Particles, atoms, and crystals 2

Hydrogen atom radial solutions

Modern physics for engineers

David Miller

Radial solutions

We remember that we had written before that

- the solution for the hydrogen atom wavefunctions can be written in the "separated" product form

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

We have now discussed the angular part $Y(\theta,\phi)$

- which we found was described by spherical harmonics

Now we return to examining the radial part $R(r)$

Hydrogen atom solution – radial functions

The radial functions are formally

$$R_{nl}(r) \propto \left(\frac{2r}{na_o}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_o}\right)\exp\left(-\frac{r}{na_o}\right)$$

where the Bohr radius is given by

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{e^2\mu} \cong 0.529\ \mathring{A} = 5.29\ \times\ 10^{-11}\mathrm{m}$$

and $L_p^j(s)$ are the associated Laguerre polynomials

and we require

n is an integer, starting at 1, with $n \geq l+1$

Eigen energies for the hydrogen atom

When we substitute the total solution

$$U_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

back into the original Schrödinger eigen equation

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_o r}\right)U(\mathbf{r}) = EU(\mathbf{r})$$

the allowed values for E are $E_{Hn} = \dfrac{-Ry}{n^2}$

where the Rydberg (energy) is

$$Ry = \frac{\hbar^2}{2\mu a_o^2} = \frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o \hbar}\right)^2 \simeq 13.6 \text{ eV}$$

Hydrogen eigen energies

Note these energies

$$E_{Hn} = \frac{-Ry}{n^2}$$

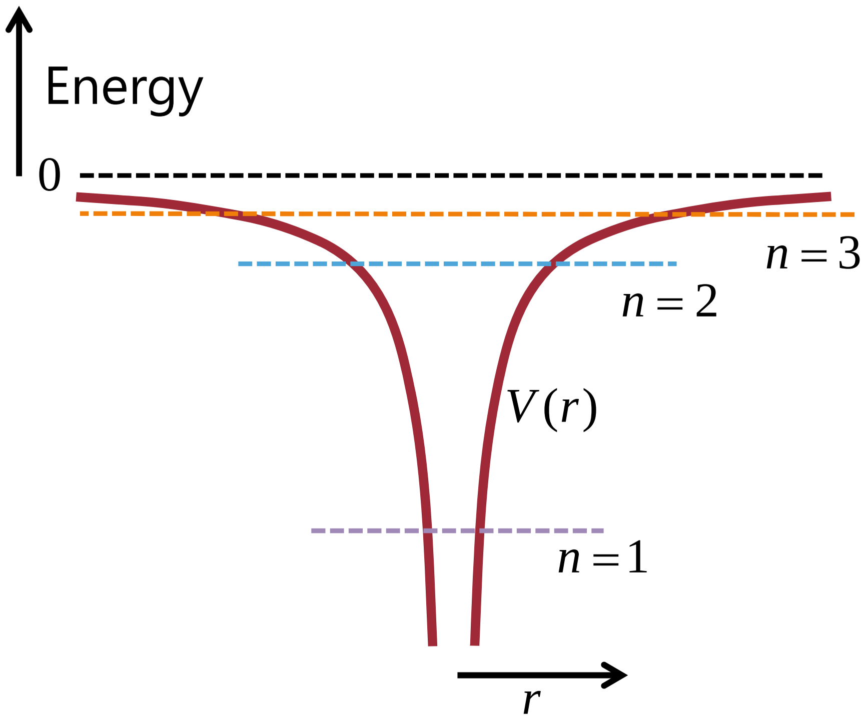
do not depend on either l or m

but only on n, the principal quantum number

Given the different shapes of the orbitals

for different n, l, and m

this is a surprising result



Radial wavefunctions - $n = 1$

We plot wavefunctions using distance units of the Bohr radius

so $\rho = r / a_o$

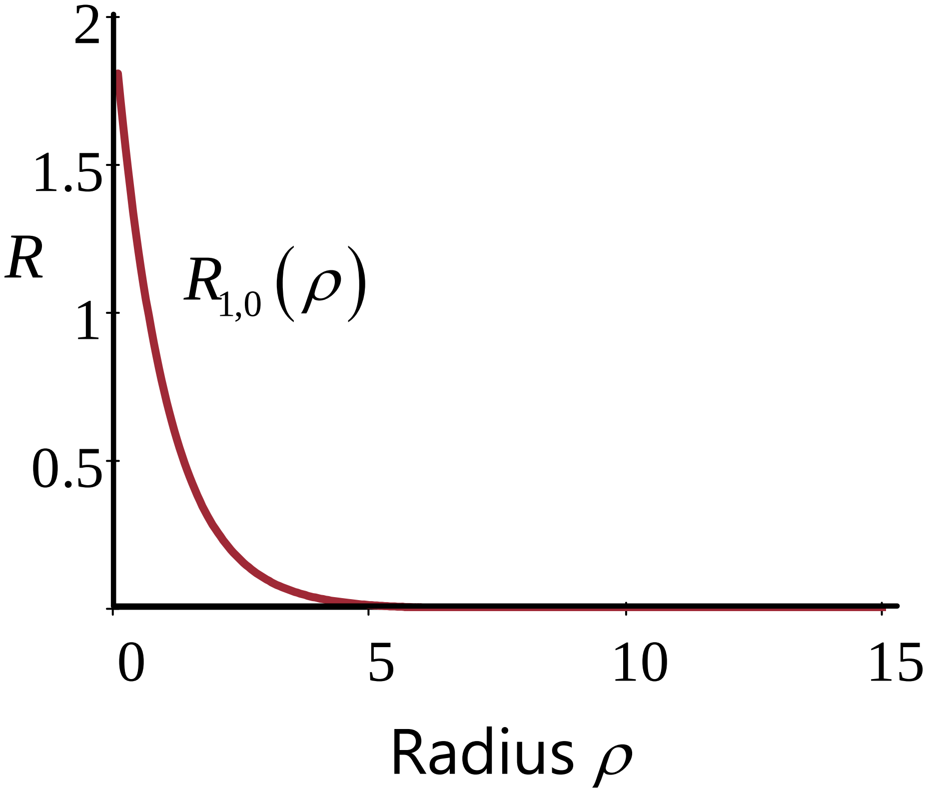
Principal quantum number

$n = 1$

Angular momentum quantum number

$l = 0$

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



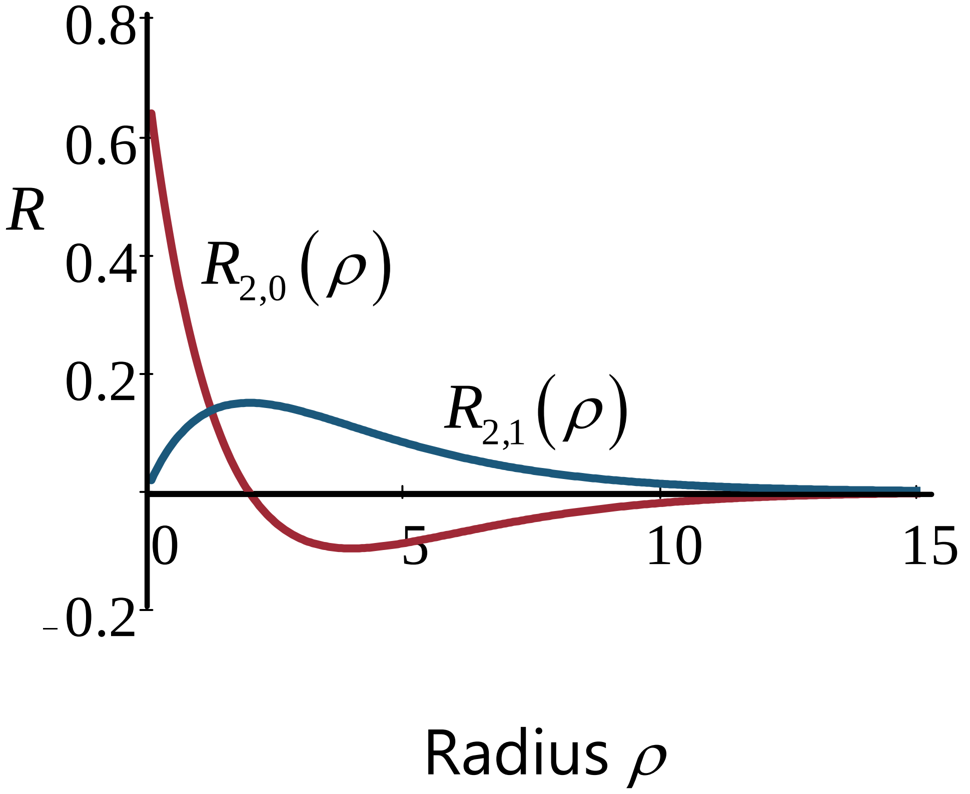
Radial wavefunctions - $n = 2$

$l = 0$

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

$l = 1$

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



Radial wavefunctions - $n = 3$

$l = 0$

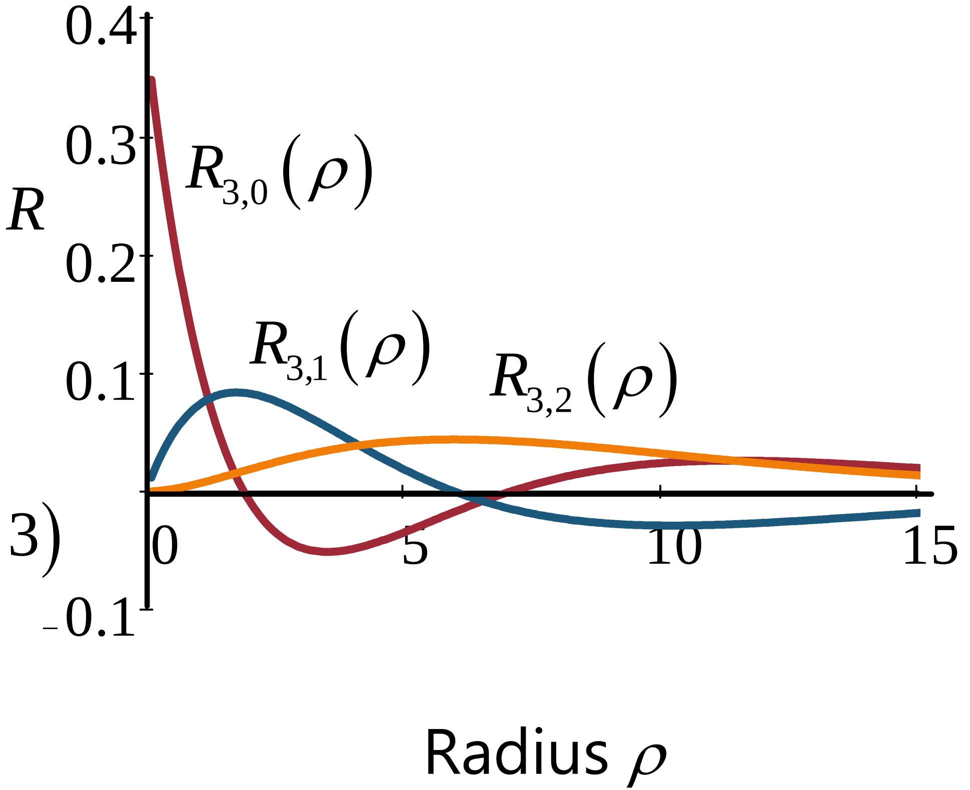
$$R_{3,0}(\rho) = \frac{2\sqrt{3}}{27}\left(3 - 2\rho + \frac{2}{9}\rho^2\right)\exp(-\rho/3)$$

$l = 1$

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

$l = 2$

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



Particles, atoms, and crystals 2

Hydrogen atom complete solutions

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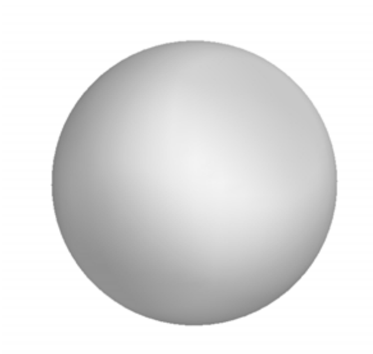
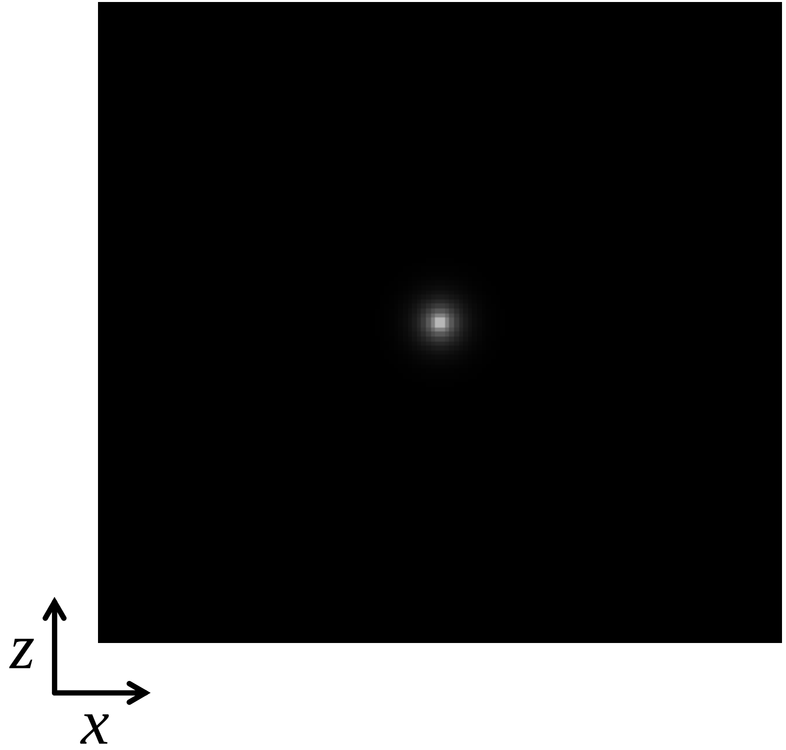
Hydrogen orbital probability density

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

spherical harmonic





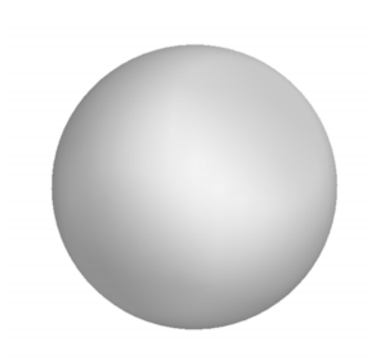
1s

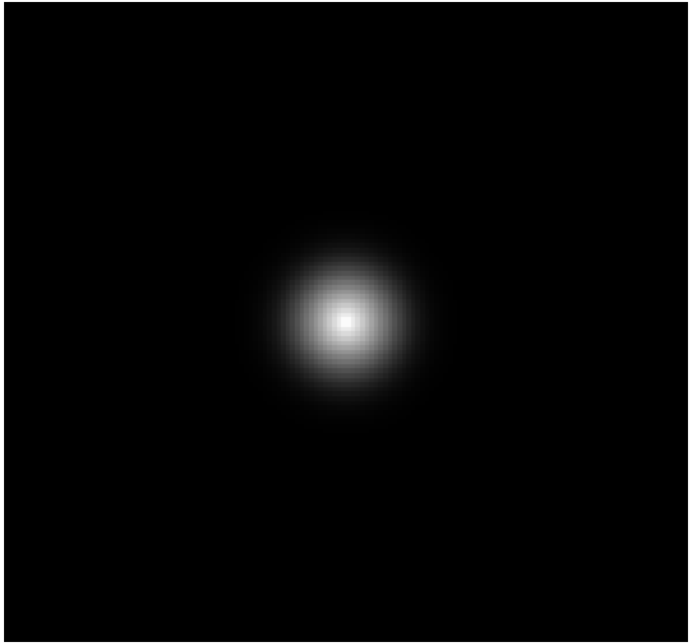
$n = 1$
$l = 0$
$m = 0$

Hydrogen orbital probability density

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

spherical harmonic





z

x

logarithmic intensity scale

1s

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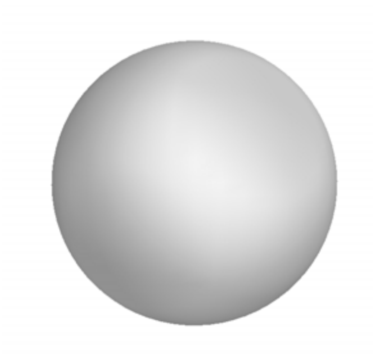
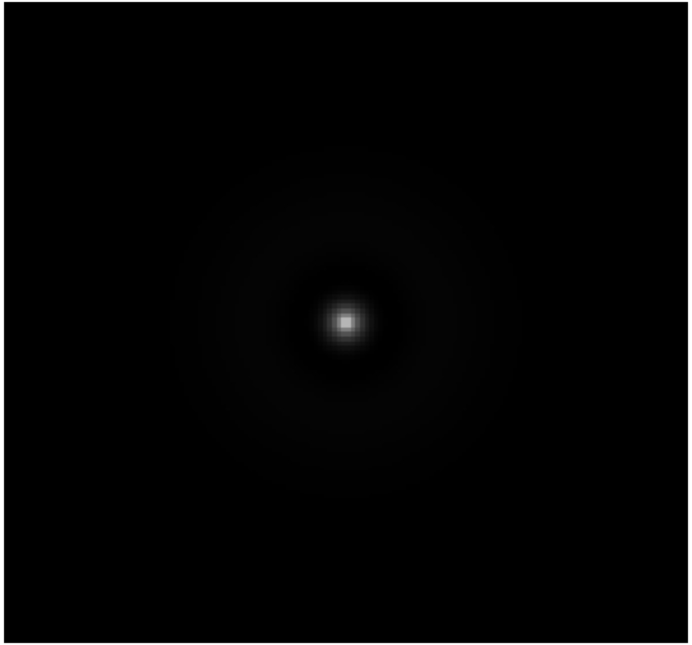
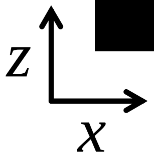
Hydrogen orbital probability density

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

spherical harmonic







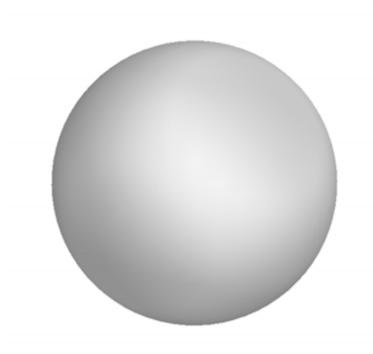
2s

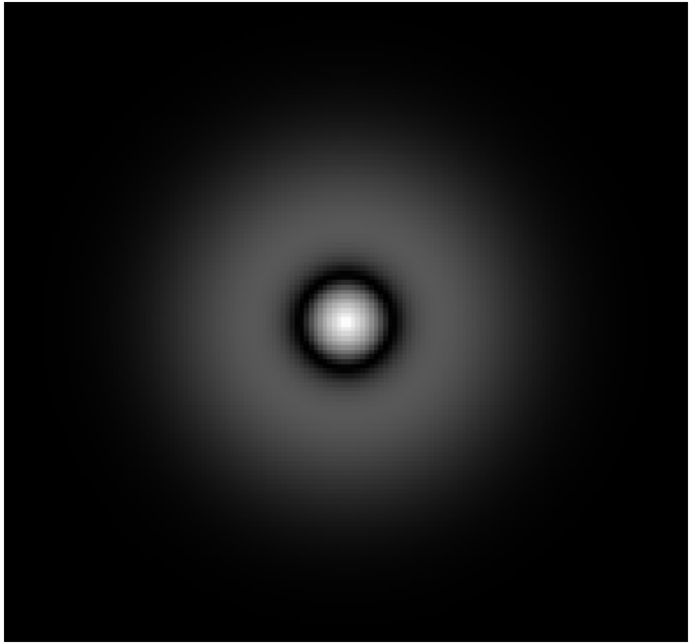
$n = 2$
$l = 0$
$m = 0$

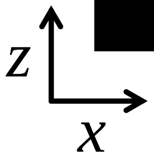
Hydrogen orbital probability density

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

spherical harmonic







logarithmic intensity scale

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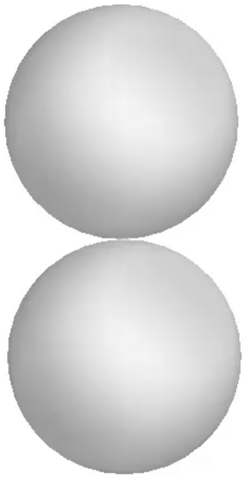
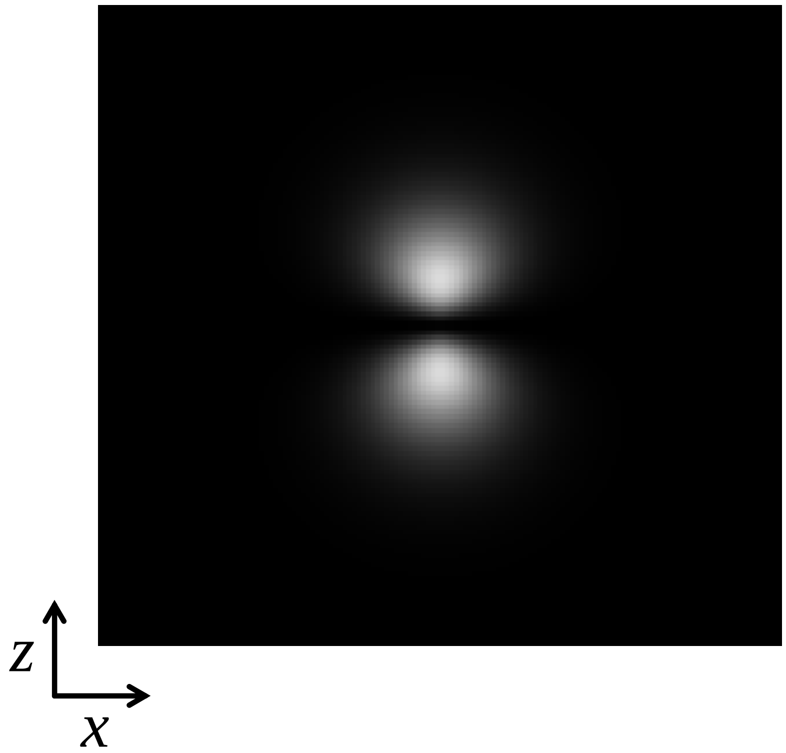


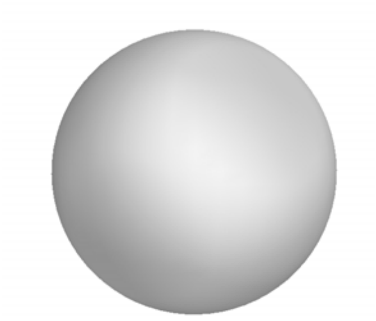


2p

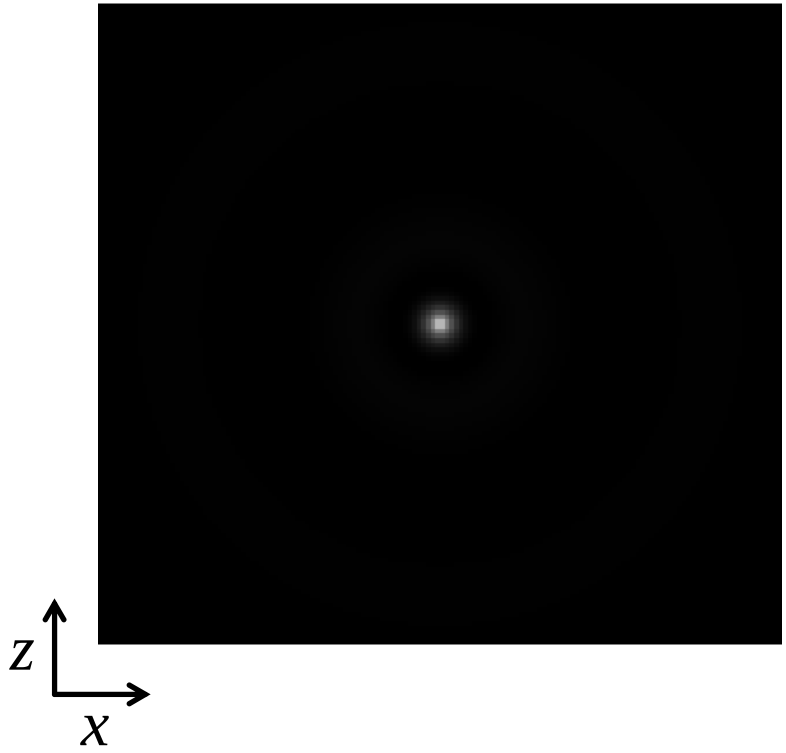
$n = 2$
$l = 1$
$m = 0$

Hydrogen orbital probability density

spherical harmonic



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



3s

$n = 3$

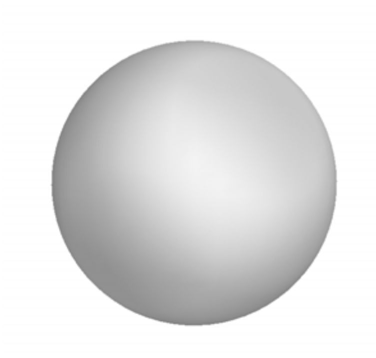
$l = 0$

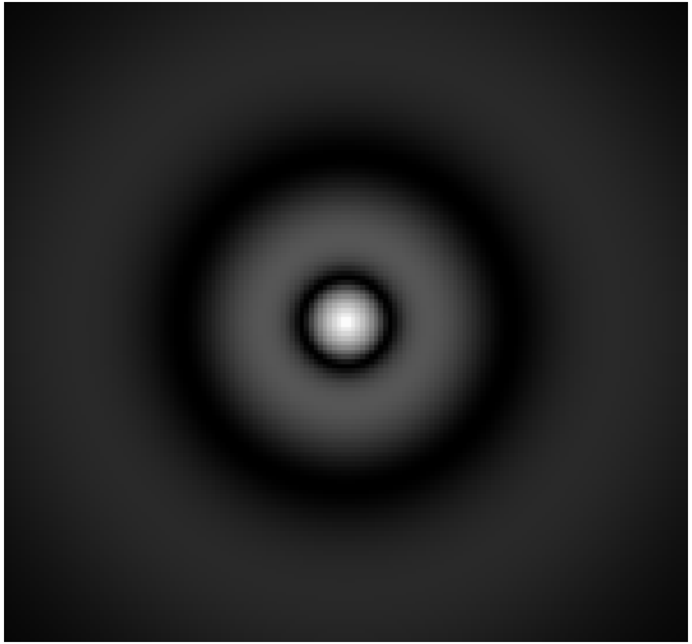
$m = 0$

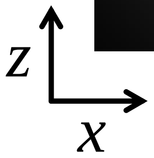
Hydrogen orbital probability density

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

spherical harmonic







logarithmic intensity scale

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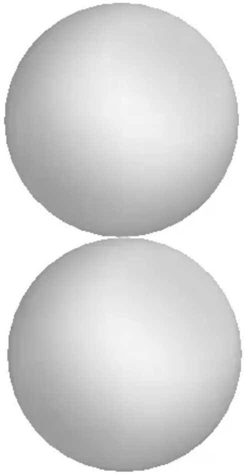
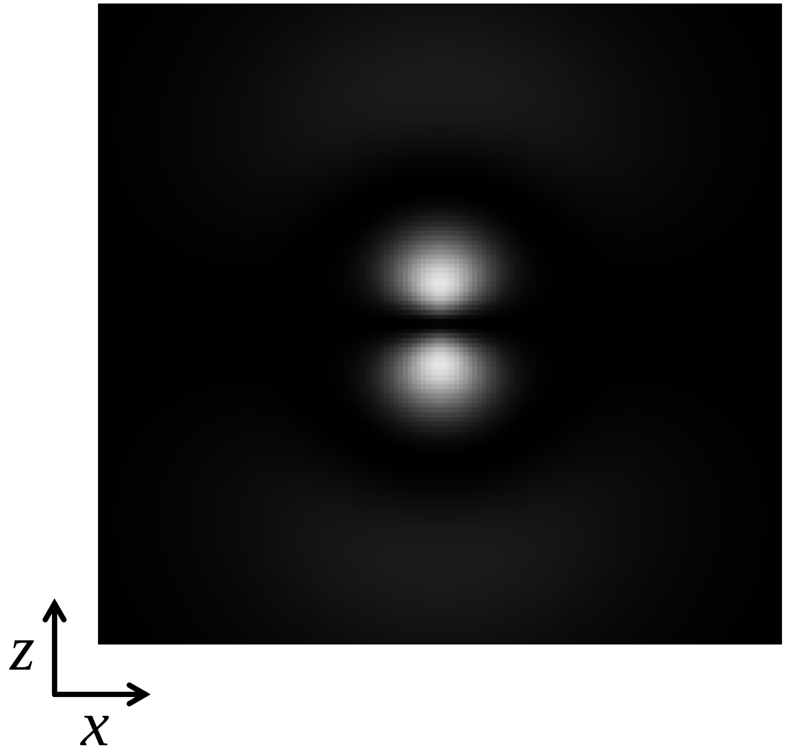
Hydrogen orbital probability density

spherical harmonic



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



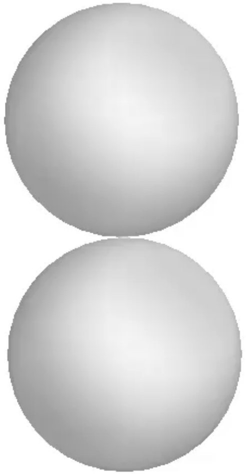
3p

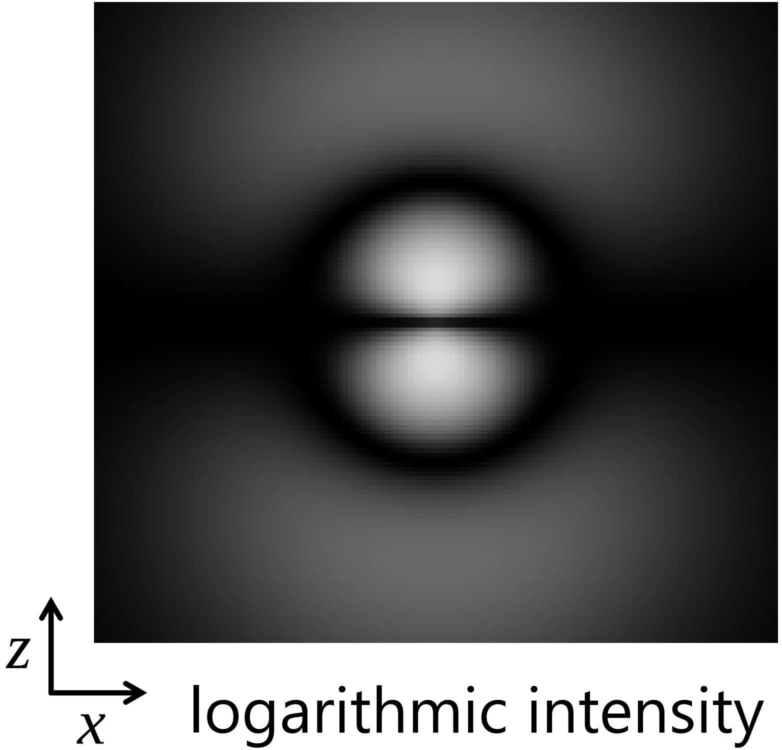
$n = 3$
$l = 1$
$m = 0$

Hydrogen orbital probability density

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

spherical harmonic





logarithmic intensity scale

3p

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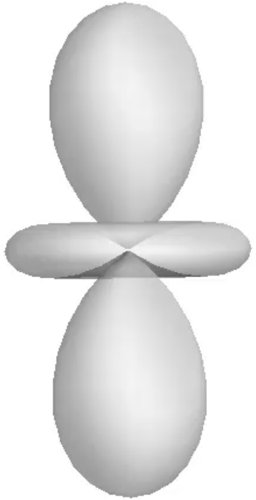
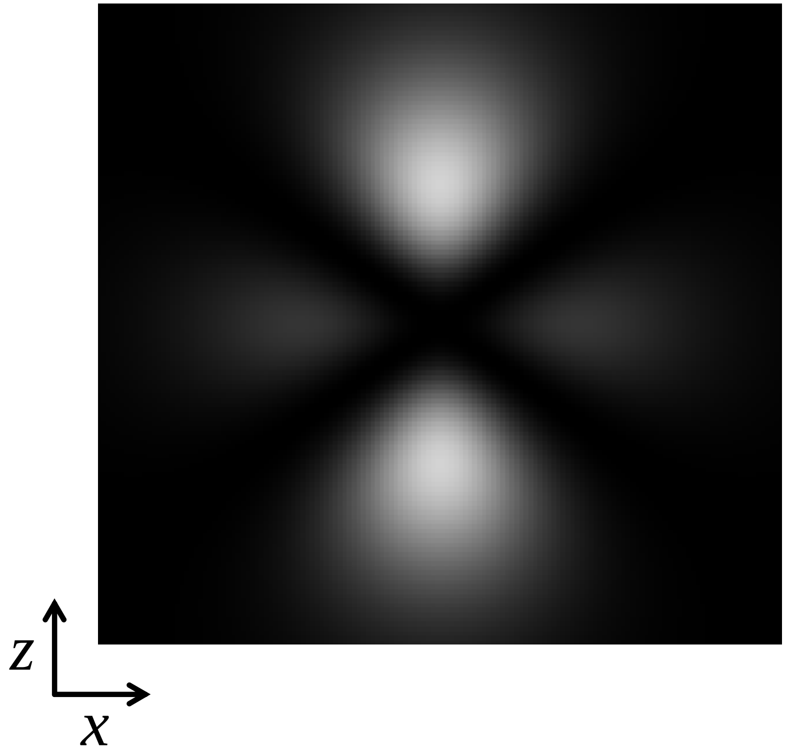
$m = 0$

Hydrogen orbital probability density

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

spherical harmonic





3d

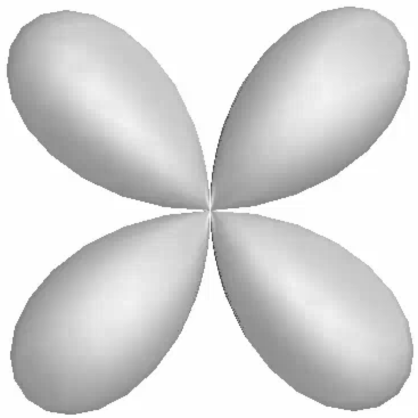
$n = 3$

$l = 2$

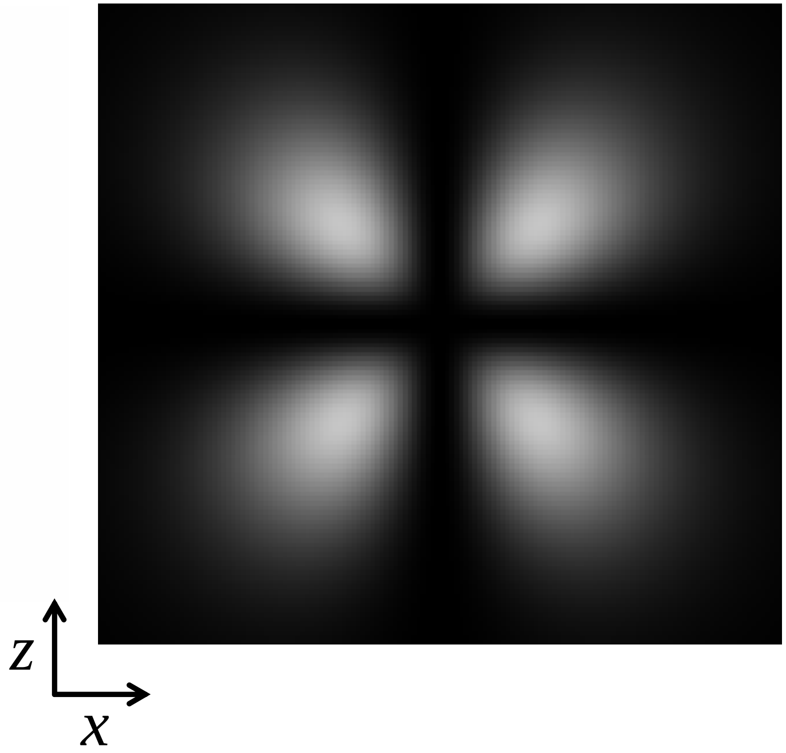
$m = 0$

Hydrogen orbital probability density

spherical harmonic



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

The wavefunctions generally have an overall exponential decay of the form $\exp\left(-r / na_o\right)$

so this exponential decay is slower with r for larger n

(ii) The radial wavefunctions have $n - l - 1$ zeros

These zeros are from the roots of the polynomial functions

This completes our mathematical solution of the hydrogen atom problem

Behavior of the complete hydrogen solutions

In summary of the quantum numbers, all integers

for the so-called principal quantum number

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

for the angular momentum quantum number

$$l \leq n - 1$$

for the magnetic quantum number

$$-l \leq m \leq l$$

We also now know the eigenenergies $E_{Hn} = -\frac{Ry}{n^2}$

Note the energy does not depend on l or m

Particles, atoms, and crystals 2

Electron spin and Pauli exclusion

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Electron spin and the Pauli exclusion principle

By the early 1920's atoms were being grouped based on "shells"

- e.g., of 2 electrons, 8 electrons, 18 electrons, …

Pauli realized in 1924 that

- introducing one more quantum number beyond the n, l, and m already present in extensions of Bohr's model
  - and allowing two values
    - now called spin-up and spin-down
      - he could explain much about atoms
        - based on only one electron per "state"

Electron spin and Pauli exclusion

The idea that

- only one electron is allowed for each different set of quantum numbers
  - or equivalently
    - we can only have one electron in a given "state"

is

- the Pauli exclusion principle

Pauli exclusion also explains

- why condensed matter has most of the volume it has

Electron spin

Later, the new quantum number introduced by Pauli

was called spin

in part because it is like the behavior

of a classical spinning particle

A classical spinning particle of some size

would have angular momentum

and, for a charged particle

would correspond to a current loop

and hence a magnetic moment

The electron has both angular momentum and a magnetic moment

Electron spin

But, quantitatively

- the electron does not correspond with any such classical spinning body

And, quantum mechanically

- the electron behaves as if the magnitude of its “spin” angular momentum is $\hbar / 2$

So, instead of an orbital angular momentum quantum number l that takes integer values

- we have a quantum number s for the electron where

$$s = \frac{1}{2}$$

Electron spin

With this half-integer value for s we see

electron spin is not associated with a spatial wavefunction corresponding to an orbit

because this non-integer value means

any such spatial wavefunction would not get back to where it started on going round in a circle

Spin is more abstract property that

we cannot completely visualize in a spatial way

Spin magnetic quantum number

We can define a magnetic spin quantum number, m_s

analogously to the (orbital) magnetic quantum number m and its relation to l, that is

$$-s \le m_s \le s$$

which means we can have

$m_s = \frac{1}{2}$, known as "spin-up"

$m_s = -\frac{1}{2}$, known as "spin-down"

and we can write the angular momentum as $m_s \hbar$

“Explanation” of spin

Spin was introduced “ad hoc” to explain electron occupation of orbitals and effects of magnetic fields

Dirac showed in 1928 that with a

- a relativistically correct equation
  - instead of the Schrödinger equation
    - he obtained spin automatically

The “explanation” of Pauli exclusion

- comes from the “spin-statistics theorem”
  - which requires relativistic quantum mechanics