Quantum Mechanics.

Classical Mechanics.

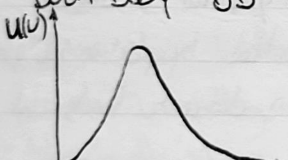
- Explains "large" and "slow" systems.
    - large here is defined by a size much greater than the atomic scale ($1 \text{Å} = 10^{-10}$ m)
    - speed here is defined by a speed much less than the speed of light ($\simeq 3 \times 10^8$ m/s).
- for "small" systems, use quantum mechanics. [Heisenberg & Schrodinger 1925-1926].
- for "fast" systems, use relativistic mechanics (special relativity). [Einstein 1905]

Motivation for Quantum Mechanics

- 3 experiments could not be explained by classical physics (Mechanics, optics, EM).
    1. "Black Body" Radiation - "explained" by Planck in 1899
    2. "Photo electric Effect - "explained" by Einstein in 1905
    3. Emission Spectrum of atomic hydrogen - "explained" by Bohr in 1913

  } Old quantum theory.

"Black Body" Radiation

- "Black Body" = BB = absorbs all EM waves falling into BB and is reemitted.
- 

  $U(\nu)$ - energy density of EM radiation per unit volume.

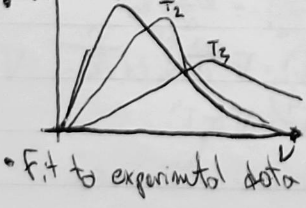
  ν - frequency of EM radiation

- Experimental Realization: ① 

  cavity

  walls @ temperature T.

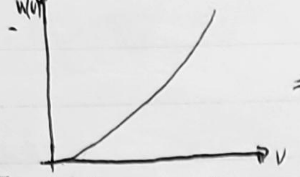
  ② "3K" cosmic microwave background radiation.

- 

  $T_1 < T_2 < T_3$.

- Fit to experimental data: - $U(\nu) \simeq \nu^3 \frac{1}{e^{\text{const} \frac{\nu}{T}} - 1}$
    - Low freq - $U(\nu) = \frac{8\pi}{c^3} \nu^2 k_B T$ (Rayleigh-Jeans Formula)
    - High freq - $U(\nu) \simeq \nu^3 \exp(-\text{const.} \frac{\nu}{T})$ (Wiens Law).

- Classical EM & Statistical physics $\Rightarrow u(\nu) = \frac{8\pi}{c^3}\nu^2 k_B T$ @ all freq.



$\Rightarrow$ "Ultraviolet Catastrophe"

- U = total energy of BB radiation $= \int_0^\infty u(\nu)\,d\nu \cdot V$ ← volume of cavity.

$$= \int_0^\infty \frac{8\pi}{c^3}\nu^2 k_B T\,d\nu \cdot V$$

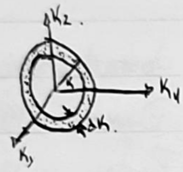
$$= \frac{8\pi}{c^3} k_B T \int_0^\infty \nu^2 d\nu \cdot V \Rightarrow \infty.$$

We see that classical mechanics fails here ($U \neq \infty$).

- Origin of Rayleigh-Jeans - system of plane waves characterized by wave vector $\vec{k}$

- Total energy of the waves @ temperature T, in volume $V \Rightarrow U = V\sum_k \left(\begin{smallmatrix}\text{AVG energy of}\\ \text{wave with } \vec{k}\end{smallmatrix}\right)\left(\begin{smallmatrix}\#\text{ of waves with}\\ \text{wave vector } \vec{k}\end{smallmatrix}\right)$

$k_B T$; $2\times$(# of k-points inside in spherical shell of radius k & thickness dk) ; 2 independent polarizations ; $= 2\times$(Volume of shell) $= 2\times\left(\frac{4\pi k^2}{(2\pi)^3}dk\right)$



$k = 2\pi\frac{\nu}{c}$

$$U = V\int_0^\infty dk\,\frac{8\pi k^2}{(2\pi)^3} k_B T.$$

$$= V\, 8\pi k_B T \int_0^\infty d\nu\,\frac{\nu^2}{c^3}$$

$$= V\int_0^\infty d\nu\, u(\nu) \Rightarrow \text{energy density} = \frac{8\pi}{c^3} k_B T \nu^2$$

- Planck's Revolutionary Ideas.
  1. The black body is a set of oscillators with frequencies ν
  2. Energies of the Planck oscillator are quantized: $E = nh\nu$; $n = 1, 2, \ldots$; h = planck's constant.
  3. EM radiation can be absorbed or emitted by portions ("quanta"), corresponding to transitions between discrete levels of the oscillators

$h \approx 6.63\times10^{-34}\frac{m^2 kg}{s}$

has the same dimensionality as angular momentum.

- Planck's Formula: $u(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{k_B T}} - 1}$
  - At low freq.: $\frac{h\nu}{k_B T} \ll 1 \Rightarrow \nu \ll \frac{k_B T}{h}$

$e^x - 1 \Rightarrow x = \frac{h\nu}{k_B T}$ use taylor series for e^x

$e^x = 1 + x + \frac{x^2}{2} + \ldots$ ($e \ll 1$)

$\therefore u(\nu) \approx \frac{8\pi h\nu^3}{c^3}\frac{1}{\frac{h\nu}{k_B T}} = \frac{8\pi\nu^2}{c^3}k_B T$

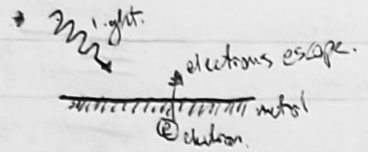
- Total energy of BB Radiation: $U = V\int_0^\infty d\nu\, u(\nu) = V\frac{8\pi h}{c^3}\int_0^\infty d\nu\,\frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} = V\frac{8\pi^4}{c^3}\left(\frac{k_B T}{h}\right)\int_0^\infty dx\,\frac{x^3}{e^x - 1}$; $\frac{\pi^4}{15}$

$$= V\frac{8\pi^5 k_B^4}{15h^3c^3}T^4 = V\sigma T^4$$

σ ← stefan-Boltzmann constant

- UV Catastrophe fixed.
- Classically: $h \to 0 \Rightarrow \sigma \to \infty \Rightarrow$ UV catastrophe

Photoelectric Effect

• 

$\frac{mv^2}{2}$ = kinetic energy of electron after escape.

$\frac{mv^2}{2} = -W + E_{light}$; Work function!! $W > 0$.

∴ • Minimum Energy needed to remove electron is when $E_{light} = W$.

∴ • It takes a minimum ~~energy~~ frequency (not intensity) of the light to remove electrons.

• Classically: energy of any ~~wave~~ wave $E_{wave} \sim \nu^2 A^2$ — ν = frequency, A = Amplitude.

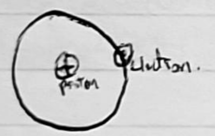
∴ • $W \sim \nu^2 A^2 \rightarrow$ inconsistent with experimental values.

• Einstein's Explanation – Quantize electromagnetic radiation

- View EM radiation as stream of particles ("photons") of energy, $E = h\nu$ (h = planck's constant) and momentum $p = \frac{h}{\lambda}$ ← wavelength

• $E_{photon} = h\nu \Rightarrow h\nu_{min} = W \Rightarrow \nu_{min} = \frac{W}{h}$

Emission Spectrum of Hydrogen (H)

• 

nuclear size ≃ 10^{-15} m

atomic size ≃ 10^{-10} m

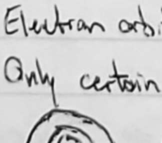
• Since the electron is constantly accelerating (centripetal), it is constantly emitting energy as EM radiation, & spirals down towards nucleus

• Classically: atoms are unstable.

• Spectrum consists of discrete lines, described by $\nu = cR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ — R – Rydberg's constant ≃ $1.09\times10^{7}\ \frac{1}{m}$; n_1, n_2 – integers; $n_1 < n_2$

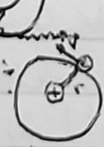
- $n_1 = 1$, $n_2 = 2, 3, 4, \ldots$ ← Lyman Series.
- $n_1 = 2$, $n_2 = 3, 4, 5 \ldots$ ← Balmer Series.

• Bohr's Explanation – Electron orbits in atoms are quantized.

- Only certain orbits (stationary states) are possible
- 

emits light as electron falls from state to lower state.

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

• Origin of Bohr's Orbits: 

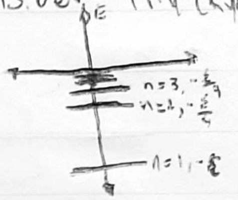
$\frac{mv^2}{r} = \frac{e^2}{r^2}$ ← Coulomb's force — Bohr's Assumption.

Angular Momentum: $L = mvr = n\hbar$ $(n = 1, 2, 3 \ldots)$ — $r = r_n = n^2 a_0$ — $a_0 = \frac{\hbar^2}{me^2} \simeq 5.29\times10^{-11}$ m ← Bohr Radius.

→ ∴ the radii of stationary orbits are quantized

- Energy of the n^{th} orbit $\Rightarrow E = \frac{mv^2}{2} - \frac{e^2}{r}$

$\Rightarrow E_n = -\frac{me^4}{2\hbar^2 n^2} = -\frac{\mathcal{E}}{n^2}$, $\mathcal{E} = \frac{me^4}{2\hbar^2} \simeq 13.6\,eV = 1\,Ry$ (Rydberg)



- $n=1 \rightarrow -\mathcal{E}$ is the ground state

$n=2 \rightarrow -\frac{\mathcal{E}}{4}$ is the first excited state

etc.

- Frequencies of the spectral lines correspond to transitions between stationary states. $(n_2 \rightarrow n_1)$ $(n_1 < n_2)$
- initial energy: $E_{n_2} = -\frac{\mathcal{E}}{n_2^2}$

Final energy $= E_{n_1} = -\frac{\mathcal{E}}{n_1^2}$

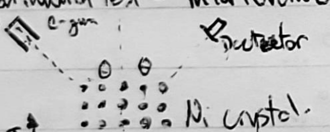
$E_{n_2} - E_{n_1} = h\nu$ .....

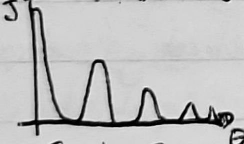
$\nu = cR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ ← agrees with experiment.

- Einstein said waves of frequency ν and wavelength λ → particles of energy $h\nu$ of momentum $\frac{h}{\lambda}$
- De Broglie particles of energy E and momentum p → waves of frequency $\nu = \frac{E}{h}$ and wavelength $\lambda = \frac{h}{p}$

De Broglie Relations.

- Experimental Test - interference / diffraction of electrons (Davisson-Germer)





Classically - expect chaotic scattering of particles (featureless J)

← Experiment - suggests wave-like diffraction of electrons

- Bragg Formula for diffraction of waves: $2d\cos\theta = n\lambda$ ⇒ constructive interference of waves which lead to a diffraction peak.

- at given λ & d ⇒ set of θ that correspond to interference.

- De Broglie - $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$

$\frac{p^2}{2m} = E \Rightarrow p = \sqrt{2mE}$

- Experimentally $\lambda(E) \sim \frac{1}{\sqrt{E}}$
- Bohr: $L = mvr = n\hbar = n\frac{h}{2\pi} \Rightarrow 2\pi r = n\frac{h}{p} \Rightarrow 2\pi r = n\lambda$
- $2\pi r = n\lambda$ - De Broglie wave fits n times into the orbit (constructive interference of the wave).

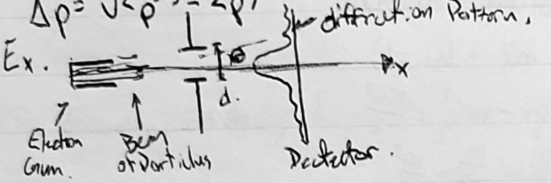
Heisenberg Uncertainty Principle

- Position and momentum cannot be measured simultaneously with arbitrary percision
- $\Delta q \Delta p \geq \frac{\hbar}{2}$ q = position

  $\Delta q = \sqrt{\langle q^2 \rangle - \langle q \rangle^2}$ ← STDEV of position, q, & momentum, p.

  $\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$

- Ex.



$\Delta p_y = p \sin\theta$, assume $\theta \ll 1$ so $p\sin\theta \simeq p\theta$ → wave optics

Uncertainty in p_y: $\Delta p_y \sim p \cdot \left(\begin{smallmatrix}\text{typical angle}\\ \text{of diffraction}\end{smallmatrix}\right) = p\frac{\lambda}{d} = \frac{h}{d}$

Uncertainty in y: $\Delta q = d$ $(q = y)$

$\Delta y \cdot \Delta p_y \sim d \cdot \frac{h}{d} = h$.

Classical Mechanics. (1 particle, in 1D, $q = x$, conservative force $F(x)$)

① • Newton's 2^{nd} Law: $-F = m\ddot{x} = m\ddot{q}$ $\Rightarrow$ $m\frac{d^2q}{dt^2} = F$

- Conservative Force $F = -\frac{\partial V}{\partial q}$
- Initial Conditions $\begin{cases} q(t=0) = q_0 \\ \dot{q}(=0) = v_0 \end{cases}$

→ Solve and find $q(t), \dot{q}(t) \Rightarrow p(t) = m\dot{q}$

② • Lagrangian Formulation of Classical Mechanics.

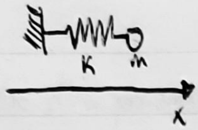
- introduce set of generalized coordinates, q and generalized velocities, $\dot{q}$
- Kinetic Energy: $K(\dot{q}, q)$

  Potential Energy: $V(q)$
- Lagrangian: $L(q, \dot{q}) = K - V$. $\Rightarrow$ Equations of motion $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)$, $p = \frac{\partial L}{\partial \dot{q}}$ Generalized momentum conjugate to q.
- $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0$ → solve for $q(t)$.

③ • Hamiltonian Formulation of Classical Mechanics.

- dynamics are describe in terms of p and q.
- $H = p\dot{q} - L = p\dot{q} - L(q, \dot{q})$ $\dot{q}(q, p)$, use $p = \frac{\partial L}{\partial \dot{q}}$
- $H(q, p)$
- Equations of Motion: $\left.\begin{aligned} \frac{dq}{dt} &= \frac{\partial H}{\partial p} \\ \frac{dp}{dt} &= -\frac{\partial H}{\partial q} \end{aligned}\right\}$ solve for $q(t)$, $p(t)$.

• Ex: 1D Linear Harmonic Oscillator (LHO).



$q = x$

Potential Energy: $V(x) = \frac{Kx^2}{2} \Rightarrow F = -\frac{\partial V}{\partial x} = -Kx.$ ← Hooke's Law

Newton 2nd Law: $m\ddot{x} = -Kx \Rightarrow \ddot{x} + \omega x = 0, \; \omega = \sqrt{\frac{K}{m}}$

Lagrangian: $L = K - V = \frac{m\dot{x}^2}{2} - \frac{Kx^2}{2}$, generalized momentum $p = \frac{\partial L}{\partial \dot{x}} = m\dot{x}$

EOM: $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = \frac{d}{dt}(m\dot{x}) + Kx = 0$

$$m\ddot{x} + Kx = 0.$$

Hamiltonian: $H = p\dot{x} - L = p\dot{x} - \frac{m\dot{x}^2}{2} + \frac{Kx^2}{2}$, use $p = m\dot{x}$, eliminate $\dot{x}$: $\dot{x} = \frac{p}{m}$.

$$= \frac{p^2}{m} - \frac{p^2}{2m} + \frac{Kx^2}{2}.$$

$$= \frac{p^2}{2m} + \frac{Kx^2}{2}$$ ← total energy expressed in terms of x & p.

EOM: $\frac{dq}{dt} = \frac{\partial H}{\partial p} = \frac{\partial}{\partial p}\left(\frac{p^2}{2m} + \frac{Kx^2}{2}\right) = \frac{p}{m} \rightarrow p = m\dot{x}$

$\frac{dp}{dt} = -\frac{\partial H}{\partial q} = -\frac{\partial}{\partial q}\left(\frac{p^2}{2m} + \frac{Kx^2}{2}\right) = -Kx. \Rightarrow m\ddot{x} = -Kx.$

$$m\ddot{x} + Kx = 0.$$

• State of the system is determined by $x(t), p(t)$

- for N degrees of freedom: $x_1(t), p_1(t); \ldots \; x_n(t) p_n(t)$

Quantum Mechanics.

• Simultaneous determination of x and p is not possible due to the Heisenberg uncertainty.

Schrödinger Idea:

• Dynamical state of a quantum system is described by a "wave function" Ψ, which satisfies a "wave equation":

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

• For 1 particle in 1D: $\Psi = \Psi(x,t)$

• ~~Classical Mechanics: state = $\{q(t), p(t)\} \equiv \Gamma(t)$~~, ~~initial state: $\{q(0), p(0)\} = \Gamma(0)$~~ ← Time evolution is described by Eqn

~~Quantum Mechanics:~~

Time Evolution

- Classical Mechanics - state $= \{q(t), p(t)\} \equiv \Gamma(t)$, initial state $= \{q(0), p(0)\} \equiv \Gamma(0)$
  - → time evolution described by EOM (Hamiltonian) → $\{q(t), p(t)\}$
- Quantum Mechanics - state $= \Psi(x,t)$; initial state $= \Psi(x, t=0)$
  - → time evolution described by quantum EOM (Schrödinger Equation) → $\Psi(x,t)$

How to solve Schrödinger Equation?

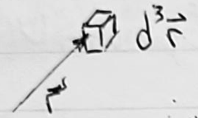
S.E → Schrödinger Eqn.

EOM = Equations of Motion

- $i\hbar \frac{\partial \Psi}{\partial x} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial t^2} + V(x,t)\Psi$ ← time dependent potential energy.
- If V is time independent → S.E can be solved by separation of variables.
  - seek solution in the form: $\Psi(x,t) = \psi(x) f(t)$ $\quad \psi \neq \Psi$
  - $i\hbar \psi \frac{df}{dt} = -\frac{\hbar^2}{2m} f \frac{d^2\psi}{dx^2} + V(x)\psi f$
  - $\underbrace{\frac{1}{f} i\hbar \frac{df}{dt}}_{\text{Function of } t} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x)}_{\text{function of } x}$
  - $i\hbar \frac{1}{f}\frac{df}{dt} = \mathcal{E}$, $\quad -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) = \mathcal{E}$
  - $\frac{df}{dt} = \frac{\mathcal{E} f}{i\hbar} = -\frac{i\mathcal{E} f}{\hbar} \xrightarrow{\text{soln}} f(t) = c e^{-\frac{i\mathcal{E}t}{\hbar}}$
  - $\Psi(x,t) = \psi(x)\, c e^{-\frac{i\mathcal{E}t}{\hbar}}$
    - $\psi(x)$: depends on the system, satisfies
    - $c e^{-\frac{i\mathcal{E}t}{\hbar}}$: same for all systems (if $V = V(x)$)
  - $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = \mathcal{E}\psi$
  - Conservative system → total mech. energy E is conserved
  - De Broglie relation: particle of energy E → frequency, $\nu = \frac{E}{h}$, angular freq. $\omega = \frac{E}{\hbar}$
  - Wave function Ψ oscillating: $\Psi(x,t) = \psi(x) e^{-i\omega t}$
  - $\mathcal{E} = E$
  - $\Psi(x,t) = \psi(x) e^{-\frac{iEt}{\hbar}}$, ψ is found by solving time-indep. S.E.
  - N Particles in 1D → $\Psi(x_1, x_2, \ldots, x_N, t)$ → SE: $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \ldots \frac{\partial^2}{\partial x_N^2}\right)\Psi + V(x_1 \ldots x_N)\Psi$
    - $\Rightarrow \Psi = \psi(x_1, \ldots x_N) e^{-\frac{i}{\hbar}Et}$
  - 1 particle in 3D (Spherical Coord) → $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\vec{r})\Psi$
    - → $\Psi(\vec{r}, t) = \psi(\vec{r}) e^{-\frac{i}{\hbar}Et}$
    - Time-independent SE in D dimension. → $-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi = E\psi$

$A = \int \tau$

Interpretation of ψ

- ψ is a complex function → not measurable
- $|\psi|^2$ can be interpreted probabilistically:
  - $|\psi(\vec{r},t)|^2 d^3\vec{r} = dP$ ← Probability to find the particle in the small volume $d^3\vec{r}$ near $\vec{r}$, at time t
  -  $d^3\vec{r}$ $\quad$ H atom: $\vec{r}_1$ $\vec{r}_2$ $\vec{r}_3$ $\vec{r}_4$
    $\underbrace{\qquad\qquad\qquad}_{N >> 1 \text{ atoms, all in the same state } \psi}$
  - Data Points:  $d^3\vec{r}$
    - achieve a density cloud
    - # of points inside $d^3\vec{r} = dn(\vec{r},t) = N d^3\vec{r}\,\underset{\text{density}}{\rho}(\vec{r},t)$
    - $\rho(\vec{r},t) = |\psi|^2$

Normalization of ψ:

- $\underset{\text{entire space (any dimension)}}{\int} d^3\vec{r}\,|\psi(\vec{r},t)|^2 = 1$
- $\underbrace{\sum_{d^3\vec{r}} dn}_{\text{total \# of points} = N} = \sum_{d^3\vec{r}} \rho N d^3\vec{r} = N \sum_{d^3\vec{r}} \rho\, d^3\vec{r}\Big|_{d^3\vec{r}\to 0} = N \int_{\text{all } \vec{r}} \rho\, d^3\vec{r} = N \int |\psi(\vec{r},t)|^2 d^3\vec{r}$
- Conservation of Probability: $\frac{d}{dt}\int d^3\vec{r}\,|\psi|^2 = \frac{d}{dt}\int d^3\vec{r}\,\rho = \int d^3\vec{r}\,\frac{d\rho}{dt} = \int d^3\vec{r}\,\frac{d(\psi^*\psi)}{dt}$

$$= \int d^3\vec{r}\left(\frac{d\psi^*}{dt}\psi - \psi^*\frac{d\psi}{dt}\right)$$

- SE: $i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$

$$\Rightarrow \frac{\partial\psi}{\partial t} = \frac{1}{i\hbar}\left[-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right]$$

$$= \frac{i\hbar}{2m}\nabla^2\psi - \frac{i}{\hbar}V\psi$$

$$\psi^*\frac{\partial\psi}{\partial t} = \frac{i\hbar}{2m}\psi^*\nabla^2\psi - \frac{i}{\hbar}V|\psi|^2$$

$$-\int d^3\vec{r}\left(-\frac{i\hbar}{2m}\psi\nabla^2\psi^* + \frac{i}{\hbar}V|\psi|^2 + \frac{i\hbar}{2m}\psi^*\nabla^2\psi - \frac{i}{\hbar}V|\psi|^2\right)$$

$$\frac{\partial P}{\partial t} = \frac{i\hbar}{2m}\int d^3\vec{r}\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right) = \dots$$

$$\frac{\partial\rho}{\partial t} = \frac{i\hbar}{2m}\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right)$$

$$= \frac{i\hbar}{2m}\vec{\nabla}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right)$$

$$= \frac{i\hbar}{2m}\left[(\vec{\nabla}\psi^*)\cdot(\vec{\nabla}\psi) + \psi^*(\nabla^2\psi) - (\vec{\nabla}\psi)\cdot(\vec{\nabla}\psi^*) - \psi(\nabla^2\psi^*)\right]$$

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

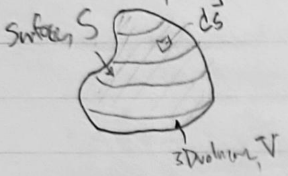
$-\frac{i\hbar}{2m}\left[\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*\right] = \frac{\hbar}{2}\,\mathrm{Im}\left(\psi^*\vec{\nabla}\psi\right)$

Probability Current → $\vec{J}(\vec{r},t) = -\frac{i\hbar}{2m}\left(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi\right)$

Probability Conservation Law → $\frac{\partial\rho}{\partial t} = -\vec{\nabla}\cdot\vec{J}$ or $\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0$

- Charge Density - $\rho_c(\vec{r},t) = e\rho(\vec{r},t)$

  Charge Current Density - $\vec{J}_c(\vec{r},t) = e\vec{J}(\vec{r},t) \Rightarrow \frac{\partial \rho_c}{\partial t} + \vec{\nabla}\cdot\vec{J}_c = 0$ ← charge conservation
- Arbitrary volume, V, enclosed by surface, S.



$$\underbrace{\int_V d^3\vec{r}\,\frac{\partial \rho}{\partial t}}_{\parallel} = -\underbrace{\int_V d^3\vec{r}\,(\vec{\nabla}\cdot\vec{J})}_{\text{Gauss Theorem}}$$

$$\frac{\partial}{\partial t}\underbrace{\left(\int_V d^3\vec{r}\,\rho\right)}_{} = -\underbrace{\oint_S \vec{J}\cdot d\vec{S}}_{\text{Probability flux}}$$

Total probability of finding particle in volume at time, t.

$$\frac{d}{dt}\left(\begin{matrix}\text{total probability}\\ \text{to be inside } V\end{matrix}\right) = -\left(\begin{matrix}\text{flux through}\\ \text{the surface}\end{matrix}\right)$$

$$\frac{d}{dt}\int_V \rho\, d^3\vec{r} = -\oint_S \vec{J}\cdot d\vec{S}$$

V = universe, $S \to \infty$, ψ has to be normalizable $\Rightarrow \psi(|\vec{r}| \to \infty) \to 0$, sufficiently fast

$\frac{d}{dt}\int_{\text{whole space}} \rho\, d^3\vec{r} = 0 \Rightarrow \int_{\text{whole space}} \rho\, d^3r = \text{constant} = 1$

$\Rightarrow J \to 0$; fast @ $|\vec{r}| \to 0$

$\Rightarrow$ the flux of $\vec{J}$ through $S = 0$

$\Rightarrow \int d^3\vec{r}\, |\psi(\vec{r},t)|^2 = 1$ @ all t

if the wave function is normalized @ $t=0 \Rightarrow \psi$ will stay normalized

Average (= mean, = expectation) Value of $\vec{r}$

- x - random quantity: discrete values x_i, with probabilities p_i
- Average $\langle x \rangle = \sum_i x_i p_i$ $(i = 1, \ldots N) \doteq M_1$

  moments $M_n = \langle x^n \rangle = \sum_{i=1}^{N} x_i^n p_i$

  $M_0 = 1 = \sum_{i=1}^{N} p_i$
- Continuous Random Quantity - characterized by the probability density $\rho(x)$

  - x probability that x is between x and $x+dx$: $dp = \rho(x)dx$, $dx \to 0$

- $\langle x \rangle = \int_{-\infty}^{+\infty} x\, dp = \int_{-\infty}^{+\infty} x\rho(x)$

  Moments: $M_n = \langle x^n \rangle = \int_{-\infty}^{\infty} x^n \rho(x) dx$

  $M_0 = \int_{-\infty}^{\infty} \rho(x) dx = 1$

  $M_2 = \langle x^2 \rangle = \int_{-\infty}^{\infty} dx\, x^2 \rho(x)$
- STDEV of x - $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$

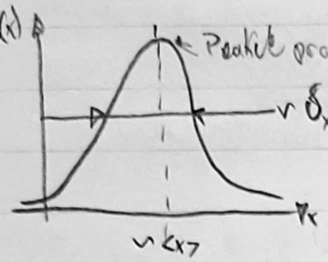
• $\delta x = x - \langle x\rangle$ ← measure deviation of x from its average value

$\langle \delta x\rangle = \langle (x-\langle x\rangle)\rangle = \langle x\rangle - \langle x\rangle = 0$

$\langle \delta x^2\rangle = \langle (x-\langle x\rangle)^2\rangle = \langle (x^2 - 2x\langle x\rangle + \langle x\rangle^2)\rangle$

$= \langle x^2\rangle + \langle x\rangle^2 - 2\langle x\rangle^2$

$= \langle x^2\rangle - \langle x\rangle^2$

• 

• Quantum Mechanics - $\rho = |\psi|^2$

- $\langle \vec r\rangle = \int d^3 r\, \vec r\, |\psi(\vec r,t)|^2$ - average position in the state ψ
- Average velocity $\langle \vec v\rangle = \frac{d}{dt}\langle \vec r\rangle = \int d^3 r\, \vec r\left(\underbrace{\frac{\partial}{\partial t}|\psi|^2}_{-\vec\nabla\cdot\vec J}\right) =$

$= -\int d^3 r\, \vec r\,(\vec\nabla\cdot\vec J)$

Integration by parts in 3D

$\int_V \vec a(\vec\nabla\cdot\vec b)\, d^3 r$, $\vec a(\vec r), \vec b(\vec r)$, V=volume, S=surface of V

$= -\int_V \underbrace{(\vec b\cdot\vec\nabla)\vec a}_{b_x \frac{\partial \vec a}{\partial x} + b_y\frac{\partial\vec a}{\partial y} + b_z \frac{\partial \vec a}{\partial z}}\, d^3 r + \oint_S \vec a\,(\vec b\cdot d\vec S)$

- V = universe, $S\to\infty \Rightarrow$ surface term = 0, $\vec a = \vec r$, $\vec b = \vec J$
- $-\int d^3 r\, \vec r\,(\vec\nabla\cdot\vec J) = \int_V \underbrace{(\vec J\cdot\vec\nabla)\vec r}_{\vec f}\, d^3 r = \vec\nabla[\psi^*\vec\nabla\psi - \psi\vec\nabla\psi^*]$

$\vec f = \vec J$ where $\begin{cases} f_x = (J_x\frac{\partial}{\partial x} + J_y\frac{\partial}{\partial y} + J_z\frac{\partial}{\partial z})x = J_x \\ f_y = J_y \\ f_z = J_z \end{cases}$

$= \int d^3 r\, \vec J(\vec r,t)$

$= \frac{i\hbar}{2m}\int d^3 r\,(\psi^*\vec\nabla\psi - \psi\vec\nabla\psi^*)$

$= \frac{i\hbar}{2m}\left[\int d^3 r\,\psi^*\vec\nabla\psi - \int d^3 r\,\psi\vec\nabla\psi^*\right]$ by parts $= -\int d^3 r\,(\vec\nabla\psi)\psi^* +$ surface term $= 0$

$\langle\vec v\rangle = \frac{i\hbar}{2m}\left[\int d^3 r\,\psi^*\vec\nabla\psi + \int d^3 r\,(\vec\nabla\psi)\psi^*\right]$

$= \frac{i\hbar}{m}\int d^3 r\,\psi^*\vec\nabla\psi$

$= \frac{1}{m}\int d^3 r\,\psi^*(-i\hbar\vec\nabla)\psi$

• Classical Mechanics - $\vec p = m\vec v$

Quantum Mechanics - $\langle\vec p\rangle = m\langle\vec v\rangle = \int d^3 r\,\psi^*(-i\hbar\vec\nabla)\psi$ ← average momentum in state ψ

- $\langle\vec r\rangle = \int d^3 r\,\psi^*\,\vec r\,\psi$

- Obeservable Quantity - $Q(\vec{r},\vec{p})$, $\vec{r}$, $\vec{p}$, $K=\frac{\vec{p}^2}{2m}$, $\vec{L}=\vec{r}\times\vec{p}$

  Average value of Quantity - $\langle Q\rangle = \int d^3\vec{r}\ \psi^*(\hat{Q}\psi)$

  Operator $\hat{Q}$ - $\hat{Q}=Q(\hat{\vec{r}},\hat{\vec{p}})$

  $\vec{r}\to$ the position operator $\hat{\vec{r}}=\vec{r}$ - multiplication by $\vec{r}$

  $\vec{p}\to$ the momentum operator $\hat{\vec{p}}=i\hbar\vec{\nabla}$ - differentiation by $\vec{r}$

Here hats denote operator

- $\langle\vec{r}\rangle=\int d^3\vec{r}\ \psi^*\vec{r}\psi$

  $\hat{\vec{p}}=-i\hbar\vec{\nabla}$ ← momentum operator

  $\langle p\rangle=\int d^3\vec{r}\ \psi^*(-i\hbar\vec{\nabla}\psi)$

- Potential Energy Operator - $Q=V(\vec{r})\to\hat{Q}=V(\vec{r})$

  Kinetic Energy Operator - $Q=\frac{p^2}{2m}=K\to\hat{K}=\frac{\hat{p}^2}{2m}=\frac{(-i\hbar\nabla)^2}{2m}=-\frac{\hbar^2\nabla^2}{2m}$

  Total Energy - $Q=H=\frac{\vec{p}^2}{2m}+V(\vec{r})\to\hat{H}=\frac{\hat{p}^2}{2m}+V(r)=-\frac{\hbar^2}{2m}\nabla^2+V(r)$

  Classical Hamiltonian   quantum Hamiltonian

  Angular Momentum - $\vec{L}=\vec{r}\times\vec{p}$

  $L_x=yp_z-zp_y\to\hat{L}_x=\hat{y}\hat{p}_z-\hat{z}\hat{p}=-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$

  $\vec{r}\times\vec{p}=\begin{vmatrix}\hat{i}&\hat{j}&\hat{k}\\x&y&z\\p_x&p_y&p_z\end{vmatrix}$

- $\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})$ is very important
- $i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi$ ← schrodinger equation

  $i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi$ ← time evolution of the system is denoted by Hamiltonian, $\hat{H}$

Ehrenfest Theorem

- Ehrenfest Theorem = quantum-mechanical analogue of the 2nd Law
- $\frac{d\vec{p}}{dt}=\vec{F}$, $\vec{F}=-\frac{\partial V}{\partial\vec{r}}$

  quantum mechanics: $\frac{d\langle\vec{p}\rangle}{dt}=-\frac{\partial V}{\partial\vec{r}}$

- QM - $\frac{d\langle\vec{p}\rangle}{dt}=\frac{d}{dt}\left[\int d^3\vec{r}\ \psi^*(i\hbar\nabla\psi)\right]=i\hbar\int d^3\vec{r}\left(\frac{\partial\psi^*}{\partial t}\frac{\partial\psi}{\partial\vec{r}}+\psi^*\frac{\partial}{\partial\vec{r}}\frac{\partial\psi}{\partial t}\right)$

  $=-i\hbar\int d^3\vec{r}\left[\frac{\partial\psi^*}{\partial t}\frac{\partial\psi}{\partial\vec{r}}-\frac{\partial\psi^*}{\partial\vec{r}}\frac{\partial\psi}{\partial t}\right]$ ← use schrodinger equation.

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

  $-i\hbar\frac{\partial\psi^*}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi^*+V\psi^*$ ← Complex Conjugate

  $=\int_{\vec{r}}\Big[\frac{\hbar^2}{2m}(\nabla^2\psi^*)(\vec{\nabla}\psi)+V\psi^*(\vec{\nabla}\psi)-\frac{\hbar^2}{2m}(\vec{\nabla}\psi^*)(\nabla^2\psi)$

  $+V(\vec{\nabla}\psi^*)\psi\Big]=$ ← integrate by parts

  integrate by parts & cancel 3rd term

  $=\int_{\vec{r}}\left[-\vec{\nabla}(V\psi^*)\psi+V(\vec{\nabla}\psi^*)\psi\right]$

  $=\int_{\vec{r}}\left[(-\vec{\nabla}V)|\psi|^2-V(\vec{\nabla}\psi^*)\psi\right]$

  $=\int d^3\vec{r}\ \psi^*\left(-\frac{\partial V}{\partial\vec{r}}\right)\psi=\langle-\frac{\partial V}{\partial\vec{r}}\rangle$

• Solve the S.E. with the initial condition $\psi(\vec{r}, t=0) = \underbrace{\psi_0(\vec{r})}_{\text{initial state}}$

- Find $\psi(\vec{r}, t)$
- Calculate expectation values of the observables $\vec{r}, \vec{p}, K$, etc.
- Properties of ψ - ① $\psi(\vec{r}, t)$ & $\vec{\nabla}\psi(\vec{r}, t)$ are complex, single valued functions of $\vec{r}$

② $\psi(\vec{r}, t)$ is a continuous function of $\vec{r}$
$\vec{\nabla}\psi(\vec{r}, t)$ is continuous for non-singular potentials

③ $\psi(\vec{r}, t)$ is normalized: $\int d^3\vec{r}\, |\psi(\vec{r}, t)|^2 = 1 \rightarrow \psi \to 0$, as $|\vec{r}| \to \infty$

$|\psi(\vec{r}, t)|^2$ - probability density of finding the particle near $\vec{r}$

- Normalization of ψ:
  - it is sufficient to normalize $\psi(\vec{r}, t=0)$
  - Ex. $\psi_0(x) = \psi(x, t=0) = A e^{-\frac{ax^2}{2}}$

$$1 = \int_{-\infty}^{\infty} dx\, |\psi_0|^2 = |A|^2 \int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}\, |A|^2$$

$$\Rightarrow \sqrt{\frac{a}{\pi}} = |A|^2 \; ; \; \sqrt[4]{\frac{a}{\pi}} = |A|$$

phase of A $(A = |A| e^{i\varphi})$ cannot be determined from the normalization

$\int e^{-ax^2} dx$ ← important, put on cheat sheet

$\int e^{-ax^2} dx = I_0(a)$.

$\iint e^{-a(x^2+y^2)} dx\, dy = I^2$

$\int_0^{\infty} r\, dr \int_0^{2\pi} d\phi\, e^{-ar^2} =$

$2\pi \int_0^{\infty} r\, dr\, e^{-ar^2} =$

$2\pi \frac{1}{2} \int_0^{\infty} ds\, e^{-as} =$

$\frac{\pi}{a} = I^2$

$\sqrt{\frac{\pi}{a}} = I$

- Expectation Values:
  - $\langle Q \rangle = \int_{-\infty}^{\infty} dx\, \psi^* \hat{Q} \psi = \int_{-\infty}^{\infty} dx\, \tilde{\psi}^* \hat{Q} \tilde{\psi}$

    ↳ rotate the phase: $\psi(x, t) \to e^{i\varphi} \psi(x, t) = \tilde{\psi}(x, t)$
  - the phase of ψ does not affect **any** observable quantities.

• Normalized wave function:
  - $\psi_0(x) = \sqrt[4]{\frac{a}{\pi}}\, e^{-\frac{ax^2}{2}} = \psi(x, t=0)$
  - Probability of finding the particle @ $x \geq 0$
  - $P_{x \geq 0} = \int_0^{\infty} dx\, \rho(x, t=0) = \int_0^{\infty} dx\, |\psi_0(x)|^2 = \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_0^{\infty} dx\, e^{-ax^2}$

$$= \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \left[\frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}\right] = \frac{1}{2}$$

$I_n(a) = \int_{-\infty}^{\infty} dx\, x^n e^{-ax^2}$, $I_n = 0$ for odd n

$I_2(a) = -\frac{\partial}{\partial a} \int_{-\infty}^{\infty} dx\, e^{-ax^2}$, $I_n \neq$ for even n.

$= -\frac{\partial}{\partial a}\left(\sqrt{\frac{\pi}{a}}\right)$

$= \sqrt{\frac{\pi}{a}}\, \frac{1}{2a}$

- $\langle x \rangle = \int_{-\infty}^{\infty} dx\, x\, |\psi(x, t=0)|^2 = \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx\, x\, e^{-ax^2} = 0$

  average position @ $t=0$

- $\langle x^2 \rangle = \int_{-\infty}^{\infty} dx\, x^2 |\psi|^2 = \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \underbrace{\int_{-\infty}^{\infty} dx\, x^2 e^{-ax^2}}_{I_2(a)} = \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \left[\sqrt{\frac{\pi}{a}}\, \frac{1}{2a}\right] = \frac{1}{2a}$
- $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{1}{2a}}$

$p = p_x$

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

- $\langle p \rangle = \int_{-\infty}^{\infty} dx\, \psi_0^*(x)\, \hat{p}\, \psi_0(x) = -i\hbar \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx\, e^{-\frac{ax^2}{2}} \left(\frac{\partial}{\partial x} e^{-\frac{ax^2}{2}}\right)$.

  @ $t=0$ $= -i\hbar \left(\frac{a}{\pi}\right)^{\frac{1}{2}} (-a) \underbrace{\int_{-\infty}^{\infty} dx\, x\, e^{-ax^2}}_{0} = 0$.

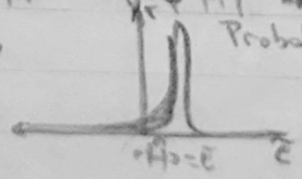
For this to work need to know x at all t values. → - $\langle p \rangle = m \frac{d}{dt} \langle x \rangle = ?$

Schrödinger Equation:

- $i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$
- Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t)$
- Wave Function $\psi(\vec{r}, t)$
- Time Independent Potential: $V(\vec{r})$
  - Particular solution of the S.E. has the form $\psi(\vec{r}, t) = \psi(\vec{r})\, e^{-\frac{i}{\hbar} E t}$ ← energy

$\int d^3_r |\psi(\vec{r})|^2 = 1$ ↑ Normal

- Time Independent SE: $\hat{H}\psi = E\psi$ + the normalization $\int d^3_r |\psi(\vec{r})|^2 = 1$ + the boundary conditions
- $\int d^3_r\, \psi^*(\vec{r})\, e^{\frac{i}{\hbar}Et}\, \psi(\vec{r})\, e^{-\frac{i}{\hbar}Et} \Rightarrow \int d^3_r |\psi(\vec{r})|^2 = 1$
- Property of the Stationary State.
  1. probability density $\rho(\vec{r}, t) = |\psi(\vec{r}, t)|^2 = |\psi(\vec{r})|^2$ ← time independent.
  2. Expectation values of observables are time independent.
     $\langle Q \rangle = \int d^3_r\, \psi^* \hat{Q} \psi = \int d^3_r\, \psi^* e^{\frac{i}{\hbar}Et}\, Q(\hat{\vec{r}}, \hat{\vec{p}})\, \psi(\vec{r})\, e^{-\frac{i}{\hbar}Et}$
     $= \int d^3_r\, \psi^*(\vec{r})\, \hat{Q}\, \psi(\vec{r})$
     $\langle \vec{r} \rangle = \int d^3_r\, \vec{r}\, |\psi|^2$
     $\langle \vec{p} \rangle = m \frac{d\langle \vec{r} \rangle}{dt}$ or by $\int d^3_r\, \psi^* \hat{\vec{p}} \psi$
     $= 0 \rightarrow$ in any stationary state
     $\langle \vec{F} \rangle = \frac{d}{dt}\langle \vec{p} \rangle = 0$
  3. $\int d^3_r |\psi|^2 = 1$
  4. The stationary states correspond to a definite value, E, of the total energy; every measurement of $\hat{H}$ returns E. Standard Deviation of total energy $\sigma_H = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}$. In stationary state $\langle \hat{H}^2 \rangle = \int_r \psi^* \hat{H} \psi \Rightarrow E^2$, $\langle \hat{H} \rangle \Rightarrow E$.
     $\sigma_H = 0 \Rightarrow$

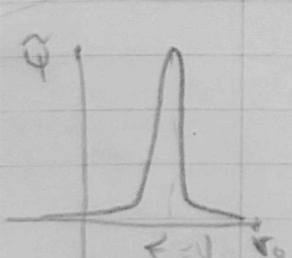


- Given $\hat{H}$, the equation $\hat{H}\psi = E\psi$ has normalizable solutions only @ certain values of E = the energy levels E_n
- SE has an infinite number of solutions:
  $\psi_1(\vec{r}), \psi_2(\vec{r}), \ldots \; \{\psi_n\}$, corresponding to the energy levels $E_1, E_2, \ldots \{E_n\}$
  $\hat{H}\psi_n = E_n\psi_n$

  * Mathematically: Solving SE = Eigenvalue problem
  $\underbrace{\hat{A}\psi_n}_{\text{Eigenstates of } \hat{A}} = \underbrace{E_n}_{\text{Eigenvalues of } \hat{A}}\psi_n$

- Dirac Notation: $\psi_n(\vec{r}) \equiv \langle \vec{r} | n \rangle$
  $\psi_n = |n\rangle$
  $\hat{H}|n\rangle = E_n|n\rangle$
- n^{th} stationary state: $\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-\frac{i}{\hbar}E_n t}$
- General QM state: $\Psi(\vec{r},t) = \sum_n c_n \Psi_n(\vec{r},t) = \underbrace{c_1\Psi_1(\vec{r},t) + c_2\Psi_2(\vec{r},t)}_{\text{superposition (linear combination) of stationary state}} + \ldots$

- $i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$ ← linear equation.
  - if Ψ_1 is a solution, if Ψ_2 is a solution $\Rightarrow c_1\Psi_1 + c_2\Psi_2$ is a solution
  - $c_1, c_2, c_3 \ldots$ are complex coefficients.
- $c_1, c_2, \ldots$ are determined by the initial condition
  $\Psi(\vec{r}, t=0) = \Psi_0(\vec{r})$
- ① Given $V(\vec{r}) \to$ solve the SE to find the stationary states $\hat{H}\psi_n = E_n\psi_n$
  ② Prepare the system in the initial state $(\Psi_0(\vec{r}))$.
  + find the coefficients c_n
  ③ QM state @ time $t>0$: $\Psi(\vec{r},t) = \sum_n c_n \psi_n(\vec{r})\, e^{-\frac{i}{\hbar}Et}$.
  ④ Calculate observables: $\langle Q \rangle = \int_{\vec{r}} \Psi^* Q \Psi$ ← Time-independent
- Measurements in QM
  - Measurement destroys the wave function:
    eg. measure the position in the state $\Psi(\vec{r}) \to$ find the particle at $\vec{r}_0 \to$ immediately after the measured, $\Psi(\vec{r})$ = sharply localized wave $\vec{r} = \vec{r}_0$



  - Wavefunction collapse - act of measurement has changed the state of the system
    - cannot repeat the measurement on the system

QM in 1D

- Wave function: $\Psi(x,t)$ ← Satisfies 1D SE

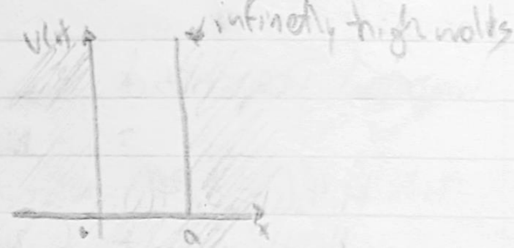
Stationary state: $\Psi(x,t) = \psi(x)\, e^{-\frac{i}{\hbar}Et}$

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

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

- Particle in a Box.

$$V(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{outside} \end{cases}$$



$$\begin{cases} \psi(x) - \text{continuous} \\ \psi(x) = 0 \text{ outside the box} \end{cases}$$

2 boundary conditions $\psi(0) = 0$, $\psi(a) = 0$

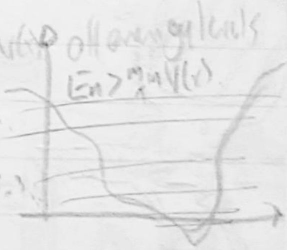
SE inside the box:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \Rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi \qquad k = \sqrt{\frac{2mE}{\hbar^2}},\ E > 0$$

General solution: $\psi(x) = A\sin kx + B\cos kx$

Boundary Conditions: $\psi(0) = 0 = B \Rightarrow B = 0$

$\psi(x) = A\sin k_n x$



$n = \pm 1, \pm 2, \ldots$ can take

$$\psi(a) = A\sin(ka) = 0 \Rightarrow \begin{cases} A = 0 \\ ka = n\pi \end{cases} \quad n = 1, 2, 3$$

if $n = 0$

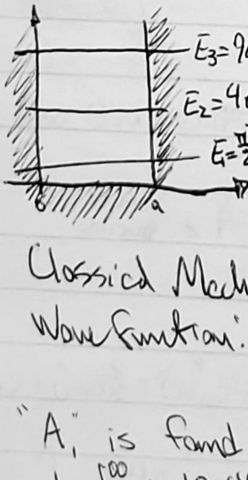
$\psi(x) = 0$ everywhere & non-normalizable & unphysical

$k = \sqrt{\frac{2mE}{\hbar^2}}$

$k_n = \frac{\pi n}{a}$

$k_n = \frac{n\pi}{a}$ ← k is quantized

$$E = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m}\frac{\pi^2 n^2}{a^2} = \frac{\pi^2\hbar^2}{2ma^2}n^2$$ ← E_n = energy levels (or eigenvalues of $\hat{H}$)



$E_3 = 9E_1$ ← 2nd excited state.

$E_2 = 4E_1$ ← 1st excited state

$E_1 = \frac{\pi^2\hbar^2}{2ma^2}$ ← ground state

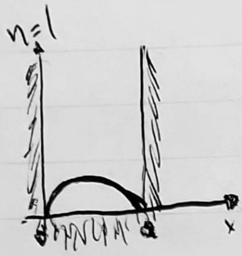
Classical Mechanics: $E = \frac{p^2}{2m} = \frac{mv^2}{2}$ & all $E \ge 0$ are possible.

Wave function: $\psi_n(x) = \begin{cases} A\sin k_n x, & 0 \le x \le a \\ 0, & \text{outside} \end{cases}$

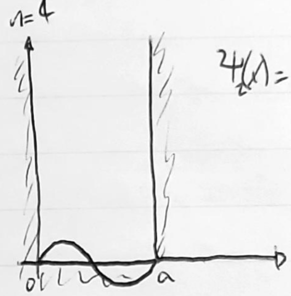
"A" is found from the normalization condition:

$$1 = \int_{-\infty}^{\infty} dx\, |\psi_n(x)|^2 = |A|^2 \int_0^a dx\, \sin^2\left(\frac{\pi n}{a}x\right) = |A|^2\left(\frac{a}{2}\right) \Rightarrow |A| = \sqrt{\frac{2}{a}}$$

Choose the phase of the wave function such that $A = \sqrt{\frac{2}{a}}$



$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$



$\psi_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$

classical analogy = the standing waves.

Important Properties of the Stationary States

- $\hat{H}\psi_n(x) = E_n \psi_n(x)$
- 1) Orthonormality of ψ_n's
  - orthogonality + normalization
  - $\int_{-\infty}^{\infty} dx\, \psi_m^*(x)\psi_n(x) = \delta_{mn} = \begin{cases} 1, & \text{if } m=n \leftarrow \text{normalization} \\ 0, & \text{if } m \neq n \leftarrow \text{orthogonality} \end{cases}$

    δ_{mn}: Kronecker delta symbol
  - Dirac notation: $\psi_n(x) = \langle x|n\rangle$, $\langle m|n\rangle = \delta_{mn}$

  2) Completeness of ψ_n's
  - any "good" square-integrable function $f(x)$ can be represented in the form, $f(x) = \sum_n c_n \psi_n(x)$, c_n = complex coefficients

    $\int_{-\infty}^{\infty} dx\, |f(x)|^2 = 1$
- Orthonormality of Standing Waves:

  $\int_{-\infty}^{\infty} dx\, \psi_m^* \psi_n = \frac{2}{a}\int dx \sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{a}x\right) = \frac{2}{a}\frac{1}{2}\int_0^a dx \left[\cos\left(\frac{\pi(m-n)x}{a}\right) - \cos\left(\frac{\pi(m+n)x}{a}\right)\right]$

  $= \frac{1}{\pi}\left[\frac{\sin(m-n)\pi}{m-n} - \frac{\sin(m+n)\pi}{m+n}\right] = \begin{cases} 1, & m=n \\ 0, & m\neq n \end{cases} = \delta_{mn}$.
- Completeness of Standing Waves

  any function $f(x)$ such that $f(x)=0$ @ $x<0$ and $x>a$ and $\int_0^a dx\,|f|^2 = 1$ can be written as

  $f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{\pi n}{a}x\right)$ ✱ Fourier series.

  How to find c_n, given $f(x)$?

  $f(x) = \sum_n c_n \psi_n(x)$.

  $\int_{-\infty}^{\infty} dx\, f(x)\psi_m^* = \sum_n c_n \int_{-\infty}^{\infty} dx\, \psi_n(x)\psi_m^*(x) = \sum_n c_n \delta_{mn} = c_m$

  $c_m = \int_{-\infty}^{\infty} dx\, f(x)\psi_m^*(x)$

  $c_n = \underbrace{\int_{-\infty}^{\infty} dx\, \psi_n^*(x) f(x)}_{\text{"overlap" of } \psi_n \text{ \& } f}$

Dirac: $f(x) = \langle x|f\rangle$

$c_n = \langle n|f\rangle$

Particle in a Box: General Time dependent wave function:

$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-\frac{i}{\hbar}E_n t}$ stationary states. (*)

Initial State: $\Psi(x, t=0) = \Psi_0(x)$

$\Psi_0(x) = \sum_n c_n \psi_n(x) \Rightarrow$ Given $\Psi_0 \to$ Find c_n: $c_n = \langle n|\Psi_0\rangle = \int_{-\infty}^{\infty} dx\, \psi_n^*(x)\Psi_0(x)$.

$f(x)$ insert into (*)

Normalization in terms of c_n:

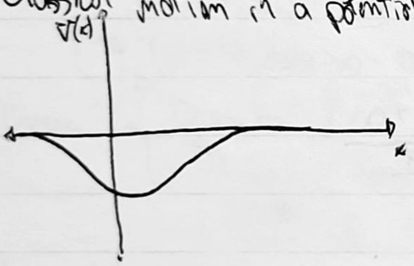
$\sum_n |c_n|^2 = 1$.

$\Psi(x,t) = \sum_n c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-\frac{i\pi^2\hbar n^2}{2ma^2}t}$ $\quad E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2$

$\hookrightarrow$ calculate the observables. $\langle Q\rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t)\hat{Q}\Psi(x,t)$.

Finite Potential Wells, Bound vs Scattered States.

- Classical motion in a potential well



QM

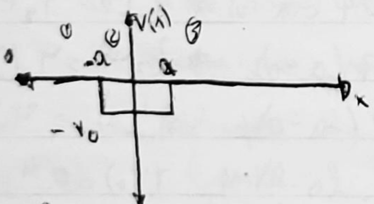
$V(+\infty) = V(-\infty) = 0$

if $E > 0$, motion is unbound (can reach $x = \pm\infty$) $\to$ Scattering States

if $E < 0$, motion is bound (finite) (cannot reach $\pm\infty$) $\to$ Bound States.

motion takes place between classical turning points

x_1 & $x_2 \Rightarrow V(x_1) = V(x_2) = E$.



$V(x)\begin{cases} -V_0, & |x| \leq a \\ 0, & |x| > a. \end{cases}$

- Scattering States @ $E > 0$

Bound States @ $E < 0$

- Bound States - ① Find the general solutions of the S.E in the 3 Regions. (1 $x < -a$, 2 $-a < x < a$, 3 $x > a$.)

② Select physical (normalizable) solutions

③ Use the boundary conditions to match ψ's in the 3 regions $\to$ find $\psi(x)$ valid @ all x.

④ Find the values of E at which the matching conditions have solution.

$-|E|$

$\varkappa$ - kappa

$\varkappa = \sqrt{\frac{2m|E|}{\hbar^2}}$

① $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$ region 1: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

$\frac{\partial^2\psi}{\partial x^2} = \varkappa^2\psi$

general solution

$\psi(x) = Ae^{-\varkappa x} + Be^{\varkappa x}$ $A \neq 0 \Rightarrow \psi \to \infty$ @ $x \to -\infty$

$\psi(x) = Be^{\varkappa x}$ physical sln corresponds to $A=0$.

Region 3: $\frac{\partial^2\psi}{\partial x^2} = \varkappa^2\psi$

General Solution: $\psi(x) = Fe^{-\varkappa x} + Ge^{\varkappa x}$

physically $G=0$, $\psi_3(x) = Ge^{\varkappa x}$.

Region 2: $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} - V_0\psi = E\psi$

$-V_0 < E < 0$ (bound states).

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

$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi$. $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$

General Solution: $\psi(x) = C\sin kx + D\cos kx$.

② Physical Solutions:

$\psi_1(x) = Be^{\varkappa x}$ @ $x < -a$

$\psi_2(x) = C\sin kx + D\cos kx$ @ $-a<x<a$

$\psi_3(x) = Fe^{-\varkappa x}$ @ $x > a$

$\varkappa = \sqrt{\frac{2m|E|}{\hbar^2}}$; $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$

③ Boundary Conditions:

ψ is continuous, $\psi(-a-0) = \psi(-a+0) \Rightarrow \psi_1(-a) = \psi_2(-a)$

$\psi(a-0) = \psi(a+0) \Rightarrow \psi_2(a) = \psi_3(a)$,

$V(x)$ is non-singular $\Rightarrow \psi' \Rightarrow \psi_1'(-a-0) = \psi_1'(a) = \psi_2'(-a)$

$\psi_2'(a-0)$, $\psi_1'(a) = \psi$.

$Be^{-\varkappa a} = -C\sin ka + D\cos ka$. $\varkappa Be^{\varkappa a} = kC\cos ka + kD\sin ka$

$C\sin ka + D\cos ka = Fe^{-\varkappa a}$ $kC\cos ka - kD\sin ka = -\varkappa Fe^{-\varkappa a}$

$\psi_1'(x) = \varkappa Be^{\varkappa x}$

$\psi_2'(x) = kC\cos kx - kD\sin kx$ 4 homogeneous linear equations

$\psi_3'(x) = -\varkappa Fe^{-\varkappa x}$

$\hat{M}\begin{pmatrix} B \\ C \\ D \\ F \end{pmatrix} = 0$ - has nontrivial solutions only if $\det \hat{M} = 0$

$\det(\hat{M}) = 0 \to$ solve for E.

• More efficient approach: Use symmetry of $V(x)$

If the potential is symmetric: $V(-x) = V(x)$, then the solutions of the SE have definite parity:

$\psi(x) = \psi(-x)$ ← even

or $\psi(x) = -\psi(-x)$ ← odd.

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

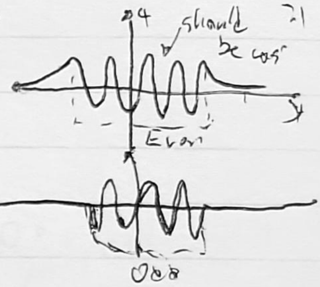
$$x \to -x: \quad -\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(-x)\psi(-x) = E\psi(-x) \Rightarrow$$

$\psi(x)$ & $\psi(-x)$ satisfy the same eq.

$\psi(-x) = \alpha\,\psi(x)$ ← phase factor

$\psi(x) = \alpha\psi(-x) = \alpha^2\psi(x)$ $\quad \alpha^2 = 1 \Rightarrow \alpha = \pm 1$

• Consider even & odd bound states separately:



Even: $C = 0$, $B = F \Rightarrow \psi_{Even}(x) = \begin{cases} D\cos kx, & 0 \le x \le a \\ Fe^{-\kappa x}, & x > a \\ \psi(-x), & x < 0 \end{cases}$

Odd: $D = 0$, $B = -F \Rightarrow \psi_{Odd}(x) = \begin{cases} C\sin kx, & 0 \le x \le a \\ Fe^{-\kappa x}, & x > a \\ -\psi(-x), & x < 0 \end{cases}$

• Use the boundary conditions @ $x = a$.

$$\begin{cases} \psi_2(a) = \psi_3(a) \\ \psi_2'(a) = \psi_3'(a) \end{cases}$$

• Even: $\begin{cases} D\cos ka = Fe^{-\kappa a} \\ -Dk\sin ka = -F\kappa e^{-\kappa a} \end{cases}$ } Divide

$-k\frac{\cos ka}{\sin ka} = -\kappa \Rightarrow k\tan ka = \kappa$ ← solve for E graphically.

$ka\tan ka = \kappa a$.

Dimensionless variables: $z_1 = ka$, $z_2 = \kappa a$; $z_1 z_2$

$$k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}} \qquad \kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$$

$z_1 \tan z_1 = z_2$.

• Odd: $\begin{cases} C\sin ka = Fe^{-\kappa a} \\ Ck\cos ka = -F\kappa e^{-\kappa a} \end{cases}$ } Divide

$k\cot ka = -\kappa$

$ka\cot ka = -\kappa a$.

$z_2 = -z_1\cot z_1$

• $z_2 = \kappa a = a\sqrt{\frac{2m|E|}{\hbar^2}} \Rightarrow z_2^2 = a^2\frac{2m|E|}{\hbar^2}$

$z_1 = ka = a\sqrt{\frac{2m(V+E)}{\hbar^2}} \Rightarrow z_1^2 = a^2\frac{2m(E+V)}{\hbar^2}$

$z_1^2 + z_2^2 = \frac{2ma^2}{\hbar^2}(|E| + E + V_0) = \frac{2ma^2V_0}{\hbar^2} = z_0^2$

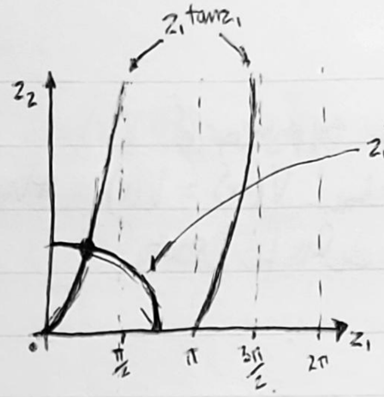
E-independent.

• Solve $z_1\tan z_1 = z_2$ & $z_1^2 + z_2^2 = z_0^2$ graphically:

$z_2 = -z_1\cot z_1$

$z_0^2 = \frac{2mV_0a^2}{\hbar^2}$

• Even:



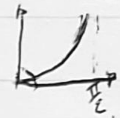
Intersection points give us the energy at the bound states.

• Deep Well ($V_0 \to \infty$) → $z_0 >> 1$

Intersections: $z_1 = \frac{\pi}{2} n$, $n = 1, 3, 5 \ldots$

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

• Shallow Well ($V_0 \to 0$) → $z_0 << 1 \Rightarrow z_{1,2} << 1$



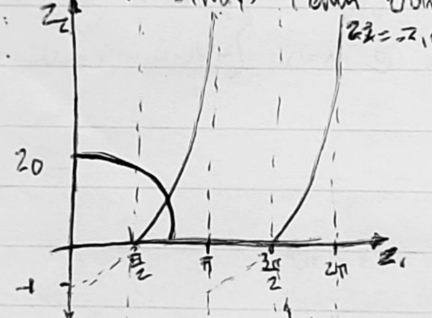
Use taylor series: $\tan z_1 \approx z_1 \Rightarrow z_2 = z_1^2$

$$z_0^2 = z_1^2 + z_2^2 \Rightarrow z_1^2 + z_1^4 \simeq z_1 \Rightarrow z_0 = z_1 \Rightarrow z_0^2 = z_2$$

$$\Rightarrow \sqrt{\frac{2m|E|}{\hbar}}\, a = \frac{2mV_0 a}{\hbar^2} \Rightarrow |E| = \frac{2mV_0^2 a^2}{\hbar^2}$$

There is always 1 even bound state with energy $E = -\frac{2mV_0^2 a^2}{\hbar^2}$

• Odd:



Number of intersections depends on z_0

• Deep Well ($z_0 >> 1$)

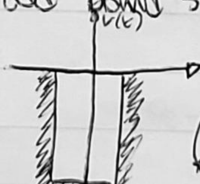
$z_1 = \pi m$, $m = 1, 2, 3 \ldots$

$ka = \pi m \Rightarrow k = \frac{\pi}{a} m$

• Shallow Well ($z_0 < \frac{\pi}{2}$) → no intersections

No odd bound states.

• Deep Well



Even ψ_s: $k = k_n = \frac{\pi}{2a} n$, $n = 1, 3, 5 \ldots$

Odd ψ_s: $k = \frac{\pi}{2a} 2m \underset{2m=n}{\Rightarrow} k = k_n = \frac{\pi}{2a} n$, $n = 2, 4, 6 \ldots$

$k_n = \frac{\pi}{2a} n$, $n = 1, 2, 3, \ldots$

• $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}} = \frac{\pi}{2a} n \Rightarrow$

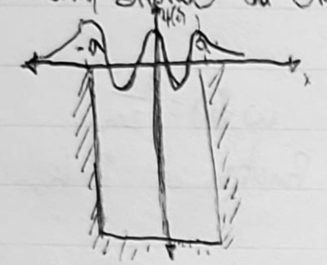
$$E = E_n = -V_0 + \frac{\hbar^2 \pi^2}{2m(2a)^2} n^2$$

• Shallow Well:

$$\hat{K} = \frac{-\hbar^2}{2m} p^2$$

$$\langle K \rangle = \int dx\, \psi^* \hat{K} \psi \neq \int dx\, \hat{K} |\psi|^2$$

· Classically allowed and classically forbidden regions.



Inside well: $\psi(x)$ is oscillating $\to E > V(x)$ (classically allowed region).

Outside well: $\psi(x)$ is exponentially decaying $\to E < V(x)$ classically forbidden region.

Free Particles, Plane Waves.

- $V(x) = 0$ everywhere

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \;\Rightarrow\; \frac{d^2\psi}{dx^2} = -k^2\psi \qquad k = \sqrt{\frac{2mE}{\hbar^2}}, \quad E > 0$$

$e^{ikx} = \cos kx + i \sin kx$.

- General Solution: $\psi(x) = Ae^{ikx} + Be^{-ikx}$.
- Time-dependence: $\psi(x) = Ae^{ikx}e^{-i\frac{E_k t}{\hbar}} + Be^{-ikx}e^{-i\frac{E_{-k}t}{\hbar}}$; $E_k = \frac{\hbar^2 k^2}{2m}$, $E_k = E_{-k}$.

$$= A\underbrace{e^{ikx}e^{-i\frac{\hbar k^2}{2m}t}}_{\text{True plane wave}} + Be^{-ikx}e^{-i\frac{\hbar k^2}{2m}t} = C_k\psi_k(x,t) + C_{-k}\psi_{-k}(x,t)$$

complex coefficients

- Most General Solution: $\Psi(x,t) = \underbrace{\sum_k C_k \psi_k(x,t)}_{\text{superposition of the plane waves.}}$
- A single ~~[illegible]~~ plane wave is unphysical.

$$\psi_k(x,t) \sim e^{ikx}e^{-i\frac{\hbar k^2}{2m}t} = e^{ik(x - \frac{\hbar k}{2m}t)} = e^{ik(x-vt)}$$

translating with v phase

$v = v_{phase} = \frac{\hbar k}{2m}$ - the phase velocity.

DeBroglie: $\hbar k = p = mv_{physical}$

$v_{phase} = \frac{1}{2} v_{physical}$. ← particle wave correspondence breaks down!

- ψ_k is not normalizable: $\int_{-\infty}^{\infty} dx\, |\psi_k|^2 = \infty$.
- Instead of individual plane waves, use wave packets = superpositions of plane waves

$$\Psi(x,t) = \int_{-\infty}^{\infty} \frac{dk}{2\pi}\, \phi(k)\, \psi_k(x,t)$$

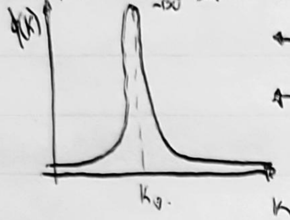
$$= \int_{-\infty}^{\infty} \frac{dk}{2\pi}\, \phi(k)\, e^{i(kx - \frac{\hbar k^2}{2m}t)}$$

$\phi(k)$: continuous analog of C_k.

Wave Packets

- $\Psi(x,t) = \int_{-\infty}^{+\infty} \frac{dk}{2\pi} \underbrace{\phi(k)}_{\text{wieght function}} e^{i(kx - \omega(k)t)}$, $\omega(k) = \frac{\hbar k^2}{2m}$
- $\phi(k)$ ← sharply peaked function at $k = k_0$

  ← $\int_{-\infty}^{+\infty} \frac{dk}{2\pi} |\phi(k)|^2 = 1$



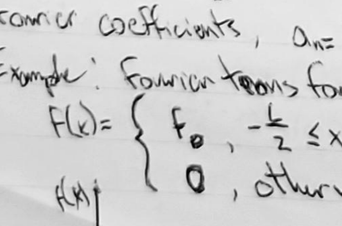
- ① The initial state $\Psi(x,t) = \Psi_0(x)$, $t=0$.
  ② $\Psi_0(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ikx}$; represent initial state as superposition of plane waves.
  ③ "Invert" the waves. → $\phi(k)$. [$\phi(k)$ = the Fourier transform of $\Psi_0(k)$].
  ④ Insert $\phi(k)$ into $\Psi(x,t)$:
  find $\Psi(x,t)$
  ⑤ Calculate the observables, e.g. $\langle x \rangle = \int_{-\infty}^{\infty} dx\, \Psi^* x \Psi$

Fourier Transforms

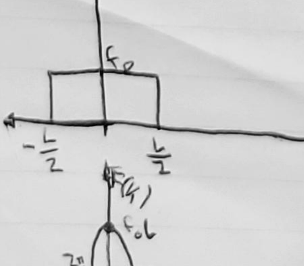
- Function $f(x)$ ← square-integrable $\int_{-\infty}^{\infty} dx |f|^2 < \infty$
- Fourier transform of f: $F(k) = \int_{-\infty}^{\infty} dx\, f(x) e^{-ikx}$
- Inverse fourier transform: $f(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} F(x) e^{ikx}$

  } Fourier Integrals.
- Parceval Theorem: $\int_{-\infty}^{\infty} dx |f(x)|^2 = \int_{-\infty}^{\infty} \frac{dk}{2\pi} |F(k)|^2$
- Function $f(x)$ ← periodic: $f(x+L) = f(x)$.
  then $f(x) = \sum_{n=-\infty}^{\infty} a_n e^{i\frac{2\pi}{L}nx}$ ← Fourier Series.
- Fourier coefficients, $a_n = \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} dx\, f(x) e^{-i\frac{2\pi}{L}nx}$, $k = k_n = \frac{2\pi}{L}n$
- Example: Fourier transform of a finite pulse.

$$f(x) = \begin{cases} f_0, & -\frac{L}{2} \le x \le \frac{L}{2} \\ 0, & \text{otherwise} \end{cases}$$



$F(k) = f_0 \int_{-\frac{L}{2}}^{\frac{L}{2}} dx\, e^{-ikx} = 2f_0 \frac{\sin(\frac{kL}{2})}{k}$.



1st node when $kL/2 = \pi$, $k = \frac{2\pi}{L}$.

GENERALIZED Gaussian integrals $\int_{-\infty}^{\infty} dx \, e^{-A}$

$-Ax^2 + Bx = A(x-x_0)^2 + Ax_0^2 = Ax^2 + 2Axx_0 - Ax_0^2 + Ax_0^2 \Rightarrow x_0 =$

- Δk = width of $F(k) \sim \frac{1}{L} \Rightarrow \begin{cases} \text{short pulse } (L \to 0) \Rightarrow \text{broad spectrum} \\ \text{long pulse } (L \to \infty) \Rightarrow \text{narrow spectrum.} \end{cases}$

Group Velocity.

- If $\phi(k)$ is sharply peaked at k_0, and if $\omega(k)$ is analytical near k_0; Expand $\omega(k)$ in the vicinity of k_0
- Taylor: $\omega(k) = \underbrace{\omega(k_0)}_{\omega_0} + \underbrace{\frac{d\omega}{dk}\Big|_{k=k_0}}_{\omega_0'} (k-k_0) + O((k-k_0)^2)$
- $\Psi(x,t) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ikx} e^{-i[\omega_0 + \omega_0'(k-k_0)]t} = e^{-i\omega_0 t} e^{i\omega_0' k_0 t} \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ikx} e^{-i\omega_0' kt}$

$= e^{-i(\omega_0 - \omega_0' k_0)t} \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ik(x-\omega_0' t)}$

compare to initial state. $\Psi_0 = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ikx}$

- $\Psi(x,t) = \begin{pmatrix} \text{phase} \\ \text{fac.} \end{pmatrix} \Psi_0(x - \omega_0' t)$

the initial state moves along (translates) with a constant velocity $\omega_0' = v_{group}$

- $\Psi_0(x) \to \Psi_0(x - v_{group} t)$
- $v_{group} = \frac{d}{dk}\left(\frac{\hbar k^2}{2m}\right)\Big|_{k_0} = \frac{\hbar k}{m}\Big|_{k_0} = \frac{p_0}{m}$
- Example: Initial state $\Psi(x, t=0) = Ae^{-ax^2}$.

⓪ Normalize $1 = |A|^2 \int_{-\infty}^{\infty} dx \, e^{-ax^2} = |A|^2 \sqrt{\frac{\pi}{2a}} \Rightarrow A = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}}$

①, ② $\Psi_0(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ikx}$.

③ $\phi(k) = \int_{-\infty}^{\infty} dx \, \Psi_0(x) e^{-ikx} = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \int_{-\infty}^{\infty} dx \, e^{-ax^2 - ikx}$.

$\left[I = e^{Ax_0^2} \int_{-\infty}^{\infty} dx \, e^{-A(x-x_0)^2} \right.$ $y = x - x_0$

$\left. \Rightarrow \int_{-\infty}^{\infty} dy \, e^{-Ay^2} = \sqrt{\frac{\pi}{A}} = \sqrt{\frac{\pi}{A}} e^{Ax_0^2} = \sqrt{\frac{\pi}{A}} e^{\frac{B^2}{4A}} \right]$

$\phi(k) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \sqrt{\frac{\pi}{a}} e^{-\frac{k^2}{4a}}$

④ $\Psi(x,t) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \phi(k) e^{ikx} e^{-i\frac{\hbar k^2}{2m}t} = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \sqrt{\frac{\pi}{a}} \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-\left(\frac{k^2}{4a}\right)} e^{-i\frac{\hbar k^2}{2m}t} e^{ikx}$.

$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \, e^{-\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right)k^2} e^{ikx} = \frac{1}{2\pi} \sqrt{\frac{\pi}{\frac{1}{4a} + \frac{i\hbar t}{2m}}} e^{-\frac{x^2}{4\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right)}}$

$= \frac{1}{2\pi} \sqrt{\frac{\pi}{\frac{1}{4a} + i\frac{\hbar t}{2m}}} e^{-\frac{x^2}{4\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right)}}$

Probability Density: $|\Psi(x,t)|^2 = \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} \frac{\pi}{a} \frac{1}{(2\pi)^2} \sqrt{\frac{\pi}{\frac{1}{4a} - i\frac{\hbar t}{2m}}} e^{-\frac{x^2}{\frac{1}{a} - i\frac{2\hbar t}{m}}} e^{-\frac{x^2}{\frac{1}{a} + i\frac{2\hbar t}{m}}} \sqrt{\frac{\pi}{\frac{1}{4a} + i\frac{\hbar t}{2m}}}$

$= (\ldots) \frac{\pi}{\sqrt{\left(\frac{1}{4a}\right)^2 + \left(\frac{\hbar t}{2m}\right)^2}} e^{-Cx^2}$, $C = \frac{1}{\frac{1}{a} - i\frac{2\hbar t}{m}} + \frac{1}{\frac{1}{a} + i\frac{2\hbar t}{m}}$

$= \frac{\frac{2}{a}}{\left(\frac{1}{a}\right)^2 + \left(\frac{2\hbar t}{m}\right)^2}$

Question 3

- $\psi(x,0) = \cos k_0 x = \frac{1}{2}e^{ik_0x} + \frac{1}{2}e^{-ik_0x}$

  use Euler formula

$$\psi(x,t) = \frac{1}{2}e^{ik_0x}e^{-\frac{iE(k_0)t}{\hbar}} + \frac{1}{2}e^{-ik_0x}e^{-\frac{iE(-k_0)t}{\hbar}} \qquad E = \frac{\hbar^2k^2}{2m}$$

Fourier Transform

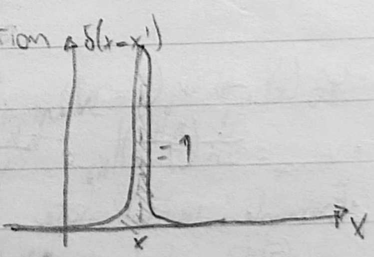
- $f(x) = \int_{-\infty}^{\infty}\frac{dk}{2\pi}F(k)e^{ikx}$
- If $F(k)=1$; $f(x) = \int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{ikx} = $ " $\begin{cases}\infty, & x=0\\ 0, & x\neq 0\end{cases}$ "
- Dirac Delta Function: $\delta(x) = \int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{ikx}$

  generalized function or distribution
- The Sifting Property (Proper definition of $\delta(x)$):
  - $f(x)$ - non-singular function

    $\int_{-\infty}^{\infty}dx'\, f(x')\,\delta(x-x') = f(x)$
  - if $f(x)=1$

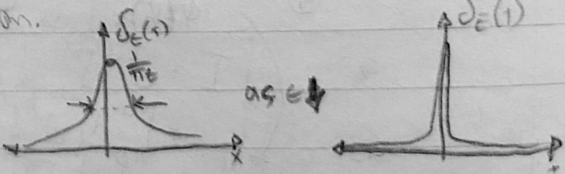
    $\int_{-\infty}^{\infty}dx'\,\delta(x-x') = 1$
  - if $x=0$

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



- $\delta(x) = \lim_{\epsilon\to 0}\delta_\epsilon(x) \leftarrow$ bell shaped function.
  - $\int_{-\infty}^{\infty}dx\,\delta_\epsilon(x) = 1$
  - Examples: $\delta_\epsilon(x) = \frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2}$

    $\int_{-\infty}^{\infty}dx\,\frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2} = 1$



- Interpreting the Sifting Property

  FT: $f(x) = \int_{-\infty}^{\infty}\frac{dk}{2\pi}F(k)e^{ikx}$

  $F(k) = \int_{-\infty}^{\infty}dx\, f(x)\,e^{-ikx}$

  $f(x) = \int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{ikx}\left(\int_{-\infty}^{\infty}dx'\,f(x')\,e^{-ikx'}\right)$

  $= \int_{-\infty}^{\infty}dx'\,f(x')\int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{ik(x-x')} \leftarrow \delta(x-x')$

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

"Proof" of the Parceval Theorem (A Physicists Proof)

- $f(x)$ - square-integrable: $\int_{-\infty}^{\infty} dx\, |f(x)|^2 = 1$

$\int_{-\infty}^{\infty} \frac{dk}{2\pi} |F(k)|^2 = ?$

$\int_{-\infty}^{\infty} \frac{dq}{2\pi} e^{iqb} = \delta(b)$

$$1 = \int_{-\infty}^{\infty} dx\, f^*(x) f(x) = \int_{-\infty}^{\infty} dx \underbrace{\left[\int_{-\infty}^{\infty} \frac{dk_1}{2\pi} F^*(k_1) e^{-ik_1 x}\right]}_{f^*(x)} \left[\int_{-\infty}^{\infty} \frac{dk_2}{2\pi} F(k_2) e^{-ik_2 x}\right]$$

$$= \iint_{-\infty}^{\infty} \frac{dk_1}{2\pi} \frac{dk_2}{2\pi} F^*(k_1) F(k_2) \underbrace{\int_{-\infty}^{\infty} dx\, e^{i(k_2 - k_1)x}}_{2\pi\delta(k_2 - k_1)}$$

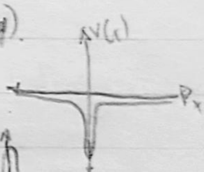
$$= \int_{-\infty}^{\infty} \frac{dk_1}{2\pi} F^*(k_1) \underbrace{\int_{-\infty}^{\infty} dk_2\, \delta(k_2 - k_1) F(k_2)}_{F(k_1)}$$

$$= \int_{-\infty}^{\infty} \frac{dk_1}{2\pi} |F(k_1)|^2 = \int_{-\infty}^{\infty} \frac{dk}{2\pi} F(k)$$

$$\int_{-\infty}^{\infty} dx\, |f(x)|^2 = 1 = \int_{-\infty}^{\infty} \frac{dk}{2\pi} |F(k)|^2$$

Dirac Delta Function

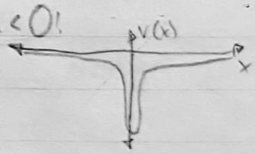
- In 2-D, $\iint_{-\infty}^{\infty} \frac{dk_x}{2\pi} \frac{dk_y}{2\pi} e^{i\vec{k}\cdot\vec{r}} \equiv \iint_{-\infty}^{\infty} \frac{d^2k}{(2\pi)^2} e^{i\vec{k}\cdot\vec{r}} = \delta(x)\delta(y)$.
- Delta-Function Potential: $V(x) = \alpha\,\delta(x)$



if $\alpha < 0$, attractive δ-potential

if $\alpha > 0$, repulsive δ-potential

- Focus on the bound states ($E < 0$) for $\alpha < 0$!



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

Integrate S.E.!

From $-\epsilon$ to ϵ

$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon} dx \frac{\partial^2\psi}{\partial x^2} + \alpha\int_{-\epsilon}^{\epsilon} dx\,\delta(x)\psi(x) = E\int_{-\epsilon}^{\epsilon} dx\,\psi(x)$

$\alpha\psi(0)$

$-\frac{\hbar^2}{2m}\left(\psi'(+0) - \psi'(-0)\right) = \alpha\psi(0)$

$\psi'(+0) - \psi'(-0) = \frac{2m\alpha}{\hbar^2}\psi(0)$

Region 1 ($x < 0$)

$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = -|E|\psi \Rightarrow \frac{d^2\psi}{dx^2} = \kappa^2\psi$ $\qquad \kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$

general solution: $\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}$

physical solution: $\psi(x) = Be^{\kappa x}$ ($\to 0$ @ $x \to -\infty$)

Region 2 ($x > 0$)

general solution: $\psi(x) = Fe^{-\kappa x} + Ge^{\kappa x}$

physical solution: $\psi(x) = Fe^{-\kappa x}$ ($\to 0$ @ $x \to +\infty$)

Region 3 ($x = 0$)

$-\kappa F - \kappa B = \frac{2m\alpha}{\hbar^2}\psi(0) \Rightarrow -2\kappa F = \frac{2m\alpha}{\hbar^2}F \Rightarrow \kappa = \frac{m|\alpha|}{\hbar^2}$

$\psi(x) = \begin{cases} Fe^{-\kappa x}, & x > 0 \\ Fe^{\kappa x}, & x < 0 \end{cases}$

Boundary Conditions:

(1) $\psi(x)$ is continuous

$\Rightarrow \psi(+0) = \psi(-0)$

(2) $\psi'(x)$ is continuous only for nonsingular potential

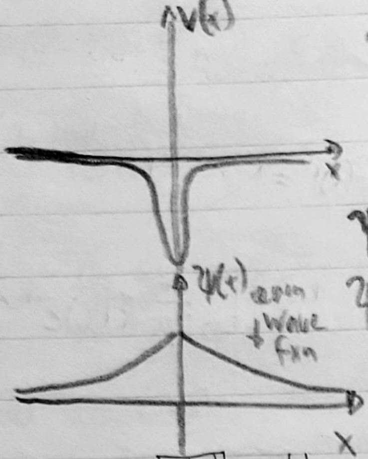
(3) $\psi'(+0) - \psi'(-0) = \frac{2m\alpha}{\hbar^2}\psi(0)$

Bound state energy,

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

only one bound state

$V(-x) = V(x) \to \psi(x)$ one other option of deduction



- $\psi(x) = F e^{-\kappa|x|}$

  $\kappa = \frac{\sqrt{2m|E|}}{\hbar}$

  $V(x) = \alpha\,\delta(x) \qquad \alpha < 0$

  $\psi'(+0) - \psi'(-0) = \frac{2m\alpha}{\hbar^2}\psi(0)$

  $\psi(+0) = \psi(-0) = \psi(0)$

  $1 = \int_{-\infty}^{\infty} dx\, |\psi|^2 = |F|^2 \int_{-\infty}^{\infty} dx\, e^{-2\kappa|x|} = 2|F|^2 \int_{-\infty}^{\infty} dx\, e^{2\kappa x}$

  $= |F|^2 \frac{1}{\kappa} \Rightarrow F = \sqrt{\kappa}$

$\psi(x) = \sqrt{\frac{m|\alpha|}{\hbar^2}}\, e^{-\frac{m|\alpha|}{\hbar^2}x}$

Scattering States $(E > 0)$

- $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \alpha\,\delta(x)\psi = E\psi$
- Region 1: $x < 0$

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

  $\frac{d^2\psi}{dx^2} = -k\psi \quad , \quad k = \sqrt{\frac{2mE}{\hbar^2}} > 0.$

  General Solution: $\psi(x) = Ae^{ikx} + Be^{-ikx}$ (finite, non-normalizable)

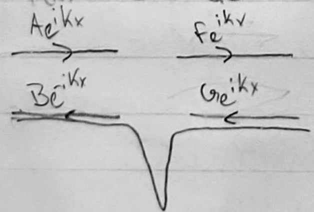
  (ψ_1)

Region 2: $x > 0$

$\psi(x) = Fe^{ikx} + Ge^{-ikx}$ (finite, non-normalizable).

(ψ_2)

- So that,



Relation between A, B, F, G are found by the boundary conditions.

- ① $\underbrace{F + G}_{\psi(+0)} = \underbrace{A + B}_{\psi(-0)}$

  ② $\psi_2'(x) = ikFe^{ikx} - ikGe^{-ikx} \Rightarrow \psi'(+0) = \psi_2'(0) = ik(F - G)$

  $\psi_1'(x) = ikAe^{ikx} - ikBe^{-ikx} \Rightarrow \psi'(-0) = \psi'(0) = ik(A - B)$

  $ik(F - G - A + B) = \frac{2m\alpha}{\hbar^2}\underbrace{(A + B)}_{\psi(0)}$

- $F + G = A + B$

  $F - G - A + B = \frac{2m\alpha}{\hbar^2 k}(A + B)$

  2 equations, 4 unknowns

- Use physical arguments to select a solution probability

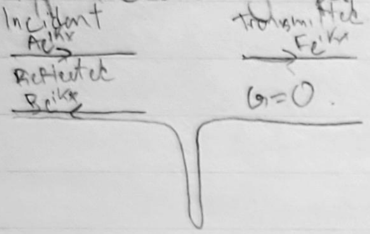
- Current carried by $\psi(x)$: $J = -\frac{i\hbar}{2m}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)$ velocity.
- If $\psi(x) = Ae^{ikx} \to J_A = \frac{\hbar k}{m}|A|^2 = \frac{p}{m}|A|^2 = v\,|A|^2$

deBroglie Relation: $\hbar k = p$.

$\psi(x) = Be^{-ikx} \to J_B = -\frac{\hbar k}{m}|B|^2$

$\psi(x) = Fe^{ikx} \to J_F = \frac{\hbar k}{m}|F|^2$

$\psi(x) = Ge^{-ikx} \to J_G = \frac{-\hbar k}{m}|G|^2$

- $J_A, J_F > 0$ & $J_B, J_G < 0$
- Typical Scattering Experiment: Particles are coming from one direction (eg $-\infty$)
- 

$F = A+B$

$F + A - B = -\frac{2m\alpha}{i\hbar^2 k}(A+B) = 2i\beta\, b \implies$

$\frac{2m\alpha}{i\hbar^2 k} = 2i\beta$

$\beta = \frac{m|\alpha|}{\hbar^2 k}$

$\beta(E) = m|\alpha$

divide by A $\Rightarrow$ $\begin{cases} t = 1 + r \\ t + 1 - r = 2i\beta \end{cases}$, $t = \frac{F}{A}$ Fraction Transmitted, $r = \frac{B}{A}$ Fraction Reflected.

- $t = \frac{1}{1-i\beta}$

$r = \frac{i\beta}{1-i\beta}$

- Reflection Coefficient: $R = \frac{|J_B|}{J_A} = \left|\frac{J_B}{J_A}\right|$

Transmission Coefficient: $T = \frac{|J_F|}{J_A} = \left|\frac{J_F}{J_A}\right|$

- $R + T = 1$
- Conversation of Current: $\underbrace{J_A + J_B}_{\text{Current to the left}} = \underbrace{J_F}_{\text{2nd Current}}$ $\to$ centered around E, $\to$ all components of a wave packet scatter in the same way

$J_A = J_F - J_B = J_F + |J_B|$

R, T weakly dependent energy

- $R = \frac{|J_B|}{J_A} = \frac{\frac{\hbar k}{m}|B|^2}{\frac{\hbar k}{m}|A|^2} = \frac{|B|^2}{|A|^2} = |r|^2 = \frac{-i\beta}{1+i\beta}\,\frac{i\beta}{1-i\beta} = \frac{\beta^2}{1+\beta^2}$

$T = \frac{J_F}{J_A} = \frac{\frac{\hbar k}{m}|F|^2}{\frac{\hbar k}{m}|A|^2} = \frac{|F|^2}{|A|^2} = |t|^2 = \frac{1}{1+i\beta}\,\frac{1}{1-i\beta} = \frac{1}{1+\beta^2}$

- Energy dependence:

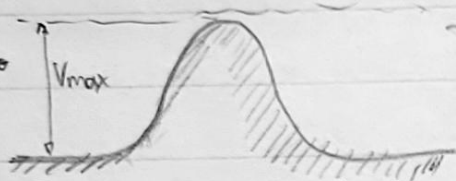
$\beta = \frac{m|\alpha|}{\hbar^2 k} = \frac{m|\alpha|}{\hbar^2}\sqrt{\frac{\hbar^2}{2mE}} = \frac{|\alpha|}{\hbar}\sqrt{\frac{m}{2E}}$

$R(E) = \frac{1}{1+\frac{1}{\beta^2}} = \frac{1}{1+\frac{2\hbar^2 E}{m\alpha^2}}$ higher energy: $E \gg \frac{m\alpha^2}{\hbar^2}$ $R \to 0, T \to 1$ almost all transmitted

$T(E) = \frac{1}{1+\beta^2} = \frac{1}{1+\frac{m\alpha^2}{2\hbar^2 E}}$ low energy: $E \ll \frac{m\alpha^2}{\hbar^2}$ $R \to 1, T \to 0$ almost all reflected

$\to$ Depend only on $|\alpha| \to$ same R & T for a repulsive delta function: $\alpha\delta(x)$, $\alpha > 0$.

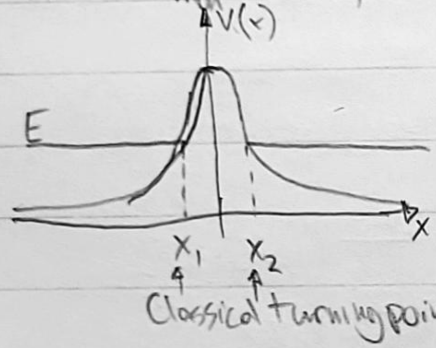
Classical Scattering

- 

  Potential Barrier $V_{max} = \max V(x)$
  $V(x) > 0$

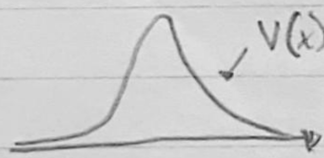
- if $E > V_{max}$: $T = 1$, $R = 0$ ← Perfect Transmission
  if $E < V_{max}$: $T = 0$, $R = 1$ ← Perfect Reflection ← because the classical probability to be found at $x_1 < x < x_2$ is 0

  ↑ not the case in QM.

- 

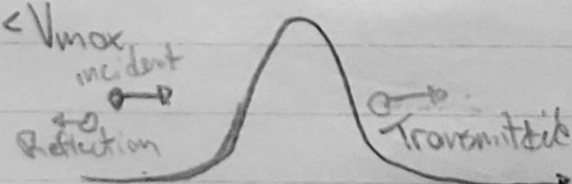
  $V(x_1) = E$
  $V(x_2) = E$

Tunneling

- 

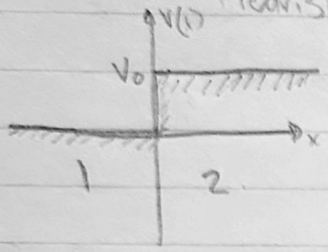
$R + T = 1$.

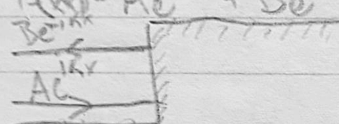
- if $E > V_{max}$; $T = 1$ } Classically
  if $E < V_{max}$; $T = 0$ }
- if $E < V_{max}$; $0 < T < 1$ } QM
  if $E > V_{max}$; $0 < R < 1$ }
- $E < V_{max}$

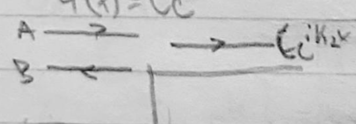


- Statistical Interpretation
  - $N \gg 1$ incident particles.
  - TN, RN - Transmitted & reflected

Step Barrier

- $V(x) = V_0\,\Theta(x) = \begin{cases} V_0, & x>0 \\ 0, & x<0 \end{cases}, \quad V_0 > 0$
  - Heaviside Step Function $\Theta(x) = \begin{cases} 1, & x>0 \\ 0, & x<0 \end{cases}, \quad \Theta'(x) = \delta(x)$
- 

- Region 1: $x<0$, $V(x)=0$
  - $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad (E>0)$
  - $\frac{d^2\psi}{dx^2} = -k^2\psi \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}}$
  - General solution
  - $\psi(x) = Ae^{ikx} + Be^{-ikx}$
  - 

- Region 2: $x>0$, $V(x) = V_0$
  - $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi$
  - $\frac{d^2\psi}{dx^2} = \frac{-2m}{\hbar^2}(E-V_0)\psi$
  - if $E>V_0$: $\frac{d^2\psi}{dx^2} = -k_2^2\psi$; $k_2 = \sqrt{\frac{2m}{\hbar^2}(E-V_0)}$
  - General Solution
  - $\psi(x) = Ce^{ik_2x} + De^{-ik_2x}$, no particles from $+\infty$ so $D=0$
  - $\psi(x) = Ce^{ik_2x}$
  - 

- Boundary Conditions: $\psi(+0) = \psi(-0) \Rightarrow C = A + B$
  - $\psi'(+0) = \psi'(-0) \Rightarrow ik_2C = ik_1A - ik_1B$
  - $r = \frac{B}{A},\ t = \frac{C}{A}$
  - $\begin{cases} t = 1 + r \\ k_2 t = k_1(1-r) \end{cases} \Rightarrow \dots \Rightarrow \quad r = \frac{k_1-k_2}{k_2+k_1}, \quad t = \frac{2k_1}{k_1+k_2}$
- Reflection Coefficient: $R = \frac{|J_B|}{J_A}$, $J_A = \frac{\hbar k_1}{m}|A|^2$, $J_B = -\frac{\hbar k_1}{m}|B|^2$, $J_C = \frac{\hbar k_2}{m}|C|^2$
  - $= \frac{|B|^2}{|A|^2} = |r|^2 = \left(\frac{k_1-k_2}{k_1+k_2}\right)^2 =$
- Transmition Coefficient: $T = \frac{J_C}{J_A} = \frac{k_2|C|^2}{k_1|A|^2} = \frac{k_2}{k_1}|t|^2 = \left(\frac{2k_1}{k_1+k_2}\right)^2\frac{k_2}{k_1} =$
- $R+T = \frac{(k_1-k_2)^2 + 4k_1k_2}{(k_1+k_2)^2} = \frac{k_1^2+k_2^2-2k_1k_2+4k_1k_2}{(k_1+k_2)^2} = \frac{(k_1+k_2)^2}{(k_1+k_2)^2} = 1$

• Region 2: • $x>0$, $V(x)=0$ $(E<V_0)$

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

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

$$\frac{d^2\psi}{dx}=\varkappa_2^2\psi \quad ; \varkappa_2=\sqrt{-\frac{2m}{\hbar^2}(E-V_0)}$$

• General Solution

$$\psi(x)=Ce^{-\varkappa_2 x}+De^{\varkappa_2 x}$$

• Physical Solution $(D=0)$.

$$\psi(x)\,Ce^{-\varkappa_2 x}$$

• Boundary Conditions: $\psi(+0)=\psi(-0) \Rightarrow C=A+B$

$\psi'(+0)=\psi'(-0) \Rightarrow i\varkappa_2 C=K_1(A-B)$

$\frac{C}{A}=\frac{2K_1}{K_1+i\varkappa_2}$, $\frac{B}{A}=\frac{K_1-i\varkappa_2}{K_1+i\varkappa_2}$

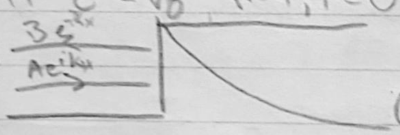
• Reflection Coefficient: $J_C=0$, $J_B=-\frac{\hbar K_1}{m}|B|^2$, $J_A=$

$R=\frac{|J_B|}{J_A}=\frac{|B|^2}{|A|^2}=\left|\frac{K_1-i\varkappa_2}{K_1+i\varkappa_2}\right|^2=\dots=1$

• Transmission Coefficient $J_C=0$, $T=0$.

• $R+T=1+0=1$.

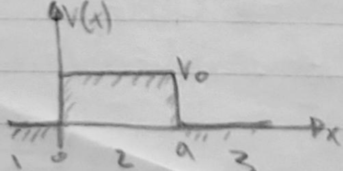
• if $E<V_0$ $R=1, T=0$.



but the probability $|\psi(x)|^2$ to find the particle @ $x>0$ is non-zero.

Finite Barrier

• $V(x)=V_0\,\Theta(x)\,\Theta(a-x)=\begin{cases}V_0, & 0<x<a\\ 0, & \text{otherwise}\end{cases}$; $V_0>0$

• 

$E<V_0$

• Region 1 & 3: $V_0=0$, $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=E\psi \to \frac{d^2\psi}{dx^2}=-K^2\psi$ $K=\sqrt{\frac{2mE}{\hbar}}$

• $\psi(x)=Ae^{ikx}+Be^{-ikx}$

Region 3: $V_0=0 \longrightarrow \psi(x)=Fe^{ikx}+\underbrace{Ge^{-ikx}}_{=0}=Fe^{ikx}$

- Region 2: $V = V_0$; $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V_0\psi = E\psi$

  $\frac{\partial^2\psi}{\partial x^2} = \varkappa^2\psi$, $\varkappa = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$

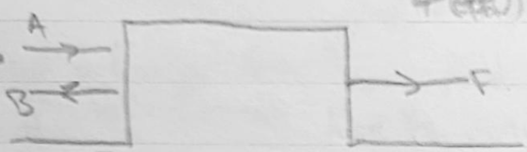
  $\psi(x) = Ce^{\varkappa x} + De^{-\varkappa x}$

- 5 unknowns (A, B, C, D, F), 4 Boundary Conditions
- Boundary Conditions: $\psi(+0) = \psi(-0)$ ← $x = 0$ $C + D = A + B$

  $\psi'(+0) = \psi'(-0)$ $\qquad \varkappa(C - D) = ik(A - B)$

  $\psi(a+0) = \psi(a-0)$ ← $x = a$ $Fe^{ika} = Ce^{\varkappa a} + De^{-\varkappa a}$

  $\psi'(a+0) = \psi'(a-0)$ $\qquad ikFe^{ika} = \varkappa Ce^{\varkappa a} - \varkappa De^{-\varkappa a}$

- 

- $r = \frac{B}{A} = ?$ $\quad t = \frac{F}{A} = ?$
- $\gamma = \frac{\varkappa}{k}$ ⇒

  $C + D = A + B$ ①

  $C - D = \frac{i}{\gamma}(A - B)$ ②

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

  $Fe^{ika} = -i\gamma Ce^{\varkappa a} + i\gamma De^{-\varkappa a}$ ④

- Step 1: Use ① & ② to express C & D in terms of A & B

  Step 2: Insert $C(A,B)$ & $D(A,B)$ into ③ & ④

  Step 3: Solve ③ & ④ for $r = \frac{B}{A}$, & $t = \frac{F}{A}$

- $t =$

$\coth x = \frac{\cosh x}{\sinh x} = \mathrm{cth}$

$= \frac{e^{x} + e^{-x}}{e^{x} - e^{-x}}$

$\mathrm{cth}^2(\varkappa a) - 1 = \frac{1}{\sinh^2(\varkappa a)}$

- $r = \frac{B}{A} = \frac{\frac{1}{\gamma} + \gamma}{(\frac{1}{\gamma} - \gamma) + 2i\,\mathrm{cth}(\varkappa a)}$, $k = \sqrt{\frac{2mE}{\hbar^2}}$, $\varkappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$; $\gamma = \frac{\varkappa}{k}$.

  ⇒ $R = \frac{|J_B|}{J_A} = \frac{|B|^2}{|A|^2} = |r|^2 = \frac{(\frac{1}{\gamma} + \gamma)^2}{(\frac{1}{\gamma} - \gamma)^2 + 4\,\mathrm{cth}^2(\varkappa a)}$

  $(\frac{1}{\gamma} - \gamma)^2 = \frac{1}{\gamma^2} + \gamma^2 - 2 = \frac{1}{\gamma^2} + \gamma^2 + 2 - 4$

  $= \frac{(\frac{1}{\gamma} + \gamma)^2}{(\frac{1}{\gamma} + \gamma)^2 + 4(\mathrm{cth}^2(\varkappa a) - 1)} = \frac{(\frac{1}{\gamma} + \gamma)^2 \sinh^2(\varkappa a)}{4 + (\frac{1}{\gamma} + \gamma)^2 \sinh^2(\varkappa a)}$

- $T = 1 - R = 1 - \frac{(\frac{1}{\gamma} + \gamma)^2 \sinh^2(\varkappa a)}{4 + (\frac{1}{\gamma} + \gamma)^2 \sinh^2(\varkappa a)} = \frac{4}{4 + (\frac{1}{\gamma} + \gamma)^2 \sinh^2(\varkappa a)} = \frac{1}{1 + \frac{1}{4}(\frac{1}{\gamma} + \gamma)^2 \sinh^2(\varkappa a)}$

  sub $\gamma = \frac{\varkappa}{k}$. ⇒ $(\gamma + \frac{1}{\gamma})^2 = \gamma^2 + \frac{1}{\gamma^2} + 2 = \frac{\varkappa^2}{k^2} + \frac{k^2}{\varkappa^2} + 2 = \frac{V_0 - E}{E} + \frac{E}{V_0 - E} + 2 = \frac{V_0^2}{E(V_0 - E)}$

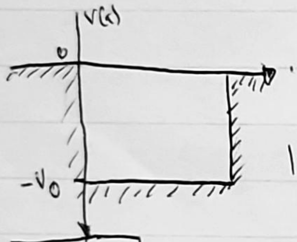
  $T = \frac{1}{1 + \frac{V_0^2}{E(V_0 - E)4}\sinh^2(\varkappa a)}$

- If $E \ll V_0$ ⇒ $T \to 0$.

- If $E > V_0$:
- Solution in Region 2: $\psi(x) = Ce^{ik_1x} + De^{-ik_1x}$; $k_1 = \sqrt{\frac{2m}{\hbar^2}(E-V_0)}$
- If $E < V_0$:
  Solution in Region 2: $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$ (*) obtained by replacing $ik_1 \to \kappa$.
- $T = \dfrac{1}{1 + \frac{V_0^2}{4E(V_0-E)}\sinh^2(\kappa a)}$, $\sinh(xi) = \dfrac{e^{ix} - e^{-ix}}{2} = i\sin x$.

  $= \dfrac{1}{1 + \frac{V_0^2}{4E(E-V_0)}\sin^2(k_1 a)}$, $k_1 = \sqrt{\frac{2m}{\hbar^2}(E-V_0)}$

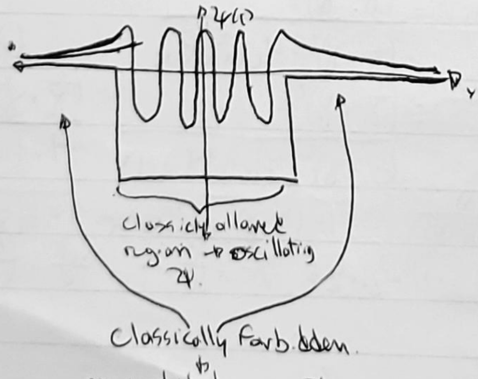
Potential Well ($V_0 > 0$)



- $T = \dfrac{1}{1 + \frac{V_0^2}{4E(E+V_0)}\sin^2(k_1 a)}$, $k_1 = \sqrt{\frac{2m}{\hbar^2}(E+V_0)}$

  If $k_1 a = \pi n$, then $\sin^2(k_1 a) = 0$ & $T = 1$
- $\sqrt{\frac{2m}{\hbar^2}(E+V_0)}\, a = \pi n \Rightarrow E = -V_0 + \underbrace{\frac{\pi^2\hbar^2}{2ma^2} n^2}_{\text{energies of a particle in a box of size } a.}$
- This is the Ramsauer effect.

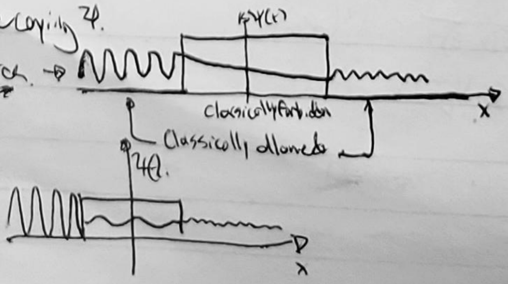
Wave Functions:



- Scattering states →

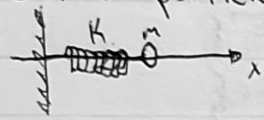
  $E < V_0$ →

  $E > V_0$ →



Harmonic Oscillator.

- Classical particle in 1D of mass m + spring of stiffness k.



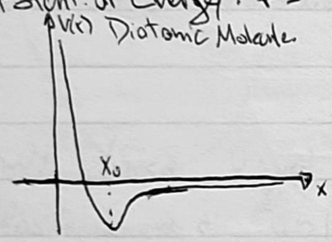
Hooke's Law: $F = -kx$.

$m\ddot{x} = -kx$

$\ddot{x} = -\omega^2 x \Rightarrow \omega = \sqrt{\frac{k}{m}}$

$x(t) = \underbrace{A}_{\text{amplitude}}\sin(\omega t + \underbrace{\phi}_{\text{phase}})$

- Potential Energy: $F = -\frac{\partial V}{\partial x}$, $V = \frac{kx^2}{2}$.



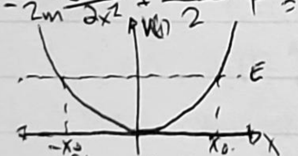
Near the minimum: $V(x) = V(x_0) + \underbrace{V'(x_0)}_{=0}(x-x_0) + \frac{1}{2}V''_0(x-x_0)^2 + \frac{1}{6}V'''_0(x-x_0)^3 + \dots$ Taylor Series

Small oscillations $\rightarrow V(x) = \text{const.} + \underbrace{\frac{V''(x_0)}{2}x^2}_{\text{"Stiffness" } k.} + \underbrace{\frac{\alpha}{6}x^3 + \dots}_{\text{describe anharmonic effects.}}$

$x - x_0 \to x$

- In the harmonic approximations:
  - $V(x) = \frac{m\omega^2x^2}{2}$
- Schrödinger Equation:

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



$V(|x| \to \infty) \to \infty \Rightarrow$ only bound states.

- Classically allowed Region: $-x_0 \le x \le x_0$.

$\pm x_0 \rightarrow$ Classical turning points.

$V(\pm x_0) = E \Rightarrow \frac{m\omega^2x_0^2}{2} = E \Rightarrow x_0 = \sqrt{\frac{2E}{m\omega^2}}$

- We expect that @ $|x| >> x_0$, ψ is exponentially decaying:

$\hookrightarrow \psi(x) \underset{x\to+\infty}{\sim} e^{-\mathcal{X}x}$; $\mathcal{X} = \sqrt{\frac{2m}{\hbar^2}(V-E)}$

$\mathcal{X}(x) = \sqrt{\frac{2m}{\hbar^2}(V(x)-E)}$

$= \sqrt{(\dots)x^2} \sim x.$

seek solutions of $\rightarrow$ - $\psi(x) = h(x)\,e^{-\lambda x^2}$

$\frac{\partial\psi}{\partial x} = h'e^{-\lambda x^2} - 2\lambda h x e^{-\lambda x^2}$

$\frac{\partial^2\psi}{\partial x} = h''e^{-\lambda x^2} - 2\lambda h' x e^{-\lambda x^2} - 2\lambda h e^{-\lambda x^2} - 2\lambda x h' e^{-\lambda x^2} + 4\lambda^2 h x^2 e^{-\lambda x^2}$

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

$-\frac{\hbar^2}{2m}\left(h'' - 4\lambda h' x - 2\lambda h + 4\lambda^2 h x^2\right) + \frac{m\omega^2x^2}{2}h = Eh.$

$-\frac{\hbar^2}{2m}h'' + \frac{\hbar^2}{2m}4\lambda x h' + \frac{\hbar^2}{2m}2\lambda h \underbrace{- \frac{\hbar^2}{2m}4\lambda^2x^2h + \frac{m\omega^2}{2}x^2h}_{\text{choose } \lambda \text{ to cancel the } x^2h \text{ terms.}} = Eh.$

$-\frac{\hbar^2}{2m}4\lambda^2 + \frac{m\omega^2}{2} = 0 \Rightarrow \lambda = \frac{+m\omega}{2\hbar}, ~~-\frac{m\omega}{2\hbar}~~$

- Wave Function: $\psi(x) = h(x)\,e^{-\frac{m\omega}{2\hbar}x^2}$

$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2 x^2}{2}$

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

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

- h is found from the equation, $-\frac{\hbar^2}{2m}\frac{d^2h}{dx^2} + \frac{\hbar^2}{2m}x\frac{2m\omega}{\hbar}\frac{dh}{dx} + \frac{\hbar^2}{2m}\frac{m\omega}{\hbar}h = Eh$.
  - $-\frac{\hbar^2}{2m}\frac{d^2h}{dx^2} + \hbar\omega x\frac{dh}{dx} + \hbar\omega h/2 = Eh$.
  - Dimensionless Energy: $\epsilon = \frac{E}{\hbar\omega/2} \Rightarrow E = \frac{\hbar\omega}{2}\epsilon$
    Dimensionless Position: $\xi = \frac{x}{\sqrt{\hbar/m\omega}} \Rightarrow x = \sqrt{\frac{\hbar}{m\omega}}\,\xi$
  - $-\frac{\hbar^2}{2m}\frac{1}{\frac{\hbar}{m\omega}}\frac{d^2h}{d\xi^2} + \hbar\omega\xi\frac{dh}{d\xi} + \frac{\hbar\omega}{2}h = \frac{\hbar\omega}{2}\epsilon\xi$
  - $-\frac{d^2h}{d\xi^2} + 2\xi\frac{dh}{d\xi} + h = \epsilon h \Rightarrow$ solve for $h(\xi)$.
  - ~~Solution:~~ $\cancel{\psi(\xi) = h(\xi)e^{-\frac{\xi^2}{2}}}$
  - $\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (\epsilon-1)h = 0 \Rightarrow$ solve for h
- Hermite Equation, solve by the Forbenius method, seek solutions of the form of a power series.
- $h(\xi) = \sum_{k=0}^{\infty} a_k\xi^k = a_0 + a_1\xi + a_2\xi^2 + \dots$
- The power series must terminate ($a_k = 0$, $k > n$), otherwise $h(\xi) \sim e^{\xi^2}$ @ $|\xi| \to \infty$, & $\psi(\xi) \sim e^{\frac{\xi^2}{2}}$ is nonnormalizable.
- $\frac{dh}{d\xi} = \sum_k k a_k\xi^{k-1} = a_1 + 2a_2\xi + 3a_3\xi^2 \dots$, $\frac{d^2h}{d\xi^2} = \sum_k k(k-2)a_k\xi^{k-2} = \dots$

$k-2 = m$, $k = m+2$ →

- $\sum_k k(k-1)a_k\xi^{k-2} - 2\sum_k k a_k\xi^{k-1} + (\epsilon+1)\sum_k a_k\xi^k = 0$.
  $\sum_m (m+2)(m+1)a_{m+2}\xi^m$ $\vdots$ $\vdots$

$m = k$ →

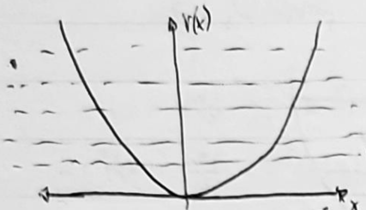
  $\sum_k (k+2)(k+1)a_{k+2}\xi^k$ $\vdots$ $\vdots$

- $\sum_{k=0}^{\infty}\underbrace{[(k+2)(k+1)a_{k+2} - 2ka_k + (\epsilon-1)a_k]}_{0}\xi^k = 0$
- $(k+2)(k+1)a_{k+2} - 2ka_k + (\epsilon-1)a_k = 0$.
- recursion relation: $a_{k+2} = \left[\frac{2k+1-\epsilon}{(k+2)(k+1)}\right]a_k$.

Agrees with → Parity

- Start with $a_0 \Rightarrow a_2, a_2 \Rightarrow a_4 \dots$
  Start with $a_1 \Rightarrow a_3, a_3 \Rightarrow a_5 \dots$
- Asymptotic behaviour of h @ $|\xi| \to \infty$ is determined by the large-k terms. ($k \gg 1$, $k \gg \epsilon$)
- $a_{k+2} \approx \frac{2k}{k^2}a_k = \frac{1}{\frac{k}{2}}a_k$
  $a_{k+4} = \frac{1}{(k+2)/2}a_{k+2} = \frac{1}{(\frac{k}{2}+1)\frac{k}{2}}a_k$
  $a_{k+6} = \frac{1}{(k+4)/2}a_{k+4} = \frac{1}{(\frac{k}{2}+2)(\frac{k}{2}+1)\frac{k}{2}}a_k$.
- $k \to \infty$: $a_k \approx \frac{const}{(\frac{k}{2})!}$
- $h(\xi) \approx \sum_k \frac{const}{(\frac{k}{2})!}\xi^k \sim \sum_m \frac{1}{(m)!}\xi^{2m} = \frac{\xi^{2m}}{(m)!} \Rightarrow h(\xi) \sim e^{\xi^2} \Rightarrow \psi(\xi) \sim e^{\frac{\xi^2}{2}}$
- Taylor series $e^x = \sum_m \frac{1}{m!}x^m$

- $h(\xi)$ and $\psi(\xi)$ diverge @ $|\xi| \to \infty$ unless the power series terminates @ some $k=n$: $a_n \neq 0$ but $a_{n+2} = a_{n+n} = \ldots = 0$.
- If $\epsilon = 2n+1$ $\longrightarrow$
- $h(\xi)$ is a polynomial of degree n
  - if n is even: $h(\xi) = a_0 + a_2\xi^2 + \ldots + a_n\xi^n = h(-\xi)$
  - if n is odd: $h(\xi) = a_1\xi + a_3\xi^3 + \ldots + a_n\xi^n = -h(-\xi)$.
- Physical energy is quantized.
  - $E = (2n+1)\frac{\hbar\omega}{2} \Rightarrow E_n = \hbar\omega(n+\frac{1}{2})$ ← energies of the stationary state of the harmonic oscillator.



$n=1$, $E_1 = \frac{3}{2}\hbar\omega$, first excited stat.
$n=0$, $E_0 = \frac{\hbar\omega}{2}$, ground state

- Classical Energy: $E = \frac{p^2}{2m} + \frac{m\omega^2x^2}{2}$
- Minimum Classical Energy $= 0$, for $x = 0 = p$.
  Minimum QM Energy $= \frac{\hbar\omega}{2}$, corresponds to the zero-point oscillations.
- The wave functions:
  $\psi_n(x) = ?$, $\epsilon = (2n+1)$, $a_{k+2} = \frac{2(k-n)}{(k+2)(k+1)} a_k$
- $n=0$; $a_0 \neq 0$, $a_2 = 0 \Rightarrow h(\xi) = a_0$.
  $n=1$; $a_1 \neq 0$, $a_{k+2} = \frac{2(k+1)}{(k+2)(k+1)} a_k = 0 \Rightarrow h(\xi) = a_1\xi$
  $n=2$; $a_2 \neq 0$, $a_{k+2} = \frac{2(k+2)}{(k+2)(k-1)} a_k = 0 \Rightarrow h(\xi) = a_0(1-2\xi^2)$.
  $n=3$; . . . . $\Rightarrow h(\xi) = a_1(\xi - \frac{2}{3}\xi^3)$.
- By convention: a_0 (for even n), a_1 (for odd n), are chosen so that $a_n = 2^n$
- $\left.\begin{array}{l} h_0(\xi) = 1 \\ h_1(\xi) = 2\xi \\ h_2(\xi) = -2 + 4\xi^2 \end{array}\right\}$ by convention.
- Hermite Polynomials:
  $h_n(\xi) = H_n(\xi)$
  $h_0(\xi) = 1$
  $h_1(\xi) = 2\xi$
  $h_2(\xi) = -2 + 4\xi^2$
  $h_3(\xi) = -12\xi + 8\xi^3$
  $h_4(\xi) = 12 - 48\xi^2 + 16\xi^4$

Put on formula sheet. $\longrightarrow$

Useful formula: Rodriguez Formula.
$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$

Orthogonality of Hermite Polynomials:
$\int_{-\infty}^{\infty} d\xi\, H_n(\xi) H_m(\xi) e^{-\xi^2} = (\sqrt{\pi}\, 2^n n!)\, \delta_{nm}$

- $\psi_n(x) = \underset{\uparrow}{C_n} H_n(\xi) e^{-\frac{\xi^2}{2}}$

  normalization coefficient.

- $1 = \int_{-\infty}^{\infty} dx\, |\psi|^2 = |C_n|^2 \underbrace{\int_{-\infty}^{\infty} dx\, H_n^2(\xi)\, e^{-\xi^2}} \Rightarrow |C_n|^2 \sqrt{\frac{\hbar}{m\omega}} \times \underbrace{\int_{-\infty}^{\infty} d\xi\, H_n^2(\xi) e^{-\xi^2}}_{\sqrt{\pi}\, 2^n n!}$

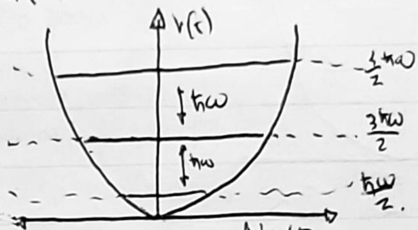
$|C_n|^2 \sqrt{\frac{\hbar\pi}{m\omega}}\, 2^n n! = 1$

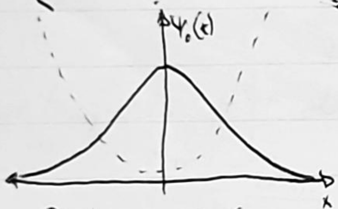
$C_n = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}}$

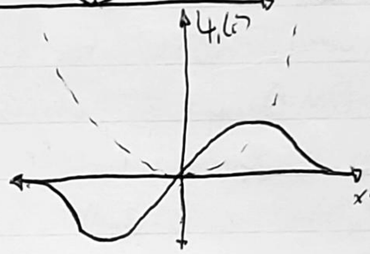
- Normalized Stationary States:

  $\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}\, x\right) e^{-\frac{m\omega}{2\hbar} x^2}$, $n = 0, 1, 2 \ldots$

- Hermite Polynomials
  $\begin{cases} H_0(\xi) = 1 \\ H_1(\xi) = 2\xi \\ H_2(\xi) = 4\xi^2 - 2 \end{cases}$



- 



ψ_n has n zeros.

- Example: Initial State of the LHO.
  - $\psi_0(x) = \psi(x,0) = Ax^2 e^{-\frac{m\omega^2}{2\hbar} x^2}$

    $\psi(x,t) = ?$

    $|\psi(x,t)|^2 = ?$
  - $\langle x \rangle, \langle p \rangle, \langle H \rangle, \langle K \rangle, \langle V \rangle = ?$
  - $\psi(x,0) = \sum_n C_n \psi_n(x)$

    $\psi(x,0) = \sum_n C_n \psi_n(x)\, e^{-\frac{i}{\hbar} E_n t}$
  - $C_n = ?$, $C_n = \int_{-\infty}^{\infty} dx\, \psi_n^*(x) \psi(x,0)$
    - Guess that only ψ_0 & ψ_2 contribute to $\psi(x,0)$
    - $\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar} x^2}$

      $\psi_2(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{2\sqrt{2}} H_2\left(\sqrt{\frac{m\omega}{\hbar}}\, x\right) e^{-\frac{m\omega}{2\hbar} x^2} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \left(\sqrt{2} \frac{m\omega}{\hbar} x^2 - \frac{1}{\sqrt{2}}\right) e^{-\frac{m\omega}{2\hbar} x^2}$
  - $\psi(x,0) = C_0 \psi_0(x) + C_2 \psi_2(x)$

    $A\cancel{x^2} \cancel{e^{-(\ldots)}} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \left[C_0 + C_2 \left(\sqrt{2} \frac{m\omega}{\hbar} x^2 - \frac{1}{\sqrt{2}}\right)\right] e^{-(\ldots)}$

    $Ax^2 = \left(C_0 - C_2 \frac{1}{\sqrt{2}}\right) \left(\frac{m\omega}{\pi\hbar}\right)^{2} + \sqrt{2}\, C_2 \left(\frac{m\omega}{\hbar}\right) x^2 \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$

    $C_0 - C_2 \frac{1}{\sqrt{2}} = 0$, $A = \sqrt{2}\, C_2 \left(\frac{m\omega}{\hbar}\right)\left(\frac{m\omega}{\pi\hbar}\right)^{2}$, $|C_0|^2 + |C_2|^2 = 1$.

$C_0 = \frac{1}{\sqrt{3}}$, $C_2 = \frac{\sqrt{2}}{\sqrt{3}}$, where A is $= \frac{2}{\sqrt{3}} \left(\frac{m\omega}{\pi}\right)\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$

- $\Psi(x,t) = \frac{1}{\sqrt{3}} \psi_0(x) e^{-\frac{i}{\hbar}E_0 t} + \sqrt{\frac{2}{3}}\psi_2(x) e^{-\frac{i}{\hbar}E_2 t} = \frac{1}{\sqrt{3}}\psi_0(x) e^{-\frac{i\omega t}{2}} + \sqrt{\frac{2}{3}}\psi_2(x) e^{-\frac{5i\omega t}{2}}$

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

- $|\Psi|^2 = \left(\frac{1}{\sqrt{3}}\psi_0 e^{\frac{iE_0 t}{\hbar}} + \sqrt{\frac{2}{3}}\psi_2 e^{\frac{iE_2 t}{\hbar}}\right)\left(\frac{1}{\sqrt{3}}\psi_0 e^{-\frac{iE_0 t}{\hbar}} + \sqrt{\frac{2}{3}}\psi_2 e^{-\frac{iE_2 t}{\hbar}}\right) =$

$= \frac{1}{3}\psi_0^2(x) + \frac{2}{3}\psi_2^2(x) + \frac{2\sqrt{2}}{3}\psi_0\psi_2\left(e^{\frac{i(E_0-E_2)t}{\hbar}} + e^{-\frac{i(E_2-E_0)t}{\hbar}}\right)$

$= \frac{1}{3}\psi_0^2 + \frac{2}{3}\psi_2^2 + \frac{2\sqrt{2}}{3}\psi_0\psi_2\cos(2\omega t)$

$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}$

$\psi_2 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(\sqrt{2}\frac{m\omega}{\hbar}x^2 - \frac{1}{\sqrt{2}}\right)e^{-\frac{m\omega x^2}{2\hbar}}$

- $\langle x\rangle = \int_{-\infty}^{\infty}dx\, \Psi^*(x,t)\, x\, \Psi(x,t) = \int_{-\infty}^{\infty}dx\, x\, |\Psi(x,t)|^2 =$

$= \frac{1}{3}\underbrace{\underbrace{\int_{-\infty}^{\infty}dx\, \psi_0^2 x}_{\text{odd in } x}}_{=0} + \frac{2}{3}\underbrace{\underbrace{\int_{-\infty}^{\infty}dx\, x\psi_2^2}_{\text{odd in } x}}_{=0} + \underbrace{\frac{2\sqrt{2}}{3}\cos(\omega t)\int_{-\infty}^{\infty}dx\, \underbrace{x\psi_0\psi_2}_{}}_{\text{odd in } x \; =0}$

$= 0$

Stationary states of the same parity result in zero expectation value.

- $\langle p\rangle = m\frac{d\langle x\rangle}{dt} = 0$

- $\langle H\rangle = \int_{-\infty}^{\infty}dx\, \underbrace{\Psi^*(x,t)}_{\sum_m C_m^*\psi_m^*(x)e^{\frac{i}{\hbar}E_m t}} H(x,t)\underbrace{\Psi(x,t)}_{\sum_n C_n\psi_n(x)e^{-\frac{i}{\hbar}E_n t}} = \sum_{mn} C_m^* C_n e^{\frac{i}{\hbar}(E_m - E_n)t}\overbrace{\int_{-\infty}^{\infty}dx\, \psi_m^* \underbrace{\hat{H}\psi_n}_{E_n\psi_n}}^{E_n\delta_{mn}}$

$= \sum_n E_n |C_n|^2$, $C_0 = \frac{1}{\sqrt{3}}$, $C_2 = \sqrt{\frac{2}{3}}$

$= E_0|C_0|^2 + E_2|C_2|^2 = \frac{1}{3}E_0 + \frac{2}{3}E_2 = \frac{11}{6}\hbar\omega$

- $\langle V\rangle = \frac{m\omega^2}{2}\langle x^2\rangle = \frac{m\omega^2}{2}\int_{-\infty}^{\infty}dx\, \Psi^* x^2\Psi = \frac{m\omega^2}{2}\left[\frac{1}{3}\underbrace{\int_{-\infty}^{\infty}dx\, \psi_0^2(x)x^2}_{I_1} + \frac{2}{3}\underbrace{\int_{-\infty}^{\infty}dx\, \psi_2^2(x)x^2}_{I_2} + \frac{2\sqrt{2}}{3}\cos(2\omega t)\underbrace{\int_{-\infty}^{\infty}dx\, x^2\psi_0\psi_2}_{III}\right]$

$I_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty}dx\, x^2 e^{-\frac{m\omega}{\hbar}x^2} = \frac{\hbar}{2m\omega}$

$II_2 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty}dx\, x^2\left(\sqrt{2}\frac{m\omega^2}{\hbar^2}x^2 - \frac{1}{\sqrt{2}}\right)^2 e^{-\frac{m\omega}{\hbar}x^2} = \frac{5\hbar}{2m\omega}$

$III = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty}dx\, x^2\left(\sqrt{2}\frac{m\omega^2}{\hbar^2}x^2 - \frac{1}{\sqrt{2}}\right)^2 e^{-\frac{m\omega}{\hbar}x^2} = \frac{\hbar}{\sqrt{2}m\omega}$

$\int_{-\infty}^{\infty}dx\, x^M e^{-ax^2}$

$= J_M(a)$

$= J_M = 0$, if M is odd

$J_M = \int_{-\infty}^{\infty}dx\,(x^2)^N e^{-ax^2}$ if M is even ($M=2N$)

$J_0(a) = \int_{-\infty}^{\infty}dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$

$J_2(a) = \int_{-\infty}^{\infty}dx\, x^2 e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$

$\vdots$

$J_{2N}(a) = (-1)^N\frac{d^N}{da^N}\sqrt{\frac{\pi}{a}}$

$= \frac{1\cdot 3\cdot 5\cdots(2N-1)}{2^N a^N}\sqrt{\frac{\pi}{a}}$

- $\langle x^2\rangle = \frac{1}{3}\frac{\hbar}{2m\omega} + \frac{2\cdot 5\hbar}{3\cdot 2m\omega} + \frac{2\sqrt{2}}{3}\cos(2\omega t)\cdot\frac{\hbar}{\sqrt{2}m\omega}$

$= \frac{11}{6}\frac{\hbar}{2m\omega} + \frac{2}{3}\frac{\hbar}{2m\omega}\cos(2\omega t)$

- $\langle V\rangle = \frac{11}{12}\hbar\omega + \frac{1}{3}\hbar\omega\cos(2\omega t)$

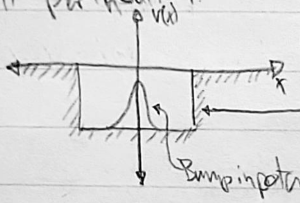
- $\langle K\rangle = \langle H\rangle - \langle V\rangle = \frac{11}{12}\hbar\omega - \frac{1}{3}\hbar\omega\cos(2\omega t)$

- time average of $\langle V\rangle$ = time average of $\langle K\rangle = \frac{1}{2}\langle E\rangle$

Pertubation Theory

- Partubation Theory - method of approximate solution for S.E.
- Hamiltonian: $\hat{H} = \hat{H}_0 + \delta\hat{H}$
  - $\hat{H}_0$ - unperturbed Hamiltonian: SE can be solved exactly.
    - $\hat{H}_0 \psi_n^{(0)}(x) = E_n^{(0)} \psi_n^{(0)}(x)$

      Exact Eigenstates of $\hat{H}_0$; Exact Eigenvalues of $\hat{H}_0$
  - $\delta\hat{H}$ - "small" perturbation
    - Ex.



$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + V_0(x)$$

  - Anharmonic Oscillator:

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + \frac{m\omega^2 x^2}{2}}_{\text{harmonic}} + \underbrace{\frac{\beta}{3}x^3 + \frac{\gamma}{4}x^4 + \ldots}_{\text{anharmonic}}$$

- $\hat{H}\psi_n(x) = E_n\psi_n(x)$ ← stationary states of $\hat{H}$ are not known exactly; can be calculated perturbatively in $\delta\hat{H}$
- Formal Trick: - Introduce $\hat{H}_\lambda = \hat{H}_0 + \lambda\delta\hat{H}$
  - If $\lambda = 0$, $\hat{H}_0$ is solvable
  - If $\lambda = 1$, $\hat{H}_1 = \hat{H}$
- Seek the stationary states of $\hat{H}_\lambda$ in the form
  - $\psi_n^{(\lambda)}(x) = \psi_n^{(0)}(x) + \lambda\psi_n^{(1)}(x) + \lambda^2\psi_n^{(2)}(x) \ldots$
  - $E_n^{(\lambda)} = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$
  - $\psi_n^{(1)}(x), E_n^{(1)}$ ← 1st order corrections

    $\psi_n^{(2)}(x), E_n^{(2)}$ ← 2nd order corrections
- $(\hat{H}_0 + \lambda\delta\hat{H})[\psi_n^{(0)} + \lambda\psi_n^{(1)} + \ldots] = [E_n^{(0)} + \lambda E_n^{(1)} + \ldots][\psi_n^{(0)} + \lambda\psi_n^{(1)} + \ldots]$
- Collect the powers of λ on both sides:

  λ^0: $\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ ← unperturbed S.E.

  λ^1: $\hat{H}_0\psi_n^{(1)} + \delta\hat{H}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$

  $\vdots$

- $(\hat{H}_0 - E_n^{(0)})\psi_n^{(1)}(x) = [E_n^{(1)} - \delta\hat{H}]\psi_n^{(0)}(x)$

  ↳ solve for $E_n^{(1)}$ & $\psi_n^{(1)}(x)$

  ← Focus on this.

- Seek solution in the form.
  - $\psi_n^{(1)}(x) = \sum_m C_m^{(n)} \psi_m^{(0)}(x)$ ← sub into eqn.
  - $\psi_m^{(0)}(x)$ form a complete and orthonormal (infinite) set of functions.

- $\sum_m C_m^{(n)} \underbrace{\hat{H}_0 \psi_m^{(0)}}_{= E_m^{(0)}\psi_m^{(0)}} - E_n^{(0)} \sum_m C_m^{(n)} \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} - \delta\hat{H}\psi_n^{(0)}$

$\sum_m [E_m^{(0)} - E_n^{(0)}] C_m^{(n)} \psi_m^{(0)} = E_n^{(1)} \psi_n^{(0)} - \delta\hat{H}\psi_n^{(0)}$

- Multiply by $\psi_\ell^{(0)*}(x)$ and integrate
  - $\sum_m [E_m^{(0)} - E_n^{(0)}] C_m^{(n)} \underbrace{\int_{-\infty}^{\infty} dx\, \psi_\ell^{(0)*}(x) \psi_m^{(0)}(x)}_{=\delta_{\ell m}} = E_n^{(1)} \underbrace{\int_{-\infty}^{\infty} dx\, \psi_\ell^{(0)*}(x)\psi_n^{(0)}(x)}_{\delta_{\ell n}} - \int_{-\infty}^{\infty} dx\, \psi_\ell^{(0)*}(x)\,\delta\hat{H}\,\psi_n^{(0)}(x)$

    due to orthonormality of $\psi^{(0)}$'s

  - $\sum_m [E_m^{(0)} - E_n^{(0)}] \delta_{\ell m} C_m^{(n)} = E_n^{(1)} \delta_{\ell n} - \langle \ell | \delta\hat{H} | n \rangle$ ← Dirac notation, using as shortform for now, means the matrix element of $\delta\hat{H}$ between $\psi_\ell^{(0)}$ and $\psi_n^{(0)}$
  - If $\ell = n$:

    $\sum_m \underbrace{[E_m^{(0)} - E_n^{(0)}]}_{\text{when } m=n,\ \Delta E = 0} \delta_{nm} C_m^{(n)} = E_n^{(1)} - \langle n | \delta\hat{H} | n \rangle$

  - 1st order correction to the n^{th} level

    $E_n^{(1)} = \langle n | \delta\hat{H} | n \rangle = \int_{-\infty}^{\infty} dx\, \psi_n^{(0)*}(x)\, \delta\hat{H}\, \psi_n^{(0)}(x)$

- Corrected Energy of the n^{th} state: $E_n^{(0)} + E_n^{(1)} + \ldots$ usually neglect higher order terms.
- Ex. Anharmonic oscillator: $\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + \frac{m\omega^2 x^2}{2}}_{= \hat{H}_0} + \underbrace{\frac{\gamma}{4}x^4}_{= \delta\hat{H}}$ ← quartic anharmonicity.

$E_0^{(1)} = ?$, $E_1^{(1)} = ?$

$E_0^{(1)} = \int_{-\infty}^{\infty} dx\, \psi_0^{(0)}(x) \frac{\gamma x^4}{4} \psi_0^{(0)}(x)$, $\psi_0^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}$

$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{\gamma}{4} \int_{-\infty}^{\infty} dx\, x^4 e^{-\frac{m\omega x^2}{\hbar}} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{\gamma}{4} \left[\frac{3}{4}\left(\frac{\hbar^2}{m^2\omega^2}\right)\sqrt{\frac{\pi\hbar}{m\omega}}\right] = \frac{3}{16}\gamma\left(\frac{\hbar}{m\omega}\right)^2$

should be small compared to the level spacing. $\gamma \frac{\hbar^2}{m^2\omega^2} \ll \hbar\omega$

Perturbation theory is applicable if $\gamma \ll \frac{m\omega^2}{\hbar}$

$\int_{-\infty}^{\infty} dx\, x^4 e^{-ax^2} = \frac{3}{4a^2}\sqrt{\frac{\pi}{a}}$

$\int dx\, x^6 e^{-ax^2} = \sqrt{\frac{\pi}{a}} \frac{15}{8} a^3$

$E_1^{(1)} = \int_{-\infty}^{\infty} dx\, \psi_1^{(0)*}(x) \frac{\gamma}{4} x^4 \psi_1^{(0)}(x)$, $\psi_1^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}} \left(2\sqrt{\frac{m\omega}{\hbar}}\, x\right) e^{-\frac{m\omega x^2}{2\hbar}}$

$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} 4 \frac{m\omega}{\hbar} \frac{1}{4} \frac{1}{2} \int_{-\infty}^{\infty} dx\, x^6 e^{-\frac{m\omega x^2}{\hbar}} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \gamma \frac{m\omega}{\hbar 2} \left[\sqrt{\frac{\pi\hbar}{m\omega}} \frac{15}{8}\left(\frac{\hbar}{m\omega}\right)^3\right]$

$= \frac{15}{8}\gamma\left(\frac{\hbar}{m\omega}\right)^2 \ll \hbar\omega$

Mathematical Formalism of Quantum Mechanics

- Superposition Principle - if $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$ are states of a quantum system ($i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$; ψ_1, ψ_2 satisfy)
  $\psi_3(\vec{r},t) = c_1\psi_1(\vec{r},t) + c_2\psi_2(\vec{r},t)$ is also a possible state
  Similar to the usual vectors: $\vec{a}_1, \vec{a}_2 \Rightarrow a_3 = c_1\vec{a}_1 + c_2\vec{a}_2$

- Wave functions, ψ, can be regarded as 'state vectors'
  - elements of an infinitely-dimensional complex vector Space (Hilbert Space), satisfying $\int d^3r\, |\psi|^2 = 1$
- Dirac notation for the wave function
  - Complex vectors in 3D space: $\vec{a} = a_1\vec{e}_1 + a_2\vec{e}_2 + a_3\vec{e}_3$
    $\vec{e}_1, \vec{e}_2, \vec{e}_3$ - the basis vector
    a_1, a_2, a_3 - complex components
    $a_i = (\vec{e}_i \cdot \vec{a})$
  - Column: $\vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \equiv |\vec{a}\rangle$ Hermition Conjugation ("dagger")
  - Row: $\langle\vec{a}| \equiv |\vec{a}\rangle^{\dagger} = (a_1^*, a_2^*, a_3^*)$
  - "bra" x "ket" = inner product = $\langle\vec{a}|\vec{b}\rangle = a_1^* b_1 + a_2^* b_2 + a_3^* b_3$
  - $\vec{e}_1 = |\vec{e}_1\rangle = |1\rangle$
    $\vec{e}_2 = |\vec{e}_2\rangle = |2\rangle \Rightarrow a_i = \langle i|\vec{a}\rangle$
    $\vec{e}_3 = |\vec{e}_3\rangle = |3\rangle$

- Wave function
  - "Universe" = set of N points
  - Wave function $\psi = \underbrace{\{\psi_1, \psi_2, \dots \psi_N\}}_{N \text{ complex numbers}}$
  - $|\psi_i|^2$ = probability to find the particle on the i^{th} state
    $= \sum_{i=1} |\psi_i|^2 = 1$
  - Dirac: $|\psi\rangle = \begin{pmatrix} \psi_1 \\ \vdots \end{pmatrix}$, $\psi_i = \langle i|\psi\rangle$, $\langle\psi| = (\psi_1^*, \dots, \psi_N^*)$
  - Dirac Normalization: $\langle\psi|\psi\rangle = 1$, $\sum_i \psi_i^* \psi_i$
  - Physical Universe: $|\psi\rangle$, $\psi(x) = \langle x|\psi\rangle$
- Inner product of 2 functions: $f(x)$ & $g(x)$
  $\langle f|g\rangle = \int_{-\infty}^{\infty} dx\, f^*(x) g(x)$
  $\langle f|f\rangle = \int_{-\infty}^{\infty} dx\, |f(x)|^2$

• Basis in the Hilbert Space: Infinite set of basis "vectors", or basis functions.

$$f_1, f_2, f_3, \ldots ; \; f_n(x) = \langle x | n \rangle$$

$$f_1 = |f_1\rangle = |1\rangle, \; f_2 = |f_2\rangle = |2\rangle$$

① Orthonormality. $\langle n | m \rangle = \delta_{nm}$

$$\int_{-\infty}^{\infty} dx\, f_n^*(x) f_m(x)$$

② Complete: Any element of the Hilbert space can be represented as

$$|\psi\rangle = \sum_n c_n |n\rangle$$ Complex coefficients.

$$\langle x | \psi \rangle = \sum_n c_n \langle x | n \rangle$$

$$\psi(x) = \sum_n c_n f_n(x)$$

• Operators = linear transformations in the Hilbert Space.

- Operator $\hat{T}$: $\hat{T} f(x) = g(x)$, $\hat{T}|f\rangle = |g\rangle$

- Lin Operator: $\hat{T}(c_1 f_1 + c_2 f_2) = c_1 g_1 + c_2 g_2$. $g_1 = \hat{T} f_1$, $g_2 = \hat{T} f_1$

Anti-linear: $\hat{T}(c_1 f_1 + c_2 f_2) = c_1^*(\hat{T} f_1) + c_2^*(\hat{T} f_2)$

- Example: Multiplication by x, $\hat{T}_1 = x$, $\hat{T}_1 f(x) = x f(x)$

Differentiation by x, $\hat{T}_2 = \frac{d}{dx}$, $\hat{T}_2 f(x) = \frac{df(x)}{dx}$

- Order of applications is important. $\hat{T}_1 \hat{T}_2 \neq \hat{T}_2 \hat{T}_1$

- Commutator: $[\hat{T}_1, \hat{T}_2] = \hat{T}_1 \hat{T}_2 - \hat{T}_2 \hat{T}_1$

$$[x, \tfrac{d}{dx}] f = x \frac{d}{dx} f - \frac{d}{dx}(xf)$$

- Hermitian Conjugate Operator: Operator $\hat{T}$ → Consider 2 state vectors $|f\rangle$ & $|g\rangle$

$$\rightarrow \langle f | \hat{T} g \rangle = \langle \hat{T}^+ f | g \rangle$$ ← Hermitian Conjugate Operator

$$\langle x | \hat{T} g \rangle = (\hat{T} g)(x)$$

$$\int_{-\infty}^{\infty} dx\, f^*(x) \hat{T} g(x) = \int_{-\infty}^{\infty} dx\, (\hat{T}^+ f)^*(x)\, g(x)$$

$$\int_{-\infty}^{\infty} dx\, f^*(x)\, x\, g(x) = \int_{-\infty}^{\infty} x f^* g\, dx = \int_{-\infty}^{\infty} (xf)^* g\, dx$$

$$\hat{T}_1 = x \; ; \; \hat{T}_1^+ \stackrel{?}{=} x$$

$$\int_{-\infty}^{\infty} dx\, f^* \frac{d}{dx} g \underset{\text{by parts}}{=} - \int_{-\infty}^{\infty} dx \left(\frac{d}{dx} f^*\right) g = \int_{-\infty}^{\infty} \left(-\frac{df}{dx}\right)^* g$$

$$\hat{T}_2 = \frac{d}{dx} \; ; \; \hat{T}_2^+ \stackrel{?}{=} -\frac{d}{dx} \Rightarrow \hat{T}_2 \neq \hat{T}_2^+$$

Hermitian operators are ones that which the operator equates its complex conjugate ($\hat{T}_1$ is, $\hat{T}_2$ isn't)

$$\int_{-\infty}^{\infty} f^* \hat{p} g\, dx = -i\hbar \int_{-\infty}^{\infty} f^* \frac{d}{dx} g\, dx \underset{\text{by parts}}{=} \underbrace{-i\hbar\, f^* g \Big|_{-\infty}^{\infty}}_{0} + i\hbar \int_{-\infty}^{\infty} \frac{df^*}{dx} g\, dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{df}{dx}\right)^* g\, dx = \int_{-\infty}^{\infty} (\hat{p} f)^* g\, dx$$

$$\hat{T} = \hat{p} = -i\hbar \frac{d}{dx}, \; \hat{T}^+ \stackrel{?}{=} \hat{p}$$

So, $\hat{p}$ is Hermitian.

$$\hat{p} = \hat{p}^+$$

• Eigenfunction & Eigenvalues

- $\hat{T} f(x) = \lambda f(x) \rightarrow \hat{T}|f\rangle = \lambda|f\rangle$

  Eigenfunction of $\hat{T}$ — Eigenvalue of $\hat{T}$

- $\hat{T}|f_n\rangle = \lambda_n |f_n\rangle$ n, labels the eigen functions

- if $\hat{T} = \frac{d}{dx}$: eigenfunctions $\rightarrow e^{\lambda x}$, $\hat{T} e^{\lambda x} = \lambda e^{\lambda x}$

  Eigenvalues $\rightarrow \lambda$

- if $\hat{T} = x\frac{d}{dx}$: eigenfunctions $\rightarrow x^{\alpha}$, $\hat{T} x^{\alpha} = x\alpha x^{\alpha-1} = \alpha x^{\alpha}$

  eigenvalues $\rightarrow \alpha$

- if $\hat{T} = \hat{p}$: eigenfunctions $\rightarrow e^{ikx}$, $\hat{p} e^{ikx} = -i\hbar\frac{\partial}{\partial x} e^{ikx} = (\hbar k) e^{ikx}$ → $e^{ikx} = \langle x|k\rangle$, $\hat{p}|k\rangle = \hbar k|k\rangle$

  eigenvalues $\rightarrow \hbar k$

- if $\hat{T} = \hat{x} = x$: eigenfunctions $\rightarrow \delta(x-x_0)$, $\hat{x}\,\delta(x-x_0) = x\delta(x-x_0) = x_0\delta(x-x_0)$ → $\delta(x-x_0) = \langle x|x_0\rangle$, $= \hat{x}|x_0\rangle$, $= x_0|x_0\rangle$

  eigenvalues $\rightarrow x_0$

• Important Property of Hermitian Operators.

- ① All eigenvalues of a hermitian operator are real:

  $\hat{T}|f_n\rangle = \lambda_n|f_n\rangle$

  $\lambda_n^* = \lambda_n$

  ② The eigenfunctions of a hermitian operator form a complete and orthonormal set in the Hilbert space

  $\left.\begin{array}{l} \langle f_n|f_m\rangle = \int_{-\infty}^{\infty} dx\, f_n^*(x) f_m(x) = \delta_{mn} \\ \Psi(x) = \sum_n c_n f_n(x) \end{array}\right\} \Rightarrow \{|f_n\rangle\}$ = basis in the hilbert space.

$|f_n\rangle \equiv |n\rangle$

$f_n(x) = \langle x|n\rangle$

• Given the basis $\{|f_n\rangle\}$ in the Hilbert Space → matrix elements of an operator $\hat{O}$ in this basis:

$$O_{mn} = \langle m|O|n\rangle = \int_{-\infty}^{\infty} dx\, f_m^*(x)\, \hat{O} f_n(x)$$

• If operator $\hat{O}$ is a hermitian operator: $\hat{O}^{\dagger} = \hat{O}$

$$O_{mn} = \int_{-\infty}^{\infty} dx\, f_m^* \hat{O} f_n = \int_{-\infty}^{\infty} dx\, (\hat{O}^{\dagger} f_m)^* f_n = \underline{\int_{-\infty}^{\infty} dx\, (\hat{O} f_m)^* f_n}$$

$$O_{nm}^* = \int_{-\infty}^{\infty} dx\, f_m (\hat{O} f_n)^* = \underline{\int_{-\infty}^{\infty} dx\, (\hat{O} f_n)^* f_m}$$

$$O_{mn} = O_{nm}^*$$

$(\text{matrix})^T$ = matrix ← symmetric

$(\text{matrix})^*$ = matrix ← real.

∴ The matrix representing $\hat{O}$ in an arbitrary basis is Hermitian, A matrix is Hermitian if $((\text{matrix})^T)^*$ = Matrix.

• Matrix of $\hat{O}$ = $\begin{bmatrix} O_{11} & O_{12} & O_{13} & \cdots \\ O_{21} & O_{22} & O_{23} & \cdots \\ O_{31} & O_{32} & O_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$, ∞ rows & columns

• Diagonal of matrix elements: $O_{nn}=\int_{-\infty}^{\infty}dx\, f_n^*(x)\,\hat{O}\,f_n(x)$ - expectation value of $\hat{O}$ in the state $f_n(x) \equiv \langle x|n\rangle$

• $\hat{T}_1, \hat{T}_2$ - Operators do not necessarily commute: $\hat{T}_1\hat{T}_2 \neq \hat{T}_2\hat{T}_1$

• Commutator, $[\hat{T}_1, \hat{T}_2] = \hat{T}_1\hat{T}_2 - \hat{T}_2\hat{T}_1 \neq 0$, in general

- $[\hat{x}, \hat{x}] = ? = 0$

$[\hat{p}, \hat{p}] = ? = 0$

$[\hat{x}, \hat{p}] = ? = x(-i\hbar\frac{\partial}{\partial x})f - (-i\hbar\frac{\partial}{\partial x})f x = i\hbar f$, $[\hat{x}, \hat{p}] = i\hbar$ ⇐ do not commute

• In 3D, $\hat{x}_1 = x$; $\hat{p}_1 = -i\hbar\frac{\partial}{\partial x} = p_x$

$\hat{x}_2 = y$; $\hat{p}_2 = -i\hbar\frac{\partial}{\partial y} = p_y$

$\hat{x}_3 = z$; $\hat{p}_z = -i\hbar\frac{\partial}{\partial z} = p_z$

$[\hat{x}_i, x_j] = 0$ $\quad i, j = 1, 2, 3$ or (x, y, z).

$[\hat{p}_i, \hat{p}_j] = 0$

$[\hat{x}_i, \hat{p}_j] = -i\hbar\,\delta_{ij}$

Postulates of Quantum Mechanics.

• ① States: the state of a quantum system is represented by the wave function ψ = vector in a Hilbert space the state vector is normalized: $\langle\psi|\psi\rangle = 1$. The state vectors differing by a phase factor, ψ and $e^{i\alpha}\psi$, describe same physical state.

② Observables: Observable quantities, $Q(\vec{r}, \vec{p})$, are represented by Hermitian operators, $\hat{Q} = Q(\vec{r}, \vec{p})$, which act on state vectors. The expectation value of $\hat{Q}$ in the state ψ is given by $\langle\psi|\hat{Q}|\psi\rangle$

③ Measurements: If you measure an observable $\hat{Q}$, in any state $|\psi\rangle$, the measurement returns to one of the eigenvalues of $\hat{Q}$. Measurement of $\hat{Q}$ in the state is certain to return to the value λ if and only if ψ is an eigenstate of $\hat{Q}$: $\hat{Q}\psi = \lambda\psi$. If ψ is not an eigenstate of $\hat{Q}$: $|\psi\rangle = \sum_n C_n|f_n\rangle$, $|f_n\rangle$ are the eigenstates of $\hat{Q}$: $\hat{Q}|f_n\rangle = \lambda_n|f_n\rangle$

⇒ Probability of measuring $\lambda_n = |C_n|^2$.

$\sum|C_n|^2 = 1$.

- Compatible Observables: $[\hat{Q}_1, Q_2] = 0 \to \hat{Q}_1 \,\&\, \hat{Q}_2$ have the same eigen functions : $\hat{Q}_1|f_n\rangle = \lambda_n^{(1)}|f_n\rangle$
  but different eigenvalues. $\hat{Q}_2|f_n\rangle = \lambda_n^{(2)}|f_n\rangle$
- InCompatible Observables: $[\hat{Q}_1, Q_2] \neq 0$.
- Proof: $\underset{0}{[\hat{Q}_1, Q_2]}\psi = \sum_n C_n(\hat{Q}_1\hat{Q}_2 - \hat{Q}_2\hat{Q}_1)f_n = \sum_n C_n(\lambda_n^{(1)}\lambda_n^{(2)}f_n - \lambda_n^{(2)}\lambda_n^{(1)}f_n) = 0$
  $|\psi\rangle = \sum_n C_n|f_n\rangle$

$\langle\hat{O}\rangle = \langle\psi|\hat{O}|\psi\rangle$

- Generalized Uncertainty Principle
  - measure A and B in the state ψ, then $\sigma_A\sigma_B \geq |\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle|$
  - $\sigma_{A,B} = \sqrt{\langle\hat{A}^2\rangle - \langle A\rangle^2}$ or $\sqrt{\langle\hat{B}^2\rangle - \langle B\rangle^2}$
- Define 2 state vectors $|\alpha\rangle = (\hat{A} - \langle\hat{A}\rangle)|\psi\rangle$
  $|\beta\rangle = (\hat{B} - \langle\hat{B}\rangle)|\psi\rangle$
- Normals: $\langle\alpha|\alpha\rangle = \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^\dagger(\hat{A} - \langle\hat{A}\rangle)|\psi\rangle = \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2|\psi\rangle$
  $= \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2 = \sigma_A^2$
  $\langle\beta|\beta\rangle = \sigma_B^2$
- Schwartz Inequality
  - $\sigma_A^2\sigma_B = \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2$
  - $\langle\alpha|\beta\rangle = z$ ← complex number
    $\langle\beta|\alpha\rangle = z^*$
  - $|z|^2 \geq (\text{Im}z)^2 = \left(\frac{z - z^*}{2i}\right)^2$
  - $|\langle\alpha|\beta\rangle|^2 \geq \left(\frac{1}{2i}(\langle\alpha|\beta\rangle - \langle\beta|\alpha\rangle)\right)^2$
  - $\langle\alpha|\beta\rangle = \langle\psi|(\hat{A} - \langle\hat{A}\rangle)(\hat{B} - \langle\hat{B}\rangle)|\psi\rangle$
    $= \langle(\hat{A}\hat{B} - \hat{A}\langle B\rangle - \langle\hat{A}\rangle B + \langle\hat{A}\rangle\langle\hat{B}\rangle)\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$
    $\langle\beta|\alpha\rangle = \langle\hat{B}\hat{A}\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle$
  - $\langle\alpha|\beta\rangle - \langle\beta|\alpha\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{B}\hat{A}\rangle = \langle\hat{A}\hat{B} - \hat{B}\hat{A}\rangle = \langle[\hat{A},\hat{B}]\rangle$.
  - $|\langle\alpha|\beta\rangle|^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2$
  - $\sigma_A^2\sigma_B^2 \geq \frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle$.
- Example: $\hat{A} = \hat{x}$, $\hat{B} = \hat{p}$
  We know the commutator is non zero ($i\hbar$)
  $\sigma_x\sigma_p \geq \frac{\hbar}{2}$
- Example: Angular Momentum: classically, $\vec{L} = \vec{r} \times \vec{p}$
  In QM, angular momentum operat.

Angular Momentum

- Classically, $\vec{L} = \vec{r} \times \vec{p}$
- In QM, angular momentum operator $\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = \hat{\vec{r}} \times \left(-i\hbar \frac{\partial}{\partial \vec{r}}\right)$

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = i\hbar\left(z\hat{p}_x - x\hat{p}_z\right)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

- The acts on $\psi(\vec{r}) = \psi(x,y,z)$.
- Different components of $\hat{\vec{L}}$ donot commute.

~~Different components of $\hat{L}$ d~~

- $$\left.\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}\right\}$$ the components of $\vec{L}$ cannot be measured simultaneously.

- Proof: $[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$

$$\hat{L}_x\hat{L}_y f(\vec{r}) = -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial z}\right) = -\hbar\left(y\frac{\partial f}{\partial x} + yz\frac{\partial^2 f}{\partial z \partial x} - yx\frac{\partial^2 f}{\partial z^2} - z^2\frac{\partial^2 f}{\partial y \partial x} + zx\frac{\partial^2 f}{\partial y \partial z}\right)$$

$$\hat{L}_y\hat{L}_x f(\vec{r}) = -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial z}\right) = -\hbar\left(zy\frac{\partial^2 f}{\partial z \partial x} - z^2\frac{\partial^2 f}{\partial y \partial x} - xy\frac{\partial^2 f}{\partial z^2} + x\frac{\partial f}{\partial y} + xz\frac{\partial^2 f}{\partial z \partial y}\right).$$

- $$[\hat{L}_x, \hat{L}_y]f = -\hbar^2\left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right]f = (i\hbar)\underbrace{(-i\hbar)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}_{\hat{L}_z} f = i\hbar\hat{L}_z f.$$

- $\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

$$[\hat{\vec{L}}, \hat{L}_x] = [\hat{\vec{L}}^2, L_y] = [\hat{\vec{L}}^2, L_z] = 0$$

$$[\hat{\vec{L}}, \hat{L}_x] = \underbrace{[\hat{L}_x^2, \hat{L}_x]}_{0} + [\hat{L}_y^2, L_x] + [\hat{L}_z^2, \hat{L}_x]$$

$$[\hat{L}_y^2, L_x] = \hat{L}_y^2 \hat{L}_x - L_x L_y^2$$

$$= L_y L_y L_x - L_x L_y L_y - L_y L_x L_y + L_y L_x L_y =$$

$$\hat{L}_y\underbrace{[\hat{L}_y, \hat{L}_x]}_{-i\hbar \hat{L}_z} \qquad \underbrace{[\hat{L}_y, \hat{L}_x]}_{-i\hbar \hat{L}_z} L$$

- $[\hat{\vec{L}}^2, \hat{L}_{x,y,z}] = 0. \rightarrow$ One ~~component~~ can simultaneously measure $\hat{\vec{L}}^2$ and any one component of $\vec{L}$

usually choose $\hat{L}_z$

Eigenfunctions and Eigenvalues of $\hat{L}^2$ and $\hat{L}_z$

- Eigenfunctions - the spherical harmonics. $Y_{\ell m}(\theta, \varphi)$ $\quad \ell = 0, 1, 2, \ldots \leftarrow$ orbital quantum number (azimutal)

  @ given ℓ: $m = -\ell, -\ell+1, 0 \ldots \ell$; $m = 2\ell + 1$ magnetic quantum number

  Eigenvalues - $\hat{L}_z Y_{\ell m} = \underbrace{\hbar m}_{\text{Eigenvalues of } \hat{L}_z} Y_{\ell m}$

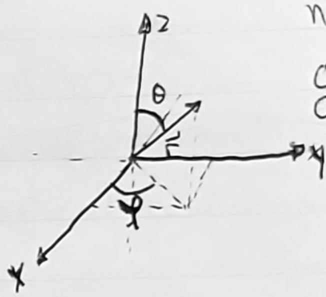
  - $\hat{L}^2 Y_{\ell m} = \underbrace{\hbar^2 \ell(\ell+1)}_{\text{Eigenvalues of } \hat{L}^2} Y_{\ell m}$

- Dirac Notation
  - Eigenfunctions - $Y_{\ell m}(\theta, \varphi) = \langle \theta, \varphi | \ell, m \rangle$

    θ, φ - spherical angles.

  - $\hat{L}_z |\ell m\rangle = \hbar m |\ell m\rangle$

    $\hat{L}^2 |\ell m\rangle = \hbar^2 \ell(\ell+1) |\ell m\rangle$



$0 \le \theta \le \pi$
$0 \le \varphi \le 2\pi$

- Cartesian to Spherical Coordinates.
  - $x = r \sin\theta \cos\varphi$

    $y = r \sin\theta \sin\varphi$

    $z = r \cos\theta$

- Do this for the angular momentum operators.

$$\left.\begin{aligned} \hat{L}_x &= -i\hbar\left(-\sin\varphi \frac{\partial}{\partial\theta} - \cos\varphi \cdot \cot\theta \frac{\partial}{\partial\varphi}\right) \\ \hat{L}_y &= -i\hbar\left(\cos\varphi \frac{\partial}{\partial\theta} - \sin\varphi \cdot \cot\theta \frac{\partial}{\partial\varphi}\right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial\varphi} \end{aligned}\right\} \text{act on } f(\theta, \varphi)$$

- Eigen functions of $\hat{L}_z$
  - $\hat{L}_z Y(\theta, \varphi) = \underset{\substack{\uparrow \\ \text{Eigenvalues}}}{\lambda} Y(\theta, \varphi)$

Seperation of variables

$\varphi \to \varphi + 2\pi$

WAVE FXN DOES NOT CHANGE

$f(\varphi + 2\pi) = f(\varphi) \leftarrow$ single valued

$-i\hbar \frac{\partial}{\partial\varphi} Y(\theta, \varphi) = \lambda Y(\theta, \varphi)$, seek solutions of the form $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$

$-i\hbar \frac{\partial}{\partial\varphi} \Theta(\theta)\Phi(\varphi) = \lambda \Theta(\theta)\Phi(\varphi) \Rightarrow -i\hbar \frac{\partial\Phi}{\partial\varphi} = \lambda\Phi$

- Solution: $\Phi(\varphi) = e^{i\frac{\lambda}{\hbar}\varphi}$

$$\Phi(\varphi + 2\pi) = \Phi(\varphi)$$

$$e^{i\frac{\lambda}{\hbar}\varphi} e^{i\frac{2\pi\lambda}{\hbar}} = e^{i\frac{\lambda}{\hbar}\varphi}$$

$$e^{i\frac{2\pi\lambda}{\hbar}} = 1 \qquad \frac{\lambda}{\hbar} = \text{integer} = m$$

$$e^{2\pi i m} = 1$$

- Eigenvalues $\hat{L}_z = \hbar m$
- Eigenfunctions $\Rightarrow Y(\theta, \varphi) = \Theta(\theta) e^{im\varphi}$

- $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \ldots = -\hbar^2 \frac{1}{\sin^2\theta}\left[\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\varphi^2}\right]$
- $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$
- $\hat{L}^2 Y(\theta,\varphi) = \lambda_{L^2} Y(\theta,\varphi)$, $Y(\theta,\varphi) = \Theta(\theta)e^{im\varphi}$, m=integer.
  $\hat{L}_z Y(\theta,\varphi) = \lambda_{L_z} Y(\theta,\varphi)$
- Finding Θ
  $\Rightarrow -\hbar^2 \frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\varphi^2}\right]\Theta e^{im\varphi} = \lambda_{L^2}\Theta e^{im\varphi}$
  - $-\hbar^2\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - m^2\right]\Theta = \lambda_{L^2}\Theta$
- Legendre Equation
  - $\frac{d}{d\xi}\left[(1-\xi^2)\frac{dP}{d\xi}\right] + \left[l(l+1) - \frac{m^2}{1-\xi}\right]P = 0$
  - Solution: $P(\xi)$; $|\xi| \le 1$

$\xi = x_i$

  - Change of variables: $\xi = \cos\Theta$
    $\lambda_{L^2} = \hbar^2 l(l+1)$, $l = 0,1,2,3\ldots$
  - $P(\xi) = \frac{1}{2^l l!}(1-\xi^2)^{\frac{|m|}{2}}\left(\frac{d}{d\xi}\right)^{l+|m|}(\xi^2-1)^l = P_l^m(\xi)$ ← the associated Legendre function
    $\Rightarrow l + |m| \le 2l$ $|m| \le l$
- The common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$
  - $Y_l^m(\theta,\varphi) = C_l^m P_l^m(\cos\theta)e^{im\varphi}$, $l = 0,1,2,3\ldots$ $|m| \le l$
- Normalization:
  - $\underbrace{\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi}_{\int d\Omega}\, |Y_l^m(\theta,\varphi)|^2 = 1 \Rightarrow$ Normalized spherical harmonics

Formula sheet →

  - Normalized Spherical Harmonic: $Y_l^m(\theta,\varphi) = (-1)^{\frac{m+|m|}{2}}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\,P_l^m(\cos\theta)e^{im\varphi}$
  - In Dirac $= \langle\theta,\varphi|lm\rangle$
  - At given $2l+1$ - spherical harmonics, $m = -l, -l+1, \ldots 0 \ldots, l-1, l$
- Ex: $l=0$, $m=0$
  $Y_0^0(\theta,\varphi) = \sqrt{\frac{1}{4\pi}}\,P_0^0(\cos\theta) = \sqrt{\frac{1}{4\pi}}$

$P_0^0(\xi) = 1$
$P_1^1(\xi) = \frac{1}{2}\left[1-\xi^2\right]^{\frac{1}{2}}\frac{d}{d\xi^2}(\xi^2-1)$
$= \sqrt{1-\xi^2}$

- Ex: $l=1$, $m=-1$, $Y_1^{-1}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cdot\frac{1}{2}P_1^1(\cos\theta)e^{-i\varphi} = \sqrt{\frac{3}{8\pi}}\sqrt{1-\cos^2\theta}\,e^{-i\varphi} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
  $m=0$, $Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$
  $m=1$, $Y_1^1(\theta,\varphi) = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\varphi}$
- Ex $l=2$, $m=-2$, $Y_2^{-2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{-2i\varphi}$
  $m=-1$, $Y_2^{-1}(\theta,\varphi) = \sqrt{\frac{15}{16\pi}}\sin\theta\cos\theta\, e^{-i\varphi}$
  $m=0$ $Y_2^0(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
  $m=1$, $Y_2^1(\theta,\varphi) = -\sqrt{\frac{15}{16\pi}}\sin\theta\cos\theta\, e^{i\varphi}$
  $m=2$, $Y_2^2(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\varphi}$

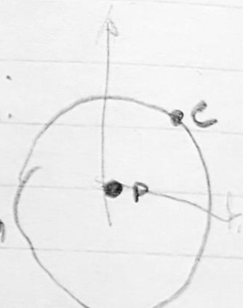
- The common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ are the spherical harmonics $Y_l^m(\theta,\varphi)$.
- $\lambda_{L^2} = \hbar^2 l(l+1)$, $\lambda_{L_z} = \hbar m$.

Quantum Mechanics in 3D: Hydrogen Atoms

- In 1D: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = E\psi$
- In 3D: $-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi + V(\vec{r})\psi = E\psi$

$$\left.\begin{array}{l}\psi = \psi(x,y,z)\\ V = V(x,y,z)\\ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\end{array}\right\}\text{ in Cartesian}$$

Hydrogen atom:
Coulomb Attraction
$V = -\frac{e^2}{r} = \frac{-e^2}{\sqrt{x^2+y^2+z^2}}$
Gaussian Units



$r = |\vec{r}|$

- If $V(\vec{r}) = V(r) \Rightarrow$ use the 3D spherical coordinates instead of Cartesian $(x,y,z) \to (r,\theta,\varphi)$
- Laplacian in Spherical Coordinates
  - $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]}_{= -\frac{1}{\hbar^2}\hat{L}^2}$

- Schrödinger Equation for any isotropic system in 3D:
  - $-\frac{\hbar^2}{2M}\nabla^2\psi + V(r)\psi = E\psi$, $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\hat{L}^2$

mass now equals M

- Solve the S.E. by the separation of variables (seek solutions ψ in the form $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$
- $\to -\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)RY + \frac{1}{2Mr^2}\hat{L}^2(RY) + V(r)RY = ERY$

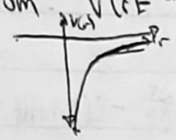
  $-\frac{\hbar^2}{2M}Y\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + R\frac{1}{2Mr^2}(\hat{L}^2Y) + V(r)RY = ERY$
- If $Y = Y_l^m(\theta,\varphi) \Rightarrow \hat{L}^2 Y_l^m = \hbar^2 l(l+1)Y_l^m$
  - $-\frac{\hbar^2}{2M}Y_l^m\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + Y_l^m\frac{\hbar^2 l(l+1)}{2Mr^2}R + V(r)RY_l^m = ERY_l^m$, if $\psi(\vec{r}) = R(r)Y_l^m(\theta,\varphi)$
  - Radial Equation: $-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right) + \left[V(r) + \frac{\hbar^2 l(l+1)}{2Mr^2}\right]R = ER$
- Angular dependence of ψ for any isotropic potential is given by $Y_l^m(\theta,\varphi)$, the radial dependence ($R(r)$) is determined by $V(r)$.
- $\underbrace{V(r) + \underbrace{\frac{\hbar^2 l(l+1)}{2Mr^2}}_{\text{centrifugal potential}}}_{\text{Effective Potential}}$

The spherical harmonics are orthonormal
$\int d\Omega\, Y_{l_1}^{m_1 *}(\theta,\varphi)\, Y_{l_2}^{m_2}(\theta,\varphi) = \delta_{l_1 l_2}\delta_{m_1 m_2}$
or $\langle l_1 m_1 | l_2 m_2\rangle$
and complete.
$Y(\theta,\varphi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{ml} Y_l^m(\theta,\varphi)$
any Y can be represented as a linear combination of Y_l^m

- 3D isotropic potential $V(r) \Rightarrow \psi(\vec{r}) = R(r)\underbrace{Y_l^m(\theta,\varphi)}_{\text{spherical harmonics}}$ $\quad l=0,1,2\ldots$ $\quad m=-l,\ldots l$

- $R(r)$ is found by solving the radial equation
  - $-\frac{\hbar^2}{2M}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[V(r) + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2}\right]R = ER.$

- Hydrogen atom $V(r) = -\frac{e^2}{r}$

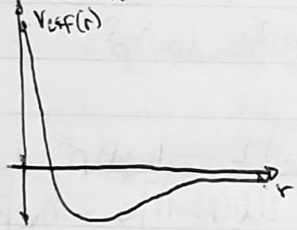


for the bound states $E = -|E| < 0$

- Seek solution in the form $R(r) = \frac{1}{r}u(r).$
  - $\frac{dR}{dr} = -\frac{1}{r^2}u + \frac{1}{r}\frac{du}{dr}$
  - $\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{d}{dr}\left(-u + r\frac{du}{dr}\right) = -\frac{du}{dr} + \frac{du}{dr} + r\frac{d^2u}{dr^2} = r\frac{d^2u}{dr}$
  - $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{1}{r}\frac{d^2u}{dr^2}$
  - $-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2}\right]u = -|E|u.$

- Hydrogen atom
  - $-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{r} + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2}\right]u = -|E|u.$

- 1D Radial Potential



- How to make Schrödinger equation dimensionless:
  - $-\frac{\hbar^2}{2M|E|}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{r|E|} + \frac{\hbar^2}{2M|E|}\frac{l(l+1)}{r^2}\right]u = -u.$
  - Introduce dimensionless length $\Rightarrow$

    $\rho^2 = r^2\frac{2M|E|}{\hbar^2} \Rightarrow$ dimensionless distance $\left(\rho = \sqrt{r^2\frac{2M|E|}{\hbar^2}} = r\sqrt{\frac{2M|E|}{\hbar^2}}\right)$ $\quad r = \rho\sqrt{\frac{\hbar^2}{2M|E|}}$
  - $-\frac{d^2u}{d\rho^2} + \left[-\underbrace{\frac{e^2}{|E|\sqrt{\frac{\hbar^2}{2M|E|}}}}\frac{1}{\rho} + \frac{l(l+1)}{\rho^2}\right]u = -u.$

    $\to \frac{e^2}{|E|\sqrt{\frac{\hbar^2}{2M|E|}}} = \frac{e^2}{\hbar}\sqrt{\frac{2M}{|E|}} = \rho_0.$
  - $\rho = r\sqrt{\frac{2M|E|}{\hbar^2}}$; $\rho_0 = \frac{e^2}{\hbar}\sqrt{\frac{2M}{|E|}}$
  - $\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho}\right]u \to$ solve for $u(\rho)$
  - Asymptotics of $u(\rho)$:

    @$\rho \to \infty$: $\frac{d^2u}{d\rho^2} = u \Rightarrow$ general solution: $u(\rho) = Ae^{-\rho} + Be^{\rho} = Ae^{-\rho} \simeq e^{-\rho}$

    normalizable physical solution: $B=0$

    @$\rho \to 0$: $\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u \Rightarrow$ general solution: $u(\rho) = \rho^\alpha$

    physical solution $\alpha = l+1 \Rightarrow u(\rho) \simeq \rho^{l+1}$

$u(\rho) = \rho^\alpha$

$\frac{d^2u}{d\rho^2} = \alpha(\alpha-1)\rho^{\alpha-2}$

$= l(l+1)\rho^{\alpha-2}$

$\Rightarrow \alpha(\alpha-1) = l(l+1)$

$\alpha = l+1$ or $-l$.

P

· Seek solution of $\left[1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}\right]u$ in this Form $u(\rho)=e^{-\rho}\rho^{l+1}v(\rho)$

- $\frac{du}{d\rho} = -e^{-\rho}\rho^{l+1}v + (l+1)e^{-\rho}\rho^{l}v - e^{-\rho}\rho^{l(l+1)}\frac{dv}{d\rho}$
- $\frac{d^2u}{d\rho^2} = e^{-\rho}\rho^{l+1}v - (l+1)e^{-\rho}\rho^{l}v - e^{-\rho}\rho^{l+1}\frac{dv}{d\rho} +$

$$-(l+1)e^{-\rho}\rho^{l}v + l(l+1)e^{-\rho}\rho^{l-1}v + (l+1)e^{-\rho}\rho^{l}\frac{dv}{d\rho} - e^{-\rho}\rho^{l+1}\frac{dv}{d\rho}$$

$$+(l+1)e^{-\rho}\rho^{l}\frac{dv}{d\rho} + e^{-\rho}\rho^{l+1}\frac{d^2v}{d\rho^2}$$

$$= e^{-\rho}\rho^{l+1}v - \rho_0 e^{-\rho}\rho^{l}v + l(l+1)e^{l}$$

$$= \rho\frac{d^2v}{d\rho^2} - 2\rho\frac{dv}{d\rho} + 2(l+1)\frac{dv}{d\rho} - 2(l+1)v = -\rho_0 v.$$

· Equation for $v(\rho)$:

Forbenius → Method

- $\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$

· Seek solutions in the form of a power series:

- $v(\rho)=\sum_{k=0}^{\infty} b_k\rho^k = b_0+b_1\rho+b_2\rho^2+\dots$
- $\frac{dv}{d\rho} = \sum_k b_k\rho^{k-1}k.$
- $\frac{d^2v}{d\rho^2} = \sum_k b_k k(k-1)\rho^{k-2}$

⇒ $\sum_k b_k k(k-1)\rho^{k-1} + 2(l+1)\sum_k b_k k\rho^{k-1} - 2\sum_k b_k k\rho^k + [\rho_0 - 2(l+1)]\sum_k b_k\rho^k = 0.$

- $k-1=p$, $k=p+1$
- $\sum_p b_{p+1}p(p+1)\rho^p + 2(l+1)\sum_p b_{p+1}(p+1)\rho^p$

  $p=k$ $\qquad$ $p=k$

- $\sum_k b_k(k+1)k\rho^k + 2(l+1)\sum_k b_{k+1}(k+1)\rho^k.$
- $\sum_k \rho^k \underbrace{\left\{b_{k+1}\left[k(k+1)+2(l+1)(k+1)\right] - b_k\left[2k-\rho_0+2(l+1)\right]\right\}}_{=0} = 0.$
- Recursion Relation: $b_{k+1} = b_k\frac{2(k+l+1)-\rho_0}{(k+1)(k+2l+2)}$ → start with $b_0, b_1, b_2, \dots$

· Asymptotical behaviour of $v(\rho)$ @ $\rho\to\infty$ is determined by $k\gg1$;

- $b_{k+1}\simeq b_k\frac{2k}{k^2} = b_k\frac{2}{k}.$
- ⇒ $b_k \simeq C\frac{2^k}{k!}$ @ $k\gg1$
- @ $\rho\to\infty$: $v(\rho)\simeq C\sum_k\frac{2^k}{k!}\rho^k = C\sum_k\frac{(2\rho)^k}{k!} = Ce^{2\rho}$

· $u(r)=e^{-\rho}\rho^{l+1}v(\rho)$

- @ $\rho\to\infty$: $u\sim e^{\rho}$

ψ cannot be normalized → one has to terminate power series at some $k_{max}=K$.

· $b_{k_{max}}\neq 0$, but $b_{k_{max}+1}=b_{k_{max}+2}=\dots=0.$

· $2(k_{max}+l+1)-\rho_0=0$ ⇒ $\rho_0=2(k_{max}+l+1)$ ⇒ $v(\rho)$ = polynomial of degree k_{max}

· $k_{max}\geq 0$

- $k_{max} + l + 1 = n$; $n \geq 1$ - the principle quantum number.
- $\rho_0 = 2n \Rightarrow \frac{e^2}{\hbar}\sqrt{\frac{2M}{|E|}} = 2n \Rightarrow |E| = \frac{Me^4}{2\hbar^2}\frac{1}{n^2} \Rightarrow E_n = -\frac{Me^4}{2\hbar^2}\frac{1}{n^2}$

$\frac{Me^4}{2\hbar^2} = 1\,R_y = 13.6\,eV$

R_y = Rydberg

energies with stationary bound states.

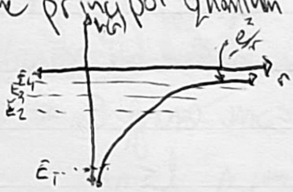
- Ground State: $n=1$
  - Energy = $-13.6\,eV$.
- For the n^{th} bound state:
  - $k_{max} = n - l - 1 \geq 0$
  - @ given n: $l \leq n-1$
- Radial Wave function: $R(r) = \frac{1}{r}u(r)$.

$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$; $\rho = \sqrt{\frac{2M|E|}{\hbar^2}}\, r$

terminates @ $k = k_{max}$ if $\rho_0 = 2(k_{max}+l+1) = 2n$ $\rightarrow v(\rho) = \sum_k b_k \rho^k$, $b_{k+1} = b_k \frac{2(k+l+1) - \rho_0}{(k+1)(k+2l+2)}$

- $n \geq 1$ ← the principal quantum number
- Bound Energies - $E_n = -\left(\frac{Me^4}{2\hbar^2}\right)\frac{1}{n^2}$

$\approx 13.6\,eV$.



- $k_{max} = n - l - 1 \geq 0 \Rightarrow$ @ given n, $l \leq n-1$
- $v(\rho)$ is a polynomial of degree $n-l-1$
  - $b_{k+1} = b_k \frac{2(k+l+1-n)}{(k+1)(k+2l+2)}$ ← use the recursion relation to obtain $v(\rho)$ @ n & l.
  - $v(\rho) = L^{2l+1}_{n-l-1}(2\rho)$

    The associated Laguerre polynomial
  - $n=1, l=0 \Rightarrow L^1_0(x) = 1$ $(b_0 = 1)$
  - $n=2, l=0,1 \Rightarrow L^1_1(x) = -2x+4$. $(b_0 = 4)$

    $L^3_0(x) = 6$ $(b_0 = 6)$.
  - $n=3, l=0 \Rightarrow L^1_2(x) = 3x^2 - 18x + 18$ $(b_0 = 18)$

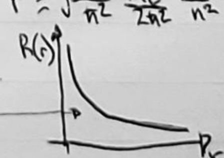
    $l = 1 \Rightarrow L^3_1(x) = -24x + 96$ $(b_0 = 96)$

    $l = 2 \Rightarrow L^5_0(x) = 120$ $(b_0 = 120)$.

the characteristic size of hydrogen atom

is the Bohr radius $a_0 = \frac{\hbar^2}{Me^2} \approx 5.29\times10^{-11}\,m$

- In the n^{th} bound state: $\rho = \sqrt{\frac{2M|E|}{\hbar^2}}\, r = \sqrt{\frac{2M}{\hbar^2}\frac{Me^4}{2\hbar^2}\frac{1}{n^2}}\, r = \left(\frac{Me^2}{\hbar^2}\right)\frac{1}{n} r = \frac{1}{n}\frac{r}{a_0}$.
- $R(r) = \frac{1}{r}\left(\frac{1}{n}\frac{r}{a_0}\right)^{l+1} e^{-\frac{r}{na_0}} L^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right)$



$= \left(\frac{1}{na_0}\right)^{l+1} r^l e^{-\frac{r}{na_0}} L^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right)$

- The wave function corresponding to n, l, m:
  - $\psi_{nlm}(\vec{r}) = C R_{nl}(r) Y_l^m(\theta, \varphi)$

    $\equiv \langle r, \theta, \varphi | nlm \rangle$

- Normalization:
  - $\int d^3\vec{r}\, |\psi_{nlm}(\vec{r})|^2 = 1$
  - $\int_0^\infty r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi\, |\psi_{nlm}|^2 = |C|^2 \underbrace{\left[\int_0^\infty r^2 dr\, R_{nlm}^2(r)\right]}_{=1} \underbrace{\left(\int_0^\pi \sin\theta\, d\theta\right)\left(\int_0^{2\pi} d\varphi\, |Y_l^m(\theta,\varphi)|^2\right)}_{=1}$

  - $\psi_{nlm}(\vec{r}) = \left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n((n+l)!)^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} \cdot$ Solve for C

    $L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta, \varphi)$

    depends on n, l, m; n = principal, l = orbital, m = magnetic — quantum number.

- Energy depends only on n: $E_n = -(1 R_y)\frac{1}{n^2}$
- At given n, there are several different stationary states corresponding to the same energy $E_n \Rightarrow$ the energy level E_n is degenerate
- At given n: $l \leq n-1$.

  At given n and l: $-l \leq m \leq l$ ($2l+1$ values).
- The degeneracy of the n^{th} level:
  - $d_n = \sum_{l=0}^{n-1} (2l+1) = n^2$.
- Ground State: $n=1,\ l=0,\ m=0$ $\quad d_1 = 1$

  1^{st} Excited State: $\left.\begin{array}{l} n=2,\ l=0,\ m=0 \\ n=2,\ l=1,\ m=\pm 1, 0 \end{array}\right\} \rightarrow d_2 = 4$
- Actual degeneracy $= 2n^2$, due to spin (spin = intrinsic angular momentum)

• Example: Hydrogen atom in the state $n_r=2,\ l=1,\ m=0$

$$\psi_{210}(\vec{r}) = \frac{1}{\sqrt{24}} a_0^{-\frac{3}{2}} \frac{r}{a_0} e^{-\frac{r}{a_0}} \underbrace{Y_1^0(\theta,\varphi)}_{\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta}$$

$\langle x\rangle = ?\ ;\ \langle x^2\rangle = ?$

~~Angular~~

$$\langle x\rangle = \int d^3\vec{r}\, x|\psi_{210}(\vec{r})|^2 = \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi\ r\sin\theta\cos\varphi \cdot \frac{1}{24}\frac{1}{a_0}\left(\frac{r}{a_0}\right)^2 e^{-\frac{2r}{a_0}} \frac{3}{4\pi}\cos^2\theta$$

$$= \frac{1}{24}\frac{1}{a_0^3}\frac{3}{4\pi}\left(\int_0^\infty dr\, r^3 e^{-\frac{2r}{a_0}}\right)\left(\int_0^\pi d\theta \sin^2\theta\cos^2\theta\right)\left(\int_0^{2\pi} d\varphi \cos\varphi\right)$$

$= 0$.

Start with φ, usually 0.

If asked for dipole moment, $\vec{d} = -e\vec{r}$

$\langle d_x\rangle = -e\langle x\rangle$

or Angular momentum $\hat{L}_z = i\hbar\frac{\partial}{\partial\varphi}$.

$\int_{\vec{r}} \psi_{210}^* \hat{L}_z \psi_{210} = \hbar m = 0$

$\int_{\vec{r}} \psi_{nlm}^* \hat{L}_z \psi_{210} = \hbar m$

$\int_{\vec{r}} \psi_{nlm}^* \hat{L}_z^N \psi_{210} = (\hbar m)^N$

$$\langle x^2\rangle = \int d^3\vec{r}\, x^2|\psi_{210}(\vec{r})|^2 = \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi\ r^2\sin^2\theta\cos^2\varphi \cdot \frac{1}{24}\frac{1}{a_0}\left(\frac{r}{a_0}\right)^2 e^{-\frac{2r}{a_0}} \frac{3}{4\pi}\cos^2\theta$$

$$= \frac{1}{32\pi a_0^5}\underbrace{\left[\int_0^\infty dr\, r^6 e^{-\frac{2r}{a_0}}\right]}_{I}\underbrace{\left[\int_0^\pi d\theta \sin^3\theta\cos^2\theta\right]}_{s=\cos\theta,\ ds=-\sin\theta d\theta}\left[\int_0^{2\pi} d\varphi\cos^2\varphi\right]$$

$$-\int_1^{-1} ds\,(1-s^2)s^2 = \int_{-1}^1 ds\, s^2(1-s^2) = 2\int_0^1 ds\, s^2(1-s^2) = 2\left(\int_0^1 ds\, s^2 - \int_0^1 ds\, s^4\right) = \frac{4}{15}$$

$$= \left(\frac{1}{32\pi a_0^5}\right)\left(a_0^7\, 720\right)\left(\frac{4}{15}\right)(\pi)$$

$= 6a_0^2$

$\rho = \frac{r}{a_0}$

$$I = \int_0^\infty dr\, r^6 e^{-\frac{2r}{a_0}} = a_0^7 \underbrace{\int_0^\infty d\rho\, \rho^6 e^{-\rho}}_{720}.$$

Put simple trig integrals on Formula sheet.

$J(a) = \int_0^\infty d\rho\, \rho^6 e^{-a\rho}$

$\frac{\partial^6 J}{\partial a^6} = \rho$