QUANTUM CHEMISTRY

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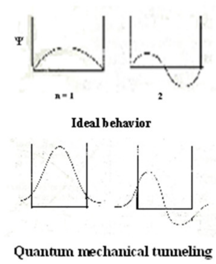
QC-3.3: QUANTUM EFFECTS

(i) Tunneling effect

- The probability of finding the particle **outside** the box is not zero.
- There is penetration of the probability of the particle outside box and go into the classically **forbidden** region.



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- Such quantum mechanical tunneling behavior is more predominant as the **classical behavior** of the system is **reduced**.
- **Radiation** (α , β or γ emission) is due to quantum mechanical tunneling
- Calculations show that an α-particle knocks at its confining wall 10^{21} times per second and may have to wait for $\mathbf{10^{10}}$ **years** to escape from the same nucleus. But emission occurs due to tunneling.
- **Outer-sphere** electron transfer $t_{2g} \rightarrow t_{2g}$, for example electron-transfer between $[Fe(CN)_6]^{4-}$ and $[Co(NH_3)_6]^{3+}$, arises due to such quantum mechanical tunneling.

(ii) Free particles

- Un like an electron in an atom or molecule, the free particle is not bound to any external force not even to gravitational force and can move within the container without any restriction. Hence, its potential energy is constant and may be taken as zero.
- Its Schrodinger equation will be of the form $\frac{d^2\psi}{dx^2} + k^2\psi = 0$
- The standard solution is of the form $\psi = Ce^{ikx} + De^{-ikx}$; Where ; $k^2 = \frac{8\pi^2 mE}{h^2}$

There are **no restrictions to k**. Hence, the free particle has any **energy** in a **continuous** form as translational energy.

(iii) Bohr's correspondence principle

In the limit of classical sized system, the quantum mechanical results had to go over in to the classical results.

That is the ***quantum mechanical results become identical to the classical results*** when the **quantum number** describing the system becomes **large**.

Illustrations:

- Calculate the value of n necessary to give energy of ½kT for O_2 molecule at 298K in a box of length (a) 1nm (b) 1cm.

  $$E_n = \frac{n^2h^2}{8ml^2} = \frac{1}{2}kT$$ (NB: *n will work out to be large making energy levels close & energy continuous leading to classical behavior*)

- Compare the quantum mechanical behavior & calculate the ground state energy of

  (i) an electron in a box of length 2Å (QM behavior)

  (ii) a particle of mass 0.1 mg in a box of length 1 cm. (Classical behavior)

  Ground state energy: n = 1

In the case of a particle in a box, as the particle becomes **heavier** and the dimension of the box larger, the **energy levels become closer**. Thus energy becomes **continuous** as expected by **classical mechanics**.