What's the AVERAGE distance?

$$\langle r \rangle = \int_0^\infty r\, P_{10}(r)\, dr$$

$$= \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0}\, dr$$

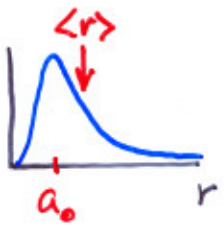
like a class of integrals:

$$\int_0^\infty z^n e^{-z}\, dz = n!$$

change variables: $z = 2r/a_0$

$$\langle r \rangle = \frac{a_0}{4}(3!)$$

$$\langle r \rangle = 3/2\, a_0$$



Where is the electron? can't ask that, as you know.

The likelihood of finding the electron between some $r = a$ and $r = b$ will be

$$P_{10}(ab) = \int_a^b P_{10}(r)\, dr$$

So... what is the likelihood that the electron spends time OUTSIDE of the Bohr orbit?

(still the 1s state of Hydrogen)

$$P(r>a_0) = \int_{a_0}^{\infty} P_{10}(r)\,dr$$

$$= \frac{4}{a_0^3}\int_{a_0}^{\infty} r^2 e^{-2r/a_0}\,dr$$

another class of integrals.

$$\int z^2 e^{-z}\,dz = -\tfrac{1}{2}(z^2+2z+2)e^{-z}$$

let $z = 2r/a_0$ again

$$P(r>a_0) = \tfrac{1}{2}\int_2^{\infty} z^2 e^{-z}\,dz = 5e^{-2} \sim 0.68$$

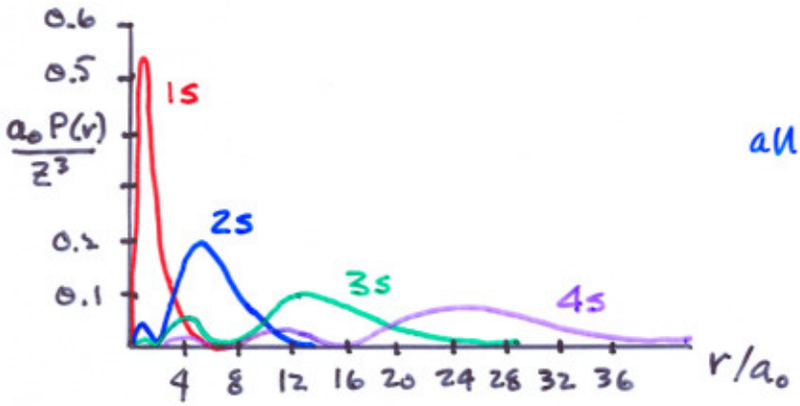
$\sim 2/3$ of the time the electron wanders beyond the Bohr orbit.

Excited states...

say 2s Again Y_{00} is relevant, so again, spherically symmetric probability distribution

$$R_{20}(r) = \frac{1}{\sqrt{(2a_0)^3}}\left(2 - \frac{r}{a_0}\right) e^{-r/a_0 2}$$ (hydrogen)

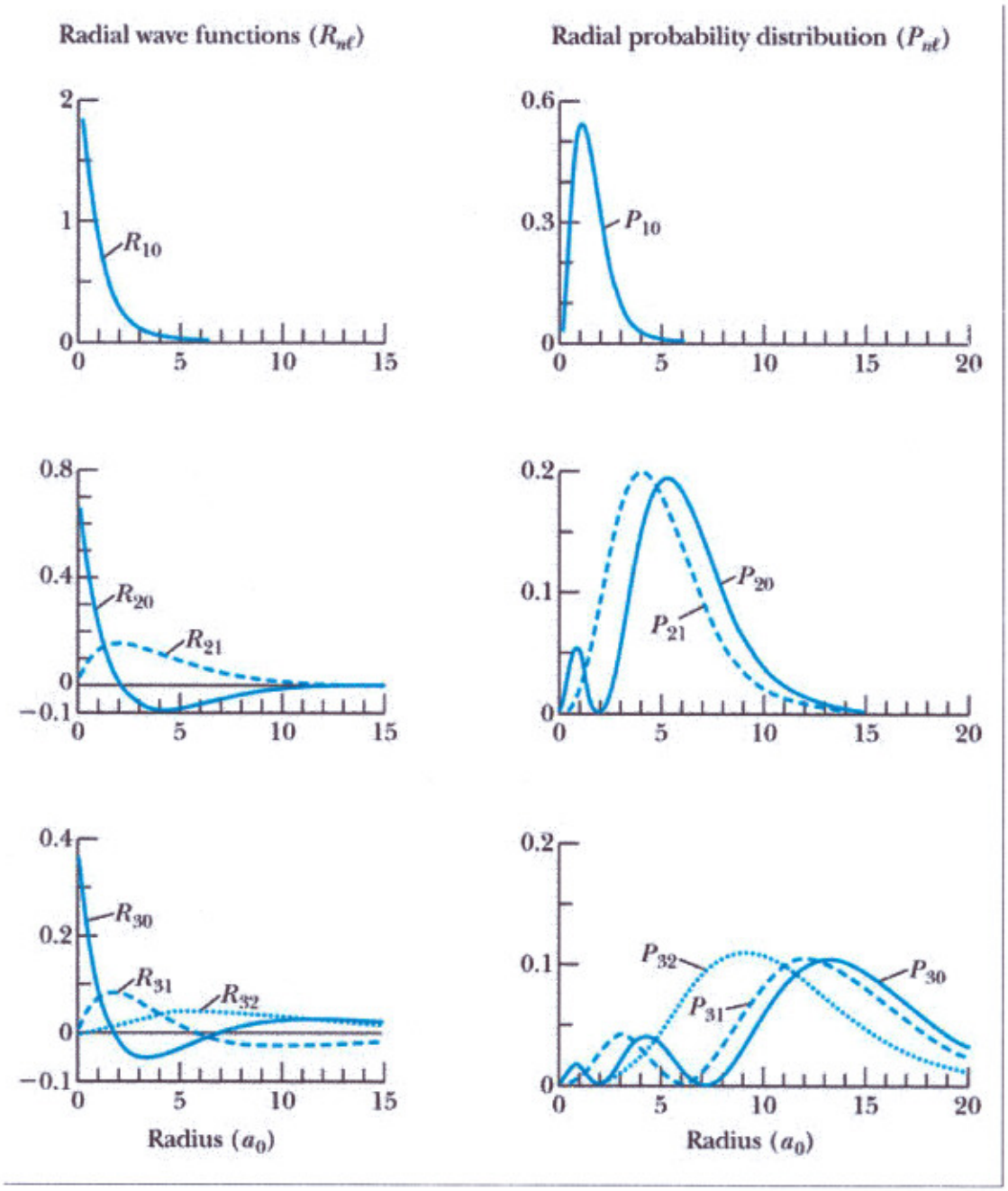
strange density peaks



all spherically symmetric

notice that at any radius -- especially around $1a_0$, there is a non-negligible probability of electrons from excited states being where the 1s electrons might likely be

But... obviously, the higher the principle quantum number, the farther away from the nucleus is the most likely.


Radial wave functions ($R_{n\ell}$)
Radial probability distribution ($P_{n\ell}$)
R_{10}
P_{10}
R_{20}
R_{21}
P_{20}
P_{21}
R_{30}
R_{31}
R_{32}
P_{32}
P_{31}
P_{30}
Radius (a_0)
Radius (a_0)

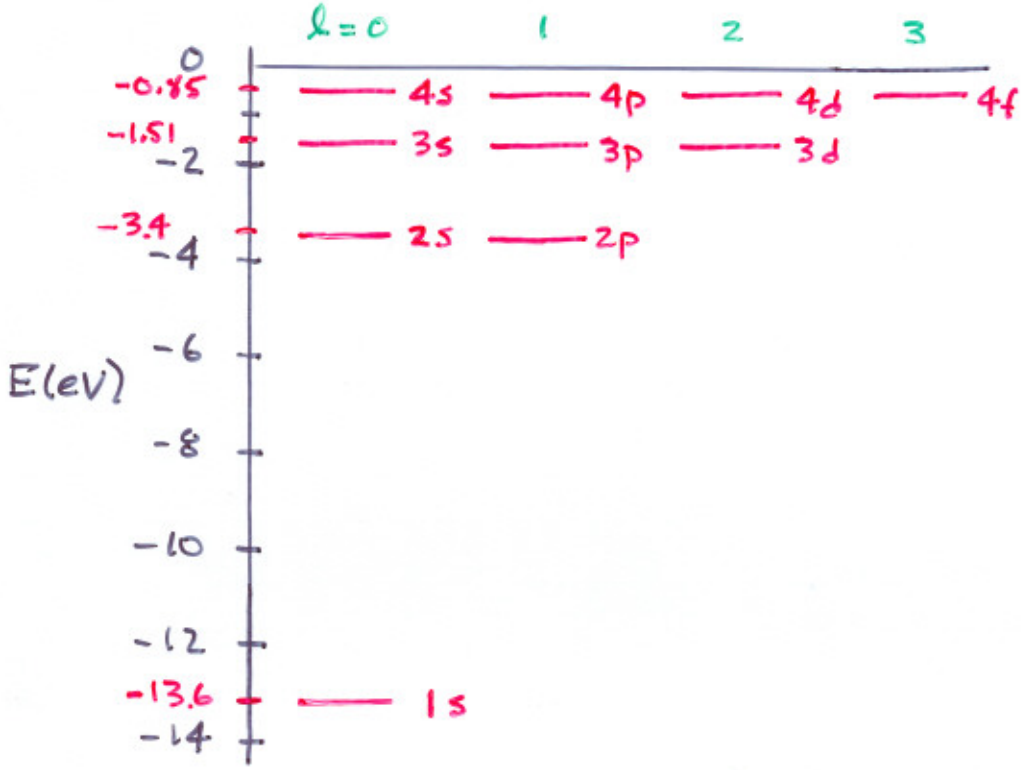
Energy.

Remember, E depends only on n.

$$E_n = -\frac{E_0}{n^2} \qquad E_0 = \frac{\hbar^2}{2Ma_0^2}$$

But, each n can result in many values of ℓ.
↳ and m_ℓ

→ substantial Degeneracy in Hydrogen



* states

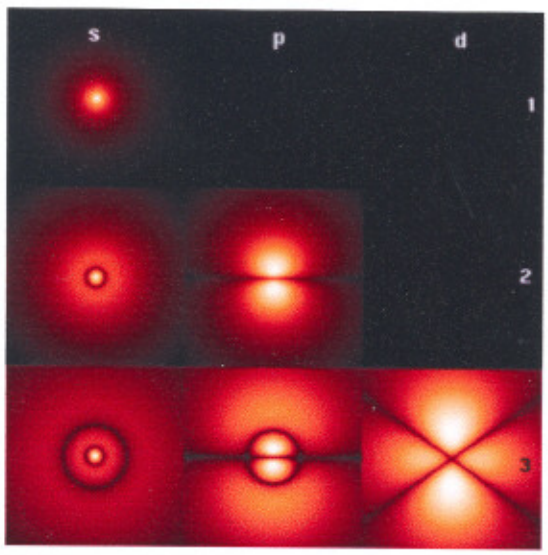
$1 + 3 + 5 + 7 = 16$

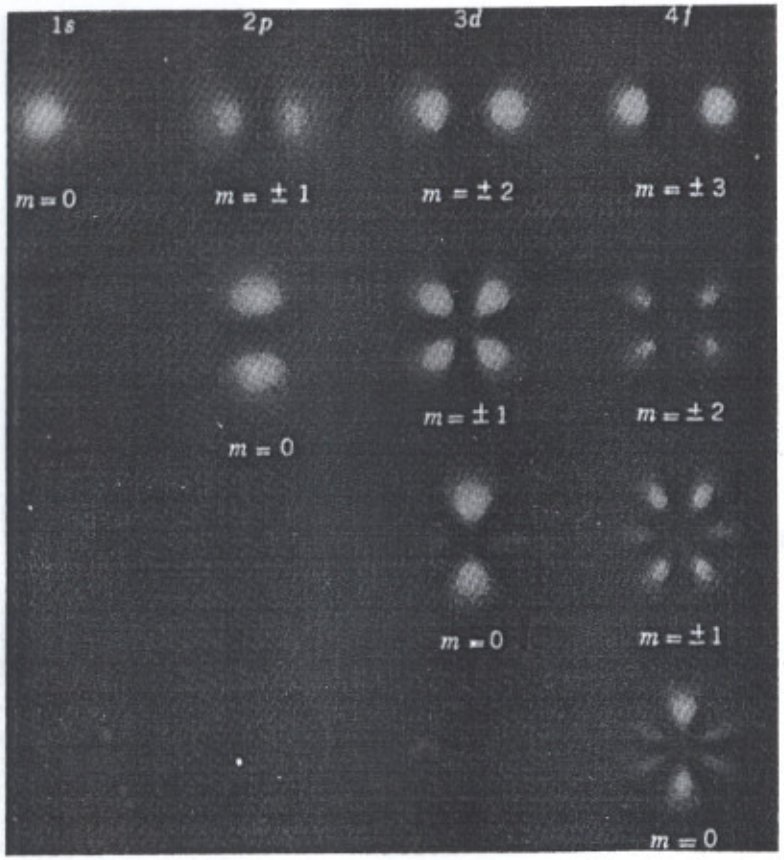
$1 + 3 + 5 = 9$

$1 + 3 = 4$

1

degeneracies = n^2


s
p
d
1
2
3



e 7-7 Photographic representation of the electron probability density distribution eral energy eigenstates. These may be regarded as sectional views of the distributions ontaining the polar axis, which is vertical and in the plane of the paper. The scale varies to figure. (From *Principles of Modern Physics* by R. B. Leighton. Copyright 1959 by ll Book Company. Used with permission of McGraw-Hill Book Company.)

e the energy levels are independent of the quantum numbers ℓ and m, xpress the degeneracy of each level by the sum

$$\sum_{\ell=0}^{n-1}(2\ell+1) = 1 + 3 + 5 + \cdots + 2n - 1 = n^2.$$

$+ 1)$-fold degeneracy of the m-values is characteristic of all spherically ic potentials, while the n-fold degeneracy of the ℓ-values occurs only ential such as the Coulomb potential, which satisfies a specific invari- ıdition.[5] Historical usage has coined the unfortunate phrase "acci- egeneracy" to describe the latter. The reader can anticipate some of lts of later sections by speculating that any alteration of the physical hich destroys the spherical symmetry or the pure Coulombic potential . to the removal of some or all of the degeneracies.

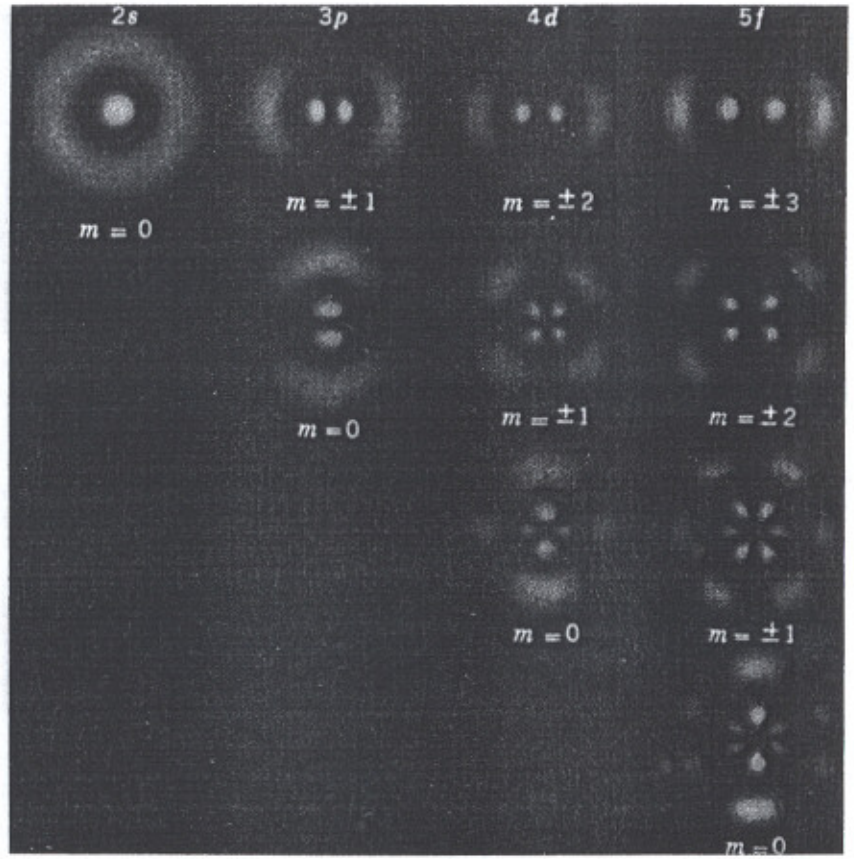


Figure 7-7 *Continued.*

The total hydrogenic wave functions can now be written as

$$\Psi_{n\ell m}(r, \theta, \phi, t) = \psi_{n\ell m}(r, \theta, \phi) \cdot e^{-iE_n t/\hbar} = R_{n\ell}(r) Y_\ell^m(\eta, \phi) e^{-iE_n t/\hbar},$$

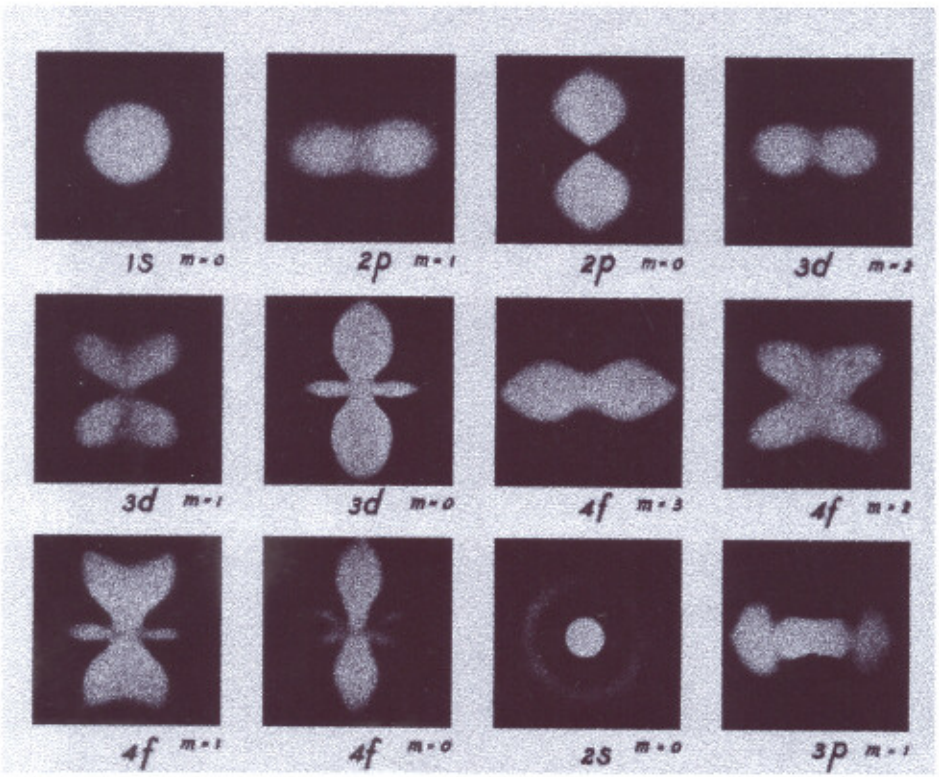
where n can be any integer, ℓ can take on the values $0, 1, 2, \ldots, (n-1)$, and m can have any of the values $\ell, \ell-1, \ldots, 0, -1, \ldots, -\ell$. Although the radial and angular functions have been given above, a few of the normalized spatial, hydrogenic wave functions are tabulated below to facilitate their use in the problems:

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

$$\psi_{2s} = \psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot \left(2 - \frac{Zr}{a_0}\right) \cdot e^{-Zr/2a_0}$$

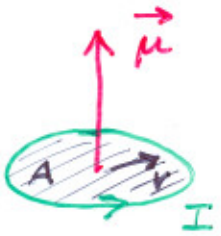
$$\psi_{2p} = \psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot \frac{Zr}{a_0} \cdot e^{-Zr/2a_0} \cos\theta$$

$$\frac{1}{} \left(\frac{Z}{}\right)^{\frac{3}{2}} \frac{Zr}{}$$


1s m=0
2p m=1
2p m=0
3d m=2
3d m=1
3d m=0
4f m=3
4f m=2
4f m=1
4f m=0
2s m=0
3p m=1

Orbiting electrons should actually show magnetic phenomena.

Recall classical E&M...



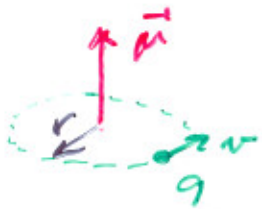
a current loop gives rise to a Magnetic Moment

$|\mu| = IA$ (RH rule gives direction)

Suppose it's a charge going in a circle...

$$I = \frac{dq}{dt} \rightarrow \frac{q}{T}$$

T ← period.



If a circular orbit...

angular momentum $L = mvr$

$$v = \frac{2\pi r}{T} \qquad A = \pi r^2$$

$$L = m\left(\frac{2\pi r}{T}\right) r = 2m\frac{\pi r^2}{T}$$

$$L = 2m\left(\frac{A}{T}\right) \qquad \text{(Kepler's Law)}$$

$$\Rightarrow \quad \frac{A}{T} = \frac{L}{2m}$$

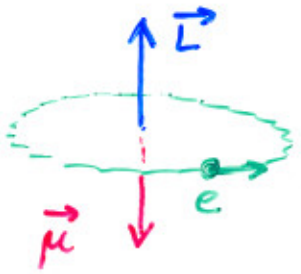
So,

$$\mu = IA = \frac{q}{T} A = \frac{q}{2m} L$$

or

$$\vec{\mu} = \frac{q}{2m} \vec{L}$$

if an electron: $\vec{\mu} = -\frac{e}{2m} \vec{L}$



What about atomic electrons.

Thinking in some strange superposition of classical & quantum mechanical ways (!)...

We just found that some orbits – levels – in Hydrogen have specific angular momenta.

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

which is a vector, but which has a quantized projection onto one axis... we define as z – of

$$L_z = m_\ell \hbar$$

But... what's the z direction?

NO DIRECTIONS ARE PREFERRED

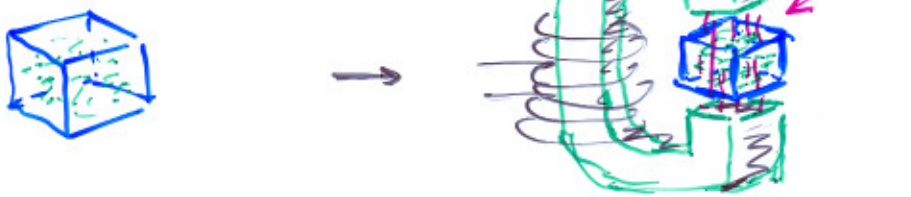
– symmetrical, so the $\vec{L}$'s point randomly

unless

something BREAKS that symmetry

and "picks out" or establishes a PARTICULAR direction in space as special.

An external magnetic field does that!



$\vec{B}$ field

↑

DEFINES A Z AXIS...

An "axis of quantization"

Now those angular momenta...

and through $\mu = \frac{-e}{2m} L$

the atomic magnetic moments... come alive.

$$\mu_3 = \frac{-e}{2m} L_3 = \frac{-e\hbar}{2m} m_\ell$$

$$\mu_z = -\frac{e}{2m}\hbar m_\ell$$

This encompasses a famous quantity..

"Bohr magneton"

$$\mu_B = \frac{e\hbar}{2m} = 9.274\times10^{-24}\ J/T$$

$$\mu_z = -\mu_B m_\ell$$

So, atomic magnetic moments can be thought of as multiples of μ_B.

REMEMBER E & M:

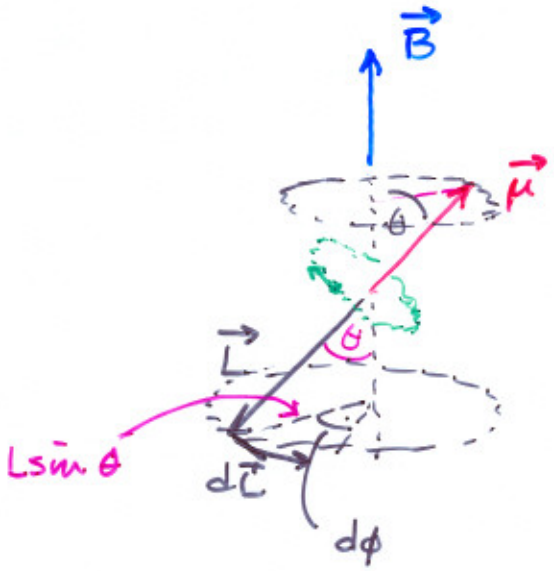
$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

a torque is applied to a magnetic moment by $\vec{B}$. trying to align the moment and $\vec{B}$

But, it doesn't align.. it precesses.. $\mu \propto L$

$$\vec{\tau} = \frac{d\vec{L}}{dt} = \cancel{\mu_B \vec{L} \times \vec{B}} = \frac{q}{2m}\vec{L} \times \vec{B}$$

change in $\vec{L}$ $\perp$ $\vec{L}$ and $\vec{B}$



$d\vec{L} \perp$ plane of $\vec{B}$ and $\vec{L}$

$\Rightarrow$ around the circle

$$|dL| = L\sin\theta\, d\phi$$

$$d\phi = \frac{|dL|}{L\sin\theta} \qquad \left|\frac{dL}{dt}\right| = |\tau|$$

$$d\phi = \frac{|\tau|\,dt}{L\sin\theta}$$

$$d\phi = \frac{q/2m\,(LB\sin\theta)\,dt}{L\sin\theta} = \frac{Bq}{2m}\,dt$$

precession frequency -- called Larmor frequency, ω_L

$$\omega_L = \frac{d\phi}{dt} = \frac{qB}{2m}$$

Since there is a torque through an angular displacement... work is done

$$dW = \tau\, d\theta$$

$$dW = -\mu B \sin\theta\, d\theta$$

(external torque opposes that of B)

$$= d(\mu B \cos\theta)$$

$$dW = d(\vec{\mu} \cdot \vec{B})$$

The work done .. is stored as a potential energy

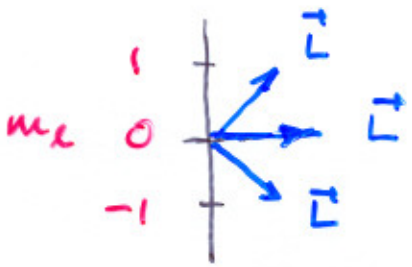
$$dW = -dV$$

So... there is an induced magnetic potential energy:

$$V = -\vec{\mu} \cdot \vec{B}$$

- depends on the external B
- the more aligned .. the less is V

BUT.. μ is quantized according to L_z



for $\ell = 1$ for example

SO, THE MAGNETIC POTENTIAL ENERGY IS QUANTIZED!

So, if we DEFINE the z direction to be along $\vec{B}$...

$$V = \frac{e}{2m} \vec{L} \cdot \vec{B} = \frac{e|B|}{2m} L_z$$

$$V = \mu_B m_\ell B$$

↑ can range over values $-\ell$ to $+\ell$

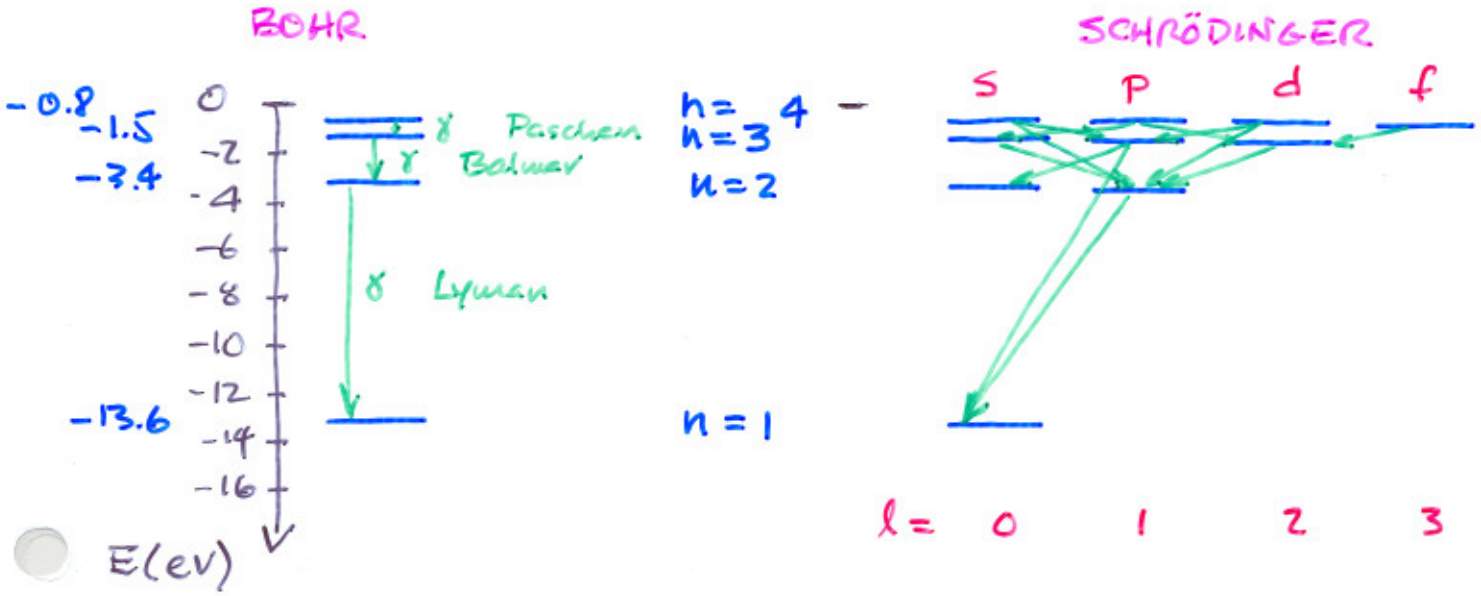
So, when a magnetic field is applied -- the energy levels change

→ that's what Lorentz predicted and Zeeman found.

But. the Schrödinger approach changed even the $B = 0$ situation.

B = 0

Remember the Bohr atom & spectra:



Something comes out of Schrödinger's theory:

- RESTRICTIONS on allowed transitions
- PROBABILITIES -- intensities of emitted light.

* Selection Rule *

$\Delta l = \pm 1$

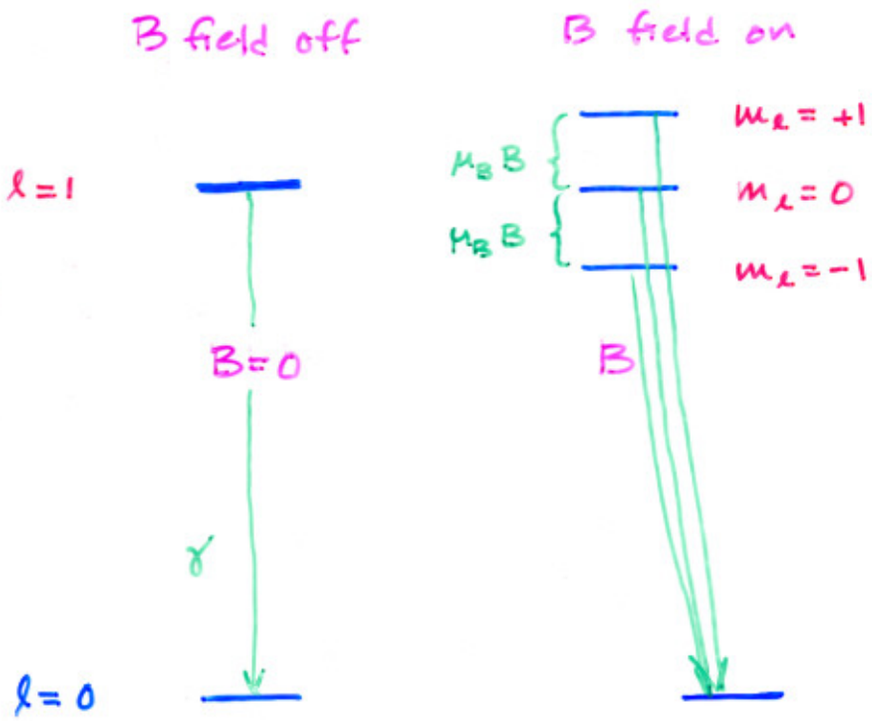
like: $2p \rightarrow 1s$ OKAY

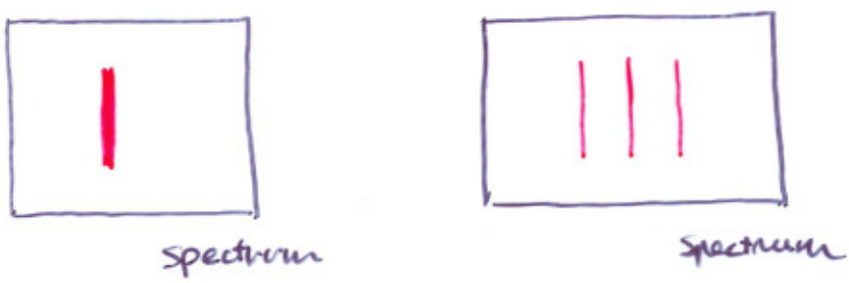
$2s \rightarrow 1s$ forbidden

for γ emission

What about a magnetic field?

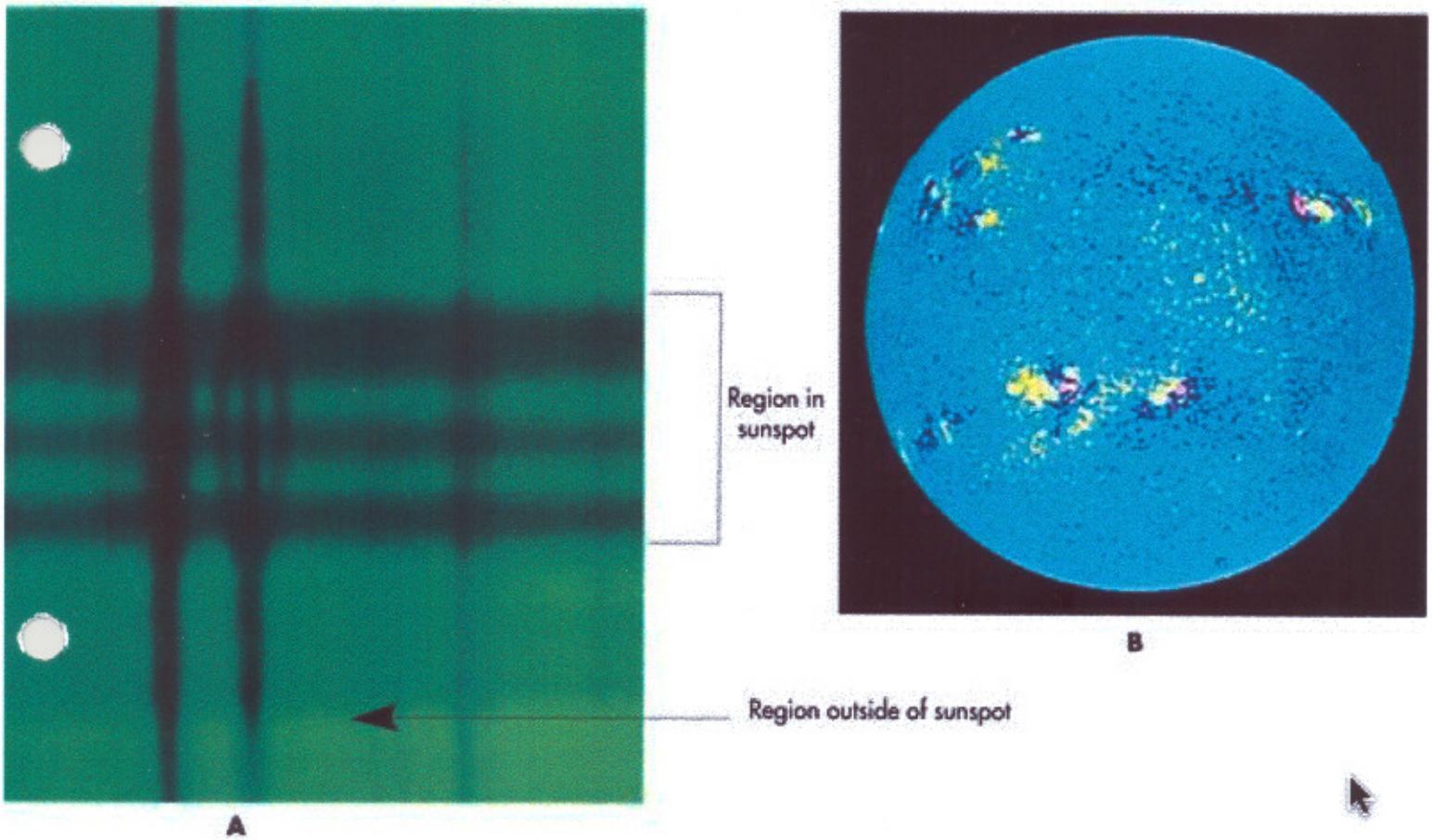
The potential associated with $\vec{\mu} \cdot \vec{B}$ is added to the energy of the state with $B = 0$





* Selection Rule *

$$\Delta m_\ell = 0, \pm 1$$


Region in sunspot
Region outside of sunspot
A
B

This splitting into 3 is called the

Normal Zeeman Effect

You guessed it... there's such a thing as the

Anomalous Zeeman Effect

There's a history here...

Known from the beginning... the Anomalous Z.E. had no classical features ("normal" meant that Lorentz could explain it with classical ideas...)

Instead of splitting into 3's...

atoms exhibiting the Anomalous Zeeman Effect split into quartets or sextuplets!

For 2 different P↔S
transitions, one would
expect triplets from the
Schrodinger model...but
what one sees is:

say, in Sodium...the first one was called
originally the "Sodium Doublet" as
resolution could only see 2, not 4 lines