Assignment 5

Problem 1

The wave function of the $3p_z$ atomic orbital in spherical polar coordinates is given by:

$$\psi_{3p_z}(r,\theta,\phi) = R_{31}(r)Y_{10}(\theta,\phi)$$

where $R_{31}(r)$ is the radial part:

$$R_{31}(r) = \frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2} \rho\,(6-\rho)\,e^{-\rho/3}, \qquad \rho = \frac{Zr}{a_0},$$

and $Y_{10}(\theta,\phi)$ the angular part (spherical harmonic):

$$Y_{10}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta.$$

(a) Write a Python function that computes the ψ_{3p_z} wave function for the hydrogen atom for given values of the radius r and polar angle θ. Use atomic units, where the Bohr radius $a_0 = 1$.

(b) Plot the radial wave function $R_{31}(r)$ for $r \in [0, 25]$ Bohr, and create a 2D contour plot of ψ_{3p_z} in the xz-plane for $x, z \in [-15, 15]$ Bohr. How many radial nodes can you identify? Compare with the number of radial nodes obtained using the formula $n - l - 1$, where n and l are the principal and angular momentum quantum numbers, respectively. *Note*: the point at $r = 0$ is not considered a node.

Hint: For the 2D plot, convert Cartesian to spherical coordinates using

$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \arccos\left(\frac{z}{r}\right).$$

(c) Find the approximate location of the radial node between $r = 2.5$ and 7.5 Bohr using the bisection and the Newton-Raphson methods. Use $[2.5, 7.5]$ Bohr as the initial interval for the bisection method and $r_0 = 2.5$ Bohr as the initial guess for the Newton method.

(d) For each method, save the error at each iteration (*for the bisection method it is best to take the length of the interval as the error*). Then, plot the error ϵ_i versus the iteration number using a logarithmic scale for the y-axis and create a log-log plot of ϵ_{i+1} versus ϵ_i. Roughly estimate the slope for each method from the log-log plot. The slope is the *order of convergence*, which measures the rate of convergence of the algorithm. Comment on the differences between the two methods.

Hint: To set the log scale in Matplotlib use `plt.xscale('log')`/`plt.yscale('log')`.

(e) Find the approximate location of the maximum along r using the Newton-Raphson method with an initial guess of $r_0 = 1$ Bohr. What happens if you use $r_0 = 7$ Bohr? Comment.

Problem 2

The paiwise Lennard-Jones potential can be used to model the interatomic interactions of noble-gas atoms. The Lennard-Jones interaction energy between atoms is given by:

$$E_{LJ} = \sum_{i=1}^{N} \sum_{j>i}^{N} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

where N is the number of atoms and r_{ij} the distance between atoms i and j. The positive r^{-12} term describes the repulsive part of the potential, while the negative r^{-6} term describes the attractive part.

(a) Create a Python class called `Atoms` that represents a cluster of atoms with attribute the (x, y, z) coordinates of the atoms in the cluster (NumPy array). Include a `set_positions` method to update the atom positions and a `get_pairwise_distances` method that computes and returns a vector of pairwise distances between all atoms.

(b) Create a `LennardJonesCalculator` class that computes the Lennard-Jones energy of the cluster of atoms with attributes `epsilon` and `sigma`. The class should have a `calculate_energy` method that takes the `Atoms` object and returns the total Lennard-Jones energy.

(c) Calculate the energy of the following two configurations (atomic coordinates in Å) of a cluster of four Ar atoms ($\epsilon = 8.0$ meV and $\sigma = 3.54$ Å).
Linear chain:

$$\texttt{positions} = \begin{bmatrix} 0.0 & 0.0 & 0.0 \\ 4.0 & 0.0 & 0.0 \\ 8.0 & 0.0 & 0.0 \\ 12.0 & 0.0 & 0.0 \end{bmatrix}$$

Square arrangement:

$$\texttt{positions} = \begin{bmatrix} 0.0 & 0.0 & 0.0 \\ 4.0 & 0.0 & 0.0 \\ 0.0 & 4.0 & 0.0 \\ 4.0 & 4.0 & 0.0 \end{bmatrix}$$

Which configuration has the lowest energy?