

Gauge invariant formulation of molecular electrodynamics and the multipolar Hamiltonian

Vladimir Chernyak, Shaul Mukamel

Department of Chemistry, University of Rochester, Rochester, NY 14627, USA

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Abstract

The multipolar Hamiltonian has many advantages for describing the electrodynamics of nonrelativistic material systems. Usually it is derived by performing a canonical transformation on the minimal coupling Hamiltonian. We show that both the minimal coupling and the multipolar Hamiltonians are two forms of the same Hamiltonian corresponding to two choices of gauge: $\text{div } A = 0$ and $\mathbf{r} \cdot A(\mathbf{r}) = 0$ respectively. We further discuss the use of the multipolar Hamiltonian in electronically extended systems.

1. Introduction

A large class of problems in linear and nonlinear optics is connected with the interaction of radiation (i.e., the transverse electromagnetic field) with nonrelativistic material systems. Two forms of the Hamiltonian are most often used in theoretical investigations of these problems: the minimal coupling and the multipolar Hamiltonian [1]. Systems interacting with the radiation field possess a specific kind of symmetry-gauge invariance, which leads to the appearance of constraints when constructing the Hamiltonian [2]. There are different ways to proceed in such a case. One possibility is to fix the gauge with the condition

$$\text{div } A(\mathbf{r}) = 0, \quad (1.1)$$

in the action of the system. We will use the notation $A_0(\mathbf{r})$ and $A(\mathbf{r})$ for the scalar and the vector potentials of the electromagnetic field. After that, the system has no constraints on the Hamiltonian level

and can be quantized canonically [3–5]. This procedure leads to the minimal coupling Hamiltonian. The multipolar Hamiltonian is usually obtained from the minimal coupling Hamiltonian by applying a canonical transformation which mixes the material and the field variables [1,6–9].

An alternative way to obtain the multipolar Hamiltonian involves the Lagrangian formalism in classical mechanics. Power and Thirunamachandran [10] considered a transformation of variables in the classical Lagrangian, whereas Babiker and Loudon [11] used a procedure of gauge fixing and gauge transformation in the Lagrangian formalism. In both approaches transformations affect the classical Lagrangians, and different forms of the classical Lagrangian lead to different forms of classical Hamiltonians written in terms of canonical variables, which in turn lead to different forms of the quantum Hamiltonian after canonical quantization. The quantum Hamiltonians are then connected by a quantum canonical transformation.

In this paper we propose an approach which connects the quantum canonical transformations with gauge transformation. Quantizing the system before the gauge fixing we obtain a procedure of gauge fixing on the level of the quantum Hamilton formalism; gauge transformations then become canonical transformations.

The proposed approach is based on the gauge invariant scheme of quantization introduced by Dirac [12]. This scheme involves an extended space of states with the Hamiltonian defined uniquely on the subspace of physical states denoted the physical subspace. This subspace is determined by the condition that the result of acting with all constraints (which become operators after quantization) on a physical state gives zero. Due to the constraints, a physical state being a wave function depending on the vector potential is determined completely by its values on an infinite-dimensional surface in the space of all possible vector potentials. A choice of such a surface is equivalent to the choice of a gauge. Therefore, different choices of gauge lead to different realizations of the physical subspace, and different forms of the Hamiltonian. We shall show that the minimal coupling and the multipolar Hamiltonians correspond to two specific choices of gauge. Both gauges are “transverse”, the first in the momentum domain, the second in the coordinate space.

In Section 2 we present a formulation of quantum electrodynamics with nonrelativistic matter in an arbitrary gauge. Details of the derivation starting with the gauge invariant quantization are given in Appendices A, B, and C. In Section 3 we consider “linear” gauges and show that the minimal coupling and the multipolar Hamiltonians correspond to the gauges $\text{div } A(\mathbf{r}) = 0$ and $\mathbf{r} \cdot A(\mathbf{r}) = 0$ respectively. Several applications of the multipolar Hamiltonian are discussed in Section 4.

2. Quantum electrodynamics of nonrelativistic matter in an arbitrary gauge

In this section we formulate the quantum electrodynamics of nonrelativistic material systems in an arbitrary gauge. In Appendix A we introduce the gauge invariant quantization scheme based on disregarding the constraints on the first step of quantiza-

tion to obtain a broader space of states \mathcal{H} . The physical subspace of states $\mathcal{H}_{\text{ph}} \subset \mathcal{H}$ is obtained by imposing the quantum versions of the constraints. The quantum Hamiltonian \hat{H} is uniquely defined on \mathcal{H}_{ph} . In Appendix B we describe the procedure of gauge fixing and define the gauge transformations on the language of quantum Hamiltonian formalism. For each gauge, denoted by \mathcal{M} we obtain a specific realization $\mathcal{H}_{\mathcal{M}}$ of the physical space of states \mathcal{H}_{ph} . The isomorphism $\rho_{\mathcal{M}}^*: \mathcal{H}_{\text{ph}} \rightarrow \mathcal{H}_{\mathcal{M}}$ leads to a Hamiltonian $\hat{H}_{\mathcal{M}}$ acting on $\mathcal{H}_{\mathcal{M}}$ which corresponds to \hat{H} and is called the Hamiltonian in the gauge \mathcal{M} . In Appendix C we introduce the canonical variables for an arbitrary gauge \mathcal{M} and express the Hamiltonians $\hat{H}_{\mathcal{M}}$ in terms of them.

The gauge is usually fixed by a set of equations which specify constraints on the vector potential $A(\mathbf{r})$:

$$F_{\mathcal{M}}(A) = 0. \quad (2.1)$$

The solutions of Eq. (2.1), i.e., the vector potentials $A(\mathbf{r})$ satisfying the gauge condition can be presented in a form

$$A(\mathbf{r}) \equiv A^{\perp}(\mathbf{r}) + \frac{\partial}{\partial \mathbf{r}} \varphi_{\mathcal{M}}(\mathbf{r}, [A^{\perp}]), \quad (2.2)$$

where $A^{\perp}(\mathbf{r})$ is the transverse part of the vector potential, and the functional $\varphi_{\mathcal{M}}$ is determined from $F_{\mathcal{M}}$. The canonical field variables are the operators of the transverse vector potential $\hat{A}^{\perp}(\mathbf{r})$ and transverse electric displacement $\hat{D}^{\perp}(\mathbf{r})$ which satisfy the commutation relations

$$[\hat{D}^{\perp}(\mathbf{r}), \hat{A}^{\perp}(\mathbf{r}')] = -4\pi i \delta^{\perp}(\mathbf{r} - \mathbf{r}'), \quad (2.3)$$

and commute with all material operators. Here δ^{\perp} is the transverse δ -function. The complete vector potential operator $\hat{A}(\mathbf{r})$ can be expressed in terms of its transverse part $\hat{A}^{\perp}(\mathbf{r})$ by applying Eq. (2.2) in an operator form, which yields:

$$\hat{A}(\mathbf{r}) \equiv \hat{A}^{\perp}(\mathbf{r}) + \frac{\partial}{\partial \mathbf{r}} \varphi_{\mathcal{M}}(\mathbf{r}, [\hat{A}^{\perp}]). \quad (2.4)$$

The canonical material variables are the operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^{\dagger}(\mathbf{r})$ (we adopt the second quantized form for the electrons) with the commutation relations

$$[\hat{\psi}^{\dagger}(\mathbf{r}), \hat{\psi}(\mathbf{r}')]_{+} = -\delta(\mathbf{r} - \mathbf{r}'), \quad (2.5)$$

$[\ , \]_{\pm}$ denotes the anticommutator, and we set $\hbar = 1$.

The operators of the charge density $\hat{\rho}(\mathbf{r})$ and the current $\hat{j}(\mathbf{r})$ are given by

$$\hat{\rho}(\mathbf{r}) = -e\hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r}), \quad (2.6a)$$

$$\hat{j}(\mathbf{r}) = -ie\left[\hat{\psi}^+(\mathbf{r})\partial\hat{\psi}(\mathbf{r}) - \partial\hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r})\right]. \quad (2.6b)$$

The transverse electric field operator $\hat{E}^-(\mathbf{r})$ is connected to the electric displacement operator $\hat{D}^-(\mathbf{r})$ by the relation

$$\hat{D}^-(\mathbf{r}) = \hat{E}^-(\mathbf{r}) + 4\pi\hat{P}_{\mathcal{A}}^-(\mathbf{r}), \quad (2.7a)$$

with

$$\hat{P}_{\mathcal{A}}^-(\mathbf{r}) \equiv -\int d\mathbf{r}' \hat{\rho}(\mathbf{r}') \frac{\delta\varphi_{\mathcal{A}}(\mathbf{r}', [\hat{A}^+])}{\delta\hat{A}^-(\mathbf{r})}. \quad (2.7b)$$

We will refer to $\hat{P}_{\mathcal{A}}^-(\mathbf{r})$ as the microscopic gauge-dependent polarization, where \mathcal{A} specifies the gauge.

The Hamiltonian $\hat{H}_{\mathcal{A}}$ in the gauge defined by \mathcal{A} (or equivalently by $\varphi_{\mathcal{A}}$) has the form (for derivation, see Appendix C)

$$\hat{H}_{\mathcal{A}} = \hat{H}_e + \hat{H}_{\text{rad}} + \hat{H}_{\text{int}}. \quad (2.8a)$$

In Eq. (2.8a) \hat{H}_e is the Hamiltonian of electrons with Coulomb interaction

$$\hat{H}_e = \int d\mathbf{r} \left(\frac{1}{2m} \frac{\partial\hat{\psi}^+}{\partial\mathbf{r}} \frac{\partial\hat{\psi}}{\partial\mathbf{r}} + U(\mathbf{r})\hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r}) \right) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}'), \quad (2.8b)$$

where $U(\mathbf{r})$ is the potential induced by nuclei. \hat{H}_{rad} is the free field Hamiltonian

$$\hat{H}_{\text{rad}} = \frac{1}{8\pi} \int d\mathbf{r} \left\{ \left[\hat{D}^-(\mathbf{r}) \right]^2 + \left[\text{rot } \hat{A}^-(\mathbf{r}) \right]^2 \right\}, \quad (2.8c)$$

and \hat{H}_{int} describing the electron interaction with the transverse electromagnetic field is

$$\hat{H}_{\text{int}} = \hat{H}_{\text{int}}^{(0)} + \hat{H}_{\text{int}}^{(\text{magn})}, \quad (2.8d)$$

with

$$\hat{H}_{\text{int}}^{(0)} \equiv -\frac{1}{2} \int d\mathbf{r} \left[\hat{D}^-(\mathbf{r})\hat{P}_{\mathcal{A}}^-(\mathbf{r}) + \hat{P}_{\mathcal{A}}^-(\mathbf{r})\hat{D}^-(\mathbf{r}) \right] + 2\pi \int d\mathbf{r} \left[\hat{P}_{\mathcal{A}}^-(\mathbf{r}) \right]^2, \quad (2.8e)$$

and

$$\hat{H}_{\text{int}}^{(\text{magn})} \equiv \int d\mathbf{r} \left(\hat{j}(\mathbf{r}) \cdot \hat{A}(\mathbf{r}) - \frac{e}{2m} \hat{\rho}(\mathbf{r}) \hat{A}^2(\mathbf{r}) \right). \quad (2.8f)$$

We denote $H_{\text{int}}^{(\text{magn})}$ the ‘‘magnetic interaction’’ since it can be expressed in terms of the magnetic field $\hat{B}(\mathbf{r})$ using Eq. (C.18) to find $\hat{A}^-(\mathbf{r})$, and Eq. (2.4). This terminology which applies to an arbitrary gauge is somewhat unusual. Using the gauge $\mathbf{r} \cdot \mathbf{A}(\mathbf{r}) = 0$ related to the multipolar Hamiltonian (see Section 3) it coincides with the conventional definitions. However, in the gauge $\text{div } \mathbf{A}(\mathbf{r}) = 0$ related to the minimal coupling Hamiltonian the entire interaction is ‘‘magnetic’’.

3. Linear gauge and the minimum coupling and multipolar Hamiltonians

In this section we consider the case of ‘‘linear’’ gauges and show that the gauges $\text{div } \mathbf{A}(\mathbf{r}) = 0$ and $\mathbf{r} \cdot \mathbf{A}(\mathbf{r}) = 0$ lead to the minimal coupling and the multipolar Hamiltonians respectively. We will call a gauge linear if the gauge fixing conditions Eq. (2.1) are linear in $\mathbf{A}(\mathbf{r})$. If $F_{\mathcal{A}}$ is linear in $\mathbf{A}(\mathbf{r})$ then $\varphi_{\mathcal{A}}$ is linear in $\mathbf{A}^-(\mathbf{r})$ and can be presented in a form

$$\varphi_{\mathcal{A}}(\mathbf{r}, [\mathbf{A}^-]) = \int \varphi_{\mathcal{A}}(\mathbf{r}', \mathbf{r}) \cdot \mathbf{A}^-(\mathbf{r}') d\mathbf{r}'. \quad (3.1)$$

For ‘‘linear’’ gauges when Eq. (3.1) is satisfied the microscopic polarization adopts a form

$$\hat{P}_{\mathcal{A}}^-(\mathbf{r}) = -\int d\mathbf{r}' d\mathbf{r}'' \delta^-(\mathbf{r}-\mathbf{r}') \varphi_{\mathcal{A}}(\mathbf{r}', \mathbf{r}'') \hat{\rho}(\mathbf{r}''). \quad (3.2)$$

We now turn to specific gauges. First, we take for Eq. (2.1) the condition $\text{div } \mathbf{A} = 0$. We then have

$$\varphi_{\mathcal{A}} \equiv 0, \quad (3.3a)$$

which by using Eq. (3.2) leads to

$$\hat{P}_{\mathcal{A}}^-(\mathbf{r}) \equiv 0, \quad \hat{D}^-(\mathbf{r}) = \hat{E}^-(\mathbf{r}) \quad (3.3b)$$

and from Eq. (2.4) yields

$$\hat{A}(\mathbf{r}) = \hat{A}^-(\mathbf{r}). \quad (3.3c)$$

We then have

$$\hat{H}_{\text{int}}^{(0)} = 0, \quad (3.3d)$$

and we obtain the Hamiltonian

$$\hat{H}_{\#} = \hat{H}_e + \hat{H}_{\text{rad}} + \hat{H}_{\text{int}}^{(\text{magn})}, \quad (3.4)$$

with $\hat{A}^\perp(\mathbf{r})$ substituted into $\hat{H}_{\text{int}}^{(\text{magn})}$ instead of $\hat{A}(\mathbf{r})$. This is the minimal coupling Hamiltonian.

To obtain the multipolar Hamiltonian we fix the gauge (Eq. (2.1)) with the condition

$$\mathbf{r} \cdot \mathbf{A}(\mathbf{r}) = 0, \quad (3.5)$$

which means that the vector potential is transverse in coordinate space. Since Eq. (3.5) is linear in $\mathbf{A}(\mathbf{r})$, $\hat{P}_{\#}^\perp(\mathbf{r})$ becomes a purely material operator (see Eq. (3.2)) and $\hat{H}_{\text{int}}^{(0)}$ can be recast in a form

$$\begin{aligned} \hat{H}_{\text{int}}^{(0)} = & - \int d\mathbf{r} \hat{P}_{\#}^\perp(\mathbf{r}) \hat{D}^\perp(\mathbf{r}) \\ & + 2\pi \int d\mathbf{r} [\hat{P}_{\#}^\perp(\mathbf{r})]^2. \end{aligned} \quad (3.6)$$

We can also express $\hat{A}(\mathbf{r})$ in terms of the magnetic field $\hat{B}(\mathbf{r})$ by making use of the gauge fixing condition of Eq. (3.5). Taking into account Eq. (3.5), Eq. (C.18) can be written as

$$\frac{\mathbf{r}}{|\mathbf{r}|} \frac{\partial \hat{A}(\mathbf{r})}{\partial \mathbf{r}} + \frac{\hat{A}(\mathbf{r})}{|\mathbf{r}|} = - \frac{1}{|\mathbf{r}|} \mathbf{r} \times \hat{B}(\mathbf{r}), \quad (3.7)$$

whose solution is

$$\hat{A}(\mathbf{r}) = - \frac{1}{|\mathbf{r}|} \int_{C_r} d\mathbf{r}' \cdot \mathbf{r}' \frac{1}{|\mathbf{r}'|} [\mathbf{r}' \times \hat{B}(\mathbf{r}')], \quad (3.8a)$$

where C_r is a segment of a straight line $[0, \mathbf{r}]$, or alternatively

$$\hat{A}(\mathbf{r}) = - \int_0^1 d\lambda \lambda \int d\mathbf{r}' \delta(\mathbf{r}' - \lambda \mathbf{r}) [\mathbf{r}' \times \hat{B}(\mathbf{r}')]. \quad (3.8b)$$

Substituting Eq. (3.8b) into Eq. (2.8) and taking $\hat{H}_{\text{int}}^{(0)}$ in the form of Eq. (3.6), the Hamiltonian $\hat{H}_{\#}$ assumes the multipolar second quantized form, with $\hat{H}_{\text{int}}^{(\text{magn})}$ representing the magnetic terms. The only remaining point is to show that the expression for the polarization Eq. (3.2) is the same as the one used in the multipolar Hamiltonian. To that end we need to

find $\varphi_{\#}(\mathbf{r}, \mathbf{r}')$. It follows from Eqs. (2.4) and (3.5) that $\varphi_{\#}$ satisfies the following relation

$$\left(\hat{A}^\perp(\mathbf{r}) + \frac{\partial}{\partial \mathbf{r}} \varphi_{\#}(\mathbf{r}, [\hat{A}^\perp]) \right) \cdot \mathbf{r} = 0. \quad (3.9)$$

Solving Eq. (3.9) we get

$$\varphi_{\#}(\mathbf{r}, [A^\perp]) = - \int_{C_r} d\mathbf{r}' \cdot \mathbf{A}^\perp(\mathbf{r}'). \quad (3.10a)$$

Combining Eqs. (3.10a) and (3.1) results in

$$\varphi_{\#}(\mathbf{r}', \mathbf{r}'') = - \int_0^1 d\lambda \mathbf{r}'' \delta(\mathbf{r}' - \lambda \mathbf{r}''). \quad (3.10b)$$

Substituting $\varphi_{\#}(\mathbf{r}', \mathbf{r}'')$ from Eq. (3.10b) into Eq. (3.2) we obtain the expression for the polarization as used in the multipolar Hamiltonian [1,8].

4. Discussion

The multipolar Hamiltonian has been successfully used to describe the interaction of molecules with the transverse electromagnetic field [1]. Calculations using this form of the Hamiltonian become particularly simple when it is possible to neglect the magnetic terms ($\hat{H}_{\text{int}}^{(\text{magn})}$) in the interaction, which leads to an interaction which is linear in the transverse field.

The magnetic terms are smaller in nonrelativistic systems by a factor of v/c , where c is the speed of light and v is a typical electron speed. In the expansion in multipoles the expansion parameter is L/λ where L is the size of a system, and λ is the optical wavelength. For a hydrogen atom these parameters coincide, and are equal the fine structure constant $e^2/\hbar c$. Therefore, when neglecting the magnetic terms we can also invoke the dipole approximation. However, in large molecules the parameter L/λ can be much larger than v/c so that we can neglect the magnetic terms, yet need to keep higher terms in the multipolar series. This justifies using the multipolar Hamiltonian while neglecting the magnetic terms.

In the remainder of the section we will comment on applying the multipolar Hamiltonian without the magnetic terms. The ‘‘self-interaction’’ (the last term in the rhs of Eq. (3.6)) which looks complicated in the Hamiltonian is very important, and leads to a compact form of the interaction terms when solving

dynamical problems. It has been shown in [13] that the equation of motion for the Heisenberg operator $\tilde{Q}(t)$ related to an arbitrary material operator \hat{Q} assumes the form

$$\frac{d\tilde{Q}}{dt} = i[\hat{H}_c, \tilde{Q}] + \frac{i}{2} \int d\mathbf{r} \left\{ [\tilde{P}^\perp(\mathbf{r}), \tilde{Q}] \cdot \tilde{E}^\perp(\mathbf{r}) + \tilde{E}^\perp(\mathbf{r}) \cdot [\tilde{P}^\perp(\mathbf{r}), \tilde{Q}] \right\}. \quad (4.1a)$$

Note that $\tilde{E}^\perp(\mathbf{r})$ is a mixed (field and material) operator which does not commute with $[\tilde{P}^\perp(\mathbf{r}), \tilde{Q}]$. Making use of Eq. (3.10) we can recast Eq. (4.1a) in a form

$$\frac{d\tilde{Q}}{dt} = i[\hat{H}_c, \tilde{Q}] - \frac{i}{2} \int d\mathbf{r} \left\{ [\tilde{\rho}(\mathbf{r}), \tilde{Q}] \tilde{\varphi}_{\text{eff}}(\mathbf{r}) + \tilde{\varphi}_{\text{eff}}(\mathbf{r}) [\tilde{\rho}(\mathbf{r}), \tilde{Q}] \right\}, \quad (4.1b)$$

with

$$\tilde{\varphi}_{\text{eff}}(\mathbf{r}) \equiv - \int_{c_r} d\mathbf{r}' \cdot \tilde{E}^\perp(\mathbf{r}'). \quad (4.1c)$$

Eq. (4.1b) shows that when the magnetic terms are neglected, the second term has a form of the interaction of the charge density $\tilde{\rho}(\mathbf{r})$ with the effective potential $\tilde{\varphi}_{\text{eff}}(\mathbf{r})$ induced by the transverse field according to Eq. (4.1c).

The interaction terms also assume a compact form if we adopt the path-integral approach [12], using the action S which has a form related to the partition given by Eq. (2.8a):

$$S = S_c + S_{\text{rad}} + S_{\text{int}}, \quad (4.2a)$$

where the interaction term is [14]

$$S_{\text{int}} = \int d\mathbf{r} d\tau P^\perp(\mathbf{r}, \tau) E^\perp(\mathbf{r}, \tau), \quad (4.2b)$$

and

$$E^\perp(\mathbf{r}, \tau) \equiv \frac{\partial A^\perp(\mathbf{r}, \tau)}{\partial \tau}. \quad (4.2c)$$

The interaction term can be represented also as the interaction of the charge density with the effective potential:

$$S_{\text{int}} = - \int d\mathbf{r} d\tau \rho(\mathbf{r}, \tau) \varphi_{\text{eff}}(\mathbf{r}, \tau). \quad (4.2d)$$

Finally we show how to apply the multipolar Hamiltonian for systems with size larger than the wavelength and with extended electron states such as semiconductors. In such systems, it is not possible to apply the dipole approximation to the entire system; however, it is possible to introduce a dipole moment per unit cell [15].

We consider a one-dimensional tight binding model for the system in the z -direction [16]. The charge density is given by

$$\hat{\rho}(\mathbf{r}) = -e \sum_n \delta(\mathbf{r} - \mathbf{R}_n) \hat{c}_n^+ c_n, \quad (4.3)$$

where \hat{c}_n^+ (c_n) is the creation (annihilation) operator of an electron on the site n . We assume that \mathbf{R}_n form a one-dimensional regular lattice along the z -axis, with two sites per unit cell. Treating the transverse field classically for the sake of simplicity we obtain the interaction term in the Hamiltonian

$$\hat{H}_{\text{int}} = \int dz \hat{\rho}(z) \varphi_{\text{eff}}(z), \quad (4.4a)$$

with

$$\varphi_{\text{eff}}(z) = - \int_{z_0}^z dz' E_z(z'). \quad (4.4b)$$

It follows from Eq. (4.4b), that

$$E_z = - \frac{\partial \varphi_{\text{eff}}}{\partial z}. \quad (4.4c)$$

For a long chain, we can switch to a basis set of the Bloch functions determined by momentum k and a two-dimensional vector $w_i(k)$ ($i = c, v$ denotes the conduction and the valance bands), which describes the Bloch function in a unit cell. Switching to the momentum domain we obtain

$$\begin{aligned} \hat{H}_{\text{int}} = & -e \int dq \varphi_{\text{eff}}(-q) \\ & \times \int dk (w_i(k+q), w_j(k)) \hat{c}_i(k+q) \hat{c}_j(k), \end{aligned} \quad (4.5)$$

where (w_i, w_j) is the scalar product of the Bloch functions in a unit cell and $\hat{c}_i^+(k)$, $\hat{c}_i(k)$ are the electron creation and annihilation operators in the

Bloch basis set. Considering the cross terms in Eq. (4.5) ($i = c, j = v$) we have

$$(w_c(k), w_v(k)) = 0, \quad (4.6)$$

since the states in different bands are orthogonal, and for $qa \ll 1$ (a is the lattice constant) we have

$$(w_c(k+q), w_v(k)) \approx i e^{-1} \mu(k) q, \quad (4.7a)$$

with

$$\mu(k) \equiv -i e \left(\frac{\partial w_c(k)}{\partial k}, w_v(k) \right). \quad (4.7b)$$

Substituting Eq. (4.7a) into Eq. (4.5) and making use of Eq. (4.4c) we obtain

$$\hat{H}_{int} = - \int dk \int dq E_z(q) \mu(k) \hat{c}_c^+(k+q) \hat{c}_v(k). \quad (4.8)$$

Eq. (4.8) has a form of the dipole approximation with respect to a unit cell, $\mu(k)$ being the k -dependent dipole moment of a unit cell.

Appendix A. Gauge invariant quantization

We start with presenting the gauge invariant scheme of quantization. Consider a system containing nonrelativistic electrons in an external potential, interacting with the electromagnetic field. The Coulomb interaction of electrons is taken into account by the longitudinal field. We start with the classical action in the second quantized form [17]

$$\begin{aligned} S[\bar{\psi}, \psi, A_0, A] &= \int d\mathbf{r} dt \left[i \bar{\psi} \left(\frac{\partial}{\partial t} - i e A_0 \right) \psi \right. \\ &\quad - U \bar{\psi} \psi - \frac{1}{2m} \bar{\nabla} \bar{\psi} \nabla \psi \\ &\quad \left. + \frac{1}{8\pi} (\dot{A} - \partial A_0)^2 - \frac{1}{8\pi} (\text{rot } A)^2 \right], \quad (A.1a) \end{aligned}$$

with

$$\nabla_m = \partial_m - i e A_m \quad (A.1b)$$

$$\bar{\nabla}_m = \partial_m + i e A_m. \quad (A.1c)$$

Switching to the Hamilton formalism by means of the canonical procedure, we obtain the Poisson bracket for the canonical variables $A, A_0, E, E_0, \bar{\psi}, \psi$

$$\{E(\mathbf{r}), A(\mathbf{r}')\} = 4\pi \delta(\mathbf{r} - \mathbf{r}'), \quad (A.2a)$$

$$\{E_0(\mathbf{r}), A_0(\mathbf{r}')\} = 4\pi \delta(\mathbf{r} - \mathbf{r}'), \quad (A.2b)$$

$$\{\bar{\psi}(\mathbf{r}), \psi(\mathbf{r}')\} = -i \delta(\mathbf{r} - \mathbf{r}'). \quad (A.2c)$$

The Hamiltonian has the form

$$\begin{aligned} H = \int d\mathbf{r} &\left(\frac{1}{2m} \partial \bar{\psi} \partial \psi + U \bar{\psi} \psi + \frac{1}{8\pi} [E^2 + (\text{rot } A)^2] \right. \\ &\left. + j \cdot A - \frac{e}{2m} \rho A^2 - \frac{1}{4\pi} A_0 (\partial \cdot E - 4\pi \rho) \right), \quad (A.3) \end{aligned}$$

with the constraints

$$E_0(\mathbf{r}) = 0, \quad \partial \cdot E(\mathbf{r}) + 4\pi \rho(\mathbf{r}) = 0. \quad (A.4)$$

In Eqs. (A.3) and (A.4) we use the notation

$$\rho(\mathbf{r}) = -e \bar{\psi}(\mathbf{r}) \psi(\mathbf{r}), \quad (A.5a)$$

is the charge density and

$$j(\mathbf{r}) = -i e (\bar{\psi} \partial \psi - \partial \bar{\psi} \psi), \quad (A.5b)$$

is the current. The basic idea of the gauge invariant quantization scheme [12] is to use the canonical quantization, disregarding the constraints at first, and obtaining the commutation relations for the canonical operators from the Poisson bracket. The second step is to form the space of states, providing an irreducible representation of the operator algebra. The third step is to introduce the physical states subspace, which includes the states which are nullified by the quantized version of the constraints Eqs. (A.4).

The commutation relations for the operators, quantized canonical variables (we denote by \hat{Q} the operator corresponding to a classical variable Q) have the form

$$[\hat{E}(\mathbf{r}), \hat{A}(\mathbf{r}')] = -4\pi i \delta(\mathbf{r} - \mathbf{r}'), \quad (A.6a)$$

$$[\hat{E}_0(\mathbf{r}), (\hat{A}_0)] = -4\pi i \delta(\mathbf{r} - \mathbf{r}'), \quad (A.6b)$$

$$[\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}(\mathbf{r}')]_+ = -\delta(\mathbf{r} - \mathbf{r}'). \quad (A.6c)$$

$[\ , \]_+$ denotes the anticommutator, and we set $\hbar = 1$. The algebra defined by Eqs. (A.6) can be realized on

the space of wavefunctions $\psi[A, A_0]$ depending on the scalar and vector potentials (we use the square brackets for listing functional variables), and taking values in the space of material states with the natural action of the material operators. The action of the field operators on the wavefunctions is defined as follows:

$$(\hat{A}(\mathbf{r})\psi)[A, A_0] = A(\mathbf{r})\psi[A, A_0], \quad (\text{A.7a})$$

$$(\hat{E}(\mathbf{r})\psi)[A, A_0] = -4\pi i \frac{\delta\psi[A, A_0]}{\delta A(\mathbf{r})}, \quad (\text{A.7b})$$

with the action of the operators \hat{E}_0 and \hat{A}_0 defined in the same manner.

The physical states are those satisfying the conditions

$$\hat{E}_0(\mathbf{r})\psi = 0, \quad (\text{A.8a})$$

$$(\partial \cdot \hat{E}(\mathbf{r}) - 4\pi\hat{\rho}(\mathbf{r}))\psi = 0. \quad (\text{A.8b})$$

The Hamiltonian \hat{H} is the quantum version of (A.3) and has the form

$$\begin{aligned} \hat{H} = & \hat{H}_m + \frac{1}{8\pi} \int d\mathbf{r} \left[\hat{E}^2 + (\text{rot } \hat{A})^2 \right] \\ & + \int d\mathbf{r} \left(\hat{j}(\mathbf{r}) \cdot \hat{A}(\mathbf{r}) - \frac{e}{2m} \hat{\rho}(\mathbf{r}) \hat{A}^2(\mathbf{r}) \right), \end{aligned} \quad (\text{A.9a})$$

with

$$\hat{H}_m = \int d\mathbf{r} \left(\frac{1}{2m} \frac{\partial\hat{\psi}^\dagger}{\partial\mathbf{r}} \frac{\partial\hat{\psi}}{\partial\mathbf{r}} + U(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}) \right). \quad (\text{A.9b})$$

We omitted the last terms of Eq. (A.3) since due to Eq. (A.8b) this term vanishes on the physical subspace.

It is well known [2] that one can add to the Hamiltonian terms which vanish on the physical subspace; therefore, in the present formalism we have a unique Hamiltonian on the physical subspace. Note, that the physical subspace is the correct space of states of the system, and the physical quantities correspond to gauge invariant operators, i.e., operators for which the physical subspace is invariant [12].

The constraints of Eqs. (A.8) can be solved, leading to a convenient description of the physical subspace. Making use of the analogue of Eq. (A.7b)

for \hat{E}_0 , we see that Eq. (A.8) means that a physical wavefunction does not depend on A_0 .

$$\psi[A, A_0] = \psi[A]. \quad (\text{A.10})$$

Introducing the longitudinal and the transverse parts of the vector potential

$$A = A^\parallel + A^\perp = \partial\varphi + A^\perp, \quad (\text{A.11})$$

we obtain for a variation of a wavefunction ψ with respect to $\varphi(\mathbf{r})$

$$\delta\psi = - \int d\mathbf{r} \delta\varphi(\mathbf{r}) \frac{\partial}{\partial\mathbf{r}} \frac{\delta\psi}{\delta A(\mathbf{r})}, \quad (\text{A.12})$$

which after taking Eq. (A.7b) into account leads to

$$\partial \cdot \hat{E}(\mathbf{r})\psi = 4\pi i \frac{\delta\psi}{\delta\varphi(\mathbf{r})}. \quad (\text{A.13})$$

Making use of Eqs. (A.3b), (A.8b) and (A.10) we obtain the general form of a physical state

$$\psi = \exp\left(-i \int d\mathbf{r} \varphi(\mathbf{r}) \hat{\rho}(\mathbf{r})\right) \psi[A^\perp]. \quad (\text{A.14})$$

The results of this appendix will be used in Appendix B to introduce the gauge fixing and transformations and in Appendix C to obtain Hamiltonians at fixed gauges.

Appendix B. Gauge fixing and transformations

In this appendix we turn to the problem of gauge fixing and transformations. Let \mathcal{V} be the space of vector potential $A(\mathbf{r})$. It can be decomposed according to Eq. (A.11)

$$\mathcal{V} = \mathcal{V}_\parallel \oplus \mathcal{V}_\perp, \quad (\text{B.1a})$$

with

$$A^\parallel \in \mathcal{V}_\parallel, \quad A^\perp \in \mathcal{V}_\perp. \quad (\text{B.1b})$$

It follows from Eq. (a.14) that a physical wavefunction ψ , which is a mapping of $\psi: \mathcal{V} \rightarrow \mathcal{W}$, \mathcal{W} being the space of the material system, is determined by its values on a submanifold $\mathcal{M} \subset \mathcal{V}$ with the following property: the projection $p: \mathcal{M} \rightarrow \mathcal{V}_\perp$ is a one-to-one mapping. The latter condition implies that \mathcal{M} can be described by a mapping $\varphi_\# : \mathcal{V}_\perp \rightarrow \mathcal{V}_\parallel$, \mathcal{M} then consists of vector potentials $A(\mathbf{r})$ of the form

$$A(\mathbf{r}) = A^\perp(\mathbf{r}) + \partial\varphi_\#(\mathbf{r}, [A^\perp]) \quad (\text{B.2})$$

for all possible transverse vector potentials $A^\perp(\mathbf{r})$. The choice of \mathcal{M} is the gauge fixing procedure. Usually the gauge is fixed by a system of equations.

$$F_{\mathcal{M}}(A) = 0, \quad (\text{B.3})$$

\mathcal{M} being the space of solutions of Eq. (B.3).

The gauge fixing (i.e., the choice of \mathcal{M}) allows us to describe the physical space of wavefunctions $\psi: \mathcal{V} \rightarrow \mathcal{W}$ satisfying Eq. (A.14) as a space of functions $\psi_{\mathcal{M}}: \mathcal{M} \rightarrow \mathcal{W}$, confining a function ψ on \mathcal{M} to obtain $\psi_{\mathcal{M}}$. We can return to ψ starting with $\psi_{\mathcal{M}}$ making use of Eq. (A.14). We will denote the space of all functions $\psi: \mathcal{V} \rightarrow \mathcal{W}$ with \mathcal{H} , its physical subspace of functions satisfying Eq. (A.14) \mathcal{H}_{ph} , and the space of functions $\psi_{\mathcal{M}}: \mathcal{M} \rightarrow \mathcal{W}$ with $\mathcal{H}_{\mathcal{M}}$, we have an isomorphism $p_{\mathcal{M}}^*: \mathcal{H}_{\text{ph}} \rightarrow \mathcal{H}_{\mathcal{M}}$. We call the space $\mathcal{H}_{\mathcal{M}}$ the space of states of the system at the gauge given by \mathcal{M} . We can choose the transverse part of the vector potential A^\perp as a set of coordinates on \mathcal{M} , then $\mathcal{H}_{\mathcal{M}}$ can be described as the space of functions $\psi_{\mathcal{M}}[A^\perp(\mathbf{r})]$ and the isomorphism between \mathcal{H}_{ph} and $\mathcal{H}_{\mathcal{M}}$ can be given by

$$\psi_{\mathcal{M}}[A^\perp(\mathbf{r})] = \psi[A^\perp(\mathbf{r}) + \partial\varphi_{\mathcal{M}}(\mathbf{r}, [A^\perp])]. \quad (\text{B.4})$$

Let \mathcal{M} and \mathcal{M}' define two different gauges. It follows from Eqs. (B.4) and (A.14) that

$$\begin{aligned} \psi_{\mathcal{M}}[A^\perp(\mathbf{r})] &= \exp\left(-i \int d\mathbf{r} (\varphi_{\mathcal{M}}(\mathbf{r}, [A^\perp]) \right. \\ &\quad \left. - \varphi_{\mathcal{M}'}(\mathbf{r}, [A^\perp])) \hat{\rho}(\mathbf{r})\right) \psi_{\mathcal{M}'}[A^\perp(\mathbf{r})]. \end{aligned} \quad (\text{B.5})$$

We can recast Eq. (B.5) in the form

$$\psi_{\mathcal{M}} = \hat{U}_{\mathcal{M}, \mathcal{M}'} \psi_{\mathcal{M}'}, \quad (\text{B.6a})$$

where $\hat{U}_{\mathcal{M}, \mathcal{M}'}$ is a unitary operator which has the form

$$\begin{aligned} \hat{U}_{\mathcal{M}, \mathcal{M}'} &\equiv \exp\left(-i \int d\mathbf{r} (\varphi_{\mathcal{M}}(\mathbf{r}, [\hat{A}^\perp]) \right. \\ &\quad \left. - \varphi_{\mathcal{M}'}(\mathbf{r}, [\hat{A}^\perp])) \hat{\rho}(\mathbf{r})\right). \end{aligned} \quad (\text{B.6b})$$

Eqs. (B.6) imply that wavefunctions in two different gauges are connected with a unitary (canonical) transformation. This means that quantum gauge

transformations are canonical (unitary) transformations of a special form given by Eq. (B.6).

In Section 3 we show that the minimal coupling and the multipolar Hamiltonians are two forms of \hat{H} corresponding to the gauges $\text{div } A = 0$ and $\mathbf{r} \cdot A(\mathbf{r}) = 0$. This means that the canonical transformation used to obtain the multipolar Hamiltonian from the minimal coupling Hamiltonian [1,8] is a gauge transformation.

Appendix C. Hamiltonian for a fixed gauge and canonical variables

In Appendix B we have defined the procedure for gauge fixing and transformations. In this appendix we will find the form $\hat{H}_{\mathcal{M}}$ of the Hamiltonian \hat{H} of Eqs. (A.9) related to a gauge given by \mathcal{M} . Making use of the facts that \hat{H} acts on \mathcal{H}_{ph} and $p_{\mathcal{M}}^*$ is an isomorphism between \mathcal{H}_{ph} and $\mathcal{H}_{\mathcal{M}}$ given by Eq. (B.4), it is natural to define $\hat{H}_{\mathcal{M}}$ acting on $\mathcal{H}_{\mathcal{M}}$ as

$$\hat{H}_{\mathcal{M}} \equiv p_{\mathcal{M}}^{*-1} \hat{H} p_{\mathcal{M}}^*. \quad (\text{C.1})$$

It is convenient to express $\hat{H}_{\mathcal{M}}$ in terms of canonical variables, i.e. operators acting on the space of functions $\psi_{\mathcal{M}}[A^\perp(\mathbf{r})]$. We choose the canonical variables to be the operators $\hat{A}^\perp(\mathbf{r})$ and $\hat{D}^\perp(\mathbf{r})$ defined as

$$\hat{A}^\perp(\mathbf{r}) \psi_{\mathcal{M}}[A^\perp] \equiv A^\perp(\mathbf{r}) \psi_{\mathcal{M}}[A^\perp], \quad (\text{C.2a})$$

$$\hat{D}^\perp(\mathbf{r}) \psi_{\mathcal{M}}[A^\perp] \equiv -4\pi i \frac{\delta \psi_{\mathcal{M}}[A^\perp]}{\delta A^\perp(\mathbf{r})}, \quad (\text{C.2b})$$

where

$$A^\perp(\mathbf{r}) = \int \delta^\perp(\mathbf{r} - \mathbf{r}') A(\mathbf{r}') d\mathbf{r}', \quad (\text{C.3a})$$

$$\frac{\delta}{\delta A^\perp(\mathbf{r})} = \int d\mathbf{r}' \delta^\perp(\mathbf{r} - \mathbf{r}') \frac{\delta}{\delta A(\mathbf{r}')}, \quad (\text{C.3b})$$

and δ^\perp is the transverse δ -function.

It follows from Eqs. (C.2) that \hat{A}^\perp and \hat{D}^\perp commute with all material operators and

$$[\hat{D}^\perp(\mathbf{r}), \hat{A}^\perp(\mathbf{r}')] = -4\pi i \delta^\perp(\mathbf{r} - \mathbf{r}'). \quad (\text{C.4})$$

We will also consider the full vector potential

$$\hat{A}(\mathbf{r}) \equiv \hat{A}^\perp(\mathbf{r}) + \frac{\partial}{\partial \mathbf{r}} \varphi_{\mathcal{M}}(\mathbf{r}, [\hat{A}^\perp]) \quad (\text{C.5})$$

and according to Eq. (C.5) the operator $A(\mathbf{r})$ is a functional of the transverse vector potential \hat{A}^\perp .

We can now express the Hamiltonian $\hat{H}_\#$ in terms of the canonical variables. From Eqs. (A.9), we see that \hat{H} can be partitioned as

$$\hat{H} = \hat{H}_1 + \hat{H}_2, \quad (\text{C.6a})$$

with

$$\hat{H}_1 \equiv \frac{1}{8\pi} \int d\mathbf{r} \hat{E}^2(\mathbf{r}), \quad (\text{C.6b})$$

and \hat{H}_2 contains other terms which can be expressed in terms of $\hat{A}(\mathbf{r})$ and material operators. Both Hamiltonians \hat{H}_1 and \hat{H}_2 are gauge invariant, i.e., they commute with the constraints (Eqs. (A.8)), hence the physical subspace of states is invariant with respect to both. To obtain the Hamiltonian $(\hat{H}_2)_\#$ related to \hat{H}_2 by means of Eq. (C.1) we make use of Eq. (B.4) connecting $\psi_\#$ and ψ . $(\hat{H}_2)_\#$ has the same form as \hat{H}_2 where the operators $\hat{A}(\mathbf{r})$ are defined by Eqs. (C.2a) and (C.5) and for a material operator \hat{Q} ,

$$(\hat{Q}\psi_\#)[A^\perp(\mathbf{r})] \equiv \hat{Q}(\psi_\#[A^\perp(\mathbf{r})]). \quad (\text{C.7})$$

This means that $(\hat{H}_2)_\#$ has the form

$$\begin{aligned} (\hat{H}_2)_\# = & \hat{H}_m + \frac{1}{8\pi} \int [\text{rot } \hat{A}(\mathbf{r})]^2 d\mathbf{r} \\ & + \int d\mathbf{r} \left(\hat{j}(\mathbf{r}) \cdot \hat{A}(\mathbf{r}) - \frac{e}{2m} \hat{\rho}(\mathbf{r}) \hat{A}^2(\mathbf{r}) \right). \end{aligned} \quad (\text{C.8})$$

To obtain $(\hat{H}_1)_\#$ it is convenient to represent \hat{H}_1 in a form of a sum of its longitudinal and transverse parts

$$\hat{H}_1 = \hat{H}_1^\parallel + \hat{H}_1^\perp, \quad (\text{C.9a})$$

$$\hat{H}_1^\parallel \equiv \frac{1}{8\pi} \int d\mathbf{r} [\hat{E}^\parallel(\mathbf{r})]^2, \quad (\text{C.9b})$$

$$\hat{H}_1^\perp \equiv \frac{1}{8\pi} \int d\mathbf{r} [\hat{E}^\perp(\mathbf{r})]^2, \quad (\text{C.9c})$$

where $\hat{E}^\parallel(\mathbf{r})$ and $\hat{E}^\perp(\mathbf{r})$ are given by

$$\hat{E}(\mathbf{r}) = \hat{E}^\perp(\mathbf{r}) + E^\parallel(\mathbf{r}), \quad (\text{C.10a})$$

$$\hat{E}^\perp(\mathbf{r}) = -4\pi i \frac{\delta}{\delta A^\perp(\mathbf{r})}, \quad (\text{C.10b})$$

$$\hat{E}^\parallel(\mathbf{r}) = -4\pi i \frac{\delta}{\delta A^\parallel(\mathbf{r})}. \quad (\text{C.10c})$$

The dependence of a physical wavefunction on the longitudinal part of the vector potential $A^\parallel = \partial\varphi$ is given by Eq. (A.14) which follows from the constraint Eq. (A.8b), and we obtain on the physical subspace

$$\hat{E}^\parallel = \partial \Delta^{-1} (4\pi \hat{\rho}), \quad (\text{C.11})$$

where Δ^{-1} is the operator form of the Green function of the Laplace operator Δ . Substituting Eq. (C.11) into Eq. (C.9) and taking into account the fact that $\hat{\rho}(\mathbf{r})$ is a material operator we obtain

$$(\hat{H}_1^\parallel)_\# = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}'), \quad (\text{C.12})$$

i.e., $(\hat{H}_1^\parallel)_\#$ represents the Coulomb energy.

The most interesting term is \hat{H}_1^\perp . To find $(\hat{H}_1^\perp)_\#$ we need to connect the operators $\hat{E}^\perp(\mathbf{r})$ to $\hat{D}^\perp(\mathbf{r})$. To that end we note that we know how the operators $\hat{E}^\perp(\mathbf{r})$ act on \mathcal{H}_{ph} and how $\hat{D}^\perp(\mathbf{r})$ act on $\mathcal{H}_\#$. Let $\psi_\# \in \mathcal{H}_\#$ and $\psi \in \mathcal{H}_{\text{ph}}$ represent the same state, i.e., $\psi_\# = p_\#(\psi)$. This means that ψ and $\psi_\#$ satisfy Eq. (B.4), which when combined with Eq. (C.2b) yields

$$\begin{aligned} \hat{D}^\perp(\mathbf{r})\psi = & -4\pi i \frac{\delta}{\delta A^\perp(\mathbf{r})} \psi[A^\perp(\mathbf{r}')] \\ & + \partial\varphi_\#(\mathbf{r}', [A^\perp]). \end{aligned} \quad (\text{C.13})$$

For a physical function ψ we have

$$\hat{E}^\perp(\mathbf{r})\psi = -4\pi i \frac{\delta}{\delta A^\perp(\mathbf{r})} \psi, \quad (\text{C.14a})$$

$$\frac{\delta}{\delta\varphi(\mathbf{r})} \psi = -i\hat{\rho}(\mathbf{r})\psi. \quad (\text{C.14b})$$

Combining Eqs. (C.13) and (C.14) we obtain

$$\begin{aligned} \hat{D}^\perp(\mathbf{r})\psi & = \hat{E}^\perp(\mathbf{r})\psi - 4\pi \int d\mathbf{r}' \frac{\delta\varphi_\#(\mathbf{r}', [A^\perp])}{\delta A^\perp(\mathbf{r})} \hat{\rho}(\mathbf{r}')\psi \end{aligned} \quad (\text{C.15})$$

for an arbitrary physical state $\psi \in \mathcal{H}_{\text{ph}}$. This means that a relation between $\hat{D}^\perp(\mathbf{r})$ and $\hat{E}^\perp(\mathbf{r})$ can be written in the form

$$\hat{D}^\perp(\mathbf{r}) = \hat{E}^\perp(\mathbf{r}) + 4\pi \hat{P}_\#^\perp(\mathbf{r}), \quad (\text{C.16a})$$

alently $\varphi_{\mathcal{H}}$ is a linear functional of $A^{\perp}(\mathbf{r})$, i.e., $\varphi_{\mathcal{H}}$ can be written as

$$\varphi_{\mathcal{H}}(\mathbf{r}, [A^{\perp}]) = \int \varphi_{\mathcal{H}}(\mathbf{r}', \mathbf{r}) \cdot A^{\perp}(\mathbf{r}') d\mathbf{r}', \quad (\text{C.19})$$

which leads to the following expression for the polarization

$$\begin{aligned} \hat{P}_{\mathcal{H}}^{\perp}(\mathbf{r}) \\ = - \int d\mathbf{r}' d\mathbf{r}'' \delta^{\perp}(\mathbf{r} - \mathbf{r}') \varphi_{\mathcal{H}}(\mathbf{r}', \mathbf{r}'') \hat{\rho}(\mathbf{r}''). \end{aligned} \quad (\text{C.20})$$

Our formalism points out a geometric origin of the microscopic polarization $\hat{P}_{\mathcal{H}}^{\perp}$. This is illustrated in Fig. 1. In the derivation of Eqs. (C.16) we noticed that on the space \mathcal{H}_{ph} , $\hat{E}^{\perp}(\mathbf{r})$ acts as a variational derivative in a transverse direction, and $\hat{D}^{\perp}(\mathbf{r})$ acts as a derivative in a direction tangent to \mathcal{H} . Therefore, the difference $\hat{D}^{\perp} - \hat{E}^{\perp}$ represented by $4\pi\hat{P}_{\mathcal{H}}^{\perp}$ is given by a derivative in the longitudinal direction, i.e., a functional derivative with respect to the longitudinal part of the vector potential which is defined by its transverse part (see Eq. (2.2)), which yields $\hat{P}_{\mathcal{H}}^{\perp}$ proportional to $\hat{\rho}$, in agreement with Eqs. (A.13) and (A.14).

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