

# Wave-particle Duality

De Broglie wavelength  $\lambda = h/p$ ;  $p = mv$  = momentum

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What is the de Broglie wavelength of 75 kg boy and an electron each traveling at 10 mph?

$$\lambda_{boy} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} J \cdot s}{75 \text{ kg} \times 10 \frac{\text{miles}}{\text{hour}}} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{75 \text{ kg} \times 10 \frac{\text{miles}}{\text{hour}} \times \frac{1.6093 \text{ km}}{\text{miles}} \times \frac{\text{hour}}{3600 \text{ s}} \times \frac{1000 \text{ m}}{\text{km}}} = 1.98 \times 10^{-36} \text{ m}$$

Too small to be detectable

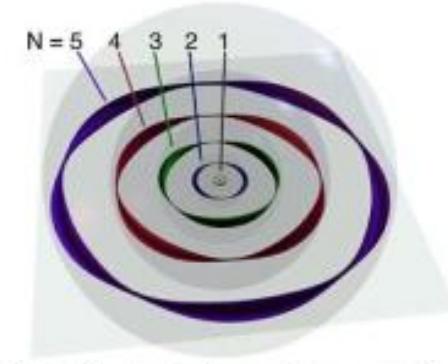
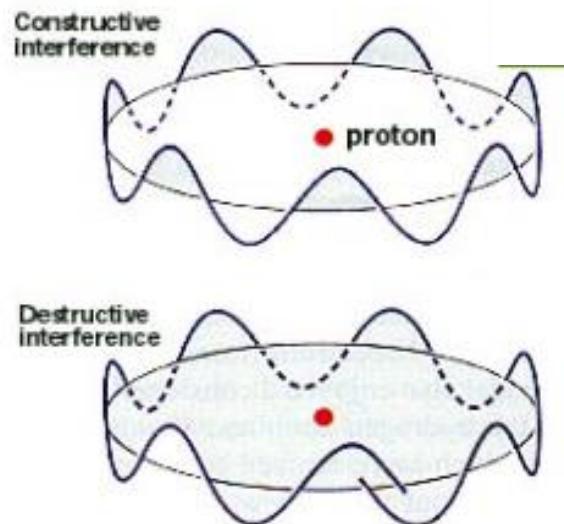
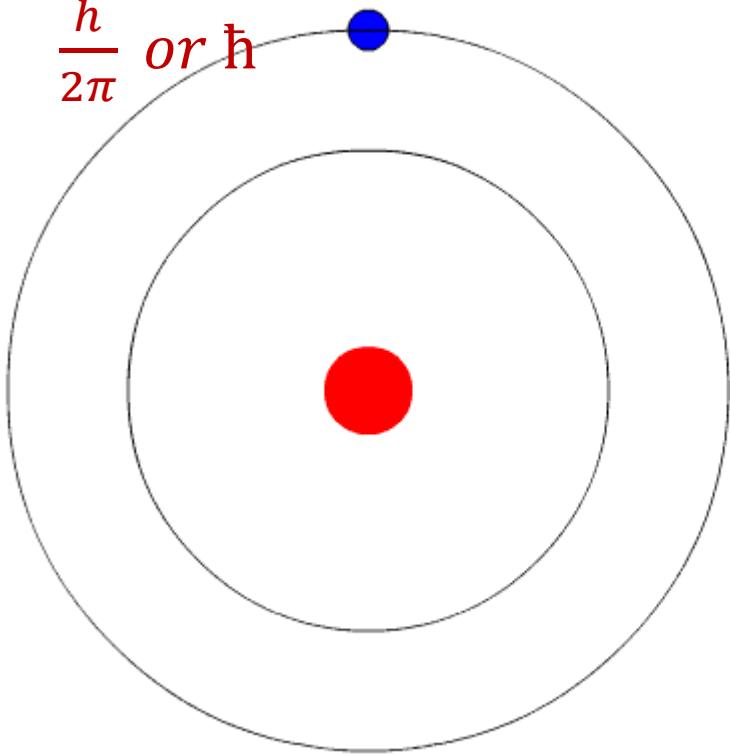
$$\lambda_e = \frac{h}{mv} = \frac{6.626 \times 10^{-34} J \cdot s}{9.109 \times 10^{-31} \text{ kg} \times 10 \frac{\text{miles}}{\text{hour}}} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{9.109 \times 10^{-31} \text{ kg} \times 10 \frac{\text{miles}}{\text{hour}} \times \frac{1.6093 \text{ km}}{\text{miles}} \times \frac{\text{hour}}{3600 \text{ s}} \times \frac{1000 \text{ m}}{\text{km}}} = 1.63 \times 10^{-7} \text{ m}$$

# Bohr - de Broglie Theory

For an hydrogen atom

➤ Combining  $\lambda = \frac{h}{mv}$  and  $2\pi r = n\lambda \rightarrow m_e v r = \frac{nh}{2\pi}$

Angular momentum is quantized and integral multiples of  $\frac{h}{2\pi}$  or  $\hbar$

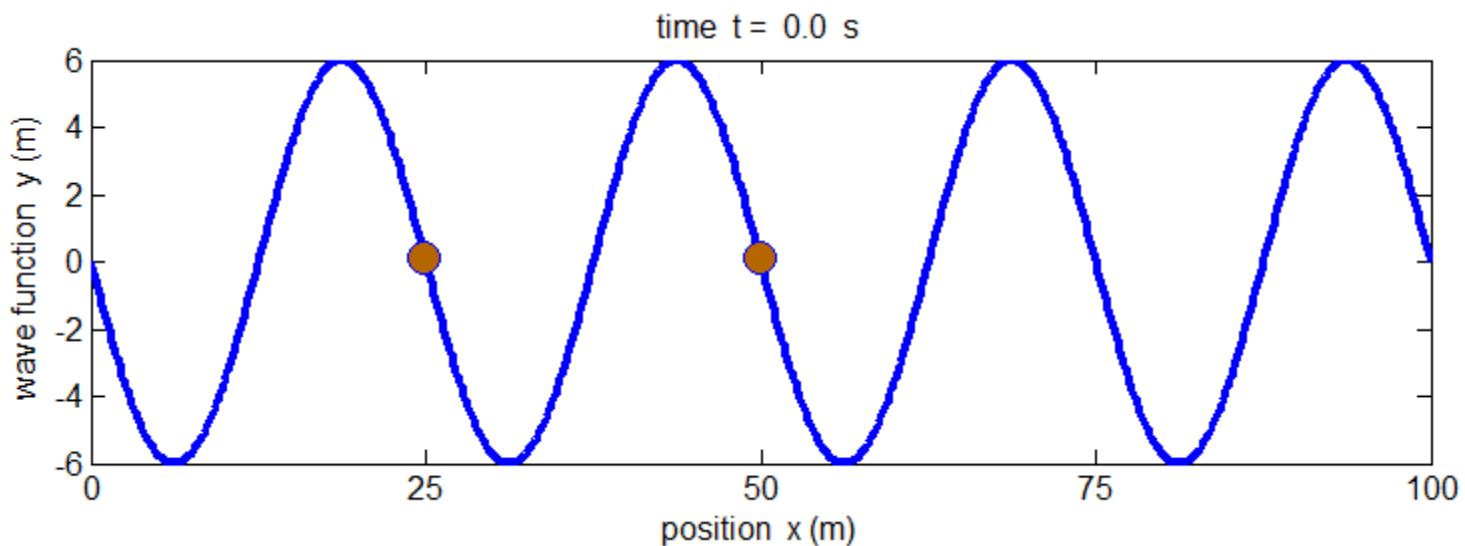


Bohr-de Broglie electron matterwave orbits  
shells 1-5

# Energy Conversion

	1	27.21139	219474.63	627.503	2625.438228	
	hartree	eV	cm-1	kcal/mol	kJ/mol	k
hartree	1	27.21139	219474.63	627.503	2625.438228	
eV	0.036749322	1	8065.544	23.06031	96.4830761	
cm-1	4.55634E-06	0.000124	1	0.002859	0.011962377	
kcal/mol	0.001593618	0.043365	349.7587	1	4.183945301	
kJ/mol	0.000380889	0.010365	83.595428	0.239009		1
k	3.16679E-06	8.62E-05	0.6950305	0.001987	0.008314216	
J	2.29E+17	6.24E+18	5.03E+22	1.44E+20	6.02E+20	
Hz	1.52E-16	4.14E-15	3.34E-11	9.54E-14	3.99E-13	
nm	45.56335253	1239.842	10000000	28591.14	119623.7675	

# Uncertainty Principle (1927)



de Broglie Hypothesis,  $\lambda = h/p$ ;

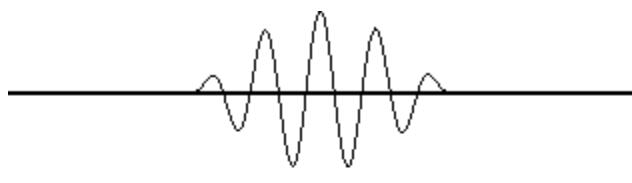
# Uncertainty Principle (1927)

How to understand wave/particle duality:

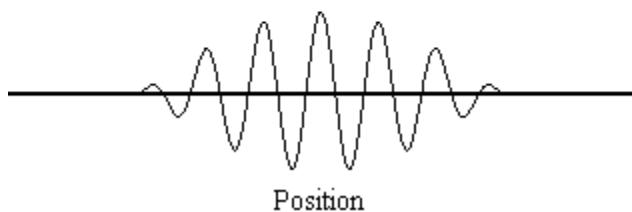
- a) a wave with a definite frequency and wavelength (e.g., a nice sine wave) does not have a definite location.

[At a definite location at a specific time the wave would have a definite phase, but the wave would not be said to be located there.]

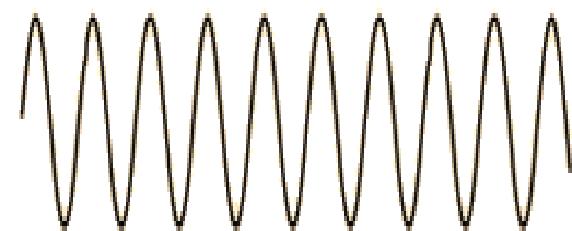
[ a nice travelling sine wave =  $A \sin(kx - \omega t)$  ]



Momentum ( $\rightarrow$  wavelength  $\rightarrow$  colour)



Position



**de Broglie Hypothesis,  $\lambda = h/p$ ;  
momentum is precisely determined**

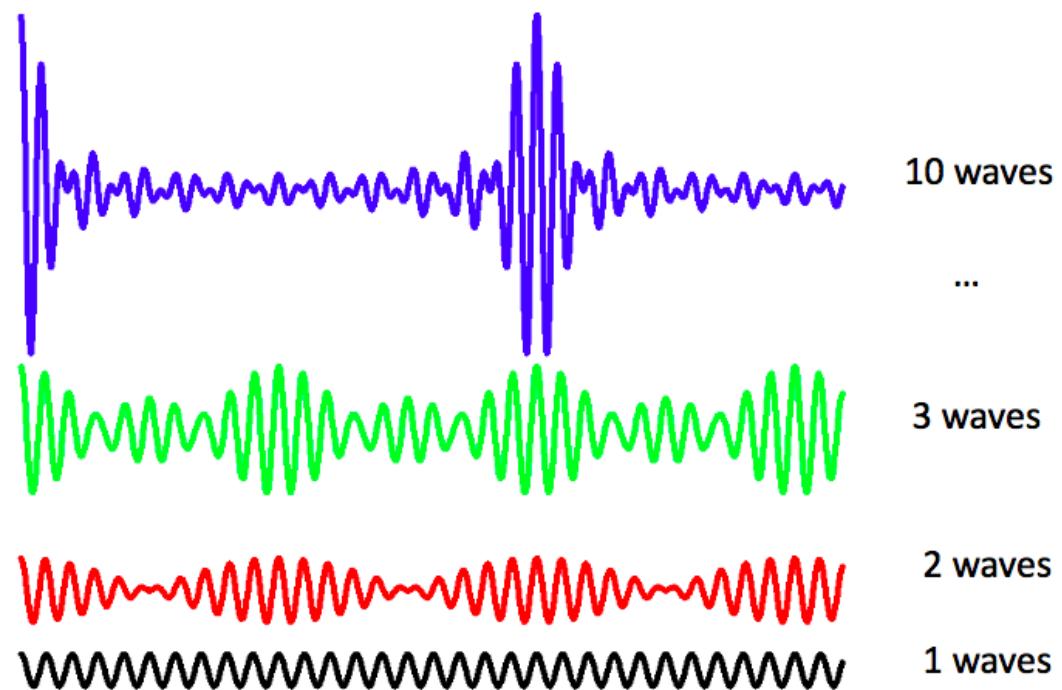
# Uncertainty Principle

- b) A particle does have a definite location at a specific time, but it does not have a frequency or wavelength.

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- c) In-between case: a group of sine waves can add together (via Fourier analysis) to give a semi-definite location: a result of Fourier analysis is this: the more the group shows up as a spike, the more waves it takes to make the group.

To know the location of a particle with some degree of certainty, we sacrificed the certainty of momentum



# Uncertainty Principle

Thus the **Heisenberg's Uncertainty Principle**

**Position and Momentum:**  $\Delta x \times \Delta p_x \geq h/4\pi$

**A generalized form of the uncertainty Principle:**

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

where the **root mean square deviation** of  $A$  is defined as

$$\Delta A = \left\{ \langle A^2 \rangle - \langle A \rangle^2 \right\}^{1/2}$$

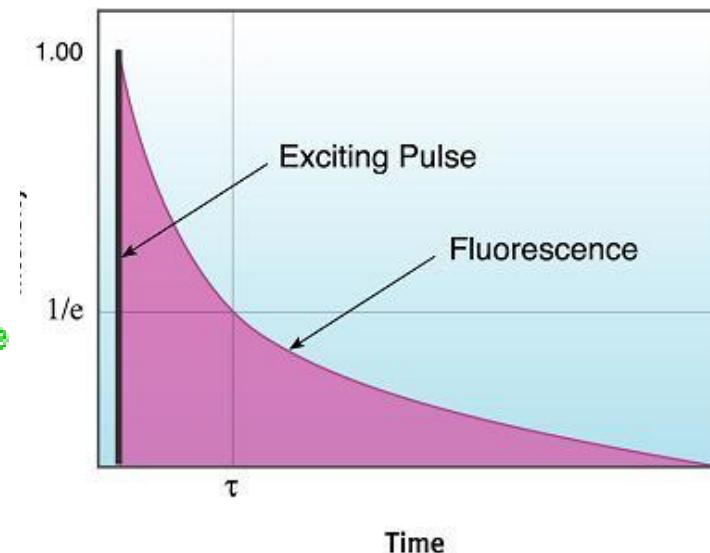


# Uncertainty in Time and Energy

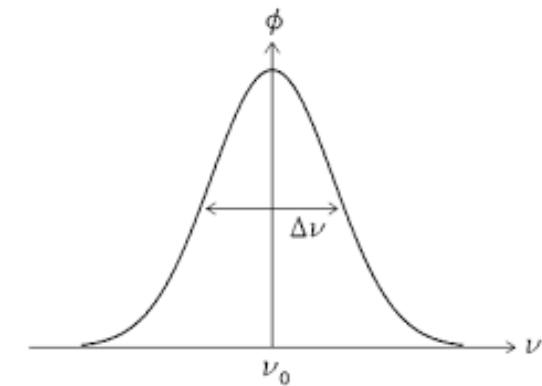
Excited State



Absorbance



Ground State



$T_{1/2}$  = half life =  $\Delta t$  = 1 ns; Find out the spectral line width:

$$\Delta t^* \Delta E = h/2\pi; \Rightarrow \Delta t^* h \Delta v = h/2\pi;$$

$$\Rightarrow \Delta v = 1/(2\pi * \Delta t) \sim 160 \text{ MHz} \sim 0.006 \text{ cm}^{-1}$$

# Quantum Theory

But if an **electron** acts as a wave when it is moving, **WHAT IS  
WAVING?**

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When **light acts as a wave** when it is moving, we have identified the **ELECTROMAGNETIC FIELD** as waving.

We have laws governing the electric and magnetic fields:  
**MAXWELL'S EQUATIONS.**

Classical Mechanics takes care of a particle's motion.

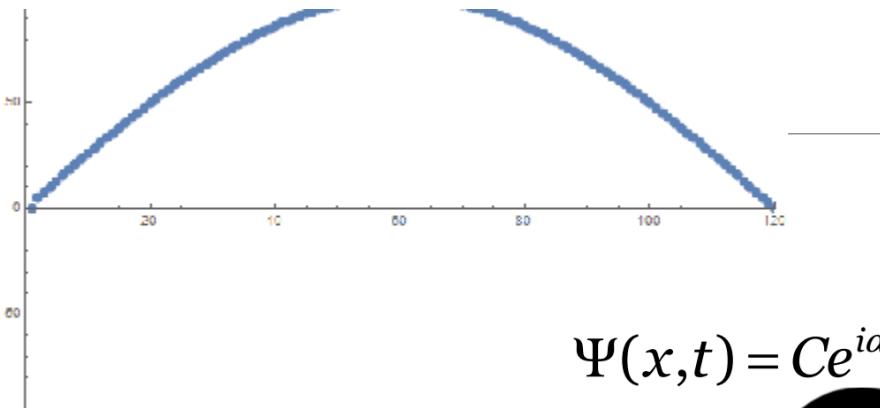
**But what do we do for electron waves (wavy particle)?**

# **Quantum Theory**

- New theory is required to explain the behavior of electrons, atoms and molecules

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- Should be Probabilistic, not deterministic (non-Newtonian) in nature
- Wavelike equation for describing sub/atomic systems

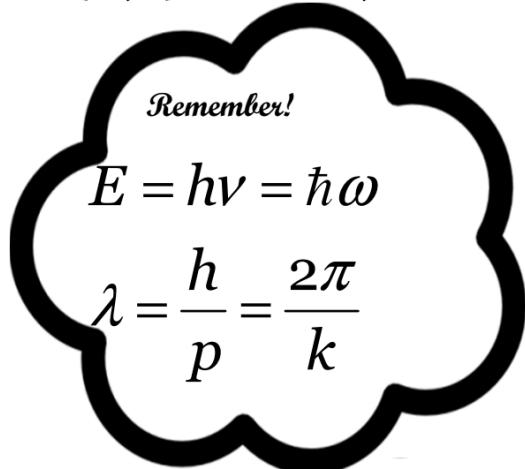
# Classical Wave Equation



$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2}$$

$\Psi(x,t)$  = Amplitude

$\Psi(x,t) = Ce^{i\alpha}$  ; Where  $\alpha = 2\pi\left(\frac{x}{\lambda} - vt\right)$  is the phase



$$\alpha = 2\pi\left(\frac{x}{\lambda} - vt\right) = \frac{x \cdot p - E \cdot t}{\hbar}$$

# Classical Wave Equation

$$\Psi(x,t) = Ce^{i\alpha} \quad \text{and} \quad \alpha = \frac{x \cdot p - E \cdot t}{\hbar}$$

$$\frac{\partial \Psi(x,t)}{\partial t} = iCe^{i\alpha} \cdot \frac{\partial \alpha}{\partial t} = i \cdot \Psi(x,t) \cdot \frac{\partial \alpha}{\partial t} = i \cdot \Psi(x,t) \cdot \left( \frac{-E}{\hbar} \right)$$

$$\frac{-\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = E \cdot \Psi(x,t)$$

# Classical Wave Equation

$$\Psi(x,t) = Ce^{i\alpha} \quad \text{and} \quad \alpha = \frac{x \cdot p - E \cdot t}{\hbar}$$

$$\frac{\partial \Psi(x,t)}{\partial x} = iCe^{i\alpha} \cdot \frac{\partial \alpha}{\partial x} = i \cdot \Psi(x,t) \cdot \frac{\partial \alpha}{\partial x} = i \cdot \Psi(x,t) \cdot \left( \frac{p_x}{\hbar} \right)$$

$$\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x} = p_x \cdot \Psi(x,t)$$

# Concept of an Operator

$$\Psi(x,t) = Ce^{i\alpha} \quad \text{and} \quad \alpha = \frac{x \cdot p - E \cdot t}{\hbar}$$

$$\frac{\partial \Psi(x,t)}{\partial t} = iCe^{i\alpha} \cdot \frac{\partial \alpha}{\partial t} = i \cdot \Psi(x,t) \cdot \frac{\partial \alpha}{\partial t} = i \cdot \Psi(x,t) \cdot \left( \frac{-E}{\hbar} \right)$$

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$$\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x} = p_x \cdot \Psi(x,t)$$

# Operators

$$\frac{-\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = E \cdot \Psi(x,t)$$

$$\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x} = p_x \cdot \Psi(x,t)$$

$$\frac{-\hbar}{i} \frac{\partial}{\partial t} \Psi(x,t) = E \cdot \Psi(x,t)$$

$$\frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x,t) = p_x \cdot \Psi(x,t)$$

$$\frac{-\hbar}{i} \frac{\partial}{\partial t} = i\hbar \frac{\partial}{\partial t} = \hat{E}$$

$$\frac{\hbar}{i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x} = \hat{p}_x \quad \text{Operators}$$

## Operators

- A symbol that tells you to do something to whatever follows it
- Operations might be simple multiplication or differentiation
- Operators can be real or complex
- Operators can also be represented as matrices

# More on Operators

- An operator is an instruction, a symbol which tells us to perform one of more mathematical acts on a function, say  $f(x)$ .  
The essential fact is that they act on a function
- Operator act on everything to the right, unless the action is constrained by brackets

# More on Operators

- Linear Operator
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$$\Omega(af + bg) = a\Omega f + b\Omega g$$

- Here a and b are constants, f and g are functions
- Multiplication is a linear operation; so is differentiation and integration.
- An example of a nonlinear operation is that of taking the logarithm of a function

# Operators and Eigen Values

Operator operating on a function results in re-generating the same function multiplied by a number

$$\hat{A} \cdot f(x) = a \cdot f(x) \quad \text{Eigen Value Equation}$$

The function  $f(x)$  is eigenfunction of operator  $\hat{A}$  and  $a$  its eigenvalue

$$f(x) = \sin(\alpha x)$$

$$\frac{d}{dx} f(x) = \alpha \cdot \cos(\alpha x)$$

$\sin(\alpha x)$  is an eigenfunction of operator  $\frac{d^2}{dx^2}$  and  $-\alpha^2$  is its eigenvalue

$$\frac{d^2}{dx^2} f(x) = \frac{d}{dx} [\alpha \cdot \cos(\alpha x)] = -\alpha^2 \cdot \sin(\alpha x) = -\alpha^2 \cdot f(x)$$

# Operators and Eigen Values

- Linear combination of degenerate wavefunctions is also an Eigen function
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- Linear combinations:

$$g = \sum_n c_n f_n$$

- Degenerate wavefunctions:

$$\Omega f_n = \omega f_n \text{ with } n = 1, 2, \dots, k$$

$$\Omega g = \Omega \sum_{n=1}^k c_n f_n = \sum_{n=1}^k c_n \Omega f_n = \sum_{n=1}^k c_n \omega f_n = \omega \sum_{n=1}^k c_n f_n = \omega g$$

# Operators and Eigen Values

- Linear combination of degenerate wavefunctions is also an Eigen function
- 

$$\frac{d^2}{dx^2} e^{\pm 2ix} = \frac{d}{dx} (\pm 2ie^{\pm 2ix}) = -4e^{\pm 2ix}$$

$$\frac{d^2}{dx^2} (ae^{2ix} + be^{-2ix}) = -4(ae^{2ix} + be^{-2ix})$$

# **Dynamics of Chemical Systems-1**

## **Lecture 4**

**CY-1020 (total credit = 1)**

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# Commutation and non-Commutation

- A commutator in quantum mechanics tells us if we can measure two 'observables' at the same time.

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- If the commutator of two 'observables' is zero, then they CAN be measured at the same time, otherwise there exists an uncertainty relation between the two.
- In general,  $\hat{A}_1 \hat{A}_2 \neq \hat{A}_2 \hat{A}_1$  :  $\hat{A}_1$  operates on  $\hat{A}_2$  is not equal to  $\hat{A}_2$  operates on  $\hat{A}_1$
  
- For example,  $x$  and  $p_x$  are position and momentum operators and  $x p_x \neq p_x x$ ; check for a specific function  $x^2$

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

$$(xp_x)x^2 = x(2\hbar/i)x = (2\hbar/i)x^2$$
$$(p_xx)x^2 = p_xx^3 = (3\hbar/i)x^2.$$

- Two operators commute if they obey the simple operator expression:  $[\hat{A}_1, \hat{A}_2] = \hat{A}_1 \hat{A}_2 - \hat{A}_2 \hat{A}_1 = 0 \Rightarrow \hat{A}_1 \hat{A}_2 = \hat{A}_2 \hat{A}_1$

# Commutation and non-Commutation

Evaluate the commutator  $[x, p_x]$  in the position representation.

**Method.** To evaluate the commutator  $[A, B]$  we need to remember that the operators operate on some function, which we shall write  $f$ . So, evaluate  $[A, B]f$  for an arbitrary function  $f$ , and then cancel  $f$  at the end of the calculation.

**Answer.** Substitution of the explicit expressions for the operators into  $[x, p_x]$  proceeds as follows:

$$\begin{aligned}[x, p_x]f &= (xp_x - p_x x)f = x \times \frac{\hbar}{i} \frac{\partial f}{\partial x} - \frac{\hbar}{i} \frac{\partial(xf)}{\partial x} \\ &= x \times \frac{\hbar}{i} \frac{\partial f}{\partial x} - \frac{\hbar}{i} f - x \times \frac{\hbar}{i} \frac{\partial f}{\partial x} = i\hbar f\end{aligned}$$

where we have used  $(1/i) = -i$ . This derivation is true for any function  $f$ , so in terms of the operators themselves,

$$[x, p_x] = i\hbar$$

The right-hand side should be interpreted as the operator ‘multiply by the constant  $i\hbar$ ’.

# Laws of Quantum Mechanics

On information about a state

**Postulate 1.** The state of a system is fully described by a function  $\Psi(r_1, r_2, \dots, t)$ .

The state of a quantum mechanical system is completely specified by a wavefunction  $\Psi(x, t)$ , which can be complex

All possible information can be derived from  $\Psi(x, t)$

From the analogy of classical wave equation, Intensity is replaced by Probability. The probability is proportional to the square of the of the wavefunction  $|\Psi(x, t)|^2$ , known as probability density  $P(x)$

# Laws of Quantum Mechanics

## On the selection of operators:

**Postulate 2.** Observables are represented by hermitian operators chosen to satisfy the commutation relations

$$[q, p_{q'}] = i\hbar\delta_{qq'} \quad [q, q'] = 0 \quad [p_q, p_{q'}] = 0$$

where  $q$  and  $q'$  each denote one of the coordinates  $x, y, z$  and  $p_q$  and  $p_{q'}$  the corresponding linear momenta.

An operator is **hermitian** if it satisfies the following relation:

$$\int f_m^* \Omega f_n \, d\tau = \left\{ \int f_n^* \Omega f_m \, d\tau \right\}^*$$

**Property 1.** The eigenvalues of hermitian operators are real.

**Property 2.** Eigenfunctions corresponding to different eigenvalues of an hermitian operator are orthogonal.

## Laws of Quantum Mechanics

An operator is hermitian if it satisfies the following relation:

$$\int f_m^* \Omega f_n d\tau = \left\{ \int f_n^* \Omega f_m d\tau \right\}^*$$

All the eigenfunctions of Quantum Mechanical operators are “Orthogonal”

$$A\psi_1 = a_1\psi_1$$

$$A\psi_2 = a_2\psi_2.$$

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \langle \psi_m | \psi_n \rangle = 0 \quad \text{for } m \neq n$$

Now we compute  $\langle \psi_2 | A | \psi_1 \rangle$  two ways.

$$\begin{aligned} \langle \psi_2 | A \psi_1 \rangle &= a_1 \langle \psi_2 | \psi_1 \rangle \\ \langle \psi_2 | A \psi_1 \rangle &= \langle A \psi_2 | \psi_1 \rangle = a_2 \langle \psi_2 | \psi_1 \rangle \end{aligned} \quad \boxed{0 = (a_2 - a_1) \langle \psi_2 | \psi_1 \rangle}$$

If  $a_1 \neq a_2$  then  $\langle \psi_2 | \psi_1 \rangle = 0$ .

# Laws of Quantum Mechanics

Only real eigenvalues will be observed, which will specify a number corresponding to the classical variable

If  $\Psi(x) = \sin(cx)$

$$\frac{d}{dx} \Psi(x) = c \cdot \cos(cx)$$

$$\frac{d^2}{dx^2} \Psi(x) = -c^2 \cdot \sin(cx) = -c^2 \cdot \Psi(x)$$

If  $\Psi(x) = e^{\alpha x}$

$$\frac{d}{dx} \Psi(x) = \alpha \cdot e^{\alpha x}$$

$$\frac{d^2}{dx^2} \Psi(x) = \alpha^2 \cdot e^{\alpha x} = \alpha^2 \cdot \Psi(x)$$

There may be, and typically are, many eigenfunctions for the same QM operator!

# Laws of Quantum Mechanics

Link between wavefunction/operators with the experimental observations

**Postulate 3.** When a system is described by a wavefunction  $\psi$ , the mean value of the observable  $\Omega$  in a series of measurements is equal to the expectation value of the corresponding operator.

The expectation value of an operator  $\Omega$  for an arbitrary state  $\psi$  is denoted  $\langle \Omega \rangle$  and defined as

$$\langle \Omega \rangle = \frac{\int \psi^* \Omega \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{\langle \psi | \Omega | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.23)$$

If the wavefunction is chosen to be normalized to 1, then the expectation value is simply

$$\langle \Omega \rangle = \int \psi^* \Omega \psi \, d\tau = \langle \psi | \Omega | \psi \rangle \quad (1.24)$$

Unless we state otherwise, from now on we shall assume that the wavefunction is normalized to 1.

# Laws of Quantum Mechanics

The average value of the observable corresponding to operator  $\hat{A}$  is

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi dv$$

From classical correspondence we can define average values for a distribution function  $P(x)$

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) \cdot dx \text{ and } \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \cdot dx$$

$\langle a \rangle$  corresponds to the average value of a classical physical quantity or observable , and  $\hat{A}$  represents the corresponding Quantum mechanical operator

$$\langle a \rangle = \int_{-\infty}^{+\infty} \hat{A} \cdot P(x) dx = \int_{-\infty}^{+\infty} \hat{A} \cdot |\Psi|^2 dx \approx \int_{\text{all space}} \Psi^* \hat{A} \Psi dx = \langle \Psi | \hat{A} | \Psi \rangle$$

# Laws of Quantum Mechanics

The next postulate concerns the interpretation of the wavefunction itself, and is commonly called the **Born interpretation**:

**Postulate 4.** The probability that a particle will be found in the volume element  $d\tau$  at the point  $r$  is proportional to  $|\psi(r)|^2 d\tau$ .

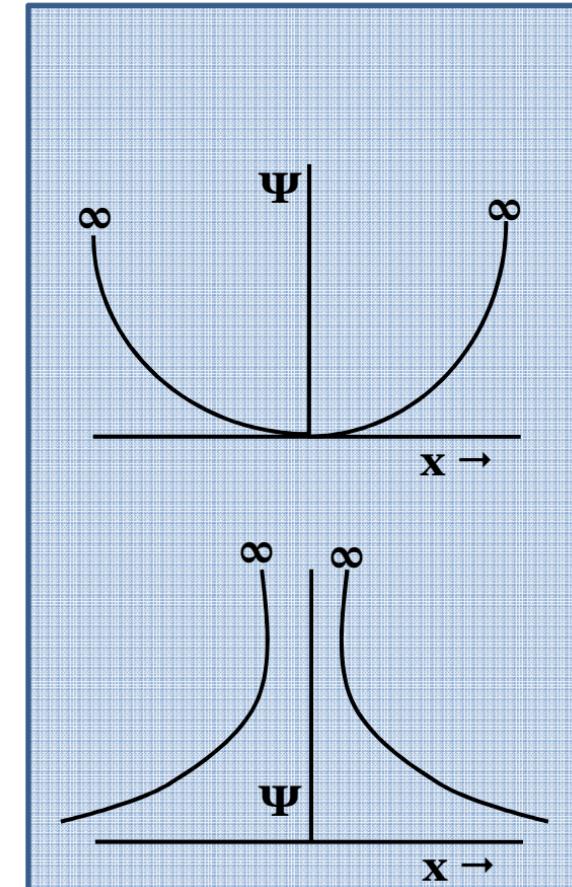
# Born Interpretation

## Normalization of Wavefunction

Since  $\Psi^* \Psi d\tau$  is the probability, the total probability of finding the particle somewhere in space has to be unity

$$\iiint_{\text{all space}} \Psi^*(x, y, z) \cdot \Psi(x, y, z) dx dy dz = \int_{\text{all space}} \Psi^* \Psi d\tau = \langle \Psi | \Psi \rangle = 1$$

If integration diverges, i.e.  $\rightarrow \infty$ :  $\Psi$  can not be normalized, and therefore is NOT an acceptable wave function. However, a constant value  $C \neq 1$  is perfectly acceptable.



Unacceptable wavefunction

$\Psi$  must vanish at  $\pm\infty$ , or more appropriately at the boundaries and  $\Psi$  must be finite

# Born Interpretation



## Probability density

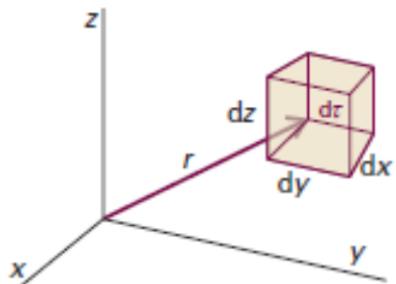
$$P(x) = |\Psi(x, t)|^2 = \Psi^*(x, t) \cdot \Psi(x, t)$$

## Probability

$$P(x_a \leq x \leq x_a + dx) = |\Psi(x, t)|^2 dx = \Psi^*(x_a, t) \cdot \Psi(x_a, t) dx$$

## Probability in 3-dimensions

$$\begin{aligned} P(x_a \leq x \leq x_a + dx, y_a \leq y \leq y_a + dy, z_a \leq z \leq z_a + dz) \\ &= \Psi^*(x_a, y_a, z_a, t') \cdot \Psi(x_a, y_a, z_a, t') dx dy dz \\ &= |\Psi(x_a, y_a, z_a, t')|^2 d\tau \end{aligned}$$



## Restrictions on wavefunction

$\psi$  must be a solution of the Schrodinger equation

$\psi$  must be normalizable:  $\psi$  must be finite and  $\rightarrow 0$  at boundaries/  $\pm\infty$

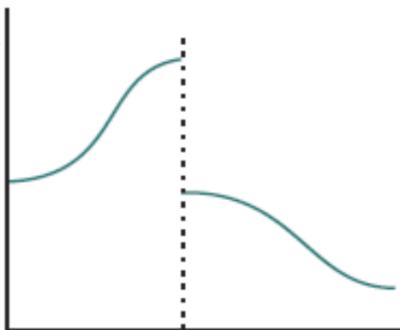
$\Psi$  must be a continuous function of x,y,z

$d\Psi/dq$  must be must be continuous in x,y,z

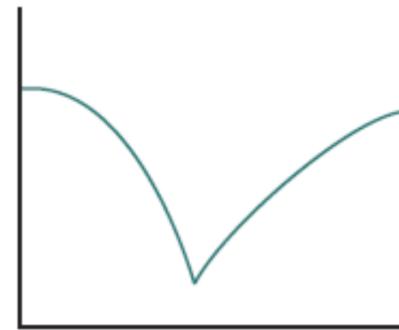
$\Psi$  must be single-valued

$\Psi$  must be quadratically-intergrable  
(square of the wavefunction should be integrable)

## Restrictions on wavefunction



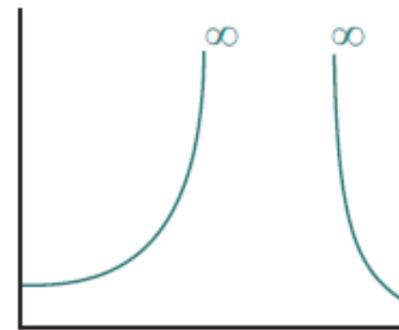
Unacceptable because  
 $\psi$  is not continuous



Unacceptable because  
 $d\psi/dq$  is not continuous



Unacceptable because  
 $\psi$  is not single-valued



Unacceptable because  
 $\psi$  goes to infinity

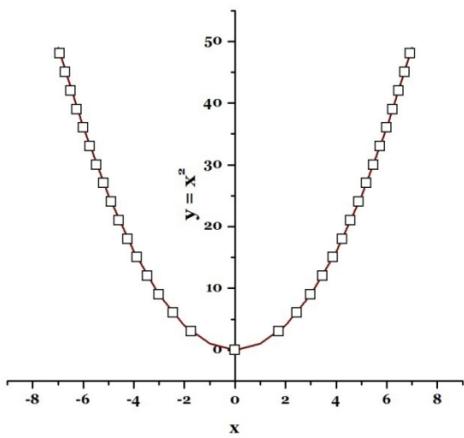
## Restrictions on wavefunction

Because of these restrictions, solutions of the Schrodinger equations do not in general exist for arbitrary values of energy

In other words, a particle may possess only certain energies otherwise its wavefunction would be Unacceptable

The energy of a particle is quantized

## Quantization?



The function  $f(x) = x^2$  can take any values

If we impose arbitrary condition that  $f(x)$  can only be multiples of three, then values if  $x$  are restricted.

Quantization!

Physically meaningful boundary conditions lead to quantization ☺

## Essence of Quantum Mechanics

Not deterministic: Can not precisely determine many parameters in the system, but  $\Psi$  can provide all the information (spatio-temporal) of a system.

Only average values and probabilities can be obtained for classical variables, now in new form of “operators”.

Total energy is conserved, but quantization of energy levels come spontaneously from restriction on wave function or boundary condition

Final outputs tally very well with experimental results, and does not violate Classical mechanics for large value of mass.

# Laws of Quantum Mechanics

The final postulate concerns the dynamical evolution of the wavefunction with time:

**Postulate 5.** The wavefunction  $\Psi(r_1, r_2, \dots, t)$  evolves in time according to the equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (1.27)$$

The state of a system is completely specified by the wavefunction  $\Psi(x, y, z, t)$  which evolves according to time-dependent Schrodinger equation

# Representation of Operators

**Classical Variable**

Position,  $x$

Momentum,  $p_x = mv$

Kinetic Energy,  $T_x = \frac{p_x^2}{2m}$

Kinetic Energy,  $T = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$

Potential Energy,  $V(x)$

**QM Operator**

$\hat{x}$

$$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} = -i\hbar \frac{d}{dx}$$

$$\hat{T}_x = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

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

$\hat{V}(x)$

# Schrödinger's Wave Equation

$$E = T + V = \frac{p_x^2}{2m} + V(x)$$

---

Time-dependent Schrodinger equation

$$i\hbar \frac{\widehat{\partial}}{\partial t} \Psi(x, t) = \left[ -\frac{\hbar^2}{2m} \widehat{\nabla}_x^2 + \widehat{V}(x, t) \right] \Psi(x, t)$$

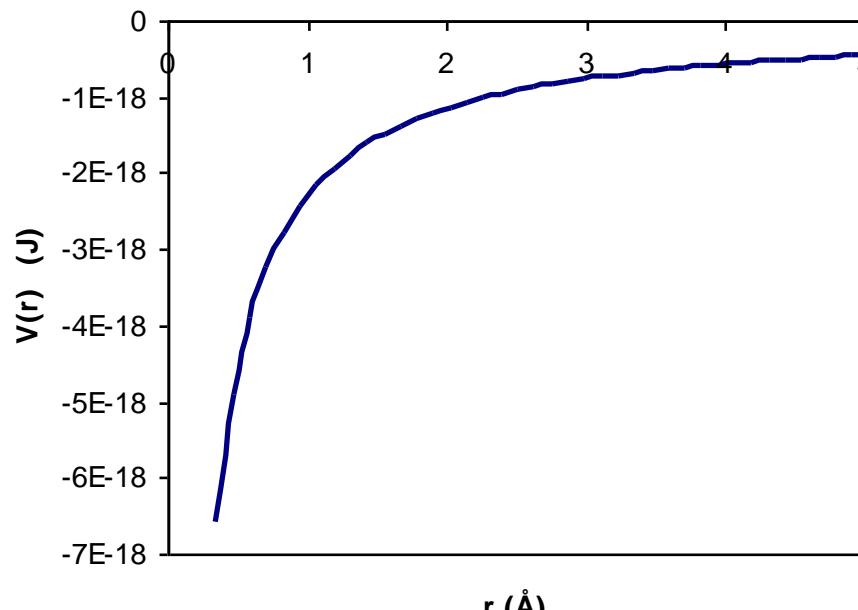
where

$$\widehat{H} = -\frac{\hbar^2}{2m} \widehat{\nabla}_x^2 + \widehat{V}(x, t) \quad \widehat{\nabla}_x^2 = \frac{\partial^2}{\partial x^2}$$

# The Potential Energy Function

The potential energy of interaction between a proton and an electron is described by the equation  $V(r) = -e^2/4\pi\epsilon_0 r$

$V(r)$  is zero when the proton and electron are an infinite distance apart, but is negative at all values of  $r < \infty$ . That is, the potential energy of the electron bound to the nucleus is lower than that of a free electron.



# Time-dependent Schrodinger Equation

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

Equations of this form can be solved by the technique of **separation of variables**, in which a trial solution takes the form

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

When this substitution is made, we obtain

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

Division of both sides of this equation by  $\psi\theta$  gives

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) = i\hbar\frac{1}{\theta}\frac{d\theta}{dt}$$

# Time-dependent Schrodinger Equation

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V(x) = i\hbar \frac{1}{\theta} \frac{d\theta}{dt}$$

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

$$i\hbar \frac{d\theta}{dt} = E\theta$$

## **Examples of Exactly Solvable Systems**

### **Time Independent Schrodinger Equation**

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \cdot \psi(x)$$

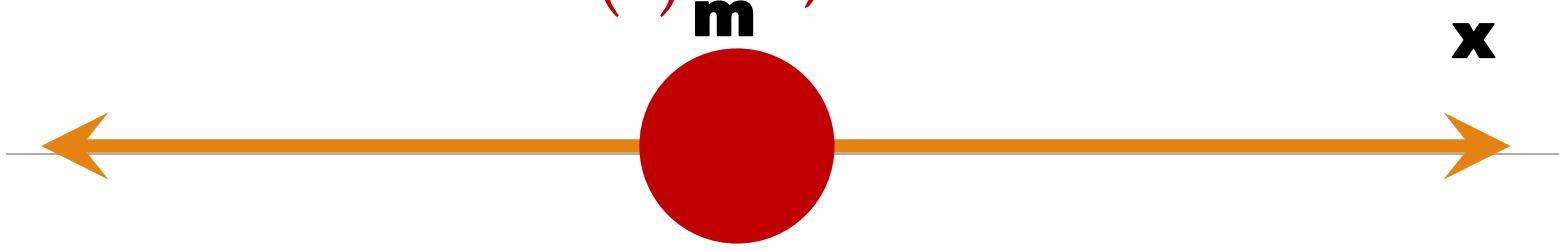
1. Free Particle
  2. Particle in a 1D/2D/3D box
-

# Free Particle

## Schrodinger Equation

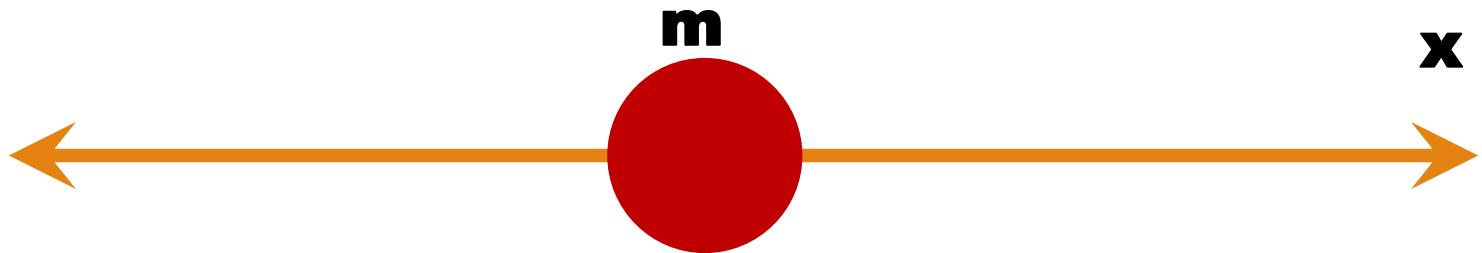
$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \cdot \psi(x)$$

Free Particle:  $V(x) = 0$ ; No external forces



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

# Free Particle



Free Particle:  $V(x) = 0$ ; No external forces

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

---

Second-order linear differential equation

Try with a trial solution:

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

# Free Particle

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

Try with a trial solution:  
 $\Psi(x) = A \sin kx + B \cos kx$

Eigenvalue function and eigenvalue?

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

# Free Particle

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

Try with a trial solution:  
 $\Psi(x) = A \sin kx + B \cos kx$

$$\frac{\partial^2}{\partial x^2} \psi(x) = -k^2 (A \sin kx + B \cos kx) = -k^2 \psi(x)$$

Solution: Energy and Wavefunction

$$\frac{\hbar^2}{2m} k^2 \psi(x) = E \cdot \psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm \frac{\sqrt{2mE}}{\hbar}$$

There are no restrictions on  $k$  and  $E$  can have any value  
Energies of free particles are continuous

No quantization, all energies are allowed

# Free Particle

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

Try with a trial solution:  
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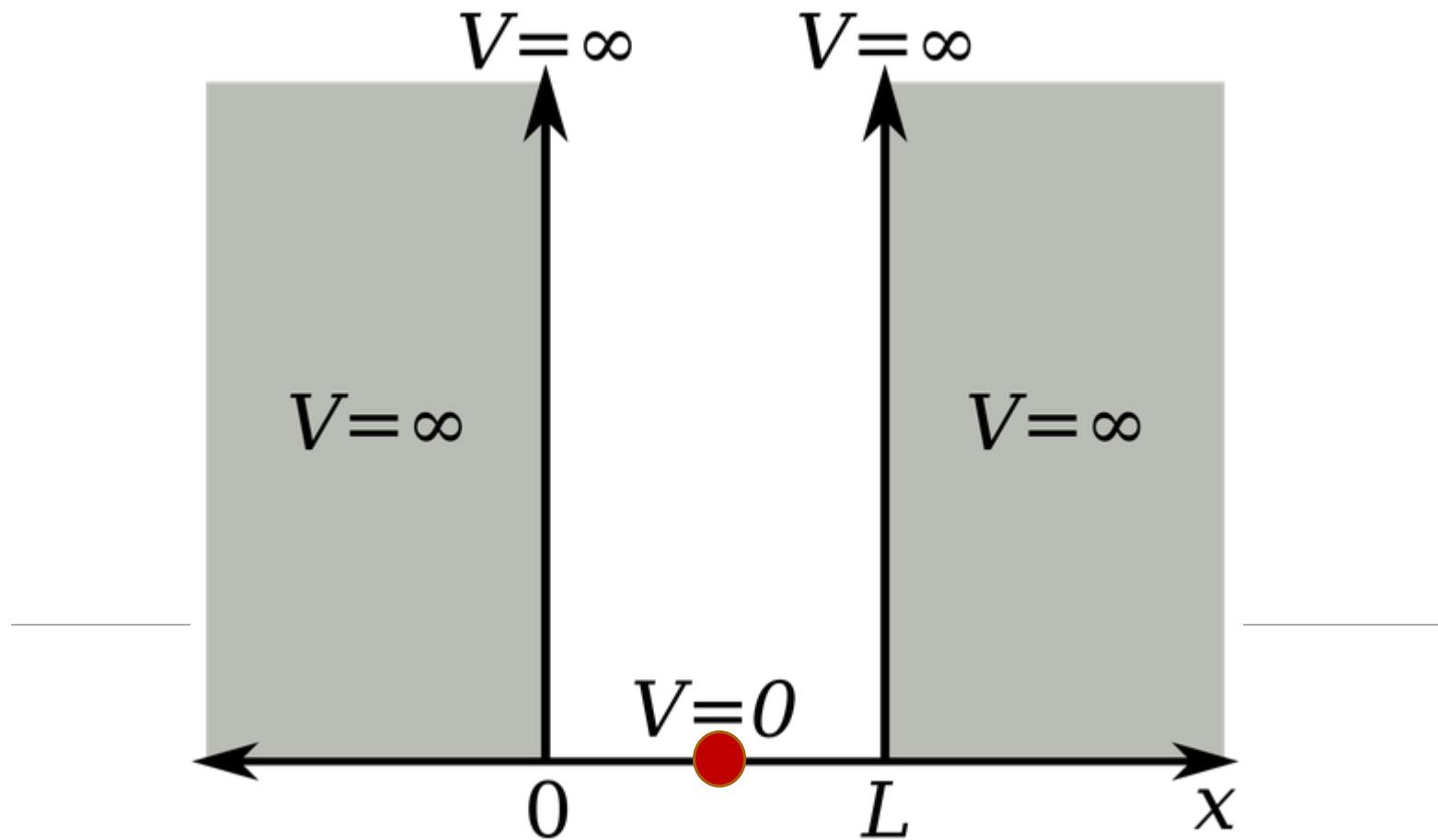
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$$\Psi(x) = A \sin kx + B \cos kx$$

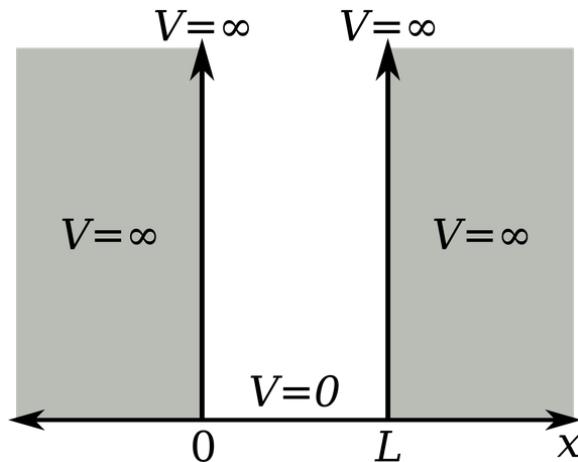
No quantization, all energies are allowed

# Particle in an one dimensional box



$V(x) = 0$  when  $0 \leq x \leq L$   
 $= \infty$  at any other values of  $x$

# Particle in an one dimensional box



$V(x) = 0$  when  $0 \leq x \leq L$   
 $= \infty$  at any other values of  $x$

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

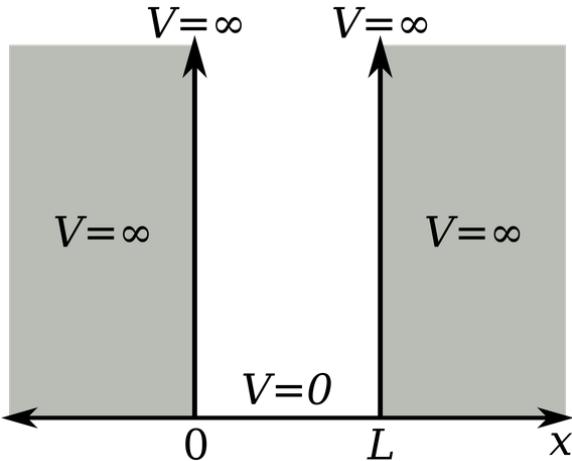
For regions in the space  $x < 0$  and  $x > L \Rightarrow V = \infty$

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

Normalization condition not satisfied

$$\Psi(x < 0) = 0; \Psi(x > L) = 0$$

# Particle in an one dimensional box



$V(x) = 0$  when  $0 \leq x \leq L$

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

Try with a trial solution:

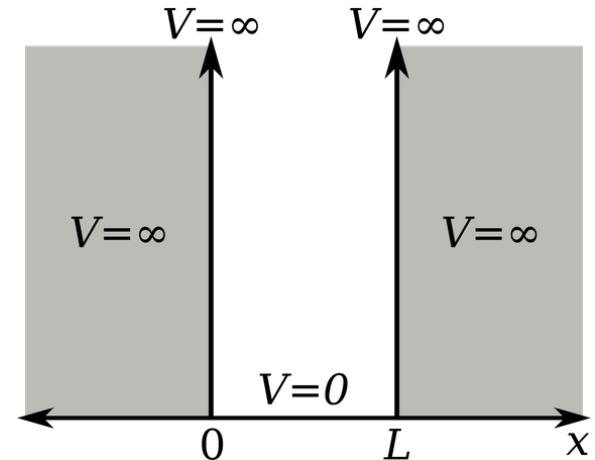
$$\Psi(x) = A \sin kx + B \cos kx$$

$$\frac{\hbar^2}{2m} k^2 \psi(x) = E \cdot \psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm \frac{\sqrt{2mE}}{\hbar}$$

# Particle in an one dimensional box

$V(x) = 0$  when  $0 \leq x \leq L$

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



Boundary Condition  $x = 0 \Rightarrow \psi(x) = 0$

$$\psi(x) = A \sin kx \quad \because \cos 0 = 1$$

Boundary Condition  $x = L \Rightarrow \psi(L) = 0$

$$\psi(L) = 0 \Rightarrow A \sin kL = 0 \Rightarrow A = 0 \text{ or } \sin kL = 0$$

But the wavefunction  $\psi(x)$  CANNOT be ZERO everywhere

$$\sin kL = 0 \Rightarrow kL = n\pi \quad n=1,2,3,4\dots$$

# Particle in an one dimensional box

$V(x) = 0$  when  $0 \leq x \leq L$

Wavefunction  $\psi(x) = A \sin kx$

Energy  $E = \frac{\hbar^2 k^2}{2m}$  and  $k = \frac{n\pi}{L}$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad n=1,2,3,4\dots$$

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