Engineering Physics (2025)
Course code 25PY101
Module 1 Unit 2: Quantum mechanics

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December 7, 2025

M1U2 Plan

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Quantum mechanics jigsaw puzzle

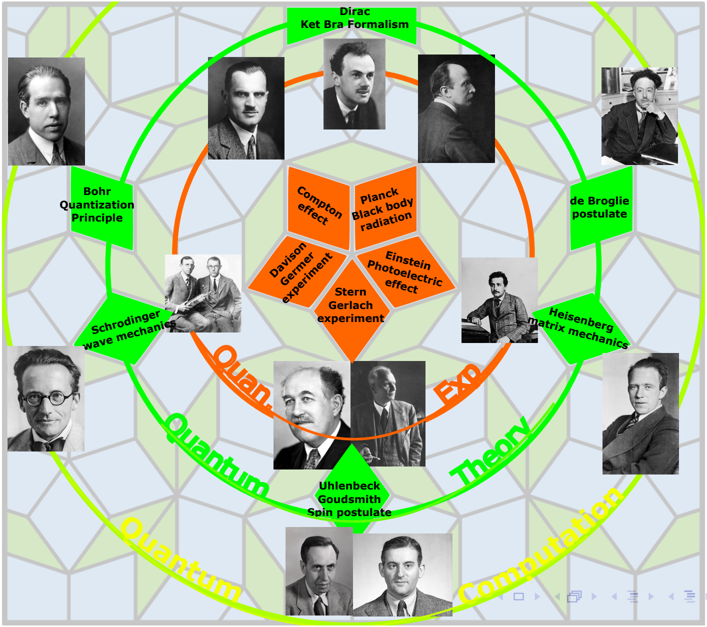
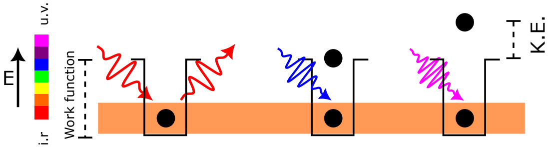
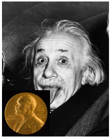


Photo-electric effect

Definition

Light of **suitable** frequency leads to **instantaneous** emission of electron from a metal surface.



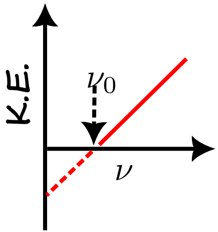


A. Einstein

- Discovered by Albert Einstein in 1905.
- The emitted electron is called the **photo-electron**.
- The minimum energy required to emit an electron is a material property and is called the **work function** of the metal.

Classical explanation of photo-electric effect

- Light is a wave with energy given by its intensity.
- Therefore, even low-frequency light (if sufficiently intense) should eventually provide enough energy to eject electrons — though perhaps after some time delay.
- But it is observed that
  - Emission of electrons is instantaneous – even for low intensity light as long as frequency of light is above a certain threshold ν_0.
  - No electrons are emitted if the frequency is below the threshold, no matter how intense the light is.
  - The kinetic energy of emitted electrons depends on the frequency of light, not its intensity.



Key Insight

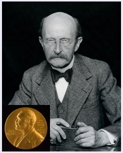
Classical electromagnetic theory cannot explain photoelectric effect!

Quantum mechanical explanation of Photoelectric effect

- Albert Einstein borrowed the idea of **quantum**[1] from Max Planck's theory of blackbody radiation and applied to photoelectric effect.

Planck's law

- Max Planck postulated that the light energy is absorbed or emitted by matter in is a packet of energy. The quantum of energy is related to the frequency ν by $E = h\nu$ where h is the **Planck's constant** given by 6.625×10^{-34} J s.
- The quantum of light energy is called **photon**.



Max Planck

Estimate: Energy of infra-red photon

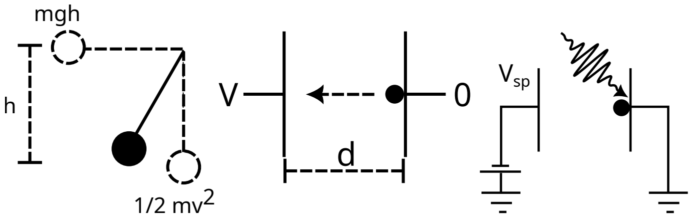
Wavelength of infra-red photon is 1 μm. [Hint: $c = \nu\lambda$]

[1] "Quantum" is Latin for "a certain amount". In the context of physics, the word quantum refers to a **packet**.

Photoelectric effect: experiment

Theorem

An electron under potential difference of V gains kinetic energy of eV.



Proof.

- Electric field is $E = \frac{V}{d}$.
- Acceleration is $|a| = \frac{eE}{m}$.
- Initial velocity $u = 0$. Final velocity is $v^2 = 2ad$.
- Kinetic energy K.E. $= \frac{1}{2}mv^2 = eV$.

Photoelectric effect: energy equation

- Photon with energy $E = h\nu$ transfers energy to the electron, to overcome the work function Φ. The rest of the energy is photoelectron's kinetic energy.

$$\text{K.E.} = h\nu - \Phi$$

- The photoelectrons generate photocurrent.
- In the experiment, the photo electron emitted is decelerated by applying a **stopping potential** V_{sp} till the photocurrent is zero. Thus,

$$\text{K.E.} = eV_{sp}$$

- Therefore, frequency is related to stopping potential as

$$eV_{sp} = h\nu - \Phi$$

- The plot of $\nu(\rightarrow x)$ vs $V_{sp}(\rightarrow y)$ is a straight line $y = mx + c$ with slope $m = h/e$ and y-intercept $c = -\Phi$.
- The x-intercept is the minimum frequency of photon to generate photo-current and is called the **threshold frequency** $\nu_0 = \frac{\Phi}{h}$.

Photoelectric effect: momentum equation

- From Einstein's special theory of relativity, the momentum of a particle of mass m is related to its total energy E by

$$E^2 = p^2c^2 + m^2c^4$$

where c is the velocity of light.

- If the light is considered as a massless particle i.e. $m_{\text{photon}} = 0$, then

$$E = p_{\text{photon}}c \Rightarrow p_{\text{photon}} = \frac{E}{c}$$

- However, the velocity of light is related to its wavelength and frequency by

$$c = \nu\lambda$$

- Using the Planck's law for the energy of photon, the momentum is given by

$$p_{\text{photon}} = \frac{h}{\lambda}$$

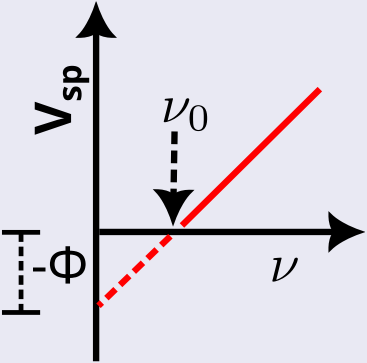
Photoelectric effect: problems

Estimate: Energy of X-ray photon

Wavelength of X-ray photon is 0.708 Å.

[Hint: (a). $E \propto 1/\lambda$. (b). $E_{\lambda=1\,\mu\text{m}} = 1.24\,\text{eV}$]

Problem



The work function Φ of Au is 4.90 eV.

1. *A blue photon is incident on Au. Does it emit photo-electron? If yes, what is the stopping potential required to have zero photocurrent.* [$\lambda_{\text{blue}} = 460\,\text{nm}$]
2. *Determine the threshold frequency ν_0 for photon emission of electrons for Au.*

Repeat the above steps for Cs with work function 1.90 eV.

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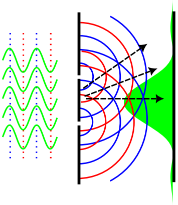
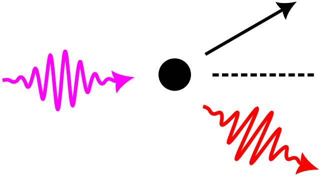
Radiation: Wave vs Particle

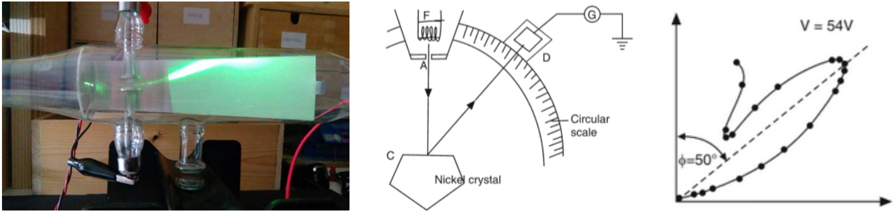




- Young's double slit experiment
- Discovered in 1801
- Light is a wave with amplitude, frequency and wavelength
- **Principle of superposition**: Waves superpose leading to constructive and destructive fringes.
- Animation for double slit experiment [Click]

- Compton effect
- Discovered in 1923.
- Light is a particle with momentum!
- **Conservation of momentum**: Light redshifts (wavelength increases) upon scattering off an electron.

Matter: Particle vs Wave



(a)cathode ray tube, Davison-Germer experiment (b) and data (c).

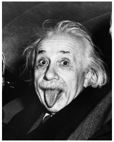
- Thomson's cathode ray tube experiment
- Discovered in 1897
- Electron is a particle

- Davisson and Germer experiment
- Discovered in 1927.
- Electron is a wave!

Key Insight

The name of the game is light-matter interaction. And nature plays the game in a **symmetric** fashion!

Summary of nature of light-matter interaction

	Wave	Particle
Light	 Young's double slit[2]	    Einstein's photo-electric effect Compton's scattering effect
Electron	   Davison's and Germer's diffraction experiment	  Thomson's cathode ray tube experiment

[2] British polymath who has been described as "The Last Man Who Knew Everything" and disproved Newton's corpuscular theory of light.

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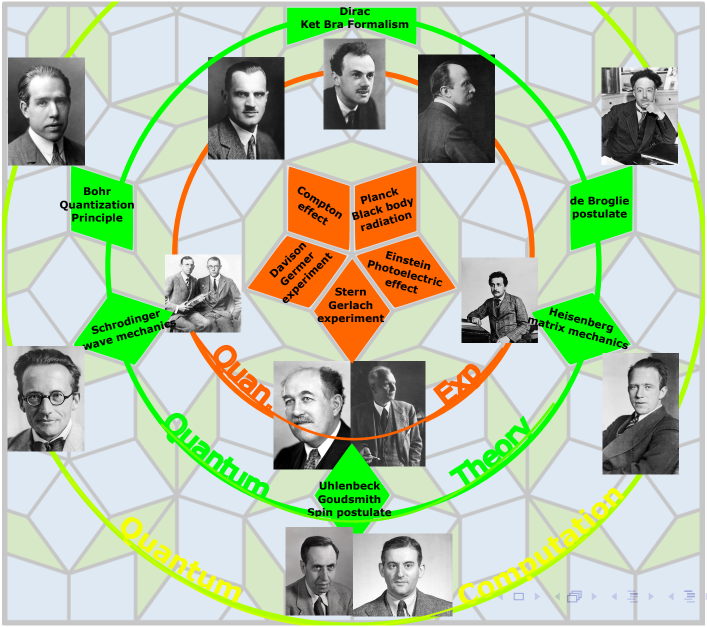
Quantum mechanics jigsaw puzzle



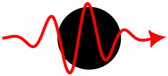
Theories of quantum physics

- Max Planck's postulate of quantization of light energy absorbed or emitted by electron in quanta (plural for quantum)
- Louis de Broglie's postulate of existence of matter waves
- Werner Heisenberg's principle of uncertainty
- Erwin Schrödinger's wave equation

Wave-Particle Duality

de Brogie hypothesis

Any moving particle is associated with a wave. The waves associated with particles are called **de Broglie waves** or **matter waves**.



- Louis de Broglie in 1924 postulated the existence of **matter waves**.
- He suggested since light wave exhibits particle like behaviour, matter particles should be expected to show wave-like properties. This is the hypothesis of **wave-particle duality**.
- The wavelength λ of the matter wave is related to the momentum p of the matter particle by

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

Matter wave: properties

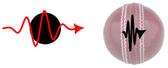
- Matter waves are due to motion of particle and are independent of charge. Therefore, they are neither electromagnetic waves nor acoustic waves. They are a new kind of waves.
- Can propagate/travel through vacuum and do not require any medium for propagation.
- Smaller the mass, longer the de Broglie wavelength.
- Smaller the velocity, longer the de Broglie wavelength.
- Velocity of matter waves depends on velocity of particle and is not a constant quantity.

Estimate: de Broglie wavelength of thermal electron

Estimate at room temperature.

Estimate: de Broglie λ of macroscopic particle

Cricket ball of mass 150 g is bowled at 140 km h^{-1}.



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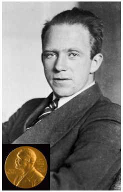
Heisenberg uncertainty principle

Uncertainty principle/hypothesis

Precise values of position and momentum of a particle cannot be determined **simultaneously**. If the uncertainty in position is Δx and uncertainty in momentum is Δp, then

$$\Delta x \, \Delta p \geq \frac{\hbar}{2}, \qquad \text{where} \quad \hbar = \frac{h}{2\pi}$$

where $\hbar$ is the reduced/modified Planck's constant.



- Werner Heisenberg postulated the uncertainty principle in 1927.
- In classical mechanics, position and momentum are **deterministic**. In quantum mechanics, they are not deterministic and are associated with **uncertainties**.
- If position is measured with low uncertainty, then measurement of momentum has high uncertainty and vice versa.

Uncertainty → Probability

- The uncertainty principle relates any pair of **conjugate** variables.
- Position – momentum is a pair of conjugate variables.
- Energy – time is also a conjugate variable pair.
- So the uncertainty in energy ΔE is related to the uncertainty in time by Δt by

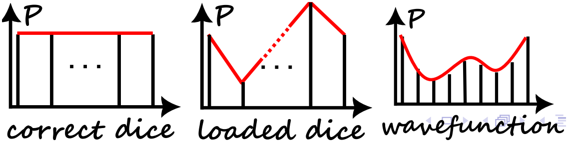
$$\Delta E \, \Delta t \geq \frac{\hbar}{2}$$

  This is the second statement/corollary of Heisenberg's uncertainty principle.
- Due to the smallness of reduced Planck's constant, the uncertainty principle is significant for subatomic particles.
- The cause of uncertainty is **limitation of measurement**.

Key Insight

Since the position cannot be measured with certainty, we determine the **probability** of finding an electron at a particular position.

- The way to deal with uncertainty is to talk in terms of probability.
- If a system has N events, the probability of event A is defined as number of times event A has occured over total number of outcomes.
- A coin is a "2-sided polyhedron/dice". The probability of coin having heads is $\frac{1}{2}$. Similarly for N-sided dice the probability is $\frac{1}{N}$.
- A "loaded" dice can different probability for each outcome.
- In the limit of ∞-sided dice, the probability of a outcome becomes a function.



Uncertainty in function of variable

- If uncertainty in variable x is Δx, then the uncertainty in variable $f(x)$ is given by

$$\Delta f = \frac{\mathrm{d}f}{\mathrm{d}x}\Delta x$$

- Kinetic energy E is related to momentum p by

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

- If uncertainty in momentum is Δp, then uncertainty in kinetic energy E is given by

$$\Delta E = \frac{\mathrm{d}E}{\mathrm{d}p}\Delta p = \frac{p}{m}\Delta E$$

Problem

- *Uncertainity in position of electron is* $12\,\text{Å}$.
- *Nominal energy of electron is* $16\,\mathrm{eV}$.
- *Determine the uncertainty in momentum and kinetic energy*

M1U2 Plan

Schrödinger's wave equation

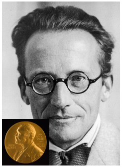
Wave equation hypothesis

If the **wave function** of a particle of mass m is $\Psi(x, t)$, then it satisfies the **wave equation** given by

$$-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) = j\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

where $V(x)$ is the potential function[a] and j is the imaginary constant $\sqrt{-1}$.

[a] Potential energy and not electric potential difference



- Erwin Schrödinger postulated the wave equation in 1926 that incorporated principles of quanta introduced by Planck and wave-particle duality introduced by de Broglie.
- The wave function $\Psi(x, t)$ describes the behaviour of particle
- $\Psi(x, t)$ can be a **complex** quantity.

Analysis of the wave equation (W.E.)

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)=j\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

1. The independent variables/quantities are position x and time t whereas the dependent variable is the wave function Ψ. Therefore, wave function is a function of position and time
$$\Psi(x,t)$$
2. W.E. is a **partial** differential equation.
   - A differential equation relates dependent variable y to the independent variable x. The relationship is given by derivatives $\frac{\mathrm{d}\,y}{\mathrm{d}\,x},\frac{\mathrm{d}^2\,y}{\mathrm{d}\,x^2},\ldots$
   - A partial differential equation relates dependent variable z to the independent variables x and y. The relationship is given by partial derivatives $\frac{\partial\,z}{\partial\,x},\frac{\partial\,z}{\partial\,y},\frac{\partial^2\,z}{\partial\,x^2},\ldots$
3. W.E. is a **second order** differential equation.
   - A first order differential equation has only first order derivative.
   - A second order differential equation has upto second order derivatives.
4. The potential energy $V(x)$ is a parameter whereas $\hbar$, m, j are constants.

Solution of the W.E. : Separation of variables

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2 \Psi(x,t)}{\partial x^2}+V(x)\,\Psi(x,t)=j\hbar\frac{\partial \Psi(x,t)}{\partial t}$$

- The goal is to find the solution $\Psi(x,t)$ for a given $V(x)$.
- We assume form of the solution as

$$\Psi(x,t)=\psi(x)\,\phi(t)$$

where $\psi(x)$ is a function of the position only and $\phi(t)$ is a function of the time only.

- Upon substitution of above form, W.E. reduces to

$$-\frac{\hbar^2}{2m}\phi(t)\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)\,\psi(x)\,\phi(t)=j\hbar\,\psi(x)\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}$$

W.E. $$-\frac{\hbar^2}{2m}\phi(t)\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)\psi(x)\phi(t)=j\hbar\,\psi(x)\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}$$

W.F. $$\Psi(x,t)=\psi(x)\phi(t)$$

- Divide the above equation by total wave function so that

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)=j\hbar\frac{1}{\phi(t)}\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}$$

- Since L.H.S. is a function of x only and R.H.S. is a function of t only, each side must be equal to constant. Let us call this the **separation constant** η.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)=\eta,\qquad j\hbar\frac{1}{\phi(t)}\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}=\eta$$

Solution: Time dependent part of W.F

$$j\hbar \frac{1}{\phi(t)} \frac{\mathrm{d}\,\phi(t)}{\mathrm{d}t} = \eta$$

- The time dependent side of W.E. is then given by

$$\frac{\mathrm{d}\,\phi(t)}{\mathrm{d}t} = -j\frac{\eta}{\hbar}\phi(t) \qquad \text{related to} \qquad \frac{\mathrm{d}\,y}{\mathrm{d}\,x} = cx$$

- The solution is a sinusoidal wave given by

$$\phi(t) = e^{-j\left(\frac{\eta}{\hbar}\right)t} \qquad \text{related to} \qquad y = e^{-j\omega t}$$

with angular frequency ω given by $[\nu = \frac{\omega}{2\pi}]$

$$\omega = \frac{\eta}{\hbar}, \quad \Rightarrow \eta = \hbar\omega = \frac{h}{2\pi}\cdot 2\pi\nu = h\nu$$

- From Planck's law, $E = h\nu$. Therefore,

$$\eta = E, \qquad \text{and} \qquad \phi(t) = e^{-j\left(\frac{E}{\hbar}\right)t} = e^{-j\omega t}$$

Solution: Time independent part of W.F

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)=\eta$$

- The time independent portion can now be written as

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

  where the separation constant is replaced by the total energy E.
- Therefore, the time independent part of W.E. is

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+\frac{2m}{\hbar^2}(E-V(x))=0$$

- This is called the time independent Schrödinger wave equation. The aim is to solve for the time independent wave function $\psi(x)$ for a given potential $V(x)$.

Physical meaning of wave function

Probability density hypothesis

If the **wave function** of a particle is $\Psi(x, t)$, then the probability density function is given by

$$|\Psi(x, t)|^2$$

- Max Born in 1926 postulated the **interpretation** of wave function.
- Let us assume that we have solved for the time independent part of wave function. Thus,

$$\Psi(x, t) = \psi(x)e^{-j\omega t}$$

- Since $\Psi(x, t)$ is a complex function, it cannot represent physical quantity. Its modulus squared is the **probability density** of finding particle between x and $x + \mathrm{d}x$ and is given by

$$|\Psi(x, t)|^2 = \Psi(x, t) \cdot \Psi^*(x, t) = \psi(x)e^{-j\omega t} \cdot \psi^*(x)e^{+j\omega t} = |\psi(x)|^2$$

- The probability of finding particle between x and $x + \mathrm{d}x$ is then

$$|\psi(x)|^2 \cdot \mathrm{d}x$$

Boundary conditions

- Total probability is unity.

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

  This condition is called **normality condition**.
- Continuity condition
  1. $\psi(x)$ must be finite, single-valued and continuous.
  2. $\frac{\partial \psi(x)}{\partial x}$ must be finite, single-valued and continuous.
- $\psi(x)$ must vanish at infinity.

$$\lim_{x \to \infty} \psi(x) = 0, \qquad \lim_{x \to -\infty} \psi(x) = 0$$

  This condition is due to the **physicality condition**.

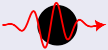
Problem

Normalization of wave function

1. *Consider the wave function* $\Psi(x,t) = A\cos\left(\frac{\pi x}{2}\right)e^{-j\omega t}$ *for* $-1 \leq x \leq +3$*. Determine* A *so that* $\int_{-1}^{+3} |\Psi(x,t)|^2 \, dx = 1$*.*

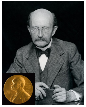
Summary

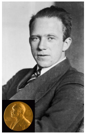
Postulates of quantum mechanics

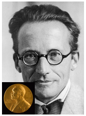


The work of Planck, de Broglie, Heisenberg, Born, and Schrödinger can be summarized as

1. The state of a particle is given by the wave function $\Psi(x, t)$.
2. The probability density of the particle is $|\Psi(x, t)|^2$. The probability of finding the particle in between x and $x + \mathrm{d}x$ is $|\Psi(x, t)|^2 \mathrm{d}x$.
3. If the uncertainty in position is Δx and uncertainty in position is Δp, then $\Delta x \, \Delta p \geq \frac{\hbar}{2}$.
4. The de Broglie wavelength of particle with momentum p is $\lambda = \frac{h}{p}$.
5. The energy E of the particle with frequency ν is $E = h\nu$.







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$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x) = 0 \qquad \Psi(x,t) = \psi(x)e^{-j\omega t}$$

- The aim is to solve for the time independent wave function $\psi(x)$ for a given potential $V(x)$.
- The potential functions that are useful to describe commonly occurring physical systems are

$V(x)$	Name	Physical systems
0	Constant potential	Particle in free space
$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$	Infinite potential well	Ideal atom
$V(x) = \begin{cases} 0 & -\frac{a}{2} < x < \frac{a}{2} \\ V_0 & \text{otherwise} \end{cases}$	Finite potential well	Work function
$V(x) = \begin{cases} V_0 & -\frac{a}{2} < x < \frac{a}{2} \\ 0 & \text{otherwise} \end{cases}$	Finite barrier	Nuclear fission
		Scanning Tunneling Micros

Particle in free space

$V(x)$: Constant potential

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \qquad \Psi(x,t) = \psi(x)e^{-j\omega t}$$

- Let us define the wave vector k as

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

so that the Time Independent Schrödinger Equation (TISE) is reduced to

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + k^2\psi(x) = 0$$

so that

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = -k^2\psi(x)$$

$V(x)$: Constant potential – Solution of TISE

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = -k^2\psi(x)$$

- The solution of above differential equation can be written as

$$\psi(x) = Ae^{jkx} + Be^{-jkx}$$

- If we use the Euler's formula

$$e^{jx} = \cos x + j\sin x$$

then the solution can be written also as

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

$V(x)$: Constant potential – Wave vector, Momentum and Energy

- All the wave vectors are allowed

$$k = -\infty \text{ to } + \infty$$

- The momentum is given by

$$p = \frac{h}{\lambda} \Rightarrow p = \hbar k \qquad [\because k = \frac{2\pi}{\lambda}]$$

- The corresponding energy levels are given by

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

$V(x)$: Constant potential – Solution of TDSE

- The solution of Time Dependent part of Schrödinger Equation (TDSE) is given by

$$\phi(t) = e^{-j\omega t}, \qquad \text{where} \qquad \omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}$$

- The total wave function is given by

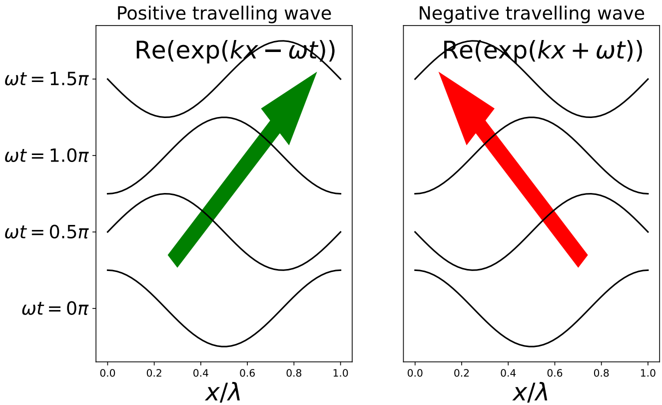
$$\Psi_k(x,t) = \psi_k(x)\phi_k(t) = e^{j\overline{kx - \omega t}}.$$

where the subscript k is the quantum number.

$V(x)$: Constant potential – Nature of solutions

- The solutions are **traveling** waves.
- The energy E can be any positive real number and is related to the wave vector k by

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



Constant potential: problems

Problem

An electron in free space is described by a plane wave given by $\Psi(x,t) = A\exp(j(kx - \omega t))$. *If* $k = 8 \times 10^{8}\,\mathrm{m}^{-1}$ *and* $\omega = 8 \times 10^{12}\,\mathrm{rad\,s}^{-1}$, *determine*

1. *phase velocity and wavelength of the plane wave*
2. *momentum and kinetic energy (in* eV*)*

Repeat the steps for $k = -1.5 \times 10^{9}\,\mathrm{m}^{-1}$ *and* $\omega = 1.5 \times 10^{13}\,\mathrm{rad\,s}^{-1}$.

Problem

Determine the wave number, wavelength, angular frequency, and period of wavefunction that describes an electron traveling in free space at a velocity of (a) $5 \times 10^{6}\,\mathrm{cm\,s}^{-1}$.

Summary of particle in free space

- For a particle in free space, all wave vectors are allowed $k = -\infty$ to $+\infty$.
- The corresponding energy levels are given by

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

- The time independent part of wave function is given by

$$\psi(x) = e^{jkx}$$

- The time dependent part of wave function is given by

$$\phi(t) = e^{-j\omega t}, \qquad \text{where} \qquad \omega = \frac{E}{\hbar}$$

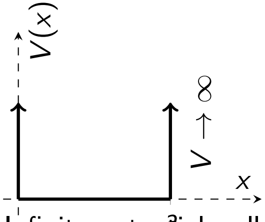
- The total wave function is given by

$$\Psi_k(x,t) = \psi_k(x)\phi_k(t) = e^{j\overline{kx-\omega t}}.$$

Particle in a 1D box

$V(x)$: Infinite potential

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$



Infinite potential well

- Consider a particle in a 1-dimensional infinite potential well.
- The well can be considered as a box.

Outside infinite box

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}(E - \infty)\psi(x) = 0$$

Inside infinite box

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

$V(x)$: Infinite potential well – Solution of TISE

Outside infinite box

- There is no wave function!

$$\psi(x) = 0$$

- Upon applying boundary conditions

Inside infinite box

- The wavefunction is

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

Left B.C.

$$\psi(x = 0) = 0$$
$$A\cos kx = 0$$
$$\Rightarrow A = 0$$

Right B.C.

$$\psi(x = a) = 0$$
$$B\sin ka = 0$$
$$\Rightarrow \sin ka = 0$$

$V(x)$: Infinite potential well – Solution of TISE

- The equation $\sin ka = 0$ is valid if

$$ka = n\pi$$

where n is a positive integer, or $n = 1, 2, 3, \ldots$. The parameter is referred to as quantum number. In terms of the quantum number, the wave vector is given by

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

- The prefactor B can be found by applying the **normality condition** of wave function.

$$\int_0^a |B \sin kx|^2 \, \mathrm{d}x = 1, \qquad \Rightarrow \qquad \int_0^a B^2 \sin^2 kx \, \mathrm{d}x = 1$$

$$\therefore B = \sqrt{\frac{2}{a}}$$

- Therefore, the time independent wave function is given by

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

$V(x)$: Infinite potential well – Energy levels

- Recall that the wave vector k is related to the energy E by

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \qquad \Rightarrow \qquad E = \frac{\hbar^2 k^2}{2m}$$

- Therefore, the energy is given by

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

Problem

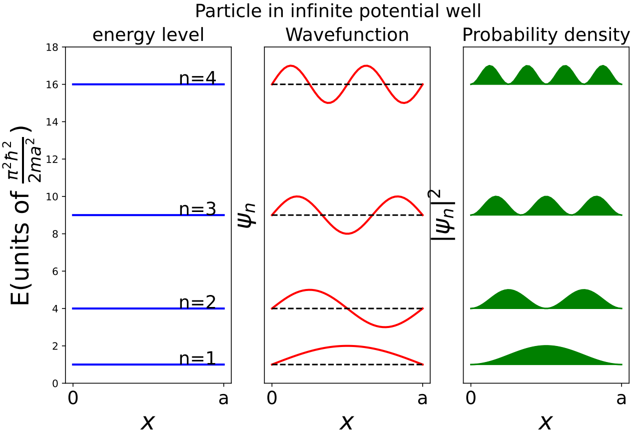
Electron in an infinite potential well of width 5 Å. *Calculate the first three energy levels.*

Key Insight

The energy of particle is **quantized** i.e. it can only have particular **discrete** values.

$V(x)$: Infinite potential well – Nature of solutions

- The solutions are **standing** waves.



Orthogonality condition

- Wave function associated with an energy level is normalized.
- In addition to normality, wave functions $\psi_m(x), \psi_n(x)$ corresponding to any two levels m, n of infinite potential well are orthogonal to each other i.e.

$$\int_0^a \psi_m^*(x)\psi_n(x)\,\mathrm{d}x = 0.$$

This is called the **orthogonality condition**.

Theorem

Prove the orthogonality condition for solutions of infinite potential well.

1D infinite well: problems

Problem

1. *A particle with mass of* 15 mg *is bound in a 1D infinte potential well that is* 1.2 cm *wide.*
2. *If the energy of the particle is* 15 mJ, *determine the value of n for that state.*
3. *What is the energy of the* $(n+1)$ *state?*
4. *Would quantum effects be observable for this particle?*

Summary of particle in infinite potential well

- For a particle in an infinite potential well, discrete wave vectors are allowed and are given by

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

- The corresponding energy levels are given by

$$E_n = \frac{\hbar^2 k^2}{2m}, \qquad \text{or} \qquad E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2}$$

- The time independent part of wave function is given by

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

- The time dependent part of wave function is given by

$$\phi_n(t) = e^{-j\omega_n t}, \qquad \text{where} \qquad \omega_n = \frac{E_n}{\hbar}$$

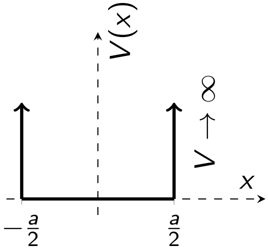
- The total wave function is given by

$$\Psi_n(x,t) = \psi_n(x)\phi_n(t),$$

Particle in a symmetric form infinite potential well

$V(x)$: Symmetric Infinite potential

$$V(x) = \begin{cases} 0 & -\frac{a}{2} \leq x \leq +\frac{a}{2} \\ \infty & \text{otherwise} \end{cases}$$



- Consider a particle in a **symmetric form** of 1-dimensional infinite potential well.
- The analysis for this potential is similar to the analysis for the asymmetric form discussed earlier.
- However, the general form of wave function can be considered as linear combination of exponential functions instead of trigonometric functions due to the symmetry of the problem.
- Thus, let the wave function inside the well be

$$\psi(x) = Ae^{jkx} + Be^{-jkx}$$

$V(x)$: Symmetric Infinite potential – Solution of TISE

$$\psi(x) = Ae^{jkx} + Be^{-jkx}$$

- Upon applying left boundary condition,

$$\psi(x = -\frac{a}{2}) = 0$$

$$\Leftrightarrow A \exp\big(-j\frac{ka}{2}\big) + B \exp\big(+j\frac{ka}{2}\big) = 0$$

$$\Leftrightarrow (A+B)\cos\big(\frac{ka}{2}\big) + j(-A+B)\sin\big(\frac{ka}{2}\big) = 0$$

$$\Leftrightarrow (A+B)\cos\big(\frac{ka}{2}\big) = 0 \text{ and } (-A+B)\sin\big(\frac{ka}{2}\big) = 0$$

$$\Leftrightarrow \Big[A+B = 0 \text{ or } \cos\big(\frac{ka}{2}\big) = 0\Big] \text{ and } \Big[A-B = 0 \text{ or } \sin\big(\frac{ka}{2}\big) = 0\Big]$$

$$\Leftrightarrow \Big[A-B = 0 \text{ and } \cos\big(\frac{ka}{2}\big) = 0\Big] \text{ or } \Big[A+B = 0 \text{ and } \sin\big(\frac{ka}{2}\big) = 0\Big]$$

- Same cases arise for the right boundary condition due to **symmetry** of the problem!

$V(x)$: Symmetric Infinite potential – Solution of TISE

$$\psi(x) = Ae^{jkx} + Be^{-jkx}$$

Case (i) Even wave functions

$$A - B = 0 \quad \Leftrightarrow \psi(x) = A\cos kx$$

and

$$\cos\left(\frac{ka}{2}\right) = 0 \quad \Leftrightarrow \frac{ka}{2} = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots \quad \Leftrightarrow k = \frac{\pi}{a}, \frac{3\pi}{a}, \ldots$$

Case (ii) Odd wave functions

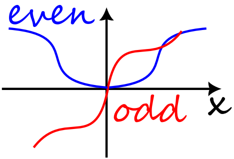
$$A + B = 0 \quad \Leftrightarrow \psi(x) = A\sin kx$$

and

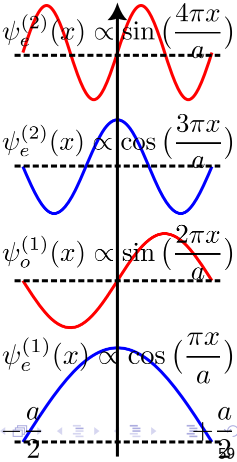
$$\sin\left(\frac{ka}{2}\right) = 0 \quad \Leftrightarrow \frac{ka}{2} = \pi, 2\pi, \ldots \quad \Leftrightarrow k = \frac{2\pi}{a}, \frac{4\pi}{a}, \ldots$$

$V(x)$: Symmetric Infinite potential – Nature of solutions

$$f(x) := \begin{cases} \text{even} & \text{if} \quad f(-x) = f(x) \\ \text{odd} & \text{if} \quad f(-x) = -f(x) \end{cases}$$



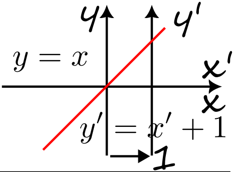
- The potential function is an even function as $V(-x) = V(x)$.
- The wave functions belonging to first case are even functions as $\cos x$ is an even function whereas the wave functions belonging to second case are odd functions as $\sin x$ is an odd function.
- There are two subfamilies of even and odd wave functions
- If we order the wave functions with increasing wave vector, then wave functions alternate between even and odd.



$V(x)$: Symmetric Infinite potential – Alternative solution

- Translation of origin by α transforms the function in new coordinate frame

$$f^{\text{new}}(x) = f^{\text{old}}(x + \alpha)$$



- The solutions to the symmetric form of infinite potential well can be obtained from the solutions to the asymmetric form by translating the coordinate frame by $\frac{a}{2}$.

$$x \to x + \frac{a}{2}$$

- The wave functions of the symmetric potential well are given by

$$\psi^{\text{sym}}(x) = \psi^{\text{asym}}(x + \frac{a}{2})$$

$$\begin{aligned}\psi^{\text{sym}}(x) &= \psi^{\text{asym}}(x + \frac{a}{2}) \\ &= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}\overline{x + \frac{a}{2}}\right) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a} + \frac{n\pi}{2}\right)\end{aligned}$$

$V(x)$: Symmetric Infinite potential – Alternative solution

- Upon substituting for $n = 1, 2, \ldots$, we have

$$\psi^{\text{sym}}(x) \propto \begin{cases} \sin\left(\frac{\pi x}{a} + \frac{\pi}{2}\right) & n = 1 \\ \sin\left(\frac{2\pi x}{a} + \frac{2\pi}{2}\right) & n = 2 \\ \sin\left(\frac{3\pi x}{a} + \frac{3\pi}{2}\right) & n = 3 \\ \sin\left(\frac{4\pi x}{a} + \frac{4\pi}{2}\right) & n = 4 \\ \vdots & \vdots \end{cases}$$

- Using the trigonometric relations, we have

$$\psi^{\text{sym}}(x) \propto \begin{cases} \cos\left(\frac{\pi x}{a}\right) & n = 1 \\ \sin\left(\frac{2\pi x}{a}\right) & n = 2 \\ \cos\left(\frac{3\pi x}{a}\right) & n = 3 \\ \sin\left(\frac{4\pi x}{a}\right) & n = 4 \\ \vdots & \vdots \end{cases}$$

  In some cases, prefactor of -1 can be absorbed into normalizing factor.
- Thus, the solutions are grouped into even and odd families.

Summary of particle in symmetric infinite potential well

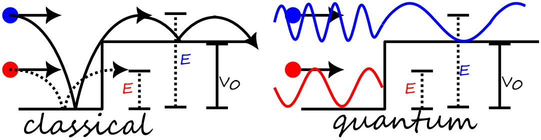
- For a particle in a symmetric infinite potential well, the allowed wave vectors are same as that of asymmetric infinite potential well.
- The corresponding energy levels are also same
- The potential well function is an even function i.e.

$$V(-x) = V(x).$$

Due to the symmetry of the potential well function, the wave functions are either **odd** or **even**.

Particle in a finite potential well

Potential energy barrier – Classical vs Quantum



- There are two regions – (I) without barrier and (II) with barrier

Region I

- Total energy E is kinetic energy T_I $$T_I = E$$
- Wave vector is real $$k_I = \sqrt{\frac{2mT_I}{\hbar^2}}$$
- Wave function has sinusoidal form $$\psi_I(x) = A \exp jk_I x + B \exp -jk_I x$$

Region II

- There are two cases – (i) total energy is greater than potential energy barrier and (ii) total energy is lesser than potential energy barrier.

Case (i) – $E > V_0$

- Classically, the particle overcomes the potential barrier with decreased kinetic energy.
- Quantum mechanically, the particle overcomes the potential barrier with decreased wave vector.

Region II

- Kinetic energy is reduced by V_0 $T_{II} = E - V_0$
- The wave function is given by

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{2m(E - V_0)}{\hbar^2}\psi(x) = 0$$

- Wave vector is real

$$k_{II} = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

- Wave vector is reduced compared to region I
- Wave function has sinusoidal form $\psi_{II}(x) = A \exp jk_{II}x + B \exp -jk_{II}x$

Curious case – $E < V_0$

- Classically, the particle **cannot** overcome the potential barrier.
- However, quantum mechanically, it is possible!
- Negative kinetic energy is allowed in quantum mechanics.

Region II

- Total energy E is less than potential barrier
- Kinetic energy is negative! $T_{II} = E - V_0 < 0$
- Wavevector is imaginary

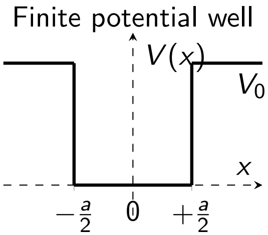
$$k_{II} = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} = j\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = j\kappa_{II}$$

- Wave function has exponential form

$$\begin{aligned}\psi_{II}(x) &= A \exp jk_{II}x + B \exp -jk_{II}x \\ &= A \exp -\kappa_{II}x + B \exp +\kappa_{II}x\end{aligned}$$

$V(x)$: Finite potential well

$$V(x) = \begin{cases} 0 & -\frac{a}{2} < x < \frac{a}{2} \\ V_0 & \text{otherwise} \end{cases}$$



- There are three regions – (I) well, (II) right of well, and (III) left of well.
- There are two cases – (i) total energy is less than potential barrier and (ii) total energy is greater than potential barrier
- Let us solve for case (i).

$V(x)$: Finite potential well – Case (i): $E < V_0$

Region I

- Kinetic energy is positive so $\psi_I(x) = A\exp(jk_I x) + B\exp(-jk_I x)$
- Apply the **symmetry condition** of even or odd wave function

$$\text{Case (1): } A = B \quad \text{or} \quad \text{Case (2): } A = -B$$

Region II

- Kinetic energy is negative so

$$\psi_{II}(x) = C\exp(-\kappa_{II}x) + D\exp(+\kappa_{II}x)$$

- Apply the **finiteness condition**

$$\lim_{x\to\infty} \psi_{II}(x) = \text{finite}$$
$$\Leftrightarrow D = 0.$$

Region III

- Kinetic energy is negative so

$$\psi_{III}(x) = E\exp(-\kappa_{III}x) + F\exp(\kappa_{III}x)$$

- Apply the **finiteness condition**

$$\lim_{x\to-\infty} \psi_{III}(x) = \text{finite}$$
$$\Leftrightarrow \quad E = 0.$$

- Due to **symmetry** of potential well $\kappa_{III} = \kappa_{II}$.

$V(x)$: Finite potential well – case (1): $A = B$

- Interface of Region I and Region II i.e. $x = \frac{+a}{2}$

Continuity condition of ψ

$$\psi_{\text{I}}\left(+\frac{a}{2}\right) = \psi_{\text{II}}\left(+\frac{a}{2}\right)$$

$$\Leftrightarrow A\left[\exp\left(j\frac{k_{\text{I}}a}{2}\right) + \exp\left(-j\frac{k_{\text{I}}a}{2}\right)\right]$$

$$= C\exp\left(-\frac{\kappa_{\text{II}}a}{2}\right)$$

$$\Leftrightarrow 2A\cos\frac{k_{\text{I}}a}{2} = C\exp-\frac{\kappa_{\text{II}}a}{2} \qquad (1)$$

Continuity condition of $\frac{d\psi}{dx}$

$$\frac{d\psi_{\text{I}}}{dx}\left(+\frac{a}{2}\right) = \frac{d\psi_{\text{II}}}{dx}\left(+\frac{a}{2}\right)$$

$$\Leftrightarrow jAk_{\text{I}}\left[\exp\left(j\frac{k_{\text{I}}a}{2}\right) - \exp\left(-j\frac{k_{\text{I}}a}{2}\right)\right]$$

$$= -C\kappa_{\text{II}}\exp-\frac{\kappa_{\text{II}}a}{2}$$

$$\Leftrightarrow 2Ak_{\text{I}}\sin\frac{k_{\text{I}}a}{2} = C\kappa_{\text{II}}\exp-\frac{\kappa_{\text{II}}a}{2} \qquad (2)$$

- Dividing (1) by (2) gives the **quantization condition** for wave vector.

$$\boxed{\tan\frac{k_{\text{I}}a}{2} = \frac{\kappa_{\text{II}}}{k_{\text{I}}}}$$

$V(x)$: Finite potential well – case (1): $A = B$

$$\tan \frac{k_I a}{2} = \frac{\kappa_{II}}{k_I} \qquad (3)$$

- This is a transcendental type of equation [3] and **cannot** be solved analytically!
- We have to employ numerical techniques.
- First let us introduce dimensionless variable z and constant z_0

$$z = \frac{k_I a}{2} = \frac{a}{2}\sqrt{\frac{2mE}{\hbar^2}}, \qquad z_0 = \frac{a}{2}\sqrt{\frac{2mV_0}{\hbar^2}}$$

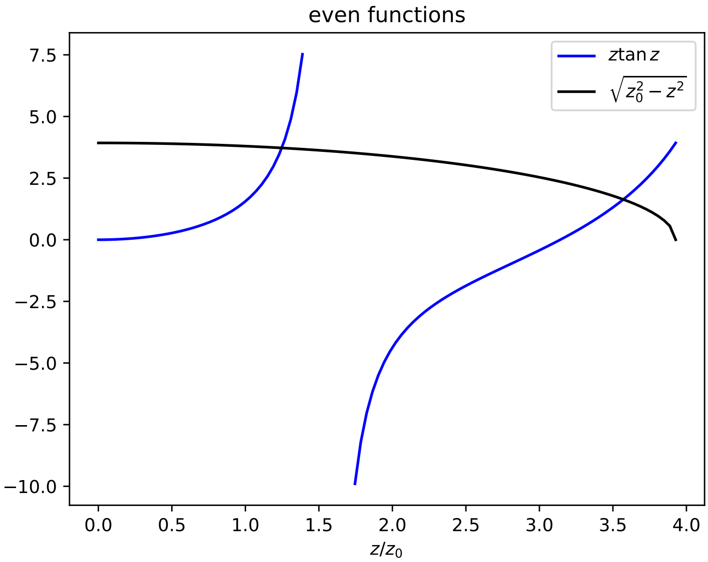
so that (3) is reduced to

$$z \tan z = \sqrt{z_0^2 - z^2}.$$

- Now let us plot the graph of LHS and RHS of above equation. The points of intersection given you quantized values of z. From this, we can get quantized wave vectors and quantized energies.
- The depth of the well determines the number of

[3] Transcendental means beyond conventional knowledge.

$V(x)$: Finite potential well – case (1): $A = B$



$V(x)$: Finite potential well – case (1): $A = B$

- By symmetry the other interface between Region I and Region III gives the same quantization condition.
- Let us denote the quantized wave vectors as

$$k_{\text{I}}^{(1)}, k_{\text{I}}^{(2)}, k_{\text{I}}^{(3)}, \ldots, \qquad \text{and} \qquad \kappa_{\text{II}}^{(1)}, \kappa_{\text{II}}^{(2)}, \kappa_{\text{II}}^{(3)}, \ldots$$

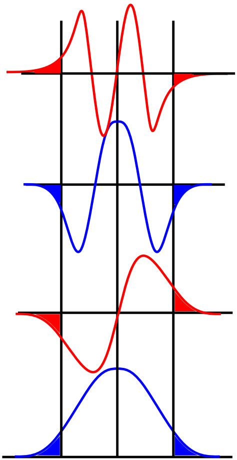
- By symmetry $F = C$.
- C can be expressed in terms of A from (1).
- Therefore, the wave functions are given by

$$\psi^{(n)}(x) = \begin{cases} C \exp\left(+\kappa_{\text{II}}^{(n)} x\right) & x < -\frac{a}{2} \\ 2A \cos \frac{k_{\text{I}}^{(n)} x}{2} & -\frac{a}{2} < x < +\frac{a}{2} \\ C \exp\left(-\kappa_{\text{II}}^{(n)} x\right) & x > +\frac{a}{2} \end{cases}$$

- The solutions corresponding to $E < V_0$ are called **bound states**.

$V(x)$: Finite potential well – Nature of solutions

- Wave function penetrates into the finite potential barrier.
- The wave function is either odd or even function.
- The depth of the well determines the number of bound states.
- In the limiting case of very large depth, the penetration tends to zero and the number of bound states tends to infinity leading to particle in infinite potential well.



Key Insight

The wave function penetrates into the finite potential barrier. This is called **Quantum Penetration**.

$V(x)$: Finite potential well – case (2): $A = -B$

- Similar analysis for the case(2): $A = -B$ gives the quantization condition as

$$\cot \frac{k_{\mathrm{I}} a}{2} = -\frac{\kappa_{\mathrm{II}}}{k_{\mathrm{I}}}$$

Problem

Prove the above quantization condition for the odd wave functions.