6 Quantization of the Radiation Field

So far, we have treated the electric and magnetic fields as classical quantities when studying quantum mechanical problems. In this chapter we study the quantization of electromagnetic radiation and its interaction with matter in an entirely quantum mechanical setting.

Some of the material presented in this chapter is taken from Auletta, Fortunato and Parisi, Chap. 13, and Grynberg, Aspect and Fabre, Chaps. 4-6.

6.1 Classical Formulation of the Free Radiation Field

We are first concerned with the free electromagnetic field, i.e., when no charges or current are present, whose behaviour and evolution is classically governed by ***Maxwell's equations***

$$\begin{aligned}
\nabla \cdot \mathbf{E}(\mathbf{r},t) &= 0 && (6.1)\\
\nabla \cdot \mathbf{B}(\mathbf{r},t) &= 0 && (6.2)\\
\nabla \times \mathbf{E}(\mathbf{r},t) &= -\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r},t) && (6.3)\\
\nabla \times \mathbf{B}(\mathbf{r},t) &= \frac{1}{c^2}\frac{\partial}{\partial t}\mathbf{E}(\mathbf{r},t). && (6.4)
\end{aligned}$$

Adapting these equations to the realm of quantum mechanics necessitates the identification of conjugate canonical variables, which would become operators in the quantum mechanics version of electrodynamics and subjected to the same commutation relations as $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. The procedure to be taken here is fairly similar to the one we used for the one-dimensional harmonic oscillator (see Exercise 1.6 in Chapter 1).

6.1.1 Expansion using Normal Modes

Since a radiation field can exist in different ***modes***, i.e., it can propagate along different directions, at different frequencies and exhibit different polarization states, it will be to our advantage to express the fields (i.e., electric, magnetic and potentials) with a Fourier series. To do so, we must define a volume over which the radiation field will evolve. In some cases, that volume is physical and can easily be identified (e.g., the interior of a cavity) but there does not always exist clear boundaries to delimitate the region where this evolution takes place. We will therefore subjectively introduce a cube of length L for that volume, with the understanding that any physical results stemming from the quantization process cannot depend on the exact nature of the volume (also note that a Fourier series expansion always implies a periodic signal, which also does not need to be realized physically). Because of this we expect and require that any mathematical "trace" of the chosen volume "disappears" from or is absorbed in the relevant physical quantities appearing in the equations. We therefore define the electric field as follows

$$\mathbf{E}(\mathbf{r},t) = \sum_{\mathbf{n}} \overline{\mathbf{E}}_{\mathbf{n}}(t)\, e^{i\mathbf{k}_{\mathbf{n}}\cdot\mathbf{r}}, \tag{6.5}$$

where $\mathbf{n} = n_x\mathbf{e}_x + n_y\mathbf{e}_y + n_z\mathbf{e}_z$ is a unit vector defining the direction of propagation and

$$\overline{\mathbf{E}}_{\mathbf{n}}(t) = \frac{1}{L^3}\int_V \mathbf{E}(\mathbf{r},t)\, e^{-i\mathbf{k}_{\mathbf{n}}\cdot\mathbf{r}} d^3x \tag{6.6}$$

are the Fourier coefficients (also $V = L^3$). The wave vector is thus defined with

$$\mathbf{k}_{\mathbf{n}} = \frac{2\pi}{L}\left(n_x\mathbf{e}_x + n_y\mathbf{e}_y + n_z\mathbf{e}_z\right). \tag{6.7}$$

With this formalism the divergence relations of Maxwell's equations (i.e, equations (6.1) and (6.2)) reduce to

$$\begin{aligned} \mathbf{k}_{\mathbf{n}} \cdot \overline{\mathbf{E}}_{\mathbf{n}} &= 0 && (6.8)\\ \mathbf{k}_{\mathbf{n}} \cdot \overline{\mathbf{B}}_{\mathbf{n}} &= 0 && (6.9) \end{aligned}$$

since all modes in equation (6.5) must independently equal zero. Equations (6.8)-(6.9) also make clear that the fields are transverse to the direction of propagation, which imply that two mutually orthogonal polarization modes can exist for them. For example, the electric field can be decomposed into linear polarization states $\boldsymbol{\varepsilon}_{\mathbf{n},1}$ and $\boldsymbol{\varepsilon}_{\mathbf{n},2}$ such that

$$\begin{aligned} \boldsymbol{\varepsilon}^*_{\mathbf{n},1} \cdot \boldsymbol{\varepsilon}_{\mathbf{n},2} &= \boldsymbol{\varepsilon}_{\mathbf{n},1} \cdot \boldsymbol{\varepsilon}_{\mathbf{n},2} \\ &= 0, && (6.10) \end{aligned}$$

and (with $j = 1, 2$)

$$\mathbf{k}_{\mathbf{n}} \cdot \boldsymbol{\varepsilon}_{\mathbf{n},j} = 0. \tag{6.11}$$

We therefore redefine the modes by combining the polarization state j to $\mathbf{n}$ such that

$$p = (\mathbf{n}; j) \tag{6.12}$$

and

$$\begin{aligned} \mathbf{E}(\mathbf{r},t) &= \sum_p \boldsymbol{\varepsilon}_p \overline{E}_p(t)\, e^{i\mathbf{k}_p\cdot\mathbf{r}} && (6.13)\\ \overline{E}_p(t) &= \frac{1}{L^3}\int_V \boldsymbol{\varepsilon}_p \cdot \mathbf{E}(\mathbf{r},t)\, e^{-i\mathbf{k}_p\cdot\mathbf{r}} d^3x. && (6.14) \end{aligned}$$

We note here a few relations that will be useful later on

$$\begin{aligned} \boldsymbol{\varepsilon}_{-p} &= \boldsymbol{\varepsilon}_p & (6.15)\\ \mathbf{k}_{-p} &= -\mathbf{k}_p, & (6.16) \end{aligned}$$

i.e., the polarization state $\boldsymbol{\varepsilon}_p$ is not affected by reversing the sense of propagation, and

$$\begin{aligned} \boldsymbol{\varepsilon}'_p &= \mathbf{n} \times \boldsymbol{\varepsilon}_p \\ &= \frac{\mathbf{k}_p}{k_p} \times \boldsymbol{\varepsilon}_p & (6.17) \end{aligned}$$

with $k_p = |\mathbf{k}_p|$. We should also note that, contrarily to $\boldsymbol{\varepsilon}_p$, $\boldsymbol{\varepsilon}'_{-p} = -\boldsymbol{\varepsilon}'_p$. It is easy to verify from equations (6.3) that the magnetic induction field is expressed by

$$\begin{aligned} \mathbf{B}(\mathbf{r}, t) &= \sum_p \boldsymbol{\varepsilon}'_p \overline{B}_p(t)\, e^{i\mathbf{k}_p \cdot \mathbf{r}} & (6.18)\\ \overline{B}_p(t) &= \frac{1}{L^3} \int_V \boldsymbol{\varepsilon}'_p \cdot \mathbf{B}(\mathbf{r}, t)\, e^{-i\mathbf{k}_p \cdot \mathbf{r}} d^3x. & (6.19) \end{aligned}$$

Equation (6.18) follows from the fact that only $\overline{B}_p(t)$ is dependent on time in the Fourier expansion, i.e.,

$$\begin{aligned} \sum_p \boldsymbol{\varepsilon}'_p \frac{\partial \overline{B}_p(t)}{\partial t} e^{i\mathbf{k}_p \cdot \mathbf{r}} &= \frac{\partial}{\partial t} \sum_p \boldsymbol{\varepsilon}'_p \overline{B}_p(t)\, e^{i\mathbf{k}_p \cdot \mathbf{r}} \\ &= \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t}. & (6.20) \end{aligned}$$

As is well known, Maxwell's equations are invariant under certain gauge transformations. For our purpose, it will be advantageous to choose the ***Coulomb gauge*** that constrains the potential vector $\mathbf{A}(\mathbf{r}, t)$ with

$$\nabla \cdot \mathbf{A}(\mathbf{r}, t) = 0, \tag{6.21}$$

which leaves the magnetic and electric fields unchanged at

$$\begin{aligned} \mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t) & (6.22)\\ \mathbf{E}(\mathbf{r}, t) &= -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} - \nabla \Phi(\mathbf{r}, t) & (6.23) \end{aligned}$$

with $\Phi(\mathbf{r}, t)$ the electric scalar potential. Applying equation (6.1) to equation (6.23) simplifies our problem since

$$\begin{aligned}\nabla\cdot\mathbf{E}(\mathbf{r},t) &= -\frac{\partial}{\partial t}\nabla\cdot\mathbf{A}(\mathbf{r},t)-\nabla\cdot\nabla\Phi(\mathbf{r},t)\\ &= -\nabla\cdot\nabla\Phi(\mathbf{r},t)\\ &= 0\end{aligned}\tag{6.24}$$

and we choose[1] $\Phi(\mathbf{r},t)=0$. It follows from equations (6.13), (6.18), (6.22) and (6.23) that

$$\mathbf{A}(\mathbf{r},t) = \sum_p \boldsymbol{\varepsilon}_p \overline{A}_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} \tag{6.25}$$

$$\overline{A}_p(t) = \frac{1}{L^3}\int_V \boldsymbol{\varepsilon}_p\cdot\mathbf{A}(\mathbf{r},t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}d^3x \tag{6.26}$$

and

$$\overline{B}_p(t) = ik_p\overline{A}_p(t) \tag{6.27}$$

$$\overline{E}_p(t) = -\frac{d}{dt}\overline{A}_p(t). \tag{6.28}$$

We can eliminate one of the fields from these two equations with the Ampère-Maxwell Law, i.e., equation (6.4)

$$\frac{d}{dt}\overline{E}_p(t) = -ic^2k_p\overline{B}_p(t), \tag{6.29}$$

and from equation (6.27)

$$\frac{d}{dt}\overline{E}_p(t) = \omega_p^2\overline{A}_p(t) \tag{6.30}$$

with $\omega_p = ck_p$. Equations (6.28) and (6.30) form a set of two coupled differential equations involving two variables. Despite their appearance, however, they are not constrained to only one radiation mode since

$$\overline{E}_{-p}(t) = \overline{E}_p^*(t) \tag{6.31}$$

$$\overline{A}_{-p}(t) = \overline{A}_p^*(t) \tag{6.32}$$

from equations (6.14) and (6.26) and the fact that these (classical) fields are real. The modes p and $-p$ are thus coupled, which is something we would like to avoid when we apply the aforementioned commutation relation in the quantum mechanical version. We

[1] Although, for example, $\Phi(\mathbf{r},t)\propto x$ would verify equation (6.24), it must be rejected on the grounds that the potential must be finite everywhere in space. The scalar potential can thus only be equal to a constant, which we choose to be zero.

therefore need to find quantities that do not exhibit this interdependency between these modes.

Let us now consider

$$\begin{aligned}\alpha_p(t) &= \frac{1}{2\mathcal{E}_p}\left[\omega_p\overline{A}_p(t) - i\overline{E}_p(t)\right] && (6.33)\\ \beta_p(t) &= \frac{1}{2\mathcal{E}_p}\left[\omega_p\overline{A}_p(t) + i\overline{E}_p(t)\right] && (6.34)\end{aligned}$$

with $\mathcal{E}_p$ is a constant to be evaluated. Equivalently, we have

$$\begin{aligned}\overline{E}_p(t) &= i\mathcal{E}_p\left[\alpha_p(t) - \beta_p(t)\right] && (6.35)\\ \overline{A}_p(t) &= \frac{\mathcal{E}_p}{\omega_p}\left[\alpha_p(t) + \beta_p(t)\right]. && (6.36)\end{aligned}$$

Combining equations (6.28), (6.30), (6.33) and (6.34) we find that

$$\begin{aligned}\frac{d}{dt}\alpha_p(t) + i\omega_p\alpha_p(t) &= 0 && (6.37)\\ \frac{d}{dt}\beta_p(t) - i\omega_p\beta_p(t) &= 0, && (6.38)\end{aligned}$$

which admit for solutions

$$\begin{aligned}\alpha_p(t) &= \alpha_p(0)\,e^{-i\omega_p t} && (6.39)\\ \beta_p(t) &= \beta_p(0)\,e^{i\omega_p t}. && (6.40)\end{aligned}$$

Unlike $\overline{E}_p(t)$ and $\overline{A}_p(t)$ in equations (6.28) and (6.30), the ***normal variables*** $\alpha_p(t)$ and $\beta_p(t)$ are found to be decoupled in equations (6.37)-(6.38). Equations (6.31)-(6.32) also show that $\beta_p^*(t) = \alpha_{-p}(t)$ and we can write from equations (6.35)-(6.36)

$$\begin{aligned}\mathbf{E}(\mathbf{r},t) &= i\sum_p \mathcal{E}_p\boldsymbol{\varepsilon}_p\left[\alpha_p(t) - \alpha_{-p}^*(t)\right]e^{i\mathbf{k}_p\cdot\mathbf{r}}\\ &= i\sum_p \mathcal{E}_p\boldsymbol{\varepsilon}_p\left[\alpha_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} - \alpha_p^*(t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right] && (6.41)\\ \mathbf{A}(\mathbf{r},t) &= \sum_p \frac{\mathcal{E}_p}{\omega_p}\boldsymbol{\varepsilon}_p\left[\alpha_p(t) + \alpha_{-p}^*(t)\right]e^{i\mathbf{k}_p\cdot\mathbf{r}}\\ &= \sum_p \frac{\mathcal{E}_p}{\omega_p}\boldsymbol{\varepsilon}_p\left[\alpha_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} + \alpha_p^*(t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right] && (6.42)\\ \mathbf{B}(\mathbf{r},t) &= \nabla\times\mathbf{A}(\mathbf{r},t)\\ &= i\sum_p \frac{\mathcal{E}_p}{c}\boldsymbol{\varepsilon}_p'\left[\alpha_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} - \alpha_p^*(t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right]. && (6.43)\end{aligned}$$

6.1.2 The Hamiltonian for the Free Radiation Field and The Conjugate Canonical Variables

The energy, or Hamiltonian, contained in an electromagnetic field is given by

$$H_{\mathrm{R}} = \frac{\epsilon_0}{2}\int_V \left[E^2(\mathbf{r},t) + c^2 B^2(\mathbf{r},t)\right] d^3x. \tag{6.44}$$

We must then evaluate the following integrals (dropping the explicit time dependency for the moment)

$$\int_V E^2(\mathbf{r},t)\, d^3x = -\sum_{p,q}\mathcal{E}_p\mathcal{E}_q\boldsymbol{\varepsilon}_p\cdot\boldsymbol{\varepsilon}_q\int_V\left(\alpha_p e^{i\mathbf{k}_p\cdot\mathbf{r}} - \alpha_p^* e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right)\left(\alpha_q e^{i\mathbf{k}_q\cdot\mathbf{r}} - \alpha_q^* e^{-i\mathbf{k}_q\cdot\mathbf{r}}\right) \tag{6.45}$$

$$\int_V c^2B^2(\mathbf{r},t)\, d^3x = -\sum_{p,q}\mathcal{E}_p\mathcal{E}_q\boldsymbol{\varepsilon}'_p\cdot\boldsymbol{\varepsilon}'_q\int_V\left(\alpha_p e^{i\mathbf{k}_p\cdot\mathbf{r}} - \alpha_p^* e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right)\left(\alpha_q e^{i\mathbf{k}_q\cdot\mathbf{r}} - \alpha_q^* e^{-i\mathbf{k}_q\cdot\mathbf{r}}\right) \tag{6.46}$$

But we know that

$$\begin{aligned}
\int_{-L/2}^{L/2} e^{i(k_i+k_j)x}dx &= \int_{-L/2}^{L/2}\left\{\cos\left[(n_i+n_j)\frac{2\pi x}{L}\right] + i\sin\left[(n_i+n_j)\frac{2\pi x}{L}\right]\right\}dx \\
&= \int_{-L/2}^{L/2}\cos\left[(n_i+n_j)\frac{2\pi x}{L}\right]dx \\
&= L\delta_{(i)(-j)}
\end{aligned} \tag{6.47}$$

as well as $\boldsymbol{\varepsilon}_p\cdot\boldsymbol{\varepsilon}_q = \boldsymbol{\varepsilon}'_p\cdot\boldsymbol{\varepsilon}'_q = \delta_{|p||q|}$ and $\boldsymbol{\varepsilon}'_{-p} = -\boldsymbol{\varepsilon}'_p$, thus we have

$$\begin{aligned}
\int_V E^2(\mathbf{r},t)\, d^3x &= -L^3\sum_p \mathcal{E}_p^2\left(\alpha_p\alpha_{-p} - \alpha_p\alpha_p^* - \alpha_p^*\alpha_p + \alpha_p^*\alpha_{-p}^*\right) \\
&= L^3\sum_p \mathcal{E}_p^2\left(2\alpha_p\alpha_p^* - \alpha_p\alpha_{-p} - \alpha_p^*\alpha_{-p}^*\right)
\end{aligned} \tag{6.48}$$

$$\begin{aligned}
\int_V c^2B^2(\mathbf{r},t)\, d^3x &= -L^3\sum_p \mathcal{E}_p^2\left(-\alpha_p\alpha_{-p} - \alpha_p\alpha_p^* + \alpha_p^*\alpha_p + \alpha_p^*\alpha_{-p}^*\right) \\
&= L^3\sum_p \mathcal{E}_p^2\left(2\alpha_p\alpha_p^* + \alpha_p\alpha_{-p} + \alpha_p^*\alpha_{-p}^*\right).
\end{aligned} \tag{6.49}$$

It follows that

$$\begin{aligned}
H_{\mathrm{R}} &= 2\epsilon_0 L^3\sum_p \mathcal{E}_p^2\left|\alpha_p(t)\right|^2 \\
&= 2\epsilon_0 L^3\sum_p \mathcal{E}_p^2\left(\mathrm{Re}^2\{\alpha_p(t)\} + \mathrm{Im}^2\{\alpha_p(t)\}\right).
\end{aligned} \tag{6.50}$$

We have now expressed the Hamiltonian for the free radiation field in a form similar to that for an harmonic oscillator (see equation (1.189) in Chapter 1). Importantly, we note that the modes are now completely decoupled. We thus introduce the quantities

$$Q_p(t) = 2\mathcal{E}_p\sqrt{\frac{\epsilon_0 L^3}{\omega_p}}\mathrm{Re}\{\alpha_p(t)\} \tag{6.51}$$

$$P_p(t) = 2\mathcal{E}_p\sqrt{\frac{\epsilon_0 L^3}{\omega_p}}\mathrm{Im}\{\alpha_p(t)\}, \tag{6.52}$$

which can be verified to be ***conjugate canonical variables*** since they are linked through Hamilton's canonical equations of motions (see equation (6.37))

$$\frac{d}{dt}Q_p = \frac{\partial H_\mathrm{R}}{\partial P_p} \tag{6.53}$$

$$\frac{d}{dt}P_p = -\frac{\partial H_\mathrm{R}}{\partial Q_p} \tag{6.54}$$

with

$$H_\mathrm{R} = \frac{1}{2}\sum_p \omega_p\left[Q_p^2(t) + P_p^2(t)\right]. \tag{6.55}$$

6.2 Quantum Mechanical Formulation for the Free Electromagnetic Field

To proceed with the quantization of the free electromagnetic field we will associate to the conjugate canonical variables $Q_p(t)$ and $P_p(t)$ the quantum mechanical operators $\hat{Q}_p$ and $\hat{P}_p$ and impose the canonical commutation relations

$$\left[\hat{Q}_p, \hat{P}_q\right] = i\hbar\hat{1}\delta_{pq} \tag{6.56}$$

$$\left[\hat{Q}_p, \hat{Q}_q\right] = \hat{0} \tag{6.57}$$

$$\left[\hat{P}_p, \hat{P}_q\right] = \hat{0}. \tag{6.58}$$

We note that because we will be working in the Schrödinger representation these operators will be assumed time-independent (conversely, time dependencies would be used for the Heisenberg representation).

Keeping our analogy with our previous classical formulation, we introduce the (time-independent) operator $\hat{a}_p$ corresponding to the variable $\alpha_p(t)$

$$\hat{Q}_p + i\hat{P}_p = 2\mathcal{E}_p\sqrt{\frac{\epsilon_0 L^3}{\omega_p}}\hat{a}_p. \tag{6.59}$$

If we define

$$\mathcal{E}_p = \sqrt{\frac{\hbar\omega_p}{2\epsilon_0 L^3}}, \tag{6.60}$$

then we have

$$\begin{aligned}
\left[\hat{a}_p, \hat{a}_q^\dagger\right] &= \hat{1}\delta_{pq} &(6.61)\\
\left[\hat{a}_p, \hat{a}_q\right] &= \hat{0} &(6.62)\\
\left[\hat{a}_p^\dagger, \hat{a}_q^\dagger\right] &= \hat{0}. &(6.63)
\end{aligned}$$

The $\hat{a}_p$ and $\hat{a}_p^\dagger$ operators are, respectively, the ***annihilation and creation operators*** we previously encountered in our analysis of the harmonic oscillator (see Exercise 1.6 in Chapter 1). The Hamiltonian can written as

$$\begin{aligned}
\hat{H}_{\mathrm{R}} &= \sum_p \hbar\omega_p\left(\hat{a}_p\hat{a}_p^\dagger + \hat{a}_p^\dagger\hat{a}_p\right)\\
&= \sum_p \hbar\omega_p\left(\hat{a}_p^\dagger\hat{a}_p + \frac{1}{2}\right)\\
&= \sum_p \hbar\omega_p\left(\hat{N}_p + \frac{1}{2}\right), &(6.64)
\end{aligned}$$

where the ***number operator***

$$\hat{N}_p = \hat{a}_p^\dagger\hat{a}_p \tag{6.65}$$

was introduced. We note that fields are also (time-independent) operators since

$$\begin{aligned}
\hat{\mathbf{A}}(\mathbf{r}) &= \sum_p \frac{\mathcal{E}_p}{\omega_p}\boldsymbol{\varepsilon}_p\left[e^{i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p + e^{-i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p^\dagger\right]\\
&\equiv \hat{\mathbf{A}}^+(\mathbf{r}) + \hat{\mathbf{A}}^-(\mathbf{r}) &(6.66)\\
\hat{\mathbf{E}}(\mathbf{r}) &= i\sum_p \mathcal{E}_p\boldsymbol{\varepsilon}_p\left[e^{i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p - e^{-i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p^\dagger\right]\\
&\equiv \hat{\mathbf{E}}^+(\mathbf{r}) + \hat{\mathbf{E}}^-(\mathbf{r}) &(6.67)\\
\hat{\mathbf{B}}(\mathbf{r}) &= i\sum_p \frac{\mathcal{E}_p}{c}\boldsymbol{\varepsilon}'_p\left[e^{i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p - e^{-i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p^\dagger\right]\\
&\equiv \hat{\mathbf{B}}^+(\mathbf{r}) + \hat{\mathbf{B}}^-(\mathbf{r}). &(6.68)
\end{aligned}$$

We should also note that $\left[\hat{\mathbf{A}}^{+}(\mathbf{r})\right]^{\dagger}=\hat{\mathbf{A}}^{-}(\mathbf{r})$, etc.

This formalism, based on the annihilation and creation operators, their commutation relations (i.e., equations (6.61)-(6.63)), the resulting form of the Hamiltonian (equation (6.64)) and the number operator (equation (6.65)), is the same we have encountered in Exercise 1.6 of Chapter 1 with the harmonic oscillator. We therefore use the same kind of basis $\{|n_p\rangle\}$ (generalized to an arbitrary number of dimensions) where, for $n_p \geq 0$,

$$\begin{aligned} \hat{a}_p^{\dagger}|n_p\rangle &= \sqrt{n_p+1}\,|n_p+1\rangle & (6.69)\\ \hat{a}_p|n_p\rangle &= \sqrt{n_p}\,|n_p-1\rangle & (6.70)\end{aligned}$$

and

$$\hat{N}_p|n_p\rangle = n_p|n_p\rangle . \tag{6.71}$$

It is easy to verify from equation (6.70) the following relation between the lowest energy state $|0_p\rangle$ and any other states

$$|n_p\rangle = \frac{\left(\hat{a}_p^{\dagger}\right)^{n_p}}{\sqrt{n_p!}}|0_p\rangle . \tag{6.72}$$

However, the system is made of a large (potentially infinite) number of independent modes p that will result in the total state of the radiation field to be given by the ket $|n_1, n_2, \ldots, n_p, \ldots\rangle$, with the eigenvalue equation

$$\hat{H}_{\mathrm{R}}|n_1, n_2, \ldots, n_p, \ldots\rangle = \sum_p \left(n_p+\frac{1}{2}\right)\hbar\omega_p|n_1, n_2, \ldots, n_p, \ldots\rangle . \tag{6.73}$$

It is interesting and important to note that the ground state of the system

$$|0\rangle \equiv |n_1=0, n_2=0, \ldots, n_p=0, \ldots\rangle , \tag{6.74}$$

called the ***radiation vacuum state***, has a non-zero energy content. That is,

$$\begin{aligned} \hat{H}_{\mathrm{R}}|0\rangle &= E_V|0\rangle \\ &= \frac{1}{2}\sum_p \hbar\omega_p|0\rangle . & (6.75)\end{aligned}$$

We can also generalize equation (6.72), given for one mode, to the entire radiation field with

$$|n_1, n_2, \ldots, n_p, \ldots\rangle = \prod_p \frac{\left(\hat{a}_p^{\dagger}\right)^{n_p}}{\sqrt{n_p!}}|0\rangle . \tag{6.76}$$

We are then left with the picture of the vacuum state $|0\rangle$ devoid of any "particle" can be altered by the creation operator $\hat{a}_p^\dagger$ by adding a particle to the mode p, i.e.,

$$\hat{a}_p^\dagger |0\rangle = |n_1 = 0, n_2 = 0, \ldots, n_p = 1, \ldots\rangle . \tag{6.77}$$

This interpretation is reinforced by a comparison of the energy contents between the two states

$$\begin{aligned} E\left(n_1 = 0, n_2 = 0, \ldots, n_p = 1, \ldots\right) - E_V &= \left(E_V + \hbar\omega_p\right) - E_V \\ &= \hbar\omega_p, \end{aligned} \tag{6.78}$$

where we find that the creation of a particle is accompanied by a quantum of energy $\hbar\omega_p$. The associated particle is called a ***photon***.

Finally, the kets forming the basis $\{|n_1, n_2, \ldots, n_p, \ldots\rangle\}$, commonly known as ***Fock states***, can be used to generate or expand any other radiation state $|\psi\rangle$ in the usual manner, i.e.,

$$|\psi\rangle = \sum_{n_1, n_2, \ldots, n_p, \ldots = 0}^{\infty} c_{n_1, n_2, \ldots, n_p, \ldots} |n_1, n_2, \ldots, n_p, \ldots\rangle , \tag{6.79}$$

with $c_{n_1, n_2, \ldots, n_p, \ldots}$ a complex number and $\langle \psi \mid \psi \rangle = 1$.

6.3 Interaction between Matter and the Quantized Radiation Field

If we are to describe the interaction of radiation and matter in a fully quantum mechanical formalism, then we must augment the form of the (classical) Maxwell's equations used in Section 6.1 to include the charges and currents that are sources of, and interact with, electromagnetic fields. Equations (6.1)-(6.4) are then replaced with

$$\nabla \cdot \mathbf{E}(\mathbf{r}, t) = \frac{1}{\epsilon_0} \rho(\mathbf{r}, t) \tag{6.80}$$

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0 \tag{6.81}$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t} \mathbf{B}(\mathbf{r}, t) \tag{6.82}$$

$$\nabla \times \mathbf{B}(\mathbf{r}, t) = \frac{1}{c^2} \frac{\partial}{\partial t} \mathbf{E}(\mathbf{r}, t) + \mu_0 \mathbf{J}(\mathbf{r}, t) , \tag{6.83}$$

where $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ are the charge and current densities, respectively. These quantities can be broken down into the contributions of the elementary charges q_j, of mass m_j located at $\mathbf{r}_j$ and moving at velocity $\mathbf{v}_j$ at time t, composing the system under studies with

$$\begin{aligned}
\rho(\mathbf{r},t) &= \sum_j q_j \delta\left[\mathbf{r}-\mathbf{r}_j(t)\right] && (6.84)\\
\mathbf{J}(\mathbf{r},t) &= \sum_j q_j \mathbf{v}_j \delta\left[\mathbf{r}-\mathbf{r}_j(t)\right] && (6.85)
\end{aligned}$$

These quantities interact with the electromagnetic field through the ***Lorentz Force***

$$m_j \frac{d\mathbf{v}_j}{dt} = q_j\left[\mathbf{E}(\mathbf{r},t) + \mathbf{v}_j \times \mathbf{B}(\mathbf{r},t)\right]. \tag{6.86}$$

Keeping with the same Fourier expansion as before, i.e., we have for the charge and current densities

$$\begin{aligned}
\rho(\mathbf{r},t) &= \sum_{\mathbf{n}} \overline{\rho}_{\mathbf{n}}(t)\, e^{i\mathbf{k_n}\cdot\mathbf{r}} && (6.87)\\
\mathbf{J}(\mathbf{r},t) &= \sum_{\mathbf{n}} \overline{\mathbf{J}}_{\mathbf{n}}(t)\, e^{i\mathbf{k_n}\cdot\mathbf{r}} && (6.88)
\end{aligned}$$

with

$$\begin{aligned}
\overline{\rho}_{\mathbf{n}}(t) &= \frac{1}{L^3}\int_V \rho(\mathbf{r},t)\, e^{-i\mathbf{k_n}\cdot\mathbf{r}} && (6.89)\\
\overline{\mathbf{J}}_{\mathbf{n}}(t) &= \frac{1}{L^3}\int_V \mathbf{J}(\mathbf{r},t)\, e^{-i\mathbf{k_n}\cdot\mathbf{r}}, && (6.90)
\end{aligned}$$

equations (6.80)-(6.83) yield

$$\begin{aligned}
i\mathbf{k_n}\cdot\overline{\mathbf{E}}_{\mathbf{n}}(t) &= \frac{1}{\epsilon_0}\overline{\rho}_{\mathbf{n}}(t) && (6.91)\\
i\mathbf{k_n}\cdot\overline{\mathbf{B}}_{\mathbf{n}}(t) &= 0 && (6.92)\\
i\mathbf{k_n}\times\overline{\mathbf{E}}_{\mathbf{n}}(t) &= -\frac{d}{dt}\overline{\mathbf{B}}_{\mathbf{n}}(t) && (6.93)\\
i\mathbf{k_n}\times\overline{\mathbf{B}}_{\mathbf{n}}(t) &= \frac{1}{c^2}\frac{d}{dt}\overline{\mathbf{E}}_{\mathbf{n}}(t) + \mu_0\overline{\mathbf{J}}_{\mathbf{n}}(t). && (6.94)
\end{aligned}$$

Clearly this set of equations implies situations that are more complicated than what was considered for the free radiation field. For example, although equation (6.92) shows that the magnetic induction field is still perpendicular to it, equation (6.91) reveals the presence of an electric field component parallel to $\mathbf{k_n}$. We therefore write for the electric field

$$\begin{aligned}
\mathbf{E}(\mathbf{r},t) &= \mathbf{E}_{\parallel}(\mathbf{r},t) + \mathbf{E}_{\perp}(\mathbf{r},t)\\
&= E_{\parallel}(\mathbf{r},t)\,\mathbf{e}_n + \mathbf{E}_{\perp}(\mathbf{r},t), && (6.95)
\end{aligned}$$

where $\mathbf{e}_n \equiv \mathbf{n} = \mathbf{k_n}/k_\mathbf{n}$ (see equation (6.91)) and $\mathbf{E}_\perp(\mathbf{r},t)$ has components in the $(\boldsymbol{\varepsilon}_{\mathbf{n},1}, \boldsymbol{\varepsilon}_{\mathbf{n},2})$-plane perpendicular to $\mathbf{e}_n$. The Fourier coefficients can be likewise broken down

$$\overline{\mathbf{E}}_\mathbf{n}(t) = \mathbf{E}_{\parallel,\mathbf{n}}(t) + \overline{\mathbf{E}}_{\perp,\mathbf{n}}(t). \tag{6.96}$$

Equations (6.80)-(6.82), (6.91)-(6.93) and (6.95) can be combined to give

$$\begin{aligned} \nabla\cdot\mathbf{E}_\parallel(\mathbf{r},t) &= \frac{1}{\epsilon_0}\rho(\mathbf{r},t) &(6.97)\\ \nabla\times\mathbf{E}_\parallel(\mathbf{r},t) &= \mathbf{0}. &(6.98)\end{aligned}$$

The last of these relations implies that $\mathbf{E}_\parallel(\mathbf{r},t)$ can be expressed as (minus) the gradient of some potential $\Phi_\parallel(\mathbf{r},t)$, as in electrostatic, and from equation (6.97)

$$\nabla^2\Phi_\parallel(\mathbf{r},t) = -\frac{1}{\epsilon_0}\rho(\mathbf{r},t), \tag{6.99}$$

or equivalently

$$\mathbf{E}_\parallel(\mathbf{r},t) = \frac{1}{4\pi\epsilon_0}\sum q_j\frac{\mathbf{r}-\mathbf{r}_j(t)}{|\mathbf{r}-\mathbf{r}_j(t)|^3}. \tag{6.100}$$

The longitudinal component of the electric field is then similar in form to the electrostatic due to a charge distribution (i.e., Coulomb's Law), except for the fact that it dynamically evolves with time as the positions of the individual charges change. Since we know from classical electrodynamics that radiation fields are due to the acceleration of charges, we conclude that *the longitudinal electric field is not a radiation field.*

We already stated that the magnetic field is transverse because of equation (6.92), i.e., $\mathbf{B}_\parallel(\mathbf{r},t) = 0$. Its transverse component is contained in the remaining two of Maxwell's equations

$$\begin{aligned} \nabla\times\mathbf{E}_\perp(\mathbf{r},t) &= -\frac{\partial}{\partial t}\mathbf{B}_\perp(\mathbf{r},t) &(6.101)\\ \nabla\times\mathbf{B}_\perp(\mathbf{r},t) &= \frac{1}{c^2}\frac{\partial}{\partial t}\mathbf{E}_\perp(\mathbf{r},t) + \mu_0\mathbf{J}_\perp(\mathbf{r},t), &(6.102)\end{aligned}$$

which can be combined to yield (with $\nabla\cdot\overline{\mathbf{E}}_\perp(\mathbf{r},t) = 0$)

$$\begin{aligned} \nabla\times[\nabla\times\mathbf{E}_\perp(\mathbf{r},t)] &= -\nabla^2\mathbf{E}_\perp(\mathbf{r},t)\\ &= -\frac{\partial}{\partial t}[\nabla\times\mathbf{B}_\perp(\mathbf{r},t)]\\ &= -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}_\perp(\mathbf{r},t) - \mu_0\frac{\partial}{\partial t}\mathbf{J}_\perp(\mathbf{r},t), &(6.103)\end{aligned}$$

or

$$\nabla^2 \mathbf{E}_\perp(\mathbf{r},t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}_\perp(\mathbf{r},t) = \mu_0 \frac{\partial}{\partial t}\mathbf{J}_\perp(\mathbf{r},t). \tag{6.104}$$

In the same manner we can derive

$$\nabla^2 \mathbf{B}_\perp(\mathbf{r},t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{B}_\perp(\mathbf{r},t) = -\mu_0 \nabla \times \mathbf{J}_\perp(\mathbf{r},t). \tag{6.105}$$

As equations (6.104)-(6.105) are inhomogeneous forms of the wave equation, yielding retarded solutions for the fields, we conclude that *the transverse components of the electric and magnetic fields form the radiating electromagnetic field.*

Just as we did in Section 6.1 we proceed by trying to formulate the problem using normal variables in order to separate the different modes of radiation in the Hamiltonian. We thus introduce, once again, the magnetic vector potential, which, like $\mathbf{B}_\perp(\mathbf{r},t)$, will be transverse when using the Coulomb gauge since $\nabla \cdot \mathbf{A}_\perp(\mathbf{r},t) = 0$. With the Fourier expansion for all the transverse quantities, i.e., $\mathbf{E}_\perp(\mathbf{r},t)$, $\mathbf{B}_\perp(\mathbf{r},t)$, $\mathbf{A}_\perp(\mathbf{r},t)$ and $\mathbf{J}_\perp(\mathbf{r},t)$, Maxwell's equations (i.e., equations (6.93)-(6.94)) can be transformed to

$$\begin{aligned} \frac{d}{dt}\overline{B}_{\perp p}(t) &= -ik_p\overline{E}_{\perp p}(t) && (6.106)\\ \frac{d}{dt}\overline{E}_{\perp p}(t) &= -ic^2k_p\overline{B}_{\perp p}(t) - \frac{1}{\epsilon_0}\overline{J}_{\perp p}(t). && (6.107) \end{aligned}$$

Using $\mathbf{B}_\perp(\mathbf{r},t) = \nabla \times \mathbf{A}_\perp(\mathbf{r},t)$ to relate $\overline{B}_{\perp p}$ and $\overline{A}_{\perp p}$ (see equation (6.27)) we can write

$$\begin{aligned} \frac{d}{dt}\overline{A}_{\perp p}(t) &= -\overline{E}_{\perp p}(t) && (6.108)\\ \frac{d}{dt}\overline{E}_{\perp p}(t) &= \omega_p^2\overline{A}_{\perp p}(t) - \frac{1}{\epsilon_0}\overline{J}_{\perp p}(t). && (6.109) \end{aligned}$$

Defining the normal variables $\alpha_p(t)$ and $\beta_p(t)$ in a manner similar as when dealing with the free field

$$\begin{aligned} \alpha_p(t) &= \frac{1}{2\mathcal{E}_p}\left[\omega_p\overline{A}_{\perp p}(t) - i\overline{E}_{\perp p}(t)\right] && (6.110)\\ \beta_p(t) &= \frac{1}{2\mathcal{E}_p}\left[\omega_p\overline{A}_{\perp p}(t) + i\overline{E}_{\perp p}(t)\right] && (6.111) \end{aligned}$$

we find that equations (6.108)-(6.109) decouple to

$$\begin{aligned} \frac{d}{dt}\alpha_p(t) + i\omega_p\alpha_p(t) &= \frac{i}{2\epsilon_0\mathcal{E}_p}\overline{J}_{\perp p}(t) && (6.112)\\ \frac{d}{dt}\beta_p(t) - i\omega_p\beta_p(t) &= -\frac{i}{2\epsilon_0\mathcal{E}_p}\overline{J}_{\perp p}(t) && (6.113) \end{aligned}$$

We therefore see that the transverse current density acts as a forcing term for these differential equations, unlike for the free field where we had homogeneous equations. However, it is still the case that $\beta_p^*(t) = \alpha_{-p}(t)$ and we can again write

$$\begin{aligned}
\mathbf{A}_\perp(\mathbf{r},t) &= \sum_p \frac{\mathcal{E}_p}{\omega_p}\boldsymbol{\varepsilon}_p\left[\alpha_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} + \alpha_p^*(t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right] && (6.114)\\
\mathbf{E}_\perp(\mathbf{r},t) &= i\sum_p \mathcal{E}_p\boldsymbol{\varepsilon}_p\left[\alpha_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} - \alpha_p^*(t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right] && (6.115)\\
\mathbf{B}_\perp(\mathbf{r},t) &= i\sum_p \frac{\mathcal{E}_p}{c}\boldsymbol{\varepsilon}'_p\left[\alpha_p(t)\,e^{i\mathbf{k}_p\cdot\mathbf{r}} - \alpha_p^*(t)\,e^{-i\mathbf{k}_p\cdot\mathbf{r}}\right] && (6.116)
\end{aligned}$$

when following the technique used for the free field.

6.3.1 The Hamiltonian with Radiation-Matter Interaction

When dealing with the Lagrangian or Hamiltonian formulation for a charge q of mass m interacting with an electromagnetic field, it is possible to show that (see the Third Problem List) the Hamiltonian can be written as

$$H' = \frac{1}{2m}\left[\mathbf{p} - q\mathbf{A}(\mathbf{r},t)\right]^2 + q\Phi(\mathbf{r},t)\,, \tag{6.117}$$

where $\mathbf{A}(\mathbf{r},t)$ and $\Phi(\mathbf{r},t)$ are, respectively the magnetic vector and electric scalar potentials at the position $\mathbf{r}$ of the charge at time t, and the generalized momentum $\mathbf{p}$ of the charge is given by

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A}(\mathbf{r},t)\,. \tag{6.118}$$

This Hamiltonian is found to produce the Lorentz force for equations of motion, and is generalized for an arbitrary number of charge in a straightforward manner. As we will soon see, the Hamiltonian in equation (6.117) contains the kinetic energy of the charge and the interaction term between the charge and the field. To obtain the complete Hamiltonian for the radiation-matter system we should add a component containing the energy of the radiation field. For the system we are concerned with in this section, we write for the total Hamiltonian

$$\begin{aligned}
H &= \frac{1}{2}\sum_j m_j v_j^2 + \frac{\epsilon_0}{2}\int_V\left[E^2(\mathbf{r},t) + c^2B_\perp^2(\mathbf{r},t)\right]d^3x\\
&= \sum_j \frac{1}{2m_j}\left[\mathbf{p}_j - q_j\mathbf{A}_\perp(\mathbf{r}_j,t)\right]^2 + \frac{\epsilon_0}{2}\int_V E_\parallel^2(\mathbf{r},t)\,d^3x\\
&\quad + \frac{\epsilon_0}{2}\int_V\left[E_\perp^2(\mathbf{r},t) + c^2B_\perp^2(\mathbf{r},t)\right]d^3x,
\end{aligned} \tag{6.119}$$

where we recognize the radiation part of the Hamiltonian in the last term (see equations (6.44) and (6.50))

$$
\begin{aligned}
H_{\mathrm{R}} &= \frac{\epsilon_0}{2}\int_V \left[E_\perp^2(\mathbf{r},t) + c^2 B_\perp^2(\mathbf{r},t)\right] d^3x \\
&= 2\epsilon_0 L^3 \sum_p \mathcal{E}_p^2 \left|\alpha_p(t)\right|^2 \\
&= 2\epsilon_0 L^3 \sum_p \mathcal{E}_p^2 \left(\mathrm{Re}^2\{\alpha_p(t)\} + \mathrm{Im}^2\{\alpha_p(t)\}\right) \\
&= \frac{1}{2}\sum_p \omega_p \left[Q_p^2(t) + P_p^2(t)\right]. \qquad (6.120)
\end{aligned}
$$

The generalized momenta $\mathbf{p}_j$ in equation (6.119) was obtained with a relation similar to equation (6.118) and equations (6.51)-(6.52) were used for the last line of equation (6.120) .

Let us now consider the following

$$
\begin{aligned}
E_\parallel^2 &= \left(-\nabla\Phi_\parallel\right)\cdot\left(-\nabla\Phi_\parallel\right) \\
&= \nabla\cdot\left(\Phi_\parallel\nabla\Phi_\parallel\right) - \Phi_\parallel\nabla^2\Phi_\parallel \qquad (6.121) \\
&= \nabla\cdot\left(\Phi_\parallel\nabla\Phi_\parallel\right) + \frac{1}{\epsilon_0}\Phi_\parallel\rho \qquad (6.122)
\end{aligned}
$$

and therefore (using the divergence theorem with S the boundary surface of the volume V)

$$
\begin{aligned}
\frac{\epsilon_0}{2}\int_V E_\parallel^2(\mathbf{r},t)\, d^3x &= \frac{\epsilon_0}{2}\int_S \left(\Phi_\parallel\nabla\Phi_\parallel\right)\cdot d^2\mathbf{a} + \frac{1}{2}\int_V \Phi_\parallel\rho d^3x \\
&= \frac{1}{2}\sum_j\int_V q_j\Phi_\parallel\delta\left[\mathbf{r}-\mathbf{r}_j(t)\right] d^3x \\
&= \frac{1}{2}\sum_j q_j\Phi_\parallel(\mathbf{r}_j,t) \\
&= \frac{1}{8\pi\epsilon_0}\sum_j\sum_{k\neq j}\frac{q_j q_k}{\left|\mathbf{r}_j(t)-\mathbf{r}_k(t)\right|} \\
&= V_{\mathrm{Coul}}(\mathbf{r}_1,\ldots,\mathbf{r}_j,\ldots). \qquad (6.123)
\end{aligned}
$$

In other words, the energy associated with the longitudinal electric field is nothing more than the Coulomb potential energy due to the "electrostatic" interaction between the different charges. We can now write the total Hamiltonian as

$$
H = H_{\mathrm{P}} + H_{\mathrm{R}} + H_{\mathrm{I}} \qquad (6.124)
$$

where

$$
\begin{aligned}
H_{\mathrm{P}} &= \sum_j \frac{p_j^2}{2m_j} + V_{\mathrm{Coul}} && (6.125)\\
H_{\mathrm{R}} &= \frac{1}{2}\sum_p \omega_p \left[Q_p^2(t) + P_p^2(t)\right] && (6.126)\\
H_{\mathrm{I}} &= \sum_j \left[-\frac{q_j}{m_j}\mathbf{p}_j \cdot \mathbf{A}_\perp(\mathbf{r}_j, t) + \frac{q_j^2}{2m_j} A_\perp^2(\mathbf{r}_j, t)\right] && (6.127)
\end{aligned}
$$

for the Hamiltonians of the particles, radiation and interaction components, respectively.

6.4 Quantization of the Radiation-Matter System

We are now in a position to proceed with the quantization of the total Hamiltonian. To do so, we introduce the quantum mechanical version of the transverse component of the classical fields of equations (6.114)-(6.116)

$$
\begin{aligned}
\hat{\mathbf{A}}_\perp(\mathbf{r}) &= \sum_p \frac{\mathcal{E}_p}{\omega_p}\boldsymbol{\varepsilon}_p \left[e^{i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p + e^{-i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p^\dagger\right]\\
&\equiv \hat{\mathbf{A}}_\perp^+(\mathbf{r}) + \hat{\mathbf{A}}_\perp^-(\mathbf{r}) && (6.128)\\
\hat{\mathbf{E}}_\perp(\mathbf{r}) &= i\sum_p \mathcal{E}_p\boldsymbol{\varepsilon}_p \left[e^{i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p - e^{-i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p^\dagger\right]\\
&\equiv \hat{\mathbf{E}}_\perp^+(\mathbf{r}) + \hat{\mathbf{E}}_\perp^-(\mathbf{r}) && (6.129)\\
\hat{\mathbf{B}}_\perp(\mathbf{r}) &= i\sum_p \frac{\mathcal{E}_p}{c}\boldsymbol{\varepsilon}'_p \left[e^{i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p - e^{-i\mathbf{k}_p\cdot\mathbf{r}}\hat{a}_p^\dagger\right]\\
&\equiv \hat{\mathbf{B}}_\perp^+(\mathbf{r}) + \hat{\mathbf{B}}_\perp^-(\mathbf{r}), && (6.130)
\end{aligned}
$$

while the total Hamiltonian becomes

$$
\hat{H} = \hat{H}_{\mathrm{P}} + \hat{H}_{\mathrm{R}} + \hat{H}_{\mathrm{I}} \tag{6.131}
$$

with

$$
\begin{aligned}
\hat{H}_{\mathrm{P}} &= \sum_j \frac{\hat{p}_j^2}{2m_j} + \hat{V}_{\mathrm{Coul}} && (6.132)\\
\hat{H}_{\mathrm{R}} &= \sum_p \hbar\omega_p \left[\hat{a}_p^\dagger\hat{a}_p + \frac{1}{2}\right] && (6.133)\\
\hat{H}_{\mathrm{I}} &= \sum_j \left[-\frac{q_j}{m_j}\hat{\mathbf{p}}_j \cdot \hat{\mathbf{A}}_\perp(\mathbf{r}_j) + \frac{q_j^2}{2m_j}\hat{A}_\perp^2(\mathbf{r}_j)\right]. && (6.134)
\end{aligned}
$$

When dealing with atoms or molecules the quantum mechanical Hamiltonian $\hat{H}_\mathrm{P}$ is the one that is used with the Schrödinger equation to determine the (potentially degenerate) eigenvalues E_n and corresponding eigenstates $|u_n\rangle$ that characterize their stationary states (i.e., $\hat{H}_\mathrm{P}|u_n\rangle = E_n|u_n\rangle$). For example, these states are usually labeled $|n,\ell,m\rangle$ for the hydrogen atom, with $n = 1, 2, \ldots$ the *principal quantum number* (determining the energy of the states), ℓ the *orbital angular momentum quantum number* $(0 \leq \ell < n-1)$ and m the *magnetic quantum number* $(|m| \leq \ell)$. This Hamiltonian does not include any interaction between the charges beyond the $\hat{V}_\mathrm{Coul}$ term (e.g., spin-obit coupling).

The Hamiltonian for the radiation $\hat{H}_\mathrm{R}$ has exactly the same form and properties as for the case of the free field, except that the annihilation and creation operators are specifically associated with the transverse fields of equations (6.128)-(6.130). That is, in the free radiation field case all the fields were transverse, while here the electric field also possesses a longitudinal component $\hat{E}_\parallel$. It is often advantageous to combine $\hat{H}_\mathrm{P}$ and $\hat{H}_\mathrm{R}$ such that, for example,

$$\hat{H}_0 = \hat{H}_\mathrm{P} + \hat{H}_\mathrm{R} \tag{6.135}$$

is the "unperturbed" Hamiltonian of the radiation-matter system, which we treat as one. The associated eigenvalue problem is

$$\hat{H}_0|u_n;n_1,\ldots,n_p,\ldots\rangle = \left[E_n + \sum_{j=1,\ldots}\left(\hbar\omega_j + \frac{1}{2}\right)\right]|u_n;n_1,\ldots,n_p,\ldots\rangle, \tag{6.136}$$

where $|u_n;n_1,\ldots,n_p,\ldots\rangle \equiv |u_n\rangle \otimes |n,\ldots,n_p,\ldots\rangle$.

With this picture the interaction Hamiltonian[2] $\hat{H}_\mathrm{I}$ can be seen as a "perturbation" on the radiation-matter system of Hamiltonian $\hat{H}_0$. It is important to note that the inclusion of this term implies that the kets $|u_n;n_1,\ldots,n_p,\ldots\rangle$ are not eigenstates for the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_\mathrm{I}$ (i.e., $\left[\hat{H}_0,\hat{H}_\mathrm{I}\right] \neq \hat{0}$). As we will see, $\hat{H}_\mathrm{I}$ will instead be responsible for transitions between different states $|u_n;n_1,\ldots,n_p,\ldots\rangle$. Finally, the form of $\hat{H}_\mathrm{I}$ is often simplified from the fact that the radiation field may only substantially vary on spatial scales that are much larger than the size of the matter system. For example, when dealing with an atom or a molecule we have

$$\hat{H}_\mathrm{I} = \sum_j\left[-\frac{q_j}{m_j}\hat{\mathbf{p}}_j\cdot\hat{\mathbf{A}}_\perp(\mathbf{r}_0) + \frac{q_j^2}{2m_j}\hat{A}_\perp^2(\mathbf{r}_0)\right], \tag{6.137}$$

where $\mathbf{r}_0$ is the position of the atom/molecule. Equation (6.137) is commonly referred to as the ***long-wavelength approximation***.

[2]The form for $\hat{H}_\mathrm{I}$ given in equation (6.134) is appropriate for the Coulomb gauge, but one must be careful while making the transition from the classical to the quantum mechanical versions of this Hamiltonian (see the Third Problem List).

6.4.1 Interaction Processes

For convenience, we will consider an atom for which one the electrons (of charge q and mass m) interacts much more strongly with the transverse field than the other charges in the system (the nucleus is much heavier than the electrons an can therefore be neglected; perhaps the other electron are strongly tied to the nucleus on inner orbits, or the atom only has one electron). We will also split the interaction Hamiltonian in its two components, while setting $\mathbf{r}_0 = 0$,

$$\begin{aligned}
\hat{H}_{\mathrm{I1}} &= -\frac{q}{m}\hat{\mathbf{p}} \cdot \hat{\mathbf{A}}_{\perp} \\
&= -\frac{q}{m}\sum_{p}\frac{\mathcal{E}_p}{\omega_p}\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p\left(\hat{a}_p + \hat{a}_p^{\dagger}\right) \qquad (6.138)\\
\hat{H}_{\mathrm{I2}} &= \frac{q^2}{2m}\hat{A}_{\perp}^2 \\
&= \frac{q^2}{2m}\sum_{p,q}\frac{\mathcal{E}_p\mathcal{E}_q}{\omega_p\omega_q}\boldsymbol{\varepsilon}_p \cdot \boldsymbol{\varepsilon}_q\left(\hat{a}_p\hat{a}_q^{\dagger} + \hat{a}_p^{\dagger}\hat{a}_q + \hat{a}_p\hat{a}_q + \hat{a}_p^{\dagger}\hat{a}_q^{\dagger}\right), \qquad (6.139)
\end{aligned}$$

as they are different in character. More precisely, $\hat{H}_{\mathrm{I1}}$ is of first-order since the creation and annihilation operators appear linearly, while they appear quadratically in $\hat{H}_{\mathrm{I2}}$ (thus a second-order process).

6.4.1.1 Absorption and Emission of a Photon

Let us assume the atom in the initial state

$$|\psi_i\rangle = |u_i; n_1, \ldots, n_p, \ldots\rangle \qquad (6.140)$$

an eigenstate of $\hat{H}_0$, i.e., the atom is in the discrete state $|u_i\rangle$ and the radiation field in the state $|n_1, \ldots, n_p, \ldots\rangle$. We now apply to this ket the first interaction Hamiltonian $\hat{H}_{\mathrm{I1}}$, which we assume to have only one mode p such that

$$\begin{aligned}
\hat{H}_{\mathrm{I1}}|\psi_i\rangle &= -\frac{q}{m}\frac{\mathcal{E}_p}{\omega_p}\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p\left(\hat{a}_p + \hat{a}_p^{\dagger}\right)|u_i; n_1, \ldots, n_p, \ldots\rangle \\
&= -\frac{q}{m}\frac{\mathcal{E}_p}{\omega_p}\left[\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p|u_i\rangle\right]\left[\left(\hat{a}_p + \hat{a}_p^{\dagger}\right)|n_1, \ldots, n_p, \ldots\rangle\right] \\
&= -\frac{q}{m}\frac{\mathcal{E}_p}{\omega_p}\left[\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p|u_i\rangle\right]\left[\sqrt{n_p}\,|n_1, \ldots, n_p - 1, \ldots\rangle\right. \\
&\qquad \left. + \sqrt{n_p + 1}\,|n_1, \ldots, n_p + 1, \ldots\rangle\right]. \qquad (6.141)
\end{aligned}$$

Evidently, we end up with two new radiation states where one photon was either removed or added to mode p. These are the well-known photon ***absorption*** and ***emission*** processes. However, since a photon carries an energy of $\hbar\omega_p$ and that energy must be conserved overall, the initial atomic state $|u_i\rangle$ must be replaced by states that ensure that this condition is fulfilled (see Exercise 6.1 below).

For the absorption of a photon the two atomic states are related through

$$\left\langle u_f; n_1, \ldots, n_p - 1, \ldots \middle| \hat{H}_{\mathrm{I}1} \middle| u_i; n_1, \ldots, n_p, \ldots \right\rangle = -\frac{q}{m} \frac{\mathcal{E}_p}{\omega_p} \sqrt{n_p} \left\langle u_f \,|\, \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \right\rangle, \quad (6.142)$$

with

$$E_f = E_i + \hbar\omega_p. \quad (6.143)$$

Considering first-order perturbation theory (see Chapter 5) we find that the probability of absorption is proportional the number of photons n_p, i.e., the intensity of the radiation field.

For the emission of a photon we have

$$\left\langle u_f; n_1, \ldots, n_p + 1, \ldots \middle| \hat{H}_{\mathrm{I}1} \middle| u_i; n_1, \ldots, n_p, \ldots \right\rangle = -\frac{q}{m} \frac{\mathcal{E}_p}{\omega_p} \sqrt{n_p + 1} \left\langle u_f \,|\, \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \right\rangle \quad (6.144)$$

with

$$E_f = E_i - \hbar\omega_p. \quad (6.145)$$

Conservation of energy implies that this process cannot take place when the initial state $|u_i\rangle$ corresponds to the atomic ground state. As for the absorption process, first-order theory predicts that the emission rate is proportional to $\approx n_p$ (when $n_p \gg 1$). This corresponds to the ***stimulated emission*** of a photon. But interestingly, we note that a photon can still be emitted even when no photon is present in the initial radiation state (i.e, $n_p = 0$; this is also true if all radiation modes are empty of photons). This corresponds to the ***spontaneous emission*** process.

Exercise 6.1. Given a radiation mode p of polarization $\boldsymbol{\varepsilon}_p$.

a) Calculate the commutator $\left[\hat{\mathbf{r}} \cdot \boldsymbol{\varepsilon}_p, \hat{H}_0\right]$ and show how it can used to find an expression for $\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p$.

b) Using the properties of spherical harmonics determine the final atomic states arising in equation (6.141). That is, what are their orbital angular momentum quantum numbers in relation to that of the initial atomic state $|u_n\rangle$?

c) Use the result obtained in b) to relate the interaction Hamiltonian $\hat{H}_{\mathrm{I}1}$ to an electric dipole coupling.

Solution.

a) We define $\hat{x}_p = \hat{\mathbf{r}} \cdot \boldsymbol{\varepsilon}_p$. Since position operators commute with the radiation fields (i.e., $[\hat{x}_p, \hat{a}_q] = \left[\hat{x}_p, \hat{a}_q^\dagger\right] = \hat{0}$), we have

$$\begin{aligned}
\left[\hat{x}_p, \hat{H}_0\right] &= \left[\hat{x}_p, \hat{H}_\mathrm{P}\right] \\
&= \left[\hat{x}_p, \frac{\hat{p}^2}{2m}\right] \\
&= \frac{i\hbar}{m}\hat{p}_p \\
&= \frac{i\hbar}{m}\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p.
\end{aligned} \tag{6.146}$$

b) Let us now consider the following matrix element

$$\begin{aligned}
\langle u_f \,|\, \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \rangle &= \frac{m}{i\hbar}\left\langle u_f \,\middle|\, \left[\hat{x}_p, \hat{H}_0\right] \,\middle|\, u_i \right\rangle \\
&= \frac{m}{i\hbar}\left\langle u_f \,\middle|\, \hat{x}_p\hat{H}_0 - \hat{H}_0\hat{x}_p \,\middle|\, u_i \right\rangle \\
&= \frac{m}{i\hbar}\left(E_i - E_f\right)\langle u_f \,|\, \hat{x}_p \,|\, u_i \rangle .
\end{aligned} \tag{6.147}$$

Because the spherical harmonics verify the relation $Y_{\ell m} \propto x^a y^b z^c$ with $\ell = a + b + c$ (see equations (3.88)-(3.93) in Chapter 3, while using $x = r\sin(\theta)\cos(\phi)$, $y = r\sin(\theta)\sin(\phi)$ and $z = r\cos(\theta)$), we find that $\hat{x}_p$ transforms as $\hat{L}_\pm$ as far as the orbital angular momentum number is concerned. We therefore write

$$\begin{aligned}
\langle u_f \,|\, \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \rangle &\propto \langle u_f \,|\, \hat{x}_p \,|\, u_i \rangle \\
&\Rightarrow \left\langle u_f \,\middle|\, \hat{L}_\pm \,\middle|\, u_i \right\rangle,
\end{aligned} \tag{6.148}$$

which implies that if $|u_i\rangle$ has a quantum number ℓ, then $|u_f\rangle$ can only have $\ell' = \ell \pm 1$.

c) Using equation (6.147) we write

$$\begin{aligned}
\left\langle u_f \,\middle|\, \hat{H}_{\mathrm{I}1} \,\middle|\, u_i \right\rangle &= -\frac{q}{m}\left\langle u_f \,\middle|\, \hat{\mathbf{p}} \cdot \hat{\mathbf{A}}_\perp \,\middle|\, u_i \right\rangle \\
&= -\frac{q}{m}\frac{\mathcal{E}_p}{\omega_p}\langle u_f \,|\, \hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \rangle \left(\hat{a}_p + \hat{a}_p^\dagger\right) \\
&= iq\mathcal{E}_p\frac{\omega_{if}}{\omega_p}\langle u_f \,|\, \hat{\mathbf{r}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \rangle \left(\hat{a}_p + \hat{a}_p^\dagger\right),
\end{aligned} \tag{6.149}$$

with $\hbar\omega_{if} = E_i - E_f$. We note, however, that if for the emission of a photon (under the action of $\hat{a}_p^\dagger$) $\omega_{if} = \omega_p > 0$, for the absorption process $\omega_{if} = -\omega_p < 0$. These relations imply that equation (6.149) can be transformed to

$$\begin{aligned}
\left\langle u_f \,\middle|\, \hat{H}_{\mathrm{I}1} \,\middle|\, u_i \right\rangle &= -i\mathcal{E}_p\langle u_f \,|\, q\hat{\mathbf{r}} \cdot \boldsymbol{\varepsilon}_p \,|\, u_i \rangle \left(\hat{a}_p - \hat{a}_p^\dagger\right) \\
&= -\left\langle u_f \,\middle|\, \hat{\mathbf{d}} \cdot \hat{\mathbf{E}}_\perp \,\middle|\, u_i \right\rangle
\end{aligned} \tag{6.150}$$

from equation (6.129) and with $\hat{\mathbf{d}} = q\hat{\mathbf{r}}$ is the electric dipole operator. We therefore find that $\hat{H}_{\mathrm{I}1}$ corresponds to the electric dipolar coupling between the radiation and the atom. This result is easily generalized to an arbitrary number of charges and modes.

6.4.1.2 Scattering Processes

Because the interaction term $\hat{H}_{\mathrm{I}2}$ does not involve the generalized momentum $\hat{\mathbf{p}}$ it cannot alter the internal state of the atom. Let us consider the case where only two modes of radiation p and q are present such that

$$\begin{aligned} \hat{H}_{\mathrm{I}2}\left|u_i; n_p, n_q\right\rangle = \left|u_i\right\rangle \cdot \frac{q^2}{2m} \Bigg[& \frac{\mathcal{E}_p^2}{\omega_p^2}\left(\hat{a}_p\hat{a}_p^\dagger + \hat{a}_p^\dagger\hat{a}_p + \hat{a}_p\hat{a}_p + \hat{a}_p^\dagger\hat{a}_p^\dagger\right) \\ & + 2\frac{\mathcal{E}_p\mathcal{E}_q}{\omega_p\omega_q}\boldsymbol{\varepsilon}_p \cdot \boldsymbol{\varepsilon}_q\left(\hat{a}_p\hat{a}_q^\dagger + \hat{a}_p^\dagger\hat{a}_q + \hat{a}_p\hat{a}_q + \hat{a}_p^\dagger\hat{a}_q^\dagger\right) \\ & + \frac{\mathcal{E}_q^2}{\omega_q^2}\left(\hat{a}_q\hat{a}_p^\dagger + \hat{a}_q^\dagger\hat{a}_q + \hat{a}_q\hat{a}_q + \hat{a}_q^\dagger\hat{a}_q^\dagger\right)\Bigg]\left|n_p, n_q\right\rangle. \end{aligned} \tag{6.151}$$

It should be clear that terms of the forms $\hat{a}_p\hat{a}_q$ and $\hat{a}_p^\dagger\hat{a}_q^\dagger$ have a very low probability of occurrence, as they do not conserve energy (i.e., they either remove or add two photons from the radiation field). It follows that only the terms in $\hat{a}_p\hat{a}_q^\dagger$ and $\hat{a}_p^\dagger\hat{a}_q$ can lead to realizable processes, as long as $\omega_p = \omega_q$ (terms involving only one mode, e.g., $\hat{a}_p\hat{a}_p^\dagger$ and $\hat{a}_p^\dagger\hat{a}_p$, leave the radiation field is unaltered by this process). We therefore consider, for example,

$$\begin{aligned} \left\langle u_i; n_p - 1, n_q + 1 \middle| \hat{H}_{\mathrm{I}2} \middle| u_i; n_p, n_q \right\rangle & \simeq 2\frac{\mathcal{E}_p^2}{\omega_p^2}\boldsymbol{\varepsilon}_p \cdot \boldsymbol{\varepsilon}_q \left\langle n_p - 1, n_q + 1 \middle| \hat{a}_p\hat{a}_q^\dagger + \hat{a}_p^\dagger\hat{a}_q \middle| n_p, n_q \right\rangle \\ & \simeq 2\frac{\mathcal{E}_p^2}{\omega_p^2}\boldsymbol{\varepsilon}_p \cdot \boldsymbol{\varepsilon}_q \left\langle n_p - 1, n_q + 1 \middle| \hat{a}_p\hat{a}_q^\dagger \middle| n_p, n_q \right\rangle \quad (6.152) \\ & \simeq 2\frac{\mathcal{E}_p^2}{\omega_p^2}\boldsymbol{\varepsilon}_p \cdot \boldsymbol{\varepsilon}_q \sqrt{n_p\left(n_q + 1\right)}. \quad (6.153) \end{aligned}$$

This photon exchange between modes, and which cannot take place when the modes are polarized in orthogonal states, corresponds to an ***elastic scattering*** process.

Scattering can also happen through second-order perturbation processes involving the $\hat{H}_{\mathrm{I}1}$ interaction term. We again consider a radiation field containing two modes

$$\hat{H}_{\mathrm{I}1} = -\frac{q}{m}\hat{\mathbf{p}} \cdot \left[\frac{\mathcal{E}_p}{\omega_p}\boldsymbol{\varepsilon}_p\left(\hat{a}_p + \hat{a}_p^\dagger\right) + \frac{\mathcal{E}_q}{\omega_q}\boldsymbol{\varepsilon}_q\left(\hat{a}_q + \hat{a}_q^\dagger\right)\right] \tag{6.154}$$

Referring to equation (5.97) in Chapter 5, we know that the second-order transition amplitude between the states $\left|u_i; n_p, n_q\right\rangle$ and $\left|u_f; n_p, n_q\right\rangle$ is of the form

$$S_{if} \propto \sum_{j\neq i,f} \frac{\left\langle u_f; n_p, n_q \middle| \hat{H}_{\mathrm{I}1} \middle| u_j; n'_p, n'_q \right\rangle \left\langle u_j; n'_p, n'_q \middle| \hat{H}_{\mathrm{I}1} \middle| u_i; n_p, n_q \right\rangle}{\left(E_j + n'_p \hbar\omega_p + n'_q \hbar\omega_q\right) - \left(E_i + n_p \hbar\omega_p + n_q \hbar\omega_q\right)}. \tag{6.155}$$

The most interesting situation happens when both modes happen in the same scattering terms, such as

$$\begin{aligned} S'_{if} \quad \propto \quad & \sum_{j\neq i,f} \frac{\left\langle u_f; n_p+1, n_q-1 \middle| \hat{p}_p \hat{a}_p^\dagger \middle| u_j; n_p, n_q-1 \right\rangle \left\langle u_j; n_p, n_q-1 \,|\, \hat{p}_q \hat{a}_q \,|\, u_i; n_p, n_q \right\rangle}{E_j - E_i - \hbar\omega_q} \\ & + \sum_{j\neq i,f} \frac{\left\langle u_f; n_p+1, n_q-1 \,|\, \hat{p}_q \hat{a}_q \,|\, u_j; n_p, n_q+1 \right\rangle \left\langle u_j; n_p+1, n_q \middle| \hat{p}_p \hat{a}_p^\dagger \middle| u_i; n_p, n_q \right\rangle}{E_j - E_i + \hbar\omega_q}. \end{aligned} \tag{6.156}$$

The scattering process must conserve energy between the initial and final states with

$$E_i + n_p \hbar\omega_p + n_q \hbar\omega_q = E_f + (n_p+1)\,\hbar\omega_p + (n_q-1)\,\hbar\omega_q. \tag{6.157}$$

However, there is no requirement for energy conservation between the initial and intermediate states since the latter is not available to observation or measurement. Such intermediary states are called ***virtual states***. On the other hand, the denominators in each term favour intermediate states for which $E_j \simeq E_i + \hbar\omega_q$ and $E_j \simeq E_i - \hbar\omega_q$, respectively.

Finally, it is interesting to note that the virtual state in the second term of equation (6.156) has one more photon than the initial and final states. That is, the atom emits a virtual photon of mode p before absorbing a photon of mode q. This implies that if $|u_i\rangle$ is the ground state of the atom, its intermediate state must involve an excited state[3] with $E_f > E_i$ and one more photon than the initial state; a situation clearly at odds with the conservation of energy. But still, this combination must be included in calculations since we are dealing with a virtual state.

[3]Notably, Rayleigh scattering is defined as a low-energy elastic scattering process where all of the intermediate atomic states have higher energy than the initial atomic state.