APPENDIX

QUANTUM ELECTRODYNAMICS IN THE COULOMB GAUGE—SUMMARY OF THE ESSENTIAL RESULTS

This appendix briefly summarizes the procedure for quantizing the electromagnetic field in the Coulomb gauge and gathers together the essential formulas that are used in this volume (*).

The system studied in electrodynamics is composed of two interacting subsystems: the electromagnetic field on the one hand, and an ensemble of charged particles on the other. Quantum electrodynamics attempts to describe, within the framework of quantum mechanics, the states and the dynamics of these two subsystems whose evolutions are coupled. The charged particles are actually the sources of the field and the field exerts forces on the particles.

We first introduce the variables used to describe the field (§1) and the particles (§2) in classical and quantum theories. Then we introduce the Coulomb-gauge Hamiltonian which governs the dynamics of the global system (§3). We then review a few important quantum states of the field (§4), and last we introduce the electric dipole representation currently used to describe localized systems of charges such as atoms or molecules (§5).

1. Description of the Electromagnetic Field

a) Electric Field E and Magnetic Field B

In classical electrodynamics, the fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$ obey the Maxwell equations

$$\nabla \cdot \mathbf{E}(\mathbf{r}, t) = \frac{1}{\varepsilon_0}\rho(\mathbf{r}, t) \tag{1.a}$$

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0 \tag{1.b}$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r}, t) \tag{1.c}$$

$$\nabla \times \mathbf{B}(\mathbf{r}, t) = \frac{1}{c^2}\frac{\partial}{\partial t}\mathbf{E}(\mathbf{r}, t) + \frac{1}{\varepsilon_0 c^2}\mathbf{j}(\mathbf{r}, t) \tag{1.d}$$

(*) It is, of course, impossible to discuss in a short appendix all the aspects of the quantization of the electromagnetic field or to prove all the results cited here. The reader can refer to *Photons and Atoms—Introduction to Quantum Electrodynamics* for a more detailed presentation.

where the charge density $\rho(\mathbf{r}, t)$ and current density $\mathbf{j}(\mathbf{r}, t)$ are those associated with the particles. After a spatial Fourier transformation, the Maxwell equations become (*)

$$i\mathbf{k} \cdot \mathscr{E}(\mathbf{k}, t) = \frac{1}{\varepsilon_0}\rho(\mathbf{k}, t) \tag{2.a}$$

$$i\mathbf{k} \cdot \mathscr{B}(\mathbf{k}, t) = 0 \tag{2.b}$$

$$i\mathbf{k} \times \mathscr{E}(\mathbf{k}, t) = -\frac{\partial}{\partial t}\mathscr{B}(\mathbf{k}, t) \tag{2.c}$$

$$i\mathbf{k} \times \mathscr{B}(\mathbf{k}, t) = \frac{1}{c^2}\frac{\partial \mathscr{E}(\mathbf{k}, t)}{\partial t} + \frac{1}{\varepsilon_0 c^2}\mathscr{j}(\mathbf{k}, t) \tag{2.d}$$

where $\mathbf{E}(\mathbf{r}, t)$ and $\mathscr{E}(\mathbf{k}, t)$, for example, are related by:

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}}\int \mathrm{d}^3k\, \mathscr{E}(\mathbf{k}, t)\, \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}. \tag{3}$$

The two equations (2.a) and (2.b) fix the longitudinal parts $\mathscr{E}_\parallel$ and $\mathscr{B}_\parallel$ of the electric and magnetic fields, i.e., the projections onto $\mathbf{k}/k$ of $\mathscr{E}$ and $\mathscr{B}$:

$$\mathscr{E}_\parallel(\mathbf{k}, t) = -\frac{i\mathbf{k}}{\varepsilon_0 k^2}\rho(\mathbf{k}, t) \tag{4.a}$$

$$\mathscr{B}_\parallel(\mathbf{k}, t) = 0 \tag{4.b}$$

In real space, these relations become

$$\mathbf{E}_\parallel(\mathbf{r}, t) = \frac{-1}{4\pi\varepsilon_0}\int \mathrm{d}^3r'\, \rho(\mathbf{r}', t)\nabla_\mathbf{r}\frac{1}{|\mathbf{r} - \mathbf{r}'|} \tag{5.a}$$

$$\mathbf{B}_\parallel(\mathbf{r}, t) = 0. \tag{5.b}$$

The magnetic field is purely transverse, whereas the longitudinal electric field coincides with the Coulomb field associated with the distribution of charge $\rho(\mathbf{r}, t)$ at the same time. The longitudinal fields are thus not really

(*) We systematically use the following notation: a scalar or vectorial field in real space is written with a Roman letter, whereas its spatial Fourier transform is designated by the same cursive or italic letter.

independent variables for the field. They are either zero, or they can be expressed through ρ as a function of the particle variables. By contrast, the transverse fields $\mathscr{E}_\perp$ and $\mathscr{B}_\perp = \mathscr{B}$, which are the projections of $\mathscr{E}$ and $\mathscr{B}$ in the plane perpendicular to $\mathbf{k}$, are independent variables whose equations of motion can be deduced from (2.c) and (2.d)

$$\frac{\partial}{\partial t}\mathscr{B}(\mathbf{k}, t) = -i\mathbf{k} \times \mathscr{E}_\perp(\mathbf{k}, t) \tag{6.a}$$

$$\frac{\partial}{\partial t}\mathscr{E}_\perp(\mathbf{k}, t) = c^2 i\mathbf{k} \times \mathscr{B}(\mathbf{k}, t) - \frac{1}{\varepsilon_0}\mathscr{j}_\perp(\mathbf{k}, t). \tag{6.b}$$

b) Vector Potential A and Scalar Potential U

In quantum theory, it is necessary to consider the potentials $\mathbf{A}$ and U related to the fields $\mathbf{E}$ and $\mathbf{B}$ by the equations

$$\mathbf{E}(\mathbf{r}, t) = -\nabla U(\mathbf{r}, t) - \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} \tag{7.a}$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \tag{7.b}$$

which, in reciprocal space, become

$$\mathscr{E}(\mathbf{k}, t) = -i\mathbf{k}\mathscr{U}(\mathbf{k}, t) - \frac{\partial \mathscr{A}(\mathbf{k}, t)}{\partial t} \tag{8.a}$$

$$\mathscr{B}(\mathbf{k}, t) = i\mathbf{k} \times \mathscr{A}(\mathbf{k}, t). \tag{8.b}$$

The fields $\mathbf{E}$ and $\mathbf{B}$ are invariant in the gauge transformation associated with the function $F(\mathbf{r}, t)$

$$\mathbf{A}(\mathbf{r}, t) \to \mathbf{A}'(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \nabla F(\mathbf{r}, t) \tag{9.a}$$

$$U(\mathbf{r}, t) \to U'(\mathbf{r}, t) = U(\mathbf{r}, t) - \frac{\partial F(\mathbf{r}, t)}{\partial t} \tag{9.b}$$

which can also be written

$$\mathscr{A}(\mathbf{k}, t) \to \mathscr{A}'(\mathbf{k}, t) = \mathscr{A}(\mathbf{k}, t) + i\mathbf{k}\mathscr{F}(\mathbf{k}, t) \tag{10.a}$$

$$\mathscr{U}(\mathbf{k}, t) \to \mathscr{U}'(\mathbf{k}, t) = \mathscr{U}(\mathbf{k}, t) - \frac{\partial \mathscr{F}(\mathbf{k}, t)}{\partial t}. \tag{10.b}$$

It is clear from Equations (10) that only $\mathscr{A}_\parallel$ and $\mathscr{U}$ change in a gauge

transformation, whereas $\mathscr{A}_\perp$ is gauge invariant

$$\mathscr{A}'_\perp(\mathbf{k},t) = \mathscr{A}_\perp(\mathbf{k},t). \tag{11}$$

Equations (8) prove also that the transverse fields $\mathscr{E}_\perp$ and $\mathscr{B}$ depend only on $\mathscr{A}_\perp$

$$\mathscr{E}_\perp(\mathbf{k},t) = -\frac{\partial}{\partial t}\mathscr{A}_\perp(\mathbf{k},t) \tag{12.a}$$

$$\mathscr{B}(\mathbf{k},t) = i\mathbf{k}\times\mathscr{A}_\perp(\mathbf{k},t). \tag{12.b}$$

c) Coulomb Gauge

The Coulomb gauge ($\nabla\cdot\mathbf{A}=0$) corresponds to the choice

$$\mathscr{A}_\parallel(\mathbf{k},t) = 0 = \mathbf{A}_\parallel(\mathbf{r},t). \tag{13}$$

By comparing the longitudinal part of (8.a) with (4.a), we then obtain

$$\mathscr{U}(\mathbf{k},t) = \frac{1}{\varepsilon_0 k^2}\rho(\mathbf{k},t) \tag{14}$$

or, equivalently,

$$U(\mathbf{r},t) = \frac{1}{4\pi\varepsilon_0}\int \mathrm{d}^3r'\,\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}. \tag{15}$$

In the Coulomb gauge, the longitudinal vector potential is zero and the scalar potential coincides with the Coulomb potential associated with the charge distribution $\rho(\mathbf{r},t)$ at the same time. Therefore, in this gauge the independent variables of the field are the transverse vector potential $\mathscr{A}_\perp(\mathbf{k},t)$ and its velocity $\dot{\mathscr{A}}_\perp(\mathbf{k},t) = -\mathscr{E}_\perp(\mathbf{k},t)$.

d) Normal Variables

The simple form for the equations of motion (6) of the transverse fields suggests the introduction of the following linear combination of $\mathscr{B}$ and $\mathscr{E}_\perp$ [or, using (12), of $\mathscr{A}_\perp$ and $\dot{\mathscr{A}}_\perp$]

$$\begin{aligned}\boldsymbol{\alpha}(\mathbf{k},t) &= \lambda(k)\left[\mathscr{E}_\perp(\mathbf{k},t) - c\frac{\mathbf{k}}{k}\times\mathscr{B}(\mathbf{k},t)\right]\\ &= \lambda(k)\left[-\dot{\mathscr{A}}_\perp(\mathbf{k},t) + i\omega\mathscr{A}_\perp(\mathbf{k},t)\right]\end{aligned} \tag{16}$$

where $\lambda(k)$ is a normalization constant that we will later on take to be equal to $-i\sqrt{\varepsilon_0/2\hbar\omega}$. The evolution equation for $\boldsymbol{\alpha}$ is then quite simple:

$$\dot{\boldsymbol{\alpha}}(\mathbf{k},t) + i\omega\boldsymbol{\alpha}(\mathbf{k},t) = \frac{i}{\sqrt{2\varepsilon_0\hbar\omega}}\mathscr{j}_\perp(\mathbf{k},t). \tag{17}$$

In the absence of sources ($\mathbf{j}_\perp = \mathbf{0}$), the variables $\boldsymbol{\alpha}(\mathbf{k},t)$ corresponding to the different possible values for $\mathbf{k}$ evolve independently of each other, with a time dependence $\exp(-i\omega t)$ where $\omega = ck$. The variables $\boldsymbol{\alpha}$ thus describe the normal modes of vibration of the free field and are for this reason called normal variables.

Equation (16) shows that $\boldsymbol{\alpha}$ is, like $\mathscr{E}_\perp$ and $\mathscr{B}$, a transverse field. For each value of $\mathbf{k}$, we can introduce two unitary vectors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$, orthogonal to each other and both perpendicular to $\mathbf{k}$. Each ensemble $\mathbf{k}, \boldsymbol{\varepsilon}$ defines a normal vibrational mode of the field and the normal variable associated with this mode

$$\alpha_\varepsilon(\mathbf{k}) = \boldsymbol{\varepsilon}\cdot\boldsymbol{\alpha}(\mathbf{k}) \tag{18.a}$$

obeys, according to (17), the evolution equation

$$\dot{\alpha}_\varepsilon(\mathbf{k},t) + i\omega\alpha_\varepsilon(\mathbf{k},t) = \frac{i}{\sqrt{2\varepsilon_0\hbar\omega}}\boldsymbol{\varepsilon}\cdot\mathscr{j}(\mathbf{k},t). \tag{18.b}$$

By using the reality conditions for the fields $\mathbf{E}_\perp$, $\mathbf{B}$, and $\mathbf{A}_\perp$, which, for example, for $\mathbf{E}_\perp$ are written

$$\mathscr{E}_\perp(\mathbf{k},t) = \mathscr{E}^*_\perp(-\mathbf{k},t), \tag{19}$$

we can invert Equations (16) and express $\mathscr{E}_\perp(\mathbf{k},t)$, $\mathscr{B}(\mathbf{k},t)$, and $\mathscr{A}_\perp(\mathbf{k},t)$ as a function of $\alpha_\varepsilon(\mathbf{k},t)$ and $\alpha^*_\varepsilon(-\mathbf{k},t)$. A Fourier transformation then gives the expansions of the various transverse fields as functions of the normal variables. Later on, these expansions are written directly as a function of the operators $a_\varepsilon(\mathbf{k})$ and $a^+_\varepsilon(\mathbf{k})$ which are associated, in quantum theory, with the normal variables $\alpha_\varepsilon(\mathbf{k})$ and $\alpha^*_\varepsilon(\mathbf{k})$. The set of degrees of freedom associated with the transverse field is usually designated as "radiation". The state of the radiation is thus defined at time t by the given normal variables $\alpha_\varepsilon(\mathbf{k},t)$ for all $\mathbf{k}$ and all $\boldsymbol{\varepsilon}$.

e) Principle of Canonical Quantization in the Coulomb Gauge

The canonical quantization procedure requires pairs of conjugated dynamical variables to be identified, which, after quantization, become operators whose commutators equal $i\hbar$.

For the electromagnetic field, we can introduce a Lagrangian which contains only the really independent variables of the field ($\mathscr{A}_\perp$ and $\dot{\mathscr{A}}_\perp$) and the variables of the particles (standard Lagrangian in the Coulomb gauge) and which leads to the Maxwell equations for the field and to the Newton–Lorentz equations for the particles. With regard to this Lagrangian, the conjugate moment of the generalized coordinate $\mathscr{A}_\varepsilon(\mathbf{k})$ is found to be equal to $\pi_\varepsilon(\mathbf{k}) = \varepsilon_0 \dot{\mathscr{A}}_\varepsilon(\mathbf{k})$ and the canonical commutation relations are written

$$\left[\mathscr{A}_\varepsilon(\mathbf{k}), \pi_{\varepsilon'}^+(\mathbf{k}')\right] = i\hbar\delta_{\varepsilon\varepsilon'}\delta(\mathbf{k}-\mathbf{k}'). \tag{20.a}$$

The operator $a_\varepsilon(\mathbf{k})$ associated with the normal variable $\alpha_\varepsilon(\mathbf{k})$ is expressed as a function of the operators $\mathscr{A}_\varepsilon(\mathbf{k})$ and $\pi_\varepsilon(\mathbf{k}) = \varepsilon_0 \dot{\mathscr{A}}_\varepsilon(\mathbf{k})$ by an equation analogous to (16). By choosing an appropriate normalization constant $\lambda(k)$ [$\lambda(k) = -i\sqrt{\varepsilon_0/2\hbar\omega}$], we then find that relation (20.a) is equivalent to

$$\left[a_\varepsilon(\mathbf{k}), a_{\varepsilon'}^+(\mathbf{k}')\right] = \delta_{\varepsilon\varepsilon'}\delta(\mathbf{k}-\mathbf{k}') \tag{20.b}$$

with all the other commutators being zero.

To follow the quantum electrodynamic calculations presented in this book, it is sufficient to know the commutation relations (20.b) and the expressions for the physical variables as a function of the operators a and a^+ which are discussed in the next subsection.

f) Quantum Fields in the Coulomb Gauge

As we explained above, it is possible to invert Equations (16) between operators and to use the Hermiticity conditions of these operators to obtain, by Fourier transformation, the expansions of the field operators in a_ε and a_ε^+. We find in this way that

$$\mathbf{A}_\perp(\mathbf{r}) = \int \mathrm{d}^3k \sum_\varepsilon \mathscr{A}_\omega \left[\boldsymbol{\varepsilon} a_\varepsilon(\mathbf{k})\, \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} + \boldsymbol{\varepsilon} a_\varepsilon^+(\mathbf{k})\, \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\right] \tag{21}$$

$$\mathbf{E}_\perp(\mathbf{r}) = \int \mathrm{d}^3k \sum_\varepsilon i\mathscr{E}_\omega \left[\boldsymbol{\varepsilon} a_\varepsilon(\mathbf{k})\, \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} - \boldsymbol{\varepsilon} a_\varepsilon^+(\mathbf{k})\, \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\right] \tag{22}$$

$$\mathbf{B}(\mathbf{r}) = \int \mathrm{d}^3k \sum_\varepsilon i\mathscr{B}_\omega \left[(\boldsymbol{\kappa}\times\boldsymbol{\varepsilon}) a_\varepsilon(\mathbf{k})\, \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} - (\boldsymbol{\kappa}\times\boldsymbol{\varepsilon}) a_\varepsilon^+(\mathbf{k})\, \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\right] \tag{23}$$

where

$$\omega = ck \tag{24.a}$$

$$\boldsymbol{\kappa} = \mathbf{k}/k \tag{24.b}$$

$$\mathscr{A}_\omega = \left[\hbar/2\varepsilon_0\omega(2\pi)^3\right]^{1/2} \qquad \mathscr{E}_\omega = \omega\mathscr{A}_\omega \qquad \mathscr{B}_\omega = \mathscr{E}_\omega/c. \tag{24.c}$$

The total electric field $\mathbf{E}(\mathbf{r})$ is written

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_\perp(\mathbf{r}) + \mathbf{E}_\parallel(\mathbf{r}) \tag{24.d}$$

where $\mathbf{E}_\parallel(\mathbf{r})$ is given in (5.a).

It is often convenient to consider the field as being contained in a cubic box with periodic boundary conditions. The dimension L of this box is taken as being large compared with all the characteristic dimensions of the problem under consideration. The components of the wave vectors are then multiples of $2\pi/L$ and the modes form a discrete ensemble designated by the subscript j. The Fourier integrals are replaced by series following the rule

$$\int \mathrm{d}^3k \sum_\varepsilon f(\mathbf{k},\varepsilon) \leftrightarrow \sum_j \left(\frac{2\pi}{L}\right)^3 f(\mathbf{k}_j, \boldsymbol{\varepsilon}_j). \tag{25}$$

The creation and annihilation operators are redefined by

$$a_j = \left(\frac{L}{2\pi}\right)^{3/2} \int_{C_j} \mathrm{d}^3k\, a_{\varepsilon_j}(\mathbf{k}) \tag{26}$$

where C_j is the elementary cell of volume $(2\pi/L)^3$ about $\mathbf{k}_j$. The a_i and a_j^+ satisfy the simple commutation relation

$$\left[a_i, a_j^+\right] = \delta_{ij}. \tag{27}$$

The fields are expressed as a function of the a_j in the form

$$\mathbf{A}_\perp(\mathbf{r}) = \sum_j \sqrt{\frac{\hbar}{2\varepsilon_0\omega_j L^3}} \left[a_j\boldsymbol{\varepsilon}_j\, \mathrm{e}^{i\mathbf{k}_j\cdot\mathbf{r}} + a_j^+\boldsymbol{\varepsilon}_j\, \mathrm{e}^{-i\mathbf{k}_j\cdot\mathbf{r}}\right] \tag{28}$$

$$\mathbf{E}_\perp(\mathbf{r}) = \sum_j i\sqrt{\frac{\hbar\omega_j}{2\varepsilon_0 L^3}} \left[a_j\boldsymbol{\varepsilon}_j\, \mathrm{e}^{i\mathbf{k}_j\cdot\mathbf{r}} - a_j^+\boldsymbol{\varepsilon}_j\, \mathrm{e}^{-i\mathbf{k}_j\cdot\mathbf{r}}\right] \tag{29}$$

$$\mathbf{B}(\mathbf{r}) = \sum_j \frac{i}{c}\sqrt{\frac{\hbar\omega_j}{2\varepsilon_0 L^3}} \left[a_j\boldsymbol{\kappa}_j\times\boldsymbol{\varepsilon}_j\, \mathrm{e}^{i\mathbf{k}_j\cdot\mathbf{r}} - a_j^+\boldsymbol{\kappa}_j\times\boldsymbol{\varepsilon}_j\, \mathrm{e}^{-i\mathbf{k}_j\cdot\mathbf{r}}\right]. \tag{30}$$

Last, to finish this subsection, we give several useful formulas. In the bilinear expressions with respect to the fields, the following sums involving the Cartesian components of the transverse polarization vectors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$, perpendicular to $\mathbf{k}$ are often encountered:

$$\sum_{\varepsilon} \varepsilon_l \varepsilon_m = \delta_{lm} - \kappa_l \kappa_m \tag{31}$$

$$\sum_{\varepsilon} \varepsilon_l (\boldsymbol{\kappa} \times \boldsymbol{\varepsilon})_m = \sum_{n} e_{lmn} \kappa_n \tag{32}$$

$$\sum_{\varepsilon} (\boldsymbol{\kappa} \times \boldsymbol{\varepsilon})_l (\boldsymbol{\kappa} \times \boldsymbol{\varepsilon})_m = \delta_{lm} - \kappa_l \kappa_m \tag{33}$$

where l and $m = x, y, z$, e_{lmn} is the antisymmetric tensor, and where $\boldsymbol{\kappa}$ is defined in (24.b). Expression (31) represents, in reciprocal space, the projector onto the subspace of transverse fields. In real space, this projector is represented by the transverse delta function

$$\begin{aligned} \delta_{lm}^{\perp}(\mathbf{r} - \mathbf{r}') &= \frac{1}{(2\pi)^3} \int \mathrm{d}^3 k \, \mathrm{e}^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} (\delta_{lm} - \kappa_l \kappa_m) \\ &= \frac{2}{3} \delta_{lm} \delta(\mathbf{r} - \mathbf{r}') + \frac{Y(|\mathbf{r} - \mathbf{r}'|)}{4\pi |\mathbf{r} - \mathbf{r}'|^5} \times \\ &\quad \times \left[3(r_l - r_l')(r_m - r_m') - (\mathbf{r} - \mathbf{r}')^2 \delta_{lm} \right] \end{aligned} \tag{34}$$

where $Y(|\mathbf{r} - \mathbf{r}'|)$ is a regularization function equal to 1 everywhere except inside a small sphere around $|\mathbf{r} - \mathbf{r}'| = 0$, where it tends to zero. Finally, from (27)–(29), we obtain the following commutation relations for the fields in real space:

$$[A_{\perp l}(\mathbf{r}), A_{\perp m}(\mathbf{r}')] = 0 \qquad [E_{\perp l}(\mathbf{r}), E_{\perp m}(\mathbf{r}')] = 0 \tag{35.a}$$

$$[A_{\perp l}(\mathbf{r}), E_{\perp m}(\mathbf{r}')] = \frac{-i\hbar}{\varepsilon_0} \delta_{lm}^{\perp}(\mathbf{r} - \mathbf{r}'). \tag{35.b}$$

2. Particles

Particles are described within a nonrelativistic framework: their velocity is assumed to be small compared with c, and their number is invariant. In this limit, we can describe each particle α by the conjugate variables $\mathbf{r}_\alpha$ (position) and $\mathbf{p}_\alpha$ (momentum), rather than using a field theory. In quantum theory these variables become observables obeying the canonical

commutation relations

$$[r_{\alpha i}, p_{\beta j}] = i\hbar \delta_{\alpha\beta} \delta_{ij}. \tag{36}$$

In the presence of the vector potential, the velocity $\mathbf{v}_\alpha$ of the particle is related to $\mathbf{p}_\alpha$ by

$$m_\alpha \mathbf{v}_\alpha = \mathbf{p}_\alpha - q_\alpha \mathbf{A}_\perp(\mathbf{r}_\alpha) \tag{37}$$

(m_α and q_α are, respectively, the mass and the charge of the particle α). The charge density and the current density are expressed as a function of the preceding variables

$$\rho(\mathbf{r}) = \sum_{\alpha} q_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha) \tag{38.a}$$

$$\mathbf{j}(\mathbf{r}) = \sum_{\alpha} q_\alpha \mathbf{v}_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha). \tag{38.b}$$

We will also use their spatial Fourier transforms

$$\rho(\mathbf{k}) = \sum_{\alpha} \frac{q_\alpha}{(2\pi)^{3/2}} \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}_\alpha} \tag{39.a}$$

$$\mathbf{j}(\mathbf{k}) = \sum_{\alpha} \frac{q_\alpha \mathbf{v}_\alpha}{(2\pi)^{3/2}} \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}_\alpha} \tag{39.b}$$

3. Hamiltonian and Dynamics in the Coulomb Gauge

a) Hamiltonian

The Hamiltonian H describing the dynamics of the system formed by the transverse field and the particles can be written as

$$\begin{aligned} H = &\sum_{\alpha} \frac{1}{2m_\alpha} [\mathbf{p}_\alpha - q_\alpha \mathbf{A}_\perp(\mathbf{r}_\alpha)]^2 + \\ &+ \sum_{\alpha} \left(-g_\alpha \frac{q_\alpha}{2m_\alpha} \right) \mathbf{S}_\alpha \cdot \mathbf{B}(\mathbf{r}_\alpha) + V_{\mathrm{Coul}} + H_R. \end{aligned} \tag{40}$$

The first term of H is the kinetic energy of the particles [see expression (37) for the velocity].

The second term represents the interaction energy of the spin magnetic moments possibly carried by the particles (g_α is the g factor for the particle α) with the magnetic field $\mathbf{B}(\mathbf{r}_\alpha)$.

The third term, V_{Coul}, is the energy of the longitudinal field (Coulomb energy)

$$V_{\text{Coul}} = \frac{\varepsilon_0}{2}\int \mathrm{d}^3r\, \mathbf{E}_{\parallel}^2(\mathbf{r}) = \frac{\varepsilon_0}{2}\int \mathrm{d}^3k\, |\mathscr{E}_{\parallel}(\mathbf{k})|^2 \tag{41}$$

which, using (4.a) and (39.a), equals

$$V_{\text{Coul}} = \frac{1}{2\varepsilon_0}\int \mathrm{d}^3k\, \frac{\rho^*(\mathbf{k})\rho(\mathbf{k})}{k^2} = \sum_\alpha \varepsilon_{\text{Coul}}^\alpha + \frac{1}{8\pi\varepsilon_0}\sum_{\alpha\neq\beta}\frac{q_\alpha q_\beta}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|}. \tag{42}$$

$\varepsilon_{\text{Coul}}^\alpha$ is the Coulomb self-energy of particle α, which is expressed in reciprocal space in the form of a divergent integral, unless a cutoff k_c is introduced

$$\varepsilon_{\text{Coul}}^\alpha = \frac{q_\alpha^2}{2\varepsilon_0}\int \frac{\mathrm{d}^3k}{(2\pi)^3k^2} = \frac{q_\alpha^2}{4\varepsilon_0\pi^2}\int_0^{k_c}\mathrm{d}k = \frac{q_\alpha^2 k_c}{4\varepsilon_0\pi^2}. \tag{43}$$

The fourth term of H represents the energy of the transverse field

$$H_R = \frac{\varepsilon_0}{2}\int \mathrm{d}^3r\left[\mathbf{E}_\perp^2(\mathbf{r}) + c^2\mathbf{B}^2(\mathbf{r})\right] \tag{44}$$

which, using expressions (29) and (30) for $\mathbf{E}_\perp$ and $\mathbf{B}$, can be put in the form

$$H_R = \sum_i \hbar\omega_i\left(a_i^+a_i + \tfrac{1}{2}\right). \tag{45}$$

In the presence of external fields described by the potentials $\mathbf{A}_e(\mathbf{r}, t)$ and $U_e(\mathbf{r}, t)$, the Hamiltonian (40) must be modified as follows:

$$\mathbf{A}_\perp(\mathbf{r}_\alpha) \to \mathbf{A}_\perp(\mathbf{r}_\alpha) + \mathbf{A}_e(\mathbf{r}_\alpha, t) \qquad V_{\text{Coul}} \to V_{\text{Coul}} + \sum_\alpha q_\alpha U_e(\mathbf{r}_\alpha, t). \tag{46}$$

Finally, note that the momentum of the field + particles global system has a simple expression in the Coulomb gauge:

$$\mathbf{P} = \sum_\alpha \mathbf{p}_\alpha + \mathbf{P}_R. \tag{47}$$

The first term represents the momentum of the particles and the momentum of the longitudinal field associated with them; the second term is the momentum of the transverse field

$$\mathbf{P}_R = \varepsilon_0\int \mathrm{d}^3r\, \mathbf{E}_\perp(\mathbf{r}) \times \mathbf{B}(\mathbf{r}) = \sum_j \hbar\mathbf{k}_j a_j^+ a_j \tag{48}$$

where the fields have been replaced by their expressions (29) and (30).

b) Unperturbed Hamiltonian and Interaction Hamiltonian

It is interesting to split the Hamiltonian H of the global system into three parts:

$$H = H_P + H_R + H_I \tag{49}$$

where H_P depends only on the variables $\mathbf{r}_\alpha$ and $\mathbf{p}_\alpha$ of the particles (particle Hamiltonian), H_R depends only on the variables a_j and a_j^+ of the field (radiation Hamiltonian), H_I depends both on $\mathbf{r}_\alpha, \mathbf{p}_\alpha$ and a_j, a_j^+ (interaction Hamiltonian). Starting with expression (40) for H, we obtain, beside H_R given by (45),

$$H_P = \sum_\alpha \frac{\mathbf{p}_\alpha^2}{2m_\alpha} + V_{\text{Coul}} \tag{50}$$

$$H_I = H_{I1} + H_{I2} + H_{I1}^S \tag{51}$$

where H_{I1} and H_{I1}^S are linear with respect to the fields

$$H_{I1} = -\sum_\alpha \frac{q_\alpha}{m_\alpha}\mathbf{p}_\alpha \cdot \mathbf{A}_\perp(\mathbf{r}_\alpha) \tag{52}$$

$$H_{I1}^S = -\sum_\alpha g_\alpha \frac{q_\alpha}{2m_\alpha}\mathbf{S}_\alpha \cdot \mathbf{B}(\mathbf{r}_\alpha) \tag{53}$$

and where H_{I2} is quadratic

$$H_{I2} = \sum_\alpha \frac{q_\alpha^2}{2m_\alpha}\mathbf{A}^2{}_\perp(\mathbf{r}_\alpha). \tag{54}$$

For systems of bound particles, the relative orders of magnitude of the different interaction terms are the following:

$$\frac{H_{I2}}{H_{I1}} \simeq \frac{q^2A^2/m}{qAp/m} = \frac{qAp/m}{p^2/m} \simeq \frac{H_{I1}}{H_P}. \tag{55}$$

For low radiation intensities, the ratio H_{I1}/H_P is small, which results in the ratio H_{I2}/H_{I1} also being small. The ratio H_{I1}^S/H_{I1} is on the order of

$$\frac{H_{I1}^S}{H_{I1}} \simeq \frac{q\hbar B/m}{qAp/m} \simeq \frac{\hbar kA}{pA} = \frac{\hbar k}{p} \tag{56}$$

which is the ratio between the momentum $\hbar k$ of the photon and the momentum p of the particle. For low-energy photons (for example, in the optical or microwave domain) and a bound electron, this ratio is very small compared with 1.

c) Equations of Motion

In the Heisenberg representation, the equations of motion can be deduced from expression (40) for H and the canonical commutation relations (20.b) and (36).

For the position and the velocity of the particles, we find, respectively, the relation (37) between the velocity $\mathbf{v}_\alpha$ of the particle and the momentum $\mathbf{p}_\alpha$, and the Newton–Lorentz equation, appropriately symmetrized, giving the acceleration of the particle in the presence of the fields **E** and **B**.

For the transverse fields, we recover the Maxwell equations between operators. Because the transverse fields are linear functions of a_j and a_j^+, these equations are equivalent to the equations of motion for the a_j:

$$\begin{aligned}\dot{a}_j &= \frac{1}{i\hbar}[a_j, H] \\ &= -i\omega_j a_j + \frac{i}{\sqrt{2\varepsilon_0\hbar\omega L^3}} \int \mathrm{d}^3r\, \mathrm{e}^{-i\mathbf{k}_j\cdot\mathbf{r}}\, \boldsymbol{\varepsilon}_j \cdot \mathbf{j}(\mathbf{r})\end{aligned} \tag{57}$$

which are the quantum equivalents of Equations (18.b), and which have the structure of harmonic oscillator equations with source terms. In general, it is not possible to explicitly calculate their solutions, because the source term depends on the motion of the particles, which are themselves affected by the transverse field that we are looking for. However, in the absence of particles, the evolutions of the operators a_j are decoupled and Equation (57) can be integrated to give

$$a_j(t) = a_j(0)\exp(-i\omega_j t). \tag{58}$$

The evolution of the free fields can be immediately deduced from (58). They appear as sums of traveling plane waves with wave vector $\mathbf{k}_j$, frequency $\omega_j = ck_j$ and polarization $\boldsymbol{\varepsilon}_j$. For example:

$$\begin{aligned}\mathbf{E}_{\text{free}}(\mathbf{r}, t) = \sum_j i\sqrt{\frac{\hbar\omega_j}{2\varepsilon_0 L^3}} \times \\ \times\left\{a_j(0)\boldsymbol{\varepsilon}_j \exp\left[i(\mathbf{k}_j\cdot\mathbf{r} - \omega_j t)\right] - a_j^+(0)\boldsymbol{\varepsilon}_j \exp\left[-i(\mathbf{k}_j\cdot\mathbf{r} - \omega_j t)\right]\right\}.\end{aligned} \tag{59}$$

In certain calculations, particularly calculations of photodetection signals, it is necessary to isolate the components of fields with positive and negative frequencies. For the free fields, formulas of the same type as (59) give an explicit expression for these components. For example,

$$\mathbf{E}_{\text{free}}^{(+)}(\mathbf{r}, t) = \sum_j i\sqrt{\frac{\hbar\omega_j}{2\varepsilon_0 L^3}}\, a_j(0)\boldsymbol{\varepsilon}_j \exp\left[i(\mathbf{k}_j\cdot\mathbf{r} - \omega_j t)\right] \tag{60.a}$$

$$\mathbf{E}_{\text{free}}^{(-)}(\mathbf{r}, t) = \left[\mathbf{E}_{\text{free}}^{(+)}(\mathbf{r}, t)\right]^+. \tag{60.b}$$

In the Schrödinger representation, observables are time independent and the state vector evolves in state space according to the Schrödinger equation.

4. State Space

In the Coulomb gauge, the dynamics of the global system is equivalent to the dynamics of an ensemble of nonrelativistic particles and an infinite collection of harmonic oscillators representing the modes of the transverse field. In quantum theory, the state space $\mathscr{E}$ of the system is the tensor product of the state spaces $\mathscr{E}_P$ and $\mathscr{E}_R$ associated with each of these subsystems. The spaces $\mathscr{E}_P$ and $\mathscr{E}_R$ are themselves tensor products of spaces relative to each of the particles, and to each of the modes of the transverse field:

$$\mathscr{E}_P = \cdots \otimes \mathscr{E}_\alpha \otimes \cdots \tag{61}$$

$$\mathscr{E}_R = \cdots \otimes \mathscr{E}_j \otimes \cdots. \tag{62}$$

We now consider $\mathscr{E}_R$ in more detail. An orthonormal basis of each of the spaces $\mathscr{E}_j$ is composed of the basis $\{|n_j\rangle\}$ of the energy eigenstates of the oscillator j. Using expressions (45) and (48) for H_R and $\mathbf{P}_R$, the state $|n_1\rangle \cdots |n_j\rangle \cdots$, written more concisely as $|\{n_j\}\rangle$, is an eigenstate of these two observables:

$$H_R|\{n_j\}\rangle = \left[\sum_j \left(n_j + \tfrac{1}{2}\right)\hbar\omega_j\right]|\{n_j\}\rangle \tag{63.a}$$

$$\mathbf{P}_R|\{n_j\}\rangle = \left(\sum_j n_j\hbar\mathbf{k}_j\right)|\{n_j\}\rangle. \tag{63.b}$$

It represents a state of the field containing n_1 *photons* of the mode $1, \ldots, n_j$ *photons* of the mode j, with each photon of a mode j contributing to the total energy and momentum by the elementary "quanta" $\hbar\omega_j$ and $\hbar\mathbf{k}_j$.

The vacuum is the ground state of H_R corresponding to $n_1 = \cdots = n_j = \cdots = 0$. It is written more concisely as $|0\rangle$ and is characterized by the property

$$a_j|0\rangle = 0 \qquad \text{for each } j. \tag{64}$$

In each of the spaces $\mathscr{E}_j$, the $|n_j\rangle$ are not the only interesting states. The "coherent" states $|\alpha_j\rangle$ play a particular role in the discussion of quasi-classical situations. They can be deduced from the vacuum $|0\rangle$ by a unitary transformation

$$|\alpha_j\rangle = T^+(\alpha_j)|0\rangle \tag{65}$$

defined by

$$T(\alpha_j) = \exp\left[\alpha_j^* a_j - \alpha_j a_j^+\right] \tag{66}$$

whose action is a translation of the operator a_j by the quantity α_j

$$T(\alpha_j)a_j T^+(\alpha_j) = a_j + \alpha_j. \tag{67}$$

The state $|\alpha_j\rangle$ is an eigenstate of the annihilation operator a_j having the eigenvalue α_j

$$a_j|\alpha_j\rangle = \alpha_j|\alpha_j\rangle \tag{68}$$

and its expansion onto the basis $\{|n_j\rangle\}$ is given by

$$|\alpha_j\rangle = e^{-|\alpha_j|^2/2} \sum_{n_j=0}^{\infty} \frac{(\alpha_j)^{n_j}}{\sqrt{n_j!}}|n_j\rangle. \tag{69}$$

5. The Long-Wavelength Approximation and the Electric Dipole Representation

Atoms and molecules are composed of charged particles (electrons and nuclei) forming bound states whose size a_0 is typically on the order of a few Bohr radii. Assume that such a system interacts with radio frequency, infrared, visible, or ultraviolet radiation. The wavelength λ of this radiation is large compared with a_0 and it is legitimate to neglect the spatial variations of the electromagnetic field over the size of the system of particles: all the particles see the same field. This is the long-wavelength approximation.

For the sake of simplicity, consider an atom (or a molecule) that is globally neutral and located close to the origin **0**. To lowest order in a_0, its electrical properties are characterized by its electric dipole moment

$$\mathbf{d} = \sum_\alpha q_\alpha \mathbf{r}_\alpha \tag{70}$$

A unitary transformation on the Hamiltonian (40) can cause the coupling between the atom and the field to appear explicitly in the form of an electric dipole interaction between the atomic dipole **d** and the radiation. To higher orders in a_0/λ, the same procedure would result in the appearance of electric quadrupole and magnetic dipole interactions, etc. Because we neglect them here, we also omit in H the spin magnetic coupling H_{I1}^S, so that we start with the approximate Hamiltonian:

$$H = \sum_\alpha \frac{1}{2m_\alpha}\left[\mathbf{p}_\alpha - q_\alpha \mathbf{A}_\perp(\mathbf{0})\right]^2 + V_{\text{Coul}} + \sum_j \hbar\omega_j\left(a_j^+ a_j + \tfrac{1}{2}\right). \tag{71}$$

a) The Unitary Transformation

The transformation

$$T = \exp\left[-\frac{i}{\hbar}\mathbf{d}\cdot\mathbf{A}_\perp(\mathbf{0})\right] = \exp\left\{\sum_j\left(\lambda_j^* a_j - \lambda_j a_j^+\right)\right\} \tag{72}$$

where

$$\lambda_j = \frac{i}{\sqrt{2\varepsilon_0 \hbar \omega_j L^3}} \boldsymbol{\varepsilon}_j \cdot \mathbf{d} \tag{73}$$

is a translation concerning both the operators $\mathbf{p}_\alpha$ and the operators a_j and a_j^+. The fundamental operators are in fact transformed according to the following rules

$$T\mathbf{r}_\alpha T^+ = \mathbf{r}_\alpha \tag{74.a}$$

$$T\mathbf{p}_\alpha T^+ = \mathbf{p}_\alpha + q_\alpha \mathbf{A}(\mathbf{0}) \tag{74.b}$$

$$Ta_j T^+ = a_j + \lambda_j \tag{74.c}$$

$$Ta_j^+ T^+ = a_j^+ + \lambda_j^*. \tag{74.d}$$

Because the transformation is time independent, the new Hamiltonian is written

$$\begin{aligned} H' &= THT^+ \\ &= \sum_\alpha \frac{\mathbf{p}_\alpha^2}{2m_\alpha} + V_{\text{Coul}} + \varepsilon_{\text{dip}} + \sum_j \hbar\omega_j \left(a_j^+ a_j + \tfrac{1}{2}\right) - \\ &\quad - \mathbf{d} \cdot \sum_j \mathscr{E}_{\omega_j} \left[i a_j \boldsymbol{\varepsilon}_j - i a_j^+ \boldsymbol{\varepsilon}_j \right] \end{aligned} \tag{75}$$

where

$$\varepsilon_{\text{dip}} = \sum_j \frac{1}{2\varepsilon_0 L^3} (\boldsymbol{\varepsilon}_j \cdot \mathbf{d})^2. \tag{76}$$

b) The Physical Variables in the Electric Dipole Representation

The physical variables in the new representation are represented by the transforms G' of the observables G which represent them in the original representation

$$G' = TGT^+. \tag{77}$$

Starting with expressions (37), (21), (23), and (22) for the operators representing, respectively, the velocity of the particle α, the transverse vector potential, the magnetic field and the transverse electric field, we obtain expressions for the new observables which represent these variables:

$$\mathbf{v}'_\alpha = T\mathbf{v}_\alpha T^+ = \frac{\mathbf{p}_\alpha}{m_\alpha} \tag{78}$$

$$\begin{aligned} \mathbf{A}'_\perp(\mathbf{r}) &= T\mathbf{A}_\perp(\mathbf{r})T^+ = \mathbf{A}_\perp(\mathbf{r}) \\ &= \sum_j \mathscr{A}_{\omega_j} \left[a_j \boldsymbol{\varepsilon}_j e^{i\mathbf{k}_j \cdot \mathbf{r}} + a_j^+ \boldsymbol{\varepsilon}_j e^{-i\mathbf{k}_j \cdot \mathbf{r}} \right] \end{aligned} \tag{79}$$

$$\mathbf{B}'(\mathbf{r}) = \mathbf{B}(\mathbf{r}) \tag{80}$$

$$\begin{aligned} \mathbf{E}'_\perp(\mathbf{r}) &= T\mathbf{E}_\perp(\mathbf{r})T^+ \\ &= \sum_j \mathscr{E}_{\omega_j} \left[i(a_j + \lambda_j) \boldsymbol{\varepsilon}_j e^{i\mathbf{k}_j \cdot \mathbf{r}} + \text{h.c.} \right] \\ &= \mathbf{E}_\perp(\mathbf{r}) - \frac{1}{\varepsilon_0} \mathbf{P}_\perp(\mathbf{r}) \end{aligned} \tag{81}$$

where $\mathbf{P}_\perp(\mathbf{r})$ is the transverse part of the polarization density $\mathbf{P}(\mathbf{r})$ associated with the atom when it is considered as a pointlike dipole:

$$\mathbf{P}(\mathbf{r}) = \mathbf{d}\, \delta(\mathbf{r}) \tag{82}$$

$$\mathbf{P}_\perp(\mathbf{r}) = \sum_j \frac{\boldsymbol{\varepsilon}_j (\boldsymbol{\varepsilon}_j \cdot \mathbf{d})}{L^3} e^{i\mathbf{k}_j \cdot \mathbf{r}}. \tag{83}$$

Note that, according to (74.a), $\mathbf{r}'_\alpha = \mathbf{r}_\alpha$, so that the position of the particles, the atomic dipole and the polarization density are represented by the same operators in the two representations.

c) The Displacement Field

Starting with the total electric field $\mathbf{E}(\mathbf{r})$ and the polarization density $\mathbf{P}(\mathbf{r})$, we introduce the displacement field

$$\mathbf{D}(\mathbf{r}) = \varepsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r}). \tag{84}$$

We study its properties in reciprocal space, where it is written:

$$\mathscr{D}(\mathbf{k}) = \varepsilon_0 \mathscr{E}(\mathbf{k}) + \frac{\mathbf{d}}{(2\pi)^{3/2}}. \tag{85}$$

[Relation (82) has been used to calculate the Fourier transform of $\mathbf{P}(\mathbf{r})$].

With expression (39.a) for $\rho(\mathbf{k})$, the Maxwell equation (2.a) is written:

$$i\varepsilon_0 \mathbf{k}\cdot\mathscr{E}(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}}\sum_\alpha q_\alpha e^{-i\mathbf{k}\cdot\mathbf{r}_\alpha}$$
$$= \frac{1}{(2\pi)^{3/2}}\left[\sum_\alpha q_\alpha - i\mathbf{k}\cdot\sum_\alpha q_\alpha \mathbf{r}_\alpha + \cdots\right]. \qquad (86)$$

The expansion in powers of $\mathbf{k}\cdot\mathbf{r}_\alpha$ made in formula (86) is justified in the long-wavelength approximation because $kr_\alpha \simeq ka_0 \ll 1$. The first term inside the brackets of formula (86) is zero because the system of charges is assumed to be globally neutral. The second term is expressed as a function of the electric dipole. We then have, in the dipole approximation,

$$\varepsilon_0 \mathbf{k}\cdot\mathscr{E}(\mathbf{k}) + \frac{\mathbf{k}\cdot\mathbf{d}}{(2\pi)^{3/2}} = 0. \qquad (87)$$

From (85) and (87), it is clear that $\mathbf{k}\cdot\mathscr{D}(\mathbf{k})$ is zero so that the displacement field is transverse for a globally neutral system.

Moreover, the polarization $\mathbf{P}(\mathbf{r})$ is zero outside the system of charges ($r > a_0$), and (84) is reduced to

$$\mathbf{E}(\mathbf{r}) = \mathbf{D}(\mathbf{r})/\varepsilon_0 \qquad \text{for } |\mathbf{r}| > a. \qquad (88)$$

The displacement field is thus the transverse field which coincides, except for the factor ε_0, with the *total* electric field outside the system of charges. One advantage of the new representation is that a very simple operator describes $\mathbf{D}(\mathbf{r})/\varepsilon_0$, and thus the total electric field. Indeed, according to (84), the transversality of $\mathbf{D}$ results in the fact that $\mathbf{D} = \varepsilon_0\mathbf{E}_\perp + \mathbf{P}_\perp$. As a consequence of (81),

$$\mathbf{D}'(\mathbf{r})/\varepsilon_0 = \mathbf{E}'_\perp(\mathbf{r}) + \frac{1}{\varepsilon_0}\mathbf{P}'_\perp(\mathbf{r})$$
$$= \mathbf{E}_\perp(\mathbf{r})$$
$$= i\sum_j \mathscr{E}_{\omega_j}\left(a_j\boldsymbol{\varepsilon}_j e^{i\mathbf{k}_j\cdot\mathbf{r}} - a_j^+\boldsymbol{\varepsilon}_j e^{-i\mathbf{k}_j\cdot\mathbf{r}}\right). \qquad (89)$$

d) Electric Dipole Hamiltonian

We now return to the Hamiltonian H'. The last term of (75) is the new interaction Hamiltonian. Using (89), it is written

$$H'_I = -\mathbf{d}\cdot\mathbf{D}'(\mathbf{0})/\varepsilon_0 \qquad (90)$$

and represents the interaction energy between the electric dipole and the displacement field. It is frequently written in the form

$$H'_I = -\mathbf{d}\cdot\mathbf{E}_\perp(\mathbf{0}) \qquad (91)$$

it being understood that $\mathbf{E}_\perp(\mathbf{r})$ is the mathematical operator defined by (29) or (89) as a function of a_j and a_j^+. It is usually designated by the term "electric field", although it coincides with this variable only outside the system of charges. H' is thus written

$$H' = H'_P + H_R + H'_I. \qquad (92)$$

H_R is given by (45), H'_I by (90), and H'_P by

$$H'_P = H_P + \varepsilon_{\text{dip}}. \qquad (93)$$

The new particle Hamiltonian is obtained simply by adding to H_P given in (50) a dipolar self-energy described by expression (76). However, it should be noted that, in H'_P, $\mathbf{p}_\alpha^2/2m_\alpha$ is indeed the kinetic energy of the particle α, according to (78), whereas this is not the case in (50), because the velocity is given by (37) in this representation.

In all the foregoing, the atom is assumed to be at rest at the origin of the coordinate system. In certain problems, it is important to take into account the motion of the center of mass $\mathbf{R}$ of the atom. If the atom is globally neutral, it is sufficient, in the electric dipole representation, to replace $\mathbf{0}$ by $\mathbf{R}$ in H'_I:

$$H'_I = -\mathbf{d}\cdot\frac{\mathbf{D}'(\mathbf{R})}{\varepsilon_0} = -\mathbf{d}\cdot\mathbf{E}_\perp(\mathbf{R}). \qquad (94)$$

References

For more details, see *Photons and Atoms—Introduction to Quantum Electrodynamics*.

Refer also to the work of Kroll, Heitler, Power, Loudon, and Haken.