constant. we then attempt to calculate the probability of finding the system in some other state

Under these circumstances

and $\phi(r)$ is time independent. (7)

From (1) and (2)

$$\Rightarrow i\hbar \frac{\delta}{\delta t}\left[\sum a_n(t)\phi_n(r)e^{-iE_nt/\hbar}\right] = (H_0 + H')\left[\sum_n a_n(t)\phi(r)e^{-iE_nt/\hbar}\right]$$

$$\Rightarrow \left[\sum_n i\hbar \dot{a}_n(t)\phi_n(r)e^{(-iE_nt)/\hbar} + \sum_n a_n E_n \phi_n(r) e^{(-iE_nt)/\hbar}\right]$$

$$= \sum_n a_n H_0 \phi_n(r) e^{(-iE_nt)/\hbar} + \sum a_n H'\phi_n(r) e^{(-iE_nt)/\hbar}$$

using (3) $H_0\phi_n = E_n\phi_n$

$$\Rightarrow \sum_n i\hbar \dot{a}_n \phi_n(r) e^{-iE_nt/\hbar} + \sum_n a_n E_n \phi_n(r) e^{-iE_nt/\hbar} = \sum_n a_n E_n \phi_n(r) e^{iE_nt/\hbar} + \sum_n a_n H'\phi_n(r) e^{-iE_nt/\hbar}$$

$$\Rightarrow \sum i\hbar \dot{a}_n \phi_n(r) e^{(-iE_nt)/\hbar} = \sum a_n H'\phi_n(r) e^{(-iE_nt)/\hbar} \quad (5)$$

Multiplying both sides by ϕ_k^* and integrating over configuration space we get

(2)

$$i\hbar \dot{a}_n e^{-iE_n t/\hbar} \int \phi_k^* \phi_n \, d\tau$$

$$= \sum_n a_n e^{-iE_n t/\hbar} \int \phi_k^* H' \phi_n \, d\tau$$

Now using orthogonormality condition of ϕ's, i.e;

$$\int \phi_k^* \phi_n \, d\tau = \delta_{kn} = \begin{cases} 0 & \text{for } n \neq k \\ 1 & \text{for } n = k \end{cases}$$

$$i\hbar \dot{a}_n e^{(-iE_n t)/\hbar} \delta_{kn} = \sum_n a_n e^{(-iE_n)t/\hbar} \int \phi_k^* H' \phi_n \, d\tau$$

Because in L.H.S. all terms will be zero except $k=n$ term due to the properties of Kronecker delta δ_{kn}, we have

$$i\hbar \dot{a}_k e^{-iE_k t/\hbar} = \sum_n a_n e^{-iE_n t/\hbar} \int \phi_k^* H' \phi_n \, d\tau \quad (6)$$

The integral $\int \phi_k^* H' \phi_n \, d\tau$ at R.H.S. is a matrix

$|n\rangle$ (ket) $\langle\psi| = |\psi^*\rangle$

$\langle k|$ (Bra)

(4)

$$\langle k|H'|n\rangle = H'_{kn}$$

$$i\hbar\,\dot{a}_k = \sum_n a_n e^{i(E_k - E_n)t/\hbar} H'_{kn} \quad (7)$$

But $\frac{E_k - E_n}{\hbar} = \omega_{kn}$

is the Bohr's angular frequency.

Time dependent constants a_n's are given by

$$\left.\begin{aligned} \dot{a}_k &= (i\hbar)^{-1} \sum_n a_n H'_{kn} e^{i\omega_{kn}t} \\ &= (i\hbar)^{-1} \sum_n a_n^{(t)} \langle k|H'|n\rangle e^{i\omega_{kn}t} \end{aligned}\right\} \quad (9)$$

$$\boxed{\frac{d}{dt} a_k = \frac{1}{i\hbar} \sum_n a_n^{(t)} \langle k|H'|n\rangle e^{i\omega_{kn}t}} \quad (9)(b)$$

This is the required eq^n for the perturbation theory which shows that the perturber components (a_k (unitary ~~operator~~ parameter)), a_n are strongly dependent of time 't'.

$\Rightarrow$ Again considering

$$H = H_0 + \lambda H'$$

'λ' is known as switching parameter. It is real b/w $\lambda = 0$ to 1, i.e λ is very small

i.e, H' is replaced in eq^n 2 by $\lambda H'$.

Now, on expanding the coefficients a_K and a_n as follows

$$a_n = \underbrace{\lambda a_n(0)}_{} + \lambda^2 a_n^{(1)} + \lambda^3 a_n^{(2)} + \ldots \quad \text{— (10)}$$

$$a_K = \underbrace{a_K(0)}_{\text{unperturbed terms}} + \underbrace{\lambda a_K^{(1)}}_{\text{First order correction}} + \underbrace{\lambda^2 a_K^{(2)}}_{\text{Second order correction}}$$

Put these value in 9(b).

$$\Rightarrow \frac{d}{dt}\left[a_K^{(0)} + \lambda a_K^{(1)} + \lambda^2 a_K^{(2)} + \ldots\right]$$

$$= \frac{1}{i\hbar}\left[a_n^{(0)} + \lambda^2 a_n^{(1)} + \lambda^3 a_n^{(2)} + \ldots\right] \langle k|H'|n\rangle e^{i\omega_{Kn}t}$$

$$\Rightarrow \dot{a}_K^{(0)} + \lambda \dot{a}_K^{(1)} + \lambda^2 \dot{a}_K^{(2)} + \ldots = (i\hbar)^{-1}\sum_n (a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \ldots) H'_{Kn} e^{i\omega_{Kn}t}$$

Now equating the coefficients of different powers of λ on both the sides.

Equating coefficients of λ^0

$$i\hbar \dot{a}_k^0 = 0$$

Equating the coefficients of λ^1

$$i\hbar \dot{a}_k^{(1)} = \sum a_n^{(0)} \langle k|H'|n\rangle e^{i\omega_{kn}t}$$

(First order)

For λ^2

$$i\hbar \dot{a}_k^{(2)} = \sum a_n^{(1)} \langle k|H'|n\rangle e^{i\omega_{kn}t}$$

(second order)

$$i\hbar \dot{a}_k^{(s+1)} = \sum a_n^{(s)} \underbrace{\langle k|H'|n\rangle} e^{i\omega_{kn}t} \quad (11)$$

$$\underbrace{\int \psi_k^* \psi_n d^3r}_{\text{Schroedinger}} = \underbrace{\langle H'_{kn}\rangle}_{\text{Matrix}} = \underbrace{\langle k|H'|n\rangle}_{\text{Dirac}}$$

$$i\hbar \dot{a}_k^{(s+1)} = \sum_n a_n^{(s)} \langle H'_{kn}\rangle e^{i\omega_{kn}t}$$

Zero order Calculation :-

$$i\hbar \dot{a}_k = 0$$

$$\Rightarrow \dot{a}_k = 0$$

$$\Rightarrow \frac{d}{dt} a_k = 0$$

$$\Rightarrow \boxed{a_k = \text{constant}}$$

i.e, No effect of time on Zero order.

Let $a_k^{(0)} = \langle k | n \rangle = \delta_{kn}$

i.e, $a_k^{(0)} = \delta_{kn}$

If $k = n$ then

$$a_n^{(0)} = 1$$

$$k \neq n$$

then $a_n^{(0)} = 0$

$$\dot{a}_k = \frac{1}{i\hbar} \langle k | H' | n \rangle e^{i\omega_{kn} t}$$

Fi...