

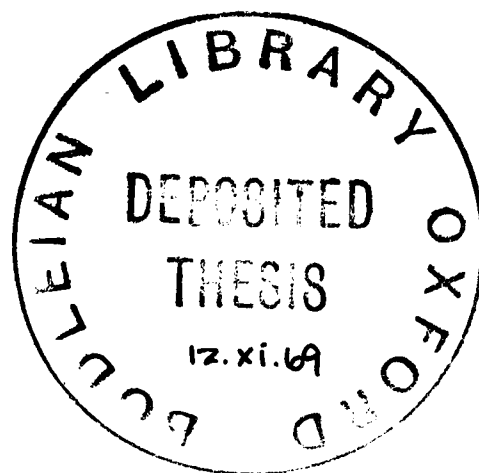
**THE THEORY OF  
OPTICAL  
BIREFRINGENCE**

# THE THEORY OF OPTICAL BIREFRINGENCE

**L.D. Barron**

Lincoln College, Oxford

June 1969



Submitted for the Degree of  
Doctor of Philosophy  
of the University of Oxford

# Acknowledgements

The author wishes to thank Dr. P. W. Atkins for his valuable guidance and inexhaustible patience during the course of this work.

The award of a Research Studentship by the Science Research Council is also gratefully acknowledged.

# Abstract

The theory of optical birefringence is discussed from the point of view of the scattering of polarized photons by molecules using the framework of formal scattering theory and quantum electrodynamics.

In Part One, those features from noncovariant quantum electrodynamics relevant to the molecular scattering of photons are reviewed. Chapter One contains an outline of classical electrodynamics in the Coulomb gauge, including the Stokes parameter and density matrix formulations of polarization. Chapter Two deals with the quantization of the radiation field, and the occupation number representation is defined. The quantum mechanical description of polarized light is outlined in Chapter Three: operator equivalents of the density matrix and Stokes parameters are invoked, the parameters themselves being obtained from the expectation values of the Stokes operators with the state vector of the photon. The Stokes parameter and density matrix are then applied to the polarization of a general beam containing an arbitrary number of photons, and some new methods are developed.

The interaction of the electromagnetic field with bound electrons is formulated in Chapter Four in terms of a canonically transformed interaction Hamiltonian in which the multipole terms are explicit. Since each term is then gauge-invariant, this Hamiltonian is particularly suited to the application of diagrammatic perturbation theory which follows from the iteration of

the scattering matrix in the interaction representation (Chapter Five). Also the extension of the theory to multiphoton processes is facilitated because the field strength is explicit in the transformed Hamiltonian. The S-matrix connects the initial and final asymptotic states of the scattering system, and in Chapter Six the state vector and density operator of the scattered photon beam are obtained from those of the incident beam.

Part Two contains the application of the above methods to a variety of linear and nonlinear optical birefringence effects in the absence or presence of external fields. In Chapter Seven, general equations are obtained for the polarization changes imposed on a forward scattered photon in terms of matrix elements of the reaction operator between plane polarized photon base states; whereas Chapter Eight extends this treatment to an n-photon beam, thereby encompassing the hyperpolarizability contributions to the polarization changes of the forward scattered beam. It is then demonstrated that the fundamental process in optical birefringence can be interpreted as an infinitesimal unitary transformation of the polarization spinor. Also the S-matrix approach to birefringence is compared with the methods used in crystal optics, and with the classical treatments of the scattering of polarized light by molecules.

The general equations obtained for the polarization changes of the forward scattered beam are subsequently interpreted in the light of the physical circumstances appropriate to the bire-

fringe effect of interest. In Chapters Nine, Ten, and Eleven, diagrammatic perturbation theory is used to obtain explicit expressions, in terms of molecular polarizability and rotation tensors, for the linear and nonlinear contributions to the polarization changes involved in natural optical activity, and in birefringence phenomena induced by static and optical electric and magnetic fields.

The nonforward scattering of polarized photons by molecules is discussed in Part Three. General equations are calculated in Chapter Twelve for the azimuth, ellipticity, and depolarization ratio of the Rayleigh beam at any scattering angle and for any polarization of the incident beam. Explicit expressions in terms of molecular quantities are then obtained for the polarization at scattering angles of  $90^\circ$  and almost zero from both optically inactive and optically active molecules. It is demonstrated that a determination of the precise polarization state of the scattered beam can provide useful molecular information additional to that obtained from depolarization ratios alone. This is because the depolarization ratio depends on only the diagonal elements of the polarization density matrix and so does not convey all the information about the system.

Raman scattering processes are contained in the formulation and the polarization of the Raman light at any scattering angle can be obtained. This is shown to be particularly useful for predicting the polarization of stimulated Raman light for any

Raman-active liquid placed within a laser cavity.

By extending the nonforward scattering formulation to incorporate multiphoton processes, equations are obtained in Chapter Thirteen for the ellipticity, azimuth, and depolarization ratio of the second harmonic wave at any scattering angle as a function of the incident polarization. Several specific situations are subsequently investigated.

Finally, it is shown in Chapter Fourteen that the near-forward Rayleigh and Raman scattering formulations provide an explanation for the observed polarization, as a function of the initial polarization, of the self-trapped filaments that arise from the self-focusing of an intense laser beam.

# Contents

|              |   |
|--------------|---|
|              | x |
| Abstract     | v |
| Introduction | 1 |

## PART 1: SOME FEATURES FROM QUANTUM ELECTRODYNAMICS

### CHAPTER 1. THE CLASSICAL RADIATION FIELD

|     |                                                               |    |
|-----|---------------------------------------------------------------|----|
| 1.1 | Maxwell's Equations                                           | 6  |
| 1.2 | Gauge Transformations                                         | 7  |
| 1.3 | Force and Energy                                              | 10 |
| 1.4 | Plane Electromagnetic Waves                                   | 12 |
| 1.5 | The Lagrangian and Hamiltonian Form of the Field<br>Equations | 13 |
| 1.6 | The Polarized Radiation Field                                 | 17 |

### CHAPTER 2. THE QUANTIZED RADIATION FIELD

|     |                                                             |    |
|-----|-------------------------------------------------------------|----|
| 2.1 | The Field Operators                                         | 24 |
| 2.2 | The Occupation Number Representation of the Photon<br>Field | 26 |

### CHAPTER 3. POLARIZED LIGHT IN QUANTUM MECHANICS

|     |                                                          |    |
|-----|----------------------------------------------------------|----|
| 3.1 | The polarization of a Single Photon                      | 31 |
| 3.2 | The Description of a Beam of Polarized Photons           | 33 |
| 3.3 | The Polarization Density Matrix for a Beam of<br>Photons | 35 |

|     |                                             |    |
|-----|---------------------------------------------|----|
| 3.4 | The Stokes Parameters for a Beam of Photons | 40 |
|-----|---------------------------------------------|----|

## CHAPTER 4. THE INTERACTION OF THE ELECTROMAGNETIC FIELD WITH BOUND ELECTRONS

|     |                                                                                 |    |
|-----|---------------------------------------------------------------------------------|----|
| 4.1 | The Lagrangian and Hamiltonian for a Particle in<br>the Electromagnetic Field   | 42 |
| 4.2 | The Hamiltonian for Bound Charges Interacting with<br>the Electromagnetic Field | 43 |

## CHAPTER 5. THE SCATTERING MATRIX

|     |                                               |    |
|-----|-----------------------------------------------|----|
| 5.1 | The Transition Amplitude                      | 47 |
| 5.2 | Connectedness-Structure                       | 49 |
| 5.3 | The S-Matrix in the Interaction Picture       | 50 |
| 5.4 | The Adiabatic Hypothesis                      | 54 |
| 5.5 | Noncovariant Diagrammatic Perturbation Theory | 56 |

## CHAPTER 6. THE POLARIZATION OF THE SCATTERED PHOTON BEAM

|     |                                     |    |
|-----|-------------------------------------|----|
| 6.1 | The Scattering of a Single Photon   | 66 |
| 6.2 | The Scattering of a Beam of Photons | 69 |

# PART 2: OPTICAL BIREFRINGENCE

## CHAPTER 7. FORWARD SCATTERING OF A SINGLE PHOTON

|     |                                                          |    |
|-----|----------------------------------------------------------|----|
| 7.1 | The Master Equations for Birefringent Scattering         | 72 |
| 7.2 | The Stokes Parameters of the Forward Scattered<br>Photon | 74 |

|                                                                           |                                                                                         |     |
|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|-----|
| 7.3                                                                       | The Density Matrix of the Forward Scattered Photon                                      | 76  |
| 7.4                                                                       | Non-Absorptive Forward Scattering                                                       | 77  |
| 7.5                                                                       | Forward Scattering with Absorption                                                      | 80  |
| 7.6                                                                       | The Spinor Transformation Description of<br>Birefringence                               | 81  |
| 7.7                                                                       | The Connexion Between the S-Matrix and the Semi-<br>Classical Theories of Birefringence | 84  |
| CHAPTER 8. FORWARD SCATTERING OF A BEAM OF PHOTONS                        |                                                                                         |     |
| 8.1                                                                       | The Master Equations for Multiphoton Birefringent<br>Scattering                         | 90  |
| 8.2                                                                       | The Density Matrix of the Forward Scattered Beam                                        | 91  |
| 8.3                                                                       | The Application to Birefringence Phenomena                                              | 97  |
| CHAPTER 9. BIREFRINGENCE INDUCED BY STATIC AND OPTICAL<br>ELECTRIC FIELDS |                                                                                         |     |
| 9.1                                                                       | Introduction                                                                            | 104 |
| 9.2                                                                       | The Kerr Effect                                                                         | 105 |
| 9.3                                                                       | The Optical Kerr Effect                                                                 | 110 |
| 9.4                                                                       | Intensity-Dependent Rotation of the Polarization<br>Ellipse                             | 113 |
| CHAPTER 10. NATURAL OPTICAL ACTIVITY                                      |                                                                                         |     |
| 10.1                                                                      | Introduction                                                                            | 117 |
| 10.2                                                                      | Linear Optical Rotation                                                                 | 118 |
| 10.3                                                                      | Intensity-Dependent Optical Rotation                                                    | 120 |

## CHAPTER 11. BIREFRINGENCE INDUCED BY MAGNETIC FIELDS

|      |                                 |     |
|------|---------------------------------|-----|
| 11.1 | Introduction                    | 125 |
| 11.2 | The Faraday Effect              | 125 |
| 11.3 | Optically Induced Magnetization | 130 |

**PART 3: NONFORWARD SCATTERING**

## CHAPTER 12. NONFORWARD SCATTERING OF A SINGLE PHOTON

|      |                                                |     |
|------|------------------------------------------------|-----|
| 12.1 | Introduction                                   | 134 |
| 12.2 | The Master Equations for Nonforward Scattering | 135 |
| 12.3 | Rayleigh Scattering at $90^\circ$              | 140 |
| 12.4 | Rayleigh Scattering Near the Forward Direction | 147 |
| 12.5 | Raman Scattering                               | 151 |
| 12.6 | Depolarization Ratios                          | 153 |

## CHAPTER 13. THE POLARIZATION OF THE SECOND HARMONIC

|      |                                               |     |
|------|-----------------------------------------------|-----|
| 13.1 | Introduction                                  | 157 |
| 13.2 | The Second Harmonic                           | 158 |
| 13.3 | The Second Harmonic in the Forward Direction  | 160 |
| 13.4 | Second Harmonic Scattering at $90^\circ$      | 166 |
| 13.5 | Depolarization Ratios for the Second Harmonic | 168 |

## CHAPTER 14. POLARIZATION EFFECTS IN SELF-FOCUSING

|      |                                                |     |
|------|------------------------------------------------|-----|
| 14.1 | Self-Focusing                                  | 169 |
| 14.2 | The Polarization of the Self-Trapped Filaments | 170 |

|           |                                        |     |
|-----------|----------------------------------------|-----|
| APPENDIX. | Tensor Averages in a Rotating Molecule | 176 |
|-----------|----------------------------------------|-----|

|             |  |     |
|-------------|--|-----|
| REFERENCES. |  | 179 |
|-------------|--|-----|

# Introduction

Many phenomena in chemistry and physics involve the scattering of polarized light by assemblies of molecules. Such scattering may occur elastically or inelastically, with or without a change in the polarization of the beam, and in the direction of the incident beam or out of its path.

In the range of effects designated optical birefringence, attention is centred on the polarization change suffered by a light beam on passing through a molecular medium. Forward scattering is relevant here, and the phenomena observed include optical activity, the Faraday effect, the Kerr effect, the Cotton-Mouton effect, and the double refraction of crystal optics. Now that laser technology has provided intense light beams, many intensity-dependent birefringence effects have become potentially observable: in particular the optical Kerr, Faraday, and Cotton-Mouton effects, auto-rotation of the polarization ellipse, non-linear optical rotation, and the polarization dependence of the power threshold for self-focusing.

The polarization of Rayleigh and Raman scattered photons is also of some interest. Former work on molecular properties has been concerned mainly with the depolarization ratio of the nonforward scattered beam rather than with the polarization itself, but additional molecular information should accrue from a determination of the precise polarization state. For example, the ellipticity of the Rayleigh scattered beam from an optically-active molecule could provide a direct measurement of the ratio

of the oscillator strength to the rotational strength. There are also some intensity-dependent nonforward scattering phenomena, such as multiharmonic scattering and self-focusing, in which interesting polarization effects occur.

The theory of all these phenomena may be derived from a common starting point by considering the scattering of polarized photons by electrons bound to some atomic or molecular system, for then the powerful techniques of formal scattering theory and quantum electrodynamics can be applied to the problem. Both forward and nonforward scattering may be accommodated, for the difference lies only in the importance of the interference between the scattered and unscattered components.

In addition to unifying the theory of all birefringence effects, the photon-scattering formulation provides a rather more succinct method of calculating the associated polarization changes, especially the intensity-dependent contributions, than the usual semi-classical approach. This is because it is unnecessary to construct phenomenological equations in terms of the various refractive indices of the medium.

All classical scattering treatments of optical birefringence appear to be valid only for samples containing a large number of molecules, for the effect is ascribed to the interference in the forward direction between the transmitted wave and the resultant of the wavelets scattered from an almost continuous distribution of molecules. By contrast, the quantum theory

presented below is meaningful even if the sample volume consists just of a single molecule, for the lack of knowledge as to the precise location of the molecule when the scattering event occurs means that the wave function of the scattered photon must contain a weighted sum of contributions, each corresponding to scattering from one of the continuous spectrum of possible positions that that the molecule may have within the sample volume.

The theory is restricted to photon frequencies far from absorption regions so that, except where otherwise stated, resonance phenomena are excluded. Dilute fluid media only are considered, so additivity is assumed and intermolecular effects such as degeneracy of the molecular ensemble and exciton transfer are neglected.

# PART ONE

## Some Features from Quantum Electrodynamics

## 1

## THE CLASSICAL RADIATION FIELD

## 1.1. MAXWELL'S EQUATIONS [1]

Maxwell's equations provide a relationship between a system of currents and charges and the electromagnetic fields set up by them. In Gaussian units these equations have the form

$$\nabla \cdot \mathbf{D} = 4\pi \rho \quad (1.1)$$

$$\nabla \wedge \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0 \quad (1.2)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (1.3)$$

$$\nabla \wedge \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4\pi}{c} \mathbf{j} , \quad (1.4)$$

where  $\mathbf{E}$  and  $\mathbf{H}$  are the electric and magnetic field strength vectors, and  $\mathbf{D}$  and  $\mathbf{B}$  are the electric displacement and magnetic induction, being related to the free fields in macroscopic media by the constitutive relations  $\mathbf{D} = \epsilon \mathbf{E}$  and  $\mathbf{B} = \mu \mathbf{H}$ , where  $\epsilon$  is the dielectric constant and  $\mu$  is the magnetic permeability. From (1.1) and (1.4), the charge density  $\rho$  and current density  $\mathbf{j} = \rho \mathbf{v}$  are seen to satisfy the equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 . \quad (1.5)$$

It is convenient to reduce the four Maxwell equations to two equations involving vector and scalar potentials. Thus since  $\nabla \cdot \mathbf{B} = 0$ , we can define  $\mathbf{B}$  in terms of a vector potential  $\mathbf{A}$ :

$$\mathbf{B} = \nabla \wedge \mathbf{A} . \quad (1.6)$$

Then (1.2) becomes

$$\nabla \wedge \left( \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right) = 0 , \quad (1.7)$$

and since  $\nabla \wedge \nabla \phi = 0$  we can set

$$\mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad (1.8)$$

where  $\phi$  is the scalar potential. Using (1.1) and (1.4) the two required differential equations for the potentials are

$$\nabla^2 \mathbf{A} - \frac{e\mu}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla \left( \nabla \cdot \mathbf{A} + \frac{e\mu}{c} \frac{\partial \phi}{\partial t} \right) = -\frac{4\pi\mu}{c} \mathbf{j} \quad (1.9)$$

$$\nabla^2 \phi + \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot \mathbf{A}) = -\frac{4\pi}{\epsilon} \rho . \quad (1.10)$$

The microscopic form of these equations obtains when  $\epsilon$  and  $\mu$  are replaced by their free space values of unity.

## 1.2. GAUGE TRANSFORMATIONS [2]

Equations (1.9) and (1.10) can be uncoupled by exploiting the arbitrariness involved in the definition of the potentials. Thus  $\mathbf{B}$  and  $\mathbf{E}$  are unchanged by the gauge transformation

$$\left. \begin{aligned} \mathbf{A} &\rightarrow \mathbf{A} + \nabla\Lambda \\ \phi &\rightarrow \phi - \frac{1}{c} \frac{\partial\Lambda}{\partial t} \end{aligned} \right\}. \quad (1.11)$$

The choice of  $\nabla \cdot \mathbf{A}$  is said to determine the gauge, where

$$\nabla \cdot \mathbf{A} + \frac{1}{c} \frac{\partial\phi}{\partial t} = 0 \quad (1.12)$$

defines the Lorentz gauge, and

$$\nabla \cdot \mathbf{A} = 0 \quad (1.13)$$

the Coulomb gauge. Clearly the Lorentz gauge is preserved in the gauge transformation (1.11) provided that the Lorentz condition

$$\nabla^2 \Lambda - \frac{1}{c^2} \frac{\partial^2 \Lambda}{\partial t^2} = 0 \quad (1.14)$$

is satisfied, whereas the Coulomb gauge is similarly preserved if

$$\nabla^2 \Lambda = 0. \quad (1.15)$$

We now have two alternative pairs of uncoupled electromagnetic field equations, namely

$$\left. \begin{aligned} \nabla^2 \mathbf{A} - \frac{\epsilon\mu}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} &= - \frac{4\pi\mu}{c} \mathbf{j} \\ \nabla^2 \phi - \frac{\epsilon\mu}{c^2} \frac{\partial^2 \phi}{\partial t^2} &= - \frac{4\pi}{\epsilon} \rho \end{aligned} \right\} \quad (1.16)$$

in the Lorentz gauge, and

$$\left. \begin{aligned} \nabla^2 \mathbf{A} - \frac{\epsilon\mu}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \frac{\epsilon\mu}{c} \nabla \frac{\partial\phi}{\partial t} &= - \frac{4\pi\mu}{c} \mathbf{j} \\ \nabla^2 \phi &= - \frac{4\pi}{\epsilon} \rho \end{aligned} \right\} \quad (1.17)$$

in the Coulomb gauge. The Lorentz gauge is used in relativistic situations, for the two equations (1.16) constitute a single covariant wave equation for the four-vector  $A_\mu$  with components  $A_x, A_y, A_z, i\phi$ . Notice that in the Coulomb gauge the scalar potential satisfies Poisson's equation, with solution

$$\phi(\mathbf{r}, t) = \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' , \quad (1.18)$$

and so  $\phi$  is just the instantaneous Coulomb potential due to the charge density. Since  $\phi$  then follows the fluctuations in  $\rho(\mathbf{r}, t)$  without any retardation, it follows that the Coulomb gauge is noncovariant.

If the current vector  $\mathbf{j}$  is split into its transverse and longitudinal parts

$$\mathbf{j} = \mathbf{j}^l + \mathbf{j}^t \quad (1.19)$$

so that, according to Helmholtz's theorem ([3], p.53),  $\nabla \cdot \mathbf{j}^t = 0$  and  $\nabla \wedge \mathbf{j}^l = 0$ , the first equation (1.17) provides two equations:

$$\nabla \frac{\partial \phi}{\partial t} = \frac{4\pi}{\epsilon} \mathbf{j}^l \quad (1.20)$$

$$\nabla^2 \mathbf{A} - \frac{\epsilon \mu}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = -\frac{4\pi \mu}{c} \mathbf{j}^t . \quad (1.21)$$

Therefore the source in the wave equation for  $\mathbf{A}$  can be expressed entirely in terms of the transverse current.

In the Coulomb gauge the division of  $\mathbf{E}$  into its transverse and longitudinal parts is automatic, for if we write

$$\mathbf{E} = \mathbf{E}^t + \mathbf{E}^l \quad (1.22)$$

and use (1.8) together with  $\nabla \cdot \mathbf{E}^t = 0$  and  $\nabla \wedge \mathbf{E}^l = 0$ , we obtain

$$\mathbf{E}^t = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad (1.23)$$

$$\mathbf{E}^l = -\nabla \phi. \quad (1.24)$$

It can be seen from (1.3) that  $\mathbf{B}$  is always transverse.

The advantage of the Coulomb gauge, therefore, is that the division of the fields into their longitudinal and transverse parts is automatic even in the presence of free charge, whereas this division is only possible in the Lorentz gauge in the absence of free charge. We shall be concerned with the interaction of electromagnetic fields with atomic and molecular charges and currents, and since the latter will be treated from a nonrelativistic viewpoint, the use of the Coulomb gauge is entirely appropriate.

### 1.3. FORCE AND ENERGY [1]

The Lorentz force density acting on a region of charge-current density is

$$\mathbf{F} = \rho \mathbf{E} + \frac{1}{c} \mathbf{j} \wedge \mathbf{B}. \quad (1.25)$$

The rate at which the Lorentz forces within a finite volume  $V$  do work is

$$\int_V \mathbf{F} \cdot \mathbf{v} dV = \int_V \rho \left[ \mathbf{v} \cdot \mathbf{E} + \frac{1}{c} (\mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{v} \right] dV = \int_V \mathbf{j} \cdot \mathbf{E} dV. \quad (1.26)$$

This power represents a conversion of electromagnetic energy into mechanical or thermal energy, and must be balanced by a corresponding rate of decrease of electromagnetic energy within  $V$ . Use (1.4) to write

$$\int_V \mathbf{j} \cdot \mathbf{E} dV = \frac{1}{4\pi} \int_V \left[ c \mathbf{E} \cdot (\nabla \wedge \mathbf{H}) - \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} \right] dV, \quad (1.27)$$

and with the aid of (1.2) together with the vector identity

$$\nabla \cdot (\mathbf{E} \wedge \mathbf{H}) = \mathbf{H} \cdot (\nabla \wedge \mathbf{E}) - \mathbf{E} \cdot (\nabla \wedge \mathbf{H}), \quad (1.28)$$

this becomes

$$\int_V \mathbf{j} \cdot \mathbf{E} dV = - \int_V \left\{ \frac{\partial}{\partial t} \left( \frac{\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}}{8\pi} \right) + \nabla \cdot \left( \frac{c}{4\pi} \mathbf{E} \wedge \mathbf{H} \right) \right\} dV. \quad (1.29)$$

The total energy density can now be identified as

$$U = \frac{1}{8\pi} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}), \quad (1.30)$$

and the energy flux density (Poynting vector) as

$$\mathbf{S} = \frac{c}{4\pi} (\mathbf{E} \wedge \mathbf{H}), \quad (1.31)$$

for then (1.29) can be written

$$\frac{\partial}{\partial t} \int_V (U + \mathbf{j} \cdot \mathbf{E}) dV = - \int_V \nabla \cdot \mathbf{S} dV = - \int_S \mathbf{n} \cdot \mathbf{S} ds \quad (1.32)$$

which corresponds to the total rate of change of energy within

the volume being equal to the loss of energy through the boundary surface  $S$ .

#### 1.4. PLANE ELECTROMAGNETIC WAVES

The electromagnetic field in vacuo is completely determined by the vector potential  $\mathbf{A}$ , satisfying the wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \quad (1.33)$$

and the transversality condition  $\nabla \cdot \mathbf{A} = 0$ , which may be imposed within the lorentz gauge by choosing  $\Lambda$  so that  $\phi$  is normalized to zero, or imposed directly by using the Coulomb gauge. The field vectors and potentials must be real, so the general solution of (1.33) is written as a linear combination of some complete set of real plane waves:

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\mathbf{k}} \left[ \mathbf{A}_{\mathbf{k}}(t) e^{i\mathbf{k} \cdot \mathbf{r}} + \mathbf{A}_{\mathbf{k}}^*(t) e^{-i\mathbf{k} \cdot \mathbf{r}} \right], \quad (1.34)$$

The denumerably infinite set of plane waves  $\mathbf{u}_{\mathbf{k}}(\mathbf{r})$  that can be accomodated in a cube of volume  $V = L^3$  is suitable, where

$$\mathbf{u}_{\mathbf{k}}(\mathbf{r}) = V^{-1/2} \boldsymbol{\epsilon} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad \hat{\mathbf{k}} \cdot \boldsymbol{\epsilon} = 0 \quad (1.35)$$

$$\int \mathbf{u}_{\mathbf{k}}^* \cdot \mathbf{u}_{\mathbf{k}'} d^3\mathbf{r} = \delta_{\mathbf{k}\mathbf{k}'} \quad (1.36)$$

$$u_{\mathbf{k},i}(i = L/2) = u_{\mathbf{k},i}(i = -L/2), \quad i = x, y, z. \quad (1.37)$$

The periodic boundary conditions (1.37) impose the discrete values  $2\pi n_i/L_i$  on the wave vector; furthermore the number of solutions with  $\mathbf{k}_i$  in the range  $d\mathbf{k}_i$  is

$$d_n(\mathbf{k}) = \frac{dk_x}{2\pi} L_x \frac{dk_y}{2\pi} L_y \frac{dk_z}{2\pi} L_z = \frac{d^3\mathbf{k}}{(2\pi)^3} V \quad (1.38)$$

and this will be the number of states in  $d^3\mathbf{k}$ . If  $V$  is sufficiently large that very many modes are contained within  $d^3\mathbf{k}$ , the summation in (1.34) can be replaced by the integral

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3\mathbf{k}. \quad (1.39)$$

The electric and magnetic field strengths obtained from the vector potential (1.34) are

$$\mathbf{E}(\mathbf{r}, t) = i \sum_{\mathbf{k}} \mathbf{k} [A_{\mathbf{k}}(t) e^{i\mathbf{k} \cdot \mathbf{r}} - A_{\mathbf{k}}^*(t) e^{-i\mathbf{k} \cdot \mathbf{r}}] \quad (1.40)$$

$$\mathbf{H}(\mathbf{r}, t) = i \sum_{\mathbf{k}} \mathbf{k} \wedge [A_{\mathbf{k}}(t) e^{i\mathbf{k} \cdot \mathbf{r}} - A_{\mathbf{k}}^*(t) e^{-i\mathbf{k} \cdot \mathbf{r}}], \quad (1.41)$$

and from these equations, together with (1.30) and (1.36), the total field energy within  $V$  is found to be

$$U = \frac{V}{4\pi} \sum_{\mathbf{k}} k^2 [A_{\mathbf{k}} A_{\mathbf{k}}^* + A_{\mathbf{k}}^* A_{\mathbf{k}}]. \quad (1.42)$$

## 1.5. THE LAGRANGIAN AND HAMILTONIAN FORM OF THE FIELD EQUATIONS [4]

A field is a physical system with an infinite number of degrees of freedom, the equivalent of the generalized coordinates  $q_i(t)$  for each degree of freedom being the field functions  $\psi(\mathbf{r}, t)$ , where  $\mathbf{r}$  is a continuous index analogous to the discrete index  $i$ . The transformation is considered of a mechanical system with a finite number of degrees of freedom into a continuous system.

The appropriate mechanical system comprises a set of oscillators which may be reduced to a system of normal vibrational modes, each characterized by a normal coordinate  $q_i$ . One can write a Lagrangian  $\mathcal{L}_i$ , being the difference between the kinetic and potential energies, for each oscillator, and express the total Lagrangian as

$$L = \sum_{i=1}^n a \mathcal{L}_i(q_i) \quad (1.43)$$

where  $a$  is the separation of the vibrating "mass points". The transition to a continuous system is made by letting the number of degrees of freedom tend to infinity, whereupon

$$\begin{aligned} \sum_i a &\rightarrow \int_{x_1}^{x_2} dx; \quad \mathcal{L}_i(q_i) \rightarrow \mathcal{L}(\psi(x)) \\ \text{and} \quad L &= \int \mathcal{L}(\psi(x)) dx \end{aligned} \quad (1.44)$$

where  $\mathcal{L}$  is now called the Lagrangian density. In addition to a dependence on  $\psi(x)$  and  $\dot{\psi}(x)$ ,  $\mathcal{L}$  is also dependent upon  $d\psi/dx$ .

According to Hamilton's principle of least action, for a conservative system the action integral

$$A = \int_{t_1}^{t_2} L(q_i, \dot{q}_i) dt \quad (1.45)$$

is a constant. In other words the path of the system from  $t_1$  to  $t_2$  is such that

$$\delta_{q_i} \int_{t_1}^{t_2} L(q_i, \dot{q}_i) dt = 0 \quad (1.46)$$

i.e. the variation of the line integral is zero. The Euler-

Lagrange equations follow from this principle, and for a single component  $q_i$  we have

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0 . \quad (1.47)$$

In the case of the Lagrangian density (1.44) the dependence on the spatial derivative of the field function means that the action integral is now, in three space dimensions,

$$A = \iint \mathcal{L} d^3r dt \equiv \int \mathcal{L} d^4x , \quad (1.48)$$

so that the Euler-Lagrange equations become

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\psi}} \right) + \sum_{k=1}^3 \frac{\partial}{\partial x_k} \left[ \frac{\partial \mathcal{L}}{\partial (\partial \psi / \partial x_k)} \right] - \frac{\partial \mathcal{L}}{\partial \psi} = 0 . \quad (1.49)$$

The generalized momentum for particles in the system described by (1.47) is defined as

$$p_i = \frac{\partial L}{\partial \dot{q}_i} , \quad (1.50)$$

and from the Hamiltonian function  $H(p, q)$  representing the total energy, where

$$H(p, q) = \sum_{i=1}^n p_i \dot{q}_i - L , \quad (1.51)$$

one obtains Hamilton's equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i} = p_i , \quad \dot{p}_i = - \frac{\partial H}{\partial q_i} . \quad (1.52)$$

The generalized coordinates  $q_i$  and momenta  $p_i$  are called canonically conjugate variables. In the case of the Lagrangian density

for the field, we can define a generalized momentum density  $\pi$  that is canonically conjugate to  $\psi$  :

$$\pi = \frac{\partial \mathcal{L}}{\partial \dot{\psi}} . \quad (1.53)$$

A Hamiltonian density  $\mathcal{H}$  can now be introduced by writing

$$H = \int \mathcal{H} d^3\mathbf{r} = \int d^3\mathbf{r} (\pi \dot{\psi} - \mathcal{L}). \quad (1.54)$$

A suitable Lagrangian density for the free electromagnetic field is

$$\mathcal{L} = \frac{1}{8\pi} (\mathbf{E}^2 - \mathbf{B}^2)$$

and in the Coulomb gauge this becomes

$$\mathcal{L} = \frac{1}{8\pi} \left\{ \frac{1}{c^2} \dot{\mathbf{A}}^2 - (\nabla \wedge \mathbf{A})^2 \right\} \quad (1.55)$$

with  $\mathbf{A}(\mathbf{r}, t)$  comprising the generalized coordinates. The momentum field conjugate to  $\mathbf{A}(\mathbf{r}, t)$  is then

$$\pi = \frac{1}{4\pi c^2} \frac{\partial \mathbf{A}}{\partial t} = -\frac{1}{4\pi c} \mathbf{E} . \quad (1.56)$$

It is easily verified that the Lagrangian density (1.55) reproduces the field equation (1.33) when substituted into the Lagrange equation (1.49), and that the energy density (1.30) obtains from (1.54).

This imposition of the Coulomb gauge within the Lagrangian formulation is equivalent to introducing a modified Hamilton's principle

$$\delta_t \iint \mathcal{L} d^3\mathbf{r} dt = 0 \quad (1.57)$$

such that only variations of  $\mathbf{A}$  within the manifold of transverse vector fields are allowed ([5], p.77). This procedure parallels the expansion (1.34) of  $\mathbf{A}(\mathbf{r}, t)$  in terms of a complete set of plane waves and then assigning a normal vibrational coordinate  $q_{\mathbf{k}}$  to each plane wave mode. The Hamiltonian and Lagrangian for each mode are then

$$H_{\mathbf{k}} = \frac{1}{2} (p_{\mathbf{k}}^2 + \omega_{\mathbf{k}}^2 q_{\mathbf{k}}^2), \quad L_{\mathbf{k}} = \frac{1}{2} (p_{\mathbf{k}}^2 - \omega_{\mathbf{k}}^2 q_{\mathbf{k}}^2) \quad (1.58)$$

and one can verify that ([5], p.18)

$$\sum_{\mathbf{k}} H_{\mathbf{k}} = \int_V \mathcal{H} d^3\mathbf{r} = \frac{V}{8\pi} (E^2 + B^2) \quad (1.59)$$

$$\sum_{\mathbf{k}} L_{\mathbf{k}} = \int_V \mathcal{L} d^3\mathbf{r} = \frac{V}{8\pi} (E^2 - B^2). \quad (1.60)$$

## 1.6. THE POLARIZED RADIATION FIELD

In free space the electric field vector satisfies the wave equation

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0 \quad (1.61)$$

with real plane wave solutions

$$\mathbf{E} = [\mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \mathbf{E}_0^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}]. \quad (1.62)$$

If the wave propagates along the 3-axis,  $\mathbf{k} \cdot \mathbf{r} = k r_3$  and (1.61) reduces to the two independent equations

$$\left. \begin{aligned} \frac{\partial^2 E_1}{\partial r_3^2} - \frac{1}{c^2} \frac{\partial^2 E_1}{\partial t^2} &= 0 \\ \frac{\partial^2 E_2}{\partial r_3^2} - \frac{1}{c^2} \frac{\partial^2 E_2}{\partial t^2} &= 0 \end{aligned} \right\}. \quad (1.63)$$

We can therefore associate two linearly independent polarization vectors with  $E_1$  and  $E_2$ , and so write

$$\mathbf{E} = [\mathbf{e}_1 E_1 + \mathbf{e}_2 E_2] e^{i(k r_3 - \omega t)} + \text{complex conjugate}. \quad (1.64)$$

where the unit vectors  $\mathbf{e}_1$ ,  $\mathbf{e}_2$ , and  $\hat{\mathbf{k}}$  form a right-handed system such that  $\mathbf{e}_1 \wedge \mathbf{e}_2 = +\hat{\mathbf{k}}$  (Figure 1.1).

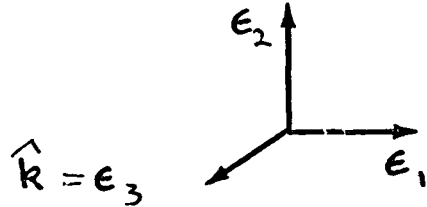


Figure 1.1. The system of unit vectors that characterize  $\mathbf{E}$ .

The nature of the polarization is determined by the relative phases and magnitudes of  $E_1$  and  $E_2$ , and these may be combined into complex amplitudes by considering the geometry of the polarization ellipse [6,7,8] (Figure 1.2). The positive sense of rotation, corresponding to a positive ellipticity or right-handed circularity, is usually taken as a clockwise rotation of  $\mathbf{E}$  when looking towards the source of the wave. Our convention in this respect follows that of Born & Wolf [6]. In terms of

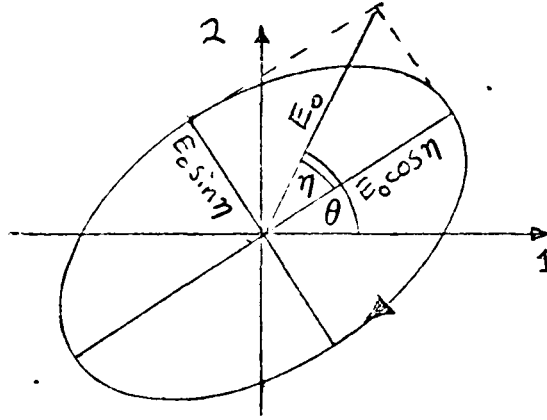


Figure 1.2. The polarization ellipse, showing a positive sense of rotation.

the azimuth  $\Theta$  and ellipticity  $\eta$ , the required amplitudes are

$$\left. \begin{aligned} E_1 &= E_0 (\cos \eta \cos \Theta + i \sin \eta \sin \Theta) \equiv E_0 b_1 \\ E_2 &= E_0 (\cos \eta \sin \Theta - i \sin \eta \cos \Theta) \equiv E_0 b_2 \end{aligned} \right\} \quad (1.65)$$

so that, using (1.64), the electric field vector may be written in terms of a two-dimensional polarization vector  $\pi$  with complex components:

$$\mathbf{E} = \pi E_0 e^{i(kr_3 - \omega t)} + c.c. ; \quad \pi \equiv \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}. \quad (1.66)$$

Notice that the  $\mathbf{E}$  calculated from this equation is always real.

The polarization characteristics  $\Theta$  and  $\eta$  may be extracted from the electric field vector by means of the Stokes parameters  $S_i$  ( $i=0,1,2,3$ ), where [6,7,8,9]

$$\left. \begin{aligned} S_0 &= E_1 E_1^* + E_2 E_2^* = E_0^2 (b_1 b_1^* + b_2 b_2^*) \\ S_1 &= E_1 E_2^* + E_2 E_1^* = E_0^2 (b_1 b_2^* + b_2 b_1^*) \\ S_2 &= i(E_2 E_1^* - E_1 E_2^*) = iE_0^2 (b_2 b_1^* - b_1 b_2^*) \\ S_3 &= E_1 E_1^* - E_2 E_2^* = E_0^2 (b_1 b_1^* - b_2 b_2^*). \end{aligned} \right\} \quad (1.67)$$

From (1.65) we then have

$$\left. \begin{aligned} S_0 &= E_0^2 & (= 2\pi U/V \text{ from (1.42)}) \\ S_1 &= S_0 \cos 2\eta \sin 2\theta \\ S_2 &= S_0 \sin 2\eta \\ S_3 &= S_0 \cos 2\eta \cos 2\theta. \end{aligned} \right\} \quad (1.68)$$

so that

$$\left. \begin{aligned} \tan 2\theta &= S_1/S_3 \\ \tan 2\eta &= S_2/(S_1^2 + S_3^2)^{1/2} \end{aligned} \right\} \quad (1.69)$$

The Stokes parameters correspond exactly to the set of four independent measurements required for the experimental determination of  $\theta$  and  $\eta$  ([9], p.313). Thus

- $S_0$ : The intensity of the beam.
- $S_1$ : The degree of plane polarization with respect to a set of axes oriented at  $\pi/4$  to the 1- and 2-axes.
- $S_2$ : The degree of circular polarization.
- $S_3$ : The degree of plane polarization with respect to the 1- and 2-axes.

The absolute phase of the wave does not appear in the Stokes parameters. This enables them to be used for the specification of an incoherent beam comprising a superposition of several waves with the same propagation direction but different phases and possibly different polarizations; one simply adds the Stokes parameters for each coherent wavelet. For a pure polarized beam we have

$$S_0^2 = S_1^2 + S_2^2 + S_3^2 \quad (1.70)$$

and this implies that  $\theta$  and  $\eta$  of all the constituent wavelets are the same. When waves of different polarization are incoherently superimposed, it is necessary to define the degree of polarization  $P$ , where

$$P = (S_1^2 + S_2^2 + S_3^2)^{1/2} / S_0, \quad (1.71)$$

so that

$$\left. \begin{aligned} S_1 &= S_0 P \cos 2\eta \sin 2\theta \\ S_2 &= S_0 P \sin 2\eta \\ S_3 &= S_0 P \cos 2\eta \cos 2\theta. \end{aligned} \right\}. \quad (1.72)$$

The Stokes parameters may be regarded as constituting a vector  $\mathbf{S}$  of length  $S_0$  in a three-dimensional real space called Poincaré' space. The locus of the tip of the vector is the Poincaré' sphere [6,7,8,9], and all possible polarization conditions are encompassed by the surface of the sphere. In fact the three components in Poincaré' space, together with the intensity component  $S_0$ , constitute a four-vector that is invariant under a Lorentz transformation; but this relativistic viewpoint is only required if the observer is in motion relative to the source of the light beam as in astrophysical observations [10].

An alternative method of handling the polarization, entirely equivalent to the Stokes parameters, involves the use of

a polarization density matrix [11] with elements

$$\rho_{\sigma\tau} = E_{\sigma} E_{\tau}^* / E_0^2 \equiv b_{\sigma} b_{\tau}^* \quad (1.73)$$

With the aid of (1.65), these matrix elements can be written explicitly in terms of  $\theta$  and  $\eta$  :

$$\begin{aligned} \rho &= \begin{pmatrix} b_1 b_1^* & b_1 b_2^* \\ b_2 b_1^* & b_2 b_2^* \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} 1 + \cos 2\eta \cos 2\theta & \cos 2\eta \sin 2\theta + i \sin 2\eta \\ \cos 2\eta \sin 2\theta - i \sin 2\eta & 1 - \cos 2\eta \cos 2\theta \end{pmatrix} \end{aligned} \quad (1.74)$$

The relationship of the density matrix to the Stokes parameters can be established by writing

$$\begin{aligned} \rho &= \frac{1}{2S_0} \begin{pmatrix} S_0 + S_3 & S_1 + iS_2 \\ S_1 - iS_2 & S_0 - S_3 \end{pmatrix} \\ &= 1/2S_0 (1S_0 + \mathbf{S} \cdot \boldsymbol{\sigma}) \end{aligned} \quad (1.75)$$

where  $\boldsymbol{\sigma}$  is the set of Pauli matrices. In terms of a polarization vector  $\mathbf{P}$ , where  $\mathbf{P} = \mathbf{S}/S_0$ , we have

$$\rho = \frac{1}{2} (1 + \mathbf{P} \cdot \boldsymbol{\sigma}) , \quad (1.76)$$

and so the density matrix can accommodate conditions of partial polarization. Indeed the density matrix is usually invoked in both classical and quantum mechanics to deal with impure states.

The two-dimensional complex polarization vector  $\boldsymbol{\pi}$  defined in (1.66) may be regarded as a first rank spinor. The elements

of the density matrix are the components of a second rank spinor  $\rho$ , which is equivalent to a dyadic in spin space ([3], p.101):

$$\rho = \begin{pmatrix} \epsilon_1 & \epsilon_2 \end{pmatrix} \begin{pmatrix} b_1 b_1^* & b_1 b_2^* \\ b_2 b_1^* & b_2 b_2^* \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \end{pmatrix} \quad (1.77)$$

A second rank spinor represents in the two-dimensional complex spin space a four-dimensional real vector in space-time, in this case the Stokes vector  $\mathbf{S}$ . Equation (1.75) displays the actual connection between the two representatives.

The first and second rank spinor descriptions of photon polarization bear the same relation to each other as do the Jones and Stokes vector formulations of polarized light in crystal optics [12,13]. Thus the second rank spinor, like the Stokes vector, can automatically include states of partial polarization, whereas the first rank spinor and the Jones vector do not display explicitly the degree of polarization. Another point of difference is that in the second rank spinor and the Stokes vector the absolute phase of the wave is lost, but the first rank spinor and the Jones vector carry the absolute phase. This means that if the net effect is required at a point of beams from different sources, the second rank spinor components or Stokes parameters are summed if the sources are incoherent, whereas the first rank spinor or Jones vector components are summed if the sources are coherent.

## 2

## THE QUANTIZED RADIATION FIELD

## 2.1. THE FIELD OPERATORS [2,5,14,15,16,etc.]

The quantization procedure consists in replacing the generalized field coordinates, in this case the vector potential  $A(\mathbf{r}, t)$ , and conjugate momenta  $\pi(\mathbf{r}, t)$ , by appropriate operators satisfying well-defined commutation relations. By analogy with the commutation relations for particle coordinates and momenta in the Schrodinger picture,

$$[\tilde{r}_\lambda, \tilde{r}_\mu] = [\tilde{p}_\lambda, \tilde{p}_\mu] = 0; \quad [\tilde{r}_\lambda, \tilde{p}_\mu] = i\hbar \delta_{\lambda\mu}, \quad (2.1)$$

we can assume for the field operators the relations

$$[A_\lambda(\mathbf{r}, t), A_\mu(\mathbf{r}', t)] = [\pi_\lambda(\mathbf{r}, t), \pi_\mu(\mathbf{r}', t)] = 0 \quad (2.2)$$

$$[A_\lambda(\mathbf{r}, t), \pi_\mu(\mathbf{r}', t)] = i\hbar \delta_{\lambda\mu} \delta(\mathbf{r} - \mathbf{r}') \quad (2.3)$$

provided that the operators are always taken at the same time.

Equations (2.2) and (2.3) hold for both the real and the complex vector potential, but the complex vector potential in addition satisfies the commutation relation

$$[A_\lambda(\mathbf{r}, t), A_\mu^*(\mathbf{r}', t)] = (4\pi\hbar c/k) \delta_{\lambda\mu} \delta(\mathbf{r} - \mathbf{r}') \quad (2.4)$$

which can be obtained from (2.3) together with

$$\pi_\lambda^* = \frac{1}{4\pi c^2} \frac{\partial A_\lambda^*}{\partial t} = -\frac{i\omega}{4\pi c^2} A_\lambda^* \quad (2.5)$$

It is convenient to take the basic region of space as a cube of volume  $V$ , and to use the plane wave expansion

$$\left. \begin{aligned} A_\lambda(\mathbf{r}, t) &= \sum_{\mathbf{k}} a_{\mathbf{k}\lambda}(t) \phi_{\mathbf{k}}(\mathbf{r}) \\ A_\lambda^*(\mathbf{r}, t) &= \sum_{\mathbf{k}} a_{\mathbf{k}\lambda}^\dagger(t) \phi_{\mathbf{k}}^*(\mathbf{r}) \end{aligned} \right\} \quad (2.6)$$

for the complex vector potential, with  $\phi_{\mathbf{k}}(\mathbf{r})$  normalized so that

$$\left. \begin{aligned} \phi_{\mathbf{k}}(\mathbf{r}) &= (4\pi\hbar c/Vk)^{1/2} e^{i\mathbf{k}\cdot\mathbf{r}} \\ \int \phi_{\mathbf{k}}^*(\mathbf{r}) \phi_{\mathbf{k}'}(\mathbf{r}) d^3\mathbf{r} &= (4\pi\hbar c/k) \delta_{\mathbf{k}\mathbf{k}'} \end{aligned} \right\} \quad (2.7)$$

Then  $a_{\mathbf{k}\lambda}(t)$  and  $a_{\mathbf{k}\lambda}^\dagger(t)$  become

$$\left. \begin{aligned} a_{\mathbf{k}\lambda}(t) &= (k/4\pi\hbar c) \int A_\lambda(\mathbf{r}, t) \phi_{\mathbf{k}}(\mathbf{r}) d^3\mathbf{r} \\ a_{\mathbf{k}\lambda}^\dagger(t) &= (k/4\pi\hbar c) \int A_\lambda^*(\mathbf{r}, t) \phi_{\mathbf{k}}^*(\mathbf{r}) d^3\mathbf{r} \end{aligned} \right\} \quad (2.8)$$

The commutation relations for these new operators can be obtained from those of  $\mathbf{A}(\mathbf{r}, t)$  and  $\mathbf{A}^*(\mathbf{r}, t)$ . Thus

$$\begin{aligned} [a_{\mathbf{k}\lambda}(t), a_{\mathbf{k}'\mu}^\dagger(t)] &= (k/4\pi\hbar c)^2 \int [A_\lambda(\mathbf{r}, t), A_\mu^*(\mathbf{r}', t)] \phi_{\mathbf{k}}(\mathbf{r}) \phi_{\mathbf{k}'}^*(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}' \\ &= \delta_{\lambda\mu} \delta_{\mathbf{k}\mathbf{k}'} \end{aligned} \quad (2.9)$$

$$[a_{\mathbf{k}\lambda}(t), a_{\mathbf{k}'\mu}(t)] = [a_{\mathbf{k}\lambda}^\dagger(t), a_{\mathbf{k}'\mu}^\dagger(t)] = 0 \quad (2.10)$$

The following expressions can now be written for the

operators corresponding to the real field vectors:

$$\mathbf{A} = (2\pi\hbar c/Vk)^{1/2} \sum_{\mathbf{k}, \lambda} \mathbf{e}_{\mathbf{k}, \lambda} [a_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{r}} + a_{\mathbf{k}, \lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}] \quad (2.11)$$

$$\mathbf{E} = i(2\pi\hbar ck/V)^{1/2} \sum_{\mathbf{k}, \lambda} \mathbf{e}_{\mathbf{k}, \lambda} [a_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{r}} - a_{\mathbf{k}, \lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}] \quad (2.12)$$

$$\mathbf{B} = i(2\pi\hbar c/Vk)^{1/2} \sum_{\mathbf{k}, \lambda} (\mathbf{k} \wedge \mathbf{e}_{\mathbf{k}, \lambda}) [a_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{r}} - a_{\mathbf{k}, \lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}] \quad (2.13)$$

Equation (1.42) for the total field energy within  $V$  then provides the following equation for the Hamiltonian operator:

$$H = \frac{1}{2} \sum_{\mathbf{k}, \lambda} \hbar \omega_{\mathbf{k}} [a_{\mathbf{k}, \lambda}^\dagger a_{\mathbf{k}, \lambda} + a_{\mathbf{k}, \lambda} a_{\mathbf{k}, \lambda}^\dagger]$$

which becomes, with the help of (2.9),

$$H = \sum_{\mathbf{k}, \lambda} \hbar \omega_{\mathbf{k}} [a_{\mathbf{k}, \lambda}^\dagger a_{\mathbf{k}, \lambda} + \frac{1}{2}] . \quad (2.14)$$

This parallels the expression  $\sum_{\mathbf{k}, \lambda} \hbar \omega_{\mathbf{k}} (n_{\mathbf{k}, \lambda} + \frac{1}{2})$  that is obtained for the total field energy by quantizing the normal vibrations assigned to each plane wave mode, provided that the operator  $a_{\mathbf{k}, \lambda}^\dagger a_{\mathbf{k}, \lambda}$  is identified with the number of excitation quanta (photons)  $n_{\mathbf{k}, \lambda}$  in the  $\mathbf{k}'$ th mode plane polarized along the  $\mathbf{e}_{\lambda}$ -axis. The number of  $\mathbf{k}'$ s is infinite, so the vacuum state energy  $\sum_{\mathbf{k}, \lambda} \frac{1}{2} \hbar \omega_{\mathbf{k}}$  is infinite; consequently the field energy is calculated relative to the vacuum state energy as zero.

## 2.2. THE OCCUPATION NUMBER REPRESENTATION OF THE PHOTON FIELD [14, 16, 17, 18]

The Hermitian operator  $a_{\mathbf{k}}^\dagger a_{\mathbf{k}}$  was introduced in the previous

section and identified with the number of photons  $n_{\mathbf{k}}$  present in the  $\mathbf{k}$ 'th mode of the radiation field. We wish to find the eigenvectors  $|\mathbf{k}[n]\rangle$  of this operator, where

$$a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} |\mathbf{k}[n]\rangle = n_{\mathbf{k}} |\mathbf{k}[n]\rangle. \quad (2.15)$$

The eigenvectors of a Hermitian operator are normalizable, so

$$\langle \mathbf{k}[n] | a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} | \mathbf{k}[n] \rangle = n_{\mathbf{k}} \langle \mathbf{k}[n] | \mathbf{k}[n] \rangle = n_{\mathbf{k}}. \quad (2.16)$$

Rewriting (2.16) as

$$n_{\mathbf{k}} = (a_{\mathbf{k}} |\mathbf{k}[n]\rangle)^{\dagger} (a_{\mathbf{k}} |\mathbf{k}[n]\rangle) = |a_{\mathbf{k}} |\mathbf{k}[n]\rangle|^2 \geq 0 \quad (2.17)$$

we see that the eigenvalues of  $a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}$  are all positive since the length of an element of Hilbert space cannot be negative.

The effect of the individual operators  $a_{\mathbf{k}}^{\dagger}$  and  $a_{\mathbf{k}}$  on  $|\mathbf{k}[n]\rangle$  must now be determined. From (2.15) together with the commutation relation (2.9), it is easy to deduce that

$$\left. \begin{aligned} a_{\mathbf{k}}^{\dagger} |\mathbf{k}[n]\rangle &= (n_{\mathbf{k}} + 1)^{1/2} |\mathbf{k}[n+1]\rangle \\ a_{\mathbf{k}} |\mathbf{k}[n]\rangle &= n_{\mathbf{k}}^{1/2} |\mathbf{k}[n-1]\rangle \end{aligned} \right\}. \quad (2.18)$$

The operators  $a_{\mathbf{k}}^{\dagger}$  and  $a_{\mathbf{k}}$  are therefore called creation and annihilation operators, respectively, since they can change the number of photons present in a mode by plus or minus one.

According to (2.17) the eigenvalue spectrum is bounded from below, so there must exist a Hilbert vector  $|\mathbf{k}[0]\rangle$  such that

$$a_k |k[0]\rangle = 0 \quad ; \quad a_k^\dagger a_k |k[0]\rangle = 0 . \quad (2.19)$$

A single application of the creation operator to this vacuum state therefore produces a state with a single  $k$ -photon:

$$a_k^\dagger |k[0]\rangle = (0+1)^{1/2} |k[1]\rangle . \quad (2.20)$$

Consequently any state  $|k[n]\rangle$  may be generated by the  $n$ -fold application of the creation operator to the vacuum state:

$$|k[n]\rangle = \frac{(a_k^\dagger)^{n_k}}{(n_k!)^{1/2}} |k[0]\rangle . \quad (2.21)$$

The operators  $a_k$  and  $a_k^\dagger$  were introduced in (2.6) as time-dependent amplitudes for the complete set of functions  $A_k(t)$ ; the subscripts  $k$  therefore cover the complete set of orthogonal radiation modes. Clearly the set of Hermitian operators  $a_k^\dagger a_k$  will similarly be complete, and since these operators commute,

$$[(a_k^\dagger a_k), (a_{k'}^\dagger a_{k'})] = 0 , \quad (2.22)$$

the corresponding eigenvalues  $n_k$  and  $n_{k'}$  may be simultaneously measured. Thus the Hilbert space can be spanned by the simultaneous eigenvectors of the complete maximal set  $a_k^\dagger a_k$ . An eigenvector of this basis set may be labelled by the simultaneous eigenvalues  $n_a, n_b, \dots$  and so can be written

$$\begin{aligned} \Phi_{n_a n_b \dots} &= |k_a[n_a] k_b[n_b] \dots \rangle \\ &= (n_a! n_b! \dots)^{-1/2} (a_a^\dagger)^{n_a} (a_b^\dagger)^{n_b} \dots \Phi_0 \end{aligned} \quad (2.23)$$

where  $\Phi_0$  is the vacuum state:

$$\Phi_0 = |k_a[0]k_b[0] \dots \rangle. \quad (2.24)$$

Any general state can be written as a linear superposition of the states (2.23).

A relationship must now be established between the base vectors (2.23) in occupation number space and the base vectors

$$\Phi_{k(1)k(2)\dots} = |k_a(1)k_a(2) \dots k_a(n_a)k_b(n_a+1)k_b(n_a+2) \dots k_b(n_a+n_b)\dots \rangle \quad (2.25)$$

in wave vector space, being direct products of the eigenstates for the individual photons 1,2,3,-- n, there being n photons in all. The single photon eigenstates in  $\mathbf{k}$ -space may be written

$$|\mathbf{k}\rangle = V^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.26)$$

so that, c.f. (1.36),

$$\langle \mathbf{k}' | \mathbf{k} \rangle = \delta_{\mathbf{k}\mathbf{k}'}.$$

Only symmetrical boson states are found in nature, so we must work with symmetrical n-photon eigenstates of the form

$$\Phi^S = N^{-1/2} \sum P |k_a(1)k_a(2) \dots k_a(n_a)k_b(n_a+1)k_b(n_a+2) \dots k_b(n_a+n_b)\dots \rangle \quad (2.27)$$

the sum being taken over all the  $n!$  permutations of the photon labels 1,2,3,-- n. The normalization condition

$$\begin{aligned} N^{-1} \langle k_a(1) \dots k_a(n_a)k_b(n_a+1) \dots k_b(n_a+n_b) | \sum P \sum \overleftrightarrow{P} | k_a(1) \dots k_a(n_a)k_b(n_a+1) \dots k_b(n_a+n_b) \rangle \\ = 1 \end{aligned} \quad (2.28)$$

provides the normalization factor

$$N = (n!)(n_a! n_b! \dots) \quad (2.29)$$

since, in addition to the  $n!$  equal bras and kets of (2.28) that arise when every photon is in a different state, those bras and kets will be equal which arise from permutations which merely interchange photons in the same state.

The state (2.27) is, like the occupation number state (2.23), a simultaneous eigenstate of the numbers  $n_a, n_b, \dots$  of photons with wave vectors  $\mathbf{k}_a, \mathbf{k}_b, \dots$ , and so the required relation between the base vectors in occupation number space and the base vectors in  $\mathbf{k}$ -space is

$$\begin{aligned} & |\mathbf{k}_a [n_a] \mathbf{k}_b [n_b] \dots \rangle \\ &= [(n!)(n_a! n_b! \dots)]^{-1/2} \sum P |\mathbf{k}_{a(1)} \dots \mathbf{k}_{a(n_a)} \mathbf{k}_{b(n_a+1)} \dots \mathbf{k}_b(n_a+n_b) \dots \rangle. \end{aligned} \quad (2.30)$$

# 3

## POLARIZED LIGHT IN QUANTUM MECHANICS

### 3.1. THE POLARIZATION OF A SINGLE PHOTON

The state of a plane wave photon is specified uniquely if its wave vector  $\mathbf{k}$  and polarization vector  $\boldsymbol{\pi}$  are known, where  $\boldsymbol{\pi}$  is the first rank polarization spinor introduced in (1.66). If a wave packet description of the photon is required, a suitable superposition of the  $\mathbf{k}$ -states must be taken.

It is convenient to work in a representation in which the general pure polarization state  $|\boldsymbol{\pi}\rangle$  is written as a coherent superposition of the plane polarized base states  $|\boldsymbol{\epsilon}_\lambda\rangle$ ,  $\lambda=1,2,3$ , being the quantum mechanical equivalents of the unit vectors defined in Section 1.6. (Figure 1.1.). The state of a transverse photon is written in this representation as

$$|\mathbf{k}, \boldsymbol{\pi}\rangle = \sum_{\lambda} |\mathbf{k}, \boldsymbol{\epsilon}_\lambda\rangle \langle \boldsymbol{\epsilon}_\lambda | \boldsymbol{\pi} \rangle \quad (\lambda = 1, 2, 3). \quad (3.1)$$

The transversality condition is imposed by choosing  $\langle \boldsymbol{\epsilon}_3 | \boldsymbol{\pi} \rangle$  to be zero. The remaining transformation coefficients may be identified with the amplitudes  $b_1$  and  $b_2$  defined in (1.65):

$$\left. \begin{aligned} \langle \epsilon_1 | \pi \rangle &= \cos \eta \cos \theta + i \sin \eta \sin \theta \equiv b_1 \\ \langle \epsilon_2 | \pi \rangle &= \cos \eta \sin \theta - i \sin \eta \cos \theta \equiv b_2 \end{aligned} \right\} \quad (3.2)$$

It was seen in Section 1.6 that the azimuth and ellipticity of the radiation field could be extracted from the classical wave function (1.66) by means of the Stokes parameters. Here we must invoke the operational equivalents of the Stokes parameters and take their expectation values with the state vector (3.1). The required operators are

$$\left. \begin{aligned} \Sigma_0 &= \sum_{\mathbf{k}} (a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_1} + a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_2}) \\ \Sigma_1 &= \sum_{\mathbf{k}} (a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1} + a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}) \\ \Sigma_2 &= \sum_{\mathbf{k}} i(a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} - a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1}) \\ \Sigma_3 &= \sum_{\mathbf{k}} (a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_1} - a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_2}) \end{aligned} \right\} \quad (3.3)$$

It can be verified that the expectation values of these operators with the state (3.1) reproduce the Stokes parameters (1.67).

For example

$$\begin{aligned} S_1 &= \langle \mathbf{k}, \pi | \Sigma_1 | \mathbf{k}, \pi \rangle \\ &= (b_1^* \langle \mathbf{k}, \epsilon_1 | + b_2^* \langle \mathbf{k}, \epsilon_2 |) \sum_{\mathbf{k}} (a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1} + a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}) (b_1 | \mathbf{k}, \epsilon_1 \rangle + b_2 | \mathbf{k}, \epsilon_2 \rangle) \\ &= b_1^* b_2 + b_2^* b_1. \end{aligned} \quad (3.4)$$

The density operator provides an alternative formulation of quantum mechanics that avoids the need to take expectation

values [11]; furthermore impure states are automatically accommodated, whereas only pure states are exhaustively characterized by specifying a single state vector of the type (3.1). A density operator  $\mathbf{D}$  may therefore be defined for the photon state and factorized into an operator  $\rho$  in polarization space and an operator  $\chi$  in wave vector space:

$$\mathbf{D} = |\mathbf{k}, \pi\rangle\langle\mathbf{k}, \pi| \equiv \chi \rho \quad (3.5)$$

with

$$\chi = |\mathbf{k}\rangle\langle\mathbf{k}| \quad (3.6)$$

and

$$\rho = |\pi\rangle\langle\pi| = \sum_{\lambda, \mu} |\epsilon_\lambda\rangle b_\lambda b_\mu^* \langle\epsilon_\mu|. \quad (3.7)$$

The elements of  $\rho$  in the  $\epsilon_\lambda$ -representation are

$$\rho_{\sigma\tau} = \langle\epsilon_\sigma|\rho|\epsilon_\tau\rangle = b_\sigma b_\tau^* \quad (3.8)$$

and these are the same as the elements (1.74) of the classical density dyadic (1.77).

### 3.2. THE DESCRIPTION OF A BEAM OF POLARIZED PHOTONS

In order to deal with multiphoton interactions between polarized light and molecules, it is necessary to construct a state vector in a polarization space that is a direct product of the two-dimensional polarization spaces spanned by the individual photon states.

We shall consider only the case of  $n$  photons confined to

a single plane wave mode of the radiation field; each photon therefore has the same wave vector  $\mathbf{k}$  and polarization  $\pi$ . Field states that are coherent superpositions of single modes will not be considered. The required state vector  $|k_\pi[n]\rangle$  may be constructed in occupation number space by the  $n$ -fold application of the creation operator  $a_{k_\pi}^\dagger$  to the vacuum state. In terms of the creation operators  $a_{k_\lambda}^\dagger$  for the plane polarized plane wave states, where  $a_{k_1}^\dagger$  creates a photon of wave vector  $\mathbf{k}$  and polarization along  $\epsilon_1$ , and  $a_{k_2}^\dagger$  creates the same, but with polarization along  $\epsilon_2$ , we may write

$$a_{k_\pi}^\dagger = b_1 a_{k_1}^\dagger + b_2 a_{k_2}^\dagger \quad (3.9)$$

where  $b_1$  and  $b_2$  are the transformation coefficients defined in (3.2). Therefore

$$\begin{aligned} |k_\pi[n]\rangle &= (n!)^{-1/2} (a_{k_\pi}^\dagger)^n |k_1[0] k_2[0]\rangle \\ &= (n!)^{-1/2} (b_1 a_{k_1}^\dagger + b_2 a_{k_2}^\dagger)^n |k_1[0] k_2[0]\rangle \\ &= (n!)^{-1/2} \sum_{r=0}^n \binom{n}{r} b_1^{n-r} b_2^r (a_{k_1}^\dagger)^{n-r} (a_{k_2}^\dagger)^r |k_1[0] k_2[0]\rangle \\ &= \sum_{r=0}^n \left[ \binom{n}{r} \right] b_1^{n-r} b_2^r |k_1[n-r] k_2[r]\rangle, \end{aligned} \quad (3.10)$$

where  $\left[ \binom{n}{r} \right]$  is the square root of the binomial coefficient:

$$\left[ \binom{n}{r} \right] \equiv \left( \binom{n}{r} \right)^{1/2} \equiv [n! / (n-r)! r!]^{1/2}. \quad (3.11)$$

Clearly (3.10) constitutes a linear superposition of states of the type (2.23) since the number of photons in states

with the same wave vector but different plane polarization base vectors are simultaneous eigenvalues. One could, for example, simultaneously determine the number of photons from the polarized  $n$ -photon beam passing through each of two nicol prisms, one oriented along the  $\epsilon_1$ -axis, and the other oriented along the  $\epsilon_2$ -axis. The sum (3.10) covers all observational possibilities: thus if in a particular experiment  $(n - r)$  photons passed through the  $\epsilon_1$ -filter,  $r$  photons must have passed through the  $\epsilon_2$ -filter, the amplitude for this observation being proportional to  $b_1^{n-r} b_2^r$ , which in turn depends on the polarization of the beam.

For the special case of  $\theta = \pi/4$ , Equation (3.10) reproduces (39) of [32], namely

$$|k_\pi[n]\rangle = 2^{-n/2} e^{in\eta} \sum_{r=0}^n \begin{bmatrix} n \\ r \end{bmatrix} e^{-2ir\eta} |k_1[n-r]k_2[r]\rangle \quad (3.12)$$

and for a single photon the expected result

$$|k_\pi[1]\rangle = b_1 |k_1[1]k_2[0]\rangle + b_2 |k_1[0]k_2[1]\rangle \quad (3.13)$$

is obtained, which is equivalent to the state (3.1).

### 3.3. THE POLARIZATION DENSITY MATRIX FOR A BEAM OF PHOTONS

The density operator corresponding to the state (3.10) is

$$\begin{aligned} \rho &= |k_\pi[n]\rangle \langle k_\pi[n]| \\ &= \sum_{r,r'=0}^n \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} n \\ r' \end{bmatrix} |k_1[n-r]k_2[r]\rangle \langle k_1[n-r']k_2[r']| b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \end{aligned} \quad (3.14)$$

with matrix elements in the occupation number representation

$$\rho_{rr'} = \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} n \\ r' \end{bmatrix} b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \quad (3.15)$$

Notice that the trace of this matrix provides the correct normalization:

$$\begin{aligned} \text{Tr}_\pi \rho &= \sum_{r=0}^n \rho_{rr} \\ &= \sum_{r=0}^n \begin{bmatrix} n \\ r \end{bmatrix} |b_1^{n-r}|^2 |b_2^r|^2 \\ &= \{|b_1|^2 + |b_2|^2\}^n = 1. \end{aligned} \quad (3.16)$$

Since the subscripts  $r, r'$  range from zero to  $n$ , the order of the matrix will be  $n+1$ . When  $n=1$  we have

$$\rho = \begin{pmatrix} b_1 b_1^* & b_1 b_2^* \\ b_2 b_1^* & b_2 b_2^* \end{pmatrix}$$

in agreement with (3.8), whereas in general

$$\rho = \begin{pmatrix} b_1^n b_1^{*n} & n^{1/2} b_1^n b_1^{*n-1} b_2^* & \dots & b_1^n b_2^{*n} \\ n^{1/2} b_1^{n-1} b_1^{*n} b_2 & n b_1^{n-1} b_1^{*n-1} b_2 b_2^* & & n^{1/2} b_1^{n-1} b_2 b_2^{*n} \\ [n/2(n-1)]^{1/2} b_1^{n-2} b_1^{*n} b_2^2 & \vdots & & [n/2(n-1)]^{1/2} b_1^{n-2} b_2^2 b_2^{*n} \\ \vdots & & & \vdots \\ [n/2(n-1)]^{1/2} b_1^2 b_1^{*n} b_2^{n-2} & & & [n/2(n-1)]^{1/2} b_1^2 b_2^{n-2} b_2^{*n} \\ n^{1/2} b_1 b_1^{*n} b_2^{n-1} & & & n^{1/2} b_1 b_2^{n-1} b_2^{*n} \\ b_2^n b_1^{*n} & & & b_2^n b_2^{*n} \end{pmatrix} \quad (3.17)$$

The unusual notation and dimensionality of this density matrix is a consequence of the matrix elements being written in

the occupation number representation. The relation of such a matrix to the one of dimensionality  $n^2$  obtained in  $\mathbf{k}$ -space can be seen from a consideration of the two photon case. The direct product in polarization space of two single photon  $\mathbf{k}$ -space eigenstates is

$$\begin{pmatrix} |k_1(1)\rangle \\ |k_2(1)\rangle \end{pmatrix} \times \begin{pmatrix} |k_1(2)\rangle \\ |k_2(2)\rangle \end{pmatrix} = \begin{pmatrix} |k_1(1)k_1(2)\rangle \\ |k_1(1)k_2(2)\rangle \\ |k_2(1)k_1(2)\rangle \\ |k_2(1)k_2(2)\rangle \end{pmatrix} \quad (3.18)$$

Using (2.30) we can connect the direct product polarization eigenstates in  $\mathbf{k}$ -space and occupation number space by writing

$$\sum P \prod_{i=1}^{n-r} \prod_{j=n-r+1}^n |k_1(i)k_2(j)\rangle = [n!(n-r)!r!]^{1/2} |k_1[n-r]k_2[r]\rangle \quad (3.19)$$

so that

$$\left. \begin{aligned} |k_1(1)k_1(2)\rangle &= |k_1[2]k_2[0]\rangle \\ |k_1(1)k_2(2)\rangle + |k_2(1)k_1(2)\rangle &= 2^{1/2} |k_1[1]k_2[1]\rangle \\ |k_2(1)k_2(2)\rangle &= |k_1[0]k_2[2]\rangle \end{aligned} \right\} \quad (3.20)$$

The density matrix in  $\mathbf{k}$ -space for two photons is then written as the direct product of two single photon density matrices:

$$\rho(1) \times \rho(2) = \begin{pmatrix} \underline{b_1 b_1^*} \underline{b_1 b_1^*} & \underline{b_1 b_1^*} \underline{b_1 b_2^*} & \underline{b_1 b_2^*} \underline{b_1 b_1^*} & \underline{b_1 b_2^*} \underline{b_1 b_2^*} \\ \underline{b_1 b_1^*} \underline{b_2 b_1^*} & \underline{b_1 b_1^*} \underline{b_2 b_2^*} & \underline{b_1 b_2^*} \underline{b_2 b_1^*} & \underline{b_1 b_2^*} \underline{b_2 b_2^*} \\ \underline{b_2 b_1^*} \underline{b_1 b_1^*} & \underline{b_2 b_1^*} \underline{b_1 b_2^*} & \underline{b_2 b_2^*} \underline{b_1 b_1^*} & \underline{b_2 b_2^*} \underline{b_1 b_2^*} \\ \underline{b_2 b_1^*} \underline{b_2 b_1^*} & \underline{b_2 b_1^*} \underline{b_2 b_2^*} & \underline{b_2 b_2^*} \underline{b_2 b_1^*} & \underline{b_2 b_2^*} \underline{b_2 b_2^*} \end{pmatrix} \quad (3.21)$$

and this, on transforming to occupation number space with the aid of (3.20), coalesces to

$$\begin{pmatrix} b_1^2 b_1^{*2} & 2^{1/2} b_1^2 b_1^* b_2 & b_1^2 b_2^{*2} \\ 2^{1/2} b_1 b_1^{*2} b_2 & 2 b_1 b_1^* b_2 b_2^* & 2^{1/2} b_1 b_2^{*2} b_2 \\ b_2^2 b_1^{*2} & 2^{1/2} b_2^2 b_1^* b_2^* & b_2^2 b_2^{*2} \end{pmatrix} \quad (3.22)$$

which is just the matrix (3.17) for  $n=2$ .

Since every photon in the beam has the same polarization, the above analysis provides a justification for extracting the polarization parameters  $\Theta$  and  $\eta$  of the beam from the  $n$ 'th roots of the four corner elements of the matrix (3.17).

An alternative approach to the problem of determining the polarization of the  $n$ -photon beam is to generate the density matrix for a single photon by taking the trace over all but one photon. To this end we must evaluate the trace of the density operator (3.14) in the  $\mathbf{k}$ -representation. That is

$$\text{Tr}_\pi \rho = \sum_{r,r'} \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} n \\ r' \end{bmatrix} b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \text{Tr}_\pi \mathbf{B}(r, r'), \quad (3.23)$$

where

$$\mathbf{B}(r, r') \equiv |e_1[n-r] e_2[r] \rangle \langle e_1[n-r'] e_2[r']|. \quad (3.24)$$

The wave vector label has been omitted since it is a superfluous label, for we are concerned only with the trace over the polarization states of the photon. Then

$$\text{Tr}_\pi \mathbf{B}(r, r') =$$

$$\int \langle \epsilon_{\sigma_1}(1) \epsilon_{\sigma_2}(2) \dots \epsilon_{\sigma_n}(n) | \epsilon_1[n-r] \epsilon_2[r] \rangle \langle \epsilon_1[n-r'] \epsilon_2[r'] | \epsilon_{\sigma_1}(1) \epsilon_{\sigma_2}(2) \dots \epsilon_{\sigma_n}(n) \rangle d\sigma_1 d\sigma_2 \dots d\sigma_n$$

$$= \prod_{\lambda} \prod_{\mu} \prod_{\nu} \int \langle \epsilon_{\sigma_\lambda}(\lambda) | \epsilon_1[n-r] \epsilon_2[r] \rangle \langle \epsilon_1[n-r'] \epsilon_2[r'] | \epsilon_{\sigma_\mu}(\mu) \rangle d\sigma_\nu \quad (3.25)$$

where the integral  $\int d\sigma_\nu$  is really a sum over the two values  $1_\nu$  and  $2_\nu$  of  $\sigma$ , and  $\nu$  ranges from 1 to  $n$ . Furthermore, if the expansion (3.19) is used it is clear that, since the photons are indistinguishable, we may write

$$\text{Tr}_\pi \mathbf{B}(r, r') = \sum_s \binom{n}{s} \int (d1)^{n-s} (d2)^s \{ (n!)^2 (n-r)! (n-r')! r! r'! \}^{-1/2}$$

$$\times \sum_{PP'} \langle \epsilon_1^{n-s} \epsilon_2^s | P | \epsilon_1^{n-r} \epsilon_2^r \rangle \langle \epsilon_1^{n-r'} \epsilon_2^{r'} | P' | \epsilon_1^{n-s} \epsilon_2^s \rangle. \quad (3.26)$$

Therefore

$$\text{Tr}_\pi \mathbf{B}(r, r') = \sum_s \binom{n}{s} \left[ \binom{n}{r} \right]^{-1} \left[ \binom{n}{r'} \right]^{-1} \delta_{rs} \delta_{r's} = \delta_{rr'} \quad (3.27)$$

and so

$$\text{Tr}_\pi \rho = \sum_r \binom{n}{r} |b_1|^{2(n-r)} |b_2|^{2r}$$

$$= \{ |b_1|^2 + |b_2|^2 \}^n = 1 \quad (3.28)$$

in agreement with (3.16).

In a similar way it can be shown that by taking the trace over all but one photon we generate the density matrix for a single photon. For example, calling  $\text{Tr}'_\pi$  the trace over all but one photon, we obtain

$$(\text{Tr}'_\pi \rho)_{rr'} = \sum_{r'', r'''} \left[ \binom{n}{r''} \right] \left[ \binom{n}{r'''} \right] b_1^{n-r''} b_2^{r''} b_1^{*n-r'''} b_2^{*r'''} \{ \text{Tr}'_\pi \mathbf{B}(r'', r''') \}_{rr'} \quad (3.29)$$

with

$$\begin{aligned}
 \{Tr_{\pi}' B(r, r')\}_{11} &= \sum_s \binom{n-1}{s} (d1)^{n-1-s} (d2)^s [(n!)^2 (n-r)! (n-r')! r! r'!]^{-1/2} \\
 &\times \langle \epsilon_1 | \{ \sum_{P, P'} \langle \epsilon_1^{n-1-s} \epsilon_2^s | P | \epsilon_1^{n-r} \epsilon_2^r \rangle \langle \epsilon_1^{n-r'} \epsilon_2^{r'} | P' | \epsilon_1^{n-1-s} \epsilon_2^s \rangle \} | \epsilon_1 \rangle \\
 &= \sum_s \binom{n-1}{s} (d1)^{n-1-s} (d2)^s [(n!)^2 (n-r)! (n-r')! r! r'!]^{-1/2} \\
 &\times \sum_{P, P'} \langle \epsilon_1^{n-s} \epsilon_2^s | P | \epsilon_1^{n-r} \epsilon_2^r \rangle \langle \epsilon_1^{n-r'} \epsilon_2^{r'} | P' | \epsilon_1^{n-s} \epsilon_2^s \rangle \\
 &= \sum_s \binom{n-1}{s} \left[ \binom{n}{r} \right]^{-1} \left[ \binom{n}{r'} \right]^{-1} \delta_{rs} \delta_{r's} .
 \end{aligned} \tag{3.30}$$

The required partial trace is then

$$\begin{aligned}
 \{Tr_{\pi}' \rho\}_{11} &= \sum_r \binom{n-1}{r} |b_1|^2 |b_2|^2 |b_1|^{2(n-r-1)} \\
 &= [|b_1|^2 + |b_2|^2]^{n-1} |b_1|^2 = |b_1|^2
 \end{aligned} \tag{3.31}$$

The remaining elements of the single photon polarization density matrix may be generated in like fashion.

### 3.4. THE STOKES PARAMETERS FOR A BEAM OF PHOTONS

Yet another method for extracting the polarization characteristics of the n-photon beam involves calculating the Stokes parameters by taking the expectation values of the Stokes operators (3.3) with the state (3.10). Thus

$$\begin{aligned}
 S_0 &= \langle k_{\pi} [n] | \Sigma_0 | k_{\pi} [n] \rangle \\
 &= \sum_{r, r'} \left[ \binom{n}{r} \right] \left[ \binom{n}{r'} \right] b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \langle k_1 [n-r'] k_2 [r] | a_{k_1}^+ a_{k_1} a_{k_2}^+ a_{k_2} | k_1 [n-r] k_2 [r] \rangle
 \end{aligned}$$

$$\begin{aligned}
& = \sum_{r,r'} [\hat{n}_1^r] [\hat{n}_2^{r'}] b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} (n-r+r') \delta_{rr'} \\
& = n \sum_r \binom{n}{r} |b_1|^2 |b_2|^2 \\
& = n (b_1 b_1^* + b_2 b_2^*)^n \\
& = n
\end{aligned} \tag{3.32}$$

The next Stokes parameter is found to be

$$\begin{aligned}
S_1 & = \langle \mathbf{k}_\pi [n] | \Sigma | \mathbf{k}_\pi [n] \rangle \\
& = \sum_{r,r'} [\hat{n}_1^r] [\hat{n}_2^{r'}] b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \langle \mathbf{k}_1 [n-r'] \mathbf{k}_2 [r'] | a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1} + a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} | \mathbf{k}_1 [n-r] \mathbf{k}_2 [r] \rangle \\
& = \sum_{r,r'} [\hat{n}_1^r] [\hat{n}_2^{r'}] b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \langle \mathbf{k}_1 [n-r'] \mathbf{k}_2 [r'] | \\
& \quad \times \{ [(n-r)(r+1)]^{1/2} | \mathbf{k}_1 [n-r-1] \mathbf{k}_2 [r+1] \rangle + [(n-r+1)r]^{1/2} | \mathbf{k}_1 [n-r+1] \mathbf{k}_2 [r-1] \rangle \} \\
& = \sum_{r,r'} [\hat{n}_1^r] [\hat{n}_2^{r'}] b_1^{n-r} b_2^r b_1^{*n-r'} b_2^{*r'} \{ [(n-r)(r+1)]^{1/2} \delta_{r',r+1} + [(n-r+1)r]^{1/2} \delta_{r',r-1} \} \\
& = n \sum_r \binom{n-1}{r} |b_1|^2 |b_2|^2 (b_1 b_2^* + b_1^* b_2) \\
& = n (b_1 b_2^* + b_1^* b_2)
\end{aligned} \tag{3.33}$$

The remaining Stokes parameters can be shown in a similar manner to be

$$S_2 = in (b_1^* b_2 - b_2^* b_1) \tag{3.34}$$

$$S_3 = n (b_1^* b_1 - b_2^* b_2). \tag{3.34}$$

## 4

# THE INTERACTION OF THE ELECTROMAGNETIC FIELD WITH BOUND ELECTRONS

## 4.1. THE LAGRANGIAN AND HAMILTONIAN FOR A PARTICLE IN THE ELECTROMAGNETIC FIELD [2,3 etc.]

The Lagrangian appropriate to a particle of charge  $e$  and mass  $m$  in an electromagnetic field is

$$L = \frac{1}{2} m \dot{\mathbf{q}}^2 - e\phi(\mathbf{q}) + \frac{1}{c} e \dot{\mathbf{q}} \cdot \mathbf{A}(\mathbf{q}). \quad (4.1)$$

It is easily verified that this Lagrangian generates the correct equations of motion: thus the momentum conjugate to  $\mathbf{q}$  is

$$\mathbf{p} = \frac{\partial L}{\partial \dot{\mathbf{q}}} = m \dot{\mathbf{q}} + \frac{e}{c} \mathbf{A}; \quad (4.2)$$

and so the Euler-Lagrange equation (1.47) yields

$$m \ddot{\mathbf{q}} + \frac{e}{c} \dot{\mathbf{A}} = \nabla \left\{ -e\phi + \frac{1}{c} e \dot{\mathbf{q}} \cdot \mathbf{A} \right\}. \quad (4.3)$$

Using the vector identity

$$\nabla(\mathbf{a} \cdot \mathbf{b}) = (\mathbf{a} \cdot \nabla) \mathbf{b} + (\mathbf{b} \cdot \nabla) \mathbf{a} + \mathbf{a} \wedge (\nabla \wedge \mathbf{b}) + \mathbf{b} \wedge (\nabla \wedge \mathbf{a})$$

(4.3) reduces to Newton's law with the Lorentz force (1.25):

$$m\ddot{\mathbf{q}} = e\mathbf{E} + \frac{e}{c}(\dot{\mathbf{q}} \wedge \mathbf{B}) \quad (4.4)$$

where  $\mathbf{E}$  contains both longitudinal and transverse components.

From the definition (1.51) the Hamiltonian corresponding to (4.1) is

$$\begin{aligned} H &= \frac{1}{m} \mathbf{P} \cdot \left( \mathbf{P} - \frac{e}{c} \mathbf{A} \right) - \frac{1}{2m} \left( \mathbf{P} - \frac{e}{c} \mathbf{A} \right)^2 + e\phi - \frac{e}{mc} \left( \mathbf{P} - \frac{e}{c} \mathbf{A} \right) \cdot \mathbf{A} \\ &= \frac{1}{2m} \left( \mathbf{P} - \frac{e}{c} \mathbf{A} \right)^2 + e\phi \end{aligned} \quad (4.5)$$

One advantage of the Coulomb gauge is that the order of the factors  $\mathbf{p}$  and  $\mathbf{A}$  in the first term of (4.5) is immaterial despite the non-commutativity of  $\mathbf{p}$  and  $\mathbf{q}$  in the quantum theory.

#### 4.2. THE HAMILTONIAN FOR BOUND CHARGES INTERACTING WITH THE ELECTROMAGNETIC FIELD [5,20,21,22]

In a neutral molecule, the electrons and protons comprising each atom, or indeed each "charge cluster", give rise to net electric and magnetic multipole potentials at sufficiently large distances. Denoting the net electric dipole moment for atom  $a$  by  $\mathbf{d}_a$ , the net electric quadrupole moment by  $\mathbf{Q}_a$ , and the net magnetic dipole moment by  $\mathbf{m}_a$ , we can write

$$\mathbf{d}_a = \sum_{i_a} e_{i_a} \mathbf{r}_{i_a} \quad (4.6)$$

$$\mathbf{Q}_a = \frac{1}{2} \sum_{i_a} e_{i_a} \mathbf{r}_{i_a} \mathbf{r}_{i_a} \quad (4.7)$$

$$\mathbf{M}_a = \sum_{i_a} \frac{e_{i_a}}{2m_{i_a}c} (\mathbf{q}_{i_a} \wedge \mathbf{p}_{i_a}) \quad (4.8)$$

where the particles labelled  $i_a$  make up atom  $a$  which is at  $\mathbf{x}_a$ , being the coordinate origin from which the  $\mathbf{q}_{i_a}$  are measured. The complete molecule may be associated with a net electric polarization vector field  $\mathbf{P}(\mathbf{x})$ , where

$$\mathbf{P}(\mathbf{x}) = \sum_a \sum_{i_a} e_{i_a} \mathbf{q}_{i_a} \delta(\mathbf{x} - \mathbf{x}_a) + \frac{1}{2} \sum_a \sum_{i_a} e_{i_a} \mathbf{q}_{i_a} (\mathbf{q}_{i_a} \cdot \nabla) \delta(\mathbf{x} - \mathbf{x}_a) + \dots \quad (4.9)$$

and a net magnetic polarization vector field  $\mathbf{M}(\mathbf{x})$ , where

$$\mathbf{M}(\mathbf{x}) = \sum_a \sum_{i_a} \frac{e_{i_a}}{2m_{i_a}c} (\mathbf{q}_{i_a} \wedge \mathbf{p}_{i_a}) \delta(\mathbf{x} - \mathbf{x}_a) + \dots \quad (4.10)$$

The resulting average charge and current densities over the region occupied by the molecule are

$$\rho = \sum_a \sum_{i_a} e_{i_a} \delta(\mathbf{q} - \mathbf{q}_{i_a}) = -\nabla \cdot \mathbf{P} \quad (4.11)$$

$$\mathbf{j} = \sum_a \sum_{i_a} e_{i_a} \dot{\mathbf{q}}_{i_a} \delta(\mathbf{q} - \mathbf{q}_{i_a}) = c(\nabla \wedge \mathbf{M}) + \dot{\mathbf{P}} \quad (4.12)$$

(see Section 6.10 of [1], or Chapter 15 of [9]), so that the Lagrangian for the molecule in the field is

$$\begin{aligned} L &= \sum_a \sum_{i_a} \frac{1}{2} m_{i_a} \dot{\mathbf{q}}_{i_a}^2 + \int (-\rho \phi + \frac{1}{c} \mathbf{j} \cdot \mathbf{A}) dV \\ &= \sum_a \sum_{i_a} \frac{1}{2} m_{i_a} \dot{\mathbf{q}}_{i_a}^2 + \int (\phi \nabla \cdot \mathbf{P} + \frac{1}{c} \dot{\mathbf{P}} \cdot \mathbf{A} + \mathbf{A} \cdot \nabla \wedge \mathbf{M}) dV. \end{aligned} \quad (4.13)$$

The vector identity (1.28) enables the last term to be written

$$\mathbf{A} \cdot (\nabla \cdot \mathbf{M}) = \mathbf{M} \cdot (\nabla \wedge \mathbf{A}) + \nabla \cdot (\mathbf{M} \wedge \mathbf{A})$$

and since the integral of a divergence over all space equals the net outflow integral at infinity, which is zero, we obtain

$$L = \sum_a \sum_{i_a} \frac{1}{2} m_{i_a} \dot{\mathbf{q}}_{i_a}^2 + \int \left( \frac{1}{c} \dot{\mathbf{P}} \cdot \mathbf{A} + \mathbf{M} \cdot \mathbf{B} \right) dV. \quad (4.14)$$

The equations of motion are not altered by the addition to the Lagrangian of a total time derivative of some quantity which does not depend explicitly on the time (see [22] or [4], Chapter 8). It will therefore prove convenient to subtract the term

$$\frac{1}{c} \frac{\partial}{\partial t} \int \mathbf{P} \cdot \mathbf{A} dV = \frac{1}{c} \int \dot{\mathbf{P}} \cdot \mathbf{A} dV - \int \mathbf{P} \cdot \mathbf{E}^t dV \quad (4.15)$$

from the Lagrangian (4.14):

$$L' = \sum_a \sum_{i_a} \frac{1}{2} m_{i_a} \dot{\mathbf{q}}_{i_a}^2 + \int (\mathbf{P} \cdot \mathbf{E}^t + \mathbf{M} \cdot \mathbf{B}) dV. \quad (4.16)$$

The momentum conjugate to  $\mathbf{q}$  is now simply  $m\dot{\mathbf{q}}$ , whereupon the Hamiltonian becomes

$$H = \sum_a \sum_{i_a} \frac{1}{2} m_{i_a} \dot{\mathbf{q}}_{i_a}^2 - \int (\mathbf{P} \cdot \mathbf{E}^t + \mathbf{M} \cdot \mathbf{B}) dV. \quad (4.17)$$

Using the expressions (4.9) and (4.10) for  $\mathbf{P}$  and  $\mathbf{M}$ , the interaction part of this Hamiltonian may be written

$$V = - \sum_a \mathbf{d}_a \cdot \mathbf{E}^t(\mathbf{x}_a) - \sum_a \mathbf{m}_a \cdot \mathbf{B}(\mathbf{x}_a) - \sum_a (\mathbf{Q}_a \cdot \nabla) \cdot \mathbf{E}^t(\mathbf{x}_a) + \dots \quad (4.18)$$

This multipole form of the interaction Hamiltonian, in which each term is gauge-invariant, will prove very useful for the application of diagrammatic perturbation theory. In particular the extension to multiphoton processes becomes very simple because the field strength dependence is explicit. By contrast the conventional interaction Hamiltonian obtained from (4.15) as

$$V = \sum_i \frac{e_i}{m_i c_i} \mathbf{p}_i \cdot \mathbf{A}(\mathbf{q}_i) + \sum_i \frac{e_i^2}{2m_i c_i^2} A^2(\mathbf{q}_i) + \sum_i e_i \phi(\mathbf{q}_i) \quad (4.19)$$

is rather less convenient for dealing with the interaction of the radiation field with electrons bound to atomic or molecular systems.

The above derivation of the multipole interaction Hamiltonian is based on a treatment by McLachlan [22], which in turn follows the work of Richards [21]. An alternative derivation, based on a canonical transformation of the complete Hamiltonian, can be found in the paper by Power & Zienau [20].

## 5

## THE SCATTERING MATRIX

## 5.1. THE TRANSITION AMPLITUDE [14,15,16,17,22,23,etc.]

The S-matrix is introduced as a means of describing collision phenomena in terms of observable quantities only, thereby eliminating the need to specify state vectors other than those of free systems. The physical processes are thought of as transformations which convert the free input states into corresponding free output states. No attempt is made to visualize the interaction process, which is regarded as occurring within a "black box" region of space and time.

The free input and output states are connected formally by the S-operator:

$$|\Psi^{\text{out}}\rangle = S |\Psi^{\text{in}}\rangle. \quad (5.1)$$

The precise nature of these in and out states depends on whether a time-independent or a time-dependent formulation is used. If we employ the latter, the in and out states refer to times in the remote past and future with respect to the interaction, that is

$$\left. \begin{aligned} |\Psi^{\text{in}}\rangle &= \lim_{t \rightarrow -\infty} |\Psi(t)\rangle \\ |\Psi^{\text{out}}\rangle &= \lim_{t \rightarrow +\infty} |\Psi(t)\rangle \end{aligned} \right\} \quad (5.2)$$

Conservation of probability requires that the in and out states have the same inner product:

$$\langle \Psi^{\text{out}} | \Psi^{\text{out}} \rangle = \langle \Psi^{\text{in}} | S^\dagger S | \Psi^{\text{in}} \rangle = \langle \Psi^{\text{in}} | \Psi^{\text{in}} \rangle \quad (5.3)$$

which implies that

$$S^\dagger S = S S^\dagger = 1. \quad (5.4)$$

Consequently the S-matrix is unitary.

The elements of the S-matrix connect the eigenstates of the maximal set of observables in terms of which the initial and final asymptotic states have been expanded. Suppose that the initial state is prepared as the eigenstate  $|i\rangle$  of the complete orthonormal set of states  $|n\rangle$ . The superposition principle now permits us to write the final state as

$$|\Psi^{\text{out}}\rangle = \sum_n c_n |n\rangle \quad (5.5)$$

and so the transition amplitude from  $|i\rangle$  to some final eigenstate  $|f\rangle$  is simply the weight  $c_f$  of  $|f\rangle$  in  $|\Psi^{\text{out}}\rangle$ . Thus

$$c_f = \langle f | \Psi^{\text{out}} \rangle = \langle f | S | \Psi^{\text{in}} \rangle = \langle f | S | i \rangle \equiv S_{fi}. \quad (5.6)$$

and so the S-matrix elements are simply the transition amplitudes between the initial and final eigenstates for the infinite time interval  $-\infty < t < +\infty$ , the interaction being assumed located near  $t = 0$ .

## 5.2. CONNECTEDNESS-STRUCTURE

The S-operator can usefully be separated into a unit matrix corresponding to no interaction between the sub-states of the system, and a reactance operator  $R$  describing any such interaction:

$$S = 1 + R \quad (5.7)$$

This is known as the assumption of connectedness-structure of the S-matrix elements, and for two-particle  $\rightarrow$  two-particle scattering may be represented diagrammatically as follows:

$$\text{---} \bigcirc \text{---} = \text{---} + \text{---} \bigoplus \text{---} \quad (5.8)$$

This decomposition is strictly valid only for short range forces and is not, at least in principle, admissible for electromagnetic interactions [22]. Indeed, our theory of optical birefringence is critically dependent on the lack of validity of (5.8) for the photon-molecule scattering system, for as we shall see, it is the interference between the unscattered component and the forward scattered component that gives rise to birefringent polarization changes. Since the scattering amplitude for

a single molecule and a photon is extremely small, the connected part of (5.8) may be considered a minute perturbation to the unconnected part. It is therefore possible that there are no polarization changes analogous to those involved in optical birefringence for the forward scattering of particles that interact through strong forces.

The invariance of the S-matrix under proper Lorentz transformations implies that energy and momentum are conserved in interactions. It is convenient to take this conservation law out of the matrix element  $R_{fi}$ , but since the extremely large mass of the molecule relative to that of the photon implies that the latter effectively scatters from a fixed target, a momentum conserving  $\delta$ -function is irrelevant and we may use an R-matrix on the energy shell. Therefore we define

$$S_{fi} = \delta_{fi} - 2\pi i \delta(E_f - E_i) R_{fi} . \quad (5.9)$$

### 5.3. THE S-MATRIX IN THE INTERACTION PICTURE

For practical calculations it is necessary to obtain specific expressions for the S-matrix elements. The noncovariant form of the usual perturbation series in the interaction picture from conventional quantum electrodynamics [8,16,17,26] will be employed, rather than the latest methods that eliminate the need to specify an interaction Hamiltonian density [23,24,25].

In the interaction picture, the operators and state vectors are defined in such a way that any changes with time in the state vectors arise solely from the interaction. Let  $|\Psi_s(t)\rangle$  be the time-dependent state vector in the Schrodinger picture, satisfying the Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi_s(t)\rangle = H_s |\Psi_s(t)\rangle \quad (5.10)$$

where the Hamiltonian  $H_s$  in this picture is independent of time. In the presence of some sort of interaction,  $H_s$  will contain a part  $H_{cs}$  representing the Hamiltonian of the unperturbed system, and a perturbing energy  $V_s$  which can have an intrinsic time dependence. Now define the interaction picture vector  $|\Psi_I(t)\rangle$  by

$$|\Psi_I(t)\rangle = e^{iH_{cs}t/\hbar} |\Psi_s(t)\rangle \quad (5.11)$$

which by virtue of (5.10) satisfies

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\Psi_I(t)\rangle &= e^{iH_{cs}t/\hbar} V_s e^{-iH_{cs}t/\hbar} |\Psi_I(t)\rangle \\ &= V_I(t) |\Psi_I(t)\rangle, \end{aligned} \quad (5.12)$$

where

$$V_I(t) = e^{iH_{cs}t/\hbar} V_s e^{-iH_{cs}t/\hbar} \quad (5.13)$$

is the perturbing Hamiltonian in the interaction picture. Therefore the temporal change of the state vector in the interaction picture depends entirely on the perturbation.

We now introduce the operator  $U(t, t_0)$  to formally describe the temporal evolution of the state vector. Thus

$$|\Psi_I(t)\rangle = U(t, t_0) |\Psi_I(t_0)\rangle \quad (5.14)$$

and so

$$i\hbar \frac{\partial}{\partial t} |\Psi_I(t)\rangle = i\hbar \frac{\partial}{\partial t} U(t, t_0) |\Psi_I(t_0)\rangle = V_I(t) U(t, t_0) |\Psi_I(t_0)\rangle. \quad (5.15)$$

Consequently  $U(t, t_0)$  satisfies the operator equation

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = V_I(t) U(t, t_0) \quad (5.16)$$

together with the boundary condition

$$U(t, t) = 1. \quad (5.17)$$

It is easy to show that the evolution operator satisfies the group property (see [16], p.40)

$$U(t, t_0) = U(t, t_1) U(t_1, t_0), \quad (5.18)$$

the inverse relation

$$U^{-1}(t, t_0) = U(t_0, t), \quad (5.19)$$

and the unitarity condition

$$U(t, t_0) U^\dagger(t, t_0) = U^\dagger(t, t_0) U(t, t_0) = 1. \quad (5.20)$$

In view of the unitarity of  $U$  it is reasonable to identify

the S-operator with  $U(+\infty, -\infty)$ :

$$S = \lim_{\substack{t_0 \rightarrow -\infty \\ t \rightarrow +\infty}} U(t, t_0) \quad (5.21)$$

A solution of (5.16) will, through (5.21), automatically provide a specific form for the S-matrix. In general this equation does not permit of a simple solution, and one method of treating it is to expand  $U$  into a perturbation series by iterative methods and hope that succeeding terms converge rapidly to zero. It is therefore assumed that  $V_I(t)$  is a small quantity of first order, and that  $U(t, t_0)$  may be expanded as

$$\begin{aligned} U(t, t_0) &= 1 + U_1(t, t_0) + U_2(t, t_0) + U_3(t, t_0) + \dots \\ &= \sum_{m=0}^{\infty} U_m(t). \end{aligned} \quad (5.22)$$

From (5.16) we now find

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} U_1(t, t_0) &= V_I(t) \\ i\hbar \frac{\partial}{\partial t} U_2(t, t_0) &= V_I(t) U_1(t, t_0) \\ &\dots \end{aligned} \quad (5.23)$$

which equations possess the solutions

$$\begin{aligned} U_1(t, t_0) &= (-i/\hbar) \int_{t_0}^t dt_1 V_I(t_1) \\ U_2(t, t_0) &= (-i/\hbar)^2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 V_I(t_1) V_I(t_2) \\ &\dots \\ U_m(t, t_0) &= (-i/\hbar)^m \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{m-1}} dt_m V_I(t_1) V_I(t_2) \dots V_I(t_m). \end{aligned} \quad (5.24)$$

The S-matrix may therefore be written

$$S = 1 + \sum_{n=1}^{\infty} (-i/\hbar)^n \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \dots \int_{-\infty}^{t_{n-1}} dt_n V_I(t_1) V_I(t_2) \dots V_I(t_n) \quad (5.25)$$

and a noncovariant expression can be developed from this by performing the space and time integrations independently. To carry out the time integrations we must make use of the adiabatic hypothesis.

#### 5.4. THE ADIABATIC HYPOTHESIS [8,14,16,17,etc.]

When using the S-matrix operator (5.25) to calculate the transition amplitude  $S_{fi}$ , one would want to specify  $|i\rangle$  and  $|f\rangle$  as free states. However, the logical application of field theory renders such an approach inadequate, for although the particles in the free states are well separated and no longer interacting with each other, they are nonetheless real particles interacting with their self-fields. Thus the electron would be regarded as a bare core "dressed" in a cloud of soft photons.

This problem can be avoided by introducing the adiabatic hypothesis, in which the interaction is switched on and off at infinity by rewriting the interaction Hamiltonian as

$$V_I(t, \epsilon) = e^{-\epsilon|t|} V_I(t) ; \quad \epsilon \rightarrow 0^+ \quad (5.26)$$

where  $\epsilon$  is an infinitesimally small but positive quantity. This device also enables plane wave initial and final states to be used instead of wave packets; the potential (5.26) then ensures

that these plane waves interact in the time region that one would expect colliding wave packets to interact.

We can appreciate the meaning of the Hamiltonian (5.26) by considering the second order term in (5.25). Thus the second order S-matrix element for a transition from  $|i\rangle$  to  $|f\rangle$  which are eigenstates of  $H_0$  is given by

$$\langle f|S_2|i\rangle = (-i/\hbar)^2 \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \langle f|V_I(t_1)V_I(t_2)|i\rangle. \quad (5.27)$$

Making use of the definition (5.13) of the Schrodinger operator  $V_S$ , and introducing the complete set of eigenstates  $|n\rangle$  of  $H_0$ , we obtain

$$\langle f|S_2|i\rangle = (-i/\hbar)^2 \sum_n \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 e^{i(E_f - E_n)t_1/\hbar} e^{i(E_n - E_i)t_2/\hbar} \langle f|V_S|n\rangle \langle n|V_S|i\rangle \quad (5.28)$$

The integral over  $t_2$  is an oscillatory function. In order to make it convergent at its lower limit, an infinitesimal positive term  $\varepsilon$  can be inserted in the exponent:

$$\begin{aligned} \int_{-\infty}^{t_1} dt_2 e^{i(E_n - E_i)t_2/\hbar} &\rightarrow \int_{-\infty}^{t_1} dt_2 e^{i(E_n - E_i - i\varepsilon)t_2/\hbar} \\ &= \frac{i\hbar e^{i(E_n - E_i - i\varepsilon)t_1/\hbar}}{E_i - E_n + i\varepsilon} \end{aligned} \quad (5.29)$$

This result obtains automatically when the adiabatic potential (5.26) is used. Equation (5.27) is now simply

$$\langle f|S_2|i\rangle = -i \sum_n \frac{\langle f|V_S|n\rangle \langle n|V_S|i\rangle}{E_i - E_n + i\varepsilon} \int_{-\infty}^{+\infty} dt_1 e^{i(E_f - E_i)t_1/\hbar}$$

$$= -2\pi i \delta(E_f - E_i) \sum_n \frac{\langle f | V_s | n \rangle \langle n | V_s | i \rangle}{E_i - E_n + i\epsilon} \quad (5.30)$$

This is the same as the matrix element of the second order term in conventional time dependent perturbation theory. The extension to the  $m^{\text{th}}$  order is obvious, so we may write

$$S_{fi} = S_{fi} - 2\pi i \delta(E_f - E_i) \left\{ \langle f | V_s | i \rangle + \sum_n \frac{\langle f | V_s | n \rangle \langle n | V_s | i \rangle}{E_i - E_n + i\epsilon} + \sum_{n, n'} \frac{\langle f | V_s | n' \rangle \langle n' | V_s | n \rangle \langle n | V_s | i \rangle}{(E_i - E_n + i\epsilon)(E_i - E_{n'} + i\epsilon)} + \dots \right\}. \quad (5.31)$$

### 5.5. NONCOVARIANT DIAGRAMMATIC PERTURBATION THEORY [5,16,27,28]

The noncovariant iteration solution (5.31) for the S-matrix, together with the decomposition (5.9), provides the following equation for the matrix elements of the R-operator:

$$R_{fi} = \langle f | V_s | i \rangle + \sum_n \frac{\langle f | V_s | n \rangle \langle n | V_s | i \rangle}{E_i - E_n + i\epsilon} + \sum_{n, n'} \frac{\langle f | V_s | n' \rangle \langle n' | V_s | n \rangle \langle n | V_s | i \rangle}{(E_i - E_n + i\epsilon)(E_i - E_{n'} + i\epsilon)} + \dots \quad (5.32)$$

We are concerned with the interaction of a molecule and a single plane wave mode of the radiation field containing  $n$  photons, each of which carries the polarization  $\pi$ . The occupation number representation is used and so the state vector  $|k_\pi[n]\rangle$ , given by (3.10), is appropriate for the field. The molecular state is described in terms of the complete set of energy eigen-

states  $|m\rangle$  of the molecular Hamiltonian  $H_{mol}$ , where

$$H_{mol} |m\rangle = E_m |m\rangle. \quad (5.33)$$

Considerable simplification is achieved by using the multipole Hamiltonian (4.18) for the interaction of the quantized electromagnetic field with the bound charges. For a single charge cluster we have

$$V_s = -\mathbf{d} \cdot \mathbf{E}^E - \mathbf{m} \cdot \mathbf{B} - (\mathbf{Q} \cdot \nabla) \cdot \mathbf{E}^E + \dots \quad (5.34)$$

The electric and magnetic field vectors in this potential can be replaced immediately by their operator equivalents (2.12) and (2.13), obtained from the quantization of the electromagnetic field in the Coulomb gauge:

$$\begin{aligned} \mathbf{E} &= i(2\pi\hbar c/V)^{1/2} \sum_{\mathbf{k}, \lambda} \boldsymbol{\epsilon}_{\mathbf{k}, \lambda} (a_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{r}} - a_{\mathbf{k}, \lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}) \\ &\equiv \sum_{\mathbf{k}} (\mathbf{E}_{\mathbf{k}}^- + \mathbf{E}_{\mathbf{k}}^+) \end{aligned} \quad (5.35)$$

$$\begin{aligned} \mathbf{B} &= i(2\pi\hbar c/V)^{1/2} \sum_{\mathbf{k}, \lambda} (\mathbf{k} \wedge \boldsymbol{\epsilon}_{\mathbf{k}, \lambda}) (a_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{r}} - a_{\mathbf{k}, \lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}) \\ &\equiv \sum_{\mathbf{k}} (\mathbf{B}_{\mathbf{k}}^- + \mathbf{B}_{\mathbf{k}}^+). \end{aligned} \quad (5.36)$$

The matrix elements required to calculate the R-matrix for the photon-molecule system can now be written down. For example

$$\langle f | \mathbf{d} \cdot \mathbf{E}^+ | i \rangle = -i(2\pi\hbar\omega/V)^{1/2} \langle m'; \mathbf{k}_\pi [n'] | \sum_{\mathbf{k}, \lambda} \mathbf{d} \cdot \boldsymbol{\epsilon}_{\mathbf{k}, \lambda} a_{\mathbf{k}, \lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}} | m; \mathbf{k}_\pi [n] \rangle$$

$$\begin{aligned}
&= -i(2\pi\hbar\omega/V)^{1/2} \sum_{r,r'} \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} n' \\ r' \end{bmatrix} b_2^r b_1^{n-r} b_2^{*r'} b_1^{*n'-r'} \langle m'; k_1[n-r] k_2[r'] | \\
&\quad \times d.(\mathbf{e}_1 a_{k_1}^\dagger + \mathbf{e}_2 a_{k_2}^\dagger) e^{-i\mathbf{k} \cdot \mathbf{r}} | m; k_1[n-r] k_2[r] \rangle \\
&= -i(2\pi\hbar\omega/V)^{1/2} (n+1)^{1/2} \delta_{n',n+1} \sum_r \begin{bmatrix} n \\ r \end{bmatrix} |b_2|^{2r} |b_1|^{2(n-r)} \\
&\quad \times \langle m' | d. (b_1^* \mathbf{e}_1 + b_2^* \mathbf{e}_2) | m \rangle \\
&= -i(2\pi\hbar\omega/V)^{1/2} (n+1)^{1/2} \delta_{n',n+1} \sum_\lambda b_\lambda^* \langle m' | d. \mathbf{e}_\lambda | m \rangle. \tag{5.37}
\end{aligned}$$

The wavelength has been assumed long compared with molecular dimensions so that the exponential can be replaced by unity. Similarly,

$$\langle f | d. \mathbf{E}^- | i \rangle = i(2\pi\hbar\omega/V)^{1/2} n^{1/2} \delta_{n',n-1} \sum_\lambda b_\lambda \langle m' | d. \mathbf{e}_\lambda | m \rangle \tag{5.38}$$

$$\langle f | \mathbf{m} \cdot \mathbf{B}^+ | i \rangle = -i(2\pi\hbar\omega/V)^{1/2} (n+1)^{1/2} \delta_{n',n+1} \sum_\lambda b_\lambda^* \langle m' | \mathbf{m} \cdot (\hat{\mathbf{k}}_\lambda \mathbf{e}_\lambda) | m \rangle \tag{5.39}$$

$$\langle f | \mathbf{m} \cdot \mathbf{B}^- | i \rangle = i(2\pi\hbar\omega/V)^{1/2} n^{1/2} \delta_{n',n-1} \sum_\lambda b_\lambda \langle m' | \mathbf{m} \cdot (\hat{\mathbf{k}}_\lambda \mathbf{e}_\lambda) | m \rangle \tag{5.40}$$

$$\langle f | (\mathbf{Q} \cdot \nabla) \cdot \mathbf{E}^+ | i \rangle = -(2\pi\hbar\omega/V)^{1/2} (n+1)^{1/2} \delta_{n',n+1} \sum_\lambda b_\lambda^* \langle m' | (\mathbf{Q} \cdot \mathbf{k}) \cdot \mathbf{e}_\lambda | m \rangle \tag{5.41}$$

$$\langle f | (\mathbf{Q} \cdot \nabla) \cdot \mathbf{E}^- | i \rangle = -(2\pi\hbar\omega/V)^{1/2} n^{1/2} \delta_{n',n-1} \sum_\lambda b_\lambda \langle m' | (\mathbf{Q} \cdot \mathbf{k}) \cdot \mathbf{e}_\lambda | m \rangle \tag{5.42}$$

Both the magnetic dipole and the electric quadrupole interaction energies are of the order of  $10^3$  smaller than the electric dipole interaction energy. This ratio is important in deciding which terms are going to provide the dominant contributions in particular physical situations.

Consider now the diagrammatic representation of the terms in the expansion (5.32). The propagation of a free state is depicted by a straight line. A vertex corresponding to an electromagnetic interaction between two states is drawn as a wavy line. The first term in (5.32) is therefore represented as in Figure 5.1, with time increasing to the right. The interaction

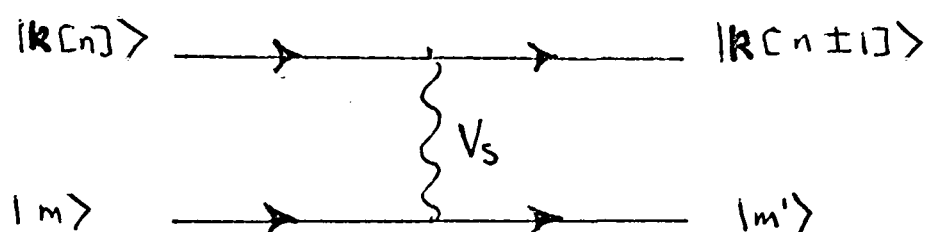


Figure 5.1. Diagrammatic representation of the first order contribution to  $R_{fi}$ .

results in the emission or absorption of a photon by the molecule, so the wavy line may be taken as representing a photon transfer between the molecule and the field. If the photon is absorbed by the molecule, the wavy line is drawn approaching the molecular line with increasing time; if the photon is emitted, the wavy line diverges from the molecular line.

It is convenient to distinguish electric and magnetic dipole interactions by drawing the latter as a broken line. Furthermore, we shall omit the radiation field line and draw simply the molecule and the emitted or absorbed photon. Figure 5.2 shows several possible contributions to the first order R-matrix element

$$\langle f | V_s | i \rangle = \langle f | d \cdot E^- | i \rangle + \langle f | d \cdot E^+ | i \rangle + \langle f | m \cdot B^- | i \rangle + \langle f | m \cdot B^+ | i \rangle \quad (5.43)$$

+ - - -

$$\begin{array}{c}
 \text{d.E}^- \quad k_\pi \\
 \nearrow \\
 \longrightarrow \\
 |m\rangle \quad |m'\rangle
 \end{array}
 \equiv \langle m'; k_\pi [n-1] | \text{d.E}^- | m; k_\pi [n] \rangle$$

$$\begin{array}{c}
 \text{d.E}^+ \quad k_\pi \\
 \nearrow \\
 \longrightarrow \\
 |m\rangle \quad |m'\rangle
 \end{array}
 \equiv \langle m'; k_\pi [n+1] | \text{d.E}^+ | m; k_\pi [n] \rangle$$

$$\begin{array}{c}
 \text{m.B}^- \quad k_\pi \\
 \nearrow \\
 \longrightarrow \\
 |m\rangle \quad |m'\rangle
 \end{array}
 \equiv \langle m'; k_\pi [n-1] | \text{m.B}^- | m; k_\pi [n] \rangle$$

$$\begin{array}{c}
 \text{m.B}^+ \quad k_\pi \\
 \nearrow \\
 \longrightarrow \\
 |m\rangle \quad |m'\rangle
 \end{array}
 \equiv \langle m'; k_\pi [n+1] | \text{m.B}^+ | m; k_\pi [n] \rangle$$

Figure 5.2. Some explicit first order contributions to  $R_{fi}$

We turn now to the second order term in (5.32). This contains the following product of two interaction matrix elements:

$$\begin{aligned}
 \langle f | V_S | n \rangle \langle n | V_S | i \rangle = & \\
 & \langle f | \text{d.E}^- | n \rangle \langle n | \text{d.E}^- | i \rangle + \langle f | \text{d.E}^+ | n \rangle \langle n | \text{d.E}^+ | i \rangle \\
 & + \langle f | \text{d.E}^- | n \rangle \langle n | \text{d.E}^+ | i \rangle + \langle f | \text{d.E}^+ | n \rangle \langle n | \text{d.E}^- | i \rangle \\
 & + \langle f | \text{d.E}^- | n \rangle \langle n | \text{m.B}^+ | i \rangle + \langle f | \text{d.E}^+ | n \rangle \langle n | \text{m.B}^- | i \rangle \\
 & + \langle f | \text{m.B}^- | n \rangle \langle n | \text{d.E}^+ | i \rangle + \langle f | \text{m.B}^+ | n \rangle \langle n | \text{d.E}^- | i \rangle \\
 & + \text{-----}
 \end{aligned}$$

where, for example,

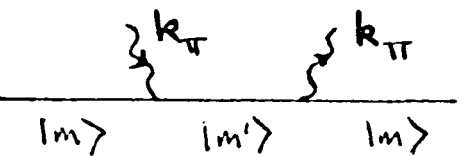
$$\langle f | \text{d.E}^- | n \rangle \langle n | \text{d.E}^- | i \rangle = -(2\pi \hbar \omega / V) n^{1/2} n'^{1/2} \delta_{n', n-1} \delta_{n'', n'-1} \sum_{\lambda, \lambda'} b_\lambda b_{\lambda'} \langle m'' | \text{d.E}_\lambda | m' \rangle \langle m' | \text{d.E}_\lambda | m \rangle$$

(5.44)

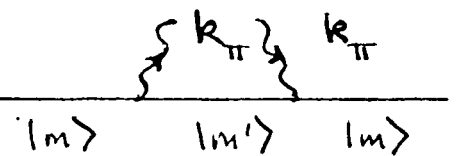
A few of these possible contributions to the two vertex term are drawn in Figure 5.3. Obviously only a few diagrams can contr-

a)   $\equiv$

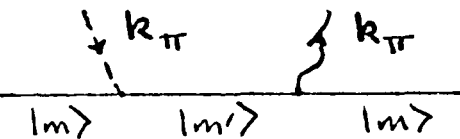
$$-(2\pi\hbar\omega/V) n^{1/2} n'^{1/2} \delta_{n',n-1} \delta_{n'',n'-1} \sum_{\lambda,\lambda'} b_{\lambda} b_{\lambda'} \sum_{m'} \frac{\langle m'' | d \cdot \epsilon_{\lambda'} | m' \rangle \langle m' | d \cdot \epsilon_{\lambda} | m \rangle}{E_m - E_{m'} + \hbar\omega + i\epsilon}$$

b)   $\equiv$

$$(2\pi\hbar\omega/V) n^{1/2} (n'+1)^{1/2} \delta_{n,n'+1} \sum_{\lambda,\lambda'} b_{\lambda} b_{\lambda'}^* \sum_{m'} \frac{\langle m | d \cdot \epsilon_{\lambda'} | m' \rangle \langle m' | d \cdot \epsilon_{\lambda} | m \rangle}{E_m - E_{m'} + \hbar\omega + i\epsilon}$$

c)   $\equiv$

$$(2\pi\hbar\omega/V) (n+1)^{1/2} n'^{1/2} \delta_{n,n'-1} \sum_{\lambda,\lambda'} b_{\lambda}^* b_{\lambda'} \sum_{m'} \frac{\langle m | d \cdot \epsilon_{\lambda'} | m' \rangle \langle m' | d \cdot \epsilon_{\lambda} | m \rangle}{E_m - E_{m'} - \hbar\omega + i\epsilon}$$

d)   $\equiv$

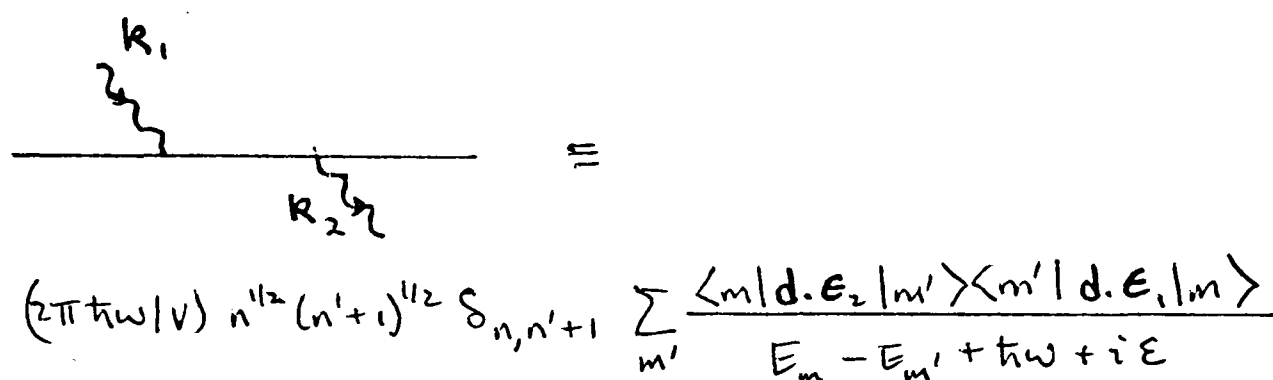
$$(2\pi\hbar\omega/V) n^{1/2} (n'+1)^{1/2} \delta_{n,n'+1} \sum_{\lambda,\lambda'} b_{\lambda} b_{\lambda'}^* \sum_{m'} \frac{\langle m | d \cdot \epsilon_{\lambda'} | m' \rangle \langle m' | m \cdot \hat{k}_{\lambda} \epsilon_{\lambda} | m \rangle}{E_m - E_{m'} + \hbar\omega + i\epsilon}$$

Figure 5.3. Some explicit second order contributions to  $R_{fi}$

tribute to a particular fundamental process. Thus a) is relevant for double photon absorption, b) and c) contribute to the elastic scattering of a single photon, and d) is only non-zero if

the molecule can support the interference of electric and magnetic dipole interactions.

Expressions obtained later for the polarization changes induced in a light beam through birefringent scattering specify R-matrix elements between plane polarized base states. It is therefore useful to adopt the convention that photons plane polarized along the  $\epsilon_1$ -direction be confined to the area above the molecular line, with those polarized along  $\epsilon_2$  confined below this line (Figure 5.4).



$$(2\pi\hbar\omega/V) n^{1/2} (n'+1)^{1/2} \delta_{n,n'+1} \sum_{m'} \frac{\langle m | d \cdot \epsilon_2 | m' \rangle \langle m' | d \cdot \epsilon_1 | m \rangle}{E_m - E_{m'} + \hbar\omega + i\epsilon}$$

Figure 5.4. A second order contribution to  $R_{21}$ .

It will often be necessary to formulate the interaction of a molecule with an externally applied static electric or magnetic field. Such fields provide a classical perturbation to the molecular energy states, and an extra term

$$V_S(0) = -d \cdot E(0) - m \cdot B(0) \quad (5.45)$$

must be added to the interaction Hamiltonian (5.34). These electrostatic and magnetostatic interactions will be depicted as unbroken and broken vertical lines, respectively. In addition

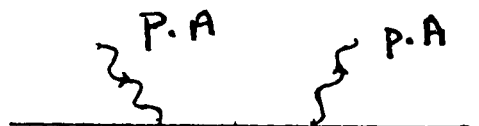
to providing mixed perturbations with the optical field, the static fields can produce permanent Zeeman and Stark modifications to the molecular energy levels: such interactions are independent of the photon scattering event, and may be incorporated in an ad-hoc fashion by substituting appropriate expressions for the permanently perturbed molecular energy levels in the energy denominators of the R-matrix and by using perturbed wave functions in the matrix elements. We therefore introduce the notation that a molecular eigenstate permanently perturbed by an external static field be drawn as a double line; the second line is continuous if the field is electric, and broken if it is magnetic (Figure 5.5).



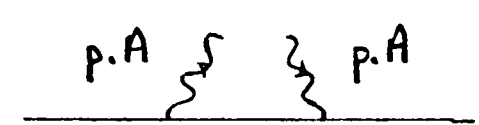
Figure 5.5. The interaction of a molecule with static fields.

There appears to be no place for two-photon vertices when the transformed interaction potential (4.18) is used, since terms bilinear in the field strength do not occur: the paper by Wallace [27] appears to be misleading in this respect. On the other hand, when the untransformed Hamiltonian (4.19) is employed, double photon vertices are obtained from the second term. Diagrams such as those in Figure 5.6 illustrate the application of

the untransformed potential to the elastic scattering of a single photon. The contribution of c) to the Kramers-Heisenberg disp-

a)   $\equiv$

$$(e/mc)(2\pi\hbar c/Vk)n^{1/2}(n'+1)^{1/2}\delta_{n,n'+1}\sum_{\lambda,\lambda'}b_{\lambda}b_{\lambda'}^*\sum_{m'}\frac{\langle m|P.E_{\lambda}|m'\rangle\langle m'|P.E_{\lambda'}|m\rangle}{E_m-E_{m'}+\hbar\omega+i\varepsilon}$$

b)   $\equiv$

$$(e/mc)(2\pi\hbar c/Vk)n^{1/2}(n'+1)^{1/2}\delta_{n,n'+1}\sum_{\lambda,\lambda'}b_{\lambda}^*b_{\lambda'}\sum_{m'}\frac{\langle m|P.E_{\lambda}|m'\rangle\langle m'|P.E_{\lambda'}|m\rangle}{E_m-E_{m'}-\hbar\omega+i\varepsilon}$$

c)   $\equiv$

$$(e^2/2mc^2)(2\pi\hbar c/Vk)n^{1/2}(n'+1)^{1/2}\delta_{n,n'+1}\sum_{\lambda,\lambda'}b_{\lambda}b_{\lambda'}^*\langle m|E_{\lambda'}\cdot E_{\lambda}|m\rangle$$

Figure 5.6.

ersion formula is known as the Waller term. One can show that these three contributions are equivalent to the sum of b) and c) of Figure 5.3 using a method due to Dirac (see [18]p.247, or [26] p.490).

Theories of absorption and damping would, in the present context, be built around the term  $i\varepsilon$  that occurs in the propagators in the R-matrix expansion (7.1). These effects are not discussed in the present work, so henceforth the  $i\varepsilon$  term will be omitted.

Self energy effects, other than radiation damping, provide

only small radiative corrections to bound states, and will not be considered [2,5,8,etc.,and particularly 20 and 29 ].

## 6

THE POLARIZATION OF THE  
SCATTERED PHOTON BEAM

## 6.1. THE SCATTERING OF A SINGLE PHOTON

We are concerned for the moment with the scattering of a single plane wave photon by a single molecule. General states of the photon and molecule will be written  $|\psi\rangle$  and  $|\phi\rangle$ , respectively. The uncoupled input state comprises a molecule in its ground state  $|g\rangle$ , and a plane wave photon with wave vector  $\mathbf{k}^i$  and polarization  $\pi^i$ , and so having a state vector  $|\mathbf{k}^i, \pi^i\rangle$ .

Subsequent to scattering, the final photon state  $|\psi^f\rangle$  consists of a transmitted plane wave component together with a spherical scattered wave, the molecule being in some final state  $|\phi^f\rangle$  which is a superposition of the complete set  $|m\rangle$  of molecular eigenstates (5.33). These initial and final states are connected by the S-operator (5.1), so we may write

$$|\phi^f; \psi^f\rangle = S|\mathbf{g}; \mathbf{k}^i, \pi^i\rangle. \quad (6.1)$$

The corresponding initial and final density operators for the entire system may be related as follows:

$$\begin{aligned}
D &= |\phi^f; \psi^f\rangle \langle \phi^f; \psi^f| \equiv M^f \chi^f \rho^f \\
&= S |g; \mathbf{k}^i, \pi^i\rangle \langle g; \mathbf{k}^i, \pi^i| S^\dagger \\
&= S D^i S^\dagger
\end{aligned} \tag{6.2}$$

where  $M$  denotes the density operator for the molecular states.

In order to proceed further, it is necessary to consider the photon detection apparatus and to invoke an operational equivalent of the detection process. A spherical wave may be considered a plane wave over a small region at great distances from the target, so it may be assumed that the detector is sensitive to plane wave photons with wave vector  $\mathbf{k}$  in a manner determined by a shape function  $A(\mathbf{k}^d - \mathbf{k})$  peaked sharply around  $\mathbf{k}^d$ . The operator representing the detection operation is then

$$\mathcal{Q}(\mathbf{k}^d - \mathbf{k}) = |\mathbf{k}\rangle A(\mathbf{k}^d - \mathbf{k}) \langle \mathbf{k}|, \tag{6.3}$$

and is independent of the polarization of the photon. Operationally we may consider the detector to be a gate for photons of a particular frequency travelling in a particular direction, and an application of  $\mathcal{Q}$  enables the polarization of photons with a particular wave vector to be studied by eliminating all others.

The polarization of the scattered wave can be determined by taking the expectation values of the Stokes operators with the state vector of the beam admitted by the detector, this being obtained from (3.1), (5.5), and (6.1) as

$$|\phi^f; \psi^d\rangle = \sum_{\mathbf{k}, m, \sigma, \lambda} A(\mathbf{k}^d - \mathbf{k}^f) |m; \mathbf{k}^f, \epsilon_\sigma^f\rangle \chi_m, \mathbf{k}^f, \epsilon_\sigma^f | S |g; \mathbf{k}^i, \epsilon_\lambda^i\rangle b_\lambda^i \tag{6.4}$$

where  $\mathbf{e}_\lambda^i$  are the unit vectors defined in terms of the direction of propagation of the incident beam, and  $\mathbf{e}_\tau^f$  are the corresponding vectors referred to the propagation direction of the final beam.

Alternatively, the polarization can be extracted from the density matrix of the scattered wave. Thus from (6.2) we can write

$$\mathcal{D}_{\sigma\tau}^f = \sum_{\lambda\mu} \langle \mathbf{e}_\sigma^f | s | g; \mathbf{k}^i, \mathbf{e}_\lambda^i \rangle \rho_{\lambda\mu}^i \langle g; \mathbf{k}^i, \mathbf{e}_\mu^i | s^\dagger | \mathbf{e}_\tau^f \rangle. \quad (6.5)$$

If the trace over the polarization states is denoted  $\text{Tr}_\pi$ , then since

$$\text{Tr}_\pi \rho^f = \sum_{\sigma} \rho_{\sigma\sigma}^f = 1, \quad (6.6)$$

it follows that

$$\mathbf{M}^f \chi^f = \sum_{\sigma} \mathcal{D}_{\sigma\sigma}^f. \quad (6.7)$$

The polarization density matrix of the photon admitted by the detector can now be obtained by writing

$$\text{Tr}_m \text{Tr}_k^A \mathcal{D}_{\sigma\tau}^f \equiv \sum_{\mathbf{k}, m} A(\mathbf{k}^d - \mathbf{k}^f) \langle m; \mathbf{k}^f | \mathcal{D}_{\sigma\tau}^f | m; \mathbf{k}^f \rangle \quad (6.8)$$

where  $\text{Tr}_m$  is a trace over the molecular states, and  $\text{Tr}_k^A$  is a trace over the photon momenta that are admitted by the detector.

We therefore deduce that

$$\begin{aligned} \rho_{\sigma\tau}^d = & \left\{ \sum_{\mathbf{k}, \lambda, \mu, m} A(\mathbf{k}^d - \mathbf{k}^f) \langle m; \mathbf{k}^f, \mathbf{e}_\tau^f | s | g; \mathbf{k}^i, \mathbf{e}_\lambda^i \rangle \rho_{\lambda\mu}^i \langle g; \mathbf{k}^i, \mathbf{e}_\mu^i | s^\dagger | m; \mathbf{k}^f, \mathbf{e}_\tau^f \rangle \right\} \\ & \times \left\{ \sum_{\mathbf{k}, \lambda, \mu, \sigma, m} A(\mathbf{k}^d - \mathbf{k}^f) \langle m; \mathbf{k}^f, \mathbf{e}_\sigma^f | s | g; \mathbf{k}^i, \mathbf{e}_\lambda^i \rangle \rho_{\lambda\mu}^i \langle g; \mathbf{k}^i, \mathbf{e}_\mu^i | s^\dagger | m; \mathbf{k}^f, \mathbf{e}_\sigma^f \rangle \right\}^{-1} \end{aligned} \quad (6.9)$$

The corresponding polarization density operator is

$$\rho^d = \left\{ \text{Tr}_{\mathbf{R}}^A \text{Tr}_m S \rho^i S^\dagger \right\} / \left\{ \text{Tr}_{\mathbf{R}}^A \text{Tr}_m \text{Tr}_\pi S \rho^i S^\dagger \right\}. \quad (6.10)$$

## 6.2. THE SCATTERING OF A BEAM OF PHOTONS

The treatment has been concerned so far with the scattering of a single photon; in other words the density matrix (3.8) is normalized so as to provide the input and output for the calculation of elementary processes involving one photon at a time. To describe processes involving a beam of photons, (3.8) is simply multiplied by the intensity of the incident beam and so the same expressions are obtained for the polarization changes of a beam as for a single photon. There is the restriction, however, that the elementary interaction processes between the beam and the molecule can be described only in terms of the scattering of a single photon, so multiphoton scattering cannot be accommodated.

To calculate the contributions to the polarization changes arising from the simultaneous scattering of two or more photons from the same molecule, that is the hyperpolarizability and multiphoton contributions, an n-photon representation of the beam must be used. The results obtained above may be directly applied with the single photon state vectors in (6.4) replaced by n-photon

state vectors of the type (3.10), and the single photon density operators of the type (3.14).

The results obtained in this chapter provide the master equations for all the later calculations, including linear and nonlinear optical birefringence, and polarization effects in Rayleigh, Raman, and multiharmonic scattering.

# PART TWO

## Optical Birefringence

## 7

## FORWARD SCATTERING OF A SINGLE PHOTON

### 7.1. THE MASTER EQUATIONS FOR BIREFRINGENT SCATTERING

The fundamental process responsible for optical birefringence phenomena is the forward scattering of photons by molecules. The forward scattered component interferes with the transmitted component of the photon state vector due to the lack of strict validity for electromagnetic interactions of the S-matrix decomposition (5.7). We shall call this process "birefringent scattering".

The master equations obtained in Chapter 6 can be applied directly to the present situation. Thus in an experiment arranged to observe the forward elastically scattered component, the idealized detector shape function has the form

$$A(\mathbf{k}^d - \mathbf{k}) = \delta(\mathbf{k}^i - \mathbf{k}). \quad (7.1)$$

The state vector of the detected beam (6.4) then becomes

$$|\phi^f; \psi^f\rangle = \sum_{\mathbf{k}, \lambda, \sigma} \delta(\mathbf{k}^i - \mathbf{k}^f) |g; \mathbf{k}^f, \epsilon_\sigma^f\rangle \langle g; \mathbf{k}^f, \epsilon_\sigma^f | S | g; \mathbf{k}^i, \epsilon_\lambda^i \rangle b_\lambda^i \quad (7.2)$$

and the corresponding density matrix (6.9) is now

$$\rho_{\sigma\tau}^d = \left\{ \sum_{\mathbf{k}, \lambda, \mu} \delta(\mathbf{k}^i - \mathbf{k}^f) \langle g; \mathbf{k}^f, \mathbf{e}_\sigma^f | S | g; \mathbf{k}^i, \mathbf{e}_\lambda^i \rangle \rho_{\lambda\mu}^i \langle g; \mathbf{k}^i, \mathbf{e}_\mu^i | S^\dagger | g; \mathbf{k}^f, \mathbf{e}_\tau^f \rangle \right\} \\ \times \left\{ \sum_{\mathbf{k}, \lambda, \mu, \sigma} \delta(\mathbf{k}^i - \mathbf{k}^f) \langle g; \mathbf{k}^f, \mathbf{e}_\sigma^f | S | g; \mathbf{k}^i, \mathbf{e}_\lambda^i \rangle \rho_{\lambda\mu}^i \langle g; \mathbf{k}^i, \mathbf{e}_\mu^i | S^\dagger | g; \mathbf{k}^f, \mathbf{e}_\sigma^f \rangle \right\}^{-1} \quad (7.3)$$

In view of the decomposition (5.9) of the S-matrix elements, we can separate the final photon state vector into parts corresponding to a transmitted plane wave and a spherical scattered wave:

$$|\psi^f\rangle = |\mathbf{k}^i\rangle - 2\pi i \sum_{\mathbf{k}} \delta(E_f - E_i) |\mathbf{k}^f\rangle R_{fi} \quad (7.4)$$

where the polarization vector has been suppressed for clarity. The sum over final wave vector states is in fact the integral (1.39) over the continuous spectrum of  $\mathbf{k}$ , but since Equation (7.2) for the detected beam specifies a sum over just those photons scattered precisely into the forward direction, a one dimensional density of states is appropriate, that is

$$\sum_{\mathbf{k}} \rightarrow \frac{L}{2\pi} \int d\mathbf{k} = \frac{L}{2\pi \hbar c} \int dE, \quad (7.5)$$

where  $L$  is the length of the quantization volume in the direction of propagation of the incident plane wave. This length may be identified with the sample length provided the latter is not too small. The state vector of the detected beam may therefore be

written

$$|\psi^d\rangle = |k^i\rangle - (iL/\hbar\omega) |k^i\rangle \langle g; k^i | R | g; k^i \rangle. \quad (7.6)$$

If we define the polarization matrix elements of the forward scattering S-matrix element to be

$$\langle g; k^i, \epsilon_\sigma^i | S | g; k^i, \epsilon_\lambda^i \rangle \equiv S_{\sigma\lambda}^0 \quad (7.7)$$

then from (7.6)

$$S_{\sigma\lambda}^0 = S_{\sigma\lambda} - (iL/\hbar\omega) R_{\sigma\lambda}^0, \quad (7.8)$$

and so the state vector of the forward scattered beam may be written

$$|\psi^d\rangle = \sum_\lambda |k^i, \epsilon_\lambda^i\rangle b_\lambda^i - (iL/\hbar\omega) \sum_{\sigma,\lambda} |k^i, \epsilon_\sigma^i\rangle \langle g; k^i, \epsilon_\sigma^i | R | g; k^i, \epsilon_\lambda^i \rangle b_\lambda^i \quad (7.9)$$

## 7.2. THE STOKES PARAMETERS OF THE FORWARD SCATTERED PHOTON

The polarization characteristics of the forward scattered photon can be obtained by way of the Stokes parameters, and these in turn can be calculated by applying the Stokes operators (3.3) to the state (7.9). The Stokes operators were first applied to the calculation of polarization changes in certain optical birefringence effects by Stephen [30]: he used a final state vector obtained from conventional time-dependent perturbation theory, but his approach was rather specialized. The Stokes operators have since been applied to a variety of optical birefringence

effects by Atkins and Barron [31,32] and by Atkins and Miller [33,34] ; also Go [35] has applied them to certain aspects of optical activity.

Consider first the calculation of  $S_0$ :

$$\begin{aligned}
 S_0^d &= \langle \Psi^d | \Sigma_0 | \Psi^d \rangle \\
 &= \left\{ \sum_{\lambda} \langle \mathbf{k}^i, \mathbf{e}_{\lambda}^i | b_{\lambda}^{i*} + (iL/\hbar c) \sum_{\lambda, \sigma} \langle \mathbf{k}^i, \mathbf{e}_{\sigma}^i | R_{\sigma\lambda}^{0*} b_{\lambda}^{i*} \right\} \sum_{\mathbf{k}} (a_{\mathbf{k}_1}^{\dagger} a_{\mathbf{k}_1} + a_{\mathbf{k}_2}^{\dagger} a_{\mathbf{k}_2}) \\
 &\times \left\{ \sum_{\lambda} | \mathbf{k}^i, \mathbf{e}_{\lambda}^i \rangle b_{\lambda}^i - (iL/\hbar c) \sum_{\lambda, \sigma} | \mathbf{k}^i, \mathbf{e}_{\sigma}^i \rangle R_{\sigma\lambda}^0 b_{\lambda}^i \right\} \\
 &= (b_1^{i*} b_1^i + b_2^{i*} b_2^i) + (iL/\hbar c) \sum_{\lambda} [ b_1^{i*} b_1^i R_{1\lambda}^{0*} + b_1^{i*} b_2^i R_{2\lambda}^{0*} \\
 &\quad - b_1^{i*} b_{\lambda}^i R_{1\lambda}^0 - b_2^{i*} b_{\lambda}^i R_{2\lambda}^0 ] \\
 &= S_0^i + (2L/\hbar c) g_m \sum_{\lambda} (b_1^{i*} b_{\lambda}^i R_{1\lambda}^0 + b_2^{i*} b_{\lambda}^i R_{2\lambda}^0) \quad (7.10)
 \end{aligned}$$

where we have neglected quantities of the order  $(L/\hbar c)^2 R^2$  because  $(L/\hbar c) R^0 \ll 1$ .

The remaining Stokes parameters are obtained in like fashion. It is found that

$$S_1^d = S_1^i + (2L/\hbar c) g_m \sum_{\lambda} (b_1^{i*} b_{\lambda}^i R_{2\lambda}^0 + b_2^{i*} b_{\lambda}^i R_{1\lambda}^0) \quad (7.11)$$

$$S_2^d = S_2^i - (2L/\hbar c) g_m \sum_{\lambda} (b_2^{i*} b_{\lambda}^i R_{1\lambda}^0 - b_1^{i*} b_{\lambda}^i R_{2\lambda}^0) \quad (7.12)$$

$$S_3^d = S_3^i + (2L/\hbar c) g_m \sum_{\lambda} (b_1^{i*} b_{\lambda}^i R_{1\lambda}^0 - b_2^{i*} b_{\lambda}^i R_{2\lambda}^0) . \quad (7.13)$$

### 7.3. THE DENSITY MATRIX OF THE FORWARD SCATTERED PHOTON

The polarization density matrix was first applied to the birefringent scattering of photons by Atkins and Barron [36]. It provides a rather more succinct calculation of the polarization changes than the Stokes operator method.

By inserting (7.8) into (7.3), the polarization density matrix of the forward scattered photon is found to be

$$\begin{aligned}
 \rho_{\sigma\tau}^d &= \left\{ \rho_{\sigma\tau}^i - (iL/\hbar c) \sum_{\lambda} (R_{\sigma\lambda}^0 \rho_{\lambda\tau}^i - \rho_{\sigma\lambda}^i R_{\lambda\tau}^{0+}) \right\} \\
 &\times \left\{ 1 - (iL/\hbar c) \sum_{\sigma,\lambda} (R_{\sigma\lambda}^0 - R_{\sigma\lambda}^{0+}) \rho_{\lambda\sigma}^i \right\}^{-1} \\
 &\sim \rho_{\sigma\tau}^i - (iL/\hbar c) \sum_{\lambda} (R_{\sigma\lambda}^0 \rho_{\lambda\tau}^i - \rho_{\sigma\lambda}^i R_{\lambda\tau}^{0+}) \\
 &\quad + (iL/\hbar c) \rho_{\sigma\tau}^i \sum_{\lambda,\mu} (R_{\mu\lambda}^0 - R_{\mu\lambda}^{0+}) \rho_{\lambda\mu}^i
 \end{aligned} \tag{7.14}$$

where again quantities of the order  $(L/\hbar c)^2 R^2$  have been neglected.

In operator form this equation is

$$\rho^d = \rho^i + (iL/\hbar c) \overleftrightarrow{R}^0 \rho^i \tag{7.15}$$

with the notation

$$\overleftrightarrow{A}B \equiv (\langle A \rangle - A)B - B(\langle A^+ \rangle - A^+); \quad \langle A \rangle = \text{Tr}(\rho^i A). \tag{7.16}$$

We may now proceed to a derivation of explicit expressions for the azimuth  $\theta^d$  and ellipticity  $\eta^d$  of the detected beam in the forward direction if initially it was prepared with polarization parameters  $\theta^i$  and  $\eta^i$ . Both the absorptive and nonabsorptive

situations will be analysed.

#### 7.4. NONABSORPTIVE FORWARD SCATTERING

In the absence of absorption,  $R^0$  is Hermitian and so (7.10) reduces to

$$S_o^d = S_o^i \quad (7.17)$$

corresponding to the expected result that the forward scattered intensity equals the incident intensity. The other Stokes parameters become

$$S_1^d = \cos 2\eta^i \sin 2\theta^i + (L/\hbar c) [ \operatorname{Re}(R_{11}^0 - R_{22}^0) \sin 2\eta^i + 2g_m R_{21}^0 \cos 2\eta^i \cos 2\theta^i ] \quad (7.18)$$

$$S_2^d = \sin 2\eta^i - (L/\hbar c) [ \operatorname{Re}(R_{11}^0 - R_{22}^0) \cos 2\eta^i \sin 2\theta^i - \operatorname{Re} R_{21}^0 \cos 2\eta^i \cos 2\theta^i ] \quad (7.19)$$

$$S_3^d = \cos 2\eta^i \cos 2\theta^i - (L/\hbar c) [ 2\operatorname{Re} R_{21}^0 \sin 2\eta^i + 2g_m R_{21}^0 \cos 2\eta^i \sin 2\theta^i ] . \quad (7.20)$$

The density operator (7.15) reduces here to

$$\rho^d = \rho^i - (iL/\hbar c) [ R^0, \rho^i ] , \quad (7.21)$$

with elements

$$\rho_{\sigma\tau}^d = \rho_{\sigma\tau}^i - (iL/\hbar c) \sum_{\lambda} (R_{\sigma\lambda}^0 \rho_{\lambda\tau}^i - \rho_{\sigma\lambda}^i R_{\lambda\tau}^{0*}) . \quad (7.22)$$

It is convenient to write the diagonal elements as

$$\rho_{\sigma\sigma}^d = \rho_{\sigma\sigma}^i + (2L/\hbar c) \sum_{\lambda} g_m R_{\sigma\lambda}^0 \rho_{\lambda\sigma}^i . \quad (7.23)$$

Using either the Stokes parameters or density matrix, one can deduce that

$$\sin 2\gamma^d = \sin 2\gamma^i + (L/4\pi) [ \operatorname{Re}(R_{22}^0 - R_{11}^0) \cos 2\gamma^i \sin 2\theta^i + 2 \operatorname{Re} R_{21}^0 \cos 2\gamma^i \cos 2\theta^i ] \quad (7.24)$$

$$\begin{aligned} \tan 2\theta^d = & \left\{ \sin 2\theta^i + (L/4\pi) [ \operatorname{Re}(R_{11}^0 - R_{22}^0) \tan 2\gamma^i + 2 \operatorname{Im} R_{21}^0 \cos 2\theta^i ] \right\} \\ & \times \left\{ \cos 2\theta^i - (2L/4\pi) [ \operatorname{Re} R_{21}^0 \tan 2\gamma^i + \operatorname{Im} R_{21}^0 \sin 2\theta^i ] \right\}^{-1}. \end{aligned} \quad (7.25)$$

It will be seen in Section 7.6 that the associated polarization changes are infinitesimal. Then

$$\left. \begin{aligned} \sin 2\gamma^d - \sin 2\gamma^i & \sim \delta\gamma \cdot 2 \cos 2\gamma^i \\ \tan 2\theta^d - \tan 2\theta^i & \sim 2 \delta\theta / \cos^2 2\theta^i \end{aligned} \right\} \quad (7.26)$$

so that, after some manipulation, the infinitesimal polarization changes can be extracted from (7.24) and (7.25) as

$$\delta\gamma = (L/2\pi) [ 2 \operatorname{Re} R_{21}^0 \cos 2\theta^i + \operatorname{Re}(R_{22}^0 - R_{11}^0) \sin 2\theta^i ] \quad (7.27)$$

$$\begin{aligned} \delta\theta = (L/2\pi) [ & 2 \operatorname{Im} R_{21}^0 + 2 \operatorname{Re} R_{21}^0 \tan 2\gamma^i \sin 2\theta^i \\ & + \operatorname{Re}(R_{11}^0 - R_{22}^0) \tan 2\gamma^i \cos 2\theta^i ]. \end{aligned} \quad (7.28)$$

These equations immediately reduce to those obtained in the special circumstances investigated in [31 to 34]. Consider first an optically inactive molecule. Electric dipole transitions only are involved because a symmetric molecule cannot support a process involving interference between electric and magnetic

dipole interactions, so the imaginary R-matrix elements will vanish if the molecular wave functions are chosen to be real. Equation (7.27) then reproduces (7) of [32] under the conditions specified there, namely an initial azimuth of zero:

$$\delta\eta = (L/\hbar c) \operatorname{Re} R_{21}^0. \quad (7.29)$$

Notice that the ellipticity changes are independent of the ellipticity of the incident beam. Similarly, (7.28) reduces to (58) of [32] for the first order contribution to the ellipticity-dependent angle of rotation for an optically inactive molecule when the initial azimuth is  $\pi/4$ :

$$\delta\theta = (L/\hbar c) \operatorname{Re} R_{21}^0 \tan 2\eta^i. \quad (7.30)$$

If the molecule is optically active, or has an asymmetry imposed by an externally applied field (for example, an axial magnetic field in the Faraday effect), then imaginary R-matrix elements can exist even in the absence of absorption due to the presence of a static or optical magnetic dipole interaction. Equation (7.28) shows that the angle of rotation in this situation will be

$$\delta\theta = (L/\hbar c) \operatorname{Im} R_{21}^0, \quad (7.31)$$

a result that is independent of both the ellipticity and the azimuth of the incident beam. This agrees with (40) of [31] and (16) of [33].

## 7.5. FORWARD SCATTERING WITH ABSORPTION

In the case of absorptive forward scattering,  $R^o$  is no longer Hermitian so the matrix elements of the anti-Hermitian operator  $\delta R^o = R^o - R^{o\dagger}$  are retained in (7.14). Using the same procedure as above, we can derive the following expressions for the polarization parameters of the forward scattered beam:

$$\sin 2\eta^d = \sin 2\eta^i - (L/2\pi c) \left\{ \delta R_{12}^o + \delta R_{21}^o - 2(R_{12}^o + R_{21}^o) + (\delta R_{12}^o - \delta R_{21}^o) \cos^2 2\eta^i + i(\delta R_{11}^o - \delta R_{22}^o) \cos 2\eta^i \sin 2\eta^i \right\} \quad (7.32)$$

$$\tan 2\theta^d = \left\{ (iL/2\pi c) [ (R_{12}^o + R_{12}^{o\dagger} - R_{21}^o - R_{21}^{o\dagger}) \cos 2\eta^i - \delta R_{21}^o + \delta R_{12}^o + (R_{22}^o + R_{22}^{o\dagger} - R_{11}^o - R_{11}^{o\dagger}) \sin 2\eta^i ] \right\} \\ \times \left\{ \cos 2\eta^i + (L/2\pi c) [ \delta R_{22}^o - \delta R_{11}^o - i(\delta R_{11}^o + \delta R_{22}^o) \cos 2\eta^i + (\delta R_{12}^o - \delta R_{21}^o) \sin 2\eta^i + 2(R_{12}^o + R_{21}^{o\dagger}) \sin 2\eta^i ] \right\}^{-1} \quad (7.33)$$

In obtaining these equations we have, for simplicity, chosen an initial azimuth  $\theta^i$  of zero.

Equations (7.29) and (7.30) reduce to more familiar expressions in specific physical situations. Thus if the molecule is optically active, (7.32) becomes

$$\delta \eta = (L/\pi c) \operatorname{Re} R_{21}^o \quad (7.34)$$

which is the same as (47) of [31] describing the phenomenon of circular dichroism. For an optically inactive molecule, (7.33) reduces to

$$\delta \theta = (L/\pi c) \operatorname{Im} R_{21}^o, \quad (7.35)$$

which represents the angle of rotation due to linear dichroism. A more familiar form of (7.35) is obtained by specifying an initial azimuth of  $\pi/4$  rather than zero. Then

$$\delta\theta = (L/2\hbar c) g_m (R_{zz}^o - R_{ii}^o). \quad (7.36)$$

No further discussion of birefringent scattering in the presence of absorption will be presented in this work.

## 7.6. THE SPINOR TRANSFORMATION DESCRIPTION OF BIREFRINGENCE

It was seen in Chapter 7 that the transformation of the first rank photon polarization spinor  $|\pi\rangle$  in a birefringent scattering event is effected by the operator (7.8), that is

$$|\pi^d\rangle = [1 - (iL/\hbar c) R^o] |\pi^i\rangle. \quad (7.37)$$

By writing

$$[1 - (iL/\hbar c) R^o] [1 - (iL/\hbar c) R^o]^\dagger = 1 + (L/\hbar c)(R^{o\dagger} - R^o) + (L/\hbar c)^2 R^o R^{o\dagger} \quad (7.38)$$

we see that when  $R^o$  is Hermitian, corresponding to the absence of absorption and neglect of nonforward scattering, and the term  $(L/\hbar c)^2 R^o R^{o\dagger}$  is neglected, (7.37) represents an infinitesimal unitary transformation generated by  $(L/\hbar c) R^o$ . Equation (7.15) describing the transformation of the density operator  $\rho$ , which is the second rank spinor equivalent of  $|\pi\rangle$ , now reduces to

$$\rho^d = \rho^i - (iL/\hbar c) [R^o, \rho^i] \sim e^{-(iL/\hbar c) R^o} \rho^i e^{(iL/\hbar c) R^o} \quad (7.39)$$

in which the infinitesimal unitary nature of the transformation is displayed explicitly.

In view of the equivalence of the second rank polarization spinor to a real polarization vector in the three dimensional Poincaré space (Section 1.6), we see that the infinitesimal transformations of the density operator are equivalent to infinitesimal rotations of the Poincaré sphere. Any polarization condition of the forward scattered beam may be reached from any polarization condition of the incident beam by suitable infinitesimal rotations of the sphere; indeed calculations in crystal optics can be performed using just such a technique [13].

If in a particular experiment both  $\Theta$  and  $\eta$  are changing simultaneously so that changes in one may affect the other, the Poincaré sphere executes some general rotation around all three Euler angles, and calculations of the net polarization changes become very complicated. Fortunately, most molecular optics experiments are arranged so that only one polarization parameter is changing. Thus in the Kerr effect the azimuth remains constant as the ellipticity changes, and in an optical activity experiment the azimuth changes with the ellipticity remaining constant (but notice that even if the ellipticity is simultaneously changing through circular dichroism, (7.28) predicts that this will not affect the angle of rotation because the latter is independent of the incident ellipticity).

The treatment so far has been concerned with the scattering

of photons by a single molecule located anywhere within the sample volume. If there are  $N$  molecules distributed within the volume, the infinitesimal transformation must be applied  $N$  times. An average molecular density might be about  $10^{20}$  per cubic centimetre, so a finite transformation could be generated. We must therefore generate finite rotations of the Poincaré sphere from the infinitesimal changes given in (7.27) and (7.28). Thus in an experiment such as the Kerr effect where ellipticity changes are not accompanied by azimuth changes, we obtain for the finite ellipticity change

$$\Delta\eta = (NL/\pi c) [2\operatorname{Re} R_{21}^0 \cos 2\theta^i + \operatorname{Re} (R_{22}^0 - R_{11}^0) \sin 2\theta^i]. \quad (7.40)$$

The second and third terms in Equation (7.28) for the infinitesimal angle of rotation are dependent on the initial azimuth, and this will be changing at each subsequent scattering event. Therefore we cannot build up a finite rotation simply by multiplying by  $N$ . However the first term is independent of the initial polarization parameters, so in phenomena where just this term contributes, such as natural optical activity and the Faraday effect, the finite angle of rotation is simply

$$\Delta\theta = (NL/\pi c) g_m R_{21}^0. \quad (7.41)$$

## 7.7. THE CONNEXION BETWEEN THE S-MATRIX AND THE SEMI-CLASSICAL THEORIES OF OPTICAL BIREFRINGENCE

It is interesting to speculate on the relationship between the S-matrix formulation of birefringence and the classical description. We recall that the classical picture considers the net effect of the spherical wavelets scattered from a plane of molecules (see [37], Chapter 15). The wavelength of the light must be long compared to the interparticle distance. The phase of each scattered wavelet is retarded by  $\pi$  relative to the transmitted beam, but since the net plane wave front of the wavelets scattered from molecules in a single plane is advanced by  $\pi/2$  relative to each constituent wavelet, the resultant plane wave front is now  $\pi/2$  retarded relative to the transmitted wave.

In addition to describing refraction, this retardation accounts for the ellipticity imposed by birefringent materials on a plane polarized wave; the net plane wave of the scattered wavelets with plane polarized components orthogonal to the transmitted beam will be  $\pi/2$  out of phase with the latter, thereby producing an elliptically polarized resultant (Figure 7.1).

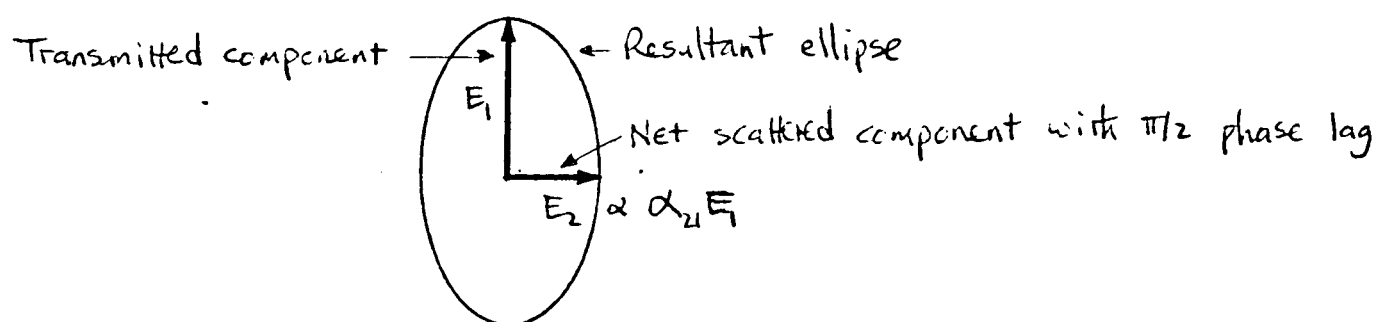


Figure 7.1. The origin of the ellipticity imposed by birefringent materials.

Optical rotation arises because the scattered component that is plane polarized at right angles to the incident polarization is produced by a magnetic field-induced oscillating electric dipole moment: this scattered component will therefore be  $3\pi/2$  phase retarded in relation to the transmitted beam. The net plane wave front from these wavelets will now lag the transmitted component by  $\pi$ , so the resultant is a plane polarized beam with the plane of polarization rotated relative to the incident beam (Figure 7.2).

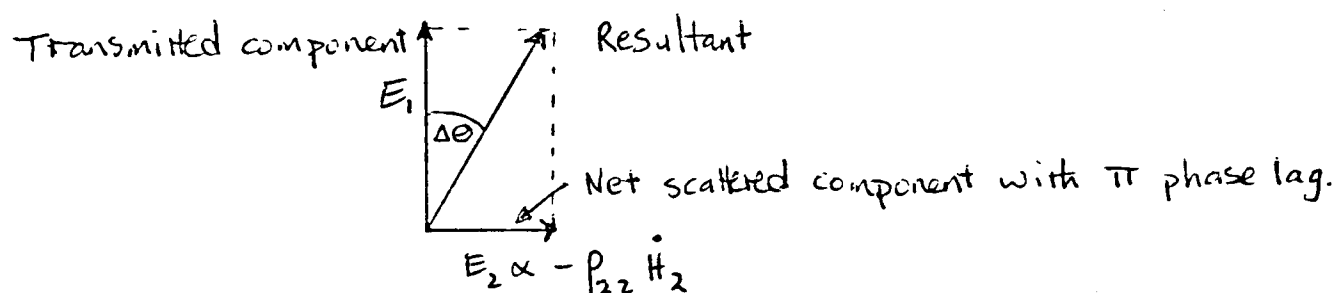


Figure 7.2. The origin of optical rotation.

The S-matrix description considered the scattering of a single plane wave photon by a single molecule. The phase difference would therefore appear to be  $\pi/2$  too large to produce the correct polarization changes; for there are no other spherical scattered waves to produce a net scattered wavefront with the correct phase. So at first sight the scattering from a single molecule seems to predict an ellipticity when there should be a rotation, and vice-versa.

Classical calculations of the light wave emergent from the sample volume in the forward direction are usually based on

either the short wavelength approximation ([7],p.24) or the long wavelength approximation ([37],p.600); the two simply provide different ways of replacing the sum over all scatterers by an integral over a continuous distribution. We, however, are concerned with the forward part of the state vector of a photon scattered from a single molecule located somewhere within the sample volume which, if not too small, may be taken as the quantization volume  $V$ . Observations are made on the asymptotic input and output photon wave, but no knowledge is available of the precise location of the molecule in space and time when the scattering event occurs. The lack of knowledge as to the time provides a justification for using the orientational average of a single molecule, whereas the lack of knowledge as to the location implies that a sum is required of all the amplitudes for all possible paths that the photon may take between the initial and the final observations (this is in accordance with the Feynman path integral philosophy [38]). Consequently the final photon state vector must contain a sum of components corresponding to wavelets scattered from all possible positions of the molecule, each component being weighted according to the probability of finding the molecule at the appropriate point. In a fluid medium there is the same probability  $1/V$  of finding the molecule at any point within  $V$  and so, in a quantum mechanical sense, we are dealing with a truly continuous distribution of scattering centres.

When the three-dimensional sum over all photon modes (1.39) is used in the S-matrix decomposition (7.4), one obtains

$$|\psi^f\rangle = e^{i\mathbf{k}^i \cdot \mathbf{r}} - 2\pi i \frac{V}{(2\pi)^3} \int d^3\mathbf{k} \delta(E_f - E_i) e^{i\mathbf{k}^f \cdot \mathbf{r}} R_{fi}. \quad (7.42)$$

If the element  $d^3\mathbf{k}$  corresponds to light scattered into a cone of solid angle  $d\Omega = \sin\theta d\theta d\phi$ , then

$$d^3\mathbf{k} = k^2 dk d\Omega = (k^2/\hbar c) d\Omega dE, \quad (7.43)$$

so that

$$\begin{aligned} \int d^3\mathbf{k} \delta(E_f - E_i) e^{i\mathbf{k}^f \cdot \mathbf{r}} &= (1/\hbar c) \int k^2 d\Omega e^{i\mathbf{k}^f \cdot \mathbf{r}} \\ &= (k^2/\hbar c) \int_0^{2\pi} \int_0^\pi e^{ikr \cos\theta} \sin\theta d\theta d\phi \\ &= (k^2/\hbar c) \int_{-1}^1 d(\cos\theta) e^{ikr \cos\theta} \int_0^{2\pi} d\phi \\ &= (k^2/\hbar c) (2\pi/ikr) [e^{ikr} - e^{-ikr}]. \end{aligned} \quad (7.44)$$

This corresponds to a superposition of incoming and outgoing spherical waves. The asymptotic solution at  $r \rightarrow \infty$  contains just the outgoing wave, so (7.42) becomes

$$|\psi^f\rangle = e^{i\mathbf{k}^f \cdot \mathbf{r}} - \left( \frac{kV}{2\pi\hbar c} \right) \frac{e^{ikr}}{r} R_{fi}. \quad (7.45)$$

The component received at  $P(0,0,z)$  from scattering centres  $Q(x,y,0)$  continuously distributed in an infinitely thin slice at right angles to the propagation direction will now be evaluated.

Assume the dimensions of the slice are small relative to its distance from P (Figure 7.3) so that

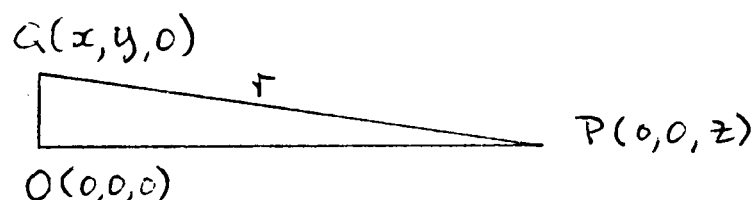


Figure 7.3.

$$r = [z^2 + (x^2 + y^2)]^{1/2} \sim z + (1/2z)(x^2 + y^2). \quad (7.46)$$

The probability of finding the molecule in an infinitesimal volume element in the slice is  $dx dy dz/V$ , so (7.45) gives the component at P as

$$\langle \psi^P \rangle = \left\{ 1 - (k dz / 2\pi \hbar c z) \int dx dy e^{ik(x^2+y^2)/2z} R_{ii} \right\} |k^i\rangle \quad (7.47)$$

where the restriction (7.46) has allowed us to replace  $R_{fi}$  by  $R_{ii}$  since only forward or near forward scattered components are detected at P. If the dimensions of the plane are large enough so that on its edge  $k(x^2+y^2)/z \gg 2\pi$ , but still sufficiently small that  $x^2+y^2 \ll z^2$ , the integral over the plane may be extended to infinity with negligible error. It then becomes Gauss's integral, where

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (1/z) e^{ik(x^2+y^2)/2z} dx dy = 2\pi i/k, \quad (7.48)$$

and so

$$|\psi^p\rangle = [1 - (idz/\hbar c) R_{ii}] |k^i\rangle. \quad (7.49)$$

There will be a contribution to the final wave from each plane within the sample length  $L$ , and since no phase difference occurs in the forward direction by moving a plane along  $Oz$ , summation over the entire sample volume yields

$$|\psi^p\rangle = [1 - (iL/\hbar c) R_{ii}] |k^i\rangle, \quad (7.50)$$

provided the scattered wave is very much smaller than the transmitted wave.

This expression is the same as (7.6), which was obtained intuitively by replacing the sum over all final modes by a one-dimensional sum corresponding to final modes precisely in the forward direction.

## 8

# FORWARD SCATTERING OF A BEAM OF PHOTONS

## 8.1. THE MASTER EQUATIONS FOR MULTIPHOTON BIREFRINGENT SCATTERING

In view of the discussion in Section 6.2, the master equations obtained in Section 7.1 for the forward scattering of a single photon can be adapted at once to the scattering of an n-photon beam; the single photon state vectors and density operators are simply replaced by their n-photon equivalents. Using (3.10), therefore, the state vector of the detected beam becomes, in place of (7.9),

$$\begin{aligned}
 |\psi^d\rangle &= \sum_{r=0}^n [\hat{r}] b_1^{n-r} b_2^r |k_1[n-r] k_2[r]\rangle - \\
 (iL/\hbar c) \sum_{r,r'=0}^n [\hat{r}] b_1^{n-r} b_2^r |k_1[n-r] k_2[r]\rangle &\langle g; k_1[n-r] k_2[r'] | R | g; k_1[n-r] k_2[r]\rangle
 \end{aligned}
 \tag{8.1}$$

whereas the density matrix (7.14) becomes, using (3.15),

$$\begin{aligned}
 \rho_{rr'}^d &= \rho_{rr'}^i - (iL/\hbar c) \sum_{s=0}^n (R_{rs}^0 \rho_{sr'}^i - \rho_{rs}^i R_{sr'}^{0+}) \\
 &\quad + (iL/\hbar c) \rho_{rr'}^i \sum_{s,s'=0}^n (R_{s's}^0 - R_{s's}^{0+}) \rho_{ss'}^i.
 \end{aligned}
 \tag{8.2}$$

where

$$R_{r',r}^0 = \langle g; k_1[n-r] k_2[r] | R | g; k_1[n-r] k_2[r] \rangle \quad (8.3)$$

The polarization parameters of the beam may be evaluated by taking expectation values of the Stokes operators with the state (8.1) using the methods of Section 3.4, or extracted directly from the density matrix (8.2) using the methods of Section 3.3. The Stokes operator method was employed in [31,32,33,34], but in fact the density matrix method, used in [39], is the most succinct for calculating the polarization of the forward scattered n-photon beam, and will be used here.

## 8.2. THE DENSITY MATRIX OF THE FORWARD SCATTERED BEAM

The polarization characteristics of the n-photon beam will be extracted from the density matrix (8.2) using the first method described in Section 3.3, namely by taking the n'th roots of the four corner elements.

Each R-matrix element can be expressed as a sum of contributions from single photon scattering, double photon scattering, and so on; furthermore we can use the concept of a reduced R-matrix element, denoted  $\mathcal{R}$ , from which all occupation number dependence has been removed [32]. Thus an off-diagonal polarization matrix element corresponding to the forward scattering of a single photon from the n-photon beam becomes

$$\begin{aligned}
& \langle g; \mathbf{k}_1, [n-r-1] \mathbf{k}_2, [r+1] | R(i) | g; \mathbf{k}_1, [n-r] \mathbf{k}_2, [r] \rangle \\
& \equiv [(n-r)(r+1)]^{1/2} \langle g; \mathbf{k}_1, [0] \mathbf{k}_2, [1] | R(i) | g; \mathbf{k}_1, [1] \mathbf{k}_2, [0] \rangle \\
& = [(n-r)(r+1)]^{1/2} \mathcal{R}_{21}
\end{aligned} \tag{8.4}$$

where  $\mathcal{R}_{21}$  is the same as the single photon R-matrix elements used in Chapter 7. With reduced R-matrix elements that describe the scattering of a photon back into the same mode with the same polarization, the two contributions corresponding to the different chronological orderings of the emission and absorption vertices have different photon number coefficients. For example, using the results of Chapter 5,

$$\begin{aligned}
& \langle g; \mathbf{k}_1, [n-r] \mathbf{k}_2, [r] | R(i) | g; \mathbf{k}_1, [n-r] \mathbf{k}_2, [r] \rangle \equiv \\
& \left( \frac{2\pi\hbar\omega}{V} \right) \sum_{m'} \left\{ (n-r) \frac{\langle m | \mathbf{d} \cdot \boldsymbol{\epsilon}_1 | m' \rangle \langle m' | \mathbf{d} \cdot \boldsymbol{\epsilon}_1 | m \rangle}{E_{mm'} + \hbar\omega} + (n-r+1) \frac{\langle n | \mathbf{d} \cdot \boldsymbol{\epsilon}_1 | m' \rangle \langle m' | \mathbf{d} \cdot \boldsymbol{\epsilon}_1 | m \rangle}{E_{mm'} - \hbar\omega} \right\}
\end{aligned} \tag{8.5}$$

If, however, the beam contains a large number of photons,  $n \pm 1$  can be replaced by  $n$ , thereby removing the ambiguity. Consequently one could not talk about the refractive index of a medium as revealed from the scattering of a single photon: it is necessary to discuss the scattering of a photon from a beam of many. But it appears from (8.4) that the scattering of a single photon involving polarization flip is meaningful because the photon number coefficients are the same for the two chronological orderings since the initial and final photon states are distinguishable.

Consider the density matrix element  $\rho_{co}^d$ . From (8.2) we have, when R is Hermitian,

$$\rho_{co}^d = \rho_{co}^i + (2L/\hbar c) \sum_{s=0}^n g_m R_{os}^0 \rho_{so}^i \quad (8.6)$$

The prescribed R-matrix elements can now be written in terms of reduced R-matrix elements:

$$R_{oo}^0 = \langle g; k_1[n] k_2[0] | R | g; k_1[n] k_2[0] \rangle \equiv n R_{11} + n^2 R_{11,11} + \dots \quad (8.7a)$$

$$R_{o1}^0 = \langle g; k_1[n] k_2[0] | R | g; k_1[n-1] k_2[1] \rangle \equiv n^{1/2} R_{12} + n^{3/2} R_{11,12} + \dots \quad (8.7b)$$

$$R_{o2}^0 = \langle g; k_1[n] k_2[0] | R | g; k_1[n-2] k_2[2] \rangle \equiv 2^{1/2} n R_{11,22} + \dots \quad (8.7c)$$

-----

Terms beyond  $R_{o2}^0$  are extremely small and may be neglected. The  $n^{\text{th}}$  root of (8.6) is

$$(\rho_{co}^d)^{1/n} = (\rho_{co}^i)^{1/n} + \frac{1}{n} (\rho_{co}^i)^{1/n-1} \left( \frac{2L}{\hbar c} \right) \sum_{s=0}^n g_m R_{os}^0 \rho_{so}^i + \dots \quad (8.8)$$

which becomes, with the help of (8.7) and (3.17),

$$\begin{aligned} b_1^d b_1^{d*} = & b_1^i b_1^{i*} + (2L/\hbar c) g_m \{ b_1^i b_1^{i*} [R_{11} + n R_{11,11}] \\ & + b_2^i b_1^{i*} [R_{12} + n R_{11,12}] + n (b_2^{i2} b_1^{i*} / b_1^i) R_{11,22} + \dots \} \end{aligned} \quad (8.9)$$

The other diagonal element is

$$(\rho_{nn}^d)^{1/n} = (\rho_{nn}^i)^{1/n} + \frac{1}{n} (\rho_{nn}^i)^{1/n-1} \left( \frac{2L}{\hbar c} \right) \sum_{s=0}^n g_m R_{ns}^0 \rho_{sn}^i \quad (8.10)$$

where

$$R_{nn}^0 = \langle g; \mathbf{k}_1[0] \mathbf{k}_2[n] | R | g; \mathbf{k}_1[0] \mathbf{k}_2[n] \rangle \equiv n R_{22} + n^2 R_{22,22} + \dots \quad (8.11a)$$

$$R_{n(n-1)}^0 = \langle g; \mathbf{k}_1[0] \mathbf{k}_2[n] | R | g; \mathbf{k}_1[1] \mathbf{k}_2[n-1] \rangle \equiv n^{1/2} R_{21} + n^{3/2} R_{22,21} + \dots \quad (8.11b)$$

$$R_{n(n-2)}^0 = \langle g; \mathbf{k}_1[0] \mathbf{k}_2[n] | R | g; \mathbf{k}_1[2] \mathbf{k}_2[n-2] \rangle \equiv 2^{1/2} n R_{22,11} + \dots \quad (8.11c)$$

-----

Therefore (8.10) becomes

$$\begin{aligned} b_2^d b_2^{d*} = & b_2^i b_2^{i*} + (2L/\hbar c) \mathcal{J}_m \left\{ b_2^i b_2^{i*} [R_{22} + n R_{22,22}] \right. \\ & \left. + b_1^i b_2^{i*} [R_{21} + n R_{22,21}] + n (b_1^i b_2^{i*} / b_2^i) R_{22,11} + \dots \right\} \end{aligned} \quad (8.12)$$

The relevant off-diagonal matrix elements may be obtained in like fashion. Thus from (8.2)

$$\begin{aligned} p_{no}^d &= p_{no}^i - (iL/\hbar c) \sum_{s=0}^n (R_{ns}^0 p_{so}^i - p_{ns}^i R_{so}^{0*}) \\ &= p_{no}^i - (iL/\hbar c) \sum_{s=0}^n (R_{ns}^0 p_{so}^i - R_{os}^{0*} p_{sn}^{i*}) \end{aligned} \quad (8.13)$$

Taking the  $n^{\text{th}}$  root yields

$$(p_{no}^d)^{1/n} = (p_{no}^i)^{1/n} - \frac{1}{n} (p_{no}^i)^{1/n-1} \left( \frac{iL}{\hbar c} \right) \sum_{s=0}^n (R_{ns}^0 p_{so}^i - R_{os}^{0*} p_{sn}^{i*}) + \dots \quad (8.14)$$

From (8.7), (8.11), and (3.17) we then have

$$b_2^d b_1^{d*} = b_2^i b_1^{i*} - (iL/\hbar c) \left\{ b_2^i b_1^{i*} (R_{22} + n R_{22,22}) + \right.$$

$$\begin{aligned}
& + b_i^i b_i^{i*} (R_{21} + n R_{22,21}) + n (b_i^{i2} b_i^{i*} / b_i^i) R_{22,11} + \dots \\
& - b_i^i b_i^{i*} (R_{11}^* + n R_{11,11}^*) - b_i^i b_i^{i*} (R_{12} + n R_{11,12}^*) - n (b_i^i b_i^{i*2} / b_i^{i*}) R_{11,22}^* + \dots \}
\end{aligned} \tag{8.15}$$

Since both  $\rho$  and  $\mathcal{R}$  are Hermitian, the real and imaginary parts of (8.15) can be written

$$\begin{aligned}
\text{Re } b_i^d b_i^{d*} &= \text{Re } b_i^i b_i^{i*} + (L/\hbar c) \mathcal{I}_m \{ b_i^i b_i^{i*} (R_{22} + n R_{22,22}) \\
& + b_i^i b_i^{i*} (R_{21} + n R_{22,21}) + n (b_i^{i2} b_i^{i*} / b_i^i) R_{22,11} + \dots \\
& + b_i^i b_i^{i*} (R_{11} + n R_{11,11}) + b_i^i b_i^{i*} (R_{12} + n R_{11,12}) \\
& + n (b_i^{i2} b_i^{i*} / b_i^i) R_{11,22} + \dots \}
\end{aligned} \tag{8.16}$$

$$\begin{aligned}
\mathcal{I}_m b_i^d b_i^{d*} &= \mathcal{I}_m b_i^i b_i^{i*} - (L/\hbar c) \text{Re} \{ b_i^i b_i^{i*} (R_{22} + n R_{22,22}) \\
& + b_i^i b_i^{i*} (R_{21} + n R_{22,21}) + n (b_i^{i2} b_i^{i*} / b_i^i) R_{22,11} + \dots \\
& - b_i^i b_i^{i*} (R_{11} + n R_{11,11}) - b_i^i b_i^{i*} (R_{12} + n R_{11,12}) \\
& - n (b_i^{i2} b_i^{i*} / b_i^i) R_{11,22} + \dots \} .
\end{aligned} \tag{8.17}$$

The polarization of the forward scattered beam may be extracted from (8.12), (8.15), (8.16), and (8.17) in the usual manner. Many terms are zero due to the Hermiticity of  $\mathcal{R}$ . The ellipticity is found to be

$$\begin{aligned}
\sin 2\eta^d = & \sin 2\eta^i + (L/tc) \left\{ [\operatorname{Re}(R_{22} - R_{11}) + n \operatorname{Re}(R_{22,22} - R_{11,11})] \cos 2\eta^i \sin 2\theta^i \right. \\
& + 2(\operatorname{Re} R_{21} + n \operatorname{Re} R_{21,11}) \cos 2\eta^i \cos 2\theta^i + (1 - \cos^2 2\eta^i \cos^2 2\theta^i)^{-1} \times \\
& \left. 4n(\operatorname{Re} R_{22,11} \cos^2 2\eta^i - \operatorname{Im} R_{22,11} \sin 2\eta^i \cos 2\eta^i) \cos 2\theta^i \right\} \quad (8.18)
\end{aligned}$$

corresponding to the infinitesimal ellipticity change

$$\begin{aligned}
\delta\eta = & (L/2tc) \left\{ [\operatorname{Re}(R_{22} - R_{11}) + n \operatorname{Re}(R_{22,22} - R_{11,11})] \sin 2\theta^i \right. \\
& + 2(\operatorname{Re} R_{21} + n \operatorname{Re} R_{21,11}) \cos 2\theta^i + (1 - \cos^2 2\eta^i \cos^2 2\theta^i)^{-1} \times \\
& \left. 4n(\operatorname{Re} R_{22,11} \cos 2\eta^i \sin 2\theta^i - \operatorname{Im} R_{22,11} \sin 2\eta^i) \cos 2\theta^i \right\}. \quad (8.19)
\end{aligned}$$

The azimuth is given by

$$\begin{aligned}
\tan 2\theta^i = & \left[ \sin 2\theta^i + (L/tc) \left\{ [\operatorname{Re}(R_{11} - R_{22}) + n \operatorname{Re}(R_{11,11} - R_{22,22})] \tan 2\eta^i \right. \right. \\
& + 2(\operatorname{Im} R_{21} + n \operatorname{Im} R_{21,11}) \cos 2\theta^i + (1 - \cos^2 2\eta^i \cos^2 2\theta^i)^{-1} \times \\
& \left. \left. 4n(\operatorname{Im} R_{22,11} \cos 2\eta^i \sin 2\theta^i + \operatorname{Re} R_{22,11} \sin 2\eta^i) \cos 2\theta^i \right\} \right] \\
& \times \left[ \cos 2\theta^i - (2L/tc) \left\{ (\operatorname{Im} R_{21} + n \operatorname{Im} R_{21,11}) \sin 2\theta^i \right. \right. \\
& + (\operatorname{Re} R_{21} + n \operatorname{Re} R_{21,11}) \tan 2\eta^i + (1 - \cos^2 2\eta^i \cos^2 2\theta^i)^{-1} \times \\
& \left. \left. n \operatorname{Im} R_{22,11} (\cos 2\eta^i \sin^2 2\theta^i - \tan 2\eta^i \sin 2\eta^i) + 2n \operatorname{Re} R_{22,11} \sin 2\eta^i \sin 2\theta^i \right\} \right]^{-1} \quad (8.20)
\end{aligned}$$

with the corresponding infinitesimal angle of rotation

$$\begin{aligned}
\delta\theta = (L/2\pi c) \bigg\{ & [\text{Re}(R_{11} - R_{22}) + n \text{Re}(R_{11,11} - R_{22,22})] \cos 2\theta^i \tan 2\eta^i \\
& + 2(\text{Im} R_{21} + n \text{Im} R_{21,11}) + 2(\text{Re} R_{21} + n \text{Re} R_{21,11}) \tan 2\eta^i \sin 2\theta^i \\
& + 2n(1 - \cos^2 2\eta^i \cos^2 2\theta^i)^{-1} [2 \text{Re} R_{22,11} \sin 2\eta^i (\cos^2 2\theta^i + \sin^2 2\theta^i) \\
& + \text{Im} R_{22,11} (2 \cos^2 2\theta^i \cos 2\eta^i \sin 2\theta^i + \cos 2\eta^i \sin^3 2\theta^i - \tan 2\eta^i \sin 2\eta^i \sin 2\theta^i)] \bigg\}
\end{aligned}
\tag{8.21}$$

Notice that the linear parts of (8.19) and (8.21) agree with the single-photon scattering equations (7.27) and (7.28).

It was seen in Section 3.3 that an alternative method for extracting the polarization parameters from the n-photon density matrix is to take the trace of the density operator over all but one photon. This method has in fact been used in [39], and provides the same equations as (8.19) and (8.21) for the polarization changes of the forward scattered n-photon beam.

### 8.3. THE APPLICATION TO BIREFRINGENCE PHENOMENA

The observables in optical birefringence experiments are the changes in azimuth and ellipticity of the forward scattered light beam. The corresponding infinitesimal changes are given by (8.21) and (8.23). These complicated equations are simplified considerably for phenomena in which the infinitesimal polarization changes are independent of the initial polarization so that, as discussed in Section 7.6, the finite changes may be generated simply by multiplying by the number N of molecules in

the sample volume, with the initial polarization parameters selected arbitrarily.

The contribution of the various R-matrix elements in (8.19) and (8.21) depends on the phenomenon under investigation. For example, the real R-matrix elements must contain electric dipole interactions, electric quadrupole interactions, an even number of magnetic dipole interactions, or some combination of these three possibilities only. The imaginary R-matrix elements must contain an odd number of magnetic dipole interactions with or without electric quadrupole interactions; however terms containing more than one magnetic dipole or electric quadrupole interaction may be neglected because they will be very small. These statements must be qualified if the presence of degenerate molecular states is admitted, for then the molecular states can be complex. In what follows it is assumed that such degeneracy is absent unless otherwise indicated.

In fact the contribution to birefringent scattering of terms containing an electric quadrupole interaction can be neglected. This is because such terms provide non-zero spatial averages in just the same situations as terms containing electric dipole interactions only, and since the former terms will be about  $10^3$  smaller than the latter, they will be undetectable. It is, however, possible to isolate a measurable contribution from electric quadrupole interactions by using an inhomogeneous electric field [40], but this feature will not be discussed here.

In the case of a solid, the contributions of the various terms depend, in addition to the nature of the individual molecules, on the symmetry properties of the medium. But we shall confine our attention to the scattering of light from molecules in dilute gases or liquids only, so the orientational averages of the specified R-matrix elements must be taken. The tensor averages we shall require are listed in the Appendix.

In the presence of electric or magnetic fields the ensemble of molecules is not distributed uniformly, and a statistical average must be taken. For our purposes the classical Boltzmann average for a system in thermodynamic equilibrium at the temperature  $T$  is adequate:

$$\begin{aligned} \overline{A(\Omega)} &= \frac{\int d\Omega A(\Omega) e^{-U(\Omega)/kT}}{\int d\Omega e^{-U(\Omega)/kT}} \\ &= \langle A(\Omega) \rangle + (1/kT) [\langle A(\Omega) \rangle \langle U(\Omega) \rangle - \langle A(\Omega) U(\Omega) \rangle] + \\ &\quad (1/k^2 T^2) \left[ \frac{1}{2} \langle A(\Omega) U(\Omega)^2 \rangle - \frac{1}{2} \langle A(\Omega) \rangle \langle U(\Omega)^2 \rangle - \langle A(\Omega) U(\Omega) \rangle \langle U(\Omega) \rangle \right] + \dots \end{aligned} \quad (8.22)$$

where  $U(\Omega)$  is the interaction energy between the molecule at the orientation  $\Omega$  and the field, and  $\langle A(\Omega) \rangle$  is the isotropic spatial average of the quantity  $A$ . The use of a classical statistical average rather than its quantum mechanical equivalent means that our results will be valid only for liquid samples in which free rotation is quenched. Also the effect of molecular relaxation on the statistical averaging will not be discussed.

An expression for the potential energy  $U(\Omega)$  is required. The molecular dipole moment  $\mathbf{d}$  in the presence of a field  $\mathbf{F}$  may be written as a Taylor expansion about the value when  $\mathbf{F}$  is zero:

$$\begin{aligned} \mathbf{d}(\mathbf{F}) &= \boldsymbol{\mu} + \left( \frac{\partial \mathbf{d}(\mathbf{F})}{\partial \mathbf{F}} \right) \cdot \mathbf{F} + \frac{1}{2} \left( \frac{\partial^2 \mathbf{d}(\mathbf{F})}{\partial \mathbf{F}^2} \right) : \mathbf{F} \mathbf{F} + \dots \\ &= \boldsymbol{\mu} + \boldsymbol{\alpha} \cdot \mathbf{F} + \frac{1}{2} \boldsymbol{\beta} : \mathbf{F} \mathbf{F} + \dots \end{aligned} \quad (8.23)$$

where  $\boldsymbol{\mu}$  is the permanent electric dipole moment,  $\boldsymbol{\alpha}$  is the polarizability tensor, and  $\boldsymbol{\beta}$  is the first hyperpolarizability tensor. For an infinitesimal change  $d\mathbf{F}$  in the field, the change in the interaction energy is

$$dU(\Omega) = -\mathbf{d} \cdot d\mathbf{F}$$

so that

$$\begin{aligned} U(\Omega) &= -\int_0^{\mathbf{F}} \mathbf{d} \cdot d\mathbf{F} \\ &= -\boldsymbol{\mu} \cdot \mathbf{F} - \frac{1}{2} \boldsymbol{\alpha} : \mathbf{F} \mathbf{F} - \frac{1}{6} \boldsymbol{\beta} : \mathbf{F} \mathbf{F} \mathbf{F} + \dots \end{aligned} \quad (8.24)$$

If a field gradient is also present, terms involving quadrupole polarizabilities must be included. Thus we see that terms in (8.19) and (8.21) which have zero spatial averages in isotropic systems may provide non-zero averages under the influence of a suitable electromagnetic field.

If the orienting field is the optical field of an intense laser beam, a time average of (8.24) is taken; furthermore the

first term then provides no contribution because the torque exerted on the permanent electric dipole moments by the optical fields varies at the optical frequency and so cannot be coupled to the much slower molecular motion. Consequently the potential energy becomes

$$U(\Omega) = -\frac{1}{2} \alpha(\omega) : \langle \mathbf{E} \mathbf{E} \rangle_t \quad (8.25)$$

where  $\langle \mathbf{E} \mathbf{E} \rangle_t$  denotes a time average. By defining a real electric field vector for a light beam of arbitrary polarization  $\pi$ ,

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) &= \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \mathbf{E}_0^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \\ &= 2 \operatorname{Re} \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \end{aligned} \quad (8.26)$$

the required time average is obtained as

$$\langle \mathbf{E} \mathbf{E} \rangle_t = 2 E_0^2 (b_1 \mathbf{e}_1 + b_2 \mathbf{e}_2)(b_1 \mathbf{e}_1 + b_2 \mathbf{e}_2)^*. \quad (8.27)$$

The potential energy is then

$$\begin{aligned} U(\Omega) &= -\frac{1}{2} E_0^2 \alpha : [(\mathbf{e}_1 \mathbf{e}_1 + \mathbf{e}_2 \mathbf{e}_2) + (\mathbf{e}_1 \mathbf{e}_1 - \mathbf{e}_2 \mathbf{e}_2) \cos 2\eta \cos 2\Theta \\ &\quad + (\mathbf{e}_1 \mathbf{e}_2 + \mathbf{e}_2 \mathbf{e}_1) \cos 2\eta \sin 2\Theta + i(\mathbf{e}_1 \mathbf{e}_2 - \mathbf{e}_2 \mathbf{e}_1) \sin 2\eta] \end{aligned} \quad (8.28)$$

It is interesting that the same expression for the potential energy (8.28) is obtained if the interaction responsible for the optical orientation is regarded as brought about through the scattering of a photon that has the same wave vector  $\mathbf{q}$  and polarization  $\pi$  as the orienting field, that is we make the

identification

$$U(\Omega) \equiv -\text{Re } R_{\pi\pi} \quad (8.29)$$

The appropriate diagrams are shown in Figure 8.1, corresponding

$$\text{Diagram 1} + \text{Diagram 2} \equiv \text{Re } R_{\pi\pi}$$

Figure 8.1. Diagrams representing optical orientation.

to the R-matrix element

$$\begin{aligned} R_{\pi\pi} &= \left( \frac{2\pi n \hbar \omega}{V} \right) \sum_{\lambda, \lambda'} b_{\lambda} b_{\lambda'}^* \sum_m \left\{ \frac{d_{gm} \cdot \epsilon_{\lambda'} d_{mg} \cdot \epsilon_{\lambda}}{E_{gm} + \hbar \omega} + \frac{d_{gm} \cdot \epsilon_{\lambda} d_{mg} \cdot \epsilon_{\lambda'}}{E_{gm} - \hbar \omega} \right\} \\ &= E_0^2 \alpha(\omega) : (b_1 \epsilon_1 + b_2 \epsilon_2) (b_1 \epsilon_1 + b_2 \epsilon_2)^* \end{aligned} \quad (8.30)$$

with the polarizability tensor  $\alpha(\omega)$  defined as

$$\alpha_{\alpha\beta}(\omega) = \sum_m \frac{2E_{gm}}{E_{gm}^2 - \hbar^2 \omega^2} d_{gm}^{\alpha} d_{mg}^{\beta} \quad (8.31)$$

and the electric field intensity identified as

$$E_0^2 = (2\pi n \hbar \omega / V) \quad (8.32)$$

(compare (8.26) with (5.35)).

It is often necessary to take account of the influence of the surrounding medium on the electromagnetic fields experienced by the molecule. For example, the Lorentz correction to

the local field enhances the electric vector by a factor  $(n^2+2)/3$ . A further complication when nonlinear effects are considered is that the refractive index is itself intensity-dependent. For simplicity, such corrections will not be made to our final formulae.

We now have an algorithm for calculating the polarization changes involved in any linear or nonlinear optical birefringence effect. It is merely a matter of using diagrammatic perturbation theory to calculate explicit expressions, in terms of molecular polarizability and optical rotation tensors, for the space-averaged R-matrix elements relevant to the phenomenon of interest.

# 9

## BIREFRINGENCE INDUCED BY STATIC AND OPTICAL ELECTRIC FIELDS

### 9.1. INTRODUCTION

Electrically induced birefringence refers to those phenomena where the polarization changes of a light beam passing through a molecular medium depend on the presence of electric fields. When the electric field is static and externally applied, the Kerr effect obtains. The electric field in an intense light beam produces a similar effect, and the use of a second, weak beam to probe this optically induced birefringence constitutes the optical Kerr effect. The polarization characteristics of the intense beam itself can be altered by the birefringence it induces: the intensity dependent rotation of the polarization ellipse of a laser beam is one manifestation of such an effect. A useful review of many relevant nonlinear optical phenomena can be found in [53].

With fluid samples, these effects originate in the tendency for the electric fields to provide non-zero spatial averages

of one or more of the R-matrix elements specified in (8.19) or (8.21). The physical mechanisms responsible include molecular reorientation in the field, nonlinear electronic polarizability (hyperpolarizability), and electrostriction; but only the first two contributions are considered here. For discussions of various models of the molecular medium see, for example, [42-44]. Much of the material in this chapter has been published by Atkins and Barron [32].

## 9.2. THE KERR EFFECT

The application of a uniform, static electric field  $\mathbf{F}$  across an isotropic fluid causes the system to become birefringent with the optic axis in the direction of  $\mathbf{F}$  [45]. The Kerr experiment involves the measurement of the ellipticity of a light beam emergent in the forward direction from such a system, the incident beam being plane polarized at  $\pi/4$  to  $\mathbf{F}$ . This birefringence arises because not all the orientations available to the molecules are sampled equally. The most important attributes of molecules that enable them to show this effect are a permanent electric dipole moment, an anisotropic polarizability, or both. Hyperpolarizability can sometimes be important: the applied field distorts the molecular wave function with the result that the electronic structure of the molecule changes as it rotates, thereby upsetting the averaging process.

The linear parts of (8.19) are applicable here. If the

coordinate axes are chosen so that the incident beam is plane polarized along the  $\mathbf{e}_1$ -axis then, since the azimuth remains unchanged in the experiment, the macroscopic ellipticity change for  $N$  molecules in the sample volume can be written

$$\Delta\eta = (NL/\hbar c) \text{Re} \mathcal{R}_{21}. \quad (9.1)$$

The term  $\text{Re} \mathcal{R}_{21}$  requires careful interpretation because the static field has not been consistently incorporated into the total state vector of the system: if it were, (9.1) would contain R-matrix elements in which vertices involving the static field as well as the optical field would be specified. Thus we introduce the appropriate R-matrix elements in an ad-hoc fashion by means of the diagrams in Figure 9.1, which are drawn and interpreted in accordance with the rules of Section 5.5. We obtain

$$\begin{aligned}
 & \text{Diagram 1: } |g\rangle \xrightarrow{k_1} |m\rangle \xrightarrow{k_2} |g\rangle + \text{Diagram 2: } |g\rangle \xrightarrow{k_1} |g\rangle \quad \equiv \text{Re } \mathcal{R}_{21} \\
 & \text{Diagram 3: } |g\rangle \xrightarrow{F} |m\rangle \xrightarrow{F} |m'\rangle \xrightarrow{F} |g\rangle + 5 \text{ other time orderings} \quad \equiv \text{Re } \mathcal{R}_{21F} \\
 & \text{Diagram 4: } |g\rangle \xrightarrow{F} |m\rangle \xrightarrow{F} |m'\rangle \xrightarrow{F} |m'\rangle \xrightarrow{F} |g\rangle + 11 \text{ other time orderings} \quad \equiv \text{Re } \mathcal{R}_{21FF}
 \end{aligned}$$

Figure 9.1. Diagrams appropriate to the Kerr effect.

$$\text{Re } R_{21} + \text{Re } R_{21F} + \text{Re } R_{21FF}$$

$$\begin{aligned}
&= \left( \frac{2\pi\hbar\omega}{V} \right) \sum_{n,m,m''} \left\{ \frac{2E_{gm}}{E_{gm}^2 - \hbar^2\omega^2} d_{gm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2 \right. \\
&\quad - F \cdot \left[ \frac{2(E_{gm}E_{gm'} + \hbar^2\omega^2)}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)} d_{gm} \cdot \epsilon_1 d_{m'm} d_{mg} \cdot \epsilon_2 \right. \\
&\quad + \frac{2E_{gm}}{E_{gm'}(E_{gm}^2 - \hbar^2\omega^2)} d_{gm'} d_{m'm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2 \\
&\quad \left. + \frac{2E_{gm'}}{E_{gm}(E_{gm'}^2 - \hbar^2\omega^2)} d_{gm'} \cdot \epsilon_1 d_{m'm} \cdot \epsilon_2 d_{mg} \right] \\
&\quad + FF: \left[ \frac{2E_{gm} d_{gm'} d_{m''m'} d_{m'm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_1}{(E_{gm}^2 - \hbar^2\omega^2) E_{gm'} E_{gm''}} \right. \\
&\quad + \frac{2(E_{gm}E_{gm'}E_{gm''} + E_{gm}\hbar^2\omega^2 + E_{gm'}\hbar^2\omega^2 + E_{gm''}\hbar^2\omega^2)}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)(E_{gm''}^2 - \hbar^2\omega^2)} d_{gm} \cdot \epsilon_2 d_{m''m'} d_{m'm} d_{mg} \cdot \epsilon_1 \\
&\quad + \frac{2(E_{gm'}E_{gm''} + \hbar^2\omega^2)}{E_{gm}(E_{gm'}^2 - \hbar^2\omega^2)(E_{gm''}^2 - \hbar^2\omega^2)} d_{gm''} \cdot \epsilon_2 d_{m''m'} d_{m'm} \cdot \epsilon_1 d_{mg} \\
&\quad + \frac{2E_{gm'} d_{gm''} d_{m''m'} \cdot \epsilon_2 d_{m'm} \cdot \epsilon_1 d_{mg}}{E_{gm}(E_{gm'}^2 - \hbar^2\omega^2) E_{gm''}} + \frac{2E_{gm''} d_{gm''} \cdot \epsilon_2 d_{m''m'} \cdot \epsilon_1 d_{m'm} d_{mg}}{E_{gm} E_{gm'} (E_{gm''}^2 - \hbar^2\omega^2)} \\
&\quad \left. + \frac{2(E_{gm}^2 + \hbar^2\omega^2)}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2) E_{gm''}} d_{gm'} d_{m''m'} \cdot \epsilon_2 d_{m'm} d_{mg} \cdot \epsilon_1 \right] \left. \right\} \quad (9.2)
\end{aligned}$$

where we have anticipated the equivalence of the orientational averages of  $d_{ab} \cdot \epsilon_1 d_{cd} \cdot \epsilon_2$  and  $d_{ab} \cdot \epsilon_2 d_{cd} \cdot \epsilon_1$ .

The orientational average of (9.2) must now be evaluated using the classical Boltzmann average (8.22) together with the interaction energy (8.24) between the molecule and the static

field  $\mathbf{F}$ . The only non-zero terms containing up to four vertices are then

$$\overline{\text{Re } R_{21}(\omega)} = (1/2kT) \langle (\mathbf{F} \mathbf{F} : \alpha) X(\text{Re } R_{21}) \rangle + (1/2k^2 T^2) \langle (\boldsymbol{\mu} \cdot \mathbf{F})^2 (\text{Re } R_{21}) \rangle \quad (9.3)$$

$$\overline{\text{Re } R_{21F}(\omega)} = (1/kT) \langle (\boldsymbol{\mu} \cdot \mathbf{F}) (\text{Re } R_{21F}) \rangle \quad (9.4)$$

$$\overline{\text{Re } R_{21FF}(\omega)} = \langle \text{Re } R_{21FF} \rangle. \quad (9.5)$$

The static field  $\mathbf{F}$  is related to the  $\mathbf{e}_1$  and  $\mathbf{e}_2$ -axes as follows:

$$\mathbf{F} = (F/\sqrt{2})(\mathbf{e}_1 + \mathbf{e}_2). \quad (9.6)$$

If we use the following averages of fourth-rank tensor components (see the Appendix)

$$\begin{aligned} \langle a \cdot \mathbf{e}_\sigma b \cdot \mathbf{e}_\sigma c \cdot \mathbf{e}_\sigma d \cdot \mathbf{e}_\sigma \rangle &= \frac{1}{15} (a \cdot b c \cdot d + a \cdot c b \cdot d + a \cdot d b \cdot c) \\ \langle a \cdot \mathbf{e}_\sigma b \cdot \mathbf{e}_\sigma c \cdot \mathbf{e}_\tau d \cdot \mathbf{e}_\tau \rangle &= \frac{1}{30} (4 a \cdot b c \cdot d - a \cdot c b \cdot d - a \cdot d b \cdot c) \end{aligned}$$

together with the dynamic polarizability and hyperpolarizability tensors  $\alpha(\omega)$ ,  $\beta(\omega)$ , and  $\gamma(\omega)$ , where

$$\alpha_{\alpha\beta}(\omega) = \sum_m \frac{2E_{gm}}{E_{gm}^2 - \hbar^2 \omega^2} d_{gm}^\alpha d_{mg}^\beta \quad (9.7)$$

$$\begin{aligned} \beta_{\alpha\beta\gamma}(\omega) = \sum_{m,m'} \bigg\{ & \frac{E_{gm'}}{E_{gm}(E_{gm'}^2 - \hbar^2 \omega^2)} (d_{gm'}^\alpha d_{m'm}^\beta d_{mg}^\gamma + d_{gm'}^\beta d_{m'm}^\alpha d_{mg}^\gamma) \\ & + \frac{E_{gm}}{(E_{gm}^2 - \hbar^2 \omega^2) E_{gm'}} (d_{gm'}^\gamma d_{m'm}^\beta d_{mg}^\alpha + d_{gm'}^\gamma d_{m'm}^\alpha d_{mg}^\beta) \\ & + \frac{(E_{gm} E_{gm'} + \hbar^2 \omega^2)}{(E_{gm}^2 - \hbar^2 \omega^2)(E_{gm'}^2 - \hbar^2 \omega^2)} (d_{gm'}^\beta d_{m'm}^\gamma d_{mg}^\alpha + d_{gm'}^\alpha d_{m'm}^\gamma d_{mg}^\beta) \bigg\} \quad (9.8) \end{aligned}$$

$$\begin{aligned}
\gamma_{\alpha\beta\gamma\delta}(\omega) = & \sum_{m,m',m''} \left\{ \frac{E_{gm}(\alpha\beta\gamma\delta + \alpha\beta\delta\gamma)}{(E_{gm}^2 - \hbar^2\omega^2) E_{gm'} E_{gm''}} \right. \\
& + \frac{E_{gm'}(\gamma\delta\alpha\beta + \alpha\delta\gamma\beta)}{E_{gm}(E_{gm'}^2 - \hbar^2\omega^2) E_{gm''}} + \frac{E_{gm''}(\gamma\delta\alpha\beta + \delta\gamma\alpha\beta)}{E_{gm} E_{gm'}(E_{gm''}^2 - \hbar^2\omega^2)} \\
& + \frac{(E_{gm'} E_{gm''} + \hbar^2\omega^2)(\gamma\alpha\delta\beta + \delta\alpha\gamma\beta)}{E_{gm}(E_{gm'}^2 - \hbar^2\omega^2)(E_{gm''}^2 - \hbar^2\omega^2)} + \frac{(E_{gm}^2 + \hbar^2\omega^2)(\alpha\gamma\beta\delta + \alpha\delta\beta\gamma)}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2) E_{gm''}} \\
& \left. + \frac{(E_{gm} E_{gm'} E_{gm''} + E_{gm} \hbar^2\omega^2 + E_{gm'} \hbar^2\omega^2 + E_{gm''} \hbar^2\omega^2)(\gamma\alpha\beta\delta + \delta\alpha\beta\gamma)}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)(E_{gm''}^2 - \hbar^2\omega^2)} \right\} \quad (9.9)
\end{aligned}$$

with the abbreviation

$$\alpha\beta\gamma\delta \equiv d_{gm''}^{\alpha} d_{m''m'}^{\beta} d_{m'm}^{\gamma} d_{mg}^{\delta},$$

then

$$\langle FF: \alpha Re R_{21} \rangle = (F^2/30)(2\pi\hbar\omega/V)[3\alpha_{\alpha\beta}(\omega)\alpha_{\alpha\beta}(0) - \alpha_{\alpha\alpha}(\omega)\alpha_{\beta\beta}(0)] \quad (9.10)$$

$$\langle (\mu \cdot F)^2 Re R_{21} \rangle = (F^2/30)(2\pi\hbar\omega/V)[3\alpha_{\alpha\beta}(\omega)\mu_{\alpha}\mu_{\beta} - \alpha_{\alpha\alpha}(\omega)\mu_{\beta}\mu_{\beta}] \quad (9.11)$$

$$\langle \mu \cdot F Re R_{21F} \rangle = (F^2/30)(2\pi\hbar\omega/V)[3\beta_{\alpha\beta\alpha}(\omega)\mu_{\beta} - \beta_{\alpha\alpha\beta}(\omega)\mu_{\beta}] \quad (9.12)$$

$$\langle Re R_{21FF} \rangle = (F^2/30)(2\pi\hbar\omega/V)[3\delta_{\alpha\beta\alpha\beta}(\omega) - \delta_{\alpha\alpha\beta\beta}(\omega)]. \quad (9.13)$$

The ellipticity may finally be written as

$$\begin{aligned}
\Delta\eta = & (4\pi^2 N F^2 / 30 \lambda) \left\{ [3\delta_{\alpha\beta\alpha\beta}(\omega) - \delta_{\alpha\alpha\beta\beta}(\omega)] \right. \\
& + (1/kT)[3\beta_{\alpha\beta\alpha}(\omega)\mu_{\beta} - \beta_{\alpha\alpha\beta}(\omega)\mu_{\beta}] + (1/2kT)[3\alpha_{\alpha\beta}(\omega)\alpha_{\alpha\beta}(0) - \alpha_{\alpha\alpha}(\omega)\alpha_{\beta\beta}(0)] \\
& \left. + (1/2k^2T^2)[3\alpha_{\alpha\beta}(\omega)\mu_{\alpha}\mu_{\beta} - \alpha_{\alpha\alpha}(\omega)\mu_{\beta}\mu_{\beta}] \right\} \quad (9.14)
\end{aligned}$$

for unit path length in a medium containing  $N$  molecules per unit volume. This equation has the same form as the Born-Langevin equation, a classical derivation of which has been presented by Buckingham and Pople [46]. The dispersion with frequency of the quantum mechanical expression has been investigated by Buckingham [47].

### 9.3. THE OPTICAL KERR EFFECT

It was Buckingham [41] in 1956 who first appreciated that the electric field vector of an intense light beam could cause an isotropic material to become birefringent. His suggestion of an experiment involving a second weaker beam to measure the birefringence did not materialize until the advent of the laser, and in particular the work of Mayer and Gires [48] and Paillette [49].

The optical Kerr effect, otherwise known as the Buckingham effect, originates like its static analogue from the tendency for certain orientations of the molecule to be favoured in the electric field. One point of difference, however, is that in dipolar liquids the permanent molecular dipole moment makes an important contribution to the Kerr effect but not to the optical Kerr effect because in the latter the permanent dipole moments cannot follow the optical frequency.

Equation (9.1) is applicable for the ellipticity change, but again requires careful interpretation because the orienting optical field has not been consistently incorporated into the

total state vector. If it were, then "half reduced" hyperpolarizability terms such as  $\text{Re } \tilde{\mathcal{R}}_{2\pi,1\pi}$  would arise, where  $\pi$  is the polarization of the orienting beam which has a wave vector  $q$ . Such terms will therefore be introduced in an ad-hoc manner, and may be represented diagrammatically as in Figure 9.2b. Also the Boltzmann average  $\overline{\text{Re } \mathcal{R}_2(\omega)}$  is now evaluated using  $-\mathcal{R}_{\pi\pi}$  as the potential energy term in accordance with the interpretation introduced in Section 8.3 (Equation (8.30)). This scattering from an optically oriented molecule may be represented as in Figure 9.2a, where the time ordering of the vertices to the left and right of the double line through the molecular propagator must be kept separate.

$$\begin{aligned}
 \text{a)} \quad & \text{Diagram with vertices } g, m, g, m, g \text{ and wavy lines } q_\pi, q_\pi, k_1, k_2. \text{ + 3 other time orderings} \equiv \text{Re } \mathcal{R}_2 \text{ Re } \mathcal{R}_{\pi\pi} \\
 \text{b)} \quad & \text{Diagram with vertices } g, m, m', m'' \text{ and wavy lines } q_\pi, q_\pi, k_1, k_2. \text{ + 23 other time orderings} \equiv \text{Re } \tilde{\mathcal{R}}_{2\pi,1\pi}
 \end{aligned}$$

Figure 9.2. Diagrams which contribute to the optical Kerr effect.

If the orienting light beam is plane polarized with an azimuth of  $\pi/4$ , then from (8.30) we have

$$\text{Re } \mathcal{R}_{\pi\pi} = \frac{1}{2} E_0^2 \alpha(\omega_q) : (\epsilon_1 \epsilon_1 + \epsilon_2 \epsilon_2 + \epsilon_1 \epsilon_2 + \epsilon_2 \epsilon_1) \quad (9.15)$$

so that the required Boltzmann average becomes

$$\overline{\text{Re } R_{2,1}(-2)} \sim (1/kT) \langle \text{Re } R_{2,1} \text{Re } R_{\pi\pi} \rangle$$

$$= [E_0^2(\omega_q)/30kT] (2\pi\hbar\omega_k/V) [3\chi_{\alpha\beta}(\omega_q)\chi_{\alpha\beta}(\omega_k) - \chi_{\alpha\alpha}(\omega_q)\chi_{\beta\beta}(\omega_k)] \quad (9.16)$$

The hyperpolarizability R-matrix element can be written

$$\overline{\text{Re } \tilde{R}_{2\pi,1\pi}} = [E_0^2(\omega_q)/30] (2\pi\hbar\omega_k/V) [3\delta_{\alpha\beta\alpha\beta}(\omega_k, \omega_q) - \delta_{\alpha\alpha\beta\beta}(\omega_k, \omega_q)] \quad (9.17)$$

with the fourth rank tensor  $\delta(\omega_k, \omega_q)$  defined as

$$\delta_{\alpha\beta\gamma\delta}(\omega_k, \omega_q) = \sum_{m, m', m''} \left\{ \begin{aligned} & \frac{(E_{gm}E_{gm'}E_{gm''} + E_{gm}\hbar^2\omega_1\omega_3 + E_{gm'}\hbar^2\omega_1^2 + E_{gm''}\hbar^2\omega_1\omega_3)(\delta\alpha\beta\delta + \delta\alpha\beta\delta)}{(E_{gm}^2 - \hbar^2\omega_1^2)(E_{gm'}^2 - \hbar^2\omega_3^2)(E_{gm''}^2 - \hbar^2\omega_1^2)} \\ & + \frac{(E_{gm}E_{gm'}E_{gm''} + E_{gm}\hbar^2\omega_2\omega_3 + E_{gm'}\hbar^2\omega_1\omega_2 + E_{gm''}\hbar^2\omega_1\omega_3)(\alpha\delta\beta\delta + \alpha\delta\beta\delta)}{(E_{gm}^2 - \hbar^2\omega_1^2)(E_{gm'}^2 - \hbar^2\omega_3^2)(E_{gm''}^2 - \hbar^2\omega_2^2)} \\ & + \frac{2E_{gm}E_{gm''}(\alpha\beta\delta\gamma + \alpha\beta\delta\delta)}{(E_{gm}^2 - \hbar^2\omega_1^2)E_{gm'}(E_{gm''}^2 - \hbar^2\omega_2^2)} + \frac{2E_{gm}E_{gm''}(\delta\delta\alpha\beta + \delta\delta\alpha\beta)}{(E_{gm}^2 - \hbar^2\omega_2^2)E_{gm'}(E_{gm''}^2 - \hbar^2\omega_1^2)} \\ & + \frac{(E_{gm}E_{gm'}E_{gm''} + E_{gm}\hbar^2\omega_1\omega_3 + E_{gm'}\hbar^2\omega_2\omega_3 + E_{gm''}\hbar^2\omega_1\omega_3)(\delta\alpha\gamma\beta + \delta\alpha\gamma\beta)}{(E_{gm}^2 - \hbar^2\omega_2^2)(E_{gm'}^2 - \hbar^2\omega_3^2)(E_{gm''}^2 - \hbar^2\omega_1^2)} \\ & + \frac{(E_{gm}E_{gm'}E_{gm''} + E_{gm}\hbar^2\omega_3\omega_2 + E_{gm'}\hbar^2\omega_2^2 + E_{gm''}\hbar^2\omega_2\omega_3)(\alpha\delta\delta\beta + \alpha\delta\delta\beta)}{(E_{gm}^2 - \hbar^2\omega_2^2)(E_{gm'}^2 - \hbar^2\omega_3^2)(E_{gm''}^2 - \hbar^2\omega_2^2)} \\ & + \frac{(E_{gm}E_{gm'}E_{gm''} - E_{gm}\hbar^2\omega_2\omega_4 - E_{gm''}\hbar^2\omega_2\omega_4 + E_{gm''}\hbar^2\omega_2^2)(\alpha\delta\gamma\beta + \alpha\delta\gamma\beta)}{(E_{gm}^2 - \hbar^2\omega_2^2)(E_{gm'}^2 - \hbar^2\omega_4^2)(E_{gm''}^2 - \hbar^2\omega_2^2)} \end{aligned} \right.$$

$$\begin{aligned}
& + \frac{(E_{g,m}E_{g,m'}E_{g,m''} - E_{g,m}\hbar^2\omega_z\omega_4 - E_{g,m'}\hbar^2\omega_1\omega_z + E_{g,m''}\hbar^2\omega_1\omega_4)(\alpha\gamma\beta\delta + \alpha\delta\beta\gamma)}{(E_{g,m}^2 - \hbar^2\omega_1^2)(E_{g,m'}^2 - \hbar^2\omega_4^2)(E_{g,m''}^2 - \hbar^2\omega_z^2)} \\
& + \frac{(E_{g,m}E_{g,m'}E_{g,m''} + E_{g,m}\hbar^2\omega_1\omega_4 - E_{g,m'}\hbar^2\omega_1\omega_z - E_{g,m''}\hbar^2\omega_z\omega_4)(\delta\alpha\delta\beta + \delta\alpha\delta\beta)}{(E_{g,m}^2 - \hbar^2\omega_z^2)(E_{g,m'}^2 - \hbar^2\omega_4^2)(E_{g,m''}^2 - \hbar^2\omega_1^2)} \\
& + \frac{(E_{g,m}E_{g,m'}E_{g,m''} + E_{g,m}\hbar^2\omega_1\omega_4 + E_{g,m'}\hbar^2\omega_1^2 + E_{g,m''}\hbar^2\omega_1\omega_4)(\delta\alpha\beta\gamma + \gamma\alpha\beta\delta)}{(E_{g,m}^2 - \hbar^2\omega_1^2)(E_{g,m'}^2 - \hbar^2\omega_4^2)(E_{g,m''}^2 - \hbar^2\omega_z^2)} \Bigg\} \quad (9.18)
\end{aligned}$$

where  $\omega_1, \omega_2, \omega_3$ , and  $\omega_4$  represent the possible combinations of  $\omega_k$  and  $\omega_q$ :

$$\omega_1 = \omega_k, \quad \omega_2 = \omega_q, \quad \omega_3 = \omega_k + \omega_q, \quad \omega_4 = \omega_k - \omega_q.$$

The optical Kerr ellipticity is finally obtained as

$$\begin{aligned}
\Delta\eta = [4\pi^2 N E_0^2(\omega_q)/30\lambda] \Big\{ [3\delta_{\alpha\beta\alpha\beta}(\omega_k, \omega_q) - \delta_{\alpha\alpha\beta\beta}(\omega_k, \omega_q)] \\
+ (1/kT)[3\chi_{\alpha\beta}(\omega_k)\chi_{\alpha\beta}(\omega_q) - \chi_{\alpha\alpha}(\omega_k)\chi_{\beta\beta}(\omega_q)] \Big\} \quad (9.19)
\end{aligned}$$

for unit path length, and  $N$  molecules per unit volume.

Takatsuji [50] has developed quantum mechanical expressions for the optical Kerr polarizations by semi-classical methods, and we refer to his work for detailed discussions of the implications of these equations.

#### 9.4. INTENSITY-DEPENDENT ROTATION OF THE POLARIZATION ELLIPSE

Equation (8.21) contains terms contributing to the angle of rotation that need not involve optically active molecules. An example of this is the intensity-dependent rotation of the

polarization ellipse of an intense laser beam [52,52]. The classical theory ascribes the effect to the intensity-dependence of the refractive index: an elliptically polarized beam may be considered as a superposition of two circularly polarized beams of different intensity, so the two components will propagate through the medium at different velocities thereby causing the ellipse to rotate.

Equation (8.21) for the infinitesimal angle of rotation is simplified considerably if an initial azimuth of  $\pi/4$  could be chosen; but certain terms are dependent on the initial azimuth, which changes as the beam traverses the medium. If, however, the coordinate axes are rotated at each subsequent scattering event so that the initial azimuth is maintained at  $\pi/4$ , we can write for the macroscopic rotation

$$\Delta\theta = (NL/\pi c) \left[ \Im_m R_{21} + n \Im_m R_{21,11} + (\Re R_{21} + n \Re R_{21,11}) \tan 2\eta' + n \Im_n R_{22,11} (2 \cos 2\eta' - \sec 2\eta') + 2n \Re R_{22,11} \sin 2\eta' \right]. \quad (9.20)$$

If the molecules are not optically active, only the real R-matrix elements can contribute to the angle of rotation, which will be ellipticity-dependent. Of the two real hyperpolarizability terms, only  $\Re R_{22,11}$  can provide a non-zero spatial average. A temperature-dependent contribution obtains from  $\Re R_{21}$  if the molecules are optically oriented. The relevant diagrams are shown in Figure 9.3.

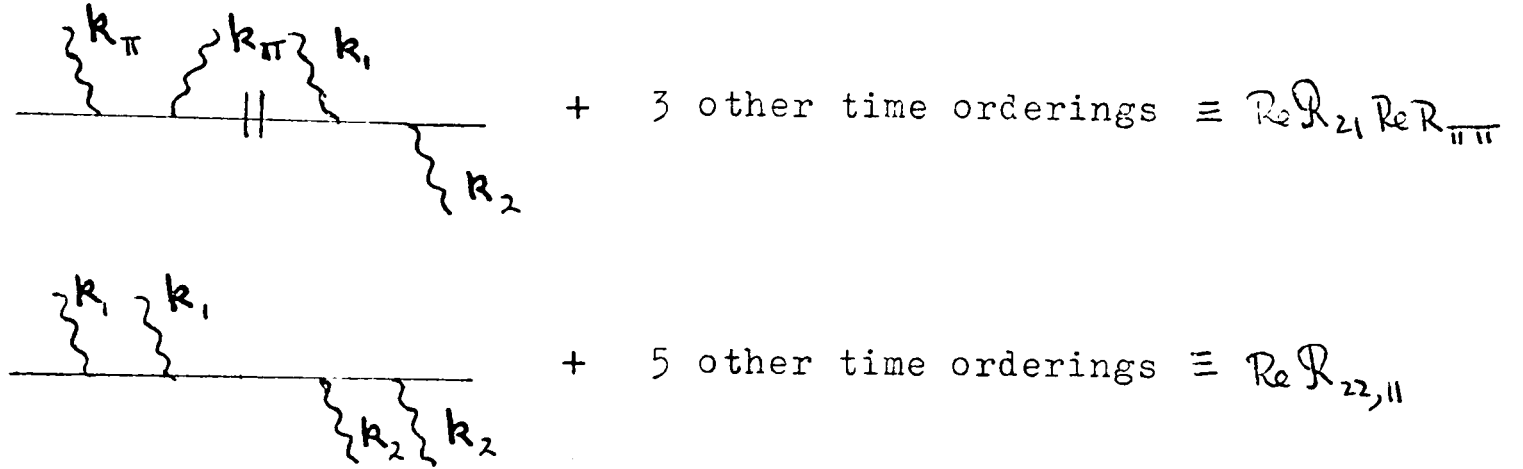


Figure 9.3. Diagrams which contribute to the rotation of the polarization ellipse.

The temperature-dependent term is directly analogous to (9.16), with the orienting beam now having the polarization and frequency of the measuring beam, that is

$$\overline{\text{Re } R_{21}(\Omega)} = [E_0^2(\omega)/30kT](2\pi\hbar\omega/V)[3\alpha_{\alpha\epsilon}(\omega)\alpha_{\alpha\epsilon}(\omega) - \alpha_{\alpha\alpha}(\omega)\alpha_{\epsilon\epsilon}(\omega)]\cos 2\eta_i \quad (9.21)$$

The hyperpolarizability term is

$$\begin{aligned} \text{Re } R_{22,11} = (2\pi\hbar\omega/V)^2 \sum_{m,m',m''} & \left\{ \frac{d_{gm''} \cdot \epsilon_2 d_{m''m'} \cdot \epsilon_2 d_{m'm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_1}{(E_{gm} + \hbar\omega)(E_{gm'} + 2\hbar\omega)(E_{gm''} + \hbar\omega)} \right. \\ & + \frac{d_{gm''} \cdot \epsilon_2 d_{m''m'} \cdot \epsilon_1 d_{m'm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_1}{(E_{gm} + \hbar\omega) E_{gm'} (E_{gm''} + \hbar\omega)} + \frac{d_{gm''} \cdot \epsilon_2 d_{m''m'} \cdot \epsilon_1 d_{m'm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2}{(E_{gm} - \hbar\omega) E_{gm'} (E_{gm''} + \hbar\omega)} \\ & + \frac{d_{gm''} \cdot \epsilon_1 d_{m''m'} \cdot \epsilon_2 d_{m'm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2}{(E_{gm} - \hbar\omega) E_{gm'} (E_{gm''} - \hbar\omega)} + \frac{d_{gm''} \cdot \epsilon_1 d_{m''m'} \cdot \epsilon_2 d_{m'm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_1}{(E_{gm} + \hbar\omega) E_{gm'} (E_{gm''} - \hbar\omega)} \\ & \left. + \frac{d_{gm''} \cdot \epsilon_1 d_{m''m'} \cdot \epsilon_1 d_{m'm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_2}{(E_{gm} - \hbar\omega)(E_{gm'} - 2\hbar\omega)(E_{gm''} - \hbar\omega)} \right\} \quad (9.22) \end{aligned}$$

so that, by introducing the dynamic hyperpolarizability tensor  $\chi(\omega)$  as

$$\gamma_{\alpha\beta\gamma\delta}(\omega) = \sum_{m,m',m''} \left\{ \frac{[E_{gm}E_{gm'}E_{gm''} + (E_{gm} + E_{gm'} + E_{gm''})\hbar^2\omega^2]\alpha\delta\beta\gamma}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - 4\hbar^2\omega^2)(E_{gm''}^2 - \hbar^2\omega^2)} \right. \\ \left. + \frac{(E_{gm}E_{gm''} + \hbar^2\omega^2)\alpha\beta\gamma\delta + (E_{gm}E_{gm'} - \hbar^2\omega^2)\alpha\delta\beta\gamma}{(E_{gm}^2 - \hbar^2\omega^2)E_{gm'}(E_{gm''} - \hbar^2\omega^2)} \right\} \quad (9.23)$$

we obtain

$$\overline{n \operatorname{Re} R_{22,11}} = [E_0^2(\omega)/30](2\pi\hbar\omega/v)[3\gamma_{\alpha\beta\alpha\beta}(\omega) - \gamma_{\alpha\alpha\beta\beta}(\omega)] . \quad (9.24)$$

The angle of rotation is now obtained as

$$\Delta\theta = [4\pi^2 N E_0^2(\omega)/30\lambda] \left\{ 2[3\gamma_{\alpha\beta\alpha\beta}(\omega) - \gamma_{\alpha\alpha\beta\beta}(\omega)] \right. \\ \left. + (1/kT)[3\alpha_{\alpha\beta}(\omega)\alpha_{\alpha\beta}(\omega) - \alpha_{\alpha\alpha}(\omega)\alpha_{\beta\beta}(\omega)] \right\} \sin 2\eta' . \quad (9.25)$$

Measurements of the angle of rotation of the polarization ellipse could provide an alternative method to the Kerr effect for determining molecular polarizability and hyperpolarizability tensors.

# 10

## NATURAL OPTICAL ACTIVITY

### 10.1. INTRODUCTION

A molecule or crystal is naturally optically active if in its natural state it rotates the plane of polarization of light, as distinct from, for example, Faraday rotation where an externally applied magnetic field is necessary to produce a rotation. There are only two terms in (8.21) that can provide non-zero contributions to the optical rotation angle for an ensemble of freely tumbling molecules, and since they are independent of the polarization of the incident beam we obtain for the macroscopic rotation

$$\Delta\theta = (NL/4\pi c)(g_m R_{21} + n g_m R_{21,11}). \quad (10.1)$$

From the discussion in Section 8.3,  $\text{Im } Q_u$  contains a magnetic dipole interaction and an electric dipole interaction;  $\text{Im } Q_{u,11}$  contains a single magnetic dipole interaction and three electric dipole interactions, and will provide an intensity-dependent hyperpolarizability contribution to the angle of rotation. Thus we immediately have the condition that only naturally

asymmetric molecules can show optical activity, for a process involving the interference of electric and magnetic dipole interactions can be supported only by systems where parity is not defined.

Earlier work on the quantum field theory of optical rotation includes that of Stephen [30] and Hameka [54]; the use of the transformed interaction Hamiltonian (5.34) in the treatment of optical rotation was first suggested by Power and Shail [55], and Power [5] has employed diagrammatic perturbation theory to this end, although his treatment is obscure. Kielich [56] has briefly discussed the possibility of observing intensity-dependent optical rotation. The present chapter is based largely on the Paper by Atkins and Barron [31].

## 10.2. LINEAR OPTICAL ROTATION

The term  $\text{Im } \mathcal{R}_2$  determines the first order contribution to optical rotation. Figure 10.1 shows the appropriate diagrams.

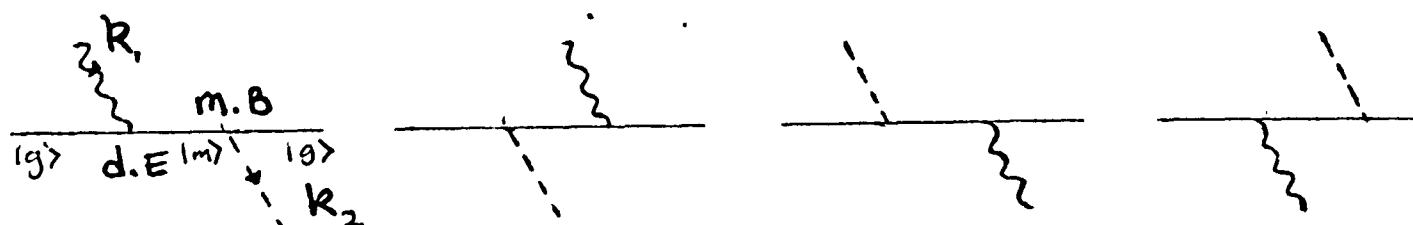


Figure 10.1. Diagrams which contribute to optical rotation.

From Section 5.4 it is clear that the required R-matrix element is

$$\begin{aligned}
g_m R_{21} &= (2\pi\hbar\omega/V) g_m \sum_m \left\{ \frac{m_{gm} \cdot \hat{k}_\perp \epsilon_2 d_{mg} \cdot \epsilon_1}{E_{gm} + \hbar\omega} \right. \\
&+ \frac{d_{gm} \cdot \epsilon_1 m_{mg} \cdot \hat{k}_\perp \epsilon_2}{E_{gm} - \hbar\omega} + \frac{d_{gm} \cdot \epsilon_2 m_{mg} \cdot \hat{k}_\perp \epsilon_1}{E_{gm} + \hbar\omega} + \left. \frac{m_{gm} \cdot \hat{k}_\perp \epsilon_1 d_{gm} \cdot \epsilon_2}{E_{gm} - \hbar\omega} \right\} \\
&= (2\pi\hbar\omega/V) g_m \sum_m \left\{ \frac{d_{gm} \cdot \epsilon_2 m_{mg} \cdot \epsilon_2 - m_{gm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2}{E_{gm} + \hbar\omega} \right. \\
&+ \left. \frac{m_{gm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_2 - d_{gm} \cdot \epsilon_1 m_{mg} \cdot \epsilon_1}{E_{gm} - \hbar\omega} \right\}. \tag{10.2}
\end{aligned}$$

Invoking the Hermiticity of the operators, this reduces to

$$\begin{aligned}
g_m R_{21} &= -(4\pi\hbar^2\omega^2/V) g_m \sum_m \left\{ \frac{d_{gm} \cdot \epsilon_1 m_{mg} \cdot \epsilon_1 + d_{gm} \cdot \epsilon_2 m_{mg} \cdot \epsilon_2}{E_{gm}^2 - \hbar^2\omega^2} \right\} \\
&= -(2\pi\hbar\omega/V) \rho : (\epsilon_1 \epsilon_1 + \epsilon_2 \epsilon_2) \tag{10.3}
\end{aligned}$$

with the optical rotation tensor  $\rho$  defined as

$$\rho_{\alpha\beta} = \sum_m \frac{2\hbar\omega}{E_{gm}^2 - \hbar^2\omega^2} g_m (d_{gm}^\alpha m_{mg}^\beta). \tag{10.4}$$

This differs from the usual definition of  $\rho$  by the factor  $2\hbar\omega$ , so as to parallel the definition of  $\alpha$ . After spatial averaging we obtain

$$\begin{aligned}
\overline{g_m R_{21}} &= -\frac{8\pi\hbar^2\omega^2}{3V} \sum_m g_m \frac{d_{gm} \cdot m_{mg}}{E_{gm}^2 - \hbar^2\omega^2} \\
&= -(2/3)(2\pi\hbar\omega/V) \rho_{\alpha\alpha}. \tag{10.5}
\end{aligned}$$

By substituting this result into (10.1), the Rosenfeld

equation [57] is reproduced:

$$\Delta\theta = -\frac{8\pi N}{3\pi c} \sum_m f_m \frac{\omega^2 \mathbf{d}_{g,m} \cdot \mathbf{m}_{mg}}{\omega_{gm}^2 - \omega^2} \quad (10.6)$$

for unit path length in a solution containing  $N$  optically active molecules per unit volume. The different sign to (43) of [31] is due to the use of a different set of coordinate axes.

### 10.3. INTENSITY-DEPENDENT OPTICAL ROTATION

The simultaneous scattering of two photons by an optically active molecule will provide a hyperpolarizability contribution to intensity-dependent optical rotation determined by  $\text{Im } \mathcal{R}_{21,11}$  (hyper-rotation). The associated forty eight diagrams may be divided into the six classes which are illustrated in Figure 10.2.

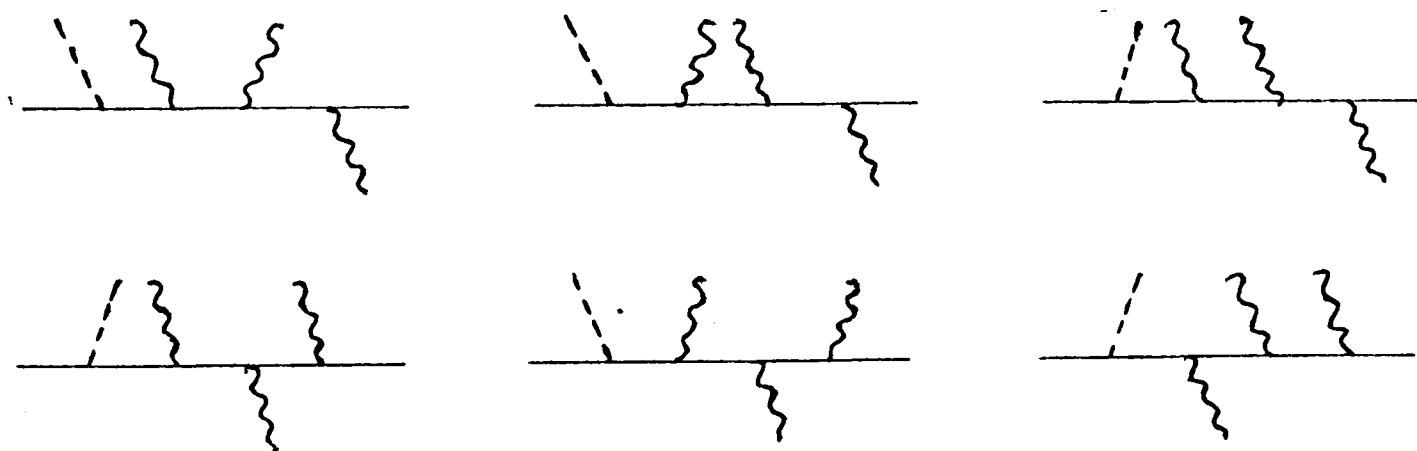


Figure 10.2. Typical members of the six classes of diagrams which contribute to hyper-rotation.

The other diagrams may be generated by replacing in turn each electric dipole vertex by a magnetic dipole vertex and then interchanging the time ordering of the two emission vertices in

each of the twenty four diagrams so obtained. The complete expression for  $\text{Im } \mathcal{R}_{21,11}$  is very long and will not be reproduced here. By using the Hermiticity of the operators  $\mathbf{d}$  and  $\mathbf{m}$  and the symmetry properties of the energy denominators, we obtain after spatial averaging

$$\overline{g_m \mathcal{R}_{21,11}} = -(2/15)(2\pi\hbar\omega/V)^2 [3\sigma_{\alpha\beta\alpha\beta}(\omega) - \sigma_{\alpha\alpha\beta\beta}(\omega)] \quad (10.7)$$

with the fourth rank dynamic hyper-rotation tensor  $\gamma(\omega)$  defined as

$$\begin{aligned} \sigma_{\alpha\beta\gamma\delta}(\omega) = & \hbar\omega g_m \sum_{m,m',m''} \left\{ \right. \\ & - \frac{(2E_{gm}E_{gm''} + E_{gm}E_{gm'} + E_{gm'}E_{gm''} + 2\hbar^2\omega^2)(\bar{\alpha}\beta\gamma\delta + \bar{\alpha}\beta\delta\gamma + \alpha\bar{\beta}\delta\gamma + \alpha\bar{\beta}\gamma\delta)}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - 4\hbar^2\omega^2)(E_{gm''}^2 - \hbar^2\omega^2)} \\ & + \frac{(E_{gm''} - E_{gm})(\alpha\gamma\bar{\delta}\beta + \alpha\delta\bar{\gamma}\beta - \bar{\alpha}\gamma\delta\beta - \bar{\beta}\gamma\delta\alpha)}{(E_{gm}^2 - \hbar^2\omega^2)E_{gm'}(E_{gm''}^2 - \hbar^2\omega^2)} \\ & \left. + \frac{(E_{gm''} + E_{gm})(\alpha\bar{\gamma}\beta\delta + \alpha\bar{\delta}\beta\gamma + \alpha\gamma\bar{\beta}\delta + \alpha\delta\bar{\beta}\gamma)}{(E_{gm}^2 - \hbar^2\omega^2)E_{gm'}(E_{gm''}^2 - \hbar^2\omega^2)} \right\} \quad (10.8) \end{aligned}$$

where

$$\bar{\alpha}\beta\gamma\delta \equiv m_{gm''}^{\alpha} d_{m''m'}^{\beta} d_{m'm}^{\gamma} d_{mg}^{\delta}.$$

There will be a further nonlinear contribution to the angle of rotation that is temperature-dependent, arising from the orientational anisotropy induced by the intense beam itself. We must therefore evaluate the Boltzmann average  $\overline{\text{Im } \mathcal{R}_{21}(\omega)}$  corresponding to optically active scattering from molecules .

that have been oriented through electric dipole scattering (Figure 10.3). The required average is obtained from (8.22)

$$+ 7 \text{ other time orderings} \equiv g_m R_{21} \text{Re } R_{\pi\pi}$$

Figure 10.3. Optically active scattering from an optically oriented molecule.

and (8.29) as

$$\overline{g_m R_{21}(\omega)} \sim (1/kT) [\langle g_m R_{21} \text{Re } R_{\pi\pi} \rangle - \langle g_m R_{21} \rangle \langle \text{Re } R_{\pi\pi} \rangle] \quad (10.9)$$

which becomes, using (8.30), (10.3), and (10.5),

$$\begin{aligned} \overline{g_m R_{21}(\omega)} &\sim (E_0^2/kT)(2\pi\hbar\omega/V) [\langle p_i(\epsilon_1\epsilon_1 + \epsilon_2\epsilon_2) \alpha(\omega) : \epsilon_1\epsilon_1 \rangle \\ &\quad - \langle p_i(\epsilon_1\epsilon_1 + \epsilon_2\epsilon_2) \rangle \langle \alpha(\omega) : \epsilon_1\epsilon_1 \rangle] \\ &= -(E_0^2/45kT)(2\pi\hbar\omega/V) [3\rho_{\alpha\beta} \alpha_{\alpha\beta}(\omega) - \rho_{\alpha\alpha} \alpha_{\beta\beta}(\omega)]. \end{aligned} \quad (10.10)$$

This result has been obtained by assuming that the light beam is plane polarized along the  $\epsilon_1$ -axis. However, the beam rotates as it passes through the medium and so the azimuth of the orienting photon changes. But (10.10) is still applicable if it is understood that the coordinate axes are rotated after each scattering event so that an initial azimuth of zero is maintained at each subsequent scattering event (c.f. the rotation of the polarization ellipse).

The complete expression for the angle of rotation is now

$$\Delta \theta = - (2\pi^2 N / 3\lambda) \left\{ \rho_{\alpha\alpha} + (E_0^2 / 5) [3\sigma_{\alpha\beta\alpha\beta}(\omega) - \sigma_{\alpha\alpha\beta\beta}(\omega)] \right. \\ \left. + (E_0^2 / 30kT) [3\rho_{\alpha\beta}\alpha_{\alpha\beta}(\omega) - \rho_{\alpha\alpha}\alpha_{\beta\beta}(\omega)] \right\}. \quad (10.11)$$

A study of the intensity-dependence of optical rotation could provide additional structural information. Different transitions contribute to  $\rho$  than to  $\sigma$ , and it is quite possible that a molecule in which  $\rho$  is very small will possess a  $\sigma$  that is large. Also, the excited states of a chromophore will extend over much of an optically active molecule, and as excited states contribute strongly to  $\sigma$  its study will provide information about them. The intensity-dependent effect could be enhanced by approaching electronic excitation frequencies: double photon resonances would be of particular interest. We refer to Woolley [58], and Atkins and Woolley [59] for further discussion of the consequences of (10.11).

There is one important reservation in all considerations of the practical application of intensity-dependent optical rotation to chemistry, namely that the beam will always have a slight ellipticity, which would become large near absorption bands due to circular dichroism. Consequently, at the intensities required to produce observable effects, one would expect an appreciable intensity-dependent rotation of the polarization ellipse (Section 9.4), so perhaps intensity-dependent optical

rotation could never be observed.

Notice that a static analogue of intensity-dependent optical rotation could be obtained by applying a static electric field across an optically active solution, preferably along the plane of polarization of the incident beam so that no Kerr-ellipticity would arise. In addition to the static analogues of the temperature-dependent and hyperpolarizability terms in (10.11), there would be further terms containing the permanent electric dipole moment of the molecule. In fact Tinoco has investigated this effect [60], but has not discussed the hyperpolarizability contribution.

# 11

## BIREFRINGENCE INDUCED BY MAGNETIC FIELDS

### 11.1. INTRODUCTION

All of the electrically induced birefringence phenomena discussed in Chapter 9 have magnetic analogues. For example, the Cotton-Mouton and optical Cotton-Mouton effects parallel the Kerr and optical Kerr effects. One point of difference, however, is that if the ground state of the molecule is a spin or an orbital multiplet, there will be a first order Zeeman correction to the energy. We shall not reproduce here the explicit expressions for the polarization changes since they are basically the same as their electrical equivalents. Atkins and Miller [33,34] have considered a number of these phenomena from the photon scattering viewpoint.

### 11.2. THE FARADAY EFFECT

There is one important magnetically induced birefringence effect having no electric analogue, and that is the Faraday effect. This is observed for all molecules when a plane

polarized beam of light suffers a rotation on passing through a material subjected to a magnetic field in a direction parallel to the propagation direction. The actual calculation presented here was first performed by Atkins and Miller [33], but it is being included for the sake of completeness.

Equation (8.21) is relevant, with the R-matrix elements interpreted in the light of the present physical situation. The static magnetic field must be incorporated in an ad-hoc manner (Figure 11.1), and it will transpire that, with the magnetic field along the  $\hat{\mathbf{k}}$ -axis and with the photon scattering effected from the optically inactive molecule by electric dipole interactions only, the terms  $\text{Im } \mathcal{R}_2$  and  $\text{Im } \mathcal{R}_{21B}$  are the only ones to provide non-zero spatial averages. It will also be seen that only terms linear in  $\mathbf{B}$  will contribute.

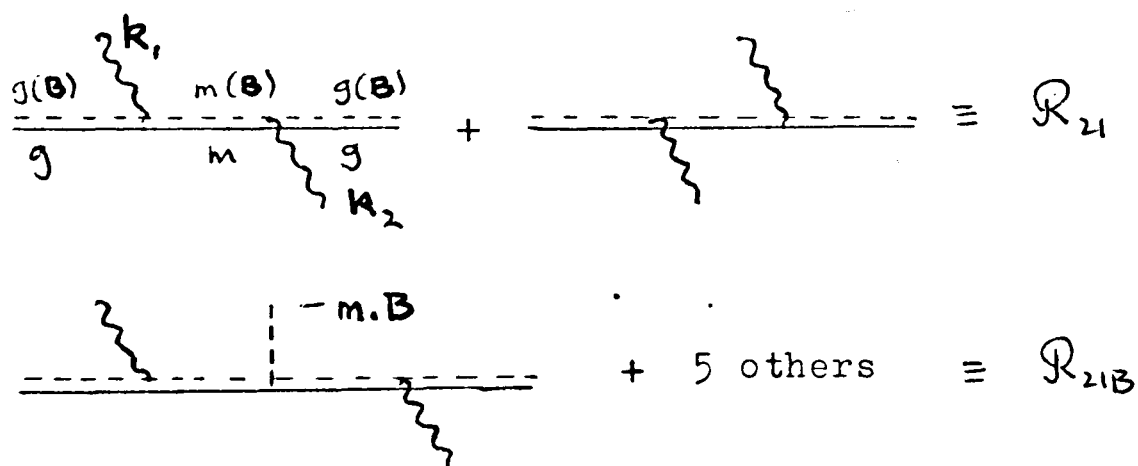


Figure 11.1. Contributions to the Faraday effect.

From these diagrams, using the methods of Section 5.5, the R-matrix elements are found to be

$$\begin{aligned}
R_{21} + R_{21B} = & (2\pi\hbar\omega/V) \sum_{m,m'} \left\{ \frac{d_{gm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_1}{E_{gm} + \hbar\omega} + \frac{d_{gm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2}{E_{gm} - \hbar\omega} \right. \\
& + B \cdot \left[ \frac{d_{gm'} \cdot \epsilon_2 m_{m'm} d_{mg} \cdot \epsilon_1}{(E_{gm} + \hbar\omega)(E_{gm'} + \hbar\omega)} + \frac{d_{gm'} \cdot \epsilon_1 m_{m'm} d_{mg} \cdot \epsilon_2}{(E_{gm} - \hbar\omega)(E_{gm'} - \hbar\omega)} \right. \\
& + \frac{d_{gm'} \cdot \epsilon_2 d_{m'm} \cdot \epsilon_1 m_{mg}}{E_{gm}(E_{gm'} + \hbar\omega)} + \frac{d_{gm'} \cdot \epsilon_1 d_{m'm} \cdot \epsilon_2 m_{mg}}{E_{gm}(E_{gm'} - \hbar\omega)} \\
& \left. \left. + \frac{m_{gm'} d_{m'm} \cdot \epsilon_2 d_{mg} \cdot \epsilon_1}{(E_{gm} + \hbar\omega) E_{gm'}} + \frac{m_{gm'} d_{m'm} \cdot \epsilon_1 d_{mg} \cdot \epsilon_2}{(E_{gm} - \hbar\omega) E_{gm'}} \right] \right\} \quad (11.1)
\end{aligned}$$

with Zeeman modifications to the energies and wavefunctions implied. The first order Zeeman energy may be introduced into the first two terms by writing

$$\begin{aligned}
E_{gm} &= E_{gm}^0 + \langle g | \mu \cdot B | g \rangle - \langle m | \mu \cdot B | m \rangle \\
&\equiv E_{gm}^0 + (\mu_g - \mu_m) \cdot B \quad (11.2)
\end{aligned}$$

and then by expanding the denominator:

$$(E_{gm}^2 - \hbar^2 \omega^2)^{-1} \sim (E_{gm}^{02} - \hbar^2 \omega^2)^{-1} \left\{ 1 - \frac{2(\mu_g - \mu_m) \cdot B E_{gm}^0}{(E_{gm}^{02} - \hbar^2 \omega^2)} \right\} \quad (11.3)$$

The superscript zero will henceforth be omitted from  $E_{gm}^0$ . The last six terms in (11.1) are not modified to take account of this energy shift because the resulting terms will be quadratic in the magnetic field strength and will vanish after spatial averaging.

Equation (11.1) now becomes

$$\begin{aligned}
R_{21} + R_{21B} = & -(2\pi\hbar\omega/V) \sum_{m,m'} \left\{ \right. \\
& \frac{2i\hbar\omega g_m d_{gm} \cdot e_2 d_{mg} \cdot e_1 - 2E_{gm} \text{Re} d_{gm} \cdot e_2 d_{mg} \cdot e_1}{(E_{gm}^2 - \hbar^2\omega^2)} \\
& - 2B \cdot \left[ \frac{2E_{gm}^2 (\mu_g - \mu_m) \text{Re} d_{gm} \cdot e_2 d_{mg} \cdot e_1 - 2i\hbar\omega E_{gm} (\mu_g - \mu_m) g_m d_{gm} \cdot e_2 d_{mg} \cdot e_1}{(E_{gm}^2 - \hbar^2\omega^2)} \right. \\
& + \frac{(E_{gm} E_{gm'} + \hbar^2\omega^2) \text{Re} d_{gm'} \cdot e_2 m_{m'} d_{mg} \cdot e_1 - i\hbar\omega (E_{gm} + E_{gm'}) g_m d_{gm'} \cdot e_2 m_{m'} d_{mg} \cdot e_1}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)} \\
& \left. - \frac{E_{gm} \text{Re} d_{mg} \cdot e_2 d_{m'm} \cdot e_1 m_{gm'} - i\hbar\omega g_m d_{mg} \cdot e_2 m_{m'm} d_{mg} \cdot e_1}{E_{gm} (E_{gm'}^2 - \hbar^2\omega^2)} \right] \left. \right\} \quad (11.4)
\end{aligned}$$

The Boltzmann average of (11.4) is required with  $-\mu \cdot B$  as the potential energy. We need the tensor average

$$\langle a \cdot e_\alpha b \cdot e_\gamma c \cdot e_\nu \rangle = \frac{1}{6} a \cdot b \wedge c$$

(see the Appendix). It can then be shown that the real components of (11.4) are zero [33]. In any event, it is the imaginary part of the R-matrix element that is specified in the equation for the angle of rotation, so even if the real parts did not average to zero, for example in a solid, they still would not contribute. We now obtain

$$\begin{aligned}
\overline{g_m R_{21}(\omega)} + \overline{g_m R_{21B}(\omega)} = & (2\pi\hbar\omega/V) (B\hbar\omega/3) \sum_{m,m'} \left\{ \right. \\
& \frac{g_m \mu \cdot d_{gm} \wedge d_{mg}}{kT (E_{gm}^2 - \hbar^2\omega^2)} + \frac{2E_{gm} g_m (\mu_g - \mu_m) \cdot d_{gm} \wedge d_{mg}}{(E_{gm}^2 - \hbar^2\omega^2)^2}
\end{aligned}$$

$$\left. + \frac{(E_{g,m} + E_{g,m'}) g_m m_{m'}. d_{g,m'} \wedge d_{mg}}{(E_{g,m}^2 - \hbar^2 \omega^2)(E_{g,m'}^2 - \hbar^2 \omega^2)} + \frac{2 g_m m_{g,m'}. d_{mg} \wedge d_{m'm}}{E_{g,m'}(E_{g,m}^2 - \hbar^2 \omega^2)} \right\}. \quad (11.5)$$

Since

$$g_m m_{m'}. d_{g,m'} \wedge d_{mg} = g_m m_{mm'}. d_{g,m} \wedge d_{m'g}, \quad (11.6)$$

then if

$$E_{mm'} = E_{g,m'} - E_{g,m},$$

it is simple to show that

$$\sum_{m,m'} \frac{g_m m_{m'}. d_{g,m'} \wedge d_{mg} (E_{g,m} + E_{g,m'})}{(E_{g,m}^2 - \hbar^2 \omega^2)(E_{g,m'}^2 - \hbar^2 \omega^2)} = 2 \sum_{m,m'} \frac{g_m m_{m'}. d_{g,m'} \wedge d_{mg}}{(E_{g,m}^2 - \hbar^2 \omega^2) E_{mm'}}. \quad (11.7)$$

The angle of rotation is finally

$$\begin{aligned} \Delta\theta = (4\pi^2 N/3\lambda)(B\hbar\omega) \sum_{m,m'} \left\{ \frac{g_m \mu. d_{g,m} \wedge d_{mg}}{kT(E_{g,m}^2 - \hbar^2 \omega^2)} + \frac{2E_{g,m} g_m (\mu_g - \mu_m). d_{g,m} \wedge d_{mg}}{(E_{g,m}^2 - \hbar^2 \omega^2)} \right. \\ \left. + \frac{2 g_m m_{m'}. d_{g,m'} \wedge d_{mg}}{(E_{g,m}^2 - \hbar^2 \omega^2) E_{mm'}} + \frac{2 g_m m_{g,m'}. d_{mg} \wedge d_{m'm}}{E_{g,m'}(E_{g,m}^2 - \hbar^2 \omega^2)} \right\} \quad (11.8) \end{aligned}$$

for  $N$  molecules per unit volume and unit path length. The first two terms disappear if the ground state is not degenerate for then the directions of  $d_{g,m}$  and  $d_{mg}$  are necessarily parallel. We refer to Buckingham and Stephens [61] for a discussion of the consequences of this equation.

It was seen at the end of Section 10.3 that the application of a static field in any direction would, for optically active molecules only, provide an additional contribution to the angle of rotation that was quadratically dependent on the static

field strength. Consequently if the Faraday experiment were performed on an optically active molecule, there would be an additional contribution to the rotation angle quadratically dependent on the static magnetic field strength. The calculation of the corresponding angle of rotation is similar to that for nonlinear optical rotation, with the addition of terms containing the permanent magnetic dipole moment of the molecule. Atkins and Miller [33] have performed the calculation explicitly.

The direct optical analogue of the Faraday effect is the interaction of the molecule with the magnetic vector of an intense beam propagating at right angles to the direction of the measuring beam. But the Faraday rotation is linear in  $\mathbf{B}$  so there will be no optical analogue because the time average of  $\mathbf{B}(\omega)$  is zero.

### 11.3. OPTICALLY INDUCED MAGNETIZATION

The inverse Faraday effect occurs when a circularly polarized light beam passes through a transparent medium and induces a magnetic moment in the sample. Atkins and Miller [34] have calculated this optically induced magnetization by considering the perturbation of the molecules by a beam of elliptically polarized photons. They then suggest that an intense circularly polarized light beam collinear with a plane polarized measuring beam could induce a magnetization that would cause the measuring beam to rotate as in the Faraday effect: this they call the

optical Faraday effect.

The Optical Faraday rotation would be determined by

$$\delta\theta = (L/\hbar c)(g_m R_{z1} + g_m R_{z\pi, 1\pi}) \quad (11.9)$$

where we have incorporated the magnetizing field, with polarization  $\pi$ , into the hyperpolarizability term. The molecules are optically inactive, so electric dipole interactions only are involved. The temperature-dependent contribution that arises from an optically oriented molecule is given by

$$g_m R_{z1}(\omega) \sim (1/kT) \langle g_m R_{z1} R_{\pi\pi} \rangle$$

and this will not necessarily be zero if the presence of degenerate states is admitted, for then terms containing imaginary R-matrix elements can be extracted from  $\text{Re} R_{\pi\pi}$ . We refer to [34] for explicit calculations of these R-matrix elements.

# **PART THREE**

## **Nonforward Scattering**

# 12

## NONFORWARD SCATTERING OF A SINGLE PHOTON

### 12.1. INTRODUCTION

There is a fundamental distinction between forward and nonforward scattering. In the former case the component scattered into the forward direction interferes with the transmitted beam, whereas this cannot occur in nonforward scattering. Furthermore, there is no phase difference introduced between the waves scattered into the forward direction by different molecules, so birefringence effects depend on the molecular density because the amplitudes of the individual forward scattered waves must be summed. In contrast, the phases of waves scattered into any nonforward direction, other than anti-parallel to the incident beam, from randomly distributed molecules in a fluid, are incoherent. Therefore the intensities of the individual waves are summed so that the polarization of the nonforward scattered beam is independent of the sample density.

Classical discussions of the polarization of light scattered away from the forward direction by molecules can be found

in a number of sources [7,62], but quantum mechanical treatments seem to have been confined to the scattering of photons by free electrons [63]. This chapter derives largely from the quantum mechanical discussion by Atkins and Barron [64].

## 12.2. THE MASTER EQUATIONS FOR NONFORWARD SCATTERING

Since the S-matrix can be decomposed into a unit matrix and a reaction matrix (5.9), wherever  $S_{fi}$  occurs in the master equations (6.4) and (6.9) for the state vector and density matrix of the nonforward scattered beam it may be replaced by

$$S_{fi} \rightarrow -2\pi i \delta(E_f - E_i) R_{fi}.$$

The R-operator will occur in a mixed  $(\mathbf{e}^f; \mathbf{e}^i)$ -representation; but the ensuing difficulties are usually avoided by defining  $\mathbf{e}_1$  and  $\mathbf{e}_2$  to be perpendicular and parallel, respectively, to the scattering plane. General equations can then be obtained in a relatively simple manner for the polarization of the scattered beam, but the evaluation of the R-matrix elements becomes rather complicated. In view of this we shall adopt an alternative approach by rewriting (6.4) and (6.9) in the pure  $\mathbf{e}^i$ -representation, thereby increasing the complexity of the general equations, but facilitating the computation of the specified elements of the R-matrix. The necessary transformation is effected as follows:

$$\begin{aligned}
|k^f; \epsilon_\mu^f\rangle &\equiv |k^f \epsilon_3^f, \epsilon_\mu^f\rangle \\
&= \sum_{\nu} |k^f \epsilon_3^f, \epsilon_\nu^i\rangle \langle \epsilon_\nu^i | \epsilon_\mu^f\rangle \\
&= \sum_{\nu, \nu'} |k^f \epsilon_{\nu'}^i, \epsilon_\nu^i\rangle \langle \epsilon_\nu^i | \epsilon_\mu^f\rangle \langle \epsilon_{\nu'}^i | \epsilon_3^f\rangle \\
&\equiv \sum_{\nu, \nu'} |k^f \epsilon_{\nu'}^i, \epsilon_\nu^i\rangle b_{\nu\mu}^{if} b_{\nu'3}^{if}
\end{aligned} \tag{12.1}$$

with  $\mu \neq 3, \nu' \neq \nu$ , and

$$b_{\nu\mu}^{if} \equiv \langle \epsilon_\nu^i | \epsilon_\mu^f \rangle. \tag{12.2}$$

These transformation coefficients may be determined by reference to Figure 12.1:

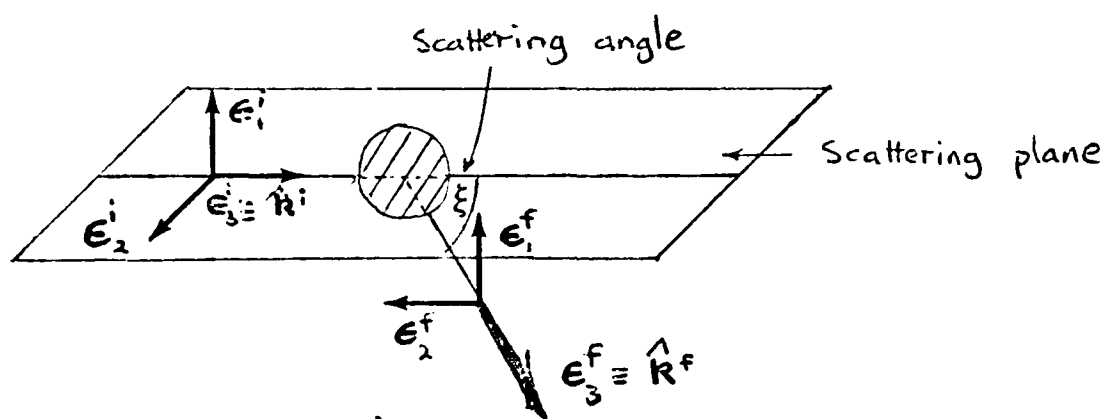


Figure 12.1. The system of unit vectors that specify nonforward scattering.

$$\begin{aligned}
b_{11}^{if} = b_{11}^{fi} = 1 \quad ; \quad b_{12}^{if} = b_{13}^{if} = b_{21}^{fi} = b_{31}^{fi} = 0 \\
b_{22}^{if} = b_{33}^{if} = \cos \xi \quad ; \quad b_{23}^{if} = -b_{32}^{if} = \sin \xi .
\end{aligned} \tag{12.3}$$

The transversality conditions  $\mu \neq 3$  and  $v \neq v'$  are absorbed into (12.1) most succinctly by defining the (real) symbol

$$\begin{pmatrix} v & \mu \\ v' & \mu' \end{pmatrix}^{if} \equiv b_{v\mu}^{if} b_{v'\mu'}^{if} (1 - \delta_{\mu\mu'}) (1 - \delta_{vv'}) , \quad (12.4)$$

which disappears if any column has the same elements. It possesses the following useful symmetry properties:

$$\begin{pmatrix} v & \mu \\ v' & \mu' \end{pmatrix}^{if} = \begin{pmatrix} v' & \mu' \\ v & \mu \end{pmatrix}^{if} = \begin{pmatrix} \mu & v \\ \mu' & v' \end{pmatrix}^{if} . \quad (12.5)$$

Then (12.1) can be written

$$|k^f; \epsilon_\mu^f\rangle = \sum_{v,v'} |k^f \epsilon_{v'}^i, \epsilon_v^i\rangle \begin{pmatrix} v & \mu \\ v' & 3 \end{pmatrix}^{if} . \quad (12.6)$$

Only photons Rayleigh-scattered along  $\hat{k}^d$  are detected and so the detector shape function may be idealized by the expression

$$A(k^d - k) = \delta(k^d - k^i) \delta(\hat{k}^d \cdot \epsilon_3^f - 1). \quad (12.7)$$

Using the last two equations, the polarization density matrix for the nonforward scattered photon may be obtained from (6.9) as

$$\rho_{\sigma\tau}^d = (\text{num})_{\sigma\tau} / (\text{den}) \quad (12.8)$$

where

$$\begin{aligned} (\text{num})_{\sigma\tau} = \sum_{v,v',v,v',\lambda,\mu} \begin{pmatrix} \sigma & v \\ 3 & v' \end{pmatrix}^{di} \langle g; k^i \epsilon_{v'}^i, \epsilon_v^i | R | g; k^i \epsilon_\lambda^i \rangle \rho_{\lambda\mu}^i \\ \times \langle g; k^i \epsilon_\mu^i | R^\dagger | g; k^i \epsilon_{v'}^i, \epsilon_v^i \rangle \begin{pmatrix} v & \tau \\ v' & 3 \end{pmatrix}^{id} \end{aligned} \quad (12.9)$$

and

$$(\text{den}) = \sum_{\gamma} (\text{num})_{\gamma\gamma} . \quad (12.10)$$

The formulation could be extended to Raman scattering by including the complete set of vibrational and rotational states in the molecular density matrix, and then specifying the particular Stokes or anti-Stokes frequencies of interest in the detector shape function.

The numerator and denominator of  $\rho_{\sigma\tau}$  may be evaluated quite simply. We first define the quantity

$$\begin{aligned} \langle p(q) \| p'(q') \rangle &\equiv \sum_{\lambda, \mu} \langle g; k^i \epsilon_q^i, \epsilon_p^i | R | g; k^i \epsilon_3^i, \epsilon_\lambda^i \rangle \rho_{\lambda\mu}^i \\ &\times \langle g; k^i \epsilon_3^i, \epsilon_\mu^i | R^\dagger | g; k^i \epsilon_{q'}^i, \epsilon_{p'}^i \rangle \end{aligned} \quad (12.11)$$

and then, with the help of (12.3) and (12.4), deduce that

$$\begin{aligned} (\text{num})_{\sigma\tau} &= \begin{pmatrix} \sigma & 1 \\ 3 & 3 \end{pmatrix}^{di} \langle 1(3) \| 1(3) \rangle \begin{pmatrix} 1 & \tau \\ 3 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 1 \\ 3 & 3 \end{pmatrix}^{di} \langle 1(3) \| 2(3) \rangle \begin{pmatrix} 2 & \tau \\ 3 & 3 \end{pmatrix}^{id} \\ &+ \begin{pmatrix} \sigma & 2 \\ 3 & 3 \end{pmatrix}^{di} \langle 2(3) \| 1(3) \rangle \begin{pmatrix} 1 & \tau \\ 2 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 2 \\ 3 & 3 \end{pmatrix}^{di} \langle 2(3) \| 2(3) \rangle \begin{pmatrix} 2 & \tau \\ 3 & 3 \end{pmatrix}^{id} \\ &+ \begin{pmatrix} \sigma & 1 \\ 3 & 2 \end{pmatrix}^{di} \langle 1(2) \| 1(3) \rangle \begin{pmatrix} 1 & \tau \\ 3 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 1 \\ 3 & 3 \end{pmatrix}^{di} \langle 1(3) \| 1(2) \rangle \begin{pmatrix} 1 & \tau \\ 2 & 3 \end{pmatrix}^{id} \\ &+ \begin{pmatrix} \sigma & 1 \\ 3 & 2 \end{pmatrix}^{di} \langle 1(2) \| 1(2) \rangle \begin{pmatrix} 1 & \tau \\ 2 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 2 \\ 3 & 3 \end{pmatrix}^{di} \langle 2(3) \| 1(2) \rangle \begin{pmatrix} 1 & \tau \\ 2 & 3 \end{pmatrix}^{id} \\ &+ \begin{pmatrix} \sigma & 1 \\ 3 & 2 \end{pmatrix}^{di} \langle 1(2) \| 2(3) \rangle \begin{pmatrix} 2 & \tau \\ 3 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 3 \\ 3 & 2 \end{pmatrix}^{di} \langle 3(2) \| 3(2) \rangle \begin{pmatrix} 3 & \tau \\ 2 & 3 \end{pmatrix}^{id} \\ &+ \begin{pmatrix} \sigma & 3 \\ 3 & 2 \end{pmatrix}^{di} \langle 3(2) \| 2(3) \rangle \begin{pmatrix} 2 & \tau \\ 3 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 2 \\ 3 & 3 \end{pmatrix}^{di} \langle 2(3) \| 3(2) \rangle \begin{pmatrix} 3 & \tau \\ 2 & 3 \end{pmatrix}^{id} \\ &+ \begin{pmatrix} \sigma & 3 \\ 3 & 2 \end{pmatrix}^{di} \langle 3(2) \| 1(3) \rangle \begin{pmatrix} 1 & \tau \\ 3 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 1 \\ 3 & 3 \end{pmatrix}^{di} \langle 1(3) \| 3(2) \rangle \begin{pmatrix} 3 & \tau \\ 2 & 3 \end{pmatrix}^{id} \end{aligned}$$

$$\begin{aligned}
& + \begin{pmatrix} \sigma & 3 \\ 3 & 2 \end{pmatrix}^{di} \langle 3(2) \| 1(2) \rangle \begin{pmatrix} 1 & 1 \\ 2 & 3 \end{pmatrix}^{id} + \begin{pmatrix} \sigma & 1 \\ 3 & 2 \end{pmatrix}^{di} \langle 1(2) \| 3(2) \rangle \begin{pmatrix} 3 & 1 \\ 2 & 3 \end{pmatrix}^{id} \\
& = \delta_{\sigma 1} \delta_{\tau 1} \{ \langle 1(3) \| 1(3) \rangle \cos^2 \xi + \langle 1(2) \| 1(3) \rangle \cos \xi \sin \xi \\
& \quad + \langle 1(3) \| 1(2) \rangle \cos \xi \sin \xi + \langle 1(2) \| 1(2) \rangle \sin^2 \xi \} \\
& + \delta_{\sigma 2} \delta_{\tau 1} \{ \langle 2(3) \| 1(3) \rangle \cos^3 \xi + \langle 2(3) \| 1(2) \rangle \cos^2 \xi \sin \xi \\
& \quad - \langle 3(2) \| 1(3) \rangle \cos \xi \sin^2 \xi - \langle 3(2) \| 1(2) \rangle \sin^3 \xi \} \\
& + \delta_{\sigma 1} \delta_{\tau 2} \{ \langle 1(3) \| 2(3) \rangle \cos^3 \xi + \langle 1(2) \| 2(3) \rangle \cos^2 \xi \sin \xi \\
& \quad - \langle 1(3) \| 3(2) \rangle \cos \xi \sin^2 \xi - \langle 1(2) \| 3(2) \rangle \sin^3 \xi \} \\
& - \\
& + \delta_{\sigma 2} \delta_{\tau 2} \{ \langle 2(3) \| 2(3) \rangle \cos^4 \xi + \langle 3(2) \| 3(2) \rangle \sin^4 \xi \\
& \quad - \langle 3(2) \| 2(3) \rangle \cos^2 \xi \sin^2 \xi - \langle 2(3) \| 3(2) \rangle \cos^2 \xi \sin^2 \xi \} \quad (12.12)
\end{aligned}$$

Using this result with (12.10) we have

$$\begin{aligned}
(\text{den}) & = \langle 1(3) \| 1(3) \rangle \cos^2 \xi + \langle 1(2) \| 1(3) \rangle \sin \xi \cos \xi \\
& \quad + \langle 1(2) \| 1(2) \rangle \sin^2 \xi + \langle 1(3) \| 1(2) \rangle \sin \xi \cos \xi \\
& \quad + \langle 2(3) \| 2(3) \rangle \cos^4 \xi + \langle 3(2) \| 3(2) \rangle \sin^4 \xi \\
& \quad - \langle 2(3) \| 3(2) \rangle \sin^2 \xi \cos^2 \xi - \langle 3(2) \| 2(3) \rangle \sin^2 \xi \cos^2 \xi. \quad (12.13)
\end{aligned}$$

From these equations it is possible to calculate the elements of the density matrix, and therefore the polarization characteristics, of the light beam scattered by a molecule into

any nonforward direction, for an incident beam with arbitrary ellipticity, azimuth, and degree of polarization. Several specific situations will now be considered.

### 12.3. RAYLEIGH SCATTERING AT $90^\circ$

When the scattering angle  $\xi = \pi/2$ , the elements of the density matrix for Rayleigh-scattered photons may be obtained from

$$\begin{aligned} \rho_{\sigma_1}^{\pi/2} = & \{ \delta_{\sigma_1} \delta_{\tau_1} \langle 1(z) \| 1(z) \rangle - \delta_{\sigma_1} \delta_{\tau_2} \langle 1(z) \| 3(z) \rangle - \delta_{\sigma_2} \delta_{\tau_1} \langle 3(z) \| 1(z) \rangle \\ & + \delta_{\sigma_2} \delta_{\tau_2} \langle 3(z) \| 3(z) \rangle \} \{ \langle 1(z) \| 1(z) \rangle + \langle 3(z) \| 3(z) \rangle \}^{-1}. \end{aligned} \quad (12.14)$$

Thus

$$\begin{aligned} \rho_{11}^{\pi/2} & \equiv \frac{1}{2} (1 + \cos 2e^{\pi/2} \cos 2\eta^{\pi/2}) \\ & = \frac{\langle 1(z) \| 1(z) \rangle}{\langle 1(z) \| 1(z) \rangle + \langle 3(z) \| 3(z) \rangle}, \text{ etc.} \end{aligned}$$

The required polarization parameters are therefore given by

$$\sin 2\eta^{\pi/2} = i \left\{ \frac{\langle 1(z) \| 3(z) \rangle - \langle 3(z) \| 1(z) \rangle}{\langle 1(z) \| 1(z) \rangle + \langle 3(z) \| 3(z) \rangle} \right\} \quad (12.15)$$

$$\tan 2e^{\pi/2} = - \left\{ \frac{\langle 1(z) \| 3(z) \rangle + \langle 3(z) \| 1(z) \rangle}{\langle 1(z) \| 1(z) \rangle - \langle 3(z) \| 3(z) \rangle} \right\}. \quad (12.16)$$

In the absence of absorption,  $R$  is Hermitian and so, for example,

$$\begin{aligned}
\langle 1(z) || 3(z) \rangle + \langle 3(z) || 1(z) \rangle &= \sum_{\lambda, \mu} \left\{ R_{1(z)\lambda(3)} \rho_{\lambda\mu}^i R_{\mu(3)3(z)}^+ \right. \\
&\quad \left. + R_{3(z)\lambda(3)} \rho_{\lambda\mu}^i R_{\mu(3)1(z)}^+ \right\} \\
&= 2 \operatorname{Re} \sum_{\lambda, \mu} R_{1(z)\lambda(3)} \rho_{\lambda\mu}^i R_{\mu(3)3(z)}^+
\end{aligned} \tag{12.17}$$

where

$$R_{p(q)p'(q')} \equiv \langle g; k^i \epsilon_{q'}^i, \epsilon_p^i | R | g; k^i \epsilon_q^i, \epsilon_{p'}^i \rangle. \tag{12.18}$$

The terms in (12.15) and (12.16) can now be expanded as follows:

$$\begin{aligned}
\langle 1(z) || 3(z) \rangle + \langle 3(z) || 1(z) \rangle &= \\
&\operatorname{Re} \left\{ R_{1(z)1(3)} R_{1(3)3(z)} (1 + \cos 2\eta^i \cos 2\theta^i) \right. \\
&\quad + R_{1(z)1(3)} R_{2(3)3(z)} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\
&\quad + R_{1(z)2(3)} R_{1(3)3(z)} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\
&\quad \left. + R_{1(z)2(3)} R_{2(3)3(z)} (1 - \cos 2\eta^i \cos 2\theta^i) \right\}
\end{aligned} \tag{12.19}$$

$$\begin{aligned}
\langle 1(z) || 3(z) \rangle - \langle 3(z) || 1(z) \rangle &= \\
&i g_m \left\{ R_{1(z)1(3)} R_{1(3)3(z)} (1 + \cos 2\eta^i \cos 2\theta^i) \right. \\
&\quad + R_{1(z)1(3)} R_{2(3)3(z)} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\
&\quad + R_{1(z)2(3)} R_{1(3)3(z)} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\
&\quad \left. + R_{1(z)2(3)} R_{2(3)3(z)} (1 - \cos 2\eta^i \cos 2\theta^i) \right\}
\end{aligned} \tag{12.20}$$

$$\langle 1(2) || 1(2) \rangle \pm \langle 3(2) || 3(2) \rangle =$$

$$\begin{aligned} & \frac{1}{2} (R_{1(2)1(3)} R_{1(3)1(2)} \pm R_{3(2)1(3)} R_{1(3)3(2)}) (1 + \cos 2\theta^i \cos 2\eta^i) \\ & + \frac{1}{2} (R_{1(2)1(3)} R_{2(3)1(2)} \pm R_{3(2)1(3)} R_{2(3)3(2)}) (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\ & + \frac{1}{2} (R_{1(2)2(3)} R_{1(3)1(2)} \pm R_{3(2)2(3)} R_{1(3)3(2)}) (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\ & + \frac{1}{2} (R_{1(2)2(3)} R_{2(3)1(2)} \pm R_{3(2)2(3)} R_{2(3)3(2)}) (1 - \cos 2\theta^i \cos 2\eta^i). \quad (12.21) \end{aligned}$$

The parallel expressions for the absorptive situation, when  $R$  is no longer Hermitian, are more complex but can be written just as easily if required.

Explicit expressions for the  $R$ -matrix elements will now be derived using diagrammatic perturbation theory (Section 5.5). To facilitate this, the following expansion is required:

$$R_{ab} R_{cd} = \text{Re} R_{ab} \text{Re} R_{cd} - \text{Im} R_{ab} \text{Im} R_{cd} + i (\text{Re} R_{ab} \text{Im} R_{cd} + \text{Im} R_{ab} \text{Re} R_{cd}). \quad (12.22)$$

Scattering from an optically inactive molecule will involve only electric dipole interactions; we ignore contributions from electric quadrupole interactions because such terms are very small and give non-zero spatial averages in the same situations as terms containing just electric dipole interactions. The predominant contribution comes, therefore, from the diagrams in Figure 12.2, and so the appropriate  $R$ -matrix element is

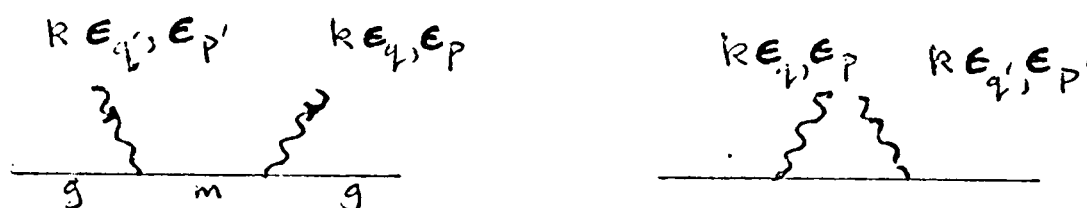


Figure 12.2. The electric dipole scattering of a photon with polarization  $\epsilon_{p'}$  and propagation direction  $\epsilon_{q'}$  into a photon with polarization  $\epsilon_p$  and propagating along  $\epsilon_q$ .

$$R_{p(q)p'(q')} = (2\pi\hbar\omega/V) \sum_m (E_{gm}^2 - \hbar^2\omega^2)^{-1} \{ E_{gm} [d_{gm} \cdot \epsilon_{p'} d_{mg} \cdot \epsilon_p + d_{gm} \cdot \epsilon_p d_{mg} \cdot \epsilon_{p'}] + \hbar\omega [d_{gm} \cdot \epsilon_{p'} d_{mg} \cdot \epsilon_p - d_{gm} \cdot \epsilon_p d_{mg} \cdot \epsilon_{p'}] \}. \quad (12.23)$$

In terms of the polarizability tensor  $\alpha(\omega)$  defined in (8.31), this equation becomes

$$R_{p(q)p'(q')} = (2\pi\hbar\omega/V) \alpha(\omega) : \epsilon_{p'} \epsilon_p. \quad (12.24)$$

Imaginary R-matrix elements will arise if the molecule is optically active, for the absence of particular symmetry elements permits interference between electric and magnetic dipole interactions. The relevant diagrams are shown in Figure 12.3, and the corresponding R-matrix element is



Figure 12.3. Diagrams which contribute to optically active nonforward scattering.

$$\begin{aligned}
R_{P(q)P'(q')} &= (2\pi\hbar\omega/v) \sum_m \left\{ \frac{m_{gm} \cdot \mathbf{E}_q \wedge \mathbf{E}_P d_{mg} \cdot \mathbf{E}_{P'}}{E_{gm} + \hbar\omega} \right. \\
&\quad + \frac{d_{gm} \cdot \mathbf{E}_{P'} m_{mg} \cdot \mathbf{E}_q \wedge \mathbf{E}_P}{E_{gm} - \hbar\omega} + \frac{d_{gm} \cdot \mathbf{E}_P m_{mg} \cdot \mathbf{E}_{q'} \wedge \mathbf{E}_{P'}}{E_{gm} + \hbar\omega} \\
&\quad \left. + \frac{m_{gm} \cdot \mathbf{E}_{q'} \wedge \mathbf{E}_{P'} d_{mg} \cdot \mathbf{E}_P}{E_{gm} - \hbar\omega} \right\} \\
&= i(2\pi\hbar\omega/v) \rho : \{ \mathbf{E}_{P'} \mathbf{E}_q \wedge \mathbf{E}_P - \mathbf{E}_P \mathbf{E}_{q'} \wedge \mathbf{E}_{P'} \} \quad (12.25)
\end{aligned}$$

where  $\rho$  is the optical rotation tensor defined in (10.4).

In the absence of externally applied fields, photon scattering occurs from freely tumbling molecules if the sample is fluid, so the products  $RR$  must be averaged over all orientations of the molecule. The averages of the fourth rank tensor components listed in the Appendix are required; these are valid if the Raman rotational shifts are negligible [65].

From equations (12.15), (12.20), (12.21), (12.22), (12.24), and (12.25), it can be seen on close inspection that the ellipticity of the beam scattered at  $\xi = \pi/2$  is zero under all conditions for an optically inactive molecule because all the specified  $R$ -matrix elements disappear upon averaging, but can differ from zero if the molecule is active. The calculation of the ellipticity of the beam scattered from an optically active molecule is rather complicated for an incident beam of arbitrary polarization, so we shall first consider the case of a plane polarized incident beam with zero azimuth. Equation (12.15) then becomes

$$\sin 2\eta^{\pi/2} = - \frac{2[\operatorname{Re} R_{1(2)1(3)} \operatorname{Im} R_{1(3)3(2)} + \operatorname{Im} R_{1(2)1(3)} \operatorname{Re} R_{1(3)3(2)}]}{\operatorname{Re} R_{1(2)1(3)} \operatorname{Re} R_{1(3)1(2)} + \operatorname{Re} R_{3(2)1(3)} \operatorname{Re} R_{1(3)3(2)}} \quad (12.26)$$

The appropriate spatial averages are

$$\langle \operatorname{Re} R_{1(2)1(3)} \operatorname{Re} R_{1(3)1(2)} \rangle = (2\pi\hbar\omega/V)^2 (1/15) (\alpha_{\alpha\alpha} \alpha_{\beta\beta} + 2\alpha_{\alpha\beta} \alpha_{\alpha\beta}) \quad (12.27)$$

$$\langle \operatorname{Re} R_{3(2)1(3)} \operatorname{Re} R_{1(3)3(2)} \rangle = (2\pi\hbar\omega/V)^2 (1/30) (3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta}) \quad (12.28)$$

$$\langle \operatorname{Re} R_{1(2)1(3)} \operatorname{Im} R_{1(3)3(2)} \rangle = -(2\pi\hbar\omega/V)^2 (1/15) (\alpha_{\alpha\alpha} \rho_{\beta\beta} + 2\alpha_{\alpha\beta} \rho_{\alpha\beta}) \quad (12.29)$$

$$\langle \operatorname{Im} R_{1(2)1(3)} \operatorname{Re} R_{1(3)3(2)} \rangle = -(2\pi\hbar\omega/V)^2 (1/30) (3\alpha_{\alpha\beta} \rho_{\alpha\beta} - \alpha_{\alpha\alpha} \rho_{\beta\beta}) \quad (12.30)$$

and so

$$\sin 2\eta^{\pi/2} = \frac{2(\alpha_{\alpha\alpha} \rho_{\beta\beta} + 7\alpha_{\alpha\beta} \rho_{\alpha\beta})}{\alpha_{\alpha\alpha} \alpha_{\beta\beta} + 7\alpha_{\alpha\beta} \alpha_{\alpha\beta}} \quad (12.31)$$

Notice that if the molecule is isotropically polarizable so that

$\alpha_{\alpha\beta} = \alpha \delta_{\alpha\beta}$ , this reduces to

$$\sin 2\eta^{\pi/2} = 2\rho/\alpha \quad (12.32)$$

where  $\alpha = \frac{1}{3} \alpha_{\alpha\alpha}$  and  $\rho = \frac{1}{3} \rho_{\alpha\alpha}$  with implied summation over the repeated indices. The determination of the ellipticity of the beam would therefore provide a measure of  $\rho/\alpha$ , which is related to the ratio of the rotational strengths and the oscillator strengths for various transitions. This latter ratio is Kuhn's anisotropy factor [66].

A more general calculation for an incident beam of

arbitrary polarization yields the result that

$$\sin 2\eta^{\pi/2} = \frac{2[(13\alpha_{\alpha\beta}\rho_{\alpha\beta} - \alpha_{\alpha\alpha}\rho_{\beta\beta}) + (\alpha_{\alpha\beta}\rho_{\alpha\beta} + 3\alpha_{\alpha\alpha}\rho_{\beta\beta})\cos 2\epsilon'\cos 2\eta']}{(13\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}) + (\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta})\cos 2\epsilon'\cos 2\eta'} \quad (12.33)$$

of which (12.31) is a special case.

Equations (12.16), (12.19), (12.22), (12.24), and (12.25) show that the azimuth of the beam scattered at  $\xi = \pi/2$  is zero for optically inactive molecules. This implies that the major axis of the polarization ellipse will be perpendicular to the scattering plane, irrespective of the polarization condition of the incident beam. When the molecules are optically active, however, (12.16) contains the following term which provides a non-zero spatial average:

$$\tan 2\theta^{\pi/2} = \frac{[g_m R_{1(2)1(3)} g_m R_{2(3)3(2)} + g_m R_{1(2)2(3)} g_m R_{1(3)3(2)}] \cos 2\eta' \sin 2\epsilon'}{[\text{Re} R_{1(2)1(3)} \text{Re} R_{1(3)1(2)} - \text{Re} R_{3(2)1(3)} \text{Re} R_{1(3)3(2)}] (1 + \cos 2\epsilon' \cos 2\eta')} \quad (12.34)$$

Using

$$\langle g_m R_{1(2)1(3)} g_m R_{2(3)3(2)} \rangle = (2\pi\kappa\omega/V)^2 (1/15) (3\rho_{\alpha\beta}\rho_{\alpha\beta} - \rho_{\alpha\alpha}\rho_{\beta\beta}) \quad (12.35)$$

$$\langle g_m R_{1(2)2(3)} g_m R_{1(3)3(2)} \rangle = -(2\pi\kappa\omega/V)^2 (1/30) (7\rho_{\alpha\beta}\rho_{\alpha\beta} + \rho_{\alpha\alpha}\rho_{\beta\beta}) \quad (12.36)$$

together with (12.27) and (12.28), the azimuth becomes

$$\tan 2\theta^{\pi/2} = - \frac{2(\rho_{\alpha\beta}\rho_{\alpha\beta} + 3\rho_{\alpha\alpha}\rho_{\beta\beta}) \cos 2\eta' \sin 2\epsilon'}{(\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta}) (1 + \cos 2\epsilon' \cos 2\eta')} \quad (12.37)$$

The beam will emerge only very slightly rotated away from the

perpendicular to the scattering plane unless it is initially plane polarized parallel to the scattering plane. In this case the trigonometric quotient in the last equation is infinite:

$$\lim_{\substack{\eta \rightarrow 0 \\ \theta \rightarrow \pi/2}} \frac{\cos 2\eta \sin 2\theta}{1 + \cos 2\theta \cos 2\eta} = \lim_{\theta \rightarrow 0} \frac{\sin \theta}{1 - \cos \theta} \\ \sim \lim_{\theta \rightarrow 0} \frac{\theta}{1 - 1 + \theta^2/2} \rightarrow \infty \quad (12.38)$$

so the beam will emerge polarized at  $-\pi/4$  to the scattering plane so long as  $(\rho_{\alpha\beta} \rho_{\alpha\beta} + 3\rho_{\alpha\alpha} \rho_{\beta\beta})$  is not identically zero. We therefore obtain a method for investigating very small optical rotation angles, for rotating the plane of the incident beam will produce a beam at  $45^\circ$  to the scattering plane only if the molecules are optically active, and only when the incident beam is plane polarized parallel to the scattering plane. The rotation is independent of the sample density and so should be apparent at very low concentrations.

#### 12.4. RAYLEIGH SCATTERING NEAR THE FORWARD DIRECTION

For scattering angles other than  $90^\circ$ , both the azimuth and ellipticity will vary even for optically inactive molecules, and will depend on the polarization of the incident beam. The general equations are too complicated to be reported here, but may be extracted from the equations already given. However, the equations for a scattering angle of zero are fairly simple.

At first sight it might appear pointless to discuss Rayleigh scattering in the forward direction because it would be unobservable owing to the overwhelming preponderance of birefringent scattering. There are, however, certain nonlinear effects, such as self-focusing, that can be attributed to Rayleigh scattering very close to the forward direction, and the equations we shall derive can easily be extended to forward Raman scattering for there is then no transmitted component of the correct frequency to interfere with the forward scattered Stokes or anti-Stokes components.

Using (12.12) and (12.13), the elements of the polarization density matrix for a beam scattered at  $\xi=0$  are found from

$$P_{\sigma\tau}^0 = \{ \delta_{\sigma 1} \delta_{\tau 1} \langle 1(3) \| 1(3) \rangle + \delta_{\sigma 1} \delta_{\tau 2} \langle 1(3) \| 2(3) \rangle + \delta_{\sigma 2} \delta_{\tau 1} \langle 2(3) \| 1(3) \rangle + \delta_{\sigma 2} \delta_{\tau 2} \langle 2(3) \| 2(3) \rangle \} \{ \langle 1(3) \| 1(3) \rangle + \langle 2(3) \| 2(3) \rangle \}^{-1} \quad (12.39)$$

so that the ellipticity and azimuth are given by

$$\sin 2\eta^0 = i \left\{ \frac{\langle 2(3) \| 1(3) \rangle - \langle 1(3) \| 2(3) \rangle}{\langle 1(3) \| 1(3) \rangle + \langle 2(3) \| 2(3) \rangle} \right\} \quad (12.40)$$

$$\tan 2\theta^0 = \left\{ \frac{\langle 2(3) \| 1(3) \rangle + \langle 1(3) \| 2(3) \rangle}{\langle 1(3) \| 1(3) \rangle - \langle 2(3) \| 2(3) \rangle} \right\} \quad (12.41)$$

where

$$\begin{aligned} \langle 2(3) \| 1(3) \rangle + \langle 1(3) \| 2(3) \rangle &= \text{Re} \{ R_{21} R_{11} (1 + \cos 2\eta^i \cos 2\theta^i) + \\ &R_{21} R_{21} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) + R_{22} R_{11} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\ &+ R_{22} R_{21} (1 - \cos 2\eta^i \cos 2\theta^i) \} \end{aligned} \quad (12.42)$$

$$\begin{aligned}
\langle 1(3) \| 1(3) \rangle \pm \langle 2(3) \| 2(3) \rangle &= \frac{1}{2} (R_{11} R_{11} \pm R_{21} R_{12}) (1 + \cos 2\theta^i \cos 2\eta^i) \\
&+ \frac{1}{2} (R_{11} R_{21} \pm R_{21} R_{22}) (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\
&+ \frac{1}{2} (R_{12} R_{11} \pm R_{22} R_{12}) (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\
&+ \frac{1}{2} (R_{12} R_{21} \pm R_{22} R_{22}) (1 - \cos 2\theta^i \cos 2\eta^i)
\end{aligned} \quad (12.43)$$

$$\begin{aligned}
\langle 2(3) \| 1(3) \rangle - \langle 1(3) \| 2(3) \rangle &= i g_m \{ R_{21} R_{11} (1 + \cos 2\eta^i \cos 2\theta^i) \\
&+ R_{21} R_{21} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) + R_{22} R_{11} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\
&+ R_{22} R_{21} (1 - \cos 2\eta^i \cos 2\theta^i) \}.
\end{aligned} \quad (12.44)$$

We have omitted from the R-matrix elements the subscripts indicating the direction of propagation of the photons, for now both incident and scattered photons are moving along  $\mathbf{e}_3^i$ .

For an optically inactive molecule in a fluid we now obtain

$$\begin{aligned}
\sin 2\eta^i &= \left\{ \frac{\operatorname{Re} R_{22} \operatorname{Re} R_{11} - \operatorname{Re} R_{21} \operatorname{Re} R_{21}}{\operatorname{Re} R_{11} \operatorname{Re} R_{11} + \operatorname{Re} R_{21} \operatorname{Re} R_{21}} \right\} \sin 2\eta^i \\
&= \left\{ \frac{5(\alpha_{\alpha\alpha} \alpha_{\beta\beta} - \alpha_{\alpha\beta} \alpha_{\alpha\beta})}{(\alpha_{\alpha\alpha} \alpha_{\beta\beta} + 7\alpha_{\alpha\beta} \alpha_{\alpha\beta})} \right\} \sin 2\eta^i
\end{aligned} \quad (12.45)$$

$$\begin{aligned}
\tan 2\theta^i &= \left\{ \frac{\operatorname{Re} R_{22} \operatorname{Re} R_{11} + \operatorname{Re} R_{21} \operatorname{Re} R_{21}}{\operatorname{Re} R_{11} \operatorname{Re} R_{11} - \operatorname{Re} R_{21} \operatorname{Re} R_{21}} \right\} \tan 2\theta^i \\
&= \left\{ \frac{(3\alpha_{\alpha\alpha} \alpha_{\beta\beta} + \alpha_{\alpha\beta} \alpha_{\alpha\beta})}{(3\alpha_{\alpha\alpha} \alpha_{\beta\beta} + \alpha_{\alpha\beta} \alpha_{\alpha\beta})} \right\} \tan 2\theta^i = \tan 2\theta^i.
\end{aligned} \quad (12.46)$$

Thus the azimuth of the forward Rayleigh scattered beam is the same as that of the incident beam and is independent of the molecular polarizability characteristics. On the other hand, the ellipticity does depend on the nature of the molecule, unless  $\alpha$  is isotropic, when the ellipticities of the incident and forward Rayleigh scattered beams are the same.

If the molecule is optically active, there will be a contribution to the ellipticity that is independent of the polarization of the incident beam. Specifically, the term

$$\frac{2(3\alpha_{xx} p_{\beta\beta} + \alpha_{\alpha\beta} p_{\alpha\beta})}{(\alpha_{xx} \alpha_{\beta\beta} + 7\alpha_{\alpha\beta} \alpha_{\alpha\beta})} \quad (12.47)$$

must be added to (12.45). If the molecule is isotropic, this contribution reduces to  $2\rho/\alpha$ , which is the same as the result obtained for  $90^\circ$  scattering.

It is possible to understand in semi-classical terms why the light that is Rayleigh scattered from an optically active molecule should be elliptical. The scattered beam does not interfere with the transmitted beam, so the resultant is required only of the scattered electric field vector that arises from the oscillating electric dipole moment induced by the incident electric field vector, with the electric field vector, plane polarized perpendicular to the first, that arises from the oscillating electric dipole moment induced by the time derivative of the incident magnetic field vector. These two components will be

$\pi/2$  out of phase, so the resultant is elliptically polarized but not rotated (Figure 12.4).

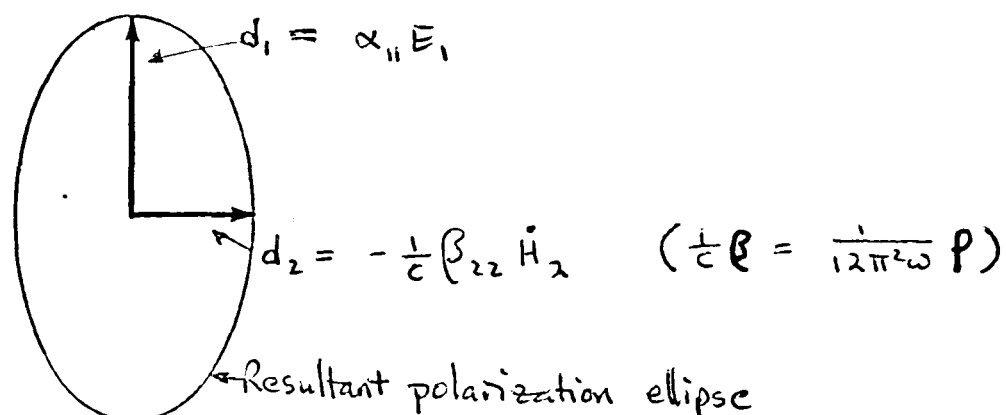


Figure 12.4. The origin of the ellipticity of Rayleigh scattered light from an optically active molecule.

The ellipticity discussed above would be rather small, perhaps of the order  $m/d \sim 1/300$ . Since transitions with high rotational strengths can have low oscillator strengths, measurable ellipticities could arise, particularly if the dispersion of the effect with frequency were investigated.

## 12.5. RAMAN SCATTERING

The preceding equations can be applied to the Raman scattered beam. The actual expressions for the polarizability tensors must take into account the molecular process responsible for producing Stokes or anti-Stokes photons. One could use, for example, explicit expressions for the vibrational Raman polarizability tensors obtained by Albrecht [67], who calculated the vibrational perturbations to the electronic energy states.

The polarization of the stimulated Raman light that arises when a Raman-active sample is placed within a laser cavity [68] ought to be given for the forward direction by equations (12.45) and (12.46), provided that the appropriate Raman polarizability tensors are substituted. Measurements have been reported [69] of the polarization states of Raman laser radiation from hydrogen gas for different states of polarization of the stimulating laser beam: with the laser elliptically polarized the Raman beam was found to have the same eccentricity and sense. Equation (12.45) may be used to estimate the ellipticity on the assumption that a classical rotational average is permissible.

The hydrogen molecule is axially symmetric and so

$$\alpha_{zz} = \alpha_{\parallel} \quad ; \quad \alpha_{xx} = \alpha_{yy} = \alpha_{\perp} \quad .$$

Then the mean polarizability becomes -

$$\alpha = \frac{1}{3} (\alpha_{\parallel} + 2\alpha_{\perp})$$

so that (12.45) may be written

$$\sin 2\eta^c = \frac{5(\alpha_{\perp}^2 + 2\alpha_{\parallel}\alpha_{\perp})}{(4\alpha_{\parallel}^2 + 9\alpha_{\perp}^2 + 2\alpha_{\perp}\alpha_{\parallel})} \sin 2\eta^i \quad . \quad (12.48)$$

Typical measured values of the components of the Raman polarizability tensor for hydrogen between the ground and first excited vibrational states are [70]

$$(\alpha_{\parallel})_{01} = 0.066 \times 10^{-24} \text{ cm}^3 ; \quad (\alpha_{\perp})_{01} = 0.138 \times 10^{-24} \text{ cm}^3$$

and so

$$\sin 2\eta^0 \sim 0.84 \sin 2\eta^i.$$

We would therefore expect some decrease in the ellipticity of the Raman beam in the forward direction, even though none was observed.

It might prove interesting to use a Raman active material that was also optically active, and see if the stimulated Raman beam in the forward direction had the ellipticity predicted by (12.47). Although such a contribution would be independent of the polarization of the laser beam, it would be revealed most clearly if the laser beam were plane polarized, for then no contribution would arise from (12.45).

## 12.6. DEPOLARIZATION RATIOS

The depolarization ratio is defined as the ratio of the intensity components polarized along the  $\epsilon_2^f$  and  $\epsilon_1^f$  axes of the scattered beam, that is

$$\Delta = I_2^f / I_1^f. \quad (12.49)$$

These intensity components are given directly by the density matrix elements  $\rho_{22}^f$  and  $\rho_{11}^f$ , respectively. Equations (12.12) and (12.13) enable us to write down the depolarization ratio for

an incident beam in any polarization condition and for any scattering angle:

$$\Delta = \frac{\langle 2(3) \| 2(3) \rangle \cos^4 \xi + \langle 3(2) \| 3(2) \rangle \sin^4 \xi - [\langle 3(2) \| 2(3) \rangle + \langle 2(3) \| 3(2) \rangle] \cos^2 \xi \sin^2 \xi}{\langle 1(3) \| 1(3) \rangle \cos^2 \xi + \langle 1(2) \| 1(2) \rangle \sin^2 \xi + [\langle 1(2) \| 1(3) \rangle + \langle 1(3) \| 1(2) \rangle] \sin \xi \cos \xi} \quad (12.50)$$

The application of this equation to a few specific physical situations will now be considered.

For a scattering angle of  $\pi/2$  the depolarization ratio is

$$\Delta = \langle 3(2) \| 3(2) \rangle / \langle 1(2) \| 1(2) \rangle \quad (12.51)$$

and in the absence of absorption the terms in this equation are

$$\begin{aligned} 2 \langle 3(2) \| 3(2) \rangle &= |R_{3(2)1(3)}|^2 + |R_{3(2)2(3)}|^2 + (|R_{3(2)1(3)}|^2 - |R_{3(2)2(3)}|^2) \cos 2\eta^i \cos 2\theta^i \\ &+ 2 \operatorname{Re} R_{3(2)2(3)} R_{1(3)3(2)} \cos 2\eta^i \sin 2\theta^i \\ &+ 2 \operatorname{Im} R_{3(2)2(3)} R_{1(3)3(2)} \sin 2\eta^i \end{aligned} \quad (12.52)$$

$$\begin{aligned} 2 \langle 1(2) \| 1(2) \rangle &= |R_{1(2)1(3)}|^2 + |R_{1(2)2(3)}|^2 + (|R_{1(2)1(3)}|^2 - |R_{1(2)2(3)}|^2) \cos 2\eta^i \cos 2\theta^i \\ &+ 2 \operatorname{Re} R_{1(2)2(3)} R_{1(3)1(2)} \cos 2\eta^i \sin 2\theta^i \\ &+ 2 \operatorname{Im} R_{1(2)2(3)} R_{1(3)1(2)} \sin 2\eta^i. \end{aligned} \quad (12.53)$$

If the incident beam has zero azimuth and ellipticity we obtain

$$\Delta = |R_{3(2)1(3)}|^2 / |R_{1(2)1(3)}|^2 \quad (12.54)$$

and this, subsequent to spatial averaging, becomes

$$\Delta = \frac{(3\alpha_{xe}\alpha_{xe} - \alpha_{xx}\alpha_{ee})}{2(\alpha_{xx}\alpha_{ee} + 2\alpha_{xe}\alpha_{xe})}$$

$$= 3K^2 / (5 + 4K^2) \quad (12.55)$$

where

$$K^2 = \frac{(3\alpha_{xe}\alpha_{xe} - \alpha_{xx}\alpha_{ee})}{2\alpha_{xx}\alpha_{ee}} \quad (12.56)$$

in agreement with the standard result [71]. When the initial ellipticity is  $\pi/4$ , that is the beam is circularly polarized, then

$$\Delta = \frac{2(3\alpha_{xe}\alpha_{xe} - \alpha_{xx}\alpha_{ee}) + 4(3\alpha_{xe}P_{xe} - \alpha_{xx}P_{ee})}{\alpha_{xx}\alpha_{ee} + 7\alpha_{xe}\alpha_{xe} + 2(\alpha_{xx}P_{ee} + 7\alpha_{xe}P_{xe})} \quad (12.57)$$

and so if the molecule is optically active, the optical rotation tensor can affect the depolarization ratio. In general, there will be a contribution to the depolarization ratio from optically active molecules that is dependent on the ellipticity of the incident beam.

Should the incident beam be only partially polarized, we can use (1.76) and write, in place of (12.54),

$$\Delta = \frac{|R_{3(2)1(3)}|^2 + |R_{3(2)2(3)}|^2 + (|R_{3(2)1(3)}|^2 - |R_{3(2)2(3)}|^2) P}{|R_{1(2)1(3)}|^2 + |R_{1(2)2(3)}|^2 + (|R_{1(2)1(3)}|^2 - |R_{1(2)2(3)}|^2) P}$$

$$= \frac{2(3\alpha_{xe}\alpha_{xe} - \alpha_{xx}\alpha_{ee})}{(\alpha_{xx}\alpha_{ee} + 7\alpha_{xe}\alpha_{xe}) + P(3\alpha_{xx}\alpha_{ee} + \alpha_{xe}\alpha_{xe})} \quad (12.58)$$

Thus if the incident beam is fully polarized ( $P=1$ ) we reproduce (12.55), whereas if it is unpolarized ( $P=0$ ) we obtain the standard result

$$\Delta = \frac{6k^2}{(5+7k^2)} . \quad (12.59)$$

# 13

## THE POLARIZATION OF THE SECOND HARMONIC

### 13.1. INTRODUCTION

Second and higher harmonic generation arises from the simultaneous scattering of two or more photons into a single photon with a frequency that is a multiple of the incident frequency [72,73,74,75,76,etc.]. Much work has been done on the depolarization ratios of the second harmonic from molecules in fluid media, but there has been little discussion of the precise polarization state, although some recent work has been done on the polarization from crystalline media [77,78].

Second harmonic generation involving just electric dipole interactions is supported only by molecules lacking inversion symmetry, that is optically active molecules. This is because electric dipole transitions connect states of opposite parity so that the successive absorption of two photons produces an excited state with the same parity as the ground state. Thus the subsequent emission of the second harmonic photon by an electric dipole process is forbidden, unless parity is not

defined. But the subsequent emission of the second harmonic photon through a magnetic dipole interaction can be supported by an optically inactive molecule, although the amplitude for such a process is very small. Second harmonic generation can also be induced in non-optically active molecules by applying a static electric or magnetic field.

The polarization of the second and higher harmonic photons must be formulated in terms of nonforward scattering because there can be no transmitted second harmonic component to interfere with the scattered beam even in the forward direction (c.f. Raman scattering). The nonforward scattering description must be modified to incorporate an incident radiation field that contains more than one photon, since the discussion in Section 6.2 is pertinent here.

Only the second harmonic will be considered. The polarization of the third and higher harmonics could be obtained by an obvious extension of the methods used for the second harmonic, but the calculations become very laborious. We shall not consider the intensity-dependent contribution to first harmonic nonforward scattering that could arise from the simultaneous scattering of two first harmonic photons into another two first harmonic photons.

### 13.2. THE SECOND HARMONIC

It is sufficient to consider the intense beam incident

upon the molecule as giving rise to a single second harmonic photon, for the probability of such an event is extremely small for a particular molecule in the medium. This means that we may use the same transformed polarization basis (12.1) for the second harmonic as was used for the first harmonic nonforward beam. In addition, considerable simplification is achieved by considering an incident beam containing just two photons: this is permissible since the polarization of the second harmonic is not intensity-dependent, even though the associated scattering amplitude will be.

The complete nonforward scattering formulation can be applied immediately, provided that (12.11) is reinterpreted as

$$\begin{aligned} \langle p(q) || p'(q') \rangle &= \langle g; 2k^i \epsilon_q^i, \epsilon_p^i | R | g; k_\pi^i [2] \rangle \\ &\times \langle g; k_\pi^i [2] | R^\dagger | g; 2k^i \epsilon_{q'}^i, \epsilon_{p'}^i \rangle \end{aligned} \quad (13.1)$$

where  $|2k^i \epsilon_q^i, \epsilon_p^i\rangle$  is the state vector for a second harmonic photon plane polarized along  $\epsilon_p^i$  and propagating along the  $\epsilon_q^i$ -direction, and  $|k_\pi^i [2]\rangle$  is the occupation number state vector for the two first harmonic incident photons. In expanded form this equation becomes

$$\begin{aligned} \langle p(q) || p'(q') \rangle &= \sum_{r, r'=0}^2 \langle g; 2k^i \epsilon_q^i, \epsilon_p^i | R | g; k_1^i [2-r] k_2^i [r] \rangle \rho_{rr'} \\ &\times \langle g; k_1^i [2-r] k_2^i [r] | R^\dagger | g; 2k^i \epsilon_{q'}^i, \epsilon_{p'}^i \rangle \end{aligned} \quad (13.2)$$

with the two-photon density matrix elements  $\rho_{rr'}$  given by (13.22). By analogy with (12.18) we may define, for example,

$$R_{p(q),1(3)2(3)} \equiv \langle g; 2k^i e_q^i, \epsilon_p^i | R | g; k_1^i [1] k_2^i [1] \rangle. \quad (13.3)$$

### 13.3. THE SECOND HARMONIC IN THE FORWARD DIRECTION

Equations (12.40) and (12.41) for the ellipticity and azimuth of the first harmonic in the forward direction can be applied to the second harmonic, where now

$$\begin{aligned} \langle 2(3) || 1(3) \rangle + \langle 1(3) || 2(3) \rangle = & \frac{1}{2} \text{Re} \{ R_{2,11} R_{11,1} (1 + \cos 2\eta^i \cos 2\theta^i)^2 \\ & + R_{2,11} R_{12,1} \sqrt{2} (1 + \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\ & + R_{2,11} R_{22,1} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i)^2 \\ & + R_{2,12} R_{11,1} \sqrt{2} (1 + \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\ & + R_{2,12} R_{12,1} 2 (1 + \cos 2\eta^i \cos 2\theta^i) (1 - \cos 2\eta^i \cos 2\theta^i) \\ & + R_{2,12} R_{22,1} \sqrt{2} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) (1 - \cos 2\eta^i \cos 2\theta^i) \\ & + R_{2,22} R_{11,1} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i)^2 \\ & + R_{2,22} R_{12,1} \sqrt{2} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) (1 - \cos 2\eta^i \cos 2\theta^i) \\ & + R_{2,22} R_{22,1} (1 - \cos 2\eta^i \cos 2\theta^i)^2 \} \end{aligned} \quad (13.4)$$

$$\langle 2(3) || 1(3) \rangle - \langle 1(3) || 2(3) \rangle = \frac{1}{2} i \text{Im} \{ \text{as above} \} \quad (13.5)$$

$$\begin{aligned}
\langle 1(3) || 1(3) \rangle \pm \langle 2(3) || 2(3) \rangle = & \frac{1}{4} \{ (R_{1,11} R_{11,1} \pm R_{2,11} R_{11,2}) (1 + \cos 2\eta' \cos 2\theta')^2 \\
& + (R_{1,11} R_{12,1} \pm R_{2,11} R_{12,2}) \sqrt{2} (1 + \cos 2\eta' \cos 2\theta') (\cos 2\eta' \sin 2\theta' + i \sin 2\eta') \\
& + (R_{1,11} R_{22,1} \pm R_{2,11} R_{22,2}) (\cos 2\eta' \sin 2\theta' + i \sin 2\eta')^2 \\
& + (R_{1,12} R_{11,1} \pm R_{2,12} R_{11,2}) \sqrt{2} (1 + \cos 2\eta' \cos 2\theta') (\cos 2\eta' \sin 2\theta' - i \sin 2\eta') \\
& + (R_{1,12} R_{12,1} \pm R_{2,12} R_{12,2}) 2 (1 + \cos 2\eta' \cos 2\theta') (1 - \cos 2\eta' \cos 2\theta') \\
& + (R_{1,12} R_{22,1} \pm R_{2,12} R_{22,2}) \sqrt{2} (\cos 2\eta' \sin 2\theta' + i \sin 2\eta') (1 - \cos 2\eta' \cos 2\theta') \\
& + (R_{1,22} R_{11,1} \pm R_{2,22} R_{11,2}) (\cos 2\eta' \sin 2\theta' - i \sin 2\eta')^2 \\
& + (R_{1,22} R_{21,1} \pm R_{2,22} R_{21,2}) \sqrt{2} (\cos 2\eta' \sin 2\theta' - i \sin 2\eta') (1 - \cos 2\eta' \cos 2\theta') \\
& + (R_{1,22} R_{22,1} \pm R_{2,22} R_{22,2}) (1 - \cos 2\eta' \cos 2\theta')^2 \} . \quad (13.6)
\end{aligned}$$

The subscripts indicating the direction of propagation of the photons have been omitted from the R-matrix elements since both incident and scattered photons are moving along  $\mathbf{e}_3^i$ .

We are now in a position to evaluate the polarization of the second harmonic in the forward direction with an incident beam of arbitrary polarization. Explicit equations for the ellipticity and azimuth of the second harmonic in terms of molecular hyperpolarizability tensors will not be calculated since they are very complicated and are not particularly useful. But general equations for the R-matrix elements will be written down

so that the polarization parameters can be obtained if required.

If the molecule is optically active, a process involving only electric dipole interactions can be supported. Figure 13.1 shows the appropriate diagrams, and the corresponding R-matrix

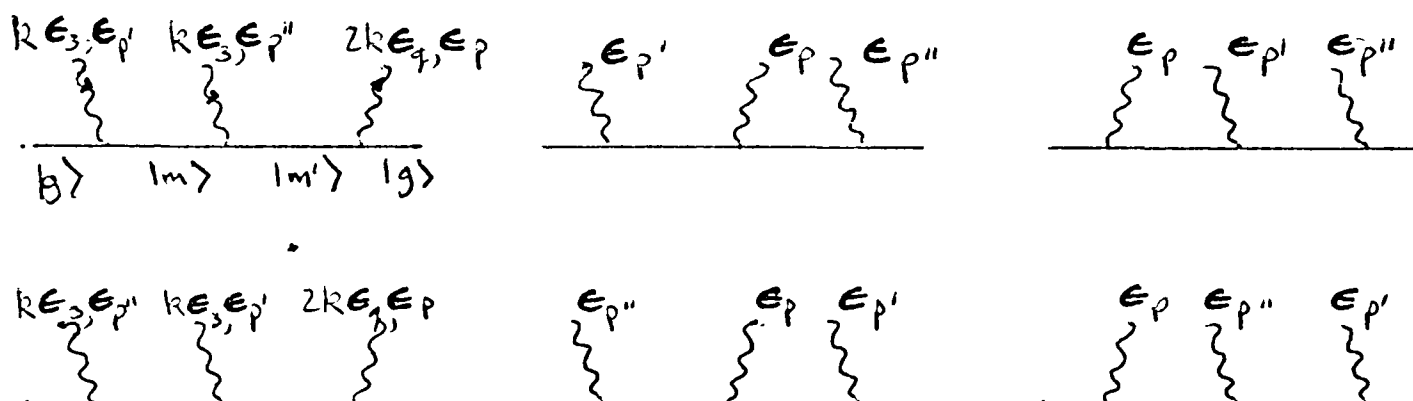


Figure 13.1. Second harmonic generation through electric dipole scattering.

is found to be

$$\begin{aligned}
 R_{p(4), p'(3)p''(3)} &= i n_{p'}^{1/2} n_{p''}^{1/2} \lambda^{1/2} (2\pi\hbar\omega/V)^{3/2} \sum_{m, m'} \left\{ \right. \\
 &+ \frac{d_{gm'} \cdot \epsilon_p d_{m'm} \cdot \epsilon_{p'} d_{mg} \cdot \epsilon_{p'}}{(E_{gm} + \hbar\omega)(E_{gm'} + 2\hbar\omega)} + \frac{d_{gm'} \cdot \epsilon_{p''} d_{m'm} \cdot \epsilon_p d_{mg} \cdot \epsilon_{p'}}{(E_{gm} + \hbar\omega)(E_{gm'} - \hbar\omega)} \\
 &\frac{d_{gm'} \cdot \epsilon_{p''} d_{m'm} \cdot \epsilon_{p'} d_{mg} \cdot \epsilon_p}{(E_{gm} - 2\hbar\omega)(E_{gm'} - \hbar\omega)} + \frac{d_{gm'} \cdot \epsilon_p d_{m'm} \cdot \epsilon_{p'} d_{mg} \cdot \epsilon_{p''}}{(E_{gm} + \hbar\omega)(E_{gm'} + 2\hbar\omega)} \\
 &\frac{d_{gm'} \cdot \epsilon_{p'} d_{m'm} \cdot \epsilon_p d_{mg} \cdot \epsilon_{p''}}{(E_{gm} + \hbar\omega)(E_{gm'} - \hbar\omega)} + \left. \frac{d_{gm'} \cdot \epsilon_{p'} d_{m'm} \cdot \epsilon_{p''} d_{mg} \cdot \epsilon_p}{(E_{gm} - 2\hbar\omega)(E_{gm'} - \hbar\omega)} \right\} \\
 &= i n_{p'}^{1/2} n_{p''}^{1/2} 2^{1/2} (2\pi\hbar\omega/V)^{3/2} \beta : \epsilon_p \epsilon_{p''} \epsilon_{p'} \quad (13.7)
 \end{aligned}$$

with the first hyperpolarizability tensor  $\beta$  defined as

$$\beta_{\alpha\beta\gamma} = \sum_{n,m'} \left\{ \frac{\alpha\beta\gamma + \alpha\gamma\beta}{(E_{g,n} + \hbar\omega)(E_{g,m'} + 2\hbar\omega)} + \frac{\beta\alpha\gamma + \gamma\alpha\beta}{(E_{g,m} + \hbar\omega)(E_{g,m'} - \hbar\omega)} + \frac{\beta\gamma\alpha + \gamma\beta\alpha}{(E_{g,m} - 2\hbar\omega)(E_{g,m'} - \hbar\omega)} \right\} \quad (13.8)$$

where

$$\alpha\beta\gamma \equiv d_{g,n'}^{\alpha} d_{m'm}^{\beta} d_{mg}^{\gamma}.$$

Notice that for second harmonic scattering it is the terms with just electric dipole interactions that are imaginary; those with a magnetic dipole interaction are real. If it is assumed that the important intermediate states have energies much greater than the photon energy, the photon frequencies in the denominators of (13.8) can be neglected and the tensor  $\beta_{\alpha\beta\gamma}$  becomes symmetric in all its indices. This is very useful when spatial averages are taken.

If the incident beam is plane polarized, we see that both optically active and inactive molecules can provide the following contribution to the ellipticity:

$$\sin 2\eta_{2\omega}^{\circ} = \frac{(\text{Re } R_{2,||} g_m R_{1,||} - g_m R_{2,||} \text{Re } R_{1,||})}{\text{Re}(R_{1,||} R_{1,||} + R_{2,||} R_{2,||})}. \quad (13.9)$$

The real R-matrix elements contain one magnetic dipole interaction with two electric dipole interactions. The diagrams shown in Figure 13.2 provide the R-matrix element

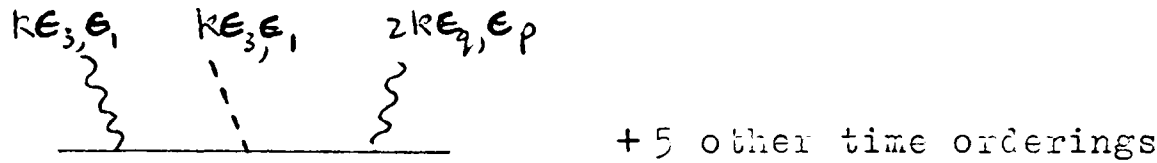
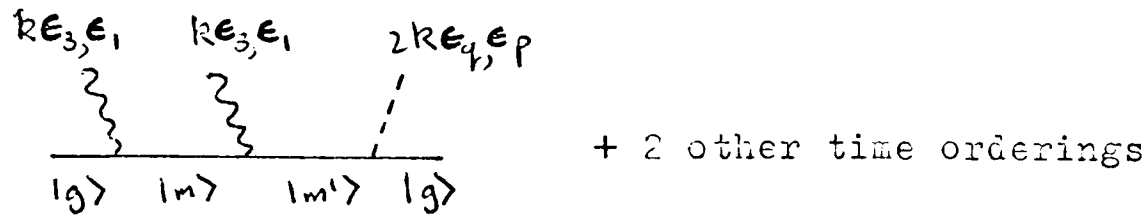


Figure 13.2. Second harmonic scattering involving one magnetic dipole interaction.

$$\begin{aligned}
 R_{P(q),1(3)1(3)}^m &= -4\pi\omega(2\pi\hbar\omega/V)^{3/2} g_m \sum_{m,m'} \left\{ (2E_{gm} + E_{gm'}) \right. \\
 &\times [(E_{gm}^2 - 4\hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)]^{-1} [d_{gm'} \cdot \epsilon_i d_{m'm} \cdot \epsilon_f m_{mg} \cdot \epsilon_q \wedge \epsilon_p \\
 &+ m_{gm'} \cdot \epsilon_3 \wedge \epsilon_i d_{m'm} \cdot \epsilon_i d_{mg} \cdot \epsilon_p + d_{gm'} \cdot \epsilon_p m_{m'm} \cdot \epsilon_3 \wedge \epsilon_i d_{mg} \cdot \epsilon_i] + \\
 &[(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)]^{-1} [d_{gm'} \cdot \epsilon_i m_{m'm} \cdot \epsilon_q \wedge \epsilon_p d_{mg} \cdot \epsilon_i \\
 &\left. + m_{gm'} \cdot \epsilon_3 \wedge \epsilon_i d_{m'm} \cdot \epsilon_p d_{mg} \cdot \epsilon_i] (E_{gm} - E_{gm'}) \right\}. \quad (13.10)
 \end{aligned}$$

By introducing the third rank tensor  $\lambda$  as a sum of two tensors  $\lambda'$  and  $\lambda''$ , where

$$\begin{aligned}
 \lambda'_{\alpha\beta\gamma} &= 2\hbar\omega g_m \sum_{m,m'} \left\{ \frac{(2E_{gm} + E_{gm'}) (\bar{\alpha} \gamma \beta + \beta \bar{\alpha} \gamma)}{(E_{gm}^2 - 4\hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)} \right. \\
 &\left. + \frac{(E_{gm} - E_{gm'}) \bar{\alpha} \beta \gamma}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)} \right\} \quad (13.11)
 \end{aligned}$$

$$\lambda''_{\alpha\beta\gamma} = 2\hbar\omega g_m \sum_{m,m'} \left\{ \frac{(2E_{gm} + E_{gm'}) \gamma \alpha \bar{\beta}}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)} + \frac{(E_{gm} - E_{gm'}) \alpha \bar{\gamma} \beta}{(E_{gm}^2 - \hbar^2\omega^2)(E_{gm'}^2 - \hbar^2\omega^2)} \right\} \quad (13.12)$$

with

$$\bar{\alpha}\beta\gamma \equiv m_{gm'}^\alpha d_{m'm}^\beta d_{mg}^\gamma,$$

we obtain

$$R_{P(1),1(3)1(3)}^m = -2(2\pi\hbar\omega/V)^{3/2} [\lambda' : \epsilon_2 \epsilon_p \epsilon_1 + \lambda'' : \epsilon_q \wedge \epsilon_p \epsilon_1 \epsilon_1]. \quad (13.13)$$

The tensor  $\lambda_{\alpha\beta\gamma}$  does not appear to be symmetric in any of its indices when the photon frequencies in the denominators are neglected, so the spatial averages become very complicated. But we may still conclude that there will be a small contribution, of magnitude  $m/d$ , to the ellipticity of all second harmonic waves independent of the polarization of the incident beam.

Other general conclusions for the second harmonic in the forward direction are that the azimuth is always the same as that of the incident beam, and that there will be a further contribution to the ellipticity dependent on the incident ellipticity.

13.4. SECOND HARMONIC SCATTERING AT  $90^\circ$ 

The ellipticity and azimuth of the second harmonic at a scattering angle  $\xi$  of  $\pi/4$  can be obtained by adapting the first harmonic equations (12.15) and (12.16). Thus

$$\begin{aligned}
 \langle 1(2) \| 3(2) \rangle + \langle 3(2) \| 1(2) \rangle = & \frac{1}{2} \operatorname{Re} \{ R_{1(2), 1(3) 1(3)} R_{1(3) 1(3), 3(2)} (1 + \cos 2\eta^i \cos 2\theta^i)^2 \\
 & + R_{1(2), 1(3) 1(3)} R_{1(3) 2(3), 3(2)} \sqrt{2} (1 + \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\
 & + R_{1(2), 1(3) 1(3)} R_{2(3) 2(3), 3(2)} (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i)^2 \\
 & + R_{1(2), 1(3) 2(3)} R_{1(3) 1(3), 3(2)} \sqrt{2} (1 + \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\
 & + R_{1(2), 1(3) 2(3)} R_{1(3) 2(3), 3(2)} 2 (1 + \cos 2\eta^i \cos 2\theta^i) (1 - \cos 2\eta^i \cos 2\theta^i) \\
 & + R_{1(2), 1(3) 2(3)} R_{2(3) 2(3), 3(2)} \sqrt{2} (1 - \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i) \\
 & + R_{1(2), 2(3) 2(3)} R_{1(3) 1(3), 3(2)} (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i)^2 \\
 & + R_{1(2), 2(3) 2(3)} R_{2(3) 1(3), 3(2)} \sqrt{2} (1 - \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i - i \sin 2\eta^i) \\
 & + R_{1(2), 2(3) 2(3)} R_{2(3) 2(3), 3(2)} (1 - \cos 2\eta^i \cos 2\theta^i)^2 \} \quad (13.14)
 \end{aligned}$$

$$\langle 1(2) \| 3(2) \rangle - \langle 3(2) \| 1(2) \rangle = \frac{1}{2} i \operatorname{Im} \{ \text{as above} \} \quad (13.15)$$

$$\langle 1(2) \| 1(2) \rangle \pm \langle 3(2) \| 3(2) \rangle = \frac{1}{4} \{$$

$$(R_{1(2), 1(3) 1(3)} R_{1(3) 1(3), 1(2)} \pm R_{3(2), 1(3) 1(3)} R_{1(3) 1(3), 3(2)}) (1 + \cos 2\eta^i \cos 2\theta^i)^2$$

$$+ (R_{1(2), 1(3) 1(3)} R_{1(3) 2(3), 1(2)} \pm R_{3(2), 1(3) 1(3)} R_{1(3) 2(3), 3(2)}) \sqrt{2} (1 + \cos 2\eta^i \cos 2\theta^i) (\cos 2\eta^i \sin 2\theta^i + i \sin 2\eta^i)$$

$$\begin{aligned}
& + (R_{1(2),1(3)1(3)} R_{2(3)2(3),1(2)} \pm R_{3(2),1(3)1(3)} R_{2(3)2(3),3(2)}) (\cos 2\eta' \sin 2\theta' + i \sin 2\eta')^2 \\
& + (R_{1(2),1(3)2(3)} R_{1(3)1(3),1(2)} \pm R_{3(2),1(3)2(3)} R_{1(3)1(3),3(2)}) \sqrt{2} (1 + \cos 2\eta' \cos 2\theta') (\cos 2\eta' \sin 2\theta' - i \sin 2\eta') \\
& + (R_{1(2),1(3)2(3)} R_{1(3)2(3),1(2)} \pm R_{3(2),1(3)2(3)} R_{1(3)2(3),3(2)}) 2(1 + \cos 2\eta' \cos 2\theta') (1 - \cos 2\eta' \cos 2\theta') \\
& + (R_{1(2),1(3)2(3)} R_{2(3)2(3),1(2)} \pm R_{3(2),1(3)2(3)} R_{2(3)2(3),3(2)}) \sqrt{2} (1 - \cos 2\eta' \cos 2\theta') (\cos 2\eta' \sin 2\theta' + i \sin 2\eta') \\
& + (R_{1(2),2(3)2(3)} R_{1(3)1(3),1(2)} \pm R_{3(2),2(3)2(3)} R_{1(3)1(3),3(2)}) (\cos 2\eta' \sin 2\theta' - i \sin 2\eta')^2 \\
& + (R_{1(2),2(3)2(3)} R_{2(3)1(3),1(2)} \pm R_{3(2),2(3)2(3)} R_{2(3)1(3),3(2)}) \sqrt{2} (1 - \cos 2\eta' \cos 2\theta') (\cos 2\eta' \sin 2\theta' - i \sin 2\eta') \\
& + (R_{1(2),2(3)2(3)} R_{2(3)2(3),1(2)} \pm R_{3(2),2(3)2(3)} R_{2(3)2(3),3(2)}) (1 - \cos 2\eta' \cos 2\theta')^2 \}. \quad (13.16)
\end{aligned}$$

Since none of the terms in (13.14) and (13.15) provide a non-zero spatial average if only electric dipole interactions are involved, we conclude that the contribution of these terms to the ellipticity and azimuth of the second harmonic scattered at  $90^\circ$  is zero. However, there will still be a small ellipticity arising from the presence of a magnetic dipole interaction. Only the case of an incident ellipticity and azimuth of zero will be considered, whereupon

$$\sin 2\eta'_{2\omega} = \frac{\text{Re } R_{1(2),1(3)1(3)} \mathcal{J}_m R_{3(2),1(3)1(3)} - \mathcal{J}_m R_{1(2),1(3)1(3)} \text{Re } R_{3(2),1(3)1(3)}}{\text{Re}(R_{1(2),1(3)1(3)} R_{1(2),1(3)1(3)} + R_{3(2),1(3)1(3)} R_{3(2),1(3)1(3)})}. \quad (13.17)$$

These R-matrix elements can be evaluated from (13.7) and (13.13), but we shall not reproduce the explicit expression for  $\sin 2\eta'_{2\omega}$  here because it is very complicated.

## 13.5. DEPOLARIZATION RATIOS FOR THE SECOND HARMONIC

The depolarization ratio for the second harmonic, at any scattering angle and with any incident polarization, can be obtained from (12.50) provided that the terms are interpreted in the manner of (13.1). One can also systematically include the contributions from terms containing a magnetic dipole interaction, as was done for the first harmonic; but one point of difference is that whereas such terms are always present for the second harmonic, they only occur for the first harmonic if the molecule is optically active.

One simple example will be calculated here, the electric dipole contribution to the depolarization ratio for scattering at  $90^\circ$  with a plane polarized incident beam of zero azimuth:

$$\begin{aligned}\Delta &= \langle 3(2) || 3(2) \rangle / \langle 1(2) || 1(2) \rangle \\ &= |R_{\alpha(2), 1(3) 1(3)}|^2 / |R_{1(2), 1(3) 1(3)}|^2.\end{aligned}\quad (13.18)$$

Using the averages of six direction cosines (Appendix), we find

$$\langle |R_{1,||}|^2 \rangle = -(2\pi\hbar\omega/V)^3 (1/35) (3\beta_{\alpha\beta\beta}\beta_{\alpha\gamma\gamma} + 2\beta_{\alpha\beta\gamma}\beta_{\alpha\beta\gamma}) \quad (13.19)$$

$$\langle |R_{3,||}|^2 \rangle = -(2\pi\hbar\omega/V)^3 (1/105) (4\beta_{\alpha\beta\gamma}\beta_{\alpha\beta\gamma} - \beta_{\alpha\beta\beta}\beta_{\alpha\gamma\gamma}). \quad (13.20)$$

Consequently,

$$\Delta = \frac{4\beta_{\alpha\beta\gamma}\beta_{\alpha\beta\gamma} - \beta_{\alpha\beta\beta}\beta_{\alpha\gamma\gamma}}{9\beta_{\alpha\beta\beta}\beta_{\alpha\gamma\gamma} + 6\beta_{\alpha\beta\gamma}\beta_{\alpha\beta\gamma}} \quad (13.21)$$

in agreement with, for example, Kielich [74].

# 14

## POLARIZATION EFFECTS IN SELF-FOCUSING

### 14.1. SELF-FOCUSING

A pencil of laser light above a certain power threshold collimates itself when passing through a transparent medium, and produces extremely intense self-trapped filaments [52,53,68,79, 80,etc.]. Self-focusing can be qualitatively understood using the language of geometrical optics. Because of the non-uniform intensity distribution inherent in a beam of finite cross-section, the intensity-dependent index of refraction causes different parts of the beam to propagate with different phase velocities: a lens effect is thus produced whereby the rays move towards the region of higher intensity and further increase the intensity there (Figure 14.1).

Optical orientation and electrostriction are the dominant mechanisms of intensity-dependent refractive index, and hence of self-focusing, although nonlinear electronic polarizability appears to be responsible for self-trapping with picosecond light pulses [82]. A power threshold exists for the onset of self-

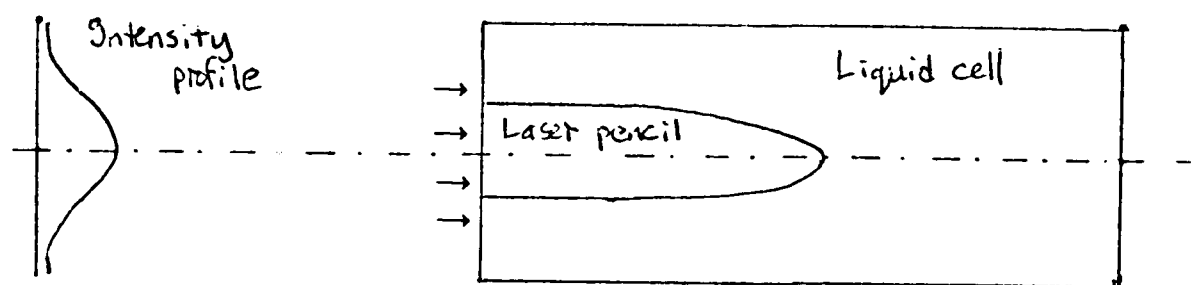


Figure 14.1. Self-focusing of a laser beam. The intensity profile corresponds to a refractive index profile.

focusing, as this effect must overcome the spreading of the beam due to diffraction. It can be shown that this power threshold is inversely proportional to the intensity-dependent refractive index [79], from which it follows that the power threshold for a circularly polarized beam is four times greater than for a plane polarized beam if molecular reorientation is the predominant mechanism [80].

Self-focusing could assume enormous technological importance in view of the recent investigations into the use of laser beams to trigger nuclear fusion reactions. Presumably the self-trapped filaments provide stable channels of dense plasma maintained at extremely high temperatures.

#### 14.2. THE POLARIZATION OF THE SELF-TRAPPED FILAMENTS

It has been observed that a plane polarized laser beam produces plane polarized self-trapped filaments with the same azimuth as the incident beam, whereas a circularly polarized beam

produces plane polarized filaments of arbitrary azimuth [80,81]. In the literature these filaments are sometimes said to be depolarized, but this terminology is not quite correct because although the azimuth may be arbitrary, the filament itself is pure plane polarized.

The observed polarization of the self-trapped filaments could perhaps be explained with reference to the following model. It is assumed that as the beam starts to focus itself, some photons are scattered slightly off-axis towards the region of higher intensity. This means that the scattering becomes increasingly of the Rayleigh type, and so the polarization of these scattered photons is more properly described in terms of the near-forward Rayleigh scattering formulation (Chapter 12). The diminution of the beam is not permitted to reach a focus: some other nonlinear mechanism takes over to produce the self-trapped filaments. In these filaments birefringent scattering may presumably occur once more, and one particular polarization will be maintained in the filament.

Stimulated Raman scattering occurs simultaneously with self-focusing, and the power thresholds for the two processes coincide. Indeed Stokes and anti-Stokes self-trapped filaments are observed. These facts are in accord with the above model, for as the beam narrows there is less stimulation for the molecules to scatter coherently because of the off-axis propagation direction, and so Stokes and anti-Stokes scattering can compete

on more equal terms with coherent scattering. As the point is approached where a trapped filament is about to form, there could be an appreciable flux of incoherent photons, leading to the formation of a Stokes or anti-Stokes filament.

We shall consider just the optical orientation mechanism. The basic process in self-focusing would then be the near-forward Rayleigh and Raman scattering of photons by optically oriented molecules, and the polarization of the self-trapped filaments should be related to the polarization of these photons.

Equations (12.45) and (12.46) are applicable here, provided we use the following type of Boltzmann average:

$$\overline{\text{Re} R_{ab} \text{Re} R_{cd}} = (1/kT) [\langle \text{Re} R_{ab} \text{Re} R_{cd} \text{Re} R_{\pi\pi} \rangle - \langle \text{Re} R_{ab} \text{Re} R_{cd} \rangle \langle \text{Re} R_{\pi\pi} \rangle] \quad (14.1)$$

where  $\pi$  is the polarization of the incident beam. The following tensor averages are required:

$$\langle \text{Re} R_{22} \text{Re} R_{11} \rangle = (2\pi\hbar\omega/v)^2 (1/15) (2\alpha_{\alpha\alpha}\alpha_{\beta\beta} - \alpha_{\alpha\beta}\alpha_{\alpha\beta}) \quad (14.2)$$

$$\langle \text{Re} R_{21} \text{Re} R_{21} \rangle = (2\pi\hbar\omega/v)^2 (1/30) (3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}) \quad (14.3)$$

$$\langle \text{Re} R_{11} \text{Re} R_{11} \rangle = (2\pi\hbar\omega/v)^2 (1/15) (\alpha_{\alpha\alpha}\alpha_{\beta\beta} + 2\alpha_{\alpha\beta}\alpha_{\alpha\beta}) \quad (14.4)$$

$$\langle \text{Re} R_{\pi\pi} \rangle = n(2\pi\hbar\omega/v)(1/3)\alpha_{\alpha\alpha} \quad (14.5)$$

$$\begin{aligned} \langle \text{Re} R_{22} \text{Re} R_{11} \text{Re} R_{\pi\pi} \rangle = n(2\pi\hbar\omega/v)^3 (1/210) (6\alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} \\ + 8\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\beta\gamma} - 8\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma}) \end{aligned} \quad (14.6)$$

$$\begin{aligned} \langle \text{Re} R_z, \text{Re} R_z, \text{Re} R_{\pi\pi} \rangle &= n(2\pi\hbar\omega/V)^3 (1/210) (6\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma} \\ &\quad + \alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} - \alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\gamma\beta}) \end{aligned} \quad (14.7)$$

$$\begin{aligned} \langle \text{Re} R_{xx}, \text{Re} R_{xx}, \text{Re} R_{\pi\pi} \rangle &= n(2\pi\hbar\omega/V)^3 (1/210) (4\alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} \\ &\quad + 10\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\gamma\beta} + 4\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma}) \end{aligned} \quad (14.8)$$

where we have chosen an initial azimuth of  $\pi/4$  so that the second term in (8.28) disappears.

The required polarization parameters are therefore

$$\sin 2\eta^o = \frac{7(4\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\gamma\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} - 3\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma})}{(\alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} - 8\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\gamma\beta} + 15\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma})} \sin 2\eta^i \quad (14.9)$$

$$\begin{aligned} \tan 2\theta^o &= \frac{(10\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\gamma\beta} - 3\alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} - 3\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma})}{(10\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\alpha_{\gamma\beta} - 3\alpha_{\alpha\alpha}\alpha_{\beta\beta}\alpha_{\gamma\gamma} - 3\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\alpha_{\beta\gamma})} \tan 2\theta^i \\ &= \tan 2\theta^i. \end{aligned} \quad (14.10)$$

Notice that the numerator and denominator of both equations reduce to zero if the molecules are isotropic, for no optical orientation would then occur.

From (14.10) it can be seen that the azimuth of the near-forward Rayleigh scattered photon from the optically oriented molecule is the same as that of the incident beam, irrespective of the molecular polarizability characteristics. The ellipticity of the scattered photon will be rather less than that of the

incident beam; in particular, if the molecule is axially symmetric,

$$\sin 2\eta^0 = \frac{7(2\alpha_{\perp}^3 - 4\alpha_{\perp}^2\alpha_{\parallel} + 2\alpha_{\perp}\alpha_{\parallel}^2)}{(8\alpha_{\parallel}^3 + 6\alpha_{\perp}^3 - 4\alpha_{\perp}^2\alpha_{\parallel} - 10\alpha_{\perp}\alpha_{\parallel}^2)} \sin 2\eta^i. \quad (14.11)$$

These results are in broad agreement with the observed polarization of the self-trapped filaments. Thus if the incident beam is plane polarized, we predict that the filaments are plane polarized with the same azimuth as the incident beam, whereas for a circularly polarized incident beam the filaments will be elliptically polarized with arbitrary azimuth because the incident azimuth is undefined. Furthermore, the ellipticity becomes progressively less at each subsequent near-forward scattering event, so the limit of plane polarization is approached.

Similar calculations could be performed for the hyperpolarizability contribution to self-focusing, which would be temperature-independent. The results would be particularly useful for predicting the polarization of the self-trapped filaments arising from picosecond laser pulses. The calculations, which are very tedious and will not be reproduced here, involve a multiphoton scattering formulation in which two incident photons are scattered into two others of the same frequency but away from the forward direction.



# Appendix

# TENSOR AVERAGES IN A ROTATING MOLECULE

The expressions obtained for the R-matrix elements contain scalar products of matrix elements of molecular dipole moment operators  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ , - - with unit vectors  $\mathbf{e}_z, \mathbf{e}_y, \mathbf{e}_x$ , - - along space-fixed Cartesian axes. The dipole moment operators are expressed in terms of unit vectors  $\mathbf{e}_\alpha, \mathbf{e}_\beta, \mathbf{e}_\gamma$ , - - along the molecule-fixed axes. The dyadics  $\mathbf{abc}$  - - constitute tensors characteristic of the molecular polarizability. We shall denote such tensors by  $a_\alpha b_\beta c_\gamma$  - -, which represents the complete set of components with  $\alpha, \beta, \gamma$ , - - = 1, 2, 3; also summation over repeated indices is implied. In terms of the direction cosines  $w_{\alpha\sigma}, w_{\beta\tau}$ , - - between the space-fixed and molecule-fixed axes, the  $\sigma\tau\nu$  - - component of the tensor  $\mathbf{abc}$  - - can be written as

$$\mathbf{a} \cdot \mathbf{e}_\sigma \mathbf{b} \cdot \mathbf{e}_\tau \mathbf{c} \cdot \mathbf{e}_\nu - - - = a_\alpha b_\beta c_\gamma - - - w_{\alpha\sigma} w_{\beta\tau} w_{\gamma\nu} - - - , \quad (\text{A.1})$$

The direction cosines comprise  $3 \times 3$  matrices, the rows (or columns) of which form a set of orthonormalized vectors:

$$w_{\alpha\sigma} w_{\alpha\tau} = \delta_{\sigma\tau} \quad ; \quad w_{\alpha\sigma} w_{\beta\sigma} = \delta_{\alpha\beta} . \quad (\text{A.2})$$

If the molecule is freely tumbling, the space-fixed components of the tensor  $\mathbf{abc}$  - - will be observed as an average over all molecular orientations. The problem of calculating these tensor averages reduces to averaging the product of the direction cosines over a sphere, and this may be done by trigonometrical analysis [83, 84, 85].

The following averages of tensor components are required in the text:

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} \rangle = \frac{1}{3} a \cdot b \quad (\text{A.3})$$

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\tau} \rangle = 0 \quad (\text{A.4})$$

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\tau} c \cdot \epsilon_{\nu} \rangle = \frac{1}{6} a \cdot b \wedge c \quad (\text{A.5})$$

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\tau} \rangle = \langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\sigma} \rangle = 0 \quad (\text{A.6})$$

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\sigma} d \cdot \epsilon_{\sigma} \rangle = \frac{1}{15} (a \cdot b c \cdot d + a \cdot c b \cdot d + a \cdot d b \cdot c) \quad (\text{A.7})$$

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\tau} d \cdot \epsilon_{\tau} \rangle = \frac{1}{30} (4 a \cdot b c \cdot d - a \cdot c b \cdot d - a \cdot d b \cdot c) \quad (\text{A.8})$$

$$\langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\sigma} d \cdot \epsilon_{\tau} \rangle = 0 \quad (\text{A.9})$$

$$\begin{aligned} \langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\tau} c \cdot \epsilon_{\sigma} d \cdot \epsilon_{\tau} e \cdot \epsilon_{\tau} f \cdot \epsilon_{\tau} \rangle &= \\ \langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\sigma} d \cdot \epsilon_{\sigma} e \cdot \epsilon_{\sigma} f \cdot \epsilon_{\tau} \rangle &= 0 \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} \langle a \cdot \epsilon_{\sigma} b \cdot \epsilon_{\sigma} c \cdot \epsilon_{\sigma} d \cdot \epsilon_{\tau} e \cdot \epsilon_{\sigma} f \cdot \epsilon_{\sigma} \rangle &= \frac{1}{105} (a \cdot b c \cdot d e \cdot f \\ &+ a \cdot b c \cdot e d \cdot f + a \cdot b c \cdot f d \cdot e + a \cdot e c \cdot d b \cdot f + a \cdot f c \cdot d b \cdot e \\ &+ a \cdot c e \cdot f b \cdot d + a \cdot d e \cdot f b \cdot c + a \cdot c b \cdot e d \cdot f + a \cdot c b \cdot f d \cdot e \\ &+ a \cdot e b \cdot c d \cdot f + a \cdot f b \cdot c d \cdot e + a \cdot d b \cdot e c \cdot f + a \cdot d b \cdot f c \cdot e \\ &+ a \cdot e b \cdot d c \cdot f + a \cdot f b \cdot d c \cdot e) \end{aligned} \quad (\text{A.11})$$

$$\begin{aligned}
\langle a.\epsilon_\sigma b.\epsilon_\sigma c.\epsilon_\tau d.\epsilon_\tau e.\epsilon_\tau f.\epsilon_\tau \rangle &= \frac{1}{210} \{ 6(a.b.c.d.e.f \\
&+ a.b.c.e.d.f + a.b.c.f.e.d) - (a.e.c.d.b.f + a.f.c.d.b.e \\
&+ a.c.e.f.b.d + e.f.a.d.b.c + a.c.b.e.d.f + a.c.b.f.e.d \\
&+ b.c.a.e.d.f + b.c.a.f.d.e + a.d.b.e.c.f + a.d.b.f.c.e \\
&+ b.d.a.e.c.f + b.d.a.f.c.e) \} \quad (A.12)
\end{aligned}$$

$$\begin{aligned}
\langle a.\epsilon_\sigma b.\epsilon_\sigma c.\epsilon_\tau d.\epsilon_\tau e.\epsilon_\nu f.\epsilon_\nu \rangle &= \frac{1}{210} \{ 16 a.b.c.d.e.f \\
&- 5(a.b.c.e.d.f + a.b.c.f.d.e + a.e.c.d.b.f + a.f.c.d.b.e \\
&+ a.c.b.d.e.f + a.d.b.c.e.f) + 2(a.c.b.e.d.f + a.c.b.f.d.e \\
&+ a.d.b.e.c.f + a.d.b.f.c.e + a.e.b.c.d.f + a.e.b.d.c.f \\
&+ a.f.b.c.d.e + a.f.b.d.c.e) \} \quad (A.13)
\end{aligned}$$

# References

1. Jackson, J. D. 1962 Classical Electrodynamics. Wiley.
2. Heitler, W. 1954 quantum Theory of Radiation. Oxford.
3. Morse, P. M. and Feshbach, H. 1953 Methods of Theoretical Physics. McGraw-Hill.
4. Goldstein, H. 1950 Classical Mechanics. Addison-Wesley.
5. Power, E. A. 1964 Introductory Quantum Electrodynamics. Longmans.
6. Born, M. and Wolf, E. 1964 Principles of Optics. Pergamon.
7. Newton, R. G. 1966 Scattering Theory of Waves and Particles. McGraw-Hill.
8. Jauch, J. M. and Rohrlich, F. 1955 Theory of Photons and Electrons. Addison-Wesley.
9. Stone, J. M. 1963 Radiation and Optics. McGraw-Hill.
10. De Young, D. S. 1966 J. Math. Phys. 7, 1916.
11. Fano, U. 1957 Rev. Mod. Phys. 29, 74.
12. Shurcliff, W. A. and Ballard, S. S. 1964 Polarized Light. Van Nostrand.
13. Ramachandran, G. N. and Ramaseshan, S. 1961 Crystal Optics, in Encyclopedia of Physics XXV/1. Springer-Verlag.
14. Davydov, A. S. 1965 Quantum Mechanics. Pergamon.
15. Schiff, L. I. 1968 Quantum Mechanics. McGraw-Hill.
16. Roman, P. 1965 Advanced Quantum Mechanics. Addison-Wesley.
17. Schweber, S. S. 1961 Relativistic Quantum Field Theory. Harper and Row.

18. Dirac, P. A. M. 1958 Principles of Quantum Mechanics. Oxford.
19. Kaempffer, F. A. 1965 Concepts in Quantum Mechanics. Academic Press.
20. Power, E. A. and Zienau, S. 1959 Phil. Trans. Roy. Soc. 251, 427.
21. Richards, P. I. 1948 Phys. Rev. 73, 3.
22. McLachlan, A. D. 1963 Proc. Roy. Soc. 271, 387.
23. Eden, R. J., Landsdorf, P. V., Olive, D. I. and Polkinghorne, J. C. 1966 The Analytic S-Matrix. Cambridge.
24. Barut, A. O. 1967 The Theory of the Scattering Matrix. Macmillan.
25. Chou, T. T. and Dresden, M. 1967 Rev. Mod. Phys. 39, 1.
26. Akhiezer, A. I. and Berestetskii, V. B. 1965 Quantum Electrodynamics. Interscience.
27. Wallace, R. 1966 Molec. Phys. 11, 457.
28. Ward, J. F. 1965 Rev. Mod. Phys. 37, 1.
29. Bethe, H. A. and Salpeter, E. E. 1957 Quantum Mechanics of One and Two Electron Atoms. Springer-Verlag.
30. Stephen, M. J. 1958 Proc. Camb. Phil. Soc. 54, 81.
31. Atkins, P. W. and Barron, L. D. 1968 Proc. Roy. Soc. A 304, 303.
32. Atkins, P. W. and Barron, L. D. 1968 Proc. Roy. Soc. A 306, 119.
33. Atkins, P. W. and Miller, M. 1969 Molec. Phys. 15, 5, 491.
34. Atkins, P. W. and Miller, M. 1969 Molec. Phys. 15, 5, 503.
35. Go, N. 1967 J. Phys. Soc. Jap. 23, 1.

36. Atkins, P. W. and Barron, L. D. 1969 Molec. Phys. Submitted.
37. Kauzmann, W. 1957 Quantum Chemistry. Academic Press.
38. Feynman, R. P. and Hibbs, A. R. 1965 Quantum Mechanics and Path Integrals. McGraw-Hill.
39. Atkins, P. W. and Barron, L.D. 1969 Molec. Phys. Submitted.
40. Buckingham, A. D. and Longuet-Higgins, H. C. 1968 Molec. Phys. 14, 1, 63.
41. Buckingham, A. D. 1956 Proc. Phys. Soc. B 69, 344.
42. Zel'dovich, Ya. B. and Raizer, Yu. P. 1966 Sov. Phys. J. E. T. P. Lett. 3, 86.
43. Hellwarth, R. W. 1966 Phys. Rev. 152, 156.
44. Kielich, S. 1966 Acta Phys. Polon. 30, 683.
45. Kerr, J. 1875 Phil Mag. 50, 337.
46. Buckingham, A. D. and Pople, J. A. 1956 Proc. Phys. Soc. B 69, 344.
47. Buckingham, A. D. 1962 Proc. Roy. Soc. A 267, 271.
48. Mayer, G. and Gires, F. 1964 C. R. Acad. Sci. 258, 2039.
49. Paillette, M. 1966 C. R. Acad. Sci. 262, 264.
50. Takatsuji, M. 1967 Phys. Rev. 155, 3, 980.
51. Maker, P. D., Terhune, R. W. and Savage, C. M. 1964 Phys. Rev. Lett. 12, 18.
52. Wang, C. C. 1966 Phys. Rev. 152, 149.
53. Minck, R. W., Terhune, R.W. and Wang, C. C. 1966 Applied Optics 5, 10, 1595.

54. Hameka, H. F. 1965 Advanced Quantum Chemistry. Addison-Wesley.
55. Power, E. A. and Shail, R. 1959 Proc. Camb. Phil. Soc. 55, 87.
56. Kielich, S. 1967 Phys. Lett. 25A, 7, 517.
57. Rosenfeld, L. 1928 Z. Phys. 52, 161.
58. Woolley, R. G. 1968 Part II Thesis. Oxford University.
59. Atkins, P. W. and Woolley, R. G. 1969 J. Chem. Soc. A 3, 515.
60. Tinoco, I. 1959 J. Am. Chem. Soc. 81, 1540.
61. Buckingham, A. D. and Stephens, P. J. 1966 A. Rev. Phys. Chem. 17, 399.
62. Perrin, F. 1942 J. Chem. Phys. 10, 415.
63. McMaster, W. H. 1961 Rev. Mod. Phys. 33, 8.
64. Atkins, P. W. and Barron, L. D. 1969 Molec. Phys. In press.
65. Bridge, N. J. and Buckingham, A. D. 1966 Proc. Roy. Soc. A 295, 334.
66. Kuhn, W. 1930 Trans. Far. Soc. 26, 293.
67. Albrecht, A. C. 1961 J. Chem. Phys. 34, 5.
68. Bloembergen, N. 1967 Am. J. Phys. 35, 989.
69. Maker, P. D. and Terhune, R. W. 1964 Phys. Rev. 137, 3A, 801.
70. Terhune, R. W. and Peters, C. W. 1959 J. Mol. Spectr. 3, 138.
71. Fabelinskii, L. 1968 Molecular Scattering of Light. Plenum Press.
72. Franken, P. A. and Ward, J. F. 1963 Rev. Mod. Phys. 35, 23.
73. Bloembergen, N. 1965 Nonlinear Optics. Benjamin.
74. Bersohn, R., Pao, Y. H. and Frisch, H. L. 1966 J. Chem. Phys. 45, 3184.

75. Kielich, S. 1968 Acta Phys. Polon. 33, 89.
76. Buckingham, A. D. and Orr, B. J. 1967 Quart. Rev. Chem. Soc. 21, 195.
77. Bey, P. P. and Rabin, H. 1967 Phys. Rev. 162, 794.
78. Simon, H. J. and Bloembergen, N. 1968 Phys. Rev. 171, 1104.
79. Chiao, R. Y., Garmire, E. and Townes, C. H. 1964 Phys. Rev. Lett. 13, 479.
80. Close, D. H., Giuliano, C. R., Hellwarth, R. W., Hess, L. D., McClung, F. J. and Wagner, W. G. 1966 IEEE J. Quant. Electr. QE-2, 553.
81. Chaban, A. A. 1967 J. E. T. P. Lett. 5, 48.
82. Brewer, G. B. and Lee, C. H. 1968 Phys. Rev. Lett. 21, 267.
83. Jeffreys, H. 1965 Cartesian Tensors. Cambridge.
84. Kielich, S. 1961 Acta Phys. Polon. 20, 433.
85. Carrington, A. and McLachlan, A. D. 1967 Introduction to Magnetic Resonance. Harper and Row.