CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-04, 15-01-2018

Summary: Lecture-03

Time independent Schröndinger Equation

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

Well behaved wave function for a physical system:

- Ψ must be single-valued.
- Ψ must be finite everywhere.
- Ψ must be continuous.
- $\frac{d\psi}{dx}$ must be continuous.

Normalization of wavefunction is a consequence of Born Interpretation.

$$\int_{-\infty}^{\infty}[N\Psi(x)]\,[N\,\Psi(x)]dx = 1$$

Work out: Normalize the following wavefunction, $\phi = sin\frac{n\pi x}{a}$

Summary: Lecture-03

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Postulates of Quantum Mechanics

Postulate 1: Quantum mechanical system is completely specified by wavefunction.

Postulate 2: To every observable in classical mechanics there is an operator in quantum mechanics.

Postulate 3: Quantum Mechanical operators are **special in nature**. In any measurement of the observable associated with the operator $\hat{A}$, the only values that will be ever observed are the eigenvalues a, which satisfy the eigen value equation:

$$\boldsymbol{\widehat{A}\,\psi = a\,\psi}$$

Schröndinger Equation using operators:

Time independent Schröndinger Equation (ODE)

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

We can rewrite as, $\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + u(x)\right\}\psi(x) = E\,\psi(x)$

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + u(x)\right\} = \widehat{H};$$

Energy Operator or Hamiltonian

Schröndinger Equation using operators:

Schröndinger Equation as energy eigen value problem:

$$\widehat{\boldsymbol{H}}\,\boldsymbol{\psi} = \boldsymbol{E}\,\boldsymbol{\psi}$$

For a physical system which is having more than one eigen state, such as, H-Atom – 1s, 2s, 2p, 3s, 3p and so on . . . .

$$\widehat{\boldsymbol{H}}\,\boldsymbol{\psi}_{\boldsymbol{n}} = \boldsymbol{E}_{\mathbf{n}}\,\boldsymbol{\psi}_{\boldsymbol{n}}$$

What would be the form of $\widehat{\boldsymbol{H}}$ for a two particle system (masses m_1 and m_2) interacting through Coulomb's potential in one dimension? The distance between the two particles is x_{12}

Application: Free Particle, Momentum

- Free particle in 1D: A particle which is not under any forces {Simplest system}
- Start with the Schröndinger representation of momentum operator:

$$\hat{P} = \text{-i}\,\hbar\,\frac{d}{dx}$$

Let us start with a trial function:

$$\psi_p = \text{C}\; e^{\pm ipx/\hbar}$$

(c is a constant other than zero)

What would be the momentum value?

We'll determine the eigen value? {Ans: $\pm$p)

Energy, E = $\frac{p^2}{2m} \Rightarrow behaves\ as\ a\ classical\ system$

Application in Free Particle: Energy

Particle subject to no forces: U(x) = 0

Schröndinger equation becomes: $\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi(x) = 0$

ODE of order 2: General solution would be,

$$\psi_E = C_1\, e^{i\sqrt{(2mE)}\,x/\hbar} + C_2\, e^{-i\sqrt{(2mE)}\,x/\hbar}$$

$$\equiv C_3 \cos kx + C_4 \sin kx;\ k = \frac{(2mE)^{1/2}}{\hbar}$$

Ψ will remain finite as x$\rightarrow \pm\infty$; $E \geq 0$ $(Boundary\ condition)$

Particle in one-dimensional Box (PIB):

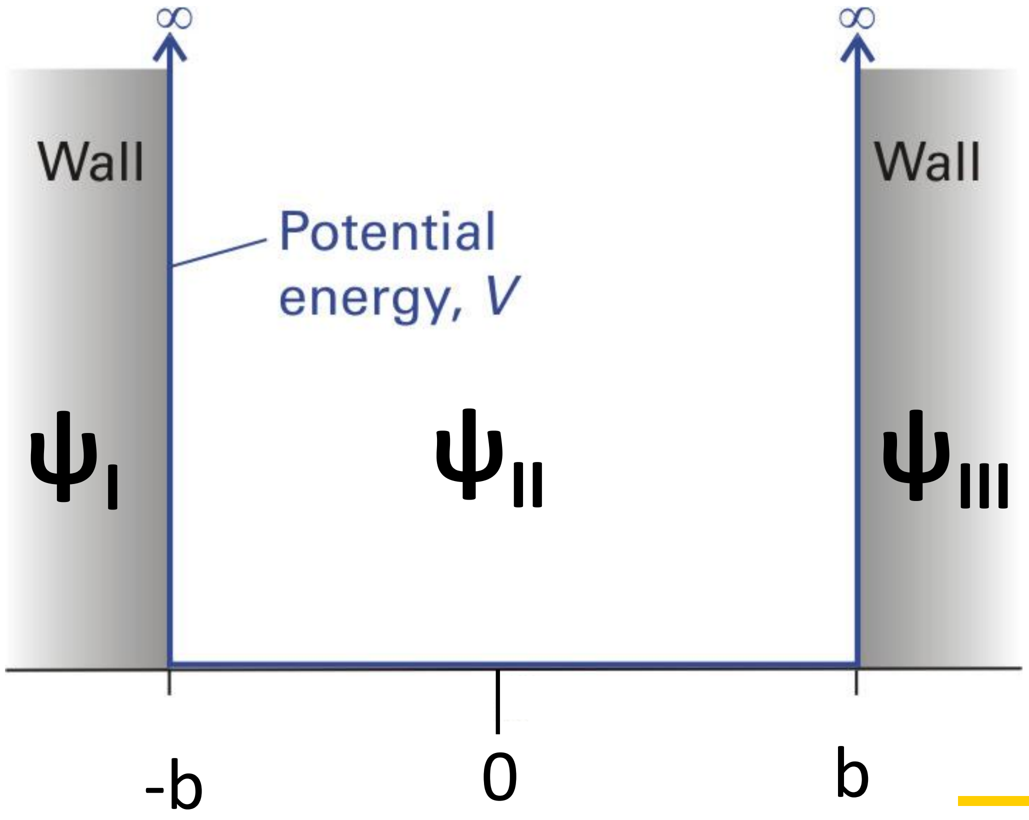
Classical analogue

- One-dimensional racquet ball court with infinitely massive walls.
- Perfect ball: collisions are perfectly elastic.
- There is no resistance in this racquet ball court.
- If a player hits a ball against the wall – no loss of kinetic energy; Continue to bounce between the walls indefinitely.
- Energy of the ball is only kinetic energy (KE).
- The ball can be hit hard or soft to provide more or less KE.
- Energy for this classical particle in a box is continuous.
- Energy can take on any value – even can have zero energy at point X.
- Probability of finding the ball is equally likely at every point

Particle in one-dimensional Box (PIB):

The quantum mechanical particle in a box:

- Consists of a particle, such as an electron,
- The box is small in an **absolute sense** (~ nanometer).



$$U(x) = 0 \; for \; -b < x < b$$

What would be the value of ψ_I and ψ_{III}?

How do we obtain the form of ψ_{II}?

Particle in one-dimensional Box (PIB):

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Schröndinger Equation:

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

$\psi(x)$ is the eigen function for PIB with E as the energy eigen value

What would be the form of PE?

$$U(x) = 0,\ |x| < b \ and\ U(x) = \infty,\ |x| \geq b$$

Interest is in the regions $|x| < b$ $\{\psi_{II}\}$

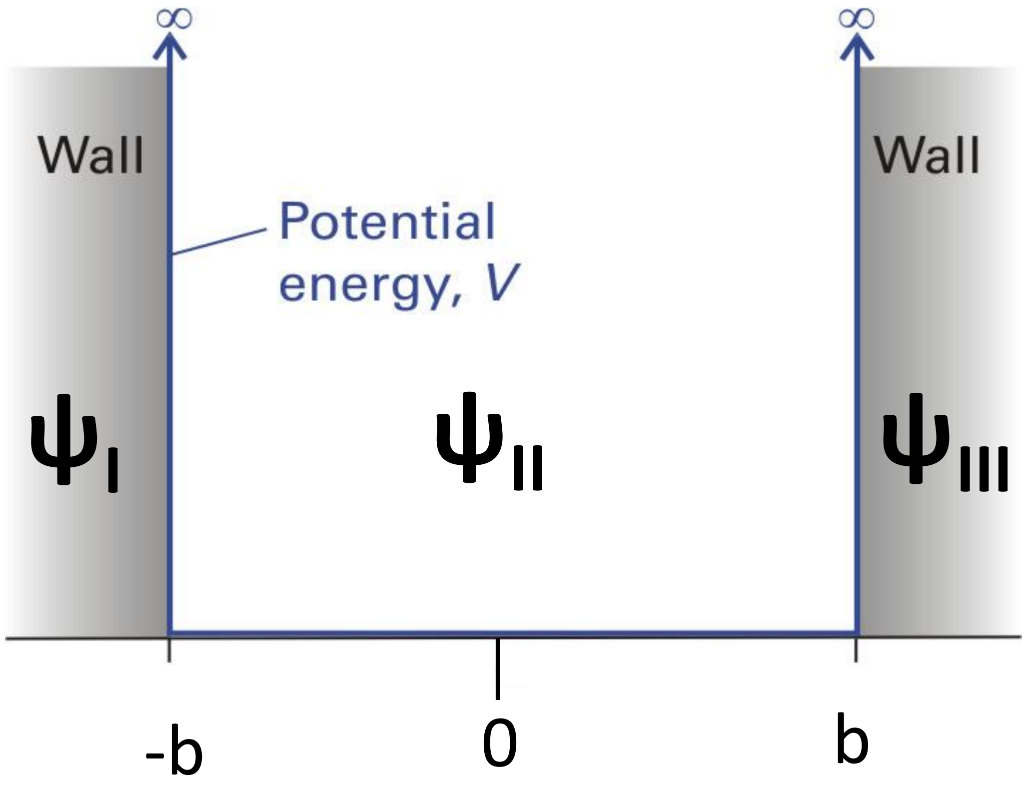
$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

Particle in one-dimensional Box (PIB):

Schröndinger Equation for 1D PIB:

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

- Solution of ODE of 2nd order yield: $\psi(x)$
- $\psi(x)$ will be acceptable if,
  1. Ψ (x) is single-valued.
  2. Ψ (x) is finite everywhere
  3. Ψ (x) is continuous
  4. $\frac{d\psi}{dx}$ is continuous



Solution of 1D PIB

Schröndinger Equation for 1D PIB:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\,\psi(x) \quad \text{……………………Equn. 1}$$

Rearrange Equn. 1

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2mE}{\hbar^2}\psi(x) \quad \text{……………………Equn. 2}$$

Can we guess any solution for this ODE?

2nd derivative of a function is equals the function times a –ve const.

Solution of 1D PIB

Consider **sin(ax)** and **cos(ax)**

$$\frac{d^2}{dx^2}\sin(ax) = -a^2\sin(ax)$$ ....Equn. 3

$$\frac{d^2}{dx^2}\cos(ax) = -a^2\cos(ax)$$ ....Equn. 4

$$\frac{\mathbf{d}^2}{\mathbf{dx}^2}\,\boldsymbol{\psi}(\mathbf{x}) = -\frac{\boldsymbol{2mE}}{\boldsymbol{\hbar}^2}\,\boldsymbol{\psi}(\mathbf{x})$$ ....Equn. 2

Solution of 1D PIB

Either the **sin** or **cos** functions or any combination of **sin** and **cos** function solve the differential equation. Compare Equn. (2), (3), and (4)

$$\frac{d^2}{dx^2}\sin(ax) = -a^2\sin(ax) \text{ ......Equn. 3}$$

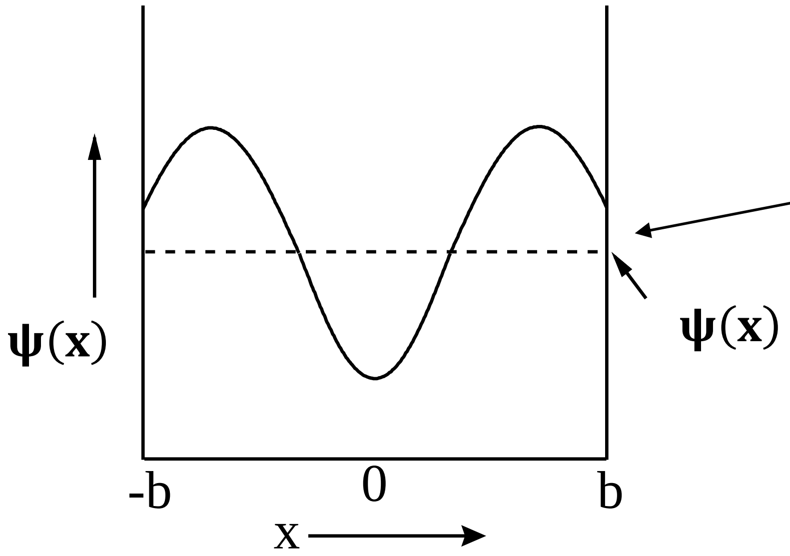
Physical condition

$$\frac{d^2}{dx^2}\cos(ax) = -a^2\cos(ax) \text{ ......Equn. 4}$$

$$a^2 = \frac{2mE}{\hbar^2}$$

$$\frac{\mathbf{d^2}}{\mathbf{dx^2}}\,\boldsymbol{\psi}(\mathbf{x}) = -\frac{\mathbf{2}\boldsymbol{mE}}{\hbar^2}\,\boldsymbol{\psi}(\mathbf{x}) \text{ ......Equn. 2}$$

Solution of 1D PIB: Is it acceptable?



Well is infinitely deep.

Particle has zero probability of being found outside the box.

Function as drawn discontinuous at $|x| \geq b$

To be an acceptable wavefunction for PIB

$\Psi \Rrightarrow \sin$ and $\cos \Rrightarrow 0$ at $|x| = b$

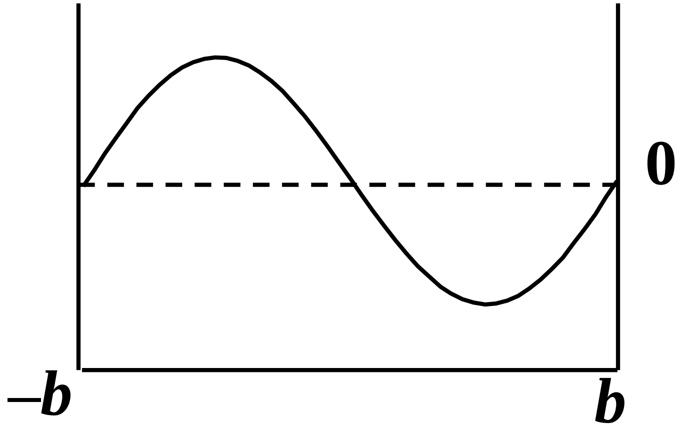
Solution of 1D PIB: Acceptable solution?

Ψ will vanish at |x| = b if

$$a = \frac{n\pi}{2b} \equiv a_n$$ n is an integer

$$\cos a_n x \qquad n = 1, 3, 5\ldots$$

$$\sin a_n x \qquad n = 2, 4, 6\ldots$$



Integral number of half wavelengths in box. Zero at walls.

We have two condition for a^2, solve for E

$$a_n^2 = \frac{n^2\pi^2}{4b^2} = \frac{2mE}{\hbar^2}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{8mb^2} = \frac{n^2h^2}{8mL^2}$$

Energy eigenvalues,

$L = 2b$ – **length of box.**

Energy levels are not continuous

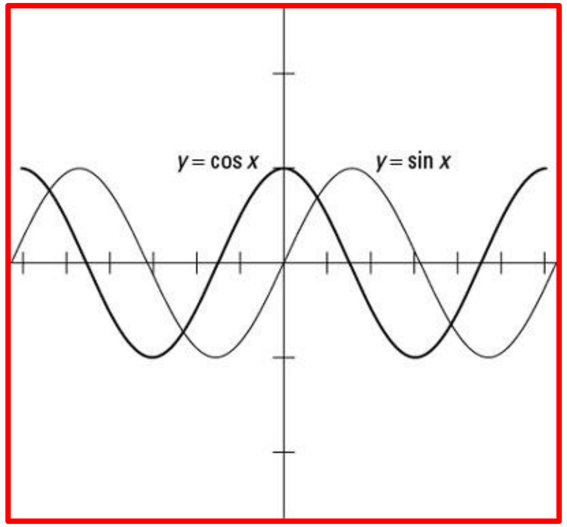
What do we learn from PIB problem?

- Energy in PIB is discrete
- Energy eigen values are labelled by the integer n
- n is referred to as quantum number
- Lowest energy state is for $n = 1 \Rrightarrow E \neq 0$
- Lowest state is having finite kinetic energy
- Particle is never perfectly localized and stationary – uncertainty principle is not violated.

PIB wavefunctions

$$\Psi_n(x) = \left(\frac{1}{b}\right)^{1/2} \cos\frac{n\pi x}{2b} \quad |x| \leq b \qquad \text{n = 1, 3, 5 ......}$$

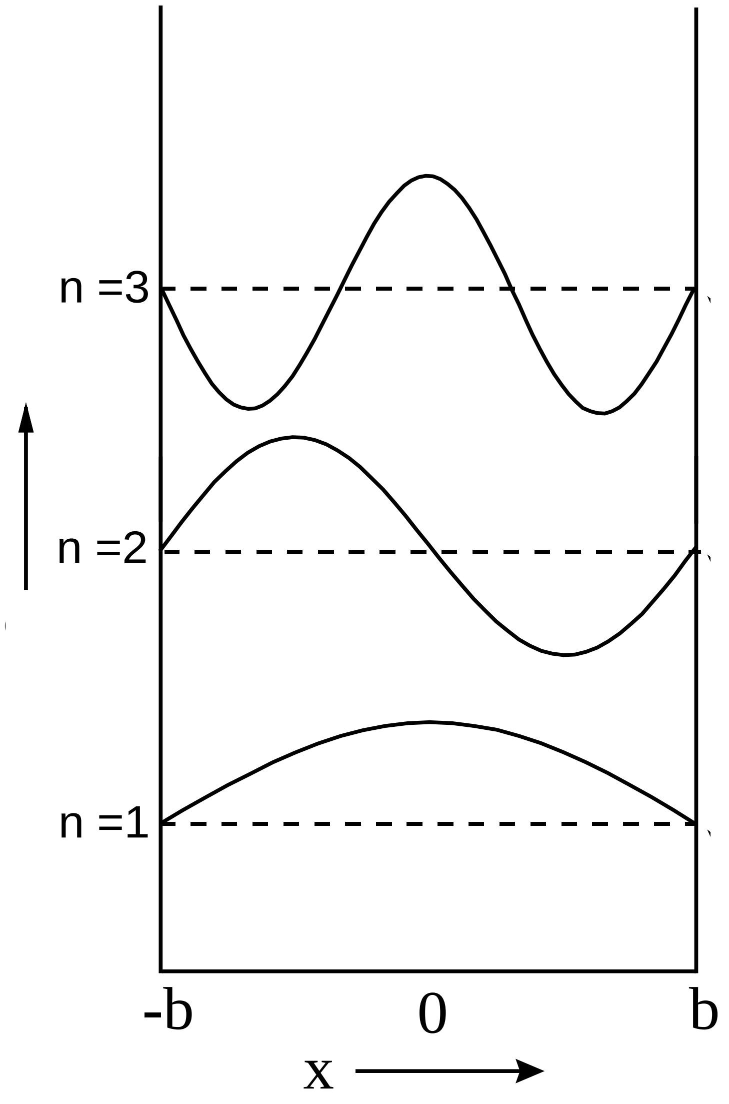
$$\Psi_n(x) = \left(\frac{1}{b}\right)^{1/2} \sin\frac{n\pi x}{2b} \quad |x| \leq b \qquad \text{n = 2, 4, 6 ......}$$



General form of the wavefunctions:

$$\Psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a} \quad 0 \leq x \leq a, \text{ n = 1, 2, 3 .....}$$

Wave functions & Born Conditions



- Quantization is forced by Born condition – boundary condition
- Wave function must be finite everywhere.
- Wave function is single valued.
- Wave function is continuous.
- What about the 4th condition: $\frac{d\psi}{dx}$???

Consider $\frac{d\psi}{dx}$ at |x| = b

Outside the box at |x| = b, $\frac{d\psi}{dx} = 0$

Inside the box at |x| = b, $\frac{d\psi}{dx} \neq 0$, finite