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CIRCULAR AND UNI-AXIAL DICHROISM AND BIREFRINGENCE: THE EMERGENCE OF NONLINEAR OPTICAL NMR AND ESR

M. W. EVANS*

433 Theory Center, Cornell University, Ithaca, NY 14853, USA

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The last decade has seen the emergence of new circular and uni-axial, or forward backward, birefringence and dichroism due to magnetic, nonlinear electromagnetic, and under the correct conditions, alternating electric fields. In this review, we explain some of our contributions to this new area of chemical physics, with special reference to fundamental and applied phenomena such as parity violation and nonlinear optical resonance effects set up by various conjugate products of the Maxwellian electromagnetic field.

Introduction

The first theoretical prediction of uni-axial, or forward backward, birefringence and dichroism appears to have been made by Wagnière and Meier[1] in 1982. They proposed a new uni-axial equivalent of the Faraday effect,[2] which is circular birefringence and dichroism. Both uni-axial and circular effects are due to static magnetic flux density **B**. In the Faraday effect, **B** causes the well-known rotation of the plane of polarised electromagnetic probe radiation, and occurs in chiral and achiral atomic and molecular ensembles. Forward backward birefringence[1,3,4] occurs only in chiral media, and can be observed with unpolarised probe radiation, the refractive index of which is different for the probe propagation vector (**κ**) parallel or antiparallel with **B**. It is a much smaller effect, has been estimated to be about one part in a million by Barron and Vrbancich,[5] and is capable of providing unique information on molecular property tensors of chiral molecules, thus supplementing the information available from natural optical activity. Under the appropriate experimental conditions, discussed by Wagnière,[6] forward backward (FB) birefringence and dichroism can be used to investigate the fundamental phenomenon[7] of parity non-conservation.[8–10] The latter manifests itself, for example, as a very small circular birefringence in achiral ensembles such as heavy metal atoms, and is due to the theoretical unification of weak and electromagnetic fields, the "electroweak" theory of matter. FB birefringence and

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[*] 1990/1991, Guest of the University of Zurich, Switzerland.

dichroism is therefore potentially important for the investigation of the chiral properties of atoms and molecules in several different contexts,[11–14] nuclear, electronic, and electroweak.

Note that FB phenomena occur in one axis only (are "uni-axial"), and should be distinguished from the well known phenomenon sometimes known as magnetic linear dichroism, the Cotton-Mouton effect,[15] which is proportional to magnetic flux density squared and which is usually observed as elliptical polarisation of a probe beam by a magnetic field applied perpendicular to the direction of propagation and at 45° to the plane of polarisation. The Cotton-Mouton effect is also a type of circular dichroism, and is not uni-axial in nature. Note that the Cotton-Mouton effect has an electrically induced analogue, the optical Kerr effect, which is proportional to the square of the electric field strength, whereas there is no analogue of FB birefringence due to a static electric field. The latter would violate reversality, as discussed in Sec. 1. We note that Stedman[16] and Wozniak *et al.*[17] appear to have implied the presence of forward backward birefringence to first order in **B**, a phenomenon which appears[18] to have been referred to as "magnetic linear dichroism" by Stedman and co-workers.

In this review we introduce several new birefringent and dichroic effects due to an intense pump laser. Among these is the optical equivalent of magnetic FB birefringence and dichroism, which is due to the conjugate product ($\mathbf{\Pi}$) of a circularly polarised laser, or electromagnetic field. This conjugate product is responsible for the Pershan, or "inverse Faraday" effect,[19–21] which is magnetism due to an intense circularly polarised pump laser's nonlinear electromagnetic nature. The conventional Faraday effect is accompanied by FB birefringence[1] due to static magnetic flux density, as we have seen, and recent work by Evans[22–25] has shown that there is a forward backward analogue of the inverse Faraday effect due to $\mathbf{\Pi}$. This was first proposed in 1988[22] and tentatively named "spin chiral dichroism". This nomenclature was adopted as the optical analogue of the forward backward birefringence first proposed by Wagnière and Meier,[1] and termed "magnetochiral dichroism" by Barron and Vrbancich.[5] The semi-classical theory of spin chiral dichroism (or "optical uni-axial, or forward backward, dichroism" is another possibility) has been developed by Evans,[23–25] and Evans and Wagnière[26] have demonstrated the existence of frequency dependent, or dynamic, electric polarisation in chiral ensembles due to the interaction of $\mathbf{\Pi}$ with the imaginary part of the dynamic electronic polarisability. This appears at present to have important consequences in two directions: 1) the experimental investigation of parity non-conservation in atomic and molecular spectroscopy; 2) the development of nonlinear optical NMR and ESR, in which a circularly polarised laser is used in an NMR spectrometer to generate additional magnetisation both in chiral and achiral ensembles.

These directions are explored in this review article, and a classification scheme developed for new circular and forward backward dichroic effects in nonlinear optics. Several of these effects have by now a solid theoretical foundation in semi-classical and (in the case of the inverse Faraday effect) quantum field theory,[27] and part of the purpose of this review is to encourage the development of experimental observation.

1. Fundamental Symmetries

This is an area of chemical physics in which symmetry plays an important role in several different contexts.[28,29] The familiar rules of molecular point group theory are supplemented by the concepts of parity inversion (P) and motion reversal (T), applied both to complete experiments and to individual variables. Overall conservation of P and T in the complete experiment should always be a first consideration.[5] Finally the three principles of group theoretical statistical mechanics, developed by Evans[30–35] from the well-known Neumann-Curie Principle, have proven to be useful in relating cause and effect, and in the identification of non-vanishing ensemble averages of the molecular dynamics of circular and uni-axial dichroism. Some of these dynamical phenomena have been computer simulated[36,37] and animated on video[38] for general distribution and broadcasting. A detailed discussion of the symmetry principles is available in recent reviews by Barron[39,40] and Evans.[41] Here we summarise the most relevant and fundamental details.

1.1. *Symmetry of the complete experiment*

1.1.1. *The conservation of reversality, or motion reversal symmetry, T*

The concept of conservation of reversality in a complete experiment appears to have been introduced by Wigner in 1927.[42] Its implementation in contemporary semi-classical theory is illustrated by Barron.[39,40] Essentially, when the motion reversal operator

$$(\mathbf{q}, \mathbf{p}) \xrightarrow{T} (\mathbf{q}, -\mathbf{p})$$

where $\mathbf{q}$ is position and $\mathbf{p}$ is linear momentum, is applied to the variables of a complete, realizable, experiment, the result must be indistinguishable for conservation of reversality. If not, then reversality is not conserved, and any observable must violate T. Violation of T has been observed only once,[43] in nuclear physics, and then only indirectly.

1.1.2. *The conservation of parity inversion, P, in the complete experiment*

This is Wigner's second conservation principle of 1927.[42] When the parity inversion operator

$$(\mathbf{q}, \mathbf{p}) \xrightarrow{P} (-\mathbf{q}, -\mathbf{p})$$

is applied to the variables of a complete, realizable, experiment, the result must be indistinguishable from the original. Otherwise there is parity non-conservation.[39] Any observables in this context violate P, and are measured, for example, in electroweak phenomena[44–46] such as natural optical activity in atoms due to the neutral intermediate vector boson, detected in the well-known CERN experiment.[47]

In practice, the application of these principles requires considerable physical insight, because each experiment is necessarily different, and rules have been devised by Evans[48] in an attempt to help the non-specialists in their application to optical activity caused by static electric and magnetic fields and field combinations. These rules complement those of Stedman *et al.*,[12,14] but appear to be much simpler to apply. The rules of Evans and Stedman *et al.* lead to the same physical conclusions.[49] It can be shown, for example,[50,51] that circular dichroism due to a static electric field $\mathbf{E}$ violates $\mathbf{T}$, and appears never to have been observed experimentally. Faraday himself looked for this effect,[52] and obtained a negative result. "Electric circular dichroism" also violates P in achiral ensembles. Similarly, natural optical activity violates P in achiral ensembles, but conserves T in all ensembles, so that it is observed in chiral media[40] only. (Electroweak theory, as we have seen, leads to P non-conservation, and to the observation of very small optical rotations in achiral ensembles such as atoms.) These considerations can be extended[1,5] to forward backward birefringence due to $\mathbf{B}$, which conserves T in all ensembles, but violates P when the medium is achiral.[6] It is observable in consequence only in chiral ensembles if P is to be conserved. This is the origin of the nomenclature "magnetochiral birefringence", due originally to Barron and Vrbancich,[5] i.e. the birefringence is magnetic in origin, and occurs only in chiral media. Note that the terms "magnetochiral", "uni-axial" and "forward-backward" are all used interchangeably to describe the same $\mathbf{B}$ induced phenomenon. When $\mathbf{\Pi}$ is used to induce forward backward birefringence, "magnetochiral" is replaced by "spin chiral".

1.1.3. *P and T symmetries of individual variables*

At this point it is convenient to consider the P and T symmetries of some of the individual variables of the complete experiments considered in this article, such as the applied external fields $\mathbf{B}$ and $\mathbf{\Pi}$, the conjugate product[53–55] of nonlinear optics.

It is well known from fundamental theory[56] that static magnetic flux density, $\mathbf{B}$, is negative to T and positive to P. One consequence of this is that the Faraday effect is "activated" by $\mathbf{B}$ through the intermediacy[57] of the T negative, P positive imaginary part of the dynamic electronic polarisability, α''_{ij}, which is related to the complex electronic polarisability of semi-classical theory[56] by

$$\alpha_{ij} \equiv \alpha'_{ij} - i\alpha''_{ij} \ . \tag{1}$$

Note carefully that the real part of the polarisability, α'_{ij}, is a T positive quantity, a symmetric second rank tensor quantity with no vector (i.e. rank one tensor) equivalent, whereas the imaginary part α''_{ij} is an antisymmetric T negative polar tensor, mathematically equivalent to an axial vector quantity,

$$i\alpha''_k = i\varepsilon_{ijk}\alpha''_{ij} \tag{2}$$

known[58–61] as "the angular polarisability" (Sec. 2). Here ε_{ijk} is the third rank totally antisymmetric unit tensor,[56] known as the Levi-Civita symbol. The angular polarisability vanishes in the absence of **B** because it is a T negative quantity.

Recently, it has been shown[58–61] that the angular polarisability is also the molecular property tensor responsible for the optical Faraday effect, which is the rotation of the plane of rotation of a linearly polarised probe laser by an intense, circularly polarised, pump laser. The latter generates the conjugate product, **Π**, which is defined[7] by

$$\mathbf{\Pi} = \mathbf{E}_L^+ \times \mathbf{E}_L^- = -\mathbf{E}_R^+ \times \mathbf{E}_R^- = -2E_0^2\, i\mathbf{k} \ . \tag{2a}$$

Here the **E** symbols denote various electric field strengths (in volts m^{-1}) of the plane wave solutions of Maxwell's equations of the electromagnetic field. The superscripts + and − denote plus and minus complex conjugate solutions,[58] and the subscripts L and R denote left and right circularly polarised. If **i**, **j**, and **k** be unit vectors in the X, Y, and Z axes of the laboratory frame (X, Y, Z), and i denote the square root of minus one, then

$$\mathbf{E}_R^+ = E_0(\mathbf{i} - i\mathbf{j})e^{i\phi_R}\,; \quad \mathbf{E}_R^- = E_0(\mathbf{i} + i\mathbf{j})e^{-i\phi_R}$$

$$\mathbf{E}_L^+ = E_0(\mathbf{i} + i\mathbf{j})e^{i\phi_L}\,; \quad \mathbf{E}_L^- = E_0(\mathbf{i} - i\mathbf{j})e^{-i\phi_L} \tag{3}$$

where the phases are defined by

$$\phi_R = \omega t - \boldsymbol{\kappa}_R \cdot \mathbf{r}\,; \quad \phi_L = \omega t - \boldsymbol{\kappa}_L \cdot \mathbf{r} \ . \tag{4}$$

Here $\boldsymbol{\kappa}_L$ and $\boldsymbol{\kappa}_R$ are propagation vectors of left and right circularly polarised components of the electromagnetic plane wave, directed along the Z axis, **r** the position vector in (X, Y, Z), ω the angular frequency of the plane wave in $\mathrm{rad\,s}^{-1}$; and t the time.

Note that the conjugate product, **Π**, is an imaginary quantity which is directed in the Z axis and which is proportional to the square of the amplitude E_0 of the electric field of the plane wave. It reverses sign with circular polarity, and in consequence vanishes in a plane polarised wave, or in unpolarised, incoherent, radiation such as daylight. The T symmetry of $\mathbf{\Pi}$ is established through the fact that T reverses the circular polarity of a plane wave from right to left (traditionally clockwise and anticlockwise rotation, respectively, of the electric field vector of a beam of light travelling towards an observer). Equation (2) shows that $\mathbf{\Pi}$ is reversed in sign by reversing the circular polarity, which is equivalent to the T operation. Accordingly, $\mathbf{\Pi}$ is negative to T. Its positive P symmetry is established through the fact that it is the product of two P negative electric field strengths. Finally, the conjugate product is independent of the phases of electromagnetic plane waves, and does not time average to zero.

We arrive at the conclusion that $\mathbf{\Pi}$ is a T negative, P positive, axial vector, mathematically equivalent to an antisymmetric, T negative, rank two polar tensor

$$\Pi_k = \varepsilon_{ijk}\Pi_{ij} \ . \tag{5}$$

Note that $\mathbf{\Pi}$ and the angular polarisability have the same symmetry characteristics. This T negative, P positive axial symmetry is also the same as those of $\mathbf{B}$, and the magnetic dipole moment $\mathbf{m}$.[56] The latter, in turn, is well known to have the same T and P symmetries as angular momentum. For example

$$\hat{m}_i = \gamma_e(\hat{L}_i + 2.002\,\hat{S}_i) \tag{6}$$

where γ_e is the well known gyromagnetic ratio, and $\hat{L}_i$ and $2.002\,\hat{S}_i$ are respectively the quantised orbital and relativistic, quantised, spin electronic angular momenta. It is therefore possible to write the OPERATOR DEFINITION

$$i\alpha''_i = \gamma_\Pi(\hat{L}_i + 2.002\,\hat{S}_i) \tag{7}$$

where γ_Π is a scalar quantity called the gyroptic ratio[58–61] recently introduced in the context of nonlinear optical NMR and ESR spectroscopy (Sec. 4).

Another important consequence of fundamental symmetry is that $i\hat{\alpha}''_i$ and Π_i form[58–61] a P positive, T positive, scalar interaction hamiltonian

$$\Delta H_1 = \frac{i}{2}\hat{\alpha}''_i\Pi_i \tag{8}$$

in analogy with the well-known[62] interaction hamiltonian

$$\Delta H_2 = -\hat{m}_i B_i \tag{9}$$

between B_i and $\hat{m}_i$. The hamiltonian (8) is important in the description of several new phenomena due to $\mathbf{\Pi}$ of a circularly polarised pump laser, some of which are detailed in this article.

1.2. *The principles of group theoretical statistical mechanics*

A final symmetry consideration in this context is group theoretical statistical mechanics,[30–35] which is founded on three principles of general applicability.[41] The first is the Neumann-Curie Principle, in contemporary group theoretical language; the second is principle (1) applied to a molecule fixed frame of reference; the third is a general cause effect principle which is useful for anticipating the statistical effects of an external influence such as **B** or **Π**.

Principle 1

The thermodynamic average $\langle A_i B_j C_k \ldots \rangle$ exists in the laboratory frame (X, Y, Z) if the product of symmetry representations $\Gamma(A_i)\Gamma(B_j)\Gamma(C_k)\ldots$ of the molecular quantities **A**, **B**, **C**, ... contains at least once the totally symmetric irreducible representation $D_g^{(0)}$ of the rotation reflection group $R_h(3)$

Principle 2.

The thermodynamic ensemble average $\langle A_i B_j C_k \ldots \rangle$ exists in frame (x, y, z) of the molecular point group if the product of symmetry representations $\Gamma(A_i)$ $\Gamma(B_j)\ldots$ in this point group contains at least once the totally symmetric irreducible representation of the molecular point group itself.

Principle 3

If an external vector field of force is applied to an atomic or molecular ensemble which subsequently reaches a steady state in the presence of that field, new vector ensemble averages may be created whose symmetry is that of the applied field.

Principle three is particularly useful in the context of circular and forward backward birefringence caused both by **B** and the conjugate product **Π**. The symmetry of **B** and $\mathbf{\Pi}$[30–35] in the rotation reflection point group $R_h(3)$ of achiral ensembles is $D_g^{(1)}(-)$, where the D symbol means "irreducible representation",[41] the subscript implies g, i.e. positive, to P, and the superscript the tensor rank (one of an axial vector). The quantity in brackets is the T symmetry. Therefore, $D_g^{(1)}(-)$ is the irreducible representation of **B** or **Π** in the point group $R_h(3)$ of achiral ensembles.[35] The same vectors **B** and **Π** are represented differently, however, in the point group of all rotations, $R(3)$, of chiral ensembles, where the irreducible representation becomes $D^{(1)}(-)$. The g subscript is missing because in chiral ensembles, the reflection operation generates the opposite molecular enantiomer (a different, mirror image, molecule), and cannot be a valid point group operator. In point group theory,[62] valid symmetry operations must always leave the molecular structure unaltered.

Using principle three, the symmetry $D_g^{(1)}(-)$is imparted by the vector fields **B** and **Π** to achiral ensemble averages of vector rank (rank one tensors), and the symmetry $D^{(1)}(-)$ to chiral ensemble averages.

This means, for example, that either **B** or **Π** can set up magnetisation or angular momentum both in chiral and achiral ensembles (see estimate in Sec. 2). In chiral ensembles ONLY, **B** and **Π** have the additional capability of producing dynamic, or alternating, or time varying, electric polarisation,[26] which in $R(3)$ has the same $D^{(1)}(-)$ symmetry as magnetisation. Note that this alternating polarisation, as the name implies, is T negative, unlike static electric polarisation, which is T positive. This phenomenon has recently been proposed by Evans and Wagnière,[26] and verified using computer simulation in the S enantiomer of bromochlorofluoromethane. It is mediated by the angular polarisability $i\hat{\alpha}''_k$, which has the same negative T and positive P symmetries as magnetisation, angular momentum, $\mathbf{B}$ and the conjugate product $\mathbf{\Pi}$.

Note that according to principle three, this phenomenon is NOT supported in achiral ensembles, because both dynamic and static electric polarisation are negative to P. Its irreducible representation in the point group $R_h(3)$ is therefore $D_u^{(1)}(-)$, which has a u subscript, denoting negative[30–35,41] to P. The field vector symmetry is on the other hand $D_g^{(1)}(-)$, as we have seen, and by principle three cannot impart this to a vector ensemble average of a different symmetry.

Principle three is also useful in the realisation that forward backward birefringence due to $\mathbf{B}$ or $\mathbf{\Pi}$ must also involve a vector ensemble average of $D^{(1)}(-)$ symmetry in $R(3)$. This is the symmetry in a chiral ensemble of the time odd polar vector which Barron[39,40] has described as the "magnetochiral observable". Note carefully that in $R_h(3)$, the symmetry of a time odd polar vector is $D_u^{(1)}(-)$, and by principle three, achiral ensembles cannot sustain forward backward birefringence due either to $\mathbf{B}$ or $\mathbf{\Pi}$. This time odd polar vector has the same T and P symmetries as the propagation vector,[41,48] $\boldsymbol{\kappa}$, of the circularly polarised laser, a vector which is negative both to P and T.

Forward backward birefringence, as the name implies, is generated by switching the propagation vector of a probe laser from forward (parallel to $\mathbf{B}$ of a magnet or $\mathbf{\Pi}$ of a pump laser) to backward (antiparallel).

To conclude this section, note that it is always important to apply these symmetry principles in a given order: 1) the complete experiment symmetry, aided by principles one to three and related rules, such as those given by Evans[48] and Stedman *et al.*[12,14]; 2) consideration of the symmetry of individual variables and their irreducible representations; 3) point group theory. Using symmetry with care can result in a great saving of computational[41] and analytical[40] effort, and conversely can also be used to indicate whether a given observable indicates P and/or T non-conservation, of fundamental importance.

Principle three must be applied with the necessary care, for example, a vector influence such as $\mathbf{B}$ results in magnetisation (a vector ensemble average of the same symmetry), but also in optical rotation, which is a pseudo scalar. The pseudo scalar is generated through the intermediacy of the Maxwell equations[41,56] and molecular property tensors of rank higher than one (the vector rank of tensor). The Faraday effect is mediated by the rank two angular polarisability, for example. Symmetry principles can provide limited information only, and are not intended to substitute for mathematical analysis.

2. The Interaction of Intense Electromagnetic Radiation with Atomic and Molecular Ensembles — the Nonlinear Interaction Hamiltonian

In this section the hamiltonian governing the interaction of intense electromagnetic radiation with molecular matter is set up in terms of a novel[63] double Taylor expansion of the interaction energy as a function of the electric and magnetic components of the electromagnetic field. This is compared term by term with results from scattering theory (*n*th order quantum perturbation theory) and related to the fundamental Lorentz interaction hamiltonian and dynamic multipole interaction hamiltonian (DMIH).[56] The new general hamiltonian is used to show the presence of several phenomena based on the conjugate product **Π**, and is a rigorous basis for the hamiltonian (8) of optical NMR and ESR.

There have been several approaches to the problem of describing the in general nonlinear interaction hamiltonian of intense electromagnetic radiation with atomic and molecular ensembles. The linear semi-classical approach assumes that the field is classical and that the molecular property tensors are quantised,[56] and described by the time dependent Schrödinger equation. The well-known nonlinear approach used by Ward[64] is based on scattering theory and expands the wave functions in terms of propagators (Green's functions). These two approaches can be unified by expanding the interaction energy in terms of **E** and **B** of the electromagnetic field.[63]

A straightforward application of Taylor's Theorem for the function H of the two complex variables **E** and **B** produces a result such as

$$H = H_0 + \left(\frac{\partial H}{\partial E_i}\right)_0 E_i + \left(\frac{\partial H}{\partial B_i}\right)_0 B_i + \frac{1}{2!}\left[\left(\frac{\partial^2 H}{\partial E_i \partial E_j}\right)_0 E_i E_j + \left(\frac{\partial^2 H}{\partial E_i \partial B_j}\right)_0 E_i B_j\right.$$

$$\left. + \left(\frac{\partial^2 H}{\partial B_i \partial E_j}\right)_0 B_i E_j + \left(\frac{\partial^2 H}{\partial B_i \partial B_j}\right)_0 B_i B_j\right] + \ldots$$

$$+ \left(\frac{\partial H}{\partial \nabla_i E_j}\right)_0 \nabla_i E_j + \left(\frac{\partial H}{\partial \nabla_i B_j}\right)_0 \nabla_i B_j + \ldots + \ldots \tag{10}$$

whose molecular property tensors are summarised in Table 1. Here the energy of interaction, H, is expanded about the point

$$(\mathbf{E}_0, \mathbf{B}_0) = (\mathbf{0}, \mathbf{0}) \tag{11}$$

the origin of the complex space $(\mathbf{E}_0, \mathbf{B}_0)$. The term H_0 is the energy in the absence of the field. In this representation, tensor notation has been used, so that the usual summation over repeated indices is implied. The zero subscripts imply that the subscripted quantity is defined in the limit (11). The coefficients of E_i and B_i, and of the gradients $\nabla_i E_j$ and $\nabla_i \mathrm{B}_j$ and so on in this expansion define complex

Table 1. Fundamental definitions of the complex dynamic molecular property tensors from the hamiltonian (10)

Property	Definition	P Symmetry
Electric Dipole	$\mu_i \equiv -\left(\frac{\partial H}{\partial E_i}\right)_0$	$-$
Magnetic Dipole	$m_i \equiv -\left(\frac{\partial H}{\partial B_i}\right)_0$	$+$
Polarisability	$\alpha_{1ij} \equiv -\left(\frac{\partial^2 H}{\partial E_i \partial E_j}\right)_0$	$+$
Rosenfeld Tensor 1	$\alpha_{2ij} \equiv -\left(\frac{\partial^2 H}{\partial E_i \partial B_j}\right)_0$	$-$
Rosenfeld Tensor 2	$\alpha_{3ij} \equiv -\left(\frac{\partial^2 H}{\partial B_i \partial E_j}\right)_0$	$-$
Magnetisability	$\alpha_{4ij} \equiv -\left(\frac{\partial^2 H}{\partial B_i \partial B_j}\right)_0$	$+$
Electric Quadrupole	$\mathbf{\Theta}_{1ij} \equiv -\left(\frac{\partial H}{\partial \nabla_i \partial E_j}\right)_0$	$+$
Magnetic Quadrupole	$\mathbf{\Theta}_{2ij} \equiv -\left(\frac{\partial H}{\partial \nabla_i \partial B_j}\right)_0$	$-$
Quadrupole Polarisability	$\mathbf{\Phi}_{1ijkl} \equiv -\left(\frac{\partial^2 H}{\partial \nabla_i E_j \partial \nabla_k E_l}\right)_0$	$+$
Quadrupole Magnetisability	$\mathbf{\Phi}_{4ijkl} \equiv -\left(\frac{\partial^2 H}{\partial \nabla_i B_j \partial \nabla_k B_l}\right)_0$	$+$
Quadrupole Rosenfeld 1	$\mathbf{\Phi}_{2ijkl} \equiv -\left(\frac{\partial^2 H}{\partial \nabla_i E_j \partial \nabla_k B_l}\right)_0$	$-$
Quadrupole Rosenfeld 2	$\mathbf{\Phi}_{3ijkl} \equiv -\left(\frac{\partial^2 H}{\partial \nabla_i B_j \partial \nabla_k E_l}\right)_0$	$-$

molecular property tensors which can be related to equivalent expressions in the nonlinear theory of Ward.[64] In mathematical terms, the energy H is a complex quantity, the physical significance of this can be discussed in terms of P and T non-conservation.

The terms E_i and B_i can be developed analytically as plane wave solutions of the Maxwell equations. In general, there are plus and minus conjugates both for right and left circularly polarised plane waves, defined earlier in Eqs. (3). In general therefore, each molecular property tensor is complex, and defined by the quantities

$$E_i = E'_i + iE''_i \tag{12}$$

Table 2. Electric and magnetic components, Eqs. (12) and (13).

Electric	E_i'	E_i''	Magnetic	B_i'	B_i''
E_{LX}^-	$E_0\cos\theta_L$	$-E_0\sin\theta_L$	B_{LX}^-	$-B_0\sin\theta_L$	$-B_0\cos\theta_L$
E_{LX}^+	$E_0\cos\theta_L$	$E_0\sin\theta_L$	B_{LX}^+	$-B_0\sin\theta_L$	$B_0\cos\theta_L$
E_{RX}^-	$E_0\cos\theta_R$	$-E_0\sin\theta_R$	B_{RX}^-	$B_0\sin\theta_R$	$B_0\cos\theta_R$
E_{RX}^+	$E_0\cos\theta_R$	$E_0\sin\theta_R$	B_{RX}^+	$B_0\sin\theta_R$	$-B_0\cos\theta_R$
E_{LY}^-	$E_0\sin\theta_L$	$E_0\cos\theta_L$	B_{LY}^-	$B_0\cos\theta_L$	$-B_0\sin\theta_L$
E_{LY}^+	$E_0\sin\theta_L$	$-E_0\cos\theta_L$	B_{LY}^+	$B_0\cos\theta_L$	$B_0\sin\theta_L$
E_{RY}^-	$-E_0\sin\theta_R$	$-E_0\cos\theta_R$	B_{RY}^-	$B_0\cos\theta_R$	$-B_0\sin\theta_R$
E_{RY}^+	$-E_0\sin\theta_R$	$E_0\cos\theta_R$	B_{RY}^+	$B_0\cos\theta_R$	$B_0\sin\theta_R$

and

$$B_i = B_i' + iB_i'' . \tag{13}$$

For Z axis propagation, these are summarised in Table 2.

It is convenient to develop the complex electric field strengths and complex electric flux densities in terms of their positive and negative conjugates, identified respectively by + and − superscripts. With the definitions

$$E_i^+ \equiv E_i' + iE_i'' \equiv E_0(\mathbf{i} - i\mathbf{j})e^{i\theta_L} \quad \text{or} \quad E_0(\mathbf{i} + i\mathbf{j})e^{i\theta_R} \tag{14}$$

and

$$E_i^- \equiv E_i' - iE_i'' \equiv E_0(\mathbf{i} + i\mathbf{j})e^{-i\theta_L} \quad \text{or} \quad E_0(\mathbf{i} - i\mathbf{j})e^{-i\theta_R} \tag{15}$$

for the + and − conjugates the following identities are obtained algebraically

$$E_i^+ \equiv \left[\frac{1}{2}(E_i^+ + E_i^-)\right] + i\left[\frac{1}{2i}(E_i^+ - E_i^-)\right] \tag{16}$$

$$E_i^- \equiv \left[\frac{1}{2}(E_i^+ + E_i^-)\right] - i\left[\frac{1}{2i}(E_i^+ - E_i^-)\right] \tag{17}$$

$$E_i' = \frac{1}{2}(E_i^+ + E_i^-); \quad E_i'' = \frac{1}{2i}(E_i^+ - E_i^-) . \tag{18}$$

These allow comparison with the linear DMIH[56] and the Ward diagrammatic perturbation theory[64] that forms the basis of nonlinear optics in this context. They also allow molecular property tensors to be defined directly in terms of field conjugates. A careful inspection of these various terms allows the identification of new nonlinear optical effects involving various conjugate products.

2.1. *The complex conjugate dynamic electronic dipole moments*

These are defined by the partial derivatives of the energy with respect to the electric field strength conjugates

$$\mu_i^+ = -\left(\frac{\partial H}{\partial E_i^+}\right)_0 \tag{19}$$

$$\mu_i^- = -\left(\frac{\partial H}{\partial E_i^-}\right)_0 \tag{20}$$

It is convenient to express these as the products

$$\left.\begin{aligned} \mu_i^+ &= -(\partial H(\partial E_i^+)^{-1})_0 \\ \mu_i^- &= -(\partial H(\partial E_i^-)^{-1})_0 \end{aligned}\right\} \tag{21}$$

expressions which follow from the fundamental analytical definition of the partial derivatives. Thus, the complex positive and negative conjugates of the dynamic electronic dipole moment are defined in their most general form by

$$\left.\begin{aligned} \mu_i^+ &= -(\partial H \partial E_i^-)_0 / E_0^2 \equiv \mu_i^{+\prime} - i\mu_i^{+\prime\prime} \\ \mu_i^- &= -(\partial H \partial E_i^+)_0 / E_0^2 \equiv \mu_i^{-\prime} + i\mu_i^{-\prime\prime} \end{aligned}\right\} \tag{22}$$

The semi-classical DMIH[56] and the nonlinear theory of Ward[64] are based on particular approximations to the electronic dipole moment. For example, Barron[56] approximates

$$E_i' = E_0(\cos\theta_{\mathrm{L}}\,\mathbf{i} - \sin\theta_{\mathrm{L}}\,\mathbf{j}) = \frac{1}{2}(E_i^+ + E_i^-) \tag{23}$$

by its *T* positive part (Table 2)

$$(E_i')_{TP} \equiv \frac{E_0}{2}(e^{i\theta_{\mathrm{L}}} + e^{-i\theta_{\mathrm{L}}})\,\mathbf{i} \tag{24}$$

which is used to multiply the real part of the dynamic polarisability in his Eq. (2.6.26) of Ref. 56. The real part (24) in this approximation is positive to motion reversal symmetry *T*. Barron also approximates

$$\left.\begin{aligned} E_i'' &= E_0(-\sin\theta_{\mathrm{L}}\,\mathbf{i} + \cos\theta_{\mathrm{L}}\,\mathbf{j}) \\ &= \frac{1}{2i}(E_i^+ - E_i^-) \end{aligned}\right\} \tag{25}$$

by

$$(E''_i)_{\mathrm{TN}} \equiv -\frac{E_0}{2i}(e^{i\theta_{\mathrm{L}}} - e^{-i\theta_{\mathrm{L}}})\,\mathbf{i} \tag{26}$$

a T negative quantity which multiplies the T negative imaginary part of the dynamic polarisability. More generally, E'_i has a T positive real part (the X component) and a T negative real part (the Y component). Ward[64] also makes similar approximations in developing his nonlinear diagrammatic perturbation theory. It follows from the approximation made by Barron that the dynamic complex electronic dipole moment has a T positive real part

$$(\mu_i^{+})'_{\mathrm{TP}} \equiv -\frac{1}{E_0}(\partial H \partial \cos\theta_{\mathrm{L}})_0\,\mathbf{i} \tag{27}$$

and a T negative imaginary part

$$(\mu_i^{+})''_{\mathrm{TN}} \equiv -\frac{1}{E_0}(\partial H \partial \sin\theta_{\mathrm{L}})_0\,\mathbf{i} \tag{28}$$

both being negative to parity inversion P. Rigorously, however, the real part of the dynamic electronic dipole moment has a real X component which is T positive and a real Y component which is T negative, an imaginary X component which is T negative, and an imaginary Y component which is T positive.

These considerations allow a comparison of the general nonlinear interaction hamiltonian (10) with the DMIH, using

$$E'_i = E_0(\cos\theta_{\mathrm{L}}\,\mathbf{i} + \cos\theta_{\mathrm{L1}}\,\mathbf{j})\,, \tag{29}$$

$$\theta_{\mathrm{L1}} = \theta_{\mathrm{L}} + \frac{\pi}{2}(t + \mathbf{k}\cdot\mathbf{r}) \tag{30}$$

$$E_i^{+} = E_0(e^{i\theta_{\mathrm{L}}}\,\mathbf{i} + e^{i\theta_{\mathrm{L1}}}\,\mathbf{j})\,; \quad E_i^{-} = E_0(e^{-i\theta_{\mathrm{L}}}\,\mathbf{i} + e^{-i\theta_{\mathrm{L1}}}\,\mathbf{j}) \tag{31}$$

so that E'_i is chosen to be T positive. Similarly

$$E''_i = -E_0(\sin\theta_{\mathrm{L}}\,\mathbf{i} - \sin\theta_{\mathrm{L1}}\,\mathbf{j}) \tag{32}$$

$$= -\frac{E_0}{2i}((e^{i\theta_{\mathrm{L}}} - e^{-i\theta_{\mathrm{L}}})\,\mathbf{i} - (e^{i\theta_{\mathrm{L1}}} - e^{-i\theta_{\mathrm{L1}}})\,\mathbf{j}) \tag{33}$$

so that E''_i is T negative. Using these fundamental symmetries, and Table 1, the dynamic complex electric dipole moment is expanded in the two variable complex Taylor series

$$\mu_i = \mu_0 + \alpha_{1ij}E_j + \alpha_{3ij}B_j + \dots \tag{34}$$

$$\alpha_{1ij} = \left(\frac{\partial \mu_i}{\partial E_j}\right)_0 = -\left(\frac{\partial}{\partial E_i}\left(\frac{\partial H}{\partial E_j}\right)\right)_0 = -\left(\frac{\partial^2 H}{\partial E_i \partial E_j}\right)_0 \ ;$$

$$\alpha_{3ij} = \left(\frac{\partial \mu_i}{\partial B_j}\right)_0 = -\left(\frac{\partial}{\partial B_i}\left(\frac{\partial H}{\partial E_j}\right)\right)_0 = -\left(\frac{\partial^2 H}{\partial B_i \partial E_j}\right)_0 \ ;$$

with an analogous expansion for the complex dynamic magnetic dipole moment. An inspection of the terms in (34) linear in E_j and B_j leads to a direct comparison with the linear DMIH. In order to match the notation used[56] in the DMIH we write

$$\mathrm{Re}\,(\mu_i) = \mu'_i = \alpha'_{1ij}E'_j - \alpha''_{1ij}E''_j + \dots \tag{35}$$

where the real and imaginary parts of the dynamic electronic polarisability, respectively α'_{1ij} and α''_{1ij}, are defined more closely later. The real part of the dynamic electronic dipole moment from (35) is

$$\mathrm{Re}\,(\mu_i) = \alpha'_{ij}\left(\frac{1}{2}(E_j^+ + E_j^-)\right) - \alpha''_{ij}\left(\frac{1}{2i}(E_j^+ - E_j^-)\right) + \dots \tag{36}$$

and using

$$\dot{E}'_j = -\omega E''_j \ , \tag{37}$$

$$\mathrm{Re}\,(\mu_i) = \alpha'_{ij}E'_j + \frac{\alpha''_{ij}}{\omega}\,\dot{E}'_j + \dots \tag{38}$$

we recover the first two terms of Barron's representation,[56] his Eq. (2.6.26a), of the real part of the electronic dipole moment from the linear DMIH, his Eq. (2.5.30). Note that the quantities α'_{ij} and α''_{ij} in our Eq. (38) are respectively T positive and negative, following upon our definitions (29) and (32). Barron's result equivalent to our Eq. (38), his Eq. (2.6.26a), was obtained using the Placzek expansion of the wavefunction in the time dependent Schrödinger equation. Our Eq. (36), clearly, was obtained without the use of an equation of motion.

We are now in a position to extend the DMIH to terms nonlinear in the complex oscillating electric and magnetic fields, and to check the result term by term against the expressions obtained by Ward[64] using diagrammatic perturbation theory. In the latter approach the energy is developed through

$$H = H_0 + \langle \psi^{\oplus *} | H' | \psi^{\oplus} \rangle \tag{39}$$

where ψ is a wave function defined at long positive times[64] and expanded in terms of Green's functions (propagators):

$$|\psi^{\oplus}\rangle = (1 + GH' + GH'GH' + \ldots)|g\rangle \, . \tag{40}$$

The energy is therefore expanded as

$$\begin{aligned} H = H_0 &+ \langle g | H' | g \rangle + (\langle g | H'G^*H' | g \rangle + \langle g | H'GH' | g \rangle) + (\langle g | H'G^*H'GH' | g \rangle \\ &+ \langle g | H'G^*H'G^*H' | g \rangle + \langle g | H'GH'GH' | g \rangle) + \ldots \end{aligned} \tag{41}$$

where G^* is the conjugate of the Green's function, and g the ground state. Feynman diagrams[64] are then used to evaluate each term in the expansion. In this section, Eqs. (41) and (10) are compared term by term to give quantum definitions of the various molecular property tensors without the need to solve the time dependent Schrödinger equation, and to show that Eq. (10) encompasses the results of n order (nonlinear) diagrammatic quantum perturbation theory.

The latter depends on a definition of H', the "core perturbation energy". Ward[64] defines this through his Eq. (II.11) as

$$H' = -e\mathbf{E}^{\omega} \cdot \mathbf{r} \sin \omega t \equiv H^{+} e^{i\omega t} + H^{-} e^{-i\omega t} \tag{42}$$

in the "electric dipole approximation". Here e is the electronic charge and $\mathbf{r}$ a position vector. This is an approximation, given in our notation by the imaginary part of the linear electric field term of Eq. (10)

$$\mathrm{H}' = -\left(\frac{\partial H}{\partial E''_i}\right)_0 \mathrm{E}''_i \, . \tag{43}$$

Ward also makes the approximation

$$\theta_{\mathrm{L}} = \theta_{\mathrm{R}} \div \omega \mathrm{t} \tag{44}$$

i.e. develops the theory without regard to left or right circular polarisation. His core hamiltonian H' leaves the magnetic terms out of consideration, and finally, he proceeds without defining T and P symmetries in his molecular property tensors. Nonetheless, the theory has proven to be useful in nonlinear optics, and many of the predictions made have been verified experimentally.[65]

Table 3 is a comparison of the first, second, and third order terms from Eqs. (41) and (10).

From this table it is clear that Ward perturbation theory, with its core hamiltonian, his equation (II.11), is equivalent term by term to an approximation

Table 3. Comparison of terms, general nonlinear hamiltonian (10) and N Order diagrammatic perturbation theory.

Order	From Eq. (10)	Ward[64*]
1	$\left(\frac{\partial H}{\partial E''_i}\right)_0 E''_i$	$\langle g \mid H' \mid g\rangle$
2	$\frac{1}{2!}\left(\frac{\partial^2 H}{\partial E''_i \partial E''_j}\right)_0 E''_i E''_j$	$\langle g \mid H' G^* H' \mid g\rangle$ $+ \langle g \mid H' G H' \mid g\rangle$
3	$\frac{1}{3!}\left(\frac{\partial^3 H}{\partial E''_i \partial E''_j \partial E''_k}\right)_0 E''_i E''_j E''_k$	$\langle g \mid H' G^* H' G H' \mid g\rangle$ $+ \langle g \mid H' G^* H' G^* H' \mid g\rangle$ $+ \langle g \mid H' G H' G H' \mid g\rangle$

* $H' = -\left(\frac{\partial H}{\partial E''_i}\right)_0 E''_i$

of Eq. (10) which substitutes E_i by its imaginary part, and neglects the magnetic terms at all orders. Higher order Taylor differentiation in Eq. (10) is equivalent at all orders to operating with Green's functions and integrating over all configuration space. Furthermore, it can be seen that the Ward type core interaction hamiltonian needed to generate the full equation (6) is in our notation

$$H'_1 = \left(\frac{\partial H}{\partial E_i}\right)_0 E_i + \left(\frac{\partial H}{\partial B_i}\right)_0 B_i \tag{45}$$

which includes the real and imaginary parts both of the electric and magnetic components of the Maxwellian electromagnetic field. Reinstating these terms leads to a more complete understanding of the approximate theory by Ward,[64] and also to new and useful nonlinear optical phenomena.

2.2. *The dynamic electronic polarisabilities*

It is convenient to develop the hamiltonian in terms of products of complex conjugates of electric and magnetic components. In so doing, the relevant dynamic mutipoles and molecular property tensors are defined in terms of conjugate products, with appropriate T and P symmetries which signal the existence of various nonlinear optical phenomena by inspection of terms. This method is exemplified in this section by the four dynamic electronic polarisabilities

$$\begin{aligned}\alpha_{ij}^{++} &= -\left(\frac{\partial}{\partial E_i^+}\left(\frac{\partial H}{\partial E_j^+}\right)\right)_0; \quad \alpha_{ij}^{+-} = -\left(\frac{\partial}{\partial E_i^+}\left(\frac{\partial H}{\partial E_j^-}\right)\right)_0;\\ \alpha_{ij}^{-+} &= -\left(\frac{\partial}{\partial E_i^-}\left(\frac{\partial H}{\partial E_j^+}\right)\right)_0; \quad \alpha_{ij}^{--} = -\left(\frac{\partial}{\partial E_i^-}\left(\frac{\partial H}{\partial E_j^-}\right)\right)_0;\end{aligned} \tag{46}$$

which involve conjugate products at order two in the oscillating complex electric field. These are the four conjugate products of the dynamic electronic polarisability, two of which, Eqs. (46a) and (46d), signal frequency doubling,[64] and two, Eqs. (46b) and (46c), optical rectification.[64–67] Types (46b, c) can generate magnetisation through the Pershan effect,[19] often known in the literature as the inverse Faraday effect.[3,4] This means that the angular polarisability (Sec. 1) can generate an optical Zeeman splitting, and optical NMR and ESR. This is potentially of great practical utility when a circularly polarised laser is used to generate magnetisation in a conventional NMR or ESR spectrometer, because the laser induces extra magnetisation which leads to a blue shift in the NMR or ESR resonance frequencies, and to a higher resolution (absolute frequency difference between NMR resonances at different nuclear sites). Some of the concepts of optical NMR and ESR are introduced in Sec. 4 of this review, and are summarised in the appendix with reference to the notation used in a standard NMR text such as that of Slichter.[68] The negative T symmetries of these interesting new effects serve to distinguish them from the well-known and observed optical Stark effect.[69–72]

In discussing T and P symmetries of the dynamic polarisabilities, the real part E'_i of E_i is taken as T positive, P negative (Eq. (29)), and the imaginary part E''_i as T negative, P negative (Eq. (32)). With these definitions, the double positive conjugate of the dynamic electronic polarisability is

$$\alpha_{ij}^{++} = -(\partial^2 H \partial(E'_i - iE''_i)\partial(E'_j - iE''_j))_0 / E_0^2 \equiv \alpha'^{++}_{ij} - i\alpha''^{++}_{ij} \tag{47}$$

which has a T positive, P positive real part

$$\alpha'^{++}_{ij} = -(\partial^2 H(\partial E'_i \partial E'_j - \partial E''_i \partial E''_j))_0 / E_0^2 \tag{48}$$

and a T negative, P positive imaginary part

$$\alpha''^{++}_{ij} = -(\partial^2 H(\partial E''_i \partial E'_j + \partial E'_i \partial E''_j))_0 / E_0^2 \ . \tag{49}$$

In the hamiltonian (10) both parts multiply the tensor $E_i^+ E_j^+$ and produce frequency doubling.[64] The only part of this described by Ward[64] is the term proportional to the tensor product $\partial E''_i \partial E''_j$ in the real part of α_{ij}^{++}. This is simply because Ward approximated E_i by its imaginary part E''_i. The other three terms in (47) and (48) produce other frequency doubling phenomena, which appear to be new. Of particular interest is the imaginary, T negative, polarisability, which multiplies the imaginary, T negative tensor product of oscillating electric field components

$$\left.\begin{aligned} \Delta H_3 &= \frac{i}{2}\varepsilon_{ijk}\alpha_{ij}''^{+-}\,(\mathbf{E}^+\times\mathbf{E}^-)_k\ ; \\ \alpha_{ij}^{+-} &= \alpha_{ij}'^{+-} - i\alpha_{ij}''^{+-} \end{aligned}\right\} \tag{50}$$

to give a REAL, measurable, scalar contribution to the energy H in Eq. (10). The conjugate product $\mathbf{E}^+\times\mathbf{E}^-$ changes sign from left to right circular polarisation as in Eq. (2) of Sec. 1

$$\mathbf{\Pi} \xrightarrow{T} -\mathbf{\Pi} \tag{51}$$

and vanishes if there is no circular polarisation.

In terms of the phases θ_{L} and θ_{R} of the electromagnetic field we have

$$(\alpha_{ij}^{++})_{\mathrm{L}}''\,\delta_{ij} = (\alpha_{ij}^{++})_{\mathrm{R}}''\,\delta_{ij} = \left(\frac{\partial^2 H\partial}{E_0^2}\begin{bmatrix} \sin 2\theta_{\mathrm{L}} & 0 & 0 \\ 0 & -\sin 2\theta_{\mathrm{L}} & 0 \\ 0 & 0 & 0 \end{bmatrix}\right)_0 \tag{52}$$

for the diagonal part, and

$${}^{s}(\alpha_{ij}^{++})_{\mathrm{L}}'' = -\,{}^{s}(\alpha_{ij}^{++})_{\mathrm{R}}'' = \left(\frac{\partial^2 H\partial}{E_0^2}\begin{bmatrix} 0 & -\cos 2\theta_{\mathrm{L}} & 0 \\ -\cos 2\theta_{\mathrm{L}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}\right)_0 \tag{53}$$

for the symmetric tensor part. Both parts are T negative, and are non-zero only in the presence of a T negative influence. The latter is generated through the diagonal and symmetric tensor components of the imaginary part of the complete tensor product

$$E_i^+\,E_j^+ \equiv (E_i^+\,E_j^+)' - i\,(E_i^+\,E_j^+)'' \tag{54}$$

so that the contribution to the hamiltonian is a T positive P positive scalar formed by a tensor contraction of the polarisability and field product. Equations (52) and (53) signal the presence of one out of several new types of frequency doubling phenomena.

2.3. *The electronic angular polarisability*

Of central importance to the new circular and uni-axial birefringence effects of this review, and in particular to optical NMR and ESR, is the electronic angular polarisability (Sec. 1 and Appendix).

Consider the phase independent conjugate product polarisability α_{ij}^{+-}, which multiplies the conjugate field product $E_i^+\,E_j^-$ to form a scalar energy. In this case the trace and symmetric tensor parts vanish, leaving the antisymmetric, T negative, P positive, dynamic electronic polarisability

$$i\alpha''_{ij} = \frac{i}{2}(\alpha_{ij}^{+-''} - \alpha_{ji}^{+-''}) \equiv i^{a}\alpha_{ij}^{+-''} \ . \tag{55}$$

This is defined as the electronic angular polarisability.

The angular polarisability multiplies the phase independent conjugate product (**Π**) of Sec. 1 to give the interaction hamiltonian

$$\Delta H_1 = \frac{i}{2}\alpha''_{ij}\Pi_{ij} \tag{56}$$

which can be written (Sec. 1) as the scalar product of two T negative P positive axial vectors (rank one tensors)

$$\Delta H_1 = \frac{i}{2}\hat{\alpha}''_k\Pi_k \tag{57}$$

where

$$\hat{\alpha}''_k = \varepsilon_{ijk}\alpha''_{ij}; \quad \Pi_k = \varepsilon_{ijk}\Pi_{ij} \tag{58}$$

with ε_{ijk} as the third rank totally antisymmetric unit tensor (the Levi-Civita tensor). Using Eq. (2) of Sec. (1) we arrive at a hamiltonian

$$\Delta H_1 = -\hat{\alpha}''_z E_0^2 \tag{59}$$

which is closely analogous to the interaction hamiltonian

$$\Delta H_2 = -\hat{m}_z B_z \tag{60}$$

of a magnetic dipole moment and applied static magnetic flux density, the basic hamiltonian of the theory of nuclear magnetic resonance[68] (see Appendix 1, where further analogies of this nature are made).

We note that semi-classical theory (Table 3) gives the EXPECTATION VALUE of the angular polarisability as

$$\alpha''_{\alpha\beta} = -\alpha''_{\beta\alpha} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\operatorname{Im}\langle n|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|n\rangle \tag{61}$$

where $\hat{\mu}_\alpha$ and $\hat{\mu}_\beta$ are electric dipole matrix element operators with transition frequency

$$\omega_{jn} = \omega_j - \omega_n \tag{62}$$

in rads s^{-1}. This expression[56] gives the necessary T negative, P positive, antisymmetric symmetry for the expectation value of the angular polarisability in its second rank polar tensor form.

Note carefully that the angular polarisability has both an operator definition (Eq. (7)), and an expectation value (Eq. (61)) in direct analogy (Appendix 1) with the magnetic dipole moment. The angular polarisability and magnetic dipole operators are proportional through

$$i\hat{\alpha}_i'' = \frac{\gamma_\pi}{\gamma_e}\hat{m}_i \tag{63}$$

where γ_e is the gyromagnetic and γ_π the gyroptic ratio. The latter is developed in Sec. 4. It has the units and approximate magnitude as tabulated in Appendix 1.

In consequence of this operator definition of angular polarisability, it is natural to define a non-vanishing product such as

$$\langle n \,|\, \hat{\alpha}_i'' | j\rangle \equiv \int \psi_n^* \,\hat{\alpha}_i'' \psi_j \, d\tau \tag{64}$$

in which the OPERATOR $\hat{\alpha}_i''$ is implied, and not the expectation value (61). This is entirely analogous with the standard practice of writing the magnetic dipole moment as either an operator or expectation value, as necessary.

2.4. *Comparison of magnetizations produced by a magnet and a circularly polarised laser*

In consequence to this theoretical development of $\hat{\alpha}_i''$ as a quantum mechanical operator with the same P and T symmetries as both the magnetic dipole moment and angular momentum, we emphasise in this section that a circularly polarised laser's conjugate product $\mathbf{\Pi}$ can produce the same order of magnitude of magnetization as a 1.0 Tesla magnet for a laser electric field strength amplitude of about 100,000 volts per centimetre (an intensity of the order 4,000 watts per cm^2). This is an important rule of thumb for optical NMR, because a laser of this intensity is easily available, and can be used to supplement the magnetisation of the conventional NMR magnet.

The magnetisation produced by a 1.0 Tesla magnet is estimated through[73]

$$\langle m_Z \rangle = m_{0Z} + \xi_{ZZ}\frac{B_Z}{\mu_0} + \dots \tag{65}$$

where m_{0Z} is the permanent magnetic dipole moment, ξ_{ZZ} is the molecular magnetizability, B_Z the applied magnetic flux density, μ_0 the vacuum permeability.

The magnetizability is estimated through its diamagnetic part[73]

$$\xi_{ZZ} = -\frac{e^2\mu_0}{6m_e}\langle r^2\rangle \tag{66}$$

where e is the charge on the electron, and m_e its mass. The mean square orbital radius $\langle r^2\rangle$ is estimated to be about $10^{-20}\,\mathrm{m}^2$. This gives a diamagnetic magnetizability of about

$$\xi_{ZZ} \doteqdot 5 \times 10^{-35}\ \mathrm{Js^2m\ kgm^{-1}}\ . \tag{67}$$

The magnetisation in amps m^{-1} is then

$$N\langle m_Z\rangle = N\xi_{ZZ}B_Z/\mu_0 \tag{68}$$

which for N of about 6×10^{26} molecules per m^3 is

$$N\langle m_Z\rangle = 0.01\ Am^{-1} \tag{69}$$

for an applied **B** of 1.0 Tesla. This is the order of magnitude of the number density diamagnetic magnetization in amperes per metre produced by an applied magnetic flux density of 1.0 Tesla.

In comparison, the diamagnetic part of the magnetization produced by a circularly polarised laser has been given by Wagnière[74] as

$$\begin{aligned} M_Z^{(d)} &= N\langle m_Z^{(d)}\rangle \\ &= -\frac{iN\omega}{3\hbar^2}\sum_k\sum_l\Bigg[\mathrm{Im}\,(\boldsymbol{\mu}_{ka}\cdot\mathbf{m}_{al}\times\boldsymbol{\mu}_{lk})\frac{2}{\omega_{la}(\omega_{ka}^2-\omega^2)} \\ &\quad -\mathrm{Im}\,(\mathbf{m}_{lk}\cdot\boldsymbol{\mu}_{ka}\times\boldsymbol{\mu}_{al})\frac{(\omega_{la}+\omega_{ka})}{(\omega_{la}^2-\omega^2)(\omega_{ka}^2-\omega^2)}\Bigg](\mathbf{E}_-\times\mathbf{E}_+) \end{aligned} \tag{70}$$

where ω is the angular frequency of the laser in rad s^{-1}; $\hbar$ is the reduced Planck constant; and where the matrix element shorthand notation

$$\begin{aligned} \boldsymbol{\mu}_{ka} &= \langle k|\hat{\boldsymbol{\mu}}|a\rangle\ ; \\ \boldsymbol{\mu}_{al} &= \langle a|\hat{\boldsymbol{\mu}}|l\rangle\ ; \\ \boldsymbol{\mu}_{lk} &= \langle l|\hat{\boldsymbol{\mu}}|k\rangle\ ; \\ \mathbf{m}_{al} &= \langle a|\hat{\mathbf{m}}|l\rangle\ ; \\ \mathbf{m}_{lk} &= \langle l|\hat{\mathbf{m}}|k\rangle\ ; \end{aligned} \tag{71}$$

has been used for the quantum states a, l, and k. Using angular frequencies corresponding to electronic transition energies

$$\omega \doteqdot \omega_{la} \doteqdot \omega_{ka} \doteqdot 10^{14}\ \mathrm{rad}\ s^{-1} \tag{72}$$

and $\hbar$ of the order 10^{-34} Js, estimating an order of magnitude

$$\boldsymbol{\mu}_{ka} \doteqdot \boldsymbol{\mu}_{al} \doteqdot \boldsymbol{\mu}_{lk} \doteqdot 10^{-29}\ \mathrm{Cm} \tag{73}$$

for the electric dipole moments, we obtain the order of magnitude magnetisation

$$\mathbf{M}^{(d)} \doteqdot 10^{8}\,|\mathbf{m}_{al}|\,E_0^2\ \mathrm{Am}^{-1} \tag{74}$$

in amperes per metre. Taking an order of magnitude for the diamagnetic magnetic dipole moment of about a tenth of the Bohr magneton

$$|\mathbf{m}_{al}| \doteqdot 10^{-25}\ JT^{-1} \tag{75}$$

gives a diamagnetic magnetisation from the circularly polarised laser of the order of magnitude

$$\mathbf{M}^{(d)} \doteqdot 10^{-16}\ E_0^2\ \mathrm{Am}^{-1}\ . \tag{76}$$

For a laser electric field strength amplitude of the order

$$E_0 \doteqdot 10^{6}\ \mathrm{Vm}^{-1} = 10^{4}\ \mathrm{Vcm}^{-1} \tag{77}$$

the magnetisation is 0.01 amp m^{-1}; which is the same order of magnitude as obtained for an applied magnetic flux density of 1.0 Tesla. It is useful to note that $10^6\ \mathrm{Vm}^{-1}$ is $10^4\ \mathrm{Vcm}^{-1}$, which corresponds to an intensity of about $4 \times 10^2\ \mathrm{Wcm}^{-2}$. This is easily obtainable in contemporary laser technology with several different kinds of laser.

Provided therefore that the laser is acccurately circularly polarised, and it is expected to shift significantly the NMR resonance frequency to split it through Landé coupling as described[75] in the literature and summarised later in this article. The shift should be towards higher frequencies if the conjugate product $\mathbf{\Pi}$ is parallel to $\mathbf{B}$, and vice versa. This is also a kind of "forward/backward" effect therefore. The shift to higher frequencies is particularly useful for increasing the resolution of an NMR spectrometer by greatly increasing the effective magnetisation using a combination of magnet and applied circularly polarised laser. This can be particularly useful for the ultra high resolution optical NMR of proteins and other complex specimens in which the many different proton resonances occur at much the same frequency, and with low resolution cannot be distinguished. The circularly polarised laser in this context increases the absolute frequency separation between the various chemically shifted proton resonances by effectively increasing the magnetization of the sample. The proton resonances are therefore separated out on an absolute frequency scale, i.e. the effective resolution of the instrument is greatly increased. The difficulties introduced by fluctuations (inhomogeneities) in the electric field strength amplitude of the laser can be overcome[76] in principle by using a combination of factors such as specially designed pulse sequencies and stable lasers such as a nitrogen cooled diode laser in the visible.

2.5. *The Hellman-Feynman Theorem for the conjugate product* $\mathbf{\Pi}$

Finally in this section we define the Hellman-Feynman Theorem[73] for the conjugate product $\mathbf{\Pi}$. The Theorem relates the change in energy due to $\mathbf{\Pi}$ to the expectation value of the change in the hamiltonian due to $\mathbf{\Pi}$.

Consider a system characterised by a hamiltonian that depends on the conjugate product of Eq. (2) of Sec. 1. The exact wave function describing the system is a solution of the Schrödinger equation, and also depends on $\mathbf{\Pi}$. The energy of the system therefore depends on $\mathbf{\Pi}$ through the equation

$$E_n(\mathbf{\Pi}) = \int \psi^* H \psi \, d\tau \tag{78}$$

where H, and the wave function ψ, and its conjugate ψ^*, are all functions of $\mathbf{\Pi}$:

$$H = H(\mathbf{\Pi}) ; \quad \psi = \psi(\mathbf{\Pi}) ; \quad \psi^* = \psi^*(\mathbf{\Pi}) \; . \tag{79}$$

Differentiating Eq. (78) with respect to $\mathbf{\Pi}$ gives

$$\begin{aligned} \frac{dE_n}{d\mathbf{\Pi}} &= \int \left(\frac{\partial\psi^*}{\partial\mathbf{\Pi}}\right) H\psi d\tau + \int \psi^*\left(\frac{\partial H}{\partial\mathbf{\Pi}}\right)\psi \, d\tau + \int \psi^* H \left(\frac{\partial\psi}{\partial\mathbf{\Pi}}\right) d\tau \\ &= E_n\left(\frac{d}{d\mathbf{\Pi}} \int \psi^*\psi d\tau\right) + \int \psi^*\left(\frac{\partial H}{\partial\mathbf{\Pi}}\right)\psi d\tau \end{aligned} \tag{80}$$

which reduces to the Hellman-Feynman Theorem

$$\frac{dE_n}{d\mathbf{\Pi}} = \left\langle\frac{\partial H}{\partial\mathbf{\Pi}}\right\rangle = \int \psi^*\left(\frac{\partial H}{\partial\mathbf{\Pi}}\right)\psi \, d\tau \tag{81}$$

where the angular brackets denote expectation value. The Theorem immediately provides the definition of the angular polarisability in the form

$$-\alpha'' = \frac{\partial H}{\partial\mathbf{\Pi}} \tag{82}$$

which corresponds to a particular term in the expansion of the hamiltonian

$$E_n(\mathbf{\Pi}) = (E_n)_0 + \left(\frac{\partial E_n}{\partial \mathbf{\Pi}}\right)_0 \mathbf{\Pi} + \dots \tag{83}$$

as described earlier in this section.

The Hellman-Feynman Theorem shows that the differential of energy with respect to the conjugate product is the expectation value of the angular polarisability.

3. Voigt-Born Perturbations: Approximate Expressions for Uni-Axial and Circular Birefringence and Dichroism

The molecular property tensors of Sec. 2 can themselves be expanded in Taylor series in terms of external field perturbations such as **B** and **Π**, the Voigt-Born series.[77] Of fundamental importance to the theory of circular and forward backward birefringence is the Voigt-Born expansion of molecular property tensors such as the complex polarisability of Eq. (1):

$$\alpha_{ij}(B_k) = \alpha_{ij}(0) + \alpha_{ijk}B_k + \dots\ . \tag{84}$$

This type of expansion was used by Barron and Vrbancich[5] to derive forward backward birefringence due to **B** using both Rayleigh refringent scattering theory and the Maxwell equations. A later description by Evans[22–25] of forward backward dichroism and birefringence due to Π_k has been based on a similar Voigt-Born perturbation. In this section a summary of a simple, approximate, method of solving the Maxwell equations for both circular and forward backward birefringence due either to **B** or **Π** is based on a recent long paper.[78]

In the Voigt-Born expansions of molecular property tensors such as the complex polarisability, α_{ij}, and the complex Rosenfeld tensor, α_{2ij}, it is assumed that Taylor expansions are possibly analogous to those of Sec. 2. Thus, a perturbation due to the conjugate product Π_k is developed as the Taylor series

$$\alpha_{ij}(\Pi_k) = \alpha_{ij}(0) + \alpha_{ijk}\Pi_k + \dots \tag{85}$$

$$\alpha_{2ij}(\Pi_k) = \alpha_{2ij}(0) + \alpha_{2ijk}\Pi_k + \dots \tag{86}$$

which define the T and P symmetries of higher rank perturbing tensors such as

$$\alpha_{ijk} \quad \text{and} \quad \alpha_{2ijk}\ .$$

Confining the Taylor expansions to first order in Π_k gives the perturbation expressions

$$\alpha_{ij}(\pi_k) = \alpha_{ij}(0) \pm \alpha_{ijk}\pi_k ;$$

$$\alpha_{2ij}(\pi_k) = \alpha_{2ij}(0) \pm \alpha_{2ijk}\pi_k ; \tag{87}$$

where the plus sign denotes Π_k in the $+z$ direction and vice versa. Note that the third rank tensor α_{ijk} mediating the effect of Π_k on molecular polarisability is positive to P, and is supported by achiral ensembles. The tensor α_{2ijk} mediating the effect of Π_k on the negative parity optical activity tensor α_{2ij} is also negative to P, and is supported only in chiral ensembles.

These tensors can be incorported within "core equations" derived from the Maxwell equations[78] and which describe spectral effects such as uni-axial and circular birefringence due to the conjugate product Π_k. The Maxwell equation is written as

$$\frac{1}{\mu_0}\nabla \times \mathbf{B}^{(1)} = \varepsilon_0 \frac{\partial \mathbf{E}^{(1)}}{\partial t} + N\frac{\partial}{\partial t}(\alpha_{ij}E_j^{(1)} + \alpha_{2ij}B_j^{(1)}) \tag{88}$$

where μ_0 is the vacuum permeability (in S.I. units), and ε_0 the vacuum permittivity. $\mathbf{B}^{(1)}$ is the magnetic and $\mathbf{E}^{(1)}$ the electric field component of the probe electromagnetic field. Solving this equation[78] in the approximation $\mathbf{M} \ll \mathbf{P}$, where $\mathbf{M}$ is the bulk magnetisation and $\mathbf{P}$ the bulk polarisation, gives the necessary core equations for the spectra effects in which we are interested.

3.1. *Uni-Axial birefringence due to* Π *or* B

In this case the probe is unpolarised, and measures the average of the refractive and absorption indices measured by a left and right circularly polarised probe beam. The core equations are

$$n'_{\text{av}z} = \frac{\mu_0 c}{B_0^{(1)}}(\varepsilon_0 E_0^{(1)} + NE_0^{(1)}\alpha'_{XX} + NB_0^{(1)}\alpha'_{2XY}) \tag{89}$$

$$n''_{\text{av}z} = \frac{\mu_0 cN}{B_0^{(1)}}(E_0^{(1)}\alpha''_{XX} + B_0^{(1)}\alpha''_{2XY}) . \tag{90}$$

The power absorption coefficient in neper cm^{-1} is obtained directly from Eq. (90) as

$$A^{\text{axial}}_{\text{av}z}(\text{neper cm}^{-1}) = \frac{2\omega\mu_0 N}{B_0^{(1)}}(E_0^{(1)}\,\alpha''_{XX} + B_0^{(1)}\,\alpha''_{2XY}) \tag{91}$$

and the real and imaginary parts of the complex permittivity are obtained from

$$\varepsilon' = n'^2 - n''^2 ; \quad \varepsilon'' = 2n''n' . \tag{92}$$

3.2. *Circular birefringence*

The refractive and absorption indices for circular birefringence are obtained from the core equations

$$(n'_{\mathrm{L}Z} - n'_{\mathrm{R}Z}) = 2\mu_0\, cN\left(\frac{E_0^{(1)}}{B_0^{(1)}}\,\alpha''_{XY} - \alpha''_{2XX}\right) \tag{93}$$

$$(n''_{\mathrm{L}Z} - n''_{\mathrm{R}Z}) = 2\mu_0\, cN\left(\alpha'_{2XX} - \frac{E_0^{(1)}}{B_0^{(1)}}\,\alpha'_{XY}\right) \tag{94}$$

i.e. are expressions for the difference in refractive index in left and right circularly polarised probe radiation. The angle of rotation of a plane polarised probe is

$$\Theta = l\mu_0\, N\omega\left(\frac{E_0^{(1)}}{B_0^{(1)}}\,\alpha''_{XY} - \alpha''_{2XX}\right). \tag{95}$$

3.3. *Field induced axial and circular birefringence*

3.3.1. *Static magnetic flux density*

The difference between ensemble averaged refractive indices parallel and antiparallel with the externally applied static magnetic flux density B_z is the Wagnière-Meier effect, described by our simple core equations as

$$\langle n_{\uparrow\uparrow} - n_{\downarrow\uparrow}\rangle = 2\mu_0\, cNB_Z\,\langle\alpha^{(B)'}_{2XYZ}\rangle \tag{96}$$

$$\langle A^{\mathrm{axial}}_{\uparrow\uparrow} - A^{\mathrm{axial}}_{\downarrow\uparrow}\rangle = 4\mu_0\, N\omega B_Z\,\langle\alpha^{(B)''}_{2XYZ}\rangle\ . \tag{97}$$

This depends[78] on an odd parity totally antisymmetric tensor element $\langle\alpha^{(B)}_{2XYZ}\rangle$, which survives ensemble averaging, and conserves parity only in chiral ensembles. If the uni-axial effect were to be observed in achiral ensembles, it would signal parity non-conservation due to such causes as electroweak interactions between nucleus and electron, mediated[40] by the appropriate boson.

The original Faraday effect, circular birefringence due to B_Z, is described in this approximation ($\mathbf{M} \ll \mathbf{P}$) by

$$\langle\Theta_{\uparrow\uparrow} - \Theta_{\downarrow\uparrow}\rangle = 2l\mu_0\, N\omega c\, B_Z\,\langle\alpha^{(B)''}_{XYZ}\rangle \tag{98}$$

$$\langle A^{\mathrm{circ}}_{\uparrow\uparrow} - A^{\mathrm{circ}}_{\uparrow\uparrow}\rangle = -8\omega\mu_0\, NcB_Z\,\langle\alpha^{(B)'}_{XYZ}\rangle \tag{99}$$

giving the Verdet constant

$$V = l\mu_0 N\omega c \langle \alpha^{(B)''}_{XYZ} \rangle \tag{100}$$

$$\Theta = VB_Z \ . \tag{101}$$

It is seen that the Faraday effect depends on the even parity, totally antisymmetric component, $\langle \alpha^{(B)}_{XYZ} \rangle$, which survives ensemble averaging.[56,79] Note that the Faraday effect is c times greater, effectively, than the Wagnière-Meier effect. In this treatment we have left out of consideration the effect of field gradients. A more complete treatment includes these to eliminte the possibility of origin dependence in the molecular property tensors. For details, see the paper by Barron and Vrbancich.[5] The treatment given here is simplified, but sufficient to compare the origins of uni-axial and circular spectral effects of magnetic flux density.

3.3.2. *Circular and uni-axial spectral effects due to the electric conjugate product of a circularly polarised pump laser*

The P and T symmetries of the electric conjugate product of a circularly polarised pump laser, defined in Eq. (2) of this review, are the same as those of static magnetic flux density, i.e. P positive, T negative. On the grounds of fundamental symmetry we expect similar uni-axial and circular spectral effects. Writing the conjugate product as

$$\Pi_Z = \pm 2E_0^2 i\mathbf{k} = \pm (2E_0^2)_Z \, i \tag{102}$$

and the Voigt-Born perturbation as

$$\begin{aligned} \alpha'_{ij}(\Pi_k) &= \alpha'_{ij} \mp \alpha^{(\pi)''}_{ijZ} (E_0^2)_Z \ ; \\ \alpha''_{ij}(\Pi_k) &= \alpha''_{ij} \pm \alpha^{(\pi)'}_{ijZ} (E_0^2)_Z \ ; \end{aligned} \tag{103}$$

and similarly for α_{2ij}, we obtain the uniaxial birefringence[78]

$$\langle n_{\uparrow\uparrow \mathrm{L}} - n_{\uparrow\uparrow \mathrm{R}} \rangle = -2\mu_0 c N (E_0^2)_Z \langle \alpha^{(\pi)''}_{2XYZ} \rangle \tag{104}$$

which depends on the square of the electric field strength amplitude (volts per metre) of the pump laser, and is proportional to the odd parity ensemble average $\langle \alpha^{(\pi)''}_{2XYZ} \rangle$. This result leads to the interesting possibility of using intense pump lasers to observe parity non-conservation in achiral ensembles in the form of symmetry forbidden uni-axial birefringence.[78] Using mode locking and focusing, E_0 can reach 10^9 volts per metre.

The corresponding axial dichroism in the power absorption coefficient measured by the probe is

$$\langle A^{\text{axial}}_{\uparrow\uparrow \mathrm{L}} - A^{\text{axial}}_{\uparrow\uparrow \mathrm{R}} \rangle = 4\omega\mu_0 N(E_0^2)_Z \langle \alpha^{(\pi)\prime}_{2XYZ} \rangle \tag{105}$$

and has the same P characteristics as the axial birefringence.

The circular birefringence, the Pershan effect,[19–21] produced by switching the pump laser from left to right circular polarisation, and measured with a plane polarised probe, is

$$\langle \Theta_{\uparrow\uparrow \mathrm{L}} - \Theta_{\uparrow\uparrow \mathrm{R}} \rangle = 2l\mu_0 N\omega c(E_0^2)_Z \langle \alpha^{(\pi)\prime}_{XYZ} \rangle \tag{106}$$

and the corresponding circular dichroism is

$$\langle A^{\text{circ}}_{\uparrow\uparrow \mathrm{L}} - A^{\text{circ}}_{\uparrow\uparrow \mathrm{R}} \rangle = 8\omega\mu_0\, cN(E_0^2)_Z \langle \alpha^{(\pi)\prime}_{XYZ} \rangle\ . \tag{107}$$

For both birefringence and dichroism, the mediating property tensors are even to P, and the effects are observable without P violation in achiral and chiral ensembles of atoms and molecules. The same is true for the difference in rotation angle generated by the left to right switch in circular polarity of the pump, and measured by the plane of the probe.

These are examples of class one spin chiral effects,[78] class two effects depend on conjugate products such as

$$\mathbf{\Pi}_2 = \mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{B}_{\mathrm{L}}^{-} = \mathbf{E}_{\mathrm{R}}^{+} \times \mathbf{B}_{\mathrm{R}}^{-} = 2E_0B_0\mathbf{k} \tag{108}$$

which mediate inverse magnetochiral birefringence.[74] For more details see Ref. 78.

4. Optical NMR and ESR, Theory, Simulation, and Animation

As we have seen, the conjugate product of a circularly polarised laser field, $\mathbf{\Pi}$, produces circular and forward backward birefringence and dichroism. It also produces magnetisation through a phenomenon which has become known as the "inverse Faraday effect",[73] first proposed by Pershan[19] and measured by Pershan *et al.*[20,21] It appears that only this one measurement of the magnetisation has been reported. The symmetry characteristics of the circular birefringence accompanying the magnetisation of the Pershan effect have been discussed in Sec. 3. The pump laser induced magnetisation is potentially of great importance in what has become known as "nonlinear optical NMR and ESR",[58–61] in which an intense, circularly polarised, laser is used to supplement the customary homogeneous superconducting magnetic field of contemporary NMR and ESR spectrometers.

Magnetisation due to an intense, circularly polarised, laser was introduced theoretically by Pershan[19] in 1963, and shortly afterwards demonstrated experimentally by Pershan *et al.*[20,21] The quantum field theory of the effect was developed by Atkins and Miller,[80] and it is described by Shen[81] and Atkins[73] as the "inverse Faraday effect". Wagnière has demonstrated theoretically[4] that the inverse Faraday effect is due to the conjugate product (**Π**) of this article. He has also shown[74] that the related conjugate product

$$\mathbf{\Pi}_2 = \mathbf{E}^{+}_{\substack{\mathrm{L}\\ \mathrm{R}}} \times \mathbf{B}^{-}_{\substack{\mathrm{L}\\ \mathrm{R}}} \tag{109}$$

is responsible for magnetisation in a chiral ensemble, an effect which he has named "inverse magnetochiral birefringence or dichroism". As in the original magnetochiral effect of Wagnière and Meier,[1] the birefringence vanishes in an achiral ensemble such as water. An order of magnitude of the magnetisation produced by the inverse Faraday and the (smaller) inverse magnetochiral effects has been given by Wagnière,[4] (see Sec. 2). Using the interaction hamiltonian (59), Evans has demonstrated recently the phenomenon of spectral splitting due to **Π** of a circularly polarised pump laser, a contribution to which is the "inverse, or optical, Zeeman effect".[58] The *A* term of the semi-classical theory of the inverse Faraday effect[4] is the inverse Zeeman effect.

This analogy with the conventional Zeeman effect (spectral splitting due to **B**) has led naturally to the expectation[58–61] that **Π** can produce resonance phenomena analogous to those produced by **B** in a contemporary NMR or ESR spectrometer. By using a combination of **B** and **Π** in the same spectrometer, a blue shift of the resonance frequency can be induced,[59] which is potentially of great practical utility in the ultra high resolution resonance spectroscopy of complex systems[60] such as proteins.

Nuclear magnetic resonance (NMR) and electron spin resonance (ESR) are important contemporary analytical techniques which have been developed in many different directions. The conventional NMR of proteins, however, is constrained by contemporary technological limits, because a protein may have about two hundred peptide units, for example, and there are only about twenty amino acids, so that the proton resonances of the spectrum overlap heavily. Two-dimensional Fourier transform techniques effectively spread out the spectral information[60] over two different time delays of a pulse sequence, and generate a greater NMR "spectral dispersion", the term used for absolute frequency separation between different resonances, usually proton resonances. A typical pulse sequence of this type is $90° - t_1 - 90° - t_2$ with magnetism measured as a function of t_1 and t_2. If a technique can be devised that increases the resonance frequency by a significant amount during the t_1 period, it would allow a greatly increased resolution in the NMR investigation of proteins. Such a technique, based on the application of a circularly polarised pump laser, is proposed in this section, and referred to as "optical NMR".

Appendix 1 compares some of the basic concepts of magnetic and optical resonance. In both cases, simple interaction hamiltonians are used as a basis for the theoretical development, in terms respectively of the magnetic flux density, **B**, and the conjugate product, **Π**. Landé coupling develops between the parts of the interaction hamiltonian that depend on the magnet and the circularly polarised laser, a coupling which effectively mixes quantum numbers, allowing more transitions and resonances, analogously with the theory of the anomalous Zeeman effect.[73] This enriches the conventional NMR spectrum in addition to increasing the spectral resolution, the absolute frequency separation between proton resonances.

The nonlinear optical equivalent of the gyromagnetic ratio is the gyroptic ratio, the scalar ratio between the T negative, P positive angular polarisability and the electronic angular momentum. Classical considerations show that the gyroptic ratio is proportional to the effective electronic orbital area, inversely proportional to the magnitude of the resultant electronic orbital momentum, and proportional to the angular frequency in radians per second. It becomes infinite, theoretically, when the laser is tuned to a natural transition frequency of the molecule or atom, i.e. can be greatly amplified by resonance tuning of the circularly polarised laser to a natural transition frequency. It is also possible to develop the theory in optical NMR and ESR of chemical shifts, shielding constants, g values, Overhauser enhancement, spin-spin coupling, and hyperfine interaction.

The simplest representation of the combined hamiltonian of both laser and magnet is

$$\Delta H_c = -\hat{m}_k B_k - \hat{\alpha}_k'' E_0^2 \cdot \mathbf{k} \tag{110}$$

and it is possible to use this to provide an order of magnitude estimate of the shift to higher frequency produced in a conventional NMR spectrometer by the application of a laser field. In Sec. 2, an order of magnitude estimate produced an equivalent magnetisation for a laser intensity of about 400 watts per centimetre squared and a magnetic field of 1.0 Tesla. This was based on an order of magnitude estimate of the angular polarisability of $10^{-40}\,\mathrm{c^2m^2J^{-1}}$, a value which can also be obtained from measurements[82] of the Verdet constant in diamagnetic materials.

The additional electronic angular momentum imparted to a molecule by the circularly polarised pump laser enriches the conventional NMR or ESR spectrum by Landé coupling.[6] For simplicity, we develop the Landé factor for the angular momentum sum

$$\hat{\mathbf{J}} = \hat{\mathbf{I}} + \hat{\mathbf{L}} \tag{111}$$

where $\hat{\mathbf{L}}$ is the orbital electronic angular momentum and $\hat{\mathbf{I}}$ the nuclear angular momentum. Other combinations can be used for further theoretical development. Landé splitting can be shown using a simple hamiltonian such as

$$\Delta H_4 = -\gamma_N \hat{\mathbf{I}}\cdot\mathbf{B} - \gamma_\Pi \hat{\mathbf{L}}\cdot E_0^2\,\mathbf{k} \ . \tag{112}$$

Here $\mathbf{k}$ is a unit vector in the Z axis of the laboratory frame. The factor γ_π is the gyroptic ratio, defined by Eq. (7) in the operator definition of $\hat{\alpha}''$. The physical properties of γ_π are developed classically later in this section.

We first note the approximate vector relations

$$\hat{\mathbf{I}}\cdot\mathbf{B} \doteqdot (\hat{\mathbf{I}}\cdot\hat{\mathbf{J}})\,\hat{\mathbf{J}}\cdot\mathbf{B}/|\hat{\mathbf{J}}|^2 \tag{113}$$

$$\hat{\mathbf{L}}\cdot\mathbf{k} \doteqdot (\hat{\mathbf{L}}\cdot\hat{\mathbf{J}})\,\hat{\mathbf{J}}\cdot\mathbf{k}/|\hat{\mathbf{J}}|^2 \tag{114}$$

similar to those used in the theory of the anomalous Zeeman effect.[73] Here

$$2\hat{\mathbf{L}}\cdot\hat{\mathbf{J}} = \hat{J}^2 + \hat{L}^2 - \hat{I}^2 \tag{115}$$

$$2\hat{\mathbf{I}}\cdot\hat{\mathbf{J}} = \hat{J}^2 + \hat{I}^2 - \hat{L}^2 \tag{116}$$

from Eq. (115) in (113) and (116) in (114)

$$\Delta H_4 = -\gamma_N\left(\frac{\hat{J}^2 + \hat{I}^2 - \hat{L}^2}{2|\hat{\mathbf{J}}|^2}\right)\hat{\mathbf{J}}\cdot\mathbf{B} - \gamma_\pi\left(\frac{\hat{J}^2 + \hat{L}^2 - \hat{I}^2}{2|\hat{J}|^2}\right)E_0^2\hat{\mathbf{J}}\cdot\mathbf{k} \tag{117}$$

allowing one hamiltonian (117) to be written in terms of the z component of the total angular momentum $\hat{\mathbf{J}}$:

$$\Delta H_4 = -g_J\hat{\mathbf{J}}\cdot\mathbf{k} = -g_J\hat{M}_J, \quad M_J = J, \quad J-1, \ldots, -J \ . \tag{118}$$

where the Landé factor is

$$\begin{aligned} g_J = {} & \gamma_N B_Z\left(\frac{J(J+1) + I(I+1) - L(L+1)}{2J(J+1)}\right) \\ & + \gamma_\pi E_0^2\left(\frac{J(J+1) + L(L+1) - I(I+1)}{2J(J+1)}\right) . \end{aligned} \tag{119}$$

With the selection rule

$$\Delta M_J = \pm 1 \tag{120}$$

for the Z component M_J of the quantum number J, the NMR resonance frequency is defined simply by

$$\omega_R = g_J \, . \tag{121}$$

This result allows several contributions of practical interest. In the simple scheme used here the presence of two quantum numbers in the Landé factor g_J allows extra transitions which split the original NMR lines in a manner analogous with the textbook treatment[73] of the anomalous Zeeman effect due to **B**. This appears to give plenty of scope for analytical implementation of optical NMR.

4.1. *The gyroptic ratio*

In the specific case of a paramagnetic molecule or atom the gyroptic ratio can be developed simply in classical terms as follows. We begin by writing the angular polarisability for a given m and n from Eq. (61) as

$$\alpha''_k = -\frac{2e^2\omega}{\hbar(\omega_{mn}^2 - \omega^2)} \varepsilon_{ijk} r_{0i} r_{0j} \tag{122}$$

where

$$r_{0i} = \int \psi_m^* r_i \psi_n \, d\tau \tag{123}$$

$$r_{0j} = \int \psi_m^* r_j \psi_n \, d\tau \tag{124}$$

are expectation values of the position vectors defining the electric dipole moments

$$\mu_{0i} = e r_{0i} \, ; \quad \mu_{0j} = e r_{0j} \, . \tag{125}$$

We note that the quantity

$$A_{0k} = \varepsilon_{ijk} r_{0i} r_{0j} \tag{126}$$

is an electronic orbital area.

Classically[73] the magnetic dipole moment is defined as

$$|\mathbf{m}^{(c)}| = IA \tag{127}$$

where

$$I = e\left(\frac{v}{2\pi r}\right) \tag{128}$$

is the charge per unit time passing some point of an orbit r traversed by an electron travelling at speed v. For a circular orbit, the area A is

$$A = \pi r^2 \tag{129}$$

so that

$$|\mathbf{m}^{(c)}| = \left(\frac{e}{2m}\right) mrv \equiv -\gamma_e |\mathbf{L}| \tag{130}$$

where γ_e is the gyromagnetic ratio and $|\mathbf{L}|$ is the magnitude of the electronic orbital angular momentum

$$|\mathbf{L}| = mrv \ . \tag{131}$$

Now, instead of taking a circular area A, we take

$$A_{0Z} = \varepsilon_{ijZ} r_{0i} r_{0j} \equiv -A_1 \alpha''_Z \tag{132}$$

$$A_1 = \frac{\hbar(\omega_{mn}^2 - \omega^2)}{2e^2\omega} \tag{133}$$

which defines an effective magnetic dipole moment

$$m_{0Z} = I_0 A_{0Z} \tag{134}$$

implying that

$$\frac{\gamma_e}{\gamma_\pi} = -I_0 A_1 \ . \tag{135}$$

Choosing

$$I_0 = e\left(\frac{v}{2\pi r_{\text{av}}}\right) \tag{136}$$

where r_{av} is an average effective circular orbital radius, gives

$$\gamma_\pi = -\frac{2\pi r_{\text{av}}}{ev A_1}\gamma_e = \frac{\pi r_{\text{av}}^2}{|\mathbf{L}_{\text{av}}|} \cdot \frac{2e^2\omega}{\hbar(\omega_{mn}^2 - \omega^2)} \tag{137}$$

which is the desired classical expression for the electronic gyroptic ratio γ_π in a paramagnetic molecule in which there is net orbital electronic angular momentum.

The theory of chemical shifts, spin spin coupling, shielding constants, and Overhauser enhancement in optical NMR can be developed by using the proportionality between the angular polarisability and the real, classical, magnetic dipole moment

$$\alpha''_i = \left(\frac{\gamma_\pi}{\gamma_e}\right) m_i^{(\text{classical})} . \tag{138}$$

Details of this development are given in Ref. 61. For example, the shielding constant of optical NMR is defined by

$$\mathbf{\Pi}_{\text{eff}} = \mathbf{\Pi}(1 - \sigma) \tag{139}$$

implying that the observed resonances occur at different frequencies due to the chemical shift between the applied and effective conjugate product.

4.2. *Laser induced Overhauser enhancement*

Finally the magnetisation produced by the circularly polarised laser can be shown to result in Overhauser enhancement as described in Ref. 83. The final expression for the enhancement of the nuclear magnetic resonance signal produced by a circularly polarised laser used to saturate the electronic resonance is, in terms of the gyroptic ratio[83]

$$\frac{\langle I_Z \rangle}{\langle I_Z \rangle_{\text{thermal}}} = 1 + \frac{\gamma_\pi E_0^2}{2\gamma_n B_0} + \frac{A}{4\gamma_n \hbar B_0} \div \frac{\gamma_\pi E_0^2}{2\gamma_n B_0}$$

where γ_n is the nuclear gyromagnetic ratio and A a spin-spin constant, so that the Overhauser enhencement is maximised by the same set of factors which maximise the magnitude of the gyroptic ratio itself.

These considerations allow plenty of scope therefore for the practical development of laser NMR. Overhauser enhancement appears to be a particularly interesting possibility, because it is not adversely affected by inhomogeneities in the pump laser intensity. It appears that problems of power broadening due to pump laser inhomogeneities can be surmounted with a $90^\circ - t_1 - 90^\circ - t_2$ pulse sequence and conventional spin echo implementation, keeping the laser in CW mode with relatively low electric field strengths.

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Appendix 1: Tabular Comparison of Basic Concepts in Magnetic and Nonlinear Optical Resonance

This appendix tabulates the basic concepts of magnetic and optical resonance in terms of the gyromagnetic and gyroptic ratios. It is developed using the notation employed by Slichter[68] in the first chapters of his well-known text on conventional NMR and ESR.

Concept	Magnetic	Optical
Hamiltonian	$H = -\hat{\mathbf{m}} \cdot \mathbf{B}$ $= -\gamma_e \hbar B_0 I_Z$	$H = -E_0^2 \hat{\boldsymbol{\alpha}}'' \cdot \mathbf{k}$ $= -\gamma_e \hbar E_0^2 I_Z$
Eigenvalues of the hamiltonian	Multiples of $\gamma_e \hbar B_0$	Multiples of $\gamma_\pi \hbar E_0^2$
Allowed energies	$E_n = -\gamma_e \hbar B_0 M$ $M = I, I-1, \ldots, -I$ $\hat{\mathbf{J}} = \hbar \hat{\mathbf{I}}$	$E_n = -\gamma_\pi \hbar E_0^2 M$ $M = I, I-1, \ldots, -I$ $\hat{\mathbf{J}} = \hbar \hat{\mathbf{I}}$
Resonance condition	$\Delta E_n = \hbar\omega = \gamma_e \hbar B_0$ $\omega_{\mathrm{L}}^{B} = \gamma_e B_0$	$\Delta E_n = \hbar\omega = \gamma_\pi \hbar E_0^2$ $\omega_{\mathrm{L}}^{\pi} = \gamma_\pi E_0^2$
Gyromagnetic ratio (paramagnetic resonance)	$\gamma_e = -\dfrac{e}{2m}$ $\doteqdot 10^{12}\ \mathrm{C\,kgm^{-1}}$	–
Gyroptic ratio (paramagnetic resonance)	–	$\gamma_\pi = \dfrac{\pi r_{\mathrm{av}}^2}{\lvert \mathbf{J}_{\mathrm{av}} \rvert \hbar} \dfrac{2e^2\omega}{(\omega_{mn}^2 - \omega^2)}$ $\doteqdot 10^{-6}\ (\mathrm{V/m})^{-2}\mathrm{s}^{-1}$
Operator definitions	$\hat{\mathbf{m}} = \gamma_e \hat{\mathbf{J}}$ $\hat{J}_X = \dfrac{\hbar}{i}\left\{Y\dfrac{\partial}{\partial Z} - Z\dfrac{\partial}{\partial Y}\right\}$ etc.	$i\hat{\alpha}'' = \gamma_\pi \hat{\mathbf{J}}$
Expectation values	$\langle n \vert \hat{m}_i \vert n \rangle$	$-\dfrac{2e^2}{\hbar} \sum_{m \neq n} \dfrac{\omega}{\omega_{mn}^2 - \omega^2}$ $\times\, \varepsilon_{ijk} \operatorname{Im}(\langle n \vert r_i \vert m \rangle \langle m \vert r_j \vert n \rangle)$
Precession equation (classical)	$\dfrac{d\mathbf{m}}{dt} = \mathbf{m} \times (\gamma_e \mathbf{B})$	$\dfrac{d\boldsymbol{\alpha}''}{dt} = \boldsymbol{\alpha}'' \times (\gamma_\pi E_0^2 \mathbf{k})$
Rotating frame representation	$\mathbf{B}_{\mathrm{eff}} = \mathbf{B} - \dfrac{\boldsymbol{\Omega}}{\gamma_e}$ $\boldsymbol{\Omega} = -\gamma_e B_0 \mathbf{k}$	$(E_0^2\mathbf{k})_{\mathrm{eff}} = E_0^2\mathbf{k} - \dfrac{\boldsymbol{\Omega}}{\gamma_\pi}$ $\boldsymbol{\Omega} = -\gamma_\pi E_0^2 \mathbf{k}$

Spin lattice relaxation time	$\frac{1}{T_1} = W_\downarrow + W_\uparrow$ $\frac{W_\downarrow}{W_\uparrow} = \exp\left(\frac{\gamma_e \hbar B_0}{kT}\right)$ $\mathbf{B} = B_0 \mathbf{k}$	$\frac{1}{T_1} = W_\downarrow + W_\uparrow$ $\frac{W_\downarrow}{W_\uparrow} = \exp\left(\frac{\gamma_\pi \hbar E_0^2}{kT}\right)$
Eigenfunctions of the time dependent Schrödinger equation	$\Phi_{l,m}^{(B)}(t) =$ $\sum_{m=-l}^{l} C_m^{(B)} u_{l,m}^{(B)} e^{-iE_m^{(B)}(t)/\hbar}$ $E_m^{(B)} = -\gamma_e \hbar B_0 M$	$\Phi_{l,m}^{(\pi)}(t) =$ $\sum_{m=-l}^{l} C_m^{(\pi)} u_{l,m}^{(\pi)} e^{-iE_m^{(\pi)}(t)/\hbar}$ $E_m^{(\pi)} = -\gamma_\pi \hbar E_0^2 M$
Time dependent expectation values	$\langle \hat{\mathbf{m}}(t) \rangle$ $= \int \Psi^*{}_B(t) \hat{\mathbf{m}} \Psi_B(t) d\tau$ $= \gamma_e \int \Psi_B^*(t) \hat{\mathbf{J}} \Psi_B(t) d\tau$	$i \langle \hat{\boldsymbol{\alpha}}''(t) \rangle$ $= \int \Psi^*{}_\pi(t) \hat{\boldsymbol{\alpha}}'' \Psi_\pi(t) d\tau$ $= \gamma_\pi \int \Psi_\pi^*(t) \hat{\mathbf{J}} \Psi_\pi(t) d\tau$
Quantum representation of the classical precession frequency	$\langle \hat{\mathbf{m}}(t) \rangle$ $= \sum_{mm'} \gamma_e \hbar C_{m'}^{(B)*} C_m^{(B)}$ $\times \langle m' \| \hat{\mathbf{I}} \| m \rangle$ $\times \exp\left(\frac{i}{\hbar}(E_{m'}^{(B)} - E_m^{(B)})t\right)$ $\times \langle m' \| \hat{\mathbf{I}} \| m \rangle$ $= \int u_{lm}^* \hat{\mathbf{I}} u_{lm} d\tau$ $= 0;$ unless $m' = m \pm 1$	$i \langle \hat{\boldsymbol{\alpha}}(t) \rangle$ $= \sum_{mm'} \gamma_\pi \hbar C_{m'}^{(\pi)*} C_m^{(\pi)}$ $\times \langle m' \| \hat{\mathbf{I}} \| m \rangle$ $\times \exp\left(\frac{i}{\hbar}(E_{m'}^{(\pi)} - E_m^{(\pi)})t\right)$ $\times \langle m' \| \hat{\mathbf{I}} \| m \rangle$ $= \int u_{lm}^* \hat{\mathbf{I}} u_{lm} d\tau$ $= 0;$ unless $m' = m \pm 1$
Time derivative of the operator definition: $d\hat{F}/dt = i[H, \hat{F}]/\hbar$	$\hat{\mathbf{F}} = \hat{\mathbf{m}}$ $H = -\gamma_e \hbar B_0 I_Z$ $[I_X, I_Y] = i I_Z$	$\hat{\mathbf{F}} = i \hat{\boldsymbol{\alpha}}''$ $H = -\gamma_\pi \hbar E_0^2 I_Z$ $[I_X, I_Y] = i I_Z$
Vector operator equation of motion	$\frac{d\mathbf{I}}{dt} = \mathbf{I} \times \gamma_e \mathbf{B}$ $\frac{dI_X}{dt} = \gamma_e B_0 I_Y$ etc.	$\frac{d\mathbf{I}}{dt} = \mathbf{I} \times \gamma_\pi E_0^2 \mathbf{k}$ $\frac{dI_X}{dt} = \gamma_\pi E_0^2 I_Y$ etc.
Expectation value equation of motion, equivalent to the classical equation	$\frac{d}{dt} \langle \hat{\mathbf{m}} \rangle = \langle \hat{\mathbf{m}} \rangle \times \gamma_e \mathbf{B}$	$\frac{d}{dt} \langle \hat{\boldsymbol{\alpha}}'' \rangle = \langle \hat{\boldsymbol{\alpha}}'' \rangle \times \gamma_\pi E_0^2 \mathbf{k}$
Effect of alternating probe magnetic field	$\mathbf{B}_{\text{eff}} = \mathbf{k}\left(B_0 - \frac{\omega}{\gamma_e}\right) + B_1 \mathbf{i}$	$\mathbf{B}_{\text{eff}} = \mathbf{k}\left(E_0^2 - \frac{\omega}{\gamma_\pi}\right)$ $+ \frac{\gamma_e}{\gamma_\pi} B_1 \mathbf{i}$
$\pi/2$ pulse	$\gamma_e B_1 t = \frac{\pi}{2}$	$\frac{\gamma_e}{\gamma_\pi} B_1 t = \frac{\pi}{2}$

Bloch equation	$M_0 = \chi_0^B B_1$; $\frac{dM_Z}{dt} = \frac{M_0 - M_Z}{T_1}$ $+ \gamma_e (\mathbf{m} \times \mathbf{B})_Z$	$M_0 = \chi_0^\pi E_0^2$; $\frac{dM_Z}{dt} = \frac{M_0 - M_Z}{T_1}$ $+ \gamma_\pi (\mathbf{m} \times \mathbf{k})_Z E_0^2$

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