Quantum Theory

Basics of Quantum Mechanics
- Why Quantum Physics? -

- Classical mechanics (Newton's mechanics) and Maxwell's equations (electromagnetics theory) can explain MACROSCOPIC phenomena such as the motion of billiard balls or rockets.
- Quantum mechanics is used to explain microscopic phenomena such as photon-atom scattering and the flow of electrons in a semiconductor.
- QUANTUM MECHANICS is a collection of postulates based on a huge number of experimental observations.
- The differences between classical and quantum mechanics can be understood by examining both
  - The classical point of view
  - The quantum point of view

Basics of Quantum Mechanics
- Classical Point of View -

- In Newtonian mechanics, the laws are written in terms of PARTICLE TRAJECTORIES.
- A PARTICLE is an indivisible mass point object that has a variety of properties that can be measured, which we call observables. The observables specify the state of the particle (position and momentum).
- A SYSTEM is a collection of particles, which interact among themselves via internal forces, and can also interact with the outside world via external forces. The STATE OF A SYSTEM is a collection of the states of the particles that comprise the system.
- All properties of a particle can be known to infinite precision.
- **Conclusions:**
  - TRAJECTORY ➔ state descriptor of Newtonian physics,
  - EVOLUTION OF THE STATE ➔ Use Newton's second law
  - PRINCIPLE OF CAUSALITY ➔ Two identical systems with the same initial conditions, subject to the same measurement will yield the same result.0

Basics of Quantum Mechanics
- Quantum Point of View -

- Quantum particles can act as both particles and waves ➔ WAVE-PARTICLE DUALITY
- Quantum state is a conglomeration of several possible outcomes of measurement of physical properties ➔ Quantum mechanics uses the language of PROBABILITY theory (random chance)
- An observer cannot observe a microscopic system without altering some of its properties. Neither one can predict how the state of the system will change.
- QUANTIZATION of energy is yet another property of "microscopic" particles.

Basics of Quantum Mechanics
- Heisenberg Uncertainty Principle -

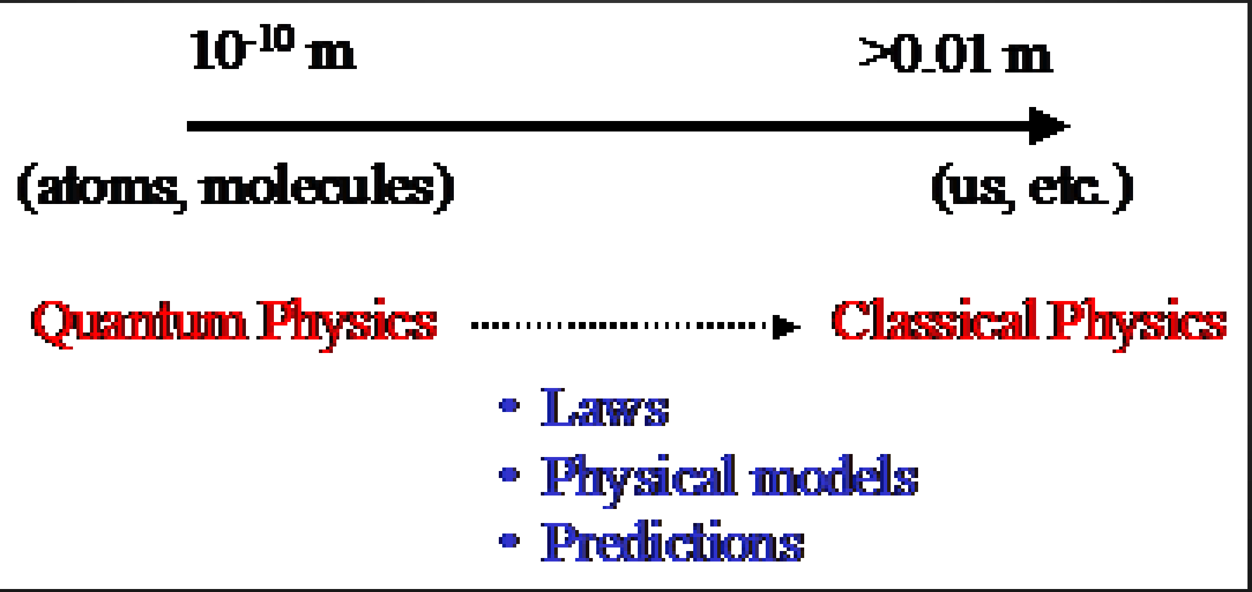
- One cannot unambiguously specify the values of particle's position and its momentum for a microscopic particle, i.e.

$$\Delta x(t_0) \cdot \Delta p_x(t_0) \geq \frac{1}{2}\frac{h}{2\pi}$$

- Position and momentum are, therefore, considered as incompatible variables.
- The Heisenberg uncertainty principle strikes at the very heart of the classical physics => the particle trajectory.

Basics of Quantum Mechanics
- The Correspondence Principle -

When Quantum physics is applied to macroscopic systems, it must reduce to the classical physics. Therefore, the nonclassical phenomena, such as uncertainty and duality, must become undetectable. Niels Bohr codified this requirement into his Correspondence principle:



Basics of Quantum Mechanics
- Particle-Wave Duality -

- The behavior of a "microscopic" particle is very different from that of a classical particle:
  - ➔ in some experiments it resembles the behavior of a classical wave (not localized in space)
  - ➔ in other experiments it behaves as a classical particle (localized in space)
- Corpuscular theories of light treat light as though it were composed of particles, but can not explain DIFRACTION and INTERFERENCE.
- Maxwell's theory of electromagnetic radiation can explain these two phenomena, which was the reason why the corpuscular theory of light was abandoned.

Basics of Quantum Mechanics
- Particle-Wave Duality -

- Waves as particles:

  - Max Plank work on black-body radiation, in which he assumed that the molecules of the cavity walls, described using a simple oscillator model, can only exchange energy in quantized units.

  - 1905 Einstein proposed that the energy in an electromagnetic field is not spread out over a spherical wavefront, but instead is localized in individual clumbs - quanta. Each quantum of frequency n travels through space with the speed of light, carrying a discrete amount of energy and momentum =photon => used to explain the photoelectric effect, later to be confirmed by the *x*-ray experiments of Compton.

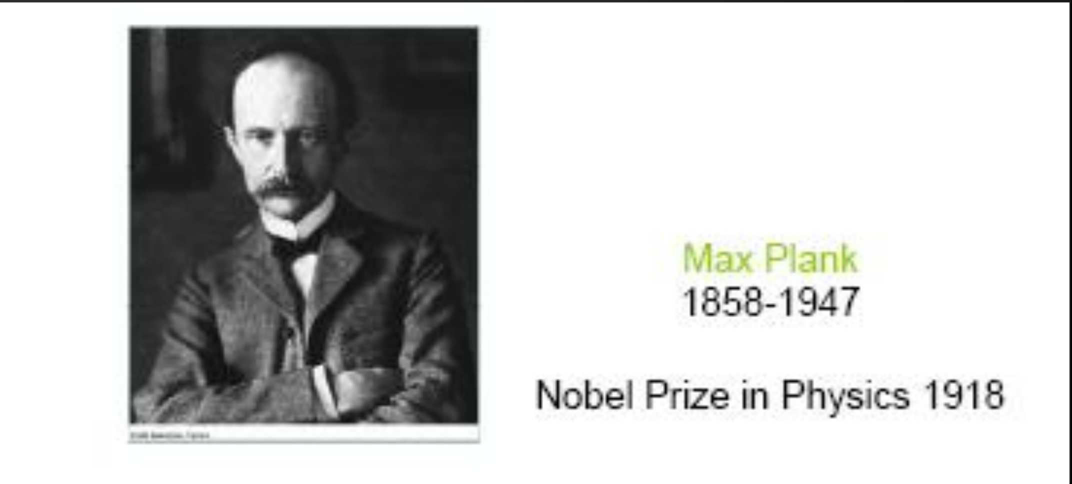
- Particles as waves

  - Double-slit experiment, in which instead of using a light source, one uses the electron gun. The electrons are diffracted by the slit and then interfere in the region between the diaphragm and the detector.

Waves as Particles

Basics of Quantum Mechanics
- Blackbody Radiation -

- Known since centuries that when a material is heated, it radiates heat and its color depends on its temperature
- Example: heating elements of a stove:
  – Dark red: 550ºC
  – Bright red: 700ºC
  – Then: orange, yellow and finally white (really hot !)
- The emission spectrum depends on the material
- Theoretical description: simplifications necessary Blackbody

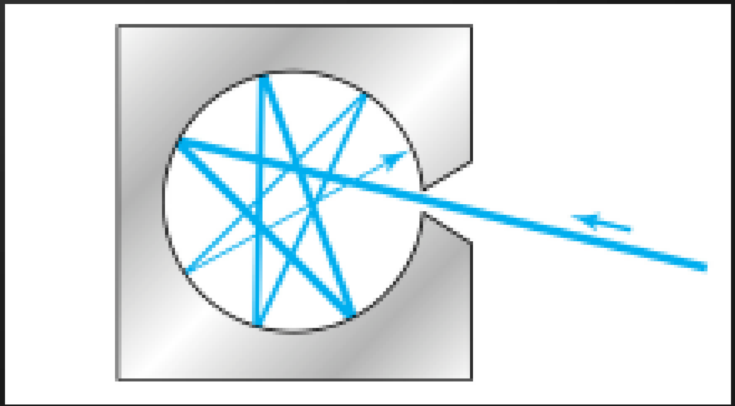


Blackbody?

- A material is constantly exchanging heat with its surroundings (to remain at a constant temperature):
  - It absorbs and emits radiations
  - Problem: it can reflect incoming radiations, which makes a theoretical description more difficult (depending on the environment)
- A blackbody is a perfect absorber:
  - Incoming radiation is totally absorbed and none is reflected

Blackbody Radiation

- Blackbody = a cavity, such as a metal box with a small hole drilled into it.
  - Incoming radiations entering the hole keep bouncing around inside the box with a negligible change of escaping again through the hole => Absorbed.
  - The hole is the perfect absorber, e.g. the blackbody Radiation emission does not depend on the material the box is made of => Universal in nature



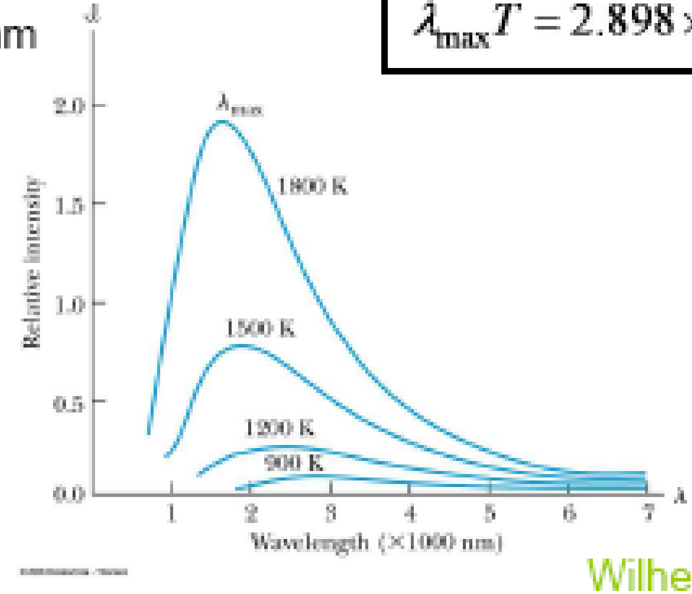
Wien's displacement law

- The intensity $\mathcal{I}(\lambda, T)$ is the total power radiated per unit area per unit wavelength at a given temperature
- Wien's displacement law: The maximum of the distribution shifts to smaller wavelengths as the temperature is increased.

Visible light: 400 – 700 nm
UltraViolet: <400 nm
Infrared: >700 nm

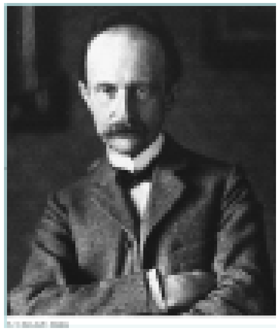
$$\boxed{\lambda_{max} T = 2.898 \times 10^{-3}\ \mathrm{m \cdot K}}$$

Empirical Formula



Wilhem Wien: Nobel Prize 1911

Max Planck and the blackbody problem



- Max Planck 1858-1947
  - Expert in thermodynamics and statistical mechanics
  - Around 1900: Proposes first an empirical formula (based on real physics) to reproduce both the high and low wavelength parts of the emission spectrum
    → Remarkable agreement with experimental results
  - Then, works on a theoretical basis of the formula

1918 Nobel Prize

Planck's radiation law

- Planck assumed that the radiation in the cavity was emitted (and absorbed) by some sort of "oscillators" contained in the walls. He used Boltzman's statistical methods to arrive at the following formula:

$$\boxed{\mathscr{I}(\lambda,T)=\frac{2\pi c^2 h}{\lambda^5}\frac{1}{e^{hc/\lambda kT}-1}}$$

Planck's radiation law

- Planck made two modifications to the classical theory:
  1) The oscillators (of electromagnetic origin) can only have certain discrete energies determined by $E_n = nh\nu$, where n is an integer, ν is the frequency, and h is called Planck's constant.

     $h = 6.6261 \times 10^{-34}$ J·s.

  2) The oscillators can absorb or emit energy in discrete multiples of the fundamental quantum of energy given by

     $\Delta E = h\nu$

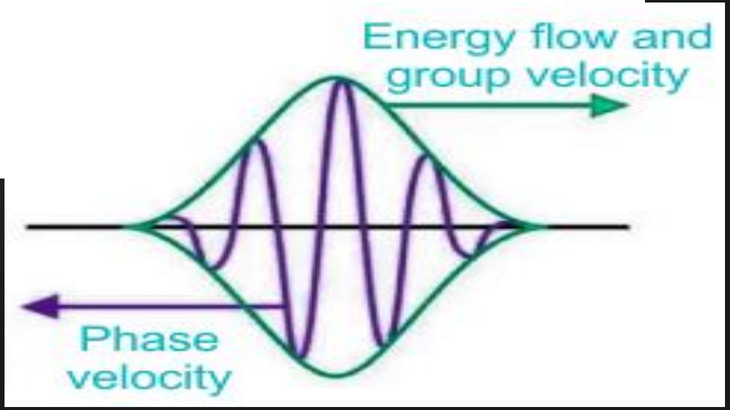
Wave packet, phase velocity and group velocity

- The velocities of the individual waves which superpose to produce the wave packet representing the particle are different - the wave packet as a whole has a different velocity from the waves that comprise it
- Phase velocity: The rate at which the phase of the wave propagates in space
- Group velocity: The rate at which the envelope of the wave packet propagates

Phase velocity

- Phase velocity is the rate at which the phase of the wave propagates in space.
- This is the velocity at which the phase of any one frequency component of the wave will propagate.
- You could pick one particular phase of the wave and it would appear to travel at the phase velocity.
- The phase velocity is given in terms of the wave's angular frequency ω and wave vector *k* by

$$v_{\mathrm{p}} = \frac{\omega}{k}$$



$$y = A\sin(\omega t - kx) \qquad \text{...(i)}$$

The particle velocity

$$v_p = \frac{dy}{dt} = A\omega\cos(\omega t - kx) \qquad \text{...(ii)}$$

Slope of displacement curve or strain

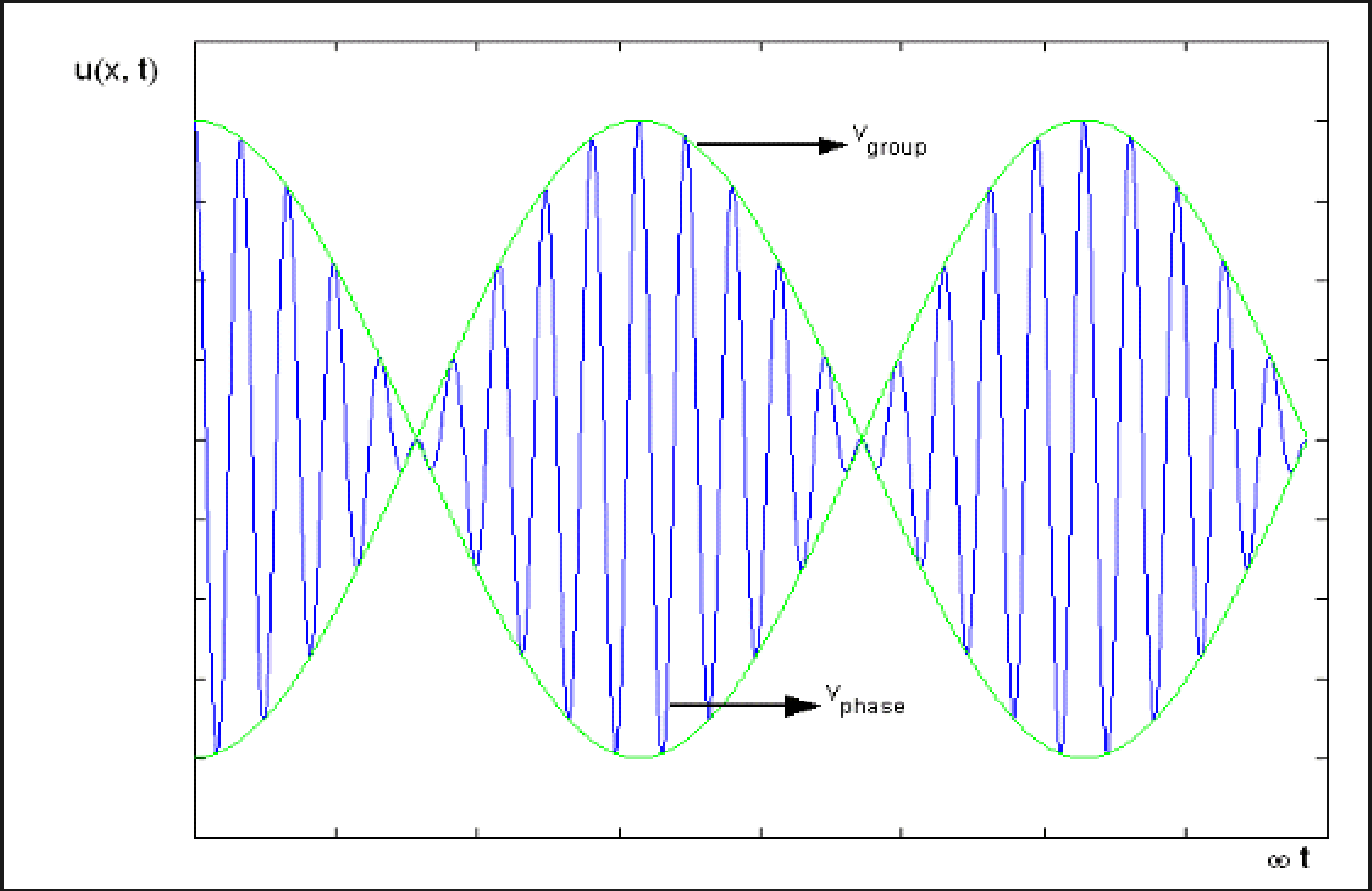
$$\frac{dy}{dx} = -Ak\cos(\omega t - kx) \qquad \text{...(iii)}$$

Dividing eq^n. (ii) by (iii), we get

$$\frac{dy/dt}{-dy/dx} = \frac{\omega}{k}$$

$$\Rightarrow \frac{v_p}{-dy/dx} = v \qquad \left(\text{since } \frac{\omega}{k} = v\text{, wave velocity}\right)$$

$$\Rightarrow v_p = -v.\frac{dy}{dx}$$



Phase and Group velocity

Difference between phase velocity and group velocity

Phase Velocity	Group Velocity
•It is the velocity with which a definite phase of the wave propagates in the medium.	•The average velocity with which group of waves having slightly different wavelength travel along the same direction.
•$v_p = \omega/k$	•$v_g = d\omega/dk$
•Characteristics of individual wave	•Characteristics of group of waves
•For non relativistic particle, $v_p = v/2$ and for relativistic particle, $v_p = c^2/v$	•For non relativistic particle and relativistic particle, $v_g = v$

we know phase velocity $v_p = \frac{\omega}{K}$

and group velocity $v_g = \frac{d\omega}{dK}$

Here

$$v_p = cK^{-\frac{1}{2}} \quad \text{—— (1)}$$

$$\frac{\omega}{K} = cK^{-\frac{1}{2}}$$

$$\omega = cK^{-\frac{1}{2}} . K = cK^{\frac{1}{2}}$$

$$\frac{d\omega}{dK} = \frac{1}{2} cK^{-\frac{1}{2}} = \frac{1}{2} v_p \text{ [using (1)]}$$

$$\therefore \frac{d\omega}{dK} = \frac{v_p}{2}$$

$$\boxed{v_g = \frac{v_p}{2}}$$

Derivation of the Schr¨odinger Wave Equation

The Time Dependent Schr¨odinger Wave Equation

In the discussion of the particle in an infinite potential well, it was observed that the wave function of a particle of fixed energy E could most naturally be written as a linear combination of wave functions of the form

$$\Psi(x,t) = Aei(kx-\omega t) \qquad (1)$$

representing a wave travelling in the positive x direction, and a corresponding wave travelling in the opposite direction, so giving rise to a standing wave, this being necessary to satisfy the boundary conditions.

This corresponds intuitively to our classical notion of a particle bouncing back and forth between the walls of the potential well, which suggests that we adopt the wave function above as being the appropriate wave function for a free particle of momentum p = ℏ k and energy E = ℏ ω. With this in mind, we

$$E = hf = \hbar w$$

$$\psi = e^{i(kx - wt)} \quad \text{---------} \quad (1)$$

$$\frac{d\psi}{dt} = -iw\psi \quad \text{----------} \quad (2)$$

From Eq(A), $E\psi = \psi\hbar w$ -- (3)

Now 'x'ing (-i) to both sides of Eq(3)

$$-iE\psi = -i\,\psi\hbar w \quad \boxed{\text{Or}} \quad \frac{-i}{\hbar}E\psi = -iw\psi = \frac{d\psi}{dt} \text{---------} (4)$$

Now from Eq (4) so, $E\psi = \frac{\hbar}{-i}\frac{d\psi}{dt} = i\hbar\frac{d\psi}{dt}$ -------- (5)

Now from the time Independent SE equation,we have

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

$$\boxed{i\hbar\frac{d\psi}{dt} = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + u\psi}$$

Time Dependent Schrodinger Equation

where Ψ is now the wave function of a particle moving in the presence of a potential V (x).

Even though this equation does not look like the familiar wave equation that describes, for instance, waves on a stretched string, it is nevertheless referred to as a 'wave equation' as it can have solutions that represent waves propagating through space. We have seen an example of this: the harmonic wave function for a free particle of energy E and momentum p,

i.e. $\Psi(x,t) = Ae{-}i(px{-}Et)$

is a solution of this equation with, as appropriate for a free particle, V (x) = 0. But this equation can have distinctly non-wave-like solutions whose form depends, amongst other things, on the nature of the potential V (x) experienced by the particle.

The Time Independent Schr¨odinger Equation

We have seen what the wave function looks like for a free particle of energy E – one or the other of the harmonic wave functions – and we have seen what it looks like for the particle in an infinitely deep potential well though we did not obtain that result by solving the Schr¨odinger equation.

But in both cases, the time dependence entered into the wave function via a complex exponential factor $\exp[-iEt/\hbar]$. This suggests that to 'extract' this time dependence we guess a solution to the Schr¨odinger wave equation of the form $\Psi(x,t) = \psi(x)e{-iEt/\hbar}$

i.e. where the space and the time dependence of the complete wave function are contained in separate factors.

The idea now is to see if this guess enables us to derive an equation for $\psi(x)$, the spatial part of the wave function. If we substitute this trial solution into the Schr¨odinger wave equation, and make use of the meaning of partial derivatives, we get:

$$E = KE + PE$$

$$E = \frac{1}{2}mv^2 + u$$

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

$$\psi = e^{i(kx - \omega t)}$$

$$\frac{d\psi}{dx} = ike^{i(kx-\omega t)} = ik\psi$$

$$\frac{d^2\psi}{dx^2} = (ik)^2\psi$$

$$k = \frac{p}{\hbar} \qquad k = \frac{2\pi}{\lambda}$$

$$p = \frac{h}{\lambda} \Rightarrow p = \frac{hk}{2\pi} \Rightarrow p = \hbar k$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{p^2}{\hbar^2}\right)\psi$$

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

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

$$E\psi = \frac{p^2\psi}{2m} + u\psi$$

$$\boxed{E\psi = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + u\psi} \Longrightarrow \text{Time Independent}$$

We note here that the quantity E, which we have identified as the energy of the particle, is a free parameter in this equation. In other words, at no stage has any restriction been placed on the possible values for E. Thus, if we want to determine the wave function for a particle with some specific value of E that is moving in the presence of a potential V (x), all we have to do is to insert this value of E into the equation with the appropriate V (x), and solve for the corresponding wave function. In doing so, we find, perhaps not surprisingly, that for different choices of E we get different solutions for $\psi(x)$.

We can emphasize this fact by writing $\psi E(x)$ as the solution associated with a particular value of E. But it turns out that it is not all quite as simple as this. To be physically acceptable, the wave function $\psi E(x)$ must satisfy two conditions, one of which we have seen before namely that the wave function must be normalizable, and a second, that the wave function and its derivative must be continuous.

Together, these two requirements, the first founded in the probability interpretation of the wave function, the second in more esoteric mathematical necessities which we will not go into here and usually only encountered in somewhat artificial problems, lead to a rather remarkable property of physical systems described by this equation that has enormous physical significance: the quantization of energy.

Particle in a 3D box

- This is just 3 Schrodinger eqs in one!

  - One for x $$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E_x\,\psi(x)$$
  - One for y $$\frac{-\hbar^2}{2m}\frac{d^2\psi(y)}{dy^2} = E_y\,\psi(y)$$
  - One for z $$\frac{-\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2} = E_z\,\psi(z)$$

- These are just for 1D particles in a box and we have solved them already!

Particle in a 3D box

- Assuming x, y and z motion is independent, we can use separation of variables:

$$\psi(x, y, z) = \psi(x)\,\psi(y)\,\psi(z)$$

- Substituting: $$\frac{-\hbar^2}{2m}\nabla^2\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\psi(x)\,\psi(y)\,\psi(z) + \frac{\partial^2}{\partial y^2}\psi(x)\,\psi(y)\,\psi(z) + \frac{\partial^2}{\partial z^2}\psi(x)\,\psi(y)\,\psi(z)\right) = E\psi(x)\,\psi(y)\,\psi(z)$$

- Dividing through by: $\psi(x)\,\psi(y)\,\psi(z)$

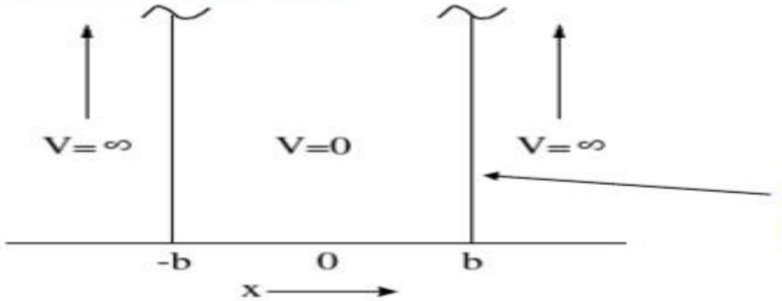
$$\frac{-\hbar^2}{2m}\left(\frac{1}{\psi(x)}\,\frac{\partial^2\psi(x)}{\partial x^2} + \frac{1}{\psi(y)}\,\frac{\partial^2\psi(y)}{\partial y^2} + \frac{1}{\psi(z)}\,\frac{\partial^2\psi(z)}{\partial z^2}\right) = E$$

Schrodinger Equation

Again, we said that the time independent SE for a particle of mass m moving under a potential energy V is

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

Particle in a One Dimensional Box



Particle inside box. Can't get out because of impenetrable walls.

Classically ⟶ E is continuous. E can be zero. One D racquet ball court.

Q.M. ⟶ $\Delta x \Delta p \geq \hbar/2$ E can't be zero.

$\underline{H}|\varphi\rangle = E|\varphi\rangle$ Energy eigenvalue problem

Schrödinger Equation

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

$V(x) = 0 \qquad |x| < b$

$V(x) = \infty \qquad |x| \geq b$

For $|x| < b$

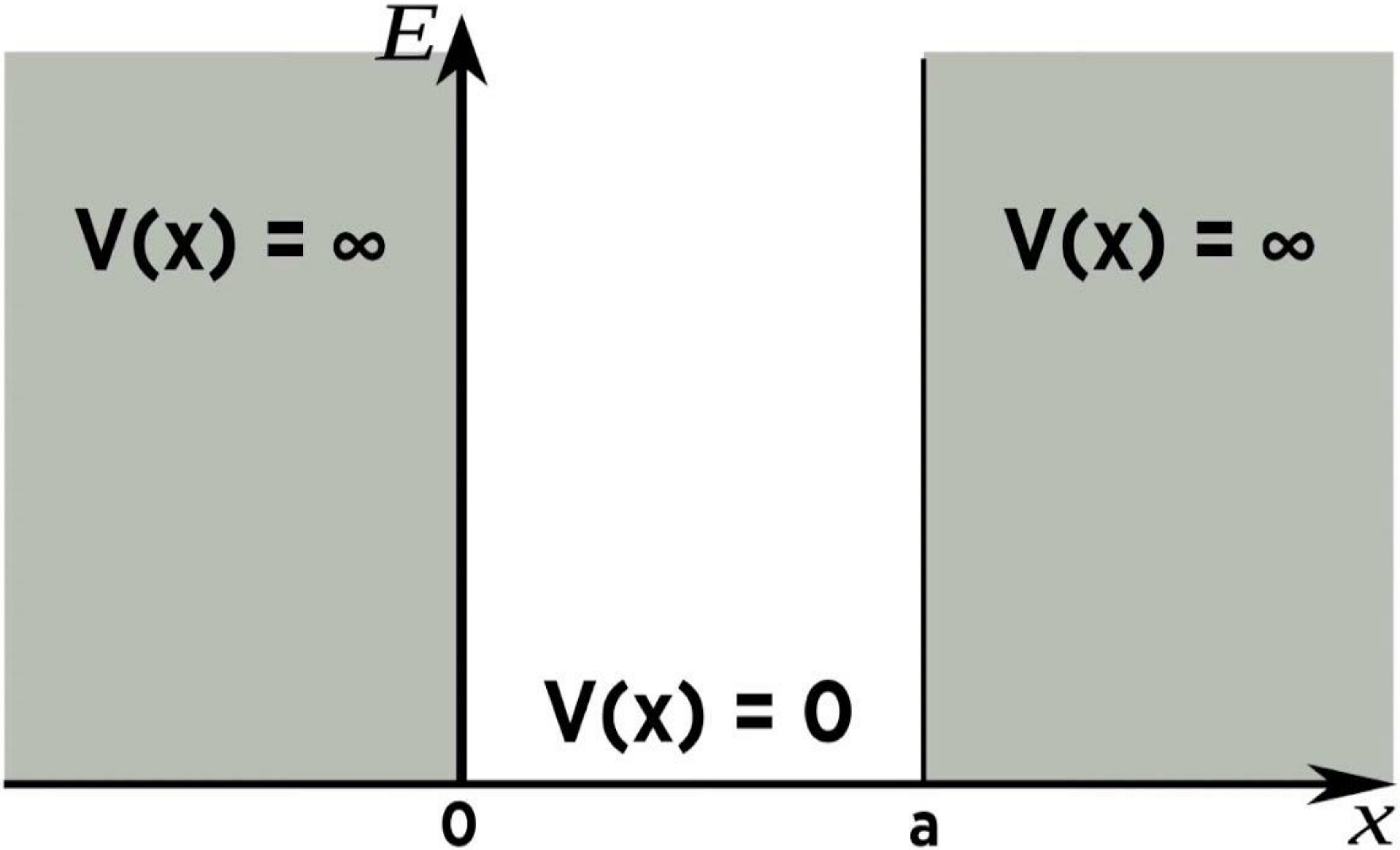
$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} = E\,\varphi(x)$$

Want to solve differential Equation, but
Solution must by physically acceptable.

Born Condition on Wavefunction to make physically meaningful.

1. The wave function must be finite everywhere.
2. The wave function must be single valued.
3. The wave function must be continuous.
4. First derivative of wave function must be

Which $\psi(x)$ satisfy the Schrödinger equation?



$V = 0$ for $0 < x < L$

$V = \infty$ for $x \leq 0$ and $x \geq L$

The particle present in the box co outside the box wave function ψ is 0

$\psi = 0$ for $x \leq 0$ & $x \geq L$

In the potential box Schrodinger's time independent wave equation is given by

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

Inside the box $V = 0$ hence

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E)\psi = 0 \qquad (1)$$

put

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

$$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0 \qquad (3)$$

So, the general solution of above equation is

$$\psi = A \sin kx + B \cos kx \qquad (4)$$

Now at $x = 0$ and $\psi = 0$ equation (4) becomes

$$0 = A \sin k\,0 + B \cos k\,0$$

Particle in a 1D box

We know the solution for : $\psi'' + c\,\psi = 0$

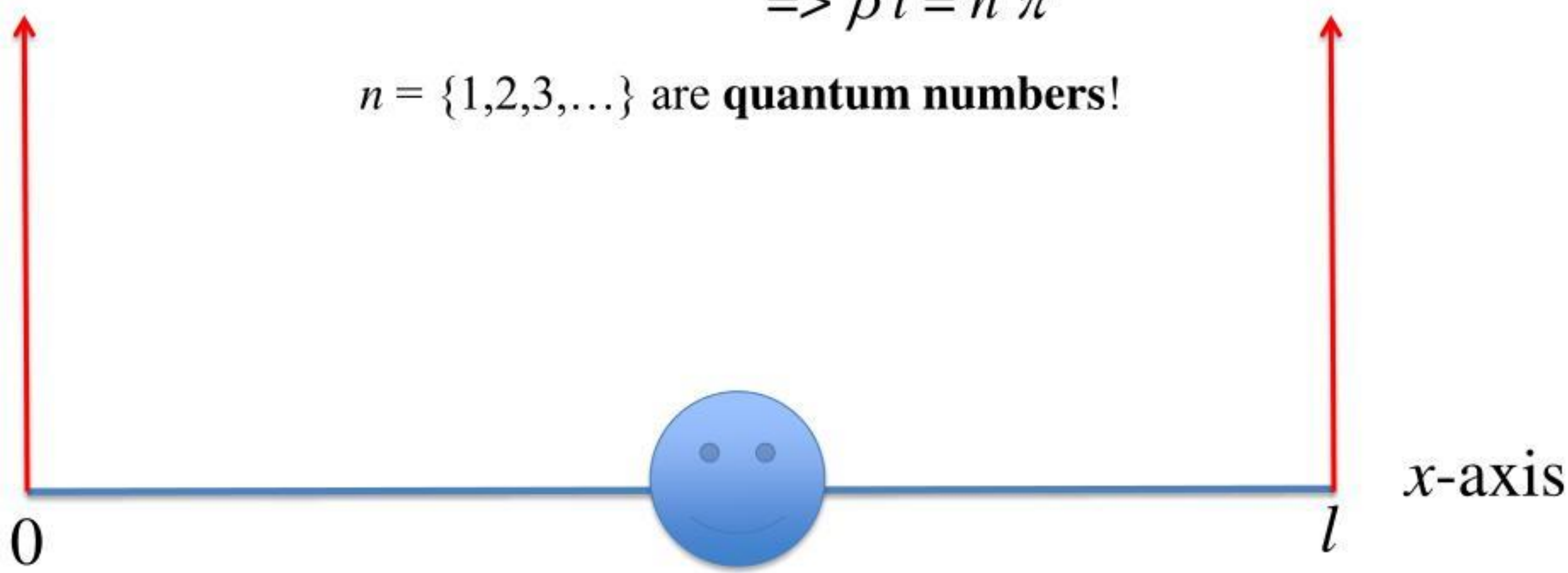
Boundary conditions: $\psi(0) = 0,\ \psi(l) = 0$

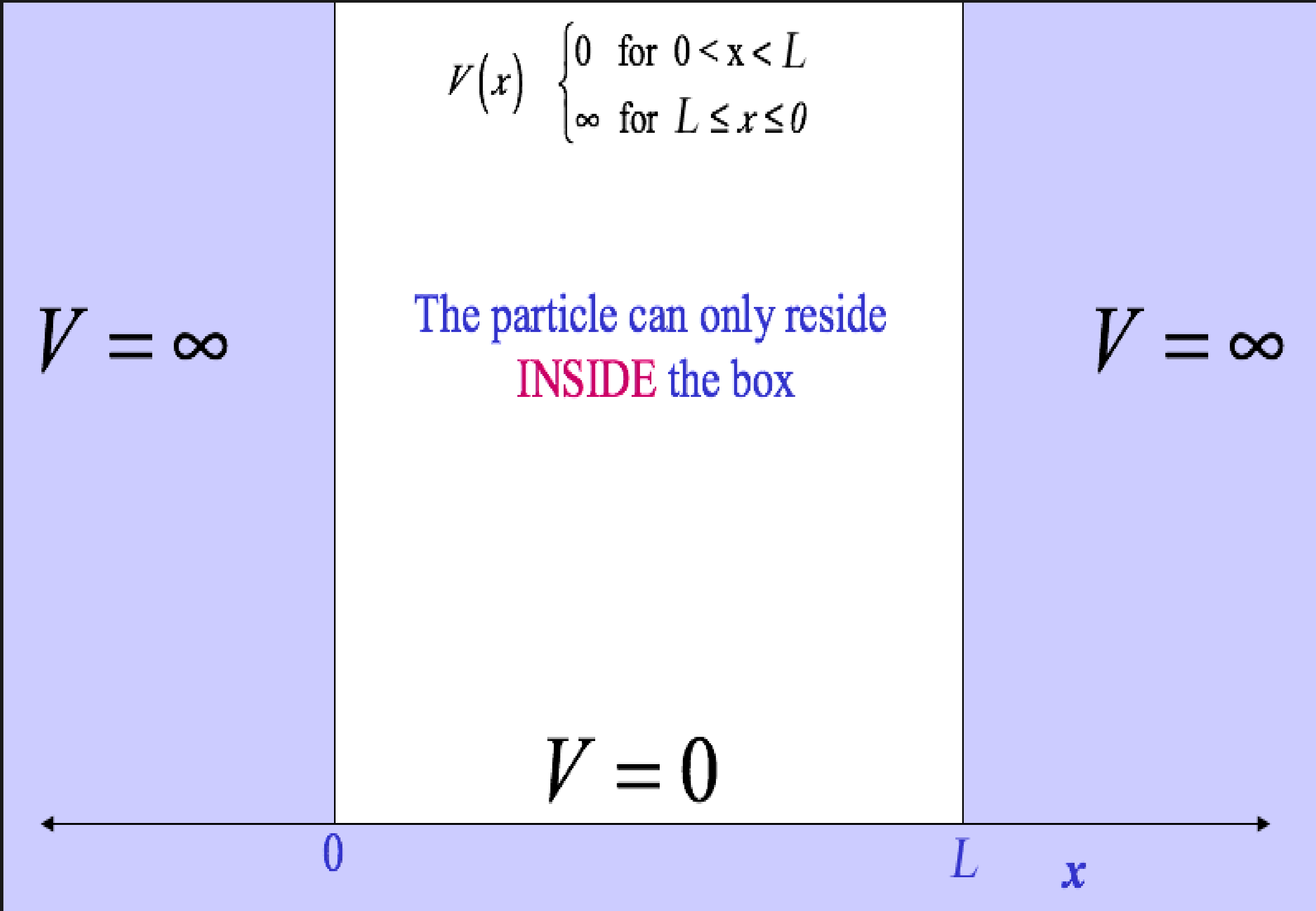
Solution: $\psi(x) = B\sin(\beta x)$

$\psi(l) = B\sin(\beta l) = 0$ $\sin(\bullet) = 0$ every π units

$\Rightarrow \beta l = n\pi$

$n = \{1,2,3,\ldots\}$ are **quantum numbers**!




$V(x) \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{for } L \le x \le 0 \end{cases}$
$V = \infty$
The particle can only reside INSIDE the box
$V = \infty$
$V = 0$
0
L
x