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QUANTUM OPTICS IN NMR SPECTROSCOPY

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A circularly polarised laser is shown to produce a static magnetic field, $\mathbf{B}_\pi$, in its axis of propagation. The field $\mathbf{B}_\pi$ is expressed in quantum optical form and is shown to interact with a nuclear dipole moment to produce a real interaction energy which produces a frequency shift in a standard NMR spectrum. The observed shift is two orders of magnitude smaller than that predicted with a classical $\mathbf{B}_\pi$. This is explained qualitatively using the fact that the classical $\mathbf{B}_\pi$ produces an interaction energy which is the upper bound of the energy produced by the quantised $\hat{B}_\pi$. The quantum field in NMR appears to behave quite differently, therefore, from its classical counterpart.

1. Introduction

A circularly polarised laser can magnetize atomic and molecular material, as demonstrated theoretically and experimentally by Pershan *et al.*,[1–4] and called the inverse Faraday effect[5–10] (IFE). The theory of the IFE has until recently been based on the imaginary, nonlinear conjugate product

$$\pi^{(A)} = \mathbf{E} \times \mathbf{E}^* = \pm 2E_0^2 i\mathbf{k} \tag{1}$$

of the circularly polarised laser. Here $\mathbf{E}^*$ denotes the complex conjugate of $\mathbf{E}$, the laser's electric field strength vector in volts per metre, E_0 is the scalar electric field strength amplitude, and $\mathbf{k}$ is a unit AXIAL vector in the laser's propagation axis. However, it has recently been realized[9–14] that $\pi^{(A)}$ is made up of a real magnetic flux density vector, $\mathbf{B}_\pi$, that is capable of forming a real interaction energy with a magnetic dipole moment, specifically a nuclear magnetic dipole moment, $\mathbf{m}^{(N)}$. This letter introduces the concept of a quantised $\hat{B}_\pi$ in NMR spectroscopy, using the experimental results of Warren and co-workers,[15] who have shown recently that a circularly polarised laser shifts NMR resonances in the liquid state of matter.

Section 2 introduces and defines $\mathbf{B}_\pi$ using classical electrodynamics, a definition which is extended to quantum optics in Sec. 3. Section 4 works out the form of the interaction energy between the quantum field $\hat{B}_\pi$ and the quantised $\hat{m}^{(N)}$. Finally, Sec. 5 compares the theory with experimental data.

2. The Classical $\mathbf{B}_\pi$

It is easy to show that the following relations exist between the nonlinear conjugate product $\boldsymbol{\pi}^{(A)}$ and the real, classical $\mathbf{B}_\pi$:

$$\begin{aligned}\boldsymbol{\pi}^{(A)} &= 2E_0cB_0\mathbf{k}_i \equiv 2E_0c\mathbf{B}_\pi i \text{ (right)}\\ \boldsymbol{\pi}^{(A)} &= -2E_0cB_0\mathbf{k}_i \equiv -2E_0c\mathbf{B}_\pi i \text{ (left)}\\ \boldsymbol{\pi}^{(A)} &= 0 \text{ (linear polarisation)}\end{aligned} \tag{2}$$

Note that $\mathbf{B}_\pi$ changes sign with circular polarisation and vanishes in a linearly polarised laser. It is an axial vector with the units of tesla, negative to motion reversal T and positive to parity inversion P. It has all the properties of a magnetostatic flux density, but is generated by an electromagnetic field. Clearly, if $\boldsymbol{\pi}^{(A)}$ vanishes, so does $\mathbf{B}_\pi$, and whenever $\boldsymbol{\pi}^{(A)}$ interacts with atomic or molecular material, so must $\mathbf{B}_\pi$. The interaction energy of $\mathbf{B}_\pi$ with a nuclear magnetic dipole moment $\mathbf{m}^{(N)}$ is semiclassical, because $\mathbf{B}_\pi$ is classical and $\mathbf{m}^{(N)}$ is quantised, and is

$$\Delta En_1 = -\mathbf{m}^{(N)} \cdot \mathbf{B}_\pi \tag{3}$$

which is formally identical with the interaction of a permanent magnet's flux density, $\mathbf{B}_0$, with $\mathbf{m}^{(N)}$. If a circularly polarised laser is applied to the sample in a standard contemporary NMR spectrometer, therefore, in a direction parallel with that of $\mathbf{B}_0$, the total interaction energy is

$$\Delta En_2 = -\mathbf{m}^{(N)} \cdot (\mathbf{B}_0 + \mathbf{B}_\pi) \tag{4}$$

and there is a shift in the original NMR resonance, a shift which depends on the relative magnitudes of $\mathbf{B}_0$ and $\mathbf{B}_\pi$.

It is possible to show[14] that

$$|\mathbf{B}_\pi| = B_0 \sim 10^{-7} I_0^{1/2} \text{ T} \tag{5}$$

where I_0 is the laser's intensity in watts per square metre (S.I. units), and for an intensity of 1.0 watt per square centimetre, $|\mathbf{B}_\pi|$ is about 10^{-5} T. A laser of such intensity used in a permanent magnet of 1.0 T is expected, semiclassically, to produce a shift of ten parts per million. For a 270 MHz NMR spectrometer,[15] a magnet of 6.4 T, we expect an unshielded proton shift due to a laser of 1.0 watt per square centimetre intensity[15] of about 400 Hertz from the semiclassical Eq. (3). The observed shift[15] is real, free of artifact, but is about two orders of magnitude smaller. The experimentally observed shift disappears with a linearly polarised laser, and has a more complicated dependence on the intensity of the laser than allowed for by the simple square root dependence of Eq. (5).

In the next section we explore the quantum field definition of the vector $\mathbf{B}_\pi$ and form the fully quantum mechanical interaction energy between this quantised field

and the quantised nuclear magnetic dipole moment. This turns out to be much more intricate in nature than the semiclassical interaction energy.

3. The Quantised $\hat{B}_\pi$

We seek the definition of $\hat{B}_\pi$ in terms of quantum field theory using the link

$$\mathbf{B}_\pi = \pm\left(\frac{\varepsilon_0}{8I_0c}\right)^{1/2} S_3\,\mathbf{k} \tag{6}$$

between the classical $\mathbf{B}_\pi$ and the classical third Stokes parameter S_3,[16] which is a real scalar quantity. Here ε_0 is the permittivity in vacuo and c the speed of light. It is well known that in quantum field theory the classical S_3 is the expectation value

$$S_3 = \langle\alpha|\hat{S}_3|\alpha\rangle \tag{7}$$

where $\hat{S}_3$ is the third Stokes operator, and where a coherent state of the quantum field is defined by

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle \tag{8}$$

where $\hat{a}$ is an annihilation operator. The third Stokes operator can be expressed as[16]

$$\hat{S}_3 = -i(\hat{a}_x^+\hat{a}_y - \hat{a}_y^+\hat{a}_x) \tag{9}$$

where ω is the field frequency in radians per second, V the quantisation volume, $n(\omega)$ the refractive index, and where $\hat{a}^+$ denotes a creation operator. In (9), the field propagates in Z of the laboratory frame.

The quantum field definition of $\hat{B}_\pi$ rests therefore on a boson operator

$$\hat{B}_\pi \equiv \left(\frac{\varepsilon_0}{8I_0c}\right)^{1/2}\left(\frac{2\pi\hbar\omega}{n^2(\omega)V}\right)\hat{S}_3\,. \tag{10}$$

Since $\hbar\hat{S}_3$ is a quantised quantity which is negative to T and positive to P, it is proportional to quantised angular momentum and has all the well known quantum properties[17] of angular momentum. The component of $\hat{B}_\pi$ in Z can therefore be written as in analogy with the Z component of a quantized angular momentum operator, $\hat{J}$, describing the angular momentum of quantised radiation[18]

$$\hat{J}_Z|JM_J\rangle = M_J\hbar|JM_J\rangle \tag{11}$$

with

$$\hat{\mathbf{J}} \equiv \hbar\hat{S}_3\,. \tag{12}$$

Defining a quantum number J associated with the boson operator $\hat{B}_\pi$, the latter's observable magnitude is in turn defined in analogy with angular momentum theory as

$$\hat{J}^2|JM_J\rangle = J(J+1)\hbar^2|JM_J\rangle\,. \tag{13}$$

It also follows that the values of the quantum number M_J are given by

$$M_J = -J, \ldots, J \tag{14}$$

with the selection rule

$$\Delta M_J = 0, \pm 1 \tag{15}$$

again in direct analogy with quantum mechanics applied to angular momentum.

Finally the cartesian components of the boson operator $\hat{J}$ obey a commutator equation

$$[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_Z \tag{16}$$

and are governed by Heisenberg's Uncertainty Principle. It is interesting to note that the Stokes operators of quantised radiation also form a commutation relation[16,19]

$$[\hat{S}_1, \hat{S}_2] = 2_i \hat{S}_3 \tag{17}$$

and this brings out the similarity between the Stokes operators and angular momentum cartesian operators of quantised radiation.

4. The Interaction Energy and Resonance Condition

We are now in a position to construct the interaction energy between the quantum field operator $\hat{B}_x$ and the quantised nuclear magnetic dipole moment $m^{(N)}$:

$$\Delta En_3 = -\left(\frac{\varepsilon_0}{8I_0 c}\right)^{1/2} \left(\frac{2\pi\omega}{n^2(\omega)V}\right) g_N \gamma_N \langle IJFM_F | \hat{I} \cdot \hat{J} | IJFM_F \rangle . \tag{18}$$

Here $\hat{I}$ is the nuclear spin quantum operator, and a resultant F quantum number is formed from the quantum numbers I and J through a Clebsch Gordan series:

$$F = J + I, \ldots, |J - I| . \tag{19}$$

Standard quantum theory and the Wigner Eckart Theorem give

$$\begin{aligned} \Delta En_3 &= -\left(\frac{\varepsilon_0}{8I_0 c}\right)^{1/2} \left(\frac{2\pi\omega\hbar}{n^2(\omega)V}\right) \gamma_N g_N g \hbar M_F ; \\ g &= \left(\frac{3(2F+1)I(I+1)(2I+1)J(J+1)(2J+1)}{F(F+1)}\right)^{1/2} \begin{Bmatrix} I & I & 1 \\ J & J & 1 \\ F & F & 0 \end{Bmatrix} ; \\ M_F &= -F, \ldots, F , \end{aligned} \tag{20}$$

where the quantity in braces is the well known $9-j$ symbol of quantum angular momentum coupling theory.[20–23] Here g_N is the nuclear g factor,[24] and γ_N the nuclear gyromagnetic ratio.

It is immediately clear therefore that the fully quantum mechanical interaction energy of $\hat{B}_\pi$ and $\hat{m}^{(N)}$ is different from the semiclassical counterpart, which is simply

$$\Delta En_1 = -B_\pi \gamma_N g_N \hbar M_I \,. \tag{21}$$

From Eq. (20) a resonance condition can be defined through the equation,[24] using the selection rule $\Delta M_F = \pm 1$,

$$\hbar\omega = En_3(M_F - 1) - En_3(M_F) \tag{22}$$

and the resonance frequency in hertz is

$$\mathcal{J}_V = \left(\frac{\varepsilon_0}{8I_0 c}\right)^{1/2} \frac{\omega\hbar\gamma_N g_N g}{n^2(\omega)V} \,. \tag{23}$$

This compares with a semiclassical resonance frequency in hertz for the same mechanism of

$$\mathcal{J}_c = \frac{B_\pi \gamma_N g_N}{2\pi} \,. \tag{24}$$

5. Comparison with Data and Discussion

In Figs. 1 and 2 the g factor in Eq. (23) is shown as a function of the quantum number J for the two cases $F = J + 1/2$ and $F = J - 1/2$ respectively allowed by the Clebsch Gordan series (19). Also illustrated is the behaviour of the $9-j$ symbol as J is increased. It can be seen that the g factor saturates at levels of about -0.5 and 0.5 respectively. Since $\hat{J}$ is a boson operator, its quantum number is considered to take integral values only, and at $J = 0$, there is no resonance. The initial g value is therefore taken for $J = 1$, and g is worked out until $J = 100$ by direct computation of the $9 - j$ symbol with standard code.[20] These results enable some points of comparison with the semiclassical (24) and with the available experimental data[15] of Warren *et al.*, the only data in the literature at the time of writing.

1) Firstly, intercomparison of quantum field and semiclassical expressions for the resonance condition, Eqs. (23) and (24) respectively, shows that in the quantum field theory, more than one resonance is possible, corresponding to two different F values and therefore two different g values (Figs. 1 and 2). It may be possible to resolve these experimentally.[15] For $I = 1/2$, two resonances are present theoretically. For higher I more than two are present. In the semiclassical theory, only one resonance is possible for $I = 1/2$. This is a clear quantum optical effect therefore in optically enhanced NMR.[14]

2) From Figs. 1 and 2, the sum of the absolute values of the g factors for the two F numbers is precisely one. This implies that as J goes to infinity the two possible resonances present for low J (e.g. $J = 1$) merge into one frequency, which is always, of course, positive. This is the semiclassical result (24), with the infinity value of the third Stokes operator

$$\hat{B}_\pi(J \to \infty) \propto (\hat{S}_3\hbar)_\infty \,. \tag{25}$$

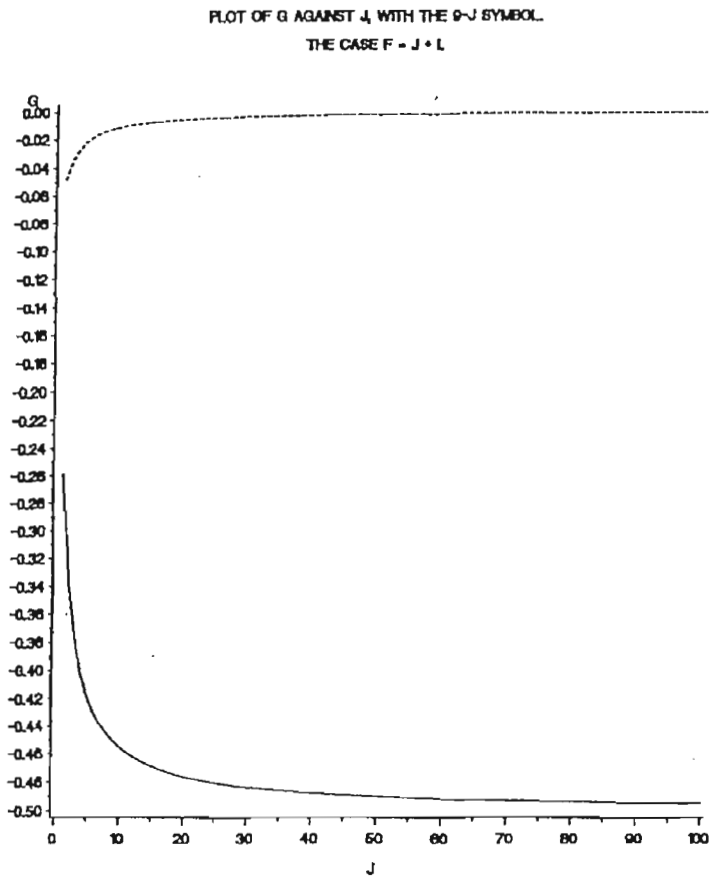

Fig. 1. The g factor (Eq. (20)) as a function of J for $F = J + 1/2$, solid line. The dashed line is the $9 - j$ symbol as a function of J.

Clearly, this means that for every intense radiation, the quantum field theory goes over properly (quantum-classical equivalence) into the classical $\mathbf{B}_\pi$, defined by the expectation value of the boson operator $\hat{B}_\pi$. (Note that the resonance frequency must be positive to be physically meaningful, so the absolute value of g is designated for use in Eq. (23). It follows that the laser induced NMR shift is always to higher frequency, as observed experimentally.[15]

3) It may be possible to use the quantum field theoretical result (23) to explain why the laser induced NMR shifts observed by Warren *et al.*[15] are two orders of magnitude smaller than the semiclassical theory (24) expects. From Eq. (23), the shift due to the quantum field operator $\hat{B}_\pi$ depends on several individual quantities such as the frequency ω and quantisation volume V which merge into the classical laser intensity I_0, which is proportional to the angular frequency (ω) multiplied by the number of photons. From Eq. (23) it might well be possible for example that the effective intensity is much smaller than the measured laser intensity[15] which is inevitably based on the measured output power of the laser and the effective sample area, two macroscopic quantities. In particular, it appears that the microscopic quantisation volume V might well be effectively much larger than that deduced from the macroscopic I_0, meaning that the number of photons actually interacting with the nuclear dipole moment operator $\hat{m}^{(N)}$ is much smaller than the number of

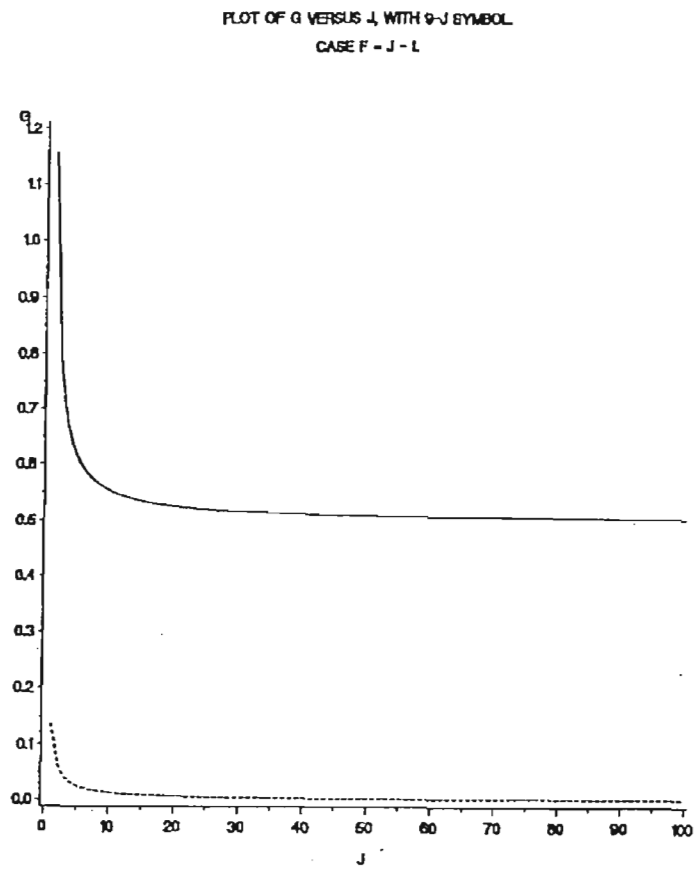

Fig. 2. As for Fig. 1, $F = J - 1/2$.

photons actually delivered by the laser as measured through its macroscopic intensity I_0 in watts per square meter. Many handed photons could be prevented from reaching the nucleus by the electronic environment of that nucleus, which would also explain why the observed laser induced shifts are different for different resonating protons in the sample molecule.[15] This appears to be entirely plausible, especially if some photons are absorbed by the electronic environment before reaching the nuclear part of the nuclear/electronic wave function. In other words, the shielding factor σ in the expression

$$\hat{B}_\pi(\text{eff.}) = (1 - \sigma)\hat{B}_\pi \tag{26}$$

is far bigger than the factors encountered in conventional NMR.

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