Intro to QM & Black Body radiation
Emma Physics & Maths Summer work 2020

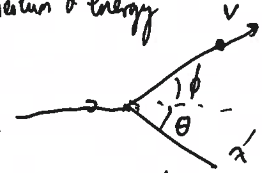
s.d. in black body radiation

$$(\sigma E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$
$$= hf(N + N^2)$$
$$= kT^2 \frac{dE}{dT}$$

↳ particle fluctuation : $\sigma^2 = N$
wave fluctuation ~~waves~~ $\sigma^2 = N^2$

Compton Scattering

change of λ due to conservation of momentum & energy



Energy conservation
$(\hbar \underline{k} = M \underline{v} + \hbar \underline{k}')$
$E = hf$ $\quad w = 2\pi f$
$= \hbar w$
$\hbar = \frac{h}{2\pi}$ $\quad k = \frac{2\pi}{\lambda}$

$$\Delta\lambda = \cancel{\frac{h}{M_e c}} \frac{h}{M_e c}(1 - \cos\theta)$$
derived from term 1 notes

using $mv = \frac{h}{\lambda}$
on a head on head collision by cons^n of momentum

$$\frac{h}{\lambda} = M_e v - \frac{h}{\lambda'} \Rightarrow \left(\frac{h}{\lambda} + \frac{h}{\lambda'}\right)^2 \frac{1}{M_e^2} = M_e v^2$$

AND by $E = mc^2$
$= mvc$ AND $E = hf$
$= pc$ $\quad = \frac{hc}{\lambda}$

also we get $E_{tot} = E_{e^-} + E_{photon}$

$$\cancel{E}\ \frac{hc}{\lambda} = \frac{M_e v^2}{2} + \frac{hc}{\lambda'}$$
split 2

classical model ⇒ e/ treated as an oscillator connected by a 'spring' to a nucleus
(*) AND : Light is treated ~~as an oscillator~~ as an external force driving the oscillator.
↳ which can be used to explain Reyleigh Scattering
BUT → fail to explain compton scattering and black body radiation.

$$\cancel{h}\left(\frac{\cancel{h}c}{\lambda} - \frac{\cancel{h}c}{\lambda'}\right) = \frac{h^{\cancel{2}}}{2M_e}\left(\frac{1}{\lambda} + \frac{1}{\lambda'}\right)^2$$

$$c\left(\frac{\lambda' - \lambda}{\lambda\lambda'}\right) = \frac{h}{2M_e}\left(\frac{\lambda' + \lambda}{\lambda\lambda'}\right)^2$$

We make $\lambda \approx \lambda'$
$\Rightarrow \Delta\lambda \approx 0$
$\lambda\lambda' = \lambda^2$
$\lambda' + \lambda = 2\lambda$

$$cM_e\left(\frac{\lambda' - \lambda}{\lambda^2}\right) = \frac{h}{2}\frac{4\lambda^2}{\lambda^4}$$

$$\lambda' = \lambda + \frac{2h}{M_e c}$$

which coincides w/ Compton's formula for head on collision, $\theta = \pi$

Treating system as a simple harmonic oscillator:
We write Newton's ~~2nd to~~ 2^{nd} law of motion

$$\ddot{x} + w_0^2 x = \frac{eE}{M_e}\cos wt$$

$$x = A\cos(w_0 t - \phi) + B\cos wt$$

$$x = A\cos(w_0 t - \phi) + \frac{eE}{M_e(w_0^2 - w^2)}$$

$$B = \frac{eE}{M_e(w_0^2 - w^2)}$$

evaluating

$$\int_0^\infty \frac{u^3}{e^u - 1}\, du$$

Same result can be derived using

$$I = \int \frac{\cancel{2c^2 ch}\ 2c^2 \pi h}{\lambda^5 \left(e^{hc/kT\lambda} - 1\right)}\, d\lambda$$

Bohr's model:
The 4 postulates:

- circular orbit $\frac{mv^2}{r} = \frac{q^2}{4\pi\varepsilon_0 r^2}$

- ~~No~~ Infinite orbits are not possible by classical mech
  ↳ only possible for an e⁻ to move in an orbit for which its orbital angular momentum
  $\vec{L} = n\hbar$
  $= \frac{nh}{2\pi}$

- total energy is constant
  → e⁻ is constantly accelerating but does not radiate EM energy

- EM energy only emitted if an electron discontinuously changes its motion so that from $E_i \to E_f$
  $f = \frac{E_f - E_i}{h}$

remaining stuff in phy. chem notes:
Problems: bad for other elements
- more complex systems, liquid or gases, molecules

incomplete: the Wilson-Sommerfield quantisation rule 2nd Bohr postulate is a special case
↳ can only applied to periodic systems
↳ no way of ~~approa~~ approaching non-periodic quantum behaviour
eg. scattering

Eta function: $\eta(s) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^s}$ relating zeta func: $\overset{\zeta(s)}{\cancel{\zeta(s)}} = \sum_{n=1}^{\infty} \frac{1}{n^s}$

$$\zeta(s) - \eta(s) = \cancel{\frac{1}{1^s}} + \frac{1}{2^s} + \frac{1}{3^s} + \frac{1}{4^s} + \dots - \left[\cancel{\frac{1}{1^s}} - \frac{1}{2^s} + \frac{1}{3^s} - \frac{1}{4^s} + \dots\right]$$

$$= 2 \cdot \frac{1}{2^s} + 2 \cdot \frac{1}{4^s} + \frac{2}{6^s} + \frac{2}{8^s} + \dots$$

$$= 2^s \cdot 1^s + 2^s \cdot 2^s + 2^s \cdot 3^s + 2 \cdot 4^s + \dots = \frac{2}{2^s} \underbrace{\sum_{n=1}^{\infty} \frac{1}{n^s}}_{\zeta(s)}$$

$$\zeta(s) - \eta(s) = 2^{1-s} \zeta(s)$$

$$\eta(s) = \left[1 - 2^{(1-s)}\right] \zeta(s)$$

integral representation

$$\int_0^\infty \frac{x^{s-1}}{e^x + 1} dx = \int_0^\infty \frac{e^{-x} x^{s-1}}{1-(-e^{-x})} dx = \int_0^\infty e^{-x} x^{s-1} \sum_{n=0}^{\infty} (-e^{-x})^n dx = \int_0^\infty e^{-x} x^{s-1} \underbrace{\sum_{n=1}^{\infty} e^{-nx} (-1)^n}_{\text{converges}} dx$$

$$= \sum_{n=0}^{\infty} (-1)^n \int_0^\infty x^{s-1} e^{-x(n+1)} dx \quad \Big| \quad \text{Let } t = x(n+1), \; dt = (n+1)dx, \; dx = \frac{dt}{n+1}$$

$$= \sum_{n=0}^{\infty} (-1)^n \int_0^\infty \frac{t^{s-1}}{(n+1)^{s-1}} e^{-t} \frac{dt}{(n+1)} = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)^s} \underbrace{\int_0^\infty t^{s-1} e^{-t} dt}_{\Gamma(s)}$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)^s} \Gamma(s) \quad \Big| \quad \cancel{k+1 \to k}, \; n+1 \to n, \; n \to n-1$$

$$\int_0^\infty \frac{x^{s-1}}{e^x+1} dx = \sum_{n=0}^{\infty} \frac{(-1)^{n-1}}{n^s} \Gamma(s)$$

$$= \eta(s)\Gamma(s)$$

$$\eta(s) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{x^{s-1}}{e^x+1} dx$$

from BPRP

Pi function: $\Pi(n) = \int_0^\infty t^n e^{-t}\,dt$

- ① $f(1) = 1$ $\qquad \Pi(n) = n!$
- ② $f(n) = n \cdot f(n-1)$ $\qquad = \cancel{n(n-1)! \cdot \Pi(n) \cdot f(n)}$

checking ①

$$\Pi(1) = \int_0^\infty t e^{-t}\,dt$$

using DI method

	D	I
+	t	e^{-t}
−	1	$-e^{-t}$
+	0	e^{-t}

$$\Pi(1) = \left[\left(-te^{-t} - e^{-t}\right)\right]_0^\infty$$

using $\lim_{t\to\infty}\left(\frac{-t}{e^t}\right) = \lim_{t\to\infty}\left(\frac{-1}{e^t}\right) = 0$

L'Hopital's rule

$$\Pi(1) = \left(0 - e^{-\infty}\right) + \left(e^{-0}\right)$$

$$\Pi(1) = 1$$

checking ②:

$$\Pi(x) = \int_0^\infty t^n e^{-t}\,dt$$

using DI method:

	D	I
+	t^n	e^{-t}
−	$-nt^{n-1}$	$-e^{-t}$

$$\Pi(x) = \underbrace{\left[t^n e^{-t}\right]_0^\infty}_{A} + \int n t^{n-1} e^{-t}\,dt$$

$\lim_{t\to\infty}\left(\frac{-t^n}{e^t}\right) = \dots$ 無限 L'Hopital's rule: diff.

$= \lim_{t\to\infty} \frac{-n!}{e^t} = 0 \qquad \therefore A = 0 - 0 = 0$

~~$\Pi(x) = \dots$~~

$$\Pi(x) = n\int_0^\infty t^{n-1} e^{-t}\,dt$$

$$1 = n \cdot \Pi(n-1) - n \cdot f(n-1)$$

Gamma & zeta function $\Rightarrow$ $\zeta(x) = \sum_{n=1}^{\infty} \frac{1}{x^n}$

$$\Gamma(n) = (n-1)!$$

$$\Gamma(x) = \int_{t=0}^{t=\infty} t^{x-1} e^{-t}\,dt \qquad \text{set } t = n\cdot u, \quad dt = n\,du$$

$$= \int_{u=0}^{u=\infty} (nu)^{x-1} e^{-nu}\, n\,du$$

$$= \int_0^\infty n^{x-1} u^{x-1} e^{-nu}\, n\,du$$

$$\sum_{n=1}^{\infty}\left(\frac{\Gamma(x)}{n^x}\right) = \sum_{n=1}^{\infty}\left(\frac{\int_0^\infty u^{x-1} e^{-nu}\,du}{n^x}\right)$$

new) $\Gamma(x) \cdot \sum_{n=1}^\infty \frac{1}{n^x} = \int_0^\infty u^{x-1} \sum_{n=1}^\infty (e^{-u})^n\,du$

inf geo series $r = \frac{1}{e^u}$; first term / $1-r$

$$\Gamma(x)\zeta(x) = \int_0^\infty u^{x-1} \frac{e^u (e^{-u})}{e^u(1-e^{-u})}\,du$$

$$= \int_0^\infty \frac{u^{x-1}}{e^u - 1}\,du$$

$$\Gamma(s)\zeta(s) = \int_0^\infty \frac{u^{s-1}}{e^u-1}\,du$$

$x \to s$, u changes to s

Lambert function

Gamma function

Zetla function

~~ζ function~~

Evaluating $\int_0^\infty \frac{e^x x^3}{e^x - 1}\,dx$

↳ Classic way:

$$\int_0^\infty \frac{x^m \div e^x}{(e^x-1)\div e^x}\,dx$$

$$= \int_0^\infty \frac{e^{-x} x^m}{1-e^{-x}}\,dx$$

$$= \int_0^\infty x^m e^{-x} \times \underbrace{\frac{1}{1-e^{-x}}}_{\sum_{n=1}^{\infty}(e^{-x})^n}\,dx$$

$$= \int_0^\infty x^m e^{-x} \sum_{n=1}^{\infty} (e^{-x})^n dx = \int_0^\infty \frac{x^m}{e^x} \sum_{n=1}^{\infty} e^{-xn}\,dx$$

$$= \sum_{n=1}^{\infty} \int_0^\infty x^m e^{-x} e^{-xn}\,dx = \sum_{n=1}^{\infty} \int_0^\infty x^m e^{-(n+1)x}\,dx$$

Setting ~~$n+1=u$~~

$u = (n+1)x$

$du = (n+1)\,dx$

$dx = \frac{du}{(n+1)}$

$x = \frac{u}{(n+1)}$

$$= \sum_{n=1}^{\infty} \int_0^\infty x^m e^{-u} \times \frac{1}{(n+1)}\,du$$

$$= \sum_{n=1}^{\infty} \int_0^\infty \left(\frac{u}{n+1}\right)^m \frac{1}{n+1} e^{-u}\,du$$

$$= \sum_{n=1}^{\infty} \int_0^\infty u^m \frac{1}{(n+1)^{m+1}} e^{-u}\,du$$

$$= \sum_{n=1}^{\infty} \int_0^\infty u^{m+1-1} e^{-u} \frac{1}{(n+1)^{m+1}}\,du$$

$$= \sum_{n=1}^{\infty} \frac{1}{(n+1)^{m+1}} \int_0^\infty u^{m+1-1} e^{-u}\,du$$

$$= \Gamma(m+1) \cdot \zeta(m+1)$$

$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t}\,dt$

and

$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}$

Lambert func: $W(x) = xe^x$

Gamma func: $\Gamma(n) = (n-1)!$ ~~$n \in \mathbb{Z}$~~

$$\Gamma(z) = \int_0^\infty e^{z-1} e^{-x}\,dx \quad \mathbb{R}(z) > 0$$

for ~~$x \in \mathbb{C}$~~ $z \in \mathbb{C}$

$\mathbb{R}(z) > 0$

Zeta function: $\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}$

$\Rightarrow$ what if

for $s \in \mathbb{C}$ $\quad \zeta(s) = 0$

$s = ?$

Pi func:

$$\Pi(x) = \int_0^\infty t^x e^{-t}\,dt = n!$$

$$= n \cdot \Gamma(x)$$

Eta func: $\eta(s) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^s} = \frac{1}{\Gamma(s)} \int_0^\infty \frac{x^{s-1}}{e^x+1}\,dx$

when $m = 3$

$$\Gamma(4) \cdot \zeta(4)$$

$$= (4-1)! \cdot \sum_{n=1}^{\infty} \frac{1}{n^4}$$

$$= 3 \cdot 2 \cdot 1 \cdot \sum_{n=1}^{\infty} \frac{1}{n^4} = 6 \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{6\pi^4}{90} = \frac{\pi^4}{15}$$

Series

Evaluating $\sum_{n=1}^{\infty} \frac{1}{n^4}$: using Fourier coefficients

Parseval's theorem

$$\sigma = \frac{2\pi k^4}{c^2 h^3} \frac{\pi^4}{15}$$

$$\sigma = \frac{2\pi^5 k^4}{15 c^2 h^3}$$

$$= 5.67 \times 10^{-8}\ \mathrm{W m^{-2} K^{-4}}$$

Perseval's Theorem, using Fourier series:

Fourier Series: Computationally using some integral identities: from Wolfram Alpha

$$\int_{-\pi}^{\pi} \sin(mx)\sin(nx)\,dx = \pi\delta_{mn} \quad -(1)$$

$\delta_{mn} \Rightarrow$ Kronecker delta $\quad m,n \neq 0$

$$\int_{-\pi}^{\pi} \cos(mx)\cos(nx)\,dx = \pi\delta_{mn} \quad -(2)$$

$$\int_{-\pi}^{\pi} \sin(mx)\,dx = 0 \quad -(4)$$

$$\int_{-\pi}^{\pi} \sin(mx)\cos(nx)\,dx = 0 \quad -(3)$$

$$\int_{-\pi}^{\pi} \cos(mx)\,dx = 0 \quad -(5)$$

Taking $f_1(x) = \cos x$, $f_2(x) = \sin x$, giving a generalised Fourier series and these func from a complete orthogonal system

$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} a_n\cos(nx) + \sum_{n=1}^{\infty} b_n\sin(nx)$$

How?

$$a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\,dx \qquad a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\cos(nx)\,dx \qquad b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\sin(nx)\,dx$$

purpose symmetry

- complete orthogonal system?

- generalised Fourier series ?

using this $f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n\cos(nx) + \sum_{n=1}^{\infty} b_n\sin(nx)$

In other notes:

$$\int_{-\pi}^{\pi} (f(x))^2\,dx = \int_{-\pi}^{\pi}\left(\frac{a_0}{2}\right)^2 dx + \int_{-\pi}^{\pi} 2a_0\sum_{n=1}^{\infty}(a_n\cos(nx) + b_n\sin(nx))\,dx + \int_{-\pi}^{\pi}\sum_{n=1}^{\infty}(a_n\cos(nx) + b_n\sin(nx))\sum_{m=1}^{\infty}(a_m\cos(mx) + b_m\sin(mx))$$

$$= \frac{2\pi(a_0)^2}{4_2} + 2a_0\sum_{n=1}^{\infty}\int_{-\pi}^{\pi} a_n\cos(nx) + b_n(\sin(nx))\,dx + \sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\int \begin{pmatrix} a_n\cos(nx)a_m\cos(mx) + a_n\cos(nx)b_m\sin(mx) \\ + b_n\sin(nx)a_m\cos(mx) + b_n\sin(nx)b_m\sin(mx)\end{pmatrix}$$

using ⑤ and ④ $\Rightarrow$ 2nd term $= 0$

using ②: $\int_{-\pi}^{\pi} \cos(nx)\cos(mx)\,dx = \begin{cases} 0 & \text{if } (n \neq m) \\ \pi & \text{if } (n = m) \end{cases}$

③: $\because$ odd func.

①: $\int_{-\pi}^{\pi} \sin(nx)\sin(mx)\,dx = \begin{cases} 0 & \text{if } n \neq m \\ \pi & \text{if } n = m \end{cases}$

$$\frac{1}{\pi}\int_{-\pi}^{\pi}(f(x))^2\,dx = \frac{2(a_0)^2}{2} + \sum_{n=1}^{\infty}((a_n)^2 + (b_n)^2)$$

note $a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\,dx$

when $m = n$

$$\sum_{n=1}^{\infty}\int_{-\pi}^{\pi} a_n\cos(nx)\,a_n\cos(nx)\,dx = \pi\sum_{n=1}^{\infty}(a_n)^2 \quad \text{using ②}$$

$$+ \sum_{n=1}^{\infty}\int_{-\pi}^{\pi} b_n^{\,2}\sin(nx)\sin(nx)\,dx = \pi\sum_{n=1}^{\infty}(b_n)^2$$

Evaluating $\sum_{n=1}^{\infty} \frac{1}{n^4}$ using Parseval's theorem

where $a_0 = \frac{1}{2\pi}\int_{-\pi}^{\pi} f(x)\,dx$

Recalling $f(x) = \cancel{\frac{a_0}{2}}\ a_0 + \sum_{n=1}^{\infty}[a_n\cos(nx) + b_n\sin(nx)]$

$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\cos(nx)\,dx$

$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\sin(nx)\,dx$

Using Parseval's theorem:

$$\frac{1}{\pi}\int_{-\pi}^{\pi}(f(x))^2\,dx = 2(a_0)^2 + \sum_{n=1}^{\infty}((a_n)^2 + (b_n)^2)$$

So $f(x) = x^2$

for a_0: $a_0 = \frac{1}{2\pi}\int_{-\pi}^{\pi} x^2\,dx = \frac{1}{2\pi}\left[\frac{x^3}{3}\right]_{-\pi}^{\pi} = \frac{1}{\cancel{2}\pi}\frac{\cancel{2}\pi^{3\,2}}{3} = \frac{\pi^2}{3}$

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} x^2\cos(nx)\,dx$$

	D	I
+	x^2	$\cos(nx)$
−	$2x$	$\frac{1}{n}\sin(nx)$
+	2	$-\frac{1}{n^2}\cos(nx)$
−	0	$-\frac{1}{n^3}\sin(nx)$

$$= \frac{1}{\pi}\left(\cancel{\frac{x^2\sin(nx)}{n}} + \frac{2x\cos(nx)}{n^2} - \cancel{\frac{2\sin(nx)}{n^3}}\right)_{-\pi}^{\pi}$$

$$= \frac{1}{\pi}\left[\frac{2\pi\cos n\pi}{n^2}\times 2\right]$$

$$= \frac{4}{n^2}\cos(n\pi) = \frac{4(-1)^n}{n^2}$$

$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} \underbrace{x^2}_{\text{even}}\,\underbrace{\sin(nx)}_{\text{odd}}\,dx = 0$

integrate odd function $x \in [-\pi, \pi]$ $\Rightarrow b_n = 0$

$$\frac{1}{\pi}\int_{-\pi}^{\pi}(x^2)^2\,dx = 2\left(\frac{\pi^2}{3}\right)^2 + \sum_{n=1}^{\infty}\left(\frac{4(-1)^n}{n^2}\right)^2$$

$$\frac{1}{\pi}\int_{-\pi}^{\pi} x^4\,dx = \frac{2\pi^4}{9} + \sum_{n=1}^{\infty}\frac{16}{n^4}$$

$$\frac{1}{\cancel{\pi}}\frac{2\pi^{\cancel{5}\,4}}{5} = \frac{2\pi^4\times 5}{9\cdot 5} + \sum_{n=1}^{\infty} 16\times\frac{1}{n^4}$$

$$\frac{8\pi^4}{45\times 16} = \sum_{n=1}^{\infty}\frac{1}{n^4}$$

$$\sum_{n=1}^{\infty}\frac{1}{n^4} = \frac{\pi^4}{90}$$

$\sum_{r=1}^{\infty} e^{-2r} =$

$r \to r+1$

$\sum_{r=1}^{\infty} e^{-2(r+1)}$ $\cancel{= \sum_{r=0}^{\infty} \frac{e^{r+1}}{e^{-2}}}$

$\cancel{= \sum_{r=0}^{\infty} e^{-2r-2}}$

Energy density: $E = hf \dfrac{1}{e^{hf/kT} - 1}$

For calculating the total energy output of the black body

$\because$ density of states $\propto$ Area of sphere

↳ knowing how many frequencies there are around frequency (f)

density of state per unit volume: $(4\pi f^2 \quad f = \text{radius})$

think as diff state lying on sphere w/ radius (f)

$$g(f) = \frac{8\pi}{c^3} f^2 = \underbrace{\left(\frac{2}{c^3}\right)}_{\text{Constant}} 4\pi f^2$$

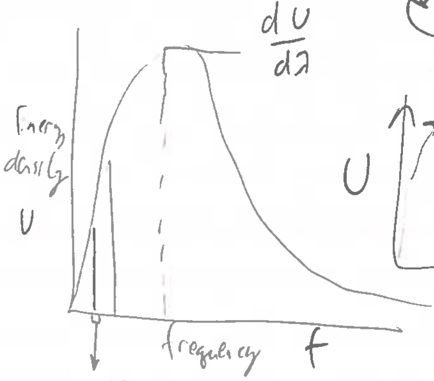
$g(f) \propto f^2$

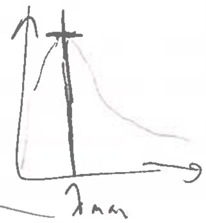
?.??

Black body energy density:

$$U(f) = g(f) E$$

$$= \frac{8\pi h}{c^3} f^3 \frac{1}{e^{hf/kT} - 1}$$





$Udf \rightarrow$ energy in the interval $\lambda \in [f, df + f]$

$f = \frac{c}{\lambda} \qquad f^2 = \frac{c^2}{\lambda^2}$

$df = \frac{c}{d\lambda}$

$\frac{df}{d\lambda} = -\frac{c}{\lambda^2}$

$df = -\frac{c}{\lambda^2} d\lambda \qquad df = -\frac{c}{\lambda^2} d\lambda$

$(df)^3 = \frac{c^3}{\lambda^5} d\lambda^3$

$U(\lambda) = \frac{8\pi}{c^3} \times \frac{c^2}{\lambda^2} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$

$U(\lambda) = \frac{8\pi hf}{} hf \times \frac{8\pi h}{c^3} f^2 \times \frac{1}{e^{hc/\lambda kT} - 1} = \cancel{\frac{8\pi h}{c^3}\frac{c^3}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}}$

$= \frac{hc}{\lambda^3 c} \frac{8\pi}{} \times \frac{1}{e^{hc/\lambda kT} - 1}$

$-\frac{6a}{\lambda^6} \quad -\frac{5a}{\lambda^6}\frac{1}{e^{b/\lambda\phi} - 1} + \frac{a}{\lambda^5}$

$\int_0^\infty U\,df$ = total energy

$Udf = \frac{8\pi h}{\lambda^3} \frac{1}{e^{hc/\lambda kT} - 1} df$

↳ $U(d\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} d\lambda$

$a = 8\pi hc$
$b = hc$
$\phi = kT$

$U(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$

finding λ_{max}:

$$\frac{dU}{d\lambda} = \frac{d}{d\lambda}\left(\frac{a}{\lambda^5} \frac{1}{e^{b/\lambda\phi} - 1}\right) = 0$$

$hc = b \quad kT = \phi \quad a = 8\pi hc$

$$\frac{dU}{d\lambda} = \frac{d}{d\lambda}\left(\frac{\overbrace{8\pi hc}^{a}}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}\right) = 0$$

$$\frac{d}{d\lambda}\left(\frac{a}{\lambda^5}\frac{1}{e^{\frac{b}{\phi}\frac{1}{\lambda}}-1}\right) = 0 \Rightarrow \frac{d}{d\lambda}\left(a\lambda^{-5} \times \left(e^{\frac{b}{\phi}\times\frac{1}{\lambda}}-1\right)^{-1}\right) = 0$$

$$-5a\lambda^{-6}\left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)^{-1} + (a\lambda^{-5}) \times \left(\frac{b}{\phi}\cancel{(-1)(-1)}\left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)^{-2}\right) = 0$$

$$-\frac{5a}{\lambda^6}\left(\frac{1}{e^{\frac{b}{\phi}\frac{1}{\lambda}}-1}\right) + \frac{a}{\lambda^5} \times \frac{b}{\phi}\frac{1}{\left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)^2} = 0$$

$$-\frac{5}{\lambda} + \frac{hc}{kT}\frac{1}{e^{\frac{b}{\phi}\frac{1}{\lambda}}-1} = 0$$

$$\lambda\frac{hc}{kT} = \frac{5}{\lambda} \times \left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)$$

$$\lambda = \frac{5kT}{hc}\left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)$$

$$\lambda = \frac{5kT}{hc}e^{\frac{hc}{kT}\frac{1}{\lambda}} - \frac{5kT}{hc}$$

$$\frac{d}{d\lambda}\left(\frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}\right) = 0$$

$$\frac{d}{d\lambda}\left[\frac{a}{\lambda^5}\left(e^{\frac{b}{\phi}\lambda^{-1}}-1\right)^{-1}\right] = 0$$

$$\cancel{-\frac{5a}{\lambda^6}\left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)^{-1}} + \frac{a}{\lambda^5}\left(-\frac{\frac{b}{\phi}e^{\frac{b}{\phi\lambda}}}{\lambda^2}\right)\left(e^{\frac{b}{\phi}\frac{1}{\lambda}}-1\right)^{-2} = 0$$

$$-\frac{5}{\lambda} + \left(-\frac{hc\, e^{\frac{hc}{kT\lambda}}}{kT\lambda^2}\right)\left(e^{\frac{hc}{kT}\frac{1}{\lambda}}-1\right)^{-1} = 0$$

$$-hce^{\frac{hc}{kT\lambda}} = 5\left(e^{\frac{hc}{kT}\frac{1}{\lambda}}-1\right)$$

$$-hce^{\frac{hc}{kT}\frac{1}{\lambda}} = 5e^{\frac{hc}{kT}\frac{1}{\lambda}} - 5$$

$$\ln\frac{5}{5+hc} = \ln\left(e^{\frac{hc}{kT}\frac{1}{\lambda}}\right)$$

$$\ln\frac{5}{5+hc} = \frac{hc}{kT}\frac{1}{\lambda}$$

$$\lambda = \frac{hc}{kT} \div \left(\ln\frac{5}{5+hc}\right)$$

$$\lambda = \left(\frac{hc}{k\ln\frac{5}{5+hc}}\right)\frac{1}{T}$$

$$\frac{hc}{k\ln\left(\frac{5}{5+hc}\right)}$$

$\frac{1}{k}$

8π

$$U(\lambda) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right) \qquad a = 8\pi hc \quad \beta = \frac{hc}{kT}$$

$$\frac{dU}{d\lambda} = \frac{d}{d\lambda}\left(\frac{a}{\lambda^5}\times\left(\frac{1}{e^{\beta/\lambda}-1}\right)\right) = \frac{d}{d\lambda}\left[(a\lambda^{-5})\times\underbrace{\left(e^{\beta\lambda^{-1}}-1\right)^{-1}}_{\left(e^{\beta\lambda^{-1}}-1\right)^{-1}}\right]$$

$$= \frac{-5a}{\lambda^6}\times\frac{1}{e^{\beta/\lambda}-1} + \frac{a}{\lambda^5}\times(-1)(-1)\frac{\beta e^{\beta/\lambda}}{\lambda^2\left(e^{\beta\lambda^{-1}}-1\right)^2}$$

$$= \frac{-5\cancel{\lambda}}{\cancel{\lambda^6}}\left[\frac{1}{\cancel{(e^{\beta/\lambda}-1)}}\right] + \frac{\cancel{a}}{\lambda^{\cancel{5}}}\left[\frac{\beta e^{\beta/\lambda}}{\cancel{\lambda^2}\,(e^{\beta/\lambda}-1)^{\cancel{2}}}\right] = 0$$

$$\cancel{-\frac{5}{e}}$$

$$-5 + \frac{1}{\lambda}\frac{\beta e^{\beta/\lambda}}{(e^{\beta/\lambda}-1)} = 0$$

$$-5\lambda + \frac{\beta e^{\beta/\lambda}}{e^{\beta/\lambda}-1} = 0$$

$$\frac{-5\lambda \quad + \beta e^{\beta/\lambda}}{e^{\beta(\lambda)^{-1}}-1} = 0$$

$$5\lambda - \beta e^{\beta/\lambda} = 0$$

$$5\lambda - \frac{hc}{kT}e^{\frac{hc}{kT\lambda}} = 0$$

$$\frac{kT5\lambda}{hc} = \frac{h\cancel{c}}{\cancel{k}T}e^{\frac{hc}{kT\lambda}}$$

$$=$$

$$\ln\frac{kT5\lambda}{hc} = \ln\left(e^{\frac{hc}{kT\lambda}}\right)$$

$$\cancel{kT\lambda\,\ln\frac{kT5\lambda}{hc} = \frac{hc}{kT\lambda}}$$

Using Lambert's W function: $f(W) = We^W$

$$\cancel{\frac{-5a}{\lambda^5}\frac{1}{e^{hc/}}}$$

$$f(x)\ \lambda e^{\lambda} = W_0$$

$$\frac{-5\cancel{a}}{\cancel{\lambda^6}}\frac{1}{(\cancel{e^{\beta/\lambda}-1})} + \frac{\cancel{a}}{\cancel{\lambda^7}}\frac{\beta e^{\beta/\lambda}}{(e^{\beta/\lambda}-1)^{\cancel{2}}} = 0$$

$$\frac{\beta e^{\beta/\lambda} \div e^{\beta/\lambda}}{\lambda(e^{\beta/\lambda}-1) \div e^{\beta/\lambda}} = 5$$

$$\cancel{\beta = 5\lambda\left(1-\frac{1}{e^{\beta\lambda}}\right)}$$

$$\cancel{= 5\lambda -}$$

$$\beta e^{\beta/\lambda} = 5\lambda(e^{\beta/\lambda}-1)$$

$$\beta e^{\beta/\lambda} = 5\lambda e^{\beta/\lambda} - 5\lambda$$

$$\cancel{\frac{\beta}{\lambda\left(1-\frac{1}{e^{\beta/\lambda}}\right)} = 5}$$

$$\cancel{\lambda - \lambda}$$

$$\cancel{\lambda\left(1-\frac{1}{e^{\beta\lambda}}\right) = \frac{\beta}{5}}$$

$$\cancel{e^{\beta/\lambda}\frac{\lambda}{e^{\beta/\lambda}} - \frac{\lambda}{e^{\beta/\lambda}} = \frac{\beta}{5}}$$

$$\cancel{\frac{\lambda(e^{\beta/\lambda}-1)}{e^{\beta/\lambda}} = \frac{\beta}{5}}$$

$$\cancel{5\lambda e^{\beta/\lambda} - 5\lambda = \beta e^{\beta/\lambda}}$$

$$\cancel{(5\lambda-\beta)e^{\beta/\lambda} - 5\lambda = 0}$$

$$\cancel{\frac{(5\lambda-\beta)}{\lambda}e^{\beta/\lambda} = \frac{5\lambda}{\lambda}}$$

$$\cancel{\left(5-\frac{\beta}{\lambda}\right)e^{\beta/\lambda} = \cancel{5}\ 5}$$

$$\cancel{\frac{1}{\beta}} + \frac{\beta e^{\beta/\lambda}}{\lambda(e^{\beta/\lambda}-1)} - 5 = 0$$

$$\beta e^{\beta/\lambda} - 5\lambda e^{\beta/\lambda} + 5\lambda = 0$$

$$\frac{hc}{kT}e^{\frac{hc}{kT\lambda}} - 5\left(\lambda e^{\frac{hc}{kT\lambda}} - \lambda\right) = 0$$

set $\underbrace{\frac{hc}{kT\lambda}} = u$

$$u\cancel{\lambda}e^u - 5\cancel{\lambda}(\cancel{\lambda}e^u - 1) = 0$$

$$ue^u - 5(e^u - 1) = 0$$

$$ue^u - 5e^u + 5 = 0$$

$$(u-5)e^u + 5 = 0$$

$$(u-5)e^u = -5$$

$$W = u-5$$

$$u = W+5$$

$$e^{-5}(We^{W+5}) = (-5)e^{-5}$$

$$We^W = -5e^{-5}$$

$$\cancel{W = WW}$$

$$W = W_0(-5e^{-5})$$ ← non-zero solution

$$W = W_0(-5e^{-5})$$

$$f(W) = We^{W}$$
$$= -5e^{-5}$$

$$W_0 = \frac{w}{-5e^{-5}}$$

$$w = u - 5$$

$$w = \frac{hc}{kT\lambda} - 5$$

$$\frac{hc}{kT\lambda} \cancel{-5} = W_0(-5e^{-5}) + 5$$

$$\lambda = \frac{hc}{[W_0(-5e^{-5}) + 5]\, kT}$$

$$\lambda = \frac{b}{T}$$

$$b = \lambda T$$

$$b = \frac{hc}{W_0(-5e^{-5}) + 5}$$
$$= \frac{(6.626\times10^{-34})(3\times10^{8})}{W_0(-5e^{-5}) + 5}$$

$$b = \frac{hc}{\frac{\frac{hc}{kT\lambda} - 5}{\cancel{(-5e^{-5})}}\cancel{(-5e^{-5})} + 5}$$

$$b = \frac{\cancel{hc}}{\frac{\cancel{hc}}{kT\lambda}\cancel{+5-5}}$$

$$b = kT\lambda$$

$$\lambda = \frac{b}{kT}$$

$$\lambda = \frac{hc}{[k(W_0(-5e^{-5}) + 5]\, T}$$

$$\lambda T = \frac{hc}{k(W_0(-5e^{-5}) + 5)} = b$$

$$\cancel{W_0 =} \ ?$$

$$\cancel{2.99}$$
$$2.893\times10^{-3} = \frac{hc}{W_0(-5e^{-5}) + 5}$$

$$W_0 = \frac{(6.626\times10^{-34})(3\times10^{8})}{2.893\times10^{-3}\times(-5e^{-5}) + 5}$$

$$W_0 = 2.9757\times10^{-26}$$

$$\cancel{W_0 = w}$$

$$w = W_0(-5e^{-5})$$

$$\frac{\cancel{u+5}\ u - 5}{-5e^{-5}} = W_0$$

$$w = u - 5$$
$$= \frac{hc}{kT\lambda} - 5$$

$$\frac{\frac{hc}{kT\lambda} - 5}{-5e^{-5}} = W_0$$

$$\frac{hc}{k\left(\frac{u-5}{\cancel{(-5e^{-5})}}\cancel{(-5e^{-5})} + 5\right)} = \frac{hc}{ku}$$

$$b = \frac{\cancel{hc}}{\frac{\cancel{k}\cancel{hc}}{\cancel{k}T\lambda}}$$

$$b = \lambda T$$

$(u-5)e^{\frac{u}{5}}+5=0$ $\qquad u-5 = \frac{hc}{kT\lambda}-5$

using newton's method:

$u = \frac{hc}{kT\lambda}$

$\cancel{(u-5)e^{5} = -5}$ $\qquad \lambda = \frac{hc}{kTu}$

$\cancel{5-u} = \frac{5}{e^5}$

$\lambda = \underbrace{\frac{hc}{ku}}_{b} \times \frac{1}{T}$

$(u-5)e^{u} = -5$

$\cancel{u=}$ $\qquad (u-5)e^{u}+5=0$

$\cancel{u_0}$

$u_1 = u_0 - \frac{f(u)}{f'(u)}$ $\qquad \cancel{(0-5)e^{0}+5 = 0}$

$\cancel{-5+5} = 0$

$u_1 = (-5e^{-5}+5) - \frac{(u-5)e^{u}}{(u-5)e^{u}+e^{u}}$

$n=0$

$u_1 = u_0 - \frac{(u_0-5)e^{u_0}+5}{e^{u_0}+(u_0-5)e^{u_0}} = \frac{(u_0-5)e^{u_0}+5}{e^{u_0}(1+u_0-5)}$

$= \frac{(u_0-5)e^{u_0}+5}{e^{u_0}(u_0-4)}$

$\cancel{u_1 = 0 - \frac{(-5)+5}{}}$

$\cancel{u_0 - 4}$

$u_0 = 5$

$u_1 = \frac{e^5+5}{e^5}$

$= \frac{e^5}{5}$

$= 29.68263$

$\frac{(29.68263-5)e^{29.68263}+5}{e^{29.68263}(29.68213-4)}$

$\Delta E = T\Delta S$

where $S = k\ln W \Rightarrow \Delta S = \cancel{k\ln \Delta W}\ k\Delta\ln W$

from thermodynamics:

for ΔE, ~~the~~ assume change in energy cannot be smaller than a certain unit → a quantum

$$I = \int \frac{2c^2\pi h}{\lambda^5\left(e^{hc/k T\lambda} - 1\right)}\, d\lambda$$

$\Delta E = hf$ $[E = Nhf]$

↳ determining the size of the energy packet

available states of energy can only be in discrete chunks, say $N+1 \to N$

$hf = \cancel{k[\ln W_{n+1}}\ k\Delta[\ln W]\,T$ where $N = \frac{E}{hf}$

$hf = k[\ln(N+1) - \ln N]T$

$\frac{hf}{kT} = \cancel{kT}\ \cancel{\frac{\ln N + \ln 1}{\ln N}}\ \cancel{\ln N+1}\ \ln\frac{N+1}{N}$

$e^{\frac{hf}{kT}} = \frac{N+1}{N}$ $N = \frac{1}{e^{hf/kT} - 1}$

$e^{\frac{hf}{kT}} - 1 = \cancel{1+}\ \frac{1}{N}$ $\boxed{E = \frac{hf}{e^{hf/kT} - 1}}$

$N = \cancel{\frac{1}{e^{hf} - 1}}$

$\cancel{\int \frac{2\pi}{c^3}\frac{hf^3/(kT)^3}{e^{hf/kT} - 1}}\, df$ Let $u = \frac{hf}{kT}$

$I = \int \frac{2\pi}{c^2}\frac{hf^3}{e^{hf/kT} - 1}\, df$ $du = \frac{h}{kT}\,df$ $df = \frac{kT}{h}\,du$

$I = \frac{2\pi}{c^2}\left(\frac{kT}{h^2}\right)\int \frac{\frac{h^2}{(kT)^3}(hf)^3}{e^u - 1}\frac{kT}{h}\,du$

$I = \underbrace{\frac{2\pi k^4 T^4}{c^2 h^3}}\underbrace{\int \frac{u^3}{e^u - 1}\,du}$

$\int_0^\infty \frac{u^3}{e^u - 1}\,du = \frac{\pi^4}{15}$

$= \int_0^\infty u^3(e^u - 1)^{-1}\,du$

$e^u - 1 = x$

$x = e^u - 1$

$\frac{dx}{du} = e^u$ $\frac{dx}{e^u} = du$

?? $I = \underbrace{\frac{2\pi^5 k^4}{15c^2h^3}}_{\sigma} T^4$

$\sigma = \frac{2(3.14)^2(1.38\times10^{-23})^4}{15(3\times10^8)(6.626\times10^{-34})^3}$

$I = \sigma T^4$

↳ energy of a black body which falls on a unit area per unit time

for total intensity of the black body:

remembering: $g(f) = \frac{8\pi}{c^3}f^2$

$= \frac{2}{c^3}4\pi f^2$

$I = \underbrace{\frac{c}{4}}_{?}\int \underbrace{g(f)}_{?}\ \underbrace{E(f)}_{\text{Lore}}\,df$

let $\frac{1}{kT} = \alpha$

$= \frac{c}{4}\frac{8\pi}{c^3}\int \frac{hf^3}{e^{hf/kT} - 1}\,df$

$= \frac{2\pi k}{c^2h^3}\int \cancel{\frac{(hf)^3}{e^{hf/kT} - 1}}\,df$ $u = hf$

$\frac{du}{df} = h$

$df = \frac{du}{\alpha h}$

$= \frac{2\pi}{c^2h^3}\int \cancel{\frac{u^3}{e^{\alpha u} - 1}}\left(\frac{1}{h}\right)\cancel{df}\,(du)$

solving $(u-5)e^{u}+5=0$

$u = W_0(-0.033690) = -5$

$= W_0(-5e^{-5}) - 5$

$u = -0.033690+5 \; (W_1)$

$u = 4.96371 \; (W_0)$

$\cancel{u = \frac{hc}{}}$

$$T\lambda = \frac{(6.626\times10^{-34})\,\cancel{(3\times10^{8})}\,(2.998\times10^{8})}{(1.3806\times10^{-23})\,(4.965\cancel{114})\,\cancel{(W_0)}}$$

$= 2.893\times10^{-3}\,mK$

$(u-5)e^{u}+5=0$

$w = u-5$

$\cancel{w =}$

$\cancel{We\,e}$

$(we^{w+5})e^{-5} = -5e^{-5}$

$\underbrace{we^{w}} = -5e^{-5}$

or $(u-5)e^{u-5} = -5e^{-5}$

$we^{w} = -5e^{-5}$

$W(we^{w}) = W(-5e^{-5})$

$w = W(-5e^{-5})$

$u\cancel{-5} = \text{product log}(-5e^{-5})+5$

$\cancel{\approx}$ by wolfram alpha:

4.965114

$h(x) = g^{-1}(x)$ where $g(x) = e^{x}$

$D:(0,\infty)\; R:(-\infty,\infty)$ $\qquad D:(-\infty,\infty)\; R:(0,\infty)$

① $h(g(x)) = \ln(e^{x}) = x$

② $g(h(x)) = e^{\ln x} = x$

note: $W(x) = f^{-1}(x)$ where $f(x) = xe^{x}$

$D:[-\frac{1}{e},\infty)\; R:[-1,\infty) \quad D:[-1,\infty)\; R:[-\frac{1}{e},\infty)$

① $W(f(x)) = W(xe^{x}) = x$

② $f(W(x)) = W(x)e^{W(x)} = x \quad \Rightarrow \quad e^{W(x)} = \frac{x}{W(x)}$

$\cancel{W}$

③ $W(x)$ = product log

$u = \frac{hc}{\lambda kT}$

$$\lambda T = \frac{hc}{uk} = \text{const} = \frac{(6.626\times10^{-34})\,\cancel{(3\times10^{8})}\,(2.998\times10^{8})}{(4.965)(1.381\times10^{-23})} = 2.898\times10^{-3} \quad \cancel{2.98\times10^{-3}}\,mK$$

$$= \frac{(6.626070\cancel{04}\times10^{-34})(2.998\cancel{2458}\times10^{8})}{(4.965\cancel{114})(1.3806\cancel{4852}\times10^{-23})} = 2.898\times10^{-3}\,mK$$

$\approx 2.9\times10^{-3}\,mK$

Photon Energy & momentum

$E = hf = pc$

p

$E = pc$

$p = \frac{hf}{c}$

$f = \frac{c}{\lambda} \rightarrow p = \frac{h}{\lambda}$

$h = 6.626\times10^{-34}\ Js$

$4.1357\times10^{-15}\ eV\cdot s$

Def: wave number:

$k = \frac{2\pi}{\lambda}$

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

$E_k = \frac{p^2}{2m_e} \quad p = \hbar k = \frac{h}{\lambda}$

$\lambda = \frac{h}{\sqrt{2mE_k}}$

- Compton scattering:

↳ scattering of high energy X-ray photons from free e^-'s → establishing photons have quantised momentum as well as quantised Energy

☆ - derivation from other notes

$\lambda_c = \frac{h}{m_e c}$

$\Delta\lambda = \lambda_c(1-\cos\theta)$

- Double slit from other notes

fringe separation for small Ls:

$\Delta y \approx \frac{D\lambda}{d}$

$d\sin\theta_n = n\lambda$

wave-particle ~~Wave~~ duality

Light: exhibits diffraction & interference phenomena (only for wave)

- always ~~trv~~ as individual packets; never observe half a photon

photons ∝ energy density ∝ $(E\text{-field})^2$

Uncertainty principle:

$\Delta q \Delta p_q \geq \frac{\hbar}{2}$

→ errors in ~~pred~~ prediction

components of position $\underline{r}$ and momentum $\underline{p}$ cannot be known w/ absolute precision @ the same time.

↳ we can never know x & p_x w/ precision better than $\hbar/2$

Adding several waves of different λ tgt

↳ begin to localise the wave

∴ strongly localised wave packet requires more frequencies

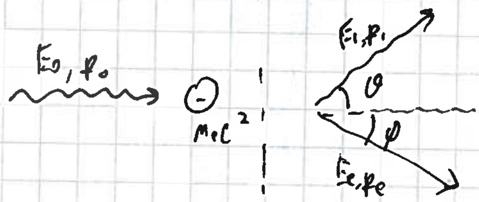
∴ perfectly localised particle requires ∞ spread of momenta

→ process spreads wave number, $k = \frac{2\pi}{\lambda}$ & makes it more uncertain

$\Delta k \uparrow$ when $\Delta x \downarrow$

$\Delta k \Delta x \approx 1$

Bf4 After



Classical Wave Eq^{n}.

$$\frac{\partial^2 A}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 A}{\partial t^2}$$

$\Rightarrow$ $A(x,t) = A_0 \cos(kx - wt)$ ← 1

$$\frac{\partial A}{\partial x} = -kA_0 \sin(kx-wt) \qquad \frac{\partial A}{\partial t} = wA_0 \sin(kx-wt)$$

$$\frac{\partial^2 A}{\partial x^2} = -k^2 A_0 \cos(kx-wt) \qquad \frac{\partial^2 A}{\partial t^2} = -wA_0\cos(kx-wt)$$

$$= -k^2 A \qquad = -w^2 A_0 \; A$$

LHS = RHS

$$-k^2 = -\frac{w^2}{v^2} \qquad w = \frac{2\pi}{f} = 2\pi\frac{v}{\lambda}$$

$$\alpha \quad \beta$$

$$\Rightarrow k^2 = \left(\frac{2\pi}{\lambda}\right)^2 \qquad \Rightarrow \cancel{w}$$

$$k = \frac{2\pi}{\lambda}$$

$\therefore$ $A = A_0\cos(kx-wt)$ is a sol^{n} to Eq^{n}

$\Rightarrow$ $A(x,t) = A_0 \exp(i(kx-wt))$ ← 2 for plane waves:

$$= A_0 e^{i(kx-wt)}$$

$\Rightarrow$ insert into Eq 2.4

$$k^2 = \frac{w^2}{v^2}$$

$$w^2 = v^2 k^2$$

$$w = v|k|$$

in Quant mech: $\rightarrow$ $E = \hbar w$ or using 2

de Broglie's relations:

$p = \hbar k$

$E = \hbar w$

$E = p^2/2m$

$$w = \frac{2\pi v}{\lambda}$$

$$E = \frac{h}{2\pi}\frac{2\pi v}{\lambda}$$

$$= \frac{hv}{\lambda}$$

$$E = hf \checkmark$$

$E = \hbar v|k|$

$E = vp \Rightarrow E \propto p$

$\Rightarrow$ not the expression we were expecting

$\therefore$ Classical Phy:

$\hookrightarrow E = \frac{p^2}{2m} = \frac{1}{2}mv^2$

$\cancel{E \propto p^2}$

$E \propto p^2$

In order to satisfy simultaneously:

$$E = \hbar w \quad \& \quad E = \frac{p^2}{2m}$$

We require $E \propto p^2$, not $E \propto p$ from sol^{n}

$\therefore$ $\Rightarrow$ Come w/ new wave eq^{n}

if we want to have $E \propto p^2$ $\Rightarrow$ we don't want β: $k^2 = \frac{w^2}{v^2}$

Wave eq^n where the 2nd derivative wrt position but 1st derivative wrt time

Consider: $\frac{\partial^2 A}{\partial x^2} = \alpha \frac{\partial A}{\partial t}$

Insert plane wave eq^n: $A(x,t) = A_0 \exp(i(kx-wt))$

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

$= A_0 e^{i(kx-wt)}$

$= \cancel{A_0 e}\ A_0[\cos(kx-wt) + i\sin(kx-wt)]$

$\frac{\partial A}{\partial x} = ikA_0 e^{i(kx-wt)}$

$\frac{\partial^2 A}{\partial x^2} = -k^2 A_0 e^{i(kx-wt)}$

$= -k^2 A$

$\frac{\partial A}{\partial t} = iw A_0 e^{i(kx-wt)}$

$= iwA$

$-k^2 A = iwA\alpha$

$-k^2 = i\alpha w$

We want

$\hbar w = \frac{p^2}{2m}$

~~but~~ $-k^2 = i\alpha m$

let $\alpha = \frac{2m}{i\hbar}$

$\Rightarrow$ multiply by $\frac{\hbar^2}{2m}$

$\frac{\hbar^2 k^2}{2m} = \hbar w$

$\frac{p^2}{2m} = \hbar w$

$\Rightarrow$ wave eq^n (matter)

$$\boxed{\frac{\partial^2 A}{\partial x^2} = \frac{2m}{i\hbar}\frac{\partial A}{\partial t}} \quad ; \times \frac{(i\hbar)^2}{2m}$$

$\Rightarrow$

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

$A(x,t) = A_0 e^{i(kx-wt)}$ insert

We will have

$$\underbrace{\hbar w}_{\text{Total energy}} = \underbrace{\frac{\hbar^2 k^2}{2m}}_{\text{Kinetic energy}} \left(+ \text{ Potential energy}\right)$$

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

Time dependent Schrödinger eq^n

should hold for not only plane wave, but ~~oth~~ to any other wave

$\Rightarrow$ all general solutions

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

$\nexists$ no formal derivation $\qquad \Psi(x,t)$

if $V(x,t) \equiv V(x)$

$\rightarrow$ we can apply separation of variables

$\hookrightarrow$ look for solutions of the form

$\Rightarrow \Psi(x,t) = \psi(x)T(t)$

$\Rightarrow$

4

$$i\hbar\,\partial_t\,\psi(x)T(t) = -\frac{\hbar^2}{2m}\partial_x^2\psi(x)T(t) + V(x)\psi_x T(t)$$

$$\frac{1}{\psi T}\left(i\hbar\,\psi\frac{dT}{dt}\right) = \left(-\frac{\hbar^2}{2m}T\frac{d^2\psi}{dx^2} + V\psi T\right)\frac{1}{\psi T}$$

$$\frac{i\hbar}{T}\frac{dT}{dt} = -\frac{\hbar^2}{2m\psi}\frac{d^2\psi}{dx^2} + V$$

Full Solution of TDSE

$$\boxed{\Psi(x,t) = \psi(x)\,e^{-\frac{iE}{\hbar}t}}$$

$\hookrightarrow$ $\frac{i\hbar}{T}\frac{dT}{dt} = E$

$$\frac{dT}{dt} = \frac{-iE}{\hbar}T(t)$$

$$T(t) = e^{-\frac{iEt}{\hbar}}$$

describes the time dependence of the wavefunction

in the case where P.E does not vary w/ time

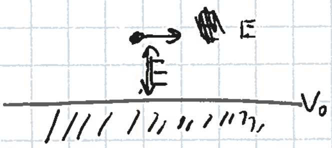
$$-\frac{\hbar^2}{2m\psi}\frac{d^2\psi}{dx^2} + V = E$$

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

Time ~~ir~~ independent Schrödinger eq^n $\Rightarrow$ for spatial dependence

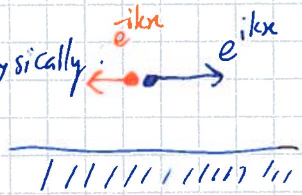
need to know $V(x)$ / the form of $V(x)$

Example: time independent Schrödinger eq^n for a free particle



$V(x) = V_0$

Physically:



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

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

- trying: $\psi = e^{\alpha x}$

$$\frac{d^2 e^{\alpha x}}{dx^2} = \alpha^2\psi$$

$\hookrightarrow$ $-\frac{\hbar^2}{2m}\alpha^2\psi = (E - V_0)\psi$

$\Rightarrow$ $-\frac{\hbar^2\alpha^2}{2m} = \underbrace{E - V_0}_{+ve}$

L.H.S $\frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

$\rightarrow$ need to get rid of -ve sign

$\Rightarrow$ $\alpha = \pm ik$

$\hookrightarrow$ Soln

$$\psi(x) = \begin{cases} e^{+ikx} \\ e^{-ikx} \end{cases}$$

check putting $\psi(x) = e^{ikx}$ back into TISE

$$-\frac{\hbar^2}{2m}\underbrace{\frac{d^2 e^{ikx}}{dx^2}}_{\downarrow\; -k^2 e^{ikx}} = (E - V_0)e^{ikx}$$

$\Rightarrow$ $\frac{\hbar^2 k^2}{2m}\cancel{e^{ikx}} = (E - V_0)\cancel{e^{ikx}}$

$$\underbrace{\frac{\hbar^2 k^2}{2m}}_{KE} + \underbrace{V_0}_{PE} = \underbrace{E}_{TE}$$

De Broglie, momentum

$\psi(x) = e^{ikx}$ $\quad p = \hbar k$ (右行)

$\psi(x) = e^{-ikx}$ $\quad p = -\hbar k$ (左行)

algebraic expression for k

$$\frac{\hbar^2 k^2}{2m} = E - V_0$$

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

General solution:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

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

Postulates of quantum mechanics

– cannot be derived from ~~[illegible]~~ classical sense

Postulates:

1. A wave function exists & contains all info about the system

2. Operators are used to extract observable quantities from the wave function

3. How we construct operators

4. What happens when we make a measurement

5. Time evolution of the wave function

Wavefunction: describing the universe in terms of a mathematical object (ψ)
(in classical mech: describe the universe in terms of positions & velocities of particles)

Postulate ~~one~~ 1:

There exists a wave function which describes all possible predictions about the physical properties of the system can be obtained

$\psi \Rightarrow$
- continuous
- square – integrable
- single-valued

of the parameters of all parameters and of time

~~ψ is~~ ψ is complex $\Rightarrow$ difficult to ascribe it a physical interpretation

→ a mathematical description of the system of interest
↳ can determine various properties from it

Notations

$\Psi(\underline{r}, t)$

$\psi(\underline{r})$

$\hat{Q} \Rightarrow$ operator

$\phi(\underline{r}) \Rightarrow \psi$ is an eigenfunction

$\underline{r} = \underline{r}(x, y, z)$

or

$\underline{r} = \underline{r}(r, \theta, \phi)$

6

The Born rule:

- in double slit expt, probability of a particle arriving at a particular point $\propto$ to intensity / square magnitude of the wave

- probability of finding the particle @ dx at t : $|\Psi(x,t)|^2 dx$

$$\Rightarrow \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

Ψ' representing an unnormalised wave function

$\Rightarrow$ calculating normalised Ψ $\quad \int_{-\infty}^{\infty} |\Psi'(x,t)|^2 dx = N$

$$\Rightarrow \Psi(x,t) = \frac{1}{\sqrt{N}} \Psi'(x,t)$$

Boundary conditions: no jumps, gaps, undefined pts, no discontinuities

1: continuous, single-valued function of position & time $\boxed{\Psi = \Psi(x,t)}$

2: continuous first derivative wrt position everywhere Ψ $\partial_x \Psi$ $\Rightarrow$ continuous

EXCEPT : infinite discontinuity in the PE function

3: finite squared modulus over all values of position

$\int |f(x)|^2 dx < \infty$ must remain finite for all values of x

$\rightarrow$ ensured that :

1. probability of finding the particle @ any pt is unambiguously defined
   - $\hookrightarrow$ other quantity can be calculated from the Ψ

e.g. $f(x) = e^{-x^2}$ ✓

2. Infinities DO NOT occur in $\partial_x^2 \Psi$
   - $\hookrightarrow$ ∵ implies ($E \to \infty$)

$f(x) = e^{x}$ ✗

3. Ψ can be normalized

Postulate 2: (how to extract info)

- There is an associated linear, Hermitian operator to each observable quantity
- eigenvalues of the operator represent the possible results of carrying out a measurement of the ~~correct~~ corresponding quantity
- after taking the measurement → Ψ_E

- using mathematical operator $\hat{Q}$

$\hat{Q}\phi = q\phi$ => eigenvalue eq^n

q ↓ measurement result

eigenvalues are quantised by one or more quantum numbers (eg. n), only discrete values of a certain property

=> $\hat{Q}\phi_n = q_n\phi_n$

Eg.

TISE

$$\underbrace{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)}\psi = E\psi$$

→ $\hat{H}$, Hamiltonian

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

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

↖ real ←

For ~~linear~~ linear, Hermitian operators

* eigenvalues must be ~~re~~ real

=> Hermitian operators guarantee real eigen values

Eigenvalues of Hermitian operators are real!

$\hat{Q}\phi_m = q_m\phi_m$

$(\hat{Q}\phi_m)^* = (q_m\phi_m)^* = q_m^*\phi_m^*$

If $\hat{Q}$ is Hermitian,

$$\int \phi_m^*\hat{Q}\phi_m \,d\tau = \int \phi_m(\hat{Q}\phi_m)^* d\tau$$

$$\int \phi_m^* q_m\phi_m d\tau \qquad \int\phi_m(q_m\phi_m)^* d\tau$$

$$= q\int\phi_m^*\phi_m d\tau \qquad = \int\phi_m q_m^*\phi_m^* d\tau$$

$$= q_m\int|\phi_m|^2 d\tau \qquad = q_m^*\int|\phi_m|^2 d\tau$$

=> L.H.S = R.H.S

$q_m = q_m^*$

∴ q_m are real

① **Definition** of Hermitian Operator:

$$\int f^*\hat{Q}g\,d\tau = \int g(\hat{Q}f)^* d\tau$$

* f & g are well behaved functions that ~~g~~ vanish @ ∞

integrals are over all space

$d\tau = dx\,dy\,dz$.

1D: $\displaystyle\int_{-\infty}^{\infty} f^*\hat{Q}g\,dx = \int_{-\infty}^{\infty} g(\cancel{f\ominus}\,\hat{Q}f)^* dx$

Hermitian operator:

are these hermitian? → def: $\int f^* \hat{Q} g \, d\tau = \int g (\hat{Q} f)^* d\tau$

eg.

$\hat{Q} = \frac{d}{dx}$

$$\int_{-\infty}^{\infty} f^* \hat{Q} g \, dx = \int_{-\infty}^{\infty} f^* \frac{dg}{dx} dx$$

$u = f^*$ $\quad v' = \frac{dg}{dx}$

$u' = \frac{df^*}{dx}$ $\quad v = g$

$$\int_{-\infty}^{\infty} f^* \hat{Q} g \, dx = \underbrace{\left[f^* g \right]_{-\infty}^{\infty}} - \int g \frac{df^*}{dx} dx = - \int g \left(\frac{df}{dx} \right)^* dx$$

$$= - \int g (\hat{Q} f)^* dx$$

$f(x), g(x) \to 0$ as $x \to \pm\infty$

∵ well behaved function, goes to 0 at infinit

↳ not hermitian

$\hat{Q} = \frac{d}{dx}$ is not an Hermitian operator

? $\hat{Q} = x$

? $\hat{Q} = -i\hbar \frac{d}{dx}$

Defining Linearity

Def:

Linear operators

$\hat{Q}$ is linear if & only if

=> for any two functions f_1 and f_2

any any two constants C_1 and C_2.

[which may be complex]

$$\hat{Q}(c_1 f_1 + c_2 f_2) = c_1 \hat{Q}(f_1) + c_2 \hat{Q}(f_2)$$

→ operators which represent physical observables

to be linear

↳ construct superpositions of quantum states

↳ we want to able to add two or more quantum state together, to create another valid quantum state.

eg. TISE in a region of const $V(x)$

↳ $\psi(x) = Ae^{ikx} + Be^{-ikx}$

The effect of measurement

$$\hat{Q}\phi = q\phi$$

Measure some quantity

general wavefunction

result

after measurement, system is in eigenstate ϕ

ψ may not be same as ϕ

wavefunction B4 measurement

wave function after measurement.

$$\psi \xrightarrow{\hat{Q}} \phi \xrightarrow{\hat{Q}} \phi$$

measure again immediately

act of measurement

changes the wave function, IF the ~~wavefunction~~ system is not in some eigenstate

But we will be getting the same result if we immediately measure again the same quantity, ∵ system is now in an eigenstate of operator $\hat{Q}$ //

Postulate 3

→ identifying the operator $\hat{X} = x$ $\hat{p} = -i\hbar\frac{d}{dx}$

$\hat{\underline{R}} = \underline{r}$ $\hat{\underline{p}} = -i\hbar\nabla$

Eg:

The classical ~~KE~~ expression of energy

$$T = \frac{p^2}{2m} \Rightarrow \hat{T} = \frac{\hat{p}^2}{2m}$$

$$= \frac{\hat{p}\hat{p}}{2m}$$

$$= \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right)$$

$$\underline{\underline{\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}}$$

From $\hat{H} = \hat{T} + \hat{V}$

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

Eg. KE in 3D

Eg. Angular momentum operator

About the momentum operator:

$\hat{P}\phi = p\phi$

$\Rightarrow -i\hbar \frac{d}{dx}\phi = p\phi$

$\Rightarrow$ looking at an eigenfunction

using plane wave sol^n

$\phi(x) = Ae^{ikx}$

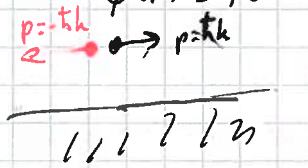
$-i\hbar \frac{d}{dx} Ae^{ikx} = \hbar k A e^{ikx} = \hbar k \phi$

eigenvalue

↳ $p = \hbar k$ (postulated earlier from de Broglie)

→ physically

$\phi(x) = Ae^{ikx}$



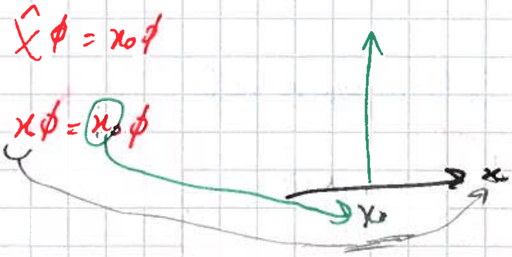
If instead, $\phi(x) = Ae^{-ikx}$

↳ $\hat{P}\phi \Rightarrow p = -\hbar k$

About the position operator:

$\hat{X}\phi = x_0\phi$

$x\phi = x_0\phi$



We know the operator: x

$\Rightarrow$ we know the eigenvalue: x_0

BUT don't know wt are the eigenfunctions

We know $|\phi|^2 dx \Rightarrow$ probability of finding the particle within some element dx of the point x_0.

we know $\Rightarrow$ highly localized at x_0 and zero everywhere else

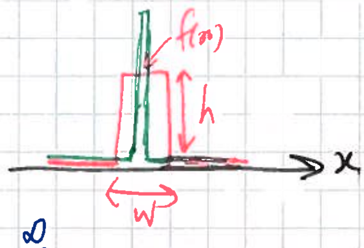
satisfies

Dirac delta function. [Def]

$$\delta(x-x_0) = \begin{cases} +\infty & \text{if } x = x_0 \\ 0 & \text{if } x \neq x_0 \end{cases}$$

$$\int_{-\infty}^{\infty} f(x)\,\delta(x-x_0)\,dx = f(x_0)$$

eg. $\int_{-\infty}^{\infty} \delta(x-x_0)\,dx = 1$



$\Rightarrow \int_{-\infty}^{\infty} f(x)\,dx \approx w \times h$

→ decrease w, $w \to 0 \Rightarrow h \to \infty$

Area is constant

$\lim w \to 0 \quad h \to \infty$

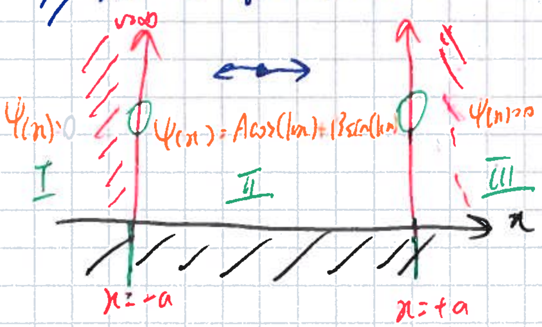
$x\phi = x_0\phi$

$\phi(x) = A\delta(x-x_0)$

$xA\delta(x-x_0) = x_0 A\delta(x-x_0)$

4/. One-dimensional time-independent problems.

4.1/ Infinite square well. $V=\infty$



$$V(x)=\begin{cases}0 & \text{if } -a\le x\le a\\ \infty & \text{if } |x|>a\end{cases}$$

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

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

Region I & III, $V(x)=\infty$

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + \infty\,\phi = E\phi$$

$$\Rightarrow \phi(x)=0$$

Region II $V(x)=0$ $E>0$

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

$\Rightarrow$ General solⁿ: $\psi(x)=Ae^{ikx}+Be^{-ikx}$ $\quad k=\frac{\sqrt{2mE}}{\hbar}$

Alternate solⁿ:

$$\psi(x)=A_2\cos(kx)+B_2\sin(kx)$$

* $\psi(x)$ must be continuous everywhere

$$\left.\begin{aligned}\psi_I(-a)&=\psi_{II}(-a)\\ \psi_{II}(a)&=\psi_{III}(a)\end{aligned}\right]\text{— Boundary Conditions (B.C.)}$$

$$\left.\begin{aligned}0&=A\cos(-ka)+B\sin(-ka)\\ A\cos(ka)&+B\sin(ka)=0\end{aligned}\right\}$$

$\Rightarrow A\cos(ka)-B\sin(ka)=0$ — ①

$A\cos(ka)+B\sin(ka)=0$ — ②

$\Rightarrow 2A\cos(ka)=0$ or ①+②

$$\left[\begin{aligned}&2A\cos(ka)=0\\ &①-②\\ &2B\sin(ka)=0\end{aligned}\right.$$

Letting $B=0$

$\Rightarrow A\cos ka=0$

$\rightarrow ka=\frac{n\pi}{2}$

$n=1,3,5,\dots$] → quantum number

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

$\psi(x)=A\cos\left(\frac{n\pi x}{2a}\right)$ $n=1,3,5\dots$] — I

Letting $A=0$

$B\sin ka=0$

$ka=n\pi$ $\quad n=1,2,3\dots$

or

$ka=\frac{n\pi}{2}$ $\quad n=2,4,6\dots$

$\psi(x)=B\sin\left(\frac{n\pi x}{2}\right)$ $n=2,4,6\dots$] — II

$\psi_n(x)=A\cos\left(\frac{n\pi x}{2a}\right)$ for $n=1,3,5,\dots$

OR

$B\sin\left(\frac{n\pi x}{2a}\right)$ for $n=2,4,6,\dots$

Finding the Normalization constant

$$\int_{-\infty}^{\infty}|\psi(x)|^2dx=\int_{-a}^{a}|A|^2\cos^2\left(\frac{n\pi x}{2a}\right)dx$$

$$=|A|^2a \Rightarrow A=\frac{1}{\sqrt{a}},\quad B=\frac{1}{\sqrt{a}}$$

$$\therefore \psi_n(x)=\begin{cases}\frac{1}{\sqrt{a}}\cos\left(\frac{n\pi x}{2a}\right) & \text{for odd } n\text{'s}\\ \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right) & \text{for even } n\text{'s}\end{cases}$$

$k=\frac{n\pi}{2a}$

$n=1,2,3,4\dots$

for Energy of a particle:

$$E = \frac{\hbar^2 k^2}{2m} \qquad k = \frac{n\pi}{2a} \quad n = 1, 2, 3, 4$$

$$\Rightarrow E_n = \frac{\hbar^2 \pi^2 n^2}{8ma^2} \qquad n = 1, 2, 3 \ldots$$

Sol^n to the infinite square well.

See moodle notes Section 4

for

E, $\psi_n(x)$ & $|\psi_n(x)|^2$

$E_n \propto n^2 \rightarrow$ discrete energies

E_1 is the ground state, or lowest energy level

~~A=3~~

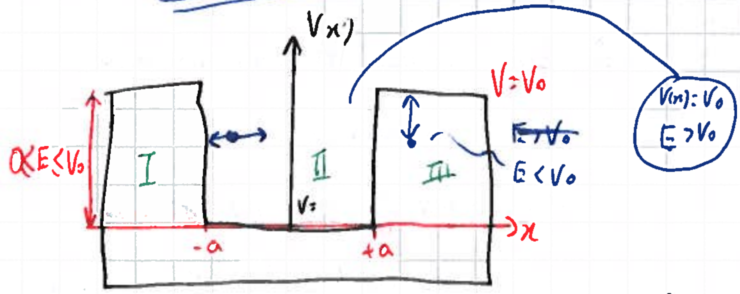
$n = 1, 3, 5$ cosine functions symmetrical (odd) at y axis $\rightarrow$ even valued $\Rightarrow$ even parity

$n = 2, 4, 6 \ldots$ sine function antisymmetrical / mirror symmetry about y axis $\rightarrow$ odd valued $\Rightarrow$ odd parity

P.D.Fs ~~pro~~ $\rightarrow$ physically meaningful

$\hookrightarrow$ ~~pro~~ gives probabilities

The finite square well



$$V(x) \begin{cases} 0 & -a \le x \le a \ (\text{II}) \\ V_0 & |x| \ge a \ (\text{I} \& \text{III}) \end{cases}$$

Region II:

$$\psi_{\text{II}} = A\cos(kx) + B\sin(kx)$$

where $k = \sqrt{2mE}/\hbar$

Using TISE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \underbrace{V(x)}_{=V_0}\psi = E\psi$$

for $E < V_0$

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

$$\Rightarrow \psi(x) = e^{\alpha x}$$

$$\Rightarrow -\frac{\hbar^2\alpha^2}{2m} = E - V_0$$

$$\Rightarrow \frac{\hbar^2\alpha^2}{2m} = \underbrace{V_0 - E}$$

$E < V_0 \Rightarrow$ R.H.S. is +ve when α is real

By convention $\alpha = K$

$$\psi(x) = e^{\pm Kx}$$

$$\frac{\hbar^2 K^2}{2m} = V_0 - E \Rightarrow K = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

General sol^n

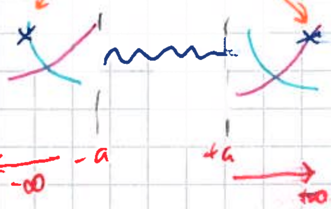
$$\psi(x) = Ae^{+Kx} + Be^{-Kx}$$

is not square integrable

$\Rightarrow$ for regions I & III

$$\rightarrow \psi_{\text{I}}(x) = Ce^{Kx} + \underbrace{De^{-Kx}}_{=0}$$

$$\psi_{\text{III}}(x) = \underbrace{Fe^{Kx}}_{0} + \underbrace{Ge^{-Kx}}$$



$$\therefore \psi_{\text{I}}(x) = Ce^{Kx} \quad (x > a)$$

$$\psi_{\text{III}}(x) = Ge^{-Kx} \quad (x < -a)$$

14

Having $\psi_I = Ce^{Kx}$ $x > a$

$\psi_{III} = Ge^{-Kx}$ $x < -a$

→ Boundary conditions require the wavefunction to be continuous everywhere

↳ our functions are continuous, now matching them at steps in $V(x)$

$$\psi_I(-a) = \psi_{II}(-a)$$

$$\psi_{II}(a) = \psi_{III}(a)$$

→ ~~call~~ also noting that the first derivative $\Rightarrow \frac{d\psi}{dx} = \psi'$ has to be continuous

$$\psi'_I(a) = \psi'_I(-a)$$

$$\psi'_{II}(a) = \psi'_{III}(-a)$$

I.E:

$$\psi_I(x) = Ce^{Kx}$$

$$\psi_{II}(x) = A\cos(kx) + B\sin(kx)$$

$$\psi_{III}(x) = Ge^{-Kx}$$

$\frac{d}{dx}$

$$\Rightarrow \psi'_I(x) = KCe^{Kx}$$

$$\psi'_{II}(x) = -kA\sin kx + kB\cos(kx)$$

$$\psi'_{III}(x) = -KGe^{-Kx}$$

⇒ Applying boundary conditions:

$$A\cos(ka) - B\sin(ka) = Ce^{-Ka} \quad - (1)$$

$$A\cos(ka) + B\sin(ka) = Ge^{-Ka} \quad - (2)$$

$$kA\sin(ka) + kB\cos(ka) = KCe^{-Ka} \quad - (3)$$

$$-kA\sin(ka) + kB\cos(ka) = -KGe^{-Ka} \quad - (4)$$

(1) + (2)

$$2A\cos(ka) = (C+G)e^{-Ka} \quad - (5)$$

(2) − (1) $$2B\sin(ka) = (G-C)e^{-Ka} \quad - (6)$$

(3) + (4) $$2kB\cos(ka) = -K(G-C)e^{-Ka} \quad - (7)$$

(3) − (4) $$2kA\sin(ka) = K(C+G)e^{-Ka} \quad - (8)$$

– 4 values, C, G, k, K

– 4 sim^{t} eq^{n}s ∴ simultaneously satisfied.

Considering $C = G$ & $B = 0$, (6) & (7) will vanish

↳ (8) ÷ (5) : $\boxed{k\tan ka = K}$ – (9)

Or

Considering $C = -G$, $A = 0$ (5) & (8) will vanish

↳ (7) ÷ (6) : $\underline{k\cot(ka) = K}$ – (10)

Boundary conditions are ~~st~~ satisfied when:

$$k\tan(ka) = K, \quad C = G \text{ \& } B = 0 \quad - (11)$$

OR

$$k\cot(ka) = -K, \quad C = -G \text{ \& } A = 0 \quad - (12)$$

The above ~~soln~~ has to be solved numerically

values of k & K in these eq^{n} are given by:

$$k = \frac{\sqrt{2mE}}{\hbar} \; ; \; K = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

$V = 0$ $\qquad V_0 > E$

Cannot use these conditions to write simple analytic expressions for allowed energy levels

– Solve (12) numerically, graphically or iteratively

↳ expressing K as:

$$K = \sqrt{\frac{2mV_0}{\hbar^2} - \frac{2mE}{\hbar^2}} = \sqrt{k_0^2 - k^2}$$

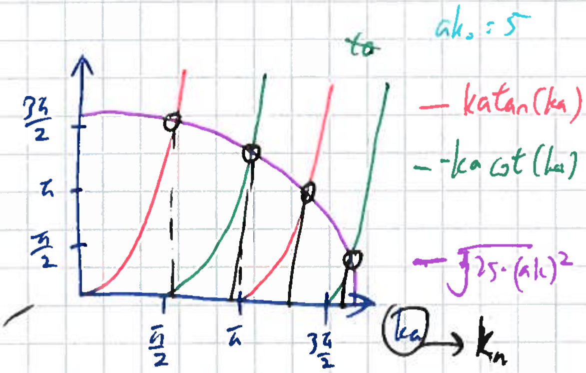
where $k_0^2 = \frac{2mV_0}{\hbar}$

- Multiply (11) & (12)

(11) × (12)

- $ka\tan ka = \sqrt{(ak_0)^2 - (ak)^2}$
- $ka\cot ka = \sqrt{(ak_0)^2 - (ak)^2}$

=> using Mathematica



we know $k_n = \frac{\sqrt{2mE}}{\hbar}$

intersections of the traces on this graph provides sol'n to (11) for values of ak for a given value of ak_0

↳ determined by both the width & depth of the well

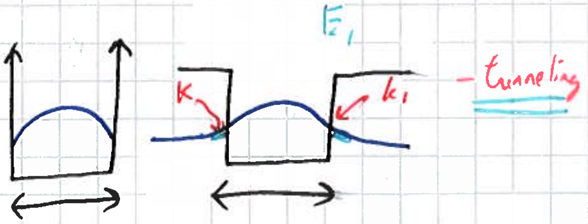
$ak = 1.32, 2.60,$ ~~2.6~~ $3.84, 4.91$ ← intersect values

for a given well width, a, and the product ak_0,

well ~~tuff~~ depth: $V_0 = \frac{(ak_0)^2 \hbar^2}{2a^2 m_e}$

See table for Section 4:

$E_{finite} < E_{infinite}$



it less squished, more spread out

for the finite square well

- similar to the ∞ square well
- potentials are even, but ψ are even or odd

★ Penetration to classically forbidden region $|x| > a$

↳ there is a finite probability for finding the particle there

↳ results in energies lower than the ∞ ~~well~~ □ well.

↳ noticeable for states near the top of the well

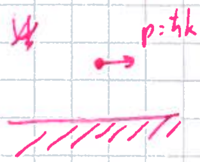
- There is a finite number of bound states.

↳ depending on depth of potential well

↳ for very deep wells, lowest lying states will be similar to that of ∞ □ wells too

Plane waves

$\psi(x) = Ae^{ikx}$



But all wavefunctions must satisfy the boundary conditions of Postulate 1

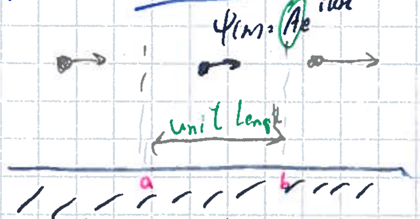
→ square integrability

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \text{finite}$$

eg: $\int_{-\infty}^{\infty} |A|^2 e^{ikx} e^{-ikx} dx = \int_{-\infty}^{\infty} |A|^2 dx \rightarrow$ not finite

✱ Plane waves are not ~~normalizable~~ square integrable

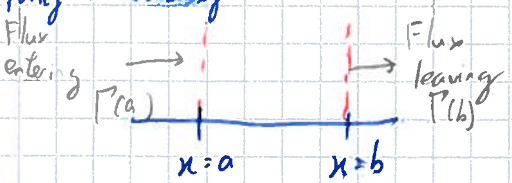
The concept of Particle flux ($\Gamma(x)$)



- instead of treating the system as one particle
  ↳ treat the system as a beam of particles

∴ We can integrate from ~~from~~ the a to b where ab is the average distance between the particles

Doing it formally



Pt Probability of finding the particle between points $x=a$ & $x=b$:

$$P_{a,b} = \int_a^b |\psi|^2 dx = \int_a^b \psi^* \psi \, dx$$

✱ Net flux passing through the region at time t is

$$\Gamma(a) - \Gamma(b)$$

entering − leaving

16.

Particle flux $\Gamma(x)$ → or current density

→ represents the average of particles passing a pt x per unit time

i.e.

$$\Gamma(a) - \Gamma(b) = \frac{dP_{a,b}}{dt} = \frac{d}{dt}\int_a^b \psi^* \psi \, dx$$

$$= \int_a^b \frac{\partial}{\partial t}(\psi^* \psi) \, dx$$

- Differentiating the integral sign

∵ $\psi(x,t)$, when we have $\frac{d}{dt}\int_a^b \psi^* \psi \, dx$, only integrating out spatial dependence

→ derivative is only w.r.t time

→ when we bring in the $\frac{d}{dt}$ into the integral sign, only want to ~~do~~ diff. w.r.t time ∂_t

Using Product rule:

$$\Rightarrow \int_a^b \psi \, \partial_t \psi^* + \psi^* \, \partial_t \psi \, dx \quad \text{— (A)}$$

using TDSE:

$$i\hbar \, \partial_t \psi = -\frac{\hbar^2}{2m} \partial_x^2 \psi + V\psi$$

$$\Rightarrow \frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi\right)$$

TDSE*

$$\frac{\partial^* \psi}{\partial t} = \frac{1}{i\hbar}\left(\frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + V\psi^*\right)$$

Putting back these in (A)

$$\frac{1}{i\hbar}\int_a^b \psi \frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} - \psi V \psi^* - \psi^* \frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \psi^* V \psi \, dx$$

$$= -\frac{i\hbar}{2m}\int_a^b \psi \frac{\partial^2 \psi^*}{\partial x^2} - \psi^* \frac{\partial^2 \psi}{\partial x^2} \, dx$$

$$= \frac{i\hbar}{2m}\left(\int_a^b \psi^* \frac{\partial^2 \psi}{\partial x^2} dx - \int_a^b \psi \frac{\partial^2 \psi^*}{\partial x^2} dx\right)$$

$$\left[\int_a^b \psi \frac{\partial^2 \psi^*}{\partial x^2}\,dx\right]$$

$u = \psi \qquad v' = \frac{\partial^2 \psi^*}{\partial x^2}$

$\frac{du}{dx} = \frac{\partial \psi}{\partial x} \qquad v = \frac{\partial \psi^*}{\partial x}$

$$\Rightarrow \left[\psi \frac{\partial \psi^*}{\partial x}\right]_a^b - \int_a^b \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x}\,dx$$

Similarly:

$$\left[\int_a^b \psi^* \frac{\partial^2 \psi}{\partial x^2}\,dx\right] = \left[\psi^* \frac{\partial \psi}{\partial x}\right]_a^b - \int_a^b \frac{\partial \psi}{\partial x}\frac{\partial \psi^*}{\partial x}\,dx$$

$$\Gamma(x) = \Gamma(a) - \Gamma(b) = \frac{i\hbar}{2m}\left(\int_a^b \psi^* \frac{\partial^2 \psi}{\partial x^2}\,dx - \int_a^b \psi \frac{\partial^2 \psi^*}{\partial x^2}\,dx\right)$$

$$\Rightarrow \frac{i\hbar}{2m}\left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right]_a^b$$

$$= \frac{i\hbar}{2m}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)\Big|_{x=b}$$

$$- \frac{i\hbar}{2m}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)\Big|_{x=a}$$

$$= -\frac{i\hbar}{2m}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)\Big|_a \quad \Big] \; \Gamma(a)$$

$$- \left(\frac{-i\hbar}{2m}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)\right)\Big|_b \quad \Big] \; \Gamma(b)$$

$$\boxed{\Gamma(x) = -\frac{i\hbar}{2m}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)}$$

Eq^n for particle flux

17

Ex/

Calculate the $\Gamma(x)$ for plane wave

$\psi(x,t) = Ae^{i(kx-\omega t)}$

$$\Gamma(x) = \frac{i\hbar}{2m}\left(\psi^*(ik\psi) - \psi(-ik\psi^*)\right)$$

$$= -\frac{i\hbar}{2m}(2ik)\psi^*\psi$$

$$\underbrace{\Gamma(x)}\; = \underbrace{\frac{\hbar k}{m}}_{\text{velocity}} |A|^2$$

- interpreting this result:

$p = \hbar k$, classically, $p = mv$

$$\boxed{\frac{\text{particle}}{\text{unit time}} = \frac{\text{unit length}}{\text{unit time}} \times \frac{\text{particles}}{\text{unit length}}}$$

- if we normalize $|A|^2 = 1$

↳ implies one particle per unit length

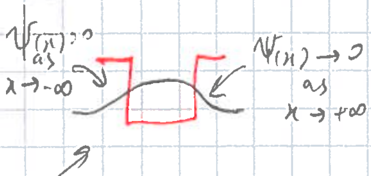
- Setting amplitude constant, $A=1$,

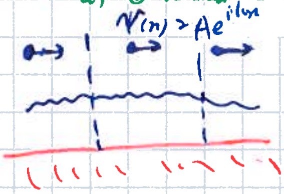
we will have one particle per unit length

$\psi(x) = Ae^{ikx}$

For Boundary Conditions

Postulate 1: Ψ must be square integrable so as to normalize it





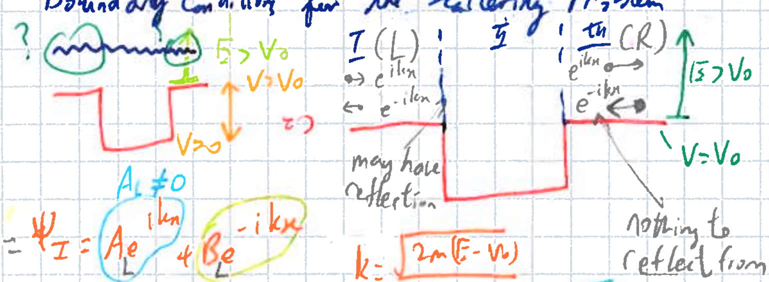
For Bound states

$\Psi(x) \to 0$ as $x \to \pm\infty$

$|A|^2 = 1$

$\to$ one particle per unit length

Boundary Condition for the Scattering Problem



$A_L \neq 0$

$\Psi_L = \Psi_I = A_L e^{ikx} + B_L e^{-ikx}$

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

$\Psi_R = \Psi_{III} = Ce^{ikx} + De^{-ikx}$

$= A_R e^{ikx} + B_R e^{-ikx}$, $B_R = 0$

A beam of particles incident on our potential from the left

$\therefore$ conditions to conclude: $A_L \neq 0$, $B_R = 0$

if we normalize the incident beam

$\Psi(x) = e^{ikx} + Be^{-ikx}$ to one particle per unit length

$\hookrightarrow |A_L| = 1$

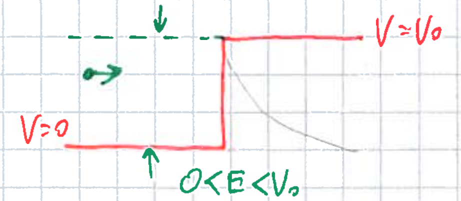
For $E > V_L, V_R$ (Free particle beam)

$\Rightarrow \Psi_L(x) = e^{ikx} + B_L e^{-ik_L x}$ $\quad k_L = \frac{\sqrt{2m(E-V_L)}}{\hbar}$

$\Rightarrow \Psi_R(x) = A_R e^{ik_R x}$ $\quad k_R = \frac{\sqrt{2m(E-V_R)}}{\hbar}$

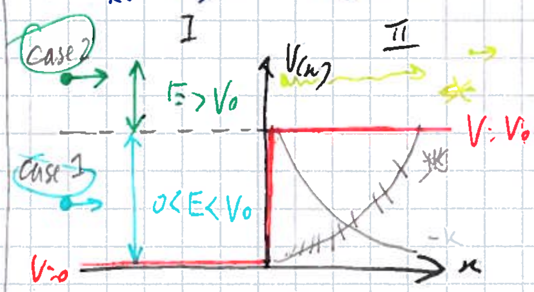
$\Rightarrow$ Boundary ~~cor~~ for scattering

Mixture of boundary conditions … for scattering & bound states.



$\Psi_L(x) = e^{ikx} + Be^{-ikx}$

$\Psi_R(x) \to 0$ as $x \to +\infty$



$$V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } x \geq 0 \end{cases}$$

Considering Case 1: $0 < E < V_0$

$\Psi_I(x) = Ae^{ikx} + Be^{-ikx}$, $A \neq 0$ $\quad k = \frac{\sqrt{2mE}}{\hbar}$

$\hookrightarrow$ representing a beam of particles incident on this V_0 on the left

Boundary conditions:

$A \neq 0$ $\because$ there must be a beam, incident on the L.H.S

Normalise beam to one particle per unit length

$\hookrightarrow |A|^2 = 1$

$\Psi_{II}(x) = Ce^{kx} + De^{-kx}$ $\quad k = \frac{\sqrt{2m(V_0-E)}}{\hbar}$

$Ce^{kx} = 0$

$C = 0$ $\because$ not allow diverging sol^n/s

$\Psi_I(x) = e^{ikx} + Be^{-ikx}$

$\Psi_{II}(x) = De^{-kx}$

Boundary Conditions @ the point $x=0$

$$\psi_I(0) = \psi_{II}(0)$$

$$\psi_I'(0) = \psi_{II}'(0)$$

$$\Rightarrow \psi_I'(x) = ike^{ikx} - ikBe^{-ikx}$$

$$\psi_{II}'(x) = -KDe^{-Kx}$$

$$\Rightarrow 1+B=D$$

$$ik - ikB = -KD$$

$\Rightarrow$ solving simultaneously

$$\rightarrow D = \frac{2k}{k+iK}$$

$$B = \frac{k-iK}{k+iK}$$

~~[illegible]~~

$$\psi(x) = \begin{cases} \underbrace{e^{ikx}}_{\text{incident } a} + \underbrace{\frac{k-iK}{k+iK}e^{-ikx}}_{\text{reflected } b} & (x<0) \\ \underbrace{\frac{2k}{k+iK}e^{-Kx}}_{\text{decay } c} & (x \geq 0) \end{cases}$$

穿[illegible]

case 2

: 100% reflection

Reflected & transmitted flux

↳ do not know exact precise location of the beam that turns around

$$\Gamma(x) = \frac{-i\hbar}{2m}\left(\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx}\right)$$

For a wavefunction:

$$\psi(x) = Ae^{ikx}$$

Reflected:

$$\Rightarrow \Gamma(x) = |A|^2 \frac{\hbar k}{m}$$

$$\Gamma_{incident} = \frac{\hbar k}{m} \quad (|A|^2 = 1)$$

$$\Gamma_{reflected} = -\frac{\hbar k}{m}|B|^2 \qquad B^*B = |B|^2$$

$$= -\frac{\hbar k}{m}\underbrace{\left(\frac{k-iK}{k+iK}\right)\left(\frac{k+iK}{k-iK}\right)}_{=1}$$

$$= -\frac{\hbar k}{m}$$

~~[illegible]~~

Transmitted flux

$\because$ real wavefunction into flux expression

$$\Gamma_{transmitted} = 0$$

Probability of reflection or transmission

$$P(R) = R = \left|\frac{\Gamma_{reflected}}{\Gamma_{incident}}\right| \qquad T + R = 1$$

$$P(T) = T = \left|\frac{\Gamma_{transmitted}}{\Gamma_{incident}}\right|$$

Potential Step $0 < E < V_0$

$T = 0$

$R = 1$ for this case

Considering now for Case 2

$$E > V_0$$

using also the plane wave sol^n

as from B4:

$$I: \quad \psi_I = e^{ikx} + Be^{-ikx} \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

$$II: \quad \psi_{II}(x) = Fe^{ik_{II}x} + Ge^{-ik_{II}x} \qquad k_{II} = \frac{\sqrt{2m(E-V_0)}}{\hbar}$$

☆ No reflections for particles to scatter from

$$\therefore G = 0$$

$$\Rightarrow \psi_{II}(x) = Fe^{ik_{II}x}$$

$$\left.\begin{aligned} \psi_I'(x) &= ik - ikBe^{-ikx} \\ \psi_{II}'(x) &= ik_{II}Fe^{ik_{II}x} \end{aligned}\right\} \begin{aligned} \psi_I(0) &= \psi_{II}(0) \quad - ① \\ \psi_I'(0) &= \psi_{II}'(0) \quad - ② \end{aligned}$$

↳ $1 + B = F$ from ①

$ik - ikB = ik_{II}F$ from ②

Solving Simultaneously

$$F = \frac{2k}{k+k_{II}} \; ; \; B = \frac{k-k_{II}}{k+k_{II}}$$

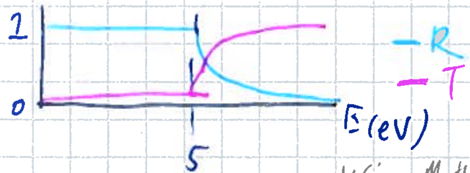
$$\psi(x) = \begin{cases} e^{ikx} + \frac{k-k_{II}}{k+k_{II}} e^{-ikx} & (x<0) \\ \frac{2k}{k+k_{II}} e^{ikx} & (x>0) \end{cases}$$

For probabilities for reflection & transmission

$$R = \left| \frac{\Gamma_{reflected}}{\Gamma_{incident}} \right| = \left| \frac{-\frac{\hbar k}{m}|B|^2}{\frac{\hbar k}{m}} \right| = |B|^2 = \frac{(k-k_{II})^2}{(k+k_{II})^2}$$

$$T = \left| \frac{\Gamma_{transmitted}}{\Gamma_{incident}} \right| = \left| \frac{\frac{\hbar k_{II}}{m}|F|^2}{\frac{\hbar k}{m}} \right| = \frac{k_{II}}{k}|F|^2 = \frac{4kk_{II}}{(k+k_{II})^2}$$

$R+T=1$

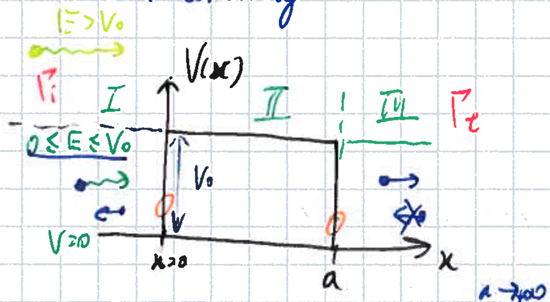


Using Mathematica

[try playing with the codes given]

Quantum tunnelling

20.



- finite thickness a
- height V_0
- particle beam of energy $0 \leq E \leq V_0$

$$\psi_I(x) = e^{ikx} + Be^{-ikx} \qquad \psi_I'(x) = ike^{ikx} - ikBe^{-ikx}$$

$$\psi_{II}(x) = Ce^{\kappa x} + De^{-\kappa x} \qquad \psi_{II}'(x) = \kappa Ce^{\kappa x} - \kappa De^{-\kappa x}$$

$$\psi_{III}(x) = Fe^{ikx} \qquad \psi_{III}'(x) = ikFe^{ikx}$$

$$k = \frac{\sqrt{2mE}}{\hbar} \qquad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

* for continuity of the wave function

$\psi_I(0) = \psi_{II}(0)$ => same as ψ'

$\psi_{II}(a) = \psi_{III}(a)$ => same as ψ'

↳ $1 + B = C + D$ — ①

$1 - B = \frac{\kappa}{ik}C - \frac{\kappa}{ik}D$ — ②

$Ce^{\kappa a} + De^{-\kappa a} = Fe^{ika}$ — ③

$Ce^{\kappa a} - De^{-\kappa a} = \frac{ik}{\kappa}Fe^{ika}$ — ④

① + ②

$2 = \left(1 + \frac{\kappa}{ik}\right)C + \left(1 - \frac{\kappa}{ik}\right)D$ — ⑤

③ − ④

$2De^{-\kappa a} = \left(1 - \frac{ik}{\kappa}\right)Fe^{ika}$ — ⑥

$\Rightarrow 2Ce^{\kappa a} = \left(1 + \frac{ik}{\kappa}\right)Fe^{ika}$ — ⑦

I : $\Gamma_i = \frac{\hbar k}{m}$

III : $\Gamma_t = |F|^2\frac{\hbar k}{m}$

$T = |F|^2$

Now we are interested in getting $|F|^2$

- Rearranging (5):

$$C = \frac{2 - \left(\frac{ik-K}{ik}\right) D}{\frac{ik+K}{ik}}$$

$$\Rightarrow C = \frac{2ik - (ik-K)D}{ik+K}$$

- Relating D to F

Divide (7) by $2e^{KA}$ & sub above expression for C

$$\frac{2ik-(ik-K)D}{ik+K} = \frac{\left(\frac{K+ik}{K}\right) F e^{ika}}{2e^{Ka}}$$

$$-(ik-K)D = \frac{\frac{(K+ik)^2}{K} F e^{ika}}{2e^{Ka}} - 2ik$$

$$D = \frac{2ik}{ik-K} - \frac{(K+ik)^2 F e^{ika}}{(ik-K)K\,2e^{Ka}} \quad \text{— (8)}$$

(6) $\div\ 2e^{-KA}$

$$D = \left(\frac{K-ik}{K}\right)\frac{e^{ika}}{2e^{-Ka}} F \quad \text{— (9)}$$

Equating (9) to (8)

$$\left(\frac{K-ik}{K}\right)\frac{e^{ika}}{2e^{-Ka}} F = \left[\frac{e^{-ika}\,2ik}{ik-K} - \frac{(K+ik)^2 e^{ika}}{(ik-K)K\,2e^{Ka}} F\right]$$

$$\left[\left(\frac{(K-ik)^2}{K\,2e^{-Ka}}\right) + \frac{(K+ik)^2}{\cancel{(ik-K)}K\,2e^{Ka}}\right] F = \frac{2ik e^{-ika}}{\cancel{ik-K}}$$

$$\left[(K-ik)^2 e^{Ka} + (K+ik)^2 e^{-Ka}\right] F = 4ikK e^{-ika}$$

$$F = \frac{4ikK e^{-ika}}{(K+ik)^2 e^{-Ka} + (K-ik)^2 e^{Ka}}$$

$$T = |F|^2 = |F^* F| = \frac{16k^2K^2}{|(ik+K)^2 e^{-Ka} - (K-ik)^2 e^{Ka}|^2}$$

for $E < V_0$

We can ignore the e^{-Ka}

~~Ka<~~ $Ka \gg 1$

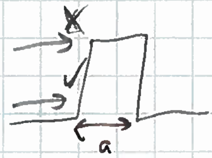
$\Rightarrow e^{Ka} \gg e^{-Ka}$

$$F \approx \frac{4ikK}{-(K-ik)^2 e^{Ka}} e^{-ika}$$

$$\Rightarrow T = |F^* F| = |F|^2 = \frac{16k^2K^2}{|(K-ik)^2 e^{Ka}|^2} = \frac{16k^2K^2}{(K^2+k^2)^2 e^{2Ka}}$$

$$T = \frac{16k^2K^2}{(K^2+k^2)^2} e^{-2Ka}$$

$$K = \frac{\sqrt{2m(V_0-E)}}{\hbar} \qquad k = \frac{\sqrt{2mE}}{\hbar}$$



if higher position of well, $(V_0 - E) \to 0$

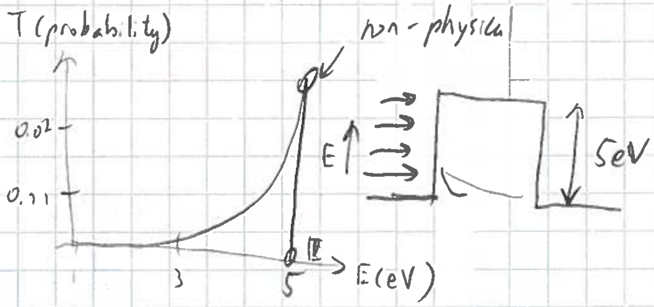
violate $Ka \gg 1$

∴ Simplified expression of T approximates particles near at the bottom of the well.

☆ transmission probability depends exponentially on the width of the barrier

Subbing expressions for K & k

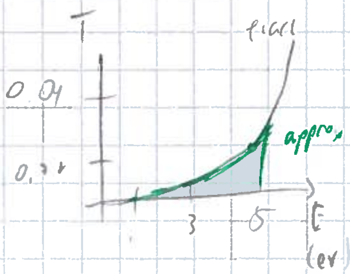
$$T = \frac{16E(V_0-E)}{V_0^2} e^{-2Ka}$$

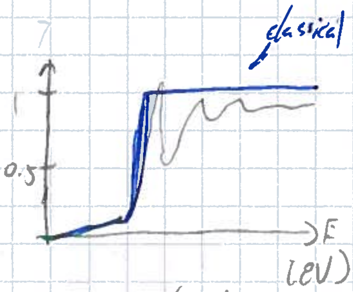


Repeating for $E > V_0$

- $\psi_{II} = Ce^{ik_{II}x} + De^{-ik_{II}x}$

$$T = \frac{16k^2k_{II}^2}{|(k+k_{II})^2 e^{-ik_{II}a} - (k-k_{II})^2 e^{ik_{II}a}|^2}$$





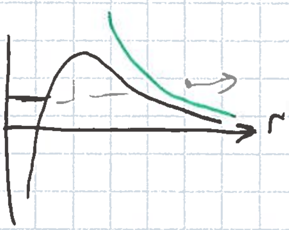
大概
[illegible]詳情睇 notes pdf.

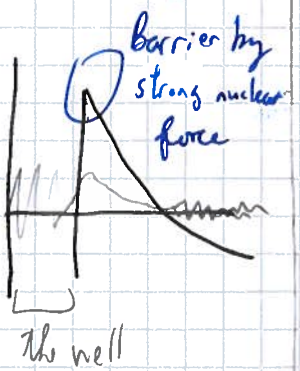
Eg. Alpha particle emission from a nucleus

→ finite probability for a particle to tunnel through a potential energy barrier which would be forbidden classically

↳ alpha particle - experiences attractive strong nuclear force, and a longer range repulsive force

- if it occupies an energy state less than zero, it will remain indefinitely → atom will be stable
- if it occupies energy state > 0, it can escape nucleus via Quantum tunnelling



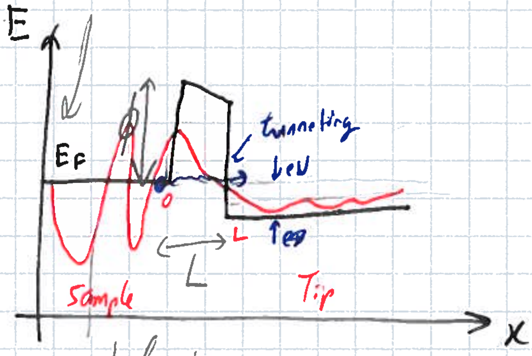


Scanning tunnelling microscope.

→ sharp needle scanned across the surface

1. Bringing a tip close to the surface, but not touching [5 atoms wide]
2. Apply electric voltage & measure tunnelling current
   - volts for semiconductors
   - mV for metals
   - pA to nA of tunneling current

Fermi level



work function

$$\left|\frac{\psi_n(L)}{\psi_n(0)}\right|^2 \propto e^{-2kL} \qquad k = \frac{\sqrt{2m(U-E)}}{\hbar}$$

[LQR]

3. Raster scan the tip while maintaining constant current
   ↳ TIP height to generate STM img

→ can also move atoms

One dimensional energy eigenvalue problems

energy eigenvalue

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

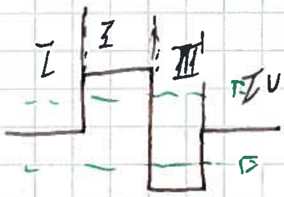
(TISE)

Energy operator

Eigenfunction

$$\overbrace{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)}^{\hat{H}}\phi = E\phi$$

for constant V_0:



$E>V_0$: plane wave sol^n

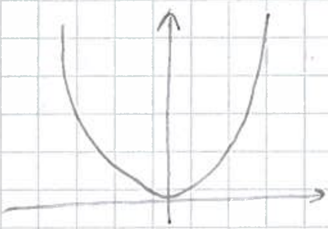
$\psi(x)=Ae^{ikx}+Be^{-ikx}$

$E<V_0$: $\psi(x)=Ce^{kx}+De^{-kx}$

Simple Harmonic Oscillator

$V(x)=\frac{1}{2}kx^2$

spring constant



classical natural frequency of oscillation

classically, mass m oscillates w/ angular frequency $\omega_0=\sqrt{\frac{k}{m}}$

$$\Rightarrow V(x)=\frac{\omega_0^2 m}{2}x^2=\frac{1}{2}kx^2$$

TISE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{\omega_0^2 m}{2}x^2\psi=E\psi$$

Change of variable

$$y=\sqrt{\frac{m\omega_0}{\hbar}}\,x \quad \& \quad \alpha=\frac{2E}{\hbar\omega_0}$$

$$\psi(x)\to\psi(y)$$

TISE $\times \frac{2}{\hbar\omega_0}$

$$-\frac{\hbar}{m\omega_0}\frac{d^2\psi}{dx^2}+\frac{\omega_0 m x^2}{\hbar}\psi=\frac{2E}{\hbar\omega_0}\psi$$

$$\Rightarrow -\frac{\hbar}{m\omega_0}\frac{d^2\psi}{dx^2}+y^2\psi=\alpha\psi$$

$\psi(y(x)) \to$ need $\frac{d^2\psi}{dy^2}$

using chain rule:

$$\frac{d(\psi(y(x)))}{dx}=\frac{d\psi}{dy}\times\frac{dy}{dx}$$

for 2nd derivative:

$$\frac{d^2\psi}{dx^2}=\frac{d^2\psi}{dy^2}\left(\frac{dy}{dx}\right)^2+\frac{d\psi}{dy}\frac{d^2y}{dx^2}$$

$$\Rightarrow \frac{dy}{dx}=\sqrt{\frac{m\omega_0}{\hbar}} \qquad \frac{d^2y}{dx^2}=0$$

$$\frac{d^2\psi}{dx^2}=\frac{d^2\psi}{dy^2}\frac{m\omega_0}{\hbar}+\frac{d\psi}{dy}(0)$$

$$\Rightarrow \frac{d^2\psi}{dy^2}=\frac{\hbar}{m\omega_0}\frac{d^2\psi}{dx^2}$$

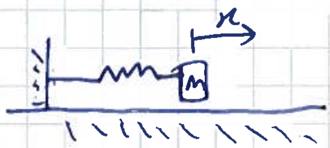
$\Rightarrow$ TISE

$$-\frac{d^2\psi(y)}{dy^2}+y^2\psi(y)=\alpha\psi(y)$$

$\Rightarrow$ Rearranging:

$$\boxed{\begin{gathered}\psi''(y)+(\alpha-y^2)\psi(y)=0\\ \& \quad y=\sqrt{\frac{m\omega_0}{\hbar}}\,x, \quad \alpha=\frac{2E}{\hbar\omega_0}\end{gathered}}$$

Asymptotic sol^n for large y

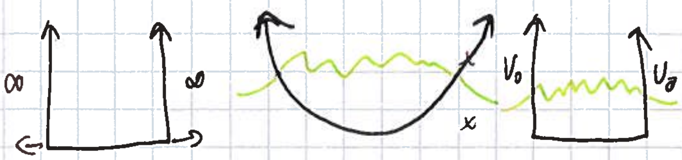


y^2 dominate over α

$$\Rightarrow \psi''(y)-y^2\psi=0$$

$$\psi''=y^2\psi \leftarrow \circledast$$

Trial: $\psi(y) = y^n e^{-\frac{y^2}{2}}$



maybe similar

But different for H.O. ∵ have finite value for potential energy

↳ comparing to finite square well

$$\psi = y^n e^{-y^2/2}$$

$$\psi' = n y^{n-1} e^{-y^2/2} - y e^{-y^2/2} y^n$$

$$= n y^{n-1} e^{-y^2/2} - y^{n+1} e^{-y^2/2}$$

$$\psi'' = n(n-1) y^{n-2} e^{-y^2/2} - n y^n e^{-y^2/2} - (n+1) y^n e^{-y^2/2} + y^{n+2} e^{-y^2/2}$$

$$= e^{-y^2/2} \left[n(n-1) y^{n-2} - (2n+1) y^n + \underline{y^{n+2}} \right]$$

y is large

$$\cong y^{n+2} e^{-y^2/2}$$

$$\psi'' = y^2 y^n e^{-y^2/2} = \boxed{y^2 \psi = \psi}$$

↳ Confirms this is the eigenfunction of the ~~ord~~ diff eqⁿ

Recalling:

$$\psi'' + (\alpha - y^2)\psi = 0$$

⇒ $\psi = y^n e^{-y^2/2}$ is a solⁿ if $y \gg 1$.

⇒ Suggest a full solⁿ:

$$\boxed{\psi(y) = H(y) e^{-y^2/2}}$$ → trial func.

might be solⁿ for TISE for all values of y

Repeating the same procedure:

$$\psi' = H' e^{-y^2/2} - y H e^{-y^2/2}$$

$$\psi'' = H'' e^{-y^2/2} - y e^{-y^2/2} H' - \left(H e^{-y^2/2} + y H' e^{-y^2/2} - y^2 H e^{-y^2/2} \right)$$

$$\psi'' = e^{-y^2/2} \left(H'' - 2y H' + (y^2 - 1) H \right)$$

↳ inserting into the diff eqⁿ

$$\psi'' + (\alpha - y^2)\psi = 0$$

$$e^{-y^2/2}\left(H'' - 2yH' + (y^2-1)H\right) + (\alpha - y^2) H e^{-y^2/2} = 0$$

$y = \sqrt{\frac{m\omega_0}{\hbar}}\, x$

$\alpha = \frac{2E}{\hbar\omega_0}$

using $\psi(y) = H(y) e^{-y^2/2}$

↳ $e^{-y^2/2}\left(H'' - 2yH' + (\alpha - 1)H\right) = 0$

$$\underline{\underline{H'' - 2yH' + (\alpha - 1) H = 0}}$$

Solving in MMIII using Frobenius method

$$H(y) = \sum_{p=0}^{\infty} a_p y^p$$

$$H'(y) = \sum_{p=0}^{\infty} a_p\, p\, y^{p-1}$$

$$H''(y) = \sum_{p=0}^{\infty} a_p\, p(p-1)\, y^{p-2}$$

$$= \sum_{p=2}^{\infty} a_p (p(p-1))\, y^{p-2} \quad \text{[first two terms vanish]}$$

$$\underset{p \to p-2}{=} \sum_{p=0}^{\infty} a_p (p+1)(p+2) y^p$$

Inserting back into to the eqⁿ/

$$\sum_{p=0}^{\infty} \left[a_{p+2}(p+2)(p+1) y^p - 2y a_p p y^{p-1} + (\alpha - 1) a_p y^p \right] = 0$$

$$\Rightarrow \sum_{p=0}^{\infty} y^p \left[\underbrace{a_{p+2}(p+2)(p+1) - 2p\, a_p + (\alpha - 1) a_p}_{=0 \text{ for all values of } p} \right] = 0$$

$$\Rightarrow a_{p+2}(p+2)(p+1) = (2p - \alpha + 1) a_p$$

$$a_{p+2} = \frac{(2p - \alpha + 1)}{(p+2)(p+1)} a_p$$

when $p=0$

$$a_2 = \frac{0-\alpha+1}{(1)(2)} = \frac{1-\alpha}{2}a_0$$

Examining the recurrence relationship

$$\frac{a_{p+2}}{a_p} = \frac{2p-\alpha+1}{(p+1)(p+2)}$$

$$\lim_{p\to\infty}\left|\frac{a_{p+2}}{a_p}\right| \to \frac{2}{p}$$

Relationship between successive term : $a_{p+2} = \frac{2}{p}a_p$

↳ same as : $\exp(y^2)$

$$= \sum_{n=0}^{\infty} \frac{y^{2n}}{n!} = 1 + y^2 + \frac{y^4}{2!} + \frac{y^6}{3!} + \dots$$

Examining the terms

p	0	2	4	6
Terms	1	y^2	$\frac{y^4}{2}$	$\frac{y^6}{3}$
Coeff	$a_0=1$	$a_2=\frac{2}{p}a_0$	$a_4=\frac{2}{p}a_2$	$a_6=\frac{2}{p}a_4$

↳ $H(y)$ will diverge

↳ $\Psi(y)$ will diverge

$\because \Psi = H(y)\, e^{-y^2/2}$

$= e^{y^2} e^{-y^2/2}$

$= e^{y^2/2} e^{\frac{3y^2}{2}}$

↳ $\because y \propto x \Rightarrow \Psi$ is not normalisable

★ Applying boundary conditions

↳ we ~~need~~ would want the series to terminate at some value of p

↳ i.e. $\frac{a_{p+2}}{a_p} = 0$

$2p - \alpha + 1 = 0$

$\alpha = 2p+1$

$\alpha = 2n+1 \quad p=n$

introducing a quantum no., n

$n = 1, 2, 3 \dots$

→ forcing the other series to vanish by setting its first coefficient $=0$

$\Rightarrow \alpha = 2n+1 \quad n = 0, 1, 2, 3 \dots$

$a_1 = 0$ if n is even

$a_0 = 0$ if n is odd.

Values of a_0 & a_1 are chosen to ensure the wavefunction is properly normalised

$a_0 = 1$, $a_1 = 2$ } just by convention

Recalling $\alpha = \frac{2E}{\hbar\omega_0}$

$$\Rightarrow E_n = \frac{\hbar\omega_0\alpha}{2} = \hbar\omega_0\left(n+\frac{1}{2}\right)$$

Writing down solⁿ:

$$H_n(y) = \sum_{p=0}^{n} a_p y^n$$

$H_0(y) = a_0$

$H_1(y) = a_0 + a_1 y$

$H_2(y) = a_0 + a_1 y + a_2 y^2$

$H_3(y) = a_0 + a_1 y + a_2 y^2 + a_3 y^3$

Applying the boundary conditions on

$a_0 = 0$ for odd n

$a_1 = 0$ for even n

$$\int_{-\infty}^{\infty} \left| H_n(y) e^{-\frac{y^2}{2}} \right|^2 dy = 1$$

using $a_0 = 1$; $a_1 = 2$

↳ $H_0(y) = 1$

$H_1(y) = 2y$

$H_2(y) = 4y^2 - 2$

$H_3(y) = 8y^3 - 12y$

} Hermite polynomials

Summary:

$$H''(y) - 2yH'(y) + (\alpha-1)H(y) = 0$$

where

$$H(y) = \sum_{p=0} a_p y^p$$

or

$$H(y) = a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \dots \infty$$

→ We want the wavefunction to be ~~not~~ normalizable;

series must terminate at some power of y

↳ $H_n(y) = a_0 + a_1 y + a_2 y^2 + \dots + a_n y^n$

$$a_{p+1} = \frac{2p-\alpha+1}{(p+1)(p+2)} a_p$$

$\alpha = 2n+1$ $n = 1, 2, 3 \dots$

↳ to terminate the series

$E_n = \hbar\omega_0(n+\frac{1}{2})$ ~~n = 1, 2, 3...~~ $n = 0, 1, 2, 3 \dots$

Eigenfunctions of H.O.:

$$\phi_n(y) = H_n(y)\, e^{-y^2/2}$$

Hermite polynomials are not normalized

↳ ∴ need a normalisation constant A_n

Rewriting everything:

eigenfunctions of the H.O.

$$\phi_n(x) = A_n H_n\left(\sqrt{\frac{m\omega_0}{\hbar}}\,x\right) e^{-\frac{m\omega_0 x^2}{2\hbar}}$$

$n = 0, 1, 2, 3$

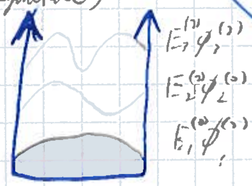
$$E = \hbar\omega_0\left(n+\frac{1}{2}\right)$$

See chem Q.M. notes or pdf for Phy Quant Phy for H.O. graphs

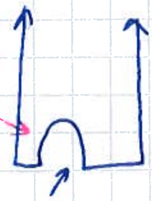
Perturbation theory

(first order, time independent, non-degenerate)

$$\hat{H}^{(0)}\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)} \quad - ①$$



↳ Adding a small perturbation



Full Hamiltonian

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}'$$

↳ λ has values between 0 & 1 } see this as an adjustable knob that can control the "size" of the perturbation

Write ϕ_n & E_n as power series

$$\phi_n = \phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)} + \dots \quad - ②$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad - ③$$

higher order corrections to eigenvalues & eigenfunctions

unperturbed eigenfunction & eigenvalue

Now we want to determine the first order correction to the original eigenvalues

①, ②, ③ → $\hat{H}\phi_n = E_n\phi_n$

$$(\hat{H}^{(0)} + \lambda\hat{H}')(\phi_n^{(0)} + \lambda\phi_n^{(1)}) = (E_n^{(0)} + \lambda_n E^{(1)})(\phi_n^{(0)} + \lambda\phi_n^{(1)})$$

$$\hat{H}^{(0)}\phi_n^{(0)} + \lambda\hat{H}^{(0)}\phi_n^{(1)} + \lambda\hat{H}'\phi_n^{(0)} + \lambda^2\hat{H}'\phi_n^{(1)} + \dots$$

$$= E_n^{(0)}\phi_n^{(0)} + \lambda E_n^{(0)}\phi_n^{(1)} + \lambda E_n^{(1)}\phi_n^{(0)} + \lambda^2 E_n^{(1)}\phi_n^{(1)} + \dots$$

Lowest order:

$$\hat{H}^{(0)}\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)}$$

First order correction term

$$\hat{H}^{(0)}\phi_n^{(1)} + \hat{H}'\phi_n^{(0)} = E_n^{(0)}\phi_n^{(1)} + E_n^{(1)}\phi_n^{(0)}$$

$\lambda = 1$

Multiply the expression by $\phi_n^{(0)*}$ & integrate.

$$\int \phi_n^{(0)*} \hat{H}^{(0)} \phi_n^{(1)} d\tau + \int \phi_n^{(0)*} \hat{H}' \phi_n^{(0)} d\tau$$

$$= \int \phi_n^{(0)*} E_n^{(0)} \phi_n^{(1)} d\tau + \underbrace{\int \phi_n^{(0)*} E_n^{(1)} \phi_n^{(0)} d\tau}_{E_n^{(1)}}$$

→ Hermitian operator

First term on L.H.S

$$\int \phi_n^{(0)*} \hat{H}^{(0)} \phi_n^{(1)} d\tau = \int \phi_n^{(1)} (\underbrace{\hat{H}^{(0)}}_{\text{unperturbed Hamiltonian}} \phi_n^{(0)})^* d\tau$$

$$= \int \phi_n^{(1)} (\underbrace{E_n^{(0)}}_{\text{real constant}} \phi_n^{(0)})^* d\tau$$

$$= \int \phi_n^{(0)*} E_n^{(0)} \phi_n^{(1)}$$

= First ~~term~~ term of R.H.S

Second term on R.H.S:

$$\int \phi_n^{(0)*} E_n^{(1)} \phi_n^{(0)} d\tau$$

$$= E_n^{(1)} \underbrace{\int \phi_n^{(0)*} \phi_n^{(0)} d\tau}_{=1} = E_n^{(1)}$$

(∵ normalized)

$$\boxed{E_n^{(1)} = \int \phi_n^{(0)*} \hat{H}' \phi_n^{(0)} d\tau}$$

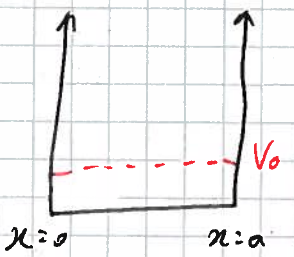
– First order energy correction using perturbation theory

Eg// Infinite square well

$$\phi_n^{(0)} = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) \quad n = 1, 2, 3, \ldots$$

Perturbation

$\hat{H}' = V_0$



$$E_n^{(1)} = \int_{-\infty}^{\infty} \phi_n^{(0)*} \hat{H}' \phi_n^{(0)} d\tau$$

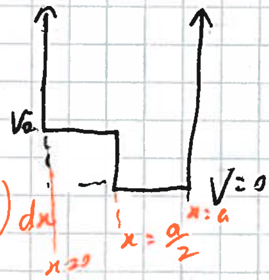
$$= \int_0^a V_0 \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$E_n^{(1)} = V_0$$

In this case, $E^{(1)}$ is exact

Eg

$$E_n^{(1)} = \int_{-\infty}^{\infty} \phi_n^{(0)*} \hat{H}' \phi_n^{(0)} dx$$



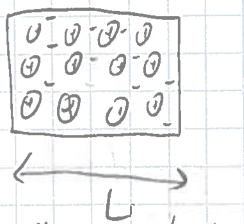
$$= \int_0^{a/2} V_0 \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$E_n^{(1)} = \frac{V_0}{2}$$

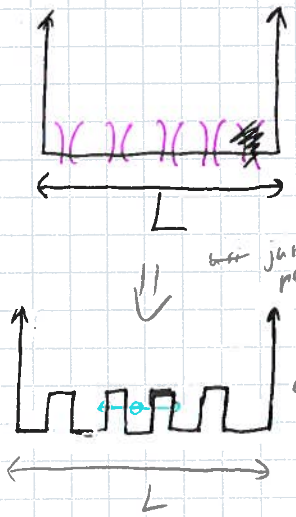
Periodic Potentials

Metal

infinite square well



<=>



- Macroscopic length.

just some perturbations caused by the coulomb potentials

Assumptions:

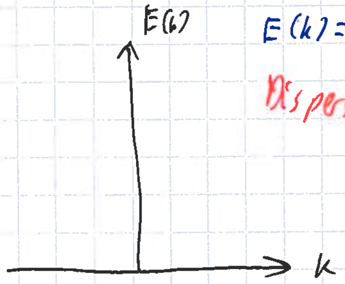
- Born-Oppenheimer approximation
  - consider the motion of e's for fixed lattice
- Independent electrons
  - we do not consider e⁻/e⁻ interaction
- One-dimension

- Completely free e⁻ TISE $V(x)=V_0$, $E>V_0$

$$\Rightarrow E = \frac{\hbar^2 k^2}{2m}$$

$$E(k) = \frac{\hbar^2 k^2}{2m}$$

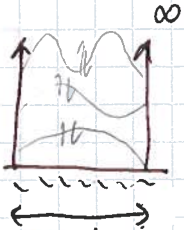
Dispersion relation



We would want to derive such relationships for e's moving in metals

---

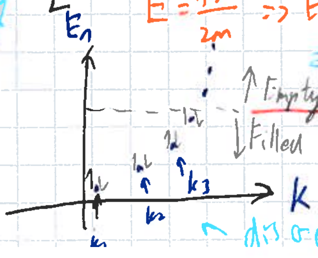
∞-square well



$k = \frac{n\pi}{L}$, $n = 1,2,3\ldots$

$$\phi_k(x) = \sqrt{\frac{2}{L}}\sin(kx)$$

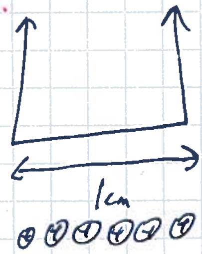
$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow E_n = \frac{\hbar^2 \pi^2}{2m}\frac{n^2}{L^2}$$



Fermi Energy
↳ Topmost filled level
↳ always have an unoccupied lvl

discrete levels

Eg.



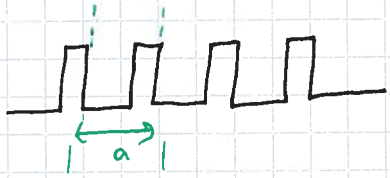
- 1D chain Na atoms,
- Spacing between atoms 3.7Å
- $\frac{1\text{cm}}{3.7\text{Å}} = 2.7\times10^7$ atoms

if we have 2e's per state
→ 1.35×10^7 filled energy levels

$$E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{1.35\times10^7}{1\times10^{-2}}\right)^2 = 0.69\,\text{eV}$$

Adding Periodic boundary conditions

$V(x+na) = V(x)$ $n = 1,2,3\ldots$



Boundary conditions

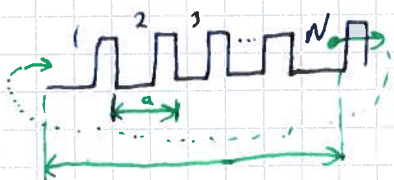
$|A_L|^2 \neq 0$ $B_R = 0$ — reflected wave's amplitude

$\psi(x) \to 0$ $x \to \pm\infty$

- Periodic Boundary Conditions

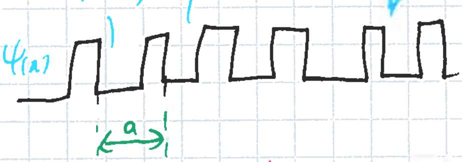
A particle moving to the right side of the N^{th} state finds itself back @ site 1

$$\psi(x+Na) = \psi(x)$$



looping

Finding the eigenfunctions for a periodic pot^n



$$\psi(x+a) = c\,\psi(x)$$

The wavefunction in adjacent unit cells are different by a constant, c, which can be complex

$$\psi(x+2a) = \psi(x+a+a) = c\,\psi(x+a)$$
$$= c^2 \psi(x)$$

$\Rightarrow$ continuing to the N^{th} region by symmetry of the system

$$\psi(x+Na) = c^N \psi(x) \quad -\ ①$$

From periodic boundary conditions: $\psi(x+Na) = \psi(x)$ — ②

① & ②:

$$\psi(x) = c^N \psi(x)$$

Trivially: $c^N = 1$

or

Non-trivially: $c^N = e^{i2\pi n}$ $\quad n = 0, \pm1, \pm2, \pm3, \dots$

$\hookrightarrow c = e^{\frac{i2\pi n}{N}}$

$c = e^{ika}$ $\quad k = \frac{2\pi n}{Na}$ $\quad n = 0, \pm1, \pm2, \pm3 \dots$

For a periodic pot^{l}: $V(x) = V(x+na)$

Subject to Periodic Boundary Conditions $\psi(x+Na) = \psi(x)$

Eigenfunction: $\psi(x+a) = \psi(x)e^{ika}$

$k = \frac{2\pi n}{Na}$ $\quad n = 0, \pm1, \pm2 \dots$

~~Bloch~~ Bloch's Theorem [Alternate form]

- The eigenfunction of the Schrödinger eq^{n} for a pot^{l} $V(x+a) = V(x)$, are the product of a plane wave: e^{ikx} time func $u(x)$:

$$\psi(x) = u(x)e^{ikx}$$

where $u(x)$ has the periodicity of the lattice

$$u(x) = u(x+a)$$

Bloch's Theorem: (B.T.)

$$\psi(x) = u(x)e^{ikx}$$

$x \to x+a$

$$\psi(x+a) = \underbrace{u(x+a)}_{u(x)} e^{ik(x+a)}$$

$$= \underbrace{u(x)e^{ikx}}_{\psi(x)} e^{ika}$$

$$\psi(x+a) = \psi(x)e^{ika}$$

Alternate form of Bloch's Theorem

B.T.1: $\psi(x) = u(x)e^{ikx}$

B.T.2: $\psi(x+a) = \psi(x)e^{ika}$ relating $\psi(x)$

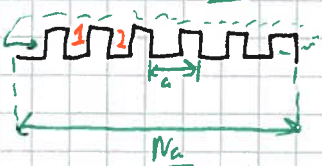
$\hookrightarrow$ to wavefunction in neighbouring region

$\hookrightarrow$ complex phase difference

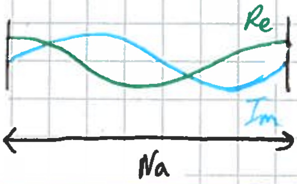
from 1 & 2

$u(x+a) = u(x)$

$k = \frac{2\pi n}{Na}$; $n = 0, \pm1, \pm2 \dots$



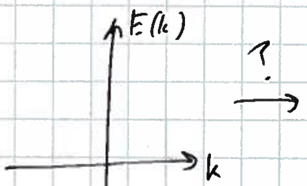
when: $n = 1$ $\quad k = \frac{2\pi}{Na}$ $\quad e^{ikx} = e^{i\frac{2\pi x}{Na}}$



More visualizations in Moodle, using Mathematica.

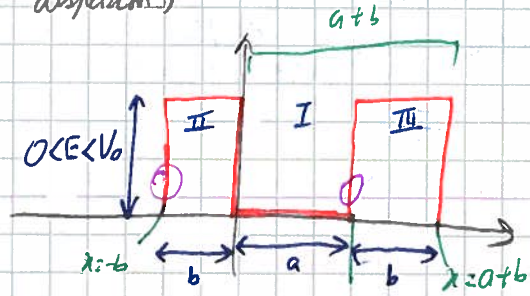
The Kronig-Penny Model

- Periodic Boundary Conditions
- Bloch waves



(free particle dispersion)

What is the dispersion relation for a periodic pot^{l}?



$$\Rightarrow \psi_I(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$$
$$\alpha = \frac{\sqrt{2mE}}{\hbar}$$

$$\Rightarrow \psi_{II}(x) = Ce^{\beta x} + De^{-\beta x}$$
$$\beta = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

$$\Rightarrow \psi_{III}(x) = \psi_{II}(x)e^{ik(a+b)}$$

using B.T.

$\hookrightarrow$ repeating cell

$\psi(x+a) = \psi(x)e^{ika}$

$\Rightarrow$ Alternate Bloch wave

$$\Rightarrow \psi_{III}(x) = (Ce^{\beta x} + De^{-\beta x})e^{ik(a+b)}$$

3.?

Applying Boundary conditions:

$$\left.\begin{aligned}\psi_I(0) &= \psi_{II}(0)\\ \psi'_I(0) &= \psi'_{II}(0)\end{aligned}\right] *$$

$$\left.\begin{aligned}\psi_I(a) &= \psi_{III}(a)\\ \psi'_I(a) &= \psi'_{III}(a)\end{aligned}\right]$$

using B.T. subbing

$$\left.\begin{aligned}\psi_{III}(a) &= \psi_{II}(-b)\,e^{ik(a+b)}\\ \psi'_{III}(a) &= \psi'_{II}(-b)\,e^{ik(a+b)}\end{aligned}\right]$$

$$\left.\begin{aligned}\psi_I(a) &= \psi_{II}(-b)\,e^{ik(a+b)}\\ \psi'_I(a) &= \psi'_{II}(-b)\,e^{ik(a+b)}\end{aligned}\right] *$$

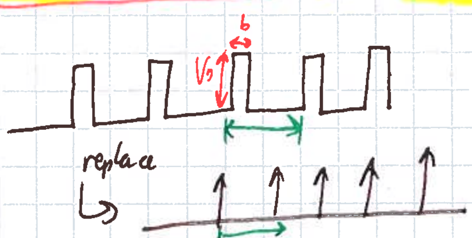
Need to satisfy eq^n marked by *

$$*\left[\begin{aligned}&A+B = C+D\\ &i\alpha A - i\alpha B = \beta C - \beta D\\ &Ae^{i\alpha a} + Be^{-i\alpha a} = (Ce^{-\beta b} + De^{\beta b})\,e^{ik(a+b)}\\ &i\alpha Ae^{i\alpha a} - i\alpha Be^{-i\alpha a} = (\beta Ce^{-\beta b} - \beta De^{\beta b})\,e^{ik(a+b)}\end{aligned}\right.$$

Solve by matrix manipulations using the textbook "Introductory Nanoscience" ~ M. Kuno [solve as exercise]

Sol^n to these eq^{n}s

$$\boxed{\begin{aligned}&\text{Kronig-Penney}\\ &\frac{\beta^2-\alpha^2}{2\alpha\beta}\sinh(\beta b)\sin(\alpha a) + \cosh(\beta b)\cos(\alpha a) = \cos[k(a+b)]\end{aligned}}$$

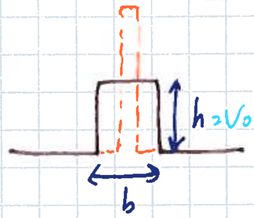


[Barriers replaced by the Dirac-Delta functions]

"Strength" = $V_0 \times b$

↳ construct delta functions so the barrier maintains the same strength //

Dirac-Delta function



$$\int_0^b h\,dx = \underbrace{b\times h}_{} \equiv \underbrace{V_0}_{\text{Strength}}$$

Shrink b, increase h, but maintain the "strength"

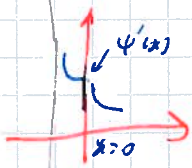
limit $b\to 0$, $h \to \infty$

$$\int_{-\infty}^{\infty} V_0\,\delta(x-x_0) = V_0$$

Dirac-Delta function barrier potential:

$$V(x) = V_0 \sum_n \delta(x-x_0)$$

$\psi'(x)$ across a Dirac-delta func



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

$$\Rightarrow -\frac{\hbar^2}{2m}\int_{-\varepsilon}^{\varepsilon}\frac{d^2\psi}{dx^2}dx + \underbrace{V_0\int_{-\varepsilon}^{\varepsilon}\delta(x)\,\psi(x)\,dx}_{\text{↳ defined when } x=0 \text{ then } \psi(x) \text{ and } \delta(x)} = \underbrace{E\int_{-\varepsilon}^{\varepsilon}\psi(x)\,dx}_{=0 \text{ in the limit } \varepsilon\to 0,\ \because \psi \text{ is continuous}}$$

$$-\frac{\hbar^2}{2m}\left[\frac{d\psi}{dx}\right]_{-\varepsilon}^{\varepsilon} + V_0\,\psi(0) = 0$$

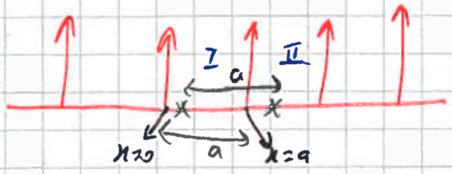
$$\cancel{-\frac{\hbar^2}{2m}\left[\frac{d\psi}{dx}\right]^{\varepsilon}}$$

$$-\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\Big|_{\varepsilon} - \frac{d\psi}{dx}\Big|_{-\varepsilon}\right) + V_0\psi = 0$$

$$\boxed{\underbrace{\frac{d\psi}{dx}\Big|_{\varepsilon} - \frac{d\psi}{dx}\Big|_{-\varepsilon}}_{\to 0 \text{ as } \varepsilon\to 0} = \frac{2mV_0}{\hbar^2}\,\psi(0)} \quad (\dagger)$$

but $\neq 0$ ⇒

Kronig Penny - δ fn potentials



$\psi_I(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$ $\quad \alpha = \frac{\sqrt{2mE}}{\hbar}$

using B.T.

$\psi_{II}(x) = \psi_I(x) e^{ika}$ $\left[\psi_{II}(x) = \psi(x-a)e^{ika}\right.$

not correct

∵ ψ evaluated at region I but also evaluated at the exact same spot

$\Rightarrow \psi_{II}(x) = (Ae^{i\alpha(x-a)} + Be^{-i\alpha(x-a)})e^{ika}$

Matching wavefunction at x=a

⇒ Applying Boundary Conditions

$\psi_I(a) = \psi_{II}(a)$

$Ae^{i\alpha a} + Be^{-i\alpha a} = (A+B)e^{ika}$ //

Rearranged to give us

$A(e^{i\alpha a} - e^{ika}) + B(e^{-i\alpha a} - e^{ika}) = 0$ ✱

$\psi'_{II}|_{x=a+\varepsilon} - \psi'_I|_{x=a-\varepsilon} = \frac{2mV_0}{\hbar^2}\psi_I(a)$

or II

∵ ψ is continuous

Computing derivatives

$\psi'_{II}(x) = (i\alpha A e^{i\alpha(x-a)} - i\alpha Be^{-i\alpha(x-a)}) \times e^{ika}$

$\psi'_{II}(x)|_{x=a+\varepsilon} = [i\alpha Ae^{i\alpha\varepsilon} - i\alpha Be^{-i\alpha\varepsilon}]e^{ika}$

$\psi'_{II}(x)|_{x=a+\varepsilon} = [i\alpha A - i\alpha B]e^{ika}$ //
$\lim_{\varepsilon\to 0}$

$\psi'_I(x)|_{x=a-\varepsilon} = i\alpha Ae^{i\alpha a} - i\alpha Be^{i\alpha a}$ //
$\lim_{\varepsilon \to 0}$

Putting it altogether & rearranging

$(i\alpha A - i\alpha B)e^{ika} - \frac{2mV_0}{\hbar^2}(A+B)e^{ika} = i\alpha Ae^{i\alpha a} - i\alpha Be^{i\alpha a}$

$\left(i\alpha(e^{ika} - e^{i\alpha a}) - \frac{2mV_0}{\hbar^2}e^{ika}\right)A + \left(-i\alpha(e^{ika} - e^{-i\alpha a}) - \frac{2mV_0}{\hbar^2}e^{ika}\right)B = 0$

✱ under what values of k can we satisfy the ✱✱ 1st 2nd eq^n ✱✱

Eq^{n} ✱ + ✱✱ have sol^n when

$$\boxed{\frac{mV_0}{\alpha\hbar^2}\sin(\alpha a) + \cos(\alpha a) = \cos(ka)}$$

$V_0 \leftarrow V\times b$

Kronig-Penny result for δ-fn pot^e

entirely equivalent model to the Kronig Penny model result

b → 0 btw

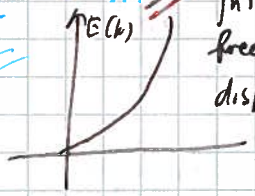
solved using matrix (solve as exercise as well)

- Well, wtf is going on!
  ↳ implications of the Kronig-Penney Eq^n

Case 1: $V_0 \to 0$

$\cos(\alpha a) = \cos(ka)$

$k = \alpha = \frac{\sqrt{2mE}}{\hbar}$ $\quad E = \frac{\hbar^2 k^2}{2m}$



just a free particle dispersion

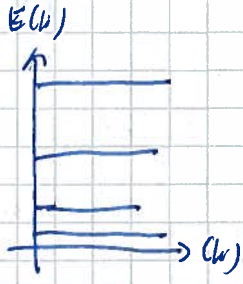
Case 2: $V_0 \to \infty$

↳ $\sin(\alpha a) \to 0$

to have the L.H.S remain within the ±1 limit set by the R.H.S of eq^n

$\alpha a = n\pi \Rightarrow \sqrt{\frac{2mE}{\hbar^2}}\, a = n\pi$

$n = 1, 2, 3 \ldots$



$\Rightarrow E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$

↳ ∞-square well with width a

Case 3: General sol^n

L.H.S oscillates $\quad (\alpha = \frac{\sqrt{2mE}}{\hbar^2})$

日本 moodle for graph

✱ values within ±1 → allowed energy values
↳ allowed energy band

✱ if function output exceeds ±1
↳ there are no sol^{n}s, are the Forbidden Energy Gap / Band Gaps

For determining full E(k) relationship ⇒ solve numerically & plot parametrically

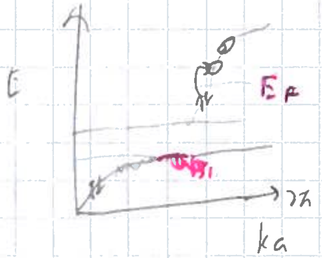
$\arccos\left(\frac{mV_0}{\sqrt{2mE}\hbar}\sin\left(\frac{\sqrt{2mE}\,a}{\hbar}\right) + \cos\left(\frac{\sqrt{2mE}}{\hbar}a\right)\right) = ka$

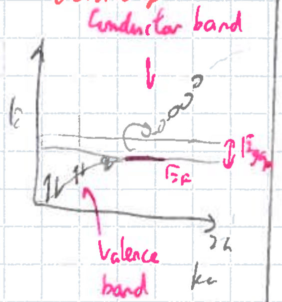
✱ Band gaps develop @ $ka = n\pi$
↳ defining the zone edges

✲ Bands have only discrete allowed values of k
→ filling up w/ e's according to the Pauli exclusion Principle

✲ Metallic
- partially filled band
- Fermi Energy (E_F) higher than the Band gap
↳ when energy is applied, e/ excited above E_F
↳ free e/

✲ Semiconductor (eg Si w/e)
- a band is filled up to the bottom of a band gap
- E_F is @ bottom of band gap
- need supply energy bigger than band gap to conduct electricity





✲ Insulator
↳ band gap becomes very large (>~3eV) eg Diamond

✲ Band structure is usually plotted in the "reduced" zone scheme, where the bands are folded back called the Brillouin zone

月¥ moodle for 図

Postulates of Quantum Mechanics (4) Probability

Concept of orthogonality as of MM III

Orthogonal Eigenfunctions

The eigenfunctions of a Hermitian operator belonging to ~~the~~ diff. eigenvalues are orthogonal.

$\hat{Q}\phi_n = q_n \phi_n$ where $q_n \neq q_m$

$\hat{Q}\phi_m = q_m \phi_m$

$$\boxed{\int \phi_n^* \phi_m \, d\tau = 0 \qquad (n \neq m)}$$

Showing this is true:

since $\hat{Q}$ is Hermitian:

$$\int \phi_n^* \hat{Q}\phi_m \, d\tau = \int \phi_m (\hat{Q}\phi_n)^* \, d\tau$$

L.H.S: $\int \phi_n^* \underbrace{\hat{Q}\phi_m}_{q_m\phi_m} d\tau$

$= \int \phi_n^* q_m \phi_m \, d\tau$

$= q_m \int \phi_n^* \phi_m \, d\tau$

R.H.S: $\int \phi_m \underbrace{(\hat{Q}\phi_n)}_{q_n\phi_n}{}^* d\tau$

$= \int \phi_m (q_n \phi_n)^* d\tau$

$= \int \phi_m q_n^* \phi_n^* d\tau$

$= q_n^* \int \phi_m \phi_n^* d\tau = q_n \int \phi_m \phi_n^* d\tau$

Eigenvalues of Hermitian operators are real

L.H.S = R.H.S

$\Rightarrow q_m \int \phi_m^* \phi_n \, d\tau = q_n \int \phi_m \phi_n^* \, d\tau$

$q_m \neq q_n$

$\therefore$ for the above to be true

$\Rightarrow \int \phi_m^* \phi_n \, d\tau = 0$

$\int \phi_m \phi_n^* \, d\tau = 0$

Orthonormal Eigenfunctions

If orthogonal eigenfunctions are normalised

$$\int \phi_m^* \phi_n \, d\tau = \delta_{n,m} \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$$

$\int \phi_n^* \phi_n \, d\tau = \int |\phi_n|^2 d\tau = 1$

if ϕ_n are normalized

Eg. Showing the normalised energy eigenfunctions of the infinite □ well are orthonormal

$$\phi_n = \begin{cases} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & \text{odd } n \\ \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & \text{even } n \end{cases} \quad \text{for } -a \leq x \leq a$$

$$\int_{-\infty}^{\infty} \phi_n^* \phi_m = \int_{-a}^{a} \frac{1}{a} \cos\left(\frac{n\pi x}{2a}\right) \cos\left(\frac{m\pi x}{2a}\right) dx$$

$$= \frac{1}{2a} \int_{-a}^{a} \cos \frac{\pi x}{2a}(n-m) + \cos \frac{\pi x}{2a}(n+m) \, dx$$

$= 0$ for odd n, m & $n \neq m$

always even $\because$ odd ± odd = even

Similar to MM III

3 Cases:

1. → n & m are odd → Case 1 only
2. → n & m are even
3. → n is odd, m is even

See Visualisation in moodle notes

Complete sets

Definition: Complete sets

- Eigenfunctions ϕ_n of a Hermitian operator form a complete set.
- Any well behaved function satisfying the same boundary conditions can be expanded as a linear combination of the eigenfunction

$$\psi = \sum_n a_n \phi_n$$

If we know ψ, ϕ_n (orthonormal), we can determine weighting coeffs a_n:

$$\int \phi_n^* \psi \, d\tau = \int \phi_n^* \sum_m a_m \phi_m$$

$$= \sum_m a_m \underbrace{\int \phi_n^* \phi_m \, d\tau}_{\delta_{n,m} = 1 \text{ if } n=m}$$

$$a_m = a_n = \int \phi_n^* \psi \, d\tau$$

Explicit representation:

$$\phi_n(x) = \begin{cases} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & (\text{odd } n) \\ \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) & (\text{even } n) \end{cases} \quad \text{for } -a \le x \le a$$

$$\psi(x) = \sum_{\text{odd}} a_n \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) + \sum_{\text{even}} a_n \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)$$

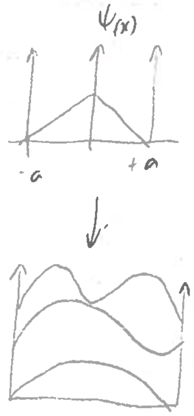
$$a_n = \begin{cases} \int_{-a}^{a} \psi(x) \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) dx & (\text{odd } n) \\ \int_{-a}^{a} \psi(x) \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) dx & (\text{even } n) \end{cases}$$

As per Fourier series

Given the wave function

$$\psi(x) = \sqrt{\frac{3}{2a^3}} (a - |x|)$$

determine a_n



wave functions are even, ∴ only even eigenfunctions appear [cos terms]

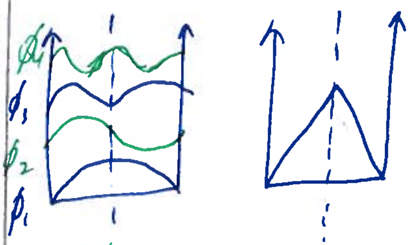
Finding a_n for odd n

$$a_n = \int_{-a}^{a} \phi_n^*(x) \psi(x) \, dx$$

$$= \int_{-a}^{a} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) \sqrt{\frac{3}{2a^3}} (a - |x|) \, dx \quad \text{for odd } n$$

do as exercise

$$a_n = \begin{cases} \frac{4\sqrt{6}}{n^2 \pi^2} & \text{for odd } n \\ 0 & \text{for even } n \end{cases}$$



ϕ_2 & ϕ_4
→ antisymmetric about centre axis

ϕ_n for even n = 0

= 0 ∵ nothing antisymmetric

Recalling the normalisation condition for an arbitrary wave function

$$\int \psi^* \psi \, d\tau = \int \sum_n (a_n \phi_n)^* \sum_m (a_m \phi_m) \, d\tau$$

$$= \sum_{n,m} a_n^* a_m \underbrace{\int \phi_n^* \phi_m \, d\tau}_{\delta_{m,n}}$$

$$= \sum_{n,m} a_n^* a_m \delta_{n,m}$$

if $n=m$
$\delta = 1$

$$= \sum_n |a_n|^2$$

∴ with:
↳ $\psi = \sum_n a_n \phi_n$, $\int \psi^* \psi \, d\tau = 1 \Rightarrow \sum_n |a_n|^2 = 1$

Basis for Postulate 4:
$|a_n|^2$ is the probability of finding the system in state ϕ_n

Definition:
When a measurement of a physical variable represented by a Hermitian operator $\hat{Q}$ is carried out on a system of which the wave function is ψ
↳ probability of the result being equal to a particular eigenvalue q_m is

$|a_m|^2$

with: $\psi = \sum_n a_n \phi_n$ $\quad \hat{Q}\psi = q_n \phi_n$

IF a system is definitely in state ϕ_n, the result of measuring $\hat{Q}$ is definitely the corresponding eigenvalue q_n

Best is we predicting the probability

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For a set of repeated measurements on identical systems

⇒ average value of such measurements is called the expectation value

$$\langle \hat{Q} \rangle = \int \psi^* \hat{Q} \psi \, d\tau = \langle \psi | \hat{Q} | \psi \rangle$$

$$\langle \hat{Q} \rangle = \sum_n |a_n|^2 q_n$$

Classically:
→ Ch. 1 Griffiths

$$\int \psi^* \hat{Q} \psi \, d\tau = \int \Big(\sum_m a_m^* \phi_m^* \Big) \hat{Q} \Big(\sum_n a_n \phi_n \Big) d\tau$$

using complete set representation

$$= \sum_{n,m} a_m^* a_n q_n \int \phi_m^* \phi_n \, d\tau$$

$$= \sum_{n,m} a_m^* a_n q_n \underbrace{\delta_{n,m}}_{=1 \text{ if } n=m}$$

$$= \sum_n |a_n|^2 q_n$$

☆ $|a_n|^2$ is the probability of finding q_n for a given measurement

☆ outcome of measurement is real
∴ $\langle \hat{Q} \rangle^* = \langle \hat{Q} \rangle$

$$\int \psi^* \hat{Q} \psi \, d\tau = \Big(\int \psi^* \hat{Q} \psi \, d\tau \Big)^* = \int \psi (\hat{Q}\psi)^* \, d\tau$$

↳ def of Hermitian

letting $f^* = \psi^*$, $g = \psi$

Show that $\int f^* \hat{Q} g \, d\tau = \int g (\hat{Q} f)^* \, d\tau$

Exercise:
first let $\psi = f + g$
then let $\psi = f + ig$

~~Commutation Relations~~

Commutation Relations:

In general: do NOT commute

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

Def: Commutator

$$[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

if $\hat{A}$ & $\hat{B}$ commute, $[\hat{A},\hat{B}] = 0$

$[\hat{A},\hat{A}] = 0$

$[\hat{A},\hat{B}] = -[\hat{B},\hat{A}]$

eg// $\hat{P}_x$ $\hat{X}$ $\hat{P} = (\hat{P}_x, \hat{P}_y, \hat{P}_z)^T$

$\hat{P}_x = -i\hbar\partial_x$

$\hat{X} = x$

Looking @ commutator

$$[\hat{P}_x, \hat{X}]\psi = (\hat{P}_x\hat{X} - \hat{X}\hat{P}_x)\psi$$

$$= \hat{P}_x\hat{X}\psi - \hat{X}\hat{P}_x\psi$$

$$= (-i\hbar\partial_x)x\psi - x(-i\hbar\partial_x)\psi$$

$$= -i\hbar\frac{\partial(x\psi)}{\partial x} + i\hbar x\frac{\partial\psi}{\partial x}$$

$$= -i\hbar\psi - i\hbar x\partial_x\psi + i\hbar x\partial_x\psi$$

$$= -i\hbar\psi \neq 0$$

$\therefore$ $\hat{P}_x$ & $\hat{X}$ do not commute

$$[\hat{P}_x, \hat{X}] = -i\hbar$$

eg// $[\hat{P}_y, \hat{X}] = 0$

left as exercise

In general:

different spatial components $\hat{R}$ & $\hat{P}$ commute

$\hat{R}$ & $\hat{P}$ do not commute for a given spatial coordinate

$[\hat{X}_i, \hat{X}_j] = 0$

$[\hat{P}_i, \hat{P}_j] = 0$

$[\hat{P}_i, \hat{X}_j] = -i\hbar\delta_{ij}$

$\hat{X}_1 \equiv \hat{X}$, $\hat{X}_2 \equiv \hat{Y}$, $\hat{X}_3 \equiv \hat{Z}$

$\hat{P}_1 \equiv \hat{P}_x$, $\hat{P}_2 \equiv \hat{P}_y$, $\hat{P}_3 \equiv \hat{P}_z$

Compatible Operators

two physical observables are said to be compatible IF the operators representing them have a common set of eigenfunctions

→ if one quantity is measured

↳ resulting wave function of the system will be in one of the common eigenfunctions

→ a subsequent measurement of the other quantity will have a completely ~~un~~predictable result

Assuming non-degenerate eigenfunctions

$$\psi \xrightarrow{\hat{Q}} \phi \xrightarrow{\hat{R}} \phi \quad | \quad \psi \xrightarrow{\hat{R}} \phi \xrightarrow{\hat{Q}} \phi$$

- The operators representing the observables commute

Compatible operators commute

Assume $\hat{Q}\phi_n = q_n \phi_n$

$\hat{R}\phi_n = r_n \phi_n$

$\psi = \sum_n a_n \phi_n$

$\hookrightarrow [\hat{Q},\hat{R}]\psi = (\hat{Q}\hat{R} - \hat{R}\hat{Q})\sum_n a_n\phi_n$

$= \sum_n a_n (\hat{Q}\hat{R}\phi_n - \hat{R}\hat{Q}\phi_n)$

$= \sum_n a_n (\hat{Q}r_n\phi_n - \hat{R}q_n\phi_n)$

$= \sum_n a_n (r_n q_n \phi_n) - q_n r_n \phi_n$

$= 0$

Taking $[\hat{Q},\hat{R}] = 0$

$\Downarrow$

$\hat{Q}\phi_n = q_n\phi_n$

$\hat{Q}\hat{R}\phi_n = \hat{R}\hat{Q}\phi_n$

$= \hat{R}q_n\phi_n$

$= q_n\hat{R}\phi_n$

$\hookrightarrow$ $\hat{R}\phi_n$ is an eigenfunction of $\hat{Q}$

$\hat{Q}(\hat{R}\phi_n) = q_n(\hat{R}\phi_n)$

* $\hat{R}\phi_n$ differs from ϕ_n by a constant

$\hookrightarrow \hat{R}\phi_n = r_n\phi_n$

✱ $\hat{Q}$ & $\hat{R}$ have common eigenfunctions ϕ_n

$\therefore$ are compatible operators

[if only ϕ_n are non-degenerate]

Degenerate eigenfunctions

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def: if 2 or more eigenfunctions share the same eigenvalue $\Rightarrow$ degenerate

unique property: any linear combination of them is also an eigenfunction w/ the same eigenvalue

Consider: $\hat{Q}\phi_1 = q\phi_1$

$\hat{Q}\phi_2 = q\phi_2$

$\hat{Q}(c_1\phi_1 + c_2\phi_2) \underset{\text{linearity of } \hat{Q}}{=} c_1\hat{Q}\phi_1 + c_2\hat{Q}\phi_2$

$= c_1 q\phi_1 + c_2 q\phi_2$

$= q(c_1\phi_1 + c_2\phi_2)$

Generally: for degenerate eigenstates:

$\hat{Q}\sum_n c_n\phi_n = \sum_n c_n\hat{Q}\phi_n$

$= q\sum_n c_n\phi_n$

degenerate for $\hat{H}$ but not $\hat{P}_x = -i\hbar\partial_x$

Time evolution of the system

Between measurements, the development of the wave function w/ time is governed by the TDSE

$$\hat{H}\Psi = i\hbar\partial_t\Psi$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r},t)$$

- considering cases where $\hat{H}$ is time independent
  ↳ conservation of energy $V(x,t) \equiv V(x)$

Starting from TDSE:

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

Separation of variables:

$$\Psi(x,t) = \phi(x)T(t)$$

$$\Rightarrow i\hbar\phi(x)\frac{dT(t)}{dt} = -\frac{\hbar^2}{2m}T(t)\frac{d^2\phi(x)}{dx^2} + V(x)\phi(x)T(t)$$

$$\Rightarrow \underbrace{i\hbar\frac{1}{T(t)}\frac{dT(t)}{dt}}_{E} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\phi(x)}\frac{d^2\phi(x)}{dx^2} + V(x)}_{E}$$

① $E\phi(x) = -\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} + V(x)\phi(x)$ &

② $\frac{dT(t)}{dt} = -\frac{iE}{\hbar}T(t)$

$$T(t) = e^{-\frac{iE}{\hbar}t}$$

$\Rightarrow$ TDSE: $\Psi(x,t) = \phi(x)e^{-\frac{iE_t}{\hbar}}$

$\Rightarrow$ called stationary state ∵ probability density does not depend on time

$$|\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t) = |\phi(x)|^2$$

including time-dependence on a complete set

$$\Psi(x,t) = \sum_n a_n\Psi_n(x,t)$$

$$= \sum_n a_n\phi_n(x)e^{-\frac{iE_n}{\hbar}t}$$

complex phase factor
↳ oscillate

$$= a_1\phi_1 e^{-iE_1t/\hbar} + a_2\phi_2 e^{-iE_2t/\hbar} + a_3\phi_3 e^{-iE_3t/\hbar} + \dots$$

E_i: dependent on ϕ_i

when $t=0$: $\Psi(x,0) = \sum_n^{\infty} a_n\phi_n(x)$

Given $V(x)$ & $\Psi(x,0)$

① Solve TISE
determine ϕ_n & E_n

② Determine coefficients a_n which determines
$\Psi(x,0) = \sum_n a_n\phi_n(x)$ @ $t=0$

③ Construct $\Psi(x,t)$, tack onto each term its characteristic time dependence

---

Supposing Ψ in an ∞ □ well @ $t=0$ is at a superposition of $n=1$, $n=2$ states

wavefunction: $\Psi(x,0) = c_1\phi_1(x) + c_2\phi_2(x)$

Probability density: $|\Psi(x,0)|^2 = \Psi^*(x,0)\Psi(x,0)$

$$= |c_1|^2|\phi_1|^2 + |c_2|^2|\phi_2|^2 + c_1^*c_2\phi_1^*\phi_2 + c_2^*c_1\phi_2^*\phi_1$$

$$\Psi(x,t) = c_1\phi_1(x)e^{-iE_1t/\hbar} + c_2\phi_2(x)e^{-iE_2t/\hbar}$$

↑ @ some time later

Probability density some time later

$$|\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t)$$

$$= |c_1|^2|\phi_1|^2 + |c_2|^2|\phi_2|^2$$

$$+ c_1^*c_2\phi_1^*\phi_2 e^{-i\boxed{\frac{\Delta E}{\hbar}}t}$$

$$+ c_2^*c_1\phi_2^*\phi_1 e^{+i\boxed{\frac{\Delta E}{\hbar}}t} \quad (\omega)$$

$$\Delta E = E_1 - E_2$$

* Not a stationary state

$\therefore |\Psi(x,t)|^2 \neq |\Psi(x,0)|^2$

[not stationary in general]

* Last two terms oscillate w/ time w/ angular frequency

$$\omega = \frac{\Delta E}{\hbar}$$

See programming example in Moodle using Mathematica

Rate of change of expectation value $\langle \hat{Q} \rangle$

$$\frac{d\langle\hat{Q}\rangle}{dt} = \frac{d}{dt}\int_{-\infty}^{\infty}\Psi^*\hat{Q}\Psi\,dx$$

diff under integral sign

$$= \int_{-\infty}^{\infty}\frac{\partial}{\partial t}(\Psi^*\hat{Q}\Psi)\,dx$$

$$= \int_{-\infty}^{\infty}\frac{\partial\Psi^*}{\partial t}\hat{Q}\Psi + \Psi^*\frac{\partial\hat{Q}}{\partial t}\Psi + \Psi^*\hat{Q}\frac{\partial\Psi}{\partial t}\,dx$$

using $\partial_t\Psi = \frac{1}{i\hbar}\hat{H}\Psi$

$\partial_t\Psi^* = -\frac{1}{i\hbar}(\hat{H}\Psi)^*$

$$\Rightarrow \frac{d}{dt}\langle\hat{Q}\rangle = -\frac{1}{i\hbar}\int_{-\infty}^{\infty}(\hat{H}\Psi)^*\hat{Q}\Psi\,dx \quad] - ①$$

$$+ \int_{-\infty}^{\infty}\Psi^*\frac{\partial\hat{Q}}{\partial t}\Psi\,dx \quad] \rightarrow \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle$$

$$+ \frac{1}{i\hbar}\int_{-\infty}^{\infty}\Psi^*\hat{Q}\hat{H}\Psi\,dx$$

Considering ①

$$\cancel{\frac{1}{i\hbar}}\int_{-\infty}^{\infty}(\hat{H}\Psi)^*\hat{Q}\Psi\,dx = \int_{-\infty}^{\infty}\hat{Q}\Psi(\hat{H}\Psi)^*\,dx$$

$\hat{H}$ is Hermitian

$$= \left(\int_{-\infty}^{\infty}(\hat{Q}\Psi)^*\hat{H}\Psi\,dx\right)^*$$

$$= \left(\int_{-\infty}^{\infty}\Psi(\hat{H}\hat{Q}\Psi)^*\,dx\right)^*$$

$$= \int_{-\infty}^{\infty}\Psi^*(\hat{H}\hat{Q}\Psi)\,dx$$

$$\therefore \frac{d}{dt}\langle\hat{Q}\rangle = \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle - \frac{1}{i\hbar}\int_{-\infty}^{\infty}\Psi^*(\hat{H}\hat{Q}\Psi)\,dx$$

$$+ \frac{1}{i\hbar}\int_{-\infty}^{\infty}\Psi^*(\hat{Q}\hat{H}\Psi)\,dx$$

$$= \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle + \frac{1}{i\hbar}\int_{-\infty}^{\infty}\Psi^*(\hat{Q}\hat{H} - \hat{H}\hat{Q})\Psi\,dx$$

$$= \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle + \frac{1}{i\hbar}\int\Psi^*[\hat{Q},\hat{H}]\Psi\,dx$$

$$= \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle + \frac{1}{i\hbar}\langle[\hat{Q},\hat{H}]\rangle$$

$$\hookrightarrow \frac{d}{dt}\langle\hat{Q}\rangle = \underbrace{\left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle}_{\text{intrinsic time dependence of the operator}} + \underbrace{\frac{1}{i\hbar}\langle[\hat{Q},\hat{H}]\rangle}_{\text{time dependence from changing wave function}}$$

Angular momentum

Classically: $\underline{L} = \underline{r} \times \underline{p}$

QM: $\underline{r} \to \hat{R}$, $\underline{p} \to -i\hbar\underline{\nabla}$ $\Big\} \Rightarrow \hat{\underline{L}} = -i\hbar\,\underline{r}\times\underline{\nabla}$

In cartesian coordinate

$$\hat{\underline{L}} = -i\hbar\begin{pmatrix}x\\y\\z\end{pmatrix}\times\begin{pmatrix}\partial x\\\partial y\\\partial z\end{pmatrix}$$

$$\begin{pmatrix}\hat{L}_x\\\hat{L}_y\\\hat{L}_z\end{pmatrix} = -i\hbar\begin{bmatrix}y\partial z - z\partial y\\ z\partial x - x\partial z\\ x\partial y - y\partial x\end{bmatrix} = \begin{pmatrix}\hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y\\ \hat{Z}\hat{P}_x - \hat{X}\hat{P}_z\\ \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x\end{pmatrix}$$

$\hat{R} = \hat{X}\underline{\hat{e}}_i + \hat{Y}\underline{\hat{e}}_j + \hat{Z}\underline{\hat{e}}_z$

$$\hat{L}^2 = \hat{L}\cdot\hat{L}$$
$$= \begin{pmatrix}\hat{L}_x\\\hat{L}_y\\\hat{L}_z\end{pmatrix}\cdot\begin{pmatrix}\hat{L}_x\\\hat{L}_y\\\hat{L}_z\end{pmatrix}$$
$$= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Commutation relationships:

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$
$$= (\hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y)(\hat{Z}\hat{P}_x - \hat{X}\hat{P}_z) - (\hat{Z}\hat{P}_x - \hat{X}\hat{P}_z)(\hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y)$$

$$= \hat{Y}\hat{P}_z\hat{Z}\hat{P}_x - \cancel{\hat{Y}\hat{P}_z\hat{X}\hat{P}_z} - \cancel{\hat{Z}\hat{P}_y\hat{Z}\hat{P}_x} + \hat{Z}\hat{P}_y\hat{X}\hat{P}_z - \hat{Z}\hat{P}_x\hat{Y}\hat{P}_z + \cancel{\hat{Z}\hat{P}_x\hat{Z}\hat{P}_y} + \cancel{\hat{X}\hat{P}_z\hat{Y}\hat{P}_z} - \hat{X}\hat{P}_z\hat{Z}\hat{P}_y$$

$$= \hat{Y}\hat{P}_z\hat{Z}\hat{P}_x - \hat{Z}\hat{P}_x\hat{Y}\hat{P}_z + \hat{Z}\hat{P}_y\hat{X}\hat{P}_z - \hat{X}\hat{P}_z\hat{Z}\hat{P}_y$$

$$= -\hat{Y}\hat{P}_x(\hat{Z}\hat{P}_z - \hat{P}_z\hat{Z}) + \hat{X}\hat{P}_z(\hat{Z}\hat{P}_y - \hat{Z}\hat{P}_y)$$

$$\Rightarrow -\hat{Y}\hat{P}_x[\hat{Z}, \hat{P}_z] + \hat{X}\hat{P}_y[\hat{Z}\hat{P}_z]$$
$$= (\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x)\underbrace{[\hat{Z}, \hat{P}_z]}_{= i\hbar}$$
$$= i\hbar(\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x) = i\hbar\hat{L}_z$$

$\therefore$ We get cyclic permutations

$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$
$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$
$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$
$[\hat{L}_x, \hat{L}_z] = -i\hbar\hat{L}_y$

Different components of $\hat{L}_i$ do not commute
↳ Cannot find simultaneous eigenfunctions of all 3 components of angular momentum
↳ if system is an eigenstate of one component ↳ it cannot simultaneously be in an eigenstate of either of the others

$\hat{L}^2$ commute w/ $\hat{L}_z$

$$[\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_z]$$
$$= [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] + [\hat{L}_z^2, \hat{L}_z]$$

$[A^2, B] = A^2B - BA^2$
$= A^2B + ABA - ABA - BA^2$
$= A[AB - BA] + [BA - AB]A$
$= A[A,B] + [A,B]A$

Similarly:

$$[\hat{L}_x^2, \hat{L}_z] = L_x\underbrace{[\hat{L}_x, \hat{L}_z]}_{-i\hbar L_y} + \underbrace{[\hat{L}_x, \hat{L}_z]}_{-i\hbar L_y}L_x$$
$$= -i\hbar[\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x]$$

$[\hat{L}_y^2, \hat{L}_z] = i\hbar[\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x]$

$[\hat{L}_z^2, \hat{L}_z] = 0$

$\therefore [\hat{L}^2, \hat{L}_z] = 0$ $\Rightarrow$ we can find simultaneous eigenfunctions of the square magnitude, $\hat{L}^2$ & $\hat{L}_i$

Similarly: $[\hat{L}^2, \hat{L}_x] = 0$

$[\hat{L}^2, \hat{L}_y] = 0$

$\therefore$ total angular momentum can be measured compatibly w/ any one component

Goal: find a set of functions that are simultaneously eigenfunctions of the total angular momentum $\hat{L}^2$ & the z component of angular momentum L_z

using spherical coordinates:

$x = r\sin\theta\cos\phi \quad r \in [0, r]$

$y = r\sin\theta\sin\phi \quad \theta \in [0, \pi]$

$z = r\cos\theta \quad \phi \in [0, 2\pi]$

Andrew vid

See MM II notes for conversion of $\partial_x \to \partial_r$ etc

? is there an easier, less rigorous conversion?

$\hat{e}_r = \hat{e}_i \sin\theta\cos\phi + \hat{e}_j \sin\theta\sin\phi + \hat{e}_k\cos\theta$

$\hat{e}_\theta = \hat{e}_i\cos\theta\cos\phi + \hat{e}_j\cos\theta\sin\phi - \hat{e}_k\sin\theta$

$\hat{e}_\phi = \hat{e}_i(-\sin\phi) + \hat{e}_j\cos\phi$?

$\hat{L} = -i\hbar\, \underline{r} \times \underline{\nabla}$

$\hat{e}_i$

$i \Rightarrow r$
$2 \Rightarrow \theta$
$3 \Rightarrow \phi$

$= -i\hbar r \underline{\hat{e}_r} \times \underline{\nabla}$

$$= -i\hbar \begin{pmatrix} r \\ 0 \\ 0 \end{pmatrix} \times \begin{pmatrix} \partial_r \\ \frac{1}{r}\partial_\theta \\ \frac{1}{r\sin\theta}\partial_\phi \end{pmatrix}$$

$$= -i\hbar \begin{pmatrix} 0 \\ -\frac{1}{\sin\theta}\partial\phi \\ \partial\theta \end{pmatrix}$$

$$\hat{L} = -i\hbar\left(\hat{e}_\phi \frac{\partial}{\partial\theta} - \hat{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$\underline{\nabla} = \frac{\partial}{\partial r}\hat{e}_r + \frac{1}{r}\frac{\partial}{\partial\theta}\hat{e}_\theta + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat{e}_\phi$$

MM III

$L_z = \hat{e}_k \cdot L$

$$= -i\hbar(\hat{e}_r\cos\theta - \hat{e}_\theta\sin\theta)\cdot\left(\hat{e}_\phi\frac{\partial}{\partial\theta} - \hat{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$= -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$\hat{e}_i = \hat{e}_r\sin\theta\cos\phi + \hat{e}_\theta\cos\theta\cos\phi - \hat{e}_\phi\sin\phi$

$\hat{e}_j = \hat{e}_r\sin\theta\sin\phi + \hat{e}_\theta\cos\theta\sin\phi + \hat{e}_\phi\cos\phi$

$\hat{e}_k = \hat{e}_r\cos\theta - \hat{e}_\theta\sin\theta$?

Expression for the magnitude:

$$\hat{L}^2 = \hat{L}\cdot\hat{L} = (-i\hbar\,\underline{r}\times\underline{\nabla})\cdot(-i\hbar\,\underline{r}\times\underline{\nabla})$$
$$= \hbar^2(\underline{r}\times\underline{\nabla})\cdot(\underline{r}\times\underline{\nabla})$$

using the scalar quadruple product

$(A\times B)\cdot(C\times D) = (A\cdot C)(B\cdot D) - (A\cdot D)(B\cdot C)$

using the Laplacian of spherical coordinates

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

$$\Rightarrow \hat{L}^2 = -\hbar^2\left[r^2\nabla^2 - (r\partial_r)(\partial_r r)\right]$$

$$(r\partial_r)(\partial_r r)f = r\frac{\partial}{\partial r}\frac{\partial}{\partial r}rf = r\frac{\partial}{\partial r}\left(f + r\frac{\partial f}{\partial r}\right)$$

$$= r\left(\frac{\partial f}{\partial r} + \frac{\partial f}{\partial r} + r\frac{\partial^2 f}{\partial r^2}\right) = 2r\frac{\partial f}{\partial r} + r^2\frac{\partial^2 f}{\partial r^2}$$

$$= \frac{\partial}{\partial r}\left[r^2\frac{\partial f}{\partial r}\right] \Leftrightarrow \left[r\frac{\partial}{\partial r}, \frac{\partial}{\partial r}r\right]f = 0$$

$$\hat{L}^2 = -\hbar^2\left[r^2\nabla^2 - \left(r\frac{\partial}{\partial r}\right)\left(\frac{\partial}{\partial r}r\right)\right]$$

$$= -\hbar^2\left[r^2\nabla^2 - \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]$$

✱ $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$

↳

$$\hat{L}^2 = -\hbar^2\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$$

$$\Rightarrow \hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

↳ $\hat{L}^2$ depends only on the angular behaviour of the wavefunction

Now searching for eigenvalues & the common set of eigenfunctions for operators $\hat{L}_z$ & $\hat{L}^2$

✱ $[\hat{L}^2, L_z] = 0$

using

eigenfunction of L_z

$$\hat{L}_z\Phi(\phi) = \lambda\Phi(\phi)$$

$$\Rightarrow -i\hbar\frac{d}{d\phi}\Phi(\phi) = \lambda\Phi\phi$$

$$\Rightarrow \Phi(\phi) = Ae^{i\frac{\lambda}{\hbar}\phi}$$

We now apply boundary conditions:

✱ $\Phi(\phi+2\pi) = \Phi(\phi)$ ∵ $\phi \in [0, 2\pi]$

✱ wavefunction must have single value for every value of ϕ

$$\Phi(\phi+2\pi) = Ae^{i\frac{\lambda}{\hbar}\phi+2\pi} = Ae^{i\frac{\lambda}{\hbar}\phi}\underbrace{e^{i\frac{\lambda}{\hbar}2\pi}}_{=1}$$

$e^{i\frac{\lambda}{\hbar}2\pi} = 1$ if $\frac{\lambda}{\hbar} = m$, $m \in \mathbb{Z}$

$\lambda = m\hbar$

↳ quantum number m

$$\Rightarrow \Phi = Ae^{im\phi}$$

$m = 0, \pm1, \pm2, \ldots$

for the normalization constant

$$\int_0^{2\pi} A^2 e^{im\phi}e^{-im\phi}\,d\phi = 1$$

$$A = \frac{1}{\sqrt{2\pi}}$$

$$\Rightarrow \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \qquad \hat{L}_z\Phi(\phi) = m\hbar\Phi_m(\phi)$$

To ensure sol^n remain eigenfunctions of $\hat{L}_z$, we look for eigenfunctions of $\hat{L}^2$

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

$$= \Theta(\theta)e^{im\phi}$$

$\Rightarrow$ giving our eigenvalue eq^n

$$\hat{L}^2 Y(\theta,\phi) = \beta\hbar^2 Y(\theta,\phi)$$

↳ eigenvalue, need to determine expression for β

$$-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Theta e^{im\phi} = \beta\hbar^2\Theta e^{im\phi}$$

$$-\left(\frac{e^{im\phi}}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\Theta \cancel{e^{im\phi}}\right) = \beta\Theta e^{im\phi}$$

$$\Rightarrow -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{m^2}{\sin^2\theta}\Theta = \beta\Theta$$

solving using Legendre Polynomials as per MMIII

Letting $\mu = \cos\theta$

$$\frac{\partial}{\partial\theta} = \frac{\partial\mu}{\partial\theta}\frac{\partial}{\partial\mu} = -\sin\theta\frac{\partial}{\partial\mu} \Rightarrow \frac{\partial}{\partial\mu} = \frac{-1}{\sin\theta}\frac{\partial}{\partial\theta}$$

$\sin^2\theta = 1 - \mu^2$ ℏ

$$\Rightarrow \frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial \Theta}{\partial \mu}\right) + \left(\beta - \frac{m^2}{1-\mu^2}\right)\Theta = 0$$

$\hookrightarrow P(\mu) = \Theta(\theta) = \sum_{p=0}^{\infty} a_p \mu^p$

force recurrence relation to terminate

as per MMIII

$\beta = l(l+1)$

$\therefore$ eigenvalues of $\hat{L}^2$ are:

$l(l+1)\hbar^2$ for $l = 0, 1, 2, 3 \ldots$

Eigenfunctions:

$$Y_{lm}(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

$$= (-1)^m\left[\frac{(2l+1)(l-|m|)!}{4\pi\,(l+|m|)!}\right]^{1/2} P_l^m(\cos\theta)\, e^{im\phi}$$

$-l \le m \le l$

Revising MMIII

$\Rightarrow$ Legendre functions:

$$P_l^m(\mu) = (1-\mu^2)^{\frac{|m|}{2}}\left(\frac{d}{d\mu}\right)^{|m|} P_l(\mu)$$

$\Rightarrow$ Legendre polynomials:

$$P_l(\mu) = \frac{1}{2^l l!}\left(\frac{d}{d\mu}\right)^l (\mu^2-1)^l$$

- See more examples in MMIII & QM ~~pr~~ notes week 7 for ~~special~~ spherical harmonics
- See 3D polplot using Mathematica

Eigenfunctions of $\hat{L}_z Y_{lm}(\theta,\phi)$

$$\hat{L}_z Y_{lm} = -i\hbar\frac{\partial Y_{lm}}{\partial \theta} = -i\hbar(im)Y_{lm}$$

$$= m\hbar\, Y_{lm}$$

$\therefore$ eigenvalue of $\hat{L}_z \Rightarrow m\hbar$

where $-l \le m \le +l$

P_l are order-l polynomials

$\Rightarrow m^{th}$ derivative $= 0$ if $|m| > |l|$

$\hookrightarrow$ making spherical coordinates

$\therefore \psi = 0$ everywhere $\therefore$ non-physical

ALSO: $m\hbar \le \sqrt{l(l+1)\hbar^2}$ when $-l \le m \le l$

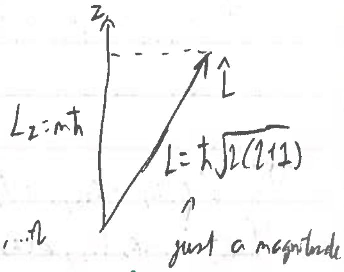
$\hookrightarrow$ individual component of L_z cannot be greater than the total L

$\hat{L}^2 \Rightarrow$ 出 $l(l+1)\hbar^2$

$l = 0, 1, 2, 3$

$\hat{L}_z \Rightarrow$ 出 $m\hbar$

$m = -l, \ldots, -1, 0, 1, \ldots, l$



$\Rightarrow$ These states do not correspond to well-defined values of $\hat{L}_x$ & $\hat{L}_y$ $\because$ operators don't commute w/ $\hat{L}_z$.

Eg. Determine allowed $\hat{L}_z$ components of L for $l = 2$

$(l(l+1))\hbar^2 = 2(2+1)\hbar^2 = 6\hbar^2$

佢係唔會知 L_x & L_y

$\Rightarrow$ uncertainty one.

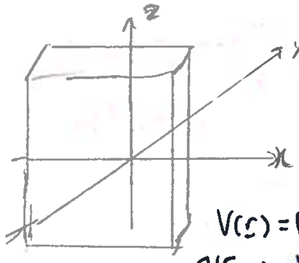
$\Rightarrow$ magnitude $= \hbar\sqrt{6}$

$\Rightarrow$ allowed components of $L_z \Rightarrow m\hbar$ w/ $m = -l, \ldots, -1, 0, +1 \ldots l$

$\Rightarrow -2\hbar, -\hbar, 0, \hbar, 2\hbar$

3-D Potentials

3-D box first : [equivalent to a 3D box]



$V(\underline{r}) = V_1(x) + V_2(y) + V_3(z)$

$\Psi(\underline{r}) = X(x) Y(y) Z(z)$

3D ~~TDI~~ TDSE :

$$i\hbar \partial_t \Psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})\right)\Psi$$

TISE :

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})\right)\Psi = E\Psi$$

Probability :

$$P(\underline{r}, t) = |\Psi(\underline{r}, t)|^2$$

Using separation of variables (cartesian)

$V(\underline{r}) = V_1(x) + V_2(y) + V_3(z)$

$\Psi(\underline{r}) = X(x) Y(y) Z(z)$

$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\underline{r})\Psi = E\Psi$$

$$-\frac{\hbar^2}{2m}\left(YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} + VXYZ\right) = EXYZ$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2}\right) + V_1 + V_2 + V_3 = E$$

$$\underbrace{-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} + V_1}_{x} \underbrace{-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + V_2}_{y} \underbrace{-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} + V_3}_{z} = E$$

$= E_x \qquad = E_y \qquad = E_z$

$$E = E_x + E_y + E_z$$

$$\left.\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} + V_1 X &= E_x X \\ -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} + V_2 Y &= E_y Y \\ -\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} + V_3 Z &= E_z Z \end{aligned}\right\} 3 \times 1D \text{ eq}^{n}$$

using solution for 1D particle in a box sol^n

$E_x = \frac{\hbar^2\pi^2}{8ma^2} n_x^2 \qquad n_x = 1, 2, 3 \ldots$

$E_y = \frac{\hbar^2\pi^2}{8ma^2} n_y^2 \qquad n_y = 1, 2, 3 \ldots$

$E_z = \frac{\hbar^2\pi^2}{8ma^2} n_z^2 \qquad n_z = 1, 2, 3 \ldots$

$$E = \frac{\hbar^2\pi^2}{8ma^2}\underbrace{(n_x^2 + n_y^2 + n_z^2)}$$

→ 3 quantum numbers to specify 3D system.

★ Degeneracy :

→ Energy can have the same value for 2 different sets of eigenvalues [eg. $n_x = 1$, $n_y = 1$, $n_z = 2$]

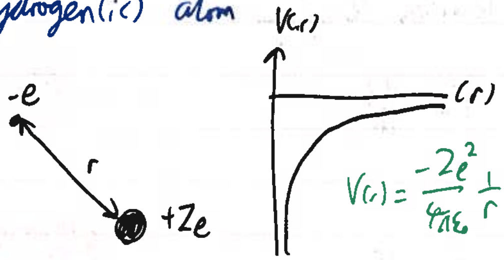
The bound state wave function :

if n is odd

$$\phi_{n_x n_y n_z} = \sqrt{\frac{1}{a^3}}\begin{bmatrix}\cos\\ \sin\end{bmatrix}\left(\frac{n_x\pi x}{2a}\right)\begin{bmatrix}\cos\\ \sin\end{bmatrix}\left(\frac{n_y\pi y}{2a}\right)\begin{bmatrix}\cos\\ \sin\end{bmatrix}\left(\frac{n_z\pi z}{2a}\right)$$

if n is even

The hydrogen(ic) atom



⇒ single electron moving under the influence of a +vely charged proton, with charge +Ze (apply in He^+ & Li^{2+})

& solving radial wavefunction & using spherical harmonics

& spherical symmetry

↳ potential only depends on r

$$\hat H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Using spherical coordinates:

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

Hamiltonian:

$$\hat H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \overbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}^{\frac{\hat L^2}{r^2\hbar^2}}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat H = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat L^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

- function of only r & $\hat L^2(\theta,\phi)$

[$\hat L^2$ & $\hat L_z$ are independent of r]

∴ $[\hat H, \hat L^2] = 0$ & $[\hat L^2, \hat L_z] = 0$

$[\hat H, \hat L_z] = 0$ for commutation relationships

$\hat H, \hat L^2, \hat L_z$ are compatible operators

↳ we can measure compatibly — can find a common set of eigenfunctions
- total L
- L_z
- energy

$V(r) \propto \frac{1}{|r|}$

TISE:

$$\left(-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat L^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = E\psi$$

⇒ looking for sol^n of the form

$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

via separation of variable again

$$\underbrace{\left[-\frac{\hbar^2}{2m_e}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - E r^2 - \frac{Ze^2 r}{4\pi\varepsilon_0}\right]}_{(r)\ = -\lambda} + \underbrace{\frac{(\hat L^2 Y)}{2m_e Y}}_{\theta,\phi\ = \lambda} = 0$$

⇒ $\frac{1}{Y}\frac{\hat L^2 Y}{2m_e} = \lambda$ — (θ,ϕ)

⇒ $-\frac{\hbar^2}{2m_e R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - E r^2 - \frac{Ze^2 r}{4\pi\varepsilon_0} = -\lambda$ — r

Angular eq^n: $\hat L^2 Y = 2m_e\lambda Y$
[eigenvalue eq^n for $\hat L^2$]

Radial eq^n: $\left(-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\lambda}{r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)R = ER$

∴ using $\hat L^2 Y_{lm}(\theta,\phi) = \underbrace{l(l+1)\hbar^2}_{2m_e\lambda} Y_{lm}(\theta,\phi)$

By comparison: $\lambda = \frac{\hbar^2 l(l+1)}{2m_e}$

Subbing back λ in the Radial eq^n

$$-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{\hbar^2 l(l+1)}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)R = ER$$

→ depend on orbital angular momentum l

⇒ involves magnitude of the angular momentum, not orientation

4b

Simplifying the term

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)$$

$R(r) = \frac{\chi(r)}{r}$ (2) $\chi(r) = rR(r)$

for the Radial Eq^n

$$R(r) = \frac{\chi(r)}{r}$$

$$\frac{dR}{dr} = \frac{1}{r}\frac{d\chi}{dr} - \frac{\chi}{r^2}$$

$$r^2\frac{dR}{dr} = r\frac{d\chi}{dr} - \chi$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r\frac{d^2\chi}{dr^2} + \cancel{\frac{d\chi}{dr}} - \cancel{\frac{d\chi}{dr}}$$

$\div r^2$

$$\underbrace{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{1}{r}\frac{d^2\chi}{dr^2}}$$

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right] + \left(\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)R = ER$$

$$\Rightarrow -\frac{\hbar^2}{2m_e}\cancel{\frac{1}{r}}\frac{d^2\chi}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\frac{\chi}{\cancel{r}} = E\frac{\chi}{\cancel{r}}$$

$$-\frac{\hbar^2}{2m_e}\frac{d^2\chi}{dr^2} + \underbrace{\left(\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r}\right)}_{=V_{eff}(r)}\chi = E\chi$$

$\Rightarrow$ Identical in form to the 1D TISE

with

$$V_{eff}(r) = \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Examining the forces:

2nd term:

$$F = -\frac{dV}{dr} = -\frac{d}{dr}\left(-\frac{Ze^2}{4\pi\varepsilon_0}r^{-1}\right) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r^2}$$

1st term:

$$F = -\frac{dV}{dr} = \left(\frac{\hbar^2 l(l+1)}{2m_e}r^{-2}\right) = \frac{\hbar^2 l(l+1)}{m_e}\frac{1}{r^3}$$

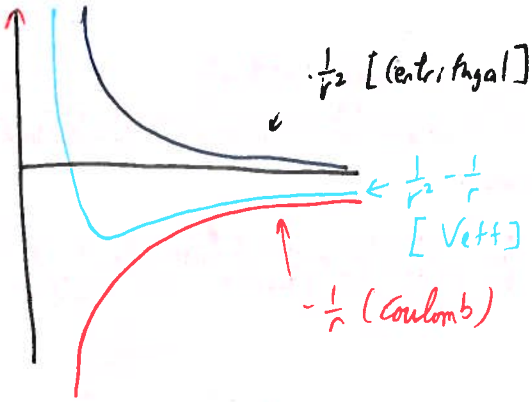
eigenvalue for $\hat{L}^2$ $\Rightarrow L^2$

Classically:

$$F = \frac{L^2}{m_e r^3} = \frac{(m_e v r)^2}{m_e r^3} = \frac{m_e v^2}{r}$$

↳ which is the classical centrifugal force that tends to throw the particle outward

V_{eff}



$\Rightarrow$ Centrifugal term dominates @ small r

$\Rightarrow$ Coulomb term dominates @ large r

Atomic Unit:

$$\text{a.u} \xrightarrow{\times a_0} \text{SI}, \quad \text{SI} \xrightarrow{\div a_0} \text{a.u}$$

Symbol	SI	a.u.
$\hbar$	1.05×10^{-34} Js	1
m_e	9.11×10^{-31} kg	1
e	1.60×10^{-19} C	1
$\frac{1}{4\pi\varepsilon_0}$	8.99×10^{9} kg m^3 s^{-2} C^{-2}	1

Natural unit of length: Bohr radius a_0

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2 m_e} = 5.29\times10^{-11}\,\text{m}$$

Natural unit of Energy $\Rightarrow$ Hartree E_H

$$E_H = \frac{\hbar^2}{m_e a_0^2} = m_e\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2$$

$$= 4.36\times10^{-18}\,\text{J} = 27.21\,\text{eV}$$

Radial Eq^n in atomic units:

$$-\frac{1}{2}\frac{d^2\chi}{dr^2} + \underbrace{\left(\frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)}\chi = E\chi$$

$$V_{eff} = \frac{l(l+1)}{2r^2} - \frac{Z}{r}$$

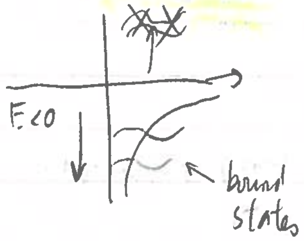
$r\to\infty$, $V_{eff}\to 0$

Looking for Asymptotic sol^n 1. ($r\to\infty$)

$V_{eff}\to 0$, looking for boundstates
↳ where e^- does not have enough energy to escape to infinity

$$\frac{d^2\chi}{dr^2} = -2E\chi$$

~~Veff~~



Let $E = -\frac{k^2}{2}$ ($E<0$)

$$\Rightarrow \frac{d^2\chi}{dr^2} = k^2\chi$$

$$\Rightarrow \chi(r) = Ae^{-kr} + Be^{kr}$$

∵ $\chi(r)$ Be^{kr} cannot be normalized for $r\to\infty$

∴ for large r

$$\Rightarrow \chi(r) \sim e^{-kr}$$

for 2. ($r\to0$)

$$-\frac{1}{2}\frac{d^2\chi}{dr^2} + \left[\underbrace{\frac{l(l+1)}{2r^2}}_{\text{dominates as } r\to0} - \frac{Z}{r} - E\right]\chi = 0$$

Radial eq^n becomes:

$$\frac{d^2\chi}{dr^2} = \frac{l(l+1)}{r^2}\chi$$

$$\Rightarrow \chi(r) = Cr^{l+1} + Dr^{-l}$$

↳ cannot be normalized for $r\to0$

for small r:

$$\Rightarrow \chi(r) \sim r^{l+1}$$

sol^{n}s for $r\to\infty \Rightarrow \chi(r) \sim e^{-kr}$

$r \to 0 \Rightarrow \chi(r) \sim r^{l+1}$

$\therefore$ looking for sol^n in the form

$$\chi(r) = F(r)e^{-kr}$$

↳ looking for power series sol^n

d 两次:

$$\chi'' = \frac{d^2F}{dr^2}e^{-kr} - 2k\frac{dF}{dr}e^{-kr} + k^2Fe^{-kr}$$

↓ subbing back into radial eq^n
- cancelling e^{-kr} terms as well
- $E = -k^2/2$

$$-\frac{1}{2}\left(F'' - 2kF' + k^2F\right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)F = -\frac{k^2}{2}F$$

$$-\frac{1}{2}\left(F'' - 2kF'\right) - \cancel{\frac{k^2F}{2}} + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)F = -\cancel{\frac{k^2F}{2}}$$

$$\times -2: \quad \underbrace{\frac{d^2F}{dr^2} - 2k\frac{dF}{dr} + \left(\frac{2Z}{r} - \frac{l(l+1)}{r^2}\right)F = 0}_{\text{solve in MMPII}}$$

eq^n in the form:

$$y'' + p(x)y' + q(x)y = 0$$

$\therefore$ using Frobenius's method

Assume: $F(r) = \sum_{p=0}^{\infty} c_p r^{p+l+1}$

$\Rightarrow$ subbing back after d 完

recurrence relationship:

$$\frac{c_p}{c_{p-1}} = \frac{2(k(p+l) - Z)}{(p+l+1)(p+l) - l(l+1)}$$

for large p: $\frac{c_p}{c_{p-1}} \approx \frac{2k}{p}$

$$\Rightarrow \sum \frac{(2kr)^p}{p!} = e^{2kr}$$

which diverges, $\therefore$ wavefunction cannot be normalized

$\therefore$ we require the series to terminate after some # of terms

At some value, $p = N$

$\Rightarrow$ we will have $c_N = 0$ ~~&~~ & $c_{N-1} \neq 0$

($c_N = 0$ implies that all c_p where $p > N$ will also be zero)

$$\Rightarrow c_p = c_N = k(N+l) - Z = 0$$

$$\Rightarrow k = \frac{Z}{N+l}$$

Recalling $E = -\frac{k^2}{2}$

$$\Rightarrow E = -\frac{Z^2}{2(N+l)^2} \quad \text{where } N = 1,2,3..$$

$$E_n = -\frac{Z^2}{2n^2}$$

defining the principle quantum number, $n = N + l$

$n = 1,2,3..$ (in a.u.)

$\because n = N+l$, $N \geq 1$, $l \geq 0$ gives us: $n \geq 1$, and $l \leq n-1$

$l = 0,1,2,3$

$\because F \to \chi \to R$

$$\psi_{nlm}(r) = R_n(r)Y_{lm}(\theta,\phi)$$

$n = 1,2,3$ from $\hat{H}$

$l = 0,1,2,\ldots,n-1$ from $\hat{L}^2$

$m = -l,\ldots,-1,0,1,2\ldots,l$ from $\hat{L}_z$

from n:

$$E_n = -\frac{Z^2}{2n^2}E_h = -\frac{m_e Z^2 e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}$$

Energy is specified by n only

$\therefore$ has a degeneracy:

$$2\sum_{l=0}^{n-1}(2l+1) = 2n^2$$

values of m for a given l

comes from spin states

$\because$ each state has spin up spin down

H-energy spectrum from chem

Traditional nomenclature

$l=3$ f
$l=2$ d
$l=1$ p
$l=0$ s

The radial wave functions:

$$R(r) = \frac{\chi(r)}{r} = \frac{F(r)e^{-kr}}{r}$$

$$F(r) = \sum_{p=0} c_p r^{p+l+1}$$

$$c_p = \frac{2\left[\left(\frac{Z}{n}\right)(p+l)-Z\right]}{(p+l+1)(p+l)-l(l+1)} c_{p-1}$$

for $k = \sqrt{2E} = \frac{Z}{n}$

✱ initial value in the recurrence relation c_0 is determined by normalisation

eg. for $n=1$, $l=0$
check for that the series terminates at c_1 & determine the expression for $R(r)$

$$c_1 = \frac{2[(Z)(1)-Z]}{(1+0+1)(1)-0} c_0 = 0$$

$$F_{10}(r) = \sum_{p=0} c_p r^{p+l+1} = c_0 r$$

=> value of c_0 is determined later when $R(r)$ is normalised

for $n=2$, $l=0$

$$c_1 = 2\frac{\left(\frac{Z}{2}\right)-Z}{2(1)-0} = -\frac{1}{2}Zc_0$$

$$c_2 = 0$$

$\therefore$ series has $p=0$ & $p=1$ terms

$$F_{20}(r) = \sum_{p=0} c_p r^{p+l+1} = c_0 r - \frac{1}{2}Zc_0 r^2$$

$$R_{20}(r) = c_0(1-kr)e^{-kr}$$

for $n=2$, $l=1$

$$c_1 = 2\frac{\left(\frac{Z}{2}\right)2-Z}{3(2)-2} c_0 = 0$$

$\therefore$ containing only the $p=0$ term

$$F(r) = \sum_{p=0} c_p r^{p+l+1} = c_0 r^2$$

$$R(r) = c_0 r e^{-kr}$$

n, l	$F_{nl}(r)$	$R_{nl}(r)$
$n=1$ $l=0$	$c_0 r$	$c_0 e^{-kr}$
$n=2$, $l=0$	$c_0 r - kc_0 r^2$	$c_0(1-kr)e^{-kr}$
$n=2$, $l=1$	$c_0 r^2$	$\cancel{c_0 e}$ $c_0 r e^{-kr}$

Normalisation:

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr \int_0^{2\pi}\underbrace{\int_0^\pi |Y_{lm}(\theta,\phi)|^2 \sin\theta \, d\theta \, d\phi}_{\text{already normal}} = 1$$

✱ $\because$ spherical harmonics are normalized:

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1$$

eg. Normalising the radial ~~of~~ wavefunction for $n=1, l=0$

$$\int_0^\infty |R_{10}(r)|^2 r^2 dr = \int_0^\infty |C_0 e^{-kr}|^2 r^2 dr = \frac{C_0^2}{4k^3} = 1$$

$$C_0 = 2\sqrt{k^3}$$

$$\Rightarrow R_{10}(r) = 2k^{\frac{3}{2}} e^{-kr} = 2Z^{3/2} e^{-Zr}$$

A.U $\quad E = -\frac{k^2}{2}$; $E_n = -\frac{Z^2}{2n^2}$ $\quad k = \frac{Z}{n}$

↓

SI $\quad E = -\frac{\hbar^2 k^2}{2m_e}$; $E_n = -\frac{Z^2}{2n^2} E_H$ $\quad k = \frac{Z}{a_0}$

$$= \frac{-Z^2\hbar^2}{2n^2 m_e a_0^2}$$

$$\hookrightarrow R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

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

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}}$$

* See Radial wave function
&
Radial probability density
in moodle notes

See Feynman Lectures as well

QM

* $L_z = m\hbar \quad m = -l, \dots, l$

$$\langle \frac{1}{r} \rangle = \frac{Z}{n^2 a_0}$$

Energy quantized solely by principle quantum number, not by angular momentum:

$$E_n = -\frac{Z^2}{2n^2} E_H$$

Further refinements :

approximations we have made:

- nucleus is not precisely fixed & we should replace mass m w/ reduced mass μ
- non-relativistic treatment
- neglection of spin
- neglection of quantum electrodynamic correction

fine structure — e^- spin

hyperfine structure — e^- AND nuclei spin

Electron spin & total angular momentum

Some revision:

l: orbital angular quantum number $\hbar\sqrt{l(l+1)}$
↳ magnitude of angular momentum

m: magnetic quantum number
↳ determine the component of angular momentum along the chosen axis (usually z-axis)

- $\hat{L}_x$ & $\hat{L}_y$ do not commute w/ $\hat{L}_z$ and do not have well defined values

- semiclassically: in each state, L is likely to be found anywhere on a cone, symmetrical to the z-axis
→ it has definite magnitude & $\hat{L}_z$, but not for $\hat{L}_x$ & $\hat{L}_y$

$\psi = \psi_{n,l,m}$

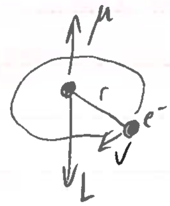
$n = 1, 2, 3, \ldots, \infty$

$l = 0, 1, 2, 3, \ldots, n-1$

$m = -l, \ldots, -1, 0, 1, \ldots +l$
for each value of l, there are $(2l+1)$

won't discuss full quantum mech approach.

→ semiclassical approach using Bohr model:



- orbiting e⁻ behaves like a current loop

loop current $= \dfrac{-ev}{2\pi r}$

using classical magnetic moment $\underline{\mu}$

$\underline{\mu}$ is a vector normal to the plane w/ magnitude:

$$\mu = IA = \frac{-ev}{2\cancel{\pi} \cancel{r}}\cancel{\pi} r^{\cancel{2}} = -\frac{evr}{2}$$

$$= \frac{-e\,\overbrace{m_e v r}^{L}}{2m_e} = -\frac{e\underline{L}}{2m_e}$$

$$\underline{\mu} = -\frac{e\hbar}{2m_e\hbar}\underline{L} = -\frac{\mu_B}{\hbar}\underline{L}$$

μ_B is the Bohr magneton: $\mu_B = \dfrac{e\hbar}{2m_e}$

Classical magnetic moment:

$$\underline{\mu} = \frac{-\mu_B}{\hbar}\underline{L}$$

-ve sign: $\underline{\mu}$ is opposite direction of $\underline{L}$

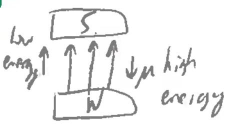
$$\mu = \frac{-\mu_B}{\hbar} L$$

Magnetic potential energy

magnetic dipole moment in B-field possesses a Magnetic potential energy
↳ depends upon its orientation w.r.t field

$$V_{magnetic} = -\mu \cdot B$$
$$= \frac{\mu_B}{\hbar} L \cdot B$$

↓ applying postulate 3 to this classical expression



classically:
- any orientation is ok

quantum:
- only certain orientation is allowed

getting QM operator:

$$\hat{H}_{magnetic} = -\hat{\mu} \cdot B$$
$$= \frac{\mu_B}{\hbar} \hat{L} \cdot B$$

$$\hat{\mu} = -\frac{\mu_B}{\hbar} \hat{L}$$

Splitting atomic energy levels in a B-field

suppose we have a uniform B-field in z-dir

$$B = B_z \hat{e}_z$$

potential $\Rightarrow$ $\hat{H}_{magnetic} = \frac{\mu_B}{\hbar} B_z \hat{L}_z$

treat this as a small perturbation to our Hydrogen atom Hamiltonian for calculating expected energy shifts

$$\hat{H}^{(0)} \psi_{nlm} = E_n^{(0)} \psi_{nlm} \quad \text{if} \times B\text{-field}$$

if ✓ B-field: $B\hat{e}_z$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}_{magnetic}$$
$$= \hat{H}^{(0)} + \frac{\mu_B}{\hbar} B_z \hat{L}_z$$

eigenfunctions ψ_{nlm} are eigenfunctions of $\hat{L}_z$

$$\Rightarrow \hat{L}_z \psi_{nlm} = m\hbar\, \psi_{nlm}$$

m: magnetic angular momentum quantum number

$\therefore$ for the new perturbed Hamiltonian:

$$\hat{H}\psi_{nlm} = \left(\hat{H}^{(0)} + \frac{\mu_B}{\hbar} B_z \hat{L}_z\right)\psi_{nlm}$$
$$= \underbrace{\left(E_n^{(0)} + m\mu_B B_z\right)}_{\text{new energy eigenvalue}}\psi_{nlm}$$

- m takes integer values between $\pm l$

$\therefore$ splitting of energy levels:

$$\Delta E = m\mu_B B_z$$

Applying eq^n for 1st order, nondegenerate energy perturbation:

✡ orbital magnetic moment has an exact sol^n

∵ unperturbed eigenfunctions are eigenfunctions of perturbing Hamiltonian

$$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau$$

$$= \frac{\mu_B B_z}{\hbar} \int \psi^*_{nlm} \hat{L}_z \psi_{nlm} \, d\tau$$

$$= \frac{\mu_B B_z}{\hbar} m\hbar \underbrace{\int \psi^*_{nlm} \psi_{nlm} \, d\tau}_{=1 \text{ ∵ normalized}}$$

$$= m \mu_B B_z$$

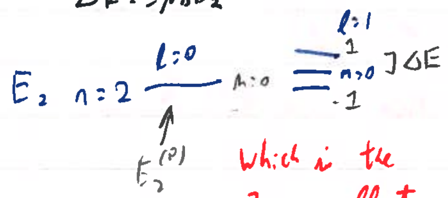
which is the same result

Visualising the result

for: $n=2 \quad l=0 \quad m=0$

$n=2 \quad l=1 \quad m=-1,0,1$

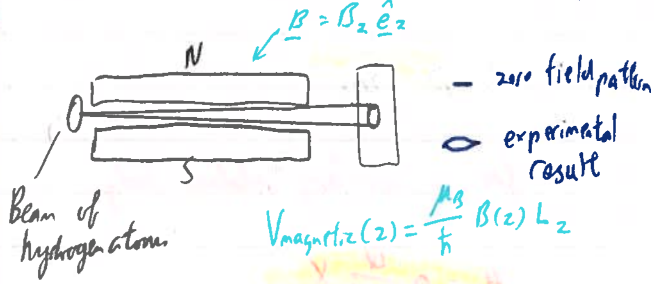
$\Delta E = \pm \mu_B B_z$



which is the Zeeman effect

See Zeeman effect in moodle notes

The Stern-Gerlach experiment



$$V_{magnetic}(z) = \frac{\mu_B}{\hbar} B(z) L_z$$

∴ will have a force:

$$F = -\frac{\partial V}{\partial z} = \frac{-\mu_B L_z}{\hbar} \frac{\partial B}{\partial z} = \mu_z \frac{\partial B}{\partial z}$$

$$F = \mu_z \frac{\partial B}{\partial z} \quad \Big\| \quad \mu_z = -\frac{\mu_B}{\hbar} L_z$$

z-component of the magnetic moment

if the magnetic field has a uniform gradient $\frac{\partial B}{\partial z}$

=> beam is expected to deflect ∝ μ_z

– classically, μ_z can take any value

↳ expect a uniform distribution

↳ might expect deflection to be quantized according to $L_z = m\hbar$

↳ always expect odd number of beam deflection according to allowed values of m_l

=> Stern-Gerlach experiment gives 2 groups of atoms, deflected in opposite directions

$$\mu_z = \pm \mu_B$$

∴ need additional source of angular momentum

✡ e⁻ has an intrinsic angular momentum

↳ SPIN

Magnetic moment of a rotating body

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

for an arbitrary rotating body

charge — angular momentum

$\mu_x = g_x \frac{Q}{2M} X$ — mass

g_x : g-factor

⇒ gyromagnetic factor

↳ depends on the details of the rotating charge distribution

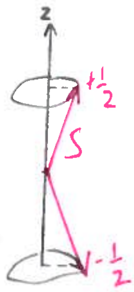
Intrinsic magnetic moment:

$\hat{\mu}_s = g_s \frac{(-e)}{2m_e}\hat{S} = -g_s \frac{\mu_B}{\hbar}\hat{S}$

↳ g-spin factor

$\hat{\mu}_{s_z}$ has allowed values of:

$-g_s \mu_B m_s$



∵ beam splits into 2 components

m_s must have 2 equal values that are opposite in sign

By analogy to $\hat{L}$ ⇒ possible value of m_s differ by unity / 1, & range from -s to s

$\mu_z = \pm\mu_B$

$S_z\chi = m_s\hbar\chi$

Spin quantum numbers:

$m_s = \pm\frac{1}{2}$; $s = \frac{1}{2}$

∴ $g_s = 2$ from above

$\mu_z = \pm \mu_B$

$S_z \chi = m_s \hbar \chi$

$\hat{\mu}_{S_z} = -g_s \frac{\mu_B}{\hbar}\left(\pm\frac{1}{2}\right)\hbar$

$= -g_s\mu_B\left(\pm\frac{1}{2}\right) = \mu_z$

$\mu_B = \mu_z$

⇒ $g_s = 2$

Complete set of quantum numbers

$\hat{H}\psi = \hat{H}^{(0)}\psi + \frac{\mu_B}{\hbar}B\cdot\hat{L}\,\psi + \frac{\mu_B}{\hbar}B\cdot 2\hat{S}$ ↳ g-factor

the general interaction w/ B-field must take into account orbital & spin momenta:

$\hat{H} = \hat{H}^{(0)} + \frac{\mu_B}{\hbar} B\cdot(\hat{L}+2\hat{S})$

expression of $\hat{H}$ for atom in presence of B-field

w/ eigenfunction:

$\psi_{n,l,m_l,s,m_s}(r,\theta,\phi)$

$= \underbrace{R_{n,l}(r)\,Y_{l,m}(\theta,\phi)}_{\text{continuous}}\;\underbrace{\chi_{s,m_s}}_{\text{discrete}}$

w/ complete set of quantum numbers

n, l, m_l, s, m_s | $s = \frac{1}{2}$

spin function χ_{s,m_s} do not depend on e/ coordinates

↳ thus representing a purely internal degree of freedom

w/ eigenvalues of $(\hat{L}_z + 2\hat{S}_z)$

⇒ $(m_l + g_s m_s)\hbar$

$L_z \psi\ m_l\hbar$

$\hat{S}_z \psi\ m_s\hbar$

$m_s = \pm\frac{1}{2}$; $s = \frac{1}{2}$

Total angular momentum, $\underline{J}$

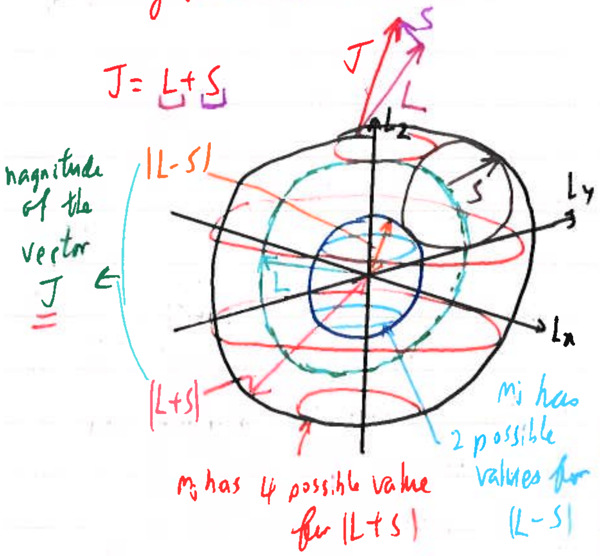
an e/ has 2 sources of angular momentum

→ Orbital angular momentum, $\underline{L}$
↳ from its motion through the atom

→ intrinsic angular momentum, $\underline{S}$
↳ intrinsic property of the e/

→ obtaining total angular momentum $\underline{J}$ using vector addition:

$\underline{J} = \underline{L} + \underline{S}$



$j = |l - \frac{1}{2}|, l + \frac{1}{2}$

$m_j = -j, \dots, +j$ ⇒ projection of the z-component of j

eg for 1s state:
$l = 0$; $m_l = 0$; $s = \frac{1}{2}$; $m_s = \pm\frac{1}{2}$

⇒ $j = |l - s| = l + s = \frac{1}{2}$, $m_j = \pm\frac{1}{2}$

for 2p state:
$l = 1$ $m_l = \{-1, 0, 1\}$, $s = \frac{1}{2}$, $m_s = \pm\frac{1}{2}$

$j = |l - s| = \frac{1}{2}$ $m_j = \pm\frac{1}{2}$

$j = l + s = \frac{3}{2}$ $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

Intrinsic angular momentum $\underline{S}$ (spin)

Analogous to orbital angular momentum

$\hat{L}$ orbital angular momentum	$\hat{S}$ intrinsic angular momentum
l	s ⇒ spin quantum number
$m_l = -l \dots l$	$m_s = -s, \dots s$ ⇒ magnetic spin quantum num
$\hat{L}^2 Y_{lm_l} = l(l+1)\hbar^2 Y_{lm_l}$	$\hat{S}^2 \chi_{sm_s} = s(s+1)\hbar^2 \chi_{sm_s}$
$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$	$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z$
$[\hat{L}^2, \hat{L}_z] = 0$	$[\hat{S}^2, \hat{S}_z] = 0$

χ_{sm_s} do not depend on e/ coordinates r, θ, ϕ:
↳ just representing a purely internal degree of freedom