## 4. Second order Perturbation:-

We next expand $\psi_n^{(2)}$ as a linear combination of the eigenfunctions of $H_0$; thus, we write

$$\psi_n^{(2)} = \sum_m a_m^{(2)} u_m \qquad (22)$$

where the superscripts (2) refer to the fact that we are considering second order perturbation. Substituting the above expansions eqn (22) & (13) in eqn (10), we get

$$H_0 \sum_m a_m^{(2)} u_m + H' \sum_m a_m^{(1)} u_m$$

$$= W_n^{(0)} \sum_m a_m^{(2)} u_m + W_n^{(1)} \sum_m a_m^{(1)} u_m + W_n^{(2)} u_n$$

[From eqn (11), (13) & (22)]

Multiplying by $u_k^*$ and integrating

$$\sum_m a_m^{(2)} E_m \delta_{km} + \sum_m a_m^{(1)} H'_{km}$$

$$= E_n \sum_m a_m^{(2)} \delta_{km} + H'_{nn} \sum_m a_m^{(1)} \delta_{km} + W_n^{(2)} \delta_{kn}$$

$$a_k^{(2)} (E_n - E_k) + W_n^{(2)} \delta_{kn} = \sum_m a_m^{(1)} H_{km} - a_k^{(1)} H'_{nn} \qquad (23)$$

For $k = n$, we get,

$$W_n^{(2)} = \sum_m a_m^{(1)} H'_{nm} - a_n^{(1)} H'_{nn}$$

$$= \sum_m{}' a_m^{(1)} H'_{nm} \quad ; m \neq n.$$

where the prime over the summation indicates that we have omitted the term $m = n$. Thus using eqn (19) we have

$$W_n^{(2)} = \sum_m{}' \frac{|H'_{mn}|^2}{E_n - E_m} \qquad (24)$$

where we have used the relation $H'_{nm} = (H'_{mn})^*$. The above equation gives the second order perturbation to the energy eigenvalue. Further, for $k \neq n$. Eqn. (23) gives

$$a_k^{(2)} = \sum_m{}' \frac{H'_{km} H'_{mn}}{(E_n - E_k)(E_n - E_m)} - \frac{H'_{kn} H'_{nn}}{(E_n - K_k)^2} \qquad (25)$$

lly we obtain $W_n^{(3)}$. the final result is

$$W_n = W_n^{(0)} + W_n^{(1)} + W_n^{(2)} + W_n^{(3)} + \cdots \qquad (26)$$

on substitution we have

$$W_n = E_n + H'_{nn} + \sum_m{}' \frac{|H'_{mn}|^2}{E_n - E_m} + \left[ \sum_m{}' \frac{|H'_{mn}|^2 (H'_{mn} - H'_{nn})}{(E_n - E_m)^2} + \frac{1}{3} \sum_m{}' \sum_k \left\{ \frac{1}{E_m - E_k} + \frac{1}{E_n - E_k} \right\} \frac{H'_{nk} H'_{km} H'_{mn} + H'_{nm} H'_{mk} H'_{kn}}{E_n - E_m} \right] \qquad (27)$$

$k \neq n$
$k \neq m$.

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