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AND CIRCULAR DIFFERENTIAL IMAGING

D.J. Keller
(Ph.D. Thesis)
February 1984

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SCATTERING OPTICAL ACTIVITY OF CHIRAL MOLECULES:
CIRCULAR INTENSITY DIFFERENTIAL SCATTERING
AND CIRCULAR DIFFERENTIAL IMAGING

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(Ph.D. Thesis)

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Scattering Optical Activity of Chiral Molecules:
Circular Intensity Differential Scattering
and Circular Differential Imaging

David John Keller

Abstract

Theoretical treatments are presented for two new techniques based on the ability of chiral molecules to preferentially scatter or absorb right and left circularly polarized light. The two techniques are circular intensity differential scattering (CIDS) and circular differential imaging (CDI). Circular intensity differential scattering is the fractional difference in the scattering cross sections for left and right circularly polarized light for optically active (chiral) molecules. A circular differential image is the difference in images formed under a microscope using right and left circularly polarized illumination.

For circular intensity differential scattering we first present a theory based on classical electrodynamics for scattering in the second Born approximation. This theory is based on earlier work by Bustamante, Maestre, and Tinoco,1-4 for scattering in the first Born approximation. The extension of the CIDS theory to the second Born approximation has resulted in the prediction of qualitatively new behavior in the CIDS patterns, most notably CIDS for forward scattered light and CIDS for systems of isotropic scatterers. A number of model computations are presented. Next, a quantum mechanical theory for CIDS is presented. This theory is similar in approach to the work done by Barron and
The quantum mechanical theory uses the first Born approximation, but is valid for cases where magnetic effects are important (notably spin effects) and where the size of the scatterer is not small compared to the wavelength of the incident light. The quantum mechanical theory also describes inelastic scattering processes such as Raman CIDS.

For circular differential imaging we present a theory based in part on the classical theory for CIDS mentioned above. Two types of differential images are possible: a) darkfield images formed from light reflected or scattered by the sample, and b) brightfield images formed from light transmitted through the sample. The sign and magnitude of each feature in a circular differential image are proportional to the optical activity of the corresponding feature in the sample. For incident light with wavelengths in the visible, the darkfield circular differential images are mostly sensitive to large features with dimensions similar to the wavelength, while the brightfield images are most sensitive to the short range molecular order.

Let the words of my mouth
and the meditation of my heart
be acceptable in Thy sight O Lord,
my Rock and my Redeemer.

Psalm 19:14
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Emil Scoffone can only be described in italian.

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CONTENTS

Dedication.........................................................................................1

Acknowledgments..............................................................................ii

Contents............................................................................................iv

Introduction.........................................................................................1
   A. Circular Intensity Differential Scattering.........................3
   B. The Geometrical Basis of Optical Activity.....................7
   C. Circular Differential Imaging...........................................10

Chapter 1  Introduction to CIDS Theory.................................15
   A. Overview of Classical Scattering Theory...................15
   B. Classical Expression for CIDS in the First Born
      Approximation............................................................35
   C. Rotationally Averaged CIDS.........................................43

Chapter 2  CIDS in the Second Born Approximation.............50
   A. The Second Born Approximation...............................51
   B. Higher-Order Approximations...................................56
   C. CIDS..............................................................................58
   D. Rotationally Averaged Differential Scattering
      in the Second Born Approximation.............................60
   E. Rotationally Averaged Total Scattering......................63
   F. CIDS of Spherically Symmetric Scatterers With...
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Quantum Mechanical Calculation of the Circular Intensity Differential Scattering</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>A. Overview of the Quantum Theory of Light Scattering</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>B. CIDS</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>C. CIDS of a Collection of Independent Systems</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>D. Discussion</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>Appendix 3A</td>
<td>124</td>
</tr>
<tr>
<td>4</td>
<td>CIDS Model Computations</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>A. Twisted Ladder</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>B. Liquid Crystals</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>C. General Helix</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>D. Rotationally Averaged Helix</td>
<td>161</td>
</tr>
<tr>
<td>5</td>
<td>Circular Differential Imaging</td>
<td>168</td>
</tr>
<tr>
<td></td>
<td>A. Imaging Theory</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>Darkfield Circular Differential Imaging</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>Brightfield Circular Differential Imaging</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>B. Summary and Discussion</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>Appendix A</td>
<td>196</td>
</tr>
<tr>
<td>Appendix</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Appendix B</td>
<td>Some Notes on Polarizabilities</td>
<td>198</td>
</tr>
<tr>
<td>Appendix C</td>
<td>Notes on the Tensor Green's Function</td>
<td>201</td>
</tr>
<tr>
<td>Appendix D</td>
<td>Computer Programs</td>
<td>205</td>
</tr>
</tbody>
</table>
Introduction

The purpose of this report is to describe two new techniques for probing biological structure based on optical activity: circular intensity differential scattering (CIDS) and circular differential imaging (CDI). Both techniques are of recent origin, and the emphasis will be on theoretical results, though experimental results will be mentioned where appropriate and available. Before beginning the details of the theory however, a brief overview of the various kinds of optical activity and of what is known about CIDS and CDI is in order.

One of the hallmarks of biological systems is their chirality. Most small biological molecules (sugars, amino acids, etc) are chiral, and the biopolymers, made up of chiral subunits, also have a larger-order chirality of their own: DNA has the well known double helix structure, and proteins frequently have $\alpha$-helical regions. On a higher order of complexity it is found that these biopolymers are themselves frequently the subunits of large molecular aggregates. DNA is wound into chromatin fibers during the process of cell replication and these chromatin fibers are in turn gathered into chromosomes. Proteins are also frequently wound into fibers and microtubules. Many of these high order structure are chiral in every order of complexity. For example, the DNA in a chromosome is composed, ultimately, of chiral nucleotide units which are wound into a chiral double helix of DNA, which is thought to be wound into a helical form in the chromatin fiber, which is wound into a possibly helical chromosome.

With all this chirality, a natural approach for probing biological structure is to take advantage of the optical activity of chiral
structures, that is, the ability of chiral objects to interact differently with right circularly polarized light than with left circularly polarized light. There are several ways in which the optical activity of a biological sample can manifest itself, corresponding to the different ways in which light can interact with matter. The ability of chiral samples to preferentially absorb right or left circularly polarized light is the basis for circular dichroism (CD). The ability to transmit right and left circularly polarized light at different speeds (that is, a difference in the indices of refraction for right and left circularly polarized light) is called optical rotatory dispersion (ORD). If the system fluoresces, its optical activity can also be measured by fluorescence detected circular dichroism (FDCD). The CD, ORD, and FDCD are well established, standard techniques. They are very sensitive to chiral structure on the molecular level, and have been used extensively to study the conformations of DNA and proteins.

Most of the studies done with CD, ORD, and FDCD have been on small molecules or biological macromolecules at the largest. When circular dichroism studies began to be done on large biological aggregates a number of "artifacts" appeared, some of which were later found to be caused by the preferential scattering of right or left circularly polarized light by the chiral aggregates.\(^2,12-13\) This scattering optical activity has since been named circular intensity differential scattering (CIDS).\(^3\) The CIDS effect was not discovered when small molecules were studied because the dimensions of the molecules were too small to have a significant scattering cross section at visible and UV wavelengths. The large biological aggregates have dimensions similar to visible and UV wavelengths however, and their scattering cross sections can be of the
same order of magnitude as their absorption cross sections. For a more detailed overview of the genesis of the CIDS effect, see Bustamante, chapter 1.

A. Circular Intensity Differential Scattering

In a CIDS experiment a scattering sample is placed at the center of a goniometer device which is capable of moving a light-sensitive detector to view the sample from all directions in space. The scattered light intensity at each direction is measured when left circularly polarized light is incident on the sample, and then again when right circularly polarized light is incident. The CIDS is defined as the difference in these two intensities divided by their sum:

\[
CIDS(\theta, \phi) = \frac{I_L(\theta, \phi) - I_R(\theta, \phi)}{I_L(\theta, \phi) + I_R(\theta, \phi)}
\]

where \(\theta\) and \(\phi\) are the polar and azimuthal angles that define the direction of view with respect to the direction of the incident light (see figure I.1). The sample may be rotationally disordered as in a solution of virus particles or it may be oriented with respect to the incident light beam as in the case of a macroscopic single crystal. For either case the CIDS pattern is sensitive to chiral structure with dimensions similar to the wavelength of the incident light. If visible or UV wavelengths are used this means that the CIDS pattern carries
Figure I.1  Schematic diagram for a CIDS apparatus. Left and right circularly polarized light are incident from the bottom of the figure toward the top. The angles $\theta$ and $\phi$ which determine a direction of view for the detector are always defined with respect to the direction of the incident light. The scattered intensity is measured for each incident circular polarization in each direction.
information about structure on the order of several thousand angstroms. This sensitivity to long-range structure is complementary to circular dichroism, optical rotatory dispersion, or fluorescence detected circular dichroism, which are sensitive to shorter range structure on the molecular and atomic level.

In principle, CIDS measurements could be made in the vacuum ultraviolet and soft X-ray regions of the spectrum with dimensions between 2000 angstroms and 10 angstroms. Circular dichroism has been measured at wavelengths as low as 1400 angstroms using synchrotron radiation, and one measurement of the ORD of a quartz crystal has also been made with 1.54 angstrom radiation.

At wavelengths in the hard X-rays (λ < 1 Å) the energy of the radiation is greater than the electronic binding energies of most "biological" elements (hydrogen, carbon, nitrogen, oxygen, phosphorous) and it is expected that optical activity will be very small in most cases. This expectation is supported by the measurement of the optical activity of quartz at 1.54 angstroms mentioned above. It was found that the same sample which showed an optical rotation of 2.30° in the visible (HeNe laser light) showed an optical rotation of only 0.047° at 1.54 angstroms.

At the time of this writing CIDS measurements have been carried out only for wavelengths in the visible. The systems studied make a short list: T2 and T4 bacteriophages, the helical sperm cell of the mediterranean octopus Eledona Cirrhosa, and several cholesteric liquid crystals. Of these systems the liquid crystals were oriented, and all the others were studied in solution.
B. The Geometrical Basis of Optical Activity

All forms of optical activity data are usually more sensitive to the structure and conformation of the sample than techniques based on unpolarized light. For example, the circular dichroism spectrum of a solution of _E. Coli_ DNA changes considerably with changes in the water activity or temperature, but the corresponding absorption curves change relatively little. The high sensitivity of optically active techniques comes from the special chiral properties of circularly polarized light and the relationship of this chirality to the chirality of the sample. The chirality of circularly polarized light is apparent in the shape of the electric field of the light. Figure I.2 shows the electric fields for right and left circularly polarized light at a single instant of time. The fields shown are plane waves travelling from the bottom to the top of the page parallel to the _z_ axis. There is an electric vector associated with each point in space, and the electric vectors lying in a plane perpendicular to the direction of propagation all point in the same direction. The direction pointed by the electric vectors in each plane rotates as one proceeds from plane to plane upwards along the _z_ axis. For right circularly polarized light the rotation is counter clockwise and the field as a whole has the shape and sense of a right-handed helix with the length of one helical turn (called the pitch) equal to the wavelength of the light. For left circularly polarized light the rotation is clockwise and the shape and sense of the field are left-handed.*

* It should be noted that there are two conflicting definitions for the terms "right" and "left" circularly polarized light. The convention we
Figure I.2 Electric field distributions for left and right circularly polarized plane waves: a) right circularly polarized light, and b) left circularly polarized light. The light is travelling upwards from the bottom of the figure.
As an example of how these helical fields interact with chiral objects, consider the helical structure in figure I.3. The helix is composed of a collection of small scattering groups and is right handed. If right circularly polarized light is incident along the helix axis, and if the pitch of the helical object is the same as the wavelength of the light, then the shape of the electric field exactly matches the shape of the object. The result is that the wave is strongly reflected backwards along the helix axis. On the other hand, if left circularly polarized light is incident, the shape of the field does not match the object and the light is either transmitted or scattered forward.

The mechanisms by which the other forms of optical activity arise are somewhat different than in the example above. For the purposes of probing biological structure however, the important thing is that there is a direct dependence of the optical activity on the structure of the sample. This dependence is rooted in the matching of the chirality of circularly polarized light and the chirality of the sample in all forms of optical activity.

C. Circular Differential Imaging

If a lens is placed between the sample and the detector in a CIDS experiment, and if the detector is replaced by a photographic plate, an image of the sample can be recorded. If the sample is chiral, an image formed under left circularly polarized illumination will not be the same as an image formed under right circularly polarized illumination. The difference between these two images is called a circular differential
Figure I.3 A chiral object composed of small scattering groups.
image (CDI). The circular differential imaging technique is an even more recent development than CIDS. However, as it turns out, much of the experience gained in the study of CIDS also applies to circular differential imaging. In chapter 5 a theoretical treatment of the circular differential image will be presented.

Bibliography

Chapter 1  Introduction to CIDS Theory

The work to be presented in later chapters is in part an extension of earlier work on CIDS theory done by a number of workers, most notably Bustamante, Maestre, and Tinoco,\(^1\)-\(^6\) who used classical scattering theory to describe the scattering of circularly polarized light by a collection of small scatterers arranged in a chiral fashion. The first work on CIDS theory was done by Barron and Buckingham,\(^9\)-\(^13\) who took a primarily quantum mechanical approach, and derived several expressions for the CIDS of molecules small compared to the wavelength of light. The results of Barron and Buckingham are also applicable to Raman CIDS, in which the light is scattered by an inelastic Raman process rather than the elastic process assumed by Bustamante, Maestre, and Tinoco. Harris and McClain have given a very general treatment of scattering which includes CIDS.\(^{14}-\(^17\) In this chapter we will consider the classical theory of scattering used by Bustamante, Maestre, and Tinoco in some detail. We will try to emphasize the qualitative ideas involved in the scattering process with an eye toward making the later developments (especially chapters 2 and 4) more easily understood.

A. Overview of Classical Scattering Theory

In a typical scattering experiment a beam of light is sent in from a source far from the sample. The beam strikes the sample, light is scattered in all directions, and the intensity of the light deflected in each direction is measured. We wish to calculate the pattern of scattered light intensity from a knowledge of the incident electric field
and the nature of the scattering object. There are two problems to be overcome to achieve this goal:

1) the description of the interaction between the sample and the incident light, and

2) calculation of the scattered electric field that results from this interaction.

As an example, consider the water molecule in figure 1.1. When the incident light beam strikes the water molecule the electric field of the light causes a distortion of the molecular charge density. The way in which the charge density is distorted depends on the way in which the electrons are bound (that is, on the energies and shapes of the stationary states of the molecule) and on the spatial variation of the electric field across the length of the molecule. In general then, calculating the response of a system to the incident light may require a quantum mechanical treatment. In chapter 3 we will consider how such a treatment is done, and what effects it can have on the CIDS patterns. However, if the wavelength of the light is very long compared to the dimensions of the scatterer (so that the scatterer "looks" like a single point to the light) the distortion of the charge density may be described as a dipole moment, $\mu$, induced in the molecule by the action of the light:

$$\mu = \alpha \cdot E$$

Eqn (1.1)

where $\alpha$ is a second rank tensor called the polarizability of the molecule, and $E$ is the electric field felt by the molecule. The assignment of polarizabilities to scattering systems is valid for any
Figure 1.1 A water molecule responding to the electric field of an incoming beam of light. The oscillating, distorted molecular charge density that results from the interaction between the light and the molecule creates secondary electric fields. The secondary electric fields may be short ranged electrostatic fields (near fields) or long ranged radiation fields (far fields).
system that is small compared to the wavelength of the light. (The crucial quantity is \( \frac{2\pi d}{\lambda} \), where \( d \) is the largest dimension of the system. A safe criterion is \( \frac{2\pi d}{\lambda} \lesssim 0.10 \).

Even systems that are large compared to the wavelength of the incident light can be described by the use of polarizability tensors if the larger system can be broken into a collection of small independent subsystems. In this case each small subsystem is assigned a polarizability tensor, and the distortion of the overall charge density is described as a collection of induced point dipoles of the form of eqn (1.1). The way in which the larger system is broken into smaller groups is somewhat arbitrary. For short incident wavelengths (say, in the soft X-ray region or shorter) separate polarizabilities would be assigned to each atom in the system. For longer wavelengths (say, in the visible region) even whole proteins may be small enough to be described by a single polarizability. For more on the properties of polarizabilities and the behavior they imply, see appendix B.

The distortion of the molecular charge density causes a change in the electric fields surrounding the molecule. If the molecule has no time-dependent behavior of its own (that is, if vibrational and rotational motion can be ignored, as is usually the case) then the distortions of the charge density will oscillate harmonically with the frequency of the incident light. Calculating the electric field scattered by the molecule is therefore equivalent to calculating the electric field produced by the oscillating distorted charge density created by the action of the light on the molecule. For very low flux of incident radiation the quantum nature of the electromagnetic field becomes important. But for almost all experimental situations the
incident flux is very high and a classical description of the electromagnetic field is appropriate.

If the system responds to the incident light as a collection of polarizabilities would, then the scattered electric field is just the electric field produced by a collection of oscillating point dipole moments. To find this scattered field, Bustamante\(^1,2\) made use of the elegant theory developed by Saxon.\(^7\) In this theory the system is treated as a continuous collection of small polarizable groups described by a polarizability density \(\kappa(x)\). The central result is an integral equation for the electric field:

\[
\mathbf{E}(x) = \mathbf{E}_0(x) + 4\pi k^2 \int \frac{\mathbf{\tau}(x, x') \cdot \kappa(x') \cdot \mathbf{E}(x')}{4\pi |x-x'|^2} \, d^3x',
\]

\text{eqn (1.2)}

where \(\mathbf{E}_0(x)\) is the electric field of the incident light, \(k = \frac{2\pi}{\lambda}\), and \(\mathbf{\tau}(x, x')\) is a tensor Green's function which satisfies

\[
\nabla_x \left[ \nabla_x \mathbf{\tau}(x, x') \right] + k^2 \mathbf{\tau}(x, x') = \frac{1}{4\pi} \delta^3(x-x')
\]

\text{eqn (1.3)}

\(\mathbf{\tau}(x, x')\) is given explicitly by

\[
\mathbf{\tau}(x, x') = (1 - \frac{i}{k^2} \nabla \nabla) \left( \frac{e^{ik|x-x'|}}{4\pi |x-x'|} \right)
\]
\[
(1 - \frac{\hat{R}^2}{\infty R^2}) e^{\frac{ik\hat{R}}{4\pi R}} + (3 \frac{\hat{R}^2}{\infty R^2} - 1) \left( \frac{1}{k^2 R^2} - \frac{i}{\hbar k R} \right) e^{\frac{ik\hat{R}}{4\pi R}}
\]

\[- \frac{1}{3k^2} \delta^3(R)\]

eqn (1.4)

where \( R = x - x', R = 1 \frac{x - x'}{l} \), and \( \hat{R} = \frac{R}{R} \). A list of further properties of \( \mathcal{F}(x, x') \) can be found in appendix C.

We will rederive equation (1.2) by a somewhat different approach than the one used by Saxon and Bustamante. This derivation is not as elegant, but has the advantage of providing a simple physical interpretation for equation (1.2). Let us begin by considering a system small compared to the wavelength of the incident light so that the oscillating charge density is effectively just the oscillating dipole moment given by eqn (1.1). The electric field of the incident light may be taken to be a monochromatic plane wave:

\[
E_0(x, t) = E_0 \hat{\varepsilon}_0 e^{i k_0 \cdot x - i\omega t}
\]

eqn (1.5)

where \( E_0, \hat{\varepsilon}_0, \) and \( k_0 \) are the amplitude, polarization, and wavevector of the incident light respectively. The frequency \( \omega \) is given by \( \omega = \frac{ck}{\lambda} = \frac{2\pi c}{\lambda} \). We take the molecule to have no time dependent behavior of its own, so the induced dipole moment oscillates with the same frequency as the incident light:

\[
\mu(t) = \hat{\mu} \cdot E_0 \hat{\varepsilon}_0 e^{i k_0 \cdot x - i\omega t}
\]

eqn (1.6)
where \( \alpha \) is not time dependent. The electric field produced by an harmonically oscillating dipole located at \( x' \) is given by:\(^8\)

\[
\mathbf{E}_{\text{dipole}}(x,t) = \mathbf{E}_{\text{scatt}}(x,t)
\]

\[
= k^2 \left( \hat{\mathbf{r}} \times \hat{\mathbf{m}} \right) \times \hat{\mathbf{r}} \frac{e^{ikR}}{R}
\]

\[
+ \left[ 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \hat{\mathbf{m}}) - \hat{\mathbf{m}} \right] \left( \frac{1}{R^2} - \frac{ik}{R} \right) \frac{e^{ikR}}{R}
\]

\[
= 4\pi k^2 \left[ \left( 1 - \hat{\mathbf{r}} \hat{\mathbf{r}} \right) \frac{e^{ikR}}{4\pi R}
\right]
\]

\[
+ \left( 3\hat{\mathbf{r}}\hat{\mathbf{r}} - 1 \right) \left( \frac{1}{k^2 R^2} - \frac{ik}{kR} \right) \frac{e^{ikR}}{4\pi R} \right] \cdot \mathbf{m}
\]

\[
= 4\pi k^2 \sum (x,x') \cdot \mathbf{m}
\]

\[
= 4\pi k^2 \sum (x,x') \cdot \alpha \cdot \mathbf{E}_0(x,t) \quad \text{eqn (1.7)}
\]
where $\hat{R}$, $R$, and $\hat{R}$ are the same as in equation (1.4). In this simple case the scattered field, $E_{\text{scatter}}(x)$, is just the field of a single oscillating electric dipole moment being driven by the incident electric field. It is apparent from equation (1.7) that the tensor Green's function $\mathbf{G}(x, x')$ can be interpreted as a tensor that gives the electric field at all points in space, $x$, due to an harmonically oscillating dipole located at $x'$. The total electric field at any point in space is then $E(x, t) = E_0(x, t) + E_{\text{scatter}}(x, t)$. In the limit of very large $R$ (that is, when the field is observed at a distance $|x - x'| \gg \lambda \}$ the dipole field becomes

$$
E_{\text{dipole}}(x, t) = \lim_{R \to \infty} 4\pi k^2 \mathbf{G}(x, x') \cdot \mathbf{\mu}(t)
$$

$$
\cong k^2 \left( 1 - \hat{k} \cdot \hat{R} \right) \frac{e^{ikR}}{R} \cdot \mathbf{\mu}(t) \quad \text{eqn (1.8)}
$$

where $\hat{k}$ is a unit vector equal to $\hat{R}$ and may be thought of as the wavevector of a plane wave travelling from the location of $\mathbf{\mu}$ to the observer. Equation (1.8) has the form of a spherical wave centered on $x'$. Figure 1.2 shows what this spherical wave looks like. The phase of $E_{\text{dipole}}$, given by $e^{ikR}$, is constant everywhere on any sphere having $x'$, the location of the dipole, as its center (hence the name spherical wave). The amplitude of the wave drops off as $1/R$ as the light radiates away from $x'$. The polarization of the light is determined by the quantity $(1 - \hat{k} \cdot \hat{R}) \cdot \mathbf{\mu}$. The tensor $(1 - \hat{k} \cdot \hat{R})$
Figure 1.2  Spherical wave produced by an harmonically oscillating point dipole moment at distances many wavelengths from the location of the dipole. The spherical surfaces in figure 1.2a are surfaces of constant phase (hence the name spherical wave). The polarization of the field is tangential to these spheres at all points. Figure 1.2b shows the radiated intensity in each direction. Notice that there is no radiation emitted in directions parallel to $\mathbf{\hat{n}}$. 
may be thought of as a projection operator which changes $\mathbf{A}$ into a vector that is the projection of $\mathbf{A}$ onto the plane perpendicular to $\hat{k}$. Since $\hat{k}$ is the direction in which the scattered light is travelling, $(1 - \hat{k}\hat{k})$ assures that the electric field will be transversal, that is, perpendicular to the direction of propagation of the wave at all points. The magnitude of the projection of $\mathbf{A}$ onto the plane perpendicular to $\hat{k}$ diminishes when $\hat{k}$ starts to become parallel to $\mathbf{A}$. In the direction parallel to $\mathbf{A}$, no light is emitted at all. The result is the toroidal pattern of emitted intensity shown in figure 1.2b.

In the limit of very short $R$ (that is, when the field is observed at a distance $|x - x'| \ll \lambda$) the dipole field (eqn (1.7)) becomes:

$$\mathbf{E}_{\text{dipole}}(x, t) = \lim_{R \to 0} 4\pi k^2 \frac{\mathbf{P}(x, x') \cdot \mathbf{A}}{R^3}$$

$$= \frac{3R^3 - 1}{R^3} \cdot \mathbf{A}$$

Eqn (1.9)

The dependence of the field on wavelength has disappeared from this expression and equation (1.9) is just the field produced by a static dipole moment. This field is not transversal, and drops off as $1/R^3$. The field in eqn (1.9) is therefore felt significantly only very close to the location of the dipole.

The two limits eqn (1.8) and eqn (1.9) are known as the far zone (or radiation zone) and near zone (or static zone) respectively. It is often
useful to think of these two zones separately, even though the fields arise from the same source. For scattering calculations it is the radiation zone that we are most concerned with of course, but the static zone fields can have indirect effects on the CIDS pattern. These effects will be investigated in chapter 2.

If there is more than one scattering group present the field felt by each group is no longer just the incident electric field. Each group feels both the incident field and the fields produced by each of its neighboring groups. But the field produced by each neighbor depends in turn on the field produced by the original group. In this situation we cannot write down the scattered field simply in terms of known fields and polarizabilities as in eqn (1.7). The best we can do is write an equation that the field must satisfy, and perhaps solve this equation approximately. If the system is composed of \( N \) scattering groups located at positions \( \mathbf{x}_i \), \( i = 1, \ldots, N \), and having polarizabilities \( \mathbf{\alpha}_i \), \( i = 1, \ldots, N \), then the field observed at \( \mathbf{x} \) due to the entire collection will be:

\[
E(\mathbf{x}, t) = E_0(\mathbf{x}, t) +
4\pi k^2 \sum_{i=1}^{N} \mathbf{\nabla}(\mathbf{x}, \mathbf{x}_i) \cdot \mathbf{\alpha}_i \cdot E(\mathbf{x}_i, t) \quad \text{eqn (1.10)}
\]

where \( E(\mathbf{x}_i, t) \) is the total electric field felt by the group located at position \( \mathbf{x}_i \). The first term in equation (1.10), \( E_0(\mathbf{x}, t) \), is
just the incident electric field, while the second term, the scattered field, is just the sum of fields produced by each oscillating dipole moment. The scattered electric field is therefore a superposition of spherical waves of the sort shown in figure 1.2. It is the interference between these waves that produces the scattering pattern observed in a scattering experiment.

If the number of scattering groups becomes very large and very closely spaced the polarizabilities \( \chi_i \) may be replaced by a polarizability density \( \chi(x') \), and the sum in eqn (1.10) goes over to an integral. The result is the integral equation, equation (1.2).

As it stands equation (1.10) is very difficult to solve exactly. In the calculations done by Bustamante, Maestre, and Tinoco\(^\text{1-6} \), the first Born approximation was used. In this approximation the electric field felt by each scattering group is taken to be the incident electric field, \( \mathbf{E}_0(x_i, t) \), alone:

\[
\mathbf{E}(x, t) \approx \mathbf{E}_0(x, t) + 4\pi k^2 \sum_{i=1}^{N} \nabla(x, x_i) \cdot \mathbf{\chi}_i \cdot \mathbf{E}_0(x_i, t).
\]

Clearly this approximation is valid only if the scattering groups are located far enough apart so that the near zone fields of each group have a negligible effect on the other groups, and if the scattering fields of each group are very weak compared to the incident field. Since we are interested only in the radiation zone fields, we may make the further approximations
\[ 4 \pi k^2 \sum (x, x_i) \cdot \alpha_i \cdot E_0 (x_i, t) \equiv \]

\[ 4 \pi k^2 \left( 1 - \hat{k} \hat{k} \right) \cdot \frac{e^{i k |x-x_i|}}{4 \pi r} \alpha_i \cdot E_0 (x_i, t) \equiv \]

\[ 4 \pi k^2 \frac{e^{i k n}}{4 \pi r} \left( 1 - \hat{k} \hat{k} \right) \cdot e^{-i \hat{k} \cdot x_i} \alpha_i \cdot E_0 (x_i, t) \]

\text{eqn (1.12)}

where \( r = |x| \), \( k = \frac{2 \pi \hbar}{\lambda} \), and we have made use of the approximations

\[ \frac{1}{|x-x_i|} \equiv \frac{1}{|x|} \quad \text{for} \quad (|x| \gg |x_i|), \]

\[ \hat{k} = \frac{x-x_i}{|x-x_i|} \equiv \frac{x}{|x|}, \]

and

\[ k |x-x_i| \equiv k |x| - k \hat{k} \cdot x_i + \ldots \]
for \( k\left(\mathbf{x}_i^2\right) = 2\pi \frac{1}{\lambda} \), \( \lambda \ll l \). This last series of approximations may appear quite severe at first glance, but in fact they are virtually exact in most experimental situations, where the detector is always very far away from the sample compared to both the dimensions of the sample and the wavelength of light. The effect of these approximations is to say that the intensity and direction of the waves scattered by each group is the same as if the groups were all located at the center of the system \( \mathbf{k}_i = \frac{\mathbf{k}}{l^2} \) and \( \frac{1}{l} \mathbf{x}_i - \mathbf{x}_i^2 = \frac{1}{l^2} \), but the relative phases of the waves vary depending on the actual position of each group (hence the factor \( e^{-i \mathbf{k}_i \cdot \mathbf{x}_i} \) in eqn (1.12)).

If we substitute eqn (1.5) for the incident field \( E_0(x^2, t) \), and combine eqns (1.11) and (1.12) we obtain

\[
\mathbf{E}(\mathbf{x}, t) = \left[ E_0 \mathbf{\hat{e}}_0 e^{i \mathbf{k}_0 \cdot \mathbf{x}} + E_0 k^2 \frac{e^{i \mathbf{k} \cdot \mathbf{r}}}{r} \left( 1 - \frac{\mathbf{k} \cdot \mathbf{k}}{2} \right) \right] e^{-i \omega t} \tag{1.13}
\]

with the scattered field alone given by

\[
\mathbf{E}_{\text{scat}}(\mathbf{x}, t) = E_0 e^{-i \omega t} k^2 \frac{e^{i \mathbf{k} \cdot \mathbf{r}}}{r} \left( 1 - \frac{\mathbf{k} \cdot \mathbf{k}}{2} \right) \cdot \mathbf{\hat{e}}_0 \tag{1.14}
\]
where $\Delta \mathbf{k} = \mathbf{k} - k_0$. We may rewrite eqn (1.14) in the form

$$E_{\text{scatt}}(\mathbf{x}, t) = (E_0 e^{-i\omega t}) k^2 \frac{e^{ikr}}{r} \quad (1 - \mathbf{e} \cdot \mathbf{e}_0) \quad \text{eqn (1.15)}$$

where

$$\Pi = \frac{N}{\omega} \sum_{i=1}^{N} e^{-i\Delta \mathbf{k} \cdot \mathbf{x}_i} \mathbf{x}_i \quad \text{eqn (1.16)}$$

Except for the factor $E_0 e^{-i\omega t}$, $E_{\text{scatt}}$ has a form like $E_{\text{dipole}}$ in eqn (1.12). Like the field of a single dipole, $E_{\text{scatt}}$ is a transversal spherical wave that falls off with distance as $1/r$. The important difference is that $\Pi$ (which plays the role of $\Pi$ in eqn (1.12)) is a function of $k$ instead of being a function only of the properties of the scatterer. This means that the intensity pattern will not be the toroidal shape in figure 1.2, but will depend on the overall arrangement of the collection of scattering groups.

For a continuous scattering system described by a polarizability density $\mathbf{a}(\mathbf{x'})$ equation (1.15) is unaltered except that $\Pi$ becomes

$$\Pi = \int e^{-i\Delta \mathbf{k} \cdot \mathbf{x'}} \mathbf{a}(\mathbf{x'}) d^3\mathbf{x'} \quad \text{eqn (1.17)}$$

From equation (1.17) it can be seen that $\Pi$ is just the Fourier transform of $\mathbf{a}(\mathbf{x'})$. If we consider the special case where $\mathbf{a}(\mathbf{x'})$ is
isotropic everywhere we may write

\[ \omega(x') = \frac{1}{2} \alpha \rho(x') \quad \text{eqn (1.18)} \]

where \( \rho(x') \) is the scatterer density of the system. In this case \( \Pi \) becomes

\[ \Pi = \frac{1}{2} \int e^{-i \Delta k \cdot x'} \rho(x') \, d^3x' \]

\[ = \frac{1}{2} F(\Delta k) \quad \text{eqn (1.19)} \]

where \( F(\Delta k) \) is just the structure factor familiar in the theory of X-ray diffraction. The \( \Pi \) matrix is therefore a generalization of the structure factor for the case where the electronic binding energy is important compared to the energy of the incident light, and the polarizability is therefore not isotropic.

In an actual experiment the quantity measured is the intensity of the scattered light in a particular direction, \( \hat{k} \). The intensity is related to the Poynting vector:

\[ I = \mathbf{S} \cdot \hat{k} \quad \text{eqn (1.20)} \]

where

\[ \mathbf{S} = \frac{\epsilon}{8\pi} \mathbf{E} \times \mathbf{B}^*. \quad \text{eqn (1.21)} \]
To find $\mathbf{B}$ we use one of Maxwell's equations and the fact that $\mathbf{B}$, like $\mathbf{E}$, must have harmonic time dependence $e^{-i\omega t}$:

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0$$

$$\frac{\partial \mathbf{B}}{\partial t} = -i\omega \mathbf{B}$$

therefore

$$\mathbf{B} = \frac{-i}{k} \nabla \times \mathbf{E} = \mathbf{k} \times \mathbf{E} \quad k = \omega/c$$

Eqn (1.22)

The last result is true only for radiation fields, and says that $\mathbf{B}$ is perpendicular to $\mathbf{E}$ and $\mathbf{k}$, as would be expected. The intensity is therefore given by

$$I = \frac{c}{8\pi} \left[ \mathbf{E} \times (\mathbf{k} \times \mathbf{E}) \right] \cdot \mathbf{k}$$

$$= \frac{c}{8\pi} \left| \mathbf{E} \right|^2$$

Eqn (1.23)
The scattered intensity is therefore given by

\[ I_{\text{scatt}} = \frac{c}{8\pi} |E_{\text{scatt}}|^2 \]

\[ = \frac{c |E_0|^2 k^4}{8\pi r^2} \left| \left( \mathbf{1} - \hat{k} \hat{k} \right) \cdot \hat{\pi} \cdot \hat{\xi}_0 \right|^2 = I_0 \frac{k^4}{r^2} \sum_i \sum_j \left( e^{-i\Delta k \cdot (\mathbf{x}_j - \mathbf{x}_i)} \hat{\xi}_0^* \hat{\alpha}_i^\dagger \left( \mathbf{1} - \hat{k} \hat{k} \right) \cdot \hat{d}_j \cdot \hat{\xi}_0 \right) \]

\[ \text{eqn (1.24)} \]

where \( I_0 = \frac{c |E_0|^2}{8\pi} \), and we have used

\[ \left[ \left( \mathbf{1} - \hat{k} \hat{k} \right) \cdot \hat{\alpha}_i \cdot \hat{\xi}_0 \right]^* = \hat{\xi}_0^* \hat{\alpha}_i^\dagger \left( \mathbf{1} - \hat{k} \hat{k} \right) \]

and

\[ \left( \mathbf{1} - \hat{k} \hat{k} \right) \cdot \left( \mathbf{1} - \hat{k} \hat{k} \right) = \mathbf{1} - \hat{k} \hat{k} \].

In equation (1.24) the intensity is proportional to \( k^4 \) (or \( 1/\lambda^4 \)) which is the well known wavelength dependence of Rayleigh scattering intensities (and the famous explanation for the blue sky). Also, the factors \( e^{-i\Delta k \cdot (\mathbf{x}_j - \mathbf{x}_i)} \) appear. These quantities keep track of the phase differences in the waves scattered from different parts of the system. It is these phase differences that give rise to interference and give detail to the scattering pattern. Detail in the pattern is greatest when these phase differences are large. Since
\[ \Delta \mathbf{k} \cdot (\mathbf{x}_j - \mathbf{x}_i) = \frac{2\pi}{\lambda} \mathbf{r}_{ij} \cdot \mathbf{r}_{ij} \]

(Where \( \mathbf{r}_{ij} = \mathbf{x}_j - \mathbf{x}_i \) is the distance vector between groups i and j), the interference is significant only when \( \frac{2\pi \mathbf{r}_{ij}}{\lambda} \) is on the order of unity or greater. It is therefore possible for light with wavelength \( \lambda \) to "see" details of a structure that has dimensions of \( \mathbf{r}_{ij} \geq \frac{\lambda}{2\pi} \).

If \( \mathbf{r}_{ij} \) is too much larger than \( \lambda \) however, small variations in distances due to fluctuations or disorder in the system can cause the interference to be averaged away, and the scattering pattern again loses detail. The condition for maximum detail in a scattering pattern is therefore that the relevant dimensions of the system be of the order of the incident wavelength.

B. Classical Expression for CIDS in the First Born Approximation

We are now in a position to compute the CIDS. We need the quantities \( I_{\text{scatt}}^L \) and \( I_{\text{scatt}}^R \), where L and R denote left and right circularly polarized light. These intensities are obtained by replacing \( \mathbf{E}_0 \) in eqn (1.24) with appropriate circular polarization vectors. In the conventions we have adopted (see page 7, Introduction) the polarization vectors are

\[ \mathbf{E}_L = \frac{1}{\sqrt{2}} (\mathbf{x} + i\mathbf{y}) \quad \mathbf{E}_R = \frac{1}{\sqrt{2}} (\mathbf{x} - i\mathbf{y}) \]
where \( \hat{\mathbf{x}} \) and \( \hat{\mathbf{y}} \) are two real unit vectors which together with \( \hat{\mathbf{z}}_0 \) form a right handed orthogonal coordinate system. With these definitions:

\[
\mathcal{I}_{\text{scat}}^{L,R} = I_0 \frac{k_0^4}{r^2} \left| (1 - \hat{\mathbf{z}}_0 \cdot \hat{\mathbf{z}}_0) \cdot \mathbf{\Pi} \cdot \hat{\mathbf{e}}_{L,R} \right|^2
\]

and the CIDS is

\[
\Delta = \frac{\mathcal{I}_{\text{scat}}^L - \mathcal{I}_{\text{scat}}^R}{\mathcal{I}_{\text{scat}}^L + \mathcal{I}_{\text{scat}}^R} = \frac{\left| (1 - \hat{\mathbf{z}}_0 \cdot \hat{\mathbf{z}}_0) \cdot \mathbf{\Pi} \cdot \hat{\mathbf{e}}_L \right|^2 - \left| (1 - \hat{\mathbf{z}}_0 \cdot \hat{\mathbf{z}}_0) \cdot \mathbf{\Pi} \cdot \hat{\mathbf{e}}_R \right|^2}{\left| (1 - \hat{\mathbf{z}}_0 \cdot \hat{\mathbf{z}}_0) \cdot \mathbf{\Pi} \cdot \hat{\mathbf{e}}_L \right|^2 + \left| (1 - \hat{\mathbf{z}}_0 \cdot \hat{\mathbf{z}}_0) \cdot \mathbf{\Pi} \cdot \hat{\mathbf{e}}_R \right|^2}
\]

eqn (1.25)

The quantities in the numerator and denominator of eqn (1.25) can be simplified somewhat by taking advantage of the fact that \( \hat{\mathbf{e}}_L = \hat{\mathbf{e}}_R^* \). The algebra is somewhat tedious and will not be reproduced here (but see pages 110 - 111, Chapter 3). The final result is

\[
\Delta = \frac{-i (\mathbf{\Pi} \times \mathbf{\Pi}^\dagger)_{\alpha\beta \gamma} (\delta_{\lambda \gamma} - \hat{\mathbf{k}}_\alpha \hat{\mathbf{k}}_\gamma) \hat{\mathbf{k}}_{\kappa \rho}}{\prod_{\alpha \beta} \prod_{\gamma \delta} (\delta_{\beta \gamma} - \hat{\mathbf{k}}_{\kappa \rho} \hat{\mathbf{k}}_{\kappa \gamma}) (\delta_{\alpha \delta} - \hat{\mathbf{k}}_{\alpha \rho} \hat{\mathbf{k}}_{\delta \rho})}
\]

eqn (1.26)

where repeated indices imply a summation, and the quantity \( \mathbf{\Pi} \times \mathbf{\Pi}^\dagger \) is defined as

\[
(\mathbf{\Pi} \times \mathbf{\Pi}^\dagger)_{\alpha\beta \gamma} = \epsilon_{\beta \gamma \rho} \mathbf{\Pi}_{\alpha \delta} \mathbf{\Pi}^\dagger_{\delta \rho}
\]

eqn (1.27)

where the dagger, \( ^\dagger \), indicates the Hermitian conjugate of a matrix:
\((\pi^+)_{ij} = \pi_{ji}^\ast\). The symbol \(\epsilon_{\rho ij}\) is the Levi-Civita symbol

\[
\epsilon_{\rho ij} = \begin{cases} 
0 & \text{i} = \text{j} \text{ or } \text{j} = \rho \text{ or } \text{i} = \rho \\
1 & \text{any cyclic permutation} \\
-1 & \text{any odd permutation}
\end{cases} \\
\text{of }\ i=1, j=2, \rho = 3
\]

Less formally, \(\epsilon_{\rho ij}\) is a "cross product" tensor, and the quantity \(\pi \times \pi^\dagger\) is the cross product of two tensors. For example, the result of a cross product of two dyadic tensors is a "triadic":

\[
(a \otimes c) \times (c \otimes d) = a \otimes (b \times c) \otimes d \quad \text{eqn (1.28)}
\]

where \(b \times c\) is the usual cross product of two vectors. Since any second rank tensor can be written as a sum of dyadics, eqn (1.28) can be considered an alternate definition of the cross product of tensors.

Under global rotations the quantity \(\pi \times \pi^\dagger\) transforms as a third-rank pseudovector, that is, under rotations

\[
(\pi \times \pi^\dagger)_{\alpha \rho \gamma} \rightarrow (\pi \times \pi^\dagger)_{\mu \nu \lambda} R_{\mu \alpha} R_{\nu \rho} R^{-1}_{\lambda \gamma}
\]

A global rotation is a simultaneous rotation of the wave vectors \(\mathbf{\ell}_0\) and \(\mathbf{\ell}_1\), and the sample (i.e., a rotation of both the sample and the measuring device). Later we will consider samples which are rotationally disordered. This involves rotations of the sample independent of the wave vectors and vice-versa. \(\pi\) is not a tensor of well defined rank under these latter, non-global rotations.
but $\vec{\Pi} \times \vec{\Pi}^+$ does not change sign under spatial inversion of the coordinates. At first glance it may seem that this last property is a manifestation in the CIDS theory of one of the properties characteristic of all forms of optical activity, namely that mirror-image structures (enantiomers) give CIDS patterns of identical shape but opposite sign. (By an argument based only on the conservation of parity it can be shown that for all forms of optical activity, enantiomers give signals of identical magnitudes but opposite sign.) However, the CIDS should not change sign under global inversion of coordinates (by conservation of parity); it should change sign only under an inversion of the sample alone. In eqn (1.26) it appears that $\Delta$ changes sign under a global inversion, but $\hat{k}_0$ in the numerator of eqn (1.26) is actually a pseudovector, $\vec{\varepsilon}_L \times \vec{\varepsilon}_R = -i \hat{k}_0$. Therefore the numerator has the form of a contraction of two pseudotensors, and $\Delta$ does not change sign under global inversion.

If we substitute eqn (1.16) into eqn (1.26) we obtain an explicit expression for CIDS in terms of individual polarizabilities:

$$\Delta = \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} e^{-i \Delta k \cdot \vec{\nu}_{ij}} (\vec{\alpha}_j \times \vec{\alpha}_i)^{\alpha \rho \gamma} (\vec{s}_\gamma \hat{k}_\alpha \hat{k}_\rho \hat{k}_\gamma) \hat{k}_{\rho \gamma}}{\sum_{i=1}^{N} \sum_{j=1}^{N} e^{-i \Delta k \cdot \vec{\nu}_{ij}} \epsilon_{i \rho \sigma} \epsilon_{j \sigma \gamma} (\vec{s}_\gamma \hat{k}_\alpha \hat{k}_\rho \hat{k}_\sigma \hat{k}_\gamma \hat{k}_{\rho \sigma})}$$

eqn (1.31)

The same phase factors $e^{-i \Delta k \cdot \vec{\nu}_{ij}}$ appear in eqn (1.31) for the CIDS
as in eqn (1.24) for the scattered intensity. This means that the CIDS pattern, like the scattered intensity pattern, will be largest and most detailed when \( \frac{2\pi r_{ij}}{\lambda} \sim 1 \). In the CIDS the magnitude of the contribution made by each pair of groups \( i \) and \( j \) is controlled by the quantity 

\[
(\alpha_i \times \alpha_j^\dagger) \alpha_\rho \gamma (S_{\omega \gamma} - \hat{k}_\omega \hat{k}_\gamma) \hat{k}_0 \beta
\]

To see what this means, let us consider two uniaxial groups with polarizabilities \( \alpha_1 = \alpha_1 \hat{e}_1 \hat{e}_1 \) and \( \alpha_2 = \alpha_2 \hat{e}_2 \hat{e}_2 \):

\[
(\alpha_2 \times \alpha_1^\dagger) \alpha_\rho \gamma (S_{\omega \gamma} - \hat{k}_\omega \hat{k}_\gamma) \hat{k}_0 \beta =
\]

\[
\alpha_1^* \alpha_2 \left[ \hat{e}_2 \alpha (\hat{e}_2 \times \hat{e}_1) \cdot \hat{e}_1 \gamma \right] (S_{\omega \gamma} - \hat{k}_\omega \hat{k}_\gamma) \hat{k}_0 \beta
\]

\[
= \alpha_1^* \alpha_2 \left[ \hat{e}_2 \cdot (\hat{e}_2 \times \hat{e}_1) \cdot \hat{e}_1 \right] (\hat{e}_2 \times \hat{e}_1) \cdot \hat{k}_0
\]

\[
= \alpha_1^* \alpha_2 \left[ \hat{e}_2 \cdot \hat{e}_1 - (\hat{e}_2 \cdot \hat{k}_\omega)(\hat{e}_1 \cdot \hat{k}_\omega) \right] (\hat{e}_2 \times \hat{e}_1) \cdot \hat{k}_0
\]

\[
eqn (1.32)
\]

If the groups are arranged as shown in figure 1.3 and \( \hat{k}_0 \) is along the axis that joins the midpoints of the groups, then the pair of groups will have a non-zero contribution to the CIDS pattern except when \( \phi_{12} = 0^\circ \).
Two scattering groups with uniaxial polarizabilities \( \alpha_1 = \alpha_1 \, \hat{e}_1 \, \hat{e}_1 \) and \( \alpha_2 = \alpha_2 \, \hat{e}_2 \, \hat{e}_2 \). The groups have been arranged so that they are both lying in planes perpendicular to the axis that joins their midpoints. The groups are arranged in a chiral fashion so long as \( \phi_{12} \) is not 0° or 90°.
or $\phi_{12} = 90^\circ$. At these two angles the groups are not chirally arranged. The quantity $(\alpha_j \times \alpha_i^\dagger) \alpha \gamma (S_{\alpha r} - \hat{k}_d \hat{k}_r) \hat{k}_{0\beta}$ is therefore responsible for picking out the chiral relationships that exist between various parts of the sample.

There are two other properties of CIDS patterns that are easily proven using eqn (1.31):

1) the CIDS in the forward direction ($\Theta = 0^\circ$) is zero, and

2) the CIDS of a collection of purely isotropic polarizabilities is zero.

First we show that the CIDS in the forward direction is zero. In the forward direction $\Delta \hat{k} = 0$, and the numerator in eqn (1.31) is given by

$$
\sum_{i=1}^{N} \sum_{j=1}^{N} (\alpha_j \times \alpha_i^\dagger) \alpha \gamma (S_{\alpha r} - \hat{k}_d \hat{k}_r) \hat{k}_{0\beta}
$$

Since

$$(\alpha_j \times \alpha_i^\dagger) \alpha \gamma (S_{\alpha r} - \hat{k}_d \hat{k}_r) \hat{k}_{0\beta}$$

$$= -(\alpha_i \times \alpha_j^\dagger) \alpha \gamma (S_{\alpha r} - \hat{k}_d \hat{k}_r) \hat{k}_{0\beta}$$

the terms in the double sum cancel in pairs.
The second proof is equally straightforward. If all the groups in the system are isotropic, the polarizabilities may be written

$$\alpha_i = \alpha_i \frac{1}{2}$$

The numerator in eqn (1.31) is then given by

$$(\sum \sum e^{-i \Delta k \cdot r_{ij}} \alpha_i \alpha_j) \left( \frac{1}{\omega} \frac{1}{\omega} \right) d\rho \left( S_{kr} \hat{k}_k \hat{k}_r \right) k_0 \beta$$

But,

$$\left( \frac{1}{\omega} \frac{1}{\omega} \right) d\rho \left( S_{kr} \hat{k}_k \hat{k}_r \right) k_0 \beta = (\hat{\mathbf{k}} \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{k}}_0 = 0$$

Therefore the CIDS of a system of isotropic groups is zero.

Both of the above properties depend on the fact that eqn (1.31) was derived using the first Born approximation. In chapter 2 this approximation will be improved upon and it will be found that there can be forward CIDS and that systems of isotropic groups can have non-zero CIDS. Even so, in most situations the CIDS in the forward direction is small, and the CIDS diminishes as scattering groups become more and more isotropic.

C. Rotationally Averaged CIDS

Equation (1.26) gives the CIDS for a stationary, well oriented scattering object. If the system is, say a suspension of bacteriophages
in solution however, there is no well-defined orientation of the scatterers with respect to the incident light. In this case eqn (1.26) must be averaged over all possible orientations. The averaging process has been described in detail in references 1 and 5. Briefly, we first choose the polarizabilities to be uniaxial:

\[ \bar{\chi}_i = \chi_i \hat{e}_i \hat{e}_i \quad i = 1, \ldots, N \]

where \( \hat{e}_i \) is the principle axis of \( \bar{\chi}_i \). Substituting eqn (1.16) for \( \Pi \) into eqn (1.26) we obtain

\[
\Delta = \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} e^{-i \Delta \vec{k} \cdot \vec{r}_{ij}} \alpha_i^* \alpha_j \left[ \left( \hat{e}_i \cdot \hat{e}_j \right) \cdot \hat{k}_o \right] \times \left[ \hat{e}_i \cdot \left( 1 - \hat{k}_o \hat{k} \right) \cdot \hat{e}_j \right]}{\sum_{i=1}^{N} \sum_{j=1}^{N} e^{-i \Delta \vec{k} \cdot \vec{r}_{ij}} \alpha_i^* \alpha_j \left[ \left( \hat{e}_i \cdot \hat{e}_j \right) \cdot \hat{k}_o \right] \times \left[ \hat{e}_i \cdot \left( 1 - \hat{k}_o \hat{k} \right) \cdot \hat{e}_j \right]} \]

\text{eqn} \ (1.33)

The numerator and denominator are now averaged separately. The result is:

\[
\langle \Delta \rangle_{\text{ave}} = \frac{\langle I_{\text{scatt}}^L - I_{\text{scatt}}^R \rangle}{\langle I_{\text{scatt}}^L + I_{\text{scatt}}^R \rangle} \quad \text{eqn} \ (1.34)
\]

with
\[
\langle I_{\text{scatt}}^L - I_{\text{scatt}}^R \rangle = \left( \frac{c |E_0|^2 k^4}{8 \pi r^2} \right)
\]

\[
\times \sum_{i=1}^{N} \sum_{j=1}^{N} \alpha_i^* \alpha_j \left( \hat{e}_j \times \hat{e}_i \right) \cdot r_{ij} \sum \left[ \left( \hat{e}_i \cdot \hat{e}_j \right) \left( j_{2/q} - j_i \right) \right.
\]

\[
- \left( \hat{e}_j \cdot r_{ij} \times \hat{e}_i \cdot r_{ij} \right) \left( 5 j_{2/q} - j_i \right) \left( \sin \beta + \sin^3 \beta \right) \left[ \sin \beta + \sin^3 \beta \right]
\]

and

\[
\langle I_{\text{scatt}}^L + I_{\text{scatt}}^R \rangle = \left( \frac{c |E_0|^2 k^4}{8 \pi r^2} \right)
\]

\[
\times \frac{8}{15} \sum_i |\alpha_i|^2 \left( 1 - \sin \beta \cos^2 \beta \right) + \sum_i \sum_j \alpha_i^* \alpha_j \sum \left( \hat{e}_i \cdot \hat{e}_j \right) \left( \hat{e}_j \cdot \hat{e}_i \right) \sum \left[ \left( j_0 - j_{1/q} \right) \right.
\]

\[
+ \sin^2 \beta \left( 3 j_{1/q} - j_0 \right) \left( \hat{e}_i \cdot \hat{e}_j \right) -
\]

\[
2 \left( \hat{e}_i \cdot \hat{e}_j \right) \left( \hat{e}_j \cdot \hat{e}_i \right) \left[ \left( j_{1/q} - 4 j_{2/q} \right) - \sin^2 \beta \left( j_{2/q} \right) \right.
\]

\[
+ \sin^4 \beta \left( j_{1/q} - 3 j_{2/q} \right) \left[ \sin \beta + \sin^3 \beta \right] \]
\[(\hat{e}_i \times \hat{e}_j) \cdot (\hat{e}_j \times \hat{e}_i) \approx \frac{1}{2}[(j_0 + j_1/q) + \sin^2 \rho (j_0 - 3j_1/q)](\hat{e}_i \cdot \hat{e}_j) \]

\[-\frac{1}{2}(\hat{e}_i \cdot \hat{e}_j)(\hat{e}_j \cdot \hat{e}_j)[(16j_2/q^2 - 3j_1/q + j_0) + \sin^2 \rho (4j_2/q^2 - 3j_1/q + j_0)] + \sin^4 \rho (5j_2/q^2 - 3j_1/q) \]

\[-\frac{1}{2}[(\hat{e}_i \times \hat{e}_j)^2 + (\hat{e}_i \times \hat{e}_j) \hat{e}_j] \sin^2 \rho (j_0 - j_1/q) - \sin^4 \rho (j_0 - 3j_2/q^2) \]

\[-[\hat{e}_i \cdot (\hat{e}_i \times \hat{e}_j)]^2 [(\sqrt{8})(-9j_2/q^2 + 2j_1/q + j_0) - \frac{1}{8} \sin^2 \rho (9j_2/q^2 + 2j_1/q + 3j_0)] \]

\[-[\hat{e}_j \cdot (\hat{e}_i \times \hat{e}_i)]^2 [\frac{1}{8} (5j_2/q^2 + 2j_1/q - j_0) + \frac{1}{8} \sin^2 \rho (3j_2/q - 4j_1/q - j_0)] \]
\[
\frac{1}{4} \sin^2 \beta \left(-5j_2/q + 2j_1/q + j_0\right) + \frac{1}{8} \sin^4 \beta \left(3j_2/q^2 - 6j_1/q - j_0\right) \]

\text{eqn (1.36)}

where

\[\alpha_i = \hat{e}_i \cdot \hat{e}_i, \quad \hbar_{ij} = \hbar_{ij}/r_{ij}, \quad q = 4\pi r_{ij} \sin \beta / \lambda, \quad \beta = \theta/2 \quad (\theta \text{ is the scattering angle, the angle between } \hat{e} \text{ and } \hat{e}_{0}),\]

and \(j_0, j_1, \) and \(j_2\) are the spherical Bessel functions of order 0, 1, and 2 respectively. The unit vectors \(\hat{e}_i\) are taken to be real in this expression. (This means that the polarizabilities \(\alpha_i\) cannot represent groups which are optically active all by themselves. See appendix B.)

These expressions may be generalized for polarizabilities with three principle axes

\[\alpha_i = \sum_{k=1}^{3} \alpha_{ik} \hat{e}_k \cdot \hat{e}_k\]

by replacing each \(\hat{e}_i\) with \(\hat{e}_k\), each \(\hat{e}_j\) with \(\hat{e}_l\), and the quantity \(\alpha_i \cdot d_j\) with \(\sum_{k=1}^{3} \alpha_{ik} \alpha_{kl} \).

A detailed interpretation of these equations is given by Bustamante,\(^1\) pp 213-222 and pp 228-230.

The theory summarized in this chapter suffers from several shortcomings. First the scattered electric fields were calculated using the first Born approximation. This amounts to saying that the electric field felt by any one scattering group is the incident electric field alone, and that the electric fields produced by neighboring groups are small enough to be neglected. This approximation is not valid for many of the dense scattering systems encountered in biology. In the next chapter we will extend the theory to the second Born approximation, in which the scattering groups are allowed to interact with each other via their induced electric fields.
Second, we assumed that the response of each scattering group could be described as an induced point dipole moment. This cannot always be done however. If the various parts of a sample are strongly statically coupled to each other so that a perturbation of one part causes the other parts to move as well, then the system cannot be broken up into a collection of small, independent subunits. In principle even for groups which are small compared to the incident wavelength the response would include induced electric quadrupole, octupole, and higher moments, as well as induced magnetic dipole and higher moments.

Finally, in eqns (1.5) and (1.6) we assumed that the time dependence of the response of the system was purely harmonic, with frequency equal to the frequency of the incident light. This is equivalent to saying that the scattering system has no internal motion of its own, but is only capable of a passive response to the electric driving forces. The result is that our equations predict that all of the scattered light has the same frequency as the incident light, that is, all the light is elastically scattered. In practice however, some light is inelastically scattered, and the scattered light has a spectrum of frequencies. This spectrum contains information about the dynamic aspects of the scatterer. Raman scattering and dynamic light scattering are two examples of physical techniques based on inelastic scattering effects. In chapter 3 we will present a quantum mechanical theory for the CIDS which accounts properly for the finite size of the scatterer and inelastic scattering processes.

Bibliography
In the last chapter we presented a theory for the difference in the scattering cross-sections for incident right and left circularly polarized light by chiral objects of arbitrary size and shape. The theory was developed within the framework of the first Born approximation, that is, the internal field of the scatterer was assumed to be that of the incident electromagnetic wave. Several general properties of CIDS pattern were found in this approximation: 1-4, 7

1) Mirror-image chiral structures give mirror-image CIDS patterns, except that the signs of the signals are reversed. This reversal of sign occurs both when the system is rotationally averaged, where the scattering patterns are symmetric about the direction of the incident light, and when the system is oriented, where CIDS patterns need not be symmetric. 3 These results are consequences of parity conservation, and have analogs in all types of optical activity.

2) The CIDS patterns are very sensitive to parameters which characterize the chirality of the scattering system, but insensitive to parameters which characterize overall size. In particular, it will be shown that the CIDS of oriented periodic structures depend only on the chiral properties of one unit cell.

3) There is no CIDS in the direction parallel to the incident light beam (the forward direction).

4) There is no CIDS for structures composed solely of isotropic scattering groups, even though the groups may be arranged in a chiral fashion.

The first Born approximation is expected to be valid when the
density of scattering centers is relatively low, or when the polarizabilities of the scatterer are not very different from the solvent. This is not always the case in aggregates of biological origin, however.

In this chapter we present a theory for CIDS in the second Born approximation. The second Born approximation accounts for some of the effects of the multiple scattering of light and of dipole-dipole coupling between scatterers. The presence of multiple scattering and dipole-dipole coupling alters the third and fourth conclusions listed above, so that now there can be CIDS in the forward direction and systems of isotropic scatterers can have non-zero CIDS.7

A. The Second Born Approximation

In previous derivations the effective perturbation field at each point polarizable group was assumed to be the incident field, \( \mathbf{E}_0 \). This is the first Born approximation for the internal field. A more realistic approach should account for the electric fields scattered by other groups in the same structure; it should also account for the mutual interaction between groups caused by the dipole moments that are induced by the incident field. This may be done simply and consistently by use of the second Born approximation.

The electric field produced by a traveling electromagnetic wave interacting with a distribution of polarizable point groups can be found by solving the integral equation in chapter 1, eqn (1.2):

\[
\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + 4\pi k^2 \int \mathbf{G}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') \cdot \mathbf{E}(\mathbf{r}') d^3r'
\]

\[\text{eqn (2.1)}\]
where \( E' \) is the incident wave, the wavelength \( \lambda = \frac{2\pi}{k} \), and \( \alpha' (r') \) is the polarizability density for the scattering system. In the case where the system is a discrete collection of \( N \) scattering groups, eqn (2.1) becomes

\[
E(\vec{r}) = E'_0(\vec{r}) + 4\pi k^2 \sum_{i=1}^{N} \Gamma(\vec{r}, \vec{r}_i) \cdot \alpha_i \cdot \vec{E}(\vec{r}_i) \quad \text{eqn (2.2)}
\]

where \( \alpha_i \) is the polarizability of the \( i \)th group. The quantity \( \Gamma(\vec{r}, \vec{r}_i) \) is the tensor Green's function described in chapter 1, eqns (1.2)-(1.4), and in appendix C.

As was pointed out in chapter 1, equation (2.2) can be given a simple physical interpretation by noticing that the electric field produced by an oscillating dipole located at \( \vec{r}_i \) and measured at \( \vec{r} \) is:

\[
\vec{E}_{\text{dipole}}(\vec{r}) = 4\pi k^2 \sum_{i=1}^{N} \Gamma(\vec{r}, \vec{r}_i) \cdot \alpha_i \quad \text{eqn (2.3)}
\]

If the oscillating dipole is an induced dipole we may write

\[
\alpha_i = \alpha_i \cdot \vec{E}_{\text{int}}(\vec{r}_i) \quad \text{eqn (2.4)}
\]

where \( \vec{E}_{\text{int}} \) is the internal field of the scattering system, the field actually felt inside the system at the group at \( \vec{r}_i \). If the electric field \( \vec{E}(\vec{r}) \) were known exactly inside the system, the internal field, \( \vec{E}_{\text{int}}(\vec{r}_i) \), would be \( \vec{E}(\vec{r}_i) \). Equation (2.2) is therefore a statement that in the absence of any explicit charges or currents the electric field is the sum of the fields produced by oscillating induced
dipoles.

It is usually not feasible to find the exact electric field at all points in space, and the electric fields inside and outside the system are best treated separately. To solve eqn (2.2) we must therefore find an adequate approximation to the internal field, $E_{\text{int}}$. We may write

$$E_{\text{int}}(r_i) = E_0(r_i) + E_{\text{ind}}(r_i)$$  \hspace{1cm} \text{eqn (2.5)}$$

where $E_{\text{ind}}$ is the field induced by the action of $E_0$ on the polarizable groups surrounding $r_i$. In the first Born approximation $E_{\text{ind}}$ is now considered negligible compared to $E_0$. This approximation is valid only when the polarizabilities are so weak and the dipoles are so far apart that each dipole may be considered not to be affected by any of the others. A first order correction for the interaction between polarizable groups may be made by adding an approximate induced field. Using equations (2.3), (2.4), and (2.5):

$$E_{\text{ind}}(r_i) \cong 4\pi k^2 \sum_{j \neq i}^{N} \hat{r}_{ij} \cdot \hat{d}_j \cdot E_0(r_j)$$  \hspace{1cm} \text{eqn (2.6)}$$

where $\hat{r}_{ij} = \hat{r}(r_i, r_j)$. This says that the induced electric field is the sum of dipole fields produced by all groups in the system if each group sees only the incident electric field. The internal field (eqn (2.5)) now has a contribution from the fields of surrounding groups. This allows some weak coupling between the scattering groups and amounts to the second Born approximation. Combining equations (2.5) and (2.6), and substituting into eqn (2.2) we find

$$E(r) \cong E_0(r) + 4\pi k^2 \sum_{i=1}^{N} \hat{r}(r, r_i) \cdot \hat{d}_i .$$
\[ E_0(r_i) + 4\pi k^2 \sum_{j \neq i} \vec{a}_{ij} \cdot \vec{a}_j \cdot E_0(r_j) \]  

**eqn (2.7)**

Equation (2.7) should be compared to eqn (1.11) for the electric field in the first Born approximation.

If we now make the usual far-field approximation to the scattered wave (see eqn (1.12), chapter 1) we obtain

\[ E_{\text{scat}}(r) = \frac{k^2 e^{i k r}}{r} (1 - \vec{k} \cdot \vec{k}_0) \cdot \sum_{i=1}^{N} e^{-i \vec{k} \cdot \vec{r}_i} \vec{a}_i. \]

\[ [ E_0 \hat{E}_0 e^{i k_0 \cdot \vec{r}_i} + 4\pi k^2 \sum_{j \neq i} \vec{a}_{ij} \cdot \vec{a}_j \cdot E_0 \hat{E}_0 e^{i k_0 \cdot \vec{r}_j} ] \]

**eqn (2.8)**

where \( k \) and \( k_0 \) are the wave vectors of the scattered and incident light respectively, and we have taken the incident field to be \( E_0 = E_0 \hat{E}_0 e^{i k_0 \cdot \vec{r}_i} \).

In many applications it may be that the distance over which polarizable groups interact significantly is very short compared to the wavelength of the incident light. In this case \( \alpha \ll |\vec{r}_j - \vec{r}_i|/4\pi k^2 \) and \( k |\vec{r}_j - \vec{r}_i| \ll 1 \) the Green's function is effectively reduced to

\[ \Gamma_{ij} = \frac{3 \hat{\kappa}_{ij} \cdot \hat{\kappa}_{ij} - 1}{4\pi k^2 r_{ij}^3} \]

where \( \hat{\kappa}_{ij} = \kappa_{ij} - \kappa_i \). This approximation is equivalent to saying that the incident wave has a wavelength so long that it appears to be uniform over the distance in which interactions are significant. In our calculations we have used the full \( \Gamma_{ij} \) tensor, eqn (1.4), for finding
the CIDS of oriented systems, and the short-ranged $\Gamma_{ij}$ tensor, eqn (2.9), for finding the CIDS of rotationally averaged systems.

The scattered electric field produced by left or right circularly polarized incident light is given by

$$E_{\text{scatter}, L,R} = \frac{e^{i kn}}{n} k^2 \left( 1 - \hat{k} \cdot \hat{k} \right) \cdot \sum_{i=1}^{N} e^{-i \hat{k} \cdot \vec{r}_i} \left[ \alpha_i \left( 1 + 4\pi k^2 \sum_{j \neq i} \prod_{ij} \alpha_j \cdot e^{i k_0 \cdot (\vec{r}_j - \vec{r}_i)} \right) \right].$$

Notice that the terms in the square brackets can be interpreted as a new, effective polarizability (in general complex) of the nth group resulting from its interaction with surrounding groups. Physically the existence of this effective polarizability means that in the presence of interaction the incident light does not perturb a single isolated group, but rather causes a collective response of groups coupled through their mutual interaction in the molecule. When the groups are close together the dominant term of this interaction is a dipole-dipole coupling among the groups of its nearest neighbors. This coupling is described by eqns (2.9) and (1.9). When the groups are far apart the interaction takes place through radiation coupling which is equivalent to multiple scattering effects among the groups in the molecule (see eqn (1.8)).

If the scattering system is continuous, with scattering properties described by a polarizability density $\alpha(\vec{r})$, the electric field in the second Born approximation is given by an equation similar to eqn (2.10):

$$E_{\text{scatter}, L,R} = \frac{e^{i kn}}{n} k^2 \left( 1 - \hat{k} \cdot \hat{k} \right) \cdot \int e^{-i \hat{k} \cdot \vec{r} \cdot \vec{r}}$$
\[
\left[ \alpha_i(r) \cdot \left( \frac{1}{2} + 4\pi k^2 \int \frac{1}{r} \cdot \alpha_j(r') \cdot e^{i k_0 (r-r')} \, d^3 r' \right) \right] 
\cdot E_0 e^{ik_0 \cdot r} \, d^3 r
\]
eqn (2.11)

where \( \Pi(r, r') \) is given by eqn (1.4). As in eqn (2.10), the quantity in the square brackets may be interpreted as an effective polarizability resulting from interactions between the polarizability at position \( r \) and all the other parts of the system.

In chapter 1 we found it convenient to express the scattered electric field in terms of a matrix \( \Pi \), such that

\[
E_{\text{scatt}} = E_0 \frac{e^{ik_0 \cdot r}}{r} \left( 1 - \hat{k} \hat{r} \right) \cdot \Pi \cdot \hat{r}_0
\]
eqn (2.12)

When \( E_{\text{scatt}} \) is computed in the second Born approximation it can still be given by an expression with the form of eqn (2.12), but now the \( \Pi \) matrix is given by

\[
\Pi = \sum_i e^{-i \Delta k \cdot \hat{r}_j} \alpha_i
\]
eqn (2.13)

with the effective polarizability \( \alpha_i' \) given by

\[
\alpha_i' = \alpha_i \cdot \left( 1 + 4\pi k^2 \sum_{j \neq i} \frac{1}{r_{ij}} \cdot \alpha_j e^{i k_0 (r_j - r_i)} \right)
\]
eqn (2.14)

Similar expressions can be obtained for continuous systems by comparing eqn (2.11) with eqn (2.12).

B. Higher-Order Approximations
In general, higher-order approximations than the second Born approximation are possible (for example, see section G of this chapter), and may be necessary for dense and strongly polarizable systems. In these higher-order approximations the scattered fields remain in the form of eqn (2.12), with a matrix given by (2.13), and only the definition of the effective polarizabilities, $\alpha'_i$, changes. It can be shown that the effective polarizabilities obey the recursion relation

$$\alpha'_i^{(n+1)} = \alpha'_i^{(n)} \cdot \left( 1 + 4\pi k^2 \sum_{j \neq i} \Gamma_{ij} \cdot \alpha'_j^{(n)} e^{i k \cdot (r_j - r_i)} \right)$$

eqn (2.15)

where the polarizabilities $\alpha'_i^{(n)}$ and $\alpha'_i^{(n+1)}$ are effective polarizabilities in the nth or (n+1)th "Born" approximation. For example, the ordinary polarizabilities $\alpha_i$ are equivalent to $\alpha'_i^{(1)}$, and the effective polarizabilities in the second Born approximation, $\alpha'_i^{(2)}$, in eqn (2.14), are equivalent to $\alpha'_i^{(2)}$. In principle then, the scattered electric field may be computed to any desired level of approximation by use of eqns (2.12), (2.13), and (2.15). In practice however the computations become increasingly difficult and are seldom carried out beyond the second Born approximation.

For systems that can be described by a relatively small number of polarizabilities ($N < 100$) an exact solution for the internal electric field can be obtained by setting up a system of $3N$ equations in $3N$ unknowns:

$$\vec{E}_i = \vec{E}_0 + 4\pi k^2 \sum_{j \neq i} \Gamma_{ij} \cdot \vec{a}_j \cdot \vec{E}_j, \quad i = 1, \ldots, N$$

eqn (2.16)
where $\mathbf{E}_i$ is the electric field at the position of the $i$th polarizability, and $\mathbf{E}_0$ is the incident electric field at the same position. These equations are then solved numerically for the quantities $\mathbf{E}_i$, and the scattered electric field calculated by eqn (1.10):

$$E_{\text{scatt}}(\mathbf{r}) = 4\pi k^2 \sum_{i=1}^{N} T(\mathbf{r}, \mathbf{r}_i) \cdot \mathbf{\alpha}_i \cdot \mathbf{E}_i$$

$$= \frac{k^2 e^{i k \mathbf{r}}}{r} (1 - k^2 \mathbf{a}) \cdot \sum_{i=1}^{N} e^{-i k \cdot \mathbf{r}_i} \mathbf{\alpha}_i \cdot \mathbf{E}_i \quad \text{eqn (2.17)}$$

This is essentially the approach taken by DeVoe for calculating the circular dichroism of strongly interacting polarizable groups. For the remainder of this chapter we will concern ourselves only with the second Born approximation.

C. CIDS

The intensities necessary to compute the CIDS are obtained by squaring eqn (2.11) with the appropriate right and left incident electric vector, $\hat{\mathbf{E}}_0, L, R$. For simplicity of notation we choose the polarizabilities to be uniaxial:

$$\mathbf{\alpha}_i = \mathbf{\alpha}_i \hat{\mathbf{a}}_i \hat{\mathbf{a}}_i$$

where $\hat{\mathbf{a}}_i$ is the principle axis of the $i$th group, and $\mathbf{\alpha}_i$ is the magnitude of the polarizability along the principle axis. The
expressions to be derived here can be generalized for triaxial polarizabilities by use of the prescription on page 47.

Using eqn (2.16) and squaring eqn (2.10) we obtain:

\[ I_{\text{scatt}} = \frac{c}{8\pi} E_{\text{scatt}} \cdot E_{\text{scatt}}^* = \]

\[ |c|^2 \left( \sum_i \sum_j e^{-i\Delta k \cdot \mathbf{r}_{ij}} \alpha_i \alpha_j^* \left[ \hat{e}_i \cdot \hat{e}_j - (\hat{e}_i \times \hat{e}_j) \cdot (\hat{e}_i \times \hat{e}_j) \right] \right. \]

\[ \times \left[ \Lambda_{ji} + \sum_s \alpha_s \Lambda_{si} \sum_s \lambda_{js} e^{ik_0 \cdot \mathbf{r}_{js}} + \sum_{m \neq i} \alpha_m^* \Lambda_{im}^* \sum_m \lambda_{im}^* e^{-i\Delta k \cdot \mathbf{r}_{im}} \right] \]

where

\[ c = \sqrt{\frac{c}{8\pi}} \frac{E_0 e^{ikr}}{r} k^2 \]

and

\[ \Lambda_{ij} = (\hat{e}_i \cdot \hat{e}_0 \times \hat{e}_j \cdot \hat{e}_0)^* \text{ eqn (2.18)} \]

To compute the quantities \( I_L - I_R \) and \( I_L + I_R \) (the differential and total scattered intensities) we apply eqn (2.17) with the appropriate choices for \( \hat{e}_0 \) in eqn (2.18). We have adopted the definitions of right and left circular polarization described in chapter 1. After algebraic manipulation the differential scattering intensity for oriented systems is given by:

\[ \frac{I_L - I_R}{|c|^2} = -i \sum_i \sum_j e^{-i\Delta k \cdot \mathbf{r}_{ij}} \alpha_i \alpha_j^* \left[ \hat{e}_i \cdot \hat{e}_j - (\hat{e}_i \times \hat{e}_j) \cdot (\hat{e}_i \times \hat{e}_j) \right] \]
arriving at eqn (2.19) we have neglected a term which is fourth power in the polarizabilities. Usually this term will not contribute significantly. However, it can be shown that when the system is composed entirely of isotropic groups, only this fourth-power term contributes.

Eqn (2.19) and the rotationally averaged equations which follow are therefore valid only when the scattering groups are significantly anisotropic.

The perturbation due to the interaction between polarizabilities appears in the terms $V_i s$ and $V_j m$. If the interaction is turned off by setting $V_i s$ and $V_j m$ equal to zero then only the simple first Born approximation contribution to the CIDS is left, $\Omega_{ji}$. When the interaction is turned on, the second and third terms in the square brackets in equation (2.19) contain the interference between waves scattered from waves i and j, modulated by the interaction of these groups with the groups surrounding them.

D. Rotationally Averaged Differential Scattering in the Second Born Approximation

Just as in the first Born approximation, a rotationally averaged CIDS pattern can be computed for an arbitrary distribution of scatterers which interact among themselves. Harris and McClain\textsuperscript{5} have derived very
general expressions for the rotationally averaged scattering cross section of a system of interacting scatterers. The calculation begins with a general form for the exact scattering amplitude to all orders in the "Born" approximations. The scattering cross section is then rotationally averaged using an analysis based on the cross section's irreducible tensor structure. The approach we will take here is to rotationally average eqn (2.19) directly. The results will be equivalent to the results obtained by Harris and McClain for the special case where: 1) the interaction between scatterers is given by the second Born approximation, 2) the interaction is short ranged compared to the wavelength of the light, and 3) the scatterers are anisotropic. In performing the rotational average of eqn (2.19) it is useful to note that the $V_{ij}$ factors are molecule fixed and are therefore invariant under rotations. The phase factors $e^{-i k_0 \cdot L_m}$ and $e^{i k_0 \cdot L_i}$ that appear multiplying the dipole coupling terms will complicate the averaging so that it cannot be done analytically. However, if the polarizabilities of the scattering groups are small enough so that only closely spaced groups interact significantly, phase factors of the type

$$e^{-i k_0 \cdot L_m} V_{im} d^*_{im}$$

will remain approximately constant within the range of values of $L_m$ for which $V_{im}$ (multiplying the phase factors) are different from zero. We therefore make the approximation

$$e^{-i k_0 \cdot L_m} \approx 1$$
This approximation is consistent with choosing a short-ranged coupling between groups, and from now on it will be understood that in all rotationally averaged expressions the quantities $V_{ij}$ will contain the short-ranged coupling tensor $\Gamma_{ij}$ given by eqn (2.9). The general term to be averaged is of the type

$$\langle e^{-i\Delta \mathbf{k} \cdot \mathbf{x}} [\hat{e}_i \cdot \hat{e}_j - (\hat{e}_i \cdot \hat{k}) (\hat{e}_j \cdot \hat{k})] (\hat{e}_s \times \hat{e}_m) \cdot \hat{k}_o \rangle$$

The results are:

$$\frac{\langle I_+ - I_- \rangle}{l c l^2} = \sum_i \sum_j \frac{\alpha_i^* \alpha_j}{2} \left[ (\hat{e}_j \times \hat{e}_i) \cdot \hat{r}_{ij} - \sum_{s \neq j} \alpha_s V_{js} (\hat{e}_s \times \hat{e}_j) \cdot \hat{r}_{ij} - \sum_{m \neq i} \alpha_m^* V_{im} (\hat{e}_j \times \hat{e}_m) \cdot \hat{r}_{ij} \right]$$

$$x \left[ (\hat{e}_i \cdot \hat{e}_j)(\frac{j_2^2}{4} - j_1) - (\hat{e}_i \cdot \hat{r}_{ij})(\hat{e}_j \cdot \hat{e}_i)(\frac{5j_2}{4} - j_1) \right] (\sin \beta + \sin^3 \beta)$$

$$\sum_i \sum_j \frac{\alpha_i^* \alpha_j}{2} \left[ \sum_{s \neq j} \alpha_s V_{js} (\hat{e}_j \times \hat{e}_i) \cdot \hat{e}_s (\hat{e}_i \cdot \hat{e}_j) + \sum_{m \neq i} \alpha_m^* V_{im} (\hat{e}_j \times \hat{e}_i) \cdot \hat{e}_m (\hat{e}_i \cdot \hat{e}_j) \right]$$

$$x \left[ \sin \beta (\frac{2}{5} j_1 - \frac{j_2}{10}) + \sin^3 \beta (-\frac{3}{5} j_1 - \frac{j_2}{10}) \right]$$

where $j_1 = j_1(\xi)$ is the spherical Bessel function of order 1, $j_2$ of order 2 etc. with argument $\xi = \frac{4\pi r_{ij} \sin \beta}{\lambda}$, $r_{ij} = |\mathbf{r}_{ij}|$, and $\beta$ is half the angle of scattering.

It can be seen that for this level of approximation there is no CIDS at zero angle of scattering ($\beta = 0$). To get differential scattering in the forward direction higher terms in the expansion...
must be kept. The linear term is the one that is usually kept in circular dichroism computations. The CIDS patterns computed using eqn (2.20) will therefore be similar to the CIDS patterns computed using eqn (1.35) (first Born approximation used), in that there will be no CIDS for systems of purely isotropic groups, and no CIDS in the forward direction. The differences caused by the presence of interactions will be quantitative, not qualitative. However, in chapter 4 and in section F of this chapter we will show that when CIDS is calculated using eqn (2.10) (that is, without neglecting the phases $e^{i k \cdot r_{ij}}$ or the terms that are fourth power in the polarizabilities) the CIDS is not zero for systems of isotropic groups, or zero in the forward direction. The second Born approximation therefore leads to qualitative differences in the CIDS patterns, and this may be of considerable help in interpreting experimental measurements. These more exact calculations can only be done for oriented systems at present.

E. Rotationally Averaged Total Scattering

In a fashion analogous to the section above the total scattering for oriented distributions of scatterers can be obtained. For oriented systems the total scattering is given by:
\[ \frac{I_i + I_a}{1/c^2} = 2 \sum_i \sum_j e^{-i \mathbf{k} \cdot \mathbf{r}_{ij}} \alpha_i^* \alpha_j [\mathbf{e}_i \cdot \mathbf{e}_j - (\mathbf{e}_i \cdot \mathbf{k})(\mathbf{e}_j \cdot \mathbf{k})] \]

\[ x \left[ \Phi_{ji} - \sum_{m \neq i} a_m^* e^{-i k \cdot r_{im}} \Phi_{jm} V_{im}^* - \sum_{s \neq j} \alpha_s e^{i k \cdot r_{js}} \Phi_{is} V_{js} \right] \]

**Eqn (2.21)**

where

\[ \Phi_{ij} = (\mathbf{e}_i \cdot \mathbf{e}_j) - (\mathbf{e}_i \cdot \mathbf{k}) (\mathbf{e}_j \cdot \mathbf{k}) \]

for all values of \( i \) and \( j \). Making the same approximations for the \( e^{-i k \cdot r_{im}} \) factors as before, we can compute the rotationally averaged total scattering:

\[ \left\langle \frac{I_i + I_a}{1/c^2} \right\rangle_{\text{ave}} = \sum_i |\alpha_i|^2 \left\{ \frac{8}{15} (1 - \sin^2 \beta \cos^2 \beta) - \sum_{m \neq i} (a_m^* + a_m) V_{im} \right. \]

\[ \left. x \left[ \frac{2}{3} - (\mathbf{e}_i \cdot \mathbf{e}_m)^2 \right] \frac{2}{15} (1 + 4 \sin^2 \beta \cos^2 \beta) \right\} + \]

\[ \sum_{i,j \neq i} \alpha_i^* \alpha_j \left[ 1 - \sum_{m \neq i} a_m^* V_{im} (\mathbf{e}_j \cdot \mathbf{e}_m) - \sum_{s \neq j} \alpha_s V_{js} (\mathbf{e}_i \cdot \mathbf{e}_s) \right] \]

\[ x \left[ S_1 + S_2 \sin^2 \beta + S_3 \sin^4 \beta \right] + \]
\[
\left( \hat{e}_i \cdot \hat{e}_j \right)^2 - \sum_{m \neq i} \alpha_m^* V_{im} (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_j \cdot \hat{e}_m) - \sum_{s \neq j} \alpha_s V_{js} (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_i \cdot \hat{e}_s) \right]
\]
\[
\times \left[ S4 + S5 \sin^2 \beta + S6 \sin^4 \beta \right] +
\]
\[
\left( \hat{e}_i \cdot \hat{e}_j \right) \left( \hat{e}_i \cdot \hat{e}_j \right) -
\sum_{m \neq i} \alpha_m^* V_{im} \left[ (\hat{e}_i \cdot \hat{e}_i) (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_j \cdot \hat{e}_m) + (\hat{e}_i \cdot \hat{e}_m) (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_j \cdot \hat{e}_j) \right] -
\sum_{s \neq j} \alpha_s V_{js} \left[ (\hat{e}_i \cdot \hat{e}_i) (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_j \cdot \hat{e}_s) + (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_j \cdot \hat{e}_s) \right] \right]
\]
\[
\times \left[ S7 + S8 \sin^2 \beta + S9 \sin^4 \beta \right] +
\]
\[
\left[ (\hat{e}_i \cdot \hat{e}_i) + (\hat{e}_j \cdot \hat{e}_j) \right] -
\sum_{m \neq i} \alpha_m^* V_{im} \left[ (\hat{e}_i \cdot \hat{e}_i) (\hat{e}_i \cdot \hat{e}_m) + (\hat{e}_i \cdot \hat{e}_m) (\hat{e}_i \cdot \hat{e}_m) \right] -
\sum_{s \neq j} \alpha_s V_{js} \left[ (\hat{e}_i \cdot \hat{e}_i) (\hat{e}_i \cdot \hat{e}_j) + (\hat{e}_i \cdot \hat{e}_j) (\hat{e}_i \cdot \hat{e}_j) \right] \right]
\[ x \left[ S_{10} + S_{11} \sin^2 \beta + S_{12} \sin^4 \beta \right] + \\
\left[ (\hat{e}_{ij} \cdot \hat{e}_{ij})^2 - \sum_{m \neq i} a_m V_{im} (\hat{e}_{ij} \cdot \hat{e}_i)(\hat{e}_{ij} \cdot \hat{e}_m)(\hat{e}_{ij} \cdot \hat{e}_j)^2 - \right. \\
\left. \sum_{s \neq j} a_s V_{js} (\hat{e}_{ij} \cdot \hat{e}_s)^2 (\hat{e}_{ij} \cdot \hat{e}_i)(\hat{e}_{ij} \cdot \hat{e}_s) \left( \frac{3}{8} j_4 + \frac{1}{4} j_4 \sin^2 \beta + \frac{3}{8} j_4 \sin^4 \beta \right) \right] \\
\text{eqn (2.22)}
\]

where \( \hat{e}_{ij} = (\hat{e}_j - \hat{e}_i)/(\hat{e}_j \cdot \hat{e}_i) \) and the \( S_1, S_2, \) etc are combinations of spherical Bessel functions as follow:

\[ S_1 = j_{0/15} - j_{2/21} + 3j_{4/280} \]

\[ S_2 = -2j_{0/5} - j_{2/7} + j_{4/140} \]

\[ S_3 = 2j_{0/5} + 2j_{2/7} + 3j_{4/280} \]

\[ S_4 = 7j_{0/15} + 5j_{2/21} + 3j_{4/140} \]

\[ S_5 = -2j_{0/15} - 13j_{2/21} + j_{4/70} \]
This equation represents a generalization of the expression obtained previously by Bustamante et al.\textsuperscript{4}

In arriving at eqns (2.20) and (2.22) we have assumed that the polarizability eigenvectors, \( \hat{\xi}_i \), are real. For a scattering group to be optically active by itself, its polarizability eigenvectors must be complex. Eqns (2.20) and (2.22) are therefore not capable of describing
systems with groups that are individually optically active. All optical activity must result from the spatial relationships between groups in the system.

This concludes the general results for the CIDS in the second Born approximation. In the following sections we will illustrate the behavior predicted by these results in several specific cases.

F. CIDS of Spherically Symmetric Scatterers With and Without Interactions

Consider a scattering structure composed entirely of isotropic point polarizable groups arranged in a chiral shape. It can be shown that in this special case the first Born approximation predicts no CIDS despite the overall chirality of the structure.

For a spherically symmetric polarizability

\[ \alpha_i = \sum_{\gamma} \hat{\alpha}_\gamma \hat{\alpha}_\gamma = \alpha_i \frac{1}{\omega} \]

where \( \gamma = 1,2,3 \). The scattered intensity for incoming left circularly polarized light in the absence of multiple scattering and interactions is proportional to:

\[
\left[ (1 - \hat{k} \hat{k}) \cdot \sum_j e^{-i \Delta k \cdot r_j} \hat{\alpha}_j \hat{\xi}_L \right] \cdot \left[ (1 - \hat{k} \hat{k}) \cdot \sum_i e^{i \Delta k \cdot r_i} \hat{\alpha}_i \hat{\xi}^*_L \right]
\]
$$= \sum_i \sum_j e^{-i \Delta_{ij} \cdot \mathbf{r}} \alpha_i^* \alpha_j (1 - |\hat{\mathbf{E}}_L \cdot \hat{\mathbf{k}}|^2)$$

An identical expression is obtained for incoming right circularly polarized light with $\hat{\mathbf{E}}_L$ replaced by $\hat{\mathbf{E}}_R$. But $\hat{\mathbf{E}}_L = \hat{\mathbf{E}}_R^*$, and therefore $I_L = I_R$ and there is no CIDS.

However, if we allow multiple scattering and dipole-dipole interactions, that is, if we include the second Born approximation in the treatment, the scattered field is

$$\mathbf{E}_{\text{scatt}} = E_0 \frac{e^{ikr}}{r} k^2 (\mathbf{1} - \mathbf{k} \cdot \mathbf{k}) \cdot \sum_i e^{-i \Delta_{ij} \cdot \mathbf{r}_i} \left[ \alpha_i \cdot (\hat{\mathbf{E}}_0 + 4\pi k^2 \sum_{j \neq i} \mathbf{I}_{ij} \cdot \alpha_j \hat{\mathbf{E}}_0 e^{i \mathbf{k}_0 \cdot \mathbf{r}_{ij}}) \right]$$

This may be rewritten in the form

$$\mathbf{E}_{\text{scatt}} = E_0 \frac{e^{ikr}}{r} k^2 (\mathbf{1} - \mathbf{k} \cdot \mathbf{k}) \cdot \left[ \sum_i e^{-i \Delta_{ij} \cdot \mathbf{r}_i} \sum_{\gamma} \alpha_i \hat{\alpha}_\gamma (\hat{\alpha}_\gamma \cdot \hat{\mathbf{E}}_0) \right.$$ 

$$+ \sum_{j \neq i} \sum_{\gamma} \alpha_i \hat{\alpha}_\gamma \hat{\alpha}_\rho \cdot \mathbf{I}_{ij} \cdot \sum_{\beta} \alpha_j \hat{\alpha}_\rho \hat{\alpha}_\beta \cdot \hat{\mathbf{E}}_0 e^{i \mathbf{k}_0 \cdot \mathbf{r}_{ij}} \right]$$
We now define \( V^{\alpha}_{ij} = -4\pi k^2 \hat{\alpha}_\gamma \cdot \hat{n}_{ij} \cdot \hat{\alpha}_\beta \) and the above equation can be written

\[
E_{\text{scatt}} = E_0 \frac{e^{i k r}}{r} k^2 \left( 1 - \hat{\kappa} \cdot \hat{\kappa} \right) \left\{ \sum_i e^{-i \Delta \hat{\kappa} \cdot \hat{\kappa}_i} \left[ \sum_{\gamma} \alpha_i \hat{\alpha}_\gamma \hat{\alpha}_\gamma - \sum_{j \neq i} \sum_{\gamma} \xi_{ij} \xi_{ij} V^{\alpha}_{ij} \hat{\alpha}_\beta \right] e^{i \hat{\kappa} \cdot \hat{\kappa}_{ij}} \right\}.
\]

The term in square brackets is the effective polarizability in this case which can be seen by inspection to have non-diagonal terms and is (in general) not isotropic. This will cause the presence of CIDS in chiral organizations of systems made of spherically symmetric groups allowed to interact with each other.

G. CIDS of Periodic Arrays

Here we will demonstrate that the CIDS of a periodic scattering structure depends only on the properties of one unit cell and does not depend on the lattice repeat.

Consider a continuous, periodic structure whose polarizability density is

\[
\chi(x) = \chi(x + \xi_{pq}) \quad \text{eqn (2.13)}
\]
where \( \mathbf{r}_{pq} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c} \), \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) are unit cell vectors of a crystalline lattice, and \( p, q, r \) are integers. A plane wave \( \mathbf{E}_0 = E_0 \mathbf{e}_0 e^{i\mathbf{k}\cdot\mathbf{r}} \) is incident on the structure. A formal solution for the general electric field may be obtained iteratively:

\[
\mathbf{E}_1(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + 4\pi k^2 \int \mathbf{\Gamma}(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r} + \mathbf{\gamma}) \cdot \mathbf{E}_0(\mathbf{r} + \mathbf{\gamma}) d^3\mathbf{R},
\]

\[
\mathbf{E}_2(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + 4\pi k^2 \int \mathbf{\Gamma}(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r} + \mathbf{\gamma}) \cdot \mathbf{E}_1(\mathbf{r} + \mathbf{\gamma}) d^3\mathbf{R},
\]

\[\vdots\]

\[
\mathbf{E}_{n+1}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + 4\pi k^2 \int \mathbf{\Gamma}(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r} + \mathbf{\gamma}) \cdot \mathbf{E}_n(\mathbf{r} + \mathbf{\gamma}) d^3\mathbf{R}
\]

\text{eqn (2.24)}

where the fact that \( \mathbf{\Gamma}(\mathbf{r}, \mathbf{r}') = \mathbf{\Gamma}(\mathbf{r}' - \mathbf{r}) = \mathbf{\Gamma}(\mathbf{r}) \) has been used and the variable of integration has been changed accordingly. In eqn (2.24) \( \mathbf{E}_1(\mathbf{r}), \mathbf{E}_2(\mathbf{r}), \ldots \) are the electric fields in the first Born approximation, second Born approximation, and so on. As \( n \) goes to
infinity, $E_n(r)$ approaches an exact solution. Inspection of eqn (2.24) shows that for a polarizability that satisfies eqn (2.23) we have:

$$E_1(r + r_{pqr}) = e^{i k_0 r_{pqr}} E_1(r) \quad \text{eqn (2.25)}$$

It can be seen that an analogous property holds for $E_2, E_3, \text{etc}$, and thus, for the general field, $E(r + r_{pqr}) = e^{i k_0 r_{pqr}} E(r)$. Now let $r'$ be written as:

$$r' = r_{pqr} + r_c$$

i.e., as the sum of a vector $r_{pqr}$ that defines the particular unit cell in the array that contains the point $r'$, plus a vector $r_c$ from the center of that unit cell to the scattering point. The $(n+1)$th approximation to the electric field can then be written as the sum of the contributions from each of the unit cells in the array:

$$E_{n+1}(r) = E_n(r) + 4\pi k^2 \sum_{pqr} \int_{V_c} \delta(r_c + r_{pqr} - r) \cdot d(r_c + r_{pqr}) \cdot E_n(r_c + r_{pqr}) d^3 r_c \quad \text{eqn (2.26)}$$

Using eqn (2.23):

$$E_{n+1}(r) = E_n(r) + 4\pi k^2 \sum_{pqr} \int_{V_c} e^{i k_0 r_{pqr}} \delta(r_c + r_{pqr} - r) \cdot d(r_c) \cdot E_n(r_c) d^3 r_c \quad \text{eqn (2.27)}$$

where the integration is now over the volume $V_c$ of only one unit cell of the array. In the far-field approximation:
Combining eqns (2.27) and (2.28) we obtain, for the scattered field:

\[
E_{\text{scatt}} = E - E_0 = \left( \sum pqr \right)
\]

In equation (2.29) the effect of the lattice on the scattered field has been factored from the effect of the contents of the unit cell. The lattice factor does not depend on the polarization of the incident light, and we may therefore write:

\[
\frac{I_L - I_R}{I_L + I_R} = \frac{\left| E_{\text{scatt},L}^c \right|^2 - \left| E_{\text{scatt},R}^c \right|^2}{\left| E_{\text{scatt},L}^c \right|^2 + \left| E_{\text{scatt},R}^c \right|^2} \quad \text{eqn (2.30)}
\]
where $E_{\text{scatt}}^{c, L, R}$ is the scattered field due to one unit cell, equal to the second bracket in eqn (2.29). It should be pointed out that although the scattered field is proportional to the field of one unit cell, the internal field depends on interactions that in general can come from all unit cells. The argument therefore depends on $\alpha(r)$ being periodic for every value of $r$. For a finite array there will be values of $r$ for which $\alpha(r + r_{pq}) \neq \alpha(r)$, that is, the conclusion above is valid only for infinite arrays. However, if the interaction between dipoles is short-ranged compared to the dimensions of the array these boundary effects can be neglected.

H. Discussion and Conclusions

Several new effects have been described earlier, and we will summarize them here:

1) The CIDS in the forward direction ($k = k_0$) need no longer be zero. The CIDS is a manifestation of wave interference, and in the first Born approximation there can be no net interference effects when the scattered light is parallel to the incident light. In the second Born approximation however, phase shifts in the forward scattered light may be introduced by multiple scattering and dipole-dipole coupling between groups. The forward CIDS is similar in this regard to the circular dichroism, which arises from interactions between groups, and optical rotatory dispersion, which arises from multiple scattering effects.*
Because the forward CIDS is a second order effect, it will tend to be smaller than CIDS at other angles.

2) The CIDS of systems composed entirely of isotropic polarizabilities need no longer be zero. Earlier we showed that the CIDS of chiral arrays of isotropic groups could be understood in terms of anisotropy induced in each scattering group by multiple scattering and interactions. The CIDS of a collection of isotropic groups can be also understood in another way. In the first Born approximation the CIDS is the result of the interference between electric fields scattered by pairs of groups. But for an object composed of isotropic groups, chirality is not apparent unless the interference from at least four groups at a time is considered. (Three of fewer groups must always have a plane of symmetry.) In the second Born approximation, each group is capable of sensing each of the other groups, and the chirality of the object becomes apparent.

3) The CIDS of a strictly periodic structure depends on the characteristics of only one unit cell of the periodic array, and does not depend on the fact that the unit cell is repeated many times in space. The lattice-independence of the CIDS holds only for oriented systems, but previous calculations show that even in rotationally averaged systems the CIDS is often only weakly lattice-dependent.4,7

Bibliography

It is worth emphasizing at this point that the forward CIDS is not the same as the circular dichroism. The forward CIDS is the difference in the right and left intensities of the forward scattered light, while the circular dichroism is the difference in the right and left extinction coefficients for the incident light.
Chapter 3  Quantum Mechanical Calculation of the Circular
Intensity Differential Scattering

In this chapter we take up the quantum mechanical theory for CIDS. The main objective in using quantum mechanics is to improve our ability to describe the details of the response of the system to the incident electric fields. There are two aspects of this response that we wish to address in particular: 1) the response of systems that have dimensions equal to or greater than the wavelength of the incident light, and 2) the effect of motion in the system that is not due to the electric driving forces of the incident light (inelastic scattering). A quantum mechanical theory for the CIDS has been developed previously by Barron and Buckingham\(^1,2\) for molecules small compared to the wavelength of light. This theory is capable of describing CIDS due to inelastic scattering processes, but does not describe systems large compared to the wavelength of light. Our purpose here is to generalize the theory of Barron and Buckingham and of chapter 1 by combining a quantum electrodynamical treatment of the scattering with the general strategy adopted in chapter 1 for dealing with large systems. In the first section we review the quantum theory of light scattering. In section B we derive an expression for the CIDS of an arbitrary quantum mechanical system using time-dependent perturbation theory. In section C we present some special cases pertaining to a collection of non-interacting scatterers. Finally, in section D we discuss the main features of the theory.

A. Overview of the Quantum Theory of Light Scattering
Our purpose in this section is to review briefly the important features in the quantum theory for the interaction of radiation with matter. A full description of the theory is beyond the scope of this presentation, and we will present only a brief outline here. For a more detailed discussion see Loudon,\textsuperscript{3} chapters 6, 7, and 8. We follow the notation and conventions of Sakurai,\textsuperscript{4} chapters 1 and 2, but we have changed the units to conform with the units used in the previous chapters. (Sakurai uses Heaviside-Lorentz units, we will use Gaussian units. See Jackson,\textsuperscript{5} Appendix on Units and Dimensions, pp811-821.) We will also continue to use the conventions for right and left circularly polarized light described in chapter 1. Some helpful background on the treatment of the electromagnetic field using continuum mechanics can be found in Jackson, chapter 12, and Goldstein,\textsuperscript{6} chapter 12.

The system we wish to treat is a combination of molecular and electromagnetic parts. The quantum mechanical treatment is quite different than the electrodynamical treatment given in previous chapters. The primary reason for this is the need to describe both the molecular parts and the electromagnetic parts of the system in detail within a single formalism. To do this we abandon the approach used earlier based on Maxwell's equations for the electric and magnetic fields alone, and consider the entire system, both electrons and photons, as a single system describable by a wavefunction $|\Psi(t)\rangle$ that contains both electronic and photon parts. We are then interested not in the scattered electric field per se, but in transitions between various states of the combined molecule/photon system. It is worth noting that this approach automatically includes the effects of magnetic interactions
between the molecule and the photons in addition to the electric effects.

Suppose that initially the scattering molecule is in a molecular state described by a wavevector $|i\rangle$ and there is a single incoming photon described by a photon wavevector $|k_0, \hat{\xi}_0\rangle$ with wavelength given by $|k_0| = \frac{2\pi}{\lambda}$, and polarization vector $\hat{\xi}_0$. The state of the combined molecule/photon system is then $|I\rangle = |i\rangle |k_0, \hat{\xi}_0\rangle$. When the atom and photon interact (via the oscillatory vector potential associated with the electric and magnetic fields of the photon), they create a transient atom-photon time dependent state, denoted by $|\Psi(t)\rangle$. At some time after the interaction has taken place, we may measure the states of the atom and the photon. The results of these measurements are then denoted $|f\rangle$ and $|k, \hat{\xi}\rangle$ for the final states of the atom and the photon respectively. The quantity of interest to us is then the probability of making the transition $|I\rangle \rightarrow |F\rangle$ where $|F\rangle = |f\rangle |k, \hat{\xi}\rangle$. This probability is given by

$$P_{FI} = |A_{FI}|^2$$  \hspace{1cm} \text{eqn (3.1)}$$

where $A_{FI}$, the transition amplitude, is given by

$$A_{FI} = \langle F | \Psi(t \rightarrow \infty) \rangle$$  \hspace{1cm} \text{eqn (3.2)}$$

where the wavefunction $|\Psi(t)\rangle$ depends on the initial state of the system $|I\rangle$. Our task is therefore to find $\langle F | \Psi(t \rightarrow \infty) \rangle$. We can do this by setting up a Hamiltonian, $H$, and then using the Schrödinger equation to find the time development of the system due to
the interaction of the photon with the molecule. Finding a Hamiltonian for the molecule/photon system is not a simple procedure. Once again, we refer the reader to Loudon (chapter 8) for a detailed treatment.

The derivation begins by finding a classical Lagrangian capable of describing a system comprised of both discrete particles with mass (like electrons), and continuous, massless fields (like the electromagnetic fields). In arriving at a Lagrangian, the electromagnetic fields must be treated relativistically, but the particles are usually moving slowly enough to be treated in the non-relativistic limit. An appropriate Lagrangian is (Goldstein, chapter 12, pp581-586, eqn 12-133, non-relativistic limit):

\[
L = \frac{1}{2} \sum \limits_{l} m_{l} \dot{r}_{l}^{2} + \frac{1}{8\pi} \int (\mathbf{E}^{2} - \mathbf{B}^{2}) \cdot d^{3}r \\
+ \frac{1}{c} \int \mathbf{j} \cdot \mathbf{A} \cdot d^{3}r - \int \rho \Phi \cdot d^{3}r
\]

\[\text{eqn (3.4)}\]

where \( m_{l} \) and \( \mathbf{r}_{l} \) are the mass and position of the \( l \)th particle. The current and charge densities \( \mathbf{j} \) and \( \rho \) are given by

\[
\mathbf{j}(\mathbf{r}) = \sum \limits_{l} z_{l} e \hat{\mathbf{r}}_{l} \int \delta^{3}(\mathbf{r}_{l} - \mathbf{r}) \]

\[\text{eqn (3.5)}\]

\[
\rho(\mathbf{r}) = \sum \limits_{l} z_{l} e \delta^{3}(\mathbf{r}_{l} - \mathbf{r})
\]

\[\text{eqn (3.6)}\]
where \( \frac{2}{\hbar} e \) is the charge of the lth particle. The quantities \( E, B, A \), and \( \Phi \) are the electric field, magnetic field, vector potential, and scalar potential respectively. They describe the properties of the photon parts of the system. In terms of the potentials \( A \) and \( \Phi \), the electric and magnetic fields are given by

\[
B = \nabla \times A \quad \text{eqn (3.7)}
\]

\[
E = -\nabla \Phi - \frac{1}{c} \frac{\partial A}{\partial t} \quad \text{eqn (3.8)}
\]

It can be shown that the Lagrangian of eqn(3.4) yields the correct classical Lagrangian equations of motion. For the particles, the equations of motion are given by

\[
\frac{d}{dt} \left( \frac{2L}{\gamma \gamma_l} \right) - \frac{\partial L}{\partial \gamma_l} = 0 \quad \text{eqn (3.9)}
\]

which gives

\[
m_l \ddot{\gamma}_l = \frac{2}{\hbar} e E(\gamma_l) + \frac{2}{\hbar c} \frac{\partial A}{\partial t} \times B(\gamma_l) \quad \text{eqn (3.10)}
\]
For the fields the equations of motion are given by

\[
\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{A}_\lambda}\right) + \sum_{\mu=1,2,3} \frac{d}{dr_\mu}\left(\frac{\partial \mathcal{L}}{\partial (\partial A_\lambda/\partial r_\mu)}\right) - \frac{\partial \mathcal{L}}{\partial A_\lambda} = 0
\]

\text{eqn (3.11)}

where \(A_\lambda = (A_x, A_y, A_z, \Phi)\) and \(\mathcal{L}\) is a Lagrangian density:

\[
\mathcal{L} = \frac{1}{8\pi} (E^2 - B^2) + \frac{1}{c} \mu \cdot A - \rho \Phi
\]

\text{eqn (3.12)}

Equation (3.11) then results in the Maxwell equations for \(E\) and \(B\) or an equivalent set of equations for the potentials \(A\) and \(\Phi\).

Having established that the Lagrangian (3.4) gives the correct classical equations of motion and that \(\mathcal{L}\) is therefore an appropriate Lagrangian for our purposes, we may obtain the classical Hamiltonian by a Legendre transformation (Goldstein, chapters 8 and 12; Loudon, chapter 8). After considerable manipulation the result is

\[
H = \sum_l \frac{1}{2m_l} \left[ p_l - \frac{e_l}{c} A(\mathbf{r}_l) \right]^2 +
\]
\[ \sum_{l<j} \frac{z_l z_j e^2}{|r_l - r_j|} + \frac{1}{8\pi} \int (E^2 + B^2) \, d^3r \]  
\text{eqn (3.13)}

where \( p_t \) is the conjugate momentum

\[ p_t = \frac{\partial}{\partial r} \rightleftharpoons \frac{m c^2}{\omega} A (r_e) \]  
\text{eqn (3.14)}

and \( E_T \) is the transversal part of the electric field (this will be explained more later). In arriving at eqn (3.13) an important step was made, namely, a particular gauge was chosen for the potentials \( A \) and \( \Phi \). As is described in many texts on electrodynamics and as can be seen from eqns (3.7) and (3.8), the electric and magnetic fields are not affected if the potentials \( A \) and \( \Phi \) are changed by a transformation of the form

\[ A' = A + \nabla \Lambda \]  
\text{eqn (3.15)}

\[ \Phi' = \Phi - \frac{1}{c} \frac{\partial \Lambda}{\partial t} \]  
\text{eqn (3.16)}

Transformations of this sort are called gauge transformations, and they
allow considerable arbitrariness in the properties of $\mathbf{A}$ and $\Phi$. In this case we have chosen $\mathbf{A}$ such that

$$\nabla \cdot \mathbf{A} = 0 \quad \text{eqn (3.17)}$$

This choice is called the Coulomb guage (or transverse guage or radiation guage). The advantage it has in our situation is explained as follows. First, we may separate any vector field $\mathbf{F}$ into two parts

$$\mathbf{F} = \mathbf{F}_L + \mathbf{F}_T \quad \text{eqn (3.18)}$$

called the longitudinal and transverse parts respectively, where

$$\nabla \times \mathbf{F}_L = 0 \quad \text{eqn (3.19)}$$

and

$$\nabla \cdot \mathbf{F}_T = 0 \quad \text{eqn (3.20)}$$

Using eqn (3.7) for the electric field we have

$$\nabla \cdot \mathbf{E} = \nabla \cdot (\mathbf{E}_L + \mathbf{E}_T) = \nabla \cdot \mathbf{E}_L$$

$$= -\nabla^2 \Phi - \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot \mathbf{A}) = -\nabla^2 \Phi \quad \text{eqn (3.21)}$$

and
\[ \nabla \times \vec{E} = \nabla \times (\vec{E}_L + \vec{E}_T) = \nabla \times \vec{E}_T = -\frac{1}{\varepsilon_0 c^2} (\nabla \times \vec{A}) \]

\text{eqn (3.22)}

Therefore only \( \Phi \) contributes to the longitudinal part, \( \vec{E}_L \), and only \( \vec{A} \) contributes to the transversal part, \( \vec{E}_T \). Also, from Maxwell's equations, or eqn (3.8), we have \( \nabla \cdot \vec{B} = 0 \), so \( \vec{B} \) is always purely transversal. This means that the radiation fields (photons), which are always transversal, may be described using the vector potential alone. The electric fields due to the scalar potential are the "static" fields associated with the electron charges. The scalar potential is therefore given by:

\[ \Phi(r) = \sum_l \frac{z_l e}{|r - r_l|} \]

\text{eqn (3.23)}

The potential energy due to this scalar potential is

\[ V = \int \rho(r) \Phi(r) \, d^3r = \frac{1}{2} \sum_j z_j e \Phi(r_j) \]

\[ = \sum_{l<j} \sum \frac{z_l z_j e^2}{|r_l - r_j|} \]

\text{eqn (3.24)}

This is just the well known Coulomb potential of atomic and molecular
quantum mechanics, and is the second term in our Hamiltonian (eqn (3.13)) for the combined molecule/photon system. We may write the Hamiltonian as a sum of three terms:

\[ H = H_M + H_{\text{int}} + H_{EM} \quad \text{eqn (3.25)} \]

where \( H_M \) is the pure molecular energy,

\[ H_M = \sum \frac{p_l^2}{2m_l} + \sum \sum \frac{Z_l Z_j e^2}{r_{lj}} \quad \text{eqn (3.26)} \]

\( H_{EM} \) is the pure photon field energy,

\[ H_{EM} = \frac{1}{8\pi} \int (E_r^2 + B_r^2) d^3 r \quad \text{eqn (3.27)} \]

and \( H_{\text{int}} \) is the interaction energy between the photons and the molecule,

\[ H_{\text{int}} = \sum \frac{Z_l e}{m_l c} A_r(x_l) \cdot p_l + \]

\[ \sum \frac{Z_l^2 e^2}{2m_l^2 c^2} A_r^2(x_l) \quad \text{eqn (3.28)} \]

The interaction Hamiltonian \( H_{\text{int}} \) depends only on the vector potential and not on the scalar potential, due to the choice of the Coulomb
guage. Up to now we have been treating the system as if the electrons and nuclei had no spin associated with them. Spin arises naturally only in a relativistic treatment of the particles, so to include the effects of spin we must add another term to the interaction Hamiltonian at this point:

\[ H_{\text{int}} = \sum_{l} \frac{z_{l} e}{m_{l} c} A(r_{l}) \cdot p_{l} + \sum_{l} \frac{z_{l}^{2} e^{2}}{2 m_{l}^{2} c^{2}} A^{2}(r_{l}) \]

\[ - \sum_{l} \frac{z_{l} e g_{l}}{2 m_{l} c} \mathbf{S}_{l} \cdot \nabla \times \mathbf{A}(r_{l}) \]  

\text{eqn (3.29)}

where \( g_{l} \) is the spin g-factor of the \( l \)-th particle and \( \mathbf{S}_{l} \) is the spin angular momentum of the \( l \)-th particle. The third term in eqn (3.29) is the energy of interaction between the magnetic field of the photons \( (\mathbf{B} = \nabla \times \mathbf{A}) \) and the spin magnetic moments of the electrons and nuclei \( (\mathbf{m} = \frac{z_{l} e g_{l}}{2 m_{l}} \mathbf{S}_{l}) \).

Now that the form of the Hamiltonian has been established our next task is to obtain the quantum mechanical Hamiltonian operator. This is straightforward for the parts of the Hamiltonian that describe the particles; we just let the coordinates \( \mathbf{r}_{l} \) and momenta \( \mathbf{p}_{l} \) become the corresponding operators. The field operators \( \mathbf{A}, \mathbf{E}, \) and \( \mathbf{B} \) require more work however. First note that because of eqns (3.7) and (3.22) we need only deal with the vector potential, \( \mathbf{A} \). This vector potential is therefore the operator that will contain all the information on the nature of the quantized photon field. We begin by expanding \( \mathbf{A} \) in a
Fourier series:

\[ A = \frac{1}{\sqrt{V}} \sum_{k} \sum_{\alpha} \left( c_{\alpha k} \hat{e}_{k} e^{-i k \cdot r} + c_{\alpha k}^* \hat{e}_{k}^* e^{-i k \cdot r} \right) \]

\[ \text{eqn (3.30)} \]

Since \( \nabla \cdot A = 0 \), we must have \( \hat{e}_{k} \cdot k = 0 \) for all \( k, \alpha \). The vectors \( \hat{e}_{1k}, \hat{e}_{2k} \), and \( k \) may be chosen to form an orthogonal set of unit vectors. Then equation (3.30) may be interpreted as a superposition of transversal plane waves or "photons". The direction and wavelength of each photon is given by \( k \), and the polarization and amplitude are given by \( A^0 = c_{1k} \hat{e}_{1k} + c_{2k} \hat{e}_{2k} \).

As the first step toward quantizing the vector potential, we introduce the idea of a photon state. Each photon in a photon state is conceived of as a completely delocalized photon wave or photon mode filling up all parts of space. The allowed modes are labelled by their polarization, \( \hat{e}_{k} \), direction of propagation, \( k \), and frequency, \( \omega \). A given photon state may be composed of a single photon or may contain many photons. Formally, we denote the photon states by a ket

\[ \left| n_{k_1}, n_{k_2}, \ldots, n_{k_N} \right> \]

where each number \( n_{k_1}, n_{k_2}, \ldots, n_{k_N} \) is the number of photons having wavevector \( k_i \) and polarization \( \hat{e}_{k_i} \). So far this is just notation. To concretely define what we mean by these photon states we must now decide how the vector potential \( A \) operates on \( \left| n_{k_1}, \ldots, n_{k_N} \right> \). There are no a
priori rules for how this should be done, and we simply put forth a postulate:* The quantum mechanical vector potential operator is obtained from the classical vector potential, eqn (3.30), by the replacement

\[
  c_k \rightarrow c \sqrt{\frac{2\pi \hbar}{\omega}} a_k \\
  c_k^* \rightarrow c \sqrt{\frac{2\pi \hbar}{\omega}} a_k^* \quad \text{eqn (3.31)}
\]

where \( \omega = c |k| \), and \( a_k \) and \( a_k^* \) are operators such that

\[
  [a_k, a_{k'\alpha'}] = \delta_{kk'} \delta_{\alpha\alpha'} \\
  [a_k, a_{k'\alpha'}] = 0 \\
  [a_k^+, a_{k'\alpha'}] = 0 \quad \text{eqn (3.32)}
\]

There are ways to motivate these choices. For example, in classical mechanics the coefficients \( C_k \) can be considered canonical variables whose Poisson brackets correspond to the commutators in eqn (3.32).
The operators $a_{k\alpha}$ and $a_{k\alpha}^+$ act like the ladder operators in the theory of the quantum harmonic oscillator. Indeed, it can be shown that the classical electromagnetic Hamiltonian $H_{EM}$ can be put into a form which is identical with the Hamiltonian of a large number of independent harmonic oscillators.

$$H_{EM} = \frac{1}{8\pi} \int \left( \frac{E^2}{c^2} + B^2 \right) d^3r =$$

$$\frac{1}{8\pi} \int \left[ \left( \frac{1}{c} \frac{\partial A}{\partial t} \right)^2 + (\nabla \times A)^2 \right] d^3r \quad \text{eqn (3.34)}$$

To evaluate eqn (3.34) we need to find $\frac{\partial A}{\partial t}$. For a pure photon field (no charges or currents present) the classical vector potential...
obeys the wave equation

$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = 0$$

(Jackson, p220). This equation is satisfied by eqn (3.30) if we choose

$$c_{k\alpha}(t) = c_{k\alpha}(0) e^{-i \omega t}$$

Using this time dependence for $A$, we find

$$H_{EM} = \frac{1}{\pi} \sum_k \left( \frac{\omega}{c} \right)^2 |c_{k\alpha}|^2$$

$$= \sum_k \frac{1}{2} \left( P_{k\alpha}^2 + \omega^2 Q_{k\alpha}^2 \right) \quad \text{eqn (3.34)}$$

where

$$P_{k\alpha} = -i \sqrt{\frac{\omega^2}{2\pi c^2}} \left( c_{k\alpha} - c_{k\alpha}^* \right)$$

and

$$Q_{k\alpha} = \sqrt{\frac{1}{2\pi c^2}} \left( c_{k\alpha} + c_{k\alpha}^* \right) \quad \text{eqn (3.35)}$$

In eqn (3.34) the quantities $P_{k\alpha}$ and $Q_{k\alpha}$ play the role of the canonical variables of an harmonic oscillator, and the classical Hamiltonian
becomes the quantized Hamiltonian operator by eliminating $C_{k\alpha}$ and $C_{k\alpha}^*$ in eqn (3.35) using eqn (3.31). We are implicitly working in the Schrödinger picture here, so $a_{k\alpha}$ and $a_{k\alpha}^+$ are not time dependent even though the classical $c_{k\alpha}$ and $c_{k\alpha}^*$ are. In terms of the $a_{k\alpha}$ and $a_{k\alpha}^+$ operators the quantum Hamiltonian is

$$H_{Em} = \sum_{k\alpha} \left( \hat{N}_{k\alpha} + \frac{1}{2} \right) \hbar \omega$$

where $\hat{N}_{k\alpha} = a_{k\alpha}^+ a_{k\alpha}$. Equations (3.26), (3.27), and (3.29), together with eqns (3.31), (3.33), and (3.29) complete the specification of the Hamiltonian for the combined molecule/photon system. In the following we show how the scattering amplitude $A_{FI} = \langle F | \Phi(t \rightarrow \infty) \rangle$ is obtained using this Hamiltonian and the Schrödinger equation.

With the choices for the operators and photon states made above the states $|n_{k\alpha 1}, \ldots, n_{k\alpha N_2}\rangle$ are eigenvectors of $H_{Em}$:

$$H_{Em} |n_{k\alpha 1}, \ldots, n_{k\alpha N_2}\rangle =$$

$$\sum_{k\alpha} \left( \hat{N}_{k\alpha} + \frac{1}{2} \right) \hbar \omega |n_{k\alpha 1}, \ldots, n_{k\alpha N_2}\rangle =$$

$$\left( \sum_{k\alpha} \left( n_{k\alpha} + \frac{1}{2} \right) \hbar \omega \right) |n_{k\alpha 1}, \ldots, n_{k\alpha N_2}\rangle$$

$$\text{eqn (3.37)}$$

We may therefore form a basis set for the Hilbert space of the combined
molecule/photon system from kets of the form

\[ |N\rangle = |n\rangle |\gamma\rangle \quad \text{eqn (3.38)} \]

where \( |n\rangle \) is a molecular state which is an eigenvector of the pure molecular Hamiltonian, \( H_M \), and \( |\gamma\rangle \) is a photon state of the sort described above, an eigenvector of the pure photon Hamiltonian, \( H_{Em} \). Any state of the combined system may be written as a superposition of the \( |N\rangle \) states:

\[ |\Psi(t)\rangle = \sum_n \sum_{\gamma} c_{n\gamma}(t) |n\rangle |\gamma\rangle \]

\[ = \sum_N c_N |N\rangle \quad \text{eqn (3.39)} \]

where the sum over \( N \) actually represents a multiple sum over all the quantum numbers describing the eigenstates of the molecular and photon parts of the system. In the total Hamiltonian (3.25) the pure molecule Hamiltonian \( H_M \) acts only on the \( |n\rangle \) states and the pure photon Hamiltonian \( H_{Em} \) acts only on the \( |\gamma\rangle \) states, but the interaction Hamiltonian \( H_{int} \) acts on both molecule and photon states. If the total Hamiltonian did not have the interaction term the eigenstates of the molecule/photon system would be the \( |N\rangle \) states. The presence of \( H_{int} \) causes the photon and molecule parts of the system to mix, and the result is in general a form like eqn (3.39).

To find the scattering amplitude \( A_{\Phi*} \), we use time-dependent perturbation theory. The Schrödinger equation for our system is:
\[(H_M + H_{\text{int}} + H_{\text{EM}})|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle \quad \text{eqn (3.40)}\]

where all three terms $H_M$, $H_{\text{int}}$, and $H_{\text{EM}}$ are time independent since we are working in the Schrödinger picture. We want to solve this equation for the quantity $\langle F | \Psi(t) \rangle$ where $|F\rangle$ is the final state of the system $|k, \xi \rangle f \rangle$ (scattered photon and final molecular state) and where $|\Psi(t)\rangle$ is subject to the boundary condition that as $t$ goes to infinity, $|\Psi(-t)\rangle \to |I\rangle$ where $|I\rangle$ is the initial state of the system, $|k_0, \xi_0 \rangle i \rangle$ (incident photon and initial molecular state).

Equation (3.40) may be simplified by means of partial picture transformations. Suppose we let $|\Psi(t)\rangle$ have the form

\[|\Psi(t)\rangle = e^{-iH_{\text{EM}}t/\hbar} |\Psi'(t)\rangle \quad \text{eqn (3.41)}\]

where $H_{\text{EM}}$ is the electromagnetic Hamiltonian operator, and

\[U_{\text{EM}}(t) = e^{-iH_{\text{EM}}t/\hbar}\]

is in effect a time development operator for the time dependence due to the pure electromagnetic Hamiltonian alone. We also define new operators $H'_M, H'_{\text{EM}}$ and $H'_{\text{int}}$ according to
\[ H_M = e^{-iH_{EM}t/\hbar} H_M e^{iH_{EM}t/\hbar} = H_M' \]

\[ H_{EM} = e^{-iH_{EM}t/\hbar} H_{EM} e^{iH_{EM}t/\hbar} = H_{EM}' \]

\[ H_{int} = e^{-iH_{EM}t/\hbar} H_{int} e^{iH_{EM}t/\hbar} \]

\[ \text{eqn (3.42)} \]

where

\[ e^{iH_{EM}t/\hbar} = (e^{-iH_{EM}t/\hbar})^\dagger \]

\[ = U_{EM}^+(t) = U_{EM}^{-1}(t). \]

Since \( H_M \) and \( H_{EM} \) commute with \( H_{EM}' \), \( H_M' = H_M \) and \( H_{EM}' = H_{EM} \). Notice however that \( H_{int}'(t) \) is time dependent, that is, \( H_{int}' \) is no longer an operator in the Schrödinger picture, but is in a picture half way between the Schrödinger picture and the Heisenberg picture. With these definitions equation (3.40) becomes

\[ (H_M + U_{EM}^{-1}(t) H_{int}'(t) U_{EM}^+(t) + H_{EM}) U_{EM}(t) | \Phi(t) \rangle = \]
Multiplying on both sides by $U_{EM}^\dagger(t)$ we obtain

$$\left[ H_M + H'_{int}(t) \right] |\Phi'(t)\rangle = i\hbar \frac{\partial |\Phi'(t)\rangle}{\partial t}$$

\text{eqn (3.43)}

Equation (3.43) is a new Schrödinger equation, equivalent in every way to eqn (3.40), but simplified in that there is no $H_{EM}$ term in the Hamiltonian. The price paid for this simplification is that now $H'_{int}(t)$ is time dependent.

We may now perform a second transformation to eliminate $H_M$. Let

$$|\Phi(t)\rangle = U_M(t)|\Psi''(t)\rangle$$

$$H_M = U_M(t) H_M U_M^\dagger(t) = H_M$$

$$H'_{int} = U_M(t) H'_{int} U_M^\dagger(t) \quad \text{eqn (3.44)}$$
where

\[ U_m(t) = e^{-iH_M t/\hbar} \]

Then, by the same process as before

\[ H_{int}''(t) | \Psi''(t) > = \frac{i\hbar}{2} \left( \frac{\partial | \Psi''(t) >}{\partial t} \right) \]

**eqn (3.45)**

In equation (3.45) only the interaction Hamiltonian is shown explicitly. The time dependence due to \( H_M \) and \( H_{EM} \) is now buried in \( H_{int}''(t) \) and \( | \Psi''(t) > \). From eqns (3.41), (3.42), and (3.44):

\[ | \Psi''(t) > = [U_m(t)U_{EM}(t)]^\dagger | \Psi > \]

\[ = U_o^\dagger(t) | \Psi > \]

\[ H_{int}''(t) = [U_m(t)U_{EM}(t)]^\dagger H_{int} [U_m(t)U_{EM}(t)] \]
where
\[ U_0(t) = e^{-i(H_M + H_{EM})t/h} \]

We may solve eqn (3.45) formally by the use of yet another time development operator:

\[ |\Psi''(t)\rangle = e^{-i\int_{-\infty}^{t} H_{int}(t')dt'/h} |\Psi''(-\infty)\rangle \]

It can be verified by direct substitution that \(|\Psi''(t)\rangle\) in eqn (3.47) satisfies eqn (3.45). We now use our requirement that \(|\Psi(-\infty)\rangle = |I\rangle\). From (3.46) we see that

\[ |\Psi''(-\infty)\rangle = U_0^+(t)|\Psi(+\rightarrow-\infty)\rangle = U_0^+(t)|I\rangle \]

Since \(|I\rangle\) is an eigenvector of both \(H_M\) and \(H_{EM}\) the effect of the operators \(U_M\) and \(U_{EM}\) is to multiply \(|I\rangle\) by a phase factor \(e^{iE_I t/h}\). The scattering amplitude is therefore
\[
A_{FI} = \langle F | \Psi(t) \rangle = \langle F'' | \Psi''(t) \rangle
\]

\[
= e^{-i(E_F - E_I) t / \hbar} \langle F | e^{-i \int_{-\infty}^{t} H_{int}(t') dt'} | I \rangle
\]

\text{eqn (3.48)}

\[
| F'' \rangle = U_o^\dagger(t) | F \rangle = e^{i E_F t / \hbar} | F \rangle
\]

The global phase factor \( e^{i(E_F - E_I) t / \hbar} \) multiplying \( A_{FI} \) has no physical significance (since we are interested only in \( P_{FI} = |A_{FI}|^2 \)), and we may ignore it. In the limit of large times,

\[
A_{FI}(t \to \infty) = \langle F | e^{-i \int_{-\infty}^{\infty} H_{int}(t') dt' / \hbar} | I \rangle
\]

\text{eqn (3.49)}

So far this has been nothing but a formal manipulation. The advantage to the final form we have arrived at is that if \( H_{int}(t) \) is a "small" perturbation, we may expand the exponential in eqn (3.49) and obtain a
workable approximate expression for \( A_{FII} \):

\[
A_{FII} \approx \langle F | \left[ 1 + \left( \frac{1}{i\hbar} \right) \int_{-\infty}^{t'} H_{int}(t') dt' \right.
\]

\[
+ \left. \left( \frac{1}{i\hbar} \right)^2 \int_{-\infty}^{t'} \int_{-\infty}^{t'} H_{int}(t') H_{int}(t'') dt' dt'' + \cdots \right] I \rangle
\]

\[
= \langle F | I \rangle + \left( \frac{1}{i\hbar} \right) \int_{-\infty}^{t'} \langle F | H_{int}(t') | I \rangle dt'
\]

\[
+ \left( \frac{1}{i\hbar} \right)^2 \int_{-\infty}^{t'} \int_{-\infty}^{t'} \langle F | H_{int}(t') H_{int}(t'') | I \rangle dt' dt'' + \cdots
\]

eqn (3.50)

The matrix elements in eqn (3.50) can be simplified by using the definition of \( H_{int}(t) \). First, it can be shown that the effect of the transformation

\[
H_{int}(t) = U_{EM}^+ H_{int} U_{EM}(t)
\]

is just to make the photon creation and destruction operators \( a_{k\alpha} \) and \( a_{k\alpha}^+ \) time dependent:
\[ a_{k\alpha} \rightarrow a_{k\alpha}(0) e^{-i\omega t} \]
\[ a_{k\alpha}^+ \rightarrow a_{k\alpha}^+(0) e^{i\omega t} \quad \text{eqn (3.51)} \]

where \( a_{k\alpha}(0) \) and \( a_{k\alpha}^+(0) \) act on the photon states exactly as did \( a_{k\alpha} \) and \( a_{k\alpha}^+ \). \( H_{\text{int}}(t) \) is therefore given by eqn (3.29) with \( A \) given by eqn (3.30), but with the time dependent \( a_{k\alpha} \)'s given by (3.51).

\( H_{\text{int}}''(t) \) is then

\[ H_{\text{int}}''(t) = U_M^+(t) H_{\text{int}}'(t) U_M(t) \]

which gives

\[ \langle F \mid H_{\text{int}}'' \mid I \rangle = \]

\[ \langle F \mid e^{iH_M t'/\hbar} H_{\text{int}}'(t') e^{-iH_M t'/\hbar} \mid I \rangle = \]

\[ e^{i(E_f - E_i) t'/\hbar} \langle F \mid H_{\text{int}}'(t') \mid I \rangle \quad \text{eqn (3.52)} \]

and
\[
\langle F | H_{\text{int}}(t') H_{\text{int}}(t'') | I \rangle = 
\]

\[
\sum \langle F | H_{\text{int}}(t') | N \rangle \langle N | H_{\text{int}}(t'') | I \rangle = 
\]

\[
\sum \sum e^{i(E_f - E_n)t'/\hbar} e^{i(E_n - E_i)t''/\hbar} 
\]

\[
x \langle F | H_{\text{int}}(t') | N \rangle \langle N | H_{\text{int}}(t'') | I \rangle \quad \text{eqn (3.53)}
\]

In arriving at eqn (3.52) we have used the fact that the \( |N \rangle \) states are a complete set:

\[
\sum |N \rangle \langle N | = 1
\]

With expressions (3.52) and (3.53), the scattering amplitude becomes

\[
A_{FI} \equiv \int_{F_1} + 
\]

\[
(\frac{i}{\hbar}) \int_{-\infty}^{\infty} e^{i(E_f - E_i)t'/\hbar} \langle F | H_{\text{int}}(t') | I \rangle dt' + 
\]

\[
(\frac{1}{i\hbar}) \int_{-\infty}^{\infty} \int_{-\infty}^{t'} \sum \sum e^{i(E_f - E_n)t'/\hbar} e^{i(E_n - E_i)t''/\hbar} 
\]

The probability amplitude in eqn (3.54) is now in the form of a sum of contributions of decreasing magnitude:

\[ A_{FI} = A_{FI}^{(0)} + A_{FI}^{(1)} + A_{FI}^{(2)} + \ldots \]  

\text{eqn (3.55)}

The next step is to substitute eqn (3.29) for the interaction Hamiltonian into eqn (3.54). The expression for the scattering amplitude can then be further simplified by acting the creation and destruction operators \( a_k^+ \) and \( a_k \) in \( A \) on the photon parts of \( |F\rangle \), \( |I\rangle \), and \( |N\rangle \). When this is done the roles that the various contributions play in the scattering may be understood in terms of microscopic processes: \( A_{FI}^{(0)} = \delta_{FI} \) is the amplitude for the case when no interaction occurs between the atom and the photon. This term vanishes for scattering at angles away from the incident beam (\( |F\rangle \neq |I\rangle \)). \( A_{FI}^{(1)} \) is the amplitude for the simultaneous absorption and re-emission of the incident photon (elastic Thompson scattering) and arises from the \( \left( \frac{2e^2}{m_c^2} \right) A_{\infty}^2 \left( \frac{p_i}{\hbar}, t \right) \) terms of the interaction Hamiltonian. \( A_{FI}^{(2)} \) is the amplitude when the absorption and emission of the photon take place at two different times (either elastic or
inelastic scattering) and arises from the \( \left( \frac{z e^2}{m_l c} \right) A(\mathbf{r}_2, t) \cdot \mathbf{p}_l \)
and \( \left( \frac{z e^2 e^2}{2 m_l c} \right) \mathbf{l} \cdot \nabla \times A(\mathbf{r}_2, t) \) terms. Other higher-order contributions can arise from various combinations of these two processes and collectively amount to a quantum mechanical description of multiple scattering and multiple photon effects. In these calculations we will concern ourselves solely with single photon, single scattering effects and will therefore consider only \( A_{\text{FI}}^{(1)} \) and \( A_{\text{FI}}^{(2)} \) in equation (3.55).

These amplitudes are given by:

\[
A_{\text{FI}}^{(1)} = \left( \frac{-i}{\mathcal{V}} \right) \frac{1}{2 \sqrt{\omega \omega_0}} (2\pi) \int (\omega_1 + \omega - \omega_i - \omega_0) \hat{\xi}^* \hat{\xi}_0 \\
\times \langle f | \sum_l \frac{z^2 e^2}{m_l^2} e^{-i \cdot \mathbf{k} \cdot \mathbf{r}_l} | i \rangle \quad \text{eqn (3.56a)}
\]

\[
A_{\text{FI}}^{(2)} = \left( \frac{-i}{\mathcal{V}} \right) \left( \frac{-i}{\mathcal{V}} \right) \frac{1}{2 \sqrt{\omega \omega_0}} (2\pi) \int (\omega_1 + \omega - \omega_i - \omega_0) \\
\times \sum_n \left[ \frac{1}{\omega_n - \omega_0} \right] \langle f | \sum_l \frac{z e}{m_l} e^{i \cdot \mathbf{k} \cdot \mathbf{r}_l} \hat{\xi}^*(\mathbf{p}_l - \frac{ie q l}{\hbar} \mathbf{k} \times \mathbf{s}_l) | n \rangle
\]
with \( \omega_f = E_f/\hbar \), \( \omega_n = E_n/\hbar \), \( \omega_i = E_i/\hbar \), \( \omega_{ni} = (E_n - E_i)/\hbar \)

etc., and where \( |n\rangle \) is an eigenstate of the atomic Hamiltonian, \( H_m \),

with eigenvalue \( E_n \), and \( \vec{e}_n \), \( \vec{e}_o \), \( \omega \), \( \omega_0 \), \( k \), \( k_0 \) are the polarizations, angular frequencies, and wavevectors of the scattered and initial photons respectively. \( V \) is a normalization volume. The total scattering amplitude can be written conveniently as a product of the incident and final polarization vectors with a matrix:

\[
A_{FI} = A_{FI}^{(1)} + A_{FI}^{(2)} =
\]
\[
\left( \frac{-i}{2V} \right) (2\pi) \delta'(\omega_f + \omega - \omega_i - \omega_0) \tilde{E}^* \cdot \tilde{E}_0 \quad \text{eqn (3.57)}
\]

with \( \Pi \) given by:

\[
\Pi = -\frac{1}{\sqrt{\omega_0 \omega}} \left\langle f \left| \sum \frac{\sqrt{2} e^{i \Delta k \cdot \eta}}{m_l} e^{-i \Delta k \cdot \eta} \right| i \right\rangle +
\]

\[
\frac{1}{\sqrt{\omega_0 \omega}} \frac{1}{h} \sum_n \left( \frac{1}{\omega_n - \omega} \right) \left\langle f \left| \sum \frac{\sqrt{2} e^{i \Delta k \cdot \eta}}{m_l} e^{-i \Delta k \cdot \eta} (p_l - \frac{ig e}{2} k \times s_l) \right| n \right\rangle
\]

\[
x \left\langle h \left| \frac{\sqrt{2} e^{i \Delta k \cdot \eta}}{m_l} e^{-i \Delta k \cdot \eta} (p_l + \frac{ig e}{2} k \times s_l) \right| i \right\rangle +
\]

\[
\left( \frac{1}{\omega_n + \omega_0} \right) \left\langle h \left| \sum \frac{\sqrt{2} e^{i \Delta k \cdot \eta}}{m_l} e^{-i \Delta k \cdot \eta} (p_l - \frac{ig e}{2} k \times s_l) \right| i \right\rangle
\]

\[
x \left\langle f \left| \sum \frac{\sqrt{2} e^{i \Delta k \cdot \eta}}{m_l} e^{i \Delta k \cdot \eta} (p_l + \frac{ig e}{2} k \times s_l) \right| n \right\rangle \quad \text{eqn (3.58)}
\]

where \( \Delta k = k - k_0 \). The terms \( \frac{ig e}{2} k \times s_l \) and
\[ \frac{ig\ell}{2} \mathbf{k}_0 \times \mathbf{\ell} \]

describe a scattering process due to the interaction of the spin of the particles and the magnetic fields of the incoming photon.\(^7\)\(^-\)\(^9\) Although these terms can give rise to differential scattering of circularly polarized light, we will not explicitly discuss these processes here.

The \( \Pi \) matrix is not a tensor of well defined rank under rotations of the scattering system. However, if the exponentials in eqn (3.58) are expanded in power series, it is possible to write the \( \Pi \) matrix as a sum of rotational tensors of all ranks (hyper-polarizabilities) tensorially contracted with powers of \( \mathbf{k} \) and \( \mathbf{k}_0 \). The \( \Pi \) matrix has been defined so that the leading term is the familiar electric polarizability tensor. This can be obtained by setting:

\[ e^{-i\mathbf{k} \cdot \mathbf{r}_\ell} = e^{i\mathbf{k}_0 \cdot \mathbf{r}_\ell} \approx 1 \]

and choosing \(|f\rangle = |i\rangle\). This approximation is valid whenever the volume where the charge density of the system is located is much smaller than the wavelength of light. Then we can write:

\[ \Pi_{\text{dipole}} = \alpha = \frac{2}{\hbar} \sum_n \left( \frac{1}{\omega_n^2 - \omega^2} \right) \]

\[ \times \left[ \omega_n \Re \left\{ \langle i | \mu_n | nXn | \mu_i \rangle \right\} \right] + \]

\[ i\omega_0 \Im \left\{ \langle i | \mu_n | nXn | \mu_i \rangle \right\} \]

eqn (3.58a)
where \( M = \sum \frac{\mathbf{z}_k \cdot \mathbf{r}_k}{r_k^3} \).

B. CIDS

If the volume from which the scattered light is collected is small compared to the distance, \( r \), between the volume and the detector (that is, if the scattering volume can be approximated as a single point) then the differential scattering cross section \( \frac{d\sigma}{d\Omega} \) is related to the intensity by

\[
\frac{I}{I_0} = \frac{1}{r^2} \frac{d\sigma}{d\Omega}
\]

where \( I_0 \) is the intensity of the incident beam and \( \Omega \) is the solid angle intercepted by the light sensitive detector used to make the intensity measurement. If the incident intensities for right and left circularly polarized light are equal, then the CIDS is given by

\[
\Delta = \frac{\frac{d\sigma_L}{d\Omega} - \frac{d\sigma_R}{d\Omega}}{\frac{d\sigma_L}{d\Omega} + \frac{d\sigma_R}{d\Omega}}
\]

The differential cross section is given in terms of \( P_{FL} \) by:\(^5\)

\[
\frac{d\sigma}{d\Omega} = \lim_{t \to 0} \frac{V}{(2\pi)^3 c^3 t} \frac{1}{I_0} \int P_{FL}(\omega) \omega^3 d\omega
\]
where $I_0 = (c/\nu)^2 \omega_0$ is the intensity of the incident beam.
Substituting $P_{FI} = |A_{FI}|^2$ into eqn (3.61) and performing the integral, we obtain:

$$\frac{d\sigma_{L,R}}{d\Omega} = \left(\frac{1}{4\pi c^2}\right)^2 (\omega_0 - \omega_f + \omega_i)^3 \times |\hat{\mathbf{E}}_\omega \times \Pi(\omega = \omega_i + \omega_0 - \omega_f) \cdot \hat{\mathbf{E}}_{L,R}|^2$$

where $\hat{\mathbf{E}}_{L,R}$ are the polarization vectors for left (L) and right (R) circularly polarized light. This expression assumes that the incident light is travelling in a single direction, given by $\mathbf{k}_0$. Suppose now that the light source is a continuous beam of photons which is collimated so that all photons are travelling along $\mathbf{k}_0$, but which may not be monochromatic. Then the scattering cross sections are given by:

$$\frac{d\sigma_{L,R}}{d\Omega} = \left(\frac{1}{4\pi c^2}\right)^2 \sum_{\omega_0} \left(\frac{I_{\omega_0}}{I_0}\right)(\omega_0 - \omega_f + \omega_i)^3 \times |\hat{\mathbf{E}}_\omega \times \Pi(\omega = \omega_i + \omega_0 - \omega_f) \cdot \hat{\mathbf{E}}_{L,R}|^2$$

**eqn (3.63)**
where \( I_{\omega_0} / I_0 \) is the fraction of the incident intensity which has angular frequency \( \omega_0 \). Substituting equation (3.63) in equation (3.60) we obtain for the CIDS:

\[
\Delta = \frac{\sum \left( \frac{I_{\omega_0}}{I_0} \right) (\omega_0 - \omega_i)^3 \left( |\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_l|^2 - |\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_R| |^2 \right)}{\sum \left( \frac{I_{\omega_0}}{I_0} \right) (\omega_0 - \omega_i)^3 \left( |\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_l|^2 + |\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_R|^2 \right)}
\]

\( \text{eqn} (3.64) \)

where \( \omega_i = \omega_f - \omega_i \). From now on it will be understood that \( \hat{\mathbf{p}} \) is to be evaluated at \( \omega = \omega_0 - \omega_i \). The quantities \( |\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_l|^2 \) can be simplified somewhat:

\[
|\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_l|^2 - |\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_R|^2 =
\]

\[
(\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_l \times \hat{\mathbf{E}}_l^* \cdot \hat{\mathbf{E}}_l) - (\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \hat{\mathbf{E}}_l^* \cdot \hat{\mathbf{E}}_l \times \hat{\mathbf{E}}_l^*) =
\]

\[
= [ (\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \mathbf{E}_l^*) \times (\hat{\mathbf{x}} \cdot \hat{\mathbf{p}} \cdot \mathbf{E}_l)^* ] \cdot (\hat{\mathbf{E}}_l \times \hat{\mathbf{E}}_R) =
\]
\[
\begin{align*}
\left[ (\hat{\varepsilon}^* \pi) \times (\hat{\varepsilon}^* \pi)^* \right] \cdot (-i \hat{k}_o) &= \\
- i \left( \pi \times \pi^\dagger \right)_{\alpha \beta \gamma} \hat{k}_o \hat{\varepsilon}_\alpha \hat{\varepsilon}_\beta & \quad \text{eqn (3.65)}
\end{align*}
\]

where \((\pi \times \pi^\dagger)_{\alpha \beta \gamma} \equiv \varepsilon_{\beta ij} \pi_{\alpha i} \pi_{\gamma j}\), and \(\hat{k}_o\) is a unit vector along the direction of propagation of the incident light. Similarly:

\[
\begin{align*}
|\hat{\varepsilon}^* \cdot \hat{\varepsilon}_l|^2 + |\hat{\varepsilon}^* \cdot \hat{\varepsilon}_R|^2 &= \\
\hat{\varepsilon}^* \left[ \pi \cdot (1 - \hat{k}_o \hat{k}_o) \cdot \pi^\dagger \right] \cdot \hat{\varepsilon} &= \\
\pi_{\alpha \beta} \pi_{\gamma \delta}^\dagger \left( \delta_{\beta \gamma} - \hat{k}_o \hat{k}_o \right) \hat{\varepsilon}_\alpha \hat{\varepsilon}_\delta & \quad \text{eqn (3.66)}
\end{align*}
\]

Substituting equation (3.66) in equation (3.64), the expression becomes:

\[
\Delta = \left\{ -i \left[ \sum_{\omega_o} I_{\omega_o} (\omega_o - \omega_{\text{fi}})^3 (\pi \times \pi^\dagger)_{\alpha \beta \gamma} \hat{k}_o \hat{k}_\rho \right] \hat{\varepsilon}_\alpha \hat{\varepsilon}_\gamma \right\}
\]
Equation (3.67) is our most general expression for the CIDS ratio. It is valid whenever: 1) there is no multiple scattering, 2) the response of the system is linear in the electric and magnetic fields (no multiple photon effects are taken into account), 3) the incident beam is made up of photons which are all travelling parallel to one another along the direction given by \( \hat{k}_0 \), 4) the observation is made at long times after the scattering event, 5) the incident beam is perfectly polarized, and 6) the scattering volume is effectively a single point.

Equation (3.67) gives the CIDS ratio for a specific polarization state of the scattered photons. To obtain the CIDS ratio in the case in which the final state of the scattered photons is not measured, we must average this expression over all final polarizations. Performing the average of equation (3.67) amounts to averaging the dyadic \( \hat{\varepsilon}_\alpha \hat{\varepsilon}_\beta \), which appears in both the numerator and the denominator:

\[
\langle \hat{\varepsilon}_\alpha \hat{\varepsilon}_\beta \rangle_{\kappa \rho} = \frac{1}{2} ( \hat{\varepsilon}_\alpha \hat{\varepsilon}_\beta - \hat{k}_\alpha \hat{k}_\beta )
\]

Also, in most experimental situations the incident beam is approximately monochromatic. Under these conditions:

\[
\Delta = \frac{-i( \Pi x \Pi^t )_{\kappa \rho \gamma} \hat{k}_{\rho \beta} ( \delta_{\alpha \gamma} - \hat{k}_\alpha \hat{k}_\gamma )}{\Pi_{\kappa \rho} \Pi_{\gamma \delta}^t ( \delta_{\beta \gamma} \hat{k}_{\rho \delta} \hat{k}_{\gamma \delta} - \hat{k}_\alpha \hat{k}_\delta )} \quad \text{eqn (3.68)}
\]
In the next section, we will give expressions appropriate for the CIDS of a polymer or aggregate scatterer, but before proceeding to this special case, it should be mentioned that the expressions derived above are valid for the CIDS of an oriented system, and do not describe the differential scattering of rotationally disordered systems. To be applicable to disordered systems, our results would have to be rotationally averaged. Although this averaging can be performed in principle, the process in very involved and the final expressions would probably be too complicated to be useful.

C. CIDS of a Collection of Independent Systems

The application of equation (3.67) directly to a large polymer or aggregate is not practical, but it is often possible to approximate the scattering of a large object as the scattering of a collection of independent scatterers. 10-11 The expressions presented in this section are essentially generalizations of earlier results (chapter 1) to allow for situations where the individual scatterers do not behave as point polarizabilities.

Let us consider a scatterer made up of N non-interacting scattering groups described by N Hamiltonians $H_1$, $H_2$, ..., $H_N$ having eigenvectors $|n_1\rangle, |n_2\rangle, ..., |n_N\rangle$. It can be shown that the total scattering amplitude for the combined system is the sum of the scattering amplitudes for each of the individual systems:
I It is useful to define here an effective scattering amplitude $A_{Fr}$ such that

$$\frac{d\varphi}{d\Omega} = |A_{Fr}|^2.$$ 

$$(A_{Fr}^*)_{L,R} = \frac{1}{4\pi c^2} (\omega_0 - \omega_{fi})^{3/2} \hat{\xi}^* \Pi \cdot \hat{\xi}_{L,R}$$ 

Eqn (3.70)

In the case considered here

$$(A_{Fr}^*)_{L,R} = \frac{1}{4\pi c^2} (\omega_0 - \omega_{fi})^{3/2} \hat{\xi}^* \left( \sum_{r} \Pi^r \right) \cdot \hat{\xi}_{L,R}$$

Eqn (3.71)

Our task is therefore to find the quantities $\Pi^r$. The calculation can be carried out in a straightforward manner by making use of the general definition of the $\Pi$ matrix with the substitutions $|f> = |f_1, f_2> ... |f_N>$, $|n> = |n_1, n_2> ... |n_N>$, and $|i> = |i_1, i_2> ... |i_N>$. Care must be taken however, since the $\Pi$ matrix is not independent of the origin of coordinates. Imagine one of the scattering groups located at a position $\vec{r}_o$ relative to a "global" coordinate frame (see figure 3.1). Suppose we know the $\Pi$ matrix in a local coordinate frame centered on the
Figure 3.1  A local coordinate frame relative to the global coordinate frame. The axes of both frames are assumed to be parallel.
group. Then it is not difficult to show that the matrix in the local frame is related to the matrix in the global frame by a phase factor:

\[
\Pi_{\text{global frame}} = \Pi_{\text{local frame}} e^{-i\Delta k \cdot r_0}
\]

where \( r_0 \) is the vector which points from the origin of the global frame to the origin of the local frame, and \( \Delta k = k - k_0 \) as before. The phase factor appearing in equation (3.72) is responsible for keeping track of the relative positions of the scattering groups in space. With this transformation rule, the matrix for a composite system of \( N \) independent scatterers may be computed (see appendix 3A):

\[
\Pi = \sum_{r} \Pi_r' = \sum_{r} \Pi_r e^{-i\Delta k \cdot r_0} S_{FI}^{(r)}
\]

with

\[
\Pi_r' = \Pi_r e^{-i\Delta k \cdot r_0} S_{FI}^{(r)}
\]

and where
\[
\delta_\mathcal{F}_I^{(r)} = \delta f_{i_1} \delta f_{i_2} \cdots \delta f_{i_{r-1}} \delta f_{i_r+1} \cdots \delta f_{i_N}
\]

and \( \prod r \) is the \( \Pi \) matrix (computed according to (3.58)) for the \( r \)th scattering group alone in the \( r \)th local frame. The CIDS is then

\[
\Delta = \left< \left\{ -i \sum_r \sum_r' \left[ (\prod r \times \prod r')_{\alpha\beta} \hat{k}_\alpha \hat{k}_\beta \right] \right. \right. \\
\left. \left. \times \delta_\mathcal{F}_I^{(r)} \delta_\mathcal{F}_I^{(r')} e^{-i \Delta \hat{k} \cdot (\mathbf{x}_{or} - \mathbf{x}_{or'})} \right\} \right>
\]

\[
\left\{ \sum_r \sum_r' \left[ (\prod r)_{\alpha\beta} (\prod r')_{\gamma\delta} \left( \delta_{\beta\gamma} - \hat{k}_\alpha \hat{k}_\beta \right) \left( \delta_{\delta\gamma} - \hat{k}_\alpha \hat{k}_\delta \right) \right] \\
\times \delta_\mathcal{F}_I^{(r)} \delta_\mathcal{F}_I^{(r')} e^{-i \Delta \hat{k} \cdot (\mathbf{x}_{or} - \mathbf{x}_{or'})} \right\}
\]
eqn (3.74)

Equation (3.74) is the general result, but there are two qualitatively different special cases, the inelastic case (where the atom changes state during the scattering process and the final atomic state \( |f> \) is not the same as the initial state \( |i> \)), and the elastic case (where \( |f> \) is the same as \( |i> \)). For the inelastic case
\[ \Delta_{\text{inelastic}} = \left( \sum_{r}^{N} \Delta I_{r} \right) / \left( \sum_{r}^{N} I_{r} \right) \]  

Eqn (3.75)

where

\[ \Delta I_{r} = -i \left( \underline{\pi}_{r} \times \underline{\pi}_{r}^{+} \right) \alpha_{\rho} \gamma \hat{k}_{\rho \gamma} \left( \delta_{\alpha r} - \hat{k}_{\alpha} \hat{k}_{r} \right) \]

and

\[ I_{r} = \left( \underline{\pi}_{r} \right)_{\alpha \beta} \left( \underline{\pi}_{r}^{+} \right)_{\gamma \delta} \left( \delta_{\rho \gamma} - \hat{k}_{\rho} \hat{k}_{\gamma} \right) \left( \delta_{\delta \alpha} - \hat{k}_{\delta} \hat{k}_{\alpha} \right) \]

In the elastic case

\[ \Delta_{\text{elastic}} = \left\{ -i \sum_{r}^{N} \sum_{r'}^{N} \left[ \left( \underline{\pi}_{r} \times \underline{\pi}_{r'}^{+} \right)_{\alpha \rho} \gamma \hat{k}_{\rho \gamma} \left( \delta_{\alpha r} - \hat{k}_{\alpha} \hat{k}_{r} \right) \right] \right\} / \left( x e^{-i \Delta \xi} \left( \xi_{or} - \xi_{or'} \right) \right) \]

\[ \left\{ \sum_{r}^{N} \sum_{r'}^{N} \left[ \left( \underline{\pi}_{r} \right)_{\alpha \beta} \left( \underline{\pi}_{r'}^{+} \right)_{\gamma \delta} \left( \delta_{\rho \gamma} - \hat{k}_{\rho} \hat{k}_{\gamma} \right) \left( \delta_{\delta \alpha} - \hat{k}_{\delta} \hat{k}_{\alpha} \right) \right] \right\} \]
The most common inelastic scattering process in Raman scattering, where the molecular system changes vibrational levels during the course of scattering. As is well known, the scattered light has a different wavelength than the incident light in Raman scattering: the change in the molecular energy levels allows energy to be transferred from the light beam to the molecule and vice-versa. Classically this same phenomenon occurs if the scattering system is time dependent, that is, if the system has internal vibration or some other time-varying property that causes it to respond to the incident light with frequencies of oscillation other than the frequency of the incident light.

Raman scattering is not the only kind of inelastic scattering process. Any scattering process in which the final molecular state $|f\rangle$ is not the same as the initial state $|i\rangle$ (even though $|f\rangle$ and $|i\rangle$ may have the same energy) is termed an inelastic process. The distinguishing feature of inelastic scattering is that it is incoherent, i.e., light scattered by one part of the system does not interfere with light scattered by another part. In equation (3.75) the intensity scattered by the collection of independent groups is the sum of intensities scattered by each individual group. No interference cross terms survive, due to the $\delta_{FP}^{(r)}$ factors in eqn (3.74). In appendix 3A we give a brief quantum mechanical explanation for this phenomenon. The incoherence of inelastic scattering means that the angular dependence of the scattered intensity does not carry any information on the spatial
relationship between groups. In inelastic scattering experiments the interesting quantity is the frequency spectrum of the scattered light, which carries information on the dynamic properties of the subunits, rather than the angular intensity variations. The information contained in Raman CIDS data should be similar to the information in infrared circular dichroism spectroscopy. For more information on Raman CIDS (sometimes called Raman optical activity, "ROA") see references 2 and 12.

In the elastic scattering process the initial and final molecular states are identical, and the frequencies of the incident and scattered light must be the same. In this case there is no information in the frequency spectrum of the scattered light, but now the scattering is coherent, and there is structural information in the angular dependence of the scattered intensity. The effects of interference between light waves scattered from various parts of the system is contained in the cross terms proportional to \((\Pi_r \times \Pi_{r'})\) \(( \mathbf{r} \neq \mathbf{r}'\)) in equation (3.76). In fact, eqn (3.76) has exactly the same form as eqn (1.31) for the CIDS of a system of classical electric polarizabilities. The \(\Pi_r\) matrices are capable of describing the scattering by a molecule of any size or shape (or groups with magnetic polarizabilities), unlike the electric polarizabilities, which can describe only point groups.

D. Discussion

The expressions presented here are valid for all wavelengths of the incident light, for arbitrary geometry and size of the scattering molecules, for molecules which have both electric and magnetic properties, and for both elastic and inelastic scattering processes. The
expressions can also describe the anomalous CIDS effect caused by scattering at wavelengths within the absorption bands of the system. The chief shortcoming is that the effects of multiple scattering and induced coupling between parts of the system are not taken into account. This means, for example, that no CIDS is predicted for systems composed entirely of isotropic groups, in contrast to the theory of chapter 2 where multiple scattering and induced couplings are taken into account.

Bibliography


Appendix 3A

To illustrate the derivation of equation (3.73), we consider a scattering system composed of two non-interacting groups. Here we have neglected all terms dealing with spin angular momentum for convenience. For such a system the states \(| f \rangle, |n \rangle, \text{ and } |i \rangle\) appearing in the definition of the \(\Pi\) matrix are \(| f \rangle = |f_1 \rangle |f_2 \rangle, |n \rangle = |n_1 \rangle |n_2 \rangle\), and \(|i \rangle = |i_1 \rangle |i_2 \rangle\) with eigenvalues of \(\Omega_f = \Omega_{f_1} + \Omega_{f_2}, \Omega_n = \Omega_{n_1} + \Omega_{n_2}, \text{ and } \Omega_i = \Omega_{i_1} + \Omega_{i_2}\). Substituting into equation (3.58) we obtain

\[
\Pi = \frac{-1}{\sqrt{\omega \omega_0}} \langle f_1 | f_2 | (O_1 + O_2) | i_1 \rangle | i_2 \rangle \frac{1}{\omega_0} + \frac{1}{\sqrt{\omega \omega_0}} \frac{1}{\hbar} \sum_{n_1} \sum_{n_2} \left( \langle \frac{1}{\omega_{n_1} - \omega_0} \rangle \langle f_1 | f_2 | (I_1^*(k_{z_0}) + I_2^*(k_{z_0})) | n_1 \rangle | n_2 \rangle \right)
\]

\[
\times \langle n_1 | n_2 | (I_1^*(k_{z_0}) + I_2^*(k_{z_0})) | i_1 \rangle | i_2 \rangle + \left( \frac{1}{\omega_{n_f} + \omega_0} \right) \langle f_1 | f_2 | (I_1^*(k_{z_0}) + I_2^*(k_{z_0})) | i_1 \rangle | i_2 \rangle
\]

\[
\times \langle f_1 | f_2 | (I_1^*(k_{z_0}) + I_2^*(k_{z_0})) | n_1 \rangle | n_2 \rangle \right] = \Omega_n (3A.1)
\]
where $O_{1,2}$, $I_{1,2}(k)$ and $\tilde{I}_{1,2}(k_0)$ are operators acting on the wavevectors of systems 1 and 2 respectively:

$$O_{1,2} = \sum_{\text{particles of system } 1,2} \frac{2e^2}{m_l^2} e^{-i \Delta k \cdot \mathbf{r}_l} \quad \text{eqn (3A.2a)}$$

$$I_{1,2}(\mathbf{k}) = \sum_{\text{particles of system } 1,2} \frac{e^2}{m_l^2} e^{i \mathbf{k} \cdot \mathbf{r}_l} \quad \text{eqn (3A.2b)}$$

$$\tilde{I}_{1,2}(\mathbf{k}_0) = \sum_{\text{particles of system } 1,2} \frac{e^2}{m_l} e^{i \mathbf{k}_0 \cdot \mathbf{r}_l} \quad \text{eqn (3A.2c)}$$

Using the orthogonality of the wavevectors and after some manipulation, equation (3A.1) becomes:

$$\Pi = \langle f_1 | O_{1,2} | i_1 \rangle \delta_{f_2 i_2} \frac{1}{\sqrt{\omega \omega_0}} \left( \frac{-1}{\sqrt{\omega \omega_0}} \right)$$

$$+ \frac{1}{\sqrt{\omega \omega_0}} \frac{1}{\hbar} \sum \left[ \frac{1}{\left( \omega n_i - \omega_0 \right)} \langle f_1 | I^*_1(k) | n_i \times n_l | I_{1,2}(k_0) | i_1 \rangle \right]$$
\[ + \left( \frac{1}{\omega_{n_1 f_1 + \omega_0}} \right) \left\langle n_1 | T_1^* (k) | i_1 \times f_1 | T_1 (k_0) | n_1 \right\rangle S_{f_1 i_1} \]

\[ + \left( f_2 | O_2 | i_2 \right) S_{f_1 i_1} \left( \frac{-1}{\sqrt{\omega_0}} \right) \frac{1}{n_2} \sum_{n_2} \left( \frac{1}{\omega_{n_2 f_2 + \omega_0}} \right) \left\langle n_2 | T_2^* (k) | n_2 \times f_2 | T_2 (k_0) | i_2 \right\rangle \]

\[ + \left( \frac{1}{\omega_{n_1 f_1 + \omega_0}} \right) \left\langle n_2 | T_1^* (k) | i_1 \times f_1 | T_1 (k_0) | n_2 \right\rangle S_{f_1 i_1} \]

\[ + \frac{1}{\sqrt{\omega_0}} \frac{1}{\hbar} \left( \frac{1}{\omega_{n_1 f_1 + \omega_0}} \right) \left\langle f_1 | T_1^* (k) | i_1 \times f_1 | T_1 (k_0) | i_2 \right\rangle \]

\[ + \frac{1}{\sqrt{\omega_0}} \frac{1}{\hbar} \left( \frac{1}{\omega_{n_2 f_2 + \omega_0}} \right) \left\langle f_2 | T_2^* (k) | i_2 \times f_2 | T_2 (k_0) | i_1 \right\rangle \]

\[ + \frac{1}{\sqrt{\omega_0}} \frac{1}{\hbar} \left( \frac{1}{\omega_{n_1 f_1 + \omega_0}} \right) \left\langle f_1 | T_1^* (k) | i_1 \times f_1 | T_1 (k_0) | i_2 \right\rangle \]

\[ + \frac{1}{\sqrt{\omega_0}} \frac{1}{\hbar} \left( \frac{1}{\omega_{n_2 f_2 + \omega_0}} \right) \left\langle f_2 | T_2^* (k) | i_2 \times f_2 | T_2 (k_0) | i_1 \right\rangle \]

\text{eqn (3A.3)}
The last four "cross terms" cancel each other. Transforming the integrals in equation (3A.3) into their local coordinate frames gives the desired result:

\[ \Pi = \sum_1 e^{-i\Delta k \cdot R_{01}} S_{f_2 i_2} + \sum_2 e^{-i\Delta k \cdot R_{02}} S_{f_1 i_1} \]

**eqn (3A.4)**

The form of equation (3A.4) helps to illustrate the origin of the coherent nature of Rayleigh (elastic) scattering as opposed to the incoherent nature of Raman (inelastic) scattering. In the Rayleigh process the initial and final states of both atoms are identical, and the kronecker delta's in equation (3A.4) are both unity. The scattering amplitude (computed according to equation (3.57)) will therefore contain two terms, which will lead to interference cross terms when the amplitude is squared.

On the other hand, in the Raman case the initial and final states of one of the two atoms (the atom that the photon actually scatters from) will be different, and only one term in the sum on the right hand side of equation (3A.4) survives. In this case, no interference terms are obtained in the squared amplitude.

This difference is the result of the laws for calculating probabilities in quantum mechanics. In the Rayleigh case it is not possible to decide which atom has done the actual scattering of the photon, since no state change has taken place in the process. The probability that the scattering event has occurred is therefore the square of the sum of the probability amplitudes for scattering from each
individual atom. In the Raman case on the other hand, the atom that scatters the photon is "tagged" by the change of state it undergoes in the scattering process, i.e., it is possible to decide which of the two atoms scattered the photon. In this case the probability that the scattering event has occurred is obtained by summing the squares of the probability amplitudes.
Chapter 4  CIDS Model Computations

In order to get a fuller picture of the CIDS behavior predicted by our earlier work, we will present here the results of detailed CIDS calculations for particular model geometries. First we consider a linear array of polarizable point groups whose polarizability axes twist as one proceeds down the axis of the array. This geometry can be considered a model for the CIDS of a cholesteric liquid crystal. The calculated CIDS expression for this model has a simple analytical form that shows various properties of the CIDS patterns clearly. We then consider a more general helical array which allows us to investigate questions that cannot be addressed by the first model. Finally, we consider the case where the CIDS of an arbitrary helix has been averaged over all orientations of the scatterer. This case may be considered a model for the CIDS of a helical chromosome in solution. Recently McClain et al.\textsuperscript{1} have made some similar model calculations for rotationally averaged systems of point polarizabilities, but which do not include interaction between groups.

The computations presented in this chapter were done using the FORTRAN programs RIBLIN2 (twisted ladder model), RIBBON (liquid crystal model), CIDSC (oriented general helices), and CIDSAVE (rotationally averaged general helices), which appear in appendix D.

A. Twisted Ladder

Consider the array shown in fig 4.1a. In this structure the scattering points have been arranged on a line parallel to the \( z \) axis, and the principal axes of the polarizabilities of the groups are arranged
Figure 4.1 Geometries used in the CIDS calculations: a) the twisted ladder geometry, and b) a general helical geometry. In a) the rods represent uniaxial point polarizable groups with polarizable axes parallel to the rods. In b) the ellipsoids represent point polarizable groups with anisotropic polarizabilities.
in a spiral fashion. For the nth group of this system the polarizability is:

\[ \alpha_n = \alpha \hat{\tau}_n \]

eqn (4.1)

with

\[ \hat{\tau}_n = \cos\left(\frac{2\pi n \Delta z}{P}\right) \hat{x} + \sin\left(\frac{2\pi n \Delta z}{P}\right) \hat{y} \]

eqn (4.2)

where \( \alpha \) is the magnitude of the polarizability, \( P \) is the pitch of the helix, and \( \Delta z \) is the spacing between groups along the helix axis. We have taken the polarizabilities to be uniaxial with identical magnitudes for all groups. For simplicity all the end effects in this model have been neglected. That is, we have ignored the fact that a group near the ends of a helix experiences a somewhat different interaction with its neighbors than one near the middle. This can be done if the helix is very long compared to the distance over which groups interact significantly. Notice also that the direction of the incident light is parallel to the helix axis. With these choices, eqns (1.23) and (2.10) may be used to find the scattered intensities for right and left circularly polarized light. After considerable algebra we obtain:

\[ I_L = |C|^2 |S_L|^2 \left[ (A^2 + B_L^2) \left( \frac{1 + \cos^2 \theta}{2} \right) - AB_L \sin^2 \theta \cos 2\phi \right] \]
eqn (4.3)

\[ I_R = |C|^2 |S_L|^2 [(A_L^2 + B_R^2)(1 + \cos^2 \theta) - AB_R \sin^2 \theta \cos 2\phi] \]

eqn (4.4)

where

\[ C = (2\pi/\lambda)^2 \frac{E_o}{\sqrt{2\pi}} \frac{e^{i2\pi r/\lambda}}{r} \]

and

\[ A = \frac{\sin[N \left( (\pi \Delta z/\lambda) (\cos \theta - 1) \right)]}{\sin[N \left( (\pi \Delta z/\lambda) (\cos \theta - 1) \right)]} \]

eqn (4.5)

\[ B_{L,R} = \frac{\sin[N \left( (\pi \Delta z/\lambda) (\cos \theta - 1) \mp 2\pi \Delta z/\lambda \right)]}{\sin[N \left( (\pi \Delta z/\lambda) (\cos \theta - 1) \mp 2\pi \Delta z/\lambda \right)]} \]

eqn (4.6)

where \( N \) is the number of scattering groups in the system, \( \lambda \) is the wavelength of the incident light, and the upper (lower) sign refers to \( B_L \) (\( B_R \)). The interaction factors \( S_L \) and \( S_R \) are

\[ S_{L,R} = 1 + 4\pi k^2 a_{\lambda}^2 \sum_{\ell=-M}^{M} \left( \frac{1}{|k\Delta z|\ell} - \frac{1}{|k^2 \Delta z^2|\ell^2} \right) \frac{e^{i k \Delta z \ell}}{4\pi \Delta z |\ell|} \]
\[ x = e^{i(2\pi \Delta z / \lambda \pm 2\pi \Delta z / P)} \cos(2\pi \Delta z / P) \]  

eqn (4.7)

where \(|l|\) indicates the absolute value of the index \(l\), \(M\) is the number of neighboring groups which interact significantly with any given group, and as before the upper (lower) sign refers to \(S_L(S_R)\). The second Born approximation adopted in these calculations is valid only if \(S_L\) and \(S_R\) are not too different from unity (less than 1.1). In eqns (4.3) and (4.4) the effect of interactions is contained entirely in the factors \(|S_L|^2\) and \(|S_R|^2\), while only \(A\) and \(B_{L,R}\) depend on the scattering angles. The overall form of eqns (4.3) and (4.4) is \(|S_{L,R}|^2 I_{L,R}^{(o)}\) where \(I_{L,R}^{(o)}\) is the scattered intensity for left and right circularly polarized incident light in the absence of interactions between groups. This result is due to our neglect of end effects and the fact that the direction of the incident light is perpendicular to all of the polarizabilities in the system.

Figure 4.2 shows the behavior of the CIDS as a function of the polar angle, \(\theta\), for the twisted ladder model for various ratios of pitch to wavelength. In fig 4.2 the effect of interactions has been completely suppressed. The azimuthal angle, \(\phi\), has been chosen to be 45° to give the simplest patterns. All the patterns in fig 4.2 have been calculated for one turn of a right handed helix containing 50 groups evenly spaced along the \(z\) axis.

When the pitch equals the wavelength of the incident light the CIDS pattern shows a large backward lobe. This lobe has a maximum value of \(\text{CIDS} = -1\), indicating that one of the circular polarizations is being
Figure 4.2  CIDS vs. polar angle for the twisted ladder geometry for different ratios of pitch to wavelength:  a) $P/\lambda = \frac{1}{2}$, b) $P/\lambda = 1$, c) $P/\lambda = 2$, d) $P/\lambda = 5$, and e) $P/\lambda = 10$. In these calculations the groups that make up the system are not allowed to interact. For these calculations $N = 50$, $P = 100$ nm, and $\Delta z = 2$ nm. Notice that for $P/\lambda > 1$ the CIDS always reaches a value of $-1$. Also, the angle at which the CIDS is a maximum moves toward the forward direction with increasing $P/\lambda$. 
a. $P/\lambda = 1/2$

b. $P/\lambda = 1$

c. $P/\lambda = 2$

d. $P/\lambda = 5$

e. $P/\lambda = 10$
reflected by the chiral structure while the other is completely transmitted. The polarization of light being reflected is that which matches the handedness of the scatterer. In this way the lobe is negative for right-handed scatterers and positive for their mirror images. The reflection of like-handed waves by chiral objects is a common feature in CIDS patterns in general, and has been observed experimentally in the light scattered by cholesteric liquid crystals, and also found theoretically in macroscopic models of the optical properties of liquid crystals (Chandrasekhar$^2$, pp202-221). At wavelengths longer than the pitch the CIDS signals diminish rapidly as $P/\lambda$ becomes smaller. At wavelengths shorter than the pitch the CIDS remains large, and the lobe of maximum CIDS moves forward with increasing $P/\lambda$.

Figure 4.3 shows the CIDS patterns for which the interactions have been included. For this geometry and direction of incidence the effect of interactions is very simple. Using eqns (4.3) and (4.4) we obtain:

$$\Delta = \frac{|S_L|^2 |I_L^{(o)}| - |S_R|^2 |I_R^{(o)}|}{|S_L|^2 |I_L^{(o)}| + |S_R|^2 |I_R^{(o)}|}$$

$$= \frac{|S_L|^2 - |S_R|^2}{|S_L|^2 + |S_R|^2} \frac{I_L^{(o)} - I_R^{(o)}}{I_L^{(o)} + I_R^{(o)}}$$

eqn (4.8)

The last expression on the right in eqn (4.8) holds only when

$$\frac{|S_L|^2 - |S_R|^2}{|S_L|^2 + |S_R|^2}$$

and

$$\frac{I_L^{(o)} - I_R^{(o)}}{I_L^{(o)} + I_R^{(o)}}$$

are both small. Since $S_L$ and $S_R$ do not vary with angle, eqn (4.8) tells us that within the approximations noted above the effect of interactions is
Figure 4.3  CIDS vs. polar angle for the twisted ladder geometry for the case where the groups are allowed to interact. For this calculation $N=50$, $P = 100$ nm, $\Delta z = 2$ nm, and $\alpha = 1$ nm$^3$. The primary difference between this CIDS pattern and the one in figure 4.2c is the presence of CIDS at $0^\circ$.
merely to add a baseline shift wherever the CIDS is small. In particular, the CIDS without interactions \( \frac{(I_L^{(o)} - I_R^{(o)})}{(I_L^{(o)} + I_R^{(o)})} \) must be zero in the forward direction (\( \theta = 0 \)), so the quantity
\[
\frac{|S_L|^2 - |S_R|^2}{|S_L|^2 + |S_R|^2}
\]
is responsible for the CIDS in the forward direction.

B. Liquid Crystals

It was suggested earlier that the twisted ladder geometry might make an approximate model for the CIDS of a cholesteric liquid crystal. In figure 4.4 the liquid crystal is considered to be an infinite array of twisted ladders side by side with each other. This model for the structure of a cholesteric liquid crystal is similar to models used in earlier calculations on the optical properties of cholesteric liquid crystals (Chandrasekhar, p202-221). The CIDS pattern depends on only one unit cell of this array, so the CIDS of one turn of one twisted ladder is the CIDS for the cholesteric liquid crystal. In computing the CIDS for a cholesteric liquid crystal we have used a continuous twisted ladder of scatterers rather than the discrete twisted ladder described above. To do this we used eqn (2.11) for the electric field rather than eqn (2.10), and used polarizability density

\[
\alpha(x) = \alpha(x) \delta(y) \hat{e}(z) \hat{e}(z)
\]
eqn (4.9)

where
Figure 4.4 An infinite array of side-by-side twisted ladders as a model for the structure of a cholesteric liquid crystal. The small rods represent long, rod-like liquid crystal molecules. The direction pointed by the molecules in each plane twists in a right handed helical fashion. The unit cell of such an array is one turn of the twisted ladder geometry shown in figure 4.1, where the uniaxial point polarizabilities represent liquid crystal molecules.
\[ \hat{c}(z) = \cos(2\pi z/P)\hat{x} + \sin(2\pi z/P)\hat{y} \]

eqn (4.10)

and \( \alpha \) is a linear polarizability density. Also, we allowed the scattering groups to interact with the groups on neighboring twisted ladders as well as with other groups on the same twisted ladder. The result is identical in form to eqns (4.3) and (4.4) with the quantities \( A, B_L, B_R, S_L, \) and \( S_R \) given by:

\[ A = \frac{\sin[(\pi P/\lambda)(\cos \theta - 1)]}{(2\pi/\lambda)(\cos \theta - 1)}, \]

eqn (4.11)

\[ B_{L,R} = \frac{\sin[(\pi P/\lambda)(\cos \theta - 1)]}{(2\pi/\lambda)(\cos \theta - 1) + 4\pi/P}, \]

eqn (4.12)

and

\[ S_{L,R} = 1 + \rho \alpha \frac{2\pi}{(1 \pm 2\lambda/P)^2 - 1}, \]

eqn (4.13)

where \( \rho \) is the number of twisted ladders per unit cross sectional area in the liquid crystal. As before, the second Born approximation is valid.
only for cases where $S_L$ and $S_R$ are close to unity. The quantities $S_L$ and $S_R$ were computed using some of the special properties of the tensor Green's function listed in appendix B. The reader interested in these details should contact the author.

To measure the CIDS of a cholesteric liquid crystal, the liquid crystal material is placed between two quartz plates with a 10 micron spacer ring between them. The quartz plates insure that the liquid crystal forms a monodomain that can be described approximately by the model in figure 4.4. The incident light is passed through the sample at 90° to the plates (that is, along the helical axis of the liquid crystal), and the scattered light is collected at various angles to the incident beam. However, at angles greater than about 35° from the forward direction or less than about 145° (35° from the backward direction), the scattered light does not pass cleanly through the quartz plates, but is mostly reflected at the air-quartz interface. Also, even at scattering angles less than 35° or greater than 145° the air-quartz interface tends to selectively transmit or reflect the scattered light depending on its polarization, and this can introduce artifacts into the CIDS signals.

The experimental data is shown in figure 4.5 a-d. All data were collected with an incident wavelength of 442 nm. As can be seen, data are lacking in the region from about 35° to 145°. Also, in figures 4.5a and 4.5d, large variations in the CIDS are seen near 35° and 145°. These are most likely due to the polarization-selective reflection of the quartz plates mentioned above. A complete report on the experimental aspects of the measurements is in preparation.

Because of the narrow range in which good data can be collected from
Figure 4.5  Measured CIDS of cholesteric liquid crystals: a) $P/\lambda = 1.17$, b) $P/\lambda = 1.52$, c) $P/\lambda = 2.26$, and d) $P/\lambda = 4.52$. The incident wavelength was 442 nm in all measurements, and the incident beam was oriented parallel to the helix axis. The absence of data in the region between 35° and 145° is due to experimental limitations (see the main text). The liquid crystal molecules used in the experiments were: a) 40 % CB15 cholesteric liquid crystal + 60 % E7 nematic liquid crystal, b) 30 % CB15 + 70 % E7, c) 20 % CB15 + 80 % E7, and d) 12 % CB15 + 88 % E7.
the liquid crystals, a direct comparison between the calculated and measured CIDS patterns is not possible. The most characteristic feature of the calculated patterns is the large lobe that always reaches a value of -1 when the pitch is longer than the wavelength. But this lobe always falls into the gaps in the experimental data for the pitches measured so far.

The magnitudes of the calculated CIDS signals are much larger than the magnitudes of the measured signals, and this is a serious problem that has not yet been fully explained. One reasonable possibility is that the model on which the calculations are based is for a perfectly ordered crystalline array, but the actual liquid crystals have considerable disorder. Some preliminary investigations have been made into this explanation but the jury is still out.

Though direct comparison of calculated and measured CIDS patterns is not possible, we may still compare the calculated and experimental trends of the CIDS at one angle as a function of pitch. Table 4.1 shows the calculated and experimental CIDS values at 180° for cholesteric liquid crystals with 5 different pitches. The angle 180° was chosen because the measured CIDS seems most stable and reproducible in the backward direction. The values of the measured CIDS "at 180°" are actually the largest value of the CIDS in the region between 145° and 175°.

In the last column on the right in table 4.1 it can be seen that the ratio of the measured value to the calculated value is fairly constant for all pitches. Figure 4.6 is a plot of CIDS at 180° vs. pitch. The experimental values have all been multiplied by 10 in figure 4.6. It can be seen that the theory and experiment agree quite well except for the constant factor of 10. This agreement suggests that the model structure
Table 4.1 CIDS at 180° for Cholesteric Liquid Crystals

<table>
<thead>
<tr>
<th>Pitch/Wavelength</th>
<th>CIDS exp</th>
<th>CIDS theory</th>
<th>CIDS theory/CIDS exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.17</td>
<td>-0.095</td>
<td>-0.948</td>
<td>10.0</td>
</tr>
<tr>
<td>1.52</td>
<td>-0.070</td>
<td>-0.750</td>
<td>10.7</td>
</tr>
<tr>
<td>2.26</td>
<td>-0.050</td>
<td>-0.480</td>
<td>9.6</td>
</tr>
<tr>
<td>4.52</td>
<td>-0.035</td>
<td>-0.227</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Figure 4.6  CIDS at 180° vs. pitch to wavelength ratio. The solid curve is the theoretical dependence of the CIDS at 180° on \( \frac{P}{\lambda} \), and the X's are the measured values multiplied by 10.
has some qualitative features in common with the structure of the real
liquid crystal, though clearly there are also significant differences.

Equations (4.11) and (4.12) together with eqns (4.3) and (4.4) can
be used to find an analytical expression for the CIDS at 180°:

\[ \Delta(\theta=180^\circ) = \frac{-(P/\lambda)^3}{(P/\lambda)^6 - 1/2(P/\lambda)^2 + 1/2} \]

**eqn (4.14)**

The effects of multiple scattering and interactions have been neglected
in eqn (4.14). As can be seen, the model predicts that the CIDS at 180°
depends only on the ratio of the pitch to the wavelength, and the curve
in figure 4.6 is therefore a constant for all cholesteric liquid crystals
with geometries approximated by the geometry of figure 4.4. Deviations
from eqn (4.14) are then indicative of the effects of disorder or
multiple scattering and interactions in the liquid crystal.

Equations (4.13) and (4.8) can be used to find the CIDS in the
forward direction:

\[ \Delta(\theta=0^\circ) = \frac{-2ar^2(1 + (a - 1)r^2)}{(r^2 - 1)^2 - ar^2(1 + r^2) - 2(r^2 - 1)} \]

**eqn (4.15)**

where \( r = P/\lambda \) and \( a = \pi \rho a/2 \). According to eqn (4.15), the forward CIDS
depends only on the ratio of pitch to wavelength and the polarizability
density, \( \rho a \). Deviations from eqn (4.15) are indicative of the effects
of disorder in the liquid crystal, or of higher-order multiple scattering
than is accounted for by the second Born approximation.

C. General Helix

In section A we considered a twisted ladder-like helix of anisotropic polarizabilities, for incidence parallel to the helix axis. In this section we consider a more general arrangement where the helix may have a non-zero radius. We have also allowed the groups on the helix to have general, triaxial polarizabilities, and have considered directions of incidence other than parallel to the helix axis. The CIDS of a general helix can be computed by straightforward applications of equation (2.10). It has not proven possible to significantly simplify the expressions and we will not present any new equations here. In performing calculations with finite helices we have not neglected end effects. The geometry of a general helix also provides the possibility of investigating the CIDS of a system composed entirely of isotropic scattering groups, a case for which the CIDS is zero for the geometry of section A.

Figures 4.7a and 4.7b show the CIDS patterns of the helices. In each figure the solid line represents the CIDS computed when interactions between the scattering groups are included, and the dashed line is the CIDS for the same helix without interactions. The pitches and radii of the helices are equal to the wavelength of the incident light. The incident light is parallel the the helix axis in figure 4.7a and perpendicular to the helix axis in figure 4.7b. The helices in both figures are composed of uniaxial polarizable groups tangential to the helix at each point. The polarizabilities are all identical in
Figure 4.7  CIDS patterns of an oriented helix: a) incident light parallel to the helix axis, and b) incident light perpendicular to the helix axis. For these calculations the pitch, radius, and wavelength are all 100 nm. The helix is one turn in length, with 10 polarizable groups per turn. The polarizabilities are uniaxial with the polarizable axes tangent to the helix. The solid lines are the CIDS patterns when the groups are allowed to interact with each other (α = 5000 nm\(^3\)), and the broken lines are the CIDS patterns for the same helix and orientation without interaction.
magnitude. Only one turn of the helix is used in the computations and there are 10 groups evenly spaced in this turn.

The properties of CIDS patterns for general helices without interactions have been discussed in references 3 and 4 at the end of the chapter. It is of interest to note however, that the pattern in figure 4.7a shows the same like-handed reflection feature (the large backward lobe) as that calculated for the simple ladder model in section A (figs. 4.2 and 4.3).

For these relatively small values of the polarizability the effect of interactions at angles away from the forward direction are rather small, and the CIDS patterns are still very nearly symmetric. The most apparent effect of the interactions is the presence of non-zero forward CIDS.

In the case where the scattering object is composed entirely of isotropic groups the presence of interactions between groups is necessary for the system to show CIDS. Figure 4.8 shows the CIDS pattern for a helix identical in shape and orientation to the one in fig 4.7a, only in this case its polarizabilities are triaxial and isotropic rather than uniaxial and tangential. The CIDS pattern in figure 4.8 bears a marked resemblance to the pattern in figure 4.7a. This resemblance is not accidental, and can be understood by considering the interaction effect more closely. As was shown in chapter 2, the effect of interaction is formally equivalent to altering the polarizabilities associated with each scattering group. When interactions are significant the effective polarizability of a given group becomes a property of the scattering system as a whole rather than a property of the isolated group. In the case shown in figure 4.8, the spherical polarizabilities of each group
Figure 4.8. CIDS pattern of an oriented helix composed of isotropic, interacting scatterers. The incident light is parallel to the helix axis. The number of scattering groups, the pitch, radius, and length of the helix are the same as in figure 4.7. The polarizability is 5000 nm$^3$. 
are effectively elongated by interaction with their neighboring groups. These effective polarizabilities therefore play the role of the anisotropic polarizabilities in the cases shown in figure 4.7.

D. Rotationally Averaged Helix

The range of applicability of the rotationally averaged CIDS expressions of chapter 2 is somewhat more restricted than those obtained for oriented scatterers. The conditions of their validity are: 1) that the only scattering groups which interact significantly are very close together compared to the wavelength of the incident light, and 2) that the magnitudes of the polarizabilities of the scattering groups are small enough so that there is no significant multiple scattering. The net effect of these restrictions is to reduce all interactions between scattering groups to short range, dipole-dipole couplings. For comparison with the results of sections A, B and C, we have chosen a helical geometry as our scattering system.

Figure 4.9 shows the rotationally averaged CIDS patterns of a helix with pitch and radius identical to that in figure 4.7. The helix in figure 4.9 is 20 turns in length. For the oriented helices in fig. 4.7 the length has no effect on the CIDS, and the patterns of figures 4.7 and 4.9 can therefore be compared. For rotationally averaged structures the scattering is independent of the azimuthal angle $\phi$ and depends only on the polar angle $\theta$. The dashed lines in figure 4.9 show the CIDS pattern with no interaction effects, and the solid line shows the CIDS pattern including interaction effects.

The effect of interaction appears as a marked decrease in the
Figure 4.9  Rotationally averaged CIDS pattern of a helix. Broken lines indicate the CIDS pattern when no interactions are present and solid lines indicate the CIDS pattern with interactions. The pitch and radius are the same as in figure 4.7. The polarizabilities are uniaxial and tangent to the helix. For the pattern where interactions are present, $\alpha = 8\times10^4$ nm$^3$. The helix is 20 turns in length, 10 groups per turn. The presence of interactions between groups results in a marked decrease in the size of the CIDS signals, but no apparent change in the shape of the pattern.
magnitude of the CIDS, but little change in the shape of the pattern. This is the opposite of the effect that interaction between groups had on the oriented helix of isotropic groups in figure 4.8. In the latter case the groups were initially completely isotropic and the effect of interactions was to make them appear somewhat anisotropic. In the present case the groups are initially completely anisotropic and the effect of interactions is to make them appear more spherical. This reduction of the anisotropy of the groups is also visible in the CIDS patterns of the oriented helices in figure 4.7, though it is not as pronounced.

A comparison of the patterns in figure 4.9 with the corresponding patterns in figure 4.7 shows little resemblance between the CIDS patterns of a rotationally disordered system and the CIDS of the same system in a particular orientation. This is not surprising since the averaged CIDS patterns are superpositions of the CIDS patterns from all possible orientations of the scattering system, and need not resemble any one orientation. The averaged CIDS patterns are generally smaller in magnitude, and have more lobe structure than the CIDS patterns for oriented systems. Both of these results are a consequence of the fact that the differential intensity can be both positive and negative. The superposition of many patterns will tend to diminish the overall magnitude of the CIDS and break up any smooth regions in the patterns. There does not seem to be any tendency for rotationally averaged helices to preferentially scatter circularly polarized light of like handedness in the back direction (see the previous discussion), and therefore the "reflection" lobes visible in figures 4.2, 4.3, 4.7a, and 4.8 are absent in figure 4.9.
In a previous publication it was suggested that the CIDS patterns for rotationally averaged helices are largely independent of the length of the helix. This appears to be true when the incident light has a wavelength much longer than the pitch and radius of the helix, but not when the wavelength is similar in length to the helix parameters. Figure 4.10 shows the CIDS pattern of a helix of only one turn, otherwise identical to the one in figure 4.9. The two patterns differ in magnitude, number of lobes, and sign of the backward lobe.

Bibliography

Figure 4.10 Rotationally averaged CIDS pattern of the same helix as in figure 4.9, but only one turn in length. The CIDS patterns of rotationally disordered systems depend on the size of the system, even though the CIDS patterns of oriented systems do not.
Chapter 5  Circular Differential Imaging

In the previous chapters we have dealt exclusively with circular intensity differential scattering. Here we take up our second topic, circular differential imaging. Much less is known about this technique than is known about CIDS; few experimental measurements have been made to date, and even the theoretical investigation presented here is only a few months old. The emphasis will therefore be on qualitative ideas and examples rather than quantitative predictions.

In a normal optical activity experiment, the transmitted or scattered intensity is measured directly as it emerges from a chiral sample. This is the way CD, ORD, and CIDS are measured. But what happens if we now view the chiral system through a microscope? The image produced using left circularly polarized illumination will be different than the image produced when the illumination is right circularly polarized. The difference between these two images can be called a circular differential image. The information contained in a circular differential image will not be the same as the information in an image produced using unpolarized light. In the latter case the optical contrast that distinguishes one feature of the sample from another is provided by differences in the absorption and index of refraction of the various parts of the sample. In a circular differential image the contrast is provided by differences in the interaction of different parts of the sample with left and right circularly polarized light.

It will be shown below that the intensity with which each feature in a circular differential image appears is proportional to the "optical activity" of that feature in the particular direction from which the
sample is being viewed. This "optical activity" may take the form of circular dichroism or circular intensity differential scattering. As the wavelength of the illumination changes or the direction of view changes, the optical activity of each feature also changes, highlighting different features at each point. In order to see more clearly how a differential image comes about, let us now turn to the imaging theory.

A. Imaging Theory

In describing the properties of a circular differential image, we will treat the interaction of the incident light with the sample in much the same way we treated the problem in the CIDS calculations, i.e., we will consider a sample made up of a collection of small groups that respond to the electric field so as to produce oscillating induced electric dipole moments. Each of the small groups may be as large as several hundred angstroms for incident light in the visible region, or as small as a few angstroms for shorter wavelengths. As before, this division of the system into groups is somewhat arbitrary. It is only necessary that the groups be small compared to the wavelength of the incident light so that each one can be treated as a single point. The scattering and absorptive properties of each group can then be described by a polarizability tensor, \( \alpha \). Some of the optical activity of the sample will result from the intrinsic properties of each individual group, and this information is contained in the polarizability tensors associated with the groups. This optical activity is due to the short-range structure of the sample and is manifested primarily as circular dichroism. The remainder of the optical activity arises from the long-
range spatial organization of the collection of groups as a whole, and is manifested primarily in the CIDS.

After the light has interacted with the sample, two qualitatively different imaging experiments are possible:

a) Brightfield imaging, in which the microscope and detector are placed directly behind the sample. In this experiment the measured intensity is due mainly to the transmitted light, with contributions from light that has been scattered directly forward.

b) Darkfield imaging, in which the microscope and detector are placed at an angle to the incident beam. In this experiment the measured intensity is due entirely to the scattered light.

In the brightfield experiment the circular differential image can contain contributions from both the circular dichroism and the circular intensity differential scattering of the sample, while in the darkfield case only the circular intensity differential scattering contributes. Figure 5.1 shows the experimental geometry. We will treat the image calculation in the following way:

1. The electric field scattered or transmitted by the sample is calculated using classical scattering theory. The field is different for the brightfield and darkfield experiments. For the darkfield experiment $\mathbf{E}(\mathbf{r}')$ is the field scattered by the sample:\textsuperscript{1}

\[
\mathbf{E}(\mathbf{r}') = \mathbf{E}_{\text{scatt}}(\mathbf{r}') = \frac{2 \, \mathbf{k} \, r_0 \, e^{ikr'/2r_0}}{r_0} \left(1 - \hat{k} \hat{k}\right).
\]
Figure 5.1  Geometry for the differential imaging calculations. The vectors $k_o$ show the direction of the incident light for the brightfield (B) and darkfield (D) experiments. The other variables are: the distance between the sample and the lens, $r_0$, the distance between the lens and the detector screen, $d$, the lens aperture diameter, $a$, the direction of propagation of the scattered light, $k$, the position in the lens plane, $r_l$, and the position in the detector screen plane, $r$. Variables used in describing the relation between the sample and the imaging system are shown in the lower half of the figure.
where \( k = 2\pi/\lambda \) is the wavenumber of the incident light, \( \mathbf{r}' \) is a position vector in the lens plane, \( r_0 \) is the distance between the sample and the lens plane, \( \mathbf{E} \) is a unit vector pointing from the sample toward the center of the lens, \( \mathbf{r}_0 \) is the vector from the center of the lens to the sample, \( \mathbf{r}_i = \mathbf{R}_i - \mathbf{r}_0 \) where \( \mathbf{R}_i \) is the vector pointing from the center of the lens to the \( i \)th group (see inset, Fig. 5.1), \( \alpha_i \) is the polarizability tensor of the \( i \)th group, and \( E_0, \mathbf{E}_0, \) and \( k_0 \) are the amplitude, polarization, and wavevector of the incident light. In eqn (5.1) we have assumed that the lens aperture and the dimensions of the sample are much smaller than the distance \( r_0 \) between the scatterer and the lens. Also, the field in eqn (5.1) is computed in the first Born approximation, that is, we have assumed that there is no appreciable induced dipole-induced dipole interaction between groups or multiple scattering in the sample. Some of the effects of dipole-dipole interactions and multiple scattering can be taken into account by the use of the second Born approximation. This amounts to replacing \( \alpha_i \) in eqn (5.1) with an effective polarizability which contains the coupling information (see chapter 2).

For the brightfield experiment the electric field at the near face of the lens includes both incident and scattered waves:

\[
E(\mathbf{r}') = E_0 \varepsilon_0 \mathbf{e}_0 \ + \ E_{\text{scatt}}(\mathbf{r}')
\]

eqn (5.2)
2. We take the imaging apparatus to be a single thin lens. That is, after the scattered or transmitted light has left the sample and arrived at the lens, the effect of the imaging system is to modulate the phase of the field as a function of position in the lens plane. The polarization and magnitude of the field are not altered at all. Specifically, we take the electric field on the far face of the lens (after passing through the lens, but before beginning to propagate toward the detector screen) to be

\[ E_f(r') = e^{i\phi(r')} E(r') \quad \text{eqn (5.3)} \]

where \( E_f \) and \( E \) are the electric fields on the far and near faces respectively, and \( r' \) is a position vector in the lens plane (see Fig. 5.1). The phase function \( \phi(r') \) is given by

\[ \phi(r') = k n \Delta_o - kr'^2 / 2f \quad \text{eqn (5.4)} \]

where \( n \) is the index of refraction of the lens material, \( \Delta_o \) is the thickness of the lens at its widest point, and \( f \) is the focal length of the lens.

3) Once the electric field is known on the lens, we calculate the propagation of the field outward from the lens toward the detector screen using vector diffraction theory. If the lens aperture is small compared to the distance \( d \) between the detector screen and the lens plane (see Fig. 5.1), the electric field on the detector plane is given by

\[
E(r) = \frac{i e^{-ikr}}{2\pi r} kr x[\int_{\text{aperture}} x E_f(r') e^{-ikr'r'} + \frac{ikr'^2}{2r} \, ds]
\]
where $r$ is a position vector pointing from the center of the lens to a
spot in the detector plane, $r = |r|$, $\hat{r} = r/r$, and $\hat{n}$ is a unit vector
normal to the surface of the lens plane. The integration in eqn (5.5) is
over the surface of the lens aperture. We choose the lens and detector
planes to be parallel to the $xy$ plane, so that the normal to the surface,
$\hat{n}$, is along $z$.

Darkfield Circular Differential Imaging. All parts of the
calculation are now specified. To obtain the image electric field (i.e.,
the field arriving at the detector) in the darkfield case we substitute
eqns (5.1), (5.3), and (5.4) into eqn (5.5):

$$
E(x) = C \sum_i F(k, r_i) e^{-i\Delta k \cdot r_i} \hat{r} \times [\hat{k} \times (\hat{a} \cdot \hat{e}_o)]
$$
eqn (5.6)

where $\Delta k = k - k_o$ is the momentum transfer vector for scattering in the $k$
direction,

$$
C = iE_o k^3 \left[ \exp(i(kn\Delta o + k_o \cdot r_o)) e^{ik(r + r_o)} \right] \frac{e}{2\pi r_o}
$$

and $F(k, r_i)$ is given by
The integral in eqn (5.7) is commonly found in imaging theories based on scalar diffraction theory. It is this integral which gives the localized field intensity that will produce an image of the scattering sample. In eqn (5.7) the quantity \( \frac{1}{r_0} + \frac{1}{r} - \frac{1}{f} \) appears. According to geometric optics, the condition for a thin lens to produce a focused image is

\[
\frac{1}{r_0} + \frac{1}{d} - \frac{1}{f} = 0
\]

where \( d \) is the distance from the lens plane to the detector plane (see Fig. 5.1). For points in the detector plane near the lens axis \( d \approx r \), and we may set the first term in the argument of the exponential in eqn (5.7) to zero. The second term in the exponential can be rewritten in terms of the magnification of the imaging system:

\[
(k + \frac{kr_i}{r_0}) \cdot r' = \frac{k}{r} \sqrt{(x + mx_i)^2 + (y + my_i)^2} \ r' \cos \phi
\]

where \( x_i \) and \( y_i \) are the \( x \) and \( y \) components of \( r_i \), \( x \) and \( y \) are the \( x \) and \( y \) components of \( r \), and \( m = r/r_0 \) is the lens magnification. The remaining integral may be performed directly:
\[ F(k, r) \equiv F(\rho) = 2\pi a^2 \left[ \frac{J_1\left(\frac{2\pi}{\Lambda} \rho \right)}{\frac{2\pi}{\Lambda} \rho} \right] \]  

where \( J_1 \) is the Bessel function of the first kind of order 1, \( \rho = \sqrt{(x + mx_i)^2 + (y + my_i)^2} \) and \( \frac{\Lambda}{\lambda} = \frac{(m + 1)f}{a} \). The function \( F(\rho) \) reaches a maximum when \( \rho = 0 \), that is, when \( x = -mx_i \) and \( y = -my_i \), and diminishes for all non-zero values of \( \rho \).

To calculate the darkfield circular differential image we must calculate the image intensity at the detector for right and left circularly polarized illumination and then subtract. To do this we substitute left and right circular polarization vectors for the incident polarization vector \( \epsilon_0 \) in eqn (5.6) and square the electric fields to obtain left and right circular intensities. The unit vectors for left and right circular polarization are

\[ \hat{\epsilon}_L = \frac{1}{\sqrt{2}} (\hat{\epsilon}_1 + i \hat{\epsilon}_2) \quad \text{and} \quad \hat{\epsilon}_R = \frac{1}{\sqrt{2}} (\hat{\epsilon}_1 - i \hat{\epsilon}_2) \]

respectively, where \( \hat{\epsilon}_1, \hat{\epsilon}_2 \), and \( \hat{\epsilon}_0 \) form a right-handed orthogonal coordinate frame. After some algebra we obtain:

\[ I_L - I_R = |c|^2 \sum_{i<j} F(\rho_i)F(\rho_j) \Delta I_{ij}(k, k_o) \]

where the differential intensity \( \Delta I_{ij} \) is given by
\[ \Delta I_{ij}(k, k_0) = \]
\[
2 \text{Re} \left[ e^{-i \Delta k \cdot r_{ij}} \left( \varepsilon_{L}^{*} \cdot a_{i}^{+} \cdot (1 - \hat{k} \hat{k}) \cdot a_{j} \cdot \varepsilon_{R} \right) \right]
\]

with \( r_{ij} = r_j - r_i \), and \( a_i^* \) is the Hermitian conjugate of \( a_i \) (i.e., \([a_i^+]_{ij} = [a_i^*]_{ji}\)). In arriving at eqn (5.11) we have taken \( r \equiv k \), which is valid for images in the portion of the detector screen close to the lens axis.

The differential intensity \( \Delta I_{ij}(k, k_0) \) is the scattering optical activity of the sample in the \( k \) direction due to the pair of groups \( i \) and \( j \). In a normal CIDS experiment what is measured is the total differential intensity in a given direction, which is a sum of contributions from all single groups \( \sum_i \Delta I_{ii} \) and pairs of groups \( \sum_{i<j} \Delta I_{ij} \) in the sample. It is usually not possible to tell how much each group has contributed. On the other hand, in a darkfield differential imaging experiment the individual contributions from the self and pairwise differential intensities of the groups are spatially resolved. To see this more clearly, consider the case where the sample contains only two groups. From eqn (5.10) the circular differential image is proportional to:

\[
|c|^2 \left[ F_1^2(\rho_1) \Delta I_{11} + 2F(\rho_1)F(\rho_2)\Delta I_{12} + F_2^2(\rho_2)\Delta I_{22} \right].
\]
Eqn (5.12) has three terms: two proportional to the self differential intensities $\Delta I_{11}$ and $\Delta I_{22}$, which give the optical activity due to the individual groups, and one proportional to the pair differential intensity $\Delta I_{12}$, which gives the optical activity due to the chiral orientation between the groups. If the two groups are well resolved so that there is no overlap between their image spots $[F(p_1)F(p_2) = 0]$ only the self differential intensities will contribute. The differential image will then consist of two image spots, each spot having intensity proportional to the self differential intensity of the corresponding group in the direction of observation, $E$. Fig. 5.2 shows the differential image of a pair of groups. The presence of intrinsic differential intensity in Fig. 5.2a shows that each group is chiral individually, and in Fig. 5.2b the differential intensity due to coupling shows that the spatial relationship between groups is also chiral.

On the other hand, if the groups have no self differential intensity ($\Delta I_{11} = \Delta I_{22} = 0$), but bear a chiral orientation with respect to each other and are closely enough spaced to overlap in the image, $[F(p_1)F(p_2) \neq 0]$, then only the pairwise differential intensity contributes. Fig. 5.3a shows the circular differential image for the pair of groups shown in Fig. 5.2. Because the pairwise differential image arises from the interference term, $F(p_1)F(p_2)\Delta I_{12}$, Fig. 5.3a shows more structure than the images in Fig. 5.2. In Fig. 5.3b a differential image is shown in which all of the effects leading to a darkfield differential image are present.

The circular differential image can reveal structural information in images formed under unpolarized light. In figure 5.4 the image of a
Figure 5.2  The circular differential image of a pair of scattering groups: a) groups well-resolved and having intrinsic optical activity, but not interacting with each other, and b) groups well-resolved and interacting, but having no intrinsic optical activity. Solid lines indicate positive differential intensity and broken lines negative differential intensity. The point of view in the images is from perpendicular to the axis that joins the two groups, and at an angle of 60° to each group. The light is incident parallel to the intergroup axis from below. The distance between groups is equal to 3/4 the incident wavelength for these calculations. In figure 5.2a the sign of the differential intensity does not depend on the orientation between the groups. In figure 5.2b the sign does depend on the orientation, and would be opposite for a mirror-image system.
Figure 5.3  The circular differential image of the pair of groups shown in Fig. 5.2: a) groups not well-resolved so that pairwise differential intensity contributes, and b) combination of the cases shown in Fig. 5.2a, 5.2b, and 5.3a: groups with intrinsic optical activity, interacting with each other, and not well-resolved. The wavelength, direction of the incident light, and point of view are the same as in Fig. 5.2. As before, broken lines indicate negative differential intensity.
Figure 5.4 Images of a helix in unpolarized light and circular differential images of a helix: a) image in unpolarized light at high resolution, b) circular differential image at high resolution, c) image in unpolarized light at low resolution, and d) circular differential image at low resolution. Shaded regions denote negative differential intensity. The polarizabilities of the groups that make up the helix are uniaxial with principal axes tangent to the helical curve. The groups are individually non-chiral and all contributions to the circular differential images are due to pairwise differential intensity. The incident wavelength is the same in all images, and is equal to one tenth the pitch of the helix. The light is incident from the left along the helix axis, and the point of view is perpendicular to the direction of incidence.
helix is shown at two different image resolutions, all other conditions being identical. The helix used for the calculations in figure 5.4 is similar to the helix in figure 4.1. At high resolution a zig-zag pattern appears in the image formed under unpolarized light, but it is not clear that this is a helix. The circular differential image shows that there are chiral relationships between adjacent groups and therefore confirms that the object is helical. At low resolution, the image under unpolarized light reveals only that the object is elongated somewhat in one direction. The circular differential image shows the object to be chiral, and clearly shows the axial symmetry one would expect of a helix.

A sample may show a differential image even if it is not optically active overall, or if the total scattered differential intensity in a given direction of observation is zero. In figure 5.4 the total differential intensity in the direction of view is zero, as can be seen by the symmetrical regions of positive and negative differential image intensity. But because each pair of groups in the helix contributes individually, the differential image is not zero. In general, all that is necessary for a differential image is that some group of the system bear a chiral relationship to another group and that these groups either interact or have overlapping images.

As the wavelength of the incident light changes, both the self and pairwise contributions to the differential image also change. The self contributions are greatest inside the absorption bands of the groups where the intrinsic optical activity is greatest, and the coupling between groups is increased by the large induced dipoles and the anomalous scattering within an absorption band.

**Brightfield Circular Differential Imaging.** When the lens and
detector are placed directly behind the sample the electric field arriving at the lens plane has two parts: the forward scattered electric field and the incident electric field. In classical electrodynamics it is the interference between these two fields that leads to absorptive effects. The primary difference between the brightfield and darkfield differential imaging experiments is the presence of these absorptive effects in the brightfield image.

When eqn (5.2) for the electric field at the near face of the lens is substituted into eqns (5.3) and (5.4), two image fields will result, one originating from the incident field and one originating from the scattered field:

\[ E(r, \hat{e}_o) = E_I(r, \hat{e}_o) + E_S(r, \hat{e}_o) \]  

**eqn (5.13)**

where \( \hat{e}_o \) is the incident polarization, \( E \) is the total image field, \( E_I \) is the image field due to the incident light, and \( E_S \) is the image field due to the forward scattered light (given by eqn (5.6) with \( k = k_o \)). The field \( E_I \) is given by

\[ E_I(r, \hat{e}_o) = C' \hat{r} \times (k_o \times \hat{e}_o) \int_{\text{aperture}} \exp \left[ i \frac{k}{2} \left( \frac{r}{r'} - \frac{r}{r} \right) r'^2 - i(kr - k_o \cdot r') \right] dS \]  

**eqn (5.14)**

where \( C' = \frac{ie^{ikr}}{2\pi r} \frac{iknA}{k_o \cdot \hat{e}_o} \). If the lens aperture has a finite diameter, the integration in eqn (5.14) is very difficult. However, this field is the one that provides the bright background illumination in a
brightfield experiment, and therefore we expect it to be very slowly varying over the surface of the detector screen. The smaller the aperture the more slowly varying the background field is. It can be shown that even if the aperture is taken to be infinite however, $E_I$ is still approximately constant for the portion of the detector screen near the lens axis. For an infinite aperture then, eqn (5.14) becomes

$$E_I(r, \hat{e}) = C' r x (\hat{k}_o \times \hat{e}) \left( \frac{2\pi i r_o}{r} \right) \exp \left[ i \frac{r o k}{2r^2} (x^2 + y^2) \right]$$

$$= C' \hat{e}_o \left( \frac{2\pi i r_o}{k} \right) \text{ eqn (5.15)}$$

where we have used $\frac{1}{r} - \frac{1}{k} = \frac{1}{r_o}$, and the second equation holds for portions of the detector screen near the lens axis ($r = r_o$).

To find the brightfield differential image we square eqn (5.13) with $\hat{e}_o = \hat{e}_L$ or $\hat{e}_R$ [as defined in eqn (5.9)] and subtract:

$$I_L - I_R = (I_L - I_R)_I +$$

$$2\text{Re}[E_I(r, \hat{e}_L) \cdot E^*_I(r, \hat{e}_L) - E_I(r, \hat{e}_L) \cdot E^*_S(r, \hat{e}_L)] +$$

$$= (I_L - I_R)_S \text{ eqn (5.16)}$$
where \((I_L - I_R)_I = |E_I(x, \hat{e}_L)|^2 - |E_I(x, \hat{e}_R)|^2 = 0\),

and \((I_L - I_R)_S = |E_S(x, \hat{e}_L)|^2 - |E_S(x, \hat{e}_R)|^2\).

The quantity \((I_L - I_R)_I\), the background illumination, does not contribute to the differential image. The quantity \((I_L - I_R)_S\) is just the darkfield differential image evaluated for scattering in the forward direction and has already been discussed. The cross terms in eqn (5.16) contain the absorptive effects. Usually the incident field is much larger than the scattered field and so these absorption terms should give the primary contributions to the brightfield image. Substituting eqns (5.6) and (5.15) into eqn. (5.16) we obtain, for the absorption terms:

\[
CDI = 2C^* \frac{2\pi a}{k} \sum_i F(\rho_i) \text{Im} \left( \hat{e}_L \cdot \alpha_i^* \cdot \hat{e}_L - \hat{e}_R \cdot \alpha_i^* \cdot \hat{e}_R \right)
\]

\[
= K \sum_i F(\rho_i) \Delta I_{1i}^{\text{abs}} \quad \text{eqn (5.17)}
\]

where \(K = \frac{|E_0|^2 k^3}{2\pi r^2}\), and \(\Delta I_{1i}^{\text{abs}}\) is proportional to the difference in the absorbed intensities for left and right circularly polarized light. For optically thin samples (\(c\varepsilon \ll 1\), where \(\varepsilon\) is the extinction coefficient,
c is the concentration, and \( l \) is the path length) the absorption differential intensity \( \Delta I_{\text{abs}}^1 \) is approximately proportional to the circular dichroism. In the brightfield experiment therefore the circular differential image is essentially a map of the circular dichroism of each feature of the sample. Figure 5.5 shows the image in unpolarized light and the brightfield circular differential image of the helix in figure 5.4. In the differential image it can be seen that the groups all have different intrinsic chirality, even though the image in unpolarized light is similar to the image of the helix in figure 5.4, where the groups have no intrinsic optical activity.

Usually the circular dichroism is sensitive to molecular structure on the order of a few tens of angstroms. The differential image in the brightfield case will therefore mainly contain information on short-range structure in the sample. However, if the sample is capable of scattering appreciably, the difference in total scattering cross-sections for left and right circularly polarized light can also contribute to the apparent circular dichroism. This contribution is largest when the dimensions of the scatterer are on the order of the incident wavelength. For incident wavelengths outside the absorption bands of the groups only the differential scattering effects contribute to the circular dichroism. Inside the absorption bands the absorptive circular dichroism is usually dominant, though the scattering contribution also increases as the absorption bands are approached.

B. Summary and Discussion

The circular differential image can be thought of as a two-dimensional
Figure 5.5  Brightfield images of a helix at high resolution: a) image in unpolarized light, and b) circular differential image. The groups that make up the helix have intrinsic optical activity, but are not interacting with each other. The intrinsic optical activity varies from group to group. Since the helix is being viewed from directly opposite the incident beam the differential image contains none of the darkfield scattering effects (since there can be no interference in the forward scattered light). The optical activity is therefore due entirely to circular dichroism.
mapping of the optical activity of the sample. Each feature in the image is differentiated from surrounding features by the differences in its optical activity rather than differences in absorption or refractive index. This has two advantages. First, samples that have little or no contrast in an ordinary optical image may show contrast in a differential image. In effect, areas of differing chemical composition are "stained" by their differing optical activity properties. Second, the sign and magnitude of the optical activity of each feature are characteristic of structural properties that are too small to be resolved by the microscope directly. This should be especially valuable for parts of the system whose structure changes with time or environment, for example, the folding and unfolding of chromatin.

The optical activity of each feature in the sample manifests itself differently at different angles of observation with respect to the incident light, and at different wavelengths of the light. When the sample is viewed from directly opposite the source of illumination (brightfield experiment) the optical activity is primarily circular dichroism, and is sensitive mainly to short-range molecular structure when the incident wavelength is inside the absorption bands. When the sample is viewed at an angle to the illuminating beam (darkfield experiment) the optical activity is due to circular differential scattering and is sensitive mainly to structures with dimensions similar to the incident wavelength. In the visible and UV regions this means very long-range macromolecular structure on the order of thousands of angstroms. The circular differential scattering of each feature is different at each angle of observation, and as the angle is changed some features in the differential image will change sign or disappear and
others will become more prominent. We have spoken primarily in terms appropriate to microscopy at visible and UV wavelengths. In principle, however, circular differential images could also be formed using short wavelengths in the far UV or X-ray regions.

If the sample fluoresces or if it is treated with a fluorescent dye it should also be possible to form differential images from the fluorescence emission. In this case the darkfield differential image will contain a contribution from the fluorescence detected circular dichroism (FDCD) which may dominate the contribution from differential scattering. Also, if the sample is placed in a magnetic field even non-chiral parts of the sample will acquire a magnetically induced optical activity and contribute to the differential image.

REFERENCES

The electric fields for plane wave left and right circularly polarized light are:

LCP \[ \mathbf{E}_L = E_0(\hat{x} + i\hat{y})e^{ikz-i\omega t} \]

RCP \[ \mathbf{E}_R = E_0(\hat{x} + i\hat{y})e^{ikz-i\omega t} \]

where \( k = 2\pi/\lambda , \omega = kc \), and the light is propagating along \( z \) from negative values of \( z \) toward positive values of \( z \). We wish to visualize these fields in space and time. The physically meaningful parts of the fields are their real parts:

\[ \mathbf{F}_L = \text{Re}\mathbf{E}_L = E_0[\cos(kz-\omega t)\hat{x} - \sin(kz-\omega t)\hat{y}] \]

\[ \mathbf{F}_R = \text{Re}\mathbf{E}_R = E_0[\cos(kz-\omega t)\hat{x} + \sin(kz-\omega t)\hat{y}] \]

At a fixed point in space (say, \( z = 0 \)):

\[ \mathbf{F}_L = E_0(\cos\omega t\hat{x} + \sin\omega t\hat{y}) \]

eqn (A.1a)

\[ \mathbf{F}_R = E_0(\cos\omega t\hat{x} - \sin\omega t\hat{y}) \]

eqn (A.1b)

To an observer standing at \( z = 0 \) and facing the light beam (looking back toward negative values of \( z \)) the vector \( \mathbf{F}_L \) in eqn (A.1a) would rotate in
a counter-clockwise direction and the vector $F_R$ in eqn (A.1b) would rotate in a clockwise direction.

At a fixed point in time (say, $t = 0$):

$$F_L = E_o (\cos kzx - \sin kzy)$$

eqn (A.2a)

$$F_R = E_o (\cos kzx + \sin kzy)$$

eqn (A.2b)

These fields look like the fields in figure 1.2. $F_L$ is a left handed helix and corresponds to figure 1.2b. $F_R$ is a right handed helix and corresponds to figure 1.2a.

Combining the space and time dependence, the fields may be visualized as left handed ($E_L$) or right handed ($E_R$) helices moving forward along $\hat{z}$ at the speed of light.
Appendix B        Some Notes on Polarizabilities

1) The electric polarizability is defined by the equation

\[ \mu = \alpha \cdot E \]

where \( E \) is the electric field at the position of the polarizability, and \( \mu \) is the electric dipole moment induced by the field.

2) The polarizability transforms under rotations as a second rank tensor:

\[ \alpha' = U^\dagger \alpha U \]

where \( U \) is a rotation matrix which rotates the original coordinate axes into a new coordinate system, and \( \alpha' \) is the polarizability in the rotated coordinate system.

3) The polarizability is most conveniently represented as a sum of dyadics formed from the principle axis vectors of the polarizability (i.e., the eigenvectors of the polarizability matrix):

\[ \alpha = \alpha_1 \hat{t}_1 \hat{t}_1^* + \alpha_2 \hat{t}_2 \hat{t}_2^* + \alpha_3 \hat{t}_3 \hat{t}_3^* \]

where \( \alpha_1, \alpha_2, \alpha_3, \) and \( \hat{t}_1, \hat{t}_2, \hat{t}_3 \) are the eigenvalues and eigenvectors of the polarizability respectively. Physically, the eigenvectors are determined by the symmetry of the polarizable group. The eigenvalues and...
eigenvectors are complex quantities in general.

4) The rate at which a group absorbs energy from an incident light beam is related to the imaginary parts of the polarizability eigenvalues:

$$P_{\text{abs}} = \text{Im}(\varepsilon_0^* \cdot \alpha^* \cdot \varepsilon_0) = \text{Im} \alpha_1 |\hat{\varepsilon}_o \cdot \hat{\tau}_1|^2 + \text{Im} \alpha_2 |\hat{\varepsilon}_o \cdot \hat{\tau}_2|^2 + \text{Im} \alpha_3 |\hat{\varepsilon}_o \cdot \hat{\tau}_3|^2$$

where $\hat{\varepsilon}_o$ is the polarization vector of the incident light.

5) The circular dichroism is related to the cross products of the eigenvectors with their complex conjugates:

$$\text{CD} = P_{\text{abs}, L} - P_{\text{abs}, R} = \text{Im} \alpha_1 (|\hat{\varepsilon}_L \cdot \hat{\tau}_1|^2 - |\hat{\varepsilon}_R \cdot \hat{\tau}_1|^2) + \text{Im} \alpha_2 (|\hat{\varepsilon}_L \cdot \hat{\tau}_2|^2 - |\hat{\varepsilon}_R \cdot \hat{\tau}_2|^2) + \text{Im} \alpha_3 (|\hat{\varepsilon}_L \cdot \hat{\tau}_3|^2 - |\hat{\varepsilon}_R \cdot \hat{\tau}_3|^2)$$

$$= -i \text{Im} \alpha_1 (\hat{\tau}_1 \times \hat{\tau}_1^*) + \text{Im} \alpha_2 (\hat{\tau}_2 \times \hat{\tau}_2^*) + \text{Im} \alpha_3 (\hat{\tau}_3 \times \hat{\tau}_3^*) \cdot \hat{k}_o$$

Clearly, if the CD is to be non-zero both the eigenvalues and the eigenvectors must be complex.

6) The intensity scattered by a polarizable group is second order in the polarizability:

$$I = |\varepsilon^* \cdot \alpha \cdot \varepsilon_0|^2$$

where $\varepsilon$ is the polarization vector of the scattered light in the
direction of observation. Both the real and imaginary parts of the polarizability eigenvalues and eigenvectors contribute to the scattered intensity.

7) The scattering optical activity is related to the cross product of the real part of the polarizability with the imaginary part:

\[
I_L - I_R = |\hat{\mathbf{e}}^* \cdot \mathbf{a}_L \hat{\mathbf{e}}^*|^2 - |\hat{\mathbf{e}}^* \cdot \mathbf{a}_R \hat{\mathbf{e}}^*|^2 = -i(\mathbf{a} \times \mathbf{a}^\dagger)_{\alpha\beta} \alpha^\gamma k_{\alpha^\gamma} \\
= 2(\text{Im} a \times \text{Re} a)_{\alpha\beta} \alpha^\gamma k_{\alpha^\gamma}
\]
Appendix C  Notes on the Tensor Green's Function

1) \( \nabla \times [\nabla \times \Gamma(\mathbf{x} - \mathbf{x}')] - k^2 \Gamma(\mathbf{x} - \mathbf{x}') = \delta^3(\mathbf{x} - \mathbf{x}') \)

2) \( \Gamma(\mathbf{x} - \mathbf{x}') = (1 - \frac{1}{k^2} \mathbf{V} \mathbf{V}) \frac{e^{ik|\mathbf{x} - \mathbf{x}'|}}{4\pi |\mathbf{x} - \mathbf{x}'|} = (1 + \frac{1}{k^2} \mathbf{V} \mathbf{V}) \frac{e^{ik|\mathbf{x} - \mathbf{x}'|}}{4\pi |\mathbf{x} - \mathbf{x}'|} \)

3) \( \Gamma(\mathbf{x} - \mathbf{x}') = \Gamma(\mathbf{x}' - \mathbf{x}) = \tilde{\Gamma}(\mathbf{x} - \mathbf{x}') \)

where the ~ symbol indicates the transpose of a matrix.

4) \( \Gamma(\mathbf{x} - \mathbf{x}') = \Gamma(\mathbf{R}) = (1 + \frac{1}{k^2} \mathbf{V} \mathbf{V}) \frac{e^{ik\mathbf{R}}}{4\pi \mathbf{R}} \)

where \( \mathbf{R} = \mathbf{x} - \mathbf{x}' \). Since the radial part of \( \mathbf{V} \mathbf{V} \) is

\[
\frac{\partial^2}{\partial \mathbf{R}^2} + (1 - \frac{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}}{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}}) \frac{1}{\mathbf{R} \frac{\partial}{\partial \mathbf{R}}} \]

we have

\[
\Gamma(\mathbf{R}) = (1 + \frac{1}{k^2} \frac{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}}{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}}) \frac{1}{\mathbf{R} \frac{\partial}{\partial \mathbf{R}}} \frac{e^{ik\mathbf{R}}}{4\pi \mathbf{R}} \]

5) Under rotations \( \Gamma \) behaves like a second-rank tensor:

\[
\Gamma^\prime(\mathbf{R}) = \mathbf{U}^\dagger \Gamma(\mathbf{R}) \mathbf{U} \]

6) By explicit use of 4) we obtain:

\[
\Gamma(\mathbf{R}) = (1 - \frac{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}}{4\pi \mathbf{R}}) \frac{e^{ik\mathbf{R}}}{4\pi \mathbf{R}} + (3\frac{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}}{\mathbf{R} \cdot \frac{\partial}{\partial \mathbf{R}}} - 1) \frac{1}{k^2 \mathbf{R}^2} - \frac{1}{k^2 \mathbf{R}^2} \frac{e^{ik\mathbf{R}}}{4\pi \mathbf{R}} \]
However, if we take the trace of $\Gamma$ we obtain

$$\text{tr}\Gamma = (3 + \frac{1}{k^2} \psi^2)(\frac{\i k R}{4\pi R}) ,$$

and since

$$\left(\nabla^2 + k^2\right)(\frac{\i k R}{4\pi R}) = -\delta^3(R)$$

we have

$$\text{tr}\Gamma = 2(\frac{\i k R}{4\pi R}) - \frac{1}{k^2} \delta^3(R) .$$

We must therefore add a quantity $-\frac{1}{3k^2} \delta^3(R)$ to $\Gamma$ to obtain the correct trace:

$$\Gamma(R) = (1 - \frac{1}{3k^2})(\frac{\i k R}{4\pi R}) + (3\delta^3 - 1)(\frac{1}{2k^2} - \frac{1}{kR}\frac{\i k R}{4\pi R}) - \frac{1}{3k^2} \delta^3(R)$$

7) The electric field produced by a point dipole oscillating with time dependence $e^{-i\omega t}$ is

$$E(x) = 4\pi k^2 (x - x') \cdot u(x').$$

If the oscillation is due to an applied electric field, and the point has polarizability $\alpha(x')$

$$E(x) = 4\pi k^2 (x - x') \cdot \alpha(x') \cdot E_0(x')$$
where \( E_0(x') \) is the applied field. Finally, the coupling energy between two oscillating dipoles located at \( x \) and \( x' \) is

\[
U = \mu(x) \cdot 4\pi k^2 \Gamma(x - x') \cdot \mu(x').
\]

8) For a medium with no explicit sources, with no magnetic susceptibility, which responds passively and linearly to applied electric fields, the total electric field is given by the integral equation:

\[
E(x) = E_0(x) + 4\pi k^2 \int \Gamma(x - x') \cdot \alpha(x') \cdot E(x') d^3x.
\]

The magnetic field is then

\[
B(x) = -\frac{1}{k} \nabla \times E(x).
\]

9) The tensor Green's function acts as a partial inverse for the operator \( \nabla \times (\nabla \times ) - k^2 = \nabla \nabla - \nabla^2 - \frac{2}{k} \). That is, \( \Gamma \) inverts the operator up to within an element of its nullspace:

\[
\int \Gamma(x - x') \cdot [\nabla' \nabla' - \nabla^2 - k^2] \cdot F(x') d^3x' = F_0(x) + F(x)
\]

where \( F_0 \) satisfies \( \nabla \times (\nabla \times F_0) - F_0 = 0 \). \( F_0 \) is an element of the vector space spanned by

\[
\{ F_0 e^{\pm ik \cdot x} \mid \epsilon \cdot k = 0, F_0 \text{ complex} \},
\]

that is,
\[ F_0 = \sum_{i=1,2} \left[ \int d\Omega_k F_{0i}(\mathbf{k}) \varepsilon_i(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{x}} + \int d\Omega_k F'_{0i}(\mathbf{k}) \varepsilon_i(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{x}} \right] . \]
Appendix D  Computer Programs

The programs listed in this appendix were used to make the calculations that appear in the main text. Program RIBLIN2 was used to make the twisted ladder calculations of figures 4.2 and 4.3, program CIDSC was used to make the oriented general helix calculations for figures 4.7 and 4.8, program CIDSAVE was used for the rotationally averaged general helix calculations of figures 4.9 and 4.10, and program IMAGEC was used to make the differential image calculations for the figures in chapter 5. Programs CIDSC, CIDSAVE, and IMAGEC have very similar input and output conventions. There are three auxiliary programs, HGEN, HGENAVE, and IMHGENC, that generate input data files for CIDSC, CIDSAVE, and IMAGEC respectively, for scattering systems with helical geometries ("HGEN" stands for Helix GENerator). In the following we will give a brief description of the input requirements for these programs, and examples of input and output files.

A. RIBLIN2

Program RIBLIN2 calculates the CIDS for the twisted ladder geometry in figure 4.1. This program evaluates eqns (4.3) and (4.4) and includes the effects of interactions and multiple scattering, but neglects end effects. Program RIBLIN2 has very simple input requirements (due to the highly specialized geometry) and is designed to run interactively. Upon running RIBLIN2, the program asks the operator "ENTER THE PITCH, WAVELENGTH, HELIX PHASE, POLARIZABILITY, DIPOLE SPACING, NUMBER OF DIPOLES, AND INTERACTION INTEGER". Most of these quantities are self
expansory. The quantity "helix phase" is the angle $\phi$ in eqns (4.3) and (4.4), and the interaction integer is the number of neighboring groups that are allowed to interact with any one group (the number $M$ in eqn (4.7)). The term "dipole" means "scattering group".
### Example output data file for RIBLIN2

**Program RIBLIN2: helical ribbon interacting with itself.**

**End Effects "Not" included**

<table>
<thead>
<tr>
<th>Pitch</th>
<th>Wavelength</th>
<th>Fix Phase</th>
<th>Polarizability</th>
<th>Dipolar Spacing</th>
<th>Dipolar Number</th>
<th>Interaction Integer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Example output data file for RIBLIN2**

<table>
<thead>
<tr>
<th>ANGLE</th>
<th>CIDS</th>
<th>IL+IR</th>
<th>IL</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>0.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>1.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>1.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>2.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>2.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>3.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>3.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>4.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>4.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>5.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>5.500000000E+00</td>
<td>0.06632221-01</td>
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<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>6.000000000E+00</td>
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<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>6.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>7.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>7.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>8.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>8.500000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
<tr>
<td>9.000000000E+00</td>
<td>0.06632221-01</td>
<td>168.8342</td>
<td>100.4158</td>
<td>87.51816</td>
</tr>
</tbody>
</table>

**Notes:**
- The table above shows output data for a helical ribbon interacting with itself.
- The data includes various parameters such as angle, CIDS, IL+IR, IL, and IR, indicating specific values for each parameter at different angles.

*Example values in the table are illustrative and do not represent actual data.*
PROGRAM BIELIN2
REAL P.*,PHI,ALPHA,DZ,AK,AKP,DA,CPHI,A,CIDS,SCATT,IL,IX,
* DEG,SD,SL,SL2,PI,
CCMIX=16.5,SL,SR 
OPEN(NAM=’BISON.DAT’,UNIT=10,TYPE=’NEW’)
PI=3.14159 2D535 69795 22E46E80
DA=1/2E6.0D00
#BIT=5,102
101 FCPHAI(’’ THIS PROGRAM CALCULATES THE CIDS OF A BICAL’’
* RIBON OF RADIAL POLARIZABILITIES’’ INTERACTING WITH’’,
* ITSELF, THE Ev EFFECTS OF A FINITE ARRAY ARE NOT TAKEN’’/
* INTO ACCOUNT’’/
WRITE(5,102)
102 FORMAT(’’ ENTER THE PITCH, WAVELENGTH, HELIX PHASE,
POLARIZABILITY, ‘’ DIPOLE SPACING, NUMBER OF DipoLES, AND
INTERACTION INTEGER ’’)
READ(5,*)P.,P.,ALPHA,IL,IN,NL
#BIT=2,144)P.,P.,PHI,ALPHA,DZ,IN,NL
104 FCPHAI(’’ PROGRAM BIELIN2: HELICAL BONBON INTERACTING WITH’’,
* ITSELF, Ev EFFECTS N’’ NOT INCLUDED’’/
* PITCH, WAVELENGTH’’,
* HELIX PHASE’’, T, G16.7’’ POLARIZABILITY’’,
* DIPOLE SPACING’’, T, G16.7’’ DIPOLE NUMBER’’,
* INTERACTION INTEGER’’, T, I66.7’’/
WRITE(12,103)
103 FORMAT(’’ input’’, ‘’ ANGLAE’, ‘’ IL7,E’’, ‘’ CIDS’, ‘’ T33,GX’, ‘’ IL+IS’’,
T,GX, ’’ IL’, ’’ T56,EX’, ’’ IX’’)
AK=2.2000*PI/P
AKP=2.2000*PI/P
DEG=PI/180.E0E0
CPHI=DCOS((N-1)*AKP=DZ-2.E0E0+PHI*DEG)
C
SI=S(ALPHA,AK,AKP,IL,IN,IN)
SI=S(ALPHA,AK,-AKP,IL,IN,IN)
SL=SL=DCONJG(SL)
SL2=SR=DCONJG(SR)
C
A=0.8002

DO 1 I=1,481
CALL BIEBON(AK,AKP,DZ,CPHI,SL2,SR2,AN,N,CIDS,SCATT)
XI=0.5D0*SCATT*(1.0D0*CIDS)
XR=0.5D0*SCATT*(1.0D0*CIDS)
AL=A/CG0
WRITE(12,100)AD,CIDS,SCATT,IL,IX
A=A+DA
1
C
100 FORMAT(5G16.7)
STOP
END

SUBROUTINE BIEBON(AK,AKP,DZ,CPHI,SL2,SR2,AN,N,
CIDS,SCATT)
HEAL=9 AK,AKP,DZ,CPHI,AN,CIDS,SCATT,SA,CA,IL,IB,SL2,SR2,
C CP1,CM1,Q4.4,4,U,V,W,L=5,IX,IX,A,Bl,Br
S=USIN(AA)
CA=DCOS(AA)
CP1=2.2000*(CA+1.0D0)
CM1=0.5D0*DA*(CA-1.0D0)
QZ=AKP=DZ
Z=DCONJG(N)
U=USIN(A=0.14)
V=DSIN(CM1)
*1=DSIN(Z*(CP1-Q2))
*2=DSIN(Z*(CM1-Q2))
X1=DSIN(CP1-Q2)
X2=DSIN(CP1-Q2)

IF(V.EQ.2.000) THEN
  A=2
ELSE
  A=U/V
END IF
IF(XL.EQ.2.000) THEN
  BL=2
ELSE
  BL=U/XL
END IF
IF(X3.EQ.2.000) THEN
  BR=2
ELSE
  BR=U/XR
END IF

II=SI2=((A*A+BL*BL)*C2P1+A*PI*SA*SA*CPHI)
IB=SB2=(((A*A+BR*BR)*C2F1+A*BI*SA*SA*CPHI)
SCATT=II+IR
IF(SCATT.NE.0.000) THEN
  CIDS=(II-IR)/SCATT
ELSE
  CIDS=0.0000
END IF
RETURN
END

FUNCTION S(ALPHA, AK, AKP, DZ, NL)
COMPLEX*16 S,F1,F2,F3,C1
REAL*8 ALPHA, AK, AKP, DZ, AKPZ, R2
C1=(0.0000,1.0000)
AKZ=AK*DZ
AKPZ=AKP*DZ
Y3=(0.0000,0.0000)

DC 1 L=-NI,NL
IF(L.EQ.0) GO TO 1
R2=DSQAT(L)
R=DAABS(R2)
F1=(1.0000,0.0000)-((1.0000,0.0000)/DCMPLX(AKZ*AKZ*R*R)+
  CI/DCMPIT(AKZ*R))
F2=CDMPF(CI/DCMPLX(AKZ*R*AKZ*R2+AKPZ*R2))"
F3=F3*F1*F2
CONTINUE
*RITE(5,*):1,F2

C
S=1.0000+DCMPLX(AK*AK=ALPHA)*F3
RETURN
END
B. CIDSC

Program CIDSC calculates the CIDS of an arbitrary oriented collection of up to 1000 polarizable point groups in the second Born approximation. It was used for the oriented general helix calculations in chapter 4, but can also be used for geometries other than helices. Program CIDSC is capable of computing the CIDS of systems with groups that absorb and have intrinsic optical activity (i.e., have complex polarizability eigenvalues and eigenvectors, hence the name CIDSC).

Programs CIDSC, CIDSAVE, and IMAGEC read input data from a separate file. The only question they ask of the operator is the file name for the input data file. The input data files for CIDSC, CIDSAVE, and IMAGEC are very similar, and can be created (for helical scattering systems) by using the programs HGEN, HGENAVE, and IMHGENC. Most of the input variables are self-explanatory, and can be understood by looking at the comments in the program listings, running HGEN, HGENAVE, or IMHGENC (these are interactive programs with explanatory prompts), and examining the sample input files. For CIDSC the polarizabilities of the scattering groups can be input in two forms: 1) as polarizability eigenvalues and a set of three Euler angles to define the orientation of the polarizability eigenvectors for each group, or 2) as pre-formed polarizability matrices. The program HGEN writes input data files that use the first input option. The second input option is necessary for systems with groups that have complex polarizability eigenvectors.
Example input data file for CIDSC

```
MILIY, ISO PCLS, F=1.00, a=100, AIPEA=500, 11 GROUPS
1 TURN, NO INTERM, INT
MIIA.OUT

100.0000
0.0000000E+00
0.0000000E+00

180
0.0000000E+00
0.0000000E+00
0.0000000E+00

80.50172  50.77653  10.00000
30.50169  50.12565  20.00000
-30.50173  55.12566  30.00000
-60.50172  55.77650  40.00000
-100.0000  -3.250413E-05  50.00000
-60.50166  -66.77655  60.00000
-30.50176  -66.12563  70.00000
30.50175  -55.77645  80.00000
80.50172  -55.12566  90.00000
100.0000  1.1265155E-04  100.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
500.0000  500.0000  200.0000
```
212
Example output data file for

erose

11-JAN-e-i
Pi0GU.P1 CIDSC
SCAiTliii ViSCiiPTION: ii.LU. ISO POLS. E•101, 1•101, ALPRA•5el. 11 GROUPS •
1 lOlLNo NO INTRINSIC OPTICAL .ACTIVlTI
INTiiiCTICN iiilCT IhClUDiD
IIIU.ti!
GiO~iliiC&L FABJ~iTiiS STOiAGi iii.Ia
ue.1eee
lNCltiNT •AViliNGTli:
Gl .IUI00GI001+11
AZI~~THAL SCATTIRING ANGllt
0. 101111110001:+10
I~Itl&L POLAi ANGLi1
361.1GIU
ilN~L POlAR ANGII:
361
NU~EiR 01 POI~tS IVAICAT!Dt
1.01U0UI+01
Pils
GLOBAL iuLiR ROTATION ANGLIS
0.11211001+00
UITA:
I. IGIII!G101U+IGI
11:
11
NUM!ii 01 POLAB~AilLITIIS IN SCU'Iiilla
POLU AN~U
GI.I0011UI+U
1.i10Ui0
~ .011!1/!UGI
~.111102011

4.U0111i0
!.011liUGI
e.ee0eu
?.a~lll0216

e.1110eee0
s.0n0u
u.uue
11.0102:1
12.l10il
13.!oi0U3
14.i0UI
15.11!111020
lS.Irlk"!U
1? .~eue
18.11!0121
19.00e£0
2~.0e021

.21. 20UGI
.22.eeeu
2~.eeue

24 .eeue
z:.eeue
26.0001/!QI
c7.Ue1Ze
ze.e:~~eze

c9.eeue
:!a.0fiiiiiZ3
~l.UUI
~2.~aeee
~~.e0eee

Jt.eeue

CIDS
1.1111!UI-0i

SCATT
1.:!28729Si+ll

0.!631E3~i-2~

~-~:!ll!a56i+U

e.U6fllo25I-21c

1.:!270785E+U

0.155c~55i-lc
t.:. hle»ieJi~c
a.2377~5~i-0c

if.27tS796I-ec
Gl •.:inte2s-e«
0.31437:,31-12
0 • .!1E!:IS17i-0:i:
e •.3w.51E54A-ec
~ .2685!:761-ic
2.1S4£:~2Ji-0:i:

e .e7::eiue:-~~
-1.1.Ui72ii-12
-1.4752.2!~&-a«

-e .U05:t,76-lrl1
•2.1642S22E-01
-0.J133E24i-t111
-e .4-.S4W15i-tU
-a. 'i.2522:!Jli-11
-e.;e::us2I-11
-e.;;~4U6i-21

-2.E36S76JI-11
-1. 7a:!f.2251-e 1
-e .5562 ea6 1-11
-i.4J:bll35i-11
-t • .!41eee~I-u

e.2J281~i•lili

~ .7642~sei-Ic
fii.C::i327c6•-t~

e.U17c33I-ill

fil .~270~1/!SI+ISil

-2.2cit~e7i-a1

-i .2121 995i-81
-e.1eEEi75.E-et
-1.1i»•i96a-t1
-t.S»27ca4a-ec
-1.?313311!41-0c
-&.!Ula1i-ec
-•.~e203S9i-1£
-1.1225~~41-t£
11!.4S~7E7Si-~J

~S.rlUU

e.~51E!SU-0c

.a.uue
41.2111!21
t2.eeu1
43 .0U21
44.11Jf821
4S.IIlliiUI

0 .cil269Ui+U
".2740713!+10
W: .25c77 Ui+U
Gl.229451fE•U
l.cUS16U:+UI
li1.1795876i+ll
Gl.15447-i3i+U
li1.1:!01457i+U
0.1272277i+lli1
0.a618177t+e9
I .d74BS20i+09
e.! 1438S2E+0;
e .Je22383E+e9
e .£7918SeE+e9
1. e: t48S ~" •e 9
fll.1578644i+f9
e .1J5E&04E+t9
e .t:!59189E+I9
1.15438321+19
1.1873701£+09
Gl. 26269011 +19
e.J33168EE•fiiS
0.:!847729£+09
1.4324E35i+e9
1.47:!8:52EE+e9
e.ees9:534i+i5il
e .::~11l5139t•e9
l.!oi3ES5E£+19
lll.546:il543i+e9
Ill. !4015941+19
1.!239S61i+0;
~~: •• a;&7S7t•09
0 .4691577E+e9
0. 4~:!11J2E2E +e9
e .~9J3432i+l;
e .~515~S5E+I9
e. !190507E+e'
e.c6719411+i9

~~.ee1ee
~e.aeu1

:!7 .eeue
:!e.eerra

1.~19529cE+U
1.~11!8041U+U

2.213526:51-tc

e ·••..!•571~-e.c

1.6311 ?4ii-lc

46.UUt

e .t.:h:BH-e 1

e .1asset5i:+e9
e .1S5SII!i7i.+19

4?.eeeee

1.1~55~?1i-ll

1.1254~221-+e~

e.u~e~&SJI-01

II

I. 1Eoi3E!Gii+ 1GI
1.1E51658i+li
1.1E~7160£+ 10
1 .1E00E:!:3i•ll
1.1:43272i+ll
1.14669:!51+10
1.1~7U70i+11

II
0 .1643S50i+UI
0.164i179Si+1111
0.16:336251+U
1.15S5o5SI+UJ
0 .1537UH•11
GI.143SI976i+U
0.135564~i+U

fil.12600iEi+10
I. 1C:E7612i+ 11
8.11oi364SI+U
e.u:0asu:•u
0.102GISUI+10
e.u2n47l+te
li1.9U687U+I/!9 - e.8a51S67i•t9
0.7711:2S7~1+09
1.774U5Si+0;
0.64S4611JEi+il9
t.E!1SS64E+V!i
•• ~356766[+09
GI.!::!SU23I+09
0.4:5151671+e9
0.4.!030101+09
e.33Seoieet+t9
I. 3~~B414E+GI9
t~t.~5~7E1ei•09
e.2!4607-ii+f9
1.1946415E•09
0.1E75973i+l!'9
IIJ.143S6S2I+09
e.t:!52t9wi+I!S.
e.U7~4SU•e9
t.ii'i31E16E+I8
0 .646~653I+e8
e.n2t7641+ea
I. 741271 S£+08
e.e17o~c21+28
e. 7443S27i+llle
1.61479SSE+f8
t.836067SI+f6
1.72576451+28
Gl.lfii~27SSI+IS
e.a'it9J1U+ee
t.12t8274i•tw
e. ue9S79i+29
1.14645E5i+fll9
1.1~42316i+lll9
e.172275U•ea
0.1Ee8Sc7E•IIJ9
e.1i756cei+e9
11.1E72U7i+09
1.21165411+29
1.22fii83UI+I9
1.24087051+29
1.2~296231+09
1.2~U?17E+29

0.,~6761Ei+l9

1.2E26236i+19
0.2E99!S0i+29
1.2'i209S:i+09
a.ze92125E+e9
I. 2Elo82JI+I9
0.,!00!58i+e9

0.2678904[+09
e.27393Sci+0&
0.4:74855EI+0SI
e .27184691 •11!9
e.252313SI+09
1.24962201+09
1.23411J515I•29
1.21575231+09
e .1.~711l01i•09
e .1 7465841 •IIJ 9
3.15334441+09
11J.132403fi+09
1.11238!#71+09
i.93752f0i+0E
e.76S3264i•ee
1.61Sti114I+08

e.2~5il0ti2E•e9

1.21727591:+09
1.1i7f4~11+29

1.17687721+19
111.1~~70E~!+2S
1.1~47~84i+09

t.1U71111+QI9
III.S!:SI89SI+I/!8
e. 7E?7? 111•ea
1.6~561071+18


PROGRAM CIDSC

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CI
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LABELING THE OUTPUT FILE

OPEN (NAME=NOUT, UNIT=9, ILEF= "NE")
CALL DATE(ND1TE)
#illi(6,163)NDAL,NDESC1,NDESC2
103
FORMA (' "PROGRAM CIDSC",A9/
' SCATTER DESCRIPTION: T25,A50/T25,A50)
IF(NINT.EQ.0)THEN
   WRITE(95,"(""INTERACTION EFFECT NEGLECTED""
ELSE
   WRITE(95,"(""INTERACTION EFFECT INCLUDIC"
END IF
WRITE(95,102) NIN, M, PHI, THETA1, THETA2, NANGLE, IPHI.
102
SUBROUTINE GEN GENERATES THE POLARIZAbILITIES FROM THE EULER ANGLES IN THE INPUT. CAN ALSO APPLY THE GLOBAL ROTATION [PSI,ECHTA,EXI) WICH ORIENTS THE SCATTERER RELATIVE TO THE INCIDENT LIGHT.

SUBROUTINE BORN2 CALCULATES THE INTERACTION EFFECT IN THE SECOND FORM APPROXIMATION. AINT(I,J,X) IS THE EFFECTIVE 'INTERACTION POLARIZABILITY'.

IF(NINT.NE.6)THEN
   CALL BORN2(N,W,X,I,AIN)
ELSE
   DO = I=1,N
   DO = J=1,J
   DO = K=1,K
   AINT(I,J,K)=T(I,J,K)
END IF

PARAMETER SET UP

DEG=3.14159 26525 E775128/180.0DG
CI=(0.62831.0DG)
C=2.0460' T.1456 26525 E7752000/W
CPF=CCS(PHI,DEG)
SPA=DSSIN(PHI*DEG)
TA=(THETA2-THETA1)*DEG/NANGLE
A=THETA1+DEG

THIS LOOP Computes THE CICS AT EACH ANGLE

DO = I=1,NANGLE+1
CA=CCS(A)
SA=DSIN(A)
THIS LOOP COMPUTES THE PI MATRIX AT EACH ANGLE

DO 3 J=1,N
PHASE=(*1(Le(1)*X(J,1)+Dk(2)*X(J,2)+Dk(3)*X(J,3))
*CI*PHASE)
DO 3 K=1,N
DO 3 I=1,N
PI(I,K)=PI(K,L)+*AINT(J,K,L)

3 SUBROUTINE XEACT CALCULATES THE RIGHT AND LEFT SCATTERING CROSS-
      SECTIONS FOR THE PI MATRIX.

DX(3)=CA
CALL XEACT(WK,PI,IL,IR)
AI=A*DG
SCATT=IL-IR
IF(SCATT.EQ.0.000)THEN
  C1S=0.0000
ELSE
  C1S=*(IL-IR)/SCATT
END IF
WRITE(5,16.7)AI,C1S,SCATT,IL,IR
A=A+DA
STOP
160 FORMAT(5w16.7)
STOP

AND
SUBROUTINE ESEM2(N,W,X,T,AINT)
COMPLEX*16 AINT(1000,2,2),CI,B2,R2,R,Q,RB(3,3),
I XI(3),FJ,3,A,GB,RA(2,2),A,B,C,TI(3,3),TI(3,2),
I T2(3,3),T2(3,2)
REAL*8 X(1000,3)

C SET UP PARAMETERS
Q=2.0000*1.4105 265.35 3059.200/W
IF=4.0000*2.14155 26511 3059.200
CI=(0.0000,0.0000)

C THIS LOOP COMPUTES THE INDUCED INTERACTION FIELDS FILL AT EACH
C POLARIZABLE SITE

DO 1 I=1,N
DC 6 1=1,3
DC 6 L=1,3
BE(K,L)=(0.0000,0.0000)

2 TI(K,L)=T(I,K,L)

C THIS LOOP SUMS UP THE INDUCED FIELDS FROM THE GROUPS WHICH INTERACT WITH
C POSITION I

DO 2 J=1,N
IF(J.EQ.I)GO TO 2
C COMPUTE THE DISTANCE VECTORS, ETC.
XI(1)=X(J,1)-X(I,1)
XI(2)=X(J,2)-X(I,2)
XI(3)=X(J,3)-X(I,3)
H2=2*(XI(1)**2+XI(2)**2+XI(3)**2)*XI(3)
A=CDSCRT(H2)
DO 5 K=1,3
DO 5 L=1,3

5 Continue
5  IJ(4,1)=IJ(1,1)
   C COMPUTE THE PHASE FACTOR
   F1=CCOS(I(+1)*XIIJ(3))
   C BEGIN COMPUTING THE GREEN'S FUNCTION
   F2=CLSSF(I(+)*R)/(R*FP)
   #F2=(1.000,0.000)/(Q*Q*F2)-CI/(Q*R)
   GA=(1.000,0.000)-F2*F2
   GB=(-1.000,0.000)+(1.000,0.000)*F2*F2
   C MULTIPLY THE GREEN'S FUNCTION BY THE JTH POLARIZABILITY
   A=IJI(1)*TJ(1,1)+IJI(2)*TJ(2,1)+IJI(3)*TJ(3,1)
   B=IJI(1)*TJ(1,2)+IJI(2)*TJ(2,2)+IJI(3)*TJ(3,2)
   C=IJI(1)*TJ(1,3)+IJI(2)*TJ(2,3)+IJI(3)*TJ(3,3)
   DC 3 X 1,3
   RA(K,1)=CA*TJ(K,1)+GB*IJI(K)*A/R2
   RA(K,2)=CA*TJ(K,2)+GB*IJI(K)*B/R2
   RA(K,3)=CA*TJ(K,3)+GB*IJI(K)*C/R2
   C SUM UP THE INTERACTIONS TIMES PROPER PHASE FACTORS
   DO 4 K=1,3
   DC 4 X 1,3
   RA(K,1)=RA(K,1)+BA(K,1)*F1
   4  CCMINU
   C COMPUTE AINV. (ADD THE UNIT MATRIX AND MULTIPLY BY THE ITH
   C POLARIZABILITY)
   DC 7 X 1,3
   DO 7 L=1,3
   7  AINV(I(L,L))=TI(L,L)+
      I F1=2*Q*(TJ(I,1)*EA(1,1)+TJ(I,2)*EB(2,1)+TJ(I,3)*EB(3,1))
   1  CCMINU
   BITURN
END
SUBROUTINE GEN(W,ALPHA,PSI,EPHI,ETHETA,EII,X,T)
   CCMFII=X*G ALPHA(1000,3),T(1200,3,3)
   RIAL=E PSI(1000,3),T(1200,3,3)
   X E1(3),E2(3),E3(3),T1(3),T2(3),T3(3),R(3)
   X DC,CP,SEP,CST,STI,CIX,SCI,CTI,STI,CII
   X ECII,ETHETA,EXII
   DATA A1 /1.0000, 0.0000, 2.0000/
   DATA A2 /2.0000, 1.0000, 2.0000/
   DATA A3 /2.0000, 1.0000, 0.0000/
   DATA D1 /1.0000, 2.0000, 2.0000, 1.0000, 2.0000/
   DATA D2 /25535 25535 186.2500 186.2500
   CIP=DCOS(EPHI*DEG)
   SIP=DSIN(EPHI*DEG)
   CII=DCOS(EII*DEG)
   SII=DSIN(EII*DEG)
   CIX=DCOS(XII*DEG)
   SIX=DSIN(XII*DEG)
   DC 3 X 1,3
   CPI=DCOS(PSI(I,1)*DEG)
   SFI=DSIN(PSI(I,1)*DEG)
   CTI=DCOS(PSI(I,2)*DEG)
   SII=DSIN(PSI(I,2)*DEG)
   CI=DCOS(PSI(I,3)*DEG)
   SII=DSIN(PSI(I,3)*DEG)
   CALL EUER(CPI,SPI,CTI,STI,CIX,SCI,STI,EXI,EL,T1)
   CALL EUER(CIP,SIP,CTI,STI,CIX,SCI,STI,EXI,EL,T1)
   CALL EUER(CPI,SPI,CTI,STI,CII,SCI,STI,EXI,EL,T2)
   CALL EUER(CIP,SIP,CTI,STI,CII,SCI,STI,EXI,EL,T2)
   CALL EUER(CPI,SPI,CTI,STI,CII,SCI,STI,EXI,EL,T3)
   CALL EUER(CIP,SIP,CTI,STI,CII,SCI,STI,EXI,EL,T3)
   DO 2 J=1,2
   DO 2 K=1,3
T(I,J,K)=ALPHA(I,1)*T1(J)*T1(K)+
ALPHA(1,2)*T2(J)*T2(K)+
ALPHA(1,3)*T3(J)*T3(K)

R(1)=X(I,1)
R(2)=X(I,2)
R(3)=X(I,3)
CALL KULIR(CP,SP,CT,ST,CI,SI,Al,E)
X(I,1)=R(1)
X(I,2)=R(2)
X(I,3)=R(3)
CONTINUE
RETURN
END

SUBROUTINE KULIR(CP,SP,CT,ST,CI,SI,Al,E)

REAL*8 A(3),Z(3),CP,SP,CT,ST,CI,SI,Al,E
DATA U(0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000),
     (0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000),
     (0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000)/
DATA U(0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000),
     (0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000),
     (0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000)/
DATA U(0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000),
     (0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000),
     (0.8000,0.8000), (0.8000,0.8000), (0.8000,0.8000)/
DO 1 I=1,3
DC 1 J=1,3
1 T(I,J)=U(I,J) -X(I)*X(J)
DO 2 J=1,3
AL(J)=E(1)*E(J)
AB(J)=E(J)*E(J)
DC 2 J=1,3
AL(J)=AL(J)*T(I,J)*T(J)*E(L)
AB(J)=AB(J)*T(I,J)*T(J)*E(L)
IL=E(J)*E(J)
IX=E(J)*E(J)
DO 3 J=1,3
II=II+AL(J)*DCOM(JJ(AB(J))
3 IF =II-AB(J)*DCOM(JJ(AB(J))
RETURN
END
C. CIDSAVE

Program CIDSAVE calculates the CIDS of a rotationally averaged arbitrary collection of polarizable point groups. The program evaluates eqns (2.20) and (2.22), and therefore includes the limited interaction effects described in chapter 2. The program can be used for systems that absorb, but not for systems with intrinsic optical activity. (This last limitation is also due to the limitations of the basic equations (2.20) and (2.22).) Program CIDSAVE has only one input option: polarizabilities are read in as eigenvalues and orientation Euler angles.
**Example input data file for CIDSAVE**

```
HILII, 2 GROUPS, P=3V, A=0, UNIAAXIAL POLS,
11FIV=10000, w=150
W1GPS.OUT

150.0000
  0.000000E+00   300.0000
  360

  2

  0.000000E+00   0.000000E+00   0.000000E+00
  0.200000E+00   0.200000E+00   100.0000
  0.000000E+00   0.000000E+00   100.0000
  0.000000E+00   0.000000E+00   100.0000
  0.000000E+00   50.00000   50.0000
  100.0000   50.00000   50.0000
```
Example output data file for CIDSAVE

```
PROGRAM CIDSAVE  14-JAN-84
SCATTER E DESCRIPTION:  MAXIX, 2 GROUPS, P=300, R=0, UNIAxIAL FCS,
ALPHA=100.00, W=150

GEOMETRICAL PARAMETERS STORAGE FILE:  HX2GPS.DAT
INCIDENT WAVELENGTH:  150.000
INITIAL POLAR ANGLE:  0.000000E+00
FINAL POLAR ANGLE:  360.0000
NUMBER OF POINTS EVALUATED:  360
NUMBER OF POLAR ABILITIES IN SCATTER:  2

<table>
<thead>
<tr>
<th>POLAR ANGLE</th>
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<th>II-B</th>
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<tbody>
<tr>
<td>0.000000E+00</td>
<td>8.4098035E-06</td>
<td>8.4098035E-06</td>
<td>8.7223335E+00</td>
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<tr>
<td>0.000000E+00</td>
<td>8.4098035E-06</td>
<td>8.4098035E-06</td>
<td>8.7223335E+00</td>
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<td>8.4098035E-06</td>
<td>8.4098035E-06</td>
<td>8.7223335E+00</td>
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<tr>
<td>0.000000E+00</td>
<td>8.4098035E-06</td>
<td>8.4098035E-06</td>
<td>8.7223335E+00</td>
</tr>
</tbody>
</table>
```

220
PROGRAM CIDS

REAL*8 ALPH(1000), VEC(250,3), VEC(250,3), VEC(250,3)
REAL*8 DEL, DA, AD, CIDS, SCATT, X, PSI(250,3)

C INPUT PARAMETERS: MIN=NAME OF CONTROL INPUT DATA FILE, NDESC1, NDESC2=
C DESCRIPTION OF SCATTERING SYSTEM, OUT=NAME OF OUTPUT DATA FILE. 
C N=NUMBER OF PHASES, TETA1, TETA2=POLAR ANGLE LIMITS, NANGLE=NUMBER 
C OF POLAR ANGLES, N=NUMBER OF POLARIZABLE GROUPS IN THE SCATTERER. 
C X(J,J)=POSITION VECTOR OF JTH GROUP, ALPH(1,J)=EIGENVALUES OF 
C POLARIZABILITY OF JTH GROUP, PSI(J,J)=SOLID ANGLES GIVING THE 
C ORIENTATION OF THE EIGENVECTORS (PRINCIPLE AXIS) OF POLARIZABILITY 
C OF JTH GROUP.

DC 2000 I=1,100
DC 2000 J=1,3
ALPH(I,J)=0.0000
X(I,J)=0.0000
PSI(I,J)=0.0000
DC 2000 I=1,3
VETI(I,J)=2.0000

2000 T(I,J,J)=0.0000
DC 2000 I=1,3
A(1)=0.0000
AD(1)=0.0000
SCATT=0.0000
#0.0000
TETA1=2.0000
TETA2=2.0000
SCATT=0.0000
J1=1.0000
J1=2.0000
PROGRAM CIDS

WRITE(6,*) 'ENTER THE NAME OF THE DATA INPUT FILE'
READ(5,121)IN

101 FORMAT(A50)
OPEN(NAM=MIN,UNIT=10,TYP='OLD')
MIN=10
READ('MIN,105')INDISC1
READ(MIN,106)NINDISC2

105 FORMAT(A50)
READ('MIN,101')NOUT
READ('MIN,'*)
READ(MIN,'*')THETA1,THETA2
READ(MIN,'*')MANGLE
READ(MIN,'*')M
DO 7 I=1,N
READ('MIN,'*)(X(I,J),J=1,3)
7 DO 6 I=1,N
6 READ('MIN,'*)(ALPHA(I,J),J=1,3)
EC

LABELING THE OUTPUT FILE

OPEN(NAM=MOUT,UNIT=99,TYP='NEW')
CALL DATE(HDATE)
WRITE(99,132)HDATE

103 FORMAT(' PROGRAM CIDS','A9)
WRITE(99,132)INDISC1,INDISC2
106 FORMA'I(' SCATTERER IDENTIFICATION: A50/
WRITE(99,132)MIN,W,THETA1,THETA2,MANGLE,M
102 FORMAT(' GEOMETRICAL PARAMETERS STORAGE FILE: ',T52,'A36/
' INCIDENT #WAVELENGTH: ',T52,'G14.7/
' INITIAL POLAR ANGLE: ',T52,'G14.7/'FINITE POLAR ANGLE: ',T52,'G14.7/
' NUMBER OF POINTS EVALUATED: ',T52,'G110/
' NUMBER OF POLARIZABILITIES IN SCATTERER: ',T52,'G110/
WRITE(99,132)W,THETA1,THETA2,MANGLE,M
104 FORMAT(' POLAR ANGLE',T17,',' CIDS',T33,',' IL-IB',
T49,',' IL-IB')

SUBROUTINE GEN GENERATES THE POLARIZABILITIES FROM THE ANGLES IN THE INPUT.

CALL GEN(A,PSI)

PARAMETER SET UP

SUMO=6.8008
DO 1 I=1,A
1 SUM=SUM+1.3
AI=ALPHA(I,M)
IF(AI.EQ.6.8008)GO TO 1
II(I)=T(I,M,1)
II(2)=T(I,M,2)
II(3)=T(I,M,3)

SUBROUTINE VECTR CALCULATES AN INTERMEDIATE IN THE CALCULATION.
FOR CALL VECIR(M, N, I, AI, VECT) THE RETURNED QUANTITY (VECT) IS:
SUM ON \* I TO M OF THE PRODUCT
(AI*POLARIZABILITY)*(COUPLING CONSTANT VIE)*
(UNIT VECTOR OF THE KTH POLARIZABLE AXIS).

CALL VECIR(M, N, I, AI, VECT)
VECT(1,1,1)=VECT(1)
VECT(1,1,2)=VECT(2)
VECT(1,1,3)=VECT(3)
SUM=SUM+AI*AI
CCNIUA
DIG=-3.14159 26535 8975D00/180.0D00
CG=4.0D00-3.14159 26535 8975D00/W
EA=(TNEITA1-TNEITA1)*DIG/NANGLE
AE=IAEITA1*DIG
DO 13 IA=1,NANGLE+1
DI(IA)=E.0D00
TI(IA)=E.0D00

THESE ICCFS SUM UP CONTRIBUTIONS FROM EACH PAIR OF POLARIZABILITIES

DO 2 I=1,N
DO 2 PI=1,3
AI=ALPHA(I,PI)
IF(AI*EQ.-2.D00)GO TO 2
DC 3 I=1,3
VECT(I)=VECT(I,1,1)
XI(I)=XI(1,1,1)
DI=DCI(VECT,II)
DC 2 J=I+1,N
XI(J)=XI(1,1,1)
RIJ=DOT(XI, XI)
RIJ=SQRT(RIJ)
UIJ(1)=UIJ(1)/RIJ
UIJ(2)=UIJ(2)/RIJ
UIJ(3)=UIJ(3)/RIJ

DC 4 M2=1,3
AJ=ALPHA(J,M2)
IF(AJ*EQ.-2.D00)GO TO 4
DC 5 I=1,3
VECT(I)=VECT(1,1,1)
EIJ=DOT(VECT, IJ)
CALL CRCSS(EI, IJ, EIJ)
EIJI=DOT(EI, IJ)
EIJI=DOT(EJ, IJ)
EIJI=DOT(EI, UE)
EIJI=DOT(EJ, UIJ)
VIJ=(EIJI-3.0D00*XIJI)*XIJI/(RIJ*RRIJ)
SUM3=2.0D00*AI(AJ)*VIJ/3.0D00
SUM2=2.0D00*AI(AJ)*VIJ/EIJI/15.0D00
CALL CRCSS(AJ, VEKCT, EK)
CALL CRCSS(VEKCT, EK, VIJ)
SUM1=DCI(EK, VIJ)
SUM1=DCI(VIJ, UE)
SUM2=DCI(VEKCT, EK)*EIJI

224
SUM2J=DCT(VICT,J,I)*IIXIJ
SUM4I=DCT(VACT,I,J)
SUM5I=SUM4I*IIXJ
SUM5J=SUM4J*IIXJ
S1=COI(VACT,I,J)
SI=DCT(VICT,J,I)
SUM6I=0.5*2P*(SUM4I*IIXIJ*EJXIJ+SI*EJXIJ*IIXJ)
SUM6J=0.5*2P*(SUM4J*IIXIJ*EJXIJ+SJ*EJXIJ*IIXJ)
SUM7I=SIXIXIJ+DII*EJXIJ*IIXJ
SUM7J=SI*EJXIJ+DII*IIXIJ*IIXJ
SUM8I=SI*EJXIJ+DII*IIXIJ*IIXJ
SUM8J=SI*EJXIJ+DII*IIXIJ*IIXJ
J3=(1.0D00-SUM4I-SUM4J)
F4=(EIIJ*IIIJ-SUM5I-SUM5J)
F6=(EIIJ*IIIJ-IIXJ-IIXJ-IIXJ-SUM7I-SUM7J)
F7=(EIIJ*IIIIJ-IIXJ-IIXJ-SUM8I-SUM8J)

THIS LOOP ADDS THE CONTRIBUTIONS AT EACH ANGLE

A=AE
LC 15 IA=1,NANGLI+1
BETA=A/2.0D00
SI=DSIN(BETA)
CS=DCOS(BETA)
S12=SI*SE
S13=SI*SE
S14=SE*SE
S15=G*IIJ*SI

SUBROUTINE BESSEL CALCULATES THE SPHERICAL BESSEL FUNCTIONS J0 THROUGH J6
CALL BESSEL(QIJ)

SUBROUTINE S CALCULATES THE FACTORS S1 THROUGH S12
CALL S
IF(GL.JE.0.0D00)THEN
   IA=(IALJ+(J2/QI-J1)-EIIJ*EIIJ*J3)
ELSE
   F1=0.0D00
   SUM3=SUM3A-(1.0D00*4.0D00*SB2*CB*CB)*SUM3B
   F11=F1*(SB2+SE2)
   F21=(4.40D00*J1-0.10D00*J3)*SB-(2.60D00*J1+0.10D00*J3)*SB3
   F31=F3*(SI-S2*SB2+SB3*SE4)
   F41=F4*(S4-S2*SB2+SB3*SE4)
   F51=F5*(SB2+SB2+SB2*SE4)
   F61=F6*(SI-S2*SB2+SB3*SE4)
   F71=F7*(0.375D00*0.375D00*SE4+0.25D00*SB2)*J4
   D1(J1)=D1(J1)-A-J1*(J1.D00*(IJIIJ-SUM11-SUM11)*+11-
   (SUM21+SUM2J)*F21)
   D1(J1)=T1(J1)-SUM3+A1*(F21+F41+F51+F61+F71)
A=A-1
15 CONTINUE
4 CONTINUE
2 CONTINUE
A=AE
LC 12 IA=1,NANGLI+1
BETA=A/2.0D00
SI=DSIN(BETA)
CE=DCS(EITA)
SCATT=T(IA)*SUM*(1.0D62-5B=5B*CB*CB)*4.0D00/15.0D00
AE=4.0D00
IF(SCATT.EQ.0.0D00)THEN
CIDS=0.0D00
ISTAB="*
ELSE
CIDS=DJ(IA)/SCATT
ISTAB="*
END IF
#RITE(SG,100)AD,CIDS,DJ(IA),SCATT,ISTAB
12 A=A+DA
100 FCRAI(4G1C,7,A4)
STOP
END
SUBROUTINE GIM(N,FSI)
COMMON /MAIN/ T(250,3,2),ALPHA(250,3),X(250,3)
REAL*8 FSI(250,3),X,ALPHA,
I XI(C),X2(C),X3(C),T1(3),T2(3),T3(3),T
X DIG,CFI,SP,CTI,STI,XI,SI
DATA E1 /1.0D00,0.0D00,0.0D00/
DATA E2 /0.0D00,1.0D00,0.0D00/
DATA E3 /0.0D00,0.0D00,1.0D00/
DATA E4 /3.14159*25535*8.75100/182.0D00
DO 1 I=1,N
CFI=CSI(FSI(I,1)*DEG)
SPI=DSIN(FSI(I,1)*DEG)
CTI=DCOS(FSI(I,2)*DEG)
STI=DSIN(FSI(I,2)*DEG)
CII=DCOS(FSI(I,3)*DEG)
SII=DSIN(FSI(I,3)*DEG)
CALL EULER(CFI,SPI,CTI,STI,CII,SII,SI,E1,T1)
CALL EULER(CFI,SPI,CTI,STI,CII,SII,SL,E2,T2)
DC = D+1.3
T(I,1,K)=T1(K)
T(I,2,K)=T2(K)
T(I,3,K)=T3(K)
1 CONTINUE
RETURN
END
SUBROUTINE S
COMMON /MAIN/ T(250,3,2),ALPHA(250,3),X(250,3)
REAL*8 S1,S2,S3,S4,S5,S6,S7,S8,S9,S10,S11,S12
COMMON /J/ J6,J1,J2,J3,J4,J5,J6,J7,J8,J9,J10,J11,J12
S1=J8/15.0D00-J2/21.0D00+3.0D00*J4/280.0D00
S2=2.0D00*J6-J2/7.0D00-J4/14.0D00
S3=2.0D00*J6-J2/7.0D00-J4/14.0D00
S4=7.0D00*J6-J2/7.0D00-J4/14.0D00
S5=7.0D00*J6-J2/7.0D00-J4/14.0D00
S6=7.0D00*J6-J2/7.0D00-J4/14.0D00
S7=7.0D00*J6-J2/7.0D00-J4/14.0D00
S8=13.0D00*J6-J2/7.0D00-J4/14.0D00
S9=2.0D00*J6-J2/7.0D00-J4/14.0D00
S10=J8/15.0D00-J2/21.0D00+3.0D00*J4/280.0D00
S11=J8/15.0D00-J2/21.0D00+3.0D00*J4/280.0D00
S12=J8/15.0D00-J2/21.0D00+3.0D00*J4/280.0D00
RETURN
END
SUBROUTINE CROSS(A,B,C)
REAL*8 A(3),B(3),C(3),U, V, W
U=A(2)*B(3)-A(3)*B(2)
V=A(3)*B(1)-A(1)*B(3)
W=A(1)*B(2)-A(2)*B(1)
W = A(1) * E(2) - B(1) * A(2)
C(1) = U
C(2) = V
C(3) = w
RETURN
END

SUBROUTINE VECRA(M, N, K, V)
COMMON /MAIN/ T(250, 3, 3), ALPHA(250, 3), X(250, 3)
REAL*E T, ALPHA, X, K, V(3), X(3)
REAL*E DOT, AK, Z(3), BZ, RE, BXK, XIXK, PIK, XIK, YIK
DO 4 L = 1, 3
V(L) = D.E00
DO 1 I = 1, M
IF(X(I, J) GO TO 1
DO 5 J = 1, 3
AK = ALPHA(K, J)
DO 2 L = 1, 3
EX(I) = T(I, M, J)
2 XIX(I) = X(I, J) - X(I, L)
B2IK = DOT(XIX, XIX)
BZIK = DSBI(B2IK)
XIK = DOT(XIX, XIK)
XIXK = DOT(XIX, XIXK) / EIK
V(K) = XIXK - (3.0D00 * XIKK * XIXK) / (EIK * B2IK)
LC 3 L = 1, 3
3 V(L) = V(I) * AK * VIK * EX(L)
CONTINUE
5 CONTINUE
4 CONTINUE
RETURN
END

SUBROUTINE BESSEL(N)
COMMON /J/ J0, J1, J2, J3, J4, JN
REAL*E J0, J1, J2, J3, J4, SQ, Q2
I(A(Q, E, 1, 3, 0.0E-0.0E, 1.0E-0.0E)) THEN
SQ = DSIN(Q)
CQ = DCOS(Q)
J1 = SQ / Q
J2 = 3.0D00 * J1 / Q - J0
J3 = 5.0D00 * J2 / Q - J1
J4 = 7.0D00 * J3 / Q - J2
ELSE
J2 = Q * Q
J3 = J0 - Q2 / 6.0D00
J4 = J2 - Q2 / 12.0D00
J3 = J3 - Q2 / 14.0D00
J4 = J4 - Q2 / 11.0D00
END IF
RETURN
END

SUBROUTINE RULER(CP, SP, CT, ST, CI, SI, A, E)
REAL*E A(3), CP, SP, CT, ST, CI, SI, U, V, W
U = (C1 * CT * CP - S1 * SP) = A(1) - (S1 * CP + C1 * SP) = A(2) * CT + ST = A(3)
V = (C1 * CP - S1 * SP) = A(1) - (C1 * CT + S1 * ST) = A(2) + ST + CP = A(3)
W = -C1 * ST = A(1) + ST + CT = A(2) + CT = A(3)
RETURN
END

FUNCTION DOT(A, E)


REAL A(3), B(3), C(3)

C(1) = A(1) * B(1) * C(1) + A(2) * B(2) * C(2) + A(3) * B(3)

RETURN

END
D. IMAGEC

Program IMAGEC calculates the circular differential image of an arbitrary collection of polarizable point groups in the second Born approximation. As is explained in the comments on the program listing, the geometry implicit in the program is such that the incident light is parallel to the z axis travelling from negative values of z toward positive values of z, and the image is formed in a viewing plane specified by the viewing angle \( \theta \). The y axis of the viewing plane is always parallel to the y axis of the global coordinate system, and the x axis of the viewing plane varies depending on the value of \( \theta \). The direction of view must therefore always be in the xz plane of the global coordinate system. The program rotates the sample rather than the viewing plane for effective directions of view outside the xz plane. (For example, for \( \theta = 90^\circ \), the viewing plane x axis is parallel to the global z axis, for \( \theta = 0^\circ \) the viewing plane x axis is anti-parallel to the global x axis, and for other values of \( \theta \) the viewing plane tilts so as to remain perpendicular to the direction from which the sample is being viewed.) IMAGEC can be used for systems with absorbing groups or intrinsically optically active groups. If the viewing angle \( \theta \) is 0° the program automatically computes a brightfield image, otherwise it computes a darkfield image. Program IMAGEC can read in polarizability data in three forms: 1) as polarizability eigenvalues and orientation Euler angles, 2) as polarizability eigenvalues and eigenvectors, and 3) as preformed polarizability matrices. Option 2 or 3 is necessary for groups with complex polarizability eigenvectors.
Example input data file for IMAGEC

BELLI, P=10, R=16, 5 GROUPS/TUN, 16 GROUPS, NO INTERACTION, INTRINSIC CIDS, TANG. REAL PARTS
HPhi4.out

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1.000000
2.000000
-15.000000
-30.000000

58
58

20.000000

6.000000*01+00 -50.000000*00 0.000000*00

16

15.000000

0

2

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3.00000000000000003+00 0.51256162651532 2.000000000
-8.00000000000000001+00 5.8778252525252525

-8.00000000000000001+00 -5.8778252525252525 6.000000000

3.000000000000000001+00 -5.8778252525252525 8.000000000

12.200000000000000001+00 -6.4621769735347214 10.000000000

3.000000000000000001+00 -5.8778252525252525 12.000000000

-8.000000000000000001+00 5.8778252525252525 14.000000000

-8.000000000000000001+00 -5.8778252525252525 16.000000000

3.000000000000000001+00 -5.8778252525252525 18.000000000

12.000000000000000001+00 -1.3146012438575265 20.000000000

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-8.000000000000000001+00 5.8778252525252525 24.000000000

3.000000000000000001+00 -5.8778252525252525 26.000000000

-8.000000000000000001+00 5.8778252525252525 28.000000000

12.000000000000000001+00 -1.3638624192941055 30.000000000

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(1.000000000000000001+00, 0.000000000000000001+00)
(0.000000000000000001+00, 0.000000000000000001+00)
(0.000000000000000001+00, 0.000000000000000001+00)

**Example output data file for IMAGEC**

**PROGRAM IMAGEC**  12-JAN-84  
**SCATTERER DESCRIPTION:**  BALL, E=10, R=10, 5 GROUPS/TURN, 15 GROUPS,  
NO INTERACTION, INTRINSIC CIDS, TANG. REAL PARTS  
**INTERACTION EFFECT NEGLECTED**  
**GEOMETRICAL PARAMETERS STORAGE FILE:**  IMEB4.DAT  
**INCIDENT WAVELENGTH:**  1.000000  
**LENS APERTURE:**  1.000000  
**LENS FOCAL LENGTH:**  2.000000  
**IMAGE PLANES X LIMITS:**  -15.20000  45.00000  
**Y LIMITS:**  -30.20000  30.00000  
**NUMBER OF X GRID LINES:**  50  
**NUMBER OF Y GRID LINES:**  50  
**POLAR SCATTERING ANGLE:**  0.000000+00  
**GLOBAL EULER ROTATION ANGLES**  
**THETA:**  -58.220000  
**XI:**  0.000000+00  
**NUMBER OF POLARIZABILITIES IN SCATTERER:**  16  
**BRIGHTFIELD BACKGROUND ILLUMINATION:**  15.200000  
**POLARIZABILITY INPUT CODE OPTION:**  2

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PROGRAM IMAGC

THIS PROGRAM EVALUATES THE DIFFERENTIAL IMAGE PRODUCED
WHEN A LENS IS USED TO MAKE AN IMAGE OF A SCATTERING OBJECT ILLUMINATED
BY RIGHT AND LEFT CIRCULARLY POLARIZED LIGHT, AND THE TWO
IMAGES ARE THEN SUBTRACTED. THE SCATTERING OBJECT IS SPECIFIED
BY THE POSITIONS AND POLARIZABILITIES OF ITS CONSTITUENT GROUPS
IN A COORDINATE FRAME WITH THE INCIDENT LIGHT TRAVELLING ALONG
THE X AXIS (TRAVELLING FROM NEGATIVE VALUES OF Z TOWARD POSITIVE
VALUES OF Z). THE IMAGE IS PRODUCED IN A PLANE PERPENDICULAR TO THE
DIRECTION IN WHICH THE SCATTERED LIGHT IS DETECTED. THE Y AXIS
OF THE IMAGE PLANE IS ORIENTED TO CoinCIDE WITH THE Y AXIS OF
THE OBJECT COORDINATE SYSTEM. THAT IS, THE SCATTERING VECTOR
IS TAKEN TO BE IN THE XL PLANE OF THE OBJECT COORDINATE SYSTEM.
AND THE IMAGE PLANE IS PERPENDICULAR TO THE SCATTERING VECTOR.
THE MAGNIFICATION OF THE IMAGING SYSTEM HAS BEEN FIXED AT 1.0,
SO THE IMAGE WILL BE SCALRED THE SAME SIZE AS THE SCATTERING
OBJECT. (THE IMAGE MAY BE A BIT LARGER THAN THE OBJECT IF THE
INPUT PARAMETERS ARE SUCH THAT THE RESOLUTION OF THE IMAGE IS
LOW. THE RADIUS OF RESOLUTION IS APPROXIMATELY 2*FOCAL/(Q*APER)
WHERE FOCAL IS THE FOCAL LENGTH OF THE LENS, Q IS THE WAVELENGTH
OF THE INCIDENT LIGHT, AND APER IS THE LENS APERTURE.)

CCM, FOCAL(100,0,3), ALM (100,0,3), CL, PHASE(1000), F, FI (3, 3).
X ALPHA(1000,2), 3, 3, ABS
REAL = DEC, CPHI, SPhi, A, Ca, Dk(3), AD, CD, SCAT, 
X IL, I, X1 (1000, 3), PS1 (1000, 2), W, PHI, TE, ETA, APHI, THETA, 
X TE, ETA (3), EANG
REAL = FREAL, TAL, 
CHARACTER = 50 MIN, NOUT
CHARACTER = 50 NG, 
CHARACTER = 30 ND, 
CHARACTER = 50 M, NOUT
CHARACTER = 70 NAME2

INPUT PARAMETERS: MIN=NAME OF CONTROL INPUT DATA FILE, NAME1, NAME2=
DESCRIPTION OF A SAMPLE SYSTEM, NOUT=NAME OF OUTPUT DATA FILE, 
W=WAVELENGTH, APER=APERATURE OF THE LENS IMAGING SYSTEM,
FOCAL=FOCAL LENGTH OF LENS, X1, X2, Y1, Y2=THE
X AND Y LIMITS ON THE REGION OF THE IMAGE PLANE
WHERE THE DIFFERENTIAL IMAGE IS TO BE APPLIED, NPOINT=THE
NUMBER OF GRID POINTS ALONG EACH OF THE X AND Y AXES WHERE THE
IMAGE INTENSITY IS TO BE EVALUATED (THE TOTAL NUMBER OF POINTS AT
WHICH THE IMAGE WILL BE EVALUATED IN THE AREA CHOSEN BY X1, X2
AND Y1, Y2 IS (NPOINT+1)*(NPOINT+1)), TE=POLAR ANGLE,
THETA, EPHI, ETA=THE EULER ANGLES THAT DEFINE THE GLOBAL ORIENTATION
OF THE SCATTERER, N=NUMBER OF POLARIZABLE GROUPS IN SCATTERER,
BGP=THE EFFECTIVE BACKGROUND ILLUMINATION POLARIZABILITY (FOR BRIGHTFIELD
IMAGES, Theta=0.0, THIS PARAMETER DETERMINES THE INTENSITY OF THE
BACKGROUND ILLUMINATION, BGP SHOULD BE NO LARGER THAN THE SUM OF THE
TESES OF THE POLARIZABILITY TENSORS IN THE SAMPLE, FOR DARKFIELD
IMAGES, Theta=0.0, BGP IS NOT USED IN THE PROGRAM. IF BGP IS
SET TO ZERO THERE WILL BE NO ABSORPTIVE EFFECTS IN THE BRIGHTFIELD
IMAGES. ), IGEN=POLARIZABILITY INPUT MODE OPTION (IF IGEN=1 THE PROGRAM
READS IN POLARIZABILITY EIGENVALUES AND ROTATION EULER ANGLES FOR THE
POLARIZABILITY EIGENVECTORS. IF IGEN=2, THE PROGRAM READS IN
POLARIZABILITY EIGENVALUES AND EIGENVECTORS. IF IGEN=3, THE PROGRAM
READS IN POLARIZABILITIES DIRECTLY AS 3 BY 3 MATRICES.), 
NT=NUMBER OF REACTION SUPPRESSOR (IF NT=0 ONLY THE FIRST BORN
CONTRIBUTION TO THE CLS IS COMPUTED), X(I, J)=POSITION
VECTORS OF I TH GROUP, ALPHA(I, J)=EIGENVALUES OF POLARIZABILITY OF
ITH GROUP, PSI(I,J)=EULER ANGLES GIVING THE ORIENTATION OF THE EIGENVECTORS (PRINCIPLE AXES) OF POLARIZABILITY OF ITH GROUP.

NOTE: CHOOSING AN AZIMUTHAL ANGLE PHI IS EQUIVALENT TO A ROTATION (USING THE GLOBAL EULER ANGLES) BY PHI1=PHI, ETA1=ETA, 01=0 OR PHI1=0, ETA1=0, 01=PHI.

WRITE(6,*,'(PROGRAM IMAGEC')
WRITE(6,*,'')
WRITE (6,*,'ENTER THE NAME OF THE DATA INPUT FILE')
READ(5,112)MIN
101 FORMAT(A58)
OPEN(NAM=MIN,CMNT=10,TIPL='OLD')
MINF=10
READ(MINF,105)NDESC
105 FORMAT(A58)
READ(MINF,107)NDESC2
107 FORMAT(A78)
READ(MINF,I01)NGOT
READ(MINF,*)APER
READ(MINF,*)FOCAL
READ(MINF,*)XLM1,XLM2
READ(MINF,*)YLM1,YLM2
READ(MINF,*)NPOINT,NPOINT
READ(MINF,*)ALPHA
READ(MINF,*)ETA
READ(MINF,*)PHI
READ(MINF,*)XI
READ(MINF,*)N
READ(MINF,*)BEGIN
READ(MINF,*)INIT
READ(MINF,*)IGEN
IF(IGEN.EQ.3.OR.IGEN.EQ.1)THEN
   WRITE(6,*,'INVALID INPUT OPTION: IGEN= ',IGEN,STOP
END IF
DC 7 I=1,N
DC 8 J=1,3
IF(IGEN.EQ.1)THEN
   DC 6 I=1,N
   READ(MINF,*)ALPHA(I,J),J=1,3
   DC 1 I=1,N
   READ(MINF,*)PSI(I,J),J=1,3
END IF
10 IF(IGEN.EQ.2)THEN
   DC 10 I=1,N
   READ(MINF,*)ALPHA(I,J),J=1,3
   DC 11 I=1,N
   DC 11 J=1,3
   READ(MINF,*)T(I,J,K),K=1,3
END IF
11 IF(IGEN.EQ.3)THEN
   DC 12 I=1,N
   DC 12 J=1,3
   READ(MINF,*)T(I,J,K),K=1,3
END IF
CALL LABELING THE OUTPUT FILE
OPEN(NAM=ACUT,UNIT=DG,TYPE='NEW')
CALL DATA(NDATI)
WRITE(GS,123)NDATI
103 FORMAT(130,130,130)
WRITE(GS,123)NDATI,NDESC2
SUBROUTINE GEN1 GENERATES THE POLARIZABILITIES FROM THE EULER ANGLES IN THE INPUT UNDER INPUT OPTION 1. GEN1 ALSO APPLIES THE GLOBAL ROTATION (EPHI,ETHETA,EXI) Ssince ORIENTS THE SCATTERER RELATIVE TO THE INCIDENT LIGHT. GEN2 GENERATES POLARIZABILITY MATRICES FROM EIGENVALUE INPUT DATA UNDER INPUT OPTION 2. GEN2 ALSO DOES THE GLOBAL ROTATIONS. GEN3 APPLIES FOR INPUT OPTION 3, AND ONLY DOES THE GLOBAL ROTATIONS.

IF(IGEN.EQ.1)CALL GEN1(N,ALPHA,PSI,EPHI,ETHETA,EXI,X,T)
IF(IGEN.EQ.2)CALL GEN2(N,ALPHA,PSI,EPHI,ETHETA,EXI,X,T)
IF(IGEN.EQ.3)CALL GEN3(N,EPHI,ETHETA,EXI,X,T)

SUBROUTINE BCWN2 CALCULATES THE INTERACTION EFFECT IN THE SECOND BCRN APPROXIMATION. AINT(I,J,K) IS THE EFFECTIVE 'INTERACTION POLARIZABILITY'.

IF(NINT.NE.W)THEN
   CALL SCRN2(N,W,1,1,AIMT)
ELSE
   DO 5 I=1,N
   DO 5 J=1,K
   DO 5 K=1,3
   AINT(I,J,K)=T(I,J,K)
5   END IF

PARAMETER SET UP

SIG=3.1415
E0=1.0
Q=EPHI*SIG/3.1415
R0=SIG
R=SQRT(SQRT(Q))

THE QUANTITY R00 IS THE EFFECTIVE RADIUS OF RESOLUTION FOR THE IMAGING SYSTEM

R00=R*I0/(C*APSX)
APSX=(2.44*0.18)*SIG

106 FORMAT(′ , SCATTERING DESCRIPTION: ′, AS0/11,A?2) IF(NINT.EQ.0) THEN
   WRITE(6,′ , "INTERACTION EFFECT NEGLECTED") ELSE
   WRITE(6,′ , "INTERACTION EFFECT INCLUDED") END IF

102 FORMAT(′ GEOMETRICAL PARAMETERS STORAGE FILE: ′,TS0,AS0/)
I1 = INCIDENT WAVELENGTH: ′,TS0,AS0/  
I2 = LENS APERTURE: ′,TS0,AS0/  
I3 = LENS FOCAL LENGTH: ′,TS0,AS0/  
I4 = IMAGE PLANE X LIMITS: ′,TS0,AS0/  
I5 = IMAGE PLANE Y LIMITS: ′,TS0,AS0/  
I6 = NUM OF X GRID LINES: ′,TS0,AS0/  
I7 = NUM OF Y GRID LINES: ′,TS0,AS0/  
I8 = POL SCATTERING ANGLE: ′,TS0,AS0/  
I9 = GLOBE EULER ROTATION ANGLES PHI: ′,TS0,AS0/  
10 = ETHETA: ′,TS0,AS0/  
11 = EXI: ′,TS0,AS0/  
12 = NUM OF POLAR ABILITIES IN SCATTERER: ′,TS0,AS0/  
13 = BRIGHTFIELD BACKGROUND ILLUMINATION: ′,TS0,AS0/  
14 = POL SCATTERING INPUT MODE OPTION: ′,TS0,AS0/)

104 FORMAT(′ SCATTERING IMAGE′)
A = THETA * DIG
CA = COS(THETA)
SA = SIN(THETA)
DLK(1) = SA
DLK(2) = 2.0 * DK
DLK(3) = CA - 1.0 * DK
BE(1) = SA
BE(2) = 0.5
BE(3) = CA
X2 = XI
WX = (XI[2] - XI[1]) / NPOINT
WY = (Y[2] - Y[1]) / NPOINT
DO 5 J = 1, N
7 = EXP(-CI * XI * XI(J, 1) + DI * XI(J, 2) + DI * XI(J, 3) * XI(J, 3))
CONTINUE

5

CONTINUE

These loops compute the differential image intensity at each point

DO 2 I1 = 1, NPOINT + 1
Y2 = Y[1]
DO 2 I2 = 1, NPOINT + 1
DO 4 J = 1, 3
DO 3 I = 1, 3
F(J, I) = (C + 0.0 * Y1 / 2.0) * Y2
CONTINUE

3

This loop computes the II matrix for each image point

DO 3 J = 1, N
SX = X * CA * XI(J, 1) * SA * XI(J, 3)
SY = Y * XI(J, 2)
TAU = SQRT(SX * SX + SY * SY) / REO
IF (TAU > N * B) THEN
   I = DCMFLX(PI * SQR(TAU), IER) / TAU * PHASE(J)
ELSE
   I = PHASE(J) / (0.0000, 0.0000)
END IF
DO 3 J = 1, 3
DO 3 I = 1, 3
F(I, J) = F(I, J) + I * AIAT(J, K, L)
CONTINUE

SUBROUTINE XSCFT CALCULATES THE RIGHT AND LEFT IMAGE CROSS-SECTIONS FROM THE II MATRIX.

IF (THETA.EQ.0.000) THEN
   DO 14 I = 1, 3
      I = I + 1
   END IF
   CALL XSCFT(X, FI, IL, IR)
   SCATT = I - 2
   CEI = I - 2
   WRITE(6, 10) X, IF, CD1, SCATT
10  FORMAT(4G14.7)
   STOP
END

SUBROUTINE BORNE(H, A, X, T, AI)
   COMPLEX = A
   AI = X
   IF (H.EQ.3.3, 0, 0)
   X = I / 2.0
   REAL = X
100 FORMAT(4G14.7)
   END

C SET UP PARAMETERS
C THIS LOCP CCFFUTES THE INDUCTED INTERACTION FIELDS FILT AT EACH
C POLARIZABLE SITE
C
DC 1 I=1,N
   JC G I=1,3
   BE(X,L)=(W.ZD6E,6.ED6E)
   TI(X,L)=T(I,X,L)
C THIS LOCP SUMS UP THE INDUCTED FIELDS FROM THE GROUPS WHICH INTERACT WITH
C POSITION I
DO 2 J=1,N
   IF(J,EQ,1)GO TO 2
C COMPUTE THE DISTANCE VECTORS, IIC.
   I1J(1)=X(I,J,1)-X(I,1)
   I1J(2)=X(I,J,2)-X(I,1)
   I1J(3)=X(I,J,3)-X(I,1)
   E2=I1J(1)*T1J(1,1)+I1J(2)*T1J(2,1)+I1J(3)*T1J(3,1)
   B=CISBET(B2)
   DO 5 K=1,3
      DO 5 L=1,3
      TJ(I,K,L)=T(I,K,L)
5 CONTINUE
C COMPUTE THE PHASE FACTOR
   F1=CDEIF(CI=I1J(3))
C BEGIN COMPUTING THE GRIEM'S FUNCTION
   F2=CDEIF(CI=I1J(1))/(F1*P)
   F3=(1.ED22,0.ED00)/(Q*Q)+CI/(Q*R)
   GA=(1.ED22,0.ED00)-F2-F3=F2
C MULTIPLY THE GRIEM'S FUNCTION BY THE JTH POLARIZABILITY
   A=I1J(1)*TJ(1,1)+I1J(2)*TJ(2,1)+I1J(3)*TJ(3,1)
   X=I1J(1)*TJ(1,2)+I1J(2)*TJ(2,2)+I1J(3)*TJ(3,2)
   C=I1J(1)*TJ(1,3)+I1J(2)*TJ(2,3)+I1J(3)*TJ(3,3)
   DC 3 K=1,3
      EA(X,K,1)=GA*TJ(K,1)-GA*I1J(K)*A/B2
      EA(X,K,2)=GA*TJ(K,2)-GA*I1J(K)*B/B2
      EA(X,K,3)=GA*TJ(K,3)-GA*I1J(K)*C/B2
3 CONTINUE
C SUM UP THE INTERACTIONS TIMES PROPER PHASE FACTORS
   DC 4 K=1,3
      DO 4 L=1,3
      BB(K,L)=BB(K,L)+EA(K,L)*F1
4 CONTINUE
C CONTINUE
C CCFFUTE AIN. (ADD THE UNIT MATRIX AND MULTIPLY BY THE JTH
C POLARIZABILITY)
C
DC 7 K=1,3
   DC 7 I=1,3
7 CONTINUE
   X FF=Q*G=(T1J(1,1)*BB(1,1,1)+T1J(2,1,1)*BB(2,1,1)+T1J(3,1,1)*BB(3,1,1))
1 CONTINUE
RETURN
END
DATA E3/(0.000, 0.000), (0.000, 0.000), (1.000, 0.000)/
L1G=3.1415 26535 6979180/180.000
CPI=DCOS(EPSI*DIL)
SIP=DSIN(EPSI*DIL)
CII=DCOS(ETHETA*DII)
SIT=DSIN(ETHETA*DII)
CXX=DCOS(AAXI*DIX)
SIX=DSIN(AAXI*DIX)
DO 1 J=1,N
CFI=DCOS(PHI(I,1)*DIL)
SPI=DSIN(PHI(I,1)*DIL)
CTI=DCOS(PHI(I,2)*DIL)
STI=DSIN(PHI(I,2)*DIL)
CII=DCOS(PHI(I,3)*DIL)
SIT=DSIN(PHI(I,3)*DIL)
CALL CEULER(CFI,SPI,CTI,STI,CXX,SIT,E1,T1)
CALL CEUER(CF,SEP,CTI,STI,CXX,SIT,E1,T1)
CALL CEULER(CFI,SPI,CTI,STI,CXX,SIT,E2,T2)
CALL CEULER(CFI,SPI,CTI,STI,CXX,SIT,E3,T3)
CALL CEULER(CFI,SPI,CTI,STI,CXX,SIT,E3,T3)
CALL CEULER(CFI,SPI,CTI,STI,CXX,SIT,E3,T3)
DO 2 J=1,3
DO 2 K=1,3
2 T(I,J,K)=ALPHA(I,1)*T1(J)*DCCNJG(T1(K))+
ALPHA(I,2)*T2(J)*DCCNJG(T2(K))+
ALPHA(I,3)*T3(J)*DCCNJG(T3(K))
R(1)=X(I,1)
R(2)=X[I,2]
R(3)=X[I,3]
CALL CEULER(CF,SEP,CTI,STI,CXX,SIT,E,R,R)
A(I,1)=R(1)
A(I,2)=R(2)
A(I,3)=R(3)
CONTINUE
RETURN
END
SUBROUTINE GEN(E,ALPHA,EPHI,ETHETA,E11,E2,T)
CIMAL=EPHI(I,1), I1(I), I2(I)
I3M=I1(I), I2(I), I3(I)
DIM=EPSI(I), I1(I), I2(I), I3(I)
DC 1 I=1,N
DC 3 J=1,3
3 T(I,J)=T(I,1,J)
T2(J)=T(I,2,J)
T3(J)=T(I,3,J)
CALL CEULER(CF,SEP,CTI,STI,CXX,SIT,E1,T1)
CALL CEULER(CF,SEP,CTI,STI,CXX,SIT,E2,T2)
CALL CEULER(CF,SEP,CTI,STI,CXX,SIT,E3,T3)
DO 2 J=1,3
DO 2 K=1,3
2 T(I,J,K)=ALPHA(I,1)*T1(J)*DCCNJG(T1(K))+
ALPHA(I,2)*T2(J)*DCCNJG(T2(K))+
ALPHA(I,3)*T3(J)*DCCNJG(T3(K))
R(I)=X(I,1)
R(2)=X(I,2)
R(3)=X(I,3)
CALL CEULER(CEP,SEP,CET,SIT,CEX,SEX,R,R)
I(I,1)=R(1)
I(I,2)=R(2)
I(I,3)=R(3)
CONTINUE
RETURN
END

SUBROUTINE CIULI(X,EPHI,ETAYA,SII,X,T)
CCMFLX*10 T1(J),T2(J),T3(J),T(1000,3,3).
CIP*SEP,CET,SIT,CET,SEX,TI,TJ
CCMFLX*R(X,EPHI*DEG)
SEC=CCS(EPHI,ETAYA*DEG)
SET=CCS(ETAYA*DEG)
SEX=CCS(X*DEG)
EO 1 I=1,1
DO 3 J=1,3
T(I,J)=T(I,J,1)
T(I,J)=T(I,J,2)
T(I,J)=T(I,J,3)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,TI,TJ)
END

CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T1,T1)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T2,T2)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T3,T3)
END

DO 2 J=1,3
T(I,J)=T(I,J,1)
T(I,J)=T(I,J,2)
T(I,J)=T(I,J,3)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,TI,TJ)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T2,T2)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T3,T3)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T1,T1)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T2,T2)
CALL CEULER(CEP,SEP,CET,SIT,CET,SEX,T3,T3)
CONTINUE
RETURN
END

SUBROUTINE CALLER(CP,SP,CT,ST,CI,SI,A,B)
COMPLEX*16 A(3),B(3),CP,SP,CT,ST,CI,SI,A,B,U,V,W,
U=(CT*CP-ST*SP)*A(1)-(SI*CT-CP*X*SP)*A(2)*ST*CP*A(3)
V=(CT*SP-ST*CP)*A(1)-(SI*CT+SP*X*CP)*A(2)*ST*SP*A(3)
W=-CT*ST*A(1)-SI*ST*A(2)*CT*A(3)
B(1)=U
B(2)=V
B(3)=W
RETURN
END

SUBROUTINE IXECT(K,FI,IL,IR)
CCMFLX16 FL(I,J),ER(I,J),AL(I,J),T(J,J),U(J,J)
REAL*2 K(I,J),IL,IR
DATA U / (1.0000, 0.0000), (0.0000, 0.0000), (0.0000, 0.0000),
(0.0000, 0.0000), (0.0000, 0.0000), (0.0000, 0.0000),
(0.0000, 0.0000), (0.0000, 0.0000), (0.0000, 0.0000),
(0.0000, 0.0000), (0.0000, 0.0000), (0.0000, 0.0000),
(0.0000, 0.0000), (0.0000, 0.0000), (0.0000, 0.0000),
(0.0000, 0.0000), (0.0000, 0.0000), (0.0000, 0.0000),
(0.0000, 0.0000), (0.0000, 0.0000) /
DATA IL / (1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000) /
DATA IR / (1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000), (1.0000, 0.0000),
(1.0000, 0.0000), (1.0000, 0.0000) /
DO 1 I=1,3
2 DO 1 J=1,3
T(I,J)=U(I,J)*K(I)*K(J)
DO 2 I=1,3
AL(I)=(2.0000, 0.0000)
AB(I)=(2.0000, 0.0000)
DO 2 J=1,3
CC 2 L=1,3
AL(I)=AL(I)+T(I,J)*I(J,L)*EL(L)
AB(I)=AB(I)+T(I,J)*I(J,L)*EL(L)
II=II+II
IR=IR+IR
DC 3 I=1,3
IL=IL+AL(I)*CONJG(AL(I))
IB=IB+AB(I)*CONJG(AB(I))
RETURN
END
E. HGEN, HGENAVE, and IMHGENC

Programs HGEN, HGENAVE, and IMHGENC are interactive programs that set up input data files for CIDSC, CIDSAVE, and IMAGEC respectively, for helical scatterer geometries. These programs were used to make the example input data files shown above.
PROGRAM HGEN

C

CHARACTER*5@NDISC1,NDISC2,NIN,NOUT

WRITE(5,'(A50)') 'ENTER THE SCATTERER DESCRIPTION (TWO LINES)'
READ(5,500)NDISC1,NDISC2

500

WRITE(5,'(A50)') 'ENTER THE CONTROL PARAMETERS INPUT FILE NAME'
READ(5,100)NIN
WRITE(5,'(A50)') 'ENTER THE CIDS DATA OUTPUT FILE NAME'
READ(5,100)NOUT

WRITE(5,'(A50)') 'ENTER W, PHI, THETA1, THETA2, NANGLES'
READ(5,100)W,PHI,THETA1,THETA2,NANGLES
WRITE(5,'(A50)') 'ENTER PHI, THETA, XI, N, NINT'
READ(5,100)PHI,THETA, XI,N,NINT

100

READ(A,NIN,UNIT=10,TYP= 'NEW')
WRITE(10,'(A50)') NOUT

WRITE(10,101)@PHI,THETA1,THETA2,NANGLES,PHI,THETA, XI,N,NINT

101

WRITE(5,'(A50)') 'ENTER THE PITCH, RADIUS, SPACING'
READ(5,100)R,DZ
DG3=D2=DG
WRITE(5,'(A50)') 'THE DISTANCE BETWEEN NEIGHBORING GROUPS ALONG THE
XHULL IS:'
WRITE(5,'(A50)') 'D = ',DG,'DG3 = ',DG3
WRITE(5,'(A50)') 'ENTER THE PRINCIPAL POLARIZABILITIES'
WRITE(5,'(A50)') '(PARALLEL, TANGENTIAL, RADIAL)
READ(5,100)A1,A2,A3
DIG=3.141553/180.0
THETA=3.141
IF(0.0<.0)THEN
 XI=ATAN(P/(2.0*3.141553*R))/DIG
 ELSE
 XI=36.0
 END IF

DFPHI=3.141553*R/P
PHI=0.0

DC 1 I=1,A
X=R*COS(PHI)
Y=D*Sin(PHI)
Z=(I-1)*DZ
WRITE(10,10)I,X,1,Z

1

PHI=PHI+DFPHI
DC 2 I=1,A
WRITE(10,10)I,X,1,Z

2

3

WRITE(10,10)I,X,1,Z

PHI=PHI+DFPHI
STOP
END
PROGRAM HGENAVE

CHARACTER*20 NIN,NOUT
CHARACTER*20 NDESC1,NDESC2
READ(5,*),NDESC1,NDESC2
WRITE(5,*),"ENTER THE SCATTERER DESCRIPTION (TWO LINES)"
READ(5,**),NDESC1,NDESC2
FORMAT(A56/A56)
WRITE(5,*),"ENTER THE CONTROL PARAMETERS INPUT FILE NAME"
REAL(5,100),NIN
WRITE(5,*),"ENTER THE CIDS DATA OUTPUT FILE NAME"
READ(5,120),NOUT
FORMAT(42)
WRITE(5,*),"ENTER THE INCIDENT WAVELENGTH"
READ(5,*),W
WRITE(5,*),"ENTER THE INITIAL AND FINAL SCATTERING ANGLES"
WRITE(5,*),"AND THE NUMBER OF POINTS TO BE EVALUATED"
WRITE(5,*),THETA1,THETA2,NANGLES
WRITE(5,*),"ENTER THE NUMBER OF SCATTERING GROUPS"
READ(5,*),N
OPEN(NAME=HAIR,UNIT=10,TYPE="NEW")
WRITE(12,560),NDESC1,NDESC2
WRITE(10,121),THETA1,THETA2,NANGLES,N
FORMAT(C16.7/EG16.7/I7/I7)
WRITE(5,*),"ENTER THE PITCH, RADIUS, SPACING"
READ(5,*),P,R,DZ
DG=SQRT(2.0*PI*R/(1.0-COS(2.0*3.141592654*DZ/P)))/R=DZ
WRITE(5,*),"THE DISTANCE BETWEEN NEIGHBORING GROUPS ALONG THE"
X AXIX IS:
WRITE(5,*),"D = ',DG,' I= ',I1,' DG3"
WRITE(5,*),"ENTER THE PRINCIPAL POLARIZABILITIES"
WRITE(5,*),"(PARALLEL, TANGENTIAL, RADIAL)"
READ(5,*),A1,A2,A3
DIG=3.141593/180.0
THETA=0.0
IF(EX2.6E.0)THEN
   XI=ATAN(P/(2.0*3.141593*R))/DEG
ELSE
   XI=50.0
END IF
DO1=2.0*3.141593*DZ/P
PHI=0.0
DO 1 I=1,N
   X=SCOS(PHI)
   Y=SSIN(PHI)
   Z=-(I-1)*DZ
   WRITE(12,1)*X,Y,Z
1    PHI=PHI+DFSI
   GO TO 1
DO 2 I=1,N
   WRITE(12,2)*A1,A2,A3
2    PHI=PHI+DFSI
   GO TO 2
DO 3 N=1,N
   WRITE(12,3)*PHI,THETA,XI
3    PHI=PHI+DFSI
STOP
END
PROGRAM PREPARES INPUT FILES FOR PROGRAM

"THIS PROGRAM PREPARES INPUT FILES FOR PROGRAM"
"FILES USE INPUT MODE 2"
"ENTER THE CONTROL PARAMETERS INPUT FILE NAME"
"ENTER THE CIDS DATA OUTPUT FILE NAME"
"ENTER THE SCATTERER DESCRIPTION (Two LINES)"
"ENTER THE #WAVELENGTH, APERTURE, AND focal LENGTH"
"ENTER THE I X GRID LIMITS AND Y GRID LIMITS"
"ENTER THE NUMBER CP I AND Y GRID DIVISIONS, X AND THE VIEW ANGLE"
"ENTER THE THREE ORIENTATION EULER ANGLES" 
"ENTER THE NUMBER OF GROUPS IN THE SCATTERER"
"ENTER THE BACKGROUND ILLUMINATION POLARIZABILITY"
"IF INTERACTIONS ARE TO BE INCLUDED, ENTER 1.
"OTHERWISE ENTER 0"
"OPEN INPUT FILES"
"READ I X, A2, A3"
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