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

--Niels Bohr

Physics Colloquium TODAY!

"Quantum Optomechanics" – Prof. Markus Aspelmeyer, U. Vienna

Massive mechanical objects are now becoming available as new systems for quantum science. Recent experiments, including laser-cooling of micro- and nanomechanical resonators into their quantum ground state of motion, provide the primary building blocks for full quantum optical control of mechanics, i.e., quantum optomechanics. This new frontier opens fascinating perspectives both for various applications and for unique tests of the foundations of quantum theory, for example table-top experiments exploring the interface between quantum physics and gravity.

- 4 pm, 141 Loomis

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. 24
  - 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:

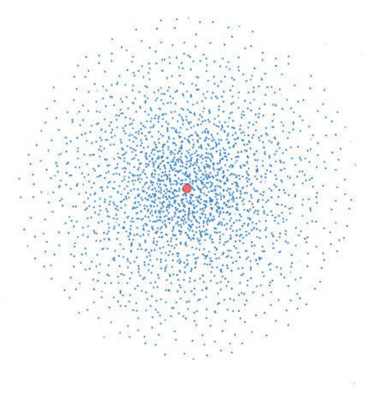
- 3 dimensions, angular momentum, electron spin, H atom
- Exclusion principle, periodic table of atoms

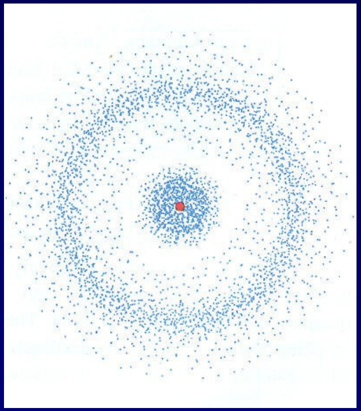
Next week:

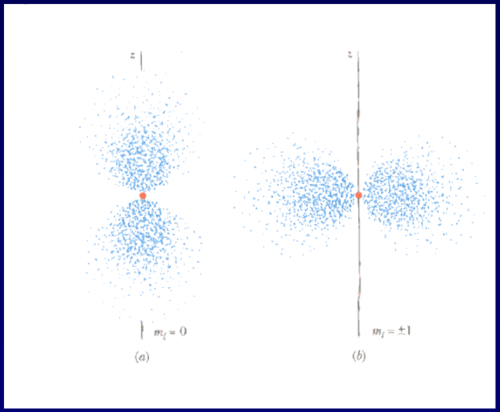
- Molecules and solids, consequences of Q. M., Schrodinger's cat
- Metals, insulators, semiconductors, superconductors, lasers, . .

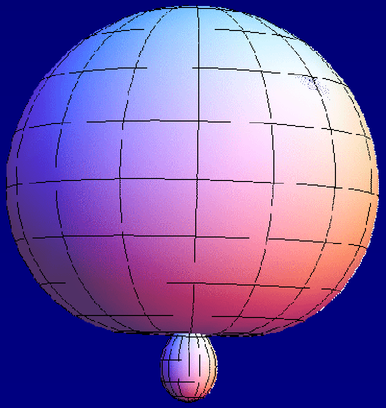
Final Exam: Monday, Mar. 4
Homework 6: Due Saturday (March 2), 8 am

Lecture 17:
Atomic States, Angular Momentum & 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

Atomic Transitions

- Selection rules

Summary of S-states of H-atom

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

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

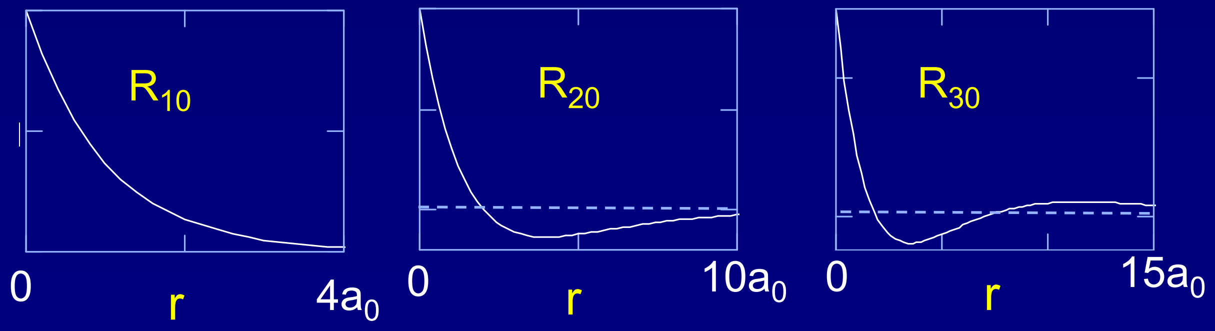
but:

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

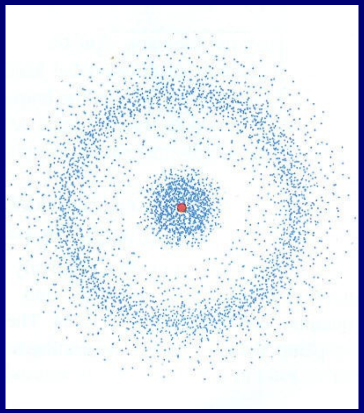
because $Y_{00}(\theta,\phi)$ is a constant.

S-state wave functions are spherically symmetric.

Some s-state wave functions (radial part):



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



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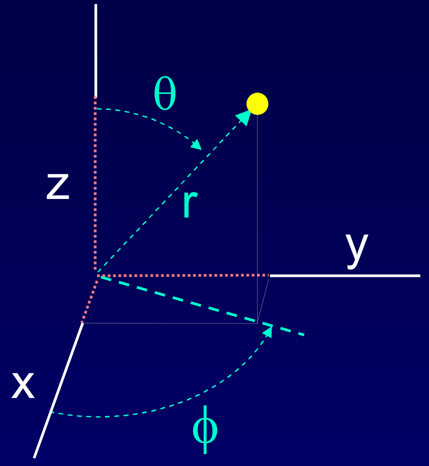
Total Wave Function of the H-atom

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



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

$$\begin{array}{lll} \bullet\; n & \text{“principal”} & (n \geq 1) \\ \bullet\; l & \text{“orbital”} & (0 \leq l < n-1) \\ \bullet\; m & \text{“magnetic”} & (-l \leq m \leq +l) \end{array}\left.\vphantom{\begin{array}{l}a\\a\end{array}}\right\}^{*}$$

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

They are related to the angular momentum of the electron.

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* 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

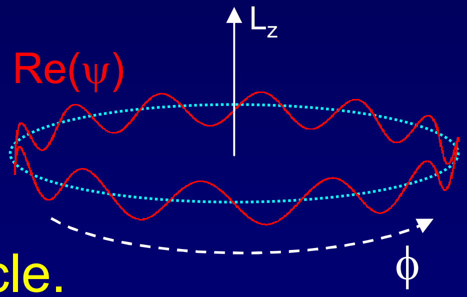
Linear momentum depends on the wavelength ($k=2\pi/\lambda$):

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

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.

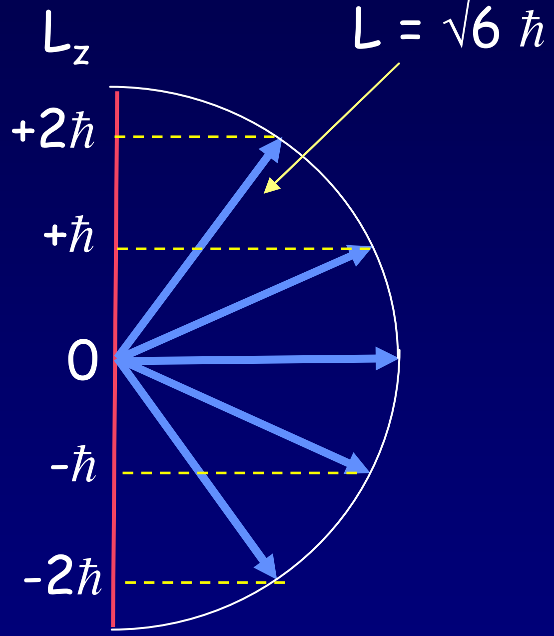
This logic only works for $L \neq 0$. L = (0,0,0) is allowed. It's the s-state.

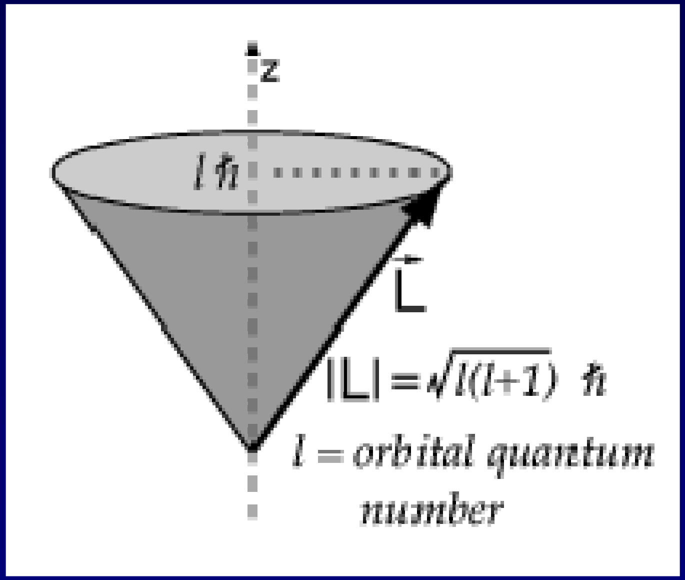
All physical quantities are subject to uncertainty relations, not just position and momentum.

Classical Picture of L-Quantization

e.g., $l = 2$

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





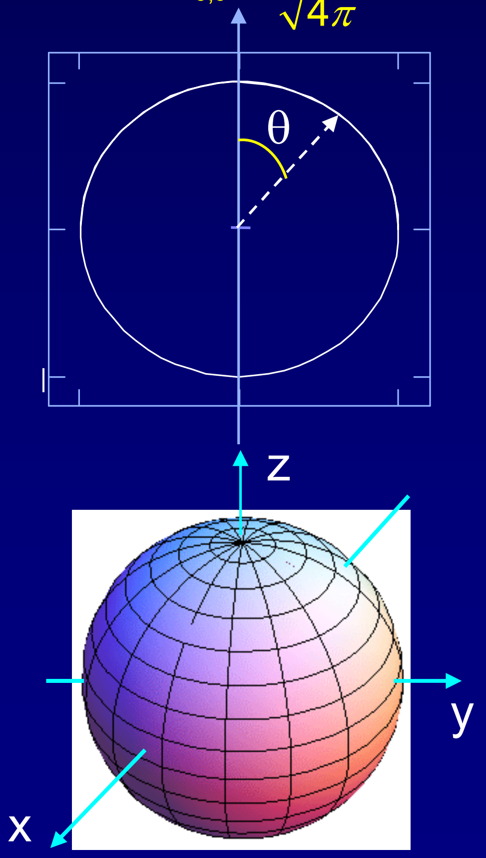
$$\vec{L} = \vec{r} \times \vec{p}$$

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

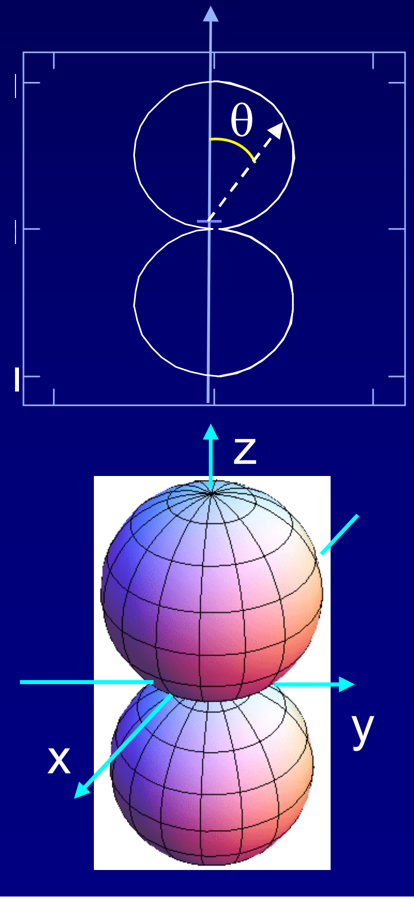
$l = 0$

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

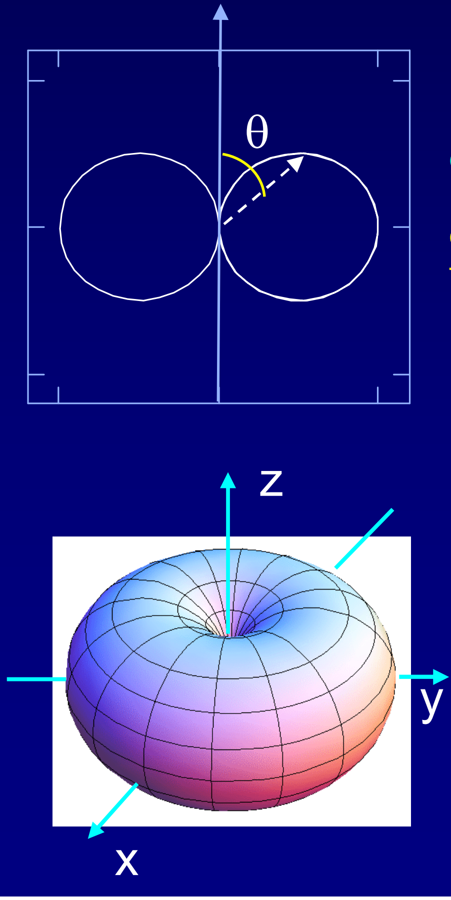


$l = 1$

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



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



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

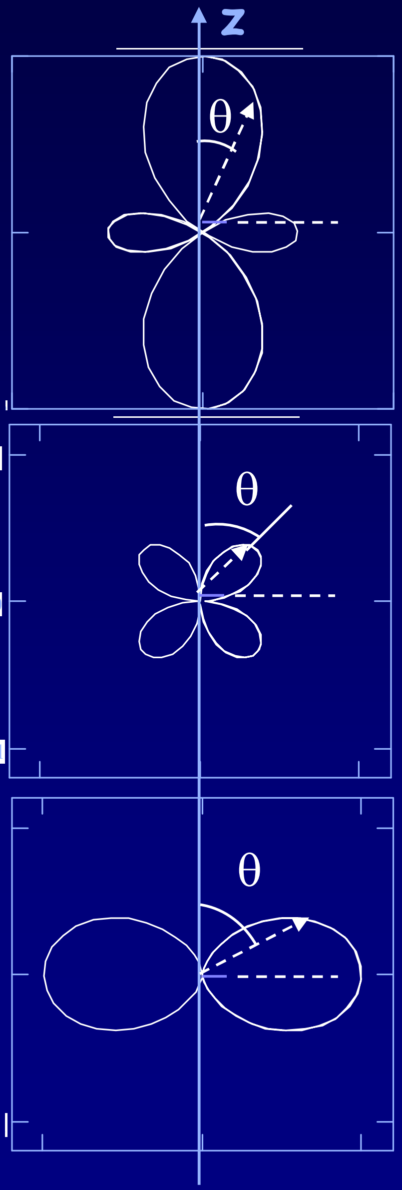
The Angular Wave Function, $Y_{lm}(\theta,\varphi)$

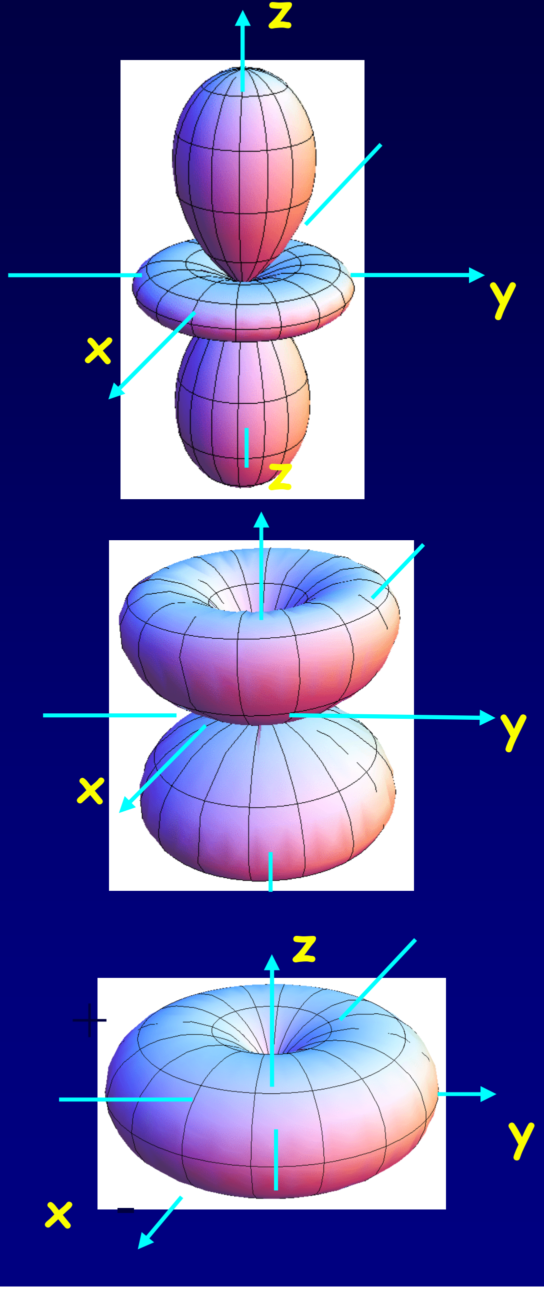
$l = 2$

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

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

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



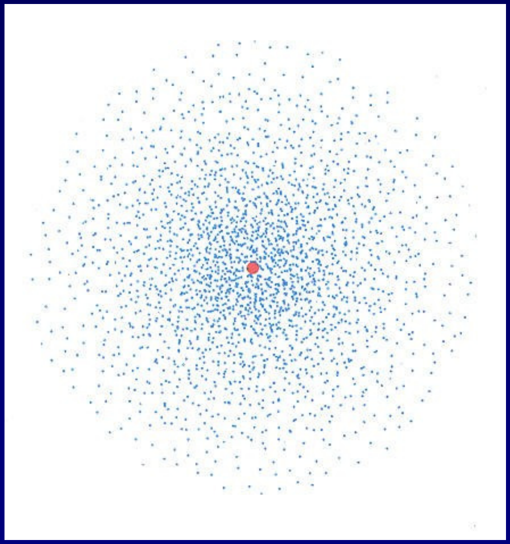


Probability Density of Electrons

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

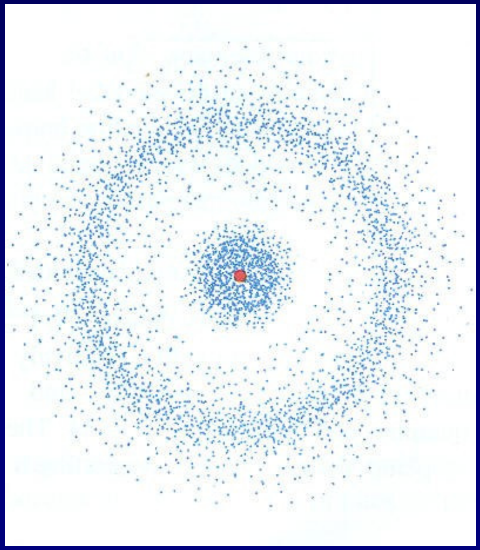
Probability density = Probability per unit volume = $|\psi_{nlm}|^2 \propto R_{nl}^2 Y_{lm}^2$.
The density of dots plotted below is proportional to $|\psi_{nlm}|^2$.

1s state



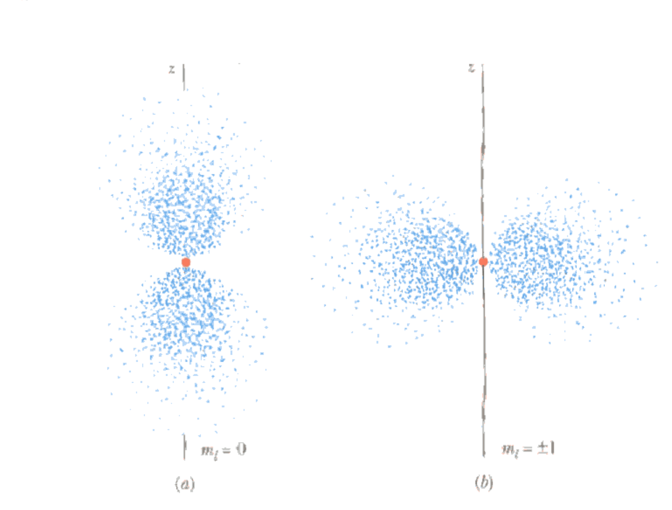
n,*l*,*m* = 1,0,0

2s state



2,0,0

2p states



2,1,{0,±1}

Act 1

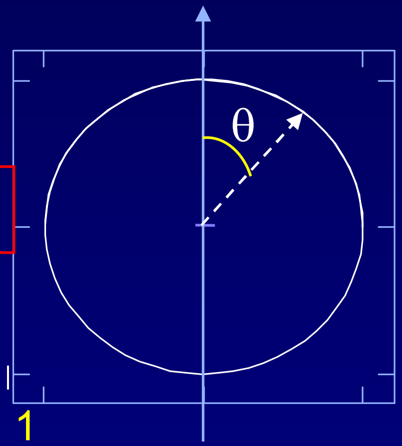
1. Suppose the electron is in the l=1, m=1 state. In what direction(s) (at what θ), is the electron most likely to be found? $Y_{1,\pm 1} \propto \sin\theta$
   - a. θ = 0° (north pole)
   - b. θ = 45°
   - c. θ = 90° (equator)

Solution

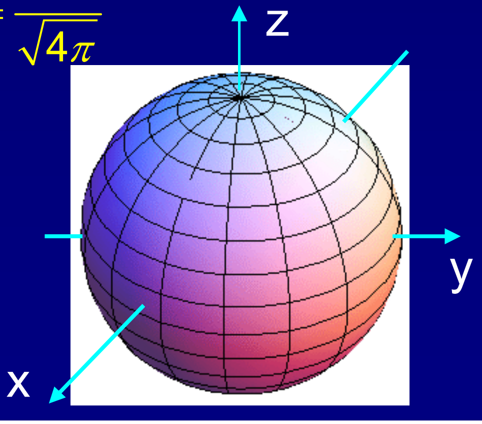
1. Suppose the electron is in the l=1, m=1 state. In what direction(s) (at what θ), is the electron most likely to be found? $Y_{1,\pm1} \propto \sin\theta$
   - a. θ = 0° (north pole)
   - b. θ = 45°
   - c. $\boxed{\theta = 90° \text{ (equator)}}$

sinθ is maximum at θ = 90°.

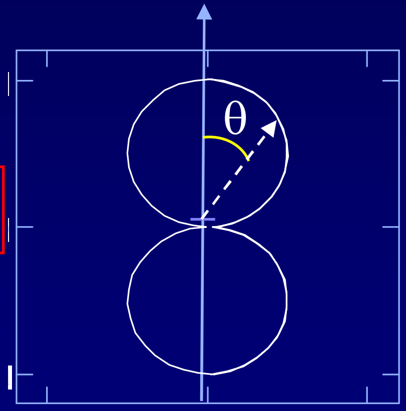
$\boxed{l = 0}$



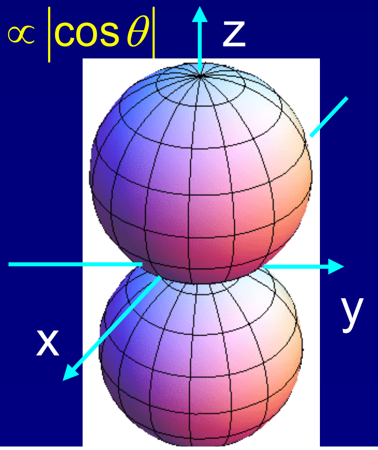
$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

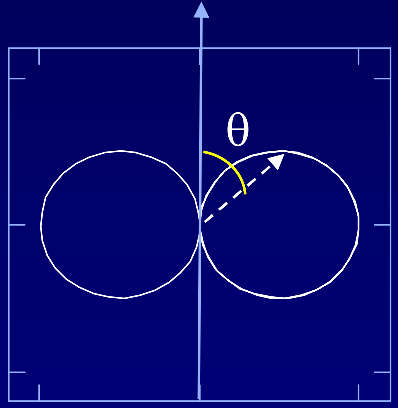


$\boxed{l = 1}$

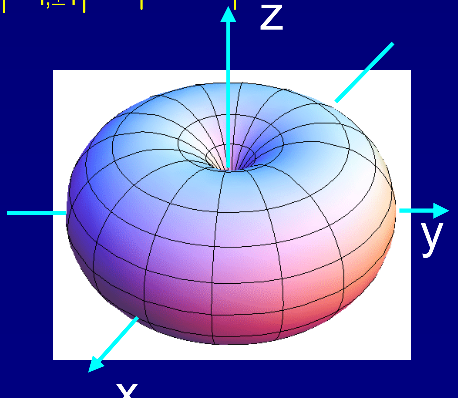


$$|Y_{1,0}| \propto |\cos\theta|$$



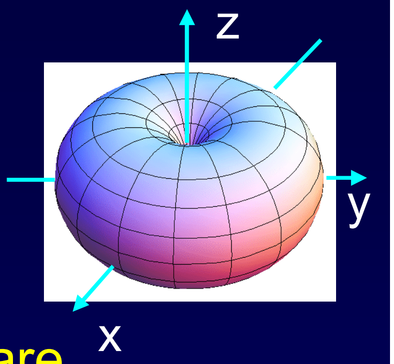


$$|Y_{1,\pm1}| \propto |\sin\theta|$$



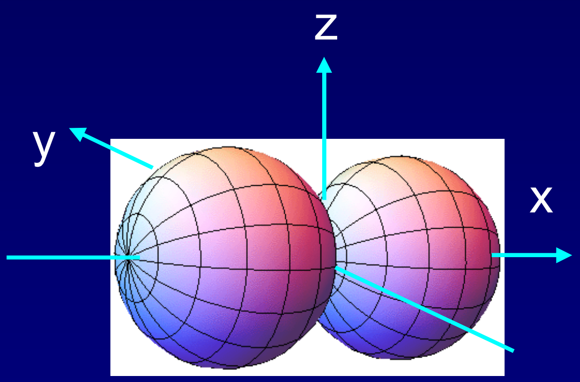
Length of the dashed arrow is the magnitude of Y_{lm} as a function of θ.

Cylindrical Symmetry



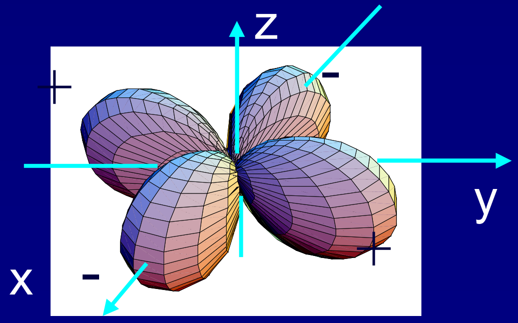
Why do none of the graphs display ϕ-dependence?
(They all have cylindrical symmetry.)

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:

→ 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”

Act 2

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?

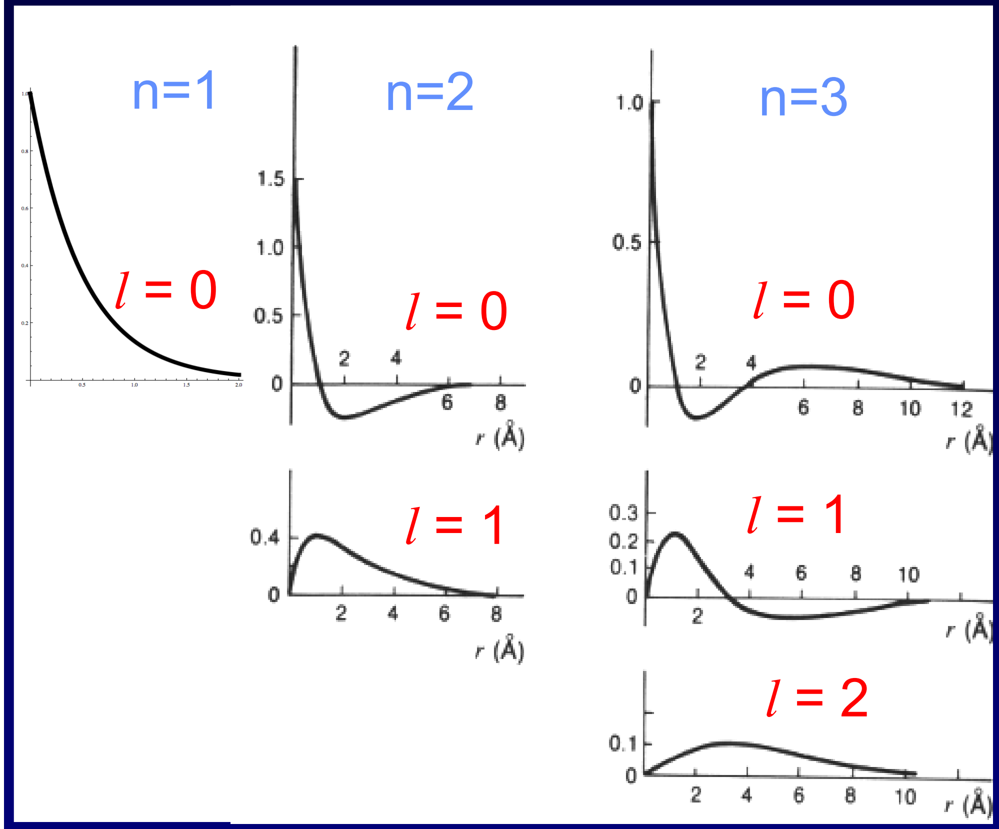
a. The number of "lobes" increases as n increases.

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.

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 #

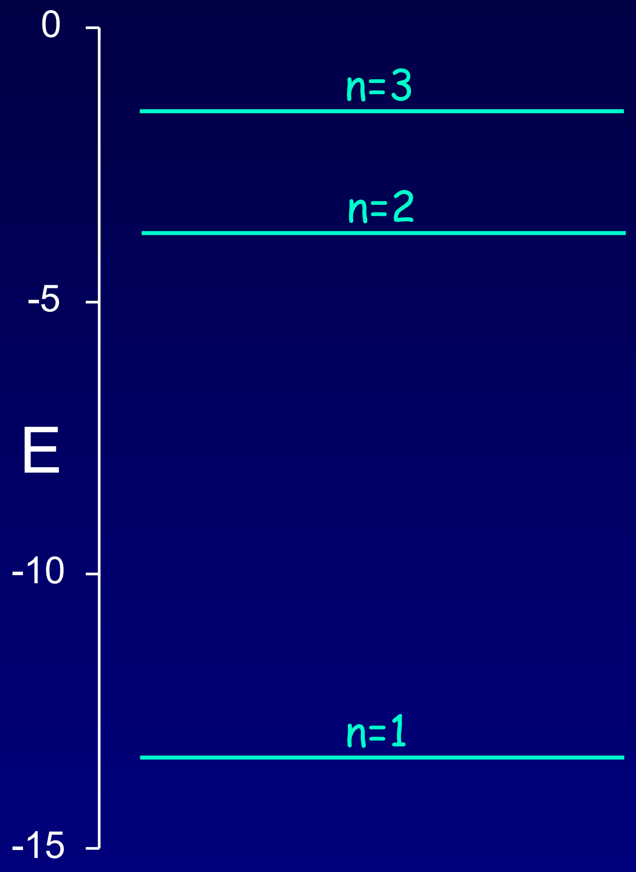
Energy depends only on n

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

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

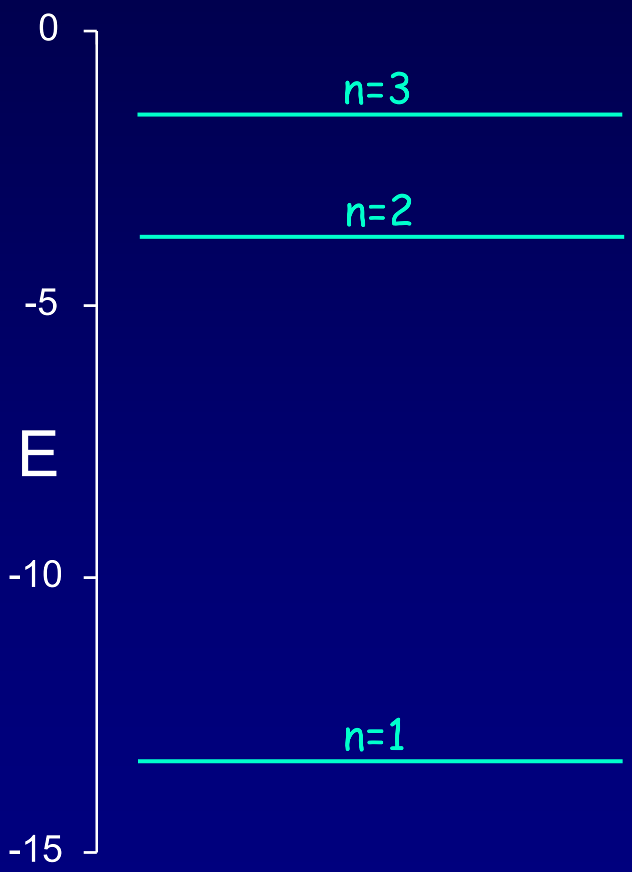
$l = 0, 1, ..., n-1$

For a given l, there are $2l + 1$ 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)

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

$E = -13.6\ \text{eV}/n^2$, 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.

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

hc = 1240 eV·nm

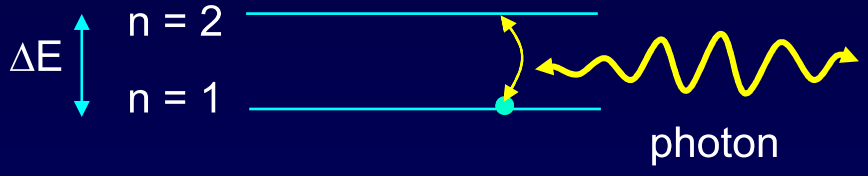
$\left.\begin{array}{l}\lambda_{21} = 122\ \text{nm}\\ \lambda_{31} = 102\ \text{nm}\end{array}\right\}$ Two wavelengths are in the ultraviolet.

λ_{32} = 653 nm

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

Optical Transitions between Atomic Levels

Consider the n = 1 and 2 levels of hydrogen:



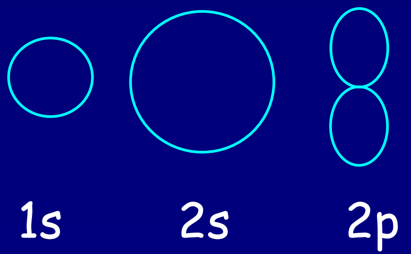
$$f = \frac{\Delta E}{h} = \frac{c}{\lambda}$$

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

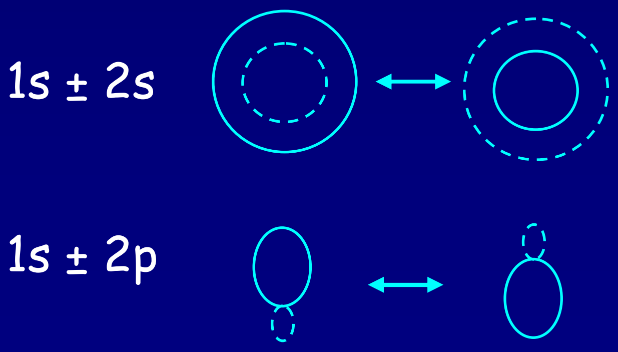
The atom can make transitions by emitting (n: 2→1) or absorbing (n: 1→2) a photon. In general, the time-dependent solution of the SEQ in the time-dependent EM field shows the wave function oscillating between the two eigenstates of the energy (that is, they were eigenstates before the field showed up!).

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

Stationary States:



Superpositions:



No electric-dipole moment

Forbidden transition
Δ*l* = 0

Oscillating electric-dipole couples to photons

Allowed transition
Δ*l* = ±1

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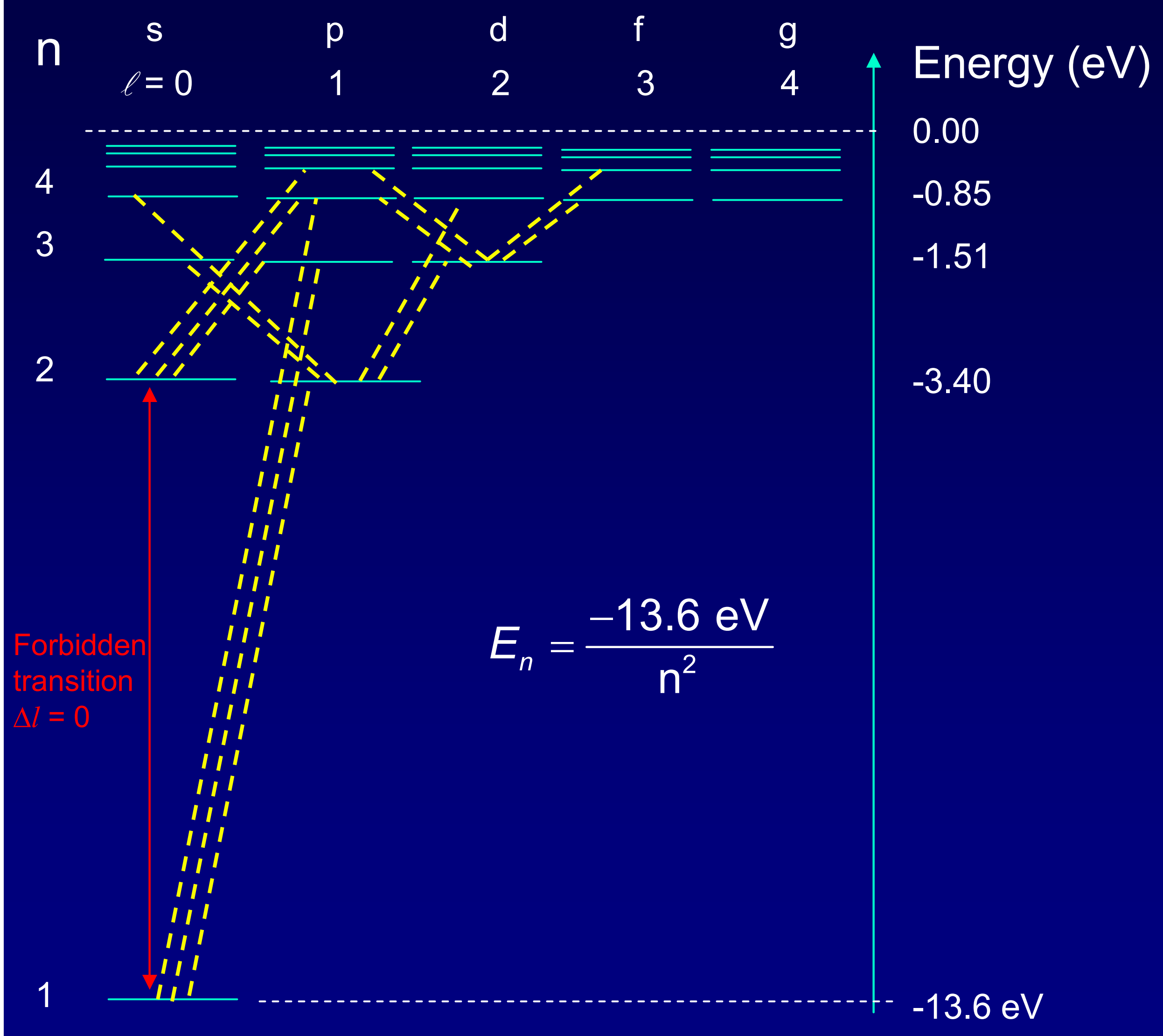
Each photon carries 1 ħ of angular momentum.

Allowed Transitions for H

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



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.

Next Time

Electron ‘spin’ and the Stern-Gerlach experiment

Next Week

Multi-electron Atoms

Covalent bonds

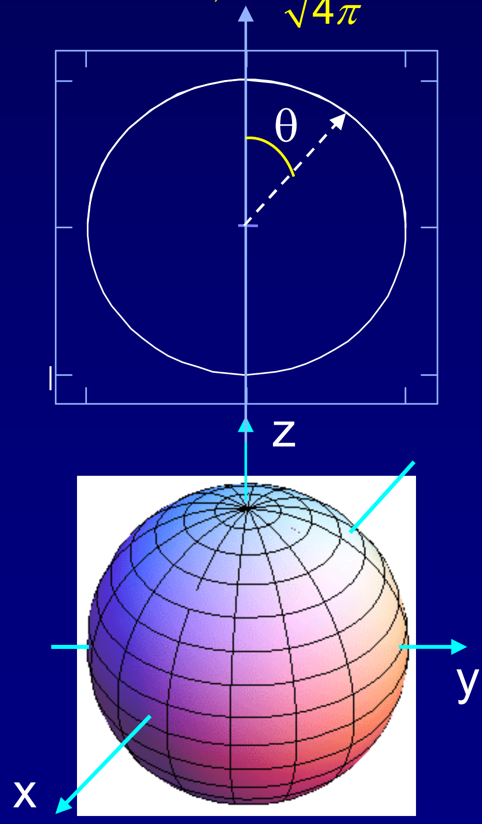
Electron energy bands in Solids

QM in everyday life

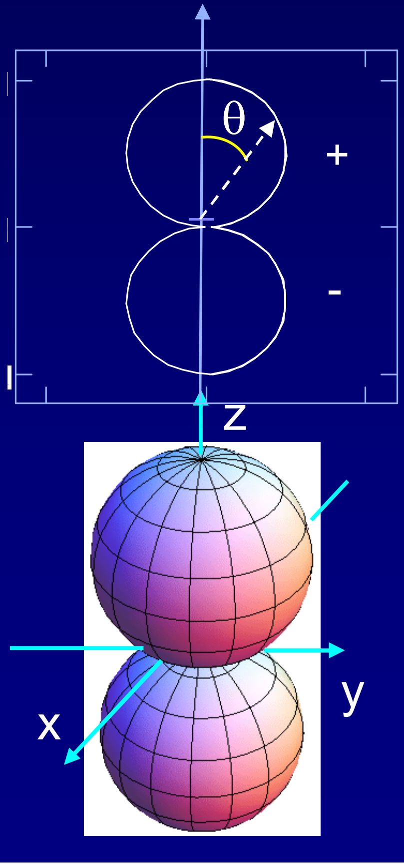
Supplement: Superposition and Chemical Bonding

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”:

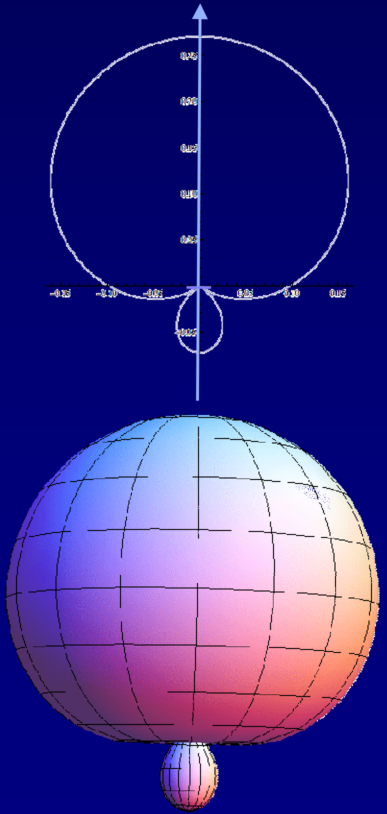
$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$



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



$Y_{00} + Y_{10}$



Supplement: Chemistry Notation

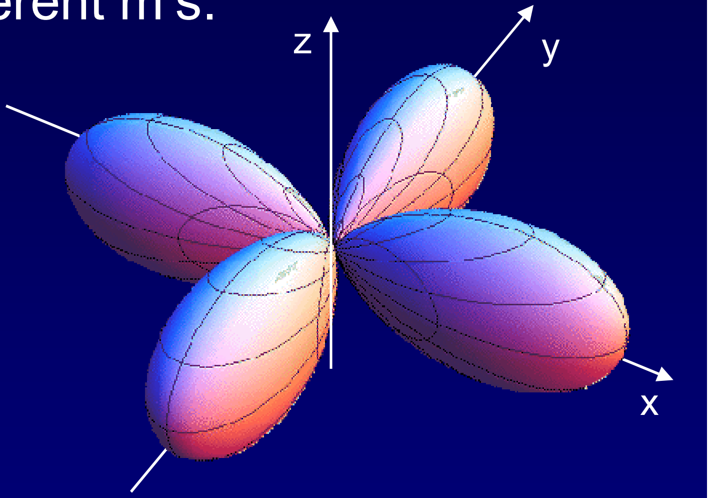
From chemistry you may be familiar with states like $d_{xy,}$ etc.

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.