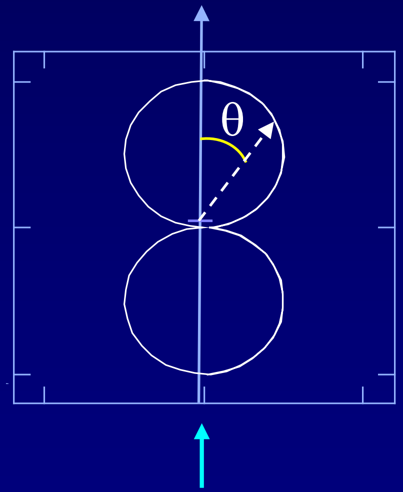
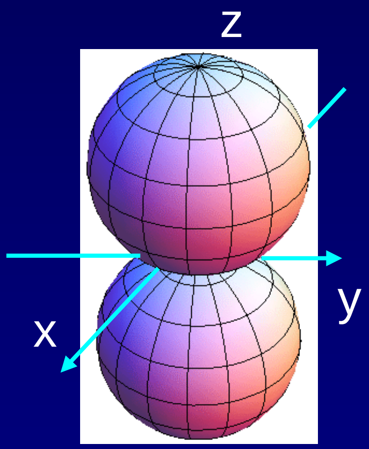
Lecture 18:
Orbitals, Spin,
and Selection Rules





Today

Angular wave functions for the Hydrogen Atom

- Orbitals

Atomic Transitions

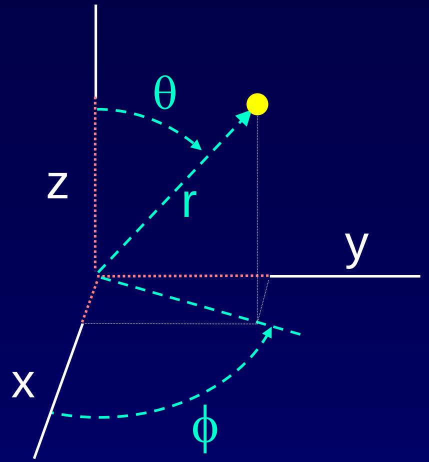
- Selection rules

Stern-Gerlach Experiment

- Electron “spin”

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.

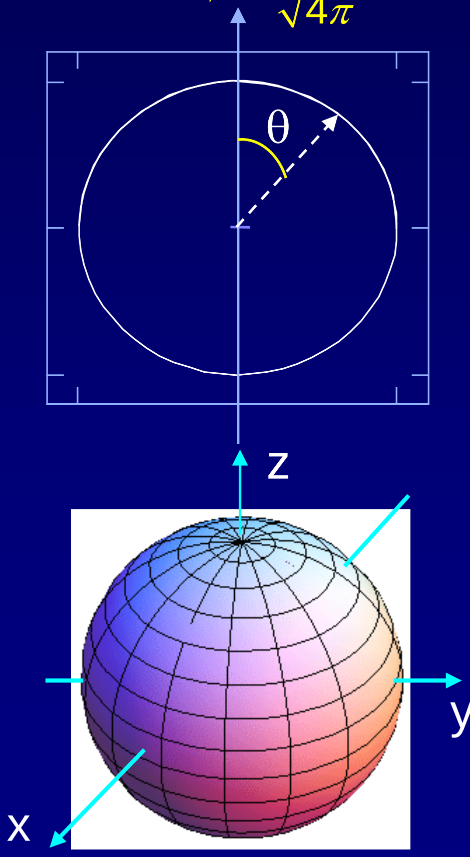
* The constraints on *l* and *m* come from the boundary conditions one must impose on the solutions to the Schrodinger equation. We’ll discuss them briefly.

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., $P(\theta)$):

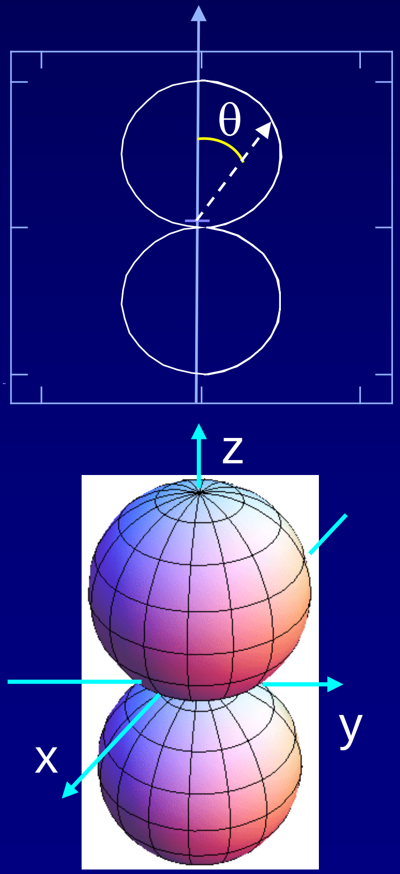
$l = 0$

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

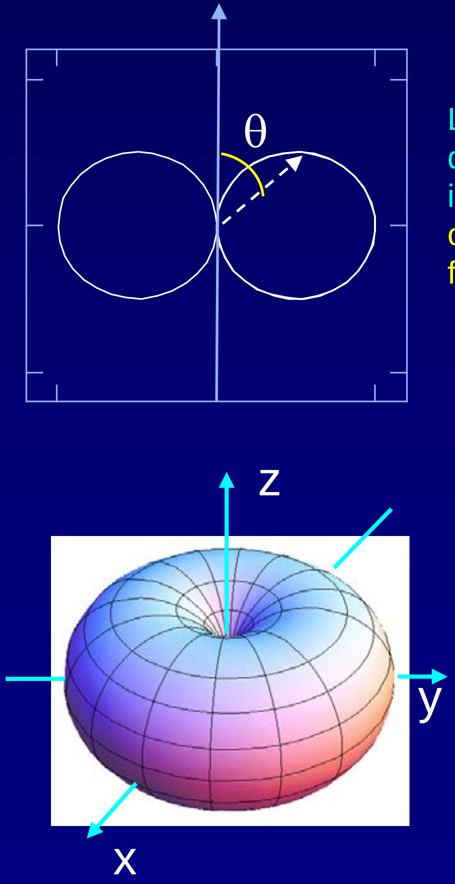


$l = 1$

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



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



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

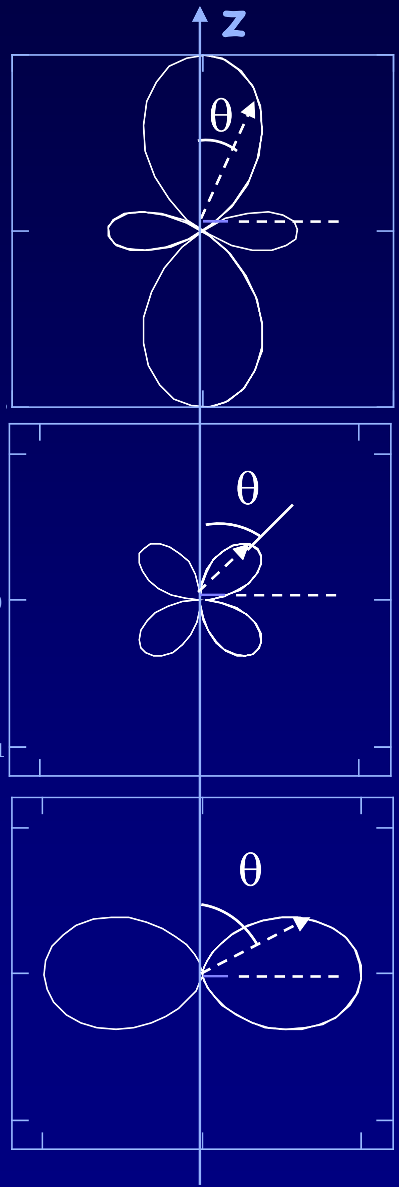
The Angular Wave Function, $Y_{lm}(\theta,\varphi)$

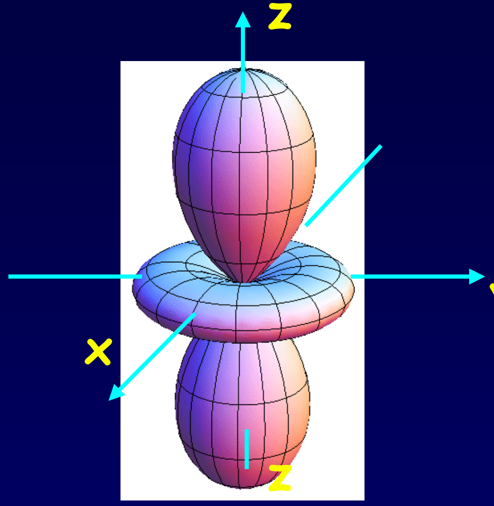
$l = 2$

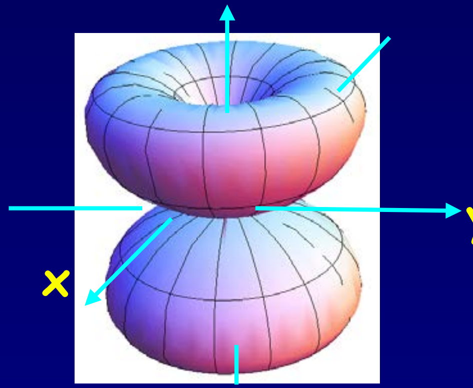
$$|Y_{2,0}| \propto |(3\cos^2\theta - 1)|$$

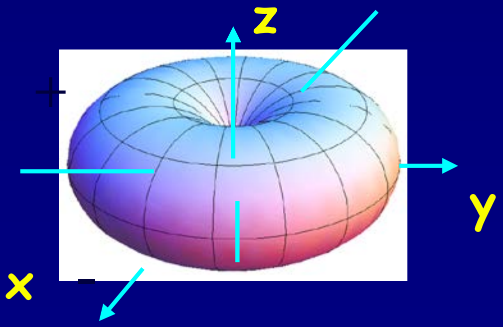
$$|Y_{2,\pm1}| \propto |\sin\theta\cos\theta|$$

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









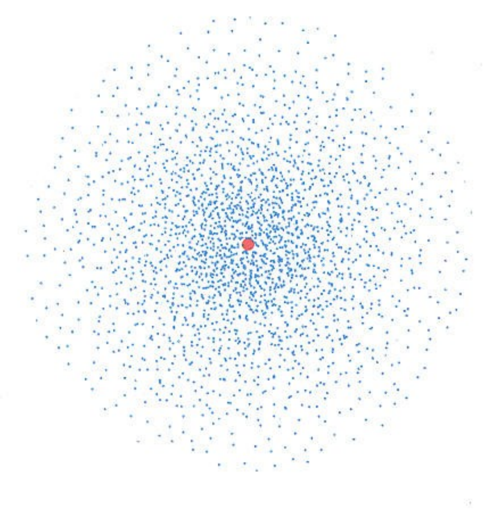
Probability Density of Electrons

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

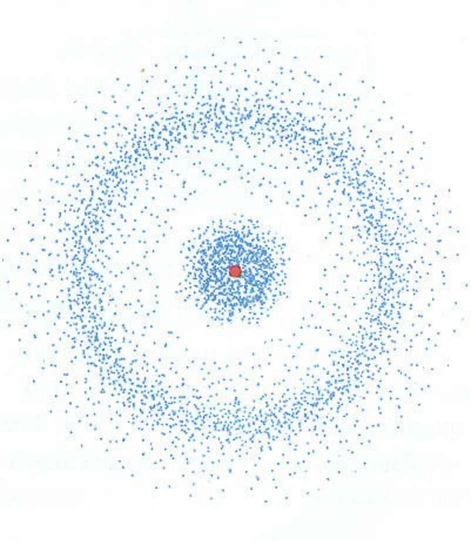
Probability density = Probability per unit volume = $|\psi_{nlm}|^2 \propto R_{nl}^2 Y_{lm}^2$.

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

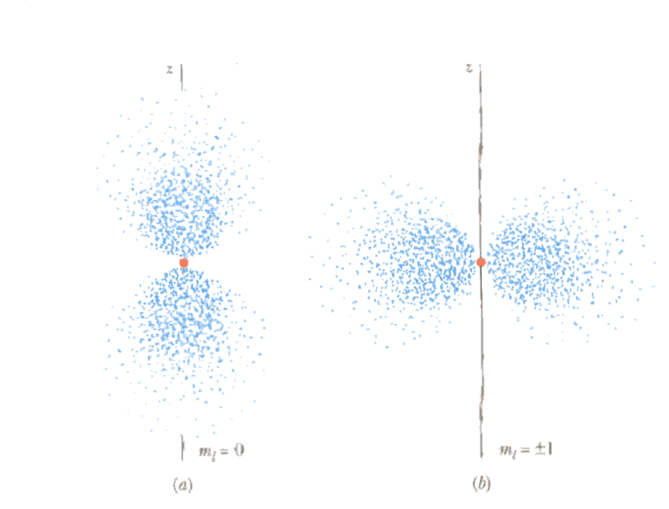
1s state



2s state



2p states



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

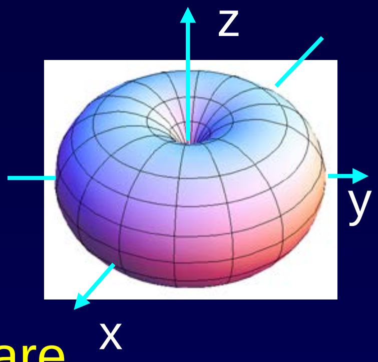
2,0,0

2,1,{0,±1}

Act 1

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. θ = 0° (north pole)
    b. θ = 45°
    c. θ = 90° (equator)

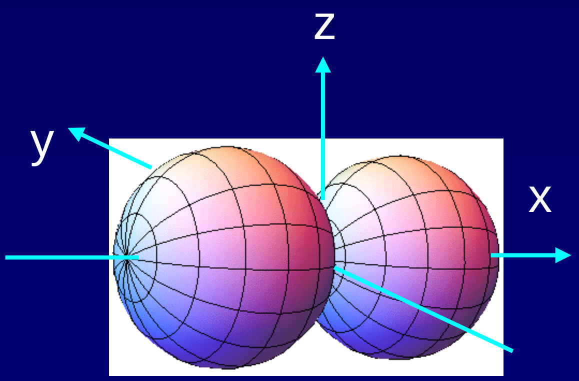
Cylindrical Symmetry



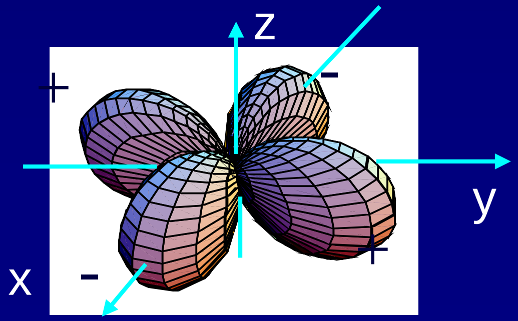
Why do none of the graphs display ϕ-dependence?
(They all have cylindrical symmetry.)

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 $l = 2$, $m = \pm 2$ superpositions:



See Supplement for more info.

Why are these distributions important?

They govern the bonding and chemistry of atoms.

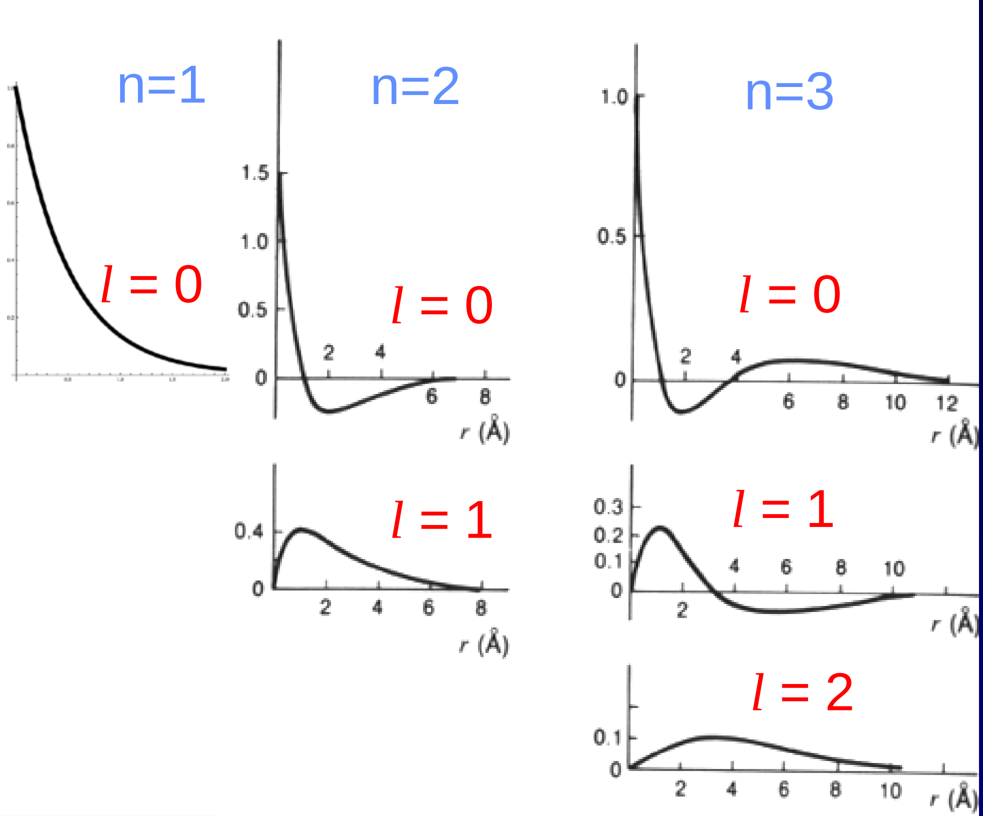
In particular, they determine the angles at which different atoms bond:

→ 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.

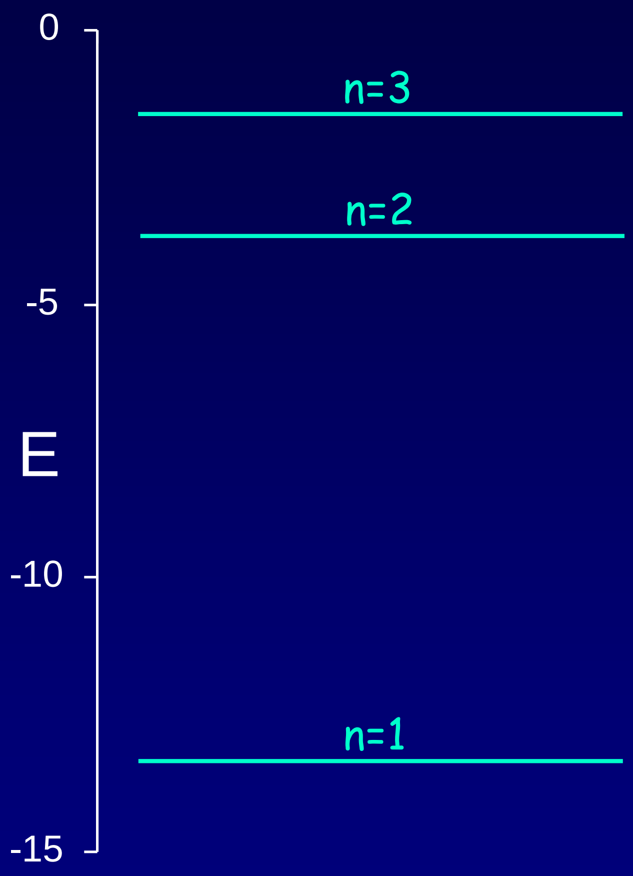
Hydrogen Atom States: Summary

Key Points:

n: principal quantum #

l: orbital quantum #

m_l: orbital magnetic quantum #



Energy depends only on n

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

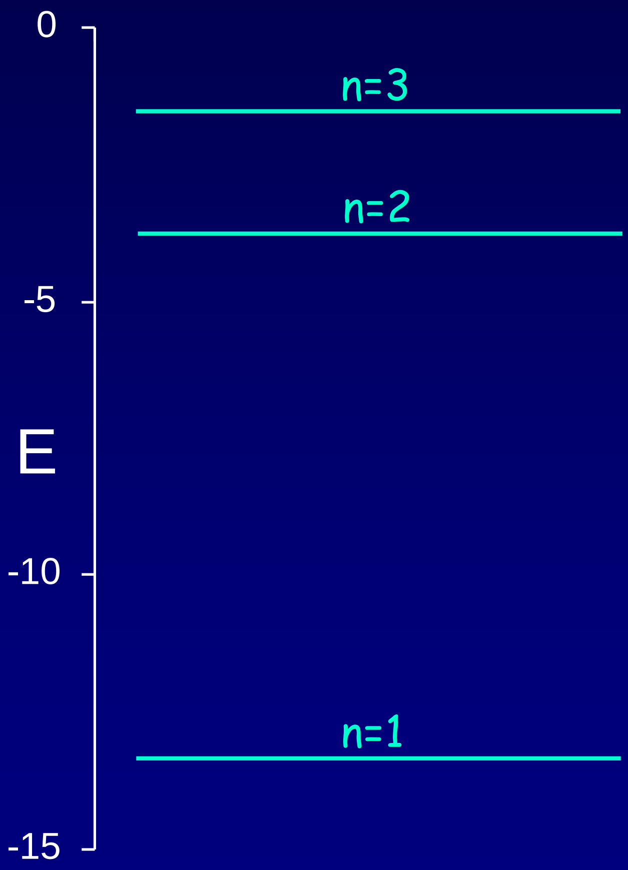
For a given n, there are n possible angular momentum states:

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

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

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

Hydrogen Atom States: Summary


0
-5
-10
-15
E
n=3
n=2
n=1

(n, l, m_l)

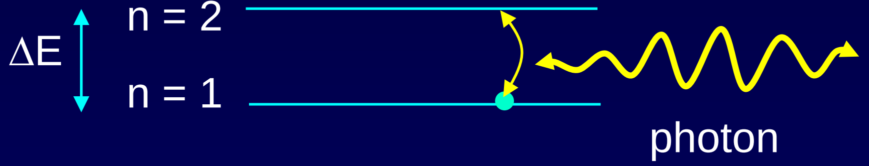
(3,0,0)
(3,1,-1), (3,1,0), (3,1,1)
(3,2,-2), (3,2,-1), (3,2,0), (3,2,1), (3,2,2)

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

(1,0,0)

Optical Transitions between Atomic Levels

Consider the n = 1 and 2 levels of hydrogen:



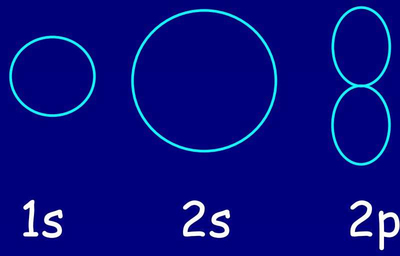
$$f = \frac{\Delta E}{h} = \frac{c}{\lambda}$$

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

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 oscillating between the two eigenstates of the energy (that is, they were eigenstates before the field showed up!).

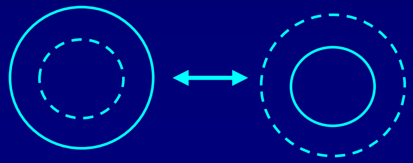
Not all transitions are possible.
For example, one must conserve angular momentum (and the photon has l = 1).

Stationary States:



Superpositions:

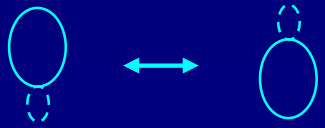
1s ± 2s



No electric-dipole moment

Forbidden transition
Δ*l* = 0

1s ± 2p



Oscillating electric-dipole couples to photons

Allowed transition
Δ*l* = ±1

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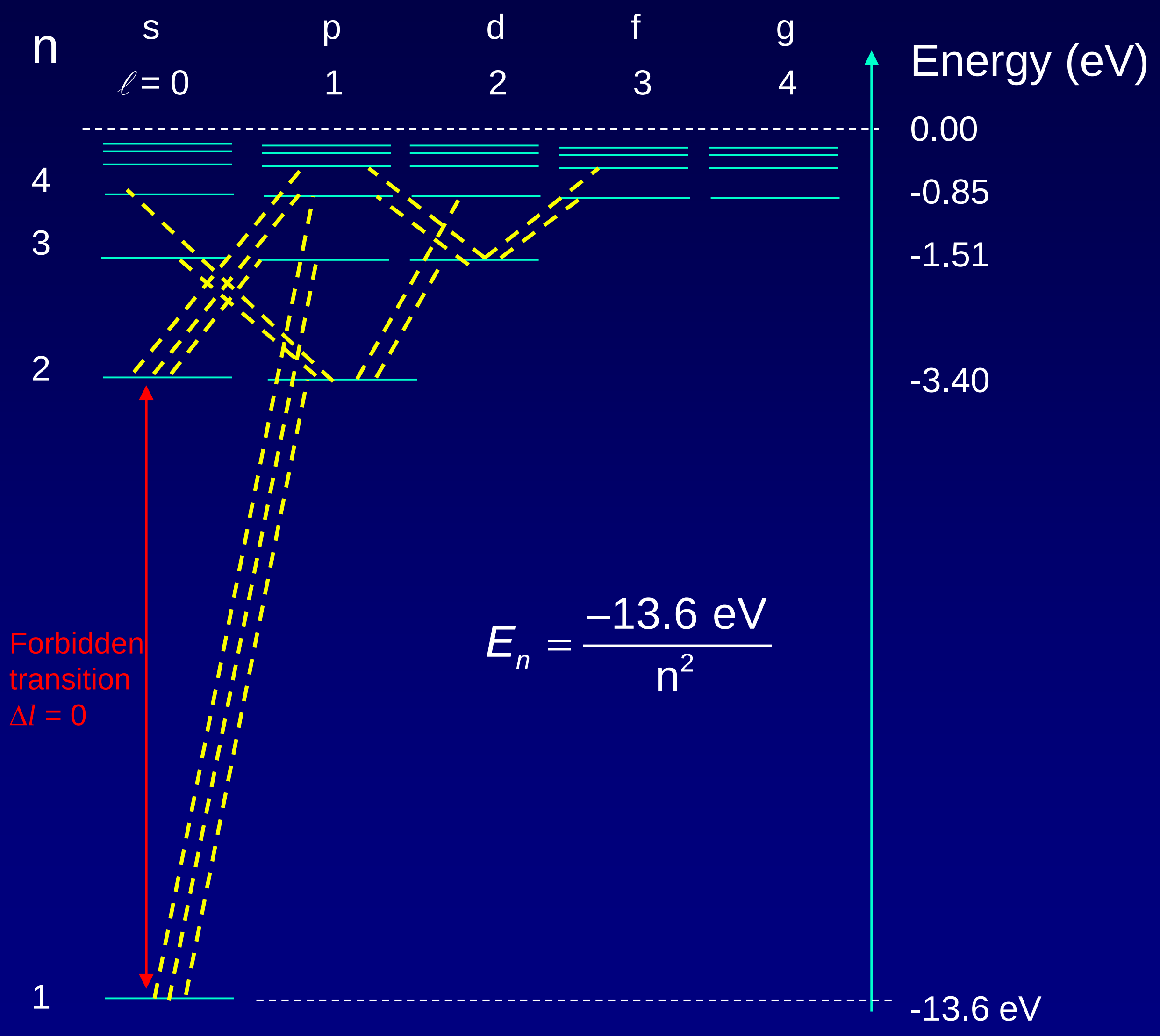
Each photon carries 1 ħ of angular momentum.

Allowed Transitions for H

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


n
s
p
d
f
g
ℓ = 0
1
2
3
4
4
3
2
1
Energy (eV)
0.00
-0.85
-1.51
-3.40
-13.6 eV

Forbidden transition $\Delta l = 0$

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

Selection Rule for “electric-dipole” (photon has l = 1) transitions:

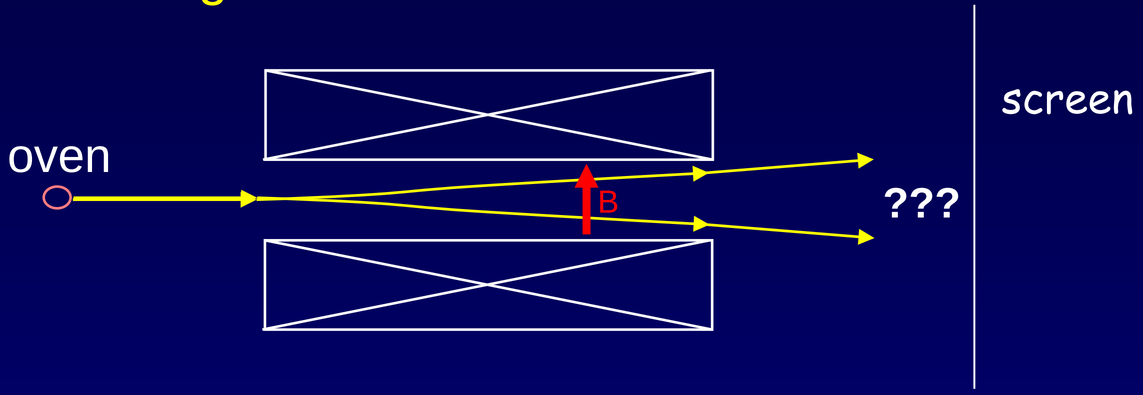
$$\boxed{\begin{aligned}\Delta l &= \pm 1 \\ \Delta m &= 0, \pm 1\end{aligned}}$$

NOTE:

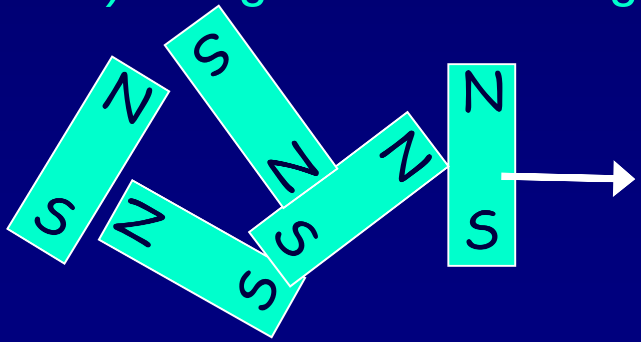
It is possible (but unlikely) for the photon to have $\ell \neq 1$ or for more than one photon to be involved. This permits other Δl and Δm.

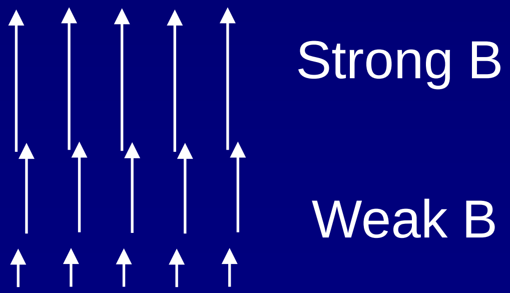
Stern-Gerlach Experiment & Electron Spin

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
B
???
screen

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

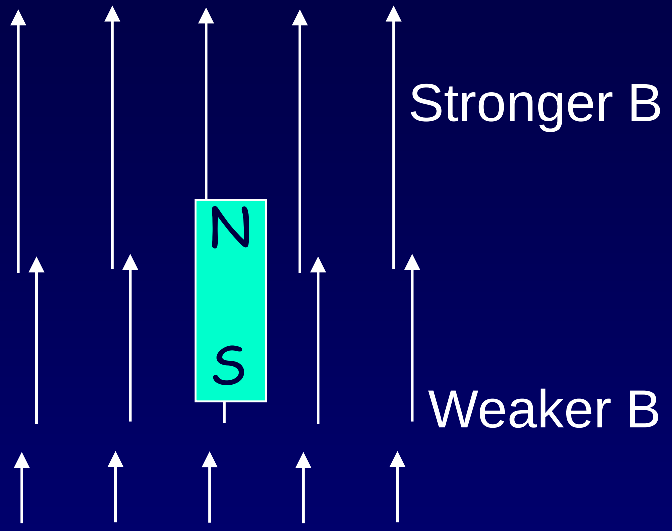

N
S
S
N
N
S
N
S
N
S


Strong B
Weak B

Act 2

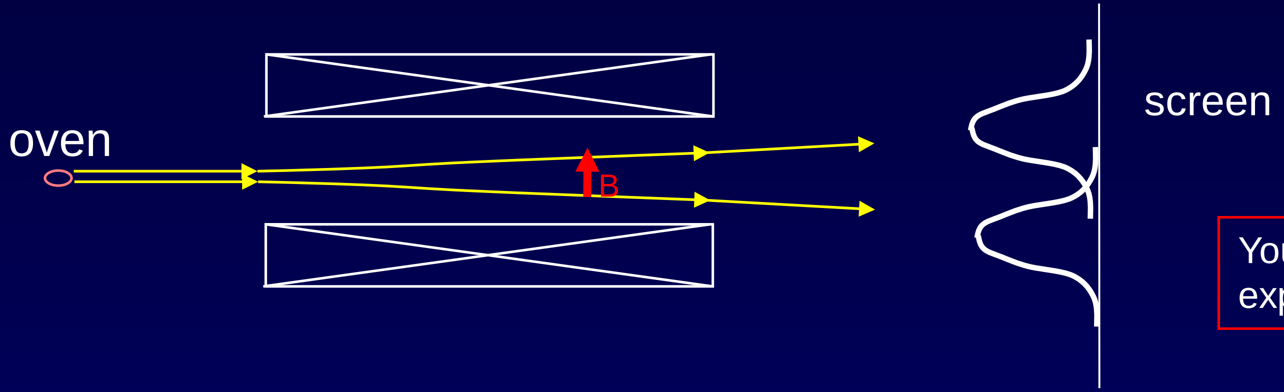
1. Consider a magnet in an inhomogeneous field, as shown.
   Which way will the magnet feel a force?

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



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

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: 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 $m_s = -½$ 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.

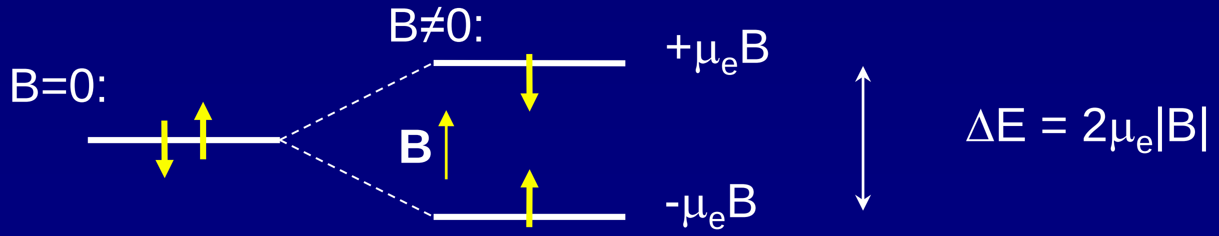
Electron Magnetic Moment

Because the electron has a charge and angular momentum, it has a magnetic moment, with magnitude: $\mu_e = 9.2848\times10^{-24}$ 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:

$+\mu_e B$

$-\mu_e B$

B

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

Note: These arrows represent magnetic moment, not spin...

FYI: The *real* value of μ_e

- There are relatively simple arguments that predict

  $\mu_e = \mu_B \equiv e\hbar/2m = 9.2740 \times 10^{-24}$ J/T

- In reality, the measured mag. moment of the electron is a bit bigger:

  $\mu_e = -9.2848 \times 10^{-24}$ J/T

- The effect is small:

  $|\mu_e/\mu_B| = 1.00115965218073\ (28)$

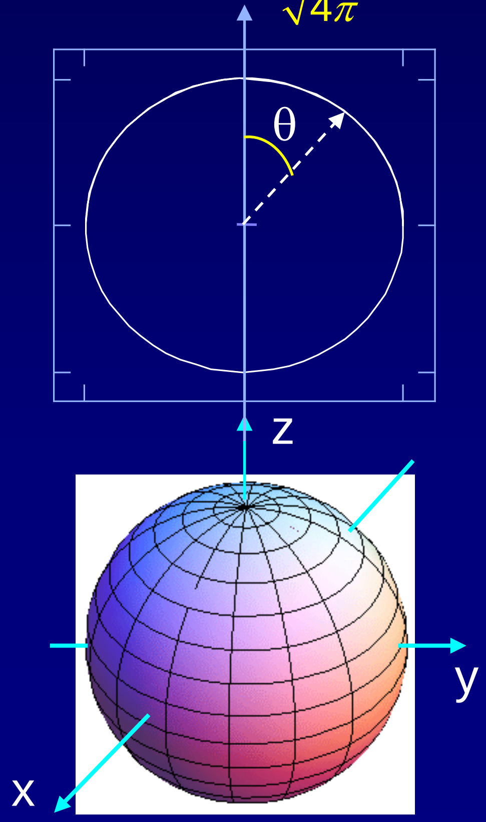
[Yes, it has been measured *that* well – in fact, it's one of the most precisely known quantities today.]

- 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!!

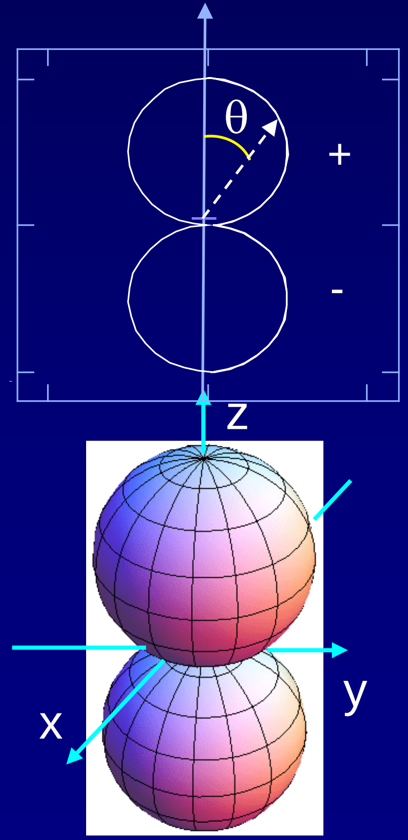
Supplement:
Superposition and Chemical Bonding

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”:

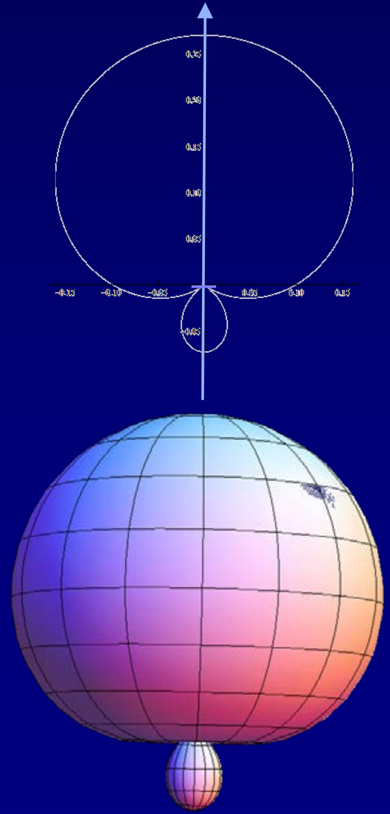
$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$



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



$$Y_{00} + Y_{10}$$



Supplement: Chemistry Notation

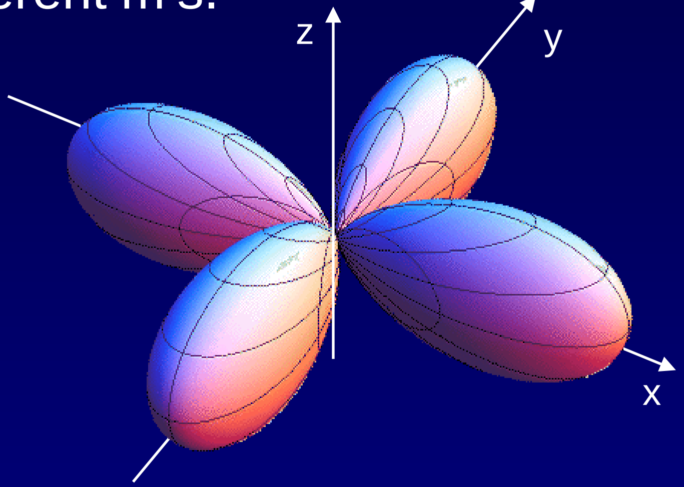
From chemistry you may be familiar with states like $d_{xy,}$ etc.

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.