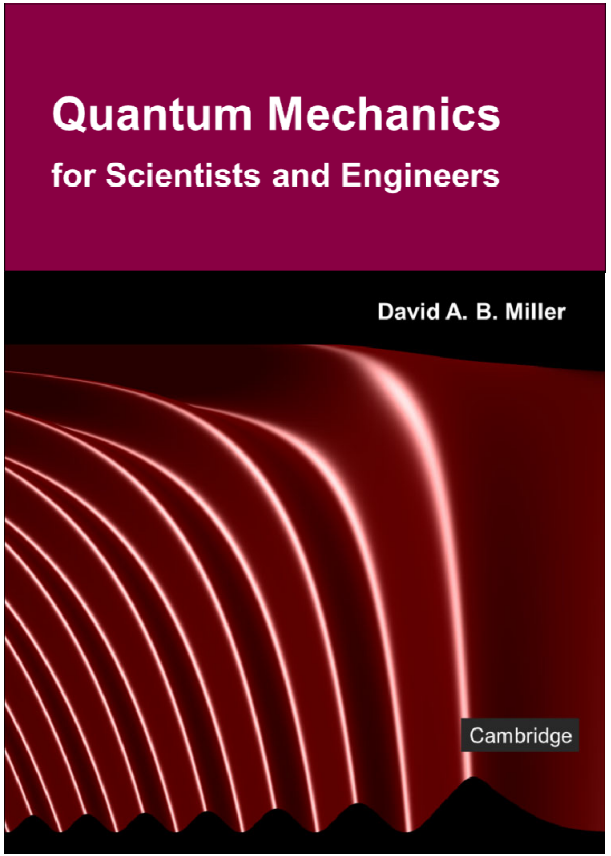
21 The hydrogen atom solutions

Slides: Lecture 21a Separating for the radial equation

Text reference: Quantum Mechanics for Scientists and Engineers

Section 10.4 (up to “Solution of the hydrogen radial wavefunction”).



The hydrogen atom solutions

Separating for the radial equation

Quantum mechanics for scientists and engineers

David Miller

Internal states of the hydrogen atom

We start with the equation for

the relative motion of electron and proton

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = E_H U(\mathbf{r})$$

We use the spherical symmetry of this equation

and change to spherical polar coordinates

From now on, we drop the subscript $\mathbf{r}$ in the operator ∇^2

Internal states of the hydrogen atom

In spherical polar coordinates, we have

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

where the term in square brackets

is the operator $\nabla^2_{\theta,\phi} \equiv -\hat{L}^2/\hbar^2$ we introduced

in discussing angular momentum

Knowing the solutions to the angular momentum problem

we propose the separation

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

Internal states of the hydrogen atom

The mathematics is simpler using the form

$$U(\mathbf{r}) = \frac{1}{r}\chi(r)Y(\theta,\phi)$$

where, obviously

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

This choice gives a convenient simplification of the radial derivatives

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\frac{\chi(r)}{r} = \frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}$$

Internal states of the hydrogen atom

Hence the Schrödinger equation becomes

$$-\frac{\hbar^2}{2\mu}Y(\theta,\phi)\frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}+\frac{\chi(r)}{r^3}\frac{1}{2\mu}\hat{L}^2Y(\theta,\phi)+Y(\theta,\phi)V(r)\frac{\chi(r)}{r}$$

$$=E_H\frac{1}{r}\chi(r)Y(\theta,\phi)$$

Dividing by $-\hbar^2\chi(r)Y(\theta,\phi)/2\mu r^3$

and rearranging, we have

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)$$

Internal states of the hydrogen atom

In

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)=l(l+1)$$

in the usual manner for a separation argument

the left hand side depends only on $\mathbf{r}$

and the right hand side depends only on θ and ϕ

so both sides must be equal to a constant

We already know what that constant is explicitly

i.e., we already know that $\hat{L}^2Y_{lm}(\theta,\phi)=\hbar^2l(l+1)Y_{lm}(\theta,\phi)$

so that the constant is $l(l+1)$

Internal states of the hydrogen atom

Hence, in addition to the $\hat{L}^2$ eigenequation

which we had already solved

from our separation above, we also have

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=l(l+1)$$

or, rearranging

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

which we can write as an ordinary differential equation

All the functions and derivatives are in one variable, r

Internal states of the hydrogen atom

Hence we have mathematical equation

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

for this radial part of the wavefunction

which looks like a Schrödinger wave equation

with an additional effective potential energy

term of the form

$$\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$$

Central potentials

Note incidentally that

though here we have a specific form for $V(r)$

in our assumed Coulomb potential

$$V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right) = -\frac{e^2}{4\pi\varepsilon_o \left|\mathbf{r}_e - \mathbf{r}_p\right|}$$

the above separation works for any potential

that is only a function of r

sometimes known as a central potential

Central potentials

The precise form of the equation

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

will be different for different central potentials

but the separation remains

We can still separate out the $\hat{L}^2$ angular momentum eigenequation

with the spherical harmonic solutions

Central potentials

Since a reasonable first approximation for more complicated atoms

is to say that the potential is still approximately "central"

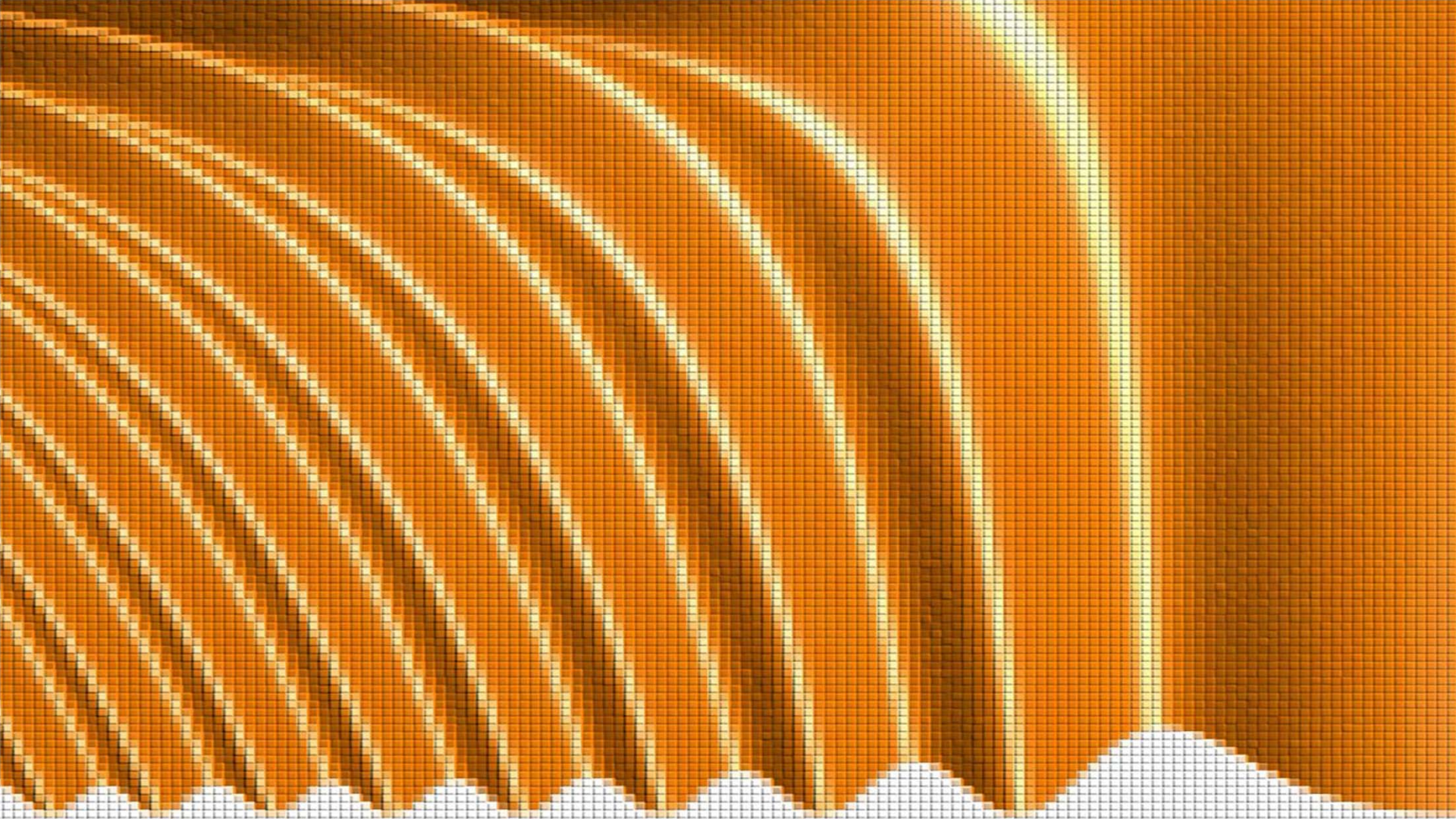
approximately independent of angle

we can continue to use the spherical harmonics

as the first approximation to the angular form of the orbitals

and use the "hydrogen atom" labels for them

e.g., s, p, d, f, etc.



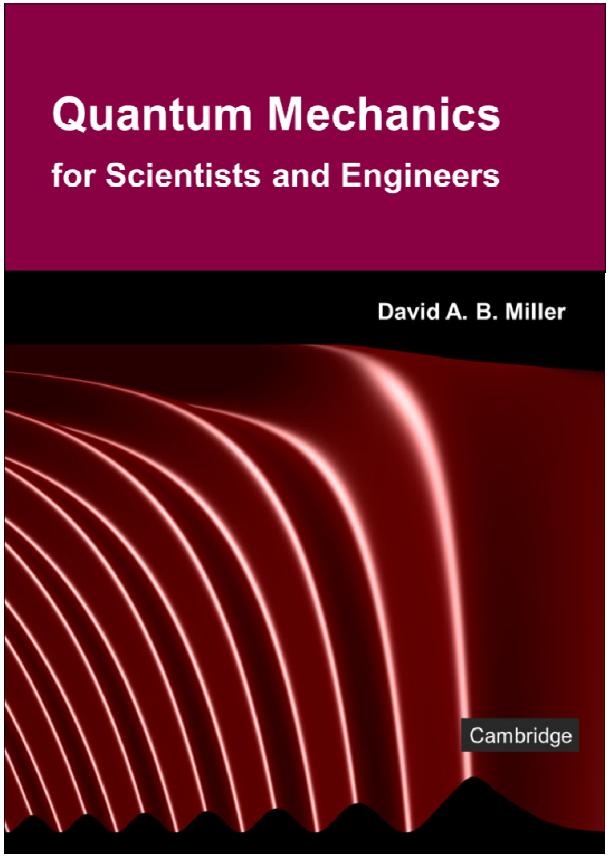
21 The hydrogen atom solutions

Slides: Lecture 21b 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: 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 Section 10.4, is optional.



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

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

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

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

Radial equation solutions

The technique to solve this equation

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

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

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

then become the finite power series

known as the associated Laguerre polynomials

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

or equivalently

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

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

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

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

Radial equation solutions - normalization

We formally introduce a normalization coefficient A so

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

The full normalization integral of the wavefunction

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

would be

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

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 - $n = 1$

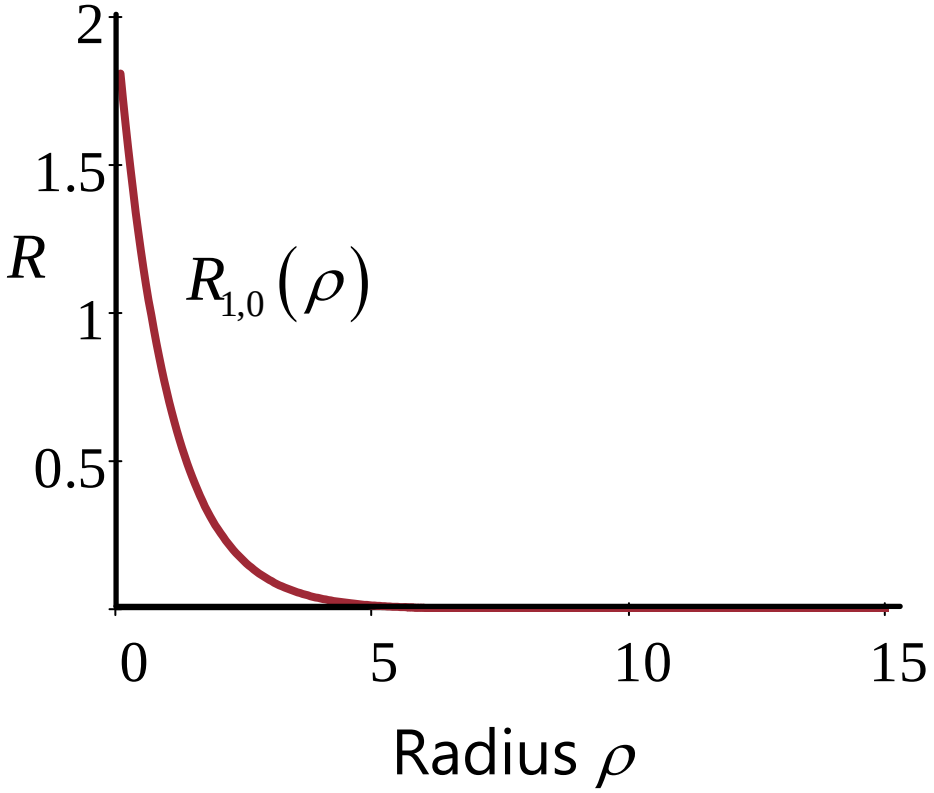
Principal quantum number

$n = 1$

Angular momentum quantum number

$l = 0$

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



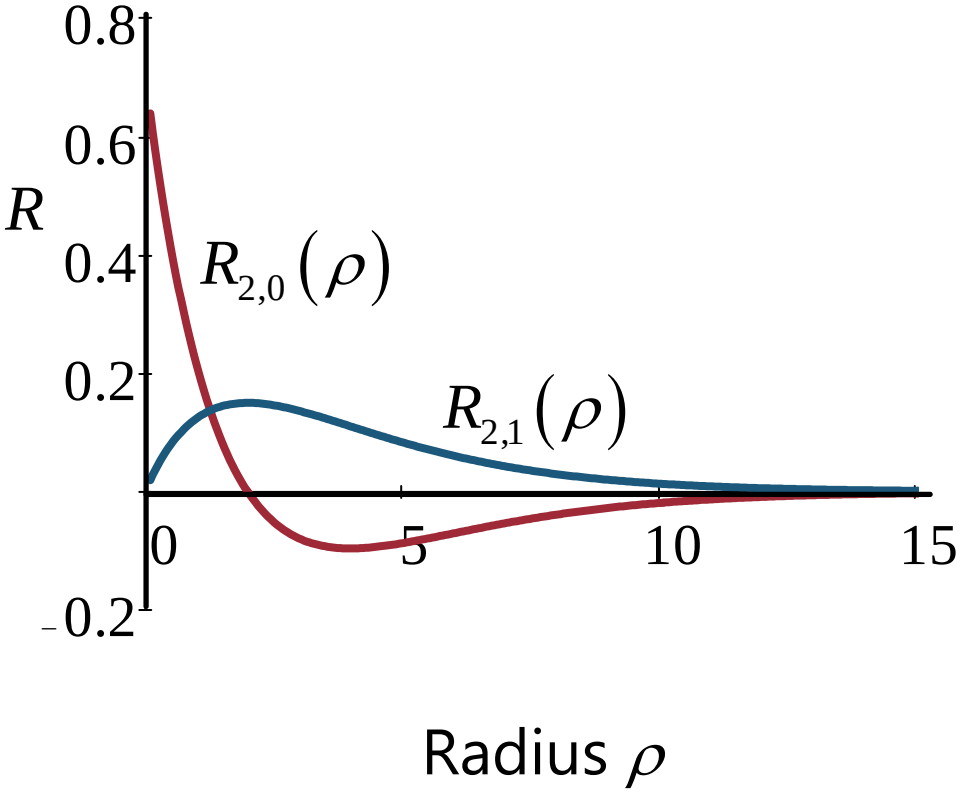
Radial wavefunctions - $n = 2$

$l = 0$

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

$l = 1$

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



Radial wavefunctions - $n = 3$

$l = 0$

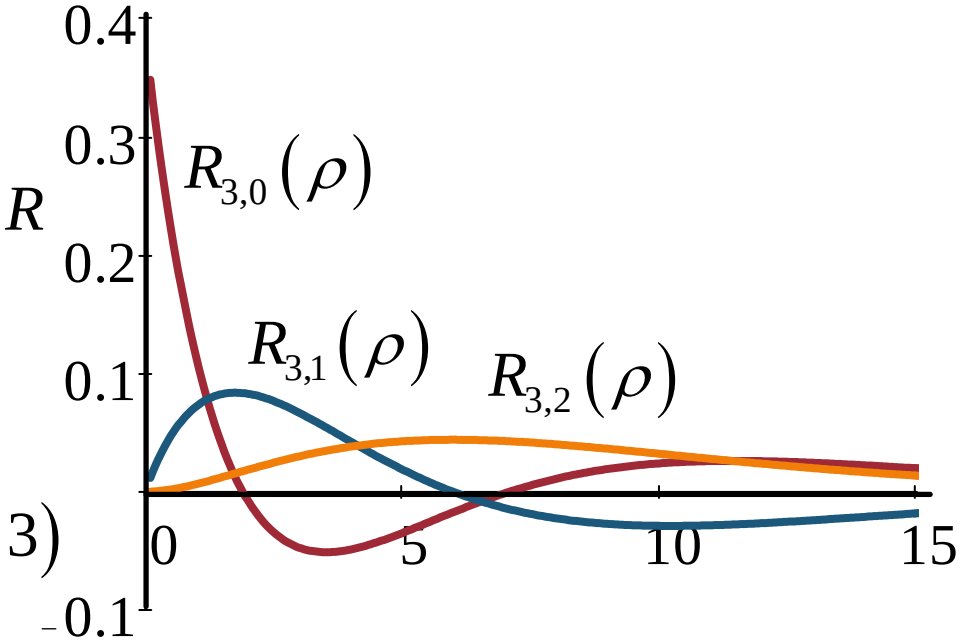
$$R_{3,0}(\rho) = \frac{2\sqrt{3}}{27}\left(3 - 2\rho + \frac{2}{9}\rho^2\right)\exp(-\rho/3)$$

$l = 1$

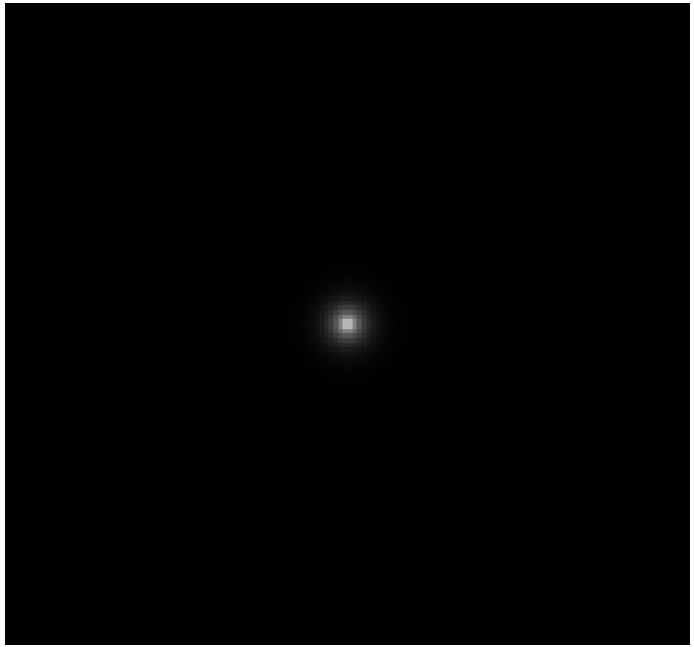
$$R_{3,1}(\rho) = \frac{\sqrt{6}}{81}\rho\left(4 - \frac{2}{3}\rho\right)\exp(-\rho/3)$$

$l = 2$

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



Hydrogen orbital probability density

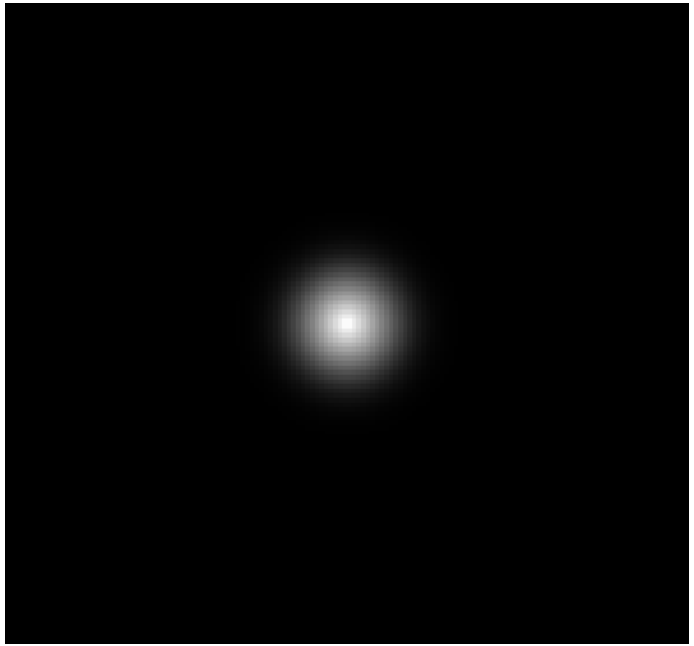


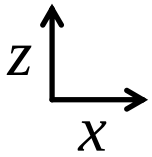
x - z
cross-section
at $y = 0$

1s

$n = 1$
$l = 0$
$m = 0$

Hydrogen orbital probability density





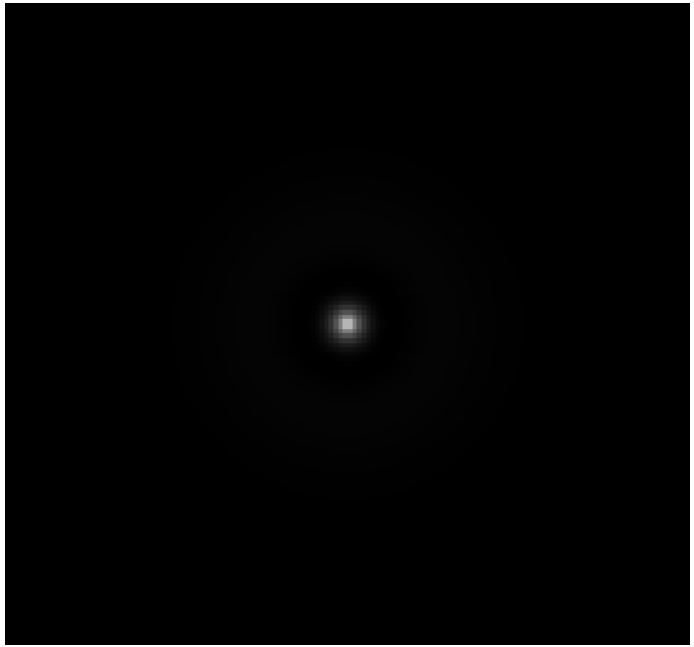
x - z
cross-section
at $y = 0$

logarithmic intensity scale

1s

$n = 1$
$l = 0$
$m = 0$

Hydrogen orbital probability density

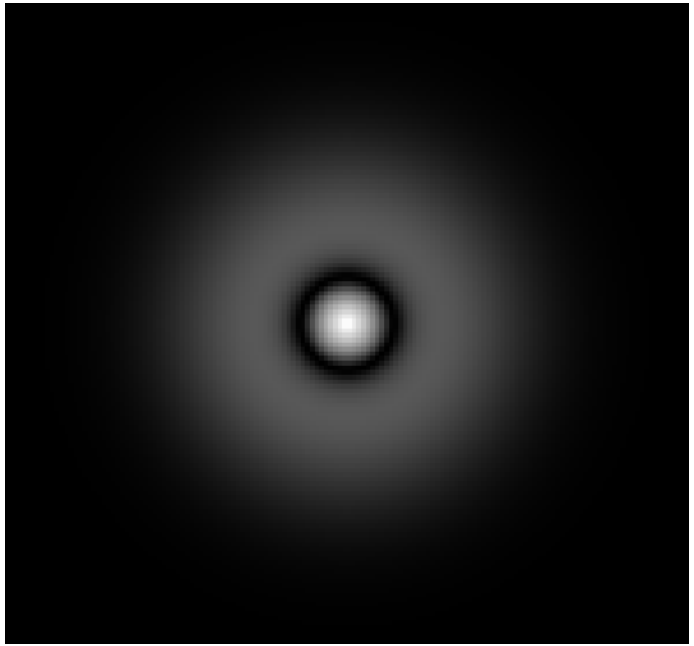


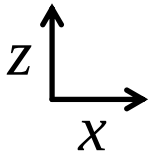
x - z
cross-section
at $y = 0$

2s

$n = 2$
$l = 0$
$m = 0$

Hydrogen orbital probability density





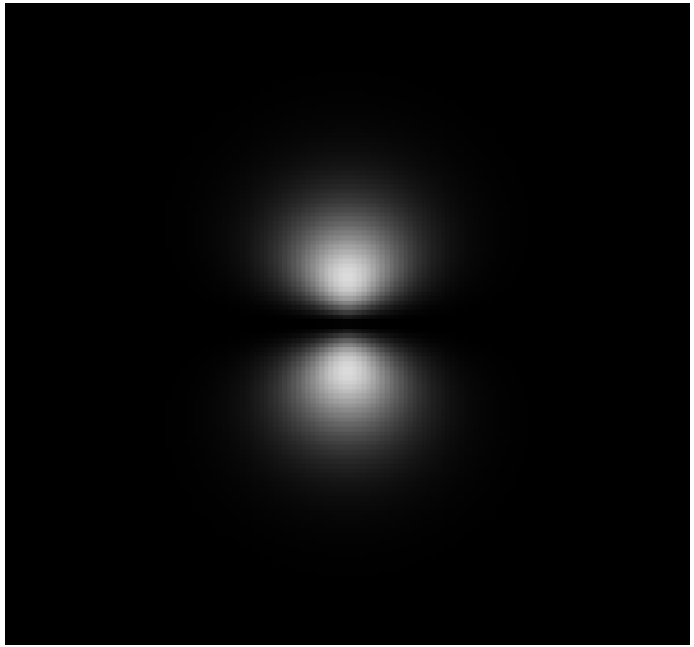
x - z
cross-section
at $y = 0$

logarithmic intensity scale

2s

$n = 2$
$l = 0$
$m = 0$

Hydrogen orbital probability density



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

2p

$n = 2$
$l = 1$
$m = 0$

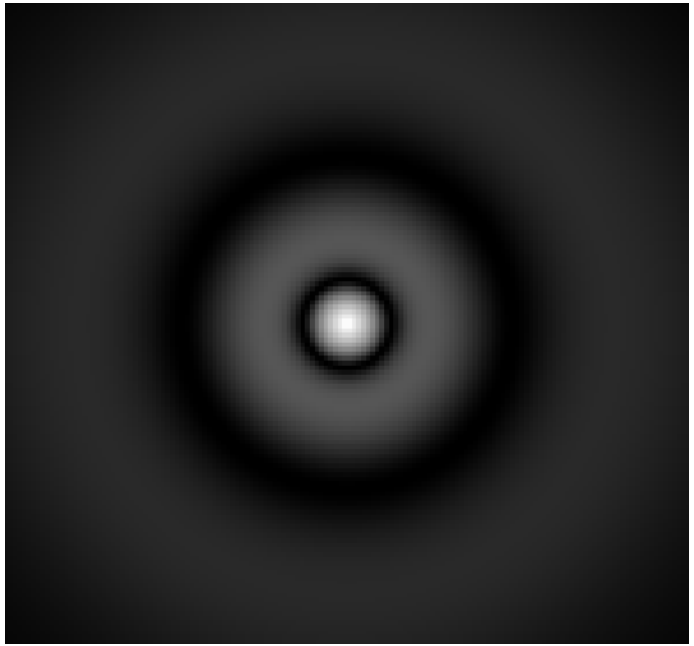
Hydrogen orbital probability density

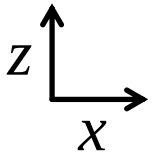
x - z
cross-section
at $y = 0$

3s

$n = 3$
$l = 0$
$m = 0$

Hydrogen orbital probability density





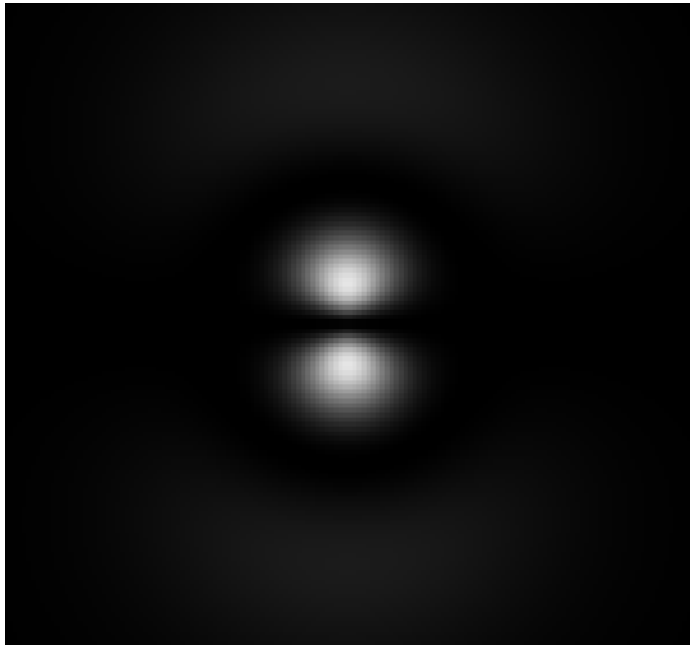
x - z
cross-section
at $y = 0$

logarithmic intensity scale

3s

$n = 3$
$l = 0$
$m = 0$

Hydrogen orbital probability density

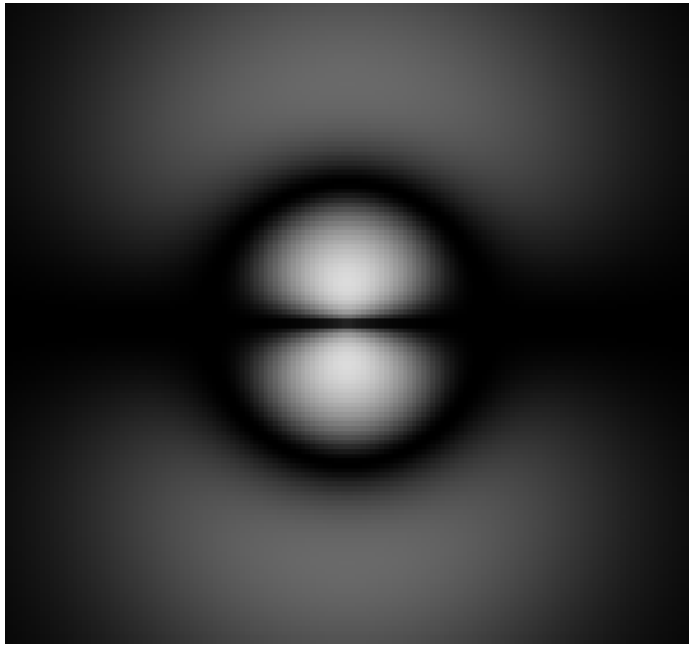


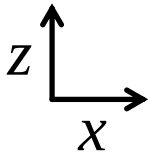
x - z
cross-section
at $y = 0$

3p

$n = 3$
$l = 1$
$m = 0$

Hydrogen orbital probability density





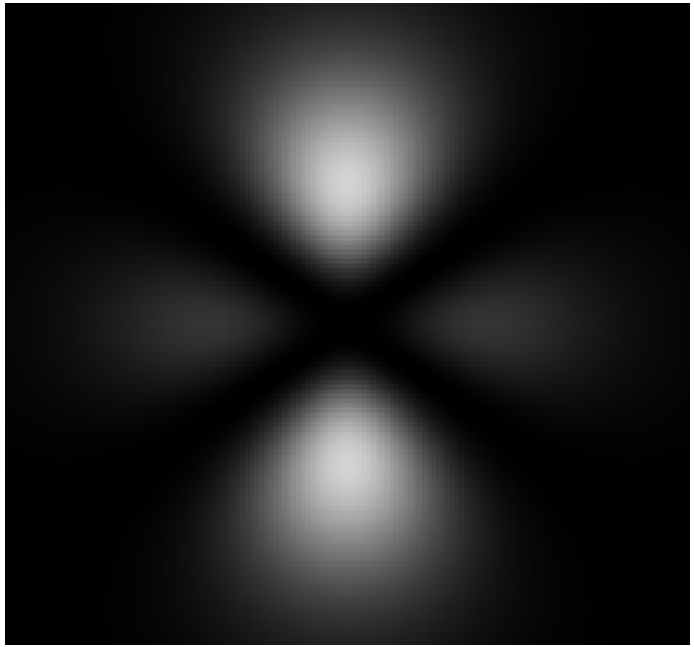
x - z
cross-section
at $y = 0$

logarithmic intensity scale

3p

$n = 3$
$l = 1$
$m = 0$

Hydrogen orbital probability density

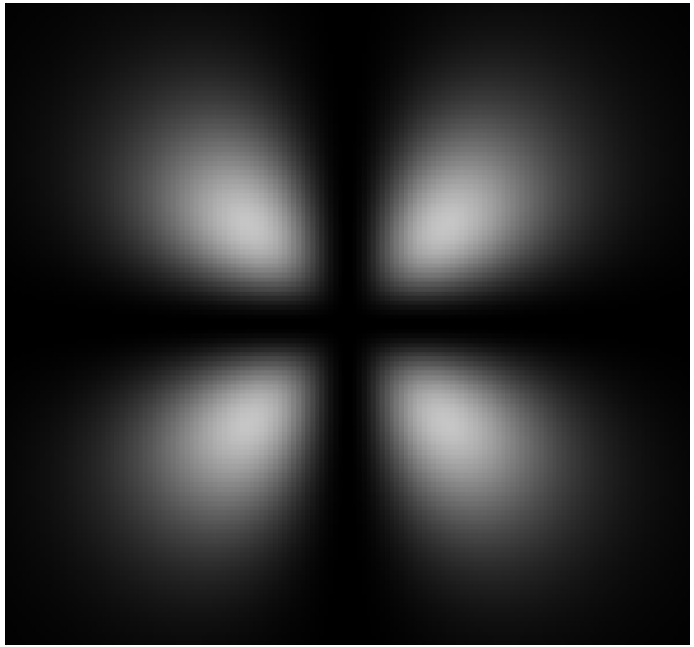


x - z
cross-section
at $y = 0$

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 $r \to 0$ in these cases

Behavior of the complete hydrogen solutions

In summary of the quantum numbers

for the so-called principal quantum number

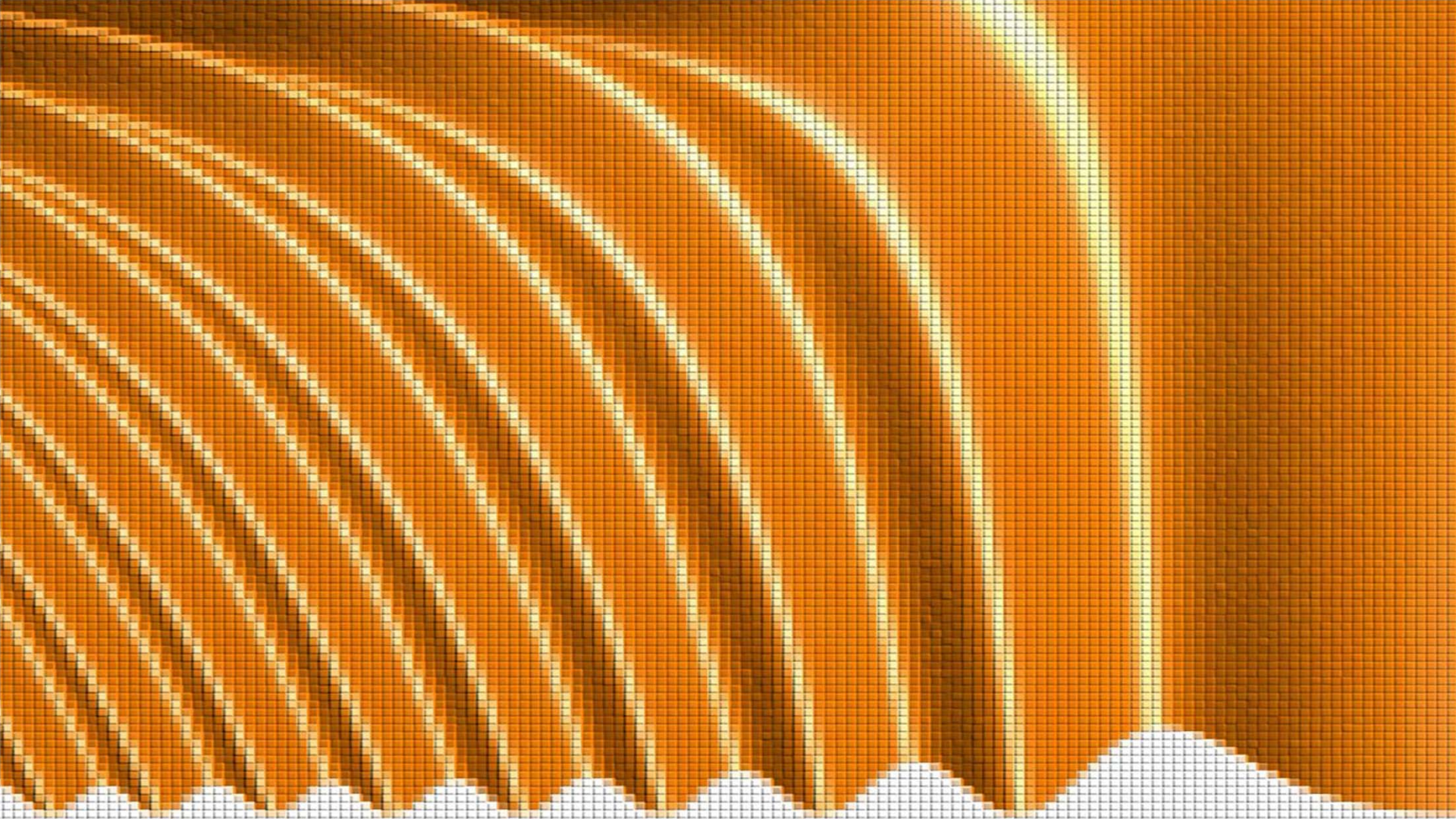
$$n = 1, 2, 3, \ldots$$

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)