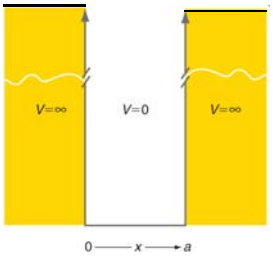
Particle in a Box and the Real World
Chapter 16

The particle in a 1D box system:



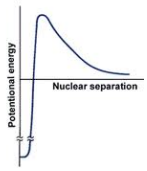
n = 1,2 ,3…∞

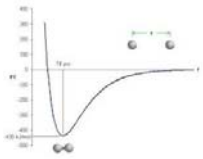
BC: $\psi(0) = 0$ and $\psi(a) = 0$

$$V(x) = 0, \quad \text{for } a \geq x \geq 0$$
$$V(x) = \infty, \quad \text{for } x > a, x < 0$$

The potential energy function of the 1D box is an infinitely deep well. An infinitely 'deep' potential well is only a theoretical construct and do not look like any real system.

Potential energy functions that could have a substantially deep but with a finite depth, are as follows.



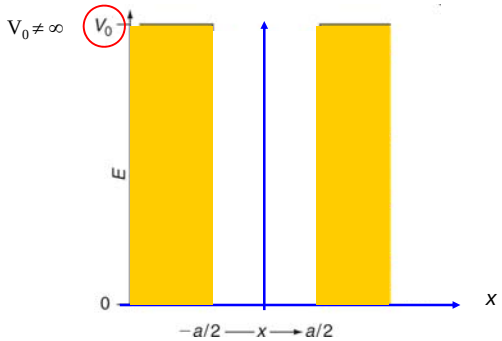


Potential well with an infinitely deep potential well implies the energy barriers are very high and impenetrable.

Impenetrable barrier would mean that the probability of finding the particle outside the 'box' is practically be zero. Thus, the wavefunction itself is zero outside the box, ψ^2 (outside) = 0 .

Any potential barrier that is not infinitely deep could and would have a non-zero probability in the barrier itself. Thus the wavefunction at the potential barrier wall is non-zero, as opposed to an infinitely deep potential well.

The particle in a 1D box system of finite potential energy:



$$V(x) = 0, \quad \text{for } -a/2 \leq x \leq a/2$$
$$V(x) = V_0, \quad \text{for } x > a/2, x < -a/2$$

Schrodinger Equation

$$\hat{H}\psi(x) = E\psi(x)$$
$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\psi(x)$$
$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = (E - V(x))\psi(x)$$
$$\frac{d^2\psi}{dx^2} = -\frac{2m(E - V_0)}{\hbar^2}\psi(x)$$

KE = E – PE

Inside the box

KE = E

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

√ Different BC than before

Outside the box

KE = E – V_0

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi(x)$$

Solutions of the SE for the region outside the box;

Solving the SE invokes the *continuity requirement* of the wave function in the 'two regions'; *ψ and (dψ/dx) at the 'wall' are the same from inside and from outside the 'box'*.

$$\frac{d^2\psi}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi(x) \Rightarrow \frac{d^2\psi}{dx^2} = \kappa^2\psi(x)$$

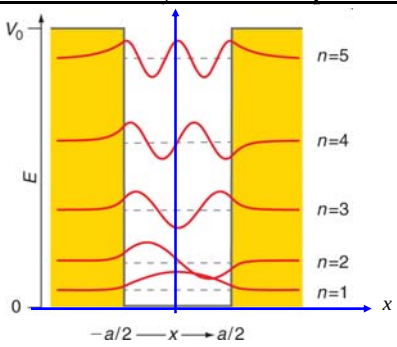
RHS $\psi(x) = A\,e^{-\kappa x} + Be^{+\kappa x}$ for $\infty \geq x \geq a/2$ and

LHS $\psi(x) = A'\,e^{-\kappa x} + B'e^{+\kappa x}$ for $-\infty \leq x \leq -a/2$

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

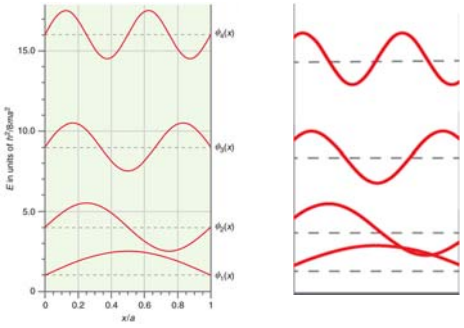
BC - (finiteness of ψ) would make B = 0, A' = 0, so that the functions are well behaved.

The particle in a 1D box system of finite potential energy:



$V(x) = 0$, for $-a/2 \leq x \leq a/2$

$V(x) = V_0$, for $x > a/2, x < -a/2$

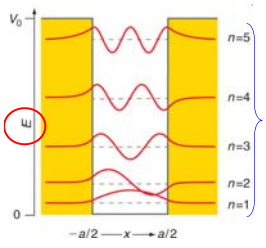


RHS $\psi(x) = Ae^{-\kappa x}$ Right wall $(x > 0)$

LHS $\psi(x) = B'e^{+\kappa x}$ Left wall $(x < 0)$

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

κ = decay constant, related to $(V_0 - E)$



n = 1,2 ,3…n' (n' finite)

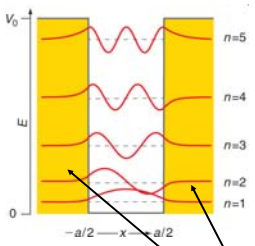
$\psi(-a/2) \neq 0$ and $\psi(a/2) \neq 0$

Finite number of bound states, and the number depends on V_0.

Wave function 'falls off' exponentially in the $V=V_0$ region.

Lower the energy E of the state compared to V_0 the 'fall off' is shorter.

Forbidden regions:



For any state in any region; total energy E = KE + PE

For the region with $V = V_0$

the KE = E – PE

$KE = (E - V_0) < 0$!

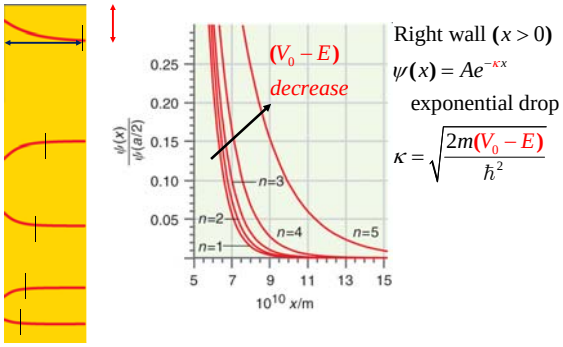
Because $KE = p^2/2m$

$\Rightarrow p$ = *imaginary number* !!

for KE to be negative.

Interpretation: Imaginary momentum! It is a ***classically forbidden region***.

Fall off in the classically forbidden region depends on the energy (stability) of the state; fall off is faster the lower the energy of the state is.



Right wall $(x > 0)$

$\psi(x) = Ae^{-\kappa x}$

exponential drop

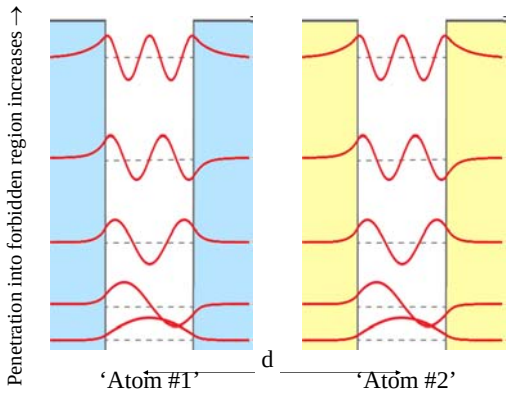
$\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$

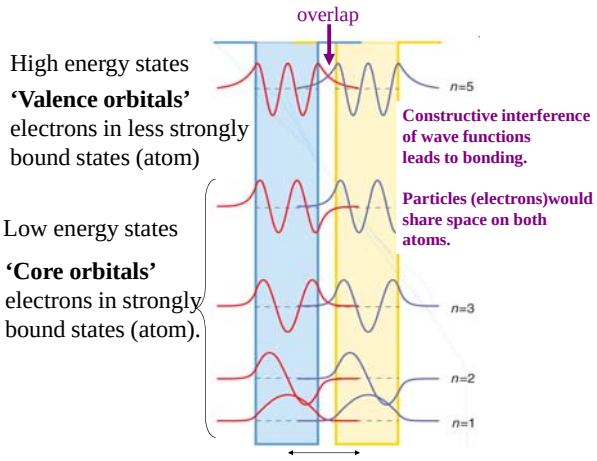
It is the confinement of the particle by way of trapping the particle in a 'potential well' that leads to quantization!

The successful model of the atom by Bohr has the same general characteristic of confinement of electrons into 'shells' with finite attractive potentials. Each shell with a well defined energy.

Approximately, therefore the particle in a box in a finite potential energy well can be considered as a first (crude) approximation model of an atom. At least for the purpose of demonstrating the quantum mechanical concepts.

A very approximate explanation of the Covalent Bond





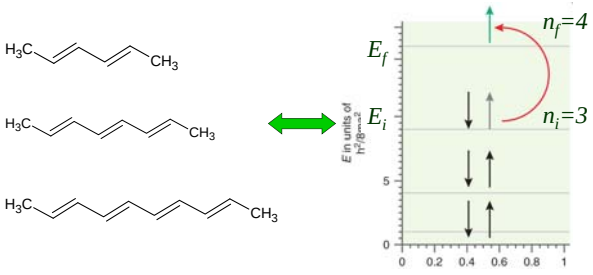
Chemical bonds involve the less strongly bound electrons, termed valence electrons.

The strongly bound electrons are termed core electrons.

Conjugated molecules absorb light in the UV-Vis region. The electrons in the pi system can be approximated as electrons in a 1D- box.

Calculating effective length 'a' using λ_{max}.

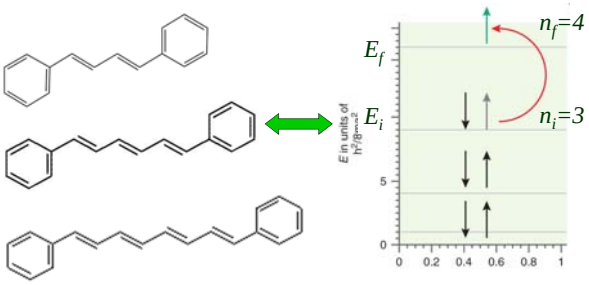
Particle in a 1D box model approximates pi electrons (conjugated) in a molecule.



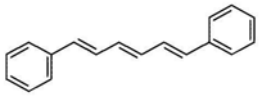
$n_e = 6$

Calculating effective length 'a' using λ_{max}.

Particle in a 1D box model approximates pi electrons (conjugated) in a molecule.



$n_e = 6$



λ_{max} = 375 nm

$$E_n = \frac{h^2}{8m}\frac{n^2}{a^2}$$

$$\Delta E = E_f - E_i = \frac{h^2}{8m}\frac{n_f^2}{a^2} - \frac{h^2}{8m}\frac{n_i^2}{a^2}$$

$$\Delta E = \frac{h^2}{8ma^2}\left(n_f^2 - n_i^2\right)$$

$$a = \sqrt{\frac{\left(n_f^2 - n_i^2\right)h^2}{8m\Delta E}} = \sqrt{\frac{\left(n_f^2 - n_i^2\right)h\lambda_{max}}{8mc}}$$

$$a = \sqrt{\frac{\left(n_f^2 - n_i^2\right)h\lambda_{max}}{8mc}}$$

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

$$= \sqrt{\frac{(4^2 - 3^2)\,(6.626 \times 10^{-34}\ \text{J s})\,(375 \times 10^{-9}\ \text{m})}{8\,(9.109 \times 10^{-31}\ \text{kg})\,(2.998 \times 10^{8}\ \text{m s}^{-1})}}$$

$$= 892\ \text{pm}$$

Compound	Conjugation	Apparent Network Length (pm)	Calculated Network Length (pm)
1,4-diphenyl–1,3-butadiene		723	695
1,6-diphenyl–1,3,5-hexatriene		892	973
1,8-diphenyl–1,3,5,7-octatetraene		1030	1251

Diversion: Estimate is the population ratio of 1st excited state to that of the ground state at 300K.

Boltzmann Distribution Law: $\frac{n_4}{n_3} = \frac{g_4}{g_3}e^{-\Delta E/k_B T}$

$$\Delta E = \frac{h^2(n_f^2 - n_i^2)}{8ma^2} = \frac{7 \times (6.626 \times 10^{-34}\ \text{J s})^2}{8 \times 9.109 \times 10^{-31}\ \text{kg} \times (973 \times 10^{-12}\ \text{m})^2}$$

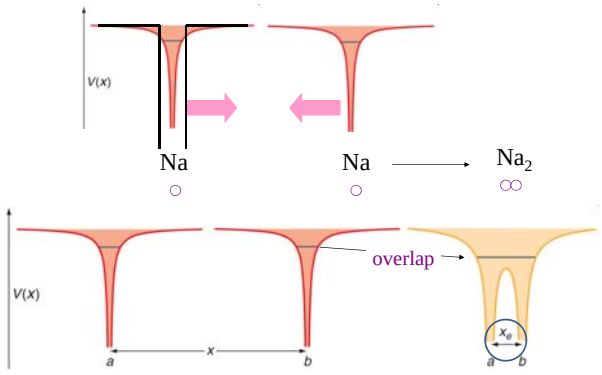
$$= \underline{4.45 \times 10^{-19}\ \text{J}}$$

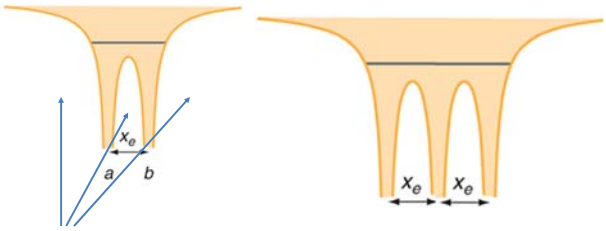
$$\frac{n_4}{n_3} = \frac{g_4}{g_3}e^{-\Delta E/k_B T} = \exp\left[-\frac{4.45 \times 10^{-19}\ \text{J}}{1.381 \times 10^{-23}\ \text{J K}^{-1} \times 300.\ \text{K}}\right]$$

$$= 2.0 \times 10^{-47}$$

n_4 negligible because $\underline{\Delta E} >> k_B T$ (=4.14×10^{-21} J)

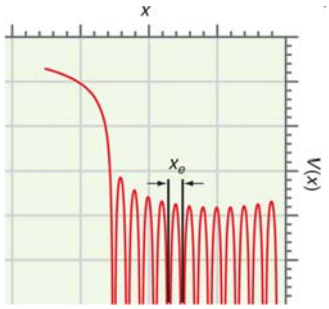
Conduction of electrons in metals



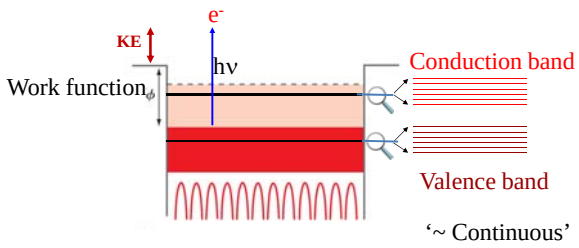


barrier

1D Na crystal - Na_n



1cm Na_n; n = 2×10^7 atoms



'~ Continuous'

If sufficient energy (> ϕ) is provided electrons of the valence band (~the top) can be taken out of the potential well to generate free electrons (classical particles)
- Photoelectric effect.)

Energy gap

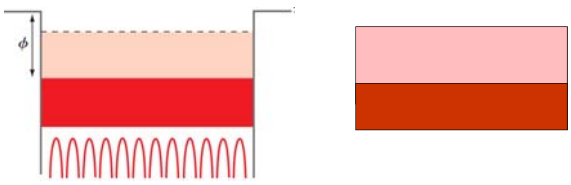
$$E_{n+1} - E_n = \frac{(n+1)^2h^2}{8ma^2} - \frac{n^2h^2}{8ma^2} = \frac{h^2}{8ma^2}(2n+1)$$

$$= (2n+1)(6.02 \times 10^{-34}\ \text{J})$$

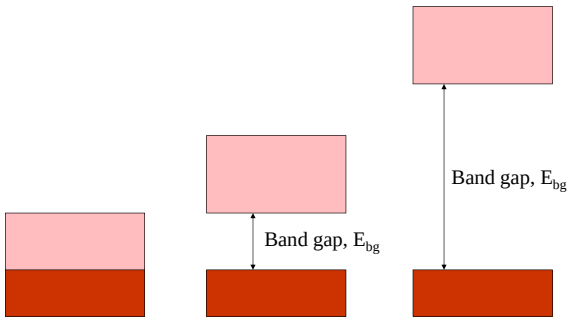
$\simeq 10^{-27}$ J $\simeq 10^{-6} k_B T$ << $k_B T$ (= 4.14×10^{-21} J) @ $T = 300K$

Thermal energy is sufficient to move electrons (populate) to the conduction band from the valence band and move electrons within energy states of the conduction band.

In metals the conduction band overlaps with the valence band.

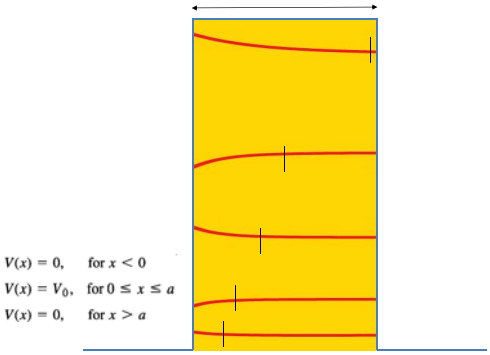


Conductors, semiconductors and insulators

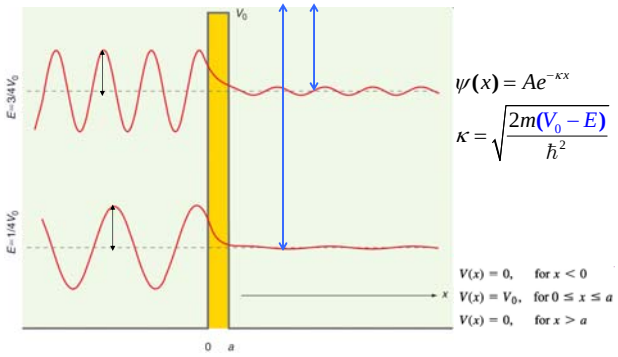


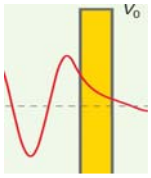
Quantum Mechanical Tunneling:

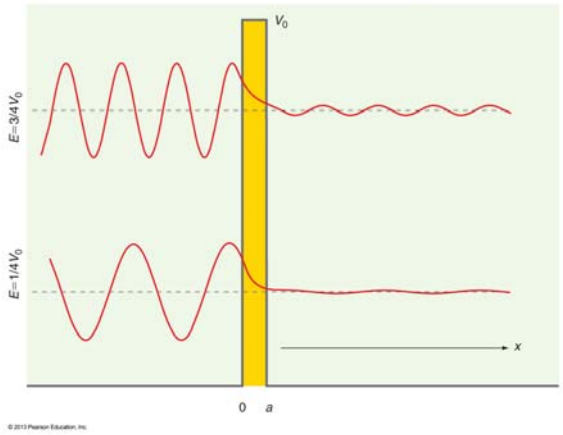
Effect of finite barrier width

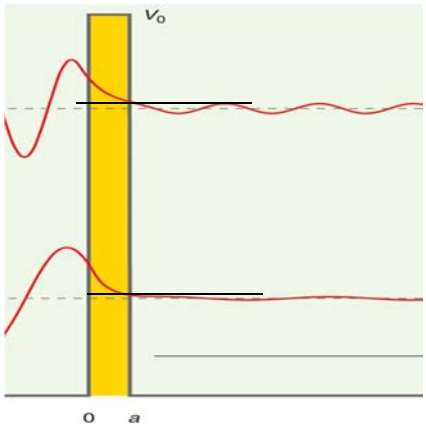


Note the amplitudes after tunneling and dependence on ($V_0 - E$) ~ probability of tunneling and a, barrier length.

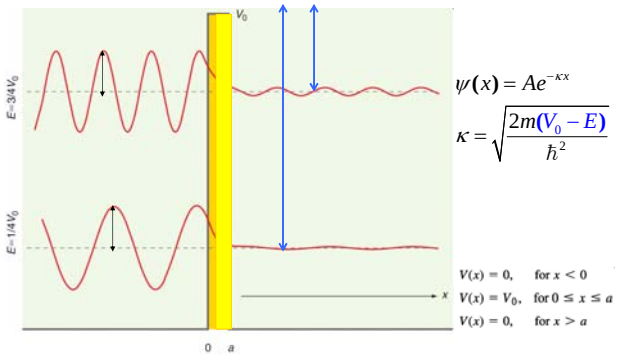


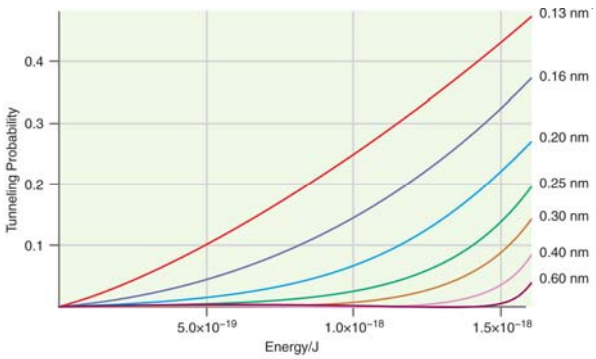




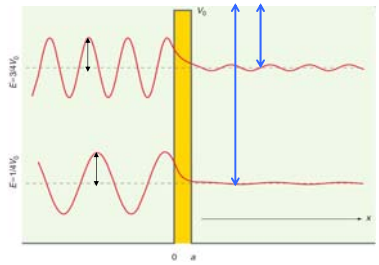


Note the amplitudes after tunneling and dependence on ($V_0 - E$) ~ probability of tunneling and a, barrier length.





E



$$\psi(x) = Ae^{-\kappa x}$$

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

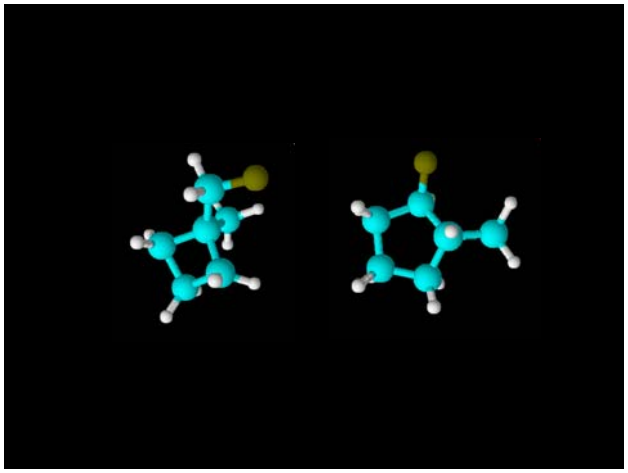
$$\text{Decay length} = \frac{1}{\kappa} = \sqrt{\frac{\hbar^2}{2m(V_0 - E)}}$$

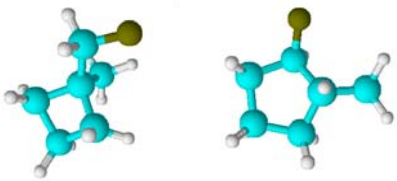
Smaller (V_0-E) slower decay (long decay length) of ψ.

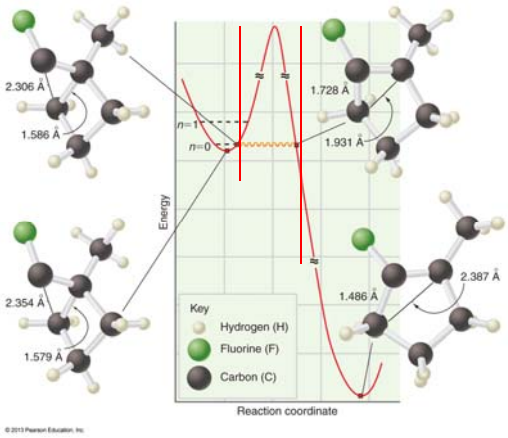
Tunneling and Chemical Reactions

Reaction rates – thermal energy used to overcome the activation energy barrier. Some reactions despite large E_a has significantly large reaction rates.

An alternate path (mechanism) is tunneling, where the reactants penetrate the energy barrier horizontally rather than going over the barrier.







The kinetic isotope effect can be used to verify tunneling mechanism, e.g. hydrogen transfer reactions such as;

Activation energy mechanism

$R_1OH + R_2O^- \xrightarrow{high,k} R_1O^- + R_2OH$

$R_1OD + R_2O^- \xrightarrow{low,k} R_1O^- + R_2OD$

$$\ln\left(\frac{k_H}{k_D}\right) = 1 - \sqrt{m_H / m_D}$$

$$= 1 - \sqrt{0.5} = 0.3$$

$$k_H = 1.34 k_D$$

The kinetic isotope effect can be used to verify tunneling mechanism, e.g. hydrogen transfer reactions such as;

Tunneling mechanism

$R_1OH + R_2O^- \xrightarrow{high,k} R_1O^- + R_2OH$

$R_1OD + R_2O^- \xrightarrow{lower,k} R_1O^- + R_2OD$

$$\psi(x) = Ae^{-\kappa x}$$

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

$$\frac{\psi(a)_H}{\psi(a)_D} = \frac{Ae^{-\kappa_H a}}{Ae^{-\kappa_D a}} = \frac{e^{-\sqrt{m_H}}}{e^{-\sqrt{m_D}}}$$

$$e^{-\sqrt{1}+\sqrt{2}} = e^{-\sqrt{1}+\sqrt{2}} = 1.5129$$

$$\psi_H = 1.5129 \psi_D$$

Quantum Wells and Quantum dots

A **quantum well** is a potential well with states of discrete energy values.

The effects of quantum confinement take place when the quantum well 'thickness' becomes comparable to the de Broglie wavelength of the carriers (generally electrons and holes), leading to energy levels called energy sub-bands.

http://en.wikipedia.org/wiki/Quantum_well

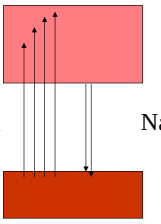
The energy levels in quantum dots can be modeled as a 'particle in a box' and the energy of the states would depend on the size of the box.

If the size of the quantum dot is small enough that the quantum confinement effects dominate (typically less than 10 nm), the electronic and optical properties are highly tunable.

The band gap energy of quantum dots strongly dependent on the diameter/size of these materials.

Quantum dots which are *semiconductors* can be synthesized in solution by controlling the crystal growth.

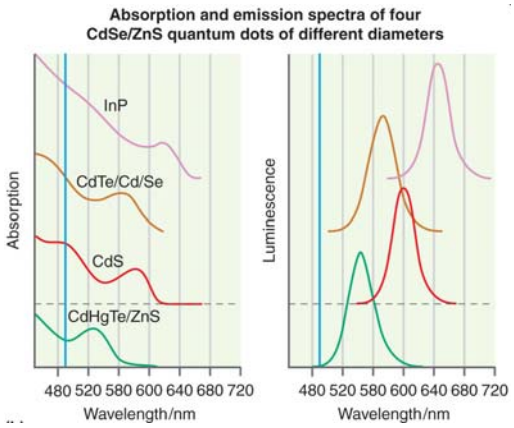
Broad absorption band

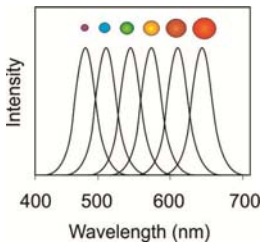


Narrow emission band

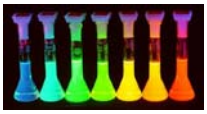
$$\lambda = \frac{hc}{E_{bg}}$$

semiconductors





$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_z^2 + n_y^2}{b^2} + \frac{n_x^2}{a^2}\right)$$



http://www.intechopen.com/books/biomedical-engineering-technical-applications-in-medicine/quantum-dots-in-biomedical-research

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_z^2 + n_y^2}{b^2} + \frac{n_x^2}{a^2}\right)$$