L24

Interaction of quantized (non-relativistic) matter with the quantized electromagnetic field

How does the quantization of the e.m. field change the picture?

The initial and final states must now have a specified number of photons (or a density matrix for a mixed state) $\Rightarrow$

$$|I\rangle = |n_i\rangle \times |\{N_i(\vec{k},\lambda)\}\rangle \equiv |n_i;\{N_i(\vec{k},\lambda)\}\rangle$$

$|n_i\rangle$: initial state of matter; $|\{N_i(\vec{k},\lambda)\}\rangle$: initial state of the e.m. field.

$$|F\rangle = |n_f\rangle \times |\{N_f(\vec{k},\lambda)\}\rangle \equiv |n_f;\{N_f(\vec{k},\lambda)\}\rangle$$

$|n_f\rangle$: final state of matter; $|\{N_f(\vec{k},\lambda)\}\rangle$: final state of e.m. field.

We specify the state of the particles by giving their initial and final quantum numbers. Similarly we specify the # of photons of each $\vec{k}$ and λ to specify the state of the e.m. field.

We recall that we can always write the Hamiltonian in the form

$$H = \sum_{i=1}^{N} \left\{ \frac{1}{2M} \left[\vec{P}_i - \frac{e}{c} \vec{A}(\vec{x}_i) \right]^2 + V(\vec{x}_i) \right\} +$$

$$+ \frac{1}{2} \int d^3x \int d^3x' \, \frac{\rho(\vec{x}) \, \rho(\vec{x}')}{|\vec{x} - \vec{x}'|} \qquad \leftarrow \text{Coulomb Interaction}$$

$$+ \int d^3k \sum_{\lambda} E(\vec{k}, \lambda) \, \hat{N}(\vec{k}, \lambda) + \underbrace{E_0}_{\text{irrelevant constant}}.$$

$$E(\vec{k}, \lambda) = \hbar \omega(\vec{k}) = \hbar c |\vec{k}| ,$$

in the eq. form

$$H = H_0 + H_{e.m} + H_{int}$$

$$H_0 = \sum_{i=1}^{N} \left[\frac{1}{2M} \vec{P}_i^{\,2} + V(\vec{x}_i) \right] + \sum_{i,j} \frac{e^2}{2} \frac{1}{|\vec{x}_i - \vec{x}_j|}$$

$$H_{em} = \int d^3k \sum_{\lambda} E(\vec{k}) \, \hat{N}(\vec{k}, \lambda) + \cancel{E_0}$$

$$H_{int} = \int d^3x \left[-\frac{e}{c} \vec{j}(\vec{x}) \cdot \vec{A}(\vec{x}) + \frac{e^2}{2mc^2} \rho(\vec{x}) \vec{A}^2(\vec{x}) \right]$$

$$\vec{j}(\vec{k}) = \frac{1}{2} \sum_{i=1}^{N} \left[\frac{\vec{P}_i}{m} e^{-i\vec{k}\cdot\vec{x}_i} + e^{-i\vec{k}\cdot\vec{x}_i} \frac{\vec{P}_i}{m} \right]$$

$$\rho(\vec{k}) = \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{x}_i}$$

Let's consider the leading term only

$$H_{int} \approx -\frac{e}{c}\int d^3x \; \vec{j}(\vec{x}) \cdot \vec{A}(\vec{x})$$

$$\equiv -\frac{e}{c}\int \frac{d^3q \sqrt{4\pi}\,\hbar c}{\sqrt{(2\pi)^3 2E(q)}} \sum_\lambda \int \frac{d^3k}{(2\pi)^3} \; \vec{j}(\vec{k}) \cdot \vec{\mathcal{E}}(\vec{q},\lambda)$$
$$(2\pi)^3 \left[\hat{a}(\vec{q},\lambda)\, \delta^3(\vec{k}+\vec{q}) + \hat{a}^\dagger(\vec{q},\lambda)\, \delta^3(\vec{k}-\vec{q})\right]$$

$$\Rightarrow H_{int} = -\int \frac{d^3q \sqrt{4\pi}\,\hbar c}{\sqrt{(2\pi)^3 2E(q)}} \sum_\lambda \frac{e}{c}\Big[\vec{j}(-\vec{q}) \cdot \vec{\mathcal{E}}(\vec{q},\lambda)\, \hat{a}(\vec{q},\lambda) +$$
$$+ \vec{j}(+\vec{q}) \cdot \vec{\mathcal{E}}(\vec{q},\lambda)\, \hat{a}^\dagger(\vec{q},\lambda)\Big]$$

This operator <u>does not</u> conserve photon number.

<u>Spontaneous Emission</u>

Consider a system in some state $|n\rangle$ and no photons, i.e.. $N(\vec{k},\vec{\lambda}) = 0 \quad \forall \vec{k},\lambda$. In other words, the e.m. field is in its gnd. state (vacuum state). What is the amplitude for a spontaneous transition from state $|n\rangle$ to the gnd. state of the atom, $|0\rangle$?

(not the vacuum of the em field!)

$\Rightarrow$ if the initial state is $|n; \{N_i(k,\lambda)\}\rangle \equiv |n;0\rangle$

$\Rightarrow$ final state $|0; \{N_f(\vec{k},\lambda)\}\rangle$

To analyze this problem we need to define the normalization of the states. In particular, for spontaneous emission we want the states $|n;0\rangle$ and $|0;p\nu\rangle$

$$\langle 0;\cdots 1(p\lambda)\cdots|\, H_{int}\, |n;0\rangle =$$

$$= -\frac{e}{c}\int \frac{d^3q\ \sqrt{4\pi}\,\hbar c}{\sqrt{(2\pi)^3\ 2E(q)}} \sum_\lambda \Big[\langle 0;p\nu|\, \vec{j}(-q)\cdot\vec{\mathcal{E}}(\vec{q}\lambda)\ \hat{a}(\vec{q},\lambda)\,|n;0\rangle$$

$$+ \langle 0;p\nu|\, \vec{j}(+\vec{q})\cdot\vec{\mathcal{E}}(\vec{q},\lambda)\ \hat{a}^+(q,\lambda)\ |n;0\rangle \Big]$$

$$= -\frac{e}{c}\int \frac{d^3q\ \sqrt{4\pi}\,\hbar c}{\sqrt{(2\pi)^3\ 2E(q)}} \sum_\lambda \Big[\langle 0|\,\vec{j}(-\vec{q})\,|n\rangle\cdot\vec{\mathcal{E}}(\vec{q},\lambda)\ \underbrace{\langle p\nu|\,\hat{a}(q,\lambda)|0\rangle}_{=0}$$

$$+ \langle 0|\,\vec{j}(+\vec{q})\,|n\rangle\cdot\vec{\mathcal{E}}(q,\lambda)\ \langle p\nu|\,\hat{a}^+(q,\lambda)|0\rangle \Big]$$

$$\langle p\nu|\,\hat{a}^+(q,\lambda)\,|0\rangle = \langle 0|\sqrt{\frac{(2\pi)^3}{V}}\ \hat{a}(\vec{p},\nu)\ \hat{a}^+(\vec{q},\lambda)|0\rangle =$$

$$= \sqrt{\frac{(2\pi)^3}{V}}\ \delta_{\lambda\nu}\ \delta(\vec{p}-\vec{q})$$

$$|\vec{p}\nu\rangle = \sqrt{\frac{(2\pi)^3}{V}}\ \hat{a}^+(\vec{p},\nu)\ |0\rangle$$

$$\Rightarrow\ \langle 0;\vec{p}\nu|\, H_{int}\,|n;0\rangle =$$

$$= -\frac{e}{c}\int \frac{d^3q\ \sqrt{4\pi}\,\hbar c}{\sqrt{(2\pi)^3\ 2E(\vec{q})}} \sum_\lambda \langle 0|\,\vec{j}(+\vec{q})\,|n\rangle\cdot\vec{\mathcal{E}}(\vec{q},\lambda)\sqrt{\frac{(2\pi)^3}{V}}\,\delta_{\lambda\nu}\,\delta(p-q)$$

$$\Rightarrow \langle 0; \vec{p}\nu | H_{int} | n; 0 \rangle =$$

$$= -\frac{e}{c} \frac{\sqrt{4\pi}\,\hbar c}{\sqrt{\cancel{(2\pi)^3}\, 2E(\vec{p})}} \langle 0 | \vec{j}(+\vec{p}) | n \rangle \cdot \vec{\mathcal{E}}(\vec{p},\nu) \sqrt{\frac{\cancel{(2\pi)^3}}{V}}$$

$$= -\frac{e}{c} \sqrt{\frac{4\pi \hbar^2 c^2}{2E(\vec{p})\, V}} \quad \langle 0 | \vec{j}(+\vec{p}) | n \rangle \cdot \vec{\mathcal{E}}(\vec{p},\nu)$$

$$= -\sqrt{\frac{2\pi \hbar e^2}{\omega V}} \quad \langle 0 | \vec{j}(+\vec{p}) | n \rangle \cdot \vec{\mathcal{E}}(\vec{p},\nu)$$

The energy change involved in this process is

$$\mathcal{E}_n - \mathcal{E}_0 - \hbar\omega(\vec{p}) = \mathcal{E}_n - \mathcal{E}_0 - \hbar c |\vec{p}|$$

$\Rightarrow$ the rate is given by the Golden Mean formula

$$\Gamma^{\text{emission}}_{n\to 0, \vec{p}\nu} = \frac{2\pi}{\hbar} \delta(\mathcal{E}_n - \mathcal{E}_0 - \hbar c|\vec{p}|) \left| \langle 0; \vec{p}\nu | H_{int} | n; 0 \rangle \right|^2$$

$$= \frac{2\pi}{\hbar} \delta(\mathcal{E}_n - \mathcal{E}_0 - \hbar c|\vec{p}|) \frac{2\pi \hbar e^2}{\omega V} \left| \langle 0 | \vec{j}(+p) \cdot \vec{\mathcal{E}}(\vec{p},\nu) | n \rangle \right|^2$$

$$= \frac{4\pi^2 e^2}{\omega V} \delta(\mathcal{E}_n - \mathcal{E}_0 - \hbar c|\vec{p}|) \left| \langle 0 | \vec{j}(+\vec{p}) \cdot \vec{\mathcal{E}}(\vec{p},\nu) | n \rangle \right|^2$$

If the initial state had $N(\vec{p},\nu) \neq 0$, the rate is

$$\Gamma^{\text{emission}}_{n\to 0; \vec{p}\nu} = \frac{4\pi^2 e^2}{\omega V} \delta(\mathcal{E}_n - \mathcal{E}_0 - \hbar c|\vec{p}|) \left| \langle 0 | \vec{j}(+\vec{p}) \cdot \vec{\mathcal{E}}(\vec{p},\nu) | n \rangle \right|^2 (N(\vec{p},\nu)+1)$$

This formula says that the state $|n\rangle$ (with $E_n > E_0$) is truly metastable and that it decays to the gnd. state $|0\rangle$ through the emission of a photon $|\vec{p},\lambda\rangle$. Since there were no photons in the initial state, this process is an interaction with the vacuum fluctuations of the e.m. field.

L25 Einstein's A and B coefficients

Einstein gave a statistical argument to determine this rate. Truly, in this case, the ~~state~~ e.m. field is <u>not</u> in a pure state but rather in a mixed state with a density matrix determined by thermodynamic equilibrium, $\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}_{e.m.}}$ $\qquad \beta = \frac{1}{k_B T}$

So, if we imagine that the photons are produced in a cavity in which the e.m. field is in thermod. eq. at temperature T, the probability of finding N photons of momentum $\vec{k}$ is $e^{-N\hbar c|k|/k_B T}$

$$\Rightarrow \overline{N(p\nu)} = \frac{\sum_{N(p\nu)=0}^{\infty} N(p\nu)\, e^{-N(p\nu)\hbar c|p|/k_B T}}{\sum_{N(p\nu)=0}^{\infty} e^{-N(p\nu)\hbar c|p|/k_B T}} = \frac{1}{e^{\frac{\hbar c|p|}{k_B T}}-1}$$

[Bose-Einstein]

and the average energy per mode is

$$\overline{N(\vec{p},\nu)} = \frac{\hbar c|\vec{p}|}{e^{\frac{\hbar c|\vec{p}|}{k_B T}} - 1}$$

Let us imagine now that the atoms of the walls of the container have electrons in certain energy levels. To simplify matters we will imagine that only two levels are relevant: the gnd state $|0\rangle$ and the excited state $|n\rangle$ with energies $\mathcal{E}_0 < \mathcal{E}_n$. The question now is the following: What relations should the absorption ~~coefficient~~ and emission rates ~~…~~ must have so that in equilibrium we get

$$\overline{N(\vec{p},\nu)} = \frac{1}{e^{\frac{\hbar c|\vec{p}|}{k_B T}} - 1} \qquad ?$$

<u>Statistical Mechanics</u>: Probability (in equilibrium) to find an atom in state $|n\rangle$ is given by the Boltzmann distribution

$P_n \propto e^{-\mathcal{E}_n/k_B T}$ and in state $|0\rangle$ is

$P_0 \propto e^{-\mathcal{E}_0/k_B T}$

$$\Rightarrow \frac{P_n}{P_0} = e^{-(\mathcal{E}_n - \mathcal{E}_0)/k_B T}$$

Let N be the # of photons of frequency $\frac{\mathcal{E}_n - \mathcal{E}_0}{\hbar}$.
~~that are absorbed by the atoms.~~ Then, the absorption rate is

$$\left(\frac{dN}{dt}\right)_{absorption} \propto - B\, N\, P_0$$

since it must be proportional to the probability to find an atom in state $|0\rangle$ and to the number of photons already present. B is called the absorption coefficient

In the presence of (equilibrium) radiation with N photons, emission is induced at a rate

$$\left(\frac{dN}{dt}\right)_{emission} = + B\, N\, P_n$$

since it must be $\propto$ the probab. of finding an atom in state $|n\rangle$ and to the # of photons present N. The emission (induced) ~~coefficient absorption~~ is the same as the absorption coeff. (as we saw). The sign is + since the # of photons increases by emission. Now, we know that there is also spontaneous emission. Then the write

$$\left(\frac{dN}{dt}\right)_{s.e.} = A \; P_n$$

since it is indep. of the # of photons present (vacuum fluctuation effect!)

If we require ~~to~~ equilibrium.

$$\Rightarrow \left(\frac{dN}{dt}\right)_{total} = 0 \quad \Rightarrow \quad N = \bar{N}$$

$$B \bar{N} \left(P_0 - P_n\right) + A \, P_n = 0$$

$$\Rightarrow A = B \; \bar{N} \; \left(e^{\frac{\varepsilon_n - \varepsilon_0}{k_B T}} - 1\right)$$

But $\bar{N} = \dfrac{1}{e^{\frac{\varepsilon_n - \varepsilon_0}{k_B T}} - 1}$

$$\Rightarrow \underline{\underline{A = B}}$$

$$\Rightarrow \left(\frac{dN}{dt}\right)_{emission} = B \; P_n \left(\bar{N} + 1\right)$$

which is exactly of the form we found (we also found the coeff. B!)

Back to <u>Spontaneous Emission</u>.

$(N(\vec{p},\nu)=0)$

Q: what is the <u>power</u> radiated spontaneously by an atom into a small solid angle $d\Omega$ in the direction $\vec{p}$?

$$dP = \sum_{\vec{p}\in d\Omega} \hbar\omega \ \Gamma^{\text{emission}}_{n\to 0;\,\vec{p}\nu}$$

$$= d\Omega \int \frac{\omega^2 d\omega}{(2\pi c)^3} \ \hbar\omega \ \frac{4\pi^2 e^2}{\omega} \left| \langle n | \vec{J}(+\vec{p}) \cdot \vec{\mathcal{E}}(\vec{p},\nu) | 0 \rangle \right|^2 \delta(\varepsilon_n - \varepsilon_0 - \hbar\omega)$$

$$\omega = c|\vec{p}|$$

$$\Rightarrow \frac{dP}{d\Omega} = \frac{\omega^2 e^2}{2\pi c^3} \left| \langle n | \vec{J}(+\vec{p}) \cdot \vec{\mathcal{E}}(\vec{p},\nu) | 0 \rangle \right|^2$$

Classically, the expression for the power radiated by a current $J_{eff}(+\vec{p})$ for radiation with polarization $\vec{\mathcal{E}}(\vec{p},\lambda)$ is

$$\left.\frac{dP}{d\Omega}\right|_{classical} = \frac{\omega^2}{2\pi c^3} \left| \vec{J}_{eff}(+\vec{p}) \cdot \vec{\mathcal{E}}(\vec{p},\lambda) \right|^2$$ (cf. Baym page 279)

$$\Rightarrow \vec{J}_{eff}(+\vec{p},t) \equiv e \langle n | \vec{J}(+\vec{p},t) | 0 \rangle$$ as the effective current.

Angular Distribution of Radiation

Consider first the problem of a ~~free~~ free particle in ∞ space interacting with the fluctuations of the e.m. field.

Q: can the particle radiate spontaneously?

Imagine that the particle is in some state $|n\rangle = |\vec{q}_n\rangle$ with well defined momentum $\hbar\vec{q}_n$ and energy $E_n = \frac{\hbar^2 \vec{q}_n^{\,2}}{2m}$

In the final state $|0\rangle$ the particle is also in a momentum eigenstate $|0\rangle = |\vec{q}_0\rangle$ with momentum $\hbar\vec{q}_0$ and energy $\frac{\hbar^2 \vec{q}_0^{\,2}}{2m}$.

The radiation is in a one photon state $|\vec{p},\lambda\rangle$ with momentum $\hbar\vec{p}$ and polarization λ.

Let's compute the matrix element

$$\langle \vec{q}_0 | \vec{J}(\vec{p}) | \vec{q}_n \rangle =$$

$$= \int d^3x \, \frac{e^{-i\vec{q}_0\cdot\vec{x}}}{\sqrt{V}} \left[\frac{\hbar}{2mi}\vec{\nabla} e^{-i\vec{p}\cdot\vec{x}} + e^{-i\vec{p}\cdot\vec{x}}\frac{\hbar}{2mi}\vec{\nabla}\right] \frac{e^{i\vec{q}_n\cdot\vec{x}}}{\sqrt{V}}$$

$$= \frac{\hbar}{2m}(\vec{q}_0 + \vec{q}_n)\frac{(2\pi)^3}{V}\,\delta^{(3)}(\vec{q}_n - \vec{q}_0 - \vec{p})$$

which vanishes unless $\hbar\vec{q}_n = \hbar\vec{q}_0 + \hbar\vec{p}$

However, energy is also conserved $\Rightarrow$

$$\frac{\hbar \vec{q}_n^{\,2}}{2m} = \frac{\hbar \vec{q}_0^{\,2}}{2m} + \hbar c |\vec{p}|$$

However, once we decided a-priori that we <u>prepared</u> the particle in the initial state ~~|~~ $|\vec{q}_n\rangle$ and that we <u>observe</u> it in state $|\vec{q}_0\rangle$ the momentum of the final photon is <u>completely</u> determined $\hbar\vec{p} = \hbar\vec{q}_n - \hbar\vec{q}_0$

$\Rightarrow$ the energy conservation condition <u>cannot</u> be satisfied for general $\vec{q}_n$ and $\vec{q}_0$ $\Rightarrow$ <u>there is no spontaneous radiation of a free particle in free space</u>

[classically such a particle moves at constant velocity and, as such, it does not radiate either].

[This effect persists to all orders in perturbation theory $\exists_c$ in the quantum case].

In general, if the initial and final states have well defined momentum $\vec{q}_n$ and $\vec{q}_0$, the photon is in state ~~|~~ $\vec{p} = \vec{q}_n - \vec{q}_0$

To show this we do the following: consider a problem with N particles and let $\vec{r}_a$ be the coord. of the a-th particle and $\vec{p}_a$ its momentum, $[(\vec{r}_a)_i, (\vec{p}_b)_j] = i\hbar\delta_{ij}\delta_{ab}$

$(a, b = 1, \ldots, N)$ $(i, j = 1, 2, 3$ $(x, y, z))$.

Since $[x, p] = i\hbar \Rightarrow x = -\frac{\hbar}{i}\frac{\partial}{\partial p}$ (p-representation)

$$\Rightarrow e^{i\frac{pa}{\hbar}} x\, e^{-i\frac{pa}{\hbar}} = e^{i\frac{pa}{\hbar}}\left[[x, e^{-i\frac{pa}{\hbar}}] + e^{-i\frac{pa}{\hbar}} x\right]$$

$$= e^{+i\frac{pa}{\hbar}}\left[-\frac{\hbar}{i}\frac{\partial}{\partial p}, e^{-ipa}\right] + x$$

and $$\left[-\frac{\hbar}{i}\frac{\partial}{\partial p}, e^{-i\frac{pa}{\hbar}}\right] = -\frac{\hbar}{i}\frac{\partial}{\partial p}\left(e^{-i\frac{pa}{\hbar}}\right) = -\frac{\hbar}{i}\left(-\frac{ia}{\hbar}\right)e^{-i\frac{pa}{\hbar}}$$

$$= a\, e^{-i\frac{pa}{\hbar}}$$

$$\Rightarrow \boxed{e^{i\frac{pa}{\hbar}} x\, e^{-i\frac{pa}{\hbar}} = x + a}$$

(conversely ~~also~~ $\cancel{e^{i\frac{pa}{\hbar}}}$ $e^{-i\frac{xq}{\hbar}}\, p\, e^{i\frac{xq}{\hbar}} = p + q$)

$$\Rightarrow e^{i\vec{p}_i\cdot\frac{\vec{a}}{\hbar}}\, \vec{r}_i\, e^{-i\vec{p}_j\cdot\frac{\vec{a}}{\hbar}} = \vec{r}_i + a$$

and $\vec{P} = \sum_{i=1}^{N} \vec{p}_i$ (total momentum.)

$$e^{i\vec{P}\cdot\frac{\vec{a}}{\hbar}}\, \vec{r}_i\, e^{-i\vec{P}\cdot\frac{\vec{a}}{\hbar}} = \vec{r}_i + \vec{a}$$ (since $\vec{p}_i$ commutes with $\vec{r}_j, i \neq j$)

$$\Rightarrow e^{i\vec{P}\cdot\frac{\vec{a}}{\hbar}} f(\vec{r}_1,\dots,\vec{r}_N; \vec{p}_1,\dots,\vec{p}_N)\, e^{-i\vec{P}\cdot\frac{\vec{a}}{\hbar}} =$$

$$= f(\vec{r}_1+\vec{a},\dots,\vec{r}_N+\vec{a};\ \vec{p}_1,\dots,\vec{p}_N)$$

and
$$e^{i\vec{P}\cdot\frac{\vec{a}}{\hbar}}\ \vec{J}(\vec{r})\ e^{-i\vec{P}\cdot\frac{\vec{a}}{\hbar}} =$$
$$= \sum_{i=1}^{N} \frac{1}{2m}\left[\vec{p}_i\,\delta(\vec{r}_i+\vec{a}-\vec{r}) + \delta(\vec{r}_i+\vec{a}-\vec{r})\,\vec{p}_i\right]$$
$$= \vec{J}(\vec{r}+\vec{a})$$
$$\Rightarrow \vec{J}(\vec{r}) = e^{+i\vec{P}\cdot\frac{\vec{r}}{\hbar}}\ \underbrace{\vec{J}(0)}_{\vec{J}(\vec{r}=0)}\ e^{-i\vec{P}\cdot\frac{\vec{r}}{\hbar}}$$
(always true!)

$$\Rightarrow \langle n|\vec{J}(+\vec{p})|0\rangle = \langle n|\int d^3r\ e^{-i\vec{p}\cdot\vec{r}}\ \vec{J}(\vec{r})\ |0\rangle$$
$$= \langle n|\int d^3r\ e^{-i\vec{p}\cdot\vec{r}}\, e^{+i\frac{\vec{P}\cdot\vec{r}}{\hbar}}\ \vec{J}(0)\, e^{-i\vec{P}\cdot\frac{\vec{r}}{\hbar}}|0\rangle$$

$$\boxed{\langle n|\vec{J}(+\vec{p})|0\rangle = \int d^3r\ e^{-i\vec{p}\cdot\vec{r}}\ \langle n|e^{+i\vec{P}\cdot\frac{\vec{r}}{\hbar}}\ \vec{J}(0)\ e^{-i\vec{P}\cdot\frac{\vec{r}}{\hbar}}|0\rangle}$$

<u>If</u> $|n\rangle$ and $|0\rangle$ are <u>eigenstates of $\vec{P}$</u> with eigenvalues $\hbar\vec{q}_n$ and $\hbar\vec{q}_0$ resp. $\Rightarrow$

$$\langle n|\vec{J}(+\vec{p})|0\rangle = \int d^3r\ e^{-i\vec{p}\cdot\vec{r}}\ e^{+i\vec{q}_n\cdot\vec{r}}\, e^{-i\vec{q}_0\cdot\vec{r}}\ \langle n|\vec{J}(0)|0\rangle$$
$$= (2\pi)^3\,\delta^3(-\vec{p}+\vec{q}_n-\vec{q}_0)\qquad \langle n|\vec{J}(0)|0\rangle$$

$\Rightarrow$ the m.e. is $\neq 0$ only for photons which conserve momentum.

L26

Electric Dipole Transitions

We now consider the case of an atom with a nucleus that is well localized in space. In this case, the initial and final states are not eigenstates of $\vec{P}$, even in the continuum. However if at least the initial or the final state is a bound state $\Rightarrow$ this state is well localized (exponentially) near the location of the nucleus, which we will take to be $\vec{r}=0$.

The matrix element

$$\langle n|\vec{J}(+\vec{p})|0\rangle = \int d^3x \; e^{+i\vec{p}\cdot\vec{x}} \langle n|\vec{J}(\vec{x})|0\rangle$$

Notice that

$$\langle n|\vec{J}(\vec{x})|0\rangle \equiv \frac{\hbar}{2mi}\left[\psi_n^*(x)\,\vec{\nabla}\psi_0(x) - (\vec{\nabla}\psi_n(x))^*\psi_0(x)\right]$$

(check it!)

$\Rightarrow$ if $\psi_0(x)$ or $\psi_n(x) \to 0$ exp. fast only the region around $\vec{x}\simeq 0$ will matter. This motivates the approximation of replacing inside the integral:

$$e^{+i\vec{p}\cdot\vec{x}} \simeq 1 + i\vec{p}\cdot\vec{x} - \frac{1}{2}(\vec{p}\cdot\vec{x})^2 + \cdots$$

Leading term:

$$\langle n|\vec{J}(+\vec{p})|0\rangle \approx \int d^3x \; \langle n|\vec{J}(\vec{x})|0\rangle = \langle n|\vec{J}(\vec{p}=0)|0\rangle$$

But

$$\vec{j}(\vec{p}=0) = \frac{\vec{P}}{m} \quad , \quad \vec{P} = \sum_{i=1}^{N} \vec{p}_i$$

and

$$\frac{\vec{P}}{m} = \frac{1}{i\hbar}[\vec{R}, H_0] \qquad \vec{R} = \sum_{i=1}^{N} \vec{r}_i$$

$$\Rightarrow \vec{j}(\vec{p}=0) = \frac{1}{i\hbar}[\vec{R}, H_0]$$

$\vec{R}$ → displacement of the C.M. ~ dipole moment

$$\langle n|\vec{j}(\vec{p}=0)|0\rangle = \frac{1}{i\hbar}\langle n|(\vec{R}H_0 - H_0\vec{R})|0\rangle$$

$$= \frac{1}{i\hbar}\left[\langle n|\vec{R}|0\rangle \mathcal{E}_0 - \langle n|\vec{R}|0\rangle \mathcal{E}_n\right]$$

$$= \frac{\mathcal{E}_0 - \mathcal{E}_n}{i\hbar}\langle n|\vec{R}|0\rangle$$

$$\mathcal{E}_n - \mathcal{E}_0 = \hbar\omega \qquad (\omega = \text{freq. of the photon})$$

$$\langle n|\vec{j}(\vec{p}=0)|0\rangle = i\omega\langle n|\vec{R}|0\rangle \equiv i\omega\, \vec{d}_{n0}$$

$\vec{d}_{n0} = \langle n|\vec{R}|0\rangle$ is the off-diag. op. of the dipole moment op.

$$\Rightarrow \text{Power:} \quad \frac{dP}{d\Omega} = \frac{\omega^2 e^2}{2\pi c^3}\left|\langle n|\vec{j}(-\vec{p})\cdot\vec{\mathcal{E}}(\vec{p},\nu)|0\rangle\right|^2$$

$$\Rightarrow \frac{dP}{d\Omega} \simeq \frac{\omega^4 e^2}{2\pi c^3}\left|\vec{d}_{n0}\cdot\vec{\mathcal{E}}(\vec{p},\nu)\right|^2 \quad \text{(dipole approx)}$$

This equation also says that the polarization of the emitted light is in the direction of $\vec{d}_{no} \perp \vec{k}$

$$(\vec{d}_{no})_\perp = \vec{d}_{no} - \frac{(\vec{d}_{no}\cdot\vec{k})\,\vec{k}}{|\vec{k}|^2}$$

Selection Rules:

We will now consider the situation in which the initial and final states $|n\rangle$ and $|0\rangle$ are chosen to be eigenstates of angular momentum (we can always do that given the isotropy of the Coulomb force).

Then $\vec{L} = \sum_i \vec{r}_i \times \vec{p}_i$ commutes with H_0.

Recall that

$$[L_i, L_j] = i\hbar\, \varepsilon_{ijk} L_k$$

$i, j, k = 1,2,3$

$$\varepsilon_{ijk} = \begin{cases} 1 & (ijk)\text{ cyclic} \\ -1 & \text{anti} \\ 0 & \text{otherwise} \end{cases}$$

Levi-Civita

but

$$[\vec{L}^2, L_i] = 0$$

eigenstates of $\vec{L}^2$ and $L_3 \equiv L_z$

$$\vec{L}^2 |l,m\rangle = \hbar^2 l(l+1)|l,m\rangle$$

$$L_z |l,m\rangle = \hbar m \; |l,m\rangle$$

with $l = 0, 1, 2, \ldots \qquad |m| \le l$

$$\Rightarrow \quad |n\rangle = |l,m\rangle$$
$$|0\rangle = |l',m'\rangle$$

$\Rightarrow$ we want $\langle n|R_i|0\rangle = \langle l,m|R_i|l',m'\rangle$

But $\quad [R_i, L_j] = i\hbar\, \varepsilon_{ijk} L_k$

$$\Rightarrow \quad [R_z, L_z] = 0$$

and $\quad [L_z, R_x] = i\hbar R_y$

$$[L_z, R_y] = -i\hbar R_x$$

$$\Rightarrow \quad \langle lm | [L_z, R_z] | l'm' \rangle = 0$$

$$\Rightarrow \langle lm | \left(L_z R_z - R_z L_z \right) | l'm' \rangle =$$

$$= m\hbar \langle lm | R_z | l'm' \rangle - m'\hbar \langle lm | R_z | l'm' \rangle$$

$$\Rightarrow \quad (m-m')\hbar \langle lm | R_z | l'm' \rangle = 0$$

$$\Rightarrow \quad \langle lm | R_z | l'm' \rangle = 0 \quad \underline{\text{unless}} \quad m = m'$$

$$\langle lm | [L_z, R_x] | l'm' \rangle = i\hbar \langle lm | R_y | l'm' \rangle$$

$$\hbar m \langle lm | R_x | l'm' \rangle - \hbar m' \langle lm | R_x | l'm' \rangle = i\hbar \langle lm | R_y | l'm' \rangle$$

$$\hbar (m-m') \langle lm | R_x | l'm' \rangle = i\hbar \langle lm | R_y | l'm' \rangle$$

and
$$\hbar (m-m') \langle lm | R_y | l'm' \rangle = -i\hbar \langle lm | R_x | l'm' \rangle$$

$$\Rightarrow \quad (m'-m)^2 \langle lm | R_x | l'm' \rangle = \langle lm | R_x | l'm' \rangle$$

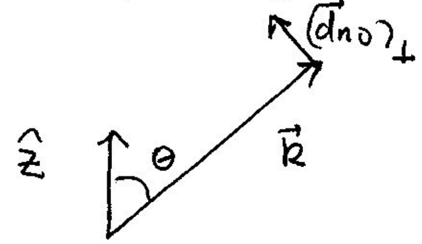
$$\Rightarrow \quad \langle lm | R_x | l'm' \rangle = 0 \quad \text{for} \quad m'-m \neq \pm 1$$

and $\quad \langle lm | R_y | l'm' \rangle = 0 \quad$ for $\quad m'-m \neq \pm 1$

$\Rightarrow$ we only get dipole transitions if $\quad m' = m,\ m \pm 1$

(a) $m = m' \Rightarrow |n\rangle = |\ell, m\rangle$ and $|0\rangle = |\ell', m\rangle$

$\Rightarrow \vec{d}_{n0} = \langle n|\vec{R}|0\rangle = \hat{z}\,\langle \ell m|R_z|\ell' m\rangle$



$$|(\vec{d}_{n0})_\perp| = |\vec{d}_{n0}|\sin\theta$$

$$\frac{dP}{d\Omega} \propto \sin^2\theta$$

(b) $m = m' - 1$, $|n\rangle = |\ell m\rangle$; $|0\rangle = |\ell', m-1\rangle$

$\hbar\,\langle n|R_x|0\rangle = i\hbar\,\langle n|R_y|0\rangle$

$\hbar\,\langle n|R_y|0\rangle = -i\hbar\,\langle n|R_x|0\rangle$

$\Rightarrow \langle n|R_x|0\rangle = i\,\langle n|R_y|0\rangle$, $\langle n|R_z|0\rangle = 0$

$$\Rightarrow \vec{d}_{n0} \sim \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}$$

$\Rightarrow$ if $\vec{k} \parallel \hat{z} \Rightarrow$ RCP ($\Delta L_z = \hbar$ and $L_z^{\text{photon}} = \hbar$ for RCP photon)

$m = m'+1 \Rightarrow \vec{d}_{n0} \sim \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \Rightarrow \Delta L_z = -\hbar \Rightarrow L_z^{\text{photon}} = -1$
$\Rightarrow$ LCP
(for $\vec{k} \parallel \hat{z}$)

(*) What about ℓ ?

We'll see later that $\ell' = \ell \pm 1$ are the only allowed dipole transitions. A direct way to see this is to use the identity

$$\left[\vec{L}^2,[\vec{L}^2,\vec{R}]\right] = 2\hbar^2\left(\vec{R}\,\vec{L}^2 + \vec{L}^2\vec{R}\right)$$

$$\Rightarrow \langle \ell m|\left[\vec{L}^2,[\vec{L}^2,\vec{R}]\right]|\ell' m'\rangle =$$

$$= 2\hbar^2 \langle \ell m|\left(\vec{R}\,\vec{L}^2 + \vec{L}^2\vec{R}\right)|\ell' m'\rangle$$

$$\Rightarrow \left[\ell(\ell+1) - \ell'(\ell'+1)\right]^2 \langle \ell m|\vec{R}|\ell' m'\rangle =$$

$$= 2\left[\ell'(\ell'+1)+\ell(\ell+1)\right]\ \langle \ell m|\vec{R}|\ell' m'\rangle$$

$$\Rightarrow (\ell+\ell')\ (\ell+\ell'+2)\left((\ell-\ell')^2-1\right)\ \langle \ell m|\vec{R}|\ell' m'\rangle = 0$$

since $\ell \geq 0,\ \ell' \geq 0 \Rightarrow \langle \ell m|\vec{R}|\ell' m'\rangle = 0$

unless $\ell+\ell'=0$ or $\ell' = \ell \pm 1$

now, $\ell+\ell'=0 \Leftrightarrow \ell=\ell'=0$ but $\langle 00|\vec{R}|00\rangle = 0$ by rotational invariance

$\Rightarrow \ell=\ell'\pm 1$ are the only possibilities

For hydrogen energy levels (single electrons)

$$\langle n',\ell',m'|\vec{r}\,|n,\ell,m\rangle = \int d^3r\ \left[R_{n'}(r)\ Y_{\ell' m'}(\theta,\varphi)\right]^* \vec{r}\left[R_n(r)\ Y_{\ell m}(\theta,\varphi)\right]$$

$$= \int_0^\infty r^3 dr\ R^*_{n'}(r)\ R_n(r)$$

$$\int d\Omega\ Y^*_{\ell' m'}(\theta,\varphi)\ Y_{\ell m}(\theta,\varphi)\ \hat{r}$$

which obey the rules we just discussed.

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Cross Sections and Dipole Sum-Rule

Total absorption cross-section (dipole app.)

$$\sigma_{abs}^{dip.} = \frac{4\pi^2 e^2 \omega}{c} \sum_n |\vec{d}_{n0} \cdot \vec{\mathcal{E}}(\vec{p}, \nu)|^2 \delta(\mathcal{E}_n - \mathcal{E}_0 - \hbar\omega)$$

$$\left[\sigma_{abs}(\omega) = \frac{4\pi^2 e^2}{\omega c} \sum_n |\langle n| \vec{j}(-\vec{p}) \cdot \vec{\mathcal{E}}(\vec{p}, \nu) |0\rangle|^2 \delta(\mathcal{E}_n - \mathcal{E}_0 - \hbar\omega) \right]$$

Sum rule:

$$\int_0^\infty d\omega \; \sigma_{abs}^{dip}(\omega) = \frac{2\pi^2 e^2 N}{mc} \qquad (N = \# \text{ of particles})$$

Proof:

$\hat{u}$ real unit vector

$$[\vec{P} \cdot \hat{u}, \vec{R} \cdot \hat{u}] = [\textstyle\sum_i \vec{p}_i \cdot \hat{u}, \sum_j \vec{r}_j \cdot \hat{u}]$$

$$= \sum_{ij} [\vec{p}_i \cdot \hat{u}, \vec{r}_j \cdot \hat{u}]$$

$$= -i\hbar \sum_{ij} \delta_{ij} = -i\hbar N$$

$$\langle 0| [\vec{P} \cdot \hat{u}, \vec{R} \cdot \hat{u}] |0\rangle = -i\hbar N \langle 0|0\rangle = -i\hbar N$$

$$\langle 0| (\vec{P} \cdot \hat{u})(\vec{R} \cdot \hat{u}) - (\vec{R} \cdot \hat{u})(\vec{P} \cdot \hat{u}) |0\rangle = -i\hbar N$$

$$\Rightarrow \sum_n \left(\langle 0| \vec{P} \cdot \hat{u} |n\rangle \langle n| \vec{R} \cdot \hat{u} |0\rangle - \langle 0| \vec{R} \cdot \hat{u} |n\rangle \langle n| \vec{P} \cdot \hat{u} |0\rangle \right) = -i\hbar N$$

$$\Rightarrow \quad \vec{P} = \frac{m}{i\hbar} [\vec{R}, H_0] \qquad [\text{no magnetic fields}]$$

$$\Rightarrow \boxed{\sum_n (\mathcal{E}_n - \mathcal{E}_0) |\langle n| \vec{R} \cdot \hat{u} |0\rangle|^2 = \frac{N\hbar^2}{2m}} \quad (\text{dipole sum rule})$$

$$\Rightarrow \int_0^\infty d\omega \; \sigma_{abs}^{dip}(\omega) = \frac{4\pi^2 e^2}{\hbar^2 c} \sum_n (\mathcal{E}_n - \mathcal{E}_0) \left| \vec{d}_{n0} \cdot \vec{\mathcal{E}}(\vec{p}, \nu) \right|^2$$

(only over states with $\mathcal{E}_n > \mathcal{E}_0$)

If $|0\rangle$ is the ground state $\Rightarrow$ sum over all n.

If $\vec{\mathcal{E}}(\vec{p}, \nu)$ is real (plane polarization) $\Rightarrow$ choose $\hat{u} \parallel \vec{\mathcal{E}}(\vec{p}, \nu)$

$$\Rightarrow \int_0^\infty d\omega \; \sigma_{abs}^{dip}(\omega) = \frac{2\pi^2 e^2 N}{m c}$$