Mathematical Tripos IB

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Quantum Mechanics

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Recommended books

- S. Gasiorowicz, *Quantum Physics*, Wiley 2003.
- P. V. Landshoff, A. J. F. Metherell and W. G. Rees, *Essential Quantum Physics*, Cambridge University Press 1997.
- A. I. M. Rae, *Quantum Mechanics*, IOP Publishing 2002.
- L. I. Schiff, *Quantum Mechanics*, McGraw Hill 1968.

Useful more advanced references

- P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press 1967, reprinted 2003.
- L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-relativistic Theory)*, Butterworth Heinemann 1958, reprinted 2003.

For an alternative perspective see Chapters 1-3 of,

- R. P. Feynman, R. B. Leighton and M. Sands, *The Feynman Lectures on Physics, Volume 3*, Addison-Wesley 1970.

Motivation

Successes of QM,

- Atomic structure → Chemistry
- Nuclear structure
- Astrophysics, Cosmology: Nucleosynthesis
- Condensed Matter: (semi-)conductors, insulators
- Optics: Lasers

Conceptual/philosophical aspects,

- Probabilistic not deterministic
- Role of observer

Mathematical aspects,

- **States** live in complex vector space
- **Observables** $\longleftrightarrow$ **Operators**
  Non-commutative algebra

Outline

1) Introduction: the need for a quantum theory

2) Wave Mechanics I: Schrödinger equation and solutions
Scattering and bound state problems in one dimension

3) Operators and expectation values
Postulates of QM
Heisenberg uncertainty

4) Wave Mechanics II: Boundstate problems in three dimensions
The Hydrogen atom

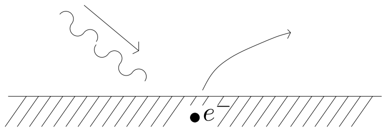


Figure 1: Incident light expels electron from metal.

1 Introduction

QM introduces a single new constant of fundamental nature: **Planck's constant**

$$\hbar \;=\; 1.055 \;\times\; 10^{-34} \;\text{Joule}\;\; \text{s}$$

We will also use Planck's original constant $h = 2\pi\hbar$
Dimensions: $[\hbar] = ML^2T^{-2} \times T = ML^2T^{-1}$

Photoelectric effect

- To liberate electron from metal requires energy $E \geq E_0 > 0$. Threshold energy E_0 is different for different metals.

- Shine monochromatic light at a metal plate (see Fig 1),

  - Intensity I

  - Angular frequency ω. Here $\omega = 2\pi c/\lambda$ where λ is the wavelength of the light.

Find,

1. Liberation of electron requires $\omega \geq \omega_0$ where,

$$\hbar\omega_0 \;=\; E_0$$

   Independent of intensity, I

2. Number of electrons emitted $\propto I$.

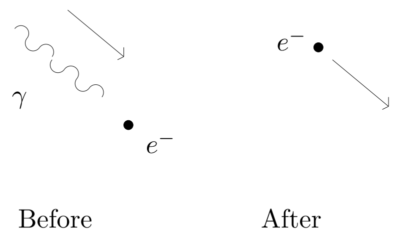


Figure 2: Collision of photon and electron.

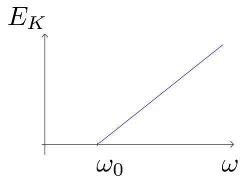


Figure 3: Plot of E_K against ω

Explanation (Einstein 1905)
Electromagnetic radiation of angular frequency ω made up of discrete quanta of energy,

$$E = \hbar\omega$$

Quanta known as *photons* (denoted γ). Intensity of light corresponds to the total number of photons emitted per second
Basic process: photon absorbed by electron (see Figure 2).

- Conservation of energy implies,

  $$E_K = \hbar\omega - E_0 = \hbar(\omega - \omega_0)$$

  where E_K is the kinetic energy of the ejected electron (See Figure 3). This relation agrees well with experiment.

- Number of electrons emitted $\sim$ Number of collisions $\sim$ Number of incident photons $\sim$ Intensity, I.

Wave-particle duality

Light exhibits **wave-like** properties,

- Refraction
- Interference
- Diffraction (see Appendix)
- Polarization

Beam of monochromatic light corresponds to plane waveform[1],

$$\mathbf{E}, \qquad \mathbf{B} \quad \sim \quad \Re\left[\exp\left(i\mathbf{k}\cdot\mathbf{x} - i\omega t\right)\right]$$

describes light of wavelength $\lambda = 2\pi/|\mathbf{k}|$ Here $\mathbf{k}$ is the wave-vector and $\omega = c|\mathbf{k}|$ is the angular frequency.

However, light also some times acts like a beam of **particles** (photons),

- Photoelectric effect
- Spectral lines

Corresponding particle has energy, $E = \hbar\omega$ and momentum $\mathbf{p} = \hbar\mathbf{k}$.
Check: as we have $\omega = c|\mathbf{k}|$, we find that $E = c|\mathbf{p}|$ which is the correct dispersion relation for a massless particle in Special Relativity.

The Hydrogen atom

Planetary model (see Fig 4),

- As $m_e/m_p \simeq 1/1837 << 1$ treat proton as stationary.
- Attractive force, F, between electron and proton given by Coulomb's law,

$$F \quad = \quad -\frac{e^2}{4\pi\varepsilon_0 r^2}$$

where r is distance between the electron and proton. Minus sign denotes attractive force. Here ε_0 is the vacuum permittivity constant.

[1]The following equation indicates the $\mathbf{x}$ and t dependence of each of the components of the vector fields $\mathbf{E}$ and $\mathbf{B}$. $\Re$ denotes the real part of the expression in brackets.

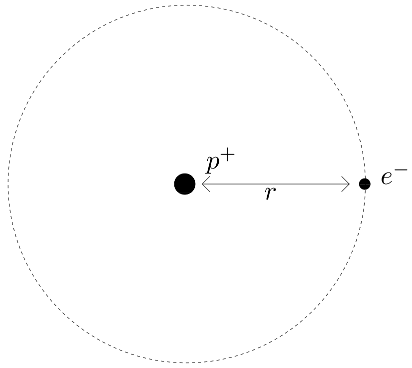


Figure 4: Planetary model of the Hydrogen atom.

- Assume electron follows circular orbit of radius r at speed v. Thus have centipetal acceleration $a = -v^2/r$. (Negative sign corresponds to acceleration towards center of circle.) Newton's second law implies,

$$F = -\frac{e^2}{4\pi\varepsilon_0 r^2} = m_e \times -\frac{v^2}{r}$$

Can then express radius r of orbit in terms of angular momentum,

$$J = m_e v r \tag{1}$$

as,

$$r = \frac{4\pi\varepsilon_0 J^2}{m_e e^2} \tag{2}$$

- Electron energy,

$$\begin{aligned} E &= \text{KE} \quad + \quad \text{PE} \\ &= \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r} \end{aligned} \tag{3}$$

eliminating v and r using Eqns (1) and (2), we obtain,

$$E = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2 J^2}$$

In classical physics the angular mometum J can take any value which implies a *continuous* spectrum of possible energies/orbits.

Problems

- Hot Hydrogen gas radiates at a **discrete** set of frequencies called **spectral lines**,

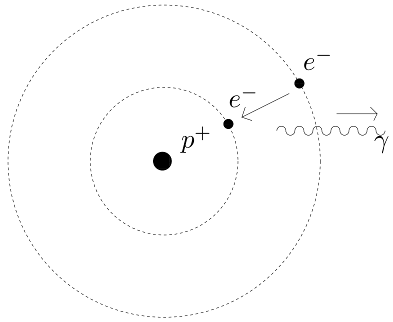


Figure 5: Classical instability of the Hydrogen atom.

Empirical formula for emitted frequencies ν_{mn} labelled by two positive integers $m > n$,

$$\nu_{mn} = R_0 \, c \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \tag{4}$$

where $R_0 \simeq 1.097 \times 10^7 \ m^{-1}$ is known as the Rydberg constant.

- Electron in circular orbit experiences centripetal acceleration $a = -v^2/r$. Classical electrodynamics implies that accelerating electric charges radiate EM waves. Hence the electron will lose energy and collapse into the nucleus (see Fig 5). This would mean that the atom was highly unstable which obviously disagrees with observation.

Bohr postulate

These two problems are solved by a simple but rather ad hoc postulate,

- The angular momentum of the electron is **quantized** according to the rule,

$$J = n\hbar$$

where $n = 1, 2, 3, \ldots$.

Check dimensions: the angular momentum $J = m_e v r$ has dimensions,

$$[J] = M \times LT^{-1} \times L = ML^2T^{-1} = [\hbar]$$

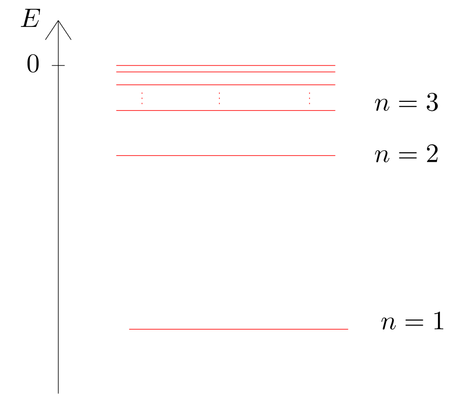


Figure 6: Energy levels of the Hydrogen atom.

Consequences

- **Quantized energy levels** Setting $J = n\hbar$ in equation (3), we immediately find a discrete set of allowed energy levels, $E_1 < E_2 < E_3 \ldots$ where,

$$E_n = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2} \times \frac{1}{n^2}$$

- **Radii** of orbit are quantized,

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \times n^2 = n^2 r_1$$

The radius of the lowest orbit,

$$r_1 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \simeq 0.529 \times 10^{-9} \ m \qquad (5)$$

is known as the **Bohr radius**.

- **Spectral lines** correspond to transitions between energy levels, electron emits a photon γ of frequency ν_{mn}

$$h\nu_{mn} = \hbar\omega_{mn} = E_m - E_n$$

thus we have,

$$\nu_{mn} = \frac{m_e e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad (6)$$

we can check that,

$$\frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \simeq 1.097 \times 10^7 \ m^{-1} \simeq R_0$$

Thus (6) agrees with the empirical formula (4).

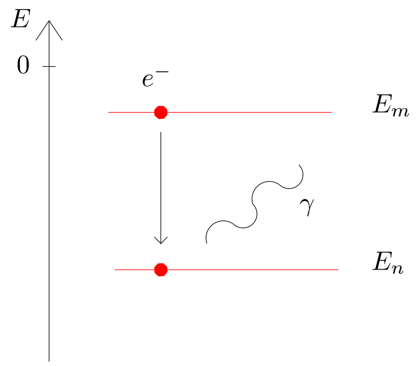


Figure 7: Transition between energy levels.

$\Rightarrow$ Bohr postulates "explain"

- stability of atoms
- observed spectral lines

Problems

- why/when do classical laws fail?
- why only circular orbits? What about elliptical orbits, orbits in different planes?
- fails for multi-electron atoms.

In fact Bohr model is not correct (but energy levels are).

de Broglie waves

We saw that EM waves of wavelength λ sometimes behave like particles of momentum,

$$p = \frac{h}{\lambda} \tag{7}$$

L. de Broglie (1924) proposed that conversely **particles** such as e^-, p^+ sometimes exhibit the properties of waves of wavelength,

$$\lambda = \hbar|\mathbf{k}| = \frac{h}{p} \tag{8}$$

where $p = |\mathbf{p}|$

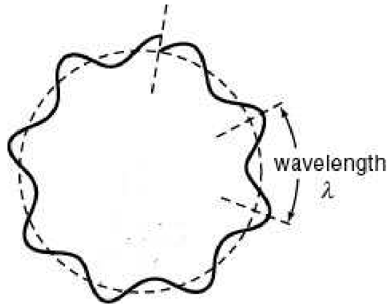


Figure 8: De Broglie argument

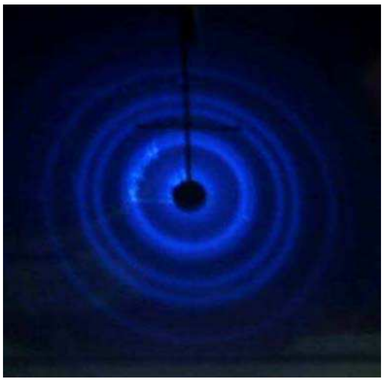


Figure 9: Electron diffraction from a crystal

This idea leads directly to Bohr's postulate.

- electron orbits should correspond to *integer* numbers of wavelengths (see Fig 8),

$$\begin{aligned} 2\pi r_n &= n\lambda = \frac{nh}{p} = \frac{nh}{m_e v} \\ \Rightarrow \quad r_n m_e v &= \frac{nh}{2\pi} \\ \Rightarrow \quad J &= n\hbar \end{aligned}$$

Experimental confirmation Davisson-Germer experiment electrons of energy $E \simeq 1eV = 1.6 \times 10^{-19}\ J$ have de Broglie wavelength,

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E}} \quad \sim \quad 10^{-9}\ m$$

are diffracted by atoms in a crystal (atomic spacing $d \sim 10^{-9}\ m$). See Figure 9

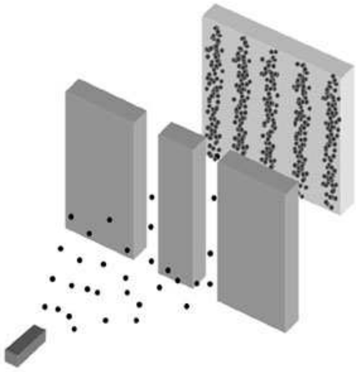


Figure 10: A double-slit experiment for electrons

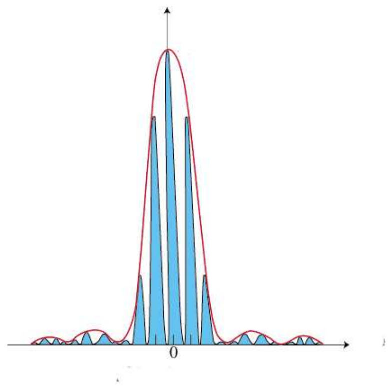


Figure 11: Double-slit diffraction pattern: plot of N against x

Double slit experiment

The optical double-slit diffraction experiment is reviewed in the Appendix.

- A source of electrons creates a beam which is diffracted through two slits (see Figure 10)
- The electrons are detected at a screen on the other side of the slits.
- Detectors count number, N, of electrons detected as a function of the transverse coordinate x. Resulting graph is shown in Figure 11. Identical to corresponding optical diffraction pattern.

Important points

- Diffraction effects are observed even when strength of the the beam is reduced so that there is only a single electron passing through the apparatus at any one time.
- We cannot predict with certainty where a given electron will be detected.
- Over a long time the total number N detected as a function of x gives a *probability distribution* for the position on the screen at which each electron is detected.

Suggests that the probability that the electron is detected at a particular point is given by $(\text{amplitude})^2$ of a wave.

2 Wave mechanics I

Describe particle by introducing a complex wave-function,

$$\psi \ : \qquad \mathbb{R}^3 \ \longrightarrow \ \mathbb{C}$$

such that the **probability** of finding a the particle in volume dV is,

$$|\psi(\mathbf{x})|^2 \ dV$$

Thus we should impose normalization condition,

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x})|^2 \ dV \ = \ 1$$

"The particle must be somewhere"

Then $\rho(\mathbf{x}) = |\psi(\mathbf{x})|^2$ is a **probability density**

Slightly different formulation: Consider possible wavefunctions,

$$\psi \; : \qquad \mathbb{R}^3 \;\longrightarrow\; \mathbb{C}$$

which are not identically zero. If,

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x})|^2 \, dV \;\; = \;\; \mathcal{N} \; < \; \infty$$

then we say that the wavefunction $\psi(\mathbf{x})$ is **normalisable**. The corresponding **normalised** wavefunction,

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

then obeys the normalisation condition,

$$\int_{\mathbb{R}^3} |\tilde{\psi}(\mathbf{x})|^2 \, dV \;\; = \;\; 1$$

Caveat For brevity we will not always denote a normalised wavefunction by $\tilde{\psi}$

Postulate Time evolution of wavefunction $\psi(\mathbf{x}, t)$ governed by the **Schrödinger equation**. For a non-relativistic particle of mass m moving in a potential $U(\mathbf{x})$ this reads,

$$i\hbar \frac{\partial \psi}{\partial t} \;\; = \;\; -\frac{\hbar^2}{2m}\nabla^2\psi \; + \; U(\mathbf{x})\psi \tag{9}$$

- First order in $t \Rightarrow \psi(\mathbf{x}, t)$ uniquely determined by Eqn (9) and initial value $\psi(\mathbf{x}, 0)$
- Second order in $\mathbf{x}$. Asymmetry between $\mathbf{x}$ and $t \Rightarrow$ Eqn (9) is non-relativistic.

Example Free particle $\Rightarrow U(\mathbf{x}) \equiv \mathbf{0}$. Schrödinger equation becomes,

$$i\hbar \frac{\partial \psi}{\partial t} \;\; = \;\; -\frac{\hbar^2}{2m}\nabla^2\psi \tag{10}$$

Look for **plane-wave** solution,

$$\psi_0(\mathbf{x}, t) \;\; = \;\; A \, \exp\left(i\mathbf{k} \cdot \mathbf{x} \; - \; i\omega t\right) \tag{11}$$

solves Eqn (10) provided we set,

$$\omega \;\; = \;\; \frac{\hbar|\mathbf{k}|^2}{2m} \tag{12}$$

Interpretation: use de Broglie relations for energy and momentum of the corresponding particle,

$$E = \hbar\omega \qquad , \qquad \mathbf{p} = \hbar\mathbf{k}$$

then, from (12), we find,

$$E = \frac{|\mathbf{p}|^2}{2m}$$

which is the correct dispersion relation for a free non-relativistic particle.

However note that plane-wave solution is **non-normalizable**,

$$|\psi_0|^2 = \psi_0\psi_0^* = |A|^2$$

$$\Rightarrow \qquad \int_{\mathbb{R}^3} |\psi_0|^2\, dV = |A|^2 \int_{\mathbb{R}^3} dV = \infty$$

We will discuss the correct resolution of this problem below.

Conservation of probability

Consider a wavefunction which is normalized at $t = 0$,

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x}, 0)|^2\, dV = 1. \tag{13}$$

Now allow ψ to evolve in time according to the Schrödinger equation (9).

We define,

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

Thus, from eqn (13), $\rho(\mathbf{x}, 0)$ is a correctly normalized probability density. We will now show that this remains true at all subsequent times, provided $|\psi(\mathbf{x}, t)| \to 0$ sufficiently fast as $|\mathbf{x}| \to \infty$.

Differentiating ρ wrt time we get,

$$\frac{\partial \rho(\mathbf{x},t)}{\partial t} \;=\; \frac{\partial}{\partial t}\left(|\psi|^2\right) = \frac{\partial \psi}{\partial t}\psi^* \;+\; \psi\frac{\partial \psi^*}{\partial t} \tag{14}$$

Now use the Schrödinger equation and its complex conjugate,

$$\begin{aligned} i\hbar\frac{\partial \psi}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2\psi \;+\; U(\mathbf{x})\psi \\ -i\hbar\frac{\partial \psi^*}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2\psi^* \;+\; U(\mathbf{x})\psi^* \end{aligned} \tag{15}$$

to eliminate time derivatives in (14) to obtain,

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{i\hbar}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] \\ &= \frac{i\hbar}{2m}\nabla\cdot\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right] \end{aligned}$$

This yields the "conservation equation",

$$\frac{\partial \rho}{\partial t} + \nabla\cdot\mathbf{j} \;=\; 0 \tag{16}$$

where we define the **probability current**,

$$\mathbf{j}(\mathbf{x},t) \;=\; -\frac{i\hbar}{2m}\;\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right]$$

- Consider a closed region $V \subset \mathbb{R}^3$ with boundary S, se Figure (12) The probability of finding the particle inside V is,

  $$P(t) \;=\; \int_V \rho(\mathbf{x},t)\;dV$$

  and we find that,

  $$\frac{dP(t)}{dt} \;=\; \int_V \frac{\partial \rho(\mathbf{x},t)}{\partial t}\,dV = -\int_V \nabla\cdot\mathbf{j}\;dV \;=\; -\int_S \mathbf{j}\cdot\mathbf{dS}$$

  where the second and third equalities follow from Eqn (16)and Gauss' theorem (also known as the divergence theorem) respectively.

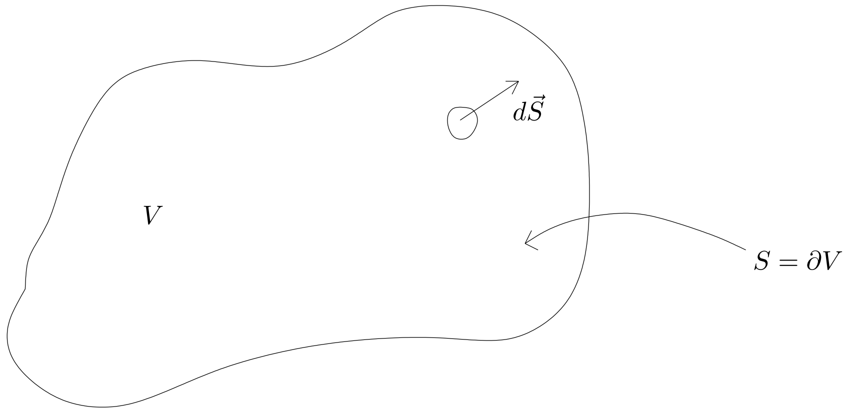


Figure 12: Gauss' Theorem

Interpretation: "Rate of change of the probability $P(t)$ of finding the particle in $V \equiv$ total flux of the probability current $\mathbf{j}(\mathbf{x},t)$ through the boundary S"

Integrating Eqn (16) over $\mathbb{R}^3$,

$$\begin{aligned}\int_{\mathbb{R}^3} \frac{\partial \rho}{\partial t} &= -\int_{\mathbb{R}^3} \nabla \cdot \mathbf{j}\, dV \\ &= -\int_{S^2_\infty} \mathbf{j} \cdot \mathbf{dS}\end{aligned}$$

where the second equality follows from Gauss' theorem. Here S^2_∞ is a sphere at infinity. More precisely, let S^2_R be a sphere in $\mathbb{R}^3$ centered at the origin having radius R. Then we define,

$$\int_{S^2_\infty} \mathbf{j} \cdot \mathbf{dS} = \lim_{R\to\infty} \int_{S^2_R} \mathbf{j} \cdot \mathbf{dS}$$

Provided that $\mathbf{j}(\mathbf{x},t) \to 0$ sufficiently fast as $|\mathbf{x}| \to \infty$, this surface term vanishes and we find,

$$\frac{d}{dt} \int_{\mathbb{R}^3} \rho(\mathbf{x},t)\, dV = \int_{\mathbb{R}^3} \frac{\partial \rho}{\partial t}\, dV = 0. \tag{17}$$

If the initial wavefunction is normalized at time $t = 0$,

$$\int_{\mathbb{R}^3} \rho(\mathbf{x},0)\, dV = \int_{\mathbb{R}^3} |\psi(\mathbf{x},0)|^2\, dV = 1,$$

then (17) implies that it remains normalised at all subsequent times,

$$\int_{\mathbb{R}^3} \rho(\mathbf{x},t)\, dV = \int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2\, dV$$

Equivalently $\rho(\mathbf{x},t)$ is a correctly normalized probability density at any time t.

Postulates of wave mechanics

- Any normalizable wavefunction $\psi(\mathbf{x}, t)$,

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \, dV \;\; = \;\; \mathcal{N} \; < \; \infty, \tag{18}$$

  (which is not identically zero), obeying the Schrödinger equation (9),

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

  corresponds to a possible state of the system.

- As before, the probability distribution for the particle position in this state is determined by the corresponding normalized wavefunction,

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

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

- Wave function $\psi_\alpha(\mathbf{x}, t) = \alpha\psi(\mathbf{x}, t)$ corresponds to the *same* state for all $\alpha \in \mathbb{C}^* = \mathbb{C} - \{0\}$.

Check: $\psi_\alpha(\mathbf{x}, t)$ obeys Schrödinger equation as $\psi(\mathbf{x}, t)$ does (by linearity of (9)) and is also normalizable,

$$\int_{\mathbb{R}^3} |\psi_\alpha(\mathbf{x}, t)|^2 \, dV \;\; = \;\; |\alpha|^2 \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \, dV = |\alpha|^2 \mathcal{N} \; < \; \infty$$

corresponding normalised wavefunction,

$$\tilde{\psi}_\alpha(\mathbf{x}, t) \;\; = \;\; \frac{\psi_\alpha(\mathbf{x}, t)}{\sqrt{|\alpha|^2 \mathcal{N}}} = \frac{\alpha}{|\alpha|}\tilde{\psi}(\mathbf{x}, t) \tag{19}$$

only depends on α through the complex phase $\alpha/|\alpha|$ and therefore yields the same probability distribution,

$$\rho(\mathbf{x}, t) \;\; = \;\; |\tilde{\psi}_\alpha(\mathbf{x}, t)|^2 = |\tilde{\psi}(\mathbf{x}, t)|^2$$

for all values of α

Principle of Superposition

- If $\psi_1(\mathbf{x}, t)$ and $\psi_2(\mathbf{x}, t)$ correspond to allowed states of the system then so does,

$$\psi_3(\mathbf{x}, t) \;=\; \alpha\psi_1(\mathbf{x}, t) + \beta\psi_2(\mathbf{x}, t) \neq 0$$

for arbitrary complex numbers α and β.

Proof

- ψ_3 satisfies (9) if ψ_1 and ψ_2 do.
- Also easy to check that ψ_3 satisfies normalizability condition (18) if ψ_1 and ψ_2 do.

…To see this let

$$\int_{\mathbb{R}^3} |\psi_1|^2 \, dV \;=\; \mathcal{N}_1 \;<\; \infty$$

$$\int_{\mathbb{R}^3} |\psi_2|^2 \, dV \;=\; \mathcal{N}_2 \;<\; \infty$$

For any two complex numbers z_1 and z_2. The triangle inequality states that,

$$|z_1 + z_2| \;\leq\; |z_1| + |z_2| \qquad\qquad \text{(A)}$$

also,

$$(|z_1| - |z_2|)^2 \geq 0 \;\;\Rightarrow\;\; 2|z_1||z_2| \leq |z_1|^2 + |z_2|^2 \qquad\qquad \text{(B)}$$

Apply these relations with $z_1 = \alpha\psi_1$ and $z_2 = \beta\psi_2$

$$\begin{aligned}
\int_{\mathbb{R}^3} |\psi_3|^2 \, dV \;&=\; \int_{\mathbb{R}^3} |\alpha\psi_1 + \beta\psi_2|^2 \, dV \\
&\leq\; \int_{\mathbb{R}^3} \left(|\alpha\psi_1| + |\beta\psi_2|\right)^2 \, dV \\
&=\; \int_{\mathbb{R}^3} \left(|\alpha\psi_1|^2 + 2|\alpha\psi_1||\beta\psi_2| + |\beta\psi_2|^2\right) \, dV \\
&\leq\; \int_{\mathbb{R}^3} \left(2|\alpha\psi_1|^2 + 2|\beta\psi_2|^2\right) \, dV \\
&=\; 2|\alpha|^2\mathcal{N}_1 + 2|\beta|^2\mathcal{N}_2 \;<\; \infty \qquad \square
\end{aligned}$$

- *Comments marked by *....* are beyond the scope of the course but might be useful.* *The superposition principle implies that the states of a quantum system naturally live in a **complex vector space**,
  - Usually infinite dimensional.
  - Extra structure: +ve definite inner product (+completeness[2]) $\Rightarrow$ Hilbert space.

The relation between states and vectors has two subtleties. First, the "zero vector" $\psi \equiv 0$ does not correspond to a state of the system. Also the correspondence between states and vectors is not one to one because, as explained above the vectors ψ and $\alpha\psi$ represent the same state for any non-zero complex number α. A more precise statement is that states correspond to *rays* in Hilbert space. A *ray*, $[\psi]$, is an equivalence class of a vector ψ under the equivalence relation*,

$$\psi_1 \sim \psi_2 \qquad \text{iff} \quad \psi_1 = \alpha\psi_2 \qquad \text{for some } \alpha \in \mathbb{C} - \{0\}$$

Stationary states

Time-dependent Schrödinger equation,

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

Seperation of variables,

$$\psi(\mathbf{x},t) \;=\; \chi(\mathbf{x})\, e^{-i\omega t}$$

Eliminate angular frequency ω using de Broglie relation $E = \hbar\omega$ to write,

$$\psi(\mathbf{x},t) \;=\; \chi(\mathbf{x}) \exp\left(-\frac{iEt}{\hbar}\right) \tag{20}$$

Substituting for (20) for ψ in the Schrödinger equation yields the **time-independent Schrödinger equation**,

$$-\frac{\hbar^2}{2m}\nabla^2\chi \;+U(\mathbf{x})\chi \;=\; E\chi \tag{21}$$

[2]This is a technical requirement for infinite sequences of vectors in a Hilbert space which demands that the limit of the sequence, if it exists, is contained in the space.

Remarks

- Typically (for boundstate problems) Eqn (21) has normalisable solutions only for certain allowed values of E.

- States of the special form (20) are known as **stationary states**. They are states of definite energy E. We will refer to $\chi(\mathbf{x})$ as the *stationary-state wavefunction* in the following.

- In a stationary state the position probability density,

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

  is time-independent.

- The general solution of the time-dependent Schrödinger equation is a *linear superposition* of stationary states,

$$\psi(\mathbf{x},t) \;=\; \sum_{n=1}^{\infty} a_n \chi_n(\mathbf{x}) \exp\left(-\frac{iE_n t}{\hbar}\right)$$

  where $\chi_n(\mathbf{x})$ solve (21) with $E = E_n$ and a_n are complex constants. In general this is not a stationary state and thus does not have definite energy. Instead the probability of measuring the particles energy as $E = E_n$ is proportional to $|a_n|^2$ (See Section 3).

Free particles

Free particle $\Rightarrow U(\mathbf{x}) \equiv 0$. Stationary state wave function $\chi(\mathbf{x})$ satisfies time-independent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\chi \;=\; E\chi \qquad (22)$$

This equation has a plane-wave solution,

$$\chi(\mathbf{x}) \;=\; A\;\exp(i\mathbf{k}\cdot\mathbf{x})$$

This satisfies (22) provided

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

- E only depends on $|\mathbf{k}|$ so there is a large *degeneracy* of states at each value of the energy.

- Complete wave-function,

$$\begin{aligned}\psi_{\mathbf{k}}(\mathbf{x},t) &= \chi(\mathbf{x})\exp\left(-\frac{iEt}{\hbar}\right)\\ &= A\ \exp(i\mathbf{k}\cdot\mathbf{x})\ \times\ \exp\left(-i\frac{\hbar|\mathbf{k}|^2 t}{2m}\right)\end{aligned}$$

  coincides with our earlier result (11,12).

As before the plane-wave solution is **non-normalizable** and thus does not give an acceptable probability density. There are several ways to resolve this problem. We will consider two of these,

- The plane wave solution $\psi_{\mathbf{k}}$ is treated as a limiting case of a **Gaussian wavepacket** describing a localized particle.

- The plane wave solution is interpreted as describing a **beam** of particles rather than a single particle

The Gaussian wave-packet

Schrödinger equation for $\psi(x,t)$ in one spatial dimension ($x\in\mathbb{R}$)

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

In one dimension we have a free particle stationary state,

$$\psi_k(x,t) = \exp(ikx)\ \times\ \exp\left(-i\frac{\hbar k^2 t}{2m}\right)$$

In one dimension the wavevector reduces to a single component $k\in\mathbb{R}$.

As in the previous section we can construct new solutions of the Schrödinger by taking a linear superposition,

$$\psi = \sum_n a_n\ \psi_{k_n}(x,t)$$

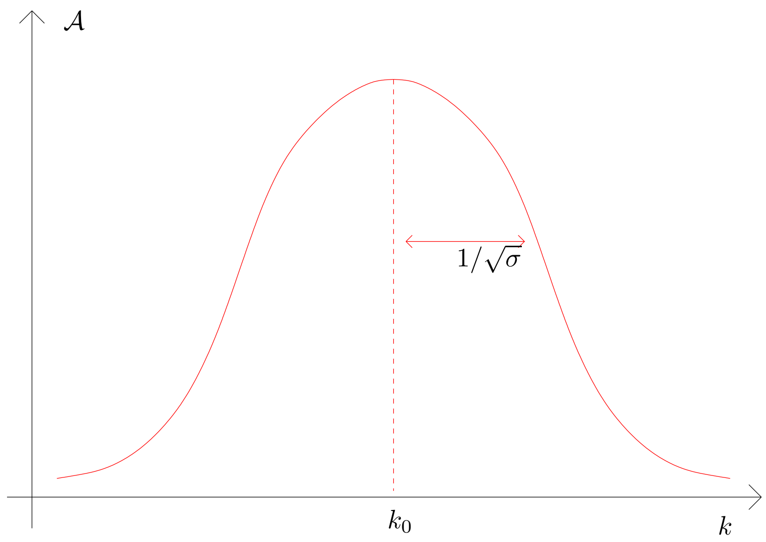


Figure 13: Gaussian distribution of wave numbers.

However, as k is a continuous variable we can also make a linear superposition by integration,

$$\begin{aligned} \psi(x,t) &= \int dk\ \mathcal{A}(k)\,\psi_k \\ &= \int dk\ \mathcal{A}(k)\ \times\ \exp(ikx)\ \exp\left(-i\frac{\hbar k^2 t}{2m}\right) \end{aligned} \tag{23}$$

where $\mathcal{A}(k)$ should go to zero sufficiently fast that the integral exists.

The Gaussian wave packet corresponds to the choice,

$$\mathcal{A}(k) = \exp\left[-\frac{\sigma}{2}(k-k_0)^2\right] \tag{24}$$

where $\sigma > 0$ which looks like a Gaussian distribution of wave numbers k centered at $k = k_0$ with width $\sim 1/\sqrt{\sigma}$ (See figure (13)) We will now evaluate the resulting wave-function by substituting (24) for $\mathcal{A}$ in (23),

$$\psi(x,t) = \int_{-\infty}^{+\infty} dk\ \exp\left(F(k)\right)$$

where the exponent in the integrand is,

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

Completing the square gives,

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

where

$$\alpha=\sigma+\frac{i\hbar t}{m} \qquad \beta=k_0\sigma+ix \qquad \delta=-\frac{\sigma}{2}k_0^2$$

Hence,

$$\begin{aligned}\psi(x,t) &= \exp\left(\frac{\beta^2}{2\alpha}+\delta\right)\int_{-\infty}^{+\infty} dk\,\exp\left(-\frac{1}{2}\alpha\left(k-\frac{\beta}{\alpha}\right)^2\right)\\ &= \exp\left(\frac{\beta^2}{2\alpha}+\delta\right)\int_{-\infty-i\nu}^{+\infty-i\nu} d\tilde{k}\,\exp\left(-\frac{1}{2}\alpha\tilde{k}^2\right)\end{aligned}$$

where $\tilde{k}=k-\beta/\alpha$ and $\nu=\Im[\beta/\alpha]$. The integral can be related to the standard Gaussian integral (Eqn (119) in the Appendix) by a straightforward application of the Cauchy residue theorem. An alternative, more elementary, approach to evaluating the integral is described in the Appendix. The result is,

$$\psi(x,t) \;=\; \sqrt{\frac{2\pi}{\alpha}}\;\times\;\exp\left(\frac{\beta^2}{2\alpha}+\delta\right)$$

- This wavefunction decays exponentially at $x\to\pm\infty$ and is therefore normalizable.

- The resulting position probability density is,

$$\rho(x,t) \;=\; |\tilde{\psi}(x,t)|^2=\tilde{\psi}(x,t)\tilde{\psi}^*(x,t)$$

  where $\tilde{\psi}$ is the normalised wavefunction corresponding to $\psi(x,t)$. After some algebra, we obtain,

$$\rho(x,t) \;=\; \frac{C}{\sqrt{\sigma^2+\frac{\hbar^2t^2}{m^2}}}\;\exp\left[-\frac{\sigma\left(x-\frac{\hbar k_0}{m}t\right)^2}{\sigma^2+\frac{\hbar^2t^2}{m^2}}\right].$$

  Exercise: The constant C is fixed by the normalization condition,

$$\int_{-\infty}^{+\infty} dx\;\rho(x,t)=1 \qquad\Rightarrow\qquad C=\sqrt{\frac{\sigma}{\pi}}$$

- $\rho(x,t)$ defines a **Gaussian probability distribution** for the position of the particle (see Figure (14)).

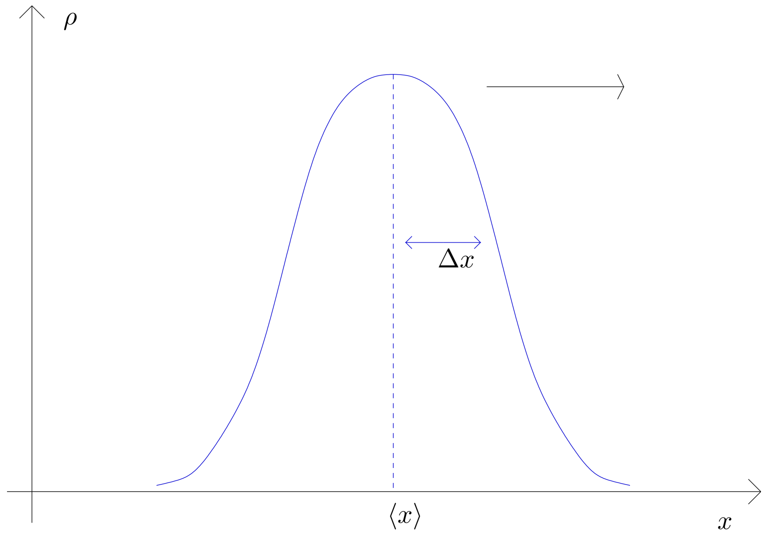


Figure 14: The probability distribution.

– The center $\langle x \rangle$ of the distribution corresponds to the average value of position.

$$\langle x \rangle = \frac{\hbar k_0}{m} t$$

which moves constant speed,

$$v = \frac{\hbar k_0}{m} = \frac{\langle p \rangle}{m}$$

Here $\langle p \rangle = \hbar k_0$ denotes the average value of the momentum.

– The width of the distribution, Δx (also known as the standard deviation) corresponds to the uncertainty in the measurement of position,

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

increases with time. (This is not a stationary state).

- Physically, the Gaussian wavepacket corresponds to a state in which the particle is localized near the point $\langle x \rangle$ with an uncertainty Δx in the measurement of its position.

- The plane wave-solution $\psi_k(x, t)$ is a limiting case of the Gaussian wavepacket where the uncertainty in position Δx becomes infinite. This an idealized state in which the momentum takes the definite value $p = \hbar k$. The uncertainty in the momentum of the particle, Δp, therefore vanishes. This is related to the Heisenberg uncertainty principle which we will discuss in Section 3.

The beam interpretation

Interpret free particle wave function,

$$\psi_{\mathbf{k}}(\mathbf{x},t) \;=\; A \;\exp(i\mathbf{k}\cdot\mathbf{x}) \;\times\; \exp\left(-i\frac{\hbar|\mathbf{k}|^2 t}{2m}\right)$$

as describing **a beam of particles** of momentum $\mathbf{p} = \hbar\mathbf{k}$ and energy,

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

- Here $\rho(\mathbf{x},t) = |\psi_{\mathbf{k}}(\mathbf{x},t)|^2 = |A|^2$ is now interpreted as the constant **average density of particles**.

- The probability current,

$$\begin{aligned}
\mathbf{j}(\mathbf{x},t) &= -\frac{i\hbar}{2m}\;(\psi^*_{\mathbf{k}}\nabla\psi_{\mathbf{k}} \;-\; \psi_{\mathbf{k}}\nabla\psi^*_{\mathbf{k}}) \\
&= -\frac{i\hbar}{2m} \;\times\; |A|^2 \;\times\; 2i\mathbf{k} \\
&= |A|^2 \;\times\; \frac{\hbar\mathbf{k}}{m} = |A|^2 \;\times\; \frac{\mathbf{p}}{m} \\
&= \text{average density} \;\times\; \text{velocity} \\
&= \text{average flux of particles}
\end{aligned}$$

Particle in an infinite potential well

Potential,

$$\begin{aligned}
U(x) &= 0 \qquad\qquad 0 < x < a \\
&= \infty \qquad\qquad \text{otherwise}
\end{aligned} \tag{25}$$

as shown in Figure (15). Stationary states,

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} \;+\; U(x)\chi = E\chi \tag{26}$$

- **Outside well**

$$U(x) = \infty \qquad \Rightarrow \qquad \chi(x) \equiv 0$$

otherwise $E = \infty$ from (26). Thus, as in classical physics, there is zero probability of finding the particle outside the well.

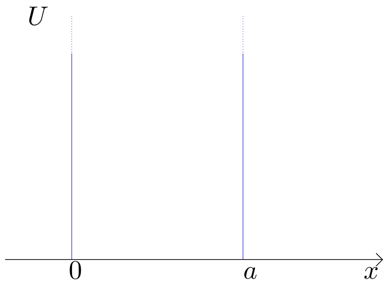


Figure 15: The infinite square well.

- **Inside well**

$$U(x) = 0 \qquad \Rightarrow \qquad -\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} = E\chi \tag{27}$$

Define $k = \sqrt{2mE/\hbar^2} > 0$. Equation (27) becomes,

$$\frac{d^2\chi}{dx^2} = -k^2\chi$$

General solution,

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

Boundary conditions from continuity of χ at $x = 0$ and $x = a$,

$$\chi(0) = \chi(a) = 0$$

- i) $\chi(0) = 0 \Rightarrow$ B=0
- ii) $\chi(a) = 0 \Rightarrow A\sin(ka) = 0 \Rightarrow ka = n\pi$ where $n = 1, 2, \ldots$

Thus solutions are,

$$\begin{aligned} \chi_n(x) &= A_n \sin\left(\frac{n\pi x}{a}\right) \qquad & 0 < x < a \\ &= 0 & \text{otherwise} \end{aligned}$$

- Normalization condition,

$$\int_{-\infty}^{+\infty} |\chi_n|^2 \, dx = |A_n|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) \, dx = \frac{|A_n|^2 a}{2} = 1$$

Thus we find,

$$A_n = \sqrt{\frac{2}{a}}$$

for all n.

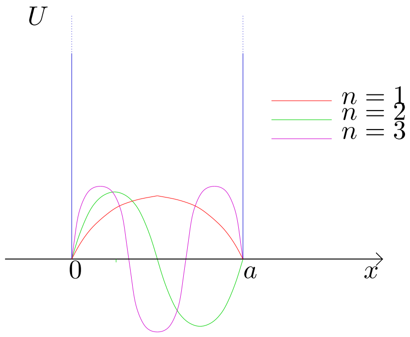


Figure 16: Lowest energy wavefunctions of the infinite square well.

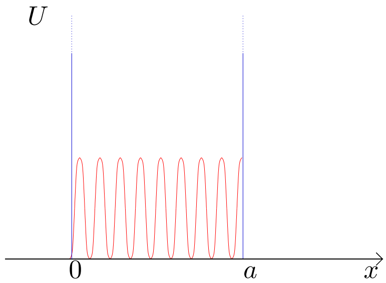


Figure 17: Wavefunction at large n.

- The corresponding energy levels are,

$$E = E_n \quad = \quad \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

for $n = 1, 2, \ldots$

  - Like Bohr atom, energy levels are **quantized**
  - Lowest energy level or groundstate,

$$E_1 \quad = \quad \frac{\hbar^2 \pi^2}{2ma^2} > 0$$

- The resulting wavefunctions are illustrated in Figure 16
  - Wave functions alternate between even and odd under reflection,

$$x \quad \rightarrow \quad \frac{a}{2} - x$$

  - Wavefunction $\chi_n(x)$ has $n+1$ zeros or *nodes* where $\rho_n(x) = |\chi_n|^2$ vanishes.
  - $n \to \infty$ limit. Correspondence principle: probability density approaches a constant $\equiv$ classical result (see Figure 17).

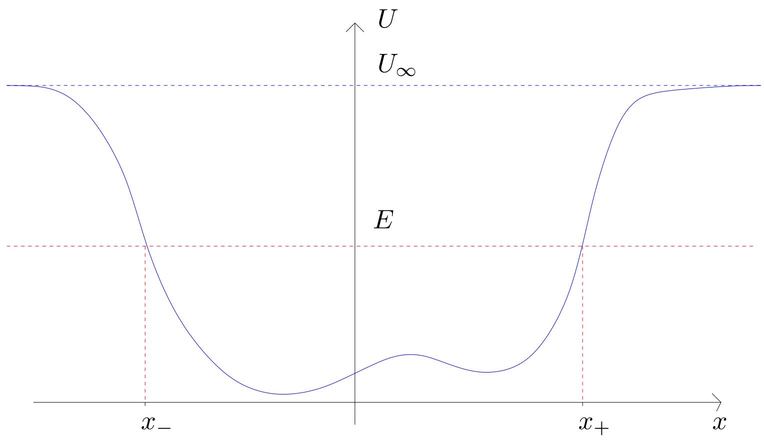


Figure 18: A generic boundstate problem.

General remarks on one-dimensional bound state problems

Consider a particle moving in one spatial dimension in the generic potential $U(x)$ plotted in Figure 18 with asymptotic values $U(x) \to U_\infty$ as $x \to \pm\infty$. Bound states correspond to a particle trapped in the well with $0 < E < U_\infty$

- **Classical mechanics** The particle follows a periodic trajectory $x(t)$ with turning points $x = x_\pm$ such that $U(x_\pm) = E$. Thus the classical particle is always found in the interval $[x_-, x_+]$.

- **Quantum mechanics** Stationary states obey,

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + U(x)\chi = E\chi \tag{28}$$

  - 2nd order linear ODE $\Rightarrow$ two linearly independent solutions; $\chi_1(x)$ and $\chi_2(x)$
  - For a bound state the particle must be localised near the well. Thus we demand a normalizable wavefunction,

$$\int_{-\infty}^{+\infty} |\chi|^2 \, dx < \infty$$

    $\Rightarrow \chi$ must vanish sufficiently fast as $x \to \pm\infty$.

    * How fast?

$$\int \frac{dx}{x^\delta} \sim \frac{1}{x^{\delta-1}}$$

      thus $|\chi(x)|^2$ must vanish faster than $1/x$ as $x \to \pm\infty$

Actual asymptotic behaviour of $\chi(x)$ as $x \to \infty$ determined by asymptotic form of Schrödinger equation (28)

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + U_\infty\chi \simeq E\chi \tag{29}$$

Define,

$$\kappa = \sqrt{\frac{2m(U_\infty - E)}{\hbar^2}} > 0$$

Note that κ is real by virtue of the bound state condition $E < U_\infty$. Eqn (29) can then be written as,

$$\frac{d^2\chi}{dx^2} = +\kappa^2\chi$$

with general solution,

$$\chi(x) = A\exp(+\kappa x) + B\exp(-\kappa x).$$

Thus the general form of the asymptotic wavefunction is

$$\chi(x) \to A_\pm \exp(+\kappa x) + B_\pm \exp(-\kappa x)$$

as $x \to \pm\infty$. For a normalizable wavefunction, we must choose a solution which decays (rather than grows) as $x \to \pm\infty$. Thus we must set $A_+ = B_- = 0$.

- Its not hard to see why these conditions lead to a discrete spectrum of boundstates. For each value of the energy E , we have two linearly independent solutions, $\chi_1(x; E)$ and $\chi_2(x; E)$. General solution,

$$\chi(x) = A\ [\chi_1(x; E) + \alpha\chi_2(x; E)]$$

  for complex constants A and α.

Normalizability $\Rightarrow$ Two independent conditions ($A_+ = B_- = 0$) for two unknowns: α and $E \Rightarrow$ isolated solutions $\Rightarrow$ Discrete spectrum.

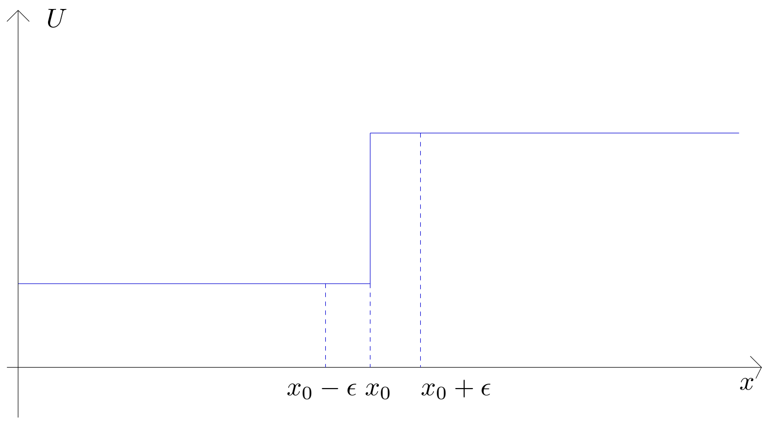


Figure 19: A discontinuous potential.

Further properties

Time-independent Schrödinger equation in one dimension,

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + U(x)\chi = E\chi \tag{30}$$

- **Continuity**
  - If $U(x)$ is smooth then so is $\chi(x)$.
  - If $U(x)$ has a finite discontinuity the $\chi(x)$ and $d\chi/dx$ remain continuous, but (30) $\Rightarrow d^2\chi/dx^2$ is discontinuous.
  - If $U(x)$ has an infinite discontinuity then $\chi(x)$ remains continuous but $d\chi/dx$ is discontinuous. Also note that $U(x) \equiv \infty \Rightarrow \chi(x) \equiv 0$ (cf infinite square-well)

To understand the second case, consider the discontinuous potential shown in Figure 19, Integrating (30) over the interval $[x_0 - \epsilon, x_0 + \epsilon]$,

$$\begin{aligned} \int_{x_0-\epsilon}^{x_0+\epsilon} \left[-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2}\right] dx &= \int_{x_0-\epsilon}^{x_0+\epsilon} (E - U(x))\chi(x)\, dx \\ \Rightarrow \quad \left.\frac{d\chi}{dx}\right|_{x_0+\epsilon} - \left.\frac{d\chi}{dx}\right|_{x_0-\epsilon} &= \mathcal{I}(\epsilon) \end{aligned}$$

where

$$\mathcal{I}(\epsilon) = \frac{2m}{\hbar^2}\int_{x_0-\epsilon}^{x_0+\epsilon} (E - U(x))\chi(x)\, dx$$

Easy to see that $\mathcal{I}(\epsilon) \to 0$ as $\epsilon \to 0$ (because integrand is bounded), $\Rightarrow d\chi(x)/dx$, and therefore $\chi(x)$ is continuous at $x = x_0$. Discontinuity of $d^2\chi/dx^2$ follows directly from Schrödinger equation (30)

- **Parity** Suppose spectrum of boundstates is **non-degenerate**

$$E_1 < E_2 < E_3 < \quad \ldots$$

If $U(-x) = U(x)$ we say that U is **reflection invariant**. In this case all stationary state wavefunctions must be either even or odd. In other words we must have $\chi(-x) = \pm\chi(x)$

Proof

  - Easy to see that time-independent Schrödinger equation (30) is reflection invariant. Thus if $\chi(x)$ is a solution of (30) with eigenvalue E then so is $\chi(-x)$.
  - Non-degeneracy of the spectrum then implies that $\chi(-x) = \alpha\chi(x)$ for some non-zero complex constant α.
  - For consistency,

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

  Thus $\alpha^2 = 1 \Rightarrow \alpha = \pm 1$ as required $\Box$.

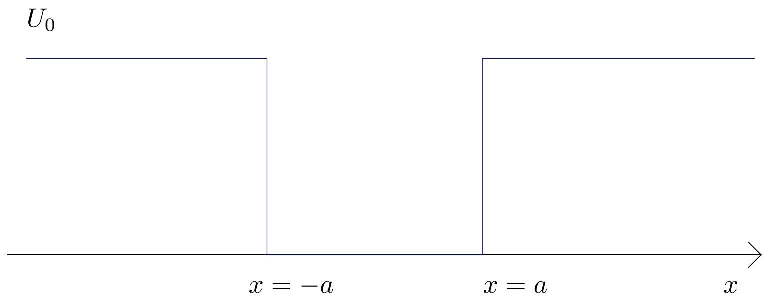


Figure 20: The finite square well.

The finite potential well

Potential,

$$\begin{aligned} \text{Region I}: \quad U(x) &= 0 \qquad -a < x < a \\ \text{Region II}: \quad &= U_0 \qquad \text{otherwise} \end{aligned} \tag{31}$$

as shown in Figure 20.

Stationary states obey,

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + U(x)\chi = E\chi \tag{32}$$

consider even parity boundstates

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

obeying $0 \leq E \leq U_0$ Define real constants

$$k = \sqrt{\frac{2mE}{\hbar^2}} \geq 0 \qquad \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} \geq 0 \tag{33}$$

- **Region I** The Schrödinger equation becomes,

$$\frac{d^2\chi}{dx^2} = -k^2\chi$$

The general solution takes the form,

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

even parity condition,

$$\chi(-x) = \chi(x) \quad \Rightarrow \quad B = 0 \quad \Rightarrow \quad \chi(x) = A\cos(kx)$$

- **Region II**

$$\frac{d^2\chi}{dx^2} = \kappa^2\chi$$

The general solution for $x > +a$,

$$\chi(x) = C\exp(+\kappa x) + D\exp(-\kappa x) \tag{34}$$

Normalizability $\Rightarrow C = 0$ thus,

$$\chi(x) = D\exp(-\kappa x)$$

for $x > +a$.

Similarly for $x < -a$ (by even parity) we have,

$$\chi(x) = D\exp(+\kappa x)$$

Imposing continuity of $\chi(x)$ at $x = +a$ gives,

$$A\cos(ka) = D\exp(-\kappa a) \tag{35}$$

and continuity of $\chi'(x)$ at $x = +a$ gives,

$$-kA\sin(ka) = -\kappa D\exp(-\kappa a) \tag{36}$$

Dividing Eqn (36) by (35) yields,

$$k\tan(ka) = \kappa \tag{37}$$

From the definitions in Eqn (33) we find a second equation relating k and κ,

$$k^2 + \kappa^2 = \frac{2mU_0}{\hbar^2} \tag{38}$$

Now define rescaled variables $\xi = ka$ and $\eta = \kappa a$ and the constant $r_0 = \sqrt{(2mU_0)/\hbar^2} \cdot a$. Equations (37) and (38) become,

$$\xi\tan\xi = \eta \tag{39}$$

$$\xi^2 + \eta^2 = r_0^2 \tag{40}$$

It is not possible to solve these transcendental equations in closed form. Instead one may easily establish some qualitative features of the solutions via a graphical solution as shown in Figure 21. Here the two equations are plotted in the (ξ, η)-plane.

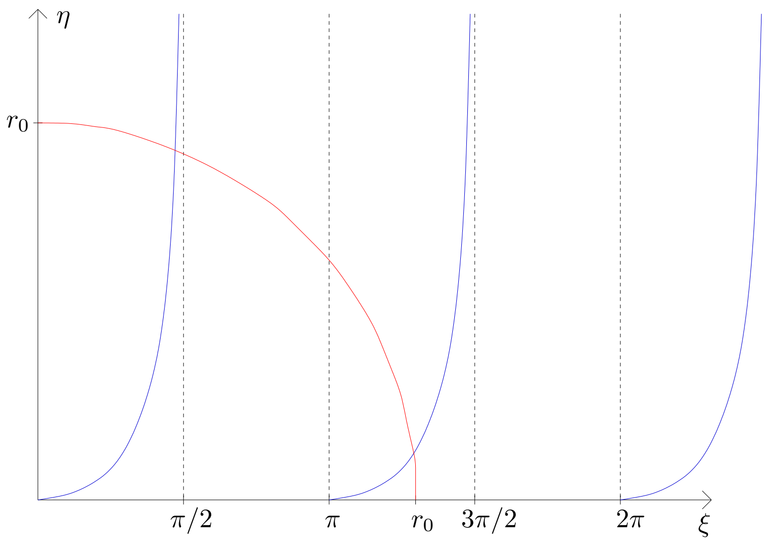


Figure 21: Graphical Solution.

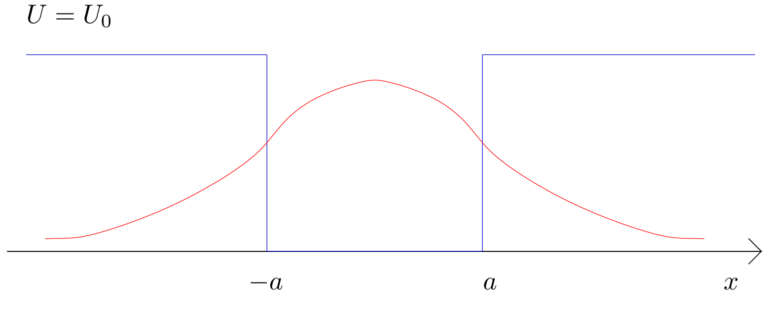


Figure 22: Groundstate probability density for the finite square well.

The solutions correspond to the intersection points $\{\xi_1, \xi_2, \ldots, \xi_K\}$.

- Number of solutions increases with the depth of the well as $r_0 = \sqrt{(2mU_0)/\hbar^2} \cdot a$ grows.

- Each solution determines an energy level via,

$$E_n = \frac{\hbar^2 \xi_n^2}{2ma^2}$$

- Always have at least one solution for $U_0 > 0$. In fact it can be proved that attractive potentials in one dimension *always* have at least one bound state.

- From the graph we see that,

$$(n-1)\pi \leq \xi_n \leq \left(n - \frac{1}{2}\right)\pi$$

- Limit of infinite square well $U_0 \to \infty \Rightarrow r_0 \to \infty \Rightarrow \xi_n \to (n - 1/2)\pi$. Resulting energy levels,

$$E_n = \frac{\hbar^2 \xi_n^2}{2ma^2} = \frac{\hbar^2 (2n-1)^2 \pi^2}{8ma^2}$$

  Agrees with earlier result for even levels of infinite well, width $2a$.

- **Still to do**

  - Use boundary conditions (35) and (36) to eliminate constant D in terms of A.
  - Find A by imposing the normalization condition,

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

  Resulting groundstate probability distribution $|\chi_1(x)|^2$ is plotted in Figure 22

  Note that there is a non-zero probability of finding particle in the classically forbidden region $|x| > a$.

Exercise Check that wavefunction goes over to our previous results in the limit of infinite well $U_0 \to \infty$.

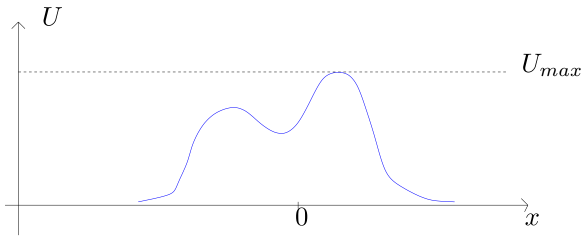


Figure 23: The potential barrier.

Scattering and Tunneling

- Consider particle scattering on the potential barrier shown in Figure 23,
  - Maximum barrier height $U = U_{\rm max}$.
  - Barrier localised near $x = 0$. $U(x) \to 0$ rapidly as $x \to \pm\infty$.

Particle of mass m and total energy E incident on the barrier from left. What happens?

Classical mechanics Two cases,

- $E > U_{\rm max} \Rightarrow$ particle gets over barrier and proceeds to $x = +\infty$.
- $E < U_{\rm max} \Rightarrow$ particle reflected back towards $x = -\infty$.

Quantum mechanics *Ideally* consider localised Gaussian wavepacket with normalised wavefunction, $\psi(x,t)$,

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

- Wavepacket centered at $x = x_0(t) << 0$ at initial time $t << 0$ with average momentum $\langle p \rangle > 0$ as shown in Figure 24.
- Evolve with Schrödinger equation, to get final state wave function for $t >> 0$. Resulting probability distribution shown in Figure 25,

Define reflection and transmission coefficients,

$$\begin{aligned} R &= \lim_{t\to\infty} \int_{-\infty}^{0} |\psi(x,t)|^2\, dx \\ T &= \lim_{t\to\infty} \int_{0}^{+\infty} |\psi(x,t)|^2\, dx \end{aligned}$$

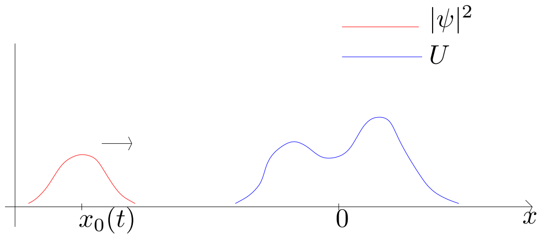


Figure 24: Initial state of wavepacket.

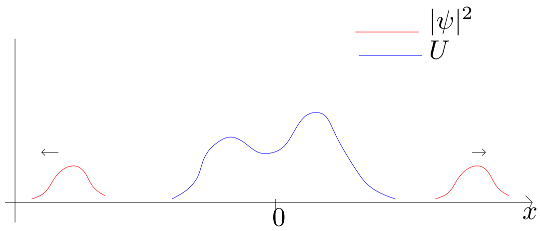


Figure 25: Final state of wavepacket.

which measure the probabilities of the particle being reflected or transmitted respectively. As total probability is conserved we have,

$$R + T \;=\; \int_{-\infty}^{+\infty} |\psi(x,t)|^2 \, dx = 1$$

In practice this is too complicated so will work with *non-normalizable* stationary states instead using the "beam interpretation" (see discussion on p24). Both approaches yield the same answers.

Beam interpretation in one dimension

Plane-wave solution,

$$\psi_k(x,t) \;=\; \chi(x)\;\exp\left(-i\frac{\hbar k^2 t}{2m}\right)$$

where,

$$\chi(x) \;=\; A\;\exp(ikx)$$

interpreted as a beam of particles with momentum $p = \hbar k$. Avererage density of particles is $|A|^2$. Particle flux/probability current,

$$\begin{aligned} j &= -\frac{i\hbar}{2m}\left[\chi^* \frac{d\chi}{dx} \;-\; \chi\frac{d\chi^*}{dx}\right] \\ &= |A|^2 \;\times\; \frac{\hbar k}{m} \end{aligned}$$

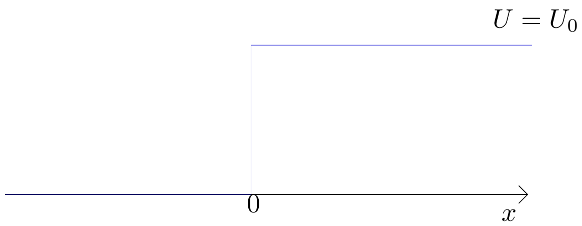


Figure 26: A potential step.

A potential step

Consider a beam of particles of mass m scattering on the potential step shown in Figure 26,

$$\begin{array}{lrcll} \text{Region I}: & U(x) & = & 0 & x < 0 \\ \text{Region II}: & & = & U_0 & x > 0 \end{array}$$

Stationary states have form,

$$\psi(x,t) \;=\; \chi(x)\exp\left(-i\frac{E}{\hbar}t\right)$$

where $\chi(x)$ obeys,

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} \;+\; U(x)\chi = E\chi \qquad (41)$$

We will start by considering the case where $E > U_0$ and comment on the other case at the end.

Region I The Schrödinger equation becomes,

$$\frac{d^2\chi}{dx^2} \;=\; -k^2\chi$$

where,

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

For $E > 0$, the general solution takes the form,

$$\chi(x) \;=\; A\exp(ikx) + B\exp(-ikx) \qquad (42)$$

Particular solutions,

- $\chi_+(x) = A\exp(ikx)$ corresponds to a beam of particles incident on the step from $x = -\infty$ with momentum $p = \hbar k$. The corresponding particle flux is given by the probability current,

$$j_+ \;=\; |A|^2 \;\times\; \frac{\hbar k}{m}$$

- $\chi_-(x) = B\exp(-ikx)$ corresponds to a beam of reflected particles moving to the left (ie towards from $x = -\infty$) with momentum $p = -\hbar k$. The corresponding particle flux is,

$$j_- \;=\; -|B|^2 \;\times\; \frac{\hbar k}{m}$$

In our scattering problem we have incident particles from the left and also expect some particles to be reflected off the barrier. Thus we retain the general solution,

$$\chi(x) \;=\; A\exp(ikx) + B\exp(-ikx) \qquad \text{for} \;\; x < 0 \tag{43}$$

as our wavefunction for $x < 0$.

The resulting expression corresponds to a superposition of the two beams χ_+ and χ_-. Total flux,

$$\begin{aligned} j &= -\frac{i\hbar}{2m}\left[\chi^*\frac{d\chi}{dx} - \chi\frac{d\chi^*}{dx}\right] \\ &= \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right) \\ &= j_+ \;+\; j_- \end{aligned}$$

Cross-terms vanish.

Region II Here we are considering the case $E > U_0$. The Schrödinger equation becomes,

$$\frac{d^2\chi}{dx^2} \;=\; -k'^2\chi$$

where,

$$k' \;=\; \sqrt{\frac{2m(E-U_0)}{\hbar^2}} \;\geq 0$$

The general solution is

$$\chi(x) \;=\; C\exp(ik'x) + D\exp(-ik'x) \tag{44}$$

Particular solutions,

- $\tilde{\chi}_+(x) = C\exp(ik'x)$ corresponds to a beam of particles in region $x > 0$ moving towards $x = +\infty$. This corresponds to a *transmitted wave* in the scattering problem.
- $\tilde{\chi}_-(x) = D\exp(-ik'x)$ corresponds to a beam of particles incident on the barrier from the right (ie from $x = +\infty$). This solution is not relevant for our scattering problem and thus we set $D = 0$ and choose the solution,

$$\chi(x) \;=\; C\,\exp(ik'x) \qquad\qquad \text{for}\;\; x > 0 \tag{45}$$

.

It remains to enforce the continuity of the stationary-state wavefunction and its derivative at $x = 0$. Comparing the solutions (43) and (45) we find,

- Continuity of $\chi(x)$ at $x = 0 \Rightarrow$

$$A + B \;=\; C \tag{46}$$

- Continuity of $\chi'(x)$ at $x = 0 \Rightarrow$

$$ikA - ikB \;=\; ik'C \tag{47}$$

Solving (46) and (47) we get,

$$B = \frac{k - k'}{k + k'}\,A \qquad\qquad C = \frac{2k}{k + k'}A$$

Interpretation Identify the particle flux corresponding to each component of the wave function,

- Incoming flux

$$j_{\rm inc} \;=\; j_+ = \frac{\hbar k}{m}\,|A|^2$$

- Reflected flux

$$j_{\rm ref} \;=\; -j_- = +\frac{\hbar k}{m}\,|B|^2 = \frac{\hbar k}{m}\left(\frac{k - k'}{k + k'}\right)^2\,|A|^2$$

- Transmitted flux

$$j_{\rm tr} \;=\; \frac{\hbar k'}{m}\,|C|^2 = \frac{\hbar k'}{m}\frac{4k^2}{(k + k')^2}\,|A|^2$$

Determine the portion of the incident beam which is reflected/transmitted. Corresponding probabilities,

$$
\begin{aligned}
R &= \frac{j_{\rm ref}}{j_{\rm inc}} = \left(\frac{k-k'}{k+k'}\right)^2 \\
T &= \frac{j_{\rm tr}}{j_{\rm inc}} = \frac{4kk'}{(k+k')^2}.
\end{aligned}
$$

Note that the undetermined constant A cancels out. Can check that,

$$
R+T = \frac{(k-k')^2+4kk'}{(k+k')^2} = 1
$$

Unlike the classical case, there is still a finite probability of reflection for $E > U_0$. However as $E \to \infty$ we have $k-k' \to 0$ which imples $R \to 0$, $T \to 1$.

Finally we consider the case $E < U_0$ where the classical particle is always reflected. In this case the Region I solution (43) remains unchanged. In Region II the time-independent Schrödinger equation becomes,

$$
\frac{d^2\chi}{dx^2} = \kappa^2\chi
$$

where

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

The general solution of this equation is then written

$$
\chi(x) = \mathcal{E}\exp(+\kappa x) + F\exp(-\kappa x) \tag{48}
$$

. The growing exponential is unphysical (non-normalizable), hence we must set $\mathcal{E}=0$. The Region II solution is therefore

$$
\chi(x) = F\exp(-\kappa x) \qquad \text{for} \quad x>0 \tag{49}
$$

. Particle flux,

$$
j_{\rm tr} = -\frac{i\hbar}{2m}\left[\chi^*\frac{d\chi}{dx} - \chi\frac{d\chi^*}{dx}\right] = 0
$$

Now impose boundary conditions on the solutions (43) and (49) at $x=0$,

- Continuity of $\chi(x)$ at $x = 0 \Rightarrow$

$$A + B = F \tag{50}$$

- Continuity of $\chi'(x)$ at $x = 0 \Rightarrow$

$$ikA - ikB = -\kappa F \tag{51}$$

Solving (50) and (51) we get,

$$B = \left(\frac{ik + \kappa}{ik - \kappa}\right) A \qquad\qquad F = \frac{2ik}{ik - \kappa} A$$

Particle flux,

$$j_{\rm tr} = -\frac{i\hbar}{2m}\left[\chi^* \frac{d\chi}{dx} - \chi \frac{d\chi^*}{dx}\right] = 0$$

Interpretation Identify the particle flux corresponding to each component of the wave function,

- Incoming flux

$$j_{\rm inc} = j_+ = \frac{\hbar k}{m} |A|^2$$

- Reflected flux

$$j_{\rm ref} = -j_- = +\frac{\hbar k}{m} |B|^2 = \frac{\hbar k}{m} |A|^2 = j_{\rm inc}$$

- Transmitted flux

$$j_{\rm tr} = 0$$

Thus the whole beam is reflected,

$$R = \frac{j_{\rm ref}}{j_{\rm inc}} = 1$$
$$T = \frac{j_{\rm tr}}{j_{\rm inc}} = 0$$

As in the classical case, the particle is certain to be reflected. Wave function decays in the classically forbidden region as shown in Figure 27.

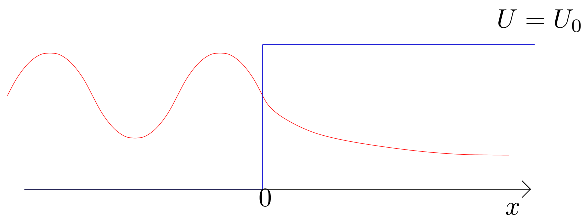


Figure 27: Wavefunction for potential step.

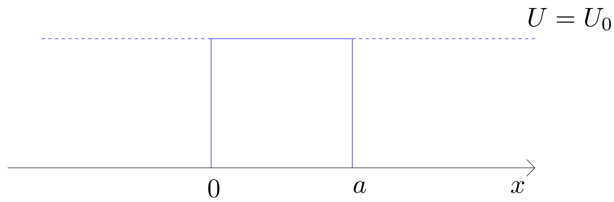


Figure 28: A square barrier.

Tunneling

Particle scattering on a square barrier

Consider incident particle with energy $E < U_0$. Look for stationary state wave function obeying,

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

Define real constants

$$k = \sqrt{\frac{2mE}{\hbar^2}} \geq 0 \qquad\qquad \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} \geq 0$$

Solution,

$$\begin{aligned} \chi(x) &= \exp(ikx) + A\ \exp(-ikx) && x < 0 \\ &= B\ \exp(-\kappa x) + C\ \exp(+\kappa x) && 0 < x < a \\ &= D\ \exp(+ikx) && x > a \end{aligned}$$

- A and D are coefficients of reflected and transmitted waves respectively.
- Coefficient of incident wave $\exp(+ikx)$ normalised to unity.

Boundary conditions

- Continuity of $\chi(x)$ at $x = 0$

$$1 + A = B + C$$

- Continuity of $\chi'(x)$ at $x = 0$

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

- Continuity of $\chi(x)$ at $x = a$

$$B \exp(-\kappa a) + C \exp(+\kappa a) = D \exp(ika)$$

- Continuity of $\chi'(x)$ at $x = a$

$$-\kappa B \exp(-\kappa a) + \kappa C \exp(+\kappa a) = ikD \exp(ika)$$

Thus we have four equations for the four unknown constants A, B, C and D. Solution,

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

Transmitted flux,

$$j_{\rm tr} = \frac{\hbar k}{m} |D|^2$$

Incident flux,

$$j_{\rm tr} = \frac{\hbar k}{m}$$

Thus the transmission probability is given as,

$$\begin{aligned} T = \frac{j_{\rm tr}}{j_{\rm inc}} &= |D|^2 \\ &= \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa a) + 4k^2\kappa^2} \end{aligned} \tag{52}$$

Hints for getting (52)

$$D = \frac{-4i\kappa k}{\exp(ika)L}$$

where

$$\begin{aligned} L &= (\kappa - ik)^2 e^{+\kappa a} - (\kappa + ik)^2 e^{-\kappa a} \\ &= G + iH \end{aligned}$$

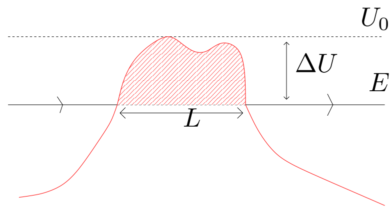


Figure 29: A generic barrier.

with

$$G = 2(\kappa^2 - k^2)\sinh(\kappa a) \qquad H = -4\kappa k \cosh(\kappa a)$$

and,

$$\sinh(\kappa a) = \frac{1}{2}\left(e^{+\kappa a} - e^{-\kappa a}\right), \qquad \cosh(\kappa a) = \frac{1}{2}\left(e^{+\kappa a} + e^{-\kappa a}\right)$$

Thus

$$|D|^2 \;=\; \frac{16k^2\kappa^2}{G^2 + H^2} = \frac{4k^2\kappa^2}{(k^2+\kappa^2)^2\sinh^2(\kappa a) + 4k^2\kappa^2}$$

as claimed.

Low energy particle scattering on very tall barrier $U_0 - E >> \hbar^2/2ma^2$. These conditions imply $\kappa a >> 1$. In this case (52) simplifies to give,

$$T \;\simeq\; f\left(\frac{k^2}{\kappa^2}\right)\,\exp(-2\kappa a) = f\left(\frac{E}{U_0 - E}\right)\,\exp\left[-\frac{2a}{\hbar}\sqrt{2m(U_0 - E)}\right] \qquad (53)$$

Eqn (53) is a particular case of of a general approximate formula for a barrier of maximum height $U_0 >> E$ and width L,

$$T \;\simeq\; \exp\left[-\frac{2L}{\hbar}\sqrt{2m\Delta U}\right]$$

where $\Delta U = U_0 - E$. See Figure 29.

Application: Radioactive decay

Consider radioactive decay of an isotope N_Z^A. Here A and Z are the atomic weight and atomic number respectively (see Appendix). The decay proceeds through emission of an α-particle (ie a Helium nucleus),

$$N_Z^A \;\rightarrow\; N_{Z-2}^{A-4} \;+\; He_2^4$$

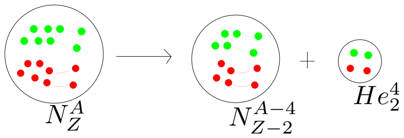


Figure 30: Radioactive decay.

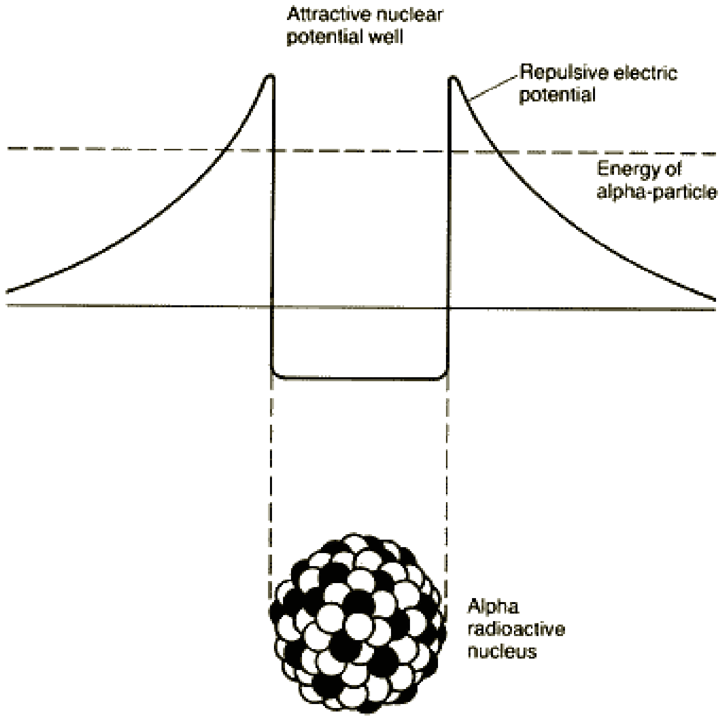


Figure 31: The nuclear potential.

In a simple model of this process due to Gammow the α-particle feels a potential due to the other particles in the nucleus which has the form shown in Figure (31). Potential has a short-range attractive component due to the strong nuclear force and a long-range component due to the electrostatic repulsion between the protons in the α-particle and those in the nucleus.

- Decay occurs when α-particle "tunnels" through potential barrier.

$$\mathrm{Half-life} \quad \sim \quad \frac{1}{T}$$

- Half-life therefore exponentially dependent on the height and width of the barrier.

- This model accounts for the huge range of half-lives of radioactive isotopes found in nature (and created in the lab). These range from 3×10^{-7} s to 2×10^{17} years!

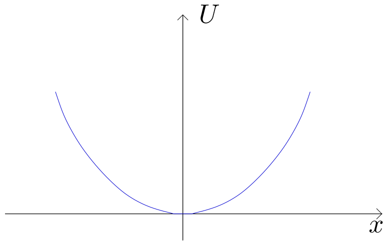


Figure 32: Harmonic oscillator potential.

The Harmonic Oscillator

The Harmonic oscillator potential (see Figure 32),

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

Classical mechanics Newton's second law implies $\ddot{x} = -\omega^2 x$. The general solution,

$$x(t) = A \sin(\omega t + \delta)$$

Particle oscillates around minimum at $x = 0$, with period $T = 2\pi/\omega$.

Quantum mechanics Stationary states described by time-independent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \chi = E\chi \tag{54}$$

subject to the normalizability condition,

$$\int_{-\infty}^{+\infty} dx\, |\chi(x)|^2 < \infty$$

Define rescaled variables

$$\xi^2 = \frac{m\omega}{\hbar}\, x^2 \qquad \epsilon = \frac{2E}{\hbar\omega}$$

In terms of these variables Eqn (54) becomes,

$$-\frac{d^2\chi}{d\xi^2} + \xi^2\chi = \epsilon\chi \tag{55}$$

For the special case $\epsilon = 1$ find normalizable solution by inspection,

$$\chi(x) = \exp\left(-\frac{1}{2}\xi^2\right)$$

Check

$$
\begin{aligned}
\frac{d\chi}{d\xi} &= -\xi\ \exp\left(-\frac{1}{2}\xi^2\right) \\
\frac{d^2\chi}{d\xi^2} &= (\xi^2-1)\ \exp\left(-\frac{1}{2}\xi^2\right) \\
\Rightarrow \qquad -\frac{d^2\chi}{d\xi^2} + \xi^2\chi &= \chi \qquad \Box
\end{aligned}
$$

Corresponding wavefunction is,

$$
\chi_0(x) = A\ \exp\left(-\frac{m\omega}{2\hbar}x^2\right)
$$

with energy $E = \hbar\omega/2$.

Now look for general solution of the form,

$$
\begin{aligned}
\chi(x) &= f(\xi)\ \exp\left(-\frac{1}{2}\xi^2\right) \\
\Rightarrow \qquad \frac{d\chi}{d\xi} &= \left(\frac{df}{d\xi} - \xi\ f\right)\ \exp\left(-\frac{1}{2}\xi^2\right) \\
\Rightarrow \qquad \frac{d^2\chi}{d\xi^2} &= \left(\frac{d^2f}{d\xi^2} - 2\xi\frac{df}{d\xi} + (\xi^2-1)\ f\right)\ \exp\left(-\frac{1}{2}\xi^2\right)
\end{aligned}
$$

Then (55) becomes,

$$
\frac{d^2f}{d\xi^2} - 2\xi\frac{df}{d\xi} + (\epsilon-1)f = 0 \tag{56}
$$

Can check that $f=1$ is a solution when $\epsilon = 1$.

Apply standard power series method ($\xi = 0$ is a regular point). Set,

$$
f(\xi) = \sum_{n=0}^{\infty} a_n\ \xi^n \tag{57}
$$

Plugging the series (57) into (56) gives the recurrence relation,

$$
(n+1)(n+2)\,a_{n+2} - 2n\,a_n + (\epsilon-1)a_n = 0
$$

$$
\Rightarrow \qquad a_{n+2} = \frac{(2n-\epsilon+1)}{(n+1)(n+2)}\ a_n \tag{58}
$$

NB Potential is reflection invariant $\Rightarrow \chi(-x) = \pm\chi(x) \Rightarrow f(-\xi) = \pm f(\xi)$. Hence, with $m = 1, 2, 3\ldots$, can set,

- **either** $a_n = 0$ for $n = 2m-1 \Leftrightarrow f(-\xi) = f(\xi)$.
- **or** $a_n = 0$ for $n = 2m \Leftrightarrow f(-\xi) = -f(\xi)$.

Derivation of (58)

$$\begin{aligned} f(\xi) &= \sum_{n=0}^{\infty} a_n\, \xi^n \qquad (57) \\ \frac{df}{d\xi} &= \sum_{n=0}^{\infty} n\, a_n\, \xi^{n-1} \\ \xi\frac{df}{d\xi} &= \sum_{n=0}^{\infty} n\, a_n\, \xi^n \end{aligned}$$

Then

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

Finally,

$$\begin{aligned} \frac{d^2 f}{d\xi^2} - 2\xi\frac{df}{d\xi} + (\epsilon-1)f &= \sum_{n=0}^{\infty} [(n+1)(n+2)\, a_{n+2} \\ &\qquad -2n\, a_n + (\epsilon-1)a_n]\; \xi^n \end{aligned}$$

Thus

$$\frac{d^2 f}{d\xi^2} - 2\xi\frac{df}{d\xi} + (\epsilon-1)f = 0 \qquad (56)$$

implies,

$$(n+1)(n+2)\, a_{n+2} - 2n\, a_n + (\epsilon-1)a_n = 0$$

There are two possibilities

- The series (57) terminates. In other words $\exists\, N > 0$ such that $a_n = 0\ \forall\, n > N$.
- The series (57) does not terminate. In other words $\nexists\, N > 0$ such that $a_n = 0\ \forall\, n > N$.

In fact the second possibility does not yield normalizable wave functions.

Why? Suppose series (57) does not terminate. The consider the large-ξ behaviour of the function,

$$f(\xi) \;=\; \sum_{n=0}^{\infty} a_n\, \xi^n.$$

This is determined by the asymptotic behaviour of the coefficients a_n as $n \to \infty$. If the series does not terminate then (58) determines the asymptotic behaviour of the coefficients as,

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

This is identical to the asymptotic behaviour of the coefficients of the Taylor series for the function,

$$\exp(+\xi^2) \;=\; \sum_{m=0}^{\infty} \frac{\xi^{2m}}{m!} \tag{59}$$

Indeed if we write the series as,

$$\exp(+\xi^2) \;=\; \sum_{n=0}^{\infty} b_n\, \xi^n$$

with coefficients,

$$\begin{aligned} b_n &= \frac{1}{m!} \qquad \text{for } \; n = 2m \\ &= 0 \qquad \text{for } \; n = 2m+1 \end{aligned}$$

we immediately find (for $n = 2m$)

$$\frac{b_{n+2}}{b_n} \;=\; \frac{(n/2)!}{(n/2+1)!} \;=\; \frac{2}{n+2} \;\to\; \frac{2}{n}$$

as $n \to \infty$. The fact that the coefficients of the two series (57) and (59) have the same behaviour as $n \to \infty$ means that the respective sums have the same asymptotics as $\xi \to \infty$. Thus, if the series does not terminate, we must have,

$$f(\xi) \;\sim\; \exp(+\xi^2)$$

or equivalently,

$$\chi(x) = f(\xi)\; \exp\left(-\frac{\xi^2}{2}\right) \;\sim\; \exp\left(+\frac{\xi^2}{2}\right)$$

as $\xi \to \infty$, which corresponds to a non-normalizable wavefunction. $\Box$.

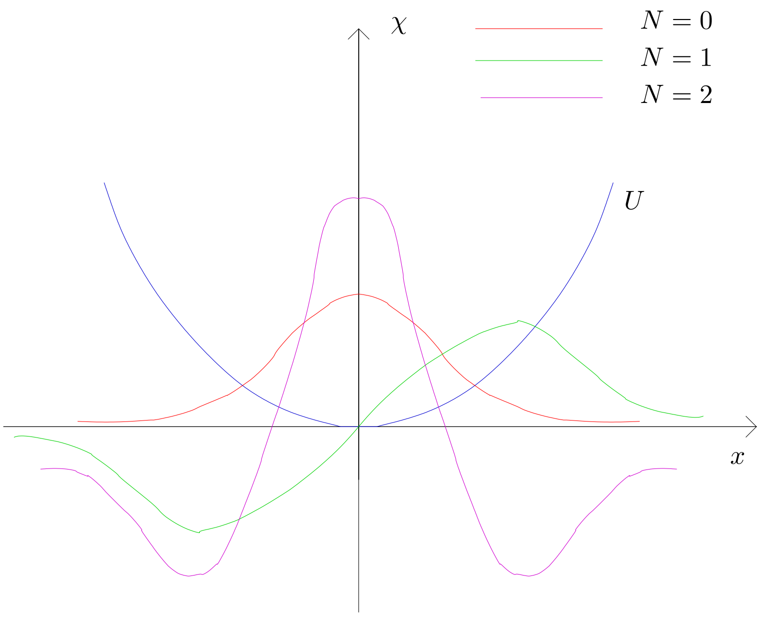


Figure 33: Harmonic oscillator wavefunctions.

Therefore the series must terminate and $\exists$ an integer $N \geq 0$ such that $a_{N+2} = 0$ with $a_N \neq 0$. Thus, from (58) we find,

$$(2N - \epsilon + 1) \;=\; 0$$

Recalling that $\epsilon = 2E/\hbar\omega$ we immediately obtain the energy spectrum of the quantum harmonic oscillator,

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

- Zero-point energy $E = \hbar\omega/2$.
- Energy levels are equally spaced with $E_{N+1} - E_N = \hbar\omega$. System can absorb or emit photons whose angular frequency is an integer multiple of $\omega \Rightarrow$ equally-spaced spectral lines

The corresponding wave-function is,

$$\chi_N(x) \;=\; f_N(\xi)\;\exp\left(-\frac{\xi^2}{2}\right)$$

- $f_N(\xi)$ is an even/odd function of $\xi = \sqrt{m\omega x^2/\hbar}$ for N even/odd,

$$\chi_N(-x) \;=\; (-1)^N\;\chi_N(x)$$

- $f_N(\xi)$ is an N'th order polynomial (known as the N'th Hermite polynomial) in ξ and therefore the wavefunction has N nodes or zeros.

- First few levels (see Figure 33),

N	E_N	$\chi_N(x)$
0	$\frac{1}{2}\hbar\omega$	$\exp\left(-\frac{\xi^2}{2}\right)$
1	$\frac{3}{2}\hbar\omega$	$\xi\ \exp\left(-\frac{\xi^2}{2}\right)$
2	$\frac{5}{2}\hbar\omega$	$(1-2\xi^2)\ \exp\left(-\frac{\xi^2}{2}\right)$
3	$\frac{7}{2}\hbar\omega$	$\left(\xi-\frac{2}{3}\xi^3\right)\ \exp\left(-\frac{\xi^2}{2}\right)$

3 Operators and Observables

Some features of Classical mechanics:

- The trajectory of a particle is described by measurable quantities or **observables**. Examples,
  - Position: $\mathbf{x} = (x_1, x_2, x_3)$.
  - Momentum: $\mathbf{p} = (p_1, p_2, p_3)$.
  - Energy:
  $$E = \frac{|\mathbf{p}|^2}{2m} + U(\mathbf{x})$$
  - Angular momentum: $\mathbf{L} = \mathbf{x} \times \mathbf{p}$

  All observables take definite real values at each moment of time which can, in principle, be measured with arbitary accuracy.

- The **state** of the system is specified by giving $\mathbf{x}$ and $\mathbf{p}$ at initial time $t = t_0$.
- Subsequent time evolution is deterministic (uniquely determined by equations of motion).

Quantum mechanics Contrasting features,

- State of the system at any given time is described by a complex wavefunction $\psi(\mathbf{x}, t)$.
- Time evolution of the wave function is determined by the time-dependent Schrödinger equation.
- Observables correspond to **operators**. An operator $\hat{O}$, acts on a complex valued function $f : \mathbb{R}^3 \to \mathbb{C}$ and produces a new such function, $g = \hat{O}f : \mathbb{R}^3 \to \mathbb{C}$. It is therefore a map from the space of such functions to itself. In Quantum Mechanics we will only be interested in *linear* operators[3] such that the corresponding map is linear,
  $$\hat{O}\left[\alpha_1 f_1 + \alpha_2 f_2\right] = \alpha_1 \hat{O} f_1 + \alpha_2 \hat{O} f_2$$
  for any complex-valued functions f_1 and f_2 and complex numbers α_1 and α_2.

[3]From now we will use the term operator to mean linear operator.

In general, the two functions $f(\mathbf{x})$ and $g(\mathbf{x}) = \hat{O}f(\mathbf{x})$ are linearly independent. However an important special case occurs when $g(\mathbf{x}) = \hat{O}f(\mathbf{x}) = \lambda f(\mathbf{x})$ for some complex number λ ($\forall\ \mathbf{x} \in \mathbb{R}^3$). In this case we say that the function $f(\mathbf{x})$ is an **eigenfunction** of the operator $\hat{O}$ with **eigenvalue** λ.

Example: Energy

- Not all states have definite energy.
- States which do are called stationary states. Wavefunction,

$$\psi(\mathbf{x}, t) \;=\; \chi(\mathbf{x})\ \exp\left(-i\frac{Et}{\hbar}\right)$$

where χ obeys,

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

It is instructive to rewrite this time-independent Schrödinger equation as,

$$\hat{H}\chi(\mathbf{x}) \;=\; E\chi(\mathbf{x}) \tag{60}$$

where we define the **Hamiltonian operator**,

$$\hat{H} \;=\; -\frac{\hbar^2}{2m}\,\nabla^2 \;+\; U(\mathbf{x}).$$

Explicitly, the function $g = \hat{H}f$ is

$$g(\mathbf{x}) \;=\; -\frac{\hbar^2}{2m}\,\nabla^2 f(\mathbf{x}) \;+\; U(\mathbf{x})f(\mathbf{x})$$

The time-independent Schrödinger equation then states that,

- The stationary-state wave-function $\chi(\mathbf{x})$ is an eigenfunction of the Hamiltonian operator $\hat{H}$ with eigenvalue E.

General feature of QM

Each observable O corresponds to an operator $\hat{O}$. States where the observable takes a definite value λ (at some fixed time) correspond to wavefunctions $\psi_\lambda(\mathbf{x})$ which are eigenfunctions of $\hat{O}$ with eigenvalue λ,

$$\hat{O}\psi_\lambda(\mathbf{x}) \;=\; \lambda\psi_\lambda(\mathbf{x}) \qquad\qquad \forall\ \ \mathbf{x} \in \mathbb{R}^3.$$

Examples

- **Momentum** in three dimensions is represented by the vector of operators $\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$ where

$$\begin{aligned}\hat{p}_1 &= -i\hbar\,\frac{\partial}{\partial x_1}\\ \hat{p}_2 &= -i\hbar\,\frac{\partial}{\partial x_2}\\ \hat{p}_3 &= -i\hbar\,\frac{\partial}{\partial x_3}\end{aligned}$$

or more concisely $\hat{\mathbf{p}} = -i\hbar\nabla$.

Check In classical mechanics the energy and momentum of a free particle of mass m are related as,

$$E = \frac{|\mathbf{p}|^2}{2m}$$

In QM the corresponding operators obey the same relation,

$$\frac{1}{2m}\hat{\mathbf{p}}\cdot\hat{\mathbf{p}} = \frac{(-i\hbar)^2}{2m}\nabla\cdot\nabla = -\frac{\hbar^2}{2m}\nabla^2 = \hat{H}_{\text{free}}$$

where $\hat{H}_{\text{free}}$ denotes the Hamiltonian for the case of a free particle (ie $U(\mathbf{x}) = 0$).

Eigenfunctions States $\psi_{\mathbf{p}}(\mathbf{x})$ of definite momentum $\mathbf{p}$ are eigenfunctions of the operator $\hat{\mathbf{p}}$,

$$\Rightarrow \qquad -i\hbar\nabla\psi_{\mathbf{p}}(\mathbf{x}) = \mathbf{p}\psi_{\mathbf{p}}(\mathbf{x})$$

Integrating this relation we obtain,

$$\psi_{\mathbf{p}}(\mathbf{x}) = A\,\exp\left(i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar}\right)$$

where A is an undetermined complex constant. Using the de Broglie relation $\mathbf{p} = \hbar\mathbf{k}$ we obtain

$$\psi_{\mathbf{p}}(\mathbf{x}) = A\,\exp\left(i\mathbf{k}\cdot\mathbf{x}\right)$$

which is just the plane-wave solution of the time-independent Schrödinger equation for a feee particle discussed earlier.

– Plane wave solution of wave vector $\mathbf{k}$ corresponds to a state of definite momentum $\mathbf{p} = \hbar\mathbf{k}$.

– Momentum eigenstates are therefore *non-normalisable*.

– Notice that eigenvalue $\mathbf{p}$ of $\hat{\mathbf{p}}$ is a continuous variable. We say that $\hat{\mathbf{p}}$ has a *continuous spectrum*. In contrast, the Hamiltonian operator relevant for boundstate problems always has a *discrete spectrum*. We verified this directly by solving the time-independent Schrödinger equation in the previous Section.

- **Position** in three dimensions, $\mathbf{x} = (x_1, x_2, x_3)$, corresponds to the operator $\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$. The action of the operator $\hat{x}_1$ is simply multiplication by the number x_1,

$$\hat{x}_1\, f(\mathbf{x}) \quad = \quad x_1\, f(\mathbf{x})$$

for all $\mathbf{x} \in \mathbb{R}^3$ and for any function $f(\mathbf{x})$ and similarly for the other components $\hat{x}_2$ and $\hat{x}_3$. Functions of the operator $\hat{\mathbf{x}}$ behave in the same way. In particular,

$$U(\hat{\mathbf{x}})\, f(\mathbf{x}) \quad = \quad U(\mathbf{x})\, f(\mathbf{x})$$

Eigenfunctions In one dimension, we have a single position operator $\hat{x}$ such that $\hat{x}f(x) = xf(x)$ for all x and for any function f. To construct a state where the particle has definite position $x = x_0$ we must solve the eigenvalue problem and find a wavefunction $\psi_{x_0}(x)$ obeying,

$$\hat{x}\psi_{x_0}(x) = x\psi_{x_0}(x) \quad = \quad x_0\psi_{x_0}(x) \tag{61}$$

for all $x \in \mathbb{R}$.

Equation (61) cannot be satisfied for any ordinary function of x (except $\psi_{x_0}(x) \equiv 0$ which is unphysical). However, it can be satisfied by the **Dirac δ-function** (see IB Methods) which formally obeys the equation,

$$x\delta(x - x_0) \quad = \quad x_0\delta(x - x_0)$$

Aside: We can verify this relation by multiplying both sides by an arbitrary function $f(x)$ and integrating over x,

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

Now evaluate the integrals on both sides to find that both sides are equal to $x_0 f(x_0)$

Thus the wavefunction $\psi_{x_0}(x) = \delta(x-x_0)$ represents a state of definite position $x = x_0$. The norm of this state,

$$|\psi_{x_0}(x)|^2 \quad \sim \quad \delta^2(x-x_0) \tag{62}$$

has an infinite spike at $x = x_0$ in accord with this interpretation but the integral of δ^2 does not exist, so the wavefunction is non-normalizable.

State of definite position $\mathbf{x} = \mathbf{X} = (X_1, X_2, X_3)$ in three dimensions corresponds to the wavefunction,

$$\Psi_{\mathbf{X}}(\mathbf{x}) \quad = \quad \delta^{(3)}(\mathbf{x}-\mathbf{X}) = \delta(x_1-X_1)\delta(x_2-X_2)\delta(x_3-X_3)$$

As before this is non-normalizable.

- Angular momentum is represented by the operator,

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

In components we have,

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

We will discuss the eigenvalues and eigenfunctions of $\hat{\mathbf{L}}$ in Section 4.

Hermitian operators

This Section has strong overlaps with the discussion of "Sturm-Liouville Theory" in IB Methods (see Chapter 5 of Methods Notes)

Given an observable O, the eigenvalues λ of the corresponding operator $\hat{O}$ determine the possible values the observable can take. An obvious requirement is that these should be real numbers. A sufficient condition for this is that $\hat{O}$ should be a **self-adjoint** or **Hermitian** operator[4]

Definition A linear operator is said to be **Hermitian** if, for any pair of normalizable functions f, $g : \mathbb{R}^3 \to \mathbb{C}$ we have,

$$\int_{\mathbb{R}^3} f^*(\mathbf{x})\ \hat{O}g(\mathbf{x})\ dV \quad = \quad \int_{\mathbb{R}^3} \left(\hat{O}f(\mathbf{x})\right)^*\ g(\mathbf{x})\ dV \qquad (63)$$

Recall that, for f and g to be normalizable, we require the existence of the integrals,

$$\int_{\mathbb{R}^3} |f(\mathbf{x})|^2\ dV \quad < \quad \infty, \qquad\qquad \int_{\mathbb{R}^3} |g(\mathbf{x})|^2\ dV \quad < \quad \infty$$

This in turn requires that f, $g \to 0$ as $|\mathbf{x}| \to \infty$ which will be important in the following.

- If $\hat{O} = h(\mathbf{x})\hat{\mathbb{I}}$ where $\hat{\mathbb{I}}$ is the unit operator (ie $\hat{\mathbb{I}}\psi(\mathbf{x}) = \psi(\mathbf{x})$ for all functions $\psi(\mathbf{x})$) then,

$$\hat{O}\ \text{ Hermitian } \ \Leftrightarrow\ h(\mathbf{x})\ \text{ real}$$

- $\hat{O}_1$, $\hat{O}_2$ Hermitian $\Rightarrow \hat{O}_1+\hat{O}_2$ and eg $\hat{O}_1^2$ Hermitian but $\hat{O}_1\hat{O}_2$ not necessarily Hermitian.

Matrix analogy Consider N component complex vectors $\mathbf{v} \in \mathbb{C}^N$

- linear map $\mu : \mathbb{C}^N \to \mathbb{C}^N$

$$\mu(\alpha_1\mathbf{v}_1 + \alpha_2\mathbf{v}_2) \quad = \quad \alpha_1\mu(\mathbf{v}_1) + \alpha_2\mu(\mathbf{v}_2)$$

[4]The term "self-adjoint" is favored by mathematicians who sometimes mean something slightly different when they talk about an Hermitian operator. However, the term "Hermitian" is universally used by physicists as synonym for "self-adjoint" and we will adopt this convention here.

corresponds to an $N \times N$ **matrix** M:
If $\mathbf{v}' = \mu(\mathbf{v})$ then, in components,

$$v_i' = M_{ij} v_j$$

- ***Roughly** operators are the generalisation of matrices relevant for the (usually) infinite-dimensional vector spaces of (wave)functions which appear in quantum mechanics.*

In general the eigenvalues of an $N \times N$ complex matrix, M are complex numbers. To obtain real eigenvalues we need to restrict to **Hermitian Matrices** *see IA Algebra and Geometry.*

- For any complex matrix define **Hermitian conjugate** $M^\dagger = (M^T)^*$. In components,

$$\left(M^\dagger\right)_{ij} = M_{ji}^*$$

- **Definition** A matrix is **Hermitian** if $M^\dagger = M$. In components,

$$M_{ji}^* = M_{ij}$$

- If M is Hermitian, then, for any two complex vectors $\mathbf{v}$ and $\mathbf{w}$,

$$M_{ji}^* v_i^* w_j = M_{ij} v_i^* w_j$$

or,

$$v_i^* M_{ij} w_j = M_{ji}^* v_i^* w_j$$

- Thus for a Hermitian matrix we have, Equivalently

$$\mathbf{v}^\dagger \cdot M\mathbf{w} = (M\mathbf{v})^\dagger \cdot \mathbf{w}$$

for any two complex vectors $\mathbf{v}$ and $\mathbf{w}$ (where $\mathbf{v}^\dagger = (\mathbf{v}^T)^*$). Compare with (63).

Examples of Hermitian operators:

- The momentum operator, $\hat{\mathbf{p}} = -i\hbar\nabla$. Verify Eqn (63) for $\hat{O} = \hat{p}_1 = -i\hbar\partial/\partial x_1$

$$\begin{aligned}\text{LHS of (63)} &= \int_{\mathbb{R}^3} f^*(\mathbf{x})\ \hat{p}_1 g(\mathbf{x})\ dV \\ &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \left[-i\hbar\ f^*(\mathbf{x})\ \frac{\partial g}{\partial x_1}\right]\ dx_1\, dx_2\, dx_3\end{aligned}$$

Integrating by parts we get,

$$\begin{aligned}\text{LHS of (63)} &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \left[\left(-i\hbar\ \frac{\partial f}{\partial x_1}\right)^*\ g(\mathbf{x})\right]\ dx_1\, dx_2\, dx_3 \\ &= \int_{\mathbb{R}^3} \left(\hat{p}_1 f(\mathbf{x})\right)^*\ g(\mathbf{x})\ dV \quad = \quad \text{RHS of (63)}\ \Box.\end{aligned}$$

Here we used the fact that f and g both vanish as $|\mathbf{x}| \to \infty$ to drop the surface term arising after integration by parts. The other components of $\hat{\mathbf{p}}$ are Hermitian by an identical argument.

- The position operator $\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$ is obviously Hermitian, as is any real function $U(\hat{\mathbf{x}})$

- The Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\hat{\mathbf{x}}) = \frac{|\hat{\mathbf{p}}|^2}{2m} + U(\hat{\mathbf{x}})$$

is also manifestly Hermitian when written in terms of the Hermitian operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{x}}$. Alternatively we can check the Hermitian property for the kinetic piece of the Hamiltonian, $\hat{H}_{\rm kin} = -(\hbar^2/2m)\nabla^2$ as follows,

$$\begin{aligned}\int_{\mathbb{R}^3} f^*(\mathbf{x})\ \hat{H}_{\rm kin} g(\mathbf{x})\ dV &= -\frac{\hbar^2}{2m}\int_{\mathbb{R}^3} f^*(\mathbf{x})\ \nabla^2 g(\mathbf{x})\ dV \\ &= -\frac{\hbar^2}{2m}\int_{\mathbb{R}^3} \left(\nabla^2 f(\mathbf{x})\right)^*\ g(\mathbf{x})\ dV \qquad \text{By Green's identity} \\ &= \int_{\mathbb{R}^3} \left(\hat{H}_{\rm kin} f(\mathbf{x})\right)^*\ g(\mathbf{x})\ dV\ \ \Box\end{aligned}$$

Again the vanishing of f and g as $|\mathbf{x}| \to \infty$ was essential for neglecting surface terms.

Properties of Hermitian matrices

See Part IA Algebra and Geometry

- The eigenvalues of a Hermitian matrix are **real**
- Eigenvectors $\mathbf{u}_n$ of a Hermitian matrix corresponding to distinct eigenvalues are **orthogonal** with respect to the usual scalar product,

$$\mathbf{u}_n^\dagger \cdot \mathbf{u}_m \;=\; 0 \qquad \text{for} \;\; n \neq m$$

Consequence The eigenvectors $\mathbf{u}_n$, $n = 1, 2, \ldots, N$, of an $N \times N$ Hermitian matrix span $\mathbb{C}^N$. This is equivalent to **completeness**:

- Any vector $\mathbf{v}$ can be expanded as,

$$\mathbf{v} \;=\; \sum_{i=1}^{N} a_n \, \mathbf{u}_n$$

for some chice of complex coefficients $\{a_n\}$.

Properties of Hermitian operators

Suppose $\hat{O}$ is an Hermitian operator with a discrete spectrum. It has eigenvalues $\{\lambda_n\}$ and corresponding normalized eigenfunctions $\{u_n(\mathbf{x})\}$ for $n = 1, 2, 3, \ldots$. Thus,

$$\hat{O} u_n(\mathbf{x}) \;=\; \lambda_n u_n(\mathbf{x}) \qquad\qquad \int_{\mathbb{R}^3} |u_n(\mathbf{x})|^2 \; dV \;=\; 1$$

For convenience we will assume that the spectrum of $\hat{O}$ is *non-degenerate*. In other words we assume that,

$$\lambda_n \neq \lambda_m \qquad \forall \;\; n \neq m$$

Now consider two eigenfunctions u_m and u_n and define,

$$\begin{aligned} \mathcal{I}_{mn} \;&=\; \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; \hat{O} u_n(\mathbf{x}) \; dV \\ &=\; \lambda_n \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; u_n(\mathbf{x}) \; dV \end{aligned} \tag{64}$$

on the other hand, as $\hat{O}$ is Hermitian we also have,

$$\begin{aligned}
\mathcal{I}_{mn} &= \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; \hat{O} u_n(\mathbf{x}) \; dV \\
&= \int_{\mathbb{R}^3} \left(\hat{O} u_m(\mathbf{x})\right)^* \; u_n(\mathbf{x}) \; dV \\
&= \lambda_m^* \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; u_n(\mathbf{x}) \; dV
\end{aligned} \tag{65}$$

Now subtracting Equation (65) from Equation (64) we obtain,

$$(\lambda_n - \lambda_m^*) \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; u_n(\mathbf{x}) \; dV = 0 \tag{66}$$

There are two cases

I: $m = n$ Then (66) reads,

$$(\lambda_m - \lambda_m^*) \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; u_m(\mathbf{x}) \, dV = (\lambda_m - \lambda_m^*) = 0$$

and hence $\lambda_m = \lambda_m^*$ for all m. Thus we have established that,

- The eigenvalues of an Hermitian operator are **real**

The proof of this statement can be extended to include the case where the spectrum of the operator is degenerate and even the case of operators with continuous spectra but this is beyond the scope of the course.

II: $m \neq n$ Then (66) reads,

$$(\lambda_n - \lambda_m^*) \int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; u_n(\mathbf{x}) \; dV = 0$$

Now as the spectrum is non-degenerate we know that $\lambda_m \neq \lambda_n$ and, as λ_n is real this imples that $\lambda_m^* \neq \lambda_n$. Therefore we must have,

$$\int_{\mathbb{R}^3} u_m^*(\mathbf{x}) \; u_n(\mathbf{x}) \; dV = 0$$

for $m \neq n$ and we have established that,

- The eigenfunctions belonging to distinct eigenvalues of an Hermitian operator are **orthogonal** with respect to the scalar product,

$$(f(\mathbf{x}), g(\mathbf{x})) = \int_{\mathbb{R}^3} f^*(\mathbf{x}) \; g(\mathbf{x}) \; dV$$

As the eigenfunctions are normalised and orthogonal we have,

$$\int_{\mathbb{R}^3} u_m^*(\mathbf{x})\; u_n(\mathbf{x})\; dV \;=\; \delta_{mn} \qquad (67)$$

where δ_{mn} is the Kronecker delta.

Another important property of Hermitian operators analogous to the completeness property for Hermitian matrices described above is,

- **Completeness** Any normalizable wavefunction $\psi(\mathbf{x})$ can be expanded as,

$$\psi(\mathbf{x}) \;=\; \sum_{n=1}^{\infty} a_n u_n(\mathbf{x})$$

  for some choice of complex constants $\{a_n\}$.

This is hard to prove in general. A one-dimensional example where we can make contact with results from the Methods course is,

Infinite square well Normalised stationary wavefunctions (see p25),

$$\begin{aligned} \chi_n &= \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right) && \text{for } 0 < x < a \\ &= 0 && \text{otherwise} \end{aligned}$$

Completeness for the eigenfunctions of the Hamiltonian operator is the statement that any wave function $\chi(x)$ can be expanded (for $0 < x < a$) as,

$$\begin{aligned} \chi(x) &= \sum_{n=1}^{\infty} a_n\; \chi_n(x) \\ &= \sqrt{\frac{2}{a}}\,\sum_{n=1}^{\infty} a_n\; \sin\left(\frac{n\pi x}{a}\right) \end{aligned}$$

Completeness is therefore equivalent to the existence of a (sine) *Fourier series* [5] for $\chi(x)$.

[5] More precisely $\chi(x)$ as defined on the interval $0 < x < a$ can be extended to an odd function on $-a < x < a$ and then to a periodic function on the line which has a Fourier sine series. See IB Methods notes 1.5.1.

Momentum eigenstates in one-dimension In one dimension the momentum operator $\hat{p} = -i\hbar d/dx$ has eigenstates (with a convenient choice of overall constant),

$$\psi_p(x) \;=\; \frac{1}{2\pi}\exp(ikx)$$

with continuous eigenvalue $p = \hbar k$. The analog of completeness is,

$$\psi(x) \;=\; \frac{1}{2\pi}\int_{-\infty}^{\infty} f(k)\;\exp(ikx)\;dk \tag{68}$$

which is equivalent to the existence of the *Fourier transform* $f(k)$ of $\psi(x)$. The analog of the orthogonality relation is,

$$\begin{aligned}\int_{-\infty}^{\infty}\psi^*_{p'}(x)\;\psi_p(x)\;dx \;&=\; \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\exp\left(i(k-k')x\right)\;dx \\ &=\; \frac{1}{2\pi}\;\delta(k-k')\end{aligned} \tag{69}$$

The last equality is the integral representation of the Dirac δ-function discussed in IB Methods.

Some consequences of completeness and orthogonality.

- Given a wavefunction $\psi(\mathbf{x})$ expanded in terms of the normalised eigenfunctions of the operator $\hat{O}$ as,

$$\psi(\mathbf{x}) \;=\; \sum_{n=1}^{\infty} a_n u_n(\mathbf{x})$$

The coefficient a_n is given by the formula,

$$a_n \;=\; \int_{\mathbb{R}^3} u_n^*\;\psi(\mathbf{x})\;dV$$

Proof

$$\begin{aligned}\text{RHS} \;&=\; \int_{\mathbb{R}^3} u_n^* \sum_{m=1}^{\infty} a_m u_m(\mathbf{x})\;dV \\ &=\; \sum_{m=1}^{\infty} a_m \int_{\mathbb{R}^3} u_n^*(\mathbf{x})\;u_m(\mathbf{x})\;dV \\ &=\; \sum_{m=1}^{\infty} a_m\;\delta_{mn} \;=\; a_n \qquad \square\end{aligned}$$

- We can calculate the normalization integral of the wavefunction $\psi(\mathbf{x})$ as,

$$\begin{aligned}\int_{\mathbb{R}^3} \psi^*(\mathbf{x})\, \psi(\mathbf{x})\, dV &= \int_{\mathbb{R}^3} \left(\sum_{n=1}^{\infty} a_n\, u_n(\mathbf{x})\right)^* \left(\sum_{m=1}^{\infty} a_m\, u_m(\mathbf{x})\right) dV \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} a_n^*\, a_m \int_{\mathbb{R}^3} u_n^*(\mathbf{x})\, u_m(\mathbf{x})\, dV \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} a_n^*\, a_m\, \delta_{mn} \\ &= \sum_{n=1}^{\infty} |a_n|^2\end{aligned}$$

Thus for a *normalised* wavefunction $\psi(\mathbf{x})$ we have,

$$\sum_{n=1}^{\infty} |a_n|^2 = 1 \tag{70}$$

The Postulates of Quantum Mechanics

I Every state of the system at a given time is described by a (normalizable) wavefunction $\psi(\mathbf{x})$.

- ψ contains all physical information about the system.
- Any (normalizable) wavefunction corresponds to a possible state of the system.

II Each observable quantity O corresponds to an Hermitian operator $\hat{O}$. The outcome of a measurement of O is always one of the *eigenvalues* of $\hat{O}$.

Suppose $\hat{O}$ has a (discrete) spectrum of eigenvalues $\{\lambda_n\}$ and corresponding normalized eigenfunctions $\{u_n(\mathbf{x})\}$. Using completeness, we can expand the normalized wave-function of any state as,

$$\psi(\mathbf{x}) = \sum_{n=1}^{\infty} a_n\, u_n(\mathbf{x}) \tag{71}$$

If a measurement of O is carried out in this state of the system, the outcome is λ_n with probability $|a_n|^2$.

III Immediately *after* such a measurement, the system is in the state with normalised wavefunction $u_n(\mathbf{x})$.

IV Subsequent time evolution of the wave function is governed by the time-dependent Schrödinger equation.

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

Remarks

- Postulate **II** states that the squared coefficients, $|a_n|^2$, in the expansion of the normalised wavefunction are interpreted as probabilities. The sum over all outcomes of these probabilities is equal to one by virtue of Eqn (70).

- If the wavefunction of the system is proportional to an eigenfunction of the operator $\hat{O}$,

$$\psi(\mathbf{x}) = a_n u_n(\mathbf{x})$$

  If $\psi(\mathbf{x})$ is normalized then $|a_n|^2 = 1$. The outcome of a measurment of the corresponding observable O will yield the value λ_n with probability one.

- Postulate **III** states that measurement of O has an instantaneous effect on the wavefunction $\psi(\mathbf{x})$ replacing it by one of the eigenfunctions of $\hat{O}$. This instantaneous change is known as "collapse of the wave-function" and leads to the several apparant paradoxes such as that of *Schrödinger 's cat*, and also the measurement problem.

The measurement problem In the absence of measurement time evolution governed by time-dependent Schrödinger equation (Postulate **IV**). When a measurement takes place we have "collapse of the wavefunction" where the wavefunction changes in a different way not governed by the Schrödinger equation (Postulate **V**). Measurement is, roughly speaking, an interaction between the experimental equipment and the particle or system being measured.

- When does "collapse occur" and what causes it? The experimental equipment is also made of atoms which should obey the rules of quantum mechanics so how can we consistently define what constitutes "a measurement".

Expectation values

From Postulate **III**, the measurement of an observable O in some state ψ yields the value λ_n with probability $|a_n|^2$. The **expectation value** of O in this state is the average value,

$$\langle O \rangle_\psi \;=\; \sum_{n=1}^{\infty} \lambda_n \, |A_n|^2.$$

We can also express this in terms of the wavefunction as,

$$\langle O \rangle_\psi \;=\; \int_{\mathbb{R}^3} \psi^*(\mathbf{x}) \; \hat{O}\psi(\mathbf{x}) \; dV \tag{72}$$

Proof Using the series (71) for ψ, the RHS of Eqn (72) becomes,

$$\begin{aligned}
\int_{\mathbb{R}^3} \psi^*(\mathbf{x}) \; \hat{O}\psi(\mathbf{x}) \; dV &= \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty} \int_{\mathbb{R}^3} a^*_{n'} a_n \; u^*_{n'}(\mathbf{x}) \; \hat{O} u_n(\mathbf{x}) \; dV \\
&= \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty} \lambda_n \; a^*_{n'} a_n \int_{\mathbb{R}^3} u^*_{n'}(\mathbf{x}) \; u_n(\mathbf{x}) \; dV \\
&= \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty} \lambda_n \; a^*_{n'} a_n \; \delta_{nn'} \\
&= \sum_{n=1}^{\infty} \lambda_n \; |a_n|^2 \;=\; \langle O \rangle_\psi \qquad \Box
\end{aligned}$$

Note that the expectation value of an observable takes definite value and therefore taking a further expectation value has no effect,

$$\langle \langle O \rangle_\psi \rangle_\psi \;=\; \langle O \rangle_\psi$$

Examples

- Expectation value of position,

$$\begin{aligned}
\langle \mathbf{x} \rangle_\psi &= \int_{\mathbb{R}^3} \psi^*(\mathbf{x}) \; \hat{\mathbf{x}}\psi(\mathbf{x}) \; dV \\
&= \int_{\mathbb{R}^3} \mathbf{x} \; |\psi(\mathbf{x})|^2 \; dV
\end{aligned}$$

  Agrees with interpretation of $|\psi(\mathbf{x})|^2$ as probability distribution.

- Expectation value of momentum,

$$\langle \mathbf{p} \rangle_\psi \;=\; -i\hbar \int_{\mathbb{R}^3} \psi^*(\mathbf{x}) \; \nabla\psi(\mathbf{x}) \; dV$$

in one-dimension this becomes,

$$\langle \mathbf{p} \rangle_\psi \;=\; -i\hbar \int_{\mathbb{R}^3} \psi^*(x)\, \frac{d}{dx}\psi(x)\; dV$$

Exercise Show using (68) and (69) that,

$$\langle \mathbf{p} \rangle_\psi \;=\; \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk\; \hbar k\; |f(k)|^2$$

where $f(k)$ is the Fourier transform of the wavefunction $\psi(x)$. Thus $|f(k)|^2$ can be interpreted as the probability distribution for the momentum $p = \hbar k$.

3.1 Commutation relations

Observables O_1 and O_2 only have definite values in a state if the wavefunction $\psi(\mathbf{x})$ of the state is an eigenfunction of *both* $\hat{O}_1$ and $\hat{O}_2$. This means that,

$$\begin{aligned} \hat{O}_1\psi &= \lambda\psi \\ \hat{O}_2\psi &= \mu\psi \end{aligned}$$

For some real constants λ and μ. Thus we have,

$$\hat{O}_1\hat{O}_2\psi = \hat{O}_2\hat{O}_1\psi \;=\; \mu\lambda\psi \tag{73}$$

Define the commutator of operators $\hat{O}_1$ and $\hat{O}_2$ as,

$$[\hat{O}_1, \hat{O}_2] \;=\; \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1$$

. Note that, from this definition,

$$[\hat{O}_2, \hat{O}_1] \;=\; -[\hat{O}_1, \hat{O}_2]$$

Equation (73) is the statement,

$$[\hat{O}_1, \hat{O}_2]\psi \;=\; 0 \tag{74}$$

If all eigenfunctions of $\hat{O}_1$ are also eigenfunctions of $\hat{O}_2$ then Eqn (74) holds for all wavefunctions ψ. More simply,

$$[\hat{O}_1, \hat{O}_2] \;=\; 0$$

In words, “the operators $\hat{O}_1$ and $\hat{O}_2$ commute”.

Exercise If $[\hat{O}_1, \hat{O}_2] = 0$, prove that any eigenfunction of $\hat{O}_1$ is also an eigenfunction of $\hat{O}_2$ assuming the spectra of these operators are non-degenerate (ie all eigenvalues distinct).

Proof Let ψ be and eigenfunction of $\hat{O}_1$ with eigenvalue λ,

$$\hat{O}_1\psi = \lambda\psi$$

Acting with $\hat{O}_2$,

$$\hat{O}_2\hat{O}_1\psi = \lambda\hat{O}_2\psi$$

Then, as $\hat{O}_1$ and $\hat{O}_2$ commute we have,

$$\hat{O}_1\hat{O}_2\psi = \lambda\hat{O}_2\psi$$

Thus $\hat{O}_2\psi$ is an eigenfunction of $\hat{O}_1$ with eigenvalue λ. Non-degeneracy then implies,

$$\hat{O}_2\psi = \mu\psi$$

for some constant μ. Thus ψ is an eigenfunction of $\hat{O}_2$ $\Box$.

An important example of **non-commuting** observables are the position and momentum operators,

$$\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$$
$$\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$$

These obey the **canonical commutation relations**,

$$[\hat{x}_i, \hat{x}_j] = 0 \tag{75}$$

$$[\hat{p}_i, \hat{p}_j] = 0 \tag{76}$$

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

where $\hat{\mathbb{I}}$ is the unit operator.

Proof Prove these relations by acting on a general function $f(\mathbf{x})$,

$$[\hat{x}_i, \hat{x}_j]\ f(\mathbf{x}) \ = \ (x_i x_j \ - \ x_j x_i)\ f(\mathbf{x}) \ = \ 0$$

while

$$[\hat{p}_i, \hat{p}_j]\ f(\mathbf{x}) \ = \ (-i\hbar)^2 \left[\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} \ - \ \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_i} \right]\ f(\mathbf{x}) \ = \ 0$$

using the symmetry of mixed partial derivatives. Finally,

$$\begin{aligned}
[\hat{x}_i, \hat{p}_j]\ f(\mathbf{x}) &= \left[x_i \left(-i\hbar \frac{\partial}{\partial x_j} \right) \ - \ \left(-i\hbar \frac{\partial}{\partial x_j} \right) x_i \right]\ f(\mathbf{x}) \\
&= -i\hbar \left[x_i \frac{\partial f}{\partial x_j} \ - \ \frac{\partial}{\partial x_j}(x_i\ f) \right] \\
&= -i\hbar \left[x_i \frac{\partial f}{\partial x_j} \ - \ f\frac{\partial x_i}{\partial x_j} \ - \ x_i \frac{\partial f}{\partial x_j} \right] \\
&= +i\hbar\ \delta_{ij}\ \hat{\mathbb{I}}\ f \qquad \square
\end{aligned} \tag{77}$$

The Heisenberg uncertainty principle

The **uncertainty**, $\Delta_\psi O$, in the measurement of an observable O in state ψ is the standard deviation of the corresponding probability distribution,

$$\begin{aligned}
(\Delta_\psi O)^2 &= \left\langle (O \ - \ \langle O \rangle_\psi)^2 \right\rangle_\psi \\
&= \left\langle O^2 \ - \ 2O\langle O \rangle_\psi + \langle O \rangle_\psi^2 \right\rangle_\psi \\
&= \langle O^2 \rangle_\psi - \langle O \rangle_\psi^2
\end{aligned}$$

Using (72), we can also express the uncertainty in a given state in terms of the wavefunction as,

$$(\Delta_\psi O)^2 \ = \ \int_{\mathbb{R}^3} \psi^*(\mathbf{x})\ \hat{O}^2 \psi(\mathbf{x})\ dV - \left[\int_{\mathbb{R}^3} \psi^*(\mathbf{x})\ \hat{O}\psi(\mathbf{x})\ dV \right]^2$$

Examples

- If $\psi(\mathbf{x})$ is a normalized eigenfunction of $\hat{O}$ with eigenvalue $\lambda \in \mathbb{R}$,

$$\hat{O}\psi \ = \ \lambda\psi$$

easy to check that,

$$
\begin{aligned}
(\Delta_\psi O)^2 &= \int_{\mathbb{R}^3} \psi^*(\mathbf{x})\ \hat{O}^2\psi(\mathbf{x})\ dV \ - \ \left[\int_{\mathbb{R}^3} \psi^*(\mathbf{x})\ \hat{O}\psi(\mathbf{x})\ dV\right]^2 \\
&= \lambda^2 \int_{\mathbb{R}^3} \psi^*(\mathbf{x})\ \psi(\mathbf{x})\ dV \ - \ \left[\lambda \int_{\mathbb{R}^3} \psi^*(\mathbf{x})\ \psi(\mathbf{x})\ dV\right]^2 \\
&= \lambda^2 - \lambda^2 = 0
\end{aligned}
$$

In this case the uncertainty vanishes and O takes the value λ with probability one.

- Particle in ground-state of the one-dimensional infinite square well,

$$
\begin{aligned}
\psi(x) &= \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) \qquad && 0 < x < a \\
&= 0 && \text{otherwise}
\end{aligned}
$$

Uncertainty in postion,

$$
\begin{aligned}
(\Delta_\psi x)^2 &= \frac{2}{a}\int_0^a dx\ x^2\ \sin^2\left(\frac{\pi x}{a}\right) - \left[\frac{2}{a}\int_0^a dx\ x\ \sin^2\left(\frac{\pi x}{a}\right)\right]^2 \\
&= \frac{2}{a}\times\left(\frac{a^3}{6}\right) - \frac{4}{a^2}\times\left(\frac{a^2}{4}\right)^2 \\
&= \frac{a^2}{12}
\end{aligned}
$$

Suppose we measure two observables O_1 and O_2,

- If $\hat{O}_1$ and $\hat{O}_2$ commute then we can find (see exercise) simultaneous eigenfunction ψ,

$$
\hat{O}_1\psi = \lambda\psi \qquad \hat{O}_2\psi = \mu\psi
$$

$$
\Rightarrow \qquad \Delta_\psi O_1 \ = \ \Delta_\psi O_2 \ = \ 0
$$

Thus O_1 and O_2 can be measured simultaneously to arbitrary accuracy.

- If $\hat{O}_1$ and $\hat{O}_2$ do not commute, then ΔO_1 and ΔO_2 cannot both be arbitarily small.

Important case Position and momentum operators in one dimension,

$$
\hat{x} = x\ \hat{\mathbb{I}} \qquad \hat{p} = -i\hbar\frac{d}{dx}
$$

As we saw above, these do not commute,

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

This implies the **Heisenberg uncertainty relation**, which asserts that, in any state Ψ of the system,

$$\Delta_\Psi x \;\cdot\; \Delta_\Psi p \;\; \geq \;\; \frac{\hbar}{2} \tag{78}$$

Proof Consider the system in a state with wavefunction $\Psi(x)$. For simplicity we will focus on states where $\langle x \rangle_\Psi = \langle p \rangle_\Psi = 0$. The extension of the proof to the general case is given in the Appendix.

Consider one-parameter family of states with wave-functions,

$$\Psi_s(x) \;\; = \;\; (\hat{p} - is\hat{x})\,\Psi(x)$$

with $s \in \mathbb{R}$. The identity,

$$\int_{-\infty}^{+\infty} |\Psi_s(x)|^2 \, dx \;\; \geq \;\; 0$$

implies,

$$\begin{aligned} 0 \;\; &\leq \;\; \int_{-\infty}^{+\infty} [(\hat{p} - is\hat{x})\,\Psi(x)]^* \, (\hat{p} - is\hat{x})\,\Psi(x) \; dx \\ &= \;\; \int_{-\infty}^{+\infty} \Psi^*(x)\,(\hat{p} + is\hat{x})\,(\hat{p} - is\hat{x})\,\Psi(x) \; dx \end{aligned}$$

using the fact that $\hat{x}$ and $\hat{p}$ are Hermitian. Thus,

$$\begin{aligned} 0 \;\; &\leq \;\; \int_{-\infty}^{+\infty} \Psi^*(x)\left(\hat{p}^2 + is[\hat{x},\hat{p}] + s^2\hat{x}^2\right)\Psi(x) \; dx \\ &= \;\; \int_{-\infty}^{+\infty} \Psi^*(x)\left(\hat{p}^2 - \hbar s + s^2\hat{x}^2\right)\Psi(x) \; dx \end{aligned}$$

using the commutation relation $[\hat{x},\hat{p}] = i\hbar\hat{\mathbb{I}}$. Which gives,

$$0 \;\; \leq \;\; \langle \hat{p}^2 \rangle_\Psi \; - \; \hbar s \; + \; s^2 \langle \hat{x}^2 \rangle_\Psi \qquad \forall \; s \in \mathbb{R} \tag{79}$$

As, by assumption $\langle \hat{p} \rangle_\Psi = \langle \hat{x} \rangle_\Psi = 0$ we have,

$$\begin{aligned} (\Delta_\Psi x)^2 \;\; &= \;\; \langle \hat{x}^2 \rangle_\Psi \\ (\Delta_\Psi p)^2 \;\; &= \;\; \langle \hat{p}^2 \rangle_\Psi \end{aligned}$$

and Eqn (79) can be rewritten as,

$$(\Delta_\Psi p)^2 \; - \; \hbar s \; + \; s^2\,(\Delta_\Psi x)^2 \;\; \geq \;\; 0 \qquad \forall \; s \in \mathbb{R} \tag{80}$$

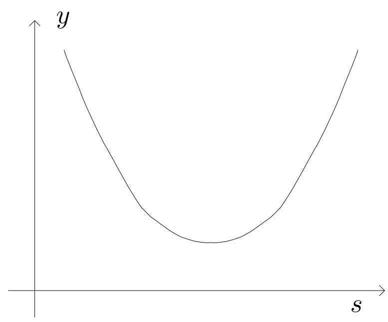


Figure 34: The quadratic equation (81) has no real roots.

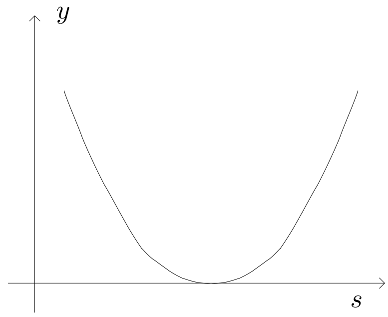


Figure 35: The quadratic equation (81) has one real root.

Lemma Let A, B and C be real numbers. If we have,

$$As^2 \ + \ Bs \ + \ C \ \geq \ 0 \qquad \forall \ s \in \mathbb{R}$$

then,

$$B^2 \ \leq \ 4AC$$

Proof The fact that

$$As^2 \ + \ Bs \ + \ C \ \geq \ 0$$

$\forall \ s \in \mathbb{R}$ is equivalent to the statement that the quadratic equation,

$$y \ = \ As^2 \ + \ Bs \ + \ C \ = \ 0 \tag{81}$$

either has no real roots if the strict inequality $y > 0$ for all s (see Figure 34) or has exactiy one real root if $y = 0$ for some value of s (see Figure 35). This immediately implies that,

$$B^2 \ \leq \ 4AC \qquad \Box$$

Now apply Lemma with $A = (\Delta_\Psi x)^2$, $B = -\hbar$ and $C = (\Delta_\Psi p)^2$ to deduce,

$$\hbar^2 \;\; \leq \;\; 4(\Delta_\Psi x)^2 (\Delta_\Psi p)^2$$

as Δx and Δp are positive we may take the square root of the above inequality to get,

$$\Delta_\Psi x \;\cdot\; \Delta_\Psi p \;\; \geq \;\; \frac{\hbar}{2}$$

as required $\Box$.

Example Consider a state with a normalized Gaussian wavefunction,

$$\psi(x) \;\; = \;\; \left(\frac{a}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{a}{2}\,x^2\right)$$

Work out expectation values,

$$\langle x \rangle_\psi \;\; = \;\; \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} dx\; x\, \exp(-ax^2) = 0$$

by symmetry.

$$\begin{aligned}
\langle p \rangle_\psi \;\; &= \;\; \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} dx\; -i\hbar\; \exp\left(-\frac{a}{2}\,x^2\right)\; \frac{d}{dx} \exp\left(-\frac{a}{2}\,x^2\right) \\
&= \;\; \sqrt{\frac{a}{\pi}}\; i\hbar a \int_{-\infty}^{+\infty} dx\; x\, \exp(-ax^2) = 0
\end{aligned}$$

also by symmetry.

$$\begin{aligned}
\langle x^2 \rangle_\psi \;\; &= \;\; \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} dx\; x^2\, \exp(-ax^2) \\
&= \;\; \sqrt{\frac{a}{\pi}} \times \frac{1}{2}\sqrt{\frac{\pi}{a^3}} \;\; = \;\; \frac{1}{2a}
\end{aligned}$$

using Eqn (120) from the appendix.

$$\begin{aligned}
\langle p^2 \rangle_\psi \;\; &= \;\; \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} dx\; -\hbar^2\; \exp\left(-\frac{a}{2}\,x^2\right)\; \frac{d^2}{dx^2} \exp\left(-\frac{a}{2}\,x^2\right) \\
&= \;\; \sqrt{\frac{a}{\pi}}\; \hbar^2 a \int_{-\infty}^{+\infty} dx\; \left(1 \;-\; ax^2\right)\, \exp(-ax^2) \\
&= \;\; \hbar^2 a\, \sqrt{\frac{a}{\pi}} \left[\sqrt{\frac{\pi}{a}} \;-\; \frac{a}{2}\sqrt{\frac{\pi}{a^3}}\right] \;\; = \;\; \frac{1}{2}\hbar^2 a
\end{aligned}$$

Finally have,

$$\Delta_\psi x = \sqrt{\langle x^2\rangle_\psi - \langle x\rangle_\psi^2} = \frac{1}{\sqrt{2a}}$$
$$\Delta_\psi p = \sqrt{\langle p^2\rangle_\psi - \langle p\rangle_\psi^2} = \hbar\sqrt{\frac{a}{2}}$$

Thus we have,

$$\Delta_\psi x \cdot \Delta_\psi p = \frac{\hbar}{2}$$

The Gaussian wavefunction *saturates* the inequality (78) and therefore represents the state of minimum uncertainty.

Physical explanation of uncertainty

- To resolve particle position to accuracy Δx, need to use light of wavelength $\lambda \sim \Delta x$.
- De Broglie relation $\Rightarrow$ corresponding photons have momentum of magnitude $p = h/\lambda \sim h/\Delta x$.
- Recoil of measured particle introduces uncertainty in its momentum of order $\Delta p \sim p \sim h/\Delta x$.
- Thus the estimated uncertainties obey,

$$\Delta x \cdot \Delta p \sim h.$$

4 Wave Mechanics II

Time-independent Schrödinger equation in three spatial dimensions,

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

In Cartesian coordinates,

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

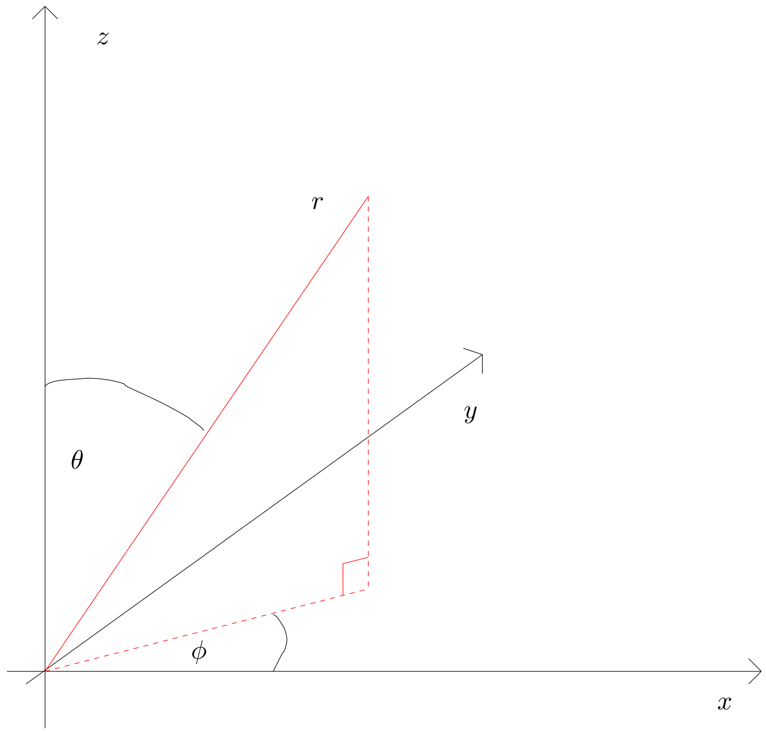


Figure 36: Spherical polars.

Spherical polars See Fig (36),

$$\begin{aligned} x &= r\cos(\phi)\sin(\theta) \\ y &= r\sin(\phi)\sin(\theta) \\ z &= r\cos(\theta) \end{aligned}$$

where,

$$0 \leq r < \infty, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi < 2\pi.$$

In spherical polars (see IA Vector Calculus),

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

Special case: Spherically symmetric potential,

$$U(r,\theta,\phi) \equiv U(r)$$

Now look for **spherically symmetric stationary state**

$$\chi(r,\theta,\phi) \equiv \chi(r)$$

for which,

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

and thus time-independent Schrödinger equation becomes,

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

or,

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\chi}{dr^2} + \frac{2}{r}\frac{d\chi}{dr}\right) + U(r)\chi = E\chi \tag{82}$$

Boundary conditions

- Wavefunction $\chi(r)$ must be finite at $r = 0$
- Recall that,

$$\int_{\mathbb{R}^3} dV = \int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos(\theta)) \int_0^\infty r^2\, dr$$

Therefore normalizability of the wavefunction requires,

$$\int_{\mathbb{R}^3} |\psi|^2\, dV < \infty \Rightarrow \int_0^\infty |\chi(r)|^2\, r^2\, dr < \infty$$

which requires that $\chi(r) \to 0$ sufficiently fast as $r \to \infty$.

Useful Trick Let $\sigma(r) = r\chi(r)$. Eqn (82) becomes,

$$-\frac{\hbar^2}{2m}\frac{d^2\sigma}{dr^2} + U(r)\sigma(r) = E\sigma(r) \tag{83}$$

This is one-dimensional Schrödinger equation on the half-line $r \geq 0$.

Now solve Schrödinger equation on whole line $-\infty < r < +\infty$ with symmetric potential $U(-r) = U(r)$. See Fig (37) Boundstate wavefunctions of odd parity $\sigma(-r) = -\sigma(r)$ solve (83) with boundary conditions,

$$\sigma(0) = 0 \qquad \text{and} \qquad \int_0^\infty |\sigma(r)|^2\, dr < \infty$$

which yields a solution to the original problem because,

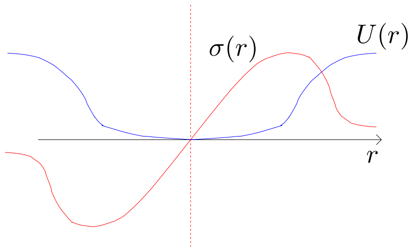


Figure 37: One-dimensional problem.

- Wavefunction $\chi(r) = \sigma(r)/r$ finite at $r = 0$ This follows from $\sigma(0) = 0$ provided $\sigma'(0)$ is finite (use L' Hôpital's rule)

- Normalizability condition,

$$\int_0^\infty |\chi(r)|^2 \, r^2 \, dr \quad < \quad \infty$$

follows for $\chi(r) = \sigma(r)/r$.

Examples

- Spherically-symmetric harmonic oscillator,

$$U(r) \quad = \quad \frac{1}{2}m\omega^2 r^2$$

Energy levels,

$$E \quad = \quad \frac{3}{2}\hbar\omega, \qquad \frac{7}{2}\hbar\omega, \qquad \frac{11}{2}\hbar\omega, \qquad \ldots$$

Odd parity boundstates of one-dimensional harmonic oscillator.

- Spherically-symmetric square well,

$$\begin{aligned} U(r) \quad &= \quad 0 \qquad\qquad \text{for} \qquad r < a \\ &= \quad U_0 \qquad\qquad \text{for} \qquad r > a \end{aligned}$$

Find odd-parity boundstates states of one-dimensional square well (see p31)

Define constants,

$$k = \sqrt{\frac{2mE}{\hbar^2}} \;\geq\; 0, \qquad\qquad \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} \;\geq\; 0$$

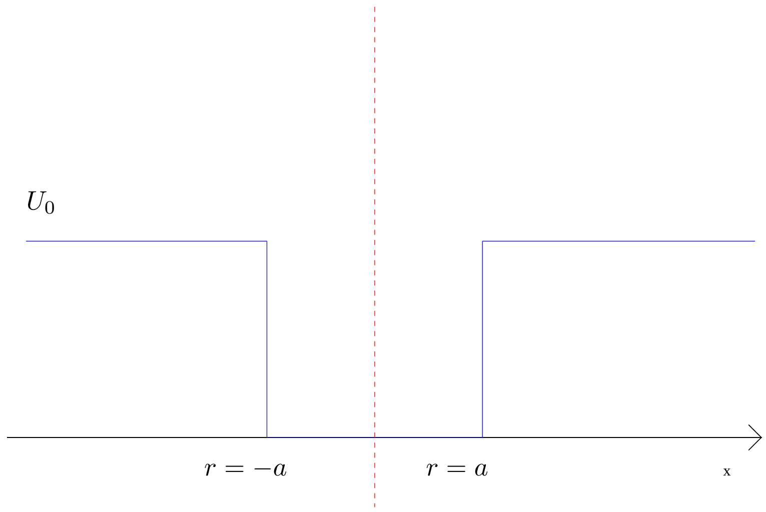


Figure 38: The finite square well.

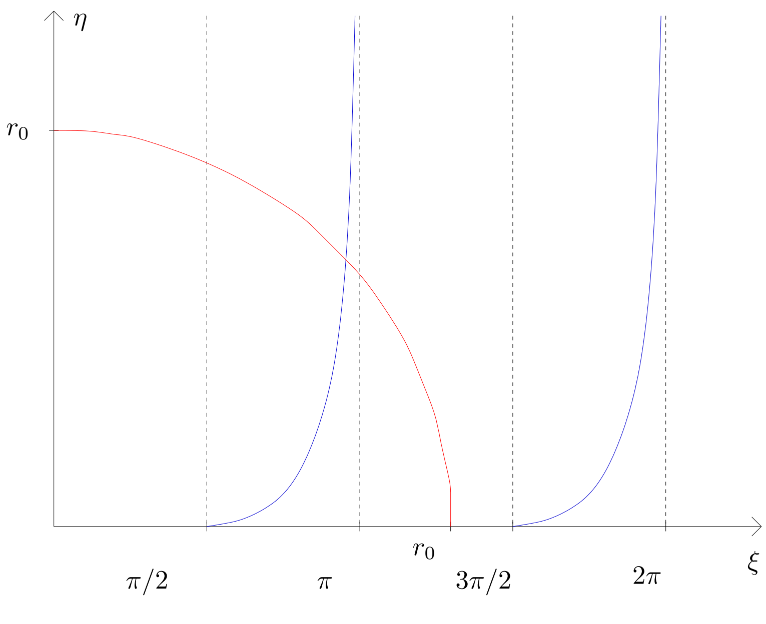


Figure 39: Graphical Solution: odd-parity levels

and select solutions of time-independent Schrödinger equation of form,

$$\begin{aligned}\sigma(r) &= A\sin(kr) && |r| < a \\ &= B\exp(-\kappa r) && r > a \\ &= -B\exp(+\kappa r) && r < -a\end{aligned}$$

Boundary conditions

- Continuity of σ and σ' at $r = a$,

$$\begin{aligned}A\sin(ka) &= B\exp(-\kappa a) \\ \text{and} \qquad kA\cos(ka) &= -\kappa B\exp(-\kappa a)\end{aligned}$$

$$\Rightarrow \qquad -k\cot(ka) = \kappa$$

- Rescaled variables,

$$\xi = ka, \qquad \eta = \kappa a, \qquad r_0 = \sqrt{\frac{2mU_0}{\hbar^2}}\, a$$

- Two equations relating unknowns ξ and η.

$$\begin{aligned}\xi^2 + \eta^2 &= r_0^2 \\ -\xi\cot(\xi) &= \eta\end{aligned}$$

- Graphical solution shown in Figure (39)

- Finite number of boundstates determined by number of intersections.

- No boundstate if $r_0 < \pi/2$ or equivalently,

$$U_0 \;\leq\; \frac{\pi^2\hbar^2}{8ma^2}$$

unlike one-dimensional case where we always find at least one boundstate.

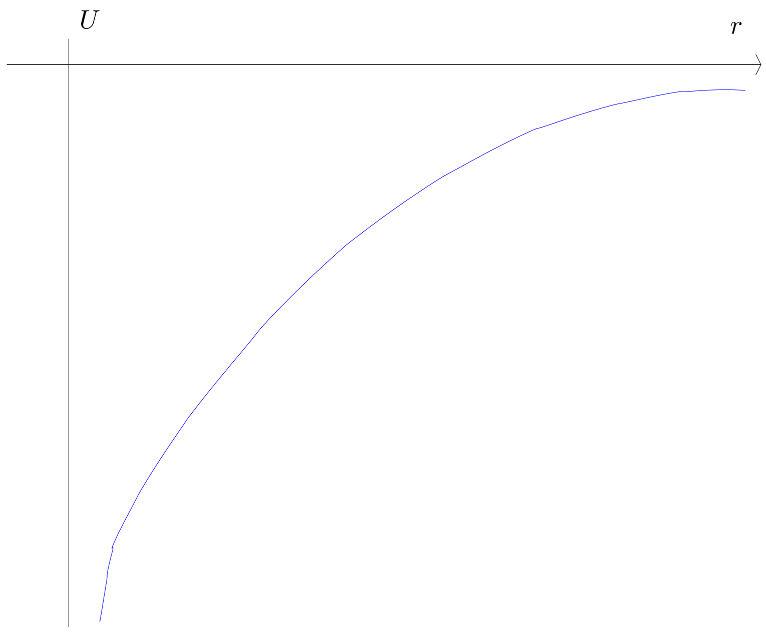


Figure 40: The Coulomb potential

The Hydrogen Atom: Part I

H-atom consists of a single proton p^+ and an electron e^-. As before treat the proton as stationary at the origin of spherical polar coordinates. Coulomb attraction,

$$F = -\frac{\partial U}{\partial r} \quad = \quad -\frac{e^2}{4\pi\varepsilon_0 r^2}$$

Corresponds to potential (see Figure 40),

$$U(r) \quad = \quad -\frac{e^2}{4\pi\varepsilon_0 r} \tag{84}$$

- The potential is infinitely deep.
- Energy defined so that particle at rest at $r = \infty$ has $E = 0$.

Look for stationary states of electron with (stationary-state) wave function $\chi(r, \theta, \phi)$. Focus on wavefunctions with spherical symmetry,

$$\chi(r, \theta, \phi) \quad = \quad \chi(r)$$

These obey the Schrödinger equation (82) with the Coulomb potential (84)

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\chi}{dr^2} \; + \; \frac{2}{r}\frac{d\chi}{dr}\right) \; - \; \frac{e^2}{4\pi\varepsilon_0 r}\,\chi \quad = \quad E\chi$$

To simplify this equation defined rescaled variables,

$$\nu^2 = -\frac{2mE}{\hbar^2} \ > \ 0, \qquad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0 \hbar^2}$$

in terms of which Schrödinger equation becomes,

$$\frac{d^2\chi}{dr^2} \ + \ \frac{2}{r}\frac{d\chi}{dr} \ + \ \frac{\beta}{r}\chi \ - \nu^2\chi \ = \ 0 \qquad (85)$$

- Large-r asymptotics of the wavefunction determined by first and last terms in (85). In the limit $r \to \infty$ we have,

  $$\frac{d^2\chi}{dr^2} - \nu^2\chi \simeq 0$$

  which implies that the solutions of (85) have behaviour,

  $$\chi(r) \ \sim \ \exp(\pm\nu r) \qquad\qquad \text{as} \ \ r \to \infty \qquad (86)$$

  We must choose an exponentially decaying solution for a normalizable wavefunction.

- Wavefunction should be finite at $r = 0$.

- As in analysis of harmonic oscillator, it is convenient to seperate out the exponential dependence of the wave-function and look for a solution of the form,

  $$\chi(r) \ = \ f(r)\exp(-\nu r)$$

  The Schrödinger equation (85) now becomes,

  $$\frac{d^2 f}{dr^2} \ + \ \frac{2}{r}(1 - \nu r)\frac{df}{dr} \ + \ \frac{1}{r}(\beta - 2\nu)f \ = \ 0 \qquad (87)$$

Equation (87) is a homogeneous, linear ODE with a *regular singular point* at $r = 0$. Apply standard method and look for a solution in the form of a power series around $r = 0$,

$$f(r) \ = \ r^c \sum_{n=0}^{\infty} a_n r^n \qquad (88)$$

Substitute series (88) for $f(r)$ in (87).

- The lowest power of r which occurs on the LHS is $a_0 r^{c-2}$ with coefficient $c(c-1)+2c = c(c+1)$. Equating this to zero yields the *indicial equation*,

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

  with roots $c = 0$ and $c = -1$.

- Root c=-1 $\Rightarrow \chi(r) \sim 1/r$ near $r = 0$. This yields a singular wavefunction which violates the boundary condition at the origin. Thus we choose root $c = 0$ and our series solution simplifies to,

$$f(r) \;=\; \sum_{n=0}^{\infty} a_n r^n \tag{89}$$

- Now collect all terms of order r^{n-2} on the LHS of (87) and equate them to zero to get,

$$n(n-1)a_n + 2na_n - 2\nu(n-1)a_{n-1} + (\beta - 2\nu)a_{n-1} \;=\; 0$$

or more simply,

$$a_n \;=\; \frac{(2\nu n - \beta)}{n(n+1)}\, a_{n-1} \tag{90}$$

This recurrence relation determines all the coeffiicents a_n in the series (89) in terms of the first coefficent a_0. As in our analysis of the harmonic oscillator, there are two possibilities,

- The series (57) terminates. In other words $\exists\; N > 0$ such that $a_n = 0 \;\forall\; n \geq N$.

- The series (57) does not terminate. In other words $\nexists\; N > 0$ such that $a_n = 0 \;\forall\; n \geq N$.

As before, the second possibility does not yield normalizable wave functions. To see this note that Eqn (90) determines the large-n behaviour of the coefficients a_n as,

$$\frac{a_n}{a_{n-1}} \;\to\; \frac{2\nu}{n} \qquad \text{as} \quad n \to \infty \tag{91}$$

We can now compare this with the power series for the function,

$$g(r) = \exp(+2\nu r) \;=\; \sum_{n=0}^{\infty} b_n r^n \qquad \text{with} \quad b_n = \frac{(2\nu)^n}{n!}$$

whose coefficients obey,

$$\frac{b_n}{b_{n-1}} \;=\; \frac{(2\nu)^n}{(2\nu)^{n-1}}\,\frac{(n-1)!}{n!} \;=\; \frac{2\nu}{n}$$

We deduce that (91) is consistent with the asymptotics,

$$f(r) \sim g(r) = \exp(+2\nu r) \quad \Rightarrow \quad \chi(r) = f(r)\exp(-\nu r) \sim \exp(+\nu r)$$

as $r \to \infty$ which is consistent with the expected exponential growth (86) of generic solutions of (85). This corresponds to a non-normalizable wavefunction which we reject.

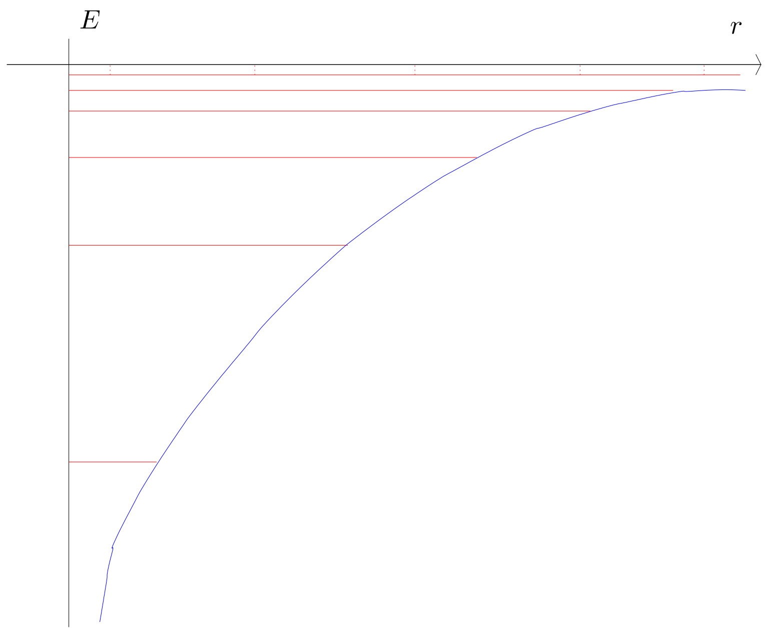


Figure 41: The energy levels of the Hydrogen atom

To give a normalisable wave-function therefore, the series (89) must therefore terminate. There must be an integer $N > 0$ such that $a_N = 0$ with $a_{N-1} \neq 0$. From the recurrence relation (90) we can see that this happens if and only if,

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

Recalling the definitions,

$$\nu^2 = -\frac{2mE}{\hbar^2} \ > \ 0, \qquad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2}$$

This yields the spectrum of energy levels,

$$E = E_N \quad = \quad -\frac{e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2}\ \frac{1}{N^2} \tag{92}$$

for $N = 1, 2, \ldots$.

- The resulting spectrum is identical to that of the Bohr atom. Thus the Schrödinger equation predicts the same set of spectral lines for Hydrogen which are in good agreement with experiment, although the degeneracies (ie number of states with the same energy) are still wrong. An important difference is that Bohr's spectrum was based on quantization of angular momentum correponding to $J = N\hbar$. In contrast the wave functions we have constructed are spherically symmetric and therefore have zero angular momentum.

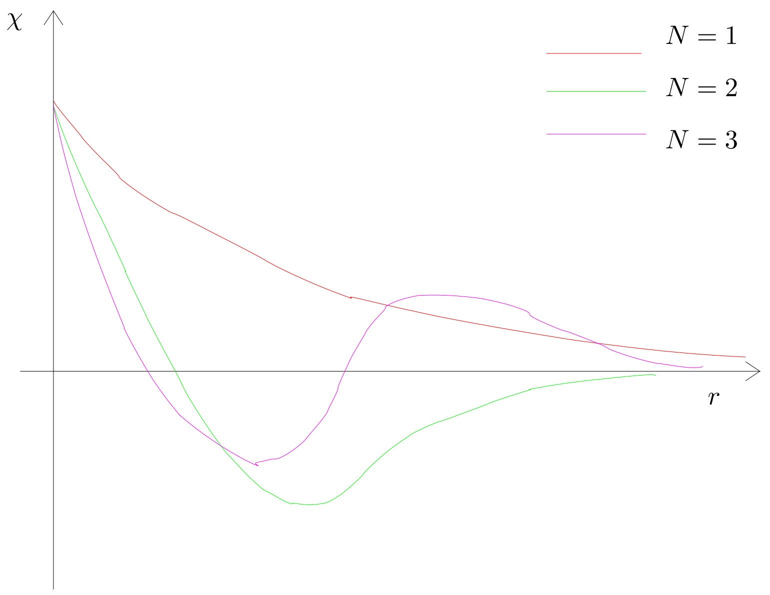


Figure 42: Spherically symmetric wavefunctions for the Hydrogen atom

Wavefunctions On setting $\nu = \beta/2N$, the recurrence relation (90) becomes,

$$\begin{aligned} \frac{a_n}{a_{n-1}} &= \frac{2\nu n - \beta}{n(n+1)} \\ &= -2\nu \left(\frac{N-n}{n(n+1)} \right) \end{aligned}$$

This formula can be used to give explict results for the first few levels (see Figure 42),

$$\begin{aligned} \chi_1(r) &= \exp(-\nu r) \\ \chi_2(r) &= (1 - \nu r) exp(-\nu r) \\ \chi_3(r) &= \left(1 - 2\nu r + \frac{2}{3}(\nu r)^2 \right) \exp(-\nu r) \end{aligned}$$

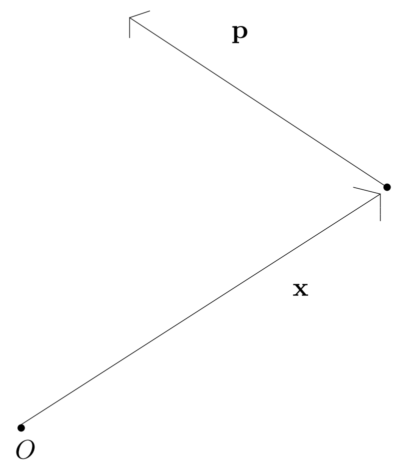
The wavefunction for the N'th level can be written as,

$$\chi_N(r) \;\; = \;\; L_N(\nu r) \;\; \exp(-\nu r)$$

where L_N is a polynomial of order $N-1$ known as the N'th **Laguerre polynomial**. The wavefunction $\chi_N(r)$ thus has $N-1$ nodes or zeros.

Normalized groundstate wavefunction $\tilde{\chi}_1(r) = A_1 \chi_1(r) = A_1 \exp(-\nu r)$. Constant A_1 fixed by normalisation condition,

$$\int_{\mathbb{R}^3} |\tilde{\chi}_1(r)|^2 \, dV \;\; = \;\; 1$$



Evaluating the integral we find,

$$|A_1|^2 \int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos\theta) \int_0^{\infty} dr\; r^2 \exp(-2\nu r) \;\; = \;\; 1$$

Thus $|A_1|^2 = 1/\mathcal{I}_2$ where,

$$\mathcal{I}_2 \;\; = \;\; 4\pi \int_0^{\infty} r^2 \exp(-2\nu r) \;\; = \;\; \frac{\pi}{\nu^3}$$

Finally we can choose,

$$A_1 \;\; = \;\; \frac{1}{\sqrt{\pi}} \left(\frac{e^2 m_e}{4\pi\varepsilon_0 \hbar^2 N}\right)^{\frac{3}{2}} \tag{93}$$

Exercise Prove that in the spherically-symmetric groundstate,

$$\langle r \rangle \;\; = \;\; \frac{3}{2}\, r_1$$

where $r_1 = 2/\beta = 4\pi\varepsilon_0\hbar^2/m_e e^2$ is the Bohr radius as defined in Section 1 (see p7)

Angular momentum

Classical angular momentum,

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

The vector $\mathbf{L}$ is a conserved quantity for systems with spherical symmetry (eg for a spherically symmetric potential $U(r, \theta, \phi) \equiv U(r)$

In Quantum Mechanics, orbital angular momentum is an observable which corresponds to the operator,

$$\begin{aligned}\hat{\mathbf{L}} &= \hat{\mathbf{x}} \times \hat{\mathbf{p}} \\ &= -i\hbar \mathbf{x} \times \nabla\end{aligned}$$

In index notation for Cartesian coordinates $\mathbf{x} = (x_1, x_2, x_3)$

$$\hat{L}_i = -i\hbar\, \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}$$

where ε_{ijk} is the Levi-Civita alternating tensor (see Appendix). Explicitly,

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

- Operators $\hat{L}_i$ are Hermitian.
- Different components of the angular momentum operator do not commute with each other: $[\hat{L}_i, \hat{L}_j] \neq 0$ for $i \neq j$. Thus different components of angular momentum cannot be measured simultaneously.

Check commutator,

$$[\hat{L}_1, \hat{L}_2]\ f(x_1, x_2, x_3) =$$

$$-\hbar^2 \left[\left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) - \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) \left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \right]\ f(x_1, x_2, x_3)$$

Check that many term cancels leaving,

$$\begin{aligned}[\hat{L}_1, \hat{L}_2]\ f &= -\hbar^2 \left(x_2 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_2} \right) f \\ &= +i\hbar\ \hat{L}_3 f \qquad (94)\end{aligned}$$

A similar calculation for the other components confirms the commutation relations,

$$[\hat{L}_2, \hat{L}_3] = i\hbar \hat{L}_1 \qquad \text{and} \qquad [\hat{L}_1, \hat{L}_3] = -i\hbar \hat{L}_2 \qquad (95)$$

The three independent commutation relations can be combined using index notation as,

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

In classical physics, magnitude of the angular momentum is $L = |\mathbf{L}|$. Thus,

$$L^2 \;=\; L_1^2 \;+\; L_2^2 \;+\; L_3^2$$

In quantum mechanics we define the **total angular momentum operator**,

$$\hat{L}^2 \;=\; \hat{L}_1^2 \;+\; \hat{L}_2^2 \;+\; \hat{L}_3^2$$

Important result Total angular momentum $\hat{L}^2$ commutes with each of the components of angular momentum $\hat{L}_i$, $i = 1, 2, 3$.

Proof For any operators $\hat{A}$ and $\hat{B}$,

$$\begin{aligned} [\hat{A},\hat{B}]\hat{B} + \hat{B}[\hat{A},\hat{B}] &= \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\hat{B} + \hat{B}\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) \\ &= \hat{A}\hat{B}^2 - \hat{B}\hat{A}\hat{B} + \hat{B}\hat{A}\hat{B} - \hat{B}^2\hat{A} \\ &= \hat{A}\hat{B}^2 - \hat{B}^2\hat{A} \end{aligned}$$

Thus we have the identity,

$$[\hat{A},\hat{B}^2] \;=\; [\hat{A},\hat{B}]\hat{B} + \hat{B}[\hat{A},\hat{B}] \tag{96}$$

Now evaluate the commutators,

$$[\hat{L}_1,\hat{L}_1^2] \;=\; 0 \tag{97}$$

and,

$$[\hat{L}_1,\hat{L}_2^2] \;=\; [\hat{L}_1,\hat{L}_2]\hat{L}_2 + \hat{L}_2[\hat{L}_1,\hat{L}_2]$$

using the identity (96). Then using (94) we obtain,

$$[\hat{L}_1,\hat{L}_2^2] \;=\; i\hbar\left[\hat{L}_3\hat{L}_2 + \hat{L}_2\hat{L}_3\right] \tag{98}$$

and,

$$[\hat{L}_1,\hat{L}_3^2] \;=\; [\hat{L}_1,\hat{L}_3]\hat{L}_3 + \hat{L}_3[\hat{L}_1,\hat{L}_3]$$

using the identity (96). Then using (95) we obtain,

$$[\hat{L}_1,\hat{L}_3^2] \;=\; -i\hbar\left[\hat{L}_3\hat{L}_2 + \hat{L}_2\hat{L}_3\right] \tag{99}$$

Finally adding equations (97), (98) and (99) we obtain,

$$[\hat{L}_1, \hat{L}^2] = [\hat{L}_1, \hat{L}_1^2] + [\hat{L}_1, \hat{L}_2^2] + [\hat{L}_1, \hat{L}_3^2] \;=\; 0$$

An identical calculation of $[\hat{L}_2, \hat{L}^2]$ and $[\hat{L}_3, \hat{L}^2]$ confirms that,

$$[\hat{L}_i, \hat{L}^2] \;=\; 0 \tag{100}$$

for $i = 1, 2, 3$ $\Box$.

Exercise Verify the following commutation relations,

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

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

From these obtain,

$$[\hat{L}_i, \hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2] \;=\; 0$$

$$[\hat{L}_i, \hat{p}_1^2 + \hat{p}_2^2 + \hat{p}_3^2] \;=\; 0$$

The Hamiltonian for a particle on mass m moving in a spherically symmetric potential has the form,

$$\begin{aligned} \hat{H} \;&=\; -\frac{\hbar^2}{2m}\nabla^2 \;+\; U(r) \\ &=\; \frac{|\hat{\mathbf{p}}|^2}{2m} \;+ U(\hat{r}) \end{aligned}$$

Here $\hat{r}$ is the operator which acts on functions $f(\mathbf{x})$ as $r\hat{\mathbb{I}}$ where r is the radial coordinate and $\hat{\mathbb{I}}$ is the unit operator. Using the above commutation relations show that $\hat{H}$ commutes with $\hat{L}_i$ for $i = 1, 2, 3$ and therefore also with $\hat{L}^2$:

$$[\hat{H}, \hat{L}_i] = [\hat{H}, \hat{L}^2] \;=\; 0 \tag{101}$$

The commutation relations (100) and (101) imply that $\hat{H}$, $\hat{L}^2$ and any one of the three operators $\hat{L}_i$, $i = 1, 2, 3$ form a set of three *mutually commuting operators*. We must choose only *one* of the $\hat{L}_i$ because they do not commute with each other (95,95). By convention we choose $\hat{L}_3$. Labelling the Cartesian coordinates in the usual way as $x_1 = x$,$x_2 = y$, $x_3 = z$, we also denote this operator as $\hat{L}_z$ or the "z-component of angular momentum". Thus we choose a set of mutually commuting operators,

$$\left\{ \hat{H} \ , \ \hat{L}^2, \ \hat{L}_3 \right\} \tag{102}$$

- As the operators commute we can find simultaneous eigenstates of all three (See Exercise in Chapter 3).
- The corresponding eigenvalues are the observables energy, total angular momentum and the z-component of angular momentum.
- The set (102) is *maximal*. In other words, we cannot construct another independent operator (other than the unit operator) which commutes with each of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$.

Eigenfunctions of angular momentum

In spherical polar coordinates we have (see Appendix),

$$\hat{L}^2 = -\frac{\hbar^2}{\sin^2(\theta)}\left[\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right] \tag{103}$$

$$\hat{L}_3 = -i\hbar\frac{\partial}{\partial\phi} \tag{104}$$

Look for simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_3$ of the form $Y(\theta)\exp(im\phi)$,

$$\hat{L}_3 \exp(im\phi) = \hbar m \exp(im\phi)$$

Wavefunctions must be single-valued functions on $\mathbb{R}^3$ and should therefore be invariant under $\phi \to \phi + 2\pi$. The function $\exp(im\phi)$ is invariant provided,

$$\exp(2\pi i m) = 1 \qquad \Rightarrow \qquad m \in \mathbb{Z}$$

Thus the eigenvalues of $\hat{L}_3$ have the form $\hbar m$ for integer m. Equivalently, the z-component of angular momentum is quantized in integer multiples of $\hbar$. This agrees with Bohr's quantization condition.

Similarly we must have,

$$\hat{L}^2\ Y(\theta)\ \exp(im\phi) \quad = \quad \lambda\, Y(\theta)\ \exp(im\phi)$$

for some eigenvalue λ. Using the explicit form (103) for $\hat{L}^2$ we find that $Y(\theta)$ must obey the equation,

$$\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) \quad - \quad \frac{m^2}{\sin^2(\theta)}\ Y(\theta) \quad = \quad -\frac{\lambda}{\hbar^2}\ Y(\theta) \tag{105}$$

This is the *associated Legendre equation.* The non-singular solutions are known as *associated Legendre functions*,

$$\begin{aligned} Y(\theta) \quad &= \quad P_{l,m}\left(\cos(\theta)\right) \\ &= \quad \left(\sin(\theta)\right)^{|m|}\ \frac{d^{|m|}}{d\left(\cos(\theta)\right)^{|m|}}\ P_l\left(\cos(\theta)\right) \end{aligned} \tag{106}$$

where $P_l(\cos(\theta))$ are (ordinary) *Legendre polynomials* (see IB Methods). The expression (106) solves equation (105) with eigenvalue,

$$\lambda = l(l+1)\ \hbar^2 \qquad\quad \text{with} \quad l = 0, 1, 2\ldots$$

There is also a further constraint on the integers l and m which reads,

$$-m \leq l \leq +m$$

The simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_3$ are therefore labelled by two integers $l > 0$ with $-m \leq l \leq +m$ and take the form,

$$Y_{l,m}(\theta,\phi) \quad = \quad P_{l,m}\left(\cos(\theta)\right)\ \exp(im\phi)$$

They obey,

$$\begin{aligned} \hat{L}^2 Y_{l,m}(\theta,\phi) \quad &= \quad l(l+1)\hbar^2 Y_{l,m}(\theta,\phi) \\ \hat{L}_3 Y_{l,m}(\theta,\phi) \quad &= \quad m\hbar Y_{l,m}(\theta,\phi) \end{aligned}$$

- The functions $Y_{l,m}$ are known as *Spherical Harmonics*
- The integer l is called the *total angular momentum quantum number* while the integer m is called the *azimuthal quantum number.*
- The constraint $-l \leq m \leq +l$ is the quantum version of the classical inequality,

  $$-L \ \leq\ L_3 \ \leq\ +L$$

  which follows because $L_3 = L\cos(\theta)$.

Some Spherical Harmonics:

$$Y_{0,0} = 1$$

$$Y_{1,-1} = \sin(\theta)\exp(-i\phi) \qquad Y_{1,0} = \cos(\theta) \qquad Y_{1,-1} = \sin(\theta)\exp(+i\phi)$$

$$Y_{2,\mp 2} = \sin^2(\theta)\exp(\mp 2i\phi) \qquad Y_{2,\mp 1} = \sin(\theta)\cos(\theta)\exp(\mp i\phi) \qquad Y_{2,0} = \big(3\cos^2(\theta) - 1\big)$$

The Hydrogen Atom: Part II

Time-independent Schrödinger equation in three spatial dimensions,

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

In Cartesian coordinates,

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

In spherical polars,

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

Thus using (103) we can write,

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

which gives,

$$\hat{H} \;\; = \;\; -\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}\, r \;\; + \;\; \frac{\hat{L}^2}{2mr^2} \;\; + \;\; U(\mathbf{x})$$

For the Hydrogen atom,

$$U(r,\theta,\phi) \equiv U(r) \;\; = \;\; -\frac{e^2}{4\pi\varepsilon_0 r}$$

and the time-independent Schrödinger equation becomes,

$$\hat{H}\chi = -\frac{\hbar^2}{2m}\left(\frac{d^2\chi}{dr^2} \;+\; \frac{2}{r}\frac{d\chi}{dr}\right) \;+\; \frac{\hat{L}^2}{2mr^2}\chi \;-\; \frac{e^2}{4\pi\varepsilon_0 r}\,\chi \;\; = \;\; E\chi \tag{107}$$

Look for a simultaneous eigenstate of,

$$\left\{ \; \hat{H} \;, \; \hat{L}^2, \; \hat{L}_3 \; \right\}$$

by setting,

$$\chi(r,\theta,\phi) \;\; = \;\; g(r)\; Y_{l,m}(\theta,\phi) \tag{108}$$

where $Y_{l,m}$ is a spherical harmonic. In particular, as above, we have,

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

Substituting (108) into (107) we obtain a second order linear homogeneous ODE for $g(r)$,

$$-\frac{\hbar^2}{2m}\left(\frac{d^2 g}{dr^2} \; + \; \frac{2}{r}\frac{dg}{dr}\right) \; + \; \frac{\hbar^2 l(l+1)}{2mr^2}g \; - \; \frac{e^2}{4\pi\varepsilon_0 r}\, g \;\; = \;\; Eg \tag{109}$$

As before define rescaled constants,

$$\nu^2 = -\frac{2mE}{\hbar^2} \; > \; 0, \qquad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2}$$

in terms of which Schrödinger equation becomes,

$$\frac{d^2 g}{dr^2} \; + \; \frac{2}{r}\frac{dg}{dr} \; - \; \frac{l(l+1)}{r^2}g \; + \; \frac{\beta}{r}g \; - \nu^2 g \;\; = \;\; 0 \tag{110}$$

Analysis proceeds exactly as for the spherically symmetric case,

- Large-r asymptotics of the wavefunction determined by first and last terms in (110). In the limit $r \to \infty$ we have,

  $$\frac{d^2\chi}{dr^2} - \nu^2\chi \simeq 0$$

  which implies that the solutions of (85) have behaviour,

  $$\chi(r) \;\; \sim \;\; \exp(\pm\nu r) \qquad\qquad \text{as} \;\; r \to \infty \tag{111}$$

  We must choose an exponentially decaying solution for a normalizable wavefunction.

- Wavefunction should be finite at $r = 0$.

- As before, it is convenient to seperate out the exponential dependence of the wavefunction and look for a solution of the form,

  $$g(r) \;\; = \;\; f(r)\exp(-\nu r)$$

  The Schrödinger equation (110) now becomes,

  $$\frac{d^2 f}{dr^2} \; + \; \frac{2}{r}(1-\nu r)\frac{df}{dr} \; - \; \frac{l(l+1)}{r^2}f \; + \; \frac{1}{r}(\beta - 2\nu)f \;\; = \;\; 0 \tag{112}$$

Equation (112) is a homogeneous, linear ODE with a *regular singular point* at $r = 0$. Apply standard method and look for a solution in the form of a power series around $r = 0$,

$$f(r) = r^\sigma \sum_{n=0}^{\infty} a_n r^n \tag{113}$$

Substitute series (113) for $f(r)$ in (112).

- The lowest power of r which occurs on the LHS is $a_0 r^{\sigma-2}$ with coefficient $\sigma(\sigma-1) + 2\sigma - l(l+1) = \sigma(\sigma+1)) - l(l+1)$. Equating this to zero yields the *indicial equation*,

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

with roots $\sigma = l$ and $\sigma = -l-1$.

- Root $\sigma = -l-1 \Rightarrow g(r) \sim 1/r^{l+1}$ near $r = 0$. This yields a singular wavefunction which violates the boundary condition at the origin. Thus we choose root $\sigma = l$ and our series solution simplifies to,

$$f(r) = r^l \sum_{n=0}^{\infty} a_n r^n \tag{114}$$

- Now collect all terms of order r^{l+n-2} on the LHS of (112) and equate them to zero to get,

$$\begin{aligned}(n+l)(n+l-1)a_n + 2(n+l)a_n - l(l+1)a_n &- \\ 2\nu(n+l-1)a_{n-1} + (\beta - 2\nu)a_{n-1} &= 0\end{aligned}$$

or more simply,

$$a_n = \frac{(2\nu(n+l) - \beta)}{n(n+2l+1)} a_{n-1} \tag{115}$$

This recurrence relation determines all the coefficents a_n in the series (114) in terms of the first coefficent a_0. As above, there are two possibilities,

- The series (114) terminates. In other words $\exists\, n_{\max} > 0$ such that $a_n = 0 \ \forall\, n \geq n_{\max}$.

- The series (114) does not terminate. In other words $\nexists\, n_{\max} > 0$ such that $a_n = 0 \ \forall\, n \geq n_{\max}$.

As before, the second possibility does not yield normalizable wave functions. To see this note that Eqn (115) determines the large-n behaviour of the coefficients a_n as,

$$\frac{a_n}{a_{n-1}} \rightarrow \frac{2\nu}{n} \qquad \text{as} \quad n \rightarrow \infty \tag{116}$$

We can now compare this with the power series for the function,

$$h(r) = \exp(+2\nu r) \;=\; \sum_{n=0}^{\infty} b_n r^n \qquad \text{with} \;\; b_n = \frac{(2\nu)^n}{n!}$$

whose coefficients obey,

$$\frac{b_n}{b_{n-1}} \;=\; \frac{(2\nu)^n}{(2\nu)^{n-1}}\,\frac{(n-1)!}{n!} \;=\; \frac{2\nu}{n}$$

We deduce that (116) is consistent with the asymptotics,

$$f(r) \sim h(r) = \exp(+2\nu r) \;\;\Rightarrow\;\; g(r) = f(r)\exp(-\nu r) \sim \exp(+\nu r)$$

as $r \rightarrow \infty$ which is consistent with the expected exponential growth (111) of generic solutions of (110). This corresponds to a non-normalizable wavefunction which we reject.

To give a normalisable wave-function therefore, the series (114) must therefore terminate. There must be an integer $n_{\text{max}} > 0$ such that $a_{n_{\text{max}}} = 0$ with $a_{n_{\text{max}}-1} \neq 0$. From the recurrence relation (115) we can see that this happens if and only if,

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

for an integer $N = n_{\text{max}} + l > l$. Recalling the definitions,

$$\nu^2 = -\frac{2mE}{\hbar^2} \;>\; 0, \qquad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2}$$

This yields the spectrum of energy levels,

$$E = E_N \;=\; -\frac{e^4 m_e}{32\pi^2\varepsilon_0^2\hbar^2}\,\frac{1}{N^2} \tag{117}$$

for $N = 1, 2, \ldots$.

- The resulting spectrum of energy eigenvalues is identical to that of the Bohr atom and to our analysis of the spherically symmetric wavefunctions.

- The new feature is that there is a large **degeneracy** at each level. To see this note that the energy E_N given in (117) only depends on N and not on the angular momentum quantum numbers,

$$0 \le l \le N-1 \qquad\qquad -l \le m \le +l$$

Thus the total degeneracy at each level is,

$$\begin{aligned} D(N) &= \sum_{l=0}^{N-1} \sum_{-l}^{+l} 1 \\ &= \sum_{l=0}^{N-1} (2l+1) \\ &= 2\left(\frac{1}{2}N(N-1)\right) + N = N^2 \end{aligned}$$

The full spectrum

$$\chi_{N,l,m}(r,\theta,\phi) = \xi^l \, L_{N,l}(\xi) \, \exp(-\xi) \, Y_{l,m}(\theta,\phi)$$

where,

$$\xi = \frac{\beta r}{2N} = \frac{e^2 m r}{4N\pi\varepsilon_0\hbar^2}$$

$L_{N,l}(\xi)$ is a *Generalised Laguerre polynomial* and $Y_{l,m}(\theta,\phi)$ is a spherical harmonic. The quantum numbers are,

- $N = 1, 2, 3, \ldots$ is the *principal quantum number*.
- $l = 0, 1, \ldots, N-1$ is the total angular momentum quantum number.
- The integer m with $-l \le m \le +l$ is the quantum number for the z-component of angular momentum.

Bohr model of atom emerges for states with $m = l \simeq N >> 1$. In this case the z-component of angular momentum $L_z = m\hbar \simeq N\hbar$ and the total angular momentum $L = \sqrt{l(l+1)\hbar^2} \simeq N\hbar$.

The radal probability distribution,

$$\begin{aligned} r^2 g(r)^2 &\sim r^{2(l+1)} \exp\left(-\frac{\beta r}{2(l+1)}\right) \\ &\sim r^{2N} \exp\left(-\frac{\beta r}{N}\right) \end{aligned}$$

Attains a maximum where,

$$\frac{2N}{r} - \frac{\beta}{N} = 0 \tag{118}$$

Thus the peak value is at,

$$r_{\text{peak}} \simeq \frac{2N^2}{\beta} = N^2 r_1$$

where $r_1 = 2/\beta$ is the Bohr radius. Thus the radial probability distribution is therefore peaked around the radius of the N'th Bohr orbit.

Appendix

Fundamental constants

- Planck's constant, $\hbar = 1.05 \times 10^{-34} \ J\, s$
- Speed of light, $c = 3 \times 10^{8} \ ms^{-1}$
- Charge of the electron, $e = 1.60 \times 10^{-19} \ C$
- Mass of the electron, $m_e = 9.11 \times 10^{-31} \ kg$
- Mass of proton, $m_p = 1.67 \times 10^{-27} \ kg$
- The vacuum permittivity constant, $\varepsilon_0 = 8.854 \times 10^{-12} \ F\, m^{-1}$.

Basic facts about atoms

An atom has a positively charged *nucleus* surrounded by negatively charged electrons. Nucleus: Z protons, each of positive charge $+e$. Z is known as the atomic number. Also has $A - Z$ neutrons, each of mass $m_n \simeq m_p$, which carry no electric charge. Total mass of the nucleus,

$$M = Zm_p + (A - Z)m_n \simeq Am_n$$

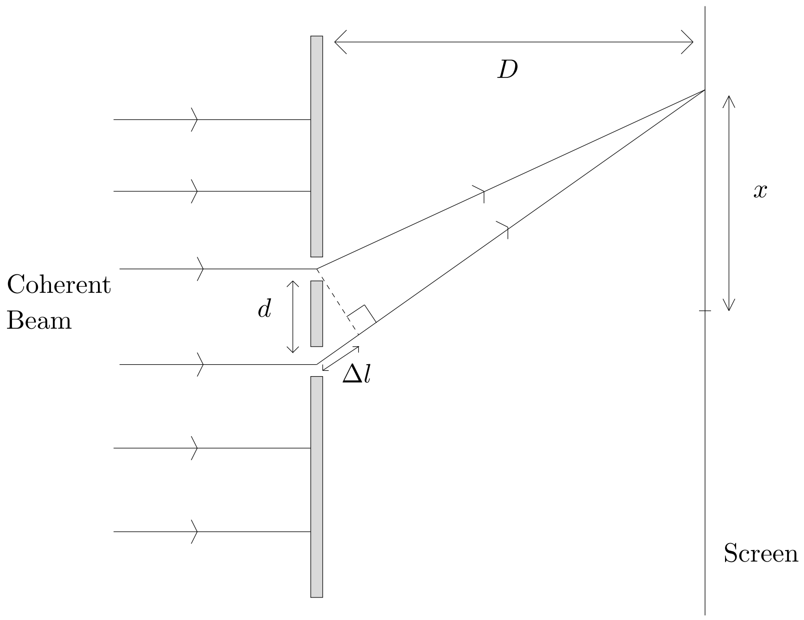


Figure 43: Double slit diffraction .

A is known as the atomic weight.

A neutral atom has Z electrons each of negative charge $-e$. If some are removed the atom becomes a positive ion.

The electrons are much lighter than the protons and neutrons of the nucleus: $m_e/m_p \simeq 1/1837$. Nearly all the mass of the atom resides in the nucleus.

Electrons are held in the atom by the electrostatic attraction between each electron and the nucleus.

Protons and neutrons are bound in the nucleus by the *strong nuclear force*. Though short-ranged, this is much stronger than the electrostatic repulsion between protons. The electrons do not feel the strong force.

Diameter of nucleus $\sim 10^{-15}\ m$. Diameter of whole atom $\sim 10^{-10}\ m$. Because the size of the nucleus is so much smaller than that of the whole atom, for the purpose of understanding atomic structure the nucleus can be treated as a point charge.

Chemical properties of atoms are determined only by the number of electrons Z.

Isotopes are atoms with the same value of Z but different A. They have the same chemistry but different radioactive properties.

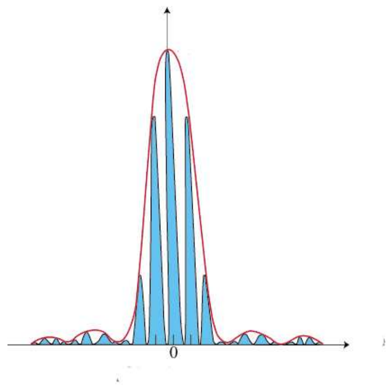


Figure 44: Double-slit diffraction pattern: plot of I against x

Diffraction

The experimental set-up for double slit diffraction is shown in Figure 43.

Coherent means that waves arrive at each slit in phase.

As shown in Figure 43 the path difference between rays from the two slits is Δl.

When $D >> d$ the path difference is approximately equal to $\simeq (d/D)x$.

Light and dark regions on the screen occur when waves from the two slits interfere constructively and destructively respectively.

In particular, dark regions occur where the paths differ by half a wavelength,

$$\Delta l \simeq \left(\frac{d}{D}\right) x \quad = \quad \left(n + \frac{1}{2}\right) \lambda$$

where n is an integer.

The resulting pattern of light and dark bands can be illustrated by plotting the intensity, I, of the light hitting the screen as a function of x as in Figure 44

Useful formulae

- **Non-relativistic mechanics** Free particle of mass m, moving at velocity $\mathbf{v}$. Speed $v = |\mathbf{v}| << c$. Momentum and energy of the particle are given as,

$$\mathbf{p} = m\mathbf{v} \qquad E = \frac{1}{2}mv^2$$

Thus we have

$$E = \frac{|\mathbf{p}|^2}{2m}$$

.

- **Relativistic mechanics** Free particle of mass m, moving at velocity $\mathbf{v}$. Speed $v = |\mathbf{v}|$. Momentum and energy of the particle are given as,

$$\mathbf{p} = \frac{m\mathbf{v}}{\sqrt{1 - v^2/c^2}} \qquad E = \frac{mc^2}{\sqrt{1 - v^2/c^2}}$$

Thus we have,

$$E = \sqrt{m^2c^4 + |\mathbf{p}|^2c^2}.$$

For the special case of a massless particle this reduces to $E = c|\mathbf{p}|$.

- **Wave motion** Complex wave-form,

$$A \exp\left(i\mathbf{k} \cdot \mathbf{x} - i\omega t\right)$$

Define the following quantities,

  - Wave-vector $\mathbf{k}$.
  - Wavelength λ is given as $\lambda = 2\pi/|\mathbf{k}|$.
  - Angular frequency ω.
  - Frequency $\nu = \omega/2\pi$.

Velocity of wave v_{wave} is given as,

$$v_{\text{wave}} = \frac{\omega}{|\mathbf{k}|} = \nu\lambda.$$

For electromagnetic waves this is equal to c.

Useful Integrals

$$\mathcal{I}(a) \;=\; \int_{-\infty}^{+\infty} dx\;\exp(-a\,x^2) \;=\; \sqrt{\frac{\pi}{a}} \qquad (119)$$

The integral exists for complex a provided $\Re[a] > 0$. The integral,

$$\mathcal{I}_2(a) \;=\; \int_{-\infty}^{+\infty} dx\; x^2\;\; exp(-a\,x^2) \;=\; \frac{1}{2}\sqrt{\frac{\pi}{a^3}} \qquad (120)$$

is obtained by differentiating (119) with respect to the parameter a.

Another useful integral is,

$$\mathcal{J}(a,b) \;=\; \int_{-\infty}^{+\infty} dx\;\cos(bx)\;\exp(-a\,x^2) \;=\sqrt{\frac{\pi}{a}}\;\exp\left(-\frac{b^2}{4a}\right) \qquad (121)$$

Again the integral exists for complex a and b provided $\Re[a] > 0$.

To prove (121), first note that

$$\mathcal{J}(a,0) \;=\; \mathcal{I}(a) = \sqrt{\frac{\pi}{a}}$$

Differentiating $\mathcal{J}(a,b)$ wrt to b yields,

$$\frac{\partial \mathcal{J}}{\partial b} \;=\; -\int_{\infty}^{+\infty} dx\; x\;\sin(bx)\;\exp(-a\,x^2)$$

Integrating by parts on the RHS then gives

$$\begin{aligned} \frac{\partial \mathcal{J}}{\partial b} \;&=\; \left[\frac{\sin(bx)}{2a}\;\exp(-ax^2)\right]_{-\infty}^{+\infty} - \int_{\infty}^{+\infty} dx\;\frac{b}{2a}\;\cos(bx)\;\exp(-a\,x^2) \\ &=\; -\frac{b}{2a}\;\mathcal{J} \end{aligned}$$

Integrating this relation we obtain,

$$\mathcal{J}(a,b) \;=\; \mathcal{J}(a,0)\exp\left(-\frac{b^2}{4a}\right) \;=\sqrt{\frac{\pi}{a}}\;\exp\left(-\frac{b^2}{4a}\right)$$

We can now use (119) and (121) to do the Gaussian integral discussed below equation (24) in the text,

$$\psi(x,t) \;=\; \int_{-\infty}^{+\infty} dk\;\exp\left(F(k)\right)$$

with,

$$F(k) \;=\; -\frac{1}{2}\alpha k^2 + \beta k + \delta$$

where the complex constants α, β and γ are defined in the text. Noting that $\exp(-iz) = \cos(z) - i\sin(z)$ for any complex number z we find,

$$\psi(x,t) \;=\; e^{\delta} \int_{-\infty}^{+\infty} dk\;\; (\cos(i\beta k) - i\sin(i\beta k))\;\; \exp\left(-\frac{1}{2}\alpha k^2\right)$$

The second term in brackets vanishes as the integrand is an odd function of k. The remaining integral can be evaluated using (121) with $b = i\beta$ and $a = \alpha/2$, to get,

$$\psi(x,t) \;=\; \sqrt{\frac{2\pi}{\alpha}}\;\exp\left(\frac{\beta^2}{2\alpha} + \delta\right)$$

as claimed in the text.

Miscellaneous

General case of uncertainty principle Extend proof given in the text to cases where $\langle x\rangle$, $\langle p\rangle \neq 0$. *drop subscript* $\langle\rangle_\Psi$ *for brevity.*

Define,

$$\begin{aligned}\hat{A} &= \hat{p} - \langle p\rangle \\ \hat{B} &= \hat{x} - \langle x\rangle\end{aligned}$$

Note that,

$$\begin{aligned}\langle A^2\rangle &= \left\langle (p - \langle p\rangle)^2\right\rangle \\ &= \left\langle p^2 - 2p\langle p\rangle + \langle p\rangle^2\right\rangle \\ &= \langle p^2\rangle - 2\langle p\rangle^2 + \langle p\rangle^2 \\ &= \langle p^2\rangle - \langle p\rangle^2 \;=\; (\Delta p)^2\end{aligned}$$

Similarly $\langle B^2\rangle = (\Delta x)^2$.

Can also check that,

$$\begin{aligned}[\hat{A},\hat{B}] &= [\hat{p},\hat{x}] - [\langle p\rangle,\hat{x}] - [\hat{p},\langle x\rangle] + [\langle p\rangle,\langle x\rangle] \\ &= [\hat{p},\hat{x}] = -i\hbar\hat{\mathbb{I}}\end{aligned}$$

Now define,

$$\Psi_s(x) \;=\; \left(\hat{A} - is\hat{B}\right)\;\Psi(x)$$

Use identical argument to that given in the text to show that,

$$\int_{-\infty}^{+\infty} |\Psi_s(x)|^2 \, dx \;\;\geq\;\; 0 \;\;\Rightarrow\;\; 4\langle A^2\rangle\langle B^2\rangle \;\;\geq\;\; \hbar$$

Heisenberg uncertainty principle then follows from the relations $\langle A^2\rangle = (\Delta p)^2$ and $\langle B^2\rangle = (\Delta x)^2$ obtained above $\Box$.

Angular momentum operators in spherical polar coordinates

Relation between cartesian and spherical polar coordinates,

$$x_1 = r\sin(\theta)\cos(\phi) \quad x_2 = r\sin(\theta)\sin(\phi) \quad x_3 = r\cos(\theta)$$

Using the chain rule,

$$\begin{aligned}\frac{\partial}{\partial x_1} &= \left(\frac{\partial r}{\partial x_1}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x_1}\right)\frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x_1}\right)\frac{\partial}{\partial \phi} \\ &= \sin(\theta)\cos(\phi)\frac{\partial}{\partial r} + \cos(\theta)\cos(\phi)\frac{1}{r}\frac{\partial}{\partial \theta} - \frac{\sin(\phi)}{r\sin(\theta)}\frac{\partial}{\partial \phi}\end{aligned}$$

and similarly for $\partial/\partial x_2$ and $\partial/\partial x_3$.

Proceeding in this way, we obtain

$$\begin{aligned}\hat{L}_1 &= -i\hbar\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right) \\ &= i\hbar\left(\cos(\phi)\cot(\theta)\frac{\partial}{\partial \phi} + \sin(\phi)\frac{\partial}{\partial \theta}\right)\end{aligned}$$

Similarly we find

$$\hat{L}_2 \;=\; i\hbar\left(\sin(\phi)\cot(\theta)\frac{\partial}{\partial \phi} - \cos(\phi)\frac{\partial}{\partial \theta}\right)$$

and,

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

Finally can check that,

$$\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2 \;=\; -\frac{\hbar^2}{\sin^2(\theta)}\left[\sin(\theta)\frac{\partial}{\partial \theta}\;\left(\sin(\theta)\frac{\partial}{\partial \theta}\right) \;+\; \frac{\partial^2}{\partial \phi^2}\right]$$

The alternating tensor Indices i, j, $k = 1, 2, 3$. $\varepsilon_{ijk} = 0$ unless all indices are different, $i \neq j \neq k \neq i$. If all indices are different, then $\varepsilon_{ijk} = +1$ if (ijk) is a cyclic permutation of (123) and -1 otherwise.