CML1001 – Structural Insights into Atoms and Molecules

Lecture 2: Time-Independent Schrödinger Equation

Department of Chemistry

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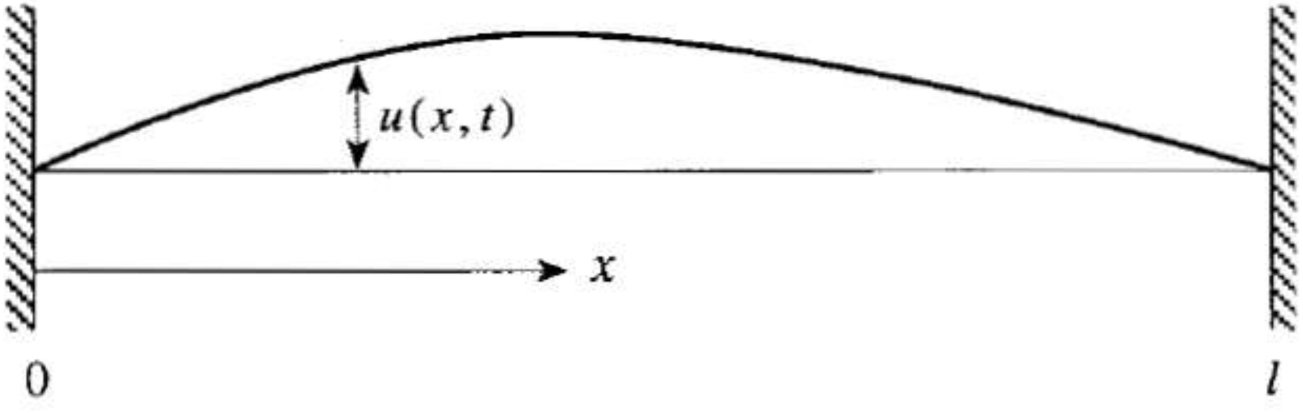
Classical Wave Equation



A vibrating string whose ends are fixed at 0 and *l*

The amplitude of the vibration at position *x* and time *t* is *u(x,* t)

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \qquad (1)$$

The Classical Wave Equation

***v* is the velocity of disturbance along the string**

The variables *x* and *t* are said to be the *independent variables*

$$u(x,t) = X(x)\,T(t) \qquad (2)$$

Separation of variables

$$\frac{\partial^2 u}{\partial x^2} = \underbrace{\frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}}$$

fn. of x

fn. of t

$$u(x,t) = f(x)\, g(t)$$

$$g f'' = \frac{1}{v^2} f g''$$

$$\frac{f''}{f} = \frac{1}{v^2}\frac{g''}{g}$$

Separation of Variables

- $u\,(x,t) = \psi(x)\cos\omega t$ **(3)**

$\psi(x)$ **is the spatial amplitude of the wave**

- **Using eq. (3) in eq. (1)** $\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{\mathrm{v}^2}\frac{\partial^2 u(x,t)}{\partial t^2}$

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{\mathrm{v}^2}\psi(x) = 0 \qquad \textbf{(4)}$$

- **Use** $\omega = 2\pi\nu$ **and** $\nu\lambda = \mathrm{v}\ (velocity)$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0 \qquad \textbf{(5)}$$

Deriving the Schrödinger Equation

- **Total energy = K.E. + P.E.** $\rightarrow E = \frac{p^2}{2m} + V(x)$ **(6)**
- **Solving for *p*:** $p = \ [2m\,\{E\ - V(x)\}]^{1/2}$ **(7)**
- **From the de Broglie formula**

$$\lambda = \frac{h}{p} = \ \frac{h}{[2m\,\{E - V(x)\}]^{1/2}} \qquad (8)$$

- **Inserting eq. 8 in eq. 5** $[\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0]$ **we have**

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E\ - V(x)]\psi(x) = 0 \qquad (9)$$

$\boxed{\hbar = h/2\pi}$ **is called *h-bar* or *h-cross***

$$\boxed{\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \ V(x)\ \psi(x) = E\psi(x)} \qquad (10)$$

de Broglie Waves

The de Broglie wavelengths of various moving objects.

Particle	Mass/kg	Speed/$m \cdot s^{-1}$	Wavelength/pm
Electron accelerated through 100 V	9.11×10^{-31}	5.9×10^{6}	120
Electron accelerated through 10,000 V	9.29×10^{-31}	5.9×10^{7}	12
α particle ejected from radium	6.68×10^{-27}	1.5×10^{7}	6.6×10^{-3}
22-caliber rifle bullet	1.9×10^{-3}	3.2×10^{2}	1.1×10^{-21}
Golf ball	0.045	30	4.9×10^{-22}

https://www.youtube.com/watch?v=PanqoHa_B6c

- **More videos on Electron Microscopes**

https://www.youtube.com/watch?v=PmfjYkKeVEA

https://www.youtube.com/watch?v=9DnnxvS6BBQ

Particle in a Box – One Dimension (PIB-1D)

T.I.S.E.

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

Linear Operators

$$\underbrace{\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]}_{\text{Operators}}\psi(x) = E\,\psi(x)$$

COMMUTING

NON-COMMUTING

Hamiltonian

$$\hat{H}\psi = E\psi$$

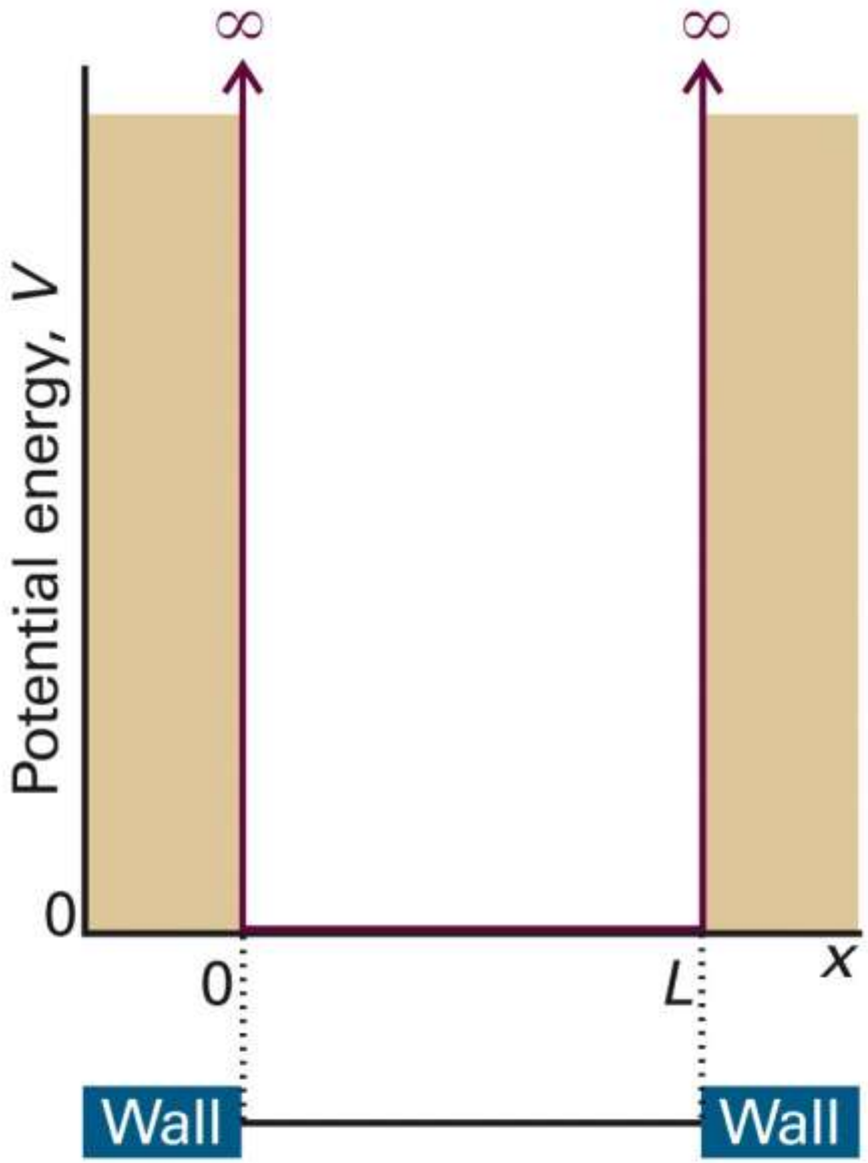


Figure 9-1
Atkins Physical Chemistry, Eighth Edition

Linear Operators

$$c\, f(x) + d\, g(x)$$

constants

$$\hat{A}\left[c f + d g\right] = c \hat{A} f(x) + d \hat{A} g(x)$$

Probability

$A e^{ikx} + B e^{-ikx}$

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

Free particle $V(x) = 0$: $\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \quad 0 \le x \le a$

The particle is restricted to the region $0 \le x \le a$ so cannot be found outside this region.

- Interpretation:

ψ is amplitude, square of amplitude is intensity

"intensity of the particle" is proportional to $|\psi|^2 = \psi^*\psi$

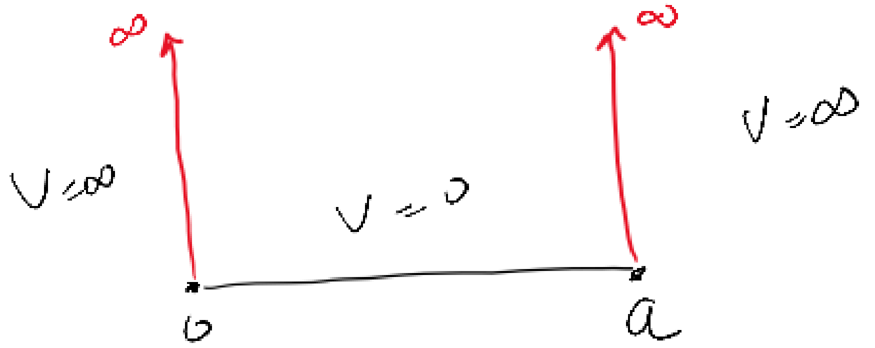
- What is "intensity of the particle"?

Schrödinger: $e\psi^*(x)\psi(x)dx$

Max Born: $\psi^*(x)\psi(x)dx$ is the probability that the particle is located between x and $x + dx$

PIB-1D

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \qquad 0 \le x \le a$$



$$\psi \sim e^{\alpha x}$$

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

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

$$\psi(x) = C \sin kx + D \cos kx$$

<u>Boundary Conditions</u>

B.C.

$\psi(0) = 0 \Rightarrow D = 0$

$$\hbar = \frac{h}{2\pi}$$

$$\psi(x) = C \sin kx$$

$\psi(a) = 0$

$$C \sin ka$$

$$\sin ka = 0 = \sin n\pi$$

integer

$$k = \frac{n\pi}{a} = \frac{\sqrt{2mE}}{\hbar}$$

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

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

Energy Levels

$$\boxed{E_n = \frac{n^2 h^2}{8 m a^2}}$$

In this communication I wish to show that the usual rules of quantization can be replaced by another postulate (the S.E.) in which there occurs no mention of whole numbers. Instead, the introduction of integers arises in the same natural way as, for example, in a vibrating string, for which the number of nodes is integral. The new conception can be generalized, and I believe that it penetrates deeply into the true nature of the quantum rules. [from Annalen. Der Physik **79**, 361 (1926)]

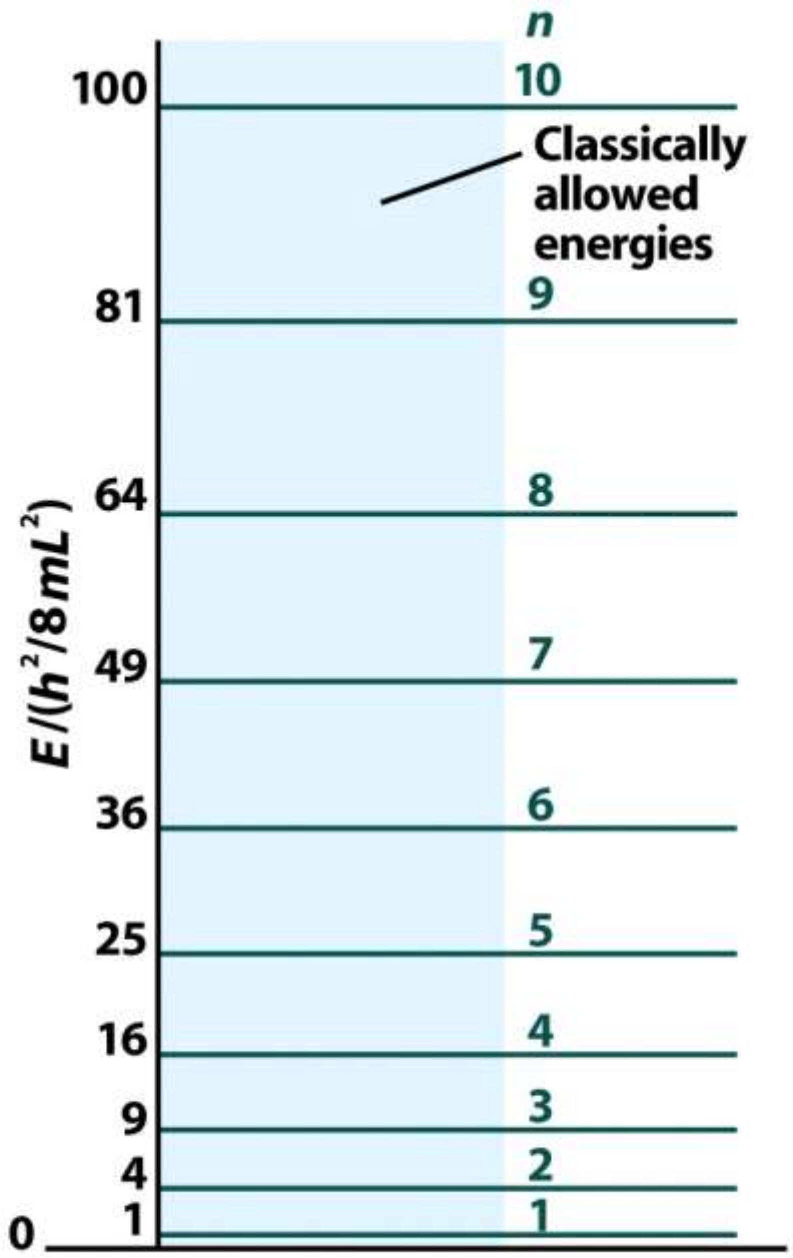


Figure 9-2
Atkins Physical Chemistry, Eighth Edition