First order perturbation theory of non degenerate states:-

Non degenerate Case:-

Hamiltonian can be written as a sum of two parts

$$H = H_0 + H' \quad \text{--- (1)}$$

where H_0 = unperturbed Hamiltonian and
H' = perturbed Hamiltonian.

We have the eigenvalue of unperturbed Hamiltonian is.

$$H_0 u_n = E_n u_n \quad \text{--- (2)}$$

where. E_n & u_n = eigenvalues and orthonormal eigenfunctions of H_0 respectively.

According to perturbation method, we solve the Schrodinger equation.

$$H\psi_n = W_n \psi_n \quad \text{--- (3)}$$

We introduce a parameter g and write

$$H = H_0 + gH' \quad \text{--- (4)}$$

We express ψ_n and W_n as power series in g, i.e.,

$$\psi_n = \psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} - - - \quad \text{--- (5)}$$

$$W_n = W_n^{(0)} + gW_n^{(1)} + g^2 W_n^{(2)} - - - \quad (6)$$

where the superscripts 0, 1, 2 ... refer to the zeroeth, First, second order perturbation and the parameter g is assumed to take a continuous range of values between zero and unity. In the final result we ~~will~~ get; $g = 1$.

substitute eqn (5) and (6) in eqn (3)

$$(H_0 + gH')(\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \cdots) = (W_n^{(0)} + gW_n^{(1)} + g^2 W_n^{(2)} + \cdots)(\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \cdots) \quad \text{—— (7)}$$

Eqn (7) is valid for all values of g lying between 0 and 1.

$$0 < g > 1 \quad \text{—— (7a)}$$

The coefficients of equal power of g on either sides of the equation must be the same, i.e.

$$H_0 \psi_n^{(0)} = W_n^{(0)} \psi_n^{(0)} \quad \text{—— (8)}$$

$$H_0 \psi_n^{(1)} + H'\psi_n^{(0)} = W_n^{(0)}\psi_n^{(1)} + W_n^{(1)}\psi_n^{(0)} \quad \text{—— (9)}$$

$$H_0 \psi_n^{(2)} + H'\psi_n^{(1)} = W_n^{(0)}\psi_n^{(2)} + W_n^{(1)}\psi_n^{(1)} + W_n^{(2)}\psi_n^{(0)} \quad \text{—— (10)}$$

where, $\psi_n^{(0)}$ = eigenfunctions of the ~~unperturbed~~ unperturbed Hamiltonian

$W_n^{(0)}$ = eigenvalues of the unperturbed Hamiltonian.

Thus $\psi_n^{(0)} = U_n$ —— (11)

and $W_n^{(0)} = E_n$ —— (12)

We will be considering the effect of the perturbation H' on the nth state which will be assumed to be discrete and non-degenerate. However, other states need neither be discrete nor be non-degenerate.