Self-consistent Mean-field Model

To explain the periodic table

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1 Introduction

In this assignment, we use a self-consistent field method to solve for atomic systems with many electrons, we will combine techniques from previous assignments to iteratively solve the coupled Schrödinger and Poisson equations using B-splines.
Our goal is to compute the electron density and total energy for a couple of neutral and ionized atoms and use those values to calculate the ionization energy.

2 Theory

2.1 Mean field potential

We model electrons in a central field by solving the radial Schrödinger equation:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} + V_{\text{ee}}(r)\right] u(r) = \epsilon u(r), \tag{1}$$

where $V_{\text{ee}}(r)$ includes two terms, the direct and exchange potential:

$$V_{\text{ee}}(r) = V_{\text{dir}}(r) + V_{\text{exch}}(r). \tag{2}$$

The potential V_{dir} is calculated by solving Poisson's equation using the collocation method:

$$\frac{d^2\phi}{dr^2} = -4\pi r\rho(r), \quad V_{\text{dir}}(r) = \frac{\phi(r)}{r}. \tag{3}$$

and the exchange potential is calculated as follows:

$$V_{\text{exch}}(r) = -3\left(\frac{3}{8\pi}\rho(r)\right)^{1/3}. \tag{4}$$

We then calculate corresponding element contributions in the Hamiltonian matrix and solve for the eigenvalues and eigenstates.

3 Numerical Method

3.1 Self consistent system

Each SCF iteration proceeds as follows:

1. Solve the radial Schrödinger equation for each ℓ using B-spline basis functions and Gauss-Legendre quadrature.
2. Compute the corresponding radial wavefunction for each orbital and construct the total electron density $\rho(r)$.
3. Compute the direct potential by integrating Poisson's equation and the exchange potential using the local density approximation.
4. Update the effective potential $V_{\text{ee}}(r)$ by mixing the new and previous potentials.
5. Repeat those steps until the total energy difference between iterations falls below a specified convergence threshold.

4 Results

4.1 Noble Gases: Neon

We first start by computing the orbital energies and corresponding ionization energy for He and He+ to serve as a reference point.
After confirming the results, we move on to Ne/Ne+, the following values were obtained:

Table 1: Orbital data for Neon and Ne^+

	Orbital	ε (Ha)	$\langle V_{ee}/2 \rangle$ (Ha)	Occ.	Contribution (Ha)
Ne	1s	-35.80	-7.25	2	-86.11
	2s	-2.18	-5.16	2	-14.68
	2p	-1.28	-5.50	6	-40.71
				Total:	-141.50
Ne^+	1s	-37.04	-6.57	2	-87.22
	2s	-3.14	-4.75	2	-15.78
	2p	-2.27	-5.16	5	-37.11
				Total:	-140.11

The ionization energy obtained was:

$$\Delta E \approx 1.394 \text{ Hartree.} \tag{5}$$

Figure 1 shows the electron probability density for both Ne and Ne^+:

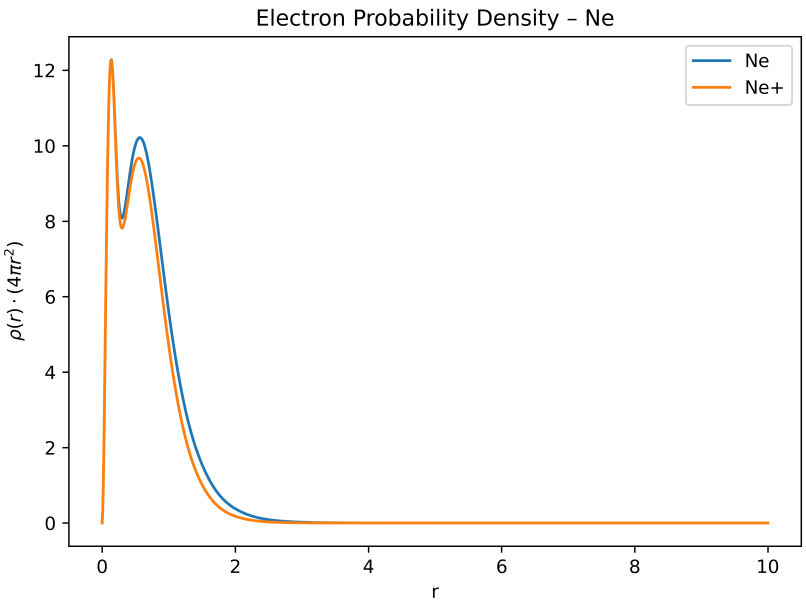

Figure 1: Electron probability density for Ne and Ne^+.

As expected, the ionization causes the density to slightly shift towards the nucleus due to reduced electron-electron repulsion.

4.2 Alkali-Metals: Potassium

The same analysis was performed for Potassium (Z = 19):

Table 2: Orbital data for Potassium and K^+

	Orbital	ε (Ha)	$\langle V_{ee}/2 \rangle$ (Ha)	Occ.	Contribution (Ha)
K	1s	-105.41	-16.01	2	-242.84
	2s	-13.28	-12.43	2	-51.40
	2p	-1.47	-7.64	6	-54.64
	3s	-1.72	-7.17	2	-17.78
	3p	-14.84	-15.00	6	-179.00
	4s	-0.40	-2.67	1	-3.07
				Total:	-548.74
K^+	1s	-105.69	-15.86	2	-243.11
	2s	-13.56	-12.29	2	-51.69
	2p	-1.75	-7.51	6	-55.53
	3s	-2.00	-7.03	2	-18.07
	3p	-15.12	-14.84	6	-179.79
				Total:	-548.18

The estimated ionization energy for Potassium is:

$$\Delta E \approx 0.554 \quad \text{Hartree} \tag{6}$$

Note that ionization energy is significantly lower than that of the Neon due to the single weakly bound valence electron in the higher-energy 4s orbital. The electron is much weakly bound because of the strong shielding from inner electrons, making the ionization less costly.

To gain a better understanding of the electron configurations in atoms, we also studied two different configurations of K: one with the outermost electron in the $4s$ orbital (Ground state) and one where the last electron is in the $3d$ shell.
We then calculated the ionization energy (to K^+) for the two different systems and got the following values:

$$\Delta E_{4s} = 0.554 \quad \text{Hartree}$$
$$\Delta E_{3d} = 0.520 \quad \text{Hartree}$$

This shows that the first system is more stable and confirms that the ground state configuration for K is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.

4.3 Ionization Energy vs. Atomic Number

Figure 2 shows a comparison between theoretical and numerical ionization energies as a function of the atomic number Z.
While the overall structure is captured correctly (Highest energy for Noble gases and lowest for Alkalis), the obtained numerical values for some atoms (those with partially filled outer shells) were much higher than expected, this can be due to numerical implementation errors or due to limitations of the local exchange approximation used in our SCF model.

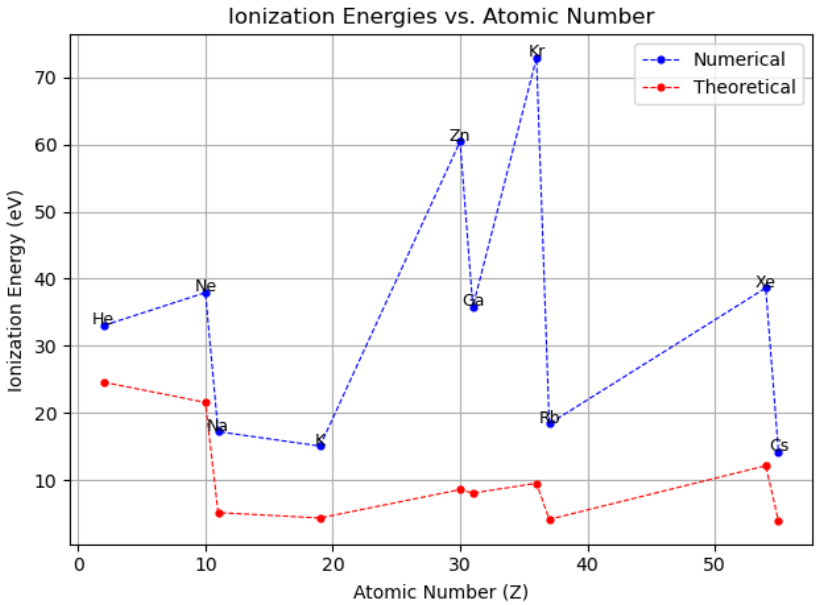

Figure 2: Ionization energy vs. atomic number for different elements.

5 Discussion

The SCF method with B-spline collocation gave the expected values and general structures for the ionization energies across different elements (with some deviations), the overall method proved effective in capturing the behavior for basic atomic structures and calculations.