Quantum Mechanics

May 24, 2023

Contents

Lectures

Start of lecture 1

1 Quantum Mechanics

1.1 Particles and Waves in Classical Mechanics

Basic concepts of classical mechanics.

Particles

Definition. Point-particle is an object carrying energy E and momentum p in infinitesimally small point of space.

Particle determined by $\mathbf{x}$ (position) and $\mathbf{v} = \dot{\mathbf{x}} = \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{x}$ (velocity). Newton's second law is that

$$m\ddot{\mathbf{x}} = \mathbf{F}(\mathbf{x}(t), \dot{\mathbf{x}}(t))$$

Solving Newton's second law determines $\mathbf{x}(t)$ and $\dot{\mathbf{x}}(t)$ for all $t > t_0$ once initial conditions known $(\mathbf{x}(t_0), \dot{\mathbf{x}}(t_0))$.

Waves

Definition. Any real or complex-valued function with periodicity in time / space.

- Take function of time t:

  $$f(t + T) = f(t)$$

  where $T \neq 0$ is the period.

  $$\nu = \frac{1}{T}$$

  is the frequency and

  $$\omega = 2\pi\nu = \frac{2\pi}{T}$$

  is the angular frequency.

- Take function of space x

  $$f(x + \lambda) = f(x)$$

  where λ is the wavelength.

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

  is the wave number.

Example. In 1 dimension, electromagnetic wave obeys equation

$$\frac{\partial^2 f(x,t)}{\partial t^2} - c^2 \frac{\partial^2 f(x,t)}{\partial x^2} = 0 \tag{1}$$

with $c \in \mathbb{R}$. Solutions:

$$f_\pm(x,t) = A_\pm \exp(\pm iKx - i\omega t)$$

with $A_\pm \in \mathbb{C}$ (amplitude of wave) and $\omega = cK$ (dispersion relation), hence

$$\lambda = \frac{2\pi c}{\omega} = \frac{c}{\nu}$$

Example. In 3 dimensions, electromagnetic wave obeys equation

$$\frac{\partial^2 f(\mathbf{x},t)}{\partial t^2} - c^2 \nabla^2 f(\mathbf{x},t) = 0 \tag{2}$$

need $f(x,t_0)$, $\frac{\mathrm{d}f}{\mathrm{d}t}(x,t_0)$ to get unique solution. Solution:

$$f(\mathbf{x},t) = A\exp(i\mathbf{K}\cdot\mathbf{x} - i\omega t)$$

with $\omega = c|\mathbf{K}|$.

Note.

- These kind of waves arise as solutions of other governing equations provided a different dispersion relation.
- For all governing equations, superposition principle holds if f_1, f_2 solutions implies $f = f_1 + f_2$ is a solution.

1.2 Particle-like Behaviour of Wave

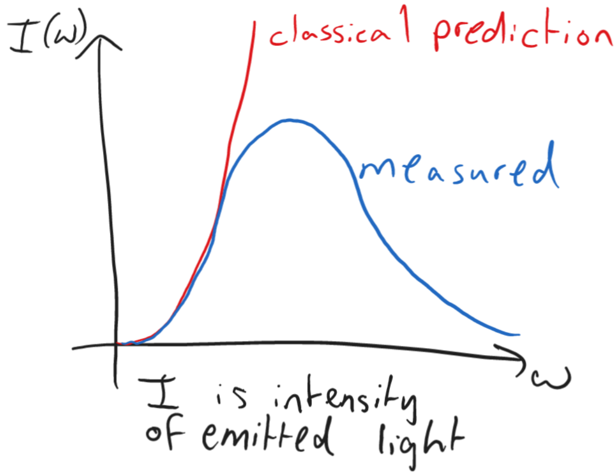
1.2.I Black-body Radiation (1900)

1.2.II Photo-electric effect (1905)

1.2.III Compton scattering (1923)

1.2.I Black Body Radiation

When a body heated at temperature T, it radiates light at different frequencies



Classical prediction:

$$E = K_B T$$

where E is energy of each wave and K_B is Boltzmann constant

$$\implies I(\omega) \propto K_B T \frac{\omega^2}{\pi^2 c^3}$$

Planck:

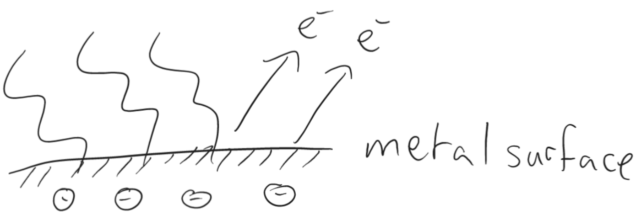
$$I(\omega) \propto \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{K_B T}\right) - 1}$$

$\hbar$ is reduced Planck constant:

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

Start of lecture 2

1.2.II Photo electric effect



As change I and ω of incident light

classical expectation:

(i) incident light carries $E \propto I$ as I increases there is enough E to break the bond of e^- with atom $\forall \omega$.

(ii) emission rate should be constant as I increases

surprising facts:

(1) Below ω_{min} no e^- emission

(2) E_{max} depended on ω not on I

(3) emission rate increases as I increases

1905 Einstein

- light quantified in small quanta, called photon
- each photon carries

$$E = \hbar\omega$$

$$\mathbf{P} = \hbar\mathbf{K}$$

- phenomenon of e^- emission comes from scattering of single photon off single e^-.

$$E_{\text{min}} = 0 = \hbar\omega_{\text{min}} - \phi$$

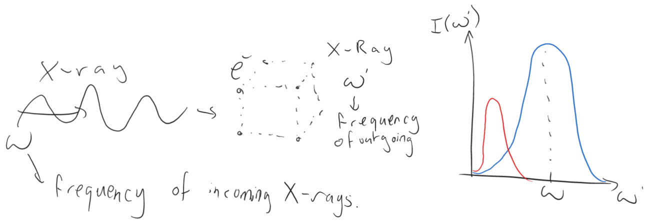
(ϕ is the binding energy of e^- with atom of metal)

$$E_{\text{max}} = \hbar\omega_{\text{max}} - \phi$$

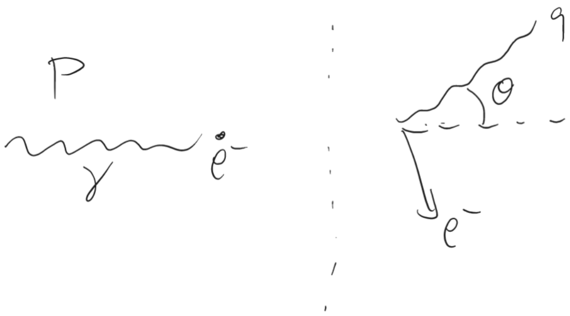
as I increases, the number of protons increases, so the amount of scattering increases, so there is a higher e^- emission rate.

!.2.III Compton scattering

1923: X-rays scattering off free electron



Recall Dynamics and Relativity example sheet 4 question 7:



$$2\sin^2\frac{\theta}{2} = \frac{mc}{|\mathbf{q}|} - \frac{mc}{|\mathbf{p}|}$$

Why is this the peak?

$$\begin{aligned} E &= \hbar\omega \\ \mathbf{P} &= \hbar\mathbf{K} \implies |\mathbf{P}| = \hbar|\mathbf{K}| = \hbar\frac{\omega}{c} \\ \mathbf{q} &= \hbar\mathbf{K}' \implies |\mathbf{q}| = \hbar|\mathbf{K}'| = \hbar\frac{\omega'}{c} \end{aligned}$$

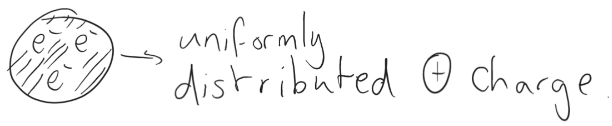
Take (2) and plug in (1)

$$\frac{1}{\omega'} = \frac{1}{\omega} + \frac{\hbar}{mc}(1-\cos\theta)$$

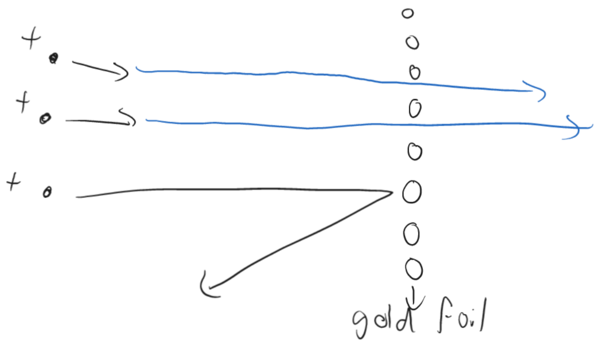
Note. $\hbar \to 0$, $\omega' \to \omega$.

1.3 Atomic spectra

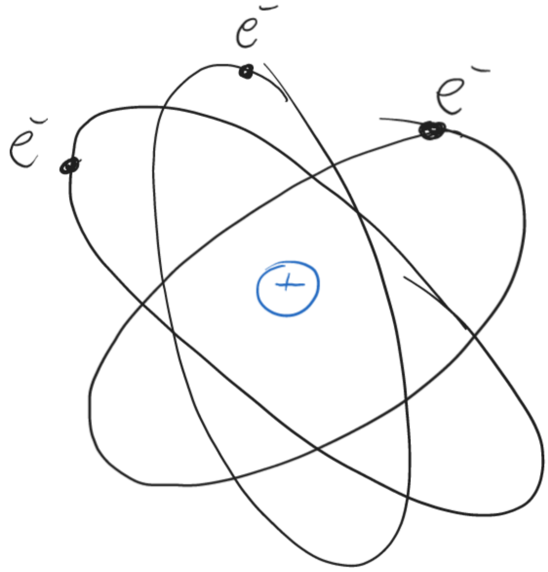
1897: Thomson, plum-pudding model of atoms.



1909: Rutherford



scattering pattern → Rutherford model



The Rutherford model did not work because

(i) e^- moves on circular orbits would radiate

(ii) e^- would collapse on nucleus due to Coulomb force

(iii) model did not explain spectra measured.

$$\omega_{\min} = 2\pi c R_0 \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

(c is the speed of light, R_0 is the Rydberg constant, $\omega_{\min}$ is the light emitted by atoms when hit by light and $n, m \in \mathbb{N}$)

1913 (Bohr): e^- orbits around nucleus are quantised so that L (= orbital angular momentum) takes discrete values

$$L_n = n\hbar$$

Proposition. Quantisation of $L \implies$ quantisation of r, v, E.

Proof.

$$L \equiv m_e v r \implies v = \frac{L}{m_e r} \implies v_n = n \frac{\hbar m_e r}{}$$

Coulomb force:

$$\mathbf{F}^{\text{Coul}} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r^2} \mathbf{e}_r$$

Newton's second law:

$$\mathbf{F}^{\text{Coul}} = m_e a_r \mathbf{e}_r$$

$$\implies \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r^2} = m_e \frac{v^2}{r} \implies r \equiv r_n = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} n^2$$

$$\implies r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$$

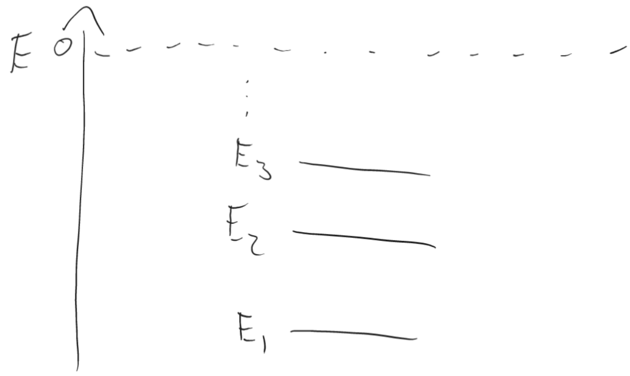
(min radius / Bohr radius)

$$E_n = \frac{1}{2} m_e v_n^2 - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_n}$$

$$= -\frac{e^2}{8\pi\varepsilon_0 r_0} \frac{1}{n^2}$$

□

$n = 1$, $E_1 = -13.6eV$ GROUND LEVEL.



$$\omega_{\min} = \frac{\Delta E_{\min}}{\hbar} = 2\pi c \left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2 \left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

1.4 The wave-like behaviour of particles

1923: De Broglie hypothesis: $\forall$ particle of $\forall$ mass associated with Q wave having

$$\omega = \frac{E}{\hbar}$$

$$\mathbf{K} = \frac{\mathbf{p}}{\hbar}$$

1927: Davison and Geemer e^- off crystals interference pattern was consistent with De Broglie.

Start of lecture 3

2 Foundation of Quantum Mechanics

Linear Algebra	Quantum Mechanics
vector (n-dimensional complex value)	state
$\mathbf{v}$, $\{e_i\}$, $\mathbf{v} \to (v_1, \dots, v_n)$	ψ, basis $\mathbf{x} \to \psi(\mathbf{x}, t)$
vector space $\mathbb{C}^n$	$L^2(\mathbb{R}^3)$ complex-valued square integrable functions
inner product $\langle \mathbf{v}, \mathbf{w} \rangle = v_1^* w_1 + \cdots + v_n^* w_n$	$\langle \psi, \phi \rangle \int_{\mathbb{R}^3} \psi^*(\mathbf{x}, t)\phi(\mathbf{x}, t) \mathrm{d}^3 x$
linear map $\mathbb{C}^n \to \mathbb{C}^n$, use matrix	$L^2(\mathbb{R}^3) \to l^2(\mathbb{R}^3)$ operators $\hat{O}$, $\phi = \hat{O}\psi$

2.1 Wave Function and Probabilistic Interpretation

Classical mechanics: $\mathbf{x}, \dot{\mathbf{x}}$ (or equivalently $\mathbf{p} = m\dot{\mathbf{x}}$) determine dynamics of the particle.

Quantum mechanics: ψ described by $\psi(\mathbf{x}, t)$ determine dynamics of the particle (in a probabilistic way)

Definition. ψ is the *state* of the particle.

Definition. $\psi(\mathbf{x}, t)$ complex coefficient of ψ in the continuous basis of $\mathbf{x}$, i.e. $\psi(\mathbf{x}, t)$ is ψ in $\mathbf{x}$ representation and is called *wavefunction*. $\psi(\mathbf{x}, t) : \mathbb{R}^3 \to \mathbb{C}$ that satisfies mathematical properties dictated by its physics interpretation.

Interpretations

Born's rule / probabilistic interpretation.

The probability density for particle to sits at $\mathbf{x}$ at given time t

$$\rho(\mathbf{x}, t) \propto |\psi(\mathbf{x}, t)|^2$$

$\rho(\mathbf{x}, t)\mathrm{d}V$ is the probability that the particle sits in some small volume V centred at $\mathbf{x}$ is proportional to square modulus of $\psi(\mathbf{x}, t)$.

Mathematical Properties

(i) Because the particle has to be somewhere implies that wavefunction has to be normalisable (or square0integrable) in $\mathbb{R}^3$:

$$\int_{\mathbb{R}^3} \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)\mathrm{d}^3 x = \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \mathrm{d}^3 x = \mathcal{N} < \infty$$

with $\mathcal{N} \in \mathbb{R}$ and $\mathcal{N} \neq 0$.

(ii) Because total probability has to be 1,

$$\overline{\psi}(\mathbf{x},t) = \frac{1}{\sqrt{\mathcal{N}}}\psi(\mathbf{x},t)$$

$$\implies \int_{\mathbb{R}^3} |\overline{\psi}(\mathbf{x},t)|^2 \mathrm{d}^3x = 1$$

$$\implies \rho(\mathbf{x},t) = |\overline{\psi}(\mathbf{x},t)|^2$$

Note. Often drop $\overline{\psi}$ and write wavefunctions as ψ, then normalise at the end.

Note. If $\tilde{\psi}(\mathbf{x},t) = e^{i\alpha}\psi(\mathbf{x},t)$ with $\alpha \in \mathbb{R}$ then $|\tilde{\psi}(\mathbf{x},t)|^2 = |\psi(\mathbf{x},t)|^2$ so ψ and $\tilde{\psi}$ are equivalent state.

Non-examinable aside:
State corresponds to rays in vector space of wave functions $[\psi]$ is the equivalence class of vectors under equivalence relation $\psi_1 \sim \psi_2 \iff \psi_1 = e^{i\alpha}\psi_2$.

Hilbert Space

Definition. The set of all square-integrable functions in $\mathbb{R}^3$ is called Hilbert space $\mathcal{H}$ or $L^2(\mathbb{R}^3)$.

Proposition. If $\psi_1, \psi_2 \in \mathcal{H}$ then $\psi = a_1\psi_1 + a_2\psi_2 \neq 0 \in \mathcal{H}$ $(a_1, a_2 \in \mathbb{C})$.

Theorem 1. If $\psi_1(\mathbf{x},t)$ and $\psi_2(\mathbf{x},t)$ are square-integrable then also $\psi(\mathbf{x},t) = a_1\psi_1(\mathbf{x},t) + a_2\psi_2(\mathbf{x},t)$ is square-integrable.

Proof.

$$\int_{\mathbb{R}^3} |\psi_1(\mathbf{x},t)|^2 \mathrm{d}^3x = \mathcal{N}_1 < \infty$$

$$\int_{\mathbb{R}^3} |\psi_2(\mathbf{x},t)|^2 \mathrm{d}^3x = \mathcal{N}_2 < \infty$$

by triangle identities for complex numbers,

$$\begin{aligned}
\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \mathrm{d}^3x &= \int_{\mathbb{R}^3} |a_1\psi_1(\mathbf{x},t) + a_2\psi_2(\mathbf{x},t)|^2 \mathrm{d}^3x \\
&\leq \int_{\mathbb{R}^3} (|a_1\psi_1(\mathbf{x},t)| + |a_2\psi_2(\mathbf{x},t)|)^2 \mathrm{d}^3x \\
&= \int_{\mathbb{R}^3} (|a_1\psi_1(\mathbf{x},t)|^2 + |a_2\psi_2(\mathbf{x},t)|^2 + 2|a_1\psi_1||a_2\psi_2|) \mathrm{d}^3x \\
&\leq \int_{\mathbb{R}^3} 2|a_1\psi_1(\mathbf{x},t)|^2 + 2|a_2\psi_2(\mathbf{x},t)|^2 \mathrm{d}^3x \\
&= 2|a_1|^2\mathcal{N}_1 + 2|a_2|^2\mathcal{N}_2 \\
&< \infty
\end{aligned}$$

□

2.2 Inner Product

Definition. Inner product in $\mathcal{H}$ is defined as

$$\langle\psi,\phi\rangle = \int_{\mathbb{R}^3} \psi^*(\mathbf{x},t)\phi(\mathbf{x},t) \mathrm{d}^3x$$

Theorem 2. If $\psi, \phi \in \mathcal{H}$ then their inner product is guaranteed to exist.

Proof.

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \mathrm{d}^3x = \mathcal{N}_1 < \infty$$

$$\int_{\mathbb{R}^3} |\phi(\mathbf{x},t)|^2 \mathrm{d}^3x = \mathcal{N}_2 < \infty$$

$$\begin{aligned}
|\langle\psi,\phi\rangle| &= \left|\int_{\mathbb{R}^3} \psi^*(\mathbf{x},t)\phi(\mathbf{x},t) \mathrm{d}^3x\right| \\
&\leq \sqrt{\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \mathrm{d}^3x \int_{\mathbb{R}^3} |\phi(\mathbf{x},t)|^2 \mathrm{d}^3x} \qquad \text{(Cauchy Schwarz)} \\
&= \sqrt{\mathcal{N}_1\mathcal{N}_2} \\
&< \infty
\end{aligned}$$

□

Start of lecture 4

Properties of inner product

(i) $\langle \psi, \phi \rangle = \langle \phi, \psi \rangle^*$

(ii) antilinear in first entry, linear in second entry. So $\forall a_1, a_2 \in \mathbb{C}$,

$$\langle a_1\psi_1 + a_2\psi_2, \phi \rangle = a_1^*\langle \psi_1, \phi \rangle + a_2^*\langle \psi_2, \phi \rangle$$

$$\langle \psi_1, a_1\phi_1 + a_2\phi_2 = a_1\langle \psi, \phi_1 \rangle + a_2\langle \psi, \phi_2 \rangle$$

(iii) inner product of $\psi \in \mathcal{H}$ with itself is non-negative

$$\langle \psi, \psi \rangle = \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \mathrm{d}^3x > 0$$

Definition. The norm of wave function ψ is the real function

$$\|\psi\| \equiv \sqrt{\langle \psi, \psi \rangle}$$

Definition. Wavefunction ψ is normalised if $\|\psi\| = 1$.

Definition. Two wave functions ψ, ϕ are orthogonal if

$$\langle \psi, \phi \rangle = 0$$

Definition. A set of wavefunctions $\{\psi_n\}$ is orthonormal if

$$\langle \psi_m, \psi_n \rangle = \delta_{mn}$$

Definition. A set of wavefunctions $\{\psi_n\}$ is complete if for all $\phi \in \mathcal{H}$ can be written as a linear combination of them

$$\forall \phi \in \mathcal{H} \qquad \phi = \sum_{n=0}^{\infty} c_n\psi_n \qquad c_n \in \mathbb{C}, \psi_n \in \mathcal{H}$$

Lemma 1. If $\{\psi_n\}$ form a complete orthonormal basis of $\mathcal{H}$ then $c_n = \langle \psi_n, \phi \rangle$.

Proof.

$$\begin{aligned}
\langle \psi_n, \phi \rangle &= \left\langle \psi_n, \sum_{m=0}^{\infty} c_m \psi_m \right\rangle \\
&= \sum_{m=0}^{\infty} c_m \langle \psi_n, \psi_m \rangle \\
&= \sum_{m=0}^{\infty} c_m \delta_{mn} \\
&= c_n
\end{aligned}$$

□

2.3 Time-dependent Schrödinger equation

Recap: first postulate of quantum mechanics is Born's rule

$$P(\mathbf{x}, t) = \rho(\mathbf{x}, t)\mathrm{d}^3\mathbf{x} = |\psi(\mathbf{x}, t)|^2 \mathrm{d}\mathbf{x}$$

The second postulate is time dependent Schrödinger equation (TDSE):

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

where $U(\mathbf{x}) \in \mathbb{R}$ (potential).

- First derivative in t: once $\psi(x, t_0)$ is known, we can find out $\psi(x, t)$ at all times.
- asymmetry between t and x, so time dependent Schrödinger equation is a non-relativistic equation.

Heuristic interpretation

e^- diffraction (interference) $\to$ e^- behaves like waves

$$\psi(x, t) \propto \exp[i(\mathbf{k} \cdot \mathbf{x} - \omega t)]$$

almost describes the dynamics of e^-. Take De-Broglie

$$kbg = \frac{\mathbf{p}}{\hbar} \qquad \omega = \frac{E}{\hbar}$$

for free particle

$$E = \frac{|\mathbf{p}|^2}{2m} \implies \omega = \frac{|\mathbf{p}|^2}{2m\hbar} = \frac{\hbar}{2m}|\mathbf{k}|^2$$

dispersion relation for a particle-wave

$$\omega \propto |\mathbf{k}|^2$$

while for light-waves

$$\omega \propto |\mathbf{k}|$$

if $\exp[i(\mathbf{k}\cdot\mathbf{x}-\omega t)]$ is a solution of the equation for the wave of e^- and if $\omega = \frac{\hbar}{2m}|\mathbf{k}|^2$ then

$$\exp[i(\mathbf{k}\cdot\mathbf{x}) - i\frac{|\mathbf{k}|^2}{2m}\hbar t] = \exp[i(kx - \frac{k^2}{2m}\hbar t)]$$

by dimensional analysis.

Properties

(i) $\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \mathrm{d}^3x = \mathcal{N} < \infty$.

Proof.

$$\begin{aligned}\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}t} &= \frac{}{t}\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \mathrm{d}^3x \\ &= \int_{\mathbb{R}^3} \frac{\partial}{\partial t}|\psi(\mathbf{x},t)|^2 \mathrm{d}^3x\end{aligned}$$

but

$$\frac{\partial}{\partial t}(\psi^*(\mathbf{x},t)\psi(\mathbf{x},t)) = \psi^*\frac{\partial\psi}{\partial t} + \frac{\partial\psi^*}{\partial t}\psi$$

Now TDSE gives

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

and TDSE* gives

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

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

$$\implies \frac{\mathrm{d}\mathcal{N}}{\mathrm{d}t} = \int_{\mathbb{R}^3}\nabla\cdot\left[\frac{i\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*\right] = 0$$

because ψ, ψ^* are such that $|\psi|, |\psi^*| \to 0$ as $|\mathbf{x}| \to \infty$. □

(ii) Normalisation of wavefunction constant in time $\implies$ probability is conserved

$$\frac{\partial\rho(\mathbf{x},t)}{\partial t} + \nabla\cdot\mathbf{J}(\mathbf{x},t) = 0$$

$$\mathbf{J}(\mathbf{x},t) = -[\cdots] = -\frac{i\hbar}{2m}[\psi^*(\mathbf{x},t)\nabla\psi(\mathbf{x},t) - \psi(\mathbf{x},t)\nabla\psi^*(\mathbf{x},t)]$$

(the conserved probability current of quantum physics states).

2.4 Expectation values and operators

How to extract info from ψ?

Definition. Observable = any property of the particle describe by ψ that can be measured.

In Quantum mechanics → operator acting on ψ, measurement → expectation value of an operator.

2.5.1 Heuristic interpretation

From probabilistic interpretation, if want to measure the position of particle:

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi(x,t)|^2 \mathrm{d}x = \int_{-\infty}^{\infty} \psi^*(x,t)x\psi(x,t)\mathrm{d}x$$

$$O_x \to \hat{x} \to x$$

Start of lecture 5

Expectation value of an observable is the mean (average) of infinite series of measurements performed on particles on the same state.

$$\begin{aligned}
\langle p\rangle &= m\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} \\
&= m\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty} \psi^* x\psi \mathrm{d}x \\
&= m\int_{-\infty}^{\infty} x\frac{\partial}{\partial t}(\psi^*\psi) \\
&= \frac{i\hbar m}{2m}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)\mathrm{d}x && \text{(TDSE)} \\
&= -\frac{i\hbar}{2}\int_{-\infty}^{\infty}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)\mathrm{d}x \\
&= -i\hbar\int_{-\infty}^{\infty}\psi^*\frac{\partial\psi}{\partial x}\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\mathrm{d}x
\end{aligned}$$

position → x
momentum → $-i\hbar\frac{\partial}{\partial x}$

2.5.2 Hermitian operators

In $\mathbb{C}^n$ linear map $\mathbb{C}^n \to \mathbb{C}^n$

$$T : \underbrace{\mathbf{v}}_{\in\mathbb{C}^n} \to \underbrace{\mathbf{w}}_{\in\mathbb{C}^n} \qquad \mathbf{w} = T\mathbf{v}$$

In quantum mechanics linear maps $\mathcal{H} \to \mathcal{H}$

$$\hat{O} : \psi \to \tilde{\psi} \quad \tilde{\psi} = (\hat{O}\psi)(x,t)$$

Definition. An operator $\hat{O}$ is any linear map $\mathcal{H} \to \mathcal{H}$ such that

$$\hat{O}(a_1\psi_1 + a_2\psi_2) = a_1\hat{O}(\psi_1) + a_2\hat{O}(\psi_2)$$

with $a_1, a_2 \in \mathbb{C}$, $\psi_1, \psi_2 \in \mathcal{H}$.

Examples

- finite differential operators
$$\sum_{m=0}^{N} p_n(X)\frac{\partial}{\partial x}$$
with $p_n(x)$ a polynomial. In particular, x and $-i\hbar\frac{\partial}{\partial x}$ are special cases.
- Translation
$$\hat{S}_a : \psi(x) \to \psi(x-a)$$
- Parity
$$\hat{P} : \psi(x) \to \psi(-x)$$

Definition. The Hermitian conjugate $\hat{O}^\dagger$ of an operator $\hat{O}$ is the operator such that

$$\langle \hat{O}^\top \psi_1, \psi_2 \rangle = \langle \psi_1, \hat{O}\psi_2 \rangle \quad \forall \psi_1, \psi_2 \in \mathcal{H}$$

Verify (from the properties of the inner product) that

- $(a_1\hat{A}_1 + a_2\hat{A}_2)^\dagger = a_1^*\hat{A}_1^\dagger + a_2^*\hat{A}_2^\dagger$ for any $a_1, a_2 \in \mathbb{C}$
- $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$.

Definition. An operator $\hat{O}$ is *Hermitian* if

$$\hat{O} = \hat{O}^\dagger \iff \langle \hat{O}\psi_1, \psi_2 \rangle = \langle \psi_1, \hat{O}\psi_2 \rangle$$

All physics quantities in quantum mechanics are represented by Hermitian operators.

Examples

(i) $\hat{x} : \psi(x,t) \to x\psi(x,t)$ verify that $\hat{x}^\dagger = \hat{x} \iff (\hat{x}\psi_1, \psi_2) = \psi_1 \hat{x}\psi_2)$ for $\psi_1, \psi_2 \in \mathcal{H}$

$$\langle x\psi_1, \psi_2\rangle = \int_{-\infty}^{\infty} (x\psi_1)^* \psi_2 \mathrm{d}x = \int_{-\infty}^{\infty} \psi_1^* x \psi_2 \mathrm{d}x = \langle \psi_1, x\psi_2\rangle$$

(ii) $\hat{P} : \psi(x,t) \to -i\hbar \frac{\partial \psi}{\partial x}(x,t)$ verify:

$$\begin{aligned}\langle \hat{P}\psi_1, \psi_2\rangle &= \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \psi_1}{\partial x}\right)^* \psi_2 \mathrm{d}x \\ &= i\hbar[\psi_1^*\psi_2]_{-\infty}^{\infty} - i\hbar \int_{-\infty}^{\infty} \psi_1^* \frac{\partial \psi_2}{\partial x} \mathrm{d}x \\ &= \int_{-\infty}^{\infty} \psi_1^* \left(-i\hbar \frac{\partial \psi_2}{\partial x}\right) \mathrm{d}x \\ &= \langle \psi_1, \hat{P}\psi_2\rangle\end{aligned}$$

(iii) Kinetic energy

$$\hat{T} : \psi(x,t) \to \frac{\hat{P}^2}{2m}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2}\psi(x,t)$$

(iv) potential energy

$$\hat{U} : \psi(x,t) \to U(\hat{X})\psi(x,t) = U(x)\psi(X,t)$$

(v) total energy

$$\hat{H} : \psi(x,t) \to (\hat{T} + \hat{U})\psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\psi(x,t)$$

Exercise: prove that $\hat{H}$ (the Hamiltonian operator) is Hermitian.

Theorem 3. The eigenvalue of Hermitian operators are real.

Proof. Let $\hat{A}$ be a Hermitian operator with eigenvalue $a \in \mathbb{C}$

$$\langle \psi, \hat{A}\psi\rangle = \langle \psi, a\psi\rangle = a\langle \psi, \psi\rangle = a$$

But $\hat{A}$ Hermitian:

$$\langle \psi, \hat{A}\psi\rangle = \langle \hat{A}\psi, \psi\rangle = \langle a\psi, \psi\rangle = a^*\langle \psi, \psi\rangle = a^*$$

$\implies a = a^*$. □

Theorem 4. If $\hat{A}$ Hermitian operator, ψ_1, ψ_2 normalised eigenfunctions of $\hat{A}$ with eigenvalues a_1, a_2 with $a_1 \neq a_2$ then ψ_1 and ψ_2 are orthogonal.

Proof. We have
$$\hat{A}\psi_1 = a_1\psi_1 \quad \hat{A}\ \psi_2 = a_2\psi_2 \qquad a_1, a_2 \in \mathbb{R}$$
Then
$$\begin{aligned} a_1\langle\psi_1, \psi_2\rangle &= a_1^*\langle\psi_1, \psi_2\rangle \\ &= \langle a_1, \psi_1, \psi_2\rangle \\ &= \langle\hat{A}\psi_1, \psi_2\rangle \\ &= \langle\psi_1, \hat{A}\psi_2\rangle \\ &= \langle\psi_1, \hat{A}\psi_2\rangle \\ &= \langle\psi_1, a\psi_2\rangle \\ &= a_2\langle\psi_1, \psi_2\rangle \end{aligned}$$
so $\langle\psi_1, \psi_2\rangle = 0$ since $a_1 \neq a_2$. □

Theorem 5. The discrete (or continuous) set of eigenfunctions of any Hermitian operator together form a complete orthonormal basis of $\mathcal{H}$.
$$\psi(x, t) = \sum_{i=1}^{N} c_i\psi_i(x, t)$$
$c_i \in \mathbb{C}$, $\{\psi_i\}$ a set of eigenfunctions of $\hat{A} = \hat{A}^\dagger$.

Start of lecture 6

2.5.3 Expectation values and operators

So far: every quantum observable is represented by a Hermitian operator $\hat{O}$.

(I) The possible outcomes of measurement of the observable O are eigenvalues of $\hat{O}$.

(II) If $\hat{O}$has discrete set of normalised eigenfunctions $\{\psi_i\}$ with distinct eigenvalues $\{\lambda_i\}$, the measurement of O on a particle described by ψ has probability
$$P(O = \lambda_I) = |a_i|^2 = |\langle\psi_i, \psi\rangle|^2$$
where $\psi = \sum_{i=1}^{N} a_i\psi_i$.

(III) If $\{\psi_i\}$ is a set of orthonormal eigenfunctions of $\hat{O}$ and $\{\psi_i\}_{i\in I}$ complete set of orthonormal eigenfunctions with some eigenvalue λ

$$P(O=\lambda)=\sum_{i\in I}|a_i|^2$$

sanity check

$$\begin{aligned}\sum_{i=1}^{N}|a_i|^2 &= \sum_{i=1}^{N}\langle a_i\psi_i, a_i\psi_i\rangle \\ &= \sum_{i,j=1}^{N}\langle a_i\psi_i, a_j\psi_j\rangle \\ &= \langle\psi,\psi\rangle \\ &= 1\end{aligned}$$

(IV) The projection postulate: If O measured on ψ at time t and the outcome of measure is λ_i then the wave function of ψ instantaneously after measurement becomes ψ_i (eigenfunction with eigenvalues) [if $\hat{O}$ has degenerate eigenfunction with some eigenvalue λ then the wavefunction becomes $\psi=\sum_{i\in I}a_i\psi_i$]

Definition (Projection operator)**.** Given $\psi=\sum_i a_i\psi_i=\sum_i\langle\psi_i,\psi\rangle\psi_i$ define

$$\hat{P}_i:\psi\to\langle\psi_i,\psi\rangle\psi_i$$

We can now define expectation value of an observable measured on state ψ

$$\begin{aligned}\langle O\rangle_\psi &+ \sum_i\lambda_i P(O=\lambda_i) \\ &= \sum_i\lambda_i|a_i|^2 \\ &= \sum_i\lambda_i|\langle\psi_i,\psi\rangle|^2 \\ &= \left\langle\sum_i\langle\psi_i,\psi\rangle\psi_i, \sum_j\lambda_j\langle\psi_j,\psi\rangle\psi_j\right\rangle \\ &= \langle\psi,\hat{O}\psi\rangle \\ &= \int\psi^*(x,t)\hat{O}\psi(x,t)\mathrm{d}x\end{aligned}$$

Property:

$$\langle a\hat{A}+b\hat{B}\rangle_\psi=a\langle\hat{A}\rangle_\psi+b\langle\hat{B}\rangle_\psi$$

$a,b\in\mathbb{R}$.

Interpretation:

- The physics implication of projection postulate is that if O is measured twice, the outcome of second measure (of Δt between measures is small) is the same as first with probability 1.
- (Born's rule) If $\phi(\mathbf{x}, t)$ is the state that gives the desired outcome of a measurement on a state $\psi(\mathbf{x}, t)$, probability of such outcome is given by

$$|\langle\psi, \phi\rangle|^2 = \left|\int_{-\infty}^{\infty} \psi^*(x,t)\phi(x,t)\mathrm{d}x\right|^2$$

2.5 Time independent Schrödinger equation (TISE)

Let's rewrite TDSE in 1D

$$i\hbar\frac{\partial\psi}{\partial t}(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}(x,t) + U(x)\psi(x,t) = \hat{H}\psi(x,t) \tag{1}$$

try ansatz (try solution)

$$\psi(x,t) = T(t)\chi(X) \tag{2}$$

Plug (2) into (1)

$$i\hbar\frac{\partial T}{\partial t}(t)\chi(x) = T(t)\hat{H}\chi(X)$$

divide by $T(t)\chi(x)$

$$\frac{1}{T(t)}i\hbar\frac{\partial T}{\partial t}(t) = \frac{\hat{H}\chi(x)}{\chi(x)} \tag{3}$$

Both LHS and RHS have to be equal to a constant E, so

$$\frac{1}{T(t)}i\hbar\frac{\partial T}{\partial t}(t) = E \implies T(t) = e^{-iEt/\hbar} \tag{4}$$

with $E \in \mathbb{R}$. So TISE is

$$\boxed{\begin{aligned} \hat{H}\chi(x) &= E\chi(x) \\ -\frac{\hbar^2}{2m}\frac{\partial^2\chi}{\partial x^2}(x) + U(x)\chi(x) &= E\chi(x) \end{aligned}} \tag{5}$$

- TDSE is eigenvalue equation for $\hat{H}$ operator.
- eigenvalues of $\hat{H}$ are all possible outcomes of measure of energy of state ψ.

2.6 Stationary states

We found *a* particular solution of TDSE

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

E eigenvalue associated with eigenfunction χ.

Definition. These solutions are called stationary states.

Why?

$$\rho(x,t) = |\psi(x,t)|^2 = |\chi(x)|^2$$

If we apply theorem 2.6 to $\hat{O} = \hat{H}$

Theorem 6. Every solution of TDSE can be written as a linear combination of stationary states.

- For system that has a discrete set of eigenvalues of $\hat{H}$,

  $$E_n = E_1, E_2, \ldots$$

  $n \in \mathbb{N}$

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

- For system that has a continuous set of eigenvalues of $\hat{H}$, $E(\alpha)$

  $$\psi(x,t) = \int A(\alpha)\chi_\alpha(\alpha) e^{-iE_\alpha t/\hbar} \mathrm{d}\alpha$$

  where $A \in \mathbb{C}$, $\alpha \in \mathbb{R}$.

- $|a_n|^2$, $|A(\alpha)|^2 \mathrm{d}\alpha$ probability of measuring the particle energy to be $E_h = E(\alpha)$.

Imagine a system with only 2 energy eigenvalues $E_1 \neq E_2$ we can write the state ψ at time t

$$\psi(c,t) = a_1\chi_1(x)e^{-iE_1t/\hbar} + a_2\chi_2(x)e^{-iE_2t/\hbar}$$
$$\implies \psi(x,0) = a_1\chi_1(x) + a_2\chi_2(x)$$

if $a_1 = 0$ then $\psi(x,0) = a_2\chi_2(\alpha)$, $\psi(x,t) = a_2\chi_2(x)e^{-iE_2t/\hbar}$ for all t, $|\psi(x,0)|^2 = |\psi(x,t)|^2$. If $a_i \neq 0$ and $a_2 \neq 0$,

$$\begin{aligned}|\psi(x,t)|^2 &= |a_1\chi_1 e^{-iE_1t/\hbar} + a_2\chi_2 e^{-iE_2t/\hbar}|^2 \\ &= a_1^2|\chi_1|^2 + a_2^2|\chi_2|^2 + 2a_1a_2\chi_1(x)\chi_2(x)\cos\left(\frac{(E_1-E_2)t}{\hbar}\right)\end{aligned}$$

Start of lecture 7

3 1 dimensional solutions of Schrödinger equation

TISE (Time independent Schrödinger equation):

$$\hat{H}\chi(X) = E\chi(x)$$

$$-\frac{\hbar^2}{2m}\chi''(x) + U(x)\chi(x) = E\chi(x)$$

with $E \in \mathbb{R}$. We will solve TISE in 3 cases:

3.1 Bound states

3.2 Free particle

3.3 scattering states.

3.1 Bound states

3.1.1 Infinite potential well

$$U(x) = \begin{cases} 0 & |x| \leq a \\ +\infty & |x| > 0 \end{cases}$$

$a \in \mathbb{R}^+$.

- for $|x| > 0$, $\chi(x) = 0$ otherwise $U \cdot \chi = \infty$ so boundary condition $\chi(\pm a) = 0$.
- for $|x| \leq a$ we look for solutions of

$$-\frac{\hbar^2}{2m}\chi''(x) = E\chi(x)$$

$$\implies \chi''(x) + k^2\chi(x) = 0$$

with $k = \sqrt{\frac{2mE}{\hbar^2}}$ and we also have $\chi(\pm a) = 0$. Solution:

$$\chi(x) = A\sin(kx) + B\cos(kx)$$

$\chi(a) = 0$, $\chi(-a) = 0$ implies

$$A\sin(ka) = 0, \quad B\cos(ka) = 0$$

so two options:

(i) $A = 0$, $\cos(ka) = 0$ then $k_n = \frac{n\pi}{2a}$, n an odd integer.

$$\chi_n(x) = B\cos(k_n x)$$

the *even solutions*.

(ii) $B = 0$, $\sin(ka) = 0$ then $k_n = \frac{n\pi}{2a}$, n even integer.

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

the *odd solutions*.

Determine A, B by requiring normalisation of eigenfunction

$$\int_{-a}^{a} |\chi_n(x)|^2 \mathrm{d}x = 0 \implies A = B = \sqrt{\frac{1}{Q}}$$

Solution: eigenvalues of $\hat{H}$ are

$$E_n = \frac{\hbar^2}{2m}k_n^2 = \hbar^2 \frac{\pi^2}{8ma^2} n^2$$

eigenfunction of $\hat{H}$

$$\chi_n(x) = \sqrt{\frac{1}{Q}} \begin{cases} \cos\left(\frac{n\pi x}{2a}\right) & n = 1, 3, \dots \\ \sin\left(\frac{n\pi x}{2a}\right) & n = 2, 4, \dots \end{cases}$$

.image

(i) Ground state has $E \neq 0$. Note (contrarily to classical mechanics)

(ii) $n \to \infty$, $|\chi_n(x)|^2 \to$ const (Classical mechanics limits)

In classical mechanics

$$P(x) \propto \frac{1}{\mathcal{N}(x)} \quad P(x) = \frac{A}{\mathcal{N}(x)}$$

In this case particle free inside the wall

$$\implies \mathcal{N}\text{constant} \implies P\text{constant}$$

Proposition. If quantum system has non-degenerate eigenstates ($E_i \neq E_j$ for $i \neq j$) then, if $U(x) = U(-x)$ the eigenfunction of $\hat{H}$ have to be either odd or even.

Proof. If $U(x) = U(-x)$ then TISE invariant under $x \to -x$. If $\chi(x)$ is a solution with eigenvalue E, then also $\chi(-x)$ solution and $\chi(-x) = \alpha\chi(x)$ solutions must be the same up to a normalisation factor α. Then

$$\chi(x) = \chi(-(-x)) = \alpha\chi(-x) = \alpha^2\chi(x)$$

$$\implies \alpha^2 = 1 \implies \alpha = \pm 1$$

$$\implies \chi(x) = \pm\chi(-x)$$

□

3.1.2 Finite potential well

$$U(x) = \begin{cases} 0 & |x| \leq a \\ U_0 & |x| > a \end{cases}$$

Consider $E > 0$ ($E < 0$ does not exist in this case) and $E < U_0$ (bound state) We look for odd / even eigenfunction

(i) even parity bound states

$$\chi(-x) = \chi(x)$$

solve

$$-\frac{\hbar^2}{2m}\chi''(x) = E\chi(x) \qquad |x| \leq a \tag{I}$$

$$-\frac{\hbar^2}{2m}\chi''(x) = (E - U_0)\chi(x) \qquad |x| > a \tag{II}$$

(I) $\chi''(x) + k^2\chi(x) = 0$ with $k = \sqrt{\frac{2mE}{\hbar^2}}$

$$\chi(x) = A\sin(kx) + B\cos(kx)$$

but $A = 0$ (even parity)

$$\chi(x) = B\cos(kx)$$

(II) $\chi''(x) - \bar{k}^2\chi(x) = 0$ with $k = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}$

$$\chi(x) = ce^{+\bar{k}x} + De^{-\bar{k}x}$$

but impose normalisability implies $x > a$, $c = 0$, $x < -a$, $D = 0$. Impose even parity $C = D$.

To summarise:

$$\chi(x) = \begin{cases} Ce^{\bar{k}x} & x < -a \\ B\cos(kx) & |x| \leq a \\ Ce^{-\bar{k}x} & x > a \end{cases}$$

Impose continuity of $\chi(x)$ at $x = \pm a$, $\chi'(x)$ at $x = \pm a$. Then

$$\chi(a) \to Ce^{-\bar{k}a} = B\cos(ka)$$

$$\chi'(a) \to -\bar{k}Ce^{-\bar{k}a} = -kB\sin(ka)$$

if take ratio from definition

$$k\tan(ka) = \bar{k}$$

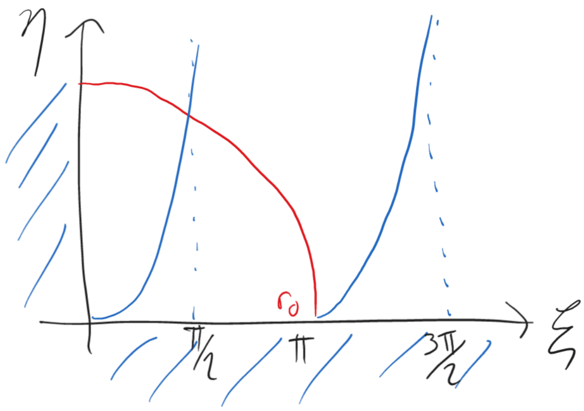
$$k^2 + \bar{k}^2 = \frac{2mU_0}{\hbar^2}$$

Define rescaled variables $\xi = ka$, $\eta = \bar{k}a$.

$$\xi \tan \xi = \eta$$

$$\xi^2 + \eta^2 = r_0^2$$

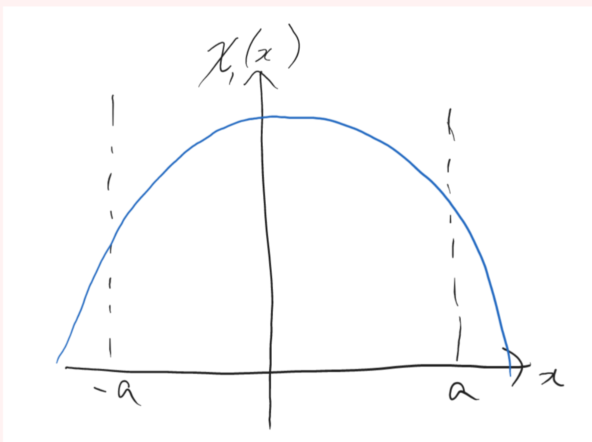
$$r_{)}^2 = \frac{2mU_0}{\hbar^2}a^2$$



eigenvalues of $\hat{H}$ corespond to points of intersection

$$E_n = \frac{\hbar^2}{2ma^2}\xi_n^2 \quad n = 1, \ldots, p$$

Note. $U_0 \to \infty \implies r_0 \to \infty \implies E_n = \frac{\hbar^2}{8ma^2}(2n-1)^2\pi^2$, $\chi \to \chi_n$ of infinite well.



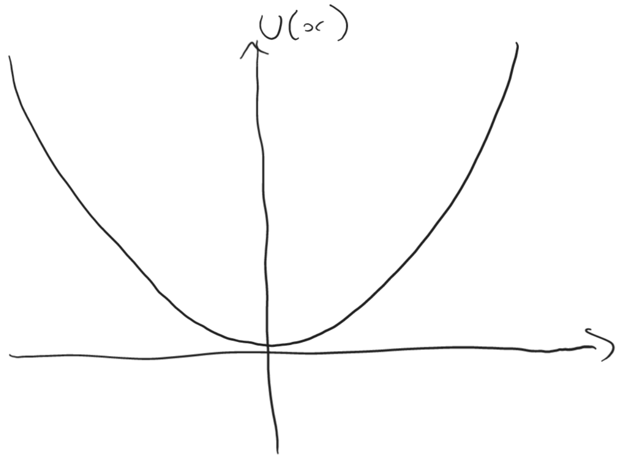
Exercise:

(1) Use the unused condition in system to write C in terms of B

(2) Impose normalisation to 1 to find B.

Start of lecture 8

3.1.3 Harmonic Oscillator



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

$k \in \mathbb{R}$ elastic constant. $\omega = \sqrt{\frac{k}{m}}$. Classical mechanics: Newton 2 is $\ddot{x}(t) = -\omega^2 x(t)$.

$$\implies x(t) = A\sin\omega t + B\cos\omega t$$

with $T = \frac{2\pi}{\omega}$ period oscillations.
Quantum mechanics:

$$-\frac{\hbar^2}{2m}\chi''(x) + \frac{1}{2}m\omega^2 x^2 \chi(x) = E\chi(x) \tag{1}$$

We know:

- Discrete eigenvalues
- even / odd eigenfunctions

Change of variables:

$$\xi^2 \equiv \frac{m\omega}{\hbar}x^2$$

$$\varepsilon \equiv \frac{2E}{\hbar\omega}$$

Plug into (1)

$$-\frac{\mathrm{d}^2\chi}{\mathrm{d}\xi^2}(\xi) + \xi^2\chi(\xi) = \varepsilon\chi(\xi) \tag{2}$$

Solve it by starting from a particular solution

$$\varepsilon = 1 \quad \left(E_0 = \frac{\hbar\omega}{2}\right)$$

ansatz:

$$\chi_0(\xi) = e^{-\xi^2/2} \tag{3}$$

Plug (3) into (2) with $\varepsilon = 1$ works. We found one eigenvalues $E_0 = \frac{\hbar\omega}{2}$, $\chi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}$
To find other eigenfunction of $\hat{H}$ take general form

$$\xi(\xi) = f(\xi)e^{-\xi^2/x} \tag{4}$$

Plug (4) into (2)

$$-\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} + 2\xi\frac{\mathrm{d}f}{\mathrm{d}\xi} + (1-\varepsilon)f = 0 \tag{5}$$

Use power series method ($\xi = 0$ regular point)

$$f(\xi) = \sum_{n=0}^{\infty} a_n \xi^n \tag{6}$$

$a_n \in \mathbb{R}$. Clearly

$$\xi\frac{\mathrm{d}f}{\mathrm{d}\xi} = \sum_{n=0}^{\infty} n a_n \xi^n \tag{7}$$

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} = \sum_{n=0}^{\infty} n(n-1)a_n\xi^{n-2} = \sum_{n=0}^{\infty}(n+1)(n+2)a_{n+2}\xi^n$$

Plug (6)-(8) into (5):

$$\sum_{n=0}^{\infty}[(n+1)(n+2)a_{n+2} - 2na_n + (\varepsilon-1)a_n]\xi^n = 0$$

$$\implies a_{n+2} = \frac{(2n-\varepsilon+1)}{(n+1)(n+2)}a_n$$

Because of parity of eigenfunction:

- Either $a_n = 0$ for odd n $(f(\xi) = f(-\xi))$ even eigenfunction
- or $a_n = 0$ for even n, $(f(\xi) = -f(-\xi))$ odd eigenfunction.

Proposition. If series (6) does *not* terminate then eigenfunction of $\hat{H}$ would *not* be normalisable.

Proof. Suppose that the series in (6) does *not* terminate. Hence can look at asymptotic behaviour of series. Take (0)

$$\frac{a_{n+2}}{a_n} \to \frac{2}{n}$$

as $n \to \infty$. This is same asymptotic behaviour as

$$g(\xi) = e^{\xi^2} = \sum_{m=0}^{\infty} \frac{\xi^{2m}}{m!} = \sum_{m=0}^{\infty} b_m \xi^m$$

where

$$b_m = \begin{cases} \frac{1}{m!} & \text{for } m \text{ even} \\ 0 & \text{for } m \text{ odd} \end{cases}$$

asymptotic behaviour of $g(\xi)$

$$\frac{b_{n+2}}{b_n} = \frac{\left(\frac{m}{2}\right)!}{\left(\frac{m}{2}+1\right)!} = \frac{2}{m+2} \to \frac{2}{m}$$

as $m \to \infty$. So if $e^{\xi^2/2}$ and $f(\xi)$ have same asymptotic behaviour

$$\chi(\xi) \sim e^{\xi^2} e^{-\xi^2/2} = e^{\xi^2/2} \to \infty$$

□

Given that the series (6) terminates then there exists Nsuch that

$$a_{N+2} = 0 \tag{10}$$

with $a_N \neq 0$. Plug (10) into (9)

$$a_{N+2} = \frac{(2N - \varepsilon + 1)}{(N+1)(N+2)} a_N = 0$$

$$\implies 2N - \varepsilon + 1 = 0$$

Plugging in definition of ε

$$\implies E_N = \left(N + \frac{1}{2}\right) \hbar\omega$$

eigenvalues $N = 0$, $E_0 = \frac{\hbar\omega}{2}$

$$E_{N+1} - E_n = \hbar\omega$$

eigenfunction $\chi_N(\xi) = f_N(\xi) e^{-\xi^2/2}$

$$\chi_N(-\xi) = (-1)^N \chi_N(\xi)$$

Hermite polynomials are defined with recursive relation

$$f_N(\xi) = (-1)^N e^{\xi^2} \frac{\mathrm{d}^N}{\mathrm{d}\xi^N} (e^{-\xi^2})$$

N	E_N	$f_N(\xi)$
0	$\frac{\hbar\omega}{2}$	1
1	$\frac{3\hbar\omega}{2}$	ξ
2	$\frac{5\hbar\omega}{2}$	$(1-2\xi^2)$
3	$\frac{7\hbar\omega}{2}$	$(\xi-\frac{2}{3}\xi^3)$

Start of lecture 9

3.2 The free particle

TISE ($U(x)=0$):

$$-\frac{\hbar^2}{2m}\chi''(X) = E\chi(x)$$

$$\chi''(x) + \frac{2mE}{\hbar^2}\chi(x) = 0$$

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

$$\chi(x) = e^{ikx}$$

$$E_k = \frac{\hbar^2k^2}{2m} \to \chi_k(x) = e^{ikx}$$

$$\psi_k(x,t) = \chi_k(x)e^{-iE_kt/\hbar} = e^{i(kx-\hbar k^2/2m)}$$

This wave function is *not* square-integrable:

$$\int_{-\infty}^{\infty} |\psi_k(x,t)|^2 \mathrm{d}x = \int_{-\infty}^{\infty} = \infty$$

This is a consequence of

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \mathrm{d}x = \mathcal{N} < \infty \implies \lim_{R\to\infty}\int_{|x|>R} \mathrm{d}x|\psi(x,t)|^2 = 0$$

How do we deal with unbound states?

Option 1 Build a linear superposition of not-normalisable states that is normalisable (section 3.2.1)

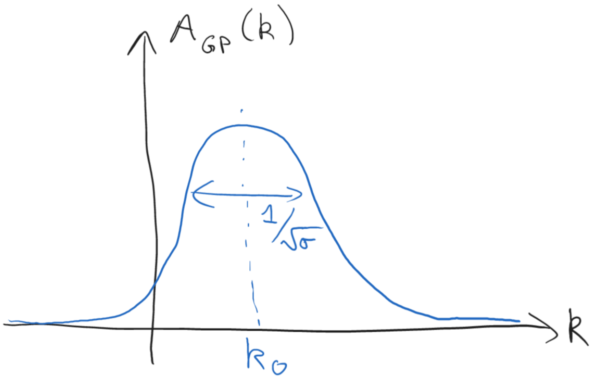
Option 2 We ignore the problem but change interpretation (section 3.2.2)

3.2.1 Gaussian Wave Packet

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k)\psi_k(x,t)\mathrm{d}k$$

($A(k)$ is a continuous coefficient of linear combination) A possible option is Gaussian wave packet:

$$A(k) = A_{\mathrm{GP}}(k) = \exp\left[-\frac{\sigma}{2}(k-k_0)^2\right] \quad \sigma \in \mathbb{R}^+, k_0 \in \mathbb{R}$$



$$\psi_{\text{GP}}(x,t) = \int_{-\infty}^{\infty} A_{\text{GP}}(k)\psi_k(x,t)\text{d}k$$

$$\psi_{\text{GP}}(x,t) = \int_{-\infty}^{\infty} \exp[F(k)]\text{d}k$$

where

$$\begin{aligned} F(k) &= -\frac{\sigma}{2}(k-k_0)^2 + ikx - \frac{i\hbar k^2}{2m}t \\ &= -\frac{1}{2}\left(\sigma + \frac{i\hbar t}{m}\right)k^2 + (k_0\sigma + ix)k \end{aligned}$$

$$\begin{aligned} \alpha &\equiv \sigma + \frac{i\hbar t}{m} \\ \beta &\equiv k_0\sigma + ix \\ \delta &= -\frac{\sigma}{2}k_0^2 \end{aligned}$$

Complete the square:

$$F(k) = -\frac{\alpha}{2}\left(k - \frac{\beta}{\alpha}\right)^2 + \frac{\beta^2}{2\alpha} + \delta$$

$$\implies Y_{\text{GP}}(x,t) = \exp\left[\frac{\beta^2}{2\alpha} + \delta\right]\int_{-\infty}^{\infty} \exp\left[-\frac{\alpha}{2}\left(k - \frac{\beta}{\alpha}\right)^2\right]\text{d}k$$

Shift contour $\tilde{k} = k - \frac{\beta}{\alpha}$. Let $\nu = \text{Im}\left(\frac{\beta}{\alpha}\right)$.

$$\psi_{\text{GP}}(x,t) = \exp\left[\frac{\beta^2}{2\alpha} + \delta\right]\int_{-\infty-i\nu}^{\infty-i\nu} \exp\left(-\frac{\alpha}{2}\tilde{k}^2\right)\text{d}\tilde{k}$$

Using standard Gaussian integral

$$I(\alpha) = \int_{-\infty}^{\infty} \exp(-ay^2)\text{d}y = \sqrt{\frac{\pi}{a}}$$

We get

$$\psi_{\mathrm{GP}}(x,t) = \sqrt{\frac{2\pi}{\alpha}} \exp\left[\frac{\beta^2}{2\alpha} + \delta\right]$$

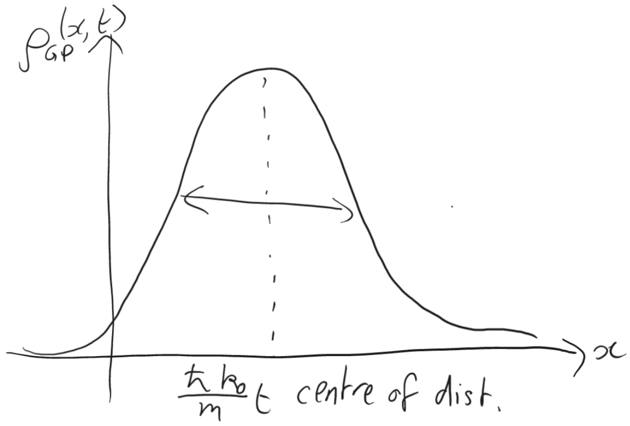
Exercise: Write $\psi_{\mathrm{GP}}(x,t)$ by substituting β, α, δ and normalise it to 1.

$$\beta = k_0\sigma + ix \quad \beta^2 = k_0^2\sigma^2 - k^2 + 2ixk_0\sigma$$

The $-x^2$ in β^2 implies that ψ_{GP} is normalisable. Once ψ_{GP} is normalised, $\overline{\psi}_{\mathrm{GP}}$ cen define

$$\rho_{\mathrm{GP}}(x,t) = |\overline{\psi}_{\mathrm{GP}}(x,t)|^2 = \sqrt{\frac{\sigma}{\pi\left(\sigma^2 + \frac{\hbar^2 t^2}{m^2}\right)}} \exp\left[\frac{-\pi\left(x - \frac{\hbar k_0 t}{m}\right)^2}{(\sigma^2 + \frac{\hbar^2 t^2}{m^2})}\right]$$

at t fixed:



width of distance

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

The centre of the distribution is $\langle x\rangle_{\psi_{\mathrm{GP}}}$:

$$\begin{aligned}
\langle x\rangle_{\psi_{\mathrm{GP}}} &= \int_{-\infty}^{\infty} \overline{\psi}^*_{\mathrm{GP}}(x,t) x \overline{\psi}_{\mathrm{GP}}(x,t)\mathrm{d}x \\
&= \int_{-\infty}^{\infty} x\rho_{\mathrm{GP}}(x,t) \\
&= \frac{\hbar k_0}{m} t
\end{aligned}$$

Error on position of particle:

$$\Delta x = \sqrt{\langle x^2\rangle_{\psi_{\mathrm{GP}}} - \langle x\rangle^2_{\psi_{\mathrm{GP}}}} = \sqrt{\frac{1}{2}\left(\sigma + \frac{\hbar^2 t^2}{m^2\sigma}\right)}$$

$\Delta x = \sqrt{\frac{\pi}{2}}$ at $t = 0$. Δx increases as t increases. Given ψ_{GP} it is interesting to compute $\langle p \rangle$, Δp

$$\begin{aligned}\langle p \rangle_{\psi_{\mathrm{GP}}} &= \int_{-\infty}^{\infty} \overline{\psi}^*_{\mathrm{GP}}(x,t) \left(-i\hbar \frac{}{x} \overline{\psi}_{\mathrm{GP}}(x,t) \right) \mathrm{d}x \\ &= \hbar k_0\end{aligned}$$

$$\Delta p = \sqrt{\langle p^2 \rangle_{\psi_{\mathrm{GP}}} - \langle p \rangle^2_{\psi_{\mathrm{GP}}}}$$

To calculate Δp on ψ_{GP} we have

$$\langle p \rangle^2_{\psi_{\mathrm{GP}}} = \hbar^2 k_0^2$$

we need

$$\langle p^2 \rangle_{\psi_{\mathrm{GP}}} = \int_{-\infty}^{\infty} \overline{\psi}^*_{\mathrm{GP}}(x,t) \left(-\hbar^2 \frac{\mathrm{d}^2}{\mathrm{d}x^2} \overline{\psi}_{\mathrm{GP}}(x,t) \right) \mathrm{d}x$$

If you compute it and plug it into Δp THE FOLLOWING SECTION IS ALL WRONG, IGNORE UNTIL TOLD TO STOP IGNORING.

$$\Delta p = \frac{\hbar}{\sqrt{2\left(\sigma + \frac{\hbar^2 t^2}{m\sigma}\right)}}$$

at $t = 0$, $\Delta p = \hbar\sqrt{\frac{2}{\sigma}}$, as $t \to \infty$, Δp decreases as $\frac{1}{\sqrt{a+t^2}}$ What we learnt is

$$\Delta x \to \infty, \Delta p \to \infty \quad \text{as } t \to \infty$$

$$\Delta x \Delta p = \frac{\hbar}{2}$$

STOP IGNORING.
At time $t = 0$, $\Delta x \Delta p = \frac{\hbar}{2}$.

The GP is a state of minimum uncertainty. Other $A(k)$ would give you a normalisable state but if you compute $\Delta x \Delta p$ you would find something $> \frac{\hbar}{2}$.
Exercise: Compare what you find for $\psi_k(x,t)$

$$\Delta x = \infty, \Delta p = 0$$

$$\langle x \rangle_{\psi_k} = 0, \langle x^2 \rangle_{\psi_k} = \infty$$

Start of lecture 10

3.3.2 Beam interpretation

The idea: ignore normalisation problem and take $\chi_k = e^{ikx}$ as eigenfunction of $\hat{H}$. Take

$$\chi_k(x) = Ae^{ikx} \quad A \in \mathbb{C}$$

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

but instead of $\chi_n(x)$ describing a single particle they describe a beam of particles with

$$p_k = \hbar k$$

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

with probability density

$$\rho_k(x,t) = |A|^2$$

representing constant average density of particles. Compute probability current

$$j_k(x,t) = -\frac{i\hbar}{2m}\left(\psi_k^* \frac{\partial \psi}{\partial x} - \psi_k \frac{\partial \psi_k^*}{\partial x}\right)$$

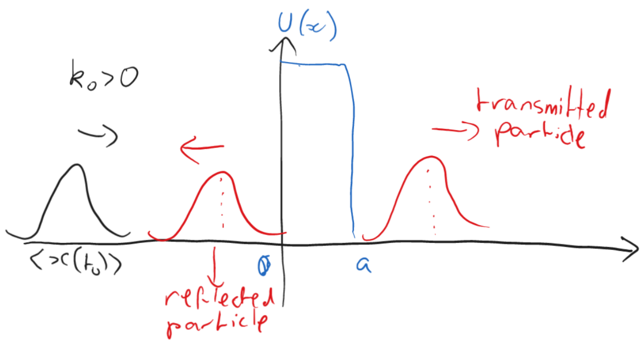
$$\left[\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0\right]$$

(lecture 3) In this case taking $(*)$

$$j_k(x,t) = |A|^2 \frac{\hbar k}{m} = |A|^2 \frac{p}{m} = \text{average flux of particles}$$

3.3 Scattering states

What happens if we have an unbound potential $U(x)$ and throw a particle on it



Definition. Probability for particle to be reflected is given by the reflection coefficient

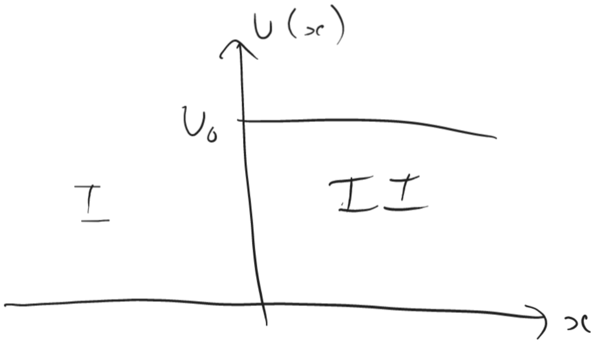
$$R = \lim_{t\to\infty} \int -\infty^0 |\psi_{\mathrm{GP}}(x,t)|^2 \mathrm{d}x$$

> **Definition.** Probability for particle to be transmitted is given by the transmission coefficient
> $$T = \lim_{t\to\infty} \int_0^\infty |\psi_{\mathrm{GP}}(x,t)|^2 \mathrm{d}x$$

Clearly $T + R = 1$. Solving scattering problems using beam interpretation gives some results for R and T, so we will use it.

3.4.1 Scattering off potential step

$$U(x) = \begin{cases} 0 & x \leq 0 \\ U_0 & x > 0 \end{cases} \quad U_0 \in \mathbb{R}^+$$



To find $\chi_k(x)$, solve TISE

$$-\frac{\hbar^2}{2m}\chi_n''(x) + U(x)\chi_n(x) = E\chi_n(x)$$

Region I, $x \leq 0$, $U(x) = 0$.

$$\chi_n''(x) + k^2\chi_n(x) = 0 \quad k = \sqrt{\frac{2mE}{\hbar^2}} > 0$$

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

(A part is the beam of incident particles, B part is the beam of reflected particles).
Region II, $x > 0$, $U(x) = U_0$.

$$\chi_{\overline{k}}''(x) + \overline{k}^2\chi_{\overline{k}}(x) = 0$$

$$\overline{k} = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}$$

$\overline{k}$ real for $E \geq U_0$, and imaginary for $E < U_0$.

- For $E \geq U_0$,
$$\alpha_{\overline{k}}(x) = Ce^{i\overline{k}x} + De^{-i\overline{k}x}$$
(the C term is the transmitted beam, and the D term is the incident beam from ∞). $D = 0$ due to initial condition.

- For $E > U_0$,
$$\chi_{\overline{k}}(x) = Ce^{-\eta x} + De^{\eta x}$$
where $\eta = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}$. $D = 0$ otherwise $\chi_{\overline{k}}$ diverges at ∞.

Putting I and II:
$$\chi_{n,\overline{k}}(x) = \begin{cases} Ae^{inx} + Be^{-inx} & x \leq 0 \\ Ce^{i\overline{k}x} & x > 0 \end{cases}$$
Impose continuity of $\chi(x), \chi'(x)$ at $x = 0$ and get
$$A + B = C$$
$$ikA - ikB = i\overline{k}C$$
$$\implies B = \frac{k-\overline{k}}{k+\overline{k}}A$$
$$C = \frac{2k}{k+\overline{k}}A$$
We can view these in terms of particle flux
$$J(x,t = -\frac{i\hbar}{2m}\left(\chi^*\frac{\partial\chi}{\partial x} - \chi\frac{\partial\chi^*}{\partial x}\right)$$
Compute for

- $E > U_0$
$$J(x,t) = \begin{cases} \frac{\hbar k}{m}(|A|^2 - |B|^2) & x < 0 \\ \frac{\hbar\overline{k}}{m}|C|^2 & x \geq 0 \end{cases}$$
$$J_{inc}(x,t) = \frac{\hbar x}{m}|A|^2$$
$$J_{ref}(x,t)\frac{\hbar k}{m}|B|^2$$
$$J_{trans}(x,t) = \frac{\hbar\overline{k}}{m}|C|^2$$
$$R = \frac{J_{refl}}{J_{inc}} = \frac{|B|^2}{|A|^2} = \left(\frac{k-\overline{k}}{k+\overline{k}}\right)^2$$
$$T = \frac{J_{trans}}{J_{inc}} = \frac{|C|^2}{|A|^2}\frac{\overline{k}}{k} = \frac{4k\overline{k}}{(k+\overline{k})^2}$$
Interpretation:

  - $R + T = 1$
  - $E \to U_0$, $\overline{k} \to 0$, $T \to 0$, $R \to 1$.
  - $E \to \infty$, $T \to 1$, $R \to 0$.

- $E < U_0$.

$$J_{inc}(x,t) = \frac{\hbar k}{m}|A|^2$$

$$J_{ref}(x,t) = \frac{\hbar k}{m}|B|^2$$

$$J_{trans}(x,t) = 0$$

  $R = 1$, $T = 0$ but $\chi_{\overline{k}}(x) \neq 0$ from $x > 0$.

Scattering off potential barrier

$$U(x) = \begin{cases} 0 & x \leq 0, x \geq a \\ U_0 & 0 < x < a \end{cases}$$

Consider $E < U_0$.

$$k = \sqrt{\frac{2mE}{\hbar^2}} > 0$$

$$\eta = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} > 0$$

Solution of TISE

$$\chi(x) = \begin{cases} e^{ikx} + Ae^{iikx} & x \leq 0 \\ Be^{-\eta x} + Ce^{\eta x} & 0 < x < a \\ De^{ikx} + \underbrace{Ee^{-ikx}}_{=0} & x \geq a \end{cases}$$

4 free coefficients with 4 boundary conditions given by continuity of $\chi(X)$ and $\chi'(x)$ at $x = 0$ and $x = a$.

$$1 + A = B + C$$

$$ik - ikA = -\eta B + \eta C$$

$$Be^{-\eta a} + Ce^{\eta a} = De^{ika}$$

$$-\eta Be^{-\eta a} + \eta Ce^{\eta a} = ikDe^{ika}$$

Find

$$D = -\frac{4\eta k}{(\eta - ik)^2 \exp[(\eta + ik)a] - (\eta + ik)^2 \exp[-(\eta - ik)a]}$$

$$\implies T = |D|^2 = 4k^2\eta^2$$

Take limit $U_0 \gg E \implies \eta a \gg 1$

$$T \to \frac{16k^2\eta^2}{(\eta^2+k^2)^2} \underbrace{e^{-2ma}}_{e^{-\frac{2a}{\hbar}\sqrt{2m(U_0-E)}}}$$

Start of lecture 11

Recap of chapter 2

Hermitian operators $\leftrightarrow$ observables

$$\hat{O}^+ = \hat{O} \iff (\hat{O}\psi, \phi) = (\psi, \hat{O}, \phi) \; \forall \psi, \phi \in \mathcal{H}$$

Have:

- Real eigenvalues (Theorem 2.1)
- If $\hat{O}\psi_1 = a\psi_1$, $\hat{O}\psi_2 = b\psi_2$ with $a \neq b$ then $(\psi_1, \psi_2) = 0$ (Theorem 2.5)
- Eigenstates of Hermitian operator form a complete basis of $\mathcal{H}$. (Theorem 2.6)

Quantum measurement:

- Eigenvalues of $\hat{O}$ are possible outcomes of measurement of the observable O.
- If $\psi = \sum_i a_i\psi_i$, ψ_i eigenstates of $\hat{O}$ then $P(O = \lambda_i) = a_i^2 = |(\psi_i, \psi)|^2$
- Immediately after a measurement with outcome λ_i, the wave function becomes ψ_i.

4 Simultaneous measurements in Quantum Mechanics

4.1 Commutators

Definition. Commutator of two operators $\hat{A}, \hat{B}$ is the operator

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Properties:

- $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$
- $[\hat{A}, \hat{A}] = 0$
- $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$
- $[\hat{A}, \hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$.

Exercise: Compute $[\hat{x}, \hat{p}]$ in 1 dimension.
Take $\psi \in \mathcal{H}$

$$\hat{x}\hat{p}\psi = x\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x) = -i\hbar x\frac{\partial\psi}{\partial x}(x)$$

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

$$\implies [\hat{x}, \hat{p}]\psi = i\hbar\psi \implies [\hat{x}, \hat{p}] = i\hbar\hat{I}$$

Canonical commutator relation.

Definition. Two Hermitian operators $\hat{A}$ and $\hat{B}$ are *simultaneously* diagonalisable in $\mathcal{H}$ is it exists a complete basis of joint eigenfunctions $\{\psi_i\}$ such that

$$\hat{A}\psi_i = a_i\psi_i$$

$$\hat{B}\psi_i = b_i\psi_i$$

with $a_i, b_i \in \mathbb{R}$.

Theorem 7. Two Hermitian operators $\hat{A}$ and $\hat{B}$ are simultaneously diagonalisable

$$\iff [\hat{A}, \hat{B}] = 0$$

Proof. $\Rightarrow$ If $\hat{A}, \hat{B}$ simultaneously diagonalisable then $\{\psi_i\}$ set of joint eigenfunctions that is a complete basis of $\mathcal{H}$.

$$\forall\psi_i \quad [\hat{A}, \hat{B}]\psi_i = \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i = (a_ib_i - b_ia_i)\psi_i = 0$$

Take $\psi \in \mathcal{H}$.

$$[\hat{A}, \hat{B} = \sum_i c_i[\hat{A}, \hat{B}]\psi_i = 0$$

$$\implies [\hat{A}, \hat{B}] = 0$$

$\Leftarrow$ If $[\hat{A}, \hat{B}] = 0$ and ψ_i eigenfunction of $\hat{A}$ with eigenvalues a_i.

$$0 = [\hat{A}, \hat{B}]\psi_i = \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i = \hat{A}\hat{B}\psi_i - a_i\hat{B}\psi_i$$

so

$$\hat{A}(\hat{B}\psi_i) = a_i(\hat{B}\psi_i)$$

$\hat{B}$ maps the eigenspace E_i of $\hat{A}$ with eigenvalue a_i into itself so $\hat{B}\mid_{E_i}$ is an Hermitian operator of E_i. Since this holds for all eigenspace E_i of $\hat{A}$, we can find a complete basis of simultaneous eigenfunctions of $\hat{A}$ and $\hat{B}$.

□

4.2 Heisenberg's Uncertainty Principle

Definition. The uncertainty in a measurement of an observable A on a state ψ is defined as

$$\Delta_\psi A = \sqrt{(\Delta_\psi A)^2}$$

where

$$\begin{aligned}(\Delta_\psi A)^2 &= \langle(\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})^2\rangle_\psi \\ &= \langle\hat{A}^2\rangle_\psi - (\langle\hat{A}\rangle_\psi)^2\end{aligned}$$

The two definitions are equivalent:

$$\begin{aligned}\langle(\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})^2\rangle_\psi &= \int_{\mathbb{R}^3} \psi^*(\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})^2\psi \mathrm{d}^3x \\ &= \int_{\mathbb{R}^3} \psi^*\hat{A}^2\psi \mathrm{d}^3x + (\langle\hat{A}\rangle_\psi)^2 \int_{\mathbb{R}^3} \psi^*\psi \mathrm{d}^3x - 2\langle\hat{A}\rangle_\psi \int_{\mathbb{R}^3} \psi^*\hat{A}\psi \mathrm{d}^3x \\ &= \langle\hat{A}^2\rangle_\psi + (\langle\hat{A}\rangle_\psi)^2 - 2(\langle\hat{A}\rangle_\psi)^2 \\ &+ \langle\hat{A}\rangle_\psi^2 - (\langle\hat{A}\rangle_\psi)^2\end{aligned}$$

Lemma 2. $(\Delta_\psi A)^2 \geq 0$ and $(\Delta_\psi A) = 0 \iff \psi$ is eigenfunction of $\hat{A}$.

Proof.

$$\begin{aligned}(\Delta_\psi A)^2 &= \langle(\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})^2\rangle_\psi \\ &= (\psi, (\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})^2 \psi) \\ &= ((\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})\psi, (\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})\psi) \\ &= \langle\phi, \phi) \\ &\geq 0\end{aligned}$$

(Call $\phi = (\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})\psi$) Now prove that $(\Delta_\psi A)^2 = 0 \iff \phi = 0$.

$\Rightarrow$ $(\Delta_\psi A)^2 = (\phi, \phi) = 0$ if $\phi = 0$ implies

$$\hat{A}\psi = \langle\hat{A}\rangle_\psi \psi$$

i.e. ψ eigenfunction of $\hat{A}$.

1. If ψ is eigenfunction of $\hat{A}$ with eigenvalue $a \in \mathbb{R}$ then

$$\langle\hat{A}\rangle_\psi = (\psi, \hat{A}\psi) = a(\psi, \psi) = a$$

$$\langle\hat{A}\rangle_\psi = (\psi, \hat{A}^2\psi) = a^2(\psi, \psi) = a^2$$

using second definition,

$$(\Delta_\psi A)^2 = \langle\hat{A}^2\rangle_\psi - (\langle\hat{A}\rangle_\psi)^2 = a^2 - a^2 = 0$$

□

Lemma 3. If $\psi, \phi \in \mathcal{H}$, then

$$|(\phi, \psi)|^2 \leq (\phi, \phi)(\psi, \psi)$$

and $|(\phi, \psi)|^2 = (\phi, \phi)(\psi, \psi)$ if and only if $\phi = a\psi$ for $a \in \mathbb{C}$.

(proof comes from Schwarz inequality and is available in Maria Ubiali's notes).

Theorem 8 (Generalised uncertainty theorem)**.** If A and B observables and $\psi \in \mathcal{H}$ then

$$(\Delta_\psi A)(\Delta_\psi B) \geq \frac{1}{2}|(\psi, [\hat{A}, \hat{B}]\psi)|$$

Proof.

$$(\Delta_\psi A)^2 = ((\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})\psi, (\hat{A} - \langle\hat{A}\rangle_\psi \hat{I})\psi)$$

Define

$$\hat{A}' = \hat{A} - \langle\hat{A}\rangle_\psi \hat{I}$$

$$\hat{B}' = \hat{B} - \langle \hat{B} \rangle_\psi \hat{I}$$

Hence

$$(\Delta_\psi A)^2 = (\hat{A}'\psi, \hat{A}'\psi)$$

$$(\Delta_\psi B)^2 = (\hat{B}'\psi, \hat{B}'\psi)$$

Using lemma 4.3:

$$(\Delta_\psi A)^2 (\Delta_\psi B)^2 \geq |(\hat{A}'\psi, \hat{B}'\psi)|^2 \tag{1}$$

and RHS is equal to $|(\psi, \hat{A}'\hat{B}'\psi)|^2$ because $\hat{A}'$ is Hermitian. Define

$$[\hat{A}', \hat{B}'] = \hat{A}'\hat{B}' - \hat{B}'\hat{A}' \tag{2}$$

$$\{\hat{A}', \hat{B}'\} = \hat{A}'\hat{B}' + \hat{B}'\hat{A}' \tag{3}$$

if $\hat{A}', \hat{B}'$ Hermitian

$$[\hat{A}', \hat{B}']^\dagger = -[\hat{A}', \hat{B}'] \tag{4}$$

Now writing

$$\hat{A}'\hat{B}' = \frac{1}{2}([\hat{A}', \hat{B}'] + \{\hat{A}', \hat{B}'\}) \tag{5}$$

Plug (5) into (1)

$$(\Delta_\psi A)^2 (\Delta_\psi B)^2 \geq \frac{1}{4} |(\psi, [\hat{A}', \hat{B}']\psi) + (\psi, \{A', B'\}\psi)|^2$$

Given that:

- $(\psi, \{\hat{A}', \hat{B}'\}\psi) \in \mathbb{R}$
- $(\psi, [\hat{A}', \hat{B}']\psi) = ir$ with $r \in \mathbb{R}$

then

$$(\Delta_\psi A)^2 (\Delta_\psi B)^2 \geq \frac{1}{4} |(\psi, [\hat{A}', \hat{B}']\psi)|^2 + \frac{1}{4} |\psi, \{\hat{A}', \hat{B}'\}\psi)|^2$$

$$\implies (\Delta_\psi A)(\Delta \psi B) \geq \frac{1}{2} |(\psi, [\hat{A}, \hat{B}]\psi)| \qquad \square$$

Start of lecture 12

Consequences of generalised uncertainty theorem

- $[\hat{A}, \hat{B}] = 0$ if and only if there exists joint set of eigenstates which form a complete basis of $\mathcal{H}$ which happens if and only if A, B can be measured simultaneously with arbitrary precision on a given state.
- Take $\hat{A} = \hat{x}$, $\hat{B} = \hat{p}$. Given that $[\hat{x}, \hat{p}] = i\hbar\hat{I}$

  $$\implies (\Delta_\psi x)(\Delta_\psi p) \geq \frac{\hbar}{2}$$

  (Heisenberg's uncertainty principle).

We had shown explicitly that, if $\psi = \psi_{\mathrm{GP}}$ then

$$(\Delta_{\psi_{\mathrm{GP}}} x)(\Delta_{\psi_{\mathrm{GP}}} p) = \frac{\hbar}{2}$$

at $t = 0$. (this is the minimum uncertainty). The reason for this lies in two lemmas:

(i) Lemma 4.5: ψ is a state of minimum uncertainty

$$\iff \hat{x}\psi = ia\hat{p}\psi \quad a \in \mathbb{R}$$

(ii) Lemma 4.6: The condition for 4.5 to hold is

$$\psi(x) = Ce^{-bx^2} \quad c \in \mathbb{C}, b \in \mathbb{R}^+$$

Exercise: Verify that $\psi_k(x,t) = e^{ikx}e^{-E_k t/\hbar}$ does not satisfy equation of Lemma 4.5.

4.3 Ehrenfest theorem

Time evolution of operators.

Theorem 9. The expectation value of an Hermitian operator $\hat{A}$ evolves according to

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{A}\rangle_\psi = \frac{i}{\hbar}\langle[\hat{H},\hat{A}]\rangle_\psi + \left\langle \frac{\partial \hat{A}}{\partial t}\right\rangle_\psi$$

Proof.

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{A}\rangle_\psi &= \frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\psi^*(x,t)\hat{A}\psi(x,t)\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\frac{\partial}{\partial t}(\psi^*\hat{A}\psi)\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\hat{A}\psi + \psi^*\frac{\partial\hat{A}}{\partial t}\psi + \psi^*\hat{A}\frac{\partial\psi}{\partial t}\right)\mathrm{d}x \\
&= \frac{i}{\hbar}\int_{-\infty}^{\infty}\psi^*(\hat{H}\hat{A} - \hat{A}\hat{H})\psi\mathrm{d}x + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle_\psi \\
&= \frac{i}{\hbar}\int_{-\infty}^{\infty}\psi^*[\hat{H},\hat{A}]\psi\mathrm{d}x + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle_\psi \\
&= \frac{i}{\hbar}\langle[\hat{H},\hat{A}]\rangle_\psi + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle_\psi
\end{aligned}$$

□

Examples

(1) Take $\hat{A} = \hat{H}$

$$\implies \frac{\mathrm{d}\langle \hat{H} \rangle_\psi}{\mathrm{d}t} = 0$$

$(\frac{\mathrm{d}E}{\mathrm{d}t} = 0)$

(2) Take $\hat{A} = \hat{p}$.

$$\begin{aligned}
[\hat{H}, \hat{p}]\psi &= \left[\frac{\hat{p}^2}{2m} + U(\hat{x}), \hat{p}\right]\psi \\
&= [U(\hat{x}), \hat{p}]\psi \\
&= U(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t) - \left(-i\hbar\frac{\partial}{\partial x}\right)[U(x)\psi(x,t) \\
&= \cancel{i\hbar U(x)\frac{\partial \psi}{\partial x}(x,t)} + \cancel{i\hbar U(x)\frac{\partial \psi}{\partial x}(x,t)} + i\hbar\frac{\partial U}{\partial x}(x)\psi(x,t) \\
\implies \frac{\mathrm{d}\langle \hat{p} \rangle_\psi}{\mathrm{d}t} &= \frac{i}{\hbar}\langle [\hat{H}, \hat{p}] \rangle_\psi \\
&= -\left\langle \frac{\partial U}{\partial x} \right\rangle_\psi
\end{aligned}$$

(3) $\hat{A} = \hat{x}$

$$\begin{aligned}
[\hat{H}, \hat{x}] &= \left[\frac{\hat{p}^2}{2m} + U(\hat{x}), \hat{x}\right] \\
&= \frac{1}{2m}[\hat{p}^2, \hat{x}^2] \\
&= \frac{1}{2m}(\hat{p}\underbrace{[\hat{p}, \hat{x}]}_{-i\hbar\hat{I}} + \underbrace{[\hat{p}, \hat{x}]}_{i\hbar\hat{I}}\hat{p}) \\
&= -\frac{i\hbar}{m}\hat{p} \\
\frac{\mathrm{d}\langle \hat{x} \rangle_\psi}{\mathrm{d}t} &= \frac{i}{\hbar}\langle [\hat{H}, \hat{x}] \rangle_\psi \\
&= \frac{\langle \hat{p} \rangle_\psi}{m}
\end{aligned}$$

(matches the classical $\dot{x} = \frac{p}{m}$)

4.4 Harmonic oscillator revisited (non-examinable)

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

($k = m\omega^2$, elastic constant). Eigenvalues, eigenfunctions of $\hat{H}$. Rewrite:

$$\begin{aligned}\hat{H} &= \frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x}) + \frac{i\omega}{2}\underbrace{[\hat{p}, \hat{x}]}_{-i\hbar\hat{I}} \\ &= \frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x}) + \frac{\hbar\omega}{2}\hat{I} \qquad (1)\end{aligned}$$

Definition. Ladder operators

$$\hat{a} = \frac{1}{\sqrt{2m}}(\hat{p} - im\omega\hat{x}) \qquad (2)$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2m}}(\hat{p} + im\omega\hat{x})$$

$$\implies \boxed{\hat{H} = \hat{a}^\dagger\hat{a} + \frac{\hbar\omega}{2}\hat{I}} \qquad (4)$$

Compute

$$\begin{aligned}[\hat{a}, \hat{a}^\dagger] &= \frac{1}{2m}[\hat{p} - im\omega\hat{x}, \hat{p} + im\omega\hat{x}] \\ &= -\frac{im\omega}{2m}[\hat{x}, \hat{p}] + \frac{im\omega}{2m}[\hat{p}, \hat{x}] \\ &= \hbar\omega\hat{I} \qquad (5) \\ [\hat{H}, \hat{a}] &= [\hat{a}^\dagger, \hat{a}, \hat{a}] \\ &= -\hbar\omega\hat{a} \qquad (6)\end{aligned}$$

$$[\hat{H}, \hat{a}^\dagger] = \hbar\omega\hat{a}^\dagger \qquad (7)$$

Suppose χ eigenfunction of $\hat{H}$ with eigenvalue E,

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

Take $(\hat{a}\chi)$. What is its energy?

$$\begin{aligned}\hat{H}(\hat{a}, \chi) &= [\hat{H}, \hat{a}]\chi + \hat{a}\hat{H}\chi \\ &= -\hbar\omega\hat{\chi} + E\hat{a}\chi \\ &= (E - \hbar\omega)\hat{a}\chi\end{aligned}$$

$\hat{a}\chi$) is eigenfunction of $\hat{H}$ with eigenvalue $(E - \hbar\omega)$ and $\hat{a}^\dagger\chi$) is eigenfunction of $\hat{H}$ with eigenvalue $(E + \hbar\omega)$. Prove by induction:

$$(\hat{a}^n\chi) \to \text{eigenfunction with eigenvalue } E - n\hbar\omega$$

$$(\hat{a}^{\dagger n}\chi) \to \text{eigenfunction with eigenvalue } E + n\hbar\omega$$

Using the fact that

$$\langle \hat{H} \rangle_\psi \geq 0$$

then $\exists$ eigenfunction χ_0 such that

$$\hat{a}\chi_0 = 0$$

Find χ_0

$$\frac{1}{\sqrt{2m}}(\hat{p} - im\omega\hat{x})\chi_0) = 0$$

$$-i\hbar\frac{\partial\chi_0}{\partial x} - im\omega x\chi_0 = 0$$

$$\implies \chi_0(x0 = ce^{-m\omega x^2/2\hbar}$$

$$\hat{H}\chi_0 = \hat{a}^\dagger\hat{a}\chi_0 + \frac{\hbar\omega}{2}\hat{I}\chi_0 = \frac{\hbar\omega}{2}\chi_0$$

The excited states with $E > E_0$

$$\begin{aligned}\chi_n &= (a^\dagger)^n\chi_0 \\ &= \frac{1}{(\sqrt{2m})^2}(\hat{p} + im\omega\hat{x})^n\chi_0 \\ &= \frac{c}{(\sqrt{2m})^n}\left(-i\hbar\frac{\partial}{\partial x} + im\omega x\right)^n e^{-m\omega x^2/2\hbar}\end{aligned}$$

Eigenvalues

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

Start of
lecture 13

5 3D solutions of Schrödinger equation

5.1 TISE in 3D for spherically symmetric potentials

$$-\frac{\hbar^2}{2m}\nabla^2\chi(\mathbf{x}) + U(\mathbf{x})\chi(\mathbf{x}) = E\chi(\mathbf{x})$$

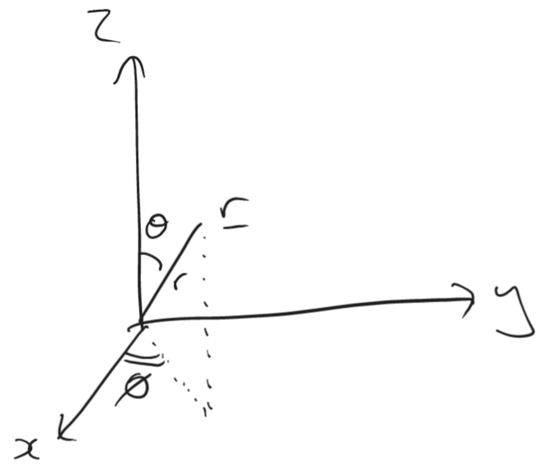
Laplacian operator ∇^2

- Cartesian coordinates (x, y, z):

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- Spherical coordinates (r, θ, ϕ)

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}(R) + \frac{1}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$



$$x = r\cos\phi\sin\theta$$
$$y = r\sin\phi\sin\theta$$
$$z = r\cos\theta$$

$0 \le r < \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$. Reminder:

$$\int_{\mathbb{R}^3} \mathrm{d}V = \int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\int_{-\infty}^{\infty}\mathrm{d}z$$

$$\int_{\mathbb{R}^3} \mathrm{d}V = \int_0^{2\pi}\mathrm{d}\phi\int_{-1}^{1}\mathrm{d}\underbrace{\cos\theta}_{\to\int_0^\pi \sin\theta\mathrm{d}\theta}\int_0^\infty r^2\mathrm{d}r$$

Definition. Spherically symmetric potential

$$U(\mathbf{x}) = U(r, \theta, \phi) \equiv U(r)$$

Clearly, even with a spherically symmetric potential $\phi(r, \theta, \phi)$.

We start by focussing on a particular sub-class of solutions of TISE, i.e. on Radial eigenfunctions $\chi(r)$. If $\chi(r, \theta, \phi) = \chi(r)$ then

$$\nabla^2 \chi(r) = \frac{1}{r} \frac{\partial^2}{\partial r^2}(r\chi(r))$$

Plugging this into TISE in 3D:

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\chi}{\mathrm{d}r}\right) + U(r)\chi = E\chi} \qquad (*)$$

Normalisation condition for $\chi \in \mathcal{H}$:

$$\int_{\mathbb{R}^3} |\chi(r, \theta, \phi)|^2 \mathrm{d}V < \infty$$

$$\implies \int_0^\infty |\chi(r)|^2 r^2 \mathrm{d}r < \infty$$

eigenfunctions $\chi(r)$ must go to 0 sufficiently fast at $r \to \infty$ and behave well ($\sim \frac{1}{r}$) (most singular behaviour) at $r \to 0$.

How to solve $(*)$? One way of doing it is to define

$$\sigma(r) \equiv r\chi(r)$$

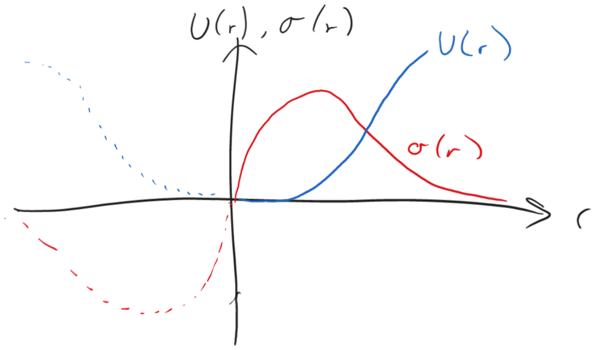
$$\implies -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\sigma(r)}{\mathrm{d}r^2} + U(r)\sigma(r) = E\sigma(r) \qquad (**)$$

This is like the 1D TISE defined only on $\mathbb{R}^+$ and with usual normalisation condition on $\mathbb{R}^2$:

$$\int_0^\infty |\sigma(r)|^2 \mathrm{d}r < \infty$$

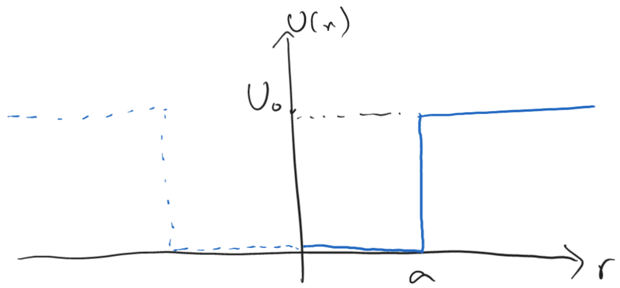
We want $\sigma(r) = 0$ at $r = 0$, $\sigma'(r)$ finite at $r = 0$.
$\implies$ Solve $(**)$ on $\mathbb{R}$ and look for odd solutions:

$$\sigma(-r) = -\sigma(r)$$



Example: Spherically symmetric potential well

$$U(r) = \begin{cases} 0 & r \leq a \\ U_0 & r > a \end{cases} \qquad a \in \mathbb{R}^+, U_0 \in \mathbb{R}^+$$



TISE as $(**)$ and solve it for $\sigma(r) = r\chi(r)$ by analytically continuation on whole $\mathbb{R}$ and looking only for *odd* solutions.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\sigma(r)}{\mathrm{d}r^2} + U(r)\sigma(r) = E\sigma(r)$$

Look for odd parity bound states

$$0 \leq E \leq U_0$$

$$K = \sqrt{\frac{2mE}{\hbar^2}} \qquad \bar{k} = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

odd solutions:

$$\sigma(r) = \begin{cases} A\sin(kr) & |r| \leq a \\ Be^{-\bar{k}r} & r > a \\ -Be^{+\bar{k}r} & r < -a \end{cases}$$

Boundary conditions for $\sigma(r)$:

- continuity of $\sigma(r)$ at $r = a$

- continuity of $\sigma'(r)$ at $r = a$.

$$\implies \begin{cases} A \sin ka = Be^{-\bar{k}a} \\ kA \cos ka = -\bar{k}Be^{-\bar{k}a} \end{cases}$$

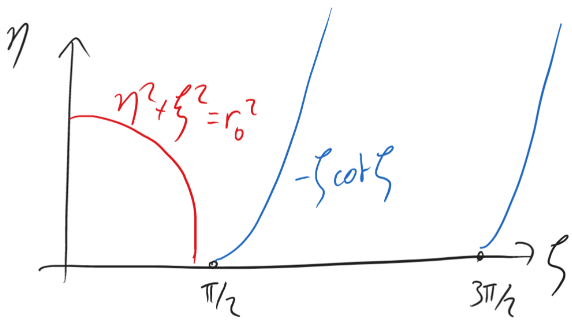
$$\implies -k \cot(ka) = \bar{k}$$

From definition:

$$k^2 + \overline{k^2} = \frac{2mU_0}{\hbar^2}$$

Solve this graphically by defining

$$\zeta = ka, \qquad \to \eta = -\zeta \cot \zeta$$
$$\eta = \bar{k}a \qquad \to \eta^2 + \xi^2 = r_0^2$$

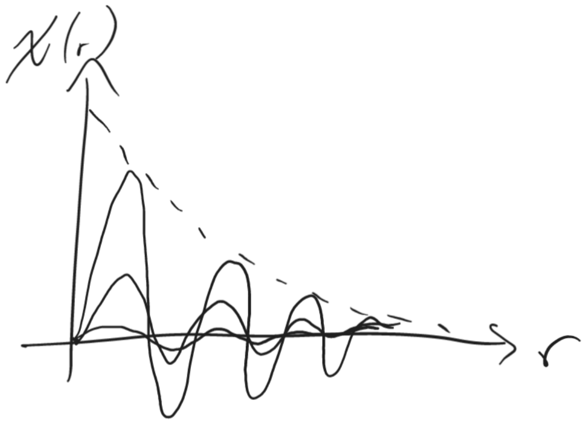


If $r_0 < \frac{\pi}{2}$ ($\iff U_0 < \frac{\pi^2\hbar^2}{3ma^2}$) then doesn't exist solution. Two differences:

(1) Below a given threshold for U_0 there does not exist bound state in 3D. (contrarily to 1D in which there exists even bound state)

(2)

$$\chi(r) = \begin{cases} A\frac{\sin(kr)}{r} & r < Q \\ B\frac{e^{-\bar{k}r}}{r} & r \geq Q \end{cases}$$



5.2 Angular momentum in Quantum Mechanics

Classical mechanics:

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}$$

When you have $U(r)$ then

$$\frac{\mathrm{d}\mathbf{L}}{\mathrm{d}t} = \dot{\mathbf{x}} \times \mathbf{p} + \mathbf{x} \times \dot{\mathbf{p}} = 0$$

In Dynamics and relativity the conservation of angular momentum implies that 3D $\to$ 2D (once take the plane $\mathbf{L} \cdot \mathbf{x} = 0$) $\to$ 1D (solve Newton's second law on $\mathbf{e}_r$).

Definition. Angular momentum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}}$$

$$\hat{\mathbf{L}} = -i\hbar \mathbf{x} \times \nabla$$

In 1D: $\hat{p} = -\hbar \frac{\partial}{\partial x}$
In 3D: $\hat{\mathbf{p}} = -\hbar \nabla$, $\hat{\mathbf{x}} = \mathbf{x}$.

Write it in cartesian coordinates (x_1, x_2, x_3)

$$\hat{L}_i = -\hbar \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k} \qquad \to (\varepsilon_{ijk} \hat{x}_j \hat{p}_k)$$

$i = 1, 2, 3.$

Start of lecture 14

Recap of Quantum Mechanics in 3D (Section 5)

- $$-\frac{\hbar^2}{2m} \nabla^2 \chi(\mathbf{x}) + U(\mathbf{x}) \chi(\mathbf{x}) = E \chi(\mathbf{x}) \qquad \mathbf{x} \in \mathbb{R}^3$$

  1D:

  $$+\frac{\partial^2}{\partial x^2}$$

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

  $$\hat{p}^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

  3D:

  $$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}$$

  $$\hat{\mathbf{p}} = -i\hbar \nabla = \left(-i\hbar \frac{\partial}{\partial x_1} + -i\hbar \frac{\partial}{\partial x_2}, -\hbar \frac{\partial}{\partial x_3} \right)$$

  $$|\hat{\mathbf{p}}|^2 = -\hbar^2 \nabla^2$$

- Useful to write ∇^2 in spherical coordinate (r, θ, ϕ)

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2 \sin^2\theta}\left[\sin\theta + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

- If $U(\mathbf{x}) = U(r)$ (spherically symmetric potential) we can find some special solutions of TISE $\chi(r)$ (radial solutions).

- If take $(xhf) = U(r)$, $\chi(r, \theta, \phi_{=}\chi(r)$

$$-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}(r\chi(r) + U(r)\chi(r) = E\chi(r)$$

if define $\sigma(r) = r\chi(r)$, TISE for $\chi(r)$ becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\sigma(r)}{\mathrm{d}r^2} + U(r)\sigma(r) = E\sigma(r)$$

in $\mathbb{R}^+$, and with normalisation condition

$$\int_0^\infty |\sigma(r)|^2 \mathrm{d}r < \infty$$

because of normalisation conditions $\sigma(r) \to a$ as $r \to 0$. But we found $a = 0$. Why? If we allowed $\sigma(r) \approx a \neq 0$ as $r \to 0$ (which means $\chi(r) \sim \frac{a}{r}$) then $\hat{H}$ would not be Hermitian.

Proof. For $\hat{H}$ to be Hermitian we need

$$(\phi, \hat{H}\chi) = (\hat{H}\phi, \chi) \qquad \forall \phi, \chi \in \mathcal{H}$$

$$\begin{aligned}
(\phi, \hat{H}\chi) &= \int_0^\infty \mathrm{d}r r^2 \phi(r)\hat{H}\chi(r) \\
&= -\frac{\hbar^2}{2m}\int_0^\infty \mathrm{d}r\phi\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\chi}{\mathrm{d}r}\right) \\
&= -\frac{\hbar^2}{2m}\left[r^2\phi\frac{\mathrm{d}\chi}{\mathrm{d}r} - r^2\chi\frac{\mathrm{d}\phi}{\mathrm{d}r}\right]_0^\infty \underbrace{-\frac{\hbar^2}{2m}\mathrm{d}r\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\phi}{\mathrm{d}r}\right)\chi}_{(\hat{H}\phi,\chi)}
\end{aligned}$$

If $\phi(r) \sim B$ as $\to 0$ with $B \neq 0$ then $\chi(r) \sim \frac{A}{r}$ as $r \to 0$ with $A \neq 0$ then

$$r^2\phi\frac{\mathrm{d}\chi}{\mathrm{d}r} - r^2\chi\frac{\mathrm{d}\phi}{\mathrm{d}r} \not\to 0$$

as $r \to 0$. □

Due to Quantum Mechanics interpretation we classify $\chi(r) \sim \frac{A}{r}$ as unphysical, hence $\sigma(r) = 0$ at $r = 0$.

Continuing from before the recap

Properties:

- $\hat{L}_i$ is Hermitian (Example sheet)
- $[\hat{L}_i, \hat{L}_j] \neq 0$ if $i \neq j$ (Example sheet). $\implies$ different components of $\mathbf{L}$ cannot be determined simultaneously.

$$[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

Proof.

$$\begin{aligned}[\hat{L}_1, \hat{L}_2]\chi(x_1, x_2, x_3) &= -\hbar^2\left[\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)\left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right) - \left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right)\left(x_2\frac{\partial}{\partial x_3} - \right.\right. \\ &= -\hbar^2\left(x_2\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_2}\right)\chi(x_1, x_2, x_3) \\ &= i\hbar\hat{L}_3\chi(x_1, x_2, x_3)\end{aligned}$$

□

> **Definition.** Total angular momentum operator $\hat{L}^2$
>
> $$\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2$$

Properties:

- $[\hat{L}^2, \hat{L}_i] = 0$ (Example sheet)
- for $U(r)$ $[\hat{L}^2, \hat{H}] = 0$ $(*)$, $[\hat{L}_i, \hat{H}] = 0$.

Proof. –

$$\begin{aligned}[\hat{L}_i, \hat{x}_j] &= [\varepsilon_{imn}\hat{x}_m\hat{p}_n, \hat{x}_j] \\ &= \varepsilon_{imn}[\hat{x}_m\hat{p}_n, \hat{x}_j] \\ &= \varepsilon_{imn}(\hat{x}_m[\hat{p}_n, \hat{x}_j] + [\hat{x}_m, \hat{x}_j]\hat{p}_n) \\ &= -i\hbar\varepsilon_{imj}\hat{x}_m \\ &= i\hbar\varepsilon_{ijm}\hat{x}_m\end{aligned}$$

–

$$\begin{aligned}[\hat{L}_i, \hat{x}_j^2] &= [\hat{L}_i, \hat{x}_j] + \hat{x}_j[\hat{L}_i, \hat{x}_j] \\ &= i\hbar\varepsilon_{ijm}(\hat{x}_m\hat{x}_j + \hat{x}_j\hat{x}_m) \\ &= 0\end{aligned}$$

- $[\hat{L}_u, U(r)] = 0$ since $r = \sqrt{\hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2}$.
- $[\hat{L}_i, \hat{p}_j] = i\hbar\varepsilon_{ijm}\hat{p}_m$ (same proof as for x_j)
- $[\hat{L}_i, \hat{p}^2] = 0$

$$\implies [\hat{L}_i, \hat{H}] = 0$$

and

$$[\hat{L}^2, \hat{H}] = 0$$

(trivially) □

$\{\hat{H}, \hat{L}^2, \hat{L}_i\}$ set of mutually commuting operators. Take $i = 3$. $\implies$

(1) Can find joint eigenstates of these 3 operators that form a basis of $\mathcal{H}$.

(2) eigenvalues of these 3 operators $|\mathbf{L}|$, L_z, E can be simultaneously measured at an arbitrary precision.

(3) The set of operators is *maximal* i.e. we cannot construct another independent operator (other than $\hat{I}$) that commutes with them.

To find joint eigenfunctions of $\hat{L}^2$ and $\hat{L}_3$ write $\hat{\mathbf{L}}$ in spherical coordinates (appendix 7 of Maria Ubiali's notes)

$$i\hbar\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}, \dots, \dots\right)$$

$$\frac{\partial}{\partial x_1} = \left(\frac{\partial r}{\partial x_1}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x_1}\right)\frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x_1}\right)\frac{\partial}{\partial \phi}$$

And put

$$\hat{L}_3 = -i\hbar\frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

Next time we will look for joint eigenfunction

$$Y(\theta, \phi)$$

such that

$$\begin{cases} \hat{L}^2 Y(\theta,\phi) = \lambda Y(\theta,\phi) & (1) \\ \hat{L}_3 Y(\theta,\phi) = \hbar m Y(\theta,\phi) & (2) \end{cases}$$

Start of lecture 15

$$-\hbar\frac{\partial}{\partial\phi}Y(\theta,\phi) = \hbar m Y(\theta,\phi)$$

Find solutions

$$\boxed{Y(\theta,\phi) = y(\theta)X(\phi)} \qquad (3)$$

Plugging (3) into (2)

$$-i\hbar\left(\frac{\partial}{\partial\phi}X(\phi)\right)\cancel{y(\theta)} = \hbar m X(\phi)\cancel{y(\theta)}$$

$$X(\phi) = e^{im\phi)}$$

Given that wave function must be simple-valued in $\mathbb{R}^3 \implies X(\phi)$ must be invariant under

$$\phi \to \phi + 2\pi$$

$$\implies e^{i2m\pi} = 1 \implies m \in \mathbb{Z} \tag{4}$$

Plug (4) into (1) and find

$$\boxed{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial y(\theta)}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}y(\theta) = -\frac{\lambda}{\hbar^2}y(\theta)} \tag{5}$$

This is the associated Legendre equation (IB Methods) and it has solution

$$y(\theta) = P_{l,m}(\cos\theta = (\sin\theta)^{|m|}\frac{\mathrm{d}^{|m|}}{\mathrm{d}(\cos\theta)^{|m|}}P_l(\cos\theta)$$

(where $P_{l,m}$ is the associate Legendre polynomial and P_l is the ordinary Legendre polynomial). Because $P_l(\cos\theta)$ is a polynomial in $\cos\theta$ of degree l, $\implies -l \leq m \leq l$ and (without proof) the eigenvalues of $\hat{L}^2$ are

$$\lambda = \hbar^2 l(l+1)$$

($l = 0, 1, 2, \ldots$) Put everything together:

$$Y_{l,m}(\theta,\phi) = P_{l,m}(\cos\theta)e^{im\phi}$$

$l = 0, 1, 2, \ldots,\ -l \leq m \leq l$. Spherical harmonics:

$$\hat{L}^2 Y_{l,m}(\theta,\phi) = \hbar^2 l(l=1)Y_{l,m}(\theta\phi)$$

$$\hat{L}_3 Y_{l,m}(\theta,\phi) = m\hbar Y_{l,m}(\theta,\phi)$$

l, m are quantum numbers that characterise:

- $l \to$ total angular momentum
- $m \to$ azimuthal number, z-component of L.

In classical mechanics

$$-|\mathbf{L}| \le L_z \le |\mathbf{L}| \leftrightarrow -l \le m \le l$$

$$Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \qquad l = 0, m = 0$$

$$Y_{1,0}(\theta, \phi) = \frac{3}{\sqrt{4\pi}} \cos\theta \qquad l = 1, m = 0$$

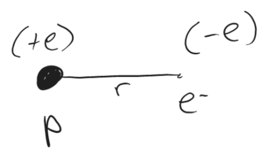
$$Y_{1,\pm 1}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \sin\theta e^{\pm i\phi} \qquad l = 1, m = \pm 1$$

All spherical harmonics are orthonormal (like all eigenfunctions of Hermitian operators)

$$(Y_{l,m}, Y_{l',m'}) = \delta_{ll'}\delta_{mm'}$$

$$\int_0^{2\pi} \mathrm{d}\phi \int_{-1}^{1} \mathrm{d}\cos\theta Y^*_{lm}(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'}\delta_{mm'}$$

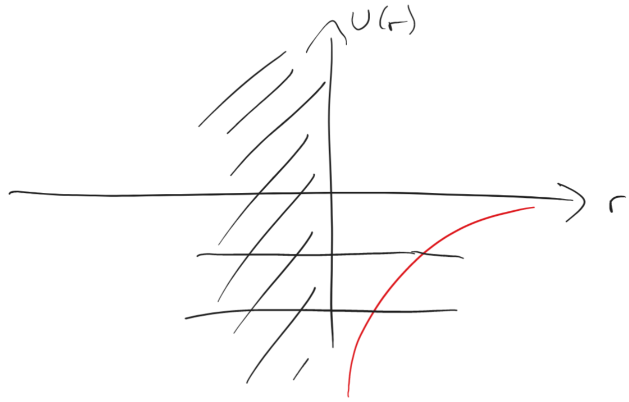
5.3 The Hydrogen atom



Model proton (nucleus) to be stationary at the origin ($m_p \to \infty$, or equivalently $m_p \gg m_e$)

$$F_{\text{coulomb}}(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2} = -\frac{\partial U_{\text{coulomb}}}{\partial r}$$

$$U_{\text{coulomb}}(r) = -\frac{e^3}{4\pi\varepsilon_0}\frac{1}{r}$$



Bound states $E < 0$.

$$-\frac{\hbar^2}{2m_e}\nabla^2\chi(r,\theta\phi) - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\chi(r,\theta,\phi) = E\chi(r,\theta,\phi) \tag{1}$$

Laplacian

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\phi^2}\right)$$

$$\hat{L}^2 = \frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\phi^2}\right]$$

$$\implies -\hbar^2\nabla^2 = -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{L}^2}{r^2} \tag{2}$$

Plug (2) into (1)

$$-\frac{\hbar^2}{2m_e}\frac{1}{r}\left(\frac{\partial^2}{\partial r^2}r\chi(r,\theta,\phi)\right) + \frac{\hat{L}^2}{2m_e r^2}\chi(r,\theta,\phi) - \frac{e^2}{4\pi\varepsilon_0 r}\chi(r,\theta,\phi) = E\chi(r,\theta,\phi) \tag{3}$$

Because of eigenfunction of $\hat{H}$ are also eigenfunction of $\hat{L}^2$ and $\hat{L}_3 \implies \chi(r,\theta,\phi)$ must also be eigenfunction of $\hat{L}^2$, $\hat{L}_3$.

$$\implies \chi(r,\theta,\phi) = R(r)Y_{l,m}(\theta,\phi)$$

$$\implies \hat{L}^2\chi = R(r)LharY_{l,m}(\theta,\phi) = \hbar^2 l(l+1)R(r)Y_{l,m}(\theta,\phi) \tag{4}$$

Plug (4) into (3)

$$-\frac{\hbar^2}{2m_e}\left(\frac{\mathrm{d}^2R(r)}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right)\cancel{Y_{l,m}(\theta,\phi)} + \frac{\hbar^2}{2m_e r^2}l(l+1)R(r)\cancel{Y_{l,m}(\theta,\phi)} - \frac{e^2}{4\pi\varepsilon_0}R(r)\cancel{Y_{l,m}(\theta,\phi)}$$
$$= ER(r)\cancel{Y_{l,m}(\theta,\phi)} \tag{5}$$

We end up with a 1D equation for radial part $R(r)$

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \underbrace{\left(-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2m_e r^2}\right)}_{V_{\text{eff}}(r)}R = ER \tag{6}$$

($V_{\text{eff}}(r)$ is a bit like in classical mechanics).

5.3.1 $l = 0$

$V_{\text{eff}}(r) \to V_{\text{coulomb}}(r)$. Rewrite (6) in terms of variables

$$\nu^2 \equiv -\frac{2mE}{\hbar^2} > 0$$

$$\beta \equiv \frac{e^2 m}{2\pi\varepsilon_0\hbar^2}$$

In terms of ν^2, β (6) becomes

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \left(\frac{\beta}{r} - \nu^2\right)R = 0 \tag{7}$$

(i) The asymptotic behaviour ($r ø \infty$) determined by

$$\frac{\mathrm{d}^2 R}{\mathrm{d}r^2} - \nu^2 R = 0$$

$$R(r) \sim e^{\pm r\nu}$$

as $r \to \infty$. Take $R(r) \sim e^{-r\nu}$ because of normalisability.

(ii) At $r = 0$ eigenfunction has to be finite ($\sim A$).

Exploiting (i) take ansatz

$$R(r) = f(r)e^{-\nu r} \tag{8}$$

Plug (8) into (7) and find

$$f''(r) + \frac{2}{r}(1 - \nu r)f'(r) + \frac{1}{r}(\beta - 2\nu)f(r) = 0 \tag{9}$$

(9) is a homogeneous linear ODE with regular point $r = 0$

$$f(r) = r^c \sum_{n=0}^{\infty} a_n r^n$$

$$f'(r) = \sum_{n=0}^{\infty} a_n (c + n) r^{c+n-1} \tag{10}$$

$$f''(r) = \sum_{n=0}^{\infty} a_n (c + n)(c + n - 1) r^{c+n-2}$$

Plug (10) into (9):

$$\sum_{n=0}^{\infty} a_n (c + n)(c + n - 1) r^{c+n-2} + \frac{2}{r}(1 - \nu r) a_n (c + n) r^{c+n-1} + (\beta - 2\nu) r^{c+n-1}] = 0$$

Constant power of r has coefficient (r^{c-2})

$$a_0 c(c - 1) + 2a_0 c = 0$$

$$\implies a_0 c(c + 1) = 0$$

$c = -1$ (then $X \sim \frac{A}{r}$) or $c = 0$ (then $X \sim A$). So $c = 0$ and the equation for the other coefficients is

$$\sum_{n=1}^{\infty} a_n n(n + 1) a_{n-1}(\beta - 2\nu n)] r^{n-2} = 0$$

$$\implies a_n = \frac{2\nu n - \beta}{n(n + 1)} a_{n-1} \tag{11}$$

Start of lecture 16

Proposition. If $f(r) = \sum_{n=0}^{\infty} a_n r^n$ is infinite then $R(r)$ is not normalisable.

Proof. Asymptotic behaviour of $f(r)$ determined by

$$\frac{a_n}{a_{n-1}} \overset{n\to\infty}{\longrightarrow} \frac{2\nu}{n}$$

This is the same asymptotic behaviour as

$$g(r) = e^{2\nu r} = \sum_{n=0}^{\infty} \frac{(2\nu)^n}{n!} r^n$$

$b_n = \frac{(2\nu)^n}{n!}$, then

$$\frac{b_n}{b_{n-1}} \overset{n\to\infty}{\longrightarrow} \frac{2\nu}{n}$$

Asymptotically $f(r) \sim e^{2\nu r}$, $R(r) = f(r)e^{-\nu r} \sin e^{\nu} r$. □

$\implies$ the series must terminate. $\exists N > 0$ such that

$$a_N = 0 \quad \text{with} \quad a_{N-} \neq 0$$

$$\implies 2\nu N - \beta = 0 \implies \nu = \frac{\beta}{2N}$$

Substituting ν, β,

$$\boxed{E_N = -\frac{e^4 m_e}{32\pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{N^2}}$$

with $N = 1, 2, 3, \ldots$ same as Bohr's energy spectrum. Eigenfunction $R_N(r)$, substitute $2N\nu = \beta$ in (11) and find

$$\frac{a_n}{a_{n-1}} = -2\nu \frac{N-n}{n(n+1)} \tag{12}$$

Can use (12) to find coefficient of $R_N(r)$.

$N = 1$, polynomial of degree 0, set $a_0 = 1$ then normalise

$$R_1(r) = A_1 e^{-\nu r}$$

$N = 2$, polynomial of degree 1, set $a_0 = 1$,

$$\frac{a_1}{a_0} \overset{(12)}{=} -2\nu \frac{2-1}{2} \implies a_1 = -\nu a_0 = -\nu$$

$$R_2(r) = A_2(1 - \nu r)e^{-\nu r}$$

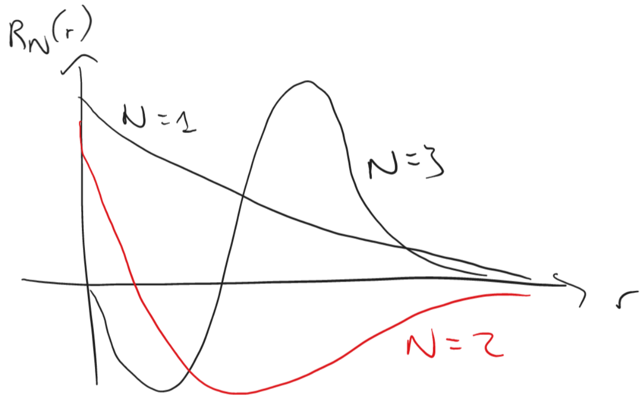
$N = 3$, polynomial of degree 2, $a_0 = 1$, $a_1 = -2\nu$, $a_2 = \frac{2}{3}\nu^2$

$$R_3(r) = A_3(1 - 2\nu r + \frac{2}{3}\nu^2 r^2)e^{-\nu r}$$

In general

$$R_N(r) = L_N(\nu r)e^{-\nu r}$$

where L_n is the Laguerre polynomial of $O(N-1)$.



$P(r) \propto r^2 |R_N(r)|^2$.

Exercise: Compute A_1 and compare closest to nucleus radius to Bohr radius

$$\langle \hat{r} \rangle_{\chi_1 = R_1 Y_{00}} = \frac{3}{2} a_0$$

(Bohr radius is $\left.\frac{\mathrm{d}P(r)}{\mathrm{d}r}\right|_{r=a_0} = 0$)

5.3.2 $l > 0$

$$\frac{\mathrm{d}^2 R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \left(\frac{\beta}{r} - 2\nu - \frac{l(l+1)}{r^2}\right) R = 0 \tag{14}$$

Asymptotic behaviour:

$$R(r) = f(r)e^{-\nu r} \tag{15}$$

$$\implies \frac{\mathrm{d}^2 f}{\mathrm{d}r^2} + \frac{2}{r}(1 - \nu r)\frac{\mathrm{d}f}{\mathrm{d}r} + \left(\frac{\beta}{r} - 2\nu - \frac{l(l+1)}{r^2}\right) f = 0 \tag{16}$$

Power series

$$f(r) = r^\sigma \sum_{n=0}^{\infty} a_n r^n \tag{17}$$

Plug (17) into (16) and identify lowest power of r and set coefficient to zero

$$a_0[\sigma(\sigma - 1) + 2\sigma - l(l+1)]r^{\sigma-2} = 0$$

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

So have $\sigma = -l-1$ or $\sigma = l$. But if $\sigma = -l-1$ then $R(r) \sim \frac{1}{r^{l+1}}$ as $r \to 0$, which is not integrable near $r = 0$. But if $\sigma = l$, then $R(r) \sim 0$ as $r \to 0$ which is fine. Now we know

$$f(r) = r^l \sum_{n=0}^{\infty} a_n r^n \tag{18}$$

Plug (18) into (16) and find

$$\boxed{a_n = \frac{2\nu(n+l) - \beta}{n(n+2l-1)} a_{n-1}} \tag{19}$$

As before easy to show that $R(r)$ would diverge unless

$$\exists n_{\max} > 0 \quad \text{such that} \quad a_{n_{\max}} = 0, a_{n_{\max}-1} \neq 0$$

Plug $a_{n_{\max}}$ in (19).

$$2\nu \underbrace{(n_{\max} + l)}_{\equiv N} - \beta = 0$$

$$\implies 2\nu N - \beta = 0 \implies \nu = \frac{\beta}{2N}$$

- $E_N = -\frac{e^4 m_E}{32\pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{N^2}$, $N = 1, 2, \ldots$
- Eigenvalues same but the degeneracy is larger $\forall N$, $N = n_{\max} + l$. Can have $l = 0, 1, \ldots, N-1$. $-l \le m \le l$.

  $$\underbrace{D(N)}_{\text{degeneracy}} = \sum_{l=0}^{N-1} \sum_{m=-l}^{l} 1 = \sum_{l=0}^{N-1} (2l+1) = N^2$$

  energy level N you have N^2 (linearly independent) states with same E_N.

- Eigenfunctions

  $$\chi_{N,l,m}(r,\theta,\phi) = R_{N,l}(r) Y_{l,m}(\theta,\phi) = r^l g_{N,l} e^{-r/2N} Y_{l,m}(\theta,\phi)$$

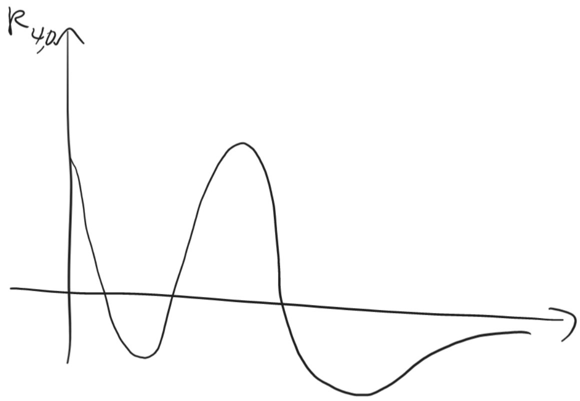
  $g_{n,l}(r)$ polynomial of degree $(N-l-1)$ defined by

  $$g_{N,l}(r) = \sum_{n=0}^{N-l-1} a_k r^k$$

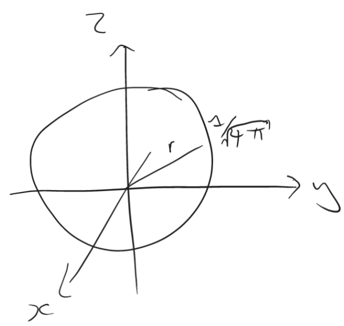
  with $a_k = \frac{2\nu}{k} \frac{k+l-N}{k+2l+1}$ (generalised Laguerre polynomials) quantum numbers $N = 0, 1, 2, \ldots$ (principal quantum numbers), $l = 0, \ldots, N-1$ (total angular momentum), $m = -l, \ldots, l$ (azimuthal quantum number).

For $N = 4$ $l = 0$,

$$R_{4,0}(r) \propto (1 + c_{4,0}r + d_{4,0}r^2 + e_{4,0}r^2)e^{-r\beta/8}$$

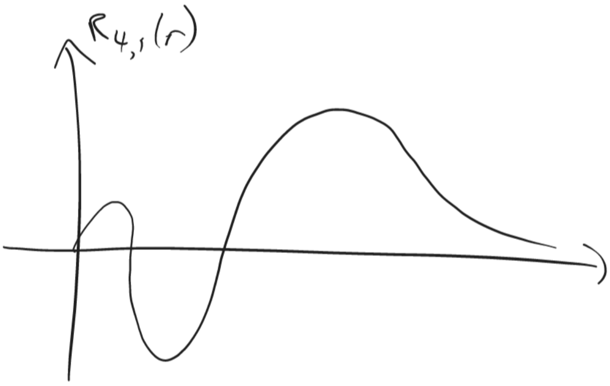


$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$,

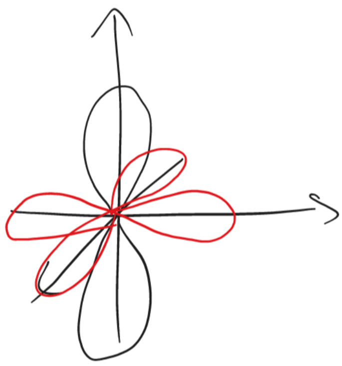


For $N = 4$, $l = 1$,

$$R_{4,1}(r) \propto r(c_{4,1} + d_{4,1}r + e_{4,1}r^2)e^{-r\beta/8}$$

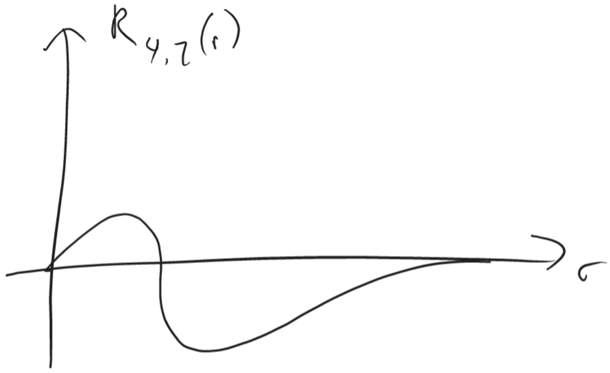


$Y_{1,0}(\theta, \phi)$, $Y_{1,1}(\theta, \phi)$, $Y_{1,-1}(\theta, \phi)$.

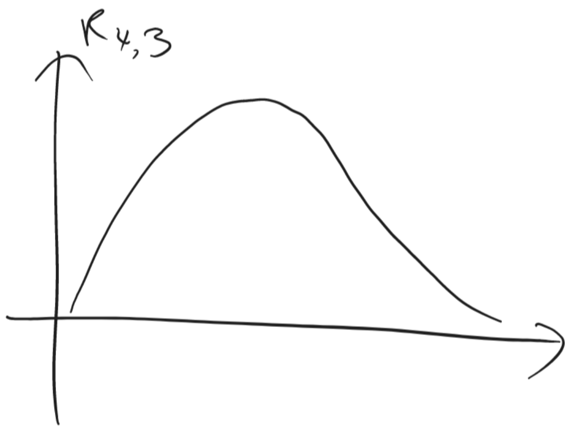


For $N = 4$, $l = 2$,

$$R_{4,2}(r) \propto r^2(c_{4,2} + d_{r,2}r)e^{-2\beta/8}$$



$Y_{2,0}(\theta, \phi)$, $Y_{2,\pm 1}(\theta, \phi)$, $Y_{2,\pm 2}(\theta, \phi)$. $N = 4$, $l = 3$



$$R_{4,3} = r^3(c_{4,3})e^{-r\beta/8}$$

$Y_{3,0}, Y_{3,\pm1}, Y_{3,\pm2}, Y_{3\pm3}$.

Bohr model:

- E_N was correct
- Bohr radius was sort of correct
- $L^2 = N^2\hbar^2$ wrong. Instead $L^2 = l(l+1)\hbar^2$ with $l < N$.
- degeneracy wrong.

5.4 Periodic table

z, e^-,

$$\chi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_z) = \chi(\mathbf{x}_1) \cdots \chi(\mathbf{x}_z)$$

$E = \sum_{j=1}^{N} E_j$. It's a poor approximation.