

# 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,  $\mu$  the particle mass,  $k_p$  a constant depending on the charge of the electron,  $r$  the radial coordinate,  $\psi$  the wave equation and  $E$  the associated energy. The associated energies of the orbits are:

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

Where  $k_e$  is also a constant depending on the charge of an electron. Expanding the Laplacian in (1) in spherical coordinates gives:

$$E\psi = -\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin(\phi)} \frac{\partial}{\partial \phi} \left( \sin(\phi) \frac{\partial \psi}{\partial \phi} \right) + \frac{1}{r^2 \sin^2(\phi)} \frac{\partial^2 \psi}{\partial \theta^2} \right] - \frac{k_p}{r} \psi \quad (3)$$

Where  $\phi$  is the polar angle and  $\theta$  the azimuthal angle. Note that often  $\theta$  is used instead of  $\phi$  to denote the polar angle and similarly  $\phi$  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 (3) 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  $r$ ,  $\theta$  and  $\phi$ . The wave equations are:

$$\psi_{nlm}(r, \theta, \phi) = C e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) e^{im\theta} P_l^m(\cos \phi) \quad (4)$$

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  $\psi$ , as given by (4), and its complex conjugate  $\psi^*$  over the domain  $V$ , equating the integral with 1 and solving for  $C$ :

$$1 = \int_V \psi \psi^* dV \quad (5)$$

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

$$L_k^\alpha(x) = \frac{2k-1+\alpha-x}{k} L_{k-1}^\alpha(x) - \frac{k-1+\alpha}{k} L_{k-2}^\alpha(x) \quad (6)$$

Where  $\alpha$  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:

$$L_0^\alpha(x) = 1 \quad (7)$$

$$L_1^\alpha(x) = 1 + \alpha - x \quad (8)$$

The associated Legendre polynomials are computed using the following relation:

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

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

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \quad (10)$$

Equation (10) can be expanded to:

$$P_l(x) = \frac{1}{2^l} \sum_{k=0}^{\lfloor l/2 \rfloor} \frac{(-1)^k (2l-2k)!}{k! (l-k)! (l-2k)!} x^{l-2k} \quad (11)$$

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

$$P_l^{-|m|}(x) = (-1)^m \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(x) \quad (12)$$

## Numerical verification

To verify that the wave functions  $\psi_{nlm}$  are solutions to the Schrödinger equation it is checked that the wave functions satisfy the discrete form of (3):

$$\begin{aligned} E\psi_{i,j,k} = & -\frac{\hbar^2}{2\mu} \left( r_{i+1}^2 \frac{\psi_{i+1,j,k} - \psi_{i,j,k}}{r_{i+\frac{1}{2}}^2 \Delta r^2} - r_i^2 \frac{\psi_{i,j,k} - \psi_{i-1,j,k}}{r_{i+\frac{1}{2}}^2 \Delta r^2} \right) + \\ & -\frac{\hbar^2}{2\mu} \left( \frac{\psi_{i,j+1,k} - \psi_{i,j,k}}{r_{i+\frac{1}{2}}^2 \sin^2(\phi_{k+\frac{1}{2}}) \Delta \theta^2} - \frac{\psi_{i,j,k} - \psi_{i,j-1,k}}{r_{i+\frac{1}{2}}^2 \sin^2(\phi_{k+\frac{1}{2}}) \Delta \theta^2} \right) + \\ & -\frac{\hbar^2}{2\mu} \left( \sin(\phi_{k+1}) \frac{\psi_{i,j,k+1} - \psi_{i,j,k}}{r_{i+\frac{1}{2}}^2 \sin(\phi_{k+\frac{1}{2}}) \Delta \phi^2} - \sin(\phi_k) \frac{\psi_{i,j,k} - \psi_{i,j,k-1}}{r_{i+\frac{1}{2}}^2 \sin(\phi_{k+\frac{1}{2}}) \Delta \phi^2} \right) - \frac{k_p}{r_{i+\frac{1}{2}}} \psi_{i,j,k} \end{aligned} \quad (13)$$

Where the indexes  $i$ ,  $j$ ,  $k$  and  $p$  denote node  $i$  in the radial  $r$  direction, node  $j$  in the  $\theta$  direction, node  $k$  in the  $\phi$  direction and the timestep, respectively. Analysis shows that the wave equations satisfy (13) 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  $\theta = 0$ .

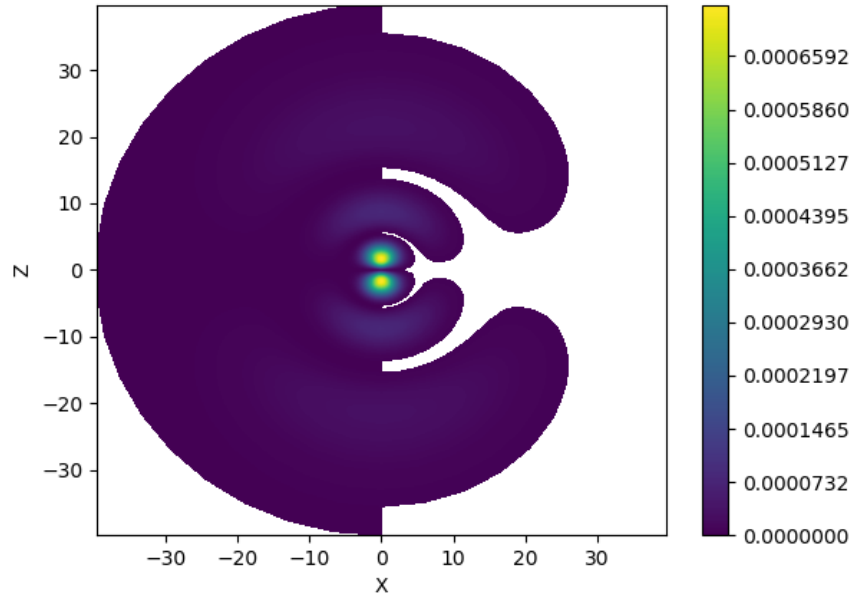


Figure 1: Probability density  $\psi^2_{410}$  of the 410 or  $4p_0$  orbital.

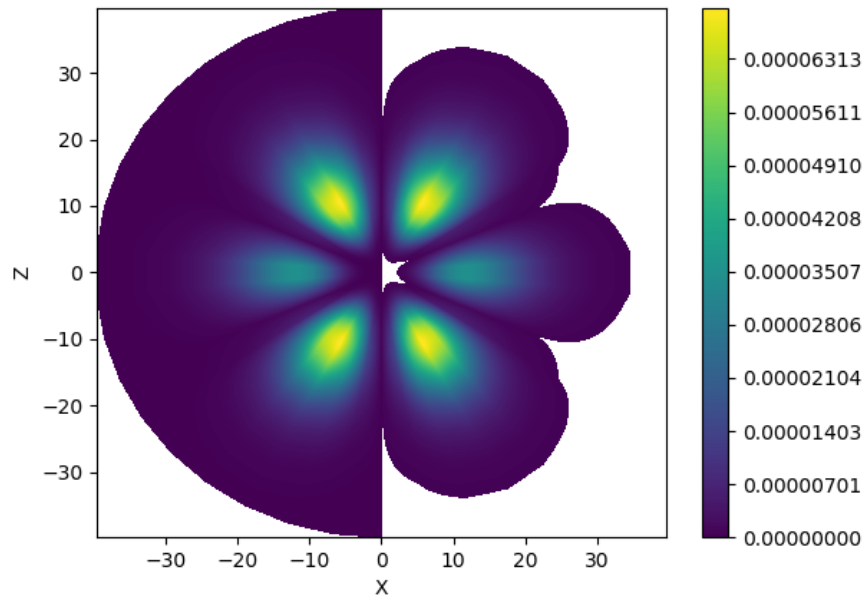


Figure 2: Probability density  $\psi_{431}^2$  of the 431 or  $4f_1$  orbital.

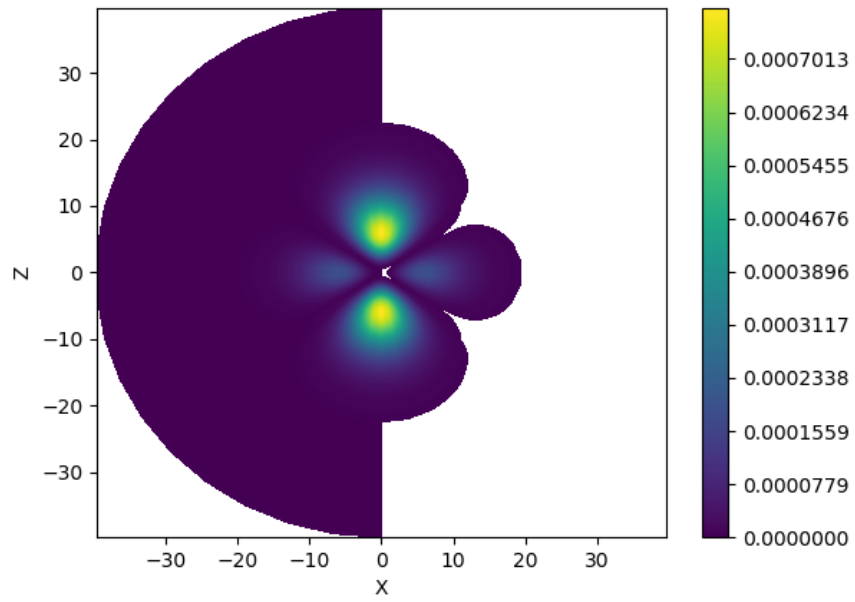


Figure 3: Probability density  $\psi_{320}^2$  of the 320 or  $3d_0$  orbital.

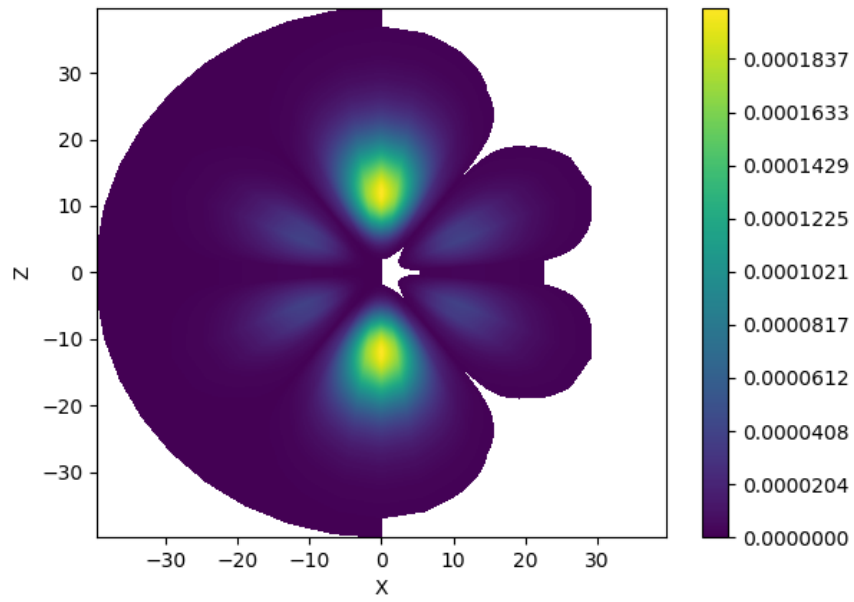


Figure 4: Probability density  $\psi_{430}^2$  of the 430 or  $4f_0$  orbital.

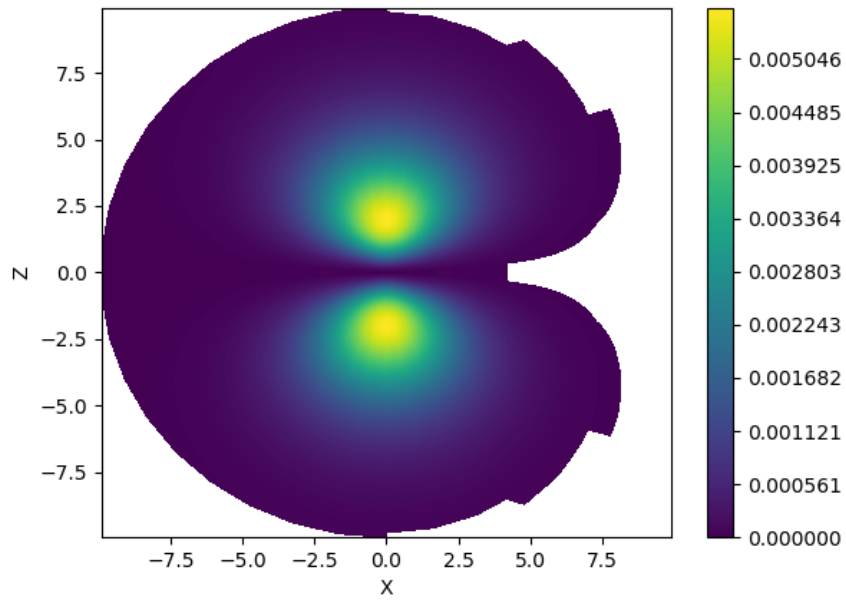


Figure 5: Probability density  $\psi_{210}^2$  of the 210 or  $2p_0$  orbital.



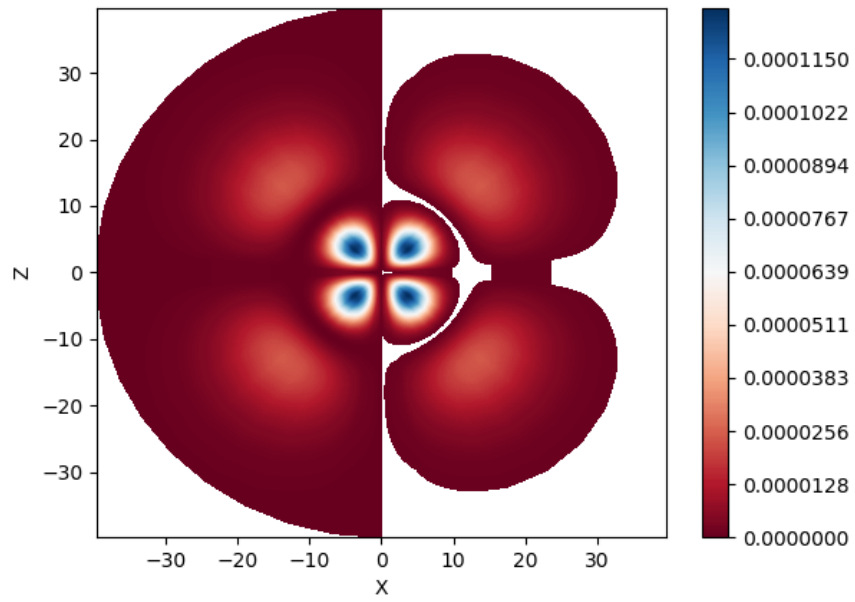


Figure 6: Probability density  $\psi_{421}^2$  of the 421 or 4d<sub>1</sub> orbital.

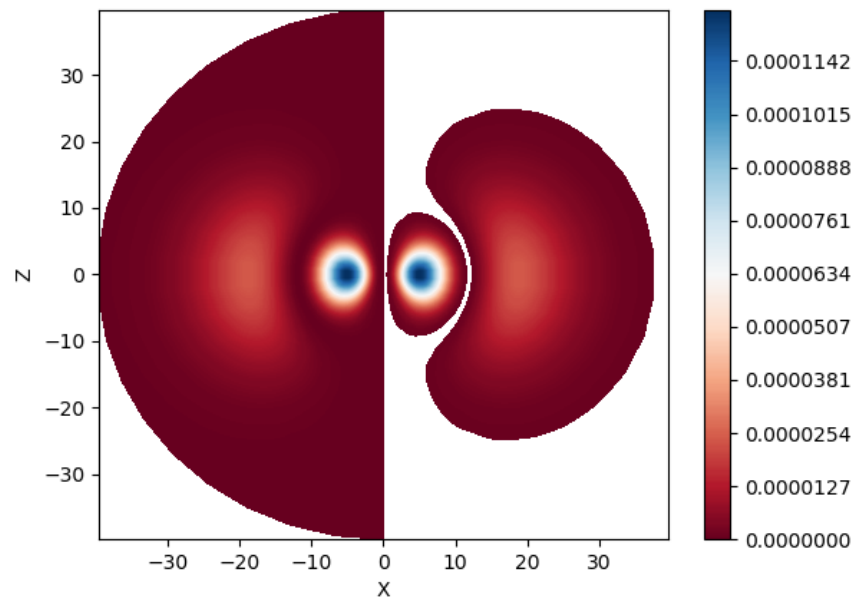


Figure 7: Probability density  $\psi_{422}^2$  of the 422 or  $4d_2$  orbital.