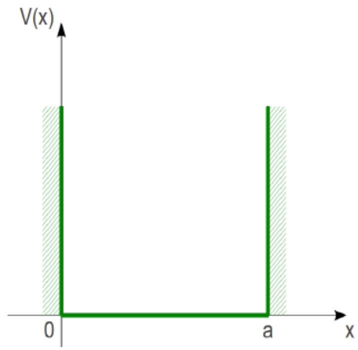
Time Independent Perturbation Theory:



<u>Remember this ?</u>

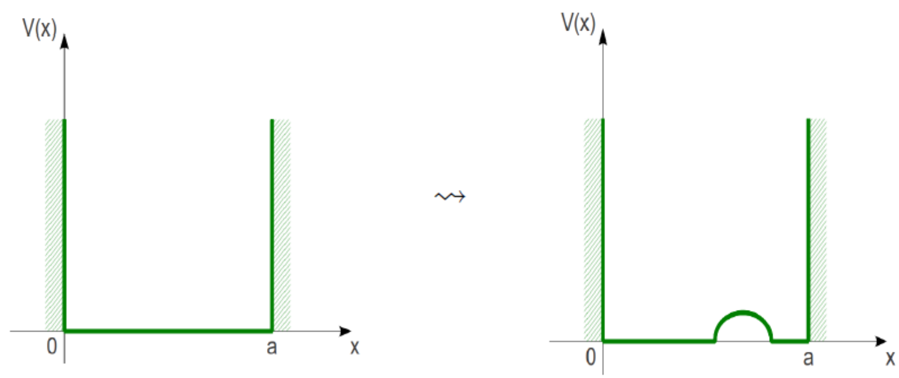
When particle in a well defined potential V(x),
we can solve the problem analytically using Sch. Eq.

$$E\,\psi_n = \hat{H}\,\psi_n$$

Where, the Hamiltonian is

$$\hat{H} = V - \frac{\hbar^2}{2m}\nabla^2$$

But, what if the potential is not a simple function,
such as :

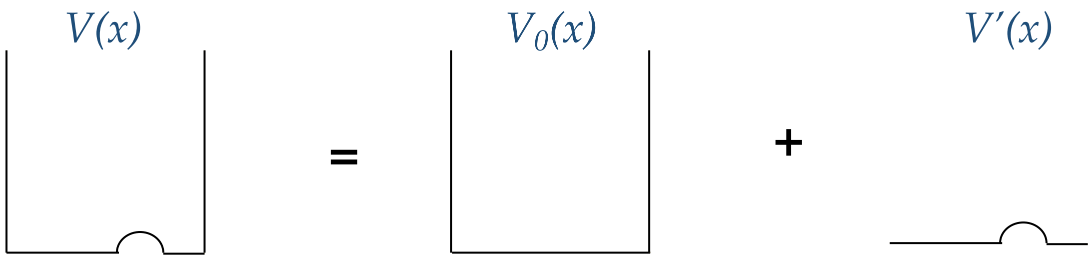


It will be difficult to find analytical solution to the problem ☹ ☹ ☹

Time Independent Perturbation Theory:

The perturbation theory is therefore developed to solve such problems.

The idea here is simple,



The T.I.S.E. can be written in this case as

$$E\,\psi_n = \hat{H}\,\psi_n$$

Where, the Hamiltonian can be expressed as

$$\hat{H} = (V_0 + V') - \frac{\hbar^2}{2m}\nabla^2$$

$$= V_0 - \frac{\hbar^2}{2m}\nabla^2 \quad + \quad V'$$

$$= \widehat{H_0} + \widehat{H'}$$

$\widehat{H_0}$ is the unperturbed system and $\widehat{H'}$ is the perturbation.

Time Independent Perturbation Theory:

When an external field is applied, this introduces an extra potential term in the Sch. Eqn. Usually this is much less than the coulomb potential of the atom and can be called a small perturbation.

For instance if an external uniform electric field Ξ is applied to an atom, the additional potential energy would be $-e\ \Xi\ z$. i.e.

$$V = -\frac{Ze^2}{r} - e\Xi z$$

$$\widehat{H_0} = -\frac{Ze^2}{r} - \frac{\hbar^2}{2m}\nabla^2, \quad \widehat{H'} = -e\Xi z$$

We express the eigenfunctions and eigenvalues ψ_k and E_{k} of $\widehat{H}$ as expansions,

$$\left(\widehat{H_0} + \widehat{H'}\right)\psi_k = E_k\,\psi_k,$$

Where, $\psi_k = \psi_{0k} + \psi_{1k} + \cdots$ and $E_k = E_{0k} + E_{1k} + \cdots$

ψ_{0k} and E_{0k} are those of the unperturbed systems. i.e.

$$\widehat{H_0}\,\psi_{0k} = E_{0k}\psi_{0k}$$

And, ψ_{1k} and E_{1k} are the ‘corrections’ or ‘perturbations’ due to $\widehat{H'}$

Time Independent Perturbation Theory:

It can be shown that the change in energy E_{1k} is given by

$$E_{1k} = \langle \widehat{H'} \rangle = \int \psi_{0k}^{*} \, \widehat{H'} \, \psi_{0k}$$

which is just the expectation value of the operator $\widehat{H'}$ using the unperturbed eigenfunctions