§6.6. Full Quantum Treatment of Radiative Transitions

The good reference books for this subject are

① "The Quantum Theory of Light" by Rodney Loudon

② "Atomic Spectra and Radiative Transitions" by Igor I. Sobelman

The good reference books for Perturbation Theory are

① "Quantum Mechanics" by L. D. Landau

② "Quantum Mechanics" by Claude Cohen-Tannoudji

As we have described in the earlier sections, the semi-classical theory can describe the stimulated/induced absorption and emission very well, but cannot naturally include the spontaneous emission. In the semi-classical theory, the radiation field strengths $\vec{E}$ and $\vec{B}$ are treated as classical variables, while the atoms are treated quantum-mechanically. Quantization conditions on the energy of the radiation field were used to derive Planck's law, but the concept of photons has played a small role in the subsequent theory. This semi-classical theory provides the correct theoretical expressions for a wide range of quantities.

The most complete description of the radiation field must be sought in quantum-mechanical terms, where the field observables $\hat{\vec{E}}$ and $\hat{\vec{B}}$ are represented by operators. This full quantum treatment is applied to the electromagnetic field. We obtain expressions for the operators that represent the various field observables and we describe the various kinds of field state that can be envisaged in the quantum picture. Quantization introduces characteristic quantum-mechanical effects into the properties of the radiation field.

1. Quantization of the Radiation Field

(1) Potential theory for the classical EM field

The quantum theory of the radiation field has many similarities with the classical theory. The field vectors in quantum theory must be taken as operators instead of the algebraic quantities of classical theory, but both theories are based on Maxwell's equations. It is not possible to derive the quantum theory from the classical equations, but the transition to quantum mechanics can be accomplished most easily if the equations of classical EM theory are first put into a suitably suggestive form. The first task here is to cast the classical equations in a form where the harmonic-oscillator dependence of the field variables is suitable for conversion to quantum mechanics.

Maxwell's Equations for EM field in nonmagnetic medium:

$$\begin{cases} \nabla \times \vec{E} = -\partial \vec{B}/\partial t \\ \frac{1}{\mu_0} \nabla \times \vec{B} = \varepsilon_0 (\partial \vec{E}/\partial t) + \vec{J} \\ \varepsilon_0 \nabla \cdot \vec{E} = U \\ \nabla \cdot \vec{B} = 0 \end{cases}$$

where U and $\vec{J}$ are the charge and current densities, respectively.

The quantization procedure is facilitated if the classical Maxwell equations are re-expressed in terms of the scalar and vector potentials, ϕ and $\vec{A}$, respectively. In terms of scalar potential ϕ and vector potential $\vec{A}$,

$$\vec{E} = -\nabla\phi - \frac{\partial \vec{A}}{\partial t} \qquad (89)$$

$$\vec{B} = \nabla \times \vec{A} \qquad (90)$$

where $\nabla \times \nabla \phi \equiv 0$, i.e., ϕ is a scalar function.

If the potentials are known, Eqs. (89) and (90) enable $\vec{E}$ and $\vec{B}$ to be found. The potentials can be determined by the followings

$$\begin{cases} \nabla(\nabla\cdot\vec{A}) - \nabla^2\vec{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\nabla\phi + \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t} = \mu_0\vec{J} & (91) \\ -\varepsilon_0\nabla^2\phi - \varepsilon_0\nabla\cdot(\partial\vec{A}/\partial t) = \sigma & (92) \end{cases}$$

where $\nabla\times\nabla\times\vec{A} \equiv \nabla(\nabla\cdot\vec{A}) - \nabla^2\vec{A}$.

It is possible to simplify the equations by the imposition of some additional conditions on the potentials $\vec{A}$ and ϕ. It is important to realize that Eqs. (89) and (90) do not completely specify the forms of the potentials $\vec{A}$ and ϕ. The potentials $\vec{A}$ and ϕ can be varied, within certain limits, without any resulting change in the observable fields $\vec{E}$ and $\vec{B}$. This kind of transformation is called "gauge" tranformation. It should be emphasized that $\vec{E}$ and $\vec{B}$, the physically measurable fields, do not depend in any way on the choice of gauge for $\vec{A}$ and ϕ. However, the freedom of choice provided by gauge invariance can often be used to obtain considerable simplifications in the calculation of $\vec{E}$ and $\vec{B}$.

(2) The Coulomb Gauge

The EM field is said to be in the Coulomb gauge when the vector potential satisfies the condition

$$\nabla\cdot\vec{A} = 0 \qquad (93).$$

For a field specified originally by a pair of potentials $\vec{A}_0$ and ϕ_0, it is alway possible to transform to the Coulomb gauge by a gauge transformation like

$$\begin{cases} \vec{A} = \vec{A}_0 - \nabla\theta & (94) \\ \phi = \phi_0 + (\partial\theta/\partial t). \end{cases}$$

Under Coulomb transformation, Eqs. (91) and (92) are simplified to

$$\begin{cases} -\nabla^2\vec{A} + \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} + \frac{1}{c^2}\frac{\partial}{\partial t}\nabla\phi = \mu_0\vec{J} & (95) \\ -\nabla^2\phi = \sigma/\varepsilon_0 & (96) \end{cases}$$

According to Helmholtz' theorem, any vector field can be written as a sum of two components, one of which has zero divergence and the other of which has zero curl. For the case of the current density $\vec{J}$, the sum is $\vec{J} = \vec{J}_T + \vec{J}_L$, (97)

where $\nabla\cdot\vec{J}_T = 0$, $\nabla\times\vec{J}_L = 0$

J_T and J_L are the transverse and longitudinal components, respectively.

Thus, Eq. (95) can be simplified to

$$-\nabla^2\vec{A} + \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = \mu_0\vec{J}_T \qquad (98).$$

in considering $\vec{J}_L = \varepsilon_0\nabla\partial\Phi/\partial t$.

The solution of Eq. (98) is

$$\vec{A}(\vec{r},t) = \frac{\mu_0}{4\pi}\int\frac{\vec{J}_T(\vec{r}',t')}{|\vec{r}-\vec{r}'|}d^3\vec{r}' \qquad (99)$$

where $t' = t - |\vec{r}-\vec{r}'|/c$ (100)

The vector potential $\vec{A}$ at position $\vec{r}$ and time t thus includes explicitly the effect of the finite velocity of light in delaying the arrival at $\vec{r}$ of the influence of the current at a distant point $\vec{r}'$. An observer at $\vec{r}$ can have a knowledge of the current distribution at $\vec{r}'$ only as it existed at the retarded time t' given by Eq. (100).

The scalar potential ϕ can be obtained from Eq. (96):

$$\phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int\frac{\sigma(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3\vec{r}' \qquad (101)$$

The electric field vector $\vec{E}$ can also be divided into transverse and longitudinal parts: $\vec{E} = \vec{E}_T + \vec{E}_L$ (102)

where $\nabla \cdot \vec{E}_T = \nabla \times \vec{E}_L = 0$ (103).

Thus, $\begin{cases} \vec{E}_T = -\partial \vec{A}/\partial t, & (104) \\ \vec{E}_L = -\nabla \phi & (105) \end{cases}$

The magnetic field vector $\vec{B}$ is entirely transverse accordig to the Maxwell equation $\nabla \cdot \vec{B} = 0$.

The great advantage of the Coulomb gauge, for the problem of the radiation field and its interaction with charges and current, lies in the separation of the field equations and Maxwell's equations into two distinct parts. The longitudinal part is associated with the scalar potential ϕ: $\begin{cases} \nabla \cdot \vec{E}_L = -\nabla^2 \phi = \sigma/\varepsilon_0 & (106) \\ \vec{J}_L = -\varepsilon_0 \partial \vec{E}_L/\partial t & (107) \end{cases}$

The longitudinal equations describe the fields arising from the charges, as determined by the equations of electrostatics.

The transverse part is associated with the vector potential $\vec{A}$:

$$\begin{cases} \nabla \times \vec{E}_T = -\partial \vec{B}/\partial t \\ \frac{1}{\mu_0} \nabla \times \vec{B} = \varepsilon_0 (\partial \vec{E}_T/\partial t) + \vec{J}_T \qquad (108) \\ \nabla \cdot \vec{E}_T = 0 \\ \nabla \cdot \vec{B} = 0 \end{cases}$$

The transverse equations describe EM waves, which are influenced only by $\vec{J}_T$.

The separation of the equations into a static part (longitudinal) associated with the charge density and a dynamic part (transverse) associated with the EM waves is a formal consequence of the Coulomb gauge condition.

(3) The free classical field

If a region of space where $\vec{J}_T = 0$, and hence

$$-\nabla^2 \vec{A} + \frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t} = 0, \qquad (109)$$

the field in such a region of space is said to be free.

The quantization of the EM field proceeds by the replacement of the classical vector potential $\vec{A}$ by a quantum-mechanical operator $\hat{A}$. The final manipulation on the classical field leads to a form of the classical equations in which the transition to quantum Mechanics is straight-forward.

Let us consider a cubic region of space of side L, merely as a region of space without any real boundaries. We take running waves and subject them to periodic boundary conditions. Thus, the vector potential in the "cavity" can be expanded in a Fourier series:

$$\vec{A} = \sum_{\vec{K}} \{ \vec{A}_K(t) \exp(i\vec{K}\cdot\vec{r}) + \vec{A}_K^*(t) \exp(-i\vec{K}\cdot\vec{r}) \} \qquad (110)$$

where the components of the wavevector $\vec{K}$ take the values

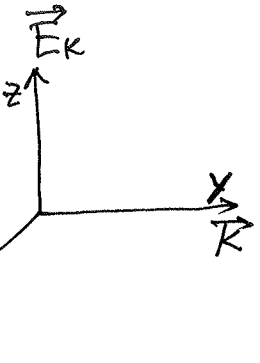
$$K_x = 2\pi N_x/L, \quad K_y = 2\pi N_y/L, \quad K_z = 2\pi N_z/L, \qquad (111)$$

with $N_x, N_y, N_z = 0, \pm 1, \pm 2, \pm 3, \cdots$

The wave vector $\vec{K} = \frac{2\pi}{L}(N_x \hat{i} + N_y \hat{j} + N_z \hat{k})$. The Coulomb gauge condition Eq. (93) is satisfied if

$$\vec{K}\cdot\vec{A}_K(t) = \vec{K}\cdot\vec{A}^*(t) = 0 \qquad (112)$$

There are two independent directions of $\vec{A}_K(t)$ for each $\vec{K}$.



The different Fourier components of $\vec{A}$ are independent and must separately satisfy the field equation Eq. (109).

Thus, $K^2 \vec{A}_K(t) + \frac{1}{c^2}\frac{\partial^2 \vec{A}_K(t)}{\partial t^2} = 0 \qquad (113)$

and $\vec{A}_K^*(t)$ satisfies the same equation.

The Fourier coefficients therefore satisfy the simple-Harmonic equation: $\left(\partial^2 \vec{A}_k(t)/\partial t^2\right) + \omega_k^2 \vec{A}_k(t) = 0$ (114)

(115)

where $\omega_k = c \cdot k$

The solution of Eq. (114) can be taken as

$$\vec{A}_k(t) = \vec{A}_k \exp(-i\omega_k t) \tag{116}$$

Thus, the complete vector potential becomes

$$\vec{A} = \sum_k \left[\vec{A}_k \exp(-i\omega_k t + i\vec{k}\cdot\vec{r}) + \vec{A}_k^* \exp(i\omega_k t - i\vec{k}\cdot\vec{r})\right]. \tag{117}$$

The cycle-averaged energy content of a single mode $\vec{k}$ is

$$\bar{\mathcal{E}}_k = \frac{1}{2}\int_{\text{cavity}} \left(\varepsilon_0 \overline{\vec{E}_k^2} + \frac{1}{\mu_0}\overline{\vec{B}_k^2}\right) dV \tag{118}$$

where the bars denote a cycle average, and $\vec{E}_k$ and $\vec{B}_k$ are the electric and magnetic fields associated with the mode. Thus, (119)

$$\begin{cases} \vec{E}_k = -\dfrac{\partial \vec{A}_k}{\partial t} = i\omega_k \left[\vec{A}_k \exp(-i\omega_k t + i\vec{k}\cdot\vec{r}) - \vec{A}_k^* \exp(i\omega_k t - i\vec{k}\cdot\vec{r})\right] \\ \vec{B}_k = \nabla \times \vec{A}_k = i\vec{k} \times \left[\vec{A}_k \exp(-i\omega_k t + i\vec{k}\cdot\vec{r}) - \vec{A}_k^* \exp(i\omega_k t - i\vec{k}\cdot\vec{r})\right] \end{cases} \tag{120}$$

(If $\vec{k}$ is along y-axis, $\vec{E}_k$ is along z-axis, then $\vec{B}_k$ is in x-axis.)

Substitute Eqs. (119) and (120) into Eq. (118), the energy

$$\bar{\mathcal{E}}_k = 2\varepsilon_0 V \omega_k^2 \vec{A}_k \cdot \vec{A}_k^* \tag{121}$$

where $V = L^3$.

The mode variables $\vec{A}_k$ and $\vec{A}_k^*$ can be replaced by a generalized mode "position" coordinate Q_k and mode "momentum" P_k in accordance with the transformations

$$\vec{A}_k = (4\varepsilon_0 V \omega_k^2)^{-1/2} (\omega_k Q_k + iP_k)\vec{e}_k \tag{122}$$

$$\vec{A}_k^* = (4\varepsilon_0 V \omega_k^2)^{-1/2} (\omega_k Q_k - iP_k)\vec{e}_k \tag{123}$$

The coordinates Q_k and P_k are scalar quantities, the directional properties of $\vec{A}_k$ and $\vec{A}_k^*$ having been separated by the introduction of a unit polarization vector $\vec{e}_k$ for the mode. Thus, the single-mode energy

$$\bar{\mathcal{E}}_k = \frac{1}{2}(P_k^2 + \omega_k^2 Q_k^2) \qquad (124).$$

This is precisely the usual form of the energy of a classical harmonic oscillator. The problem of the vector potential associated with a cavity mode has been made formally equivalent to a classical harmonic-oscillator problem. The complete classical Hamiltonian for the cavity is formed by taking a sum over $\vec{k}$, and the two independent directions of $\vec{e}_k$ of the single mode-expression Eq.(124).

(4) The quantum-mechanical harmonic oscillator

The EM field is quantized by converting Q_k and P_k into quantum-mechanical position and momentum operators $\hat{Q}_k$ and $\hat{P}_k$.

The QM Hamiltonian for a 1-D harmonic oscillator of unit mass is

$$\hat{H} = \frac{1}{2}(\hat{p}^2 + \omega^2 \hat{q}^2) \qquad (125)$$

where $\hat{p}$ and $\hat{q}$ obey the usual commutation relation:

$$[\hat{q}, \hat{p}] = i\hbar \qquad (126)$$

Define a pair of operators $\hat{a}$ and $\hat{a}^+$ to replace $\hat{q}$ and $\hat{p}$.

$$\hat{a} = (2\hbar\omega)^{-\frac{1}{2}}(\omega\hat{q} + i\hat{p}) \qquad (127)$$

$$\hat{a}^+ = (2\hbar\omega)^{-\frac{1}{2}}(\omega\hat{q} - i\hat{p}) \qquad (128)$$

Thus, $$\hat{q} = (\hbar/2\omega)^{\frac{1}{2}}(\hat{a} + \hat{a}^+) \qquad (129)$$

$$\hat{p} = -i(\hbar\omega/2)^{\frac{1}{2}}(\hat{a} - \hat{a}^+) \qquad (130)$$

The operators $\hat{a}$ and $\hat{a}^+$ are called the destruction and creation operators for the harmonic oscillator. They do not, however,

represent observables of the harmonic oscillator.

From Eqs. (127-128), we have

$$\hat{a}^+\hat{a} = (2\hbar\omega)^{-1}(\hat{p}^2 + \omega^2\hat{q}^2 + i\omega\hat{q}\hat{p} - i\omega\hat{p}\hat{q})$$

$$= (\hbar\omega)^{-1}(\hat{H} - \tfrac{1}{2}\hbar\omega) \qquad (131)$$

($i\omega[\hat{q},\hat{p}] = -\hbar\omega$)

Similarly, $\hat{a}\hat{a}^+ = (\hbar\omega)^{-1}(\hat{H} + \frac{1}{2}\hbar\omega)$ (132)

Thus, the commutator of the new operators is

$$[\hat{a}, \hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1 \qquad (133)$$

From Eq. (132), we obtain $\hat{H} = \hbar\omega(\hat{a}^+\hat{a} + \frac{1}{2})$ (134)

The operator $\hat{a}^+\hat{a}$ is called the number operator of the oscillator, and we denote it as $\hat{n} \equiv \hat{a}^+\hat{a}$. (135)

Let $|n\rangle$ be an energy eigenstate of the harmonic oscillator with eigenvalue E_n. The eigenvalue equation is

$$\hat{H}|n\rangle = \hbar\omega(\hat{a}^+\hat{a} + \tfrac{1}{2})|n\rangle = E_n|n\rangle \qquad (136)$$

Multiply both sides from the left by $\hat{a}^+$

$$\hbar\omega(\hat{a}^+\hat{a}^+\hat{a} + \tfrac{1}{2}\hat{a}^+)|n\rangle = E_n\hat{a}^+|n\rangle \qquad (137)$$

Utilizing Eq. (133), Eq. (137) becomes

$$\hbar\omega(\hat{a}^+\hat{a}\hat{a}^+ - \hat{a}^+ + \tfrac{1}{2}\hat{a}^+)|n\rangle = E_n\hat{a}^+|n\rangle, \qquad (138)$$

which can be re-arranged as

$$\hbar\omega(\hat{a}^+\hat{a} + \tfrac{1}{2})\hat{a}^+|n\rangle = (E_n + \hbar\omega)\hat{a}^+|n\rangle = \hat{H}\hat{a}^+|n\rangle \qquad (139)$$

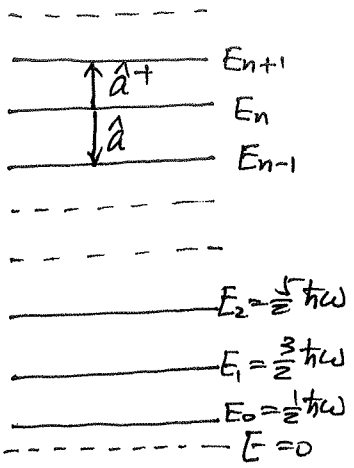
The last equation again has the form of an energy eigenvalue equation. It shows that the state $\hat{a}^+|n\rangle$ is an eigenstate ~~of~~

the harmonic oscillator with eigenvalue $E_n + \hbar\omega$. We define the new eigenstate and eigenvalue as

$$\begin{cases} |n+1\rangle = \hat{a}^+ |n\rangle & (140) \\ E_{n+1} = E_n + \hbar\omega & (141) \end{cases}$$

Thus, Eq. (139) can be written as

$$\hat{H}\,|n+1\rangle = E_{n+1}\,|n+1\rangle \qquad (142)$$



These results show that, given a harmonic-oscillator energy level E_n, there exists another level $\hbar\omega$ above the first. The energy levels thus form an equally-spaced ladder. As in classical mechanics, there is no maximum energy restriction for the harmonic oscillator, and the ladder of levels extends upwards to infinity.

The lower end of the ladder can be investigated by multiplication of Eq. (136) from the left by $\hat{a}$. We obtain

$$\hat{H}\,\hat{a}\,|n\rangle = (E_n - \hbar\omega)\,\hat{a}\,|n\rangle \qquad (143)$$

Thus, the state $\hat{a}\,|n\rangle$ is an energy eigenstate with eigenvalue $E_n - \hbar\omega$. We define

$$|n-1\rangle = \hat{a}\,|n\rangle \qquad (144)$$

$$E_{n-1} = E_n - \hbar\omega \qquad (145)$$

$$\text{So} \quad \hat{H}\,|n-1\rangle = E_{n-1}\,|n-1\rangle. \qquad (146)$$

The ladder of energy levels thus extends downwards with equal steps $\hbar\omega$. However, the ladder must have a lower end because the oscillator kinetic and potential energies are positive quantities, and the eigenvalues are not allowed to be negative.

Let $|0\rangle$ be the ground state with energy E_0. Eq. (143) gives, for the ground state,

$$\hat{H}\,\hat{a}\,|0\rangle = (E_0 - \hbar\omega)\,\hat{a}\,|0\rangle \qquad (147)$$

Since by hypothesis, there is no eigenstate of lower energy than the ground state, the only solution of Eq. (147) consistent with this physical interpretation is

$$\hat{a}\,|0\rangle = 0 \qquad (148)$$

The ground-state condition can be used to determine E_0, since Eq. (136) for the ground state becomes

$$\begin{aligned}\hat{H}\,|0\rangle &= \hbar\omega(\hat{a}^+\hat{a} + \tfrac{1}{2})|0\rangle \\ &= \hbar\omega\,\hat{a}^+(\hat{a}\,|0\rangle) + \tfrac{1}{2}\hbar\omega\,|0\rangle \\ &= 0 + \tfrac{1}{2}\hbar\omega\,|0\rangle\end{aligned}$$

$$\therefore \quad \hat{H}\,|0\rangle = \tfrac{1}{2}\hbar\omega\,|0\rangle = E_0\,|0\rangle \qquad (149)$$

Thus, the energy eigenvalue

$$E_0 = \tfrac{1}{2}\hbar\omega \qquad (150)$$

The energy eigenvalues for the harmonic oscillator are

$$E_n = (n + \tfrac{1}{2})\,\hbar\omega \qquad (151)$$

As shown in the figure on page II 151, $\hat{a}$ and $\hat{a}^+$ destroy or create a quantum $\hbar\omega$ in the oscillator's excitation energy, and thus produce a step down or up the ladder. The states $|n\rangle$ are simultaneous eigenstates of $\hat{H}$ and $\hat{n}$:

$$\hat{n}\,|n\rangle = \hat{a}^+\hat{a}\,|n\rangle = n\,|n\rangle \qquad (152)$$

The eigenvalue of $\hat{n}$ indicates the number of quanta $\hbar\omega$ excited above the oscillator ground state.

To normalize the eigenstate $|n\rangle$, i.e., to make

$$\langle n-1|n-1\rangle = \langle n|n\rangle = \langle n+1|n+1\rangle = 1 \qquad (153)$$

let us consider the effect of these conditions on Eq. (144). Insert a number factor e_n. $e_n|n-1\rangle = \hat{a}|n\rangle$

$$\langle n-1|e_n^* e_n|n-1\rangle = \langle n|\hat{a}^+\hat{a}|n\rangle = n\langle n|n\rangle = n$$

$$\Rightarrow |e_n|^2 = n \quad \Rightarrow \quad e_n = \sqrt{n}\ .$$

Thus, $\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle \qquad (154)$

Similarly, $\hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle \qquad (155)$

Different energy eigenstates of the harmonic oscillators are orthogonal and the only non-vanishing matrix elements of $\hat{a}$ and $\hat{a}^+$ are those of the types

$$\langle n-1|\hat{a}|n\rangle = \sqrt{n} \qquad (156)$$

$$\langle n+1|\hat{a}^+|n\rangle = \sqrt{n+1} \qquad (157)$$

Every Hermitian operator $\hat{O}$ has matrix elements that satisfy the condition

$$\langle i|\hat{O}|j\rangle = \langle j|\hat{O}|i\rangle^* \qquad (158)$$

It is clear that $\hat{a}$ and $\hat{a}^+$ are not Hermitian operators, and according to the general principles of QM, they cannot represent observable quantities. However, their property of destroying or creating a quantum of energy, when applied to an energy eigenstate of the oscillator is easily appreciated in a physical sense. Next, we will use $\hat{a}$ and $\hat{a}^+$ to quantize the radiation field.