“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, 151 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:

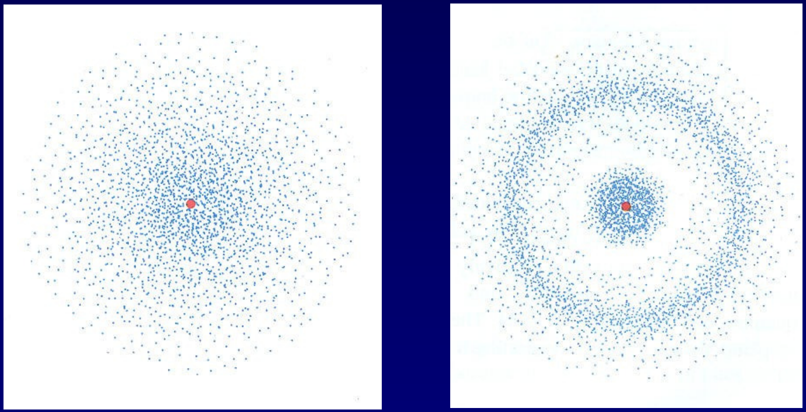
- 3 dimensions, angular momentum, electron spin, H atom
- Exclusion principle, periodic table of atoms

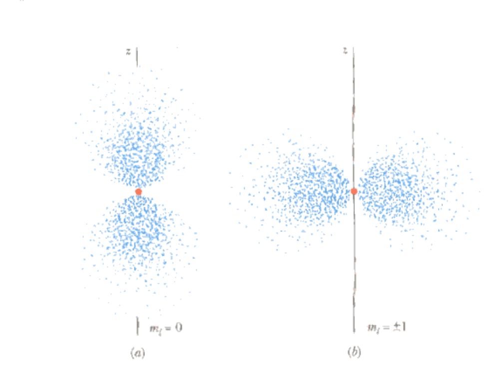
Next week:

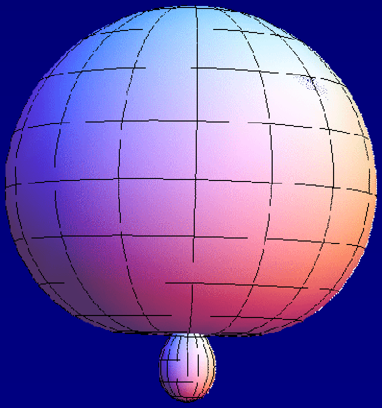
- Molecules and solids, consequences of Q. M., Schrodinger's cat
- Metals, insulators, semiconductors, superconductors, lasers, . .

| | |
|---|---|
| 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:

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

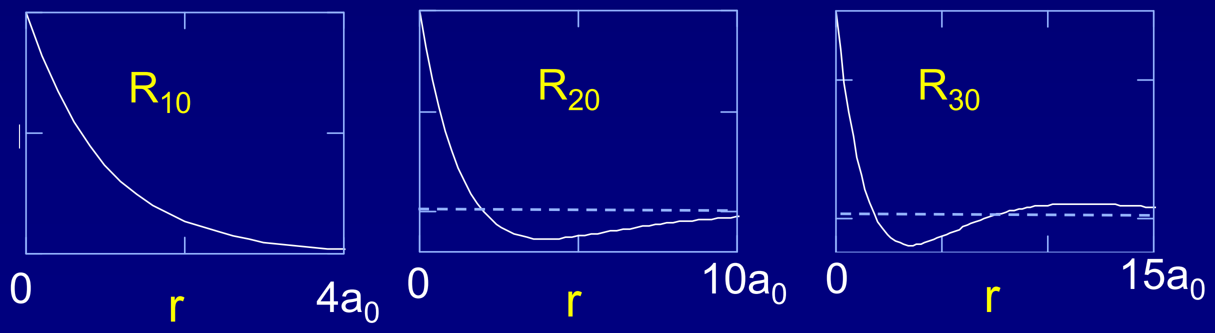
but:

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

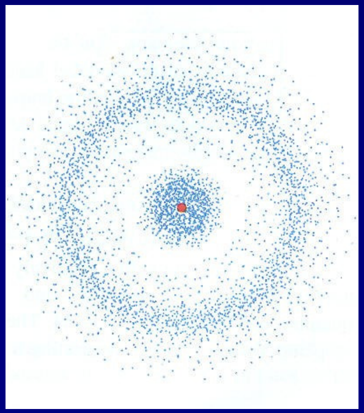
because $Y_{00}(\theta,\phi)$ is a constant.

S-state wave functions are spherically symmetric.

Some s-state wave functions (radial part):

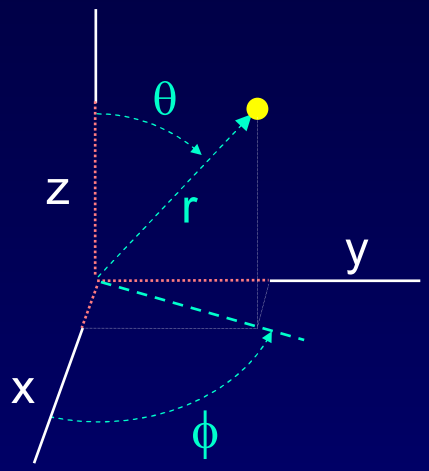


$|\psi_{20}(r,\theta,\phi)|^2$ :



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" | ($0 \leq l < n-1$) | * |
| • $m$ | "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

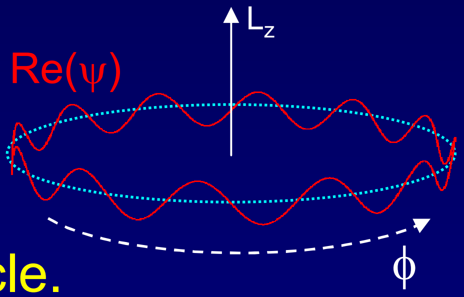
Linear momentum depends on the wavelength ($k=2\pi/\lambda$):

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

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.

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

This implies that $m = 0, \pm1, \pm2, \pm3, \ldots$

and $L_z = 0, \pm\hbar, \pm2\hbar, \pm3\hbar, \ldots$

Angular momentum is quantized!!

http://www.falstad.com/qmatom/

# The $l$ Quantum Number

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

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

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:

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

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.

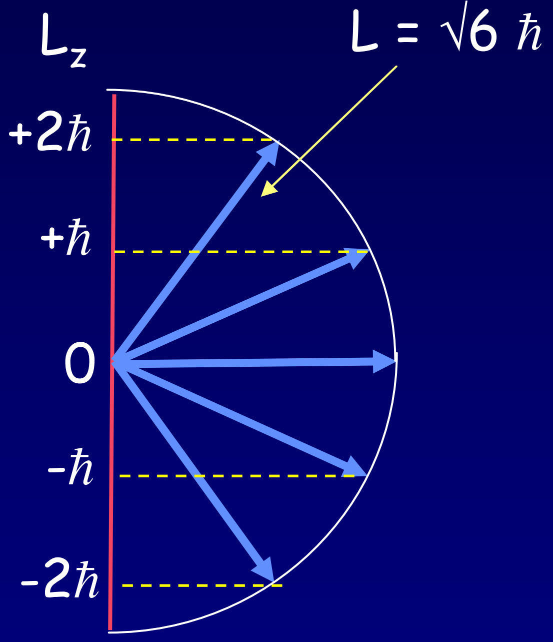
This logic only works for $L \neq 0$. L = (0,0,0) is allowed. It's the s-state.

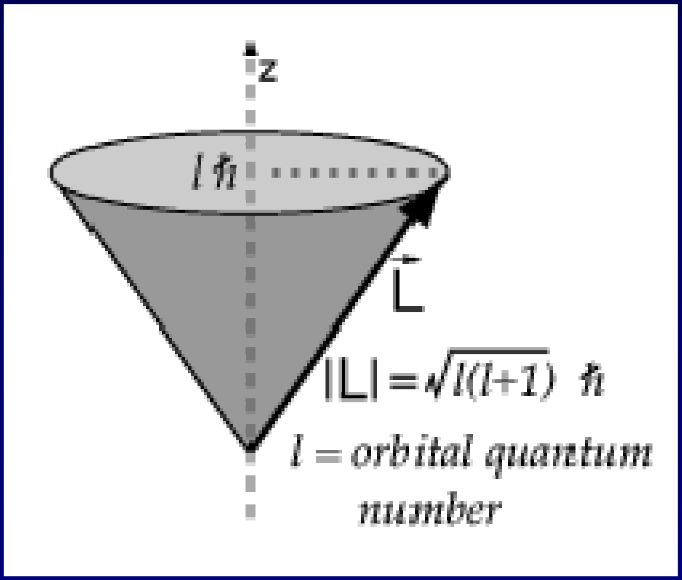
All physical quantities are subject to uncertainty relations, not just position and momentum.

# Classical Picture of L-Quantization

e.g., $l = 2$

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





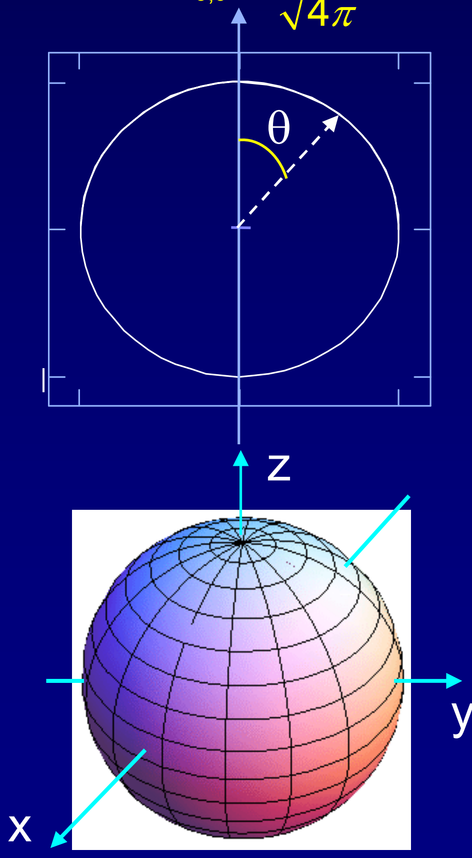
$$\vec{L} = \vec{r} \times \vec{p}$$

# 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 $\theta$-dependent part of $|Y_{lm}(\theta, \phi)|$ (i.e., $P(\theta)$):

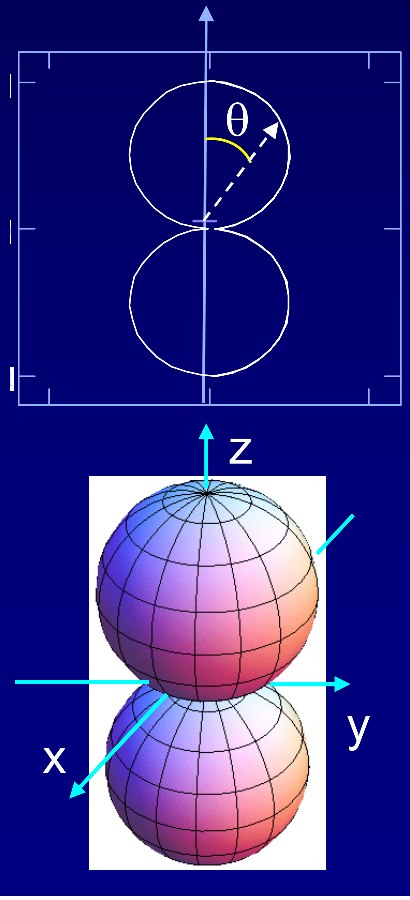
$l = 0$

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

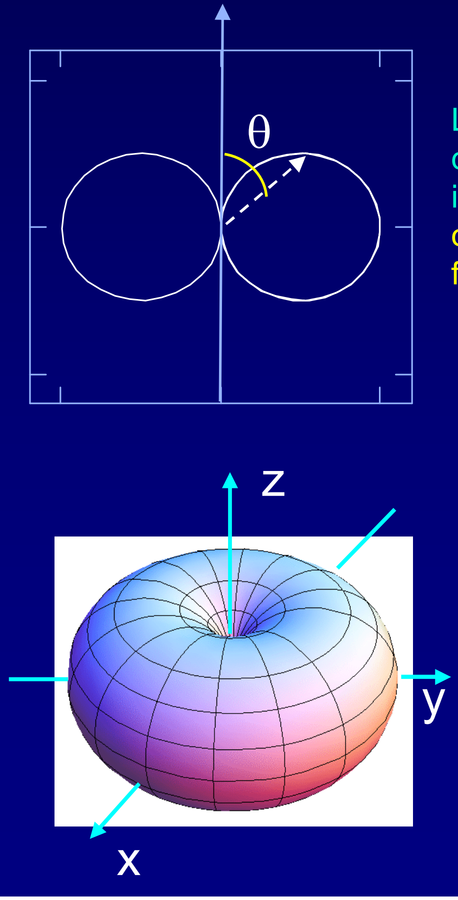


$l = 1$

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



$$\left|Y_{1,\pm1}\right| \propto \left|\sin\theta\right|$$



Length of the dashed arrow is the magnitude of $Y_{lm}$ as a function of $\theta$.

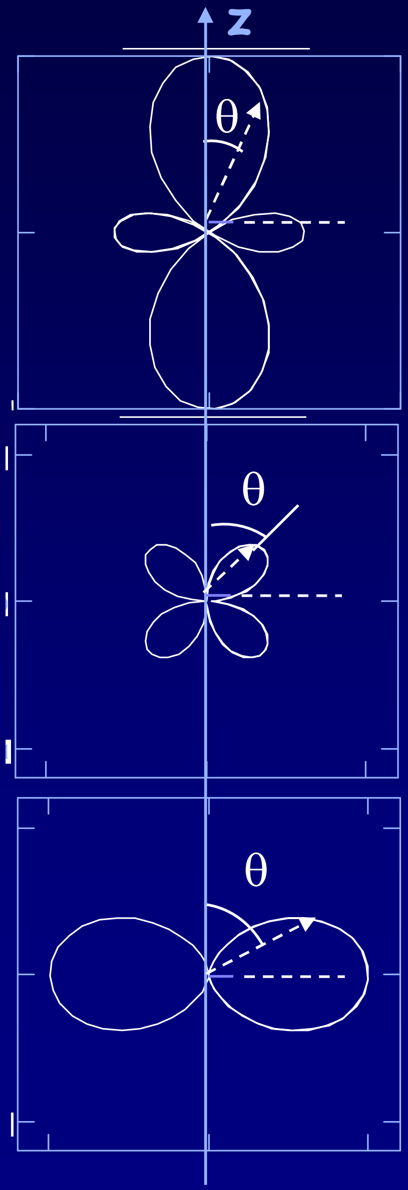
# The Angular Wave Function, $Y_{lm}(\theta,\varphi)$

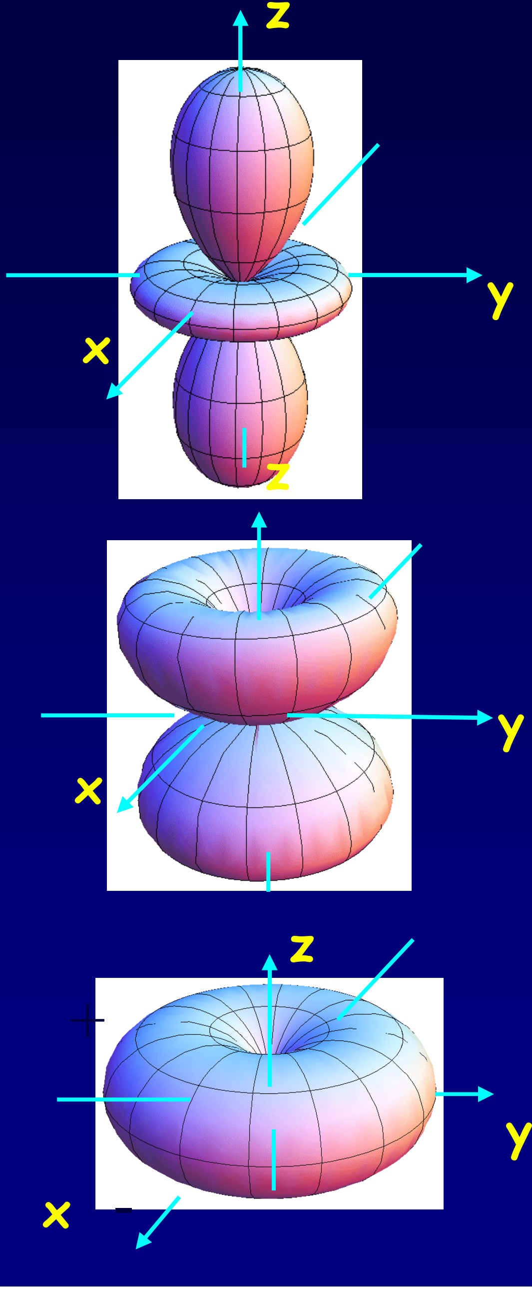
$l = 2$

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

$$|Y_{2,\pm1}| \propto |\sin\theta\cos\theta|$$

$$|Y_{2,\pm2}| \propto |\sin^2\theta|$$





# 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?

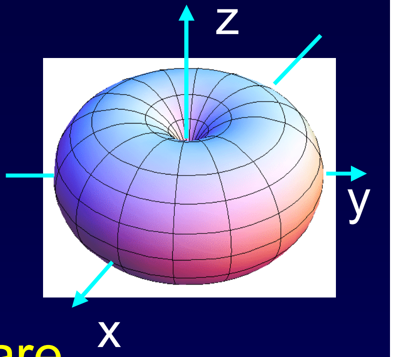
a. The number of “lobes” increases as n increases.

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.

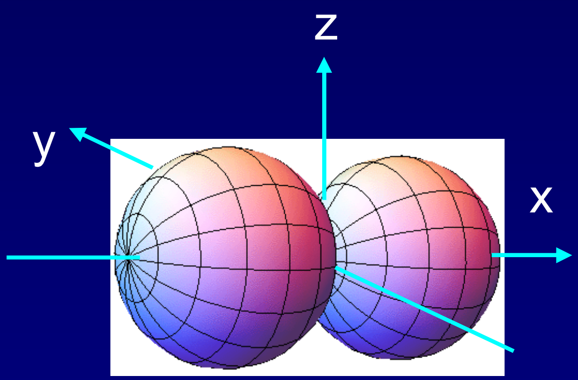
# Cylindrical Symmetry



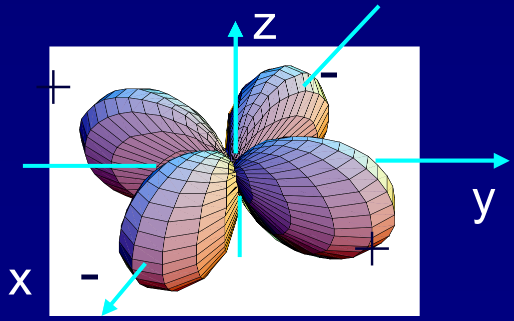
Why do none of the graphs display $\phi$-dependence?
(They all have cylindrical symmetry.)

For a given m, the $\phi$ dependence of $\psi$ is $e^{im\phi}$. When we square it to find the probability, $e^{im\phi}e^{-im\phi} = 1$.
In order to see $\phi$ 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?

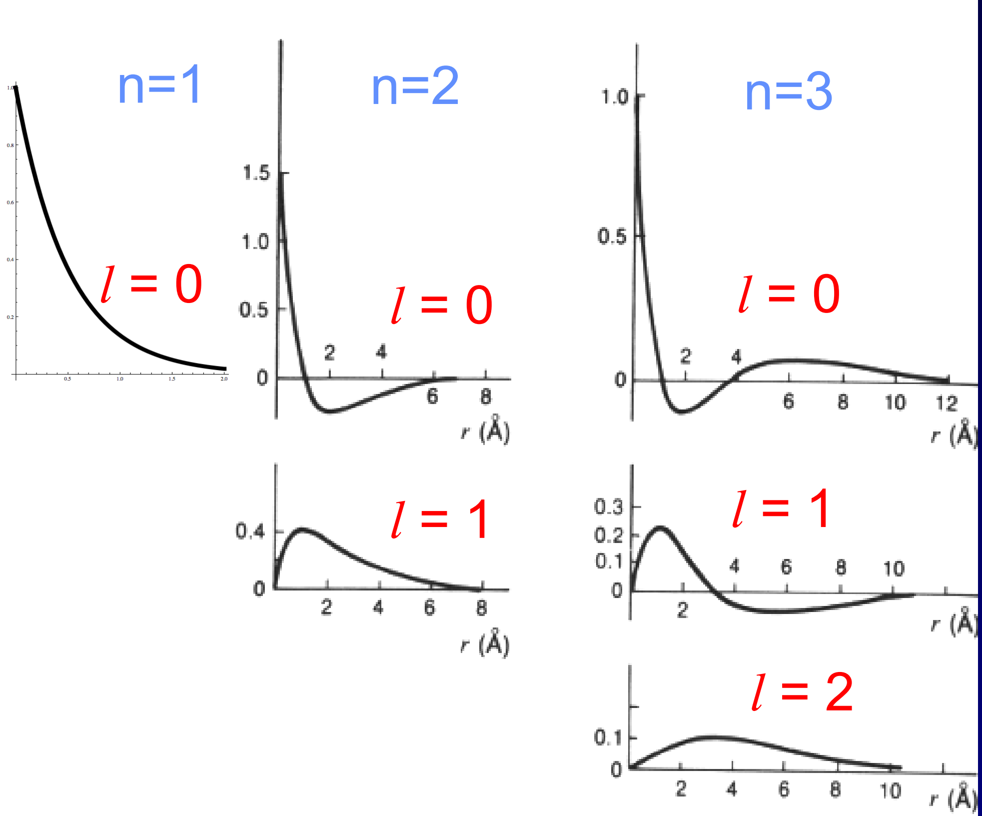
They govern the bonding and chemistry of atoms.

In particular, they determine the angles at which different atoms bond:
→ 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 $R_{n,l}$



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: $\psi(r=0) = 0$ for $l \neq 0$

Do you understand why?

(*i.e.*, a physics explanation)

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

This is only true for the Coulomb potential.

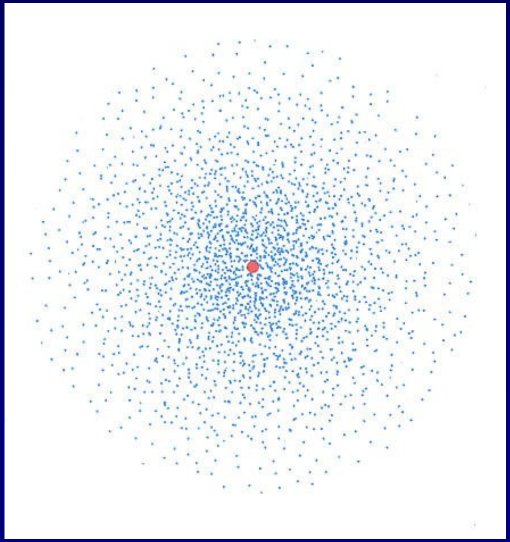
# Probability Density of Electrons

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

Probability density = Probability per unit volume = $|\psi_{nlm}|^2 \propto R_{nl}^2 Y_{lm}^2$.

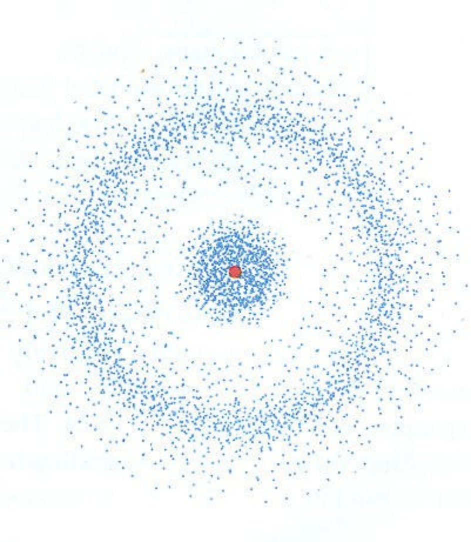
The density of dots plotted below is proportional to $|\psi_{nlm}|^2$.

1s state



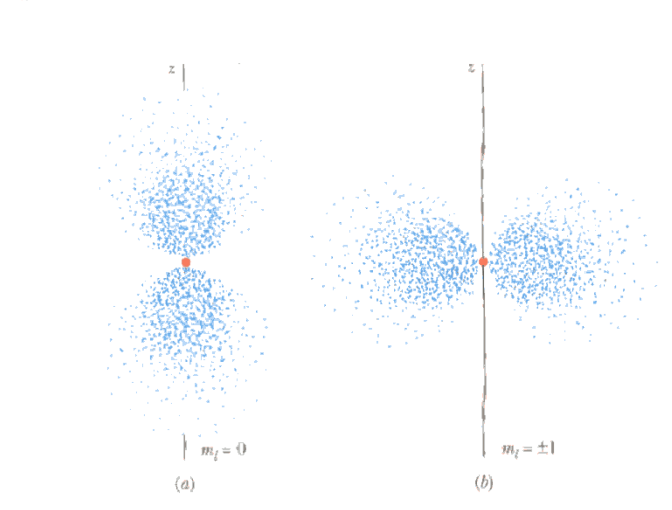
n,*l*,*m* = 1,0,0

2s state



2,0,0

2p states



2,1,{0,±1}

# Hydrogen Atom States: Summary

Key Points:

n: principal quantum #

$l$: orbital quantum #

$m_l$: orbital magnetic quantum #

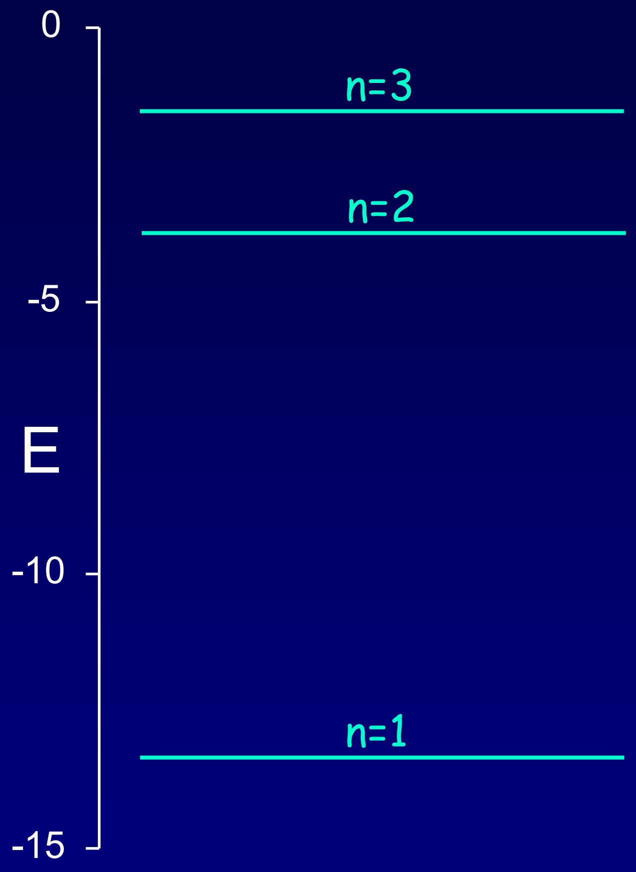
Energy depends only on n

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

For a given n, there are n possible angular momentum states:

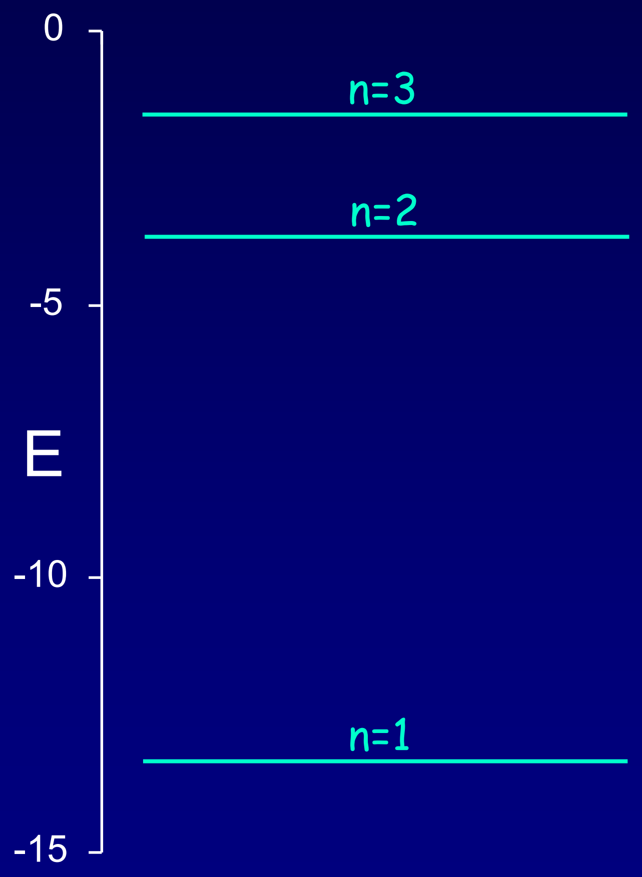
$l = 0, 1, ..., n-1$

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



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

# Hydrogen Atom States: Summary



($n,l,m_l$)

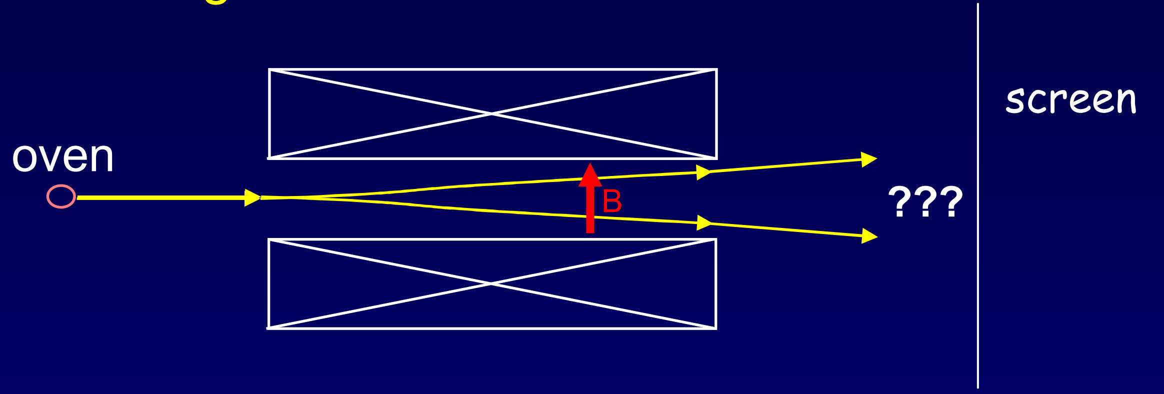
(3,0,0)
(3,1,-1), (3,1,0), (3,1,1)
(3,2,-2), (3,2,-1), (3,2,0), (3,2,1), (3,2,2)

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

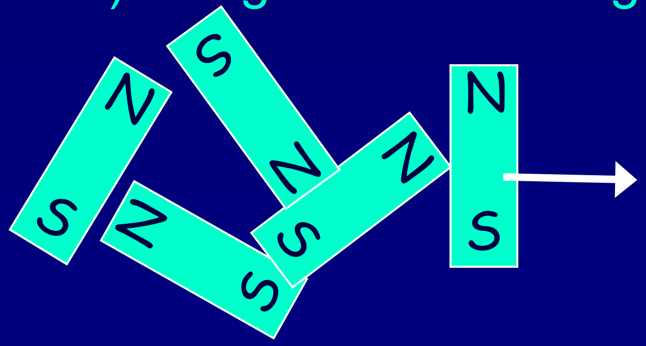
(1,0,0)

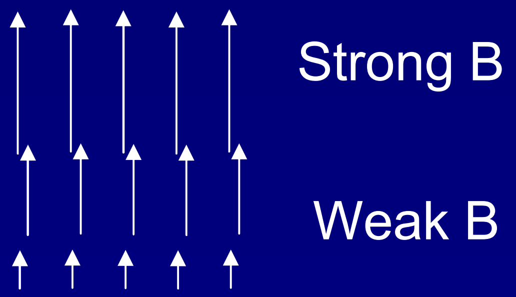
# Stern-Gerlach Experiment & Electron Spin

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



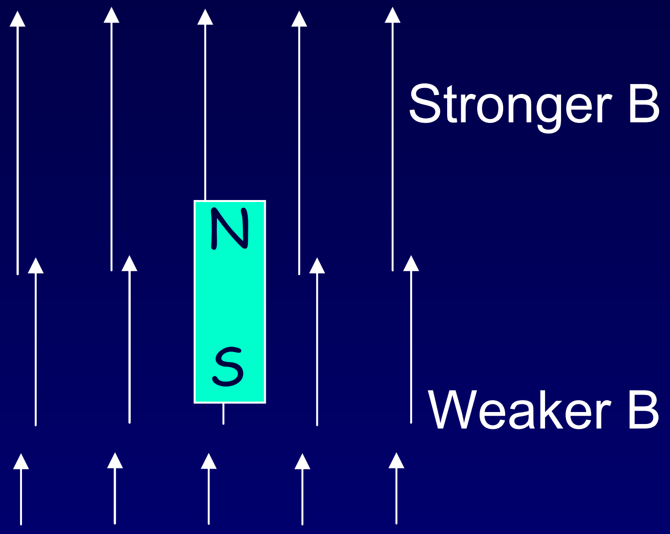
We can think of the atoms as tiny magnets (they have a magnetic moment) being directed through the field. They are randomly oriented:





# Act 2

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

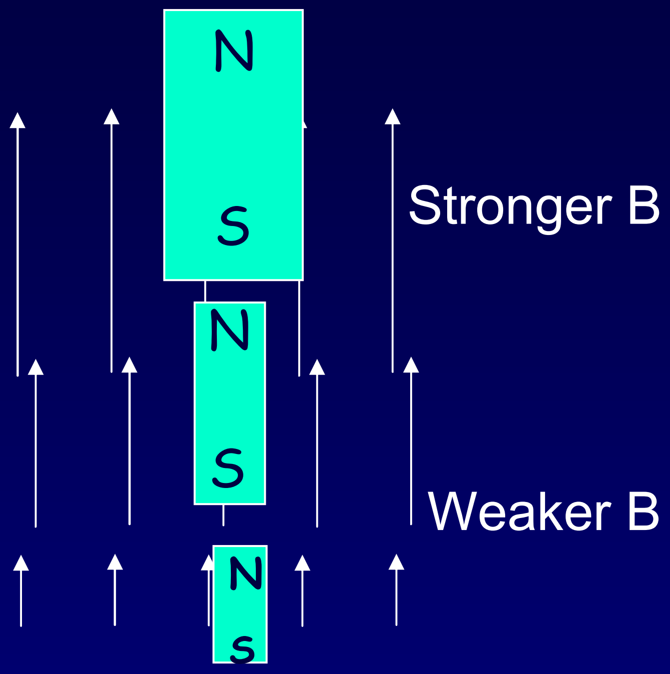


a. Up
b. Down
c. Left
d. Right
e. No force

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?



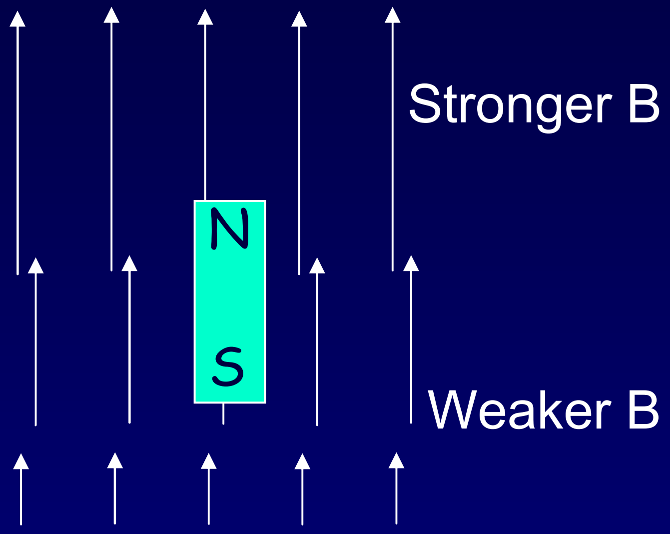
- a. Up
- b. Down
- c. Left
- d. Right
- e. No force

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

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?



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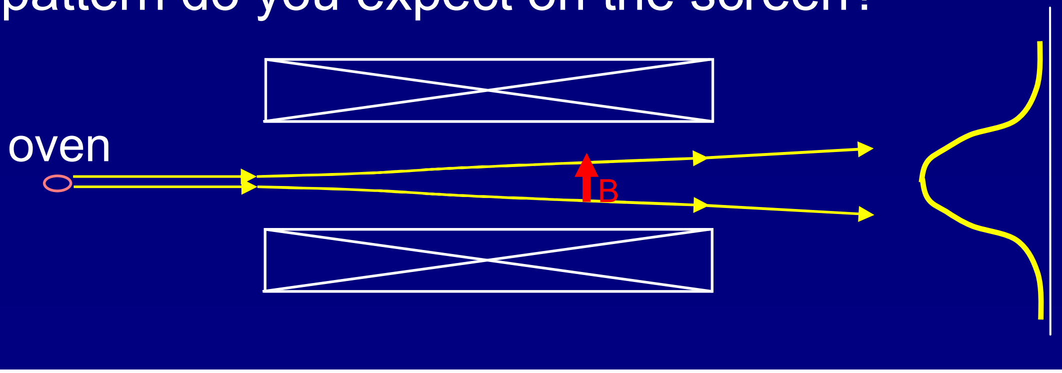
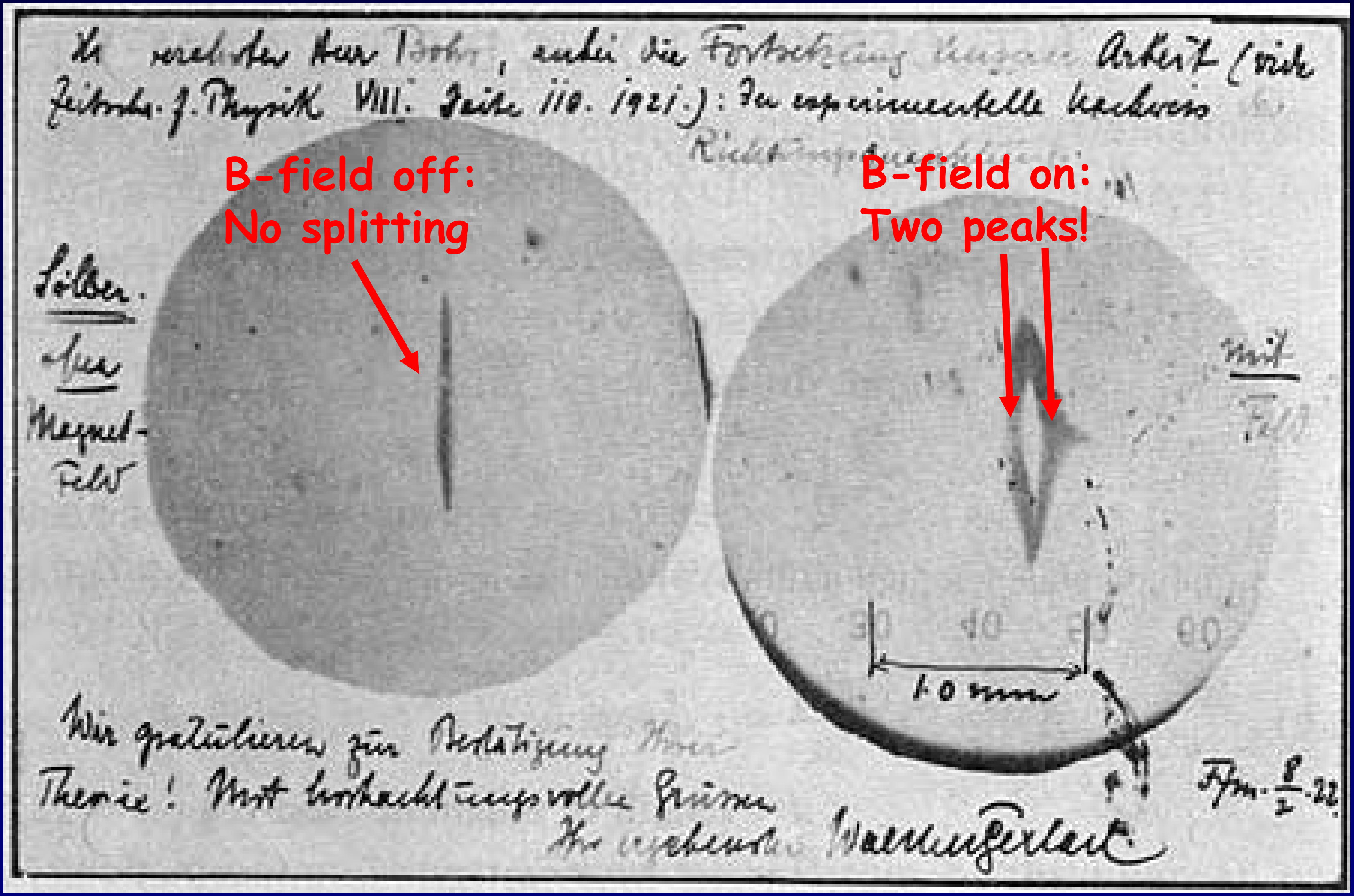


We expect a blob, because the position depends on the random rotation angle.



Hochverehrter Herr Bohr, anbei die Fortsetzung unserer Arbeit (vide Zeitschr. f. Physik VIII. Seite 110. 1921.): Der experimentelle Nachweis der Richtungsquantelung.

Silber ohne Magnetfeld

mit Feld

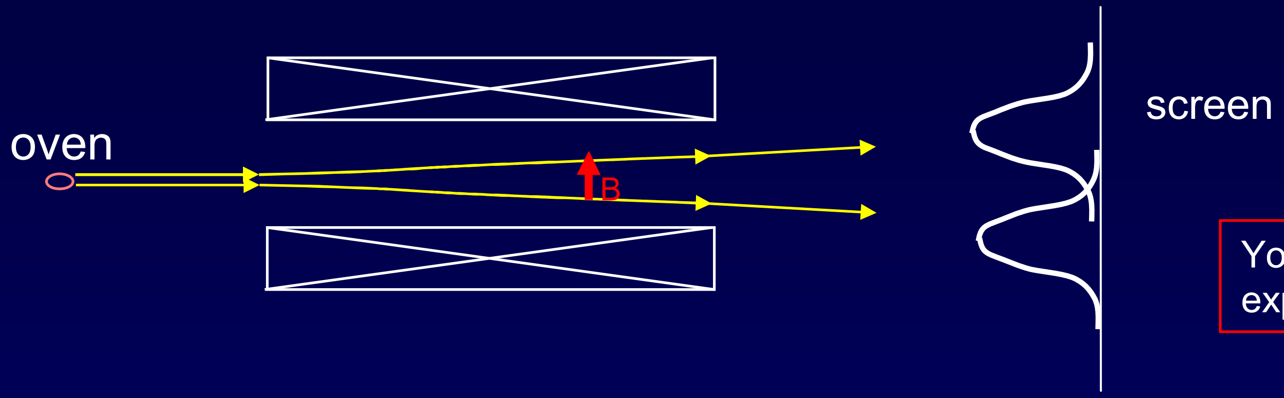
Wir gratulieren zur Bestätigung Ihrer Theorie! Mit hochachtungsvollen Grüssen

Ihr ergebener Walther Gerlach

Ffm. 8/2.22

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



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:

$$(s = \tfrac{1}{2}) \quad m_s = \pm\tfrac{1}{2}$$

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: <u>Most</u> 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 $m_s = -½$ and $+½$)

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

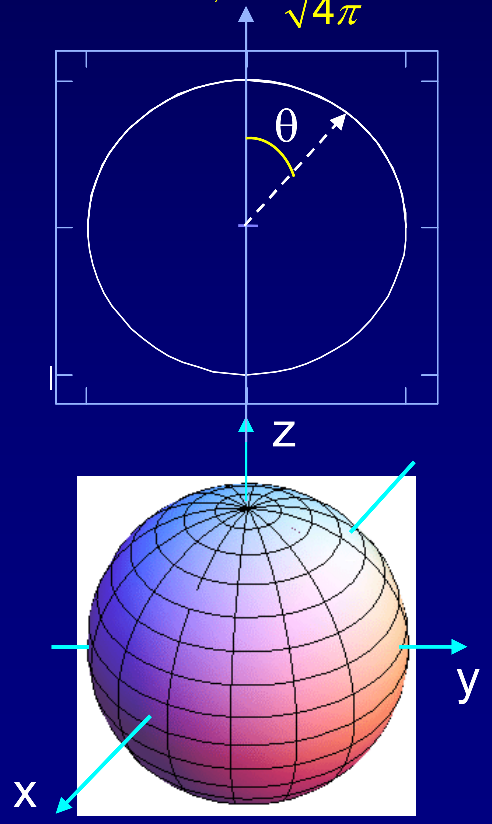
Electron energy bands in Solids

QM in everyday life

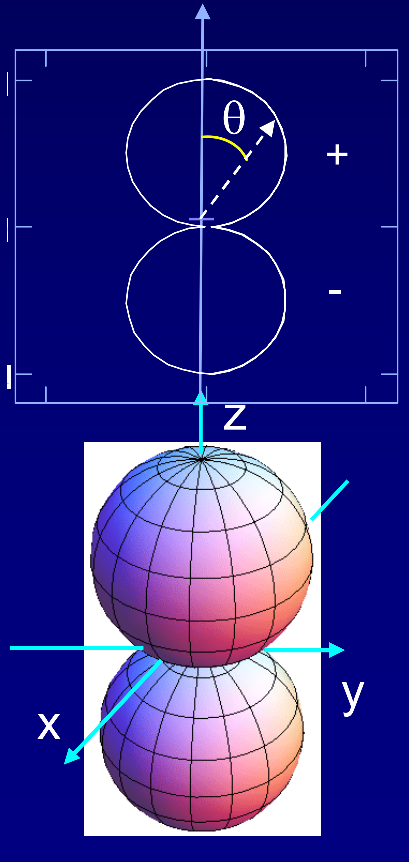
# Supplement:
# Superposition and Chemical Bonding

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”:

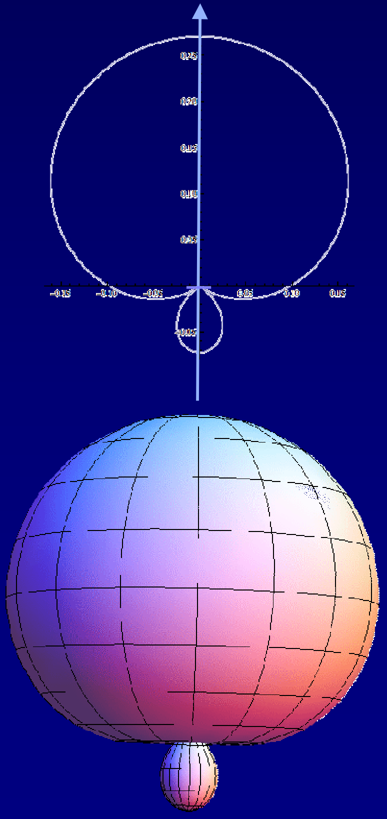
$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$



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



$Y_{00} + Y_{10}$



# Supplement: Chemistry Notation

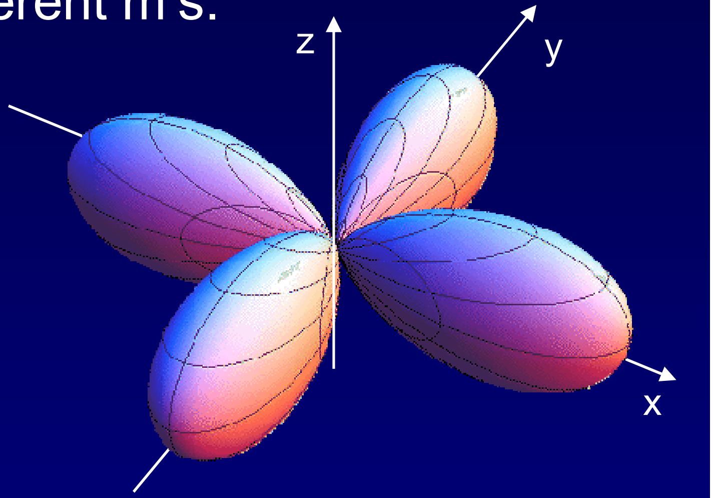
From chemistry you may be familiar with states like $d_{xy,}$ etc.

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.