PH242
Modern Physics II

Feb 7, 2018

<u>Overview</u> : all about Quantum Mechanics (QM), using the Schrödinger equation (SE)

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

↳ 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

$$\Psi(x,t) = \text{wave function}$$

→ if particle has definite values of E & p

↳ then the wave has relation : $\boxed{\lambda = \frac{h}{p}}$

freq : $\nu = \frac{E}{h}$

→ particle diffraction & interference

$\Psi(x,t)$ → exhibit interference

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

interference → e.g. $\vec{E} = c_1\vec{E_1} + c_2\vec{E_2}$ (adds)

brightness → <u>but intensity</u> : $I \sim (\vec{E})^2$ ← can be (+) or (−) { constructive intf / destructive inf

↳ $|\vec{E}|^2 = |\vec{E_1}|^2 + |\vec{E_2}|^2 + 2\vec{E_1}\vec{E_2}$

↳ $\boxed{\text{Same for } \Psi(x,t)}$

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

→ "square" → $|\Psi|^2$ → exhibit interference → "<u>modulus squar</u> of a complex-valued WF

Simplest example of a wave in 1D

$$\Psi(x,t) = \underset{\text{amplitude}}{A} \sin(\underset{\frac{2\pi}{\lambda} = \text{wave number}}{k}x - \underset{2\pi\nu \,:\, \text{angular freq}}{\omega} t)$$ (traveling wave to the right)

$\boxed{\lambda = \frac{h}{p}, \ p = \hbar k}$

$\boxed{E = \hbar\omega = h\nu}$

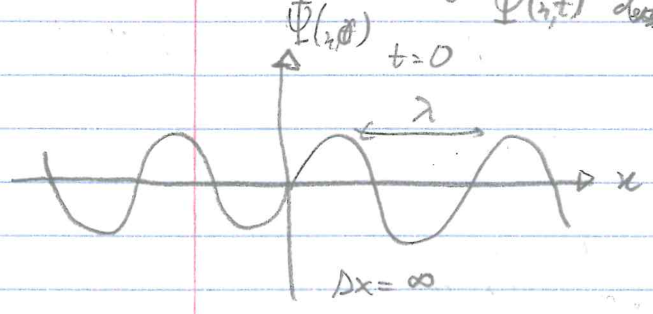
This $\Psi(x,t)$ is a pure wave → exact k, ω → λ, ν fixed = exact

⇒ p, E are both exact

$(F = \dot{p})$

since $p = \text{const}$ ⇒ no force

↳ $\Psi(x,t)$ describes a free particle



can still obey $\Delta x \Delta p_x \geq \frac{\hbar}{2}$ (λ const → $\Delta p = 0$)

wave speed: $\boxed{V = \frac{\omega}{k} = \lambda\nu}$

k ↓

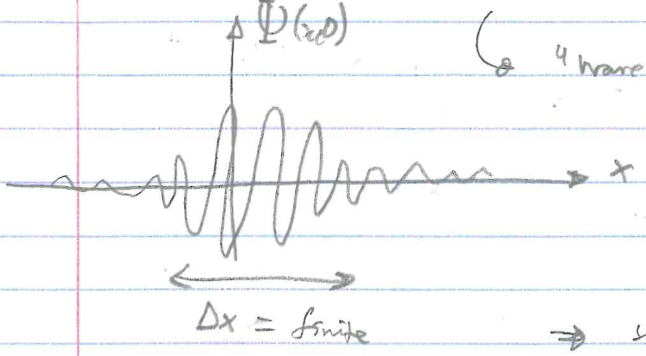
To get localized wave (finite Δx) → superimpose many $\Psi(x,t)$ of different λ

↳ "wave packet"

↳ need a range of λ

↳ a range of p values

↳ Δp = finite



⇒ still obey $\Delta x \Delta p_x \geq \frac{\hbar}{2}$

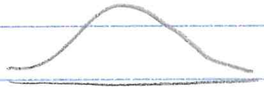
↳ group velocity $\boxed{V_g = \frac{d\omega}{dk}}$

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

Originally, Schrödinger thought it described a matter wave
→ floppy particle...

→ but this wrong → electrons are not floppy

Correct Interpretation → by Max Born



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

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

↳ probability density for finding the particle at x at time t

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

Note: QM is a probabilistic theory

Analogy with light | $\vec{E}$ → electric field ~ wave amplitude

$|\vec{E}|^2$ → intensity

Also, light has a wave equation!

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

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

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

↳ Schrödinger has a solution!

↳ lol... it's a guess / found / hypothesis...

\# heading notes 4 assumptions ~~for~~ concerning the properties of a wave function:

- consistent w/ de Broglie - Einstein postulate: $\lambda = \frac{h}{p}$; $\nu = \frac{E}{h}$
- 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
  ↳ sinusoidal WF

$E = h\nu = \hbar\omega$

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

$\parallel$

$\hbar k$

Quick "guess" process

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

$$(1) \hookrightarrow h\nu = \frac{h^2}{2m\lambda^2} + V \quad \left(+ \left\{ \begin{matrix} \omega = 2\pi\nu \\ k = \frac{2\pi}{\lambda} \end{matrix} \right\} \right)$$

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

* any derivative of Ψ is 1st order in Ψ

(3) ↳ (?)

(4) ↳ must contain 2nd derv of space & 1st derv of time

↳ (ω & k^2)

but also $\Psi(x,t)$, $V(x,t)$

$$\hookrightarrow \alpha \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\,\Psi(x,t) = \beta \frac{\partial \Psi(x,t)}{\partial t}$$

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

$$\Psi(x,t) = \gamma \sin(kx - \omega t) + \cos(kx - \omega t)$$

$$\hookrightarrow \frac{\partial \Psi(x,t)}{\partial t} = \omega \sin(kx - \omega t) - \omega\gamma \cos(kx - \omega t) \quad \boxed{\cdot}$$

$$\frac{\partial \Psi(x,t)}{\partial x} = k\gamma \cos(kx - \omega t) - k \sin(kx - \omega t)$$

$$\hookrightarrow \frac{\partial^2 \Psi(x,t)}{\partial x^2} = -k^2\gamma \sin(kx - \omega t) - k^2 \cos(kx - \omega t) \quad \boxed{\cdot}$$

Reading note, cont:

$$-\alpha\left[k^2\gamma\,\underline{\sin(kx-wt)}+k^2\cancel{\gamma}\cos(kx-wt)\right]+\overset{V_0}{\overbrace{V(x,t)}}\cdot\left(\underline{\gamma\sin(kx-wt)}+\cos(kx-wt)\right)$$

$$=\beta\cdot\left(\underline{\omega\sin(kx-wt)}-\omega\gamma\cos(kx-wt)\right)$$

$$\hookrightarrow\left(-\alpha k^2\gamma+V_0\gamma-\beta w\right)\sin(kx-wt)+\left(-\alpha k^2+V_0+\beta w\gamma\right)\cos(kx-wt)=0$$

must $= 0$
$\forall \alpha,\beta$

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

$$\rightarrow\gamma^2=-1\Rightarrow\boxed{\gamma=\pm i}$$

$$\underset{(kE)}{-\alpha k^2}+\underset{(V)}{V_0}=\underset{(E)}{\mp i\beta w}$$

$$\hookrightarrow \underline{\text{Convention}}:\begin{cases}-\alpha k^2+V_0=\mp i\beta\omega\\\dfrac{\hbar^2k^2}{2m}+V_0=\hbar w\end{cases}\rightarrow\begin{cases}\alpha=\dfrac{-\hbar^2}{2m}\\\beta=\mp\dfrac{\hbar}{i}=\mp\dfrac{\hbar i}{-1}=\pm\hbar i\\\qquad=\hbar i\end{cases}$$

$$\rightarrow\boxed{\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\frac{\Psi(x,t)}{1}=i\hbar\frac{\partial\Psi(x,t)}{\partial t}}$$

only true for non-relativistic

What about relativistic? Dirac: $E=V+\underbrace{\sqrt{\overset{kE}{c^2p^2}+\overset{\text{rest}}{(m_0c^2)^2}}}_{\text{energy due to velocity}}$

Born's interpretation: $\boxed{P(x,t)=\Psi^{\star}(x,t)\,\Psi(x,t)}$

$\Psi \rightarrow \Psi$

Expectation value $\bar{f}=\displaystyle\int_{-\infty}^{\infty}\Psi^{\star}(x,t)\cdot f\cdot\Psi(x,t)\,dx$

⑥

γ

Reading notes, cont

Differential operator : How to express p & E in terms of x, t?

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

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

$$= i^2 k\sin(kx - wt) + ik\cos(kx - wt)$$

$$= ik\,\Psi(x,t)$$

also, $p = \hbar k$
$p = \frac{h}{\lambda} = \frac{\hbar 2\pi}{\lambda}$

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

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

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

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

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

$$= -iw\left(\cos(kx - wt) + i\sin(kx - wt)\right) = -iw\,\Psi(x,t)$$

$E = \hbar w = \cancel{\frac{h}{\lambda}}$
$= h\nu$
$= \hbar(\nu 2\pi)$
$= \hbar w$

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

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

$\psi\ \psi\ \Psi\ \Psi$

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

Eg $i\hbar\frac{\partial}{\partial t}\Psi \to E.\Psi$

These operators are useful for higher dimensions ...

// end of reading note

$\boxed{\text{Schrödinger Equation}}$ → 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

$\boxed{\text{4 Conditions}}$ ⟶ looking for a differential eq. for $\Psi(x,t)$

(1) ↳ Must be consistent with $\boxed{\text{de Broglie - Einstein postulate:}}$

$$\begin{cases} \lambda = \frac{h}{p} \rightarrow p = \frac{h}{\lambda} \\ E = h\nu \end{cases}$$

potential

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

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

↳ Dirac...

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

eg if Ψ_1 & Ψ_2 are solutions, then $\Psi = c_1\Psi_1 + c_2\Psi_2$ is also a solution

(4) → The special case where $V(x,t) = V_0$ should describe a free particle.

$(V_0 = \text{const} \rightarrow F = 0)$ ⤻ $\boxed{F = -\dot{V}(x,t)}$

↳ const $p, E \Rightarrow \lambda, \nu$ const ⇒ pure wave

⇒ $\boxed{\text{SINUSOIDAL}}$

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

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

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

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

$$E = h\nu = \hbar 2\pi\nu = \hbar\omega$$

↑ schrödinger eq must be consistent w/ this

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

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

→ But it can have derivatives... → How many? what type?
↳ Work backwards from pure wave.

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

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

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

$$\boxed{\frac{\hbar^2 k^2}{2m} + V = \hbar\omega} \longrightarrow \text{suggests using}$$

$\frac{\partial^2\Psi}{\partial x^2} \to k^2$

$\frac{\partial\Psi}{\partial t} \to \omega$

$\Psi \to V$

So we guess form:

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

To find α & β → go back to free particle: → $\sin(kx-\omega t)$ or $\cos(kx-\omega t)$

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

↳ ~~$\alpha(-k)^2 + V = \beta(-\omega)$~~ → $\boxed{-\alpha k^2\sin + V\sin = \beta(-\omega)\cos}$

↳ can't find α & β

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

↳ same problem

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

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

$$\rightarrow -\alpha k^2\left[\cos(kx-\omega t)+\gamma\sin(kx-\omega t)\right]+V_0\left[\cos(kx-\omega t)+\gamma\sin(kx-\omega t)\right]$$

$$= -\beta\omega\left[-\sin(kx-\omega t)+\gamma\cos(kx-\omega t)\right]$$

$$= -\beta\gamma\omega\left[\cos(kx-\omega t)-\frac{1}{\gamma}\sin(kx-\omega t)\right]$$

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 $\Psi = -i$

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

Also,

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

However, we can $\boxed{\text{postulate}}$ the eqn holds even if $\neq V(x,t)$

if $F = -\frac{\partial V(x,t)}{\partial x} \neq 0 \rightarrow$ has forces

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

→ 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 $\Psi = c_1\Psi_1 + c_2\Psi_2$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi_1}{\partial x^2} + V\Psi_1\right]c_1 + \left[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi_2}{\partial x^2} + V\Psi_2\right]c_2$$

$$= c_1\, i\hbar\frac{\partial\Psi_1}{\partial t} + c_2\, i\hbar\frac{\partial\Psi_2}{\partial t}$$

$$= i\hbar\left[c_1\frac{\partial\Psi_1}{\partial t} + c_2\frac{\partial\Psi_2}{\partial t}\right] = i\hbar\frac{\partial\Psi}{\partial t} \quad (q.e.d)$$

//

Feb 12, 2018 Schrödinger equation

↳ Note: free-particle solution is $\cos(kx-wt) + i\sin(kx-wt)$

SE → complex-valued differential eq

Ψ → also complex-valued

Is this a problem? NOT really, because

Interpretation: $$\boxed{|\Psi(x,t)|^2 = \Psi^*(x,t)\,\Psi(x,t) = \text{probability distribution}}$$

modulus square

↳ always real, non-negative

Review of complex numbers ... $$\boxed{\begin{aligned} e^{i\theta} &= \cos\theta + i\sin\theta \\ e^{-i\theta} &= \cos\theta - i\sin\theta \end{aligned}}$$

Invert: $$\boxed{\begin{aligned} \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right) &= \sin\theta \\ \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right) &= \cos\theta \end{aligned}}$$

gives complex traveling wave to the right

Free-particle solution has form $$\boxed{\Psi(x,t) = \text{cis}(kx-wt) = e^{i(kx-wt)}}$$

$\boxed{\text{Properties of } \Psi(x,t)}$ → Solution to the SE for a given $V(x,t)$ gives $\Psi(x,t)$

$\Psi(x,t) \longrightarrow$ probability amplitude

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

↳ $|\Psi(x,t)|^2 dx \longrightarrow$ probability for finding particle in $x \rightarrow x + dx$

↳ $\boxed{\text{Must be normalized}}$! sum of all probability $= 1$

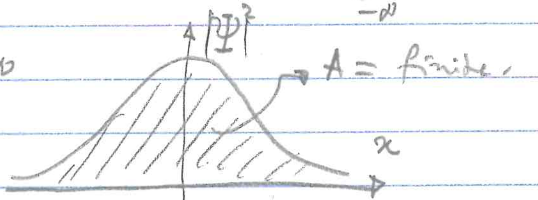
$$\boxed{\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1}$$ ⟵ must set the const inside $\Psi(x,t)$ so that this holds.

↳ Called normalization of wave function.

Good wave functions must be normalizable.

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

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



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

$\boxed{\text{Expectation values}}$ → How can we find averages/mean value of physical quantities? $\bar{x}, \bar{p}, \bar{E}, \ldots$

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

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

$$\bar{x} = \int_{-\infty}^{\infty} x P(x,t)\,dx \longrightarrow$$ We write $$\boxed{\bar{x} = \int_{-\infty}^{\infty} \Psi^*(x,t)\, x\, \Psi(x,t)\,dx}$$

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

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

This assumes $\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$. Otherwise, $\boxed{\bar{x} = \dfrac{\int_{-\infty}^{\infty} \Psi^* x \Psi \, dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}}$

- Doing the integral over x for a given Ψ at some time t gives a number $\bar{x}(t)$ (average value)

- We can also find averages of functions of x

$$\boxed{\overline{x^2} = \int_{-\infty}^{\infty} \Psi^* x^2 \Psi \, dx} \xrightarrow{\text{Generalize}} \boxed{\overline{f(x)} = \int_{-\infty}^{\infty} \Psi^* f(x) \Psi \, dx}$$

Momentum What about momentum p?

Well, $\boxed{\bar{p} = \int_{-\infty}^{\infty} \Psi^* p \, \Psi \, dx}$

Note: can't let p be a usual $f(x)$ because if $p = f(x)$, then if x exact ↳ p exact

⇒ Contradicts Uncertainty principle!

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

So how can we represent p in terms of x?

↳ for guidance, let's look at free-particle again! $\boxed{\Psi(x,t) = e^{i(kx - \omega t)}}$

↳ free particle has definite p → Observe: $\dfrac{\partial \Psi(x,t)}{\partial x} = ik\Psi$

de Broglie → Since $p = \dfrac{h}{\lambda} = \hbar k \Rightarrow \boxed{p\Psi = -i\hbar \dfrac{\partial \Psi}{\partial x}}$

↳ p is a differential ~~op~~ operator

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

↳ Define $\boxed{\hat{p} \equiv -i\hbar \dfrac{\partial}{\partial x}}$ → gives operator for momentum

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

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

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

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

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

▨ Schrödinger equation has a sign ambiguity → conventional choice $\gamma = +i$
→ this requires using $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ between Ψ^* & Ψ
(left) (right)

↳ use $\boxed{\bar{p} = \int_{-\infty}^{\infty} \Psi^* \hat{p}\, \Psi\, dx}$

Note: x is also an operator → (trivial) $\hat{x} = x$ ← multiply by x

Can also write $\boxed{\bar{x} = \int_{-\infty}^{\infty} \Psi^* \hat{x}\, \Psi\, dx}$

Recall

Feb 14, 2018 → ★ 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 $\bar{F}(x)$ of a physical quantity, put the operator between Ψ^* & Ψ and integrate.

$$\left.\begin{aligned}\bar{x} &= \int_{-\infty}^{\infty} \Psi^* x \Psi \, dx \\ \bar{p} &= \int_{-\infty}^{\infty} \Psi^* (-i\hbar) \frac{\partial}{\partial x} \Psi \, dx\end{aligned}\right\} \text{numbers!}$$

→ 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 $\bar{p}^* = \bar{p}$

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

$\boxed{\text{Integration by parts}} \rightsquigarrow \boxed{\int_a^b u\,dv = uv\Big|_a^b - \int_a^b v\,du}$

$$\left\{\begin{aligned} &\text{let } \Psi = u && \Rightarrow du = \frac{\partial \Psi}{\partial x} dx \\ &\frac{\partial \Psi^*}{\partial x} dx = dV && \Rightarrow v = \Psi^* \end{aligned}\right\}$$

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

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

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

$\boxed{\text{So } \bar{p} \text{ is real}}$

#

So we form other operators — Energy!

Energy operators — Called the Hamiltonian

↳ e.g $$\boxed{H = \frac{p^2}{2m} + V(x)} \longleftarrow \text{classical}$$

To go to QM → we promote these to operators.

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

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

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

Also, SE :

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

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

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

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

$$\boxed{\text{Energy operator} \equiv \text{Hamiltonian}}$$

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

Could compute

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

Again,

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

↳ We could also compute $\overline{x^2}$ → need both $\overline{x^2}$ & $\overline{p^2}$ to find uncertain-ties

Δx , Δp

$\boxed{\text{Uncertainties}}$ We denote Δx & Δp as standard deviation.

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

↳ $\boxed{(\Delta p)^2 = \overline{(p-\bar{p})^2}} = \overline{p^2 - 2\bar{p}p + \bar{p}^2}$

$\bar{p}$ is a number ⇝ so $\bar{\bar{p}} = \bar{p}$.

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

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

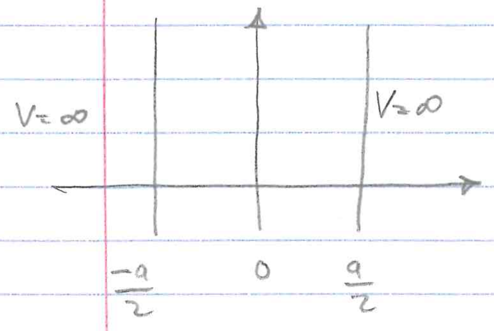
Likewise $\boxed{\Delta x = \sqrt{\overline{x^2} - \bar{x}^2}}$

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, free inside

$V \to \infty$ 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:

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

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

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

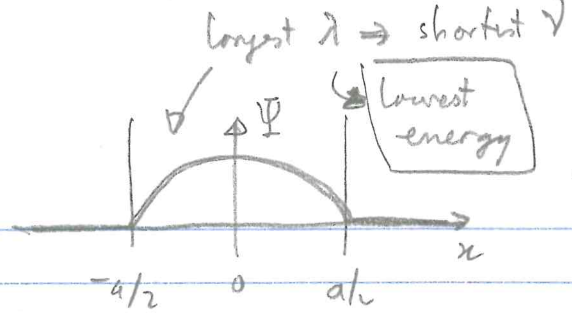
$i\hbar\frac{\partial \Psi}{\partial t} = (i\hbar) A\cos\left(\frac{\pi x}{a}\right)\left(\frac{-iE}{\hbar}\right)$.

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

↳ lowest energy solution

$$\left.\begin{aligned}\cos(2x) &= c^2 - s^2\\ &= c^2-(1-c^2)\\ &= 2c^2-1\end{aligned}\right\} \rightarrow c^2 = \frac{\cos(2)+1}{2}$$

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



→ Compute average values! But before that, we need to normalize s/n.
↳ Find A such that

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = 1 \Rightarrow \int_{-\infty}^{\infty} \left[A\cos\left(\frac{\pi x}{a}\right)\right]^2 dx = 1$$

$$\hookrightarrow A^2 \int_{-a/2}^{a/2} \cos^2\left(\frac{\pi x}{a}\right) dx = 1 \quad \left(\text{if } x > a/2 \text{ or } x < -\frac{a}{2},\ \Psi^2 = 0\right)$$

$$\longrightarrow \frac{A^2}{2}\int_{-a/2}^{a/2} \cos\left(\frac{2\pi x}{a}\right) + 1\, dx = \frac{A^2}{2}\left[\frac{a}{2\pi}\sin\left(\frac{\pi x}{a}\cdot 2\right) + x\right]\Bigg|_{-a/2}^{a/2}$$

$$\Rightarrow \frac{a}{2\pi}\frac{A^2}{2}\left(\pi\right) = \frac{a}{4}A^2 = 1 \Rightarrow \boxed{A = \sqrt{\frac{2}{a}}}$$

//

Feb 16, 2018

<u>Particle in a Box, cont.</u>

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

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

Now, find $\bar{x}, \bar{p}, \overline{x^2}, \overline{p^2}$ to find $\Delta x \Delta p$

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

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

$$= (-i\hbar)\frac{2}{a}\int_{-a/2}^{a/2}\left(-\frac{\pi}{a}\right)\underbrace{\cos\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)}_{\frac{1}{2}\sin\left(\frac{2\pi x}{a}\right)} dx = \boxed{0}$$

↑
odd function

even function

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

$$\overline{x^2} = \int_{-a/2}^{a/2} \Psi^* x^2 \Psi \, dx = \int_{-a/2}^{a/2} \frac{2}{a} x^2 \cos^2\left(\frac{\pi x}{a}\right) dx \quad . \text{ let } u = \frac{\pi x}{a} \Rightarrow du = \frac{\pi}{a} dx$$

$\{du \quad x = \frac{a}{\pi} u \Rightarrow x^2 = \left(\frac{a}{\pi}\right)^2 u^2$

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

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

$$\overline{p^2} = \int_{-a/2}^{a/2} \Psi^* \cdot (-i\hbar)^2 \frac{\partial^2}{\partial x^2} \Psi \, dx = \int_{-a/2}^{a/2} -(+\hbar)^2 \, \Psi^* \frac{\partial^2}{\partial x^2} \Psi \, dx$$

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

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

$$\overline{p^2} = +(\hbar)^2 \left(\frac{+\pi}{a}\right)^2 \underbrace{\int_{-a/2}^{a/2} \Psi^* \cdot \Psi \, dx}_{1} = \boxed{\frac{\hbar^2 \pi^2}{a^2} = \overline{p^2}}$$

<u>Recall</u>

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

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

NOW, TIME TO SOLVE THE SCHRÖDINGER EQUATION

The Time-Independent Schrödinger Eqn

If $V(x,t) = V(x)$ only, can simplify the SE

⇒ use "the separation of variables"

changes a PDE into an ODE

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

(19)

We can start ~~fro~~ $\frac{-\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \underset{\uparrow\text{ no } t \text{ dependence}}{V(x)}\,\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$

Assume that space & time dependence separates!

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

$$\hookrightarrow \boxed{\frac{-\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi(t)}{dt}}$$

ordinary derivatives

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

separated form

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

The only way this can hold $\forall x,t$, which are independent of each other is if both sides equal the same constant

↳ call it G

$$\hookrightarrow \begin{cases} \frac{1}{\psi(x)}\left[\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = G \\ (i\hbar)\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = G \end{cases} \Rightarrow \begin{cases} \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = G\psi & (x, \\ (i\hbar)\frac{d\phi(t)}{dt} = G\phi(t) & (t) \end{cases}$$

We need to find what G is...

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

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

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

$$\boxed{e^{-iGt/\hbar}\,\cancel{E} = \cos\left(2\pi \frac{G}{\hbar} t\right) - i \sin\left(2\pi \frac{G}{h} t\right)}$$

Dimensionally $\frac{G}{\hbar}$ = frequency = ν $\Rightarrow$ $G = h\nu$ }

But we know $E = h\nu$ in QM }

We know that in QM $\Rightarrow$ $G = E$ = constant (energy of particle)

↳ $\boxed{\phi(t) = e^{-iEt/\hbar}}$

Look at (x) eq: $\boxed{\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi}$ (time independent SE)

The full solution is

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

→ Recall the hamiltonian $\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x)}$

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

↳ See that the time independent SE is

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

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

↳ This is called an Eigenvalue problem

{ number → E = eigenvalue
function → $\psi(x)$ → eigenfunction/eigenvector/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, 2012 Time-independent Schrödinger equation & Eigenvalues, Eigenfunctions

- Assume $\Psi(x,t)=\psi(x)\phi(t)$, then Schrödinger Equation becomes:

↳ and $V(x,t)=V(x)$

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

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)\phi(t)}{\partial x^2}+V(x)\psi(x)\phi(t)=i\hbar\frac{\partial}{\partial t}\psi(x)\phi(t) \quad (\text{PDE})$$

↓

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

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

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

E = G by de Broglie

$\phi=e^{-iGt/\hbar}$
$=\cos()+i\sin()$
↳ $G=h\nu=E$

$$\rightarrow \begin{cases} \frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=G\psi(x)=E\psi(x) \quad " \\ i\hbar\frac{d}{dt}\phi(t)=G\phi(t) \end{cases} \rightarrow \left\{ \hat{E}\phi(t)=G\phi(t) \right.$$

↳ $G=E$

↳ $\phi(t)$ has form $e^{\alpha t}$

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

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

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

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

$\psi=$ eigenfunction

⇒ Solve the time-independent SE is the same as finding all eigenvalues & eigenfunctions of $\hat{H}$

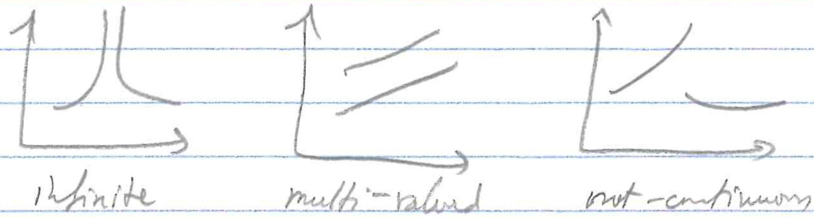
$\boxed{\text{Required properties of eigenfunctions}}$ $\begin{cases} \Psi \text{ finite} \\ \Psi \text{ single-valued} \\ \Psi \text{ continuous} \end{cases}$ $\Psi'(x)$ finite
$\Psi'(x)$ single valued
$\Psi'(x)$ continuous.

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..

$\bar{x}$ & $\bar{p}$ do not behave in unreasonable ways.

NOT well-behaved $\Psi(x)$

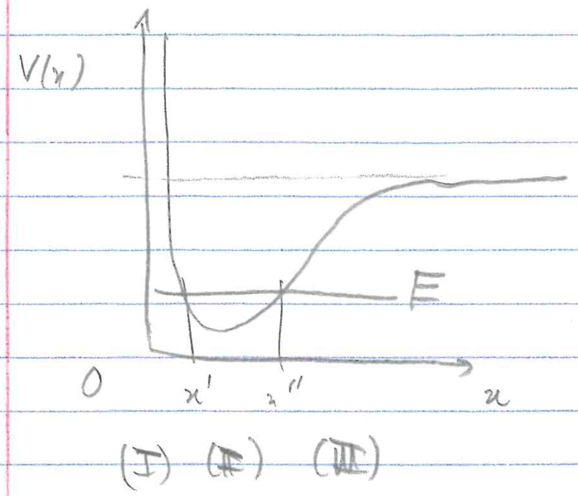


In order for $d\Psi/dx$ to be finite ⇒ Ψ must be continuous!

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

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

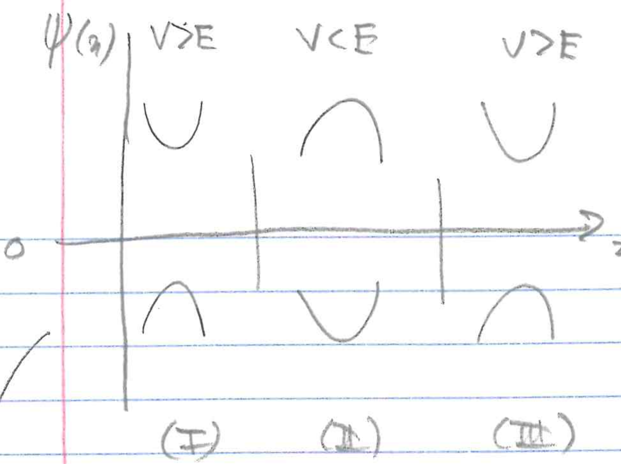
$\boxed{\text{Energy quantization}}$ Consider $\boxed{\frac{d^2\Psi(x)}{dx^2} = \frac{2m}{\hbar^2}\left[V(x)-E\right]\Psi(x)}$



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

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

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

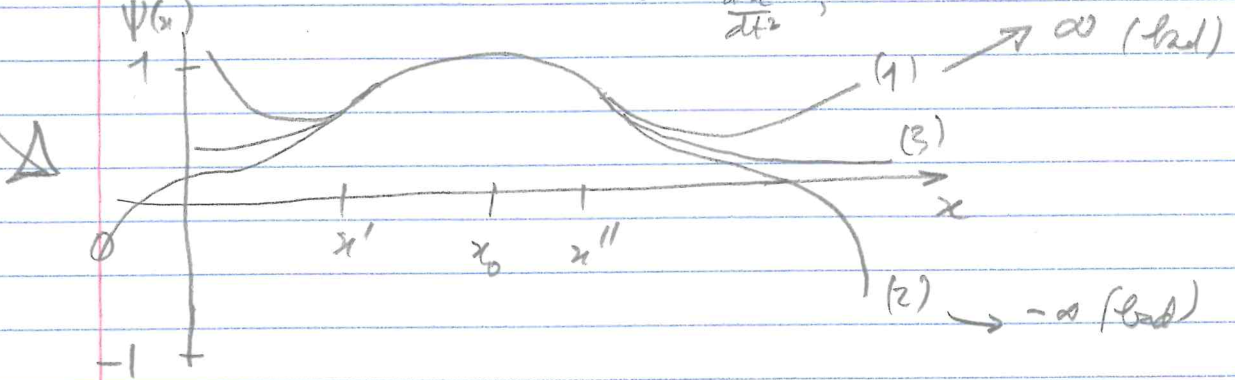


<u>Analogy</u> $\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}[V-E]\psi(x)$

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

If we specify the value of ψ & $\frac{d\psi}{dx}$, then particular behavior of ψ is determined ∀x.

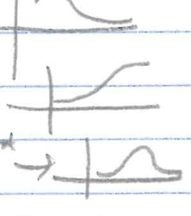
x $\frac{d^2x}{dt^2}$, x ∀t



<u>Recall</u> ψ has to be finite.

If find E^* such that

and F^* such that



→ these acceptable $E = E^* \cap F^*$ →

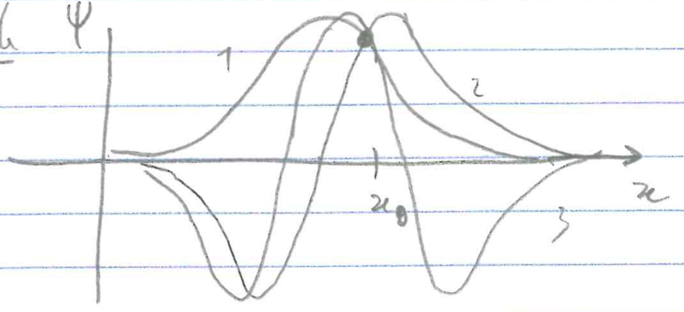
(3) $\frac{d^2\psi}{dx^2} \to 0$ as $\psi \to 0$

But hard to find ψ, $\frac{d\psi}{dt}$ such that ψ → 0 as x → ∞ or x → −∞

$E^* \cap F^*$ where these are the E level such that ψ → 0 as x → ±∞

→ But ∃ E_1, E_2 ... such that SE has acceptable solutions ψ_1, ψ_2, ψ_3 ...

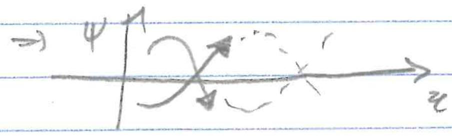
<u>Example</u>



Also $(V-E(x)) < 0$

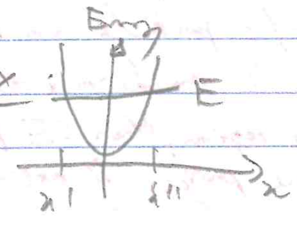
→ $\frac{d^2\psi}{dx^2}\psi(x) < 0$

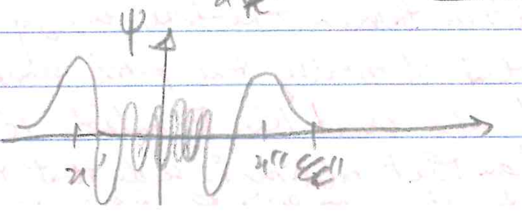
→



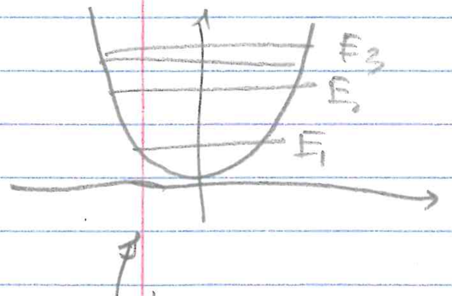
$[V(x)-E]\uparrow \to \frac{d^2\psi}{dx^2}\uparrow \Rightarrow$ <u>ψ oscillates faster!</u>

Ex

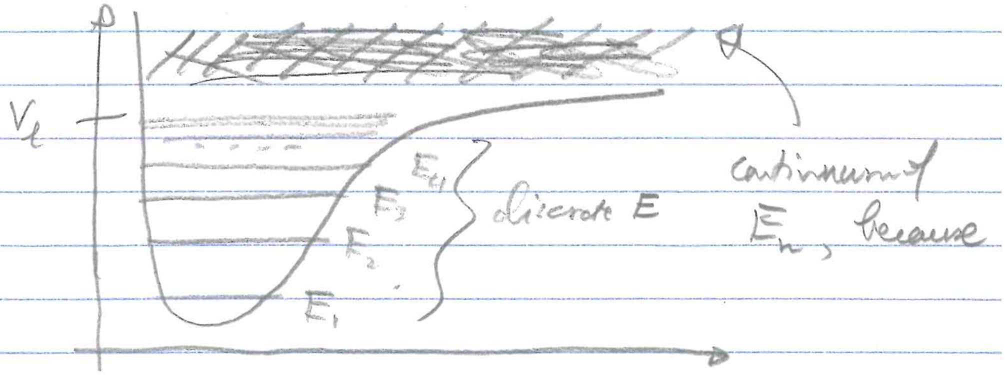




Potential "well" vs. potential with limiting value of V.



okay.



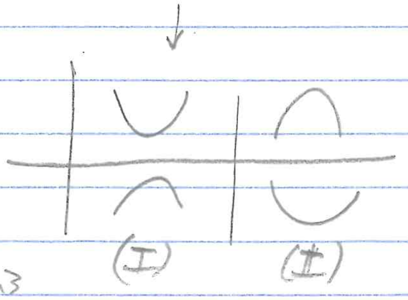
If the atom is unbound (exceed V_ℓ) $(E > V_\ell) \Rightarrow [V-E] < 0 \;\forall x$

↳ $\frac{d^2\psi}{dx^2}\psi < 0 \Rightarrow \psi$ tends to return to the axis. ⇒ oscillating fn

↳ But here E need not be discrete, but rather <u>continuum</u>

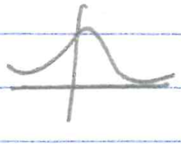
↳ Because you only have Region (I) & (II)

If there're only 2 regions, and in the second region, ψ always tend to axis



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

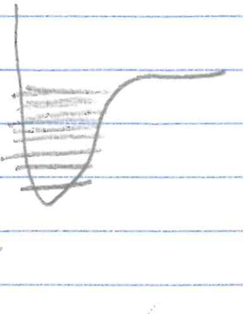
⇒ we can find E such that ψ tends to axis for region (I) ⇒ no need to satisfy



for both region ⇒

CONTINUUM of E if $E > V_\ell$

If, however $E < V_\ell$ ⇒ Bounded within "well"



then $\psi \to 0$ has to be met in (I) & (III)

↳ 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 bcz 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, then the theory predicts the total E can have any value."

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.

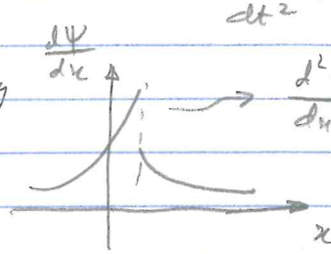
↳ Properties of the eigenfunction:

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

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

{ finite $\Rightarrow$ don't get infinite answers.
single-valued $\Rightarrow$ avoid multiple probabilities.
Continuous $\Rightarrow$ so that $\frac{d^2}{dt^2}\psi(x)$ is not infinite

e.g



$\rightarrow \frac{d^2\psi}{dx^2} \rightarrow \infty$ ← appears in Schrödinger Eq

Eigenfunctions have another important property:
$\Rightarrow$ Can look at it very generally.

Suppose $\hat{A}$ = operator for some physical quantity A (e.g.: p, x, E

ψ is an eigenfunction of A

↳ obeys:

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

where a is a number $\Rightarrow a$ = eigenvalue.

Suppose we measure quantity A, what do we get for $\bar{A}$ & ΔA?

$$\bar{A} = \int \psi^* \hat{A} \psi \, dx = \int \psi^* a \psi \, dx = a\int \psi^* \psi \, dx = 1$$

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 (ΔA)?

$\boxed{\Delta A = \sqrt{\overline{A^2} - \bar{A}^2}} \longrightarrow$ find $\overline{A^2}$

$$\overline{A^2} = \int \psi^* \hat{A}^2 \psi = \int \psi^* a^2 \psi \, dx = a^2 \int \psi^* \psi \, dx = a^2$$

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

We see that when ψ is an eigenfunction of $\hat{A}$, then the measurements of A gives "a" exactly each time.

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

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:

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

↳ so probability distribution is time independent ⇒ Externally the same

$\Rightarrow \boxed{\Delta t = \infty}$

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

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

↳ $\boxed{\hat{p}\psi = p\psi}$

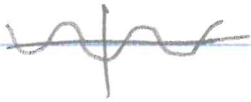
↳ $(-i\hbar)\frac{\partial}{\partial x}\psi = p\psi$ $\leftarrow e^{ikx}$

↳ get $\boxed{\psi(x) = e^{+ipx/\hbar} = e^{ipx/\hbar}}$

Here $p =$ exact $\Rightarrow \Delta p = 0$ (again, eigenvalue problem)

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

$\boxed{\Delta x = \infty} \Leftarrow$ real & imaginary part span $x = -\infty \to \infty$



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

General Solution

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

↳ separate variable $\Psi(x,t) = \psi(x)\,\phi(t)$

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

For $\psi(x)$, we need to solve the time-ind SE

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi \Rightarrow \boxed{\hat{H}\psi = E\psi}$$

→ depends on what $V(x)$ is

where $\hat{H}$ is the Hamiltonian $\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)}$

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

n : quantum number ⇐ discrete set of energy levels.

The full time dependent solutions are:

$$\Psi_1(x,t) = \psi_1(x)\,e^{-iE_1t/\hbar}$$
$$\Psi_2(x,t) = \psi_2(x)\,e^{-iE_2t/\hbar}$$
$$\vdots$$
$$\Psi_n(x,t) = \psi_n(x)\,e^{-iE_nt/\hbar}$$

■ 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)
Here $E = E_1$, $\Delta E = 0$

or • $\Psi = \Psi_4$ → excited state
has $E = E_4$, $\Delta E = 0$

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

↳ The most general solution is a superposition.

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

$$\underbrace{\boxed{\Psi(x,t) = \sum_{i=1}^{n} c_i \Psi_i(x,t)}}_{\text{wave-packet solution}} \quad c_i = \text{complex-valued constants.}$$

Note: quantum mechanical particle can exist in a superposition of different energy state ⇒ a mixture of energy states

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

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

* * *

Transitions

↳ If a particle is in a definite energy state

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

→ measure E yields $E = E_k$ exactly

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

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

→ for a quantum particle with charge ±e, then the charge density

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

↑

no t dependence.

29

→ Pure energy state have static ρ ⇒ expect NO radiation (photons)

To get radiation, need time dependent in ρ → need a mixture of states

$$\boxed{\Psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}}$$

no longer have $\Delta E = 0$

$$\boxed{\begin{aligned}|\Psi|^2 = \Psi^*\Psi = |c_1|^2|\psi_1(x)|^2 &+ |c_2|^2|\psi_2(x)|^2\\ &+ c_1^*c_2\psi_1^*\psi_2e^{-i(E_2-E_1)t/\hbar}\\ &+ c_2^*c_1\psi_2^*\psi_1e^{+i(E_2-E_1)t/\hbar}\end{aligned}}$$

→ This has time dependence
⇒ get photons (radiation)

Feb 21, 2018 Recall Transition ⇒ get radiation from oscillating charge
need $\rho = e|\Psi|^2$ to have time dependent to get $\rightsquigarrow$

⇒ need a superposition.

$$\boxed{\Psi = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}}$$

So $\left\{\begin{aligned}|\Psi|^2 = |c_1|^2|\psi_1(x)|^2 + |c_2|^2|\psi_2(x)|^2 &+ c_1^*c_2\psi_1^*\psi_2e^{-i(E_2-E_1)t/\hbar}\\ &+ c_2^*c_1\psi_2^*\psi_1e^{i(E_2-E_1)t/\hbar}\end{aligned}\right\}$

↳ has t dependence.

We look at $\boxed{e^{-i/\hbar(E_1-E_2)t} = e^{-i\omega t}}$ with $\omega = 2\pi\nu = \frac{E_2-E_1}{\hbar}$

$$\boxed{\nu = \frac{E_2-E_1}{h}}$$ ← 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)

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

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

↳ We'll look at

- free potential
- step potential
- barrier potential (★) problem 5, chap 6
- particle in a box
- SHO

⇒ all of these cases give exact solutions...

The free particle ⟶ $V = 0$ (zero potential)

Time-independent SE → $\boxed{\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x)}$

$$\Rightarrow \boxed{\frac{\partial^2\psi}{\partial x^2} = \frac{-2mE}{\hbar^2}\psi(x)}$$

let

$k = \sqrt{\frac{2mE}{\hbar^2}}$, and note $E = \frac{p^2}{2m} + \cancel{V}^{0} \rightarrow p = \sqrt{2mE} = \frac{h}{\lambda} = \hbar k$

where $k = \frac{2\pi}{\lambda}$ is the wavenumber

See that $\boxed{k = \sqrt{\frac{2mE}{\hbar^2}}}$ ⟵ 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 solut

but also

⇒ $\psi(x) = \underline{e^{ikx}}$ or $\underline{e^{-ikx}}$

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

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

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

We can see this by putting the t-dependence.

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

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

e.g. $\boxed{\Psi(x,t) = e^{-i\omega t}\cdot\sin(kx)}$ ← standing wave

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

Time dependence → fluctuating complex-valued amplitude.

↳ $\boxed{\sin(kx),\ \cos(kx)}$ → gives standing waves.

For $\psi(x) = e^{\pm ikx}$, we get <u>traveling waves</u>

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

↳ This is a traveling wave to the right.

The $\sin(kx-\omega t)$ does NOT have fixed nodes.

look at node where $kx-\omega t = 0$ → $kx - \omega t = 0$ ← zero node ~~of~~ that moves.

↓

$\sin = 0$

take $\frac{d}{dt}$ → $k\frac{dx}{dt} - \omega = 0$ → $\boxed{\frac{dx}{dt} = \frac{\omega}{k} > 0 \text{ (wave speed) (moves to the right)}}$

→ $\lambda\nu$

So the other solution

↳ $e^{-i(kx+\omega t)}$ → $\boxed{kx + \omega t = 0}$ → $\boxed{\frac{dx}{dt} = \frac{-\omega}{k}}$ ← moves to the left.

(look at node where $\sin = 0$)

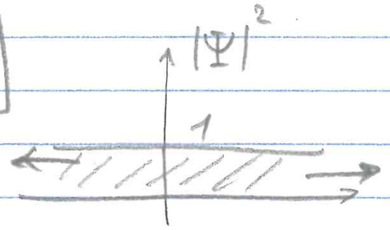
So which form of wave do we use?

- For scattering problem ⇒ Traveling waves ⇒ $e^{\pm ikx}$
- For bound systems (particle in a box) → standing waves
  → $\sin(kx)$, $\cos(kx)$

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

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

→ $|\Psi(x,t)|^2 = 1$



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

→ DOES NOT OBEY $\Psi \to 0$ as $x \to \pm\infty$

→ not square integrable.

But these are idealized solutions. → More practible free-particle solutions don't need infinite extent.

→ We can use "box normalization" → cut off Ψ at some far-away distance.

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

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

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

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

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

e.g. $\bar{p} = \int_{-L}^{L} \left(\frac{1}{\sqrt{2L}}\right)^2 e^{-ikx} (-i\hbar) \frac{\partial}{\partial x} e^{ikx}$

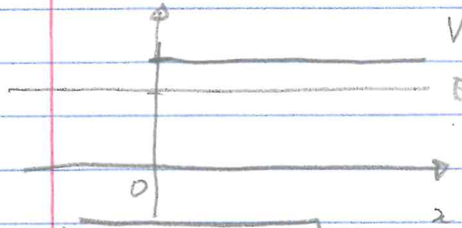
$= \frac{1}{2L}(-i\hbar)(ik) \underbrace{\int_{-L}^{L} \underbrace{e^{-ikx} \cdot e^{ikx}}_{1} dx}_{2L} = \boxed{\hbar k = \bar{p}}$

→ L doesn't matter.

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

Feb 23, 2018

$\boxed{\text{The step potential}}$ Consider a particle moving in from the left & hitting a big, thick wall.



2 cases $E < V_0$ & $V_0 < E$

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

$$\left.\begin{aligned} &\text{For } x < 0 \Rightarrow V(x) = 0 \rightarrow E = \frac{p^2}{2m} \\ &\text{For } x \geq 0 \Rightarrow E = \frac{p^2}{2m} + V_0 \end{aligned}\right\}$$

but $\frac{p^2}{2m} = E - V_0 < 0$ → NOT POSSIBLE ⇒

→ Classically, the particle bounces back to the left.

→ no motion beyond $x \geq 0$

↳ "classically forbidden region"

- What happens Quantum Mechanically? ⇒ SE is different in 2 regions

$$\left\{\begin{aligned} &(\text{left}) \quad \frac{-\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi \qquad (x<0) \\ &(\text{right}) \quad \frac{-\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V_0\Psi = E\Psi \qquad (x \geq 0) \end{aligned}\right\}$$

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

$\boxed{\text{For } x<0}$, $V=0$ → free-particle, 0 potential $\Rightarrow$ $\boxed{\psi(x) = Ae^{ik_1x} + Be^{-ik_1x}}$

general solution

Note We've chosen to use $e^{\pm ik_1x}$, not sin/cos since the problem involves a moving particle.

with $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$

→ traveling wave.

$$\boxed{\text{For } x>0} \rightarrow \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E-V_0)\psi \rightarrow \frac{d^2\psi}{dx^2} = \left[\underbrace{\frac{-2m}{\hbar^2}(E-V_0)}_{>0}\right]\psi$$

Note $E < V_0$

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

→ Now $e^{\pm ik_2x}$ / $\sin(k_2x)$ / $\cos(k_2x)$ are not solutions. Instead, e^{k_2x} or e^{-k_2x} are solutions. (or $\sinh(k_2x)$ and $\cosh(k_2x)$)

→ the general solution: $\boxed{\psi(x) = Ce^{k_2x} + De^{-k_2x}}$ $(x>0)$

The math solutions

$$\boxed{\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x} & (x<0) \\ \cancel{C}e^{k_2x} + De^{-k_2x} & (x>0) \end{cases}}$$

We find A, B, C, D by requiring $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$, and by matching $\psi(x)$, $\frac{d}{dx}\psi(x)$ at $x=0$ boundary and lastly by normalizing.

Finiteness: as $x \rightarrow +\infty$, $Ce^{k_2x} \longrightarrow \infty$. Must require $C=0$

as $x \rightarrow -\infty$,

$\psi(x) = Ae^{ik_1x} + Be^{-ik_1x}$ oscillates all the way to $-\infty$

→ must use box normalization (we won't)

Ψ continuous $\Rightarrow$ $\boxed{\Psi_{x<0}\Big|_{x=0} = \Psi_{x>0}\Big|_{x=0}}$

$\Rightarrow \left(Ae^{ik_1x} + Be^{-ik_1x}\right)\Big|_{x=0} = De^{-k_2x}\Big|_{x=0}$

$\hookrightarrow$ $\boxed{A + B = D}$ (1)

$\frac{d\psi}{dx}$ continuous $\rightarrow$ $\boxed{\frac{d\psi_{x<0}}{dx}\Big|_{x=0} = \frac{d\psi_{x>0}}{dx}\Big|_{x=0}}$

$ik_1\left(Ae^{ik_1x} - Be^{-ik_1x}\right)\Big|_{x=0} = -k_2De^{k_2x}\Big|_{x=0}$

$\Rightarrow ik_1(A-B) = -k_2D \Rightarrow \boxed{A - B = \frac{ik_2}{k_1}D}$ (2)

(1)(2) $\Rightarrow$ Solve for A & B in terms of D $\rightarrow$ add & subtract

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

Now solution is $\boxed{\psi(x) = \begin{cases} \frac{1}{2}\left(1+\frac{ik_2}{k_1}\right)De^{+ik_1x} + \frac{1}{2}\left(1-\frac{ik_2}{k_1}\right)De^{-ik_1x} & (x<0) \\ De^{-k_2x} & (x>0) \end{cases}}$

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

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

- How do we interpret the 3 terms? $\rightarrow$ need to include t dependent

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

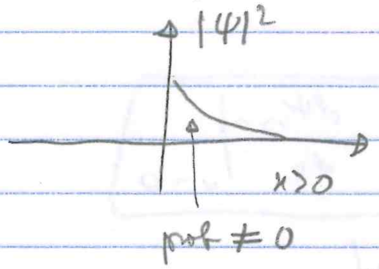
$\rightarrow$ $\boxed{\Psi(x,t) = \begin{cases} \frac{D}{2}\left(1+\frac{ik_2}{k_1}\right)e^{i(k_1x-\omega t)} + \frac{D}{2}\left(1-\frac{ik_2}{k_1}\right)e^{i(k_1x+\omega t)} & , x<0 \\ De^{-k_2x}\cdot e^{-i\omega t} & , x>0 \end{cases}}$

makes sense { 1st term is a traveling wave to the right $\Rightarrow$ (incoming wave)
2nd term is a traveling wave to the left $\Rightarrow$ (reflected wave)

QM { 3rd term is NOT a wave, be a decayed exp $\Rightarrow$ $\boxed{|\Psi|^2 = |D|^2e^{-2k_2x}}$ (x>0)

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

→ 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.
⇓ R = ratio

For $x<0$ Call ~~R~~

$$\boxed{R = \frac{\left|Be^{-i(k_1x+\omega t)}\right|^2}{\left|Ae^{i(k_1x-\omega t)}\right|^2} = \frac{B^*B}{A^*A} = \frac{|B|^2}{|A|^2}}$$

reflection coefficient

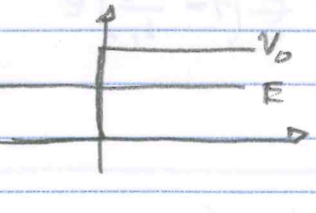
$$\Rightarrow R = \frac{\frac{D^*D}{4}\left(1-\frac{ik_2}{k_1}\right)^*\left(1-\frac{ik_2}{k_1}\right)}{\frac{D^*D}{4}\left(1+\frac{ik_2}{k_1}\right)^*\left(1+\frac{ik_2}{k_1}\right)} = \frac{\left(1+i\frac{k_2}{k_1}\right)\left(1-i\frac{k_2}{k_1}\right)}{\left(1-\frac{ik_2}{k_1}\right)\left(1+i\frac{k_2}{k_1}\right)}$$

So $\boxed{R=1}$ ⇒ 100% probability that the particle is reflecting. But it reflects with some penetration beyond $x=0 \to x>0$

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

→ new QM phenomenon → QM particle can penetrate into classically forbidden region.

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



→ particle moving in from left (classically bounce

Solving SE, matching ψ & $\frac{d\psi}{dx}$ at $x=0$

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

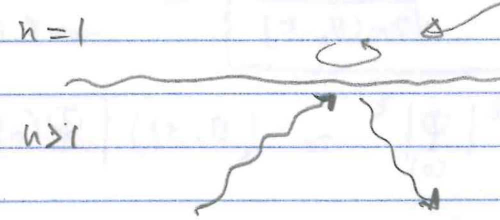
Looked at the reflection coefficient found: R = 1 → 100% probability for reflect

normal wave behavior

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

→ get penetration in classically forbidden region.

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



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

$$\boxed{\Psi(x) = \underbrace{\frac{D}{2}\left(1+\frac{ik_2}{k_1}\right)}_{A} e^{ik_1 x} + \underbrace{\frac{D}{2}\left(1-\frac{ik_2}{k_1}\right)}_{B} e^{-ik_1 x}}$$

In problem 6-1 → 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

$$\boxed{\Psi(x,t) = \underbrace{D\left(\cos k_1 x - \frac{k_2}{k_1}\sin(k_1 x)\right)}_{\text{has fixed nodes}} \underbrace{e^{-i\omega t}}_{\text{oscillating amplitude}}}, \quad x<0$$

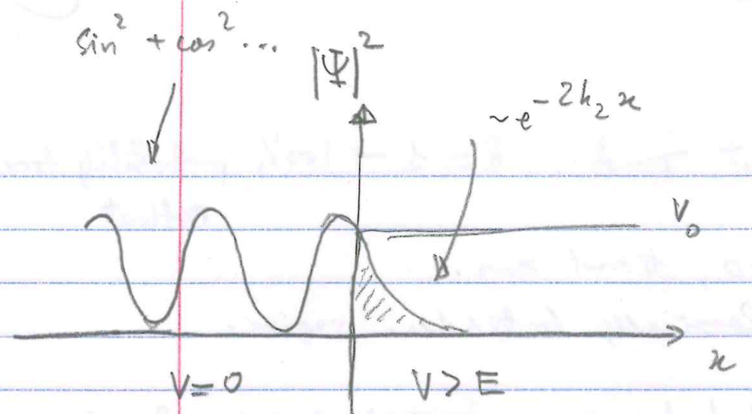
⇒ complex-valued standing wave

↳ = superposition of 2 traveling waves

Traveling waves being incident wave superpose w/ reflecting wave.

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

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



We can define a <u>penetration depth</u>

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

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

$$\rightarrow \boxed{\Delta x = \sqrt{\frac{\hbar^2}{2m(V_0-E)}} = \frac{\hbar^2}{\sqrt{2m(V_0-E)}}}$$ ← arbitrary, but useful for cross comparison

<u>At $x = \Delta x$</u>

$$\rightarrow |\Psi(\Delta x)|^2 = e^{-2}|\Psi_{(0)}|^2 \simeq (0.13)|\Psi(0)|^2$$

<u>Ex</u> tiny but microscopic object ...

$m = 4\times10^{-14}\,kg \quad v = 10^{-2}\,m/s$, suppose it hits a step with $V_0 = 2(KE)$

$$\Rightarrow V_0 - E = 2\left(\tfrac{1}{2}mv^2\right) - \left(\tfrac{1}{2}mv^2\right) \simeq 2\times10^{-10}\,J$$

$$\hookrightarrow \Delta x \simeq \frac{\hbar}{\sqrt{2m(2\times10^{-10}\,J)}} \simeq \boxed{2\times10^{-19}\,m}$$ ($\sim 1/10000$ of proton radius)

$\Rightarrow$ has no effect at all.

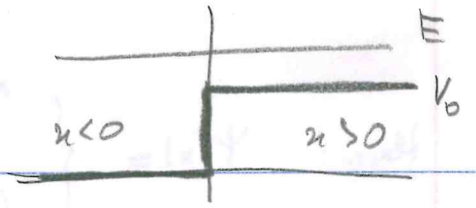
<u>Ex</u> Quantum electron, $m = 9.11\times10^{-31}\,kg$, in a block of copper.
Find Δx for an electron in a block of copper

$V_0 = 0$ inside
$V_0 > E$ outside

<u>Work function</u> $(V_0 - E) \cong 4\,eV$ needed to extract an electron.

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

↳ has consequences in atomic physics.



$\boxed{\text{Step Potential}}\ \boxed{\text{but } E>V_0}$

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

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

QM need to solve the SE
for $x>0$ & $x<0$, match ψ & $\frac{d\psi}{dx}$ at $x=0$

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

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

So, for $x<0$: Let $\boxed{k_1 = \sqrt{\frac{2mE}{\hbar^2}}} \Rightarrow \boxed{\psi = Ae^{ik_1x} + Be^{-ik_1x}}$

for $x>0$ → $\frac{d^2}{dx^2}\psi = \frac{-2m}{\hbar^2}(E-V_0)\psi$ $\qquad (E-V_0>0)$

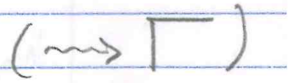
Define $\boxed{k_2 = \sqrt{\frac{2m}{\hbar^2}(E-V_0)}}$ → $\frac{d^2}{dx^2}\psi = -k_2^2\psi$

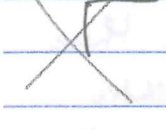
$$\boxed{\psi = Ce^{ik_2x} + De^{-ik_2x}}$$

$$\boxed{\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x} & x<0 \\ Ce^{ik_2x} + De^{-ik_2x} & x>0 \end{cases}}$$

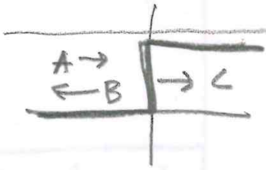
D: physical meaningless.

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

$x<0 \Rightarrow$ incoming + reflected wave (good) ()
$x>0 \Rightarrow$ transmitted wave + ???



The 4th term De^{-ik_2x} coming in to the left in $x>0$ does not make sense
⇒ $D=0$



Have: $$\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x}, & x<0 \\ Ce^{ik_2x}, & x>0 \end{cases}$$

Again, we require continuity of ψ & $\frac{d\psi}{dx}$ at $x=0$

$$\psi \Rightarrow \left(Ae^{ik_1x} + Be^{-ik_1x}\right)\Big|_{x=0} = \left(Ce^{ik_2x}\right)\Big|_{x=0}$$

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

$$\frac{d\psi}{dx}\Big|_{x=0} \Rightarrow (ik_1)Ae^{ik_1x}\Big|_{x=0} + (-ik_1)Be^{-ik_1x}\Big|_{x=0} = (ik_2)Ce^{ik_2x}\Big|_{x=0}$$

$$\hookrightarrow \boxed{k_1(A-B) = k_2C}$$

Since the original wave is A (total incident amplitude)

$\Rightarrow$ A as reference $\Rightarrow$ solve for B & C in terms of A.

leaving the rest unnormalized

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

Then get

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

So...

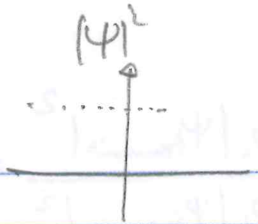
$$\boxed{\psi(x) = \begin{cases} Ae^{ik_1x} + A\left(\frac{k_1-k_2}{k_2+k_1}\right)e^{-ik_1x} & x<0 \\ A\frac{2k_1}{k_2+k_1}e^{ik_2x} & x>0 \end{cases}}$$

Want to define $\begin{cases} R = \text{reflection coeff} \\ T = \text{transmission coeff} \end{cases}$ [Classically $R=0$, $T=1$]

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

speed when crosses $x=0$

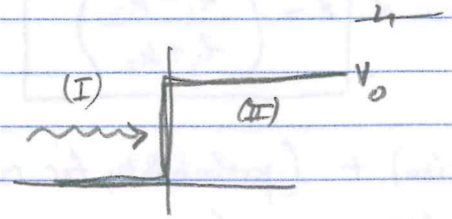
Particle slows down



Need to compare 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

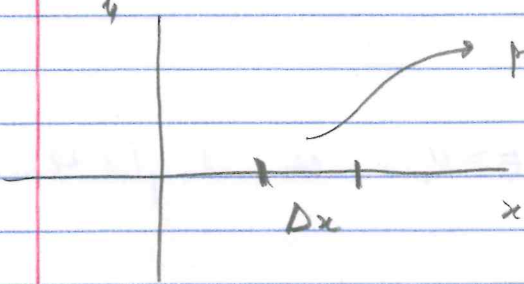
$$B = \frac{k_1 - k_2}{k_1 + k_2} A, \quad C = \frac{2k_1}{k_1 + k_2} A$$

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

↳ Need to use probability FLUXES

↳ Define a probability FLUX

↳ $\boxed{\text{Probability per second for a particle to cross some point}}$



probability in $\Delta x = \Delta|x| \cdot |\Psi|^2 = \Delta x |\Psi|^2$

divide by Δt = time to cross Δx

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

Note $\begin{cases} v_2 = \frac{p_2}{m} = \frac{\hbar k_2}{m} \\ v_1 = \frac{p_1}{m} = \frac{\hbar k_1}{m} \end{cases}$ so $\frac{v_2}{v_1} = \frac{k_2}{k_1}$

For R, the speed drops out since inc, refl waves have speed v_1

Then define R & T as ratios of probability FLUXES

For R, get ⇒ $\boxed{R = \frac{v_1 |\Psi_{reflected}|^2}{v_1 |\Psi_{incoming}|^2} = \frac{|\Psi_{ref}|^2}{|\Psi_{inc}|^2}}$ (same v_1 bcz same region)

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

→ see that $R \neq 0$ (prob for reflection)

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

$\Rightarrow \boxed{T = \frac{4k_1k_2}{(k_1+k_2)^2}}$ and $\boxed{R = \left(\frac{k_1-k_2}{k_1+k_2}\right)^2}$

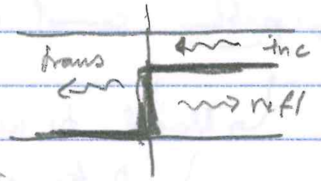
(probability for transmission) + (probability for reflection) = 1

Since the particle can't just disappear / appear

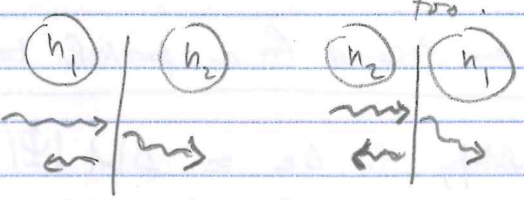
$\boxed{R + T = 1}$ (either reflect / transmit)

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.



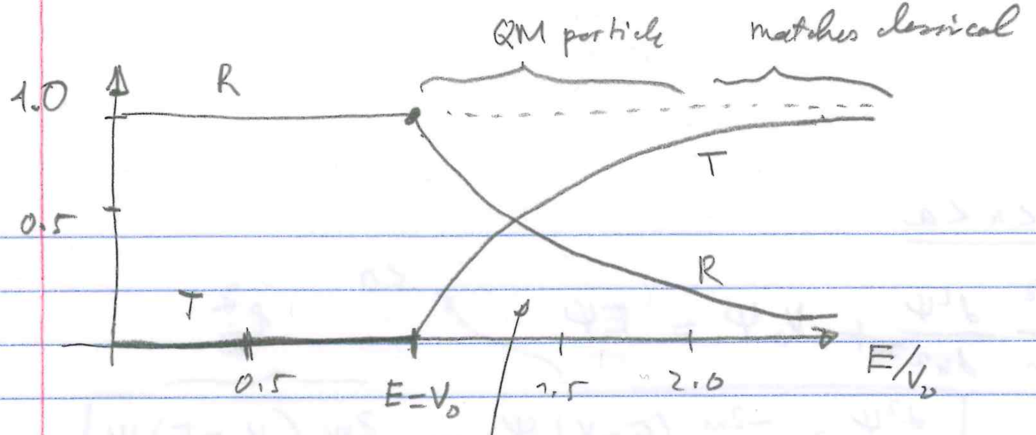
Now, we can combine $E < V_0$ & $E > V_0$ results and plot them for R & T

$E < V_0 \Rightarrow R = 1, \ T = 0$

$E > V_0 \Rightarrow R = \left(\frac{k_1-k_2}{k_1+k_2}\right)^2, \ T = \frac{4k_1k_2}{(k_1+k_2)^2}$

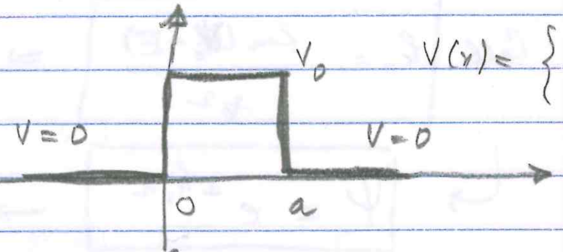
$$\boxed{R = \left(\frac{\sqrt{2mE} - \sqrt{2m(E-V_0)}}{\sqrt{2mE} + \sqrt{2m(E-V_0)}}\right)^2 = \left(\frac{\sqrt{E} - \sqrt{E-V_0}}{\sqrt{E} + \sqrt{E-V_0}}\right)^2 = \left(\frac{1-\sqrt{1-V_0/E}}{1+\sqrt{1-V_0/E}}\right)^2}$$

Plot vs. $\frac{E}{V_0}$ $\boxed{T = 1 - R}$



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

THE BARRIER POTENTIAL



$$V(x) = \begin{cases} V_0 & 0<x<a \\ 0 & x<0,\ x>a \end{cases}$$

Classically, if particle is incident from the left
↳ the probability for reflection: $R = 1$ if $E < V_0$
and $R = 0$ if $E > V_0$

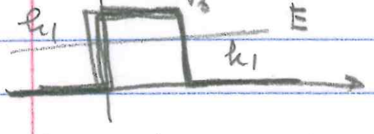
QM must solve the Schrödinger equation
↳ if $E > V_0$, can get some reflection
↳ if $E < V_0$, ⇒ get **TUNNELING**
↳ {finite probability for particle to make it to the other side.}

TUNNELING only occurs if width $a \simeq$ atomic scale
↳ cannot observe 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.

START WITH $E<V_0$. For $x<0$, $x>a$, $V=0$
• use $k_I = \sqrt{\frac{2mE}{\hbar^2}}$ → get $e^{\pm i k_I x}$ soln in both cases

(traveling wave)



For $0<x<a$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi$$

$$\hookrightarrow \boxed{\frac{d^2\psi}{dx^2} = \frac{-2m}{\hbar^2}\underset{<0}{(E-V_0)}\psi = \overbrace{\frac{2m}{\hbar}(V_0-E)}^{k_{II}^2}\psi}$$

Call $\boxed{k_2 = \frac{2m(V_0-E)}{\hbar^2}}$ ⇒ equation w/o (−) sign $\hookrightarrow \frac{d^2\psi}{dx^2} = k_{II}^2\psi$

$\hookrightarrow \boxed{\psi = e^{\pm k_2 x}}$ → regular exponential

- general solution

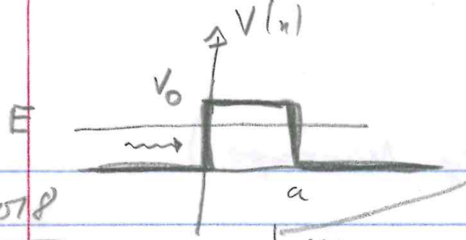
$$\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x} & x<0 \\ Ce^{ik_1x} + \cancel{De^{-ik_1x}} & x>a \\ Fe^{-k_2x} + Ge^{+k_2x} & 0<x<a \end{cases}$$

- For an incoming particle from the left, we shall not have De^{-ik_1x} coming in from the right, in $x>a$ region → $\boxed{D=0}$
- Note for $0<x<a$, neither e^{-k_2x} or e^{k_2x} blows up to ∞
  ↳ no reason to eliminate either.

- Next, match ψ & $\frac{d\psi}{dx}$ @ $x=0$, and @ $x=a$
  → get 4 equations for 5 unknowns, A, B, C, F, G. ⇒ lots of algebra
  ↳ $\boxed{\text{Problem 6.5}}$ → solve for B, C, F, G in terms of A.

- Then, compute R and T

(45)



March 2, 2018

QM ⇒ find

$$\boxed{\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x} & (x<0) \\ Ce^{ik_1x} + \cancel{De^{-ik_1x}} & (x>a) \\ Fe^{-k_2x} + Ge^{k_2x} & (0<x<a) \end{cases}}$$

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

Match ψ & $\frac{d\psi}{dx}$ at $x=0$ & $x=a$.

$$\left\{ \begin{array}{llll} \boxed{x=0} & \psi & \rightarrow & A+B = F+G \\ \boxed{x=a} & \psi & \rightarrow & Ce^{ik_1a} = Fe^{-ik_2a} + Ge^{k_2x} \\ \boxed{x=0} & \frac{d\psi}{dx} & \rightarrow & ik_1(A-B) = -k_2(F-G) \\ \boxed{x=a} & \frac{d\psi}{dx} & \rightarrow & -k_2Fe^{-k_2a} + k_2Ge^{k_2a} = ik_1Ce^{ik_1a} \end{array} \right\}$$

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.

$$\boxed{T = \frac{v_1 C^*C}{v_1 A^*A} = \frac{C^*C}{A^*A} = \left(\frac{C}{A}\right)^*\left(\frac{C}{A}\right)}$$

Do lots of algebra: → $\boxed{T = \dfrac{1}{\dfrac{(e^{k_2a}-e^{-k_2a})^2}{16\frac{E}{V_0}\left(1-\frac{E}{V_0}\right)}+1}}$ → gives probability for tunneling through a barrier

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

For tall or wide barriers: tall: $V_0 \gg E$, wide: $a \gg 1$ } ⇒ $\boxed{k_2a \gg 1}$

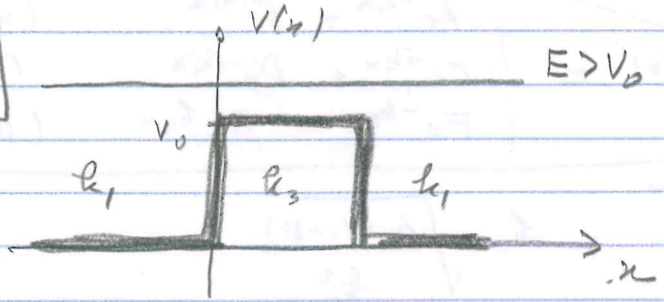
In this limit

→ $\boxed{T \simeq 16\frac{E}{V_0}\left(1-\frac{E}{V_0}\right)e^{-2k_2a}}$ (sharp exp fall off)

→ damped, but still finite

Application → STM (Scanning Tunneling Microscope)

$\boxed{E > V_0}$

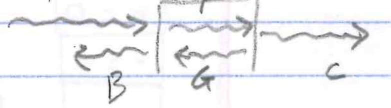


{ classically, particle slows down but then regains its speed.
→ T = 1, R = 0 classically

QM

Also, have oscillating solutions in all 3 regions.

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



⇒ General solution of traveling waves

$$\boxed{\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x} & (x<0) \\ Fe^{ik_3x} + Ge^{-ik_3x} & (0<x<a) \\ Ce^{ik_1x} & (x>a) \end{cases}}$$

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

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

where

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

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

→ QM-ly, some reflection can happen

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

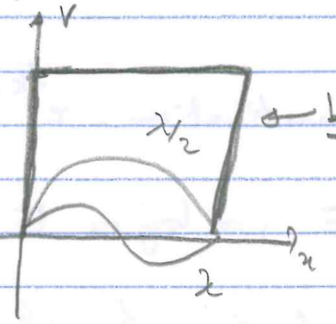
→ T = 1. No reflection!

→ This is an <u>interference</u> effect!

If we write: $k_3 a = n\pi$, n = integer > 0 }

↳ and $k_3 = \frac{2\pi}{\lambda}$

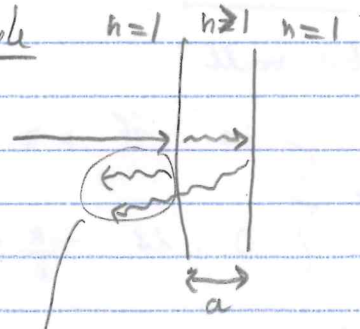
$$\Rightarrow \frac{2\pi}{\lambda} a = n\pi \rightarrow \boxed{a = n\frac{\lambda}{2}}$$



← **Box** → get destructive interference between the waves reflected off the 2 surfaces when $a = n\left|\frac{\lambda}{2}\right|$

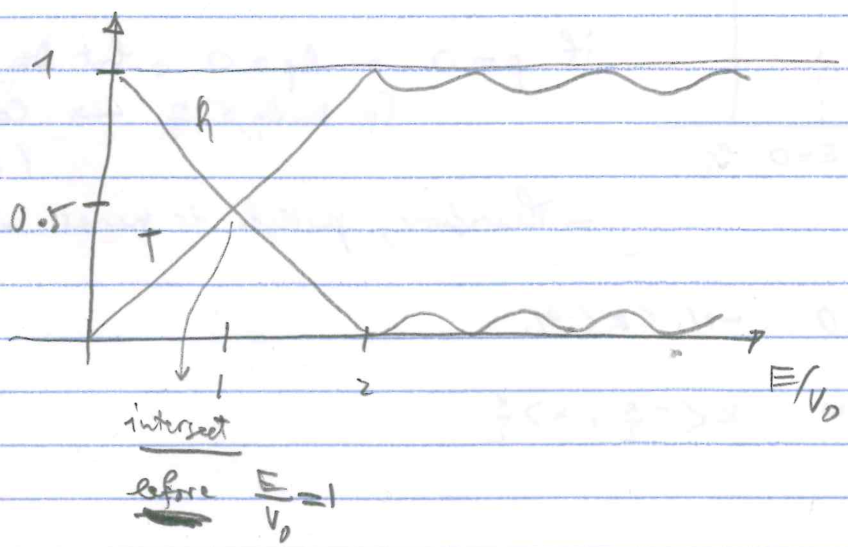
↳ This is what happens with thin film and light.
↓
width a

Example



Cancel destructively if $\boxed{2a = n\lambda}$ → This what I read about in QED (by Feynman)

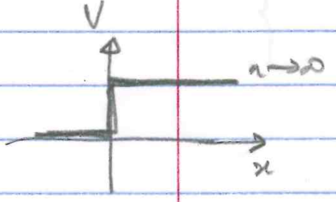
{ Lastly, can plot R & T for an electron hitting a barrier of height $V_0 = 10$ eV, with $a = 1.8\times10^{-10}$ m as a function of (E/V_0) }



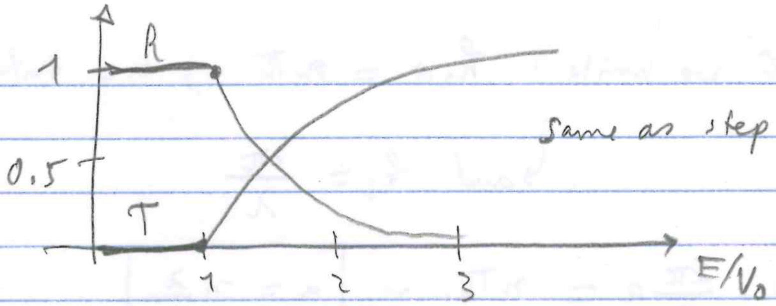
Combines $E < V_0$ and $E > V_0$

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

If $a \to \infty$



(step potential)



Same as step potential

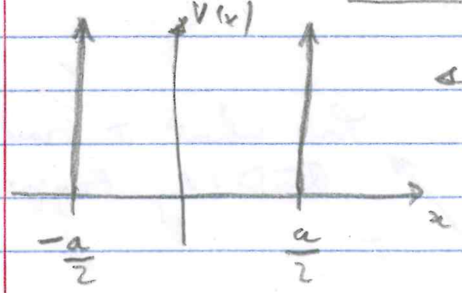
—//—

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

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

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

↳ $\boxed{\text{INFINITE SQUARE WELL}}$

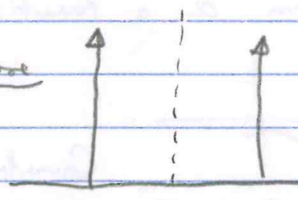


$$V(x) = \begin{cases} \infty & \text{if } x \geq \frac{a}{2},\ x \leq -\frac{a}{2} \\ 0 & \text{if } -\frac{a}{2} \leq x \leq \frac{a}{2} \end{cases}$$

↳ classically ball in room with 2 walls. → any E inside is o.k including $E = 0$

⟹ { But in QM → get E quantization. And $E = 0$ inside is not allowed! }

Suppose

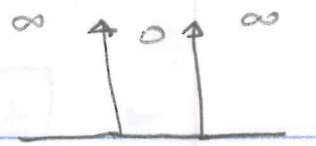


if $p = 0 \Rightarrow \Delta p = 0$, but $\Delta x \leq a$

So $\Delta x \Delta p \cancel{\leq} \frac{\hbar}{2}$ → CONTRADICTION ($\Delta x \Delta p \geq \hbar/2$)

⟹ 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, 2018

→ classically, free particle inside the box with energy E, including E=

→ QM → solve this SE:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + 0\psi = E\psi$$

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

$$\left.\begin{array}{l}\psi = 0 \text{ when particle } -a/2 \le x \le a/2 \\ \text{(walls are impenetrable, even in QM)}\end{array}\right\} \rightarrow \text{confinement in box.}$$

if $\psi \sim e^{-kx}$, but $V=\infty \Rightarrow k\to\infty \to \boxed{\psi=0}$

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

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

where $\boxed{\psi\Big|_{x=\pm a/2}=0}$

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

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

$\Rightarrow$ Want to use standing wave solutions since $\psi=0$ at walls.

→ General solution

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

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

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

$+ \quad + \quad = 0$

$- \quad + \quad = 0$

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

↳ So $2B\cos\left(\frac{ka}{2}\right) = 0 \Rightarrow$ } both of these must hold

and $2A\sin\left(\frac{ka}{2}\right) = 0 \Rightarrow$

- 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 $A \neq 0$

$\Leftrightarrow \sin\left(\frac{ka}{2}\right) = 0$

This requires $\boxed{\frac{ka}{2} = n\pi}$ → $n \neq 0$, since that gives trivial solution again

So $\boxed{k = \frac{2n\pi}{a}}$ $n = 1, 2, 3, \ldots$ $\left(\sin \sim k_n = \frac{(\text{even})\pi}{a}\right)$

So the set of solutions is

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

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

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

So the set of solutions is

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

→ Summary : 2 classes of solution : $\boxed{1^{st} \text{ set} \Rightarrow \psi = A_n \sin(k_n x)}$ (n even)

↳ $\psi_n(-x) = -\psi_n(x)$ (odd function)

↳ Called "odd parity" states.

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

↳ even function ($\psi(-x) = \psi(x)$)

↳ Called "even parity" states

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

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

Useful in problems with left/right symmetry or where

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

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

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

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

Eigenstates obey →

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

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

Can't prove this, but we will go on with this!

↳ **Now, k is quantized. What about E?**

Well, $k = \sqrt{\frac{2mE}{\hbar^2}} = k_n = \frac{n\pi}{a}$ (n alternates odd & even) $(n = 1, 2, 3, \ldots)$

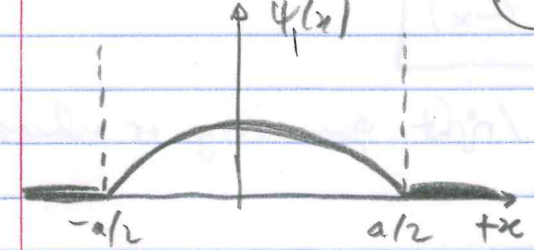
↳ So $E = E_n = \frac{\hbar^2 k_n^2}{2m}$ → So we get allowed energies

$$\boxed{E_n = \frac{\hbar^2}{2m}\cdot\left(\frac{n\pi}{a}\right)^2, \quad n = 1, 2, 3, \ldots}$$

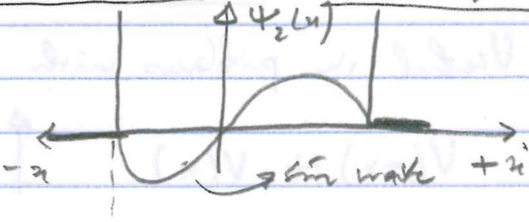
↳ Particle in a box has quantized energies, this corresponds to the fact that only certain waves fit in the box.

n odd → use cos()

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



$\boxed{\text{For } n = 2 \, , \; A_2 \sin\left(\frac{2\pi x}{a}\right) \, , \; E = E_2}$



- So E_1 is the state of lowest energy ⇒ 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 <u>non-zero</u> → called "zero-point energy"

↳ Must have $E_1 \neq 0$ for this

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

↳ 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 $\Delta p = 0$, $p =$ exact - is not allowed.

Since if $E = 0$ ⇒ at rest ⇒ $p = 0$ (exact) ⇒ This can't happen!

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

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

$\boxed{p = +\hbar k_n \text{ to the right } \& \; p = -\hbar k_n \text{ to the left.}}$

↳ So $\Delta p \neq 0$ (nonzero jiggly values)

{ Next, we would look at E_x, where we normalize ψ_n, compute $\bar{x}, \overline{x^2}, \bar{p}, \overline{p^2}$ and Δx, Δp → EXCEPT WE ALREADY DID THIS. }

↳ look at examples in chapter 5.

$\boxed{\text{CUT OFF for EXAM}}$

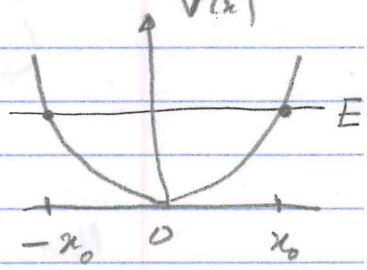
March 7, 2018

QUANTUM MECHANICAL OSCILLATOR (Appendix I chap 6)

$\boxed{V = \frac{1}{2} C x^2}$ ← C: spring constant.

← angular frequency $\omega = \sqrt{\frac{C}{m}} = 2\pi\nu$

↖ Can also write → $\boxed{C = 4\pi^2 m \nu^2}$



Classically → particle oscillate with frequency ν

Classical turning point → $\frac{1}{2} C x_0^2 = E$ total

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

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

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

Then SE, time-dependent → $\boxed{\Psi(x,t) = \psi(x) e^{-iEt/\hbar}}$

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

→ can't partition

↳ V has no abrupt changes

Using $C = 4\pi^2 m \nu^2$ → $\boxed{\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + 2\pi^2 m \nu^2 \psi = E\psi}$

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

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

Call $\boxed{\beta = \frac{2mE}{\hbar^2}}$ $\boxed{\alpha = \frac{2\pi m\nu}{\hbar}.}$

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

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

↳ so $u = \sqrt{\frac{2\pi m\nu}{\hbar}}\,x$ → gives $\boxed{\sqrt{\alpha} = \frac{(Cm)^{1/4}}{\hbar^{1/2}}}$

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

Chain rule →

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

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

↳ Rewrite SE in terms of u → $\alpha\frac{d^2\psi}{du^2} + \left(\beta - \alpha u^2\right)\psi = 0$

↳ Divide by α $\boxed{\frac{d^2\psi}{du^2} + \left(\beta/\alpha - u^2\right)\psi = 0}$ (*)

↑ all constants in one place! (preferable)

Now, solve for $\psi(u)$. Then use $u = \sqrt{\alpha}\,x = \frac{(Cm)^{1/4}}{\hbar^{1/2}}\cdot x$.

Now, how do we solve this? Can't just guess... → use a technique

↳ The power series method

The power series method Consider eqn:

guess

$$\boxed{\frac{d^2\psi}{dx^2} = -k^2\psi}$$ ← imagine we can't get a solution...

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

Instead of solving for ψ directed, we solve for its infinite power serie

(★) ↳ All good functions have power series expansions.

↳ e.g. Taylor series

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

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

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

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

↳ SE becomes $$\boxed{\sum_{l=0}^{\infty} a_l (l)(l-1) X^{l-2} = (-k^2)\sum_{l=0}^{\infty} a_l X^l}$$

Want to combine the sums.

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

$$\text{e.g. } \sum_{n=1}^{\infty} \frac{1}{n} = \sum_{j=1}^{\infty} \frac{1}{j} = \sum_{l=3}^{\infty} \frac{1}{l-2}$$

↳ We can combine the sum by shifting + relabeling the 1st sum,

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

let $l' = l-2 \rightarrow l = l'+2$

$$\boxed{\text{This sum} = \sum_{l'=0}^{\infty} a_{l'+2} (l'+2)(l'+1) X^{l'}}$$

(since $l' = 2 \rightarrow$ term $= 0$

$l' = 1 \rightarrow$ term $= 0$)

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

$$\boxed{\text{So } \sum_{\ell=0}^{\infty} a_{\ell}(\ell)(\ell-1)x^{\ell-2} = \sum_{\ell=0}^{\infty} a_{\ell+2}(\ell+2)(\ell+1)x^{\ell}}$$

→ We set eqn: $\sum_{\ell=0}^{\infty} a_{\ell+2}(\ell+2)(\ell+1)x^{\ell} = -k^2\sum_{\ell=0}^{\infty} a_{\ell}x^{\ell}$

$$\boxed{\sum_{\ell=0}^{\infty}\left[a_{\ell+2}(\ell+2)(\ell+1) + k^2 a_{\ell}\right]x^{\ell} = 0} \qquad (\text{true } \forall x)$$

Must have $a_{\ell+2}(\ell+2)(\ell+1) + k^2 a_{\ell} = 0$

$$\boxed{a_{\ell+2} = \frac{-k^2}{(\ell+2)(\ell+1)}a_{\ell}}$$ → recursion relation.

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

We can split up evens and odds. $\boxed{a_0 = \text{arbitrary}}$

$$\text{So } \begin{cases} a_2 = \frac{-k^2}{2}a_0 = \frac{-k^2}{2!}a_0 \\ a_4 = \frac{-k^2}{4\cdot 3}a_2 = \frac{+k^4}{4!}a_0 \\ a_6 = \frac{-k^2}{6\cdot 5}a_4 = \frac{-k^6}{6!}a_0 \end{cases}$$

$\vdots$

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

$$\begin{cases} a_3 = \frac{-k^2}{3!}a_1 \\ a_5 = \frac{-k^2}{5\cdot 4}a_3 = \frac{+k^4}{5!}a_1 \\ a_7 = \frac{-k^2}{7\cdot 6}a_5 = \frac{-k^6}{7!}a_1 \end{cases}$$

$\vdots$

The solution is then $\boxed{\psi(x) = \sum_{l=0}^{\infty} a_l x^l}$

So

$$\psi(x) = \left[a_0 + a_2 x^2 + a_4 x^4 + \dots\right] + \left[a_1 x + a_3 x^3 + a_5 x^5 + \dots\right]$$

$$= a_0\left[1 - \frac{(kx)^2}{2!} + \frac{(kx)^4}{4!} - \dots\right] + a_1\left[x - \frac{k^2 x^3}{3!} + \frac{k^4 x^5}{5!} - \dots\right]$$

$$= a_0\left[1 - \frac{(kx)^2}{2!} + \frac{(kx)^4}{4!} - \dots\right] + \frac{a_1}{k}\left[kx - \frac{(kx)^3}{3!} + \frac{(kx)^5}{5!} - \dots\right]$$

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

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

This gives the general solution.

Recognize the power series. $\boxed{\psi(x) = A\cos(kx) + B\sin(kx)}$

When does this method work?

↳ when we get a clean recursion relation between 2 coefficients

↳ Requires that only 2 powers appear.

↳ $\frac{d^2\psi}{dx^2} = -k^2\psi$. If $\psi \sim a_l x^l$

$$\underset{a_l x^{l-2}}{\uparrow} \qquad \underset{a_l x^l}{\uparrow} \quad \not\Leftarrow \boxed{\text{2 powers } x^{l-2}, x^l}$$

↳ method works.

But for SHO ⇒ does NOT work

↳ $$\boxed{\frac{d^2\psi}{du^2} + \left(\frac{\beta}{\alpha} - u^2\right)\psi = 0}$$

$\uparrow$ u^{l-2}

if $\psi \sim u^l$, $\frac{d^2\psi}{du^2} \sim u^{l-2}$ but $u^2\psi \sim u^{l+2}$ } 3 powers too messy

↗ relation for a_{l+2}, a_l, a_{l-2}

March 9, 2012 Recall SE: $\boxed{\frac{\partial^2\Psi}{\partial u^2}+\left(\frac{\beta}{\alpha}-u^2\right)\Psi=0}$

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

but we get too messy a recursion relation ⇒ Must do something else fir

⇒ Extract the asymptotic part of the solution

↳ solve in the limit where $|u|\to\infty$ or $\boxed{|u|>>1,\ |u|>>\frac{\beta}{\alpha}}$

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

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

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

So for $|u|>>1$ → $\boxed{\frac{\partial^2\Psi}{\partial u^2}=u^2\Psi}$

What about the exact solution?

↳ we now write the solution as: $\boxed{\Psi(u)=e^{-1/2u^2}H(u)}$

where $H(u)$ is such that $\Psi(u)$ is an exact solution. → plug in

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

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

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

$$\Rightarrow\boxed{\frac{d^2H}{du^2}-2u\frac{dH}{du}+\left(\frac{\beta}{\alpha}-1\right)H=0}\leftarrow\text{Hermite's eq.}$$

this eq. can be solved using the power series method

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

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

$\boxed{\text{Solve}}$ Hermite's eqn $\Rightarrow$ plug in power series expansion

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

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

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

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

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

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

This lets us generate all the a_l in terms of a_0 & a_1

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

The full solution is then $\boxed{\psi(u) \doteq e^{-1/2 u^2} H(u)}$

The solution $\psi(u)$ must be finite as $u \to \infty$
This means that the power series for H must converge on a function that doesn't blow up too fast ...

We can't have $e^{-1/2\, u^2} H(u) \to \infty$ as $u \to \pm\infty$

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

Then $e^{-1/2\, u^2} H \simeq e^{+1/2\, u^2} \to \infty$

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

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

$$\hookrightarrow \boxed{\sum_{\ell = 0, 2, 4 \ldots}^{\infty} a_\ell u^\ell \quad \text{where } a_\ell = \frac{1}{(\ell/2)!}}$$

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

for large ℓ $\hookrightarrow \boxed{\frac{a_{\ell+2}}{a_\ell} \simeq \frac{2}{\ell}}$ (ℓ even ...) $\longrightarrow$ same!

Compare this to what H does for large ℓ $\boxed{H: \frac{a_{\ell+2}}{a_\ell} = \frac{-(\beta/\alpha - 1 - 2\ell)}{(\ell+2)(\ell+1)} \simeq \frac{2\ell}{\ell^2} =}$

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 $\boxed{H(u) e^{-1/2\, u^2} \to 0 \text{ as } u \to \pm\infty}$

■ How do we truncate the series?

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

then $a_{n+2} = \frac{-(\beta/\alpha - 1 - 2n)}{(\ell+1)(\ell+2)} a_n = 0$

$a_{n+4} = (?)\, a_{n+2} = 0 \to$ so on $\Big\} \to$ series ends @ the n^{th} term

→ This leaves us with a finite polynomial of order n

<u>What does</u> $\left(\frac{\beta}{\alpha} - 1 - 2n = 0\right)$ mean?

<u>Recall</u> $\frac{\beta}{\alpha} = \frac{2mE/\hbar^2}{2\pi m\nu/\hbar} = \frac{E}{\pi\hbar\nu} = \frac{2E}{h\nu}$

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

Get $\boxed{E = E_n = h\nu\left(n + \frac{1}{2}\right)}$ ⇒ quantized energy levels.

$n \in \mathbb{N}$.

This gives the allowed energy levels of a QM SHO.

where ν = osc freq., $E = \frac{1}{2}h\nu$

...

$\frac{5}{2}h\nu$

$\frac{3}{2}h\nu$

$\frac{1}{2}h\nu$

0

Note → the ground state energy $\boxed{E_0 = \frac{1}{2}h\nu > 0}$ $E_0 \neq 0$

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

Why?

↳ $\boxed{E = \frac{p^2}{2m} + \frac{1}{2}Cx^2}$ $E = 0 \Longleftrightarrow \underbrace{p = 0 \text{ \& } x = 0}_{\text{exact}}$ → $\Delta p \Delta x = 0$

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

<u>Mar 12, 2018</u>

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

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

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

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

→ then the series stops at $a_n u^n$

The condition $\beta/\alpha - 1 - 2n = 0$ ⇒ $\boxed{E_n = \left(n + \frac{1}{2}\right)h\nu}$ → integers

↳ Quantized energies of QM SHO.

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

→ stop at n^{th} term (even or odd)

{ $\boxed{\text{if } n \text{ is even}}$ ⇒ we set $\boxed{a_1 = 0}$ so that the odd pwr terms are gone

keep a_0 = arbitrary, get $a_2, a_4, \ldots a_n$ in terms of a_0

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

$\boxed{\text{If } n \text{ is odd}}$ → set $\boxed{a_0 = 0}$ so the even pwrs go away.

keep a_1 = arbitrary → get $a_3, a_5, a_7, \ldots$ in terms of a_0.

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

Get an infinite set of Hermite polynomial ⤳ $\boxed{H_n(u)}$

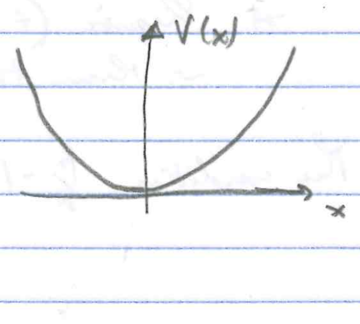
So the spatial wave function $\boxed{\Psi_n(u) = \left(e^{-\frac{1}{2}u^2}\right) H_n(u)}$

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

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

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

⇒ these are even/odd parity states (this is expected in QM whenever V(x) is left-right symmetric



$\boxed{\text{Lastly, we can generate } H_n(u)}$

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

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

So we get $\boxed{a_{l+2} = \frac{2l-2n}{(l+2)(l+1)} a_l}$

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

$\boxed{n=0} \rightarrow \boxed{a_{l+2} = \frac{2l}{(2+l)(1+l)} a_l}$. since $n=0$, $a_1 = 0$
. keep a_0 arbitrary

So $a_2 = \frac{2.0}{(2+0)(0+1)} a_0 = 0$ (recursion relation stops)

So $a_4 = a_6 = a_8 = \ldots = 0$

So $\boxed{H_0(u) = a_0}$ (just a constant) → polynomial of order 0

$\boxed{n=1} \rightarrow \boxed{a_{l+2} = \frac{2l-2}{(l+2)(l+1)} a_l}$. since $n=1$ odd $\Rightarrow a_0 = 0$
, keep a_1 arbitrary

$a_3 = \frac{2.1-2}{(1+2)(1+1)} a_1 = 0$ (poly stops at $n=1$ order)

Then $a_5 = a_7 = a_9 = \ldots 0$

So $\boxed{H_1(u) = a_1 u}$ Polynomial of order 1

$\boxed{n=2} \rightarrow \boxed{a_{l+2} = \frac{2.l-4}{(l+2)(l+1)} a_l}$ Since $n=2$ even $\rightarrow a_1 = 0$
keep a_0 arbitrary

$$\left. \begin{aligned} a_2 &= \frac{0-4}{(0+2)(0+1)} a_0 = -\frac{4}{2} a_0 = -2a_0 \\ a_4 &= \frac{2.2-4}{(2+2)(l+2)} a_2 = 0 = a_6 = a_8 = \ldots \end{aligned} \right\} \rightarrow \boxed{\begin{aligned} H_2(u) = a_0 u^0 \\ + (-2a_0)u \end{aligned}}$$

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

$\hookrightarrow$ found
$$\left| \begin{array}{l} H_0(u) = a_0 \\ H_1(u) = a_1 u \\ H_2(u) = a_0(1-u^2) \end{array} \right.$$

⊛ There are 2 steps to the normalization (2 STAGES)

① $\Rightarrow$ Mathematicians normalize $H_n(u)$ using a convention

$\boxed{\text{Rule}}$: coefficient of $u^n = 2^n$

- with $H_0(u) = a_0 u^0 \Rightarrow$ set coeff of $u^n = 2^0 = u^0 = 1$
  $\Rightarrow$ 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 $H_2(u) = a_0 u^0 + a_2 u^2 = a_0 u^0 - \underset{\uparrow}{2a_0} u^2$
  $= 2^2 \Rightarrow a_0 = -2$

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

So the mathematically normalized Hermite poly are

$$\left| \begin{array}{l} H_0(u) = 1 \\ H_1(u) = 2u \\ H_2(u) = 4u^2 - 2 \\ H_3(u) = 8u^3 - 12u \\ \quad\vdots \end{array} \right.$$

$\boxed{\text{But as a physics problem, we must "normalize"}}$

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

where $u = \frac{(Cm)^{1/4}}{\sqrt{\hbar}}\, x$ ⇒ get

$$\boxed{A_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{4\pi m\nu}{h}\right)^{1/4}}$$

Using math tables for $H_n(u)$ integrals...

⇒ The normalized wave functions:

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{4\pi m\nu}{h}\right)^{1/4} \cdot e^{-\frac{1}{2}\left[\frac{(Cm)^{1/4}x}{\sqrt{\hbar}}\right]^2} H_n\left(\frac{(Cm)^{1/4}x}{\sqrt{\hbar}}\right)}$$

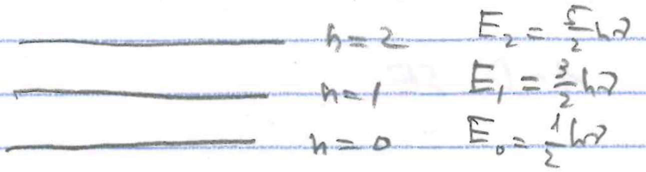
with $E_n = (n+\frac{1}{2})h\nu$ $\quad n = 0, 1, 2, \dots$

So the "full" solution

$(n+\frac{1}{2})h\nu$

$$\boxed{\Psi_n(x,t) = \psi_n(x)\,\Phi(t) = \psi_n(x)\, e^{-iE_nt/\hbar}}$$

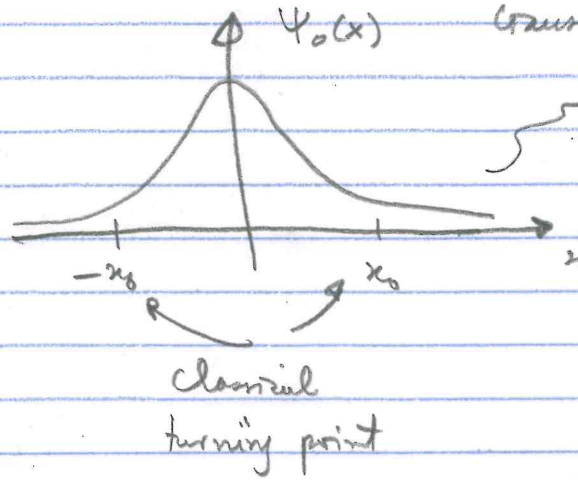
The energies are an infinite tower of equally spaced levels.



Note $E_0 = \frac{1}{2}h\nu \neq 0$

↳ zero-point energy.

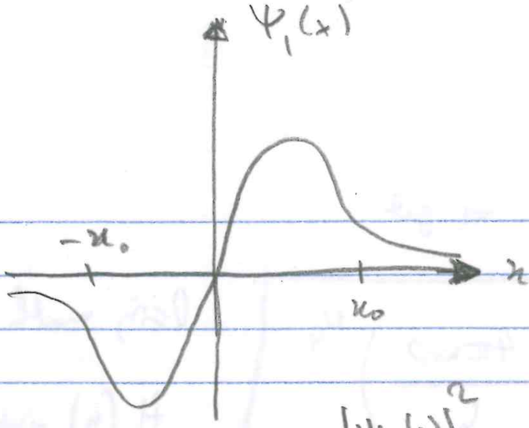
$\boxed{n = 0}$ $\quad \psi_0(x) = (\text{const})\,\underbrace{e^{-\frac{1}{2}(\text{const})x^2}}_{\text{Gaussian}} \cdot (\text{const})$



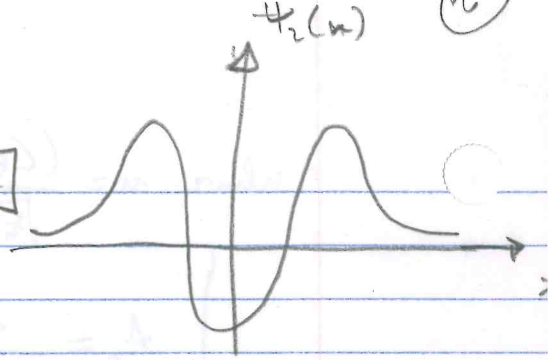
But small probability beyond classical turning point.

$\boxed{n=1}$

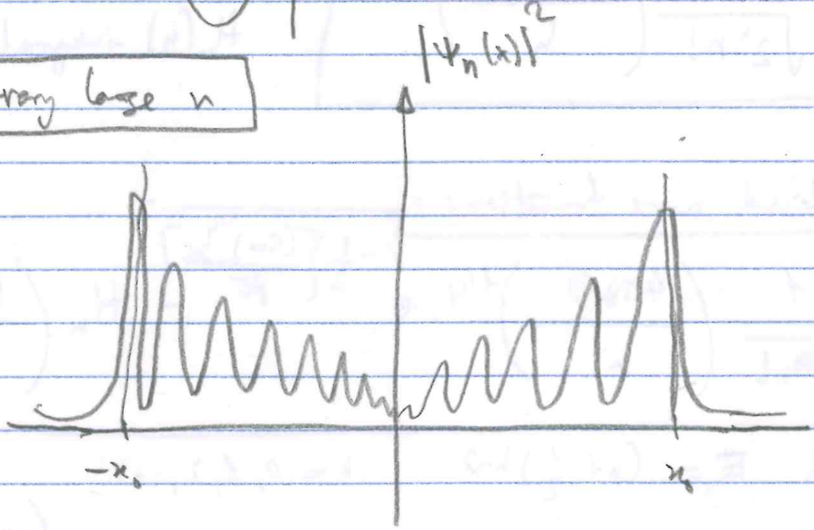
odd fn



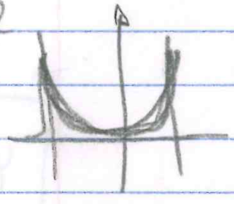
$\boxed{n=2}$



$\boxed{\text{For very large } n}$



classical



⇒ starts to match classical behavior.

Classically, the particle more likely to be found near the turning point.
↳ spends less time near $x = 0$

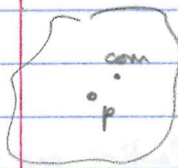
The end of 1-D SE

III. 3-D PROPLEMS & H atom

Mar 14, 2018
π Day

H is a 2-body problem in 3D

$\boxed{\text{2 body}} \longrightarrow$ electron + proton moving about their COM



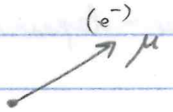
$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$ Coulomb potential

For an ion of nuclear charge Ze $\rightarrow$ $$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

To turn the 2 body problem into equivalent 1 body problem use the **REDUCED MASS**.

$$\mu = \frac{m_e m_p}{m_e + m_p}$$ $\leftarrow$ or use m_{nucleus} for ion with (Ze)

or $\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e}$, The 2 body problem is then equiv. to 1-body problem for mass μ



Same coulomb potential $$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

For H, since $m_p \gg m_e \Rightarrow \boxed{\mu \approx m_e}$

Proof $\left.\begin{array}{l}\vec{r}_1 = \vec{r}_e \text{ from COM} \\ \vec{r}_2 = \vec{r}_p \text{ from COM}\end{array}\right\} \Rightarrow$ Separation: $\boxed{\vec{r} = \vec{r}_1 - \vec{r}_2} \rightarrow$ radial difference between p^+ e^-

Set $\vec{R}_{COM} = \boxed{\frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2} = 0} \Rightarrow$ put COM @ origin.

$\Rightarrow$ Can solve for $\vec{r}_1$, $\vec{r}_2$.

$$\boxed{\vec{r}_1 = \frac{m_2}{m_1+m_2}\vec{r}, \quad \vec{r}_2 = \frac{-m_1}{m_1+m_2}\vec{r}}$$

$$\Rightarrow \left\{\begin{array}{l}\frac{d\vec{r}_1}{dt} = \frac{m_2}{m_1+m_2}\frac{d\vec{r}}{dt} \\ \frac{d\vec{r}_2}{dt} = \frac{-m_1}{m_1+m_2}\frac{d\vec{r}}{dt}\end{array}\right\} \longrightarrow \overset{+VE}{\Sigma KE} = \frac{1}{2}m_1\left(\frac{d\vec{r}_1}{dt}\right)^2 + \frac{1}{2}m_2\left(\frac{d\vec{r}_2}{dt}\right)^2 + V(r)$$

So total energy $\Rightarrow E = \frac{1}{2} m_1 \left(\frac{m_2}{m_1+m_2}\right)^2 \cdot \left(\frac{d\vec{r}}{dt}\right)^2 + \frac{1}{2} m_2 \left(\frac{m_1}{m_1+m_2}\right)^2 \left(\frac{d\vec{r}}{dt}\right)^2 + V($

$\boxed{\text{So}}$ $$\Sigma E = \frac{1}{2} \frac{m_1 m_2}{(m_1+m_2)^2} (m_1+m_2) \left(\frac{dr}{dt}\right)^2 + V(r)$$

$$\hookrightarrow \Sigma E = \frac{1}{2} \frac{m_1 \cdot m_2}{m_1+m_2} \left(\frac{d\vec{r}}{dt}\right)^2 + V(r)$$

$$\boxed{\Sigma E = \frac{1}{2} \mu \left(\frac{d\vec{r}}{dt}\right)^2 + V(r)}$$ → effective one-body problem, with reduced mass μ.

To go to 3D → need to generalize the Schrödinger eq. or upgrade operators.

Recall $\hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$ ← 1D

$\hookrightarrow \hat{H} \Psi(x,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,t)$ ← time-dependent SE

with $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

So $\boxed{\hat{H}_x = \frac{p_x^2}{2m} + V(x)}$

To generalize to 3D → replace $\hat{p}_x^2$ by $\hat{\vec{p}}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$

with $\hat{p}_y = (-i\hbar)\frac{\partial}{\partial y}$, $\hat{p}_z = (-i\hbar)\frac{\partial}{\partial z}$

So replace $$\boxed{\frac{\partial^2}{\partial x^2} \xrightarrow{\text{by}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \vec{\nabla}^2}$$

$\hookrightarrow$ gradient $\vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$

$\boxed{\text{The Laplacian}}$ $= \vec{\nabla}^2 = \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ → ☆

So the momentum operator becomes $\boxed{\hat{\vec{p}} = (-i\hbar)\vec{\nabla}}$

→ $\boxed{\frac{\hat{\vec{p}}^2}{2m} = \frac{-\hbar^2}{2m}\vec{\nabla}^2}$

$\boxed{\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}}$

The potential energy becomes → $\boxed{V(\vec{r})}$

↳ and wavefunction $\boxed{\Psi(\vec{r},t) = \Psi(x,y,z,t)}$

3D - time dependent Schrödinger Eq.

Let $m = \mu$ (reduced mass) ⇒ get 3D SE

↳ Schrödinger eqn

$$\boxed{\frac{-\hbar^2}{2\mu}\vec{\nabla}^2\Psi(\vec{r},t) + V(\vec{r},t)\,\Psi(\vec{r},t) = (i\hbar)\frac{\partial}{\partial t}\Psi(\vec{r},t)}$$

↳ Note, we're using the reduced mass $\mu \approx m_e$.

The interpretation of Ψ is similar to before

↳
- $\Psi(\vec{r},t)$ ← probability amplitude
- $|\Psi(\vec{r},t)|^2$ ← probability per volume of finding particle in $\vec{r}$ to $\vec{r}+d\vec{r}$ at time t.
- $|\Psi(\vec{r},t)|^2 d^3\vec{r}$ ← probability of being in volume $d^3\vec{r}$ @ $\vec{r}$, t.

This should be normalized

$$\boxed{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(\vec{r},t)|^2\, d^3\vec{r} = 1}$$

where $d^3\vec{r} = dx\,dy\,dz$ in Cartesian coordinates.

Calculate expectation values!

$$\boxed{\overline{f(\vec r)} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi^*(\vec r,t)\, f(\vec r)\, \Psi(\vec r,t)\, d^3\vec r}$$

$\hat f(\vec r) = f(\vec r)$

But different for $\hat{\vec p}$

$$\boxed{\hat{\vec p} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi^*(\vec r,t)\, \underbrace{(-i\hbar)\, \vec\nabla}_{\hat{\vec p}}\, \Psi(\vec r,t)\, d^3\vec r} \Rightarrow \text{gives a vector number}$$

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.

$$\boxed{-\frac{\hbar^2}{2m}\vec\nabla^2\psi(\vec r) + V(\vec r)\psi(\vec r) = E\psi(\vec r)}$$

$$\Rightarrow \boxed{\hat H\psi(\vec r) = E\psi(\vec r)} \leftarrow \text{eigenvalue problem.}$$

$\boxed{\text{For H atom}}$ → want to solve for Coulomb potential

$V(\vec{r}) = \frac{-e^2}{4\pi\varepsilon_0 r}$ ⇒ Use Cartesian coordinates where

$r = |\vec{r}|$ magnitude only

$$\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

So $r = \sqrt{x^2+y^2+z^2}$ ← rather complicated...

$$\boxed{V(x,y,z) = \frac{-e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}}$$

Get the time-independent SE for H.

$$\boxed{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y,z) - \frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\psi(x,y,z) = E\psi(x,y,z)}$$

messy! → Too complicated in Cartesian coordinates → stuck...

→ separation of variables DOES NOT work in Cartesian coordinates...

$\boxed{\text{BUT}}$ in Spherical coordinates (r,θ,φ), $V = V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$ only!

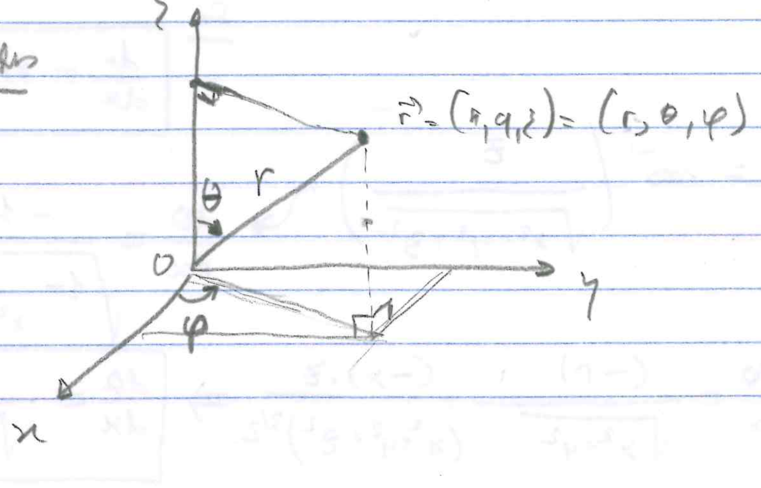
↳ spherically symmetric!

↳ Switching to spherical coordinates (r,θ,φ) → let us use separation of variables...

Spherical coordinates

These are related

$$\left\{\begin{array}{l} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{array}\right\}$$



Can invert these $\longrightarrow$
$$\left\{\begin{aligned} r &= \sqrt{x^2+y^2+z^2} \\ \theta &= \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right) \\ \varphi &= \tan^{-1}\left(\frac{y}{x}\right) \end{aligned}\right\}$$

But what does $\vec{\nabla}^2$ become?

what is $\dfrac{\partial^2}{\partial x^2}+\dfrac{\partial^2}{\partial y^2}+\dfrac{\partial^2}{\partial z^2}$?
$$\left.\begin{aligned} x &= r\sin\theta\cos\varphi \\ y &= r\sin\theta\sin\varphi \\ z &= r\cos\theta \end{aligned}\right.$$

Nov 16, 2018

Recall $V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$ → central potential, spherically symmetric
↳ has no θ, φ dep in spherical coordinate (r,θ,φ)
→ separation of variables should work

→ Need to convert SE 3D to spherical coordinates.

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi + V(r)\psi = E\psi \quad \text{need } \underline{\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}} \text{ in spherical "}$$

Now $x = x(r,\theta,\varphi)$

Chain rule
$$\boxed{\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi}}$$

what are these?

Now $r = \sqrt{x^2+y^2+z^2}$
$$\frac{dr}{dx} = \frac{x}{\sqrt{x^2+y^2+z^2}} = \frac{x}{r} = \frac{r\sin\theta\cos\varphi}{r}$$

So
$$\boxed{\frac{dr}{dx} = \sin\theta\cos\varphi}$$

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right) \longrightarrow \frac{d\theta}{dx} = \frac{-1}{\sqrt{1-\frac{z^2}{x^2+y^2+z^2}}}\cdot\frac{\partial}{\partial x}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

$$\Rightarrow \frac{d\theta}{dx} = \frac{(-r)}{\sqrt{x^2+y^2}}\,\frac{(-x)\cdot z}{(x^2+y^2+z^2)^{3/2}} \Rightarrow \boxed{\frac{d\theta}{dx} = \frac{xz}{\sqrt{x^2+y^2}}\cdot\frac{1}{r^2}}$$

$$\rightarrow \frac{d\theta}{dx} = \frac{(r^2 \cdot \sin\theta\cos\varphi)\cos\theta}{\sqrt{r^2\sin\theta^2\cos\varphi^2 + r^2\sin\theta^2 \cdot \sin^2\varphi}} \cdot \frac{1}{r^2} = \boxed{\frac{\cos\theta\cos\varphi}{r} = \frac{d\theta}{dx}}$$

and $\boxed{\frac{d\varphi}{dx} = \frac{-\sin\varphi}{r\sin\theta}}$ (with $\theta = \tan^{-1}\left(\frac{y}{x}\right)$)

So $$\boxed{\frac{\partial}{\partial x} = (\sin\theta\cos\varphi)\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\varphi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{-\sin\varphi}{r\sin\theta}\right)\frac{\partial}{\partial\varphi}}$$

→ 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) → 'called a "central potential"

→ Can use separation of variables! → 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 $\boxed{\vec{\nabla}^2\Psi + \frac{2m}{\hbar^2}(E - V(r))\Psi = 0}$

$$\rightarrow \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}(RY)\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(RY)\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}(RY) + \frac{2m}{\hbar^2}(E - V(r))\,RY = 0\right.$$

→ Divide by RY + multiply by r^2

$$\rightarrow \boxed{\frac{1}{R(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{dR(r)}{dr}\right)+\frac{2m}{\hbar^2}\left(E-V(r)\right)r^2R(r)\right] + \frac{1}{Y(\theta,\varphi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial Y(\theta,\varphi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}Y(\theta,\varphi)\right]=0}$$

Notice [1st term is a function of r ; 2nd term is a fn of θ, φ } → But eqn has to hold true ∀ r, θ, φ]

↳ ⟺ Both terms add to 0, and = constant

⇒ if $\left\{\begin{array}{l}1^{st}\text{ term} = \lambda \\ 2^{nd}\text{ term} = -\lambda\end{array}\right\} \rightarrow \lambda + (-\lambda) = 0$

Now 1st term becomes (div by r^2, mult by R)

Radial eqn
$$\boxed{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\frac{2m}{\hbar^2}\left(E-V(r)\right)R(r)-\frac{\lambda}{r^2}R(r)=0}$$

2nd term becomes : Multiply by $-Y$ — angular momentum operator

Angular eqn
$$\boxed{-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)=\lambda Y(\theta,\varphi)} \rightarrow \text{eigen problem}$$

Note : get same angular eqn + solutions $Y(\theta,\varphi)$ for any central potential $V(r)$

The full solution is a product $\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$

$$\hookrightarrow \boxed{\Psi=\psi(r,\theta,\varphi)\,\phi(t)}$$

For H $\Rightarrow V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$

Outline what we'll see → need to solve using the power series method

↳ also need to separate $\boxed{Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)}$

↳ The answers will be:

Radial solutions → depend on 2 quantum number

$$\begin{cases} n = 1, 2, 3 \ldots & \leftarrow \text{principal} \\ l = 0, 1, 2 \ldots (n-1) & \leftarrow \text{angular} \end{cases}$$

↳ So $\boxed{R_{n,l}(r) = \text{special functions} \longrightarrow \text{exponential times poly}(r)}$

Angular solutions → depend on $\begin{cases} l = 0, 1, \ldots n-1 & \leftarrow \text{ang} \\ m_l = 0, \pm 1, \ldots \pm l & \leftarrow \text{mag} \end{cases}$

$$\boxed{Y_{l,m_l}(\theta,\varphi) = \text{polys in} (\cos\theta) \text{ and } e^{i\varphi}}$$

↳ called "spherical harmonics"

The full solutions are

$$\boxed{\Psi_{n,l,m_l}(r,\theta,\varphi) = \overset{\text{radial}}{R_{n,l}(r)}\ \overset{\text{angular}}{Y_{l,m_l}(\theta,\varphi)}}$$

The 3 integers: n, l, m_l are quantum number where:

$$\left\{ \begin{array}{l} n: \text{quantized } E \\ l: \text{quantizes } L^2 \\ m_l: \text{quantizes } L_z \end{array} \right\}$$

→ Quantization is a result of using the power series method.
→ like in SHO (quantization ...)

Also the separation constant $\boxed{\lambda = l(l+1)}$ and $\boxed{E_n = \dfrac{-me^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = \dfrac{-13.6}{n^2}}$

Interestingly, $\boxed{E_n = \frac{-me^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = \frac{-13.6\,eV}{n^2}}$ ← same result found by Bohr

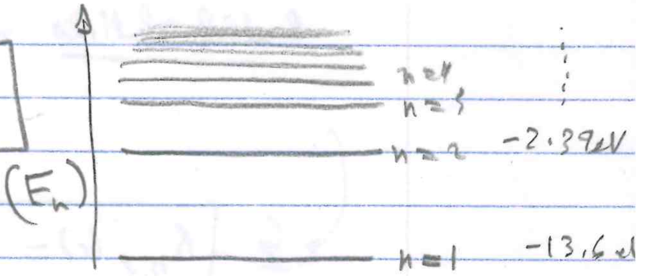
↳ comes from solving SE.

▣ Have 3 quantum numbers

$$\begin{cases} n = 1, 2, 3, \ldots \\ l = 0, 1, 2, \ldots (n-1) \\ m_l = 0, \pm 1, \pm 2, \ldots \pm l \end{cases}$$

But note $\boxed{E_n \text{ only depends on } n}$

↳ Energy levels are degenerate



For each n, there $\boxed{l = 0, 1, 2, \ldots (n-1)}$

↳ $\boxed{n \text{ states of different } l\text{, and for each } l \quad m_l = 0, \pm 1, \ldots \pm l}$

↳ 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

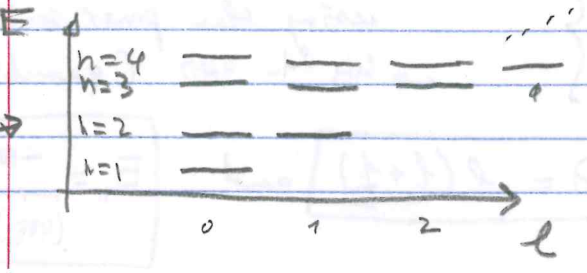
W/o spin

$$\begin{cases} n = 1 \rightarrow 1 \text{ state} \\ n = 2 \rightarrow 4 \text{ states} \\ n = 3 \rightarrow 9 \text{ states} \end{cases}$$

so that the deneracy $= n^2$ for the n^{th} level in H (note w/o spin)

Can also display states differently.

for H only →



"It's common to use spectroscopic notation →

Spectroscopic notation → $\ell = 0$: s states
$\ell = 1$: p states
$\ell = 2$: d states
$\ell = 3$: f states
...

$\boxed{\text{Table 7-2}}$ → shows $\Psi_{n\ell m_\ell}$ states for H

$Z = 1$ for H , $\boxed{a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 0.529\,\mathring{A}}$ ← Bohr radius

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

Now, where do these $\Psi_{n\ell m_\ell}$ come from?

↳ need to solve the angular & radial solution:

separation const

$$\boxed{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \frac{2\mu}{\hbar^2}\left(E - \underset{\uparrow\ -\frac{e^2}{4\pi\epsilon_0 r}}{V(r)}\right)R(r) - \frac{\lambda}{r^2}R(r) = 0}$$

Angular eqn

$$\boxed{-\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) + \frac{1}{\sin^2\theta}\frac{d^2}{d\varphi^2}\right]Y(\theta,\varphi) = \lambda Y(\theta,\varphi)}$$

note : the form is an operator, Y = number . Y
↳ eigen problem!
↳ so what is this operator?

↳ can show that the operator is related to $\hat{L}^2$ (angular p op^2)

ANGULAR MOMENTUM IN QM

Classically: $\boxed{\vec{L} = \vec{r} \times \vec{p}}$ → $\begin{cases} L_x = yP_z - zP_y \\ L_y = zP_x - xP_z \\ L_z = xP_y - yP_x \end{cases}$

and $L^2 = L_x^2 + L_y^2 + L_z^2$

In QM, p_x, p_y, p_z becomes operators!

$$\hookrightarrow \boxed{\hat{p}_x = -i\hbar\frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}}$$

$$\hookrightarrow \boxed{\begin{aligned} \hat{L}_x &= (-i\hbar)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y &= (-i\hbar)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z &= (-i\hbar)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \\ \Rightarrow \hat{L}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \end{aligned}} \longrightarrow$$

need to change into spherical coordinates! So they can act on $\psi(r,\theta,\varphi)$

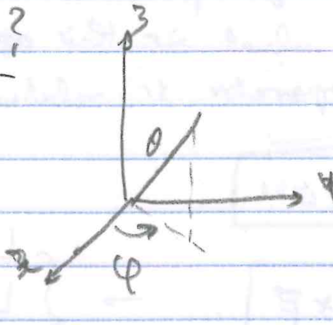
To do this, use the chain rule.

let $x = x(r,\theta,\varphi)$ $\rightarrow \boxed{\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi}}$

↳ spend some time dealing with this...

$$\hookrightarrow \boxed{\begin{aligned} \hat{L}_x &= (i\hbar)\left(\sin\varphi\frac{\partial}{\partial \theta} + \cot\theta\cos\varphi\frac{\partial}{\partial \varphi}\right) \\ \hat{L}_y &= (i\hbar)\left(-\cos\varphi\frac{\partial}{\partial \theta} + \cot\theta\sin\varphi\frac{\partial}{\partial \varphi}\right) \\ \hat{L}_z &= (i\hbar)\left(-\frac{\partial}{\partial \varphi}\right) \end{aligned}}$$

Why is z simpler?



{ φ naturally rotates about z. }

Lastly, find $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ ← important...

↳ get $$\boxed{\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]}$$

<u>Note</u> $\hat{L}^2$ very similar to $\overset{\text{angular}}{Y(\theta,\varphi)}$! → same operator as in that in $Y(\theta,\varphi)$!

↳ $$\boxed{\hat{L}^2 Y(\theta,\varphi) = \lambda\hbar^2 Y(\theta,\varphi)}$$ ← angular eq becomes an eigenvalue problem.

Units → $L \sim \hbar$ units.

<u>Later</u> will show → $\lambda = \ell(\ell+1)$ $(\ell = 0, 1, 2 \dots)$

↳ then have $\hat{L}^2 Y(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y(\theta,\varphi)$

Eigenvalues of $\hat{L}^2$ are $\boxed{(\ell)(\ell+1)\hbar^2}$

Remember that eigenvalues are <u>exact</u>

<u>Here that</u>
$$\boxed{\begin{aligned}\hat{H}\psi_{n,\ell,m_\ell} &= E\psi_{n,\ell,m_\ell}\\ \hat{L}^2\psi_{n,\ell,m_\ell} &= \ell(\ell+1)\hbar^2\psi_{n,\ell,m_\ell}\end{aligned}}$$

<u>and</u> we'll also come see that

$$\boxed{\hat{L}_z\psi_{n\ell m_\ell} = (m_\ell\hbar)\,\psi_{n\ell m_\ell}}$$

↖ z component of L

<u>But</u> still has uncertain values for L_x, L_y

Solving the angular eqn

$$\boxed{-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)=\lambda Y(\theta,\varphi)}$$

where : λ : separation constant ...

↳ suppose $\boxed{Y(\theta,\varphi)=\Theta(\theta)\,\Phi(\varphi)}$

↳ plug in + divide by $\Theta\Phi$

so, get : $-\frac{1}{\Theta(\theta)}\cdot\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\Theta(\theta)\right)-\frac{1}{\Phi(\varphi)}\cdot\frac{1}{\sin^2\theta}\frac{d^2\Phi(\varphi)}{d\varphi^2}-\lambda=0$

multiply by $\sin^2\theta$

$$\boxed{+\underbrace{\frac{\sin\theta}{\Theta(\theta)}\cdot\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right)}_{\theta\text{ dep.}}\underbrace{+\frac{1}{\Phi(\varphi)}\frac{d^2\Phi(\varphi)}{d\varphi^2}}_{\varphi\text{ dep}}=0}$$

$+\lambda\sin^2\theta$

(q) $(-q)$

→ q = separation constant → get 2 ODE.

need power series method

$$\boxed{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right)+\left(\lambda\sin^2\theta\right)\Theta(\theta)=q\,\Theta(\theta)}$$

and $\boxed{\frac{1}{\Phi(\varphi)}\frac{d^2\Phi(\varphi)}{d\varphi^2}=-q}\rightarrow\boxed{\frac{d^2\Phi}{d\varphi^2}=-\Phi(\varphi)\,q}$ can get soln

For $\Phi(\varphi)$ we guess → $e^{i\sqrt{q}\varphi}$, $e^{-i\sqrt{q}\varphi}$ (to be continued...)

Mar 21, 2018

Recall Angular Eqn

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)=\lambda Y(\theta,\varphi)$$

$$\boxed{\hat{L}^2 Y(\theta,\varphi)=\lambda\hbar^2\psi(\theta,\varphi)}$$

separation constant!

Separate again $Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$

↳ get 2 ODEs ⇒

sep. const

$$\boxed{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right)+\left(\lambda\sin^2\theta\right)\Theta(\theta)=q\,\Theta(\theta)}$$

and $\boxed{\dfrac{d^2\Phi(\varphi)}{d\varphi^2}=-q\,\Phi(\varphi)}\rightarrow\Phi(\varphi)=e^{i\sqrt{q}\Phi}+e^{-i\sqrt{q}\Phi}$

As good solutions, Φ must be single-valued

↳ must require: $\Phi(\varphi)=\Phi(\varphi+2\pi)$

↳ So $e^{i\sqrt{q}\varphi}=e^{i\sqrt{q}(\varphi+2\pi)}\Leftrightarrow 1=e^{i\sqrt{q}(2\pi)}$

↳ $\boxed{1=\cos(\sqrt{q}\,2\pi)+i\sin(\sqrt{q}\,2\pi)}$

↳ need $\sqrt{q}=0,1,2,3,\dots$

Call m_ℓ = integer ⇒ $q=m_\ell^2$

So solution $\boxed{\Phi(\varphi)=e^{im_\ell\varphi}}$

We can include $e^{-im_\ell\varphi}$ solution as well, by letting $m_\ell<0$

↳ $m_\ell=\{\pm0,\pm1,\pm2,\dots\}$

Notice what we get if $\hat{L}_z=-i\hbar\dfrac{\partial}{\partial\varphi}$ acts on $\Phi(\varphi)=e^{im_\ell\varphi}$

↳ $\hat{L}_z \Phi(\varphi) = (-i\hbar)\frac{\partial}{\partial\varphi}\Phi(\varphi) = (-i\hbar)(im_\ell)\,e^{im_\ell\varphi}$

↳ $\boxed{\hat{L}_z \Phi(\varphi) = m_\ell\hbar\,\Phi(\varphi)}$ → get $m_\ell\hbar = L_z$ eigenvalues

(also quantized)

Note that $\sin(\sqrt{q}\,\varphi)$ or $\cos(\sqrt{q}\,\varphi)$ would not give this result...

⇒ Better to use $e^{im_\ell\varphi}$, since these have definite L_z values labeled by m_ℓ

With $q = m_\ell^2$

$$\boxed{\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right) + \left(\lambda\sin^2\theta - \overset{q}{m_\ell^2}\right)\Theta(\theta) = 0}$$

divide by $\sin^2\theta$

$$\boxed{\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta\right) + \left(\lambda - \frac{m_\ell^2}{\sin^2\theta}\right)\Theta = 0} \quad (*)$$

too complicated as a fn of θ

↳ to solve $\boxed{\text{let } z = \cos\theta}$

↳ chain rule $\boxed{\frac{d}{d\theta} = \frac{dz}{d\theta}\frac{d}{dz} = -\sin\theta\frac{d}{dz} = -\sqrt{1-z^2}\frac{d}{dz}}$ (**)

So $\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta\right) = \frac{1}{\sqrt{1-z^2}}\left(-\sqrt{1-z^2}\right)\frac{d}{dz}\left(\sqrt{1-z^2}\cdot\left(-\sqrt{1-z^2}\right)\frac{d\Theta}{dz}\right)$

$= \frac{d}{dz}\left((1-z^2)\frac{d}{dz}\right)\Theta$

associated Legendre eqn

So (*) becomes $\boxed{\frac{d}{dz}\left([1-z^2]\frac{d\Theta}{dz}\right) + \left(\lambda - \frac{m_\ell^2}{\sqrt{1-z^2}}\right)\Theta = 0}$

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 solns as $\Theta_{\ell, m_\ell}(z) = \Theta_{\ell, m_\ell}(\cos\theta)$

To get an eq. that can be solved using the power series method, let

$$\boxed{\Theta_{l m_l}(z) = (1-z^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|} P_l(z)}{dz^{|m_l|}}}$$

↳ plug in.... $$\boxed{(1-z^2)\frac{d^2 P_l}{dz^2} - 2z\frac{dP_l}{dz} + \lambda P_l = 0} \quad (L)$$ ← Legendre's equation

To verify that this works, would need to take $|m_l|$ derivatives of Legendre's eqn + show it gives back the Associated Legendre eq (we won't do this)

(L) can be solved using the power series method!

Let $$\boxed{P_l(z) = \sum_{k=0}^{\infty} a_k z^k}$$ (Recall: $z = \cos\theta$)

↳ plug into (L) and find recursion relation for a^k, get:

$$\boxed{a_{k+2} = \frac{k(k+1)-\lambda}{(k+2)(k+1)} a_k}$$

↳ get 2 series: $\left\{ \begin{array}{l} \text{one with even powers,} \\ \text{one with odd powers.} \end{array} \right\}$

But find that the full infinite power series is divergent.
→ need to truncate it. (just like in SHO)

↳ So for some k value, say $k = l$ where $l = 0, 1, 2, \ldots$
require that $a_{l+2} = \frac{l(l+1)-\lambda}{(l+2)(l+1)} a_l = 0$ ← so that the series stops.

Must require that $\boxed{\lambda = l(l+1)}$ then P_l does not diverge

$(l = 0, 1, 2, \ldots)$

The solutions are then finite polynomials of order l

$$\boxed{P_l(z) = \text{Legendre Polynomials}}$$

↳ even powers for l even
odd powers for l odd

Normalized in math $\longrightarrow \boxed{P_l(1) = 1}$

The first few Legendre's polys are

$$P_0(z) = 1$$
$$P_1(z) = z$$
$$P_2(z) = \frac{1}{2}(3z^2 - 1)$$
$$P_3(z) = \frac{1}{2}(5z^3 - 3z)$$
$$\vdots$$

but remember that $\boxed{z = \cos\theta}$

Note Appendix N in book uses a nonstandard normalization

But what about the associated Legendre equations? ↘ $\Theta_{l,m_l}(z)$

Use

$$\Theta_{lm_l}(z) = (1-z^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|} P_l(z)}{dz^{|m_l|}}$$

Note since $P_l(z)$ is a poly of order l, then if $|m_l| > l$ ⇒ we get 0

↳ So we get condition: $\boxed{|m_l| \leq l}$

$\boxed{m_l = 0, \pm 1, \pm 2, \ldots \pm l}$ as allowed values ...

Note the book denotes derivatives as

$$\boxed{F_{l,m_l}(\cos\theta) = \frac{d^{|m_l|} P_l(z)}{dz^{|m_l|}}} \leftarrow \text{non standard} \rightarrow \Theta_{l,m_l}(\theta) = \sin\theta \, F_{l,m_l}(\cos$$

So the full angular solutions

$$\boxed{Y_{\ell,m_\ell}(\theta,\varphi) = \Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)}$$

called "spherical harmonics"

assc. Legendre equation

z component

this is λ

these obey

$$\boxed{\begin{aligned}\hat{L}^2 Y_{\ell,m_\ell} &= (\ell+1)\ell\hbar^2 Y_{\ell,m_\ell}\\ \hat{L}_z Y_{\ell,m_\ell} &= m_\ell \hbar Y_{\ell,m_\ell}\end{aligned}}$$

Note $\left\{\begin{array}{l} |\vec{L}| = \sqrt{\ell(\ell+1)}\,\hbar \quad \leftarrow \text{magnitude} \\ L_z = m_\ell\hbar \qquad m_\ell = 0, \pm1, \pm2, \dots \pm\ell \end{array}\right.$

$\rightarrow$ $(2\ell+1)$ values!

//

Summary on how to solve $\Psi(\vec{r},t)$

So $\Psi(r,t) \rightarrow \phi(t) = e^{-iEt/\hbar}$

$\rightarrow \psi(\vec{r}) = \psi(r,\theta,\varphi)$

} separation const $= \boxed{E}$

$\psi(\vec{r}) \rightarrow R(r)$ and $Y(\theta,\varphi)$

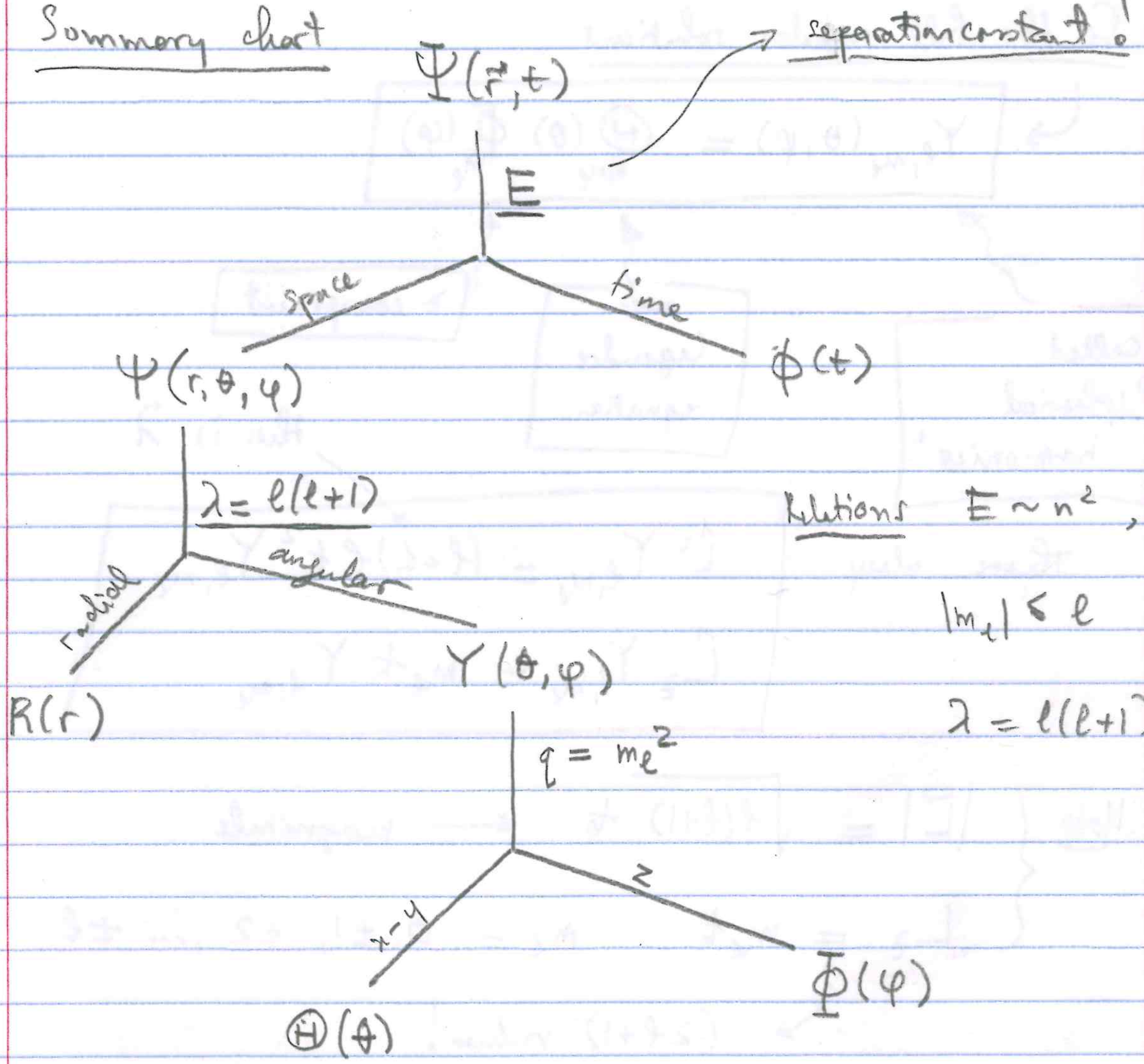
$R(r)$ separation constant $= \boxed{\lambda}$ $Y(\theta,\varphi)$

$Y(\theta,\varphi) \rightarrow \Theta(\theta)$ and $\Phi(\varphi)$

$\Theta(\theta)$ $\boxed{q = m_\ell^2}$ $\Phi(\varphi)$

Relations $\left\{\begin{array}{l} E \sim n^2, \ \ell \le n-1 \\ \lambda = (\ell+1)\ell \\ |m_\ell| \le \ell \end{array}\right\}$

Summary chart



Relations $E \sim n^2$, $n-1 \geq \ell$

$|m_\ell| \leq \ell$

$\lambda = \ell(\ell+1)$

Operators

z-angular mom • $\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi} \rightsquigarrow \Phi(\varphi) = e^{i\sqrt{q}\varphi} = e^{i m_\ell \varphi}$

So $\hat{L}_z \Phi(\varphi) = (m_\ell \hbar)\Phi(\varphi)$

angular mom • $\hat{L}^2 Y(\theta,\varphi) = \lambda\hbar^2 Y(\theta,\varphi) \rightsquigarrow \hat{L}^2 Y(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y(\theta,\varphi)$

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

Energy • Time-ind $\hat{H}\psi_{n,\ell,m_\ell} = E\psi_{n,\ell,m_\ell}$

Mar 23, 2018

Spherical Harmonics
$$\begin{cases} \hat{L}^2 Y_{\ell, m_\ell}(\theta, \varphi) = \ell(\ell+1)\hbar^2 Y_{\ell, m_\ell}(\theta, \varphi) \\ \hat{L}_z Y_{\ell, m_\ell}(\theta, \varphi) = m_\ell \hbar Y_{\ell, m_\ell}(\theta, \varphi) \end{cases}$$

where $\ell = 0, 1, \ldots$
$m_\ell = 0, \pm 1, \ldots$

We have for $\vec{L}$: $\boxed{\begin{aligned} |\vec{L}| &= \sqrt{\ell(\ell+1)}\,\hbar \\ \text{and } |\vec{L}_z| &= m_\ell \hbar \end{aligned}}$ ← quantized.

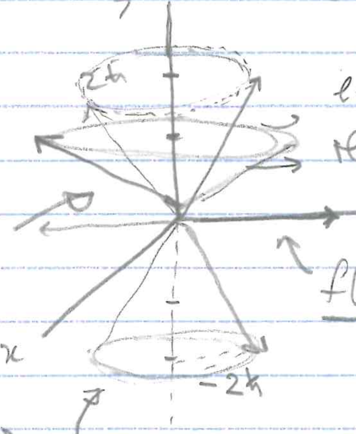
Ex let's draw a diagram for $\vec{L}$ in an $\ell = 2$ state

$$\ell = 2 \begin{cases} m_\ell = 0 \\ m_\ell = \pm 1 \\ m_\ell = \pm 2 \end{cases}$$

⇒ $|\vec{L}| = \sqrt{6}\,\hbar$ ← 1 orientation.

but $|\vec{L}_z| = \{0, \pm\hbar, \pm 2\hbar\}$

↑ 5 orientations



$\ell = 2$, $\hat{m}_z = \pm 2\hbar$
this is a cone → we don't know anything about the other components.

cone

flattened cone.

↳ we have exact value for $|\vec{L}|$, but $|\vec{L}_x|$ & $|\vec{L}_y|$ components are determined exactly

$|\vec{m}_\ell| = -2\hbar$

$$\begin{cases} \Delta x \Delta p_x \geq \frac{\hbar}{2} \\ \Delta y \Delta p_y \geq \frac{\hbar}{2} \end{cases}$$

← due to uncertainty relations.

THE RADIAL SOLUTION

→ will only outline how to solve for the radial wave function ($R(r)$)

↖ $R(r)$

→ uses power series method (See Appendix N)

Recall
$$\boxed{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r}\right]R = \ell(\ell+1)\frac{R}{r^2}}$$

(Expand

↑ $-V(r)$ ↑ λ

$$\boxed{\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r}\right]R = \ell(\ell+1)\frac{R}{r^2}}$$

↳ power series method won't work yet...

⇒ Extract parts of the solution...

- Can solve for $r \to \infty$ ⇒ $\boxed{\frac{d^2R}{dr^2} - \beta^2 R \cong 0}$

where $\boxed{\beta^2 = \frac{-2\mu E}{\hbar} > 0}$

Expect $E < 0$ for H atom bound states. Has solution: $R = e^{-\beta r}$

- Can also solve for $r \to 0$
  ↳ dominant terms in this limit are:

$$\boxed{\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} \simeq \frac{\ell(\ell+1)}{r^2} R}$$

This has solutions: $\boxed{R = r^\ell}$ ← will verify in homework...

Trial solution

$$\boxed{R(r) = r^\ell e^{-\beta r} G(r)}$$

Get an eq. for $G(r)$ that can be solved via the power series method
⇒ Find that the series diverges unless we truncate it

$$\boxed{E_n = \frac{-\mu e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = -13.6\text{ eV}\ \frac{1}{n^2}}$$

Note $n \neq 0$

- and $n = \cancel{0}, 1, 2, \ldots (\ell+1)$ or $\boxed{\ell \leq n-1}$

The solutions have the form ⇒

$$\boxed{R(r) = e^{-\frac{r}{na_0}} \cdot \left(\frac{r}{a_0}\right)^\ell G_{n,\ell}\left(\frac{r}{a_0}\right)}$$

where $\boxed{a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = 0.529\text{ Å}}$ ← Bohr radius

To summarize the exact solution to H atom

$$\boxed{\begin{aligned}\psi_{n,l,m_l}(r,\theta,\varphi) &= R_{n,l}(r)\cdot Y_{l,m_l}(\theta,\varphi)\\ &= R_{n,l}(r)\cdot\Theta_{l,m_l}(\theta)\,\Phi_{m_l}(\varphi)\end{aligned}}$$

↳ Quantum numbers obey: $\begin{cases} n = 1, 2, \ldots \\ l = 0, 1, \ldots\ n-1 \\ m_l = 0, \pm 1, \ldots\ \pm l \end{cases}$

Energies:

$$\boxed{E_n = \frac{-\mu e^4}{(4\pi\varepsilon_0)^2\, 2\hbar^2 n^2} = (-13.6\,\text{eV})\frac{1}{n^2}} \leftarrow E \text{ degenerate for } l, m_l$$

Note

↳ solutions are simultaneous of 3 operators

$$\boxed{\begin{aligned}\hat{H}\psi_{nlm_l} &= E_n\psi_{n,lm_l}\\ \hat{L}^2\psi_{n,lm_l} &= l(l+1)\hbar^2\psi_{n,l,m_l}\\ \hat{L}_z\psi_{nlm_l} &= m_l\hbar^2\psi_{n,l,m_l}\end{aligned}} \longrightarrow \text{Can look up } \psi_{nl,m_l} \text{ in Table 7-2}$$

What do solutions look like?

PROBABILITY DENSITIES The full time dep solns are

$$\Psi_{nlm_l}(\vec{r},t) = \psi_{n,l,m_l}(\vec{r})\,e^{-iE_nt/\hbar}$$

↳ But p. density (per volume)

$$\hookrightarrow |\Psi|^2 = |\psi_{nlm_l}|^2 \longrightarrow \text{no } t\text{-dep} \longrightarrow \text{stationary states!}$$

With $\Psi_{n\ell m_\ell} = R_{n\ell}\,\Theta_{\ell m_\ell}\,\Phi_{m_\ell}$

So $|\Psi_{n\ell m_\ell}|^2 = R^*_{n\ell}R_{n\ell}\,\Theta^*_{\ell m_\ell}\Theta_{\ell m_\ell}\,\Phi^*_{m_\ell}\Phi_{m_\ell}$

But remember $\Phi_{m_\ell} = e^{i m_\ell \varphi} \rightarrow \Phi^*\Phi = 1$

So $|\Psi|^2$ is symmetric about z-axis (z-L is conserved...)

So $\boxed{|\Psi_{n\ell m_\ell}|^2 = R^*_{n\ell}R_{n\ell}\,\Theta^*_{\ell m_\ell}\Theta_{\ell m_\ell}}$ (since $\Phi^*\Phi = 1$)

These are normalized so that:

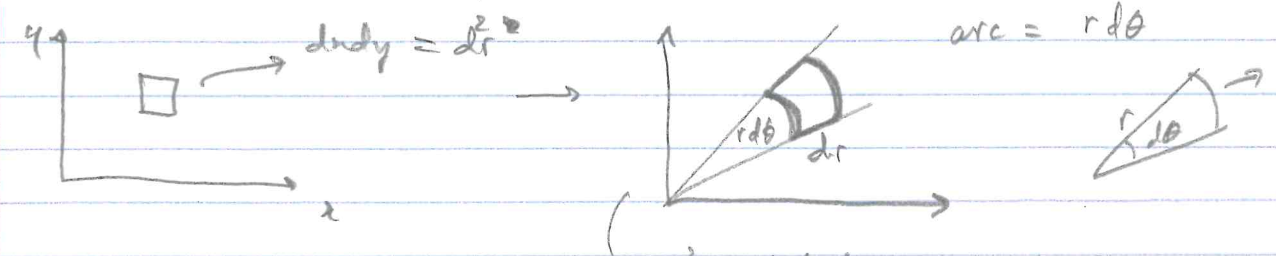
$$\boxed{\iiint |\Psi_{n\ell m_\ell}|^2\, d^3r = 1}$$

In Cartesian coordinates

$\rightarrow d^3r = dx\,dy\,dz$ and $\iiint = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}$

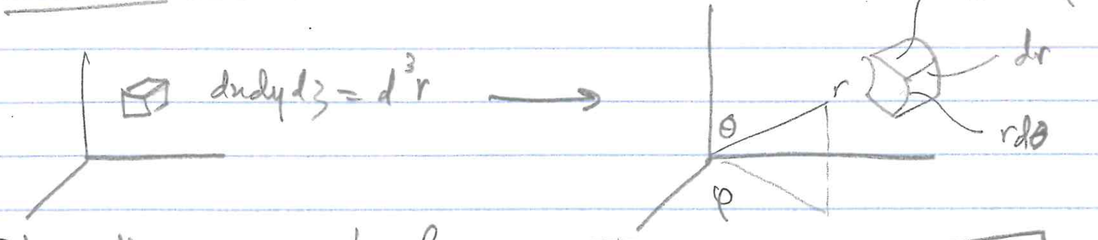
But what is d^3r in spherical coordinates? → Jacobian!

First, look in 2d @ polar coordinates



$d^2r = r\,d\theta\,dr$

So In 3D ...



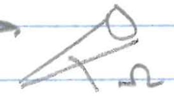
Integration ranges also change

$\boxed{d^3r = r^2\sin\theta\,dr\,d\theta\,d\varphi}$

$0 \leq r \leq \infty$
$0 \leq \theta \leq \pi$
$0 \leq \varphi \leq 2\pi$

So Int becomes $$\boxed{\int_0^\infty\int_0^\pi\int_0^{2\pi}\Psi^*_{n\ell m_\ell}\Psi_{n\ell m_\ell}\, r^2\sin\theta\, dr\, d\theta\, d\varphi} = 1$$

will often use solid angle



$$\boxed{d\Omega = \sin\theta\, d\theta\, d\varphi}$$

(unit sphere of radius 1) → $\iint d\Omega = 4\pi$ → angular opening inside a cone.

So...

$$\boxed{1 = \int_0^\infty R^*_{n\ell}R_{n\ell}\, r^2 dr \int_0^\pi\int_0^{2\pi}\Theta^*_{\ell m_\ell}(\theta)\,\Theta_{\ell m_\ell}\sin\theta\, d\theta\, d\varphi}$$

By convention, the angular part is normalized to 4π

↳ $$\boxed{1 = \int_0^\infty R^*_{n\ell}(r)\, R_{n\ell}(r)\, \underbrace{4\pi r^2}_{\text{surface of sphere}} dr}$$ ⇒ can define a radial probability distribution!

April 2, 2018 Recall $\Psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)$

↳ operators
$$\hat H\Psi = E\Psi$$
$$\hat L^2\Psi = \ell(\ell+1)\hbar^2\Psi$$
$$\hat L_z\Psi = m_\ell\hbar\Psi$$

Normalized → $$1 = \int_0^\infty\int_0^\pi\int_0^{2\pi}\Psi^*\Psi\, \underbrace{r^2\sin\theta\, dr\, d\theta\, d\varphi}_{d^3r}$$

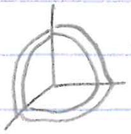
Also $d^3r = r^2 dr\, d\Omega$ where $d\Omega = \sin\theta\, d\theta\, d\varphi$ (opening of a cone)

Recall $\Phi_{m_\ell} = e^{im_\ell\varphi}$ so $\Phi^*\Phi = 1$

So $$1 = \int_0^\infty R^*_{n\ell}R_{n\ell}\, r^2 dr \int_0^\pi\int_0^{2\pi}\Theta^*_{\ell m_\ell}(\theta)\,\Theta_{\ell m_\ell}(\theta)\,\overbrace{\sin\theta\, d\theta\, d\varphi}^{d\Omega}$$

By convention, normalize $\boxed{\int_0^{\pi}\int_0^{2\pi} \Theta^* \Theta \sin\theta \, d\theta \, d\phi = 4\pi}$

So that leaves a purely radial distribution:



$$\boxed{1 = \int_0^{\infty} R^*_{n\ell}(r) R_{n\ell}(r) \underbrace{4\pi r^2 dr}_{dV}}$$

→ volume between 2 shells of radii r and r+dr

With this, we can define a radial probability dist

$$\boxed{P_{n\ell}(r)dr = R^*_{n\ell}(r) R_{n\ell}(r) \cdot 4\pi r^2 dr}$$

↳ probability of e^- between r and r+dr

Note, $P_{n\ell}(r)dr$ includes "r^2" factor from the volume element d^3r

By itself

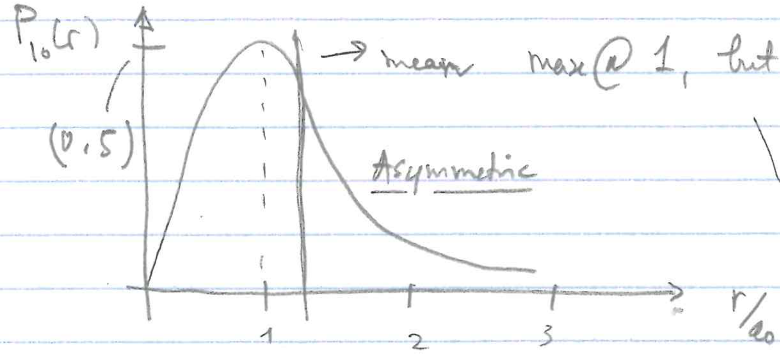
$$\boxed{\begin{aligned} P_{n\ell}(r) &= R^*_{n\ell}(r) R_{n\ell}(r) \, 4\pi r^2 \\ P_{n\ell}(r) &= |R_{n\ell}(r)|^2 \, 4\pi r^2 \end{aligned}}$$

→ probability per length in radial direction

↳ normalized $\int_0^{\infty} P_{n\ell}(r) = 1$

Now, we can look at plots of $P_{n\ell}(r)$ for the radial dist → Figure 7.5

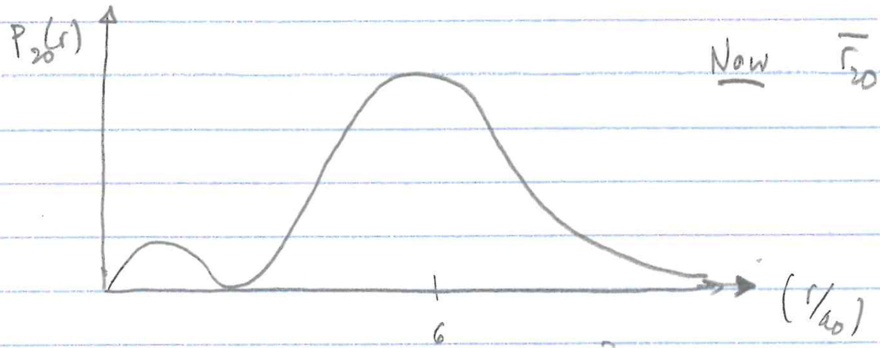
Ex $n=1$, $\ell=0$: $P_{10} \approx r^2 e^{-2r/a_0}$ (for H atom)



max @ 1, but $\boxed{\bar{r}_{10} \simeq 1.5 a_0}$ → average pos of e^-

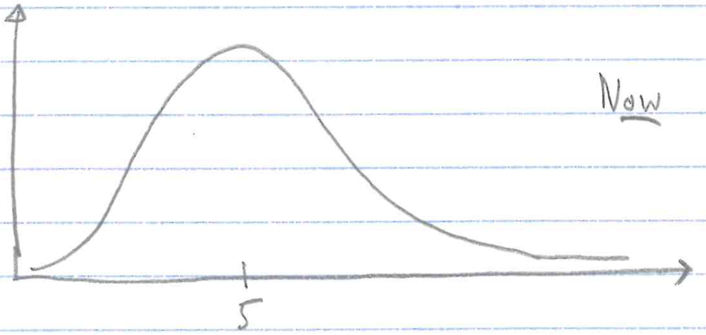
↳ but most likely @ $1 a_0$

Ex $n=2,\ l=0 \Rightarrow P_{20} \sim r^2\left(2-\frac{r}{a}\right)^2 e^{-r/a_0}$



Now $\bar{r}_{20} = 6a_0$

Ex $n=2,\ l=1 \Rightarrow P_{21} \sim r^2\left(\frac{r}{a_0}\right)^2 e^{-r/a_0}$



Now $\bar{r}_{21} = 5a_0$

Note: as 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 $r \to 0$. So if $l \neq 0$, then $r^l \ll 1$
if $l=0 \to R \sim 1$

Next, calculate expectation values...

$$\boxed{\bar{r}_{nl} = \int_0^\infty r\, P_{nl}(r)\, dr}$$

Using properties of $R_{nl}(r)$ polys, you would get

$$\boxed{\bar{r}_{nl} = a_0\left[\frac{3n^2}{2} - \frac{l(l+1)}{2}\right]}$$

Note: $n^2 \sim \bar{r}$
- also, if $n =$ fixed, then

$\bar{r} \sim -l^2$

Ex Find where $P_{n\ell}(r)$ is maximum for $n = 1$

↳ look up table $\Psi_{100} = (\text{const})\, e^{-r/a_0}$ ⇒ $R_{100} = \text{const}\cdot e^{-r/a_0}$

So $\boxed{P_{10}(r) = (\text{const})\, r^2 e^{-2r/a_0}}$ $P_{10}(r) = R^* R\, r^2 dr$

↑ where is this maximum?

$$\frac{dP}{dr} = (\text{const})\left[2re^{-2r/a_0} + \left(\frac{-2}{a_0}\right) r^2 e^{-2r/a_0}\right] = 0$$

⇒ $2r = \frac{2r^2}{a_0}$ so $\boxed{r = a_0}$ here, P is max

But remember, $\boxed{\bar{r}_{n\ell} = \bar{r}_{10} = \frac{3}{2}a_0}$ ⇒ Distribution is asymmetric

//

Angular dependence

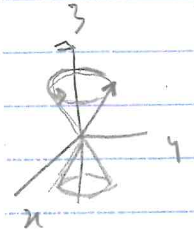
solid angle $= \sin\theta\, d\theta\, d\varphi$

$$\boxed{|\Psi_{n\ell m_\ell}|^2 d^3r = R^*_{n\ell} R_{n\ell}\, \Theta^*_{\ell m_\ell} \Theta_{\ell m_\ell}\, r^2 dr\, d\Omega}$$

Now $P_{n\ell}(r) = 4\pi r^2 R^*_{n\ell}(r) R_{n\ell}(r)$ → gives radial prob. density.

So the remaining factor $\Theta^*_{\ell m_\ell}(\theta)\, \Theta_{\ell m_\ell}(\theta)$ is prob. per unit solid angle d

↳ $\boxed{\text{says which direction matters more}}$



- Since $\Phi^*_{m\ell}(\varphi)\, \Phi_{m\ell}(\varphi) = 1$ → there's no φ dependence → prob is symmetric around z-axis. So once the r, θ dependence is found, we just rotate the picture around the z-axis...

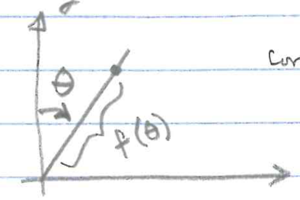
- Since we can't graph $|\Psi_{n\ell m_\ell}|^2$ versus r, θ, φ (because we'd need 4D)

  ↳ Instead, we use shadowing / shading to represent density in 3D space → DENSITY PLOT

To visualize the angular modulation caused by $\Theta^{*}_{\ell m_\ell}(\theta)\,\Theta_{\ell m_\ell}(\theta)$

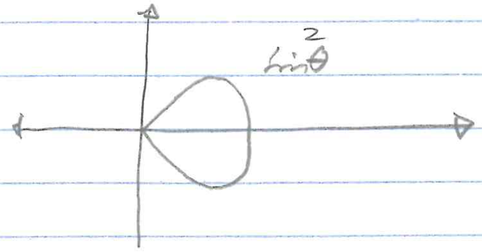
→ use POLAR DIAGRAM

e.g., $f(\theta)$ is a fn of θ

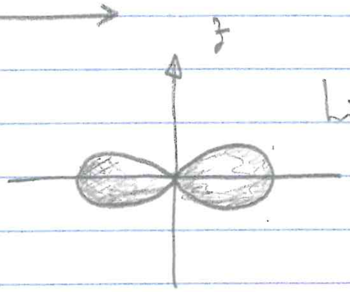


come out along θ by $f(\theta)$

Ex if $f(\theta) = \sin^2\theta$



rotate
→
abt z



higher prob. are near $\theta \cong \frac{\pi}{2}$

April 4, 2018

Recall $\boxed{P_{n\ell}(r) = |R_{n\ell}|^2\, 4\pi r^2}$

To get full prob dist, multiply by $|\Theta(\theta)|^2$ → acts as a modulating function in angle.

To visualize this, use polar plots

e.g. $f(\theta) = \cos^2\theta$ ⟶

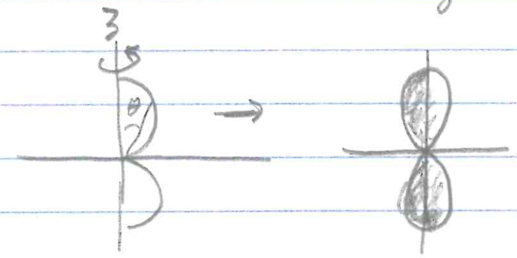
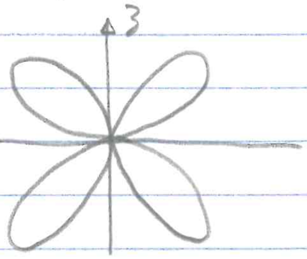


Fig 7-8 ⇒ $\ell = 3$ polar plots.

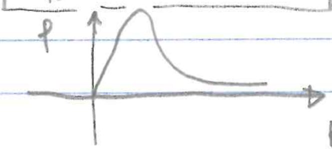
e.g. $m_\ell = \pm 2$ ⟶ $|\Theta_{32}|^2 \propto \sin^4\theta\cos^2\theta$



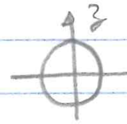
$\underbrace{P_{n\ell}(r)}$ $\underbrace{|\Theta_{n\ell}|^2}$

$\boxed{\text{DENSITY PLOTS}}$ → Combine visualization from Radial + Polar plot to make 3D plots ⇒ use shading to represent 4th dimension

Ex $\boxed{\begin{matrix} n=1 \\ \ell=0 \\ m_\ell=0 \end{matrix}}$ $\boxed{P_{10}(r) \sim r^2 e^{-r/a_0}}$ also $|\Theta(\theta)|^2 = \text{constant}$ polar ⟹

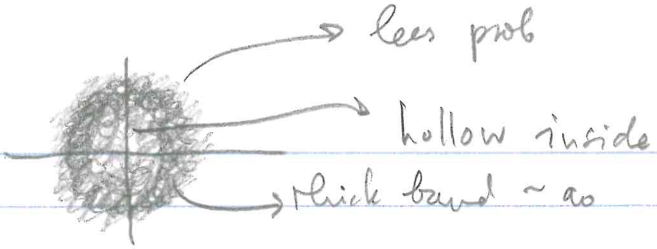


since $\Theta(\theta) = \text{constant}$



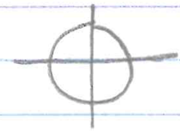
⇒ SYMMETRIC SPHERICALLY

Density plot →



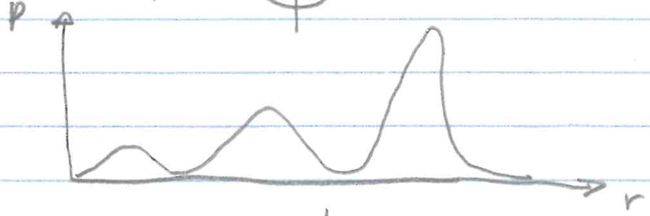
Note $\boxed{\text{all s-states } (\ell=0) \text{ are all spherically symmetric}}$

with $|\Theta(\theta)|^2$ = constant ⇒



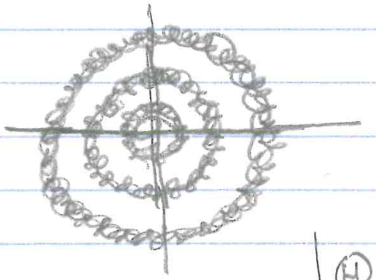
Ex $\boxed{\begin{array}{c} n=3 \\ \ell=0 \\ m_\ell=0 \end{array}}$ Recall

$P_{30}(r) =$



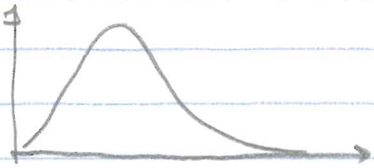
with polar

↳ so density plot ⟶

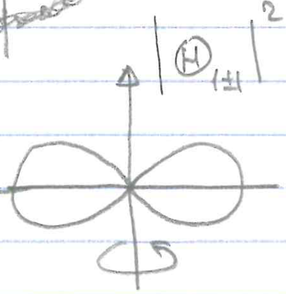


$\boxed{\text{For } \ell \neq 0 \Rightarrow \text{get angular dep}}$

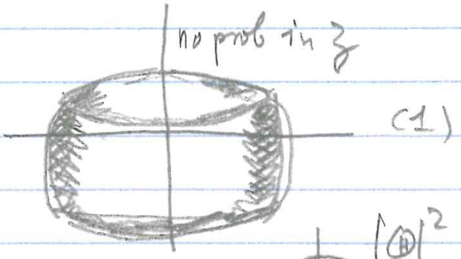
Ex $\boxed{\begin{array}{c} n=2 \\ \ell=1 \\ m_\ell=\pm1 \end{array}}$ $P_{21} =$



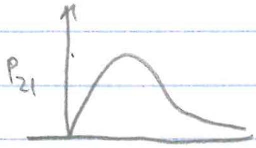
with



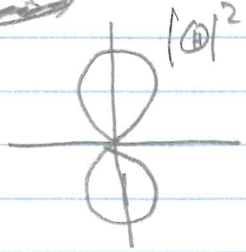
So density plot



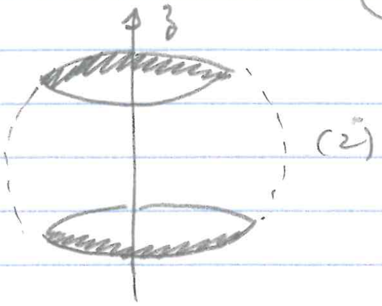
$\boxed{\begin{array}{c} n=2 \\ \ell=1 \\ m_\ell=0 \end{array}}$



with



So density plot



Note (1)(2) fill sphere

<u>Question</u> For $l \neq 0$, there is θ dep, and density is a [illegible] aligned with the z direction, but how does the atom know which way z-points? → It can't!

→ Free atoms with no external interactions can't distinguish directions

→ So z can't matter.

↳ As long as there are no external interactions (like an $\vec{E}$ or $\vec{B}$), then the solutions should be spherically symmetric.

<u>Recall</u> $E_n = \frac{-13.6\,\text{eV}}{n^2}$ has no l, m_l dependance.

If all we do is fix E_n, then any atom would be a statistical mix of the degenerate l & m_l states.

→ these mixtures are spherically symmetric.

$$\boxed{|\psi_n|^2 = \frac{1}{n^2} \sum_{l, m_l} |\psi_{n l m_l}|^2}$$

degeneracy

Any experiment looking at such a sample will see a spherically symmetric distribution

↳ Note the l, m_l states of the same n complete each other to form a spherically symmetric picture (see Fig 7-10)

(7-10: combining images for the same l, m_l gives a spherically symmetric picture)

↳ we can also prove this mathematically

<u>Ex</u> Show n=2 level for H has a spherically symmetric dist

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

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

- $$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cdot \sin\theta \, e^{\pm i\varphi}$$

The average distribution

$$|\Psi_2|^2 = \frac{1}{2^2}\left[|\Psi_{200}|^2 + |\Psi_{210}|^2 + |\Psi_{211}|^2 + |\Psi_{21-1}|^2\right]$$

$$= \frac{1}{4}\left[\frac{1}{16}\frac{1}{2\pi}\left(\frac{1}{a_0}\right)^3 \cancel{\left(2-\frac{r}{a_0}\right)}^2 e^{-r/a_0}\right]\cdot\left[\left(2-\frac{r}{a_0}\right)^2 + \left(\frac{r}{a_0}\right)^2 \cdot \cos^2\theta + \left(\frac{r}{a_0}\right)^2 \cdot \frac{1}{2}\sin^2\theta + \frac{1}{2}\left(\frac{r}{a_0}\right)^2 \sin^2\theta\right]$$

only dep on r $\longrightarrow$ $$= \left[\frac{1}{4}\,\frac{1}{16}\,\frac{1}{2\pi}\left(\frac{1}{a_0}\right)^3 e^{-r/a_0}\right]\left[\left(2-\frac{r}{a_0}\right)^2 + \left(\frac{r}{a_0}\right)^2\right]$$

<u>So</u> $|\Psi_2|^2$ is spherically symmetric!

▨ If we want to distinguish l, m_l states, we must lift the E_n degeneracy $\Rightarrow$ we can do so by applying an external E & B fields. → to select out particular l, m_l

⇒ 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 solutions for H atoms so far have been for free structureless atoms

↳ **Next**, we want to include some additional interaction!

For starters, atoms have magnetic dipole moment ⇒ 2 types of magnetic dipole moment:
- → orbital type (from e^- ↻ 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:

- → Zeeman effect
  - ↳ magnetic dipole moment w/ external B fields
  - ↘ Energy lvl chge
  - ↳ w charge
- → Fine structure → (spin-orbit interaction)
  - ↳ internal interaction between spin & orbital angular momentum
  - ⇒ splits energy levels
- → Relativistic effect → Thomas precession

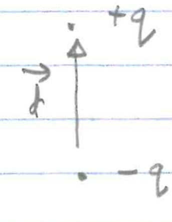
Note There are small interactions, but of approximately the same orders of magnitude

- 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

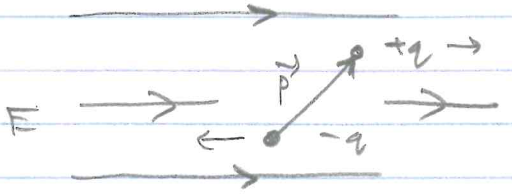
↳ Electric dipoles are made of electric charges:



↳ Def $\boxed{\vec{p} = q\vec{d}}$

∘ If we put $\vec{p}$ in an external $\vec{E}$ field

Ex



→ $\vec{p}$ wants to turn, gets a torque

$$\boxed{\vec{\tau} = \vec{p}\times\vec{E}}$$

Likewise, there's a potential energy : $\boxed{U = -\vec{p}\cdot\vec{E}}$

↑ lowest when $\vec{p} \parallel \vec{E}$

Magnetic dipoles

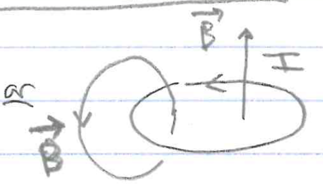
Note, there are no magnetic monopoles ...

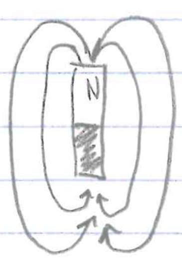
⇒ $\vec{B}$ fields come from current I → Biot-Savart

$$\boxed{d\vec{B} = \frac{\mu_0}{4\pi}\frac{I\,d\vec{s}\times\vec{r}}{r^3}\,dr} \Rightarrow$$

If

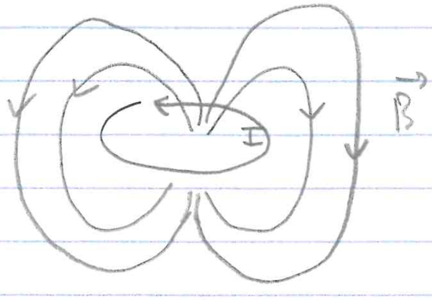
or





⇒ can still have magnetic dipoles : Ex bar magnet

↳ we can still get the same field lines from a loop of current



so $\boxed{\text{Loops of current act as magnetic dipoles}}$

So Def of magnetic dipole moment $\boxed{\mu = I\cdot A}$

area of loop

units Am^2

as a vector $\vec{\mu}$ → use right hand rule

In ext $\vec{B}$ field, get torque $\boxed{\vec{\tau} = \vec{\mu} \times \vec{B}}$

In analogous way, potential energy → $\boxed{U = -\vec{\mu} \cdot \vec{B}}$

↳ lowest when parallel ($\vec{\mu} \parallel \vec{B}$) → $U = -\mu B$

For a bar magnet, we have <u>alligned</u> atomic dipole <u>moments</u>

↳ get macroscopic $\vec{B}$ field.

<u>What about QM magnetic dipole moment?</u>

① ↳ $\boxed{\text{ORBITAL MAGNETIC DIPOLE MOMENT in QM}}$

↳ Our approach so far has been to solve SE exactly

⇒ But can't do that when we include E&M

⇒ E&M is inherently RELATIVISTIC — EM waves move at the speed of light.

↳ $\boxed{\text{Quantum Electrodynamics (QED)}}$

→ combines QM, (special) Relativity, and E&M

<u>What we'll do is to use a combined approach</u>

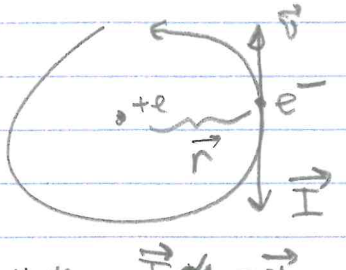
↳ QM based on SE + semiclassical methods (use Bohr model)

+ 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 ⇒ electron in a circular orbit



v = speed of e^- orbit p

$T = \frac{2\pi r}{v}$ = period

<u>current</u>

$I = \frac{e}{T} = \frac{dq}{dt}$

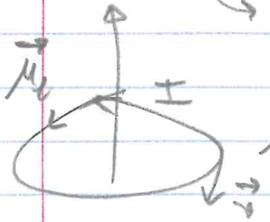
→ $I = \frac{ev}{2\pi r}$

Note $\vec{I}\ -\vec{v}$

So this loop of current has a magnetic dipole moment :

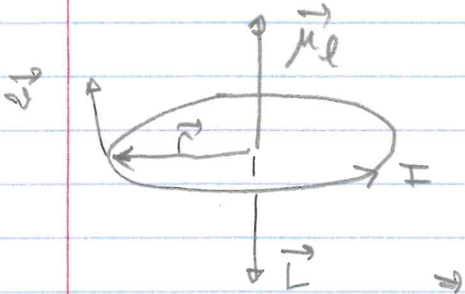
$$\boxed{\mu_\ell = IA} \longrightarrow \text{orbital magnetic dipole moment.}$$

ℓ – denotes that it's orbital (~has sth to do with angular momentum)



$\vec{\mu}_\ell$ loops with $\vec{I}$ using the right hand rule
but there's also angular momentum $\vec{L} = \vec{r} \times \vec{p}$

But since $\vec{I} \propto -\vec{v}$, $\vec{\mu}_\ell$ and $\vec{L}$ are in opposite directions!



with $\mu_\ell = IA = \frac{ev}{2\pi r} \cdot \pi r^2 = \frac{evr}{2}$

while $L = rmv$

$\Rightarrow |\vec{\mu}_\ell| = \frac{evr}{2} = \frac{e}{2} \cdot \frac{|\vec{L}|}{m}$ } note L quantized

So $\boxed{|\vec{\mu}_\ell| = \frac{e}{2m}|\vec{L}|}$ 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 $\boxed{\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24}\ \text{Am}^2}$ → Bohr magneton

Can then write → $\boxed{\mu_\ell = \frac{\mu_B}{\hbar} L}$

We can introduce a strength factor to make formulas uniform

↳ $\boxed{g_\ell = 1}$ → $\boxed{\mu_\ell = g_\ell \frac{\mu_B}{\hbar} L}$

(same type as magnetic dipole in other form

So in vector form

$$\boxed{\vec{\mu}_\ell = -\frac{g_\ell \mu_B}{\hbar} \vec{L}}$$

So orbital magnetic dipole moment $\boxed{\vec{\mu}_\ell = \frac{-g_\ell \mu_B}{\hbar}\vec{L}}$

From QM → we know $\vec{L}$ quantized

$$|\vec{L}| = \sqrt{\ell(\ell+1)}\,\hbar \quad , \cancel{|L_z| =} \; m_\ell \hbar = L_z$$

Those say

$$\boxed{\begin{aligned} \mu_\ell &= +g_\ell \mu_B \sqrt{\ell(\ell+1)} \\ \text{and} \quad \mu_{\ell_z} &= \frac{-g_\ell \mu_B}{\hbar} L_z = -g_\ell \mu_B m_\ell \end{aligned}}$$

↪ quantized magnetic moment!

Next, the spin!

April 9, 2018

→ Magnetic Dipoles in QM

↪ "classical" view: orbital $\vec{\mu}_\ell = \frac{-g_\ell \mu_B}{\hbar}\vec{L}$, $g_\ell = 1$ ↗ strength factor

and $\mu_B = \frac{e\hbar}{2m}$ $= 9.27\times10^{-24}\,\text{Am}^2$ (Bohr magneton)

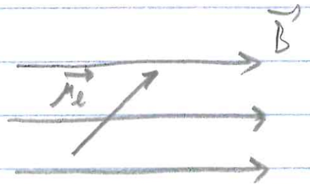
Since $\vec{L}$ quantized → $\vec{\mu}_\ell$ is also quantized.

$$\boxed{\mu_\ell = g_\ell \mu_B \sqrt{\ell(\ell+1)}} \quad \text{and} \quad \boxed{\mu_{\ell_z} = -g_\ell \mu_B m_\ell}$$

expect $(2\ell+1)$ values of μ_ℓ.

Magnetic Moment in an external $\vec{B}$ field

→ it feels a torque!



$\boxed{\vec{\tau} = \vec{\mu}_\ell \times \vec{B}}$

and has $\boxed{PE = -\vec{\mu}_\ell \cdot \vec{B} = U}$

What is the typical size of $U = -\vec{\mu}_\ell \cdot \vec{B}$ ⟶ estimate ΔE between an aligned dipole + anti-aligned

Suppose $\begin{cases} \mu_\ell \simeq \mu_B & \rightarrow \text{typical value} \\ B \simeq 1\text{T} & \rightarrow \text{typical lab magnet} \end{cases}$

↪ Estimate:

$$\Delta E = \mu_B B - (-\mu_B B) = 2\mu_B B = 2(9.27\times10^{-24})(1) \simeq \boxed{1.85\times10^{-23}\,\text{J}} \nearrow \sim \boxed{1.2\times10^{-4}\,\text{e}}$$

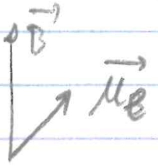
⇒ ~10,000 times smaller than typical atomic energy levels.

⇒ SMALL CORRECTIONS ...

Note → as small as this is, the dipole actually WON'T FLIP unless energy is exchanged

→ As long as NO energy is exchanged, then $PE = -\vec{\mu}_e \cdot \vec{B}$ <u>stays fixed</u>

(★) ⇒ For a dipole in an external B field where E stays fixed



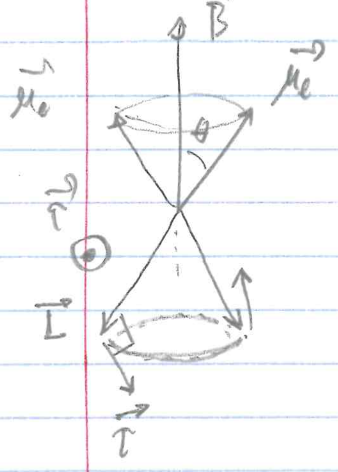
then $E = -\vec{\mu}_e \cdot \vec{B} = -\mu_e B \cos\theta$ <u>stays fixed</u>!

→ <u>so</u> θ stays fixed (if no E exchanges)

But → there is also a torque → $\vec{\tau} = \vec{\mu}_e \times \vec{B}$

<u>What does it do?</u> → $\boxed{\text{PRECESSION}}$

<u>Use</u> $\vec{\mu}_e = \dfrac{-g_e \mu_b}{\hbar} \vec{L} \Rightarrow \vec{\tau} = \dfrac{-g_e \mu_b}{\hbar} \vec{L} \times \vec{B} \sim -\vec{L} \times \vec{B}$



torque changes $\vec{L}$

→ $\vec{\tau} = \dfrac{d\vec{L}}{dt}$ ⇒ get a precession!

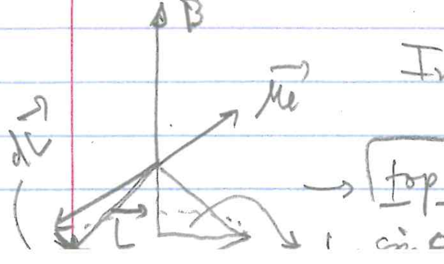
Neither $|\vec{L}|$ ~~nor~~ $|\vec{\mu}_e|$ can change, nor can the angle θ change, since this would change E

→ since $\Delta E = 0$ (and $\vec{p}$ conserved)

⇒ $\vec{\mu}_e$ will precess around $\vec{B}$

Can find angular freq. of the precession

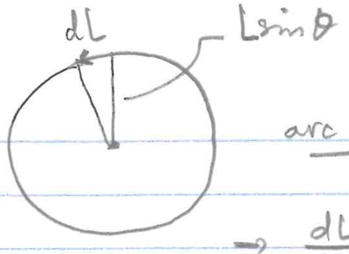
→ Call ω = angular freq of precession & dt = infinitesimal time



In time dt ⇒ get an angle (ωdt)

→ $\boxed{\underline{\text{top}}\ \text{view}}$ →

Top view



arc length $dL = L \cdot \sin\theta \cdot \overbrace{\omega dt}^{\Delta \text{angle}}$

$\rightarrow \frac{dL}{dt} = L\omega \sin\theta$ (geometrically)

We can set this equal to

$$\Rightarrow \tau = \frac{dL}{dt} = \left| \frac{-g_l \mu_B}{\hbar} \vec{L} \times \vec{B} \right|$$

We get

$$L\omega \sin\theta = \left| \frac{-g_l \mu_B}{\hbar} \vec{L} \times \vec{B} \right| = \frac{g_l \mu_B}{\hbar} LB \sin(\pi - \theta)$$

$$L\omega \sin\theta = \frac{g_l \mu_B}{\hbar} LB \sin\theta$$

So $\boxed{\omega = \frac{g_l \mu_B}{\hbar} B}$ → called the Larmor frequency (Larmor precession)

Larmor precession → precession of magnetic dipole in external $\vec{B}$ field

$\boxed{\text{Note}}$ → 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 of magnetic dipole moments of Ag atoms by sending them through non-uniform $\vec{B}$ field.

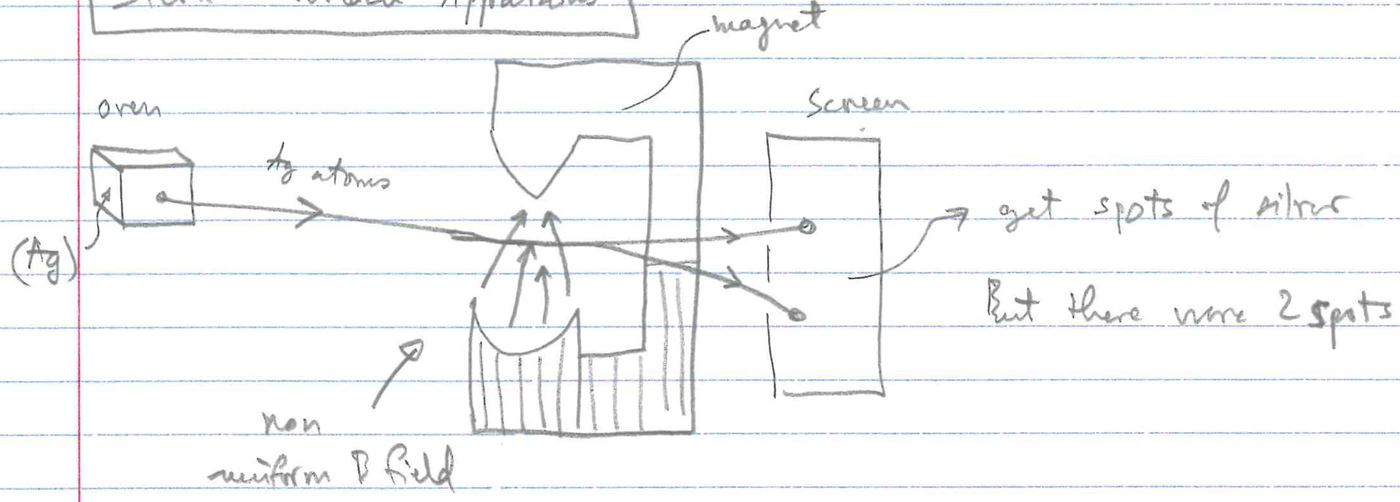
1925 → "spin" was introduced by Uhlenbeck & Goudsmit who were trying to understand the fine - structure of H

QM just invented

But 1927 → Phipps & Taylor repeated exp (S-G), except using ground - state H (and ground - state with $l = 0$) $\Rightarrow \mu_l = 0$
⇒ found evidence of ang. mom values $\neq l = 0, 1, 2 \ldots$
→ half - integer angular momentum

→ SPIN → proposed as a new kind of angular momentum where e^- have spin $= \frac{1}{2}$.

Stern-Gerlach Apparatus

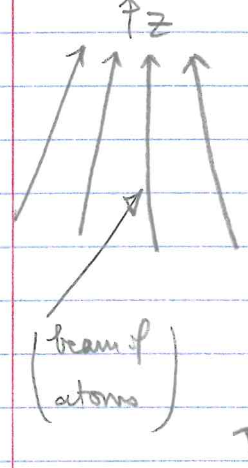


Why non-uniform $\vec{B}$ field? → neutral atoms : $q = 0 \Rightarrow \vec{F} = q\vec{v}\times\vec{B} = \vec{0}$

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 → $U = -\vec{\mu}_e \cdot \vec{B}$



along the axis : $\vec{B} = \underbrace{B_z}_{}(z)\,\hat{k}$

↳ B changes along z only

→ $\boxed{U = -\vec{\mu}_e\cdot\vec{B} = -\mu_{ez}\cdot B_z(z)}$ → only in z-dir (other x, y = 0)

Thus $\vec{\nabla}U = -\frac{\partial}{\partial z}\left(\mu_{ez}\cdot B_z(z)\right)\hat{k}$ $\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y} \text{ give } 0\right)$

So $\boxed{\vec{\nabla}U = -\mu_{ez}\cdot\left(\frac{\partial B_z}{\partial z}\right)\hat{k}}$ → field gradient!

So $\vec{F} = -\vec{\nabla} U = \mu_{\ell z}\left(\frac{\partial B_z}{\partial z}\right)\hat{k}$

Call this → $\vec{F} = F_z \hat{k}$ → only get force in z-direction

and $\boxed{F_z = \mu_{\ell z}\left(\frac{\partial B_z}{\partial z}\right)}$ → Note $F = 0$ unless there is non-uniform B

with $\mu_{\ell z} = -g_\ell \mu_B m_\ell$, assuming it's orbital!

Then m_ℓ has $(2\ell+1)$ values → so expect $2\ell+1$ force values that split the beam apart. But in the exp, $\ell = 0$ → we expect 1 beam $(2\ell+1 = 2\cdot 0+1 = 1)$. However, 2 beams were observed

↳ says $(2\ell+1 = 2)$ or $\ell = \frac{1}{2}$ → NOT allowed as orbital values

→ Instead → Introduce SPIN.

April 11, 2018

Phipps - Taylor repeats exp using ground state $\ell = 0$ H atoms
↳ expected one beam $(2\cdot 0 + 1 = 1)$
→ But 2 spots were seen.

How to explain this? → { By a 2nd type of angular momentum / a 2nd type of magnetic dipole moment }

Spin → like a spinning ball

...

But e^- are point like → So what is spin?
→ an intrinsic angular momentum
→ isolated particles have it.

→ It's a basic property of elementary particle like its mass or charge

→ Call $\vec{S}$ = spin angular momentum S_z = z-component

Since it's quantum mechanical → it's quantized

$$\boxed{\begin{array}{ll} \text{where} & |\vec{S}| = \sqrt{s(s+1)}\,\hbar \\ \text{and} & S_z = m_s\hbar \end{array}}$$

Get 2 new quantum number and $m_s = \underbrace{-s, -s+1 \dots s-1, s}_{2s+1 \text{ values}}$

For electron, there's a new associated magnetic dipole moment → call $\boxed{\vec{\mu}_s = \frac{-g_s\mu_B}{\hbar}\vec{S}}$

and $\boxed{\mu_{s_z} = -g_s\mu_B m_s}$

and

test for QED

g_s = strength factor → can be found experimentally (or calculated in QED)

For a Stern-Gerlach experiment
⇒ use $\vec{\mu_s}$ instead of $\vec{\mu_l}$

$$\boxed{F_z = \mu_{s_z}\left(\frac{\partial B_z}{\partial z}\right) = -g_s\mu_B m_s\left(\frac{\partial B_z}{\partial z}\right)}$$

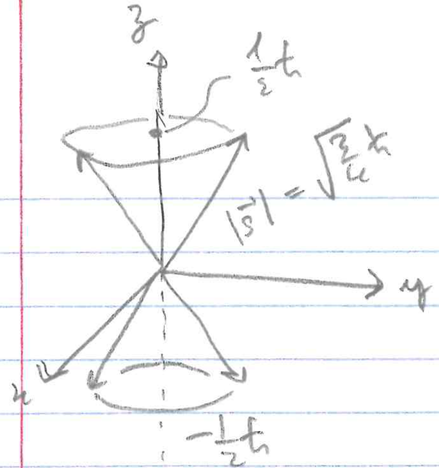
Experiment got $(2s+1)$ spots (or F_z values)

Experiment observed 2 spots → $2s+1 = 2$ → $\boxed{s = \frac{1}{2} \text{ for electrons}}$

$\boxed{\text{Electrons have spin } \frac{1}{2}}$

⇒ But if $s = \frac{1}{2}$, then $m_s = \pm\frac{1}{2}$ → and $\boxed{S_z = \pm\frac{1}{2}\hbar}$

Magnitude = $\boxed{|\vec{S}| = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \sqrt{\frac{3}{4}}\,\hbar}$



Experimentally, found that

$$g_s m_s \simeq \pm 1 \quad \text{where} \quad m_s = \pm\frac{1}{2}$$

$$\Rightarrow \quad g_s \simeq 2 \quad (\text{electron}) \qquad \text{in QED}$$

Careful experiment gives $g_s = 2.00232\ldots$

$\boxed{\text{We'll mostly use } g_s \simeq 2}$

Why are $g_\ell \cong 1$ and $g_s \cong 2$

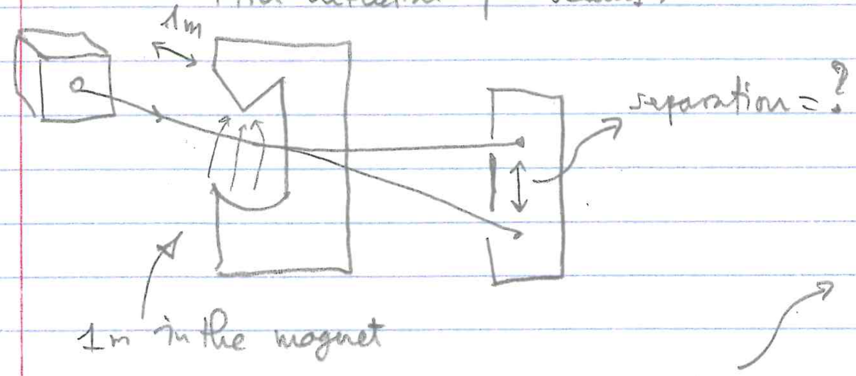
follows from Bohr model + orbital motion

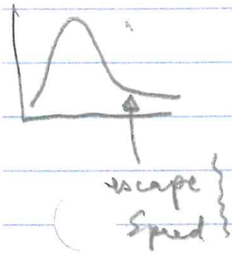
(?) Don't know. Can't really say why $g_s \cong 2$ any more than we can explain why electrons have mass m_e & charge $-e$

Example

Important (Study this)

A beam of 8 atoms comes out of an oven at 400K & goes through a 1-m magnet with a gradient of 10T/m. Find deflection of beams.





Boltzmann constants

Recall KE of hot atoms $= \frac{1}{2}kT$ per degree of freedom

Since in 3D → 3 degrees of freedom → $KE = \frac{3}{2}kT$

But $KE \simeq 2kT$ works better. Treat this as given

notes the faster ones escaping the oven

$$\boxed{KE_x = \frac{1}{2}MV_x^2 = 2kT}$$

temp

$\frac{1}{2}MV_x^2 = 2kT \rightarrow \frac{1}{2}MV_x^2 = 2\left(1.38\times10^{-23}\frac{J}{k}\right).400k$

$\frac{1}{2}MV_x^2 \simeq 1.1\times10^{-20}J = 0.069eV$

So clearly, this is non-relativistic energy! They'll also be in ground state

So $l=0 \Rightarrow$ no $\vec{\mu}_l$, only have $\vec{\mu}_s$

So

Force in magnet is $F_z = \mu_{sz}\frac{\partial B_z}{\partial z}$ → 10T/m given

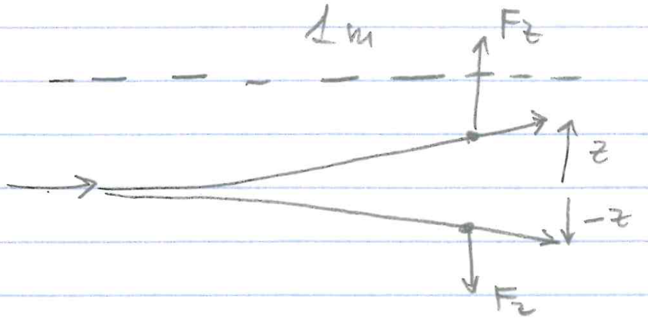
μ_B: Bohr magneton $= -\underset{\simeq 2}{g_s}\,\mu_B\,\underset{\pm\frac{1}{2}}{m_s}\left(\frac{\partial B_z}{\partial z}\right)$

• field gradient = 10T/m

So 2 values for Force

$$\boxed{F_z = \mp\mu_B\left(\frac{\partial B_z}{\partial z}\right)}$$

Sideways picture



Goal: Find z

[illegible]

$z(t) = \frac{1}{2}a_z t^2 = \frac{1}{2}\frac{F_z}{\cancel{M}_H}t^2 \Rightarrow z(t) = \mp\frac{1}{2}\frac{\mu_B}{M}\left(\frac{\partial B_z}{\partial z}\right)t^2$

↓ like "falling" (F only in z)

Need t $\frac{1}{2}MV_x^2 = 2kT \Rightarrow V_x = \sqrt{\frac{4kT}{m}}$

With no acc. along x $t = \frac{x}{V_x} = x\sqrt{\frac{M}{4kT}}$

$\rightarrow z(x) = \mp\frac{1}{2}\left(\frac{\mu_B}{M}\right)\left(\frac{\partial B_z}{\partial z}\right)x$

$$\boxed{z(1) = \mp\frac{\mu_B 1^2}{8kT}\left(\frac{\partial B_z}{\partial z}\right)}$$

Get $\boxed{z = \mp 2.1\times10^{-3}m}$ → separation ~ 0.4 cm → observable

April 13, 2018

The Zeeman Effect → first observed in 1896

⇒ splitting ~~of~~ of spectral lines for atoms placed in an external $\vec{B}$ field

How? An atom can have 2 types of magnetic dipole moments $\vec{\mu}_\ell$ & $\vec{\mu}_s$. In an external $\vec{B}$ field, you get a potential energy

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

if we allign ⟶ $\vec{B} = B\hat{k}$ → uniform along z

then $U = -\mu_z B$ → gives a splitting of the energy the depends on B

→ called the Zeeman Effect

The full Zeeman effect depends on $\vec{\mu} = \vec{\mu}_s + \vec{\mu}_\ell$ 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) → $\ell = 0$ → $m_\ell = 0$

$|\vec{\mu}_\ell| = 0$

In this case $\vec{\mu} = \vec{\mu}_s$ due to spin only

Put an H atom in an s-state in a $\vec{B}$ field → energy total

$$E = \frac{-13.6eV}{n^2} + \Delta E \qquad (n=1)$$

where $\Delta E = -\mu_{s_z} B = g_s \mu_b m_s B$ $\qquad (\vec{B} = B\hat{k})$

Plug in ⟶ $E = \frac{-13.6}{n^2} + g_s \mu_b m_s B$

Experimentally ⟶ $g_s m_s \simeq \pm 1$ so $\boxed{E = \frac{-13.6}{n^2} \pm \mu_B B}$

So an s-state is split into 2 levels

splitting $= 2\Delta E \cong \boxed{2\mu_B B}$

If B ~ 1T → splitting is on the order of 10^{-4} eV

Note the differences between:

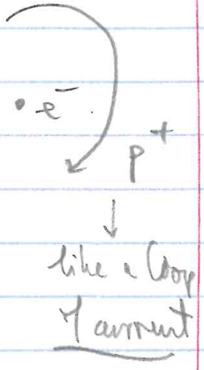
- Stern-Gerlach exp → involves a field gradient $\frac{\partial B}{\partial z}$
  → get a force that separates a beam of atoms
- Zeeman effect → involves constant B field → use atoms at rest (not a beam) (spectroscopically)
  → defines energy level splitting (observed spectroscopically)

SPIN-ORBIT INTERACTION (FINE STRUCTURE)

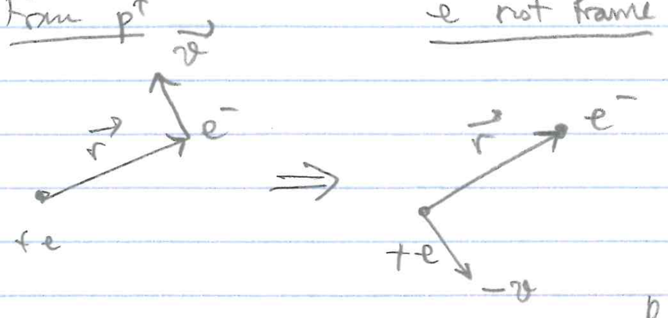
In some ways, this is like the Zeeman effect for μ_s → $\Delta E = -\vec{\mu}\cdot\vec{B}$ but where here, $\vec{B}$ is an internal $\vec{B}$ field inside an atom

⇒ 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"



Consider the motion of the nucleus (proton) from the electron's p.o.v



Note transformation between accelerating frames

→ want to find $\vec{B}$ at the location of e^- due to e^+ motion

Recall Biot-Savart law:

$$d\vec{B} = \frac{\mu_0}{4\pi}\frac{I\, d\vec{s}\times\vec{r}}{r^3}$$

where $I = \frac{e}{T}$ = current
← period

Here $d\vec{s} = -\vec{v}\,dt$ and $T = \int dt$ = period

So $\vec{B} = \int d\vec{B} = \int \frac{-\mu_0}{4\pi}\frac{I\,\vec{v}\times\vec{r}}{r^3}\,dt$

$IT = e$

Note $\vec{v}\times\vec{r}$ constant

So $\vec{B} = \frac{-\mu_0}{4\pi}\frac{I\,\vec{v}\times\vec{r}}{r^3}\int dt = \frac{-\mu_0}{4\pi}\frac{I\,\vec{v}\times\vec{r}}{r^3}\,T$

So $\boxed{\vec{B} = \frac{-\mu_0}{4\pi}\,e\,\frac{\vec{v}\times\vec{r}}{r^3}}$ → internal $\vec{B}$ field interacts with μ_s of e^-

So potential E due to this : energy shift

$$\boxed{\Delta E = -\vec{\mu}_s\cdot\vec{B}}$$

↑

$-g_s\mu_B\vec{S}/\hbar$

So $\boxed{\Delta E = \frac{g_s\mu_B}{\hbar}\vec{S}\cdot\vec{B}}$

But since $\vec{B}$ is due to orbital motion, we can relate it to $\vec{L} = \vec{r}\overset{m}{\times}\vec{v}$

if $\vec{B} = \frac{-e\mu_0}{4\pi}\frac{\vec{v}\times\vec{r}}{r^3} \leftarrow \frac{m}{m}$ $\quad \vec{L} = \vec{r}\times\vec{p}$

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 → $V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$

$\frac{dV}{dr} = \frac{e^2}{4\pi\epsilon_0 r^2} \Rightarrow \frac{1}{r}\frac{dV}{dr} = \frac{e^2}{4\pi\epsilon_0 r^3}$

So I can replace $\frac{1}{r^3}$ by $\boxed{\frac{1}{r^3} = \frac{4\pi\epsilon_0}{e^2}\frac{1}{r}\frac{dV(r)}{dr}}$

So $\vec{B} = \frac{e\mu_0}{4\pi m_e} \cdot \frac{4\pi\epsilon_0}{e^2}\frac{1}{r}\frac{dV(r)}{dr} \cdot \vec{L}$

So $\vec{B} = \frac{\mu_0\epsilon_0}{em}\frac{1}{r}\frac{dV(r)}{dr}\vec{L}$ Note $\mu_0\epsilon_0 = \frac{1}{c^2}$

Write $\boxed{\vec{B} = \frac{1}{em_ec^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{L}}$ Note m_ec^2

Plug this into ΔE to get

$$\Delta E = \frac{g_s\mu_B}{\hbar}\vec{S}\cdot\left(\frac{1}{em_ec^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{L}\right)$$

with $g_s = 2$ and
$\mu_B = \frac{e\hbar}{2m}$

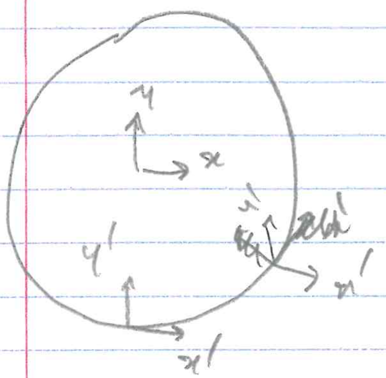
So $\boxed{\Delta E = \frac{1}{m_e^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{L}}$ → $\overrightarrow{\text{Spin} \cdot \text{orbital}}$

Now, this is the result in the e^- rest frame. What about that in the proton's rest frame?

→ We need to transform back to proton's rest frame.

But this is a transformation between accelerating frames
⇒ Must perform a sequence of infinitesimal Lorentz transform.

→ need a sequence of infinitesimal Lorentz transform because $\vec{v}$ changes direction



→ find a rotation or (precession) of axis

↳ Thomas precession (complicated)

(Appendix O)

The result of careful calculations (which we won't do) is that ΔE changes by a factor (1/2)

→ The spin-orbit interaction including Thomas precession is

↳ $$\boxed{\Delta E = \frac{1}{2m^2c^2}\cdot\frac{1}{r}\cdot\frac{dV(r)}{dr}\,\vec{S}\cdot\vec{L}}$$

(derived by Thomas (1926), agrees with relativistic QM calculations

Next

↳ incorporate ΔE into SE. How do we add spin to SE?

#

April 16, 2018

SPIN → electron: $s = \frac{1}{2}$, so $m_s = \pm\frac{1}{2}$ → up/down states

↳ Today: **FINE-STRUCTURE**

spin-orbit interaction

↳ interaction between $\vec{\mu}_s$ and internal $\vec{B}$ (caused by movement of e^- in atom)

#

→ include relativistic effect → found $$\boxed{\Delta E = \frac{1}{2m^2c^2}\,\frac{1}{r}\,\frac{dV(r)}{dr}\,\vec{S}\cdot\vec{L}}$$

$V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$ for H

Now → need to add ΔE correction to SE

but this involves spin!

↳ how do we include spin, even w/o spin-orbit interaction time-independent

↳ SE with spin (but no spin-orbit interaction) ↗

↳ Before, we had $\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + U(r)$

SE → $\hat{H}\psi_{nlm_l} = E_n\psi_{nlm_l}$

We also found that

$$\left\{\begin{array}{l} \hat{L}^2\psi_{nlm_l} = l(l+1)\hbar^2\psi_{nlm_l} \\ \text{and} \\ \hat{L}_z\psi_{nlm_l} = m_l\hbar\psi_{nlm_l} \end{array}\right.$$

But now we want to include spin, but ignoring the spin-orbit interacti

⟹ Let Ψ = wave function with spin

want it to obey:

- $\hat{H}\Psi = E_n\Psi$
- $\hat{L}^2\Psi = l(l+1)\hbar^2\Psi$
- $\hat{L}_z\Psi = m_l\hbar\Psi$

But also

- $\hat{S}^2\Psi = s(s+1)\hbar^2\Psi$ where for electrons: $s = \frac{1}{2}$
- $\hat{S}_z\Psi = m_s\hbar\Psi$ and $m_s = \pm\frac{1}{2}$

What we do is let → $\boxed{\Psi = \psi_{nlm_l}\cdot\chi_{sm_s}}$ (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_l}

and $\hat{S}^2, \hat{S}_z \rightarrow$ act on χ_{sm_s}

<u>Need</u>
$$\left\{ \begin{aligned} \hat{S}^2 \chi_{sm_s} &= s(s+1)\hbar^2 \chi_{sm_s} \\ \hat{S}_z \chi_{sm_s} &= m_s \hbar \chi_{sm_s} \end{aligned} \right\}$$

$\hat{H}, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$

So if we do this, then $\Psi = \psi \chi$ will be eigenstates of all $\underline{S}$ operators

So how are the spin operators and spin wave functions represented explicitly?

↳ Since spin is purely intrinsic, it does NOT depend on the position or momentum of electron

↳ <u>So</u> χ_{sm_s} has <u>NO</u> coordinate dependence, and for $s = \frac{1}{2}$, it only has 2 possible states

→ Can represent the spin wave functions as a 2-component matrices

$$\left. \begin{aligned} \chi_{\frac{1}{2}\frac{1}{2}} &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{spin "up" state} \\ \chi_{\frac{1}{2}-\frac{1}{2}} &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{"down" state} \end{aligned} \right\} \text{Called "spinors"}$$

<u>Then</u> $\hat{S}^2$ and $\hat{S}_z$ can be represented as 2x2 matrices

<u>eg</u>

$$\boxed{\begin{aligned} \hat{S}^2 &= \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ \hat{S}_z &= \frac{1}{2}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned}}$$

Verify $\hat{S}^2_1 \chi_{\frac{1}{2}\frac{1}{2}} = \frac{3}{4}\hbar^2 \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{3}{4}\hbar^2\begin{pmatrix}1\\ 0\end{pmatrix}$

$= s(s+1)\hbar^2 \chi_{\frac{1}{2}\frac{1}{2}} \quad (s = \frac{1}{2})$

Likewise $\hat{S}_z \chi_{\frac{1}{2}+\frac{1}{2}} = \frac{1}{2}\hbar \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = m_s \hbar \chi_{\frac{1}{2}\frac{1}{2}} \quad (m_s = +\frac{1}{2})$

So these give a good representation of spin in QM

Note Heisenberg use matrices to represent all operators in QM, including $\hat{p}$, $\hat{x}$, ...

For spin we don't have differential operator

So the full SE with spin (but no spin-orbit eqn) is a hybrid eqn

$$\boxed{\hat{H}\,\psi_{nlm_\ell}\chi_{sm_s} = E_n\,\psi_{nlm_\ell}\chi_{sm_s}}$$

differential operator on spatial wavefunction $\psi_{nlm_\ell}(r,\theta,\varphi)$

While

$$\boxed{\hat{S}^2\,\psi_{nlm_\ell}\chi_{sm_s} = s(s+1)\hbar^2\,\psi_{nlm_\ell}\chi_{sm_s}}$$

matrix operator acting on χ_{sm_s}

We won't worry about matrix representation → all we need to remember is that

$$\Psi = \psi_{nlm_\ell}\chi_{sm_s}$$

where $\hat{S}^2\Psi = s(s+1)\hbar^2\Psi$ and $\hat{S}_z\Psi = m_s\hbar\Psi$

→ With ~~those~~ no spin-orbit interaction, we still get

$$\hat{H}\,\psi_{nlm_\ell}\chi_{sm_s} = E_n\,\psi_{nlm_\ell}\chi_{sm_s}$$

where $E_n = \frac{-13.6\,\text{eV}}{n^2}$ for H — degenerate in l, m_ℓ, s, m_s

Now, the total degeneracy changes -

If we fix n → Ψ_{nlm_l} → n^2 states

χ_{sm_s} → 2 states

So the degeneracy doubles!!!

So the total degeneracy with spin = $\boxed{2n^2}$

Note All this ignores the spin-orbit interaction

SE with spin ≠ spin-orbit interaction

So our Hamiltonian changes!

Want to solve SE with Hamiltonian

$$\boxed{\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V(r)}_{\text{includes a } 2\times 2 \text{ unit matrix}} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\,\underset{\uparrow}{\vec{S}\cdot\vec{L}}}$$

a matrix...

Want to solve → $\hat{H}\Psi = E_n\Psi$

So the 3rd term in $\hat{H}$ changes everything!

- we no longer have Ψ_{nlm_l} as the spatial solution

⇒ 3rd term has ~~both~~ angular + radial + spin dependence...

⇒ MUST start over =(

Note Look at the extra term $\hat{\vec{S}}\cdot\hat{\vec{L}} = \hat{S}_x\hat{L}_x + \hat{S}_y\hat{L}_y + \hat{S}_z\hat{L}_z$

⇒ 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 → 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 $\hat{S}_x, \hat{S}_y$.

↳ Now we'll have

$$\left\{\begin{array}{ll} & \hat{L}_z\Psi \neq m_\ell\hbar\Psi \\ \text{likewise} & \hat{S}_z\Psi \neq m_s\hbar\Psi \end{array}\right\}$$

$$\boxed{\begin{array}{l}\text{So, we say } m_\ell, m_s \Rightarrow \text{no longer "good" quantum number} \\ \quad(\text{since } \hat{L}_z, \hat{S}_z \text{ no longer have eigenstates})\end{array}}$$

↳ We might think ℓ, s are no longer "good"

But ⇒ look at the total angular momentum!

Note $\vec{S}+\vec{L}$ = total angular momentum

↳ Square!

$$\boxed{\underset{\uparrow\ \text{define}}{(\vec{S}+\vec{L})^2} = \underbrace{\hat{\vec{S}}^2 + \hat{\vec{L}}^2}_{\text{can be "good" with } \ell, s} + \underbrace{2\hat{S}\cdot\hat{L}}_{\text{need to find this!}}}$$

$$\boxed{\text{total ang. mom} = \vec{J} = \vec{S}+\vec{L}}$$

↳ See that

$$\vec{J}^2 = \vec{S}^2 + \vec{L}^2 + 2\vec{S}\cdot\vec{L}$$

So

$$\boxed{\vec{S}\cdot\vec{L} = \frac{1}{2}\left(\vec{J}^2 - \vec{S}^2 - \vec{L}^2\right)}$$

keep $\hat{L}^2, \hat{S}^2$ as before → with l, s = quantum number

But now look for states of total $\vec{J}$

↳ Propose that $\vec{J}$ 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 = ang. momentum quantum number

$m_j = -j, \dots j$

↳ $2j+1$ values

April 18, 2018 Recall SE with spin-orbit interaction

$$\hookrightarrow \hat{H} = \frac{-\hbar^2}{2m}\vec{\nabla}^2 + V(r) + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{L}$$

where $\vec{S}\cdot\vec{L} = \hat{S}_x\hat{L}_x + \hat{S}_y\hat{L}_y + \hat{S}_z\hat{L}_z$

↳ can't use $\hat{S}_z\hat{L}_z$ since y, x are unknown.

So we $\vec{J}^2 = (\vec{S}+\vec{L})^2 = \vec{S}^2 + \vec{L}^2 + 2\vec{S}\cdot\vec{L}$ & $\boxed{\vec{S}\cdot\vec{L} = \frac{1}{2}\left(\vec{J}^2 - \vec{S}^2 - \vec{L}^2\right)}$

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 eigenstate of the total angular momentum. ($\vec{J}^2$)

Propose
$$\boxed{\begin{aligned}\hat{J}^2 \Psi &= j(j+1)\hbar^2 \Psi \\ \text{and} \quad \hat{J}_z \Psi &= m_j \hbar \Psi\end{aligned}}$$

j = quantum number for total angular momentum

and $m_j = -j, -j+1, \dots j-1, j$

↑ $(2j+1)$ values...

↳ To include spin-orbit } interaction

↳ we change our description

* Without S-O interaction ⇒ l, s, m_l, m_s are "good" ↗ (appear in eigenvalues...)

With spin-orbit term ⇒ m_ℓ, m_s are "bad" → introduce $\vec{J} = \vec{L} + \vec{S}$ which represents total angular momentum.

↳ good quantum numbers are $\boxed{\ell, s, \cancel{m_\ell}, m_j, j}$

<u>Then</u> $\vec{S}\cdot\vec{L}$ acting on Ψ gives

$$\vec{S}\cdot\vec{L} = \frac{1}{2}\left(\vec{J}^2 - \vec{S}^2 - \vec{L}^2\right)$$

$$\boxed{\vec{S}\cdot\vec{L} = \frac{1}{2}\left[j(j+1) - s(s+1) - \ell(\ell+1)\right]\hbar^2}$$

and,

$$\boxed{\vec{J}_z \Psi = m_j \hbar \Psi}$$

⇒ states become eigenstates of $\vec{J}^2$ and $\vec{J}_z$

$\boxed{\text{But what are } j \text{ and } m_j?}$ → what is $\vec{J} = \vec{L} + \vec{S}$?

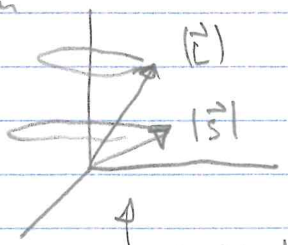
differential ↑ matrix ↗

↳ $\boxed{\text{ADDITION OF ANGULAR MOMENTUM}}$

→ 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.

↳ To find j and m_j → imagine we can <u>turn off</u> the spin-orbit interaction



⟸ L_z and S_z are "good"

m_ℓ and m_s are good ...

↑ don't know L_x, L_y, S_x, S_y

<u>But the z-component adds</u>

↳ $J_z = L_z + S_z \Rightarrow \boxed{m_j = m_\ell + m_s}$

The maximum case adds as well

$$\hookrightarrow \boxed{(m_j)_{max} = (m_\ell)_{max} + (m_s)_{max}}$$

So $\boxed{(m_j)_{max} = \ell + s}$

But we know that $m_j = -j, -j+1, \ldots j-1, \underset{\nearrow\,max}{j}$

So One possible value is $\boxed{j = \ell + s}$ or $\boxed{j = \frac{1}{2} + \ell}$ for e^-

with this $\rightarrow$ $\boxed{m_j = -j, -j+1, \ldots, j-1, j \leftarrow \text{with } j = \ell + \frac{1}{2}}$

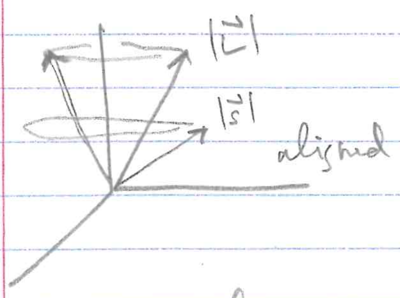
Special case $\ell = 0$ (e^- in s-state)

$\rightarrow$ get $j = \frac{1}{2}$ ($\vec{J} = \vec{S}$ since $\vec{L} = \vec{0}$)

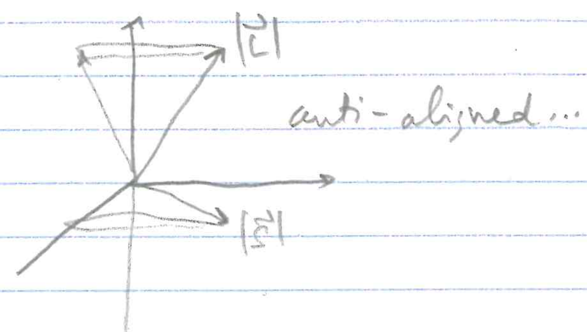
then $m_j = \pm\frac{1}{2}$

Are there other possible j values?

Since ℓ & s have 2 relative orientations, we can get 2 j values.



or



For the 2nd case

$$\hookrightarrow (m_j)_{max} = (m_\ell)_{max} - \left(\frac{1}{2}\right) \quad \text{where } j = \ell - \frac{1}{2}$$

$\Rightarrow$ $\boxed{j = \ell - \frac{1}{2}}$ for e^- $\leftarrow$ different value... $\boxed{m_j = -j, -j+1 \ldots j-1, j}$

(124)

Summary over addition rule ($\vec{J} = \vec{L} + \vec{S}$)

$$\begin{cases} \text{If } \ell = 0 \Rightarrow j = s = \frac{1}{2}, \quad m_\ell = \pm\frac{1}{2} \\ \text{If } \ell \neq 0 \xrightarrow{*} j = \ell + \frac{1}{2}, \quad m_j = -j, -j+1 \dots j, \quad j = \ell + \frac{1}{2} \text{ (spin up)} \\ \ell \neq 0 \xrightarrow{*} j = \ell - \frac{1}{2}, \quad m_j = -j, \dots j, \quad j = \ell - \frac{1}{2} \text{ (spin down)} \end{cases}$$

⇒ But remember all this assume we could turn off orbit-spin interaction
Now → turn it back on, what happens to $\vec{J}$?

The spin-orbit interaction is purely <u>internal</u> so the total angular momentum doesn't change.
→ The same rules still apply!

<u>But</u> m_ℓ, m_s become bad quantum numbers... (but we're only using ℓ, s...)

<u>Example</u> $\ell = 1$, $s = \frac{1}{2}$ (e^- in p-state)

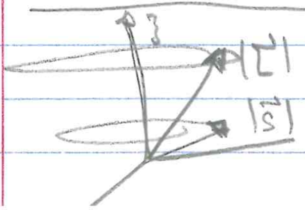
→ 2 possible values for ~~m~~ $j = \left\{\frac{3}{2}, \frac{1}{2}\right\}$

<u>So</u>
$$\left.\begin{array}{ll} m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, +\frac{3}{2} & \text{for } j = \frac{3}{2} \\ m_j = -\frac{1}{2}, \frac{1}{2} & \text{for } j = \frac{1}{2} \end{array}\right\} \underline{\text{6 states!}}$$

<u>Note</u> This is the same number as before with no spin-orbit int...

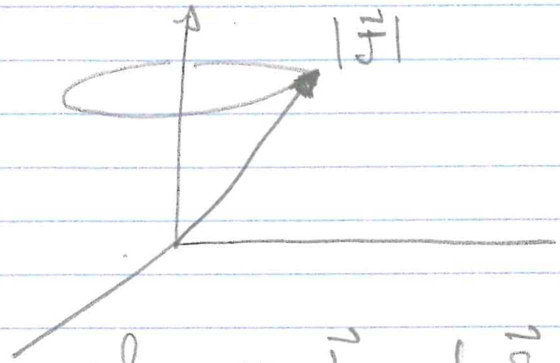
$$\left.\begin{array}{l} \ell = 1 \rightarrow m_\ell = -1, 0, 1 \\ s = \frac{1}{2}, \text{ each with } m_s = \pm\frac{1}{2} \end{array}\right\} \underline{\text{6 possible states!}}$$

<u>What about vector diagram?</u> – with no spin-orbit interaction?



← $\vec{L}$ & $\vec{S}$ lie on cone with definite z component. → m_ℓ, m_s "good"

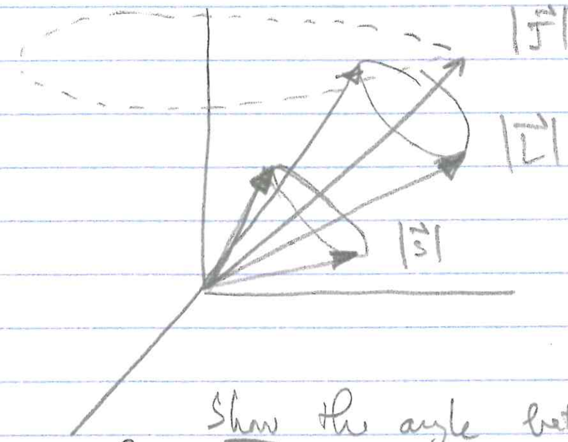
But <u>with</u> spin-orbit interaction



$|\vec{J}|$ lies on a cone with definite J_z

where are $\vec{L}$ & $\vec{S}$?

<u>where are $\vec{L}$ and $\vec{S}$?</u>



→ $\vec{S}$ & $\vec{L}$ lie on a cone along $\vec{J}$

→ $\boxed{\text{angle w.r.t } \vec{J} \text{ do not change}}$

{But S_z and L_z no longer have definite value}

<u>Show</u> the angle between $\vec{S}$ & $\vec{J}$ has a fixed definite value.

$$\vec{S}\cdot\vec{J} = |\vec{S}||\vec{J}|\cdot\cos\theta \quad , \text{ \underline{also} } \quad \vec{S}\cdot\vec{J} = \vec{S}(\vec{S}+\vec{L})$$

$$\text{\underline{so}} \quad \vec{S}\cdot\vec{J} = \vec{S}^2 + \vec{S}\cdot\vec{L} = \vec{S}^2 + \frac{1}{2}\left[J^2 - L^2 - S^2\right] = \frac{1}{2}\left(J^2 - L^2 + S^2\right)$$

$$\text{\underline{and}} \quad |\vec{S}| = \sqrt{s(s+1)}\,\hbar \quad \text{and} \quad |\vec{L}| = \sqrt{l(l+1)}\,\hbar$$

$$\text{\underline{and}} \quad |\vec{J}| = \sqrt{j(j+1)}\,\hbar$$

$$\text{\underline{so}} \quad \cos\theta = \frac{\vec{S}\cdot\vec{J}}{\|\vec{S}\|\|\vec{J}\|}$$

$$\boxed{\cos\theta = \frac{\frac{1}{2}\left(j(j+1) - l(l+1) + s(s+1)\right)\cancel{\hbar^2}}{\sqrt{s(s+1)}\sqrt{l(l+1)}\,\cancel{\hbar^2}}}$$

Similarly,
<u>$\cos\varphi = \vec{S}, \vec{L} = \text{const}$</u>

↳ has definite values for given $j, l, s, \ldots$

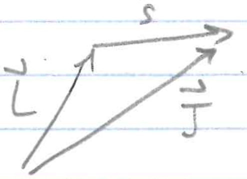
April 20, 2018

Recall Total angular momentum.

$$\hat{J}^2\Psi = j(j+1)\hbar^2\Psi \qquad \text{rule} \quad j = \begin{cases} \frac{1}{2} & l=0 \\ l\pm\frac{1}{2} & l\neq 0 \end{cases}$$
$$\hat{J}_z\Psi = m_j\hbar\Psi$$

Book ⇒ use triangle inequalities to verify this rule

$\vec{J} = \vec{L} + \vec{S}$



$|\vec{J}| \leq |\vec{S}| + |\vec{L}|$

This gives $\boxed{j \leq l+s}$

Also $|\vec{J}| \geq \big||\vec{L}| - |\vec{S}|\big|$ This gives $\boxed{\sqrt{j(j+1)} \geq \left|\sqrt{l(l+1)} - \sqrt{s(s+1)}\right|}$

Prob 8-8 has you verify that with $s=\frac{1}{2}$ the only integer-spaced j-values consistent with these are

$$j = \begin{cases} 1/2 & \text{if } l=0 \\ l\pm\frac{1}{2} & \text{if } l\neq 0 \end{cases}$$

Ex

List all j and m_j for $n=4$ state with $l=4$, $s=\frac{1}{2}$ ↳ $m_s = \pm\frac{1}{2}$

- $j = 4+\frac{1}{2} = \frac{9}{2}$
- $m_j = -\frac{9}{2}, -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ (10 values)
- $j = 4-\frac{1}{2} = \frac{7}{2}$
- $m_j = -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ (8 values)

Total 18 states total

Note 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? $\ell = 4, \quad m_\ell = 0, \pm 1, \pm 2, \pm 3, \pm 4$ 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_j, j description.

Then
$$\boxed{\vec{S}\cdot\vec{L} = \frac{1}{2}\left[j(j+1) - s(s+1) - \ell(\ell+1)\right]\hbar^2}$$

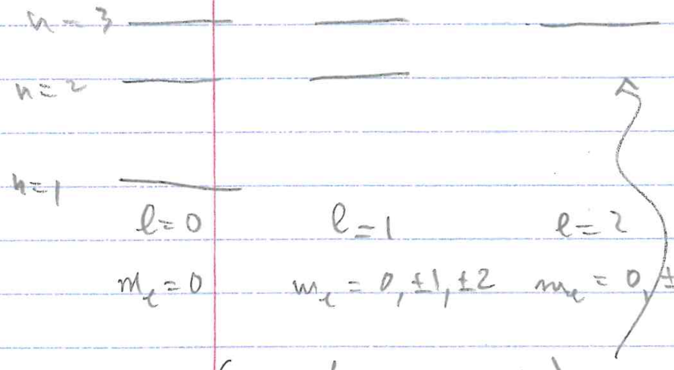
↳ And this goes into ΔE (into SE)

↳ some degeneracy gets lifted!

Hydrogen Energies with the spin-orbit interaction

↳ Before, w/o spin-orbit int: $\psi_{n\ell m_\ell}$ = spatial wave functions

$\chi_{s m_s}$ = spin wave functions



← $E_n = \dfrac{-13.6}{n^2}$ eV degeneracy $= 2n^2$

$(s = \frac{1}{2}, \ m_s = \pm \frac{1}{2})$

Now, include spin-orbit term.

need to solve this $\hat{H}\Psi = E\Psi$

$$\boxed{\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(r) + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{L}}$$

Would need to start over again! $\Psi = \psi_{nlm_l}\,\chi_{sm_s}$ are not solutions anymore!

Too hard to solve exactly → Approximation

KNOW The spin-orbit correction is very small! ($\Delta E \sim 10^{-4} E$)

↳ To first approx → we still have $\psi_{nlm_l} = R_{nl} Y_{lm_l}$ is still a solution to 1st order

Gives $E_n = -\frac{13{,}6\,eV}{n^2}$ (dominant)

↳ We can compute ΔE for the spin-orbit term as an expectation value using ψ_{nlm_l}.

$$\Delta E = \frac{1}{2m^2c^2}\left(\overline{\frac{1}{r}\frac{dV(r)}{dr}}\right)\left(\overline{\vec{S}\cdot\vec{L}}\right)$$ expectation values!

Can use
$$\overline{\vec{S}\cdot\vec{L}} = \frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]$$

① $$\overline{\vec{S}\cdot\vec{L}} = \frac{1}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]\hbar^2$$

② Compute $\left(\overline{\frac{1}{r}\frac{dV(r)}{dr}}\right)$ using the radial wave function

So
$$\left(\overline{\frac{1}{r}\frac{dV(r)}{dr}}\right) = \int R^*_{nl}\,\frac{1}{r}\frac{dV(r)}{dr}\,R_{nl}\,4\pi r^2\,dr$$

where for H

↳ $$V = \frac{-e^2}{4\pi\epsilon_0 r}$$

If done this gives a small correction to the primary energy $E = -\frac{13.6}{n^2}$

$\boxed{\text{BUT}}$ → other small corrections should then be included as well (e.g. Relativistic corrections (of ~ order of mag))

Relativisticly $KE = E - mc^2 = \sqrt{m^2c^4 + c^2p^2} - mc^2$

Perturbatively, $\boxed{KE \simeq \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots}$

↑ I showed this in problem 8-12

Note $\frac{p^2}{2m}$ already in SE → Can compute 1st order relativistic correction as an expectation value as well

$$\Delta E_{rel} = \overline{\left(\frac{-p^4}{8m^3c^2}\right)} \Rightarrow \text{compute using the } 0^{th} \text{ order wave function } R_{nl}$$

Note When spin-orbit and relativistic corrections are included, the result matches the result from (QED)!

The final answer is result in QED →

$$\boxed{E_n = \frac{-13.6\,eV}{n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]}$$

This is H atom energy levels, including the fine structure.
where

$$\boxed{\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137}} \leftarrow \text{fine structure constant has No units}$$

E.M QM Relativistic

α gives a scale of EM interaction

Note

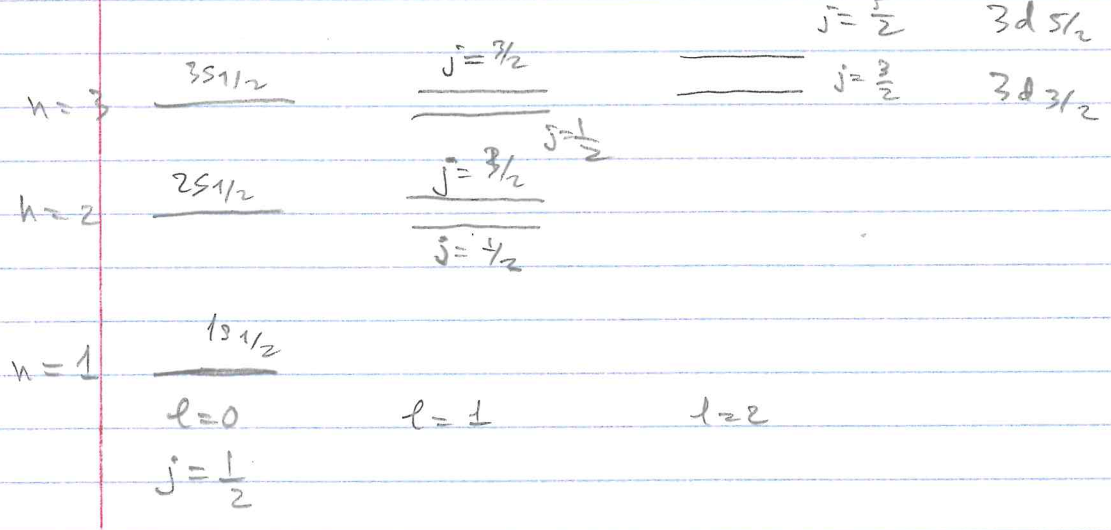
$$\boxed{E_n = \frac{-13.6\,eV}{n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]}$$

tiny splitting for the same n

Note $\alpha^2 < 10^{-4}$ ⇒ 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. $1s_{1/2}$, $2s_{1/2}$, ...

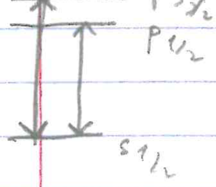
↑ use s, p, d, f ... $2p_{1/2}$, $2p_{3/2}$, ...

$3p_{1/2}$, $3p_{3/2}$ ...

Note
Alkalis are hydrogenic,
having one valence electron

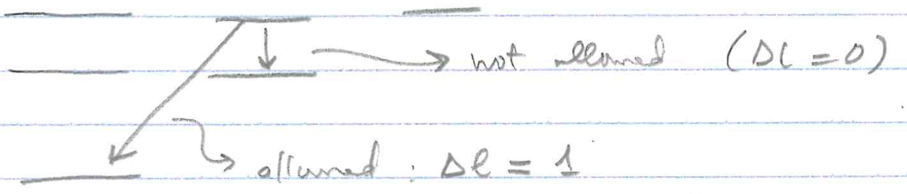
e.g. Na can use same labels, though there are also additional splittings ...

Na doublet $3p_{3/2} \longrightarrow 3s_{1/2}$
$3p_{1/2} \longrightarrow 3s_{1/2}$ } → more easily resolved.



April 23, 2012

<u>Selection Rules</u> When an atom is excited, it deexcite by emitting a photon. But not all transitions are allowed.



$\boxed{\text{Selection rule says which transition are allowed}}$

We'll also talk about <u>transition probabilities</u> ⇒ Prob./sec for a transition to occur

Selection rules says which transitions have probabilitys that aren't negligible

For the allowed transitions, the selection rules are

$$\left\{\begin{matrix}\text{electric dipole}\\ \text{transitions}\end{matrix}\right\} \longrightarrow \boxed{\begin{matrix}\Delta l = \pm 1\\ \Delta j = \pm 1, 0\end{matrix}}$$

The main reason for this is that photons have spin

$$\boxed{\begin{matrix}j = 1 \text{ for photon}\\ (j = s = 1,\ l = 0)\end{matrix}} \longrightarrow \text{photons don't have angular orbital mom.}$$

So $\Delta j = \pm 1$ makes sense ⇒ photon carries off $1\hbar$ of angular momentum

$\Delta j = 0$ is also possible.

⇒ $\vec{J}$ ⇒ changes direction but not magnitude

$\Delta \vec{J} \neq 0$

$\boxed{\text{But why } \Delta l = \pm 1 \text{ only?}}$

↳ we'll show this using parity arguments.

First, with an energy eigenstate $\Psi_{nlm_l}(\vec{r},t) = \psi_{nlm_l}(\vec{r})\, e^{-iE_n t/\hbar}$

⇒ $|\Psi_{nlm_l}(\vec{r},t)|^2$ has no t-dependence ⇒ no transitions

To get transitions, we need a mixture of states ⟶

For a mixture → $\Psi = c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2t/\hbar}$

So $|\Psi|^2$ = has cross terms that are time dependence

↳ T-dep terms $\sim e^{i(E_1-E_2)t/\hbar}$ and a frequency ν

$$\boxed{\nu = \frac{E_1-E_2}{\hbar} = \text{photon frequency}}$$

Photon goes off with $h\nu = E_1 - E_2$

In a quantum system, even a pure energy state will become mixed due to quantum fluctuations (relativistic)

⇒ Can get spontaneous transitions from excited states!

We want to know which transitions are allowed?

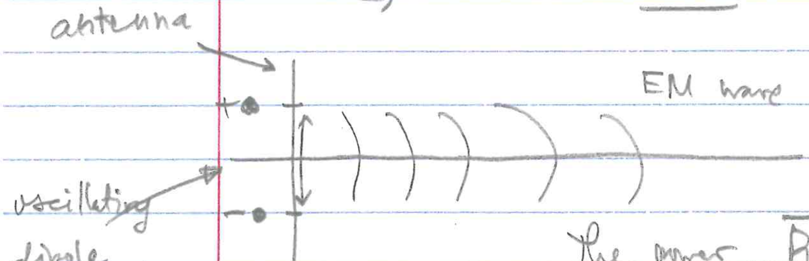
↳ Can look at classical radiation of photons, how does this occur?

How do we get radiation (light) classically? By accelerating electric charge?

↳ The simplest type of radiation, classically, is an oscillating electric dipole

⇒ with an atenna

Electric dipole moment $\vec{p} = q\vec{d}$

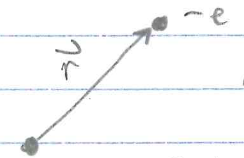


$\vec{E} \sim \vec{p}$

The power $\bar{P} \sim |\vec{p}|^2$

Relate ant and a transitioning atom → we need a non zero dipole moment, $\vec{p}$.

For atom



$q = e \quad \vec{d} = -\vec{r}$

Get $\boxed{\vec{p} = -e\vec{r}}$ for H

$$\boxed{\Psi = \psi_i e^{-iE_i t/\hbar} + \psi_f e^{-iE_f t/\hbar}}$$

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 values of $\vec{p} = -e\vec{r}$

So $\bar{\vec{p}} = \int_{-\infty}^{\infty} \Psi^* (-e\vec{r}) \Psi \, d^3r$

$\boxed{0}$??! $\boxed{= 0}$ if state has definite (depends) parity

$$= -e \Big[\int_{-\infty}^{\infty} \psi_i^* \vec{r} \psi_i \, d^3r + \int_{-\infty}^{\infty} \psi_f^* \vec{r} \psi_f \, d^3r$$

$$+ \int_{-\infty}^{\infty} \psi_i^* \vec{r} \psi_f \, d^3r \cdot \left(e^{i(E_i - E_f)t/\hbar}\right)$$

$$+ \int_{-\infty}^{\infty} \psi_f^* \vec{r} \psi_i \, d^3r \cdot \left(e^{-i(E_i - E_2)t/\hbar}\right) \Big]$$

These are complex conjugate of each other

• Both of these last-terms have the same norm $= \sqrt{|\;|^2}$

$$\boxed{\underline{\text{norm}} = \left| \int_{-\infty}^{\infty} \psi_f^* \vec{r} \psi_i \, d^3r \right| = \left| \int_{-\infty}^{\infty} \psi_i^* \vec{r} \psi_f \, d^3r \right|}$$

Get allowed transitions when $(\bar{\vec{p}} \neq 0)$

$\boxed{\text{We can evaluate these integrals using parity!}}$

$\vec{r} \rightarrow -\vec{r}$ under parity in 3D

If (as we'll show) $\psi_{nlm_l m_s}(\vec{r}) \longrightarrow \psi_{nlm_l m_s}(-\vec{r}) = \pm \psi_{nlm_l m_s}(\vec{r})$

then the $\underline{\text{1st two}}$ integrals vanish!

→ $|\Psi_i|^2$ or $|\Psi_f|^2$ even if $\Psi_i(-\vec{r}) = \pm \Psi_i(\vec{r})$

Integrand $\Psi_i^* \vec{r}\, \Psi_i = \underset{\substack{\uparrow \\ \text{odd}}}{\vec{r}}\, \underset{\substack{\uparrow \\ \text{even}}}{|\Psi_i|^2} \longrightarrow$ odd integrand

<u>Therefore</u> $\int_{-\infty}^{\infty} \Psi_i^* \vec{r}\, \Psi_i \, d^3r = 0$ <u>also</u> similarly $\int_{-\infty}^{\infty} \Psi_f^* \vec{r}\, \Psi_f \, d^3r$.

<u>So</u> all that matters for whether $\vec{p} = 0$ or not is whether the norm

$$p_{fi} = \Big| \underbrace{\int \Psi_f^* e\vec{r}\, \Psi_i \, d^3r}_{\text{involves different state}} \Big| \quad \text{is zero or not}$$

⇒ Called the "overlap integral"

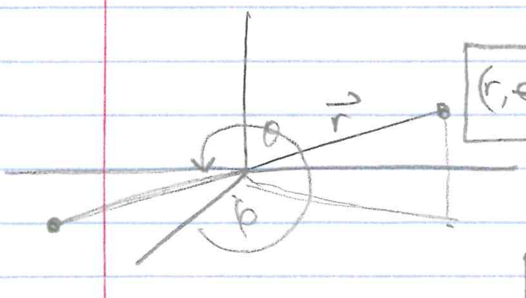
⇒ Ψ_i & Ψ_f must overlap

<u>Next</u>, we need to show that $\Psi_{nlm_l}(\vec{r})$ have definite parity (if $\underline{\Psi_{nlm_l}(-\vec{r}) = \pm \Psi_{nlm_l}(\vec{r})}$)

has definite parity

$\boxed{\text{What happens under parity in 3D?}}$

$\Psi(\vec{r}) = \Psi(r, \theta, \varphi)$ How do the coordinates r, θ, φ transform when $\vec{r} \longrightarrow -\vec{r}$?



$$\boxed{(r, \theta, \varphi) \longrightarrow (r, \pi - \theta, \pi + \varphi)}$$

In spherical coordinates

$$\boxed{\Psi(-\vec{r}) = \Psi(r, \pi - \theta, \pi + \varphi)}$$

does this have definite parity?
Is $\Psi(\vec{r})$ <u>even ~~of~~ odd</u>?

To answer this q,
<u>use</u>

$$\Psi_{nlm_l}(\vec{r}) = R_{nl}(r)\, \Theta_{lm_l}(\theta)\, \Phi_{lm_l}(\varphi)$$

So $$\boxed{\Psi_{n\ell m_\ell}(-\vec{r}) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\pi-\theta)\,\Phi_{m_\ell}(\pi+\varphi)}$$

Recall $\Phi_{m_\ell}(\varphi) = e^{im_\ell\varphi}$ So $\Phi_{m_\ell}(\pi+\varphi) = e^{im_\ell(\pi+\varphi)} = e^{im_\ell\varphi}\cdot e^{im_\ell\pi}$

Note $e^{im_\ell\pi} = \left(e^{i\pi}\right)^{m_\ell} = (-1)^{m_\ell}$

So $$\boxed{\Phi_{m_\ell}(\pi+\varphi) = (-1)^{m_\ell}\,\Phi_{m_\ell}(\varphi)}$$

Next, look at $\Theta_{\ell m_\ell}(\theta) \longrightarrow \Theta_{\ell m_\ell}(\pi-\theta)$

April 25, 2018

$P_{fi} = \left|\int \psi_f^* e\vec{r}\,\psi_i\,d^3r\right|$ is zero or not

↳ need $P_{fi} \neq 0$ for allowed transition.

Under parity → $\vec{r} \to -\vec{r}$

$\Psi_{n\ell m_\ell}(\vec{r}) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)$ becomes $R_{n\ell}(-r)\,\Theta_{\ell m_\ell}(\pi-\theta)\,\Phi_{m_\ell}(\pi+\varphi)$

Showed $$\boxed{\Phi_{m_\ell}(\pi+\varphi) = (-1)^{m_\ell}\,\Phi_{m_\ell}(\varphi)}$$

What about Θ?

even or odd function for ℓ = even or odd

Recall $$\Theta_{m_\ell}(\theta) = \sin^{|m_\ell|}\theta\,\frac{d^{|m_\ell|}P_\ell(\cos\theta)}{d^{|m_\ell|}\cos\theta}$$

$$\Rightarrow \Theta(\pi-\theta) = \sin^{|m_\ell|}(\pi-\theta)\,\frac{d^{|m_\ell|}}{d^{|m_\ell|}\cos(\pi-\theta)}\,P_\ell\left(\overset{\pi-}{\cos}\,\theta\right)$$

$$= \sin^{|m_\ell|}\theta\,\frac{d^{|m_\ell|}}{d^{|m_\ell|}(-\cos\theta)}\,\underbrace{P_\ell(-\cos\theta)}_{(-1)^\ell P_\ell(\cos\theta)}$$

$$= \sin^{|m_\ell|}\theta\,(-1)^{m_\ell}(-1)^\ell\,\Theta_{\ell m_\ell}(\theta)$$

So $$\boxed{\Theta(\pi-\theta) = \sin^{|m_\ell|}\theta\,(-1)^{m_\ell}(-1)^\ell\,\Theta_{\ell m_\ell}(\theta)}$$

So $\boxed{\psi_{nlm_l}(-r) = \underbrace{(-1)^{m_l}(-1)^{m_l}}_{}(-1)^{l}\ \psi_{nlm_l}(r)}$

↳ 1 for m_l = integer...

So $\boxed{\psi_{nlm_l}(-r) = (-1)^{l}\ \psi_{nlm_l}(r)}$

Therefore parity only depends on l;

↳ Now look at the dipole moment

$$P_{fi} = \left| \int \psi^{*}_{n'l'm_l'}\ e\tilde{r}\ \psi_{nlm_l}\ d^3r \right| \rightarrow \text{norm}$$

Under parity $\rightarrow \vec{r} \to -\vec{r}$ (odd)

↳ $\psi_{n'l'm_l'} \rightarrow (-1)^{l'}\psi_{n'l'm_l'}$

$\psi_{nlm_l} \rightarrow (-1)^{l}\psi_{nlm_l}$

Hence Integrand $\longrightarrow (-1)(-1)^{l+l'}$ Integrand

So The integral vanishes if the Integrand is odd

Hence ↳ If $\boxed{l+l' = \text{even}}$

or with $l = l' + \Delta l \rightarrow 2l + \Delta l = \text{even}$

So Vanishes if $\Delta l = 0, \pm 2, \pm 4, \ldots$

Only values (so it doesn't vanish) consistent with photons having spin = 1 are allowed

$\boxed{\Delta l = \pm 1}$ ↳ γ can't carry $3\hbar$

Then for j $j = l \pm \frac{1}{2}$, $j' = l' \pm \frac{1}{2} = \overbrace{l \pm 1} \pm \frac{1}{2}$

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 rules

$$\boxed{\begin{array}{l} \Delta l = \pm 1 \\ \Delta j = 0, \pm 1 \end{array} \text{, all other forbidden}}$$

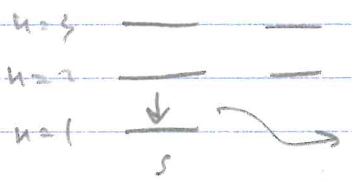
angular momentum changes in direction

electric dipole transition → with highest probability →

There are other transitions that can occur, but they have much lower probability (not electric dipole) → a million times less prob.

↳ called "forbidden transitions" → misleading since they can happen

e.g. $2s \rightarrow 1s$ in H is a forbidden transition



This can only occur as a 2γ transition

Typical lifetime for allowed transitions are $\sim 10^{-8}\, s \propto 10\, nm$

but the $2s - 1s$ lifetime is about 1s → metastable state (less probable by 10^8)

//

V · ATOMIC PHYSICS

→ Want 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 Δx of each other → we can't track them individually. This is NOT true classically → where you can always track individual trajectories

↳ This is a QM problem...

↳ Identical Particles

Consider 2 identical particles

↳ To write a 2 particle SE, we must use labels

Let $\Psi(\vec{r}_1, \vec{r}_2)$ = 2-particle wave-functions for 2 identical particles...

$$-\frac{\hbar^2}{2m}\vec{\nabla}_1^2 \Psi(\vec{r}_1,\vec{r}_2) - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 \Psi(\vec{r}_1,\vec{r}_2) + V(\vec{r}_1,\vec{r}_2)\Psi(\vec{r}_1,\vec{r}_2) = E\,\Psi(\vec{r}_1,\vec{r}_2)$$

$$\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) \qquad (\vec{r}_1 = x_1\hat{i} + y_1\hat{j} + z_1\hat{k})$$

$$(\vec{r}_2 = x_2\hat{i} + y_2\hat{j} + z_2\hat{k})$$

$$\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}$$

Mass = m for both, $V(\vec{r}_1,\vec{r}_2)$ = mutual 2-particle potential energy

E = total energy → 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 so is $\Psi(2,1)$

$(\Psi(1,2))$

Can define an exchange operator $\Psi(2,1) = \hat{P}_{12}\Psi(1,2)$

This must give ~~use~~ solution $\qquad \hat{P}$ is for Permute

If
$\hat{P}_{12}$ acts twice $\hat{P}_{12}^{2}\Psi(1,2) = \hat{P}_{12}\Psi(2,1) = \cancel{\hat{P}}\Psi(1,2)$

So $\hat{P}_{12}^{2} = 1 \longrightarrow$ eigenvalue.

So $\hat{P}_{12} = \pm 1 \longrightarrow$ eigenvalue $\rightarrow$ Get 2 types of eigenstates

If underinterchange $\boxed{\Psi(2,1) = +\Psi(1,2)} \rightarrow$ 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.

$\hookrightarrow$ All identical particle wave functions in QM are either symmetric or anti-symmetric.

April 27/2010 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 $\uparrow$ does not hold

Then, there's a 2^{nd} classification:

$\boxed{\text{Bosons}} \longrightarrow$ have integer spin | E.g: photons (1), pions (0) Higgs

$\boxed{\text{Fermions}} \longrightarrow$ have $\frac{1}{2}$-integer spin

e.g e^-, p^+, quarks, neutrinos, muons, spin $\frac{1}{2}$-int

Note 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 $n l m_\ell s m_s$

⇒ can't have 2 electrons with the same $n l m_\ell s m_s$

↳ $1^{st}\ e^- \Rightarrow n=1,\ l=0,\ m_\ell=0,\ s=\frac{1}{2},\ m_s=+\frac{1}{2}$ (up)

$2^{nd}\ e^- \Rightarrow n=1,\ l=0,\ m_\ell=0,\ s=\frac{1}{2},\ m_s=-\frac{1}{2}$ (down)

$3^{rd}\ e^- \Rightarrow n=2,\ l=0,\ m_\ell=0,\ s=\frac{1}{2},\ m_s=+\frac{1}{2}$ (up)

⋮

Have 2 classifications	→ Symmetric (Bose-Einstein)	or	Anti-symmetric (Fermi-Dirac)
	→ bosons	or	fermions
	int. spins		$\frac{1}{2}$-integers

There's a link between these

Fermions → anti symmetric wfn (obey F-D stats)

⇒ obey the exclusion principle

Bosons → symmetric wfn (obey Bose-Einstein stats)

⇒ 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 $-\frac{\hbar^2}{2m}\vec{\nabla}_1^2 \Psi(\vec{r}_1,\vec{r}_2) - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 \Psi(\vec{r}_1,\vec{r}_2) + V(\vec{r}_1,\vec{r}_2)\Psi(\vec{r}$

$$= E\Psi(\vec{r}_1,\vec{r}_2)$$

⇒ If $V(\vec{r}_1,\vec{r}_2)$ depends on $\vec{r}_1$ and $\vec{r}_2$ in a way that won't seperate, then this becomes hard to solve ...

but if $\boxed{V(\vec{r}_1,\vec{r}_2) = V(\vec{r}_1) + V(\vec{r}_2)}$, then the eqn will separate

same for V

↳ 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 $\vec{r}_1$

denotes the state (n, l, s, m_l, m_s)

single particle states

Now for identical particles, we need $\Psi(2,1) = \pm\Psi(1,2)$

We form these as the combination

$\boxed{\text{sym}}$ $\Psi_S(1,2) = \frac{1}{\sqrt{2}}\left[\Psi_\alpha(1)\Psi_\beta(2) + \Psi_\beta(1)\Psi_\alpha(2)\right]$

$\boxed{\text{anti-sym}}$ $\Psi_A(1,2) = \frac{1}{\sqrt{2}}\left[\Psi_\alpha(1)\Psi_\beta(2) - \Psi_\beta(1)\Psi_\alpha(2)\right]$

<u>Can verify</u> $\psi_s(2,1) = \frac{1}{\sqrt{2}}\left[\psi_\alpha(2)\psi_\beta(1) + \psi_\alpha(1)\psi_\beta(2)\right] = \psi_s(1,2)$

$\hookrightarrow$ always $\psi_s(1,2) = \psi_s(2,1)$

<u>also</u> $\psi_A(2,1) = \frac{1}{\sqrt{2}}\left[\psi_\alpha(2)\psi_\beta(1) - \psi_\alpha(1)\psi_\beta(2)\right] = -\psi_A(1,2)$

$\hookrightarrow$ always $\psi_A(1,2) = -\psi_A(2,1)$

$\boxed{\text{Why } 1/\sqrt{2}\text{ ?}}$ Needed for normalization

To show this, we must use a property called orthogonality.

$$\left.\begin{array}{ll} \int \psi_\alpha^*(1)\,\psi_\beta(1) = 0 & \text{if } \alpha \neq \beta \\ \int \psi_\alpha^*(1)\,\psi_\alpha(1) = 1 & \text{if } \alpha = \beta \end{array}\right] \text{You'll show this in } \underline{9\text{-}10}$$

With this, can look at normalization of $\psi_s(1,2)$

$$\iint \psi_s^*(1,2)\,\psi(1,2) = \iint \left(\frac{1}{\sqrt{2}}\right)^2 \left[\psi_\alpha^*(1)\psi_\beta^*(2) + \psi_\beta^*(1)\psi_\alpha^*(2)\right] \cdot \left[\psi_\alpha(1)\psi_\beta(2) + \psi_\beta(1)\psi_\alpha(2)\right]$$

$$= \frac{1}{2}\iint |\psi_\alpha(1)|^2|\psi_\beta(2)|^2 + |\psi_\beta(1)|^2|\psi_\alpha(2)|^2 + \psi_\alpha^*(1)\psi_\beta(1)\cdot\psi_\beta^*(2)\psi_\alpha(2) + \psi_\beta^*(1)\psi_\alpha(1)\cdot\psi_\alpha^*(2)\psi_\beta(2)$$

$$= \frac{1}{2}\left[1 + 1 + 0 + 0\right] = \frac{2}{2} = \boxed{1}$$

*

<u>Now</u>, suppose we have 3 or more identical particles

<u>Bosons</u> : symmetric under change of any pair (6 ways)

$\hookrightarrow \psi_s(\ldots i \ldots j \ldots) = \psi_s(\ldots j \ldots i \ldots)$

Fermions → must be anti-sym

$$\psi_A(\cdots i \cdots j \cdots) = -\psi_A(\cdots i \cdots j \cdots)$$

For 2 Fermions

↳ $$\psi_A = \frac{1}{\sqrt{2}}\left[\underset{(1)}{\psi_\alpha(1)\psi_\beta(2)} - \underset{(2)}{\psi_\alpha(2)\psi_\beta(1)}\right]$$

or

$$\boxed{\psi_A = \frac{1}{\sqrt{2}}\det\begin{pmatrix}\psi_\alpha(1) & \psi_\beta(2)\\ \psi_\beta(1) & \psi_\beta(2)\end{pmatrix}}$$

determinants have 2 properties...

↳ pick up a (−) under interchange of any pair of rows or column

→ they vanish if any 2 rows or columns are the same!

e.g. $\underbrace{\text{if } \alpha = \beta}$ → $\boxed{\text{get } 0}$

↳ exclusion principle (for fermions) → $\psi = 0$

For 3 particles (identical Fermions)

$$\underset{\substack{\uparrow \\ 6 = 3!}}{\psi_A = \frac{1}{\sqrt{3!}}}\begin{vmatrix}\psi_\alpha(1) & \psi_\alpha(2) & \psi_\alpha(3)\\ \psi_\beta(1) & \psi_\beta(2) & \psi_\beta(3)\\ \psi_\gamma(1) & \psi_\gamma(2) & \psi_\gamma(3)\end{vmatrix} \rightarrow \det(\,)$$

6 terms

6 = 3! → # of permutations...

April 30, 2018

Constructing anti-sym + sym. Wfns

Anti-sym

e.g 2 fermions $\Psi_A(1,2) = \frac{1}{\sqrt{2}}\left(\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)\right)$

$$= \frac{1}{\sqrt{2}} \det \begin{pmatrix} \psi_\alpha(1) & \psi_\alpha(2) \\ \psi_\beta(1) & \psi_\beta(2) \end{pmatrix}$$

$\downarrow$ Generalize to N particles

$$\boxed{\Psi_A = \underset{\uparrow \text{ \# of permutations}}{\frac{1}{\sqrt{n!}}} \det \begin{pmatrix} \psi_\alpha(1) & \cdots & \psi_\alpha(n) \\ \vdots & & \vdots \\ \psi_\gamma(1) & \cdots & \psi_\gamma(n) \end{pmatrix}}$$

slater determinant

For symmetric wfn Ψ_S ⇒ write out $n \times n$ determinant, then change all minus signs to (+) signs...

(bosons)

//

HELIUM → 2 electrons (fermions)

⇒ ignore Coulomb interaction between the electrons..

Then the single particle Wfn are hydrogenic

$$\boxed{\psi_\alpha(1) = \underset{\uparrow}{\psi_a}(1)\,\chi_{\pm\frac{1}{2}}}$$

denotes all quantum numbers but spin

Use these in

$$\boxed{\Psi_A = \frac{1}{\sqrt{2}}\left(\underset{\uparrow}{\psi_\alpha}(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)\right)}$$

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_1}, 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 $\boxed{\vec{S}' = \vec{S}_1 + \vec{S}_2}$ → total spin

Then, we form Ψ_A = (total spatial part) · (total spin part)

So $\boxed{\Psi_A = \Psi_{spatial}\,\chi_{spin}}$

We still require that under interchange, $\Psi_A \to -\Psi_A$

⇒ We can get this in 2 ways

$$\left[\begin{array}{l} \Psi_{spatial} \to -\Psi_{spatial}, \quad \chi_{spin} \Rightarrow \chi_{spin} \\ \chi_{spin} \to -\chi_{spin}, \quad \Psi_{spatial} \to \Psi_{spatial} \end{array}\right]$$

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 $\left.\begin{array}{l} |\vec{S}'| = \frac{1}{2} + \frac{1}{2} = 1 \\ \text{and } m_s' = -1, 0, 1 \end{array}\right\} \to 3 \text{ cases}$

or $\left.\begin{array}{l} |\vec{S}'| = \frac{1}{2} - \frac{1}{2} = 0 \\ \text{and } m_s' = 0 \end{array}\right\}$ 1 cases

Still have 4 cases total → two $\pm\frac{1}{2}$ spins

→ These then group into symmetric & anti-symmetric combinations

$s' = 1 \Rightarrow$ symmetric

⇒ Use labels ⟶ $\chi_{s' m_s'}$

Turns out to be more useful (we'll see why) to characterize states of the atom by their total spin.

↳ Call $\boxed{\vec{S}' = \vec{S}_1 + \vec{S}_2}$ → total spin

Then, we form Ψ_A = (total spatial part) · (total spin part)

So $\boxed{\Psi_A = \Psi_{spatial}\,\chi_{spin}}$

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⇒ We can get this in 2 ways

$$\left[\begin{array}{l} \Psi_{spatial} \to -\Psi_{spatial}, \quad \chi_{spin} \Rightarrow \chi_{spin} \\ \chi_{spin} \to -\chi_{spin}, \quad \Psi_{spatial} \to \Psi_{spatial} \end{array}\right]$$

Can have both! (either is anti-symmetric...)

⇒ Get the link between total spin & spatial wavefunction...

⇒ leads 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 $|\vec{S}'| = \frac{1}{2} - \frac{1}{2} = 0$ and $m_{s'} = 0$ } 1 cases

Still have 4 cases total → two $\pm\frac{1}{2}$ spins

↳ These then group into symmetric & anti-symmetric combinations

$s' = 1 \Rightarrow$ symmetric

⇒ Use labels ⟶ $\chi_{s' m_{s'}}$

$s'=1$ (3 sym triplet)

$$\boxed{\begin{aligned} \chi_{11} &= \chi_{\frac{1}{2}}(1)\,\chi_{\frac{1}{2}}(2) && \rightarrow m_s'=1 \\ \chi_{10} &= \frac{1}{\sqrt{2}}\left[\chi_{\frac{1}{2}}(1)\,\chi_{\frac{1}{2}}(2) + \chi_{\frac{1}{2}}(1)\,\chi_{\frac{1}{2}}(2)\right] && \rightarrow m_s'=0 \\ \chi_{1-1} &= \chi_{-\frac{1}{2}}(1)\,\chi_{-\frac{1}{2}}(2) && \rightarrow m_s=-1 \end{aligned}}$$

All threes are symmetric ⇒ called "triplet states" of He

Since χ symmetric ⇒ ψ_{spatial} has to be anti-symmetric

$s'=0 \rightarrow$ (1 anti-sym singlet)

$$\boxed{\chi_{00} = \frac{1}{\sqrt{2}}\left[\cancel{\chi}_{\frac{1}{2}}(1)\,\chi_{-\frac{1}{2}}(2) - \chi_{-\frac{1}{2}}(1)\,\chi_{\frac{1}{2}}(2)\right]} \quad m_s'=0$$

↳ χ anti-symmetric ⇒ ψ has to be symmetric

→ called "singlet state"

So the total WFn (anti-sym) → $\boxed{\psi_A = \psi_{\text{spatial}}\,\chi_{\text{spin}}}$ ← $\chi_{s' m_s'}$

and $\left\{\begin{array}{l} \psi_{\text{spatial}} \text{ symmetric for } s'=0 \\ \psi_{\text{spatial}} \text{ anti-symmetric for } s'=1 \end{array}\right\}$

What are the physical effects of this?

↳ Suppose the 2 e^- get close ⇒ $\vec{r}_1 \simeq \vec{r}_2$ ⇒ $1 \simeq 2$

Then $$\psi^{A}_{\text{spatial}} = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\,\psi_\beta(2) - \psi_\beta(1)\,\psi_\alpha(2)\right] \leftarrow \text{anti-sym}$$

So $$\simeq \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\,\psi_\beta(1) - \psi_\beta(1)\,\psi_\alpha(1)\right] \simeq 0 \rightarrow \text{spin triplet}$$

⇒ Means low probability for e^- getting close

$\boxed{s'=1}$

But $\Psi^{S}_{spatial} = \frac{1}{\sqrt{2}}\left[\Psi_\alpha(1)\Psi_\beta(2) + \Psi_\beta(1)\Psi_\alpha(2)\right]$ (spin singlet)

$\simeq \frac{1}{\sqrt{2}}\cdot 2\left[\Psi_\alpha(1)\Psi_\beta(1)\right] \neq 0$ $\pm\frac{1}{2}, S=0$

↳ Higher probability for particles to get close...

$\boxed{\text{See a correlation between spatial behavior and total spin}}$

Singlet (s'=0) $\uparrow\downarrow$ $s'=0$, $m_s'=0$ (anti-symmetric)

(so $\Psi_{spatial}$ symmetric ⇒ particles can get close)

Triplet (s'=1)

$\uparrow\ \uparrow$ $m_s'=1$

$\downarrow\ \downarrow$ $m_s'=-1$

$\uparrow\ \downarrow$ $m_s'=0$

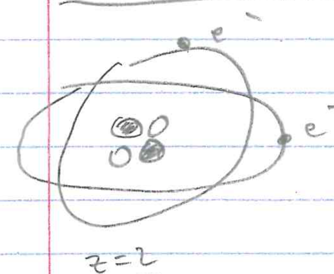
} → χ sym

↳ $\Psi_{spatial}$ is anti-sym → particle stay apart

↳ This is sort of like a force → $\boxed{\text{“exchange force”}}$

↳ But it's not really a force, rather it's an effect of having $\Psi_{spatial}$ be sym. or anti-sym...

What about energy levels of Helium?



Z=2

→ Make 3 levels of approximation!

① Ignore Coulomb potential between e^- (ignore e^--e^-)

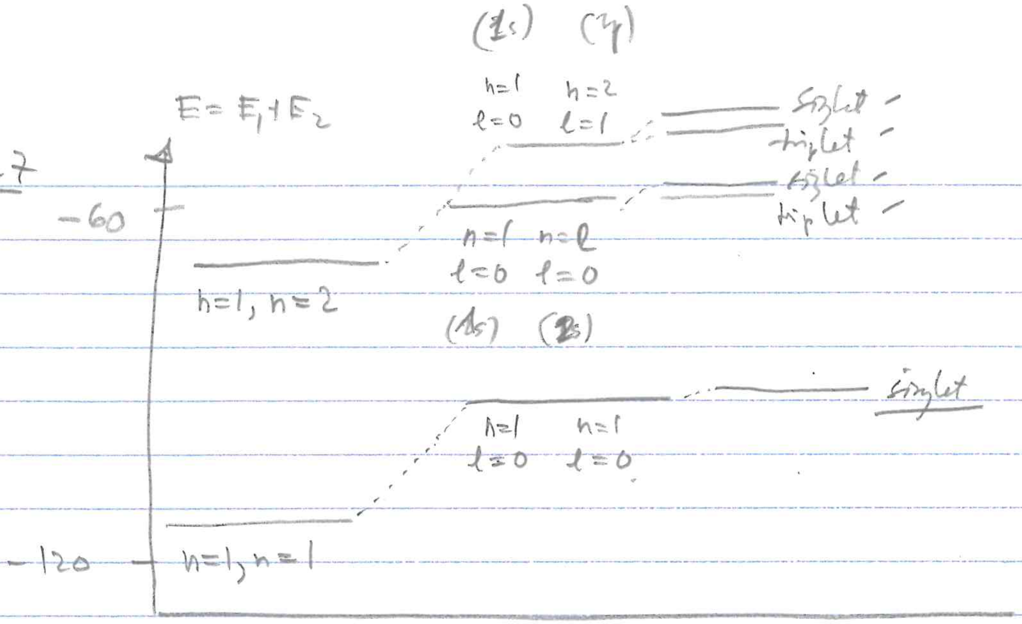
↳ $$\boxed{E_n = -Z^2\frac{(13.6\,eV)}{n^2} \qquad Z=2}$$

↳ $E_1 = -54.4eV$ ...

$E_2 = -13.6eV$ ...

⋮

Figure 9.7



② Include some of e^-e^- interaction (average Coulomb effects) between e^- (no spin yet)

$$V = \frac{e^2}{4\pi\epsilon_0 r_{1,2}}$$ ← repel force ⇒ $V > 0$

So E goes up!

→ By how much? Look at the radial probability distribution.

(p state e closer to nucleus & to each other → V higher)

③ Include spin effects

Triplet ⇒ $\Psi_{spatial}$ anti-symmetric ⇒ e stays apart more ⇒ V smaller ~~on~~

Singlet ⇒ $\Psi_{spatial}$ symmetric ⇒ e ~~stays~~ can get closer ⇒ V bigger

So

Note all triplet @ same energy (since E depends on V)

Note → there is NO triplet in the ground state.

↳ Observed spectroscopically. Why?

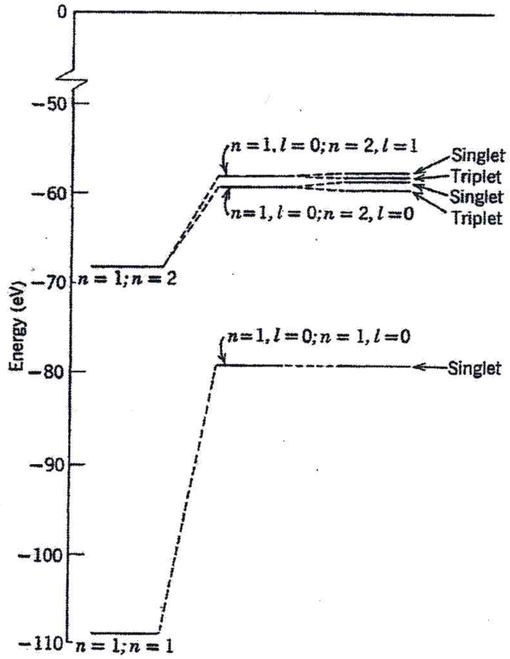
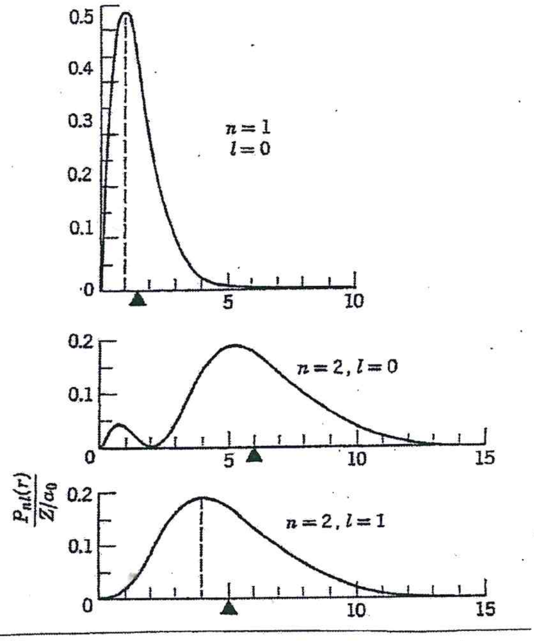


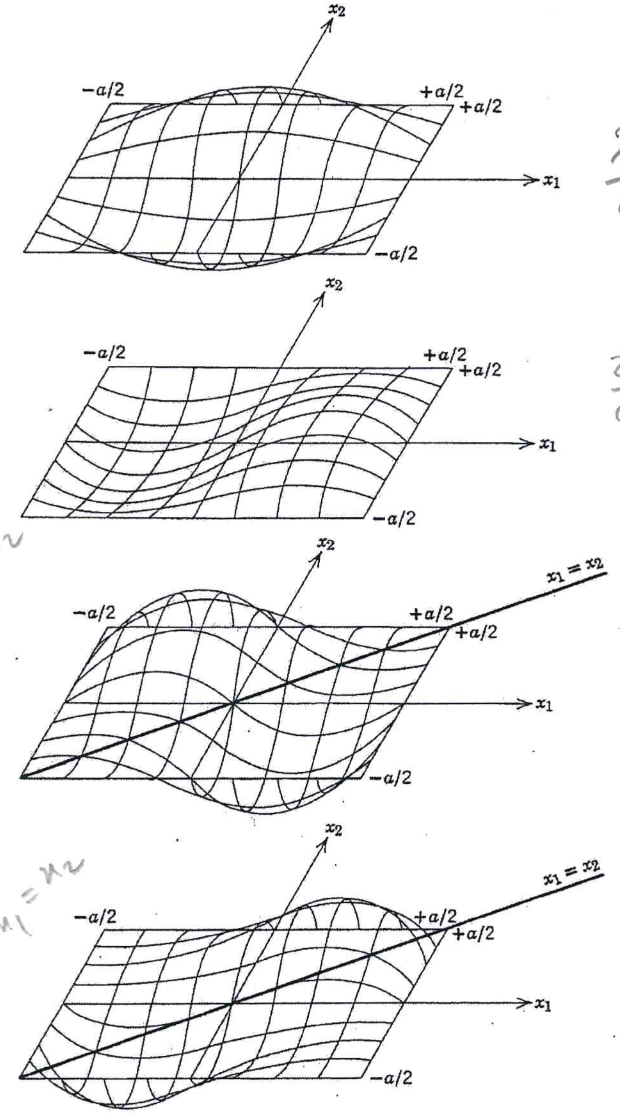
Figure 9-7 The low-lying energy levels of helium. *Left:* The levels that would be found if there were no Coulomb interaction between its electrons. *Center:* The levels that would be found if there were a Coulomb interaction but no exchange force. *Right:* The levels that would be found if there were 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.

---

n=1

n=2





$\frac{2}{a}\cos\frac{\pi x_1}{a}\sin\frac{2\pi x_2}{2}$

$\frac{2}{a}\sin\frac{2\pi x_1}{2}\cos\frac{\pi x_2}{2}$

$\psi = 0 @ x_1 = x_2$

ψ_-

when particles are close

ψ_+

$\psi \neq 0 @ x_1 = x_2$

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 $x_1 \simeq x_2$, 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.

$-\frac{e^2}{4\pi\varepsilon_0 r^2}$

$-\frac{d}{dr}\left(\frac{-e^2}{4\pi r^2}\right)\frac{1}{6}$

$= \boxed{\frac{-e^2}{4\pi\varepsilon_0 r}}$

Why? If χ_{spin} → symmetric for triplet

then $\psi_{spatial}$ → must be anti-symmetric

But both e^- have $n=1,\ l=0,\ m_l=0$ → ψ_{100}

$$\boxed{\psi^{A}_{spatial} = \frac{1}{\sqrt{2}}\left[\psi_{100}(1)\psi_{100}(2) - \psi_{100}(2)\psi_{100}(1)\right] = 0}$$

↳ No triplet! (Exclusion principle...) → Pauli...

~~April~~ May 2, 2018

Recall

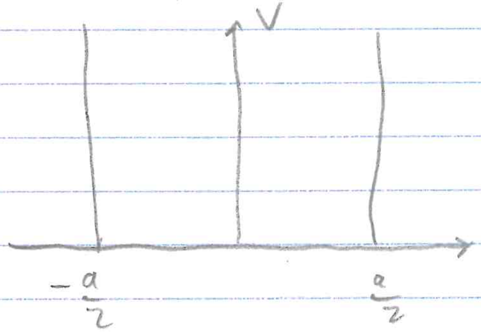
Exchange Effect $\psi_A = \psi_{spatial}\chi_{spin}$ total spin

If χ_{spin} Anti-sym, then $\psi_{spatial}$ sym → particles can get close

If χ_{spin} sym, then $\psi_{spatial}$ anti-sym → particles stay apart

Example for ψ spatial

↳ Two particles in a box



→ assume no interaction between the particles.

Recall the single particle wfn

$$\psi_1 = \sqrt{\frac{2}{a}}\cos\left(\frac{\pi x}{a}\right)$$

$$\psi_2 = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)$$

⋮

E level ↓

Suppose 1 particle in ground state, and 1 in first excited state,

let x_1 → particle 1
x_2 → particle 2

→ Can form sym & anti-sym combination of wfn...

Symmetric case

$$\hookrightarrow \Psi_+ = \frac{1}{\sqrt{2}}\left[\psi_1(x_1)\psi_2(x_2) + \psi_2(x_1)\psi_1(x_2)\right]$$

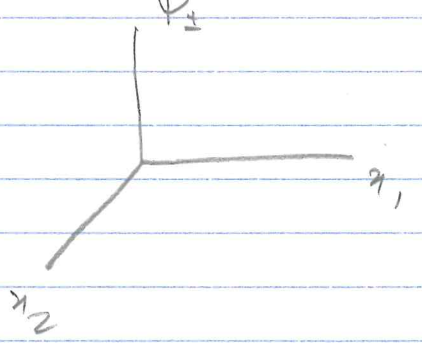
$$\boxed{\Psi_+ = \frac{2}{a}\frac{1}{\sqrt{2}}\left[\cos\frac{\pi x_1}{a}\sin\frac{2\pi x_1}{a} + \sin\frac{2\pi x_1}{a}\cos\frac{\pi x_2}{a}\right]}$$

Anti-sym

$$\boxed{\Psi_- = \frac{2}{a}\frac{1}{\sqrt{2}}\left[\cos\frac{\pi x_1}{a}\sin\frac{2\pi x_2}{2} - \sin\frac{2\pi x_1}{a}\cos\frac{\pi x_2}{a}\right]}$$

Ψ_+ and Ψ_- Obey $\left\{\begin{array}{l}\Psi_+(2,1) = \Psi_+(1,2)\\ \Psi_-(2,1) = -\Psi_-(1,2)\end{array}\right\}$

We can plot these as function of x_1 & x_2



(see Figure 9.4)

Fig 1 $\frac{2}{a}\cos\frac{\pi x_1}{a}\sin\frac{2\pi x_2}{a}$

Fig 2 $\frac{2}{a}\sin\frac{2\pi x_1}{a}\cos\frac{\pi x_2}{a}$

(anti-sym) Fig 3 $\Psi_- = \frac{\cancel{2}}{\cancel{2}}\frac{1}{\sqrt{2}}(\text{Fig 1} - \text{Fig 2})$

(sym) Fig 4 $\Psi_+ = \frac{1}{\sqrt{2}}(\text{Fig 1} + \text{Fig 2})$

Observe • Fig 3 has $\Psi = 0$ along $x_2 = x_1$

↳ no probability for being close (book cover) ($|\Psi|^2$)

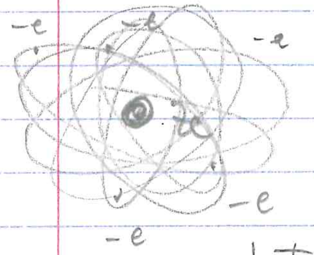
• Fig 4 has $\Psi \neq 0$ along $x_1 = x_2$

↳ There is probability of being close

→ "exchange force" → really a result of sym or anti-sym spatial wfn...

#

$\boxed{\text{Hartree Theory}}$ → Need an approximation method for multi-electron atom, let Z = atomic number...



$$\rightarrow V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots \vec{r}_Z) = \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|} + \cdots + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_{Z-1} - \vec{r}_Z|}$$
$$\frac{-Ze^2}{4\pi\varepsilon_0 \vec{r}_1} + \cdots \frac{-Ze^2}{4\pi\varepsilon_0 \vec{r}_Z}$$

| Too complicated → can't seperate variables!

↳ Must compromise → use the average effect in a way that separates

Approx

$$V(\vec{r}_1 \ldots \vec{r}_Z) = V(r_1) + V(r_2) + \cdots + V(r_Z)$$

where $V(r)$ = single particle's effective potential
→ central potential ↳ only radial distance matters
→ No angular dependence...

↳ Then the problem seperates!

$\boxed{\text{Hartree's Theory}}$ → self-consistent method for finding V(r)

(1) → Guessing a form for V(r) obeying 2 limits

$$V(r) = \begin{cases} \dfrac{-Ze^2}{4\pi\epsilon_0 r} & r \to 0 \quad \text{(no screening)} \\ \dfrac{-e^2}{4\pi\epsilon_0 r} & r \to \infty \quad \text{(full screening)} \quad (Z-Z+1) \end{cases}$$

Find V(r) that extrapolate between these...

(2) → Solve the single-particle SE for V(r) and order solution

(i) $\psi_1(r, \theta, \varphi) \rightarrow$ has E_1
(ii) $\psi_2(r, \theta, \varphi) \rightarrow$ has $E_2 > E_1$
⋮

(3) Form the ground state of the atom by filling the lowest E-levels
→ putting $1e^-$ per state

(4) Calculate the charge distribution for this solution → charge density follows the particle

$$-e|\psi_1|^2 - |\psi_2|^2 e - e|\psi_3|^2 + \ldots - e|\psi_Z|^2 + Ze \text{ @ orig}$$

(5) → Use Gauss's 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)

→ Generates a V(r) that combines the SE, Gauss's law and the exclusion principle

Remarks → Each single particle state has $Y_{lm_l}(\theta,\varphi)$ as the angular part of the solution

(i) $V(r)$ → central potential (don't matter)

And so Separation constant = $\boxed{l(l+1)}$

→ but the radial wfn for $R_{nl}(r)$ will be different from H

(ii) The same quantum numbers $n l m_l m_s$ label the states in this approx

(iii) Must solve the radial equation numerically
→ Have to use numerical methods
→ LOL 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
↳ 1s, 2s, 2p, ...

But anti-sym is too complicated ...

e.g. Ne $Z=10$ → 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 $\quad nl^{\#e^- \text{ in subshell}} \rightarrow \max = 2(2l+1)$

level/shell ↗ ↖ subshell (s, p, d, f, g, h, ...)

Subshells fill up when you put in $2(2l+1)$ electrons ...

Energies depend on nl

⇒ need to look at the ordering found by Hartree

e.g. 4s fills up before the 3d.

May 7, 2018

Ground State + Periodic Table

Use Hartree results to find the ordering of the n, l levels

→ fill them up with Z electrons...

Notation $nl^{\#e}$

$\#e \rightarrow \max = 2(2l+1)$

$l \rightarrow s, p, d, f, \ldots$

Energy depends on both n, and l

→ l degeneracy is broken

→ sometimes l matters more than n

e.g. 4s fills up before the 3d

Look at Table 9.2 → order determined by Hartree approach

subshells	Capacity $= 2(2l+1)$
1s	2
2s	2
2p	6
3s	2
3p	6

E ↓

Now fill up the ground state

Li : $Z = 3$ $1s^2\, 2s^1\, 2p^0$ → called "electron configuration"

Be $Z = 4$ $1s^2\, 2s^2$

Bo $Z = 5$ $1s^2\, 2s^2\, 2p^1$

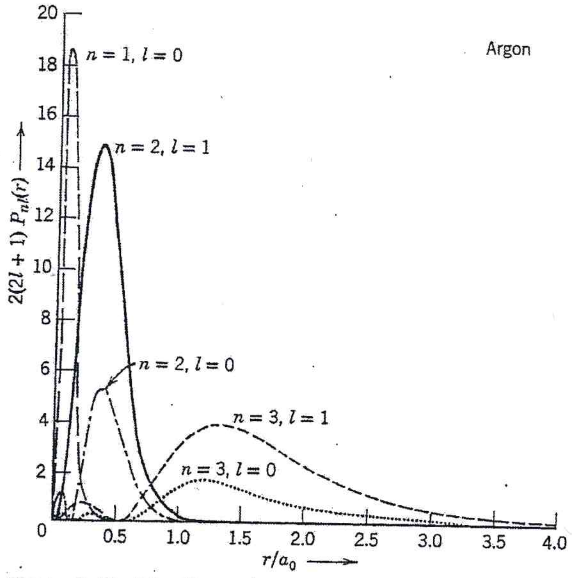


Figure 9-10 The Hartree theory radial probability densities for the filled quantum states of the argon atom, plotted as functions of r/a_0, the radial coordinate in units of the hydrogen atom first Bohr orbit radius a_0. For each n the probability density is largely concentrated in a restricted range 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.

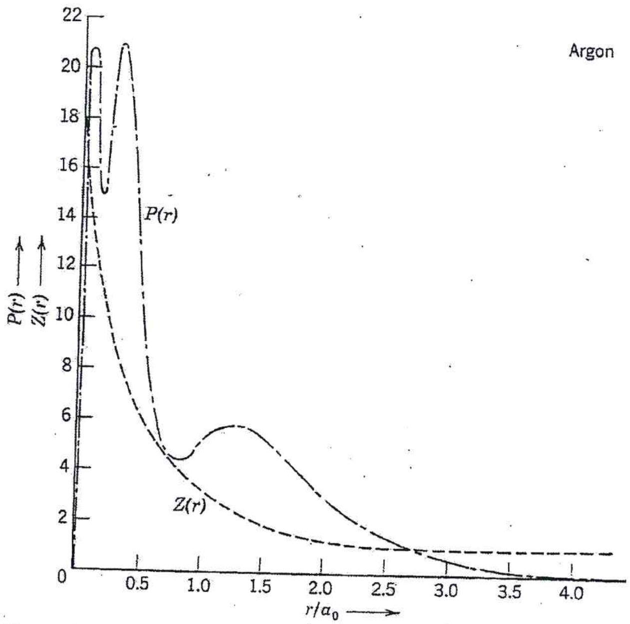
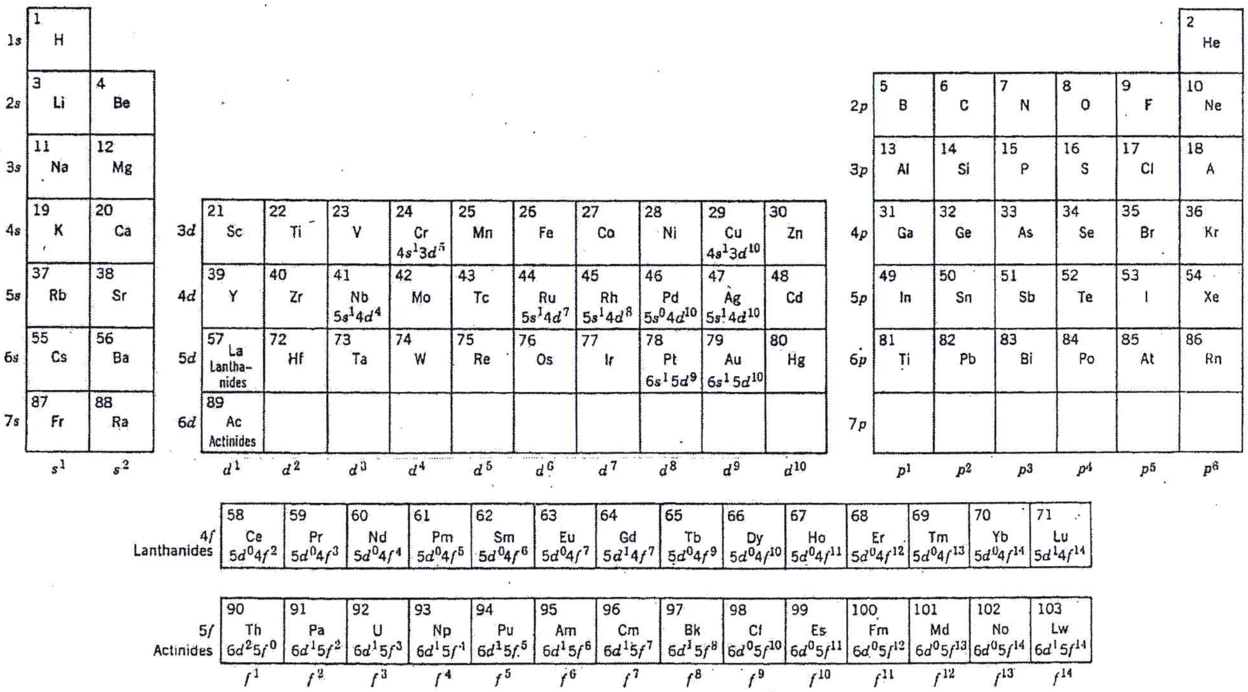


Figure 9-11 The total radial probability density $P(r)$ of the argon atom, and the quantity $Z(r)$ that specifies its net potential.

Table 9-2 The Energy Ordering of the Outer Filled Subshells

Quantum Numbers n, l	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	Increasing energy
5, 0	$5s$	2	(less negative)
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	←Lowest energy (most negative)



$1s$	1 H																			2 He
$2s$	3 Li	4 Be												$2p$	5 B	6 C	7 N	8 O	9 F	10 Ne
$3s$	11 Na	12 Mg												$3p$	13 Al	14 Si	15 P	16 S	17 Cl	18 A
$4s$	19 K	20 Ca	$3d$	21 Sc	22 Ti	23 V	24 Cr $4s^1 3d^5$	25 Mn	26 Fe	27 Co	28 Ni	29 Cu $4s^1 3d^{10}$	30 Zn	$4p$	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
$5s$	37 Rb	38 Sr	$4d$	39 Y	40 Zr	41 Nb $5s^1 4d^4$	42 Mo	43 Tc	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $5s^0 4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd	$5p$	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
$6s$	55 Cs	56 Ba	$5d$	57 La Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt $6s^1 5d^9$	79 Au $6s^1 5d^{10}$	80 Hg	$6p$	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
$7s$	87 Fr	88 Ra	$6d$	89 Ac Actinides										$7p$						
	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

$4f$ Lanthanides	58 Ce $5d^0 4f^2$	59 Pr $5d^0 4f^3$	60 Nd $5d^0 4f^4$	61 Pm $5d^0 4f^5$	62 Sm $5d^0 4f^6$	63 Eu $5d^0 4f^7$	64 Gd $5d^1 4f^7$	65 Tb $5d^0 4f^9$	66 Dy $5d^0 4f^{10}$	67 Ho $5d^0 4f^{11}$	68 Er $5d^0 4f^{12}$	69 Tm $5d^0 4f^{13}$	70 Yb $5d^0 4f^{14}$	71 Lu $5d^1 4f^{14}$
$5f$ Actinides	90 Th $6d^2 5f^0$	91 Pa $6d^1 5f^2$	92 U $6d^1 5f^3$	93 Np $6d^1 5f^4$	94 Pu $6d^1 5f^5$	95 Am $6d^1 5f^6$	96 Cm $6d^1 5f^7$	97 Bk $6d^1 5f^8$	98 Cf $6d^0 5f^{10}$	99 Es $6d^0 5f^{11}$	100 Fm $6d^0 5f^{12}$	101 Md $6d^0 5f^{13}$	102 No $6d^0 5f^{14}$	103 Lw $6d^1 5f^{14}$
	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.

^{10}Ne : $1s^2 2s^2 2p^6$

↳ For most part, the Hartree ordering works, but not all cases ...
There are exceptions to the ordering ...

^{23}V . $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ follows the ordering
^{24}Cr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ doesn't follow Hartree ordering

Gets complicated for the Lanthanides ...

Shell Structure — How do the electrons arrange themselves?
How big are atoms in their ground states?

Consider Argon $(Z = 18)$ → $1s^2 2s^2 2p^6 3s^2 3p^6$

Because of screening → $V(r) = \begin{cases} -Ze^2/4\pi\epsilon_0 r & r \to 0 \\ -e^2/4\pi\epsilon_0 r & r \to \infty \end{cases}$

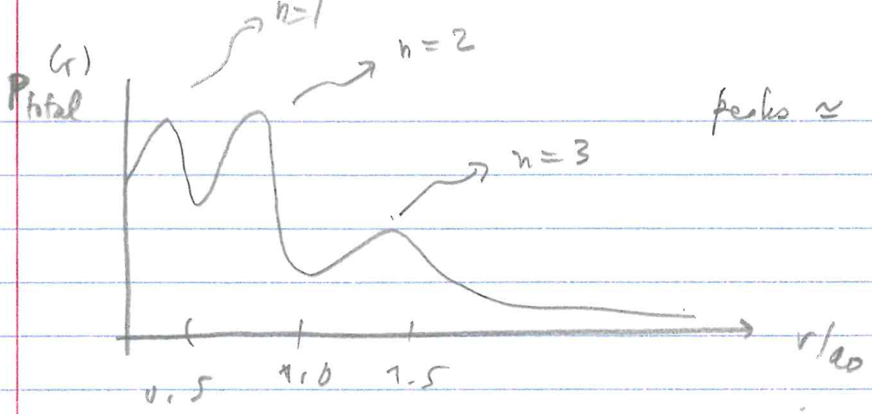
Inner electron → more tightly bound than H
outer electron → same potential as H

Size of atom = expectation value of the radius of the outermost electron

For H. → $1s^1$ electron has $\bar{r} = 1.5 a_0$
For Ar → $3p^6$ electron → also has $\bar{r} \doteq 1.5 a_0$

- Most atoms in their ground state have roughly the same size.
- Inner electrons are closer than in Hydrogen – tighter bound

↳ Fig 9-10, 9-11 combines the radial dist for the 18 e^- in Argon →



peaks ≃ "shells"

⇒ Can calculate binding energies for e^- in these shells...

(Ar) $E_{n=1} \simeq -3500$ eV → very tightly bound

$E_{n=2} \simeq -220$ eV

$E_{n=3} \simeq -14$ eV → similar to H

<u>Ionization</u> → minimum energy to remove an electron

⇒ involves outer or valence e^-

⇒ get γ in the near visible ⇒ optical

For different types of valence electrons → need different energies...

alkali atoms ⇒ s-state valence electrons...

(lowest ionization energies...)

noble gases → have filled p shells.

→ highest ionization energies...

If an inner electron is knocked out ⇒ get keV γ (x-ray) when another e^- fills the slot

<u>e.g.</u> 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.

<u>What about excited states?</u>

↳ Consider optical excitation of outer electrons (not X-ray)

<u>Alkali atoms</u> → have only 1 optically ~~excite~~ active electron
→ can label states using hydrogenic quantum #

$$\boxed{n\,l\,s\,j\,m_j}$$

But atoms with 2 or more valence e^- are best described in terms of their total spin ($\vec{S}'$) (as in He)
→ will also label by their total orbital angular momentum

$$|\vec{L}'| = \text{total angular momentum.}$$

↳ then couple these to form total angular momentum

$$\boxed{\vec{J} = \vec{L}' + \vec{S}'}$$

This labeling corresponds to using <u>3 levels</u> of approximation

(1) Use Hartree for individual nl electrons → l levels are no longer degenerate

(2) residual Coulomb + exchange effect $\vec{L}' = \vec{L}_1 + \vec{L}_2 + \ldots$ (Coulomb)
~~(3)~~ $\vec{S}' = \vec{S}_1 + \vec{S}_2 + \ldots$ (spin)

$\Rightarrow$ l' & s' levels split

(3) Spin-orbit interaction ($\vec{L}' \cdot \vec{S}'$)

$$\vec{J}' = \vec{L}' + \vec{S}' \rightarrow \text{split levels with different } \vec{J}'\text{'s}$$

→ with l', s', j' → can label excited states of multi electron atoms

May 8, 2018 — Excited States in Multi-electron Atoms

Want to use
$$\left.\begin{aligned}\vec{S}' &= \vec{s}_1 + \vec{s}_2 + \dots \\ \vec{L}' &= \vec{l}_1 + \vec{l}_2 + \dots\end{aligned}\right\}$$
for optically active e^-

Then form $\vec{J}' = \vec{L}' + \vec{S}'$

Gives quantum numbers $s', \ell', j' \dots$

⇒ need general rule :

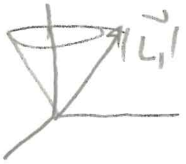
$\boxed{\text{e.g.}}$ $\ell_1 = 2, \ \ell_1 = 1$

Rule: fix the bigger one ($\ell_1 = 2$), add/subtract the smaller one ($\ell_1 = 1$), then fill in the in-between integers …
$$\left\{\begin{aligned}\ell_1 + \ell_2 &= 2+1 = 3 \\ \ell_1 - \ell_2 &= 2-1 = 1\end{aligned}\right\}$$

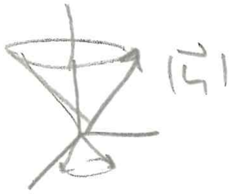
also include 2 → $\boxed{1, 2, 3 = \ell'}$

This rule follows from having 3 possible orientations for $\ell_2 = 1 \Rightarrow m_\ell = -1, 0, 1$ with $\vec{L}_1$ fixed

3



2



1

Ex $\ell_1 = 2, \ \ell_2 = 2$ add → $\ell' = 4$, subtract → $\ell' = 0$ $\Big\} \Rightarrow \ell' = 0, 1, 2, 3, 4$

Ex $s_1 = \frac{1}{2}, \ s_2 = \frac{1}{2}$ add → $s' = 1$, subtract → $s' = 0$ ← no in-between

Ex $s_1 = \frac{1}{2}, \ s_2 = \frac{1}{2}, \ s_3 = \frac{1}{2}$ → first add 2: $\frac{1}{2} \pm \frac{1}{2} = 0, 1$, then combine with the remaining $\frac{1}{2}$

$$\left.\begin{aligned}0 + \tfrac{1}{2} &= \tfrac{1}{2} \\ 1 \pm \tfrac{1}{2} &= \tfrac{1}{2}, \tfrac{3}{2}\end{aligned}\right\} \rightarrow s' = \tfrac{1}{2}, \tfrac{3}{2}$$

Using s', l', j' → called $\boxed{\text{LS coupling}}$

→ first add up to get $\vec{S}', \vec{L}'$, then get $\vec{J}' = \vec{S}' + \vec{L}'$

⇒ works best for most of the periodic table

But really heavy nuclei can use → $\boxed{\text{JJ coupling}}$

Form $\vec{J}_1 = \vec{L}_1 + \vec{S}_1$

$\vec{J}_2 = \vec{L}_2 + \vec{S}_2$ then form $\boxed{\vec{J}' = \vec{J}_1 + \vec{J}_2 + \dots}$

⋮

But we'll use $\boxed{\text{LS coupling}}$

Use notation for multi-e states $^{2s'+1}l'_{j'}$ → use capital letters

most cases ($l' \geq s'$) gives # of j' values

e.g. $^3P_2$ → $l' = 1$

$j' = 2$

$2s' + 1 = 3$ or $s' = 1$

$^1P_1$ → $l' = 1$

$j' = 1$

$s' = 0$

May 9, 2018

Excitation - $\boxed{\text{EXCITED STATES OF MULTI-}e\text{ ATOMS}}$

↳ LS coupling. Form $\vec{S}' = \vec{s}_1 + \vec{s}_2 + \dots$
and $\vec{L}' = \vec{l}_1 + \vec{l}_2 + \dots$

→ Combine, to get $\vec{J}' = \vec{S}' + \vec{L}'$

↳ get 3 quantum numbers s', l', j'
& label multi-electron configuration $^{2s'+1}l'_{j'}$

\# of states

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...

e.g. $l' = 2$, $s' = \frac{3}{2}$
To get j' add $j' = 2 + \frac{3}{2} = \frac{7}{2}$
subtract $j' = 2 - \frac{3}{2} = \frac{1}{2}$

So $\boxed{j' = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}}$ $2s'+1$ states

Note that with $\vec{J}' = \vec{L}' + \vec{S}'$, assume $l' \geq s'$ (most of the time)

$$\rightarrow \left\{ \begin{array}{l} \text{max} = l' + s' = j' \\ \text{min} = l' - s' = j' \end{array} \right\} \text{ so } j' = l'-s', l'-s'+1, \dots l'+s'$$

⇒ There are $\boxed{2s'+1}$ values

Hence the superscript

But if $l' < s'$, then $\left. \begin{array}{l} j'_{max} = s' + l' \\ \text{but } j'_{min} = s' - l' \end{array} \right\} \rightarrow \boxed{2l'+1}$ values

But we still use → $\boxed{2s'+1}$ in the labeling

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Ex $\left.\begin{array}{l} \ell'=2 \\ s'=1 \end{array}\right\} \quad j' = \cancel{0}, 1, 2, 3$

3 "configs"

Label $\quad {}^3D_1, \; {}^3D_2, \; {}^3D_3 \quad$ or $\quad {}^3D_{1,2,3}$

Ex Consider $2e^-$ in a $3f4p$ config & find all s', ℓ', j' values

$\ell_1 = 3 \qquad \ell_2 = 1 \quad \Rightarrow \quad \ell' = 2, 3, 4$

$s_1 = 1/2 \qquad s_2 = 1/2 \quad \Rightarrow \quad s' = 0, 1$

Now do j' $\quad \boxed{s'=0}$

if $\ell' = 2 \Rightarrow j' = 2 \rightarrow {}^1D_2$

if $\ell' = 3 \Rightarrow j' = 3 \rightarrow {}^1F_3$

if $\ell' = 4 \rightarrow j' = 4 \rightarrow {}^1G_4$

$\boxed{s'=1}$

$\ell' = 3 \rightarrow j' = 2, 3, 4 \rightarrow {}^3F_{2,3,4}$

$\ell' = 2 \Rightarrow j' = 1, 2, 3 \rightarrow {}^3D_{1,2,3}$

$\ell' = 4 \rightarrow j' = 3, 4, 5 \rightarrow {}^3G_{3,4,5}$

Some additional important facts..

→ filled subshells all have $\ell' \pm s' = j' = 0$

↳ so only partially filled electrons contribute to s', ℓ', j'

⇒ this is a result of the Exclusion principle

e.g

filled ns^2 level $\quad \left.\begin{array}{l} \ell_1, \ell_2 = 0 \\ m_{\ell_1}, m_{\ell_2} = 0 \end{array}\right\} \; \underline{\ell' = 0}$

$s_1 = s_2 = \frac{1}{2} \Rightarrow s' = 1, 0$

The same happens with d^{10}, p^6, f^{14}...

But for $s' = 1, 0 \rightarrow m_{s'} = 1$

requires $m_{s_1} = \frac{1}{2}$ & $m_{s_2} = \frac{1}{2}$

This would require all QM # the same

⇒ NOT POSSIBLE due to Exclusion principle

⇒ Must have $s' = 0$

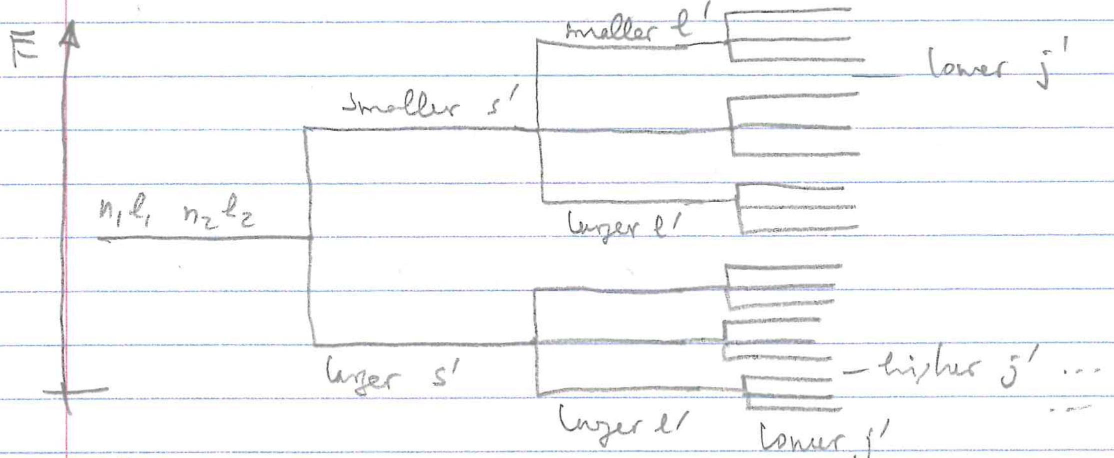
And if $s' = 0$, $\ell' = 0 \Rightarrow j' = 0$

→ There's ordering for which of s', l', j' is most important in splitting + which goes up or down in energy

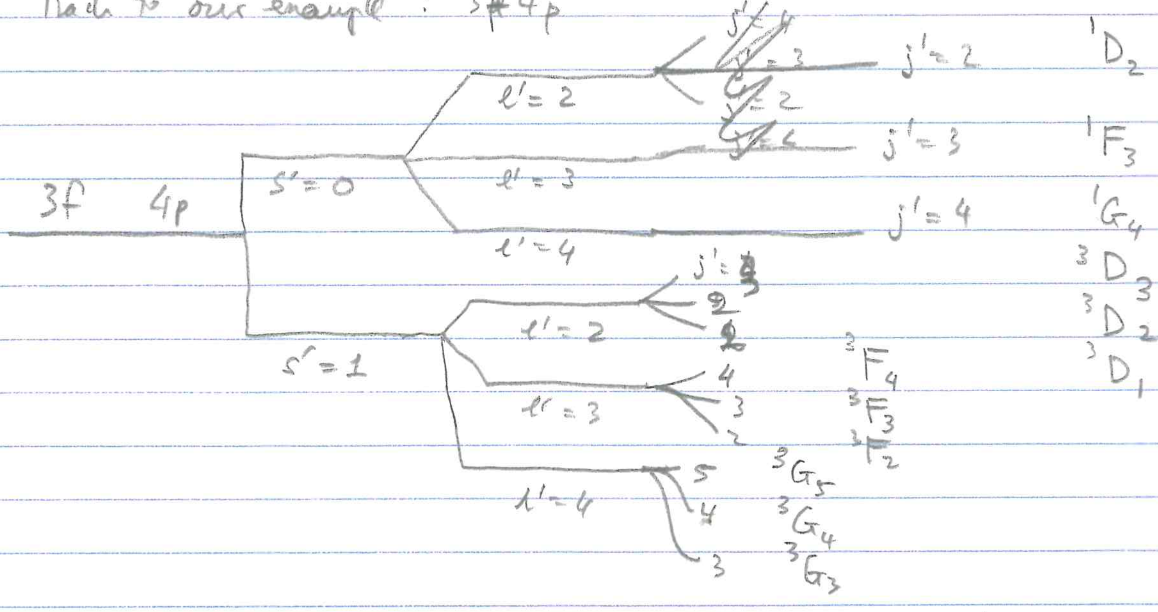
1st → split s' values (exchange effects) (dominant)
2nd → split l' values (Coulomb effects) (spatial)
3rd → split j' values (Spin-orbit correction)

Ordering with respect to energy:

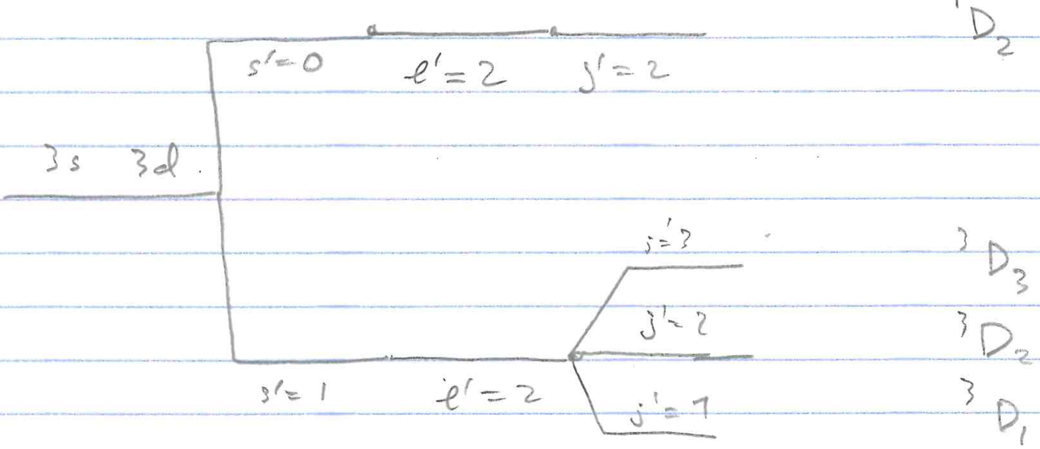
- states with larger s' → lower ... (exchange)
- states with larger l' → lower ... (Coulomb)
- states with lower j' → ~~higher~~ lower ... (Spin-orbit)



Back to our example: 3f 4p



Ex Find splitting & labels for 3s 3d level



Ex which of the following describes states that are valid/invalid

(a) $\underline{^2F_{1/2}}$ $\rightarrow$ $s'=\frac{1}{2}$, $\ell'=3$, $j'=\frac{1}{2}$ $\Big\}$ NOT valid

$\hookrightarrow j'=\frac{7}{2},\frac{5}{2}$

(b) $\underline{^3S_2}$ $\rightarrow$ $s'=1$, $\ell'=0$ $\rightarrow j'=1$ $\Big\}$ NOT valid

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
  - indistingiushable 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: $\vec{S}' = \vec{S}_1 + \vec{S}_2, \quad s' = \frac{1}{2} + \frac{1}{2} = 1, 0$
  - $\psi_A = \psi_{\text{spatial}}\,\chi_{s',m_s'}$ (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')