Time Independent Perturbation Theory

If a physical system gets disturbed or perturbed, then its energy levels and wave functions get changed.

Mathematically, Hamiltonian of perturbed system can be expressed as—

$$H = H^{(0)} + \lambda H^{(1)} \quad \text{①}$$

Where, $H^{(0)}$ = Hamiltonian of unperturbed system.
λ = perturbation parameter.
$H^{(1)}$ = perturbation effect, having smaller value than $H^{(0)}$.

Non-degenerate Case:-

In this case, there will be one eigen function corresponding to each energy level or eigen value.

In unperturbed state, Schrodinger's wave eq^n for the system can be written as—

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad \cdots (2); \left[\text{Where, } n = 1, 2, 3 \ldots\right.$$

Here, $E_n^{(0)}$ & $\psi_n^{(0)}$ represent energy and wave f^n of n^{th} level of the system respectively in unperturbed state.

In perturbed state, Schrodinger eq^n for the system can be written as—

$$H\psi_n = E_n\psi_n \quad \cdots (3)$$

Where, E_n & ψ_n represent energy & wave f^n of n^{th} level of the system respectively in perturbed state.

∴ E_n & ψ_n can be expanded in terms of 'λ' as—

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\cdots — (4)$$

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots\cdots — (5)$$

Here, $E_n^{(1)}, E_n^{(2)}$ ------ & $\psi_n^{(1)}, \psi_n^{(2)}$ ... are to be determined.

Now, eqn (3) can be expressed as — (on using eqn (1) & (2) in eqn (3))

$$(H^{(0)}+\lambda H^{(1)})(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\cdots)$$
$$=(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\cdots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\cdots)$$

$$H^{(0)}\psi_n^{(0)}+\lambda(H^{(0)}\psi_n^{(1)}+H^{(1)}\psi_n^{(0)})+\lambda^2(H^{(0)}\psi_n^{(2)}+H^{(1)}\psi_n^{(1)})+\cdots$$
$$=E_n^{(0)}\psi_n^{(0)}+\lambda(E_n^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)})+\lambda^2(E_n^{(0)}\psi_n^{(2)}+E_n^{(1)}\psi_n^{(1)}+E_n^{(2)}\psi_n^{(0)})+\cdots$$

Equating the coefficients of same powers of 'λ' from both sides, we get —

$$H^{(0)}\psi_n^{(0)}=E_n^{(0)}\psi_n^{(0)} \quad \cdots (6)$$
$$H^{(0)}\psi_n^{(1)}+H^{(1)}\psi_n^{(0)}=E_n^{(0)}\psi_n^{(1)}+E_n^{(1)}\psi_n^{(0)} \quad \cdots (7)$$
$$H^{(0)}\psi_n^{(2)}+H^{(1)}\psi_n^{(1)}=E_n^{(0)}\psi_n^{(2)}+E_n^{(1)}\psi_n^{(1)}+E_n^{(2)}\psi_n^{(0)} \quad \cdots ⑧$$

Eqns ⑥, ⑦, ⑧ represent unperturbed, first order perturbation and second order perturbation eqns respectively.

Evaluation of first order energy ($E_n^{(1)}$):—

The unknown wave fn. $\psi_n^{(1)}$ can be expanded in terms of known wave fn. as —

$$\psi_n^{(1)}=\sum_{m=1}^{\infty}C_m\psi_m^{(0)} \quad \cdots (9)$$

Using eqn ⑨ in eqn ⑦, we have —

$$\sum_m(C_m H^{(0)}\psi_m^{(0)})+H^{(1)}\psi_n^{(0)}=\sum_m(C_m E_n^{(0)}\psi_m^{(0)})+E_n^{(1)}\psi_n^{(0)}$$

$$\sum_m\left[C_m(E_m^{(0)}-E_n^{(0)})\psi_m^{(0)}\right]+H^{(1)}\psi_n^{(0)}=E_n^{(1)}\psi_n^{(0)} \quad \cdots (9.1) \; \left[H^{(0)}\psi_m^{(0)}=E_m^{(0)}\psi_m^{(0)}\right.$$

On multiplying the eqn by $\psi_n^{(0)*}$ and then integrating over the space variables, we get —

$$\int \sum_m \left[C_m \left(E_m^{(0)} - E_n^{(0)}\right) \psi_n^{(0)*} \psi_m^{(0)} (d\tau)\right] + \int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau)$$

$$= \int E_n^{(1)} \psi_n^{(0)*} \psi_n^{(0)} (d\tau) \quad \cdots ⑩$$

∴ A/c to condition of normalization,

$$\int \psi_i^{(0)*} \psi_j^{(0)} (d\tau) = \left.\begin{matrix} 0 & ; \text{if } i \neq j \\ 1 & ; \text{if } i = j \end{matrix}\right\} \cdots ⑪$$

Using eqn (11) in eqn (10), we get —

$$0 + \int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau) = E_n^{(1)}$$

$$\therefore E_n^{(1)} = \int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau) \quad \cdots (12)$$

Evaluation of first order wave fn $(\psi_n^{(1)})$:—

On multiplying eqn (9.1) by $\psi_m^{(0)*}$ and then integrating over space variables, we get—

$$\int \sum_m C_m \left[E_m^{(0)} - E_n^{(0)}\right] \psi_m^{(0)*} \psi_m^{(0)} (d\tau) + \int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau)$$

$$= \int E_n^{(1)} \psi_m^{(0)*} \psi_n^{(0)} (d\tau)$$

$$C_m \left(E_m^{(0)} - E_n^{(0)}\right) + \int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau) = 0 \; ; \left[\begin{matrix}\text{On using normalization} \\ \text{condition (11)}\end{matrix}\right.$$

$$\therefore C_m = - \frac{\int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau)}{\left(E_m^{(0)} - E_n^{(0)}\right)} \quad \cdots (13) ; [m \neq n$$

Hence, $\psi_n^{(1)} = \sum_m{}' \frac{\int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau)}{\left(E_n^{(0)} - E_m^{(0)}\right)} \psi_m^{(0)}$

Energy and wave fn of perturbed system, under first order perturbation (on using eqns ④ & ⑧) are—

$$E_n = E_n^{(0)} + \lambda \int \psi_n^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau) \quad \cdots (14) ; [\text{Using eqn (12)}$$

$$\text{And, } \psi_n = \psi_n^{(0)} - \lambda \sum_{m=1}^{\infty}{}' \frac{\int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau)}{\left(E_m^{(0)} - E_n^{(0)}\right)} \psi_m^{(0)} \cdots (15) ; \left[\begin{matrix}\text{Using eqns} \\ (9) \,\&\, (13)\end{matrix}\right.$$

Here, Σ' indicates the omission of term having $m = n$.

Evaluation of second order energy $(E_n^{(2)})$:—

The unknown wave fn $\psi_n^{(1)}$ can be expanded in terms of known wave fns as—

$$\psi_n^{(2)} = \sum_m g_m \psi_m^{(0)} \quad \text{---} (16)$$

On using eqn (9) & (16) in eqn (8), we get —

$$\sum_m g_m H^{(0)}\psi_m^{(0)} + \sum_m C_m H^{(1)}\psi_m^{(0)} = \sum_m g_m E_n^{(0)}\psi_m^{(0)} + \sum_m C_m E_n^{(1)}\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)}$$

$$\text{As, } H^{(0)}\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)}$$

$$\therefore \sum_m g_m E_m^{(0)}\psi_m^{(0)} - \sum_m g_m E_n^{(0)}\psi_m^{(0)} = \sum_m C_m E_n^{(1)}\psi_m^{(0)} - \sum_m C_m H^{(1)}\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)}$$

$$\sum_m g_m\left(E_m^{(0)} - E_n^{(0)}\right)\psi_m^{(0)} = \sum_m C_m\left(E_n^{(1)} - H^{(1)}\right)\psi_m^{(0)} + E_n^{(2)}\psi_n^{(0)} \quad (17)$$

On multiplying this eqn by $\psi_n^{(0)*}$ and then integrating over the space variables, we get —

$$\int \sum g_m\left(E_m^{(0)} - E_n^{(0)}\right)\psi_n^{(0)*}\psi_m^{(0)}(d\tau) = \int \sum \psi_n^{(0)*} C_m\left(E_n^{(1)} - H^{(1)}\right)\psi_m^{(0)}(d\tau) + \int E_n^{(2)}\psi_n^{(0)*}\psi_n^{(0)}(d\tau)$$

$$0 = -\sum' C_m \int \psi_n^{(0)*} H^{(1)}\psi_m^{(0)}(d\tau) + E_n^{(2)} \; ; \left[\text{on using normalization condition (1)}\right.$$

$$\text{So } E_n^{(2)} = \sum' C_m \int \psi_n^{(0)*} H^{(1)}\psi_m^{(0)}(d\tau)$$

$$E_n^{(2)} = -\sum' \frac{\int \psi_m^{(0)*} H^{(1)}\psi_n^{(0)}(d\tau) \int \psi_n^{(0)*} H^{(1)}\psi_m^{(0)}(d\tau)}{\left(E_m^{(0)} - E_n^{(0)}\right)} \; ; \left[\text{on using eqn } (13)\right.$$

$$\therefore E_n^{(2)} = \sum' \frac{\int \psi_m^{(0)*} H^{(1)}\psi_n^{(0)}(d\tau) \int \psi_n^{(0)*} H^{(1)}\psi_m^{(0)}(d\tau)}{\left(E_n^{(0)} - E_m^{(0)}\right)} \quad \text{---} (18)$$

This is the second order perturbed energy.

Evaluation of second order wave fn $\psi_n^{(2)}$:—

On multiplying eqn (17) by $\psi_m^{(0)*}$ and then integrating over the space variables —

$$\sum_m g_m \int \left(E_m^{(0)} - E_n^{(0)}\right)\psi_m^{(0)*}\psi_m^{(0)}(d\tau) = \sum_m C_m \int \psi_m^{(0)*}\left(E_n^{(1)} - H^{(1)}\right)\psi_m^{(0)}(d\tau) + \int E_n^{(2)}\psi_m^{(0)*}\psi_n^{(0)}(d\tau)$$

$$g_m\left(E_m^{(0)} - E_n^{(0)}\right) = \sum_m C_m\left(E_n^{(1)} - \int \psi_m^{(0)*} H^{(1)}\psi_m^{(0)}(d\tau)\right) \; ; \left[\text{on using normalization condition (1)}\right.$$

$$\therefore g_m = \sum_m \frac{C_m}{(E_m^{(0)} - E_n^{(0)})}\left[E_n^{(1)} - \int \psi_n^{(0)*} H^{(1)} \psi_m^{(0)} (d\tau)\right] \quad ③$$

Therefore, second order perturbed wave fn can be expressed as —

$$\psi_n^{(2)} = \sum_m{}' \frac{C_m}{(E_m^{(0)} - E_n^{(0)})}\left[E_n^{(1)} - \int \psi_m^{(0)*} H^{(1)} \psi_n^{(0)} (d\tau)\right]\psi_m^{(0)} \quad \text{[on using (3)+(5)]}$$

Q:- Discuss perturbation theory for non-degenerate levels in first and second order.

Or

Describe time independent perturbation theory upto second order. —

Degenerate Case :-

In this case, there are two or more eigen fns corresponding to one energy level of are s-linearly independent wave fns corresponding to same eigenvalue ~~[illegible]~~ then the system is called s-fold degenerate system ~~[illegible] unperturbed wave fn~~ ~~degenerate system [illegible] perturbation [illegible]~~ ~~[illegible] perturbed fns [illegible] perturbation [illegible]~~ In perturbed state, Schrodinger eqn for the system is,

$$H\psi_k = E_k \psi_k \quad \text{--- } ①$$

where, H, ψ_k & E_k represent perturbed Hamiltonian, perturbed wave fns and perturbed energy respectively.

Hamiltonian of perturbed system is expressed as

$$H = H^{(0)} + \lambda H^{(1)} \quad \text{--- } ②$$

here $H^{(1)}$ = perturbation Hamiltonian and is supposed to produce small changes in eigenvalues of the unperturbed Hamiltonian $H^{(0)}$ and therefore in unperturbed wave fns $\psi_k^{(0)}$

λ = perturbation parameter, having value less than —

Using eqn. (2) in eqn. (1), we have —

$$(H^{(0)} + \lambda H^{(1)})\psi_k = E_k \psi_k \quad \dots (2.1)$$

The correct zeroth order wave fn. can be expressed as

$$\psi_k^{(0)} = \sum_{l=1}^{f} \alpha_{kl} \psi_{kl}^{(0)} \quad \dots (3)$$

The eigenvalue and eigen-fn. or wave-fn. of perturbed system may be expressed as —

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots \quad \text{---} (4)$$

$$\psi_k = \psi_k^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots$$

$$\text{i.e. } \psi_k = \sum_{l=1}^{f} \alpha_{kl} \psi_{kl}^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots \quad \text{---} (5)$$

Using eqn. ④ & ⑤ in eqn. (2.1), we get —

$$(H^{(0)} + \lambda H^{(1)})\left(\sum_{l=1}^{f} \alpha_{kl} \psi_{kl}^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots\right) = (E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots)\left(\sum_{l=1}^{f} \alpha_{kl} \psi_{kl}^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} \dots\right)$$

Equating the coefficients of like power of 'λ', we get —

$$H^{(0)} \sum_{l=1}^{f} \alpha_{kl} \psi_{kl}^{(0)} = E_k^{(0)} \sum_{l=1}^{f} \alpha_{kl} \psi_{kl}^{(0)} \quad \dots (6)$$

$$(H^{(0)} - E_k^{(0)})\psi_k^{(1)} = \sum_{l=1}^{f} \alpha_{kl} (E_k^{(1)} - H^{(1)}) \psi_{kl}^{(0)} \quad \dots (7)$$

and so on.

The first order perturbed wave-fn. may be expressed in terms of unperturbed wave fn. as —

$$\psi_k^{(1)} = \sum_{mj} C_{mj} \psi_{mj}^{(0)} \quad \dots (8)$$

where C_{mj} are constants and $\psi_{mj}^{(0)}$ correspond to m^{th} state.

Now, $H^{(0)}\psi_k^{(1)} = H^{(0)} \sum_{mj} C_{mj} \psi_{mj}^{(0)}$

$$= \sum_{mj} C_{mj} H^{(0)} \psi_{mj}^{(0)} \quad \left[\because H^{(0)} \psi_{mj}^{(0)} = E_m^{(0)} \psi_{mj}^{(0)}\right]$$

$$= \sum_{mj} C_{mj} E_m^{(0)} \psi_{mj}^{(0)} \quad \dots (9)$$

Using eqns ⑧ & ⑨ in eqn ⑦, we have—

$$\sum_{mj} C_{mj}\left(E_m^{(0)}-E_k^{(0)}\right)\psi_{mj}^{(0)} = \sum_{l=1}^{s}\alpha_{kl}E_k^{(1)}\psi_{kl}^{(0)} - \sum_{l=1}^{s}\alpha_{kl}H^{(1)}\psi_{kl}^{(0)} \quad \cdots (10)$$

Multiplying this eqn by $\psi_{np}^{(0)*}$ from both sides and then integrating over all configuration space, we get—

$$\sum_{mj} C_{mj}\left(E_m^{(0)}-E_k^{(0)}\right)\int\psi_{np}^{(0)*}\psi_{mj}^{(0)}(d\tau) = \sum_{l=1}^{s}\alpha_{kl}E_k^{(1)}\int\psi_{np}^{(0)*}\psi_{kl}^{(0)}(d\tau) - \sum_{l=1}^{s}\alpha_{kl}\int\psi_{np}^{(0)*}H^{(1)}\psi_{kl}^{(0)}(d\tau)$$

$$\Rightarrow \sum_{mj} C_{mj}\left(E_m^{(0)}-E_k^{(0)}\right)\delta_{nm}\delta_{pj} = \sum_{l=1}^{s}\alpha_{kl}E_k^{(1)}\delta_{nk}\delta_{pl} - \sum_{l=1}^{s}\alpha_{kl}\int\psi_{np}^{(0)*}H^{(1)}\psi_{kl}^{(0)}(d\tau)$$

If we choose $n=k$, then we have—

$$\sum_{mj} C_{mj}\left(E_m^{(0)}-E_k^{(0)}\right)\delta_{km}\delta_{pj} = \sum_{l=1}^{s}\alpha_{kl}E_k^{(1)}\delta_{pl} - \sum_{l=1}^{s}\alpha_{kl}\int\psi_{kp}^{(0)*}H^{(1)}\psi_{kl}^{(0)}(d\tau) \quad \cdots (11)$$

In this eqn, L.H.S is always zero because when $k=m$, it is zero due to $\left(E_m^{(0)}-E_k^{(0)}\right)$ and when $k\neq m$, it is zero due to δ_{km}.

Therefore eqn (11) gives,

$$\sum_{l=1}^{s}\alpha_{kl}\int\psi_{kp}^{(0)*}H^{(1)}\psi_{kl}^{(0)}(d\tau) - \sum_{l=1}^{s}\alpha_{kl}E_k^{(1)}\delta_{pl} = 0$$

$$\sum_{l=1}^{s}\left(H_{pl}^{(1)} - E_k^{(1)}\delta_{pl}\right)\alpha_{kl} = 0 \quad \cdots (12)$$

[Using notations, $\int\psi_{kp}^{(0)*}H^{(1)}\psi_{kl}^{(0)}(d\tau) = H_{pl}^{(1)}$]

Eqn (12) gives s-simultaneous eqns in α_{kl} and that n-solutions for $E_k^{(1)}$. These simultaneous eqns can be written as—

$$\left.\begin{aligned}
&\left(H_{11}^{(1)}-E_k^{(1)}\right)\alpha_{k1} + H_{12}^{(1)}\alpha_{k2} + H_{13}^{(1)}\alpha_{k3} + \cdots + H_{1s}^{(1)}\alpha_{ks} = 0\\
&H_{21}^{(1)}\alpha_{k1} + \left(H_{22}^{(1)}-E_k^{(1)}\right)\alpha_{k2} + H_{23}^{(1)}\alpha_{k3} + \cdots + H_{2s}^{(1)}\alpha_{ks} = 0\\
&\cdots\quad \cdots\quad \cdots\quad \cdots\\
&H_{s1}^{(1)}\alpha_{k1} + H_{s2}^{(1)}\alpha_{k2} + H_{s3}^{(1)}\alpha_{k3} + \cdots + \left(H_{ss}^{(1)}-E_k^{(1)}\right)\alpha_{ks} = 0
\end{aligned}\right\} \cdots (13)$$

If neither of coefficients α_{kl} is zero, the determinant of

Coefficients of a_{kl} $(l = 1, 2, 3, \ldots, s)$ must vanish i.e.,

$$\begin{vmatrix} (H_{11}^{(1)} - E_k^{(1)}) & H_{12}^{(1)} & H_{13}^{(1)} & \cdots & H_{1s}^{(1)} \\ H_{21}^{(1)} & (H_{22}^{(1)} - E_k^{(1)}) & H_{23}^{(1)} & \cdots & H_{2s}^{(1)} \\ - & - & - & - & - \\ - & - & - & - & - \\ H_{s1}^{(1)} & H_{s2}^{(1)} & H_{s3}^{(1)} & \cdots & (H_{ss}^{(1)} - E_k^{(1)}) \end{vmatrix} = 0 \quad \text{--- (14)}$$

Eqns. (13) & (14) are generally known as "secular eqn."

Q3 :- Give the perturbation theory for a degenerate case

Application of degenerate perturbation theory:—

(First order stark effect in hydrogen atom)

The Stark effect:— When a uniform electric field is applied to an atomic system, the energy levels of the system show splitting. This is known as 'stark effect' which can be quantitatively explained by using degenerate perturbation theory. For illustration, consider the case of 'hydrogen atom'.

The perturbed Hamiltonian of a hydrogen atom in presence of a uniform electric field (E), applied along the z-direction, is

$$H = H^{(0)} + eEz \quad \text{-----} \quad ①$$

Where, $H^{(0)}$ = unperturbed Hamiltonian of hydrogen atom.

e = electric charge on an electron.

Here, first order perturbation Hamiltonian,

$$H^{(1)} = eEz \quad ; \left[\begin{array}{l} \text{In spherical polar co-ordinate} \\ \text{system, } z = r\cos\theta \end{array} \right.$$

$$\therefore H^{(1)} = eEr\cos\theta \quad \text{---} \quad (2)$$

1st order Stark effect in ground state of hydrogen atom :-

∵ For ground state, $n = 1$

∴ $l = 0$, $m = 0$.

So, ground state wave fn. of the hydrogen atom is as —

$$\psi_{100} = R_{10}(r) Y_{00}(\theta, \phi) = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} \; ; \left[\text{where, } a_0 = \hbar^2/\mu e^2 \text{ known as Bohr radius of hydrogen atom.} \right]$$

The first order perturbation energy correction in ground state is given by,

$$E^{(1)} = \int \psi_{100}^* H^{(1)} \psi_{100} (d\tau)$$

$$= \iiint \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} (eEr\cos\theta) \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} (d\theta) r^2 (dr) \sin\theta (d\phi)$$

$$= \frac{eE}{\pi a_0^3} \int_0^\infty r^3 (dr) e^{-2r/a_0} \int_0^\pi \sin\theta \cos\theta (d\theta) \int_0^{2\pi} (d\phi)$$

$$= 0 \; ; \left[\because \int_0^\pi \sin\theta \cos\theta (d\theta) = 0 \right]$$

∴ Perturbation energy correction in ground state is zero, i.e., there is no first order Stark effect in ground state of hydrogen atom.

First order Stark effect in first excited state :-

∵ For first excited state, $n = 2$,

∴ $l = 0, 1$;

Hence, for, $l = 0$, $m = 0$;

And, for, $l = 1$, $m = 1, 0, -1$.

In this case, the unperturbed states available are —

$$\psi_{200}, \psi_{211}, \psi_{210}, \psi_{21-1} = \psi_1, \psi_2, \psi_3, \psi_4 \quad \text{--- (3)}$$

$$\text{Where, } \psi_{2lm} = R_{2l}(r) Y_{lm}(\theta, \phi) \; ; \begin{cases} l = 0, m = 0 \\ l = 1, m = 1, 0, -1 \end{cases} \quad \text{--- (4)}$$

$$\text{And, } H^{(0)} \psi_{2lm} = E^{(0)} \psi_{2lm} \quad \text{--- (5)}$$

$$E^{(n)} = -\frac{Z^2 e^2}{2a_0 n^2} \quad ; \Big[\text{here, } Z=1,\ n=2$$

$$\text{i.e; } E^{(0)} = -\frac{e^2}{2a_0}\cdot\frac{1}{2^2} \quad \cdots (6)$$

A straight forward application of degenerate perturbation theory for the determination of first order perturbation energy correction $E^{(1)}$ to the energy level $E^{(0)}$, leads to,

$$\left| H^{(1)}_{pk} - E^{(1)}\delta_{pk} \right| = 0 \quad \cdots (7) ; \begin{bmatrix}\text{Replace } pk \\ \text{by } (ij)\end{bmatrix}$$

$$\text{Here, } H^{(1)}_{pk} = \int \psi_p^* H^{(1)} \psi_k (d\tau) \ ; \ p, k = 1, \cdots, 4.$$

$$\text{Now, } H^{(1)}_{pp} = eE\int \psi_p^* z\, \psi_p (d\tau) = 0 \cdots (8), \text{ due to}$$

the parity consideration.

Also, when magnetic quantum number of the states involved are not identical, then in that case,

$$H^{(1)}_{pk} = 0$$

Consequently, we have only,

$$H^{(1)}_{13} \neq 0 \text{ and } H^{(1)}_{31} \neq 0$$

Also, from the hermicity of $H^{(1)}$, we have, $H^{(1)}_{13} = H^{(1)*}_{31}$

the determinant [Eqn (7)] in its evaluation of it, then, ~~very simple~~ taken the form and we obtain,

$$\left(E^{(1)}\right)^2\left[\left(E^{(1)}\right)^2 - \left|H^{(1)}_{13}\right|^2\right] = 0 \ ; \left[\ \begin{vmatrix} -E^{(1)} & 0 & H_{13} & 0 \\ 0 & -E^{(1)} & 0 & 0 \\ H_{31} & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & E^{(1)} \end{vmatrix} = 0 \right.$$

scalar Eqn

$$\left.\begin{aligned} \text{Therefore, } E^{(1)} &= 0 \\ \text{or, } E^{(1)} &= \pm H^{(1)}_{13} \end{aligned}\right\} \cdots (8)$$

noting that $H^{(1)}_{13}$ is real.

The energy of the first excited state (E') of the hydrogen atom in the Stark field (E) thus has three levels which we raise to additional fines, the levels are —

$$E' = E^{(0)} + E^{(1)} = E^{(0)} \pm H_{13}^{(1)} \text{ ; and } E' = E^{(0)} \quad (9)$$

Identifying,

$$\psi_1 = \psi_{200}(r,\theta,\phi) = \frac{1}{(32\pi a_0^3)^{1/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0} \quad (10)$$

$$\psi_3 = \psi_{210}(r,\theta,\phi) = \frac{1}{(32\pi a_0^3)^{1/2}}\left(\frac{r}{a_0}\right)\cos\theta\, e^{-r/2a_0} \quad (11)$$

Now, we have —

$$H_{13}^{(1)} = \int \psi^* H^{(1)} \psi_3 (d\tau)$$

$$= \int \psi_{200}^* (eEr\cos\theta)\, \psi_{210}\, r^2 (dr) \sin\theta (d\theta)(d\phi)$$

$$= \frac{eE}{32\pi a_0^4}\left[\int_0^\infty r^4\left(2-\frac{r}{a_0}\right)e^{-r/a_0}(dr)\int_0^\pi \cos^2\theta (\sin\theta)(d\theta)\int_0^{2\pi}(d\phi)\right]$$

On solving, we finally get —

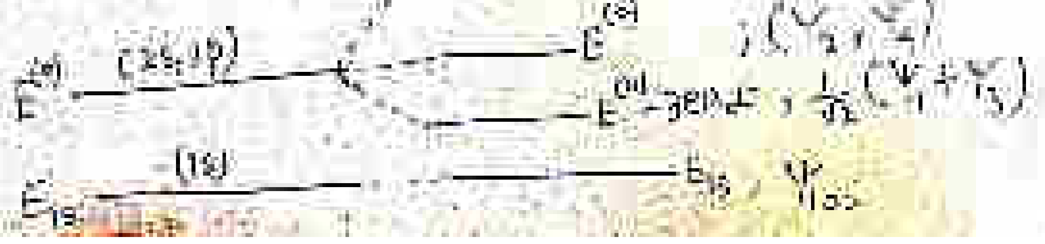
$$\boxed{H_{13}^{(1)} = -3ea_0E}$$

The degenerate wave functions corresponding to the values of $E^{(1)}$ given by eqn. (8) are —

$\frac{1}{\sqrt{2}}(\psi_1 \pm \psi_3)$; for $E^{(1)} = \pm H_{13}^{(1)}$

And, ψ_2, ψ_4 ; for $E^{(1)} = 0$

We see that the splitting is proportional to the strength of applied electric field. A diagrammatic representation of the stark effect in hydrogen atom is as —



Here, we see that the first excited state of hydrogen at. shows a linear Stark effect. This is a consequence of the fact that constituent wave fns of this state have opposite parities and therefore, expectation value of dipole moment being non-zero $(3ea_0)$. i.e., atom in this state has a permanent dipole moment which can interact with applied electric field.

Qn1 — Explain first order Stark effect in hydrogen atom by using degenerate perturbation theory.

or

Qn:- Explain stark splitting for $n=2$ level of hydrogen atom in presence of an electric field, using first order time ~~dependent~~ independent perturbation theory.