

Quantum theory of optical NMR and ESR in atoms

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The quantum theory of laser induced nuclear spin and electron paramagnetic resonance (optical NMR and ESR respectively) is developed using the irreducible spherical representations of the appropriate mediating molecular property tensors, alpha (the vectorial polarisability), and beta (a magnetic/electric/electric hyperpolarisability). The quantum structure of the theory is developed with a simple application of the Wigner/Eckart theorem in the point group of atoms, and using Griffith/Harnung theory for the point groups of molecules. The results are expressed as simple laser induced shifts and splittings in hertz for comparison with experimental data.

1. Introduction

In this paper we continue our development of the alpha [1] and beta [2] theories of optical nuclear magnetic resonance and electron spin resonance spectroscopy, hereafter referred to as "optical NMR" and "optical ESR", respectively. The basic mechanism of optical NMR relies on the application of a circularly polarised laser to an NMR spectrometer. In the alpha theory [1] there is an interaction energy generated between the vectorial, or antisymmetric, polarisability (α'') [3, 4] of an atom or molecule (alpha tensor) with net electronic angular momentum, and the conjugate product (Π) [5–8] of the laser. In the beta theory [2] there is an induction of a magnetic dipole moment by the product of a molecular or atomic magnetic/electric/electric hy-

perpolarisability (beta tensor) and the laser's Π . This induced magnetic dipole moment interacts with the static magnetic flux density $B^{(0)}$ of the permanent magnet of the NMR or ESR spectrometer. Additionally, in a chiral molecule, there is present a mechanism of direct induction of a magnetic dipole moment through the Rosenfeld tensor [9, 10], which is first order in the electric field strength of the laser. In all three mechanisms the effect of the laser on the electronic environment is transmitted, in optical NMR, to the nuclear spin, causing a shift and splitting of the original NMR resonance feature or features (referred to as the "laser shift"). The latter is site selective, i.e. depends on the electronic environment in analogy with the well-known chemical shift, the basis of NMR spectroscopy. The laser shift is proportional through the alpha and beta tensors to the laser intensity in watts per unit area (I), and as I is increased, the absolute frequency separation between laser shifted NMR features increases proportionately in theory. If this could be isolated experimentally it would give: (1) higher resolution due to the increase in absolute frequency separation; (2) extra laser shift features which could be used

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analytically; (3) laser induced splittings, extra features determined by alpha, beta and Rosenfeld tensors. In general, these laser induced features are determined by the interaction between the electronic angular momentum quantum number J and the nuclear spin quantum number I . In optical ESR spectroscopy they are determined essentially by a combination of the optical Zeeman effect [11] with conventional electron paramagnetic resonance in the permanent magnetic flux density.

Recently, Warren and co-workers [9, 10] have verified experimentally the basic theoretical expectation of optical NMR or laser enhanced NMR spectroscopy ("LENS", an acronym due to Warren [10]). It was demonstrated that a circularly polarised laser shifts a nuclear magnetic resonance line by a few hertz to the high frequency side per unit I , where I is the laser intensity in watts per square centimeter. Optical radiation was used [9, 10] far from absorption bands of the sample. LENS shifts were found experimentally to be different for different positions in a molecule, implying that such local shifts could, in principle, 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, and heating effects very carefully removed. At this frequency, the sample showed almost no optical absorption. The preliminary experimental results [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 by circularly polarised laser radiation, and the shifts were different in different solvents such as benzene and chloroform for a variety of proton sites, high and low field ring protons, methoxy protons, and high and low field methyl protons. Each of these sites showed different LENS shift patterns as a function of laser intensity in watts per square centimetre. These patterns

were different for circularly and linearly polarised laser radiation, the former effects being much larger. These data clearly reveal the presence of several contributing LENS mechanisms, which in combination produce a LENS fingerprint of the sample, in this case a fairly large chiral molecule. The detailed theoretical interpretation of such a spectrum would be numerical in nature, but clearly, the basic idea of optical NMR [1] has been verified: a circularly polarised laser shifts an NMR spectrum, a linearly polarised laser does not.

In this paper, some of the many features of optical NMR and ESR are developed simply in atomic quantum theory using irreducible spherical representations of the mediating molecular property tensors, following a treatment given originally by Manakov et al. [3, 4] for the optical Stark effects in atoms.

In section 1, the alpha theory is developed through the Wigner-Eckart theorem using 3- j and 6- j symbols for atoms and the appropriate Griffith V coefficients [12-14] for the molecular point groups. A simple example of the alpha theory is given with reference to the ground state of atomic hydrogen, with $J = \frac{1}{2}$ and $I = \frac{1}{2}$. In this case the original NMR feature ($\Delta M_I = 1$) is split into two by a circularly polarised laser, and shifted in hertz by an amount proportional to the product of I and $|\alpha''|$ divided by h , the Planck constant. The shift is to the high frequency side of the original feature according to whether the laser is left or right circularly polarised, and vanishes when the laser is linearly polarised, or otherwise if it has no degree of circular polarity.

In section 2, the beta theory is developed similarly for achiral molecules, which may be diamagnetic or paramagnetic. In the discussion section, a simple Landé, or vector, model of the theory is given, which derives the laser shift in an approximation to the Wigner-Eckart theorem. The potential interest of optical NMR and EPR is discussed in terms of its ability to probe the electronic environment and to provide, ultimately, site selective and better dispersed, or resolved, information in one- and multi-dimensional NMR spectra and maps.

2. Development of the alpha theory

The alpha theory originally considered [1] the interaction between the non-linear conjugate product (Π) of the laser and the vectorial polarisability (α''). The former is non-zero only in a circularly polarised laser, and the latter is the antisymmetric part (α''_{ij}) of the atomic or molecular polarisability tensor. The quantity α''_{ij} is an antisymmetric polar tensor, which can be related by fundamental tensor algebra [15] to an axial vector by

$$\alpha''_k = \epsilon_{ijk} \alpha''_{ij}, \quad (1)$$

where ϵ_{ijk} is the Levi-Civita symbol and where the tensor summation convention over repeated indices is used as usual. It is important to realise that the axial vector and polar tensor represent the same physical quantity. The motion reversal (T) symmetry of α'' in both representations is negative, and the parity inversion (P) symmetry is positive [16]. The axial vector therefore has the same fundamental symmetry properties as angular momentum, or of a magnetic dipole moment [1, 2, 15–17]. The vectorial polarisability has also been referred to in [15] as the “imaginary dynamic polarisability”, i.e. the imaginary part of the complete polarisability tensor α_{ij} of an atom or molecule in an electromagnetic radiation field. It vanishes if there is no net electronic angular momentum, a property which will emerge naturally and directly from our development in this section. The alpha theory is therefore suitable for atoms or molecules in which there is a net total electronic angular momentum for some reason.

The antisymmetric polarisability is the cause of inverse polarisation in Rayleigh and Raman scattering, where for incident light linearly polarised perpendicular to the scattering plane, the depolarisation ratio becomes infinite [15], a phenomenon predicted theoretically by Placzek [18] in 1934. The antisymmetric polarisability can therefore be measured experimentally through anomalous polarisation effects [15] in scattering processes. The latter occur, for example, in

Rayleigh scattering from atoms in spin degenerate ground states (such as sodium). These effects become large when the incident frequency is in the vicinity of an electronic absorption frequency [15] in the visible. Antisymmetric resonance Rayleigh and Raman scattering also occurs in molecules in degenerate states, and can also arise without degeneracy in resonance Raman scattering associated with modes of vibration that transform as components of axial vectors [19]. Antisymmetric scattering is important in haem proteins [20] in which almost pure inverse polarisation is observed in many of the vibrational bands in the resonance Raman spectra. It is also prominent [15, 21] in the vibrational resonance Raman spectra of irridium hexahalides and other odd electron transition metal complexes, and in the Raman spectra of most metal porphyrins. Electronic antisymmetric resonance Raman scattering is present in Eu^{3+} doped yttrium aluminum garnets [22].

These data from light scattering are a valuable source of information on the vectorial polarisability, which is central to our development of the alpha theory. Other sources of information include ab initio computation [23] using advanced contemporary techniques [24], and from the C term of magnetic circular dichroism [25].

A simple vector model [1] produced coupling of the interaction energy

$$En^{(1)} = \alpha'' \cdot \Pi \quad (2)$$

with the nuclear spin Hamiltonian. This produced a laser shift, a frequency change in the original laser free resonance feature of the order

$$\Delta f \text{ Hz} \sim \frac{|\alpha''| E_0^2}{h}, \quad (3)$$

where E_0 is the scalar electric field strength in volts per metre of the circularly polarised laser and h is the Planck constant. Expressed in terms of laser intensity I (watts per square metre),

$$I = \frac{1}{2} c \epsilon_0 E_0^2, \quad (4)$$

eq. (3) becomes

$$\Delta f \text{ Hz} \sim \left(\frac{2|\alpha''|}{hc\epsilon_0} \right) I, \quad (5)$$

where ϵ_0 is the permittivity in vacuo in SI units [10] and c is the speed of light. It is seen that the laser shift in the alpha theory [1] is directly proportional to laser intensity I .

The development of magneto-electric susceptibilities by Manakov et al. [3, 4] in terms of quantum theory allows the extension of the alpha and beta theories to describe the optical NMR and ESR processes in terms of J , M and I quantum numbers. The starting point of the theory for atoms (point group $R_h(3)$) is the interaction energy

$$\Delta E_n^{(2)} = \boldsymbol{\mu}_N \cdot \mathbf{B}^{(0)} + \frac{1}{2}(\alpha_{ij} E_i E_j^* + \text{complex conjugate}), \quad (6)$$

where $\boldsymbol{\mu}_N$ is the nuclear magnetic dipole moment, $\mathbf{B}^{(0)}$ the static magnetic flux density; α_{ij} is the total (i.e. complex, real plus imaginary) electronic polarisability tensor and E_i is the electric field strength of the laser in volts per metre. We develop the polarisability tensor in its irreducible spherical representations in point group $R_h(3)$ through application of the Wigner-Eckart theorem [15, 26–28]:

$$\begin{aligned} & \langle JIFM_F | \alpha_q^{(k)} | J'I'F'M'_F \rangle \\ &= (F'M'_F, kq | FM_F) \frac{\langle JIF || \alpha^{(k)} || J'I'F' \rangle}{(2F+1)^{1/2}} \quad (7) \\ &= (F'M'_F, kq | FM_F) (-1)^{J+I+F+k} \\ & \quad \times ((2F'+1)(2F+1))^{1/2} \frac{\langle J || \alpha^{(k)} || J' \rangle}{(2F+1)^{1/2}} \\ & \quad \times \begin{bmatrix} J & F & I \\ F' & J' & k \end{bmatrix} \delta_{II'}. \quad (8) \end{aligned}$$

Here J denotes the total electronic angular momentum quantum number I the nuclear angular momentum quantum number and

$$\begin{aligned} F &= J + I, J + I - 1, \dots, |J - I|, \\ M_F &= M_J + M_I, \quad (9) \end{aligned}$$

from the quantum theory of the coupling of two angular momenta. Here M denotes the usual azimuthal quantum numbers, with appropriate subscripts. Thus

$$\begin{aligned} M_F &= -F, \dots, F, \\ M_J &= -J, \dots, J, \\ M_I &= -I, \dots, I. \end{aligned} \quad (10)$$

In eqs. (6) and (7), $\alpha_q^{(k)}$ are irreducible spherical components of the polarisability α_{ij} in the laboratory frame (X, Y, Z), with

$$q = -k, \dots, k$$

and $(F'M'_F, kq | FM_F)$ denotes the Clebsch-Gordan coefficient. The number enclosed in brackets [] is a 6- j symbol [26]. Finally, $\langle || \alpha^{(k)} || \rangle$ denotes the value of $\alpha^{(k)}$ between reduced eigenstates from the Wigner-Eckart theorem [26–28]. It is seen that the M dependence of the polarisability resides completely in the Clebsch-Gordan coefficient and that this premultiplies quantities in the frame (X, Y, Z) which do not depend on M_F . The latter quantities are scalar atomic properties which can be computed without regard to the M state of the atom, using the appropriate ab initio methods.

The corresponding expression for molecules with net electronic angular momentum must be developed with the Griffith V coefficients [15, 29] computed in the presence of two T negative fields (magnetic flux density and the conjugate product of the circularly polarised laser). The theory must be based, consequently, on the Harnung double point groups [30, 31]. The appropriate Harnung theory is an extension of expressions such as

$$\begin{aligned} & \langle JIFM_F | \alpha_\beta^b | J'I'F'M'_F \rangle \\ &= [-1]^{F+M} \langle JIF || \alpha^b || J'I'F' \rangle V \begin{bmatrix} F & F' & b \\ -M_F & M'_F & \beta \end{bmatrix}. \quad (11) \end{aligned}$$

In this representation, V denotes a Griffith coefficient [29] and the state $|FM_F\rangle$ transforms according to the M_F component of the irreduc-

ible representation of F . The factor $[-1]^{F+M}$ is defined by Griffith [29] and Silver [32] and because of the presence of T negative fields, the Griffith table of complex V coefficients must be used with α_β^b in complex form. Furthermore, the extension due to Harnung [30] must be used because the molecules and atoms have net electronic angular momentum. The phase convention of Fano and Racah [33] must be used to transform from cartesian to spherical tensor representations of the alpha tensor.

Developing eq. (7) for atoms, we make use of the fact that the symmetry of the complete polarisability tensor in atoms, in the point group $R_h(3)$, is the sum of irreducible representations $D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$ [34] of its scalar, vector and tensor parts. We now consider a circularly polarized laser directed parallel to the Z axis with magnetic flux density $B^{(0)}$ of the permanent magnet of an NMR spectrometer. We have the standard relations [32, 34]

$$\begin{aligned}\alpha_0^{(0)} &= -\frac{1}{\sqrt{3}} (\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz}), \\ \alpha_0^{(1)} &= \frac{i}{\sqrt{2}} (\alpha''_{xy} - \alpha''_{yx}) = \frac{i}{\sqrt{2}} \alpha''_z, \\ \alpha_0^{(2)} &= \frac{1}{\sqrt{6}} (2\alpha'_{zz} - (\alpha'_{xx} + \alpha'_{yy})),\end{aligned}\quad (12)$$

between spherical and cartesian representations of the atomic polarisability tensor for the case $q=0$. (There are other relations [34] for $q \neq 0$ which must be considered in the case where M_F transitions are accompanied by J transitions, i.e. when a photon absorption imparts spin (change of M_F) and causes a change in the J state simultaneously. This may occur when the laser frequency is tuned to a natural optical resonance of an atom.)

We note that the M dependence in eq. (7) is transferred by the Wigner-Eckart theorem to $(F'M_F', kq | FM_F)$ and that the factor premultiplied by this coefficient does not depend on M_F . We can therefore write, using tables [26-28] of Clebsch-Gordan coefficients,

$$\langle JIFM_F | \alpha_0^{(0)} | J'I'F'M_F' \rangle = \delta_{FF'} \delta_{MM'} \alpha_0, \quad (13)$$

$$\langle JIFM_F | \alpha_0^{(1)} | J'I'F'M_F' \rangle = \frac{M_F}{(F(F+1))^{1/2}} \alpha_1, \quad (14)$$

$$\begin{aligned}\langle JIFM_F | \alpha_0^{(2)} | J'I'F'M_F' \rangle \\ = \frac{(3M_F^2 - F(F+1))\alpha_2}{(F(F+1)(2F-1)(2F+3))^{1/2}}.\end{aligned}\quad (15)$$

The interaction energy (6) can now be developed as

$$\begin{aligned}\Delta E n^{(2)} &= g_N \mu_N B_Z^{(0)} M_I \\ &+ \left(\delta_{FF'} \delta_{MM'} \alpha_0 + \frac{M_F \alpha_1}{(F(F+1))^{1/2}} \right. \\ &\left. + \frac{(3M_F^2 - F(F+1))\alpha_2}{(F(F+1)(2F-1)(2F+2))^{1/2}} \right) E_0^{(2)}\end{aligned}\quad (16)$$

where $M_I = -I, \dots, I$ and $M_F = -F, \dots, F$, with F expressed in terms of J and I through eq. (9). Using the condition

$$M_F = M_J + M_I, \quad (17)$$

it is possible to expand eq. (16) as

$$\begin{aligned}\Delta E n^{(2)} &= \left(g_N \mu_N B_Z^{(0)} + \frac{\alpha_1 E_0^2}{(F(F+1))^{1/2}} \right) M_I \\ &+ \frac{\alpha_1 E_0^2 M_J}{(F(F+1))^{1/2}} + \dots,\end{aligned}\quad (18)$$

where g_N is the nuclear g number [35] and μ_N the nuclear Bohr magneton. Nuclear resonance is achieved with electromagnetic radiation of energy $\hbar \omega_R$ at the resonance angular frequency ω_R in radians per second

$$\begin{aligned}\hbar \omega_R &= E n(M_I + 1) - E n(M_I) \\ &= g_N \mu_N B_Z^{(0)} + \frac{\alpha_1 E_0^2}{(F(F+1))^{1/2}}.\end{aligned}\quad (19)$$

The nuclear resonance frequency in hertz is

$$\begin{aligned}f_R \text{ Hz} &= \frac{g_N \mu_N B_Z^{(0)}}{h} + \frac{\alpha_1 E_0^2}{h(F(F+1))^{1/2}}, \\ F &= J + I, \dots, |J - I|,\end{aligned}\quad (20)$$

which shows that there is a laser shift and splitting of the original NMR line given by the expression [26]

$$(\Delta f)_{\text{laser}} = \frac{\alpha_1 E_0^2}{h(F(F+1))^{1/2}}, \quad F \neq 0, \quad (21)$$

where the quantity α_1 is invariant to rotation and is a scalar physical property of the atom. (In those cases where $\Delta F \neq 0$ (e.g., $F=0$, $M_F=0$ to $F=1$, $M_F=-1$), eqs. (19)–(21) need to be modified in an obvious manner.)

The split is caused by the presence of the quantum number F . For example, if $J = \frac{3}{2}$ and $I = \frac{1}{2}$, we have the possibilities $F=2$ and 1 , so that there are two possible values of $(F(F+1))^{1/2}$ in eq. (21) and two resonance features. Similarly, if $J = \frac{3}{2}$ and $I = \frac{3}{2}$, we have lines corresponding to $F=3, 2$ and 1 , all of which are laser shifted from the original resonance frequency.

Care must be taken with the case $F=0$ in eq. (21), because $M_F=0$, and the Clebsch–Gordan coefficient is identically zero. The same can be deduced from the fact that our calculations of ΔE_n and Δf amount to a first order perturbation development in which the energy shifts are estimated as the diagonal matrix elements (see also eqs. (13)–(15)) of the perturbing hamiltonian in the unperturbed basis set. (The author is indebted to a referee for this and the following remark.) Consequently shifts in states with $F=0$ are to first order zero since they involve Clebsch–Gordan coefficients $(FM, 10|FM) = (00\ 10|00) = 0$.

For example, in the ground state of atomic hydrogen, $J = \frac{1}{2}$, $I = \frac{1}{2}$ and $F=1$ or 0 . In the first case, we use eq. (21), in the second, there is no shift. The action of the laser in this case is to shift the original NMR line to $(\alpha_1)_{F=1} E_0^2/h$ from the original resonance in the absence of the laser ($\Delta M_I = 1$). Note carefully that if we also take into account hyperfine splitting between the nuclear and electron spin in atomic H there are two NMR lines in the absence of the laser [34], each of which is shifted and split in this way. A similar analysis holds for the EPR lines of atomic H, first measured [36] by Beringer and Heald. The

effect of the laser is sketched above, and this is a convenient experiment with which to test the alpha theory in the hydrogen atom electron ground state ($n=1$, $l=0$, $s=\frac{1}{2}$). If the laser is tuned [37] to a Balmer, Lyman, Brackett, Paschen, Pfund or Humphreys optical resonance in H, the simple theory giving here must be modified by the possibility of simultaneous M and J transitions, giving a rich resonance spectrum. This will be developed elsewhere.

It is clear in general that the extent of the laser shift and degree of splitting (if present) depend on the quantum numbers J , I and F , and on the vectorial polarisability $|\alpha''|$ multiplied by the applied laser intensity. For excited states of the H atom, $J > \frac{1}{2}$, the degree of shift will be different, the appropriate Clebsch–Gordan coefficients will be modified and the vectorial polarisability of the first excited state will change its value from the ground state. A simple calculation of the diagonal matrix elements may not be sufficient to calculate the shifts if couplings of I and J are of the order of or larger than the Zeeman energy, for example H in the low field limit. A referee is thanked for this remark.

2.1. The optical Stark terms in the alpha theory

The optical Stark terms are those in eqs. (13) and (15), describing respectively the optical Stark effect [38] and quadratic optical Stark effect in atoms. The T and P symmetries of the optical Stark terms are both positive, so that they do not contribute to the optical NMR shift and split as just described. This is also a consequence of the Wigner reversality theorem [15]. In this case motion reversal reverses the sign of the magnetic field of the NMR spectrometer, but leaves all other variables of the optical Stark effect with the same sign. These variables include the trace and symmetric part of the tensor product $E_i E_j^*$, which are both T positive, and the NMR observable, a scalar, T positive, resonance frequency. This means that the motion reversed experiment is not realisable, and that optical Stark terms cannot contribute to the optical NMR (or optical ESR) spectra, either in atoms or molecules. Only the optical Zeeman term (14)

can contribute. This is the same kind of fundamental symmetry argument [39] that can be used to explain why there is no Faraday effect, for example, due to a static electric field without the violation of reversality.

3. Development of the beta theory

The original semi-classical beta theory [2] relied on the interaction energy

$$En^{(3)} = \mu_N \cdot \beta^{(0)} + \frac{1}{2} (\beta_{ijk} E_i E_j^* B_k^{(0)} + \text{complex conjugate}), \quad (22)$$

where β_{ijk} is a magnetic/electric/electric hyperpolarisability tensor. The present quantum theory relies on the equivalent of eqs. (7) and (8) with $\alpha_q^{(k)}$ replaced by $\beta_q^{(k)}$, with $k = 3$ and $q = -k, \dots, k$ in general. The irreducible representation [40] of the complex molecular property tensor β_{ijk} in the appropriate $R_h(3)$ point group of atoms is

$$\begin{aligned} \Gamma(\beta_{ijk}) &= D_g^{(1)}(D_g^{(0)} + D_g^{(1)} + D_g^{(2)}) \\ &= D_g^{(1)} + D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \\ &\quad + D_g^{(1)} + D_g^{(2)} + D_g^{(3)} \\ &= D_g^{(0)} + 3D_g^{(1)} + 2D_g^{(2)} + D_g^{(3)}, \quad (23) \end{aligned}$$

so that in general there is one scalar irreducible representation, $D_g^{(0)}$, three vectorial components, $3D_g^{(1)}$, two second rank tensor components, $2D_g^{(2)}$, and one third rank, $D_g^{(3)}$. Furthermore, the tensor β_{ijk} consists of real and imaginary parts [2] whose motion reversal symmetries are respectively negative and positive. The parity inversion symmetries of both real and imaginary components are positive. Therefore the imaginary part of β_{ijk} exists in all atoms and molecules, and the real part in atoms and molecules with net electronic angular momentum. The irreducible representations in the $R_h(3)$ point group of atoms are, respectively,

$$\Gamma(\beta'_{ijk}) = 2D_g^{(1)} + D_g^{(2)} + D_g^{(3)} \quad (24)$$

and

$$\Gamma(\beta''_{ijk}) = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \quad (25)$$

so that the imaginary part of β_{ijk} is made up of one scalar, one vector and one tensor component.

To obtain a P and T positive scalar interaction energy from eq. (22), the imaginary part of β_{ijk} multiplies the antisymmetric part of $E_i E_j^*$ and the real part of β_{ijk} multiplies the symmetric component of the complete tensor product $E_i E_j^*$. This takes into account the P positive, T negative symmetry of the static magnetic flux density $B_k^{(0)}$ of the permanent magnet of the NMR or ESR instrument. The real parts β'_{ijk} all have the same symmetry as angular momentum, with negative motion reversal symmetry T . These all vanish in diamagnetic molecules, where there is no net electronic angular momentum. On this basis we develop the quantum theory for diamagnetic molecules using only the imaginary part of the beta tensor, because in atoms and paramagnetic molecules, the alpha effects (section 1) predominate.

Using the same theoretical approach as in section 1, it is possible to show that

$$\begin{aligned} \langle JIFM_F | \beta_0^{(k)} | J'I'F'M'_F \rangle \\ = (F'M'_F, k0 | FM_F) \frac{\langle JIF || \beta^{(k)} || J'I'F' \rangle}{(2F+1)^{1/2}} \quad (26) \end{aligned}$$

from the Wigner-Eckart theorem. This gives the k spherical tensor components of the beta tensor for $q = 0$, i.e. for a laser directed in the Z axis of frame (X, Y, Z) . Tables of Clebsch-Gordan coefficients (or alternatively Wigner 3- j coefficients) give directly

$$\begin{aligned} \Delta En_n^{(3)} &= \left(\gamma_N g_N M_l + E_0^2 \left(\beta_0'' \delta_{FF'} \delta_{MM'} \right. \right. \\ &\quad + \frac{M_F}{(F(F+1))^{1/2}} (\beta_1'' + \beta_{11}' + \beta_{12}') \\ &\quad + \frac{(3M_F^2 - F(F+1))(\beta_2'' + \beta_2')}{(F(F+1)(2F-1)(2F+3))^{1/2}} \\ &\quad \left. \left. - \frac{M_F(3F(F+1) - 5M_F^2 - 1)\beta_3'}{(F(F+1)(F+2)(F-1)(2F+3)(2F-1))^{1/2}} \right) \right) B_Z^{(0)}. \quad (27) \end{aligned}$$

In this notation the term in β_0'' transforms as $D_g^{(0)}$; the terms in β_1'' , β_{11}' and β_{12}' transform as $D_g^{(1)}$; those in β_2'' and β_2' as $D_g^{(2)}$; and finally, the term in β_3' as $D_g^{(3)}$. (Note carefully that these terms are all for $q=0$, and the structure of the expansion for finite positive or negative q is different. These would be needed for simultaneous J and I transitions, for example, or if the laser were at an angle to the magnetic flux density. For finite q (different from zero), the fundamental structure of the Clebsch-Gordan coefficients is different, and the relations between spherical and cartesian representations of beta by far more intricate [34].)

In general, the contributions from both real and imaginary parts of beta in eq. (27) are finite for atoms, for which the equation is valid. For molecules with net electronic angular momentum all terms are also needed in general, but the Wigner 3- j coefficients must be replaced using Harnung's double point groups [30], an extension of the Griffith V coefficients [29].

In diamagnetic molecules, the real parts of beta vanish and the 3- j coefficients multiplying the imaginary parts of beta in eq. (27) must be replaced by the Griffith V coefficients in the molecular point group being considered. In this case, the laser must be circularly polarised, because otherwise the antisymmetric part of $E_i E_j^*$ is zero [1-4]. (Note that in the beta theory, the real parts of beta play a role, and the laser need not be circularly polarised: however, in this case the beta effect is dominated by the alpha effect of section 1. In diamagnetic molecules, in which it is assumed that there is no net electronic angular momentum in the molecule as a whole, the alpha effect vanishes. However, there may be local alpha effects, involving vectorial polarisabilities localised in the electronic environment of a resonating nucleus, and we develop this idea in the discussion section.)

An estimate of the magnitude and structure of the laser shift in atoms may be obtained by examining the terms in eq. (27) involving the imaginary parts of beta. The purpose of this exercise is to provide the basic structure of the beta effect in diamagnetic molecules, where the Wigner 3- j symbols of atoms are replaced by the

Griffith V coefficients. (Recall that in diamagnetic molecules, the real part of beta vanishes.) The relevant part of the interaction energy for atoms is

$$\begin{aligned} \Delta E n^{(3)} = & \left(\gamma_N g_N M_I + E_0^2 \left(\beta_0'' \delta_{FF'} \delta_{MM'} \right. \right. \\ & + M_F \beta_1'' / (F(F+1))^{1/2} \\ & \left. \left. + \frac{(3M_F^2 - F(F+1))\beta_2''}{(F(F+1)(2F-1)(2F+3))^{1/2}} \right) \right) B_Z^{(0)}. \end{aligned} \quad (28)$$

Writing

$$M_F^2 = (M_J + M_I)^2 = M_J^2 + 2M_J M_I + M_I^2 \quad (29)$$

we have the beta laser shift (in atoms):

$$\begin{aligned} (\Delta f)_{\text{beta}} = & \frac{\beta_2''(6M_J + 3(2M_I + 1))E_0^2 B_Z^{(0)}}{h(F(F+1)(2F-1)(2F+3))^{1/2}} \\ & + \frac{\beta_1''}{(F(F+1))^{1/2}} \end{aligned} \quad (30)$$

with F taking the values $J+I, \dots, |J-I|$, and

$$M_F = M_J + M_I. \quad (31)$$

The selection rule $\Delta M_J = \pm 2$ is also allowed on the Clebsch-Gordan coefficient ($F' M_F', 20 | F M_F$), which leads to additional resonance lines for the optical Zeeman effect [11] in atomic beta theory. This phenomenon is the quadratic optical Zeeman effect in atoms. However, the rule on nuclear M_I transitions remains the same, $\Delta M_I = \pm 1$. Equation (3) shows that there are several contributions to the resonance in general, even in atoms, and that the laser shift in the beta theory depends on the initial value of both M_J and M_I . There is also a laser induced split, because the F quantum number can take several different values for given J and I , this being the usual Clebsch-Gordan series, made up of the interaction of the two quantised angular momenta J and I .

4. Discussion

In atoms there is the possibility of shifts and splittings of an NMR or ESR spectrum due to a circularly polarised laser. Equations (21) and (30) give the laser shifts in the alpha and part of the beta theories. In the alpha mechanism, the shift is proportional to the product of the appropriate vectorial polarisability and the laser intensity in watts per square metre. In the beta mechanism the shift is proportional to the appropriate part of the beta tensor multiplied by I and the permanent magnetic flux density generated by the instrument. Numerical calculations are available from Manakov et al. [3, 4] of the vectorial polarisability in the electronic states of xenon, and beta for molecules can be estimated from the Verdet constant [2, 40–42]. The vectorial polarisability mediates some scattering spectra, as discussed already, and can be estimated from these spectra for, for example, haem proteins and certain metal complexes and molecules with odd numbers of electrons. There is clearly a need, however, for ab initio computations of both alpha and beta for a range of atoms and molecules, using contemporary software [43]. In the meantime, the following rule of thumb estimates are given for reference:

$$\begin{aligned}
 (\Delta f)_{\text{alpha}} &\sim (10^{-36} - 10^{-41}) \frac{E_0^2}{h} \text{ Hz}, \\
 (\Delta f)_{\text{beta}} &\sim (10^{-42} - 10^{-45}) \frac{E_0^2 B_Z^{(0)}}{h} \text{ Hz}.
 \end{aligned}
 \tag{32}$$

In atoms, therefore, the alpha mechanism appears to be always dominant with a circularly polarised laser. (If the laser is not circularly polarised, contributions from the real part of beta are still possible for atoms and paramagnetic molecules, but these are much smaller than those expected from the alpha theory in the same samples using a fully left or right circularly polarised laser.) In general the laser shift is accompanied by splitting of the original NMR feature, a splitting which depends on the electronic state of the atom (J quantum number) and on the I quantum number of the nucleus.

The alpha mechanism also dominates in molecules where there is a net J and a net azimuthal M_J quantum number. A rigorous theory in molecules requires contemporary developments of Griffith and Harnung theory, including contemporary software [43] for generating Griffith and Harnung tables. In paramagnetic molecules and atoms, the optical NMR or ESR spectrum provides information on the fundamental molecular property tensor alpha in an entirely new context, and the laser shift clearly depends on the optical resonance properties of alpha. If the circularly polarised laser's frequency is tuned to one of these optical resonances, the laser shift will be increased, possibly by one or two orders of magnitude [44]. Suitable modulation of the laser [45] removes heating effects, and its intensity I can be varied from about half a watt per unit area (argon ion laser, CW) upwards by several orders of magnitude (e.g., mode locked dye lasers). It is basically important to recall that the laser shift is proportional to I , leading to the possibility of expanding dramatically the absolute frequency separation of a conventional (laser free) NMR or ESR spectrum. This implies a useful increase in effective NMR or ESR resolution brought about by the laser. There are two points which appear to merit further discussion at this stage in the theoretical development of optical NMR and optical ESR. Firstly, the results of the Wigner–Eckart theory, the rigorous quantum theory, for the laser shift can be obtained approximately by a simple Landé or vector coupling model, as in the original semi-classical theories [1, 2].

This leads to the same fundamental expectation for the laser shift in the example given (alpha theory), i.e. that the shift is proportional to laser intensity multiplied by the vectorial polarisability. This finding also emerged from the semi-classical approach [1], and can also be derived by developing the work of Manakov et al. [3, 4] for the optical Stark effects in atoms. Note that Manakov et al. [3, 4] appear to have proved the existence of the optical Zeeman effect independently of the present author [11], but appear not to have named the effect specifically and also did not specify or distinguish its charac-

teristic T and P symmetries. The latter may have appeared self-evident to these authors, but are fundamentally important when extending their pioneering work to NMR and ESR. In his textbook, Shen [46] appears to use a confusing nomenclature when dealing with the inverse Faraday effect, in that he appears to refer to this as an optical Stark effect. The inverse Faraday effect produces static magnetisation [47–52] of T negative, P positive symmetry, whereas the optical and quadratic optical Stark effects produce P negative, T positive electric dipole moments through the T positive, P positive parts of the electric, electronic polarisability. The optical Zeeman effect produces a frequency dependent, spatially quantised, magnetic dipole moment through the P positive, T negative vectorial polarisability. It is fundamentally important to distinguish the optical Zeeman effect both from the inverse Faraday effect and the optical Stark effects. Neither of the latter produce optical NMR nor ESR.

Secondly, it appears possible, or even probable, that in the immediate vicinity of the resonating nucleus in optical NMR, there is a residual or local vectorial polarisability, which is finite even in diamagnetic molecules in which the total electronic angular momentum vanishes on a molecular scale. This is analogous to the well developed theory of the chemical shift in conventional NMR [53], in which the magnetic field at the nucleus is calculated to be different from the applied field due to a local electronic magnetic dipole moment in the immediate vicinity of the resonating nucleus. This is the root of analytical NMR spectroscopy, a well-known example being the three lines in ethanol due to three different H environments. The latter are clearly local, or intramolecular, in nature. In optical NMR the local magnetic dipole moment is supplemented by a local vectorial polarisability with the same T negative, P positive symmetry. Again in analogy, there appears at this stage to be no reason why the local vectorial polarisability should vanish in a molecule which has no net molecular electronic angular momentum. In the same way, ethanol has no net electronic molecular angular momen-

tum, yet chemical shift theory is based on the existence of a local electronic angular momentum, proportional to the local magnetic dipole moment. The latter is responsible for inducing a magnetic field at the nucleus, causing the chemical shift and the three observed lines. If the existence of a local vectorial polarisability is accepted, the alpha theory can be used for its optical NMR effects. Note that any local laser shift is fundamentally different in nature from the chemical shift, because the former relies on the vectorial polarisability and the latter on the magnetic dipole moment.

In other contexts, the idea of local bond polarisability is well developed [54], and it follows that there are vectorial bond polarisabilities in general. It is known from the work of Manakov et al. [3, 4] that the vectorial polarisability in atoms is strikingly dependent in magnitude on the electronic state (of xenon). The theory of antisymmetric scattering (which depends on the vectorial polarisability) has been reviewed by Barron in chapter eight of his monograph [15] and is particularly well developed for resonance scattering in atomic sodium and in the totally symmetric vibrations of iridium (VI) hexahalides using Harnung's version of the Wigner–Eckart theorem. In the hexahalides, the vectorial polarisability is clearly a function of the vibrational species under consideration and is an intramolecular or local property. Again, in the theory of natural electronic optical activity, the theory is developed at the local, chromophore level [55], leading to such well known concepts as the quadrant and octant rules.

There is reason to anticipate, at least qualitatively, that optical NMR and ESR spectra will be chromophore specific, and that the details of the spectra will be both analytically useful and fundamentally informative. This paper deals with the first quantum theory of optical NMR and optical ESR in atoms.

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