"Anyone who can contemplate quantum mechanics without getting dizzy hasn't understood it."

--Niels Bohr

Special (Optional) Lecture

"Quantum Information"

- One of the most modern applications of QM
  - quantum computing
  - quantum communication – cryptography, teleportation
  - quantum metrology
- Prof. Kwiat will give a special 214-level lecture on this topic
  - Sunday, Feb. 27
  - 3 pm, 141 Loomis
- Attendance is optional, but encouraged.

Overview of the Course

Up to now:
- General properties and equations of quantum mechanics
- Time-independent Schrodinger's Equation (SEQ) and eigenstates.
- Time-dependent SEQ, superposition of eigenstates, time dependence.
- Collapse of the wave function
- Tunneling

This week:
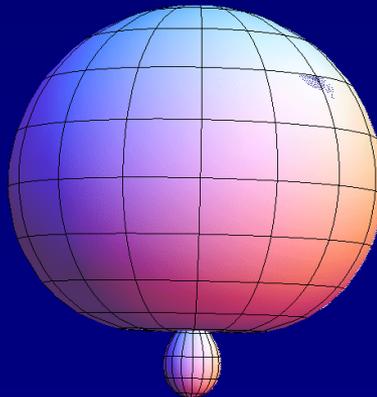- 3 dimensions, angular momentum, electron spin, H atom
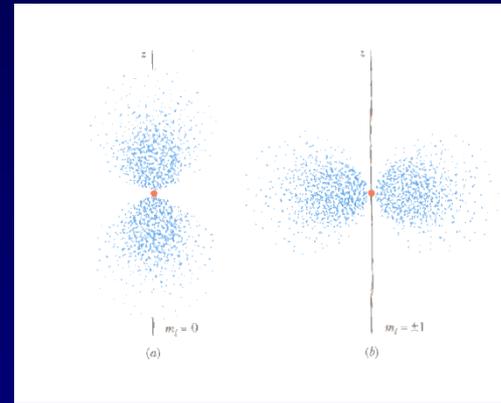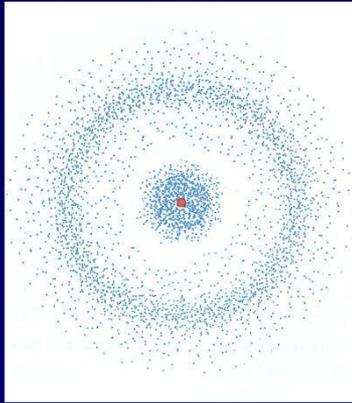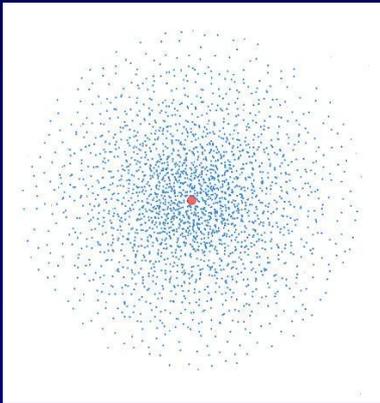- Exclusion principle, periodic table of atoms

Next week:
- Molecules and solids, consequences of Q. M., Schrodinger's cat
- Metals, insulators, semiconductors, superconductors, lasers, . .

Final Exam: Monday, Mar. 5
Homework 6: Due Saturday (March 3), 8 am

Lecture 17:
Angular Momentum, Atomic States, Spin, & Selection Rules

Today

Schrödinger's Equation for the Hydrogen Atom

- Radial wave functions
- Angular wave functions

Angular Momentum

- Quantization of L_z and L^2
- Spin and the Pauli exclusion principle
- Stern-Gerlach experiment

Summary of S-states of H-atom

The "s-states" ($l=0$, $m=0$) of the Coulomb potential have no angular dependence. In general:

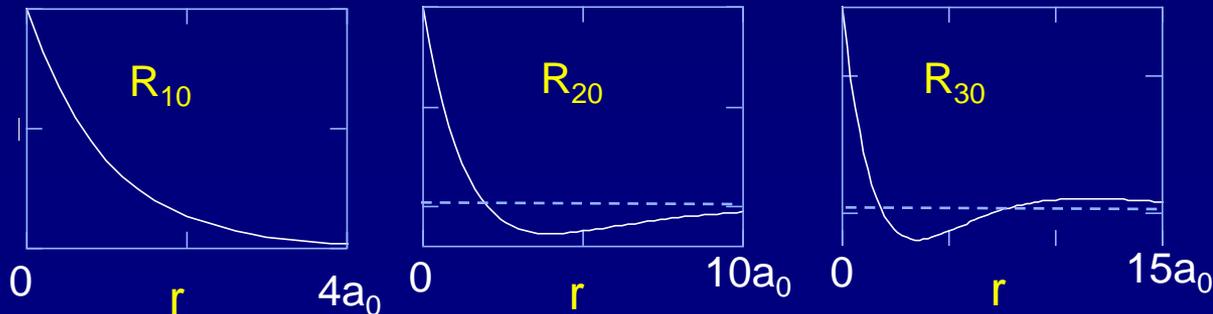$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi)$$
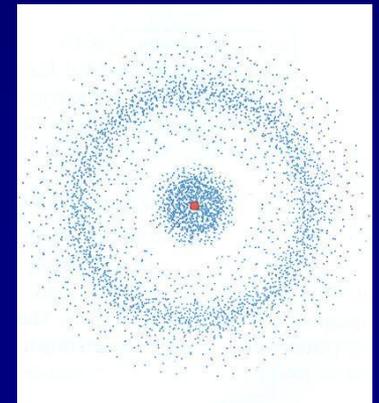
but:

$$\psi_{n00}(r,\theta,\phi) \propto R_{n0}(r)$$

because $Y_{00}(\theta,\phi)$ is a constant.

S-state wave functions are spherically symmetric.

$|\psi_{20}(r,\theta,\phi)|^2$:

Some s-state wave functions (radial part):

R_{10} 0   r $4a_0$

R_{20} 0   r $10a_0$

R_{30} 0   r $15a_0$
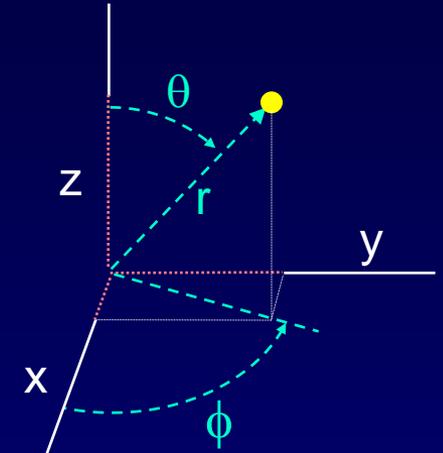
http://www.falstad.com/qmatom/

Total Wave Function of the H-atom

We will now consider non-zero values of the other two quantum numbers: l and m.

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

- n "principal"   ($n \geq 1$)
- l "orbital"   ($0 \leq l < n\text{-}1$)
- m "magnetic"   ($-l \leq m \leq +l$) } *

The $Y_{lm}(\theta,\phi)$ are known as "spherical harmonics".

They are related to the angular momentum of the electron.

* The constraints on l and m come from the boundary conditions one must impose on the solutions to the Schrodinger equation.   We'll discuss them briefly.
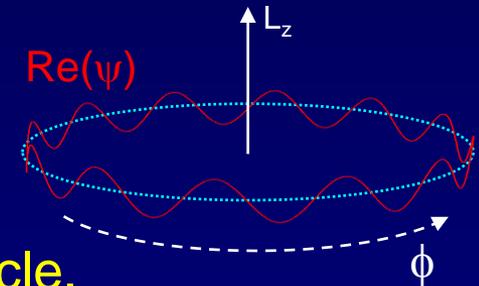
Quantized Angular Momentum

Linear momentum depends on the wavelength ($k = 2\pi/\lambda$):

$$p = \hbar k \text{ where } \psi(x) \propto e^{ikx}$$

Angular momentum depends on the tangential component of the momentum. Therefore L_z depends on the wavelength as one moves around a circle in the x-y plane. Therefore, a state with L_z has a similar form:

$$L_Z = m\hbar \text{ where } \psi(\vec{r}) \propto Y_{lm}(\theta, \phi) \propto e^{im\phi}$$

We're ignoring R(r) for now.

An important boundary condition:
An integer number of wavelengths must fit around the circle.
Otherwise, the wave function is not single-valued.

L_z

$\text{Re}(\psi)$

ϕ

Reminder:

$e^{im\phi} = \cos(m\phi) + i \sin(m\phi)$

This implies that $m = 0, \pm 1, \pm 2, \pm 3, \ldots$

and $L_z = 0, \pm\hbar, \pm 2\hbar, \pm 3\hbar, \ldots$

Angular momentum is quantized!!

The l Quantum Number

The quantum number m reflects the component of angular momentum about a given axis.

$$L_z = m\hbar \text{ where } m = 0, \pm 1, \pm 2, ...$$

In the angular wave function $\psi_{lm}(\theta, \phi)$
the quantum number l tells us the total angular momentum L.

$L^2 = L_x^2 + L_y^2 + L_z^2$ is also quantized. The possible values of L^2 are:

$$L^2 = l(l+1)\hbar^2 \text{ where } l = 0, 1, 2, ...$$

Wave functions can be eigenstates of both L^2 and L_z.
For spherically symmetric potentials, like H-atom, they can also be eigenstates of E. Such states are called "orbitals".

Summary of quantum numbers for the H-atom orbitals:

Principal quantum number: $n = 1, 2, 3, ...$
Orbital quantum number: $l = 0, 1, 2, ..., n-1$
Orbital 'magnetic' quantum number: $m = -l, -(l-1), ... 0, ... (l-1), l$

Angular Momentum & Uncertainty Principle

Note that $L^2 = l(l+1)\hbar^2$ not $(l\hbar)^2$

Also, we describe angular momentum using only two numbers, l and m.

Q: Why can't we specify all three components (*e.g.*, L =(0,0,l) so that L^2= l^2?

A: The uncertainty principle doesn't allow us to know that both $L_x = 0$ and $L_y = 0$ unless $L_z = 0$ also.

Proof by contradiction: Assume L =(0,0,l).

$\vec{L} = \vec{r} \times \vec{p}$, so if L points along the z-axis, both r and p lie in the x-y plane.
This means that $\Delta z = 0$ and $\Delta p_z = 0$, violating the uncertainty principle.

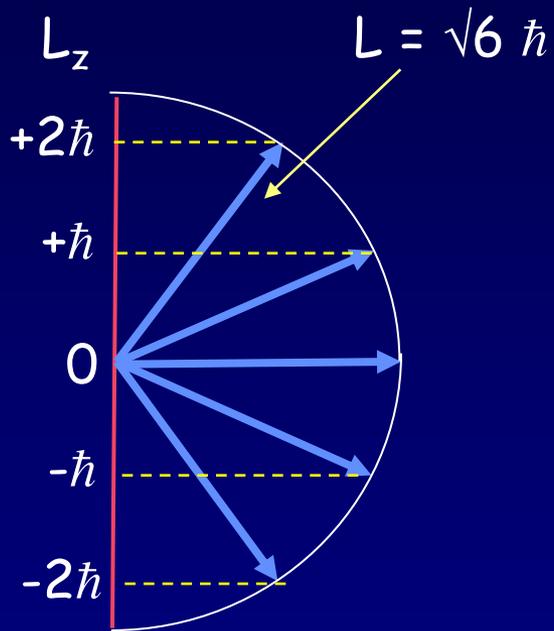Thus, L must have a nonzero L_x or L_y, making L^2 somewhat larger.
We can't specify all three components of the angular momentum vector.

This logic only works for L $\neq$ 0.   L = (0,0,0) is allowed. It's the s-state.

All physical quantities are subject to uncertainty relations, not just position and momentum.

Classical Picture of L-Quantization

e.g., $l = 2$
$$L = \sqrt{l(l+1)\hbar^2} = \sqrt{2(2+1)\hbar^2} = \sqrt{6}\,\hbar$$

L_z

$L = \sqrt{6}\,\hbar$

$+2\hbar$

$+\hbar$

0

$-\hbar$

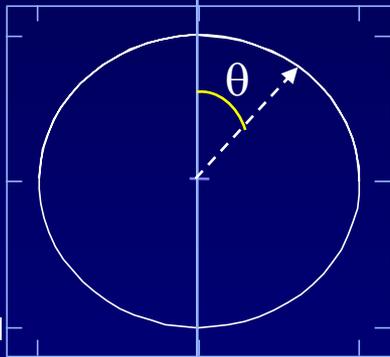$-2\hbar$
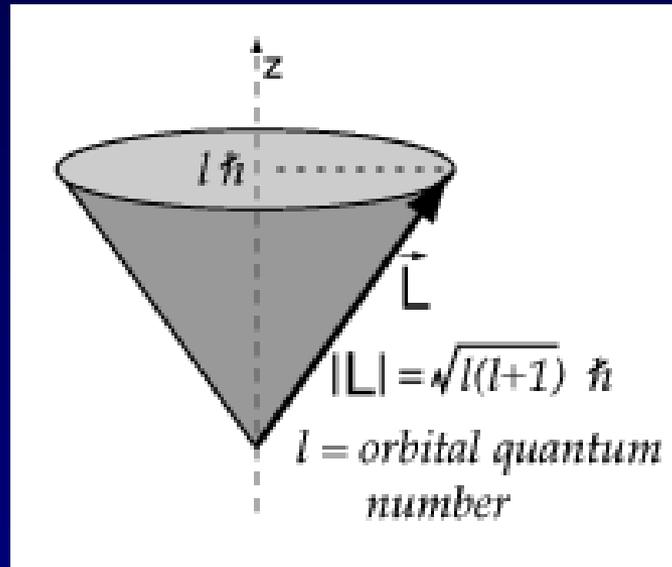
$$\vec{L} = \vec{r} \times \vec{p}$$

The Angular Wave Function, $Y_{lm}(\theta,\varphi)$

The angular wave function may be written: $Y_{lm}(\theta,\phi) = P(\theta)e^{im\phi}$
where $P(\theta)$ are polynomial functions of $\cos(\theta)$ and $\sin(\theta)$.
To get some feeling for these angular distributions, we make
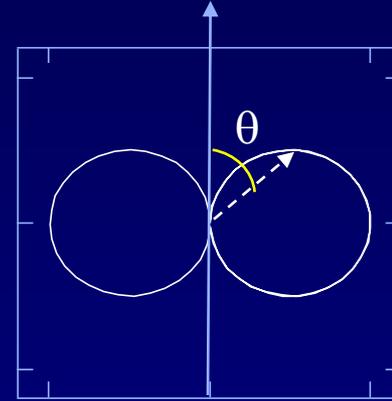polar plots of the θ-dependent part of $|Y_{lm}(\theta, \phi)|$ (i.e., $P(\theta)$):

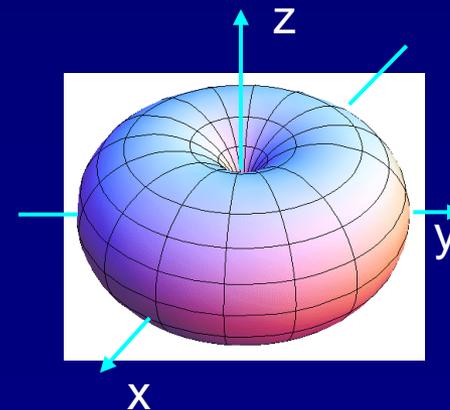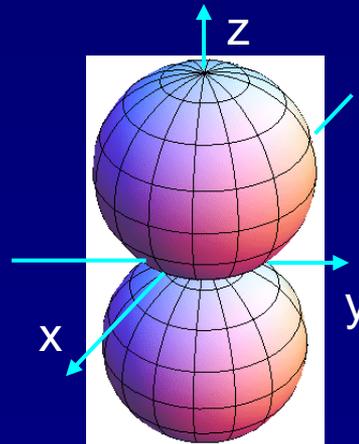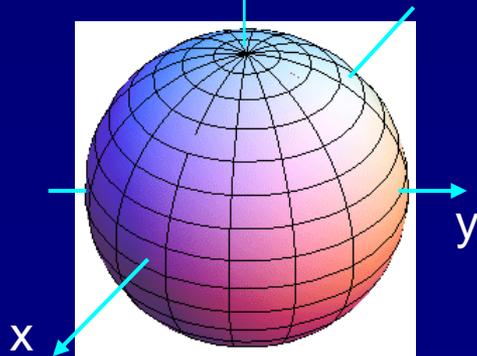$l = 0$ $Y_{0,0} = \dfrac{1}{\sqrt{4\pi}}$
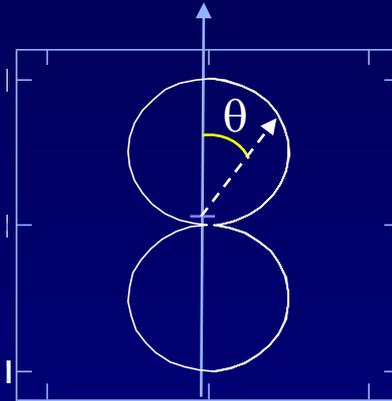
$l = 1$ $|Y_{1,0}| \propto |\cos\theta|$ $|Y_{1,\pm 1}| \propto |\sin\theta|$
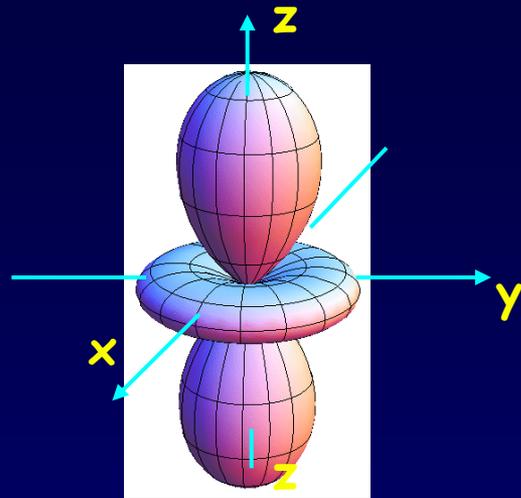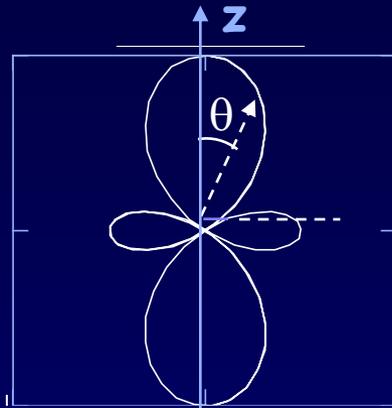
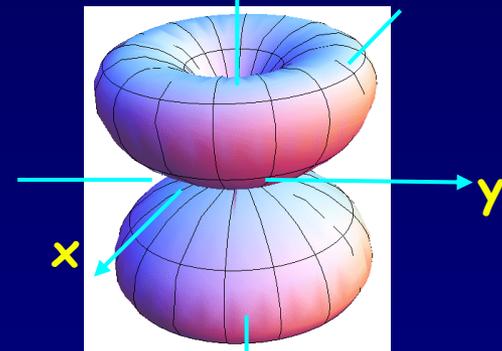Length of the dashed arrow is the magnitude of Y_{lm} as a function of θ.

The Angular Wave Function, $Y_{lm}(\theta,\varphi)$
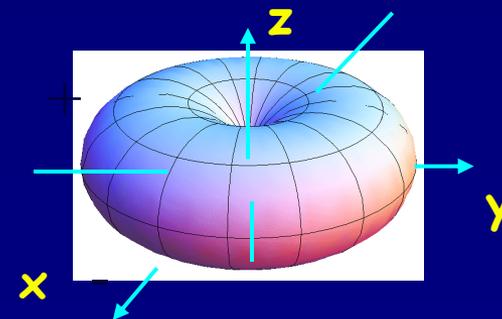
$l = 2$

$$\left|Y_{2,0}\right| \propto \left|\left(3\cos^2\theta - 1\right)\right|$$

$$\left|Y_{2,\pm 1}\right| \propto \left|\sin\theta\cos\theta\right|$$
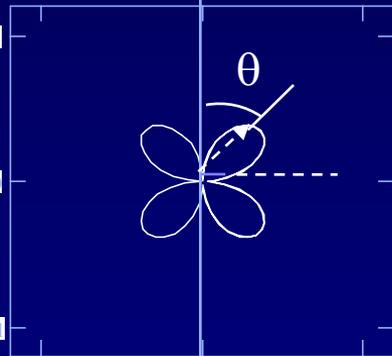
$$\left|Y_{2,\pm 2}\right| \propto \left|\sin^2\theta\right|$$
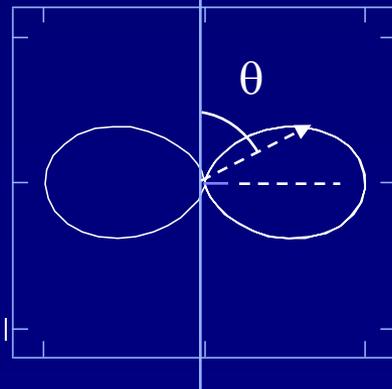
Act 1

How does the angular part of the wave function depend on the principal quantum number, n?

a. The number of "lobes" increases as n increases.

b. As n increases, the wave function becomes more concentrated in the xy plane.

c. No dependence.

Solution

How does the angular part of the wave function depend on the
principal quantum number, n?

    a. The number of "lobes" increases as n increases.

    b. As n increases, the wave function becomes
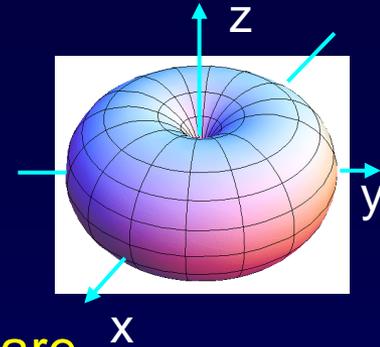   more concentrated in the xy plane.

    c. No dependence.

The principal quantum number describes the radial motion,
not the angular motion. $R_{nl}(r)$ depends on n, but $Y_{lm}(\theta,\phi)$ does not.

Cylindrical Symmetry

Why do none of the graphs display ϕ-dependence?
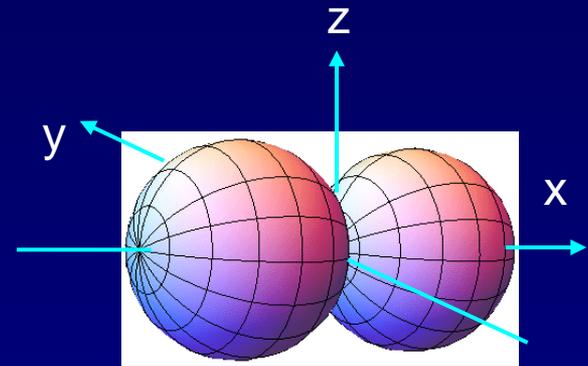   (They all have cylindrical symmetry.)

For a given m, the ϕ dependence of ψ is $e^{im\phi}$. When we square
it to find the probability, $e^{im\phi}e^{-im\phi} = 1$.
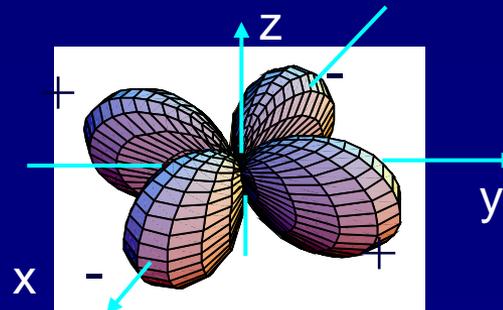In order to see ϕ dependence, we need a superposition of
different m's.

For example, consider the superposition:
(l = 1, m = +1)   &   (l = 1, m = -1).
This will have an azimuthal wave function:
   $e^{i\phi} + e^{-i\phi} \approx \cos \phi$, i.e., lobes along the x-axis:

Similar arguments explain how
to create the usual "d" lobes,
from l =2, m = ±2 superpositions:

See Supplement
for more info.

Why are these distributions important?

They govern the bonding and chemistry of atoms.

In particular, they determine the angles at which different atoms bond:
$\rightarrow$ the structure of molecules & solids.

Historical Labeling of Orbitals

Angular momentum quantum #	Notation from 19th century spectroscopy
$l = 0$	s "sharp"
$l = 1$	p "principle"
$l = 2$	d "diffuse"
$l = 3$	f "fundamental"

Effect of l on Radial Wave Functions $R_{n,l}$

n=1   n=2   n=3

$l = 0$

$l = 0$ $l = 0$

$l = 1$ $l = 1$

$l = 2$
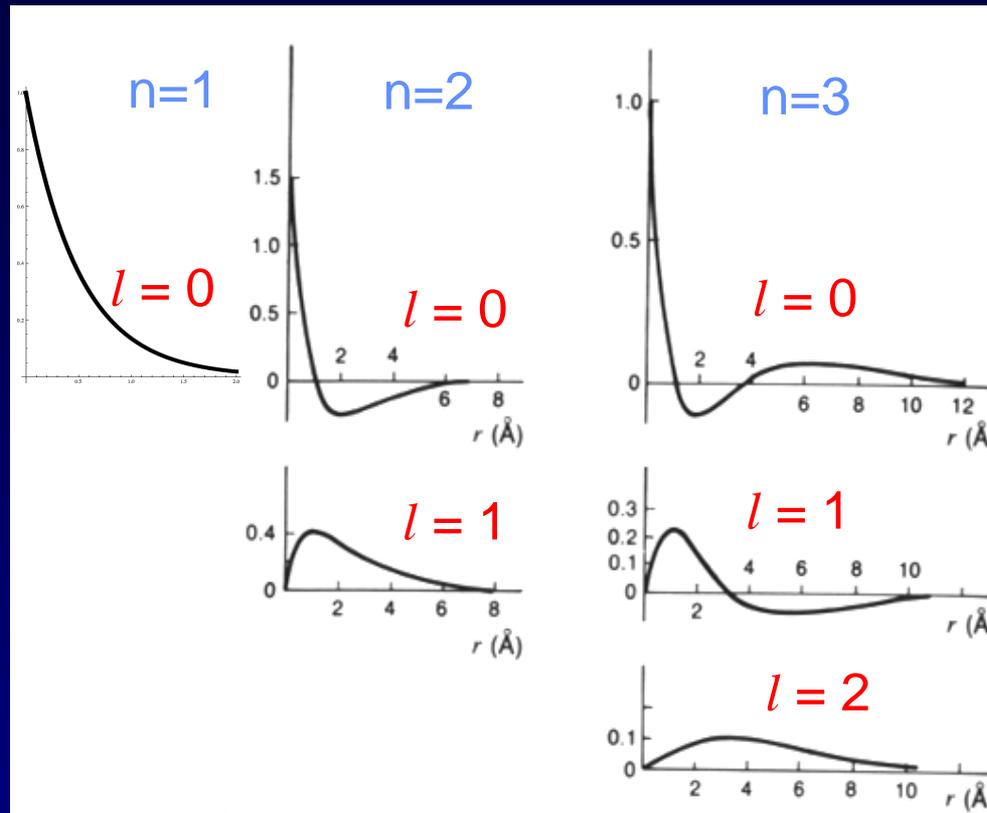
1: $l < n$ (Total energy must always be larger than rotational part.)

2: a. For fixed l, the number of radial nodes increases with n.
   b. For fixed n, the number of radial nodes decreases with l. ($E = T_{rad} + T_{rot} + U(r)$, i.e., 'radial KE' decreases as 'rotational KE' increases).

3: # radial nodes = (n-1) - l .

4: ψ(r=0) = 0 for $l \neq 0$
   Do you understand why?
   (*i.e.*, a physics explanation)

The energy eigenvalues do not depend at all on l. E_n = -13.6 eV/n^2

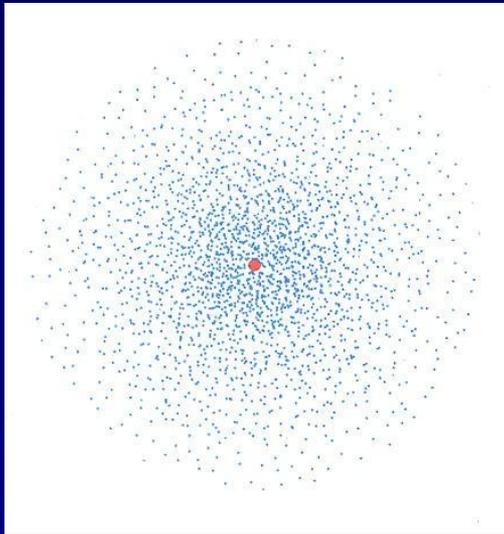This is only true for the Coulomb potential.

Probability Density of Electrons

Let's look at the angular momentum states of the hydrogen atom.

Probability density = Probability per unit volume = $|\psi_{nlm}|^2 \propto R_{nl}^2 Y_{lm}^2$.
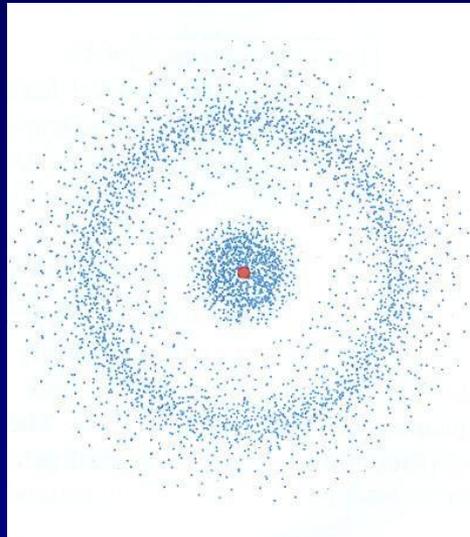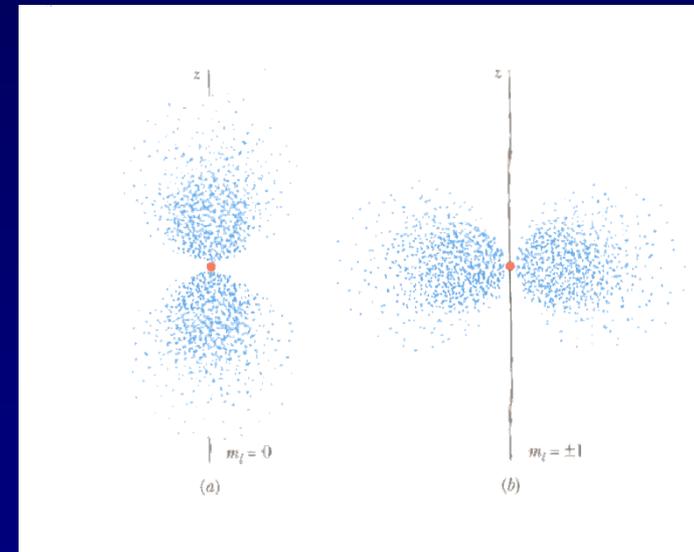The density of dots plotted below is proportional to $|\psi_{nlm}|^2$.

1s state	2s state	2p states

n,l,m = 1,0,0	2,0,0	2,1,{0,±1}

Hydrogen Atom States: Summary

Key Points:

n: principal quantum #
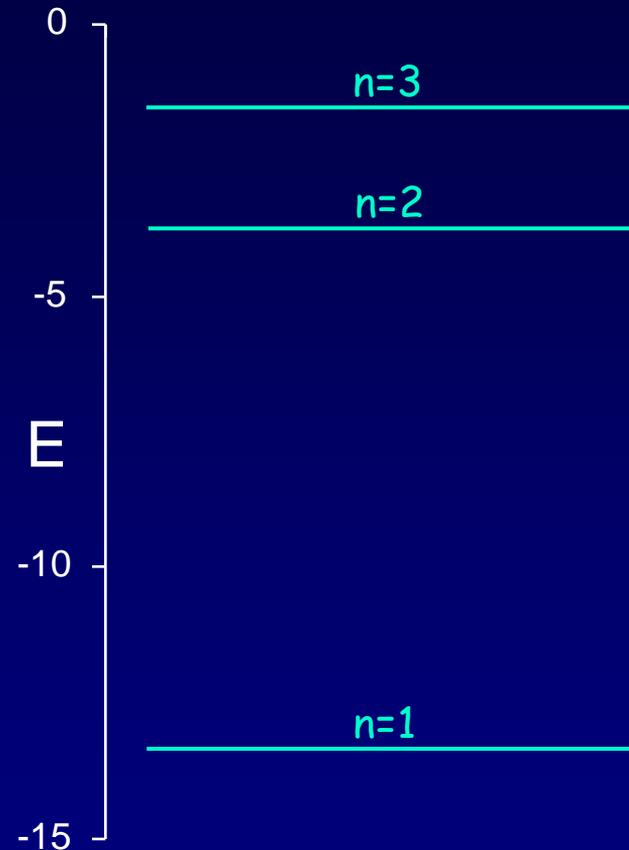
l: orbital quantum #

m_l: orbital magnetic quantum #

Energy depends only on n

$$E_n = \frac{-\kappa e^2}{2a_0}\frac{1}{n^2} = -\frac{13.6\ \text{eV}}{n^2}$$

For a given n, there are n possible angular momentum states:
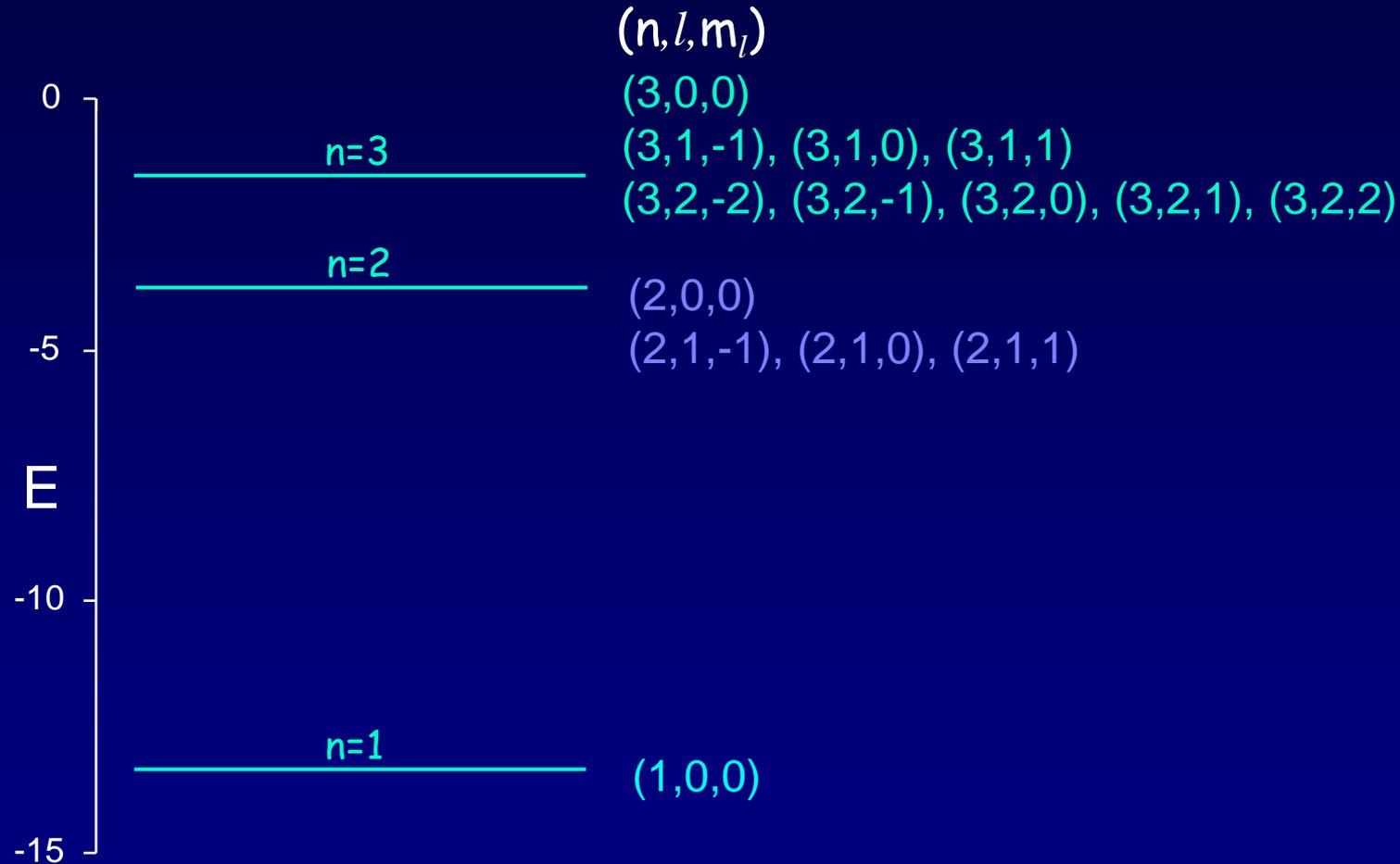
l = 0, 1, ..., n-1

For a given l, there are $2l + 1$ possible z-components: m_l = -l, -(l -1), … 0 … (l -1), l

Therefore, a level with quantum number n has n^2 degenerate states.

0

n=3

n=2

-5

E

-10

n=1

-15

Hydrogen Atom States: Summary

E

0

-5

-10

-15

n=3

n=2

n=1

(n, l, m_l)

(3,0,0)

(3,1,-1), (3,1,0), (3,1,1)

(3,2,-2), (3,2,-1), (3,2,0), (3,2,1), (3,2,2)

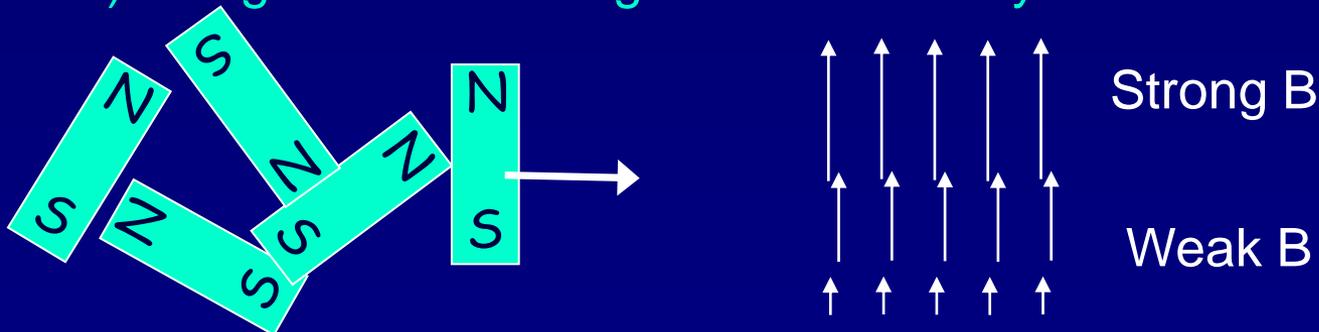(2,0,0)

(2,1,-1), (2,1,0), (2,1,1)

(1,0,0)

Stern-Gerlach Experiment & Electron Spin

In 1922, Stern and Gerlach shot a beam of Ag atoms (with $l = 0$) through a non-uniform magnetic field and detected them at a screen.
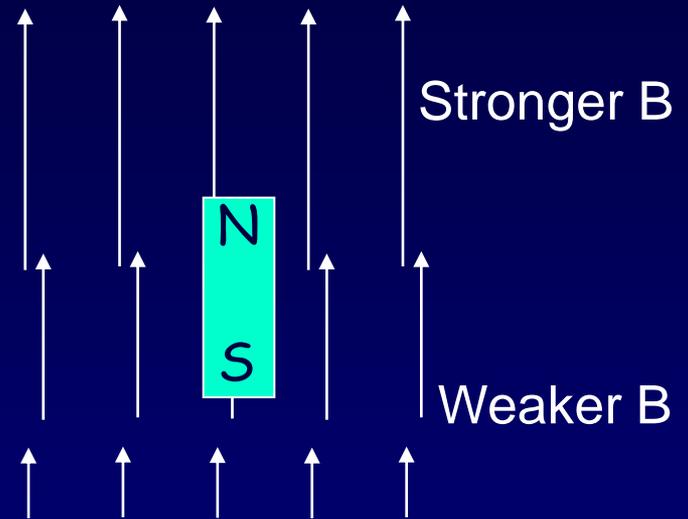
oven

screen

B

???
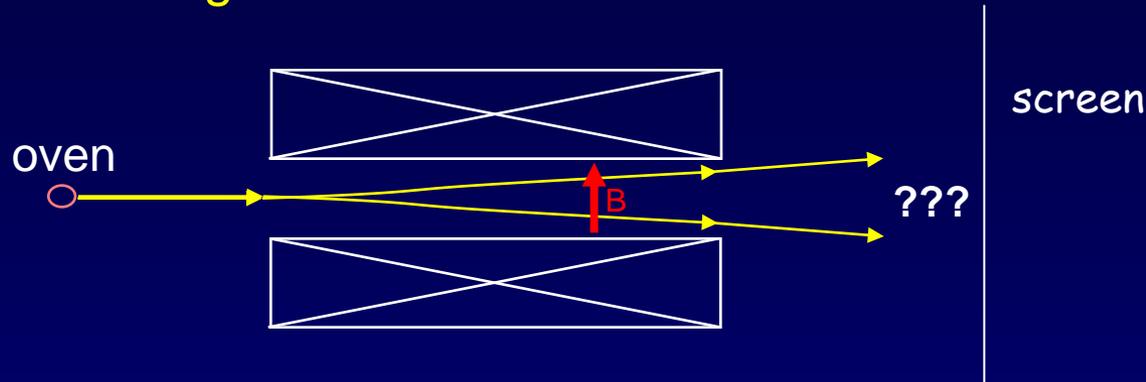
We can think of the atoms as tiny magnets (they have a magnetic moment) being directed through the field. They are randomly oriented:

Strong B

Weak B

Act 2

1. Consider a magnet in an inhomogeneous field, as shown.
   Which way will the magnet feel a force?

   a. Up
   b. Down
   c. Left
   d. Right
   e. No force

   Stronger B

   N

   S

   Weaker B

2. The magnets (i.e., atoms) leave the oven with random orientations.
   What pattern do you expect on the screen?

Solution

1. Consider a magnet in an inhomogeneous field, as shown. Which way will the magnet feel a force?

a. **Up**
b. Down
c. Left
d. Right
e. No force

The N pole is in a stronger field than the S pole, so its upward force dominates.

N
S

N
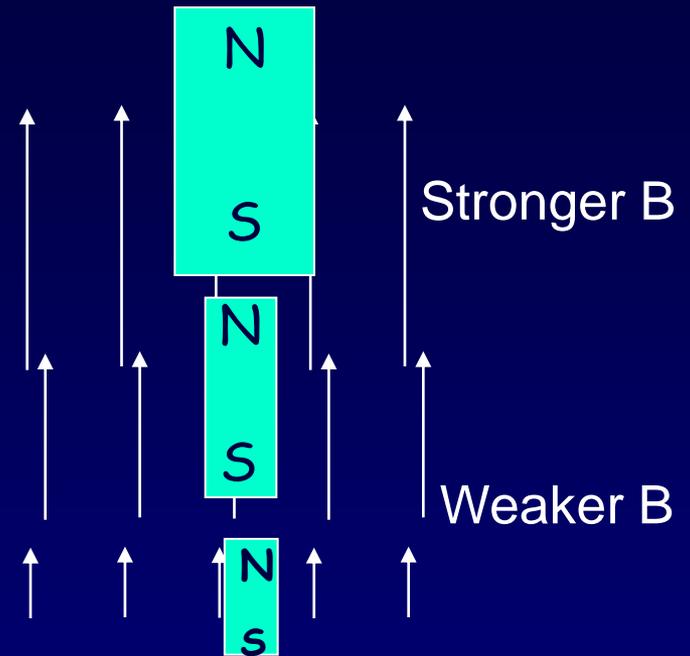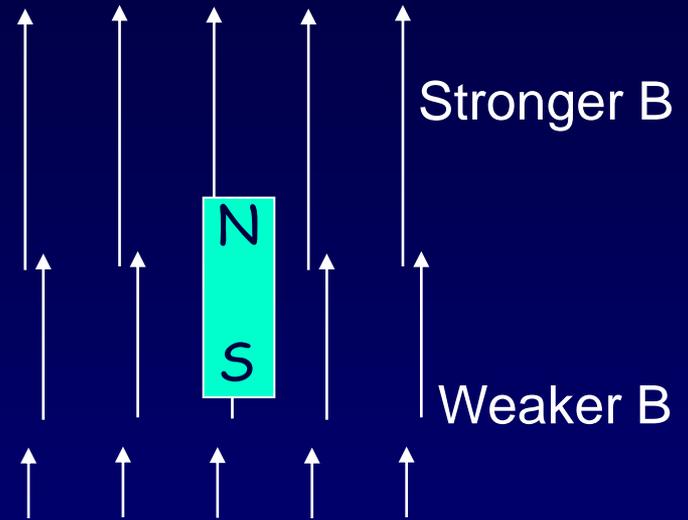**S**

N
s

Stronger B

Weaker B

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Solution

1. Consider a magnet in an inhomogeneous field, as shown. Which way will the magnet feel a force?

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b. Down
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Stronger B

N
S

Weaker B

2. The magnets (i.e., atoms) leave the oven with random orientations. What pattern do you expect on the screen?

oven

B

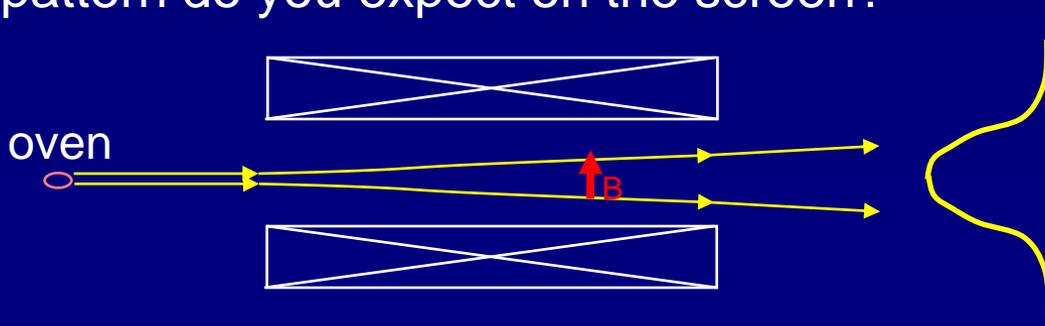We expect a blob, because the position depends on the random rotation angle.
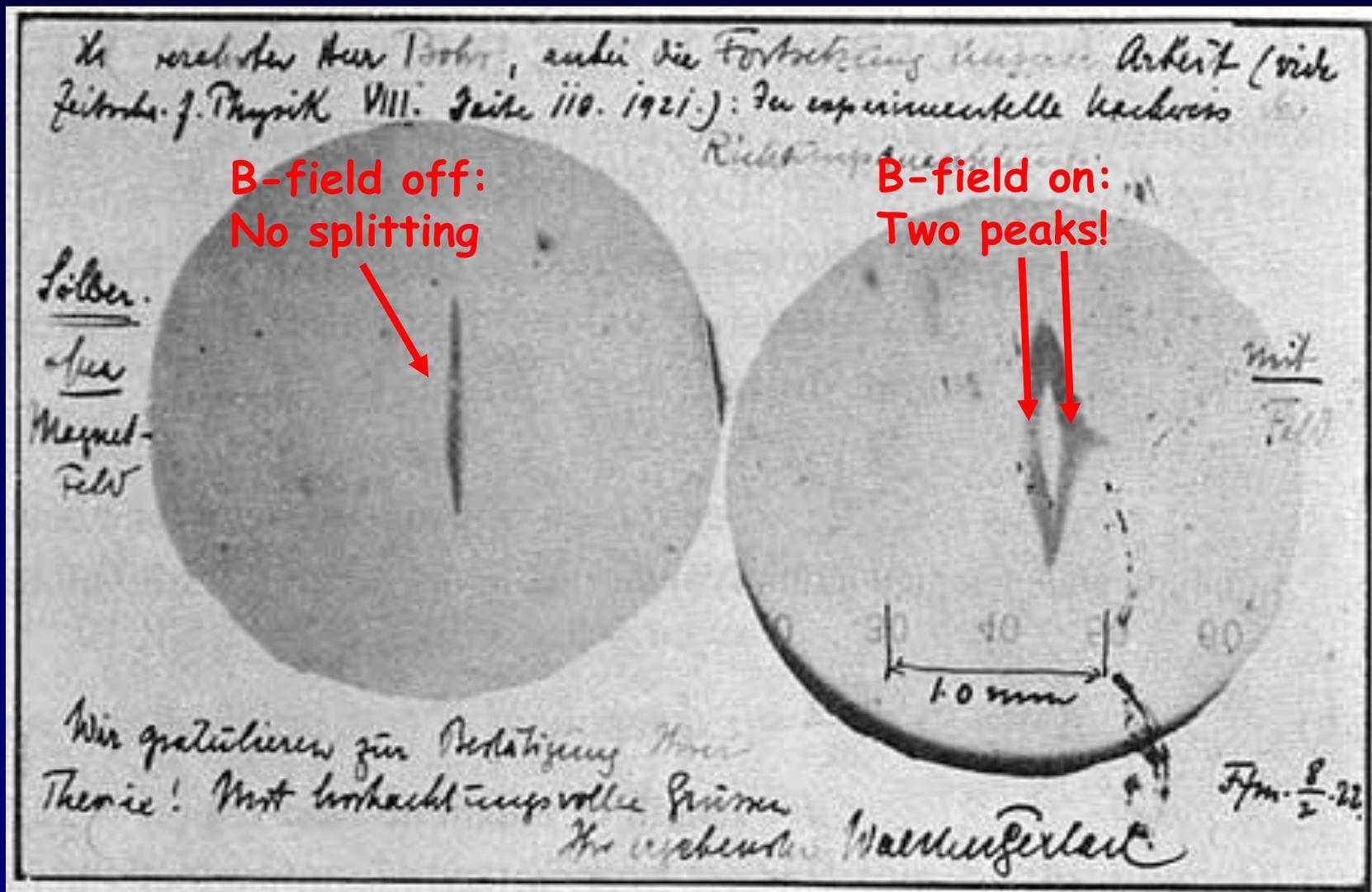
Gerlach's postcard, dated 8 February 1922, to Niels Bohr. It shows a photograph of the beam splitting, with the message, in translation: "Attached [is] the experimental proof of directional quantization. We congratulate [you] on the confirmation of your theory."

Back to the Stern-Gerlach Experiment

oven

screen

You will analyze this experiment in discussion.
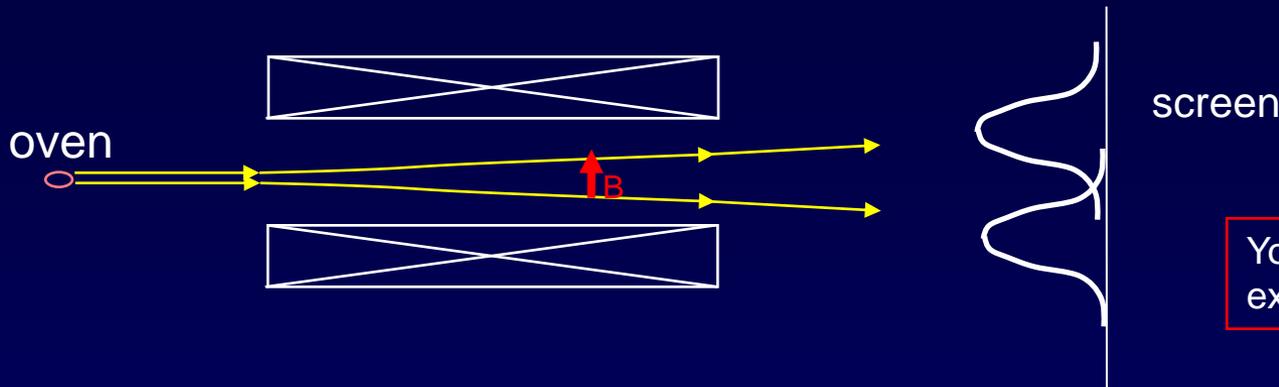
The beam split in two! This marked the discovery of a new type of angular momentum, with an m_s quantum number that can take on only two values:

$$(s = ½)   m_s = ±½$$

The new kind of angular momentum is called the electron "SPIN".   Why?

If the electron were spinning on its axis, it would have angular momentum and a magnetic moment (because it's charged) regardless of its spatial motion.

However, this "spinning" ball picture is not realistic, because it would require the point-like electron to spin so fast that parts would travel faster than c!

So we can't picture the spin in any simple way … the electron's spin is simply another degree-of-freedom available to electron.

Note: Most particles have spin (protons, neutrons, quarks, photons…)

Electron Spin

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

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

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.

Next Week

Multi-electron Atoms

Covalent bonds

Electron energy bands in Solids

QM in everyday life

Supplement: Superposition and Chemical Bonding

Chemical bonds are stronger when the bonding electrons in each atom lie on the side near the other atom. This happens as a result of superposition. A state with definite (l,m) is symmetrical, but a superposition does not have to be. The example here is called an "sp hybrid":

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$\left|Y_{1,0}\right| \propto \left|\cos\theta\right|$$

$$Y_{00} + Y_{10}$$
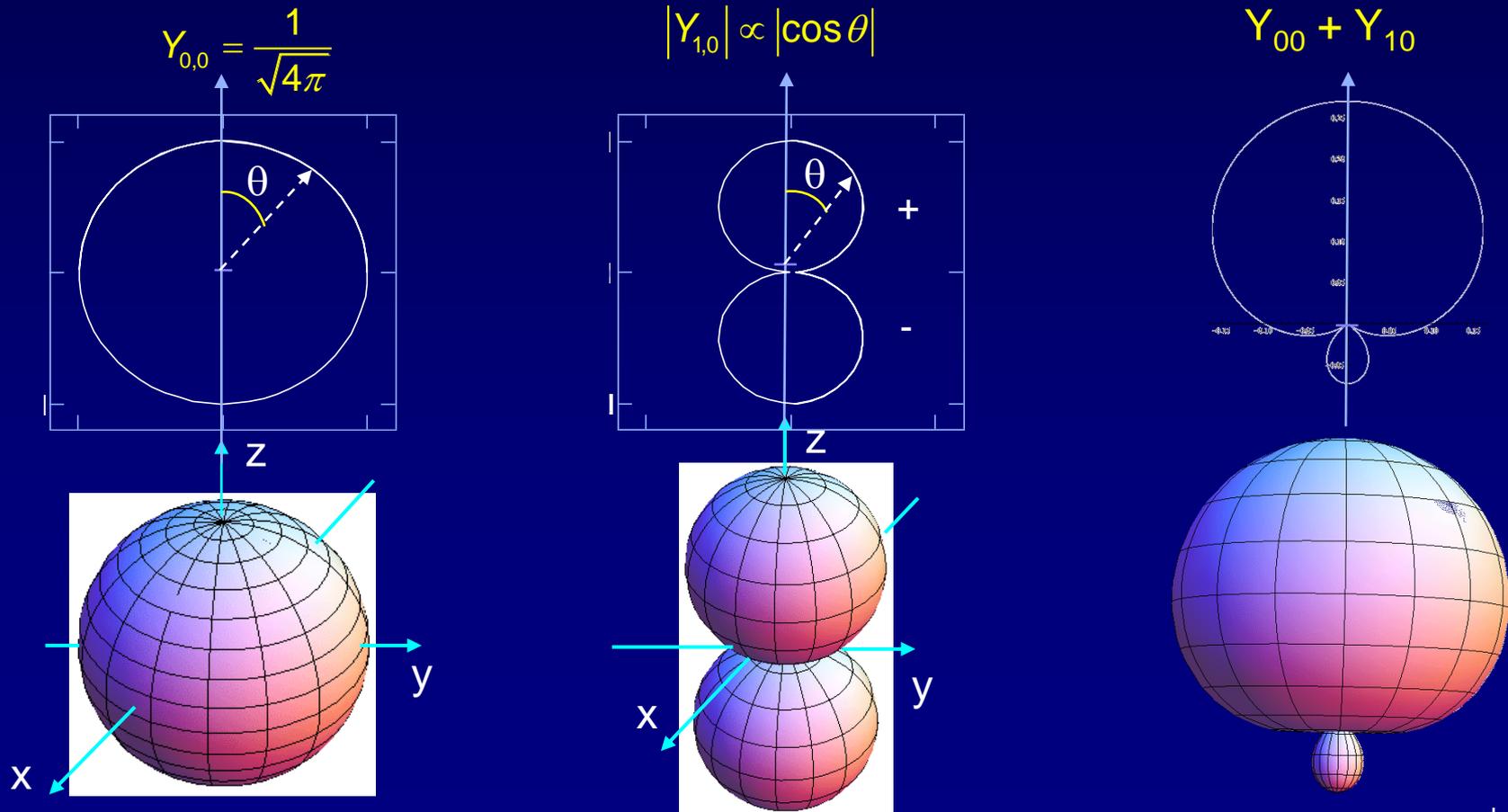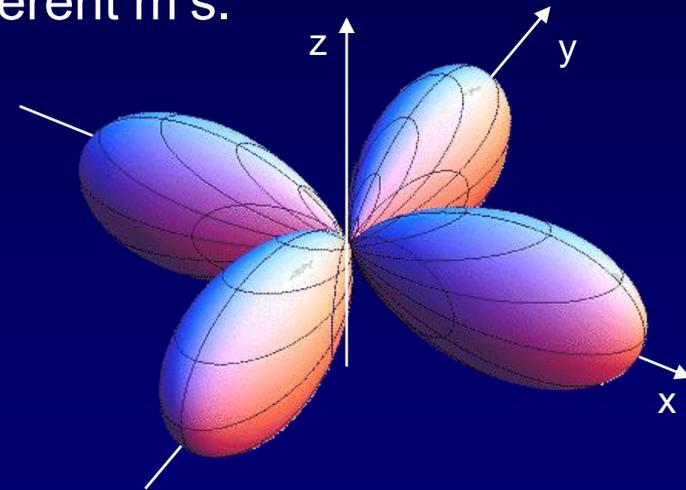
Supplement: Chemistry Notation

From chemistry you may be familiar with states like d_{xy}, etc.

How do these relate to our Y_{lm}?

- "d" means l=2.

- "xy" stands for a particular *superposition* of different m's.

  $d_{xy} = (Y_{22}+Y_{2\,-2})/ \sqrt{2}$.

  The probability distribution is shown here:

Which set of states is 'right'?

It depends on the problem you want to solve.

- In a strong magnetic field the "m" states are (approximately) the energy eigenstates, because the magnetic moment determines the energy.

- In a crystalline environment, states like "xy" may be better, because the interaction with nearby atoms dominates the energy.