Particle in finite depth box: a more realistic model for confinement

Potential defined by:

\[ V(x) = 0, \quad a/2 > x > -a/2 \]
\[ V(x) = V_0, \quad x \geq a/2, \quad x \leq -a/2 \]
\( \psi(x) \) different inside and outside box

- **Inside box** \( \frac{d^2 \psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x) \)
- **Outside box** \( \frac{d^2 \psi(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2} \psi(x) \)

\[ \psi(x) = A e^{-\kappa x} + B e^{+\kappa x} \quad \text{for } x \geq \frac{a}{2} \]

\[ \psi(x) = A' e^{-\kappa x} + B' e^{+\kappa x} \quad \text{for } x \leq -\frac{a}{2} \]

where \( \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \)

The total energy of the particle (E) must be the same everywhere (i.e. inside and outside the box).
Characteristics of EF of $\hat{H}$

- Inside box, similar to infinite box
- Add $\sim 1/2$ wavelength as increase $n$
- Outside box, $\psi(x)$ decays exponentially. Boundary conditions make $B = A` = 0$
- Finite number of bound states $\geq 0$
- $\psi(x)$ decays most rapidly for energy eigenvalues near bottom of box
Decay of $\psi(x)$ outside box

Note dependence on $n$

$$\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$
Model atoms in molecule by finite depth box

Only valence electrons overlap, allowing bond formation.
Model $\pi$-network in hexatriene using PIB model

Use the aufbau principle with the levels. Two electrons per level.

$\Delta E = E_4 - E_3 = h\nu$

### 6 $\pi$ electrons

\[ a = \sqrt{\frac{(n_f^2 - n_i^2)\hbar^2}{8m\Delta E}} = \sqrt{\frac{(n_f^2 - n_i^2)\hbar\lambda_{max}}{8mc}} \]

\[ a = \sqrt{\frac{(4^2 - 3^2) \times 6.626 \times 10^{-34} \text{Js} \times 375 \times 10^{-9} \text{m}}{8 \times 9.11 \times 10^{-31} \text{kg} \times 2.998 \times 10^8 \text{ms}^{-1}}} \]

\[ a = 892 \text{pm} \]

Calculated network length = 973 pm
Excited state populated at 298K?

\[ \Delta E \text{ given by} \]
\[ \Delta E = \frac{h^2 (n_f^2 - n_i^2)}{8ma^2} = \frac{7 \times (6.626 \times 10^{-34} \, \text{J} \, \text{s})^2}{8 \times 9.11 \times 10^{-31} \, \text{kg} \times (973 \times 10^{-12} \, \text{m})^2} \]
\[ = 4.45 \times 10^{-19} \, \text{J} \]

\[ \frac{n_4}{n_3} = \frac{g_4}{g_3} e^{-\Delta E/kT} = e^{-\frac{4.45 \times 10^{-19} \, \text{J}}{1.38 \times 10^{-23} \, \text{J} \, \text{K}^{-1} \times 300 \, \text{K}}} = 2.1 \times 10^{-47} \]
Classical physics can’t explain electrical conduction

Use “Coulomb box” for two Na atoms
Periodic array of Na atoms is 1-D wire

Looks like PIB for valence electrons
Metal in PIB model

Critical for conduction that band only partially filled.

\[ \phi \]

\[ a \]

\[ + \]

\[ b \]

\[ + \]

\[ c \]
Insulator in PIB model

For insulator, band completely filled

\[ a \]

\[ b \]

\[ c \]
Tunneling through barriers Demo 16.2

Particles go *through* as well as *over* barriers

\[ E = \frac{3}{4} V_0 \]
\[ E = \frac{1}{4} V_0 \]
Scanning tunneling microscope

Principle behind microscope

\[ \phi_t \quad \phi_s \]

\[ \text{a} \]

\[ \text{b} \]

\[ \text{c} \]
Computer: Scan Generation & Image Display

Electronics: Positioning and Feedback Control. Signal Conditioning

High Voltage Piezo Drive

Tip Bias

Current Collection

i → V conversion

Preamp

Single Tube Piezo

Sample

Probe Tip

Scanning

Sample

Sample (a)

Sample (b)

Sample (c)

Sample (d)

Sample (e)
Titanium dioxide surface
Silicon Single Crystal Surface
Electrical conduction through molecules

Use Atomic Force Microscope for this expt
Tunneling of Carbon in chemical reactions

Even Carbon atoms have been observed to tunnel.
Quantum Dots

Energy levels depend on size of particle; therefore light absorbed or emitted also depends on size.
Internal Illumination of Living Organisms Using Quantum Dots