University of Padua - Physics of Data
Academic Year: 2024-25
Course: Quantum Information with Atoms and Photons
Lecturers: Pietro Silvi, Marco Fedele di Liberto

Assignment 2 - Lithium red, crude approximation

Alessandro Miotto - 2139205 - alessandro.miotto.1@studenti.unipd.it

Lithium atom

This assignment focuses on the analysis of the electronic spectra of a lithium atom, with particular attention given to the transition from the excited state $|2p\rangle$ to the ground state $|2s\rangle$. The energy associated with this transition corresponds to a wavelength of 670.8 nm [1], which is approximately 1.85 eV. The study combines both analytical and numerical approaches, emphasizing the application of perturbative and variational methods to provide a comprehensive understanding of the system.

Analytical approach

In this section, we explore an analytical approach to solving the Hamiltonian of the lithium atom, using hydrogen-like states as the ansatz for the wavefunction. While this provides a useful starting point, it does not fully capture the effects of electron-electron repulsion, which significantly complicates the problem. To address this, we adopt a mean-field approach in two steps. First, we solve for a helium-like configuration by treating the two $|1s\rangle$ electrons as a closed-shell system, and derive their wavefunctions. This solution is then used to determine the effective potential experienced by the third electron in the valence orbital, simplifying the treatment of electron interactions.

The orbitals of interest include the closed-shell state $|1s\rangle$, the ground state $|2s\rangle$, and the excited state $|2p\rangle$. As mentioned earlier, the trial wavefunctions are modeled using hydrogen-like functions (in atomic units):

$$\psi_{1s}(\boldsymbol{r}) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr} \qquad\qquad E_{1s} = -\frac{Z^2}{2} = -4.5 \text{ Ha} \simeq -122 \text{ eV}$$

$$\psi_{2s}(\boldsymbol{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}}(2 - Zr)e^{-Zr/2} \qquad E_{2s} = -\frac{Z^2}{8} = -1.125 \text{ Ha} \simeq -30.6 \text{ eV}$$

$$\psi_{2p}(\boldsymbol{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}} Zr e^{-Zr/2} \cos\theta \qquad E_{2p} = -\frac{Z^2}{8} = -1.125 \text{ Ha} \simeq -30.6 \text{ eV}$$

By neglecting all electron-electron interactions, we significantly overestimate the system's energy, and the second orbital becomes degenerate, preventing the spectral emission at 670 nm. As a first approximation, we model the wavefunction using the Hartree product: $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \psi_{1s}(\boldsymbol{r}_1)\psi_{1s}(\boldsymbol{r}_2)\psi_{2s}(\boldsymbol{r}_3)$. For the Hamiltonian, we use the sum of the single-electron Hamiltonian.

$$E^{(0)} = \langle H_1 \rangle + \langle H_2 \rangle + \langle H_3 \rangle = 2E_{1s} + E_{2s} \simeq -274 \text{ eV}$$

This overestimation, given that the experimental value from ionization energies is approximately 203 eV, arises primarily from the shielding effect of the first-shell electrons, which reduces

the effective nuclear charge. In the next section, we aim to refine the energy calculation for the electrons in $|1s\rangle$, providing a more robust approach to determine the effective potential experienced by the valence electron.

Helium-like atom ground state for Li$^+$

To model the ground state of the lithium ion Li$^+$, we start with an helium-like system [2] with electric charge $Z = 3$. The full Hamiltonian is the following:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = K_1 + V_1 + K_2 + V_2 + V_{ee} = H_1 + H_2 + V_{ee}$$

where the zero-order Hamiltonian is $H^{(0)} = H_1 + H_2$. Neglecting the electron-electron interaction, the eigenstate is simply the product of the two hydrogen-like wavefunction in $|1s\rangle$ (antisymmetricity is enforced by the singlet spin part), therefore:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{1s}(\boldsymbol{r}_1)\psi_{1s}(\boldsymbol{r}_2) = \frac{Z^3}{\pi}e^{-Z(r_1+r_2)}$$

the zero-order energy is $E^{(0)} = \langle H_1 \rangle + \langle H_2 \rangle = 2E_{1s} = -Z^2 \simeq -244$ eV. Comparing this result with the ionization energies of lithium, the third ionization energy is nearly exact, as it corresponds to a single-electron system: $I_3 = -E_{\text{Li}^{2+}} = Z^2/2 \simeq 122.5$ eV. However, the second ionization energy at zero-order, $I_2 = E_{\text{Li}^+}^{(0)} - E_{\text{Li}^{2+}} \simeq 122.5$ eV, deviates significantly from the experimental value of 75.64 eV [1]. To improve our estimation, we can treat the electron-electron interaction as a perturbative term, yielding the first-order correction to the energy: $E^{(1)} = E^{(0)} + \Delta E^{(1)}$.

$$\Delta E^{(1)} = \langle V_{ee} \rangle = \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \frac{|\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)|^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{1}{\pi}\int \frac{d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 Z^3 e^{-Z(r_1+r_2)}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} = \frac{5}{8}Z \simeq 51 \text{ eV}$$

The first-order correction is $E^{(1)} = -Z^2 + 5Z/8 \simeq -193$ eV which is much closer to the experimental value $E_{\exp} = -(I_2 + I_3) \simeq -198$ eV. Further refinement can be achieved using the variational method, which minimizes the energy by incorporating an effective nuclear charge, Z_{eff}, accounting for the mutual shielding of the nucleus by the electrons. The effective wavefunction is given by:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{1s}(\boldsymbol{r}_1)\psi_{1s}(\boldsymbol{r}_2) = \frac{Z_{\text{eff}}^3}{\pi}e^{-Z_{\text{eff}}(r_1+r_2)}$$

From the helium-like hailtonian we compute the expected kinetic, potential and electron-electron interaction terms as:

$$\langle -\frac{1}{2}\nabla_1 \rangle = -\frac{1}{2}\int d^3\boldsymbol{r}_2 |\psi_{1s}(\boldsymbol{r}_2)|^2 \int d^3\boldsymbol{r}_1 \psi_{1s}^*(\boldsymbol{r}_1)\nabla_1^2 \psi_{1s}(\boldsymbol{r}_1) = \frac{Z_{\text{eff}}^2}{2}$$

$$\langle -\frac{Z}{r_1} \rangle = -\int d^3\boldsymbol{r}_2 |\psi_{1s}(\boldsymbol{r}_2)|^2 \int d^3\boldsymbol{r}_1 \frac{|\psi_{1s}(\boldsymbol{r}_2)|^2}{r_1} = -ZZ_{\text{eff}}$$

$$\langle \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \rangle = \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \frac{|\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)|^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{5}{8}Z_{\text{eff}}$$

Thus, the energy depends on the effective charge Z_{eff}, and minimizing it provides an approximation of the ground state.

$$E(Z_{\text{eff}}) = Z_{\text{eff}}^2 - 2ZZ_{\text{eff}} + \frac{5}{8}Z_{\text{eff}}$$

$$\min_{Z_{\text{eff}}}\{E(Z_{\text{eff}})\} \simeq -7.2 \text{ Ha} = -197 \text{ eV}$$

This result is very close to the experimental value of $E_{\exp} \simeq -198$ eV (Table 1).

Mean-field approach for $Li^+ + e^-$

In this second part, we focus on the study of the electron in the valence orbitals. To simplify the treatment of interactions between the valence electron and the electrons in the inner $|1s\rangle$ orbital, we adopt a mean-field approach. In this framework, we modify the usual hydrogen-like hamiltonian by introducing a perturbation term, Φ, which accounts for the shielding effect provided by the $|1s\rangle$ electrons. The shielding effect arises because the inner electrons partially reduce the nuclear attraction experienced by the valence electron, effectively altering its energy levels. The hydrogen-like radial wavefunction for the $|2s\rangle$ and $|2p\rangle$ electron and its perturbed hamiltonian can be expressed as follows:

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \Phi(\boldsymbol{r})$$

$$\psi_{2s}(\boldsymbol{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}}(2 - Zr)e^{-Z/2} \qquad \psi_{2p}(\boldsymbol{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}}Zre^{-Zr/2}\cos\theta$$

Proceeding as outlined previously, we begin by computing the expected values for the kinetic and potential energy terms to determine the zero-order energy of the system:

$$E^{(0)} = \langle -\frac{1}{2}\nabla^2 \rangle + \langle -\frac{Z}{r} \rangle = \frac{Z^2}{8} - \frac{Z^2}{4} = -\frac{1}{8}Z^2 \simeq -30 \text{ eV}$$

The zero-order energy is degenerate for both $|2s\rangle$ and $|2p\rangle$ states. Next, we introduce the perturbation term, Φ, which accounts for the electric potential generated by the charge density of the two inner-shell electrons. The charge density is given by $\rho(\boldsymbol{r}) = -2|\psi_{1s}(\boldsymbol{r})|^2$. Using the Poisson equation propagator, we compute the resulting potential as[1]:

$$\Phi(\boldsymbol{r}) = \int d^3\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} = \frac{1}{r}\left[(Zr + 1)e^{-2Zr} - 1\right]$$

The first-order energy correction is then given by the expectation value of $\langle\Phi\rangle$ with the unperturbed wavefunction $|2s\rangle$ and $|2p\rangle$.

$$\Delta E_{2s}^{(1)} = \langle 2s| \Phi |2s\rangle = \int d^3\boldsymbol{r}|\psi_{2s}(\boldsymbol{r})|^2\Phi(\boldsymbol{r}) = \frac{17}{81}Z \simeq 17.1 \text{ eV}$$

$$\Delta E_{2p}^{(1)} = \langle 2p| \Phi |2p\rangle = \int d^3\boldsymbol{r}|\psi_{2p}(\boldsymbol{r})|^2\Phi(\boldsymbol{r}) = \frac{59}{243}Z \simeq 19.8 \text{ eV}$$

As hoped, the first-order correction removes the degeneracy of the second orbital $n = 2$. However, the degeneracy among the magnetic quantum numbers m persists. This can be demonstrated through direct calculation, and is also evident from the fact that the difference between $\psi_{210}(\boldsymbol{r})$ and $\psi_{21\pm1}(\boldsymbol{r})$ is merely a factor of $\cos\theta$ and $\sin\theta e^{\pm i\varphi}$, which, when integrated over $\theta \in [0, \pi]$ and $\varphi \in [0, 2\pi]$, yields the same result.

Finally, we can calculate the energy difference between the $|2p\rangle$ and $|2s\rangle$ states:

$$E_{2p\rightarrow2s}^{(1)} = E_{2s}^{(1)} - E_{2p}^{(1)} = \Delta E_{2s}^{(1)} - \Delta E_{2p}^{(1)} = \frac{8}{243}Z \simeq 2.69 \text{ eV}$$

The corresponding wavelength is 461 nm. The result obtained using the perturbation method is of the same order of magnitude as the experimental value, $E_{2s\rightarrow2p,\text{ exp}} \simeq 1.85$ eV. Given the assumptions and approximations involved, this agreement is quite reasonable.

In the following section, we will attempt a second order calculation to assess whether we can further refine our results.

---

[1]These integrals are computed symbolically using the Python package `sympy`. The code is available on the following GitHub repository: https://github.com/AlessandroMiotto/LithiumAtom.

Second and third order perturbation method

To extend perturbation theory to higher-order terms, we express the hydrogen-like wave functions in a computational basis: $|1s\rangle = (1,0,0)^T$, $|2s\rangle = (0,1,0)^T$ and $|2p\rangle = (0,0,1)^T$. The last two states are degenerate and the system's Hamiltonian is given by:

$$H_0 = -\frac{Z^2}{2}|1s\rangle\langle 1s| - \frac{Z^2}{8}(|2s\rangle\langle 2s| - |2s\rangle\langle 2s|)$$

$$H = H_0 + \Phi = -\frac{Z^2}{8}\begin{pmatrix} 4 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \Phi$$

where Φ represents the perturbation matrix with elements $\Phi_{ij} = \langle i|\Phi|j\rangle$. To proceed with the perturbative corrections, we construct the projection operator onto the second orbital subspace $\Pi = |2s\rangle\langle 2s| + |2p\rangle\langle 2p|$ and the Moore-Penrose pseudoinverse $R = (-Z^2/8 - H_0)^{-1} = \frac{8}{3Z^2}|1s\rangle\langle 1s|$. Using these, we determine the energy correction Hamiltonians, whose eigenvalues provide the corresponding energy shifts:

$$H^{(1)} = \Pi\Phi\Pi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{17}{81}Z & 0 \\ 0 & 0 & \frac{59}{243}Z \end{pmatrix} \longrightarrow \begin{cases} \Delta E_{2s}^{(1)} \simeq 17.13 \text{ eV} \\ \Delta E_{2p}^{(1)} \simeq 19.82 \text{ eV} \end{cases}$$

$$H^{(2)} = \Pi\Phi R\Phi\Pi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0.0213 & 0 \\ 0 & 0 & 0 \end{pmatrix} \longrightarrow \begin{cases} \Delta E_{2s}^{(2)} \simeq 0.579 \text{ eV} \\ \Delta E_{2p}^{(2)} = 0.0 \text{ eV} \end{cases}$$

$$H^{(3)} = \Pi\Phi R\Phi R\Phi\Pi - \Pi\Phi\Pi\Phi R^2\Phi\Pi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{0.0236}{Z} & 0 \\ 0 & 0 & 0 \end{pmatrix} \longrightarrow \begin{cases} \Delta E_{2s}^{(3)} \simeq 0.214 \text{ eV} \\ \Delta E_{2p}^{(3)} = 0.0 \text{ eV} \end{cases}$$

From these calculations, the total energy difference between the $|2s\rangle$ and $|2p\rangle$ states after third-order corrections is $E_{2p\to 2s}^{(3)} = 1.894$ eV. This corresponds to a transition wavelength of 654.4 nm, achieving a discrepancy of only 2.5% from the experimental value. However, the calculated first ionization energy does not align well with experimental data. A summary of the results is presented in 1.

Variational method

Following an approach similar to that used for helium-like systems, we express the wavefunctions of the $|2s\rangle$ and $|2p\rangle$ states in terms of the effective nuclear charge $\mathcal{Z}$, which accounts for the shielding effect caused by the other electrons. The total energy of the system is then formulated as a function of $\mathcal{Z}$. Applying the variational method, we minimize this energy to obtain estimates for both the effective charges, $\mathcal{Z}_{2s}$ and $\mathcal{Z}_{2p}$, as well as the corresponding energy levels, E_{2s} and E_{2p}.

$$\psi_{2s}(\boldsymbol{r}) = \frac{\mathcal{Z}^{3/2}}{\sqrt{32\pi}}(2 - \mathcal{Z}r)e^{-\mathcal{Z}/2} \qquad \psi_{2p}(\boldsymbol{r}) = \frac{\mathcal{Z}^{3/2}}{\sqrt{32\pi}}\mathcal{Z}re^{-\mathcal{Z}r/2}\cos\theta$$

$$\text{Kinetic term: } \langle 2s| -\frac{1}{2}\nabla |2s\rangle = \langle 2p| -\frac{1}{2}\nabla_1 |2p\rangle = \frac{\mathcal{Z}^2}{8}$$

$$\text{Potential term: } \langle 2s| -\frac{Z}{r} |2s\rangle = \langle 2p| -\frac{Z}{r} |2p\rangle = -\frac{Z\mathcal{Z}}{4}$$

$$\text{Interaction term: } \langle 2s| \Phi |2s\rangle = \frac{34}{81}\mathcal{Z} \quad \text{and} \quad \langle 2p| \Phi |2p\rangle = \frac{118}{243}\mathcal{Z}$$

$$\mathcal{Z}_{2s} = \arg\min_{\mathcal{Z}} \left\{ \frac{\mathcal{Z}^2}{8} - \frac{Z\mathcal{Z}}{4} + \frac{17}{81}\mathcal{Z} \right\} = Z - \frac{68}{81} \simeq 2.16 \qquad E_{2s} \simeq -15.9 \text{ eV}$$

$$\mathcal{Z}_{2p} = \arg\min_{\mathcal{Z}} \left\{ \frac{\mathcal{Z}^2}{8} - \frac{Z\mathcal{Z}}{4} + \frac{59}{243}\mathcal{Z} \right\} = Z - \frac{234}{243} \simeq 2.04 \qquad E_{2p} \simeq -14.0 \text{ eV}$$
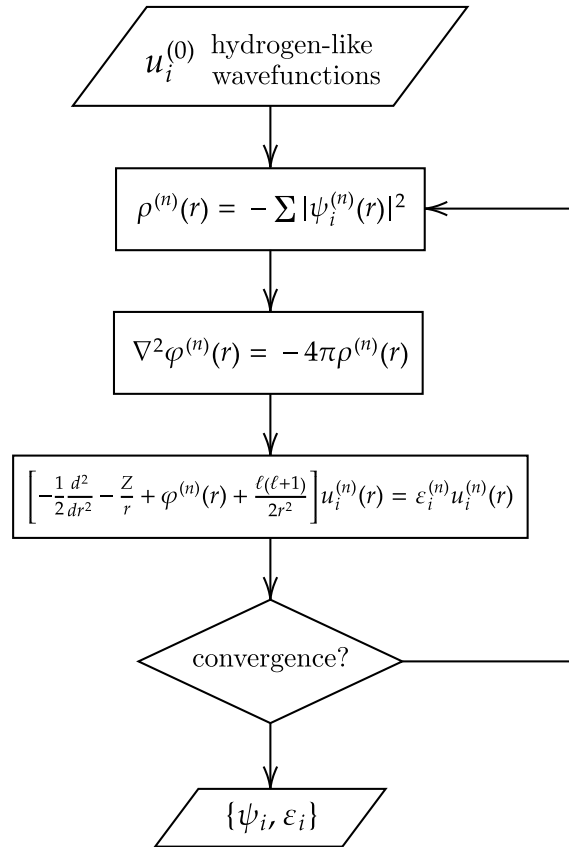
The variational method estimates the energy transition $|2p\rangle \to |2s\rangle$ in the lithium atom to be approximately 1.88 eV (corresponding to a wavelength of around 659 nm), which is close to the experimental value. However, similar to the perturbative approach, this result still exhibits a significant discrepancy in the estimation of the $|2s\rangle$ (first ionization energy) and $|2p\rangle$ state energy. A summary of the obtained results is presented in Table 1.

	pert. [eV]	var. [eV]	exp. [eV]
Excited state (2p)	10.792	14.000	3.5439
First Ionization (2s)	12.687	15.877	5.3917
Second Ionization	71.529	74.087	75.640
Third Ionization	122.45	122.45	122.45

Table 1: Ionization energy of lithium using variational an perturbative (third correction) method. The third ionization is exact because correspond to an hydrogen-like atom. Experimental data are from NIST Atomic Spectra Database [1].

Numerical approach[2]

Following the same approach as in the previous section, we use hydrogen-like wavefunctions as the starting point for our calculations. We perform a self-consistent iterative procedure in which, at each step, we compute the wavefunctions $u_i(\boldsymbol{r})$ and the corresponding energy levels ε_i for each state. These wavefunctions are then used to determine the electron charge density $\rho(\boldsymbol{r})$. Next, we solve the Poisson equation to obtain the mean-field electrostatic potential $\varphi(\boldsymbol{r})$ generated by the electrons. This potential is then incorporated to define an effective potential, which is used to refine the estimates of the wavefunctions and energy levels. The process is repeated until convergence is achieved.

$$u_i^{(0)} \quad \text{hydrogen-like wavefunctions}$$

$$\rho^{(n)}(r) = -\sum |\psi_i^{(n)}(r)|^2$$

$$\nabla^2 \varphi^{(n)}(r) = -4\pi \rho^{(n)}(r)$$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + \varphi^{(n)}(r) + \frac{\ell(\ell+1)}{2r^2} \right] u_i^{(n)}(r) = \varepsilon_i^{(n)} u_i^{(n)}(r)$$

convergence?

$$\{\psi_i, \varepsilon_i\}$$

This method represents a simplified version of more advanced self-consistent approaches for many-body systems, such as the Hartree-Fock method and Density Functional Theory.

Numerical solution of the radial equation

To solve the radial Schrödinger equation, we employ the finite difference method, discretizing the radial coordinate on a uniformly spaced grid with step size dr. In this framework, the radial Hamiltonian is represented as a tridiagonal matrix, which eigen-equation can be solved efficiently using numerical techniques.

$$-\frac{1}{2}\frac{u_{i-1} - 2u_i + u_{i+1}}{dr^2} + V_{\text{eff}}(r_i)u_i = \varepsilon_i u_i \quad \longrightarrow \quad \sum_j H_{ij}u_i = \varepsilon_i u_i$$

For an atomic system, the wavefunction must satisfy $u(0) = 0$ at the origin, and $u(R) = 0$ at a large radius R to ensure the wavefunction exponential decay at infinity. The computation for some $\ell = 0$ orbitals are plotted in Figure 1.

Using a logarithmic grid can yield more accurate results because the grid points are more densely distributed near the nucleus, where the wavefunction varies more rapidly. To further improve the accuracy of the solution, we could employ the Numerov method which is designed for second-order differential equations. Unlike the standard finite difference method, the Numerov method incorporates higher-order terms, reducing numerical errors and improving stability.
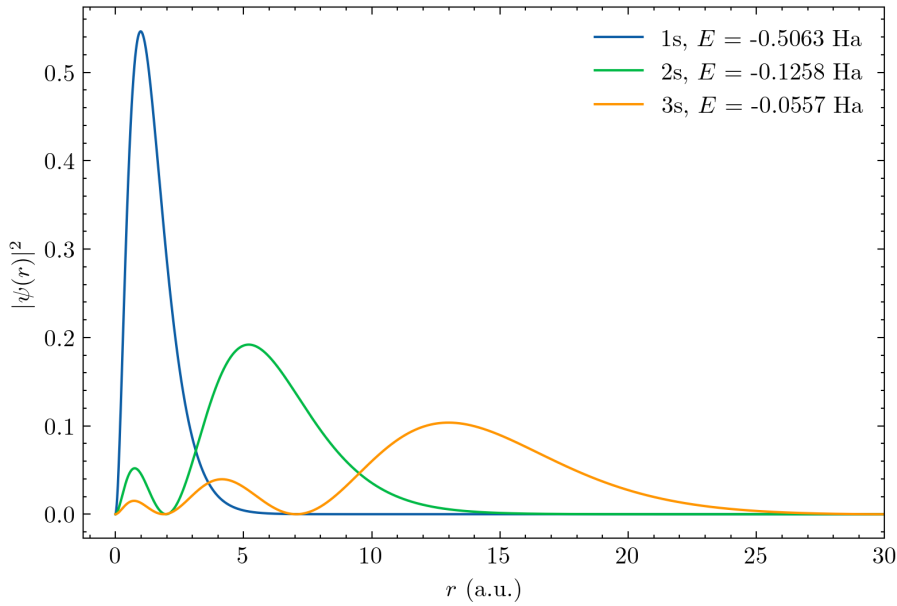

Figure 1: Probability density functions for the levels $|1s\rangle$, $|2s\rangle$ and $|3s\rangle$ of an hydrogen-like atom computed numerically. In the legend the energy (in Hartree) of the levels.

Numerical solution of the Poisson equation

As before, we discretize the Poisson equation $\nabla^2\Phi = -4\pi\rho$. In one dimension, using a uniform grid with step size dr, the Laplacian operator can be approximated using a second-order finite difference scheme:

$$\frac{\Phi_{i-1} - 2\Phi_i + \Phi_{i+1}}{dr^2} = -4\pi\rho_i \quad \longrightarrow \quad \sum_j D_{ij}\Phi_i = -4\pi\rho_i$$

this leads to a system of linear equations that can be expressed in matrix form as $D\boldsymbol{\Phi} = -4\pi\boldsymbol{\rho}$. For an atomic system, the potential Φ is required to be finite at the origin and to vanish at large distances. This is enforced through a Neumann boundary condition at $r = 0$, ensuring $d\Phi/dr|_{r=0} = 0$ to avoid singularities at the nucleus, and by setting $\Phi(R) = 0$ at a sufficiently large cutoff radius R, reflecting the decay of the potential. By solving this linear system, we obtain the electrostatic potential Φ, which can then be used to determine the mean-field interaction in the self-consistent procedure.

Due to time constraints, I was unable to complete all the code. However, I successfully solved the radial equation for $\ell = 0$ and the charge density. Based on these results, I attempted to calculate the energy of the $|2s\rangle$ orbital using the analytical $\Phi(r)$ as potential. This calculation yielded an energy for $|2s\rangle$ in a range between -6 eV and -3 eV with a strong dependence with the grid. This suggests that the method performs poorly and requires further refinement (such as implementing the Numerov method and a logarithmic grid) to obtain more reliable results.

References

[1]   A. Kramida et al. NIST Atomic Spectra Database (ver. 5.12). National Institute of Standards and Technology, Gaithersburg, MD. 2024. URL: https://physics.nist.gov/asd.

[2]   J. J. Sakurai and Jim Napolitano. *Modern Quantum Mechanics*. 3rd ed. Cambridge University Press, 2020.