

The hydrogen atom

Energy levels

Bohr formula:

$$E_n = - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots$$

The **ground state** (that is, the state of lowest energy) is the case **$n = 1$** :

$$E_1 = - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV}.$$

The **binding energy** of hydrogen (the amount of energy we would have to impart to the electron in its ground state in order to ionise the atom) is 13.6 eV.

Remember:

$$n \equiv N + \ell,$$
$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$$

Thus, $\ell = 0$ and $m = 0$:

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell}^m(\theta, \phi) \quad \rightarrow \quad \psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi).$$

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Energy levels for hydrogen

For arbitrary n , the possible values of ℓ are:

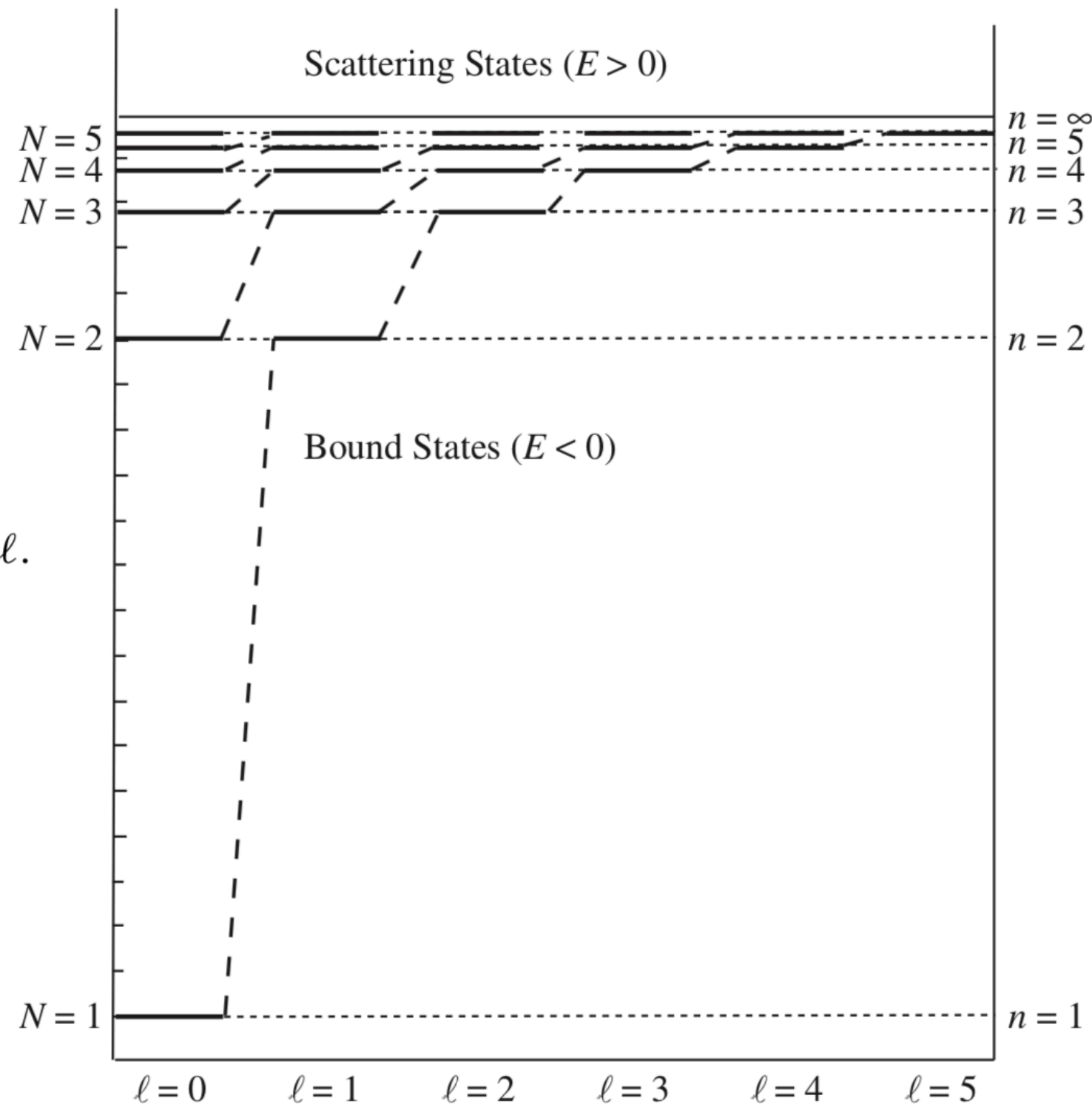
$$\ell = 0, 1, 2, \dots, n - 1$$

For each ℓ there are $(2\ell + 1)$ possible values of m .

$$m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$$

The total degeneracy of the energy level E_n is:

$$d(n) = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2.$$



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Energy levels for hydrogen

The polynomial $v(\rho)$ is a function well known to applied mathematicians; apart from normalisation, it can be written as:

$$v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)$$

where:

$$L_q^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_{p+q}(x)$$

is an **associated Laguerre polynomial**, and:

$$L_q(x) \equiv \frac{e^x}{q!} \left(\frac{d}{dx} \right)^q (e^{-x} x^q)$$

is the **q th Laguerre polynomial**.

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Laguerre polynomials

$$L_q(x) \equiv \frac{e^x}{q!} \left(\frac{d}{dx} \right)^q (e^{-x} x^q)$$

Associated Laguerre polynomials

$$L_q^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_{p+q}(x)$$

$$L_q^p(x) = \frac{x^{-p} e^x}{q!} \left(\frac{d}{dx} \right)^q (e^{-x} x^{p+q})$$

$L_0(x)$	=	1
$L_1(x)$	=	$-x + 1$
$L_2(x)$	=	$\frac{1}{2}x^2 - 2x + 1$
$L_3(x)$	=	$-\frac{1}{6}x^3 + \frac{3}{2}x^2 - 3x + 1$
$L_4(x)$	=	$\frac{1}{24}x^4 - \frac{2}{3}x^3 + 3x^2 - 4x + 1$
$L_5(x)$	=	$-\frac{1}{120}x^5 + \frac{5}{24}x^4 - \frac{5}{3}x^3 + 5x^2 - 5x + 1$
$L_6(x)$	=	$\frac{1}{720}x^6 - \frac{1}{20}x^5 + \frac{5}{8}x^4 - \frac{10}{3}x^3 + \frac{15}{2}x^2 - 6x + 1$

$L_0^0(x)$	=	1	$L_0^2(x)$	=	1
$L_1^0(x)$	=	$-x + 1$	$L_1^2(x)$	=	$-x + 3$
$L_2^0(x)$	=	$\frac{1}{2}x^2 - 2x + 1$	$L_2^2(x)$	=	$\frac{1}{2}x^2 - 4x + 6$
$L_0^1(x)$	=	1	$L_0^3(x)$	=	1
$L_1^1(x)$	=	$-x + 2$	$L_1^3(x)$	=	$-x + 4$
$L_2^1(x)$	=	$\frac{1}{2}x^2 - 3x + 3$	$L_2^3(x)$	=	$\frac{1}{2}x^2 - 5x + 10$

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Radial wave functions for hydrogen:

$$R_{10} = 2a^{-3/2} \exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a} \right) \exp(-r/2a)$$

$$R_{21} = \frac{1}{2\sqrt{6}} a^{-3/2} \left(\frac{r}{a} \right) \exp(-r/2a)$$

$$R_{30} = \frac{2}{3\sqrt{3}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a} \right)^2 \right) \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a} \right) \left(\frac{r}{a} \right) \exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a} \right)^2 \exp(-r/3a)$$

$$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a} \right)^2 - \frac{1}{192} \left(\frac{r}{a} \right)^3 \right) \exp(-r/4a)$$

$$R_{41} = \frac{5}{16\sqrt{15}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a} \right)^2 \right) \left(\frac{r}{a} \right) \exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a} \right) \left(\frac{r}{a} \right)^2 \exp(-r/4a)$$

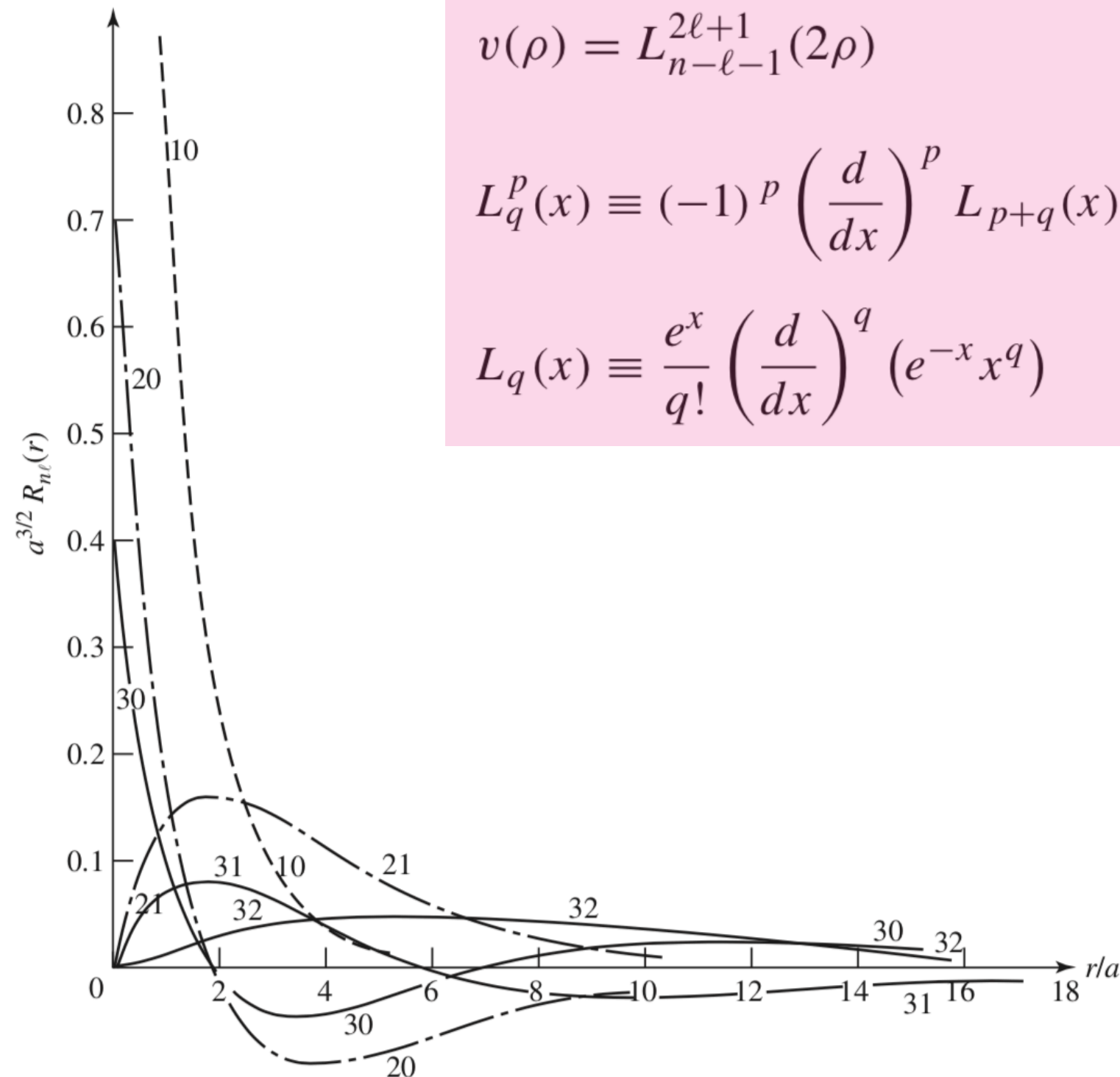
$$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a} \right)^3 \exp(-r/4a)$$

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} v(\rho),$$

$$v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)$$

$$L_q^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_{p+q}(x)$$

$$L_q(x) \equiv \frac{e^x}{q!} \left(\frac{d}{dx} \right)^q (e^{-x} x^q)$$



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Normalised hydrogen wave functions:

$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/na} \left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na) \right] Y_\ell^m(\theta, \phi).$$

The stationary states of the hydrogen atom are labeled by three quantum numbers: n , ℓ , and m .

The wave functions are mutually orthogonal:

$$\int \psi_{n\ell m}^* \psi_{n'\ell' m'} r^2 dr d\Omega = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}.$$

This follows from the orthogonality of the spherical harmonics:

$$\int_0^\pi \int_0^{2\pi} [Y_\ell^m(\theta, \phi)]^* [Y_{\ell'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{\ell\ell'} \delta_{mm'}$$

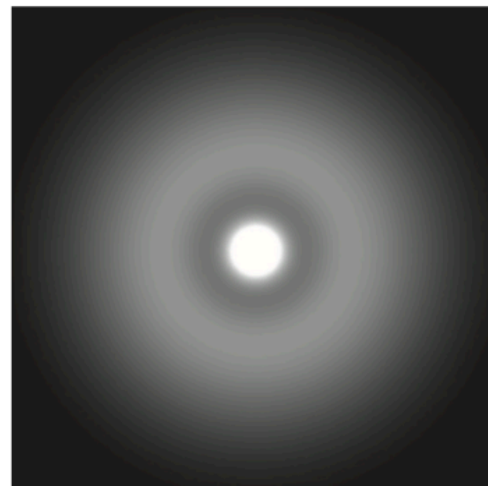
and (for $n \neq n'$) from the fact that they are eigenfunctions of \hat{H} with distinct eigenvalues.

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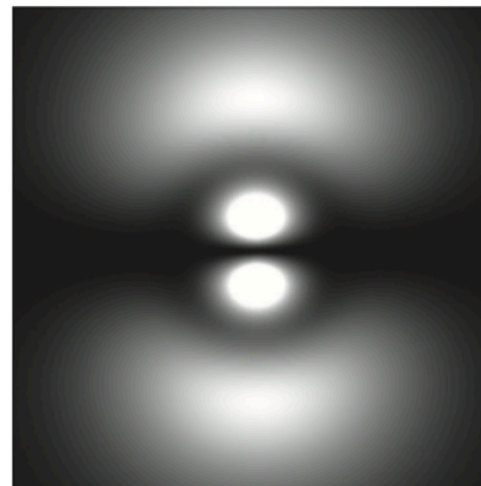
Normalised hydrogen wave functions:

$$\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/na} \left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na) \right] Y_\ell^m(\theta, \phi).$$

They can be visualised via **density plots**, in which the brightness of the cloud is proportional to $|\psi|^2$



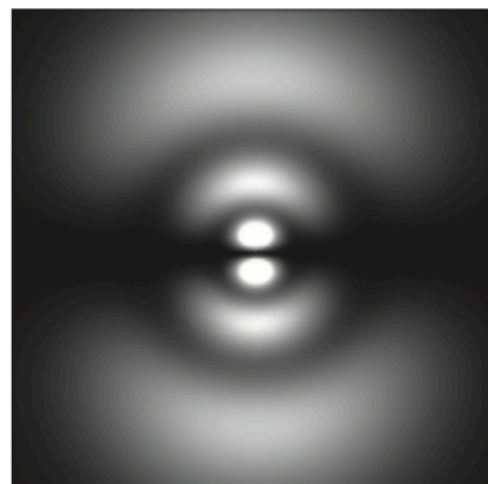
(2,0,0)



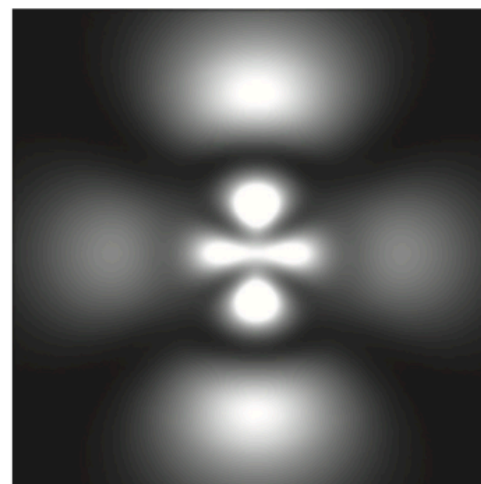
(3,1,0)



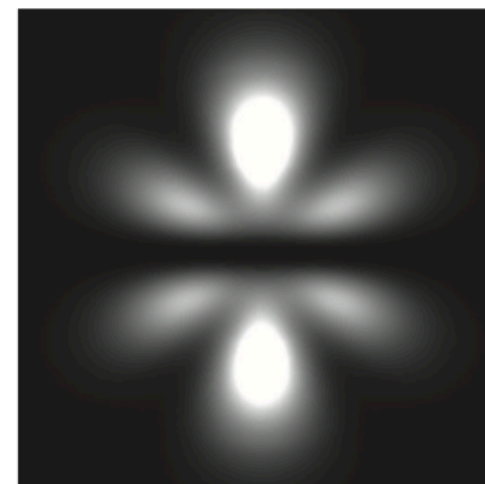
(4,0,0)



(4,1,0)

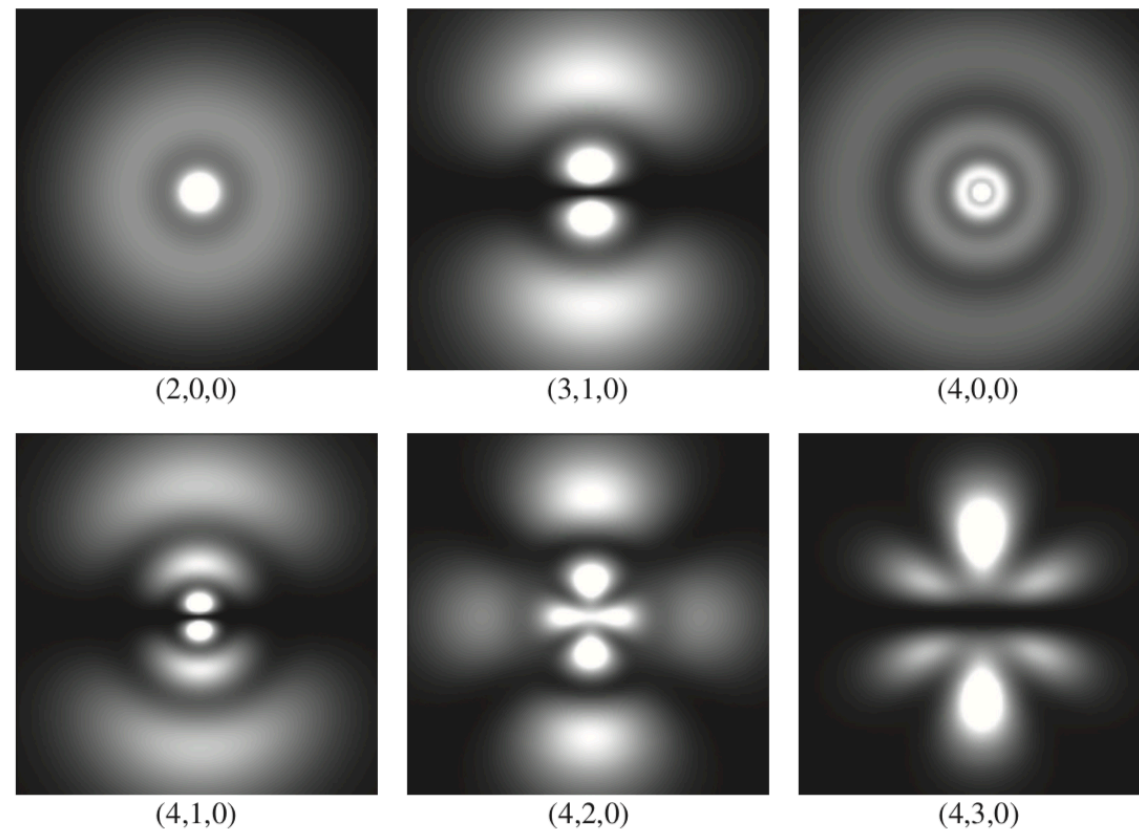


(4,2,0)



(4,3,0)

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The quantum numbers n , ℓ , and m can be identified from the nodes of the wave function.

The number of radial nodes is given by $N - 1$ (for hydrogen this is $n - \ell - 1$).

For each radial node the wave function vanishes on a sphere.

m counts the number of nodes of the real (or imaginary) part of the wave function in the ϕ direction. These nodes are planes containing the z axis on which the real or imaginary part of ψ vanishes.

$\ell - m$ gives the number of nodes in the θ direction. These are cones about the z axis on which ψ vanishes.

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Or via **surfaces of constant probability density**:

