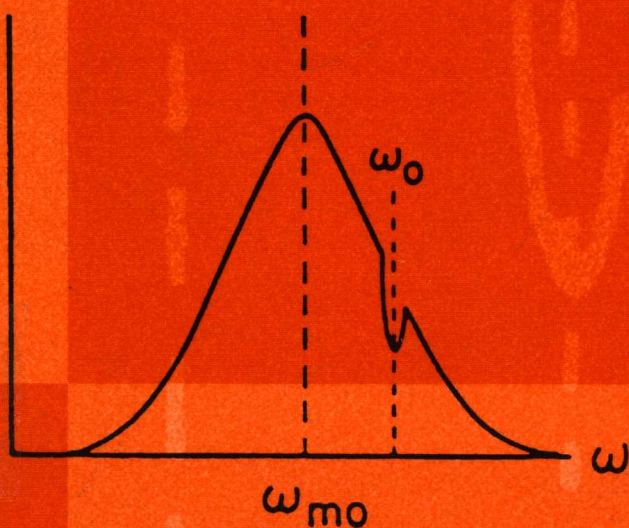D. L. Mills

Nonlinear Optics

Basic Concepts

Second, Enlarged Edition

Springer

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Basic Concepts

Second, Enlarged Edition
With 45 Figures

Springer

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Preface to the Second Edition

Since the book was first published in 1991, the field of surface nonlinear optics has grown substantially to the point where an exposition of the principles of this field will prove useful to many. Thus, in this second edition, Chapter 8 addresses this area. Also, optical probes of magnetism of very thin films and multilayers are now widely used, and magneto-optic devices of increasing sophistication have appeared. Chapter 9 is thus devoted to magneto-optics, and associated nonlinear phenomena. The earlier chapter on "Chaos" appears as Chapter 10. The philosophy which underlies the first edition was also employed in the writing of the two new chapters.

Irvine, CA
March 1998

D. L. Mills

Preface to the First Edition

One intriguing aspect of physics is its dynamic and rapidly evolving nature; exciting new fields can become moribund within relatively few years, only to revive and grow again in a dramatic and explosive manner in response to new developments. This has been the case for the fields of optics and atomic physics. In the 1950s, and perhaps into the early 1960s, both fields appeared mature, fully developed, and perhaps even a bit dull as a consequence. The appearance of the laser has turned both of these fields into dynamic areas of research, within which fundamental and profound questions are being explored. The research of the past two or three decades has led also to very important applications and to new devices. The dye laser, which enables a very narrow line to be tuned over an appreciable spectral range, has led to a virtual revolution in the spectroscopy of atoms, molecules, and the condensed phases of matter.

A parallel development, readily detectable in the recent literature of theoretical physics, has been the substantial advance in our understanding of highly nonlinear phenomena. Numerous texts are devoted to exposition of the theoretical methods which may be used to extract useful information from the important equations encountered in the various fields of physics.

A survey of the contemporary literature of nonlinear optics shows that in this area one encounters a large fraction of the basic equations and principles of nonlinear physics. For example, analysis of self-induced transparency leads to the sine-Gordon equation, and that of soliton propagation in optical fibers to the nonlinear Schrödinger equation. Other examples can be found as well. As a consequence, one has in hand real data which illustrate basic properties of those solutions of these important equations with no counterpart in linear response theory or in perturbation theoretic analyses of nonlinear terms. Other concepts central to nonlinear optics, such as the role of phase matching in various wave mixing experiments, are of very considerable importance in other subfields of physics. The field of nonlinear optics is thus a superb laboratory within which the student may encounter and explore key notions of nonlinear physics of general importance, while at the same time learning the foundations of a most important and fundamental area of contemporary physics.

Furthermore, the above issues are not addressed in many introductory graduate courses in electromagnetic theory; the emphasis is usually placed on more classical topics developed in an earlier era. This volume has its origin in a course given

at Irvine by the author, directed toward the student who has completed the first year electromagnetic theory sequence. It is intended as an extension of interest not only to students who wish to pursue thesis research in optics or laser spectroscopy but also to the general student whose ultimate research specialty may lie within a very different subfield. The focus is then on general principles, with many technical points that are important to the specialist played down or set aside. It is the author's experience that existing texts on nonlinear optics use specialized terms that are not defined fully and present introductions to important basic issues that are perhaps too concise to be grasped easily by the general reader. The purpose of this volume is to bridge the gap between the classic texts on electromagnetic theory, which omit systematic exploration of modern optics, and the (often excellent!) specialized texts full of discussion essential to those who are pursuing research in the area, but which are too detailed and too terse for the general student of physics.

The specialist may thus find important topics omitted from this volume, or discussions of a number of technical points a bit incomplete. The intention here is to provide an overview; the literature on nonlinear optics is sufficiently complete and accessible that those who wish to pursue particular aspects in more detail can proceed further without difficulty.

It is important also for the reader to acquire an understanding of the optical properties of various solid materials, to appreciate the reasons for the choice of samples for a given experiment, and the constraints that limit one's ability to explore various phenomena. Also, one must acquire a certain vocabulary in this arena to understand the literature. Chapter 2, which is quite lengthy, presents an overview of the optical properties of materials, since it is the experience of the author that many students have a very limited grasp of this area, though they may know the mathematical details associated with various models of matter.

It is hoped that this volume will broaden the horizons of graduate students in the physical sciences, by introducing them to the fascinating field of nonlinear optics, and at the same time provide them with an introduction to general aspects of the physics of nonlinear systems.

Irvine, CA   *D.L. Mills*
March 1991

Contents

1. Introductory Remarks

Throughout most of this volume, we shall be describing the interaction of electromagnetic radiation with matter within a macroscopic framework; we shall always be concerned with electric fields whose spatial variation involves length scales very large compared to the size of the atoms and molecules that are the basic constituents of the material of interest. In this regard, we note that in the visible portion of the spectrum, the wavelength of light is roughly 5×10^{-5} cm, while a typical molecular bond length or crystal lattice constant is 3×10^{-8} cm. We may then proceed by studying the solutions of Maxwell's equations, which have the form

$$\nabla \cdot \boldsymbol{D} = 0, \quad \nabla \cdot \boldsymbol{B} = 0 , \tag{1.1a}$$

$$\nabla \times \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t}, \quad \nabla \times \boldsymbol{H} = \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} . \tag{1.1b}$$

We assume no external charge is present, and no external current is present as well, so we set $\rho = \boldsymbol{J} = 0$.

To proceed, we require relations between the various fields which enter Maxwell's equations. In the limit of interest, we have [1.1]

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P} \tag{1.2a}$$

and

$$\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{M} , \tag{1.2b}$$

where $\boldsymbol{P}$ and $\boldsymbol{M}$ are the electric dipole moment per unit volume, and magnetic moment per unit volume, respectively. Until we reach Chap. 9, we shall confine our attention entirely to nonmagnetic media, and set $\boldsymbol{M} \equiv 0$. Nonlinearities very similar to those explored through Chap. 8 have their origin in the magnetic degrees of freedom of appropriate materials. Their study constitutes the very important field of magnetooptics.

We then have

$$\nabla \cdot \boldsymbol{E} + 4\pi\nabla \cdot \boldsymbol{P} = 0 \tag{1.3a}$$

and with $\boldsymbol{B} = \boldsymbol{H}$, the two remaining Maxwell equations are easily combined to give

$$\nabla^2 \boldsymbol{E} - \nabla(\nabla \cdot \boldsymbol{E}) - \frac{1}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2} - \frac{4\pi\partial^2 \boldsymbol{P}}{c^2\partial t^2} = 0 . \tag{1.3b}$$

To proceed, we require information on the relationship between P and E. In principle, one requires a full microscopic theory of the response of a particular material to relate E, the macroscopic electric field [1.1], to the dipole moment per unit volume.

It would appear that by our neglect of the term involving the current density J on the right-hand side of the $\nabla \times H$ Maxwell equation, our attention will be confined exclusively to insulating materials, rather than conductors such as metals or doped semiconductors. We shall see shortly that this is not the case; the conduction currents stimulated by time varying electric fields can in fact be viewed as contributing to the dipole moment per unit volume, as we shall come to appreciate. It is the case, however, that many of the nonlinear optical phenomena to be explored here require that the various beams involved have a long path length in the medium of interest. Thus, our attention will be directed largely toward applications to insulating materials that are nominally transparent at the relevant wavelengths. The reader should keep in mind that one encounters very interesting nonlinear optical phenomena in metals and in doped semiconductors, as discussed in the text by *Shen* [1.2].

One may proceed by noting the following: The largest electric fields encountered in practice fall into the range of 10^6 V/cm; most forms of matter exhibit electrical breakdown for fields in excess of this value. An electron bound to an atom or molecule, or moving through a solid or dense liquid, experiences electric fields in the range of 10^9 V/cm. This follows by noting that, over distances the order of an angstrom, the change in electrostatic potential can be several electron volts. The laboratory fields of interest are then small compared to the electric fields experienced by the electrons in the atoms and molecules from which dense matter is constructed. In this circumstance, we can expand the dipole moment per unit volume in a Taylor series in powers of the macroscopic field E. For the moment, we suppose the dipole moment per unit volume $P(r, t)$, depends on the electric field E at the same point r, and at the same time. We shall see shortly that in real materials, this assumption is overly restrictive. There are important qualitative implications of a more realistic relation between P and E. But this simple assertion will allow us to begin the discussion. Then the αth Cartesian component of the dipole moment per unit volume, $P_\alpha(r, t)$, is a function of the three Cartesian components of the electric field, $E_\beta(r, t)$. Here α and β range over x, y, and z. The Taylor series then takes the form

$$P_\alpha(r, t) = P_\alpha^{(0)} + \sum_\beta \left(\frac{\partial P_\alpha}{\partial E_\beta}\right)_0 E_\beta + \frac{1}{2!} \sum_{\beta\gamma} \left(\frac{\partial^2 P_\alpha}{\partial E_\beta \partial E_\gamma}\right)_0 E_\beta E_\gamma$$

$$+ \frac{1}{3!} \sum_{\beta\gamma\delta} \left(\frac{\partial^3 P_\alpha}{\partial E_\beta \partial E_\gamma \partial E_\delta}\right)_0 E_\beta E_\gamma E_\delta + \cdots . \tag{1.4}$$

In most of the common materials we encounter, the first term, which is the electric dipole moment per unit volume in zero electric field, vanishes iden-

tically. The usual situation is a dielectric material, within which the dipole moment in zero field vanishes; any dipole moment present is then induced by the external field.

There is an important class of materials, known as ferroelectrics, which possess a spontaneous electric dipole moment in zero field [1.3]. These are electrical analogues of the better known ferromagnets, which possess a spontaneous magnetization per unit volume M. In a ferromagnet, as the material is heated, the spontaneous magnetization M decreases in magnitude, to vanish at a certain temperature T_c, known as the Curie temperature. Ferroelectrics behave in a similar manner; the polarization P will decrease with increasing temperature, again to vanish above a critical temperature.

In the common ferroelectrics, the origin of the spontaneous dipole moment is in the shift of an ion from a high symmetry site to a low symmetry site as the temperature is lowered. For example, in the ferroelectric material $BaTiO_3$, in the high temperature phase for which $P_\alpha^{(0)} = 0$, the Ti^{2+} ion sits at the center of an oxygen octahedron. As the temperature is lowered below the critical temperature, the Ti^{2+} shifts off this high symmetry site, so the Ti–O complex acquires a net electric dipole moment. This is a collective phenomenon; all the Ti^{2+} ions shift in a coherent manner, so the crystal as a whole acquires an electric dipole moment. Similarly, in KH_2PO_4, it is the H that shifts.

Such materials are influenced strongly by dc or low frequency electric fields, particularly near their transition temperature, because the unstable ionic species respond strongly to an applied electric field. Ferroelectrics are thus useful in a variety of electro-optic devices.

In a ferroelectric, the dipole moment per unit volume, $P^{(0)}$, in the absence of an electric field, is independent of time, but may vary with position in the sample. In general, the presence of a nonzero polarization leads to the presence of a static, macroscopic electric field, $E^{(0)}(r)$. This static field obeys the two equations

$$\nabla \times E^{(0)} = 0 \tag{1.5a}$$

and

$$\nabla \cdot E^{(0)} = -4\pi \nabla \cdot P^{(0)} . \tag{1.5b}$$

Such fields may be analyzed by the methods of electrostatics [1.4]. We may write, from (1.5 a), $E^{(0)} = -\nabla \phi^{(0)}$, and (1.5 b) becomes Poisson's equation with effective charge density $\rho_p = -\nabla \cdot P^{(0)}$.

Our interest will be in the study of various time-dependent phenomena, in response to externally applied electric fields, usually with their origin in incident laser radiation. Thus the first term in (1.4) and the static fields it may generate in a ferroelectric are of little interest. The second and subsequent terms describe the influence of a time-dependent, macroscopic electric field; in what follows, we consider only these contributions to the dipole moment per unit

volume and their consequences, assuming the effect of $P^{(0)}$ and the static electric fields it generates are accounted for as described above, if necessary.

We may then treat the response of dielectric and ferroelectric materials within the same framework. For each, we will henceforth write

$$P_\alpha(r, t) = \sum_\beta \chi^{(1)}_{\alpha\beta} E_\beta(r, t) + \sum_{\beta\gamma} \chi^{(2)}_{\alpha\beta\gamma} E_\beta(r, t) E_\gamma(r, t)$$
$$+ \sum_{\beta\gamma\delta} \chi^{(3)}_{\alpha\beta\gamma\delta} E_\beta(r, t) E_\gamma(r, t) E_\delta(r, t) + \cdots , \qquad (1.6)$$

where $\chi^{(2)}_{\alpha\beta\gamma}$, $\chi^{(3)}_{\alpha\beta\gamma\delta}$ are referred to as the second and third order susceptibilities, respectively, and $\chi^{(1)}_{\alpha\beta}$ is the susceptibility tensor of ordinary dieletric theory.

As the notation in (1.6) indicates, the various susceptibilities are tensor objects. Thus, $\chi^{(1)}_{\alpha\beta}$ is a second rank tensor. For an isotropic material, such as a gas or liquid, $\chi^{(1)}_{\alpha\beta}$ is diagonal: $\chi^{(1)}_{\alpha\beta} = \chi^{(1)}\delta_{\alpha\beta}$. It is also established easily that for a cubic crystal, $\chi^{(1)}_{\alpha\beta}$ is diagonal. Since both P and E are vectors, and thus are odd under inversion symmetry, $\chi^{(2)}_{\alpha\beta\gamma}$ must vanish in any material that is left invariant in form under inversion. This is the case for liquids, gases, and for a number of common crystals such as the alkali halides, and also for the semiconductors Si and Ge. Notice that the fourth rank tensor $\chi^{(3)}_{\alpha\beta\gamma\delta}$ has the same transformation properties as the elastic constants of elasticity theory. One may consult analyses of elastic constants, in any given case, to investigate which elements of this tensor are nonvanishing [1.5]. *Shen* [1.2] has given very useful compilations of the nonzero elements of $\chi^{(2)}_{\alpha\beta\gamma}$ and $\chi^{(3)}_{\alpha\beta\gamma\delta}$ for crystals of various symmetry.

We separate P_α in (1.6) into two pieces, one linear in the electric field, and one nonlinear:

$$P_\alpha(r, t) = P^{(L)}_\alpha(r, t) + P^{(NL)}_\alpha(r, t) , \qquad (1.7\,a)$$

where

$$P^{(L)}_\alpha(r, t) = \sum_\beta \chi^{(1)}_{\alpha\beta} E_\beta(r, t) \qquad (1.7\,b)$$

and

$$P^{(NL)}_\alpha(r, t) = \sum_{\beta\gamma} \chi^{(2)}_{\alpha\beta\gamma} E_\beta(r, t) E_\gamma(r, t)$$
$$+ \sum_{\beta\gamma\delta} \chi^{(3)}_{\alpha\beta\gamma\delta} E_\beta(r, t) E_\gamma(r, t) E_\delta(r, t) \cdots . \qquad (1.7\,c)$$

If one retains only $P^{(L)}_\alpha(r, t)$ in the analysis, and combines this with the Maxwell equations (1.3) then one obtains a description of electromagnetic wave propagation in media, possibly crystalline in nature, and thus described by an electric susceptibility tensor $\chi_{\alpha\beta}$. The combination $\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi\chi_{\alpha\beta}$ is the

dielectric tensor of the material. Here $\delta_{\alpha\beta}$ is the Kronecker delta function, equal to unity when the two subscripts are the same, and zero otherwise. We shall assume that the reader is familiar with electromagnetic theory at this level, which is covered thoroughly in numerous excellent texts [1.1, 6].[1] However, we will cover below those aspects of the topic essential for the present discussion.

The calculation of the various nonlinear susceptibility tensor elements requires a proper microscopic theory of the material in question. One can write down formal expressions for these quantities,[2] but the resulting expressions are formidable in appearance. At the time of writing, evaluations of these formulae for anything more than schematic models of materials remain at an early stage. The simple models, however, prove most useful as a means of outlining the basic physical properties which control these parameters. We shall be content simply to regard the various coefficients in (1.7) as phenomenological parameters.

We conclude with one final remark. Throughout the present discussion, the electric field $E(r, t)$ is the macroscopic electric field, defined as in Jackson's text [1.1]. Quite often in the literature, one encounters descriptions of the linear or nonlinear response of a material based on a picture which models the atomic or molecular structure explicitly. One then relates the dipole moment per unit volume, our $P_\alpha(r, t)$, to that p_α of an atomic or molecular constituent; p_α may be written as a series similar to (1.6), where now in place of $\chi_{\alpha\beta}^{(1)}$, $\chi_{\alpha\beta\gamma}^{(2)}$, etc., one has the various linear and nonlinear polarizabilities of the individual constituents.

In this case, the electric field which enters the expansion is not the macroscopic electric field here, but the local field which acts on the individual entity; this is the external field, supplemented by that produced by the induced dipole moments which surround the entity in question. Clearly, the local field may differ substantially in value from the macroscopic field. However, it is the case that the local field is always proportional to the macroscopic field; a consequence is that the dipole moment per unit volume may always be expressed as an expansion in powers of the macroscopic field, as we do here. Particular models such as those just described can be very useful, but they can be applied only to materials in which the various atomic and molecular constituents are well separated and well defined (gases, some liquids, rare gas crystals, molecular crystals, alkali halide crystals, . . .). In dense materials, with extended chemical bonds such as those found in semiconductors, it is not clear how to isolate a basic entity, and how to calculate the local field within a simple model that is also meaningful. We thus prefer to phrase our discussion

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[1] An excellent account of the electrodynamics of crystals, within which the tensor character of the dielectric response is accounted for, is found in [1.6].

[2] A rather general microscopic description of the nonlinear optical response of materials has been given by *Armstrong* et al. [1.7].

entirely within the phenomenological framework where all nonlinear polarizabilities are related to the macroscopic field.

We now turn to a more detailed discussion of the linear response characteristics of materials, and their nonlinear response, before we enter descriptions of nonlinear optical processes.

Problems

1.1 A sphere of radius R is fabricated from ferroelectric material, and has a spatially uniform polarization $\boldsymbol{P} = \hat{\boldsymbol{z}}P_0$ parallel to the z direction everywhere.

(a) Find $\boldsymbol{D}$ and $\boldsymbol{E}$ inside and outside the material.

(b) A positive ion is attracted to, and sticks to one pole of the sphere. Calculate the work required to remove the ion and carry it off to infinity, if it is singly charged and $P_0 = 1.5 \times 10^4$ cgs units.

1.2 A point charge Q is placed at the origin of an isotropic nonlinear dielectric. Thus, both $\boldsymbol{D}$ and $\boldsymbol{E}$ are in the radial direction, by symmetry. One has, with D_r and E_r the radial fields, $D_r = E_r + 4\pi\chi^{(1)}E_r + 4\pi\chi^{(3)}E_r^3$. Assume $\chi^{(3)} > 0$, and discuss the behavior of E_r and D_r, with attention to the limits $r \rightarrow \infty$, $r \rightarrow 0$.

1.3 In an anisotropic dielectric exposed to static fields, $\chi_{\alpha\beta}^{(1)}$ is symmetric and thus we can always find a set of principal axes $x_0 y_0 z_0$ within which this tensor is diagonal. Such a material is placed between two parallel metal plates of infinite extent, separated by the distance D. The space between the plates is filled with the dielectric. The z axis is normal to the plates, which are parallel to the xy plane. The z_0 axis makes angle θ with respect to the z axis, while y and y_0 coincide. Find $\boldsymbol{D}$ and $\boldsymbol{E}$ everywhere, if V is the voltage difference between the metal plates.