Chapter 4

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

(V ≡ 0)

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

traveling wave →

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

traveling wave ←

→ $$k = \sqrt{2mE/\hbar^2}$$

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

$$p(x)dx = \frac{\psi^*\psi}{\int_{-L}^{L}\psi^*\psi\, dx} = \frac{dx}{2L}$$

← independent of x.

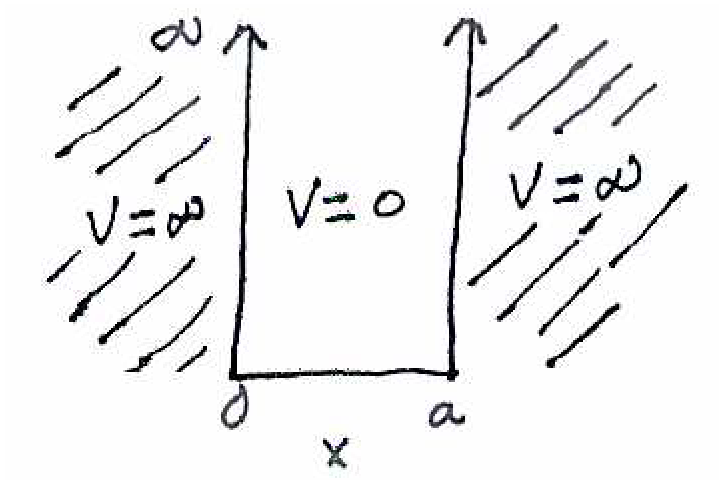
← L → ∞ in the case of a free particle

Equal probability of finding the particle anywhere

Particle the 1-D box

particle cannot escape from the box

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



Wavefunction inside box is of the form:

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

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

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

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

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

Apply Boundary Conditions

$$\psi(0) = \psi(a) = 0$$

$$\psi_n(x) = A\sin\frac{n\pi x}{a} = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$$ ← normalized

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

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

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

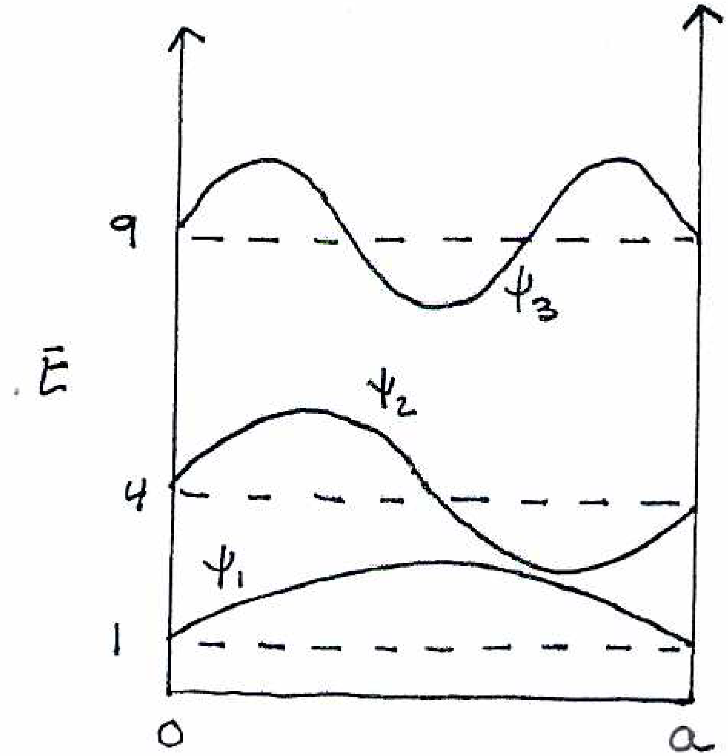
minimum energy = $\dfrac{h^2}{8ma^2}$ = zero-point energy

Consistent with the uncertainty principle.

Because *x* is constrained to be between 0 and a, the momentum cannot be zero. $\Rightarrow$ $E \neq 0$.

$$< x > \; = \; \frac{a}{2} \text{ for all } n.$$

$$< p_x > \; = \; 0 \text{ for all } n.$$



Energies get closer together as

m $\rightarrow \infty$

a $\rightarrow \infty$

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

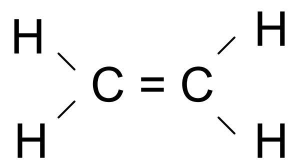
spectrum becomes continuous at large n

Excitation energy

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

Can use as a crude model for understanding the electronic spectra of polyenes.

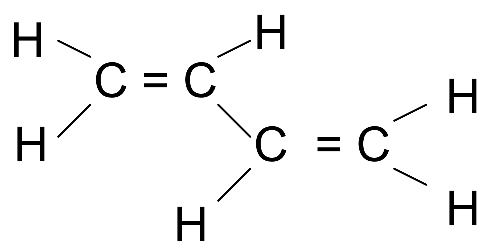
ethylene



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

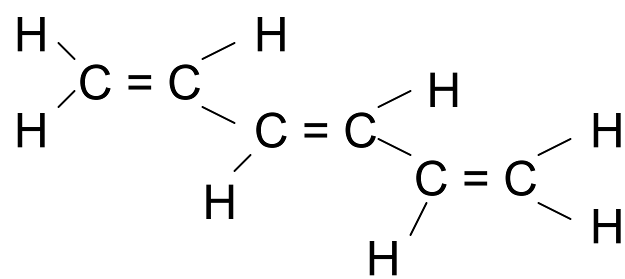
$$(L \equiv a)$$

butadiene



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

hexatriene



$$L \approx 5(1.5) + 2(.5) = 8.5 \text{ Å}$$

ethylene: 2 π electrons ΔE: n = 1 → n = 2 $\quad \dfrac{h^2}{8mL^2} = 15.4 \text{ eV}$

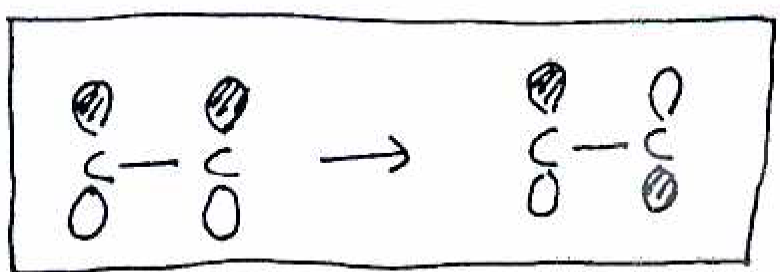
butadiene: 4 π electrons ΔE: n = 2 → n = 3 $\quad \dfrac{h^2}{8mL^2} = 3.2 \text{ eV}$

hexatriene: 6 π electrons ΔE: n = 3 → n = 4 $\quad \dfrac{h^2}{8mL^2} = 1.3 \text{ eV}$

UV
3.1 eV (400 nm)
violet

red
1.8 eV (700 nm)
IR

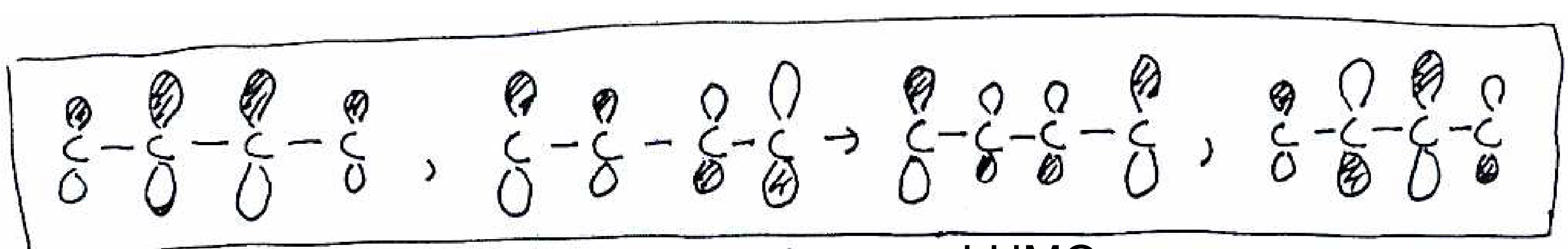
π orbitals



HOMO LUMO

ethylene

butadiene



HOMO LUMO