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Optical NMR and ESR
Dipole–dipole and Fermi contact interactions

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The quantum theory of nuclear magnetic dipole/laser induced electronic magnetic dipole interactions in optical NMR is developed for atoms in terms of the interaction between the total electronic and nuclear spin angular momenta. It is shown that a circularly polarised laser co-axial with the static magnetic flux density of a conventional NMR spectrometer (of any type) induces an electronic magnetic dipole moment in an atom or molecule, a moment which sets up a magnetic field at the nucleus, thus changing the effective magnetic field and NMR resonance frequency. This mechanism appears to be comparable in magnitude to Landé coupling between the anisotropic, or vectorial, polarisability of the atom and the nuclear spin angular momentum. Dipole–dipole and Fermi contact interaction between the vectorial polarisability and the nuclear spin angular momentum is explored through the appropriate terms in the ONMR interaction energy. Fermi contact interaction is nonzero, generally in a liquid sample.

1. Introduction

Optical NMR is a technique in which a circularly polarised laser is used to shift and split the resonance features of a conventional NMR spectrum (of any type). The first theory of ONMR was introduced [1] in simple semi-classical terms, and developed the angular momentum coupling between the anisotropic, or vectorial, polarisability ($^e\alpha^{e\prime\prime}$) and the nuclear spin angular momentum (I). This "alpha" theory is valid for atoms and molecules in which there is net total electronic angular momentum (J), to which $^e\alpha^{e\prime\prime}$ is proportional [1–3] through the gyroptic ratio (γ_Π) (see the appendix):

$$^e\alpha^{e\prime\prime} = \gamma_\Pi J \,. \tag{1}$$

Subsequently, the alpha theory has been extended in the context of optical Bloch equations [4], and has been supplemented by the beta theory [5] for molecules in which there is no net J. Recently [6, 7] the alpha theory [1] has been checked with rigorous quantum theory for

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atoms, using the Wigner–Eckart theorem to separate out the rotational (M) dependence of the interaction energy. The main result of ref. [1], its eq. (46), was rederived exactly [7] on this rigorous basis, and can be described as follows in terms of the ONMR interaction energy:

$$\Delta En = -M_F \hbar \left(g_{L1} \frac{\gamma_\Pi}{2} \Pi_Z^{(A)} + g_{L2} \gamma_N B_Z^{(0)} \right) . \tag{2}$$

Here $B_Z^{(0)}$ is the magnetic flux density in the Z axis of the laboratory frame generated by the permanent magnet of the NMR spectrometer, $\Pi_Z^{(A)}$ is the conjugate product [1–10] of the circularly polarised laser, $\hbar$ is the reduced Planck constant, g_{L1} and g_{L2} are Landé factors [11, 12];

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

$$g_{L2} = \frac{1}{2} \left(\frac{F(F+1) + I(I+1) - J(J+1)}{F(F+1)} \right) ,$$

and M_F is the azimuthal quantum number corresponding to the total quantum number F:

$$M_F = -F, \ldots, F \,. \tag{3}$$

The quantum number F takes the values

$$F = J + I, \ldots, |J - I|, \qquad (4)$$

where J is the net total electronic angular momentum quantum number of the atom (orbital plus spin), and I its net nuclear angular momentum quantum number.

The result (2) is derived directly from the fundamental quantum theory of angular momentum coupling [13–20]. In this theory, the magnetic or azimuthal quantum numbers M are added arithmetically

$$M_F = M_J + M_I, \qquad (5)$$

and the product state $|JM_J\rangle|IM_I\rangle$ can contribute to the coupled state $|FM_F\rangle$ only if condition (5) is obeyed. Theoretically [13–20], the quantum numbers J and I add vectorially through the allowed values (4) of the Clebsch–Gordan series.

Inspection of the result (2) shows: (a) that the Landé factor *premultiplies* the original resonance due to $\Delta M_I = 1$, i.e. the conventional resonance in the absence of the laser, and (b) that the Landé factors can be positive or negative, depending on the state of the atom under consideration. This is a nonclassical result, the Landé factor g_{L2} is unity, the Landé factor g_{L1} vanishes, and the original frequency and intensity of the laser free resonance is recovered if and only if the laser intensity is identically zero. Equation (2) therefore implies a counter intuitive effect of the laser, in that the original resonance will *always* be premultiplied by the Landé factor, whatever the intensity of the laser. As soon as the laser is switched on there is a "quantum leap" in the original resonance frequency caused by the Landé factor g_{L2}, which is derived directly from the fundamental theory of angular momentum coupling without the use of a Schrödinger equation or any other mechanism or model. This "quantum leap" phenomenon exists in both ^{1}H and ^{3}He and if measured experimentally gives the gyroptic ratio γ_{Π}, a new fundamental mediating property in NMR. The laser induced, "nonclassical", quantum leap was derived theoretically [6, 7] on the single assumption that the product state $|JM_J\rangle|IM_I\rangle$ contributes to the coupled state $|FM_F\rangle$.

In this paper we explore theoretically the likely order of magnitude of other effects in optical NMR of atoms. In section 2 a mechanism is considered whereby the conjugate product of a circularly polarized laser induces an electronic magnetic dipole moment in the atom, which in turn sets up a magnetic field at the nucleus, thus affecting the frequency of the orginal (laser free) resonance. In general, it appears that this semi-classical mechanism contributes in addition to the purely quantum mechanical mechanism outlined already. A comparison of orders of magnitude is given in section 3. Finally, a discussion is given of other effects likely to contribute to the atomic ONMR spectrum.

2. The laser induced electronic magnetic dipole moment

Consider a circularly polarised laser propagating along the Z axis through an ensemble of ^{1}H atoms in the ground state. Each ^{1}H atom has a permanent electronic and nuclear magnetic dipole moment, two spins [21], with $J = \frac{1}{2}$ and $I = \frac{1}{2}$, respectively, where J is the total electronic angular momentum quantum number (orbital plus spin), and I is the nuclear angular momentum quantum number. The magnetic electronic dipole moment is due to the unpaired spin of the electron, which breaks the orbital 1s symmetry in the ground state. In consequence the atomic point group of ^{1}H in the ground state is $\infty/\mathrm{m\underline{m}}$ [22], implying that there is a non-vanishing permanent electronic magnetic dipole moment component $m_3^{(0)}$ in a frame $(1, 2, 3)$ fixed by the direction of the electronic spin in the ground state $\{22\}$. The $\infty/\mathrm{m\underline{m}}$ point group also supports a non-vanishing antisymmetric, or vectorial [23] polarisability

$$\prescript{e}{}{\alpha}_{12}^{e''} = - \prescript{e}{}{\alpha}_{21}^{e''} \text{ (tensor form)}, \qquad (6)$$

or

$$\prescript{e}{}{\alpha}_{3}^{e''} \text{ (vector form)}, \qquad (7)$$

whose vector and tensor forms are related through the Levi–Civita symbol [14]:

$${}^e\alpha_i^{e\prime\prime} = \varepsilon_{ijk} \cdot {}^e\alpha_{jk}^{e\prime\prime} . \tag{8}$$

Note that the symmetry of the antisymmetry polarisability in its vectorial form is the same as that of the magnetic electronic dipole moment, a T negative, P positive, axial vector.

The $\infty/m\underline{m}$ symmetry of the ^1H ground electronic state also supports the following non-vanishing elements [22] of an electronic magnetic electric electric hyperpolarisability $\{5\}$ ${}^m\beta_{ijk}^{ee\prime\prime}$:

$${}^m\beta_{123}^{ee\prime\prime} = -{}^e\beta_{213}^{ee\prime\prime} , \quad {}^m\beta_{132}^{ee\prime\prime} = -{}^m\beta_{231}^{ee\prime\prime} ,$$
$${}^m\beta_{312}^{ee\prime\prime} = -{}^m\beta_{321}^{ee\prime\prime} . \tag{9}$$

This beta tensor mediates the induction [5, 22] by a circularly polarised laser's nonlinear optical conjugate product, $\Pi_{ij}^{(A)}$, of an electronic magnetic dipole moment, so that for each atom in the ensemble

$$m_i^{(tot)} = m_i^{(0)} + i\,{}^m\beta_{ijk}^{ee\prime\prime}\Pi_{jk}^{(A)} \tag{10}$$

where i, j, k refer to the laboratory frame (X, Y, Z). The nonlinear optical conjugate product is the antisymmetric part of the complete tensor product $E_iE_j^*$ of electric field components of the electromagnetic plane wave. Here E_j^* denotes the complex conjugate of E_j:

$$\Pi_{jk}^{(A)} = \tfrac{1}{2}(E_jE_k^* - E_kE_j^*) . \tag{11}$$

Note that $\Pi_{jk}^{(A)}$ is a T negative, P positive antisymmetric polar tensor of rank two. The algebra of tensors [14] implies immediately that there exists an axial vector

$$\Pi_i^{(A)} = \varepsilon_{ijk}\Pi_{jk}^{(A)} \tag{12}$$

which is also T negative, P positive. The vector $\Pi_i^{(A)}$ can be written as in standard vector (as opposed to tensor subscript) notation, and is consequently defined for left and right circularly polarised lasers by [23]

$$\Pi_L^{(A)} = E_L \times E_L^* = 2E_0^2\,ik ,$$
$$\Pi_R^{(A)} = E_R \times E_R^* = -2E_0^2\,ik , \tag{13}$$

showing that $\Pi^{(A)}$ is equal in magnitude but opposite in sign for left (L) and right (R) circular polarisation, and is a purely imaginary axial vector quantity directed in the laser's propagation axis. Here k is a unit vector in this axis (the Z axis of the laboratory frame). In eq. (10) therefore the induced magnetic dipole moment is a real quantity since $\Pi_{jk}^{(A)}$ is purely imaginary.

The laboratory frame ensemble average of $m_i^{(tot)}$ in the presence of the T-negative $\Pi_{jk}^{(A)}$ is not zero, as in an isotropic liquid for example, but

$$\langle m_i^{(tot)}\rangle_\Pi = \langle m_i^{(0)}\rangle_\Pi + i\langle {}^m\beta_{ijk}^{ee\prime\prime}\rangle_\Pi\Pi_{jk}^{(A)} . \tag{14}$$

The first term on the right hand side of this equation is expanded in a Boltzmann series [14]

$$\langle m_i^{(0)}\rangle_\Pi = \langle m_i^{(0)}\rangle_0 - \frac{1}{kT}\langle m_i^{(0)}U\rangle_\Pi + \cdots , \tag{15}$$

where U is the purely real T and P positive scalar interaction energy

$$U = -i\,{}^e\alpha_Z^{e\prime\prime}\Pi_Z^{(A)} \tag{16}$$

between the laser's $\Pi_Z^{(A)}$ and the ^1H atom.

After isotropic averaging [24, 25] we obtain

$$\langle m_Z^{(ind)}\rangle_\Pi = \left(\frac{\langle m_Z^{(0)e}\alpha_Z^{e\prime\prime}\rangle_\Pi}{kT} \right.$$
$$\left. + \langle {}^m\beta_{ZXY}^{ee\prime\prime}\rangle_\Pi - \langle {}^m\beta_{ZYX}^{ee\prime\prime}\rangle_\Pi \right)\Pi_Z^{(A)} \tag{17}$$

for the averaged magnetic electronic dipole moment induced by the laser, with all subscripts referring to the laboratory frame. (Quantities defined in the frame $(1, 2, 3)$ of the point group $\infty/m\underline{m}$ are related by a transformation matrix [26] to their equivalents in frame (X, Y, Z).)

We narrow consideration at this point to the case $T \to 0$ (^1H gas near absolute zero [21]). In

this case the first term on the right-hand side of eq. (17) dominates

$$\langle m_Z^{(ind)} \rangle_\Pi \xrightarrow{T \to 0} \frac{i}{kT} \langle m_Z^{(0)e} \alpha_Z^{e''} \rangle \Pi_Z^{(A)} , \qquad (18)$$

which shows that the laser induced dipole moment is proportional to the product of the permanent magnetic electronic dipole moment with the antisymmetric polarisability and conjugate product of the laser. For ease of notation we write

$$m \equiv m_i \equiv \langle m_Z^{(ind)} \rangle_\Pi . \qquad (19)$$

The averaged, induced electronic magnetic dipole moment m sets up a magnetic field, $B^{(ind)}(m)$, at the nucleus of the ^{1}H atom through the well known mechanisms [27] of dipole–dipole and Fermi contact interaction. Both can be described [27] as follows through a careful development of the vector potential associated with $B^{(ind)}(m)$. If the induced magnetic field at the nucleus survives ensemble averaging, the original NMR resonance frequency is shifted and split by the laser, providing a new spectral fingerprint, and potentially, an analytical technique of great utility in atoms, molecules and other samples.

We proceed following Appendix 22 of Atkins [27] to set up the vector potential

$$A^{(ind)} = \frac{\mu_0}{4\pi r^3} m \times r , \qquad (20)$$

whose curl defines the magnetic field at the nucleus due to m:

$$B^{(ind)} = \nabla \times A^{(ind)} . \qquad (21)$$

In eq. (20) for the vector potential μ_0 is the permeability in vacuo, and r is the distance between electron and proton in the ^{1}H ground state, which we take as the Bohr radius (see section 3). We have used the same notation as Atkins [27] and proceeding as in his Appendix 22 the magnetic field due to the induced dipole moment m at the nucleus is a sum of two terms:

$$B^{(ind)} = \nabla \times A^{(ind)}$$
$$= -\frac{\mu_0}{4\pi} (m(\nabla^2 r^{-1}) - (m \cdot \nabla)(\nabla r^{-1})) . \qquad (22)$$

The second term on the right-hand side can be rewritten as the dipolar contribution

$$(m \cdot \nabla)(\nabla r^{-1}) = -\frac{1}{r^3} (m - 3m \cdot \hat{r}\hat{r}) , \qquad (23)$$

and averages to zero in a 1s orbital [27]. Even when we deal with orbitals with a spatial characteristic which allows the survival of this term (e.g., a p orbital [27]) it vanishes when averaged over an isotropic ensemble, such as a liquid or gas. For the ground state of ^{1}H therefore, the dipolar term averages to zero, because (1) we are dealing with a 1s orbital, and (2) we consider a gas of ^{1}H atoms near absolute zero kelvin.

The first term on the right-hand side of eq. (22) is the Fermi contact term, which can be developed as [27]:

$$\langle (m \cdot \nabla) \nabla r^{-1} \rangle = \tfrac{1}{3} m(\nabla^2 r^{-1})$$
$$= -4 \frac{\pi}{3} m\delta(r) . \qquad (24)$$

This result finally leads to the magnetic field at the nucleus of the ^{1}H atom due to the spherically averaged Fermi contact interaction generated by the laser induced magnetic dipole moment m:

$$\langle \nabla \times A^{(ind)} \rangle = \langle B^{(ind)} \rangle = \tfrac{2}{3} \mu_0 m\delta(r) , \qquad (25)$$

where $\delta(r)$ is the Dirac delta function. Note that the Fermi contact interaction survives averaging both over the 1s wave function and the ensemble of atoms.

Denoting the nuclear magnetic dipole moment of ^{1}H by $m^{(N)}$, the laser sets up the interaction energy

$$\Delta En(laser) = -m^{(N)} \cdot \langle B^{(ind)} \rangle , \qquad (26)$$

which can be rewritten with eq. (25) as

$$\Delta En(laser) = -\tfrac{2}{3} \mu_0 m^{(N)} \cdot m\delta(r) . \qquad (27)$$

The frequency change (in hertz) associated with

this energy change is obtained by dividing by the Planck constant

$$\Delta f(\text{laser}) = \frac{\Delta En(\text{laser})}{h} , \qquad (28)$$

a frequency which is the product of the nuclear and permanent electronic magnetic dipole moments with the Z component of the vectorial polarisability and the conjugate product. This product is premultiplied by the Dirac delta function $\delta(r)$, and a factor which is inversely proportional to temperature T. The lower the temperature the greater the effect.

This result must now be averaged over the 1s wave function of atomic ^{1}H in the ground state [27]:

$$\Delta En(\text{av}) = -\tfrac{2}{3}\mu_0 \int \psi^* \delta(r)\psi m^{(N)} \cdot m \, d\tau$$

$$= -\tfrac{2}{3}\mu_0 |\psi(0)|^2 m^{(N)} \cdot m , \qquad (29)$$

where $|\psi(0)|^2$ is the probability density of finding the electron at the nucleus [27]. For the hydrogen atom in the ground state

$$|\psi(0)|^2 = \frac{1}{\pi a_0^3} , \qquad (30)$$

where a_0 is the Bohr radius. This leads finally to the frequency/energy change due to the Fermi contact mechanism set in action by the applied circularly polarised laser

$$\Delta f(\text{av}) = -\frac{2\mu_0}{3\pi a_0^3 h} m^{(N)} \cdot m \text{ hertz} , \qquad (31)$$

which shows clearly that we are considering a spin/induced-spin mechanism, i.e. a coupling between the laser induced electronic spin and the nuclear spin.

3. Order of magnitude estimates

In this section we use the result (31) to estimate the order of magnitude of the expected laser shift and splitting of the original NMR line

due to spin/induced-spin coupling. For ^{1}H atomic gas in the ground state the following values are used for atomic properties appearing in eq. (31). The nuclear magnetic dipole moment, $m^{(N)}$, is [27]

$$m_Z^{(N)} = g_N \mu_N I_Z = 2.821 \times 10^{-26} M_I \text{ JT}^{-1} , \qquad (32)$$

where g_N is the nuclear g factor, $g_N = 5.5857$, and μ_N is the nuclear Bohr magneton, $\mu_N = 5.051 \times 10^{-27} \text{ JT}^{-1}$. The electronic magnetic dipole moment of ^{1}H in the ground state was estimated from the experimental ratio of electronic to nuclear g factors [28]

$$g_e/g_N = -658.2277 \pm 0.0002 , \qquad (33)$$

giving

$$m_Z^{(0)} = -1.840 \times 10^{-24} M_J \text{ JT}^{-1} . \qquad (34)$$

The quantity a_0 was taken to be the Bohr radius, the maximum of the radial distribution function for the hydrogen 1s orbital

$$a_0 = r_{\text{max}} = 8\pi \frac{\varepsilon_0 \hbar^2}{\mu e^2} = 1.06 \times 10^{-10} \text{ m} , \qquad (35)$$

where ε_0 is the permittivity in vacuo ($\varepsilon_0 = 8.854 \times 10^{-12} \text{J}^{-1}\text{C}^2\text{m}^{-1}$), $\hbar$ the reduced Planck constant ($\hbar = 1.055 \times 10^{-34}$ Js) and μ the reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p} = 9.111 \times 10^{-31} \text{ kg} , \qquad (36)$$

where m_e is the mass of the electron and m_p that of the proton, and e the charge on the electron. The vacuum permeability in SI units is $\mu_0 = 4\pi \times 10^{-7} \text{ Js}^2\text{C}^{-2}\text{m}^{-1}$. Using $k = 1.381 \times 10^{-23} \text{ JK}^{-1}$ for the Boltzmann constant, and $h = 6.626 \times 10^{-34}$ Js gives the frequency change

$$\Delta f(\text{av}) = 2.16 \times 10^{31} M_I \langle M_J^e \alpha_Z^{e''} \rangle \frac{I_0}{T} \text{ hertz} , \qquad (37)$$

where I_0 is the intensity of the laser in watts per

square metre (SI units). Here we have used

$$I_0 = \tfrac{1}{2}\varepsilon_0 c E_0^2 , \tag{38}$$

where c is the velocity of light (2.998×10^8 ms^{-1} in SI), the relation between the intensity and electric field strength (Vm^{-1}) of a laser.

To complete the order of magnitude assessment an order of magnitude is also needed for the vectorial polarisability ${}^e\alpha{}_Z^{e\prime\prime}$ in the ^{1}H ground state. The most complete ab initio computation of vectorial polarisabilities for atoms is that of Kielich et al. [23]. These authors give their results in atomic units of bohr cubed:

$$1.0 \, \text{bohr}^3 = 1.335 \times 10^{-41} \, C^2 m^2 J^{-1} , \tag{39}$$

where the right-hand side gives the SI units of polarisability [27]. In these units, table 1 summarises what appear to be the only literature data available at present on vectorial polarisabilities computed ab initio.

It can be seen from table 1 that $|{}^e\alpha{}^{e\prime\prime}|$ increases considerably near optical resonance, and that it can be either positive or negative. This implies from eq. (37) that a circularly polarised laser, if tuned near an optical resonance, can be expected to produce commensurate positive or negative ONMR shifts through the dipole/induced-dipole (or "spin/induced-spin") mechanism considered in this paper. The atomic $|{}^e\alpha{}^{e\prime\prime}|$ is also sensitive from table 1 to the state of the atom, a property which can be used to advantage, potentially, in ONMR work with excited atomic states.

However, there appear to be no data for the ground state of ^{1}H or the ground state of ^{3}He in this context, the systems explored in interesting detail by Laloë et al. [21]. There are some experimentally derived data for vectorial polarisabilities [14] from antisymmetric Rayleigh/Raman scattering, but for much more complicated samples such as haem proteins. In contrast, there have been numerous ab initio computations of the real part of the polarisability of both ^{1}H and ^{3}He. For example, Karplus and Kolker [29] have given a value of 7.597×10^{-40} C^{2}m^{2}J^{-1} for the magnitude of ${}^e\alpha{}^{e\prime}$ at 1250 Å, and -2.807×10^{-40} C^{2}m^{2}J^{-1} at 1150 Å; but even for ^{1}H there appear to be little data at frequencies above the excitation threshold. In the ground state of ^{3}He Glover and Weinhold [30] have computed $|{}^e\alpha{}^{e\prime}|$ with an accurate basis set of the Hylleraas type, determining it accurately to the first excitation threshold. However, a comparison by these authors of numerous other attempts to compute $|{}^e\alpha{}^{e\prime}|$ ab initio in atomic ^{3}He in the ground state shows surprising lack of agreement, in that the various estimates differ by far more than the uncertainty bounds reported by individual authors. A similar lack of agreement was noted [30] for experimental data in ^{3}He.

In view of this it appears reasonable to assume an order of magnitude range for the vectorial polarisability in the ground state of ^{1}H about ten times smaller than the real part to about the same order of magnitude as the real part, depending on the vicinity of optical resonance.

Table 1
Some atomic vectorial polarisabilities $|{}^e\alpha{}^{e\prime\prime}|$ in SI (from Kielich et al. [23]).

Atom	Frequency [23]	$\dfrac{\text{Vectorial polarisability}}{(10^{-40} \, C^2 m^2 J^{-1})}$
K	ω_N	0.882
(ground state)	ω_R	6.208
Rb	ω_N	4.672
(ground state)	ω_R	18.221
Cs	ω_N	33.909
(ground state)	ω_R	16.554
Hg 6^3P_1	ω_N	1.749
	ω_R	3.938
	$2\omega_N$	10.907
	$2\omega_R$	-19.798
Sr 5^3P_1	ω_N	43.027
	ω_R	814.35
	$2\omega_N$	-33.468
	$2\omega_R$	0.889
Hg 6^3P_2	ω_N	7.170
	ω_R	23.549
	$2\omega_N$	-232.023
	$2\omega_R$	30.398
Sr 5^3P_2	ω_N	77.550
	ω_R	-716.895
	$2\omega_N$	78.939
	$2\omega_R$	-10.892
Tl $6^2P_{3/2}$	ω_N	6.942
	ω_R	21.627
	$2\omega_N$	-662.16
	$2\omega_r$	150.855

In ^{3}He the real part ranges from 0.184×10^{-40} C^{2}m^{2}J^{-1} at $\omega = 0$ [30] to -199×10^{-40} C^{2}m^{2}J^{-1} near the first excitation threshold. At $\omega = 0$ the vectorial polarisability of any system vanishes, but near the threshold frequency the order of magnitude known for the vectorial polarisability in bigger atoms from the work of Kielich et al. [23] is comparable with the real polarisability in ^{3}He. Kielich et al. [23] also compute real polarisabilities for atoms, which in the ground state of K, Rb, and Cs, for example, are roughly ten times bigger than the corresponding vectorial polarisabilities (table 1). However, in $6^2P_{3/2}$ T1, the vectorial polarisability is actually the bigger in magnitude.

We therefore choose a value of

$$\langle M_J \, ^e\alpha_Z^{e\prime\prime} \rangle \doteq 7 \times 10^{-41} M_J^2 \, C^2m^2J^{-1} \,, \tag{40}$$

for ^{1}H at 1250 Å; ten times smaller than the real part computed by Karplus and Kolker at this wavelength [29] in the ^{1}H ground state. This can be used in eq. (37) to give a frequency/energy change in terms of the experimental variables I_0 and T.

The quantity $^e\alpha_Z^{e\prime\prime}$ is quantised [1–3] in the same way as the total electronic angular momentum

$$^e\alpha_Z^{e\prime\prime} = \gamma_{\Pi}\hbar M_J \,, \tag{41}$$

where γ_{Π} is the gyroptic ratio [1–3] (see the appendix). Equation (37) therefore becomes

$$\Delta f(\text{av}) \doteq 2.4 \times 10^{-10} M_I M_J^2 \frac{I_0}{T} \,, \tag{42}$$

which is proportional to the nuclear magnetic quantum number, M_I, multiplied by the square of the electronic magnetic quantum number, M_J. Evidently, this shows the difference between spin/induced-spin coupling, and conventional spin–spin coupling [27], where the equivalent product is $M_I M_J$. Therefore, from eq. (42), for a nuclear transition

$$\Delta M_I = 1 \,, \tag{43}$$

resonance occurs at the ONMR resonance frequency

$$f(\text{resonance}) \doteq 2.4 \times 10^{-10} \frac{M_J^2 I_0}{T} \text{ hertz} \,. \tag{44}$$

For a given applied probe (radio frequency) of the ONMR spectrometer, there will be $(2J+1)^2$ field values which satisfy condition (44). In the ^{1}H ground state, $J = \frac{1}{2}$, and so the original, laser free, NMR resonance is split into four by the spin/induced-spin coupling mechanism considered here. This occurs in addition to the Landé mechanism discussed in the introduction.

For an applied circularly polarised laser intensity I_0 of, say, ten watts per square millimetre (10^7 W m^{-2}), and a temperature T of 0.01 K, fairly close to absolute zero [21], we obtain a shift of

$$f(\text{resonance}) \doteq 0.24 M_J^2 \text{ hertz} \,, \tag{45}$$

in the resonance frequency. This is comparable in magnitude to the Landé mechanism [1] for these values of I_0 and T. Using intense laser pulses, and by decreasing the temperature, this shift can be increased by orders of magnitude, and will also be increased by tuning near optical resonance.

4. Discussion

In this paper we have estimated the expected ONMR shift and splittings in the ground state of ^{1}H through the spin/induced-spin mechanism, using the Fermi contact interaction averaged over the 1s orbital and the ensemble of ^{1}H atoms. For a laser intensity I_0 of only ten watts per square millimetre, the original, laser free, NMR resonance is split into four and shifted, as given by eq. (45). This occurs in addition to other mechanisms, such as Landé coupling (ref. [1] and the introduction), so that a rich variety of ONMR behaviour is expected theoretically, even in a "simple" system such as atomic hydrogen gas near absolute zero.

Other mechanisms that contribute to the over-

all spectrum have been discussed clearly by Laloë and Freed [21] both for gaseous ^{1}H and liquid ^{3}He near absolute zero. The work of Laloë, Freed et al. [21] has shown elegantly the presence of purely quantum phenomena in these atomic ensembles, typified by spin waves [21]. These effects are non-classical, depending for their explanation on the different overall spin expected in ^{1}H and ^{3}He. A circularly polarised laser *induces electronic spin* through the vectorial electronic polarisability, and this can be expected to change the overall spin of the atoms under consideration. What was originally a fermion [21] for example, might become a boson under the influence of the laser, and vice versa. The laser might have profound, non-classical, and counter intuitive effects on an ensemble of ^{1}H or ^{3}He atoms near absolute zero. Further exploration of these properties would require the development of quantum molecular dynamics or quantum Monte Carlo methods to supplement the relatively simple approach of this and other early papers [1–3] on ONMR.

Finally, it is also possible to develop a theory for OESR in ^{1}H and ^{3}He in an analogous way, by substituting the electronic for nuclear spin.

Acknowledgements

Appendix

A classical theoretical development of the gyroptic ratio

Insight to the effect of the circularly polarised pump laser can be obtained by a classical treatment of the gyroptic ratio. This begins by writing the angular polarisability for final and initial m and n from semi-classical theory as follows

$$\alpha''_k = -\frac{2e^2\omega}{\hbar(\omega_{mm}^2 - \omega^2)}\,\varepsilon_{ijk}r_{oi}r_{oj}\,, \tag{A.1}$$

where

$$r_{oi} = \int \psi_m^* r_i \psi_n \, d\tau\,, \tag{A.2}$$

$$r_{oj} = \int \psi_n^* r_j \psi_m \, d\tau\,, \tag{A.3}$$

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

$$\mu_{oi} = er_{oi}\,, \quad \mu_{oj} = er_{oj}\,. \tag{A.4}$$

We note that the quantity

$$A_{ok} = \varepsilon_{ijk}r_{oi}r_{oj} \tag{A.5}$$

is an *electronic orbital area*.

Classically (27) the magnetic dipole moment is defined as

$$|m^{(c)}| = I_c A\,, \tag{A.6}$$

where

$$I_c = e\left(\frac{\nu}{2\pi r}\right) \tag{A.7}$$

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

$$A = \pi r^2\,, \tag{A.8}$$

so that

$$|m^{(c)}| = \left(\frac{e}{2m}\right)mr\nu \equiv -\gamma_e|L|\,, \tag{A.9}$$

where γ_e is the gyromagnetic ratio, and $|L|$ is the magnitude of the electronic orbital angular momentum

$$|L| = mr\nu\,. \tag{A.10}$$

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

$$A_{oz} = \varepsilon_{ijz} r_{oi} r_{oj} \equiv -A_1 \alpha''_z , \qquad (A.11)$$

$$A_1 = \frac{\hbar(\omega_{mn}^2 - \omega^2)}{2e^2 \omega} , \qquad (A.12)$$

which defines an effective magnetic dipole moment

$$m_{oz} = I_1 A_{oz} , \qquad (A.13)$$

implying that

$$\frac{\gamma_e}{\gamma_\Pi} = -I_1 A_1 . \qquad (A.14)$$

Choosing

$$I_1 = e\left(\frac{\nu}{2\pi r_{av}}\right) , \qquad (A.15)$$

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

$$\gamma_\Pi = -\frac{2\pi r_{av}}{e\nu A_1} \gamma_e = \frac{\pi r_{av}^2}{m\nu r_{av}} \cdot \frac{2e^2 \omega}{\hbar(\omega_{mn}^2 - \omega^2)}$$

$$= \frac{\pi r_{av}^2}{|L_{av}|} \cdot \frac{2e^2 \omega}{\hbar(\omega_{mn}^2 - \omega^2)} , \qquad (A.16)$$

which is the desired classical expression for the electronic gyroptic ratio γ_Π.

This equation shows that γ_Π has several properties which can be used experimentally to refine the conditions of observation of an ONMR or OESR spectrum.

(1) It is proportional to the effective orbital area πr_{av}^2, which is maximised in outer, or delocalised, electronic orbitals, such as f orbitals of lanthanides in high temperature superconducting materials, conducting polymers, and so on.

(2) It is inversely proportional to the magnitude $|L_{av}|$ of the electronic orbital angular momentum, which is minimised at low temperatures.

(3) It is proportional to the angular frequency ω of the circularly polarised pump laser, for example a visible frequency excimer pumped dye laser.

References

[1] M.W. Evans, J. Phys. Chem. 95 (1991) 2256.
[2] M.W. Evans, Phys. Lett. A 146 (1990) 185, 475.
[3] M.W. Evans, Physica B 168 (1991) 9.
[4] M.W. Evans, Int. J. Mod. Phys. B 5 (1991) 1263.
[5] M.W. Evans, Chem. Phys. 157 (1991) 1.
[6] M.W. Evans, Physica B, in press.
[7] M.W. Evans, J. Mol. Spect., in press.
[8] C.H. Townes and A.L. Schawlow, Microwave Spectroscopy (McGraw-Hill, New York, 1955) Ch. 11.
[9] J.I. Steinfeld, Molecules and Radiation, 2nd Ed. (MIT Press, Cambridge, MA, 1985).
[10] S.B. Piepho and P.N. Schatz, Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism (Wiley, New York, 1983).
[11] W.G. Richards and P.R. Scott, Structure and Spectra of Atoms (Wiley, London, 1976).
[12] G. Herzberg, Atomic Spectra and Atomic Structure (Dover, New York, 1944).
[13] M.E. Rose, Elementary Theory of Angular Momentum (Wiley, New York, 1957).
[14] L.D. Barron, Molecular Light Scattering and Optical Activity, (Cambridge Univ. Press, Cambridge, 1982).
[15] D.M. Brink and G.R. Satchler, Angular Momentum (Oxford Univ. Press, Oxford, 1968).
[16] A.R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton Univ. Press, Princeton, 1957).
[17] B.R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill, New York, 1963).
[18] M. Rotenberg, R. Bivins, N. Metropolis and J.K. Wooten Jr., The 3j and 6j Symbols (Technology Press, MIT, 1959).
[19] B.L. Silver, Irreducible Tensor Methods (Academic Press, New York, 1976).
[20] R.H. Zare, Angular Momentum (Wiley, New York, 1987).
[21] F. Laloë and J.L. Freed, Scientific American 256 (1988) 94.
[22] S. Woźniak, B. Linder and R. Zawodny, J. de Phys. 44 (1983) 403.
[23] S. Kielich, N.L. Manakov and V.D. Ovsiannikov, Acta Phys. Polon. 53A (1978) 581, 595, 737.
[24] S. Kielich, in: Dialectric and Related Molecular Processes, Vol. 1, M. Davies (senior reporter) (Chem. Soc., London, 1972).
[25] S. Kielich, Nonlinear Molecular Optics (Nauka, Moscow, 1982).
[26] M.W. Evans, Phys. Rev. A 39 (1989) 4601.
[27] P.W. Atkins, Molecular Quantum Mechanics, 2nd Ed. (Oxford Univ. Press, Oxford, 1983).
[28] R. Beringer and M.A. Heald, Phys. Rev. 95 (1954) 1474.
[29] M. Karplus and H.J. Kolker, J. Chem. Phys. 39 (1963) 1493.
[30] R.M. Glover and F. Weinhold, J. Chem. Phys. 65 (1976) 4913.