PHYSICA $\boxed{B}$

Laser enhanced (optical) NMR spectroscopy, the role of atomic hyperpolarisability

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The role of hyperpolarisability in laser enhanced NMR (LENS) spectroscopy is developed for atoms, taking into account rigorously the combined effect of three angular momenta, L, S, and I. The results show that when there is no resultant electronic angular momentum in an atom (or diamagnetic molecule) the magnetic electric electric electronic hyperpolarisability can mediate the effect of a circularly polarised laser on an NMR spectrum, producing in theory a richly varied spectrum that depends on g factors controlled by L, S and I.

1. Introduction

The technique of LENS spectroscopy has recently been developed theoretically and experimentally. LENS is an acronym for "laser enhanced NMR spectroscopy" in which a circularly polarised laser is directed into the spinning sample tube of a contemporary NMR spectrometer. As in conventional NMR there are several possible LENS mechanisms, and the dominant mechanism, clearly, will be determined by the sample and conditions. This is basically important for the potential use of LENS in the analytical laboratory, because the rich variety of behaviours expected theoretically combine to produce an easily recognisable fingerprint for a given sample under a given set of conditions. For example, the following typify the mechanisms expected theoretically.

(1) In an atom or molecule with net electronic angular momentum, the antisymmetric part of the electronic polarisability mediates the effect of the circularly polarised laser [1–3]. The expected LENS shift is controlled by g factors made up of quantum numbers L, S, and I the electronic orbital and spin angular momentum quantum numbers and the nuclear spin quantum number, respectively. The g factors may be positive or negative, so that for a given circular polarisation the shifts induced by the laser may be up frequency or down frequency.

(2) In chiral molecules with or without net electronic angular momentum a magnetic dipole moment is induced by the electric field of a laser by the Rosenfeld tensor [4, 5].

(3) In achiral molecules with no net electronic angular momentum there is always an electronic magnetic/electric/electric hyperpolarisability $({}^e\beta_{ijk}^{em\parallel})$ which mediates a LENS shift. This mechanism is developed rigorously in this paper for atoms.

(4) The processes (1)–(3) can occur far from optical resonance, i.e. do not depend on absorption. If absorption is present [6, 7] we can think of a right or left handed photon from a circularly polarised laser giving up a unit of angular momentum to the absorbing atom or molecule. This unit of angular momentum is a magnetic dipole moment which can produce a magnetic field at the nucleus through

dipole–dipole or Fermi contact interactions, thus shifting the original NMR resonance [6, 7] and providing a characteristic LENS spectrum of the absorbing sample.

Therefore, even when the net electronic angular momentum is quenched [8], it is possible theoretically for the applied circularly polarised laser of a LENS spectrometer to cause shifts in the NMR spectrum through the hyperpolarisability or by photon absorption, or in chiral molecules, through the Rosenfeld tensor. In atoms and molecules with net electronic angular momentum we expect in addition LENS shifts mediated by the antisymmetric part of the electronic polarisability. The latter vanishes, however, if there is no net electronic angular momentum. In all cases we expect the laser induced electronic magnetic dipole moment to produce a magnetic field at the nucleus, causing yet another type of LENS shift.

Recently, Warren et al. [9, 10] have verified experimentally the basic theoretical expectation of LENS spectroscopy, that a circularly polarised laser shifts a nuclear magnetic resonance line. It was demonstrated for the first time that optical radiation far from absorption bands can shift the resonances in an NMR spectrum without significant heating. It was shown that the LENS shifts are different for different positions in a molecule, implying, for example, that such local shifts could disperse resonances from identical amino acids in different positions of a polypeptide chain. A 270 MHz JEOL NMR spectrometer was used with p-methoxyphenyliminocamphor, a chiral molecule with substantial circular birefringence. Light at 514 nm was directed in the sample cavity from a Coherent Innova 200 argon ion laser. At this frequency, the sample showed almost no optical absorption, i.e. the frequency is far from any optical resonance. The preliminary experimental results of Warren and co-workers [9, 10] show both bulk and local frequency shifts in solvent and solute resonances alike. The deuterium resonance in the deuterated chloroform lock signal was also seen to have been affected [9, 10] by the laser radiation, and the shifts were different in different solvents such as benzene and chloroform. It was shown that heating effects of the laser could be removed easily and effectively [9, 10] leaving the enhanced LENS spectrum for a variety of different proton sites: high and low field ring protons, the methoxy protons, the high and low field methyl protons. Each of these sites showed different LENS shift patterns as a function of laser power in milliwatts per square centimetre. These patterns were different with and without the use of a half wave plate in the laser apparatus. These data clearly reveal the presence of several contributing LENS mechanisms, which in combination produce a LENS spectrum as a function of laser intensity which characterises the sample clearly and unambiguously. LENS is already useful therefore in the analytical laboratory provided that the necessary care is taken experimentally to remove heating artifacts. In this context it may be useful in future to use a piezoelastic modulator [11, 12] to switch the laser rapidly between linear and circular polarisation, with the aim of allowing for heating effects precisely. The idea in this context is that the heating of the sample far from optical resonance would be the same for linear and circular polarisation, whereas the LENS spectrum is expected only for circular polarisation. The extra LENS signal would be picked up with some device such as a lock-in amplifier and filtered out from the "noise" caused by sample heating due to the laser. This would allow the laser intensity to be increased using fairly long duration pulses, possibly in the millisecond range, the overall aim being to maximise the shifts seen in the LENS spectrum, i.e. to maximise the dispersion of the original NMR spectrum and to separate closely spaced proton resonances using the laser.

In this paper we aim to develop rigorously the "beta" mechanism in atoms, i.e. the LENS spectrum mediated by the hyperpolarisability tensor ($^e\beta_{ijk}^{em\parallel}$). The rigorous quantum theory in this case turns out to be complicated, but with contemporary computers it can be evaluated for given L, S, and I. In section 2 the background to the theory is given in terms of 9-j symbols. In section 3 the results of section 2 are developed for an atom in which the beta tensor mediates the effect of the laser on the nuclear characteristics of the atom. In section 4 the theory is put into a form suitable for implementation on computers and the major characteristics of the beta mechanism are evaluated.

2. Background to the rigorous quantum theory

The rigorous quantum theory of the beta mechanism in atoms depends on the appropriate coupling of quantised atomic angular momenta. The interaction energy is evaluated using the Wigner–Eckart theorem to separate out the M_F dependence of the spectrum [13] where M_F is the azimuthal part of the resultant (electronic plus nuclear) angular momentum quantum number F. The standard atomic quantum theory of angular momentum [13–16] reduces the core of the problem to

$$\langle j_1 j_2 F M_F | X_Q^K(1,2) | j_1' j_2' F' M_F' \rangle = (-1)^{F-M_F} \begin{pmatrix} F & K & F' \\ -M_F & Q & M_F' \end{pmatrix} \langle j_1 j_2 F \| X^K \| j_1' j_2' F' \rangle . \tag{1}$$

Here X_Q^K is a compound irreducible tensor operator in the group of all rotations and reflections [13–16]. The compound operator X_Q^K is built up from two operators acting on independent sets of variables in spaces 1 and 2. The matrix elements of X are constructed between eigenstates $\langle j_1 j_2 F M_F |$ and $| j_1' j_2' F' M_F' \rangle$ made up of the two angular momentum states j_1 and j_2 which couple to form the resultant angular momentum F, whose azimuthal components are M_F. The Wigner–Eckart–theorem separates out the rotational properties, (contained in the M_F quantum number) using the well known 3-j symbols [13–16]. The reduced matrix element on the right hand side of eq. (1) evaluates X^K therefore without reference to an azimuthal index Q, but only with respect to the index K which signifies the tensor rank in irreducible spherical representation in the symmetry group of atoms. As usual, the 3-j symbol depends only on the symmetry properties of the compound operator $X_Q^K(1,2)$, and determines the selection rules and overall appearance of the LENS spectrum for a particular LENS mechanism. The angular momentum states $| j_1 m_{j_1} \rangle$ and $| j_2 m_{j_2} \rangle$ are basis functions of the full rotation group [16]. The compound operator must be written in irreducible tensor form, and the reduced matrix elements must be expressed in terms of individual components using the following expression in terms of 9-j symbols [13–16] the background to which is explained by Silver [16]:

$$\langle j_1 j_2 F \| X^K(1,2) \| j_1' j_2' F' \rangle = ((2F+1)(2F'+1)(2K+1))^{1/2}$$

$$\times \begin{bmatrix} j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \\ F & F' & K \end{bmatrix} \langle j_1 \| T^{k_1}(1) \| j_1' \rangle \langle j_2 \| U^{k_2}(2) \| j_2' \rangle , \tag{2}$$

$$X^K = [T^{k_1} \otimes U^{k_2}]^K . \tag{3}$$

This is the basic equation which we shall implement repeatedly in the following section to evaluate the appropriate interaction energy between the relevant angular momentum eigenstates.

3. Development of the interaction energy

In the interaction energy of the beta mechanism we are obliged to consider the coupling of several angular momenta in several spaces. The problem can be reduced, however, to a repeated application of equations of type (2), equations which are expressed as products of 9-j symbols which can be evaluated on a computer [17–19].

Consider firstly the isotropic ensemble average [20, 21] of the electronic magnetic electric electric hyperpolarisability of a molecule or atom:

$$\langle {}^e\beta_{ijk}^{em\|} \rangle_0 = \langle \mu_i \mu_j m_k^{(e)} \rangle_0 \beta_0 , \tag{4}$$

where μ and $m^{(e)}$ denote respectively electronic electric and magnetic dipole moment components using tensor notation [21]. Equation (4) is written in the laboratory frame with Cartesian suffices i, j, k. We define a molecule fixed frame through suffices α, β and γ and unit vectors e_i, e_j and e_k. Using the transformation properties of tensors [21] gives

$$\langle \mu_i \mu_j m_k^{(e)} \rangle_0 = \langle e_{i\alpha} e_{j\beta} e_{k\gamma} \mu_\alpha \mu_\beta m_\gamma^{(e)} \rangle_0$$
$$= \tfrac{1}{6} \epsilon_{ijk} (\varepsilon_{\alpha\beta\gamma} \mu_\alpha \mu_\beta) m_\gamma^{(e)} , \tag{5}$$

where ϵ_{ijk} and $\epsilon_{\alpha\beta\gamma}$ are Levi Civita symbols [21]. Furthermore, the axial vector representation [22] of the antisymmetric electronic polarisability is given by

$$\alpha_\gamma^{\|} = \alpha_0 \epsilon_{\alpha\beta\gamma} \mu_\alpha \mu_\beta , \tag{6}$$

so that the isotropic average (5) can be written as

$$\langle {}^e\beta_{ijk}^{em\|} \rangle_0 = \frac{1}{6} \epsilon_{ijk} \frac{\alpha_\gamma^{\|} m_\gamma^{(e)}}{\alpha_0} \beta_0 , \tag{7}$$

which involves a scalar product of the antisymmetric polarisability and the magnetic dipole moment, both defined with respect to the molecule fixed frame. Any scalar product is frame invariant, and we can back-transform the result (7) to the laboratory frame:

$$\langle {}^e\beta_{ijk}^{em\|} \rangle_0 = \frac{1}{6} \epsilon_{ijk} \frac{\alpha_k^{\|} m_k^{(e)}}{\alpha_0} \beta_0 . \tag{8}$$

The isotropic ensemble average (for example in a liquid or gas) of the beta hyperpolarisability of a molecule or atom in the laboratory frame does not vanish therefore, and gives rise to a LENS spectrum through the following theory.

The interaction energy fundamental to the LENS spectrum is a sum [23]

$$\Delta En = -\langle {}^e\beta_{ijk}^{em\|} \rangle_0 \Pi_{ij}^{(A)} B_k^{(0)} - m_k^{(N)} B_k^{(0)} . \tag{9}$$

Here $m^{(N)}$ is the nuclear magnetic dipole moment, $B^{(0)}$ the static magnetic flux density generated by the permanent magnet of an NMR spectrometer, and the quantity $\Pi_{ij}^{(A)}$ is defined as the antisymmetric part of the tensor $E_i E_j^*$, where E is the electric field strength in volts per metre of the laser. For a circularly polarised laser,

$$\Pi_{ij}^{(A)} = \tfrac{1}{2} (E_i E_j^* - E_j E_i^*) , \tag{10}$$

and $\Pi_{ij}^{(A)}$ vanishes if the laser is linearly polarised or incoherently polarised. It changes sign [24] if the circular polarisation is switched from left to right. The product $\Pi_{ij}^{(A)}$ is an antisymmetric second rank polar tensor, which by fundamental tensor theory [21] can be expressed as an axial vector

$$\Pi_i^{(A)} = \epsilon_{ijk} \Pi_{jk}^{(A)} . \tag{11}$$

The theory of the LENS effect due to the beta tensor proceeds by evaluating this interaction energy quantum mechanically between the appropriate angular momentum eigenstates. The mathematics of

this procedure is complicated, but the physics of the situation is simple, we are evaluating the effect of the beta term in the interaction energy on the original NMR resonance due to the other term in eq. (9). We try to keep the complexity secondary to the physical and chemical principles involved.

Firstly it is necessary to reduce the interaction energy to a form in which it is expressed in terms of the three atomic angular momenta L, S, and I. This is accomplished using considerations of fundamental symmetry: motion reversal (T) and parity inversion (P). The antisymmetric polarisability and magnetic dipole moment both have T negative, P positive symmetries [23, 24] and it is well known [25] that the electronic magnetic dipole moment can be expressed in terms of the angular momenta L and S through the scalar gyromagnetic ratio

$$m_i^{(e)} = \gamma_e(L_i + 2.002S_i) \,. \tag{12}$$

On the grounds of P and T symmetry alone it is therefore reasonable to use a similar ansatz for the axial vector $\alpha_i^{\parallel}$:

$$\alpha_i^{\parallel} = \gamma_{\Pi}(L_i + 2.002S_i) \,, \tag{13}$$

where we have named the scalar γ_{Π} the "gyroptic ratio" [26]. Note that this assumes that the electronic spin as well as the orbital angular momentum contributes to the antisymmetric polarisability, and in this context we recall that electronic spin is not a term which can be taken too literally, it does not actually imply a spinning object (the electron), but is an outcome of the Dirac equation of relativistic quantum theory and of the need to describe the results of the Stern–Gerlach experiment. Our ansatz has implied that the electronic spin is "polarisable" [27].

The interaction energy (9) for an isotropic ensemble can therefore be written as

$$\Delta En = -\frac{1}{6} \epsilon_{ijk} \frac{\beta_0}{\alpha_0} \gamma_e \gamma_{\Pi} \langle FM_F | L_k L_k + 2.002 S_k L_k + 2.002 L_k S_k + 2.002^2 S_k S_k | F'M_F' \rangle \Pi_{ij}^{(A)} B_k^{(0)}$$
$$- \langle FM_F | m_k^{(N)} | F'M_F' \rangle B_k^{(0)} \,, \tag{14}$$

a sum of five terms, each of which consists of vectors or scalar produces of vectors. The integration energy must be evaluated between eigenstates made up of quantised angular momenta which couple to form a resultant angular momentum F. The expression for the interaction energy is therefore

$$\Delta En = -\text{Const}_1 \langle FM_F | L_k^{①} L_k^{②} + 2.002 S_k^{③} L_k^{④} + 2.002 L_k^{⑤} S_k^{⑥} + 2.002^2 S_k^{⑦} S_k^{⑧} | F'M_F' \rangle$$
$$- \text{Const}_2 \langle FM_F | I_k^{⑨} | F'M_F' \rangle \,, \tag{15}$$

in which the circled numbers denote nine angular momentum spaces [13–16] shared out among five terms. The interaction of these nine spaces in the context of Racah algebra [16] leads to g factors analogous to the well known Landé factors [13–16], but much more richly structured. All these g factors can always be expressed, however, in terms of the three atomic angular momentum quantum numbers L, S, and I.

A chain of equations can be constructed as follows, which reduces the expression for the quantised interaction energy to products of 9-j symbols, symbols which can be reduced, in turn, to simple numbers using a computer [17–19]. To start the chain consider the quantised angular momentum coupling between spaces circled 1 and 2 in eq. (15). We have a special case of the general problem described by eqs. (1) and (2) of section 2 of evaluating the compound irreducible tensor

$$X^{k_3} = [A^{k_1} \otimes B^{k_2}]^{k_3} \tag{16}$$

using an angular momentum coupling scheme:

$$j_3 = j_1 + j_2 , \tag{17}$$

with the following identities

$$A^{k_1} \equiv L_Z , \quad B^{k_2} \equiv L_Z , \quad k_1 = 1, \quad k_2 = 1, \quad k_3 = 0, \quad j_1 \equiv L , \quad j_2 \equiv L , \quad j_3 \equiv L_1 .$$

The tensor product $\otimes$ is in our case a scalar or dot product of two rank one vectors, L and L_1 both in the Z axis.

To continue the chain, we must link spaces ① and ② to the other seven spaces circled in eq. (15). It proves convenient to go about this in the following order:

$$
\begin{aligned}
j_1 + j_2 &= j_3, & X^{k_3} &= A^{k_1} \otimes B^{k_2}, & A^{k_1} &\equiv L_Z, & B^{k_2} &\equiv L_Z, \\
j_4 + j_5 &= j_6, & X^{k_6} &= C^{k_4} \otimes D^{k_5}, & C^{k_4} &\equiv S_Z, & D^{k_5} &\equiv L_Z, \\
j_7 + j_8 &= j_9, & X^{k_9} &= E^{k_7} \otimes F^{k_8}, & E^{k_7} &\equiv L_Z, & F^{k_8} &\equiv S_Z, \\
j_{10} + j_{11} &= j_{12}, & X^{k_{12}} &= G^{k_{10}} \otimes H^{k_{11}}, & G^{k_{10}} &\equiv S_Z, & H^{k_{11}} &\equiv S_Z, \\
j_3 + j_6 &= j_{14}, & X^{k_{14}} &= X^{k_3} \otimes X^{k_6}, \\
j_{14} + j_9 &= j_{15}, & X^{k_{15}} &= X^{k_{14}} \otimes X^{k_9}, \\
j_{15} + j_{12} &= j_{16}, & X^{k_{16}} &= X^{k_{15}} \otimes X^{k_{12}}, \\
j_{16} + j_{13} &= j_{17}, & X^{k_{17}} &= X^{k_{16}} \otimes I^{k_{13}}.
\end{aligned}
\tag{18}
$$

This leads to a chain of interlinked expressions which must be used for each of the five terms of eq. (14). This chain is given in appendix A because of its complexity, and referred to hereafter as eq. (A.1).

First term in eq. (A.1):

$$
\begin{aligned}
& A^{k_1} = L_Z, & B^{k_2} = L_Z, & \quad X^{k_3} = L_Z L_Z = L_Z^2, & k_1 = 1, & k_2 = 1, & k_3 = 0, \\
& C^{k_4} = 1, & D^{k_5} = 1, & \quad X^{k_6} = 1, & k_4 = 0, & k_5 = 0, & k_6 = 0, \\
& E^{k_7} = 1, & F^{k_8} = 1, & \quad X^{k_9} = 1, & k_7 = 0, & k_8 = 0, & k_9 = 0, \\
& G^{k_{10}} = 1, & H^{k_{11}} = 1, & \quad X^{k_{12}} = 1, & k_{10} = 0, & k_{11} = 0, & k_{12} = 0, \\
& X^{k_3} = L_Z^2, & X^{k_6} = 1, & \quad X^{k_{14}} = L_Z^2, & k_3 = 0, & k_6 = 0, & k_{14} = 0, \\
& X^{k_{14}} = L_Z^2, & X^{k_9} = 1, & \quad X^{k_{15}} = L_Z^2, & k_{14} = 0, & k_9 = 0, & k_{15} = 0, \\
& X^{k_{15}} = L_Z^2, & X^{k_{12}} = 1, & \quad X^{k_{16}} = L_Z^2, & k_{15} = 0, & k_{12} = 0, & k_{16} = 0, \\
& X^{k_{16}} = L_Z^2, & I^{k_{13}} = 1, & \quad X^{k_{17}} = L_Z^2, & k_{16} = 0, & k_{13} = 0, & k_{17} = 0.
\end{aligned}
\tag{19}
$$

Second term in eq. (A.1):

$$
\begin{aligned}
& A^{k_1} = 1, & B^{k_2} = 1, & \quad X^{k_3} = 1, & k_1 = 0, & k_2 = 0, & k_3 = 0, \\
& C^{k_4} = S_Z, & D^{k_5} = L_Z, & \quad X^{k_6} = S_Z L_Z, & k_4 = 1, & k_5 = 1, & k_6 = 0, \\
& E^{k_7} = 1, & F^{k_8} = 1, & \quad X^{k_9} = 1, & k_7 = 0, & k_8 = 0, & k_9 = 0,
\end{aligned}
$$

$$G^{k_{10}} = 1, \qquad H^{k_{11}} = 1, \qquad X^{k_{12}} = 1, \qquad k_{10} = 0, \quad k_{11} = 0, \quad k_{12} = 0,$$
$$X^{k_3} = 1, \qquad X^{k_6} = S_z L_z, \quad X^{k_{14}} = S_z L_z, \quad k_3 = 0, \quad k_6 = 0, \quad k_{14} = 0,$$
$$X^{k_{14}} = S_z L_z, \quad X^{k_9} = 1, \qquad X^{k_{15}} = S_z L_z, \quad k_{14} = 0, \quad k_9 = 0, \quad k_{15} = 0,$$
$$X^{k_{15}} = S_z L_z, \quad X^{k_{12}} = 1, \qquad X^{k_{16}} = S_z L_z, \quad k_{15} = 0, \quad k_{12} = 0, \quad k_{16} = 0,$$
$$X^{k_{16}} = S_z L_z, \quad I^{k_{13}} = 1, \qquad X^{k_{17}} = S_z L_z, \quad k_{16} = 0, \quad k_{13} = 0, \quad k_{17} = 0.$$
(20)

Third term in eq. (A.1):

$$A^{k_1} = 1, \qquad B^{k_2} = 1, \qquad X^{k_3} = 1, \qquad k_1 = 0, \quad k_2 = 0, \quad k_3 = 0,$$
$$C^{k_4} = 1, \qquad D^{k_5} = 1, \qquad X^{k_6} = 1, \qquad k_4 = 0, \quad k_5 = 0, \quad k_6 = 0,$$
$$E^{k_7} = L_z, \qquad F^{k_8} = S_z, \qquad X^{k_9} = L_z S_z, \quad k_7 = 1, \quad k_8 = 1, \quad k_9 = 0,$$
$$G^{k_{10}} = 1, \qquad H^{k_{11}} = 1, \qquad X^{k_{12}} = 1, \qquad k_{10} = 0, \quad k_{11} = 0, \quad k_{12} = 0,$$
$$X^{k_3} = 1, \qquad X^{k_6} = 1, \qquad X^{k_{14}} = 1, \qquad k_3 = 0, \quad k_6 = 0, \quad k_{14} = 0,$$
$$X^{k_{14}} = 1, \qquad X^{k_9} = L_z S_z, \quad X^{k_{15}} = L_z S_z, \quad k_{14} = 0, \quad k_9 = 0, \quad k_{15} = 0,$$
$$X^{k_{15}} = L_z S_z, \quad X^{k_{12}} = 1, \qquad X^{k_{16}} = L_z S_z, \quad k_{15} = 0, \quad k_{12} = 0, \quad k_{16} = 0,$$
$$X^{k_{16}} = L_z S_z, \quad I^{k_{13}} = 1, \qquad X^{k_{17}} = L_z S_z, \quad k_{16} = 0, \quad k_{12} = 0, \quad k_{17} = 0.$$
(21)

Fourth term in eq. (A.1):

$$A^{k_1} = 1, \qquad B^{k_2} = 1, \qquad X^{k_3} = 1, \qquad k_1 = 0, \quad k_2 = 0, \quad k_3 = 0,$$
$$C^{k_4} = 1, \qquad D^{k_5} = 1, \qquad X^{k_6} = 1, \qquad k_4 = 0, \quad k_5 = 0, \quad k_6 = 0,$$
$$E^{k_7} = 1, \qquad F^{k_8} = 1, \qquad X^{k_9} = 1, \qquad k_7 = 0, \quad k_8 = 0, \quad k_9 = 0,$$
$$G^{k_{10}} = S_z, \qquad H^{k_{11}} = S_z, \qquad X^{k_{12}} = S_z S_z, \quad k_{10} = 1, \quad k_{11} = 1, \quad k_{12} = 0,$$
$$X^{k_3} = 1, \qquad X^{k_6} = 1, \qquad X^{k_{14}} = 1, \qquad k_3 = 0, \quad k_6 = 0, \quad k_{14} = 0,$$
$$X^{k_{14}} = 1, \qquad X^{k_9} = 1, \qquad X^{k_{15}} = 1, \qquad k_{14} = 0, \quad k_9 = 0, \quad k_{15} = 0,$$
$$X^{k_{15}} = 1, \qquad X^{k_{12}} = S_z S_z, \quad X^{k_{16}} = S_z S_z, \quad k_{15} = 0, \quad k_{12} = 0, \quad k_{16} = 0,$$
$$X^{k_{16}} = S_z S_z, \quad I^{k_{13}} = 1, \qquad X^{k_{17}} = S_z S_z, \quad k_{16} = 0, \quad k_{13} = 0, \quad k_{17} = 0.$$
(22)

Fifth term in eq. (A.1):

$$A^{k_1} = 1, \quad B^{k_2} = 1, \quad X^{k_3} = 1, \quad k_1 = 0, \quad k_2 = 0, \quad k_3 = 0,$$
$$C^{k_4} = 1, \quad D^{k_5} = 1, \quad X^{k_6} = 1, \quad k_4 = 0, \quad k_5 = 0, \quad k_6 = 0,$$
$$E^{k_6} = 1, \quad F^{k_7} = 1, \quad X^{k_9} = 1, \quad k_6 = 0, \quad k_7 = 0, \quad k_9 = 0,$$
$$G^{k_{10}} = 1, \quad H^{k_{11}} = 1, \quad X^{k_{12}} = 1, \quad k_{10} = 0, \quad k_{11} = 0, \quad k_{12} = 0,$$
$$X^{k_3} = 1, \quad X^{k_6} = 1, \quad X^{k_{14}} = 1, \quad k_3 = 0, \quad k_6 = 0, \quad k_{14} = 0,$$
$$X^{k_{14}} = 1, \quad X^{k_9} = 1, \quad X^{k_{15}} = 1, \quad k_{14} = 0, \quad k_9 = 0, \quad k_{15} = 0,$$
$$X^{k_{15}} = 1, \quad X^{k_{12}} = 1, \quad X^{k_{16}} = 1, \quad k_{15} = 0, \quad k_{12} = 0, \quad k_{16} = 0,$$
$$X^{k_{16}} = 1, \quad I^{k_{13}} = I_z, \quad X^{k_{17}} = I_z, \quad k_{16} = 0, \quad k_{13} = 1, \quad k_{17} = 1$$
(23)

In each of the five terms the angular momentum coupling scheme is

$$
\begin{aligned}
&j_1 + j_2 = j_3, & &j_1 \equiv L, & &j_2 \equiv L, & &J_3 \equiv L_1, \\
&j_4 + j_5 = j_6, & &j_4 \equiv S, & &j_5 \equiv L, & &J_6 \equiv J, \\
&j_7 + j_8 = j_9, & &j_7 \equiv L, & &j_8 \equiv S, & &J_9 \equiv J, \\
&j_{10} + j_{11} = j_{12}, & &j_{10} \equiv S, & &j_{11} \equiv S, & &j_{12} \equiv S_1, \\
&j_3 + j_6 = j_{14}, & &j_3 \equiv L_1, & &j_6 \equiv J, & &j_{14} \equiv J_1, \\
&j_{14} + j_9 = j_{15}, & &j_{14} \equiv J_1, & &j_9 \equiv J, & &j_{15} \equiv J_2, \\
&j_{15} + j_{12} = j_{16}, & &j_{15} \equiv J_2, & &j_{12} \equiv S_1, & &j_{16} \equiv J_3, \\
&j_{16} + j_{13} = j_{17}, & &j_{16} \equiv J_3, & &j_{13} \equiv I, & &j_{17} \equiv F,
\end{aligned}
\tag{24}
$$

with the quantum numbers taking the values

$$
\begin{aligned}
&L_1 = L + L, & &L + L - 1, & &\ldots, & &0, \\
&J = S + L, & &S + L - 1, & &\ldots, & &|S - L|, \\
&J = L + S, & &L + S - 1, & &\ldots, & &|L - S|, \\
&S_1 = S + S, & &S + S - 1, & &\ldots, & &0, \\
&J_1 = L_1 + J, & &L_1 + J - 1, & &\ldots, & &|L_1 - J|, \\
&J_2 = J_1 + J, & &J_1 + J - 1, & &\ldots, & &|J_1 - J|, \\
&J_3 = J_2 + S_1, & &J_2 + S_1 - 1, & &\ldots, & &|J_2 - S_1|, \\
&F = J_3 + I, & &J_3 + I - 1, & &\ldots, & &|J_3 - I|.
\end{aligned}
\tag{25}
$$

Terms such as $\langle j_{16} \| X^{k_{16}} \| j_{16}' \rangle$ are evaluated as usual, for example

$$
\begin{aligned}
&\langle J_3 \| L_Z^2 \| j_3' \rangle = \langle J_3 \| 1 \| J_3' \rangle L_Z^2 = (2J_3 + 1)^{1/2} \delta_{J_3 J_3'} L_Z^2 , \\
&\langle I \| I \| I' \rangle = (I(I + 1)(2I + 1))^{1/2} \delta_{II'} ,
\end{aligned}
\tag{26}
$$

and so on.

4. Approximations to the rigorous theory

The rigorous theory can be reduced in complexity by suitable approximations using successive links in the chain (A.1). The first approximation consists of writing eq. (9) as

$$
\Delta En_1 = -m_Z^{(\mathrm{ind})} B_Z^{(0)} - m_Z^{(\mathrm{N})} B_Z^{(0)} = -\gamma_e J_{3Z} B_Z^{(0)} - \gamma_N I_Z B_Z^{(0)} ,
\tag{27}
$$

where $m_Z^{(\mathrm{ind})}$ is the induced magnetic dipole moment, and assuming that this is proportional to the angular momentum J_{3Z} in the coupling scheme. The component angular momenta of J_{3Z} are not considered in this approximation. In this approximation eq. (9) becomes

$$
\Delta En_1 = -B_Z^{(0)} \langle J_3 IFM_F | \gamma_e J_{3Z} + \gamma_N I_Z | J_3 IFM_F \rangle ,
\tag{28}
$$

which can be written in terms of Landé factors [28]

$$
\Delta En_1 = -B_Z^{(0)} M_F (g_{L1} \gamma_e + g_{L2} \gamma_N) \hbar ,
\tag{29}
$$

where

$$
g_{L1} = \frac{1}{2} \left(\frac{F(F + 1) + J_3(J_3 + 1) - I(I + 1)}{F(F + 1)} \right) ,
\tag{30}
$$

and

$$g_{L2} = \frac{1}{2}\left(\frac{F(F+1) + I(I+1) - J_3(J_3+1)}{F(F+1)}\right). \tag{31}$$

The 3-j symbol in the final component of eq. (A.1) determines the selection rules on the quantum number M_F, the azimuthal component of the resultant angular momentum quantum number F. The 3-j symbol vanishes unless

$$\Delta M_F = 0 \quad \text{or} \pm 1. \tag{32}$$

This rule determines the LENS resonance conditions in this approximation through

$$\omega_R = B_Z^{(0)}(g_{L1}\gamma_e + g_{L2}\gamma_N), \tag{33}$$

where ω_R is the frequency of the probe radiation in the LENS spectrometer. Even in this first approximation it can be seen that there are several possible resonance conditions, determined by the Clebsch Gordan series for F,

$$F = J_3 + I, \ldots, |J_3 - I|. \tag{34}$$

In our atomic hyperpolarisability theory, therefore, the effect of a circularly polarised laser in the LENS spectrometer is to shift the original resonance and split it into different lines.

However, we know that the quantum number J_3 is itself made up of a Clebsch–Gordan series of the angular momentum quantum numbers J_2 and S_1, as described in the foregoing coupling scheme. Furthermore, J_2 and S_1 are themselves made up of other angular momentum quantum numbers and so on. It follows that there are many LENS resonances in theory, and with sufficient resolution each of these should be present in the spectrum.

In the second approximation, therefore, we write eq. (9) as

$$\Delta En_2 = -B_Z^{(0)}\langle J_2 S_1 J_3 IF M_F | \gamma_e(J_{2Z} + S_{1Z}) + \gamma_N I_Z | J_2 S_1 J_3 IF M_F \rangle, \tag{35}$$

which consists of three angular momentum quantum numbers in different spaces. It can be shown [29] that eq. (A.1) then reduces to a sum of three terms [29] involving products of 9-j symbols. The 9-j symbols can be evaluated computationally [29], and the LENS spectrum can be constructed for any given I, J_2 and S_1. The expressions for the LENS resonances in this second approximation are given in appendix B and some results from that appendix are illustrated in figs. (1)–(3), showing that in this second approximation to eq. (A.1), the effect of the circularly polarised laser is to shift the original NMR resonance to higher frequency and in theory to split it into several different lines. This is in qualitative agreement with the available experimental data [9, 10], which refer to a large chiral molecule, not to an atom. To extend the atomic theory of this paper to molecular point groups requires the implementation of the V, W and X coefficients first devised by Griffith [30]. In this context the 3-j symbols of atomic theory go over to V coefficients, 6-j symbols to W coefficients, and 9-j symbols to X coefficients. A clear introduction is given by Silver [16]. Therefore, in order to describe the data obtained by Warren and co-workers [9, 10] the V, W, and X coefficients have to be used for the appropriate molecular symmetry, which is the chiral C_1 point group.

However, for readers primarily interested in the analytical consequences of LENS, the appropriate way forward is clearly empirical, to fingerprint the sample with LENS and to store the fingerprint for future analytical use. For the LENS dispersion [9, 10] of H resonances in a polypeptide, for example,

LENS SHIFT, SECOND ORDER APPROXIMATION.
J3 = 2.5, I = 0.5, F = 2 AND 3

LENS SHIFTS, SECOND ORDER APPROXIMATION.
J3 = 3.5, I = 0.5, F = 3 AND 4.
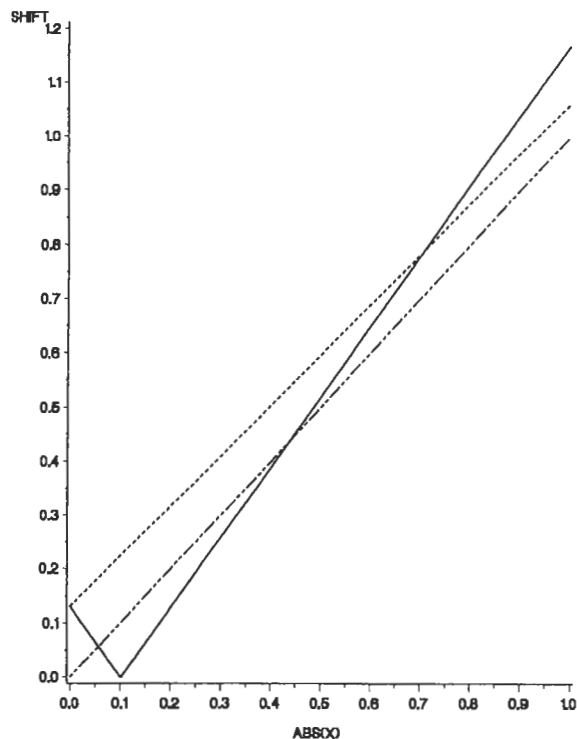
Fig. 1. Second order approximation, LENS shift as a function of the ratio $x = \gamma_e/\gamma_N$. $J_3 = \frac{5}{2}$; $I = \frac{1}{2}$. ——, $F = 2$; ------, $F = 3$; $- \cdot \cdot - \cdot \cdot$, 45° base line.
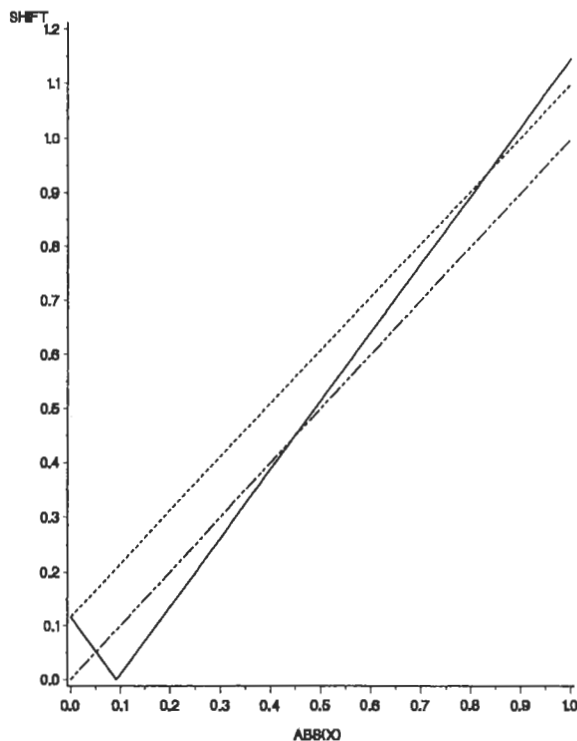
Fig. 2. As for fig. 1, $J_3 = \frac{7}{2}$; $I = \frac{1}{2}$. ——, $F = 3$; ------, $F = 4$; $- \cdot \cdot - \cdot \cdot$, 45° base line.

this is obviously the practical procedure. The analytical laboratory would probably not attempt to calculate, for example, a conventional 2-D protein map from Racah algebra. The latter is used in this and other papers [31] to give a theoretical foundation to the very existence of LENS effects, and these papers should be used in this spirit.

Recall that the whole structure of eq. (A.1) refers to only one particular mechanism, mediated by the beta tensor. The latter is non-zero in all atoms and molecules, diamagnetic or paramagnetic. In atoms and molecules with unquenched electronic angular momentum, however, the antisymmetric polarisability is also non-zero, and may be dominant in determining the LENS shift and split.

In a chiral molecule, furthermore, there is also the possibility of a magnetic dipole moment being induced through the Rosenfeld molecular property tensor, a second rank electric dipole/magnetic dipole tensor [32]

$$m_i^{(\text{ind})} = R_{ij}B_j \equiv \gamma_R J_i^{(\text{ind})} \ . \tag{36}$$

Being a magnetic dipole moment, $m_i^{(\text{ind})}$ is proportional through a scalar to an electronic angular momentum, and the latter is quantised in general. The interaction energy for the Rosenfeld mechanism is

$$\Delta En_3 = - B_Z^0 \langle J^{(\text{ind})} M_J^{(\text{ind})} | \gamma_R J_Z^{(\text{ind})} | J^{(\text{ind})} M_J^{(\text{ind})} \rangle \ , \tag{37}$$

LENS SHIFT, SECOND ORDER APPROXIMATION.
J3 = 4.5, I = 0.5, F = 4 AND 5.
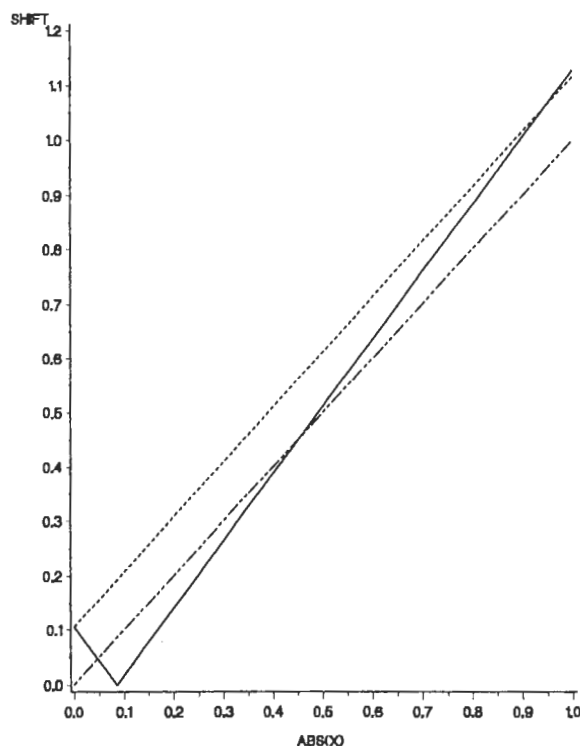
Fig. 3. As for fig. 1, $J_3 = \frac{9}{2}$; $I = \frac{1}{2}$. ——, $F = 4$; ------, $F = 5$; $- \cdot \cdot - \cdot \cdot$, 45° base line.

which again leads to a theoretical expectation of a LENS shift. We do not go into further details of the "Rosenfeld mechanism" here, but in a chiral molecule with large optical rotation at a given laser frequency, this mechanism can probably dominate, or at least be a substantial part of the observed LENS effect [6, 7]. Furthermore, the Rosenfeld tensor is defined as the second partial energy derivative

$$R_{ij} = -\left(\frac{\partial^2 H}{\partial E_i \partial B_j}\right)_0 , \tag{38}$$

where E_i and B_j are the electric and magnetic components of the laser, respectively, and the antisymmetric part of the tensor product $E_i B_j$ does not change sign on switching the laser from left to right circular polarisation. In consequence the LENS shift due to this particular Rosenfeld mechanism is always to the up frequency side. This mechanism is not present if the molecule is achiral.

The interested reader is referred to previous papers [1–3, 31] for various order of magnitude estimates from the alpha and beta mechanisms, and to other possibility based on the induction of a magnetic electronic dipole moment by the laser, an induced dipole moment which sets up a magnetic field at the nucleus, resulting in a LENS shift. The extra nuclear magnetic field can be induced by Fermi contact or dipole dipole mechanisms as circumstances allow [31].

The potentially most useful analytical feature of LENS [9, 10] appears to be the fact that the shifts are site selective, i.e. are different for local H sites in the test molecule [9, 10], with different laser intensity and solvent dependencies. The adaptation of chemical shift and shielding theory from conventional NMR [32–34] is another interesting pattern of future research now that the basic LENS

mechanisms [1–3, 6, 7] have been demonstrated [9, 10] qualitatively. In this paper we have dealt with one possible mechanism, mediated by the hyperpolarisability beta, and have confined our treatment to atomic symmetries.

Acknowledgements

Appendix A

The chain of eq. (A.1)

$$\langle j_3 \| X^{k_3} \| j_3' \rangle = [(2j_3 + 1)(2j_3' + 1)(2k_3 + 1)]^{1/2} \begin{bmatrix} j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \\ j_3 & j_3' & k_3 \end{bmatrix} \langle j_1 \| A^{k_1} \| j_1' \rangle \langle j_2 \| B^{k_2} \| j_2' \rangle \,,$$

$$\langle j_6 \| X^{k_6} \| j_6' \rangle = [(2j_6 + 1)(2j_6' + 1)(2k_6 + 1)]^{1/2} \begin{bmatrix} j_4 & j_4' & k_4 \\ j_5 & j_5' & k_5 \\ j_6 & j_6' & k_6 \end{bmatrix} \langle j_4 \| C^{k_4} \| j_4' \rangle \langle j_5 \| D^{k_5} \| j_5' \rangle \,,$$

$$\langle j_9 \| X^{k_9} \| j_9' \rangle = [(2j_9 + 1)(2j_9' + 1)(2k_9 + 1)]^{1/2} \begin{bmatrix} j_7 & j_7' & k_7 \\ j_8 & j_8' & k_8 \\ j_9 & j_9' & k_9 \end{bmatrix} \langle j_7 \| E^{k_7} \| j_7' \rangle \langle j_8 \| F^{k_8} \| j_8' \rangle \,,$$

$$\langle j_{12} \| X^{k_{12}} \| j_{12}' \rangle = [(2j_{12} + 1)(2j_{12}' + 1)(2k_{12} + 1)]^{1/2} \begin{bmatrix} j_{10} & j_{10}' & k_{10} \\ j_{11} & j_{11}' & k_{11} \\ j_{12} & j_{12}' & k_{12} \end{bmatrix} \langle j_{10} \| G^{k_{10}} \| j_{10}' \rangle \langle j_{11} \| H^{k_{11}} \| j_{11}' \rangle \,,$$

$$\langle j_{14} \| X^{k_{14}} \| j_{14}' \rangle = [(2j_{14} + 1)(2j_{14}' + 1)(2k_{14} + 1)]^{1/2} \begin{bmatrix} j_3 & j_3' & k_3 \\ j_6 & j_6' & k_6 \\ j_{14} & j_{14}' & k_{14} \end{bmatrix} \langle j_3 \| X^{k_3} \| j_3' \rangle \langle j_6 \| X^{k_6} \| j_6' \rangle \,,$$

$$\langle j_{15} \| X^{k_{15}} \| j_{15}' \rangle = [(2j_{15} + 1)(2j_{15}' + 1)(2k_{15} + 1)]^{1/2} \begin{bmatrix} j_{14} & j_{14}' & k_{14} \\ j_9 & j_9' & k_9 \\ j_{15} & j_{15}' & k_{15} \end{bmatrix} \langle j_{14} \| X^{k_{14}} \| j_{14}' \rangle \langle j_9 \| X^{k_9} \| j_9' \rangle \,,$$

$$\langle j_{16} \| X^{k_{16}} \| j_{16}' \rangle = [(2j_{16} + 1)(2j_{16}' + 1)(2k_{16} + 1)]^{1/2} \begin{bmatrix} j_{15} & j_{15}' & k_{15} \\ j_{12} & j_{12}' & k_{12} \\ j_{16} & j_{16}' & k_{16} \end{bmatrix} \langle j_{15} \| X^{k_{15}} \| j_{15}' \rangle \langle j_{12} \| X^{k_{12}} \| j_{12}' \rangle \,,$$

$$\langle j_{17} \| X^{k_{17}} \| j_{17}' \rangle = [(2j_{17} + 1)(2j_{17}' + 1)(2k_{17} + 1)]^{1/2} \begin{bmatrix} j_{16} & j_{16}' & k_{16} \\ j_{13} & j_{13}' & k_{13} \\ j_{17} & j_{17}' & k_{17} \end{bmatrix} \langle j_{16} \| X^{k_{16}} \| j_{16}' \rangle \langle j_{13} \| I^{k_{13}} \| j_{13}' \rangle \,,$$

$$\langle j_{17} \| X_Q^{k_{17}} \| j_{17}' \rangle = (-1)^{k_{17} - M_{k_{17}}} \begin{pmatrix} j_{17} & k_{17} & j_{17}' \\ -M_{k_{17}} & Q & M_{k_{17}}' \end{pmatrix} \langle j_{17} \| X^{k_{17}} \| j_{17}' \rangle \,.$$

Appendix B

In the second approximation, the LENS resonance frequency is given by

$$\omega_R = \frac{|g_{L2}|}{\hbar}, \tag{B.1}$$

where the second order g factor is

$$g_{L2} = \frac{(\gamma_e(g_{12} + 2g_{22}) + g_N\gamma_N)B_Z^{(0)}g_{32}}{(F(2F+1)(F+1))^{1/2}},$$

which is expressed as follows in terms of 9-j symbols

$$g_{12} = \langle J_2S_1J_3IF\|J_2\|J_2S_1J_3IF\rangle = 3\hbar(2F+1)(2J_3+1)(2S_1+1)^{1/2}$$

$$\times (2I+1)^{1/2}(J_2(J_2+1)(2J_2+1))^{1/2}\begin{bmatrix} J_3 & J_3 & 1 \\ I & I & 0 \\ F & F & 1 \end{bmatrix}\begin{bmatrix} J_2 & J_2 & 1 \\ S_1 & S_1 & 0 \\ J_3 & J_3 & 1 \end{bmatrix},$$

$$g_{22} = \langle J_2S_1J_3IF\|S_1\|J_2S_1J_3IF\rangle = 3\hbar(2F+1)(2J_3+1)(2J_2+1)^{1/2}$$

$$\times (2J_3+1)^{1/2}(S(S+1)(2S+1))^{1/2}\begin{bmatrix} J_3 & J_3 & 1 \\ I & I & 0 \\ F & F & 1 \end{bmatrix}\begin{bmatrix} J_2 & J_2 & 0 \\ S_1 & S_1 & 1 \\ J_3 & J_3 & 1 \end{bmatrix},$$

$$g_{32} = \langle J_2S_1J_3IF\|I\|J_2S_1J_3IF\rangle = \sqrt{3}\hbar(2F+1)(2J_3+1)(2J_1+1)^{1/2}$$

$$\times (2S_1+1)^{1/2}(I(I+1)(2I+1))^{1/2}\begin{bmatrix} J_3 & J_3 & 0 \\ I & I & 1 \\ F & F & 1 \end{bmatrix}\begin{bmatrix} J_2 & J_2 & 0 \\ S_1 & S_1 & 0 \\ J_3 & J_3 & 0 \end{bmatrix}.$$

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