RADIAL ATOMIC ORBITALS AND SHANNON INFORMATION ENTROPIES

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Introduction

The aim of this project is to determine the radial atomic orbitals in position and momentum space for the atoms from He to Ne ($2 \leq Z \leq 10$) as well as the radial distribution function in position and momentum space. Subsequently, we will calculate the Shannon information entropies in both spaces, and their sum will give us the total entropy of the atom.

To determinate the radial atomic orbital in position space $R_{nl}(r)$ and momentum space $\tilde{R}_{nl}(k)$, we use the Hartree-Fock theory, specifically the Roothaan-Hartree-Fock (RHF) electron wave functions. Finally, we use the electron density for each atom in position space $\rho(r)$ and in momentum space $n(k)$ to calculate the Shannon information entropies.

Hartree-Fock theory

Hartree Fock theory is one the simplest approximate theories for solving the many-body Hamiltonian (Kent, 1999). It is based on a simple approximation to the true many-body wavefunction: that the wavefunction is given by a single Slater determinant of N spin-orbitals.

$$\psi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N) \end{vmatrix} \tag{1}$$

The variables **r** include the coordinates of space and the $\psi(r)$ is one-electron orbital. Clemens C. J. Roothaan showed that the electron orbital could be regarded as a set of known spatial basis functions $\varphi_j(r)$.

$$\psi_i(r) = \sum_j c_{ij}\,\varphi_j(r) \tag{2}$$

The basis set can either be a linear combination of atomic orbitals (LCAO) approach, which is the usual choice within the quantum chemistry community, plane waves typically used within the solid-state community, or real-space approaches. Several types of atomic orbital sets can be used: Gaussian-type orbitals, Slater-type orbitals, or numerical atomic orbitals (Lehtola, 2019).

Numerical results

For radial atomic orbitals, we use the equation 3. The orbital expansion coefficients c_{jnl} are obtained from (Bunge C.F., 1993). The normalized primitive basis S_{jl} is taken as a Slater-type orbital set (4), where the N_{jl} is a normalization factor.

$$R_{nl}(r) = \sum_j c_{jnl}\,S_{jl}(r) \tag{3}$$

$$S_{jl}(r) = N_{jl}\,r^{n_{jl}-1}\,e^{-Z_{jl}r} \tag{4}$$

$$N_{jl} = \frac{\left(2Z_{jl}\right)^{(n_{jl}+1/2)}}{\left[(2n_{jl})!\right]^{1/2}} \tag{5}$$

For the radial atomic orbitals in the momentum space, we need to perform a Fourier transformation, which will give us the equation 6 (Chatzisavvas, et al., 2005). Here, $j_l(kr)$ is a spherical Bessel function.

$$\tilde{R}_{nl}(k) = 4\pi \int_0^\infty r^2 R_{nl}(r) j_l(kr) dr \tag{6}$$

If we take the magnitude of the radial atomic orbital in position space, square it, and multiply it by r^2, we obtain the radial distribution function in position space (equation 7). This function describes the probability density of finding an electron at a distance r from the nucleus. As we can see from Figure 1, as the atomic number increases, the orbitals appear to be tighter, and their maximum values increase linearly, as shown in the fourth graph. The least squares lines that best fit the maximum values for each orbital as a function of atomic number are described by equations 8-10. This occurs because, as the atomic number increases, the nucleus of the atom also increases, and the potential it creates impacts the electron probability distribution.

$$P(r) = r^2 |R_{nl}(r)|^2 \tag{7}$$

$$max\big(P_{1s}(r)\big) = 1.1r - 0.878 \tag{8}$$

$$max\big(P_{2s}(r)\big) = 1.216r - 2.61 \tag{9}$$

$$max\big(P_{2p}(r)\big) = 1.167r - 2.741 \tag{10}$$

For the radial distribution function in momentum space, we square the magnitude of the corresponding wavefunction and multiply it by k^2 (equation 11). This function describes the probability density of finding an electron with a momentum k. As we can see in Figure 2, as the atomic number increases, the orbitals appear wider. This observation is consistent with Heisenberg's uncertainty principle (12), a stronger nuclear attraction causes a higher electron momentum. In the fourth graph, we can see that the k k-position where the maximum appears in each orbital distribution in momentum space has a linear relationship with the atomic number, as described by equations 13-15.
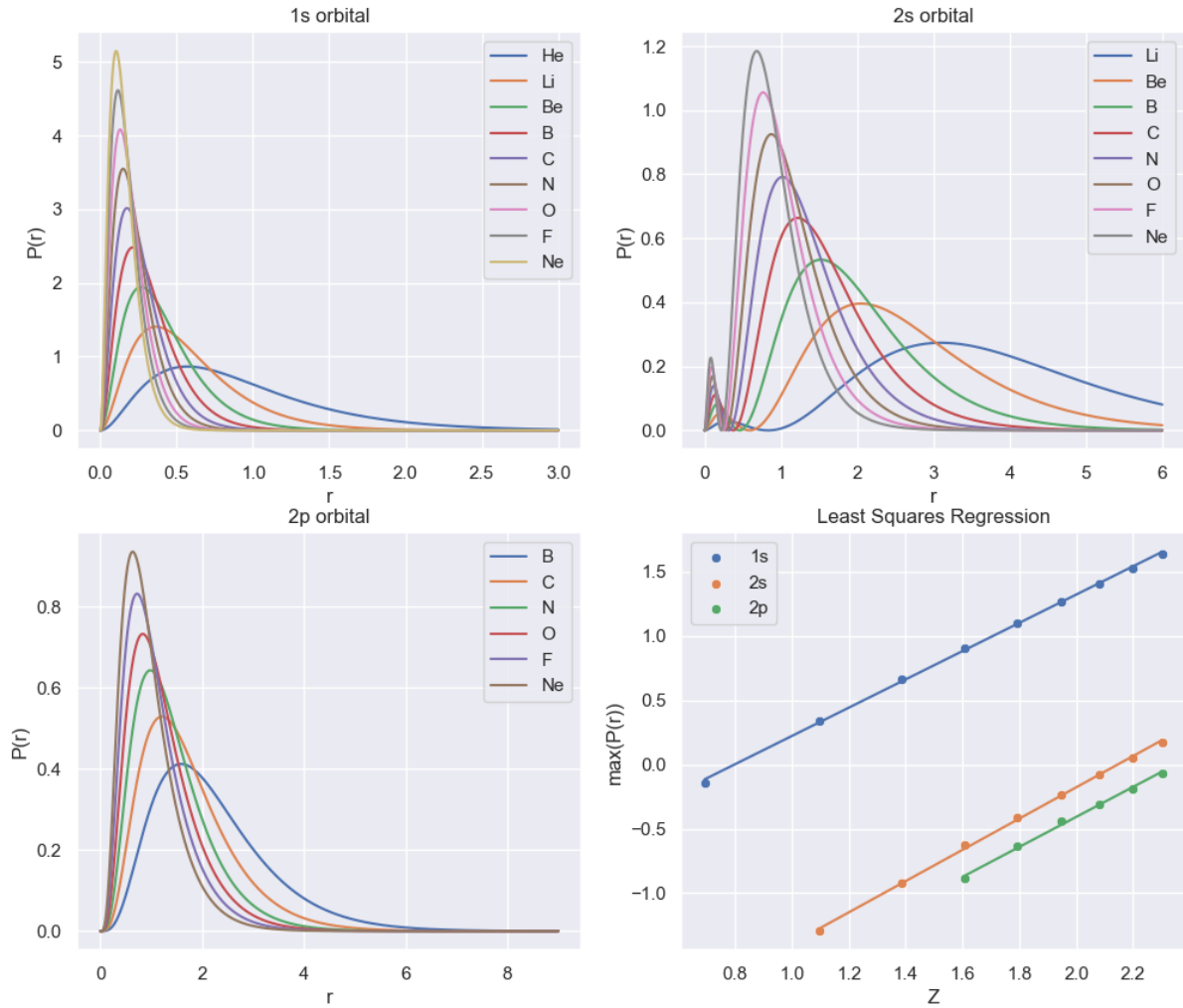
$$\tilde{P}(k) = k^2 \big|\tilde{R}_{nl}(k)\big|^2 \tag{11}$$

$$\sigma_r \sigma_k \geq \frac{1}{2} \tag{12}$$

$$max_{k_{1s}} = 1.116k - 0.862 \qquad (13)$$

$$max_{k_{2s}} = 1.167k - 2.576 \qquad (14)$$

$$max_{k_{2p}} = 1.094k - 2.044 \qquad (15)$$

Figure 1 Graphical representation of the radial distribution function $P(r)$ in position space for the first ten elements (except Hydrogen) with atomic numbers $2 \leq Z \leq 10$. The plots show $P(r)$ for 1s, 2s, and 2p orbitals. The last graph presents the maximum value of the distribution $\boldsymbol{max(P(r))}$ for each orbital as a function of atomic number Z, fitted using least squares regression.
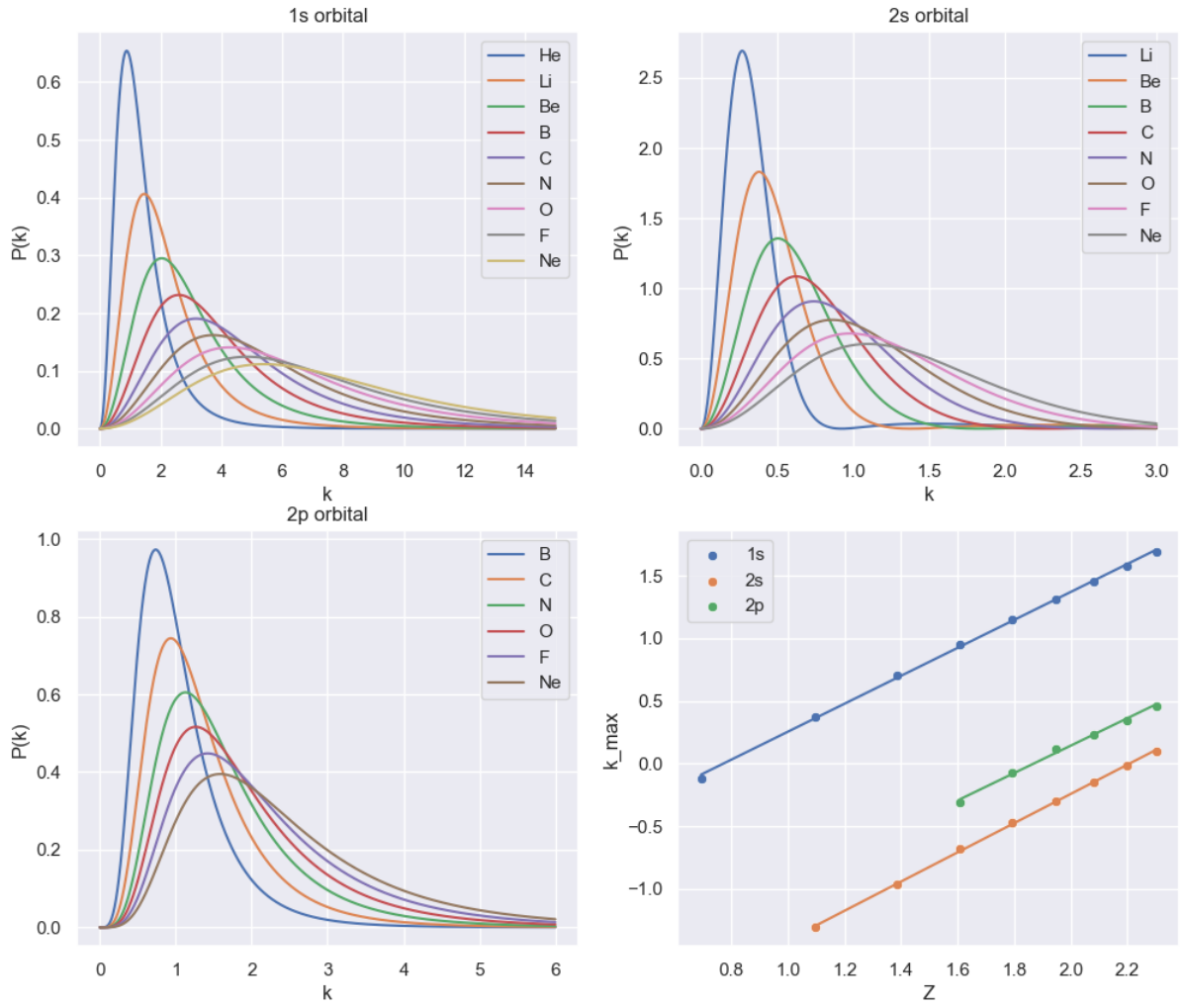
Figure 2 Graphical representation of the radial distribution function $\widetilde{P}(k)$ in momentum space for the first ten elements (except Hydrogen) with atomic numbers $2 \leq Z \leq 10$. The plots show $\widetilde{P}(k)$ for 1s, 2s, and 2p orbitals. The last graph presents the k of maximum value of the distribution max_k for each orbital as a function of atomic number Z, fitted using least squares regression.

Lastly, we determine the Shannon information entropy, which is a critically important quantity in quantum mechanics. It is used in quantum cryptography, quantum entanglement, quantum information theory, and more. The Shannon information entropy is defined in equations 16 and 17 for position and momentum space respectively, and the total entropy is simply the sum of these two (equation 18). Here, $\rho(r)$ and $n(k)$ represent the total electron density in position and momentum space respectively, which are the sums of the electron densities for each orbital (equations 19 & 20). The term $\#e$ denotes the number of electrons in an orbital for a given atom. The orbital densities are defined in equations 21 and 22. These densities are simply the squared radial atomic orbitals multiplied by a scale factor.

$$S_r = -4\pi \int_0^\infty r^2 \, \rho(r) \, ln\big(\rho(r)\big) \, dr \tag{16}$$

$$S_k = -4\pi \int_0^\infty k^2 \, n(k) \, ln\big(n(k)\big) \, dr \tag{17}$$

$$S = S_r + S_k \tag{18}$$

$$\rho(r) = \sum_i^{orbitals} \rho_i(r) \tag{19}$$

$$n(k) = \sum_i^{orbitals} n_i(k) \tag{20}$$

$$\rho_i(r) = \frac{\#e}{4\pi} R_{nl}{}^2(r) \tag{21}$$

$$n_i(k) = \frac{\#e}{4\pi} \tilde{R}_{nl}{}^2(k) \tag{22}$$

Figure 3 presents the Shannon information entropy in position space (S_r) and momentum space (S_k), along with their sum (S), as functions of the atomic number (Z).

Table 1 The values of the Shannon information entropy in position and momentum space, as well as their sum, for each atom.

Z	Atom	S_r	S_k	S
2	He	2.69850922	3.91341782	6.61192703
3	Li	3.70143890	3.99681854	7.69825745
4	Be	3.62385941	4.19018555	7.81404495
5	B	3.40544510	4.70590210	8.11134720
6	C	3.10602570	5.15657806	8.26260376
7	N	2.80168915	5.54933929	8.35102844
8	O	2.55053711	5.86735535	8.41789246
9	F	2.29882812	6.16332245	8.46215057
10	Ne	2.05513763	6.43706512	8.49220276

Conclusion

In this project, we have explored the radial atomic orbitals and their corresponding Shannon information entropies for the first ten elements (excluding Hydrogen) with atomic numbers ranging from 2 to 10. The study involved calculating the radial distribution functions in both position and momentum spaces, which were derived from the Roothaan-Hartree-Fock (RHF) electron wave functions.

References

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