

Visualization of the hydrogen atom orbitals

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Introduction

The orbitals of the hydrogen atom are visualized using the wave equations obtained from analytical solution of the Schrödinger equation.

Model equations

The three-dimensional time independent Schrödinger equation for the hydrogen atom is:

$$E\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{k_p}{r}\psi \quad (1)$$

Where \hbar is a constant, μ the particle mass, k_p a constant depending on the charge of the electron, r the radial coordinate, ψ the wave equation and E the associated energy. Expanding the Laplacian in (1) in spherical coordinates gives:

$$E\psi = -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin(\phi)} \frac{\partial}{\partial \phi} \left(\sin(\phi) \frac{\partial \psi}{\partial \phi} \right) + \frac{1}{r^2 \sin^2(\phi)} \frac{\partial^2 \psi}{\partial \theta^2} \right] - \frac{k_p}{r} \psi \quad (2)$$

Where ϕ is the polar angle and θ the azimuthal angle. Note that often θ is used instead of ϕ to denote the polar angle and similarly ϕ is used to denote the azimuthal angle, which is the opposite convention used here. The boundary conditions of the system are $\psi = 0$ at $r = 0$ and as r grows large.

Analytical solution of equation (2) produces three quantum numbers n , l and m where n is the principal quantum number, l is the azimuthal quantum number and m is the magnetic quantum number. The resulting wave equations depend on these quantum numbers in addition to the spatial coordinates r , θ and ϕ . The wave equations are:

$$\psi_{nlm}(r, \theta, \phi) = C e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) e^{im\theta} P_l^m(\cos \phi) \quad (3)$$

Where C is a normalization constant, $\rho = \frac{2r}{na_0}$ with a_0 the reduced Bohr radius, $L_{n-l-1}^{2l+1}(\rho)$ is the generalized Laguerre polynomial, i the imaginary number and $P_l^m(\cos \phi)$ the associated Legendre polynomial. The normalization constant is obtained by integrating the product of ψ , as given by (3), and its complex conjugate ψ^* over the domain V , equating the integral with 1 and solving for C :

$$1 = \int_V \psi \psi^* dV \quad (4)$$

The generalized Laguerre polynomials are given by the following recurrence relation:

$$L_k^\alpha(x) = \frac{2k-1+\alpha-x}{k} L_{k-1}^\alpha(x) - \frac{k-1+\alpha}{k} L_{k-2}^\alpha(x) \quad (5)$$

Where α and k are integers and x is the independent variable. The first two Laguerre polynomials, which form the base cases for the recurrence relation, are:

$$L_0^\alpha(x) = 1 \quad (6)$$

$$L_1^\alpha(x) = 1 + \alpha - x \quad (7)$$

The associated Legendre polynomials are computed using the following relation:

$$P_l^m(x) = (-1)^m (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_l(x) \quad (8)$$

With $P_l(x)$ the Legendre polynomial, which can be computed using the Rodrigues formula:

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \quad (9)$$

Equation (9) can be expanded to:

$$P_l(x) = \frac{1}{2^l} \sum_{k=0}^{\lfloor l/2 \rfloor} \frac{(-1)^k (2l - 2k)!}{k! (l - k)! (l - 2k)!} x^{l-2k} \quad (10)$$

Should the magnetic quantum number m be negative the associated Legendre polynomial is computed using:

$$P_l^{-|m|}(x) = (-1)^m \frac{(l - |m|)!}{(l + |m|)!} P_l^{|m|}(x) \quad (11)$$

Numerical verification

To verify that the wave functions ψ_{nlm} are solutions to the Schrödinger equation it is checked that the wave functions satisfy the discrete form of (2):

$$\begin{aligned} E\psi_{i,j,k} = & -\frac{\hbar^2}{2\mu} \left(r_{i+1}^2 \frac{\psi_{i+1,j,k} - \psi_{i,j,k}}{r_{i+\frac{1}{2}}^2 \Delta r^2} - r_i^2 \frac{\psi_{i,j,k} - \psi_{i-1,j,k}}{r_{i+\frac{1}{2}}^2 \Delta r^2} \right) + \\ & -\frac{\hbar^2}{2\mu} \left(\frac{\psi_{i,j+1,k} - \psi_{i,j,k}}{r_{i+\frac{1}{2}}^2 \sin^2(\phi_{k+\frac{1}{2}}) \Delta \theta^2} - \frac{\psi_{i,j,k} - \psi_{i,j-1,k}}{r_{i+\frac{1}{2}}^2 \sin^2(\phi_{k+\frac{1}{2}}) \Delta \theta^2} \right) + \\ & -\frac{\hbar^2}{2\mu} \left(\sin(\phi_{k+1}) \frac{\psi_{i,j,k+1} - \psi_{i,j,k}}{r_{i+\frac{1}{2}}^2 \sin(\phi_{k+\frac{1}{2}}) \Delta \phi^2} - \sin(\phi_k) \frac{\psi_{i,j,k} - \psi_{i,j,k-1}}{r_{i+\frac{1}{2}}^2 \sin(\phi_{k+\frac{1}{2}}) \Delta \phi^2} \right) - \frac{k_p}{r_{i+\frac{1}{2}}} \psi_{i,j,k} \end{aligned} \quad (12)$$

Where the indexes i , j and k denote node i in the radial r direction, node j in the θ direction and node k in the ϕ direction, respectively. The associated energies of the orbitals are:

$$E = \frac{k_e}{n^2} \quad (13)$$

Where k_e is a constant depending on, among other parameters, the charge of an electron. Plugging the wave functions into (12) shows that the wave equations satisfy (12) within 1 %.

Visualization

The probability density is computed for various values of the quantum numbers n , l and m . Results are shown in figures 1 to 7. Note that some regions in the graphs are colored white when they should be colored dark blue (or dark red for figures 6 and 7), corresponding to $\psi^2 = 0$. The graphs represent cross-sections at $\theta = 0$.

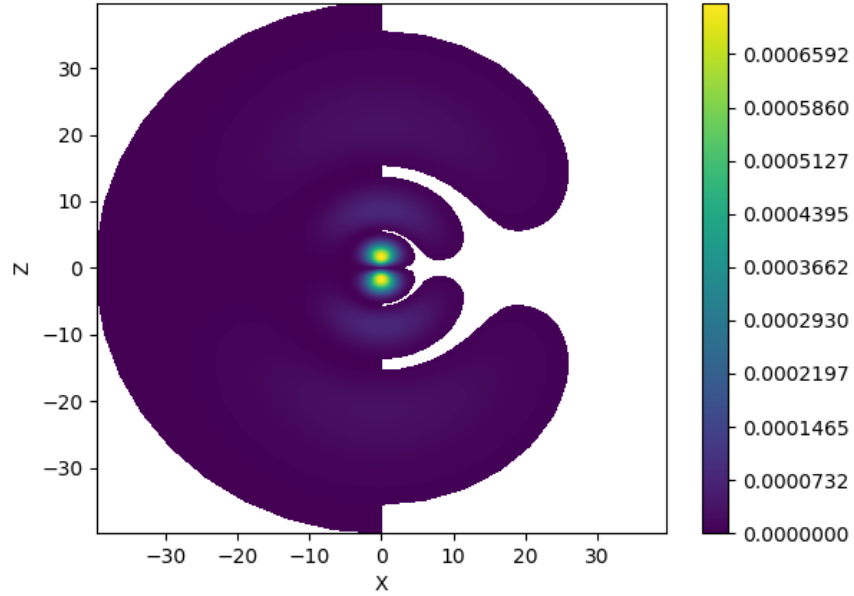


Figure 1: Probability density ψ_{410}^2 of the 410 or $4p_0$ orbital.

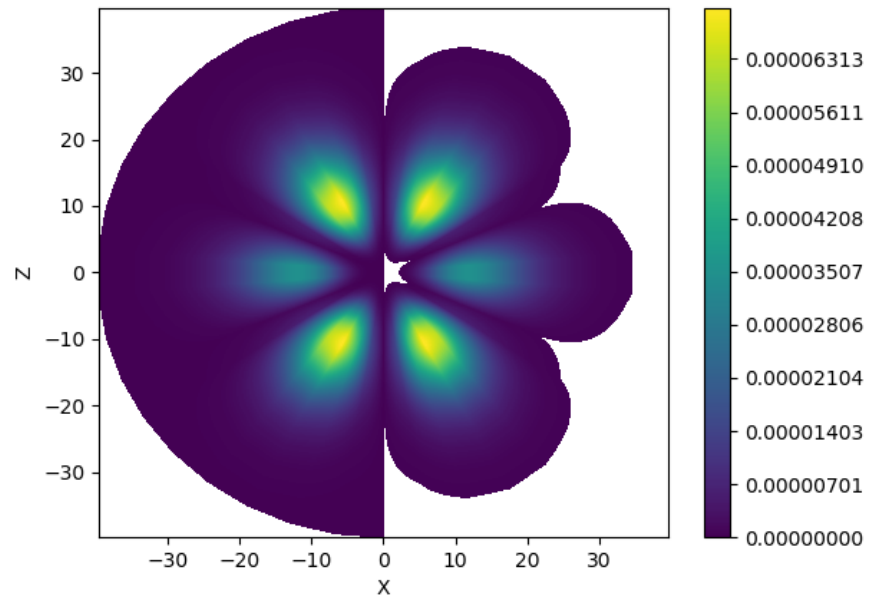


Figure 2: Probability density ψ_{431}^2 of the 431 or $4f_1$ orbital.

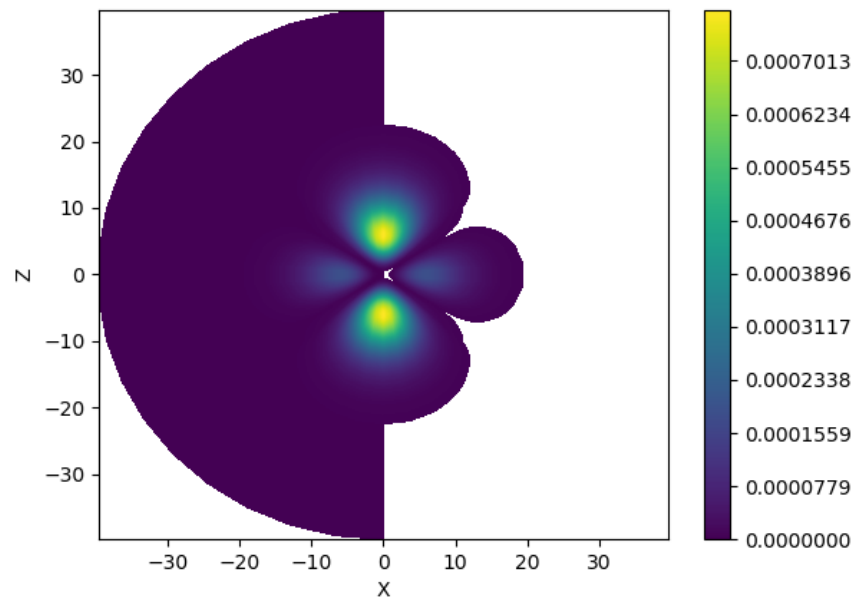


Figure 3: Probability density ψ_{320}^2 of the 320 or $3d_0$ orbital.

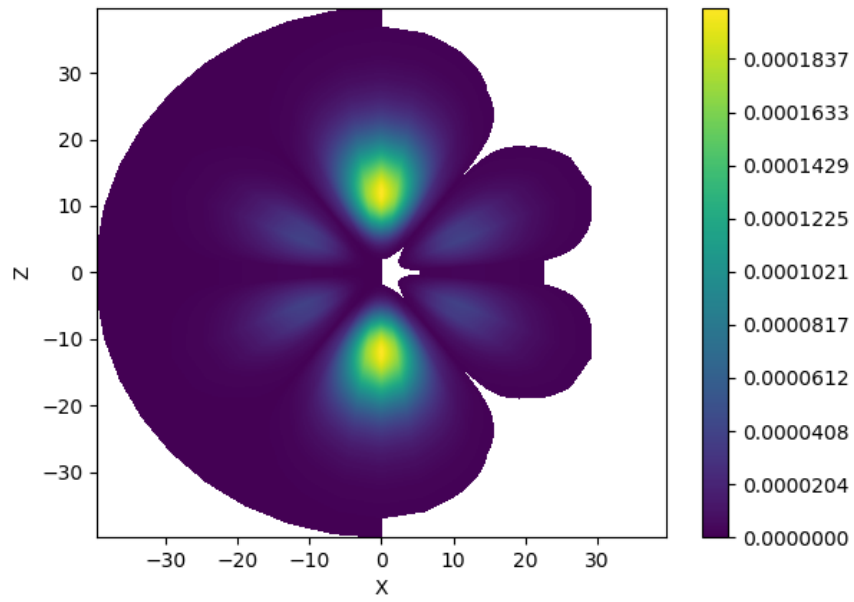


Figure 4: Probability density ψ_{430}^2 of the 430 or $4f_0$ orbital.

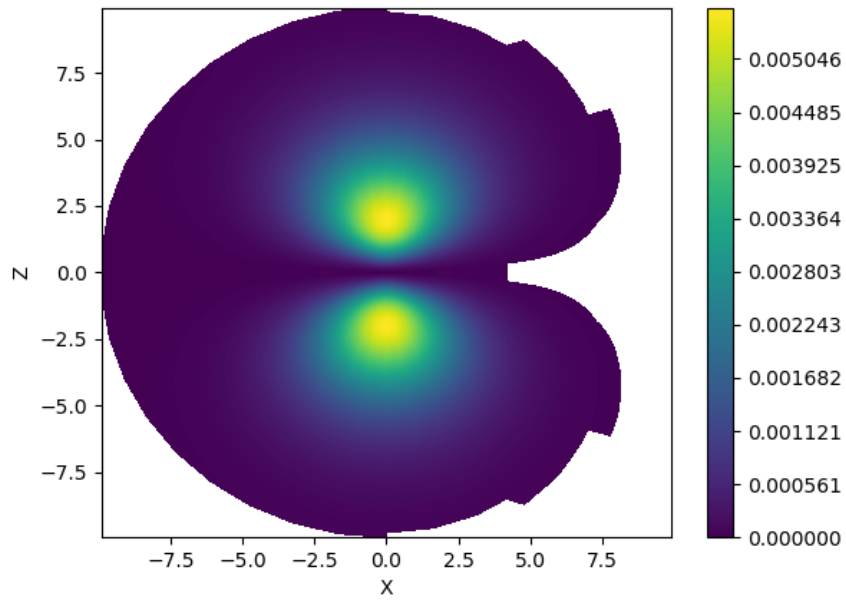


Figure 5: Probability density ψ_{210}^2 of the 210 or $2p_0$ orbital.

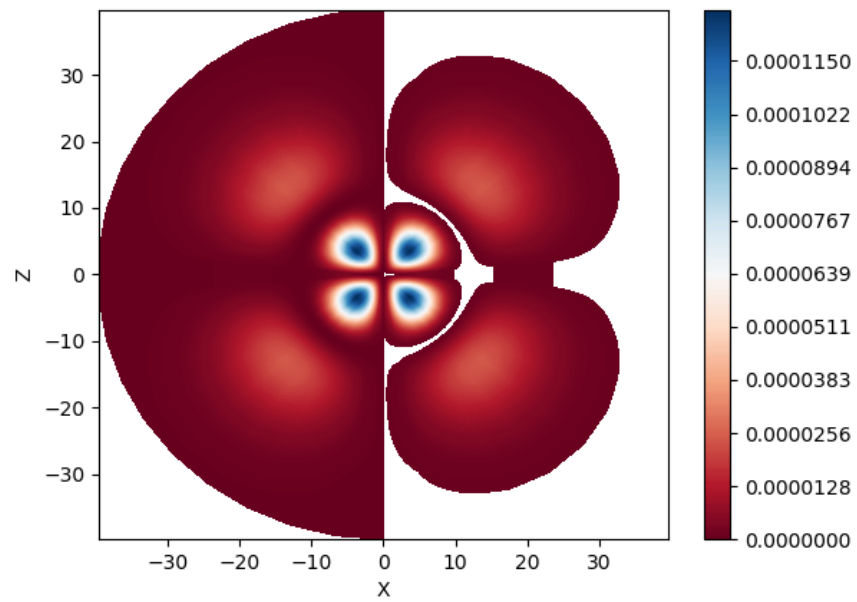


Figure 6: Probability density ψ_{421}^2 of the 421 or 4d₁ orbital.

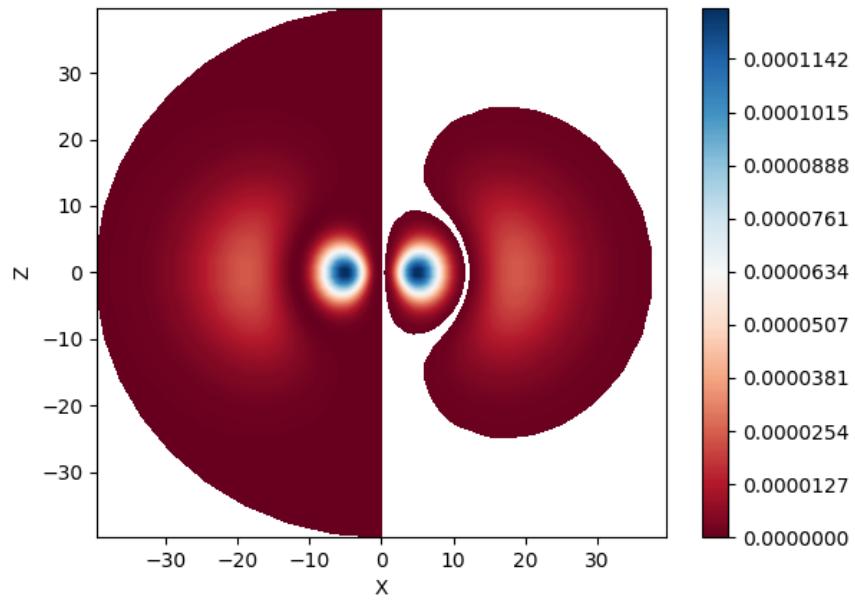


Figure 7: Probability density ψ_{422}^2 of the 422 or $4d_2$ orbital.