PHY127 FS2024

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Lecture 7
April 19th, 2024

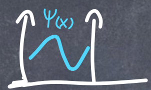
Today: quantum levels of hydrogen atom.
spherical potential in 3-D.

Review from recent lectures:

Particle trapped in $\boxed{\text{1-D box}}$

$$E_n = \frac{n^2 h^2}{8 m L^2}, \quad n = 1, 2, 3, \ldots$$

has a wave function like a standing wave

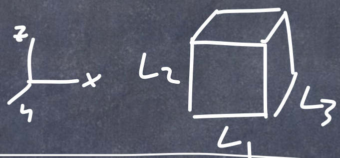


$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } n = 1, 2, 3, \ldots$$

Particle trapped in $\boxed{\text{3-D box}}$:

$$E_{n_1, n_2, n_3} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)$$

for $n_1 = 1, 2, \ldots$
$n_2 = 1, 2, \ldots$
$n_3 = 1, 2, \ldots$



$$\boxed{\psi(x,y,z) = A\,(\sin k_1 x)(\sin k_2 y)(\sin k_3 z)}$$

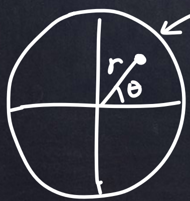
$$k_1 = \frac{n_1 \pi}{L_1}, \quad k_2 = \frac{n_2 \pi}{L_2}, \quad k_3 = \frac{n_3 \pi}{L_3}$$

Standing waves on a $\boxed{\text{2-D drum}}$

solutions to 2D circle: Bessel Functions

$$\psi(r, \theta) = \psi(r)\,\psi(\theta)$$

2 "quantum" numbers
$m = 0, 1, 2, \ldots$
$n = 0, 1, 2, \ldots$



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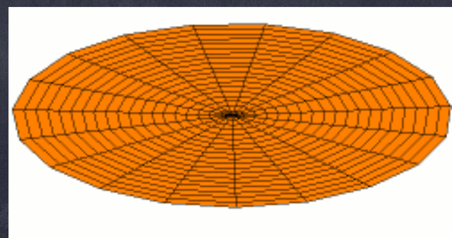
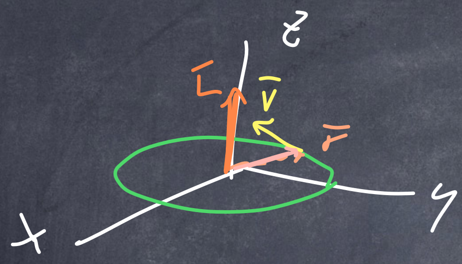


Angular momentum review

(see script 1)



A particle moving in a circle in the x-y plane with a velocity $\bar{v}$. Its speed $|\bar{v}|$ is constant.

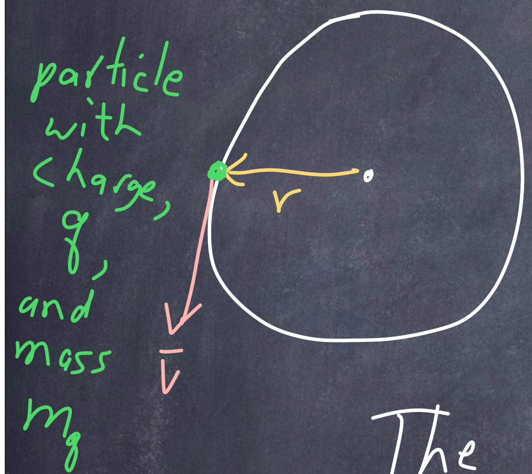
The angular momentum $\bar{L} = \bar{r} \times \bar{p} = \bar{r} \times (m\bar{v})$

we can use the right-hand rule to get $\bar{L}$.
(In our example, $\bar{L}$ points in z direction)

If the particle has an electric charge, we know that a moving electric charge generates a magnetic field. An electric charge moving in a circle generates a magnetic moment. The magnetic moment vector $\bar{\mu}$ points in the same direction as the angular momentum $\bar{L}$ (if charge is +)

The magnetic moment μ is the product of the area, A, of the circle and the electric current, I.

$$\mu = IA$$



q : charge

m_q : mass

$\bar{V}$: velocity

$\bar{r}$: radius

$$I = \frac{\text{charge}}{\text{time}} = \frac{q}{t}$$

The angular momentum is $\boxed{L = m_q V r}$ ①

$\bar{a} \times \bar{b} = |\bar{a}||\bar{b}| \sin\theta$
Here $\theta = 90°$,
So $\bar{a} \times \bar{b} = ab$

The magnetic moment $\mu = IA = I(\pi r^2)$

The current is $I = \dfrac{q}{T}$ where T is the time it takes the particle to make a circle.

$$\text{velocity} = \frac{\text{distance}}{\text{time}} = \frac{2\pi r}{T} \quad \text{so} \quad T = \frac{2\pi r}{v}$$

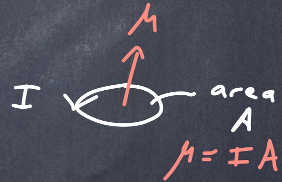
so the current is $$I = \frac{q}{t} = \frac{qv}{2\pi r}$$

Then the magnetic moment is

$$\mu = IA = \frac{qv}{2\pi r}\cdot \pi r^2 = \frac{1}{2} q v r$$

using ① we get

$$\boxed{\bar{\mu} = \frac{q}{2m_q}\bar{L}} \quad ②$$



This is the magnetic moment of a charge particle depends on angular momentum, charge, & its mass.

It is conventional to write ② as

$$\bar{\mu} = \frac{q\hbar}{2m_q}\left(\frac{\bar{L}}{\hbar}\right)$$

For an electron, $m_q = m_e$ and $q = -e$

so $$\bar{\mu} = \frac{-e\hbar}{2m_e}\frac{\bar{L}}{\hbar}$$

we define a constant $$\mu_B = \frac{e\hbar}{2m_e} = 9.27\text{E}{-24}\ A\cdot m^2$$

μ_B: Bohr magneton

Then the magnetic moment of an atom is

$$\boxed{\bar{\mu} = -\mu_B \frac{\bar{L}}{\hbar}} \quad ⓐ$$

(Negative because electrons are (−))

Last time: Hydrogen atom

$$\boxed{\epsilon_0 = \frac{k^2 e^4 m}{2\hbar^2} \approx 13.6 \text{ eV}}$$

ground state energy constant

$$\boxed{\epsilon_n = \frac{-Z^2}{n^2}\epsilon_0}$$

These are the allowed energy levels of the hydrogen atom (for $Z=1$)
$n = 1, 2, 3, \ldots$

Negative because electrons are bound to atom.

The lowest energy level is $n=1 \Rightarrow -13.6$ eV for hydrogen.

We consider an electron stuck in an atom.
The atom is 3-D. The potential is

$$U = \frac{-kZe^2}{r}$$

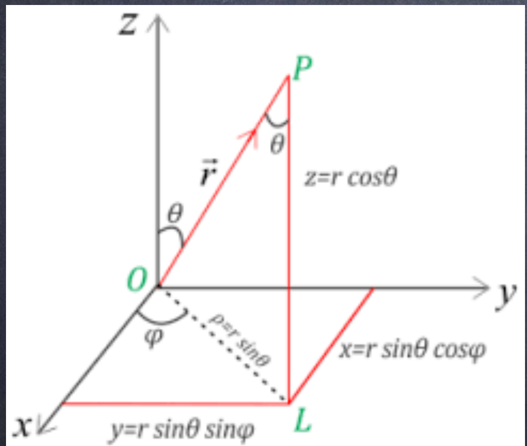
This is a spherical potential

Schroedinger wave equation in 3-D: ①

$$\boxed{\frac{-\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+U\Psi=E\Psi}$$

$$\Psi=\Psi_{(x,y,z)}=\Psi_{(x)}\,\Psi_{(y)}\,\Psi_{(z)}$$

But U is a spherical potential. We need to write ① in spherical coordinates (r,θ,ϕ)



$$x=r\sin\theta\cos\phi$$
$$y=r\sin\theta\sin\phi$$
$$z=r\cos\theta$$

In spherical coordinates, the Schroedinger wave equation becomes:

$$\frac{-\hbar^2}{2m}\left[\frac{\partial}{\partial r}r^2\frac{\partial\Psi}{\partial r}-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right]+U\Psi=E\Psi$$

Looks complicated, but like the particle in a 3-D box, we get solutions that factorize

$$\Psi(r,\theta,\phi) = \Psi_r(r)\,\Psi_\theta(\theta)\,\Psi_\phi(\phi)$$

As in the case of the 3-D box, we will get 3 quantum numbers, but they are interdependent.

$$n = 1, 2, 3, \ldots$$

$$\ell = 0, 1, 2, \ldots, n-1$$

$$m = -\ell, -\ell+1, \ldots, +\ell$$

m has $2\ell+1$ options

So n is an integer and the possible values of ℓ and m depend on n.

If $n=1$, then the allowed quantum numbers are:

$$n=1,\ \ell=0,\ m=0$$

If $n=2$: $\left[\begin{array}{l} n=2,\ \ell=0,\ m=0 \\ n=2,\ \ell=1,\ m=-1 \\ n=2,\ \ell=1,\ m=0 \\ n=2,\ \ell=1,\ m=+1 \end{array}\right.$

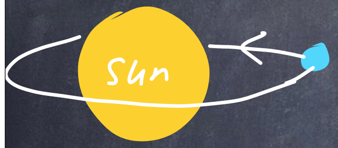
If $n=3$: $\left[\begin{array}{l} \ell=0 \Rightarrow m=0 \\ \ell=1 \Rightarrow m=-1, 0, \text{ or } 1 \\ \ell=2 \Rightarrow m=-2,-1,0,1,2 \end{array}\right.$

n: principle quantum number, comes from $\psi_r(r)$, wave function that describes the amplitude as a function of the distance r of the electron moving in a circle: $E_n = \frac{-Z^2}{n^2} E_0 \quad n=1,2,3$

The quantum numbers l + m have to do with angular momentum of the electron, and $\Psi_\phi(\phi)$, $\Psi_\theta(\theta)$ have to do with the angular dependence on the probability of finding the electron.

l: orbital quantum number

analogy:



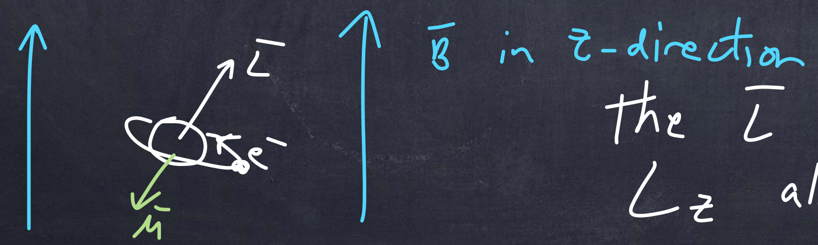
The orbital angular momentum of the electron is quantized, it is

$$L = \sqrt{l(l+1)}\,\hbar$$

From ⓐ, we see that $\mu = -\mu_B \frac{\bar{L}}{\hbar}$,

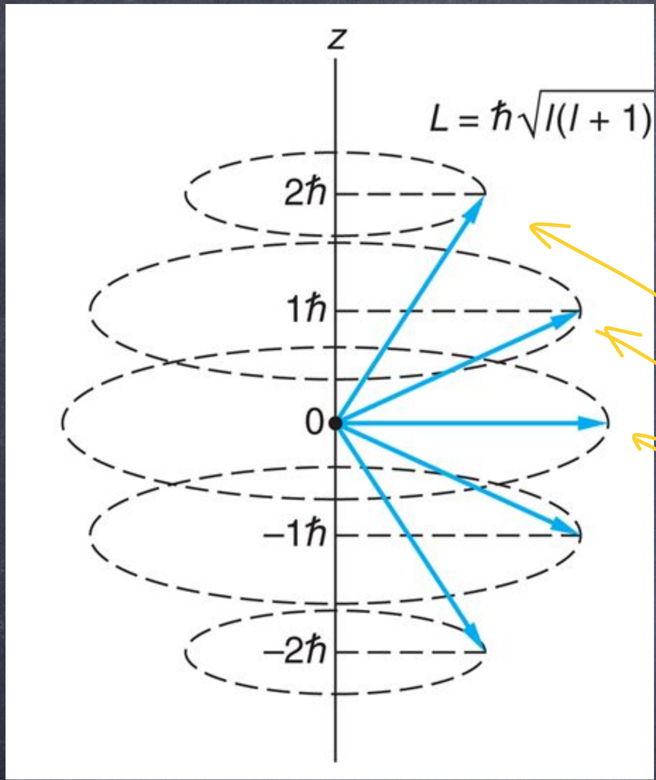
so $\mu = -\sqrt{l(l+1)}\,\mu_B$ is also quantized.

If we put the atom in a magnetic field,



the $\bar{L}$ vector has a z-component L_z along the $\bar{B}$-field direction.

$\overline{B}$



L_z can also take on only values from the integer ℓ.

$$L_z = m\hbar$$

(sketch is for the case of $\ell = 2$

$$L = \hbar\sqrt{\ell(\ell+1)} = \hbar\sqrt{6}$$

$L_z = 2\hbar$

$L_z = 1\hbar$

$L_z = 0$

$L_z = -1\hbar$

$L_z = -2\hbar$

m: is known as the magnetic quantum number

$$\mu_z = \frac{\mu_B L_z}{\hbar} = -m\mu_B$$

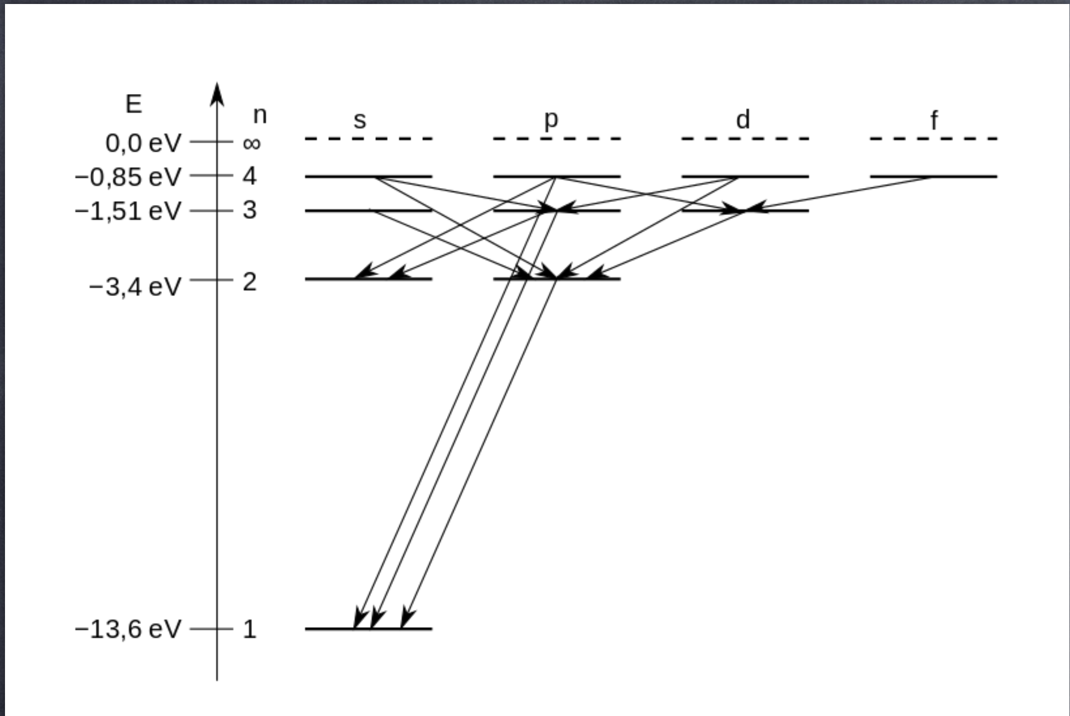
Note: $E_n = \frac{-Z^2 E_0}{n^2}$ $n = 1, 2, 3, \ldots$

The fact that the energy doesn't depend on ℓ is only true for the hydrogen atom.

For more complicated atoms with multiple electrons, E can depend on ℓ.

The energy doesn't depend on m unless the atom is in a magnetic field.

Transitions of the electron follow certain transition rules.



$l = 0 \Rightarrow$ s level

$l = 1 \Rightarrow$ p level

$l = 2 \Rightarrow$ d level

$l = 3 \Rightarrow$ f level

Transitions of the electron obey selection rules:

$\Delta l = \pm 1$

$\Delta m = 0, \pm 1$

When we absorb or emit a photon, it has an angular momentum of $\pm \hbar$.

These photons have an energy released or absorbed that is $E = h\nu = \frac{hc}{\lambda}$

The energy transitions $E_f - E_i = h\nu = \frac{hc}{\lambda}$

where is the electron in our 3-D atom?
(sperical electric potential)

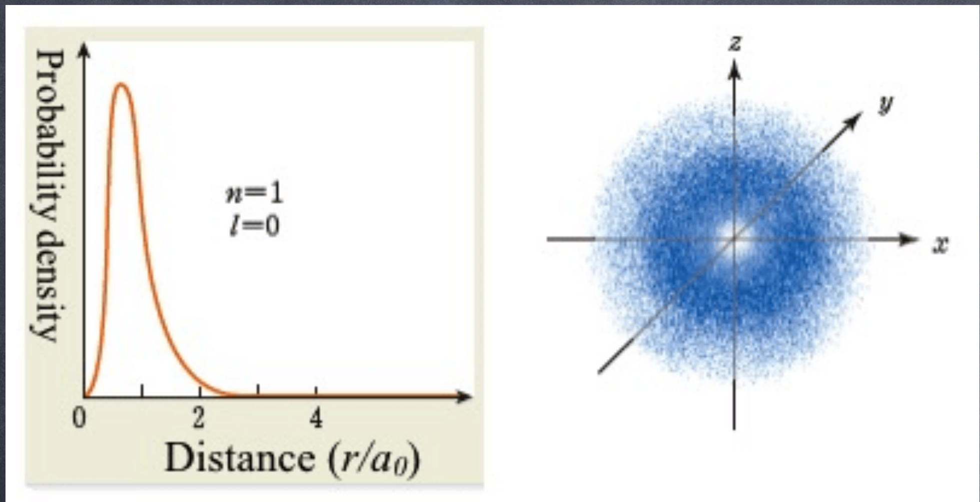
probability of the electron to be at a distance r $= \Psi^2(r)$

$$\Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$\begin{pmatrix} n=1 \\ \ell=0 \\ m=0 \end{pmatrix}$

a_0: radius of the atom

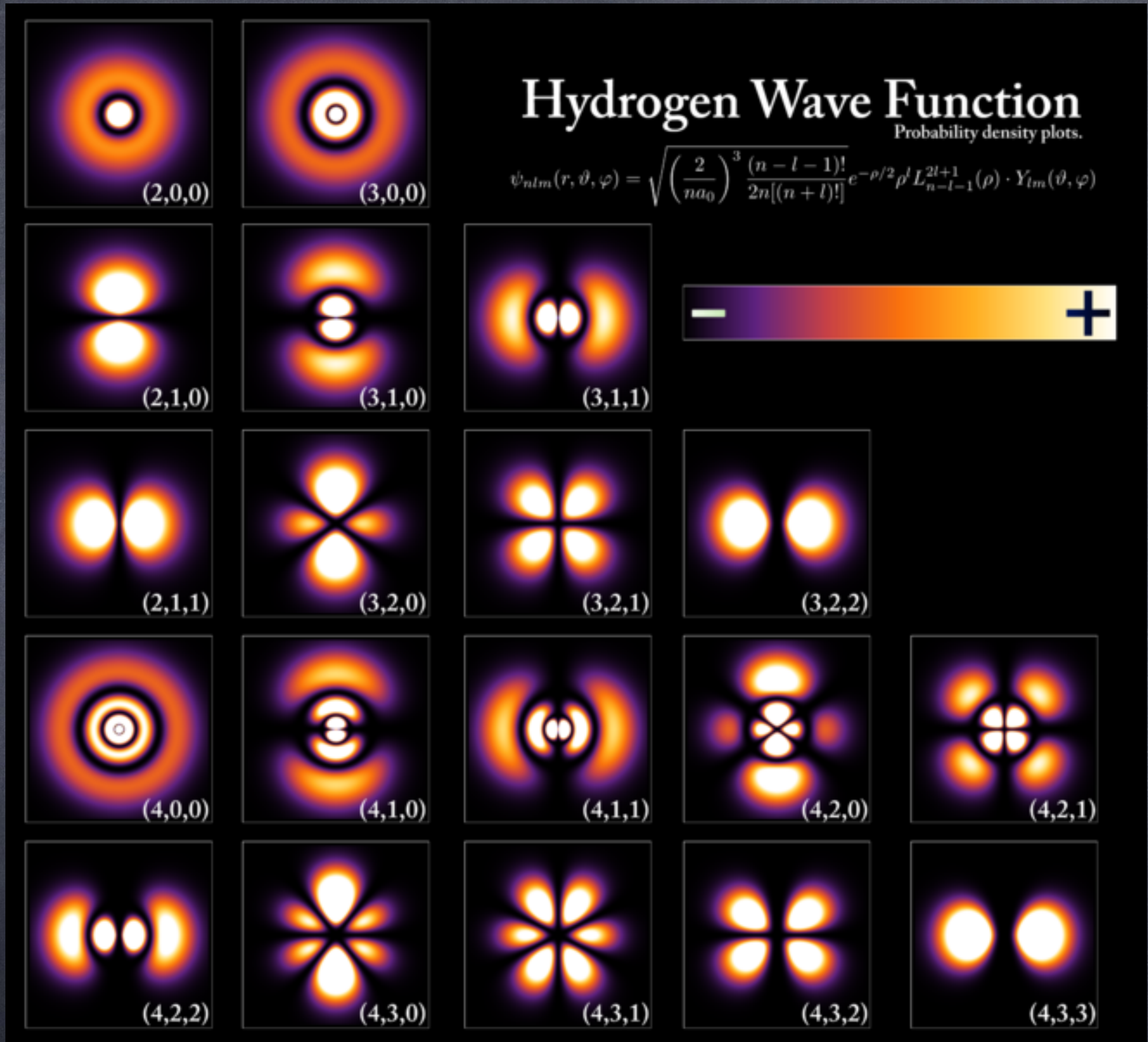
$\Psi^2(r)$



The probability of finding the electron depends only on r for $n=1, \ell=0, m=0$

Here, we see the quantized electron standing waves in a hydrogen atom that come from the 3-D Coulomb potential and the 3 quantum numbers: n, l, m

$\psi^2(r,\theta,\phi)$ depends on n, l, m and probability depends on r, θ, φ



probability of finding the electron is given by the brightness

Experiment : Chladni plate
2D

interesting frequencies

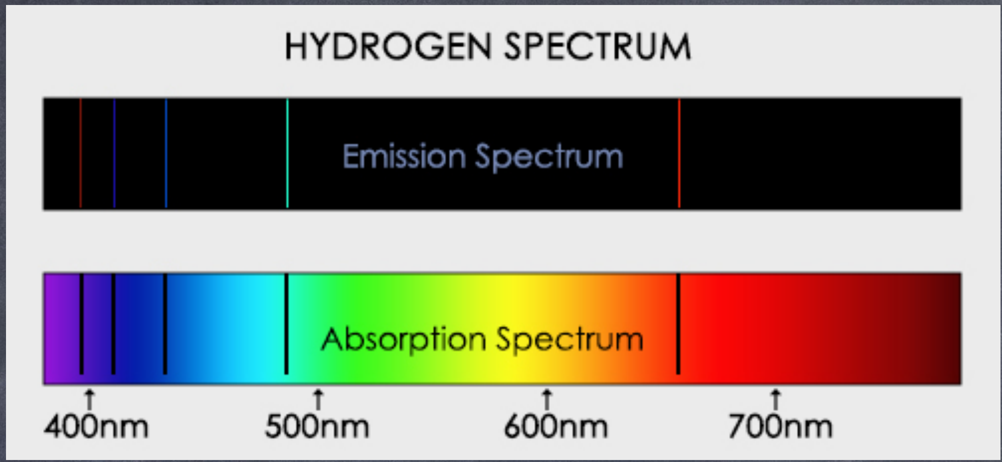
150.0 Hz
206.0
313.6
482.3
815.0
979.9
3428
4978

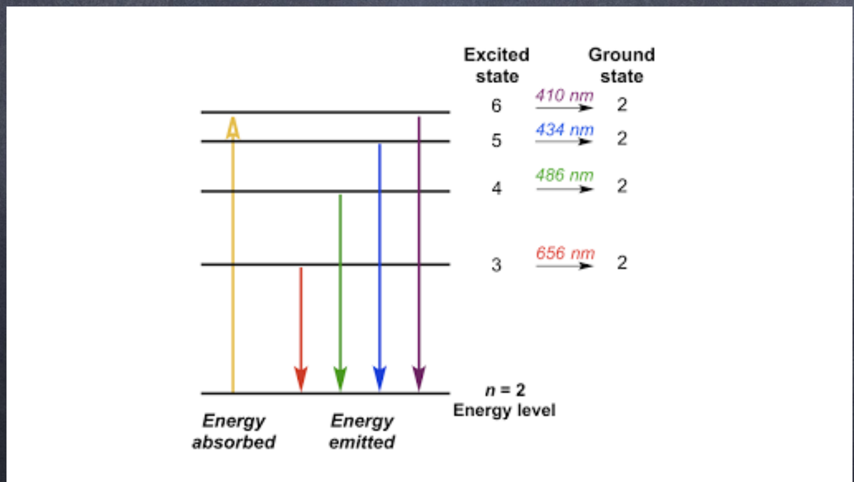
rich pattern of standing waves
dependent on frequency

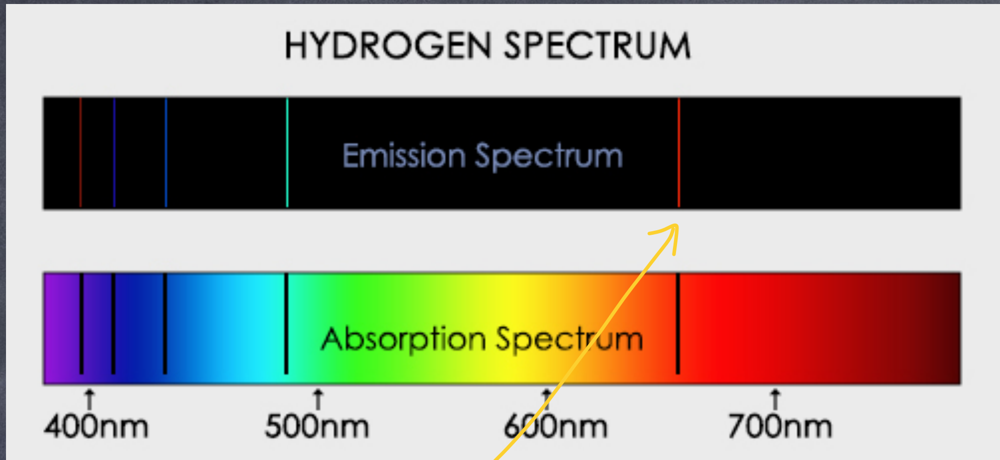
These are 2-D
standing waves
described by
~~the~~ two
"quantum number"

Higher frequency →
higher energy
of the resonance

Balmer series (transitions to $n=2$)

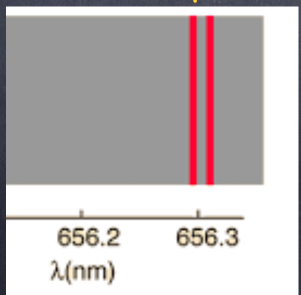






Actually, there are 2 lines here

$\lambda_1\ \lambda_2$



Difference between two lines is:

$\Delta\lambda \sim 0.016$ nm , $\lambda_{avg} \sim 656.3$ nm

$$\Delta E = hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) = hc\,\frac{\lambda_2 - \lambda_1}{\lambda_1 \lambda_2} \sim hc\,\frac{\Delta\lambda}{(\lambda_{avg})^2} = 4.6E{-5}\ eV$$

$\Rightarrow \Delta E = 4.6\ E{-5}\ eV$

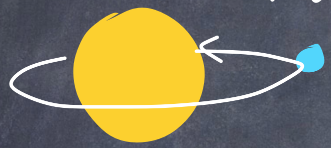
energy difference between states with different electron spin

h: 4.1357 E-15 eV.s

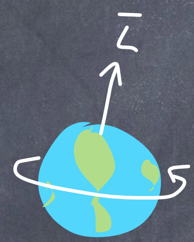
c: 2.998 E8 $\frac{m}{s}$

The reason for the 2 lines is something called spin. Spin is intrinsic angular momentum.

The earth here has orbital angular momentum.

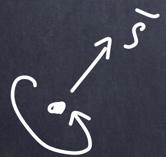


Analogy,



The earth also has spin.

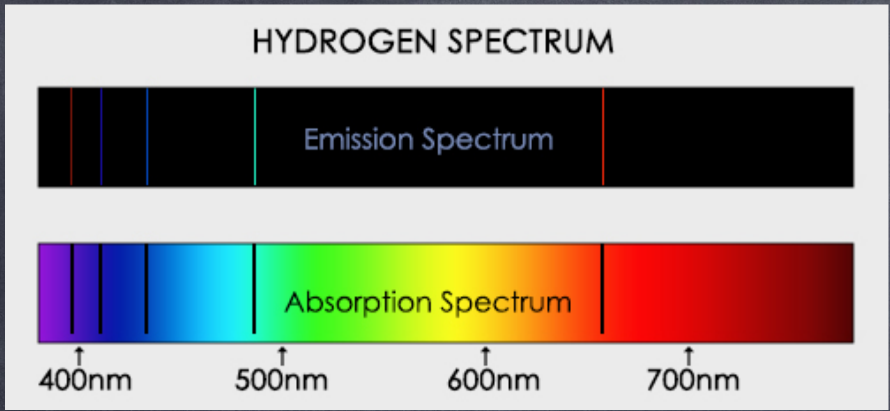
Similarly, the electron has both orbital angular momentum, and spin.

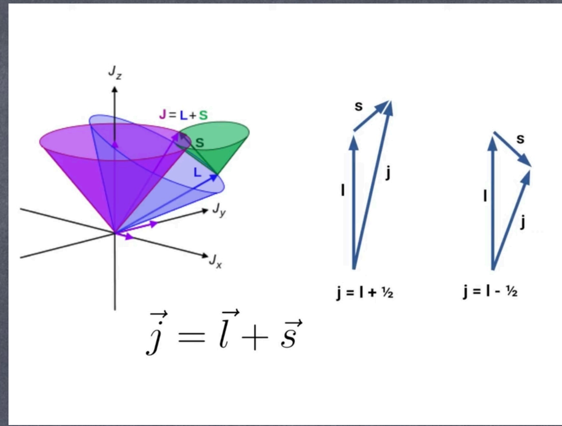


$S = \frac{1}{2}\hbar$ it can have either $-\frac{1}{2}\hbar$ or $+\frac{1}{2}\hbar$

In addition to n, l, m, the atom has an additional quantum number to describe the electron spin $m_s = \frac{1}{2}$ or $\frac{-1}{2}$

"Fine structure" is the 4th quantum number, m_s.



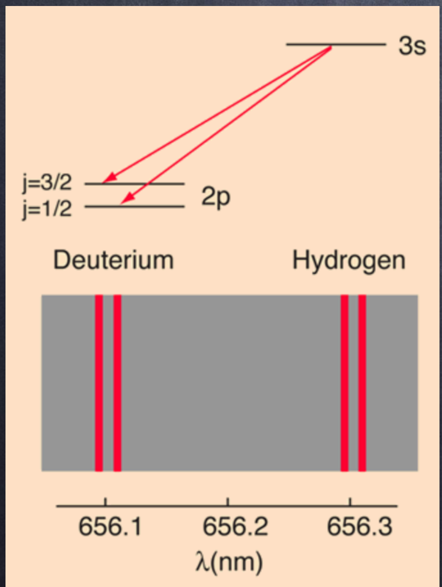


electron

↑ ↓

$+\frac{1}{2}\hbar$ $-\frac{1}{2}\hbar$

$\bar{J}$ is the sum of $\bar{L}$ plus the $\bar{S}$



The two lines correspond to

$\bar{L} + \frac{1}{2}\hbar$

or

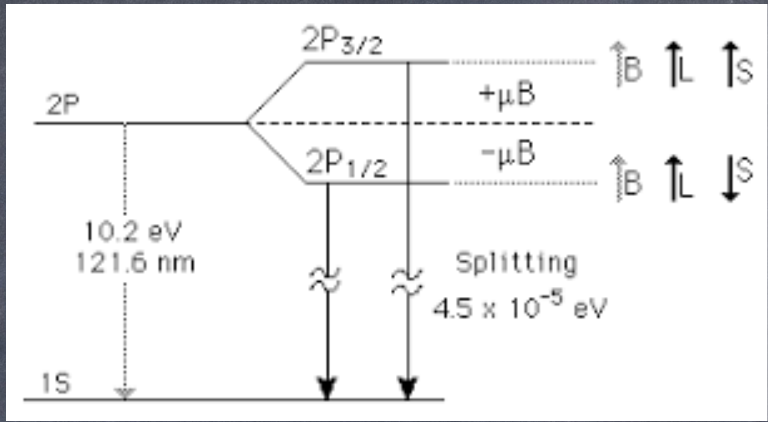
$\bar{L} - \frac{1}{2}\hbar$

transition from 3s: $n=3, \ell=0$

to $2p_{3/2}$: $n=2, \ell=1$, e is spin up

or $2p_{1/2}$; $n=2, \ell=1$, e is spin down we could further observe the effect of spin by putting the atom in a magnetic field.

Calculate μB for $B = 1T$
$\mu = 9.27 E-24 \; A \cdot m^2$
$\mu B = 9.27 E-24 \; J$
Since $1J = 6.242E-18 \, eV$,
$\mu B = 6E-5 eV$



This changes the potential energy of the electron by $+\mu B$ or $-\mu B$

This would then change the energy (and frequency) of the photons that are emitted.

In this example, if there is no magnetic field, the electron transition from $2p \to 1s$ corresponds to 10.2 eV.
But in a B-field, the 2p line is split into $2p_{3/2}$, where the electron spin is in the same direction as $\bar{B}$, or $2p_{1/2}$, where the electron spin is opposite $\bar{B}$.
The transition energy is then either $\begin{cases} \epsilon_{2p_{3/2} \to 1s} = 10.2eV + \mu B \\ \text{or} \\ \epsilon_{2p_{1/2} \to 1s} = 10.2eV - \mu B \end{cases}$

The difference $\Delta \epsilon$ is small, about 10^{-5} eV depending on $\bar{B}$