Chapter 4

Multipole interaction between atoms and their photonic environment

Macroscopic field quantization is presented for inhomogeneous nondispersive dielectrics, both with and without guest atoms. It is studied in detail how to obtain Maxwell's equations after choosing a suitable gauge. A quantum multipolar Hamiltonian is derived, starting from a classical minimal-coupling Lagrangian. Both photonic and electronic interactions of the atoms are discussed, in particular the dipole coupling of the atoms with the field.

4.1 Introduction

In this chapter it will be studied how guest atoms interact with a photonic dielectric environment that is characterized by a given spatially varying and real dielectric function $\varepsilon(r)$. A quantum mechanical description will be presented in which the guest atoms will be described microscopically, whereas the dielectric is described macroscopically. This hybrid description is more economical and probably gives more understanding of photonic effects in inhomogeneous dielectrics than a more involved theory would do in which the dielectric is also described microscopically.

The quantization of the electromagnetic field in vacuum can be found in many textbooks on quantum optics [15,45]. In [10,11] the more general problem is addressed how to quantize the electromagnetic field in a dielectric described by a real dielectric function $\varepsilon(r)$ that depends on position. The term "macroscopic quantization" has been coined for this procedure where the goal is not to derive a dielectric function from the interaction of light with the individual atoms that make up the dielectric [13]. Instead, the dielectric function is a given quantity. Material dispersion and absorption (transitions to nonradiative states in the dielectrics) are neglected. Certain sum rules [79] for modified spontaneous
emission rates when averaged over all frequencies will therefore not hold in the present formalism. Admittedly, the dielectric function is a response function that should be a dispersive and complex function of frequency. However, in the finite frequency interval of our interest, the dielectric function can be taken nondispersive and real. The same approximation is made for example when a mirror is assumed to be perfect, or in the chapters 2 and 3 of this thesis where the effective thicknesses of the plane scatterers were assumed real and frequency-independent. Also, in most band-structure calculations for photonic crystals a frequency-independent refractive-index contrast is assumed.

One can furthermore think of glass plates, optical cavities or dielectric mirrors as the type of dielectrics that can be characterized by a position-dependent dielectric function or refractive index. In these cases, the refractive index can often be considered as piecewise constant. Multimode glass fibres used in optical telecommunication do not have piecewise constant refractive indices: in the so-called graded-index fibres the refractive index in the core varies parabolically with the radius [83]. In this chapter, the relative dielectric function $\varepsilon(r)$ is left unspecified (but assume it to be piecewise continuously differentiable) so that the theory describes dielectrics in both of the situations just sketched.

This rather formal chapter generalizes standard electrodynamics in the Coulomb gauge [84] to inhomogeneous dielectrics. The results are used in chapter 5 in order to derive a point-scattering formalism for quantum optics. The present chapter consists of two parts: the first part starts with the quantization of the electromagnetic field in inhomogeneous dielectrics without guest atoms. In the second and major part, the guest atoms are added and a Lagrangian is introduced with minimal-coupling interaction between field and atoms. In the end a quantum Hamiltonian is obtained with multipolar interaction between light and matter. In particular it is found to which field a dipole couples in a quantum optical description of inhomogeneous dielectrics. Even for an atom in free space this has been a controversial subject. In the discussion at the end of the chapter it is explained why controversy and confusion could arise; the free-space case is compared to the more general situation that is presented here of an atom in an inhomogeneous dielectric.

## 4.2 Inhomogeneous dielectric without guest atoms

### 4.2.1 Classical Lagrangian and Hamiltonian

In this section the quantization of the electromagnetic field in inhomogeneous dielectrics is briefly reviewed. The goal is to simplify derivations of the original texts [10, 11] and to derive results that will be useful in the following sections, when guest atoms are added in the dielectric.

In SI-units, the source-free Maxwell equations in matter are

\[

\nabla \cdot \mathbf{D} = 0 \\
\nabla \cdot \mathbf{B} = 0 \\
\n\nabla \times \mathbf{H} - \dot{\mathbf{D}} = 0 \\
\n\nabla \times \mathbf{E} + \dot{\mathbf{B}} = 0,
\]

(4.1)
where here and in the following the dot denotes a partial time derivative. The fields \( \mathbf{E} \), \( \mathbf{B} \), \( \mathbf{D} \) and \( \mathbf{H} \) are the electric field and the magnetic induction, the displacement field and the magnetic field vector. For nonmagnetic inhomogeneous dielectrics, the constitutive relations are simply \( \mathbf{B} = \mu_0 \mathbf{H} \) and \( \mathbf{D} = \varepsilon_0 \varepsilon(r) \mathbf{E} \). (The generalization of the present theory to inhomogeneous magnetic materials will be discussed at the end of this chapter in section 4.5.) As in the case of vacuum, the electric and magnetic fields can be expressed in terms of a vector potential \( \mathbf{A} \) and a scalar potential \( \Phi \):

\[
\mathbf{E} = -\nabla \Phi - \dot{\mathbf{A}} \tag{4.2}
\]

\[
\mathbf{B} = \nabla \times \mathbf{A} \tag{4.3}
\]

There is gauge freedom in choosing pairs \((\mathbf{A}, \Phi)\) that lead to the same electric and magnetic fields. Now choose the generalized Coulomb gauge which is defined by the requirement that the vector potential satisfies

\[
\nabla \cdot [\varepsilon(r)\mathbf{A}(r)] = 0. \tag{4.4}
\]

The vector potential or any field satisfying this condition, is called "generalized transverse", because it satisfies a generalized version of the Coulomb gauge condition \( \nabla \cdot \mathbf{A} = 0 \) in free space. In this gauge, the vector potential must satisfy the wave equation

\[
\nabla \times \nabla \times \mathbf{A} + \frac{\varepsilon(r)}{c^2} \dot{\mathbf{A}} = 0. \tag{4.5}
\]

in order to be consistent with the third Maxwell equation in (4.1). The scalar potential can be chosen identically zero in the generalized Coulomb gauge.

A Lagrangian \( L_0 \) that leads to the wave equation (4.5) for the vector potential is

\[
L_0 = \int \! dr \ L_0 = \frac{1}{2} \int \! dr \left[ \varepsilon_0 \varepsilon(r) \dot{\mathbf{A}}^2 - \mu_0^{-1} (\nabla \times \mathbf{A})^2 \right]. \tag{4.6}
\]

The Lagrangian is the spatial integral over the Lagrangian density \( L_0 \). The vector potential is a canonical field variable and its canonically conjugate field can be found as a functional derivative of the Lagrangian density

\[
\Pi(r, t) \equiv \frac{\delta L_0}{\delta \dot{\mathbf{A}}} = \varepsilon_0 \varepsilon(r) \dot{\mathbf{A}} = -\mathbf{D}(r, t). \tag{4.7}
\]

(The functional derivative is used somewhat naively here, but the answer is correct, as a more detailed analysis in appendix B shows.) In other words, the field canonically conjugate to the vector potential equals minus the displacement field, which is a transverse field. The Hamiltonian is the integral over the Hamiltonian (energy) density \( \mathcal{H} \):

\[
H_0 = \int \! dr \ H_0 = \int \! dr \left[ \Pi \cdot \dot{\mathbf{A}} - L_0 \right] = \frac{1}{2} \int \! dr \left[ \frac{\Pi^2}{\varepsilon_0 \varepsilon(r)} + \frac{(\nabla \times \mathbf{A})^2}{\mu_0} \right]. \tag{4.8}
\]

This is the Hamiltonian for the classical electromagnetic field in an inhomogeneous dielectric, without the presence of guest atoms.
4.2.2 Complete sets and quantum Hamiltonian

For a quantum optical description of the dielectric, the electromagnetic fields can best be expanded in terms of harmonic solutions of the wave equation (4.5). With each of these “true modes” one can associate independent canonical variables, for which commutation rules can be given. The set of true modes is not unique. This freedom will be used below to choose a particularly convenient set. For example, in vacuum the true modes are plane waves. There one can choose linear combinations of cosine and sine solutions $\cos(k \cdot r)$ and $\sin(k \cdot r)$. The complex exponential $\exp(ik \cdot r)$ is only one such linear combination.

Now a convenient set of true modes for the dielectric will be chosen and their orthonormality relations derived. Assume that the electromagnetic fields live in a large quantization volume $V$ that can be chosen infinitely large at a later stage. Let $Q$ be an abstract operator in Hilbert space which has a local representation in real space:

$$\langle \mathbf{r}|Q|\mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}')Q(\mathbf{r}). \quad \text{with} \quad Q(\mathbf{r}) \equiv \frac{1}{\sqrt{\varepsilon(\mathbf{r})}} \nabla \times \nabla \times \frac{1}{\sqrt{\varepsilon(\mathbf{r})}}. \quad \text{(4.9)}$$

The operator $Q$ is Hermitian under the normal inner product. All eigenfunctions $g_\lambda$ of $Q$ have the property $\nabla \cdot (\sqrt{\varepsilon(\mathbf{r})}g(\mathbf{r})) = 0$. The subspace of functions in Hilbert space with the same transversality property is spanned by the eigenfunctions of $Q$. Now let $C$ be the operator which is also local in real space and whose action in real space is to take the complex conjugate. The dielectric function in this context must also be viewed as an abstract operator $\varepsilon$ with local representation in real space: $\langle \mathbf{r}|\varepsilon|\mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}')\varepsilon(\mathbf{r})$ [68]. The real-space representations of $Q$ and $C$ commute, because $\varepsilon(\mathbf{r})$ is real. Then $Q$ and $C$ commute in any representation. From the fact that $Q$ and $C$ commute it follows that an orthonormal basis of real eigenfunctions $\{g_\lambda\}$ of $Q$ can be chosen to span the subspace (with complex coefficients).

As a consequence, the vector potential $A$ can be expanded in terms of a complete set of real vector mode functions $\{h_\lambda(\mathbf{r})\} \equiv \{\sqrt{\varepsilon(\mathbf{r})}g_\lambda(\mathbf{r})\}$, which are the harmonic solutions of the wave equation (4.5):

$$-\nabla \times \nabla \times h_\lambda(\mathbf{r}) + \frac{\varepsilon(\mathbf{r})\omega^2}{c^2} h_\lambda(\mathbf{r}) = 0. \quad \text{(4.10)}$$

These mode functions satisfy the same generalized transversality condition (4.4) as the vector potential. The choice of this particular set of mode functions $\{h_\lambda\}$ simplifies the quantization of the electromagnetic field, as we will see. (Real mode functions were also used in [10], without the above motivation.) The functions are labelled with $\lambda$, where $\lambda$ is understood to count both continua and discrete sets of solutions. As is clear from Eq. (4.10), unlike the $g_\lambda$ the functions $h_\lambda$ do not satisfy a Hermitian eigenvalue equation. From the orthonormality of the $g_\lambda$ it follows that the functions $h_\lambda(\mathbf{r})$ satisfy the generalized orthonormality condition

$$\int d\mathbf{r} \varepsilon(\mathbf{r})h^*_\lambda(\mathbf{r}) \cdot h^\prime\lambda(\mathbf{r}) = \delta_{\lambda\lambda'}. \quad \text{(4.11)}$$

The complex-conjugation symbol $^*$ was written for future reference, since of course $h_\lambda$ is real. The integration volume of this integral is the quantization volume $V$. The equation
(4.11) will be called a generalized inner product of the modes $h_\lambda$ and $h_{\lambda'}$. The mode functions scale as $(V)^{-1/2}$.

In a scattering situation, where $\varepsilon(r)$ is a space-filling dielectric function plus a local modification within a scattering volume $V_\varepsilon$, the contribution of the scattering volume to the integral (4.11) scales as $V_\varepsilon/V$, which becomes of measure zero when the quantization volume $V$ is sent to infinity. As an example, mode functions of a photonic crystal with a point defect have the same orthonormality relations as the other mode functions in the absence of the defect.

The functions $h_\lambda$ are complete in the sense that they form a basis for generalized transverse functions such as the vector potential that satisfy the wave equation (4.5). In other words, a generalized transverse delta function $\delta_e^T$ (a distribution) can be defined in terms of the functions $h_\lambda$:

$$\delta_e^T(r, r') = \sum_\lambda h_\lambda(r) h_{\lambda'}(r') \varepsilon(r'). \quad (4.12)$$

For $\varepsilon(r) \equiv 1$, this expression reduces to the free-space transverse delta function that will be given explicitly in Eq. (C.5) of appendix C, and which can be written as a dyadic sum over transverse plane wave modes (see [85], p. 53). Evidently, the generalized transverse delta function (4.12) is real because the mode functions are real. The “identity” property (4.12) together with the idempotence property

$$\int dr_1 \delta_e^T(r, r_1) \cdot \delta_e^T(r_1, r') = \delta_e^T(r, r'). \quad (4.13)$$

define $\delta_e^T$ as a projector in the subspace of generalized transverse functions. The generalized transverse delta function is not symmetric in its arguments, because it is transverse in its second and generalized transverse in its first variable:

$$\nabla \cdot [\varepsilon(r) \delta_e^T(r, r')] = 0 = \nabla_{r'} \cdot [\delta_e^T(r, r')] \quad (4.14)$$

Furthermore, it has the properties that

$$X^T(r) - \int dr' X^T(r') \cdot \delta_e^T(r', r) = 0. \quad (4.15a)$$

$$X^T(r) - \varepsilon(r) \int dr' \delta_e^T(r, r') \cdot X^T(r')/\varepsilon(r') = 0. \quad (4.15b)$$

$$\int dr' \delta_e^T(r, r') \cdot X^L(r') = 0. \quad (4.15c)$$

$$\int dr' \varepsilon(r') X^L(r') \cdot \delta_e^T(r', r) = 0. \quad (4.15d)$$

for any transverse function $X^T$ (zero divergence) and longitudinal function $X^L$ (zero curl). These properties follow immediately from the transversality property (4.4) and the orthogonality relations (4.11) of the mode functions $h_\lambda$. These several properties of the generalized transverse delta function will be used in later sections and in appendix B.
The vector potential and its canonically conjugate field have normal-mode expansions

\[
A(\mathbf{r},t) = \frac{1}{\sqrt{\varepsilon_0}} \sum_\lambda q_\lambda(t) \mathbf{h}_\lambda(\mathbf{r}).
\]

(4.16a)

\[
\Pi(\mathbf{r},t) = \sqrt{\varepsilon_0} \sum_\lambda p_\lambda(t) \varepsilon(\mathbf{r}) \mathbf{h}_\lambda(\mathbf{r}).
\]

(4.16b)

If the above two expansions are substituted in the Hamiltonian (4.8) and the normalization condition (4.11) is used, then it follows that

\[
H_0 = \frac{1}{2} \sum_\lambda \left( p_\lambda^2 + \omega_\lambda^2 q_\lambda^2 \right).
\]

(4.17)

The Hamiltonian turns out to be a simple sum over the true modes of the inhomogeneous dielectric, where the energy of each mode corresponds to a one-dimensional harmonic oscillator with position \( q_\lambda \), momentum \( p_\lambda \) and frequency \( \omega_\lambda \). This is a generalization to inhomogeneous dielectrics of the result for free space.

Now comes the quantization step. Classically, the generalized coordinates \( q_\lambda(t) \) and momenta \( p_\lambda(t) \) are real variables because \( A(\mathbf{r},t) \) and \( \Pi(\mathbf{r},t) \) and the modes \( \mathbf{h}_\lambda \) are real. Real variables such as \( q_\lambda(t) \) and \( p_\lambda(t) \) turn into Hermitian operators in quantum mechanics. The independent canonical pairs satisfy the standard equal-time commutation relations

\[
[q_\lambda(t), p_{\lambda'}(t)] = i\hbar \delta_{\lambda\lambda'}.
\]

(4.18)

With the normal mode expansions (4.16a) and (4.16b), the commutation relation for the vector potential and its canonically conjugate field can be found immediately:

\[
[A(\mathbf{r},t), \Pi(\mathbf{r}',t)] = i\hbar \sum_\lambda \mathbf{h}_\lambda(\mathbf{r}) \mathbf{h}_\lambda(\mathbf{r}') \varepsilon(\mathbf{r}') = i\hbar \delta^T_\varepsilon(\mathbf{r},\mathbf{r}').
\]

(4.19)

The commutator is a dyadic quantity which turns out to be proportional to the generalized transverse delta function.

Creation and annihilation operators are introduced as

\[
\alpha_\lambda(t) = \sqrt{\frac{\omega_\lambda}{2\hbar}} q_\lambda(t) + i \sqrt{\frac{1}{2\hbar \omega_\lambda}} p_\lambda(t)
\]

(4.20a)

\[
\alpha_\lambda^\dagger(t) = \sqrt{\frac{\omega_\lambda}{2\hbar}} q_\lambda(t) - i \sqrt{\frac{1}{2\hbar \omega_\lambda}} p_\lambda(t).
\]

(4.20b)

They have standard commutation relations \([\alpha_\lambda(t), \alpha_{\lambda'}(t)^\dagger] = \delta_{\lambda\lambda'} \) and all other inequivalent commutators are zero. The Hamiltonian becomes the sum over contributions of individual modes, \( \hbar \omega_\lambda (\alpha_\lambda^\dagger \alpha_\lambda + 1/2) \). Thus the concept of a photon as the elementary excitation \( \alpha_\lambda^\dagger |0\rangle \) of a mode is as useful for inhomogeneous dielectrics as it is for free space. Number states, coherent and squeezed states etcetera can be defined analogously as for free space. The only difference for inhomogeneous dielectrics is that their true
modes are not plane waves. The vector potential and its canonically conjugate field can be expressed in terms of creation and annihilation operators as

\[ A(r, t) = \sum_\lambda \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_\lambda}} \left[ \alpha_\lambda(t) \mathbf{h}_\lambda(r) + \alpha_\lambda^\dagger(t) \mathbf{h}_\lambda(r) \right], \quad (4.21) \]

\[ \Pi(r, t) = -i\varepsilon_0 \varepsilon(r) \sum_\lambda \sqrt{\frac{\hbar \omega_\lambda}{2\varepsilon_0}} \left[ \alpha_\lambda(t) \mathbf{h}_\lambda(r) - \alpha_\lambda^\dagger(t) \mathbf{h}_\lambda(r) \right]. \quad (4.22) \]

The forms of the electric and magnetic fields as quantum mechanical operators and their commutation relations immediately follow from (4.2), (4.3) and the above equation (4.21). The time-dependence of the operators is simply harmonic, \( \alpha_\lambda(t) = \alpha(0) \exp(-i\omega_\lambda t) \), for example. The quantization of the electromagnetic field has thus been accomplished.

In practice, it can be convenient to use a set of complex true mode functions \( \{f_\mu\} \) instead of the real mode functions \( \{h_\lambda\} \). Since the complex mode functions should also satisfy the wave equation (4.10) and the generalized orthonormality condition (4.11), the two sets of mode functions are related through a unitary transformation that only relates mode function with identical eigenfrequencies:

\[ f_\mu = \sum_\lambda U^{-1}_{\mu\lambda} h_\lambda. \quad (4.23) \]

where \( U^* = U^{-1} \). Note that because of the relation (4.23), the generalized transverse delta function (4.12) can alternatively be expressed in terms of the complex mode functions \( f_\lambda \). Its effect is the substitution of one \( h_\lambda \) by \( f_\lambda \) and the other \( h_\lambda \) by \( f_\lambda^\dagger \):

\[ \delta^T_\varepsilon(r, r') = \sum_\lambda f_\lambda(r)f_\lambda^\dagger(r')\varepsilon(r'). \quad (4.24) \]

However, after this substitution it is no longer obvious that \( \delta^T_\varepsilon(r, r') \) is real-valued.

The electromagnetic fields can also be expanded in terms of the complex mode functions \( f_\lambda \) as

\[ A(r, t) = \sum_\lambda \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_\lambda}} \left[ a_\lambda^{(0)}(t) f_\lambda(r) + a_\lambda^{(0)\dagger}(t) f_\lambda^\dagger(r) \right], \quad (4.25a) \]

\[ \Pi(r, t) = -i\varepsilon_0 \varepsilon(r) \sum_\lambda \sqrt{\frac{\hbar \omega_\lambda}{2\varepsilon_0}} \left[ a_\lambda^{(0)}(t) f_\lambda(r) - a_\lambda^{(0)\dagger}(t) f_\lambda^\dagger(r) \right]. \quad (4.25b) \]

where the new annihilation operator \( a_\mu^{(0)} \) associated with the complex mode \( f_\mu \) is defined in terms of the “old” operators as

\[ a_\mu^{(0)} = \sum_\lambda U_{\mu\lambda} \alpha_\lambda. \quad (4.26) \]

and \( a_\mu^{(0)\dagger} \) is its Hermitian conjugate. The commutation relations of \( a_\mu^{(0)} \) and \( a_\mu^{(0)\dagger} \) are again the standard relations, because \( U \) is a unitary transformation. To distinguish \( a_\mu^{(0)} \)
from operators to be defined later, the superscript \((0)\) has been added, signifying that no guest atoms are present. The time dependence of the operators is harmonic.

This completes the quantization of the electromagnetic field in an inhomogeneous dielectric without guest atoms. The reason not to start the quantization procedure with complex mode functions is that the associated generalized coordinates and momenta are not Hermitian. This makes intermediate results more complicated \([11,13,86]\). These unnecessary complications were avoided here. The relations \((4.23)\) between complex and real mode functions and \((4.26)\) between their respective annihilation operators are purely formal, unless both sets of mode functions are given explicitly. It is the mere existence of the mapping \((4.23)\) of the complex modes onto the real modes that justifies the expansion of the operators \(A\) and \(\Pi\) in terms of the complex mode functions. The choice of real mode functions made explicit otherwise implicit properties of the delta function \(\delta^2\).

### 4.3 Inhomogeneous dielectric with guest atoms

In the previous section it was described how to quantize the electromagnetic field in an inhomogeneous dielectric. Now inside the inhomogeneous dielectric guest atoms are introduced. Their optical response is not included in the dielectric function \(\varepsilon(r)\) of the medium. The goal in the following sections is to find the quantum optical description of the combined system, with a multipole interaction between the electromagnetic field and the guest atoms. There are at least two reasons why the multipolar Hamiltonian is to be preferred. In the first place, it is more convenient when only approximate calculations can be done which in the minimal-coupling formalism would give gauge-dependent results \([15]\); secondly, atoms are much smaller than optical wavelengths and in the multipole-formalism this can be exploited well. Actually, atoms are so much smaller than optical wavelengths that often "atoms" are identified with "dipoles".

The starting point is the minimal-coupling Lagrangian that produces the Maxwell equations and the equations of motion for the charges that make up the guest atoms. The minimal-coupling Lagrangian can be used to find a minimal-coupling Hamiltonian and this procedure can be found in \([10,87]\). A clear exposition is also given in \([88]\). Here the Lagrangian will first be transformed to the multipolar form before constructing a Hamiltonian. The latter procedure was followed also in \([13,14]\). The present work is different in that a careful treatment of functional differentiation is given and that a qualitative connection of final results with local-field effects will be made. Helpful details of the quantization of the vacuum electromagnetic field in the presence of atoms can be found in the books \([15,84,86]\).
4.3 Inhomogeneous dielectric with guest atoms

### 4.3.1 Choice of suitable Lagrangian

Guest atoms inside an inhomogeneous dielectric can be described by a charge density \( \sigma_g \) and a current density \( J_g \) which show up as sources in Maxwell’s equations:

\[
\nabla \cdot \mathbf{B} = 0, \\
\nabla \times \mathbf{E} + \dot{\mathbf{B}} = 0, \\
\varepsilon_0 \nabla \cdot [\varepsilon(r) \mathbf{E}(r)] = \sigma_g, \\
\mu_0^{-1} \nabla \times \mathbf{B} - \varepsilon_0 \varepsilon(r) \dot{\mathbf{E}} = J_g.
\]

(4.27) \hspace{1cm} (4.28) \hspace{1cm} (4.29) \hspace{1cm} (4.30)

Whatever Lagrangians and Hamiltonians are introduced for the inhomogeneous dielectric plus guest atoms, they must lead to these four Maxwell equations. Moreover, the particles with charges \( q_{mj} \) and masses \( M_{mj} \) should respond to electric and magnetic fields as given in the equation of motion

\[
M_{mj} \ddot{\mathbf{r}}_{mj} = q_{mj} [\mathbf{E}(\mathbf{r}_{mj}) + \dot{\mathbf{r}}_{mj} \times \mathbf{B}(\mathbf{r}_{mj})].
\]

(4.31)

We assume that there are no free charges. All electrons (labelled \( j \)) are bound to atomic nuclei (label \( m \)) to form neutral atoms that are constituent of the guest atoms. Let \( Z_m e \) be the nuclear charge of atom \( m \). Then \( \sigma_g \) and \( J_g \) are given by [4]

\[
\sigma_g(r) = \sum_m \left[ Z_m e \delta(r - \mathbf{R}_m) - e \sum_j \delta(r - \mathbf{r}_{mj}) \right], \\
J_g(r) = \sum_m \left[ -e \sum_j \dot{\mathbf{r}}_{mj} \delta(r - \mathbf{r}_{mj}) \right].
\]

(4.32) \hspace{1cm} (4.33)

These are charge and current densities of the guest atoms alone, as stressed by the subscript \( g \); the dielectric is completely described by the dielectric function \( \varepsilon_0 \varepsilon(r) \) and the magnetic permeability \( \mu_0 \). The guest atoms are assumed to have fixed positions, their nuclei are their centers of mass and are stationary at positions \( \mathbf{R}_m \). From these explicit forms of \( \sigma_g \) and \( J_g \) or from the third and fourth Maxwell equation follows the equation of continuity or current conservation, namely

\[
\nabla \cdot J_g + \dot{\sigma}_g = 0.
\]

(4.34)

Again, the electric and magnetic fields can be defined through Eq (4.2) and (4.3) in terms of a vector potential \( \mathbf{A} \) and a scalar potential \( \Phi \). Then the first two Maxwell equations are automatically satisfied. The third and fourth Maxwell equations should follow from the Euler-Lagrange equations for the scalar and the vector potential, respectively. The minimal-coupling Lagrangian is

\[
L_{\text{min}} = \sum_m \left[ \sum_j \frac{1}{2} M_e \dot{\mathbf{r}}_{mj}^2 \right] + \int \text{d}r \, L_{\text{min}}.
\]

(4.35)
Here the Lagrangian density $\mathcal{L}_{\text{min}}$ describes the electromagnetic field energy and its minimal-coupling interaction with the guest atoms:

$$
\mathcal{L}_{\text{min}} = \frac{1}{2} \varepsilon_0 \varepsilon(r) \left[ \mathbf{A} + \nabla \Phi \right]^2 - \frac{1}{2 \mu_0} (\nabla \times \mathbf{A})^2 + \mathbf{J}_g \cdot \mathbf{A} - \sigma_g \Phi.
$$

(4.36)

Indeed, Maxwell's third and fourth equations can be found from the Euler-Lagrange equations for the scalar and the vector potentials, respectively. Moreover, the Euler-Lagrange equations for the canonical variables $r_{mj}$ give the equations of motion (4.31) for the charged particles. Note that the Lagrangian leads to these equations of motion, before choosing a gauge to fix $\mathbf{A}$ and $\Phi$ with: the equations of motion are gauge-independent results that should not depend on the choice of gauge.

### 4.3.2 Fixing the gauge

The electric and magnetic fields are defined in terms of a scalar and a vector potential. But there is gauge freedom, which means that the scalar and vector potentials are not uniquely defined by the requirement that physical measurable electric and magnetic fields satisfy Maxwell's equations. We need to choose a gauge in order to find in the end a quantum mechanical description of light interacting with the guest atoms. It is not necessary to choose the gauge already at this point, but is a matter of presentation to do so. In the conclusions in section 4.7 more will be said about this. As in the situation without guest atoms in section 4.2, the generalized Coulomb gauge is chosen in which $\nabla \cdot [\varepsilon(r) \mathbf{A}(r)] = 0$. In this section it will be checked whether the equations of motion for the scalar and vector potentials still lead to the third and fourth Maxwell equations after choosing the generalized Coulomb gauge. This must be the case, because the choice of gauge should not change the physical predictions of the theory.

The interaction term

$$
L_{A\Phi} \equiv \int \text{d}r \varepsilon_0 \varepsilon(r) \mathbf{A} \cdot \nabla \Phi,
$$

(4.37)

of the Lagrangian (4.35) becomes identically zero, because in the generalized Coulomb gauge it has become an inner product of a transverse and a longitudinal function. The remaining terms in the Lagrangian involving the scalar potential lead to an Euler-Lagrange equation that is the generalized Poisson equation for the scalar potential in the Coulomb gauge:

$$
\varepsilon_0 \nabla \cdot [\varepsilon(r) \nabla \Phi(r)] = -\sigma_g.
$$

(4.38)

Clearly, the scalar potential can not be chosen identically zero as in the situation without guest atoms. The gauge-fixing condition (4.4) for the vector potential, the equation (4.38) for the scalar potential, together with the definition of the electric field (4.2) in terms of the two potentials, still lead to the third Maxwell equation (4.29). This is as it should be, since Maxwell's equations should not change with the choice of the gauge.

The scalar potential is a function of the positions of the charges that make up the guest atoms. In other words, one can first solve the coupled equations of motion for the vector potential and the charges, and from the charge distribution $\sigma_g(t)$ thus found,
the scalar potential $\Phi(t)$ can be found as the solution of Eq. (4.38). Therefore, in the generalized Coulomb gauge the scalar potential is not an independent canonical field. Then the Lagrangian (4.35) can be simplified as

$$L_{\text{min}} = \sum_m \left[ \sum_j \frac{1}{2} m^2 c^2 r^2_{m,j} \right] - V_C + \int dr \ L'_{\text{min}},$$  

(4.39)

where Eqs. (4.37) and (4.38) were used. The Coulomb interaction

$$V_C = \frac{\varepsilon_0}{2} \int dr \ \varepsilon(r)(\nabla \Phi)^2$$  

(4.40)

is a function of the guest atoms alone; the Lagrangian density in (4.39) becomes

$$L'_{\text{min}} = \frac{1}{2} \frac{\varepsilon_0}{\mu} \varepsilon(r) \mathbf{A}^2 - \frac{1}{2 \mu_0} (\nabla \times \mathbf{A})^2 + \mathbf{J}_g \cdot \mathbf{A}.$$  

(4.41)

Which equation do we find for the vector potential after choosing the generalized Coulomb gauge? Let us begin at the other end: in order to be consistent with the fourth Maxwell equation, the vector potential should satisfy

$$\mu_0^{-1} \nabla \times \nabla \times \mathbf{A} + \varepsilon_0 \varepsilon(r) \mathbf{A} = \mathbf{J}_g - \varepsilon_0 \varepsilon(r) \nabla \Phi.$$  

(4.42)

It is not easy to see how the source term $-\varepsilon_0 \varepsilon(r) \nabla \Phi$ can appear at the right-hand side of this equation by functional differentiation of the Lagrangian with respect to the vector potential. Before choosing the gauge, the source term originated from the interaction term $L_{A\Phi}$ [Eq. (4.37)], which is zero after choosing the gauge. Functional derivatives of zero should of course be zero. At this point, it seems hard to find the fourth Maxwell equation after choosing the generalized Coulomb gauge.

In appendix B it is explained in detail that the usual functional derivative must be replaced by a “constrained functional derivative” after choosing a gauge. This is for mathematical reasons rather than a matter of taste or convenience. In the appendix one also finds simple rules to actually compute these constrained functional derivatives. In particular, it is shown that the Euler-Lagrange equation for the vector potential indeed gives (4.42) when the correct functional derivative is used. Interestingly, before choosing the gauge, the source term $-\varepsilon_0 \varepsilon(r) \nabla \Phi$ in (4.42) came from the $L_{A\Phi}$ interaction term (4.37) in the Lagrangian. However, after choosing the gauge the source term is produced by the constrained functional derivative of the minimal-coupling interaction term $\int dr \ \mathbf{J}_g \cdot \mathbf{A}$.

The left-hand side of the wave equation (4.42) is certainly transverse in the generalized Coulomb gauge. It is less obvious and sometimes goes unnoticed [13, 88] that the source term on the right-hand side is also transverse. A mathematical reason is that the wave equation is found by functional differentiation with respect to generalized transverse functions. In section B.2 it was shown that these derivatives are always transverse. Physically, the source term must be transverse because of current conservation, Eq. (4.34). In [88] it was shown that the vector potential satisfying the wave equation (4.42) cannot be influenced by the longitudinal part of the source term. Here one must conclude that in the generalized Coulomb gauge a longitudinal part of the source term simply does not exist.
4.4 The quantum multipolar interaction Hamiltonian

In the previous sections it was shown that the minimal-coupling Lagrangian produces the Maxwell-Lorentz equations for the electromagnetic fields and the guest charges, before and also after choosing the generalized Coulomb gauge. Now the goal is to transform the Lagrangian in order to obtain a multipole interaction between the electromagnetic field and the guest atoms. The transformed Lagrangian must lead to the same equations for the fields and charges, of course. Candidate transformations are transformations where a total time derivative of a function of the canonical variables is added to the Lagrangian [84]. Such a transformation will be used shortly, but first some new fields must be introduced.

4.4.1 Polarization, magnetization and displacement fields

In the following, it is useful to describe the guest atoms in terms of a polarization density \( P_g \) and a magnetization density \( M_g \), rather than in terms of the charge and current densities. The former and latter pairs are related through [4]:

\[
\sigma_g = -\nabla \cdot P_g, \quad J_g = \dot{P}_g + \nabla \times M_g. \tag{4.43}
\]

In terms of the new variables, the equation of continuity (4.34) is automatically satisfied. By using the definitions (4.32) and (4.33) of \( \sigma_g \) and \( J_g \) and by making a Taylor expansion around the atomic positions \( R_m \) in both the left-hand and the right-hand sides of the above definitions, one can find that

\[
P_g(r) = -e \sum_{m,j} \int_0^1 \, du \, (r_{mj} - R_m) \, \delta(r - R_m - u(r_{mj} - R_m)), \tag{4.44}
\]

\[
M_g(r) = -e \sum_{m,j} \int_0^1 \, du \, u \, (r_{mj} - R_m) \times \hat{r}_{mj} \, \delta(r - R_m - u(r_{mj} - R_m)). \tag{4.45}
\]

Finite-order multipole expansions of the polarization and magnetization fields can be found by truncating the Taylor expansion in \( u \) of the integrand on the right-hand sides of the above equations. Such approximations will be made later, in section 4.4.5.

The displacement field \( D \) and the magnetic field vector \( H \) are given by the constitutive relations

\[
D \equiv \varepsilon_0 \varepsilon(r) E + P_g, \quad H \equiv \mu_0^{-1} B - M_g, \tag{4.46}
\]

where in the latter relation it was assumed as before that the dielectric is nonmagnetic so that the magnetic permeability equals the value \( \mu_0 \) of free space. Note that the dielectric function \( \varepsilon(r) \) is a property of the dielectric alone, independent of the guest atoms. On the other hand, the displacement field (4.46) does depend on the guest atoms because it includes the polarization field produced by them. The displacement field defined here is therefore different (although the same symbol is used) from the displacement field that was defined in section 4.2.1 where no guest atoms were present. In that case, the transversality of \( D \) was evident. The displacement field is also transverse when guest atoms are present, according to eqs. (4.29) and (4.43) in combination with (4.46).
4.4.2 Classical multipolar Lagrangian and Hamiltonian

The Lagrangian will be transformed by adding to it the total time derivative

\[ -\frac{d}{dt} \int \mathrm{d}r \, \mathbf{P}_g(r) \cdot \mathbf{A}(r). \]  

(4.47)

This is the Power-Zienau-Woolley (PZW) transformation, and its effect is well-known for free space [84]. The PZW transformation was already applied to inhomogeneous dielectrics before, in [13]. There it was stated that the polarization density \( \mathbf{P}_g \) in the Lagrangian density \( \mathcal{L}' \) should be replaced by a "reduced polarization density" at this point, in order to stick to the generalized Coulomb gauge for the vector potential. However, such replacements are not necessary if functional derivatives with respect to the generalized transverse vector potential are identified as constrained functional differentiations, and if computation rules are used accordingly (see appendix B).

After adding the term \( (4.47) \), the new Lagrangian \( \mathcal{L}_{\text{multi}} \) can be rewritten as

\[ \mathcal{L}_{\text{multi}} = \sum_{m_j} \frac{1}{2} m_e \dot{r}_{m_j}^2 - V_C + \int \mathrm{d}r \, \mathcal{L}_{\text{multi}}. \]  

(4.48)

The new Lagrangian density \( \mathcal{L}_{\text{multi}} \) has the form

\[ \mathcal{L}_{\text{multi}} = \frac{1}{2} \varepsilon_0 \varepsilon(r) \dot{\mathbf{A}}^2(r) - \frac{1}{2\mu_0} [\nabla \times \mathbf{A}(r)]^2 + M_g(r) \cdot \nabla \times \mathbf{A}(r) - \mathbf{P}_g(r) \cdot \dot{\mathbf{A}}(r), \]  

(4.49)

where the definition of the magnetization density in \( (4.44) \) was used as well as Gauss's theorem. The derivation is identical to the free-space case.

In order to find a Hamiltonian, first the canonically conjugate variables must be determined. By reasoning as in section B.3, the constrained functional differentiation of the Lagrangian \( \mathcal{L}_{\text{multi}} \) with respect to \( \dot{\mathbf{A}} \) produces the following field that is canonically conjugate to the vector potential:

\[ \Pi(r, t) = \frac{\delta \mathcal{L}_{\text{multi}}}{\delta \dot{\mathbf{A}}_e^T(r)} = \varepsilon_0 \varepsilon(r) \dot{\mathbf{A}}(r) - \mathbf{P}_g(r) + \varepsilon_0 \varepsilon(r) \nabla \Phi(r) = -\mathbf{D}(r). \]  

(4.50)

In the latter identity the definition of the electric field \( (4.2) \) and the displacement field \( (4.46) \) were used. As in the case without guest atoms, the field canonically conjugate to the vector potential equals minus the displacement field. The difference is that now the displacement field also contains the polarization field produced by the guest atoms. The canonically conjugate field would have been different if the minimal-coupling Lagrangian had been used.

The canonical momenta \( \mathbf{p}_{m_j} \) corresponding to the coordinate variables \( q_{m_j} \) of the guest charges are

\[ \mathbf{p}_{m_j} = m_e \dot{r}_{m_j} - \mathbf{F}_{m_j}. \]  

(4.51)

where the field \( \mathbf{F}_{m_j} \) stems from the magnetization density in Eq. \( (4.44) \) and is defined as

\[ \mathbf{F}_{m_j} = e \int_0^1 \mathrm{d}u \, u \mathbf{B} \left[ \mathbf{R}_m - u (r_{m_j} - \mathbf{R}_m) \right] \times (r_{m_j} - \mathbf{R}_m). \]  

(4.52)
The magnetic field $\mathbf{B}$ is used as an abbreviation for $\nabla \times \mathbf{A}$. Note that unlike $\mathbf{A}$ and $\mathbf{q}_{m,j}$, their canonically conjugate variables $\Pi$ and $\mathbf{p}_{m,j}$ are not fully electromagnetic or fully atomic in nature, respectively.

All canonical momenta have now been determined, so that the multipolar Hamiltonian $H'$ can be given in terms of the canonical variables $(\mathbf{r}_{m,j}, \mathbf{p}_{m,j})$ and $(\mathbf{A}, \Pi)$:

$$H_{\text{multi}} = \sum_{m,j} \mathbf{p}_{m,j} \cdot \dot{\mathbf{r}}_{m,j} + \int \mathrm{d} \mathbf{r} \mathbf{\Pi} \cdot \dot{\mathbf{A}} - L_{\text{multi}}$$

$$= \sum_{m,j} \frac{p_{m,j}^2}{2m_e} + \int \mathrm{d} \mathbf{r} \frac{\mathbf{P}_g^2}{2\varepsilon_0\varepsilon(r)} + \int \mathrm{d} \mathbf{r} \left[ \frac{\Pi^2}{2\varepsilon_0\varepsilon(r)} + \frac{\mathbf{B}^2}{2\mu_0} \right]$$

$$+ \sum_{m,j} \frac{E_{m,j}^2}{2m_e} + \int \mathrm{d} \mathbf{r} \left[ \frac{\mathbf{P}_g \cdot \mathbf{\Pi}}{\varepsilon_0\varepsilon(r)} - \mathbf{M}_g' \cdot \mathbf{B} \right].$$

Instead of the magnetization $\mathbf{M}_g$, a reduced magnetization $\mathbf{M}_g'$ has been used in the Hamiltonian (and the difference has been corrected for by a sign change of the term quadratic in the magnetic field). The reduced magnetization is defined as the magnetization [see equation (4.44)] with the $\dot{\mathbf{r}}_{m,j}$ replaced by $\mathbf{p}_{m,j}/m_e$ [13,84]. It may seem that the Coulomb term $V_C$ (4.40) was forgotten in the Hamiltonian, but that is not the case: the Coulomb term cancels against the other term quadratic in $\nabla \Phi$ that one gets when solving Eq. (4.50) for $\dot{\mathbf{A}}$ and substituting the result in the Hamiltonian (4.53).

The first term in the Hamiltonian (4.53) represents the kinetic energy of the guest charges; the second term is the potential energy of the guest atoms, expressed as a polarisation energy. Together they constitute the atomic part of the Hamiltonian. Next come the electric and magnetic field energies, respectively, which together are the radiative part of the Hamiltonian. The last three terms are interaction terms between guest atoms and the electromagnetic field. The term quadratic in the magnetic field represents the diamagnetic energy of only the guest atoms in the nonmagnetic dielectric. It can be safely ignored from now on since it is much smaller than the other two interactions (see [15], page 312). In most cases the dominant interaction term is the next one, the inner product of the polarization field with the field $\mathbf{\Pi}/[\varepsilon_0\varepsilon(r)]$. The last term is linear in the magnetic field and represents the paramagnetic energy of the guest atoms in the dielectric.

The polarization field $\mathbf{P}_g$ [Eq. (4.44)] is simply the sum of the polarization fields $\mathbf{P}_{gm}$ produced by the individual guest atoms (labeled by $m$). Therefore, it is natural to split the polarization energy in Eq. (4.53) into an intra-atomic and an interatomic polarization energy, respectively [14,84]:

$$\int \mathrm{d} \mathbf{r} \frac{\mathbf{P}_g^2}{2\varepsilon_0\varepsilon(r)} = \sum_m \int \mathrm{d} \mathbf{r} \frac{P_{gm}^2}{2\varepsilon_0\varepsilon(r)} + \sum_{m \neq n} \int \mathrm{d} \mathbf{r} \frac{P_{gn} \cdot P_{gm}}{\varepsilon_0\varepsilon(r)}. \quad (4.54)$$

The intra-atomic polarization energy is the potential energy that keeps an atom together; the interatomic polarization energy is the only interaction term between neutral atoms in the multipolar Hamiltonian. The polarization field $\mathbf{P}_{gm}(\mathbf{r})$ (4.44) corresponding to the individual guest atom $m$ is identically zero outside the smallest sphere surrounding all
charges that make up this (neutral) atom. In this classical picture, the interatomic polarization energy (also known as contact energy) is zero unless bounding spheres of distinct guest atoms overlap. Correspondingly, in quantum mechanics the atomic wave functions of distinct guest atoms have a nonvanishing overlap that falls off exponentially with interatomic distance. The overlap is therefore negligible unless the interatomic distance is of the order of the size of the atoms.

From now on the guest atoms are assumed more than a few nanometers apart so that the contact energy can be neglected. Just like in the free-space case [84], in the multipole Hamiltonian (4.53) for the inhomogeneous dielectric there is no instantaneous interaction term left between well-separated neutral guest atoms: the effect of the Coulomb term exactly cancelled against other terms. All other interatomic interactions are radiative interactions, mediated by the (retarded) electromagnetic fields $D/\varepsilon(\mathbf{r})$ and $B$. Of course, the multipolar representation should give the same physical predictions as the minimal-coupling formalism; in [84,85] this is proved for several observables in free space. The absence of direct interatomic interactions often makes calculations simpler in the multipolar representation.

### 4.4.3 In need of a local-field model

The quantum multipolar Hamiltonian will have an atomic and a radiative part, as well as two interaction terms:

$$H_{\text{multi}} = H_{\text{rad}} + \sum_{m} \left[ H_{\text{at}}^{(m)} + V_{P}^{(m)} + V_{M}^{(m)} \right]. \quad (4.55)$$

The aim of this section is to discuss the form of the atomic Hamiltonian $H_{\text{at}}^{(m)}$; in section 4.4.4 the Hamiltonian will be given in second-quantization notation.

The Hamiltonian for a guest atom inside the dielectric is

$$H_{\text{at}}^{(m)} = \frac{1}{2m_e} \sum_{j} P_{mj}^2 + \int d\mathbf{r} \frac{P_{gm}^2}{|2\varepsilon_0 \varepsilon(\mathbf{r})|}. \quad (4.56)$$

This Hamiltonian differs from free-space atomic Hamiltonian. This point is missed if one introduces a "two-level atom" with known transition frequency into the dielectric. The second term in (4.56) is the potential energy and it consists of longitudinal (Coulomb) and transverse interactions between the charges. The potential energy is reduced by a factor $\varepsilon(\mathbf{r})$ as compared to free space. This reduction factor is well known for dielectric-filled capacitors.

Until now it was tacitly assumed that $\varepsilon(\mathbf{r})$ is a given function that characterizes the dielectric in the absence of the guest atoms. Still, it could be that $\varepsilon(\mathbf{r})$ is different locally from the situation without the guest atoms. Suppose that one neglects local changes on the grounds that the dielectric function is a macroscopically averaged quantity that does not change on atomic length scales. Then $\varepsilon(\mathbf{r})$ must be unchanged by introducing a guest atom and the Hamiltonian can be approximated by

$$H_{\text{at}}^{(m)} \approx \frac{1}{2m_e} \sum_{j} P_{mj}^2 + \frac{1}{2\varepsilon_0 \varepsilon(R_m)} \int d\mathbf{r} P_{gm}^2. \quad (4.57)$$
If the guest atom were a hydrogen atom, then its Bohr radius and dipole moments would increase by a factor $\varepsilon(R_m)$ and its energy levels would be reduced by the same factor, according to this Hamiltonian. Any visible line in free space would then be shifted to the infrared in a dielectric. The dielectric would have a huge effect on the atom’s electronic properties.

Indeed, it has been known for a long time that wave functions of impurity atoms can be severely modified by the medium from their values in free space [89]. This has important consequences, for example when doping solid silicon with phosphorus to make an $n$-type semiconductor. The high dielectric constant of Si ($\varepsilon = 11.7$) reduces the potential energy between the outermost electron and the rest of the P atom, so that the electron can enter the conduction band relatively easily, leaving a $P^+$-ion [90]. Such changes in atomic wave functions and energies with a broad term will be called electronic effects of the dielectric on the atom.

Atomic lifetime changes and line shifts can have electronic and photonic explanations. Changes due to modified atomic dipole moments are electronic effects. A macroscopic description of the dielectric is too coarse-grained to say anything quantitative about electronic effects. It is the photonic effects, the changes due to altered properties of the electromagnetic field, which are of primary interest here. However, only if the electronic changes of the atoms are somehow either absent or accounted for, can one study the photonic effects. For example, in a recent study [91] of local-field effects [4, 11, 92–95] in spontaneous emission, it was important that atomic spectra (and therefore dipole moments) do not change while varying the refractive index. As a second example, the recently observed fivefold reduction of spontaneous-emission rates inside photonic crystals [35] is a photonic effect, since possible changes in dipole moments were divided out by choosing a reference sample with identical electronic effects [96]. Some earlier observations of long lifetimes in photonic crystals must be attributed to electronic effects, according to recent calculations [97].

In practice, line shifts are often much smaller than in the estimate in Eq. (4.57) where local modifications of the dielectric function are neglected. As a first example of local modifications, outer electronic states of the atom are more affected by the dielectric than the core electrons. In other words, outer electrons feel a different dielectric function than the inner electrons. The latter are screened by the former. As a second example, in some experiments the guest atoms are surrounded by a low-index molecular complex to separate electronic from photonic effects of the dielectric [91].

The absence of large electronic effects of the dielectric on the atomic properties can not be explained within the present macroscopic quantization theory. Only from microscopic theories of the dielectric can one derive that the dielectric can not be where the guest atoms are. In the present context of macroscopic quantization, a model is needed that does justice to the above two examples of local modifications of the dielectric by the guest atoms. A real-cavity model is assumed, with atomic-sized holes in the dielectric function at the atomic positions $R_m$. In this model, the atomic Hamiltonian (4.56) can be approximated by (4.57) with $\varepsilon(R_m)$ equal to 1. The model captures the observed absence of large electronic effects of the dielectric on atomic properties of interest, but at the same time the model has consequences for photonic properties: the local changes in $\varepsilon$ will
4.4 The quantum multipolar interaction Hamiltonian

give local changes in the mode functions $f_\lambda$, and therefore in the dipole coupling (4.62) and also in the spontaneous-emission rates of the guest atoms [11]. Some quantitative consequences of adopting the real-cavity model will be given in chapter 5.

This chapter first presented the dielectric without guest atoms. Later the guest atoms were introduced. In this section we see that actually there must be three steps: first calculate the mode functions of the inhomogeneous dielectric. Second, make atomic-sized holes at the positions where the guest atoms will be introduced. Determine the locally modified mode functions of the dielectric with the tiny cavities. The third and last step is the introduction of the guest atoms themselves, which couple to the electromagnetic field through the modes of step two.

### 4.4.4 Quantum multipolar interaction Hamiltonian

The goal is now to rewrite important terms of the Hamiltonian (4.53) into a second-quantization description, where macroscopic quantization has been applied to the electromagnetic field and microscopic quantization to the guest atoms.

First start with the atomic Hamiltonian (4.57) where $\varepsilon(R_m)$ is put to 1. Following (standard) quantum mechanics, the electron coordinates $r_{mj}(t)$ and their canonical momenta $p_{mj}(t)$ (4.51), as well as the polarization and magnetization fields $\mathbf{P}_g$ and $\mathbf{M}_g$, become time-independent operators that work on the time-dependent atomic wave functions. The single-atom wave functions can be expanded in terms of eigenfunctions (labelled $k$) of the atomic Hamiltonian:

$$\Psi_m(r_1, r_2, \ldots, r_{Z_m}; t) = \sum_k c_{mk}(t) \psi_{mk}(r_1, r_2, \ldots, r_{Z_m}). \quad (4.58)$$

The time-dependence is in the probability amplitudes $c_{mk}(t)$. The time-independent functions $\psi_{mk}$ are eigenfunctions of the atomic Hamiltonian (4.57) with $\varepsilon(R_m) = 1$.

Second-quantization notation can now be introduced by promoting the probability amplitudes $c_{mk}(t)$ and $c^*_{mk}(t)$ in (4.58) to become annihilation and creation operators with standard anti-commutation relations. These operators become the atomic canonical variables in the second-quantization picture. (One could even go back and start with a Lagrangian that identifies $\Psi_m$ and $\Psi^*_m$ as canonical conjugates [98].) The atomic operators can be written as sums over matrix elements. For example, the atomic Hamiltonian of atom $m$ in standard second-quantization notation is $H^{(m)}_{at} = \sum_k E^{(m)}_k c^*_k c_k$. Within the real-cavity model that was adopted, all atomic energy levels $E_{mk}$ in this equation are numerically the same as in free space. This completes the quantization and second quantization of the atomic Hamiltonian.

Three terms of the quantum multipolar interaction Hamiltonian (4.55) must still be given in second-quantization notation. The electromagnetic field can again be quantized by expanding the vector potential and its canonically conjugate field into a complete set of true modes. The subsequent quantization steps are as presented in section 4.2.2 in the absence of guest atoms. The radiative part of the Hamiltonian becomes $H_{rad} = \sum_\lambda \hbar \omega_\lambda (a^\dagger_\lambda a_\lambda + \frac{1}{2})$. The form of this Hamiltonian has not changed by the presence of the guest atoms, but there is a slight shift in its interpretation, since the polarization of the guest atoms is included in the conjugate field.
The interaction $V_P^{(m)}$ is associated with the polarization field of the guest atom $m$ and has the form

$$V_P^{(m)} = -i \int \frac{P_{gm}(r) \cdot D(r)}{\varepsilon_0 \varepsilon(r)} dr \quad (4.59)$$

$$= -i \sum \sum \sqrt{\frac{\hbar \omega}{2 \varepsilon_0 \omega}} \left\{ a_\lambda c^\dagger_{m k} c_{m k'} \int dr P_{gm, kk'}(r) \cdot f_\lambda(r) - H.c. \right\}.$$  

where "H.c." stands for the Hermitian conjugate. The quantity $P_{gm, kk'}(r)$ is the matrix element of the polarization field $P_{gm}(r)$ with respect to states $\psi_{mk}$ and $\psi_{mk'}$ of atom $m$. These atomic states are unaffected by the dielectric, at least in the empty-cavity model that was adopted in section 4.4.3 and which is also assumed here. Thus, the polarization field and its matrix elements are functions of the atomic variables alone, whereas the displacement field depends solely on the electromagnetic canonical variables. The two interacting fields are therefore canonically independent. The interpretation of the interaction is more subtle, since in the definition (4.46) of the displacement field the polarization of the guest atoms is included. The interaction $V_P^{(m)}$ therefore includes a self-interaction of the polarization field.

The second and last interaction term $V_M^{(m)}$ in (4.55) is associated with the reduced magnetization field of the $m$th guest atom:

$$V_M^{(m)} = - \int dr M'_{gm}(r) \cdot B(r) \quad (4.60)$$

$$= - \sum \sum \sqrt{\frac{\hbar}{2 \varepsilon_0 \omega}} \left\{ a_\lambda c^\dagger_{m k} c_{m k'} \int dr M'_{gm, kk'}(r) \cdot [\nabla \times f_\lambda(r)] + H.c. \right\}.$$  

Again, the empty-cavity model entails that matrix elements $M'_{gm, kk'}$ of the reduced magnetization field do not depend on the dielectric. The magnetic field and the reduced magnetization field are canonically independent and $M'_g$ is not included in the definition of $B$. All four terms in the quantum multipolar Hamiltonian (4.55) have now been given in second-quantization notation.

### 4.4.5 Dipole approximation

The guest atoms are much smaller than an optical wavelength. One cannot spatially probe the structure of the atom with light. If light can not tell the difference, one can make the well-known assumption that the polarization and magnetization fields associated with the atom are concentrated in its center of mass $R_m$ (the nucleus, say). Mathematically, this means that the integrands in Eq. (4.44) are approximated by their values in $u = 0$. These two values are the first terms of two infinite Taylor expansions in terms of the variable $u$. The dipole approximation is made by keeping only the first term. The next terms would describe the quadrupole interaction. In the dipole approximation, the magnetization
In the last equality, the atomic dipole matrix elements $\mu_{kk'}^{(m)}$ of the guest atom $m$. These matrix elements are independent of the dielectric environment in the real-cavity model. With equation (4.59), it follows that in the dipole approximation the interaction energy of an atom with the electromagnetic field in an inhomogeneous dielectric equals

$$V_{\text{dip}}^{(m)} = -\sum_{kk'} c_{mk}'^\dagger c_{mk} \cdot \frac{\mu_{kk'}^{(m)} \cdot D(R_m)}{\varepsilon_0}$$

$$= -\frac{i}{2} \sum_\lambda \sum_{kk'} \sqrt{\frac{\hbar \omega_\lambda}{2\varepsilon_0}} \left[ a_\lambda c_{mk}'^\dagger c_{mk} \cdot \mu_{kk'}^{(m)} \cdot f_\lambda(R_m) - \text{H.c.} \right].$$ (4.62)

In the first identity it was used that $\varepsilon(R_m)$ equals unity in the real-cavity model (adopted in section 4.4.3). This gives the important result that inside an inhomogeneous dielectric, a dipole couples to the field $-D/\varepsilon_0$, but necessarily at a position where the dielectric function equals one. This is a generalisation of the free-space dipole-coupling [84,98,99] and a necessary qualification of the dipole coupling found in [13,14].

The dipole approximation is excellent for real atoms. For the guest atoms one can also think of other (larger) quantum systems in interaction with the electromagnetic field. "Artificial atoms", also known as quantum dots, are an example. Quantum dots are semiconductor nanostructures tens of nanometers in size or less in all three dimensions. Quantum dots are much larger than real atoms and so their dipole moments can be much larger as well (see for example [100] and references therein). Because of their larger size, quadrupole moments are more important for quantum dots than for real atoms, especially when excited in their near field by a scanning near field optical microscope [101].

### 4.5 Inhomogeneous magnetic media

In the past few years, old and nearly forgotten ideas about so-called left-handed materials [102] have become the subject of intense scientific discussions after a prediction that a perfect lens could be made with them [103]. Left-handed materials do not exist in nature and have the exotic property that both their relative dielectric functions $\varepsilon(\mathbf{r})$ and their relative magnetic permeabilities $\mu(\mathbf{r})$ are negative. Their index of refraction is also negative and this leads to many peculiar properties. They will also influence spontaneous-emission rates of nearby guest atoms in different ways than their right-handed counterparts, according to a recent paper [104]. Without diving into this subject here, left-handed materials make it interesting to generalize the formalism of this chapter to dielectrics with inhomogeneous magnetic properties as well. Such generalizations were already considered in [13,14] and are relatively straightforward, for reasons discussed below.
When $\mu$ becomes position-dependent, then the only term that will change in the classical multipolar Hamiltonian (4.53) is the magnetic field energy $\int dr \frac{B^2(r)}{2\mu_0 \mu(r)}$. (Confusion should not arise about the symbol $\mu$ that is used as the magnetic permeability and as the magnitude of a dipole $\mu$.) The quantum mechanical description can again be carried out by choosing the generalized Coulomb gauge. Without guest atoms, the vector potential satisfies the source-free wave equation

$$\nabla \times \left[ \frac{1}{\mu(r)} \nabla \times A(r) \right] + \frac{\varepsilon(r)}{c^2} \dot{A}(r) = 0. \quad (4.63)$$

The electromagnetic field in can be expanded in terms of new modes different from the modes $f_\lambda$. The new normal modes $m_\lambda$ are the harmonic solutions of the wave equation (4.63). These new modes are also generalized transverse, just like the modes $f_\lambda$ of the nonmagnetic medium. This is what makes the generalization of the formalism to magnetic media relatively simple. In second quantization notation, the electromagnetic field energy becomes $\sum_\lambda \hbar \omega_\lambda \left( d_\lambda^\dagger d_\lambda + \frac{1}{2} \right)$, where $d_\lambda^\dagger$ is the creation operator of a photon in the mode $m_\lambda(r)$. The new modes can have mode profiles that differ much from any of the modes $f_\lambda(r)$, but otherwise the theory of the medium is not much different. In the electric and magnetic interactions (4.59) and (4.60) of the electromagnetic field with guest atoms, the modes $f_\lambda$ can just be replaced by the $m_\lambda$ and the operators $c_\lambda^{\dagger}$ by $d_\lambda^{\dagger}$ in order to take both the electric and magnetic properties of the medium into account. As for nonmagnetic media, in the dipole approximation the magnetic interaction (4.60) is zero; the electric dipole interaction (4.59) dominates, except for optical transitions with zero dipole moments. When dipole moments are nonzero, the main effect of the dielectric becoming magnetic comes from the change in the mode functions. When in the future left-handed materials will be made with negligible dispersion and absorption in the frequency interval where $\varepsilon$ and $\mu$ are negative, then the present formalism will also be applicable to those exotic materials.

### 4.6 Dipole-coupling controversy

Many papers appeared in the nineteen-eighties about the equivalence of the minimal-coupling and the multipolar Hamiltonian in free space, for example [98, 99, 105–114]. The Hamiltonians sometimes lead to different results in calculations. Some authors argued that the minimal-coupling Hamiltonian was to be preferred [106], while others proposed to refrain from using gauge-dependent equations to stop the confusion [109]. In the multipolar picture, a controversy arose whether a dipole in free space couples to minus the displacement field ($-\mathbf{\mu} \cdot \mathbf{D}/\varepsilon_0$, see [99]) or to the transverse part of the electric field ($-\mathbf{\mu} \cdot \mathbf{E}^T$, see [115]). The book by Cohen-Tannoudji et al. helped a lot to settle the dust [84]. It is probably useful to briefly mention a few reasons why confusion is so likely to arise in a situation which is principle is not difficult.

In the first place, it is important to distinguish canonical variable transformations (new variables, same Hamiltonian and states) from unitary changes of picture (new Hamiltonian, new states, same expectation values). This distinction was excellently presented in [99].
Unlike canonical transformations, picture changes have no classical analogues. Confusion is likely to arise when after a canonical change a Hamiltonian has exactly the same form as after a picture change [99]. This is one reason why a controversy about the dipole coupling term could arise.

A second source of confusion is related to approximations. It was found in section 4.4.5 that a dipole at position \( \mathbf{R} \) inside a dielectric couples to the displacement field

\[
-D(\mathbf{R})/\varepsilon_0 = - [\mathbf{E}(\mathbf{R}) + \mathbf{P}_g(\mathbf{R})]/\varepsilon_0.
\]  

(4.64)

where \( \mathbf{P}_g \) is the polarization field of the guest atom itself; the equality in (4.64) holds because the empty-cavity model was assumed so that \( \varepsilon(\mathbf{R}) \) equals one. In free space, a dipole couples to the same field (4.64). Why then are there still authors that state that in free space [115] or in a dielectric [11] a dipole couples to minus the electric field? For the dielectric with guest atoms, the displacement field operator can be expanded as

\[
\mathbf{D}(\mathbf{r}) = i\varepsilon_0\varepsilon(\mathbf{r}) \sum_{\lambda} \sqrt{\hbar\omega_\lambda/2\varepsilon_0} \left[ a_\lambda f_\lambda(\mathbf{r}) - a_\lambda^\dagger f_\lambda^*(\mathbf{r}) \right].
\]  

(4.65)

The form of this operator is the same as in a dielectric without guest atoms [minus the equation (4.25b)], except that the equations of motion of the creation- and annihilation operators in (4.65) have terms involving the atomic variables, which the equations of motion of their counterparts \( a^{(0)}_\lambda \) and \( a^{(0)\dagger}_\lambda \) do not have. If one approximates the displacement field (4.65) and its time-derivatives by assuming free-space time-dependence, then for positions where \( \varepsilon \) equals one, the displacement field (4.65) is equal to the electric field in the absence of the guest atoms. In other words, if the guest atoms are taken into account in Maxwell’s equations, then one finds a dipole coupling to the displacement field, whereas a coupling to the electric field is found when guest atoms are left out of Maxwell’s equations. It depends on the observable under study whether the difference between the two dipole couplings can be neglected or not. An example where only one dipole coupling is correct will be given in the next chapter in section 5.2.3.

### 4.7 Summary and discussion

The aim of the chapter was to find a Hamiltonian of guest atoms in an inhomogeneous dielectric, with a multipolar interaction between the atoms and the field. The multipolar Hamiltonian is simpler than the minimal-coupling Hamiltonian, because in the former all interactions between the atoms are mediated by the retarded electromagnetic field. The main results of this chapter are therefore the quantum multipolar interaction Hamiltonian (4.55) together with its dipole approximation (4.62). With this Hamiltonian, one can study how a dielectric environment can change quantum optical processes of resonant atoms.

Another important result is that the macroscopic description of the dielectric could only be tied up to the microscopic description of the atoms by assuming that the dielectric function has the value 1 at the atomic positions. If not, the atoms in the dielectric would have huge frequency shifts. The local modification of the dielectric function will also change the dipole coupling, because mode functions change locally (see also chapter 5). If
one would start with the same two- or three-level description of the guest atoms as in free
space, one implicitly already assumes such a model for the dielectric function. Consistency
requires to also choose a local-field model when calculating the mode functions in the
dipole interaction (4.62).

In order to obtain the central results of this chapter, it was necessary to first quan-
tize the electromagnetic field in the dielectric without guest atoms. This has certainly
been carried out before, but after explaining why real optical mode functions can be used
whenever $\varepsilon(r)$ is real, the quantization becomes simpler than found in [11, 13, 86]. In par-
ticular, only when real mode functions are chosen are the associated generalized positions
and momenta Hermitian. The field that must be so quantized is the field of the dielectric
with empty cavities at the positions where the guest atoms are to be placed.

The guest atoms were introduced into the theory such that Maxwell’s equations hold
with the atomic charge and current densities as source terms. A minimal-coupling La-
grangian that gives rise to these equations was easily written down. However, after choos-
ing a generalized Coulomb gauge, it was not directly clear how to obtain all Maxwell’s
equations in this particular gauge. In the important appendix B, the mathematical ques-
tion was studied what it means to take a functional derivative after choosing a gauge. It
was shown that the derivative of the minimal-coupling Lagrangian could be found by sol-
voking a certain electrostatic potential problem. As a consequence, the gauge-independent
Maxwell’s equations were found indeed to hold in the generalized Coulomb gauge as well.

The application of the Power-Zienau-Woolley transformation to the minimal-coupling
Lagrangian was shown to produce the multipolar Lagrangian, after the generalized Cou-
lomb gauge had been chosen. Actually, the gauge was chosen earlier than strictly neces-
sary: the choice could have been postponed until the canonical momenta were determined
from the multipolar Lagrangian. The story would have been simpler up to that point.
The difficulty to find all Maxwell’s equations would then show up only after obtaining
the multipolar Lagrangian. The reason to first choose the gauge and then do the PZW
transformation, is that it more clearly shows that the difficulty to find all Maxwell’s equa-
tions was a consequence of choosing the gauge, rather than a consequence of the PZW
transformation.

More generally, the presentation given in this chapter is one among the many possibil-
ities. When going from a classical minimal-coupling Lagrangian to a quantum mechanical
multipolar Hamiltonian, one has to make four steps: one step is to choose a gauge, another
step is to transform the theory to the multipolar formalism. Yet another step is made when
going from a Lagrangian to a Hamiltonian; quantization and second quantization together
are step number four. These are now given in the order in which they occurred in this chap-
ter, but the steps can be interchanged. Not all of the 24 permutations are convenient. All
routes should lead to equivalent final results. In particular, it was shown in detail in [111]
that step two and three can be interchanged for free space: the PZW transformation of the
minimal-coupling Lagrangian is equivalent to a picture change of the minimal-coupling
Hamiltonian. The equivalence will also hold for inhomogeneous dielectrics.