Quantum Mechanics

0 Introduction

- $[\hbar] = ML^2T^{-1}$, may be thought of as a measure of the "strength" of quantum effects. We recover the classical limit as $\hbar \to 0$.

- Light Quanta: $E = \hbar\omega$, $p = \hbar k$ $\left(k = \frac{2\pi}{\lambda}\right)$ ← wavenumber.

- Photoelectric Effect: $K = \hbar\omega - W$ ← work function.
  ↑ KE of emitted particles

- Bohr model of the atom: Bohr quantisation condition quantises angular momentum : $L = mrv = n\hbar$.

Then: using $F = -\frac{e^2}{4\pi\varepsilon_0 r^2}$, we get:

$$\left.\begin{aligned} r_n &= \frac{4\pi\varepsilon_0\hbar^2 n^2}{me^2} \\ v_n &= \frac{e^2}{4\pi\varepsilon_0 n\hbar} \end{aligned}\right\} \Rightarrow E_n = -\frac{1}{2}m\left(\frac{e}{4\pi\varepsilon_0\hbar}\right)^2 \cdot \frac{1}{n^2}$$

The Bohr radius is defined to be $r_1 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \simeq 5.11 \times 10^{-11}\,m$.

1 Wavefunctions + the Schrödinger Equations

- Given a 1-D wavefunction, $\psi(x)$, we have:

$$\mathbb{P}(\text{particle in } [a,b]) = \int_a^b |\psi(x)|^2\,dx$$

So, the normalisation condition is: $\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1$.

- Gaussian wavepacket:

$$\psi(x) = C \exp\left\{-\frac{(x-c)^2}{2\alpha}\right\}$$

Then $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = |C|^2 \int_{-\infty}^{\infty} \exp\left\{-\frac{(x-c)^2}{\alpha}\right\} dx = |C|^2 (\alpha\pi)^{\frac{1}{2}}$

$$\Rightarrow C = \left(\frac{1}{\alpha\pi}\right)^{1/4} (e^{i\theta})$$

← factor which we take to be 1.

- We do require that wavefunctions are normalisable, i.e. $\int_{-\infty}^{\infty} |\psi(x)|^2 dx < \infty$, in order that ψ and $\lambda\psi$ represent the same state. Mathematically, non-normalisable wavefunctions are useful but require more

- Operators:
  1) Position: $\hat{x}\psi = x\psi(x)$
  2) Momentum: $\hat{p}\psi = -i\hbar\psi'(x)$
  3) Energy: $H\psi = -\hbar^2 \frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)$

e.g. $\psi(x) = Ce^{ikx}$ is a momentum eigenstate:

$\hat{p}\psi = -i\hbar\psi' = (\hbar k)\psi \Rightarrow$ eigenvalue is $\hbar k$.

and, for $V=0$, $H\psi = \frac{\hbar^2 k^2}{2m}\psi \rightarrow E = \frac{\hbar^2 k^2}{2m} \left(= \frac{p^2}{2m}\right)$.

We note that $|\psi(x)|^2 = |C|^2$, so only normalisable on finite interval.

Time-Dependent Schrödinger Equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

Seperating variables, and writing $\Psi(\underline{x},t) = \psi(\underline{x})T(t)$

$$\Rightarrow (*)\ i\hbar \frac{\partial T}{\partial t} = ET \quad \text{and} \quad H\psi = E\psi$$

↑ separation constant.

The solution to $(*)$ is $T(t) = \exp\left(-\frac{iEt}{\hbar}\right)$

$$\Rightarrow \underline{\Psi(x,t) = \psi(\underline{x}) \exp\left\{-\frac{iEt}{\hbar}\right\}}$$ STATIONARY STATE.

where $\psi(\underline{x})$ is an eigenfunction of the Hamiltonian.

- Conservation of probability + probability density

Let $P(\underline{x},t) = |\Psi(\underline{x},t)|^2$, then P obeys:

$$\underline{\frac{\partial P}{\partial t} = -\underline{\nabla} \cdot \underline{j}}$$ ← probability current.

where $\underline{j}(\underline{x},t) = -\frac{i\hbar}{2m}\left\{\Psi^* \cdot \underline{\nabla}\Psi - \underline{\nabla}\Psi^* \cdot \Psi\right\}$

We may prove this by considering $P = \Psi\Psi^*$ and using the Schrödinger equation. (N.B we must assume V is real).

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2 Some examples in 1D.

First take the case $V(x) = \mathcal{U}$.

i) For $\mathcal{U} > E$, we have:

$$\psi'' - k^2\psi = 0 \quad \text{where} \quad \left(\mathcal{U} - E = \frac{\hbar^2 k^2}{2m}\right)$$

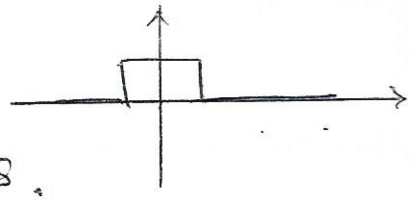
$$\Rightarrow \underline{\psi = Ae^{kx} + Be^{-kx}}.$$

ii) For $\mathcal{U} < E$, we have:

$$\psi'' + k^2\psi = 0 \quad \text{where} \quad \left(E - \mathcal{U} = \frac{\hbar^2 k^2}{2m}\right)$$

$$\Rightarrow \underline{\psi = Ae^{ikx} + Be^{-ikx}}$$

We may now examine situations e.g potential barriers where V has only a finite discontinuity.



We insist that ψ and ψ' are continuous.

- For normalisable solutions, we see that we require $\psi(x) \to 0$ as $x \to \pm\infty$. (So in the case $V \to 0$ as $x \to \pm\infty$, these solutions have $E<0$).

e.g Infinite well (width $2a$).

General solution is: $\psi = A\cos kx + B\sin kx$. $\left(\frac{\hbar^2 k^2}{2m} = E\right)$

Then boundary conditions give:

$$A\cos ka \pm B\sin ka = 0 \Rightarrow A\cos ka = B\sin ka = 0$$

So, i) $B=0$, $ka = \frac{n\pi}{2}$, $n = 1, 3, \ldots$

ii) $A=0$, $ka = \frac{n\pi}{2}$, $n = 2, 4, \ldots$

which give allowed energy levels of $E_n = \frac{\hbar^2 \pi^2 n^2}{8ma^2}$

and $$\psi_n(x) = \left(\frac{1}{a}\right)^{\frac{1}{2}} \begin{cases} \cos \frac{n\pi x}{2a} & n \text{ odd} \\ \sin \frac{n\pi x}{2a} & n \text{ even} \end{cases}$$

- Parity: Consider a symmetrical potential $(V(x) = V(-x))$.

Then, given $H\psi(x) = E\psi(x)$, we see that $\psi(-x)$ is an eigenstate of H with eigenvalue E iff $\psi(x)$ is also. So; either:

i) $\psi(x)$ and $\psi(-x)$ represent the same state i.e $\psi(x) = \eta\psi(-x)$.

which, since it is true $\forall x$ gives:

$$\psi(x) = \eta^2\psi(x) \Rightarrow \eta = \pm 1.$$

So: $\psi(-x) = \pm\psi(x)$. Then ψ has even\odd parity if $\eta = +1 \backslash -1$ respectively.

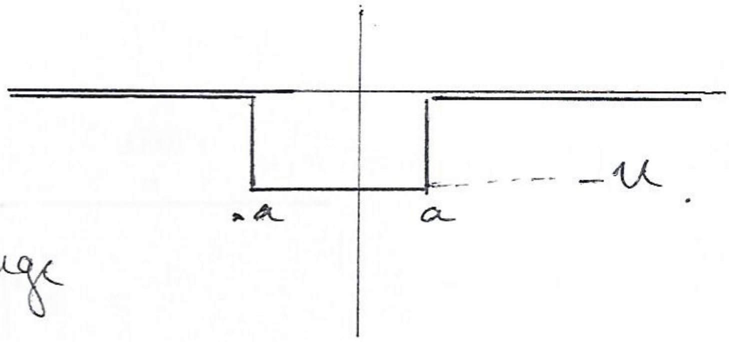
Or: ii) $\psi(x)$ and $\psi(-x)$ represent diff. states, then defining:

$\psi_\pm(x) = \alpha\left(\psi(x) \pm \psi(-x)\right)$, $\psi_\pm$ are also eigenstates of energy E and by construction $\psi_\pm(x) = \pm\psi_\pm(-x)$.

So we may restrict our attention to states of definite parity.

e.g <u>Potential Well.</u>

$$V(x) = \begin{cases} -U & |x|<a \\ 0 & |x|>a \end{cases}$$



We seek for energy levels in range

$$-U<E<0.$$

Set: $U+E = \frac{\hbar^2 k^2}{2m} > 0$ and $E = -\frac{\hbar^2 K^2}{2m}$.

noting $\boxed{k^2 + K^2 = \frac{2mU}{\hbar^2}}$

we get: $\begin{cases} \psi'' + k^2\psi = 0 & |x|<a \\ \psi'' - K^2\psi = 0 & |x|>a \end{cases}$

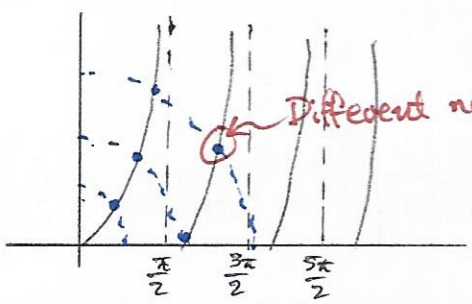
Considering even parity solutions:

$$\psi = \begin{cases} A\cos kx & |x|<a \\ Be^{-K|x|} & |x|>a \end{cases}$$ and applying BC's at $x=a$:

$$\Longrightarrow \left.\begin{aligned} A\cos ka &= Be^{-Ka} \\ -Ak\sin ka &= -KBe^{-Ka} \end{aligned}\right\} \Rightarrow k\tan ka = K.$$

Letting $\xi = ak$, $\eta = aK$, we get:

$$\eta = \xi\tan\xi \quad \text{and} \quad \xi^2 + \eta^2 = \frac{2ma^2U}{\hbar^2}$$



Different no. of bound energy states depending on magnitude of $\frac{2ma^2U}{\hbar^2}$.

- The Harmonic Oscillator.

We take $V(x) = \frac{1}{2}m\omega^2 x^2$, noting that near equilibrium points,

$$V(x) = V(x_0) + \frac{1}{2}V''(x_0)\,(x-x_0)^2 + \cdots$$ for an arbitrary potential.

We find normalisable solutions to:

$$H\psi = -\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}m\omega^2 x^2\psi = E\psi.$$

To simplify, define $y = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x$ and $\varepsilon = \frac{2E}{\hbar\omega}$

$$\Rightarrow \quad -\frac{d^2\psi}{dy^2} + y^2\psi = \varepsilon\psi \qquad (*)$$

For $y^2 >> \varepsilon$, $y^2\psi >> \varepsilon\psi$, so $e^{-\frac{1}{2}y^2}$ solves $(*)$ asymptotically.

Then, wlog, let $\psi = f(y)e^{-\frac{1}{2}y^2}$.

$$\Rightarrow \quad \frac{d^2f}{dy^2} - 2y\frac{df}{dy} + (\varepsilon-1)y = 0$$

HERMITE'S EQUATION.

Let $f(y) = \sum_{r\geq 0} a_r y^r$.

$$\Rightarrow \quad \sum_{r\geq 0}\left\{(r+2)(r+1)a_{r+2} + (\varepsilon-1-2r)a_r\right\}y^r = 0$$

$$\Rightarrow \quad a_{r+2} = \frac{2r+1-\varepsilon}{(r+2)(r+1)}a_r \qquad (r\geq 0).$$

where a_0 and a_1 may be chosen independently, generating two linearly indep. even/odd parity solutions.

We require that $f(y)$ is suppressed by $e^{-\frac{1}{2}y^2}$ so that the solutions are normalisable. Now, when y is large, unless the coefficients vanish:

$$\frac{a_p}{a_{p-2}} \sim \frac{1}{p} \Rightarrow \psi \text{ grows as } e^{\frac{1}{2}y^2}$$

which is non-normalisable. So we require f to terminate.

This occurs iff $\varepsilon = 2n+1$ for some n.

For each n, only one parity solution is normalisable.

So, for n even: $a_{r+2} = \frac{2r-2n}{(r+2)(r+1)} a_r$ for r even and $a_r = 0$ for r odd.

and vice versa for n odd.

Then, we see that:

$$\left.\begin{aligned} h_0(y) &= a_0 \\ h_1(y) &= a_1 y \\ h_2(y) &= a_0(1-2y^2) \\ h_3(y) &= a_1\left(y - \tfrac{2}{3}y^3\right) \\ &\vdots \end{aligned}\right\} \text{Hermite polynomials.}$$

We may restore the constants to see that:

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

and $$\boxed{\psi_n(x) = h_n\left\{\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x\right\} \exp\left(-\frac{1}{2}\frac{m\omega}{\hbar}x^2\right)}.$$

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3 Expectation + Uncertainty.

- Recall that

$$\left\{\begin{aligned} &(\phi, \psi) = \int_{-\infty}^{\infty} \phi(x)^* \psi(x)\, dx. \\ \text{and } &(\phi, \alpha\psi) = \alpha(\phi, \psi) = (\alpha^*\phi, \psi) \\ \text{and } &(\phi, \psi) = (\psi, \phi)^* \end{aligned}\right.$$

- Now, expectation of any observable H on the state ψ is:

$$\langle H \rangle_\psi = (\psi, H\psi).$$

The interpretation is that the expectation is the mean of the results obtained by measuring the observable many ~~times~~ with the system prepared in a state ψ before each measurement.

- Uncertainty: $(\Delta H)^2_\psi = \langle \{\hat{H} - \langle \hat{H} \rangle_\psi\}^2 \rangle_\psi$

$$(\Delta H)^2_\psi = \langle H^2 \rangle_\psi - \langle H \rangle^2_\psi .$$

- Hermition operator: Q is hermitian iff $\forall \phi, \psi$ normalisable:

$$(\phi, Q\psi) = (Q\phi, \psi).$$

i.e $\int \phi^* Q\psi \, dx = \int (Q\phi)^* \psi \, dx$

We see also that $(\psi, Q\psi) = (Q\psi, \psi) = (\psi, Q\psi)^*$

$$\Rightarrow (\psi, Q\psi) = \langle Q \rangle_\psi \in \mathbb{R} .$$

We may show that $\langle \hat{x} \rangle_\psi$, $\langle \hat{p} \rangle_\psi$ and $\langle \hat{H} \rangle_\psi$ are all hermitian by suitable integration by parts.

and further that, letting $X = \hat{x} - \alpha$, $P = \hat{p} - \beta$

$$(\psi, X^2\psi) = (X\psi, X\psi) = \|X\psi\|^2 \geq 0$$

and $(\psi, P^2\psi) = \|P\psi\|^2 \geq 0$

$$\Rightarrow (\Delta x)^2_\psi \geq 0 \text{ and } (\Delta p)^2_\psi \geq 0 .$$

- Ehrenfest's Theorem:

$$\begin{cases} \frac{d}{dt} \langle \hat{x} \rangle_\psi = \frac{1}{m} \langle \hat{p} \rangle_\psi \\ \frac{d}{dt} \langle \hat{p} \rangle_\psi = - \langle V'(\hat{x}) \rangle_\psi \end{cases}$$

Pf: $\frac{d}{dt} \langle \hat{x} \rangle_\psi = (\dot{\psi}, \hat{x}\psi) + (\psi, \hat{x}\dot{\psi})$

$$= \left(\frac{1}{i\hbar} H\psi, \hat{x}\psi\right) + \left(\psi, \hat{x}\left(\frac{1}{i\hbar} H\right)\psi\right)$$

$$= -\frac{1}{i\hbar}(\psi, H\hat{x}\psi) + \frac{1}{i\hbar}(\psi, \hat{x}H\psi)$$ since H hermitian.

But, $(\hat{x}H - H\hat{x})\psi = -\frac{\hbar^2}{2m}(x\psi'' - (x\psi)'') + (xV\psi - Vx\psi)$

$$= -\frac{\hbar^2}{m}\psi' = \frac{i\hbar}{m}\hat{p}\psi .$$

and similarly for the second equation.

- <u>Heisenberg's Uncertainty Principle</u>: If ψ is any normalised state, then:

$$(\Delta x)_\psi (\Delta p)_\psi \geq \frac{\hbar}{2}.$$

- <u>Commutation relations</u>: We define the commutator $[\cdot,\cdot]$ to be:

$$[Q, H] = QH - HQ.$$

For example, $[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$.
and from before: $[X, P] = i\hbar$ also. $(X = \hat{x} - \alpha,$
$P = \hat{p} - \beta).$

The proof of the uncertainty principle comes by considering:

$$X = \hat{x} - \alpha, \quad P = \hat{p} - \beta \quad \text{with } \alpha = \langle \hat{x} \rangle_\psi$$
$$\beta = \langle \hat{p} \rangle_\psi$$

Then: $(\Delta x)^2_\psi = \|X\psi\|^2$ and $(\Delta p)^2_\psi = \|P\psi\|^2$

Then:
$$\begin{aligned}(\Delta x)_\psi (\Delta p)_\psi &= \|X\psi\| \|P\psi\| \\ &\geq |(X\psi, P\psi)| \\ &\geq |\mathrm{Im}\{(X\psi, P\psi)\}| \\ &\geq \left|\frac{1}{2i}\{(X\psi, P\psi) - (P\psi, X\psi)\}\right| \\ &= \left|\frac{1}{2i}(\psi, [X,P]\psi)\right| = \left|\frac{\hbar}{2}(\psi,\psi)\right| = \frac{\hbar}{2}.\end{aligned}$$

4 More results in 1D.

- A wavepacket is a wavefunction localised in space.

e.g. Gaussian wavepacket:

$$\Psi_0(x,t) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\gamma(t)^{\frac{1}{2}}} \exp\left\{-\frac{x^2}{2\gamma(t)}\right\}$$

for some $\gamma(t)$. Now, if $V=0$, then $\Psi_0(x;t)$ is a soln. of the time-dependent SE if:

$$\boxed{\gamma(t) = \alpha + \frac{i\hbar}{m}t}.$$

Then, $P_0(x;t) = |\Psi_0(x;t)|^2 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{1}{|\gamma(t)|} \exp\left\{\frac{-x^2}{|\gamma(t)|^2}\right\}$

We may also consider a moving particle which has a wavefunction of the form:

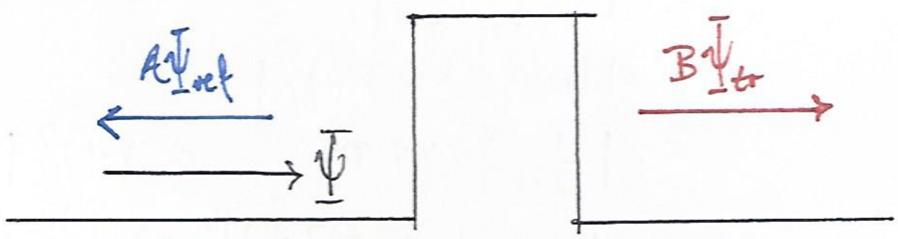
$$\underline{\Psi_u(x;t) = \Psi_0(x-ut;t) \exp\left(i\frac{mu}{\hbar}x\right) \exp\left(-i\frac{mu^2}{2\hbar}t\right)}.$$

whose probability density is:

$$P_u(x;t) = |\Psi_u(x,t)|^2 = P_0(x-ut,t).$$

and we may show that $\langle \hat{p} \rangle_{\Psi_u} = mu$

- <u>Scattering</u>: invlves sending waves towards obstacles and seeing the reflection + transmission properties.



N.B Ψ, Ψ_{tr}, Ψ_{ref} are all normalised.

Now, the probabilities of reflection and transmission are:

$$P_{ref} = |A|^2, \quad P_{tr} = |B|^2$$

To ensure mathematical clarity, we usually consider a beam of particles $\Psi(x;t)$, which is not necessarily normalisable. Now, $|\Psi(x;t)|^2$ represents the density of particles.

We may also calculate $j = -\frac{i\hbar}{2m}\{\psi^*\psi' - \psi\psi'^*\}$.

we are broadly interested in momentum eigenstates,

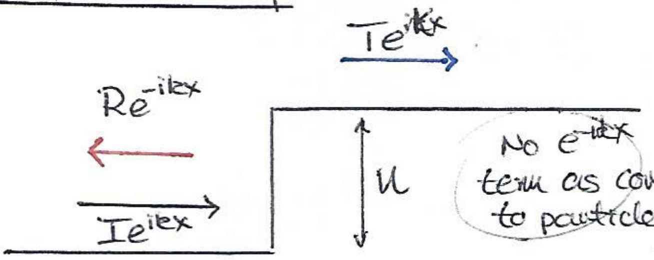
$$\psi(x) = Ce^{ikx}.$$

Then, $|\psi|^2 = |C|^2$ and $j = \frac{\hbar k}{m}|C|^2$

Then, the reflection and transmission probabilities are:

$$P_{tr} = \frac{|j_{tr}|}{|j_{inc}|}, \quad P_{ref} = \frac{|j_{ref}|}{|j_{inc}|}$$

e.g Potential step with $E > U$. (N.B for $E<U$, we get $P_{tr} = 0$ and $P_{ref} = 1$) (Although $\psi \neq 0$ for $x>0$).



No e^{-iKx} term as corresponds to particle sent in from right.

Let $E = \frac{\hbar^2 k^2}{2m}$, $E - U = \frac{\hbar^2 K^2}{2m}$, then the SE becomes:

$$\begin{cases} \psi'' + k^2\psi = 0 & (x<0) \\ \psi'' + K^2\psi = 0 & (x>0) \end{cases}$$

Matching ψ, ψ' at $x=0$ gives:

$$\left.\begin{cases} I + R = T \\ ikI - ikR = iKT \end{cases}\right\} \Rightarrow R = \frac{k-K}{k+K}I, \quad T = \frac{2k}{k+K}I$$

So; $P_{ref} = \left\{\frac{(k-K)}{(k+K)}\right\}^2$, $P_{tr} = \frac{4kK}{(k+K)^2}$

since $\begin{cases} j_{ref} + j_{inc} = |I|^2\frac{\hbar k}{m} - |R|^2\frac{\hbar k}{m} \\ j_{tr} = |T^2|\frac{\hbar K}{m}. \end{cases}$

- Potential barrier works similarly but the continuity equations are much more fiddly.

Ultimately though, it illustrates the principle of tunnelling, with a non-zero probability of transmission for $E<U$.

- General features of stationary states.

i) Bound state solutions. $(E<0)$

If we want ψ to be normalisable, we wish to have.

$$\psi \sim \begin{cases} Ae^{\kappa x} & x \to -\infty \\ Be^{-\kappa x} & x \to +\infty \end{cases}$$

Since this is an overdetermined system, bound states exist only for certain $E \Rightarrow$ quantised. The lowest energy state is the ground state, all others are excited states.

ii) Scattering state solutions. $(E>0)$.

Here we have:

$$\psi \sim \begin{cases} Ie^{ikx} + Re^{-ikx} & x \to -\infty \\ Te^{ikx} & x \to +\infty. \end{cases}$$

There are solutions for any E here, and give:

$$j \sim \begin{cases} j_{inc} + j_{ref} = |I|^2 \frac{\hbar k}{m} - |R|^2 \frac{\hbar k}{m} & x \to -\infty \\ j_{tr} = |T|^2 \frac{\hbar k}{m} & x \to +\infty \end{cases}$$

and $P_{ref} = |A_{ref}|^2 = \frac{|j_{ref}|}{|j_{inc}|}$, $P_{tr} = |A_{tr}|^2 = \frac{|j_{tr}|}{|j_{inc}|}$

where $A_{ref}(k) = \frac{R}{I}$, $A_{tr}(k) = \frac{T}{I}$ are the amplitudes.

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5 Axioms for Quantum Mechanics.

A1 • States of a quantum system correspond to non-zero elements of a complex vector space, V, with ψ and $\alpha\psi$ physically equivalent for all $\alpha \in \mathbb{C}\setminus\{0\}$. There exists an inner product on this space satisfying normal properties.

An operator, $A: V \to V$ satisfies:

$$A(\alpha\phi + \beta\psi) = \alpha A\phi + \beta A\psi.$$

and, an operator is Hermitian if:

$$Q = Q^{+}$$

where Q^{+} is defined to be the unique operator satisfying:

$$(\phi, Q^{+}\psi) = (Q\phi, \psi).$$

The set of eigenvalues of Q is called the <u>spectrum</u> of Q.

{An observable/measurable quantity corresponds to Hermitian operators.}

• <u>Measurement</u> We begin with results about Hermitian operators:

i) Eigenvalues of H are real.
ii) Eigenstates of H with distinct eigenvalues are orthogonal.
iii) Any state can be written as a (possibly infinite) linear combination of eigenstates.

Pf: i) $(\chi, Q\chi) = (Q\chi, \chi)$

$\Rightarrow (\chi, \lambda\chi) = (\lambda\chi, \chi)$

$\rightarrow \lambda(\chi,\chi) = \lambda^{*}(\chi,\chi) \Rightarrow (\lambda - \lambda^{*})(\chi,\chi) = 0$

But $(\chi,\chi) \neq 0 \Rightarrow \boxed{\lambda = \lambda^{*}}$

ii) Let $Q\phi = \mu\phi$, $Q\psi = \lambda\psi$

$\Rightarrow (\phi, Q\psi) = (Q\phi, \psi)$

$\rightarrow (\phi, \lambda\psi) = (\mu\phi, \psi) \rightarrow (\lambda - \mu)(\phi, \psi) = 0$

$\rightarrow (\lambda = \mu)$ or $\boxed{(\phi, \psi) = 0}$

Now consider an observable Q with distinct spectrum and normalised eigenstates $\{\chi_n\}$. Then any state, ψ, may be written as:

$$\boxed{\psi = \sum_n{}' \alpha_n \chi_n}$$

with $Q\chi_n = \lambda_n \chi_n$ and $(\chi_m, \chi_n) = \delta_{mn}$.

Then, $\boxed{\alpha_n = (\chi_n, \psi)}$

A2 • The outcome of a measurement is some eigenvalue of Q.

A3 • The probability of obtaining λ_n is:

$$P_n = |\alpha_n|^2$$

A4 • The measurement is instantaneous and forces the system into the state χ_n.

$\boxed{\text{N.B}}$

$$(\psi, \psi) = \left(\sum{}' \alpha_m \chi_m, \sum{}' \alpha_n \chi_n\right)$$

$$= \sum_{m,n}{}' \alpha_m^* \alpha_n (\chi_m, \chi_n)$$

$$= \sum_{m,n}{}' \alpha_m^* \alpha_n \delta_{mn}$$

$$= \sum_n{}' |\alpha_n|^2 = \sum_n{}' P_n = 1.$$ So ψ is normalised.

• Expressions for expectation + uncertainty.

(i) $\langle Q \rangle_\psi = (\psi, Q\psi) = \sum{}' \lambda_n |\alpha_n|^2 = \sum{}' \lambda_n P_n$ (*)

(ii) $(\Delta Q)_\psi^2 = \langle (Q - \langle Q \rangle_\psi)^2 \rangle_\psi = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2$

$$= \sum{}' (\lambda_n - \langle Q \rangle_\psi)^2 P_n$$ (*)

{So, ψ is an eigenstate of $Q \Leftrightarrow \langle Q \rangle_\psi = \lambda_r$, $(\Delta Q)_\psi = 0$.}

- Evolution in time.

A5 • The states of a quantum system $\Psi(t)$ obey Schrödinger's equation:

$$i\hbar \dot{\Psi} = H \Psi$$

where H, the Hamiltonian, is a hermitian operator. This holds at all times $\boxed{\text{except}}$ when a measurement is made.

Stationary states: Consider the energy eigenstates with:

$$H \psi_n = E_n \psi_n$$

Then, from before, there are simple solutions of the SE of the form:

$$\Psi_n(t) = \psi_n \exp\left(-\frac{iE_n t}{\hbar}\right).$$

$$\Rightarrow \quad \Psi(t) = \sum_n \alpha_n \exp\left(-\frac{iE_n t}{\hbar}\right) \psi_n$$

for the evolution from a state:

$$\Psi(0) = \sum_n \alpha_n \psi_n .$$

- Ehrenfest's Theorem: If Q is any operator with no explicit time dependence, then:

$$i\hbar \frac{d}{dt} \langle Q \rangle_\psi = \langle [Q, H] \rangle_\psi .$$

Pf: $i\hbar \frac{d}{dt} \langle Q \rangle_\psi = (-i\hbar \dot{\psi}, Q\psi) + (\psi, Q i\hbar \dot{\psi})$

$= (-H\psi, Q\psi) + (\psi, QH\psi)$

$= (\psi, (QH - HQ)\psi) = \langle [Q, H] \rangle_\psi$

• Continuous spectra: To solve the issue of non-normalisability, we restrict to a smaller fixed region of length l with periodic boundary conditions. $\psi(x+l) = \psi(x)$.

Consider $Q = \hat{p} = -i\hbar \frac{d}{dx}$, which has eigenstates

$$\chi_n = \frac{1}{\sqrt{l}} e^{ik_n x} \quad , \quad k_n = \frac{2\pi n}{l} .$$

$$\Rightarrow \lambda_n = \hbar k_n \text{ which are discrete.}$$

Then $\psi = \sum_i a_n \chi_n$ is a complex Fourier series. The limit that allows us to move back to a continuous spectra, $l \to \infty$ transforms this Fourier series into a Fourier integral.

• Degeneracy + simultaneous measurement.

{Definition}: For an observable Q, the degeneracy of an eigenvalue is the number of linearly independent eigenstates with eigenvalue λ. An eigenvalue is non-degenerate if it has degeneracy 1, and degenerate otherwise.

Thus, in order to distinguish between degenerate states, we must make another measurement. This is allowed when we have commuting observables.

• Commuting observables $\{A, B\}$ exist if the state χ_n is simultaneously an eigenstate of A and B.

$$\text{i.e } A\chi_n = \lambda_n \chi_n \text{ and } B\chi_n = \mu_n \chi_n .$$

This is equivalent to $\boxed{[A, B] = 0}$ ★

6 Quantum Mechanics in 3D.

- Consider two states $\psi(\underline{x})$ and $\phi(\underline{x})$, then:

$$(\phi, \psi) = \int \phi(\underline{x})^* \psi(\underline{x}) \, d^3\underline{x}$$

Now, $\hat{\underline{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$ i.e $\hat{x}_i \psi = x_i \psi$

and; $\hat{\underline{p}} = -i\hbar \underline{\nabla}$

with the canonical commutation relations:

$$\left\{ [\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij} , \quad [\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0 \right\}$$

- In this course we assume all particles are structureless. i.e may be described in terms of $\hat{x}$, and $\hat{p}$ only.

Now, we have $\hat{\underline{H}} = \dfrac{\hat{\underline{p}}^2}{2m} + V(\hat{\underline{x}}) = -\dfrac{\hbar^2}{2m}\nabla^2 + V(\underline{x})$.

and $\underline{j} = -\dfrac{i\hbar}{2m}\left(\underline{\Psi}^* \underline{\nabla} \underline{\Psi} - \underline{\Psi} \underline{\nabla} \underline{\Psi}^*\right)$

which obeys: $\dfrac{\partial |\psi(\underline{x},t)|^2}{\partial t} = -\underline{\nabla} \cdot \underline{j}$

$$\Rightarrow \frac{d}{dt} \int_V |\Psi(\underline{x},t)|^2 d^3\underline{x} = - \int_{\partial V} \underline{j} \cdot d\underline{S}$$

- $_1$ Separable eigenstate solutions. Consider case in 2D where

$$H\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right)\psi + V(x_1, x_2)\psi = E\psi$$

we look at potentials of the form $V(x_1, x_2) = U_1(x_1) + U_2(x_2)$

$$\Rightarrow H = H_1 + H_2, \quad H_i = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_i^2} + U_i(x_i).$$

Then we look for separable solutions $\chi_1(x_1)\chi_2(x_2) = \psi$.

which yields: $\left(-\frac{\hbar^2}{2m}\frac{X_1''}{X_1}+U_1\right)+\left(-\frac{\hbar^2}{2m}\frac{X_2''}{X_2}+U_2\right)=E\psi$

$$\Rightarrow H_1 X_1 = E_1 X_1 \, , \quad H_2 X_2 = E_2 X_2 \quad \text{with } \boxed{E_1+E_2=E}$$

A classic example is the harmonic oscillator.

$$\Rightarrow E_{n_1,n_2} = \hbar\omega\left(n_1+n_2+\underbrace{1}_{=\frac{1}{2}+\frac{1}{2}}\right)$$

and introduces the degeneracy clearly.

- Separable solutions also appear when when V has some symmetry e.g spherically symmetric $\Rightarrow \psi(x) = R(r)Y(\theta,\phi)$.

- Angular Momentum.

$$\underline{\hat{L}} = \hat{\underline{x}} \times \hat{\underline{p}} = -i\hbar\, \underline{x} \times \underline{\nabla}.$$

which, in components is:

$$L_i = -i\hbar\, \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}.$$

We may show that L is hermitian.

It is also helpful to consider $|\underline{L}|^2$ which is also hermitian:

$$\underline{L}^2 = L_1^2 + L_2^2 + L_3^2.$$

Commutation Relations.

- $[L_i, L_j] = i\hbar\, \varepsilon_{ijk} L_k.$

- $[L^2, L_i] = 0$ — important since we may not measure each individual component.

- $[L_i, \hat{x}_j] = i\hbar\, \varepsilon_{ijk} \hat{x}_k \, , \quad [L_i, \hat{p}_j] = i\hbar\, \varepsilon_{ijk} \hat{p}_k.$

- Spherical polars + spherical harmonics. We define:

$$\begin{cases} x_1 = r\sin\theta\cos\varphi \\ x_2 = r\sin\theta\sin\varphi \\ x_3 = r\cos\theta \end{cases}$$

Taking x_3 as our axis of rotation, we rewrite our angular momentum operators in (r,θ,φ) form, where we consider instead $L_\pm = L_1 \pm iL_2$:

$$L_3 = -i\hbar\frac{\partial}{\partial\varphi}$$

$$L_\pm = L_1 \pm iL_2 = \pm\hbar e^{\pm i\varphi}\left\{\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right\}$$

$$L^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right),$$

noting that these operators include only θ and φ.

Then, $\left\{\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{\hbar^2 r^2}\underline{L}^2\right\}$

Now, since $[L_3, \underline{L}^2] = 0$, there are simultaneous eigenfunctions of the operators, which we shall call $Y_{lm}(\theta,\varphi)$ with $\boxed{l = 0, 1, \ldots}$ and $\boxed{m = 0, \pm1, \pm2, \ldots; \pm l}$.

We have:
$$\left.\begin{matrix}\underline{L}^2 \\ L_3\end{matrix}\right\} Y_{lm}(\theta,\varphi) = \left.\begin{matrix}\hbar^2 l(l+1) \\ \hbar m\end{matrix}\right\} Y_{lm}(\theta,\varphi).$$

N.B. in general we have $Y_{lm}(\theta,\varphi) = \text{const.}\, e^{im\varphi} P_l^m(\cos\theta)$ where $P_l^m(\cos\theta)$ are the associated Legendre functions.

- Joint eigenstates for spherically symmetric potential.

Consider a particle of mass μ in a potential $V(r)$.

Then: $H = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r)$

which may be written as:

$$H = -\frac{\hbar^2}{2\mu} \cdot \frac{1}{r}\frac{\partial^2}{\partial r^2}(r) + \frac{1}{2\mu} \cdot \frac{1}{r^2}\underline{L}^2 + V(r)$$

We may show $[L_i, H] = [L^2, H] = 0$.

which implies we may label our solutions using the eigenvalues of H, L^2 and L_3. So, we have the joint eigenstates:

$$\psi(\underline{x}) = R(r)\, Y_{\ell m}(\theta, \varphi).$$

where $\begin{cases} L^2 Y_{\ell m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, Y_{\ell m}(\theta,\varphi) \\ L^3 Y_{\ell m}(\theta,\varphi) = \hbar m\, Y_{\ell m}(\theta,\varphi). \end{cases}$

N.B $\ell = 0$ is the case of a spherically symmetric solution.

We now solve $H\psi = E\psi$:

$$\Longrightarrow \left[\underbrace{-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}(rR)}_{\text{radial KE}} + \underbrace{\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)R}_{\text{angular KE/ effective potential}} + \underbrace{V(r)R}_{\text{PE}} = ER \right]$$

We often call $R(r)$ the radial part of the wavefunction, and it is often convenient to work with:

$$\boxed{\chi(r) = r R(r)} \quad \text{radial wavefunction.}$$

to obtain the radial Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\chi'' + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\chi + V\chi = E\chi \right] \; *$$

We require some boundary conditions:

(1) We want R to remain finite as $r \to 0$

$$\Rightarrow \left[\chi(r=0) = 0 \right].$$

(2) The normalisation condition is:

$$1 = \int |R(r)|^2 r^2 dr \int |Y_{lm}(\theta,\varphi)|^2 \sin\theta \, d\theta \, d\varphi .$$

$$\Rightarrow \psi \text{ normalisable} \Leftrightarrow \int |R(r)|^2 r^2 dr < \infty$$

$$\Leftrightarrow \left[\int |\chi(r)|^2 dr < \infty \right]$$

e.g <u>Three-dimensional well.</u>

$$V(r) = \begin{cases} 0 & r \geq a \\ -U & r < a . \end{cases}$$

Looking for bound state solutions $-U < E < 0$:

i) $r < a$:

$$\chi'' - \frac{l(l+1)}{r^2}\chi + k^2 \chi = 0 \quad , \quad U + E = \frac{\hbar^2 k^2}{2\mu}$$

ii) $r \geq a$:

$$\chi'' - \frac{l(l+1)}{r^2}\chi - \kappa^2 \chi = 0 , \quad E = -\frac{\hbar^2 \kappa^2}{2\mu}$$

We may solve easily for $l = 0$ and apply $\chi(0) = 0$ and χ, χ' continuous at $r = a$.

$$\Rightarrow \chi(r) = \begin{cases} A \sin kr & r < a \\ B e^{-\kappa r} & r \geq a \end{cases}$$

while matching at $r = a$ fixes $k, \kappa \Rightarrow E$.

For general l, we require spherical Bessel functions.

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7 Hydrogen Atom.

We consider the Coulomb potential:

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

Let $\mu = m_e$, the mass of the electron.

The joint eigenstates of H, L^2 and L^3 are,

$$\phi(\underline{x}) = R(r)\,Y_{lm}(\theta,\varphi).$$

$$(\text{for } l = 0, 1, \ldots, \quad m = 0, \pm 1, \ldots, \pm l)$$

Then, the radial part of the Schrödinger equation is:

$$\left[R'' + \frac{2}{r}R' - \frac{l(l+1)}{r^2}R + \frac{2\lambda}{r}R = K^2 R\right] \quad (*).$$

where $\lambda = \frac{e^2}{4\pi\varepsilon_0\hbar^2}$, $E = -\frac{\hbar^2 K^2}{2m_e}$

We aim to find all normalisation solutions to $(*)$

Now, for large r, we get:

$$[R'' \sim K^2 R] \xrightarrow{r \text{ large}} R \sim e^{-Kr} \text{ for large } r.$$

For small r, R is finite by assumption, so, multiplying through by r^2 and discounting r^2R'' and rR'

$$\rightarrow \left[r^2 R'' + 2rR' - l(l+1)R \sim 0\right]$$

$$\rightarrow R \sim r^l \quad r \text{ small.}$$

So, trying a solution of the form $R(r) = Cr^l e^{-Kr}$:

We may see that the $r^{l-2}e^{-Kr}$ and $r^l e^{-Kr}$ terms will match. However, the $r^{l-1}e^{-Kr}$ must satisfy:

$$2(l r^{l-1})(-\kappa e^{-\kappa r}) + 2(r^{l-1})(-\kappa e^{-\kappa r})$$

$$+ 2\lambda r^{l-1} e^{-\kappa r} = 0$$

$$\Rightarrow \boxed{(l+1)\kappa = \lambda}$$

which gives bound state energies:

$$E_n = -\frac{\hbar^2}{2m_e}\frac{\lambda^2}{n^2} = -\frac{1}{2}m_e\left(\frac{e^2}{4\pi\varepsilon_0\hbar^2}\right)^2 \cdot \frac{1}{n^2}, \quad \boxed{n = l+1}$$

- General solution:

we try solutions of the form:

$$\boxed{R(r) = e^{-\kappa r} f(r)}$$

$$\Longrightarrow f'' + \frac{2}{r}f' - \frac{l(l+1)}{r^2}f = 2\left(\kappa f' + (\kappa-\lambda)\frac{f}{r}\right)$$

The equation is regular singular at $r=0$, so we try:

$$f(r) = \sum' a_p r^{p+\sigma}, \quad a_0 \neq 0.$$

$$\Rightarrow \sum' \{(p+\sigma)(p+\sigma-1) - l(l+1)\} a_p r^{p+\sigma-2}$$

$$= \sum' 2(\kappa(p+\sigma-1) - \lambda) a_p r^{p+\sigma-1}$$

Giving us the indicial equation:

$$\sigma(\sigma+1) - l(l+1) = (\sigma - l)(\sigma + l + 1) = 0$$

$$\Rightarrow \sigma = l \quad \text{or} \quad \cancel{\sigma = -(l+1)}$$ dismiss since $\rightarrow f$ singular at $r=0$.

Then, with $\sigma = l$:

$$\boxed{a_p = \frac{2(\kappa(p+l) - \lambda)}{p(p+2l+1)} a_{p-1}} \quad p \geq 1.$$

Unless this series terminates,

$$\frac{a_p}{a_{p-1}} \sim \frac{2\kappa}{p} \quad \text{as } p \to \infty$$

which matches behaviour of $r^0 e^{2\kappa r}$. So $R(r)$ is normalisable only if series terminates.

$$\Rightarrow \boxed{\lambda = \kappa n} \quad \text{for some } n \geq l+1.$$

which generates the same energy levels

$$E_n = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0 \hbar^2}\right)^2 \cdot \frac{1}{n^2}$$

n is called the principal quantum number.

and l, m may take on values: for a given n.

$$l = 0, 1, \ldots, n-1$$
$$m = 0, \pm 1, \ldots, \pm l.$$

Then: $\{\psi_{nlm}(\underline{x}) = R_{nl}(r) Y_{lm}(\theta, \varphi)\}$

where $\{R_{nl}(r) = r^l g_{nl}(r) e^{-\lambda r/n}\}$

$\propto$ to associated Laguerre polynomials.

We note that there exist spherically symmetric solutions

$$\psi_{n00}(\underline{x}) = g_{n0}(r) e^{-\lambda r/n}.$$

and the degeneracy of each energy level E_n is:

$$\sum_{l=0}^{n-1} \sum_{m=-l}^{l} 1 = \sum_{l=0}^{n-1} (2l+1) = n^2.$$

• Assumptions: ① Proton stationary.
② Spin $\Rightarrow$ degeneracy of $2n^2$.
③ Many electron atoms $\Rightarrow$ predicted energy levels.