Chapter 5. The Particle in the Box and the Real World

Real particles in boxes:

Conjugated molecules with alternating single and double bonds

Butadiene: CH_2=CH-CH=CH_2

The π electrons are delocalized, excitation energy:

$$\Delta E_{2\to 3} = \frac{5h^2}{8mL^2} = \frac{5(6.626\times 10^{-34}\,Js)^2}{8(9.1\times 10^{-31}\,kg)(4.5\times 10^{-10}\,m)^2}$$
$$= 1.5\times 10^{-18}\,J$$

$$\nu = \frac{\Delta E}{h} = \frac{1.5\times 10^{-18}\,J}{6.626\times 10^{34}\,Js} = 2.2\times 10^{15}\,Hz$$

$$\lambda = \frac{c}{\nu} = \frac{3.0\times 10^{8}\,m/s}{2.2\times 10^{15}\,s^{-1}} = 133nm$$

If two more bonds are added,

$$\lambda = 369nm$$

Change of size increase the wave length of absorption, color change!

Quantum dots ~ 3D boxes.

Finite-depth box

$$V(x) = 0, \quad 0 \le x \le L$$
$$= V_0, \quad x < 0, and \ x > L$$

Schrodinger equations

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \quad \text{inside the well}$$

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi(x) \quad \text{outside the well}$$

Solutions

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \qquad k = \sqrt{2mE}/\hbar$$

$$\psi(x) = A'e^{\kappa x} + B'e^{-\kappa x}, \qquad \kappa = \sqrt{2m(V_0 - E)}/\hbar$$

By imposing continuity at the boundaries, the solutions become

Probabilities in classically forbidden region.

Tunneling: Due its wave nature, a quantum particle can penetrate a potential barrier and enter into a classically forbidden region (quantum effect).

Scattering of a quantum particle by a square barrier.

An incoming wave is split into transmission and reflection waves. The transmission probability is given

$$T = \left\{ 1 + \frac{\left(e^{\kappa L} - e^{-\kappa L}\right)^2}{16\varepsilon(1-\varepsilon)} \right\}^{-1}$$

with

$$\varepsilon = \frac{E}{V_0}, \qquad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

Tunneling depends on mass ($\propto e^{-\sqrt{m}}$) and barrier width ($\propto e^{-L}$), a smaller mass and narrow barrier aid tunneling.

App: kinetic isotope effects

App: scanning tunneling microscopy (STM)