Chapter 2

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 ←

$$\longrightarrow k = \sqrt{2mE/\hbar^2}$$

$$e^{\pm ikx} = \cos kx \pm i \sin kx$$

$$\left| e^{\pm ikx} \right| = 1$$

$$p = k\hbar, \quad \lambda = 2\pi / k$$

$$p = \frac{h}{\lambda}$$

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

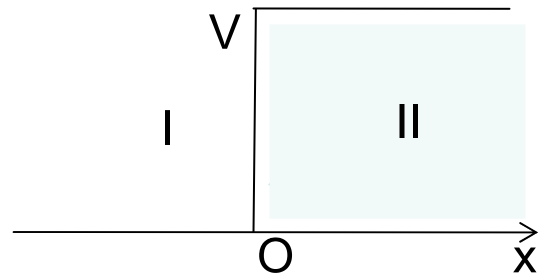
$$p(x)dx = \frac{\psi^*\psi}{\int_{-L}^{L}\psi^*\psi dx} = \frac{dx}{2L}$$

← independent of x.

← L → ∞ in the case of a free particle

Equal probability of finding the particle anywhere

Particle incident on a step potential



$$I \qquad \psi_I = Ae^{ikx} + Be^{-ikx}$$

$$k = \sqrt{2mE/\hbar^2}$$

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

$$II \qquad \psi_{II} = Ce^{ik'x} + De^{-ik'x}$$

$$k' = \sqrt{2m(E-V)/\hbar^2}$$

$$H_{II} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V$$

$$E < V$$

$$k' = i\kappa \quad (\kappa \text{ real})$$

$$\psi_{II} = Ce^{-\kappa x} + De^{\kappa x}$$

For proper wavefunction, D = 0

ψ exponentially decaying in region II

$$\psi_I(0) = \psi_{II}(0) \Rightarrow A + B = C$$

$$\psi'_I(0) = \psi'_{II}(0) \Rightarrow Aik - Bik = -Ck$$

If $E > V$

Transmission, T = $\dfrac{\text{\# particles transmitted}}{\text{\# particles incident}}$

Reflection, R = $\dfrac{\text{\# particles reflected}}{\text{\# particles incident}}$

$$R + T = 1$$

$$T = \frac{4kk'}{\left(k + k'\right)^2} = \frac{|C|^2}{|A|^2}\frac{k'}{k}$$

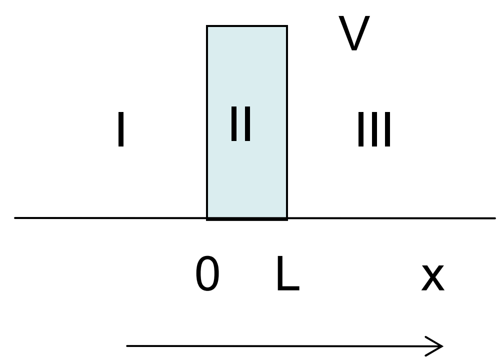
$$R = 1 - \frac{4kk'}{\left(k + k'\right)^2} = \frac{|B|^2}{|A|^2}$$

Barrier of finite width

$$\psi_I = Ae^{ikx} + Be^{-ikx}, \qquad k\hbar = \sqrt{2mE}$$

$$\psi_{II} = A'e^{i'x} + B'e^{-ik'x}, \qquad k'h = \sqrt{2m(E-V)}$$

$$\psi_{III} = A''e^{ik''x} + B''e^{-ik''x}, \quad k''\hbar = \sqrt{2mE}$$

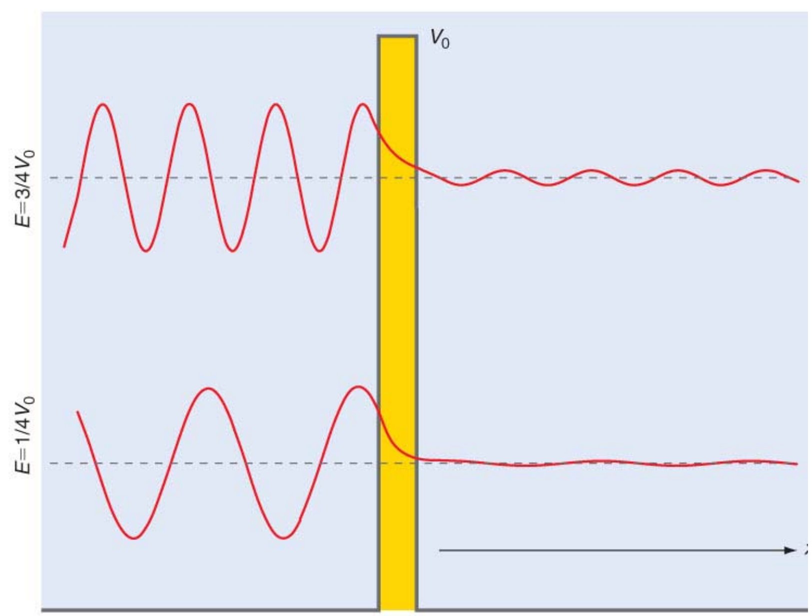


E < *V*, assume particle incident from left

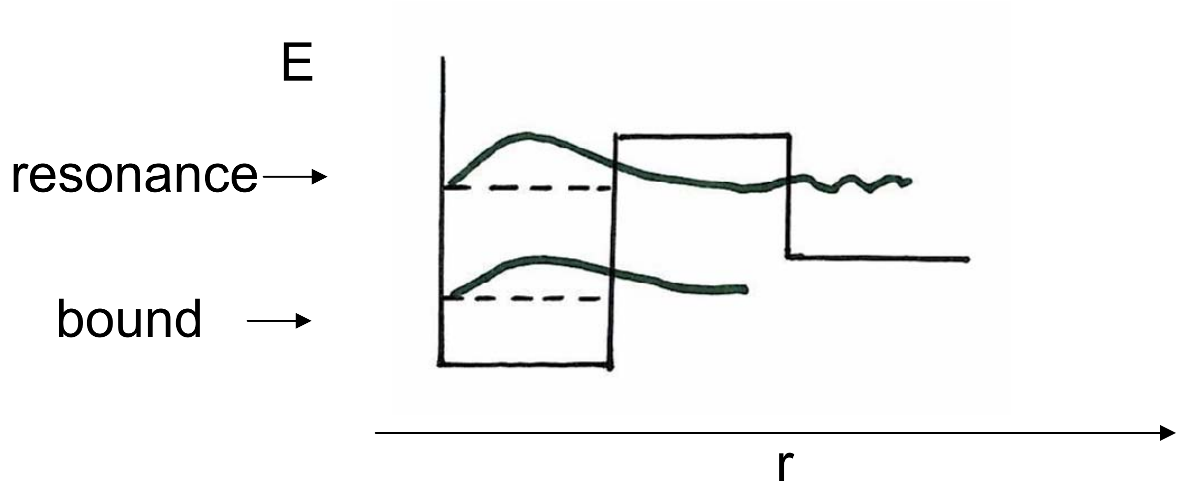
$$R = \frac{|B|^2}{|A|^2}, \quad T = \frac{|A''|^2}{|A|^2} = \frac{1}{1+\left(e^{\kappa L}-e^{-\kappa l}\right)\Big/\left[16\frac{E}{V}\left(1-\frac{E}{V}\right)\right]}$$

$$E << V \quad T \sim \frac{1}{1+\dfrac{e^{\kappa L}-e^{-\kappa L}}{16}} \qquad k' = i\kappa$$

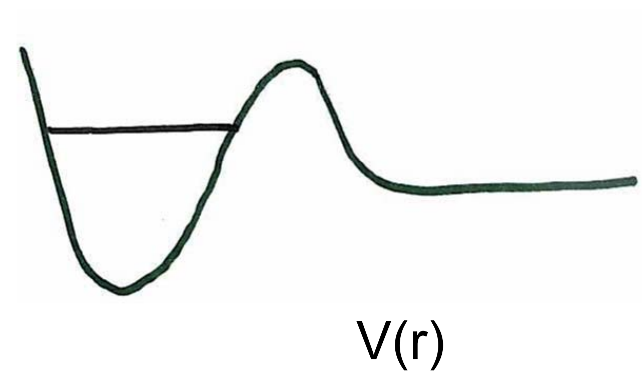
$$T \sim e^{-2L\sqrt{2m(V_o - E)/\hbar^2}}$$



resonances:
particle can escape by tunneling

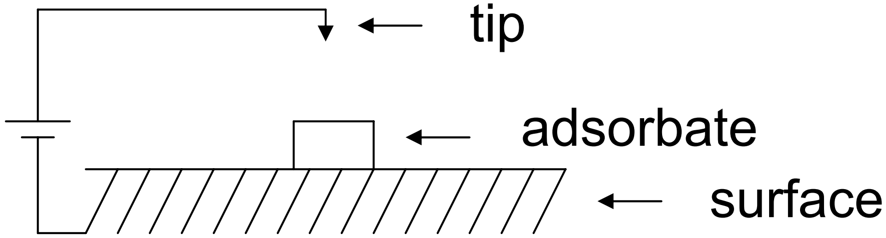


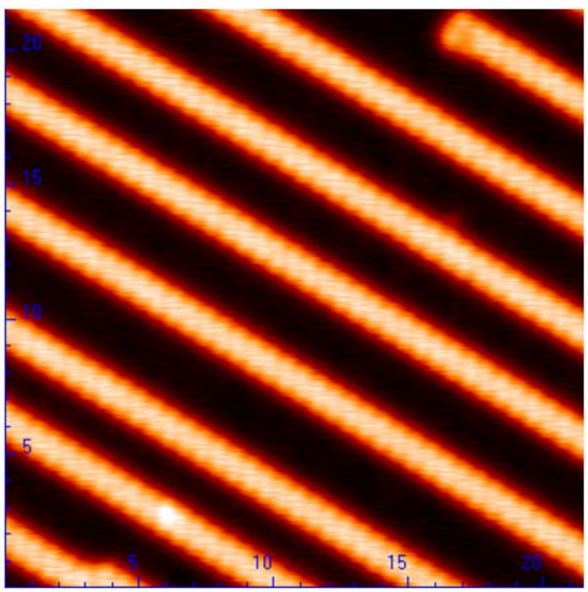
Examples:
- radioactive decay
- temporary anions: Be^-, N_2^-, benzene$^-$ electron falls off in $\approx 10^{-14}$ sec



How can one measure something with such a short lifetime?

Scanning tunneling microscopy (STM) – invented ~20 years ago at IBM Research Labs, Zürich





22 x 22nm^2

Water chains on the Cu(110) surface, from Yates et al.

Apply voltage – measure current

often run so that as the tip is scanned over the surface, the height is varied so as to keep the current constant

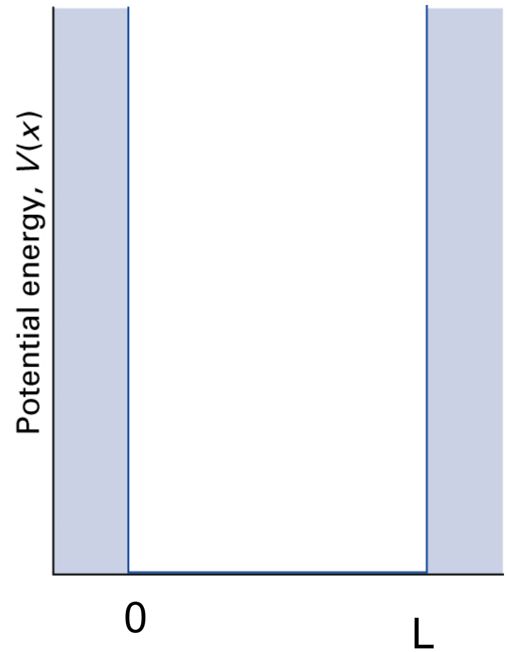
the tip does not actually touch the surface

electrons tunnel between tip and surface

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:

$$\psi(x) = D\sin kx + C\cos kx$$

$$\psi(0) = 0 = D\sin kx + C\cos kx \Rightarrow C = 0$$

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

$$\psi(L) = 0 = D\sin kL \Rightarrow kL = n\pi, \quad n = 1, 2, 3, \ldots$$

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

Apply Boundary Conditions

$$\psi(0) = \psi(L) = 0$$

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

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

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

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

Consistent with the uncertainty principle.

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

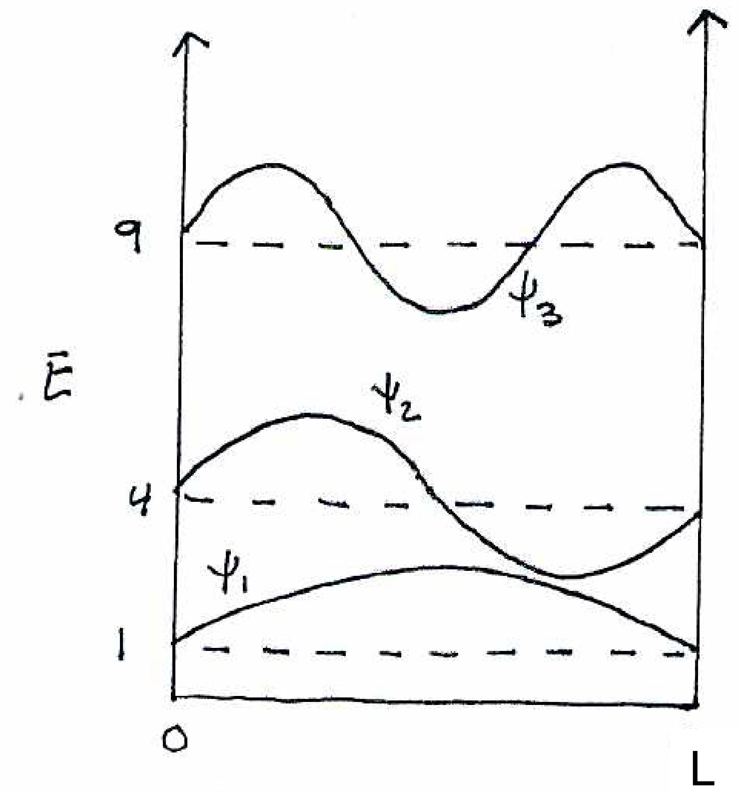
$$< x > \ = \ \frac{L}{2} \text{ for all } n.$$

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

Energies get closer together as

m $\rightarrow \infty$

L $\rightarrow \infty$

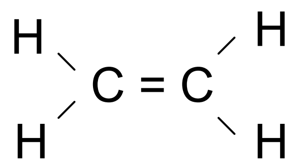


Excitation energy

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

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

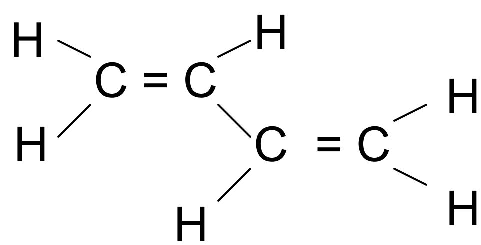
ethylene



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

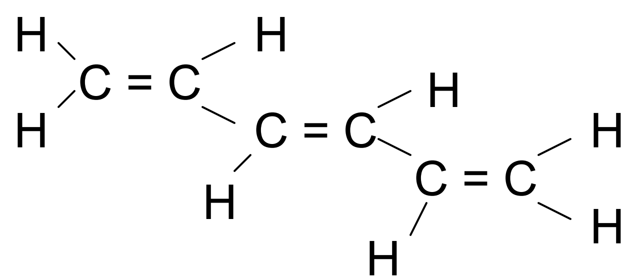
$$(L \equiv a)$$

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 $\frac{h^2}{8mL^2} = 15.4$ eV

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

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

UV

3.1 eV (400 nm)

violet

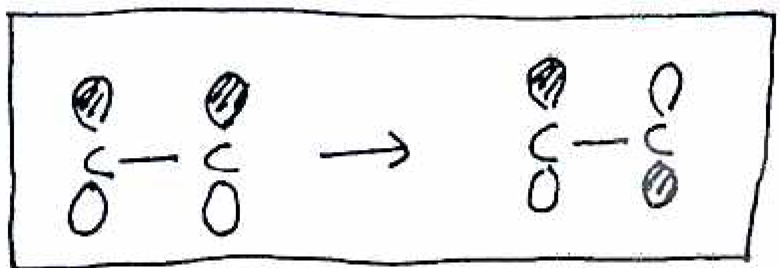
red

1.8 eV (700 nm)

IR

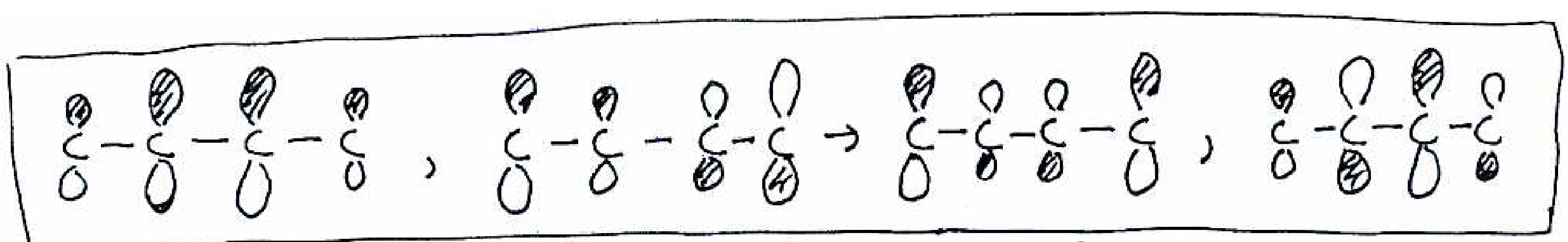
π orbitals

ethylene



HOMO LUMO

butadiene



HOMO LUMO

Particle in a finite box

Finite # of bound levels

Tunneling into classically forbidden regions