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 for the hydrogen atom.

Model equations

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

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

Where $\hbar$ is a constant, m the particle mass, k 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:

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

Where ϕ is the angle between the direction vector $\mathbf{r}$ and the z axis and θ the angle between the projection of $\mathbf{r}$ onto the xy plane and the x axis. The boundary conditions of the system are $\psi = 0$ at $r = 0$ and at $r = R$ with R the length of the domain in the r direction.

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:

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

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, setting the integral to 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:

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

Visualization

The probability density is computed for various values of the quantum numbers n, l and m. Results are shown in figures 1 to 5. Note that some regions in the graphs are colored white when they should be colored dark blue, corresponding to $\psi^2 = 0$. The graphs represent cross-sections at $\theta = 0$.

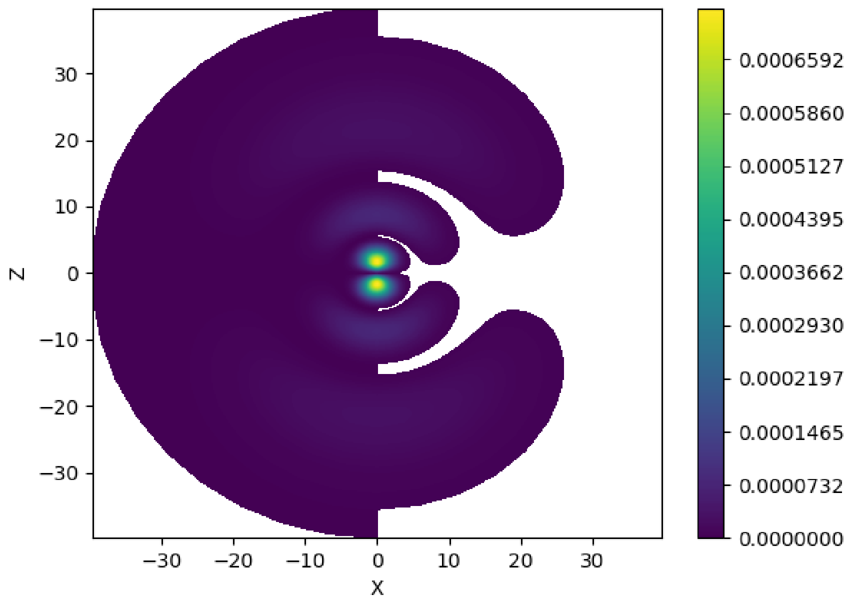

Figure 1: 410 or $4p_z$ orbital

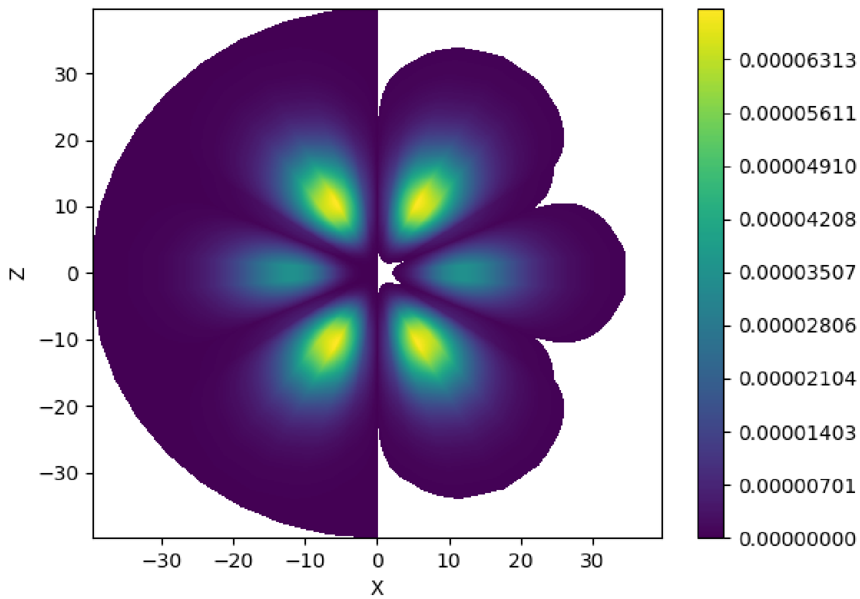

Figure 2: 431 or $4f_{xz^2}$ orbital

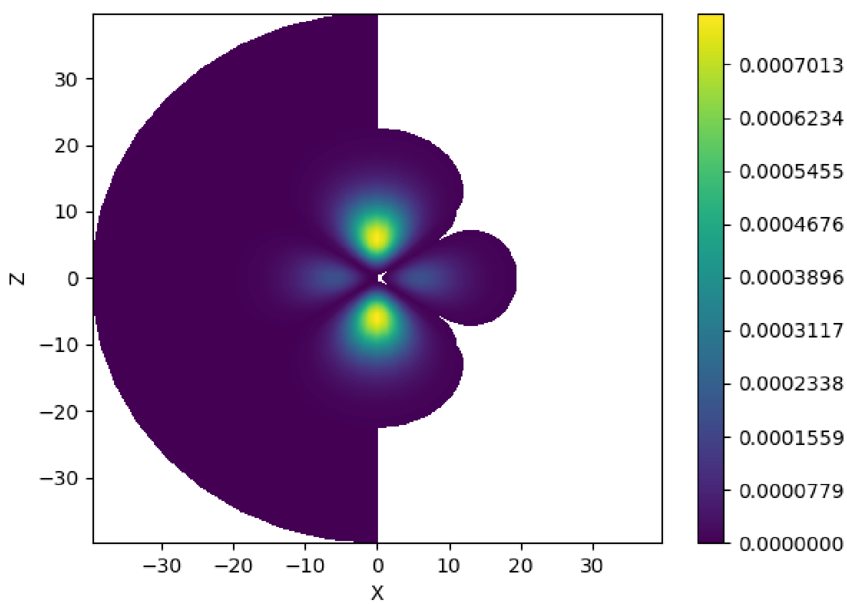

Figure 3: 320 or $3d_{z^2}$ orbital

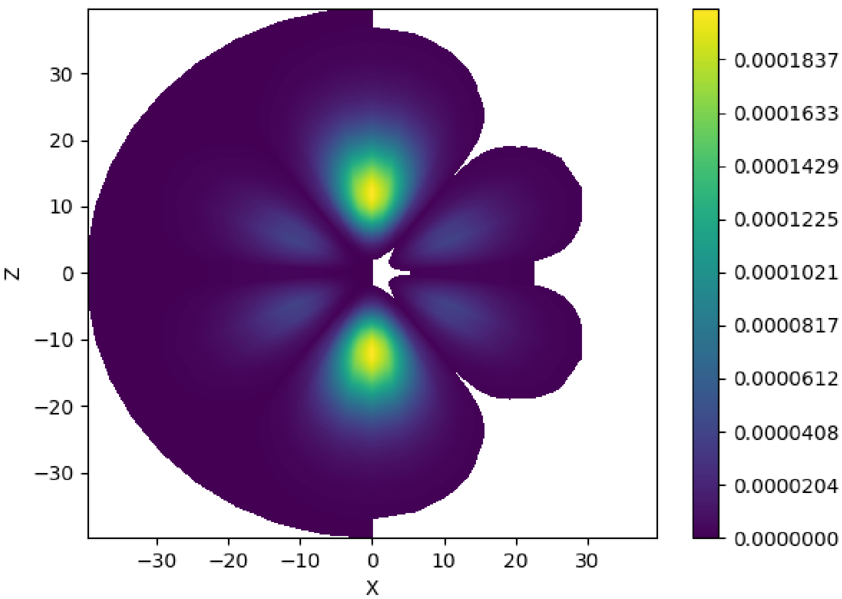

Figure 4: 430 or $4f_{z^3}$ orbital

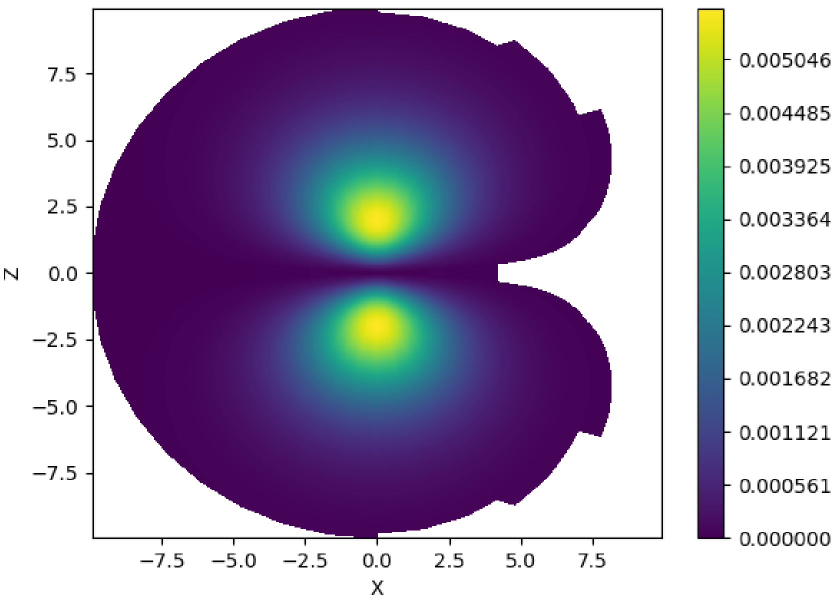

Figure 5: 210 or $2p_z$ orbital