Week 10

PHY 106 Quantum Physics
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3.4) Quantum Hydrogen atom

We have seen that a rigorous equation for the **quantum** behaviour of particles (their wave-function) is given by Schrödinger's equation (SE).

We had required a "better atomic theory" than Bohr's model at the end of "week 7".

This can now be provided by **quantum mechanics**, based on the SE.

3.4.1) Schrödinger's equation for Hydrogen

Let us apply QM to the simplest atom: Hydrogen

Problem: 3D, can no longer use simple 1D eqns.

Recall Eq. (87), 3D SE. Now we need time-indep:

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

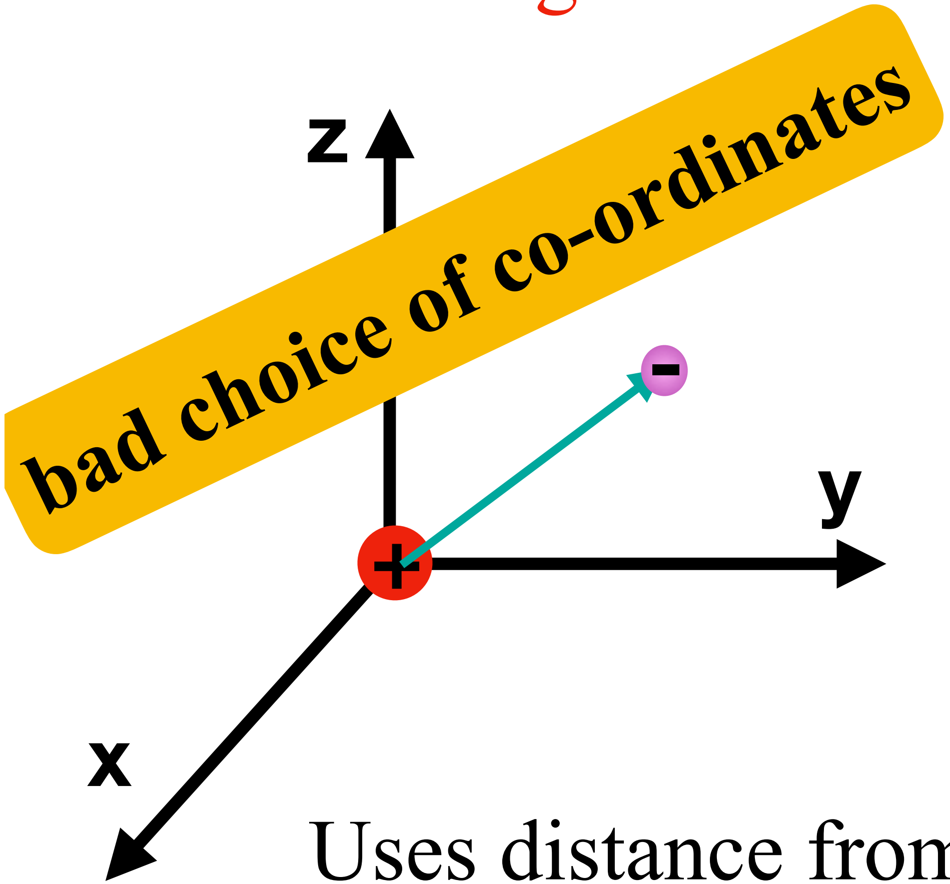
Assume proton infinitely heavy, only electron moving.

$$m = m_e$$

Schrödinger's equation for Hydrogen

$$E_n\Psi(x,y,z) = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+U(x,y,z)\right]\Psi(x,y,z) \quad \textbf{(118)}$$

Proton at origin of co-ordinate system



x,y,z electron position

Electrostatic potential from nucleus [see Eq. (67) for **force**]

$$U(x,y,z) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \quad \textbf{(118b)}$$

Uses distance from origin: $r = \sqrt{x^2+y^2+z^2}$

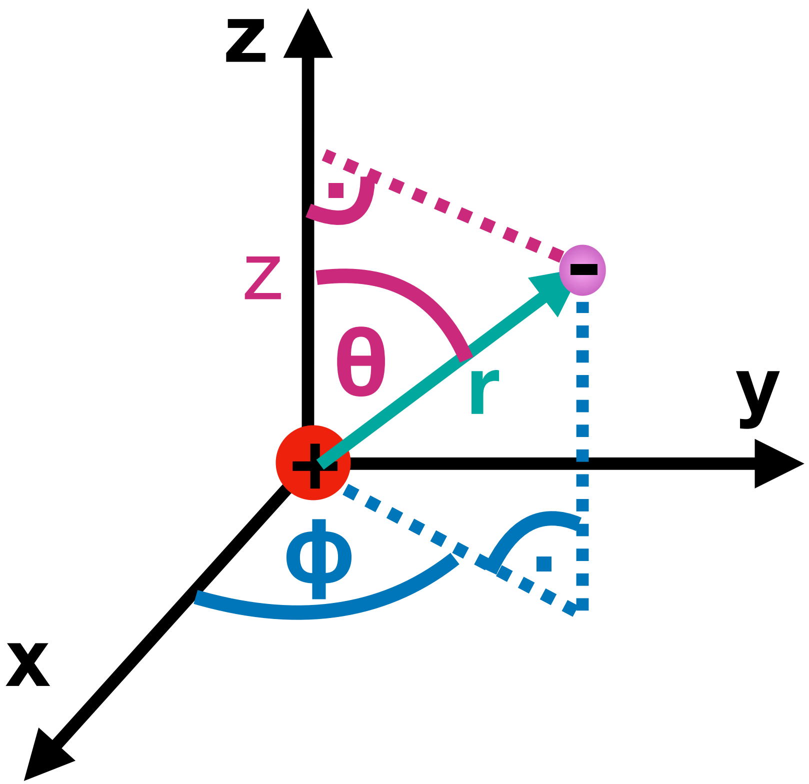
Excursion/Reminder: Spherical polar coords.

We want one coordinate to be:

$$r = \sqrt{x^2 + y^2 + z^2} \quad \textbf{(119)}$$

Add to that, angle between z-axis and vector **r** = [x,y,z]^T

$$\theta = \arccos\left(\frac{z}{r}\right) \quad \textbf{(120)}$$



Finally, we need the angle between x axis and **projection** of **r** into x-y plane

$$\phi = \arctan\left(\frac{y}{x}\right) \quad \textbf{(121)}$$

Schrödinger's equation for Hydrogen

We can rewrite the SE in spherical polar coordinates.

Difficult conversion of derivatives (advanced math)

TISE for the 3D Hydrogen atom

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \Psi}{\partial \theta}\right)$$

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2} + \frac{2m}{\hbar^2}[E - U(r)] = 0 \qquad \textbf{(122)}$$

Wave function in polar coordinates $\Psi = \Psi(r,\theta,\phi)$

Coulomb potential $U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$

3.4.2) Product wave function

Eq. (122) seems much harder than Eq. (118)

However, polar coordinates allow

Product Ansatz

$$\Psi = \Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{123}$$

$R(r)$: Function that only depends on co-ordinate r

$\Theta(\theta)$: Function that only depends on co-ordinate θ

$\Phi(\phi)$: Function that only depends on co-ordinate ϕ

Product wave function

This in turn, allows "separation of variables":

Schematically:

1. Start with Eq. (122), insert (123)

2. Can write this as $f(r,\theta) = g(\phi)$

some function   some other function

equation supposedly true for ANY value of r,theta,phi!!!

3. This means they have to be equal to a constant $f(r,\theta) = \boxed{const. = g(\phi)}$

equation for phi

4. Then again $h(r) = const_2. = y(\theta)$

(more see book)

equation for r **equation for theta**

Product wave function

Get three

Seperated equations for Hydrogen wavefunction

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 \qquad \textbf{(124)}$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0 \qquad \textbf{(125)}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0 \qquad \textbf{(126)}$$

Integers: m_l $\;l$ Energy: E

3.4.3) Hydrogen wave functions

As we have seen earlier [e.g. Eq. (115), harmonic oscillator], to get admissible solutions, **quantum numbers** may pop up

Hydrogen atom **quantum numbers**

from Eqn 126

Principal quantum number $n = 1,2,3,\ldots,\infty$ **(127)**

from Eqn 125

Orbital quantum number $l = 0,1,2,\ldots,n-1$ **(128)**

from Eqn 124

Magnetic quantum number $m_l = 0, \pm 1, \pm 2,\ldots, \pm l$ **(129)**

We skip the math of where they come from, but shall learn now what they mean….

Principal quantum number

The principal quantum number is linked to the **energy E** in Eq. (126) via

Hydrogen electron energies

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n^2}\right) \qquad (75)$$

= Bohr's theory correctly predicts energies in the Schrödinger model (Eq. 124-126).

Here the principal quantum number arises, because mathematically, Eq. (126) does not have a useful solution for any other energies.

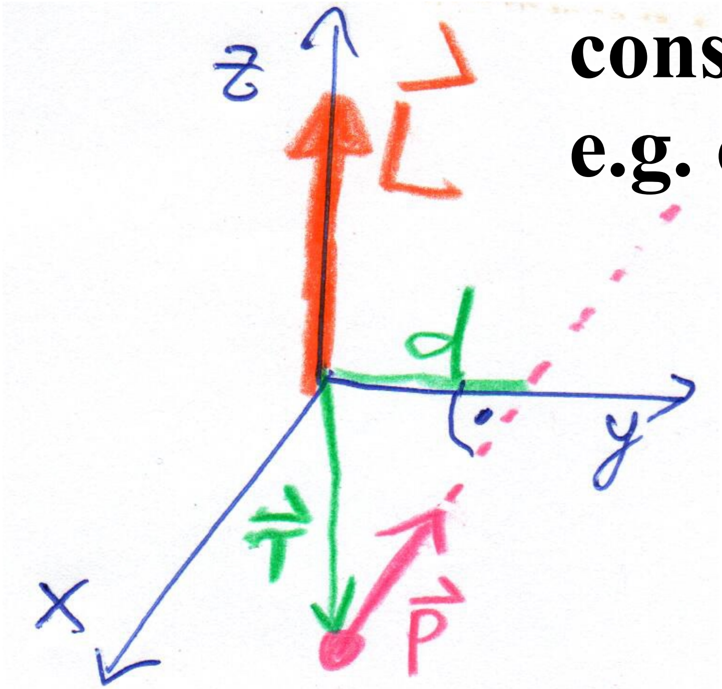
Excursion/reminder: Angular Momentum

To understand the other two quantum numbers, let us revise angular momentum:

Angular momentum
of particle with momentum p around origin

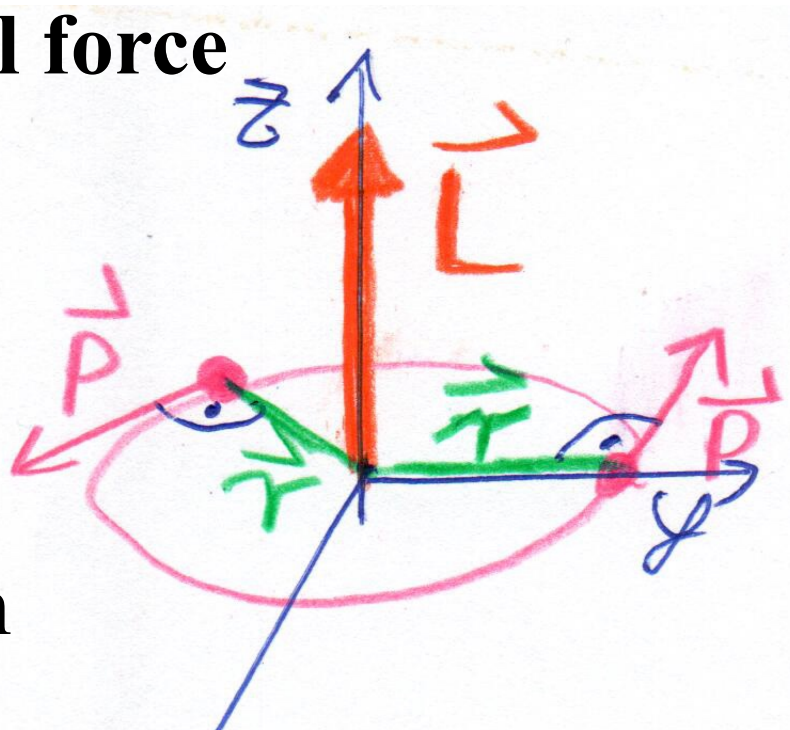
$$\vec{L} = \vec{r} \times \vec{p} \qquad (130)$$

conserved if no torque,
e.g. only central force



straight motion

rotation



Orbital quantum number

It turns out orbital quantum number decides the

Magnitude of angular momentum of the electron

$$L = |\vec{L}| = \sqrt{l(l+1)}\hbar \qquad (131)$$

- Thus angular momentum is also quantized, since l is an integer.
- Note from Eq. (128), that the n=1 ground-state must have **zero** angular momentum.
- In atomic physics, we use letter code:

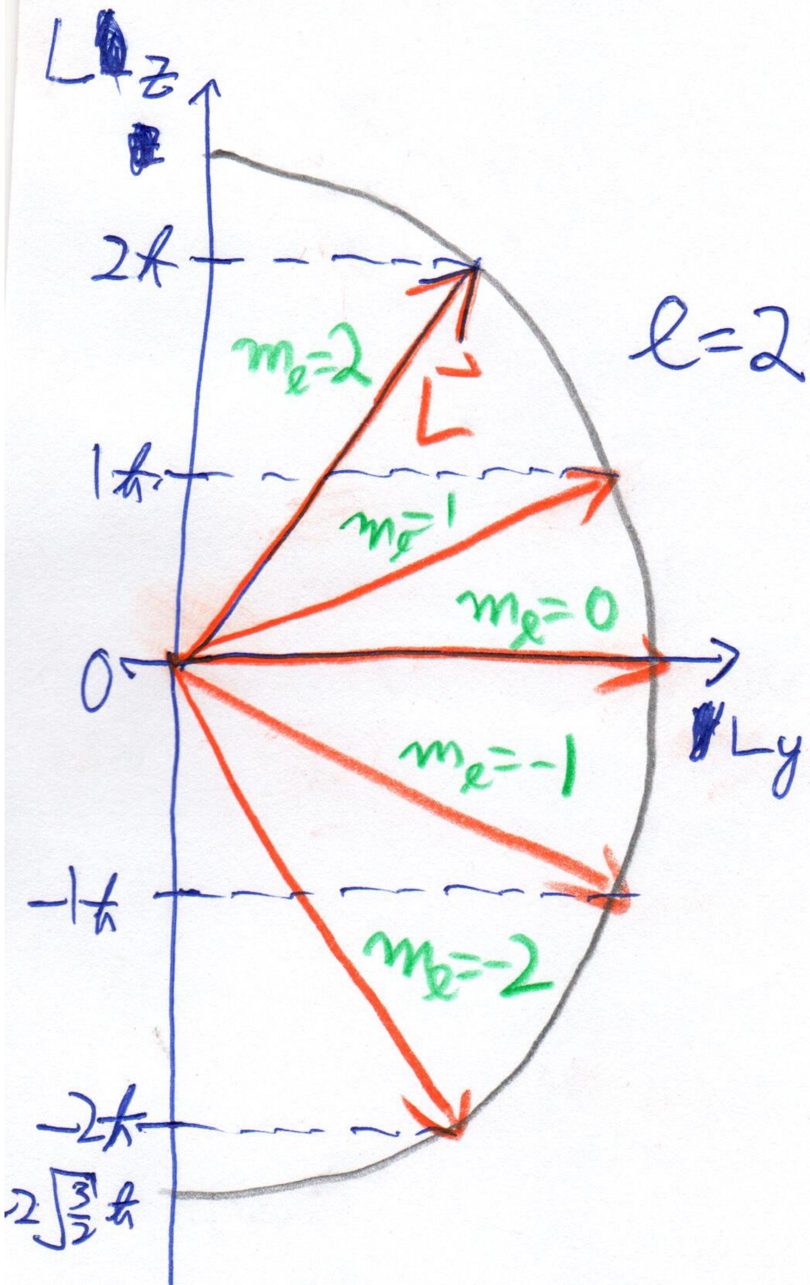
l = 0,	1,	2,	3,	4,	e.g. n=3, l=2
s,	**p,**	**d,**	**f,**	**g,**	=> 3d state

Magnetic quantum number

Finally the magnetic quantum number decides the

z-component of angular momentum of the electron

$$L_z = \hat{k} \cdot \vec{L} = m_l \hbar \qquad \textbf{(132)}$$



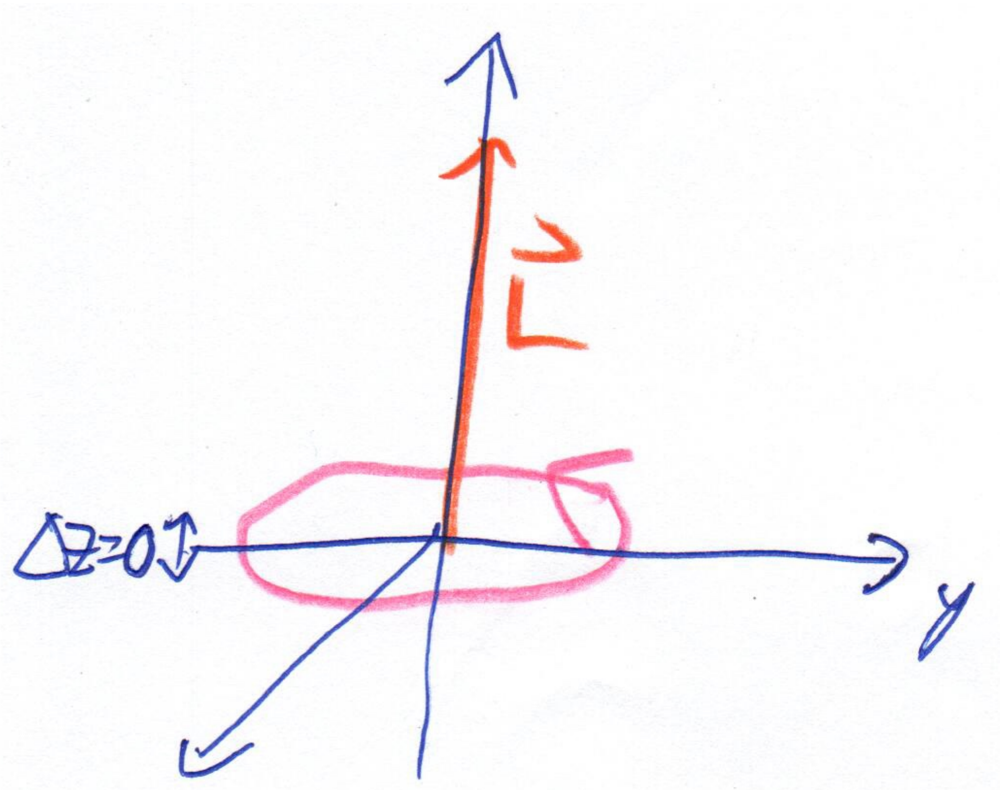
- This determines the **orientation** of angular momentum
- Note other components L_x and L_y are **completely unknown**…

Uncertainties of angular momentum

…the latter is required due to the uncertainty relation (64).

Suppose we **knew all three:**

$$\vec{L} = [0,0,L_z]^T$$



- In this case we know, motion must be in the x,y plane (see pic)

- Thus uncertainty in z-direction $\Delta z = 0$

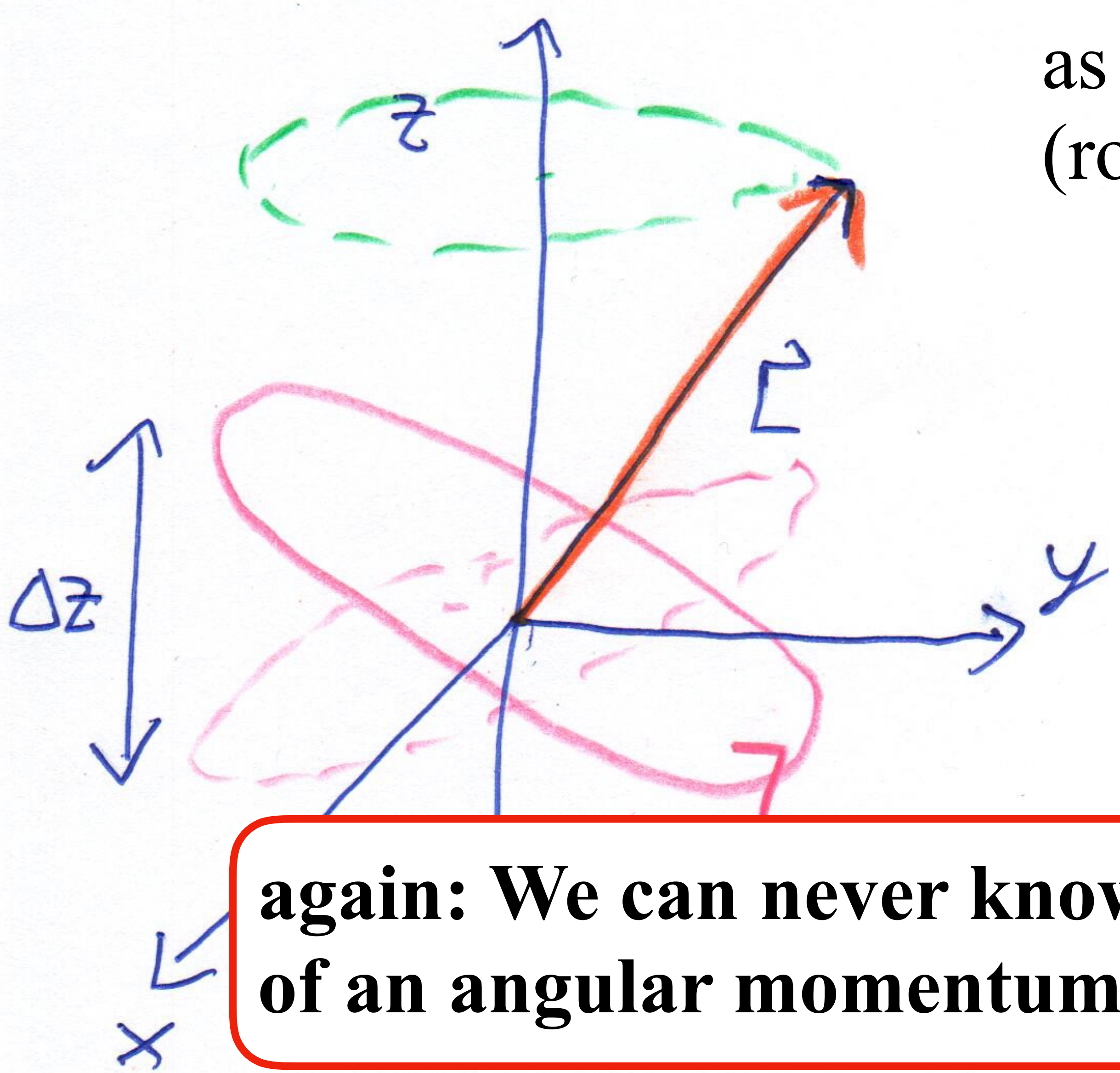
- From Eq. (64): infinite momentum uncertainty

$$\Delta p_z = \infty$$

…which can't be

Uncertainties of angular momentum

The latter is fixed by keeping L_x, L_y uncertain and having $L_z < |\vec{L}|$



- Think of uncertain L_x, L_y as $\vec{L}$ precessing (rotating) on the - - - - line

- "Matching" classical orbital motion (red) then has $\Delta_z \neq 0$ as shown

again: We can never know all three components of an angular momentum precisely (133)

Hydrogen wave functions

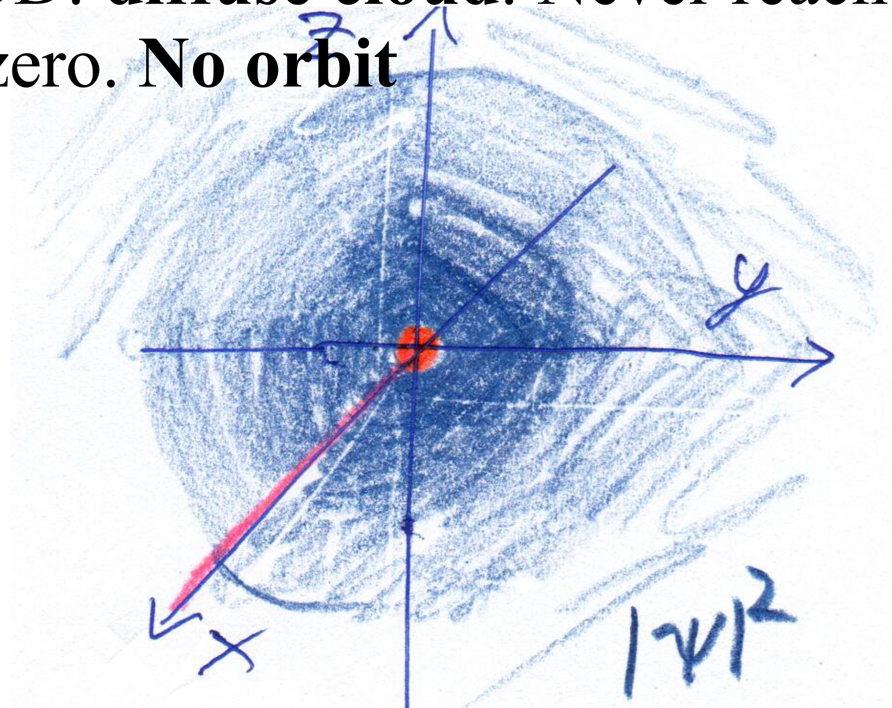
Let us finally take a look at how the electron wave functions in Hydrogen look like:

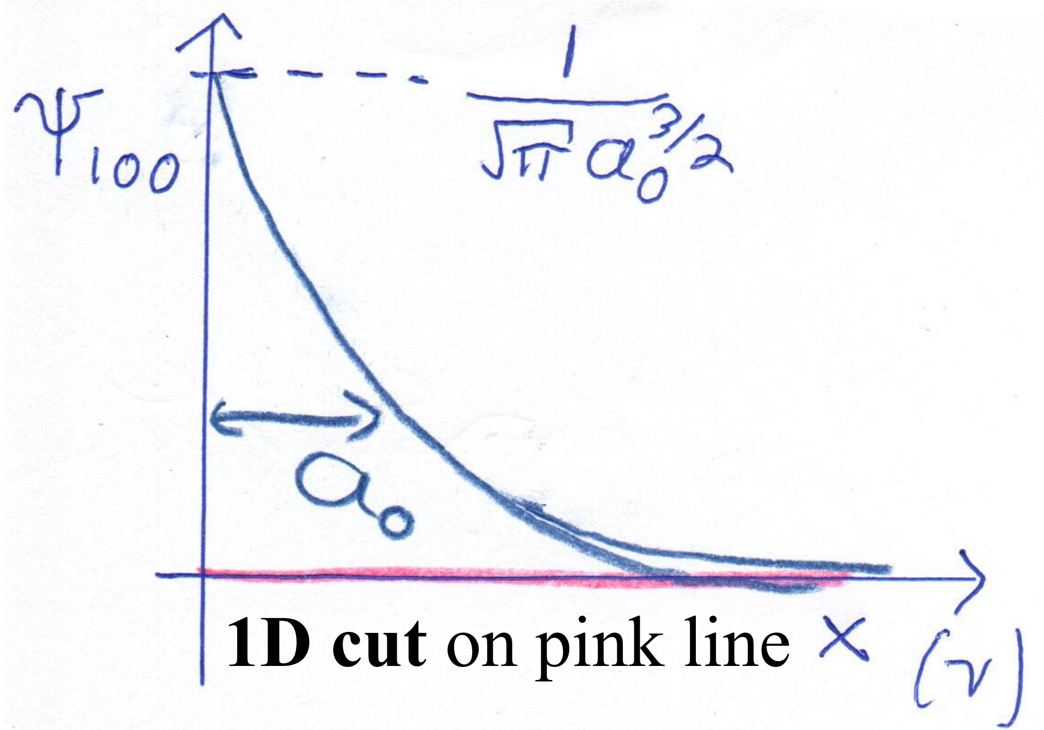
Ground-state: $n = 1, l = 0, m = 0$ or $1s$

$$\Psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} \quad (134)$$

a_0= Bohr radius, Eq. (74b)

3D: **diffuse cloud**. Never reaches zero. **No orbit**





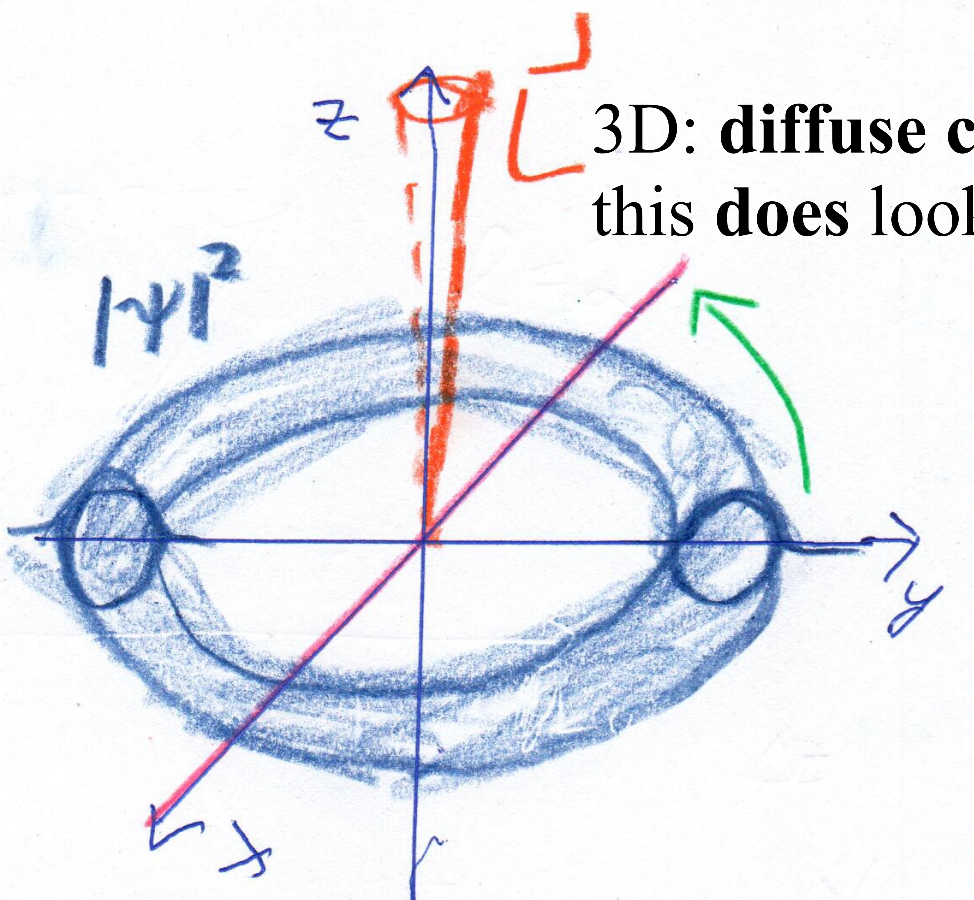
1D cut on pink line

Hydrogen wave functions

Rydberg-state: $n = 50, l = 49, m = 49$

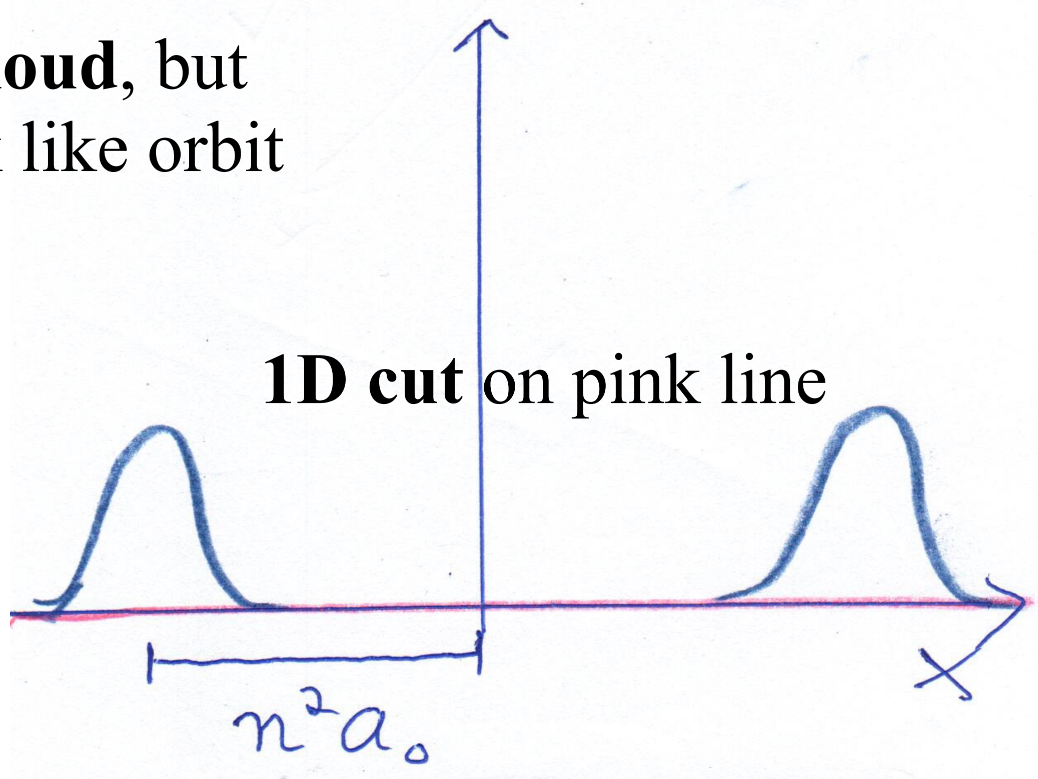
(=very high excited state)

$$\Psi_{n,n-1,n-1}(r,\theta,\phi) \sim \left(\sin[\theta]e^{i\phi}\right)^{n-1}\left(\frac{r}{a_0}\right)^{n-1} e^{-\frac{r}{a_0 n}} \qquad \textbf{(135)}$$



3D: **diffuse cloud**, but this **does** look like orbit

1D cut on pink line

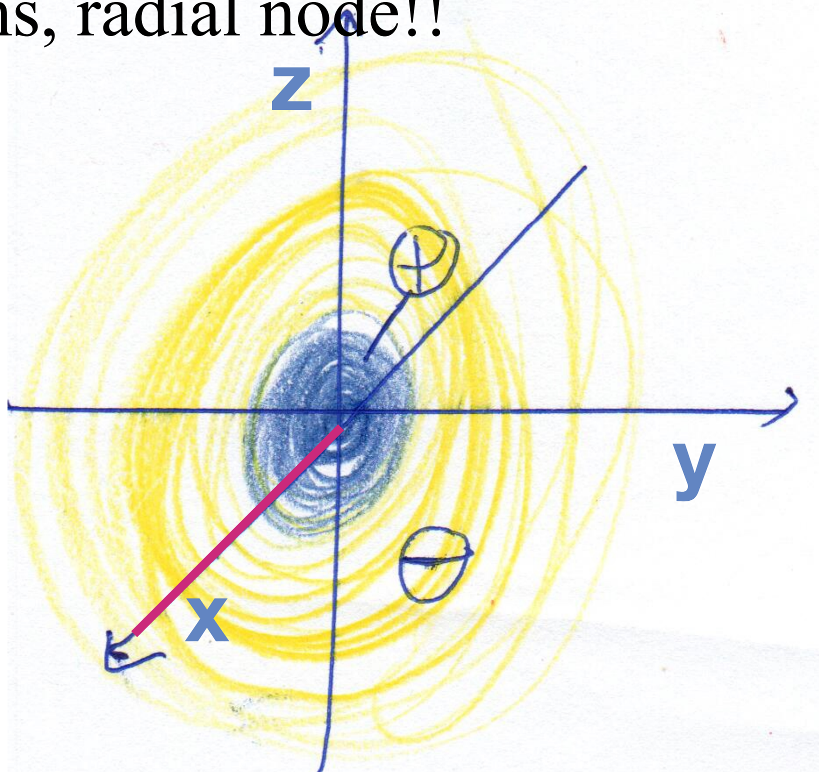


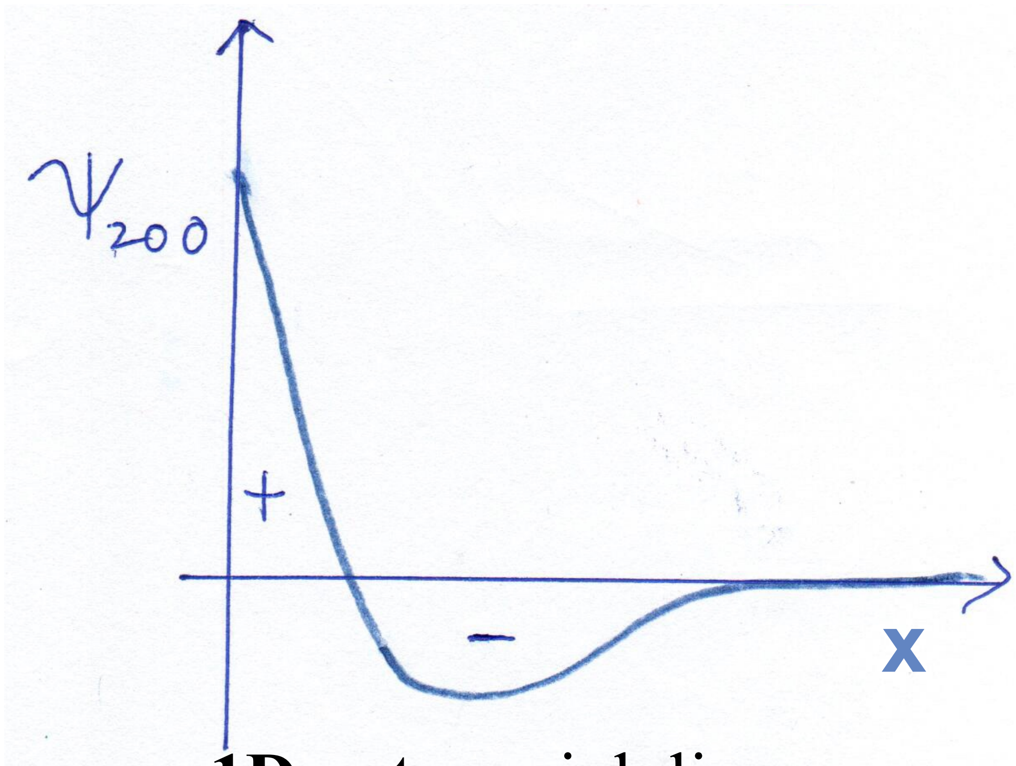
Hydrogen wave functions

Low excited states: $n = 2, l = 0, m = 0$ or $2s$

$$\Psi_{200}(r, \theta, \phi) = \sim \left(2 - \frac{r}{a_0}\right) e^{-r/(2a_0)} \qquad \textbf{(136)}$$

3D: **diffuse cloud**, different signs, radial node!!





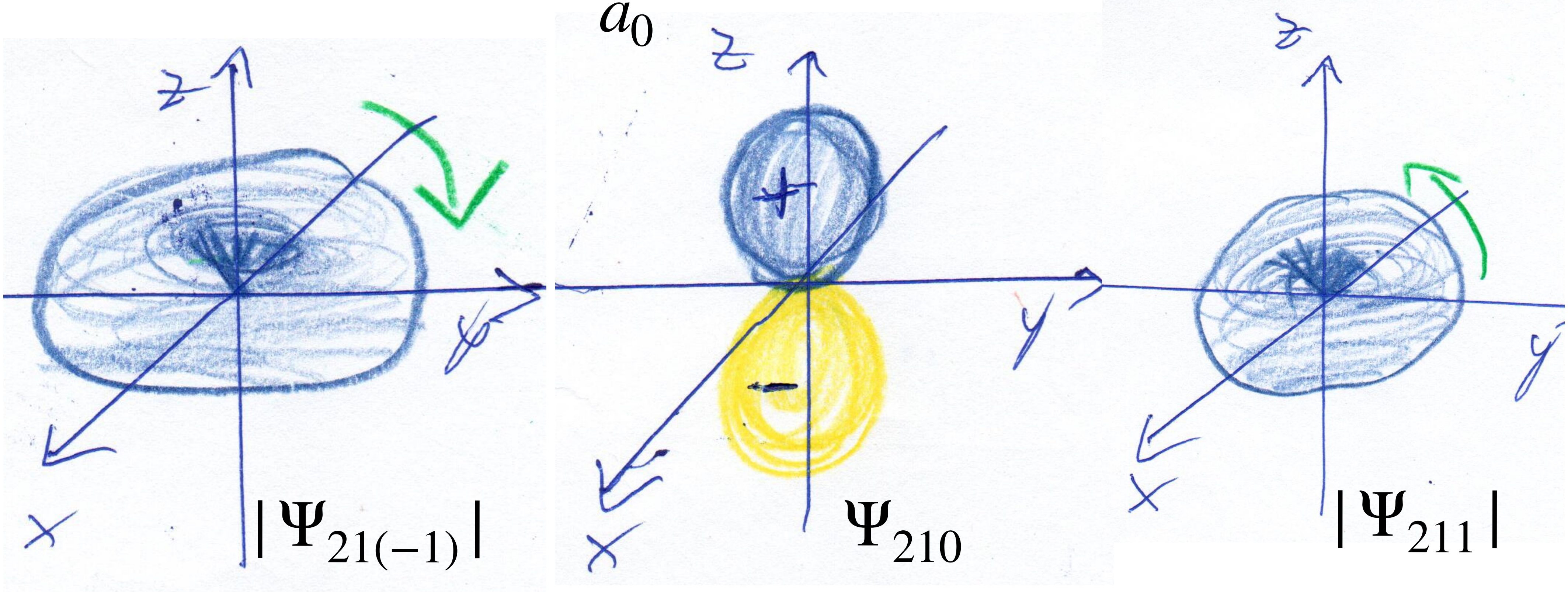
1D cut on pink line

Hydrogen wave functions

Low excited states: $n = 2, l = 1, m = 0, \pm 1$ $\quad 2p$

$$\Psi_{210}(r, \theta, \phi) = \sim \frac{r}{a_0} e^{-r/(2a_0)} \cos(\theta) \qquad \textbf{(137)}$$

$$\Psi_{21\pm1}(r, \theta, \phi) = \sim \frac{r}{a_0} e^{-r/(2a_0)} \sin(\theta) e^{\pm i\phi}$$



Hydrogen wave functions

Summary:

- We can analytically solve the TISE for the Hydrogen atom, to find wave functions with three **quantum numbers** n,l,m, see Eq. 127-129.

- These describe **energy** and **angular-momentum** quantisation

- They are essential for understanding the periodic table (later ~week12) and for calculating probabilities for atomic processes…

Example: Use of Hydrogen wave functions

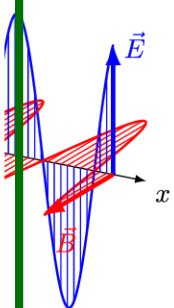
- Schematic how to calculate a stimulated emission probability:

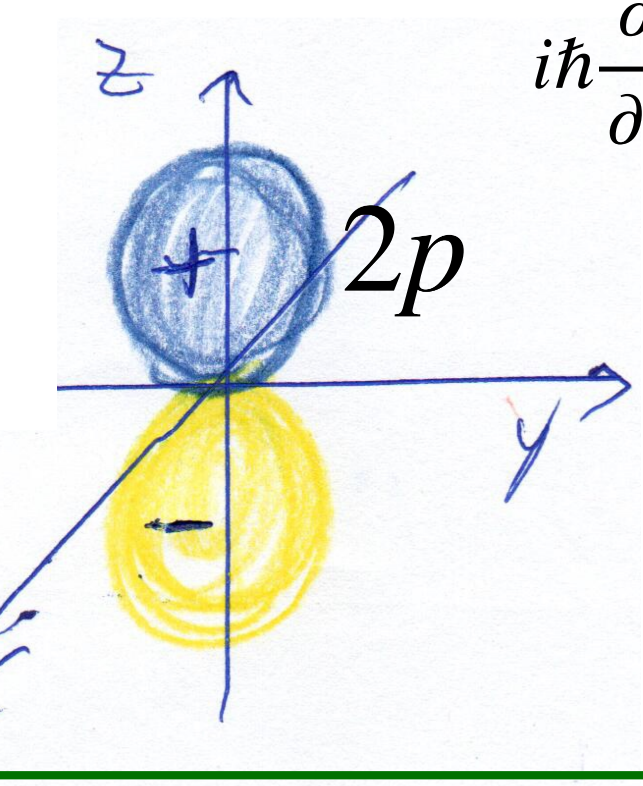
Atomic state at t=0:

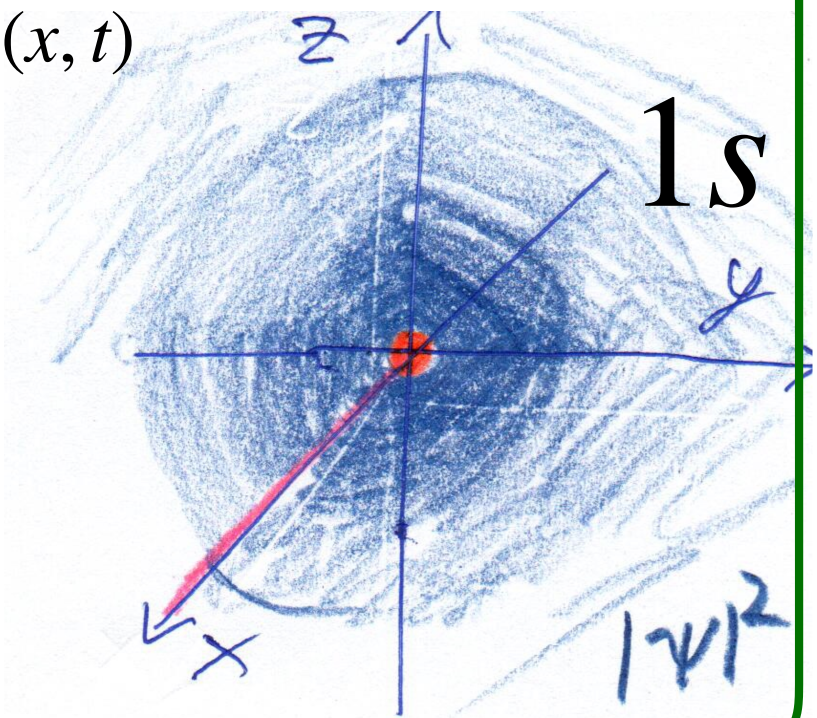
Time-dependence from photon **E**-field

Atomic state at t=T

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t)=\hat{H}(t)\Psi(x,t)$$







3.4.4) Magnetic fields

The TISE (106) can treat atom in **E** or **B** field

electric magnetic

Hamiltonian (101) on the rhs= total energy, hence add **interaction energy** (operators) due to e.g. interaction of **current** (due to electron) with **magnetic field**

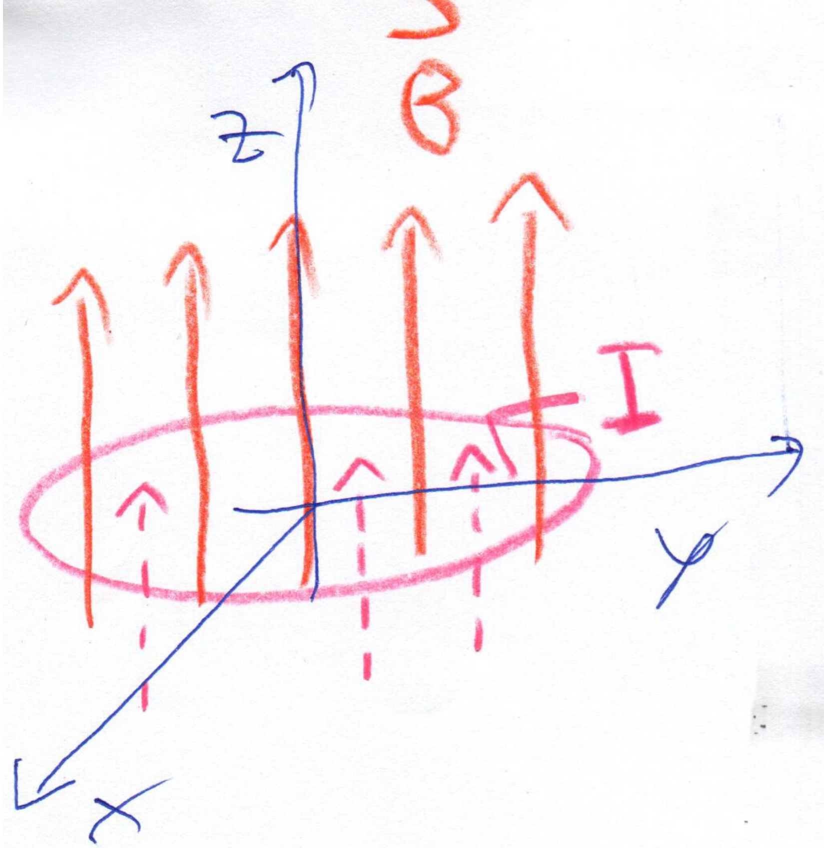
Let us assume magnetic field in z-direction:

$$\overrightarrow{B} = B_0 \hat{k} \qquad \textbf{(138)}$$

There is a magnetic moment associated with angular momentum, that has an energy shift in a field

$$ang.\ mom. \leftrightarrow motion \leftrightarrow currentloop \leftrightarrow energy\ in\ field$$

Magnetic fields



ang. mom. $\leftrightarrow$ *motion* $\leftrightarrow$
currentloop $\leftrightarrow$ *energy in field*

From the calculation we find the

Normal Zeeman effect: energy shift of Hydrogen atom in external magnetic field Eq. (138)

$$\Delta E_{mag} = \frac{\mu_B B_0 m_l}{\hbar} \qquad (139)$$

$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24}$ **J/T** is called **Bohr magneton**

Magnetic fields

splitting small vs energy for typical fields, but if zoom into line…

3.5) (Electron) spin

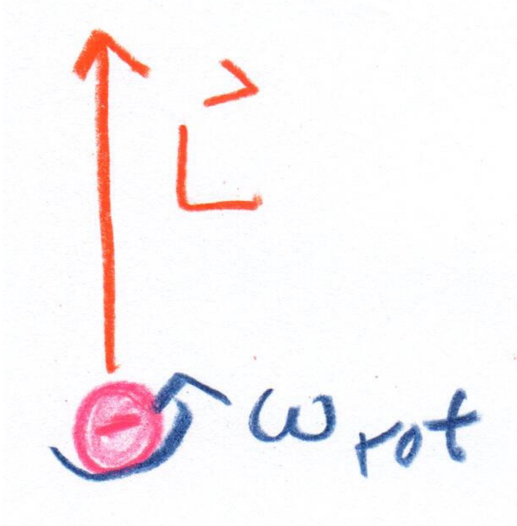
Eq. (139) predict **no shift** for e.g. Hydrogen ground-state $n=1$, $l=0$, $m_l=0$ **But we see one**

even worse: lines are split even **without** field

it turns out

Electron (and most other particles) have an **intrinsic angular momentum** called **spin**

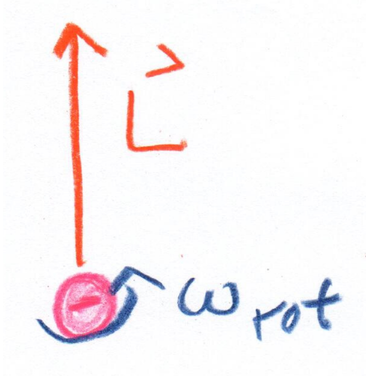
- First idea was "rotation about its axis", see drawing:
- Not true: Since size of electron so tiny, surface would need v>>c



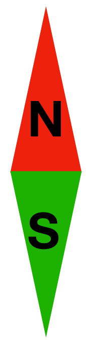
(Electron) spin

Electron (and most other particles) have an **intrinsic angular momentum** called **spin**

- Still frequently helps to (carefully) have "rotation about its axis" in mind.



- Better though is to think of spin as making the electron in to a "tiny magnet" due to magnetic moment.



(Electron) spin

Electron has an **intrinsic angular momentum** called **spin**

- Electron spin is quantized with quantum numbers

$$s = \frac{1}{2} \qquad m_s = -\frac{1}{2}, \frac{1}{2} \tag{140}$$

- These have the same meaning as l and m_l for **orbital** (the other) **angular momentum**

Spin

Turns out most other fundamental (and composite) particles also have spin. It is fundamentally required to construct **relativistic quantum physics**

We classify particles (also compound ones like atoms) as follows

Particles with half-integer spin are called **Fermions**

$$s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$$

Examples: electron, quark, proton, atoms with odd number of neutrons

Particles with integer spin are called **Bosons** (141)

$$s = 0, 1, 2, \ldots$$

Examples: photon, gluon, W-Boson, atoms with even number of neutrons

- We see next (week 11) why this is important