

# Computational Quantum Mechanics - Project

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# Abstract/Objective

This project aims to study the amount of information which is lost by the quantum-mechanical description of every atom whose atomic number  $Z$  follows the following equation  $2 \leq Z \leq 10$ . To do so we calculate the Shannon information entropy in position  $S_r$  and k space  $S_k$  for every atom mentioned above.

To achieve this, the wave function of each atom will have to be defined in position  $\Psi_r$  and k-space  $\Psi_k$  respectively. In this project, we use Roothaan-Hartree-Fock (RHF) electron wave functions for this purpose, which were then used to calculate the electron density of each atom in both spaces ( $\rho(r)$  and  $\eta(K)$ ). Finally by using  $\rho(r)$  and  $\eta(k)$  we can calculate each atom's Shannon information entropy in position  $S_r$  and k space  $S_k$ . The final part of this project is concerned with checking the validity of its results by comparing them to those presented in [1].

# Chapter 1

## Theoretical Introduction

This chapter will discuss the theory needed to comprehend this project. We will begin by examining the RHF wave function's uses and applications in both the position and k-space. After that, we will explore the Shannon entropy and why we are interested in calculating it in the first place.

### 1.1 Roothaan-Hartree-Fock wave-functions

The Hartree-Fock (HF) equations can be regarded as a form of the non-relativistic Schrodinger equations for the motion of electrons of an atom. Each atom moves under a different potential, which is calculated by taking into account every positive and negative charge of the system (atom). These potentials are corrected by removing an exchange charge that surrounds the electron that's been investigated. All of this makes HF equations complex, and thus their only possible exact solution is a numerical one. Because of this, physicists were incentivized to look for approximative analytical solutions to the HF equations.[2],[3].

Those analytical solutions were given by the RHF method. The RHF wave functions aren't as precise as the numerical RF ones, but their advantage is that they can be defined and used in a computer program more easily. The RHF wave-functions are approximations of the HF wavefunctions, and more specifically, their radial atomic part  $R_{nl}$ , which in this approach, are expanded as a superposition of primitive radial functions  $S_{jl}(r)$ :[3].

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

In this work the primitive radial functions  $S_{jl}$  are the normalized Slater-Type Orbitals (STOs):

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

where the normalization constant  $N_{jl}$  is given by:

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

where  $n_{jl}$  is the principal quantum number,  $Z_{jl}$  is the orbital exponent, and  $l$  is the azimuthal quantum number [1], [3].

The wavefunctions describing each electron of an atom in position space  $\phi_i(r)$  and k space  $\tilde{\phi}_i(k)$  can be written in the form:

$$\phi_i(r) = \phi_{nlm}(r) = R_{nl}(r)Y_{lm}(\Omega_R) \quad (1.4)$$

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

where  $1 \leq i \leq Z$ . It is important to note that in this project we are only going to be interested in the radial aspects of each electron wavefunction, namely  $R_{nl}(r)$  and  $\tilde{R}_{nl}(k)$ .

Using eqs. 1.2 and 1.3, we can define all the needed position space STOs  $R_{nl}$  in our Python program (1s, 2s, 3s, 2p). To define the k-space STOs we would have to perform a Fourier transformation on  $R_{nl}$ . Luckily, the calculations have been made for us in [4], where we get the STOs in momentum space. It's quite simple to acquire the k-space STOs  $\tilde{R}_{nl}(k)$  (or as we have named them in our program  $K_{nl}$ ) by applying  $p = \hbar k$ .

Using [3], we get the values of  $C_{jnl}$  and the orbital exponents  $Z_{jl}$  for every STO we need. This means that by using these values in eq. 1.1 can define the wave functions of each electron both in position space  $R_{nl}(r)$  and k-space  $\tilde{R}_{nl}(k)$ . All of  $R_{nl}(r)$  and  $\tilde{R}_{nl}(k)$  must be normalized for us to be able to continue. If everything goes well we expect that:

$$I_{R_{nl}} = \int_{r=0}^{\infty} R_{nl}(r) r^2 dr \text{ and } I_{K_{nl}} = \int_{k=0}^{\infty} \tilde{R}_{nl}(k) k^2 dk = 1 \quad (1.6)$$

where  $n$  represents the principal quantum number and  $l$  represents the azimuthal quantum number of each atom's electron.

Now, we can define the atom wavefunction both in position space  $\Psi(r)$  and k-space  $\tilde{\Psi}(k)$  as:

$$\Psi(r) = \frac{1}{2\pi\sqrt{Z}} \sum_i \sqrt{A_i} \times R_{nl}(r) \text{ and } \tilde{\Psi}(k) = \frac{1}{2\pi\sqrt{Z}} \sum_i \sqrt{A_i} \times \tilde{R}_{nl}(k) \quad (1.7)$$

where  $Z$  represents the atom's atomic number and  $A_i$  represents the atom's number of electrons described by the quantum numbers  $n$  and  $l$  (or the number of electrons described by the wavefunctions  $R_{nl}(r)$  and  $\tilde{R}_{nl}(k)$ ) respectively.

The Densities of States of each atom in the position space  $\rho(r)$  and in k-space  $\eta(k)$  are defined as [1]:

$$\rho(r) = \|\Psi(r)\|^2 = \Psi^*(r) \times \Psi(r) \text{ and } \eta(k) = \|\tilde{\Psi}(k)\|^2 = \tilde{\Psi}^*(k) \times \tilde{\Psi}(k) \quad (1.8)$$

Using eq. 1.7, we can write eq. 1.8 as:

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

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

In our Python program, we use eq. 1.9 and eq. 1.10 to calculate the DOS. If  $\rho(r)$  and  $\eta(k)$  have been calculated correctly, we expect them to be normalized, meaning:

$$I_\rho = 4\pi \int_{r=0}^{\infty} \rho(r) r^2 dr = 1 \text{ and } I_\eta = 4\pi \int_{k=0}^{\infty} \eta(k) k^2 dk = 1 \quad (1.11)$$

It's important to note that the integrals in eqs. 1.6 and 1.11 are really complex and thus they were calculated numerically.

## 1.2 Shannon Information Entropy

The Shannon information entropy  $S$  of a system that's described by a probability density  $p(x)$  that ranges from  $x = x_{min}$  to  $x = x_{max}$ , is calculated by: [5]:

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

Statistical entropy was introduced by Shannon as a measure for the average missing information in a random source. If we are studying a deterministic binary system, and thus there is no randomness involved (no missing information), the Shannon entropy of said system would be the minimum possible:

$$S = 0$$

On the other hand, if the binary discrete system that we are studying has the largest amount of randomness, meaning an equal probability density  $p_0$  between both results (maximum missing information), the Shannon entropy of said system would be the maximum possible:

$$S_{max} = \ln 2$$

In our case, having calculated the electron DOS from eqs. 1.9 and 1.10, we can calculate the Shannon entropy of each atom both in position space  $S_r$  and in k-space  $S_k$  by using eq. 1.12:

$$S_r = -4\pi \int_{r=0}^{r=\infty} \rho(x) \ln(\rho(x)) x^2 dx \quad (1.13)$$

$$S_k = -4\pi \int_{k=0}^{k=\infty} \eta(k) \ln(\eta(k)) k^2 dk \quad (1.14)$$

where the term  $4\pi$  exists because in reality, we have integrated over the other two coordinates (integration on  $\phi$  and  $\theta$  in spherical coordinates).

We define the total entropy of each atom  $S$  by:

$$S = S_r + S_k \quad (1.15)$$

By calculating  $S_r$ ,  $S_k$  and  $S$  for each atom we will study the amount of information that is lost from each atom's wavefunction definition as a function of  $Z$ .

## Chapter 2

# Numerical Results and Figures

This chapter is split into two sections. The first section presents the numerical results we got from our Python program, namely the values of the integrals defined on 1.6 and 1.11, the values of  $S_r$ ,  $S_k$  and  $S$  for each atom with  $2 \leq Z \leq 10$  and, the electron Density of States, both in position space  $\rho(r)$  and k-space  $\eta(K)$ . The second section is concerned with the presentation of how the Shannon entropy changes as  $Z$  increases and contains the figures for  $S_r(Z)$ ,  $S_k(Z)$ , and  $S(Z)$ .

### 2.1 Atomic study

#### 2.1.1 $Z = 2$ : Helium (He)

The orbital configuration of Helium is:  $1s^2$ . This means that Helium has two electrons in the  $1s$  orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sHe}(r)$ ,  $K_{1sHe}(k)$ ) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the Helium atom:

$$\rho_{He}(r) = \|\Psi_{He}(r)\|^2 = \frac{1}{4\pi 2} 2 \times R_{1sHe}(r)^2 \quad (2.1)$$

$$\eta_{He}(k) = \|\tilde{\Psi}_{He}(k)\|^2 = \frac{1}{4\pi 2} 2 \times K_{2sHe}(k)^2 \quad (2.2)$$

Finally, by using the DOS we have calculated (eqs. 2.1 and 2.2) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Helium atom in position space  $S_{rHe}$ , in k-space  $S_{kHe}$  and in general  $S_{He}$ . All of our numerical results are presented in table 2.1.

Quantity	Numerical Results
$I_{R_{1sHe}}$	1.0000016264426703
$I_{\rho_{He}}$	1.000001626442671
$I_{K_{1sHe}}$	1.0000016264426548
$I_{\eta_{He}}$	1.0000016264426703
$S_{rHe}$	2.698510983703346
$S_{kHe}$	3.913418758101825
$S_{He}$	6.611929741805171

Table 2.1: The numerical results we got for Helium from running our Python program.

From table 2.1 see that:

$$I_{R_{1sHe}} \approx I_{K_{1sHe}} \approx 1$$

and:

$$I_{\rho_{He}} \approx I_{\eta_{He}} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Helium's electron DOS using eqs. 2.1 and 2.2 is correct.

Finally, the electron Densities of States that were calculated for Helium, are plotted:

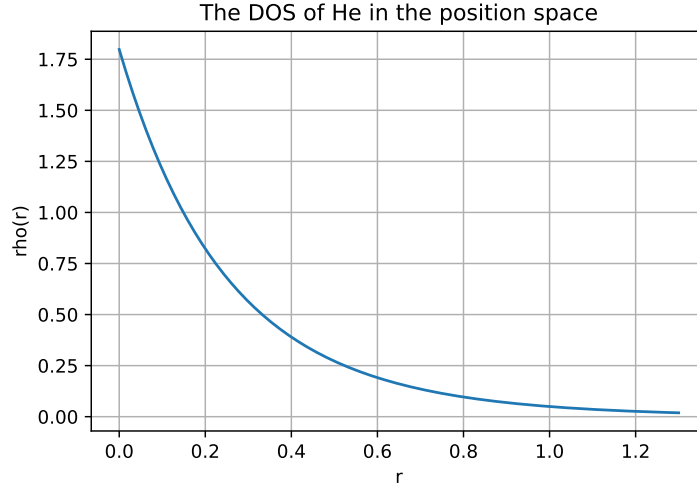


Figure 2.1: The plot of the electron Density Of States for the Helium atom in position space  $\rho_{He}(r)$ .

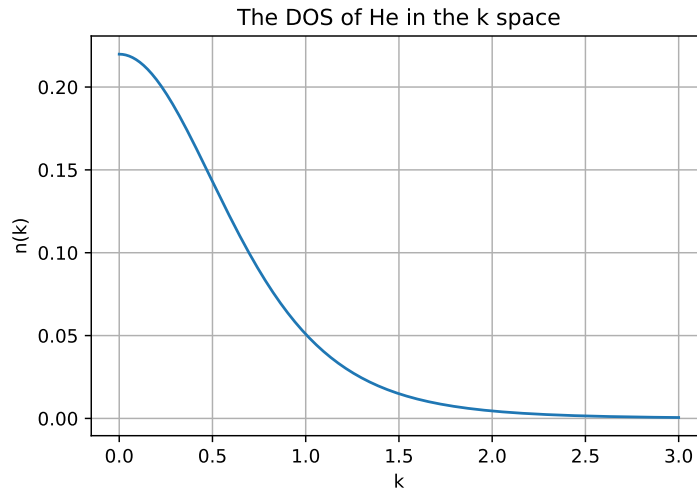


Figure 2.2: The plot of the electron Density Of States for the Helium atom in k-space  $\eta_{He}(k)$ .

### 2.1.2 $Z = 3$ : Lithium (Li)

The orbital configuration of Lithium is:  $1s^2 2s^1$ . This means that Lithium has two electrons in the 1s orbital and one in the 2s orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sLi}(r)$ ,  $K_{1sLi}(k)$ ,  $R_{2sLi}(r)$ ,  $K_{2sLi}(k)$ ) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the



electron DOS of the Li atom:

$$\rho_{Li}(r) = \|\Psi_{Li}(r)\|^2 = \frac{1}{4\pi 3} (2 \times R_{1sLi}(r)^2 + 1 \times R_{2sLi}(r)^2) \quad (2.3)$$

$$\eta_{Li}(k) = \|\tilde{\Psi}_{Li}(k)\|^2 = \frac{1}{4\pi 3} (2 \times K_{2sLi}(k)^2 + 1 \times K_{2sLi}(k)^2) \quad (2.4)$$

Finally, by using the DOS we have calculated (eqs. 2.3 and 2.4) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Lithium atom in position space  $S_{rLi}$ , in k-space  $S_{kLi}$  and in general  $S_{Li}$ . All of our numerical results are presented in table 2.2.

Quantity	Numerical Results
$I_{R_{1sLi}}$	0.9999996201070366
$I_{R_{2sLi}}$	0.9999997504434142
$I_{\rho_{Li}}$	0.9999996635524931
$I_{K_{1sLi}}$	0.9999996201070324
$I_{K_{2sLi}}$	0.9999997504434215
$I_{\eta_{Li}}$	0.9999996201070366
$S_{rLi}$	3.701436920399277
$S_{kLi}$	3.996819024119102
$S_{Li}$	7.69825594451838

Table 2.2: The numerical results we got for Lithium from running our Python program.

From table 2.2 see that:

$$I_{R_{1sLi}} \approx I_{R_{2sLi}} \approx I_{K_{1sLi}} \approx I_{K_{2sLi}} \approx 1$$

and:

$$I_{\rho_{Li}} \approx I_{\eta_{Li}} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Lithium's electron DOS using eqs. 2.3 and 2.4 is correct.

Finally, the electron Densities of States that were calculated for Lithium, are plotted:

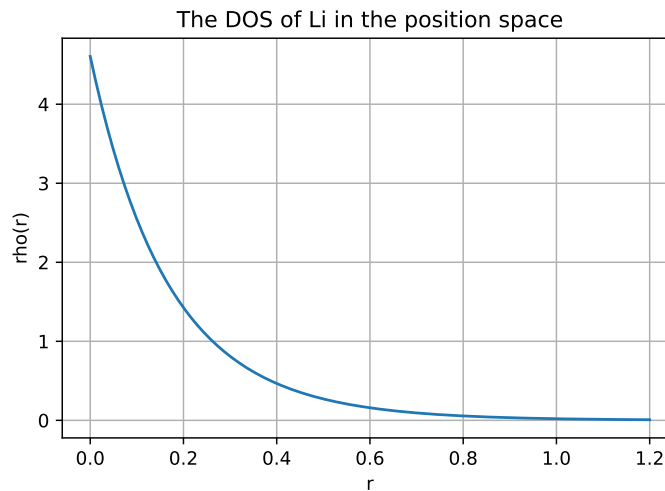


Figure 2.3: The plot of the electron Density Of States for the Lithium atom in position space  $\rho_{Li}(r)$ .

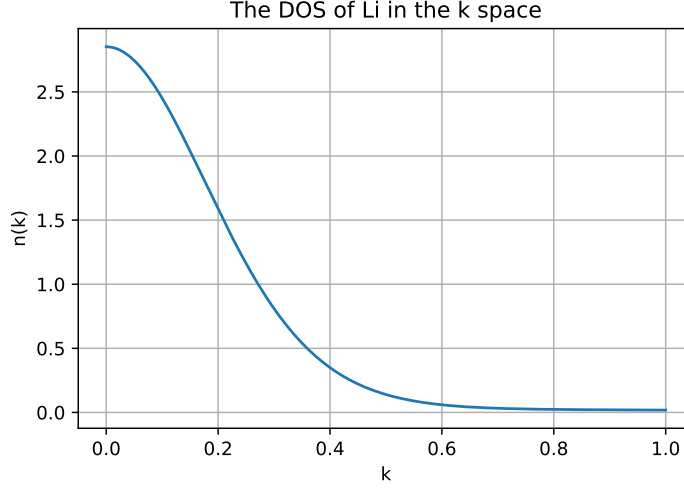


Figure 2.4: The plot of the electron Density Of States for the Lithium atom in k-space  $\eta_{Li}(k)$ .

### 2.1.3 $Z = 4$ : Beryllium (Be)

The orbital configuration of Beryllium is:  $1s^2 2s^2$ . This means that Beryllium has two electrons in the 1s orbital and two in the 2s orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sBe}(r)$ ,  $K_{1sBe}(k)$ ,  $R_{2sBe}(r)$ ,  $K_{2sBe}(k)$ ) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the Be atom:

$$\rho_{Be}(r) = \|\Psi_{Be}(r)\|^2 = \frac{1}{4\pi 4} (2 \times R_{1sBe}(r)^2 + 2 \times R_{2sBe}(r)^2) \quad (2.5)$$

$$\eta_{Be}(k) = \|\tilde{\Psi}_{Be}(k)\|^2 = \frac{1}{4\pi 4} (2 \times K_{2sBe}(k)^2 + 2 \times K_{2sBe}(k)^2) \quad (2.6)$$

Finally, by using the DOS we have calculated (eqs. 2.5 and 2.6) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Beryllium atom in position space  $S_{r_{Be}}$ , in k-space  $S_{k_{Be}}$  and in general  $S_{Be}$ . All of our numerical results are presented in table 2.3.

Quantity	Numerical Results
$I_{R_{1sBe}}$	0.9999996143650673
$I_{R_{2sBe}}$	1.0000011217653966
$I_{\rho_{Be}}$	1.00000036806523
$I_{K_{1sBe}}$	0.9999996143650658
$I_{K_{2sBe}}$	1.0000011217653932
$I_{\eta_{Be}}$	0.9999996143650673
$S_{r_{Be}}$	3.623859022676
$S_{k_{Be}}$	4.1901875514254705
$S_{Be}$	7.814046574101471

Table 2.3: The numerical results we got for Beryllium from running our Python program.

From table 2.3 see that:

$$I_{R_{1sBe}} \approx I_{R_{2sBe}} \approx I_{K_{1sBe}} \approx I_{K_{2sBe}} \approx 1$$

and:

$$I_{\rho_{Be}} \approx I_{\eta_{Be}} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Beryllium's electron DOS using eqs. 2.5 and 2.6 is correct.

Finally, the electron Densities of States that were calculated for Beryllium, are plotted:

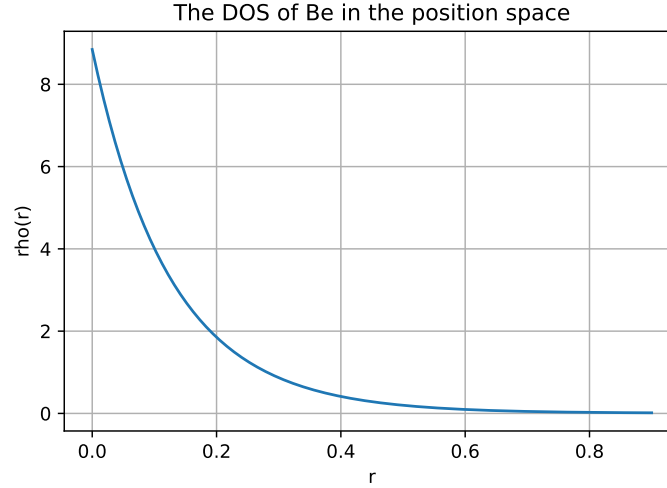


Figure 2.5: The plot of the electron Density Of States for the Beryllium atom in position space  $\rho_{Be}(r)$ .

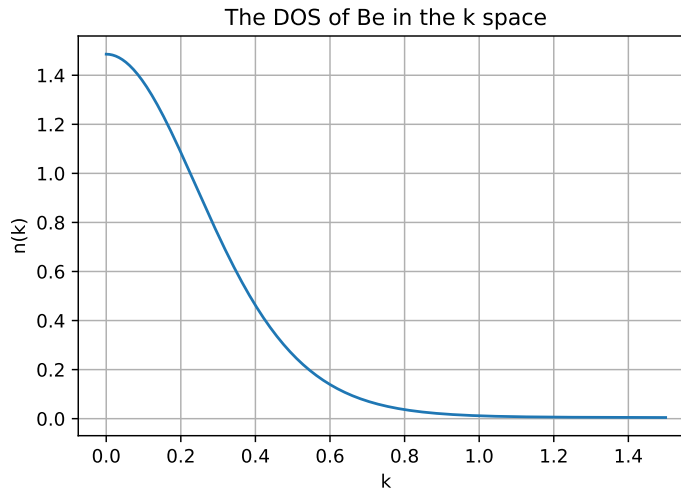


Figure 2.6: The plot of the electron Density Of States for the Beryllium atom in k-space  $\eta_{Be}(k)$ .

#### 2.1.4 $Z = 5$ : Boron (B)

The orbital configuration of Boron is:  $1s^2 2s^2 2p^1$ . This means that Boron has two electrons in the 1s orbital, two in the 2s orbital, and one electron in the 2p orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sB}(r)$ ,  $K_{1sB}(k)$ ,  $R_{2sB}(r)$ ,  $K_{2sB}(k)$ ,  $R_{2pB}(r)$ ,  $K_{2pB}(k)$ ,) by applying the values of [3] to eqs. 1.2, 1.3 and

1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the B atom:

$$\rho_B(r) = \|\Psi_B(r)\|^2 = \frac{1}{4\pi 5} (2 \times R_{1sB}(r)^2 + 2 \times R_{2sB}(r)^2 + 1 \times R_{2pB}(r)^2) \quad (2.7)$$

$$\eta_B(k) = \|\tilde{\Psi}_B(k)\|^2 = \frac{1}{4\pi 5} (2 \times K_{2sB}(k)^2 + 2 \times K_{2sB}(k)^2 + 1 \times K_{2pB}(k)^2) \quad (2.8)$$

Finally, by using the DOS we have calculated (eqs. 2.7 and 2.8) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Boron atom in position space  $S_{r_B}$ , in k-space  $S_{k_B}$  and in general  $S_B$ . All of our numerical results are presented in table 2.4.

Quantity	Numerical Results
$I_{R_{1sB}}$	1.0000003597104683
$I_{R_{2sB}}$	1.0000001111028303
$I_{R_{2pB}}$	1.0000007814633793
$I_{\rho_B}$	1.0000003446179961
$I_{K_{1sB}}$	1.0000003597105
$I_{K_{2sB}}$	1.0000001111028356
$I_{K_{2pB}}$	1.0000007814633796
$I_{\eta_B}$	1.0000003597104683
$S_{r_B}$	3.4054452271461058
$S_{k_B}$	4.70590177803336
$S_B$	8.111347005179466

Table 2.4: The numerical results we got for Boron from running our Python program.

From table 2.4 see that:

$$I_{R_{1sB}} \approx I_{R_{2sB}} \approx I_{R_{2pB}} \approx I_{K_{1sB}} \approx I_{K_{2sB}} \approx I_{K_{2pB}} \approx 1$$

and:

$$I_{\rho_B} \approx I_{\eta_B} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Boron's electron DOS using eqs. 2.7 and 2.8 is correct.

Finally, the electron Densities of States that were calculated for Boron, are plotted:

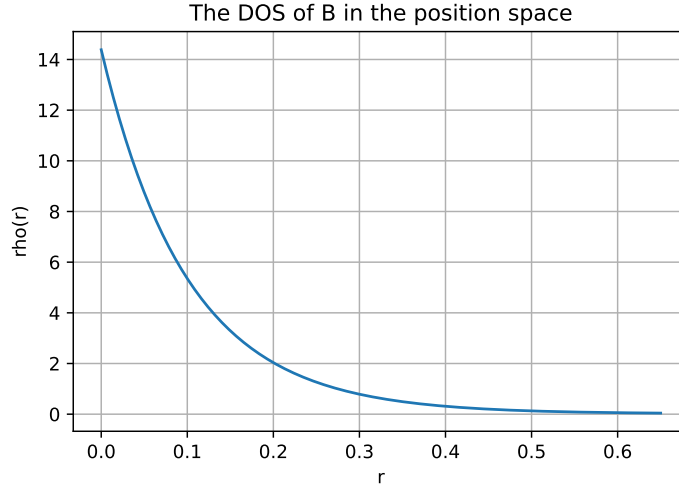


Figure 2.7: The plot of the electron Density Of States for the Boron atom in position space  $\rho_B(r)$ .

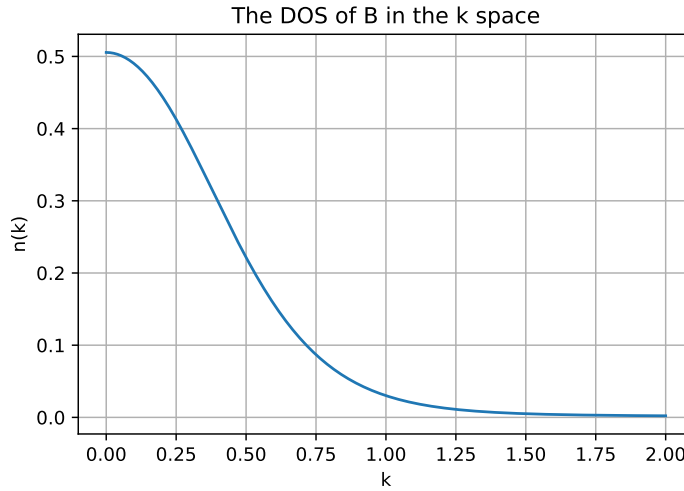


Figure 2.8: The plot of the electron Density Of States for the Boron atom in k-space  $\eta_B(k)$ .

### 2.1.5 $Z = 6$ : Carbon (C)

The orbital configuration of Carbon is:  $1s^2 2s^2 2p^2$ . This means that Carbon has two electrons in the 1s orbital, two in the 2s orbital, and two electrons in the 2p orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sC}(r)$ ,  $K_{1sC}(k)$ ,  $R_{2sC}(r)$ ,  $K_{2sC}(k)$ ,  $R_{2pC}(r)$ ,  $K_{2pC}(k)$ ,) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the C atom:

$$\rho_C(r) = \|\Psi_C(r)\|^2 = \frac{1}{4\pi 6} (2 \times R_{1sC}(r)^2 + 2 \times R_{2sC}(r)^2 + 2 \times R_{2pC}(r)^2) \quad (2.9)$$

$$\eta_C(k) = \|\tilde{\Psi}_C(k)\|^2 = \frac{1}{4\pi 6} (2 \times K_{2sC}(k)^2 + 2 \times K_{2sC}(k)^2 + 2 \times K_{2pC}(k)^2) \quad (2.10)$$

Finally, by using the DOS we have calculated (eqs. 2.9 and 2.10) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Carbon atom in position space  $S_{r_C}$ , in k-space  $S_{k_C}$  and in general  $S_C$ . All of our numerical results are presented in table 2.5.

Quantity	Numerical Results
$I_{R_{1s}C}$	1.0000002258427496
$I_{R_{2s}C}$	0.9999985063081371
$I_{R_{2p}C}$	0.9999997486127455
$I_{\rho_C}$	0.9999994935878771
$I_{K_{1s}C}$	1.0000002258427478
$I_{K_{2s}C}$	0.9999985063383648
$I_{K_{2p}C}$	0.9999997486127447
$I_{\eta_C}$	1.0000002258427496
$S_{r_C}$	3.106024953798885
$S_{k_C}$	5.156576265110764
$S_C$	8.262601218909648

Table 2.5: The numerical results we got for Carbon from running our Python program.

From table 2.5 see that:

$$I_{R_{1s}C} \approx I_{R_{2s}C} \approx I_{R_{2p}C} \approx I_{K_{1s}C} \approx I_{K_{2s}C} \approx I_{K_{2p}C} \approx 1$$

and:

$$I_{\rho_C} \approx I_{\eta_C} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Carbon's electron DOS using eqs. 2.9 and 2.10 is correct.

Finally, the electron Densities of States that were calculated for Carbon, are plotted:

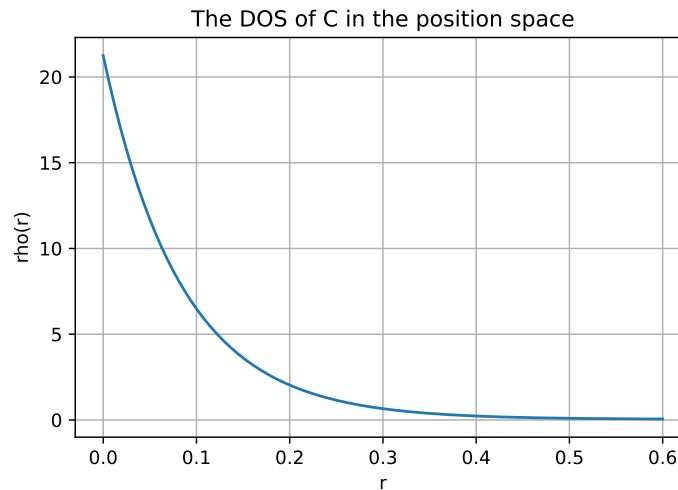


Figure 2.9: The plot of the electron Density Of States for the Carbon atom in position space  $\rho_C(r)$ .

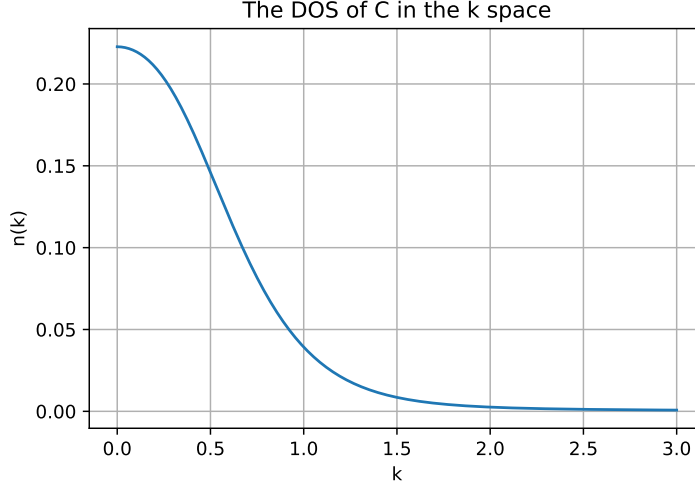


Figure 2.10: The plot of the electron Density Of States for the Carbon atom in k-space  $\eta_C(k)$ .

### 2.1.6 $Z = 7$ : Nitrogen (N)

The orbital configuration of Nitrogen is:  $1s^2 2s^2 2p^3$ . This means that Nitrogen has two electrons in the 1s orbital, two in the 2s orbital, and three electrons in the 2p orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sN}(r)$ ,  $K_{1sN}(k)$ ,  $R_{2sN}(r)$ ,  $K_{2sN}(k)$ ,  $R_{2pN}(r)$ ,  $K_{2pN}(k)$ ) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the N atom:

$$\rho_N(r) = \|\Psi_N(r)\|^2 = \frac{1}{4\pi 7} (2 \times R_{1sN}(r)^2 + 2 \times R_{2sN}(r)^2 + 3 \times R_{2pN}(r)^2) \quad (2.11)$$

$$\eta_N(k) = \|\tilde{\Psi}_N(k)\|^2 = \frac{1}{4\pi 7} (2 \times K_{2sN}(k)^2 + 2 \times K_{2sN}(k)^2 + 3 \times K_{2pN}(k)^2) \quad (2.12)$$

Finally, by using the DOS we have calculated (eqs. 2.11 and 2.12) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Nitrogen atom in position space  $S_{r_N}$ , in k-space  $S_{k_N}$  and in general  $S_N$ . All of our numerical results are presented in table 2.6.

Quantity	Numerical Results
$I_{R_{1sN}}$	0.9999992054463795
$I_{R_{2sN}}$	0.9999991391799098
$I_{R_{2pN}}$	0.999999890536027
$I_{\rho_N}$	0.9999994801229485
$I_{K_{1sN}}$	0.9999992054463774
$I_{K_{2sN}}$	0.9999991391798264
$I_{K_{2pN}}$	0.9999998905360412
$I_{\eta_N}$	0.9999992054463795
$S_{r_N}$	2.8016881540476457
$S_{k_N}$	5.54933714446826
$S_N$	8.351025298515905

Table 2.6: The numerical results we got for Nitrogen from running our Python program.

From table 2.6 see that:

$$I_{R_{1sN}} \approx I_{R_{2sN}} \approx I_{R_{2pN}} \approx I_{K_{1sN}} \approx I_{K_{2sN}} \approx I_{K_{2pN}} \approx 1$$

and:

$$I_{\rho_N} \approx I_{\eta_N} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Nitrogen's electron DOS using eqs. 2.11 and 2.12 is correct.

Finally, the electron Densities of States that were calculated for Nitrogen, are plotted:

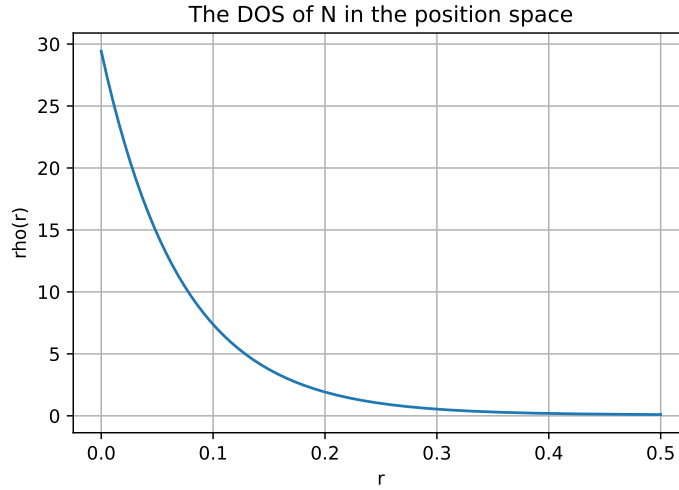


Figure 2.11: The plot of the electron Density Of States for the Nitrogen atom in position space  $\rho_N(r)$ .

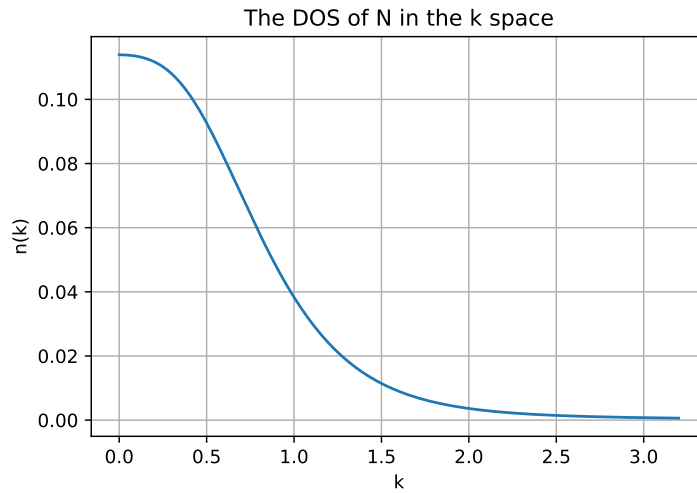


Figure 2.12: The plot of the electron Density Of States for the Nitrogen atom in k-space  $\eta_N(k)$ .

### 2.1.7 $Z = 8$ : Oxygen (O)

The orbital configuration of Oxygen is:  $1s^2 2s^2 2p^4$ . This means that Oxygen has two electrons in the 1s orbital, two in the 2s orbital, and four electrons in the 2p orbital. We cal-



culate the STOs we need to describe the electron orbitals of said atom ( $R_{1sO}(r)$ ,  $K_{1sO}(k)$ ,  $R_{2sO}(r)$ ,  $K_{2sO}(k)$ ,  $R_{2pO}(r)$ ,  $K_{2pO}(k)$ ,) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the O atom:

$$\rho_O(r) = \|\Psi_O(r)\|^2 = \frac{1}{4\pi 8} (2 \times R_{1sO}(r)^2 + 2 \times R_{2sO}(r)^2 + 4 \times R_{2pO}(r)^2) \quad (2.13)$$

$$\eta_O(k) = \|\tilde{\Psi}_O(k)\|^2 = \frac{1}{4\pi 8} (2 \times K_{2sO}(k)^2 + 2 \times K_{2sO}(k)^2 + 4 \times K_{2pO}(k)^2) \quad (2.14)$$

Finally, by using the DOS we have calculated (eqs. 2.13 and 2.14) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Oxygen atom in position space  $S_{rO}$ , in k-space  $S_{kO}$  and in general  $S_O$ . All of our numerical results are presented in table 2.7.

Quantity	Numerical Results
$I_{R_{1sO}}$	1.0000005491757415
$I_{R_{2sO}}$	0.9999994952983493
$I_{R_{2pO}}$	0.999999764149284
$I_{\rho_O}$	0.9999998931931657
$I_{K_{1sO}}$	1.0000005491757422
$I_{K_{2sO}}$	0.9999994952980159
$I_{K_{2pO}}$	0.9999997641492859
$I_{\eta_O}$	1.0000005491757415
$S_{rO}$	2.5505387339617083
$S_{kO}$	5.867353586997339
$S_O$	8.417892320959048

Table 2.7: The numerical results we got for Oxygen from running our Python program.

From table 2.7 see that:

$$I_{R_{1sO}} \approx I_{R_{2sO}} \approx I_{R_{2pO}} \approx I_{K_{1sO}} \approx I_{K_{2sO}} \approx I_{K_{2pO}} \approx 1$$

and:

$$I_{\rho_O} \approx I_{\eta_O} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Oxygen's electron DOS using eqs. 2.13 and 2.14 is correct.

Finally, the electron Densities of States that were calculated for Oxygen, are plotted:



Figure 2.13: The plot of the electron Density Of States for the Oxygen atom in position space  $\rho_O(r)$ .

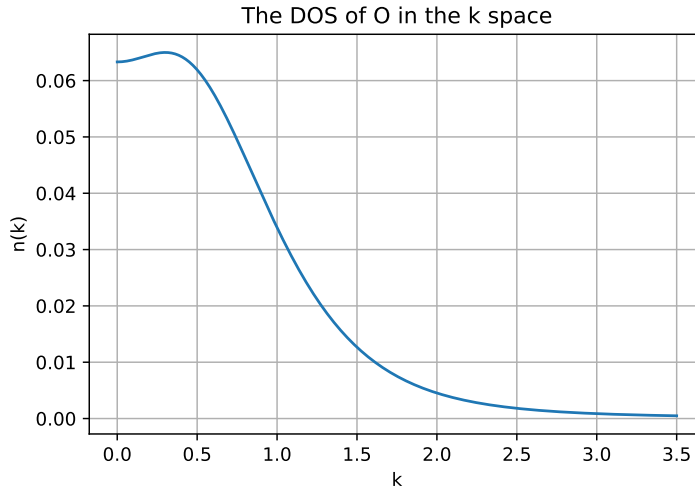


Figure 2.14: The plot of the electron Density Of States for the Oxygen atom in k-space  $\eta_O(k)$ .

### 2.1.8 $Z = 9$ : Fluorine (F)

The orbital configuration of Fluorine is:  $1s^2 2s^2 2p^5$ . This means that Fluorine has two electrons in the 1s orbital, two electrons in the 2s orbital, and five electrons in the 2p orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sF}(r)$ ,  $K_{1sF}(k)$ ,  $R_{2sF}(r)$ ,  $K_{2sF}(k)$ ,  $R_{2pF}(r)$ ,  $K_{2pF}(k)$ ,) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the F atom:

$$\rho_F(r) = \|\Psi_F(r)\|^2 = \frac{1}{4\pi 9} (2 \times R_{1sF}(r)^2 + 2 \times R_{2sF}(r)^2 + 5 \times R_{2pF}(r)^2) \quad (2.15)$$

$$\eta_F(k) = \|\tilde{\Psi}_F(k)\|^2 = \frac{1}{4\pi 9} (2 \times K_{2sF}(k)^2 + 2 \times K_{2sF}(k)^2 + 5 \times K_{2pF}(k)^2) \quad (2.16)$$

Finally, by using the DOS we have calculated (eqs. 2.15 and 2.16) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Fluorine atom in position space  $S_{r_F}$ , in k-space  $S_{k_F}$  and in general  $S_F$ . All of our numerical results are presented in table 2.8.

Quantity	Numerical Results
$I_{R_{1sF}}$	1.0000002893524889
$I_{R_{2sF}}$	1.0000002806835255
$I_{R_{2pF}}$	0.9999991341606518
$I_{\rho_F}$	0.999999645652813
$I_{K_{1sF}}$	1.0000002893524873
$I_{K_{2sF}}$	1.0000002806841517
$I_{K_{2pF}}$	0.9999991341606549
$I_{\eta_F}$	1.0000002893524889
$S_{r_F}$	2.2988269994402706
$S_{k_F}$	6.16332516670959
$S_F$	8.46215216614986

Table 2.8: The numerical results we got for Fluorine from running our Python program.

From table 2.8 see that:

$$I_{R_{1sF}} \approx I_{R_{2sF}} \approx I_{R_{2pF}} \approx I_{K_{1sF}} \approx I_{K_{2sF}} \approx I_{K_{2pF}} \approx 1$$

and:

$$I_{\rho_F} \approx I_{\eta_F} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Fluorine's electron DOS using eqs. 2.15 and 2.16 is correct.

Finally, the electron Densities of States that were calculated for Fluorine, are plotted:

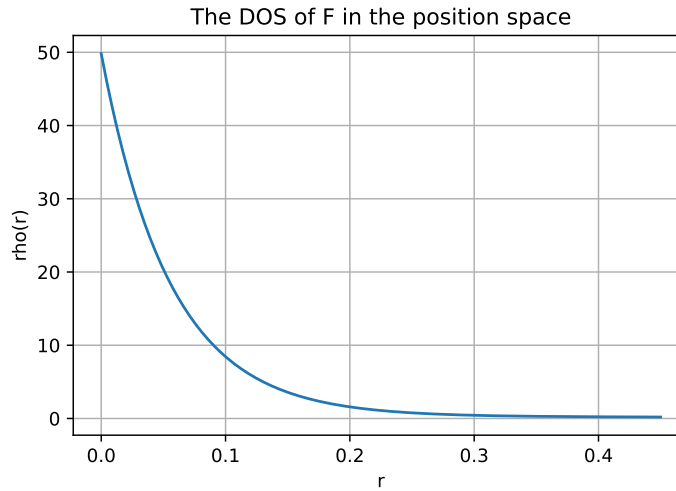


Figure 2.15: The plot of the electron Density Of States for the Fluorine atom in position space  $\rho_F(r)$ .

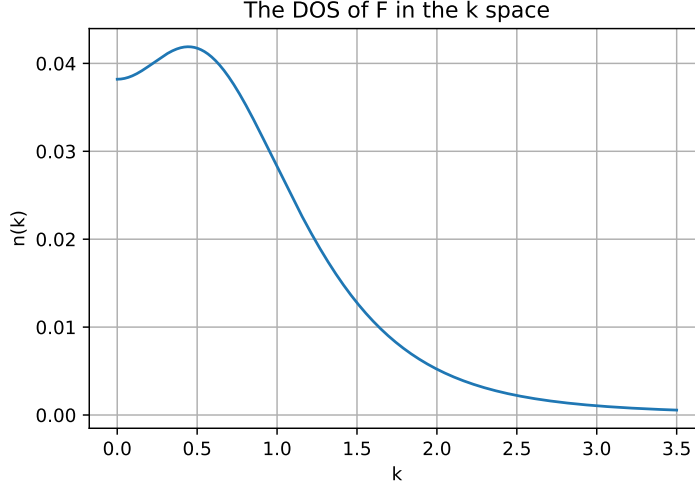


Figure 2.16: The plot of the electron Density Of States for the Fluorine atom in k-space  $\eta_F(k)$ .

### 2.1.9 $Z = 10$ : Neon (Ne)

The orbital configuration of Neon is:  $1s^2 2s^2 2p^6$ . This means that Neon has two electrons in the 1s orbital, two electrons in the 2s orbital, and six electrons in the 2p orbital. We calculate the STOs we need to describe the electron orbitals of said atom ( $R_{1sNe}(r)$ ,  $K_{1sNe}(k)$ ,  $R_{2sNe}(r)$ ,  $K_{2sNe}(k)$ ,  $R_{2pNe}(r)$ ,  $K_{2pNe}(k)$ ,) by applying the values of [3] to eqs. 1.2, 1.3 and 1.1. Then by using eqs. 1.9 and 1.10 we calculate the electron DOS of the Ne atom:

$$\rho_{Ne}(r) = \|\Psi_{Ne}(r)\|^2 = \frac{1}{4\pi 10} (2 \times R_{1sNe}(r)^2 + 2 \times R_{2sNe}(r)^2 + 6 \times R_{2pNe}(r)^2) \quad (2.17)$$

$$\eta_{Ne}(k) = \|\tilde{\Psi}_{Ne}(k)\|^2 = \frac{1}{4\pi 10} (2 \times K_{2sNe}(k)^2 + 2 \times K_{2sNe}(k)^2 + 6 \times K_{2pNe}(k)^2) \quad (2.18)$$

Finally, by using the DOS we have calculated (eqs. 2.17 and 2.18) in eqs. 1.13, 1.14 and 1.15, we calculate the Shannon entropy of the Neon atom in position space  $S_{r_{Ne}}$ , in k-space  $S_{k_{Ne}}$  and in general  $S_{Ne}$ . All of our numerical results are presented in table 2.9.

Quantity	Numerical Results
$I_{R_{1sNe}}$	1.0000016339166584
$I_{R_{2sNe}}$	0.9999998128346947
$I_{R_{2pNe}}$	1.0000006916718924
$I_{\rho_{Ne}}$	1.000000704353406
$I_{K_{1sNe}}$	1.000001633916672
$I_{K_{2sNe}}$	0.9999998128346923
$I_{K_{2pNe}}$	1.0000006916718955
$I_{\eta_{Ne}}$	1.0000016339166584
$S_{r_{Ne}}$	2.055137743242788
$S_{k_{Ne}}$	6.437068502959287
$S_{Ne}$	8.492206246202075

Table 2.9: The numerical results we got for Neon from running our Python program.

From table 2.9 see that:

$$I_{R_{1sNe}} \approx I_{R_{2sNe}} \approx I_{R_{2pNe}} \approx I_{K_{1sNe}} \approx I_{K_{2sNe}} \approx I_{K_{2pNe}} \approx 1$$

and:

$$I_{\rho_{Ne}} \approx I_{\eta_{Ne}} \approx 1$$

meaning that the normalization conditions 1.6 and 1.11 are met. Thus the calculation of Neon's electron DOS using eqs. 2.17 and 2.18 is correct.

Finally, the electron Densities of States that were calculated for Neon, are plotted:

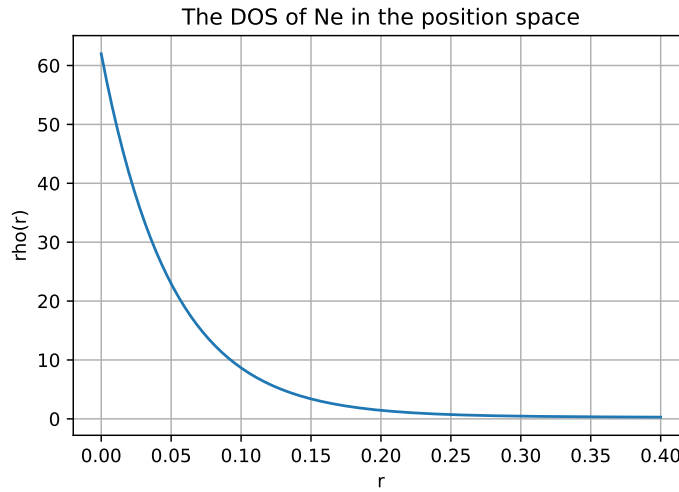


Figure 2.17: The plot of the electron Density Of States for the Neon atom in position space  $\rho_{Ne}(r)$ .

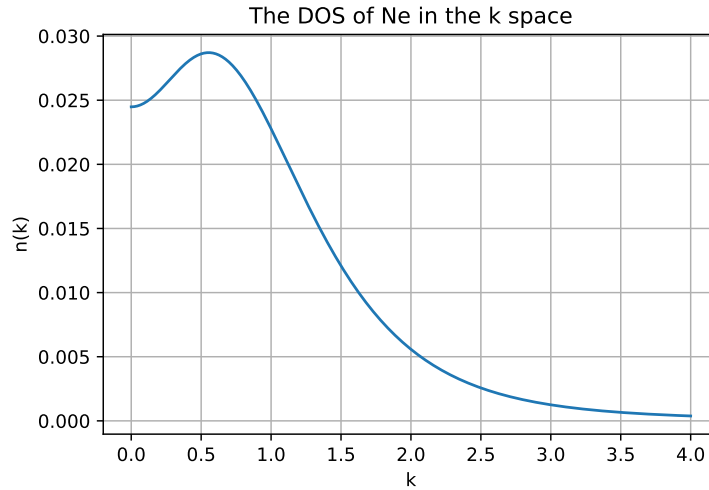


Figure 2.18: The plot of the electron Density Of States for the Neon atom in k-space  $\eta_{Ne}(k)$ .

## 2.2 Entropy (information) study

The values of the Shannon entropies of all atoms are gathered and presented in table 2.10:

$Z$	$S_r$	$S_k$	$S$
2	2.698510983703346	3.913418758101825	6.611929741805171
3	3.701436920399277	3.996819024119102	7.69825594451838
4	3.623859022676	4.1901875514254705	7.814046574101471
5	3.4054452271461058	4.70590177803336	8.111347005179466
6	3.106024953798885	5.156576265110764	8.262601218909648
7	2.8016881540476457	5.54933714446826	8.351025298515905
8	2.5505387339617083	5.867353586997339	8.417892320959048
9	2.2988269994402706	6.16332516670959	8.46215216614986
10	2.055137743242788	6.437068502959287	8.492206246202075

Table 2.10: The values of Shannon's entropies that have been calculated for different values of  $Z$  (different atoms). The first column contains the entropy in position space  $S_r$ , the second column contains the entropy in k-space  $S_k$  and the third column contains the total entropy  $S = S_r + S_k$ .

Using the values of table 2.10, we create the following figures  $S_r(Z)$ ,  $S_k(Z)$  and  $S(Z)$ :

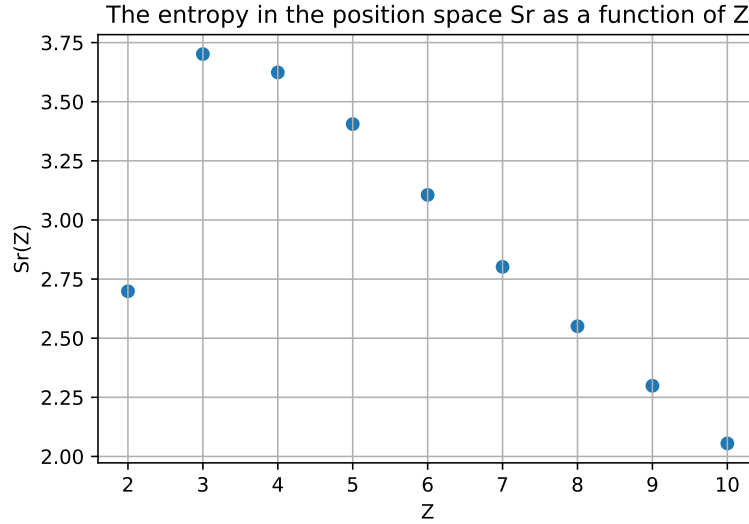


Figure 2.19: The graph of the Shannon entropy in position space  $S_r(Z)$  as a function of the atomic number  $Z$ .

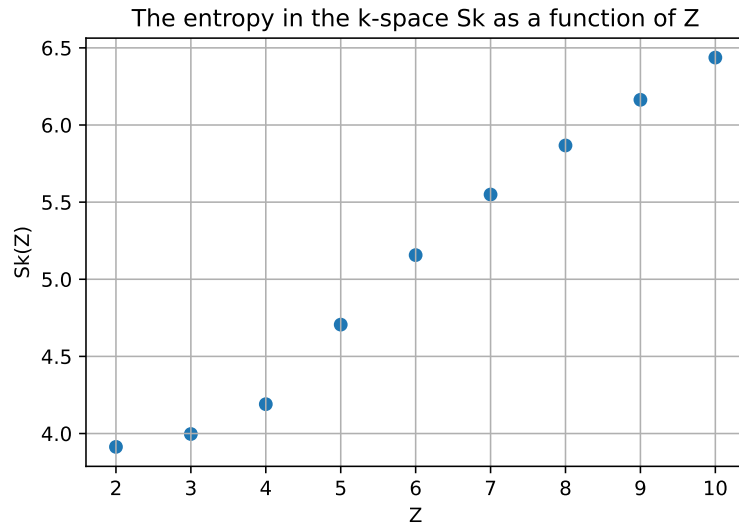


Figure 2.20: The graph of the Shannon entropy in k-space  $S_k(Z)$  as a function of the atomic number  $Z$ .

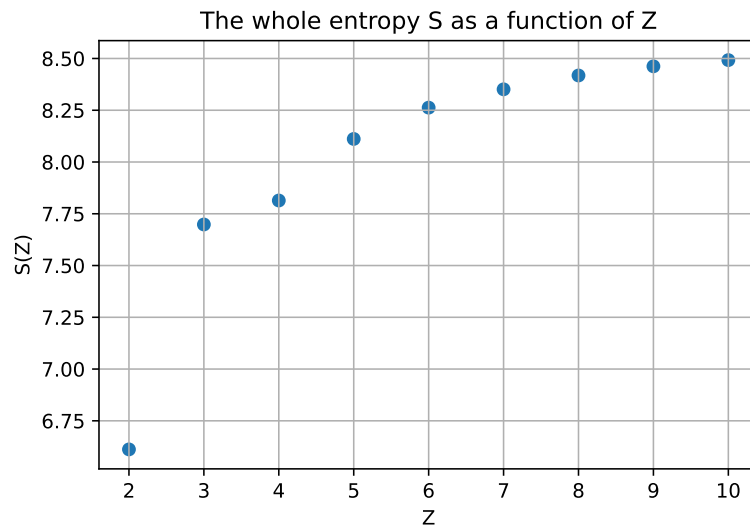


Figure 2.21: The graph of the total Shannon entropy  $S(Z)$  as a function of the atomic number  $Z$ .

## Chapter 3

# Conlusions and Discussion

This chapter contains the analysis of the results presented in the previous chapter. Our results are compared with those presented in [1] to check their validity and then, they are discussed.

### 3.1 Validity of results

By comparing the values of  $S_r(Z)$ ,  $S_k(Z)$  and  $S(Z)$  from table 2.10 with those that are presented in [1], we can see that they are equal and thus, we can conclude that our analysis and calculations are correct.

### 3.2 Analysis of results

From table 2.10 and from figures 2.19, 2.20 and 2.21 we can see that there seem to be some patterns when it comes to  $S_r(Z)$ ,  $S_k(Z)$  and  $S(Z)$ .

More specifically  $S_r(Z)$  seems to decrease as  $Z$  increases (except for  $Z = 3$ ), indicating that as  $Z$  increases the amount of information lost in position space decreases. This can be also seen by the graphs of electron Densities of States  $\rho(r)$ : as  $Z$  increases  $\rho(r)$  tend to 0 for smaller values of  $r$ , and thus the uncertainty of the atom in position space gets smaller. The exact opposite can be said for k-space: as  $Z$  increases so does  $S_k$  which can also be seen by the graphs of electron Densities of States  $\eta(k)$ : as  $Z$  increases  $\eta(k)$  tend to 0 for larger values of  $k$ . All of this is consistent with the Heisenberg uncertainty principle that states that as the uncertainty, or the amount of lost information, in position space decreases the uncertainty, or the amount of lost information, in k- space should increase such as its always true that:

$$\Delta r \times \Delta k \geq \frac{1}{2} \quad (3.1)$$

where  $\Delta r$  is the uncertainty in position space and  $\Delta k$  is the uncertainty in k-space.

If we take into consideration both spaces at the same time and focus on the total Shannon entropy  $S$  we can see (from table 2.10 and from figure 2.21) that as  $Z$  increases, so does the values of the Shannon entropy, and thus the total uncertainty of our system. In other words, we can see that the decrease of uncertainty in position space isn't proportional to the increase of uncertainty in k-space, with the latter being more significant and thus, leading to a total increase of uncertainty in our system as  $Z$  increases.



# Bibliography

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- <sup>2</sup>J. C. Slater, “A simplification of the hartree-fock method”, *Physical review* **81**, 385 (1951).
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- <sup>4</sup>F. Komarov and M. Temkin, “On the momentum representation of slater-type orbitals”, *Journal of Physics B: Atomic and Molecular Physics* **9**, L255 (1976).
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