$\boxed{\text{FREE PARTICLE}}$

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

FOR A FREE PARTICLE $V(x) = 0$

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

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi$$

$$\Rightarrow \quad \frac{d^2\Psi}{dx^2} = -\frac{2mE}{\hbar^2}\Psi$$

$$k^2 \equiv \frac{2mE}{\hbar^2}$$

$$\Psi^+(x) = A^+ e^{ikx}$$

$$\Psi^-(x) = A^- e^{-ikx}$$

$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2mE}{\hbar^2}}$$

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

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

$$\boxed{kh = 2\pi p} = 2\pi \frac{h}{\lambda}$$

$$\boxed{k = \frac{2\pi}{\lambda}}$$

$$\boxed{\hbar k = p}$$

$$|\Psi^+|^2 = |A^+|^2 = \text{CONSTANT}$$

IN 1-D

$$\int_{-\infty}^{\infty} |\Psi^+|^2 dx = \rightarrow \infty \, !$$

PICK A VERY LARGE BOX

$$\int_{-L}^{L} |\Psi^+|^2 dx = 2L\,|A^+|^2$$

PICK $\boxed{A^+ = \frac{1}{\sqrt{2L}}}$

$$P(x)dx = \frac{|A^+|^2 dx}{\int_{-L}^{L} |\Psi^+|^2 dx} = \frac{dx}{2L}$$

$$\xrightarrow[L \to \infty]{} 0$$

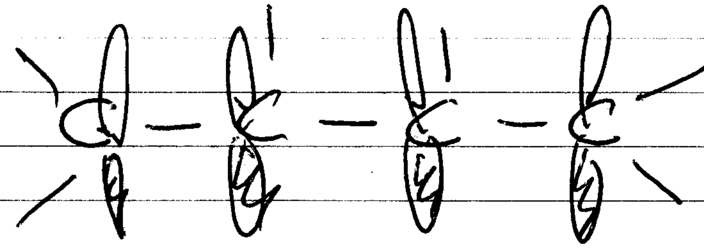
WE REALLY DO NOT KNOW WHERE IS THE PARTICLE BUT WE KNOW THE MOMENTUM

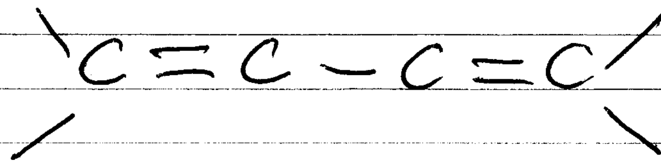
$$p = \hbar k$$

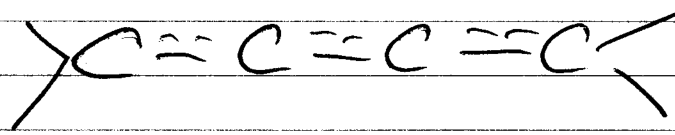
$$\hat{p} = -\frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\hat{p}\Psi^{+} = -\frac{\hbar}{i}\frac{\partial}{\partial x} A^{+} e^{-ikx}$$

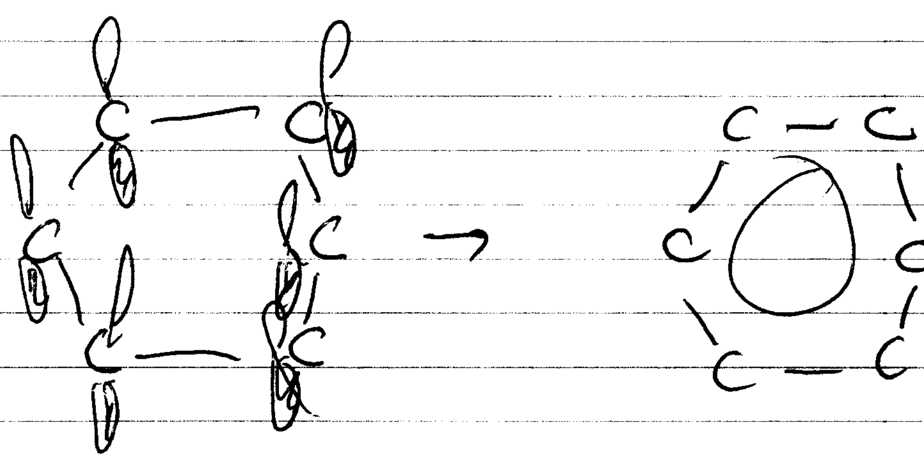
$$\boxed{\hat{p}\Psi^{+} = \hbar k \Psi^{+}}$$







DELOCALIZED e^-



PARTICLE IN BOX

BUTADIENE $H_2C=CH-CH=CH_2$

$$>C=C-C=C<$$

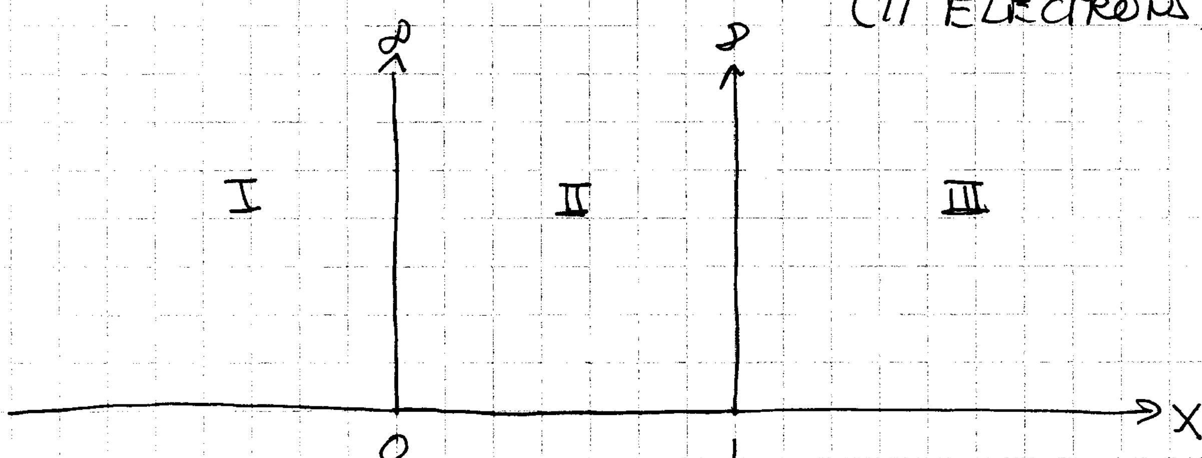
APPROXIMATE AS A 1D-BOX FOR π ELECTRONS

$$C-C \sim 154\,pm$$

$$C=C \sim 135\,pm$$

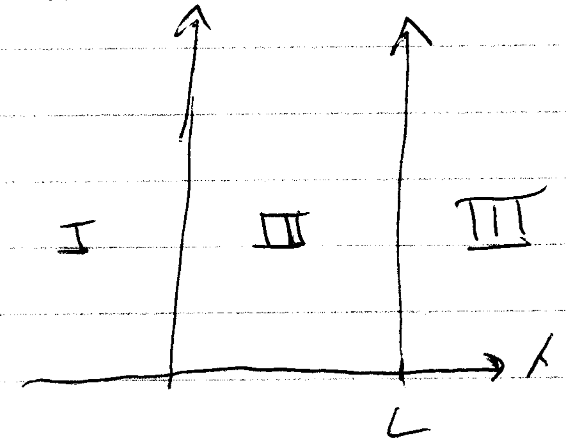
$$>C \sim 77\,pm$$

PARTICLE BOX — ELECTRONS CONSTRAINED TO A MOLECULE (π ELECTRONS)



PARTICLE IN A BOX

$$V(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < L \\ \infty & x \geq L \end{cases}$$



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

THREE REGIONS

I.- $\Psi_I(x) = 0 \qquad x \leq 0$

II.- $-\frac{\hbar^2}{2m}\frac{d^2\Psi_{II}}{dx^2} = E\,\Psi_{II}(x) \qquad 0 < x < L$

III.- $\Psi_{III}(x) = 0 \qquad x \geq L$

$$\frac{d^2\Psi_{II}}{dx^2} = -\left(\frac{2mE}{\hbar^2}\right)\Psi_{II}$$

$x = LX \qquad X \in \langle 0, 1 \rangle$ MEASURE DISTANCE IN UNITS OF L

$dx = L\,dX$

$$\frac{1}{L^2}\frac{d^2\Psi(X)}{d^2X} = \frac{d^2\Psi(x)}{dx^2}$$

$$= -\frac{E\pi^2}{\frac{h^2}{8M}}\Psi(X)$$

$$\frac{d^2\Psi(X)}{dX^2} = -\mathcal{E}\pi^2\Psi(X)$$

$$\boxed{\mathcal{E} = \frac{E}{\frac{h^2}{8ML^2}}} \qquad k \equiv \sqrt{\mathcal{E}}$$

$$\frac{d^2\Psi(X)}{dX^2} = -(k\pi)^2\Psi(X)$$

$$\Psi_{II}(X) = A\sin(k\pi X) + B\cos(k\pi X)$$

B.C

$$\Psi_{II}(0) = \Psi_{II}(1) = 0$$

THUS $B = 0$; $\cos(k\pi) = 0$

$$k\pi = m\pi \qquad m \in \mathbb{N}$$

$$\boxed{k = m}$$

$$\boxed{\mathcal{E}_m = k^2 = m^2}$$

$$\boxed{E_m = \frac{h^2}{8M}\frac{m^2}{L^2}}$$

$$\boxed{\Psi_{II}(X) = A\sin(m\pi X)} \qquad \left(X = \frac{x}{L}\right)$$

$$X \in \langle 0, 1\rangle$$

$$\int_0^1 A^2 \sin(m\pi X)^2 dX = \frac{A^2}{2} = 1$$

$$\boxed{\Psi_{II}(X) = \sqrt{2}\sin(m\pi X)} \quad X \in \langle 0, 1\rangle$$

$$\Psi_{II}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{m\pi x}{L}\right) \qquad x \in \langle 0, L\rangle$$

$$E_m = \frac{h^2}{8ML^2} m^2$$

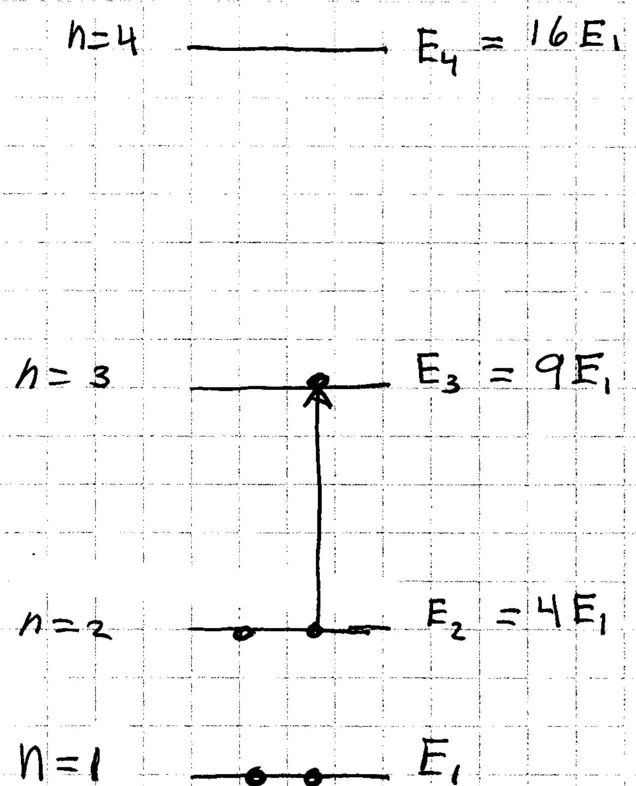
$$E_{m+1} = \frac{h^2}{8ML^2} (m+1)^2$$

$$\Delta E = E_{m+1} - E_m = \frac{h^2}{8ML^2}(2m+1) \xrightarrow[\substack{m \to 0 \\ L \to 0}]{} 0$$

$$u = \frac{h^2}{8ML^2}$$

$$\frac{\Delta E}{E_m} = \frac{2m+1}{m^2} \xrightarrow[m \to \infty]{} 0$$

ENERGY SPECTRUM



$$E_1 = \frac{h^2}{8mL^2}$$

FOR BUTADIENE

4 - π electrons

$$\Delta E_{n\to n+1} = E_{n+1} - E_n$$

$$\boxed{\Delta E_{n\to n+1} = \frac{h^2}{8mL^2}(2n+1)}$$

$$\Delta E_{2\to 3} = \frac{5h^2}{8mL^2} = 9.02 \times 10^{-19}\ J$$

$$\bar{\nu} = \frac{\Delta E}{hc} = 4.54 \times 10^{4}\ cm^{-1}$$

<u>EXP</u> ABSORPTION AT $4.61 \times 10^{4}\ cm^{-1}$