Chapter 11

QUESTIONS ABOUT THE FIELD $B^{(3)}$

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Introduction

In this summary, some questions concerning the nature of $B^{(3)}$ (see accompanying articles) are answered in a simple way by reference to the definition of $B^{(3)}$ in terms of the conjugate product. Some possible misconceptions and misinterpretations are anticipated and clarifications are made of the way in which $B^{(3)}$ should be interpreted on the basis of its definition in terms of the conjugate product, i.e. the antisymmetric part of light intensity.

1. *Is $B^{(3)}$ exactly like a static magnetic field?*

No, $B^{(3)}$ is a property of light, it is defined [1] through the antisymmetric part of the light intensity tensor, I_{ij}, in vacuo. It is a fundamental photon property [2] in the same way that the Stokes operators and Poynting vector, for example, are fundamental properties of light.

2. *If $B^{(3)}$ is a magnetic field, what is its source?*

The property $B^{(3)}$ is defined through the conjugate product of light, and has the units (tesla) and symmetry of frequency independent magnetic flux density. It vanishes if there is no electromagnetism present in the form of a travelling plane wave [3–5]. The source of $B^{(3)}$ is the same therefore as the source of the usual transverse electromagnetic plane waves which define the antisymmetric part of light intensity.

3. *Surely $B^{(3)}$, if it is a magnetic field, has an energy. If not, why?*

By using the Lorentz Lemma as in the accompanying paper [6] it is seen that $B^{(3)}$ is accompanied by an imaginary $iE^{(3)}$, the net contribution of $B^{(3)}$ and $iE^{(3)}$ to the electromagnetic energy is zero. The Poynting theorem is unchanged by the presence of $B^{(3)}$ and $iE^{(3)}$ in free space. The flux due to these fields over any closed surface is zero and no energy transport occurs in free space due to $B^{(3)}$ and $iE^{(3)}$. The frequency associated with $B^{(3)}$ and $iE^{(3)}$ is zero, and they have no Planck energy, and these fields do not contribute to the power (watts) radiated from aerials or accelerated

charges because they do not contribute to the Poynting vector. $B^{(3)}$ is proportional to the conjugate product, and the latter also does not contribute to electromagnetic energy density.

4. *If these fields have no energy, how are their effects observed?*

They do not contribute to the electromagnetic energy density, or light intensity, but these quantities take meaning [7] only when the light interacts with material. The field $B^{(3)}$ is defined as real and forms an interaction Hamiltonian with atoms and molecules. The field $iE^{(3)}$ is imaginary, and does not form a real interaction Hamiltonian. The variety of possible effects caused by $B^{(3)}$, assumed to act as a magnetic field, are described in Refs. [8–10]. Similarly, the conjugate product does not contribute to free space electromagnetic energy, but is partly responsible (with $B^{(3)}$) for the inverse Faraday effect (magnetization by light).

5. *How can $B^{(3)}$ (or the conjugate product) be created without the expenditure of energy?*

Energy is needed for transmitting electromagnetic waves (for example at a transmitting aerial as energy input to the transmitter minus heat wasted) and electromagnetic waves transmit energy to the receiving antenna, where it is picked up as a signal. Energy is carried outward in the form of electromagnetic waves [11]. The electromagnetic energy per unit area per unit time is given by the Poynting vector, and its magnitude is proportional to the *scalar* part of the radiation intensity. The *vector* part of radiation intensity is proportional to the conjugate product, or $B^{(3)}$, and cannot contribute to electromagnetic energy density. This does *not* mean that the $B^{(3)}$ vector does not exist, nor does it mean that the conjugate product does not exist. The latter is formed from a vector cross product of already formed oscillating electromagnetic fields, and energy has already been expended to create these oscillating fields at the transmitter.

6. *If $B^{(3)}$ is simply another way of describing the conjugate product, what advantage is there?*

The field $B^{(3)}$ is defined as the conjugate product divided by a scalar $iB^{(0)}$. It has the properties of frequency independent magnetic flux density, having the same symmetries and units of an ordinary uniform magnetic field. On these grounds it is indistinguishable from a regular magnetic field, and therefore it is assumed that it will interact with material matter in the same way, by, for example, setting up a Hamiltonian

with a magnetic dipole moment [8–10]. The conjugate product, in contrast, can form a Hamiltonian only with the antisymmetric part of atomic or molecular polarizability [1]. The Hamiltonian due to $\boldsymbol{B}^{(3)}$ (if it exists) should be proportional to the square root of light intensity, while the Hamiltonian due to the conjugate product should be proportional to the intensity itself. The magnitude of the conjugate product can, however, be expressed [9] as the magnitude of $\boldsymbol{B}^{(3)}$ squared. Experimental evidence for the conjugate product is also evidence for $|\boldsymbol{B}^{(3)}|^2$, and therefore for $\boldsymbol{B}^{(3)}$.

7. *If $\boldsymbol{B}^{(3)}$ is a magnetic field, what is its vector potential?*

One way of finding the vector potential, $\boldsymbol{A}^{(3)}$, associated with $\boldsymbol{B}^{(3)}$ is to express the individual fields making up the conjugate product in terms of their own vector potentials, and to carry out the cross product in terms of these. The vector potential of $\boldsymbol{B}^{(3)}$ will be independent of frequency, because the phase is eliminated by the conjugate product of the individual vector potentials, which are "retarded potentials" [12] in the usual way. In other words, causality means that the vector potential of $\boldsymbol{B}^{(3)}$ is formed from the retarded potentials of the individual fields making up the conjugate product. In a source free medium, the same procedure applies, but in this case the vector potentials of the individual fields of the conjugate product contain no reference to current or charge density, in the usual way [12].

8. *If the vacuum has no charge, how can it create a magnetic field, $\boldsymbol{B}^{(3)}$?*

In the same way that electromagnetic waves are described without reference to charge or current in a source free medium, such as a vacuum. In a source free medium the charge and current densities appearing in Maxwell's equations, or Proca's equation, are vanishingly small. Electromagnetic waves are self-propagating in a vacuum, and are transverse, as usual. The conjugate product (and therefore the antisymmetric part of light intensity) is formed from the vector product of the magnetic part of a wave with its complex conjugate, and $\boldsymbol{B}^{(3)}$ is the conjugate product divided by $iB^{(0)}$. Clearly, the electromagnetic waves must have originated from a charge and current density, but when the medium is "source free", it is stated [13] that these go to zero at infinity and the electromagnetic wave is a plane wave in vacuo.

9. *Surely, if the conjugate product is imaginary, it cannot have a physical meaning?*

It is true that the conjugate product is a pure imaginary quantity, but it can form a real interaction Hamiltonian [2, 14–16] by multiplication with another imaginary quantity, the antisymmetric part of atomic or molecular polarizability. The conjugate product $\boldsymbol{B}^{(1)} \cdot \boldsymbol{B}^{(2)}$ of the magnetic part of the electromagnetic wave, $\boldsymbol{B}^{(1)}$, with its complex conjugate, $\boldsymbol{B}^{(2)}$, is the imaginary quantity $iB^{(0)}\boldsymbol{B}^{(3)}$. The latter is $iB^{(0)}$ multiplied by the real magnetic field $\boldsymbol{B}^{(3)}$.

10. *Why is light intensity a tensor, and how can a tensor be created in a vacuum?*

Light intensity is a tensor because it is the product of two vector quantities, i.e. electric or magnetic parts of the electromagnetic wave. Mathematically, these two vectors can form the symmetric and antisymmetric parts of a rank two tensor. How do we know that this happens in a vacuum? The answer is that we know nothing whatsoever about light unless the latter interacts with material matter of some kind, a simple example being an electron. If such an interaction occurs, and light is scattered, then we know that there exists the phenomenon of antisymmetric light scattering [17] which can be explained only through the antisymmetric part of scattered light intensity. The latter is a pure imaginary quantity, but this does not mean that it is unphysical. It is directly proportional to the pure imaginary conjugate product, and therefore to the pure real $\boldsymbol{B}^{(3)}$. The latter is the most fundamental element of the antisymmetric part of light intensity. If the light beam were to consist of only one photon, there would still be a light intensity tensor, and therefore $\boldsymbol{B}^{(3)}$ is a fundamental photon property.

11. *Your assertion about a $\boldsymbol{B}^{(3)}$ contradicts the fact that electromagnetic waves are transverse?*

The individual waves making up the conjugate product [2] are both transverse to the direction of propagation and obey Gauss's theorem. The conjugate product is a longitudinal axial vector which gives $\boldsymbol{B}^{(3)}$, which in turn is independent of the phase and also obeys Gauss's theorem. The divergence (del) of $\boldsymbol{B}^{(3)}$ vanishes and there is no contradiction.

12. *You say that $\boldsymbol{B}^{(3)}$ in quantum form is proportional to angular momentum, is this compatible with fundamental symmetry in a vacuum, where there is no charge?*

The definition of $\boldsymbol{B}^{(3)}$ in quantum field theory [8] is

$$\hat{B}^{(3)} = B^{(0)} \frac{\hat{J}}{\hbar}, \qquad (1)$$

where $\hat{J}$ is a photon angular momentum, and $\hbar$ the reduced Planck constant. There are three elementary discrete symmetries in nature $\hat{C}$, the operator of charge conjugation; $\hat{P}$, the parity inversion operator, and $\hat{T}$, the motion reversal operator. In particle physics $\hat{C}$ is also the operator which produces an antiparticle from a particle [18] by reversing its charge. For precise definitions of $\hat{C}$, $\hat{P}$, and $\hat{T}$, see Ref. [18]. Equation (1) is a law of physics, and it is not changed if $\hat{C}$, for example, is applied to each symbol on both sides. In so doing, $\hat{C}(B^{(0)}) = -B^{(0)}$ because the charge parity of the photon is negative [18]. All spatio-temporal quantities of any kind are positive under $\hat{C}$ [18] by definition, so that angular momentum is unchanged by $\hat{C}$. Similarly, Eq. (1) is unchanged by (i.e. is invariant to) $\hat{P}$ and $\hat{T}$. It also has the right units, because $\hbar$ in quantum mechanics is the unit of angular momentum. Equation (1) was first derived in Ref. [1a].

13. *Yes, but how can you make a magnetic field from angular momentum when there is no charge present, as in a vacuum?*

The field $\hat{B}^{(3)}$ is formed from angular momentum by multiplying the latter by a scalar amplitude $B^{(0)}$ which is $\hat{C}$ negative. The origin of $B^{(0)}$ is the origin of electromagnetism in vacuo, because if $B^{(0)}$ vanished there would be no electromagnetism. The fact that $B^{(0)}$ is $\hat{C}$ negative means that it originates in electric charge, because the only effect of $\hat{C}$, by definition, is to reverse the sign of charge. Conventionally, $B^{(0)}$ in a source free medium originates at a current at infinity. In a medium with sources, it originates in current density. So there *is* charge present, but it is located in matter "infinitely removed from the vacuum". This is why the charge parity of the photon is negative. For example, the potential four-vector A_μ is negative to $\hat{C}$, and so are electric and magnetic field components of an electromagnetic wave. On the other hand, the spatio-temporal parts of an electromagnetic wave cannot be changed by $\hat{C}$. For example the phase of a plane wave is unchanged by $\hat{C}$, and neither is its state of polarization, usually described by unit vectors in a circular basis.

14. *If $\boldsymbol{B}^{(3)}$ is a property of light in vacuo, it must be travelling at c, and cannot be static, or uniform?*

Since $\boldsymbol{B}^{(3)}$ is the expectation value of the operator $\hat{B}^{(3)}$, a fundamental property of one photon, it travels with the photon in a vacuum at the speed of light (assuming that the photon has no mass), or more slowly if the photon has mass. The antisymmetric part of light intensity is therefore built up statistically from the $\hat{B}^{(3)}$ operators of each individual photon, to give a macroscopic average. This is the proper way to describe $\boldsymbol{B}^{(3)}$, and the latter is clearly not the same as a static magnetic field. Similarly, the vector potential $\boldsymbol{A}^{(3)}$ is a statistical property of photons, and so is the conjugate product. They are all described in terms of creation and annihilation operators [10].

15. *Since there is no experimental evidence for $\boldsymbol{B}^{(3)}$, your assertion is unfounded?*

On the contrary, there is plentiful evidence for the antisymmetric part of light intensity, for example in Refs. [19–23]. This is evidence for the conjugate product and therefore for the product $iB^{(0)}\boldsymbol{B}^{(3)}$ whose scalar magnitude is $|\boldsymbol{B}^{(3)}|^2$ squared. The fact that there is a $|\boldsymbol{B}^{(3)}|^2$ *squared* is experimentally well established, for example through data from: antisymmetric light scattering [19]; ellipse self rotation [20]; magnetization by light in the inverse Faraday effect [21]; the optical Faraday effect [22]; and light induced frequency shifts in atomic spectra [23] ("light shifts"). Recently, it has been found that circularly polarized light shifts nuclear magnetic resonances [24]. The conjugate product has actually been referred to [21, 23] as an "effective magnetic field". It is expected that if $\boldsymbol{B}^{(3)}$ acts as a magnetic field, that there should be phenomena due to it and proportional to the square root of intensity. It is clear already however that $\boldsymbol{B}^{(3)}$ is the fundamental unit of antisymmetric light intensity, and is a fundamental property of a single photon, if circularly polarized.

16. *Such data may be acceptable for the effect of $\boldsymbol{B}^{(3)}$ squared, but why have effects due to $\boldsymbol{B}^{(3)}$ itself never been observed?*

The majority of light shift data have been obtained with light which is incoherent, or linearly polarized, so that $\boldsymbol{B}^{(3)}$ is zero because the antisymmetric part of light intensity is zero. Effects due to $\boldsymbol{B}^{(3)}$ itself are expected when there is a degree of circular polarization in the pump laser, as discussed elsewhere [8]. There has been only one inverse Faraday effect experiment reported [21], and the majority of data were obtained for

diamagnetic liquids in which there is no permanent magnetic dipole moment, so that magnetization due to $|\boldsymbol{B}^{(3)}|^2$ is expected, but not due to $\boldsymbol{B}^{(3)}$. A limited amount of data were obtained [21] in doped CaF_2 glasses at low temperature. If the net magnetic dipole moment in these glasses is non-zero, magnetization due to $\boldsymbol{B}^{(3)}$ is expected, and the available data have been reinterpreted [8] to account for this possibility.

17. *You say that $\boldsymbol{B}^{(3)}$ vanishes in linear polarization, if so, how can it be a fundamental property of the photon?*

The field $\boldsymbol{B}^{(3)}$ vanishes in linear polarization because the antisymmetric part of light intensity has opposite sign for right and left circular polarization, meaning that the vector $\boldsymbol{B}^{(3)}$ nets to zero when there is 50% of right and 50% of left circularly polarized components in the beam.

18. *If the antisymmetric part of light intensity is a tensor, why is $\boldsymbol{B}^{(3)}$ a vector?*

The antisymmetric part of a rank two tensor can be expressed as a rank one axial vector through the intermediacy [25] of the Levi-Civita symbol, the rank three totally antisymmetric unit tensor ϵ_{ijk}. Therefore the conjugate product is an axial vector as well as a polar, rank two, tensor. This is consistent with the fact that the conjugate product is a cross product of two vectors, either of two polar electric field vectors, or of two axial magnetic field vectors. The conjugate product is also expressible as the antisymmetric part of a light intensity tensor. Therefore the magnetic field $\boldsymbol{B}^{(3)}$ is also either a rank one axial vector or a rank two polar tensor. In its rank two form (see accompanying article), $B_{ij}^{(3)}$ is proportional to a non-zero rotation generator, which is an angular momentum tensor within a factor of $\hbar$.

19. *If evidence is available for $|\boldsymbol{B}^{(3)}|^2$, and none becomes available for the effect of $\boldsymbol{B}^{(3)}$ at first order, where would that leave your theory?*

Such an eventuality would imply that $\boldsymbol{B}^{(3)}$ does not form a non-zero interaction Hamiltonian with a magnetic dipole moment, and would obviously not mean that $\boldsymbol{B}^{(3)}$ is zero, because effects due to the conjugate product exist experimentally. More generally, it might mean that there exists a "hidden symmetry" in nature which forbids effects due to $\boldsymbol{B}^{(3)}$, but allows effects due to $\boldsymbol{B}^{(3)}$ squared. To assert that $\boldsymbol{B}^{(3)}$ is not a magnetic field would be paradoxical in the current state of knowledge, because $\boldsymbol{B}^{(3)}$ has

the $\hat{C}$, $\hat{P}$, and $\hat{T}$ symmetries and units (tesla, or gauss) of such a field, and since $|\boldsymbol{B}^{(3)}|^2$ is non-zero, then so is $\boldsymbol{B}^{(3)}$. Also, if $\boldsymbol{B}^{(3)} - B^{(0)}\boldsymbol{k}$ were zero, then the antisymmetric part of light intensity would vanish, contradicting observation. The latter is also a solution of the Proca equation as we see in the accompanying article. This is an open question at present, because we have so little discriminating data, in the case of magnetization by light, only one series of experiments [21]. These experiments have never been repeated, and this means, perhaps, that they are difficult, or that others have tried to repeat the experiment and failed. If so, the original data are open to reasonable doubt. This would not mean that the conjugate product does not exist, because there are other sources of evidence for it, namely antisymmetric light scattering phenomena of various kinds [25]. This illustrates the present state of the art.

20. *What about your assertion of $i\boldsymbol{E}^{(3)}$, wouldn't this give rise to large effects, which should easily have been observed by now?*

The field $i\boldsymbol{E}^{(3)}$ is pure imaginary, and this is interpreted, in the conventional way described for example by Jackson [27], to mean that it has no physical existence, because its real part is zero. Light can cause electric polarization, the phenomenon of optical rectification [26], but this is observable in linear polarization, and then only in chiral media. It is not possible to form a longitudinal electric field from the conjugate product, because this would violate $\hat{T}$ symmetry, as described in the accompanying article. Therefore we interpret this to mean that there is no longitudinal electric field, and that there are no physical effects due to such a field. The emergence of $i\boldsymbol{E}^{(3)}$ from Lorentz's Lemma is a formal way of describing, and is a consequence of, the fact that the longitudinal $\boldsymbol{B}^{(3)}$ does not contribute to electromagnetic energy density in vacuo.

21. *This is all very well, but if $\boldsymbol{B}^{(3)}$ is real it magnetizes matter, and for that we need an interaction energy. If $\boldsymbol{B}^{(3)}$ does not contribute to field energy how can it magnetize?*

By reference to Jackson [27], pages 190 ff., the work done per unit time per unit volume by electromagnetic fields is $\boldsymbol{J}\cdot\boldsymbol{E}$, and represents the conversion of electromagnetic energy into mechanical or heat energy. The magnetic field does no work on a system of charges and currents, because for one charge q, the magnetic force is perpendicular to the charge's velocity $\boldsymbol{v}$. If there exists a continuous distribution of charge and current, the total rate of doing work by the fields in a finite volume V is the volume integral $\int \boldsymbol{J}\cdot\boldsymbol{E}d^3x$. The real field $\boldsymbol{B}^{(3)}$ does not contribute to this integral, and therefore does not contribute to the macroscopic

Poynting theorem, which is, essentially, a re-expression [27] of this integral in terms of the electromagnetic energy density U and the Poynting vector. If the total energy of the particles within the volume V is En, and assuming no particles move out of the volume,

$$\frac{dEn}{dt} = \int_V \boldsymbol{J}\cdot\boldsymbol{E}\,d^3x. \qquad (2)$$

So $\boldsymbol{B}^{(3)}$ does not change the total energy of particles within the volume V, and therefore does not contradict the law of conservation of energy. It follows that the concept of conjugate product is also consistent with conservation of energy.

22. *But you have still not explained why $\boldsymbol{B}^{(3)}$ can magnetize without contradicting the law of conservation of energy. If $\boldsymbol{B}^{(3)}$ does not change En how can it magnetize?*

To explain why we must consider the presence of atoms and molecules in material matter subject to $\boldsymbol{B}^{(3)}$. Following Jackson's explanation [27], electronic motion within atoms and molecules is an extra source of charge and current, a source which contributes to the conduction current $\boldsymbol{J}$. Then Poynting's theorem describes the work done on all currents by the electric field per unit time. Included is the effective molecular (or atomic) current $\partial\boldsymbol{P}/\partial t + c\nabla\times\boldsymbol{M}$ (in Gaussian units) which involves polarization and magnetization. Therefore $\boldsymbol{B}^{(3)}$ contributes to the magnetization within this current, but does not change the total energy of the system of charges and currents, made up of particles, atoms and molecules. Similarly the conjugate product contributes to the magnetization. Following Jackson's explanation [27], the energy associated with the effective molecular current is "absorbed" into the energy stored in the field, since it (the energy) is a property of the medium and is in general stored energy (i.e. reactive power) which involves no time-average dissipation.

23. *How do you explain this in molecular terms?*

Following Barron [14], the energy, W, of the system of charges and currents is expanded in a Taylor series about the system energy W_0 in the absence of the field,

$$W = W_0 + \left(\frac{\partial W}{\partial B_i^{(3)}}\right)_0 B_i^{(3)} + \ldots, \qquad m_i = -\left(\frac{\partial W}{\partial B_i^{(3)}}\right)_0. \qquad (3)$$

The field $\boldsymbol{B}^{(3)}$ forms a part of the total energy W by multiplication with a magnetic dipole moment, m_i which is a property of an atom or molecule. We find that,

$$W_0 = W - \left(\frac{\partial W}{\partial B_i^{(3)}}\right)_0 B_i^{(3)} - \ldots, \qquad (4)$$

i.e., the total energy in the absence of the field is equal to the total energy in the presence of the field, so that energy is conserved. In the same way, the conjugate product, denoted by the vector $\boldsymbol{\Pi}_i$, contributes through another type of molecular property, $(\partial W/\partial\boldsymbol{\Pi}_i)_0$.

24. *Apart from these consideration of energy, every textbook states that longitudinal fields in vacuo vanish because of the Gauss and Ampère laws. Surely your theory fails because of this?*

The textbooks refer to longitudinal *waves* of finite frequency, whereas $\boldsymbol{B}^{(3)}$ has no phase dependence. For this reason its divergence vanishes, and this is consistent with Ampère's law. It has no phase dependence because it is defined as the conjugate product divided by $iB^{(0)}$, and the conjugate product removes the phase. Therefore $\boldsymbol{B}^{(3)}$ is a wave of infinite wavelength or infinitely low frequency. In contrast a longitudinal wave must depend on the phase, and its divergence cannot be zero.

25. *But in this case the energy density associated with $\boldsymbol{B}^{(3)}$ in free space must be infinite, not zero, as you assert?*

Formally, the energy density associated with $\boldsymbol{B}^{(3)}$ at each point in space is given in S.I. units by $B^{(3)2}/2\mu_0$. However, the field $\boldsymbol{B}^{(3)}$ does not contribute to the time averaged Poynting vector. The flux of energy due to the cross product of $\boldsymbol{B}^{(3)}$ with the transverse $\boldsymbol{E}^{(1)}$ or $\boldsymbol{E}^{(2)}$ is therefore zero over any closed surface. Corson and Lorrain [28], for example, show that the expression just given for the energy density can be rewritten as $\frac{1}{2}\boldsymbol{J}\cdot\boldsymbol{A}^{(3)}$, and that this [28] is contradictory, indicating that the assignment of an energy density to a point in space is arbitrary and meaningless except as a means of computing the overall magnetic energy. The expression $B^{(3)2}/2\mu_0$ for magnetic energy density [28] assigns a finite value to all points where $\boldsymbol{B}^{(3)}$ is not zero, but the expression $\frac{1}{2}\boldsymbol{J}\cdot\boldsymbol{A}^{(3)}$ for magnetic energy density means that it is zero if there is no conduction current density $\boldsymbol{J}$. It is meaningless therefore [28] to ask whether the energy density due to $\boldsymbol{B}^{(3)}$ in free space resides in the field or in the current $\boldsymbol{J}$. As we have seen, the total rate of doing work by an electro-

magnetic field in a finite volume V is the integral $dEn/dt = \int_V \boldsymbol{J}\cdot\boldsymbol{E}d^3x$, and $\boldsymbol{B}^{(3)}$ does not contribute to this, and therefore does not contribute to the Poynting vector or to the electromagnetic energy density U. Therefore, the formal expression $B^{(3)2}/2\mu_0$ for the energy density of $\boldsymbol{B}^{(3)}$ must be interpreted to imply the existence of an equivalent energy density $\frac{1}{2}\boldsymbol{J}\cdot\boldsymbol{A}^{(3)}$ situated in a source of current density infinitely far from free space. This energy density is not transferred by the field $\boldsymbol{B}^{(3)}$ to a system of charges and currents. Similarly, the conjugate product to which $\boldsymbol{B}^{(3)}$ is proportional does not contribute to the Poynting vector, but at the same time is observed to produce effects when the light beam interacts with matter.

26. *But it is not possible for the energy density of a magnetic field to be zero, so how do you explain this?*

Following Jackson [27], the energy in the field $\boldsymbol{B}^{(3)}$ is by definition the total work done to establish it, but, as expressed by Shore [29], this work takes meaning only when $\boldsymbol{B}^{(3)}$ interacts with matter, and as we have seen, $\boldsymbol{B}^{(3)}$ does no work per unit time per unit volume on matter, because it does not contribute to the volume integral $\int_V \boldsymbol{J}\cdot\boldsymbol{E}d^3x$ which defines the macroscopic Poynting theorem. Similarly, following Duffin [11], crossed static and magnetic fields do not contribute to the Poynting vector. This does not mean, of course, that these fields do not exist. Therefore the *formal* expression $B^{(3)2}/2\mu_0$ for the energy density of $\boldsymbol{B}^{(3)}$ is just that, a formal expression.

27. *This may be acceptable classically, but what about the quantum field theory?*

The classical $\boldsymbol{B}^{(3)}$ is the expectation value of the operator $\hat{B}^{(3)}$, and the latter is an operator which has no frequency in its definition. The Planck law means then that it has no energy equivalent to frequency multiplied by h, the Planck constant. This is consistent with the fact that the classical $\boldsymbol{B}^{(3)}$ does no work per unit time per unit volume on a system of charges and currents, atoms and molecules.

28. *But if $\boldsymbol{B}^{(3)}$ has no frequency, it cannot form wave packets, doesn't this lead to profound difficulties of interpretation?*

Not at all, the conjugate product also falls into this category, and so does the symmetric and antisymmetric parts of light intensity. In a laser beam which is circularly polarized, these are constant quantities, in the same way that the intensity itself is a constant (watts per square meter). If necessary, the formation of wave packets [27] associated with $\boldsymbol{B}^{(3)}$ can be thought of in terms of the wave packets of the individual fields making up the conjugate product, (a cross product of two plane waves) and Fourier transforms applied to the cross product.

29. *Isn't your $\boldsymbol{B}^{(3)}$ just a trivial consequence of the fact that the Maxwell equations are differential equations in fields, to which a constant field makes no difference?*

The field $\boldsymbol{B}^{(3)}$ is formed from the vector cross product of the fields $\boldsymbol{B}^{(1)}$ and $\boldsymbol{B}^{(2)}$, its complex conjugate, and is not independent of these fields. As shown in detail in the accompanying article, $\boldsymbol{B}^{(1)}$, $\boldsymbol{B}^{(2)}$ and $\boldsymbol{B}^{(3)}$ form a cyclic Lie algebra, which is the same as the Lie algebra of rotation generators, and, to within a factor $\hbar$, quantized angular momentum operators. Therefore $\boldsymbol{B}^{(3)}$ is not just an arbitrary constant field plucked out of nothing. It is carefully defined in terms of the usual oscillating plane waves, which are the usual solutions of Maxwell's equations in free space.

30. *You make a great deal out of the fact that the photon may have mass, and that this allows longitudinal fields in free space, but isn't it true that these fields would be minute, that photon mass has never been observed or measured, and is so small that it is never likely to be measured?*

It is essential not to confuse the frequency independent field $\boldsymbol{B}^{(3)}$ with the *frequency dependent* longitudinal solutions of the Proca equation considered by Einstein, de Broglie, Proca, Schrodinger, Heisenberg, Vigier, Wigner, and many others, as reviewed in the accompanying article. Frequency dependent longitudinal fields are indeed minute, being a factor $(m/\nu)^2$ smaller than the transverse, frequency dependent fields from the Proca equation. As shown in the accompanying article, the field $\boldsymbol{B}^{(3)}$ from the Proca equation is scaled by $\exp(-\xi Z)$, where ξ is a minute quantity, with the dimensions of inverse meters, and which is zero in the Maxwellian limit, in which we recover $\boldsymbol{B}^{(3)}$. Therefore $\boldsymbol{B}^{(3)}$ is perfectly consistent with the existence of finite photon mass. For all practical purposes, $\boldsymbol{B}^{(3)}$ is a solution of the Proca equation, as well as the d'Alembert equation of Maxwellian electrodynamics. Therefore $\boldsymbol{B}^{(3)}$ is consistent with all that is known of the classical electromagnetic plane wave.

31. *Yes, but this is all just theory, what experimental evidence do you have for finite photon mass?*

The data on finite photon mass from the time of Cavendish to about 1970 are reviewed by Goldhaber and Nieto [30], an article which summarizes experimental limits from various sources. The data up to about 1992 are summarized by Vigier, as in the accompanying review. These are experimental upper limits on finite photon mass. These articles show that a great deal of careful experimental work has been carried out in this area. The existence of $\boldsymbol{B}^{(3)}$ is consistent with the possibility that the mass of the photon is finite. The existence of $\boldsymbol{B}^{(3)}$ is, however, also consistent with the Maxwell and d'Alembert equations, where photon mass is identically zero. Therefore the existence of $\boldsymbol{B}^{(3)}$ does not *depend* on the existence of finite photon mass, and the magnitude of $\boldsymbol{B}^{(3)}$ is such that its effects are measurable through various effects of the conjugate product, or anti-symmetric part of the light intensity tensor.

32. *If the mass of the photon is finite, how can there be a speed of light, wouldn't it have to be said that light cannot travel at the speed of light?*

The idea of finite photon mass appears to have originated with Einstein in letters to Besso circa 1916, when Einstein was developing general relativity. Therefore Einstein himself appears not to have seen any contradiction between finite photon mass and special relativity. The idea was developed by de Broglie and by Proca, who published his equation in 1930. Later, de Broglie took up the subject in some eighty papers and monographs, as summarized in the accompanying article. In the mid fifties, Bass and Schrödinger provided a thermodynamic explanation of why longitudinal, *frequency dependent*, fields from the Proca equation do not upset the Planck radiation law. Essentially, the second principle of special relativity asserts that there is a constant c, which is invariant to Lorentz transformation. This constant has been identified with the speed of light, so that in quantum field theory it is frequently asserted that the mass of the photon is identically zero in all frames of reference. This has become a tenet of gauge theory. However, there is no experimental evidence at all for this assertion, because there is no way of testing it experimentally. For example, the range of the electromagnetic field is infinite if the mass of the photon is zero. How does one test an infinite range? The contemporary explanation for finite photon mass within special relativity has been summarized by Vigier, and has been briefly described in the accompanying article. The constant c remains a constant, but is no longer the speed of light in any frame other than the rest frame of the photon. The latter becomes a relativistic particle.

33. *One moment, this is nonsense, the Michelson-Morley experiment shows that the speed of light is constant to high accuracy, and this experiment has been repeated many times by some of the best experimentalists, so what are you talking about?*

In common with several other experiments, reviewed by Goldhaber and Nieto [30] and by Vigier [31], the Michelson-Morley experiment sets an *upper limit* to photon mass. In other words the data show that the photon mass cannot be greater than some value m. The interferometric device used in this type of experiment relies on light arriving from a few miles distant, and clearly does not test the assertion that the range of electromagnetism is infinite.

34. *But cosmological sources are millions of light years distant, isn't this enough to test the range of electromagnetism?*

The light arriving at Earth from far distant sources is, in Hubble's words, "tired light". Hubble was aware of the postulate of finite photon mass, and by "tired light" he meant that its speed had slowed considerably *below* the constant c (3×10 m s^{-1}), and that the light had become "tired" after a long journey. This was inferred, as reviewed by Vigier, from anomalous red shifts and other types of astronomical measurements. The gravitational red shift, as reviewed, for example, by Bondi [32] is another sign of finite photon mass. The radius of the universe is finite, and there is no cosmological source available that can be used to test the hypothesis that the field of the photon has an infinite range. However, despite the fact that photon mass is very small indeed (maybe as small as 10^{-68} kgs), there are clear signs that it is finite. These signs arrive in several different kinds of data, so the belief that photon mass will never be measured is quite wrong. Indeed, the available data *clearly contradict* the assertion that the field of the photon has an infinite range.

35. *Yes, but then why is c always asserted to be 3×10^8 ms^{-1} if there is "tired light"?*

Because this value is arrived at using laboratory sources, or, as in the original Michelson Morley experiment, using delays caused by light travelling over a range of only a few miles. Gravitational and anomalous red shifts are observed using light arriving from sources many light years distant.

36. *Doesn't finite photon mass make a pig's breakfast out of contemporary gauge theory?*

Contemporary gauge theory [33] frequently asserts that the mass of the photon is identically zero, and freely contradicts the experimental evidence to the contrary, including all the evidence for "tired light", gravitational red shifts and so on. This assertion is at best an approximation, and should be regarded as such. There is a considerable amount of contemporary thought which is aimed at including finite photon mass in quantum field theory, an example is the work of Huang [34], who has incorporated finite photon mass in SU(5) (grand unified field theory), and GWS (unified electroweak theory). The accompanying article is an elementary account of how finite photon mass can be incorporated in field theory using the Dirac condition, for example. There are probably many other ways of modifying field theory for finite photon mass.

37. *We seem to have drifted a long way from your assertion that there is a field* $\boldsymbol{B}^{(3)}$, *what has* $\boldsymbol{B}^{(3)}$ *got to do with finite photon mass?*

The result of the Proca equation of 1930 is that $\boldsymbol{B}^{(3)} = B^{(0)} \exp(-\xi Z)\boldsymbol{k}$ where the constant ξ is about 10^{-26} m^{-1} for a photon mass of about 10^{-68} kg. This result considerably reinforces our independent result from the Maxwell equations in free space, i.e. that $\boldsymbol{B}^{(3)}$ can be obtained from the conjugate product divided by $iB^{(0)}$. The reason is that ξ is so small that the exponential is unity to an excellent approximation for any laboratory dimensions of Z (a meter perhaps): the $\boldsymbol{B}^{(3)}$ fields from these independent derivations are identical for all practical purposes. If $\boldsymbol{B}^{(3)}$ did not exist, then both field theories would be incorrect, meaning that the basic structure of electromagnetic theory would have to be re-examined. Further progress can be made by devising experiments to look for $\boldsymbol{B}^{(3)}$. This field is consistent with finite photon mass.

38. *A clever argument, perhaps, but hasn't your assertion about* $\boldsymbol{B}^{(3)}$ *been negated using simple symmetry [35]?*

The defining equations for $\boldsymbol{B}^{(3)}$ from both sources just mentioned conserve the known discrete symmetries of nature, namely $\hat{C}$, $\hat{P}$, and $\hat{T}$ and products thereof, i.e. $\hat{C}\hat{P}$, $\hat{C}\hat{T}$, $\hat{P}\hat{T}$, and $\hat{C}\hat{P}\hat{T}$. The way to see this is to apply a symmetry operator such as $\hat{C}$ to each and every symbol in the defining equations. (To do this, one must be sure to know the $\hat{C}$ symmetry of each symbol, in particular, it must be realized that $B^{(0)}$ is negative under $\hat{C}$.) If this is done properly, the same equation is recovered unchanged. Therefore the defining equation conserves the symmetry, in this case $\hat{C}$.

The law of physics being described by the defining equation does not therefore violate this fundamental natural symmetry. Professor Laurence Barron [35] has asserted that the existence of $\boldsymbol{B}^{(3)}$ violates $\hat{C}$ symmetry, but in so doing did not carry out this fundamental test. His argument [35] is based on the use of a diagram which compares the wavevector ($\boldsymbol{\kappa}$) of light with $\boldsymbol{B}^{(3)}$. He asserts that since $\hat{C}$ changes the sign of $\boldsymbol{B}^{(3)}$ but leaves $\boldsymbol{\kappa}$ unchanged, then $\boldsymbol{B}^{(3)}$ violates $\hat{C}$, and therefore $\hat{C}\hat{P}\hat{T}$. This is equivalent to saying that the $\hat{B}^{(3)}$ operator cannot be proportional to photon angular momentum because these two quantities have opposite $\hat{C}$ symmetry. This is not correct however, simply because $B^{(0)}$ in Eq. (1) is $\hat{C}$ negative.

39. *Yes, but because the photon has no charge, a magnetic field cannot ever be proportional to photon angular momentum in free space?*

The "photon" has to be defined. What do we mean by a photon? Following Shore [29], there are several possible answers. In the theory of particles and fields [18, 33], a "photon" is frequently defined through the potential four-vector A_μ and is given the standard particle symbol γ. Following Ryder [18, 33] it is well established that

$$\hat{C}(A_\mu) = -A_\mu, \qquad \hat{C}(\gamma) = -\gamma, \tag{5}$$

and it is asserted [18, 33] that the charge parity of a photon is *negative* despite the fact that it has no actual charge. This is confusing perhaps, and it has to be re-emphasized with great care that $\hat{C}$ operating on the scalar $B^{(0)}$ produces the scalar $-B^{(0)}$. This is why the magnetic field $\hat{B}^{(3)}$ is proportional to the angular momentum operator $\hat{J}$ of the photon. It is as well to remember that $\hat{C}$, by definition, cannot affect a spatio-temporal quantity. Therefore $\hat{C}$ cannot affect the phase of a plane wave, or its state of polarization, its wavevector, angular frequency, or any quantity apart from the scalar electric and magnetic field amplitudes $E^{(0)}$ and $B^{(0)}$.

The assertion that "the photon has no charge" is ill-founded because without a source of charge and current, a photon cannot be created. For a plane wave in vacuo it is conventionally accepted that the source must be at infinity, but there must have been a source, which must have consisted of charge and current. It would be more accurate to say that there are photons and concomitant electric and magnetic fields, which are described by A_μ. In gauge theory, as described in the accompanying article, electromagnetism enters through the product eA_μ, where e is the electronic charge. This product is necessary to maintain gauge invariance of the second kind, which is in turn a consequence of Noether's theorem. This $\hat{C}$ positive product has the dimensions of a four derivative: it is not

possible to describe electromagnetism (eA_μ), therefore, without charge, e, meaning that A_μ must be $\hat{C}$ negative.

40. *All very well, but isn't it well known that finite photon mass is incompatible with Noether's theorem because charge is not globally conserved?*

This is another way of stating that gauge invariance of the second kind requires a zero photon mass. As suggested in the accompanying article, this need not be the case, and the existence of non-zero photon mass becomes compatible with Noether's theorem through the use of the Dirac condition.

41. *If a longitudinal field exists from Proca's equation, doesn't this mean that symmetry arguments to the contrary are incompatible with non-zero photon mass?*

Yes, longitudinal solutions to the Proca equation in free space have been considered for over sixty years, and do not contradict $\hat{C}$ symmetry because the equations which define these solutions conserve $\hat{C}$. The $\boldsymbol{B}^{(3)}$ field from the Proca equation conserves $\hat{C}$, $\hat{P}$, and $\hat{T}$, and for all practical purposes is the same as the field $\boldsymbol{B}^{(3)}$ from the d'Alembert equation, in which photon mass is zero, and which also conserves $\hat{C}$, $\hat{P}$, and $\hat{T}$.

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42. *If fundamental equations such as the Maxwell or d'Alembert equations conserve $\hat{C}$, $\hat{P}$, and $\hat{T}$, is it possible for any solution to violate $\hat{C}$, $\hat{P}$, and $\hat{T}$?*

No, the four Maxwell equations conserve $\hat{C}$, $\hat{P}$, and $\hat{T}$. This means that application of $\hat{C}$, for example, to each and every symbol in the four

equations will produce four equations which are indistinguishable from the original. This means that any solution will also be indistinguishable and will also conserve $\hat{C}$, $\hat{P}$, and $\hat{T}$. Since $\boldsymbol{B}^{(3)}$ has all the known properties of a magnetic field, and is a solution of the Maxwell equations, symmetry arguments to the contrary [35] are incorrect. Similarly, the Maxwell equations for finite photon mass, considered for example by Moles and Vigier [36] conserve $\hat{C}$, $\hat{P}$, and $\hat{T}$, and so do all solutions thereof. The field $\boldsymbol{B}^{(3)}$ is of course well defined [37] from the equations of Moles and Vigier.

43. *Is it possible for symmetry arguments to "overrule" the d'Alembert or Proca equations, or physical laws in general?*

Not in the current state of knowledge, where physical laws are expressed as equations. It is possible to use symmetry (for example group theory) to anticipate without further calculation whether, for example, integrals in quantum mechanics will vanish. However, the symmetry analysis in such matters is always compatible with the equations themselves, if the equations allow a non-zero solution, then symmetry arguments cannot be used to the contrary.

44. *All these arguments notwithstanding, it is very difficult to accept that a basic field such as $\boldsymbol{B}^{(3)}$ should have been overlooked for so long. Very simply, angular momentum and magnetic field have the same symmetry properties under $\hat{P}$ and $\hat{T}$ but to make them proportional surely requires a charge which the vacuum does not have?*

Every theoretical development has been overlooked until it is suggested. The field $\boldsymbol{B}^{(3)}$ is a very simple consequence of the conjugate product, which is $i\boldsymbol{B}^{(0)}\boldsymbol{B}^{(3)}$, and in this sense $\boldsymbol{B}^{(3)}$ has not been overlooked at all. The conjugate product is sometimes referred to as an "effective" magnetic field. However, $\boldsymbol{B}^{(3)}$ is a *physical* magnetic field. The assertion that the vacuum does not have a charge is not sufficient to disprove the equations that are used to define $\boldsymbol{B}^{(3)}$, for example Eq. (1), or the definition in terms of the conjugate product,

$$\boldsymbol{B}^{(3)} = \frac{(\boldsymbol{B}^{(1)} \times \boldsymbol{B}^{(2)})}{(iB^{(0)})} \qquad (6)$$

The photon is uncharged, but its concomitant A_μ has negative charge parity. In consequence, the scalar magnetic flux density amplitude, $B^{(0)}$, of the electromagnetic plane wave in vacuo is negative to $\hat{C}$. It is true that angular momentum and magnetic flux density transform oppositely under

$\hat{C}$, but it is possible that one be proportional to the other through a $\hat{C}$ negative scalar. The latter is $B^{(0)}$. The vacuum does not have a charge, but $B^{(0)}$ has been formed from a current density in matter infinitely removed from the vacuum. The origin of $B^{(0)}$ is the origin of electromagnetism in vacuo.

45. *But surely the photon has no preference for the sign of charge and is even under $\hat{C}$. Since $\boldsymbol{B}^{(3)}$ is odd under $\hat{C}$ it must be zero. Why don't you respond to this simple argument?*

It is essential to define the "photon" before proceeding to assert that it cannot have preference for charge. Following Shore [29], there are several possible ways of defining a photon, but it is clear that light is made up of electromagnetic waves. A light beam made up of one photon is electromagnetic in nature, and therefore there is always a concomitant A_μ. If not, then there would be no electromagnetic field and no photon through wave particle dualism. If one considers the radiation from a rotating charge, forming a current density, the latter is related to a vector potential, whose curl is a magnetic field. It is immediately clear that the effect of $\hat{C}$ on the current density, vector potential, and magnetic field is negative. The effect of changing the sign of the rotating charge (and therefore of the current density formed by the moving charge) is to change the sign of the magnetic field. However, the spatio-temporal characteristics of the electromagnetic radiation are not changed by $\hat{C}$, meaning that the only possible explanation for the change of sign of A_μ is that the scalar amplitude $B^{(0)}$ changes sign.

46. *But isn't the only effect of changing the sign of charge a phase change, and in any case, the vacuum does not have a charge?*

The only effect of $\hat{C}$ is to change the sign of $B^{(0)}$, the $\hat{C}$ operator does not change the phase of a plane wave, because the phase $(\omega t - \boldsymbol{\kappa}\cdot\boldsymbol{r})$ is a spatio-temporal quantity. The field $\boldsymbol{B}^{(3)}$ is independent of frequency and of phase, but $\hat{C}$ changes its magnitude $B^{(0)}$, while leaving unchanged its direction (specified by an axial unit vector). This is because the axial unit vector is a spatio-temporal quantity. The magnitude $B^{(0)}$ is $\hat{C}$ negative because electromagnetism in vacuo originates at a source of charge and current at infinity, showing that the photon always has a concomitant field. In this context, the signs of the oscillating, transverse field $\boldsymbol{B}^{(1)}$ and its complex conjugate $\boldsymbol{B}^{(2)}$ are also changed by $\hat{C}$ because the sign of the *scalar* $B^{(0)}$ is changed. The phases of $\boldsymbol{B}^{(1)}$ and of $\boldsymbol{B}^{(2)}$ are unchanged by $\hat{C}$ because the phases are spatio-temporal quantities. The signs of $\boldsymbol{B}^{(1)}$ and $\boldsymbol{B}^{(2)}$ are changed by $\hat{C}$, while the sign of $\boldsymbol{\kappa}$, the propagation vector, is unchanged by $\hat{C}$, because it is a spatio-temporal quantity. This obviously does not mean that $\boldsymbol{B}^{(1)}$ and $\boldsymbol{B}^{(2)}$ vanish, as implied by Ref. [35].

47. *Doesn't the whole argument boil down to the effect of $\hat{C}$ on $B^{(0)}$?*

Essentially, yes. If, for example, a "quasi-static" $\boldsymbol{B}^{(1)}$ field of very low frequency is considered in a vacuum, $\hat{C}$ changes its sign, while leaving all its spatio-temporal characteristics unchanged. This does not imply that $\boldsymbol{B}^{(1)}$, the ordinary oscillating field, is zero. The frequency of $\boldsymbol{B}^{(1)}$ can be chosen to be infinitesimally low, so that it is essentially static. Then all components of A_μ would be essentially static, but applying $\hat{C}$ would not result in $A_\mu = 0$.

48. *It is certainly possible for a system of atoms and molecules, charges and currents, to produce a magnetic field from the angular momentum of the photon, but why should the vacuum produce such a field?*

The vacuum is uncharged, but electromagnetism is able to travel through a vacuum in the form of waves. The vacuum has not created the electromagnetism, and without electromagnetism there would be no photons. Therefore, the vacuum cannot create photons. Therefore there must be a source of electromagnetism and photons, a source which consists of matter in the form of charges and currents. The magnetic part of a circularly polarized electromagnetic field therefore has angular momentum *and* a $\hat{C}$ negative amplitude, $B^{(0)}$. The product of this amplitude with the beam angular momentum is the magnetic field $\boldsymbol{B}^{(3)}$. This field has not been created by the vacuum, but by a source (or "system") of charge and current density infinitely removed from the vacuum.

49. *In an initially unpolarized atomic medium, circularly polarized light will polarize the atoms to give them net angular momentum. This polarization would give rise to a magnetic field. In a gas of anti-atoms produced by $\hat{C}$, the imparted angular momentum would be the same, but the sign of the induced magnetic moment, and hence the field direction, would be reversed. Don't considerations such as these make the existence of $\boldsymbol{B}^{(3)}$ impossible?*

Not at all. The interaction between $\boldsymbol{B}^{(3)}$ and an atom is defined by the Hamiltonian $-\boldsymbol{m}\cdot\boldsymbol{B}^{(3)}$ where $\boldsymbol{m}$ is the magnetic dipole moment of the atom. Applying $\hat{C}$, the Hamiltonian becomes $-(-\boldsymbol{m})\cdot(-\boldsymbol{B}^{(3)})$ and is unchanged. This is consistent with the fact that a Hamiltonian is energy, a scalar quantity positive to $\hat{C}$. The induction of a magnetic dipole moment by $\boldsymbol{B}^{(3)}$

takes place through a susceptibility, which is $\hat{C}$ positive. The induced magnetic dipole is $\hat{C}$ negative as required.

50. *In a medium with charge symmetry, the angular momentum of light cannot produce a magnetic field. The vacuum has no charge at all, which amounts to the same thing, so surely the angular momentum of light cannot create a magnetic field out of nothing?*

The presence of electromagnetism in vacuo is measured through a non-zero $B^{(0)}$, because if $B^{(0)}$ were zero there would be no electromagnetism. The scalar $B^{(0)}$ has not been created by the vacuum, but by a source of current density at infinity. The fact that there is current density implies that this source cannot have been made up of a static "charge symmetry". The charges must have been moving in such a way as to create a non-zero current. The key to $\boldsymbol{B}^{(3)}$ is therefore the non-zero $B^{(0)}$, which multiplies the beam angular momentum to produce $\boldsymbol{B}^{(3)}$. It is noted that $B^{(0)}$ has already been created in the past by a system of charges and currents. As the angular momentum of the beam was being created by the source of current at infinity (i.e. infinitely distant and therefore in the infinite past), *so was the amplitude* $B^{(0)}$.

51. *What you are saying then is that electromagnetism is not just a spatio-temporal phenomenon, isn't that it?*

There are photons and fields, the former are particles, the latter are waves. According to the de Broglie-Einstein theory of light, particles and waves co-exist, according to the Copenhagen interpretation, they cannot. However, there is general agreement on the basic need for wave particle dualism. It is true that other particles such as electrons obey the same principle, otherwise there would be no quantum mechanics, but electron waves are not electric and magnetic fields. Photon waves on the other hand are electric and magnetic in nature, and this is an essential property of light. A beam of electrons or atoms is not a beam of light. Furthermore, recent experiments have shown that photons and fields co-exist, defying the Copenhagen interpretation in which there can be waves only of probability.

52. *But electrons have mass and are charged, they become positrons when acted upon by* $\hat{C}$, *and positrons are distinct particles, why is a photon not affected by* $\hat{C}$ *in this way, why is there no anti-photon?*

In the theory of particles and fields [33] it is asserted conventionally that the charge parity of the photon is negative, but that there is no

anti-photon. By this is meant that the effect of $\hat{C}$ on the concomitant A_μ of the photon is negative. A distinction must be made between the photon and its concomitant field (electromagnetic wave). The former is spatio-temporal (i.e. particulate), the latter electromagnetic (wavelike). Both concepts are needed to define the nature of light. The particle known as "the photon" is not charged, and by definition its anti-particle is not charged. By this is meant that the particle does not carry a constant unit of charge e. Therefore the particle ("photon") and anti-particle ("anti-photon") are indistinguishable. *However*, $\hat{C}$ changes the sign of the concomitant A_μ, and so the charge parity of "the photon" (this time taken to be A_μ [33]) is said to be negative.

On the other hand the electron does not produce a concomitant four-potential, but carries charge in the form of the constant e (about 10^{-19} coulombs). The electron is described by the Dirac equation, whose solution indicates the existence of the positron. The photon is not described by the Dirac equation, but by the d'Alembert or Proca equations. The essential difference between an electron and a photon is that the former carries a charge e and the latter has a concomitant field A_μ. This is the basis of quantum electrodynamics, a subject constructed from photons and electrons.

53. *This is confusing, the neutrino carries no charge, but isn't there an anti-neutrino?*

The existence of an anti-neutrino with a different handedness from the neutrino is a consequence of parity violation in beta decay. The neutrino has no charge, but despite this, there is a distinct anti-neutrino with opposite helicity [33].

54. *To return to basic magneto-statics, your* $\boldsymbol{B}^{(3)}$ *field is like the magnetic field along the axis of a long, narrow solenoid, a field which must be proportional to the current, I, in N turns per unit length. Where is your current?*

The circularly polarized laser beam that produces $\boldsymbol{B}^{(3)}$ is made up of electromagnetic *waves*, whose conjugate product produces $\boldsymbol{B}^{(3)}$ as in Eq. (6). Therefore $\boldsymbol{B}^{(3)}$, although independent of frequency, is defined in terms of magnetodynamics. This can be seen from the fact that if there is no travelling electromagnetic wave, the conjugate product is zero, and therefore so is $\boldsymbol{B}^{(3)}$. The current needed for $\boldsymbol{B}^{(3)}$ is embodied in $B^{(0)}$, radiated by a source of current at infinity. This propagates with the electromagnetic wave through a vacuum. In a rough analogy, a magnetic field along the axis of a solenoid is formed by the propagation of a current through N turns per unit length. If there is no electromagnetic

propagation, as in a standing wave, there is no $\boldsymbol{B}^{(3)}$.

55. *It is well known that electromagnetic waves depend on the existence of Maxwell's displacement current, so what role does this have in your theory?*

Following Jackson [27], pp. 177 ff., the displacement current enters into Ampère's law through the continuity equation as usual, without affecting the validity of Ampère's law for steady state phenomena. In a source free medium, the existence of electromagnetic waves depends entirely on the displacement current, i.e. on the partial derivative $\partial \boldsymbol{D}/\partial t$. The existence of $\boldsymbol{B}^{(3)}$ makes no difference to this, because electromagnetic plane waves in vacuo are transverse. Since $\boldsymbol{B}^{(3)}$ is longitudinal and independent of time, application of Ampère's law to it results in $\nabla \times \boldsymbol{B}^{(3)} = \boldsymbol{0}$. The displacement current associated with $\boldsymbol{B}^{(3)}$ is zero, i.e. the longitudinal $\partial \boldsymbol{D}^{(3)}/\partial t$ vanishes, otherwise $\boldsymbol{B}^{(3)}$ has to be time dependent from Ampère's law. The curl of $\boldsymbol{B}^{(3)}$ is zero, which is consistent with its definition as $B^{(0)}\boldsymbol{k}$. This does *not* mean that $\boldsymbol{B}^{(3)}$ is zero because there is no source present, because $\boldsymbol{B}^{(3)}$ is defined through the conjugate product, which is made up of transverse fields, which are formed from non-zero, transverse, Maxwellian displacement currents, as usual. The Maxwellian displacement current originates in the continuity equation, $\nabla \cdot \boldsymbol{J} + \partial \rho / \partial t = 0$ combined with Coulomb's law. In the absence of sources, the latter becomes $\nabla \cdot \boldsymbol{D} = 0$, so that any longitudinal $\boldsymbol{D}^{(3)}$ cannot be phase dependent. This means that the longitudinal displacement current is zero. Since $\nabla \cdot \boldsymbol{B}^{(3)} = \boldsymbol{0}$, $\boldsymbol{B}^{(3)}$ can be represented by $\boldsymbol{B}^{(3)} = \nabla \times \boldsymbol{A}^{(3)}$, where $\boldsymbol{A}^{(3)}$ is phase independent. Faraday's law then means that $\boldsymbol{B}^{(3)}$ produces a concomitant electric field, $\boldsymbol{E}^{(3)}$, whose curl and divergence are both zero, and which must be the gradient of a constant scalar potential. The only solution is $\boldsymbol{E}^{(3)} = 0$. These steps are summarized mathematically as follows:

$$\frac{\partial \boldsymbol{E}^{(3)}}{\partial t} = 0, \qquad \nabla \times \boldsymbol{E}^{(3)} = \boldsymbol{0}, \qquad \boldsymbol{E}^{(3)} = -\nabla \phi^{(3)}. \tag{7}$$

This result is entirely consistent with the fact that if there is a constant $\boldsymbol{B}^{(3)}$, then the real longitudinal $\boldsymbol{E}^{(3)}$ is zero.

56. *It is still not clear why a field such as $\boldsymbol{B}^{(3)}$ can magnetize without contributing anything to the energy of a beam. Isn't this basically contradictory?*

Following Pershan [38], and using his Gaussian units, energy conservation means that

$$\frac{c}{4\pi} \nabla \cdot (\boldsymbol{E} \times \boldsymbol{B}) + \frac{1}{4\pi} \boldsymbol{B} \cdot \frac{\partial \boldsymbol{B}}{\partial t} + \frac{1}{4\pi} \boldsymbol{E} \cdot \frac{\partial \boldsymbol{E}}{\partial t} + \boldsymbol{E} \cdot \boldsymbol{J} = 0. \tag{8}$$

In a vacuum, it is conventionally asserted that $\boldsymbol{J} = \boldsymbol{0}$, in which case the first term on the left hand side is the power flow, and the second and third terms are the time derivative of the energy density per unit volume. Since $\boldsymbol{B}^{(3)}$ is independent of frequency by definition, the term $\boldsymbol{B}^{(3)} \cdot \partial \boldsymbol{B}^{(3)}/\partial t$ vanishes, and any contribution of $\boldsymbol{B}^{(3)}$ to power flow is zero. In other words $\boldsymbol{B}^{(3)}$ cannot contribute to the Poynting vector by definition, even though $\boldsymbol{B}^{(3)}$ is non-zero by definition. In the presence of matter, $\boldsymbol{J}$ is not zero. However, as shown by Pershan [38], *$\boldsymbol{E} \cdot \boldsymbol{J}$ is not simply the contribution of the material to the energy density per unit volume*. When there is no magnetization, (when $\boldsymbol{M} = \boldsymbol{0}$), then $\boldsymbol{E} \cdot \boldsymbol{J} = \boldsymbol{E} \cdot \partial \boldsymbol{P}/\partial t$ is the time derivative of an energy density. When $\boldsymbol{M}$ is not zero, however, we have, in gaussian units [38],

$$\boldsymbol{J} = \frac{\partial \boldsymbol{P}}{\partial t} + c \nabla \times \boldsymbol{M} - \frac{\partial}{\partial t} (\nabla \cdot \boldsymbol{Q}) + \ldots, \tag{9}$$

where $\boldsymbol{P}$ is the electric dipole moment per unit volume, $\boldsymbol{M}$ is the magnetic dipole moment per unit volume, and $\boldsymbol{Q}$ the electric quadrupole moment per unit volume. If the material energy density per unit volume is U, then,

$$\frac{\partial U}{\partial t} = -\nabla \cdot \boldsymbol{S} - \frac{1}{4\pi} \left(\boldsymbol{H} \cdot \frac{\partial \boldsymbol{H}}{\partial t} + \boldsymbol{E} \cdot \frac{\partial \boldsymbol{E}}{\partial t} \right), \tag{10}$$

which is the expression for the work done on a system by external fields. Here we have

$$\boldsymbol{H} = \boldsymbol{B} - 4\pi \boldsymbol{M}, \qquad \boldsymbol{D} = \boldsymbol{E} + 4\pi \boldsymbol{P}, \tag{11}$$

in gaussian units. *The average work done on or by the material by the field $\boldsymbol{B}^{(3)}$ is zero, but the average energy stored in the material by virtue of its magnetization is not zero*. As described by Pershan [38], at an instant $t = 0$ the laser beam encounters a material (i.e. "the field is turned on") and work is done on or by the material to establish the steady state values of $\boldsymbol{P}$, $\boldsymbol{M}$, and $\boldsymbol{Q}$ after a rise transient. The final "steady state" energy density depends only on the "steady state" fields and polarizations, and not on how they were produced. As shown by Pershan [38] this leads to the definition of a time averaged free energy from which it is possible to describe all magneto-optic and electro-optic effects. From this analysis it becomes clear that the conjugate product, or $\boldsymbol{B}^{(3)}$, enters through a time averaged $(\partial U/\partial t)_{\tau}$, and therefore leads to the inverse Faraday effect described in Pershan's Eq. (5.10).

This complete analysis can be repeated in precisely the same way for

$\mathbf{B}^{(3)}$, through its definition (6), and it becomes clear that $\mathbf{B}^{(3)}$ takes meaning only when there is interaction with matter. Therefore there is no contradiction with conservation of energy and momentum.

57. *But if $\mathbf{B}^{(3)}$ takes meaning only if it interacts with something, isn't it meaningless in free space and therefore cannot exist?*

Following Shore [29], electromagnetic energy density and momentum density are also meaningless concepts unless they can be measured experimentally. In Shore's description they "take meaning" only when electromagnetism interacts with matter, and this is clear from the fact that without such interaction, electromagnetism cannot be detected, and there is no evidence for its existence. In the last analysis, electromagnetic energy density is a means of transfer of energy from a source to material through a vacuum. Poynting's theorem, following Jackson [27] is derived from a consideration of an *interaction* $\mathbf{E}\cdot\mathbf{J}$, and the fact that $\mathbf{J}$ does not appear in the Poynting theorem in vacuo is due to the fact that the source is conventionally thought of as being "infinitely removed" from free space. Similarly, the field $\mathbf{B}^{(3)}$ can only be defined through an interaction, and the same is true for all types of linear and nonlinear electro and magneto-optic phenomena.

58. *You say that $\mathbf{B}^{(3)}$ emerges from considerations of free energy, how is this done exactly?*

It is possible, for example to start from Pershan's [38] equation (3.1), rewritten in terms of its antisymmetric part, proportional to the conjugate product $\mathbf{B}^{(1)}\times\mathbf{B}^{(2)}$,

$$F = -\boldsymbol{\alpha}_B''\cdot(\mathbf{B}^{(1)}\times\mathbf{B}^{(2)}), \qquad \alpha_B'' = -\left(\frac{\partial F}{\partial(\mathbf{B}^{(1)}\times\mathbf{B}^{(2)})}\right)_0. \tag{12}$$

Here α_B'' is a molecular or atomic property tensor as usual [38] defined as the derivative of free energy F, with respect to the vector $\mathbf{B}^{(1)}\times\mathbf{B}^{(2)}$. We simply rewrite this vector using Eq. (6), and obtain,

$$F = -\mathbf{m}_B\cdot\mathbf{B}^{(3)}, \qquad \mathbf{m}_B \equiv -\left(\frac{\partial F}{\partial \mathbf{B}^{(3)}}\right)_0. \tag{13}$$

It is clear that $\mathbf{B}^{(3)}$ multiplied by the magnetic dipole moment $\mathbf{m}_B$ is also a free energy. The free energy in Eq. (12) is proportional to beam intensity, and that in Eq. (13) to the square root of beam intensity,

(i.e. to $\mathbf{B}^{(3)}$). To derive Eq. (13) from Eq. (12) we have multiplied top and bottom of Eq. (12) by $iB^{(0)}$, and have defined $\mathbf{B}^{(3)}$ as $B^{(0)}\mathbf{k}$. If it is asserted [35] that $\mathbf{B}^{(3)}$ is zero, then the free energy vanishes, contradicting the generally valid Pershan theory [38], i.e. contradicting the existence of the inverse Faraday effect and related phenomena.

59. *Surely there must be effects proportional to $\mathbf{B}^{(3)}$?*

Yes, and in principle these can be detected using the inverse Faraday effect, i.e. there should be magnetization due to $\mathbf{B}^{(3)}$ as well as $\mathbf{B}^{(1)}\times\mathbf{B}^{(2)}$.

60. *So why haven't they been detected?*

This is an open question, there are few data available on the inverse Faraday effect, and these have to be carefully analyzed in a medium in which there is a permanent magnetic dipole moment. In this case there should be effects due to $\mathbf{B}^{(3)}$ and due to $\mathbf{B}^{(1)}\times\mathbf{B}^{(2)}$.

61. *Can you give an example of an observed phenomenon involving $\mathbf{B}^{(3)}$?*

It is a straightforward matter to put the theory of the inverse Faraday effect into a form where the magnetization is proportional to $\mathbf{B}^{(3)}$ multiplied by the amplitude $B^{(0)}$. For example, a development of Eq. (30) of Woźniak et al [39], a recent paper on the inverse Faraday effect, leads to the following expression for the magnetization due to light,

$$\mathbf{M}(0) = \frac{N}{6kT}\left(\mathbf{m}_{aa}\cdot c^2 B^{(0)}\boldsymbol{\alpha}_{aa}''\right)\mathbf{B}^{(3)}, \tag{14}$$

where $\mathbf{m}$ is a magnetic dipole moment, $\boldsymbol{\alpha}''$ an antisymmetric polarizability vector, N the number of molecules, kT the thermal energy per molecule, and c the speed of light. It is important to realize that this is an expression for an *experimentally observed phenomenon*, and is therefore direct experimental proof for $\mathbf{B}^{(3)}$. The questions in this paper are all concerned with the *interpretation* of $\mathbf{B}^{(3)}$. From Eq. (14) it is clear that the magnetization is proportional to a magnetic field, $\mathbf{B}^{(3)}$, multiplied by $B^{(0)}$. This effect is therefore proportional to beam intensity, and at the same time proportional to $\mathbf{B}^{(3)}$. The question is whether $\mathbf{B}^{(3)}$ can induce magnetization through a susceptibility. It is this effect that would be proportional to the square root of intensity.

62. *Surely, if $\mathbf{B}^{(3)}$ is a magnetic field, it would do so?*

This can only be settled by further experimental work on the inverse Faraday effect and related magneto-optical phenomena. In view of Eq. (14) above, it is clear that $\mathbf{B}^{(3)}$ when multiplied by $B^{(0)}$ produces magnetization. In terms of free energy, it is well established [39] that the interaction Hamiltonian,

$$\Delta H_1 = \left(\frac{\partial H}{\partial (\mathbf{E}^{(1)} \times \mathbf{E}^{(2)})} \right)_0 \mathbf{E}^{(1)} \times \mathbf{E}^{(2)} \equiv -i\boldsymbol{\alpha}'' \cdot \mathbf{E}^{(1)} \times \mathbf{E}^{(2)}, \qquad (15)$$

defines the antisymmetric polarizability, $\boldsymbol{\alpha}''$, a vector quantity. Similarly, the antisymmetric susceptibility is defined by

$$\Delta H_2 = \left(\frac{\partial H}{\partial (\mathbf{B}^{(1)} \times \mathbf{B}^{(2)})} \right)_0 \mathbf{B}^{(1)} \times \mathbf{B}^{(2)} \equiv -i\boldsymbol{\chi}'' \cdot \mathbf{B}^{(1)} \times \mathbf{B}^{(2)}, \qquad (16)$$

and similarly, we expect that there is a magnetic dipole moment, which can be defined by

$$\Delta H_3 = \left(\frac{\partial H}{\partial \mathbf{B}^{(3)}} \right)_0 \mathbf{B}^{(3)} \equiv -\mathbf{m}^{(3)} \cdot \mathbf{B}^{(3)}. \qquad (17)$$

We note that these quantities are defined only when interaction occurs between the light and the material being magnetized by the light. *None of the quantities $\mathbf{E}^{(1)} \times \mathbf{E}^{(2)}$, $\mathbf{B}^{(1)} \times \mathbf{B}^{(2)}$ or $\mathbf{B}^{(3)}$ contributes to the Poynting vector of the radiation, and none therefore contributes to the free space electromagnetic energy density. In this sense, therefore, $\mathbf{B}^{(3)}$ is a "latent" magnetic field, or "ghost field".*

63. *What is the difference between a "latent" magnetic field and the beam magnetic fields?*

The former ($\mathbf{B}^{(3)}$) does not contribute to the Poynting vector, whereas the oscillating $\mathbf{B}^{(1)}$ and $\mathbf{B}^{(2)}$ do. Using the cyclic relations [40] derived in the accompanying article:

$$\mathbf{B}^{(1)} \times \mathbf{B}^{(2)} = iB^{(0)}\mathbf{B}^{(3)*}, \quad \text{and cyclic permutations,} \qquad (18)$$

we see that the three fields are tied together by a nonlinear algebra. It becomes clear that if we can define, for example, the molecular property $\boldsymbol{\chi}''$, we can define the property

$$\mathbf{m}^{(3)*} \equiv -\left(\frac{\partial H}{\partial \mathbf{B}^{(3)*}} \right)_0 = -\left(\frac{\partial H}{\partial (\mathbf{B}^{(1)} \times \mathbf{B}^{(2)} / iB^{(0)})} \right)_0, \qquad (19)$$

so on these grounds there should exist a magnetic dipole moment $\mathbf{m}^{(3)*}$. This means that there should be effects due to the square root of intensity, as discussed in detail [40].

64. *How can a field such as your $\mathbf{B}^{(3)}$ be thought of as uniform and time independent, and at the same time as a field which propagates in free space?*

By using the definition of $\mathbf{B}^{(3)}$ in terms of the antisymmetric part of light intensity, i.e. in terms of the third Stokes parameter. The field $\mathbf{B}^{(3)}$ can be thought of in the same way as the light intensity, which propagates through a vacuum and is also a constant, time independent, measurable. The field $\mathbf{B}^{(3)}$ is carried by the transverse fields $\mathbf{B}^{(1)}$ and $\mathbf{B}^{(2)}$.

65. *Maxwell's equations in free space contain only linear operators, so their solutions must be linear. If $\mathbf{B}^{(3)}$ is defined in terms of a cross product of transverse solutions of Maxwell's equations, then isn't this contradictory?*

The field $\mathbf{B}^{(3)}$ itself is linear in flux density amplitude, $B^{(0)}$, in the same way as the transverse fields are linear in this variable. The transverse and longitudinal fields form a cyclic Lie algebra, as described in the accompanying paper, and each field component of this algebra is linear in $B^{(0)}$. The term "nonlinear" in optics refers to products which contain $E^{(0)}$ and $B^{(0)}$ to second or higher order. It should also be noted that polarization and magnetization can enter into the linear Maxwell equations, and in nonlinear optics, these quantities are not linear in the definition used here.

66. *Transverse plane waves obey the linear superposition principle, and combinations of plane waves can be used to construct any possible plane wave with arbitrary time dependence of the amplitude or phase. Doesn't this mean that the transverse and longitudinal fields must <u>separately</u> satisfy Maxwell's equations in vacuo, and that longitudinal and transverse solutions can be tied together only by an arbitrary mathematical construction?*

The relation, Eq. (6), between $\mathbf{B}^{(3)}$ and the antisymmetric part of light intensity is not arbitrary, because the intensity is a physically

meaningful quantity which can be expressed as the product $iB^{(0)}\boldsymbol{B}^{(3)}$. The amplitude $B^{(0)}$ is physically meaningful, and therefore so is $\boldsymbol{B}^{(3)}$. A superposition of plane waves will always produce a light intensity tensor, with a non-zero antisymmetric component which is directly proportional to $\boldsymbol{B}^{(3)}$. If the latter were zero, there would be no antisymmetric light intensity component or S_3 Stokes parameter in circularly polarized light. $\boldsymbol{B}^{(1)}$, $\boldsymbol{B}^{(2)}$ and $\boldsymbol{B}^{(3)}$ are separate solutions of Maxwell's equations. If it is assumed that Eq. (6) is an arbitrary mathematical construction then it must follow that the antisymmetric part of light intensity is defined arbitrarily, a reductio ad absurdum.

67. *The fact that transverse and longitudinal field solutions are tied up together by Eq. (6) appears to be in deep conflict with accepted wisdom. How do you feel about this?*

The solutions $\boldsymbol{B}^{(1)}$, $\boldsymbol{B}^{(2)}$ and $\boldsymbol{B}^{(3)}$ form a perfectly cyclic Lie algebra within the Poincaré group, and in this sense (see accompanying article) are *more* in line with conventional wisdom (and with fundamental geometry) than the usual assertion that there is no connection at all. If there is no such connection, then fundamental geometry is contradicted so completely that the notion of zero $\boldsymbol{B}^{(3)}$ becomes absurd. Nevertheless the latter is the conventional wisdom, and asserts in effect that one dimension out of three is missing. This is discussed in the accompanying article [40].

68. *Returning to the question of energy, it is important to understand precisely the role of $\boldsymbol{B}^{(3)}$ (and of $i\boldsymbol{E}^{(3)}$) in the Poynting theorem. Can you give equations defining their role exactly, rather than playing around with words?*

Yes, the Poynting theorem in S.I. units is

$$\nabla\cdot\boldsymbol{S} = -\frac{\partial U}{\partial t} - c^2\epsilon_0\boldsymbol{E}\cdot\boldsymbol{J} \tag{20}$$

where

$$\boldsymbol{S} = \boldsymbol{E}\times\boldsymbol{B}, \qquad U = \frac{1}{2}\left(\frac{1}{c^2}\boldsymbol{E}\cdot\boldsymbol{E} + \boldsymbol{B}\cdot\boldsymbol{B}\right), \qquad \boldsymbol{J} = \frac{\partial\boldsymbol{P}}{\partial t} + \nabla\times\boldsymbol{M} + \ldots . \tag{21}$$

We note that if $\boldsymbol{B} \equiv \boldsymbol{B}^{(3)}$, $\boldsymbol{E} \equiv i\boldsymbol{E}^{(3)}$, then,

$$\boldsymbol{S} = \boldsymbol{O}, \qquad U = \frac{1}{2}\left(\frac{1}{c^2}i\boldsymbol{E}^{(3)}\cdot i\boldsymbol{E}^{(3)} + \boldsymbol{B}^{(3)}\cdot\boldsymbol{B}^{(3)}\right) = 0, \qquad \boldsymbol{J} = \boldsymbol{0}, \tag{22}$$

so that these fields obey Poynting's theorem in the presence of matter. This does not mean that the magnetization, $\boldsymbol{M}$, due to $\boldsymbol{B}^{(3)}$ is zero. In S.I. units *the energy stored in the electromagnetic field* is [38]

$$U_S = \frac{1}{\mu_0}\boldsymbol{B}\cdot\boldsymbol{B} - 2\boldsymbol{M}\cdot\boldsymbol{B} + \mu_0\boldsymbol{M}\cdot\boldsymbol{M} + \epsilon_0\boldsymbol{E}\cdot\boldsymbol{E}, \tag{23}$$

which depends on the magnetization. Therefore $\boldsymbol{B}^{(3)}$ contributes to this stored energy through its creation of magnetization. The latter is observed in the inverse Faraday effect. In S.I., *the material energy density per unit volume is [38]*

$$U_m = \mu_0\boldsymbol{H}\cdot\boldsymbol{M} + \boldsymbol{E}\cdot\boldsymbol{P} + \ldots , \tag{24}$$

where $\boldsymbol{P}$ is the polarization due to $\boldsymbol{E}$, and where the quadrupole term has been neglected for simplicity. *The average work done by the electromagnetic field on material is zero in the steady state [38],*

$$\frac{dU_m}{dt} = 0, \tag{25}$$

and there is no work done on material by $\boldsymbol{B}^{(3)}$ and $i\boldsymbol{E}^{(3)}$. If $\boldsymbol{M}$ is zero, the energy stored in the electromagnetic field due to $\boldsymbol{B}^{(3)}$ and $i\boldsymbol{E}^{(3)}$ is zero.

Therefore $\boldsymbol{B}^{(3)}$ and $i\boldsymbol{E}^{(3)}$ do not contradict basic conservation laws of electromagnetic energy.

69. *If $\boldsymbol{B}^{(3)}$ is the fundamental element of antisymmetric light intensity, then does the real $\boldsymbol{B}^{(3)}$ contribute to the observed light intensity in watts per unit area?*

To answer this question, consider the fact that in circularly polarized light, the zero'th and third Stokes parameters are equal in magnitude,

$$S_0 = S_3 = E^{(0)2} = c^2B^{(0)2}. \tag{26}$$

The observed light intensity can therefore be expressed formally in terms of a combination of S_0 and S_3, and therefore in terms of $\boldsymbol{B}^{(3)}$,

$$I_0 \equiv \epsilon_0 c|S_0| = \frac{1}{2}\epsilon_0 c(|S_0| + |S_3|) = \frac{\epsilon_0 c}{2}(\boldsymbol{E}^{(1)}\cdot\boldsymbol{E}^{(2)} - i|\boldsymbol{E}^{(1)}\times\boldsymbol{E}^{(2)}|) = \epsilon_0 c^3 \boldsymbol{B}^{(3)}\cdot\boldsymbol{B}^{(3)}, \quad (27)$$

It is important to note, however, that $\boldsymbol{B}^{(3)}$ does not *add* anything to the observed intensity, the latter has been redefined to incorporate S_3. The moduli, $|S_0|$ and $|S_3|$ ensure that the light intensity remains the same in all polarizations, linear and circular.

70. *Is there a way of demonstrating from first principles the manner in which $\boldsymbol{B}^{(3)}$ interacts with one electron?*

Yes, it can be shown from first principles that the inverse Faraday effect for one electron depends directly on $\boldsymbol{B}^{(3)}$. The magnetic dipole moment induced by the interaction of a circularly polarized light beam and one electron is a sum of two terms,

$$\boldsymbol{m} = -\chi_e \boldsymbol{B}^{(3)} - \beta_e B^{(0)} \boldsymbol{B}^{(3)}, \quad (28)$$

where χ_e is a one electron susceptibility and β_e a one electron hyperpolarizability. Clearly, if $\boldsymbol{B}^{(3)}$ were zero, $\boldsymbol{m}$ would be zero, and this contradicts fundamental theory [41, 42].

71. *Surely, if this result is from first principles, the susceptibility and hyperpolarizability for one electron can be derived in terms of fundamentals?*

Yes, the expressions are [41, 42]

$$\chi_e = \frac{e^2 r_0^2}{2m_0}, \qquad \beta_e = \frac{e^4 c^2}{2m_0^2 \omega^4}, \quad (29)$$

where e is the charge on the electron, r_0 its radius in $\boldsymbol{B}^{(3)}$, m_0 its rest mass, and ω the angular frequency of the circularly polarized light beam. It can be seen that of $\boldsymbol{B}^{(3)}$ were zero, there would be no $\boldsymbol{m}$ at any order in $\boldsymbol{B}^{(3)}$. In order for Eq. (28) to conserve $\hat{C}$ symmetry, both $B^{(0)}$ and $\boldsymbol{B}^{(3)}$ must be $\hat{C}$ negative. This is because $\boldsymbol{m}$ is $\hat{C}$ negative and so is e, the other quantities being spatio-temporal in nature and therefore $\hat{C}$ positive. This first principles calculation is consistent with the negative $\hat{C}$ symmetry of $B^{(0)}$ in our definition, Eq. (6). In the conventional theory [41] of the one electron inverse Faraday effect, the term linear in $\boldsymbol{B}^{(3)}$ is missing, and the effect is expressed in terms of the conjugate product

$\boldsymbol{E}^{(1)}\times\boldsymbol{E}^{(2)}$, proportional to the antisymmetric part of the light intensity. The conventional theory, although correct as far as it goes, does not recognize that $\boldsymbol{B}^{(3)}$ can induce $\boldsymbol{m}$ through a susceptibility.

72. *In answering question (4) you say that $\boldsymbol{B}^{(3)}$ does not contribute to free space electromagnetic energy, but in Eq. (23) we see that $\boldsymbol{M}$ appears in the expression for the energy stored in the electromagnetic field. Isn't this contradictory?*

Equation (23) is the expression for energy stored in the electromagnetic field when $\boldsymbol{M}$ is not zero, i.e. when there is non-zero magnetization. This can be true *only in the presence of matter*. In free space, $\boldsymbol{B}^{(3)}$ and $i\boldsymbol{E}^{(3)}$ formally contribute to U as in Eq. (22), but cancel each other, so that their contribution to U is zero. This explains why the Planck radiation law is not changed by the presence of $\boldsymbol{B}^{(3)}$ and $i\boldsymbol{E}^{(3)}$. Therefore $\boldsymbol{B}^{(3)}$ reveals itself by magnetizing material matter, to produce $\boldsymbol{M}$, but not through any additional contribution to beam intensity. Equation (27) means that beam intensity can be expressed formally in terms of $\boldsymbol{B}^{(3)}$, and that this is just as valid as expressing intensity in terms of the usual transverse fields.

73. *In answering question 5 you assert that $\boldsymbol{B}^{(3)}$ is created without the expenditure of energy, yet you have just said that $\boldsymbol{B}^{(3)}$ produces magnetization, which <u>does</u> contribute to energy stored in the electromagnetic field. How do you resolve this?*

Following Shore [29], classical electromagnetic theory is based on the notion that the field transmits effects from a source to matter. The electromagnetic field propagates in a vacuum, in which it can be formally assigned an energy density, U and energy flux density, $\boldsymbol{S}$. However, as described by Shore [29], U takes meaning only when there is field-matter interaction. The longitudinal $\boldsymbol{B}^{(3)}$ and $i\boldsymbol{E}^{(3)}$ have no frequency dependence, and so have no Planck energy. Their combined contribution to both U and $\boldsymbol{S}$ in free space is zero. Nevertheless, the real field $\boldsymbol{B}^{(3)}$ creates observable magnetization (as in the one electron inverse Faraday effect just discussed) when there is field-matter interaction. This can occur at first or second (or higher) order in $\boldsymbol{B}^{(3)}$. Therefore $\boldsymbol{B}^{(3)}$ contributes to the *stored* energy of the field through its ability to magnetize, but its contribution to U, the free space electromagnetic energy density, is cancelled by $i\boldsymbol{E}^{(3)}$. The stored energy due to $\boldsymbol{B}^{(3)}$ must originate in a source, and is made available to matter through the intermediacy of the field $\boldsymbol{B}^{(3)}$. The latter is therefore the agent for transmission of energy from source to matter. *During this transmission process, total energy is*

conserved. This is what is meant by the statement that $\boldsymbol{B}^{(3)}$ is created without the expenditure of energy. As shown by Pershan [38] free energy can be built up by the interaction of molecular property tensors with any power of any electromagnetic field component. The latter are solutions of Maxwell's linear field equations, but the interactions of field components with matter can be nonlinear.

74. *Surely, if $\boldsymbol{B}^{(3)}$ is a magnetic field, it obeys Faraday's law of induction and a chopped laser beam, in which $\boldsymbol{B}^{(3)}$ changes with time, should produce an easily observable voltage in an induction coil?*

Faraday's law of induction in S.I. units is

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}. \tag{30}$$

For $\boldsymbol{B}^{(3)}$ accompanied by $i\boldsymbol{E}^{(3)}$, this law is obeyed formally in a beam of light of unchanging intensity, both sides being zero. In this condition $\boldsymbol{B}^{(3)}$ is real and $i\boldsymbol{E}^{(3)}$ is imaginary, and this can be true if and only if the time derivative of $\boldsymbol{B}^{(3)}$ vanishes and the curl of $i\boldsymbol{E}^{(3)}$ vanishes. This result is obtained for a constant amplitude $E^{(0)} = cB^{(0)}$ in free space. It could be argued that if $B^{(0)}$ and $E^{(0)}$ *themselves* are made time dependent by modulating a beam (i.e. by changing the beam intensity) then a Faraday induction might occur in free space in a coil wound around a laser beam passing through a vacuum. However, changing the magnitude of $\boldsymbol{B}^{(3)}$ in this way always produces a pure imaginary $i\boldsymbol{E}^{(3)}$ which is not observable as Faraday induction without the presence of material, in which case the inverse Faraday effect occurs.

75. *You keep saying that $\boldsymbol{B}^{(3)}$ is real and $i\boldsymbol{E}^{(3)}$ is imaginary, but couldn't it be said equally well that $i\boldsymbol{B}^{(3)}$ is imaginary and $\boldsymbol{E}^{(3)}$ is real?*

This would conflict with the experimental data, because no first order electric polarization effect due to $\boldsymbol{E}^{(3)}$ has been reported to date. Here, we follow the rule that real fields are physical, imaginary fields are unphysical.

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Chapter 12

MOLECULAR THEORY OF OPTICAL NMR SPECTROSCOPY: LIGHT INDUCED BULK AND SITE SPECIFIC SHIFTS

M. W. Evans

Abstract

The molecular theory of optical NMR spectroscopy is developed and illustrated with an example of an optical NMR mechanism in which a magnetic electronic dipole moment is induced in a molecule by an applied laser field. This results in bulk and site specific shifts, both types of shift being induced simultaneously, leading to a new analytical technique of general utility. Irreducible spherical tensorial representations are given for the mediating hyperpolarizability molecular property tensor ${}^{m}\gamma^{ee}_{ijk}$ relevant to this mechanism of induction by light of a magnetic electronic dipole moment. Non-vanishing elements of ${}^{m}\gamma^{ee}_{ijk}$ are given for all the molecular point groups, and examples of point group character tables containing scalar elements of ${}^{m}\gamma^{ee}_{ijk}$ are given for a few point groups. The theory is worked out explicitly for the group O, the octahedral group without inversion, in which examples of point group character tables containing scalar elements of ${}^{m}\gamma^{ee}_{ijk}$ are given for a few point groups. The theory is worked out explicitly for the group O, the octahedral group without inversion, in which Gruffydd coefficients are available, showing that the laser shifts the original nuclear resonances in this point group in the context of the mechanism considered here. The site specific name of ONMR is developed semi-qualitatively by considering atomic and bond susceptibility and hyperpolarizability models.

Introduction

Electromagnetic radiation is capable of magnetizing molecular material in the absence or presence of an external magnetostatic field. Experimental evidence for this property first became available through the inverse Faraday effect, first proposed by Piekara and Kielich [1–5], and demonstrated experimentally by Pershan *et al.* [6–8], and Shen [9]. Recently, the present author proposed a simple atomic model [10] of optical NMR, in which the magnetizing property of light is used to shift nuclear magnetic resonances, and the prediction was verified experimentally shortly afterwards by Warren *et al.* [11] in a variety of molecular liquids, including the enantiomers of p methoxyphenyliminocamphor in the liquid state. Subsequently, several possible mechanisms of ONMR have been proposed in simple atomic systems in which there is net electronic angular momentum [12–16]. In general, it has become clear that there can be several contributory mechanisms in ONMR, leading to a richly subtle spectrum as a function of the laser's intensity and state of polarization, a spectrum which can be used without further calculation for such purposes as

chemical analysis of complex proteins in solution.

The most important experimental feature, however, is that the effect of the laser on each resonating site is different [11] in general, exhibiting a different functional dependence on laser intensity and polarization. For example, the shift pattern as a function of laser intensity of the ring protons of p methoxy phenylimino camphor was found experimentally [11] to be different from the shift pattern of the high field and other protons. Furthermore, the ONMR spectra for right and left enantiomers were different, and different again in the racemic mixture. The effect was much bigger in circular polarization (right or left) than in linear polarization, but the spectrum showed no simple dependence on circular polarization. Furthermore, there was no simple functional dependence on laser intensity at the experimental laser frequency, chosen to be far from optical resonance in the visible range. These features can be understood qualitatively [17] by using a combination of mechanisms by which light induces a magnetic electronic dipole moment. Quite generally, and independently of these details, ONMR can be interpreted as a combination of bulk and site specific shifts, whereby the applied laser is used to produce an analytically useful shift of the magnetic field seen by the resonating nucleus. The shift depends in general on the electronic topography immediately adjacent to the resonating nucleus, and is made up of several possible contributions of induction by light. These bulk and site specific mechanisms are all present simultaneously, and are mediated by several different molecular property tensors such as molecular magnetic susceptibility, ${}^{m}\chi^{m}_{ij}$, and molecular hyperpolarizability, ${}^{m}\beta^{ee}_{ijk}$, which in molecules are anisotropic, and made up of scalar components in the molecule fixed frame, components which in general are different in magnitude. This is a well known result of semi-classical theory [18]. These components can be developed, in turn, as sums of local site (e.g. atomic or chromophore) properties, well known examples being the atom and bond polarizability models of semi-classical theory [19–22]. The latter is therefore capable of providing a general framework for understanding, at least qualitatively, the several useful features of ONMR in molecules.

In this paper, we initiate the theory of bulk shifts in the optical NMR of molecules, whose point group symmetries are used in the context of the theory of angular momentum coupling in quantum mechanics developed by Gruffydd [23, 24] through his well known V, W, and X coefficients. These are the equivalents of 3-j, 6-j, and 9-j symbols in the equivalent Racah algebra [23, 24] in one electron atoms. The symbolic machinery of Gruffydd algebra is superficially complicated, but the theoretical concept in this work is simply described as follows. The applied laser is assumed to induce in the electrons of the molecule a magnetic dipole moment. For example, in the laboratory frame (X, Y, Z),

$$\hat{m}_i^{(ind)}(0) = \frac{1}{2}\,{}^{m}\hat{\alpha}^{ee}_{ijk}(0,\omega,-\omega)E_jE_k^* + \frac{1}{2}\,{}^{m}\hat{\alpha}^{ee}_{ijk}(0,-\omega,\omega)E_j^*E_k, \tag{1}$$

where ${}^{m}\beta^{ee}_{ijk}$ is the mediating molecular hyperpolarizability tensor, and $E_iE_j^*$ is a Hermitian tensor product of the oscillating electric field strength vector E_i

and its complex conjugate E_j^*, of the laser. The tensor $E_iE_j^*$ is directly proportional to the Hermitian light intensity tensor,

$$I_{ij} = \epsilon_0 c E_i E_j^*, \tag{2}$$

where ϵ_0 is the permittivity in vacuo and c the speed of light. In this mechanism, the induced dipole moment is therefore directly proportional to the laser intensity in watts m^{-2}. The mechanism (1) is one out of several possible [17] and is chosen to illustrate the application of Gruffydd algebra to the problem.

The ensemble averaged magnetization induced by the applied laser is then [25]

$$\langle M_i^{(ind)}(0)\rangle = N\langle m_i^{(ind)}(0)\rangle, \tag{3}$$

where N is the number of molecules per unit volume.

This is calculated in terms of the steady state ensemble averaged $\langle m_i^{(ind)}(0)\rangle$ induced in each molecule of a sample by light. The magnetic flux density at some point in the sample is first calculated using the magnetization $\langle M^{(ind)}(0)\rangle$. With linear Maxwellian field equations we consider the sample to be a magnetized sphere of permeability μ which is not a permanently magnetized object, but one in whose magnetization $\boldsymbol{M}$ derives from the applied flux density $\boldsymbol{B}_s$ in S.I. units, standard magnetostatics shows that the magnetic flux density and field strength inside the spherical sample are,

$$\boldsymbol{B}_{in} = \boldsymbol{B}_s + \frac{2}{3}\mu_0\boldsymbol{M}, \qquad \boldsymbol{H}_{in} = \frac{1}{\mu_0}\left(\boldsymbol{B}_s - \frac{\mu_0}{3}\boldsymbol{M}\right), \qquad \boldsymbol{B}_{in} = \mu\boldsymbol{H}_{in}, \tag{4a}$$

where μ_0 is the permeability of free space and μ that of the sample material. The macroscopic, Maxwellian, magnetic flux density inside the spherical sample is therefore

$$\boldsymbol{B}_{in} = \left(\frac{3\mu}{\mu + 2\mu_0}\right)\boldsymbol{B}_s. \tag{4b}$$

Equation (4a) allows the calculation of $\boldsymbol{B}_{in}$ from $\boldsymbol{M}$, to which there are contributions such as that in Eq. (3). Equation (4b) shows that $\boldsymbol{B}_{in}$ calculated in this

way depends only on μ, μ_0, and $\boldsymbol{B}_s$, and is independent of structural details of the spherical sample, i.e. of its atomic or molecular structure. Therefore any NMR shift calculated from the macroscopic field $\boldsymbol{B}_{La}$ inside the sample is a bulk shift, and cannot be site specific.

A magnetization such as that defined in Eq. (3) therefore contributes to the overall bulk shift observed experimentally in ref. [11]. The laser induced site specific shifts of ref. [11] need a mechanism by which the magnetic field at the resonating site differs relative to an internal standard. (One such mechanism is discussed in the Appendix B of this paper, another in ref. [11].)

In the field $\boldsymbol{B}_s$ is identified with the permanent magnetic flux density of an NMR instrument (e.g. 6.4. tesla in a 272 MHz spectrometer [11] the $\boldsymbol{B}_{La}$ of such a field is given by Eq. (4a), in which there is a relatively small contribution to $\boldsymbol{M}$ due to an applied laser. The change in $\boldsymbol{B}_{La}$ due to $\langle m_i^{(ind)}(0)\rangle$ of Eq. (3) is therefore

$$\langle B_i^{(ind)}\rangle \sim \frac{2}{3}\mu_0\langle M_i^{(ind)}(0)\rangle, \tag{4c}$$

where $\langle B_i^{(ind)}\rangle$ is an ensemble averaged, laser induced, magnetic flux density within the sample, considered as a sphere.

The laser therefore has the overall effect of changing the simple NMR Hamiltonian from

$$\Delta\hat{H}_1 = -\hat{m}_{Ni}B_{Si}, \tag{5}$$

to

$$\Delta\hat{H}_2 = -\hat{m}_{Ni}\left(B_{Si} + \langle B_i^{(ind)}\rangle\right), \tag{6}$$

i.e. produces an overall, or bulk, shift. Here $\hat{m}_{Ni}$ is a nuclear magnetic dipole moment, and $\boldsymbol{B}_{S1}$ the static magnetic field of the NMR instrument.

There are numerous elegant contemporary NMR methods available [26–28] with which the laser can be applied. The Hamiltonian (5) is the simplest possible example, chosen for the first development given in this paper.

Developing ONMR theory in molecules implies the use of the molecule fixed frame of reference to define the molecular point group [23, 24] in which Gruffydd algebra is applicable. The irreducible spherical tensorial components of the hyperpolarizability must therefore be worked out for each molecular point group in order to apply the Gruffydd theory of angular momentum coupling in quantum mechanics. The light induced electronic magnetic dipole moment must then be worked out in terms of these components in the molecule fixed frame, and finally ensemble averaged to give the laser induced magnetic flux density $\langle B_i^{(ind)}\rangle$, and bulk shift.

In Sec. 2, the fundamental properties of the mediating hyperpolarizability tensor ${}^m\mathfrak{A}^{ee}_{ijk}$ are given in terms of the symmetries of its real and imaginary parts, and its internal density matrix structure developed. The non-vanishing individual scalar components of ${}^m\gamma^{ee}_{ijk}$ are tabulated in all the molecular point groups. In Sec. 3, the tensor ${}^m\gamma^{ee}_{ijk}$ is analyzed to give its non-vanishing irreducible spherical tensorial representations in all the molecular point groups, using the method of Coope *et al.* for reducing a rank three tensor [29]. These consist of appropriate *combinations* of scalar components. Extensions for some point group character tables identify a given irreducible representation of the molecular point group with these combinations. In Sec. 4, a complex spherical basis (-1, 0, 1) is defined in the molecule fixed frame (x, y, z) for evaluating the induced dipole moment (1) in any given point group. In Sec. 5, the calculation of the ONMR spectrum is carried out explicitly in the point group O, the octahedral group without inversion, for which V, W, and X coefficients are available in the literature [23, 24]. Finally a discussion develops the individual scalar components of ${}^m\gamma^{ee}_{ijk}$ in terms of sums over site specific terms, in analogy with the well developed atom and bond polarizability models [30–34].

2. Some Fundamental Properties of the Hyperpolarizability

In general, the tensor ${}^m\mathfrak{A}^{ee}_{ijk}$ can be split into real and imaginary parts [35],

$${}^m\mathfrak{A}^{ee}_{ijk} = {}^m\beta^{ee}_{ijk} + i\,{}^m\gamma^{ee}_{ijk}, \tag{7}$$

which themselves become complex when damping is considered [35] in semi-classical theory,

$${}^m\gamma^{ee}_{ijk} = {}^m\gamma^{ee'}_{ijk} + i\,{}^m\gamma^{ee''}_{ijk}. \tag{8}$$

The axial tensors ${}^m\beta^{ee}_{ijk}$ and ${}^m\gamma^{ee}_{ijk}$ have opposite symmetries to motion reversal $\hat{T}$: ${}^m\gamma^{ee}_{ijk}$ is positive, and ${}^m\beta^{ee}_{ijk}$ is negative. Both parts are positive to parity inversion $\hat{P}$ [35]. The tensor ${}^m\beta^{ee}_{ijk}$ vanishes in molecules which have no net electronic angular momentum, therefore [36], and ${}^m\gamma^{ee}_{ijk}$ exists in all atoms and molecules. An induced magnetic dipole moment is generated from the ubiquitous tensor ${}^m\gamma^{ee}_{ijk}$ by multiplication with the imaginary, antisymmetric, $\hat{T}$ negative, $\hat{P}$ positive, component of $E_iE_j^*$, which can be represented vectorially [35] by $\boldsymbol{E}\times\boldsymbol{E}^*$.

Using density matrix formalism [37], the internal semi-classical structure of ${}^m\gamma^{ee}_{ijk}$ can be developed as,

$$
{}^{m}\varphi^{ee}_{ijk}(0,\omega,,-\omega) = \frac{1}{\hbar^2}\sum_{abc}\rho^{(0)}_{aa}\times\left[\frac{Im\left[(\hat{m}_i)_{ac}(\hat{\mu}_k)_{cb}(\hat{\mu}_j)_{ba}\right]}{(\omega_{ca}-i\Gamma_{ca})(\omega_{ba}-\omega-i\Gamma_{ba})}\right.
$$

$$
+\frac{Im\left[(\hat{m}_i)_{ac}(\mu_j)_{cb}(\hat{\mu}_k)_{ba}\right]}{(\omega_{ca}-i\Gamma_{ca})(\omega_{ba}+\omega-i\Gamma_{ba})}+\frac{Im\left[(\hat{\mu}_j)_{ac}(\hat{\mu}_k)_{cb}(\hat{m}_{i_{ba}})\right]}{(\omega_{ba}+i\Gamma_{ba})(\omega_{ca}+\omega+i\Gamma_{ca})} \qquad (9)
$$

$$
+\frac{Im\left[(\hat{\mu}_k)_{ac}(\hat{\mu}_j)_{cb}(\hat{m}_i)_{ba}\right]}{(\omega_{ba}+i\Gamma_{ba})(\omega_{ca}-\omega+i\Gamma_{ca})}+\frac{Im\left[(\hat{\mu}_j)_{ac}(\hat{m}_i)_{cb}(\hat{\mu}_k)_{ba}\right](1+K)}{(\omega_{ba}+\omega+i\Gamma_{ba})(\omega_{ca}+\omega+i\Gamma_{ca})}
$$

$$
\left.+\frac{Im\left[(\mu_k)_{ac}(m_i)_{cb}(\mu_j)_{ba}\right](1+K)}{(\omega_{ba}-\omega-i\Gamma_{ba})(\omega_{ca}-\omega+i\Gamma_{ca})}\right],
$$

where

$$
(\hat{m}_i)_{ba} \equiv \langle b|\hat{m}_i|a\rangle, \qquad (10)
$$

and

$$
(\hat{\mu}_j)_{cb} \equiv \langle c|\hat{\mu}_j|b\rangle, \qquad (11)
$$

denote magnetic and electric dipole transitions between *electronic* quantum states $|a\rangle$ and $\langle b|$ and $|b\rangle$ and $\langle c|$ respectively. Optical resonances within this semi-classical structure are defined as

$$
\omega_{ba} = \omega_b - \omega_a = \frac{(E_b - E_a)}{\hbar}, \qquad (12)
$$

and $\rho^{(0)}_{aa}$ denotes the quantum mean value of the unperturbed density matrix in the stationary state $|a\rangle$. The quantity Γ^{-1}_{ba} is a characteristic relaxation time between the states $|b\rangle$ and $|a\rangle$ and

$$
K = \frac{i(\Gamma_{bc}-\Gamma_{ba}-\Gamma_{ca})}{(\omega_{bc}-i\Gamma_{bc})}, \qquad (13)
$$

is a correction term which can be ignored whenever the combination of damping terms in Eq. (13) is small relative to the frequency ω_{bc}, and which vanishes in the absence of damping or if

$$
\Gamma_{bc} = \Gamma_{ba}+\Gamma_{ca}. \qquad (14)
$$

In general therefore the hyperpolarizability in density matrix formalism is a function of frequency, and shows optical resonances of the type illustrated recently by Woźniak *et al.* [35, 36]. It is the tensor that mediates the inverse Faraday effect in molecules without net electronic angular momentum such as water. Care must be taken not to confuse the concept of optical resonance within ${}^{m}\varphi^{ee}_{ijk}$ with the concept of nuclear magnetic resonance changes caused by ${}^{m}\varphi^{ee}_{ijk}$. The former are electronic in nature, occur typically in the visible frequency, the latter are caused by radio frequency field induced transitions between magnetic components of the net angular momentum quantum number in Eq. (6).

The hyperpolarizability ${}^{m}\beta^{ee}_{ijk}(0,\omega,-\omega)$ is given by Eq. (9) [35, 36] by replacing the imaginary part of the matrix element product in the numerators by its real part. The quantum mechanical expressions for the hyperpolarizabilities ${}^{m}\beta^{ee}_{ijk}(0,-\omega,\omega)$ and ${}^{m}\varphi^{ee}_{ijk}(0,-\omega,\omega)$ are given by replacing, ω in ${}^{m}\beta^{ee}_{ijk}(0,\omega,-\omega)$ and ${}^{m}\varphi^{ee}_{ijk}(0,\omega,-\omega)$ by $-\omega$. The electronic magnetic dipole moment operator induced by light through the mediation of these tensors is defined in general through the symmetric and antisymmetric parts of the Hermitian tensor $E_jE^*_j$,

$$
E_jE^*_k = \Pi^S_{jk}+\Pi^A_{jk}, \qquad E^*_jE_k = \left(\Pi^S_{jk}\right)^*+\left(\Pi^A_{jk}\right)^*, \qquad (15)
$$

with

$$
\Pi^S_{jk} = \frac{1}{2}\left(E_jE^*_k+E_kE^*_j\right), \qquad (16)
$$

and

$$
\Pi^A_{jk} = -\left(\Pi^A_{jk}\right)^*. \qquad (17)
$$

Note that these field products are *independent of the phase of the laser, i.e. are independent of the quantity*,

$$\phi = \omega t - \boldsymbol{\kappa}\cdot\boldsymbol{r}, \tag{18}$$

where ω is the laser's angular frequency, t the time, $\boldsymbol{\kappa}$ the laser's wave vector, and $\boldsymbol{r}$ a position vector. This is an essential and fundamental feature of the theory of molecular magneto-optics, developed extensively by the Poznań School [38], a feature which allows the induced magnetic electronic dipole moment to be time independent, i.e. to be non-zero after time averaging over many cycles of the laser's frequency. Without this feature, ONMR shifts would all vanish, in this mechanism, after time averaging. Similarly there would be no inverse Faraday effect [1–9] without using conjugate products ($E_i E_j^*$) in its theoretical description.

Note carefully that although the laser's frequency does not enter directly into products such as $E_i E_j^*$, it occurs within the internal structure of the mediating property tensor developed in Eq. (9). Clearly, if the laser is tuned to optical resonance, i.e. if

$$\omega = \omega_{ba}, \quad or, \quad \omega = \omega_{ca}, \tag{19}$$

the mediating tensor increases sharply in magnitude, and in consequence the induced magnetic dipole moment $m_i^{(ind)}(0)$ mediated by this tensor increases commensurately. This is a useful feature for ONMR—if the laser is tuned to an optical resonance of the specimen in the visible, then the ONMR shifts will increase dramatically in this theory.

With these considerations, we have the following useful relations between hyperpolarizabilities [35],

$$\begin{aligned}
{}^{m}\hat{\alpha}^{ee}_{ijk}(0,\omega,-\omega) &= {}^{m}\hat{\alpha}^{ee*}_{ijk}(0,-\omega,\omega),\\
{}^{m}\hat{\alpha}^{ee}_{ijk}(0,\omega,-\omega) &= {}^{m}\hat{\alpha}^{ee*}_{ikj}(0,\omega,-\omega),\\
{}^{m}\hat{\alpha}^{ee}_{ijk}(0,-\omega,\omega) &= {}^{m}\hat{\alpha}^{ee*}_{ikj}(0,-\omega,\omega),
\end{aligned} \tag{20}$$

and for the relevant part ${}^{m}\hat{\gamma}^{ee}_{ijk}$ considered here,

$$\begin{aligned}
{}^{m}\hat{\gamma}^{ee}_{ijk}(0,\omega,-\omega) &= -\,{}^{m}\hat{\gamma}^{ee}_{ikj}(0,\omega,-\omega),\\
{}^{m}\hat{\gamma}^{ee}_{ijk}(0,\omega,-\omega) &= -\,{}^{m}\hat{\gamma}^{ee}_{ijk}(0,-\omega,\omega),\\
{}^{m}\hat{\gamma}^{ee}_{ijk}(0,\omega,-\omega) &= {}^{m}\hat{\gamma}^{ee}_{ikj}(0,-\omega,\omega),\\
{}^{m}\hat{\gamma}^{ee}_{ijk}(0,-\omega,\omega) &= -\,{}^{m}\hat{\gamma}^{ee}_{ikj}(0,-\omega,\omega).
\end{aligned} \tag{21}$$

Therefore ${}^{m}\hat{\gamma}^{ee}_{ijk}(0,\omega,-\omega)$ is antisymmetric in its last two indices, so that only certain components are non-zero in any molecular point group. Table 1 is a convenient summary, in the molecule fixed frame (x, y, z) [35], of non-vanishing components of ${}^{m}\hat{\gamma}^{ee}_{ijk}(0,\omega,-\omega)$ in all the commonly occurring molecular point groups. In Table 1, if a component is not recorded, then it is identically zero in frame (x, y, z). In the O point group for example, there is only one independent non-zero component. Even in the point group of lowest symmetry, the chiral C_1, there are only nine independent non-zero components out of a possible total of 27. A component of the type ijj always vanishes because of the subscript symmetry recorded in Eq. (21). In the C_{2v} point group of water, there are three independent non-vanishing components only. The use of this Table greatly decreases the complexity of calculation in the following sections.

3. Irreducible Spherical Representations of ${}^{m}\hat{\gamma}^{ee}_{ijk}$

Gruffydd theory [23, 24] is worked out in terms of spherical representations of a given molecular property rather than Cartesian. In order to apply it, a given Cartesian tensor operator must be written in terms of its irreducible spherical representations in the molecular point group. In the laboratory frame, these are represented by the D symmetries [23, 24], and each D symmetry has its equivalent [23, 24] in any molecular point group. Thus, a suitable combination of scalar elements of ${}^{m}\hat{\gamma}^{ee}_{ijk}$ in frame (x, y, z) forms a basis for each irreducible representation of the molecular point group, and these irreducible representations appear in the Gruffydd V, W, and X coefficients [23, 24]. The latter in turn determine how one angular momentum couples with another in quantum mechanics applied within that point group in frame (x, y, z). This is the methodology adapted here for the calculation of ONMR spectra in any given molecular point group, a methodology which shows implicitly that the ONMR spectrum depends on the values assigned to each individual scalar component of the hyperpolarizability considered here, or more generally, of any molecular property tensor that mediates the induction of a magnetic electronic dipole moment by light.

To reduce the rank three tensor ${}^{m}\hat{\gamma}^{ee}_{ijk}$ to its irreducible spherical components of weights 0, 1, 2, and 3, we follow Coope *et al.* [29], and work in

the molecule fixed frame (x, y, z) which defines the molecular point group. (The symbols x, y, z occur in the point group character tables.)

The component at weight 0 is, in tensor notation,

$$ {}^{m}\mathcal{Q}^{ee(0)} = -\epsilon_{kji}\ {}^{m}\mathcal{Q}^{ee}_{ijk} = 2\left({}^{m}\mathcal{Q}^{ee}_{xyz} + {}^{m}\mathcal{Q}^{ee}_{yzx} + {}^{m}\mathcal{Q}^{ee}_{zxy} \right). \tag{22} $$

This component is a scalar, and forms a basis for the totally symmetric irreducible representation of the point group. In O this is A_1. Thus, the combination of scalar components $2\left({}^{m}\mathcal{Q}^{ee}_{xyz} + {}^{m}\mathcal{Q}^{ee}_{yzx} + {}^{m}\mathcal{Q}^{ee}_{zxy} \right)$ forms a basis for A_1 in O. Similar conclusions can be arrived at for all the other point groups. Using Table 1,

$$ {}^{m}\mathcal{Q}^{ee}_{xyz} = {}^{m}\mathcal{Q}^{ee}_{yzx} = {}^{m}\mathcal{Q}^{ee}_{zxy}, \tag{23} $$

and so the basis for A_1 in O is made up of only one term, $6\,{}^{m}\mathcal{Q}^{ee}_{xyz}$.

The irreducible spherical tensorial component at weight 1 of the rank three tensor in frame (x, y, z) is [29],

$$ {}^{m}\mathcal{Q}^{ee(1)}_{ijk} = \frac{1}{2}\left[\delta_{ij}\left({}^{m}\mathcal{Q}^{ee(1)}_{x} \right)_k + \delta_{ik}\left({}^{m}\mathcal{Q}^{ee(1)}_{y} \right)_j + \left({}^{m}\mathcal{Q}^{ee(1)}_{z} \right)_i \delta_{jk} \right], \tag{24} $$

where the three contributory terms are defined as

$$ \begin{aligned} \left({}^{m}\mathcal{Q}^{ee(1)}_{x} \right)_k &= {}^{m}\mathcal{Q}^{ee}_{xxk} + {}^{m}\mathcal{Q}^{ee}_{yyk} + {}^{m}\mathcal{Q}^{ee}_{zzk}, \\ \left({}^{m}\mathcal{Q}^{ee(1)}_{y} \right)_j &= {}^{m}\mathcal{Q}^{ee}_{xjx} + {}^{m}\mathcal{Q}^{ee}_{yjy} + {}^{m}\mathcal{Q}^{ee}_{zjz}, \\ \left({}^{m}\mathcal{Q}^{ee(1)}_{z} \right)_i &= {}^{m}\mathcal{Q}^{ee}_{ixx} + {}^{m}\mathcal{Q}^{ee}_{iyy} + {}^{m}\mathcal{Q}^{ee}_{izz} = 0. \end{aligned} \tag{25} $$

Within a given molecular point group, these can be identified with appropriate irreducible representations as follows. Recall that the tensor ${}^{m}\mathcal{Q}^{ee}_{ijk}$ is positive to $\hat{P}$, and in consequence its D representation at weight 1 must be $D_g^{(1)}$. This transforms [39] as a combination of irreducible representations in any given point group. For example, in the C_{2v} point group of water,

$$ D_g^{(1)} \rightarrow A_2 + B_1 + B_2. \tag{26} $$

The problem now reduces to finding which combinations of ${}^{m}\mathcal{Q}^{ee}_{ijk}$ at rank one correspond to which irreducible representation, and this can be solved by inspection of the structure in (x, y, z) of ${}^{m}\mathcal{Q}^{ee(1)}$ given by Coope *et al.* [29],

$$ {}^{m}\mathcal{Q}^{ee(1)} = \frac{1}{2}\left(\mathbf{u}\ {}^{m}\mathcal{Q}^{ee(1)}_{x} + \left[{}^{m}\mathcal{Q}^{ee(1)}_{y} \right] + {}^{m}\mathcal{Q}^{ee(1)}_{z}\,\mathbf{u} \right). \tag{27} $$

From this we see that the A_2 can be identified with ${}^{m}\mathcal{Q}^{ee(1)}_{z}$, B_1 with ${}^{m}\mathcal{Q}^{ee(1)}_{y}$, and B_2 with ${}^{m}\mathcal{Q}^{ee(1)}_{x}$. In tensor notation, alternatively, $({}^{m}\mathcal{Q}^{ee(1)}_{z})_i$ forms a basis for A_2 in the point group C_{2v}; $({}^{m}\mathcal{Q}^{ee}_{y})_j$ forms a basis for B_1; and $({}^{m}\mathcal{Q}^{ee(1)}_{x})_k$ forms a basis for B_2. The individual elements are,

$$ \begin{aligned} B_2 &: {}^{m}\mathcal{Q}^{ee}_{xxk} + {}^{m}\mathcal{Q}^{ee}_{yyk} + {}^{m}\mathcal{Q}^{ee}_{zzk}, \\ B_1 &: {}^{m}\mathcal{Q}^{ee}_{xjx} + {}^{m}\mathcal{Q}^{ee}_{yjy} + {}^{m}\mathcal{Q}^{ee}_{zjz}, \\ A_2 &: {}^{m}\mathcal{Q}^{ee}_{ixx} + {}^{m}\mathcal{Q}^{ee}_{iyy} + {}^{m}\mathcal{Q}^{ee}_{izz}, \end{aligned} \tag{28} $$

and from Table 1 we see that the bases at weight 1 for ${}^{m}\mathcal{Q}^{ee}_{ijk}$ all vanish identically in C_{2v}. Similar results can be built up for all the other commonly occurring point groups, and are summarized in Tables 2, 3, and 4.

At weight 2 the irreducible spherical representation in (x, y, z) is, in tensor notation

$$ {}^{m}\mathcal{Q}^{ee(2)}_{ml} = \frac{1}{3}\epsilon_{mnk}\left[2\left({}^{m}\mathcal{Q}^{ee(2)}_{x} \right)_{kl} + \left({}^{m}\mathcal{Q}^{ee(2)}_{y} \right)_{kl} \right] + \frac{1}{3}\left[\left({}^{m}\mathcal{Q}^{ee(2)}_{x} \right)_{lk} + 2\left({}^{m}\mathcal{Q}^{ee(2)}_{y} \right)_{lk} \right]\epsilon_{kmn}, \tag{29} $$

with

$$ \left({}^{m}\mathcal{Q}^{ee(2)}_{x} \right)_{kl} = -\frac{1}{2}\left(\epsilon_{kij}\ {}^{m}\mathcal{Q}^{ee}_{jil} + \epsilon_{lij}\ {}^{m}\mathcal{Q}^{ee}_{jik} \right) - \frac{1}{3}\ {}^{m}\mathcal{Q}^{ee(0)}\delta_{kl}, $$

$$\left({}^{m}\gamma_{y}^{ee(2)} \right)_{kl} = -\frac{1}{2}\left({}^{m}\gamma_{lij}^{ee}\epsilon_{jik} + {}^{m}\gamma_{kij}^{ee}\epsilon_{jil} \right) - \frac{1}{3}\,{}^{m}\gamma^{ee(0)}\delta_{kl}.$$

Since

$$ {}^{m}\gamma_{y}^{ee(2)} = -2\ {}^{m}\gamma_{x}^{ee(2)}, \tag{30}$$

we have

$$ {}^{m}\gamma_{ijk}^{ee(2)} = -\left({}^{m}\gamma_{x}^{ee(2)} \right)_{il}\epsilon_{ljk}. \tag{31}$$

In the point group C_{2v}, for example, this weight in a $\hat{P}$ positive tensor transforms as

$$D_g^{(2)} \to 2A_1 + A_2 + B_2 + B_1, \tag{32}$$

and we can identify the irreducible representations of the point group C_{2v} with combinations of scalar elements of ${}^{m}\gamma_{ijk}^{ee}$ as follows,

$$\begin{aligned} B_2 &: \left({}^{m}\gamma_{x}^{ee(2)} \right)_{ij} = \left({}^{m}\gamma_{x}^{ee(2)} \right)_{ji}, \qquad B_1 : \left({}^{m}\gamma_{x}^{ee(2)} \right)_{ik} = \left({}^{m}\gamma_{x}^{ee(2)} \right)_{ki}, \\ A_2 &: \left({}^{m}\gamma_{x}^{ee(2)} \right)_{jk} = \left({}^{m}\gamma_{x}^{ee(2)} \right)_{kj}, \qquad A_1 : \left({}^{m}\gamma_{x}^{ee(2)} \right)_{jj}, \end{aligned} \tag{33}$$

showing that the A_1 representations are non-zero in C_{2v} at this weight. This is recorded in the C_{2v} entry in Tables 3 and 4.

Finally at weight 3 it can be shown that all combinations of components which form bases for any irreducible representation in any molecular point group vanish identically for ${}^{m}\gamma_{ijk}^{ee}$, as summarized in Table 4. This can be seen from the fact [40] that the complete D representation of ${}^{m}\gamma_{ijk}^{ee}$ is

$$\Gamma\left({}^{m}\gamma_{ijk}^{ee} \right) = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}, \tag{34}$$

and does not contain $D_g^{(3)}$.

In the Appendix, we provide extensions of the point group character tables for some commonly occurring molecular point groups in which the hyper-

polarizability tensor ${}^{m}\gamma_{ijk}^{ee}$ is represented in terms of its irreducible representations in the point group. Alongside each Table in the Appendix is provided the transformation properties into the point group of the relevant D representations at each weight. Thus, for example, $D_g^{(1)}$ transforms as $A_2 + E$ in C_{3v}; $D_g^{(2)}$ as $A_1 + 2E$ and so forth.

Use of these Tables and the point group character table extensions given in the Appendix considerably simplifies the application of Gruffydd theory to optical NMR. In point groups the intricate theoretical structure collapses to a simple analytical result. In other point groups, such is not the case. In general, these Tables show that the ONMR spectral structure is very rich and characteristic of the molecule, and the electronic state of the molecule. It is therefore clear that characterization of a sample by optical NMR is straightforward in general, provided that the laser induced shifts can be increased a little by improvements in technology, because each sample will exhibit a clearly identifiable laser induced shift pattern as a function of a) laser intensity; b) laser frequency; c) the laser's state of polarization.

4. The Complex Spherical Basis

Before embarking on a specific calculation in Sec. 5 for the point group O of the ONMR spectrum, a clear definition must be given of the framework within which the calculation proceeds. We are interested in evaluating matrix elements between basis eigenfunctions for molecular point groups. Operators and basis functions must both transform [24] as components of representations of the molecular point group. An irreducible tensor operator must transform as a standard basis for the representations of the point group under consideration, and it is necessary to be consistent in the choice of operators and basis functions. For the group $R_h(3)$, for atoms, the complex angular momentum eigenstates $|jm_j\rangle$ form a basis. For molecular point groups and Gruffydd algebra, both real and complex bases can be used. When working with angular momentum eigenfunctions in Gruffydd algebra, it is convenient to express the components in the molecule fixed frame (x, y, z) of a given irreducible representation in a complex spherical basis [24]. For example, in the group O, the three components of the irreducible representations T_1 and T_2 are expressed as

$$T_1 1 = -\frac{i}{\sqrt{2}}(T_1 x + iT_1 y), \qquad T_1 0 = iT_1 z, \qquad T_1\ 1 = \frac{i}{\sqrt{2}}(T_1 x - iT_1 y), \tag{35}$$

and similarly for T_2, using the Fano Racah phase convention following Gruffydd [23, 24]. The angular momentum operator $\hat{J}$ is an irreducible tensor operator of rank 1, which transforms as $D_q^{(1)}$ in the laboratory frame. Since $D_q^{(1)}$ goes to T_2 in O, the operator $\hat{J}$ remains irreducible in this octahedral group without inversion, and its three real components are T_2x, T_2y, T_2z. The three complex

components are [24] $T_2 1$, $T_2 0$, $T_2 -1$. When complex components are used as bases for the irreducible representations Gruffydd algebra uses a particular form (Section 5) of the well known Wigner Eckart theorem to reduce the matrix elements which we wish to calculate in the point group of interest. These points are illustrated in the following section with a specific calculation in the point group O. For a more detailed discussion and background we refer the reader to Silver [41].

5. Calculation in the O Point Group

Consider the induction by completely circularly polarized laser light of an electronic magnetic dipole moment operator in the laboratory frame (X, Y, Z),

$$\hat{m}_i^{(ind)} = {}^{m}\hat{\gamma}^{ee}_{ijk}\Pi^{(A)}_{jk}. \tag{36}$$

The product on the right hand side must transform in molecular point groups in the same way as that on the left hand side, i.e. the product must transform with the symmetry of a magnetic dipole moment. In terms of irreducible spherical tensorial representations,

$$[\hat{m}^{(ind)}]^{(1)} = [({}^{m}\hat{\gamma}^{ee(0)} + {}^{m}\hat{\gamma}^{ee(1)} + {}^{m}\hat{\gamma}^{ee(2)})\Pi^{(A)(1)}]^{(1)}. \tag{37}$$

In the O point group the only non-zero component of ${}^{m}\hat{\gamma}^{ee}$ in Eq. (37) is ${}^{m}\hat{\gamma}^{ee(0)}$, and therefore in the laboratory frame

$$[\hat{m}^{(ind)}]^{(1)} = [{}^{m}\hat{\gamma}^{ee(0)}\Pi^{(A)(1)}]^{(1)}. \tag{38}$$

From Table (2) we find that the combination of elements that forms a basis for the A_1 representation of O is $6{}^{m}\hat{\gamma}^{ee}_{xyz}$, and so,

$$({}^{m}\hat{\gamma}^{ee})^{A_1} = 6\,{}^{m}\hat{\gamma}^{ee}_{xyz}, \tag{39}$$

forms a basis for A_1 of O. In the dihedral point groups, such as D_2, D_3, D_4 and D_5, also considered by Gruffydd [23, 24] and Silver [41], the irreducible representation ${}^{m}\hat{\gamma}^{ee(2)}$ also transforms as a non zero combination of scalar elements, and the calculation of the induced magnetic dipole moment must take this into account. In other point groups not considered by Gruffydd, yet other

irreducible representations, of ${}^{m}\hat{\gamma}^{ee(1)}$, transform as non-vanishing element combinations.

In the O point group, however,

$${}^{m}\hat{\gamma}^{ee(1)} = {}^{m}\hat{\gamma}^{ee(2)} = 0, \tag{40}$$

and the induced dipole moment is evaluated as the matrix elements,

$$\langle a\alpha|\hat{\gamma}_0^{A_1}|a'\alpha'\rangle = \langle a\|\hat{\gamma}^{A_1}\|a'\rangle V\begin{pmatrix} a & a' & A_1 \\ \alpha & \alpha' & 0 \end{pmatrix}, \tag{41}$$

using the appropriate Gruffydd form [23, 24] of the Wigner Eckart theorem. (If a complex basis is used, as defined in Sec. 4, a slightly different form [41] is required.) The V coefficient is given by

$$V\begin{pmatrix} a & a' & A_1 \\ \alpha & \alpha' & 0 \end{pmatrix} = \lambda(a)^{\frac{1}{2}}\delta_{AA'}\delta_{\alpha\alpha'}, \tag{42}$$

where $\lambda(a)$ is the dimension of the a representation in O. We obtain, finally, in the molecule fixed frame (x, y, z),

$$\langle a\alpha|\hat{\gamma}_0^{A_1}|a\alpha\rangle = 6\,{}^{m}\gamma^{ee}_{xyz}, \tag{43}$$

a result which depends on the molecular eigenstate a between which the induced dipole moment is evaluated, and on the components in the molecule fixed frame of the molecular hyperpolarizability tensor, ${}^{m}\gamma^{ee}_{xyz}$. Clearly, the shielding factor $\sigma^{(ind)}$, which is directly proportional to these expectation values, also depends on the scalar elements of the hyperpolarizability in frame (x, y, z), and on the quantum state a of the molecule, i.e. on the state between which $\hat{\gamma}_0^{A_1}$ is computed in Eq. (41). In general the molecular eigenstates are $|\zeta a\alpha\rangle$, where ζ is electronic/vibrational, and $a\alpha$ is rotational in nature.

In the absence of a magnetic field

$$V\begin{pmatrix} a & a' & A_1 \\ \alpha & \alpha' & 1 \end{pmatrix} = V\begin{pmatrix} a & a' & A_1 \\ \alpha & \alpha' & 0 \end{pmatrix} = V\begin{pmatrix} a & a' & A_1 \\ \alpha & \alpha' & -1 \end{pmatrix}, \tag{44}$$

and the magnetic sub states in frame (x, y, z) are degenerate. In the presence of a magnetic field, such as the field of an NMR spectrometer, it is possible in general, to induce transitions between previously degenerate magnetic states, leading to a resonance spectrum, but we shall not pursue this calculation here. The energy levels and transitions are as follows: e.g. for $\alpha - T_1$,

$$En(a=-1) \rightarrow En(a=0), \qquad En(a=0) \rightarrow En(a=1). \tag{45}$$

The result (43) has been obtained in the molecule fixed frame, and isotropic averaging [35] must be carried out to obtain the induced magnetic dipole moment in the laboratory frame (X, Y, Z) as an ensemble averaged induced magnetic dipole moment. This gives the final result,

$$\langle m_Z^{(ind)} \rangle = {}^{m}\gamma^{ee}_{xyz} E_0^2, \tag{46}$$

since E_0^2 is a scalar and is frame invariant. The ensemble averaged laser induced magnetization in frame (X, Y, Z) is therefore,

$$\langle M_Z^{(ind)} \rangle = N\, {}^{m}\gamma^{ee}_{xyz} E_0^2, \tag{47}$$

and the ensemble averaged laser induced magnetic flux density

$$\langle B_Z^{(ind)} \rangle = \frac{2}{3} N\mu_0\, {}^{m}\gamma^{ee}_{xyz} E_0^2. \tag{48}$$

The laser induced relative bulk shift is, finally,

$$\Delta = \frac{\langle B_Z^{(ind)} \rangle}{B_{SZ}}. \tag{49}$$

6. Discussion

From the simple result (48) it is straightforward to estimate the laser induced shielding factor $\sigma^{(ind)}$. The order of magnitude of ${}^{m}\gamma^{ee}_{xyz}$ has been given by Woźniak *et al.* from studies of the Faraday effect [42] as ~10^{-45} A m^4 V^{-2} in simple diamagnetics such as CS_2 and benzene liquids. Assuming this order of magnitude for a molecule of O symmetry, using $\mu_0 = 4\pi \times 10^{-7} J s^2 C^{-2} m^{-1}$; and taking N about 10^{28} molecules m^{-3} in a room temperature liquid, the ensemble averaged mean field is

$$\langle B_Z^{(ind)} \rangle \sim 10^{-23} E_0^2 \ tesla. \tag{50}$$

Here E_0^2 is the square of the electric field strength in V m^{-1} of the circularly polarized laser. This is related to the scalar intensity of the laser through the free space equation,

$$I_0 = \epsilon_0 c E_0^2, \tag{51}$$

where ϵ_0 is the permittivity in free space (8.854×10^{-12} J^{-1} C^2 m^{-1}), and c the speed of light. Under these conditions, we have the order of magnitude estimate, $\langle B_Z^{(ind)} \rangle \sim 10^{-20} I_0 \ tesla$. For a laser intensity of 10^4 watts m^{-2} (10 watts cm^{-2}) the estimated "shielding factor" $\sigma^{(ind)}$ for a static field of 1.0 tesla is,

$$\sigma^{(ind)} \sim 10^{-15}, \tag{52}$$

corresponding to nuclear resonance bulk shifts of the order 10^{-7} Hz for a 272 MHz instrument such as that used in the first LENS experiment [11] (i.e. 1 part in 10^{15} approximately).

Experimentally, bulk shifts of the order 1 to 10 Hz were observed [11] with laser intensities of up to 3.0 watts cm^{-2}, using several different specimens, so that the hyperpolarizability mechanism considered here produces results which appear to be several orders of magnitude too small. Moreover, the experimental data indicate the presence [11] of several different contributory mechanisms, not just one, as outlined in this paper. The data [11] did not show, for example, a simple dependence of bulk shift on laser intensity I_0, as predicted by Eq. (51), so that we must look for a linear combination of mechanisms, each proportional to a different power of I_0. The laser induced shift pattern was observed [11] to be different for different resonance sites (e.g. high field and ring protons of p methoxy phenylimino camphor [11]), i.e. to be site specific in analogy with the well known chemical shift phenomenon, the basis of analytical

NMR. (For the analytical laboratory, this is the most useful feature of optical NMR spectroscopy.) The laser induced shift pattern was not the same for left and right enantiomers and was different again [11] in the racemic mixture. This can only be explained by a combination of induction mechanisms some of which change sign between enantiomers, some of which do not. In the (chiral) O group mechanism considered here, for example, ${}^{m}\hat{\gamma}^{ee}_{ijk}$ is $\hat{P}$ positive, and in consequence does not change sign between enantiomers, and therefore does not vanish in the racemic mixture. A sign of change between enantiomers necessarily relies on a $\hat{P}$ negative molecular property tensor such as the magnetic dipole-electric dipole tensor [25].

It is also interesting to note that in theory, there are yet other possible induction mechanisms present simultaneously, and an example, in terms of site specific charge density changes due to direct perturbation of the molecular wavefunctions by the laser, is given by Warren *et al.* [11]. We consider as follows an alternative induction mechanism that is non-zero after time and ensemble averaging in a liquid sample, such as the ones used experimentally [11].

The laser property responsible for the induction of a $m^{(ind)}$ in Eq. (36) is $\boldsymbol{E}\times\boldsymbol{E}^{*}$. This has the symmetry of a magnetostatic flux density, and recently [43–46], it has been proposed that the electromagnetic plane wave generates the novel, real magnetostatic field defined by,

$$\boldsymbol{B}^{(3)} = \frac{\boldsymbol{E}\times\boldsymbol{E}^{*}}{(2E_0 c i)}, \qquad |\boldsymbol{B}^{(3)}| \sim 10^{-7} I_0^{\frac{1}{2}}, \tag{53}$$

which has the symmetry and units of magnetic flux density. Note that $\boldsymbol{B}^{(3)}$ is proportional to the square root of intensity. It has been shown [46] that $\boldsymbol{B}^{(3)}$ is rigorously consistent with the Maxwell equations, and is equivalent to a photon magnetic field operator $\hat{B}^{(3)}$ in quantum field theory [46]. The classical $\boldsymbol{B}^{(3)}$ contributes to the sample magnetization and induces a magnetic electronic dipole moment,

$$\hat{m}_i^{(ind)} = {}^{m}\hat{\chi}^{m'}_{ij} B_j^{(3)}, \tag{54}$$

where ${}^{m}\hat{\chi}^{m'}_{ij}$ is the real part of the molecular susceptibility, defined from perturbation theory [47] in the molecular frame (x, y, z) as

$${}^{m}\chi^{m'}_{\alpha\beta} = \frac{2}{\hbar}\sum \frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2} Re(\langle n|m_\alpha|j\rangle\langle j|m_\beta|n\rangle) + \sum_i \frac{e_i^2}{4m_i}\langle n|r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha\beta}|n\rangle = {}^{m}\chi^{m'}_{\beta\alpha}. \tag{55}$$

Here, the real diamagnetic susceptibility (the second term in Eq. (55)) is

defined in terms of the i'th partial charge at site i in the molecule (e.g. an atom) defined in frame (x, y, z) by the coordinate $r_{i\alpha}$, with site mass m_i. It is defined in terms of matrix elements between ground electronic eigenstates n, and is therefore non-zero in the ground state, far from optical resonance, the condition under which experimental observations were made [11]. This tensor generates an induced magnetic dipole moment which opposes the applied field $\boldsymbol{B}^{(3)}$ of the laser. The other part of the real molecular susceptibility is non-zero only when the transition magnetic dipole moment matrix elements $\langle n|m_\alpha|j\rangle$; $\langle j|m_\beta|n\rangle$ are non-zero between electronic quantum states labelled n and j, n being the ground state. The transition frequency ω_{jn} in Eq. (55) is defined as

$$\omega_{jn} = \omega_j - \omega_n, \tag{56}$$

and the sum is over all states excluding the ground state n. This part of the real molecular susceptibility tensor exhibits optical resonances at $\omega = \omega_{jn}$.

The susceptibility tensor ${}^{m}\hat{\chi}^{m'}_{\alpha\beta}$ is $\hat{T}$ and $\hat{P}$ positive, and does not change sign between enantiomers, remaining finite in a racemic mixture. The order of magnitude of the diamagnetic components can be roughly estimated as

$${}^{m}\chi^{m'}_{\alpha\beta}(diamagnetic) \sim 10^{-28}\ (\text{SI}) \tag{57}$$

It is straightforward to show that

$$\langle B_Z^{(ind)}\rangle = \frac{2}{9}\mu_0 N\left({}^{m}\chi^{m'}_{xx} + {}^{m}\chi^{m'}_{yy} + {}^{m}\chi^{m}_{zz}\right)B_{SZ}^{(3)}, \tag{58}$$

after isotropic averaging, so that the laser induced bulk shift in this mechanism is, for $B_{SZ} = 1.0$ tesla,

$$\frac{\langle B_Z^{(ind)}\rangle}{B_{SZ}} \sim 10^{-14} \text{ to } 10^{-15}, \tag{59}$$

i.e. equivalent to about (3 to 30) x 10^{7} Hz for a 222 MHz spectrometer and a laser intensity of 1.0 watt cm^{-2}.

This is several orders of magnitude less than the observed shifts, and roughly the same order of magnitude as the shifts expected from the hyperpolarizability mechanism. This mechanism is proportional to the square root of the applied laser intensity, and sums the hyperpolarizability mechanism considered earlier, proportional to I_0 itself. The overall shift pattern is therefore not

in general a simple function of laser intensity according to these basically simple considerations, involving just two molecular property tensors, ${}^{m}\gamma^{ee}_{ijk}$ and ${}^{m}\chi^{mm'}_{ij}$. When it is also considered that the susceptibility consists in general of two parts, one which opposes the field $\boldsymbol{B}^{(3)}$, and one which does not, in general, then it begins to become clear that the ONMR shift pattern in general is a sum of several terms in semi-classical theory, which depends on the concept of molecular property tensor [47].

However, these two mechanisms, based on contributions to magnetization of molecular property tensors, produce shifts which are far too small in comparison with experimental bulk shifts [11], so that the filed $\boldsymbol{B}^{(3)}$ must be acting directly to change the externally applied static magnetic field $\boldsymbol{B}_S$ to $\boldsymbol{B}_S + \boldsymbol{B}^{(3)}$. For a laser intensity of 1.0 watt m^{-2}, the free space value of $\boldsymbol{B}^{(3)}$ is about 10^{-5} tesla, which compares with a magnetic flux density of about 6.4 tesla from the permanent magnet [11]. In free space therefore, the ratio $B^{(3)}/B_S$ is approximately 10^{-6}. In the material, however, the free space $\boldsymbol{E}$ field of the laser is modified by the sample shape (a sphere) and by the presence of an internal field $\boldsymbol{E}^{(1)}$ due to the polarization of neighboring molecules. The total field at the molecule is therefore

$$\boldsymbol{E}_m = \left(\frac{3\epsilon_0}{\epsilon + 2\epsilon_0}\right)\boldsymbol{E} + \boldsymbol{E}_{(1)}, \tag{60}$$

and

$$\boldsymbol{B}^{(3)} = \frac{\boldsymbol{E}_m \times \boldsymbol{E}_m^*}{(2E_0 v i)}, \tag{61}$$

where v is the velocity of light in the spherical sample.

The free space ration $B^{(3)}/B_S$ may therefore be affected by an internal field correction, which may reduce it by perhaps an order of magnitude in the sample in comparison with free space. Even so, the direct bulk shift by $\boldsymbol{B}^{(3)}$ is several orders of magnitude greater than the two mechanisms just discussed based on susceptibility and hyperpolarizability respectively, because the shift is due to a first order effect.

Because the observed bulk shifts [11] are so much larger than those due to induction of light by magnetization through molecular property tensors, it seems likely that $\boldsymbol{B}^{(3)}$ is acting directly to augment the permanent magnetic field $\boldsymbol{B}_S$. However, the experimental evidence is unfortunately not unequivocal as yet. The experimental shifts are much smaller in linear polarization [11], which is support for a $\boldsymbol{B}^{(3)}$ mechanism. Warren *et al*. (11) did not report the magnitude of the bulk shifts in hertz, but apparently, they are too small to be due to the

free space value of $\boldsymbol{B}^{(3)}$ uncorrected for the internal field; but *many orders of magnitude* too large to be due to molecular hyperpolarizability and susceptibility. A combination of the $\boldsymbol{B}^{(3)}$ mechanism and a site specific one [11] is therefore probably responsible for the overall shift patterns observed by Warren and co workers [11]. One such site specific mechanism is discussed in Appendix B; and another is reported (without detailed calculations in Ref. [11].

Clearly, much further work is needed to resolve these issues, but the observed optical NMR bulk shifts appear to support the existence of the longitudinal magnetic field $\boldsymbol{B}^{(3)}$.

In a chiral molecule, such as the one chosen for experimental study [11], $\hat{P}$ negative molecular property tensors are also non-zero in general, and also contribute to the laser induced shielding $\sigma^{(ind)}$. This mechanism induces a magnetic electronic dipole moment through a rank three, $\hat{P}$ negative, hyperpolarizability recently considered by Woźniak, Evans, and Wagnière [36] in the context of inverse magneto-chiral birefringence. In this case, because the mediating molecular property tensor is $\hat{P}$ negative, the laser induced shift disappears in a racemic mixture, and is opposite for the two enantiomers. In general, the ONMR spectrum is a combination of terms, the probably dominant ones being mediated by $B^{(3)}$. The direct perturbation of the wavefunction as discussed in Appendix B. These are supplemented by induced dipole moments mediated by the various molecular hyperpolarizabilities, with different optical resonance patterns. Tuning of the applied laser frequency to optical resonances of any of these mediating molecular property tensors will cause enhancement of the laser induced NMR shifts.

Finally, each of the components in the molecule fixed frame of each mediating molecular property tensor can be analyzed in terms of sums of site specific contributions. The literature on semi classical theory refers to well known examples such as the atom and bond polarizability models [19–22], which can be generalized for use with any molecular property tensor. The first data on ONMR are presented [11] in terms of differential shifts (solute minus solvent) for the high and low field ring protons; methoxy protons; high field methyl group protons; and low field methyl group protons of the enantiomers of p methoxyphenyliminocamphor far from any optical resonance frequency of the sample. The differential shift patterns were different for each type of proton site, were solvent dependent, and were found to be much larger in circular polarization than linear polarization of the applied laser. Laser induced shifts were also seen in the deuteriated chloroform lock signal of the 272 MHz instrument used in the original investigation, and have now been observed in over forty different samples [48].

Table 1: [38]

Non-Vanishing Components in the Molecule Fixed Frame (x,y,z) of ${}^{mq}\gamma^{ee}_{ijk}(0,\omega,-\omega)$

Molecular Point Group	${}^{mq}\gamma^{ee}_{ijk}(0,\omega,-\omega)$
C_1, S_2	$xzx = -xxz$, $yzy = -yyz$, $xyx = xxy$, $zxz = zzx$, $yxy = -yyx$, $zyz = -zzy$, $xyz = -xzy$, $yzx = -yxz$, $zxy = -zyx$.
C_2, C_{1h}, C_{2h}	$xzx = -xxz$, $yzy = -yyz$, $xyz = -xzy$, $yzx = -yxz$, $zxy = -zyx$.
C_{2v}, D_2, D_{2h}	$xyz = -xzy$, $yzx = -yxz$, $zxy = -zyx$.
C_{3h}, C_4, S_4, C_{4h}, C_6, S_6, C_{6h}, C_∞, $C_{\infty h}$	$xzx = yzy = -xxz = -yyz$, $xyz = yzx = -xzy = -yxz$, $zxy = -zyx$
D_3, D_4, D_6, D_{2d}, D_{3d}, C_{3v}, C_{4v}, C_{6v}, D_{3h}, D_{4h}, D_{6h}, $D_{\infty h}$, $C_{\infty v}$	$xyz = yzx = -xzy = -yxz$, $zxy = -zyx$.
T, T_h, T_d, O_h, Y, Y_h, K, K_h	$xyz = yzx = zxy = -xzy = -yxz = -zyx$.

Table 2

Irreducible Representations[1] of ${}^{mq}\gamma^{ee}_{ijk}$ at Weight 0 and 1. Frame (x,y,z).

$${}^{mq}\gamma^{ee(0)}_{ijk} = \epsilon_{ijk}\,{}^{m}\gamma^{ee(0)}, \qquad {}^{mq}\gamma^{ee(1)}_{ijk} = \frac{1}{2}\left[\delta_{ij}\left({}^{mq}\gamma^{ee(1)}_{x}\right)_k + \delta_{ik}\left({}^{mq}\gamma^{ee(1)}_{y}\right)_j\right]$$

Point Groups	${}^{mq}\gamma^{ee(0)}$	$({}^{mq}\gamma^{ee(1)}_{x})_x$	$({}^{mq}\gamma^{ee(1)}_{x})_y$	$({}^{mq}\gamma^{ee(1)}_{x})_z$
C_1, S_2	$2(xyz + yzx + zxy)$	$yyx + zzx$	$xxy + zzy$	$xxz + yyz$
C_2, C_{1h}, C_{2h}	$2(xyz + yzx + zxy)$	0	0	$xxz + yyz$
C_{2v}, D_2, D_{2h}	$2(xyz + yzx + zxy)$	0	0	0
C_3, C_{3h}, C_4, S_4, C_{4h}, C_6, S_6, C_{6h}, C_∞, $C_{\infty h}$	$2(2xyz + zxy)$	0	0	$xxz + yyz$
D_3, D_4, D_6, D_{2d}, D_{3d}, C_{3v}, C_{4v}, C_{6v}, D_{3h}, D_{4h}, D_{6h}, $D_{\infty h}$, $C_{\infty v}$	$2(2xyz + zxy)$	0	0	0
T_1, T_h, T_d, O, O_h, Y_h, K, K_h	$6xyz$	0	0	0

[1] ${}^{mq}\gamma^{ee(1)}_{y} = -\,{}^{mq}\gamma^{ee(1)}_{x}$

Table 3

Irreducible Representations[2] of $^{m}\hat{\gamma}^{ee}_{ijk}$ at Weight 2; Frame (x,y,z)

Point Group	$(\hat{\gamma})_{xx}$	$(\hat{\gamma})_{yy}$	$(\hat{\gamma})_{zz}$	$(\hat{\gamma})_{xy}$	$(\hat{\gamma})_{xz}$	$(\hat{\gamma})_{yz}$
C_1, S_2	$\frac{1}{3}(yzx + zxy - 2xyz)$	$\frac{1}{3}(xyz + zxy - 2yzx)$	$\frac{1}{3}(xyz + yzx - 2zxy)$	$\frac{1}{2}(xxz - yyz)$	$\frac{1}{2}(zzy - xxy)$	$\frac{1}{2}(yyx - zzx)$
C_2, C_{1h}, C_{2h}	"	"	"	"	0	0
C_{2v}, D_2, D_{2h}	"	"	"	0	0	0
$C_3, C_{3h}, C_4, S_4, C_{4h}, C_6, S_6, C_{6h}, C_\infty, C_{\infty h}, D_3, D_4, D_6, D_{2d}, D_{3d}, C_{3v}, C_{4v}, C_{6v}, D_{3h}, D_{4h}, D_{6h}, D_{\infty h}, C_{\infty v}$	$\frac{1}{3}(zxy - xyz)$	$\frac{1}{3}(zxy - xyz)$	$-\frac{2}{3}(zxy - xyz)$	0	0	0
$T, T_h, T_d, O, O_h, Y, Y_h, K, K_h$	0	0	0	0	0	0

[2] $(\hat{\gamma}) \equiv \left({}^{m}\hat{\gamma}^{ee(2)}_{x} \right)$, $^{m}\hat{\gamma}^{ee(2)}_{y} = -2\,{}^{m}\hat{\gamma}^{ee(2)}_{x}$

Table 4

Irreducible Representations of $^{m}\hat{\gamma}^{ee}_{ijk}$ in Frame (x,y,z)

Point Group	$^{m}\hat{\gamma}^{ee(0)}$	$^{m}\hat{\gamma}^{ee(1)}$	$^{m}\hat{\gamma}^{ee(2)}$	$^{m}\hat{\gamma}^{ee(3)}$
$C_1, S_1, C_2, C_{1h}, C_{2h}, C_3, C_{3h}, C_4, S_4, C_{4h}, C_6, S_6, C_{6h}, C_\infty, C_{\infty h}$	✓	✓	✓	0
$C_{2v}, D_2, D_{2h}, D_3, D_4, D_6, D_{2d}, D_{3d}, C_{3v}, C_{4v}, C_{6v}, D_{3h}, D_{4h}, D_{6h}, D_{\infty h}, C_{\infty v}$	✓	0	✓	0
$T, T_h, T_d, O, O_h, Y, Y_h, K, K_h$	✓	0	0	0

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Appendix A: Supplementary Point Group Character Tables — $^{mQee}\gamma_{ijk}$

C_{2v}, 2mm $\quad h = 4$

A_1	$\gamma^{(0)}$; $(\gamma_x^{(2)})_{xx}$, $(\gamma_x^{(2)})_{yy}$, $(\gamma_x^{(2)})_{zz}$
A_2	$(\gamma_x^{(1)})_z$; $(\gamma_x^{(2)})_{xy}$
B_1	$(\gamma_x^{(1)})_y$; $(\gamma_x^{(2)})_{xz}$
B_2	$(\gamma_x^{(2)})_x$; $(\gamma_x^{(2)})_{yz}$

$D_g^{(0)} \rightarrow A_1$, $\quad D_g^{(1)} \rightarrow A_2 + B_1 + B_2$, $\quad D_g^{(2)} \rightarrow 2A_1 + B_1 + B_2 + A_2$

C_{3v}, 3m $\quad h = 6$

A_1	$\gamma^{(0)}$; $(\gamma_x^{(2)})_{zz}$; $(\gamma_x^{(2)})_{xx} + (\gamma_x^{(2)})_{yy}$
A_2	$(\gamma_x^{(1)})_z$
E	$\{(\gamma_x^{(1)})_x, (\gamma_x^{(1)})_y\}$; $(\gamma_x^{(2)})_{xy}$, $\{(\gamma_x^{(2)})_{xx} - (\gamma_x^{(2)})_{yy}\}$ $\{(\gamma_x^{(2)})_{xx}, (\gamma_x^{(2)})_{yz}\}$.

$D_g^{(0)} \rightarrow A_1$, $\quad D_g^{(1)} \rightarrow A_2 + E$ $\quad D_g^{(2)} \rightarrow A_1 + 2E$

$C_{\infty v}$ $\quad h = \infty$

$A_1(\Sigma^+)$	$\gamma^{(0)}$; $(\gamma_x^{(2)})_{zz}$; $(\gamma_x^{(2)})_{xx} + (\gamma_x^{(2)})_{yy}$
$A_2(\Sigma^-)$	$(\gamma_x^{(1)})_z$
$E_1(\Pi)$	$\{(\gamma_x^{(1)})_x, (\gamma_x^{(1)})_y\}$; $\{(\gamma_x^{(2)})_{xz}, (\gamma_x^{(2)})_{yz}\}$
$E_2(\Delta)$	$\{(\gamma_x^{(2)})_{xz}, \{(\gamma_x^{(2)})_{xx} - (\gamma_x^{(2)})_{yy}\}\}$

$D_g^{(0)} \rightarrow \Sigma^+$, $\quad D_g^{(1)} \rightarrow \Sigma^- + \Pi$ $\quad D_g^{(2)} \rightarrow \Sigma^+ + \Pi + \Delta$

D_2, 222 $\quad h = 4$

A_1	$\gamma^{(0)}$; $(\gamma_x^{(2)})_{xx}$; $(\gamma_x^{(2)})_{yy}$; $(\gamma_x^{(2)})_{zz}$
B_1	$(\gamma_x^{(1)})_z$; $(\gamma_x^{(2)})_{xy}$
B_2	$(\gamma_x^{(1)})_y$; $(\gamma_x^{(2)})_{xz}$
B_3	$(\gamma_x^{(1)})_x$; $(\gamma_x^{(2)})_{yz}$

$D_g^{(0)} \rightarrow A_1$, $\quad D_g^{(1)} \rightarrow B_1 + B_2 + B_3$, $\quad D_g^{(2)} \rightarrow 2A_1 + B_1 + B_2 + B_3$

D_{3h}, $\bar{6}m2$ $\quad h = 12$

A_1'	$(\gamma_x^{(2)})_{zz}$; $(\gamma_x^{(2)})_{xx} + (\gamma_x^{(2)})_{yy}$
A_2'	$(\gamma_x^{(1)})_z$
A_1''	
A_2''	
E'	$\left((\gamma_x^{(2)})_{xy}, (\gamma_x^{(2)})_{xx} - (\gamma_x^{(2)})_{yy}\right)$
E''	$\left((\gamma_x^{(1)})_x, (\gamma_x^{(1)})_y\right)$; $\left((\gamma_x^{(2)})_{xz}, (\gamma_x^{(2)})_{yz}\right)$

$$D_g^{(0)} \to A_1' \qquad D_g^{(1)} \to A_2' + E'' \qquad D_g^{(2)} \to A_1' + E' + E''$$

$D_{\infty h}$ $\quad h = \infty$

$A_{1g}(\Sigma_g^+)$	$(\gamma_x^{(2)})_{zz}$; $(\gamma_x^{(2)})_{xx} + (\gamma_x^{(22)})_{yy}$
$A_{1u}(\Sigma_u^+)$	
$A_{2g}(\Sigma_g^-)$	$(\gamma_x^{(1)})_z$
$A_{2u}(\Sigma_u^-)$	
$E_{1g}(\Pi_g)$	$\left((\gamma_x^{(1)})_x, (\gamma_x^{(1)})_y\right)$; $\left((\gamma_x^{(2)})_{xz}, (\gamma_x^{(2)})_{yz}\right)$
$E_{1u}(\Pi_u)$	
$E_{2g}(\Delta_g)$	$\left((\gamma_x^{(2)})_{xy}, (\gamma_x^{(2)})_{xx} - (\gamma_x^{(2)})_{yy}\right)$
$E_{2u}(\Delta_u)$	

$$D_g^{(0)} \to \Sigma_g^+ \qquad D_g^{(1)} \to \Sigma_g^- + \Pi_g \qquad D_g^{(2)} \to \Sigma_g^+ + \Pi_g + \Delta_g$$

T_d $\quad \bar{4}3m$ $\quad h = 24$

A_1	$(\gamma_x^{(2)})_{xx} + (\gamma_x^{(2)})_{yy} + (\gamma_x^{(2)})_{zz}$
A_2	
E	$3(\gamma_x^{(2)})_{zz} - \sum_i (\gamma_x^{(2)})_{ii}$, $\left((\gamma_x^{(2)})_{xx} - (\gamma_x^{(2)})_{yy}\right)$
T_1	
T_2	$\left((\gamma_x^{(1)})_x, (\gamma_x^{(1)})_y, (\gamma_x^{(1)})_z\right)$ $\left((\gamma_x^{(2)})_{xy}, (\gamma_x^{(2)})_{xz}, (\gamma_x^{(2)})_{yz}\right)$

$$D_g^{(0)} \to A_1, \qquad D_g^{(1)} \to T_2, \qquad D_g^{(2)} \to T_2 + E$$

0, 432 $\quad h = 24$

A_1	$(\gamma_x^{(2)})_{xx} + (\gamma_x^{(2)})_{yy} + (\gamma_x^{(2)})_{zz}$
A_2	
E	$\left(3(\gamma_x^{(2)})_{zz} - \sum_i (\gamma_x^{(2)})_{ii}, \left((\gamma_x^{(2)})_{xx} - (\gamma_x^{(2)})_{yy}\right)\right)$
T_1	
T_2	$\left((\gamma_x^{(1)})_x, (\gamma_x^{(1)})_y, (\gamma_x^{(1)})_z\right)$ $\left((\gamma_x^{(2)})_{xy}, (\gamma_x^{(2)})_{xz}, (\gamma_x^{(2)})_{yz}\right)$

$$D_g^{(0)} \to A_1, \qquad D_g^{(1)} \to T_2, \qquad D_g^{(2)} \to E + T_2$$

Appendix B

In this appendix we consider a simple model for the change in the diamagnetic shielding factor $\sigma^{(d)}$ expected through a mechanism of direct perturbation of the wave function by the external laser. It is shown that the change in $\sigma^{(d)}$ expected for an applied laser of intensity 1.0 watt cm^{-2} is minute in this mechanism compared with the ones discussed in the text – about 1 part in 10^{13}.

Consider the perturbation caused by the oscillating electric field of the laser. This can be expressed [47] as,

$$\psi_n' = \left(\psi_n^{(0)} + E_0(\mu_X \mp i\mu_Y)e^{-i\omega t}\psi_j^{(0)}\right)e^{-i\omega_n t}, \qquad \psi_n'^{*} = \left(\psi_n^{(0)} + E_0(\mu_X \mp i\mu_Y)e^{i\omega t}\psi_j^{(0)}\right)e^{i\omega_n t},$$

$$\mu_{X,Y}^2 \equiv \frac{\langle n|\mu_{X,Y}|j\rangle\langle j|\mu_{X,Y}|n\rangle}{4\hbar^2(\omega_{jn}-\omega)^2}, \tag{B1}$$

where the electric dipole moments μ_X and μ_Y are described through time dependent perturbation theory at first order. Here $\psi_n'^{*}$ is the complex conjugate of the wavefunction ψ_n'. The ground state wave function is ψ_n' and $|\psi_j'\rangle$ is an eigenstate of higher energy than that described by $|\psi_n'\rangle$>. The time independent charge density is therefore changed by the light perturbation to,

$$\rho_{ext} = -e\left(\psi_n^{(0)2} + E_0^2\left(\mu_X^2 + \mu_Y^2\right)\psi_j^{(0)2}\right), \tag{B2}$$

which is a mixture of states n and j. Here e is the electronic charge. The diamagnetic current density in the presence of this light perturbation is

$$\boldsymbol{j}^{d} = -\frac{e^2}{m_e}\boldsymbol{A}\left(\psi_n^{(0)2} + E_0^2\left(\mu_X^2 + \mu_Y^2\right)\psi_j^{(0)2}\right), \tag{B3}$$

where $\boldsymbol{A}$ is the effective vector potential associated with the light wave. Note that $\boldsymbol{A}$ vanishes unless the light beam is circularly polarized, i.e. unless there is an element of magnetostatic ($\boldsymbol{B}^{(3)}$) symmetry in the beam. $\boldsymbol{A}$ can be identified for example with the field $\boldsymbol{B}^{(3)}$ of the text. In Eq. (B3) m_e is the mass of the electron and the light perturbed wavefunction is as used in Eq. (B2). The change in the diamagnetic shielding factor due to the oscillating electric field $\boldsymbol{E}$ of the light beam is therefore,

$$\Delta\sigma^{d} = \frac{e^2\mu_0}{12\pi m_e}\left(\mu_X^2 + \mu_Y^2\right)\frac{I_0}{\epsilon_0 c}\int\frac{\psi_j^{(0)2}}{r}d\tau, \tag{B4}$$

where I_0 is the light beam's intensity in watts m^{-2}. For I_0 of 10^4 watt m^{-2} (1.0 watt cm^{-2}),

$$\frac{\Delta\sigma^{d}}{\sigma^{d}(E_0=0)} = 10^{-13}, \tag{B5}$$

which is *minute* compared with the other mechanisms considered in the text for an orbital effective radius, r, of about 10^{-10}m.

Similar results in this picture are obtained for other sources of direct perturbation of the wavefunction by the oscillating electromagnetic vectors $\boldsymbol{E}$ and $\boldsymbol{B}$ of the plane wave, to any order in $\boldsymbol{E}$ and/or $\boldsymbol{B}$.

This mechanism has recently been considered by Harris and Tinoco [49], and is very small compared with those considered in the text of this paper. The simple calculation given in this Appendix is sufficient to show this overall conclusion.