

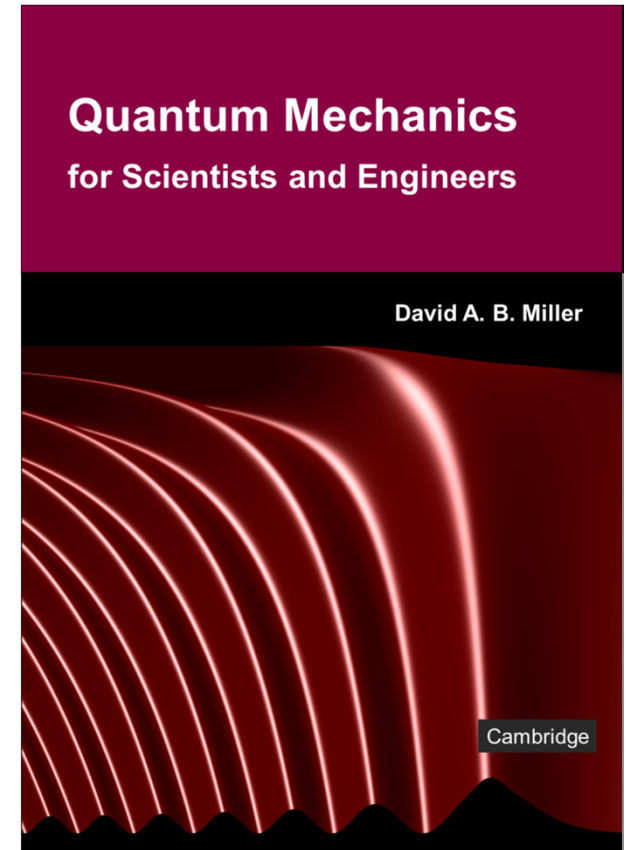
8.1 The hydrogen atom solutions

Slides: Video 8.1.3 – 8.1.4 Radial equation solutions

Text reference: Quantum Mechanics for Scientists and Engineers

Sections 10.4 starting with “Solution of the hydrogen radial wavefunction”, and 10.5

Note: The section Text reference: Quantum Mechanics for Scientists and Engineers Section 10.4 contains the complete mathematical details for solving the radial equation in the hydrogen atom problem. For this course, not all those details are required and they are consequently not all covered in the online lectures, so the additional detail, in particular on power series solutions in section Text reference: Quantum Mechanics for Scientists and Engineers Section 10.4, is optional for the student.





The hydrogen atom solutions



Radial equation solutions

Quantum mechanics for scientists and engineers

David Miller

Radial equation solutions

Using a separation of the hydrogen atom wavefunction solutions into radial and angular parts

$$U(\mathbf{r}) = R(r)Y(\theta, \phi)$$

and rewriting the radial part using

$$\chi(r) = rR(r)$$

we obtained the radial equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \chi(r)}{dr^2} - \left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} \right) \chi(r) = E_H \chi(r)$$

where we know l is 0 or any positive integer

Radial equation solutions

We now choose to write our energies in the form

$$E_H = -\frac{Ry}{n^2}$$

where n for now is just an arbitrary real number

We define a new distance unit

$$s = \alpha r$$

where the parameter α is

$$\alpha = \frac{2}{na_o} = 2\sqrt{-\frac{2\mu}{\hbar^2} E_H}$$

Radial equation solutions

We therefore obtain an equation

$$\frac{d^2 \chi}{ds^2} - \left[\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4} \right] \chi = 0$$

Then we write

$$\chi(s) = s^{l+1} L(s) \exp(-s/2)$$

so we get

$$s \frac{d^2 L}{ds^2} - [s - 2(l+1)] \frac{dL}{ds} + [n - (l+1)] L = 0$$

Radial equation solutions

The technique to solve this equation

$$s \frac{d^2 L}{ds^2} - [s - 2(l+1)] \frac{dL}{ds} + [n - (l+1)] L = 0$$

is to propose a power series in s

The power series will go on forever

and hence the function will grow arbitrarily

unless it “terminates” at some finite power

which requires that

n is an integer, and

$$n \geq l + 1$$

Radial equation solutions

The normalizable solutions of

$$s \frac{d^2 L}{ds^2} - [s - 2(l+1)] \frac{dL}{ds} + [n - (l+1)] L = 0$$

then become the finite power series

known as the associated Laguerre polynomials

$$L_{n-l-1}^{2l+1}(s) = \sum_{q=0}^{n-l-1} (-1)^q \frac{(n+l)!}{(n-l-q-1)!(q+2l+1)!} s^q$$

or equivalently

$$L_p^j(s) = \sum_{q=0}^p (-1)^q \frac{(p+j)!}{(p-q)!(j+q)!q!} s^q$$

Radial equation solutions

Now we can work back to construct the whole solution

In our definition $\chi(s) = s^{l+1} L(s) \exp(-s/2)$

we now insert the associated Laguerre polynomials

$$\chi(s) = s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2)$$

where $s = (2/na_o)r$

Since our radial solution was $\chi(r) = rR(r)$

we now have

$$\begin{aligned} R(r = na_o s / 2) &\propto \frac{1}{r} s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2) \\ &\propto s^l L_{n-l-1}^{2l+1}(s) \exp(-s/2) \end{aligned}$$

Radial equation solutions - normalization

We formally introduce a normalization coefficient A so

$$R(r = na_o s / 2) = \frac{1}{A} s^l L_{n-l-1}^{2l+1}(s) \exp(-s / 2)$$

The full normalization integral of the wavefunction

$$U(\mathbf{r}) = R(r)Y(\theta, \phi)$$

would be

$$1 = \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |R(r)Y(\theta, \phi)|^2 r^2 \sin \theta d\theta d\phi dr$$

but we have already normalized the spherical harmonics
so we are left with the radial normalization

Radial equation solutions - normalization

Radial normalization would be $1 = \int_0^{\infty} R^2(r) r^2 dr$

We could show $\int_0^{\infty} s^{2l} \left[L_{n-l-1}^{2l+1}(s) \right]^2 \exp(-s) s^2 ds = \frac{2n(n+l)!}{(n-l-1)!}$

so the normalized radial wavefunction becomes

$$R(r) = \left[\frac{(n-l-1)!}{2n(n+l)!} \left(\frac{2}{na_o} \right)^3 \right]^{1/2} \left(\frac{2r}{na_o} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na_o} \right) \exp \left(-\frac{r}{na_o} \right)$$

Hydrogen atom radial wavefunctions

We write the wavefunctions

using the Bohr radius a_o as the unit of radial distance
so we have a dimensionless radial distance

$$\rho = r / a_o$$

and we introduce the subscripts

n - the principal quantum number, and

l - the angular momentum quantum number

to index the various functions $R_{n,l}$

Radial wavefunctions - $n = 1$

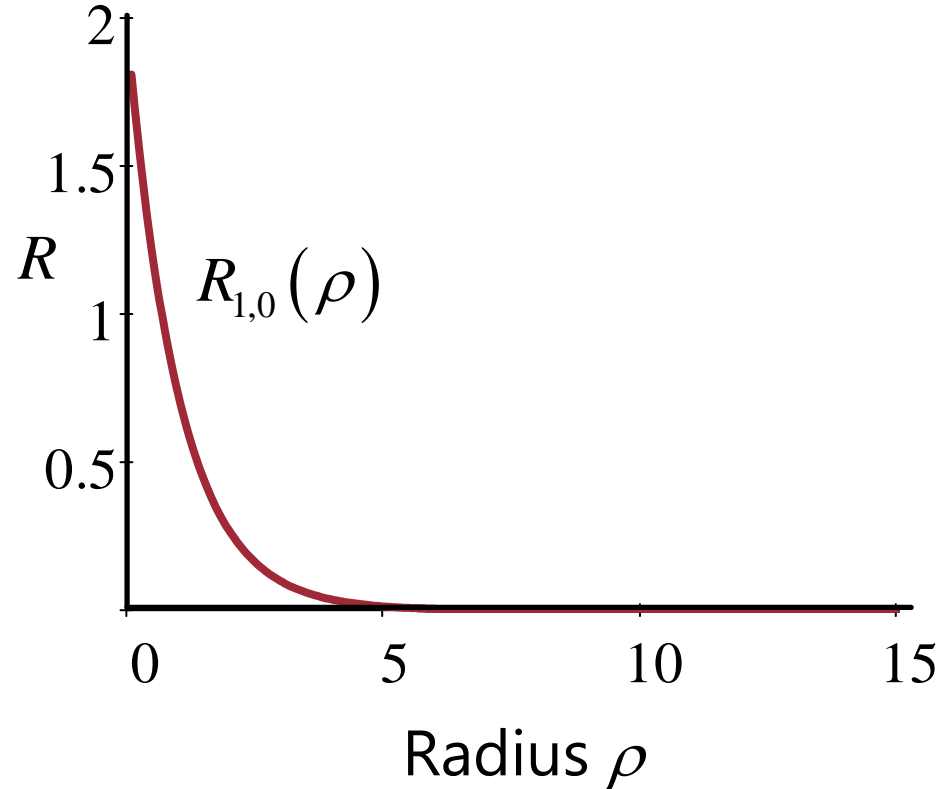
Principal quantum number

$$n = 1$$

Angular momentum
quantum number

$$l = 0$$

$$R_{1,0}(\rho) = 2\exp(-\rho)$$



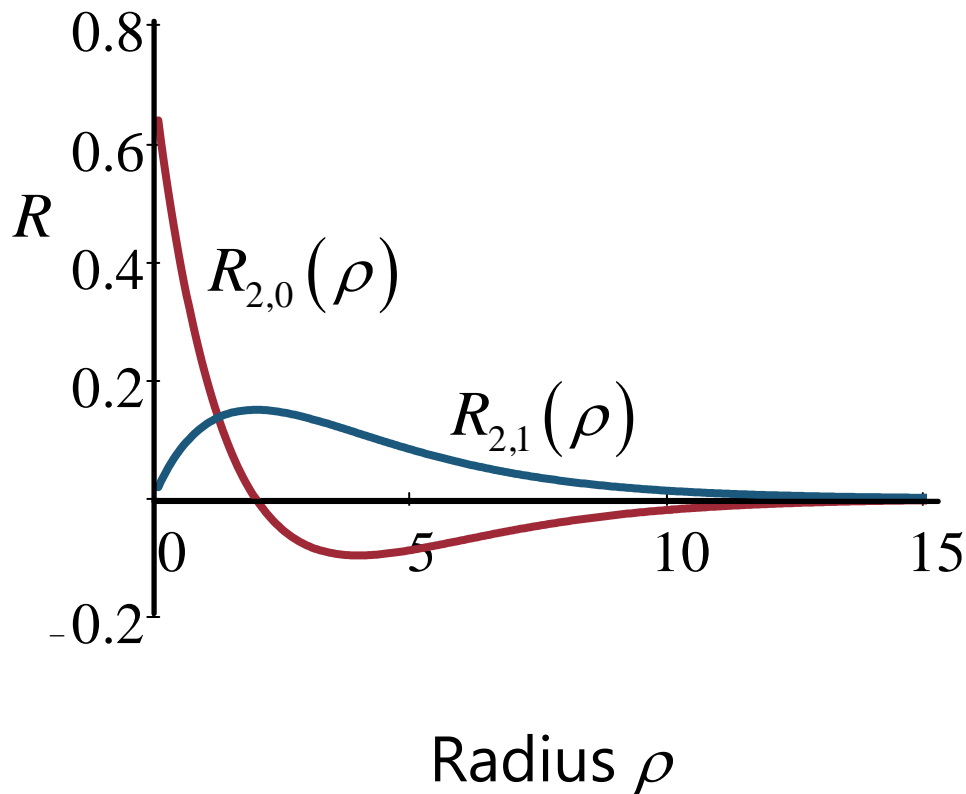
Radial wavefunctions - $n = 2$

$l = 0$

$$R_{2,0}(\rho) = \frac{\sqrt{2}}{4}(2 - \rho)\exp(-\rho/2)$$

$l = 1$

$$R_{2,1}(\rho) = \frac{\sqrt{6}}{12}\rho\exp(-\rho/2)$$



Radial wavefunctions - $n = 3$

$$l = 0$$

$$R_{3,0}(\rho) =$$

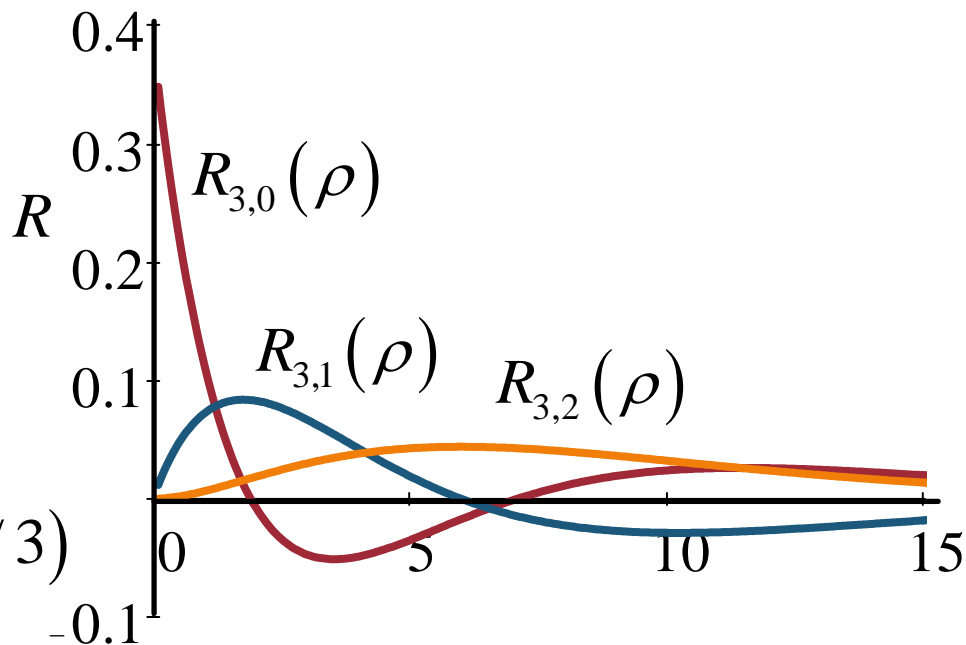
$$\frac{2\sqrt{3}}{27} \left(3 - 2\rho + \frac{2}{9}\rho^2 \right) \exp(-\rho/3)$$

$$l = 1$$

$$R_{3,1}(\rho) = \frac{\sqrt{6}}{81} \rho \left(4 - \frac{2}{3}\rho \right) \exp(-\rho/3)$$

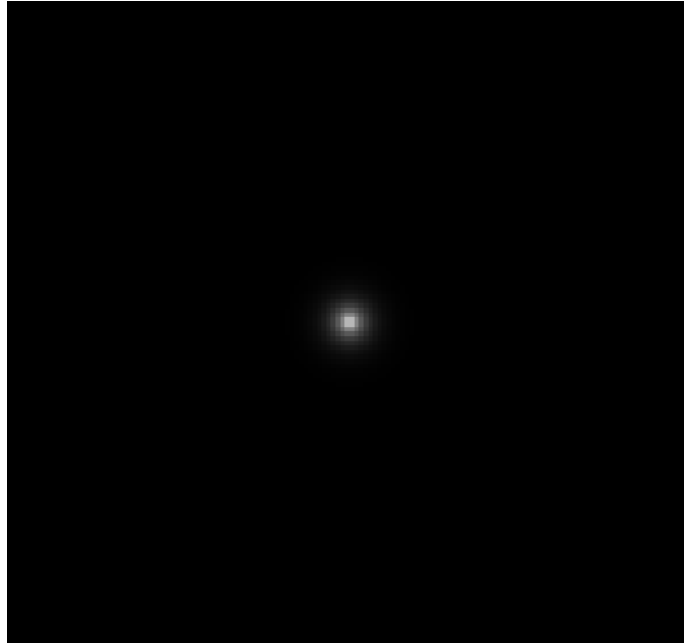
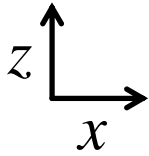
$$l = 2$$

$$R_{3,2}(\rho) = \frac{2\sqrt{30}}{1215} \rho^2 \exp(-\rho/3)$$



Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



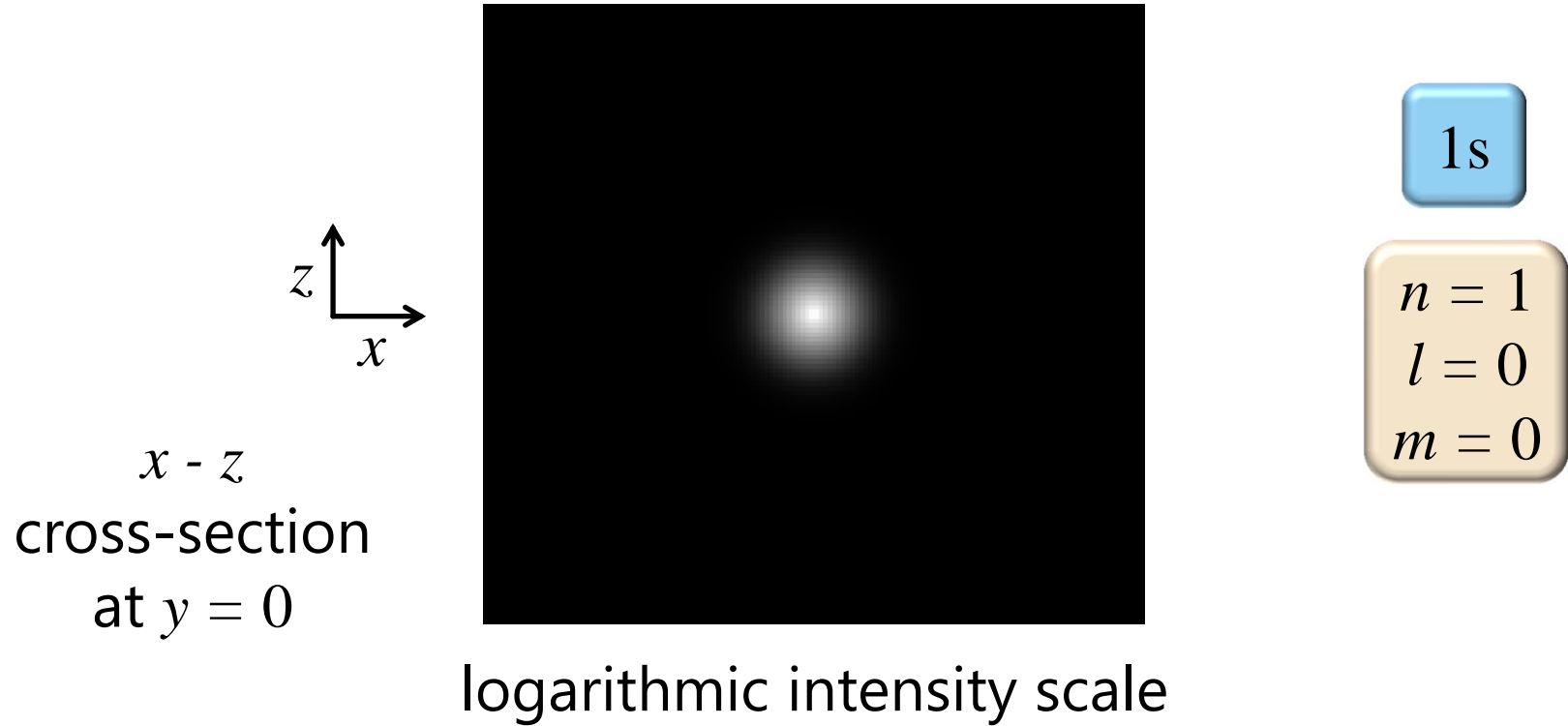
1s

$$n = 1$$

$$l = 0$$

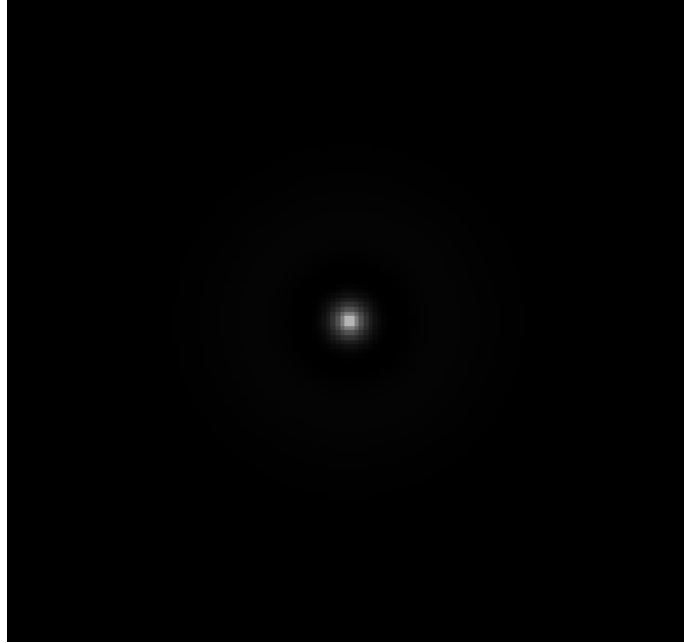
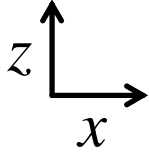
$$m = 0$$

Hydrogen orbital probability density



Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



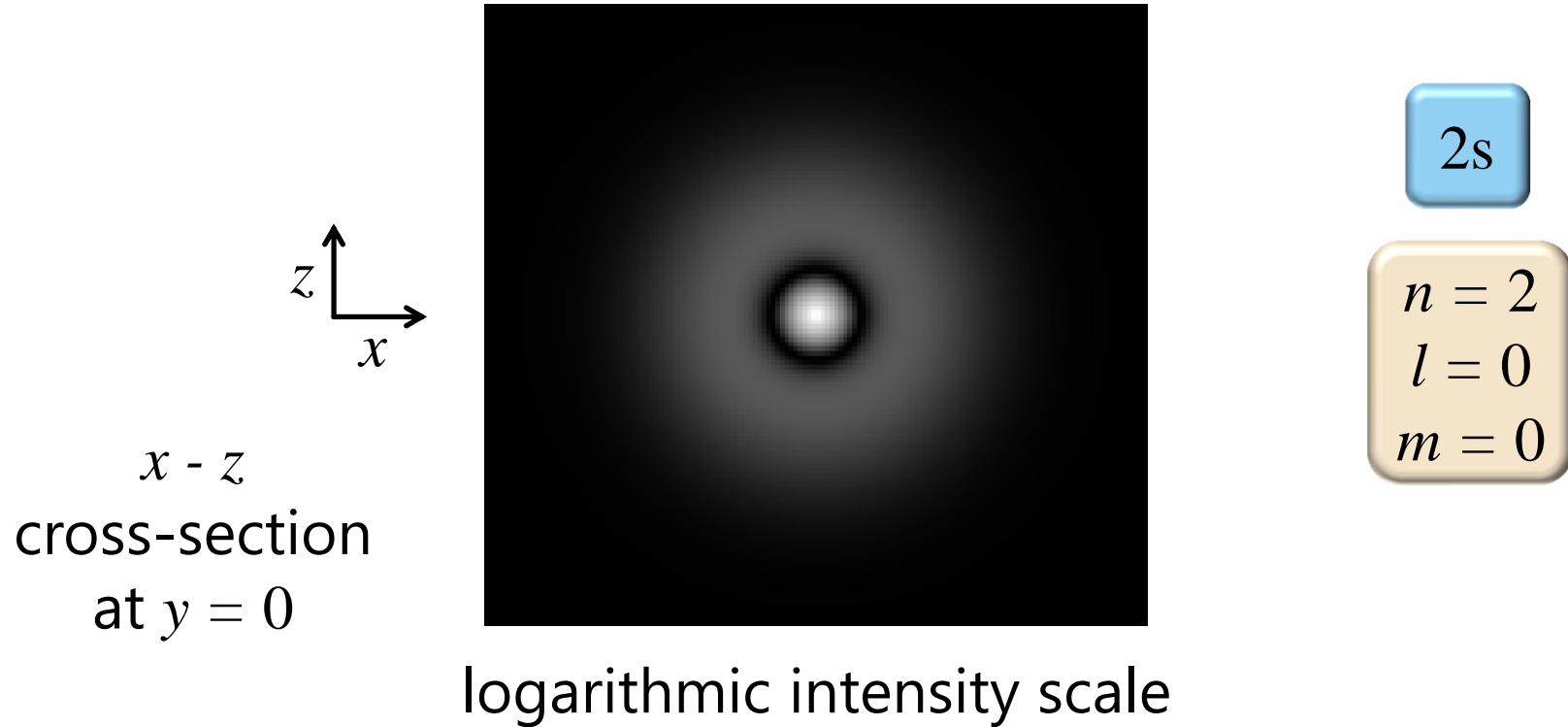
2s

$$n = 2$$

$$l = 0$$

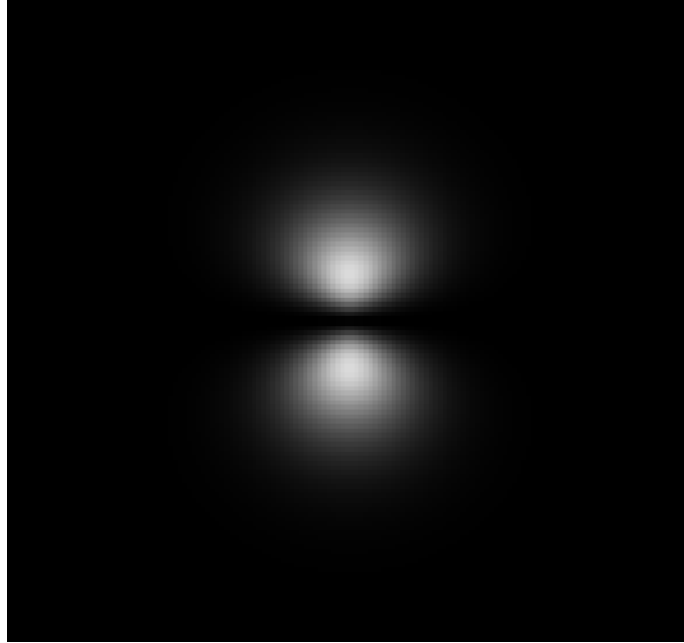
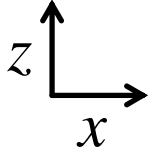
$$m = 0$$

Hydrogen orbital probability density



Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



2p

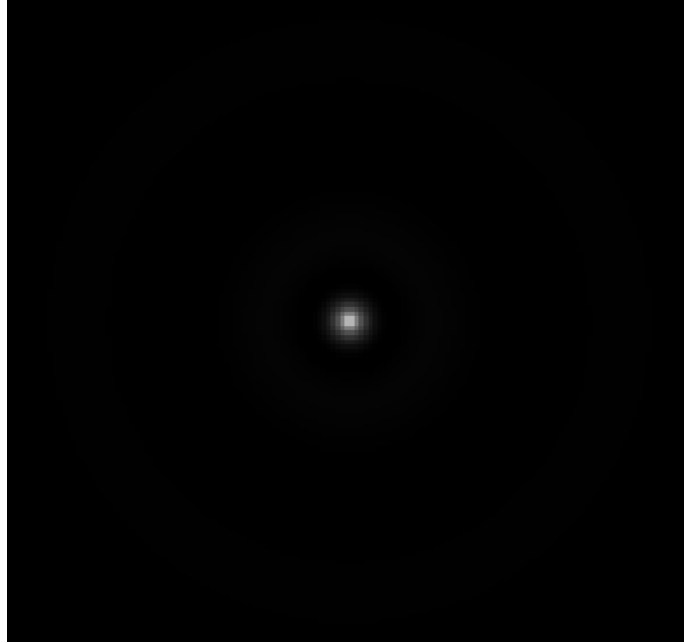
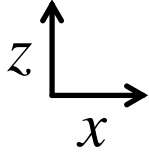
$$n = 2$$

$$l = 1$$

$$m = 0$$

Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



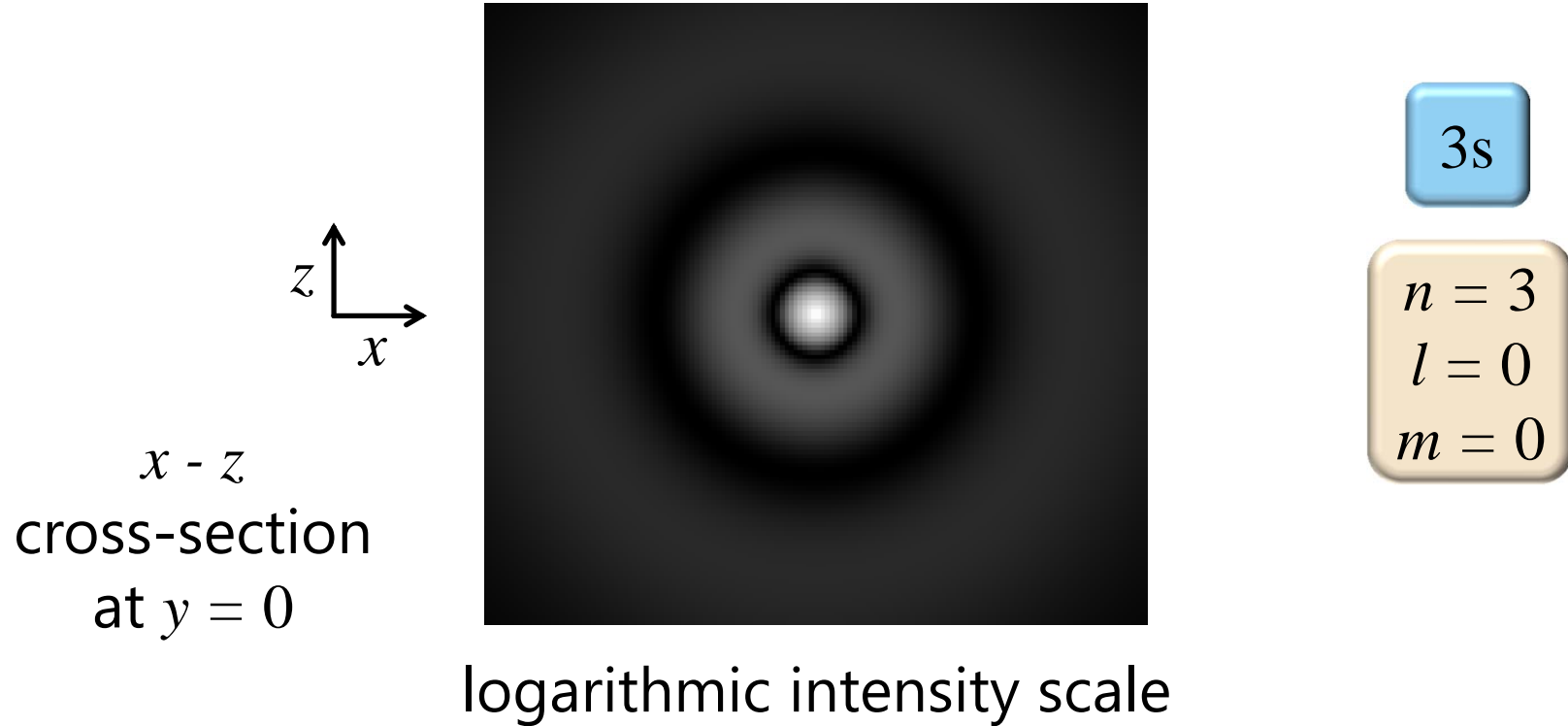
3s

$$n = 3$$

$$l = 0$$

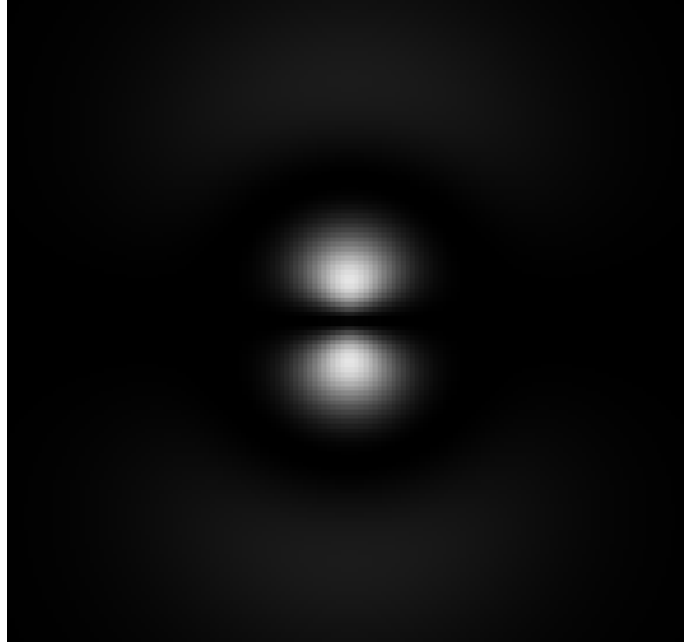
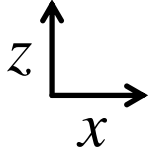
$$m = 0$$

Hydrogen orbital probability density



Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



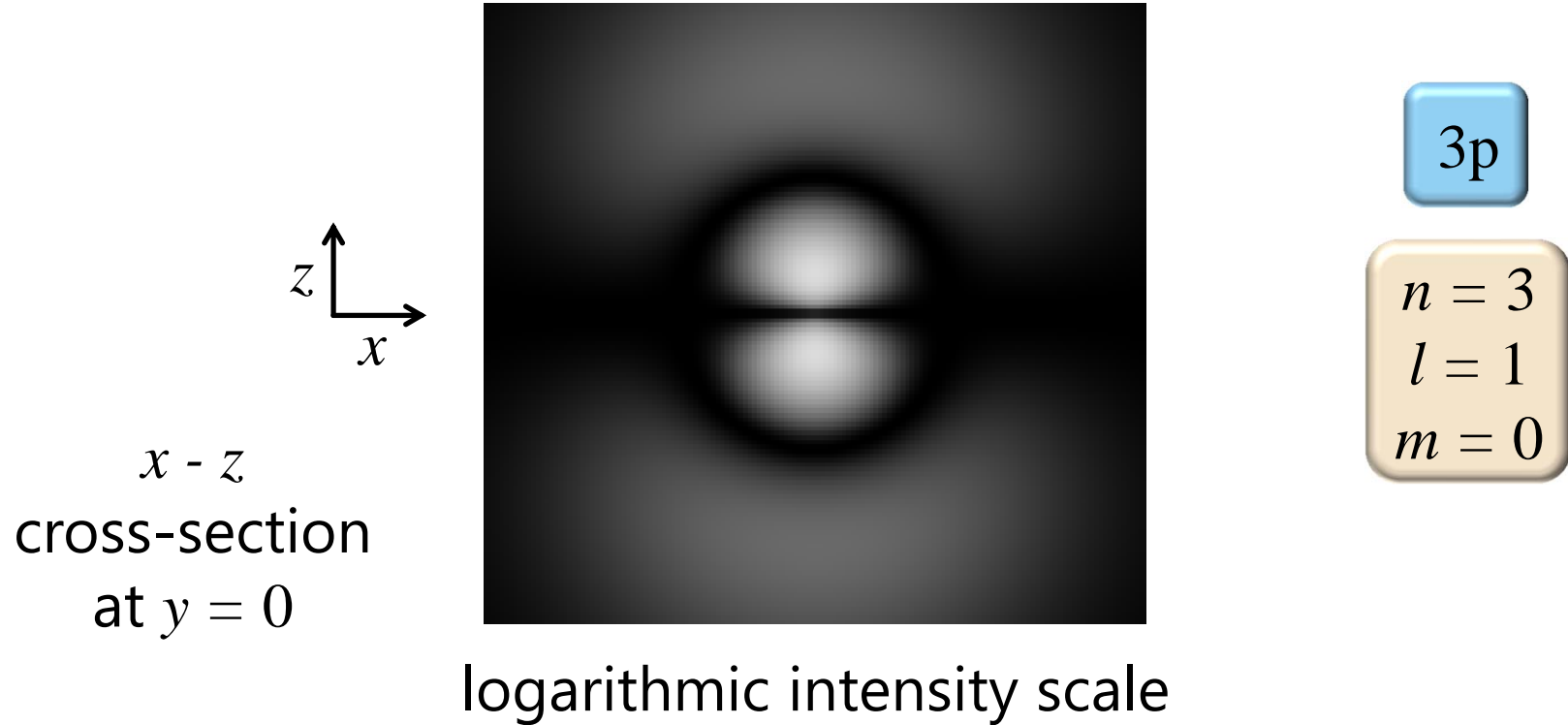
3p

$$n = 3$$

$$l = 1$$

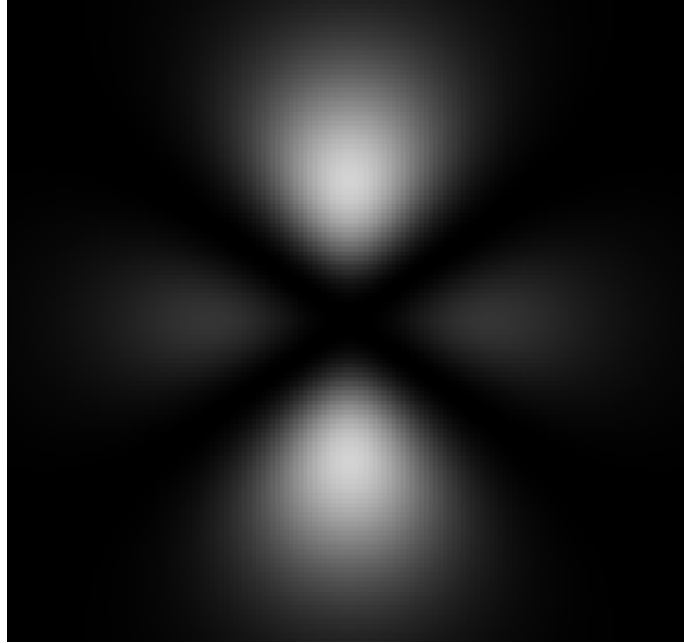
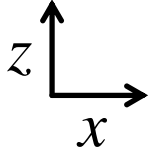
$$m = 0$$

Hydrogen orbital probability density



Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



3d

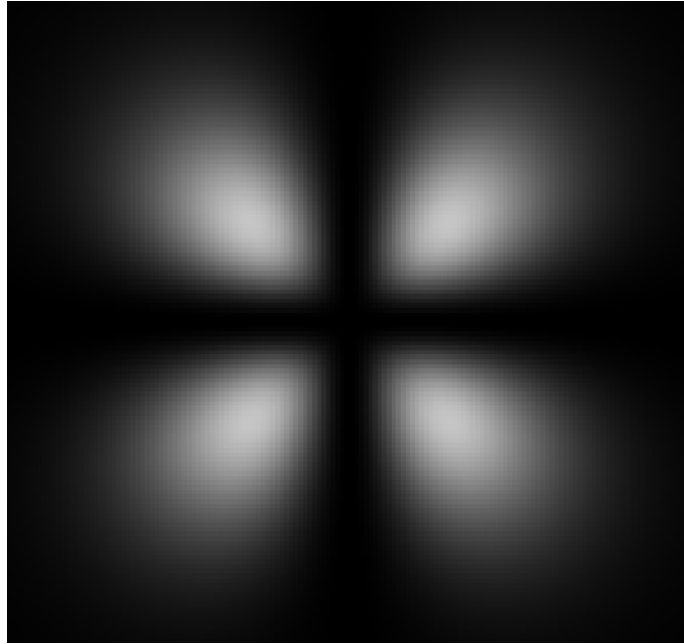
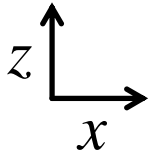
$$n = 3$$

$$l = 2$$

$$m = 0$$

Hydrogen orbital probability density

$x - z$
cross-section
at $y = 0$



3d

$$n = 3$$

$$l = 2$$

$$m = 1$$

Behavior of the complete hydrogen solutions

- (i) The overall “size” of the wavefunctions becomes larger with larger n
- (ii) The number of zeros in the wavefunction is $n - 1$

The radial wavefunctions have $n - l - 1$ zeros

and the spherical harmonics have l nodal “circles”

The radial wavefunctions appear to have an additional zero at $r = 0$ for all $l \geq 1$, but this is already counted

because the spherical harmonics have at least one nodal “circle” for all $l \geq 1$

which already gives a zero as $r \rightarrow 0$ in these cases

Behavior of the complete hydrogen solutions

In summary of the quantum numbers

for the so-called principal quantum number

$$n = 1, 2, 3, \dots$$

and

$$l \leq n - 1$$

We already deduced that l is a positive or zero integer

We also now know the eigenenergies

Given the possible values for n

$$E_H = -\frac{Ry}{n^2}$$

Note the energy does not depend on l (or m)

