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The Light Magnet, Coupling of Electronic and Nuclear Angular Momenta in Optical NMR and ESR: Quantum Theory

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Optical NMR and ESR is a recently introduced technique in which a circularly polarized laser (a "light magnet") is used in an NMR or ESR spectrometer to induce magnetization. The spectral consequencies are developed with a quantum theory similar to the rigorous theory of Zeeman splitting of Russell–Saunders states, a theory which is suitable for atoms and molecules with net electronic angular momentum, and in which the antisymmetric electronic polarizability is finite. The optical NMR and ESR Hamiltonians are developed with the Wigner–Eckhart Theorem. The circularly polarized laser shifts the original NMR or ESR resonance lines, and splits the shifted lines into analytically useful patterns. The theory gives Landé factors which are in agreement with an earlier, simple, semiclassical theory (*J. Phys. Chem.* 95, 2256–2260 (1991)).

INTRODUCTION

The first theory of optical NMR spectroscopy (*1*) was based on a simple semiclassical foundation, in which a vector coupling model was used to form Landé coefficients between the electronic and nuclear parts of the optical NMR interaction energy:

$$\Delta H = -\gamma_N \hat{\mathbf{I}} \cdot \mathbf{B}^{(0)} - \frac{i}{2} \hat{\mathbf{a}}^{\parallel} \cdot \mathbf{\Pi}. \quad (1)$$

Note that the electronic and nuclear angular momenta, J and I, respectively, are coupled through the eigenstate $|JIFM_F\rangle$, where F is the coupled angular momentum. Here the interaction energy is composed of a term $i/2\hat{\mathbf{a}}^{\parallel} \cdot \mathbf{\Pi}$ due to a circularly polarized laser, which is added to the simplest representation $-\gamma_N \hat{\mathbf{I}} \cdot \mathbf{B}^{(0)}$ of the NMR Hamiltonian. The vector $\hat{\mathbf{a}}^{\parallel}$ represents the vectorial or antisymmetric electronic polarizability (*2–4*), $\mathbf{\Pi}$ is the conjugate product of the circularly polarized laser, $\gamma_N \hat{\mathbf{I}}$ is the nuclear magnetic dipole moment, and $\mathbf{B}^{(0)}$ the static magnetic flux density of the permanent magnet of the NMR spectrometer. A simple vector model transformed the energy (1) to the Landé form

$$\frac{\Delta H}{\hbar} \doteq -\frac{\gamma_N}{2}\left[1 + \frac{I(I+1) - J(J+1)}{F(F+1)}\right] M_F B_Z^{(0)} - \frac{\gamma_\Pi}{4}\left[1 - \frac{I(I+1) - J(J+1)}{F(F+1)}\right] M_F \Pi_Z, \quad (2)$$

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which shows the way in which the nuclear angular momentum $\hat{\mathbf{I}}$ is coupled to the net electronic angular momentum $\hat{\mathbf{J}}$ (orbital plus spin). In deriving Eq. (2) the proportionality

$$i\hat{\mathbf{a}}^{\parallel} = \gamma_{\Pi}\hat{\mathbf{J}} \tag{3}$$

was constructed (*1*) between the angular (or vectorial, or antisymmetric) electronic polarizability $(i\hat{\mathbf{a}})^{\parallel}$ and $\hat{\mathbf{J}}$, each of which are axial vectors, negative to motion reversal (T) and positive to parity inversion (P). The scalar γ_{Π} was referred to as the "gyroptic ratio." The quantity γ_N in Eq. (2) is the nuclear gyromagnetic ratio, and the total (nuclear plus electronic) quantum number F ranges over

$$F = J + I, \ldots, |J - I| \tag{4}$$

with selection rules

$$\Delta M_F = 0, \pm 1 \tag{5}$$

on its azimuthal component

$$M_F = M_J + M_I. \tag{6}$$

This paper provides a rigorous quantum development of the energy (1) using the quantum theory of angular momentum. The results are then put into the Landé form of Ref. (*1*), showing that the two approaches are equivalent. In Section 1 the matrix elements of the energy (1) are derived using the theory of irreducible tensor operators in quantum mechanics. The operator is compounded from two independent spaces: space one of the nuclear angular momentum I, and space two of the angular polarizability of the electrons. In Section 2 the matrix elements of the operator are written out with the Wigner–Eckart Theorem and Racah algebra, from which Section 3 finally derives the spectral consequencies of adding circularly polarized laser radiation to a sample in an NMR spectrometer. A simple analogy anticipates similar effects of a circularly polarized laser on ESR spectra. Finally, the discussion links the analysis of Sections 1 to 3 with simple chemical shift theory, in which consideration is taken of the immediate electronic environment of the resonating nucleus, and not necessarily of the complete molecule. On such a local level net electronic angular momentum may well survive, even if it vanishes in the molecule as a whole. (In an atom there is always net electronic angular momentum, and the angular polarizability $i\hat{\mathbf{a}}^{\parallel}$ depends on the state of the atom (*3, 4*).) The laser, or optical, NMR and ESR techniques discussed in this paper are fundamentally different in nature from the technique sometimes known as optically detected ESR (*5*) in which the laser is used as a spectral source, and in which the sample is brought into resonance with the laser by adjusting the flux density of a magnet. The theory of this paper describes how a CIRCULARLY POLARIZED laser magnetizes a sample, and, essentially, develops the theory of the inverse Faraday effect (*6–10*). Our circularly polarized laser is therefore acting as a "light magnet," whose effects are detected with the highly sophisticated techniques of contemporary resonance spectroscopy, with a catalogue of pulse sequences, two- and three-dimensional capabilities, Fourier transform software, and so on (*11–15*). Optical NMR and ESR is therefore a radically new development in which there is a "laser shift" which is proportional to the intensity of the circularly polarized laser in Watts per unit area, and a "laser split." Clearly, the circularly polarized laser is capable, in theory, of increasing the absolute frequency separation of the original NMR resonance spectrum, and therefore of increasing dramatically the effective resolving power of the instrument. Both shift and splittings depend on the nature of the electrons, through electronic property tensors such as the antisymmetric polarizability, or hyperpolarizability (*2*), and on the way the electrons interact with the nuclei. The technique is therefore potentially capable of providing a great deal of fundamental information in all materials in which magnetic resonance is observable.

1. SETTING UP THE COMPOUND IRREDUCIBLE TENSOR OPERATOR

The energy (1) must be put into a form in which it can be developed with quantum theory, i.e., to the point at which the Wigner–Eckart Theorem can be applied to separate out the rotational properties responsible for the spectral nature of the shift and split due to the light magnet. Standard texts on the quantum theory of angular momentum reduce the problem to the equation (*16*)

$$\langle j_1 j_2 JM | X^K_Q(1,2) | j'_1 j'_2 J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix} \times \langle j_1 j_2 J \| X^K(1,2) \| j'_1 j'_2 J' \rangle. \quad (7)$$

Here X^K_Q is a compound tensor operator built up from two operators acting on independent sets of variables labeled in spaces 1 and 2. The matrix elements of X are constructed between eigenstates $\langle j_1 j_2 JM|$ and $|j'_1 j'_2 J'M\rangle$ made up of the two angular momentum states j_1 and j_2 which couple to form the resultant angular momentum J, whose azimuthal components are M_J. In Eq. (7) the Wigner–Eckart Theorem has been applied to separate out the rotational properties (contained in the M quantum number) in terms of the well known 3-*j* symbol (*16*). The reduced matrix element $\langle j_1 j_2 J \| X^K(1,2) \| j'_1 j'_2 J' \rangle$ evaluates X, therefore, without reference to its azimuthal index Q, but only with respect to its index K, which signifies the tensor rank in irreducible spherical representation.

It is relevant and important to recall here the steps involved in the derivation of the keystone Eq. (7), because these define the applicability of the theory of this paper, and therefore of the concepts of optical NMR and ESR.

First, the Wigner–Eckart Theorem can be derived purely from the transformation properties of wavefunctions and operators, and the 3-*j* symbol depends only on the rotational symmetry properties of the compound operator $X^K_Q(1,2)$. It determines, for example, the selection rules of spectral transitions associated with $X^K_Q(1,2)$, and therefore the appearance of the optical NMR or ESR spectra. Second, the angular momentum states $|jm\rangle$ and $|j_1 m_1\rangle$ are standard basis functions of the full rotation group (*16*). In atoms this is the group $R_h(3)$ of all rotations and reflections. In molecules the appropriate molecular point group must be used as first described by Griffith (*17*). The 3-*j* symbols become the appropriate Griffith V coefficients (*18, 19*). The compound operator must be written in irreducible tensor form, and its reduced matrix elements must be expressed in terms of those of its individual components using the appropriate 6-*j* and 9-*j* symbols (*17–22*).

It then becomes possible to make maximum use of the symmetry of the energy (1) in evaluating the effect of the light magnet.

The operator X^K_Q is usually developed as the product of operators

$$X^K_Q = \sum_{q_1 q_2} T^{k_1}_{q_1}(1) U^{k_2}_{q_2}(2) \begin{pmatrix} k_1 & k_2 & K \\ q_1 & q_2 & -Q \end{pmatrix} (2K+1)^{1/2} (-1)^{k_1-k_2+Q} \quad (8)$$

acting in spaces 1 and 2, respectively, with tensor ranks k_1 and k_2 and azimuthal indices q_1 and q_2. Of special relevance to the development of the energy (1) in atoms is a particular case of Eq. (7) when one component of the compound operator X^K_Q is the unit tensor operator **1**. In this case the general result

$$\langle j_1 j_2 J \| X^K(1,2) \| j_1' j_2' J' \rangle = \langle j_1 \| T^{k_1}(1) \| j_1' \rangle \langle j_2 \| U^{k_2}(2) \| j_2' \rangle \times [(2J+1)(2J'+1)(2K+1)]^{1/2} \begin{Bmatrix} j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \\ J & J' & K \end{Bmatrix} \quad (9)$$

reduces to two simpler results

$$\langle j_1 j_2 J \| T^{k_1}(1) \| j_1' j_2 J' \rangle = (-1)^{j_1+j_2+J'+k_1}[(2J'+1)(2J+1)]^{1/2} \begin{Bmatrix} j_1 & J & j_2 \\ J' & j_1' & k_1 \end{Bmatrix} \langle j_1 \| T^{k_1}(1) \| j_1' \rangle; \quad j_2 = j_2'; \quad K = k_1; \quad (10)$$

and

$$\langle j_1 j_2 J \| U^{k_2}(2) \| j_1 j_2' J' \rangle = (-1)^{j_1+j_2'+J+k_2}[(2J+1)(2J'+1)]^{1/2} \begin{Bmatrix} J & k_2 & J' \\ j_2' & j_1 & j_2 \end{Bmatrix} \langle j_2 \| U^{k_2}(2) \| j_2' \rangle; \quad j_1 = j_1'; \quad K = k_2. \quad (11)$$

Here the braces denote the 6-j symbols (17–22), (not to be confused with the 3-j symbols, enclosed in large brackets.) Equation (9) describes the reduced matrix elements of a simple operator T^{k_1} acting on only one set of variables of the coupled eigenstate $| j_1 j_2 JM \rangle$. Equation (10) describes the reduced matrix elements of a simple operator U^{k_2} acting on the other set of variables of the coupled eigenstate $| j_1 j_2 JM \rangle$.

In optical NMR, the (1) represents the set of coordinates describing the ELECTRONIC antisymmetric polarizability in vectorial form (the first term of the energy (1)), and (2) represents the coordinates of NUCLEAR angular momentum I.

The light magnet (circularly polarized laser) and the flux density vector of the permanent magnet ($\mathbf{B}^{(0)}$ in tesla) are now both aligned in axis Z of the laboratory frame (X, Y, Z). The coupled angular momentum state is defined as the net angular momentum **F**, the resultant of **J** and **I**. (The F notation was introduced by Townes and Schawlow (*23*) in a treatment of hyperfine effects in Zeeman splitting.) The eigenstates in Eq. (7) are therefore $| J'I'F'M_F' \rangle$ and $\langle JIFM_F |$. In general these states are not the same, i.e., at this stage in the argument off-diagonal and diagonal matrix elements are allowed. The allowed values of the quantum number F are given by the Clebsch–Gordan series

$$F = J + I,\ J + I - 1, \ldots, |J - I|$$

and the azimuthal component of F, denoted by M_F, runs from $-F$ to F, having $(2F + 1)$ values. Important for our development is the rule

$$M_F = M_J + M_I,$$

which links the azimuthal quantum numbers.

These statements arrive direct from the quantum theory of angular momentum, i.e., from the fundamental hypothesis that angular momentum is an operator, and has the properties of a commutator. Classically, **F** is the resultant of **J** and **I** of the same atom. (Recall that the electronic antisymmetric polarizability is proportional to **J**.)

The interaction energy (1) becomes

$$\Delta H = -\gamma_N \langle I'J'F'M'_{F'} | I_Z | IJFM_F \rangle B_Z - \frac{\gamma_\Pi}{2} \langle I'J'F'M'_{F'} | J_Z | IJFM_F \rangle \Pi_Z, \qquad (12)$$

and this is to be evaluated as follows:

$$\Delta H = -\gamma_N \langle I'J'F'M'_{F'} | I_0^1 | IJFM_F \rangle B_Z - \frac{\gamma_\Pi}{2} \langle I'J'F'M'_{F'} | J_0^1 | IJFM_F \rangle \Pi_Z. \qquad (13)$$

Therefore our operator $U_{q_1}^{k_1}$ is the axial vector operator J_0^1, and the operator $T_{q_1}^{k_1}$ is the axial vector operator I_0^1. Their irreducible spherical tensor forms have been used. Alignment of both laser and magnet in Z means that only the zero q indices need be considered (*17, 24*). Therefore J_0^1 acts on the electronic part of the coupled eigenstates in Eq. (7), and I_0^1 on the nuclear part.

This completes the assembly of the symbolic machinery necessary for the evaluation in atomic quantum theory of the energy (1).

2. RACAH ALGEBRA OF THE OPTICAL NMR HAMILTONIAN

It is worth detailing the reduction of Eq. (13) to Landé factors with Racah algebra (*17, 18*), because this is a key demonstration of the equivalence in optical NMR of atoms of the semiclassical and quantum theories. The analysis uses the following properties of the 6-j symbols (*17–22*)

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ 1 & j_3 & j_2 \end{Bmatrix} = (-1)^{j_1+j_2+j_3+1} \frac{2(j_2(j_2+1) + j_3(j_3+1) - j_1(j_1+1))}{[2j_2(2j_2+1)(2j_2+2)2j_3(2j_3+1)(2j_3+2)]^{1/2}}$$

$$\begin{Bmatrix} F' & 1 & F \\ J & I' & J' \end{Bmatrix} = \begin{Bmatrix} I' & J & F \\ 1 & F' & J' \end{Bmatrix}$$

$$\begin{Bmatrix} I' & F' & J' \\ F & I & 1 \end{Bmatrix} = \begin{Bmatrix} J' & I' & F' \\ 1 & F & I \end{Bmatrix}. \qquad (14)$$

The following properties of reduced matrix elements are used:

$$\langle J \| \mathbf{J} \| J' \rangle = \delta_{JJ'} (J(J+1)(2J+1))^{1/2} \hbar$$

$$\langle I \| \mathbf{I} \| I' \rangle = \delta_{II'} (I(I+1)(2I+1))^{1/2} \hbar. \qquad (15)$$

These are nonzero only for $I = I'$ and $J = J'$. These constraints, together with those on the 6-j symbols in Eqs. (10) and (11) mean that the energy (1) must be evaluated in the form

$$\Delta H = -\gamma_N \langle IJF'M'_{F'} | I_0^1 | IJFM_F \rangle - \frac{\gamma_\Pi}{2} \langle IJF'M'_F | J_0^1 | IJFM_F \rangle, \qquad (16)$$

i.e., between initial and final eigenstates in which I and J remain the same, but in which F and M_F may differ.

Landé Factors from the Racah Algebra

For the special case $F = F'$ the general expressions reduce to simple combinations of Landé factors, using the following general property of 3-j symbols:

$$\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix} = \begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} = (-1)^{j-m} \frac{m}{(j(j+1)(2j+1))^{1/2}}. \quad (17)$$

The interaction energy (16) then reduces to the form

$$\Delta H = -(-1)^{F-M} \begin{pmatrix} F & 1 & F \\ -M & 0 & M \end{pmatrix} \times [\langle IJF \| \mathbf{J} \| IJF \rangle \frac{\gamma_\Pi}{2} \Pi_Z + \langle IJF \| \mathbf{I} \| IJF \rangle \gamma_N B_Z^{(0)}] \quad (18)$$

with

$$\langle IJF \| \mathbf{J} \| IJF \rangle = (-1)^{I+J+F+1}(2F+1) \begin{Bmatrix} F & 1 & F \\ J & I & J \end{Bmatrix} \langle J \| \mathbf{J} \| J' \rangle \quad (19)$$

$$\langle IJF \| \mathbf{I} \| IJF \rangle = -(1)^{I+J+F+1}(2F+1) \begin{Bmatrix} J & I & F \\ 1 & F & I \end{Bmatrix} \langle I \| \mathbf{I} \| I' \rangle. \quad (20)$$

Some algebra (see Appendix) reduces the interaction energy to the form

$$\Delta H = -M_F \hbar \left(g_{L1} \frac{\gamma_\Pi}{2} \Pi_Z + g_{L2} \gamma_N B_Z^{(0)} \right), \quad (21)$$

where

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

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

which is identical with Eq. (46) of Ref. (*1*).

The full quantum theory for atoms has therefore reduced to the semiclassical theory (*1*) in the case $F = F'$.

In Eq. (21)

$$F = J+1, \ldots, |J-I|; \qquad M_F = M_J + M_I. \quad (22)$$

As a simple example of Eq. (21) consider the ground state of the H atom, $J = \frac{1}{2}$, $I = \frac{1}{2}$ and the state $J = \frac{3}{2}$, $I = \frac{1}{2}$. In the laser-off condition resonance occurs as usual in NMR when

$$\omega = \gamma_N B_Z^{(0)}. \quad (23)$$

The effect of the light magnet (the circularly polarized laser) is to shift the original resonance frequency (23), splitting it in the process. These features emerge as follows.

In the H ground state $J = \frac{1}{2}$ and $I = \frac{1}{2}$, so that $F = 1$ or 0. If $F = 1$, $M_F = -1, 0, 1$; and if $F = 0$, $M_F = 0$. The M_F selection rule

$$\Delta M_F = 0, \pm 1 \quad (24)$$

emerges directly from the properties of the 3-j symbol

$$\begin{pmatrix} F & 1 & F \\ -M_F & 0 & M_F \end{pmatrix}$$

and so there are two possible transitions for $F = 1$, from $M_F = -1$ to $M_F = 0$, and from $M_F = 0$ to $M_F = 1$, which satisfy $\Delta M_F = 1$. These two transitions resonate, however, at the same frequency, because

$$En(M_F - 1) - En(M_F) = En(M_F) - En(M_F + 1). \tag{25}$$

The overall ONMR spectrum of H in the ground state therefore consists of one shifted line.

If $F = 0$,

$$M_F = M_I + M_J = 0; \qquad M_I = -M_J; \tag{26}$$

and for $J = \frac{1}{2}$, $I = \frac{1}{2}$, $F = 0$, we have

$$g_{L1} = g_{L2} = 1.0 \tag{27}$$

but $\Delta M_F = 0$; so there is no resonance.

If $F = 1$, however,

$$M_F = M_I + M_J = -1, 0, 1; \qquad \Delta M_F = 0, \pm 1; \tag{28}$$

and for $J = \frac{1}{2}$, $I = \frac{1}{2}$, $F = 1$ we have

$$g_{L1} = g_{L2} = \tfrac{1}{2}, \tag{29}$$

and the laser-shifted resonance angular frequency is

$$\omega_{[F=1,J=1/2,I=1/2]} = \frac{1}{2}\left(\frac{\gamma_\Pi^{(F=1)}}{2}\Pi_Z + \gamma_N^{(F=1)} B_Z^{(0)}\right). \tag{30}$$

For the $\Delta M_I = 1$ transition therefore, there is one shifted resonance frequency in the H state $J = \frac{1}{2}$, $I = \frac{1}{2}$, $F = 1$. A similar analysis can be made for the states $J = \frac{3}{2}$, $I = \frac{1}{2}$, $F = 2$ and 1. We obtain

$$\omega_{[F=2,J=3/2,I=1/2]} = \frac{3}{8}\gamma_\Pi^{(F=2)}\Pi_Z + \frac{1}{4}\gamma_N^{(F=2)} B_Z^{(0)} \tag{31}$$

$$\omega_{[F=1,J=3/2,I=1/2]} = -\frac{5}{8}\gamma_\Pi^{(F=1)}\Pi_Z + \frac{1}{4}\gamma_N^{(F=2)} B_Z^{(0)} \tag{32}$$

so that there are *two* shifted resonance frequencies: a laser split, as well as a shift. Note that in general,

$$\gamma_\Pi^{(F=1)} \neq \gamma_\Pi^{(F=2)}; \qquad \gamma_N^{(F=1)} \neq \gamma_N^{(F=2)}. \tag{33}$$

The analogous analysis for optical ESR spectroscopy proceeds by replacing I by the electronic spin angular momentum of H, i.e., $S = \frac{1}{2}$. The theory is developed with the OESR interaction energy

$$\Delta H_1 = -2.002\gamma_e \hat{\mathbf{S}} \cdot \mathbf{B}^{(0)} - \frac{i}{2}\hat{\mathbf{a}}^{\parallel} \cdot \mathbf{\Pi}, \tag{34}$$

TABLE I

Effect of the Laser on the Ground State of Atomic ^1H

	J	I	F	M_F	g_{L1}	g_{L2}
a)	$\frac{1}{2}$	$\frac{1}{2}$	0	0	-	-
b)	$\frac{1}{2}$	$\frac{1}{2}$	1	-1, 0, 1	$\frac{1}{2}$	$\frac{1}{2}$

where γ_e is the gyromagnetic ratio and where $2.002\hat{S}$ is the electronic spin angular momentum. The F quantum number for OESR is made up of the Clebsch–Gordan series $J + S, \ldots, |J - S|$, and the Landé form of the OESR interaction energy is

$$\Delta H_1 = -M_F \hbar \left(g_{L1} \frac{\gamma_\Pi}{2} \Pi_Z + 2.002 g_{L2} \gamma_e B_Z^{(0)} \right)$$

$$g_{L1} = 0.5 \frac{(F(F+1) + J(J+1) - S(S+1))}{(F(F+1))}$$

$$g_{L2} = 0.5 \frac{(F(F+1) + S(S+1) - J(J+1))}{(F(F+1))}. \tag{35}$$

Note that in developing this OESR theory we have assumed that the angular or vectorial polarizability $\hat{a}^{\parallel}$ is still proportional (Eq. (3)) to the total electronic angular momentum (orbital and spin). On this theoretical basis the light magnet shifts the ground state H OESR resonance and splits it into two.

3. EXPECTED EFFECT OF THE LASER IN THE GROUND STATES OF ATOMIC HYDROGEN AND HELIUM

The expected effect of the laser is summarized in the ground states of atomic ^1H and ^3He in Tables I and II. These systems have been studied extensively in the gas states by Freed, Laloë, and co-workers (*25*), revealing a variety of remarkable spin-wave and heat-conduction phenomena due to counterintuitive, purely quantum, origins.

In case (a) of ground state ^1H there is no resonance, as we have seen, because $\Delta M_F = 0$. In case (b) there are two resonances at the same, shifted, frequency, so that its intensity is doubled.

TABLE II

Effect of the Laser on the Ground State of Atomic ^3He

	J	I	F	M_F	g_{L1}	g_{L2}
a)	0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	0	1
b)	1	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	$\frac{4}{3}$	$-\frac{1}{3}$
c)	1	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$	$\frac{2}{3}$	$\frac{1}{3}$

In the ground state of ^{3}He there are two electrons, with a total $L = 0$ (*26*), and a total $S = 0$ or 1, so that $J = 0$, or 1. In the nucleus of ^{3}He there are two protons and one neutron, each with nuclear spin angular momentum $\frac{1}{2}$. The resultant is $I = \frac{1}{2}$, due to pairing of proton spins (*26*). At temperatures very close to absolute zero, as used in the experiments of Freed, Laloë, and co-workers (*25*), we expect that almost all the population will be in the ground state. Table II then gives the Landé factors to be used in our Eq. (21). The outcome of Eq. (1) from Table II is that there are three cases: (a), (b), and (c). In case (a), there is no shift, because one of the Landé factors vanishes, and there is no net electronic angular momentum (i.e., $J = 0$). In case (b) the original resonance is shifted and occurs at the frequency

$$\omega_{[F=1/2, J=1, I=1/2]} = \left| \frac{1}{3} \gamma_N B_Z^{(0)} - \frac{2}{3} \gamma_\Pi \Pi_Z \right|. \tag{36}$$

In case (c) there are three shifted resonances all occurring at the same frequency, (because there are three possible $\Delta M_F = 1$). The intensity of this resonance is therefore tripled with respect to case (b), and occurs at

$$\omega_{[F=3/2, J=1, I=1/2]} = \frac{1}{3} (\gamma_N B_Z^{(0)} + \gamma_\Pi \Pi_Z). \tag{37}$$

Note that Landé factor g_{L2} PREMULTIPLIES the original resonance due to $\Delta M_I = 1$ both in ^{1}H and ^{3}He ground states. 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 resonance is recovered, if and only if the laser intensity is identically zero. Equation (21) therefore implies a counterintuitive effect of the laser, in that the original resonance frequency will ALWAYS be premultiplied by the Landé factor g_{L2}, *whatever the intensity of the laser*. There is a "quantum leap" in the original 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.

DISCUSSION

We have attempted to develop a simple first theory of the effect of a circularly polarized laser on the resonance spectra of atoms in the ground state, exemplified by ^{1}H and ^{3}He. In these systems, highly sophisticated experiments (*25*) have been performed in the gaseous state of ^{1}H and in the liquid state of ^{3}He and have detected spin waves and heat-conduction changes due to the fundamental quantum mechanical nature of these ensembles. It may be possible with the development of these experimental techniques to observe the fundamentally new predictions of Eq. (21) in the simplest cases given in Tables I and II. In particular, it would be highly significant to attempt to observe the quantum leap effect of the laser, evaluated in Eq. (21) through the *premultiplying* Landé factor g_{L2}. This is a counterintuitive, purely quantum, effect, with no classical analogue.

In deriving Eq. (21), a fundamental assumption is that the antisymmetric electronic polarizability $\mathbf{a}''$ is proportional to the TOTAL electronic angular momentum $\mathbf{J}$ (orbital and spin) through a quantity γ_Π, which was called the gyroptic ratio in the original semiclassical theory, whose Eq. (46) has been rederived rigorously as our Eq. (21). This assumption is based on well founded fundamental symmetry, but needs experimental corroboration.

APPENDIX: SOME DETAILS OF THE RACAH ALGEBRA

In this Appendix, some details are given of the algebra used in deriving Landé factors from Eqs. (19) and (20). For example,

$$
\begin{aligned}
&(-1)^{F-M}\begin{pmatrix} F & 1 & F \\ -M & 0 & M \end{pmatrix}(-1)^{I+J+F+1}(2F+1)\begin{Bmatrix} I & F & J \\ F & I & 1 \end{Bmatrix}\langle I\|\mathbf{I}\|I'\rangle \\
&\quad= \frac{(-1)^{2(F-M)}M_F(-1)^{I+J+F+1}}{((2F+1)(F+1)F)^{1/2}}(2F+1)(-1)^{I+J+F-1} \\
&\quad\times \frac{2(I(I+1)+F(F+1)-J(J+1))\langle I\|\mathbf{I}\|I'\rangle}{(2I(2I+1)(2I+2)2F(2F+1)(2F+2))^{1/2}} \\
&\quad= M_F\left(\frac{F(F+1)+I(I+1)-J(J+1)}{\sqrt{2}F(F+1)}\right)\frac{\langle I\|\mathbf{I}\|I'\rangle}{(I(2I+1)(2I+2))^{1/2}} \\
&\quad= M_F\left(\frac{F(F+1)+I(I+1)-J(J+1)}{2F(F+1)}\right)\hbar, \qquad \text{(A1)}
\end{aligned}
$$

because

$$\langle I\|\mathbf{I}\|I'\rangle = \delta_{II'}(I(2I+1)(I+1))^{1/2}\,\hbar. \qquad \text{(A2)}$$

Therefore, the very complicated 3-j and 6-j symbols reduce to simple Landé factors in the case $F = F'$. For $F \neq F'$ there is no such simple reduction.

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