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)

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

← independent of x.

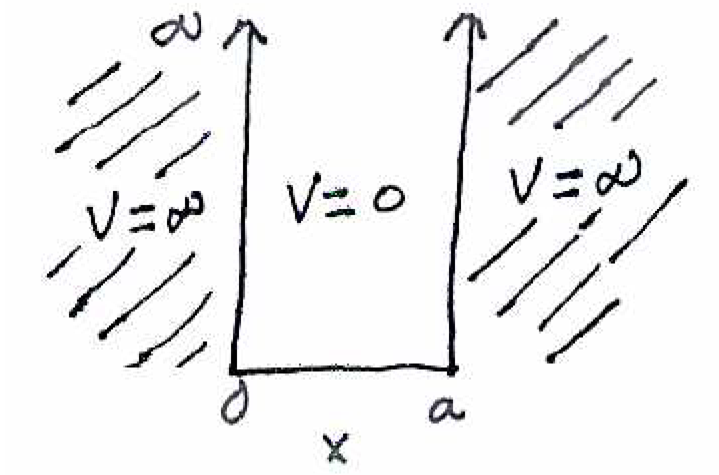
← L → ∞ in the case of a free particle

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:

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

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

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

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

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

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

Apply Boundary Conditions

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

These are also orthogonal functions. How would you show this?

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

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

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

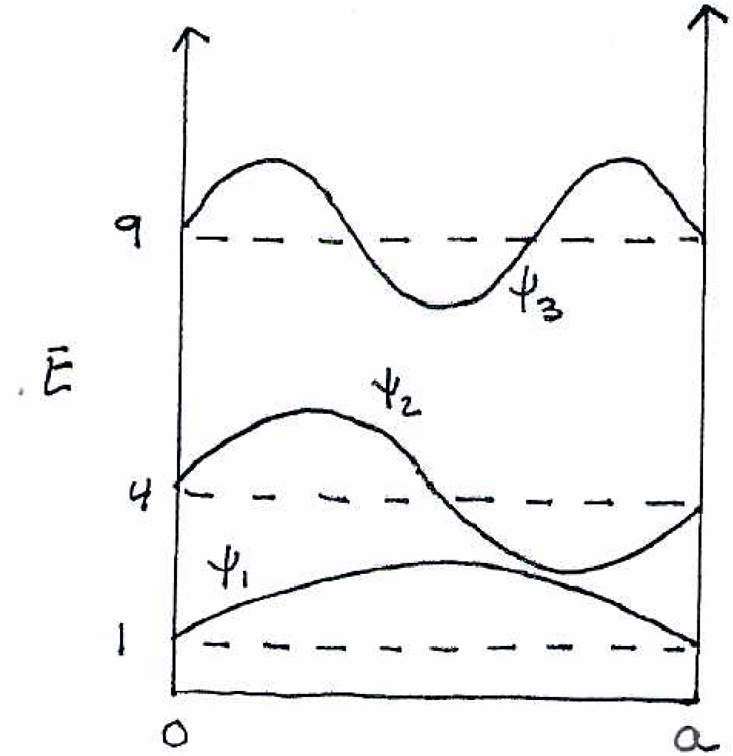
minimum energy = $\frac{h^2}{8ma^2}$ = zero-point energy

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 essentially becomes continuous at large n

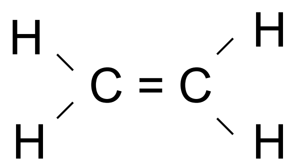
Excitation energy

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

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

Here we are assuming that only the pi electrons are important. Recall that these are perpendicular to the plane of the molecule with each C atom contributing one electron in a p orbital. (See next page)

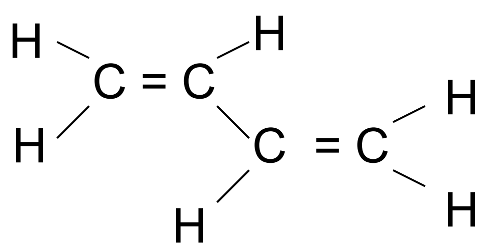
ethylene



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

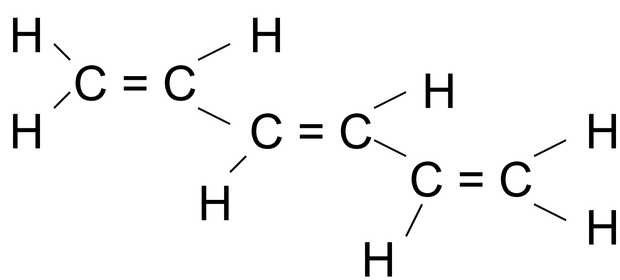
$$(L \equiv a)$$

butadiene



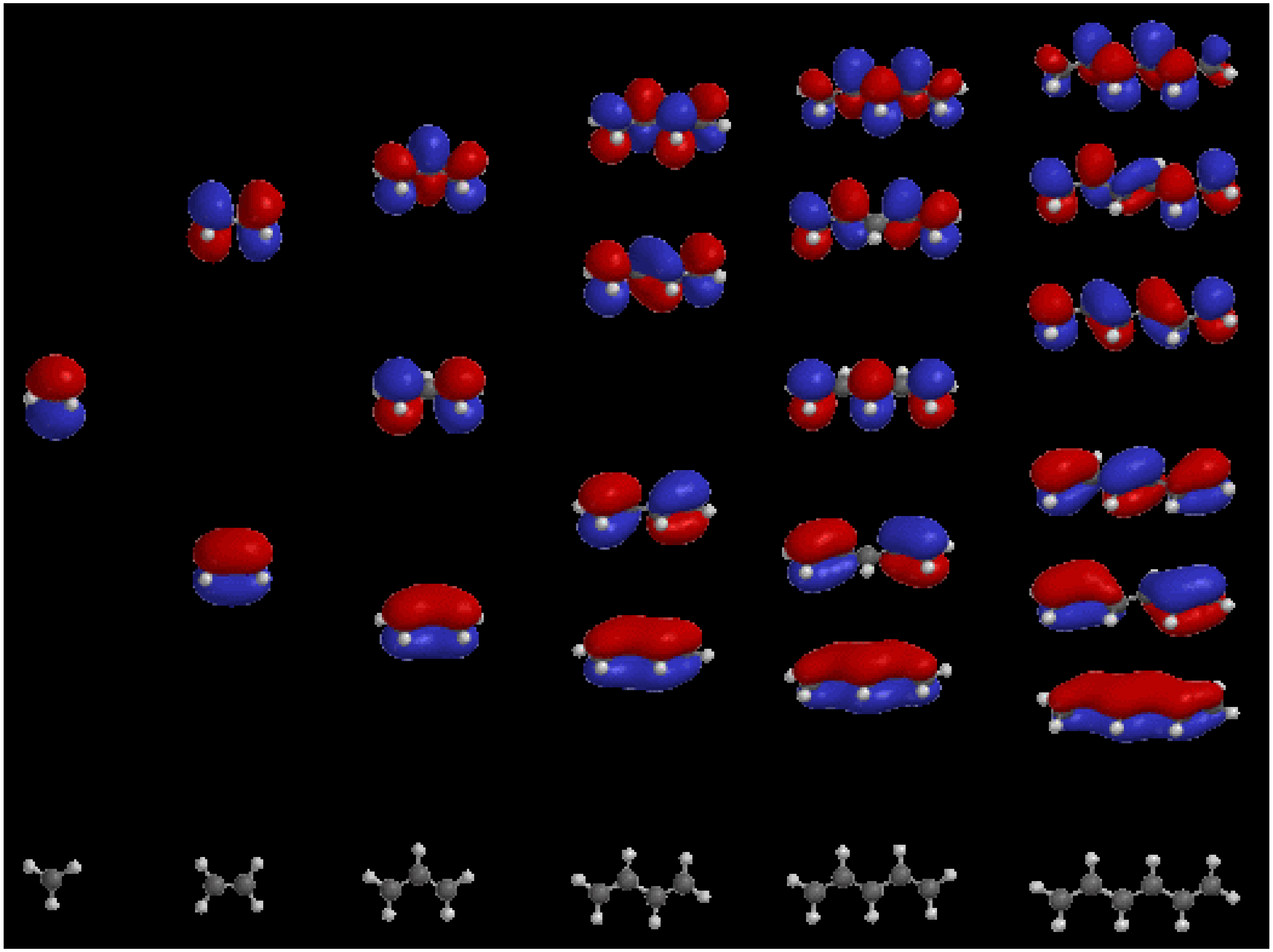
$$L \approx 3(1.5) + 2(.5) = 5.5\text{Å}$$

hexatriene



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

pi and pi* orbitals of polyenes



LUMO

HOMO

Picture from courses-chem.psu.edu/chem210 ethylene: 2 π electrons ΔE: n = 1 → n = 2

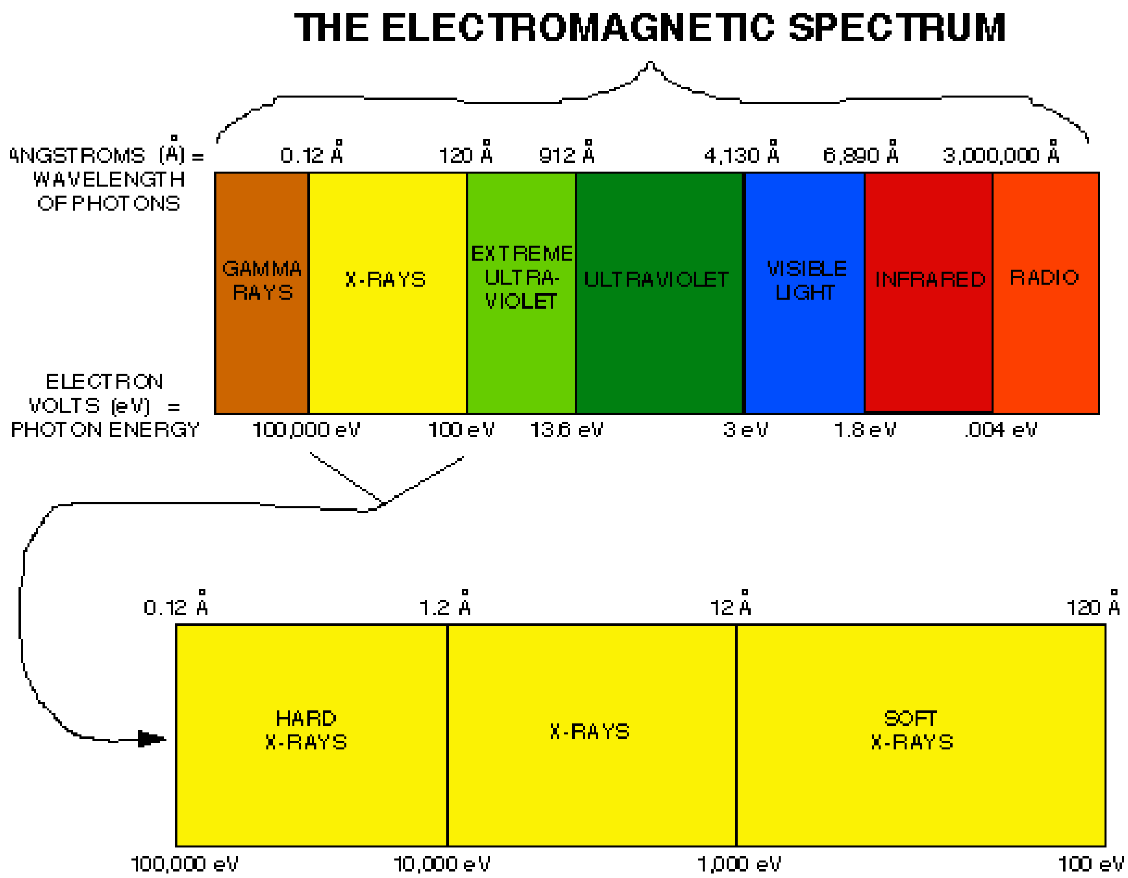
butadiene: 4 π electrons ΔE: n = 2 → n = 3

hexatriene: 6 π electrons ΔE: n = 3 → n = 4

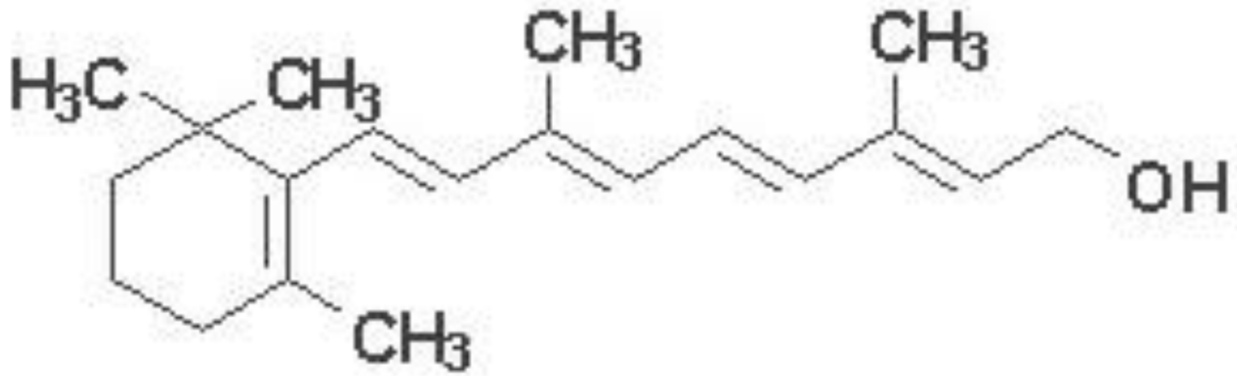
$$\frac{3h^2}{8mL^2} \approx 16\text{eV}$$

$$\frac{5h^2}{8mL^2} \approx 8\text{ eV}$$

$$\frac{7h^2}{8mL^2} \approx 6\text{ eV}$$



Qualitative agreement with expt., but predicts excitation energies somewhat too high for these three molecules.



Retinol (Vitamin A)

The related molecule, retinal, is the key to vision. Its absorption is in the yellow.