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.

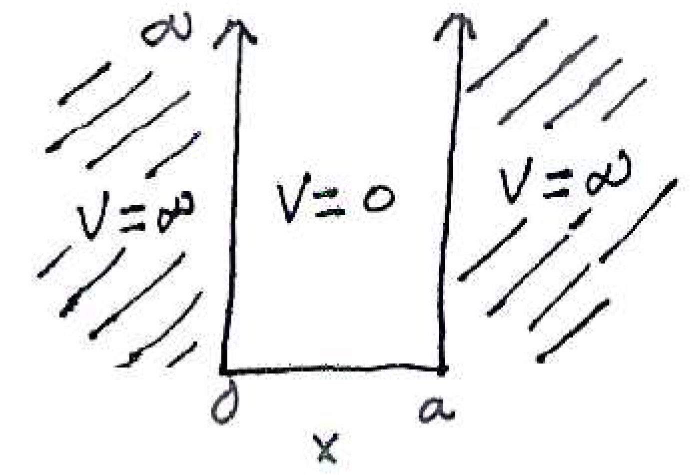
← L → ∞ in the case of a free particle

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?

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

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

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

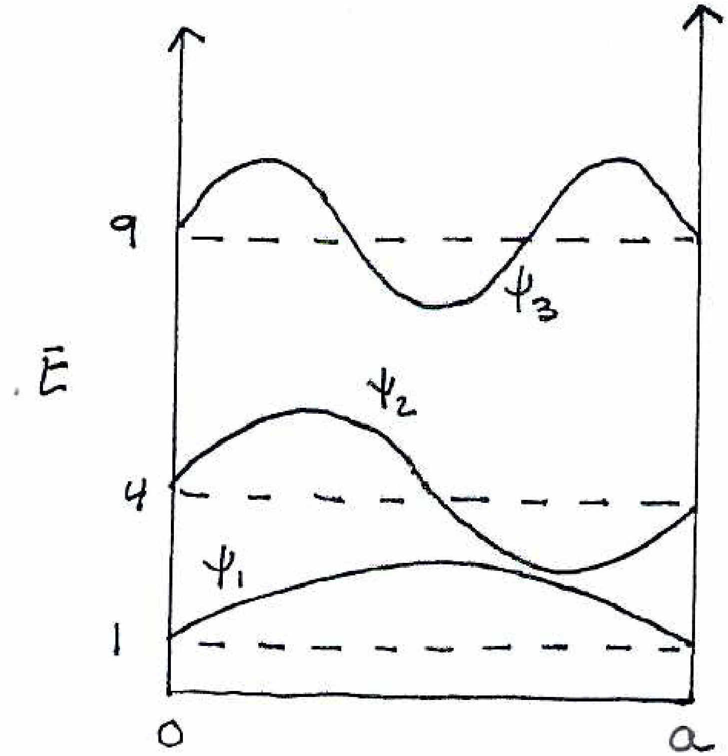
minimum energy = $\frac{h^2}{8ma^2}$ = zero-point energy

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

$m \to \infty$

$a \to \infty$

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

spectrum essentially becomes continuous at large n

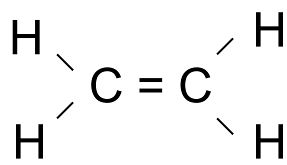
Excitation energy

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

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)

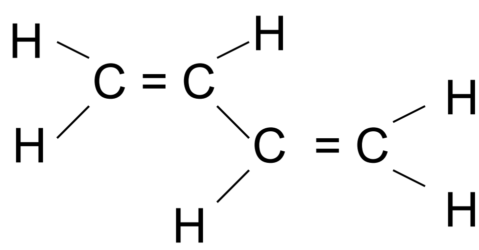
ethylene



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

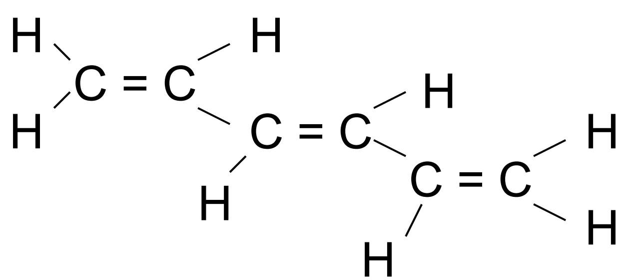
$$(L \equiv a)$$

butadiene



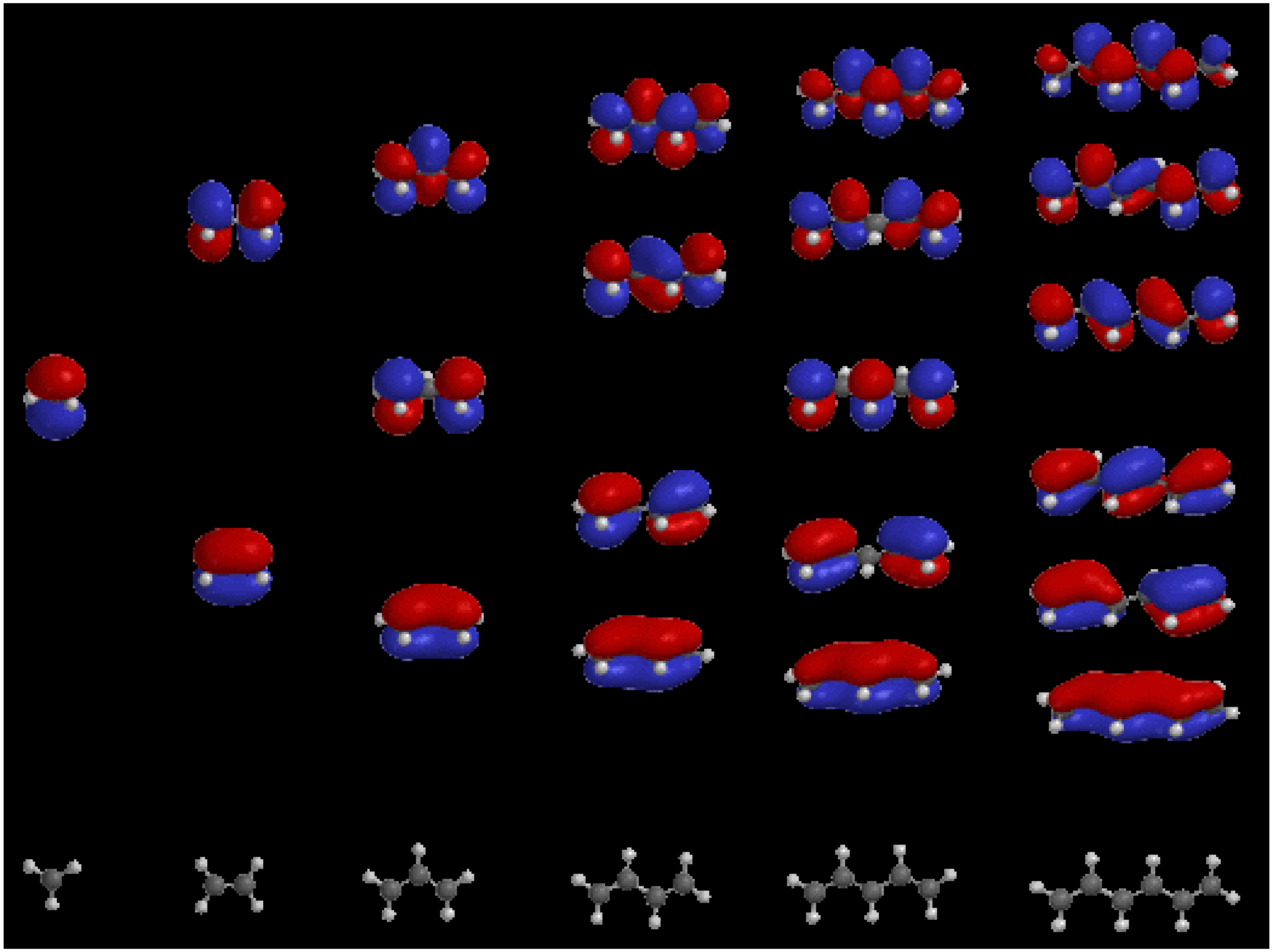
$$L \approx 3(1.5) + 2(.5) = 5.5\text{Å}$$

hexatriene



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

pi and pi* orbitals of polyenes



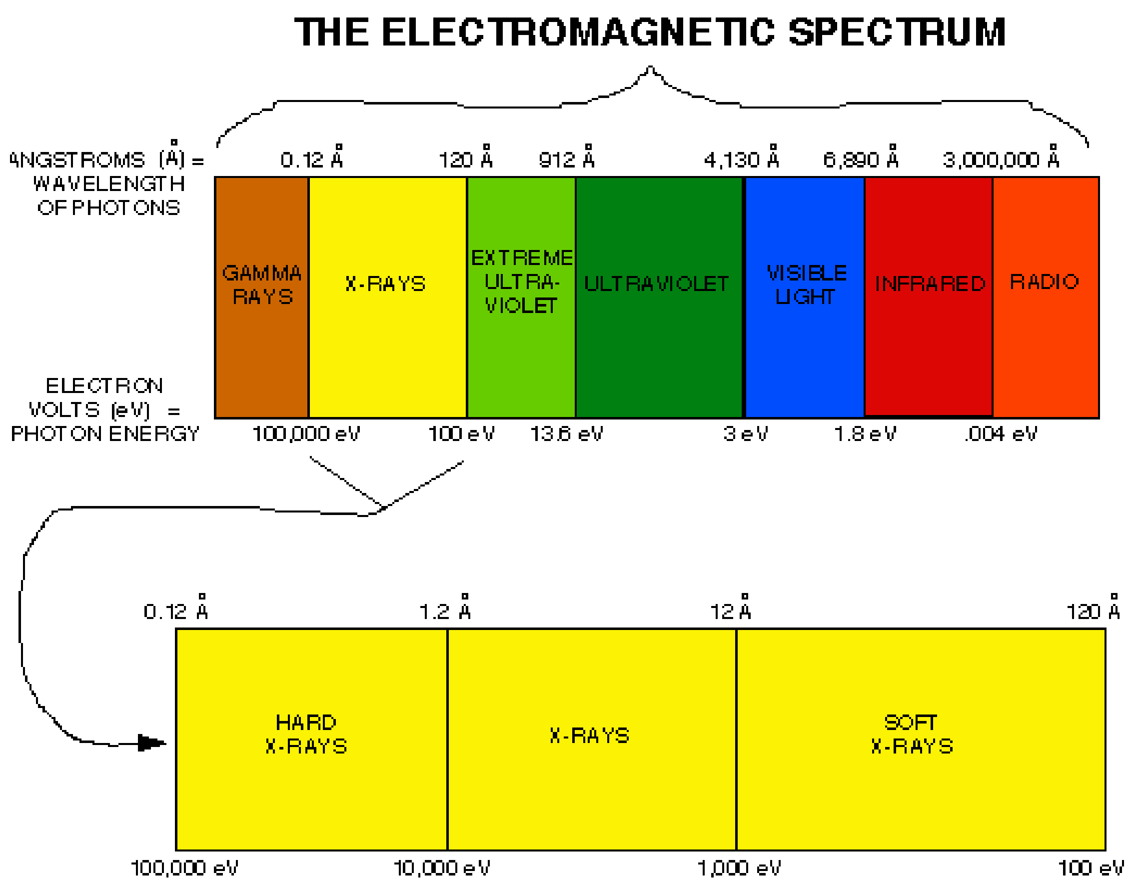
LUMO

HOMO

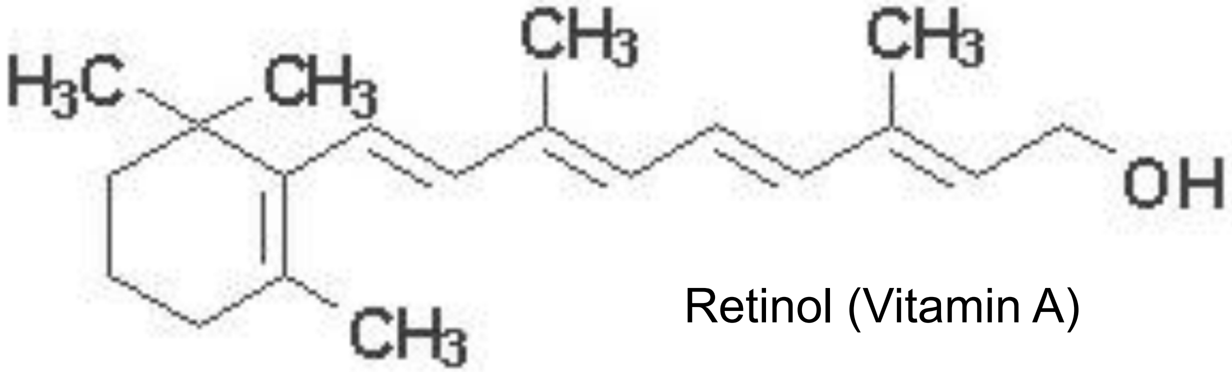
Picture from courses-chem.psu.edu/chem210 ethylene: 2 π electrons ΔE: n = 1 → n = 2 — $\frac{h^2}{8mL^2} \approx 16\ \text{eV}$ — UV

butadiene: 4 π electrons ΔE: n = 2 → n = 3 — $\frac{h^2}{8mL^2} \approx 8\ \text{eV}$

hexatriene: 6 π electrons ΔE: n = 3 → n = 4 — $\frac{h^2}{8mL^2} \approx 6\ \text{eV}$ — red

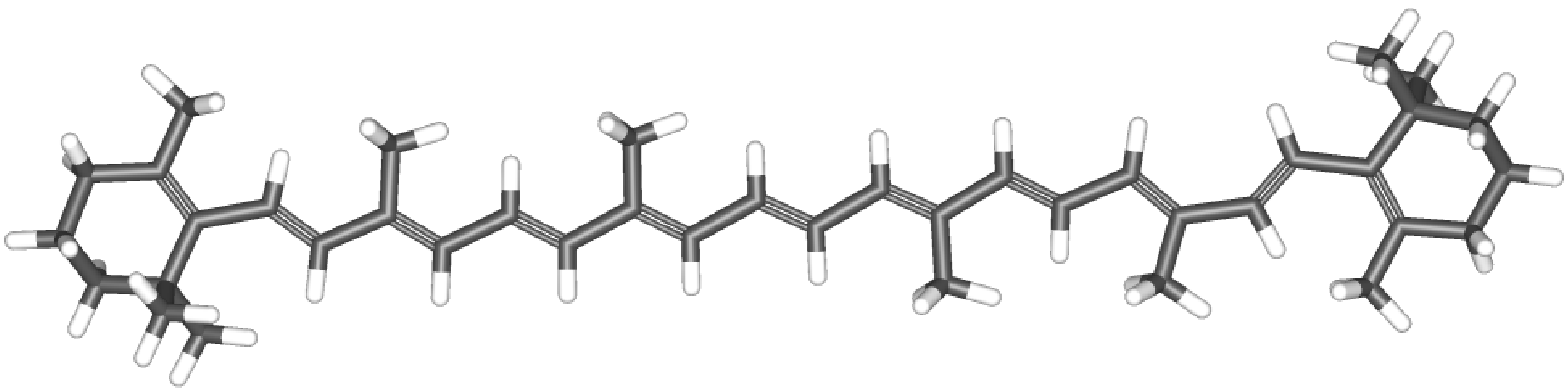


Qualitative agreement with expt., but predicts too rapid a fall off in the adsorption energy with increasing chain length.



Retinol (Vitamin A)

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



Carotene (structure from Wikipedia): absorb UV, violet blue, so appear orange/red

De Broglie (from Wikipedia)
His 1924 thesis *Recherches sur la théorie des quanta* (Research on the Theory of the Quanta) introduced his theory of electron waves. This included the wave–particle duality theory of matter, based on the work of Max Planck and Albert Einstein on light. This research culminated in the de Broglie hypothesis stating that *any moving particle or object had an associated wave*.

Heisenberg (from Wikipedia)

From September 1924 to May 1925, Heisenberg went to do research with Niels Bohr, director of the Institute of Theoretical Physics at the University of Copenhagen. His seminal paper, *Über quantentheoretischer Umdeutung* was published in September 1925.[18] He returned to Göttingen and with Max Born and Pascual Jordan, over a period of about six months, developed the matrix mechanics formulation of quantum mechanics. On 1 May 1926, Heisenberg began his appointment as a university lecturer and assistant to Bohr in Copenhagen. It was in Copenhagen, in 1927, that Heisenberg developed his uncertainty principle, while working on the mathematical foundations of quantum mechanics.

Dirac (from Wikpedia)
After reading the 1925 Heisenberg paper, he quickly developed a quantum theory that was based on non-commuting dynamical variables. This led him to a more profound and significant general formulation of quantum mechanics than was achieved by any other worker in this field.

Creation of wave mechanics (from Wikipedia)

In January 1926, Schrödinger published in *Annalen der Physik* the paper Quantization as an Eigenvalue Problem] on wave mechanics and presented what is now known as the Schrödinger equation. In this paper, he gave a "derivation" of the wave equation for time-independent systems and showed that it gave the correct energy eigenvalues for a hydrogen-like atom. This paper has been universally celebrated as one of the most important achievements of the twentieth century and created a revolution in all physics and chemistry. A second paper was submitted just four weeks later that solved the quantum harmonic oscillator, rigid rotor, and diatomic molecule problems and gave a new derivation of the Schrödinger equation. A third paper, published in May, showed the equivalence of his approach to that of Heisenberg and gave the treatment of the Stark effect. A fourth paper in this series showed how to treat problems in which the system changes with time, as in scattering problems. In this paper he introduced a complex solution to the Wave equation.These papers were his central achievement and were at once recognized as having great significance by the physics community.

Schrödinger was not entirely comfortable with the implications of quantum theory. Schrödinger wrote about the probability interpretation of quantum mechanics, saying: "I don't like it, and I'm sorry I ever had anything to do with it."[24]