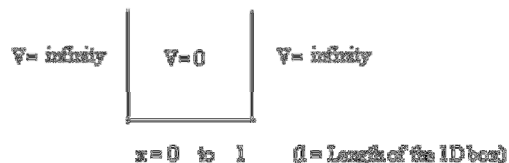


QUANTUM CHEMISTRY

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QC-3.1: PARTICLE IN A ONE DIMENSIONAL (1D) BOX



➤ $H\psi = E\psi$

➤ $\left\{ -\frac{\hbar^2}{8\pi^2m} \nabla^2 + V \right\} \psi = E\psi$

For a 1D box, $\nabla^2 = \frac{d^2}{dx^2}$

➤ *Schrödinger equation* : $\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{\hbar^2} (E - V)\psi = 0$

i.e., $\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{\hbar^2} E\psi = 0$; $V = 0$ inside the box

The particle is not at rest & has only KE

➤ Let, $k^2 = \frac{8\pi^2mE}{\hbar^2}$; *Standard differential equation* of the form $\frac{d^2\psi}{dx^2} + k^2\psi = 0$

➤ *Standard solution* : $\psi = A \sin kx + i B \cos kx$

Check: $\frac{d^2}{dx^2} (A \sin kx + i B \cos kx) = (-A \sin kx - i B \cos kx)k^2 = -k^2\psi$

➤ Apply the *first boundary condition* ($\psi = 0$ at $x = 0$) ; **B = 0**

Therefore, $\psi = A \sin kx$

➤ Apply the *second boundary condition* ($\psi = 0$ at $x = l$)

➤ $\psi = A \sin kl = 0$; A cannot be zero. Therefore $kl = n\pi$

$$\text{➤ } k = \frac{n\pi}{l}$$

$$\text{➤ } \frac{n^2\pi^2}{l^2} = \frac{8\pi^2mE}{h^2}$$

Therefore, $E_n = \frac{n^2h^2}{8ml^2}$

➤ Hence, $\psi = A \sin(n\pi/l)x$

➤ Apply *the normalization condition* to get A

$$\int \psi^* \psi dx = 1 \text{ for } 0 \leq x \leq l$$

i.e., $\int A^2 \sin^2(n\pi/l)x dx = 1$ {NB : $\cos 2x = \cos^2 x - \sin^2 x = 2\cos^2 x - 1 = 1 - 2\sin^2 x$ }

i.e., $A^2/2 \int \{1 - \cos 2(n\pi/l)x\} dx = 1$; for $0 \leq x \leq l$

$$A = (2/l)^{1/2}$$

$$\psi_n = (2/l)^{1/2} \sin(n\pi/l)x$$

➤ $E_n = \frac{n^2h^2}{8ml^2}$; ZPE = $\frac{h^2}{8ml^2}$ for n = 1

➤ $\Delta E_n = \frac{h^2}{8ml^2} (n_2^2 - n_1^2) = \frac{hc}{\lambda} = h\nu$

Discussions:

⇒ The value of “n” cannot be zero as it will mean the total energy; E is zero which is not possible.

⇒ Hence, ZPE, $E_1 = \frac{h^2}{8ml^2}$; for n = 1 (maximum degeneracy is one-non degenerate)

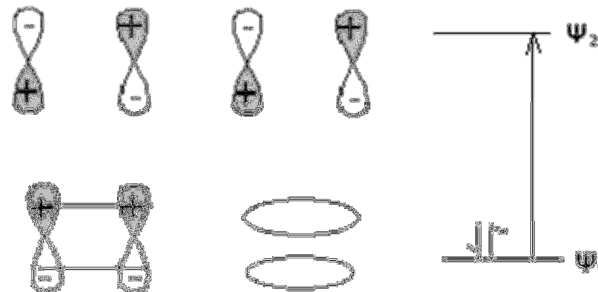
⇒ The integral values of n (1, 2, 3, ...) characterizes the energy levels, E_n (E_1, E_2, E_3, \dots) and the wave functions, ψ_n ($\psi_1, \psi_2, \psi_3, \dots$).

⇒ Generate the wave functions, ψ_n and energy levels, E_n for n=1, 2, 3, 4, 5, 6

⇒ Draw the energy levels and the wave functions for n=1, 2, 3, 4, 5, 6.

⇒ Predict the values of n for $\pi \rightarrow \pi^*$ transitions in each case.

⇒ The **energy levels are not equally spaced** and the wave functions will have nodes and anti nodes depending on n values.



⇒ Double bonds n. The $\pi \rightarrow \pi^*$ **transition** is $n \rightarrow n+1$. The number of MO's = $2n$, of which 50% levels viz., n are occupied.

⇒ Compare the particle (atom or a molecule, which can have $n = 0$ according to **statistical thermodynamics**) in a vessel with electron as a particle in a molecule, n cannot be zero.

⇒ **Mode of orbital overlap in conjugated diene like ETHENE ; E_n & Ψ_n (n = 1, 2)**

$\pi \rightarrow \pi^*$ (n : 1 \rightarrow 2)

⇒ **Mode of orbital overlap in conjugated diene like 1, 3-BUTADIENE; E_n & Ψ_n (n = 1, 2, 3, 4)**

Here, transition: $\pi \rightarrow \pi^*$; (n : 2 \rightarrow 3)

❖ *Similarly, construct energy level diagram for 1, 3, 5-Hexatriene*

❖ *Compare the energy levels of ethylene, butadiene (lie at low levels due to increase in l)*

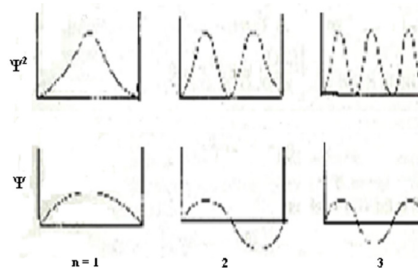
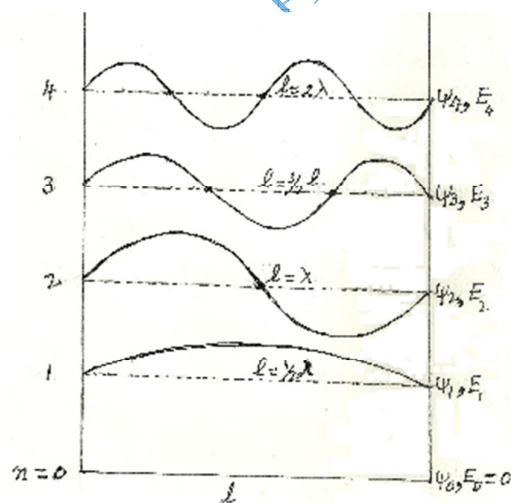
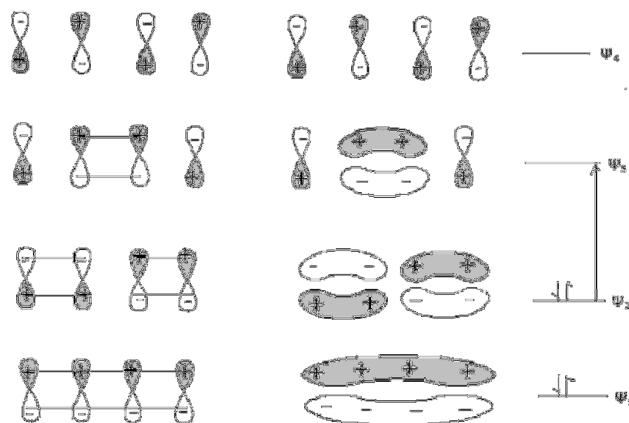


Fig: Ψ & Ψ^2 for 1D box for different n values



n	l	λ	v		$E = n^2 h^2 / 8ml^2$	$\Psi_n = (2/l)^{1/2} \sin(n\pi x/l)$
			c/λ	$c/l = k$		
1	$1/2\lambda$	$2l$	$c/2l$	$1/2k$	$h^2/8ml^2$	$(2/l)^{1/2} \sin(\pi x/l)$
2	λ	l	c/l	k	$4h^2/8ml^2$	$(2/l)^{1/2} \sin(2\pi x/l)$
3	$1 1/2\lambda$	$2/3l$	$1 1/2l$	$1 1/2k$	$9h^2/8ml^2$	$(2/l)^{1/2} \sin(3\pi x/l)$
4	2λ	$1/2l$	$2l$	$2k$	$16h^2/8ml^2$	$(2/l)^{1/2} \sin(4\pi x/l)$

Application to different conjugated olefins:

- ❖ Mass of the electron, $m_e = 9.11 \times 10^{-31} \text{ kg}$; $h = 6.625 \times 10^{-34} \text{ Js}$; $k_b = 1.38 \times 10^{-23} \text{ JK}^{-1}$
- ❖ Ethylene: $l = 1.33 \text{ \AA} = 1.33 \times 10^{-10} \text{ m}$ ($\lambda_{\text{max}} = 19.75 \text{ nm}$); NB: $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$.
- ❖ 1, 3-Butadiene: $l = 2(1.33) + 1(1.54) = 4.2 \text{ \AA} = 4.2 \times 10^{-10} \text{ m}$ ($\lambda_{\text{max}} = 117 \text{ nm}$).
- ❖ 1, 3, 5-Hexatriene (Three double bonds): $l = 3(1.33) + 2(1.54) = 7.07 \text{ \AA} = 7.07 \times 10^{-10} \text{ m}$ ($\lambda_{\text{max}} = 237.6 \text{ nm}$). Transition $3 \rightarrow 4$ (6 MOs)
- ❖ A conjugated olefin with 12 double bonds (Box length, $l = 12$ double bond distances + 11 single bond distances = $12(1.33) + 11(1.54) \text{ \AA} = 32.9 \text{ \AA} = 32.9 \times 10^{-10} \text{ m}$; ($\lambda_{\text{max}} = 1427 \text{ nm}$). Transition $n : 12 \rightarrow 13$ (12 MOs)
- ❖ The absorption increases to visible region making the compound **colored**.
- ❖ There could be an outer distribution of electron density little away from the extreme carbons - **Tunneling effect**.
- ❖ The bond angles are 120° . Hence, the **zig-zag orientation** and further twisting due to C-C free rotations (**conformations**) will make the length of the molecule shorter.