Visualization of the hydrogen atom orbitals

Derek W. Harrison

February 3, 2021

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:

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

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:

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

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:

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

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:

$$1 = \int_V \psi\psi^* dV \tag{4}$$

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

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

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:

$$L_0^\alpha(x) = 1 \tag{6}$$

$$L_1^\alpha(x) = 1 + \alpha - x \tag{7}$$

The associated Legendre polynomials are computed using the following relation:

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

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

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

Equation (9) can be expanded to:

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

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

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

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):

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

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

$$E = \frac{k_e}{n^2} \tag{13}$$

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 $\theta = 0$.

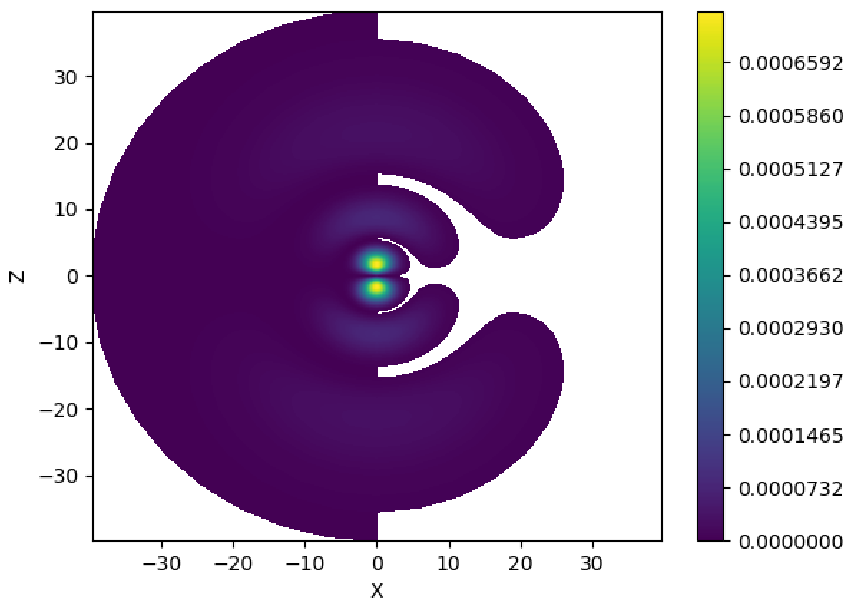

Figure 1: Probability density ψ_{410}^2 of the 410 or $4p_0$ orbital.

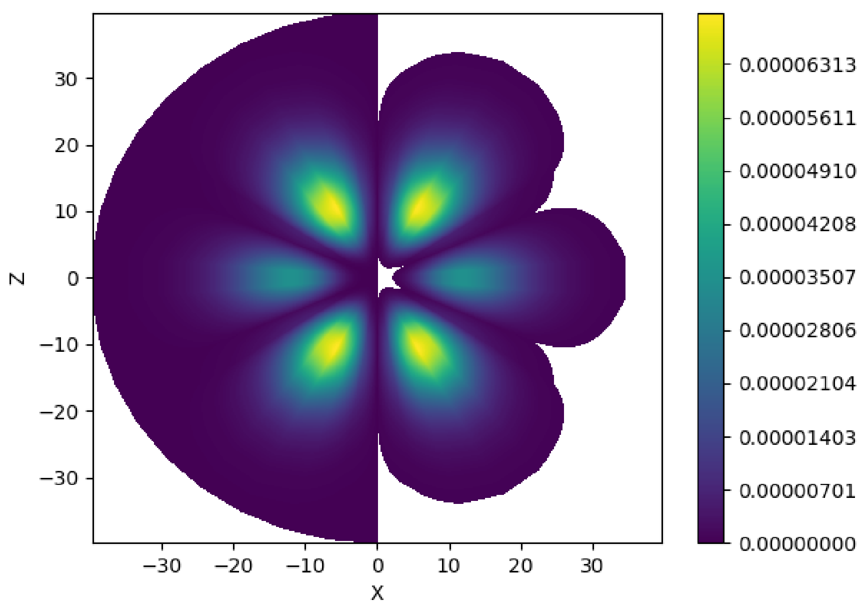

Figure 2: Probability density ψ_{431}^2 of the 431 or $4f_1$ orbital.

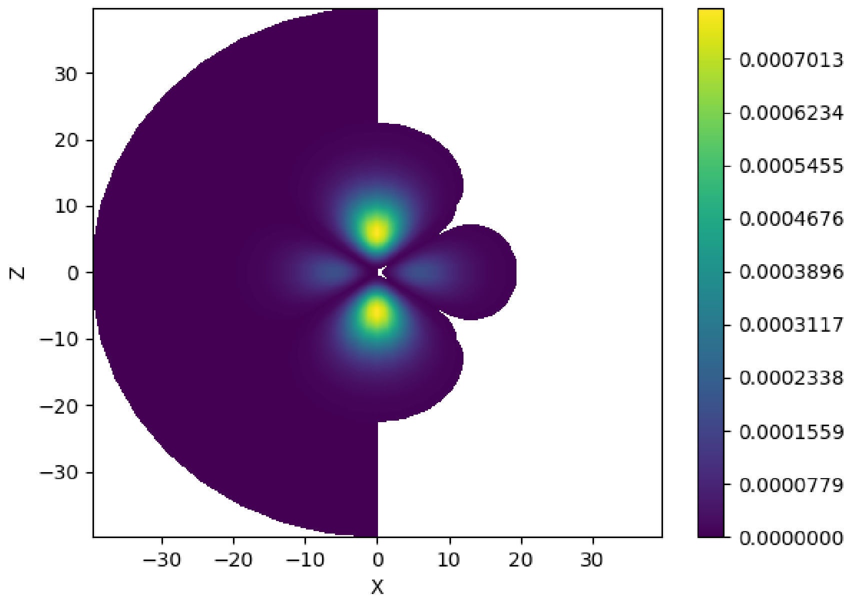

Figure 3: Probability density ψ_{320}^2 of the 320 or $3d_0$ orbital.

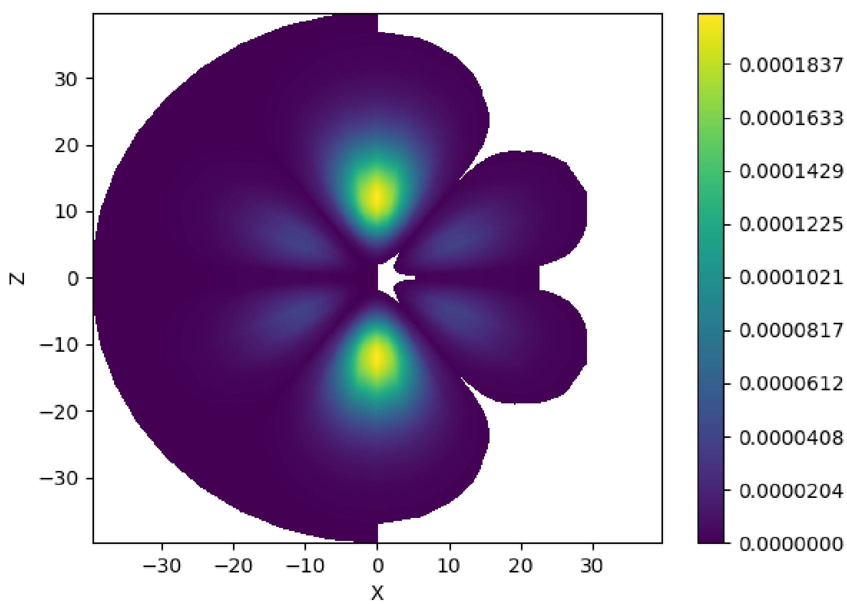

Figure 4: Probability density ψ_{430}^2 of the 430 or $4f_0$ orbital.

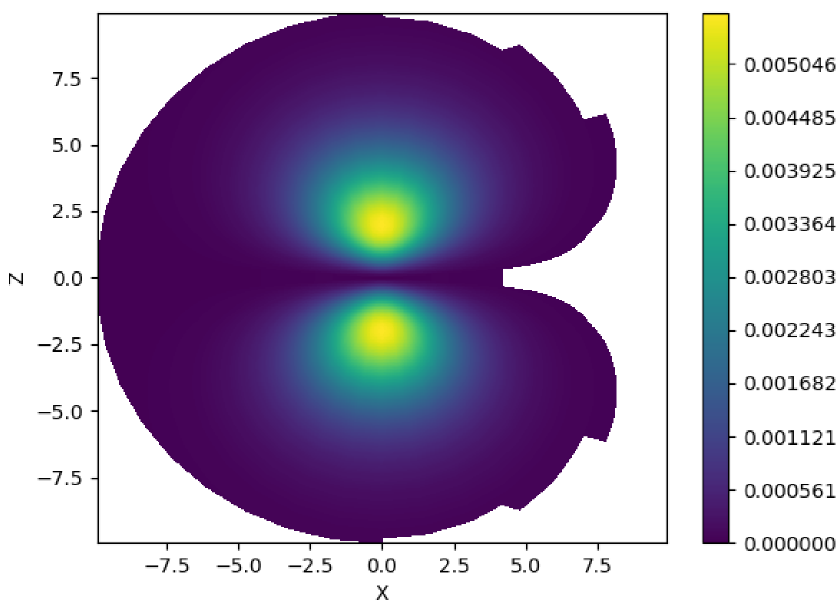

Figure 5: Probability density ψ_{210}^2 of the 210 or $2p_0$ orbital.

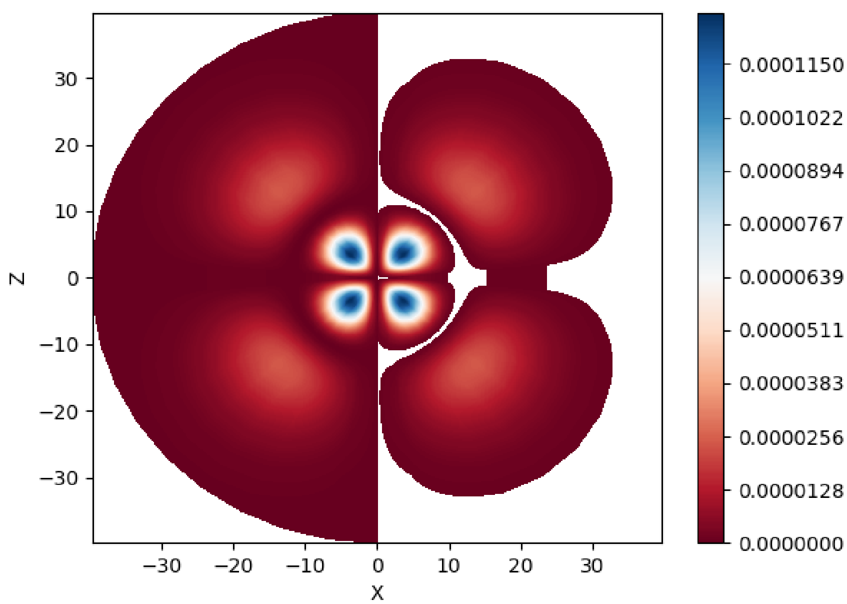

Figure 6: Probability density ψ^2_{421} of the 421 or $4d_1$ orbital.

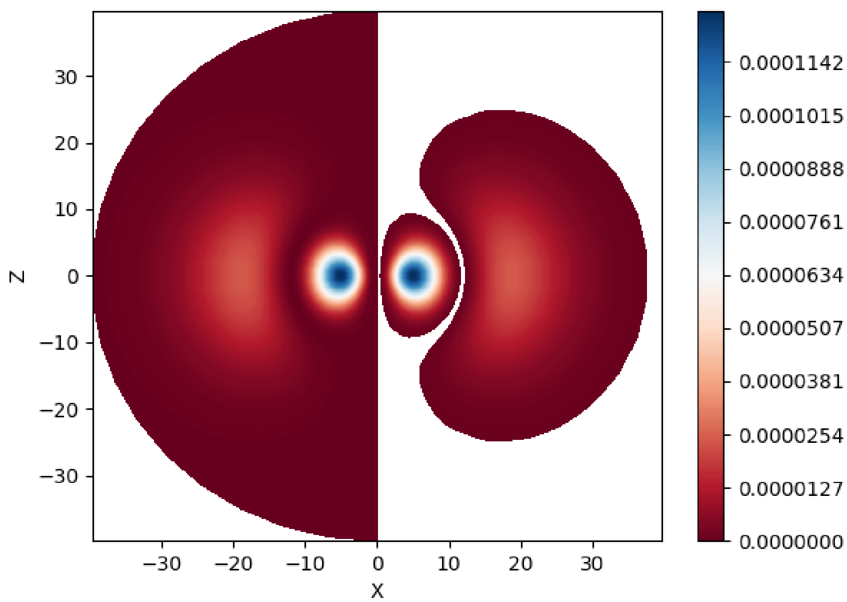

Figure 7: Probability density ψ^2_{422} of the 422 or $4d_2$ orbital.