In electromagnetic field, according to Maxwell's equations

$$\text{div } \mathbf{A} = \nabla \cdot \mathbf{A} = 0$$

In view of this equation (12) takes the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 + e\phi + \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla + \frac{e^2}{2mc^2}A^2. \quad ...(13)$$

This may be expressed as

$$H = H^0 + H' = -\frac{\hbar^2}{2m}\nabla^2 + e\phi + \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla + \frac{e^2}{2mc^2}A^2 \quad ...(14)$$

where H^0 is unperturbed hamiltonian given by

$$H^0 = -\frac{\hbar^2}{2m}\nabla^2 + e\phi = -\frac{\hbar^2}{2m}\nabla^2 + V. \quad ...(15)$$

V being potential energy and H' is perturbation or interaction term given by

$$H' = H_{int} = \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla + \frac{e^2}{2mc^2}A^2. \quad ...(16)$$

For *weak field* terms of higher order in A *i.e.* $e^2A^2/2mc^2$ may be neglected. Therefore for weak field the *interaction part of the Hamiltonian* is

$$H' = H_{int} = \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla = -\frac{e}{mc}\mathbf{A}\cdot(-i\hbar\nabla)$$

i.e.

$$H' = H_{int} = -\frac{e}{mc}\mathbf{A}\cdot\mathbf{p} \quad ...(17)$$

In the case of a number of such particles, the Hamiltonian for the system will be the sum of such Hamiltonians for individual particles. In the case of electron e may be replaced by $-e$ (if e is to be maintained as positive quantity).

9.5. APPLICATION OF TIME DEPENDENT PERTURBATION THEORY TO SEMI CLASSICAL THEORY OF RADIATION.

The subject of iinteraction of electromagnetic wave on an atom is of great importance. The theory will be semi-classical due to the fact that we shall treat the motion of the atoms to be quantised and the electromagnetic field to be classical represented by continuous potentials A and ψ.

From the knowledge of classical electrodynamics it is known that for transverse electromagnetic waves the vector potential A satisfies the equations

$$\left.\begin{aligned} \nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial \mathbf{A}}{\partial t} &= 0 \\ \text{and} \qquad \text{div } \mathbf{A} = \nabla\cdot\mathbf{A} &= 0 \end{aligned}\right\} \quad ...(1)$$

A typical plane wave-monochromatic solutions applicable to physical situations of equations (1), representing a real potential with the real polarization vector $Re\,\mathbf{A_0} = |\mathbf{A_0}|$ and propagation vector $\mathbf{k}$ can be written as

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A_0}\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + A_0^*\, e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \quad ...(2a)$$

$$= 2\,|\mathbf{A_0}|\cos(\mathbf{k}\cdot\mathbf{r} - \omega t + \alpha)\,;\ \mathbf{A_0} = |\mathbf{A_0}|\, e^{i\alpha} \quad ...(2b)$$

Equation (2a) is satisfied if $\omega = kc$, k being magnitude of propagation vector **k** and (2b) is satisfied if constant complex vector $\mathbf{A_0}$ is perpendicular to **k**.

The electric field associated with vector potential **A** (equation (1) $\phi = 0$) is

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} = -\frac{2\omega}{c}\,|\mathbf{A_0}|\,\sin\,(\mathbf{k}\cdot\mathbf{r} - \omega t + \alpha). \quad ...(3)$$

The intensity of radiation *i.e.* flow of energy per unit area per second is given by well known Poynting's vector

$$\mathbf{I} = \frac{c}{4\pi}\,(\mathbf{E}\times\mathbf{B}). \qquad \text{(C.G.S. System)} \quad ...(4)$$

In free space $|\mathbf{E}| = |\mathbf{B}|$ and **E** is normal to **B**. Thus in free space $(\mathbf{E}\times\mathbf{B})$ is a vector of magnitude $|E|^2$ and direction **k** *i.e.*

$$\mathbf{I} = \frac{c}{4\pi}\cdot\frac{4\omega^2}{c^2}\,|\mathbf{A_0}|^2\,\sin^2\,(\mathbf{k}\cdot\mathbf{r} - \omega t + \alpha)$$

Mean Poynting vector

$$\bar{\mathbf{I}} = \frac{\omega^2}{2\pi c}\,|\mathbf{A_0}|^2$$

[Since time averaged magnitude of $\sin^2\,(\mathbf{k}\cdot\mathbf{r} - \omega t + \alpha)$ is $\frac{1}{2}$]

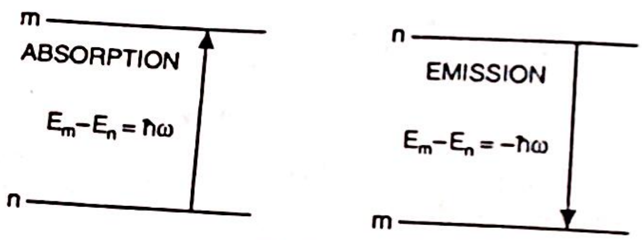

Fig. 9.4.

From the preceding section, the first order correction to Hamiltonian for a charged particle interaction with electromagnetic field is given by

$$H'_{int} = -\frac{e}{mc}\,(\mathbf{A}\cdot\mathbf{p}) = \frac{ie\hbar}{mc}\,\mathbf{A}\cdot\nabla$$

$$= \frac{ie\hbar}{mc}\,[\mathbf{A_0}\,e^{i\,(\mathbf{k}\cdot\mathbf{r} - \omega t)} + \mathbf{A_0}^*\,e^{-i\,(\mathbf{k}\cdot\mathbf{r} - \omega t)}]\cdot\nabla \quad ...(6)$$

Assuming nth state as *initial state*, equation (12) of section 8·1, for a final state m becomes

$$i\hbar\,\dot{a}_m^{(1)}(t) = (H'_{int})_{mn}\,e^{i\omega_{mn}t} \qquad \text{where } \omega_{mn} = \left(\frac{E_m - E_n}{\hbar}\right)$$

$$= H'_{mn}\,e^{i\,(\omega_{mn} - \omega)\,t} + H''_{mn}\,e^{i\,(\omega_{mn} + \omega)\,t} \quad ...(7)$$

where

$$\left.\begin{aligned} H'_{mn} &= \frac{ie\hbar}{mc}\int \psi_m^{0*}\,e^{i\,(\mathbf{k}\cdot\mathbf{r})}\,(\mathbf{A_0}\cdot\nabla)\,\psi_n^0\,d\tau \\ H''_{mn} &= \frac{ie\hbar}{mc}\int \psi_m^{0*}\,e^{-i\,(\mathbf{k}\cdot\mathbf{r})}\,(\mathbf{A_0}^*\cdot\nabla)\,\psi_n^0\,d\tau \end{aligned}\right] \quad ...(8)$$

If harmonic perturbation of frequency ω is switched on at $t = 0$, then equation (7) on integration with respect to t gives

$$a_m^{(1)}(t) = \frac{1}{i\hbar}\left[\int_0^t H'_{mn}\, e^{i(\omega_{mn}-\omega)t}\, dt + \int_0^t H''_{mn}\, e^{i(\omega_{mn}+\omega)t}\, dt\right]$$

$$= H'_{mn}\,\frac{1 - e^{i(\omega_{mn}-\omega)t}}{\hbar(\omega_{mn}-\omega)} + H''_{mn}\,\frac{1 - e^{i(\omega_{mn}+\omega)t}}{\hbar(\omega_{mn}+\omega)} \quad ...(9a)$$

Using $\omega_{mn} = \dfrac{E_m - E_n}{\hbar}$, we get

$$a_m^{(1)}(t) = H'_{mn}\left\{\frac{1 - e^{i(E_m - E_n - \hbar\omega)t/\hbar}}{E_m - E_n - \hbar\omega}\right\} + H''_{mn}\left\{\frac{1 - e^{i(E_m - E_n + \hbar\omega)t/\hbar}}{E_m - E_n + \hbar\omega}\right\} \quad ...(9b)$$

Out of the two terms in (9) only one term at a time is to be considered. If $E_m - E_n - \hbar\omega = 0$ or $E_m - E_n = \hbar\omega$ the first term will be very large compared with the second; but if

$$E_m - E_n + \hbar\omega = 0 \quad \text{or} \quad E_m - E_n = -\hbar\omega$$

the second term will be large compared to first, while if neither of these conditions is satisfied, the probability of transition is vanishingly small This means that the transitions are probable only if

$$E_m - E_n = \pm\hbar\omega \quad ...(10)$$

which is Bohr's frequency condition which appears here not as a postulate but as a deduction.

Of these two probabilities *one corresponds to an* **absorption of** *radiation from the field* and other to an **emission induced** *by the field.* It is quite remarkable that we obtain quantisation of energy even though we have not assumed the quantisation of electromagnetic field initially. Equation (10) assumes the convervation of energy between the particle and the field.

For absorption : ($E_m > E_n$) the probability is maximum for $\omega_{mn} = \omega$ or $E_m - E_n = \hbar\omega$ and first term of (9) predominates while the second term is negligible. Thus for absorption

$$a_m^{(1)}(t) = H'_{mn}\,\frac{1 - e^{(\omega_{mn}-\omega)t}}{\hbar(\omega_{mn}-\omega)} \quad ...(11)$$

∴ The probability of finding the system in m-state at the end of the interval t is

$$|a_m^{(1)}(t)|^2 = |H'_{mn}|^2\,\frac{4\sin^2\frac{1}{2}(\omega_{mn}-\omega)t}{\hbar^2(\omega_{mn}-\omega)^2}. \quad ...(12)$$

Thus for absorption the probability is proportional to $|H'_{mn}|^2$.

So far we have considered only a single frequency ω. Since the probability $|a_m^{(1)}(t)|^2$ is very small except when $\omega_{mn} = \omega$; the random motion of emitting and absorboing atoms produce a Doppler broadening of spectral lines and the radiation present in the initial state has a continnum of frequencies. If the intensity in the smaller angular frequency range $\Delta\omega$ is $I(\omega)\,\Delta\omega$, then the magnitude of Poynting vector is

$$I(\omega)\,\Delta\omega = \frac{\omega^2}{2\pi c}\,|A_0|^2 \quad \text{or} \quad |A_0|^2 = \frac{2\pi c}{\omega^2}\,I(\omega)\,\Delta\omega \quad ...(13)$$

Here A_0 is the vector potential amplitude and characterises the frequency range.

The *transition probability for absorption* is

$$|a_m^{(1)}(t)|^2 = \sum_n \frac{8\pi e^2}{m^2 c\,\omega^2}\,I(\omega)\,\Delta\omega\left|\int \psi_n^{0*}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, grad_A\, \psi_n^0\, d\tau\right|^2 \cdot \frac{\sin^2\{(\omega_{mn}-\omega)\frac{1}{2}t\}}{(\omega_{mn}-\omega)^2} \quad ...(14)$$

where grad_A is the component of the gradient operator along the polarisation vector $\mathbf{A}_0$. On account of being no phase relations between the radiation components of different frequencies, the contributions to the probability from various frequency ranges are additive. Each frequency range $\Delta\omega$ in equation (14) can be made infinitesimal and then the summation can be replaced by an integration. As the time factor has a sharp maximum at $\omega = \omega_{mn}$ the other factors involving can be taken outside the integral and the limits on ω can be extended to $\pm\infty$. By doing so the *transition probability per unit time* for an upward transition (*absorption*) becomes.

$$\frac{1}{t}\,|\,a_m^{(1)}(t)\,|^2 = \frac{8\pi e^2}{m^2\,c\omega_{mn}^2}\,I(\omega_{mn})\left|\int \psi_m^{0*}\,e^{i\mathbf{k}.\mathbf{r}}\,grad_A\,\psi_n^0\,d\tau\right|^2 \times \int_{-\infty}^{+\infty}\frac{\sin^2\{(\omega_{mn}-\omega)\frac{1}{2}t\}}{t\,(\omega_{mn}-\omega)^2}\,d\omega$$

$$= \frac{4\pi^2 e^2}{m^2 c\omega_{mn}^2}\,I(\omega_{mn})\,|\int \psi_m^{0*}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,grad_A\,\psi_n^0\,d\tau\,|^2 \qquad \text{...(15)}$$

$$\left[\text{since}\int_{-\infty}^{+\infty}\frac{\sin^2\{(\omega_{mn}-\omega)\frac{1}{2}t\}}{\{(\omega_{mn}-\omega)/2\}^2}\cdot d\omega = 2\pi t\right]$$

where the magnitude of $\mathbf{k}$ is now $\frac{\omega_{mn}}{c}$.

For **emission** *i.e.* for the downward transition there is a similar result, the only difference being that $e^{i\mathbf{k}.\mathbf{r}}$ is replaced by $e^{-i\mathbf{k}.\mathbf{r}}$ *i.e. the transition probability per unit time of a downward transition* $(E_{m'} = E_n - \hbar\,\omega)$ is given by

$$\frac{1}{t}\left|\,a_m^{(1)}(t)\right|^2 = \frac{4\pi^2 e^2}{m'^2\,c\omega_{nm'}^2}\,I(\omega_{nm'})\left|\int \psi_{m'}^*\,e^{-i\mathbf{k}.\mathbf{r}}\,grad_A\,\psi_n^0\,d\tau\right|^2 \qquad \text{...(16)}$$

where the magnitude of $\mathbf{k}$ is $\frac{\omega_{nm'}}{c}$.

Interpretation in terms of Absorption and Emission.

Equation (15) and (16) represent the transition probabilities of the particle per unit time between stationary states under the influence of a classical radiation field. Let us now interpret these expressions in terms of absorption and emission of quanta of electromagnetic radiation by assuming that such quanta exist and provide the energy units of the radiation field and that energy is conserved between the field and that particle.

In an upward transition the particle gains the amount of energy $E_m - E_n$ under the incluence of angular frequency ω_{mn}. The quantum energy of this radiation is $(E_m - E_n) = \hbar\,\omega_{mn}$, so that we may consider that the upward transition of the particle is associated with the *absorption* of the one quantum from the radiation field.

Similarly the downward transition may be considered to be associated with *emission* of the quantum whose energy corresponds to the frequency of the radiation field. According to equation (16) the transition probability of emission per unit time is proportional to the intensity of the radiation present. The process of emission is therefore called the *induced emission.*

If we rewrite equation (16) in terms of the reverse transition to that which appears in (15). Equation (15) describes the transition from an initial lower state n to a final upper state m, equation (16) can be made to describe the transition from an initial upper state m to a final lower state n if n is replaced by m and m' by n. Then equation (16) takes the form

$$\frac{4\pi^2 e^2}{m^2 c\omega_{mn}^2} I(\omega_{mn}) \left| \int (\psi_n^{0*} e^{-i\mathbf{k}\cdot\mathbf{r}}) \nabla_A \psi_m^0 d\tau \right|^2 \qquad ...(17)$$

It can be seen that the integral in (17) is just negative of the complex conjugate of integral in (15). The squares of magnitudes of both integrals in (15) and (17) are equal . This implies that the *transition probabilities of absorption and induced emission between any pair of states are the same.*

Electric-dipole Approximation.

The integral in equation (15) is usually evaluated by expanding the exponential ($e^{i\mathbf{k}\cdot\mathbf{r}}$) term by term *i.e.*

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i k\cdot r + \frac{(i\mathbf{k}\cdot\mathbf{r})^2}{2\,!} + \dots \qquad ...(18)$$

The magnitudes of the successive terms

$$1 : \mathrm{k}\cdot\mathrm{r} : \frac{(\mathrm{k}\cdot\mathrm{r})^2}{2} : \equiv 1 : \frac{2\pi r}{\lambda} = \frac{1}{2}\left(\frac{2\pi r}{\lambda}\right)^2 : \qquad ...(19)$$

i.e. the magnitude of successive terms decrease by factors of the order of magnitude r/λ. The integral is now to be taken over the space occupied by the atom and the integrand is virtually zero at distances from the origin which are greater than 10^{-8} cm. For visible and ultraviolet transitions $\lambda = 10^{-5}$ cm. Therefore r/λ is of the order of 10^{-3} and so, in this case, we approximate $e^{i\mathbf{k}\cdot\mathbf{r}} = 1$. We now show that the approximation of replacing $e^{i\mathbf{k}\cdot\mathbf{r}}$ by unity is *equivalant to replacing the atom by an electric dipole.*

The resulting integral can be simplified by expressing it as a matrix element of the momentum of the particle *i.e.*

$$\begin{aligned}\int \psi_m^{0*}\, grad_A\, \psi_n^0\, d\tau &= \int \psi_m^{0*} \left(\frac{\partial}{\partial r}\right)_A \psi_n^0\, d\tau \\ &= \frac{i}{\hbar} \int \psi_m^0\, p_A\, \psi_n^0\, d\tau \\ &= \frac{i}{\hbar} < p_A >_{mn} \qquad ...(20)\end{aligned}$$

where p_A is the component of the momentum **p** along the direction of polarisation of the incident radiation.

But
$$\begin{aligned}< \mathbf{p} >_{mn} &= m\frac{d}{dt} < \mathbf{r} >_{mn} = \frac{m}{i\hbar}\, [< \mathbf{r} >,\, H_0] \\ &= \frac{m}{i\hbar}\, [< \mathbf{r} >,\, H_0]_{mn} \\ &= \frac{m}{i\hbar} \left\{\int \psi_m^{0*}\, \mathbf{r}\, H_0 \psi_n^0\, d\tau - \int \psi_m^{0*}\, H_0\, \mathbf{r}\, \psi_n^0\, d\tau\right\} \\ &= \frac{m}{i\hbar} (E_n - E_m)\, (\mathbf{r})_{mn} = -\frac{m}{i}\, \omega_{mn}\, (\mathbf{r})_{mn} \qquad ...(21)\end{aligned}$$

$$\therefore \quad \begin{aligned}\int \psi_m^{0*}\, grad_A\, \psi_n^0\, d\tau &= -\frac{m}{\hbar}\, \omega_{mn} < r_A >_{mn} \\ &= -\frac{m}{\hbar}\, \omega_{mn} \int \psi_m^{0*}\, \mathbf{r}_A\, \psi_n^0\, d\tau \qquad ...(22)\end{aligned}$$

where r_A is the component of **r** along the direction of polarisation.

$$\therefore \quad \left|\int \psi_m^*\, grad_A\, \psi_n\, d\tau\right| = \frac{m}{\hbar}\, \omega_{mn} \int \psi_m^{0*}\, r_A\, \psi_n^0\, d\tau \qquad ...(23)$$

Then equation (15) for transition probability per unit time for absorption becomes

$$P_{mn} = \frac{1}{t} |a_m^{(1)}(t)|^2 = \frac{4\pi^2}{\hbar^2 c} I(\omega_{mn}) \; | e < \mathbf{r}_A >_{mn} |^2. \quad ...(24)$$

This involves only the matrix elements of the electric dipole moment $e\mathbf{r}$ of the particle thus indicating that replacement of $e^{i\,\mathbf{k}\cdot\mathbf{r}}$ by unity is simply the replacement of atom by an electric dipole. Thus the transition probabilities per unit time of absorption and induced emission can now we written as

$$P_{mn} = \frac{4\pi^2}{\hbar^2 c} I(\omega_{mn}) \; | e < \mathbf{r}_A >_{mn} |^2. \quad ...(25)$$

If the incident radiation is plane polarised, we calculate the x, y, z component of dipole moment and average over all orientations, so that the transition probability per unit time will be

$$P_{mn} = \frac{1}{t} | a_m^{(1)}(t) |^2 = \frac{4\pi^2}{3\hbar^2 c} I(\omega_{mn}) \; | e < \mathbf{r}_A >_{mn} |^2. \quad ...(26)$$

Einstein Transition Probabilities : It is convenient to define a transition probability per unit time per unit of radiation intensity for the transition $\psi_n \to \psi_m$ absorption $(E_m > E_n)$ denoted by Einstein B-coefficient

$$B_{n \to m} = \frac{|a_m^{(1)}(t)|^2}{t\, I(\omega_{mn})} = \frac{4\pi^2}{3\hbar^2 c} \; | e(\mathbf{r})_{mn} |^2 \quad ...(27)$$

By the principle of *detailed balance* [it may be noted that

$$\{| (\mathbf{r})_{mn} |^2 = | (\mathbf{r})_{nm} |^2\}$$

the probabilities of induced absorption $(B_{n \to m})$ and induced emission $(B_{m \to n})$ are equal for any pair of states *i.e.*

$$B_{n \to m} = B_{m \to n} \quad ...(28)$$

The above discussion does not account for spontaneous emission. It is known that a system in an excited state can emit radiation even in the absence of any external field. Einstein A-coefficient $(A_{m \to n})$ simply by considering the equilibrium of two states of different energies. If N_m and N_n are the number of systems in the states with energy E_m and E_n respectively, then according to *Boltzmann's distribution law* for equilibrium at absolute temperature T we have

$$\frac{N_m}{N_n} = \frac{e^{-E_m/kT}}{e^{-E_n/kT}} = e^{-(E_m - E_n)/kT} = e^{-\hbar\omega_{mn}/kT} \quad ...(29)$$

where k is *Boltzmann's constant.*

The number of systems emitting radiation (transition $m \to n$) per unit time is

$$N_m \{(A_{m \to n}) + B_{m \to n} I(\omega_{mn})\} \quad ...(30)$$

and the number of systems making reverse transitions (absorption) per unit time is

$$N_n B_{n \to m} I(\omega_{mn}) \quad ...(31)$$

At equilibrium these two numbers must be equal

i.e. $$N_m \{(A_{m \to n}) + A_{m \to n} I(\omega_{mn})\} = N_n B_{n \to m} I(\omega_{mn})$$

or $$\frac{N_m}{N_n} = \frac{B_{n \to m} I(\omega_{mn})}{A_{m \to n} + B_{m \to n} I(\omega_{mn})} \quad ...(32)$$

Also since $B_{n \to m} = B_{m \to n}$ and using (29), equation (32) may be expressed as

$$e^{-\hbar\omega_{mn}/kT} = \frac{B_{m \to n}I(\omega_{mn})}{A_{m \to n} + B_{m \to n}I(\omega_{mn})}$$

This gives

$$I(\omega_{mn}) = \frac{A_{m \to n}/B_{m \to n}}{e^{\hbar\,\omega_{mn}/kT} - 1} \qquad ...(33)$$

But by Planck's distribution law

$$I(\omega_{mn}) = \frac{\hbar\omega_{mn}^3}{\pi^2 c^2} \cdot \frac{1}{e^{\hbar\,\omega_{mn}/kT} - 1} \qquad ...(34)$$

Comparing (33) and (34), we note that
Einstein A-coefficient for spontaneous emission is

$$A_{m \to n} = \frac{\hbar\omega_{mn}^3}{\pi^2 c^2} B_{m \to n}$$

$$= \frac{\hbar\omega_{mn}^3}{\pi^2 c^2} \cdot \frac{4\pi^2}{3\hbar^2 c} |e\,(\mathbf{r})_{mn}|^2 \qquad \text{using (27)}$$

$$\because \quad A_{m \to n} = \frac{4\omega_{mn}^3}{3\hbar c^3} |e\,(\mathbf{r})_{mn}|^2 \qquad ...(35)$$

Selection Rules :

It is clear from equation (25) that dipole transitions between states f, i are possible only if

$$e < \mathbf{r} >_{fi} \neq 0$$

If this is the case, the states under consideration have definite angular momenta, this condition then gives the selection rule governing the change of angular momentum. From the property of spherical harmonics, it follows that

$$\int (Y_{l_f m_f})^* \, Y_{l_i m_i} \, d\tau \neq 0 \quad \text{only if } l_f - l_i = \pm 1$$

This result can be obtained more generally if it is assumed that **r** is a vector operator *i.e.* a spherical tensor of rank one. Hence its matrix element between the angular momentum eigen states are proportional to Clebsch-Gordan coeficient $< l_i \; m_i \, ; \, 1 \; l_f \; m_f >$ by Wigner Eckart theorem. Hence it vanishes if $|\Delta l| = (l_i - l_f|$ exceeds one. Further the matrix elements for $\Delta l = 0$ vanish because **r** is of odd parity.

Thus the selection rule for l remains $\Delta l = \pm 1$. From the properties of Clebsch Gorden coefficient it is also clear that $\Delta m = m_f - m_i$ is limited to $\Delta m = \pm 1, 0$. The polarisation vector **A** determines which of these cases can occur. For example of **A** is along z-axis, then $(\mathbf{r_A})_{fi} = z_{fi}$. As $z = r \cos\theta$. which is independent of ϕ this corresponds to $m = 0$ in Clebsch Gorden coefficients and hence the **selection rule** for m is $\Delta m = 0$.

Thus the selection rules are $\Delta m = 0$, $\Delta l_\cdot = \pm 1$.

The transitions which occur under dipole selection rules are called allowed transitions.

Forbidden transitions : The transitions which are forbidden by selection rules of dipole approximation may occur, but with greatly reduced probability. These arise from the higher order terms in the expansion

$$e^{i\,\mathbf{k}\cdot\mathbf{r}} = 1 + i\,\mathbf{k}\cdot\mathbf{r} + \frac{(i\,\mathbf{k}\cdot\mathbf{r})^2}{2\,!} + \ldots = \Sigma\,\frac{(i\,\mathbf{k}\cdot\mathbf{r})^r}{n\,!} \text{ (powers series)}$$

or as a series of spherical harmonics

$$e^{i\mathbf{k}\cdot\mathbf{r}} = j_0(kr) + 3i\, J_l(kr)\, P_l(\cos\theta) - 5 j_2(kr)\, P_2(\cos\theta) + \ldots$$
$$= \Sigma\,(2l+1)\, i^l\, j_l(kr)\, P_l(\cos\theta)$$

where θ is the angle between **k** and **r**. In either case the nth term of the series is of the order $(kr)^{n-1}$. The dominent factor in nth term is proportional to $(kr)^{n-1}$ for $kr << 1$. Thus if the dipole matrix element vanishes but the next term of each series does not, the transition matrix element is reduced by a factor that has the order of magnitude ka; where a is the order of the linear dimension of the particle's wave function. The typical value of ka is 10^{-3} and the correponding probability is smaller by $(ka)^2 = 10^{-6}$. Such transitions are called the forbidden transitions. Even for $l = 1$, the forbidden transitions are very much weaker than those from allowed transitions. The successive terms of the series can be interpreted in terms of electric dipole, electric quadrupole etc. transitions and involve successive higher powers of ka.

Finally we observe that the certain transitions are strictly forbidden in the sense that the exact (first order) transition matrix element vanishes; $I(\omega_{fi}) < r_A >_{fi} \rightarrow 0$ This is the case if both i and f are s-states.

If the dipole transition is forbidden we must take further terms in the expansion of $e^{i\mathbf{k}\cdot\mathbf{r}}$, but if the transition is strictly forbidden we must take higher orders of the perturbation theory and should not neglect the term $q^2A^2/2mc^2$: this then leads to the simultaneous emission of the two photons.

Questions and Problems

1. Discuss the first order time dependent perturbation theory and derive the Femi-golden rule for the transition rate from a given initial state to a final state of continuum. **(Meerut 1997, 96, 90, 82, 81)**
2. Give the time dependent perturbation theory for the case of a perturbation which is constant in time except; that it is switched on at $t = 0$ and swiched off at time t. **(Rohilkhand 85; Agra 81)**
3. Give time-dependent perturbation theory for a constant perturbation acting for a short interval of time. Relate the transition probability per unit time with the differential cross-section for scattering.
4. Prove that the transition probability per unit time is

$$\frac{2\pi}{\hbar}\,\rho(k)\,|H_{km}'|^2$$

where $\rho(k)$ denotes the density of final states and H_{km} is the matrix element of the perturbation term. **(Meerut 78; Agra 71)**

5. Show that the transition probability per unit time for a system to make a transition from an initial state to a final in the continuum is given by

$$\omega_{mn} = \frac{2\pi}{\hbar}\,\rho(k)\,|<k\,|H'|\,m>|^2$$

(Meerut 83)

6. Discuss briefly the time dependent perturbation theory and derive and expression for the transition probability to a group of states per unit time. **(Agra 72)**
7. Obtain expression for transtion probability per unit time, in the first order when constant perturbation acts on the system. Discuss limitations of any of the formula derived. **(Rohilkhand 1992)**
8. The amplitude of the k th state under the first order time dependent perturbation theory is given by $a_k^{(1)}(t) = \frac{1}{2}\hbar\int_{-\infty}^{+\infty} <k\,|H'(t')|\,m> e^{i\omega_{km}t'}\,dt'$. The sytem is subjected to a harmonic perturbation of the type $H'(t) = 2H'\sin\omega t$ which is swiched on at $t = 0$ and off at $t = t_0$. Show that the probability per unit time for an upward transition is given by

$$\omega = \frac{2\pi}{\hbar}\,|<k\,|H'|\,m>|^2\,\rho(k)$$

9. (a) Show that the first order effect of a time-dependent perturbation, varying siunsoidally in time, leads to the emission or absorption of energy **(Jivaji 1988)**
   (b) Give an outline of the derivation of the "dipole selection rule" $\Delta l = \pm 1$, $\Delta m = 0, \pm 1$. What are strictly forbidden transitions. **(Rohilkhand 1998)**
10. Give the time dependent perturbation for a harmonic perturbation. Discuss the electric dipole approximation. **(Rohilkhand 78; Raj 85)**

1 Quantum theory of radiation:

The Hamiltonian for the Radiation field:

We now whish to compute the Hamiltonian in terms of the certificate $c_k\,;\alpha(t)$. This is an important calculation because we will use the Hamiltonian formalism to do the quantization of the field. we will do the calculation using the convariant notation (while sakurai outlines an alternate using 3-vector).

we have already calculated the Hamiltonian density for a classical EM Field.

$$\mathcal{H} = F_{\mu 4}\frac{\partial A_\mu}{\partial x_4} + \frac{1}{4}F_{\mu\nu}F_{\mu\nu}$$

$$\mathcal{H} = \left(\frac{\partial A_4}{\partial x_\mu} - \frac{\partial A_\mu}{\partial x_4}\right)\frac{\partial A_\mu}{\partial x_4} + \frac{1}{4}\left(\frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\mu}{\partial x_\nu}\right)\left(\frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\mu}{\partial x_\nu}\right)$$

$$\mathcal{H} = -\frac{\partial A_\mu}{\partial x_4}\frac{\partial A_\mu}{\partial x_4} + \frac{1}{2}\left(\frac{\partial A_\nu}{\partial x_\mu}\frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\nu}{\partial x_\mu}\frac{\partial A_\mu}{\partial x_\nu}\right)$$

Now lets compute the basic element of the above formula for our decomposed radiation field.

$$A_\mu = \frac{1}{\sqrt{V}}\sum_{k}\sum_{\alpha=1}^{2}\varepsilon_\mu^{(\alpha)}\left(c_{k,\alpha}(0)e^{ik_\rho x_\rho} + c^{*}_{k,\alpha}(0)e^{-ik_\rho x_\rho}\right)$$

$$\frac{\partial A_\mu}{\partial x_\nu} = \frac{1}{\sqrt{V}} \sum_K \sum_{\alpha=1}^{2} \varepsilon_\mu^{(\alpha)} \left(C_{k,\alpha}(0)(ik_\nu)e^{ik_\rho x_\rho} + C^*_{k,\alpha}(0)(-ik_\nu)e^{-ik_\rho x_\rho} \right)$$

$$\frac{\partial A_\mu}{\partial x_\nu} = i \frac{1}{\sqrt{V}} \sum_K \sum_{\alpha=1}^{2} \varepsilon_\mu^{(\alpha)} k_\nu \left(C_{k,\alpha}(0)e^{ik_\rho x_\rho} - C^*_{,\alpha}(0)e^{-ik_\rho x_\rho} \right)$$

$$\frac{\partial A_\mu}{\partial x_4} = -\frac{1}{\sqrt{V}} \sum_K \sum_{\alpha=1}^{2} \varepsilon_\mu^{(\alpha)} \frac{\omega}{c} \left(C_{k,\alpha}(0)e^{ik_\rho x_\rho} - C_k^*{}_{,\alpha}(0)e^{-ik_\rho x_\rho} \right)$$

we have all the elements to finish the calculation of the Hamiltonian. Before pulling this all together in a brute force way, Its good to realize that almost all the terms will give zero. We see that the derivative of A_μ is proportional to a 4-vector, say k_ν and to a polarization vector, say $\varepsilon_\mu^{(\alpha)}$. The dot products of the 4-vectors, either k with itself or k with ε are zero. Going back to our expression for the Hamiltonian density, we can eliminate some ~~terms~~ terms.

$$\mathcal{H} = -\frac{\partial A_\mu}{\partial x_4}\frac{\partial A_\mu}{\partial x_4} + \frac{1}{2}\left(\frac{\partial A_\nu}{\partial x_\mu}\frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\nu}{\partial x_\mu}\frac{\partial A_\mu}{\partial x_\nu} \right)$$

$$\mathcal{H} = -\frac{\partial A_\mu}{\partial x_4}\frac{\partial A_\mu}{\partial x_4} + \frac{1}{2}(0 - 0)$$

$$\mathcal{H} = -\frac{\partial A_\mu}{\partial x_4}\frac{\partial A_\mu}{\partial x_4}$$

The remaining term ~~as~~ has a dot between polarization vectors which will be non-zero if the polarization vectors are same. (Note that this simplification is possible because we have assumed no sources in the region).

The total Hamiltonian we are aiming at, the integral of the Hamiltonian density -

$$H = \int d^3x \, \mathcal{H}$$

When we integrate over the volume only products like $e^{ik_\rho x_\rho} e^{-ik_\rho x_\rho}$ will give a nonzero result. So when we multiply one sum over k by another, only the terms with the same k will contribute to the integral, basically because the waves with different wave number are orthogonal.

$$\frac{1}{V}\int d^3x \, e^{ik_\rho x_\rho} e^{-ik'_\rho x_\rho} = \delta_{kk'}$$

$$H = \int d^3x \, \mathcal{H}$$

$$\mathcal{H} = -\frac{\partial A_\mu}{\partial x_4}\frac{\partial A_\mu}{\partial x_4}$$

$$\frac{\partial A_\mu}{\partial x_4} = -\frac{1}{\sqrt{V}}\sum_k \sum_{\alpha=1}^{2} \varepsilon_\mu^{(\alpha)} \Big(c_{k,\alpha}(0)\frac{\omega}{c} e^{ik_\rho x_\rho} - c^*_{k,\alpha}(0)\frac{\omega}{c} e^{-ik_\rho x_\rho}\Big)$$

$$H = -\int d^3x \frac{\partial A_\mu}{\partial x_4} \frac{\partial A_\mu}{\partial x_4}$$

$$H = -\int d^3x \frac{1}{V} \sum_K \sum_{\alpha=1}^{2} \left(c_{K,\alpha}(0) \frac{\omega}{c} e^{ik_\rho x_\rho} - c_{K,\alpha}(0) \frac{\omega}{c} e^{-ik_\rho x_\rho} \right)^2$$

$$H = -\sum_K \sum_{\alpha=1}^{2} \left(\frac{\omega}{c}\right)^2 \left[-c_{K,\alpha}(t) c^*_{K,\alpha}(t) - c^*_{K,\alpha}(t) c_{K,\alpha}(t) \right]$$

$$H = \sum_K \sum_{\alpha=1}^{2} \left(\frac{\omega}{c}\right)^2 \left[c_{K,\alpha}(t) c^*_{K,\alpha}(t) + c^*_{K,\alpha}(t) c_{K,\alpha}(t) \right]$$

$$H = \sum_{K,\alpha} \left(\frac{\omega}{c}\right)^2 \left[c_{K,\alpha}(t) c^*_{K,\alpha}(t) + c^*_{K,\alpha}(t) c_{K,\alpha}(t) \right]$$

This is the result we will use to quantize the field. We have been careful not to commute C and C^* here in anticipation of the fact that they do not commute.

It should not be a surprise that the terms that made up the Lagrangian gave a zero contribution because $\mathcal{L} = \frac{1}{2}(E^2 - B^2)$ and we know that E and B have the same magnitude in a radiation field. (There is one wrinkle we have glossed over, terms with $\vec{K'} = -\vec{K}$).

Fourier decomposition of Radiation oscillators:

Our goal is to write the Hamiltonian for the radiation field in terms of a sum of harmonic oscillator Hamitonians. The first step is to write the radiation field in as simple a way as possible, as a sum of harmonic components. We will work in a cublic volume $V = L^3$ and apply priodic boundary condition on our electromagnetic waves. We also assume for now that there are no sources inside the region so that we can make a gauge transformation to make $A_0 = 0$ and hence $\vec{\nabla} \cdot \vec{A} = 0$ we decompose the field into its Fourier components at $t=0$

$$\vec{A}(\vec{x}, t=0) = \frac{1}{\sqrt{V}} \sum_{K} \sum_{\alpha=1}^{2} \hat{\varepsilon}^{(\alpha)} \left(C_{K,\alpha}(t=0) e^{i\vec{K}\cdot\vec{x}} + C_{K,\alpha}(t=0) e^{-i\vec{K}\cdot\vec{x}} \right)$$

where $\hat{\varepsilon}^{(\alpha)}$ are real unit vectors, and $C_{K,\alpha}$ is the coefficient of the wave with wave vector $\vec{K}$ and polarization vector $\hat{\varepsilon}^{(\alpha)}$. Once the wave vector is chosen, the two polarization vectors must be picked so that $\hat{\varepsilon}^{(1)}$, $\hat{\varepsilon}^{(2)}$ and $\vec{k}$ form a right handed orthogonal system.

The component of the vector must satisfy,

$$k_i = \frac{2\pi n_i}{L}$$

due to the periodic boundary conditions.

The factor out front is set to normalize the states nicely since,

$$\frac{1}{V}\int d^3x\, e^{i\vec{k}\cdot\vec{x}} e^{-i\vec{k}'\cdot\vec{x}} = \delta_{\vec{k}\vec{k}'}$$

and

$$\hat{\varepsilon}^{(\alpha)} \cdot \hat{\varepsilon}^{(\alpha')} = \delta_{\alpha\alpha'}.$$

we know the time dependence of the wave from Maxwell's equations,

$$C_{k,\alpha}(t) = C_{k,\alpha}(0)\, e^{-i\omega t}$$

where $\omega = kc$. we can now write the vector potential as a function of position and time:

$$\vec{A}(\vec{x},t) = \frac{1}{\sqrt{V}} \sum_{k} \sum_{\alpha=1}^{2} \hat{\varepsilon}^{(\alpha)} \left(C_{k,\alpha}(t)\, e^{i\vec{k}\cdot\vec{x}} + C^{*}_{k,\alpha}(t)\, e^{-i\vec{k}\cdot\vec{x}} \right.$$

we may write this solution in servel different ways and use the best one for the calculation being performed. one nice way to write this is in terms 4-vector k_μ, the wave number.

$$k_\mu = \frac{p_\mu}{\hbar} = (k_x, k_y, k_z, ik) = \left(k_x, k_y, k_z, i\frac{\omega}{c}\right.$$

so that

$$k_\rho x_\rho = k.x = \vec{k}\cdot\vec{x} - \omega t$$

we can then write the radiation field in a more covariant way.

$$\vec{A}(\vec{x},t) = \frac{1}{\sqrt{V}}\sum_{k}\sum_{\alpha=1}^{2}\hat{\epsilon}^{(\alpha)}\left(c_{k,\alpha}(0)e^{ik_\rho x_\rho} + c^{\dagger}_{k,\alpha}(0)e^{-ik_\rho x_\rho}\right)$$

A convenient shorthand for calculation is possible by noticing that the second term is just the complex conjugate of the first.

$$\vec{A}(\vec{x},t) = \frac{1}{\sqrt{V}}\sum_{k}\sum_{\alpha=1}^{2}\hat{\epsilon}^{(\alpha)}\left(c_{k,\alpha}(0)e^{ik_\rho x_\rho} + c.c\right).$$

$$\vec{A}(\vec{x},t) = \frac{1}{\sqrt{V}}\sum_{k}\sum_{\alpha=1}^{2}\hat{\epsilon}^{(\alpha)}c_{k,\alpha}(0)e^{ik_\rho x_\rho} + c.c.$$

Note again that we have made this a transverse field by construction. The unit vector $\hat{\epsilon}^{(\alpha)}$ are transverse to the direction of propagation. Also note that we are working in a gauge with $A_4 = 0$, so, this can also represent the 4-vector form of the potential. The Fourier decomposition of the radiation field can be written very simply.

$$\boxed{A_\mu = \frac{1}{\sqrt{V}}\sum_{k}\sum_{\alpha=1}^{2}\epsilon_\mu^{(\alpha)}c_{k,\alpha}(0)e^{ik_\rho x_\rho} + c.c}$$

This choice of gauge makes switching between 4-vector and 3-vector expressions for the potential trivial.

Let's verify that this decomposition of the radiation field the satisfies the Maxwell equation, just for some partice. It's most convenient to use the covariant form of the equation and field. $\Box A_\mu = 0$

$$\Box\left(\frac{1}{\sqrt{V}}\sum_K\sum_{\alpha=1}^{2}\varepsilon_\mu^{(\alpha)} C_{K,\alpha}(0)\, e^{iK_\rho x_\rho} + C.C\right) =$$

$$\frac{1}{\sqrt{V}}\sum_K\sum_{\alpha=1}^{2}\varepsilon_\mu^{(\alpha)} C_{K,\alpha}(0)\,\Box e^{iK_\rho x_\rho} + C.C$$

$$= \frac{1}{\sqrt{V}}\sum_K\sum_{\alpha=1}^{2}\varepsilon_\mu^{(\alpha)} C_{K,\alpha}(0)\left(-K_\nu K_\nu e^{iK_\rho x_\rho}\right) + C.C = 0$$

The results since $K_\nu K_\nu = K^2 - K^2 = 0$

Let's also verify that $\vec{\nabla}\cdot\vec{A} = 0$

$$\vec{\nabla}\cdot\left(\frac{1}{\sqrt{V}}\sum_K\sum_{\alpha=1}^{2}\hat{\varepsilon}^{(\alpha)} C_{K,\alpha}(t)\, e^{i\vec{K}\cdot\vec{x}} + C.C\right) =$$

$$\frac{1}{\sqrt{V}}\sum_K\sum_{\alpha=1}^{2} C_{K,\alpha}(t)\,\hat{\varepsilon}^{(\alpha)}\cdot\vec{\nabla} e^{i\vec{K}\cdot\vec{x}} + C.C.$$

$$= \frac{1}{\sqrt{V}}\sum_K\sum_{\alpha=1}^{2} C_{K,\alpha}(t)\,\hat{\varepsilon}^{(\alpha)}\cdot\vec{K}\, e^{i\vec{K}\cdot\vec{x}} + C.C = 0$$

The result here is zero because $\hat{\varepsilon}^{(\alpha)}\cdot\vec{K} = 0$.

Quantized Radiation Field:

The Fourier coefficients of the expansion of the classical radiation field should now be replaced operators

$$c_{k,\alpha} \rightarrow \sqrt{\frac{\hbar c^2}{2\omega}}\, a_{k,\alpha}$$

$$c^*_{k,\alpha} \rightarrow \sqrt{\frac{\hbar c^2}{2\omega}}\, a^\dagger_{k,\alpha}$$

$$A_\mu = \frac{1}{\sqrt{V}} \sum_{k\alpha} \sqrt{\frac{\hbar c^2}{2\omega}}\, \varepsilon_\mu^{(\alpha)} \left(a_{k,\alpha}(t) e^{i\vec{k}\cdot\vec{x}} + a^\dagger_{k,\alpha}(t) e^{-i\vec{k}\vec{x}} \right).$$

A is now an operator that acts on state vectors in occupation number space. The operator is parameterized in terms of $\vec{x}$ and t.

This Hamiltonian operator can also be written in terms of the creation and annihulation operators.

$$H = \sum_{k,\alpha} \left(\frac{\omega}{c}\right)^2 \left[c_{k,\alpha} c^{*}_{k,\alpha} + c^{*}_{k,\alpha} c_{k,\alpha}\right]$$

$$= \sum_{k,\alpha} \left(\frac{\omega}{c}\right)^2 \frac{\hbar c^2}{2\omega} \left[a_{k,\alpha} a^{\dagger}_{k,\alpha} + a^{\dagger}_{k,\alpha} a_{k,\alpha}\right]$$

$$= \frac{1}{2} \sum_{k\alpha} \hbar\omega \left[a_{k,\alpha} a^{\dagger}_{k,\alpha} + a^{\dagger}_{k,\alpha} a_{k,\alpha}\right]$$

$$\boxed{H = \sum_{k,\alpha} \hbar\omega \left(N_{k,\alpha} + \frac{1}{2}\right)}$$

For our purpose, we may remove the (infinite) constant energy due to the ground state energy of all the oscillators. It is simply the energy of the vaccum which we may define as zero. note that the field fluctations that cause this energy density, also cause the spontaneous decay of excited states of atoms.. one thing that must be done is to cut off the sum at some maximum value of k. we do not ~~except~~ expect electricity and magnetism to be completely valid up to infinite energy. certainly by the gravitational or grand unifield energy scale there must be important corrections to our formulas. The energy density of the vaccum is hard to define but plays an important role in cosmology. At this time, physicists have difficulty explaning how small the energy density in the vaccum is. Until recent experiments showed otherwise, most physicists thought it was actually zero due to some unknown symmetry. In any case we are not ready to consider this problem.

$$H = \sum_{k,\alpha} \hbar\omega N_{k,\alpha}$$

with this subtraction, the energy of vaccum state has been defined to be zero.

$$H|0\rangle = 0$$

The total momentum in the (transverse) radiation field can also be computed (From the classical formula for the poynting vector).

$$\vec{P} = \frac{1}{c}\int \vec{E}\times\vec{B}\, d^3x = \sum_{k,\alpha} \hbar\vec{k}\left(N_{k,\alpha} + \frac{1}{2}\right)$$

This time the $\frac{1}{2}$ can really be dropped since the sum is over positive and negative $\vec{k}$, so its sum to zero.

$$\vec{P} = \sum_{k,\alpha} \hbar \vec{k}\, n_{k,\alpha}$$

we can compete the energy and momentum of a single photon state by operating on that state with the Hamiltonian and with the total momentum operator. The state For a single photon with a given momentum and polarization can be written as $a^{\dagger}_{k,\alpha}|0\rangle$

$$H a^{\dagger}_{k,\alpha}|0\rangle = \left(a^{\dagger}_{k,\alpha} H + [H, a^{\dagger}_{k,\alpha}] \right)|0\rangle =$$

$$0 + \hbar\omega a^{\dagger}_{k,\alpha}|0\rangle = \hbar\omega a^{\dagger}_{k,\alpha}|0\rangle$$

The energy of single photon state is $\hbar\omega$

$$P a^{\dagger}_{k,\alpha}|0\rangle = \left(a^{\dagger}_{k,\alpha} P + [P, a^{\dagger}_{k,\alpha}] \right)|0\rangle = 0 + \hbar\vec{k}\, a^{\dagger}_{k,\alpha}|0\rangle$$

$$= \hbar\vec{k}\, a^{\dagger}_{k,\alpha}|0\rangle$$

The momentum of the single photon state is $\hbar\vec{k}$, The mass of the photon can be computed

$$E^2 = p^2c^2 + (mc^2)^2$$

$$mc^2 = \sqrt{(\hbar\omega)^2 - (\hbar k)^2 c^2} = \hbar\sqrt{\omega^2 - \omega^2} = 0$$

so, the energy, momentum, and mass of a single photon state are as we would expect.

The vector potential has been given two transverse polarization as expected from classical Electricity and Magnetism. The result is two possible transverse polarization vectors in our ~~p~~ quantized field. The photon states are also labeled by one of two polarizations, that we have so far assumed were linear polarizations. The polarization vector, and therefore the vector potential, transform like a Lorentz vector. We know that the matrix element of vector operators is associated with an angular momentum of one. When a photon is emitted, selection rules indicate it is carrying away an angular momentum of one, so we deduce that the photon has spin one. We need not add anything to our theory though; the vector properities of the field are already included in our assumptions about polarization.

Of course we could equally well use circular polarizations which are related to the linear set we have been using by,

$$\hat{\varepsilon}^{(\pm)} = \mp \frac{1}{\sqrt{2}} \left(\hat{\varepsilon}^{(1)} \pm i \hat{\varepsilon}^{(2)} \right).$$

The polarization $\hat{\varepsilon}^{(\pm)}$ is associated with the $m = \pm 1$ component of the photon's spin. These are the transverse mode of the photon, $\vec{K} \cdot \hat{\varepsilon}^{(\pm)} = 0$ we have separated the field into transverse and longitudinal parts. The longitudinal part is partially responsible for static E and B fields, while the transverse ~~and longitudinal parts. The~~ part makes up radiation. The $m = 0$ component of the photon is not present in radiation but is important in understanding static fields.

By assuming the canonical coordinates and momenta in the Hamiltonian have commutators like those of the position and momentum of the a particle, led to an understanding that radiations is made up of spin-1 particles with mass zero. All fields correspond to a particles of definite mass and spin.

we now have a pretty good idea how to quantize the field for any particles.

3 Emission and Absorption of photons by Atoms:

The interaction of an electron with the quantized field is already in the standard Hamiltonian.

$$H = \frac{1}{2m}\left(\vec{P} + \frac{e}{c}\vec{A}\right)^2 + V(r)$$

$$H_{int} = -\frac{e}{2mc}\left(\vec{P}\cdot\vec{A} + \vec{A}\cdot\vec{P}\right) + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A}$$

$$= -\frac{e}{mc}\vec{A}\cdot\vec{P} + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A}$$

For completeness we should add the interaction with the spin of the electron $H = -\vec{\mu}\cdot\vec{B}$

$$\boxed{H_{int} = -\frac{e}{mc}\vec{A}\cdot\vec{P} + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A} - \frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{\nabla}\times\vec{A}}$$

For an atom with many electron, we must sum over all the electrons. The fields is evaluated at the coordinate x which should that of the electron.

This interaction Hamiltonian contains operators to create and annihilate photons with transitions between atomic states. From our previous study of time dependent perturbation theory. we know that transitions between initial and final states are proportional to the matrix element of the perturbing Hamiltonian between the states $\langle n | H_{int} | i \rangle$. The initial states $|i\rangle$ should a direct product of the atomic states and the photon state. Let concentrate on one type of photon for now - we then could write,

$$|i\rangle = |\psi_i ; n_{\vec{k},\alpha}\rangle$$

with a similar expression for the final state.

We will first consider the absorption of one photon from the field. Assume there are $n_{k,\alpha}$ photons of this type in the initial state. and that one photon is absorbed. We therefore will need a term in the interaction Hamiltonian that contains an annihilation operator (only). This will just come from the linear term in A.

$$\langle n | H_{int} | i \rangle = \langle \psi_n ; n_{\vec{k},\alpha} - 1 | -\frac{e}{mc} \vec{A} \cdot \vec{p} | \psi_i ; n_{\vec{k},\alpha} \rangle$$

$$= -\frac{e}{mc} \langle \psi_n ; n_{\vec{k},\alpha} - 1 | \frac{1}{\sqrt{V}} \sqrt{\frac{\hbar c^2}{2\omega}} \epsilon^{(\alpha)} \left(a_{k,\alpha}(0) e^{ik_\rho x_\rho} + a^{\dagger}_{k,\alpha}(0) e^{-ik_\rho x_\rho} \right) \vec{p} | \psi_i ; n_{\vec{k},\alpha} \rangle .$$

$$\langle n|H_{int}^{(abs)}|i\rangle = -\frac{e}{mc}\frac{1}{\sqrt{V}}\sqrt{\frac{\hbar c^2}{2\omega}}\langle \psi_n ; n_{\vec{k},\alpha}-1|\cdot\vec{\epsilon}^{(\alpha)}\cdot\vec{p}$$

$$(a_{k,\alpha}(0)e^{ik_p x_p})|\psi_i ; n_{\vec{k},\alpha}\rangle$$

$$= -\frac{e}{m}\frac{1}{\sqrt{V}}\sqrt{\frac{\hbar}{2\omega}}\langle \psi_n ; n_{\vec{k},\alpha}-1|\vec{\epsilon}^{(\alpha)}\cdot\vec{p}$$

$$\sqrt{n_{\vec{k},\alpha}}\, e^{ik_p x_p}|\psi_i ; n_{\vec{k},\alpha}-1\rangle$$

$$= -\frac{e}{m}\frac{1}{\sqrt{V}}\sqrt{\frac{\hbar n_{\vec{k},\alpha}}{2\omega}}\langle \psi_n|e^{i\vec{k}\cdot\vec{r}}\vec{\epsilon}^{(\alpha)}\cdot\vec{p}$$

$$|\psi_i\rangle e^{-i\omega t}$$

similarly for the emission of a photon the matrix element is,

$$\langle n|H_{int}|i\rangle = \langle \psi_n ; n_{\vec{k},a}+1|-\frac{e}{mc}\vec{A}\cdot\vec{p}|\psi_i ; n_{\vec{k},\alpha}\rangle$$

$$\langle n|H_{int}^{(emit)}|i\rangle = -\frac{e}{mc}\frac{1}{\sqrt{V}}\sqrt{\frac{\hbar c^2}{2\omega}}\langle \psi_n ; n_{\vec{k},\alpha}+1|$$

$$\vec{\epsilon}^{(\alpha)}\cdot\vec{p}\, a^{+}_{k,\alpha}(0)e^{-ik_p x_p}|\psi_i ; n_{\vec{k},\alpha}\rangle$$

$$= -\frac{e}{m}\frac{1}{\sqrt{V}}\sqrt{\frac{\hbar(n_{\vec{k},\alpha}+1)}{2\omega}}\langle \psi_n|e^{-i\vec{k}\cdot\vec{r}}\vec{\epsilon}^{(\alpha)}\cdot\vec{p}$$

$$|\psi_i\rangle e^{i\omega t}$$

These give the same result as our earlier gauess to put an $n+1$ in the emission operator.