Lecture 1 : Genesis of Quantum Theory

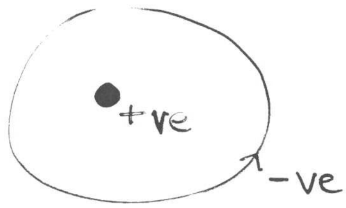
At start of 20^{th} C there were number of outstanding problems to do with structure of matter

Broadly speaking two areas

① Atoms : Stability ?

Structure ?

Radiation ?



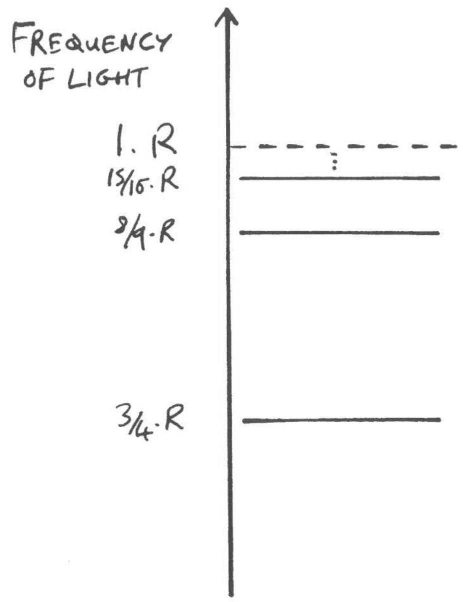
Known that atoms had both +ve and -ve charges in bound state

- But if one orbits around other then classical EM theory predicts system radiates energy (EM radiation due to accelerating charges) and collapses in very short time — so

Why atoms stable??

Moreover, experiments with discharge tubes by Balmer, Lyman, and others showed that

- Radiation (IR, visible, UV, etc) emitted by excited atoms came in discrete spectral lines eg, BALMER SERIES FROM HYDROGEN



R = Rydberg constant

$$\frac{\nu}{c} = R\left(1 - \frac{1}{n^2}\right)$$

$n = 2, 3, 4, 5, \ldots$

SEVERAL OTHER SERIES HAD ALSO BEEN IDENTIFIED TOGETHER WITH THE 'RULE' FOR THE FREQUENCIES

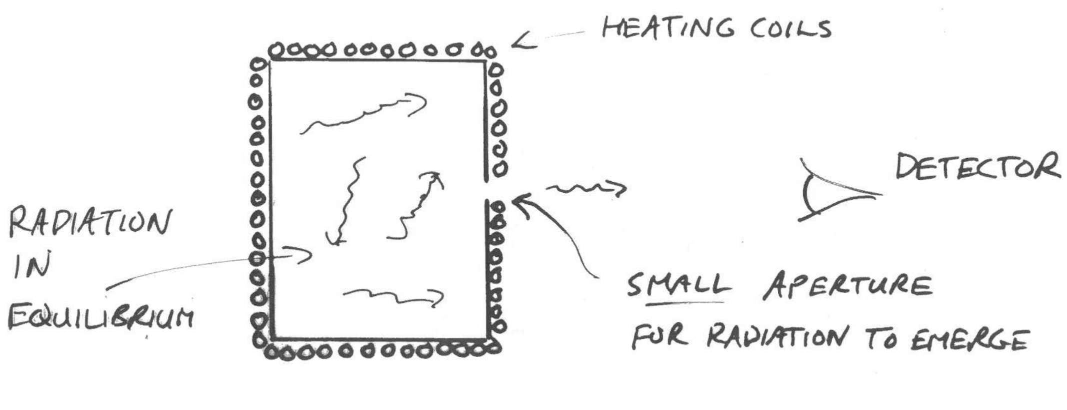
<u>WHY DISCRETE SPECTRUM</u>?

<u>WHY SIMPLE RULES FOR ν (FOR H) ?</u>

② BLACK BODY RADIATION

ALL BODIES AT TEMP $T > 0$ EMIT EM RADIATION (AND ABSORB IT IF IN EQUILIBRIUM)

SCHEMATICALLY A BLACK BODY CAN BE MADE VIA



ACCORDING TO CLASSICAL PHYSICS (STAT MECH + MAXWELL THEORY OF EM) THE AMOUNT OF EM ENERGY PER UNIT VOLUME PER UNIT FREQ. RANGE IS

$$\delta E \sim \nu^2 \delta\nu \qquad \text{IN RANGE } \nu \text{ TO } \nu + \delta\nu$$

THIS IS THE **RAYLEIGH – JEANS LAW**

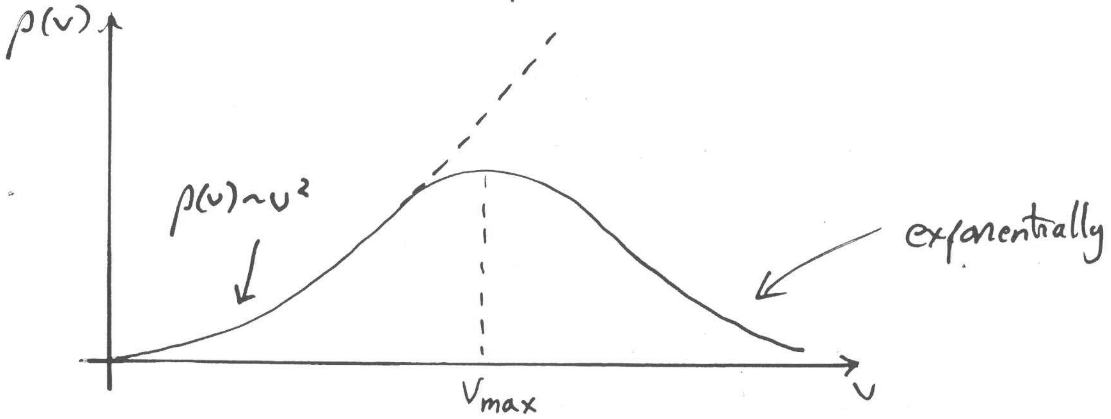
BUT IT IMPLIES THE NONSENSICAL RESULT THAT THE TOTAL ENERGY DENSITY

$$E_{TOT} \sim \int_0^\infty \nu^2 \, d\nu \longrightarrow \infty$$

INFINITE ENERGY DENSITY (AT HIGH ν) FOR ARBITRARILY SMALL T

EXPERIMENTALLY, SPECTRUM LOOKS LIKE

$$\delta E \sim \rho(\nu)\, \delta\nu$$



$$T/\nu_m = \text{CONST} \qquad \text{(WIEN'S DISPLACEMENT LAW)}$$

POSITION OF PEAK MOVES TO HIGHER ν AS T INCREASES

GREAT CONTRIBUTION OF <u>MAX PLANCK</u> TO REALIZE THAT PROBLEM WAS DUE TO CONTINUOUS NATURE OF RADIATION ENERGY IN CLASSICAL THEORY AND THAT CORRECT SPECTRUM

$$\rho(\nu)\, d\nu = (\text{constants}) \frac{\nu^3 \, d\nu}{e^{h\nu/kT} - 1}$$

PLANCK DERIVED THIS PERFECT FIT TO B-B SPECTRUM

<u>AROSE FROM ASSUMPTION THAT EM RADIATION OF FREQ. ν REQUIRES MINIMUM EXCITATION ENERGY</u>

$$\boxed{\begin{array}{c} \Delta E = h\nu \\ h \overset{\text{def}}{=} \text{Planck's constant} = 6.626 \times 10^{-34}\ \text{Js} \end{array}}$$

THIS IS COMPLETELY DIFFERENT FROM CLASSICAL THEORY

"THE BIRTH OF THE QUANTUM"

h IS A NEW FUNDAMENTAL CONSTANT OF NATURE

[MAYBE INTERESTING TO READ PARISI ARTICLE ABOUT SUBTLETIES IN PLANCK'S ARGUEMENT]

AN EQUALLY IMPORTANT CONTRIBUTION WAS <u>EINSTEIN'S</u>

ANALYSIS OF

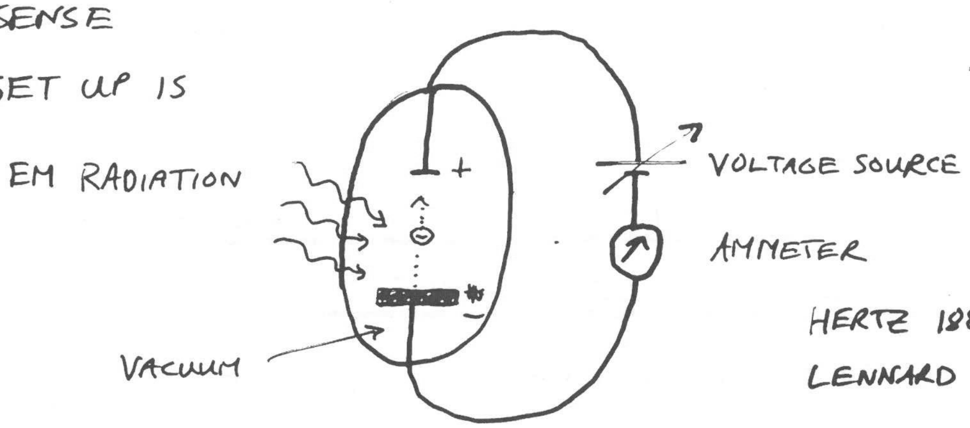
- <u>THE PHOTOELECTRIC EFFECT</u>

THE IMPORTANCE OF THIS EXPERIMENT IS THAT IT SHOWED HOW PLANCK'S QUANTA ARE

<u>REAL IRREDUCIBLE ENTITIES</u>

AND NOT JUST SOMETHING THAT EXIST IN A STATISTICAL SENSE

SET UP IS



HERTZ 1887
LENNARD 1902

RADIATION INCIDENT ON A CATHODE KNOCKS OUT ELECTRONS, WHICH ARE THEN ATTRACTED TO ANODE BY ELECTRIC FIELD ⟶ A DETECTABLE CURRENT

<u>CLASSICAL THEORY</u> SAYS:

ENERGY OF LIGHT IS DETERMINED BY INTENSITY OF LIGHT; THIS ENERGY IS DELIVERED CONTINOUSLY BY THE EM WAVES; ENERGY OF LIGHT IS INDEP^T OF FREQUENCY

THUS **CLASSICAL THEORY PREDICTS**

ONCE LIGHT IS TURNED ON, THE ELECTRONS IN CATHODE START ABSORBING ENERGY UNTIL EVENTUALLY THEY HAVE GAINED ENOUGH TO FREE THEMSELVES FROM METAL SURFACE (THIS MINIMUM AMOUNT IS THE '**WORK-FUNCTION**', W, OF THE METAL)

⟹ ① THERE SHOULD BE A **DELAY** BETWEEN SWITCHING ON LIGHT AND OBSERVING CURRENT

② IF **INTENSITY OF LIGHT IS DECREASED** THE **DELAY SHOULD INCREASE**

③ THE **FREQUENCY** OF THE LIGHT **SHOULD NOT MATTER AT ALL**, ① AND ② SHOULD STILL BE TRUE

THESE ARE THE PREDICTIONS OF THE VERY WELL VERIFIED WAVE THEORY OF LIGHT...

IN FACT WHAT HAPPENS

(i) THERE IS **NO DELAY** IN CURRENT FLOW (DELAY $< 10^{-9}$ sec.)

(ii) DECREASING INTENSITY **DECREASES SIZE OF CURRENT**, **BUT NO EFFECT OTHERWISE**

(iii) THE FREQUENCY ν IS CRUCIAL; IF ν IS TOO SMALL NO CURRENT FLOWS NO MATTER HOW LONG WE WAIT OR HOW HIGH INTENSITY

EINSTEIN (1905) EXPLAINED THESE RESULTS BY HYPOTHESIZING THAT

> LIGHT SHOULD BE REGARDED AS CONSISTING OF IRREDUCIBLE, PARTICLE LIKE OBJECTS (PHOTONS) EACH WITH ENERGY
>
> $$E = h\nu$$

THIS APPEARS TO BE IN TOTAL CONTRADICTION TO 150 YEARS OF EXPERIMENTS PROVING LIGHT WAS A WAVE (YOUNG, HUYGENS, ..., MAXWELL, HERTZ, FRAUNHOFFER, ...) AND EVEN IN 1915 WAS REGARDED AS A TREMENDOUS MISTAKE BY EINSTEIN

ANYHOW, EINSTEIN'S HYPOTHESIS HAD FOLLOWING CONSEQUENCE

IF PHOTON (γ) HITS ELECTRON (e^-) IN CATHODE ELECTRON ABSORBS ENERGY $h\nu$. FOR e^- TO ESCAPE SURFACE ITS ENERGY MUST BE GREATER THAN

$$W - V$$

THUS EINSTEIN SAID

(i) IF ν FALLS BELOW $(W-V)/h$ NO CURRENT CAN FLOW (IGNORING UNLIKELY EVENT OF 2 γ's HITTING SAME e^-!)

(ii) THERE IS NO DELAY — WE ONLY NEED ONE PHOTON TO HIT SOME ELECTRON ON CATHODE FOR CURRENT

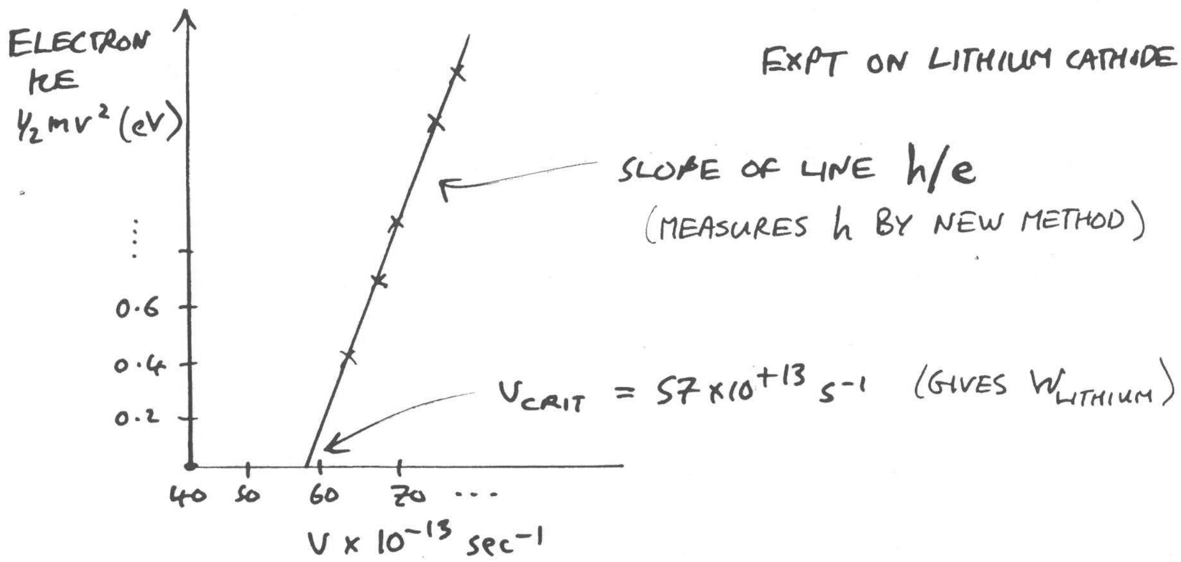
(iii) DECREASING INTENSITY DECREASES NUMBER OF γ's/UNIT TIME, HENCE RATE AT WHICH e^-'s ARE EJECTED HENCE CURRENT

THESE ALL AGREED

AND FURTHER HE PREDICTED

$$\text{KE OF } e^- = \tfrac{1}{2} m_e v^2 = h\nu - (W-V)$$

WHICH LATER EXPERIMENTS BY MILLIKAN (1916) VERIFIED!



BOHR ATOM

BOHR (1913) WAS ABLE TO DERIVE BALMER, ETC. SERIES FOR H BY SUPPOSING e^- IS IN ORBIT AROUND NUCLEUS WITH QUANTIZED ANGULAR MOMENTUM

NOTE: h HAS UNITS OF ANG. MOM'M.

$$J = \frac{nh}{2\pi} \qquad n = 1, 2, 3, \ldots$$

AND e^- CAN MAKE DISCONTINUOUS TRANSITIONS FROM ONE ORBIT TO ANOTHER, WITH CHANGE IN ENERGY $E - E'$ APPEARING AS RADIATION WITH FREQ.

$$\nu = \frac{E - E'}{h}$$

THIS WAS A VERY IMPORTANT BREAKTHROUGH AS IT SHOWED QUANTUM HYPOTHESIS WAS USEFUL FOR ATOMS, NOT JUST LIGHT.

BUT ON CLOSER INSPECTION THERE ARE A NUMBER OF THINGS PHYSICALLY WRONG WITH BOHR ATOM — SO WE'LL WAIT TO DO HYDROGEN PROPERLY VIA SCHROEDINGER EQN.

PARTICLES AND WAVES

EINSTEIN AND PLANCK ARGUED THAT LIGHT HAS PARTICLE-LIKE PROPERTIES, EVEN THOUGH IT OF COURSE IT IS ALSO WAVE-LIKE, AS SHOWN BY INTERFERENCE EFFECTS (YOUNG'S SLITS, DIFFRACTION) AND SUCCESS OF MAXWELL'S EQNS.

REALLY LIGHT IS NEITHER A PARTICLE NOR A WAVE BUT SOME NEW KIND OF ENTITY THAT HAS ASPECTS OF BOTH (FEYNMAN CALLED THESE ENTITIES 'WAVICLES' AS A SERIOUS JOKE...)

DE BROGLIE (1923) HAD THE INSIGHT TO PROPOSE THAT EVERY OBJECT – MATTER AS WELL AS LIGHT – WAS REALLY ONE OF THESE NEW ENTITIES

THUS HE WAS MOTIVATED TO ASSOCIATE A WAVELENGTH, λ, WITH MATTER (THE DE BROGLIE WAVELENGTH)

WHAT SHOULD λ BE?

RECALL FOR γ's $\quad E = h\nu = \dfrac{hc}{\lambda}$

BUT FOR PHOTONS $E = pc$ (SEE PROBLEM SET)

SO EQUALLY

$$\lambda = \frac{hc}{E} = \frac{h}{p}$$

AND DE BROGLIE TOOK FOR MATTER THE DEFINITION

$$\boxed{\lambda_{\text{DE BROGLIE}} \overset{\text{def}}{=} \frac{h}{p}}$$

PARTICLE MOM'M

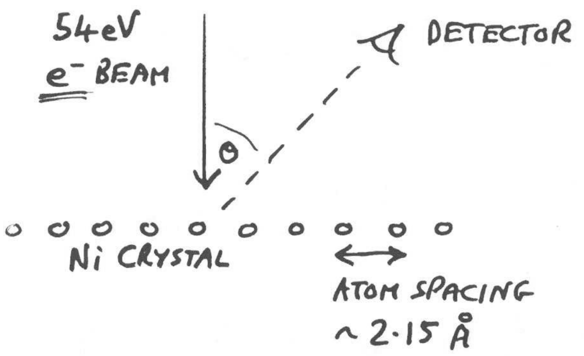
AND SUGGESTED THAT DIFFRACTION EFFECTS FOR MATTER SHOULD BE SEARCHED FOR...

THE DAVISSON AND GERNER EXPERIMENT

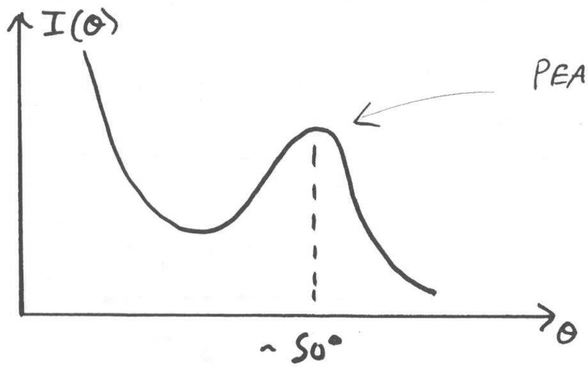
NOT SO EASY TO SEE DIFFRACTION EFFECTS FOR, EG, e^-'s AS λ IS MUCH SHORTER

EG, 10 eV e^- HAS $\lambda = 3.9\,\text{Å}$ $(1\,\text{Å} = 10^{-10}\,\text{m})$

DAVISSON AND GERMER (1925) USED A NICKEL CRYSTAL AS A DIFFRACTION GRATING



$$n\lambda = d \sin\theta$$



PEAK CORRESPONDS TO $n=1$

THUS DO GET DIFFRACTION OF MATTER!

FINALLY, COMPTON EFFECT, CONFIRMED PARTICLE NATURE OF LIGHT (SEE PROBLEMS)

QM LECTURE 2

HEISENBERG / SCHROEDINGER IN 1925/26 DEVELOPED TWO TOTALLY EQUIVALENT FORMULATIONS OF (NON-RELATIVISTIC) QUANTUM MECHANICS

WE'LL START WITH SCHROEDINGER...

DE BROGLIE HAD POSTULATED WAVE ASSOCIATED WITH EVERY PARTICLE, SO SCHROEDINGER INTRODUCED

'WAVE FUNCTION' $\psi(x, t)$

AND TOOK $\psi(x,t)$ TO SATISFY PARTIAL DIFFERENTIAL EQN.

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

"SCHROEDINGER EQN" $\hbar = h/2\pi$

$\hat{H}$ IS THE 'HAMILTONIAN' – THE PARTIAL DIFFERENTIAL OPERATOR FOR THE TOTAL ENERGY

FOR A PARTICLE MOVING IN 1D

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

WHERE IN QM THE MOMENTUM OPERATOR IS

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

THESE ARE HYPOTHESES OF QM VERIFIED BY EXPERIMENT

WITH $\hat{p}$ AS GIVEN SCH. EQN (IN 1D) READS

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

TRY SOLUTION VIA SEPARATION OF VARIABLES

$$\underline{\psi(x,t) = \phi(x)\,T(t)}$$

SO

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\,\phi(x)\right]T(t)$$

$$= \left[i\hbar\frac{\partial T(t)}{\partial t}\right]\phi(x)$$

DIVIDE BOTH SIDES BY ϕT

$$\underbrace{\frac{1}{\phi}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\phi}{\partial x^2} + V\phi\right]}_{\text{ONLY FUNCTION OF } X} = \underbrace{\frac{i\hbar}{T}\frac{\partial T(x)}{\partial t}}_{\text{ONLY FUNCTION OF } t}$$

THE ONLY WAY L.H.S. $= f(x)$ AND RHS $= g(t)$ IS IF ACTUALLY BOTH EQUAL CONSTANT (E)

THUS GET 2 EQNS:

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

$$\boxed{i\hbar\frac{dT}{dt} = ET \qquad (\mathrm{II})}$$

(II) IS EASY TO SOLVE

$$\underline{T(t) = e^{-iEt/\hbar}} \times \text{CONSTANT}$$

(I) CALLED THE 'TIME INDEPENDENT SCHROEDINGER EQN' CAN BE VERY HARD TO SOLVE - DEPENDS ON $V(x)$

TISE

EASY CASE: FREE PARTICLE

$$\underline{V = 0}$$

FOR $V=0$ TISE IS

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

WITH SOLUTIONS

$$\phi \sim e^{ikx}, \quad e^{-ikx}$$

WHERE

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

THUS PUTTING $T(t)$ AND $\phi(x)$ TOGETHER

$$\psi(x,t) \sim e^{i(kx - Et/\hbar)}$$ WAVE IN +VE X DIR'N

$$\psi(x,t) \sim e^{-i(kx + Et/\hbar)}$$ WAVE IN −VE X DIR'N

SO FIND

ANGULAR FREQ $\omega = E/\hbar$

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

SO <u>AUTOMATICALLY INCORPORATES EINSTEIN REL'N</u>

ALSO FOR CLASSICAL FREE PARTICLE $E = p^2/_{2m}$

SO GET

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

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

<u>AUTOMATICALLY INCORPORATES DE BROGLIE 'MATTER WAVE' REL'N</u>

WHAT DOES $\psi(x,t)$ MEAN?

$\psi(x,t)$ <u>CANNOT</u> BE A PHYSICAL WAVE LIKE OSCILLATING STRING, OR EM WAVE OF MAXWELL THEORY

TDSE IS <u>COMPLEX EQN</u> (THE 'i')

<u>SOLUTIONS ARE INHERENTLY COMPLEX</u> (REAL AND IMAG PARTS OF ψ DO NOT SEPARATELY SOLVE EQN)

SOMETHING WHICH IS COMPLEX CANNOT BE DIRECTLY MEASURED

(ALL EXPERIMENTS RETURN REAL RESULTS!)

ALSO NOTE THAT FOR A PHYSICAL WAVE

$$e^{ik(x - v_p t)}$$

v_p ← PHASE VELOCITY

BUT FOR $\psi(x,t)$

$$\psi(x,t) = e^{i(kx - Et/\hbar)} = e^{\frac{i}{\hbar}(px - Et)}$$

SO $$v_p = E/p = \frac{(p^2/2m)}{p} = \frac{p}{2m}$$

$$= \frac{v}{2}$$

HALF THE SPEED OF PARTICLE WITH MOM'M p AND MASS m

ON OTHER HAND GROUP VELOCITY

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp} = \frac{p}{m} = v \quad \checkmark$$

THIS IS VERY DIFFERENT TO, E.G. EM WAVES WHERE OSCILLATING $\vec{E}$ AND $\vec{B}$ HAVE

$$V_p = V_g = c$$

SO WE KNOW WHAT $\psi(x,t)$ IS <u>NOT</u>

... NEXT LECTURE WE'LL SEE WHAT $\psi(x,t)$ <u>IS</u> ...

LECTURE 3: $\psi(x,t)$ AND PROBABILITY

TO UNDERSTAND $\psi(x,t)$ MUST INTRODUCE

$$\boxed{\text{PROBABILITY DENSITY } P(x,t)}$$

BASIC IDEA IS THAT CAN NO LONGER BE CERTAIN OF EXACT POSITION OF PARTICLE

ONLY THAT <u>PROB. OF MEASURING IT BETWEEN x AND $x+\delta x$</u> IS

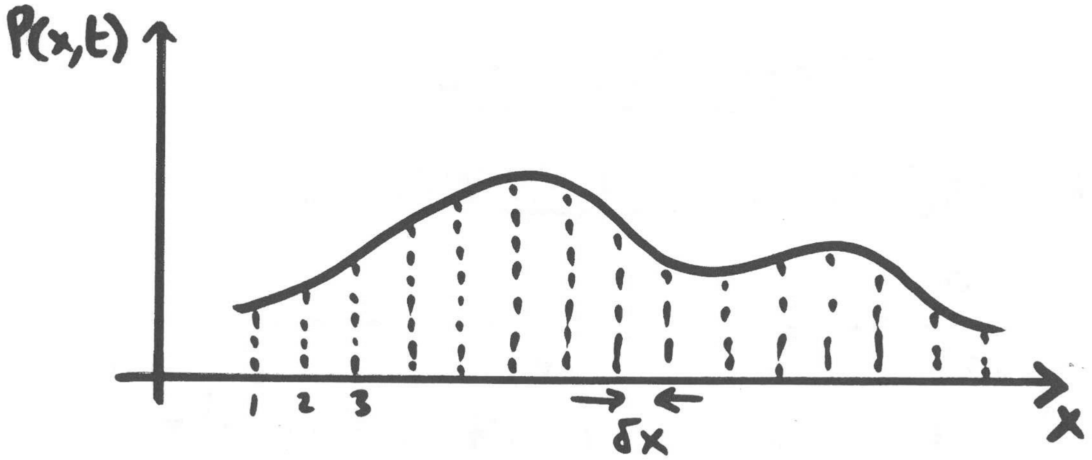
$$\text{PROB}(\text{IN } x \text{ TO } x+\delta x) = P(x,t)\,\delta x$$

AND (BORN, 1926)

A <u>POSTULATE</u> OF QM IS THAT

$$P(x,t) = \psi^*(x,t)\,\psi(x,t) = |\psi(x,t)|^2$$

IF WE KNOW $P(x,t)$ (FROM A SOLUTION $\psi(x,t)$ OF TDSE) THEN CAN CALCULATE <u>AVERAGES</u> OR <u>EXPECTATION VALUES</u>



$$\bar{x} \simeq \sum_{i=1} x_i P(x_i) \delta x$$

IN LIMIT AS $\delta x \to 0$ AND NUMBER OF SLICES $\to \infty$ $\sum_i$ BECOMES

$$\boxed{\begin{aligned} \bar{x} \overset{\text{def}}{=} \langle x \rangle &= \int_{-\infty}^{\infty} x\, P(x,t)\, dx \\ &= \int_{-\infty}^{\infty} x\, |\psi(x,t)|^2\, dx \end{aligned}}$$

SIMILARLY

$$\langle x^2 \rangle \stackrel{\text{def}}{=} \int_{-\infty}^{\infty} x^2 |\psi(x,t)|^2 dx$$

ETC...

OF COURSE, TOTAL PROBABILITY OF FINDING PARTICLE ANYWHERE MUST BE 1, SO

$$\boxed{1 = \int_{-\infty}^{\infty} P(x,t)\, dx = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx}$$

NORMALIZATION CONDITION ON $\psi(x,t)$

THIS MUST BE IMPOSED ON $\psi(x,t)$ AS SCHROEDINGER EQN IS (EXACTLY - NOT AN APPROXIMATION!) LINEAR IN ψ

IF ψ SOLVES $\hat{H}\psi = i\hbar \partial\psi/\partial t$

SO DOES $\psi \times$ CONSTANT

THUS VALUE OF UNDETERMINED CONSTANT IS FIXED (UPTO IRRELEVANT CONST. PHASE FACTOR – IGNORE) BY NORMALIZATION CONDITION

COMPLICATION FOR PLANE WAVES

$$\psi(x,t) = G\, e^{i/\hbar\,(px - Et)}$$

SO $\displaystyle\int_{-\infty}^{\infty} |\psi|^2 dx = \int_{-\infty}^{\infty} |G|^2 dx \longrightarrow \infty$

REGARDLESS OF G

$\Rightarrow$ PLANE WAVE IS NOT NORMALIZABLE!

REASON: PLANE WAVES ARE NOT PHYSICALLY REALIZABLE (THEY EXIST FOR ALL TIME AND ARE SPREAD OVER ALL SPACE)

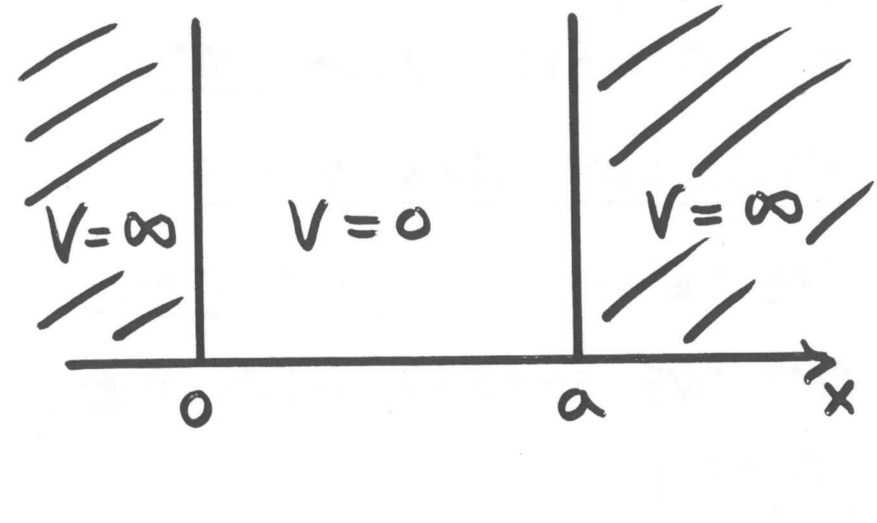
A MORE PHYSICAL SITUATION IS A 'PLANE WAVE' CONFINED TO SOME FINITE REGION (FOR EXAMPLE, OUR EXPERIMENTAL APPARATUS)

THEN $\int_{-L}^{L} dx\, |G|^2 = 1$

$$\Rightarrow \quad G = \frac{1}{\sqrt{2L}} \quad \text{OK} \checkmark$$

THE INFINITE SQUARE WELL

NOW INVESTIGATE SOL'NS TO TDSE IN FOLLOWING POTENTIAL



SINCE $V \neq V(t)$ SOL'N IS OF FORM

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

WHERE

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

- IN REGIONS WHERE $V=\infty$, ϕ MUST BE ZERO $\phi = 0$ FOR FINITE E SOL'N. (AS $KE \geq 0$)

- INSIDE WELL

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} = E\phi \quad \text{AS } V=0$$

SO $$\phi = A e^{ikx} + B e^{-ikx}$$

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

NOW HAVE TO <u>MATCH INSIDE TO OUTSIDE SOL'NS</u> VIA

BOUNDARY CONDITION ϕ MUST BE CONTINUOUS

• <u>AT $X=0$</u>

$$0 = \left(Ae^{ikx} + Be^{-ikx}\right)_{x=0} = A + B$$

• <u>AT $X=a$</u>

$$0 = Ae^{ika} + Be^{-ika}$$

SINCE 1^{st} B.C. GIVES $B = -A$ GET

$$0 = A\left(e^{ika} - e^{-ika}\right)$$

$$= 2iA \sin ka$$

$\Rightarrow$ EITHER $A=0$ – REJECT

OR $\sin ka = 0$ $\Rightarrow$ $k = \frac{n\pi}{a}$ $\quad n = 1, 2, 3, \ldots$

SUBST. BACK GET

$$\boxed{E = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2}n^2 \qquad n=1,2,\ldots}$$

POSSIBLE ENERGIES OF PARTICLE ARE <u>QUANTIZED</u>

TYPICAL FOR PARTICLES BOUND IN A POTENTIAL WELL (ATOMS,....)

ALSO <u>HAVE TO NORMALIZE SOL'N</u>

$$\phi_n(x) = A' \sin\frac{n\pi x}{a}$$

$$1 = \int_{-\infty}^{\infty} |\phi(x)|^2 dx = A'^2 \int_0^a \sin^2\frac{\pi n x}{a}\, dx$$

$$= A'^2\, a/2$$

$$\underline{A' = \sqrt{\frac{2}{a}}}$$

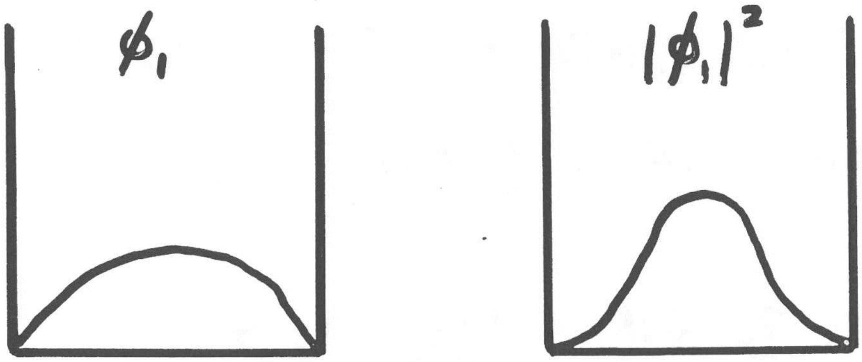
NOTE THAT ϕ_n ARE <u>ORTHOGONAL</u>

$$\int_{-\infty}^{\infty} \phi_n^*(x)\, \phi_m(x)\, dx = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}\, \sin\frac{m\pi x}{a}\, dx$$

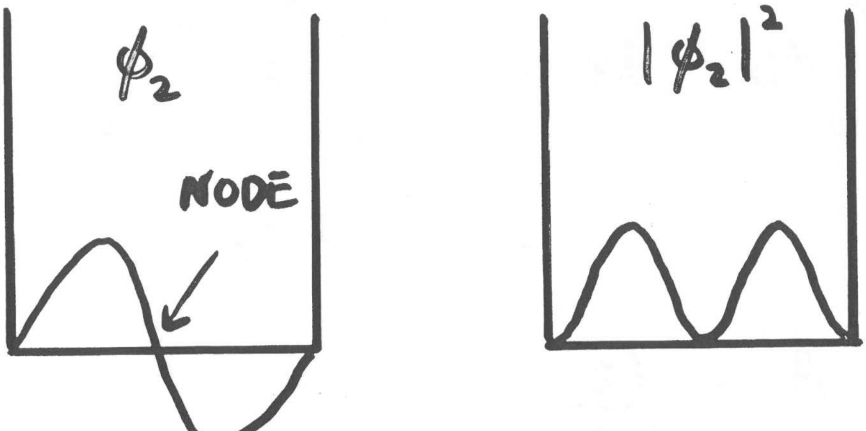
$$= 1 \text{ if } n = m$$

$$= 0 \text{ if } n \neq m$$

WHAT DO ϕ_n LOOK LIKE?



$n=1$ ('GROUND STATE') HAS NO NODES
STRONGLY PEAKED IN MIDDLE



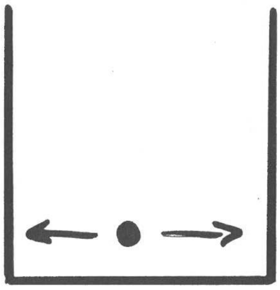
$n=2$ FIRST EXCITED STATE, 1 NODE

PHYSICS OF LOW n STATES IS VERY DIFFERENT FROM CLASSICAL EXPECTATIONS...

- CLASSICALLY

$P(x) = 1/a$

(UNIFORM!)



BALL BOUNCING BACK/FORWARD

$$\text{SO } \langle x \rangle = \int_0^a x\, P(x)\, dx = \frac{1}{a}\int_0^a x\, dx = \frac{a}{2}$$

$$\langle x^2 \rangle = \int_0^a x^2\, P(x)\, dx = a^2/3$$

BUT
- QUANTUM (PROBLEM SET)

$$\langle x \rangle_1 = a/2 \qquad \text{SAME}$$

$$\langle x^2 \rangle_1 = \frac{a^2}{3} - \frac{a^2}{2\pi^2}$$

DIFFER

'1' MEANS EVALUATED IN $n=1$ STATE

AS $n \to \infty$ FIND $\langle x^2 \rangle \to$ CLASSICAL RESULT, PROB. DIST'N. BECOMES MORE SPREAD OUT (EXAMPLE OF GENERAL BEHAVIOR)

LECTURE 4: ENERGY EIGENSTATES

WAVE FUNCTION OF FORM

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

$\psi(x,t)$ PROPORTIONAL TO SINGLE $e^{-iEt/\hbar}$

IS SPECIAL

AN ENERGY EIGENSTATE

(OR STATIONARY STATE – SAME THING)

EQUIVALENTLY

$$\underline{H\psi_n(x,t)} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\psi_n(x,t)$$

$$= i\hbar\frac{\partial}{\partial t}\psi_n(x,t) \quad \text{BY TDSE}$$

$$\underline{= E_n\psi(x,t)}$$

SO $\psi_n(x,t)$ IS AN EIGENFUNCTION OF H WITH EIGENVALUE E_n

PHYSICALLY

$$\boxed{\begin{array}{l}\text{ENERGY } \underline{\text{EIGENSTATE}} \\ \iff \text{PARTICLE IS IN } \underline{\text{STATE OF}} \\ \quad\;\; \underline{\text{DEFINITE ENERGY}} \text{ (HERE } E_n\text{)} \\ \iff \text{IF ENERGY IS } \underline{\text{MEASURED}}, \\ \quad\;\; \underline{\text{GUARANTEED}} \text{ RESULT } \underline{E_n}\end{array}}$$

PROB$(E=E_n)=1$

SUPERPOSITIONS

$\psi(x,t) = \phi_n(x)\, e^{-iE_n t/\hbar}$ IS **NOT**

MOST GENERAL SOL'N TO TDSE

SINCE TDSE IS LINEAR EQN (EXACTLY!)

GENERAL SOL'N IS SUM OF ABOVE

$$\boxed{\psi(x,t) = \sum_n a_n\, \phi_n(x)\, e^{-iE_n t/\hbar}}$$

ARBITRARY COMPLEX COEFFS

EG. SUPERPOSITION OF 2 E-EIGENSTATES

$$\psi(x,t) = a_1 \phi_1(x)\, e^{-iE_1 t/\hbar} + a_2 \phi_2(x)\, e^{-iE_2 t/\hbar}$$

ACT WITH ENERGY OPERATOR

$$H\psi = a_1 E_1 \phi_1 e^{-iE_1 t/\hbar} + a_2 E_2 \phi_2 e^{-iE_2 t/\hbar}$$

$$\underline{\neq} \text{ const.} \times \psi(x,t)$$

BUT <u>ψ IS A SOL'N OF TDSE</u>, <u>JUST NOT AN ENERGY E-STATE</u> AS $E_1 \neq E_2$

WHAT IS <u>PHYSICAL</u> SIGNIFICANCE?

FOR ψ TO BE VALID WAVEFUNCTION IT MUST BE <u>NORMALIZED</u>

$$1 = \int |\psi|^2 dx = \int_0^a dx \left\{ a_1^* \phi_1 e^{iE_1 t/\hbar} + a_2^* \phi_2 e^{iE_2 t/\hbar} \right\} \times \left\{ a_1 \phi_1 e^{-iE_1 t/\hbar} + a_2 \phi_2 e^{-iE_2 t/\hbar} \right\}$$

$$= \int_0^a dx \left\{ |a_1|^2 \phi_1^2 + |a_2|^2 \phi_2^2 + a_1 a_2^* e^{i(E_2 - E_1)t/\hbar} \times \phi_1 \phi_2 + a_1^* a_2 e^{i(E_1 - E_2)t/\hbar} \phi_1 \phi_2 \right\}$$

BUT ϕ_1, ϕ_2 ARE ORTHOGONAL AND NORMALIZED SO FIND

$$\underbrace{1 = |a_1|^2 + |a_2|^2}_{\text{A BIG HINT}} + 0 + 0$$

LOOKS LIKE A <u>SUM OF PROBABILITIES</u>

THUS: <u>INTERPRETATION OF SUPEPOSITION</u>

IF <u>MEASUREMENT MADE OF ENERGY</u> OF PARTICLE WITH THIS WAVEFUNCTION WILL <u>GET RESULT</u>

E_1	WITH AMPLITUDE	a_1,	PROBABILITY $\|a_1\|^2$
E_2	" "	a_2,	" $\|a_2\|^2$

THE EXPECTATION VALUE OF ENERGY SHOULD BE $\langle H \rangle_\psi = E_1 |a_1|^2 + E_2 |a_2|^2$

CAN CHECK THIS BY CALCULATING $\langle H \rangle$ DIRECTLY...

$$\langle H\rangle = \int_0^a dx\, \psi^* H \psi$$ <u>DEFINITION</u> OF $\langle H\rangle$ IN STATE ψ

$$= \int_0^a dx\, \psi^*(H\psi)$$

$$= \int_0^a dx \left\{a_1^*\phi_1 e^{iE_1t/\hbar} + a_2^*\phi_2 e^{iE_2t/\hbar}\right\}\left\{a_1 \overset{E_1}{\vee} \phi_1 e^{-iE_1t/\hbar} + a_2E_2\phi_2 e^{-iE_2t/\hbar}\right\}$$

$$= E_1|a_1|^2 + E_2|a_2|^2$$ USING ORTHOG OF ϕ_i's

AS EXPECTED ✓

NOTE THAT $\langle H\rangle$ IS TIME INDEPENDENT

HOWEVER <u>NOT ALL EXPECTATION VALUES ARE TIME-INDEP'T FOR ENERGY SUPERPOSITIONS</u>

- EG

$$\langle p\rangle = \int_0^a dx\, \psi^*\left(-i\hbar \frac{\partial}{\partial x}\psi\right)$$

$$= \int_0^a dx \left\{a_1^* \sin\frac{\pi x}{a} e^{iE_1t/\hbar} + a_2^* \sin\frac{2\pi x}{a} e^{iE_2t/\hbar}\right\}(-i\hbar)\frac{2}{a}\left\{a_1 \frac{\pi}{a}\cos\frac{\pi x}{a} e^{-iE_1t/\hbar} + a_2\frac{2\pi}{a}\cos\frac{2\pi x}{a} e^{-iE_2t/\hbar}\right\}$$

USING THE INTEGRALS

$$\int_0^a dx \sin\frac{\pi x}{a}\cos\frac{\pi x}{a} = 0 = \int_0^a dx \sin\frac{2\pi x}{a}\cos\frac{2\pi x}{a}$$

AND $$\int_0^a dx \sin\frac{2\pi x}{a}\cos\frac{\pi x}{a} = \frac{4a}{3\pi}$$

$$\int_0^a dx \sin\frac{\pi x}{a}\cos\frac{2\pi x}{a} = -\frac{2a}{3\pi}$$

GET

$$\langle p\rangle = -i\hbar\frac{2}{a}\Big\{a_1a_2^* e^{i(E_2-E_1)t/\hbar}\frac{\pi}{a}\frac{4a}{3\pi}$$

$$+a_1^*a_2 e^{i(E_1-E_2)t/\hbar}\frac{2\pi}{a}\left(-\frac{2a}{3\pi}\right)\Big\}$$

$$= -\frac{i\hbar 8}{3a}\left(a_1a_2^* e^{i(E_2-E_1)t/\hbar} - \text{c.c.}\right)$$

IN SIMPLE CASE WHERE a_1 AND a_2 REAL

$$\underline{\langle p\rangle = \frac{16\hbar}{3a}a_1a_2\sin\frac{(E_2-E_1)t}{\hbar}}$$

... MOM'M <u>OSCILLATES IN TIME</u> ...

OPERATORS AND OBSERVABLES

ALREADY SEEN HOW THE NUMERICAL VALUES OF CLASSICAL QUANTITIES (E.G. MOM'M, ENERGY) BECOME IN QM DIFFERENTIAL OPERATORS

X-MOMENTUM $\quad p = -i\hbar\, \partial/\partial x$

ENERGY $\quad H = \frac{p^2}{2m} + V(x) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

THIS IS A GENERAL PRINCIPLE OF QM

EVERY PHYSICAL OBSERVABLE CORRESPONDS TO AN OPERATOR Q

HOW ARE THE NUMBERS MEASURED IN EXPT'S RELATED TO OPERATOR?

FOR ENERGY FOUND

$$H\phi_n = E_n \phi_n$$

THIS IS AN EIGENVALUE EQN

$$H \phi_n = E_n \phi_n$$

EIGENVALUE EIGENFUNCTION

(JUST LIKE EIGENVALUE EQN FOR A MATRIX)

IN GENERAL FOR OPERATOR Q

$$\boxed{Q \chi_n(x) = q_n \chi_n(x)}$$

EIGENFUNCTION (LABELED BY n)

EIGENVALUE (LABELED BY n)

THE SET OF ALL q_n IS CALLED THE <u>SPECTRUM</u> OF Q

A GENERAL PRINCIPLE OF QM IS

> MEASUREMENTS OF A PHYSICAL OBSERVABLE ALWAYS GIVE A RESULT WHICH IS <u>ONE</u> OF THE <u>EIGENVALUES OF CORRESPONDING Q</u>

SINCE EXPT'S ALWAYS RETURN REAL NUMBERS AS RESULTS, CLASS OF ALLOWABLE OPERATORS MUST BE SUCH AS TO HAVE ONLY REAL EIGENVALUES

THESE ARE HERMITIAN OPERATORS

SO PRINCIPLE OF QM

EVERY OPERATOR REPRESENTING A PHYSICAL OBSERVABLE MUST BE A HERMITIAN OPERATOR

DEFINITION OF HERMITIAN OP. Q

FOR 1D QM AN OP. Q IS HERMITIAN IF $\int_{-\infty}^{\infty} \chi^* Q \psi \, dx = \int_{-\infty}^{\infty} (Q\chi)^* \psi \, dx$ FOR ANY FUNCTIONS $\chi(x), \psi(x)$ WHICH ARE NORMALIZABLE AND VANISH AT $x = \pm\infty$

WHAT KINDS OF OP. ARE HERMITIAN ?

i) THE POSITION OP.

$$\int_{-\infty}^{\infty} \chi^* x \psi \, dx = \int_{-\infty}^{\infty} (x^* \chi)^* \psi \, dx$$

$$= \int_{-\infty}^{\infty} (x \chi)^* \psi \, dx$$

SO SINCE x IS A REAL NUMBER

$$x^\dagger = x \qquad \text{(NOTATION FOR HERMITIAN OP.)}$$

AND RELATION TRIVIALLY TRUE

ii) THE POTENTIAL ENERGY $V(x)$

$$\int_{-\infty}^{\infty} \chi^* V(x) \psi \, dx = \int_{-\infty}^{\infty} (V^* \chi)^* \psi \, dx$$

SO, AS LONG AS <u>COEFFICIENTS IN $V(x)$ ARE REAL</u>, HAVE

$$V(x)^\dagger = V(x)$$

WHAT WE EXPECT AS COMPLEX POTENTIAL DOESN'T MAKE SENSE

iii) <u>MOMENTUM OP.</u>

$$\int_{-\infty}^{\infty} \chi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi \, dx = -i\hbar \int_{-\infty}^{\infty} \chi^* \frac{\partial \psi}{\partial x} \, dx$$

WE <u>NEED TO GET OP. ACTING ON</u> χ

<u>SO INTEGRATE BY PARTS</u>

$$RHS = -i\hbar \left\{ \left[\chi^* \psi\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \chi^*}{\partial x} \psi \, dx \right\}$$

SINCE x IS REAL $\partial/\partial x$ IS REAL

$$\partial f^*/\partial x = \partial f^*/\partial x^* = (\partial f/\partial x)^*$$

SO

$$RHS = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \chi}{\partial x}\right)^* \psi \, dx \quad ✓$$

<u>THUS</u> <u>p IS HERMITIAN</u>. NOTE <u>"i" IN DEF'N OF p IS VITAL</u> ($\partial/\partial x$ IS NOT HERMITIAN)

iv) IN PROBLEMS YOU SHOW K.E. OP. $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ IS HERMITIAN (INTEGRATE BY PARTS TWICE)

v) HAMILTONIAN OP.

SINCE $H = T + V$ AND T AND V HERMITIAN, $H^{\dagger} = H$ ALSO

(SUMS OF HERMITIAN OPS. ARE HERMITIAN)

- PROOF OF REALITY OF E'VALUES

LET $Q\chi_n = q_n \chi_n$, THUS $\int \chi_m^*$

$$\Rightarrow \int_{-\infty}^{\infty} \chi_m^* Q \chi_n \, dx = \int_{-\infty}^{\infty} \chi_m^* q_n \chi_n \, dx$$

BUT BY ASSUMPTION Q IS HERMITIAN SO

$$\text{LHS} = \int_{-\infty}^{\infty} (Q\chi_m)^* \chi_n \, dx$$

$$= \int_{-\infty}^{\infty} (q_m \chi_m)^* \chi_n \, dx$$

$$= \int_{-\infty}^{\infty} q_m^* \chi_m^* \chi_n \, dx$$

SO PUT THIS TOGETHER WITH RHS

$$0 = (q_n - q_m^*) \int_{-\infty}^{\infty} \chi_m^* \chi_n \, dx$$

NOW CHOOSE $n = m$

$$0 = (q_n - q_n^*) \underbrace{\int_{-\infty}^{\infty} |\chi_n|^2 \, dx}_{1 \text{ BY NORMALIZATION}}$$

$$\Rightarrow \underline{q_n = q_n^*} \quad \underline{q_n \text{ IS REAL}}$$

- BUT MORE...

CHOOSE $n \neq m$ AND USE REALITY OF q's

$$0 = (q_n - q_m) \int_{-\infty}^{\infty} \chi_m^* \chi_n \, dx$$

IF $q_m \neq q_n$ THEN MUST HAVE

$$0 = \underbrace{\int_{-\infty}^{\infty} \chi_m^* \chi_n \, dx}$$

THUS χ_m AND χ_n ARE ORTHOGONAL FUNCTIONS

THIS SHOULD REMIND YOU OF THE

$$\phi_m = \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a} \qquad \text{OF } \sqcup \text{ POT'L}$$

INDEED WE KNOW BY DIRECT CALCULATION

$$\int_{-\infty}^{\infty} \phi_n^* \phi_m \, dx = 0$$

BUT YET MORE...

WE KNOW FOR ϕ_m's (SIN FUNCTIONS) THAT HAVE FOURIER SERIES

ANY FUNCTION CAN BE EXPANDED AS

$$f(x) = \sum_{n=1}^{\infty} a_n \phi_n(x)$$

THIS IS TRUE IN GENERAL USING EIGENFUNCTIONS OF HERMITIAN OP.

THEOREM:

> LET $X_n(x)$ BE THE EIGENFUNCTIONS OF ANY HERMITIAN OPERATOR. THEN ANY NORMALIZABLE FUNCTION $f(x)$ CAN BE WRITEN AS
>
> $$f(x) = \sum_{n=1}^{\infty} a_n X_n(x)$$

- WE SAY THAT THE $\chi_n(x)$ FORM A COMPLETE SET OF FUNCTIONS (OR STATES)
- IT IS THIS EXPANSION THEOREM THAT ENABLES CONNECTION BETWEEN OPERATORS AND PROBABILITIES

LET'S SEE HOW...

SUPPOSE AT A GIVEN TIME (SAY $t=0$) WE HAVE WAVEFUNCTION $\psi(x,0)$, AND WE MEASURE Q

CAN EXPAND $\psi(x,0)$ IN E'FUNCTIONS OF Q

$$\psi(x,0) = \sum_n a_n \chi_n(x) \qquad (1)$$

FINDING a_n'S IS SIMPLE: MULTIPLY (1) BY $\chi_m^*(x)$ AND INTEGRATE

$$\text{RHS} = \int_{-\infty}^{\infty} \sum_n \chi_m^* a_n \chi_n = \sum \int_{-\infty}^{\infty} a_n \chi_m^* \chi_n$$

$$= \sum a_n \delta_{nm} \quad = a_m$$

BY ORTHOGONALITY

$$LHS = \int_{-\infty}^{\infty} \chi_m^*(x)\,\psi(x,0)\,dx$$

so $$a_m = \int_{-\infty}^{\infty} \chi_m^*(x)\,\psi(x,0)\,dx$$

NOW SUBST EXPANDED $\psi(x,0)$ IN EQN FOR $\langle Q \rangle_\psi$:

$$\langle Q \rangle_\psi = \int \left(\sum_n a_n \chi_n(x)\right)^* Q \left(\sum_m a_m \chi_m(x)\right)$$

$$= \int \left(\sum_n a_n \chi_n\right)^* \sum_m a_m q_m \chi_m$$

$$= \sum_{n,m} a_n^* a_m q_m \underbrace{\int \chi_n^* \chi_m}_{\delta_{nm}}$$

$$= \sum_n \underbrace{|a_n|^2}\, \underbrace{q_n}$$

PROBABILITY THAT RESULT OF SINGLE MEASUREMENT OF Q GIVES q_n

POSSIBLE RESULTS OF SINGLE MEAS. OF Q

NOTE: BY INSERTING Q = 1 IN ABOVE GET

$$\int_{-\infty}^{\infty} |\psi|^2 dx = \sum_n |a_n|^2 = 1 \checkmark$$

EXAMPLE:

INFINITE SQ. POT'L WELL

KNOW $H\phi_n = E_n \phi_n$ WITH

$$\phi_n = \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a} \qquad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

NOTE THAT THESE ARE NOT MOM'M E'FNCS

$$-i\hbar \frac{\partial \phi_n}{\partial x} = (-i\hbar)\sqrt{\frac{2}{a}} \frac{n\pi}{a} \underline{\cos \frac{n\pi x}{a}} \neq \text{const.} \times \phi_n$$

BUT EASY TO SEE (MOM'M E'STATES)

$$\tilde{\phi}_p = \frac{1}{\sqrt{a}} e^{ipx/\hbar} \quad \text{SATISFY} \quad -i\hbar \frac{\partial \tilde{\phi}_p}{\partial x} = p\,\tilde{\phi}_p$$

NOW WRITE ENERGY E'FNS IN TERMS OF $\tilde{\phi}_p$

$$\phi_n = \sqrt{\frac{2}{a}} \frac{1}{2i}\left(e^{in\pi x\hbar/a\hbar} - e^{-in\pi x\hbar/a\hbar}\right)$$

$$= \frac{1}{i\sqrt{2}} \tilde{\phi}_{p_n} - \frac{1}{i\sqrt{2}} \tilde{\phi}_{-p_n} \qquad \text{WHERE } p_n = \frac{n\pi\hbar}{a}$$

SO IF PARTICLE IS IN ENERGY E'STATE ϕ_n

AND WE MEASURE MOM'M WE FIND

$+p_n$ WITH PROB $= \left|\frac{1}{i\sqrt{2}}\right|^2 = \frac{1}{2}$

$-p_n$ " " $= \left|\frac{-1}{i\sqrt{2}}\right|^2 = \frac{1}{2}$