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Linear response of crystals to electromagnetic fields: Microscopic charge-current density, polarization, and magnetization

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We present an electrodynamic approach to the description of the linear response of solids to electromagnetic fields. For time and spatially varying applied fields we solve the dynamical equations satisfied by the gauge-invariant Green function and find microscopic charge and current densities that result in a form allowing for an easy construction of the multipole expansion of applied fields. Restricting ourselves to static and uniform electric and magnetic fields, we construct microscopic expressions for polarization and magnetization fields associated with each lattice site. The approach is in the spirit of the Power-Zienau-Wooley (PZW) treatment but generalized to account for the motion of the charge between lattice sites. We show that the macroscopic polarization and magnetization can be understood as the spatial average of the generalized PZW microscopic fields.

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I. INTRODUCTION

In elementary treatments of the electrodynamics of molecular fluids, the macroscopic polarization and magnetization fields are associated with the electric and magnetic dipole moments of the molecules. Systematic generalizations to include higher order moments were introduced almost half a century ago [1], where the whole analysis can be drastically simplified by introducing *microscopic* polarization and magnetization fields via the Power-Zienau-Wooley (PZW) gauge transformation [2,3]. An expansion of electromagnetic fields around the center of a molecule within expressions for polarization and magnetization fields leads in a natural way to molecular multipole moments, the effects of which can be derived up to any order.

Such an approach cannot be immediately extended to crystalline solids, where electrons cannot be assumed to be confined to particular molecules or unit cells. It was only with the advent of the "modern theory of polarization" [4], anticipated by the early work of Adams and Blount [5], that progress was made in developing a theory for the macroscopic polarization of crystals. It was argued [4,6] that only the change in any alleged macroscopic polarization has physical significance, since this corresponds to the current density. Nonetheless, that polarization could then be linked with the dipole moment of the Wannier functions, with a quantum of ambiguity in its definition linked to the ambiguity in how the Wannier functions are associated with the lattice sites. Recent work [7] has addressed the more difficult problem of determining the orbital magnetoelectric polarizability.

An additional complication arises when magnetization is considered. For an insulator in the ground state [8,9], the magnetization was shown to contain a contribution due to the magnetic dipole moment of the Wannier functions, but also a contribution due to the moment of a current involving Wannier functions at different lattice sites. The formulation of magnetization in terms of these moments was subsequently extended to systems in a uniform applied electric field [10], while the susceptibility governing the response of the orbital magnetization to the magnetic field has been extracted from the evaluation of the energy in the presence of the magnetic field [11–14].

Approaches based on the energy of systems in the presence of applied fields cannot immediately be generalized in a rigorous way to take into account the response to time-dependent fields, which is necessary for the treatment of problems in optics. Here a number of the processes one would like to describe, including forbidden second harmonic generation [15] and optical activity of solids [16,17], depend on the variation of electromagnetic fields through the crystal. Phenomenological treatments [18] of such processes, for which an underlying microscopic theory should provide expressions for the response coefficients that appear, are often based on the introduction of multipole moments per unit volume.

All this motivates the calculation of the response to electromagnetic fields from an electrodynamic perspective rather than from energy considerations, and a modern introduction of *microscopic* polarization and magnetization fields in extended solids, as an approach to the construction of macroscopic multipole moments per unit volume.

One might object to this strategy on the grounds that the freedom in choosing Wannier functions would lead to an ambiguity in the higher order moments more drastic than the quantized ambiguity that arises, for example, in the polarization of the ground state. Ambiguities in higher order moments are not just a problem for the treatment of extended solids, of course. Even in the description of a molecular fluid, if the dipole moment of a molecule is nonvanishing, then its quadrupole moment will depend on the choice of the origin. This might lead one to suspect the validity—or at least the uniqueness—of a usual description of the optical activity of such a medium, where the response of the quadrupole moment per unit volume to the electric field enters, as well as the response of the magnetic dipole moment per unit volume to the electric field and the response of the dipole moment per unit volume to the magnetic field and variation of the electric field. However, in that theory it is discovered that only combinations of these different responses that are insensitive to the choice of origin enter in the description of physical phenomena such as the rotation of the plane of polarization of light [19,20]. While the situation is more complicated for extended solids, the result

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for molecular fluid shows that higher order multipoles need not be eschewed simply because there is some ambiguity in their definition, and that examining the possibility of constructing microscopic polarization and magnetization, and using them as the basis of multipole expansions, is worth investigating. This is the program we initiate in this paper.

In this first investigation we show how the approach can be used to treat an insulator responding linearly to applied uniform and static electric and magnetic fields. With a view towards ultimate applications in the optical regime, in Sec. II we consider the linear response of an insulator of Chern class zero to an arbitrary applied electromagnetic field. In a manner that allows for a natural expansion of an electromagnetic field varying little over the distance between lattice sites, we construct the nonequilibrium Green function that results. In this initial paper we work within the independent particle approximation, but the Green function approach is generally a powerful one because it need not be restricted to considering only the Hamiltonian evolution that is often assumed in calculating the response to applied fields; any appropriate self-energy can be considered. Thus it connects naturally to modern approaches for the computation of material properties based on density functional theory and its generalizations [21]. For simplicity and to more clearly demonstrate the strategy we also neglect electron spin, assume that the bands are nondegenerate, and neglect local field corrections and any induced lattice distortion. We will turn to generalizations to include these in later communications. Once the Green function is determined, the microscopic charge and current densities immediately follow. Earlier density matrix calculations in the presence of static and uniform fields [7] can be seen as precursors to this approach.

While microscopic polarization and magnetization fields do not uniquely follow from the charge and current densities they describe, we show in Sec. III that there is a natural way to construct the microscopic polarization and magnetization fields associated with each site by employing the perturbed Wannier functions. There is some ambiguity left in the definition of the microscopic fields, which is related to the nonuniqueness of Wannier functions. However, the first moments of these fields are either gauge invariant, or have a quantum of ambiguity that simply reflects the well-known ambiguity at the macroscopic level. The higher moments do not contribute to the macroscopic response in the case of static and uniform electric and magnetic fields, nevertheless these are nonunique; this is expected, as even in the extreme case of a molecular crystal, to which a more general PZW theory of a solid should reduce in the appropriate limit, the higher moments depend on the choice of the expansion point with respect to which the moments are taken.

In Sec. IV we verify that the spatial averaging of the generalized PZW microscopic fields introduced in Sec. III results in the macroscopic polarization and magnetization in agreement with earlier calculations. In the absence of applied fields we recover the established expressions for the polarization and magnetization in the ground state [4,8]. In the presence of the perturbation we recover the established response coefficients of the polarization to the applied electric field [22,23] and of the magnetization to the magnetic field [12], what might be called the "diagonal susceptibilities." While the second of these has been calculated before, our approach does not begin from the evaluation of the energy in a magnetic field. We also recover the response coefficients that describe the response of the polarization to the magnetic field and of the magnetization to the electric field [10], which might be called the "mixed susceptibilities."

The ground state polarization and magnetization, and both the diagonal and mixed susceptibilities, have been derived from a common framework. It is based on electrodynamics, rather than energy considerations or thermodynamic potentials, and microscopic polarization and magnetization fields have been introduced associated with individual lattice sites. While only the first moments of these fields arise in the response to static and uniform fields, the theory we present provides a step towards a more general description of systems in spatially varying and time-dependent electromagnetic fields.

We present our conclusions in Sec. V.

II. LINEAR RESPONSE TO TIME AND SPATIALLY DEPENDENT FIELDS

We consider electrons interacting with an external classical electromagnetic field and with the periodic potential of a lattice, in the independent particle approximation. The interaction is described with the use of the minimal-coupling Hamiltonian

$$\hat{H}(T) = \int d^3x \hat{\psi}^\dagger(\boldsymbol{x},T)\mathcal{H}(\boldsymbol{x},T)\hat{\psi}(\boldsymbol{x},T), \tag{1}$$

with the Hamiltonian density given by

$$\mathcal{H}(\boldsymbol{x},T) = \frac{1}{2m}\left[\frac{\hbar}{i}\nabla - \frac{e}{c}\boldsymbol{A}(\boldsymbol{x},T)\right]^2 + e\mathcal{U}(\boldsymbol{x},T) + V(\boldsymbol{x}). \tag{2}$$

Here we use a notation where $\hat{\psi}(\boldsymbol{x},T)$ is a field operator, $\boldsymbol{A}(\boldsymbol{x},T)$ and $\mathcal{U}(\boldsymbol{x},T)$ are, respectively, the vector and scalar potentials of the applied electromagnetic fields, and $V(\boldsymbol{x})$ is the lattice potential. We describe the system with the use of the Green functions, and write for the usual "lesser" function

$$G^{\mathrm{GD}}(\boldsymbol{x},\boldsymbol{y};T) = i\langle\hat{\psi}^\dagger(\boldsymbol{y},T)\hat{\psi}(\boldsymbol{x},T)\rangle. \tag{3}$$

We take both coordinates in (3) to be at equal time, since the equal-time function is sufficient to describe the microscopic charge and current densities induced by electromagnetic fields. The time evolution of the Green function (3) is driven by the minimal coupling Hamiltonian,

$$i\hbar\frac{\partial G^{\mathrm{GD}}(\boldsymbol{x},\boldsymbol{y};T)}{\partial T} = [\mathcal{H}(\boldsymbol{x},T) - \mathcal{H}^*(\boldsymbol{y},T)]G^{\mathrm{GD}}(\boldsymbol{x},\boldsymbol{y};T),$$

and obviously depends on the gauge of the electromagnetic potentials.

A. Gauge-invariant Green function and the PZW transformation

The gauge-dependent formulation of the dynamics often leads to the presence of apparent divergences in the calculations of the response coefficients, and requires an identification of sum rules [12,22,24]. Therefore, rather than simply using (3), we perform a generalized Peierls transformation introduced earlier [25] to arrive at the gauge-invariant Green function

$$G(\boldsymbol{x},\boldsymbol{y};T) = e^{-i\Phi(\boldsymbol{x},\boldsymbol{y};T)}G^{\mathrm{GD}}(\boldsymbol{x},\boldsymbol{y};T), \tag{4}$$

where we put

$$\Phi(\boldsymbol{x},\boldsymbol{y};T) = \frac{e}{\hbar c}\left[\Gamma(\boldsymbol{x},\boldsymbol{y};T) - \frac{\Gamma(\boldsymbol{x},\boldsymbol{x};T)+\Gamma(\boldsymbol{y},\boldsymbol{y};T)}{2}\right],$$

with the Peierls phase $\Gamma(\boldsymbol{x},\boldsymbol{y};T)$ defined as

$$\Gamma(\boldsymbol{x},\boldsymbol{y};T) = \int_{u_{\mathrm{initial}}}^{u_{\mathrm{final}}} \frac{\partial \boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y})}{\partial u}\cdot \boldsymbol{A}(\boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y}),T)du. \tag{5}$$

Here the function $\boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y})$ parametrizes a path in space connecting the Green function coordinates $\boldsymbol{y}$ to $\boldsymbol{x}$ as u varies from u_{initial} to u_{final}. The path can be chosen arbitrarily, provided that $\boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y})$ is differentiable in all its variables and satisfies the boundary conditions $\boldsymbol{z}(u_{\mathrm{initial}};\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{y}$ and $\boldsymbol{z}(u_{\mathrm{final}};\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{x}$; there is thus a kind of freedom in the description of the system, related to the choice of a path, which replaces the gauge freedom associated with electromagnetic potentials when the usual Green function is used. For simplicity we take $\boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y}) = \boldsymbol{z}(u_{\mathrm{final}} - u + u_{\mathrm{initial}};\boldsymbol{y},\boldsymbol{x})$; that is, we assume that the path from $\boldsymbol{y}$ to $\boldsymbol{x}$ is a reverse of the path from $\boldsymbol{x}$ to $\boldsymbol{y}$; this will be true of the paths used in this paper. The dynamics of the gauge-invariant Green function (4) is described in the independent particle approximation by a kinetic equation [25],

$$\begin{aligned} i\hbar\frac{\partial G(\boldsymbol{x},\boldsymbol{y};T)}{\partial T} &= [\mathcal{H}_0(\boldsymbol{x}) - \mathcal{H}_0^*(\boldsymbol{y})]G(\boldsymbol{x},\boldsymbol{y};T) \\ &\quad + U(\boldsymbol{x},\boldsymbol{y};T)G(\boldsymbol{x},\boldsymbol{y};T), \end{aligned} \tag{6}$$

where the differential operator on the right-hand side is split into a free Hamiltonian term $\mathcal{H}_0(\boldsymbol{x}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})$, and the differential operator that depends on the externally applied fields is given by

$$\begin{aligned} U(\boldsymbol{x},\boldsymbol{y};T) &= \frac{1}{2m}\left(\boldsymbol{p}(\boldsymbol{x}) + \frac{e}{c}\boldsymbol{X}(\boldsymbol{x},\boldsymbol{y};T)\right)^2 - \frac{\boldsymbol{p}^2(\boldsymbol{x})}{2m} \\ &\quad - \frac{1}{2m}\left(\boldsymbol{p}(\boldsymbol{y}) + \frac{e}{c}\boldsymbol{Y}(\boldsymbol{x},\boldsymbol{y};T)\right)^2 + \frac{\boldsymbol{p}^2(\boldsymbol{y})}{2m} \\ &\quad + e\mathcal{T}(\boldsymbol{x},\boldsymbol{y};T). \end{aligned} \tag{7}$$

In Eq. (7) we put $p_j(\boldsymbol{x}) = -i\hbar\partial/\partial x^j$ for the momentum operator. The functions $\boldsymbol{X}(\boldsymbol{x},\boldsymbol{y};T)$, $\boldsymbol{Y}(\boldsymbol{x},\boldsymbol{y};T)$, $\mathcal{T}(\boldsymbol{x},\boldsymbol{y};T)$ are defined in terms of the derivatives of the Peierls phase $\Gamma(\boldsymbol{x},\boldsymbol{y};T)$ and electromagnetic potentials

$$X_j(\boldsymbol{x},\boldsymbol{y};T) \equiv \frac{\partial\Gamma(\boldsymbol{x},\boldsymbol{y};T)}{\partial x^j} - A_j(\boldsymbol{x},T), \tag{8}$$

$$Y_j(\boldsymbol{x},\boldsymbol{y};T) \equiv \frac{\partial\Gamma(\boldsymbol{x},\boldsymbol{y};T)}{\partial y^j} + A_j(\boldsymbol{y},T) \tag{9}$$

$$\mathcal{T}(\boldsymbol{x},\boldsymbol{y};T) \equiv \frac{1}{c}\frac{\partial\Gamma(\boldsymbol{x},\boldsymbol{y};T)}{\partial T} + \mathcal{U}(\boldsymbol{x},T) - \mathcal{U}(\boldsymbol{y},T), \tag{10}$$

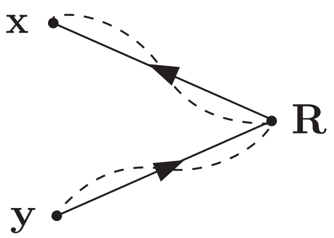

FIG. 1. The path going through a special point $\boldsymbol{R}$ leading to the PZW transformation. In the simplest case the straight line paths between points are chosen.

but they can be shown to be gauge invariant as they can be rewritten in terms of the electromagnetic fields [25],

$$X_j(\boldsymbol{x},\boldsymbol{y};T) = \int_{\boldsymbol{y}}^{\boldsymbol{x}} \frac{\partial z^k}{\partial x^j}[d\boldsymbol{z}\times\boldsymbol{B}(\boldsymbol{z},T)]_k, \tag{11}$$

$$Y_j(\boldsymbol{x},\boldsymbol{y};T) = \int_{\boldsymbol{y}}^{\boldsymbol{x}} \frac{\partial z^k}{\partial y^j}[d\boldsymbol{z}\times\boldsymbol{B}(\boldsymbol{z},T)]_k, \tag{12}$$

$$\mathcal{T}(\boldsymbol{x},\boldsymbol{y};T) = -\int_{\boldsymbol{y}}^{\boldsymbol{x}} d\boldsymbol{z}\cdot\boldsymbol{E}(\boldsymbol{z},T). \tag{13}$$

The dynamical equation (6), as well as the expressions for the microscopic charge and current densities [25]

$$\rho(\boldsymbol{x},T) = -ieG(\boldsymbol{x},\boldsymbol{x};T), \tag{14}$$

$$\begin{aligned} \boldsymbol{j}(\boldsymbol{x},T) &= -\frac{ie}{2m}\lim_{\boldsymbol{y}\to\boldsymbol{x}}[\boldsymbol{p}(\boldsymbol{x}) - \boldsymbol{p}(\boldsymbol{y})]G(\boldsymbol{x},\boldsymbol{y};T) \\ &\quad - \frac{ie^2}{2mc}[\boldsymbol{X}(\boldsymbol{x},\boldsymbol{x};T) - \boldsymbol{Y}(\boldsymbol{x},\boldsymbol{x};T)]G(\boldsymbol{x},\boldsymbol{x};T) \end{aligned} \tag{15}$$

are thus explicitly gauge invariant, with (11)–(13) valid for a general path in space.

An important special case of the general Peierls transformation (4) is the Power-Zienau-Wooley (PZW) transformation [2,3], which is a standard tool in the quantum mechanical description of the optical response of atoms and molecules. The PZW transformation is recovered within the Green function formalism for the paths $\boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y})$ in (5) that go through a special point $\boldsymbol{R}$ in space, such that the path from $\boldsymbol{y}$ to $\boldsymbol{R}$ is a reverse of the path from $\boldsymbol{R}$ to $\boldsymbol{x}$ (see Fig. 1). For the paths from this category the Peierls phase is of the form $\Gamma(\boldsymbol{x},\boldsymbol{y};T) = \gamma_{\boldsymbol{R}}(\boldsymbol{x},T) - \gamma_{\boldsymbol{R}}(\boldsymbol{y},T)$, and the Green function (4) is formed from the transformed field operators [25,26]

$$\hat{\psi}'(\boldsymbol{x},T) = e^{-\frac{ie}{\hbar c}\gamma_{\boldsymbol{R}}(\boldsymbol{x},T)}\hat{\psi}(\boldsymbol{x},T). \tag{16}$$

The interaction terms (11)–(13) take the simple form [25]

$$X_j^{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y};T) = -\Omega_j^{\boldsymbol{R}}(\boldsymbol{x},T), \tag{17}$$

$$Y_j^{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y};T) = \Omega_j^{\boldsymbol{R}}(\boldsymbol{y};T), \tag{18}$$

$$\mathcal{T}^{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y};T) = \Omega_0^{\boldsymbol{R}}(\boldsymbol{y},T) - \Omega_0^{\boldsymbol{R}}(\boldsymbol{x},T), \tag{19}$$

where

$$\Omega_0^{\boldsymbol{R}}(\boldsymbol{x},T) = \int d^3w\,\boldsymbol{E}(\boldsymbol{w},T)\cdot\boldsymbol{s}(\boldsymbol{w},\boldsymbol{x};\boldsymbol{R}), \tag{20}$$

$$\Omega_j^{\boldsymbol{R}}(\boldsymbol{x},T) = \int d^3w\,B^l(\boldsymbol{w},T)\alpha^{lj}(\boldsymbol{w},\boldsymbol{x};\boldsymbol{R}), \tag{21}$$

with the line integrals $\boldsymbol{s}(\boldsymbol{w},\boldsymbol{x};\boldsymbol{R})$ and $\alpha^{lj}(\boldsymbol{w},\boldsymbol{x};\boldsymbol{R})$ depending on the specific choice of a path; in the simplest case of points $\boldsymbol{y}$, $\boldsymbol{R}$, $\boldsymbol{x}$ connected by straight lines they are given by

$$\boldsymbol{s}(\boldsymbol{w},\boldsymbol{x};\boldsymbol{R}) = \boldsymbol{x}_{\boldsymbol{R}} \int_0^1 du\,\delta(\boldsymbol{w}_{\boldsymbol{R}} - u\boldsymbol{x}_{\boldsymbol{R}}), \tag{22}$$

$$\alpha^{lj}(\boldsymbol{w},\boldsymbol{x};\boldsymbol{R}) = x_R^m \epsilon^{lmj} \int_0^1 u\,du\,\delta(\boldsymbol{w}_{\boldsymbol{R}} - u\boldsymbol{x}_{\boldsymbol{R}}), \tag{23}$$

where we put $\boldsymbol{w}_{\boldsymbol{R}} = \boldsymbol{w} - \boldsymbol{R}$, $\boldsymbol{x}_{\boldsymbol{R}} = \boldsymbol{x} - \boldsymbol{R}$. The corresponding dynamics (6),

$$i\hbar \frac{\partial G(\boldsymbol{x},\boldsymbol{y};T)}{\partial T} = [\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x},T) - \mathcal{H}^*_{\boldsymbol{R}}(\boldsymbol{y},T)]G(\boldsymbol{x},\boldsymbol{y};T),$$

with the Hamiltonian density

$$\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x},T) = \frac{1}{2m}\left(\boldsymbol{p}(\boldsymbol{x}) - \frac{e}{c}\boldsymbol{\Omega}^{\boldsymbol{R}}(\boldsymbol{x},T)\right)^2 - e\Omega_0^{\boldsymbol{R}}(\boldsymbol{x},T) + V(\boldsymbol{x}), \tag{24}$$

can be shown to arise from the PZW Hamiltonian [25], which is formulated in terms of the polarization and magnetization fields.

Microscopic polarization and magnetization fields are the basic entities of the PZW formalism, and are related to the charge and current density operators $\hat{\rho}(\boldsymbol{x},T)$ and $\hat{\boldsymbol{j}}(\boldsymbol{x},T)$ by [2,3]

$$\hat{\boldsymbol{p}}(\boldsymbol{x},T) = \int d^3y\,\boldsymbol{s}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})\hat{\rho}(\boldsymbol{y},T), \tag{25}$$

$$\hat{m}^j(\boldsymbol{x},T) = \frac{1}{c}\int d^3y\,\alpha^{jk}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})\hat{j}^k(\boldsymbol{y},T). \tag{26}$$

Different choices of paths in Fig. 1 correspond to different polarization and magnetization fields, giving rise to a new freedom in the PZW formalism that replaces the gauge freedom of the minimal-coupling Hamiltonian; the most common choice is to use the straight line path integrals (22) and (23). In the usual applications, the fields (25) and (26) are expanded to yield multipole moments up to the order required, by formally expanding the Dirac δ function in (22) and (23),

$$\delta(\boldsymbol{x}_{\boldsymbol{R}} - u\boldsymbol{y}_{\boldsymbol{R}}) = \delta(\boldsymbol{x}_{\boldsymbol{R}}) - uy_R^i\frac{\partial}{\partial x^i}\delta(\boldsymbol{x}_{\boldsymbol{R}}) + \cdots. \tag{27}$$

Expansion (27), when used in (25) and (26) yields

$$\hat{p}^i(\boldsymbol{x},T) = \hat{\mu}^i(T)\delta(\boldsymbol{x}-\boldsymbol{R}) - \hat{q}^{ij}(T)\frac{\partial\delta(\boldsymbol{x}-\boldsymbol{R})}{\partial x^j} + \cdots, \tag{28}$$

$$\hat{m}^i(\boldsymbol{x},T) = \hat{\nu}^i(T)\delta(\boldsymbol{x}-\boldsymbol{R}) + \cdots, \tag{29}$$

with the first few multipole moments defined as

$$\hat{\boldsymbol{\mu}}(T) = \int d^3y(\boldsymbol{y}-\boldsymbol{R})\hat{\rho}(\boldsymbol{y},T), \tag{30}$$

$$\hat{q}^{ij}(T) = \frac{1}{2}\int d^3y(y^i - R^i)(y^j - R^j)\hat{\rho}(\boldsymbol{y},T), \tag{31}$$

$$\hat{\boldsymbol{\nu}}(T) = \frac{1}{2c}\int d^3y(\boldsymbol{y}-\boldsymbol{R})\times\hat{j}(\boldsymbol{y},T). \tag{32}$$

The polarization and magnetization fields couple to the electric and magnetic fields in the gauge-invariant PZW Hamiltonian. In the new representation, the interaction part of the Hamiltonian (24) is given by [27]

$$\hat{H}^{\text{int}}_{\text{PZW}}(T) = -\int d^3x\,\hat{\boldsymbol{p}}(\boldsymbol{x},T)\cdot\boldsymbol{E}(\boldsymbol{x},T) - \int d^3x\,\hat{\boldsymbol{m}}_{(P)}(\boldsymbol{x},T)\cdot \times\boldsymbol{B}(\boldsymbol{x},T) - \frac{1}{2}\int d^3x\,\hat{\boldsymbol{m}}_{(D)}(\boldsymbol{x},T)\cdot\boldsymbol{B}(\boldsymbol{x},T), \tag{33}$$

where $\hat{\boldsymbol{m}}_{(P,D)}(\boldsymbol{y},T)$ stand for the *para-* and *dia*-magnetic contributions to magnetization. The expansions (28) and (29), when used in (33), lead to the usual expression for the interaction of the electromagnetic fields and their gradients with the multipole moments. But apart from introducing a new formulation of the dynamics, expansions of the form (28) and (29) after macroscopic averaging are also typically used to formulate the material Maxwell equations [28], and to describe optical processes, such as optical activity [19,20], in systems where the molecules can be approximated as units where charges do not move from molecule to molecule.

B. Construction of the multipole Green function

The PZW formalism, although very powerful, can be usefully applied only to small systems compared with the wavelength of light. In an extended system the Peierls transformation (4) cannot globally depend on one special point in space, and the charge transfer between atoms in a solid prohibits carrying out a transformation independently for each atom. For these reasons we consider a Peierls phase that depends on $\boldsymbol{x}$ and $\boldsymbol{y}$ coordinates only, and for simplicity choose the path $\boldsymbol{z}(u;\boldsymbol{x},\boldsymbol{y})$ in (5) to be a straight line connecting the two coordinates; we will refer to the phase resulting from this choice of a path as the "global Peierls phase," and denote it by $\Gamma^{\text{GL}}(\boldsymbol{x},\boldsymbol{y};T)$. For the Green function (4) defined with the phase $\Gamma^{\text{GL}}(\boldsymbol{x},\boldsymbol{y};T)$ we seek a solution of (6) in a form such that a multipole expansion around lattice sites of the induced charges and currents and their interaction with the applied fields can easily be generated; we will refer to this form of the Green function as the "multipole Green function." The strategy we adopt resembles the PZW treatment, with the difference that we account for the motion of charge between lattice sites. Thus instead of evaluating the interaction terms $\boldsymbol{X}(\boldsymbol{x},\boldsymbol{y};T)$, $\boldsymbol{Y}(\boldsymbol{x},\boldsymbol{y};T)$, $\mathcal{T}(\boldsymbol{x},\boldsymbol{y};T)$ directly from Eqs. (11)–(13) for the straight line path, we locally rewrite this path in the neighborhood of each lattice site as a path going through a lattice site together with a path forming a closed loop (see Fig. 2). The path going through $\boldsymbol{R}$ defines a phase $\Gamma^{\boldsymbol{R}}_{\text{PZW}}(\boldsymbol{x},\boldsymbol{y};T)$ leading to the

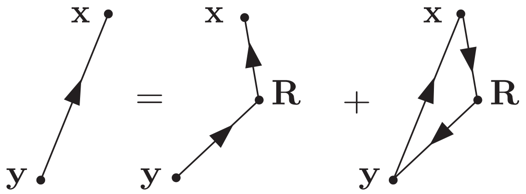

FIG. 2. The path defining the global Peierls phase $\Gamma^{\text{GL}}(\boldsymbol{x},\boldsymbol{y};T)$, represented as a sum of the path leading to the PZW transformation plus a correction.

usual PZW transformation with the multipole expansion point at $\boldsymbol{R}$. The closed loop defines a phase $\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T)$ that is a flux of the magnetic field through a triangle spanned by $\boldsymbol{x}$, $\boldsymbol{y}$, and $\boldsymbol{R}$, which we denote by $\Delta_{\boldsymbol{x}\boldsymbol{y}\boldsymbol{R}}$. For any site $\boldsymbol{R}$ we can thus write

$$\Gamma^{\mathrm{GL}}(\boldsymbol{x},\boldsymbol{y};T) = \Gamma^{\boldsymbol{R}}_{\mathrm{PZW}}(\boldsymbol{x},\boldsymbol{y};T) + \phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T), \tag{34}$$

where

$$\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T) = \int_{\Delta_{\boldsymbol{x}\boldsymbol{y}\boldsymbol{R}}} \boldsymbol{B}(\boldsymbol{s},T)\cdot\boldsymbol{n}, \tag{35}$$

with

$$\boldsymbol{n} = -\frac{(\boldsymbol{x}-\boldsymbol{R})\times(\boldsymbol{y}-\boldsymbol{R})}{|(\boldsymbol{x}-\boldsymbol{R})\times(\boldsymbol{y}-\boldsymbol{R})|}. \tag{36}$$

We now use (34) to evaluate the interaction terms (11)–(13). Differentiating (34) with respect to T and using (10) together with (19) we arrive at a relation

$$\begin{aligned}\mathcal{T}^{\mathrm{GL}}(\boldsymbol{x},\boldsymbol{y},T) = {}& -\Omega^{\boldsymbol{R}}_0(\boldsymbol{x},T) + \Omega^{\boldsymbol{R}}_0(\boldsymbol{y},T)\\ & + \frac{1}{c}\frac{\partial}{\partial T}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T).\end{aligned} \tag{37}$$

Similarly, taking space derivatives of (34) and using (8), (9), (17), and (18) we arrive at

$$X^{\mathrm{GL}}_j(\boldsymbol{x},\boldsymbol{y},T) = -\Omega^{\boldsymbol{R}}_j(\boldsymbol{x},T) + \frac{\partial}{\partial x^j}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T), \tag{38}$$

$$Y^{\mathrm{GL}}_j(\boldsymbol{x},\boldsymbol{y},T) = \Omega^{\boldsymbol{R}}_j(\boldsymbol{y},T) + \frac{\partial}{\partial y^j}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T). \tag{39}$$

Relations (37)–(39) are exact and in principle hold even for the points $\boldsymbol{x}$, $\boldsymbol{y}$, and $\boldsymbol{R}$ far apart. Physically however, the relation (34) is only useful when carried out locally, and will be applied to the projections of $G(\boldsymbol{x},\boldsymbol{y};T)$ on lattice sites rather than for the Green function itself.

With relations (37)–(39) in hand we can now construct the multipole Green function. Within the independent particle approximation, the dynamical equation (6) is exact and completely general. We now assume we are dealing with an insulator at zero temperature and neglect the spin degrees of freedom; then before any perturbing fields are applied the lesser Green function is given by

$$G^{(0)}(\boldsymbol{x},\boldsymbol{y}) = i\sum_{v}\int_{\mathrm{BZ}} d^3k\,\psi_{v\boldsymbol{k}}(\boldsymbol{x})\psi^*_{v\boldsymbol{k}}(\boldsymbol{y}), \tag{40}$$

where as indicated the integral ranges over the Brillouin zone, and we write $\psi_{n\boldsymbol{k}}(\boldsymbol{x})$ for the unperturbed Bloch function for band index n and crystal momentum $\boldsymbol{k}$,

$$\mathcal{H}_0(\boldsymbol{x})\psi_{n\boldsymbol{k}}(\boldsymbol{x}) = E_{n\boldsymbol{k}}\psi_{n\boldsymbol{k}}(\boldsymbol{x}), \tag{41}$$

normalized according to

$$\int d^3x\,\psi^*_{n\boldsymbol{k}}(\boldsymbol{x})\psi_{n'\boldsymbol{k}'}(\boldsymbol{x}) = \delta_{nn'}\delta(\boldsymbol{k}-\boldsymbol{k}'), \tag{42}$$

where v denotes valence bands. Introducing

$$I^{(1)}(\boldsymbol{x},\boldsymbol{y};T) = U(\boldsymbol{x},\boldsymbol{y};T)G^{(0)}(\boldsymbol{x},\boldsymbol{y};T), \tag{43}$$

where we restrict ourselves to terms in $U(\boldsymbol{x},\boldsymbol{y};T)$ linear in $\boldsymbol{X}(\boldsymbol{x},\boldsymbol{y};T)$, $\boldsymbol{Y}(\boldsymbol{x},\boldsymbol{y};T)$, and $\mathcal{T}(\boldsymbol{x},\boldsymbol{y};T)$, we solve (6) for $G(\boldsymbol{x},\boldsymbol{y};T)$ to linear order in the electromagnetic field, writing the first order correction to $G^{(0)}(\boldsymbol{x},\boldsymbol{y})$ as $G^{(1)}(\boldsymbol{x},\boldsymbol{y};T)$. We find

$$\begin{aligned}G^{(1)}_{n_1\boldsymbol{k}_1;n_2\boldsymbol{k}_2}(T) = {}& \lim_{\eta\to0^+}\frac{1}{i\hbar}\int_{-\infty}^{T} dt'\,I^{(1)}_{n_1\boldsymbol{k}_1;n_2\boldsymbol{k}_2}(t')\\ & \times\exp\left[\frac{i}{\hbar}(E_{n_1\boldsymbol{k}_1}-E_{n_2\boldsymbol{k}_2}-i\eta)(t'-T)\right],\end{aligned} \tag{44}$$

where the Bloch representation of a general function of the form $g(\boldsymbol{x},\boldsymbol{y};T)$ is given in terms of coefficients $g_{n_1\boldsymbol{k}_1;n_2\boldsymbol{k}_2}(T)$ by

$$\begin{aligned}g(\boldsymbol{x},\boldsymbol{y};T) = {}& \sum_{n_1n_2}\int_{\mathrm{BZ}} d^3k_1d^3k_2\,\psi_{n_1\boldsymbol{k}_1}(\boldsymbol{x})\psi^*_{n_2\boldsymbol{k}_2}(\boldsymbol{y})\\ & \times g_{n_1\boldsymbol{k}_1;n_2\boldsymbol{k}_2}(T).\end{aligned} \tag{45}$$

To make use of (37)–(39) we now recast the Green function into the Wannier function representation. We assume that for the material in the ground state a complete, orthonormal set of well localized Wannier functions can be introduced. For the case of nondegenerate bands we consider in this paper, the Wannier and Bloch functions are related through transformations [29]

$$W_{n\boldsymbol{R}}(\boldsymbol{x}) = \sqrt{\frac{V_c}{(2\pi)^3}}\int_{\mathrm{BZ}} d^3k\,e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{n\boldsymbol{k}}(\boldsymbol{x}), \tag{46}$$

$$\psi_{n\boldsymbol{k}}(\boldsymbol{x}) = \sqrt{\frac{V_c}{(2\pi)^3}}\sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}}W_{n\boldsymbol{R}}(\boldsymbol{x}), \tag{47}$$

where V_c is the volume of a unit cell and $\boldsymbol{R}$ labels lattice sites. Introducing a Wannier representation of a general function of the form $g(\boldsymbol{x},\boldsymbol{y};T)$,

$$g(\boldsymbol{x},\boldsymbol{y};T) = \sum_{\substack{n_1n_2\\ \boldsymbol{R}\boldsymbol{R}'}} W_{n_1\boldsymbol{R}}(\boldsymbol{x})W^*_{n_2\boldsymbol{R}'}(\boldsymbol{y})g_{n_1\boldsymbol{R};n_2\boldsymbol{R}'}(T), \tag{48}$$

from (44) we find

$$\begin{aligned}G^{(1)}_{n_1\boldsymbol{R};n_2\boldsymbol{R}'}(T) = {}& \frac{1}{i\hbar}\lim_{\eta\to0^+}\left[\frac{V_c}{(2\pi)^3}\right]^2\int_{\mathrm{BZ}} d^3k_1d^3k_2\int_{-\infty}^{T} dt'\exp\\ & \times\left[\frac{i}{\hbar}\big(E_{n_1\boldsymbol{k}_1}-E_{n_2\boldsymbol{k}_2}-i\eta\big)(t'-T)\right]\\ & \times\sum_{\boldsymbol{R}_1\boldsymbol{R}_2} e^{i\boldsymbol{k}_1\cdot(\boldsymbol{R}-\boldsymbol{R}_1)}e^{i\boldsymbol{k}_2\cdot(\boldsymbol{R}_2-\boldsymbol{R}')}I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(t').\end{aligned} \tag{49}$$

In each term $G^{(1)}_{n_1\boldsymbol{R};n_2\boldsymbol{R}'}(T)$ we now employ the relations (37)–(39) to arrive at the multipole expansions of the interaction with the applied electromagnetic fields around sites $\boldsymbol{R}$ and $\boldsymbol{R}'$. We do this in a symmetric way, taking the average of expansions around sites $\boldsymbol{R}$ and $\boldsymbol{R}'$,

$$I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(t') = \tfrac{1}{2}I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(t',\boldsymbol{R}) + \tfrac{1}{2}I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(t',\boldsymbol{R}'), \tag{50}$$

where the second argument in the bracket indicates an expansion point. Assuming the applied electromagnetic fields to be of the form

$$\begin{aligned}\boldsymbol{E}(\boldsymbol{x},T) &= \boldsymbol{E}(\boldsymbol{x},\omega)e^{-i\omega T} + \boldsymbol{E}(\boldsymbol{x},-\omega)e^{i\omega T},\\ \boldsymbol{B}(\boldsymbol{x},T) &= \boldsymbol{B}(\boldsymbol{x},\omega)e^{-i\omega T} + \boldsymbol{B}(\boldsymbol{x},-\omega)e^{i\omega T},\end{aligned}$$

we find

$$I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(t',\boldsymbol{R}) = I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(\omega,\boldsymbol{R})e^{-i\omega t'} + I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(-\omega,\boldsymbol{R})e^{i\omega t'}, \tag{51}$$

with

$$\begin{aligned} I^{(1)}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(\omega,\boldsymbol{R}) &= i f_{n_2n_1}\langle n_1\boldsymbol{R}_1|\hat{H}^{(1)}_{\boldsymbol{R}}(\omega)|n_2\boldsymbol{R}_2\rangle \\ &+\frac{ie}{\hbar c}\int d^3z_1d^3z_2G^{(0)}(\boldsymbol{z}_1,\boldsymbol{z}_2)\phi(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{R};\omega) \\ &\times[\mathcal{H}_0(\boldsymbol{z}_1)-\mathcal{H}_0(\boldsymbol{z}_2)-\hbar\omega]W^*_{n_1\boldsymbol{R}_1}(\boldsymbol{z}_1)W_{n_2\boldsymbol{R}_2}(\boldsymbol{z}_2). \end{aligned}$$

Here we put

$$\langle n_1\boldsymbol{R}_1|\hat{H}^{(1)}_{\boldsymbol{R}}(\omega)|n_2\boldsymbol{R}_2\rangle = \int d^3z W^*_{n_1\boldsymbol{R}_1}(\boldsymbol{z})\mathcal{H}^{(1)}_{\boldsymbol{R}}(\boldsymbol{z},\omega)W_{n_2\boldsymbol{R}_2}(\boldsymbol{z}),$$

where $\mathcal{H}^{(1)}_{\boldsymbol{R}}(\boldsymbol{z},\omega)$ is the frequency component of the PZW Hamiltonian density (24) that is linear in fields,

$$\begin{aligned} \mathcal{H}^{(1)}_{\boldsymbol{R}}(\boldsymbol{x},\omega) &= \frac{ie\hbar}{2mc}\left[2\Omega^{\boldsymbol{R}}_j(\boldsymbol{x},\omega)\frac{\partial}{\partial x^j}+\frac{\partial\Omega^{\boldsymbol{R}}_j(\boldsymbol{x},\omega)}{\partial x^j}\right] \\ &-e\Omega^{\boldsymbol{R}}_0(\boldsymbol{x},\omega), \end{aligned}$$

and in writing (51) we have employed $\sum_v[\delta_{n_1v}-\delta_{n_2v}] = f_{n_1n_2}$ with $f_{n_1n_2} = f_{n_1}-f_{n_2}$, where the occupation factor $f_n = \sum_v \delta_{nv}$. Carrying out a similar calculation for $I_{n_1\boldsymbol{R}_1,n_2\boldsymbol{R}_2}(t',\boldsymbol{R}')$, using (50) in (49), employing

$$\begin{aligned} \phi(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{R}_1;\omega) &= \phi(\boldsymbol{z}_1,\boldsymbol{z}_2,\boldsymbol{R}_2;\omega)-\phi(\boldsymbol{R}_1,\boldsymbol{z}_2,\boldsymbol{R}_2;\omega) \\ &-\phi(\boldsymbol{z}_1,\boldsymbol{R}_1,\boldsymbol{R}_2;\omega), \end{aligned} \tag{52}$$

and invoking the completeness of Wannier functions we arrive at our final result,

$$G^{(1)}(\boldsymbol{x},\boldsymbol{y};T) = G^{(1)}(\boldsymbol{x},\boldsymbol{y};\omega)e^{-i\omega T}+G^{(1)}(\boldsymbol{x},\boldsymbol{y};-\omega)e^{i\omega T}. \tag{53}$$

The frequency component of the Green function is given by

$$\begin{aligned} &G^{(1)}(\boldsymbol{x},\boldsymbol{y};\omega) \\ &= \frac{e}{c\hbar}\sum_{v\boldsymbol{R}}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};\omega)W_{v\boldsymbol{R}}(\boldsymbol{x})W^*_{v\boldsymbol{R}}(\boldsymbol{y}) \\ &-\frac{e}{2c\hbar}\sum_{\substack{nv\\ \boldsymbol{R}\boldsymbol{R}'}}W_{n\boldsymbol{R}}(\boldsymbol{x})W^*_{v\boldsymbol{R}'}(\boldsymbol{y})\langle n\boldsymbol{R}|\phi(\boldsymbol{R},\boldsymbol{R}';\omega)|v\boldsymbol{R}'\rangle \\ &-\frac{e}{2c\hbar}\sum_{\substack{nv\\ \boldsymbol{R}\boldsymbol{R}'}}W_{v\boldsymbol{R}}(\boldsymbol{x})W^*_{n\boldsymbol{R}'}(\boldsymbol{y})\langle v\boldsymbol{R}|\phi(\boldsymbol{R},\boldsymbol{R}';\omega)|n\boldsymbol{R}'\rangle \\ &+\sum_{\boldsymbol{R}\boldsymbol{R}'}\sum_{n_1n_2}W_{n_1\boldsymbol{R}}(\boldsymbol{x})W^*_{n_2\boldsymbol{R}'}(\boldsymbol{y})f_{n_2n_1}O_{n_1\boldsymbol{R};n_2\boldsymbol{R}'}(\omega), \end{aligned} \tag{54}$$

where we define

$$\begin{aligned} &\langle n_1\boldsymbol{R}|\phi(\boldsymbol{R},\boldsymbol{R}';\omega)|n_2\boldsymbol{R}'\rangle \\ &= \int d^3z W^*_{n_1\boldsymbol{R}}(\boldsymbol{z})\phi(\boldsymbol{z},\boldsymbol{R},\boldsymbol{R}';\omega)W_{n_2\boldsymbol{R}'}(\boldsymbol{z}), \end{aligned}$$

and we put

$$\begin{aligned} O_{n_1\boldsymbol{R};n_2\boldsymbol{R}'}(\omega) &= \frac{1}{i}\sum_{\boldsymbol{R}_1\boldsymbol{R}_2}\left[\frac{V_c}{(2\pi)^3}\right]^2\mathcal{F}^{\boldsymbol{R}\boldsymbol{R}'}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(\omega) \\ &\times\lim_{\eta\to0^+}\int_{\mathrm{BZ}}d^3k_1d^3k_2\frac{e^{i\boldsymbol{k}_1\cdot(\boldsymbol{R}-\boldsymbol{R}_1)}e^{-i\boldsymbol{k}_2\cdot(\boldsymbol{R}'-\boldsymbol{R}_2)}}{E_{n_1\boldsymbol{k}_1}-E_{n_2\boldsymbol{k}_2}-\hbar\omega-i\eta}, \end{aligned}$$

with

$$\begin{aligned} \mathcal{F}^{\boldsymbol{R}\boldsymbol{R}'}_{n_1\boldsymbol{R}_1;n_2\boldsymbol{R}_2}(\omega) &= \tfrac{1}{2}\langle n_1\boldsymbol{R}_1|\hat{H}^{(1)}_{\boldsymbol{R}}(\omega)|n_2\boldsymbol{R}_2\rangle \\ &+\tfrac{1}{2}\langle n_1\boldsymbol{R}_1|\hat{H}^{(1)}_{\boldsymbol{R}'}(\omega)|n_2\boldsymbol{R}_2\rangle. \end{aligned}$$

The Green function (53) is the main result of this section and gives an exact, microscopic information about the charge and current density response to the linear order in EM fields. Although no approximations regarding the spatial variation of the applied fields were made in deriving this result, the multipole expansion of the interaction with the applied fields in (53) is most useful in situations where the electron correlation length is much smaller than the distance over which the electromagnetic field varies significantly; in treating the optical response of materials, this is identified by the wavelength of light.

The response (53) takes a particularly simple form for a static, homogenous electromagnetic field to which we restrict our considerations in the remaining part of the paper. In this special case we note that (20), (21), and (35) reduce to exact expressions

$$\Omega^{\boldsymbol{R}}_0(\boldsymbol{x}) = \boldsymbol{E}\cdot(\boldsymbol{x}-\boldsymbol{R}), \tag{55}$$

$$\boldsymbol{\Omega}^{\boldsymbol{R}}(\boldsymbol{x}) = \tfrac{1}{2}\boldsymbol{B}\times(\boldsymbol{x}-\boldsymbol{R}), \tag{56}$$

$$\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R}) = \tfrac{1}{2}\boldsymbol{B}\cdot[(\boldsymbol{y}-\boldsymbol{R})\times(\boldsymbol{x}-\boldsymbol{R})], \tag{57}$$

where $\boldsymbol{E} = 2\boldsymbol{E}(\omega = 0)$, etc. We now use (55)–(57) in Eq. (53), and evaluate moments of Wannier functions as k-space integrals over Brillouin zone. We find

$$\begin{aligned} G^{(1)}_{\mathrm{DC}}(\boldsymbol{x},\boldsymbol{y}) &= \sum_{n_1n_2}\int_{\mathrm{BZ}}d^3k\psi_{n_1\boldsymbol{k}}(\boldsymbol{x})\psi^*_{n_2\boldsymbol{k}}(\boldsymbol{y})\beta_{n_1n_2}(\boldsymbol{k}) \\ &+\sum_{nv}\int_{\mathrm{BZ}}d^3k\psi_{n\boldsymbol{k}}(\boldsymbol{x})\psi^*_{v\boldsymbol{k}}(\boldsymbol{y})\gamma_{nv}(\boldsymbol{k}) \\ &+\sum_{nv}\int_{\mathrm{BZ}}d^3k\psi_{v\boldsymbol{k}}(\boldsymbol{x})\psi^*_{n\boldsymbol{k}}(\boldsymbol{y})\gamma_{vn}(\boldsymbol{k}) \\ &+\frac{e}{c\hbar}\sum_{v\boldsymbol{R}}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R})W_{v\boldsymbol{R}}(\boldsymbol{x})W^*_{v\boldsymbol{R}}(\boldsymbol{y}), \end{aligned} \tag{58}$$

where we use a notation

$$\begin{aligned} \beta_{n_1n_2}(\boldsymbol{k}) &= ie\frac{f_{n_2n_1}}{E_{n_1n_2}(\boldsymbol{k})}\Big(\boldsymbol{E}\cdot\boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k}) \\ &+\frac{1}{2mc}\boldsymbol{B}\cdot\big[\boldsymbol{L}_{n_1n_2}(\boldsymbol{k})+\boldsymbol{X}_{n_1n_2}(\boldsymbol{k})\big]\Big), \end{aligned} \tag{59}$$

$$\gamma_{n_1n_2}(\boldsymbol{k}) = -\frac{ie}{4c\hbar}\boldsymbol{B}\cdot\boldsymbol{D}_{n_1n_2}(\boldsymbol{k}). \tag{60}$$

Here we define vectors

$$\boldsymbol{L}_{n_1n_2}(\boldsymbol{k}) = \frac{1}{2}\sum_s \boldsymbol{\zeta}_{sn_2}(\boldsymbol{k}) \times \boldsymbol{p}_{n_1s}(\boldsymbol{k}) + \frac{1}{2}\sum_s \boldsymbol{\zeta}_{n_1s}(\boldsymbol{k}) \times \boldsymbol{p}_{sn_2}(\boldsymbol{k}), \tag{61}$$

$$\boldsymbol{X}_{n_1n_2}(\boldsymbol{k}) = \frac{m}{2\hbar}\left[\boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k}) \times \frac{\partial\left(E_{n_1\boldsymbol{k}} + E_{n_2\boldsymbol{k}}\right)}{\partial\boldsymbol{k}}\right], \tag{62}$$

$$\boldsymbol{D}_{n_1n_2}(\boldsymbol{k}) = \frac{\partial}{\partial\boldsymbol{k}} \times \boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k}), \tag{63}$$

and write $\boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k})$ for Berry connection

$$\boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k}) = \frac{1}{V_c}\int_{V_c} d^3x\, u^*_{n_1\boldsymbol{k}}(\boldsymbol{x})\, i\frac{\partial}{\partial\boldsymbol{k}} u_{n_2\boldsymbol{k}}(\boldsymbol{x}),$$

with $u_{n\boldsymbol{k}}(\boldsymbol{x})$ being the periodic part of the Bloch function $\psi_{n\boldsymbol{k}}(\boldsymbol{x}) = (2\pi)^{-3/2}u_{n\boldsymbol{k}}(\boldsymbol{x})e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$, and for the momentum matrix element we put $\langle n_1\boldsymbol{k}|\hat{\boldsymbol{p}}|n_2\boldsymbol{k}'\rangle = \boldsymbol{p}_{n_1n_2}(\boldsymbol{k})\delta(\boldsymbol{k}-\boldsymbol{k}')$. The first term in (58), which involves the difference of Fermi factors $f_{n_2n_1}$, is of the usual type expected in perturbation theory [30], with $\beta_{n_1n_2}(\boldsymbol{k})$ (59) indicating a perturbation energy divided by the energy difference $E_{n_1n_2}(\boldsymbol{k}) = E_{n_1}(\boldsymbol{k}) - E_{n_2}(\boldsymbol{k})$ between two Bloch states, which are eigenstates of the unperturbed Hamiltonian. Recalling that the electric and (*para*)-magnetic dipole moment matrix elements between Wannier functions at the same site, found using (46) and a partial integration, are given by [8]

$$\int d^3x\, W^*_{n\boldsymbol{0}}(\boldsymbol{x})\boldsymbol{x}\, W_{m\boldsymbol{0}}(\boldsymbol{x}) = \frac{V_c}{(2\pi)^3}\int_{\mathrm{BZ}} d^3k\, \boldsymbol{\zeta}_{nm}(\boldsymbol{k}), \tag{64}$$

$$\int d^3x\, W^*_{n\boldsymbol{0}}(\boldsymbol{x})\boldsymbol{x} \times \hat{\boldsymbol{p}}(\boldsymbol{x})W_{m\boldsymbol{0}}(\boldsymbol{x}) = \frac{V_c}{(2\pi)^3}\int_{\mathrm{BZ}} d^3k\, \boldsymbol{L}_{nm}(\boldsymbol{k}), \tag{65}$$

we see that the first two terms on the right-hand side of (59) are what one would expect were appropriate $\boldsymbol{k}$ components of the atomiclike matrix elements (64) and (65) associated with each transition energy $E_{n_1n_2}(\boldsymbol{k})$. Since the group velocity associated with a given band n and wave vector $\boldsymbol{k}$ is given by $\partial E_{n\boldsymbol{k}}/\partial(\hbar\boldsymbol{k})$, the last term on the right-hand side of (59) can be identified as a perturbation term involving the magnetic energy associated with the motion of electrons through the bands. The terms involving $\gamma_{n_1n_2}(\boldsymbol{k})$ in (58) are more complicated, and describe effects due to the variation of the Berry connections throughout the Brillouin zone. The last term in (58) we leave in a real space representation, in which it has a simple form; in the next section we indicate the physical significance of this term.

III. POLARIZATION AND MAGNETIZATION FIELDS ASSOCIATED WITH LATTICE SITES

The microscopic charge and current distribution driven by an applied electromagnetic field can be found using the expression (53) for the Green function. However, when the variation of the applied field is over a length scale much larger than the lattice constant in a normal material, a coarse-grained description with the charge and current densities averaged over the microscopic degrees of freedom is of more interest. For a fluid, this can be an ensemble average [1]; in a solid it can be a spatial average [31]. In the PZW treatment, a coarse-grained description is formulated by introducing the microscopic polarization and magnetization fields (25) and (26) in an electrodynamic approach that is also valid for systems driven out of equilibrium. The definitions (25) and (26) however, although useful in the treatment of isolated atoms and molecules, are not immediately applicable to extended systems like solids. In this section we formulate a generalized description in the spirit of the PZW treatment, where we introduce microscopic polarization and magnetization fields taking into account the motion of electrons between lattice sites. We restrict ourselves here to the case of static, uniform fields and plan to turn to the general case of arbitrary fields in future publications.

The system we consider in this section is described by the Green function $G(\boldsymbol{x},\boldsymbol{y}) = G^{(0)}(\boldsymbol{x},\boldsymbol{y}) + G^{(1)}_{\mathrm{DC}}(\boldsymbol{x},\boldsymbol{y})$, with the ground-state contribution given by (40), and the linear order correction given by (58). The difficulty in introducing polarization and magnetization fields is related to the fact that the charge and current densities that follow from $G(\boldsymbol{x},\boldsymbol{y})$ are not localized. In a material with short electron correlation lengths we can avoid these difficulties by searching for a decomposition of the Green function into contributions associated with lattice sites $G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$, each of which is nonzero only if $\boldsymbol{x}$ and $\boldsymbol{y}$ are within a few lattice constants of $\boldsymbol{R}$. We construct such a decomposition, ensuring that in the isolated atom limit $G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$ reduces to a Green function formed from the transformed field operators (16) introduced in the PZW approach.

The PZW treatment can be applied to a molecular crystal where Wannier functions associated with different lattice sites are assumed to have no common support, and it is equivalent to introducing a gauge-invariant Hamiltonian (33) at each lattice site using the Peierls phase $\Gamma^{\boldsymbol{R}}_{\mathrm{PZW}}(\boldsymbol{x},\boldsymbol{y};T)$. In this limit of a molecular crystal, the global Peierls phase $\Gamma^{\mathrm{GL}}(\boldsymbol{x},\boldsymbol{y};T)$ used to define $G(\boldsymbol{x},\boldsymbol{y};T)$ in Sec. II differs from the PZW phase by a flux term $\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R};T) = \Gamma^{\mathrm{GL}}(\boldsymbol{x},\boldsymbol{y};T) - \Gamma^{\boldsymbol{R}}_{\mathrm{PZW}}(\boldsymbol{x},\boldsymbol{y};T)$ at each $\boldsymbol{R}$. So in the more general problem we seek a decomposition of the form

$$G(\boldsymbol{x},\boldsymbol{y}) = \sum_{\boldsymbol{R}} G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})e^{-\frac{ie}{\hbar c}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R})} \tag{66}$$

in the limit of static, uniform fields [see (35) and (57)]. Here Eq. (66) does not yet define $G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$ uniquely, rather a sum $\sum_{\boldsymbol{R}} G^{(n)}_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$ at each order n in electromagnetic fields. From (40) we see than in the zeroth order we have

$$\sum_{\boldsymbol{R}} G^{(0)}_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) = i\sum_{v\boldsymbol{R}} W_{v\boldsymbol{R}}(\boldsymbol{x})W^*_{v\boldsymbol{R}}(\boldsymbol{y}), \tag{67}$$

and the obvious physical choice of $G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$ before an electromagnetic field is applied is

$$G^{(0)}_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) = i\sum_{v} W_{v\boldsymbol{R}}(\boldsymbol{x})W^*_{v\boldsymbol{R}}(\boldsymbol{y}). \tag{68}$$

Here we consider Wannier functions (46) for an insulator with nondegenerate bands, as the formalism of Sec. II is restricted to that special case. For the first order term we use (58) and

(68) to find

$$\sum_{\boldsymbol{R}} G^{(1)}_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) = \sum_{n_1 n_2} \int_{\mathrm{BZ}} d^3k \psi_{n_1\boldsymbol{k}}(\boldsymbol{x}) \psi^*_{n_2\boldsymbol{k}}(\boldsymbol{y}) \beta_{n_1 n_2}(\boldsymbol{k}) + \sum_{nv} \int_{\mathrm{BZ}} d^3k \psi_{n\boldsymbol{k}}(\boldsymbol{x}) \psi^*_{v\boldsymbol{k}}(\boldsymbol{y}) \gamma_{nv}(\boldsymbol{k}) + \sum_{nv} \int_{\mathrm{BZ}} d^3k \psi_{v\boldsymbol{k}}(\boldsymbol{x}) \psi^*_{n\boldsymbol{k}}(\boldsymbol{y}) \gamma_{vn}(\boldsymbol{k}), \quad (69)$$

showing that the last term in (58) arises from using a global rather than a local Peierls phase for each site. Note that in (67) the Wannier functions provide a Schmidt (biorthogonal) decomposition of the function $\sum_{\boldsymbol{R}} G^{(0)}_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$. Even with the application of an electromagnetic field, we can always seek a Schmidt decomposition of $\sum_{\boldsymbol{R}} G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$. Of course, if there is degeneracy in the amplitudes of the product functions [as there is in (67)], that Schmidt decomposition will not be unique; for example, both Eqs. (40) and (67) provide equivalent Schmidt decompositions of $G^{(0)}(\boldsymbol{x},\boldsymbol{y})$. Nonetheless, at least within a perturbative approach a natural strategy would be to seek a Schmidt decomposition of the form

$$G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) = i \sum_v \tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}) \tilde{W}^*_{v\boldsymbol{R}}(\boldsymbol{y}), \quad (70)$$

where the $\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x})$ are Wannier functions modified by the applied electromagnetic field but still satisfying

$$\int \tilde{W}^*_{v\boldsymbol{R}}(\boldsymbol{x}) \tilde{W}_{v'\boldsymbol{R}}(\boldsymbol{x}) d^3x = \delta_{vv'}. \quad (71)$$

Furthermore, in the special case we consider here, of a perturbative response to uniform fields, we would expect the Wannier functions associated with each lattice site to be identical except for translation; that is $\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}-\boldsymbol{R}) = \tilde{W}_{v\boldsymbol{R}'}(\boldsymbol{x}-\boldsymbol{R}')$. With this assumption we can introduce Bloch functions $\tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x})$ associated with the $\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x})$,

$$\tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x}) = \sqrt{\frac{V_c}{(2\pi)^3}} \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}), \quad (72)$$

satisfying $\tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x})$, and write

$$\sum_{\boldsymbol{R}} G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) = i \sum_v \int_{\mathrm{BZ}} d^3k \tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x}) \tilde{\psi}^*_{v\boldsymbol{k}}(\boldsymbol{y}). \quad (73)$$

These natural assumptions, together with (69), are enough to significantly constrain the possible $\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x})$, as we now show. Noting that in the absence of an applied field $\tilde{\psi}^{(0)}_{v\boldsymbol{k}}(\boldsymbol{x}) = \psi_{v\boldsymbol{k}}(\boldsymbol{x})$ [see (68) and (72)], from (73) and (69) we immediately see than one of the solutions is given by

$$\tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x}) = \phi_{v\boldsymbol{k}}(\boldsymbol{x}) \equiv \psi_{v\boldsymbol{k}}(\boldsymbol{x}) + \frac{1}{i} \sum_c \psi_{c\boldsymbol{k}}(\boldsymbol{x}) \beta_{cv}(\boldsymbol{k}) + \frac{1}{i} \sum_n \psi_{n\boldsymbol{k}}(\boldsymbol{x}) \gamma_{nv}(\boldsymbol{k}). \quad (74)$$

The general solution is a unitary transformation of (74),

$$\tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x}) = \sum_{v'} U_{v'v}(\boldsymbol{k}) \phi_{v'\boldsymbol{k}}(\boldsymbol{x}), \quad U^{(0)}_{v'v}(\boldsymbol{k}) = \delta_{v'v}, \quad (75)$$

which however does not affect the dipole moment contributions to polarization and magnetization, while the higher order moments do not contribute in the case of uniform electromagnetic fields, as we will show in Sec. IV. Thus in the simple case we consider in this paper we can choose $\tilde{\psi}_{v\boldsymbol{k}}(\boldsymbol{x}) = \phi_{v\boldsymbol{k}}(\boldsymbol{x})$. More generally, for nonuniform fields or degenerate energy bands a unitary transformation of the Bloch functions could be considered to minimize the spread of the Wannier function. The modified Wannier function follows from the inverse of (72),

$$\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}) = \sqrt{\frac{V_c}{(2\pi)^3}} \int_{\mathrm{BZ}} d^3k e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \phi_{v\boldsymbol{k}}(\boldsymbol{x}), \quad (76)$$

and the lattice-site Green function (70) can be constructed. The charge and current densities that correspond to it,

$$\rho_{\boldsymbol{R}}(\boldsymbol{x}) = -ieG_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{x}), \quad (77)$$

$$j^k_{\boldsymbol{R}}(\boldsymbol{x}) = -\frac{ie}{2m} \lim_{\boldsymbol{y}\to\boldsymbol{x}} \left[\frac{\hbar}{i} \frac{\partial}{\partial x^k} - \frac{\hbar}{i} \frac{\partial}{\partial y^k} \right] G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) + \frac{ie^2}{mc} \Omega^{\boldsymbol{R}}_k(\boldsymbol{x}) G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{x}), \quad (78)$$

when summed over lattice sites lead to the total charge and current densities

$$\rho(\boldsymbol{x}) = \sum_{\boldsymbol{R}} \rho_{\boldsymbol{R}}(\boldsymbol{x}), \quad j^k(\boldsymbol{x}) = \sum_{\boldsymbol{R}} j^k_{\boldsymbol{R}}(\boldsymbol{x}). \quad (79)$$

The densities $\rho_{\boldsymbol{R}}(\boldsymbol{x})$ and $\boldsymbol{j}_{\boldsymbol{R}}(\boldsymbol{x})$ [(77) and (78)] are localized about $\boldsymbol{R}$ and their moments are well defined. We can thus use them to introduce polarization and local circulation magnetization fields, in an approach that follows the PZW definitions (25) and (26). We write

$$p^i_{\boldsymbol{R}}(\boldsymbol{x}) = \int d^3y s^i(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R}) \rho_{\boldsymbol{R}}(\boldsymbol{y}), \quad (80)$$

$$m^i_{\boldsymbol{R}}(\boldsymbol{x}) = \frac{1}{c} \int d^3y \alpha^{ik}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R}) j^k_{\boldsymbol{R}}(\boldsymbol{y}), \quad (81)$$

where the functions $s^i(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})$ and $\alpha^{ik}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})$ are given by (22) and (23), and satisfy relations

$$\frac{\partial s^i(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})}{\partial x^i} = -\delta(\boldsymbol{x}-\boldsymbol{y}) + \delta(\boldsymbol{x}-\boldsymbol{R}), \quad (82)$$

$$\frac{\partial s^i(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})}{\partial y^k} = \delta^{ik}\delta(\boldsymbol{x}-\boldsymbol{y}) - \epsilon^{ipj} \frac{\partial \alpha^{jk}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})}{\partial x^p}, \quad (83)$$

where $\boldsymbol{R}$ is a lattice site. Using relations (82) and (83) we can rewrite the charge and current densities as

$$\rho(\boldsymbol{x}) = -\sum_{\boldsymbol{R}} \nabla \cdot \boldsymbol{p}_{\boldsymbol{R}}(\boldsymbol{x}) + \rho_{\mathrm{ref}}(\boldsymbol{x}), \quad (84)$$

$$\boldsymbol{j}(\boldsymbol{x}) = c \sum_{\boldsymbol{R}} \nabla \times \boldsymbol{m}_{\boldsymbol{R}}(\boldsymbol{x}) + \tilde{\boldsymbol{j}}(\boldsymbol{x}), \quad (85)$$

where we define the reference charge density,

$$\rho^{\mathrm{ref}}(\boldsymbol{x}) = \sum_{\boldsymbol{R}} \delta(\boldsymbol{x}-\boldsymbol{R}) Q_{\boldsymbol{R}}, \quad Q_{\boldsymbol{R}} = \int d^3y \rho_{\boldsymbol{R}}(\boldsymbol{y}), \quad (86)$$

and an additional current density,

$$\tilde{\boldsymbol{j}}(\boldsymbol{x}) = -\sum_{\boldsymbol{R}} \int d^3y\, \boldsymbol{s}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})\Theta_{\boldsymbol{R}}(\boldsymbol{y}). \tag{87}$$

A term $\partial \boldsymbol{p}_{\boldsymbol{R}}/\partial T$ would normally be present on the right-hand side of (84), but is absent because we have assumed that all fields are time independent. Were that time dependence reintroduced, both $\Theta_{\boldsymbol{R}}(\boldsymbol{x})$ and $\tilde{\boldsymbol{j}}(\boldsymbol{x})$ would also become time dependent, with $\Theta_{\boldsymbol{R}}(\boldsymbol{x},T) = \partial\rho_{\boldsymbol{R}}(\boldsymbol{x},T)/\partial T + \nabla\cdot\boldsymbol{j}_{\boldsymbol{R}}(\boldsymbol{x},T)$; in the time-independent problem we consider here, $\Theta_{\boldsymbol{R}}(\boldsymbol{x}) = \nabla\cdot\boldsymbol{j}_{\boldsymbol{R}}(\boldsymbol{x})$. This term thus describes the fact that although the total charge-current density $(\rho(\boldsymbol{x}),\boldsymbol{j}(\boldsymbol{x}))$ naturally satisfies the continuity equation, the individual charge-current densities we have introduced, $(\rho_{\boldsymbol{R}}(\boldsymbol{x}),\boldsymbol{j}_{\boldsymbol{R}}(\boldsymbol{x}))$, need not. And so we can identify $\tilde{\boldsymbol{j}}(\boldsymbol{x})$ as a current associated with the motion of electrons between sites, or a "hopping current" for short. Using (70) and (78) we find

$$\Theta_{\boldsymbol{R}}(\boldsymbol{x}) = \frac{ie}{\hbar}\sum_{v} \tilde{W}^*_{v\boldsymbol{R}}(\boldsymbol{x})\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x})\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}) + \text{c.c.}, \tag{88}$$

where $\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x})$ is the static limit of the PZW Hamiltonian (24) associated with site $\boldsymbol{R}$,

$$\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x}) = \frac{1}{2m}\left[\boldsymbol{p}(\boldsymbol{x}) - \frac{e}{2c}\boldsymbol{B}\times(\boldsymbol{x}-\boldsymbol{R})\right]^2 + V(\boldsymbol{x}) \\ - e\boldsymbol{E}\cdot(\boldsymbol{x}-\boldsymbol{R}).$$

Equation (88) is valid in general for the Green function decomposition of the form (66) and (70), with the densities defined through (77) and (78). However, since we identified the modified Wannier functions (76) only up to linear order in the applied electromagnetic fields, when using Eq. (76) in (88) only terms up to linear order should be kept; this applies also to the remaining equations in this section, for which we drop the subscripts indicating the order of the perturbation theory for a clearer notation.

Equation (85) is not yet in its final form. For a collection of isolated molecules $\Theta_{\boldsymbol{R}}(\boldsymbol{x}) = \tilde{\boldsymbol{j}}(\boldsymbol{x}) = 0$, and then $\boldsymbol{m}_{\boldsymbol{R}}(\boldsymbol{x})$ given by (81) is the total contribution to the magnetization per lattice site; but this is not the case for a solid where the hopping current $\tilde{\boldsymbol{j}}(\boldsymbol{x})$ gives rise to the itinerant part of magnetization. We note that physically the change in the charge-current densities leading to the violation of the "site continuity equation" $\Theta_{\boldsymbol{R}}(\boldsymbol{x})$ should be understood as the influx of charge from neighboring sites diminished by the outflow to other sites. To identify the hopping matrix elements in the presence of external electromagnetic fields, we first need to establish the dynamical equation satisfied by the lattice-site Green function. Using the decomposition (66) in (6) together with relations (37)–(39) we have in the static case

$$\sum_{\boldsymbol{R}} e^{-\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R})}[\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x}) - \mathcal{H}^*_{\boldsymbol{R}}(\boldsymbol{y})]G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y}) = 0. \tag{89}$$

Now we only need to integrate out one of the variables in (89). This can be easily done since the Wannier functions (76), rather than being orthonormal, satisfy

$$\int d^3x\, \tilde{W}^*_{v_1\boldsymbol{R}_1}(\boldsymbol{x})\tilde{W}_{v_2\boldsymbol{R}_2}(\boldsymbol{x})e^{-\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{R}_1,\boldsymbol{R}_2)} = \delta_{v_1v_2}\delta_{\boldsymbol{R}_1\boldsymbol{R}_2} \tag{90}$$

up to linear order. We note here that the relation (90) guarantees indempotency of the usual gauge-dependent density matrix $-iG^{\text{GD}}(\boldsymbol{x},\boldsymbol{y};T) = -iG(\boldsymbol{x},\boldsymbol{y};T)e^{i\Phi(\boldsymbol{x},\boldsymbol{y};T)}$, with $G(\boldsymbol{x},\boldsymbol{y};T)$ given by (66) and (70). Multiplying now both sides of Eq. (89) by $\exp[\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{y},\boldsymbol{R}')]\tilde{W}_{v'\boldsymbol{R}'}(\boldsymbol{y})$, using (52) and (90) and integrating over space, we arrive at

$$\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x})\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}) = \sum_{v'\boldsymbol{R}'} t^{v'v}_{\boldsymbol{R}'\boldsymbol{R}}\tilde{W}_{v'\boldsymbol{R}'}(\boldsymbol{x})e^{-\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{R},\boldsymbol{R}')},$$

with the hopping matrix elements

$$t^{v'v}_{\boldsymbol{R}'\boldsymbol{R}} = \int d^3x\, \tilde{W}^*_{v'\boldsymbol{R}'}(\boldsymbol{x})e^{-\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{R}',\boldsymbol{R})}\mathcal{H}_{\boldsymbol{R}}(\boldsymbol{x})\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x}) \\ = \int d^3x\, \tilde{W}^*_{v'\boldsymbol{R}'}(\boldsymbol{x})\mathcal{H}_{\boldsymbol{R}'}(\boldsymbol{x})e^{-\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{R}',\boldsymbol{R})}\tilde{W}_{v\boldsymbol{R}}(\boldsymbol{x})$$

satisfying $[t^{v'v}_{\boldsymbol{R}'\boldsymbol{R}}]^* = t^{vv'}_{\boldsymbol{R}\boldsymbol{R}'}$. Having identified the hopping matrix elements it is now straightforward to construct a decomposition

$$\Theta_{\boldsymbol{R}}(\boldsymbol{x}) = \sum_{\boldsymbol{R}'}[\Theta_{\boldsymbol{R}'\boldsymbol{R}}(\boldsymbol{x}) - \Theta_{\boldsymbol{R}\boldsymbol{R}'}(\boldsymbol{x})] \tag{91}$$

of the function (88), where

$$\Theta_{\boldsymbol{R}'\boldsymbol{R}}(\boldsymbol{x}) = \frac{ie}{\hbar}\sum_{vv'} t^{v'v}_{\boldsymbol{R}'\boldsymbol{R}}\tilde{W}^*_{v\boldsymbol{R}}(\boldsymbol{x})\tilde{W}_{v'\boldsymbol{R}'}(\boldsymbol{x})e^{-\frac{ie}{c\hbar}\phi(\boldsymbol{x},\boldsymbol{R},\boldsymbol{R}')}$$

describes the motion of charge from $\boldsymbol{R}'$ to $\boldsymbol{R}$. From (91) we now see that the hopping current (87) is an inherently two-site quantity, and we can identify the part of $\tilde{\boldsymbol{j}}(\boldsymbol{x})$ associated with hopping between sites $\boldsymbol{R}$ and $\boldsymbol{R}'$,

$$\tilde{\boldsymbol{j}}_{\boldsymbol{R}\boldsymbol{R}'}(\boldsymbol{x}) = -\frac{1}{2}\int d^3y[\Theta_{\boldsymbol{R}'\boldsymbol{R}}(\boldsymbol{y}) - \Theta_{\boldsymbol{R}\boldsymbol{R}'}(\boldsymbol{y})] \\ \times [\boldsymbol{s}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R}) - \boldsymbol{s}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R}')]. \tag{92}$$

Assigning half of the current (92) to site $\boldsymbol{R}$ and half to $\boldsymbol{R}'$, we put

$$\tilde{\boldsymbol{j}}_{\boldsymbol{R}}(\boldsymbol{x}) = \frac{1}{2}\sum_{\boldsymbol{R}'}[\tilde{\boldsymbol{j}}_{\boldsymbol{R}\boldsymbol{R}'}(\boldsymbol{x}) + \tilde{\boldsymbol{j}}_{\boldsymbol{R}'\boldsymbol{R}}(\boldsymbol{x})]. \tag{93}$$

The current (93) is divergenceless and thus can be represented as the curl of an itinerant magnetization

$$\tilde{m}^i_{\boldsymbol{R}}(\boldsymbol{x}) = \frac{1}{c}\int d^3y\, \alpha^{ik}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R})\tilde{j}^k_{\boldsymbol{R}}(\boldsymbol{y}). \tag{94}$$

We now arrive at the final representation of the charge and current densities,

$$\rho(\boldsymbol{x}) = -\sum_{\boldsymbol{R}}\nabla\cdot\boldsymbol{p}_{\boldsymbol{R}}(\boldsymbol{x}), \tag{95}$$

$$\boldsymbol{j}(\boldsymbol{x}) = c\sum_{\boldsymbol{R}}\nabla\times[\boldsymbol{m}_{\boldsymbol{R}}(\boldsymbol{x}) + \tilde{\boldsymbol{m}}_{\boldsymbol{R}}(\boldsymbol{x})], \tag{96}$$

where to write (95) we use the fact that in linear response the reference charge density (86) vanishes after the ionic background is included. The polarization and magnetization fields in Eqs. (95) and (96) serve as a basis for constructing a multipole expansion of the charge and current distributions that when spatially averaged leads to a macroscopic description of a system.

IV. MULTIPOLE EXPANSION OF POLARIZATION AND MAGNETIZATION FIELDS

We are interested in applying the formalism of Sec. III and its generalizations to problems where normal materials are subject to radiation with wavelengths in the optical regime or longer. In general any polarization and magnetization fields that describe charge-current densities not confined in space must be linked with those densities in a nonlocal way [25]. But for normal materials the Green function $G(\boldsymbol{x},\boldsymbol{y};T)$ can be expected to vanish as the distance between $\boldsymbol{x}$ and $\boldsymbol{y}$ is increased beyond a few lattice spacings, and the $G_{\boldsymbol{R}}(\boldsymbol{x},\boldsymbol{y})$ (70) constructed perturbatively from (68) can be expected to vanish for $\boldsymbol{x}$ and $\boldsymbol{y}$ removed from $\boldsymbol{R}$ by a few lattice spacings, a distance over which the electromagnetic field varies little. A multipole expansion of the charge and current densities associated with each site $\boldsymbol{R}$ within the expressions for polarization and magnetization fields can then be successfully introduced which, when complemented with a spatial averaging procedure to define macroscopic fields, gives a macroscopic description of the material response. In this section we construct the multipole expansion for the static case of Sec. III. We confirm that within our approach we recover the earlier results for the ground-state polarization and magnetization [4,8], the electric susceptibility [22,23], the magnetoelectric response [10], and the magnetic susceptibility [12].

We start by using the Dirac δ expansion (27) in the expressions (80) and (81) to find

$$p^i_{\boldsymbol{R}}(\boldsymbol{x}) = \mu^i_{\boldsymbol{R}}\delta(\boldsymbol{x}-\boldsymbol{R}) - q^{ij}_{\boldsymbol{R}}\frac{\partial}{\partial x^j}\delta(\boldsymbol{x}-\boldsymbol{R}) + \cdots, \tag{97}$$

$$m^i_{\boldsymbol{R}}(\boldsymbol{x}) = \boldsymbol{\nu}^i_{\boldsymbol{R}}\delta(\boldsymbol{x}-\boldsymbol{R}) + \cdots, \tag{98}$$

where the dipole, quadrupole, and the local circulation magnetic dipole moment are given by (30), (31), and (32) with the charge and current density operators replaced by $\rho_{\boldsymbol{R}}(\boldsymbol{x})$ and $\boldsymbol{j}_{\boldsymbol{R}}(\boldsymbol{x})$. For the itinerant magnetization (94) we first do the integral $\int d^3y\alpha^{ik}(\boldsymbol{x},\boldsymbol{y};\boldsymbol{R}_1)s^k(\boldsymbol{y},z;\boldsymbol{R}_2)$ and then keeping the lowest term in the expansions around $u(\boldsymbol{R}_2-\boldsymbol{R}_1)$ and $u'(z-\boldsymbol{R}_2)$ we get

$$\tilde{m}_{\boldsymbol{R}}(\boldsymbol{x}) = \delta(\boldsymbol{x}-\boldsymbol{R})\tilde{\boldsymbol{\nu}}_{\boldsymbol{R}} + \cdots, \tag{99}$$

with the itinerant magnetic dipole moment given by

$$\begin{aligned}\tilde{\boldsymbol{\nu}}_{\boldsymbol{R}} = \frac{1}{4c}\sum_{\boldsymbol{R}'}(\boldsymbol{R}'-\boldsymbol{R}) \times \int d^3z(z-\boldsymbol{R})\\ \times [\Theta_{\boldsymbol{R}'\boldsymbol{R}}(z) - \Theta_{\boldsymbol{R}\boldsymbol{R}'}(z)].\end{aligned} \tag{100}$$

The expansions (97), (98), and (99) need to be complemented with an appropriate coarse-graining procedure. We do this in the standard way [31] by defining macroscopic fields $g^{\text{mac}}(\mathbf{x})$ in terms of the corresponding microscopic fields $g(\mathbf{x})$ by spatial averaging,

$$g^{\text{mac}}(\boldsymbol{x}) = \int w(\boldsymbol{x}-\boldsymbol{x}')g(\boldsymbol{x}')d^3x',$$

where we take $w(\mathbf{x}) = w(|\mathbf{x}|)$ to be a smooth function, peaked at $|\mathbf{x}| = 0$, normalized according to $\int w(\boldsymbol{x})d^3x = 1$, and nonvanishing only for $|\mathbf{x}| \lesssim \Delta$, where the range Δ satisfies

$$a \ll \Delta \ll \lambda, \tag{101}$$

with a on the order of a lattice constant and λ indicates the range of variation of the fields one wants to describe at the macroscopic level; in optical problems, for example, it could be taken to be the wavelength of light. The detailed form of the function $w(\mathbf{x})$ is unimportant. From Eqs. (95) and (96) we then have

$$\begin{aligned}\rho^{\text{mac}}(\boldsymbol{x}) &= -\nabla\cdot\boldsymbol{\mathcal{P}}(\boldsymbol{x}),\\ \boldsymbol{j}^{\text{mac}}(\boldsymbol{x}) &= c\nabla\times\boldsymbol{\mathcal{M}}(\boldsymbol{x}),\end{aligned}$$

where using (97), (98), and (99) we have for the macroscopic polarization and magnetization fields

$$\boldsymbol{\mathcal{P}}(\boldsymbol{x}) = \boldsymbol{P}(\boldsymbol{x}) - \nabla\cdot\mathsf{Q}(\boldsymbol{x}) + \cdots, \tag{102}$$

$$\boldsymbol{\mathcal{M}}(\boldsymbol{x}) = \boldsymbol{M}(\boldsymbol{x}) + \cdots, \tag{103}$$

with

$$\begin{aligned}\boldsymbol{P}(\boldsymbol{x}) &= \sum_{\boldsymbol{R}} w(\boldsymbol{x}-\boldsymbol{R})\boldsymbol{\mu}_{\boldsymbol{R}},\\ \mathsf{Q}^{ij}(\boldsymbol{x}) &= \sum_{\boldsymbol{R}} w(\boldsymbol{x}-\boldsymbol{R})q^{ij}_{\boldsymbol{R}},\\ \boldsymbol{M}(\boldsymbol{x}) &= \sum_{\boldsymbol{R}} w(\boldsymbol{x}-\boldsymbol{R})(\boldsymbol{\nu}_{\boldsymbol{R}} + \tilde{\boldsymbol{\nu}}_{\boldsymbol{R}}).\end{aligned}$$

The terms surviving in (102) and (103) result from the terms kept in the use of the expansion (27); in general more could be included. Expansions such as (102) and (103) are common in the discussion of the electrodynamics of fluids, where the macroscopic fields are traditionally defined via ensemble averages [1]. In the case we consider here, with uniform electric and magnetic fields, the multipole moments are independent of lattice site $\boldsymbol{\mu}_{\boldsymbol{R}} = \boldsymbol{\mu}$, etc., and taking the sum over all lattice sites of $w(\mathbf{x}-\mathbf{R})$ to be essentially independent of $\mathbf{x}$ by virtue of (101), $\boldsymbol{P}(\boldsymbol{x}) = \boldsymbol{P}$, etc., we have

$$\boldsymbol{\mathcal{P}} = n\boldsymbol{\mu}, \tag{104}$$

$$\boldsymbol{\mathcal{M}} = n(\boldsymbol{\nu} + \tilde{\boldsymbol{\nu}}), \tag{105}$$

where n is the number density of lattice sites.

We now explicitly evaluate the moments in (104) and (105) to find the ground state contributions, the electric and magnetic susceptibilities, and the magnetoelectric tensor, defined as coefficients in the expansion

$$\begin{aligned}\mathcal{P}^i &= \mathcal{P}^i_{(0)} + \chi^{ij}_E E_j + \tilde{\alpha}^{ij}B_j,\\ \mathcal{M}^i &= \mathcal{M}^i_{(0)} + \chi^{ij}_B B_j + \tilde{\alpha}^{ji}E_j.\end{aligned}$$

For the ground state contribution to polarization and magnetization we find

$$\boldsymbol{\mathcal{P}}_{(0)} = e\sum_v\int_{\text{BZ}}\frac{d^3k}{(2\pi)^3}\boldsymbol{\zeta}_{vv}(\boldsymbol{k}), \tag{106}$$

$$\boldsymbol{\mathcal{M}}_{(0)} = e\sum_v\int_{\text{BZ}}\frac{d^3k}{(2\pi)^3}\boldsymbol{J}_{vv}(\boldsymbol{k}), \tag{107}$$

in agreement with King-Smith *et al.* [4] and Thonhauser *et al.* [8] and where we have introduced a shorthand

$$\boldsymbol{J}_{n_1n_2}(\boldsymbol{k}) = \frac{1}{2mc}\big[\boldsymbol{L}_{n_1n_2}(\boldsymbol{k}) + \boldsymbol{X}_{n_1n_2}(\boldsymbol{k})\big]. \tag{108}$$

Identifying the term in the expression for the polarization proportional to the electric field we find the electric susceptibility

$$\chi_E^{ij} = \sum_{n_1n_2}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{e^2 f_{n_2n_1}}{E_{n_1n_2}(\boldsymbol{k})}\zeta^i_{n_2n_1}(\boldsymbol{k})\zeta^j_{n_1n_2}(\boldsymbol{k}), \tag{109}$$

in agreement with Sipe *et al.* [22,23]. The magnetoelectric tensor we calculate both as a response of the electric dipole moment to the magnetic field and the magnetic dipole with respect to electric field; the result is

$$\begin{aligned}\tilde{\alpha}^{ij} &= \sum_{n_1n_2}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{e^2 f_{n_2n_1}}{E_{n_1n_2}(\boldsymbol{k})}\zeta^i_{n_2n_1}(\boldsymbol{k})J^j_{n_1n_2}(\boldsymbol{k})\\ &\quad - \frac{e^2}{2c\hbar}\mathrm{Re}\sum_{nv}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\zeta^i_{vn}(\boldsymbol{k})D^j_{nv}(\boldsymbol{k}),\end{aligned} \tag{110}$$

and agrees with that of Malashevich *et al.* [10] for the simple case of nondegenerate bands that we consider in this paper and in the limit where screening effects are neglected. The magnetic susceptibility tensor we write as a sum of four terms,

$$\chi_B^{ij} = \chi_a^{ij} + \chi_b^{ij} + \chi_c^{ij} + \chi_d^{ij}. \tag{111}$$

The first two terms are given by

$$\chi_a^{ij} = \sum_{n_1n_2}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{e^2 f_{n_2n_1}}{E_{n_1n_2}(\boldsymbol{k})}J^i_{n_2n_1}(\boldsymbol{k})J^j_{n_1n_2}(\boldsymbol{k}), \tag{112}$$

$$\begin{aligned}\chi_b^{ij} &= -\frac{e^2}{4mc^2}\sum_{nv}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\Big[\delta^{ij}\boldsymbol{\zeta}_{vn}(\boldsymbol{k})\cdot\boldsymbol{\zeta}_{nv}(\boldsymbol{k})\\ &\quad -\frac{1}{2}\big(\zeta^j_{vn}(\boldsymbol{k})\zeta^i_{nv}(\boldsymbol{k}) + \zeta^j_{nv}(\boldsymbol{k})\zeta^i_{vn}(\boldsymbol{k})\big)\Big],\end{aligned} \tag{113}$$

and in the limit of isolated atoms they reduce, respectively, to the usual paramagnetic and diamagnetic atomic susceptibilities. The remaining two terms involve itinerant currents, in that they would disappear were the Wannier functions at different sites to have no common support. They are given by

$$\begin{aligned}\chi_c^{ij} &= -\frac{e^2}{c\hbar}\mathrm{Re}\sum_{nv}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\Big\{J^i_{vn}(\boldsymbol{k})D^j_{nv}(\boldsymbol{k})\\ &\quad + \frac{1}{8c\hbar}E_{vn}(\boldsymbol{k})D^i_{vn}(\boldsymbol{k})D^j_{nv}(\boldsymbol{k})\Big\},\end{aligned} \tag{114}$$

$$\begin{aligned}\chi_d^{ij} &= \frac{e^2}{8\hbar^2c^2}\sum_{nv}\epsilon^{iml}\epsilon^{jus}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{\partial^2 E_{v\boldsymbol{k}}}{\partial k^l\partial k^s}\\ &\quad\times\big[\zeta^m_{vn}(\boldsymbol{k})\zeta^u_{nv}(\boldsymbol{k}) + \zeta^u_{vn}(\boldsymbol{k})\zeta^m_{nv}(\boldsymbol{k})\big],\end{aligned} \tag{115}$$

where the curly bracket indicates a symmetrization in i, j indices,

$$\{A^iB^j\} = \{A^jB^i\} = \tfrac{1}{2}(A^iB^j + A^jB^i). \tag{116}$$

Equation (111) is in agreement with the earlier result found for crystals assumed to have a cubic symmetry and derived using energy considerations [12].

The gauge transformation of Eqs. (106)–(110) was discussed in earlier works [4,8,10]. We now show that the form (111) of the magnetic susceptibility for a crystal of arbitrary symmetry is explicitly gauge invariant; to this end we introduce "gauge-covariant" matrix elements $\boldsymbol{\mathcal{J}}_{n_1n_2}(\boldsymbol{k})$ and $\boldsymbol{\mathcal{D}}_{n_1n_2}(\boldsymbol{k})$,

$$\begin{aligned}\boldsymbol{\mathcal{J}}_{n_1n_2}(\boldsymbol{k}) &= \frac{1-\delta_{n_1n_2}}{4c\hbar}\boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k})\times\frac{\partial\big(E_{n_1\boldsymbol{k}} + E_{n_2\boldsymbol{k}}\big)}{\partial\boldsymbol{k}}\\ &\quad + \frac{1}{4mc}\sum_{s\neq n_2}\boldsymbol{\zeta}_{sn_2}(\boldsymbol{k})\times\boldsymbol{p}_{n_1s}(\boldsymbol{k})\\ &\quad + \frac{1}{4mc}\sum_{s\neq n_1}\boldsymbol{\zeta}_{n_1s}(\boldsymbol{k})\times\boldsymbol{p}_{sn_2}(\boldsymbol{k}),\end{aligned} \tag{117}$$

$$\boldsymbol{\mathcal{D}}_{n_1n_2}(\boldsymbol{k}) = i\sum_{s\neq n_1,n_2}\boldsymbol{\zeta}_{n_1s}(\boldsymbol{k})\times\boldsymbol{\zeta}_{sn_2}(\boldsymbol{k}), \tag{118}$$

that differ from $\boldsymbol{J}_{n_1n_2}(\boldsymbol{k})$, $\boldsymbol{D}_{n_1n_2}(\boldsymbol{k})$ [(108) and (63)] by the absence of diagonal Berry connections [see (A1) and (A2)]. The susceptibility tensor (111) we now write as

$$\chi_B^{ij} = \tilde{\chi}_a^{ij} + \tilde{\chi}_b^{ij} + \tilde{\chi}_c^{ij} + \tilde{\chi}_d^{ij} + \tilde{\chi}_e^{ij}, \tag{119}$$

where the first four terms

$$\tilde{\chi}_a^{ij} = \sum_{n_1n_2}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{e^2 f_{n_2n_1}}{E_{n_1n_2}(\boldsymbol{k})}\mathcal{J}^i_{n_2n_1}(\boldsymbol{k})\mathcal{J}^j_{n_1n_2}(\boldsymbol{k}), \tag{120}$$

$$\begin{aligned}\tilde{\chi}_b^{ij} &= -\frac{e^2}{4mc^2}\sum_{\substack{nv\\ n\neq v}}\int\frac{d^3k}{(2\pi)^3}\Big[\delta^{ij}\boldsymbol{\zeta}_{vn}(\boldsymbol{k})\cdot\boldsymbol{\zeta}_{nv}(\boldsymbol{k})\\ &\quad -\frac{1}{2}\big(\zeta^j_{vn}(\boldsymbol{k})\zeta^i_{nv}(\boldsymbol{k}) + \zeta^j_{nv}(\boldsymbol{k})\zeta^i_{vn}(\boldsymbol{k})\big)\Big],\end{aligned} \tag{121}$$

$$\begin{aligned}\tilde{\chi}_c^{ij} &= -\frac{e^2}{c\hbar}\mathrm{Re}\sum_{nv}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\Big\{\mathcal{J}^i_{vn}(\boldsymbol{k})\mathcal{D}^j_{nv}(\boldsymbol{k})\\ &\quad + \frac{1}{8c\hbar}E_{vn}(\boldsymbol{k})\mathcal{D}^i_{vn}(\boldsymbol{k})\mathcal{D}^j_{nv}(\boldsymbol{k})\Big\},\end{aligned} \tag{122}$$

$$\begin{aligned}\tilde{\chi}_d^{ij} &= \frac{e^2}{8\hbar^2c^2}\sum_{\substack{nv\\ n\neq v}}\epsilon^{iml}\epsilon^{jus}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{\partial^2 E_{v\boldsymbol{k}}}{\partial k^l\partial k^s}\\ &\quad\times\big[\zeta^m_{vn}(\boldsymbol{k})\zeta^u_{nv}(\boldsymbol{k}) + \zeta^u_{vn}(\boldsymbol{k})\zeta^m_{nv}(\boldsymbol{k})\big],\end{aligned} \tag{123}$$

differ from (112)–(115) in that the diagonal Berry connections are now excluded; the excluded terms we collect and using appropriate sum rules outlined in the Appendix rewrite as

$$\tilde{\chi}_e^{ij} = -\frac{e^2}{2c\hbar}\sum_{v}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\big\{\mathcal{J}^i_{vv}(\boldsymbol{k})\mathcal{D}^j_{vv}(\boldsymbol{k})\big\}. \tag{124}$$

V. DISCUSSION AND FUTURE OUTLOOK

We have presented a microscopic description of the linear response of a crystal to electromagnetic fields that is based entirely on electrodynamic considerations. Our starting point was a gauge-invariant Green function [25] with a Peierls phase defined only in terms of the coordinates of the Green function. In the neighborhood of each lattice site the phase was rewritten as the Power-Zienau-Wooley (PZW) phase modified by a flux of the magnetic field, with the lattice site being the special point of the transformation. An expansion of applied fields around the lattice sites within the Green function followed in a natural way, and microscopic charge and current densities could be extracted for the response of the system exposed to time and spatially varying electromagnetic fields.

Restricting ourselves then to static and uniform electric and magnetic fields, we introduced microscopic polarization and magnetization fields associated with each site, taking into account the itinerant current "between" lattice sites that gives an additional contribution to the magnetization. Macroscopic polarization and magnetization fields were introduced as spatial averages of the microscopic fields. The results that followed for the macroscopic polarization and magnetization, both before any field is applied as well as in linear response, are all in agreement with accepted expressions. Expressions for the ground state polarization and magnetization, and the diagonal and mixed susceptibilities, have all been derived within a single framework and based on purely electrodynamic considerations.

The description of the response of solids to time-varying and spatially varying electromagnetic fields—where for transverse fields the former necessarily implies the latter through the Maxwell equations—is an outstanding problem in the optical response of materials. A formal expansion of the minimal-coupling Hamiltonian in terms of the wave vector of the applied fields is an obvious strategy and always a possible approach, but it offers little physical insight, and since the calculations are made for a particular choice of the scalar and vector potentials they are generally not manifestly gauge invariant. In contrast, only the electromagnetic fields appear in a PZW approach. But even in the usual PZW treatment of molecular fluids, nonunique polarization and magnetization fields arise once spatially varying applied fields are introduced, and moments beyond the first of the molecular charge and current densities appear in the description. Nonetheless, a unambiguous account results for both the charge and current densities in the bulk of the material, and the physics of interfaces involving such calculations as the intensity of reflected light [19,32].

In the extended PZW approach of a solid we initiate here the situation is even more complicated, but the nonuniqueness of the higher order moments of the Wannier functions does mirror that of the nonuniqueness of the higher order moments in molecular fluids. Whether the generalization of the formalism to treat optical response could provide an unambiguous account of both the charge and current densities in the bulk, and the optical properties of interfaces, is an open question and beyond the scope of this paper. But the success of such an extended PZW approach in describing all the linear response properties in the limit of static and uniform fields is promising, and its demonstration here provides an introduction to a strategy for addressing the outstanding problem of the optical response of solids to time-dependent and spatially varying electric and magnetic fields.

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APPENDIX

In this Appendix we prove the equivalence of Eqs. (111) and (119). We first establish relations between the vectors $\boldsymbol{J}_{n_1n_2}(\boldsymbol{k})$, $\boldsymbol{D}_{n_1n_2}(\boldsymbol{k})$ [(108) and (63)], and the gauge-covariant vectors $\boldsymbol{\mathcal{J}}_{n_1n_2}(\boldsymbol{k})$, $\boldsymbol{\mathcal{D}}_{n_1n_2}(\boldsymbol{k})$ [(117) and (118)],

$$\begin{aligned}\boldsymbol{J}_{n_1n_2}(\boldsymbol{k}) = \boldsymbol{\mathcal{J}}_{n_1n_2}(\boldsymbol{k}) + \frac{\delta_{n_1n_2}}{2c\hbar}\boldsymbol{\zeta}_{n_1n_1}(\boldsymbol{k}) \times \frac{\partial E_{n_1\boldsymbol{k}}}{\partial \boldsymbol{k}} \\ + (\boldsymbol{\zeta}_{n_1n_1}(\boldsymbol{k}) + \boldsymbol{\zeta}_{n_2n_2}(\boldsymbol{k})) \times \frac{\boldsymbol{p}_{n_1n_2}(\boldsymbol{k})}{4mc},\end{aligned} \quad \text{(A1)}$$

$$\begin{aligned}\boldsymbol{D}_{n_1n_2}(\boldsymbol{k}) = \boldsymbol{\mathcal{D}}_{n_1n_2}(\boldsymbol{k}) + i\boldsymbol{\zeta}_{n_1n_1}(\boldsymbol{k}) \times \boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k}) \\ - i\boldsymbol{\zeta}_{n_2n_2}(\boldsymbol{k}) \times \boldsymbol{\zeta}_{n_1n_2}(\boldsymbol{k}).\end{aligned} \quad \text{(A2)}$$

Next we use (A1) and (A2) to decompose (112)–(115),

$$\chi_p^{ij} = \tilde{\chi}_p^{ij} + g_p^{ij}, \quad p = a,b,c,d,$$

where $\tilde{\chi}_p^{ij}$ are the explicitly gauge-invariant contributions given by (120)–(123), and g_p^{ij} are the remaining contributions involving the diagonal Berry connections. The sum of g_a^{ij} and g_c^{ij} after some manipulations can be written as

$$\begin{aligned}g_{a+c}^{ij} = \mathrm{Re}\sum_{nv}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\{G_{vn}^i(\boldsymbol{k})[\boldsymbol{\zeta}_{vv}(\boldsymbol{k}) \times \boldsymbol{\zeta}_{nv}(\boldsymbol{k})]^j\} \\ - \frac{e^2}{m\hbar c^2}\sum_v\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\{D_{vv}^i(\boldsymbol{k})X_{vv}^j(\boldsymbol{k})\},\end{aligned} \quad \text{(A3)}$$

where we define

$$\begin{aligned}\boldsymbol{G}_{vn}(\boldsymbol{k}) = \frac{ie^2}{\hbar c^2}\frac{1}{m}\left(\boldsymbol{L}_{vn}(\boldsymbol{k}) - \frac{i}{2}\nabla \times \boldsymbol{p}_{vn}(\boldsymbol{k})\right) \\ + \frac{ie^2}{\hbar^2c^2}\boldsymbol{\zeta}_{vn}(\boldsymbol{k}) \times \frac{\partial E_{v\boldsymbol{k}}}{\partial \boldsymbol{k}} \\ + \frac{e^2}{2\hbar^2c^2}E_{vn}(\boldsymbol{k})\boldsymbol{\zeta}_{vv}(\boldsymbol{k}) \times \boldsymbol{\zeta}_{vn}(\boldsymbol{k}),\end{aligned} \quad \text{(A4)}$$

and the remaining two terms are

$$\begin{aligned}g_b^{ij} = -\frac{e^2}{4mc^2}\sum_v\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}[-\zeta_{vv}^i(\boldsymbol{k})\zeta_{vv}^j(\boldsymbol{k}) \\ + \delta^{ij}\boldsymbol{\zeta}_{vv}(\boldsymbol{k}) \cdot \boldsymbol{\zeta}_{vv}(\boldsymbol{k})],\end{aligned}$$

$$g_d^{ij} = e^2\frac{\epsilon^{iml}\epsilon^{jus}}{4\hbar^2c^2}\sum_v\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\frac{\partial^2 E_{v\boldsymbol{k}}}{\partial k^l\partial k^s}\zeta_{vv}^m(\boldsymbol{k})\zeta_{vv}^u(\boldsymbol{k}).$$

We now simplify expression (A3) by noting that, although formally involving sums over all bands, in fact it really depends on the properties of the valence band manifold. To show that this is the case, we rewrite the first line of (A3) using sum rules for the three contributions coming from each line in the definition (A4). For the contributions from lines two and three of (A4) we use, respectively, the expression for the Berry curvature tensor

$$\partial_l \zeta^m_{vv}(\boldsymbol{k}) - \partial_m \zeta^l_{vv}(\boldsymbol{k}) = i\sum_n \zeta^l_{vn}(\boldsymbol{k})\zeta^m_{nv}(\boldsymbol{k}) - i\sum_n \zeta^l_{nv}(\boldsymbol{k})\zeta^m_{vn}(\boldsymbol{k}), \tag{A5}$$

and the effective mass tensor sum rule

$$\begin{aligned} m\frac{\partial^2 E_{v\boldsymbol{k}}}{\partial k^m \partial k^l} &= \hbar^2\delta^{lm} + i\hbar\sum_n \zeta^m_{vn}(\boldsymbol{k})p^l_{nv}(\boldsymbol{k}) \\ &\quad - i\hbar\sum_n p^l_{vn}(\boldsymbol{k})\zeta^m_{nv}(\boldsymbol{k}). \end{aligned} \tag{A6}$$

We write the contribution from the first line of (A4) in real space in terms of the Wannier function moments of the position and orbital angular momentum operators,

$$\begin{aligned} \boldsymbol{Z}_{\boldsymbol{R}}(z) &= z - \boldsymbol{R}, \\ \boldsymbol{L}_{\boldsymbol{R}}(z) &= (z - \boldsymbol{R}) \times \boldsymbol{p}(z). \end{aligned}$$

When the first line of (A4) is inserted in (A3) we find

$$\begin{aligned} \mathrm{Re}\sum_{nv} i\int_{\mathrm{BZ}} \frac{d^3k}{(2\pi)^3}\left[\boldsymbol{L}_{vn}(\boldsymbol{k}) - \frac{i}{2}\nabla\times\boldsymbol{p}_{vn}(\boldsymbol{k})\right]^i [\boldsymbol{\zeta}_{vv}(\boldsymbol{k})\times\boldsymbol{\zeta}_{nv}(\boldsymbol{k})]^j &= \mathrm{Re}\frac{i}{V_c}\sum_{\boldsymbol{R}'\boldsymbol{R}''}\sum_{nv}\langle v\boldsymbol{R}|\hat{L}^i_{\boldsymbol{R}}|n\boldsymbol{R}'\rangle(\langle v\boldsymbol{R}''|\hat{\boldsymbol{Z}}_{\boldsymbol{R}}|v\boldsymbol{R}\rangle \\ &\quad \times \langle n\boldsymbol{R}'|\hat{\boldsymbol{Z}}_{\boldsymbol{R}''}|v\boldsymbol{R}''\rangle)^j. \end{aligned} \tag{A7}$$

Recalling now that Wannier functions are complete, and summing over n and $\boldsymbol{R}'$ we find

$$\begin{aligned} \mathrm{Re}\sum_{nv} i\int_{\mathrm{BZ}} \frac{d^3k}{(2\pi)^3}\left[\boldsymbol{L}_{vn}(\boldsymbol{k}) - \frac{i}{2}\nabla\times\boldsymbol{p}_{vn}(\boldsymbol{k})\right]^i [\boldsymbol{\zeta}_{vv}(\boldsymbol{k})\times\boldsymbol{\zeta}_{nv}(\boldsymbol{k})]^j &= \frac{i}{2V_c}\sum_{v\boldsymbol{R}''}\epsilon^{jlm}\left[\langle v\boldsymbol{R}''|\hat{Z}^l_{\boldsymbol{R}''}|v\boldsymbol{R}\rangle\langle v\boldsymbol{R}|\hat{Z}^m_{\boldsymbol{R}}\hat{L}^i_{\boldsymbol{R}''}|v\boldsymbol{R}''\rangle - \boldsymbol{R}\leftrightarrow\boldsymbol{R}''\right] \\ &\quad - \frac{2mc^2\hbar}{e^2}g^{ij}_b - \frac{1}{2}\sum_v\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\left[L^i_{vv}(\boldsymbol{k})D^j_{vv}(\boldsymbol{k}) + \epsilon^{jlm}\epsilon^{irs}\frac{\partial\zeta^l_{vv}(\boldsymbol{k})}{\partial k^r}L^{ms}_{vv}(\boldsymbol{k})\right], \end{aligned} \tag{A8}$$

where we introduced the orbital angular momentum tensor

$$L^{ms}_{vv}(\boldsymbol{k}) = \frac{1}{2}\sum_n\left[\zeta^m_{nv}(\boldsymbol{k})p^s_{vn}(\boldsymbol{k}) + \zeta^m_{vn}(\boldsymbol{k})p^s_{nv}(\boldsymbol{k})\right], \tag{A9}$$

which can be expressed in terms of the orbital angular momentum vector (61) through

$$L^{ms}_{vv}(\boldsymbol{k}) = \frac{1}{2}\epsilon^{ims}L^i_{vv}(\boldsymbol{k}) + \frac{m}{2\hbar}\zeta^s_{vv}(\boldsymbol{k})\frac{\partial E_{v\boldsymbol{k}}}{\partial k^m} + \frac{m}{2\hbar}\zeta^m_{vv}(\boldsymbol{k})\frac{\partial E_{v\boldsymbol{k}}}{\partial k^s}. \tag{A10}$$

The terms in the first line on the right-hand side of (A8) cancel out, which can be seen either by explicitly evaluating the Wannier function moments as $\boldsymbol{k}$-space integrals over Berry connections and momentum matrix elements, or more simply by expanding the periodic part of the wave function $u_{v\boldsymbol{k}}(\boldsymbol{x}) = \sum_{\boldsymbol{G}} u_{v\boldsymbol{k}}(\boldsymbol{G})e^{i\boldsymbol{x}\cdot\boldsymbol{G}}$, and formally writing

$$\begin{aligned} \frac{1}{V_c}\sum_{\boldsymbol{R}''}\epsilon^{jlm}\langle v\boldsymbol{R}''|\hat{Z}^l_{\boldsymbol{R}''}|v\boldsymbol{R}\rangle\langle v\boldsymbol{R}|\hat{Z}^m_{\boldsymbol{R}}\hat{L}^i_{\boldsymbol{R}''}|v\boldsymbol{R}''\rangle &= i\hbar\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\sum_{\boldsymbol{G}\boldsymbol{G}'}\left[\frac{\partial u^*_{v\boldsymbol{k}}(\boldsymbol{G})}{\partial\boldsymbol{k}}\times\frac{\partial u^*_{v\boldsymbol{k}}(\boldsymbol{G}')}{\partial\boldsymbol{k}}\right]^j\left[u_{v\boldsymbol{k}}(\boldsymbol{G})(\boldsymbol{k}+\boldsymbol{G}')\times\frac{\partial u_{v\boldsymbol{k}}(\boldsymbol{G}')}{\partial\boldsymbol{k}}\right]^i \\ &= \frac{1}{V_c}\sum_{\boldsymbol{R}''}\epsilon^{jlm}\langle v\boldsymbol{R}|\hat{Z}^l_{\boldsymbol{R}}|v\boldsymbol{R}''\rangle\langle v\boldsymbol{R}''|\hat{Z}^m_{\boldsymbol{R}''}\hat{L}^i_{\boldsymbol{R}}|v\boldsymbol{R}\rangle. \end{aligned}$$

Finally we establish a relation

$$\begin{aligned} \int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\left\{\epsilon^{jlm}\epsilon^{irs}\frac{\partial\zeta^l_{vv}(\boldsymbol{k})}{\partial k^r}L^{ms}_{vv}(\boldsymbol{k}) + L^i_{vv}(\boldsymbol{k})D^j_{vv}(\boldsymbol{k})\right\} &= \int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\Bigg\{mc\mathcal{J}^i_{vv}(\boldsymbol{k})\mathcal{D}^j_{vv}(\boldsymbol{k}) - D^i_{vv}(\boldsymbol{k})X^j_{vv}(\boldsymbol{k}) \\ &\quad + \frac{m}{\hbar}\epsilon^{iml}\epsilon^{jus}\zeta^m_{vv}(\boldsymbol{k})\zeta^u_{vv}(\boldsymbol{k})\frac{\partial^2 E_{v\boldsymbol{k}}}{\partial k^l\partial k^s}\Bigg\}, \end{aligned} \tag{A11}$$

by using (A10) in the first line. Using now (A11) together with (A8) we arrive at the third “sum rule”

$$\mathrm{Re}\sum_{nv} i\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\left\{[\boldsymbol{\zeta}_{vv}(\boldsymbol{k})\times\boldsymbol{\zeta}_{nv}(\boldsymbol{k})]^j\mathcal{T}^i_{vn}(\boldsymbol{k})\right\} = \frac{1}{2}\sum_v\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\left\{D^i_{vv}(\boldsymbol{k})X^j_{vv}(\boldsymbol{k})\right\} + \frac{mc^2\hbar}{e^2}\left[\tilde{\chi}^{ij}_e - 2g^{ij}_b - 2g^{ij}_d\right], \tag{A12}$$

with $\boldsymbol{\mathcal{T}}_{vn}(\boldsymbol{k}) = \boldsymbol{L}_{vn}(\boldsymbol{k}) - \frac{i}{2}\nabla\times\boldsymbol{p}_{vn}(\boldsymbol{k})$. Using now (A5), (A6), and (A12) in (A3) we arrive at

$$g^{ij}_{a+c} = \tilde{\chi}^{ij}_e - g^{ij}_b - g^{ij}_d. \tag{A13}$$

Adding now all the contributions to susceptibility, we get (119).

[1] S. R. de Groot, *The Maxwell Equations. Non-relativistic and Relativistic Derivations from Electron Theory* (Wiley Interscience, New York, 1969).

[2] W. P. Healy, *Non-relativistic Quantum Electrodynamics* (Academic, London, 1982).

[3] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms. Introduction to Quantum Electrodynamics* (John Wiley and Sons, New York, 1989).

[4] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).

[5] E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, pp. 305–373.

[6] I. Souza, J. Iniguez, and D. Vanderbilt, Phys. Rev. B **69**, 085106 (2004).

[7] A. M. Essin, A. M. Turner, J. E. Moore, and D. Vanderbilt, Phys. Rev. B **81**, 205104 (2010).

[8] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. **95**, 137205 (2005).

[9] R. Bianco and R. Resta, Phys. Rev. Lett. **110**, 087202 (2013).

[10] A. Malashevich, I. Souza, S. Coh, and D. Vanderbilt, New J. Phys. **12**, 053032 (2010).

[11] L. M. Roth, J. Phys. Chem. Solids **23**, 433 (1962).

[12] F. Mauri and S. G. Louie, Phys. Rev. Lett. **76**, 4246 (1996).

[13] T. Kita and M. Arai, J. Phys. Soc. Jpn. **74**, 2813 (2005).

[14] X. Gonze and J. W. Zwanziger, Phys. Rev. B **84**, 064445 (2011).

[15] P. N. Butcher and D. Cotter, *The Elements of Nonlinear Optics* (Cambridge University Press, Cambridge, 1990).

[16] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, Oxford, 2000).

[17] D. J. Caldwell and H. J. Eyring, *Theory of Optical Activity* (Wiley Interscience, New York, 1971).

[18] Y. R. Shen, *The Principles of Nonlinear Optics* (John Wiley and Sons, Hoboken, NJ, 2003).

[19] R. E. Raab and O. L. de Lange, *Multipole Theory in Electromagnetism: Classical, Quantum and Symmetry Aspects, with Applications.* (Oxford University Press, Oxford, 2005).

[20] E. B. Graham and R. E. Raab, J. Opt. Soc. Am. A **14**, 131 (1997).

[21] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[22] J. E. Sipe and E. Ghahramani, Phys. Rev. B **48**, 11705 (1993).

[23] J. E. Sipe and A. I. Shkrebtii, Phys. Rev. B **61**, 5337 (2000).

[24] R. Zeyher, H. Bilz, and M. Cardona, Solid State Commun. **19**, 57 (1976).

[25] S. D. Swiecicki and J. E. Sipe, Ann. Phys. (NY) **338**, 260 (2013).

[26] In atomic physics this transformation is most commonly used in a simplified form within the electric dipole approximation. See, for example, M. Scully and M. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, 1997).

[27] The procedure can be generalized to treat the situation when electromagnetic fields are quantized. Subtleties that arise there, associated with the polarization field, are not relevant in the limit of the classical fields that we consider here. For discussion and references see, for example, L. Mandel and E. Wolf, *Optical Coherence and Quantum Optics* (Cambridge University Press, Cambridge, 1995).

[28] E. B. Graham, J. Pierrus, and R. E. Raab, J. Phys. B **25**, 4673 (1992).

[29] N. Marzari, A. Mostofi, J. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys. **84**, 1419 (2012).

[30] P. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer, New York, 2010).

[31] J. D. Jackson, *Classical Electrodynamics* (John Wiley and Sons, New York, 1999).

[32] P. D. Visschere, J. Phys. D: Appl. Phys. **39**, 4278 (2006).