Lecture 18:
3D Review, MRI, Examples

A real (2D) "quantum dot"

http://pages.unibas.ch/phys-
meso/Pictures/pictures.html
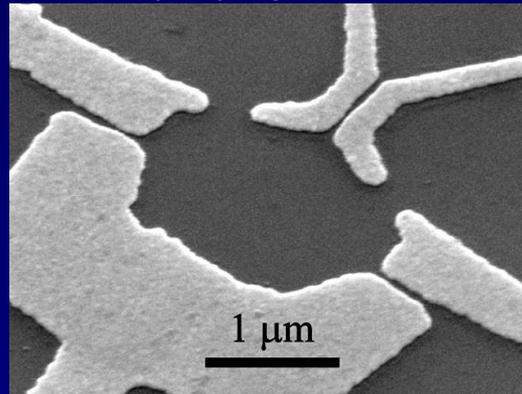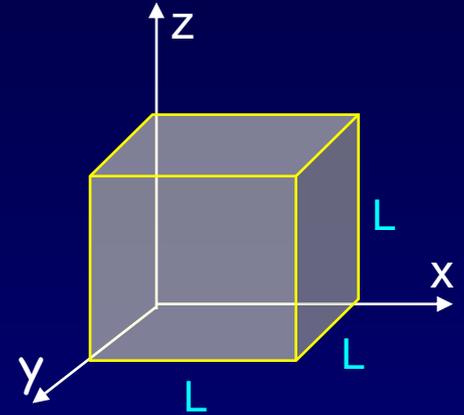
Lect. 16: Particle in a 3D Box (3)

The energy eigenstates and energy values in a 3D cubical box are:

$$\psi = N \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

where n_x, n_y, and n_z can each have values 1,2,3,….

This problem illustrates two important points:

- Three quantum numbers (n_x, n_y, n_z) are needed to identify the state of this three-dimensional system.
  That is true for every 3D system.

- More than one state can have the same energy: "Degeneracy".
  Degeneracy reflects an underlying symmetry in the problem.
  3 equivalent directions, because it's a cube, not a rectangle.

Act 1

Consider a particle in a 2D well, with $L_x = L_y = L$.

1. Compare the energies of the (2,2), (1,3), and (3,1) states?

   a. $E_{(2,2)} > E_{(1,3)} = E_{(3,1)}$

   b. $E_{(2,2)} = E_{(1,3)} = E_{(3,1)}$

   c. $E_{(2,2)} < E_{(1,3)} = E_{(3,1)}$

2. If we squeeze the box in the x-direction (*i.e.*, $L_x < L_y$) compare $E_{(1,3)}$ with $E_{(3,1)}$.

   a. $E_{(1,3)} < E_{(3,1)}$

   b. $E_{(1,3)} = E_{(3,1)}$

   c. $E_{(1,3)} > E_{(3,1)}$

Solution

Consider a particle in a 2D well, with $L_x = L_y = L$.

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   c. $E_{(2,2)} < E_{(1,3)} = E_{(3,1)}$

   $E_{(1,3)} = E_{(3,1)} = E_0 (1^2 + 3^2) = 10 E_0$

   $E_{(2,2)} \qquad = E_0 (2^2 + 2^2) = \ 8 E_0$

   $$E_0 \equiv \frac{h^2}{8mL^2}$$

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   a. $E_{(1,3)} < E_{(3,1)}$

   b. $E_{(1,3)} = E_{(3,1)}$

   c. $E_{(1,3)} > E_{(3,1)}$

Because $L_x < L_y$, for a given n, E_0 for x motion is larger than E_0 for y motion. The effect is larger for larger n. Therefore, $E_{(3,1)} > E_{(1,3)}$.

Example: $L_x = \frac{1}{2}$, $L_y = 1$:

$E_{(1,3)} \propto 4 \times 1^2 + 1 \times 3^2 = 13$
$E_{(3,1)} \propto 4 \times 3^2 + 1 \times 1^2 = 37$

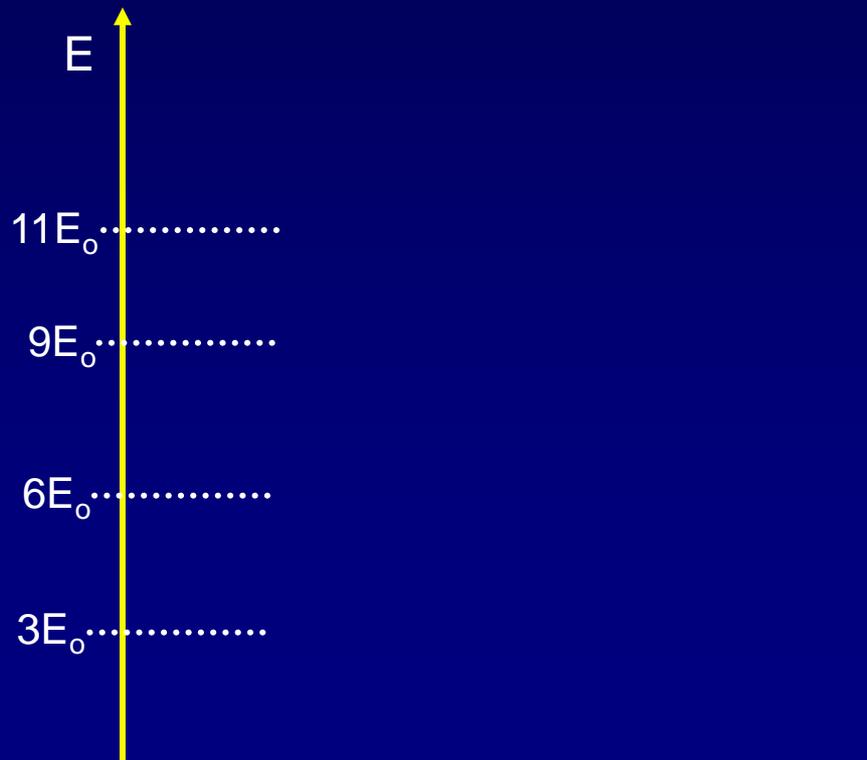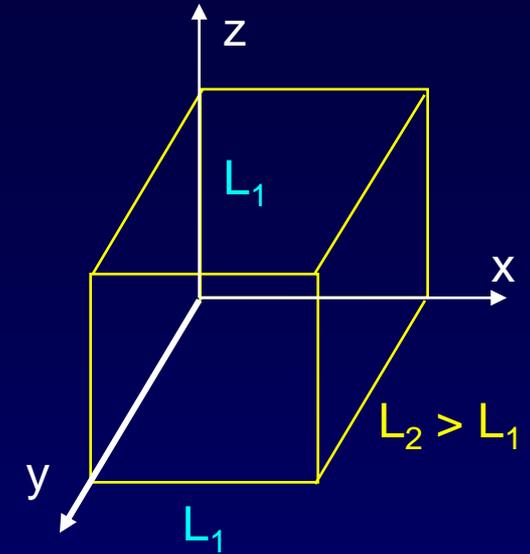We say "the degeneracy has been lifted."

Non-cubic Box

Consider a non-cubic box:

The box is stretched along the y-direction.
What will happen to the energy levels?
Define $E_o = h^2/8mL_1^2$

E

$11E_o$ ....

$9E_o$ ....

$6E_o$ ....

$3E_o$ ....

z

L_1

x

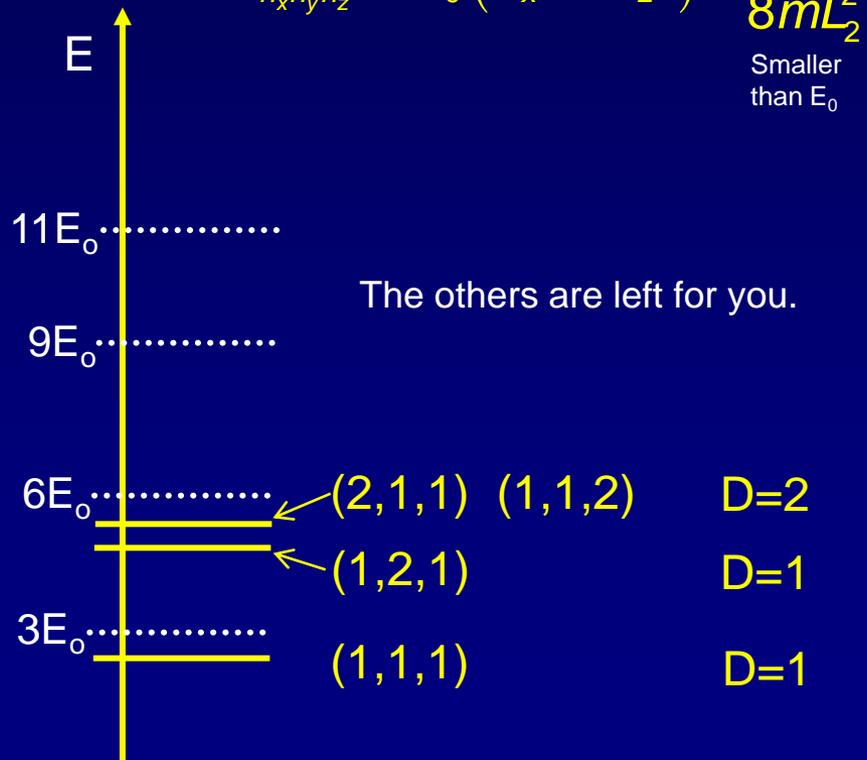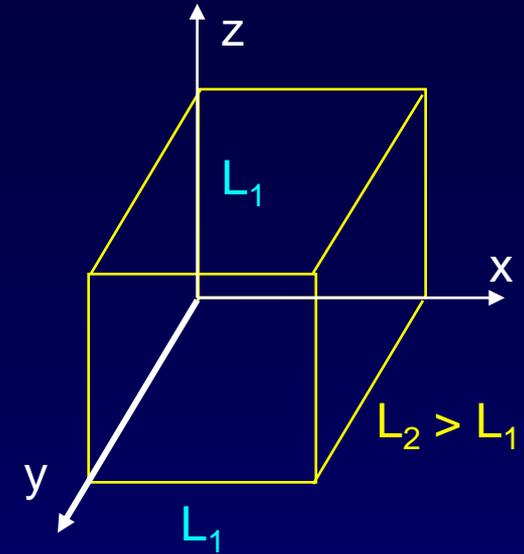$L_2 > L_1$

y

L_1

Solution

Consider a non-cubic box:

The box is stretched along the y-direction.
What will happen to the energy levels?
Define $E_o = h^2/8mL_1^2$

$$E_{n_x n_y n_z} = E_0\left(n_x^2 + n_z^2\right) + \frac{h^2}{8mL_2^2}\left(n_y^2\right)$$

Smaller
than E_0

E

11E_o ·············

9E_o ·············

The others are left for you.

6E_o ············· (2,1,1) (1,1,2)   D=2

(1,2,1)   D=1

3E_o ·············

(1,1,1)   D=1

z

L_1

x

$L_2 > L_1$

y

L_1

1: The symmetry is "broken" for y, so
    the 3-fold degeneracy is lowered.
    A 2-fold degeneracy remains,
    because x and z are still symmetric.

2: There is an overall lowering of
    energies due to decreased
    confinement along y.

Radial Eigenstates of Hydrogen

Here are graphs of the s-state wave functions, $R_{no}(r)$, for the electron in the Coulomb potential of the proton. The zeros in the subscripts are a reminder that these are states with $l = 0$ (zero angular momentum!).

E

0

-1.5 eV

R_{10}

R_{20}

R_{30}

-3.4 eV

0

0   r $4a_0$

0

0   r $10a_0$

0

0   r $15a_0$
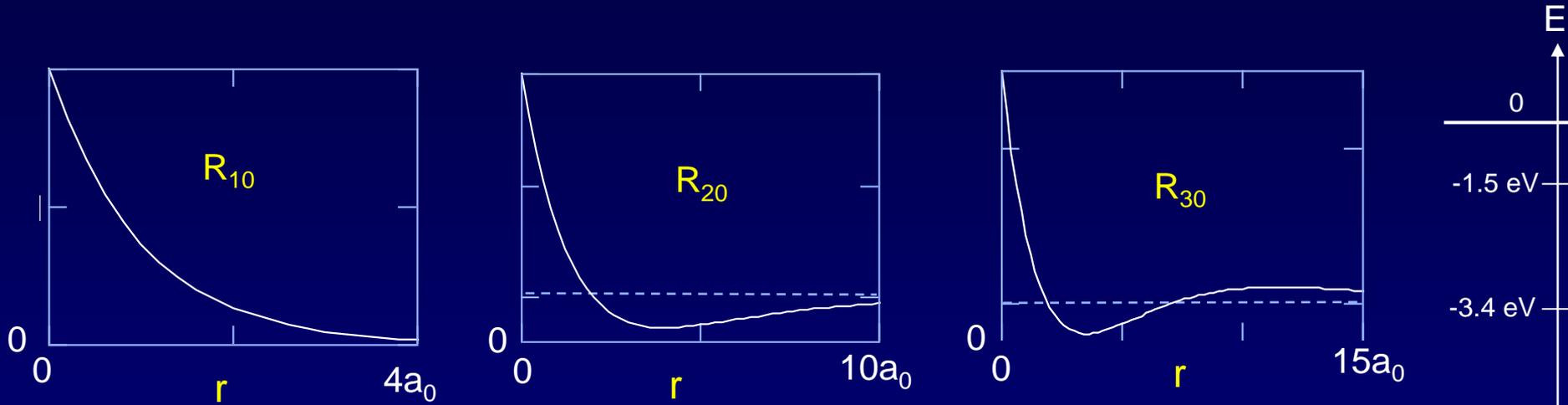
$R_{1,0}(r) \propto e^{-r/a_0}$

$R_{2,0}(r) \propto \left(1 - \dfrac{r}{2a_0}\right) e^{-r/2a_0}$

$R_{3,0}(r) \propto \left(3 - \dfrac{2r}{a_0} + 2\left(\dfrac{r}{3a_0}\right)^2\right) e^{-r/3a_0}$

$r \approx \dfrac{\hbar^2}{m\kappa e^2} \equiv a_0 = 0.053$ nm

The "Bohr radius" of the H atom.

$E \approx -\dfrac{m\kappa^2 e^4}{2\hbar^2} = -13.6$ eV
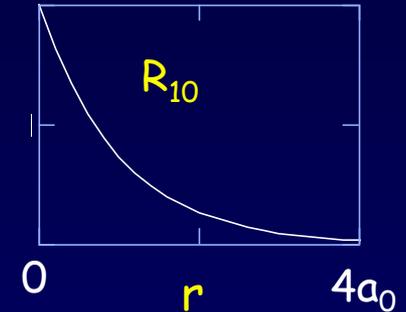
The ground state energy of the hydrogen atom.

One factor of e or e^2 comes from the proton charge, and one from the electron.

-13.6 eV

Wave Function Normalization

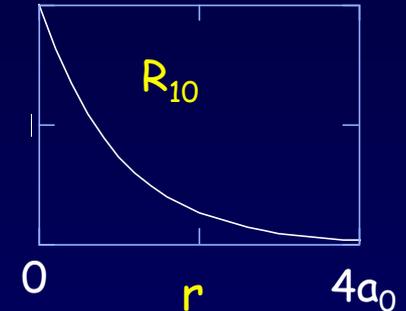What is the normalization constant for the hydrogen atom ground state?

$$\psi_{100}(r,\theta,\phi) = NR_{10}(r) = Ne^{-r/a_o}$$

Solution

What is the normalization constant for the hydrogen atom ground state?

$$\psi_{100}(r,\theta,\phi) = NR_{10}(r) = Ne^{-r/a_o}$$

The probability density is $|\psi|^2 = N^2 \exp(-2r/a_o)$. In 3D, this means "probability per unit volume".

We require that the total probability = 1: $\int |\psi|^2 \, dV = 1$

$dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$

With spherical symmetry, the angular integrals give 4π, so we are left with:

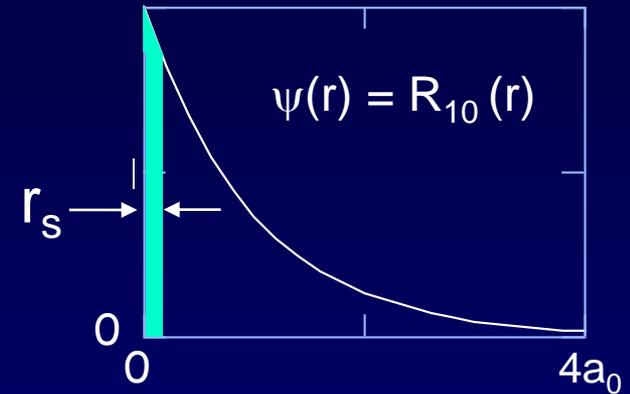$$4\pi N^2 \int_0^\infty r^2 e^{-2r/a_0} dr = 1 \quad \Rightarrow \quad N^2 = \frac{1}{\pi a_o^3}$$

"You can look it up!"

$$\boxed{\psi_{100}(r) = \sqrt{\frac{1}{\pi a_o^3}} \; e^{-r/a_o}}$$

Normalized ground-state wave function of hydrogen

Probability Calculation

Estimate the probability of finding the electron within a small sphere of radius $r_s = 0.2\, a_o$ at the origin.
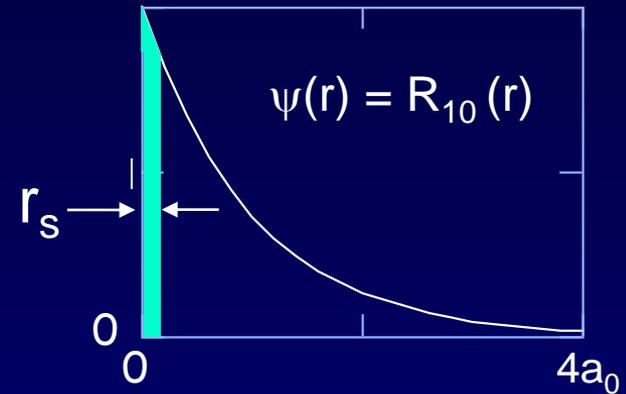

$$\psi(r) = Ne^{-r/a_o}$$

Solution

Estimate the probability of finding the electron within a small sphere of radius $r_s = 0.2\, a_o$ at the origin.

If it says "estimate", don't integrate.

The wave function is nearly constant near r = 0:

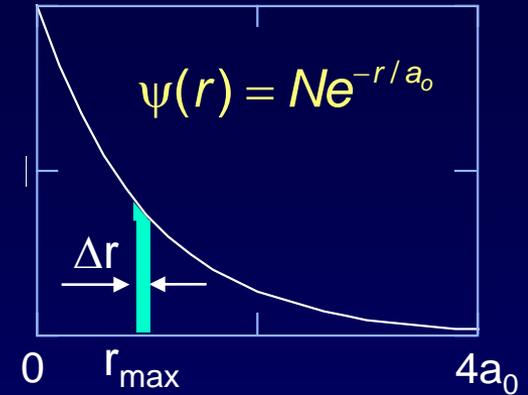$$\psi(0) = \sqrt{\frac{1}{\pi a_o^3}}\ e^{-0/a_o} = \sqrt{\frac{1}{\pi a_o^3}}$$

$\psi(r) = R_{10}(r)$

r_s

0

0          $4a_0$

$$\psi(r) = Ne^{-r/a_o}$$

Simply multiply $|\psi|^2$ by the volume $\Delta V = (4/3)\pi r_s^3$:

$$\text{Probability} \;=\; \left|\psi(0)\right|^2 \Delta V = \frac{4}{3}\left(\frac{r_s}{a_o}\right)^3 \approx 0.01$$

Maximum Radial Probability

At what radius are you most likely to find the electron?

$$\psi(r) = Ne^{-r/a_o}$$

Δr

0   r_{max} $4a_0$

Solution

At what radius are you most likely to find the electron?

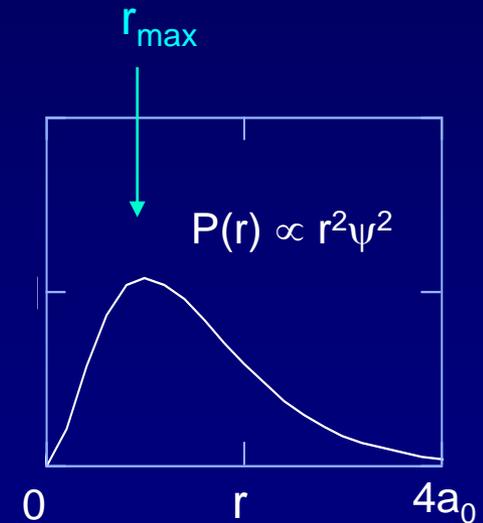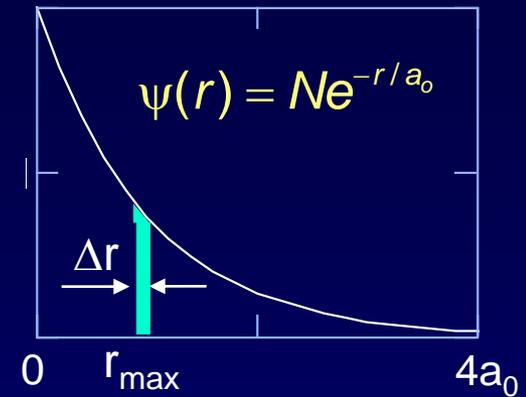Looks like a no-brainer. r = 0, of course!

Well, that's not the answer.

You must find the probability $P(r)\Delta r$ that the electron is in a shell of thickness Δr at radius r. For a given Δr the volume, ΔV, of the shell increases with radius.

The radial probability has an extra factor of r^2:

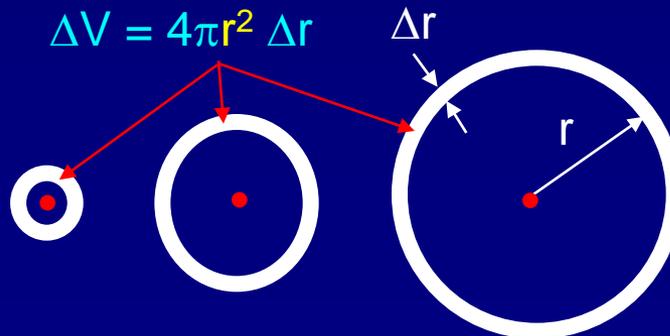$$P(r)\Delta r = \left|\psi(r)\right|^2 \Delta V = Cr^2 e^{-2r/a_o} \Delta r$$

Set dP/dr = 0 to find:

$$\boxed{r_{max} = a_0 \text{ !}}$$

$$\psi(r) = Ne^{-r/a_o}$$

$$\Delta r$$

0   r_{max} $4a_0$

r_{max}

$$P(r) \propto r^2\psi^2$$

0   r $4a_0$

More volume at larger r.

No volume at r = 0.

$$\Delta V = 4\pi r^2 \Delta r$$ Δr

r

Act 2

1. Suppose the electron is in the l=1, m=1 state. In what direction(s) (at what θ), is the electron most likely to be found? $Y_{1,\pm1} \propto \sin\theta$

    a. θ = 0° (north pole)

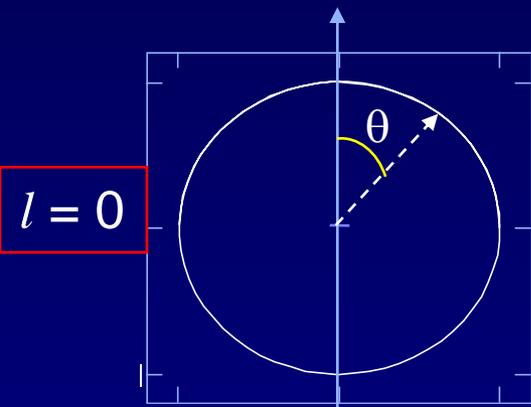   b. θ = 45°

    c. θ = 90° (equator)

Solution

1. Suppose the electron is in the $l=1$, $m=1$ state. In what direction(s) (at what θ), is the electron most likely to be found? $Y_{1,\pm 1} \propto \sin\theta$
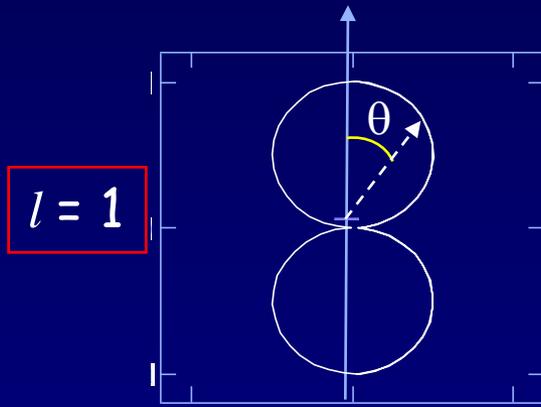
    a. $\theta = 0°$ (north pole)

    b. $\theta = 45°$
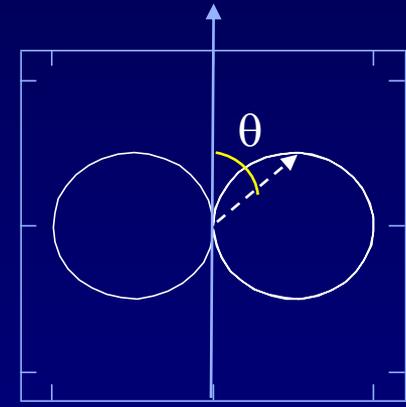
    c. $\theta = 90°$ (equator)

$\sin\theta$ is maximum at $\theta = 90°$.

$l = 0$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$
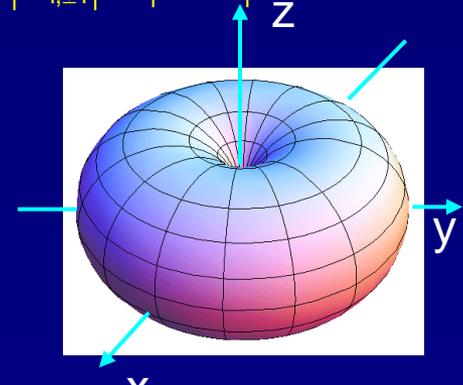
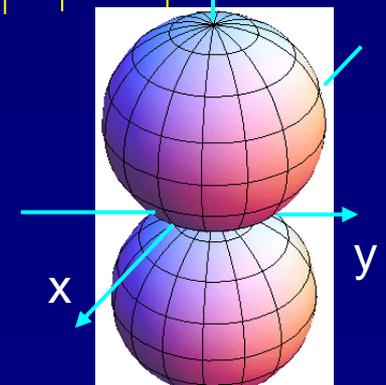$$\left|Y_{1,0}\right| \propto \left|\cos\theta\right|$$

$l = 1$

$$\left|Y_{1,\pm 1}\right| \propto \left|\sin\theta\right|$$

Length of the dashed arrow is the magnitude of Y_{lm} as a function of θ.
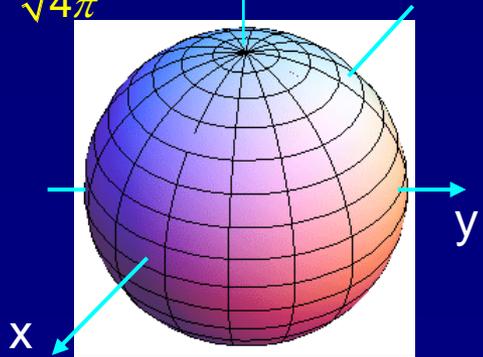
Act 3

Consider an electron around a nucleus that has two protons, like an ionized Helium atom.

1. Compare the "effective Bohr radius" $a_{0,He}$ with the usual Bohr radius for hydrogen, a_0:

   a. $a_{0,He} > a_0$

   b. $a_{0,He} = a_0$

   c. $a_{0,He} < a_0$

   > Hint:
   > Look at the expression for a_0 on the previous slide. What changes when we change H to He?

2. What is the ratio of ground state energies $E_{0,He}/E_{0,H}$?

   a. $E_{0,He}/E_{0,H} = 1$

   b. $E_{0,He}/E_{0,H} = 2$

   c. $E_{0,He}/E_{0,H} = 4$

Solution

Consider an electron around a nucleus that has two protons, like an ionized Helium atom.

1. Compare the "effective Bohr radius" $a_{0,He}$ with the usual Bohr radius for hydrogen, a_0:

    Look at how a_0 depends on the charge:

    a. $a_{0,He} > a_0$

    b. $a_{0,He} = a_0$

    c. $a_{0,He} < a_0$

    $$a_0 \equiv \frac{\hbar^2}{m\kappa e^2} \Rightarrow a_{0,He} \equiv \frac{\hbar^2}{m\kappa (2e)e} = \frac{a_0}{2}$$

    This should make sense:
    more charge → stronger attraction
    → electron sits closer to the nucleus

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Solution

Consider an electron around a nucleus that has two protons, (an ionized Helium atom).

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   Look at how a_0 depends on the charge:

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   $$a_0 \equiv \frac{\hbar^2}{m\kappa e^2} \Rightarrow a_{0,He} \equiv \frac{\hbar^2}{m\kappa(2e)e} = \frac{a_0}{2}$$

   This should make sense:
   more charge → stronger attraction
   → electron "sits" closer to the nucleus

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   b. $E_{0,He}/E_{0,H} = 2$

   c. $E_{0,He}/E_{0,H} = 4$

   Clearly the electron will be more tightly bound, so $|E_{0,He}| > |E_{0,H}|$. How much more tightly? Look at E_0:

   $$E_{0,H} = -\frac{m\kappa^2 e^4}{2\hbar^2} \Rightarrow E_{0,He} = \frac{-m\kappa^2 (2e)^2 e^2}{2\hbar^2} = 4E_{0,H}$$

In general, for a "hydrogenic" atom (only one electron) with Z protons:

$$E_{0,Z} = Z^2 E_{0,H}$$

Transitions in the Hydrogen Atom

Consider the three lowest energy levels of the hydrogen atom. What wavelengths of light will be emitted when the electron jumps from one state to another?

Transitions in the Hydrogen Atom

Consider the three lowest energy levels of the hydrogen atom.
What wavelengths of light will be emitted when the electron jumps
from one state to another?

Solution:

ΔE_{21} = 10.2 eV

ΔE_{31} = 12.1 eV

ΔE_{32} = 1.9 eV

$E = -13.6$ eV$/n^2$, so $E_1 = -13.6$ eV, $E_2 = -3.4$ eV, and $E_3 = -1.5$ eV. There are three jumps to consider, 2-to-1, 3-to-1, and 3-to-2. The photon carries away the energy that the electron loses.

$\lambda = h/p = hc/E$

λ_{21} = 122 nm

λ_{31} = 102 nm

λ_{32} = 653 nm

hc = 1240 eV·nm

Two wavelengths are in the ultraviolet.

The 3-to-2 transition gives a visible (red) photon.

Optical Transitions between Atomic Levels

Consider the n = 1 and 2 levels of hydrogen:

$$f = \frac{\Delta E}{h} = \frac{c}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{1240 \text{ eV} \cdot \text{nm}}{\Delta E}$$

n = 2

n = 1

ΔE

photon

The atom can make transitions by emitting (n: 2→1) or absorbing (n: 1→2) a photon. In general, the time-dependent solution of the SEQ in the time-dependent EM field shows the wave function <u>oscillating</u> between the two eigenstates of the energy (that is, they were eigenstates before the field showed up!).

Not all transitions are possible.
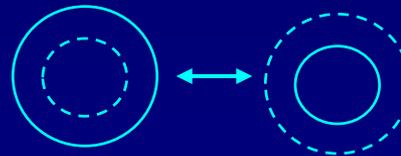For example, one must conserve angular momentum (and the photon has l = 1).

<u>Superpositions:</u>

<u>Stationary States:</u>

1s   2s   2p
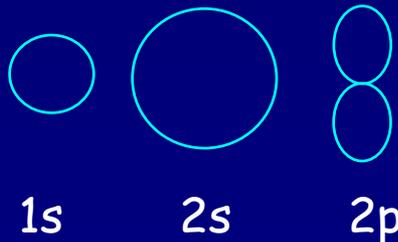
1s ± 2s

No electric-dipole moment

1s ± 2p
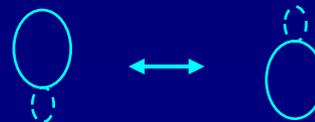
Oscillating electric-dipole couples to photons

Forbidden transition
Δl = **0**

Allowed transition
Δl = **±1**

www.falstad.com/qmatomrad

Each photon carries 1 ħ of angular momentum.

Allowed Transitions for H

(You will observe some of these transitions in Lab 4.)

n

s	p	d	f	g
$\ell = 0$	1	2	3	4

4

3

2

Forbidden
transition
$\Delta l = 0$

1

$$E_n = \frac{-13.6\ \text{eV}}{n^2}$$

Energy (eV)

0.00

-0.85

-1.51

-3.40

-13.6 eV
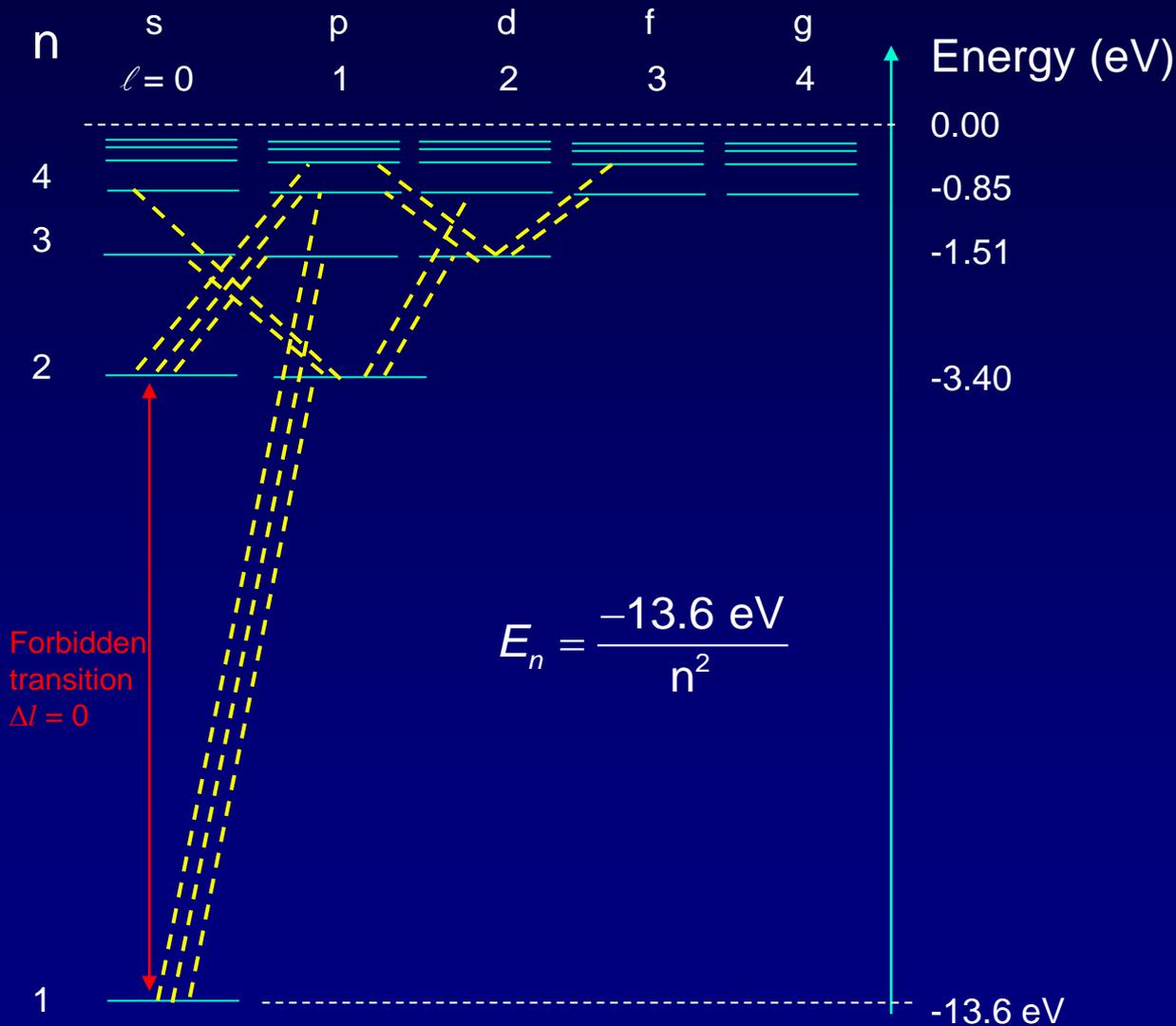
Selection Rule for "electric-dipole" (photon has $l = 1$) transitions:

$$\Delta l = \pm 1$$
$$\Delta m = 0, \pm 1$$

NOTE:
It is possible (but unlikely) for the photon to have $\ell \neq 1$ or for more than one photon to be involved. This permits other Δl and Δm.

Electron Spin

We need FOUR quantum numbers to specify the electronic state of a hydrogen atom.

$$n, l, m_l, m_s \ \text{(where } m_s = -\tfrac{1}{2} \ \text{and } +\tfrac{1}{2})$$

Actually, the nucleus (a proton) also has spin, so we must specify its m_s as well …

We'll work some example problems next time.

Electron Magnetic Moment

Because the electron has a charge and angular momentum, it has a magnetic moment, with magnitude: $\mu_e = 9.2848 \times 10^{-24}$ J/T.

One consequence of the 'quantization of angular momentum' is that we only ever measure the spin (and hence the magnetic moment) to be pointing 'up' or 'down' (where the axis is defined by any applied magnetic field). [Note: Because the charge of the electron is negative, the spin and magnetic moment point in *opposite* directions!]

In a uniform magnetic field $(\mathbf{B} = B_z\mathbf{z})$, a magnetic moment has an energy (Phys. 212): $E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B_z$

Thus, for an electron, the two spin states have two energies:

B≠0:

B=0:

$+\mu_e B$

$\mathbf{B}$

$\Delta E = 2\mu_e |B|$

$-\mu_e B$
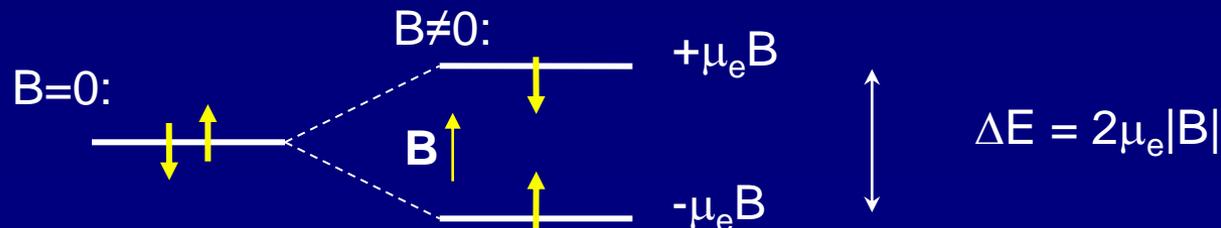
Note: These arrows represent magnetic moment, not spin...

FYI: The _real_ value of μ_e

- There are relatively simple arguments that predict
    $$\mu_e = \mu_B \equiv e\hbar/2m = 9.2740 \times 10^{-24} \text{ J/T}$$

- In reality, the measured mag. moment of the electron is a bit bigger:
    $$\mu_e = -9.2848 \times 10^{-24} \text{ J/T}$$

- The effect is small:
    $$|\mu_e/\mu_B| = 1.00115965218685 \ (42)$$

[Yes, it has been measured _that_ well – in fact, it's one of the most precisely known quantities today.]

- What causes the discrepancy? It comes from the fact that:
  - Magnetic (and electric) effects essentially arise from the exchange of "virtual" photons.
  - Sometimes these can, for a very short time, become an electron-positron pair (which then annihilate each other). There are lots of other exotic processes too.

- When all these are taken into account, our current best theoretical prediction for the value of $|\mu_e/\mu_B| = 1.001159652201 \ (27)$

- This is agreement to at least 12 decimal places!!

Nuclear Magnetic Resonance

Just like electrons, the <u>proton</u> in the H atom also has a spin, which is described by an additional quantum number, m_p, and therefore also a magnetic moment. However, it is several orders of magnitude smaller than that of the electron.

- The energy difference between the two proton spin states in a magnetic field is 660 times smaller than for electron spin states!

- But… There are many more <u>unpaired</u> proton spins than <u>unpaired</u> electron spins in ordinary matter. Our bodies have many unpaired protons in H_2O. Detect them …...

In order to image tissue of various types, Magnetic Resonance Imaging detects the small difference in the numbers of "up" and "down" hydrogen proton spins generated when the object studied is placed in a magnetic field. Nobel Prize (2003): Lauterbur (UIUC)

www.beckman.uiuc.edu/research/mri.html