

PH242

Modern Physics II

Feb 7, 2018

Theory: all about Quantum Mechanics (QM), w/ the Schrödinger equation (SE)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

↳ time dependent, 1-D Schrödinger equation.

I Wave function $\Psi(x,t)$ and the Schrödinger Equation

Recall → uncertainty principle $\Delta x \Delta p_x \geq \frac{\hbar}{2}$
 → particle-wave duality → particles have associated wave

$\Psi(x,t)$ = wave function

→ if particle has definite values of $E = p$
 ↳ then the wave has relation

$$\text{freq: } \gamma = \frac{E}{\hbar}$$

$$\lambda = \frac{\hbar}{p}$$

→ particle diffraction = interference

$\Psi(x,t)$ → exhibit interference

↳ must obey "superposition" principle, just like
 \vec{E} fields.

Interference ↳ e.g. $\vec{E} = c_1 \vec{E}_1 + c_2 \vec{E}_2$ (adds)

but intensity: $I \sim (\vec{E})^2$

can be (+) or (-)

brightness ↳ $|I| = |\vec{E}|^2 = |\vec{E}_1|^2 + |\vec{E}_2|^2 + 2\vec{E}_1 \cdot \vec{E}_2$ {constructive intf
 destructive intf}

↳ Same for $\Psi(x,t)$

$\Psi(x,t) = c_1 \Psi_1(x,t) + c_2 \Psi_2(x,t)$ → linearly combine

→ "square" → $|\Psi|^2$ → exhibit interference

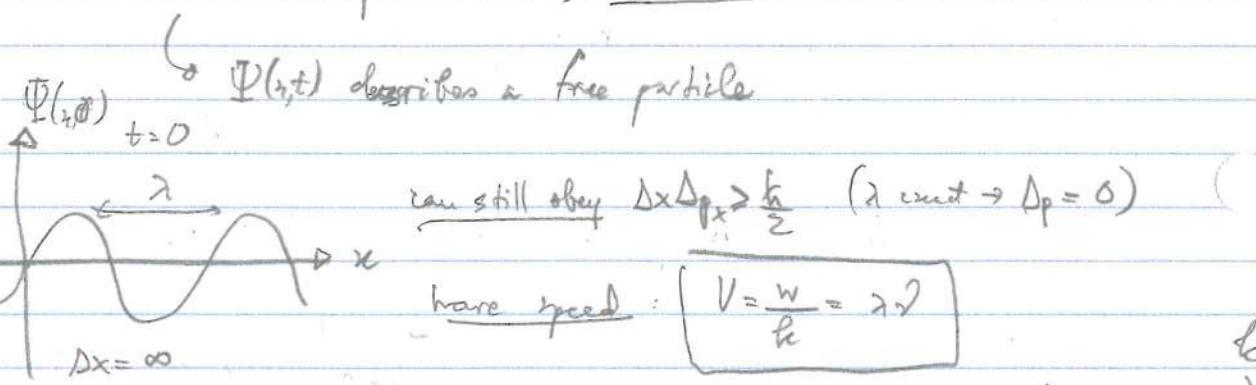
"modulus square"
 of a complex-valued WF

Simplest example of a wave in 1D

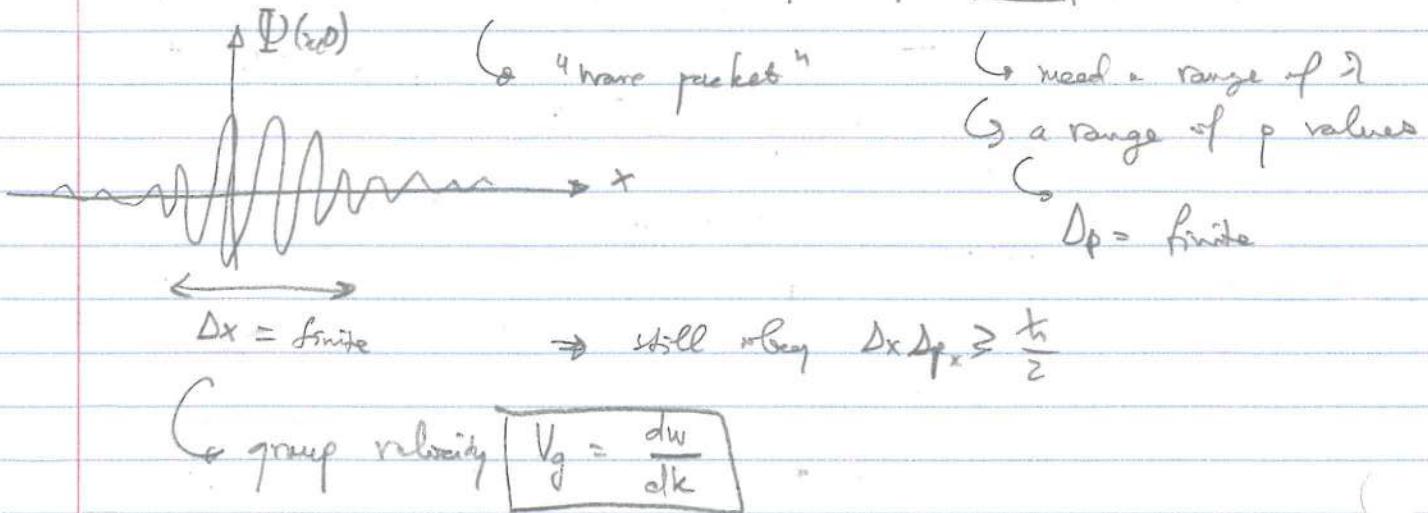
$$\Psi(x,t) = A \sin(\frac{2\pi}{\lambda}x - \omega t) \quad (\text{traveling wave to the right})$$

amplitude \uparrow angular freq \downarrow
 $\frac{2\pi}{\lambda}$ = wave number
 $\boxed{\lambda = \frac{h}{p}, p = \text{th}}$ $\boxed{E = \hbar\omega = h\nu}$

This $\Psi(x,t)$ is a pure wave \rightarrow exact bc; $w \rightarrow \lambda, \nu$ fixed = exact
 $(F = \ddot{p})$ $\Rightarrow p, E$ are both exact
 since $p = \text{const} \Rightarrow$ no force



To get localized wave (finite Δx) \rightarrow super impose many $\Psi(x,t)$ of different λ



But what exactly is $\Psi(x,t)$?

Originally, Schrödinger thought it described a matter wave
 \rightarrow floppy particle...
 \rightarrow but this wrong \rightarrow electrons are not floppy.

Correct Interpretation \rightarrow by Max Born

$\Rightarrow \Psi(x,t)$ is the probability amplitude

$$\{ P(x,t) = \Psi(x,t)^* \Psi(x,t) \} \rightarrow \text{modulus square}$$

\hookrightarrow probability density for finding the particle at x at time t

$$\boxed{P(x,t) dx} = \text{probability for particle to be in } [x \rightarrow x+dx] \text{ at time } t$$

Note: QM is a probabilistic theory

Analogy with light $|E| \rightarrow$ electric field \sim wave amplitude

$$|E|^2 \rightarrow \text{intensity}$$

Also, light has a wave equation!

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2} \cdot \frac{\partial^2 E}{\partial t^2}$$

\rightarrow and again, solutions can superimpose because it's a linear equation...

So... what is the equation for $\Psi(x,t)$?

\hookrightarrow Schrödinger has a solution!

\hookrightarrow lol... it's a guess / found / hypothesis...

(4)

heading notes 4 assumptions for ensuring the properties of a wave function:

- constant w/ de Broglie-Einstein postulate: $\lambda = \frac{h}{p}$; $E = \frac{p^2}{2m} + V$
 - obey eqn: $E = kE + V = \frac{p^2}{2m} + V$ (hence non-relativistic)
 - linear in $\Psi(x,t)$
 - $V(x,t) =$ potential function - this represents the force acting on the particle. Special case $V(x,t) = V_0 \rightarrow$ free particle
- $E = h\nu = \hbar\omega$
- $p = \frac{h}{\lambda} = \frac{\hbar z\pi}{\frac{\lambda}{\lambda}} = \cancel{\frac{\hbar z\pi}{\lambda}}$

Quick "gues" process

$$E = \frac{p^2}{2m} + V$$

$$(1) \quad \cancel{\hbar\nu} = \frac{p^2}{2m} + V \quad (+ \left\{ \begin{array}{l} \omega = 2\pi f \\ \hbar = \frac{2\pi}{\lambda} \end{array} \right\})$$

$$(2) \quad \cancel{\hbar\omega} = \frac{\hbar^2 k^2}{2m} + V$$

* any derivative of Ψ is 1st order (3) (2)

in Ψ (4) want constant 2nd deriv of space - 1st deriv of time
 (ω, k^2)

but also $\Psi_{(int)}, V_{(int)}$

$$\cancel{\alpha \frac{\partial^2 \Psi_{(int)}}{\partial x^2} + V_{(int)} \Psi_{(int)}} = \beta \frac{\partial \Psi_{(int)}}{\partial t}$$

Now.. let $V(x,t) = V_0 \rightarrow$ free particle \rightarrow sinusoidal

$$\Psi_{(int)} = A \sin(kx - \omega t) + B \cos(kx - \omega t)$$

$$\cancel{\frac{\partial \Psi_{(int)}}{\partial t}} = -\omega A \sin(kx - \omega t) - \omega B \cos(kx - \omega t) \quad \square$$

$$\frac{\partial \Psi_{(int)}}{\partial x} = kA \cos(kx - \omega t) - kB \sin(kx - \omega t)$$

$$\frac{\partial^2 \Psi_{(int)}}{\partial x^2} = -k^2 A \sin(kx - \omega t) - k^2 B \cos(kx - \omega t) \quad \square$$

Leading note, cont:

$$-\alpha \left[k^2 \gamma \sin(kx-wt) + k^2 \bar{\psi} \cos(kx-wt) \right] + V(x,t) - \left(\gamma \sin(kx-wt) + \bar{\psi} \cos(kx-wt) \right)$$

$$= \beta \cdot \left(w \sin(kx-wt) - \bar{\psi} \cos(kx-wt) \right)$$

$$\hookrightarrow (\alpha k^2 + V_0 \gamma - \beta w) \sin(kx-wt) + (-\alpha k^2 + V_0 + \beta w \bar{\psi}) \cos(kx-wt) = 0$$

$$w \sin t = 0$$

$$\nabla \alpha, \beta$$

$$\begin{cases} -\alpha k^2 + V_0 \gamma - \beta w = 0 \\ -\alpha k^2 + V_0 + \beta w \bar{\psi} = 0 \end{cases} \Rightarrow \begin{cases} -\alpha k^2 \gamma + V_0 \gamma - \beta w = 0 \\ -\alpha k^2 \bar{\psi} + V_0 \bar{\psi} + \beta w \bar{\psi} = 0 \end{cases}$$

$$\rightarrow \gamma^2 = -1 \Rightarrow \boxed{\gamma = \pm i} \quad \begin{matrix} (KE) & (V) & (F) \end{matrix}$$

$$-\alpha k^2 + V_0 = \mp i \beta w$$

$$\hookrightarrow \text{Convention: } \begin{cases} -\alpha k^2 + V_0 = +i \beta w \\ \frac{k^2 h^2}{2m} + V_0 = -i \beta w \end{cases} \rightarrow \begin{cases} \alpha = -\frac{h^2}{2m} \\ \beta = \mp \frac{h}{i} = \mp \frac{h}{-1} = \pm h \end{cases}$$

$$\rightarrow \boxed{-\frac{h^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \frac{\Psi(x,t)}{i} = ih \frac{\partial \Psi(x,t)}{\partial t}}$$

only one for non-relativistic

$$\text{what about relativistic? Dirac: } E = V + \sqrt{c^2 p^2 + (m_0 c^2)^2}$$

Born's interpretation:

$$\boxed{P(x,t) = \Psi^*(x,t) \Psi(x,t)}$$

KE rest

energy due to velocity

$$\text{Expectation value } \overline{f} = \int_{-\infty}^{\infty} \Psi^*(x,t) f \cdot \Psi(x,t) dx$$

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Reading notes, cont Differential operator: how to express $p = E$ in terms of x, t ?

Consider free-particle: $\Psi(x,t) = \cos(kx-wt) + i\sin(kx-wt)$

$$\hookrightarrow \frac{\partial \Psi(x,t)}{\partial x} = -k\sin(kx-wt) + ik\cos(kx-wt)$$

$$= ik\sin(kx-wt) + ik\cos(kx-wt)$$

$$\text{also, } p = \hbar k$$

$$p = \frac{\hbar}{\lambda} = \frac{\hbar 2\pi}{\lambda}$$

$$\hookrightarrow \frac{\partial \Psi(x,t)}{\partial x} = i \frac{p}{\hbar} \Psi(x,t) \quad (\text{multiply by } i)$$

$$\hookrightarrow i\hbar \frac{\partial \Psi(x,t)}{\partial x} = -p[\Psi(x,t)]$$

$$p \leftrightarrow -i\hbar \frac{\partial}{\partial x}$$

Similarly, for E $\frac{\partial \Psi(x,t)}{\partial t} = w\sin(kx-wt) - iw\cos(kx-wt)$

$$= -w[-\sin(kx-wt) + i\cos(kx-wt)]$$

$$= -iw(\cos(kx-wt) + i\sin(kx-wt)) = -i\hbar[\Psi(x,t)]$$

$$\begin{aligned} E &= \hbar w = \cancel{\hbar} \\ &= \hbar \gamma \\ &= \hbar(\sqrt{2}\alpha) \\ &= \hbar w \end{aligned}$$

$$\hookrightarrow \frac{\partial \Psi(x,t)}{\partial t} = -i\left(\frac{E}{\hbar}\right)\Psi(x,t) \quad (\times i)$$

$$\hookrightarrow i\hbar \frac{\partial}{\partial t} \Psi(x,t) = E[\Psi(x,t)]$$

$$\boxed{E \leftrightarrow i\hbar \frac{\partial}{\partial t} \Psi \rightarrow E \cdot \Psi}$$

$$E \leftrightarrow i\hbar \frac{\partial}{\partial t}$$

$\Psi \Psi \Psi \Psi$

These operators are useful for higher dimensions ...

// end of reading note

Schrödinger Equation

→ can't derive it (it's fundamental)

Feb 9, 2018

→ Instead, we list the conditions for it → we postulate it
→ we check consistency → test experimentally

4 Conditions → looking for a differential eq. for $\Psi(x,t)$

(1)

→ Must be consistent with [de Broglie-Einstein postulate]

$$\left\{ \begin{array}{l} \lambda = \frac{h}{p} \rightarrow p = \frac{h}{\lambda} \\ E = \hbar\nu \end{array} \right. \quad \text{potential}$$

(2)

→ Conservation of energy $E = V + KE = V + \frac{p^2}{2m}$

→ note: non-relativistic $E^2 = c^2 p^2 + (mc^2)^2$

→ Dirac...

(3)

→ Wave eq. must be linear in $\Psi(x,t)$, so that allows superposition (principle of interference)

e.g. if Ψ_1, Ψ_2 are solutions, then

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2 \text{ is also a solution}$$

(4)

→ The special case where

$V(x,t) = V_0$ should describe a free particle -

$$(V_0 = \text{const} \rightarrow F=0) \rightarrow [F = -\vec{V}(x,t)]$$

→ const $p, E \Rightarrow \lambda, \nu \text{ const} \Rightarrow \text{pure wave}$
→ SINUSOIDAL

$$[\Psi = \cos(\theta x - \omega t) + i \sin(\theta x - \omega t)]$$

Let's look closer: (1)+(2)

$$(1)+(2) \rightarrow \frac{p^2}{2m} + V = E \Rightarrow \boxed{\frac{\hbar^2 k^2}{2m} + V = \hbar\omega}$$

$$p = \frac{\hbar}{\lambda} = \frac{\hbar^2 \omega}{2m} = \hbar k$$

$$E = \hbar\nu = \hbar^2 \omega = \hbar\omega$$

Schrödinger eq. must be consistent w/ this

$$\frac{\hbar^2 k^2}{2m} + V = \frac{1}{2} m \omega^2$$

(8)

Linearity condition \Rightarrow all terms have Ψ to first power
 \Rightarrow no Ψ^2 or Ψ^0 or Ψ^{-1} ...

\Rightarrow But it can have derivatives... \rightarrow How many? what type?

Work backwards from pure wave.

Let $V_0 = \text{const} \rightarrow V(x,t) \rightarrow$ use $\Psi = \sin(kx - \omega t) = \text{solution}$

$$\frac{\partial \Psi}{\partial x} = k \cos(kx - \omega t) \rightarrow \frac{\partial^2 \Psi}{\partial x^2} = -k^2 \sin(kx - \omega t)$$

$$\frac{\partial \Psi}{\partial t} = -\omega \cos(kx - \omega t)$$

$$\boxed{\frac{\hbar^2 k^2}{2m} + V = \frac{1}{2} m \omega^2}$$

\rightarrow suggests using

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x^2} &\rightarrow k^2 \\ \frac{\partial \Psi}{\partial t} &\rightarrow \omega \\ \Psi &\rightarrow V \end{aligned}$$

So we guess form:

$$\boxed{\alpha \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = \beta \frac{\partial \Psi}{\partial t}} \rightarrow \text{what is } \alpha, \beta?$$

To find $\alpha, \beta \rightarrow$ go back to free particle: $\rightarrow \left\{ \begin{array}{l} \sin(kx - \omega t) \\ \cos(kx - \omega t) \end{array} \right.$

$$\boxed{\Psi = \sin(kx - \omega t)} \rightarrow -\alpha(k^2) \sin(kx - \omega t) + V \sin(kx - \omega t) = \beta(-\omega) \cos(kx - \omega t)$$

$$\cancel{-\alpha(k^2) \sin(kx - \omega t) + V \sin(kx - \omega t)} \rightarrow \cancel{-\alpha(k^2) \sin(kx - \omega t) + V \sin(kx - \omega t)} = \beta(-\omega) \cos(kx - \omega t)$$

$$\boxed{\Psi = \cos(kx - \omega t)} \rightarrow -\alpha(k^2) \cos(kx - \omega t) + V \cos(kx - \omega t) = \beta(-\omega) \sin(kx - \omega t) \rightarrow \text{can't find } \alpha, \beta$$

\hookrightarrow same problem

\Rightarrow We can use a linear combination of $\sin(kx - \omega t) + \cos(kx - \omega t)$

$$\Rightarrow \boxed{\Psi = C \sin(kx - \omega t) + S \cos(kx - \omega t)}$$

$$\begin{aligned} & \rightarrow -\alpha h^2 \left[\cos(kx-wt) + \gamma \sin(kx-wt) \right] + V_0 \left[\cos(kx-wt) + \gamma \sin(kx-wt) \right] \\ & = -\beta w \left[-\sin(kx-wt) + \gamma \cos(kx-wt) \right] \\ & = -\beta w \left[\cos(kx-wt) \left(-\frac{1}{\gamma} \sin(kx-wt) \right) \right] \end{aligned}$$

if $\frac{-1}{\gamma} = \gamma \Rightarrow$ we can cancel Ψ from the general form

↳ true only if $\boxed{\gamma = i}$... well actually $\Psi = \pm i$
 ↳ convention $\Psi = -i$

Also,

$$\begin{cases} -\alpha h^2 + V_0 = -i\beta w \\ \frac{\hbar^2 k^2}{2m} + V_0 = \beta w \end{cases} \Rightarrow \begin{cases} \alpha = \frac{-h^2}{2m} \\ \beta = \frac{-k}{i} = ih \end{cases}$$

$$\Rightarrow \boxed{\frac{-h^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V_0 \Psi = ih \frac{\partial \Psi}{\partial t}}, \text{ assuming } V_0 = V(x, t)$$

However, we can postulate the eqn holds even if $F + V(x, t)$

if $F = -\frac{\partial V(x, t)}{\partial x} + 0 \rightarrow$ no force

$$\boxed{\frac{-h^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t) \Psi = ih \frac{\partial \Psi}{\partial t}}$$

Time-dependent
1-Dimensional
(1925)

↳ The differential eq. that lets you solve for the associated wave function Ψ for a particle of mass m and a potential energy $V(x, t)$

Example Check if this is linear. Assume Ψ_1, Ψ_2 are solutions and see if $\Psi = c_1\Psi_1 + c_2\Psi_2$ is also a solution.

Plug in $\Psi = c_1\Psi_1 + c_2\Psi_2$

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_1}{\partial x^2} + V\Psi_1 \right] c_1 + \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_2}{\partial x^2} + V\Psi_2 \right] c_2 \\ &= c_1 i\hbar \frac{\partial \Psi_1}{\partial t} + c_2 i\hbar \frac{\partial \Psi_2}{\partial t} \\ &= i\hbar \left[c_1 \frac{\partial \Psi_1}{\partial t} + c_2 \frac{\partial \Psi_2}{\partial t} \right] = i\hbar \frac{\partial \Psi}{\partial t} \quad (\text{q.e.d}) \end{aligned}$$

→

Feb 12, 2018

Schrödinger equation

↪ Note: free-particle solution is $c_1(\hbar x - \omega t) + i c_2 \sin(\hbar x - \omega t)$

SE → complex-valued differential eq

Ψ → also complex-valued

Is this a problem? Not really, because

Interpretation:

modulus square

$$|\Psi(x,t)|^2 = \Psi^\dagger(x,t) \Psi(x,t) = \text{probability distribution}$$

↪ always real, non-negative

Reform of complex numbers...

$$e^{i\theta} = \cos \theta + i \sin \theta$$

$$e^{-i\theta} = \cos \theta - i \sin \theta$$

First:

$$\frac{1}{2i} (e^{i\theta} - e^{-i\theta}) = \sin \theta$$

$$\frac{1}{2i} (e^{i\theta} + e^{-i\theta}) = \cos \theta$$

gives complex traveling wave to the right

Free-particle solution has form

$$\Psi(x,t) = c_1 e^{i(\hbar x - \omega t)} = e^{i(\hbar x - \omega t)}$$

Properties of $\Psi(x,t)$ \rightarrow solution to the SE for a given $V(x,t)$ gives $\Psi(x,t)$

$\Psi(x,t) \rightarrow$ probability amplitude
 $|\Psi(x,t)|^2 \rightarrow$ probability density (probability per length in 1-D)

$\int |\Psi(x,t)|^2 dx \rightarrow$ probability for finding particle in $x \rightarrow x+dx$
 ↳ Must be normalized \rightarrow sum of all probability = 1

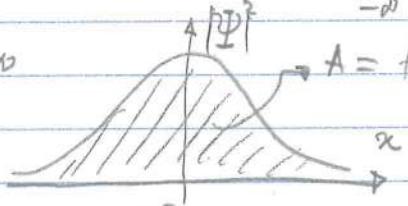
$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \quad \leftarrow \text{must set the const inside } \Psi(x,t) \text{ so that this holds.}$$

↳ Called normalization of wave function.

Good wave functions must be normalizable -

↳ must be "square integrable" $\rightarrow \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx < \infty$

\Rightarrow requires $\Psi(x,t) \rightarrow 0$ as $x \rightarrow \pm\infty$



(Will use $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$ as a condition.)

Expectation values \rightarrow how can we find averages/mean values of physical quantities? $\bar{x}, \bar{p}, \bar{E}, \dots$

Given $\int P(x,t) dx = \Psi^*(x,t) \Psi(x,t) dx =$ probability in $x \rightarrow x+dx$

Position To find $\bar{x} =$ the weighted average

$$\bar{x} = \int_{-\infty}^{\infty} x \Psi^*(x,t) dx \rightarrow$$

We write

$$\bar{x} = \int_{-\infty}^{\infty} \Psi^*(x,t) x \Psi(x,t) dx$$

Note, we flip the quantity (x, p, E) between Ψ^* & Ψ .

The order doesn't matter, but it does (sort of) in later content

This assumes $\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$. Otherwise,

$$\bar{x} = \frac{\int_{-\infty}^{\infty} \bar{P}_x^* \Psi dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}$$

- Doing the integral over time gives $\bar{x}(t)$ (average value)

We can also find averages of functions of x

$$\bar{x^2} = \int_{-\infty}^{\infty} \bar{P}_{x^2}^* \Psi dx \quad \text{Generalise} \quad \bar{f}_A = \int_{-\infty}^{\infty} \bar{P}_A^* \Psi dx$$

Momentum

What about momentum p^2 ?

Well,

$$\bar{p} = \int_{-\infty}^{\infty} \bar{P}_p^* \Psi dx$$

Note: can't let p be a usual $f(x)$
because if $p = f(x)$, then it's exact
 $\Rightarrow p$ must

\Rightarrow Contradict uncertainty principle!

but we need p in terms of x to do the integral!

So how can we represent p in terms of x ?

\Rightarrow for guidance, let's look at free-particle again!

$$\Psi(x,t) = e^{i(kx - \omega t)}$$

\hookrightarrow free particle has definite $p \rightarrow$ Observe: $\frac{\partial \Psi(x,t)}{\partial x} = ik \Psi$

Since $p = \frac{h}{\lambda} = tk \lambda \rightarrow p\Psi = -it \frac{\partial \Psi}{\partial x}$

de
Broglie

$\hookrightarrow p$ is a differential ~~op~~ operator

\hookrightarrow suggest defining p as a differential operator (\hat{p})

\hookrightarrow Define $\hat{p} = -it \frac{\partial}{\partial x}$ \rightarrow gives momentum
operator for

So... we can now proceed... $\bar{p} = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi dx \Rightarrow \bar{p} = \int_{-\infty}^{\infty} \Psi^* (-i\hbar) \frac{\partial \Psi}{\partial x} dx$

$\Rightarrow \boxed{\bar{p} = (-i\hbar) \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx}$ Given Ψ , compute $\frac{\partial \Psi}{\partial x}$, then do the integral

(\hookrightarrow we got this from free-particle, then (now) we postulate that this is always how you do it!)

★ Now we see that the ordering in the integral matters!

(1) $\int_{-\infty}^{\infty} dx \Psi^* \hat{p} \left(-i\hbar \frac{\partial}{\partial x} \right)$ \rightarrow makes no sense
(the operator does not do anything)

(2) $\int_{-\infty}^{\infty} (-i\hbar) \frac{\partial}{\partial x} (\Psi^* \Psi) dx \rightarrow -i\hbar \Psi^* \Psi \Big|_{-\infty}^{\infty} = 0$

(3) $\int_{-\infty}^{\infty} \Psi \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi^* dx \rightarrow$ doesn't give p , but $i\hbar \frac{\partial}{\partial x}$ does!

■ Schrödinger equation has a sign ambiguity \rightarrow conventional choice $\gamma = +i$
 \rightarrow this requires using $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ between Ψ^* & Ψ

\hookrightarrow use $\boxed{\bar{p} = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi dx}$ (left-right)

Note: x is also an operator \rightarrow (final) $\hat{x} = x \leftarrow$ multiply by x

Can also write

$\boxed{\hat{x} = \int_{-\infty}^{\infty} \Psi^* \hat{x} \Psi dx}$

\hookrightarrow recall

Feb 14, 2012 \hookrightarrow ★ Physical quantities in QM are represented as operators.

e.g.: $\hat{x} = x$, $\hat{p} = -i\hbar \frac{\partial}{\partial x}$; $\hat{f}(x) = f(x)$

→ To find $\bar{F}(\psi)$ of a physical quantity, put the operator between Ψ^* and Ψ and integrate.

$$\bar{x} = \int_{-\infty}^{\infty} \Psi^* x \Psi dx \quad \text{numbers!}$$

$$\bar{p} = \int_{-\infty}^{\infty} \Psi^* (-i\hbar) \frac{\partial}{\partial x} \Psi dx$$

→ These averages must be real numbers. Is \bar{p} real?

◻ Prove \bar{p} real?

$$\bar{p} = (-i\hbar) \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx$$

Want to use \bar{p} real if $\boxed{\bar{p}^* = \bar{p}}$

So, to prove $\bar{p}^* = \bar{p}$

$$\text{Well, } \bar{p}^* = \left[(-i\hbar) \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx \right]^* = (i\hbar) \int_{-\infty}^{\infty} \Psi \frac{\partial \Psi^*}{\partial x} dx \quad (\Psi^*)^* = \Psi$$

Integration by parts

$$\int_a^b u dv = uv \Big|_a^b - \int_a^b v du$$

$$\left. \begin{array}{l} \text{Let } \Psi = u \Rightarrow du = \frac{\partial \Psi}{\partial x} dx \\ \frac{\partial \Psi}{\partial x} dx = dv \Rightarrow v = \Psi^* \end{array} \right\}$$

$$\Rightarrow \bar{p}^* = (i\hbar) \int_{-\infty}^{\infty} \Psi \frac{\partial \Psi^*}{\partial x} dx = (i\hbar) \underbrace{\left[\Psi \Psi^* \right]_{-\infty}^{\infty}}_{=0} - (i\hbar) \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx$$

Recall $\Psi \rightarrow 0$ as $x \rightarrow \infty$

$$\Rightarrow \bar{p}^* = -(i\hbar) \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx = \bar{p} \Rightarrow \boxed{\bar{p}^* = \bar{p}}$$

So \bar{p} is real

#

So we form other operators — Energy!

Energy operators — Called the Hamiltonian

→ e.g. $H = \frac{\hat{p}^2}{2m} + V(x)$ ← classical

To go to QM → we promote these to operators.

→ Quantum mechanical Hamiltonian: $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x)$

where $\hat{V}(x) = V(x)$, and $\hat{p}^2 = \hat{p}\hat{p}^\dagger = (-i\hbar)^2 \frac{\partial}{\partial x} \frac{\partial}{\partial x^\dagger} = -(+i\hbar)^2 \frac{\partial^2}{\partial x^2}$

↳ See that $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

Also, SE:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

So ... $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ → As long as Ψ is a solution, we can say

$$\hat{H} = i\hbar \frac{\partial}{\partial t}$$

The book writes $\hat{E} = i\hbar \frac{\partial}{\partial t}$, but more commonly, we use $\hat{H} = \frac{\partial}{\partial t}$ as the energy operator

Energy operator ≡ Hamiltonian

∴ $\left\{ \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right\}$

Could compute

$$\hat{E} = \int_{-\infty}^{\infty} \Psi^*(i\hbar) \frac{\partial}{\partial t} \Psi dx$$

Again, $\hat{p}^2 = \int_{-\infty}^{\infty} \Psi^* (-i\hbar)^2 \frac{\partial^2 \Psi}{\partial x^2} dx$

→ We could also compute $\hat{x}^2 \rightarrow$ need both \hat{x}^2 & \hat{p}^2 to find uncertain

Uncertainties We denote Δx , Δp as standard deviation.

↳ $\sigma = \sqrt{\text{average of squares of deviation from mean}}$

$$\text{↳ } (\Delta p)^2 = \frac{(p - \bar{p})^2}{\text{number of measurements}} = \frac{p^2 - 2\bar{p}p + \bar{p}^2}{\text{number of measurements}}$$

\bar{p} is a number $\Rightarrow \text{so } \bar{\bar{p}} = \bar{p}$

$$\text{So } (\Delta p)^2 = \bar{p}^2 - 2\bar{p}\bar{p} + \bar{p}^2 = \bar{p}^2 - 2\bar{p}\bar{p} + \bar{p}^2 = \bar{p}^2 - 2\bar{p}\bar{p} + \bar{p}^2$$

$$\text{↳ } (\Delta p)^2 = \bar{p}^2 - \bar{p}^2 \Rightarrow \boxed{\Delta p = \sqrt{\bar{p}^2 - \bar{p}^2}}$$

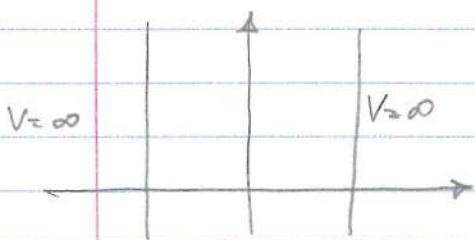
likewise $\boxed{\Delta x = \sqrt{\bar{x}^2 - \bar{x}^2}}$

We should find that with these, then $\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$

Example Consider a particle in a box where, $-\frac{a}{2} \leq x \leq \frac{a}{2}$

$V=0$ inside a box, ∞ inside

$V \rightarrow \infty$ at the walls.



We'll solve this problem later, but let's use its result now

↳ look at (1) solution @ ground state

$$\Psi(x,t) = \begin{cases} A \cos\left(\frac{\pi x}{a}\right) e^{-iEt/\hbar} & (\text{inside box}) \\ 0 & x < -\frac{a}{2} \text{ or } x > \frac{a}{2} \end{cases}$$

Verify this is a solution

↳ inside the box, $V=0$

↳ inside box:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\text{solution if } E = \frac{\hbar^2 \pi^2}{2ma^2}$$

$$\text{well } -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \left(-\frac{\hbar^2}{2m}\right)(-A) \left(\frac{\pi}{a}\right)^2 \cos\left(\frac{\pi x}{a}\right) e^{-iEt/\hbar}$$

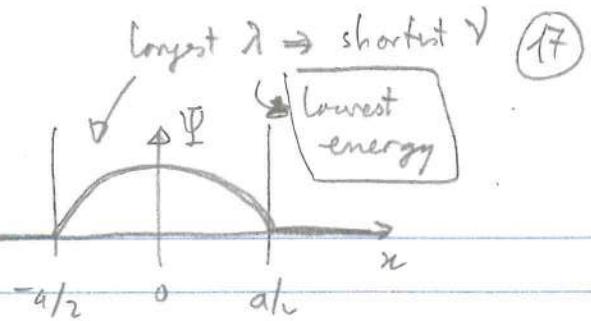
$$\text{pt } \frac{\partial \Psi}{\partial t} = (i\hbar) A \cos\left(\frac{\pi x}{a}\right) \left(-\frac{iE}{\hbar}\right)$$

$$\Rightarrow \boxed{E = \frac{\hbar^2 \pi^2}{2ma^2}}$$

Ground energy solution

$$\begin{aligned} \cos(2x) &= c^2 - s^2 \\ &= c^2 - (1 - c^2) \\ &= 2c^2 - 1 \end{aligned}$$

Well, consider $\Psi(x, 0) = A \cos\left(\frac{\pi x}{a}\right) \rightarrow$



(17)

\Rightarrow Compute energy values! But before that, we need to normalize s.l.n.
Find A such that

$$\begin{aligned} \int_{-a}^a |\Psi|^2 dx &= 1 \Rightarrow \int_{-a}^a \left[A \cos\left(\frac{\pi x}{a}\right) \right]^2 dx = 1 \\ \Rightarrow A^2 \int_{-\frac{a}{2}}^{\frac{a}{2}} \cos^2\left(\frac{\pi x}{a}\right) dx &= 1 \quad (\text{if } x > \frac{a}{2} \text{ or } x < -\frac{a}{2}, \Psi^2 = 0) \\ \Rightarrow \frac{A^2}{2} \int_{-\frac{a}{2}}^{\frac{a}{2}} \cos\left(\frac{2\pi x}{a}\right) + 1 dx &= \frac{A^2}{2} \left[\frac{a}{2\pi} \sin\left(\frac{2\pi x}{a}\right) + x \right] \Big|_{-\frac{a}{2}}^{\frac{a}{2}} \\ \Rightarrow \frac{a A^2}{2\pi^2} \left(\pi \bullet \right) - \frac{a A^2}{4\pi} &= 1 \Rightarrow A = \boxed{\sqrt{\frac{2}{a}}} \end{aligned}$$

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Feb 16, 2018 Particle in a Box, cont.

$$\text{Ground state solution } \Psi(x, 0) = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right) e^{-iEt/\hbar}$$

$$\text{provided } E = \frac{\hbar^2 n^2}{2ma^2}$$

odd function

Now, find $\bar{x}, \bar{p}, \bar{x^2}, \bar{p^2} \rightarrow$ find Dx, Dp

$$\boxed{\bar{x}} = \frac{2}{a} \int_{-a}^a x \cos^2\left(\frac{\pi x}{a}\right) dx = \frac{2}{a} \int_{-a/2}^{a/2} x \cos^2\left(\frac{\pi x}{a}\right) dx = \boxed{0}$$

$$\boxed{\bar{p}} = \frac{2}{a} \int_{-a/2}^{a/2} \cos\left(\frac{\pi x}{a}\right) \cdot (-i\hbar) \frac{d}{dx} \cos\left(\frac{\pi x}{a}\right) dx$$

$$= (-i\hbar) \frac{2}{a} \int_{-a/2}^{a/2} \left(-\frac{\pi}{a} \right) \cos\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right) dx = \boxed{0}$$

$$\frac{1}{2} \sin\left(\frac{2\pi x}{a}\right)$$

odd function

even function

$$\bar{x^2} = \int_{-a/2}^{a/2} \Psi^* x^2 \Psi dx = \int_{-a/2}^{a/2} \frac{2}{a} u \cos^2\left(\frac{\pi u}{a}\right) du . \quad \text{Let } u = \frac{\pi x}{a} \rightarrow du = \frac{\pi}{a} dx$$

$dx = \frac{a}{\pi} du$

\downarrow

$\int_{-a/2}^{a/2} \Psi^* x^2 \Psi dx \rightarrow x = \frac{a}{\pi} u \Rightarrow x^2 = \left(\frac{a}{\pi} u\right)^2$

$\hookrightarrow \bar{x^2} = \int_{-\pi/2}^{\pi/2} \left(\frac{a}{\pi}\right)^3 \cdot \left(\frac{2}{a}\right) u^2 \cos^2(u) du \rightarrow \text{look up!}$

$$\boxed{\bar{x^2}} = \frac{\pi}{4} \left(\frac{\pi^2}{6} - 1 \right) \cdot \left(\frac{2}{a} \right) \left(\frac{a}{\pi} \right)^3 = \boxed{(0.18a)^2}$$

$$\bar{p^2} = \int_{-a/2}^{a/2} \Psi^* (-ik)^2 \frac{\partial^2}{\partial x^2} \Psi dx = \int_{-a/2}^{a/2} (-ik)^2 \frac{\partial^2}{\partial x^2} \Psi^* \Psi dx$$

Can be tricky... $\Psi = \cos\left(\frac{\pi x}{a}\right)$

$$\frac{\partial^2 \Psi}{\partial x^2} = \left(\frac{\pi}{a}\right)^2 \Psi \cdot (-1)$$

$$\hookrightarrow \bar{p^2} = (-ik)^2 \left(\frac{\pi}{a}\right)^2 \int_{-a/2}^{a/2} \Psi^* \Psi dx = \boxed{\frac{k^2 \pi^2}{a^2} = \bar{p^2}}$$

1

Result $\begin{cases} (\Delta x)^2 = -(\bar{x})^2 + (\bar{x^2}) = (0.18a)^2 \\ (\Delta p)^2 = -(\bar{p})^2 + (\bar{p^2}) = \frac{k^2 \pi^2}{a^2} \end{cases} \Rightarrow \begin{cases} \Delta x = 0.18a \\ \Delta p = \frac{k\pi}{a} \end{cases}$

$\hookrightarrow \Delta x \Delta p = 0.18k\pi \approx (0.57k) > \frac{k}{2}$ as needed in QM.

Now, TIME TO SOLVE THE SCHRODINGER EQUATION

The Time-Independent Schrödinger Eqn

If $V(x, t) = V(x)$ only, can simplify the SE
 \Rightarrow use "the separation of variables"

\hookrightarrow changes a PDE into an ODE

(partial diff. eq) (ordinary diff. eq)

We can start from $\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi(x, t) = i\hbar \frac{\partial \Psi}{\partial t}$
 ↓
 no t dependence

Assume that space & time dependence separates!

↪ $\boxed{\Psi(x, t) = \Psi(x) \phi(t)}$ → okay... plug into SE

↪ $\boxed{\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x) \Psi(x) \phi(t) = i\hbar \Psi(x) \frac{d\phi(t)}{dt}}$

ordinary derivative

Divide whole eq by $\Psi(x)\phi(t)$ → becomes

$\frac{1}{\Psi(x)} \left[\frac{-\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) \right] = \left(\frac{i\hbar}{\phi(t)} \right) \frac{1}{\phi(t)} \frac{d\phi(t)}{dt}$

separated form

The only way this can hold $\Psi(x, t)$, which are independent of each other is if both sides equal the same constant
 ↪ call it G

↪ $\left\{ \begin{array}{l} \frac{1}{\Psi(x)} \left[\frac{-\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) \right] = G \\ \left(\frac{i\hbar}{\phi(t)} \right) \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = G \end{array} \right.$

⇒ $\left\{ \begin{array}{l} \frac{-\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + V(x) \Psi = G \Psi \quad (x) \\ \left(\frac{i\hbar}{\phi(t)} \right) \frac{d\phi(t)}{dt} = G \phi(t) \quad (t) \end{array} \right.$

We need to find what G is...

Look at (t) eq: $\frac{d\phi(t)}{dt} = \frac{-iG\phi(t)}{\hbar}$ Guess the solution

↪ $\{\phi(t) = e^{-iGt/\hbar}\}$

Using an Euler identity $e^{-iGt/\hbar} = \cos\left(\frac{Gt}{\hbar}\right) - i \sin\left(\frac{Gt}{\hbar}\right)$

$$e^{-iEt/\hbar} \psi = \cos\left(2\pi \frac{E}{\hbar} t\right) - i \sin\left(2\pi \frac{E}{\hbar} t\right)$$

Dimensionally $\frac{E}{\hbar}$ = frequency = $\omega \Rightarrow E = \hbar\omega$
 But we know $E = \hbar\omega$ in QM

We know that in QM $\Rightarrow E = \hbar\omega = \text{constant}$ (energy of particle)

$$\phi(x) = e^{-iEt/\hbar}$$

Look at (x) eq:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \right] \quad (\text{time independent SE})$$

The full solution is

$$\Psi(x, t) = \psi(x) \phi(t) = \psi(x) e^{-iEt/\hbar}$$

Recall the hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) = H(x)$$

See that the time independent SE is

$$\hat{H}\psi(x) = E\psi(x)$$

This has a special form: (operator)(function) = (number)(function)

→ This is called an Eigenvalue problem

{ number → E = eigenvalue
 function → $\psi(x)$ → eigenfunction/eigen vector/eigenstate

→ We often call $\psi(x)$ → the energy eigenfunction

→ The problem of solving the time independent SE is the same as finding all the eigenvalues - eigenfunctions of \hat{H}

Chapter 5, cont (Reading notes)

Feb 17, 2023

Time-independent Schrödinger equation & Eigenvalue, Eigenfunction-

Assume $\Psi(x, t) = \Psi(x)\phi(t)$, then Schrödinger Equation becomes:
 ↴ and $V(x, t) = V(x)$

$$\frac{-\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V(x, t)\Psi(x, t) = i\hbar \frac{d}{dt}\Psi(x, t)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2\Psi(x)\phi(t)}{dx^2} + V(x)\Psi(x)\phi(t) = i\hbar \frac{d}{dt}\Psi(x)\phi(t) \quad (\text{PDE})$$

$$-\frac{\hbar^2}{2m} \phi(t) \left[\frac{d^2\Psi(x)}{dx^2} \right] + V(x)\Psi(x)\phi(t) = i\hbar \Psi(x) \left[\frac{d\phi(t)}{dt} \right] \quad (\text{ODE})$$

$$\Rightarrow \underbrace{\frac{1}{\Psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) \right]}_{\text{independent of } x} = \underbrace{i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt}}_{(\text{divide by } \Psi(x)\phi(t))} \quad (\text{independent of } x)$$

but both have to be equal $\forall x, t \Rightarrow$ both equal a constant G

$E = G$ by
de Broglie

$$\Rightarrow \begin{cases} -\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = G\Psi(x) = E\Psi(x) \\ i\hbar \frac{d\phi(t)}{dt} = G\phi(t) \end{cases} \Rightarrow \begin{cases} \hat{E}\phi(t) = G\phi(t) \\ \phi(t) \text{ has form } e^{i\alpha t} \end{cases}$$

$$\phi = e^{-iGt/\hbar}$$

$$= \cos(\alpha) + i\sin(\alpha)$$

$$\hookrightarrow G = \hbar\omega = E$$

$$\Rightarrow i\hbar\alpha e^{i\alpha t} = Ge^{i\alpha t} \Rightarrow G = i\hbar\alpha \Rightarrow \alpha = \frac{G}{i\hbar} = -\frac{iG}{\hbar}$$

$$\Rightarrow \boxed{\phi(t) = e^{-iGt/\hbar}}$$

$$\text{and Recall Hamiltonian } \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$$

$$\text{and } \frac{-\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = \boxed{E\Psi(x) = \hat{H}\Psi(x)} \Rightarrow E = \text{eigenvalue}$$

$\Psi = \text{eigenfunction}$

→ Solve the time-independent SE is the same as finding all eigenvalues + eigenfunctions of \hat{H}

Required properties of eigenfunctions

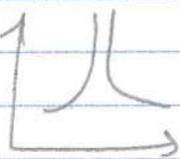
Ψ finite	$\Psi(x)$ finite
Ψ single-valued	$\Psi'(x)$ single-valued
Ψ continuous	$\Psi''(x)$ continuous.

Quantization of energy comes from the fact that acceptable solutions to time-independent SE can be found only for certain values of E .

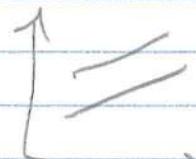
→ $\Psi(x)$ well-behaved... If $\Psi(x)$ or $d\Psi(x)/dx$ not finite/single-valued then same would be true for $\Psi(x,t) = \frac{\partial}{\partial x} \Psi(x,t)$ → unacceptable because we might not obtain finite and definite values when we evaluate measurable quantities.

x & p do not behave in unreasonable ways.

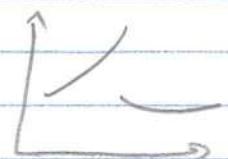
NOT well-behaved $\Psi(x)$



infinite



multi-valued



not-continuous.

In order for $d\Psi/dx$ to be finite $\Rightarrow \Psi$ must be continuous!

Consider: $\frac{-\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi \Rightarrow \frac{d^2\Psi(x)}{dx^2} = \frac{2m}{\hbar^2} [V(x) - E]\Psi(x)$

$V(x), E, \Psi(x)$ finite $\Rightarrow \frac{d^2\Psi(x)}{dx^2}$ finite. $\rightarrow \frac{d\Psi(x)}{dx}$ must also be continuous.

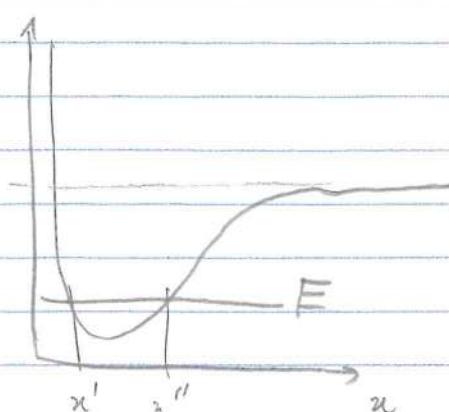
Energy quantization

Consider

$$\frac{d^2\Psi(x)}{dx^2} = \frac{2m}{\hbar^2} [V(x) - E]\Psi(x)$$

$V(x)$

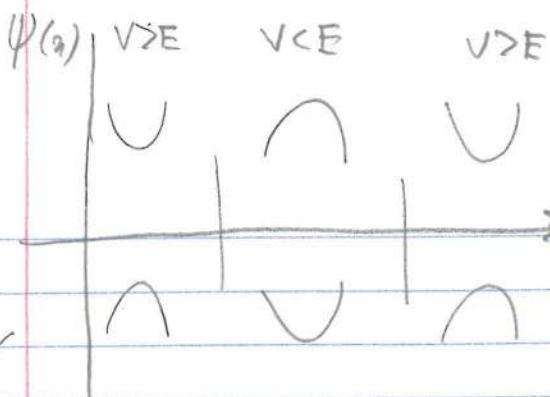
For $x < x' < x > x''$ $V(x) > E$ (III), (I)



For $x' < x < x''$ $V(x) < E$ (II)

\rightarrow sign of $\frac{d^2\Psi(x)}{dx^2} \Psi(x)$ = same in (I) & (III)
different in (II)

(I) (II) (III)



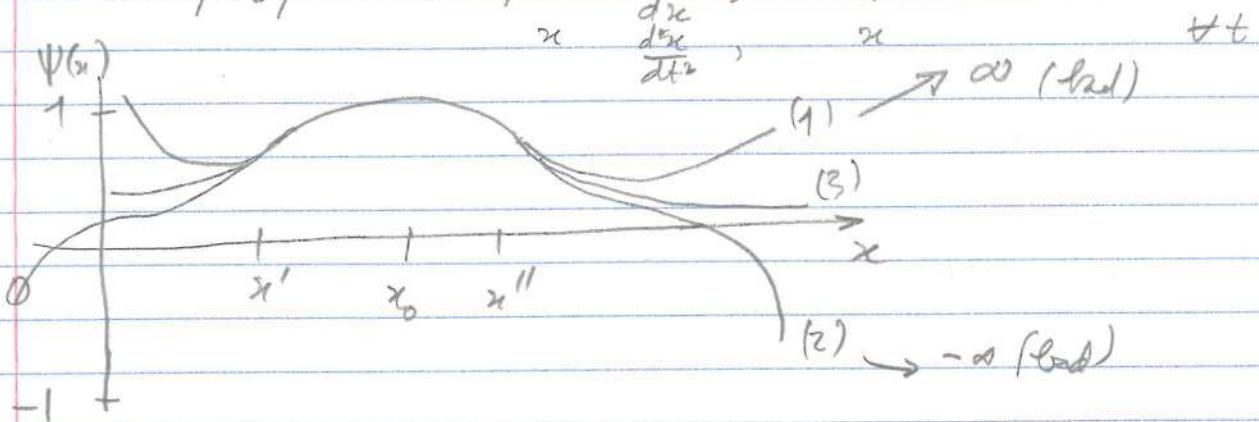
(23)

$$\text{Analogy} \quad \frac{d^2\psi(x)}{dx^2} = \frac{-2m}{\hbar^2} [V - E] \psi(x)$$

Newton's
spring $\rightarrow \frac{d^2x(t)}{dt^2} = -\frac{k}{m} x(t)$

particular behavior of

If we specify the value of $\psi = \frac{d\psi}{dx}$, then ψ is determined $\forall x$.



Recall ψ has to be finite.

If find E^* such that

and F^* such that

$$(3) \frac{d^2\psi}{dx^2} \rightarrow 0 \Leftrightarrow \psi \rightarrow 0$$

then acceptable $E = E^* \cap F^*$

But hard to find ψ such that $\psi \rightarrow 0$ as $x \rightarrow \infty$ or $x \rightarrow -\infty$

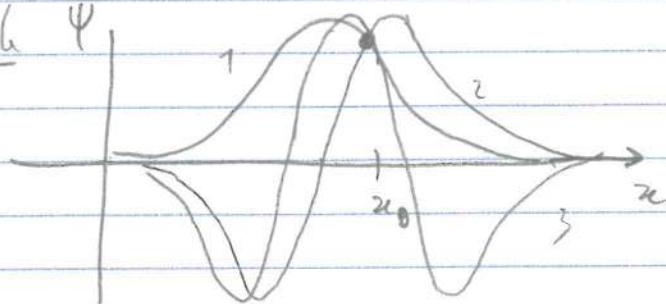
$$\frac{dV}{dx}$$

$E^* \cap F^*$ where these are the

Energy levels such that $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$

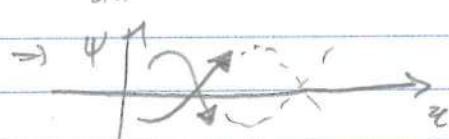
But $\exists E_1, E_2, \dots$ such that SE has acceptable solutions $\psi_1, \psi_2, \psi_3, \dots$

Example ψ



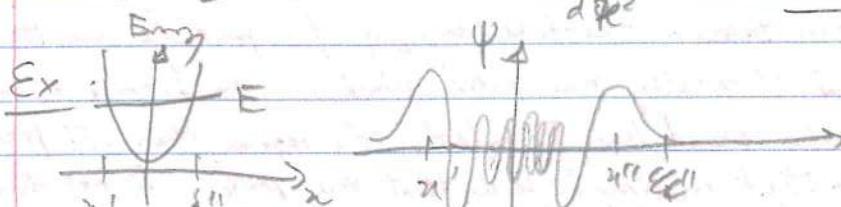
$$\text{Add } (V - E(x)) < 0$$

$$\rightarrow \frac{d^2\psi}{dx^2} \psi(x) < 0$$

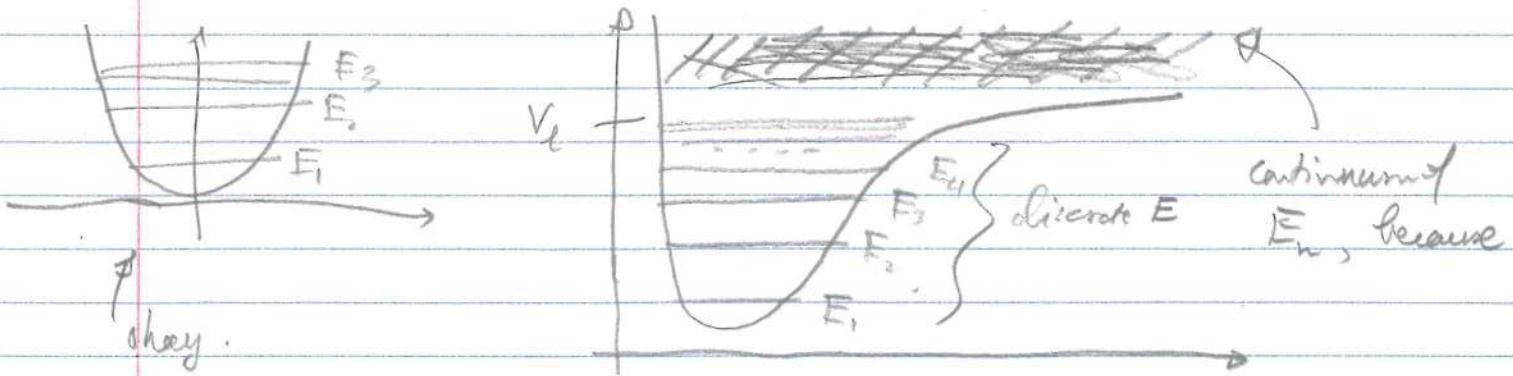


~~Effects~~ $[V(x) - E]^2 \rightarrow \frac{d^2\psi}{dx^2} \uparrow \Rightarrow \psi$ oscillates faster!

Ex:



Potential "well" vs. potential with limiting value of V .



If the atom is unbound (assumed V_c) ($E > V_c$) $\Rightarrow \nabla - E < 0$ Ψ

$\hookrightarrow \frac{d^2\Psi}{dr^2} \Psi < 0 \Rightarrow \Psi$ tends to return to the axis. \Rightarrow oscillating for

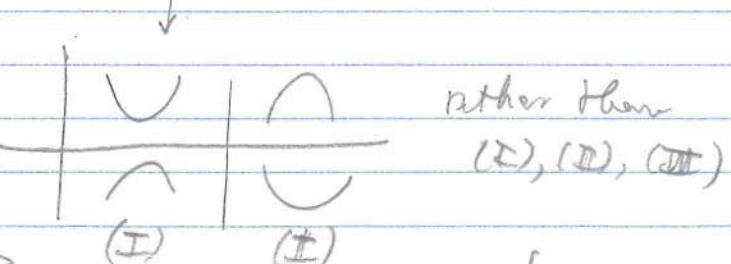
\hookrightarrow But here E need not be discrete, but rather continuum.

\hookrightarrow Because you only have Region (I) + (II)

If there's only 2 regions, and

in the second region, Ψ always tends to axis

\Rightarrow we can find E such that Ψ tends to axis

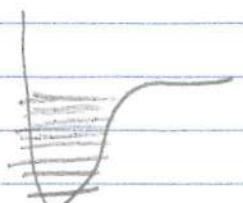


rather than (I), (II), (III)

for region (II) \Rightarrow we need to satisfy Ψ for both regions

CONTINUUM of E if $E > V_c$

If, however $E < V_c \Rightarrow$ bounded within "well"



Then $\Psi \rightarrow 0$ has to be met in (I) + (II)

\hookrightarrow QUANTIZATION

(Read p163)

"When the relation between the total energy of a particle and its potential energy is such that classically the particle would be bound to a limited region of space b/c the V would exceed the E outside the region, then SE predicts that the E is quantized. When that relation is such that the particle is not bound to a limited region b/c there exists no r for which $E = V$... then E ... can have values."

Recall $\Psi(x, t) = \psi(x)\phi(t) = \psi(x)e^{-iEt/\hbar}$

Feb 19, 2018

where $\hat{H}\Psi = E\Psi \rightarrow$ eigenvalue problem.

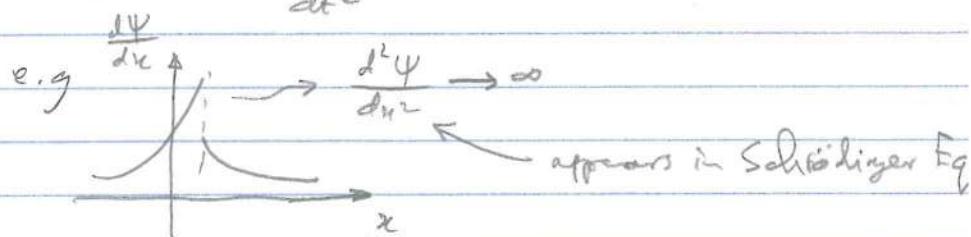
Properties of the eigenfunction:

- $\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$ (must be "square-integrable")
So ψ is normalizable.

Requirements

- $\psi(x) \text{ & } \frac{d}{dx}\psi(x)$ must be finite, single-valued, and continuous.

$\left\{ \begin{array}{l} \text{finite} \Rightarrow \text{don't get infinite answers.} \\ \text{single-valued} \Rightarrow \text{avoid multiple probabilities.} \\ \text{continuous} \Rightarrow \text{so that } \frac{d^2}{dx^2}\psi(x) \text{ is not infinite} \end{array} \right.$



Eigenfunctions have another important property:

⇒ Can look at it very generally.

Suppose \hat{A} = operator for some physical quantity A (e.g. p, n, E)
 ψ is an eigenfunction of \hat{A}

↳ obeys:

$$\hat{A}\psi = a\psi$$

where a is a number $\rightarrow a = \text{eigenvalue}$.

Suppose we measure quantity \hat{A} . What do we get for $\bar{A} = \langle A \rangle$?

$$\bar{A} = \int \psi^* \hat{A} \psi dx = \int \psi^* a \psi dx = a \int \psi^* \psi dx = a$$

Should be using $\Psi(x, t)$, but $|e^{-iEt/\hbar}|^2 = 1$

↳ Observe $\boxed{\bar{A} = a}$ expected value = eigenvalue.

Now, what do we get for $\langle Da \rangle$?

$$\Delta A = \sqrt{\bar{A}^2 - A^2} \rightarrow \text{find } \bar{A}^2$$

$$\bar{A}^2 = \int \Psi^* \bar{A}^2 \Psi = \int \Psi^* a^2 \Psi dx = a^2 \int \Psi^* \Psi dx = a^2$$

$$\text{See that } \Delta A = \sqrt{a^2 - a^2} = 0$$

■ We see that when Ψ is an eigenfunction of \hat{A} , then the measurement of A gives "a" exactly each time.

$$\left\{ \begin{array}{l} \bar{A} = a \\ \Delta A = 0 \end{array} \right\}$$

Doesn't this violate the uncertainty principle? $\hat{H}\Psi = E\Psi$

$\hat{H}\Psi = E\Psi$ means the energy of state Ψ is exact $\Rightarrow \Delta E = 0$
but Ψ depends on time.
 $\Psi = \Psi(x) e^{-iEt/\hbar}$

Observe:

$$|\Psi(x,t)|^2 = \Psi^*(x) \Psi(x) \text{ since } |\phi(x)|^2 = 1$$

↳ so probability distribution is time independent \Rightarrow Eternally the same

$$\Rightarrow \Delta t = \infty$$

$$\Rightarrow \text{Can still have } \Delta E \Delta t \geq \frac{\hbar}{2}$$

We can also look at eigenfunction of $\hat{p} = (-i\hbar) \frac{d}{dx}$

$$\hat{p}\Psi = p\Psi$$

$$(-i\hbar) \frac{d}{dx} \Psi = p\Psi$$

$$\text{get } \Psi(x) = e^{ipx/\hbar} = e^{-ipx/\hbar}$$

here $p = \text{exact} \Rightarrow \Delta p = 0$ (as in eigenvalue problem)

But at the same time $\Psi(x) = e^{ipx/\hbar} = \text{pure wave}$

$\boxed{\Delta x = \infty} \leftarrow \text{real + imaginary part spans } x = -\infty \rightarrow \infty$

$$\Rightarrow \text{again, } \Delta x \Delta p \geq \frac{\hbar}{2}$$

General Solution

Here's our approach to solving the Schrödinger Equation when $V(r) = V$ (time independent)

↪ separate variable $\Psi(r, t) = \psi(r) \phi(t)$

For $\phi(t)$, we find $\phi(t) = e^{-iEt/\hbar}$

For $\psi(r)$, we need to solve the time-independent SE

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \psi(r) + V(r) \psi(r) = E \psi \Rightarrow$$

$$\hat{H} \psi = E \psi$$

→ depends on what $V(r)$ is
where \hat{H} is the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V(r)$$

When we solve this \Rightarrow we'll get different possible solution or infinitely many $\Rightarrow E_1, E_2, \dots, E_n$ (eigenvalues)
with corresponding eigenfunctions $\psi_1(r), \psi_2(r), \dots, \psi_n(r)$

n : quantum number \neq discrete set of energy levels.

The full time dependent solutions are:

$$\Psi_1(r, t) = \psi_1(r) e^{-iE_1 t/\hbar}$$

$$\Psi_2(r, t) = \psi_2(r) e^{-iE_2 t/\hbar}$$

⋮

$$\Psi_n(r, t) = \psi_n(r) e^{-iE_n t/\hbar}$$

■ If the system is in a particular definite state, then Ψ is the WF for that state.

e.g. $\Psi = \Psi_1$ (ground state)
(lowest energy)

then $E = E_1, \Delta E = 0$

or $\Psi = \Psi_q \rightarrow$ excited state
has $E = E_q, \Delta E = 0$

But since the Schrödinger eqn is a linear equation, any linear combination of solutions are also solutions.

→ The most general solution is a superposition.

$$\Psi(z,t) = c_1 \Psi_1(z,t) + c_2 \Psi_2(z,t) + \dots$$

$$\boxed{\Psi(z,t) = \sum_{i=1}^n c_i \Psi_i(z,t)} \quad \cdot c_i = \text{complex-valued constants}$$

wave-packet solution

Note: quantum mechanical particle can exist in a superposition of different energy states \Rightarrow a mixture of energy states

$$\boxed{\Psi(z,t) = \sum_{n=1}^{\infty} c_n \Psi_n(z) e^{-iE_n t/\hbar}} \quad (E_n = E)$$

has $\Delta E \neq 0 \rightarrow$ gives a wave-packet solution.

Transitions

→ If a particle is in a definite energy state

$$\boxed{\Psi_k = \Psi_k e^{-iE_k t/\hbar}} \quad \leftarrow k^{\text{th}} \text{ state } (n=k)$$

→ measure E yields $E = E_k$ exactly

→ probability density $|\Psi|^2 = |\Psi_k|^2$ has no t -dependence.

The electric charge density $\rho(z,t) = \frac{\text{charge}}{\text{volume}}$

→ for a quantum particle with charge $\pm e$, then the charge density

$$\rho(z,t) = e \left(\frac{\text{probability}}{\text{volume}} \right) = e |\Psi|^2 = e |\Psi_k|^2 \quad \text{in state } k=n$$

no t dependence.

→ Pure energy state have static $p \Rightarrow$ expect NO radiation (photons)

To get radiation, need time dependent in $p \rightarrow$ need a mixture

$$\Psi(z,t) = c_1 \Psi_1(z) e^{-iE_1 t/\hbar} + c_2 \Psi_2(z) e^{-iE_2 t/\hbar}$$

↑ states

no longer have $\Delta E = 0$

$$|\Psi|^2 = \Psi^* \Psi = |c_1|^2 |\Psi_1(z)|^2 + |c_2|^2 |\Psi_2(z)|^2 + c_1^* c_2 \Psi_1^* \Psi_2 e^{-i(E_2 - E_1)t/\hbar} + c_2^* c_1 \Psi_2^* \Psi_1 e^{+i(E_2 - E_1)t/\hbar}$$

→ This has time dependence

⇒ get photons (radiation)

→

Feb 21, 2012 Hawell Transition ⇒ get radiation from oscillating charge

need

$$p = e |\Psi|^2 \rightarrow$$
 have time dependent to get \curvearrowright

⇒ need a superposition.

$$\Psi = c_1 \Psi_1(z) e^{-iE_1 t/\hbar} + c_2 \Psi_2(z) e^{-iE_2 t/\hbar}$$

$$\left. \begin{aligned} |\Psi|^2 &= |c_1|^2 |\Psi_1(z)|^2 + |c_2|^2 |\Psi_2(z)|^2 + c_1^* c_2 \Psi_1^* \Psi_2 e^{-i(E_2 - E_1)t/\hbar} \\ &\quad + c_2^* c_1 \Psi_2^* \Psi_1 e^{+i(E_2 - E_1)t/\hbar} \end{aligned} \right\}$$

↪ has t dependence.

We look at

$$e^{-i/\hbar(E_1 - E_2)t} = e^{-i\omega t} \quad \text{with } \omega = 2\pi\nu = \frac{E_2 - E_1}{\hbar}$$

$$\hookrightarrow \boxed{\nu = \frac{E_2 - E_1}{\hbar}}$$

↔ much like what Bohr predicted ...

⇒ radiation (photons)

go off with this frequency. We get photons when there's a transition between 2 states.

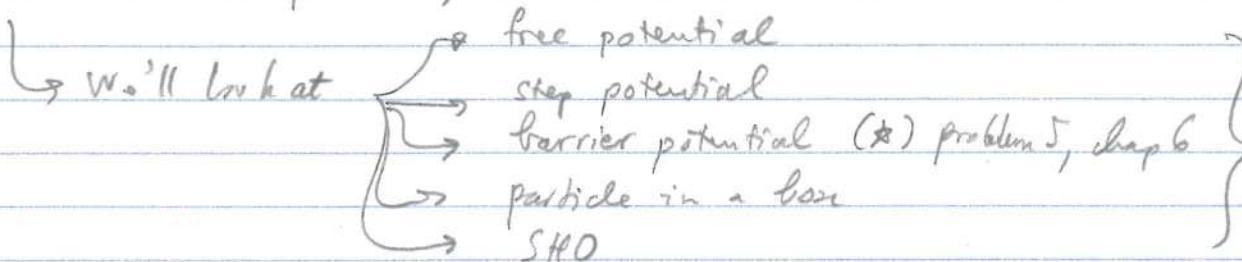
II. One-dimensional Potentials

→ we want to see how to solve the SE for 1D for potentials $V(x)$ with No time dependence.

→ can separate variables: $\Psi(x,t) = \Psi(x)e^{-iEt/\hbar}$
where $\Psi(x)$ is a solution to a 1-D SE. (time-independent)

$$\frac{-\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = (i\hbar) \frac{d}{dt}\Psi(x) = E\Psi(x)$$

→ need to look separately at different cases with different $V(x)$.



→ all of these cases give exact solutions...

(The free particle) $\xrightarrow{\text{fr}} V=0$ (zero potential)

Time-independent SE $\rightarrow \boxed{\frac{-\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi(x)}$

$$\Rightarrow \boxed{\frac{d^2\Psi}{dx^2} = -\frac{2mE}{\hbar^2}\Psi(x)}$$

Let $k = \sqrt{\frac{2mE}{\hbar^2}}$, and note $E = \frac{p^2}{2m} + \frac{k^2}{2}$ $\rightarrow p = \sqrt{2mE} = \frac{\hbar k}{2}$

See that $\boxed{k = \sqrt{\frac{2mE}{\hbar^2}}}$ where $k = \frac{2\pi}{\lambda}$ is the wavenumber
wave number.

This $k =$ wave number for the free particle wave

$$\boxed{\frac{d^2\Psi(x)}{dx^2} = -k^2\Psi(x)}$$

See that $\Psi(x) = \underline{\sin(kx)}$ or $\underline{\cos(kx)}$ are solutions
but also
 $\Rightarrow \Psi(x) = \underline{e^{ikx}}$ or $\underline{e^{-ikx}}$

But ω , \sin , e are not linearly independent due to the Euler identity.

$$e^{\pm i kx} = \cos(kx) \pm i \sin(kx)$$

It's a choice for which pair to use. But as waves, they behave differently. We can get standing waves or traveling waves depending on which choice we pick.

We can see this by putting the t -dependence.

$$\Psi(x,t) = \Psi(x) \phi(t) = \Psi(x) e^{-iEt/\hbar} = \Psi(x) e^{-iwt}$$

where $w = \frac{E}{\hbar}$. So for $\sin(kx)$, and $\cos(kx)$, we get

$$\Psi(x,t) = e^{-iwt} \cdot \sin(kx) \quad \leftarrow \text{standing wave}$$

Because Ψ has fixed nodes at $kx = 0, \pm \pi, \pm 2\pi, \dots$

Time dependence \rightarrow fluctuating complex-valued amplitude.

$$\hookrightarrow [\sin(kx), \cos(kx)]$$

\hookrightarrow gives standing waves.

For $\Psi(x) = e^{\pm ikx}$, we get traveling waves

$$\text{e.g. } \Psi(x,t) = e^{ikx} e^{-iwt} = e^{i(kx-wt)} = \cos(kx-wt) + i \sin(kx-wt)$$

\hookrightarrow This is a traveling wave to the right.

Look at node $\sin(kx-wt)$ does NOT have fixed nodes.

where $kx-wt = 0 \rightarrow kx-wt = 0$ or zero node \nexists that moves.

$$\sin = 0$$

$$-kx \frac{dx}{dt} \rightarrow k \frac{dx}{dt} - w = 0 \rightarrow \frac{dx}{dt} - \frac{w}{k} > 0 \quad (\text{wave speed})$$

\hookrightarrow $\lambda \rightarrow$

So the other solution

$$\hookrightarrow e^{-i(kx+wt)} \rightarrow [kx+wt = 0] \rightarrow \frac{dx}{dt} = \frac{-w}{k} \quad \leftarrow \text{moves to the left.}$$

Look at node where $\sin = 0$

So which form of wave do we use?

- For scattering problem \rightarrow Traveling waves $\rightarrow e^{\pm i\theta x}$

- For bound systems (particle in a box) \rightarrow Standing waves
 $\rightarrow \sin(\theta x), \cos(\theta x)$

Note: for all of these solution, the waves have infinite extent
 \rightarrow makes NORMALIZATION a problem.

e.g. $\boxed{\Psi(x,t) = \psi(x)\phi(t) = e^{i(\theta x - \omega t)}}$

$$\downarrow |\Psi(x,t)|^2 = 1 \quad \overbrace{1}^{\uparrow |\Psi|^2} \leftrightarrow / / / / / T \rightarrow$$

$$\text{So } \int_{-\infty}^{\infty} \Psi^* \Psi dx = \int_{-\infty}^{\infty} 1 dx = x \Big|_{-\infty}^{\infty} = \infty$$

\rightarrow DOES NOT OBEY $\Psi \rightarrow 0$ as $x \rightarrow \pm \infty$
 \rightarrow not square integrable.

But these are idealized solutions. \rightarrow More practical free-particle solutions don't need infinite extent.

\hookrightarrow We can use "Box normalization" \rightarrow cut off Ψ at some far-away distance.

$$\bar{\Psi} = \begin{cases} Ae^{i(\theta x - \omega t)} & -L < x < L \\ 0 & x < -L \text{ or } x > L \end{cases}$$

Then $|\bar{\Psi}|^2 = A^2$ only inside $-L < x < L$

$$\rightarrow \int_{-\infty}^{\infty} |\bar{\Psi}|^2 dx = \int_{-L}^{L} A^2 dx = A^2 x \Big|_{-L}^{L} = 2A^2 L = 1$$

Choose $A = \frac{1}{\sqrt{2L}}$

Interestingly, L won't matter most of the time.

e.g. $\bar{p} = \int_{-L}^L \left(\frac{1}{\sqrt{2L}}\right)^2 e^{-ikx} (-ik) \frac{d}{dx} e^{ikx}$

$$= \frac{1}{2L} (-ik)(ik) \int_{-L}^L \underbrace{e^{-ikx} + e^{ikx}}_1 dx = \boxed{tk = \bar{p}}$$

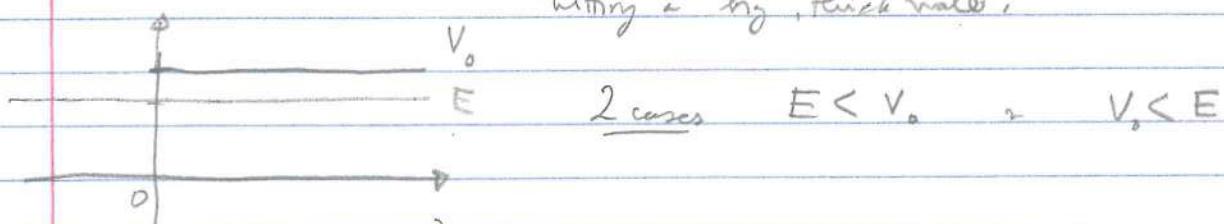
L don't matter.

↳ will often write $\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$, but where it's assumed box normalization is used

Feb 23, 2018

The Step Potential

Consider a particle moving in from the left, hitting a big, thick wall.



For $E < V_0$ → classically $E = \frac{p^2}{2m} + V(x)$

$$\text{For } x < 0 \Rightarrow V(x) = 0 \Rightarrow E = \frac{p^2}{2m}$$

$$\text{For } x > 0 \Rightarrow E = \frac{p^2}{2m} + V_0$$

$$\text{but } \frac{p^2}{2m} = E - V_0 < 0 \rightarrow \text{NOT POSSIBLE} \Rightarrow$$

→ Classically, the particle bounces back to the left.

→ no motion beyond $x > 0$

↳ "classically forbidden region"

• What happens quantum mechanically? ⇒ SE is different in 2 regions

$$(left) \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (x < 0)$$

$$(right) \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0 \psi = E\psi \quad (x > 0)$$

what we do is solve both solutions, then match Ψ , $\frac{d\Psi}{dx}$ at $x=0$
 so the overall solution is continuous.

$$\boxed{\text{For } x < 0}, V = 0 \rightarrow \text{Free particle, 0 potential} \Rightarrow \boxed{\Psi(x) = Ae^{ik_1 x} + Be^{-ik_1 x}}$$

Note We've chosen to use $e^{\pm ik_1 x}$, not \sin/\cos since
 $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ traveling wave.

The problem involves a moving particle.

$$\boxed{\text{For } x > 0} \Rightarrow -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = (E - V_0)\Psi - \frac{d^2\Psi}{dx^2} = \boxed{-\frac{2m}{\hbar^2}(E - V_0)\Psi}$$

Note $E < V_0$

$$\Rightarrow \boxed{\frac{d^2\Psi}{dx^2} = \left[\frac{2m}{\hbar^2}(V_0 - E) \right] \Psi} \text{ call } \frac{2m}{\hbar^2}(V_0 - E) = k_2^2$$

Now $e^{\pm ik_2 x}/\sin(k_2 x)/\cos(k_2 x)$ are not solutions. Instead,
 $e^{k_2 x}$ or $e^{-k_2 x}$ are solutions. (or $\sinh(k_2 x)$ and $\cosh(k_2 x)$)

∴ The general solution: $\boxed{\Psi(x) = Ce^{k_2 x} + De^{-k_2 x}} \quad (x > 0)$

The math solutions

$$\boxed{\Psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x} & (x < 0) \\ Ce^{k_2 x} + De^{-k_2 x} & (x > 0) \end{cases}}$$

We find A, B, C, D

by requiring $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$, and by matching $\Psi(x), \frac{d\Psi}{dx}$ at $x=0$ boundary and lastly by normalizing.

Finiteness • as $x \rightarrow +\infty$, $Ce^{k_2 x} \rightarrow \infty$. Must require $C = 0$
 as $x \rightarrow -\infty$,

$\Psi(x) = Ae^{ik_1 x} + Be^{-ik_1 x}$ oscillates all the way
 must use box normalization to $-\infty$
 (we won't)

$$\Psi \text{ continuous} \Rightarrow \boxed{\left. \Psi_{x<0} \right|_{x=0} = \left. \Psi_{x>0} \right|_{x=0}}$$

$$\Rightarrow (Ae^{ik_1 x} + Be^{-ik_1 x}) \Big|_{x=0} = De^{-ik_2 x} \Big|_{x=0}$$

(1)

$$\frac{d\Psi}{dx} \text{ continuous} \Rightarrow \boxed{\left. \frac{d\Psi_{x<0}}{dx} \right|_{x=0} = \left. \frac{d\Psi_{x>0}}{dx} \right|_{x=0}}$$

$$ik_1(Ae^{ik_1 x} - Be^{-ik_1 x}) \Big|_{x=0} = -k_2 D e^{ik_2 x} \Big|_{x=0}$$

$$\Rightarrow ik_1(A - B) = -k_2 D \Rightarrow \boxed{A - B = \frac{ik_2 D}{k_1}} \quad (2)$$

(1)(2) \Rightarrow solve for $A \sim B$ in terms of D → add - subtract

$$\hookrightarrow \boxed{A = \frac{1}{2} \left(1 + \frac{ik_2}{k_1} \right) D \quad \& \quad B = \frac{1}{2} \left(1 - \frac{ik_2}{k_1} \right) D} \quad (c=0)$$

Now solution is

$$\Psi(x) = \begin{cases} \frac{1}{2} \left(1 + \frac{ik_2}{k_1} \right) D e^{+ik_1 x} + \frac{1}{2} \left(1 - \frac{ik_2}{k_1} \right) D e^{-ik_1 x} & (x < 0) \\ D e^{-ik_2 x} & (x > 0) \end{cases}$$

We can find D by normalizing, but we don't bother.

\Rightarrow leave $\Psi(x)$ unnormalized.

• How do we interpret the 3 terms? → need to include t dependence

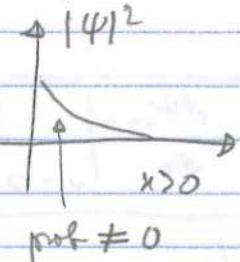
$$e^{-iEt/\hbar} = e^{-i\omega t} \quad E = \hbar\omega$$

$$\hookrightarrow \boxed{\Psi(x,t) = \begin{cases} \frac{D}{2} \left(1 + \frac{ik_2}{k_1} \right) e^{i(k_1 x - \omega t)} + \frac{D}{2} \left(1 - \frac{ik_2}{k_1} \right) e^{i(k_1 x + \omega t)} & , x < 0 \\ D e^{-ik_2 x} \cdot e^{-i\omega t} & , x > 0 \end{cases}}$$

makes sense since
 1st term is a traveling wave to the right \Rightarrow (incoming wave)
 2nd term is a traveling wave to the left \Rightarrow (reflected wave)
 3rd, i.e., NOT ... ↓ ... demand $\int |\Psi|^2 = N^2 - 2k_2 x \quad (x > 0)$

$\Rightarrow |\text{3rd term}|^2 \Rightarrow$ has exponentially falling off probability density for $x > 0$

\Rightarrow So In QM, we find nonzero probability for penetration into the "classically forbidden region".



Now, we want to see how much is reflected relative to incoming probability.
 \downarrow
 $R = \text{ratio}$

For $n \neq 0$ Calc Rec Be $R = \frac{|B e^{-ik_1 x + wt}|^2}{|A e^{ik_1 x - wt}|^2} = \frac{B^* B}{A^* A} = \frac{|B|^2}{|A|^2}$

reflection coefficient

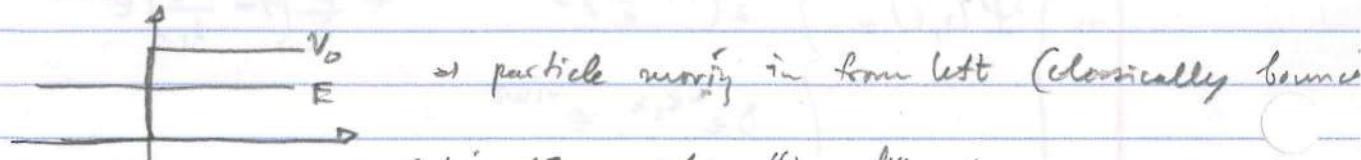
$$\Rightarrow R = \frac{\frac{D^* D}{4} \left(1 - \frac{ik_2}{k_1}\right)^* \left(1 - \frac{ik_2}{k_1}\right)}{\frac{D^* D}{4} \left(1 + \frac{ik_2}{k_1}\right)^* \left(1 + \frac{ik_2}{k_1}\right)} = \frac{\left(1 + \frac{ik_2}{k_1}\right) \left(1 - \frac{ik_2}{k_1}\right)}{\left(1 - \frac{ik_2}{k_1}\right) \left(1 + \frac{ik_2}{k_1}\right)}$$

So R = 1 \Rightarrow 100% probability that the particle is reflecting. But it reflects with some penetration beyond $x = 0 \rightarrow x > 0$

\Rightarrow No accumulation of probability at $x > 0$, since it all reflects.

\Rightarrow New QM phenomena \Rightarrow QM particle can penetrate into classically forbidden region.

Feb 26, 2018 Recall Step potential ($E < V_0$)



Solving SE, matching $\Phi_2 \frac{d\Phi}{dx}$ at $x = 0$

$$\Rightarrow k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

Looked at the reflection coefficient found: $R = 1 \rightarrow 100\%$ probability to reflect

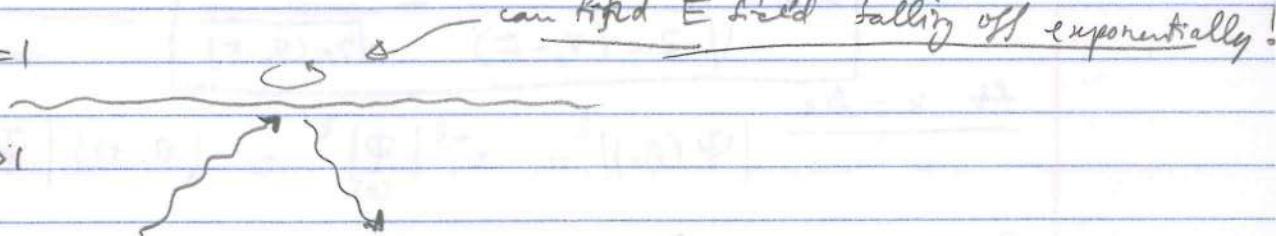
But $|\Psi|^2 = D^2 e^{-2k_2 x}$, $x > 0$, is not zero.

\Rightarrow set penetration in classically forbidden region.

normal
wave
behavior

(*) Similar thing happens with light waves with total internal reflection

$$n=1$$



Look at $\Psi(x)$ again, for $x < 0$.

$$\boxed{\Psi(x) = \frac{D}{2} \left(1 + \frac{i k_2}{k_1} \right) e^{i k_1 x} + \frac{D}{2} \left(1 - \frac{i k_2}{k_1} \right) e^{-i k_1 x}}$$

In problem 6-1 \Rightarrow show:

$$\boxed{\Psi(x) = D \left(\cos(k_1 x) - \frac{k_2}{k_1} \sin(k_1 x) \right)}$$

The full time dependence solution is

$$\boxed{\Psi(x,t) = D \left(\cos(k_1 x) - \frac{k_2}{k_1} \sin(k_1 x) \right) e^{-i \omega t}}, \quad x < 0$$

has fixed nodes oscillating amplitude

\Rightarrow complex-valued standing wave

\hookrightarrow = superposition of 2 traveling waves

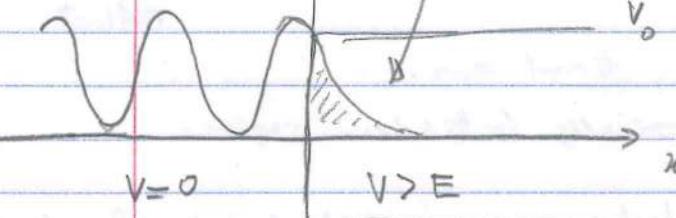
Traveling waves being incident wave superimpose w/ reflecting wave.

\hookrightarrow Probability density $= |\Psi(x,t)|^2$. Can plot it for $x < 0$ and $x > 0$ where $|\Psi(x,t)|^2 = D^2 e^{-2k_2 x}$

$$\sin^2 + \cos^2 \dots |\Psi|^2$$

$$p = \hbar k = \frac{\hbar}{2\pi} k = \frac{\hbar \omega}{2} \rightarrow \lambda = \frac{2\pi}{k}$$

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We can define a penetration depth

Since $k_2 \approx m^{-1} \sim \frac{1}{\text{length}}$

Call $\Delta x = \frac{1}{k_2}$ the penetration depth

$$\Delta x = \sqrt{\frac{k^2}{2m(V_0 - E)}} = \frac{\hbar^2}{\sqrt{2m(V_0 - E)}}$$

At $x = \Delta x$

$$|\Psi(\Delta x)|^2 = e^{-2} |\Psi_{(0)}|^2 \approx (0.13) |\Psi_{(0)}|^2 \quad \text{comparison}$$

{ Ex tiny but microscopic object ...

$m = 4 \times 10^{-14} \text{ kg}$ $v = 10^5 \text{ m/s}$, suppose it hits a step with $V_0 = 2 \text{ (keV)}$

$$\Rightarrow V_0 - E = 2\left(\frac{1}{2}mv^2\right) = \left(\frac{1}{2}mv^2\right) \approx 2 \times 10^{-10} \text{ J}$$

$$\Rightarrow \Delta x \approx \frac{\hbar}{\sqrt{2m(2 \times 10^{-10} \text{ J})}} \approx 2 \times 10^{-19} \text{ m} \quad \left(\sim \frac{1}{1000} \text{ of proton radius} \right)$$

\Rightarrow [has no effect at all.]

Ex Quantum electron, $m = 9.11 \times 10^{-31} \text{ kg}$, in a block of copper.

Find Δx for an electron in a block of copper

$V_0 = 0$ inside

work function

$(V_0 - E) \approx 4 \text{ eV}$ needed to

$V_0 > E$ outside

extract an electron.

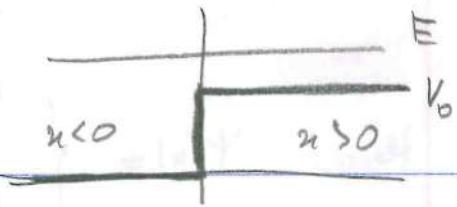
Get $\Delta x \approx 10^{-10} \text{ m} \approx \text{size of an atom}$

has consequences in atomic physics.

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39

Step Potential but $E > V_0$



→ particle coming from the left. Classically, particle slows down but keeps going.

Classically $R=0$ no reflection (R : reflection coeff)
 $T=1 \rightarrow 100\%$ transmission (T : transmission coeff)

QM need to solve the SE

for $x > 0$ & $x < 0$, match $\Psi = \frac{d\Psi}{dx}$ at $x=0$

$$x < 0 \quad -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + 0 = E\Psi \Rightarrow \frac{d^2\Psi}{dx^2} = -\frac{2mE}{\hbar^2}\Psi = -k_1^2\Psi$$

$$x > 0 \quad -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V_0\Psi = E\Psi \Rightarrow \frac{d^2\Psi}{dx^2} = -\frac{2m(E-V_0)}{\hbar^2}\Psi$$

So, for $x < 0$: let $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ $\Rightarrow \Psi = A e^{ik_1 x} + B e^{-ik_1 x}$

for $x > 0 \rightarrow \frac{d^2\Psi}{dx^2} = -\frac{2m}{\hbar^2}(E-V_0)\Psi \quad (E-V_0 > 0)$

Define $k_2 = \sqrt{\frac{2m}{\hbar^2}(E-V_0)}$ $\rightarrow \frac{d^2\Psi}{dx^2} = -k_2^2\Psi$

$\Psi = C e^{ik_2 x} + D e^{-ik_2 x}$

$\Psi(x) = \begin{cases} A e^{ik_1 x} + B e^{-ik_1 x} & x < 0 \\ C e^{ik_2 x} + D e^{-ik_2 x} & x > 0 \end{cases}$ D: physical meaningless.

To interpret these 4 terms → multiply by $e^{-i\omega t}$

$x < 0 \Rightarrow$ incoming + reflected wave (good) ($\rightarrow \Gamma$)

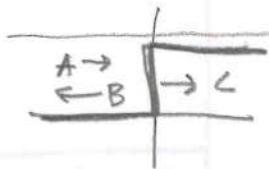
$x > 0 \Rightarrow$ transmitted wave + ???

~~X~~ The 4th term $D e^{-ik_2 x}$ coming in to the left in $x > 0$ does not make sense
 $\Rightarrow D = 0$

(40)

(40)

Here: $\Psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x}, & x < 0 \\ Ce^{ik_2 x}, & x > 0 \end{cases}$



Again, we require continuity of Ψ , $\frac{d\Psi}{dx}$ at $x=0$

$$\Psi \Rightarrow (Ae^{ik_1 x} + Be^{-ik_1 x}) \Big|_{x=0} = (Ce^{ik_2 x}) \Big|_{x=0}$$

$\hookrightarrow \boxed{A+B=C}$

$$\frac{d\Psi}{dx} \Big|_{x=0} \Rightarrow (ik_1)Ae^{ik_1 x} \Big|_{x=0} + (-ik_1)Be^{-ik_1 x} \Big|_{x=0} = (ik_2)Ce^{ik_2 x} \Big|_{x=0}$$

$\hookrightarrow \boxed{k_1(A-B) = k_2 C}$

Since the original wave is A (total incident amplitude)
 $\Rightarrow A$ as reference \Rightarrow solve for B, C in terms of A .
 having the rest unnormalized

$$A+B = \frac{k_1}{k_2} (A-B) \Rightarrow B = \frac{k_1 - k_2}{k_2 + k_1} A$$

Then get

$$C = \frac{2k_2}{k_1 + k_2} A$$

So,

$$\Psi(x) = \begin{cases} Ae^{ik_1 x} + A\left(\frac{k_1 - k_2}{k_2 + k_1}\right)e^{-ik_1 x}, & x < 0 \\ A\frac{2k_2}{k_1 + k_2} e^{ik_2 x}, & x > 0 \end{cases}$$

Want to define R = reflection coeff [Classically $R=0$]
 T = transmission coeff $T=1$

Technical problem Can't just define ... $T = \frac{|\Psi_{\text{trans}}|^2}{|\Psi_{\text{inc}}|^2}$ because these are static while the particle changes its position.

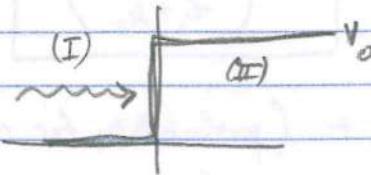
(4)

$$|\Psi|^2$$

Particle slows down

Need to compute the FLUXES of probability not just $|\Psi|^2$.

Feb 28, 2018 Recall



if $E < V_0$, then $R = 1$, $T = 0$, but $|\Psi|^2 \sim e^{-2k_2 x}$ for $x > 0$

if $E > V_0$, then SE gives

$$B = \frac{k_1 - k_2}{k_1 + k_2} A, \quad C = \frac{2k_1}{k_1 + k_2} A$$

→ problem cannot define $T = \frac{|\Psi_{\text{trans}}|^2}{|\Psi_{\text{inel}}|^2}$ ← static, whereas the speed of particle changes

→ Need to use probability FLUXES

→ Define a probability FLUX

→ Probability per second for a particle to cross some point

probability in $\Delta x = \Delta x |\Psi|^2 = \Delta x |\Psi|^2$
divide by Δt = time to cross Δx

$$\text{probability flux} = |\Psi|^2 \frac{\Delta x}{\Delta t} = v |\Psi|^2$$

$$\text{Note } v_2 = \frac{p_2}{m} = \frac{k_2 h_2}{m}$$

$$v_1 = \frac{p_1}{m} = \frac{k_1 h_1}{m} \quad \text{so} \quad v_2 = \frac{k_2}{k_1}$$

For R, the speed drops not since inc, refl waves have speed v

Then define R, T as ratios of probability FLUXES

$$\text{For } R, \text{ get } \rightarrow R = \frac{v_1 |\Psi_{\text{reflected}}|^2}{v_2 |\Psi_{\text{incoming}}|^2} = \frac{|\Psi_{\text{refl}}|^2}{|\Psi_{\text{inel}}|^2} \quad (\text{Same } V, \text{ Bc both same region})$$

$$\Rightarrow R = \frac{\left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \left(\frac{k_1 - k_2}{k_1 + k_2}\right) |A|^2}{|A|^2} = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$$

see that $R \neq 0$
(prob for reflection,

$$\text{For } T \Rightarrow T = \frac{v_2 |\Psi_{\text{transmit}}|^2}{v_1 |\Psi_{\text{incoming}}|^2} = \left(\frac{k_2}{k_1}\right) \cdot \frac{\left(\frac{2k_1}{k_1+k_2}\right)^2 \left(\frac{2k_1}{k_1+k_2}\right) |A|^2}{|A|^2}$$

$$\Rightarrow T = \frac{4k_1 k_2}{(k_1+k_2)^2} \quad \text{and} \quad R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$$

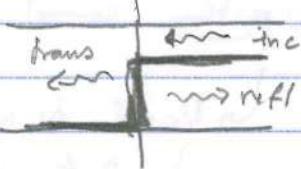
(probability for transmission) + (probability for reflection) = 1

Since the particle can't just disappear / appear

$$R + T = 1 \quad (\text{either reflect/transmit})$$

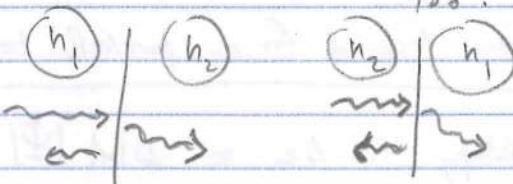
Note R and T are unchanged if we swap $k_1 \leftrightarrow k_2$

get same $R = T$ even for



• **RECIPROCITY** → light waves do this

too.



Now, we can combine $E < v_0$, $E > v_0$ results and plot them for R, T

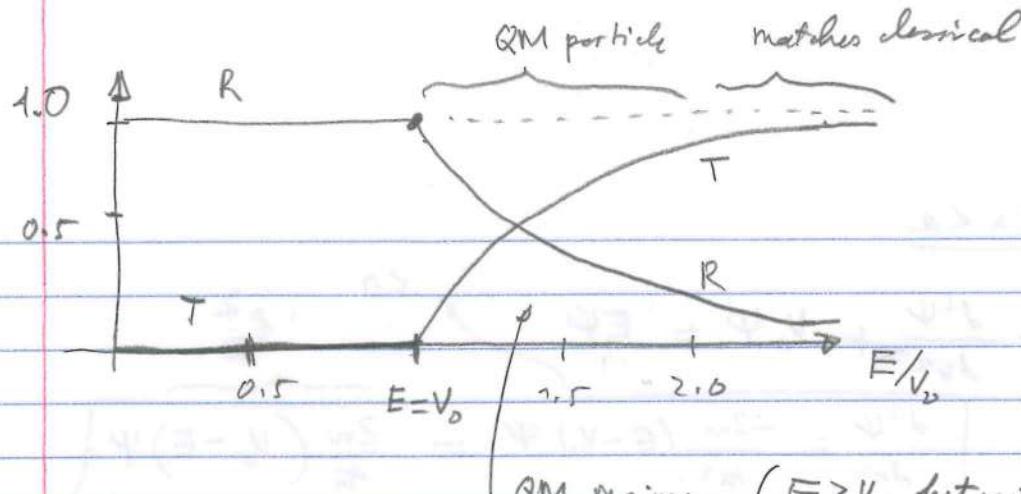
$$E < v_0 \Rightarrow R = 1, T = 0$$

$$E > v_0 \Rightarrow R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2, T = \frac{4k_1 k_2}{(k_1 + k_2)^2}$$

$$\Rightarrow R = \left(\frac{\sqrt{2mE} - \sqrt{2m(E-v_0)}}{\sqrt{2mE} + \sqrt{2m(E-v_0)}} \right)^2 = \left(\frac{\sqrt{E} - \sqrt{E-v_0}}{\sqrt{E} + \sqrt{E-v_0}} \right)^2 = \left(\frac{1 - \sqrt{1-v_0/E}}{1 + \sqrt{1-v_0/E}} \right)^2$$

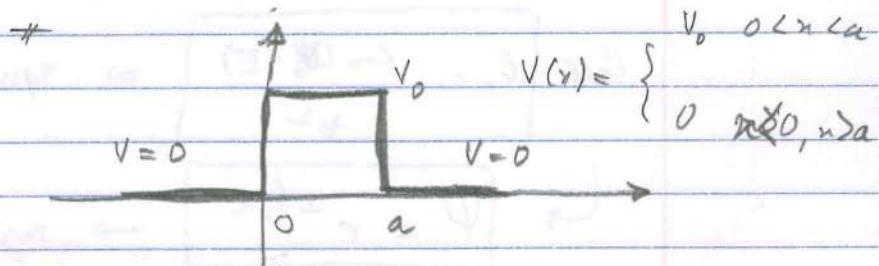
Plot vs. $\frac{E}{v_0}$

$$T = 1 - R$$



QM regime ($E > V_0$ but not much...)

THE BARRIER POTENTIAL



Classically, if particle is incident from the left

→ the probability for reflection: $R = 1$ if $E < V_0$
and $R = 0$ if $E > V_0$

QM must solve the Schrödinger equation

- ↳ if $E > V_0$, can get some reflection
- ↳ if $E < V_0$, ⇒ get **TUNNELING**

TUNNELING only occurs if
width $a \approx$ atomic scale

↳ finite probability for particle to
make it to the other side.

↳ cannot obscure the particle within the wall

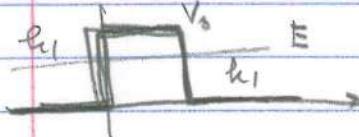
↳ only able to catch it on the other side.

↳ **SCANNING TUNNELING MICROSCOPE**

SOLVE { With the SE → get 3 regions. Solve in each, match Ψ - $d\Psi/dx$
at both boundaries $x=0$ & $x=a$
Must also do $E > V_0$ & $E < V_0$ separately. } (function
→ wave)

START WITH $E < V_0$. For $x < 0$, $x > a$, $V = 0$

$$\text{use } k_I = \sqrt{\frac{2mE}{\hbar^2}} \rightarrow \text{get } e^{\pm ik_I x} \text{ soln in both cases}$$



For $0 < x < a$

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0 \psi = E\psi \quad \text{Call } k_2^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$\downarrow \boxed{\frac{d^2\psi}{dx^2} = \frac{-2m}{\hbar^2} (E - V_0) \psi = \frac{2m}{\hbar^2} (V_0 - E) \psi}$$

Call $k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$ \Rightarrow equation w/o $(-)$ sign $\downarrow \frac{d^2\psi}{dx^2} = k_2^2 \psi$

$$\downarrow \boxed{\psi = e^{\pm k_2 x}} \rightarrow \text{regular exponential}$$

general solution

$$\psi(x) = \begin{cases} Ae^{ik_2 x} + Be^{-ik_2 x} & x < 0 \\ Ce^{ik_2 x} + De^{-ik_2 x} & x > a \\ Fe^{-k_2 x} + Ge^{+k_2 x} & 0 < x < a \end{cases}$$

- For an incoming particle from the left, we should not have $De^{-ik_2 x}$ coming in from the right, in $x > a$ region. $\rightarrow D = 0$
- Note for $0 < x < a$, neither $e^{-k_2 x}$ or $e^{+k_2 x}$ blows up to ∞

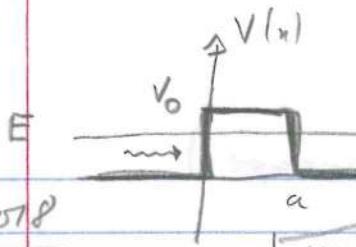
\downarrow no reason to eliminate either.

- Next, match ψ & $\frac{d\psi}{dx}$ @ $x=0$, and @ $x=a$

\rightarrow get 4 equations for 5 unknowns, A, B, C, F, G . No lots of algebra

\downarrow $\boxed{\text{Problem 6.5}}$ \rightarrow solve for B, C, F, G in terms of A .

- Then, compute R and T



March 2, 2018

QM \Rightarrow Lnd

$$Ae^{ik_1x} + B\bar{e}^{-ik_1x} \quad (x < 0)$$

$$Ce^{ik_2x} + De^{-ik_2x} \quad (x > a)$$

$$Fe^{-k_2x} + Ge^{k_2x} \quad (0 < x < a)$$

$$k_1 = \sqrt{\frac{2mE}{\hbar}} \quad , \quad k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

Match Ψ at $x=0$ and $x=a$.

$$x=0 : \Psi \rightarrow A + B = F + G$$

$$\Psi \rightarrow Ce^{ik_1a} = Fe^{-ik_2a} + Ge^{k_2a}$$

$$\frac{d\Psi}{dx} \rightarrow ik_1(A - B) = -k_2(F - G)$$

$$x=a : \frac{d\Psi}{dx} \rightarrow -k_2Fe^{-k_2a} + k_2Ge^{k_2a} = ik_1Ce^{ik_1a}$$

Plan: to solve for B, C, F, G in terms of A .↳ eliminate F, G using the 1st-3rd equations→ plug F, G answers into 2nd, 4th equations,→ eliminate B to get C in terms of A ,

then compute transmission coefficient.

$$T = \frac{\Psi C^* C}{\Psi_A A^* A} = \frac{C^* C}{A^* A} = \left(\frac{C}{A}\right)^* \left(\frac{C}{A}\right)$$

Do lots of algebra:

$$T = \frac{1}{(e^{k_2a} - e^{-k_2a})^2 + 1} \cdot \frac{16 \frac{E}{V_0} \left(1 - \frac{E}{V_0}\right)}{16 \frac{E}{V_0} \left(1 - \frac{E}{V_0}\right)}$$

gives probability
for tunneling
through a barrier

Note

$$e^{k_2a} - e^{-k_2a} = 2 \sinh(k_2a)$$

For tall or wide barriers: tall: $V_0 \gg E$ } $\Rightarrow k_2a \gg 1$
wide: $a \gg 1$

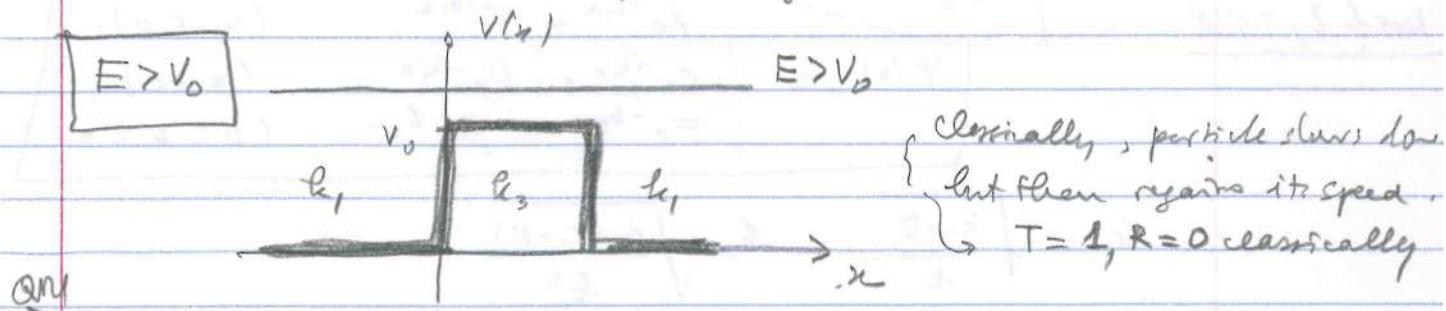
In this limit

$$T = 16 \frac{E}{V_0} \left(1 - \frac{E}{V_0}\right) e^{-2k_2a}$$

(sharp exp fall off)

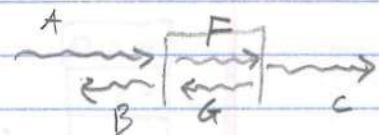
damped, but still finite

Application \rightarrow STM (Scanning Tunneling Microscope)



Also, have oscillating solutions in all 3 regions.

$$\Rightarrow k_1 = \sqrt{\frac{2mE}{\hbar^2}}, \quad k_3 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$$



\Rightarrow General solution of Schrödinger waves

$$\Psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x} & (x < 0) \\ Fe^{ik_3 x} + Ge^{-ik_3 x} & (0 < x < a) \\ Ce^{ik_1 x} & (x > a) \end{cases}$$

Again, match $\Psi, \frac{d\Psi}{dx}$ @ $x=0, x=a$. Compute T.

where

$$\sin\theta = \frac{1}{2i}(e^{i\theta} - e^{-i\theta})$$

$$T = \frac{v_1 c^* c}{v_1 A^* A} = \left(\frac{c}{A}\right)^* \left(\frac{c}{A}\right) = \frac{1}{1 + \frac{\sin^2 k_3 a}{4 \frac{E}{V_0} (\frac{E}{V_0} + 1)}}$$

See in general, $T \leq 1$. Classically, $T=1$ or $T=0$

\hookrightarrow QM-ly, some reflection can happen

Notice if $k_3 a = \pi, 2\pi, 3\pi, \dots \Rightarrow \sin^2(k_3 a) = 0$

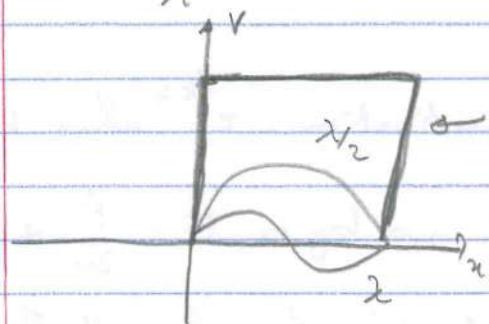
$\hookrightarrow T=1$. No reflection!

\hookrightarrow This is an interference effect!

If we write: $h_2 a = n\pi$, $n = \text{integer} > 0$

$$\text{and } h_2 = \frac{2\pi}{\lambda}$$

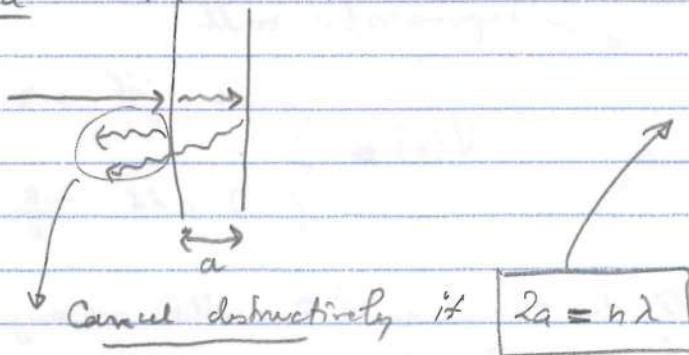
$$\Rightarrow \frac{2\pi}{\lambda} a = n\pi \Rightarrow a = n \frac{\lambda}{2}$$



\rightarrow get destructive interference between the waves reflected off the 2 surfaces when $a = n \frac{\lambda}{2}$

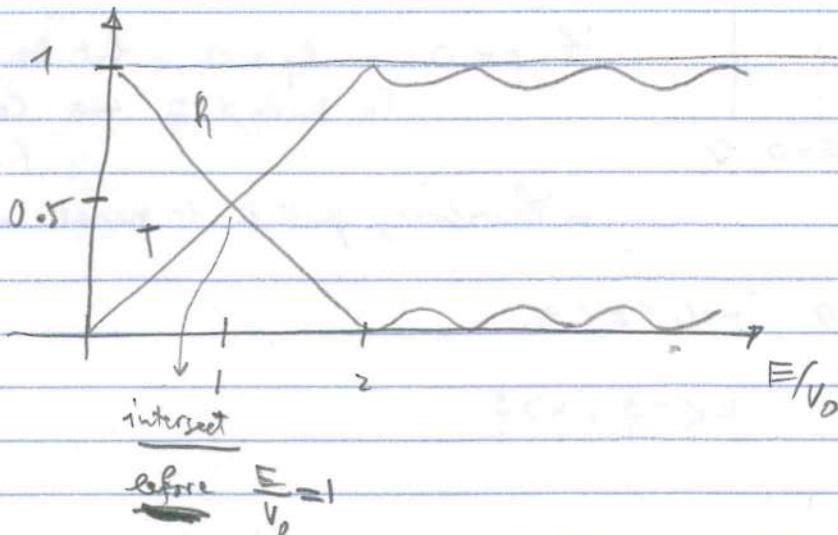
This is what happens with thin film and light.

Example $n=1$ $n \geq 1$ $n=1$



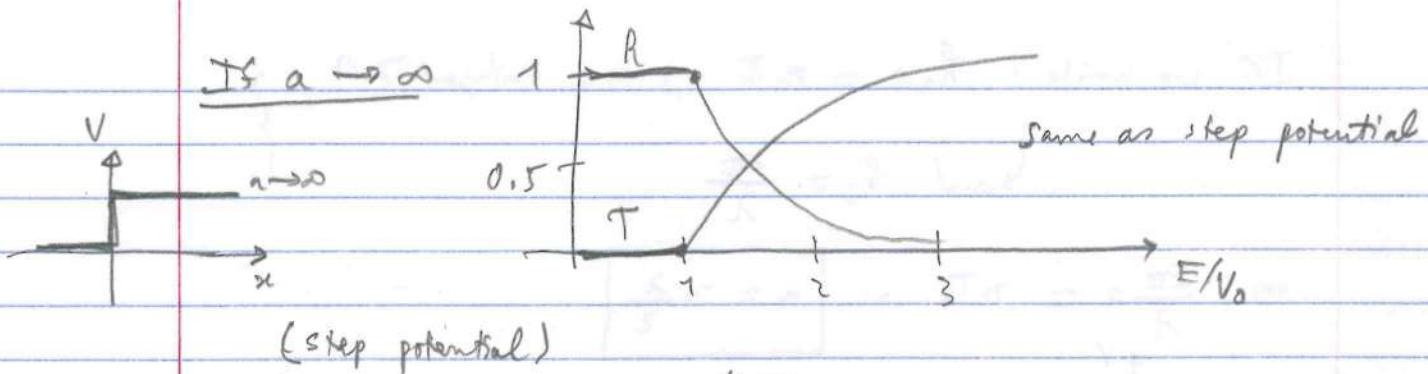
This is what I read about in QED (by Feynman)

Lastly, can plot R , T for an electron hitting a barrier of height $V_0 = 10 \text{ eV}$, with $a = 1.8 \times 10^{-10} \text{ m}$ as a function of (E/V_0)



Conditions $E < V_0$ and $E > V_0$

$$\text{and } R + T = 1$$

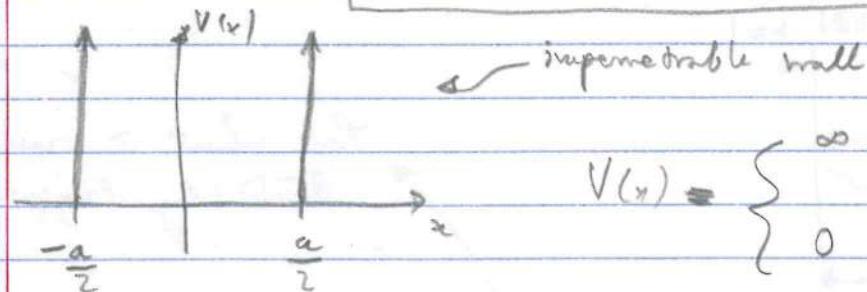


Until now, we have no E quantization. e^{ikx} where $k = \sqrt{\frac{2mE}{\hbar^2}}$

continuous \rightarrow no restrictions on E , as long as $E = \frac{p^2}{2m} + V$

Next problem: look at particle in a box where $V_0 \nearrow \infty$

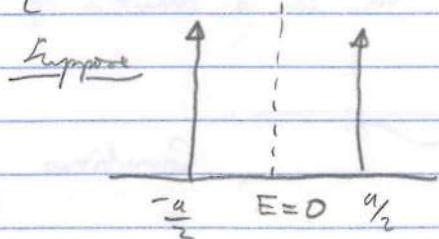
INFINITE SQUARE WELL



$$V(x) = \begin{cases} \infty & \text{if } x \geq \frac{a}{2}, x \leq -\frac{a}{2} \\ 0 & \text{if } -\frac{a}{2} \leq x \leq \frac{a}{2} \end{cases}$$

classically ball in room with 2 walls. \rightarrow any E inside is ok, including $E=0$

\Rightarrow { But in QM \rightarrow get E quantization. And $E=0$ inside is not allowed! }



if $p=0 \Rightarrow \Delta p=0$, but $\Delta x \leq a$
 $\therefore \Delta x \Delta p \leq \frac{\hbar}{2} \rightarrow \text{contradiction}$
 $(\Delta x \Delta p \geq \frac{\hbar}{2})$

\Rightarrow Therefore, particle is never at rest!

$$V(x) = \begin{cases} 0 & -a/2 < x < a/2 \\ \infty & x < -\frac{a}{2}, x > \frac{a}{2} \end{cases}$$

Infinite Square Well (Particle in a Box)

Mar 5, 2019



→ classically, free particle inside the box with energy E, including E=0QM → solve Schrödinger Eqn.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + 0\psi = E\psi$$

But the boundary conditions change. Since $V=\infty$ beyond the wall, must have:

$\psi = 0$ when particle $-a/2 \leq x \leq a/2$ } confinement in
(walls are impenetrable, even in QM) } box.

if $\psi \sim e^{-kx}$, but $V=\infty \Rightarrow k \rightarrow \infty \Rightarrow [\psi=0]$

Also, no longer have a condition on $\frac{d\psi}{dx}$ at $x = \pm \frac{a}{2}$



→ no need to avoid $\frac{d^2\psi}{dx^2} = \infty$ since $V=\infty$ at walls

Also, there's no ψ to match to outside the box.

So the problem becomes:

$$\text{where } \boxed{\psi|_{x=\pm\frac{a}{2}} = 0}$$

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi}$$

$$\text{Let } k = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow \boxed{\frac{d^2\psi}{dx^2} = -k^2\psi}$$

2 "kinds" of solution: traveling wave (c) & standing waves (trig)

→ Want to use standing wave solution since $\psi=0$ at walls.

→ General solution

$$\boxed{\psi(x) = A\sin(kx) + B\cos(kx)}$$

Require boundary condition $\psi(\pm \frac{a}{2}) = 0$

$$\text{at } x = \pm \frac{a}{2} \Rightarrow \boxed{A\sin\left(\pm \frac{ka}{2}\right) + B\cos\left(\pm \frac{ka}{2}\right) = 0}$$

$$\begin{array}{c} + & + & = 0 \\ - & + & = 0 \end{array}$$

$$\Rightarrow \boxed{\pm A \sin\left(\frac{ka}{2}\right) + B \cos\left(\frac{ka}{2}\right) = 0}$$

$$\hookrightarrow \text{So } 2B \cos\left(\frac{ka}{2}\right) = 0 \Rightarrow \left. \begin{array}{l} \text{and } 2A \sin\left(\frac{ka}{2}\right) = 0 \end{array} \right\} \text{ Both of these must hold}$$

- Picking $A=B=0$ gives a trivial solution, $\Psi(x)=0$ (no particle)
- Suppose $B=0, A \neq 0 \Leftrightarrow 2A \sin\left(\frac{ka}{2}\right) = 0$, with $A \neq 0$

This requires $\boxed{\frac{ka}{2} = n\pi} \quad \sin\left(\frac{ka}{2}\right) = 0$

$n \neq 0$, since that gives trivial solution again

$$\text{So } \boxed{k = \frac{2n\pi}{a}} \quad n = 1, 2, 3, \dots \quad (\sin \sim k_n = \frac{(2n\pi)}{a})$$

So the set of solutions is

$$\boxed{\Psi_n(x) = A_n \sin(k_n x), \text{ where } k_n = \frac{n\pi}{a}, n \text{ even}}$$

- Alternatively, we can let $A=0, B \neq 0 \Leftrightarrow 2B \cos\left(\frac{ka}{2}\right) = 0$

This requires $\boxed{\frac{ka}{2} = m\frac{\pi}{2}} \rightarrow m \text{ odd} \Rightarrow \boxed{k_n = \frac{m\pi}{a}, m \text{ odd}}$

So the set of solutions is

$$\boxed{\Psi_n(x) = B_n \cos(k_n x), \text{ where } k_n = \frac{m\pi}{a}, m \text{ odd}}$$

Summary: 2 classes of solution:

$$1^{\text{st}} \text{ set} \Rightarrow \Psi = A_n \sin(k_n x) \quad (\text{n even})$$

$$2^{\text{nd}} \text{ set} \Rightarrow \Psi = B_n \cos(k_n x), n \text{ odd}$$

even function ($\Psi(-x)=\Psi(x)$)

Called "even parity" states

$$\hookrightarrow \Psi_n(-x) = -\Psi_n(x) \quad (\text{odd function})$$

Called "odd parity" states.

(51)

(51)

What is parity? Parity is an operator \hat{P}

Definition

$$\hat{P} \Psi = \Psi(-x)$$

Useful in problems with left/right symmetry or where

$$V(-x) = V(x)$$



what are the eigenstates of \hat{P}^2 ? $\hat{P}^2 \Psi = (\text{number}) \Psi$

↳ Let \hat{P} acts twice! $\{\hat{P}^2 \Psi(x) = \Psi(x)\}$

↳ \hat{P}^2 gives $+1$! Eigenvalues of \hat{P} are (± 1)

Eigenstates always

$$\begin{aligned} \hat{P}(x) &= \Psi(-x) = (+1)\Psi(x) && (\text{even parity}) \\ \hat{P}(x) &= \Psi(-x) = (-1)\Psi(x) && (\text{odd parity}) \end{aligned}$$

Can be proved in QM that when $V(x)$ is symmetric (obeying $V(x) = V(-x)$), then you always get even or odd parity states

Now, h is quantized - what about E^2 ?

well, $h = \sqrt{\frac{2mE}{k^2}} = h_n = \frac{n\pi}{a}$ (n alternates odd-even)
 $(n=1, 2, 3, \dots)$

so $E = E_n = \frac{k^2 h_n^2}{2m} \rightarrow$ to we get allowed energies

$$E_n = \frac{k^2}{2m} \cdot \left(\frac{n\pi}{a}\right)^2, n=1, 2, 3, \dots$$

particle in a box has quantized energies, this corresponds to the fact that only certain waves fit in the box.

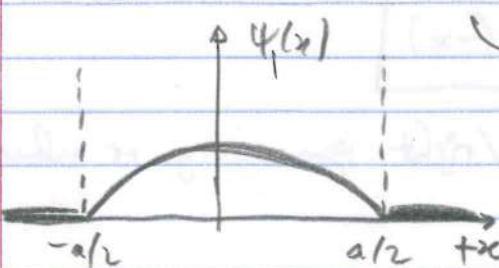
Can we prove this?
Let me tell you with k^2 .

(52)

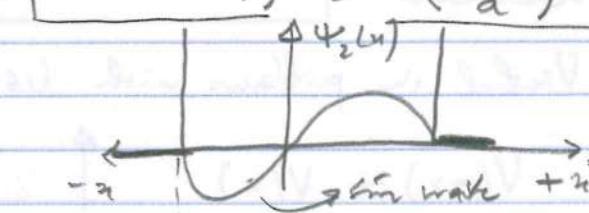
(52)

n odd \rightarrow base cos()

e.g. $n=1, \psi_1(x) = B_1 \cos\left(\frac{\pi x}{a}\right)$, with $E=E_1$,



For $n=2, \psi_2(x) = B_2 \sin\left(\frac{2\pi x}{a}\right)$, $E=E_2$



- So E_1 is the state of lowest energy \rightarrow Ground state

Note $E_1 = \frac{\pi^2 \hbar^2}{2ma^2} > 0$ We do not get $E=0$ as ground state.

When the ground state energy is non-zero \rightarrow called "zero-point energy"

\hookrightarrow Must have $E_1 \neq 0$ for this

- Why is there a zero-point energy here? \rightarrow Uncertainty principle

\hookrightarrow know $\Delta x \leq a$, so $\Delta p \geq \frac{\hbar}{2a}$ (since $\Delta x \Delta p \geq \frac{\hbar}{2}$)

So we can't have $\Delta p = 0$, $p = \text{exact} - \text{is not allowed.}$

Since if $E=0 \rightarrow$ at rest $\rightarrow p=0$ (exact) \rightarrow This can't happen.

\Rightarrow Must have a zero-point energy! ($E_1 \neq 0$)

Note $\hbar = \hbar_{k_n} = \frac{\pi n}{a}$ (exact). But the standing waves are a mix of

$p = +\hbar k_n$ to the right $\rightarrow p = -\hbar k_n$ to the left -

$\hookrightarrow \therefore \Delta p \neq 0$ (non-zero jiggly values)

Next, we look at $\underline{\Sigma E}$, where we normalize Ψ_n , compute $\bar{x}, \bar{x^2}, \bar{p}, \bar{p^2}$ and $Dx, Dp \rightarrow$ EXCEPT WE ALREADY DID THIS.

→ Look at examples in chapter 5.

CUT OFF FOR EXAM

March 7, 2018

QUANTUM MECHANICAL OSCILLATOR

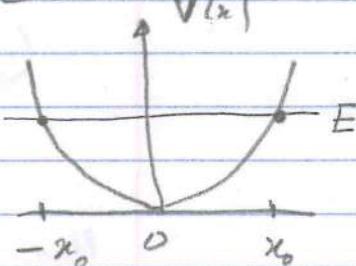
(Appendix I chap 6)

$$V = \frac{1}{2} C x^2 \quad \leftarrow C: \text{spring constant.}$$

$$\leftarrow \text{angular frequency } \omega = \sqrt{\frac{C}{m}} = 2\pi\nu \quad V(x)$$

Can also write

$$C = 4\pi^2 m \nu^2$$



Classically \rightarrow particle oscillate with frequency ν

$$\text{Classical turning point} \rightarrow \frac{1}{2} C x_0^2 = E_{\text{total}}$$

→ Classically, zero probability of going beyond the turning point.

To solve in QM \rightarrow use the SE. (time-independent)

$$\frac{-\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + \frac{1}{2} C x^2 \Psi = E \Psi$$

Then SE, time-dependent $\rightarrow \Psi(r, t) = \Psi(r) e^{-iEt/\hbar}$

Note We don't use 3 regions. Since $V(x) = \frac{1}{2} C x^2 + x$,

\rightarrow can't partition

\rightarrow V has no abrupt changes

$$\text{Using } C = 4\pi^2 m \nu^2 \rightarrow$$

$$\frac{-\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + 2\pi^2 m \nu^2 x^2 \Psi = E \Psi$$

Clear up the constants: \rightarrow divide by $-\frac{\hbar^2}{2m}$

$$\hookrightarrow \left[\frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \left(\frac{2\pi m}{\hbar} \right)^2 x^2 \right] \psi = 0 \right]$$

$\beta = \frac{2mE}{\hbar^2}$ $\alpha = \frac{2\pi m}{\hbar}$

So, we get: $\frac{d^2\psi}{dx^2} + (\beta - \alpha^2 x^2) \psi = 0$

Can do even better by making a substitution: let $u = \sqrt{\alpha} x$

$$\hookrightarrow \text{so } u = \sqrt{\frac{2\pi m}{\hbar}} x \Rightarrow \text{gives } \sqrt{\alpha} = \frac{(cm)^{1/4}}{\hbar^{1/2}}$$

Now, we have $\boxed{\psi = \psi(u|x)}$

Chain rule

$$\hookrightarrow \frac{d\psi}{dx} = \frac{d\psi}{du} \cdot \frac{du}{dx} = \boxed{\sqrt{\alpha} \frac{d\psi}{du}}$$

$$\hookrightarrow \frac{d^2\psi}{dx^2} = \boxed{\alpha \frac{d^2\psi}{du^2}} \quad \text{and } x^2 = \frac{1}{\alpha} u^2$$

$$\hookrightarrow \text{Rewrite SE in terms of } u \rightarrow \alpha \frac{d^2\psi}{du^2} + (\beta - \alpha u^2) \psi = 0$$

$$\hookrightarrow \underline{\text{divide by } \alpha} \quad \boxed{\frac{d^2\psi}{du^2} + \left(\frac{\beta}{\alpha} - u^2 \right) \psi = 0} \quad (*)$$

all constants in one place! (preferable)

Now, solve for $\psi(u)$. Then

$$\text{use } u = \sqrt{\alpha} x \Rightarrow \frac{(cm)^{1/4}}{\hbar^{1/2}} \cdot x$$

Now, how do we solve this? Can't just guess... \rightarrow use a tech
-nique

\hookrightarrow The power series method

The power series method

$$\boxed{\frac{d^2\psi}{dx^2} = -k^2 \psi}$$

Consider eqn:

guess

← imagine we can't get a solution...
 $\psi(x) = A \cos(kx) + B \sin(kx)$

Instead of solving for ψ directly, we solve for its infinite power series

- ① ↳ All good functions have power series expansions.
 ↳ e.g. Taylor series

Suppose $\boxed{\psi(x) = \sum_{l=0}^{\infty} a_l x^l}$ (al: constant coefficient)

If we can find the infinity of coefficients a_l , then we've solved the problem, since $\psi(x) = \text{power series}$.

Need to take 1st derivative $\frac{d\psi}{dx} = \sum_{l=0}^{\infty} a_l \cdot l \cdot x^{l-1}$

2nd deriv $\frac{d^2\psi}{dx^2} = \sum_{l=0}^{\infty} a_l \cdot l(l-1) x^{l-2}$

↙ SE becomes $\sum_{l=0}^{\infty} a_l \cdot l(l-1) x^{l-2} = (-k^2) \sum_{l=0}^{\infty} a_l x^l$

Want to combine the sums.

↪ the labels "l" are "dummy indices". Can always re-label them.

e.g. $\sum_{n=1}^{\infty} \frac{1}{n} = \sum_{j=1}^{\infty} \frac{1}{j} = \sum_{l=2}^{\infty} \frac{1}{l-2}$

↪ We can combine the sum by shifting + re-labeling the 1st term.

↪ $\sum_{l=0}^{\infty} a_l \cdot l(l-1) x^{l-2} = \sum_{l'=2}^{\infty} a_{l'+2} \cdot (l'+2)(l'+1) x^{l'}$

↪ let $l' = l-2 \rightarrow l = l'+2$

↪ This sum = $\sum_{l'=0}^{\infty} a_{l'+2} \cdot (l'+2)(l'+1) x^{l'}$

(since $l'=2 \rightarrow \text{term} \neq 0$)
 $l'=1 \rightarrow \text{term} = 0$

$$\text{Let } l' = l \rightarrow \text{the sum} = \sum_{l=0}^{\infty} a_{l+2} (l+2)(l+1) x^l$$

$$\boxed{\sum_{l=0}^{\infty} a_l (l)(l-1) x^{l-2} = \sum_{l=0}^{\infty} a_{l+2} (l+2)(l+1) x^l}$$

we set eqn: $\sum_{l=0}^{\infty} a_{l+2} (l+2)(l+1) x^l = -k^2 \sum_{l=0}^{\infty} a_l x^l$

$$\rightarrow \boxed{\sum_{l=0}^{\infty} [a_{l+2} (l+2)(l+1) + k^2 a_l] x^l = 0} \quad (\text{true } \forall x)$$

Must have $a_{l+2} (l+2)(l+1) + k^2 a_l = 0$

$$\rightarrow \boxed{a_{l+2} = \frac{-k^2}{(l+2)(l+1)} a_l} \quad \rightarrow \text{recursion relation.}$$

! This lets us find all a_l in terms of a_0 and a_1 !

We can split up terms and odds.

$a_0 = \text{arbitrary}$

$$\boxed{a_2 = \frac{-k^2}{2} a_0 = \frac{-k^2}{2!} a_0}$$

$$\left\{ \begin{array}{l} a_4 = \frac{-k^2}{4 \cdot 3} a_2 = \frac{+k^4}{4!} a_0 \\ a_6 = \frac{-k^2}{6 \cdot 5} a_4 = \frac{-k^6}{6!} a_0 \end{array} \right.$$

}

Repeat the whole process with the odds. Let $\boxed{a_1 = \text{arbitrary}}$

$$\left\{ \begin{array}{l} a_3 = \frac{-k^2}{3!} a_1 \\ a_5 = \frac{-k^2}{5 \cdot 4} a_3 = \frac{+k^4}{5!} a_1 \end{array} \right.$$

$$\left. \begin{array}{l} a_7 = \frac{-k^2}{7 \cdot 6} a_5 = \frac{-k^6}{7!} a_1 \end{array} \right.$$

:

The solution is then

$$\Psi(x) = \sum_{\ell=0}^{\infty} a_{\ell} x^{\ell}$$

So

$$\begin{aligned}\Psi(x) &= [a_0 + a_1 x^1 + a_2 x^2 + \dots] + [a_1 x^1 + a_2 x^2 + a_3 x^3 + \dots] \\ &= a_0 \left[1 - \frac{(hx)^2}{2!} + \frac{(hx)^4}{4!} - \dots \right] + a_1 \left[x - \frac{hx^3}{3!} + \frac{hx^5}{5!} - \dots \right] \\ &= a_0 \left[1 - \frac{(hx)^2}{2!} + \frac{(hx)^4}{4!} - \dots \right] + \frac{a_1}{h} \left[hx - \frac{(hx)^3}{3!} + \frac{(hx)^5}{5!} - \dots \right]\end{aligned}$$

Call $A = a_0$, $B = \frac{a_1}{h}$

$$\Psi(x) = A \left[1 - \frac{(hx)^2}{2!} + \frac{(hx)^4}{4!} - \dots \right] + B \left[hx - \frac{(hx)^3}{3!} + \frac{(hx)^5}{5!} - \dots \right]$$

This gives the general solution.

Recognize the power series.

$$\Psi(x) = A \cos(hx) + B \sin(hx)$$

When does this method work?

↳ when we get a clean recursive relation between 2 coefficients

↳ Requires that only 2 powers appear.

$$\hookrightarrow \frac{d^2\Psi}{dx^2} = -h^2 \Psi \quad \text{If } \Psi \sim a_{\ell} x^{\ell}$$

$$a_{\ell} x^{\ell-2} \quad a_{\ell} x^{\ell} \quad \not\in \left[\text{2 powers } x^{\ell-2}, x^{\ell} \right]$$

But for SHO \rightarrow does NOT work

↳ method works.

$$\hookrightarrow \frac{d^2\Psi}{du^2} + (\beta/\lambda - u^2)\Psi = 0$$

$$u^{t-2} \quad \not\exists \Psi \sim u^t \quad \frac{d^2\Psi}{du^2} \sim u^{t-2}$$

but $\frac{u^2 \Psi}{u^2} \sim u^{t+2}$ } 3 powers
too many

March 9, 2019

$$\text{Recall SE: } \frac{\partial^2 \Psi}{\partial u^2} + \left(\frac{\beta}{\alpha} - u^2\right) \Psi = 0$$

Want to solve this SE using a power series $\Psi = \sum_{l=0}^{\infty} a_l u^l$

but we get too messy a recursive relation \Rightarrow Must do something else first
 \rightarrow Extract the asymptotic part of the solution

\hookrightarrow Solve in the limit where $|u| \rightarrow \infty$ or $|u| \gg 1, |u| > \frac{\beta}{\alpha}$

\hookrightarrow In the limit $\frac{\partial^2 \Psi}{\partial u^2} - u^2 \Psi \approx 0$ \Rightarrow has a solution for large u

$$\Psi = e^{-\frac{1}{2}u^2}$$

$$\frac{\partial \Psi}{\partial u} = -ue^{-\frac{1}{2}u^2} \Rightarrow \frac{\partial^2 \Psi}{\partial u^2} = -e^{-\frac{1}{2}u^2} + ue^{-\frac{1}{2}u^2} = \underbrace{(u^2 - 1)e^{-\frac{1}{2}u^2}}_{\approx u^2}$$

$$\text{So for } |u| \gg 1 \rightarrow \frac{\partial^2 \Psi}{\partial u^2} \approx u^2 \Psi$$

What about the exact solution?

\hookrightarrow we now write the solution as: $\Psi(u) = e^{-\frac{1}{2}u^2} H(u)$
 where $H(u)$ is such that
 $\Psi(u)$ is an exact solution. \rightarrow plug in

$$\frac{\partial^2 \Psi}{\partial u^2} + \left(\frac{\beta}{\alpha} - u^2\right) \Psi = 0 \Rightarrow u^2 H - H - 2u \frac{dH}{du} + \frac{d^2 H}{du^2} + \left(\frac{\beta}{\alpha} - u^2\right) H = 0$$

$$\frac{d\Psi}{du} = -ue^{-\frac{1}{2}u^2} H(u) + e^{-\frac{1}{2}u^2} \frac{dH(u)}{du}$$

$$\frac{d^2 \Psi}{du^2} = u^2 e^{-\frac{1}{2}u^2} H(u) - e^{-\frac{1}{2}u^2} H(u) - 2ue^{-\frac{1}{2}u^2} \frac{dH(u)}{du} + e^{-\frac{1}{2}u^2} \frac{d^2 H(u)}{du^2}$$

$$\Rightarrow \frac{d^2 H}{du^2} - 2u \frac{dH}{du} + \left(\frac{\beta}{\alpha} - 1\right) H = 0$$

\leftarrow Hermite's eq.

\hookrightarrow this eq. can be solved using the power series method

Suppose $H \sim u^l$, then $\frac{d^2H}{du^2} \sim u^{l-2}$, $\frac{dH}{du} \sim u^l$

\Rightarrow we should end up with just 2 powers \Rightarrow should get clean recursion relation between a_{l+2}, a_l ,

Solve Hermite's eqn \Rightarrow plug in power series expansion

$$\left\{ \begin{array}{l} H(u) = \sum_{l=0}^{\infty} a_l u^l, \quad \frac{dH}{du} = \sum_{l=0}^{\infty} a_l l u^{l-1} \\ \frac{d^2H}{du^2} = \sum_{l=0}^{\infty} a_l (l)(l-1) u^{l-2} \end{array} \right\} \Rightarrow \text{plug in...}$$

$$\sum_{l=0}^{\infty} a_l (l)(l-1) u^{l-2} - 2u \sum_{l=0}^{\infty} a_l (l) u^{l-1} + \left(\frac{\beta}{\alpha} - 1\right) \sum_{l=0}^{\infty} a_l u^l = 0$$

$$= \sum_{l=0}^{\infty} a_{l+2} (l+2)(l+1) u^l$$

$$\sum_{l=0}^{\infty} [(l+2)(l+1) a_{l+2} - 2a_l l + (\beta/\alpha - 1) \cdot a_l] u^l = 0$$

This must hold for all $u \Rightarrow (l+2)(l+1) a_{l+2} - 2a_l l + (\beta/\alpha - 1) a_l = 0$

$$\text{So } a_{l+2} = \frac{-(\beta/\alpha - 1 - 2l)}{(l+2)(l+1)} a_l \rightarrow \text{recursion relation}$$

This lets us generate all the a_l in terms of $a_0 = a$,

$$\text{So } H(u) = a_0 [\text{even powers of } u] + a_1 [\text{odd powers of } u]$$

The full solution is then $\Psi(u) = e^{-1/2 u^2} H(u)$

The solution $\Psi(u)$ must be finite as $u \rightarrow \infty$

this means that the power series for H must converge on a function that doesn't blow up too fast...

We can't have $e^{-\frac{1}{2}u^2} H(u) \rightarrow 0$ as $u \rightarrow \pm\infty$

But this is what happens! Consider $H(u) = e^{u^2}$

Then $e^{-\frac{1}{2}u^2} H(u) \approx e^{-\frac{1}{2}u^2} \rightarrow \infty$

Let's compare the ratio for H with the ratio for e^{u^2}

$$\text{e.g. } e^{u^2} = 1 + u^2 + \frac{u^4}{2!} + \frac{u^6}{3!} + \dots$$

$$\hookrightarrow \sum_{l=0,2,\dots}^{\infty} a_l u^l \text{ where } a_l = \frac{1}{(l/2)!}$$

$$\text{Look at the ratio } \frac{a_{l+2}}{a_l} = \frac{1/(l+2)!}{1/(l/2)!} = \frac{(l/2)!}{(l+2/l)!} = \frac{1}{\frac{l+2}{2}} = \frac{2}{l+2}$$

for large l

$$\hookrightarrow \boxed{\frac{a_{l+2}}{a_l} \approx \frac{2}{l}} \quad (\text{l even...}) \quad \text{same!}$$

Compare this to what it does for large l

$$H: \frac{a_{l+2}}{a_l} = \frac{-\left(\frac{\beta}{\alpha} - 1 - 2l\right)}{(l+2)(l+1)} \approx \frac{2l}{l^2} =$$

This suggests (but does not prove) that $H(u)$ will blow up similarly as e^{u^2} does \Rightarrow we must do sth to fix this.

\hookrightarrow So... we can truncate the series! \Rightarrow keep $H(u)$ as a finite polynomial

Then for any finite polynomial \Rightarrow then $\boxed{H(u)e^{-\frac{1}{2}u^2} \rightarrow 0 \text{ as } u \rightarrow \infty}$

How do we truncate the series?

Suppose for some l , say $l=n$ that $\left(\frac{\beta}{\alpha} - 1 - 2n\right) = 0$

then $a_{n+2} = \frac{-(\frac{\beta}{\alpha} - 1 - 2n)}{(l+1)(l+2)} a_n = 0 \} \Rightarrow$ series ends @ the

$a_{n+4} = (?) a_{n+2} = 0 \rightarrow \text{so on}$ n^{th} term

→ This leaves us with a finite polynomial of order n
What does $\left(\frac{P}{\alpha} - 1 - 2n = 0\right)$ mean?

$$\text{Recall } \frac{P}{\alpha} = \frac{2mE/\hbar^2}{2\pi m^2/\hbar} = \frac{E}{\pi\hbar^2} = \frac{2E}{\hbar^2}$$

So for finite solutions, must have $\frac{2E}{\hbar^2} - 1 - 2n = 0$ for $n \in \mathbb{N}$

$$\text{Get } E = E_n = \hbar\gamma \left(n + \frac{1}{2}\right) \Rightarrow \begin{matrix} \text{quantized energy} \\ \text{levels.} \end{matrix}$$

This gives the allowed energy levels of a QM SHO,
where $\gamma = \text{osc freq.} \geq E = \frac{1}{2}\hbar\omega$.

Note → the ground state energy $E_0 = \frac{1}{2}\hbar\omega > 0$ $E_0 \neq 0$

↳ So we set a zero-point energy (always get wiggle)
why?

$$E = \frac{P^2}{2m} + \frac{1}{2}Cx^2 \quad E=0 \Leftrightarrow P=0 \quad x=0$$

But this violates $\Delta p \Delta x \geq \frac{\hbar}{2}$ ↳ $E \neq 0$ not possible..,

exact $\sim \Delta p \Delta x = 0$

Mar 12, 2018

$$\text{Recall } \Psi(x) = e^{-\frac{1}{2}u^2} H(u) \text{ where } u = \sqrt{\alpha}x = \frac{(Cm)^{1/4}}{\sqrt{\hbar}} x$$

$$\text{Power series } H(u) = \sum_{l=0}^{\infty} a_l u^l \quad \text{Final } a_{l+2} = \frac{-(\beta/\alpha - 1 - 2l)}{(l+2)(l+1)} a_l$$

But $H(u) \rightarrow \infty \rightarrow$ must truncate the series!

→ Require $(\beta/\alpha - 1 - 2n) = 0$ for some n

→ then the sum stops at a_n ↳ integer

The condition $\beta/\alpha - 1 - 2n = 0 \Rightarrow E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

↳ Quantized energies of QM SHO.

Our solution has the form $H(u) = a_0 [even power of u] + a_1 [odd power]$

\rightarrow stop at n^{th} term (even or odd)

{ if n is even } \Rightarrow we set $a_1 = 0$ so that the odd power terms are gone

\Rightarrow get $a_0 = \text{arbitrary} \rightarrow$ get a_2, a_4, \dots, a_n in terms of a_0

$$H(u) = \text{finite even power polynomial of power } n$$

{ If n is odd } \rightarrow set $a_0 = 0$ so the even powers go away.

\Rightarrow get $a_1 = \text{arbitrary} \rightarrow$ get a_3, a_5, a_7, \dots in terms of a_1 .

get

$$H(u) = \text{finite odd-power polynomial of power } n$$

Get an infinite set of Hermite polynomials $\rightarrow H_n(u)$

In the spatial wave function $\Psi_n(u) = (e^{-\frac{1}{2}u^2}) H_n(u)$

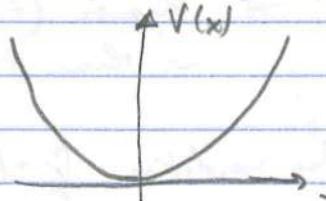
(these are finite as $u \rightarrow \pm\infty$. Since $H_n(u)$ are finite polynomials the energies are

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega$$

Note that $\begin{cases} H_n(u) = \text{odd function if } n \text{ is odd} \\ H_n(u) = \text{even function if } n \text{ is even} \end{cases}$

\Rightarrow There are even/odd parity states (This is expected in QM whenever $V(x)$ is left-right symmetric)

Lastly, we can generate $H_n(u)$



Use the recursion relation $a_{t+2} = \frac{2t - \beta/2 + 1}{(t+2)(t+1)} a_t$

where $\frac{\beta}{2} = 2n + 1$ for some $n = 0, 1, 2, \dots$

So we set $a_{t+2} = \frac{2t - 2n}{(t+2)(t+1)} a_t$

For each n , we get a different polynomial $H_n(u)$

$$n=0 \rightarrow a_{t+2} = \frac{2t}{(t+2)(t+1)} a_t \quad \begin{array}{l} \text{since } n=0, a_0=0 \\ \text{keep } a_0 \text{ arbitrary} \end{array}$$

so $a_2 = \frac{2 \cdot 0}{(2+0)(0+1)} a_0 = 0$ (recursion relation stops)

so $a_4 = a_6 = a_8 = \dots = 0$

so $H_0(u) = a_0$ (just a constant) \rightarrow polynomial of order 0

$$n=1 \rightarrow a_{t+2} = \frac{2t - 2}{(t+2)(t+1)} a_t \quad \begin{array}{l} \text{since } n=1 \text{ odd} \Rightarrow a_0=0 \\ \text{keep } a_1 \text{ arbitrary} \end{array}$$

$a_3 = \frac{2 \cdot 1 - 2}{(1+2)(1+1)} a_1 = 0$ (poly stops at $n=1$ order)

then $a_5 = a_7 = a_9 = \dots = 0$

so $H_1(u) = a_1 u$ Polynomial of order 1

$$n=2 \rightarrow a_{t+2} = \frac{2 \cdot t - 4}{(t+2)(t+1)} a_t \quad \begin{array}{l} \text{since } n=2 \text{ even} \Rightarrow a_0=0 \\ \text{keep } a_2 \text{ arbitrary} \end{array}$$

$$\left. \begin{array}{l} a_2 = \frac{0 - 4}{(0+2)(0+1)} a_0 = -\frac{4}{2} a_0 = -2a_0 \\ H_2(u) = a_0 u^0 + (-2a_0)u^2 \end{array} \right\}$$

$a_4 = \frac{2 \cdot 2 - 4}{(2+2)(2+1)} a_2 = 0 = a_6 = a_8 = \dots$

$$\Rightarrow \boxed{H_n(u) = a_0(1-2u^2)} \quad (\text{even polynomial of order 2})$$

↳ found

$$\begin{cases} H_0(u) = a_0 \\ H_1(u) = a_1 u \\ H_2(u) = a_0(1-u^2) \end{cases}$$

④ There are 2 ways to the normalization (2 stages)

→ Mathematicians normalize $H_n(u)$ using a convention

(1)

Rule: coefficient of $u^n = 2^n$

with $H_0(u) = a_0 u^0 \Rightarrow$ set coeff of $u^0 = 2^0 = u^0 = 1$
 \Rightarrow set $a_0 = 1 \Rightarrow \boxed{H_0(u) = u^0 = 1}$

with $H_1(u) = a_1 u^1 \Rightarrow$ set coeff of $u^1 = 2^1 = 2$
 \Rightarrow set $a_1 = 2 \Rightarrow \boxed{H_1(u) = 2u}$

with $H_2(u) = a_0 u^0 + a_2 u^2 = a_0 u^0 - 2a_0 u^2$
 \uparrow
 $= 2^2 \Rightarrow a_0 = -2$

$$\therefore \boxed{H_2(u) = 4u^2 - 2}$$

So the mathematically normalized Hermite poly are

$$\begin{cases} H_0(u) = 1 \\ H_1(u) = 2u \\ H_2(u) = 4u^2 - 2 \\ H_3(u) = 8u^3 - 12u \\ \vdots \end{cases}$$

But as a physics problem, we want "normalise"

$$\int_{-\infty}^{\infty} \Psi_n^*(x) \Psi_n(x) dx = 1 \Rightarrow \text{physically } \Psi_n(u) = A_n e^{-\frac{1}{2}u^2} H_n(u)$$

where $n = \frac{(Cm)^{1/4}}{\sqrt{\hbar}} x \Rightarrow$ get

$$A_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{4\pi m^2}{\hbar} \right)^{1/4}$$

Using math tables for
 $H_n(n)$ integrals...

→ The normalized wave functions:

$$\Psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{4\pi m^2}{\hbar} \right)^{1/4} e^{-\frac{1}{2} \left[\frac{(Cm)^{1/4} x}{\sqrt{\hbar}} \right]^2} H_n \left(\frac{(Cm)^{1/4} x}{\sqrt{\hbar}} \right)$$

with $E_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad n = 0, 1, 2, \dots$

→ So the "full" solution

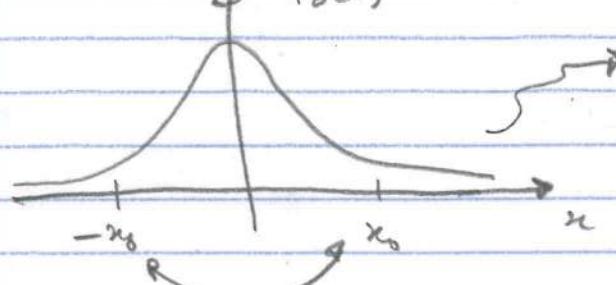
$$\Psi_n(x, t) = \Psi_n(x) \Phi(t) = \Psi_n(x) e^{-i E_n t / \hbar}$$

The energies are an infinite tower of equally spaced levels.

$$\begin{array}{c} h=3 \\ \hline h=2 \quad E_2 = \frac{5}{2} \hbar \omega \\ \hline h=1 \quad E_1 = \frac{3}{2} \hbar \omega \\ \hline h=0 \quad E_0 = \frac{1}{2} \hbar \omega \end{array} \quad \begin{array}{l} \text{Note } E_0 = \frac{1}{2} \hbar \omega \neq 0 \\ \rightarrow \text{zero-point energy} \end{array}$$

$$\boxed{n=0} \quad \Psi_0(x) = (\text{const}) e^{-\frac{1}{2} (\text{const}) x^2} \cdot (\text{const})$$

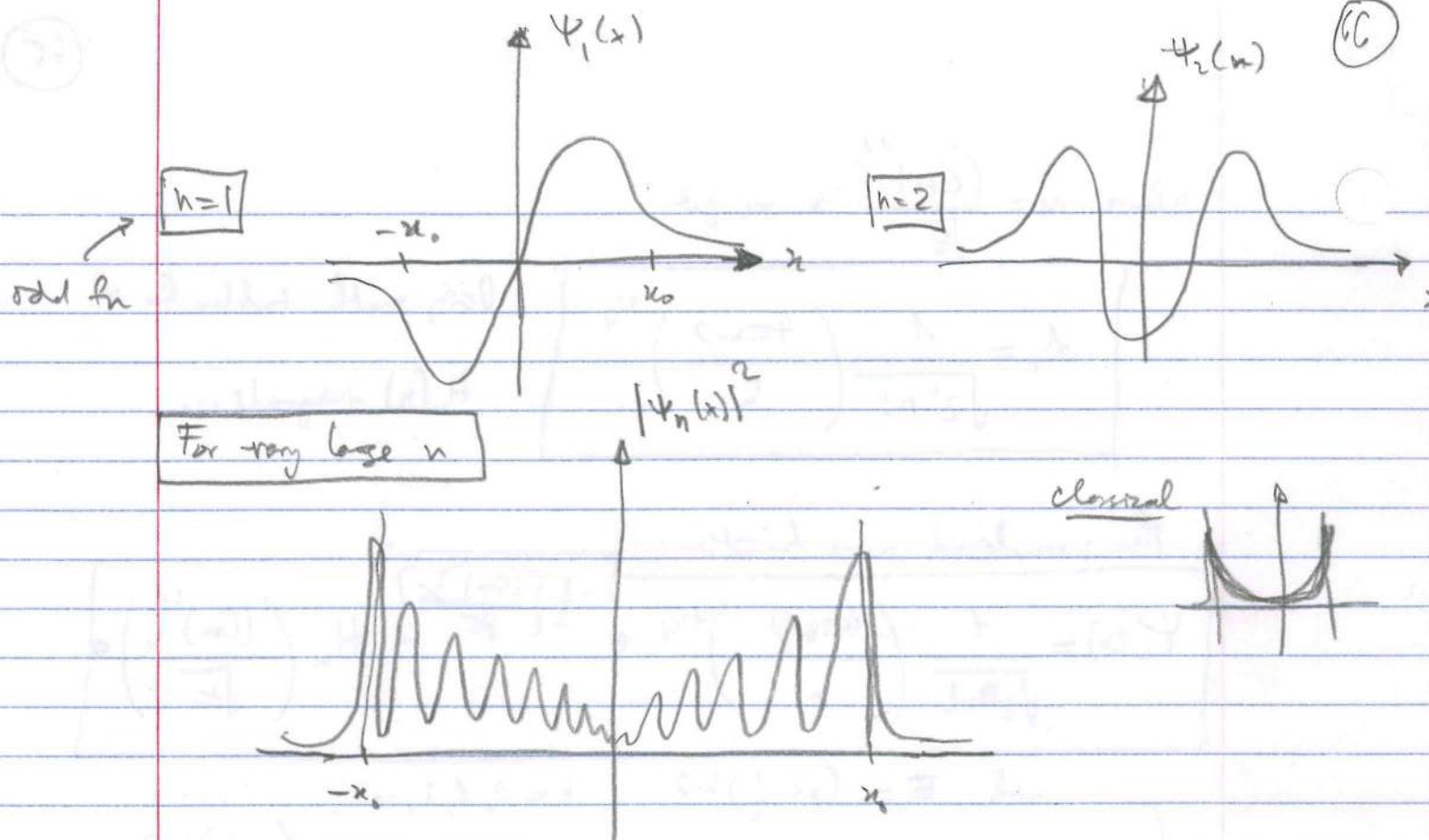
$\Phi \Psi_0(x)$ Gaussian



classical
turning point

But small probability beyond
classical turning point.

2.



\Rightarrow starts to match classical behavior.

Classically, the particle more likely to be found near the turning point.
 \hookrightarrow spends less time near $x=0$

— 4 —

The end of 1-D SE

III. 3-D PROBLEMS & H atom

Mar 14, 2018

To Day

H is a 2-body problem in 3D

2 body \rightarrow electron + proton moving about their COM

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} \quad \text{Coulomb potential}$$

For an ion of nuclear charge $Ze \rightarrow V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$

To turn the 2-body problem into equivalent 1-body problem use the REDUCED MASS.

$$\mu = \frac{m_e m_p}{m_e + m_p} \quad \text{or use } m_{\text{nucleus}}$$

for ion with (Ze)

or $\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e}$, The 2-body problem is then eqvrl. to 1-body problem for mass μ

$$\text{Same Coulomb potential } V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

For H, since $m_p \gg m_e \rightarrow \mu \approx m_e$

Proof $\vec{r}_1 = \vec{r}_1^{\text{from COM}}$ { Separation: $\vec{r} = \vec{r}_1 - \vec{r}_2$

$$\vec{r}_2 = \vec{r}_2^{\text{from COM}}$$
 { between $p + e^-$

Set $\vec{R}_{\text{COM}} = \left[\frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \right] = 0 \Rightarrow$ put COM @ origin.

\Rightarrow Can solve for $\vec{r}_1 - \vec{r}_2$:

$$\Rightarrow \left[\vec{r}_1 = \frac{m_2}{m_1 + m_2} \vec{r}, \quad \vec{r}_2 = \frac{-m_1}{m_1 + m_2} \vec{r} \right]$$

$$\Rightarrow \left\{ \begin{array}{l} \frac{d\vec{r}_1}{dt} = \frac{m_2}{m_1 + m_2} \frac{d\vec{r}}{dt} \\ \frac{d\vec{r}_2}{dt} = \frac{-m_1}{m_1 + m_2} \frac{d\vec{r}}{dt} \end{array} \right\} \rightarrow \text{+VE} \quad \sum KE = \frac{1}{2} m_1 \left(\frac{d\vec{r}_1}{dt} \right)^2 + \frac{1}{2} m_2 \left(\frac{d\vec{r}_2}{dt} \right)^2 + V(r)$$

$$\text{So total energy} \Rightarrow E = \frac{1}{2} m_1 \left(\frac{m_2}{m_1 + m_2} \right)^2 \left(\frac{dr}{dt} \right)^2 + \frac{1}{2} m_2 \left(\frac{m_1}{m_1 + m_2} \right)^2 \left(\frac{dr}{dt} \right)^2 + V(r)$$

$$\boxed{\text{So}} \quad \sum E = \frac{1}{2} \frac{m_1 m_2}{(m_1 + m_2)^2} (m_1 + m_2) \left(\frac{dr}{dt} \right)^2 + V(r)$$

$$\hookrightarrow \sum E = \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} \left(\frac{dr}{dt} \right)^2 + V(r)$$

$$\boxed{\sum E = \frac{1}{2} \mu \left(\frac{dr}{dt} \right)^2 + V(r)}$$

effective one-body problem, with reduced mass μ .

To go to 3D \rightarrow need to generalize the Schrödinger eq. \rightarrow upgrade operators.

$$\text{Recall } \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \leftarrow 1D$$

$$\hookrightarrow \hat{H} \Psi(x,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,t) \leftarrow \text{time-dependent SE}$$

$$\text{with } \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hookrightarrow \boxed{\hat{H}_x = \frac{\hat{p}_x^2}{2m} + V(x)}$$

To generalize to 3D \rightarrow replace \hat{p}_x^2 by $\hat{\vec{p}}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$

$$\left. \begin{array}{l} \text{with } \hat{p}_y = (-i\hbar) \frac{\partial}{\partial y} \rightarrow \hat{p}_z = (-i\hbar) \frac{\partial}{\partial z} \end{array} \right\}$$

$$\text{To replace} \left. \begin{array}{l} \frac{\partial^2}{\partial x^2} \xrightarrow{\text{by}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = \vec{\nabla}^2 \end{array} \right\}$$

$$\hookrightarrow \text{gradient } \vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$$

$$\boxed{\text{The Laplacian}} = \vec{\nabla}^2 = \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \rightarrow \star$$

So the momentum operator becomes

$$\hat{\vec{p}} = (-i\hbar) \vec{\nabla}$$

$$\rightarrow \frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m} \vec{\nabla}^2$$

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

The potential energy becomes \rightarrow

$$V(\vec{r})$$

and wavefunction

$$\Psi(\vec{r}, t) = \Psi(x, y, z, t)$$

3D-time dependent Schrödinger Eq.

(let $m = \mu$ (reduced mass)) \Rightarrow set 3D SE

Schrödinger eqn

$$\frac{-\hbar^2}{2\mu} \vec{\nabla}^2 \Psi(\vec{r}, t) + V(\vec{r}, t) \Psi(\vec{r}, t) = (i\hbar) \frac{\partial}{\partial t} \Psi(\vec{r}, t)$$

Note, we're using the reduced mass $\mu \approx m_e$.

The interpretation of Ψ is similar to before

$\bullet \Psi(\vec{r}, t) \leftarrow$ probability amplitude

$\bullet |\Psi(\vec{r}, t)|^2 \leftarrow$ probability per volume of finding particle in $\vec{r} \rightarrow \vec{r} + d\vec{r}$ at time t .

$\bullet |\Psi(\vec{r}, t)|^2 d^3 r \leftarrow$ probability of being in volume $d^3 r \ni \vec{r}, t$.

This should be normalized

$$\iiint_{-\infty}^{\infty} |\Psi(\vec{r}, t)|^2 d^3 r = 1$$

where $d^3 r = dx dy dz$ in Cartesian coordinates.

Calculate expectation values!

$$\boxed{\overline{f(\vec{r})} = \iiint_{-\infty \rightarrow \infty} \Psi^*(\vec{r}, t) f(\vec{r}) \Psi(\vec{r}, t) d^3 r}$$

$\hat{f}(\vec{r}) = f(\vec{r})$

But different for \hat{p}

$$\boxed{\hat{p} = \iint_{-\infty \rightarrow \infty} \int_{-\infty}^{\infty} \Psi^*(\vec{r}, t) (-i\hbar) \nabla \Psi(\vec{r}, t) d^3 r} \Rightarrow \text{gives a vector number}$$

\hat{p}

For time-independent potentials: $V = V(\vec{r})$ (no t -dep)

↪ separation of variables.

Let $\boxed{\Psi(\vec{r}, t) = \psi(\vec{r}) \phi(t)}$

Find $\boxed{\phi(t) = e^{-iEt/\hbar}}$ ← always.

and $\psi(\vec{r})$ has to satisfy t -ind SE.

↪ $\boxed{\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})}$

↪ $\boxed{\hat{H} \psi(\vec{r}) = E \psi(\vec{r})}$ ← eigenvalue problem.

For H atom \rightarrow want to solve for Coulomb potential

$$V(\vec{r}) = \frac{-e^2}{4\pi\epsilon_0 r} \Rightarrow \text{Use Cartesian coordinates where}$$

$r = |\vec{r}|$ magnitude only

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$\hookrightarrow r = \sqrt{x^2 + y^2 + z^2}$ other complicated...

$$\boxed{V(x, y, z) = \frac{-e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}}}$$

Get the time-independent SE for H.

$$\boxed{-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z) - \frac{e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} \Psi(x, y, z) = E \Psi(x, y, z)}$$

messy! \rightarrow too complicated in Cartesian coordinates \Rightarrow stuck...

\Rightarrow separation of variables DOES NOT work in Cartesian coordinates...

BUT in Spherical coordinates (r, θ, ϕ) , $V = V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$ only!

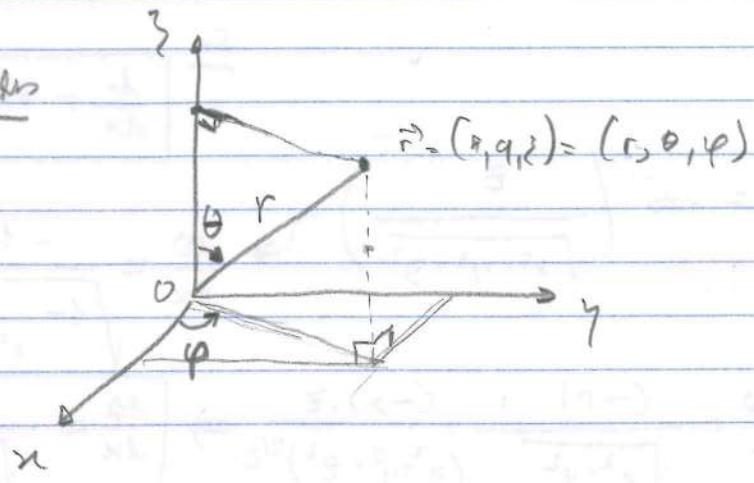
\hookrightarrow spherically symmetric!

\hookrightarrow Switching to spherical coordinates $(r, \theta, \phi) \rightarrow$ but no use separation of variables...

Spherical coordinates

These are related

$$\left\{ \begin{array}{l} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{array} \right\}$$



Can invert these $\rightarrow r = \sqrt{x^2 + y^2 + z^2}$

$$\left\{ \begin{array}{l} \theta = \cos^{-1}\left(\frac{z}{r}\right) = \sin^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right) \\ \varphi = \tan^{-1}\left(\frac{y}{x}\right) \end{array} \right.$$

But what does $\vec{\nabla}^2$ become?

What is $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$?

$$\left\{ \begin{array}{l} x = r \sin \theta \cos \varphi \\ y = r \sin \theta \sin \varphi \\ z = r \cos \theta \end{array} \right.$$

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Recall $V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$ \rightarrow central potential, spherically symmetric
 \rightarrow has no θ, φ dep in spherical coordinate (r, θ, φ)

\rightarrow separation of variables should work

\Rightarrow Need to convert SE 3D to spherical coordinates.

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi + V(r) \psi = E \psi \quad \text{and} \quad \vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{in spherical "}$$

Now $x = x(r, \theta, \varphi)$

Chain rule
$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x} \frac{\partial}{\partial \varphi}$$

what are these?

Now $r = \sqrt{x^2 + y^2 + z^2} \rightarrow \frac{dr}{dx} = \frac{x}{\sqrt{x^2 + y^2 + z^2}} = \frac{x}{r} = \frac{r \sin \theta \cos \varphi}{r}$

So

$$\boxed{\frac{dr}{dx} = \sin \theta \cos \varphi}$$

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right) \rightarrow \frac{d\theta}{dx} = \frac{-1}{\sqrt{1 - \frac{z^2}{x^2 + y^2 + z^2}}} \cdot \frac{\partial}{\partial x} \left(\frac{z}{\sqrt{x^2 + y^2 + z^2}} \right)$$

$$\Rightarrow \frac{d\theta}{dx} = \frac{(-r)}{\sqrt{x^2 + y^2}} \cdot \frac{(-x) \cdot z}{(x^2 + y^2 + z^2)^{3/2}} \Rightarrow \boxed{\frac{d\theta}{dx} = \frac{xz}{\sqrt{x^2 + y^2}} \cdot \frac{1}{r^2}}$$

$$\Rightarrow \frac{d\theta}{dx} = \frac{(r^2 \cdot \sin \theta \cos \varphi) \cos \theta}{\sqrt{r^2 \sin^2 \cos^2 + r^2 \sin^2 \theta \sin^2 \varphi}} \quad \frac{1}{r^2} = \boxed{\frac{\cos \theta \cos \varphi}{r} = \frac{d\theta}{dx}}$$

and

$$\boxed{\frac{d\varphi}{dx} = \frac{-\sin \varphi}{r \sin \theta}} \quad (\text{with } \theta = \tan^{-1}\left(\frac{y}{x}\right))$$

$$\boxed{\frac{\partial}{\partial x} = (\sin \theta \cos \varphi) \frac{\partial}{\partial r} + \left(\frac{\cos \theta \cos \varphi}{r}\right) \frac{\partial}{\partial \theta} + \left(\frac{-\sin \varphi}{r \sin \theta}\right) \frac{\partial}{\partial \varphi}}$$

Next, compute $\frac{\partial^2}{\partial x^2}$ and $\frac{\partial^2}{\partial y^2}$ and $\frac{\partial^2}{\partial z^2}$

Final answer for the laplacian

$$\boxed{\vec{\nabla}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}}$$

See Appendix M

With $V = V(r)$ only (no θ, φ dependence) \rightarrow "called a "central potential"

Can use separation of variables! \rightarrow Now SE

$$\boxed{-\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi(r, \theta, \varphi) + V(r) \Psi(r, \theta, \varphi) = E \Psi(r, \theta, \varphi)}$$

No θ, φ dependence!

Separate variable

$$\boxed{\Psi(r, \theta, \varphi) = R(r) Y(\theta, \varphi)}$$

Plug into

$$\boxed{\vec{\nabla}^2 \Psi + \frac{2m}{\hbar^2} (E - V(r)) \Psi = 0}$$

$$\boxed{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} (R\Psi) \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} (R\Psi) \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} (R\Psi) + \frac{2m}{\hbar^2} (E - V(r)) R\Psi = 0}$$

→ Divide by $R(r)$ + multiply by r^2

$$\rightarrow \frac{1}{R(r)} \left[\frac{\partial}{\partial r} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) r^2 R(r) \right]$$

$$+ \frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right] = 0$$

Notice $\begin{cases} 1^{\text{st}} \text{ term is a function of } r \\ 2^{\text{nd}} \text{ term is a function of } \theta, \phi \end{cases}$ → But eqn has to hold true $\forall r, \theta, \phi$

↳ \Leftrightarrow both terms add to 0, and = constant
 \Rightarrow if $\begin{cases} 1^{\text{st}} \text{ term} = 2 \\ 2^{\text{nd}} \text{ term} = -2 \end{cases}$ $\rightarrow 2 + (-2) = 0$

Now 1st term becomes (div by r^2 , multi by R)

Radial eqn

$$\boxed{\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) R(r) - \frac{\lambda}{r^2} R(r) = 0}$$

2nd term becomes : Multiply by $-Y$ angular momentum operator

$$\boxed{- \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = \lambda Y(\theta, \phi)}$$

eigen problem

Note : get some angular eqn + solutions $Y(\theta, \phi)$ for any central potential $V(r)$

The full solution is a product $\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$

$$\boxed{\Psi = \Psi(r, \theta, \phi) \Phi(t)}$$

$$\text{For H} \rightarrow V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

Outline what we'll see → need to solve w/ the power series method

↳ also need to separate $\Psi(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$

↳ The answers will be:

Radial solutions → depend on 2 quantum number

$$\begin{cases} n = 1, 2, 3, \dots & \text{principle} \\ l = 0, 1, 2, \dots (n-1) & \text{angular} \end{cases}$$

↳ $R_{n,l}(r)$ = special functions → exponential times poly(r)

Angular solutions → depend on $\begin{cases} l = 0, 1, \dots, n-1 & \text{any} \\ m_l = 0, \pm 1, \dots, \pm l & \text{mag} \end{cases}$

↳ $Y_{l,m_l}(\theta, \varphi) = \text{polyr in } (\cos\theta) \text{ and } e^{i\varphi}$
 ↳ called "spherical harmonics"

The full solutions are $\begin{matrix} \text{radial} \\ \downarrow \\ R_{n,l}(r) \end{matrix} \quad \begin{matrix} \text{angular} \\ \downarrow \\ Y_{l,m_l}(\theta, \varphi) \end{matrix}$

$$\Psi_{n,l,m_l}(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m_l}(\theta, \varphi)$$

The 3 integers n, l, m_l are quantum numbers where

$$\left\{ \begin{array}{l} n: \text{quantized } E \\ l: \text{quantized } L^2 \\ m_l: \text{quantized } L_z \end{array} \right\} \rightarrow \begin{array}{l} \text{Quantization is a result of} \\ \text{"using the power series method."} \\ \rightarrow \text{like in SHO (quantization...)} \end{array}$$

Also the separation constant $\lambda = l(l+1)$ and

$$E_n = \frac{-me^4}{(4\pi\epsilon_0)^2 2k^2 n^2} = \frac{-13.6}{n^2}$$

Interestingly, $E_n = \frac{-me^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = \frac{-13.6 \text{ eV}}{n^2}$ ← same result found by Bohr

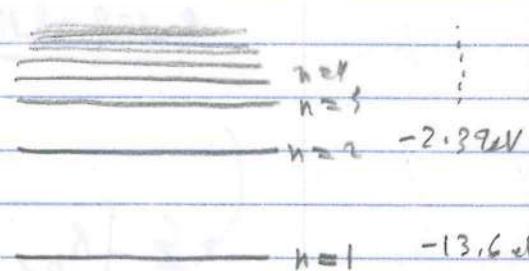
comes from solving SE.

- Have 3 quantum numbers

$$\left\{ \begin{array}{l} n = 1, 2, 3, \dots \\ l = 0, 1, 2, \dots (n-1) \\ m_l = 0, \pm 1, \pm 2, \dots \pm l \end{array} \right\}$$

But note E_n only depends on n

Energy levels are degenerate



For each n , have $l = 0, 1, 2, \dots (n-1)$

\hookrightarrow n states of different l , and for each l
 $m_l = 0, \pm 1, \dots \pm l$

\hookrightarrow there are $(2l+1)$ values of m_l

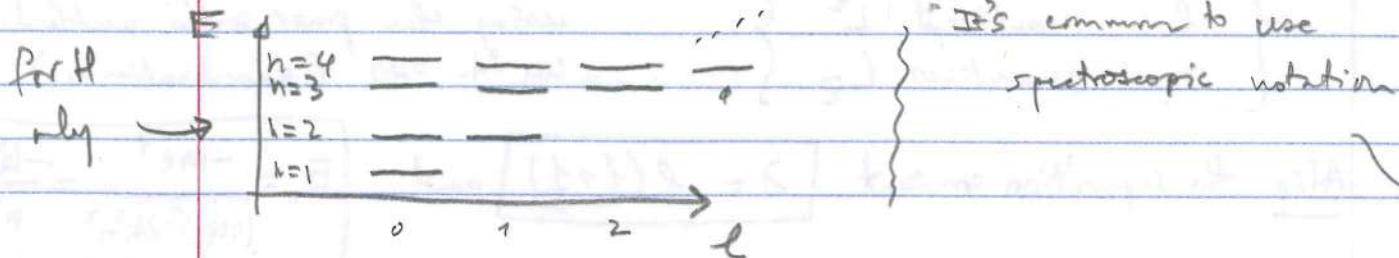
The energies E_n are said to be "degenerate" in l and m_l

Mar 29, 2018

w/o spin

$\left\{ \begin{array}{l} n=1 \rightarrow 1 \text{ state} \\ n=2 \rightarrow 4 \text{ states} \\ n=3 \rightarrow 9 \text{ states} \end{array} \right\}$ in that the degeneracy = n^2 for the n^{th} level in H
 (note w/o spin!)

Can also display states differently.



Spectroscopic notation $\rightarrow l=0 : s$ states

$l=1 : p$ states

$l=2 : d$ states

$l=3 : f$ states

...

Table 7-2 \rightarrow shows $\Psi_{n\ell m\ell}$ states for H

$$Z=1 \text{ for H} , \left[a_0 = \frac{4\pi E_0 \hbar^2}{\mu e^2} = 0.529 \text{\AA} \right] \leftarrow \text{Bohr radius}$$

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

Now, where do these $\Psi_{n\ell m\ell}$ come from?

\hookrightarrow need to solve the angular + radial equation:

$$\boxed{\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V(r)) R(r) - \frac{l(l+1)}{r^2} R(r) = 0}$$

separation eqn

Angular eqn

$$\boxed{- \left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} \right] Y(\theta, \phi) = \lambda Y(\theta, \phi)}$$

Note: the form is an operator, Y = number, Y

\hookrightarrow eigen problem!

\hookrightarrow so what is this operator?

\hookrightarrow can show that the operator is related to \vec{L}^2 (angular p op²)

ANGULAR MOMENTUM IN QM

Classically:

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

$$\rightarrow \begin{cases} L_x = yP_z - zP_y \\ L_y = zP_x - xP_z \\ L_z = xP_y - yP_x \end{cases}$$

$$\text{and } L^2 = L_x^2 + L_y^2 + L_z^2$$

In QM, p_x, p_y, p_z becomes operators!

$$\hookrightarrow \boxed{\hat{p}_x = -ik \frac{\partial}{\partial x}, \hat{p}_y = -ik \frac{\partial}{\partial y}, \hat{p}_z = -ik \frac{\partial}{\partial z}}$$

$$\hookrightarrow \left. \begin{array}{l} \hat{L}_x = (-ik) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y = (-ik) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z = (-ik) \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \\ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \end{array} \right\}$$

need to change into spherical coordinates!
So they can act on $\psi(r, \theta, \varphi)$

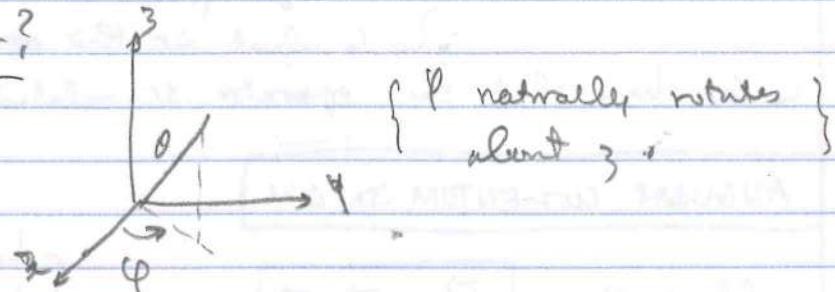
To do this, use the chain rule.

$$\text{let } x = x(r, \theta, \varphi) \rightarrow \boxed{\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x} \frac{\partial}{\partial \varphi}}$$

\hookrightarrow spent some time dealing with this...

$$\hookrightarrow \left. \begin{array}{l} \hat{L}_x = (ik) \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_y = (ik) \left(-\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_z = (ik) \left(-\frac{1}{r} \right) \end{array} \right\}$$

Why is z simpler?



lastly, find $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ important...

$$\hookrightarrow \text{get } \boxed{\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]}$$

Note \hat{L}^2 very similar to $\vec{r}^2 Y(\theta, \phi)$! \vec{r} angular \rightarrow same operators as in that in $Y(\theta, \phi)$.

$$\hookrightarrow \boxed{\hat{L}^2 Y(\theta, \phi) = \ell \hbar^2 Y(\theta, \phi)} \quad \text{angular eq becomes an eigenvalue problem.}$$

units $\rightarrow L \sim \hbar$ units.

$$\text{We will show } \lambda = \ell(\ell+1) \quad (\ell = 0, 1, 2, \dots)$$

$$\hookrightarrow \text{Then have } \hat{L}^2 Y(\theta, \phi) = \ell(\ell+1) \hbar^2 Y(\theta, \phi)$$

$$\text{Eigenvalues of } \hat{L}^2 \text{ are } \boxed{(\ell)(\ell+1)\hbar^2}$$

Remember that eigenvalues are exact.

Here that

$$\boxed{\begin{aligned} \hat{H} \Psi_{n,\ell,m_\ell} &= E \Psi_{n,\ell,m_\ell} \\ \hat{L}^2 \Psi_{n,\ell,m_\ell} &= \ell(\ell+1) \hbar^2 \Psi_{n,\ell,m_\ell} \end{aligned}}$$

and we'll also come see that

$$\boxed{\hat{L}_z \Psi_{n,\ell,m_\ell} = (m_\ell \hbar) \Psi_{n,\ell,m_\ell}}$$

\Rightarrow component of L

But still has uncertain values

for L_x, L_y

Solving the angular eqn

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] Y(\theta, \varphi) = \lambda Y(\theta, \varphi)$$

where : λ : separation constant...

↪ suppose $Y(\theta, \varphi) = \Theta(\theta) \Phi(\varphi)$

↪ plug it & divide by $\Theta \Phi$

↪ set: $-\frac{1}{\Theta(\theta)} \cdot \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{\partial}{\partial \theta} \Theta(\theta) \right) - \frac{1}{\Phi(\varphi)} \frac{1}{\sin^2 \theta} \frac{d^2 \Phi(\varphi)}{d\varphi^2} = \lambda = 0$

multiply by $\sin^2 \theta$

↪
$$\left[+ \frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Theta(\theta) \right) + \frac{1}{\Phi(\varphi)} \frac{d^2 \Phi(\varphi)}{d\varphi^2} \right] = 0$$

$\underbrace{+ \text{ dep.}}_{(\pm q)} \quad \underbrace{+ \lambda \sin^2 \theta}_{(-q)}$ $\underbrace{- \text{ dep.}}_{(\pm q)}$

→ q = separation constant \rightarrow get 2 ODE.

heat power series method

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Theta(\theta) \right) + (\lambda \sin^2 \theta) \Theta(\theta) = q \Theta(\theta)$$

and
$$\frac{1}{\Phi(\varphi)} \frac{d^2 \Phi(\varphi)}{d\varphi^2} = -q \Rightarrow \frac{d^2 \Phi}{d\varphi^2} = -\Phi(\varphi) q$$
 ↗ can set solv

For $\Phi(\varphi)$ we have $\rightarrow e^{-i\sqrt{q}\varphi}, e^{+i\sqrt{q}\varphi}$ (to be continued...)

Recall angular Eqn

Mar 21, 2018

$$-\left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] Y(\theta, \varphi) = \lambda Y(\theta, \varphi)$$

$\boxed{L^2 Y(\theta, \varphi) = \lambda t^2 Y(\theta, \varphi)}$

↑ separation constant

Separate again $Y(\theta, \varphi) = \Theta(\theta) \Phi(\varphi)$

get 2 ODEs \Rightarrow $\boxed{\sin\theta \frac{d}{d\theta} (\sin\theta \frac{d\Theta}{d\theta}) + (\lambda \sin^2\theta) \Theta(\theta) = q \Theta(\theta)}$

and $\boxed{\frac{d^2 \Phi(\varphi)}{d\varphi^2} = -q \Phi(\varphi)} \rightarrow \Phi(\varphi) = e^{i\sqrt{q}\varphi} + e^{-i\sqrt{q}\varphi}$

As good solutions, Φ must be single-valued

\Rightarrow must require: $\Phi(\varphi) = \Phi(\varphi + 2\pi)$

$\Rightarrow e^{i\sqrt{q}\varphi} = e^{i\sqrt{q}(\varphi+2\pi)} \Rightarrow 1 = e^{i\sqrt{q}(2\pi)}$

$\hookrightarrow \boxed{1 = \cos(\sqrt{q}2\pi) + i \sin(\sqrt{q}2\pi)}$

\hookrightarrow need $\sqrt{q} = 0, 1, 2, 3, \dots$

Call $m_q = \text{integer} \Rightarrow q = m_q^2$

So solution $\boxed{\Phi(\varphi) = e^{im_q\varphi}}$

We can include $e^{-im_q\varphi}$ solution as well, by letting $m_q < 0$

$\hookrightarrow m_q = \{\pm 0, \pm 1, \pm 2, \dots\}$

Notice what we get if $\hat{L}_z = -it \frac{\partial}{\partial\varphi}$ acts on $\Phi(\varphi) = e^{im_q\varphi}$

$$\hookrightarrow \hat{L}_z \Phi(\varphi) = (-i\hbar) \frac{\partial}{\partial \varphi} \Phi(\varphi) = (-i\hbar)(im_e) e^{im_e \varphi}$$

$$\boxed{\hat{L}_z \Phi(\varphi) = m_e \Phi(\varphi)} \quad \text{get } m_e \hbar = L_z \text{ eigenvalues (also quantized)}$$

Note that $\sin(\sqrt{q}\varphi)$ or $\cos(\sqrt{q}\varphi)$ would not give this result...

→ Better to use $e^{im_e \varphi}$, since there have definite L_z values labeled by m_e

With $q = m_e^2$

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Theta(\theta) \right) + \left(2\sin^2 \theta - m_e^2 \right) \Theta(\theta) = 0$$

divide by $\sin^2 \theta$

$$\boxed{\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Theta \right) + \left(2 - \frac{m_e^2}{\sin^2 \theta} \right) \Theta = 0} \quad (*)$$

too complicated
as a fn of θ

→ to solve $\boxed{\text{let } z = \cos \theta}$

chain rule $\boxed{\frac{d}{dt} = \frac{dz}{d\theta} \frac{d}{dz} = -\sin \theta \frac{d}{dz} = -\sqrt{1-z^2} \frac{d}{dz}} \quad (6)$

$$\text{So } \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Theta \right) = \frac{1}{\sqrt{1-z^2}} (-\sqrt{1-z^2}) \frac{d}{dz} \left(\sqrt{1-z^2} \frac{d}{dz} \Theta \right)$$

$$= \frac{d}{dz} \left((1-z^2) \frac{d}{dz} \Theta \right)$$

associated legendre eqn

So (*) becomes $\boxed{\frac{d}{dz} \left([1-z^2] \frac{d}{dz} \Theta \right) + \left(2 - \frac{m_e^2}{1-z^2} \right) \Theta = 0}$

can't yet use power series method? But will turn out that the solutions of z depends on 2 quantum numbers l and m_l

↪ label soln as $\Theta_{l,m_l}(z) = \Theta_{l,m_l}(\cos \theta)$

To get an eq. that can be solved using the power series method, let

$$\textcircled{H} \quad P_{l+M_l}(z) = (1-z^2)^{\frac{l+M_l}{2}} \frac{d^{l+M_l}}{dz^{l+M_l}} P_l(z)$$

Plug in...
$$(1-\frac{z}{r}) \frac{d^2 P_l}{dz^2} - 2z \frac{d P_l}{dz} + \lambda P_l = 0 \quad \text{Legendre's equation}$$
 (L)

To verify that this works, would need to take $l+M_l$ derivatives of Legendre's eqn + show it gives back the Associate Legendre eq (we won't do this)

(L) can be solved using the power series method!

Let
$$P_l(z) = \sum_{k=0}^{\infty} a_k z^k \quad (\text{Recall: } z = r \cos \theta)$$

→ plug into (L) and find recursion relation for a_k , get:

$$a_{k+2} = \frac{k(k+1) - \lambda}{(k+2)(k+1)} a_k$$

→ get 2 series: { one with even powers }
{ one with odd powers }

But find that the full infinite power series is divergent.

→ need to truncate it. (just like in SMD)

→ So for some k value, say $k=l$ where $l=0, 1, 2, \dots$

Require that $a_{l+2} = \frac{l(l+1)-\lambda}{(l+2)(l+1)} a_l = 0 \Rightarrow$ so that the series stops.

Must require that $\lambda = l(l+1)$ Then P_l does not diverge

$$(l_1 = 0, 1, 2, \dots)$$

The solutions are then finite polynomials of order l

$$P_l(z) = \text{Legendre Polynomials}$$

even powers for l even
odd powers for l odd

Normalized in math

$$\hookrightarrow P_l(1) = 1$$

The first few Legendre's poly's are

$$\begin{aligned} P_0(z) &= 1 \\ P_1(z) &= z \\ P_2(z) &= \frac{1}{2}(3z^2 - 1) \\ P_3(z) &= \frac{1}{2}(5z^3 - 3z) \\ &\vdots \end{aligned}$$

but remember that

$$z = w\theta$$

Note Appendix N in book uses a nonstandard normalization

But what about the associated Legendre equations?

Use $\left\{ \Phi_{lm_l}(z) = (1-z^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|}}{dz^{|m_l|}} P_l(z) \right.$

$$\left. \Phi_{lm_l}(z) \right)$$

Note since $P_l(z)$ is a poly of order l , then if $|m_l| > l$
we get 0

so we get condition: $|m_l| \leq l$

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

as allowed values...

Note the book denotes derivatives as

$$F_{l,m_l}(w\theta) = \frac{d^{|m_l|}}{dz^{|m_l|}} P_l(z)$$

non standard

$$\rightarrow \Phi_{l,m_l}(\theta) = \sin \theta F_{l,m_l}$$

So the full angular solutions

$$\hookrightarrow Y_{\ell, m_\ell}(\theta, \varphi) = \underset{Q_{\ell, m_\ell}}{\textcircled{H}}(\theta) \underset{M_\ell}{\textcircled{\Phi}}(\varphi)$$

called "spherical harmonics"

assoc.
Legendre
equation

\vec{z} component

This is λ

These obey

$$\begin{aligned} \vec{L}^2 Y_{\ell, m_\ell} &= (\ell + 1) \ell \hbar^2 Y_{\ell, m_\ell} \\ \vec{L}_z Y_{\ell, m_\ell} &= m_\ell \hbar Y_{\ell, m_\ell} \end{aligned}$$

Note $\left\{ \vec{L}^2 = \sqrt{\ell(\ell+1)} \hbar \right. \left. \rightarrow \text{magnitude} \right.$

$$\vec{L}_z = m_\ell \hbar \quad m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$$

$\rightarrow (2\ell+1)$ values!

Summary on how to solve $\Psi(\vec{r}, t)$

$$\hookrightarrow \Psi(r, t) \rightarrow \phi(t) = e^{-iEt/\hbar} \quad \left. \begin{array}{l} \psi(\vec{r}) = \psi(r, \theta, \varphi) \\ \text{separation const} = E \end{array} \right\}$$

$R(r)$

separation constant = λ

$Y(\theta, \varphi)$

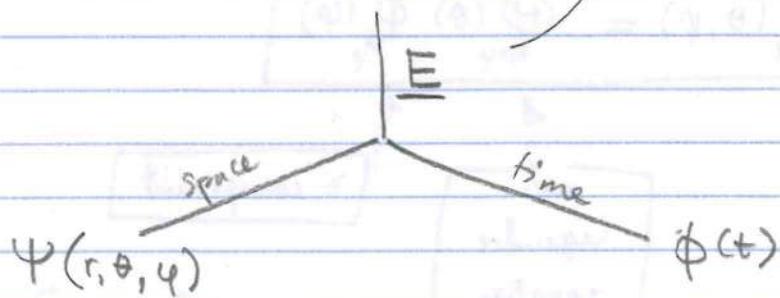
$$\begin{aligned} \text{Relations} \quad &E \sim n^2, \ell \leq n-1 \\ &\lambda = (\ell+1) \ell \\ &|m_\ell| \leq \ell \end{aligned}$$

$\textcircled{H}(\theta)$

$$q = m_\ell^2$$

$\vec{\Phi}(\varphi)$

Summary chart $\Psi(\vec{r}, t)$ \rightarrow separation constant!



$$\lambda = l(l+1)$$

Solutions $E \sim n^2$, $n-1 \geq l$

$$|m_l| \leq l$$

$$\lambda = l(l+1)$$

$$q = m_e^2$$

$$\Theta(\theta)$$

$$\Phi(\varphi)$$

Operators

\hat{L}_z -angular mom. • $\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$ $\Rightarrow \Phi(\varphi) = e^{i\sqrt{q}\varphi} = e^{im_e\varphi}$

$$\text{So } \hat{L}_z \Phi(\varphi) = (m_e \hbar) \Phi(\varphi)$$

Angular mom. • $\hat{L}^2 Y(\theta, \varphi) = \lambda \hbar^2 Y(\theta, \varphi) \Rightarrow \hat{L}^2 Y(\theta, \varphi) = l(l+1) \hbar^2 Y(\theta, \varphi)$

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

Energy • Time-ind $\hat{H} \Psi_{n_l, m_l} = E \Psi_{n_l, l, m_l}$

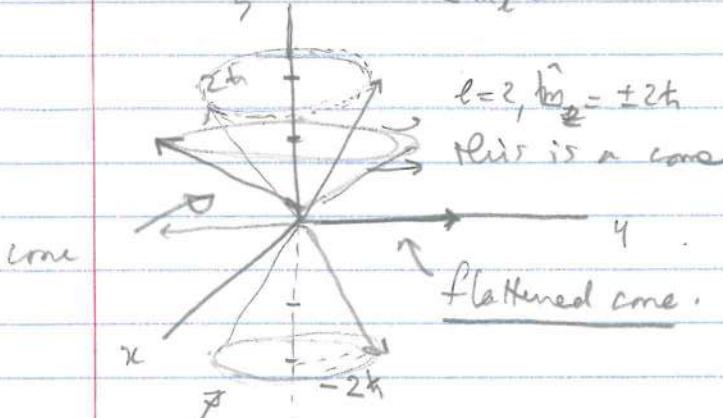
Spherical Harmonics { $\hat{Y}_{\ell m_\ell}(\theta, \phi) = \ell(\ell+1)t^\ell Y_{\ell m_\ell}(\theta, \phi)$
 where $\ell = 0, 1, \dots$
 $m_\ell = 0, \pm 1, \dots$

We have for \vec{L} : and $|\vec{L}| = \sqrt{\ell(\ell+1)}t$ ← quantized.
 $|\vec{L}_z| = m_\ell t$

Ex let's draw a diagram for

\vec{L} in an $\ell=2$ state

$$\ell=2 \quad \begin{cases} m_\ell = 0 \\ m_\ell = \pm 1 \\ m_\ell = \pm 2 \end{cases} \Rightarrow |\vec{L}| = \sqrt{6}t \quad \begin{cases} 1 \text{ orientation} \\ \text{let } |\vec{L}_z| = \{0, \pm t, \pm 2t\} \end{cases}$$



$$\ell=2, \vec{m}_\ell = \pm 2t$$

This is a cone

→ we don't know anything about the other components.

we have exact value for $|\vec{L}|$,
 but $|\vec{L}_x|, |\vec{L}_y|$ components are determined exactly

due to uncertainty relations.

THE RADIAL SOLUTION

→ will only outline how to solve for the radial wave function ($R(r)$)

→ uses power series method (See Appendix N)

well

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\epsilon_0 r} \right] R = \frac{\ell(\ell+1)}{r^2} R$$

(Expand)

$$-V(r)$$

$$\frac{d^2R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\epsilon_0 r} \right] R = \frac{\ell(\ell+1)R}{r^2}$$

→ power series method won't work yet...

→ Extract parts of the solution...

Can solve for $r \rightarrow \infty \Rightarrow \boxed{\frac{d^2R}{dr^2} - \beta^2 R \approx 0}$

where $\beta = \sqrt{-\frac{2mE}{\hbar^2}} > 0$

Expect $E < 0$ for H atom bound states. This solution: $R = e^{-\beta r}$

• Can also solve for $r \rightarrow 0$

↳ dominant terms in this limit are:

$$\left[\frac{d^2R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \approx \frac{l(l+1)}{r^2} R \right]$$

This has solutions: $R \propto r^l \leftarrow$ will verify in homework...

Trial solution

$$R(r) = r^l e^{-\beta r} G(r)$$

Get an eq. for $G(r)$ that can be solved using the power series method

⇒ Find that the series diverges unless truncate it

$$\boxed{E_n = \frac{-m\epsilon^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \leftarrow -13.6 \text{ eV} \frac{1}{n^2} \quad \text{Note } n \neq 0}$$

• and $n = 1, 2, \dots, l+1$ or $\boxed{l \leq n-1}$

The solutions have the form →

$$R(r) = e^{-\frac{r}{a_0}} \cdot \left(\frac{r}{a_0}\right)^l G_{n,l}\left(\frac{r}{a_0}\right)$$

where $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \text{ \AA}$ ← Bohr radius

To summarize the exact solution to H atom

$$\begin{aligned}\Psi_{n,l,m_l}(r, \theta, \varphi) &= R_{n,l}(r) \cdot Y_{l,m_l}(\theta, \varphi) \\ &= R_{n,l}(r) \cdot \Theta_{l,m_l}(0) \Phi_{m_l}(\varphi)\end{aligned}$$

Quantum numbers obey:
 $\begin{cases} n = 1, 2, \dots \\ l = 0, 1, \dots n-1 \\ m_l = 0, \pm 1, \dots \pm l \end{cases}$

Energies:

$$\hookrightarrow E_n = \frac{-\mu e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = (-13.6 \text{ eV}) \frac{1}{n^2}$$

\leftarrow degenerate
for l, m_l

Note

\hookrightarrow solutions are simultaneous of 3 operators

$$\begin{aligned}\hat{H}\Psi_{n,l,m_l} &= E\Psi_{n,l,m_l} \\ \hat{L}^2\Psi_{n,l,m_l} &= l(l+1)\hbar^2\Psi_{n,l,m_l} \\ \hat{L}_z\Psi_{n,l,m_l} &= m_l\hbar\Psi_{n,l,m_l}\end{aligned}$$

\rightarrow can look up Ψ_{n,l,m_l} in

Table 7-2

\hookrightarrow what do solutions look like?

\hookrightarrow PROBABILITY DENSITY: The full time dep. solns are

$$\Psi_{n,l,m_l}(\vec{r}, t) = \Psi_{n,l,m_l}(\vec{r}) e^{-iE_nt/\hbar}$$

\hookrightarrow But p. density (per volume)

$$\hookrightarrow |\Psi|^2 = |\Psi_{n,l,m_l}|^2 \rightarrow \text{no t - dep stationary states!}$$

With $\Psi_{nlm_l} = R_{nl} \Theta_{lm_l} \Phi_{ml}$

$$\underline{\Sigma} |\Psi_{nlm_l}|^2 = R_{nl}^* R_{nl} \Theta_{lm_l}^* \Theta_{lm_l} \Phi_{ml}^* \Phi_{ml}$$

But remember $\Phi_{ml} = e^{im_l \varphi} \rightarrow \Phi^* \Phi = 1$

So $|\Psi|^2$ is symmetric about z -axis \rightarrow ($z-L$ is conserved...)

$$\underline{\Sigma} \boxed{|\Psi_{nlm_l}|^2 = R_{nl}^* R_{nl} \Theta_{lm_l}^* \Theta_{lm_l}} \quad (\text{since } \Phi^* \Phi = 1)$$

They are normalized so that:

$$\iiint |\Psi_{nlm_l}|^2 dr = 1$$

In Cartesian coordinates

$$\rightarrow d^3r = dx dy dz \text{ and } \iiint = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty}$$

But what is d^3r in spherical coordinates? \rightarrow Jacobian!

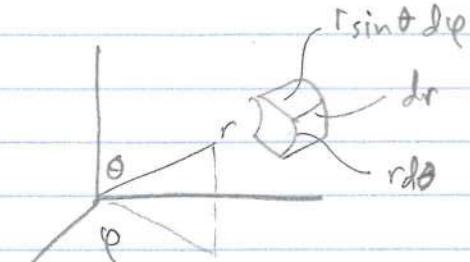
First, look in 2d @ polar coordinates

$$\begin{array}{c} \text{dy} \\ \square \\ \text{dx} \end{array} \rightarrow dxdy = dr \theta \rightarrow \text{arc} = r d\theta \rightarrow d^2r = r dr d\theta$$

$$\rightarrow d^2r = r dr d\theta$$

So In 3D...

$$\begin{array}{c} \text{dy} \\ \square \\ \text{dx} \end{array} \rightarrow dxdydz = d^3r$$



Integration ranges always

$$d^3r = r^2 \sin \theta dr d\theta d\phi$$

$$\begin{cases} 0 \leq r \leq \infty \\ 0 \leq \theta \leq \pi \\ 0 \leq \phi \leq 2\pi \end{cases}$$

So Int becomes

$$\left[\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi^* \Psi r^2 \sin\theta dr d\theta dp \right] = 1$$

will often use solid angle



$$d\Omega = \sin\theta d\theta d\phi$$

(unit sphere
of radius 1)

$$\iint d\Omega = 4\pi$$

angular opening
inside a
cone

So ...

$$1 = \int_{nl}^\infty R^* R r^2 dr \iint_{\text{cone}} \Theta_{nl}^*(\theta) \Theta_{nl}(\theta) \sin\theta d\theta dp$$

By convention, the angular part to normalized to 4π

$$1 = \int_0^\infty R_{nl}^*(r) R_{nl}(r) 4\pi r^2 dr$$

\Rightarrow can define a radial probability distribution!

surface of sphere

April 2, 2018 Recall $\Psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm_l}(\theta) \Phi_{ml}(\phi)$

operators $\hat{H}\Psi = E\Psi$

$$\hat{L}^2\Psi = l(l+1)t^2\Psi$$

$$\hat{L}_z\Psi = m_z t\Psi$$

Normalized

$$1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi^* \Psi r^2 \sin\theta dr d\theta dp$$

$$d^3r$$

Also $d^3r = r^2 dr d\Omega$ where $d\Omega = \sin\theta d\theta d\phi$ (opening of a cone)

Recall $\Phi_{ml} = e^{im_l\phi}$ so $\Phi^*\Phi = 1$

$$1 = \int_{nl}^\infty R_{nl}^* R_{nl} r^2 dr \iint_{\text{cone}} \Theta_{nl}^*(\theta) \Theta_{nl}(\theta) \sin\theta d\theta dp$$

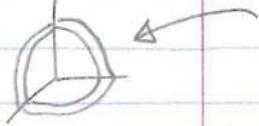
By convention, normalize

$$\int_0^{2\pi} \int_0^{\pi} R^* \Theta \sin\theta d\theta d\phi = 4\pi$$

So that leaves a purely radial distribution.

$$1 = \int_0^{\infty} R_{nl}^*(r) R_{nl}(r) \frac{4\pi r^2 dr}{dV}$$

volume between 2 shells of radii r and $r+dr$



With this, we can define a radial probability dist

$$P(r)dr = R_{nl}^*(r) R_{nl}(r) \cdot 4\pi r^2 dr$$

probability of e^- between r and $r+dr$

Note, $P(r)dr$ includes " r^2 " factor from the volume element d^3r

By itself

$$P_{nl}(r) = R_{nl}^*(r) R_{nl}(r) 4\pi r^2$$

$$P_{nl}(r) = |R_{nl}(r)|^2 4\pi r^2$$

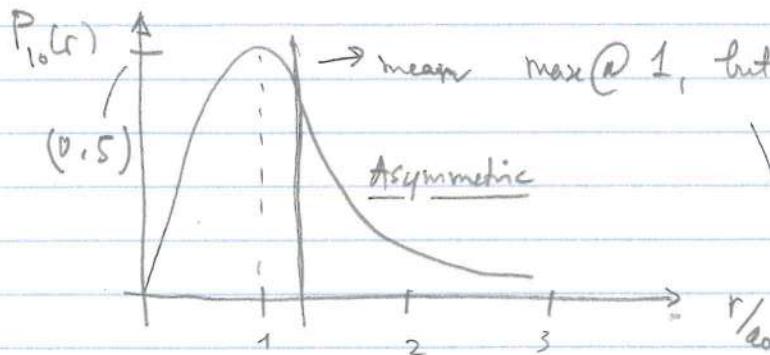
probability per length in radial direction

normalized $\int_0^{\infty} P_{nl}(r) = 1$

Now, we can look at plots of $P_{nl}(r)$ for the radial dist \rightarrow Figure 7.5

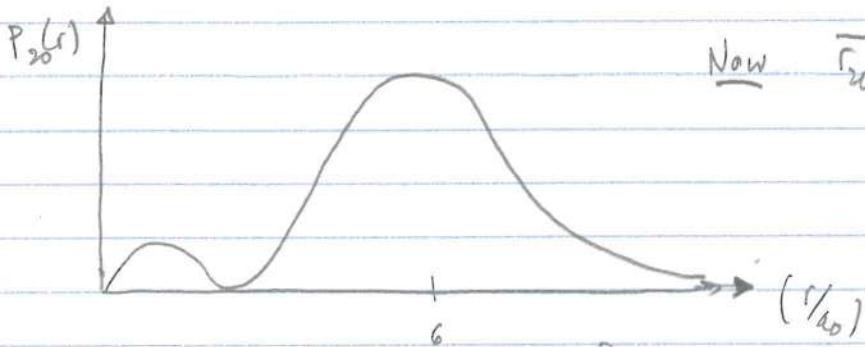
Ex $n=1, l=0 : P_{10} \propto r^2 e^{-2r/a_0}$ (for H atom)

average pos of e^-



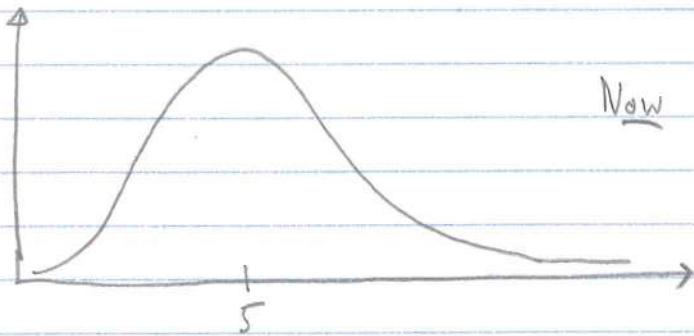
$$\bar{r}_{10} \approx 1.5 a_0$$

$$\text{Ex } n=2, l=0 \Rightarrow P_{20} \sim r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}}$$



$$\text{Now } \bar{r}_{20} = 6a_0$$

$$\text{Ex } n=2, l=1 \Rightarrow P_{21} \sim r^2 \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}}$$



$$\text{Now } \bar{r}_{21} = 5a_0$$

Note, an general observation: $\Rightarrow \bar{r}_{nl}$ increases with n

- But for fixed n , \bar{r} decreases as l increases... (higher l , e^- tucks in closer to nucleus)

- $l=0$ states have highest prob. of being near $r=0$

why? Recall $R \sim r^l$ for $r \rightarrow 0$. So if $l \neq 0$, then $r^l \ll 1$
 if $l=0 \rightarrow R \sim 1$

Next, calculate expectation values...

$$\bar{r}_{nl} = \int_0^\infty r P_{nl}(r) dr$$

Using properties of $P_{nl}(r)$ polys,
 you would get

$$\bar{r}_{nl} = a_0 \left[\frac{3n^2}{2} - \frac{l(l+1)}{2} \right]$$

Note, $n^2 \sim \bar{r}$

• also, if n = fixed, then

$$\bar{r} \sim -l^2$$

Ex Find where $P_{nl}(r)$ is maximum for $n=1$

$$\hookrightarrow \text{look up table } \Psi_{10} = (\text{const}) e^{-r/a_0} \Rightarrow R_{10} = \text{const. } e^{-r/a_0}$$

$$\text{So } P_{10}(r) = (\text{const}) r^2 e^{-2r/a_0}$$

$$P_{10}(r) = R^{\frac{1}{2}} R r^2 dr$$

Where is this maximum?

$$\frac{dP}{dr} = (\text{const}) \left[2re^{-2r/a_0} + \left(\frac{-2}{a_0}\right) r^2 e^{-2r/a_0} \right] = 0$$

$$\Rightarrow 2r = \frac{2r^2}{a_0} \quad \boxed{r = a_0} \quad \text{here, } P \text{ is max}$$

$$\text{But remember, } \boxed{R_{nl} = R_{10} = \frac{3}{2} a_0} \Rightarrow \text{Distribution is asymmetric}$$

Angular dependence-

+

solid angle
= $\sin\theta d\Omega d\varphi$

$$|\Psi_{nlm}|^2 d^3r = R_{nl} R_{lm} \Theta_{lm}^* \Phi_{ml} r^2 dr d\theta d\varphi$$

$$\text{Now } \Phi_{ml}(r) = 4\pi r^2 R_{nl}^{\frac{1}{2}}(r) R_{lm}(r) \rightarrow \text{gives radial prob density.}$$

So the remaining factor $\Theta_{lm}^*(\theta) \Theta_{lm}(\theta)$ is prob. per unit solid angle $d\Omega$

says which direction matter more

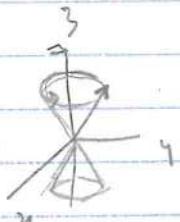
Since $\Phi_{ml}^*(\varphi) \Phi_{ml}(\varphi) = 1 \rightarrow$ there's no φ dependence \rightarrow prob is

symmetric around z -axis. So once the r, θ dependence is found,

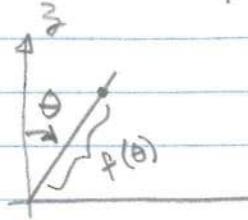
we just rotate the picture around the z -axis...

Since we can't graph $|\Psi_{nlm}|^2$ versus r, θ, φ (because we'd need 4D)

\hookrightarrow Instead, we use shadowing/shading to represent density in 3D space \rightarrow DENSITY PLOT

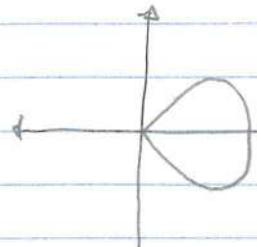


To visualize the angular modulation caused by $(\mathbb{H}_{\text{mod}}^+(\theta))^\star \mathbb{H}_{\text{mod}}^-(\theta)$
 use POLAR DIAGRAM
 e.g., $f(\theta)$ is a fn of θ



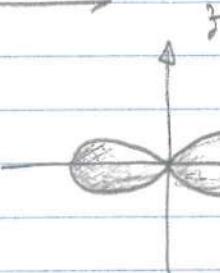
come out along θ by $f(\theta)$

Ex if $f(\theta) = \sin^2 \theta$



$$\sin^2 \theta$$

rotate
about z



higher prob.
are near
 $\theta \approx \frac{\pi}{2}$

April 4, 2018

Recall

$$P_{\text{re}}(r) = |R_m|^2 4\pi r^2$$

To get full prob dist, multiply by $|(\mathbb{H}(\theta))|^2$ → acts as a modulating function in angle.

To visualize this, use polar plots

$$\text{e.g. } f(\theta) = \cos^2 \theta$$

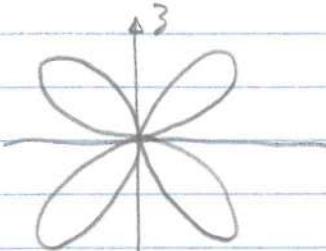


→



Fig 7-8 $\Rightarrow l=3$ polar plots.

$$\text{e.g. } m_l = +2 \rightarrow |(\mathbb{H}_{32})|^2 \approx \sin^4 \theta \cos^2 \theta$$



$$P_{\text{re}}(r) |(\mathbb{H}_{nl})|^2$$

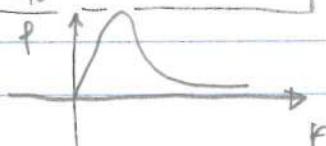
DENSITY PLOTS

→ Combine visualization from Radial + Polar plot to make 3D plots → use shading to represent 4th dimension

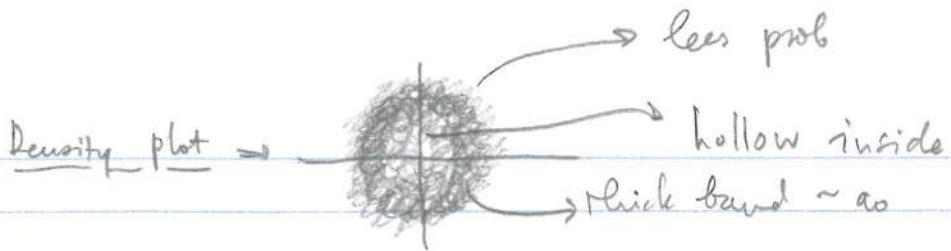
$$\begin{cases} n=1 \\ l=0 \\ m_l=0 \end{cases}$$

$$P_{10}(r) \sim r^2 e^{-r/l_{\text{eff}}}$$

$$\text{also } |(\mathbb{H}(0))|^2 = \text{constant}$$



polar
 since $(\mathbb{H}(\theta)) = \text{constant}$ ⇒ 
 ⇒ SYMMETRIC SPHERICALLY



Note all s-states ($l=0$) are all spherically symmetric

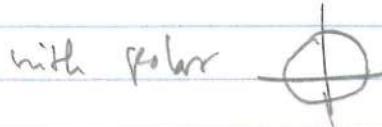
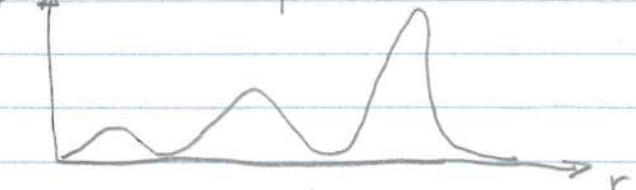
with $|(\psi(0))|^2 = \text{constant} \rightarrow$



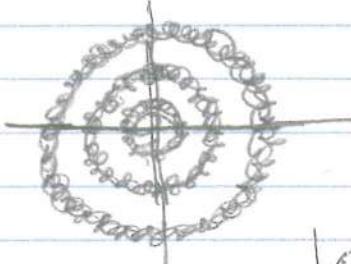
Ex $\begin{cases} n=3 \\ l=0 \\ m_e=0 \end{cases}$

Result

$$P_{30}(r) =$$



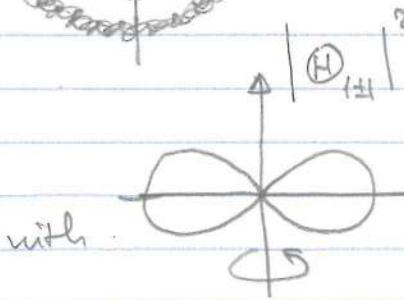
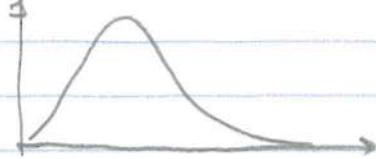
so density plot



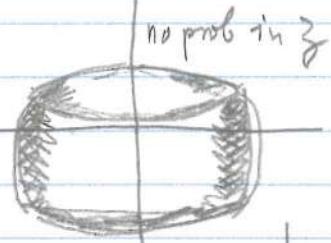
For $l \neq 0 \rightarrow$ get angular dep

Ex $\begin{cases} n=2 \\ l=1 \\ m_e=\pm 1 \end{cases}$

$$P_{21} =$$



so density plot



(1)

$\begin{cases} n=2 \\ l=1 \\ m_e=0 \end{cases}$

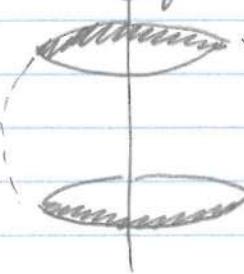
$$P_{21} =$$

with

$$|\psi|^2$$



so density plot



(2)

Note (1)(2) full sphere

Question For $\ell \neq 0$, there is a θ dep, and density is a ~~big~~ aligned with the z direction, but how does the atom know which way z -point? \rightarrow It can't!

\Rightarrow Free atoms with no external interactions can't distinguish directions
 \Rightarrow So z can't matter.

\hookrightarrow As long as there are no external interactions (like an \vec{E} or \vec{B}), then the solutions should be spherically symmetric.

Recall $E_n = \frac{-13.6 \text{ eV}}{n^2}$ has no ℓ, m_ℓ dependence.

If all we do is fix E_n , then any atom would be a statistical mix of the degenerate $\ell = m_\ell$ states.

\Rightarrow These mixtures are spherically symmetric.

$$|\Psi_n|^2 = \frac{1}{n^2} \sum_{l, m_\ell} |\Psi_{nlm_\ell}|^2$$

degeneracy

Any experiment looking at such a sample will see a spherically symmetric distribution

(7-10: combining images for the same ℓ, m_ℓ gives a spherically symmetric picture)

\hookrightarrow Note the ℓ, m_ℓ states of the same n complete each other to form a spherically symmetric picture (see Fig 7-10)

\hookrightarrow We can also prove this mathematically

Ex Show $n=2$ level for H has a spherically symmetric dist

$$\cdot \Psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/a_0}$$

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

$$\cdot \Psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-r/a_0} \sin \theta e^{\pm i\phi}$$

The average distribution

$$\begin{aligned}
 |\Psi_2|^2 &= \frac{1}{2^2} \left[|\Psi_{200}|^2 + |\Psi_{210}|^2 + |\Psi_{211}|^2 + |\Psi_{21-1}|^2 \right] \\
 &= \frac{1}{4} \left[\frac{1}{16} \frac{1}{2\pi} \left(\frac{1}{a_0}\right)^3 \left(\frac{r}{a_0} \right)^2 e^{-r/a_0} \right] \left[\left(2 - \frac{r}{a_0}\right)^2 + \left(\frac{r}{a_0}\right)^2 \cos^2\theta + \left(\frac{r}{a_0}\right)^2 \frac{1}{2} \sin^2\theta \right. \\
 &\quad \left. + \frac{1}{2} \left(\frac{r}{a_0}\right)^2 \sin^2\theta \right] \\
 \text{only dep on } r \rightarrow &= \left[\frac{1}{4} \frac{1}{16} \frac{1}{2\pi} \left(\frac{1}{a_0}\right)^3 e^{-r/a_0} \right] \left[\left(2 - \frac{r}{a_0}\right)^2 + \left(\frac{r}{a_0}\right)^2 \right]
 \end{aligned}$$

So $|\Psi_2|^2$ is spherically symmetric!

■ If we want to distinguish l, m_l states, we must lift the E degeneracy \Rightarrow we can do so by applying an external $E \perp B$ fields. \rightarrow to select not particular l, m_l

\Rightarrow But these physical vectors then introduce a physical z -direction

• Also, to trap & study 1 atom, you must use $\vec{E} + \vec{B}$ fields, these then define physical directions.

Next, we talk about SPIN. # (chapter 8)

IV ELECTRON SPIN

April 6, 2018

The solution for H atoms so far have been for free structureless atoms

→ Now, we want to include some additional interaction!

For starters, atoms have magnetic dipole moment \Rightarrow 2 types of magnetic dipole moment:

- orbital type (from e^- to nucleus)
- intrinsic → from a new type of angular momentum, called "spin"

Want to look at the discovery of "spin"

→ We'll also look at other types of interactions

(spin-orbit interaction)
 ↳ internal interaction between spin & orbital angular momentum
 \Rightarrow splits energy levels

Zeeman effect

→ magnetic dipole moment w/ external B fields

↳ Energy

↳ Int charge

↳ W charge

Fine structure

Relativistic effect

Thomas precession

Note there are

small interactions,
 but of approximately
 the same order of
 magnitude

Other interactions

Stark effect splitting of E
 levels due to external
 \vec{E} (E field)

Hyper fine structure

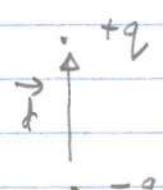
interactions with the
 nuclear magnetic
 moment. (Weak...)

Review Magnetic Dipole Moment (Classical)

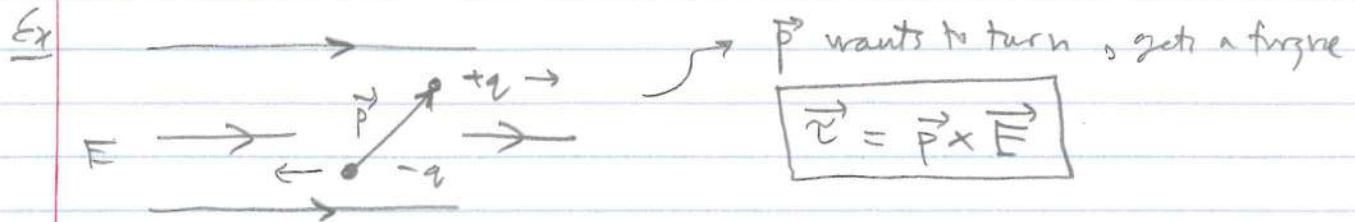
→ Electric dipole moment

→ Electric dipoles are made of electric charges:

$$\text{Def } \vec{p} = q\vec{d}$$



- If we put \vec{p} in an external \vec{E} field



Likewise, there's a potential energy : $U = -\vec{p} \cdot \vec{E}$

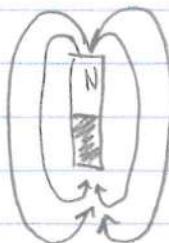
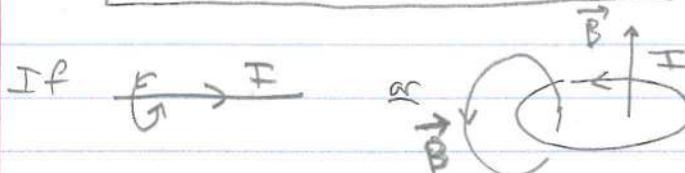
lowest when $\vec{p} \parallel \vec{E}$

Magnetic dipoles

Note, there are no magnetic monopoles ...

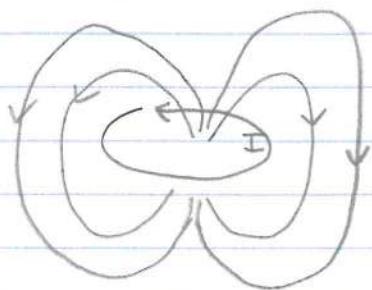
$\Rightarrow \vec{B}$ fields come from current $I \rightarrow$ Biot-Savart

$$d\vec{B} = \frac{\mu_0}{4\pi} \frac{I d\vec{s} \times \vec{r}}{dr^3} dr$$



\Rightarrow can still have magnetic dipoles : bar magnet

\hookrightarrow we can still get the same field lines from a loop of current



\hookrightarrow loops of current act as magnetic dipoles

area of loop

So Det of magnetic dipole moment

$$M = I \cdot A$$

units $A \cdot m^2$

as a vector $\vec{\mu} \rightarrow$ use right hand rule

In ext \vec{B} field, set torque $\vec{\tau} = \vec{\mu} \times \vec{B}$

In analogous way, potential energy $\rightarrow U = -\vec{\mu} \cdot \vec{B}$

\hookrightarrow lowest when parallel ($\vec{\mu} \parallel \vec{B}$) $\rightarrow U = -\mu B$

For a bar magnet, we have aligned atomic dipole moments

\hookrightarrow set macroscopic \vec{B} field.

What about QM magnetic dipole moment?

①

\hookrightarrow ORBITAL MAGNETIC DIPOLE MOMENT in QM

\hookrightarrow Our approach so far has been to solve SE exactly

\Rightarrow But can't do that when we include E-M

\Rightarrow E-M is inherently RELATIVISTIC — EM waves move at the speed of light.

\hookrightarrow Quantum Electrodynamics (QED)

(special)

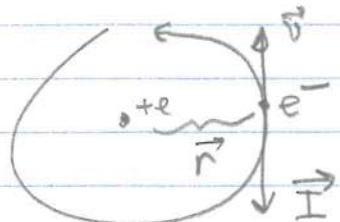
\rightarrow combines QM, Relativity, and E-M

What we'll do is to use a combined approach

\hookrightarrow QM based on SE + semiclassical methods (use Bohr model)
 + E-M (Maxwell eq.)
 + Classical Mechanics

In many cases, we will get the same results, or very close to those obtained from QED.

★ Imagine a Bohr atom \rightarrow electron in a circular orbit



v = speed of e^- orbit \oplus {current}

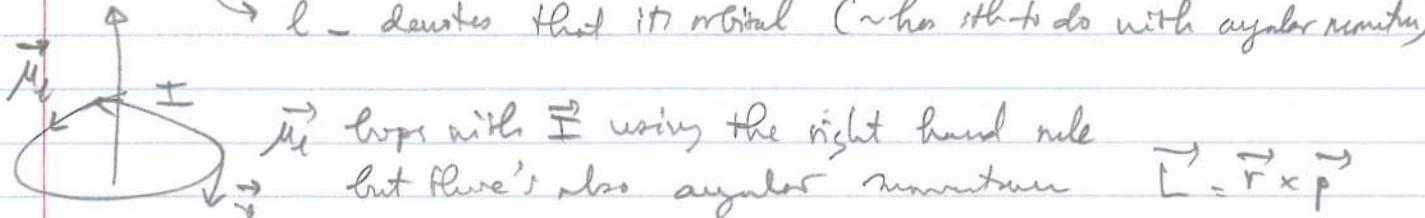
$$T = \frac{2\pi r}{v} = \text{period}$$

$$\hookrightarrow I = \frac{e}{T} = \frac{ev}{2\pi r}$$

Note $I \leftarrow -I$

So flux loop of current has a magnetic dipole moment:

$$\boxed{\mu_o = IA} \rightarrow \text{orbital magnetic dipole moment.}$$



But since $\vec{I} \propto -\vec{r}$, \vec{M}_o and \vec{L} are in opposite directions!

with $\mu_o = IA = \frac{e\pi}{2m} \cdot \pi r^2 = \frac{e\pi r^2}{2}$

$|\vec{\mu}_o| = \frac{e\pi r^2}{2} = \frac{e \cdot |L|}{2m}$ } note L quantized

So $|\vec{\mu}_o| = \frac{e}{2m} |\vec{L}|$ where $m = m_e$ (electron mass)

Note $|\vec{L}| \sim \hbar$. So dimensionally, $\frac{e\hbar}{2m}$ has a basic unit of magnetic moment

Define

$$\boxed{\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ Am}^2} \rightarrow \text{Bohr magneton}$$

Can then write $\rightarrow \boxed{\mu_o = \frac{\mu_B}{\hbar} L}$

We can introduce a strength factor to make formulas uniform

$$\hookrightarrow \boxed{g_e = 1} \rightarrow \boxed{\mu_o = g_e \frac{\mu_B}{\hbar} L}$$

So in notes from

$$\boxed{\mu_o = -\frac{g_e \mu_B}{\hbar} \vec{L}}$$

(same type vs magnetic dipole in other form)

↳ orbital magnetic dipole moment

$$\vec{\mu}_L = \frac{-g_e \mu_B \vec{L}}{\hbar}$$

From QM \rightarrow we know \vec{L} quantized

$$|\vec{L}| = \sqrt{l(l+1)} \hbar, \quad m_L \hbar = L_z$$

These say

$$\mu_L = +g_e \mu_B \sqrt{l(l+1)}$$

and

$$\mu_{Lz} = \frac{-g_e \mu_B}{\hbar} L_z = -g_e \mu_B m_L$$

→ quantized
magnetic
moment!

Next, the spin!

April 9, 2018

→ Magnetic Dipoles in QM

→ "classical" view: orbital $\vec{\mu}_L = \frac{-g_e \mu_B \vec{L}}{\hbar} \rightarrow g_e = 1 = 9.27 \times 10^{-24} \text{ A m}^2$ (Bohr magneton)

Since \vec{L} quantized $\rightarrow \vec{\mu}_L$ is also quantized.

$$\mu_L = g_e \mu_B \sqrt{l(l+1)}$$

$$\text{and } \mu_{Lz} = -g_e \mu_B m_L$$

Expect $(2l+1)$ values of μ_L .

Magnetic Moment in an external \vec{B} field

→ it feels a torque!

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

$$\text{and } \text{torq} \cdot \text{PE} = -\vec{\mu}_L \cdot \vec{B} = U$$

What is the typical size

of $U = -\vec{\mu}_L \cdot \vec{B}$ → estimate ΔE between an aligned dipole
+ anti-aligned

Suppose $\mu_L \approx \mu_B \rightarrow$ typical value

$B \approx 1 \text{ T} \rightarrow$ typical lab magnet

$$\sim 1.2 \times 10^{-4}$$

Estimate:

$$\Delta E = \mu_B B - (-\mu_B) = 2\mu_B B = 2(9.27 \times 10^{-24})(1) \approx 1.85 \times 10^{-23} \text{ J}$$

$\Rightarrow \sim 10,000$ times smaller than typical atomic energy levels.
 \Rightarrow SMALL CORRECTIONS...

Note \rightarrow as small as this is, the dipole actually WON'T FLIP unless energy is exchanged

As long as NO energy is exchanged, then $PE = -\vec{\mu}_d \cdot \vec{B}$ stays fixed

For a dipole in an external B field where E stay fixed

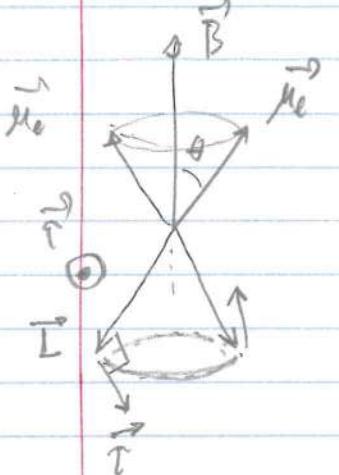
$$\begin{array}{c} \vec{B} \\ \downarrow \vec{\mu}_d \end{array} \text{ then } E = -\vec{\mu}_d \cdot \vec{B} = -\mu_d B_{\text{ext}} \text{ stays fixed!}$$

\hookrightarrow so θ stays fixed (if no E exchanges)

But \rightarrow there is also a torque $\vec{\tau} = \vec{\mu}_d \times \vec{B}$

What does it do? \rightarrow PRECESSION

$$\text{Use } \vec{\mu}_d = -g_e \frac{\mu_B}{t} \vec{l} \Rightarrow \vec{\tau} = -g_e M_B \frac{\vec{l} \times \vec{B}}{t} \sim -\vec{l} \times \vec{B}$$



Torque changes \vec{l}

$$\hookrightarrow \vec{\tau} = \frac{d\vec{l}}{dt} \Rightarrow \text{get a precession!}$$

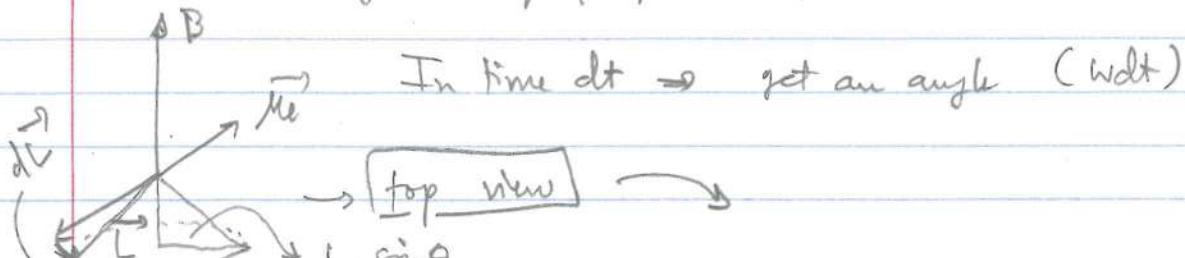
Neither $|\vec{l}|$ nor $(\vec{\mu}_d)$ can change, nor can the angle θ change, since this would change E

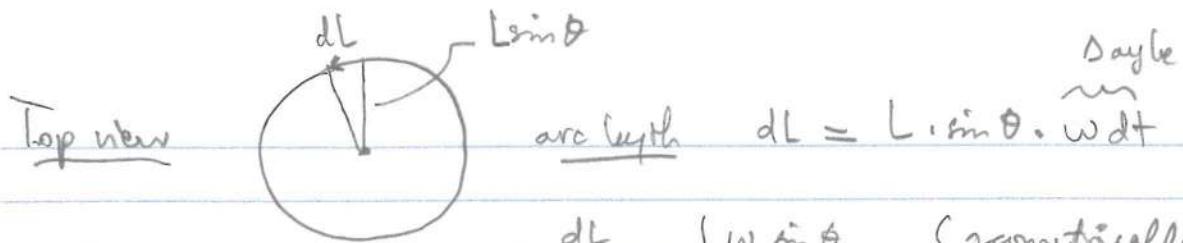
\hookrightarrow since $\Delta E = 0$ (and P conserved)

$\Rightarrow \vec{\mu}_d$ will precess around \vec{B}

Can find angular freq. of the precession

\Rightarrow Call ω = angular freq of precession νdt = infinitesimal time





We can set this
equal to

$$\Rightarrow \tau = \frac{dL}{dt} = \left| \frac{-\gamma e \mu_B}{t} \vec{L} \times \vec{B} \right|$$

We get

$$Lw \sin \theta = \left| \frac{-\gamma e \mu_B}{t} \vec{L} \times \vec{B} \right| = \frac{\gamma e \mu_B}{t} LB \sin(\pi - \theta)$$

$$Lw \sin \theta = \frac{\gamma e \mu_B}{t} LB \sin \theta$$

So

$$w = \frac{\gamma e \mu_B}{t} B$$

→ called the Larmor frequency
(Larmor precession)

Larmor precession → precession of magnetic dipole in external \vec{B} field

Note → This is a classical result

→ But the same frequency occurs in QM
(e.g. in NMR)

The STERN - GERLACH Experiment

→ reveals the existence of electron spin

1922 ⇒ Stern - Gerlach measured possible values of magnetic dipole moments of Ag atoms by sending them through non-uniform \vec{B} field.

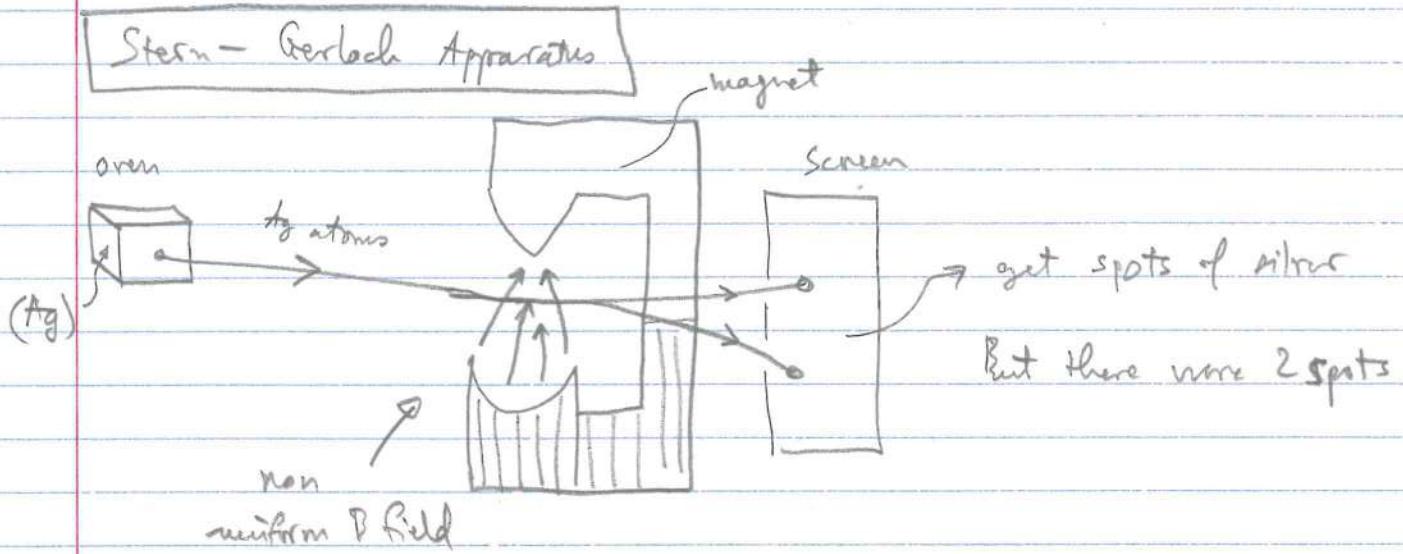
1925 → "spin" was introduced by Uhlenbeck & Goudsmit who were trying to understand the fine-structure of H

QM just
introduced

But 1927

Philips & Taylor repeated exp (S-G), except using ground-state H (and ground-state with $l=0$) $\Rightarrow \mu_l = 0$
→ found evidence of any. mom values $\neq l = 0, \pm 1, 2, \dots$
... → half-integer angular momentum

\Rightarrow SPIN \rightarrow proposed as a new kind of angular momentum where e^- have spin = $\frac{1}{2}$

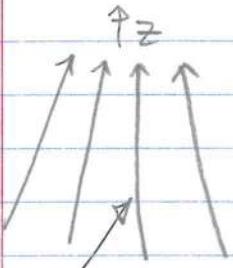


Why non-uniform \vec{B} field? \rightarrow neutral atoms: $q = 0 \Rightarrow \vec{F} = q\vec{v} \times \vec{B} = 0$

Force arises due to a magnetic dipole going thru a non-uniform \vec{B}

In general: $\vec{F} = -\vec{\nabla}U$ where U = potential energy

For a magnetic dipole $\rightarrow U = -\vec{\mu}_e \cdot \vec{B}$



along the axis: $\vec{B} = B_z(z)\hat{k}$

\hookrightarrow B changes along z only

(beam of atoms) $\rightarrow U = -\vec{\mu}_e \cdot \vec{B} = -\mu_{ez} \cdot B_z(z)$ \rightarrow only in z -dir
(other $x, y = 0$)

Then $\vec{\nabla}U = -\frac{\partial}{\partial z}(\mu_{ez} \cdot B_z(z))\hat{k}$ ($\frac{\partial}{\partial x}, \frac{\partial}{\partial y}$ give 0)

$\Rightarrow \vec{\nabla}U = -\mu_{ez} \cdot \left(\frac{\partial B_z}{\partial z} \right) \hat{k}$ \rightarrow Field gradient!

$$\text{So } \vec{F} = -\nabla U = \mu_{lz} \left(\frac{\partial B_z}{\partial z} \right) \hat{k}$$

Call this

$$\rightarrow \vec{F} = F_z \hat{k}$$

only get force in z -direction

$$\text{and } \boxed{F_z = \mu_{lz} \left(\frac{\partial B_z}{\partial z} \right)}$$

Note $F=0$ unless there is non-uniform B

with $\mu_{lz} = -g_e \mu_B m_e$, assuming it's orbital!

Then m_l has $(2l+1)$ values \rightarrow expect $2l+1$ force values

that split the beam apart. [But] in theory, $l=0 \rightarrow$ we expect 1 beam

\hookrightarrow says $(2l+1=2)$ or $l=\frac{1}{2}$ \rightarrow NOT allowed as orbital values

\rightarrow Instead \rightarrow Introduce SPIN.

April 11, 2018

Phipps-Taylor repeats exp using ground state $l=0$ H atoms

\hookrightarrow expected one beam ($2 \cdot 0 + 1 = 1$)

\rightarrow But 2 spots were seen.

How to explain this?

\rightarrow $\left. \begin{array}{l} \text{By a 2nd type of angular momentum} \\ \text{or 2nd type of magnetic dipole moment} \end{array} \right\}$

Spin \rightarrow like a spinning ball

But e^- are point like \rightarrow So what is spin?

\rightarrow an intrinsic angular momentum
 \rightarrow isolated particles have it.

\rightarrow It's a basic property of elementary particle like its mass or charge

\rightarrow Call $\vec{S} = \text{spin angular momentum } S_z = z\text{-component}$

Since it's quantum mechanical \rightarrow it's quantized

where $|\vec{S}| = \sqrt{s(s+1)}\hbar$

and $S_z = m_s\hbar$

Get 2 new quantum number and $m_s = -s, -s+1 \dots s-1, s$

For electron, there's a new associated magnetic dipole moment \rightarrow Call $\vec{\mu}_s = \frac{-g_s \mu_B}{\hbar} \vec{S}$ $2s+1$ values

and $\mu_{Sz} = -g_s \mu_B m_s$

\rightarrow test for QED

and

g_s = strength factor \rightarrow can be found experimentally
(or calculated in QED)

For a Stern-Gerlach experiment

\Rightarrow use $\vec{\mu}_s$ instead of $\vec{\mu}_d$

$\hookrightarrow \boxed{\vec{F}_z = \mu_{Sz} \left(\frac{\partial B_z}{\partial z} \right) = -g_s \mu_B m_s \left(\frac{\partial B_z}{\partial z} \right)}$

Experiment got $(2s+1)$ spots (or F_z values)

Experiment observed 2 spots $\Rightarrow 2s+1=2 \rightarrow s = \frac{1}{2}$ for electrons

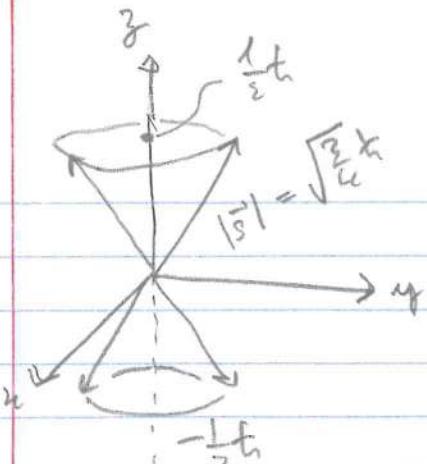
\hookrightarrow Electrons have spin $\frac{1}{2}$

\Rightarrow But if $s = \frac{1}{2}$, then $m_s = \pm \frac{1}{2}$

\rightarrow and

$$S_z = \pm \frac{1}{2}\hbar$$

Magnitude: $|\vec{S}| = \sqrt{\frac{1}{2}(\frac{1}{2}+1)}\hbar = \sqrt{\frac{3}{4}}\hbar$



Experimentally, found that

$$g_s m_s \approx \pm 1 \text{ where } m_s = \pm \frac{1}{2}$$

$$\Rightarrow g_s \approx 2 \text{ (electron) in QED}$$

Careful experiment gives $g_s = 2.00232\dots$

We'll mostly use $g_s \approx 2$

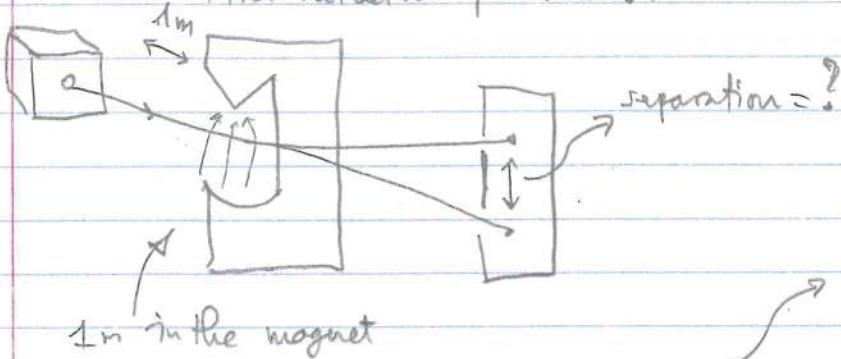
Why are $g_F \approx 1$ and $g_S \approx 2$

\uparrow
follows from
Bohr model
+ orbital
motion

(?) Don't know. Can't really say why
 $g_S \approx 2$ any more than we can
explain why electrons have mass
 $m_e > \text{charge } e^*$

Example

A beam of δ atoms comes out of an oven at $400K \approx 200s$
through a 1-m magnet with a gradient of $10T/m$
Find deflection of beams.



Boltzmann
constants

Small KE of hot atoms = $\frac{1}{2} kT$ per degree of freedom

Since in 3D $\rightarrow 3$ degrees of freedom \rightarrow KE = $\frac{3}{2} kT$

But KE $\approx 2kT$ works better. Treat this as given

notes the faster ones
escaping the oven

\hookrightarrow $\boxed{KE_H = \frac{1}{2} MV_H^2 = 2kT}$

$$\frac{1}{2}MV_x^2 = 2kT \rightarrow \frac{1}{2}MV_x^2 = 2(1.38 \times 10^{-23} \frac{\text{J}}{\text{k}}) \cdot 400 \text{K}$$

$$\frac{1}{2}MV_x^2 \approx 1.1 \times 10^{-20} \text{ J} = 0.069 \text{ eV}$$

So clearly, this is non-relativistic energy! They'll also be in ground state

So $\ell=0 \Rightarrow$ no $\vec{\mu}_\ell$; only have $\vec{\mu}_s$

do

$$\text{Force in magnet is } F_z = \mu_B \frac{\partial B_z}{\partial z} \quad \begin{matrix} 10 \text{T/m} \\ \text{given} \end{matrix}$$

μ_B : Bohr magneton

$$= -g_s \mu_B m_s \left(\frac{\partial B_z}{\partial z} \right)$$

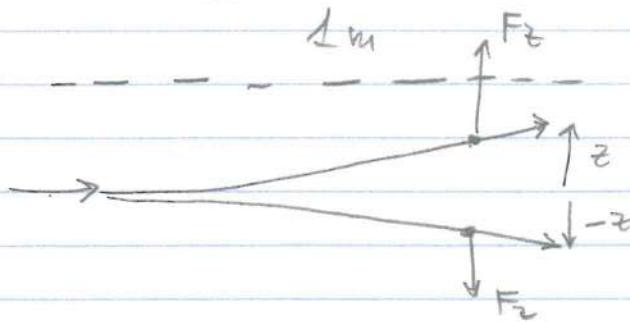
↑ ↑
 2 ±1/2

* field gradient = 10 T/m

So 2 values for force

$$F_z = \mp \mu_B \left(\frac{\partial B_z}{\partial z} \right)$$

sideways picture



Goal: Find z

$$Z(t) = \frac{1}{2} a z t^2 = \frac{1}{2} \frac{F_z}{M} t^2 \Rightarrow Z(t) = \mp \frac{1}{2} \frac{\mu_B}{M} \left(\frac{\partial B_z}{\partial z} \right) t^2$$

↓ like "falling" (F_z only $\propto z$)

$$\text{Need } t \quad \frac{1}{2}MV_x^2 = 2kT \rightarrow V_x = \sqrt{\frac{4kT}{m}}$$

$$\text{With no acc. along } x \quad t = \frac{x}{V_x} = x \sqrt{\frac{M}{4kT}}$$

$$Z(x) = \mp \frac{1}{2} \left(\frac{\mu_B}{M} \right) \left(\frac{\partial B_z}{\partial z} \right) x$$

$$Z(1) = \mp \frac{\mu_B I^2}{8kT} \left(\frac{\partial B_z}{\partial z} \right)$$

$$\text{Get } z = \mp 2.1 \times 10^{-3} \text{ m} \rightarrow \text{separation } \sim 0.4 \text{ cm} \rightarrow \text{observable}$$

The Zeeman Effect

→ first observed in 1896

April 13, 2018

⇒ splitting of spectral lines for atoms placed in an external \vec{B} field

↙ Ques? An atom can have 2 types of magnetic dipole moments $\vec{\mu}_e$ & $\vec{\mu}_s$. In an external \vec{B} field, you get a potential energy

$$U = -\vec{\mu}_s \cdot \vec{B} \quad \text{if we align } \vec{B} = \vec{B} \cdot \hat{z} \rightarrow \text{uniform along } z$$

then $U = -\mu_s B \rightarrow$ gives a splitting of the energy
the depends on B

⇒ called the Zeeman Effect

The full Zeeman effect depends on $\vec{\mu} = \vec{\mu}_s + \vec{\mu}_e$ which depends on how \vec{l} and \vec{s} add together quantum mechanically.
⇒ come back to this later

For now, look at s state (special case) → $l=0 \rightarrow m_l=0$
 $|\vec{\mu}_e| = 0$

In this case $\vec{\mu} = \vec{\mu}_s$ due to spin only

Put one atom in an s-state in a \vec{B} field → energy total

$$E = \frac{-13.6 \text{ eV}}{n^2} + \Delta E \quad (n=1)$$

$$\text{where } \Delta E = -\mu_{s_z} B = g_s \mu_B m_s B \quad (\vec{B} = B \hat{z})$$

$$\text{Plug in} \rightarrow E = \frac{-13.6}{n^2} + g_s \mu_B m_s B$$

Experimentally → $g_s m_s \approx \pm 1$ so

$$E = \frac{-13.6}{n^2} \pm \mu_B B$$

So an s-state is split into 2 levels

$$\begin{matrix} h=1 \\ l=0 \end{matrix} \xrightarrow{+B} \xrightarrow{+B}$$

$$\downarrow \text{splitting} = 2\Delta E \approx 2\mu_B B$$

If $B \sim gT \rightarrow$ splitting is on the order of 10^{-4} eV

Note the differences between:

Stern-Gerlach exp → involves a field gradient $\frac{\partial B}{\partial z}$

→ set a force that separates a beam of atoms

- Zeeman effect → involves constant B field \rightarrow use atoms at rest (not a beam) (spectroscopically)

→ defines energy level splitting (observed spectroscopically)

SPIN - ORBIT INTERACTION (FINE STRUCTURE)

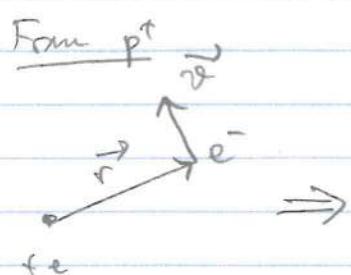
In some ways, this is like the Zeeman effect for $\vec{B}_z \rightarrow \Delta E = \vec{\mu}_s \cdot \vec{B}$ but where here, \vec{B} is an internal \vec{B} field inside an atom

→ the e^- sees the proton circling it, which creates an internal mag field \vec{B} that interacts with its spin magnetic dipole moment

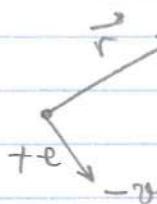
→ Get a splitting of the energy levels → called "Fine Structure"

like a (big)
current

Consider the motion of the nucleus (proton) from the electron's p.o.v



e^- not frame



Note transformation between
accelerating frames

Want to find \vec{B} at the
location of e^- due to e^+ motion

Recall Biot-Savart law.

where $I = \frac{e}{T} = \text{current}$
 $\frac{1}{\text{period}}$

$$d\vec{B} = \frac{\mu_0}{4\pi} \frac{I d\vec{s} \times \vec{r}}{r^3}$$

Here $d\vec{s} = -\vec{v} dt$ and $T = \int dt = \text{period}$

$$\text{So } \vec{B} = \int d\vec{B} = \int -\frac{\mu_0}{4\pi} \frac{I \vec{v} \times \vec{r}}{r^3} dt$$

Note $\vec{v} \times \vec{r}$ constant

$$\text{So } \vec{B} = -\frac{\mu_0}{4\pi} \frac{I \vec{v} \times \vec{r}}{r^3} \int dt = -\frac{\mu_0}{4\pi} \frac{I \vec{v} \times \vec{r}}{r^3} T$$

$$IT = e$$

$$\text{So } \boxed{\vec{B} = -\frac{\mu_0}{4\pi} e \frac{\vec{r} \times \vec{r}}{r^3}} \rightarrow \text{internal } \vec{B} \text{ field interacts with } \mu_0 \text{ of } e^-$$

So potential E due to this : energy shift

$$\boxed{\Delta E = -\vec{\mu}_s \cdot \vec{B}}$$

$$-g_s \mu_B \frac{\vec{S} \cdot \vec{B}}{k}$$

$$\text{So } \boxed{\Delta E = \frac{-g_s \mu_B}{k} \vec{S} \cdot \vec{B}}$$

But since \vec{B} is due to orbital motion, we can relate it + $\vec{L} = \vec{r} \times \vec{p}$

$$\text{if } \vec{B} = -\frac{e\mu_0}{4\pi} \frac{\vec{V} \times \vec{r}}{r^3} \leftarrow \frac{m}{m} \quad \vec{L} = \vec{r} \times \vec{p}$$

$$\text{So } \boxed{\vec{B} = \frac{e\mu_0}{4\pi} \frac{m \vec{r} \times \vec{v}}{mr^3} = \frac{e\mu_0}{4\pi m_e} \frac{\vec{L}}{r^3}} ?$$

Next, we'll rewrite $\frac{1}{r^3}$ in a way that's useful later when we talk about multi-e⁻ atoms.

Start with Coulomb potential $\rightarrow V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$

$$\frac{dV}{dr} = \frac{-e^2}{4\pi\epsilon_0 r^2} \Rightarrow \frac{1}{r} \frac{dV}{dr} = \frac{-e^2}{4\pi\epsilon_0 r^3}$$

So I can replace r^3 by $\boxed{\frac{1}{r^3} = \frac{4\pi\epsilon_0}{e^2} \frac{1}{r} \frac{dV(r)}{dr}}$

So $\vec{B} = \frac{e\mu_0}{4\pi m_e} \cdot \frac{4\pi\epsilon_0}{e^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{L}$

So $\vec{B} = \frac{\mu_0 \epsilon_0}{em_e} \frac{1}{r} \frac{dV(r)}{dr} \vec{L}$ Note $\mu_0 \epsilon_0 = \frac{1}{c^2}$

Write $\boxed{\vec{B} = \frac{1}{em_e c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{L}}$ Note $m_e c^2$

Plug this into ΔE & get

$$\Delta E = q_s \mu_B \frac{\vec{s} \cdot \vec{L}}{\hbar} \left(\frac{1}{em_e c^2} \frac{1}{r} \frac{dV(r)}{dr} \right)$$

with $q_s = 2$ and

$$\mu_B = \frac{e\hbar}{2m}$$

$\vec{s} \cdot \vec{L}$ spin-orbital

so

$$\boxed{\Delta E = \frac{1}{m_e c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{s} \cdot \vec{L}}$$

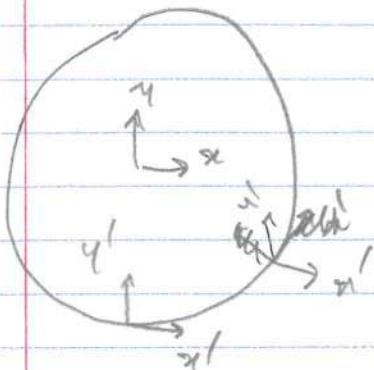
Now, this is the result in the e^- rest frame. What about that in the proton's rest frame?

\rightarrow We need to transform back to proton's rest frame.

But this is a transformation between accelerating frames

\Rightarrow Must perform a sequence of infinitesimal Lorentz transform

\Rightarrow need a sequence of infinitesimal Lorentz transform because \vec{s} changes direction



\Rightarrow find a rotation or (precession) of axis

\hookrightarrow Thomas precession (complicated)
(Appendix 0)

The result of careful calculations
(which we won't do) is that ΔE changes by
a factor ($1/2$)

\hookrightarrow The spin-orbit interaction including Thomas precession is

$$\hookrightarrow \boxed{\Delta E = \frac{1}{2m^2c^2} \cdot \frac{1}{r} \cdot \frac{dV(r)}{dr} \vec{s} \cdot \vec{L}}$$

(derived by Thomas (1926), agrees with relativistic
QM calculations)

Next

\hookrightarrow Incorporate ΔE into SE , how do we add spin to ~~old~~ SE ?

#

April 16, 2013

SPIN

\rightarrow electron: $s = \frac{1}{2}$, $\Rightarrow m_s = \pm \frac{1}{2} \rightarrow$ up/down states

\hookrightarrow Today:

FINE-STRUCTURE

Spin-orbit interaction

\hookrightarrow interaction between $\vec{\mu}_s$ and internal \vec{B} (caused by movement of e^- in atom) #

\hookrightarrow include relativistic effect \rightarrow found $\boxed{\Delta E = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{s} \cdot \vec{L}}$

Now \rightarrow need to add ΔE correction to SE

\hookrightarrow but this involves spin!

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

\hookrightarrow How do we include spin, even w/o
spin-orbit interaction

time-independent

SE with spin (but no spin-orbit interaction)

Before, we had $\hat{H} = \cancel{\frac{-\hbar^2}{2m} \nabla^2} + V(r)$

$$SE \rightarrow \hat{H} \Psi_{nlm_s} = E_n \Psi_{nlm_s}$$

We also found that $\begin{cases} \hat{L}^2 \Psi_{nlm_s} = l(l+1) \hbar^2 \Psi_{nlm_s} \\ \text{and} \\ \hat{L}_z \Psi_{nlm_s} = m_l \hbar \Psi_{nlm_s} \end{cases}$

But now we want to include spin, but ignoring the spin-orbit interaction

let Ψ = wave function with spin

want it to obey:

$$\hat{H} \Psi = E_n \Psi$$

$$\cdot \hat{L}^2 \Psi = l(l+1) \hbar^2 \Psi$$

$$\cdot \hat{L}_z \Psi = m_l \hbar \Psi$$

But also

$$\cdot \hat{S}^2 \Psi = s(s+1) \hbar^2 \Psi \quad \text{where for electrons: } s = \frac{1}{2}$$

$$\cdot \hat{S}_z \Psi = m_s \hbar \Psi \quad \text{and } m_s = \pm \frac{1}{2}$$

What we do is let

$$\boxed{\Psi = \Psi_{nlm_s} \cdot \chi_{s m_s}}$$

(note w/o time-dep)

~ adding a spin part to the wavefunction

where here,

$\hat{H}, \hat{L}^2, \hat{L}_z \rightarrow$ act on Ψ_{nlm_s}

and $\hat{S}^2, \hat{S}_z \rightarrow$ act on $\chi_{s m_s}$

$$\text{Need} \left\{ \begin{array}{l} \hat{S}^2 \chi_{sm_s} = s(s+1) \hbar^2 \chi_{sm_s} \\ \hat{S}_z \chi_{sm_s} = m_s \hbar \chi_{sm_s} \end{array} \right\} \quad \begin{matrix} \hat{H}, \hat{L}_x^2, \hat{L}_y^2, \hat{S}_x^2, \hat{S}_y^2 \\ \uparrow \end{matrix}$$

So if we do this, then $\Psi = \psi \chi$ will be eigenstates of all S operator

| So how are the spin operators and spin wavefunctions represented implicitly?

↳ Since spin is purely intrinsic, it does NOT depend on the position or momentum of electron

↳ So χ_{sm_s} has No coordinate dependence, and for $s = \frac{1}{2}$, it only has 2 possible states

→ Can represent the spin wavefunctions as a 2-component matrices

$$\chi_{\frac{1}{2}\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \begin{matrix} \text{spin "up" state} \\ \text{Called "spinors"} \end{matrix}$$

$$\chi_{\frac{1}{2}-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \begin{matrix} \text{"down" state} \end{matrix}$$

Then \hat{S}^2 and \hat{S}_z can be represented as 2×2 matrices

e.g.

$\hat{S}^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\hat{S}_z = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$\text{Verify } \hat{S}_z \chi_{\frac{1}{2}\frac{1}{2}} = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= s(s+1) \hbar^2 \chi_{\frac{1}{2}\frac{1}{2}} \quad (s = \frac{1}{2})$$

likewise

$$\hat{S}_z \chi_{\frac{1}{2}\frac{1}{2}} = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = m_s \hbar \chi_{\frac{1}{2}\frac{1}{2}} \quad (m_s = \pm \frac{1}{2})$$

So these give a good representation of spin in QM

↳ Note Heisenberg use matrices to represent all operators in QM, including \hat{p}, \hat{x}, \dots

↳ For spin we don't have differential operator

So The full SE with spin (but no spin-orbit eqn) is a hybrid eqn

$$\boxed{\hat{H} \Psi_{nlm_s} \chi_{sm_s} = E_n \Psi_{nlm_s} \chi_{sm_s}}$$

differential operator on spatial wavefunction $\Psi_{nlm_s}(r, \theta, \phi)$

$$\boxed{\hat{S}^2 \Psi_{nlm_s} \chi_{sm_s} = s(s+1) \hbar^2 \Psi_{nlm_s} \chi_{sm_s}}$$

(matrix operator acting on χ_{sm_s})

We won't worry about matrix representation \rightarrow all we need to remember is that

$$\Psi = \Psi_{nlm_s} \chi_{sm_s}$$

$$\text{where } \hat{S}^2 \Psi = s(s+1) \hbar^2 \Psi \text{ and } \hat{S}_z \Psi = m_s \hbar \Psi$$

→ With ~~that~~ no spin-orbit interaction, we still get

$$\hat{H} \Psi_{nlm_s} \chi_{sm_s} = E_n \Psi_{nlm_s} \chi_{sm_s}$$

$$\text{where } E_n = \frac{-13.6 \text{ eV}}{n^2} \text{ for H - degenerate in } l, m_l, s, m_s$$

Now, the total degeneracy changes -

$$\rightarrow \text{If we fix } n \rightarrow \Psi_{nlm} \rightarrow n^2 \text{ states } \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$x_{\text{spins}} \rightarrow 2 \text{ states} \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

\hookrightarrow So the degeneracy doubles!

$$\hookrightarrow \text{So the total degeneracy with spin} = \boxed{2n^2}$$

Note All this ignores the spin-orbit interaction

SE with spin + spin-orbit interaction

\hookrightarrow So our Hamiltonian changes!

\hookrightarrow Want to solve SE with Hamiltonian

$$\boxed{H = -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(r) + \frac{1}{2mc^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}}$$

includes a 2×2
unit matrix

a matrix...

$$\hookrightarrow \text{Want to solve} \rightarrow \hat{H} \Psi = E_n \Psi$$

\hookrightarrow So the 3rd term in \hat{H} changes everything!

\rightarrow we no longer have Ψ_{nlm} as the spatial solution

\rightarrow 3rd term has both angular + radial + spin dependence ...

\rightarrow MUST start over =

Note look at the commutator $\hat{S} \cdot \hat{L} = \hat{S}_x \hat{L}_x + \hat{S}_y \hat{L}_y + \hat{S}_z \hat{L}_z$

\Rightarrow for Ψ to be an eigenfunction, $\hat{S} \cdot \hat{L}$ with $\hat{L}_x, \hat{L}_y, \hat{S}_x, \hat{S}_y$ must

give a number \rightarrow Can't use solutions anymore with definite \hat{L}_z or

\hat{S}_z since then we know nothing about \hat{L}_x, \hat{L}_y or \hat{S}_x, \hat{S}_y .

\hookrightarrow Now we'll have

$$\left. \begin{array}{l} \hat{L}_z \Psi \neq m_{\text{th}} \Psi \\ \hat{S}_z \Psi \neq m_s \Psi \end{array} \right\}$$

So, we say $m_z, m_s \Rightarrow$ no longer "good" quantum number

(since \hat{L}_z, \hat{S}_z no longer have eigenstates)

\hookrightarrow We might think l, s are no longer "good"

But \Rightarrow look at the total angular momentum?

Note $\vec{S} + \vec{L} = \text{total angular momentum}$

\hookrightarrow Square!

$$(\vec{S} + \vec{L})^2 = \vec{S}^2 + \vec{L}^2 + 2\vec{S} \cdot \vec{L}$$

can be

"good" with
 l, s

need to find third

$$\text{total ang. mom.} = \vec{J} = \vec{S} + \vec{L}$$

\hookrightarrow See that

$$\vec{J}^2 = \vec{S}^2 + \vec{L}^2 + 2\vec{S} \cdot \vec{L}$$

$$\text{So } \boxed{\vec{S} \cdot \vec{L} = \frac{1}{2} (\vec{J}^2 - \vec{S}^2 - \vec{L}^2)}$$

use \hat{L}^2, \hat{S}^2 as before \rightarrow with $l, s = \text{quantum number}$

But now look for states of total \hat{J}

\hookrightarrow Propose that \hat{J} is quantum mechanical such that

$$\boxed{\begin{aligned}\hat{J}^2 \Psi &= j(j+1) \hbar^2 \Psi \\ \hat{J}_z \Psi &= m_j \hbar \Psi\end{aligned}}$$

where $j = \text{any, non-zero quantum number}$
 $m_j = -j, \dots, j$

$\hookrightarrow 2j+1$ values

April 18, 2018 level SE with spin-orbit interaction

$$\hookrightarrow \hat{H} = \frac{-\hbar^2}{2m} \vec{\nabla}^2 + V(r) + \frac{1}{2m c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}$$

$$\text{where } \vec{S} \cdot \vec{L} = \hat{S}_x \hat{L}_x + \hat{S}_y \hat{L}_y + \hat{S}_z \hat{L}_z$$

\hookrightarrow can't use $\hat{S}_z \hat{L}_z$ since γ_x, α are unknown.

$$\text{So use } \hat{J}^2 = (\vec{S} + \vec{L})^2 = \vec{S}^2 + \vec{L}^2 + 2\vec{S} \cdot \vec{L} \quad \& \quad \boxed{\vec{S} \cdot \vec{L} = \frac{1}{2} (\vec{j}^2 - \vec{s}^2 - \vec{l}^2)}$$

So we still want the eigenstates of \vec{s}^2 and \vec{l}^2 with quantum numbers s and l . ("good" quantum numbers). But now we want the eigenstates of the total angular momentum. (\vec{J}^2)

$$\text{Propose } \boxed{\hat{J}^2 \Psi = j(j+1) \hbar^2 \Psi}$$

$$\text{and } \boxed{\hat{J}_z \Psi = m_j \hbar \Psi}$$

$j = \text{quantum number for total angular momentum}$

$\text{and } m_j = -j, -j+1, \dots, j-1, j$

\uparrow
 $\{ (2j+1) \text{ values...} \}$

\hookrightarrow To include spin-orbit
 { interaction

\hookrightarrow we change our description

* Without S-O interaction $\Rightarrow l, s, m_l, m_s$ are "good"

$\} \text{(appear in eigenvalues...)}$

With spin-orbit term $\Rightarrow m_l, m_s$ are "bad" \rightarrow introduce $\vec{J} = \vec{l} + \vec{s}$
 which represents total angular momentum.

\hookrightarrow good quantum numbers are $[l, s, m_l, m_s, j]$

Then $\vec{S} \cdot \vec{l}$ acting on Ψ gives

$$\vec{S} \cdot \vec{l} = \frac{1}{2} (\vec{J}^2 - \vec{S}^2 - \vec{l}^2)$$

$$\hookrightarrow \boxed{\vec{S} \cdot \vec{l} = \frac{1}{2} [j(j+1) - s(s+1) - l(l+1)] \hbar^2}$$

and

$$\boxed{\vec{j}_z \Psi = m_j \hbar \Psi}$$

\Rightarrow states become eigenstates of \vec{J}^2 and \vec{j}_z

differential matrix

But what are j and m_j ?

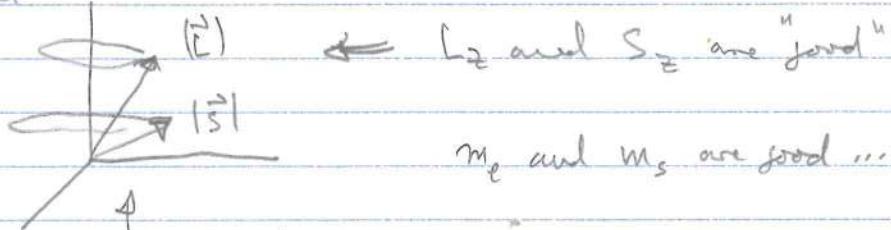
\rightarrow what is $\vec{J} = \vec{l} + \vec{s}$?

\hookrightarrow ADDITION OF ANGULAR MOMENTUM

\rightarrow we won't worry about how to represent \vec{J}^2 and \vec{j}_z as operator
 or what Ψ explicitly is...

What we want to know is what j and m_j are.

\hookrightarrow To find j and $m_j \rightarrow$ imagine we can "turn off" the spin-orbit interaction



But the z -component adds

$$\hookrightarrow J_z = L_z + S_z \Rightarrow \boxed{m_j = m_l + m_s}$$

The maximum case adds as well

$$\hookrightarrow (m_j)_{\max} = (m_e)_{\max} + (m_s)_{\max}$$

so

$$(m_j)_{\max} = l + s$$

But we know that $m_j = -j, -j+1, \dots, j-1, j$

So One possible value is $j = l+s$ or $j = \frac{1}{2} + l$ for e^-

with this $\rightarrow m_j = -j, -j+1, \dots, j-1, j \leftarrow$ with $j = l + \frac{1}{2}$

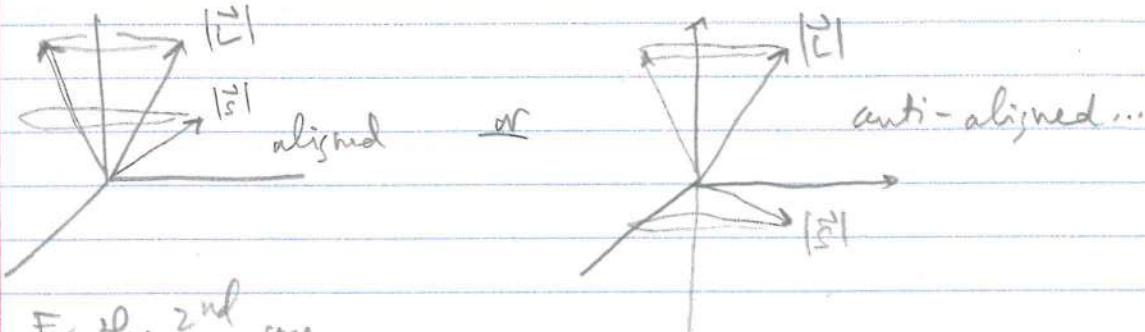
Special case $l=0$ (e^- in s -state)

$$\hookrightarrow \text{at } j = \frac{1}{2} \quad (\vec{l} = \vec{s} \text{ since } \vec{L} = \vec{0})$$

then $m_j = \pm \frac{1}{2}$

Are there other possible j values?

Since $l+s$ have 2 relative orientations, we can get 2 j values.



For the 2nd case

$$\hookrightarrow (m_j)_{\max} = (m_e)_{\max} - \left(\frac{1}{2}\right)^*$$

$\Rightarrow j = l - \frac{1}{2}$ for $e^- \leftarrow$ different value...

$m_j = -j, -j+1, \dots, j-1, j$

where $j = l - \frac{1}{2}$

Summary over addition rule ($\vec{J} = \vec{L} + \vec{S}$)

If $l=0 \rightarrow j=s=\frac{1}{2}$, $m_j = \pm \frac{1}{2}$

If $l \neq 0 \rightarrow j=l+\frac{1}{2}$, $m_j = -j, -j+1, \dots, j$, $j=l+\frac{1}{2}$ (spin up)

$l \neq 0 \rightarrow j=l-\frac{1}{2}$, $m_j = -j, \dots, l$, $j=l-\frac{1}{2}$ (spin down)

But remember all this assume we could turn off orbit-spin interaction.
Now \rightarrow turn it back on, what happens to \vec{J} ?

The spin-orbit interaction is purely internal so the total angular momentum doesn't change.

\rightarrow The same rules still apply!

But m_l, m_s become bad quantum numbers... (but we're only using l, s, m_l, m_s)

Example $l=1, s=\frac{1}{2}$ (e^- in p-state)

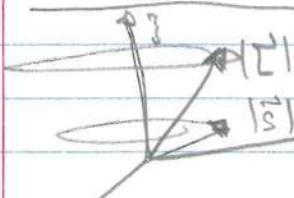
\Rightarrow 2 possible values for $j = \left\{ \frac{3}{2}, \frac{1}{2} \right\}$

So $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ for $j = \frac{3}{2}$ } 6 states!
 $m_j = -\frac{1}{2}, \frac{1}{2}$ for $j = \frac{1}{2}$

Note this is the same number as before with no spin-orbit int...

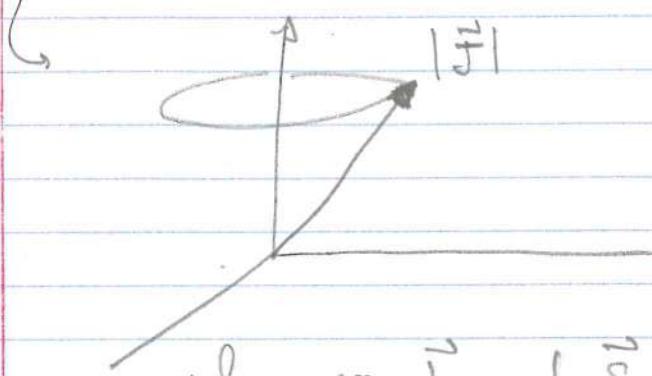
$l=1 \rightarrow m_l = -1, 0, 1$
 $s = \frac{1}{2}$, each with $m_s = \pm \frac{1}{2}$ } 6 possible states!

What about vector diagram? - with no spin-orbit interaction?



$\rightarrow \vec{L} + \vec{S}$ lie on cone with $\rightarrow m_l, m_s$ "good" definite z component.

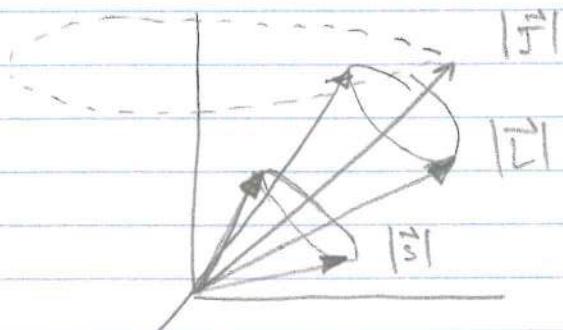
But with spin-orbit interaction



$|\vec{J}|$ lies on a cone with definite $\frac{\vec{L} \cdot \vec{S}}{|\vec{J}|}$

where are \vec{L} and \vec{S} ?

where are \vec{L} and \vec{S} ?



$|\vec{L}|, |\vec{S}|, \vec{L} \cdot \vec{S}$ lie on a cone along \vec{J}
angle w.r.t \vec{J} do not change

{ But S_z and L_z no longer have definite values }

Show the angle between $\vec{S} \cdot \vec{J}$ has a fixed definite value.

$$\vec{S} \cdot \vec{J} = |\vec{S}| |\vec{J}| \cos \theta, \text{ also } \vec{S} \cdot \vec{J} = \vec{S}(\vec{S} + \vec{L})$$

$$\therefore \vec{S} \cdot \vec{J} = \vec{S}^2 + \vec{S} \cdot \vec{L} = \vec{S}^2 + \frac{1}{2} [J^2 - L^2 - S^2] = \frac{1}{2} (J^2 - L^2 + S^2)$$

$$\text{and } |\vec{S}| = \sqrt{s(s+1)} k \text{ and } |\vec{L}| = \sqrt{l(l+1)} k$$

$$\therefore \cos \theta = \frac{\vec{S} \cdot \vec{J}}{|\vec{S}| |\vec{J}|}$$

$$\text{and } |\vec{J}| = \sqrt{j(j+1)} k$$

$$\cos \theta = \frac{\frac{1}{2} (J(j+1) - l(l+1) + s(s+1)) k^2}{\sqrt{s(s+1)} \sqrt{l(l+1)} k^2}$$

Similarly,
 $\cos \theta = \vec{S} \cdot \vec{L} = \text{const}$

has definite values for given j, l, s, \dots

April 12, 2018

Recall Total angular momentum.

$$\begin{aligned}\hat{\vec{J}}^2 \Psi &= j(j+1)h^2 \Psi \\ \hat{J}_z \Psi &= m_j \Psi\end{aligned}$$

rule $j = \begin{cases} \frac{1}{2} & l=0 \\ l \pm \frac{1}{2} & l \neq 0 \end{cases}$

Bash \Rightarrow use triangle inequalities to verify this rule

$$\vec{J} = \vec{l} + \vec{s}$$

$$|\vec{J}| < |\vec{s}| + |\vec{l}|$$

This gives $|j| \leq l+s$

Also

$$|\vec{J}| \geq ||\vec{l}| - |\vec{s}||$$

This gives $\sqrt{j(j+1)} \geq \left| \sqrt{l(l+1)} - \sqrt{s(s+1)} \right|$

Prob 8-8 has you verify that with $s = \frac{1}{2}$ the only integer-spaced j -values consistent with these are

$$j = \begin{cases} \frac{1}{2} & \text{if } l=0 \\ l \pm \frac{1}{2} & \text{if } l \neq 0 \end{cases}$$

ExList all j and m_j for $m=4$ state with $l=4$, $s=\frac{1}{2}$

$$j = 4 + \frac{1}{2} = \frac{9}{2}$$

$$m_s = \pm \frac{1}{2}$$

$$m_j = -\frac{9}{2}, -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2} \quad (10 \text{ values})$$

$$j = 4 - \frac{1}{2} = \frac{7}{2}$$

$$m_j = -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2} \quad (8 \text{ values})$$

Total 18 states totalNote all these states are distinct! e.g. $j = \frac{9}{2}$, $m_j = \frac{7}{2}$ is different from $j = \frac{7}{2}$, $m_j = \frac{7}{2}$.

Did we lose any state? $l=4$, $m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4$

each with

$$m_s = \pm \frac{1}{2}$$

→ total of 18 states!

↳ we don't lose/gain any states!

[With no spin-orbit interaction]

↳ The states are degenerate in either description.

BUT with the spin-orbit interaction → the m_l and m_s are no longer good quantum numbers

↳ need to use l, s, m_l, m_s description.

Then $\vec{S} \cdot \vec{L} = \frac{1}{2} [j(j+1) - s(s+1) - l(l+1)] \hbar^2$

↳ And this goes into DE (into SE)

↳ some degeneracy gets lifted!

Hydrogen Energies with the Spin-orbit interaction

↳ Before, w/o spin-orbit int: Ψ_{nlm_l} = spatial wave functions

$n=3$

$n=2$

$n=1$

$l=0 \quad l=1 \quad l=2$
 $m_l = 0, \pm 1, \pm 2 \quad m_l = 0, \pm 1, \pm 2$

($s = \frac{1}{2}, m_s = \pm \frac{1}{2}$)

χ_{sm_s} = spin wave functions

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

need to solve this

$$\hat{H}\Psi = E\Psi$$

Now, include spin-orbit term:

$$\hat{H} = \frac{-k^2}{2m} \vec{\nabla}^2 + V(r) + \frac{1}{2m_e c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}$$

Would need to start over again! $\Psi = \psi_{nlm_l} \chi_{s_{lm}}$ are not solutions anymore!

Too hard to solve exactly \rightarrow Approximation

KNOW The spin-orbit correction is very small! ($\Delta E \sim 10^{-4} E$)

\hookrightarrow To first approx, we still have $\psi_{nlm_l} = R_{nl} Y_{lm_l}$ is still a solution to 1st order

Gives $E_n = -\frac{13.6 \text{ eV}}{n^2}$ (dominant)

\hookrightarrow we can compute ΔE for the spin-orbit term as an expectation value, using ψ_{nlm_l} .

$$\Delta E = \frac{1}{2m_e c^2} \left(\frac{1}{r} \frac{dV(r)}{dr} \right) \underbrace{\begin{pmatrix} \vec{J} \cdot \vec{L} \\ S \cdot L \end{pmatrix}}_{\text{expectation values!}}$$

Can use $\overline{\vec{J} \cdot \vec{L}} = \frac{1}{2} \left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right]$

① $\overline{\vec{J} \cdot \vec{L}} = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] \hbar^2$

② Compute $\left(\frac{1}{r} \frac{dV(r)}{dr} \right)$ using the radial wavefunction

$$\overline{\left(\frac{1}{r} \frac{dV(r)}{dr} \right)} = \int R_{nl}^* \frac{1}{r} \frac{dV(r)}{dr} R_{nl} 4\pi r^2 dr$$

where for H

$$\rightarrow V = \frac{-e^2}{4\pi\epsilon_0 r}$$

it does this gives a small correction to the primary energy $E = -\frac{13.6}{n^2}$

BUT \rightarrow other small corrections should then be included as well (e.g. Relativistic corrections (of \sim order of mag.))

Relativistically $KE = E - mc^2 \approx \sqrt{mc^2 + c^2 p^2} - mc^2$

Perturbatively, $KE \approx \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots$

Note

$\frac{p^2}{2m}$ already in SE \rightarrow Can compute 1st order relativistic correction as an expectation value as well

$$\Delta E_{\text{rel}} = \left(\frac{-p^4}{8m^3 c^2} \right) \Rightarrow \text{compute using the } j^{\text{th}} \text{ order wave function}$$

R_{nl}

[Note] When spin-orbit and relativistic corrections are included, the result matches the result from (QED)!

\hookrightarrow the final answer is result in QED \rightarrow

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n} \left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \right]$$

This is ff atom energy levels, including the fine structure, where

$$\alpha = \frac{e^2}{4\pi\epsilon_0 hc} \approx \frac{1}{137}$$

fine structure constant has No units

$E \uparrow M \uparrow \alpha \uparrow$
Relativistic

α gives a scale of EM interaction

tiny splitting for the same n

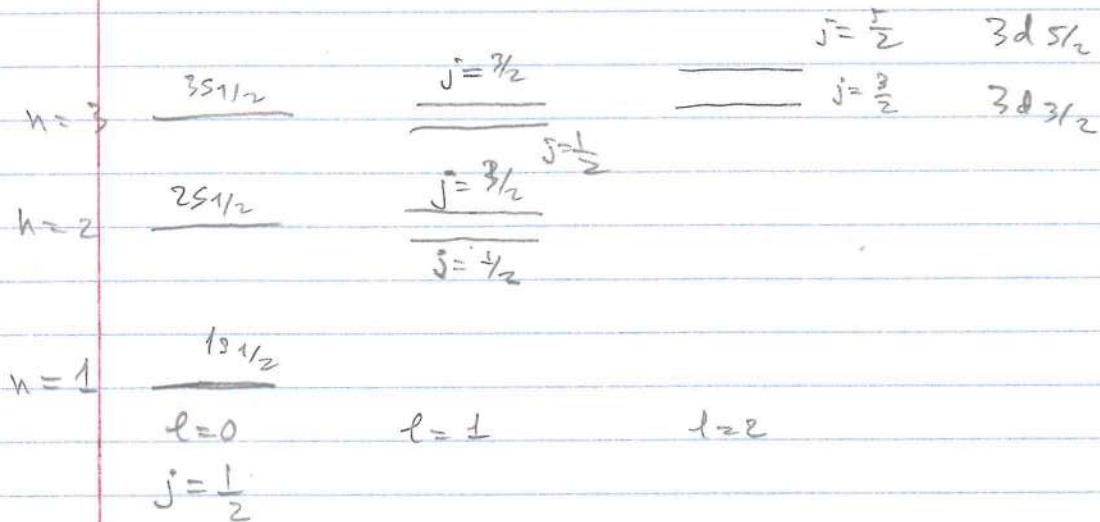
Note

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n} \left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \right]$$

Note $\alpha^2 < 10^{-4} \rightarrow$ gives small corrections to E_n

Note E depends on j, so some of the degeneracy is lifted!
(j-dependence)

→ we can look at H energy levels including the fine structure



All the non-s-states (with $l=0$) become doublets with $j=l\pm\frac{1}{2}$

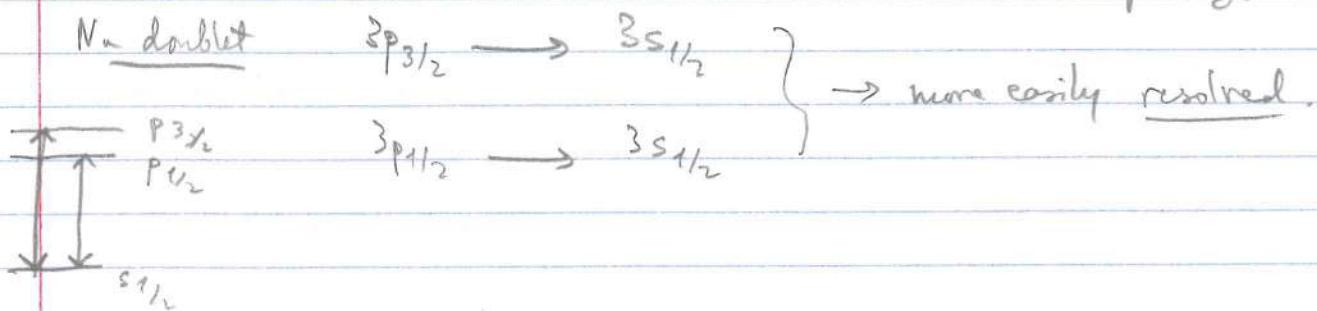
↳ Can label states nlj e.g. $1s_{1/2}, 2s_{1/2}, \dots$
 via s, p, d, f, \dots $2p_{1/2}, 2p_{3/2}, \dots$

Note

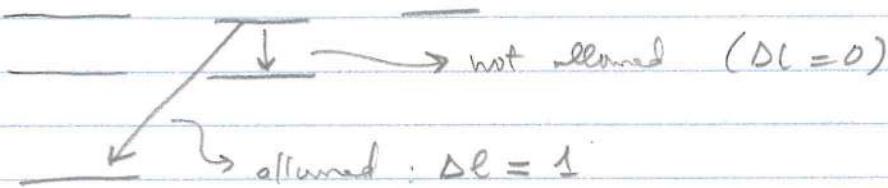
Alkalies are hydrogenic,
having one valence electron

$3p_{1/2}, 3p_{3/2}, \dots$

e.g. Na can use same labels, though there are also additional splittings...



Selection Rules When an atom is excited, it deexcite by emitting a photon. But not all transitions are allowed.



Selection rule says which transitions are allowed

We'll also talk about transition probabilities or Prob./sec for a transition to occur

Selection rule says which transitions have probabilities that aren't negligible

For the allowed transitions, the selection rules are

$$\left. \begin{array}{l} \{\text{electric dipole}\} \\ \{\text{transitions}\} \end{array} \right\} \rightarrow \boxed{\Delta l = \pm 1} \quad \boxed{\Delta j = \pm 1, 0}$$

The main reason for this is that photons have spin

$$\boxed{j = 1 \text{ for photon}} \quad (\vec{j} = \vec{s} = \vec{l}, l=0) \quad \rightarrow \text{photons don't have angular orbital mom.}$$

So $\Delta j = \pm 1$ makes sense \Rightarrow photon carries off 1h of angular momentum

$\Delta j = 0$ is also possible,

$\Rightarrow \vec{j} \Rightarrow$ changes direction but not magnitude

$$\vec{Dj} \neq 0$$

But why $\Delta l = \pm 1$ only?

\hookrightarrow we'll show this using parity arguments.

\hookrightarrow First, with an energy eigenstate $\Psi_{\text{harm}}(\vec{r}, t) = \varphi_{\text{harm}}(\vec{r}) e^{-iE_t t/\hbar}$

$\Rightarrow |\Psi_{\text{harm}}(\vec{r}, t)|^2$ has no + - dependence \Rightarrow no transitions

To get transitions, we need a mixture of states \rightarrow

$$\text{For a mixture} \rightarrow \Psi = c_1 \Psi_1 e^{-iE_1 t/\hbar} + c_2 \Psi_2 e^{-iE_2 t/\hbar}$$

$\hookrightarrow |\Psi|^2$ has cross terms that are time dependence

\hookrightarrow T-dep terms $\propto e^{i(E_1 - E_2)t/\hbar}$ and a frequency ν

$$\boxed{\nu = \frac{E_1 - E_2}{\hbar} = \text{photon frequency}}$$

Photon goes off with $\hbar\nu = E_1 - E_2$

In a quantum system, even a pure energy state will become mixed due to quantum fluctuations (relativistic)

\Rightarrow Can get spontaneous transitions from excited states!

We want to know which transitions are allowed?

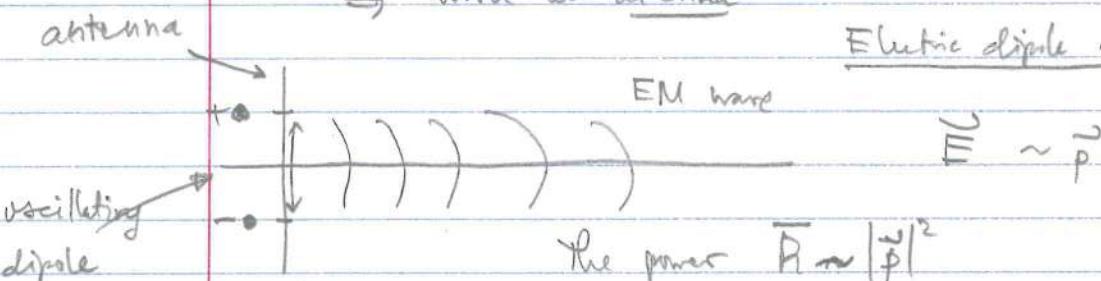
\hookrightarrow Can look at classical radiation of photons, how does this occur?

How do we get radiation (light) classically? by accelerating electric charge?

\hookrightarrow The simplest type of radiation, classically, is an oscillating electric dipole

\Rightarrow with an antenna

$$\text{Electric dipole moment } \vec{p} = q\vec{d}$$



$$\text{The power } P \sim |\vec{p}|^2$$

Back to GM and a transitioning atom \rightarrow we need a non zero dipole moment, \vec{p} .

For atom \vec{r} $-e$ $q = e$ $\vec{d} = -\vec{r}$

$$\boxed{\text{Get } \vec{p} = -e\vec{r} \text{ for H}}$$

$$\Psi = \Psi_i e^{-iE_i t/\hbar} + \Psi_f e^{-iE_f t/\hbar}$$

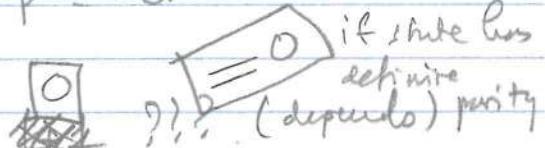
is the expectation value of \vec{p} zero or nonzero?

If $\langle \vec{p} \rangle = 0 \rightarrow$ then no transition

If $\langle \vec{p} \rangle \neq 0 \rightarrow$ get transition and photons?

→ need to calculate expectation value of $\vec{p} = -e\vec{r}$

$$\text{L} \quad \vec{p} = \int_{-\infty}^{\infty} \Psi^* (-e\vec{r}) \Psi d^3 r$$



$$\begin{aligned} &= -e \left[\int_{-\infty}^{\infty} \Psi_i^* \vec{r} \Psi_i d^3 r + \int_{-\infty}^{\infty} \Psi_f^* \vec{r} \Psi_f d^3 r \right. \\ &\quad \left. + \int_{-\infty}^{\infty} \Psi_i^* \vec{r} \Psi_f d^3 r \cdot (e^{-i(E_i - E_f)t/\hbar}) \right. \\ &\quad \left. + \left. \int_{-\infty}^{\infty} \Psi_f^* \vec{r} \Psi_i d^3 r \cdot (e^{-i(E_f - E_i)t/\hbar}) \right] \right] \end{aligned}$$

These are

complex conjugates of each other

* Both of these last terms have the same norm = $\sqrt{1^2}$

$$\text{norm} = \left| \int_{-\infty}^{\infty} \Psi_f^* \vec{r} \Psi_i d^3 r \right| = \left| \int_{-\infty}^{\infty} \Psi_i^* \vec{r} \Psi_f d^3 r \right|$$

Get allowed transitions when $(\vec{p} \neq 0)$

We can evaluate those integrals using parity!

$\vec{r} \rightarrow -\vec{r}$ under parity in 3D

If (as we'll show) $\Psi_{\text{wave}}(\vec{r}) \rightarrow \Psi_{\text{wave}}(-\vec{r}) = \pm \Psi_{\text{wave}}(\vec{r})$

then the 1st two intervals vanish!

$$\rightarrow |\Psi_i|^2 \text{ or } |\Psi_f|^2 \text{ even if } \Psi_i(-\vec{r}) = \pm \Psi_i(\vec{r})$$

Integrand $\Psi_i^* \vec{r} \Psi_i = \vec{r} |\Psi_i|^2 \rightarrow \text{odd integrated}$

Therefore $\int_{-\infty}^{\infty} \Psi_i^* \vec{r} \Psi_i d^3 r = 0$ ↑ odd ↑ even also similarly $\int_{-\infty}^{\infty} \Psi_f^* \vec{r} \Psi_f d^3 r$.

So all that matters for whether $\vec{p} = 0$ or not is whether the norm

$$P_{fi} = \left| \int \Psi_f^* \vec{r} \Psi_i d^3 r \right| \text{ is zero or not}$$

involves different state

\Rightarrow Called the "overlap integral"

$\Rightarrow \Psi_i \rightarrow \Psi_f$, overlap
must

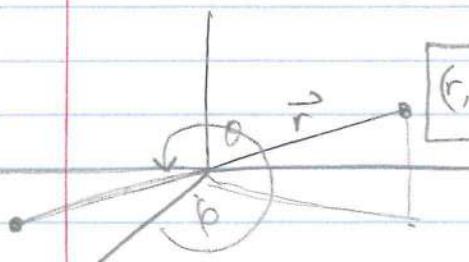
has definite parity

Next, we need to show

that $\Psi_{\text{nlm}}(\vec{r})$ have definite parity (if $\Psi_{\text{nlm}}(\vec{r}) = \pm \Psi_{\text{nlm}}(-\vec{r})$)

What happens under parity in 3D?

$\Psi(\vec{r}) = \Psi(r, \theta, \phi)$ How do the coordinates r, θ, ϕ transform when $\vec{r} \rightarrow -\vec{r}$?



$$(r, \theta, \phi) \rightarrow (r, \pi - \theta, \pi + \phi)$$

In spherical coordinates

$$\boxed{\Psi(-\vec{r}) = \Psi(r, \pi - \theta, \pi + \phi)}$$

does this have definite parity?
Is $\Psi(\vec{r})$ even or odd?

To answer this q,

use

$$\Psi_{\text{nlm}}(\vec{r}) = R_{\text{nl}}(r) Y_{\text{lm}}(\theta) \Phi(\phi)$$

$$\text{So } \Psi_{nlme}(-\vec{r}) = R_{nl}(r) \bigoplus_{lme} (\pi - \theta) \Phi_{lme}(\pi + \varphi)$$

Recall $\Phi_{lme}(\varphi) = e^{im\varphi}$ So $\Phi_{lme}(\pi + \varphi) = e^{im(\pi + \varphi)} = e^{im\pi} \cdot e^{im\varphi}$

Note $e^{im\pi} = (e^{im})^{me} = (-1)^{me}$

$$\text{So } \Phi_{lme}(\pi + \varphi) = (-1)^{me} \bigoplus_{lme}$$

Next, look at $\bigoplus_{lme} (\theta) \rightarrow \bigoplus_{lme} (\pi - \theta)$

April 25, 2018

$$P_A := \left| \int \Psi_{nlme}^* \Psi_{nlme} d^3r \right| \text{ is zero or not}$$

\hookrightarrow need $P_A \neq 0$ for allowed transition.

Under parity $\rightarrow \vec{r} \rightarrow -\vec{r}$

$$\Psi_{nlme}(\vec{r}) = R_{nl}(r) \bigoplus_{lme} (\theta) \Phi_{lme}(\varphi) \text{ becomes } R_{nl}(-r) \bigoplus_{lme} (\pi - \theta) \Phi_{lme}(\pi + \varphi)$$

Showed $\boxed{\Phi_{lme}(\pi + \varphi) = (-1)^{me} \Phi_{lme}(\varphi)}$

What about \bigoplus_{lme} ?

even or odd function for
 $l = \text{even or odd}$

Recall $\bigoplus_{lme} (\theta) = \sin^{lme} \theta \frac{d^{lme} P_l(\cos \theta)}{d^{lme} \cos \theta}$

$$\Rightarrow \bigoplus_{lme} (\pi - \theta) = \sin^{lme}(\pi - \theta) \frac{d^{lme}}{d^{lme} \cos(\pi - \theta)} P_l(\cos(\pi - \theta))$$

$$= \sin^{lme} \theta \frac{d^{lme}}{d^{lme} (-\cos \theta)} P_l(-\cos \theta)$$

$$= (-1)^l P_l(\cos \theta)$$

$$= \sin^{lme} \theta (-1)^{me} (-1)^l \bigoplus_{lme} (\theta)$$

$$\text{So } \boxed{\bigoplus_{lme} (\pi - \theta) = \sin^{lme} \theta (-1)^{me} (-1)^l \bigoplus_{lme} (\theta)}$$

So $\Psi_{nlme}(\mathbf{r}) = \underbrace{(-1)^{m_e} (-1)^{m_e}}_1 (-1)^l \Psi_{nlme}(\mathbf{r})$

1 for $m_e = \text{integer} \dots$

So $\Psi_{nlme}(\mathbf{r}) = (-1)^l \Psi_{nlme}(\mathbf{r})$

Therefore parity only depends on l :

Now look at the dipole moment

$$P_{fi} = \left| \int \Psi_{nl'm'e'}^* e \vec{r} \Psi_{nl'me} d^3r \right|$$

Under parity $\vec{r} \rightarrow -\vec{r}$ (odd)

$$\Psi_{nl'm'e'} \rightarrow (-1)^{l'} \Psi_{nl'm'e'}$$

$$\Psi_{nl'me} \rightarrow (-1)^l \Psi_{nl'me}$$

Hence Integrand $\rightarrow (-1) (-1)^{l+l'} \text{Integrand}$

So The integral vanishes if the integrand is odd

Hence \hookrightarrow If $l+l' = \text{even}$

or with $l = l' + \Delta l \rightarrow 2l + \Delta l = \text{even}$

So Vanishes if $\Delta l = 0, \pm 2, \pm 4, \dots$

Only values (so it doesn't vanish) consistent with photons having spin = 1 are allowed

$$\Delta l = \pm 1$$

\Rightarrow & can't carry 3th

$$\text{Then for } j \quad j = l \pm \frac{1}{2}, \quad j' = l' \pm \frac{1}{2} = l \mp 1 \pm \frac{1}{2}$$

$$\text{So } \Delta j = \cancel{\pm 2, \pm 1, 0} \rightarrow \boxed{\Delta j = 0, \pm 1}$$

but photons can't take spin 2

Combine, get the selection rule

$$\begin{array}{l} \hookrightarrow \boxed{\Delta l = \pm 1, \text{ all other forbidden}} \\ \Delta j = 0, \pm 1 \end{array}$$

angular momentum changes in direction

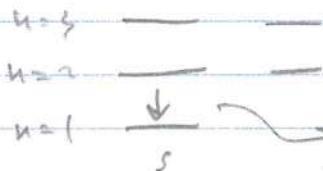
electric dipole

transition \rightarrow with highest probability \rightarrow

there are other transitions that can occur, but they have much lower probability (not electric dipole) \rightarrow a million times less prob.

\hookrightarrow called "forbidden transitions" \rightarrow misleading since they can happen

e.g. $2s \rightarrow 1s$ in H is a forbidden transition



this can only occur ^{only} as a $2 \leftarrow 1$ transition

Typical lifetime for allowed transitions are $\sim 10^{-8} \text{ s} \times 10 \text{ nm}$

but the $2s - 1s$ lifetime is about $1s$ \rightarrow metastable state
(less probable by 10^8)

$-H-$

II. ATOMIC PHYSICS

- Went to look at atoms with more than 1 electron
 → But we immediately encounter a problem
 → All electrons are alike

If 2 electrons come within some Δr of each other we can't touch them individually. This is not true classically → where you can always track individual trajectories
 → This is a QM problem...

6 Identical Particles

Consider 2 identical particles

6 To write a 2 particle SE, we must use labels

(6) $\Psi(\vec{r}_1, \vec{r}_2) = 2\text{-particle wavefunction for 2 identical particles}$

$$(6) \frac{-\hbar^2}{2m} \vec{\nabla}_1^2 \Psi(\vec{r}_1, \vec{r}_2) - \frac{\hbar^2}{2m} \vec{\nabla}_2^2 \Psi(\vec{r}_1, \vec{r}_2) + V(\vec{r}_1, \vec{r}_2) \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2)$$

$$\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) (\vec{r}_1 = x_1 \hat{i} + y_1 \hat{j} + z_1 \hat{k}) \\ \left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right) (\vec{r}_2 = x_2 \hat{i} + y_2 \hat{j} + z_2 \hat{k})$$

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

Mass = m for both, $V(\vec{r}_1, \vec{r}_2) =$ mutual 2-particle potential energy

$$E = \text{total energy} \rightarrow \text{often abbreviate } \Psi(\vec{r}_1, \vec{r}_2) = \Psi(1, 2)$$

We must use labels to write equations! But there can't be any physical meanings to them (identical particles...)

→ Must have $V(\vec{r}_1, \vec{r}_2) = V(\vec{r}_2, \vec{r}_1)$

Likewise

If $\Psi(\vec{r}_1, \vec{r}_2)$ is a solution, and τ is $\Psi(2, 1)$

$$(\Psi(1, 2))$$

Can define an exchange operator $\Psi(2,1) = \hat{P}_{12} \Psi(1,2)$

This must give us solution \hat{P} is the permute

If \hat{P}_{12} acts twice $\hat{P}_{12}^2 \Psi(1,2) = \hat{P}_{12} \Psi(2,1) = \Psi(1,2)$

$\therefore \hat{P}_{12}^2 = 1 \rightarrow$ eigenvalue.

So $\hat{P}_{12} = \pm 1 \rightarrow$ eigenvalues \rightarrow Get 2 types of eigenstates

If under interchange $\boxed{\Psi(2,1) = +\Psi(1,2)}$ \rightarrow symmetric under interchange
 \rightarrow obey Bose-Einstein statistics

$\boxed{\Psi(2,1) = -\Psi(1,2)}$ \rightarrow anti-symmetric

\rightarrow obey Fermi-Dirac statistics

Note $(\Psi(2,1))^2 = (\Psi(1,2))^2$

But there are still fundamental differences between these.

All identical particle wave functions in QM are either symmetric or anti-symmetric.

April 27/2018 Recall 2 types of wfn $\rightarrow \Psi(2,1) = \Psi(1,2) \rightarrow$ symmetric (Bose-Einstein)

or $\Psi(2,1) = -\Psi(1,2) \rightarrow$ anti-symmetric (Fermi-Dirac stats)

For different particles (e.g. e^- and photons), this does not hold

Then, there's a 2nd classification:

Bosons \rightarrow have integer spin (e.g.: photons (1), pions (0), Higgs)

Fermions \rightarrow have $\frac{1}{2}$ -integer spin

e.g. e^- , \bar{p} , quarks, neutrinos, muons, spin $\frac{1}{2}$

N.B. Fermions obey the Pauli exclusion principle

⇒ can't put two (or more) identical fermions in the same state

Suppose you have a multi-electron atom with states labeled by $n l m_l m_s$

⇒ can't have 2 electrons with the same $n l m_l m_s$,

→ 1st e⁻ ⇒ $n=1, l=0, m_l=0, s=\frac{1}{2}, m_s=+\frac{1}{2}$ (up)

2nd e⁻ ⇒ $n=1, l=0, m_l=0, s=\frac{1}{2}, m_s=-\frac{1}{2}$ (down)

3rd e⁻ ⇒ $n=2, l=0, m_l=0, s=\frac{1}{2}, m_s=+\frac{1}{2}$ (up)

Have 2 classifications

→ Symmetric or Anti-symmetric	{	
(Bose-Einstein)		(Fermi-Dirac)
→ bosons	or	fermions
→ int. spins	{	$\frac{1}{2}$ -integers

There's a link between these

Fermions → anti-symmetric wfn (sly F-D states)

⇒ obey the exclusion principle

Bosons → symmetric wfn (sly Bose-Einstein states)

⇒ don't obey the exclusion principle

We'll see later ⇒ anti-symmetric wfn give rise to the exclusion principle.

#

WAVE FUNCTIONS FOR IDENTICAL PARTICLES

Want to construct sym- and anti-sym wave functions

$$\Psi(\dots i \dots j \dots) = \pm \Psi(\dots j \dots i \dots)$$

How do we do this?

Consider 2 particles

$$\frac{-\hbar^2}{2m} \vec{\nabla}_1^2 \Psi(\vec{r}_1, \vec{r}_2) - \frac{-\hbar^2}{2m} \vec{\nabla}_2^2 \Psi(\vec{r}_1, \vec{r}_2) + V(\vec{r}_1, \vec{r}_2) \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2)$$

⇒ If $V(\vec{r}_1, \vec{r}_2)$ depends on \vec{r}_1 and \vec{r}_2 in a way that won't separate, then this becomes hard to solve ...

But if $V(\vec{r}_1, \vec{r}_2) = V(\vec{r}_1) + V(\vec{r}_2)$, then the eqn will separate

either no interaction between 2 particles or they each feel the same average interaction → will need to develop this method later

Then, with this, $\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1)\Psi(\vec{r}_2)}$ → separates --

Use notation : $\Psi_\alpha(1)$ → denotes \vec{r}_1
 $\Psi_\beta(2)$ → denotes the state (n, l, s, m_z, m_s)
 single particle state

Now for identical particles, we need $\Psi_{(2)} \pm \Psi_{(1, 2)}$

We form these as the combination

sym $\Psi_s(1, 2) = \frac{1}{\sqrt{2}} [\Psi_\alpha(1) \Psi_\beta(2) + \Psi_\beta(1) \Psi_\alpha(2)]$

anti-sym $\Psi_a(1, 2) = \frac{1}{\sqrt{2}} [\Psi_\alpha(1) \Psi_\beta(2) - \Psi_\beta(1) \Psi_\alpha(2)]$

Can verify $\Psi_s(2,1) = \frac{1}{\sqrt{2}} [\psi_\alpha(2)\psi_\beta(1) + \psi_\alpha(1)\psi_\beta(2)] = \Psi_s(1,2)$

↳ always $\Psi_s(2,1) = \Psi_s(1,2)$

also $\Psi_A(2,1) = \frac{1}{\sqrt{2}} [\psi_\alpha(2)\psi_p(1) - \psi_\alpha(1)\psi_p(2)] = -\Psi_A(1,2)$

↳ always $\Psi_A(1,2) = -\Psi_A(2,1)$

Why $\frac{1}{\sqrt{2}}$?

Needed for normalization

To show this, we must use a property called orthogonality.

$$\int \Psi_\alpha^*(1)\Psi_\beta(1) = 0 \quad \text{if } \alpha \neq \beta$$

$$\int \Psi_\alpha^*(1)\Psi_\alpha(1) = 1 \quad \text{if } \alpha = \beta$$

] You'll show this in 9-10

With this, can look at normalization of $\Psi_s(1,2)$

$$\begin{aligned} \iint \Psi_s^*(1,2)\Psi_s(1,2) &= \iint \left(\frac{1}{\sqrt{2}}\right)^2 \left[\Psi_\alpha^*(1)\Psi_\beta^*(2) + \Psi_\beta^*(1)\Psi_\alpha^*(2) \right] \cdot \\ &\quad \left[\Psi_\alpha(1)\Psi_\beta(2) + \Psi_\beta(1)\Psi_\alpha(2) \right] \\ &= \frac{1}{2} \iint |\Psi_\alpha(1)|^2 |\Psi_\beta(2)|^2 + |\Psi_\beta(1)|^2 |\Psi_\alpha(2)|^2 + \Psi_\alpha^*(1)\Psi_\beta(1) \cdot \Psi_\beta^*(2)\Psi_\alpha(2) \\ &\quad + \Psi_\beta^*(1)\Psi_\alpha(1) \cdot \Psi_\alpha^*(2)\Psi_\beta(2) \\ &= \frac{1}{2} \left[1 + 1 + 0 + 0 \right] = \frac{2}{2} = \boxed{1} \end{aligned}$$

Now, suppose we have 3 or more identical particles

Bosons : symmetric under change of any pair (6 ways)

↳ $\Psi_s(\dots i \dots j \dots) = \Psi_s(\dots j \dots i \dots)$

Fermions → must be anti-sym

$$\Psi_A(\dots i \dots j \dots) = -\Psi_A(\dots i \dots j \dots)$$

For 2 Fermions

$$\hookrightarrow \Psi_A = \frac{1}{\sqrt{2}} [\Psi_\alpha(1)\Psi_\beta(2) - \Psi_\alpha(2)\Psi_\beta(1)]$$

$$\text{or} \quad \boxed{\Psi_A = \frac{1}{\sqrt{2}} \det \begin{pmatrix} \Psi_\alpha(1) & \Psi_\beta(1) \\ \Psi_\beta(1) & \Psi_\beta(2) \end{pmatrix}}$$

determinants have 2 properties...

→ pick up a (-) under interchange of any pair of rows or columns

They vanish if any 2 rows or columns are the same:

$$\text{e.g. if } \alpha = \beta \rightarrow \boxed{\det 0}$$

→ exclusion principle (for fermions) $\rightarrow \Psi = 0$

For 3 particles (identical Fermion)

$$\Psi_A = \frac{1}{\sqrt{3!}} \det \begin{vmatrix} \Psi_\alpha(1) & \Psi_\alpha(2) & \Psi_\alpha(3) \\ \Psi_\beta(1) & \Psi_\beta(2) & \Psi_\beta(3) \\ \Psi_\gamma(1) & \Psi_\gamma(2) & \Psi_\gamma(3) \end{vmatrix}$$

$$6 = 3!$$

6 terms

→ # of permutations...

April 30, 2018

Constructing anti-sym + sym. Wfn

$$\hookrightarrow \text{e.g. 2 fermions } \Psi_A(1,2) = \frac{1}{\sqrt{2}} (\Psi_\alpha(1)\Psi_\beta(2) - \Psi_\beta(1)\Psi_\alpha(2))$$

\downarrow Generalise to N particles

$$= \frac{1}{\sqrt{2}} (\Psi_\alpha(1) \Psi_\alpha(2) - \Psi_\beta(1) \Psi_\beta(2))$$

$$\boxed{\Psi_A = \frac{1}{\sqrt{n!}} \det \begin{pmatrix} \Psi_\alpha(1) & \dots & \dots & \Psi_\alpha(n) \\ \vdots & & & \vdots \\ \Psi_\gamma(1) & \dots & \dots & \Psi_\gamma(n) \end{pmatrix}}$$

Slater determinant

\uparrow # of permutations

For symmetric wfn $\Psi_S \Rightarrow$ write out $n \times n$ determinant, then choose
 all minus signs to (+) signs and
 (lessons) \rightarrow

HELIUM \Rightarrow 2 electrons (fermions)

\Rightarrow ignore Coulomb interaction between the electrons.

Then the single particle Wfn are hydrogenic

$$\hookrightarrow \boxed{\Psi_\alpha(1) = \Psi_\alpha(1) \chi_{\pm \frac{1}{2}}}$$

denotes all quantum numbers but spin

Use these in

$$\boxed{\Psi_A = \frac{1}{\sqrt{2}} (\Psi_\alpha(1)\Psi_\beta(2) - \Psi_\beta(1)\Psi_\alpha(2))}$$

all qm numbers + spin

This gives an anti-symmetric wavefunction which does not have a total
 spin angular momentum

Instead, get a mixture of m_s, m_{s_2} states...

Turns out to be more useful (we'll see why) to characterize states of the atom by their total spin.

Call $\vec{S}' = \vec{s}_1 + \vec{s}_2$ → total spin

Thus, we form $\Psi_A = (\text{total spatial part}) \cdot (\text{total spin part})$

So $\boxed{\Psi_A = \Psi_{\text{spatial}} \chi_{\text{spin}}}$

We still require that under interchange, $\Psi_A \rightarrow -\Psi_A$

→ We can get this in 2 ways

↳ $\Psi_{\text{spatial}} \rightarrow -\Psi_{\text{spatial}}, \chi_{\text{spin}} \Rightarrow \chi_{\text{spin}}$
 ↳ $\chi_{\text{spin}} \rightarrow -\chi_{\text{spin}}, \Psi_{\text{spatial}} \rightarrow \Psi_{\text{spatial}}$

Can have both! (either is anti-symmetric...)

→ Get the link between total spin & spatial wavefunction...

⇒ lead to the "exchange force"

Adding spins: $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$ and $\vec{s}' = \vec{s}_1 + \vec{s}_2$

→ Expect 2 cases $|\vec{s}'| = \frac{1}{2} + \frac{1}{2} = 1$ }
 | and $m_{s'} = -1, 0, 1$ } → 3 cases

or $|\vec{s}'| = \frac{1}{2} - \frac{1}{2} = 0$ } 1 case
 | and $m_{s'} = 0$ }

Will have 4 cases total → two $\pm \frac{1}{2}$ spins

↳ These then group into symmetric-anti-symmetric combinations
 $s' = 1 \Rightarrow$ symmetric

⇒ Use labels → $\chi_{s'ms'}$

Turns out to be more useful (we'll see why) to characterize states of the atom by their total spin.

Call $\vec{S}' = \vec{s}_1 + \vec{s}_2$ → total spin

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 ↪ $\chi_{\text{spin}} \rightarrow -\chi_{\text{spin}}, \Psi_{\text{spatial}} \rightarrow \Psi_{\text{spatial}}$

Can have both! (either is anti-symmetric...)

→ Get the link between total spin & spatial wavefunction...

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 | and $m_{S'} = -1, 0, 1$

| or $|\vec{S}'| = \frac{1}{2} - \frac{1}{2} = 0$ } 1 case
 | and $m_{S'} = 0$

Will have 4 cases total → two $\pm \frac{1}{2}$ spins

↪ These then group into symmetric-anti-symmetric combinations
 $s' = 1 \Rightarrow$ symmetric

⇒ Use labels → $\chi_{s'm_{s'}}$

$s' = 1$

$$\chi_{11} = \frac{\chi_1(1) \chi_1(2)}{\sqrt{2}}$$

$$\rightarrow m_s' = 1$$

$$\chi_{10} = \frac{1}{\sqrt{2}} \left[\chi_{\frac{1}{2}}(1) \chi_{\frac{1}{2}}(2) + \chi_{\frac{-1}{2}}(1) \chi_{\frac{-1}{2}}(2) \right]$$

$$\rightarrow m_s' = 0$$

$$\chi_{-1-1} = \frac{\chi_{-1}(1) \chi_{-1}(2)}{\sqrt{2}}$$

$$\rightarrow m_s' = -1$$

(3 sym)
(triplet)

All three are symmetric \Rightarrow called "triplet states" of He
Since χ symmetric $\Rightarrow \Psi_{spatial}$ has to be anti-symmetric

 $s' = 0$

$$\rightarrow \boxed{\chi_{00} = \frac{1}{\sqrt{2}} \left[\chi_{\frac{1}{2}}(1) \chi_{-\frac{1}{2}}(2) - \chi_{-\frac{1}{2}}(1) \chi_{\frac{1}{2}}(2) \right]} \quad m_s' = 0$$

(1 anti-sym)
(singlet)

χ anti-symmetric $\Rightarrow \Psi$ has to be symmetric
 \rightarrow called "singlet state"

$$\text{So the total Wfn (anti-sym)} \rightarrow \boxed{\Psi_A = \Psi_{spatial} \chi_{spin}}$$

and $\begin{cases} \Psi_{spatial} \text{ symmetric for } s' = 0 \\ \Psi_{spatial} \text{ anti-symmetric for } s' = 1 \end{cases} \quad \chi_{s'm_s'}$

What are the physical effects of this?

\hookrightarrow Suppose the 2 e^- get close $\Rightarrow \vec{r}_1 \approx \vec{r}_2 \Rightarrow 1 \approx 2$

$$\text{Then } \Psi_{spatial}^+ = \frac{1}{\sqrt{2}} \left[\Psi_\alpha(1) \Psi_\beta(2) - \Psi_\beta(1) \Psi_\alpha(2) \right] \quad \leftarrow \text{anti-sym}$$

$$\text{So } \approx \frac{1}{\sqrt{2}} \left[\Psi_\alpha(1) \Psi_\beta(1) - \Psi_\beta(1) \Psi_\alpha(1) \right] \approx 0 \quad \leftarrow \begin{matrix} \text{spin} \\ \text{triplet} \end{matrix}$$

\Rightarrow Means low probability for e^- getting close

$s' = 1$

$$\text{But } \Psi_{\text{spatial}}^s = \frac{1}{\sqrt{2}} [\Psi_a(1)\Psi_p(2) + \Psi_p(1)\Psi_a(2)]$$

(spin singlet)

$$\approx \frac{1}{\sqrt{2}} \cdot 2 [\Psi_a(1)\Psi_p(1)] \neq 0$$

$\pm \frac{1}{2}, S=0$

→ Higher probability for particles to get close...

See a correlation between spatial behavior and total spin

Singlet $\uparrow \downarrow$ $s'=0, m_s'=0$ (anti-symmetric)
 $(S=0)$

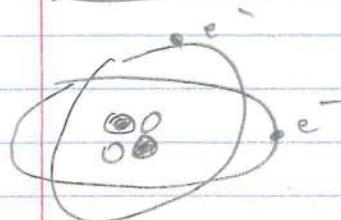
↪ Ψ_{spatial} symmetric \Rightarrow particles can get close)

Triplet $\uparrow \uparrow$ $m_s'=1$ } $\rightarrow \chi_{\text{sym}}$
 $(S=1)$ $\uparrow \downarrow$ $m_s'=-1$ } $\rightarrow \Psi_{\text{spatial}}$ is anti-sym
 $\uparrow \downarrow$ $m_s'=0$ } \rightarrow particle stay apart

↳ This is sort of like a force \rightarrow "exchange force"

↳ But it's not really a force; rather it's an effect of having Ψ_{spatial} be sym. or anti-sym.

What about energy levels of Helium?



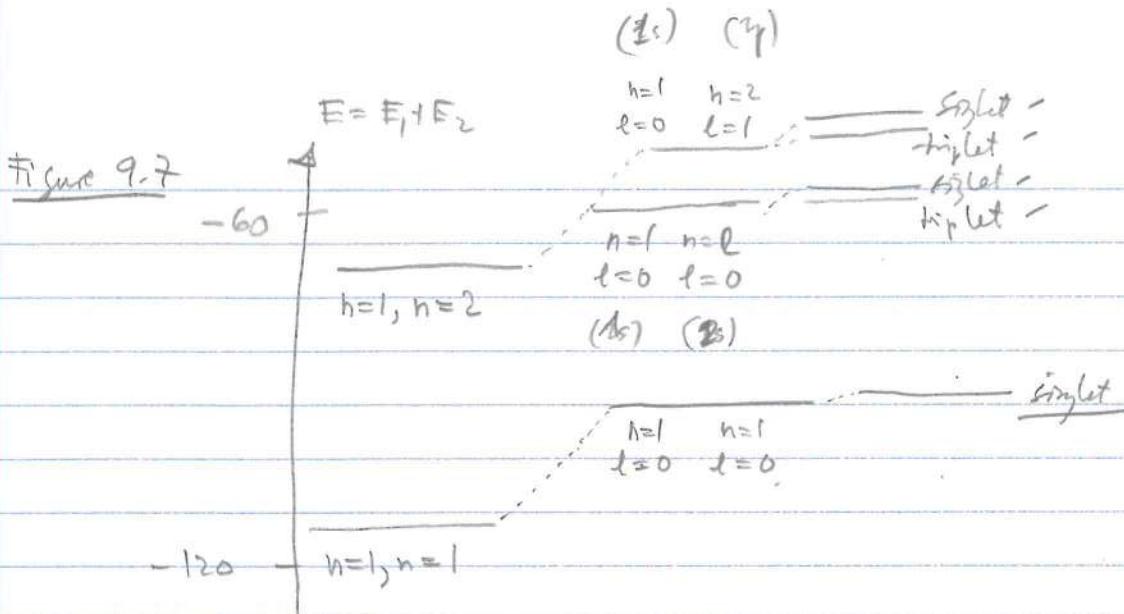
→ Make 3 levels of approximation!

① Ignore Coulomb potential between e^- (ignore e^-e^-)

$$\hookrightarrow \boxed{E_n = -\frac{z^2 (13.6 \text{ eV})}{n^2} \quad z=2}$$

$$\hookrightarrow E_1 = -54.4 \text{ eV} \dots$$

$$E_2 = -13.6 \text{ eV} \dots$$



- ② Include some of e^-e^- interaction (Coulomb effects) between e^- (no spin yet)

$$V = \frac{e^2}{4\pi\epsilon_0 r_{1,2}} \leftarrow \text{repel force} \Rightarrow V > 0$$

$\hookrightarrow E$ goes up!

\rightarrow By how much? Look at the radial probability distribution.

(p state e^- closer to nucleus \rightarrow to each other
 $\rightarrow V$ higher)

- ③ Include spin effects

Triplet $\rightarrow \Psi_{\text{spatial}}$ anti-symmetric $\rightarrow e^-$ stays apart more
 $\rightarrow V$ smaller \downarrow

Singlet $\rightarrow \Psi_{\text{spatial}}$ symmetric $\rightarrow e^-$ stay closer
 $\rightarrow V$ bigger

\hookrightarrow Singlet

triplet

Note all triplet @ same energy
 $(\text{since } E \text{ depends on } V)$

Note

\rightarrow there is No triplet in the ground state.

\hookrightarrow Observed spectroscopically, why?

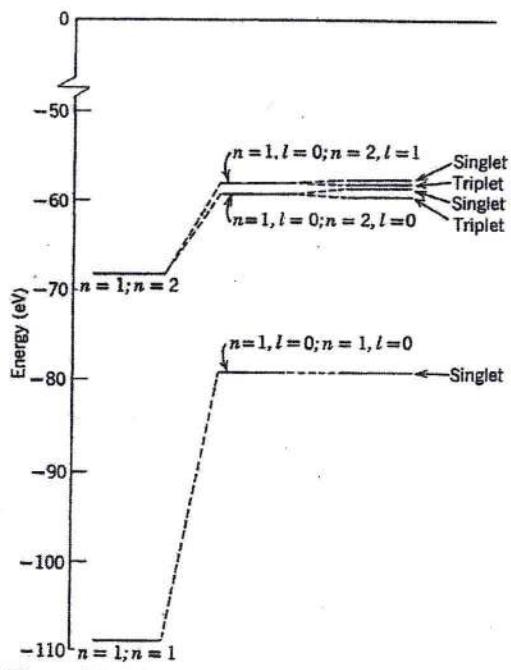
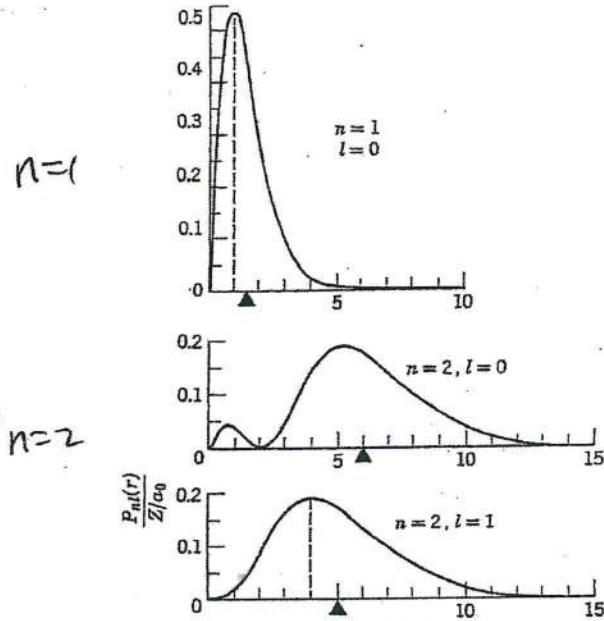


Figure 9-7 The low-lying energy levels of helium. *Left:* The levels that would be found if there were no Coulomb interaction between its electrons. *Center:* The levels that would be found if there were a Coulomb interaction but no exchange force. *Right:* The levels that would be found if there were a Coulomb interaction and an exchange force. These levels are in excellent agreement with the experimentally observed levels shown on the right in Figure 9-6.



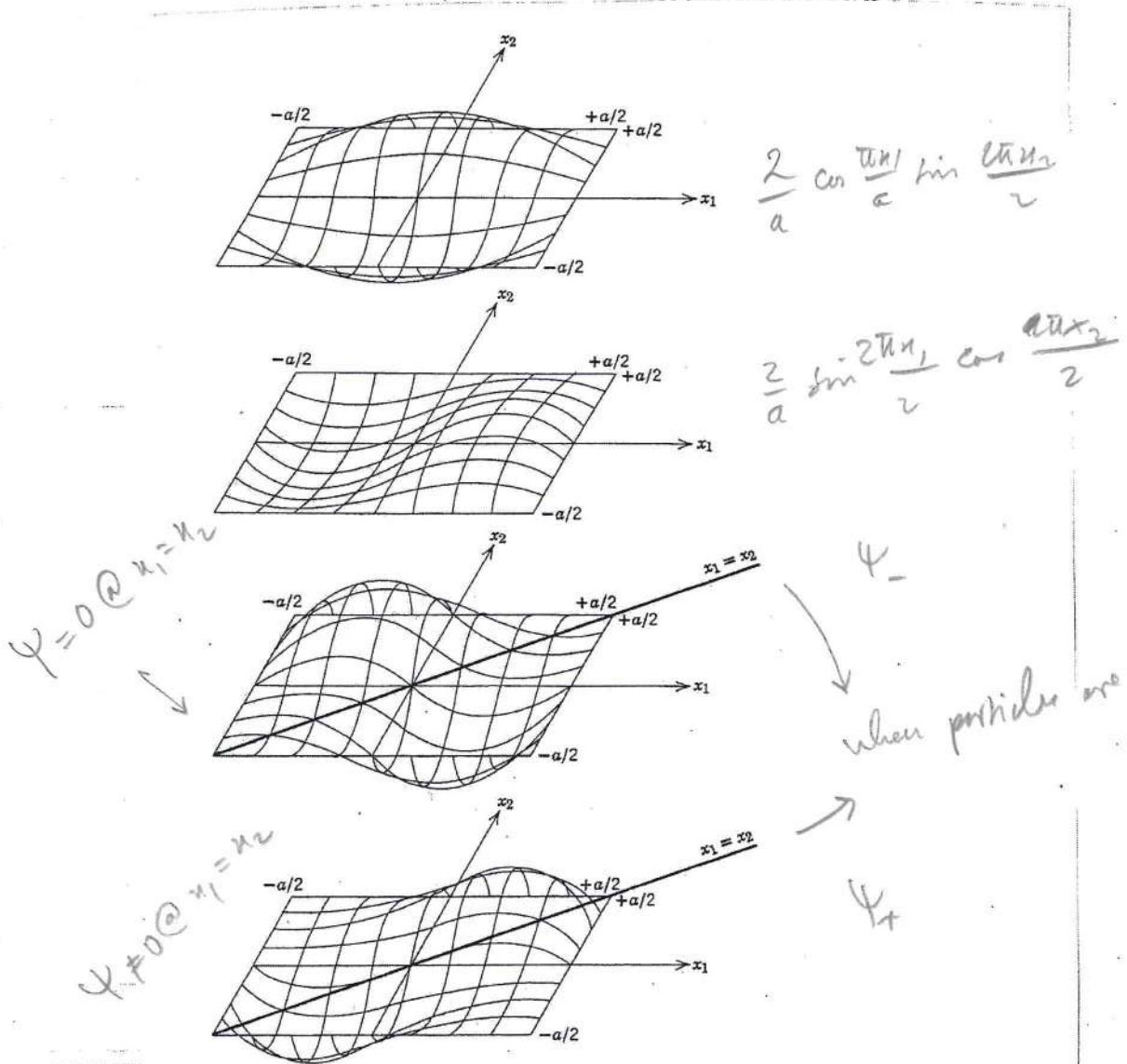


Figure 9-4 . Depicting the antisymmetric and symmetric space eigenfunctions of Example 9-1, ψ_- and ψ_+ for a system of two noninteracting identical particles in a one-dimensional infinite square well potential of width a when one particle is in the ground state with eigenfunction $\sqrt{2/a} \cos(\pi x/a)$ and the other is in the first excited state with eigenfunction $\sqrt{2/a} \sin(2\pi x/a)$. Top: The first term of ψ_- is shown by constructing the surface whose distance above or below the x_1, x_2 plane is the positive or negative value of $(2/a) \cos(\pi x_1/a) \sin(2\pi x_2/a)$. Upper middle: The surface describing the second term of ψ_- , i.e., $(2/a) \sin(2\pi x_1/a) \cos(\pi x_2/a)$. Lower middle: $1/\sqrt{2}$ times the first term minus the second term, which shows the geometry of ψ_- itself. It is apparent that the value of ψ_- is zero along the line $x_1 = x_2$, and it is small everywhere near that line. Thus the probability density $\psi_-^* \psi_-$ is very small wherever $x_1 \approx x_2$, and so the probability is very small that this condition will be achieved. Bottom: $1/\sqrt{2}$ times the sum of the term $(2/a) \cos(\pi x_1/a) \sin(2\pi x_2/a)$ and the term $(2/a) \sin(2\pi x_1/a) \cos(\pi x_2/a)$, showing the symmetric space eigenfunction ψ_+ for the system. This eigenfunction has its maximum magnitudes along the line $x_1 = x_2$. The probability density $\psi_+^* \psi_+$ therefore has its largest magnitudes if the two particles are in the same location in their one-dimensional well, and so we conclude that there is a large chance of finding them close together.

$$-\frac{e^2}{4\pi\epsilon_0 r}$$

$$= -\frac{e^2}{4\pi\epsilon_0 r}$$

Why? If $\chi_{\text{spin}} \rightarrow$ symmetric to triplet

then $\Psi_{\text{spatial}} \rightarrow$ must be anti-symmetric

But both e^- have $n=1, l=0, m_l=0 \rightarrow \Psi_{100}$

$$\boxed{\Psi_{\text{spatial}}^A = \frac{1}{\sqrt{2}} [\Psi_{100}(1)\Psi_{100}(2) - \Psi_{100}(2)\Psi_{100}(1)] = 0}$$

\hookrightarrow No triplet! (Exclusion principle...) \rightarrow Pauli ...

April

Recall

May 2, 2013

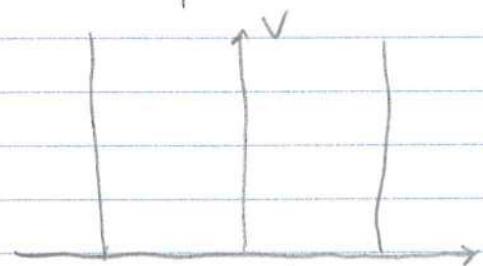
Exchange Effect $\Psi_A = \Psi_{\text{spatial}} \chi_{\text{spin}}$ total spin

If χ_{spin} Anti-sym, then Ψ_{spatial} sym \rightarrow particles can get close

If χ_{spin} sym, then Ψ_{spatial} anti-sym \rightarrow particles stay apart

Example for Ψ_{spatial}

\hookrightarrow Two particles in a box



\Rightarrow assume no interaction between the particles.

Recall the single particle wth

$$\Psi_1 = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right)$$

$$\Psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

Suppose 1 particle in ground state, and 1 in first excited state, level

Let $x_1 \rightarrow$ particle 1
 $x_2 \rightarrow$ particle 2

→ Can form sym + anti-sym combination of wfn.

Symmetric case

$$\Psi_+ = \frac{1}{\sqrt{2}} [\Psi_1(x_1)\Psi_2(x_2) + \Psi_2(x_1)\Psi_1(x_2)]$$

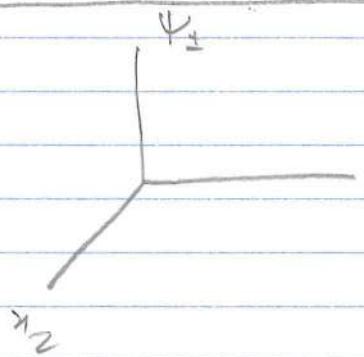
$$\Psi_+ = \frac{2}{a} \frac{1}{\sqrt{2}} \left[\cos \frac{\pi x_1}{a} \sin \frac{2\pi x_2}{a} + \sin \frac{2\pi x_1}{a} \cos \frac{\pi x_2}{a} \right]$$

Anti-sym

$$\Psi_- = \frac{2}{a} \frac{1}{\sqrt{2}} \left[\cos \frac{\pi x_1}{a} \sin \frac{2\pi x_2}{a} - \sin \frac{2\pi x_1}{a} \cos \frac{\pi x_2}{a} \right]$$

$$\Psi_+ \text{ and } \Psi_- \text{ obey } \begin{cases} \Psi_+(2,1) = \Psi_+(1,2) \\ \Psi_-(2,1) = -\Psi_-(1,2) \end{cases}$$

We can plot these as function of x_1, x_2



(See Figure 9.4)

$$\text{Fig 1 } \frac{2}{a} \sin \frac{\pi x_1}{a} \sin \frac{2\pi x_2}{a}$$

$$\text{Fig 2 } \frac{2}{a} \sin \frac{2\pi x_1}{a} \cos \frac{\pi x_2}{a}$$

$$(\text{anti-sym}) \quad \text{Fig 3 } \Psi_- = \frac{2}{a} \frac{1}{\sqrt{2}} (\text{Fig 1} - \text{Fig 2})$$

$$(\text{sym}) \quad \text{Fig 4 } \Psi_+ = \frac{1}{\sqrt{2}} (\text{Fig 1} + \text{Fig 2})$$

Observe, Fig 3 has $\Psi = 0$ along $n_1 = n_2$,

↳ no probability for being close (hook cover) (Ψ^2)

• Fig 4 has $\Psi \neq 0$ along $n_1 = n_2$

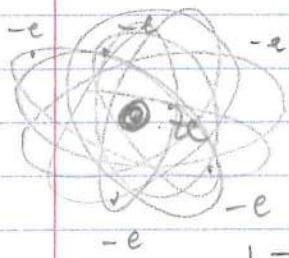
↳ There is probability of being close

⇒ "exchange force" → really a result of sym or anti-sym spatial wfn...

#

Hartree Theory

→ Need an approximation method for multi-electron atom, let z = atomic number..



$$\rightarrow V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_z) = \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} + \dots + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_z|} + \frac{-ze^2}{4\pi\epsilon_0 \vec{r}_1} + \dots + \frac{-ze^2}{4\pi\epsilon_0 \vec{r}_z}$$

| Too complicated → can't separate variables!

↳ Must compromise → use the average effect in a way that separates

Approx

$$V(\vec{r}_1, \dots, \vec{r}_z) = V(r_1) + V(r_2) + \dots + V(r_z)$$

where $V(r) = \text{single particle's effective potential}$

→ central potential

↳ only radial distance matter

→ No angular dependence...

↳ Then the problem separates!

Hartree's Theory

→ self-consistent method for finding $V(r)$

(1) → Guessing a form for $V(r)$ obeying 2 limits

$$V(r) = \begin{cases} \frac{-ze^2}{4\pi\epsilon_0 r} & r \rightarrow 0 \text{ (no screening)} \\ \frac{-e^2}{4\pi\epsilon_0 r} & r \rightarrow \infty \text{ (full screening)} \end{cases} (z=Z+1)$$

Find $V(r)$ that extrapolate between these..

(2) → Solve the single-particle SE for $V(r)$ and order solution

$$(i) \Psi_1(r, \theta, \phi) \rightarrow \text{has } E_1$$

$$(ii) \Psi_2(r, \theta, \phi) \rightarrow \text{has } E_2 > E_1$$

:

(3) Form the ground state of the atom by filling the lowest z -levels
 ⇒ putting $1e^-$ per state

(4) Calculate the charge distribution for this solution → charge density
 follows the particle

$$-e|\Psi_1|^2 - |\Psi_2|^2 e - e|\Psi_3|^2 + \dots - e|\Psi_n|^2 + ze @ \text{origin}$$

(5) → Use Gauss' law to find $V(r)$ for this charge distribution

(6) Take this $V(r)$, go to step 2, repeat.

→ repeat until self-consistent ($V(r)$ stops changing)

→ Generate a $V(r)$ that combines the SE, Gauss' law and the exclusion principle

Remarks → Each single particle state has $\Psi_{\text{one}}(r, \theta, \phi)$ as the angular part of the solution

(i) $V(r) \rightarrow$ central potential (don't matter)
And so separation constant = $[\ell(\ell+1)]$

→ but the radial wfn for $R_{nl}(r)$ will be different from H

(ii) The same quantum numbers always label the states in this approx

(iii) Must solve the radial equation numerically
 → have to use numerical methods
 → L.D.C. Hartree did this in 1928
 (use students as calculators...)

(iv) The Hartree method uses a weaker form of the exclusion principle
 → require 1 electron per state
 - but no anti-sym of wfn
 ground-state fill up
 $\uparrow 1s, 2s, 2p, \dots$

But anti-sym is too complicated...

e.g. $N_e = 10 \rightarrow 10!$ terms but $10! = 3628800$ terms...

But more modern approaches attempt to include some of these effects...

↑

Results of Hartree gives us the ordering of the n, l levels

Notation n_l $\stackrel{\# e^- \text{ in subshell}}{\uparrow}$ $\rightarrow \text{max} = 2(2l+1)$
 energy shell subshell (s, p, d, f, g, h, \dots)

Subshells fill up when you put in $2(2l+1)$ electrons...

Energy depends on n, l

\Rightarrow need to know n, l the ordering found by Hartree
e.g. $4s$ fills up before the $3d$.

May 7, 2013

Ground State + Periodic Table

Use Hartree formula to find the ordering of the n, l shells
 \Rightarrow fill them up with 2 electrons...

Notation $n, l \xrightarrow{\text{max}} s, p, d, f, \dots$ max = $2(2l+1)$

Energy depends on both n , and l
 \Rightarrow l degeneracy is broken
 \Rightarrow sometimes l matters more than n

e.g. $4s$ fills up before the $3d$

Look at Table 1.2 \rightarrow order determined by Hartree approach

Subshells	Capacity = $2(2l+1)$
1s	2
2s	2
2p	6
3s	2
3p	6

Now fill up the ground state

Li: $z = 3$ $1s^2 2s^1 2p^0$ \rightarrow called "electron configuration"
Be: $z = 4$ $1s^2 2s^2$
B: $z = 5$ $1s^2 2s^2 2p^1$

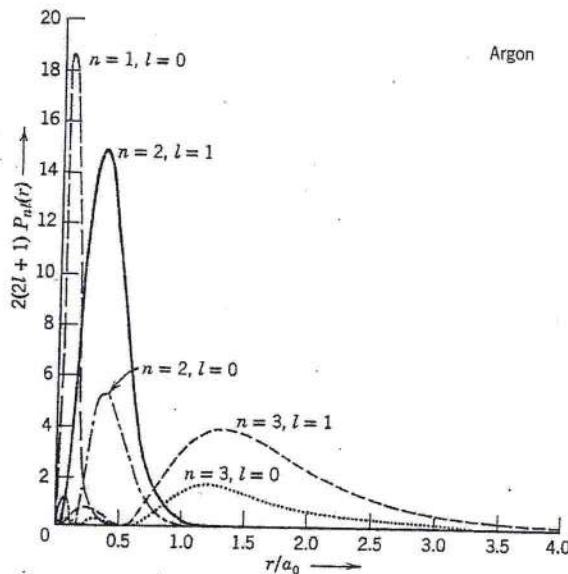


Figure 9-10 The Hartree theory radial probability densities for the filled quantum states of the argon atom, plotted as functions of r/a_0 , the radial coordinate in units of the hydrogen atom first Bohr orbit radius a_0 . For each n the probability density is largely concentrated in a restricted range of r/a_0 , called a shell. Note that the characteristic radius of the outermost shell ($n = 3$) has an r/a_0 value only a little larger than 1.0, while the characteristic radius of the innermost shell ($n = 1$) has an r/a_0 value much smaller than 1.0. That is, the outermost shell of argon is only a little larger in radius than a_0 , which is the radius of the single shell in hydrogen. The innermost shell of argon is of much smaller radius than the hydrogen shell.

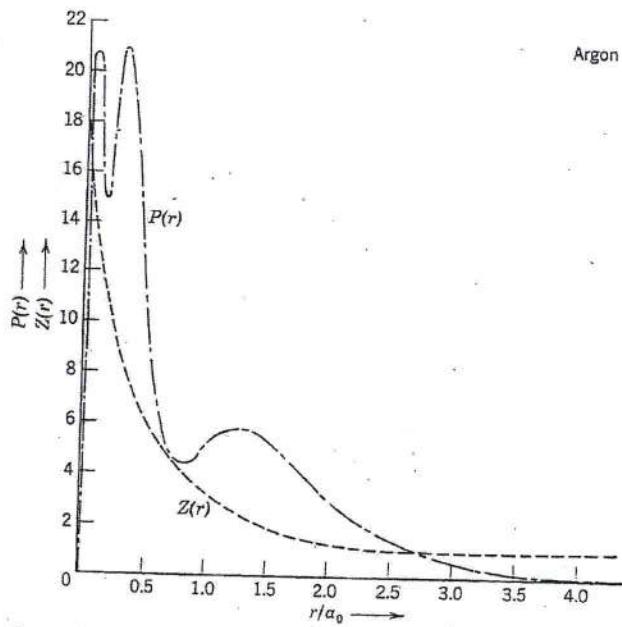


Figure 9-11 The total radial probability density $P(r)$ of the argon atom, and the quantity $Z(r)$ that specifies its net potential.

Table 9-2 The Energy Ordering of the Outer Filled Subshells

Quantum Numbers <i>n, l</i>	Designation of Subshell	Capacity of Subshell $2(2l + 1)$
—	—	—
6, 2	6d	10
5, 3	5f	14
7, 0	7s	2
6, 1	6p	6
5, 2	5d	10
4, 3	4f	14
6, 0	6s	2
5, 1	5p	6
4, 2	4d	10
5, 0	5s	2
4, 1	4p	6
3, 2	3d	10
4, 0	4s	2
3, 1	3p	6
3, 0	3s	2
2, 1	2p	6
2, 0	2s	2
1, 0	1s	2

↑
Increasing energy
(less negative)

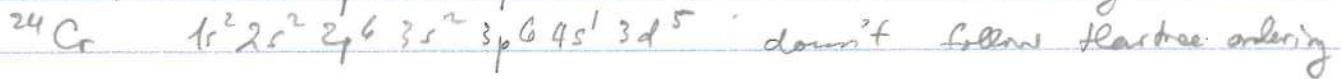
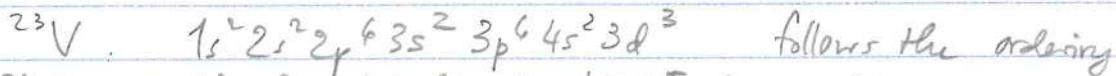
← Lowest energy
(most negative)

1	H	2	He																								
1s		2s																									
3	Li	4	Be																								
2s		3s																									
11	Na	12	Mg																								
3s		4s																									
19	K	20	Ca																								
4s		3d																									
37	Rb	38	Sr																								
5s		4d																									
55	Cs	56	Ba																								
6s		5d																									
87	Fr	88	Ra																								
7s		6d																									
s ¹	s ²	d ¹	d ²	d ³	d ⁴	d ⁵	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰	p ¹	p ²	p ³	p ⁴	p ⁵	p ⁶										
58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu
4f	$5d^0 4f^2$	$5d^0 4f^3$		$5d^0 4f^4$		$5d^0 4f^5$		$5d^0 4f^6$		$5d^0 4f^7$		$5d^1 4f^7$		$5d^0 4f^9$		$5d^0 4f^{10}$		$5d^0 4f^{11}$		$5d^0 4f^{12}$		$5d^0 4f^{13}$		$5d^0 4f^{14}$		$5d^0 4f^{14}$	
Lanthanides																											
90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lw
5f	$6d^2 5f^0$	$6d^1 5f^2$		$6d^1 5f^3$		$6d^1 5f^4$		$6d^1 5f^5$		$6d^1 5f^6$		$6d^1 5f^7$		$6d^1 5f^8$		$6d^0 5f^10$		$6d^0 5f^{11}$		$6d^0 5f^{12}$		$6d^0 5f^{13}$		$6d^0 5f^{14}$		$6d^1 5f^{14}$	
Actinides																											
f ¹	f ²	f ³	f ⁴	f ⁵	f ⁶	f ⁷	f ⁸	f ⁹	f ¹⁰	f ¹¹	f ¹²	f ¹³	f ¹⁴														

Figure 9-13 The periodic table of the elements, showing the electron configuration for each element.

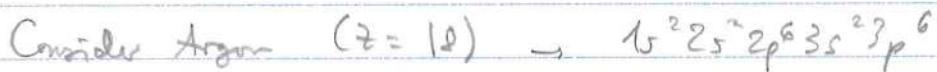


For most p-orbitals, the Aufbau ordering works, but not all cases...
There are exceptions to the ordering...



Gets complicated for the lanthanides...

Shell Structure How do the electrons arrange themselves?
How big are atoms in their ground states?



$$\text{Because of screening} \rightarrow V(r) = \begin{cases} -\frac{ze^2}{4\pi\epsilon_0 r} & r \rightarrow 0 \\ -\frac{e^2}{4\pi\epsilon_0 r} & r \rightarrow \infty \end{cases}$$

Inner electron \rightarrow more tightly bound than H
Outer electron \rightarrow same potential as H

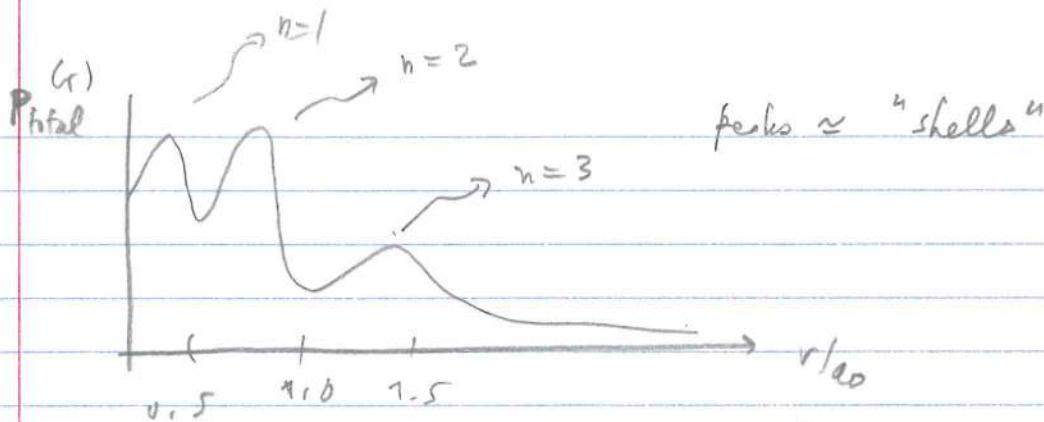
Size of atom = expectation value of the radius of the outermost electron

For H. \rightarrow 1st electron has $R = 1.5 a_0$

for Ar \rightarrow 3p⁶ electron \Rightarrow also has $R \approx 1.5 a_0$

- Most atoms in their ground state have roughly the same size.
- Inner electrons are closer than in Hydrogen - tighter bond

Fig 1-10, 9-11 combines the radial dist for the 18 e⁻ in Ar \rightarrow



→ Can calculate binding energies for e^- in these shells...

$$\text{Ar} \quad E_{n=1} \approx -3500 \text{ eV} \rightarrow \text{very tightly bound}$$

$$E_{n=2} \approx -220 \text{ eV}$$

$$E_{n=3} \approx -14 \text{ eV} \rightarrow \text{similar to H}$$

Ionization → minimum Energy to remove an electron

→ involves outer or valence e^-

⇒ get λ in the near visible ⇒ optical

For different types of valence electrons → need different energies...
alkali atoms → 1-state valence electrons...

(lowest ionization energies)

noble gases → have filled p shells

→ highest ionization energies...

If an inner electron is knocked out ⇒ get keV & (X-ray)
when another e^- fills the slot

e.g. smash e^- into copper knocking out $n=1$

→ K α line when $n=2$ fills $n=1$

K β line when $n=3$ fills $n=1$

Optical excitation

Hartree procedure \rightarrow gives ordering of nl levels
 \rightarrow use it to form ground states.

What about excited states?

\hookrightarrow Consider optical excitation of outer electrons (not X-ray)

Alkali atoms \rightarrow have only 1 optically excited active electron
 \rightarrow can label states using hydrogenic quantum #

$n l s \text{ inj.}$

But atoms with 2 or more valence e^- are best described in terms of their total spin (S') (as in He)

\rightarrow will also label by their total orbital angular momenta

$$|\vec{l}'| = \text{total angular momentum.}$$

\hookrightarrow then couple those to form total angular momentum

$$\text{Ket} \quad \boxed{\vec{j}' = \vec{l}' + \vec{s}'}$$

This labeling corresponds to using 3 levels of approximation

(1) Use Hartree for individual nl electrons \rightarrow l levels are no longer degenerate

(2) residual Coulomb + exchange effect $\vec{l}' = \vec{l}_1 + \vec{l}_2 + \dots$ (Coulomb)
 $\vec{s}' = \vec{s}_1 + \vec{s}_2 + \dots$ (spin)

$\Rightarrow l' \neq s'$ levels split

(3) Spin-orbit interaction ($\vec{l}' \cdot \vec{s}'$)

$$\vec{j}' = \vec{l}' + \vec{s}' \Rightarrow \text{split levels with different } \vec{j}'$$

\rightarrow with $l', s', j' \rightarrow$ can label excited states of multi-electron atoms

May 8, 2018

Excited States in Multi-electron Atoms

Want to use $\vec{J}' = \vec{s}_1 + \vec{s}_2 + \dots$ } for optically active e^-
 $\vec{l}' = \vec{l}_1 + \vec{l}_2 + \dots$

Then from $\vec{J}' = \vec{l}' + \vec{s}'$

Gives quantum numbers s', l', j' ...

\Rightarrow need general rule:

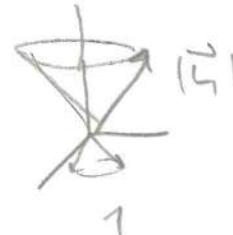
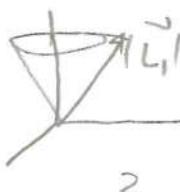
$\boxed{4 \cdot 3}$ $l_1=2, l_2=1$

Rule: fix the bigger one, add/subtract the smaller one ($l_1=2$), then
 $(l_1=2)$

fill in the in-between integers... $\left\{ \begin{array}{l} l_1 + l_2 = 2+1=3 \\ l_1 - l_2 = 2-1=1 \end{array} \right\}$

also include 2 $\rightarrow \boxed{1, 2, 3 = l'}$

This rule follows from having 3 possible orientations for $l_2=1 \Rightarrow m_l = -1, 0, 1$ with \vec{l}_2 fixed



Ex $l_1=2, l_2=1$ add $\rightarrow l'=3$ $\left\{ \begin{array}{l} l'=0, 1, 2, 3, 4 \\ \text{subtract} \rightarrow l'=0 \end{array} \right.$

Ex $s_1=\frac{1}{2}, s_2=\frac{1}{2}$ add $\rightarrow s'=1$ \leftarrow no in-between
subtract $\rightarrow s'=0$

Ex $s_1=\frac{1}{2}, s_2=\frac{1}{2}, s_3=\frac{1}{2}$ \rightarrow first add i.e. $\frac{1}{2} \pm \frac{1}{2} = 0, 1$, then
 combine with the remaining $\frac{1}{2}$

$$\left. \begin{array}{l} 0+\frac{1}{2} = \frac{1}{2} \\ 1 \pm \frac{1}{2} = \frac{1}{2}, \frac{3}{2} \end{array} \right\} \rightarrow s' = \frac{1}{2}, \frac{3}{2}$$

Using $s', l', j' \rightarrow$ called LS coupling

(160)

→ first add up to get \vec{s}', \vec{l}' , then set $\vec{J}' = \vec{s}' + \vec{l}'$

→ works best for most of the periodic table

But really heavy nuclei can use → JJ coupling

$$\text{Form } \vec{J}_1 = \vec{l}_1 + \vec{s}_1$$

$$\vec{J}_2 = \vec{l}_2 + \vec{s}_2$$

then form $\vec{J}' = \vec{J}_1 + \vec{J}_2 + \dots$

But we'll use LS coupling

Use notation for multi-electron states

$$\overset{\approx s'+1}{\vec{J}} \overset{\approx l'j'}{\downarrow}$$

use capital letters

most cases ($l' \geq s'$)

gives # of j' values

Q.8 ${}^3P_2 \rightarrow l' = 1$
 $j' = 2$
 $2s' + 1 = 3 \text{ or } s' = 1$

$${}^1P_1 \rightarrow l' = 1$$

 $j' = 1$
 $s' = 0$

Excitation - EXCITED STATES OF MULTI-E ATOMS

May 9, 2018

- ↳ LS coupling. Form $\vec{S}' = \vec{s}_1 + \vec{s}_2 + \dots$
 and $\vec{L} = \vec{l}_1 + \vec{l}_2 + \dots$ # of states
- Couline, & set $\vec{j}' = \vec{s}' + \vec{l}'$
- ↳ Get 3 quantum numbers s', l', j'
 → Label multi-electron configuration $^{2s'+1}l_j'$ capital letters

Rule for adding angular momentum

- Fix the bigger one, then add, subtract smaller one, then fill in the in-betweens jumping from the lower to the upper...

$$\text{e.g. } l' = 2, s' = \frac{3}{2}$$

To set j'

$$\text{add } j' = 2 + \frac{3}{2} = \frac{7}{2}$$

$$\text{subtract } j' = 2 - \frac{3}{2} = \frac{1}{2}$$

$$\hookrightarrow \boxed{j' = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}} \quad 2s'+1 \text{ states}$$

Note that with $\vec{j}' = \vec{L} + \vec{S}'$, assume $l' \geq s'$ (most of the time)

$$\begin{cases} \text{max} = l' + s' = j' \\ \text{min} = l' - s' = j' \end{cases} \quad \begin{cases} \text{so } j' = l' - s', l' - s' + 1, \dots, l' + s' \\ \rightarrow \text{There are } \boxed{2s'+1} \text{ values} \end{cases}$$

Hence the superscript

$$\begin{aligned} \text{But if } l' < s', \text{ then } j_{\text{max}}' = s' + l' \\ \text{but } j_{\text{min}}' = s' - l' \end{aligned} \quad \left. \right\} = \boxed{2l'+1} \text{ values}$$

But we still use $\boxed{2s'+1}$ in the labeling

$$\text{Ex} \quad l'=2 \quad \left. \begin{array}{l} \\ s'=1 \end{array} \right\} \quad j' = \cancel{1, 2, 3}$$

3 "configs"

Label

$${}^3D_1, {}^3D_2, {}^3D_3 \quad \text{or} \quad {}^3D_{1,2,3}$$

Ex Consider $2e^-$ in a $3f4p$ config & find all s', l', j' values

$$l_1 = 3 \quad l_2 = 1 \Rightarrow l' = 2, 3, 4$$

$$s_1 = 1/2 \quad s_2 = 1/2 \Rightarrow s' = 0, 1$$

Now do j'

$s' = 0$	if $l' = 2 \Rightarrow j' = 2 \rightarrow {}^1D_2$
	if $l' = 3 \Rightarrow j' = 3 \rightarrow {}^1F_3$
	if $l' = 4 \Rightarrow j' = 4 \rightarrow {}^1G_4$
$s' = 1$	$l' = 3 \Rightarrow j' = 2, 3, 4 \rightarrow {}^3F_{2,3,4}$
	$l' = 2 \Rightarrow j' = 1, 2, 3 \rightarrow {}^3D_{1,2,3}$
	$l' = 4 \Rightarrow j' = 3, 4, 5 \rightarrow {}^3G_{3,4,5}$

Some additional important facts...

→ Filled subshells all have $l' \pm s' = j' = 0$

↳ So only partially filled electrons contribute to s', l', j'

The same
happens with
 d^0, p^6, f^{14}, \dots

→ this is a result of the Exclusion principle

e.g.

Filled ns^2 level $l_1, l_2 = 0 \quad \left. \begin{array}{l} \\ \end{array} \right\} l' = 0$

$$m_{l_1}, m_{l_2} = 0$$

$$s_1 = s_2 = \frac{1}{2} \Rightarrow s' = 1, 0$$

But for $s' = 1, 0 \rightarrow m_{s_1} = 1$

$$\text{requires } m_{s_1} = \frac{1}{2} \text{ & } m_{s_2} = -\frac{1}{2}$$

This would require all $m_s \neq$ the same

→ NOT POSSIBLE due to
Exclusion principle

⇒ Must have $s' = 0$

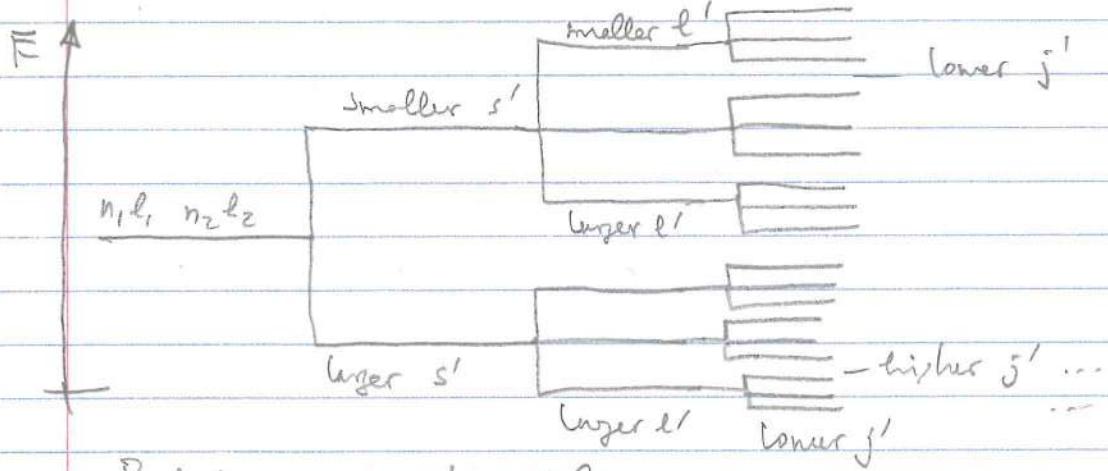
And if $s' = 0, l' = 0 \Rightarrow j' = 0$

→ There's ordering for which of s' , l' , j' is most important in splitting + which goes up or down in energy

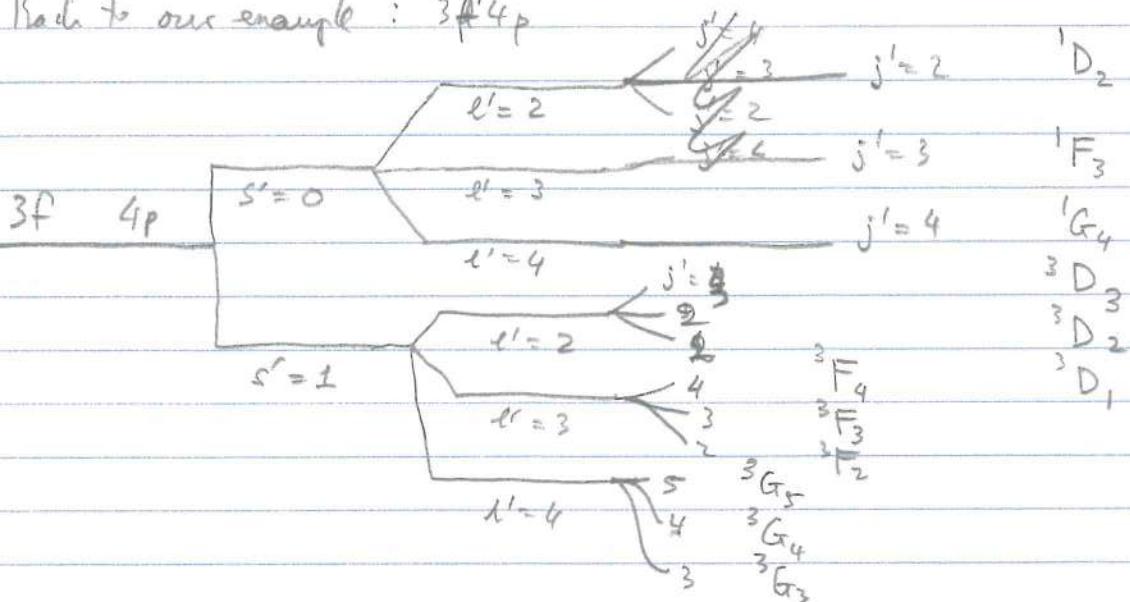
- 1st → split s' values (exchange effects) (dominant)
- 2nd → split l' values (Coulomb effects) (partial)
- 3rd → split j' values (Spin-orbit correction)

Ordering with respect to energy:

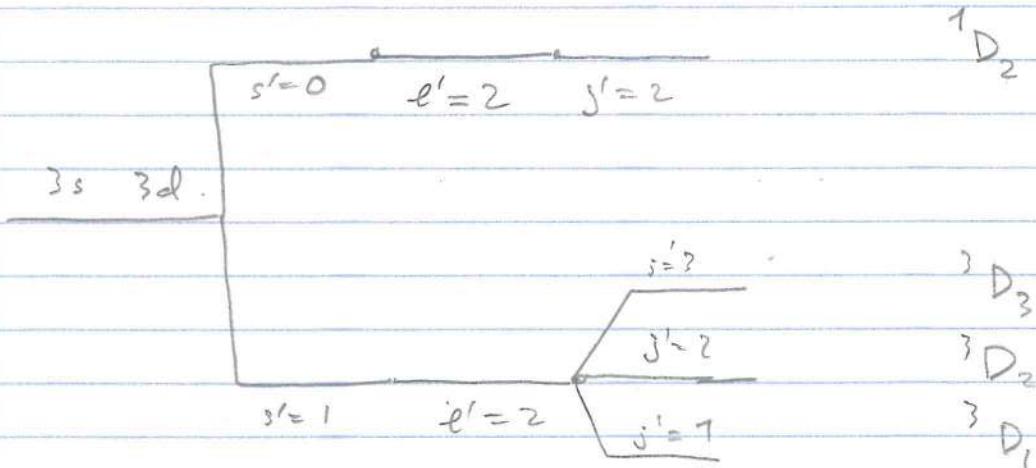
- states with larger s' → lower ... (exchange)
- states with larger l' → lower ... (Coulomb)
- states with lower j' → ~~higher~~ lower ... (spin-orbit)



Back to our example: $3f\ 4p$



Ex Find splitting & labels for $3s\ 3d$ level



Ex which of the following descents show that are valid/invalid

(a) $^2F_{1/2}$ $\rightarrow s' = \frac{1}{2}, l' = 3, j' = \frac{1}{2} \quad \left. \begin{matrix} \text{NOT} \\ \text{valid} \end{matrix} \right\}$

$\text{But } j' = \frac{2}{2}, \frac{1}{2}$

(b) 3S_2 $\rightarrow s' = 1, l' = 0 \rightarrow j' = 1 \quad \left. \begin{matrix} \text{NOT} \\ \text{valid} \end{matrix} \right\}$

But $j' = 2$

PH 242 – Review Guide #3

Be sure you know the following (including the reasoning/derivations for each one):

- addition of angular momentum
 - $\vec{J} = \vec{L} + \vec{S}$
 - “good” vs. “bad” quantum numbers
 - rules for finding j, m_j
- fine structure of H spectrum
 - splitting of energy levels
 - fine structure constant α
- selection rules
 - dipole transitions
 - $\Delta l = \pm 1, \Delta j = \pm 1, 0$
 - photons carry angular momentum (with $j = 1$)
- Identical particles
 - indistinguishable in QM, $|\psi(i, j)|^2 = |\psi(j, i)|^2$
 - Bose-Einstein statistics: $\psi(i, j) = +\psi(j, i)$ (symmetric)
 - Fermi-Dirac statistics: $\psi(i, j) = -\psi(j, i)$ (anti-symmetric)
- Fermions and bosons
 - fermions have 1/2-integral spin, e.g., electrons, protons, . . .
 - fermions obey Pauli exclusion principle (no two in same state)
 - bosons have integral spin, e.g., photons, pions, . . .
 - bosons do not obey Pauli principle (can all be in same state)
- Spin-statistics connection
 - identical fermions have anti-symmetric wave functions
 - identical bosons have symmetric wave functions

- Symmetrization/anti-symmetrization
 - combinations of one-particle states ψ_α (ignoring interactions)
 - $\psi_A = \frac{1}{\sqrt{2}}(\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2))$ (2 identical fermions)
 - Slater determinant for N identical fermions (has $N!$ terms)
 - $\psi_S = \frac{1}{\sqrt{2}}(\psi_\alpha(1)\psi_\beta(2) + \psi_\beta(1)\psi_\alpha(2))$ (2 identical bosons)
 - $N!$ permutations (all positive) for N identical bosons
- Helium (atom with two identical fermions)
 - spins add: $\vec{S}' = \vec{S}_1 + \vec{S}_2$, $s' = \frac{1}{2} + \frac{1}{2} = 1, 0$
 - $\psi_A = \psi_{\text{spatial}} \chi_{s', m_s'}$ (correlates spin & spatial behavior)
 - triplet ($s' = 1, m_s' = 1, 0, -1$) and singlet ($s' = 0, m_s' = 0$) states
 - triplet states have anti-symmetric ψ_{spatial} and symmetric $\chi_{s', m_s'}$
 - singlet state has symmetric ψ_{spatial} and anti-symmetric $\chi_{s', m_s'}$
 - “exchange force” keeps electrons in triplet states further apart
- Hartree method (effective potential $V(r)$ for multi-electron atoms)
 - results give ordering of states in ground-state atoms
 - e.g., Ar ($Z = 18$) has $1s^2 2s^2 2p^6 3s^2 3p^6$
 - note: some atoms do not follow Hartree ordering
- Periodic table
 - organizes elements according to electron configurations
 - e.g., alkali atoms have valence s -shell electrons
 - e.g., noble gases have filled p -shells (He has filled $1s$ level)
- Optical excitations of multi-electron atoms
 - low-lying excitations of outermost electrons
 - approximate using:
 1. Hartree (in terms of n and l for each valence electron)
 2. residual Coulomb effects (in terms of l' and s')
 3. spin-orbit interaction (in terms of j')