

Surprises in the multipole description of macroscopic electrodynamics

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The theory of macroscopic electrodynamics (in its multipole form) for harmonic plane-wave electric and magnetic fields in linear anisotropic media yields constitutive relations and expressions for the material constants and other macroscopic observables. It is shown that the calculated dynamic material constants are unphysical: of the 36 elements of the constitutive tensor, 27 (comprising the inverse permeability and two magnetoelectric tensors) depend on the choice of coordinate origin, while the remaining 9 (the permittivity tensor) are physical at electric dipole order, but not beyond. Thus quantities such as the time average of the instantaneous Poynting vector have origin-dependent values. We use properties of the macroscopic Maxwell equations and the equation of wave propagation to show how physically acceptable results can be obtained in a relatively simple manner for both nonmagnetic and magnetic dissipative media. In doing so, it is essential to adhere to a certain hierarchy for the pairing of electric and magnetic multipoles/polarizabilities. We also comment on the Post constraint in relation to this theory, and use the Buckingham effect to illustrate origin-dependent and origin-independent properties. © 2006 American Association of Physics Teachers. [DOI: 10.1119/1.2151213]

I. INTRODUCTION

The purpose of this paper is to present some surprising results that have been obtained in the multipole description of macroscopic electrodynamics. The theory starts with Maxwell's equations for the microscopic electric and magnetic fields \mathbf{e} and \mathbf{b} . A suitable averaging process leads to the macroscopic Maxwell equations for four fields—the macroscopic electric and magnetic fields \mathbf{E} and \mathbf{B} and two additional fields, \mathbf{D} and \mathbf{H} . Multipole concepts enter early and naturally in this approach, and \mathbf{D} and \mathbf{H} are expressed in terms of infinite series involving spatial derivatives of various macroscopic multipole moment densities (see Sec. II). This classical theory has been studied in considerable detail, is the basis for understanding a range of electromagnetic phenomena, and is a standard part of the physics curriculum.¹⁻⁴

For the theory to be workable we have to establish relations between the four macroscopic fields. To this end we will consider semiclassical electrodynamics in which matter is treated quantum-mechanically, while the electromagnetic fields are treated classically. For electromagnetic harmonic plane-wave fields, quantum-mechanical perturbation theory yields expressions for the induced multipole moment densities as infinite series involving \mathbf{E} , \mathbf{B} , and their spatial and temporal derivatives. To simplify the presentation, we initially consider only nonmagnetic media (see Secs. III–VII). The necessary modifications that must be made for magnetic media are outlined in Sec. VIII.

Constitutive relations are obtained for the response fields \mathbf{D} and \mathbf{H} of linear, homogeneous, anisotropic, dissipative media in terms of the harmonic fields \mathbf{E} and \mathbf{B} (see Sec. IV). The material constants in these relations are linear combinations of polarizability densities of various multipole orders. Each polarizability is given in terms of a quantum-mechanical expression involving matrix elements of molecular multipole moment operators.

This semiclassical extension of the theory, which draws on the quantum theory of multipole moments and polarizabilities, is less familiar than the purely classical theory, and one

of the aims of this paper is to bring it to the attention of a wider readership. The extension of the theory brings advantages and makes it possible to study certain properties (for example, symmetries, translational behavior, and absorption effects) of the dynamic material constants and other observables. Also, computational techniques can be used to obtain numerical values for observables—an area in which considerable advances have been made in recent years.

Sections II–IV form the essential background to this paper. In Sec. V we discuss the translational behavior of the theory. This behavior yields the first surprise: the theoretical results for the dynamic material constants are largely unusable because they are not translationally invariant. Specifically, 27 of the 36 components of the constitutive tensor for a linear, anisotropic medium are unphysical and the remaining 9 are physical at electric dipole order only (see Secs. V and VIII). Thus the calculated harmonic response fields have the unacceptable property that their amplitudes depend on where we choose the origin of a molecular system of coordinates. Consequently, the time average of the instantaneous Poynting vector is also origin dependent and hence unphysical.

We then consider how the theory can be adapted to avoid unphysical results. In the literature this modification has been done by means of a transformation theory.^{5,6} This theory is beyond the scope of this paper, and we therefore present a more elementary approach based on the equation for wave propagation (see Sec. VI). This approach is used in Sec. VII to obtain physically acceptable results for a nonmagnetic medium: we work to electric quadrupole-magnetic dipole order and thereby obtain results for three of the four material constants (the permittivity and the two magnetoelectric tensors). The theory is extended to magnetic media in Sec. VIII.

In Sec. IX we comment on the fourth material constant—the inverse permeability tensor. The static (dc) expression for this tensor is translationally invariant and therefore does not require transformation. However, the extension of this expression to nonzero frequency is surprisingly complicated. The reason is that in semiclassical theory the dynamic inverse permeability is a property of electric octopole-magnetic quadrupole order, and it is difficult to carry out the

necessary transformations to such a high order. In Sec. X we consider the theory in relation to the Post constraint, a topic that has attracted much recent attention.

To further illustrate the important role of origin-dependent and origin-independent quantities, we describe in Sec. XI an interesting induced effect (the Buckingham effect) that relates a macroscopic origin-independent observable to a microscopic (molecular) origin-dependent observable. The intricacy of this relation and the accuracy to which it has been established encourages confidence in the macroscopic semiclassical multipole approach, at least for phenomena to which it is applicable. A brief discussion of some applications of the semiclassical theory is given in Sec. XII.

II. THE MACROSCOPIC MAXWELL EQUATIONS

Multipole concepts arise naturally when the microscopic Maxwell equations of electrodynamics are recast in the form of macroscopic equations for bulk media. The standard procedure for doing so involves two steps. We first perform a suitable spatial average over the microscopic charge and current densities and the associated microscopic electromagnetic fields in the Maxwell equations. Then spatial Taylor-series expansions are performed for the (sufficiently slowly varying) average charge and current densities. This procedure leads to the familiar macroscopic Maxwell equations, which consist of two homogeneous equations for the macroscopic electric and magnetic fields \mathbf{E} and \mathbf{B} ,

$$\nabla \cdot \mathbf{B} = 0, \quad (1)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (2)$$

and two inhomogeneous equations for the derived fields \mathbf{D} and \mathbf{H} ,

$$\nabla \cdot \mathbf{D} = \rho, \quad (3)$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}, \quad (4)$$

in terms of the macroscopic (free) charge density ρ and current density \mathbf{J} .

The fields \mathbf{D} and \mathbf{H} are given by infinite series involving macroscopic multipole moment densities according to

$$D_i = \varepsilon_0 E_i + P_i - \frac{1}{2} \nabla_j Q_{ij} + \frac{1}{6} \nabla_k \nabla_j Q_{ijk} + \dots, \quad (5)$$

$$H_i = \mu_0^{-1} B_i - M_i + \frac{1}{2} \nabla_j M_{ij} + \dots. \quad (6)$$

Here and in the following a repeated subscript on a Cartesian tensor implies summation from 1 to 3. In Eq. (6) contributions from the motion of the medium as a whole have been neglected. The multipole densities are for the electric dipole P_i , quadrupole Q_{ij} , octopole Q_{ijk} , and the magnetic dipole M_i , and quadrupole M_{ij} . These densities are macroscopic averages^{1,4} that involve the corresponding moments of a molecule (or other charge entity), defined by

$$p_i = \sum q r_{i\alpha}, \quad q_{ij} = \sum q r_{i\alpha} r_{j\alpha}, \quad q_{ijk} = \sum q r_{i\alpha} r_{j\alpha} r_{k\alpha}, \quad (7)$$

$$m_i = \sum (q/2m) L_i, \quad m_{ij} = \sum (2q/3m) L_i r_{j\alpha}. \quad (8)$$

Here the summations are over all particles in a molecule, each having charge q , mass m , position vector \mathbf{r} , momentum $\mathbf{\Pi}$, and angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{\Pi}$.

In Eqs. (7) and (8) the position vectors \mathbf{r} of the constituents of a molecule are defined relative to some origin O . Often O is placed at the center of mass of a molecule, although a different choice such as the effective quadrupole center might be more convenient. The choice of O is constrained only by the convergence of the series expansions leading to Eqs. (5) and (6). This constraint means that \mathbf{r} should be the order of molecular dimensions (see the following). Thus O is an arbitrary origin inside or near the molecule.

Detailed accounts of the theory have been given by Russakoff,¹ Robinson,² Scaife,³ and Jackson,⁴ who provide references to earlier work on this subject. These authors exhibit the terms involving P_i , Q_{ij} , and M_i in Eqs. (5) and (6), but it is not difficult to extend the analysis to other terms in Eqs. (5) and (6).

There is another method of obtaining these results which dates back to Van Vleck⁷ and parallels the multipole expansions familiar in the electrostatics and magnetostatics of a charge distribution in vacuum. In this method multipole expansions are performed for the dynamic scalar and vector potentials at a point in the macroscopic medium. A limitation in Ref. 7 that these multipole expansions are not valid close to a molecule was removed by considering the contribution to the potentials due only to molecules inside a small (but otherwise arbitrary) volume in the medium and evaluated at a field point just outside (in the near zone of) the small volume.⁶ The same spatial average^{1,4} is used and both approaches lead to Eqs. (5) and (6).⁶ In the multipole expansion of the vector potential the electric and magnetic contributions pair up in a specific manner, for example, electric quadrupole with magnetic dipole and electric octopole with magnetic quadrupole, and their magnitudes are ordered according to the following hierarchy:^{6,8}

$$\begin{aligned} \text{electric dipole} &\gg \left\{ \begin{array}{l} \text{electric quadrupole} \\ \text{magnetic dipole} \end{array} \right. \\ &\gg \left\{ \begin{array}{l} \text{electric octopole} \\ \text{magnetic quadrupole} \end{array} \right. \gg \dots \end{aligned} \quad (9)$$

This pairing of electric multipoles of order 2^n with magnetic multipoles of order 2^{n-1} ($n=2,3,\dots$) is an important feature of the theory which extends to the semiclassical formulation.

The spatial average can be performed either by using a weighting function^{1,4} or by the aid of a truncated Fourier analysis.^{2,4} The goal is to average (filter) out enough of the complicated microscopic behavior so that the spatial Taylor-series expansions are rapidly convergent, while retaining enough detail that the macroscopic theory can still describe the phenomena. A helpful discussion of this point has been given in Ref. 2. The condition for the validity of the theory is that averaged quantities (fields and source densities) vary on a scale that is much larger than molecular dimensions ℓ , as for example in experiments in molecular physics using lasers, where the wavelength is about $10^3 \ell$. This condition differs from that for the convergence of the multipole expansion for a molecule in vacuum (distance to the field point $\gg \ell$).

It is common to assume that an electric dipole-magnetic dipole approximation (the retention of only the densities P_i and M_i) is almost always justified in Eqs. (5) and (6) and that the higher-order terms represent small corrections to the dipole terms. Surprisingly, it turns out that in the semiclassical theory the situation is considerably more subtle.

III. INDUCED MULTIPOLE MOMENT AND POLARIZABILITY DENSITIES

The usefulness of the macroscopic Maxwell equations (1)–(4) depends on the constitutive relations. We now present results from the quantum theory of multipole moments and polarizabilities that enable us to obtain these relations. At this point the theory becomes semiclassical. For reasons that will become clear, we concentrate on the polarizability densities P_i , Q_{ij} , and M_i , which appear in Eqs. (5) and (6) [see the hierarchy (9)]. It is also convenient to first consider non-magnetic media (media for which time-odd polarizability tensors are zero⁹). Magnetic media are considered in Sec. VIII.

In a seminal paper, Buckingham¹⁰ used time-dependent perturbation theory to derive quantum-mechanical expressions for the leading multipole moments induced in a molecule by the fields of a harmonic, plane electromagnetic wave. Based on Buckingham's approach and notation the macroscopic densities of these moments in a linear, homogeneous, anisotropic, nonmagnetic medium can be written as^{11,12}

$$P_i = \alpha_{ij}E_j + \frac{1}{2}a_{ijk}\nabla_k E_j + \cdots + \frac{1}{\omega}G'_{ij}\dot{B}_j + \cdots, \quad (10)$$

$$Q_{ij} = a_{kij}E_k + \cdots, \quad (11)$$

$$M_i = -\frac{1}{\omega}G'_{ji}\dot{E}_j + \cdots + \chi_{ij}B_j + \cdots, \quad (12)$$

where the fields are given by

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}, \quad \mathbf{B} = \mathbf{B}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \quad (13)$$

and ω is the angular frequency and the wave vector \mathbf{k} is complex for dissipative media.

The dynamic polarizability densities in Eqs. (10)–(12) are macroscopic averages involving the corresponding molecular quantities. The quantum expressions of the latter in the non-degenerate quantum state $|n\rangle$ were derived by Buckingham and are^{10–12}

$$\alpha_{ij} = (2/\hbar) \sum_s \omega_{sn} Z_{sn} \operatorname{Re}\{\langle p_i \rangle_{ns} \langle p_j \rangle_{sn}\} = \alpha_{ji}, \quad (14)$$

$$a_{ijk} = (2/\hbar) \sum_s \omega_{sn} Z_{sn} \operatorname{Re}\{\langle p_i \rangle_{ns} \langle q_{jk} \rangle_{sn}\} = a_{ikj}, \quad (15)$$

$$G'_{ij} = -(2/\hbar) \sum_s \omega Z_{sn} \operatorname{Im}\{\langle p_i \rangle_{ns} \langle m_j \rangle_{sn}\}, \quad (16)$$

where the quantum-mechanical moment operators have the same forms as the classical moments in Eqs. (7) and (8). (We discuss the polarizability density χ_{ij} in Sec. IX.) We have used the same symbols for the molecular equivalents of the macroscopic tensors in Eqs. (10)–(12), and we have used the notation $\langle \Omega \rangle_{sn} = \langle s | \Omega | n \rangle$ for the matrix elements of an opera-

tor. Also $\omega_{sn} = (E_s - E_n)/\hbar$ is the angular frequency of a radiation transition between states with unperturbed energy E_s and E_n , and Z_{sn} is a complex line-shape function that allows for dispersion and absorption.¹³ In the absence of absorption

$$Z_{sn} = (\omega_{sn}^2 - \omega^2)^{-1} \quad (17)$$

is real. The symmetry of the tensor subscripts of α_{ij} in Eq. (14) is due to the Hermitian property of the operator p_i in Eq. (7) and the symmetry of a_{ijk} arises from the intrinsic symmetry of q_{ij} in Eq. (7).

We remark that Eqs. (10)–(12) consist of two infinite series (one in \mathbf{E} and its derivatives and the other in \mathbf{B} and its derivatives).¹² [This remark applies also to the higher moment densities such as Q_{ijk} and M_{ij} in Eqs. (5) and (6).^{11,12}] The terms in Eqs. (10)–(12) that are most familiar are probably those involving α_{ij} and χ_{ij} . The reader may wonder why we have also chosen to display the terms involving a_{ijk} and G'_{ij} , but not any others such as magnetic terms in Q_{ij} . The answer will become clear and we will see that the terms included are the smallest set that is necessary.

The multipole orders of the polarizability densities in Eqs. (10)–(12) are evident from Eqs. (14)–(16) and Sec. IX, and are

$$\text{electric dipole: } \alpha_{ij}, \quad \text{electric quadrupole: } a_{ijk},$$

$$\text{magnetic dipole: } G'_{ij}, \quad \text{magnetic quadrupole: } \chi_{ij}. \quad (18)$$

All other terms are of electric octopole-magnetic quadrupole order and higher, as are all contributions to Q_{ijk} , M_{ij} , and other moment densities in Eqs. (5) and (6).^{6,11} Thus if we include only the terms in α_{ij} , a_{ijk} , and G'_{ij} in Eqs. (10)–(12), we are working to electric quadrupole-magnetic dipole order.

IV. CONSTITUTIVE RELATIONS

The constitutive relations for the response of a linear, anisotropic medium to the harmonic fields Eq. (13) have the form

$$\begin{pmatrix} D_i \\ H_i \end{pmatrix} = C \begin{pmatrix} E_j \\ B_j \end{pmatrix} = \begin{pmatrix} A_{ij} & T_{ij} \\ U_{ij} & X_{ij} \end{pmatrix} \begin{pmatrix} E_j \\ B_j \end{pmatrix}, \quad (19)$$

for $i, j = 1, 2, \text{ and } 3$. The components of the 6×6 matrix are the complex material constants of the medium; for a homogeneous medium they are uniform. They represent the macroscopic observables: the permittivity A_{ij} , inverse permeability X_{ij} , and the magnetoelectric coefficients T_{ij} and U_{ij} .¹⁴ In general, these observables are functions of the polarizability densities of each multipole order. The 6×6 matrix in Eq. (19) represents the constitutive tensor C .

Explicit multipole expressions for C can be obtained by using the theory of Sec. III. We simply substitute Eqs. (10)–(12) in Eqs. (5) and (6), and use the replacements $\nabla_j \rightarrow ik_j$ and $\partial/\partial t \rightarrow -i\omega$ for the harmonic fields (13). This substitution yields a series expansion

$$C = C^{(0)} + C^{(1)} + C^{(2)} + C^{(3)} + \cdots. \quad (20)$$

The vacuum contribution evident in Eqs. (5) and (6) is

$$C^{(0)} = \begin{pmatrix} \epsilon_0 \delta_{ij} & 0 \\ 0 & \mu_0^{-1} \delta_{ij} \end{pmatrix}. \quad (21)$$

The quantity

$$C^{(1)} = \begin{pmatrix} \alpha_{ij} & 0 \\ 0 & 0 \end{pmatrix} \quad (22)$$

is of electric dipole order and is the leading contribution due to the presence of a medium.

$$C^{(2)} = \begin{pmatrix} \frac{1}{2}ik_k(a_{ijk} - a_{jki}) & -iG'_{ij} \\ -iG'_{ji} & 0 \end{pmatrix} \quad (23)$$

is the contribution of electric quadrupole-magnetic dipole order, and

$$C^{(3)} = \begin{pmatrix} 3rd & 2nd \\ 2nd & -\chi_{ij} \end{pmatrix} \quad (24)$$

is the contribution of electric octopole-magnetic quadrupole order. The (\dots) in Eq. (20) indicate terms beyond electric octopole-magnetic quadrupole order.

The nine components involving a_{ijk} in Eq. (23) are a small correction to the leading contribution α_{ij} to the permittivity in Eq. (22); the reason for their retention will become clear in Sec. VII. In Eq. (24) the entries 2nd and 3rd denote second- and third-order contributions to the magnetoelectric and permittivity tensors, respectively. Both are given in terms of polarizability densities of electric octopole-magnetic quadrupole order;^{6,15} they are small corrections to the leading terms in Eqs. (22) and (23), and therefore we do not give their explicit expressions. However, it turns out that these terms play an important role in the theory (see Sec. IX and Ref. 15).

We mention that for nondissipative (lossless) media the complex material constants in Eq. (19) must satisfy the symmetries^{6,16}

$$A_{ij} = A_{ji}^*, \quad T_{ij} = -U_{ji}^*, \quad X_{ij} = X_{ji}^*. \quad (25)$$

The contributions given explicitly by Eqs. (19)–(23) and (14)–(16) clearly satisfy Eq. (25) because Z_{sn} in Eq. (17) and \mathbf{k} are real for nondissipative media. For the symmetry of X_{ij} in Eq. (24) we also require the symmetry for χ_{ij} (see Sec. IX). The conditions in Eq. (25) represent a set of 21 relations that reduce the number of independent components of the constitutive tensor for nondissipative media from 36 to 21. Even though the relations in Eq. (25) do not apply to dissipative media (as we know on general grounds^{6,16} or because Z_{sn} and \mathbf{k} are complex in such media), they play an important role in determining physically acceptable material constants.⁶

V. VIOLATION OF TRANSLATIONAL INVARIANCE

Tensors representing physical quantities can be classified into six subcategories: polar or axial (according to their behavior under improper coordinate transformations); time-even or time-odd depending on their behavior under time reversal; and origin independent or origin dependent according to their behavior under spatial translations. Our interest in this section is with translational behavior.

A tensor is origin independent (translationally invariant) if all of its components are unchanged by an arbitrary shift of the origin of coordinates. If one or more of its components is changed by this shift, the tensor is origin dependent. The value of an origin-dependent observable has meaning only with respect to a stated coordinate origin. The material con-

stants in Eq. (19) are origin-independent observables; origin dependence of material constants would result in unphysical behavior of certain phenomena such as energy flow in a medium (see the following) and reflection at a crystal surface.⁶ Thus we require that

$$\Delta A_{ij} = \Delta T_{ij} = \Delta U_{ij} = \Delta X_{ij} = 0, \quad (26)$$

where Δ denotes the change in a quantity due to an arbitrary shift in the origin O of the system of coordinates used in the evaluation of multipole moments such as Eqs. (7) and (8). Equation (26) represents a total of $4 \times 9 = 36$ relations that must be satisfied for translational invariance.

Multipole moment operators, like their classical counterparts, are (mostly) origin-dependent quantities,^{6,13} which can result in an origin dependence of the corresponding quantum-mechanical polarizabilities, such as Eqs. (14)–(16), which determine the material constants. Thus it is important to ask: do the multipole material constants satisfy the conditions (26) for translational invariance?

To answer this question we first determine the effect of an origin shift on the multipole moment operators. For a displacement \mathbf{d} of origin from O to O' , the position and momentum operators relative to O' and O are related by

$$\mathbf{r}' = \mathbf{r} - \mathbf{d}, \quad \mathbf{\Pi}' = \mathbf{\Pi}. \quad (27)$$

We work to electric quadrupole-magnetic dipole order. Then from Eqs. (7), (8), and (27) the changes in the moment operators are

$$\Delta p_i = -d_i \sum q, \quad (28)$$

$$\Delta q_{ij} = -d_i p_j - d_j p_i + d_i d_j \sum q, \quad (29)$$

$$\Delta m_i = -\varepsilon_{ijk} d_j \sum \frac{q}{2m} \Pi_k, \quad (30)$$

where $\Delta p_i = p'_i - p_i$, etc. In Eq. (30) we have used the familiar expression

$$(\mathbf{a} \times \mathbf{b})_i = \varepsilon_{ijk} a_j b_k, \quad (31)$$

where ε_{ijk} is the Levi-Civita tensor.

Next we use Eqs. (28)–(30) to determine the translational behavior of the polarizabilities (14)–(16). Because $\langle n|s \rangle = 0$ for $s \neq n$, we have

$$\langle \Delta p_i \rangle_{sn} = 0 \quad (s \neq n), \quad (32)$$

so that Eq. (14) gives

$$\Delta \alpha_{ij} = 0, \quad (33)$$

meaning the polarizability α_{ij} is translationally invariant. Similarly, if we apply Eq. (32) to the polarizability G'_{ij} in Eq. (16) we have

$$\begin{aligned} \Delta G'_{ij} &= -(2/\hbar) \sum_s \omega Z_{sn} \text{Im} \{ \langle p_i \rangle_{ns} \langle m_j + \Delta m_j \rangle_{sn} \\ &\quad - \langle p_i \rangle_{ns} \langle m_j \rangle_{sn} \} \\ &= (2/\hbar) \varepsilon_{jki} d_k \sum_s \omega Z_{sn} \text{Im} \left[\langle p_i \rangle_{ns} \left\langle \sum_\ell (q/2m) \Pi_\ell \right\rangle_{sn} \right], \end{aligned} \quad (34)$$

in which Eq. (30) was used. To simplify Eq. (34) further we use the relation

$$\langle [H^{(0)}, p_i] \rangle_{\text{sn}} = \hbar \omega_{\text{sn}} \langle p_i \rangle_{\text{sn}} = -i\hbar \left\langle \sum (q/m) \Pi_i \right\rangle_{\text{sn}}, \quad (35)$$

where $H^{(0)}$ is the unperturbed molecular Hamiltonian, which is assumed to contain only a velocity-independent potential. Then from Eqs. (34), (35), and (14) we have

$$\Delta G'_{ij} = \frac{1}{2} \omega \varepsilon_{jkl} d_k \alpha_{il}. \quad (36)$$

A similar calculation for the polarizability in Eq. (15) yields

$$\Delta a_{ijk} = -d_j \alpha_{ik} - d_k \alpha_{ij}. \quad (37)$$

To estimate the order of magnitude of these changes in the polarizabilities, we recall that the molecular origin O should be in or near the molecule. Thus, we have $d \approx \ell$ (the dimension of a molecule) and $\Delta a \approx \ell \alpha$ according to Eq. (37). An electric quadrupole moment is of order ℓ times an electric dipole moment, and it follows from Eqs. (14) and (15) that $a \approx \ell \alpha$ and $\Delta a \approx a$. Hence by shifting O we can change a_{ijk} by an amount that is comparable to its initial value. Similar results hold for all polarizabilities.

The polarizability densities in Eqs. (10)–(12) are averages of the corresponding molecular polarizabilities (14)–(16). Consequently, the polarizability densities also possess the symmetries (14) and (15) and the origin dependencies (33), (36), and (37).

From Eqs. (33) and (22) we see that the leading multipole term (electric dipole term) in the multipole expansion (20) satisfies Eq. (26). However, from Eqs. (36) and (37) it is clear that the electric quadrupole-magnetic dipole contribution (23) does not satisfy the first three equations in Eq. (26). The inverse permeability $X_{ij} = -\chi_{ij}$ in Eq. (24) also does not satisfy Eq. (26) (see Sec. IX) nor do other contributions of electric octopole-magnetic quadrupole order.⁶ We emphasize that this conclusion does not apply to static phenomena. For example, in Eq. (23) $G'_{ij} \rightarrow 0$ [see Eq. (16)] and $\mathbf{k} \rightarrow 0$ as $\omega \rightarrow 0$; thus $C^{(2)} \rightarrow 0$ and there is no violation of translational invariance at electric quadrupole-magnetic dipole order for a nonmagnetic medium. Also for magnetic media the static values are translationally invariant (see Secs. VIII and X).

We therefore reach the surprising conclusion that of the 36 components of the dynamic constitutive tensor C in Eq. (19), the multipole expansion (20) of semiclassical electrodynamics produces physically unacceptable results for 27 of them (comprising the inverse permeability and magnetoelectric tensors, X_{ij} , T_{ij} , and U_{ij}). Of the remaining 9 (comprising the permittivity tensor A_{ij}), an acceptable result is found at electric dipole order [see Eq. (22)], but not beyond [see Eq. (23)].

It is instructive to elaborate on the unphysical nature of the above-noted results. From Eqs. (19)–(23) and (13), we see that to electric quadrupole-magnetic dipole order the amplitude \mathbf{H}_0 of a harmonic, plane-wave field \mathbf{H} is given by

$$H_{0i} = -iG'_{ji} E_{0j} + \mu_0^{-1} \delta_{ij} B_j. \quad (38)$$

According to Eqs. (36) and (38),

$$\Delta H_{0i} = -\frac{1}{2} i \omega \varepsilon_{ikl} d_k \alpha_{jl} E_{0j}. \quad (39)$$

For an arbitrary shift \mathbf{d} of the origin, ΔH_{0i} is nonzero in general and hence the amplitude \mathbf{H}_0 depends on the choice of origin O .

This unphysical result carries over to the transmission of energy in a medium. Consider the time average of the instantaneous Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$, which is given by¹⁶

$$\langle \mathbf{S} \rangle = \frac{1}{2} \text{Re}(\mathbf{E} \times \mathbf{H}^*). \quad (40)$$

The origin dependence of $\langle \mathbf{S} \rangle$ follows from Eqs. (13), (39), and (40). In discussing the result, we choose the z axis along \mathbf{S} and consider linear polarization with \mathbf{E} along the x axis. Then $\mathbf{E}_0 = (E_0, 0, 0)$ is real. The result is

$$\Delta \langle S_z \rangle = -\frac{1}{4} \omega (d_z \bar{\alpha}_{xx} - d_x \bar{\alpha}_{xz}) E_0^2 e^{-2\bar{\mathbf{k}} \cdot \mathbf{r}}, \quad (41)$$

where $\bar{\alpha}_{ij}$ and $\bar{\mathbf{k}}$ are the imaginary parts of α_{ij} and \mathbf{k} . Thus, for a dissipative nonmagnetic medium $\langle S_z \rangle$ is origin dependent. For a magnetic medium, $\langle \mathbf{S} \rangle$ is also origin dependent, even in the absence of dissipation (see Sec. VIII).

We now consider how the semiclassical theory outlined in Sec. IV can be modified to obtain physically acceptable results. A transformation theory has been developed for this purpose,⁵ but this work is beyond the scope of this paper, and we provide here a simpler approach based on the wave equation.

VI. A CLUE FROM THE WAVE EQUATION

A wave equation can be obtained from the inhomogeneous Maxwell equation (4). We consider a dielectric and therefore set $\mathbf{J} = 0$. We work to electric quadrupole-magnetic dipole order and use the constitutive relations given by Eqs. (19)–(23) in Eq. (4). For the harmonic fields (13) we make the replacements $\nabla_j \rightarrow ik_j$ and $\partial/\partial t \rightarrow -i\omega$ in all terms involving derivatives of the fields \mathbf{E} and \mathbf{B} and use Faraday's law (2) in the form

$$B_j = \omega^{-1} \varepsilon_{jmn} k_m E_n \quad (42)$$

to eliminate terms involving \mathbf{B} in favor of \mathbf{E} . We also write $\mathbf{k} = (\omega n/c) \boldsymbol{\sigma}$ where n is complex for a dissipative medium, and its real part represents the refractive index for the polarization state described by the amplitude \mathbf{E}_0 in Eq. (13) when the propagation is along the unit vector $\boldsymbol{\sigma} = \mathbf{k}/k$. In this way we obtain

$$[n^2 \sigma_i \sigma_j - (n^2 - 1) \delta_{ij} + \varepsilon_0^{-1} \alpha_{ij} - i(\varepsilon_0^{-1} n/c) \beta_{ij}] E_{0j} = 0 \quad (43)$$

for the propagation of harmonic, plane-wave fields in a homogeneous, nonmagnetic, anisotropic dielectric. Here

$$\beta_{ij} = \sigma_k (\varepsilon_{ikl} V_{jl} - \varepsilon_{jkl} V_{il}), \quad (44)$$

with

$$V_{ij} = G'_{ij} - \frac{1}{2} \omega \varepsilon_{jkl} a_{kli}. \quad (45)$$

To obtain Eq. (44) we have used the relation

$$\varepsilon_{ikl} \varepsilon_{lmn} = \delta_{im} \delta_{kn} - \delta_{in} \delta_{km}. \quad (46)$$

Note that the third and fourth terms in Eq. (43) are of electric dipole and electric quadrupole-magnetic dipole order, respectively [see (18)].

This wave theory, including its extension to electric octopole-magnetic quadrupole order and magnetic media, has been used to describe a variety of transmission effects such as natural optical activity, Faraday rotation, gyrotropic birefringence, and Lorentz birefringence.¹⁷ For our purposes, the relevant aspect is the translational behavior of Eq. (43), that is, of the tensor V_{ij} . From Eqs. (36), (37), and (45),

$$\Delta V_{ij} = \frac{1}{2} \omega \varepsilon_{jkl} (d_k \alpha_{il} + d_l \alpha_{ki} + d_l \alpha_{kl}). \quad (47)$$

The second term in Eq. (47) is zero because of the symmetry of α_{kl} [see Eq. (14)] and the antisymmetry of ε_{jkl} . Hence

$$\Delta V_{ij} = \frac{1}{2} \omega (\varepsilon_{jkl} + \varepsilon_{jlk}) d_k \alpha_{il} = 0. \quad (48)$$

This invariance, together with that of α_{ij} in Eq. (33), means that Eq. (43) is translationally invariant. This result is surprising given that Eq. (43) has been obtained using a constitutive tensor that is origin dependent; it is discussed further in Secs. VII and VIII.

VII. TRANSLATIONAL INVARIANCE REGAINED

The origin independence of V_{ij} leads us to ask: can we impose translational invariance on the theory of Sec. IV by recasting it in a form that involves the origin-independent combination (45) rather than G'_{ij} and a_{ijk} separately, and that does not disturb the symmetries (25) or the propagation equation (43)? The possibility of doing so rests on an important property of the inhomogeneous Maxwell equations (3) and (4), namely that they do not define the response fields \mathbf{D} and \mathbf{H} uniquely. In fact, for complex harmonic plane-wave fields

$$\mathbf{D} = \mathbf{D}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}, \quad \mathbf{H} = \mathbf{H}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}, \quad (49)$$

Eqs. (3) and (4) have the following property: if \mathbf{H}^G is a complex harmonic field with the same form as Eq. (49), then the transformations

$$H_i \rightarrow H_i + H_i^G, \quad D_i \rightarrow D_i - \omega^{-1} \varepsilon_{ijk} k_j H_k^G, \quad (50)$$

of the fields \mathbf{H} and \mathbf{D} will leave Eqs. (3) and (4) unchanged.

We concentrate on the terms of electric quadrupole-magnetic dipole order in \mathbf{D} and \mathbf{H} , which are responsible for the lack of translational invariance discussed in Sec. V for nonmagnetic media. According to Eqs. (19)–(23), these are the contributions

$$D_i = i \frac{1}{2} k_k (a_{ijk} - a_{jki}) E_j - i G'_{ij} B_j, \quad (51)$$

$$H_i = -i G'_{ji} E_j. \quad (52)$$

We proceed in two steps.

1. The discussion in Sec. VI motivates us to convert the origin-dependent tensor G'_{ji} in Eq. (52) to the origin-independent tensor V_{ji} defined in Eq. (45). This conversion is done by adding

$$H_i^G = i \frac{1}{2} \omega \varepsilon_{ikl} a_{klj} E_j \quad (53)$$

to H_i , so that

$$H_i \rightarrow -i \left(G'_{ji} - \frac{1}{2} \omega \varepsilon_{ikl} a_{klj} \right) E_j. \quad (54)$$

According to Eqs. (50), (51), (53), and (46), we then have

$$D_i \rightarrow i \frac{1}{2} k_k (a_{kji} - a_{jki}) E_j - i G'_{ij} B_j. \quad (55)$$

Equation (55) for \mathbf{D} is not yet satisfactory because the coefficients of \mathbf{E} and \mathbf{B} are origin dependent.

2. We use the relation

$$k_k (a_{kji} - a_{jki}) E_j = \omega \varepsilon_{jkl} a_{kli} B_j, \quad (56)$$

which follows from Faraday's law (42) and Eq. (46), to express Eq. (55) as

$$D_i = -i \left(G'_{ij} - \frac{1}{2} \omega \varepsilon_{jkl} a_{kli} \right) B_j. \quad (57)$$

We have completed our goal of recasting \mathbf{D} and \mathbf{H} into physically acceptable forms where the coefficients of \mathbf{E} and \mathbf{B} are origin independent. In terms of their effect on the constitutive tensor C in Eqs. (19) and (20), the above two steps leave the vacuum and electric dipole contributions $C^{(0)}$ and $C^{(1)}$ in Eqs. (21) and (22) unchanged, and they alter the electric quadrupole-magnetic dipole contribution $C^{(2)}$ in Eq. (23) according to

$$\begin{pmatrix} \frac{i}{2} k_k (a_{ijk} - a_{jki}) & -i G'_{ij} \\ -i G'_{ji} & 0 \end{pmatrix} \xrightarrow{1} \begin{pmatrix} \frac{i}{2} k_k (a_{kji} - a_{jki}) & -i G'_{ij} \\ -i \left(G'_{ji} - \frac{1}{2} \omega \varepsilon_{ikl} a_{klj} \right) & 0 \end{pmatrix} \xrightarrow{2} \begin{pmatrix} 0 & -i \left(G'_{ij} - \frac{1}{2} \omega \varepsilon_{jkl} a_{kli} \right) \\ -i \left(G'_{ji} - \frac{1}{2} \omega \varepsilon_{ikl} a_{klj} \right) & 0 \end{pmatrix}. \quad (58)$$

The total constitutive tensor (for a nonmagnetic medium and to electric quadrupole-magnetic dipole order) is from Eqs. (20)–(22) and (58),

$$C = \begin{pmatrix} \varepsilon_0 \delta_{ij} + \alpha_{ij} & -i \left(G'_{ij} - \frac{1}{2} \omega \varepsilon_{jkl} a_{kli} \right) \\ -i \left(G'_{ji} - \frac{1}{2} \omega \varepsilon_{ikl} a_{klj} \right) & \mu_0^{-1} \delta_{ij} \end{pmatrix}. \quad (59)$$

Thus, the polarizability densities G'_{ij} and a_{ijk} have been combined to form the leading contributions to the magneto-electric tensors T_{ij} and U_{ij} of Eq. (19) and a_{ijk} no longer

contributes to the permittivity. Clearly, the origin-independent material constants in Eq. (59) satisfy the symmetries (25) if the polarizability densities are real, that is, for nondissipative media. Also, because the two steps in Eq. (58) do not alter the inhomogeneous Maxwell equations (3) and (4), they leave the propagation equation (43) unchanged. For the success of the analysis leading to Eq. (59), it is essential that we not neglect *a priori* the term involving a_{ijk} in Eq. (23), even though at that stage it is a small correction [in the sense of Eq. (9)] to the leading (electric dipole) term α_{ij} .

VIII. MAGNETIC MEDIA

A magnetic medium possesses time-odd polarizability tensors in addition to the time-even tensors introduced in Sec.

III for a nonmagnetic medium.^{6,9} Thus there are some additional contributions that should be included in discussing magnetic media. In the following we will, for brevity, give just the additional contributions. The analysis closely parallels that in Secs. III–VII for nonmagnetic media, and we give only a brief outline, emphasizing an interesting difference between the two cases.

We start with the macroscopic induced multipole moment densities Eqs. (10)–(12) to which should be added^{11,12}

$$P_i = \frac{1}{\omega} \alpha'_{ij} \dot{E}_j + \frac{1}{2\omega} a'_{ijk} \nabla_k \dot{E}_j + \cdots + G_{ij} B_j + \cdots, \quad (60)$$

$$Q_{ij} = -\frac{1}{\omega} a'_{kij} \dot{E}_k + \cdots, \quad (61)$$

$$M_i = G_{ji} E_j + \cdots + \frac{1}{\omega} \chi'_{ij} \dot{B}_j + \cdots. \quad (62)$$

The polarizability densities α'_{ij} , a'_{ijk} , and G_{ij} for magnetic systems are the time-odd counterparts of the time-even densities α_{ij} , a_{ijk} , and G'_{ij} in Eqs. (10)–(12) for nonmagnetic systems. The quantum-mechanical expressions for the corresponding molecular quantities are^{10,12}

$$\alpha'_{ij} = -(2/\hbar) \sum_s \omega Z_{sn} \text{Im}\{\langle p_i \rangle_{ns} \langle p_j \rangle_{sn}\} = -\alpha'_{ji}, \quad (63)$$

$$a'_{ijk} = -(2/\hbar) \sum_s \omega Z_{sn} \text{Im}\{\langle p_i \rangle_{ns} \langle q_{jk} \rangle_{sn}\} = a'_{ikj}, \quad (64)$$

$$G_{ij} = (2/\hbar) \sum_s \omega_{sn} Z_{sn} \text{Re}\{\langle p_i \rangle_{ns} \langle m_j \rangle_{sn}\}, \quad (65)$$

where the symbols have the same meanings as in Eqs. (14)–(16). (We postpone a discussion of the polarizability χ'_{ij} to Sec. IX.) In Eqs. (14)–(16) and (63)–(65) we have used a prime to indicate those polarizabilities that vanish in the dc limit ($\omega=0$). All the comments made at the end of Sec. III regarding the multipole orders of polarizability densities and the neglected terms in Eqs. (10)–(12) apply here as well. Thus (18) applies also to the time-odd tensors α'_{ij} , a'_{ijk} , G_{ij} , and χ'_{ij} .

Corresponding to Eqs. (60)–(62), we have the following additional contributions to the electric dipole, electric quadrupole-magnetic dipole, electric octopole-magnetic quadrupole terms (22)–(24) in the constitutive tensor (20),

$$C^{(1)} = \begin{pmatrix} -i\alpha'_{ij} & 0 \\ 0 & 0 \end{pmatrix}, \quad (66)$$

$$C^{(2)} = \begin{pmatrix} \frac{1}{2} k_k (a'_{ijk} + a'_{jki}) & G_{ij} \\ -G_{ji} & 0 \end{pmatrix}, \quad (67)$$

$$C^{(3)} = \begin{pmatrix} \text{3rd} & \text{2nd} \\ \text{2nd} & i\chi'_{ij} \end{pmatrix}. \quad (68)$$

As before, 2nd and 3rd in Eq. (68) refer to terms of electric octopole-magnetic quadrupole order, which make second- and third-order contributions to the magnetoelectric and permittivity tensors. For nondissipative media, the contributions (66)–(68) satisfy the symmetries (25).

The translational behavior obtained from Eqs. (63)–(65) is

$$\Delta \alpha'_{ij} = 0, \quad (69)$$

$$\Delta G_{ij} = -\frac{1}{2} \omega \varepsilon_{jkl} d_k \alpha'_{il}, \quad (70)$$

$$\Delta a'_{ijk} = -d_j \alpha'_{ik} - d_k \alpha'_{ij}. \quad (71)$$

When these are used in Eqs. (66) and (67), we see that there is a breakdown of translational invariance of the material constants after the electric dipole order. This breakdown again results in the origin dependence of the amplitude \mathbf{H}_0 and the energy flow. For a linearly polarized wave and the choice of coordinates used in Eq. (41), it is readily found from Eqs. (19)–(23), (66), (67), (70), and (40) that for a nondissipative medium

$$\Delta \langle S_z \rangle = -\frac{1}{4} \omega d_x \alpha'_{xz} E_0^2. \quad (72)$$

Thus in a magnetic medium $\langle \mathbf{S} \rangle$ is origin dependent even in the absence of dissipation.

To cast the theory into a physically acceptable form, we proceed as before and look to the wave equation for a clue. For a magnetic medium and to electric quadrupole-magnetic dipole order, we must include the contributions (66) and (67) in the calculations leading to Eq. (43). It is easily found that as a result, α_{ij} should be replaced by $\alpha_{ij} - i\alpha'_{ij}$ and β_{ij} by $\beta_{ij} + i\tilde{\beta}_{ij}$ in Eq. (43), where

$$\begin{aligned} \tilde{\beta}_{ij} &= \sigma_k \left[-\varepsilon_{ikl} G_{jl} - \varepsilon_{jkl} G_{il} + \frac{1}{2} \omega (a'_{ijk} + a'_{jki}) \right] \\ &= \sigma_k \left[-\varepsilon_{ikl} W_{jl} - \varepsilon_{jkl} W_{il} + S_{ijk} \right]. \end{aligned} \quad (73)$$

Here

$$S_{ijk} = \frac{1}{3} \omega (a'_{ijk} + a'_{jki} + a'_{kij}), \quad (74)$$

$$W_{ij} = G_{ij} - \frac{1}{6} \omega \varepsilon_{jkl} a'_{kli}. \quad (75)$$

In the step leading to Eq. (73) we have used Eq. (46) and the symmetry in Eq. (64).

According to Eqs. (70) and (71), S_{ijk} is origin independent⁶ but W_{ij} is not. It is easy to get around this difficulty because W_{ij} in Eq. (73) can be changed without affecting $\tilde{\beta}_{ij}$: we can add a term in δ_{ij} to W_{ij} in Eq. (73) because $\varepsilon_{ikl} \delta_{jl} + \varepsilon_{jkl} \delta_{il} = 0$. Thus, we can add $c G_{il} \delta_{ij}$ (where c is a number) to Eq. (75) without changing $\tilde{\beta}_{ij}$. [Note that according to Eq. (70) and the anti-symmetry of α'_{ij} , the trace of G_{ij} is origin dependent.] It is straightforward to show that W_{ij} is origin independent if $c=1/3$. We therefore consider

$$W_{ij} = G_{ij} - \frac{1}{3} G_{il} \delta_{ij} - \frac{1}{6} \omega \varepsilon_{jkl} a'_{kli}. \quad (76)$$

We emphasize that the change from Eq. (75) to Eq. (76) is necessitated by translational invariance. It turns out that there is an interesting physical consequence to this change (see Sec. X).

The above discussion shows that the wave equation for magnetic systems, like that for nonmagnetic systems, is origin independent even though both are based on origin-dependent constitutive relations. The invariant tensors (74) and (76) are the clue provided by the wave equation, and we now seek to recast the constitutive relations (to electric quadrupole-magnetic dipole order) in terms of them. We need concentrate only on the additional, magnetic contributions to Eqs. (51) and (52). According to Eq. (67), these are

$$D_i = \frac{1}{2}k_k(a'_{ijk} + a'_{jik})E_j + G_{ij}B_j, \quad (77)$$

$$H_i = -G_{ji}E_j. \quad (78)$$

As before there are two steps. We add

$$C^{(2)} \rightarrow \begin{pmatrix} \frac{1}{3}k_k(a'_{ijk} + a'_{jki} + a'_{kij}) & G_{ij} - \frac{1}{3}G_{ll}\delta_{ij} - \frac{1}{6}\omega\varepsilon_{jkl}a'_{kli} \\ -G_{ji} + \frac{1}{3}G_{ll}\delta_{ij} + \frac{1}{6}\omega\varepsilon_{ikl}a'_{klj} & 0 \end{pmatrix}. \quad (80)$$

The total constitutive tensor for a magnetic medium (to electric quadrupole-magnetic dipole order) is obtained by adding Eqs. (66) and (80) to the nonmagnetic contribution (59). Clearly, the result satisfies the symmetries (25) for a nondissipative medium, where the wave vector and polarizability densities are real. Also, the wave equation is unaltered by the two steps in Eqs. (58) and (80) because, by construction, these steps leave the macroscopic Maxwell equations (3) and (4) unchanged.

IX. THE INVERSE PERMEABILITY

From Eqs. (19)–(24) and (66)–(68) we see that the inverse permeability of a magnetic medium is given in the semiclassical theory by

$$X_{ij} = \mu_0^{-1}\delta_{ij} - \chi_{ij} + i\chi'_{ij}. \quad (81)$$

The quantum-mechanical expressions for the corresponding molecular polarizability tensors are^{11,12}

$$\chi_{ij} = (2/\hbar)\sum_s \omega_{sn}Z_{sn} \operatorname{Re}\{\langle m_i \rangle_{ns}\langle m_j \rangle_{sn}\} + \sum \frac{q^2}{4m}\langle r_i r_j - r^2 \delta_{ij} \rangle_{nm} = \chi_{ji}, \quad (82)$$

$$\chi'_{ij} = -(2/\hbar)\sum_s \omega Z_{sn} \operatorname{Im}\{\langle m_i \rangle_{ns}\langle m_j \rangle_{sn}\} = -\chi'_{ji}, \quad (83)$$

where the notation is the same as that used in Sec. III. In Eq. (82) the second sum is over all particles in a molecule as in Eqs. (7) and (8). The two terms in Eq. (82) are the familiar paramagnetic and diamagnetic contributions, respectively. Although χ_{ij} and χ'_{ij} appear in the leading terms involving \mathbf{B} in the macroscopic magnetic dipole moment density M_i [see Eqs. (12) and (62)], the quantum-mechanical expressions (82) and (83) show that they are of magnetic quadrupole order.

Both χ_{ij} and χ'_{ij} are origin dependent:^{11,12}

$$\Delta\chi_{ij} = \frac{1}{2}\omega(\varepsilon_{ikl}d_k G'_{lj} + \varepsilon_{jkl}d_k G'_{li}), \quad (84)$$

$$\Delta\chi'_{ij} = -\frac{1}{2}\omega(\varepsilon_{ikl}d_k G_{lj} - \varepsilon_{jkl}d_k G_{li}), \quad (85)$$

where we have, for simplicity, neglected terms quadratic in d_i . It follows that Eq. (81) is origin dependent and therefore

$$H_i^G = \left(\frac{1}{3}G_{ll}\delta_{ij} + \frac{1}{6}\omega\varepsilon_{ikl}a'_{klj}\right)E_j \quad (79)$$

to H_i and use Eq. (50). Then we use Faraday's law (42) and the relation (56) with a_{ijk} replaced by a'_{ijk} to modify D_i . The result is conveniently summarized by giving the effect on $C^{(2)}$ in Eq. (67),

cannot represent a physically acceptable inverse permeability tensor.

To find an acceptable inverse permeability we should proceed as we did for the magnetoelectric tensors; that is, we must construct an origin-independent linear combination of χ_{ij} with other nonmagnetic polarizability densities of electric octopole-magnetic quadrupole order (there are four of them) that correspond to the entries marked 2nd and 3rd in Eq. (24). In a similar manner, χ'_{ij} for a magnetic medium must be combined with polarizability tensors in the entries denoted by 2nd and 3rd in Eq. (68). These calculations are considerably more difficult than those presented in Secs. VII and VIII and the details can be found in Ref. 15. We mention that it is essential to take account of the magnetic quadrupole moment density M_{ij} and the electric octopole moment density Q_{ijk} in Eqs. (5) and (6) to obtain an origin-independent constitutive tensor to this order.

X. THE POST CONSTRAINT

This constraint, which was first proposed by Post,¹⁸ requires the equality of the traces of the magnetoelectric tensors

$$T_{ii} = U_{ii}, \quad (86)$$

thereby reducing the number of independent components of the constitutive tensor in Eq. (19) for a dissipative medium from 36 to 35 (and from 21 to 20 for a nondissipative medium). The constraint has attracted considerable attention in recent years.¹⁹ Our intention here is to comment on the results in Secs. IV, VII, and VIII in relation to the Post constraint:

1. The magnetoelectric tensors obtained directly from the semiclassical theory are given to electric quadrupole-magnetic dipole order in Eqs. (19), (23), and (67). From these equations we have

$$T_{ii} = G_{ii} - iG'_{ii}, \quad U_{ii} = -G_{ii} - iG'_{ii}. \quad (87)$$

Thus the constraint is violated in a magnetic medium if $G_{ii} \neq 0$. (At the next multipole order it is violated even for a nonmagnetic medium.^{6,15})

2. For the transformed magnetoelectric tensors, Eqs. (59) and (80) show that instead of Eq. (87), we have

$$T_{ii} = -iG'_{ii}, \quad U_{ii} = -iG'_{ii}. \quad (88)$$

[We have used $\delta_{ii}=3$ and $\varepsilon_{ikl}a_{kli}=\varepsilon_{ikl}a'_{kli}=0$ because of the antisymmetry of ε_{ijk} and the symmetry of a_{ijk} and a'_{ijk} in Eqs. (15) and (64).] Thus the Post constraint emerges automatically as a by-product of the transformations; this feature occurs also at the next multipole order.¹⁵

3. The cause of the change from Eq. (87) to (88) is seen to be due to the imposition of translational invariance on the theory, specifically with the construction of W_{ij} in Eq. (76). Because $W_{ii}=0$, the contributions of G_{ii} in Eq. (87) are removed in the transformed theory. Thus, the theory presented here has the surprising feature that the Post constraint is connected with translational invariance, at least for ac fields.

4. Because the change from Eq. (75) to (76) does not affect the wave equation, we conclude that transmission phenomena cannot be used to test the validity of the Post constraint—at least in the macroscopic theory (the long-wavelength limit). The same conclusion has been reached without using a multipole description.¹⁹

5. It is instructive to consider the dc limit ($\omega \rightarrow 0, \mathbf{k} \rightarrow 0$). We have already noted that all polarizability densities indicated with a prime vanish when $\omega=0$. Thus, the dc limit of the direct multipole results in Eqs. (19)–(24) and (66)–(68) is

$$C_0 = \begin{pmatrix} \varepsilon_0 \delta_{ij} + \alpha_{ij} & G_{ij} \\ -G_{ji} & \mu_0^{-1} \delta_{ij} - \chi_{ij} \end{pmatrix}. \quad (89)$$

[To obtain Eq. (89) we have used the result that the entries 2nd and 3rd in Eq. (24) are zero in the dc limit.²⁰] The polarizability densities in Eq. (89) are given by Eqs. (14), (65), and (82) with $\omega=0$; that is, $Z_{sn}=1/\omega_{sn}^2$. These dc polarizability densities are origin independent—see Eqs. (33), (70), and (84) with $\omega=0$. We may therefore expect that the transformed multipole results should have the same limit (89). Surprisingly, from Eqs. (59), (66), and (80) we have

$$C_0 = \begin{pmatrix} \varepsilon_0 \delta_{ij} + \alpha_{ij} & G_{ij} - \frac{1}{3} G_{ll} \delta_{ij} \\ -G_{ji} + \frac{1}{3} G_{ll} \delta_{ij} & \mu_0^{-1} \delta_{ij} - \chi_{ij} \end{pmatrix}. \quad (90)$$

[We have also used the result that the leading (electric octopole-magnetic quadrupole) contribution to the transformed X_{ij} goes to $-\chi_{ij}$ as $\omega \rightarrow 0$.¹⁵] The limits (89) and (90) agree for the permittivity and inverse permeability tensors, but not for the magnetoelectric tensors. The difference is associated with the Post constraint, see the previous remarks (1)–(3). Equation (90) satisfies this constraint, but Eq. (89) does not, at least in media for which $G_{ll} \neq 0$. It would be interesting to perform an experimental test to determine which of Eqs. (89) and (90) is correct.

6. The polarizability density χ_{ij} in Eqs. (89) and (90) is given by the dc value of Eq. (82). This expression agrees with the well-known result of Van Vleck,⁷ who, to our knowledge, was the first to mention translational invariance in this regard; when $\omega=0$, the origin dependence of the paramagnetic and diamagnetic terms in Eq. (82) cancel each other.⁶ We emphasize that although it is relatively easy to obtain Van Vleck's result, its extension to an origin-independent expression at nonzero frequency involves the complicated task mentioned in Sec. IX.

XI. THE BUCKINGHAM EFFECT

An important feature of the work we have described is the manner in which origin-independent macroscopic observables can be expressed in terms of suitable combinations of origin-dependent molecular properties (polarizabilities and in some cases also multipole moments). Often these molecular properties are also observables, and in this section we discuss a beautiful example of how values of an origin-dependent molecular property can be extracted from measurements of an origin-independent macroscopic observable. We consider the birefringence induced in a gas by an electrostatic field gradient. In recognition of the substantial contributions by Buckingham to the theoretical and experimental aspects of this phenomenon,^{21–23} the effect has been named after him.²⁴

A nonuniform electrostatic field exerts a torque $N_i = \varepsilon_{ijk} q_{jl} \nabla_l E_k$ on an electric quadrupole.⁶ In a gas of quadrupolar molecules this torque produces partial alignment of the molecules and hence anisotropy. This alignment gives rise to a linear birefringence known as electric-field-gradient-induced birefringence. The measurement of the effect provides a direct method for determining the electric quadrupole moment of a molecule.^{21–23}

The experimental arrangement devised by Buckingham consists of a gas cell in the form of a long metal cylinder, along the length of which run two thin parallel wires that are equidistant from the axis of the cylinder and on opposite sides. The wires are maintained at the same potential relative to the cylinder, and consequently the electrostatic field is zero on the axis, but the electric field gradient η is not.⁶ A laser beam parallel to the axis, centered on it, and of width smaller than the separation of the wires, is used to measure the induced birefringence.

For linearly polarized light this birefringence is given by^{23,25}

$$n_x - n_y = (\mathcal{N}/30\varepsilon_0 kT) \eta [3\alpha_{ij} q_{ij} - \alpha_{ii} q_{jj} - p_i \{3a_{jji} - a_{ijj} + 10\omega^{-1} \varepsilon_{ijk} G'_{jkj}\}]. \quad (91)$$

Here \mathcal{N} is the number density of the molecules (assumed to be constant); T is the temperature of the gas; the polarizability tensors α_{ij} , a_{ijk} , and G'_{ij} are given by Eqs. (14)–(16); and p_i and q_{ij} are (permanent) electric dipole and quadrupole moments defined in Eq. (7). The x axis is in the plane of the wires and perpendicular to them; the y axis is perpendicular to the plane of the wires. The refractive indices n_x and n_y are for incident beams linearly polarized parallel to the x and y axes, respectively. In Eq. (91) we have omitted a temperature-independent term.^{23,25}

We note the following points in relation to the present paper.

1. Equation (91) can be obtained either from the forward scattering of light by molecules,^{23,25} or by using a wave equation obtained from the macroscopic Maxwell equation (4),²⁶ or by using general arguments based on spatial properties, intrinsic symmetry, and dimensional analysis.²⁷ Each calculation is to electric quadrupole-magnetic dipole order and the results are the same.

2. In the Buckingham effect the medium is inhomogeneous, and consequently the wave equation is more complicated than that in Sec. VI; nevertheless, it is still origin independent,^{6,26} as is the right-hand side of Eq. (91). [The translational invariance of Eq. (91) can be checked using

Eqs. (28), (29), (33), (36), and (37).] This property of Eq. (91) is essential because n_x and n_y are origin-independent macroscopic observables.

3. For a nondipolar molecule ($p_i=0$), Eq. (91) simplifies to

$$n_x - n_y = (\mathcal{N}/30\epsilon_0 kT) \eta [3\alpha_{ij}q_{ij} - \alpha_{ii}q_{jj}]. \quad (92)$$

Consider a linear molecule. Relative to its main symmetry axis the molecule has only one independent component of its traceless quadrupole moment, which is the usual quoted value. This component can be obtained from Eq. (92) and measurements of the birefringence at various temperatures and the relevant components of α_{ij} . There is no question of origin dependence here because as shown by Eq. (29), $\Delta q_{ij} = 0$ for a neutral nondipolar molecule.

4. For a dipolar molecule ($p_i \neq 0$) the quadrupole moment is origin dependent [see Eq. (29)], and the situation is more subtle. As pointed out in Ref. 23, Eq. (92) still applies, provided that the origin-dependent vector in curly braces in Eq. (91) is set equal to zero:

$$3a_{jji} - a_{ijj} + 10\omega^{-1}\epsilon_{ijk}G'_{jk} = 0. \quad (93)$$

The origin-dependent moment q_{ij} obtained using Eq. (92) is with respect to an origin defined by Eq. (93). This origin is known as the effective quadrupole center;²³ it is a convenient reference point for the quadrupole moment of a dipolar molecule. The effective quadrupole center is a frequency-dependent point that, in general, does not coincide with the center of mass of a molecule.

5. Measured values of quadrupole moments are in good agreement with the results of *ab initio* calculations.^{28,29} For dipolar molecules it is essential that an accurate numerical calculation be performed to locate the position of the effective quadrupole center.²⁹ These computer calculations show that the accurate evaluation of molecular polarizability tensors such as those considered in this paper is now feasible.

6. Equation (91) illustrates how the inclusion of a third origin-dependent quantity (q_{ij} for a dipolar molecule) with a_{ijk} and G'_{ij} allows construction of an additional invariant quantity—compare the invariant scalar in square brackets in Eq. (91) with the invariant tensor (45).

We conclude that the experimental, theoretical, and computational aspects of the Buckingham effect support the multipole approach described in this paper.

XII. APPLICATIONS

It is beyond the scope of this paper to discuss the many applications of the semiclassical theory. Here we make some brief comments and refer the reader to the literature for further details.

Because of the finite wavelength of a harmonic wave, its fields are not uniform over an element of a medium, such as a molecule in a gas or a unit cell in a crystal. Thus field gradients of different order $\nabla_j E_i$, $\nabla_k \nabla_j E_i$, ... (and similarly for \mathbf{B}) may also induce multipoles. The wave also possesses time-derivative fields, and it is sufficient to consider just the zeroth and the first time derivatives. Thus the following fields of a harmonic plane wave may induce multipoles of various orders E_i , $\nabla_j E_i$, $\nabla_k \nabla_j E_i$, ..., B_i , $\nabla_j B_i$, $\nabla_k \nabla_j B_i$, ..., together with their first time derivatives [cf. Eqs. (10)–(12) and (60)–(62)].

It might be supposed that such field-gradient effects would be experimentally negligible for visible light, given its wave-

length of order 500 nm and the dimension of a unit cell in a crystal which is typically of order 0.5 nm. However, the optical activity that exists in some crystals is due to the terms $\nabla_k E_j$ and \dot{B}_j in Eq. (10), and the effect is not negligible: in quartz the rotation angle along its optic axis is about 220° per cm of path for yellow light.

The action of a field gradient of an electromagnetic wave in inducing an effect in matter is known as spatial dispersion.³⁰ This concept was used as long ago as 1878 by Lorentz in his theory of linear birefringence in certain cubic crystals.³¹ A subsequent theory by Condon and Seitz³² explained this birefringence in terms of the contribution $\nabla_k \nabla_j E_i$ to the polarization density \mathbf{P} , and this explanation was followed by a consistent multipole theory that includes all relevant contributions.¹¹ Other early work was that of Gibbs on optical activity.³³

Semiclassical multipole theory has been applied to all eight transmission effects contained in the Jones calculus;^{34,35} this theory entails working with a wave equation like Eq. (43), but including magnetic properties and extended to electric octopole-magnetic quadrupole order.¹⁷ These effects occur in nature. The theory has also been applied to effects induced by static fields, such as the Kerr effect¹⁷ and the Buckingham effect. As mentioned in Sec. VI, the wave equation is translationally invariant and it therefore produces physically acceptable results for all of these phenomena.

The material constants constructed in Secs. VII and VIII required the introduction of three invariant tensors: V_{ij} in Eq. (45), W_{ij} in Eq. (76), and S_{ijk} in Eq. (74). Some phenomena in which these tensors find application include:

1. The symmetric part of V_{ij} and its origin independence were first discussed in a theory of the optical activity of a fluid of aligned molecules.³⁶
2. Experimental confirmation of the need to include the electric quadrupole contribution [the term in a_{kli} in Eq. (45)] in the theory of optical activity in an anisotropic chiral medium is provided by the microwave measurements of Theron and Cloete.^{37,38} They measured the rotation of linearly polarized microwaves emerging from a 2-m-long sample consisting of chiral metal objects having dimensions of about 3 mm in a regular array supported by a dielectric foam. Their measurements disagreed with theoretical values in which the quadrupole contribution was omitted.
3. The tensor V_{ij} is required in the theory of reflection from nonmagnetic uniaxial and cubic crystals.⁶
4. W_{ij} and S_{ijk} are needed in the theory of reflection from magnetic crystals like Cr_2O_3 .⁶

XIII. DISCUSSION

We have shown that the multipole description of macroscopic, semiclassical electrodynamics yields unphysical results for quantities such as the dynamic material constants, response fields, and energy flow. We have also shown how the nonuniqueness of \mathbf{D} and \mathbf{H} in Maxwell's macroscopic equations allows us to construct physically acceptable results. We did this in a simple way by using the equation for wave propagation to motivate our calculations.

The nonuniqueness is a property of the Maxwell equations even when supplemented by the constitutive relations (19). The transformation theory of Refs. 6 and 15 shows that without the symmetries (25) for nondissipative media and the

invariances (26), an infinite number of solutions \mathbf{D} and \mathbf{H} can be generated within multipole theory. The propagation equation (43) (and its extensions¹⁷) is invariant under these transformations.⁶ By imposing some of the symmetries and the invariances (25) and (26), we obtain unique, physically acceptable fields \mathbf{D} and \mathbf{H} . [For a magnetic medium and to electric quadrupole-magnetic dipole order, it is sufficient to impose $U_{ij} = -T_{ji}^*$ and $\Delta T_{xx} = \Delta T_{xy} = \Delta U_{xx} = \Delta U_{xy} = 0$; the remaining 44 of the 57 conditions in Eqs. (25) and (26) are then automatically satisfied.^{6]} Thus symmetry and translational invariance are crucial to the theory.

The hierarchy of multipole orders (9) also plays an important role. This hierarchy enters in the classical multipole expansions (5) and (6) for the response fields and in the multipole orders of the polarizability densities in expansions such as Eqs. (10)–(12) for the induced macroscopic multipole moment densities. These orders are obtained from quantum-mechanical expressions such as Eqs. (14)–(16), and the first few are listed in (18). We make several comments concerning this hierarchy.

1. Properties and effects may be classified according to the lowest multipole order of polarizability densities that is necessary to describe the property or effect, based on (9). For the material constants, for example, our discussion shows that the multipole order of the leading contribution is (i) permittivity: electric dipole; (ii) magnetoelectric coefficients: electric quadrupole-magnetic dipole; (iii) inverse permeability: electric octupole-magnetic quadrupole. For the inverse permeability, this conclusion is counterintuitive: the polarizabilities χ_{ij} and χ'_{ij} in Eqs. (12) and (62) provide the leading terms involving \mathbf{B} and $\dot{\mathbf{B}}$ in the expansion of the macroscopic magnetic dipole moment density M_i . Nevertheless, according to Eqs. (82) and (83), both χ_{ij} and χ'_{ij} are of magnetic quadrupole order. The terms of magnetic dipole order in M_i are the electric field terms $-\omega^{-1}G'_{ji}\dot{E}_j$ and $G_{ji}E_j$ in Eqs. (12) and (62); they contribute to the magnetoelectric effect.
2. The contribution of higher-order terms should be treated with some care. It is, of course, true that higher-order terms will be small compared to the leading contributions. For example, the tensor $a'_{ijk} + a'_{jki} + a'_{kij}$ in Eq. (80) makes a small (electric quadrupole) contribution to the leading (electric dipole) term α_{ij} of the permittivity in Eq. (22)—here “small” means of order molecular dimension/wavelength times the leading contribution. However, this quadrupole tensor is important in its own right. More significantly, if we were to neglect the quadrupole tensors a'_{ijk} in Eq. (23) or a'_{ijk} in Eq. (67), then the resulting transformed contributions Eqs. (58) and (80) to the constitutive tensor would not be origin independent.
3. The transformation of the multipole response fields at a given order in Eq. (9) requires that we work with all the polarizabilities of that order. The reason is that the origin dependencies of polarizabilities of given multipole order 2^n involve polarizabilities of the next lowest order 2^{n-1} [examples are Eqs. (36), (37), (70), (71), (84), and (85)].⁶ Consequently, by combining polarizabilities of the same order, we can construct origin-independent forms.^{5,6,15} The use of “mixed orders,” such as an electric dipole-magnetic dipole approximation, will not yield physically acceptable results for properties such as the dynamic material constants.

4. Where the leading contribution to a property is a higher-order member of (9), it is not clear what small means. Consider, for example, the magnetoelectric effect, which is of electric quadrupole-magnetic dipole order. This effect is of considerable interest in solid-state microelectronics for its practical applications such as in sensors and microwave devices.^{39–41} Therefore, ways are sought to enhance the effect by, for example, the use of bulk and multilayer composites^{42,43} and the production of a giant magnetoelectric effect due to electromechanical resonance.⁴⁴

In conclusion, we raise some additional points that may be of further interest. (a) Why does the conventional semiclassical multipole theory for a macroscopic medium yield unphysical results that require transformation? After all, this theory is based on standard physics: the averaging and series expansions of electromagnetic quantities and the application of time-dependent perturbation theory to molecular multipole moments and polarizabilities. (b) Is it possible to obtain physical results by first making a microscopic transformation (of the molecular Hamiltonian, say), rather than by transforming macroscopic fields? (c) Is there an interesting theory underlying the aspects of nonuniqueness and transformation in the macroscopic theory? (d) Why is the Post constraint violated for the unphysical fields of the conventional theory, and why is the constraint obtained automatically for the transformed fields. In fact, is the Post constraint adequately understood? In this connection, an experimental test of the constraint for the dc magnetoelectric coefficients in Eqs. (89) and (90) would be of interest.

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¹G. Russakoff, “A derivation of the macroscopic Maxwell equations,” *Am. J. Phys.* **38**, 1188–1195 (1970).

²F. N. H. Robinson, *Macroscopic Electromagnetism* (Pergamon, Oxford, 1973).

³B. K. P. Scaife, *Principles of Dielectrics* (Clarendon, Oxford, 1989).

⁴J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1999).

⁵O. L. de Lange and R. E. Raab, “Completion of multipole theory for the electromagnetic response fields \mathbf{D} and \mathbf{H} ,” *Proc. R. Soc. London, Ser. A* **459**, 1325–1341 (2003).

⁶R. E. Raab and O. L. de Lange, *Multipole Theory in Electromagnetism* (Clarendon, Oxford, 2005).

⁷J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon, Oxford, 1932).

⁸E. B. Graham, J. Pierrus, and R. E. Raab, “Multipole moments and Maxwell’s equations,” *J. Phys. B* **25**, 4673–4684 (1992).

⁹R. R. Birss, *Symmetry and Magnetism* (North-Holland, Amsterdam, 1966). See also Ref. 6, Secs. 3.5 and 3.6.

¹⁰A. D. Buckingham, “Permanent and induced molecular moments and long-range intermolecular forces,” in *Intermolecular Forces*, edited by J. O. Hirschfelder [*Adv. Chem. Phys.* **12**, 107–142 (1967)].

¹¹E. B. Graham and R. E. Raab, “Light propagation in cubic and other anisotropic crystals,” *Proc. R. Soc. London, Ser. A* **430**, 593–614 (1990).

¹²See Ref. 6, Chap. 2, especially Eqs. (2.110)–(2.114) and Sec. 2.11.

¹³L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge U.P., Cambridge, 1982).

¹⁴T. H. O’Dell, *The Electrodynamics of Magneto-Electric Media* (North-Holland, Amsterdam, 1970).

¹⁵R. E. Raab and O. L. de Lange, “Transformed multipole theory of the

- response fields **D** and **H** to electric octupole-magnetic quadrupole order,” *Proc. R. Soc. London, Ser. A* **461**, 595–608 (2005).
- ¹⁶J. A. Kong, *Electromagnetic Wave Theory* (Wiley, New York, 1986), Secs. 2.2 and 7.10.
- ¹⁷See Ref. 6, Chap. 5 and references therein.
- ¹⁸E. J. Post, *Formal Structure of Electromagnetics* (North-Holland, Amsterdam, 1962). Reprinted by Dover, New York, 1997.
- ¹⁹F. W. Hehl and Y. N. Obukhov, “Linear media in classical electrodynamics and the Post constraint,” *Phys. Lett. A* **334**, 249–259 (2005), and references therein.
- ²⁰See Ref. 6, p. 85.
- ²¹A. D. Buckingham, “Direct method of measuring molecular quadrupole moments,” *J. Chem. Phys.* **30**, 1580–1585 (1959).
- ²²A. D. Buckingham and R. L. Disch, “The quadrupole moment of the carbon dioxide molecule,” *Proc. R. Soc. London, Ser. A* **273**, 275–289 (1963).
- ²³A. D. Buckingham and H. C. Longuet-Higgins, “The quadrupole moments of dipolar molecules,” *Mol. Phys.* **14**, 63–72 (1968).
- ²⁴G. L. D. Ritchie, J. N. Watson, and R. I. Keir, “Temperature-dependence of electric field-gradient induced birefringence (Buckingham effect) and molecular quadrupole moment of N₂. Comparison of experiment and theory,” *Chem. Phys. Lett.* **370**, 376–380 (2003), and references therein.
- ²⁵R. E. Raab and O. L. de Lange, “Forward scattering theory of electric-field-gradient-induced birefringence,” *Mol. Phys.* **101**, 3467–3475 (2003).
- ²⁶O. L. de Lange and R. E. Raab, “Reconciliation of the forward scattering and wave theories of electric-field-gradient-induced birefringence,” *Mol. Phys.* **102**, 125–130 (2004).
- ²⁷O. L. de Lange and R. E. Raab, “On the theory of the Buckingham effect,” *Mol. Phys.* (in press).
- ²⁸A. Halkier, S. Coriani, and P. Jorgensen, “The molecular electric quadrupole moment of N₂,” *Chem. Phys. Lett.* **294**, 292–296 (1998).
- ²⁹S. Coriani, A. Halkier, D. Jonsson, J. Gauss, A. Rizzo, and O. Christiansen, “On the electric field gradient induced birefringence and electric quadrupole moment of CO, N₂O, and OCS,” *J. Chem. Phys.* **118**, 7329–7339 (2003).
- ³⁰V. M. Agranovich and V. L. Ginzburg, *Crystal Optics with Spatial Dispersion, and Excitons* (Springer, Berlin, 1984).
- ³¹H. A. Lorentz, “Concerning the relation between the velocity of propagation of light and the density and composition of media,” in *H. A. Lorentz, Collected Papers*, edited by P. Zeeman and A. D. Fokker (Nijhoff, The Hague, 1936), Vol. 2, pp. 1–119.
- ³²E. B. Condon and F. Seitz, “Lorentz double refraction in the regular system,” *J. Opt. Soc. Am.* **22**, 393–401 (1932).
- ³³J. W. Gibbs, “Notes on the electromagnetic theory of light. II. On refraction in perfectly transparent media which exhibit the phenomena of circular birefringence,” *Am. J. Sci.* **23**, 460–476 (1882).
- ³⁴R. C. Jones, “A new calculus for the treatment of optical systems. VII,” *J. Opt. Soc. Am.* **38**, 671–685 (1948).
- ³⁵W. A. Shurcliff, *Polarized Light* (Harvard U. P., Cambridge MA, 1962).
- ³⁶A. D. Buckingham and M. B. Dunn, “Optical activity of oriented molecules,” *J. Chem. Soc. A* 1988–1991 (1971).
- ³⁷I. P. Theron and J. H. Cloete, “The optical activity of an artificial non-magnetic uniaxial chiral crystal at microwave frequencies,” *J. Electromagn. Waves Appl.* **10**, 539–561 (1996).
- ³⁸I. P. Theron and J. H. Cloete, “The electric quadrupole contribution to the circular birefringence of nonmagnetic anisotropic chiral media: A circular waveguide experiment,” *IEEE Trans. Microwave Theory Tech.* **44**, 1451–1459 (1996).
- ³⁹M. I. Bichurin, R. V. Petrov, and Y. V. Kiliba, “Magnetolectric microwave phase shifters,” *Ferroelectrics* **204**, 311–319 (1997).
- ⁴⁰M. I. Bichurin, V. M. Petrov, I. A. Komev, A. S. Tatarenko, Y. V. Kiliba, N. A. Konstantinov, and G. Srinivasan, “Resonance magnetolectric effect in multilayer composites,” *Ferroelectrics* **280**, 353–363 (2002).
- ⁴¹M. I. Bichurin, V. M. Petrov, R. V. Petrov, G. N. Kapralov, Y. V. Kiliba, F. I. Bukashev, A. Y. Smirnov, and A. S. Tatarenko, “Magnetolectric microwave devices,” *Ferroelectrics* **280**, 377–384 (2002).
- ⁴²M. I. Bichurin, V. M. Petrov, and G. Srinivasan, “Modeling of magnetolectric effect in ferromagnetic/piezoelectric multilayer composites,” *Ferroelectrics* **280**, 331–341 (2002).
- ⁴³M. I. Bichurin, V. M. Petrov, and G. Srinivasan, “Theory of low-frequency magnetolectric coupling in magnetostrictive-piezoelectric bilayers,” *Phys. Rev. B* **68**, 054402-1–13 (2003).
- ⁴⁴M. I. Bichurin, D. A. Filipov, V. M. Petrov, V. M. Laietsin, N. Paddubnaya, and G. Srinivasan, “Resonance magnetolectric effects in layered magnetostrictive-piezoelectric composites,” *Phys. Rev. B* **68**, 132408-1–4 (2003).