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:

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

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:

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

Where C is a normalization constant, $\rho = \frac{2r}{na_0}$ with a_0 the reduced Bohr radius, $L^{2l+1}_{n-l-1}(\rho)$ is the generalized Laguerre polynomial, i the imaginary number and $P^m_l(\cos\phi)$ 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:

$$L^\alpha_k(x) = \frac{2k-1+\alpha-x}{k}L^\alpha_{k-1}(x) - \frac{k-1+\alpha}{k}L^\alpha_{k-2}(x) \tag{5}$$

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 $\theta = 0$.

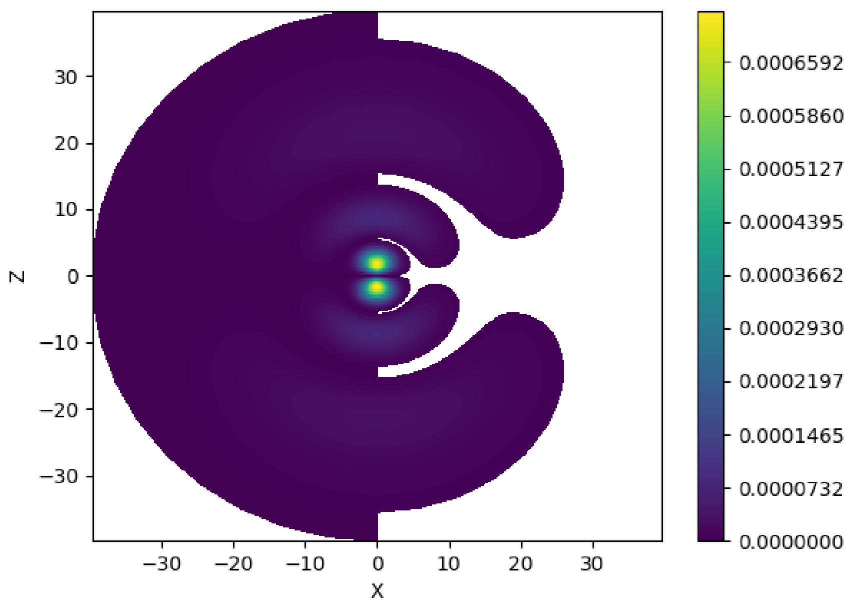

Figure 1: Probability density ψ^2_{410} of the 410 or $4p_0$ orbital.

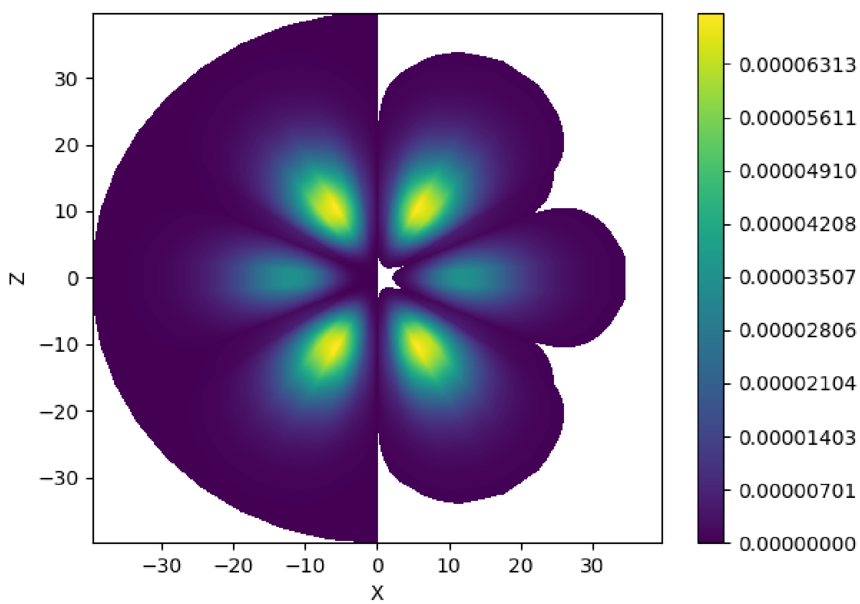

Figure 2: Probability density ψ_{431}^2 of the 431 or $4f_1$ orbital.

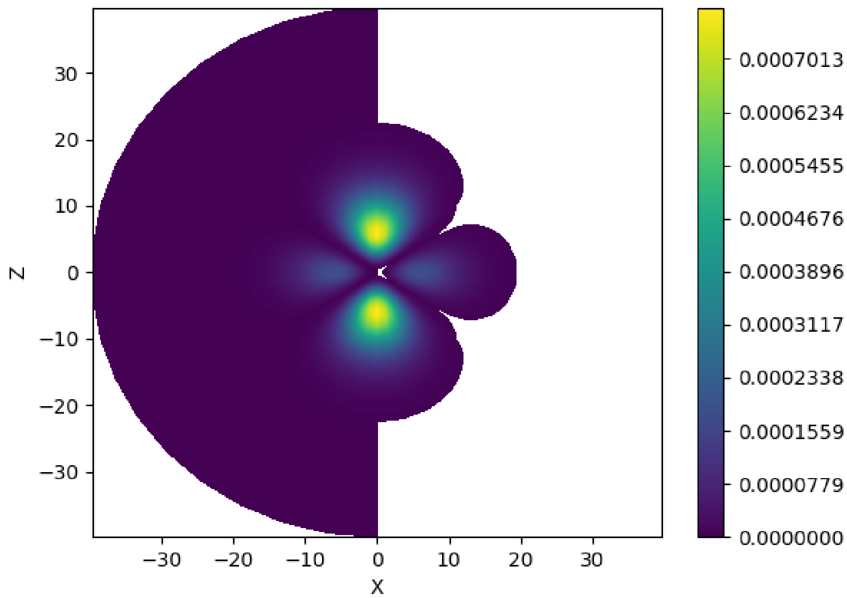

Figure 3: Probability density ψ_{320}^2 of the 320 or $3d_0$ orbital.

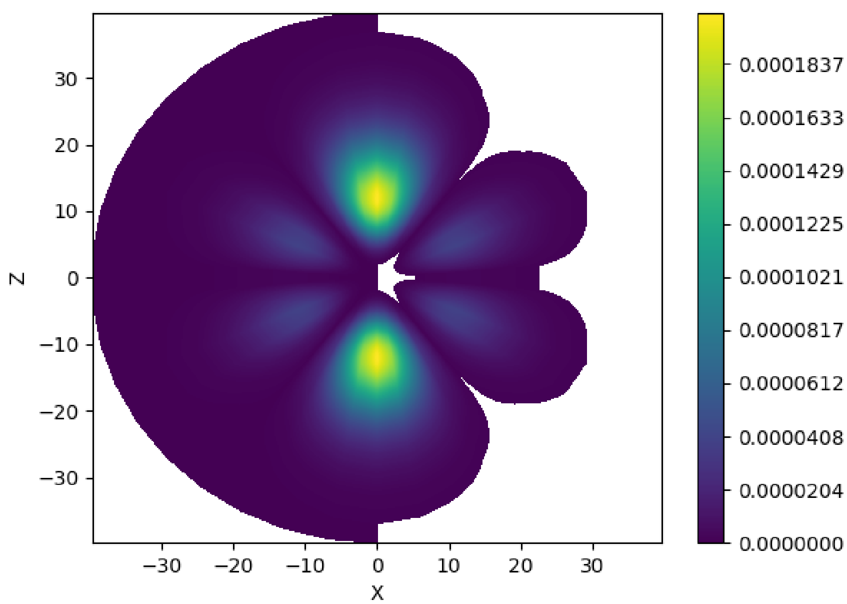

Figure 4: Probability density ψ^2_{430} of the 430 or $4f_0$ orbital.

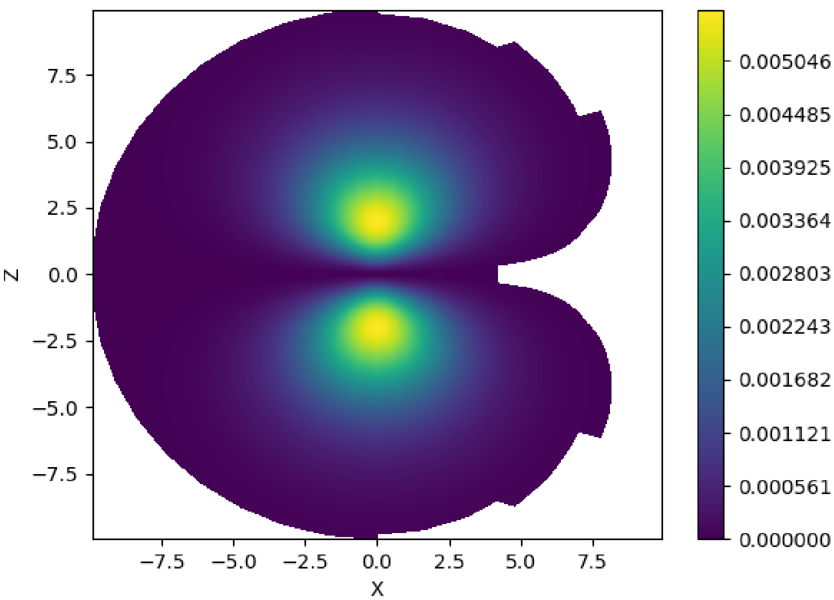

Figure 5: Probability density ψ_{210}^2 of the 210 or $2p_0$ orbital.

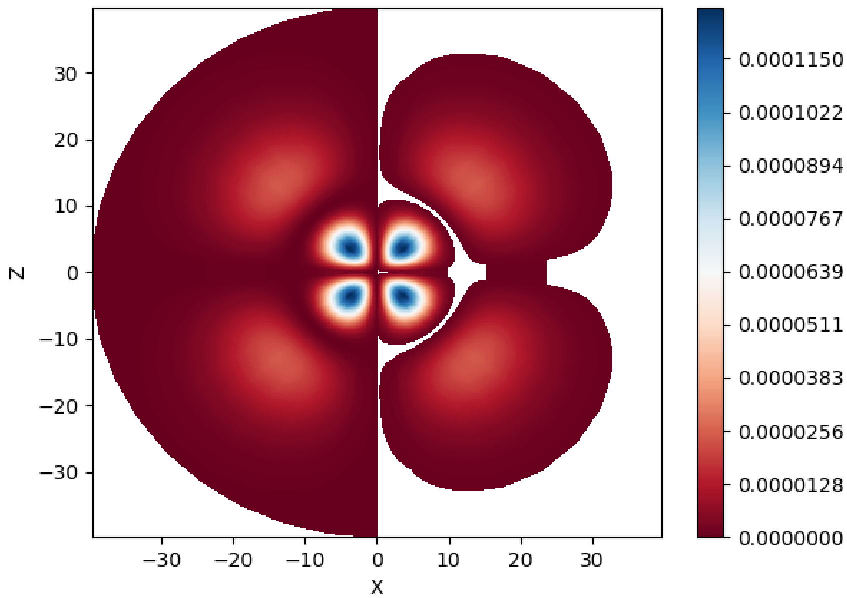

Figure 6: Probability density ψ^2_{421} of the 421 or $4d_1$ orbital.

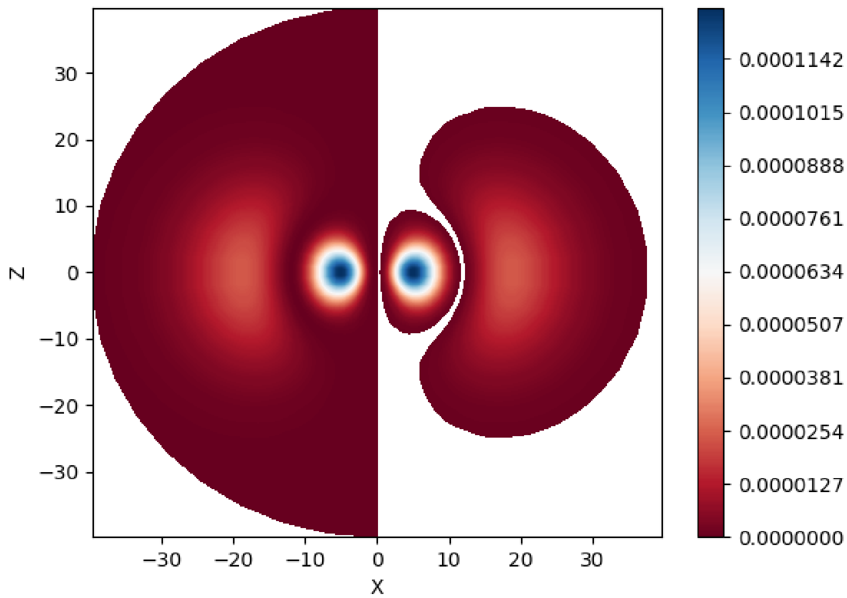

Figure 7: Probability density ψ_{422}^2 of the 422 or $4d_2$ orbital.