Free particle : $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \longrightarrow \frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}$

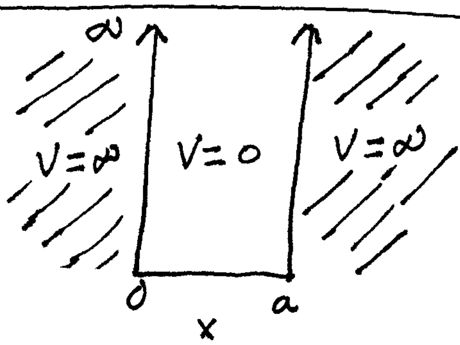
$\psi_+ = A_+ e^{ikx}$ $\qquad\qquad k = \sqrt{2mE/\hbar^2}$

$\psi_- = A_- e^{-ikx}$

Note: x can take on any value, but p_x either $\hbar k$ or $-\hbar k$ (consistent with uncertainty princ.)

$P(x)\,dx = \frac{\psi^*\psi}{\int_{-L}^{L}\psi^*\psi\,dx} = \frac{dx}{2L} \leftarrow$ independent of x.

Particle in the 1-D box



particle cannot escape from the box

Inside the box $\quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$

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

$\psi(0) = 0 = A\sin kx + B\cos kx \Rightarrow B = 0$

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

$\psi(a) = 0 = A\sin ka \Rightarrow \quad ka = n\pi,\ n = 1, 2, 3, \ldots$

$k = \frac{n\pi}{a}$

$\psi(x) = A\sin\frac{n\pi x}{a}$

$\psi(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \leftarrow$ normalized

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{a}\right) = E\sin\left(\frac{n\pi x}{a}\right)$$

$$-\frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}(-1) = E$$

$$E = \frac{n^2\hbar^2\pi^2}{2ma^2} = \frac{n^2h^2}{8ma^2}, \quad n = 1, 2, 3, \ldots$$

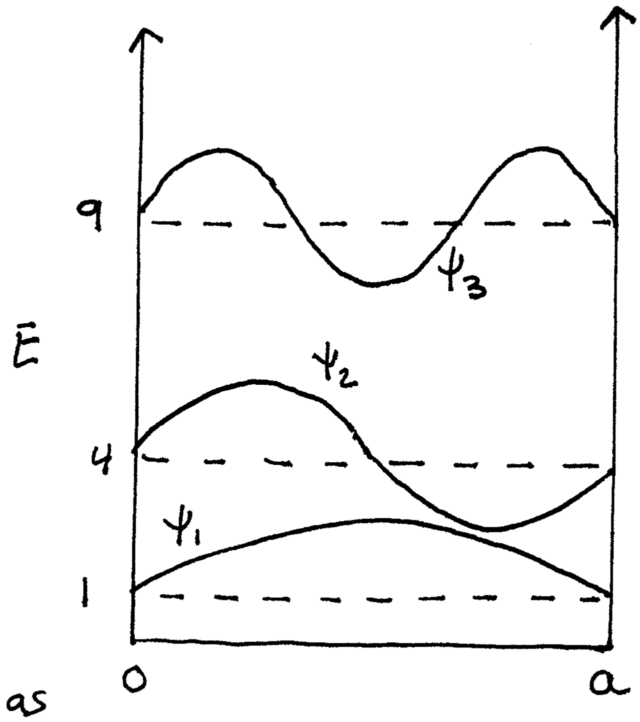
minimum energy $= \frac{h^2}{8ma^2}$ = zero-point energy

uncertainty princ.

Because x is constrained to be between 0 and a the momentum cannot be zero.

$\langle x \rangle = \frac{a}{2}$ for all n.

$\langle p_x \rangle = 0$ for all n.



Energies get closer together as

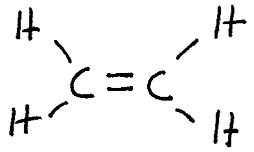
$m \to \infty$

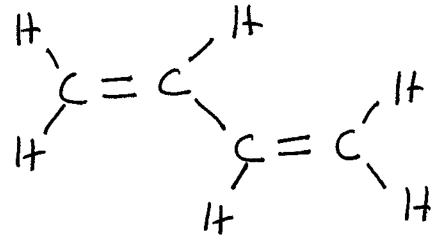
$a \to \infty$

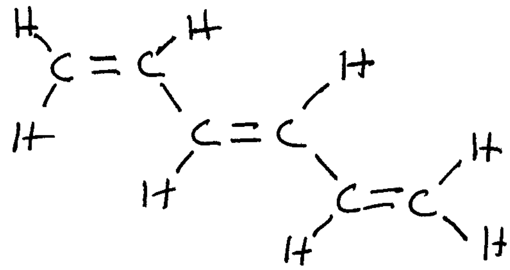
$$\frac{E_{n+1} - E_n}{E_n} = \frac{2n+1}{n^2} \to 0 \text{ as } n \to \infty$$

Spectrum becomes continuous at large n

$$\Delta E_n = E_{n+1} - E_n = \frac{h^2}{8ma^2}(2n+1)$$ ← excitation energy

ethylene  $L \approx 1.5 + 2(.5) = 2.5\,\text{Å}$

butadiene  $L \approx 3(1.5) + 2(.5) = 5.5\,\text{Å}$

hexatriene  $L \approx 5(1.5) + 2(.5) = 8.5$

ethylene:	2 π electrons	ΔE: $n=1 \rightarrow n=2$	$\frac{h^2}{8mL^2} = 15.4\,eV$
butadiene	4 π electrons	ΔE: $n=2 \rightarrow n=3$	$\frac{h^2}{8mL^2} = 3.2\,eV$
hexatriene	6 π electrons	ΔE: $n=3 \rightarrow n=4$	$\frac{h^2}{8mL^2} = 1.3\,eV$

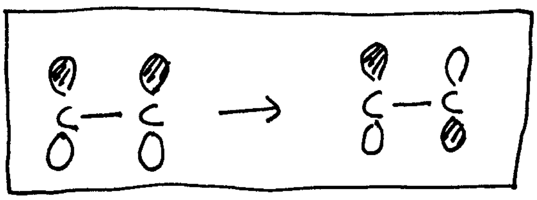
ethylene: $\Delta E = 15.4\,(3) = 46.2\,eV$

butadiene $\Delta E = 3.2\,(5) = 16.0\,eV$

hexatriene $\Delta E = 1.3\,(7)$ $9.1\,eV$

π orbitals

ethylene



butadiene