Pramāṇa, Vol. 13, No. 6, December 1979, pp. 617-624, © printed in India.

Quantum mechanical calculation of Suryan's line broadening in nuclear magnetic resonance

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MS received 20 June 1979

Abstract. The first quantum theory of the classical radiation damping in nuclear magnetic resonance is presented. Relaxation times and life times arising from the interaction of nuclear spin with the radio-frequency radiation field are calculated. Second-order line shifts are predicted and the existence of I_z and I_z^2-type operators due to photons is pointed out. The predicted line shifts as well as relaxation are found to be measurably large. Numerical estimates are given for protons in water.

Keywords. Nuclear magnetic resonance; radiation; width and shift; Suryan's line broadening; quantum mechanical calculation.

1. Introduction

The problem of line broadening due to the classical magnetic-dipole radiation damping has been well recognised for some time (Suryan 1949). It is established that this effect is large enough to be observed. It is shown by Bloembergen and Pound (1954) that in certain cases of nuclear induction the radiation damping is more important than the damping from the spin-spin and the spin-lattice relaxation mechanisms usually considered. Bruce *et al* (1956) and Sanders *et al* (1974) have shown that the effect is also important in the continuous wave magnetic resonance experiments. The measured line widths which depend on the frequency, sample size, shape and impurity concentration are often ascribed to this classical effect. These results are derived from the properties of electrical resonant circuits containing resistance, capacitance and inductance to which the magnetic resonance is matched through transformer coupling. The entire effect comes from the power emitted and it is assumed that the entire dissipated power is emitted in the form of a microwave. There is no effort to include the possible contribution of the balance term in which the microwave is actually absorbed rather than emitted. Most of the efforts are limited to the study of only the ' damping ' and perhaps there is no effort to imbibe the associated ' shift '. Besides, most of the calculations performed are classical in nature. Therefore, there is a clear need for a proper quantum mechanical calculation of this interesting quantum electrodynamic phenomenon. We have drawn attention to the possible effects in the magnetically ordered systems (Shrivastava 1979 a, b, c).

Suryan (1949) was perhaps the first to suggest the classical radiation emission from a precessing dipole as a line width mechanism in nuclear magnetic resonance. Suryan considered an electrical circuit with a damping constant

$$\tau = (2\pi \gamma \eta M_0 Q)^{-1}, \tag{1}$$

where $\gamma = g_N \beta_N/\hbar$, η is a filling factor and Q the quality factor of the coil, and arrived at a relaxation time of the order of 60 sec in the proton resonance in about 1 g of water. The calculated value of τ appears to be of the correct order of magnitude. Since it is possible to produce nuclear spin states with definite coherent phase relations between the individual spins, it appears that the classical radiation can be treated by the Bloch equations of nuclear induction. Although Dicke's (1954) theory of superradiance came more than 23 years ago, it is not obvious as to how exactly this quantum treatment applies to the magnetic resonance problem and whether the nuclear radiative relaxation can be predicted from the superradiance.

In this paper we develop the interaction of nuclear spins with the electromagnetic field as appropriate to a nuclear magnetic resonance experiment from a fundamental quantum mechanical point of view. In the lowest order we calculate the relaxation time of the nuclei due to exchange of energy with the electromagnetic field and obtain numerical estimates of the same. Then we calculate the self-energy in the second order and from that calculate the line shift of the nuclear magnetic resonance due to the nuclear-spin-photon interaction. We also separate the imaginary part of the second-order self-energy and obtain the life time. We consider the occurrence of effective magnetic moment and hence the shift in the effective value of γ. We also show the occurrence of I_z^2-type terms through the photon field and obtain numerical estimates in all cases. By going through a transformation, we also find that $-J_{ij} I_{xi} \cdot I_{xj}$-type terms appear as a result of interaction with the radio-frequency field. Our effects are found to depend on the number of nuclear spins in the system and therefore deserve comparison with Dicke's superradiance.

2. Nuclear radiative relaxation

The nuclear magnetic resonance experiments are performed by applying a radio-frequency electromagnetic field through an r.f. coil such that the magnetic vector of the radiation field makes an angle of $\pi/2$ radians with the direction of the external d.c. field. The resonance condition is $\hbar\omega_0 = \hbar\gamma H_z$ and the selection rules are provided by the radiation field which interacts with the x-component of the spin. This interaction is of the form

$$\mathcal{H}' = \sum_i \hbar\gamma h_{xi} I_{xi}, \tag{2}$$

where $\gamma = g_N \beta_N/\hbar$, g_N is the nuclear gyromagnetic ratio, β_N the nuclear magneton, H_z the external d.c. field and h_x the magnetic vector of the r.f. field which from the second quantisation of Maxwell equations appears as

$$\mathbf{h} = i \sum_{iqp} (2\pi\hbar c/qL^3)^{1/2} (\mathbf{q} \times \mathbf{e}_{qp}) [b_{qp} \exp(iq \cdot r_i) - b_{qp}^\dagger \exp(-iq \cdot r_i)], \tag{3}$$

where L^3 is the volume in which the radiation is confined, q the wave vector of the r.f. wave, c the velocity, $\mathbf{e}_{qp}$ the unit vector in the direction of polarization and $b^{\dagger}_{qp}$ and b_{qp} are the creation and annihilation operators of the photons of wave vector q and polarisation p. The interaction (2) may therefore be written as

$$\mathcal{H}' = \sum_{iq} A_{qi} \, (I_i^+ + I_i^-) \, (b_q - b^{\dagger}_{-q}), \tag{4}$$

with
$$A_{qi} = \tfrac{1}{2} \, \hbar\gamma \, (2\pi\hbar\omega_q/L^3)^{1/2} \exp{(iq.r_i)}. \tag{5}$$

The probability that a transition takes place from the nuclear state $| \, m \rangle$ to the state $| \, m - 1 \rangle$ by the absorption of a photon is given by

$$p \, (m - 1, \, n_k - 1 \leftarrow m, \, n_k)$$
$$= (2\pi/\hbar) \; A_q A_q^* \, | \, \langle m - 1, \, n_k - 1 \, | \, I_q^- \, b_q \, | \, m, \, n_k \rangle \, |^2 \, \rho_f, \tag{6}$$

where ρ_f is the density of the final states. In an experiment the r.f. frequency can be tuned to a resonant value ω_0. However, it will have certain instrumental width which is of importance to note for contact but will not enter in our calculations. The probability (6) can be written as

$$N_{m_i}(2\pi/\hbar) \int \Big| \sum_i \langle m_i - 1 \, | \, I_i^- \, | \, m_i \rangle \Big|^2 \frac{n_k\omega^2 \; V \, \delta \, (\hbar \, \omega_0 - \hbar \, \omega_{k'}) \, dE}{2\hbar \, \pi^2 \, c^3}$$
$$= N_{m_i}(2\pi/\hbar) \sum_i \{I_i \, (I_i + 1) - m_i \, (m_i - 1)\} \, n_0 \, \omega_0^2 \, V | \, A_0 \, |^2/(2 \, \hbar \, \pi^2 \, c^3), \tag{7}$$

where m_i is the projection quantum number of the nuclear spin of the ith nuclei, N_m the population on this state and n_0 is the photon number density of which the value at resonance $\hbar\omega_0 = \hbar\omega_k$ is evaluated. Similarly the probability of the emission of a photon by the nuclear spin is obtained by

$$p(m, \, n_k{+}1{\leftarrow}m{-}1, \, n_k) = N_{m_i\text{-}1} \, (2\pi/\hbar) \sum_i \{I_i \, (I_i + 1){-}m_i \, (m_i - 1)\}$$
$$(n_0 + 1)\omega_0^2 \, V | \, A_0 \, |^2/2\hbar^2\pi^2c^3 \tag{8}$$

where A_0 is the value of A_q at resonance. Following the usual procedure to define an exponential relaxation time we find

$$1/\tau_1 = \gamma^2\hbar\omega_0^3 \, N(2c^3)^{-1} \, (2n_0 + 1) \, \{I(I + 1) - m(m - 1)\}. \tag{9}$$

For $I = 1/2$, $m = 1/2$, $N = 10^{22}$, $\gamma = 1{\cdot}41049 \times 10^{-23}/\hbar$ for protons and $\omega_0 = 9{\cdot}3631 \times 10^7$ Hz at a field of 7000G

$$\tau_1 = 3{\cdot}48 \times 10^4/(2n_0 + 1) \text{ sec},$$

at a power of 1 mW, this would amount to 34 sec for protons. The dependence of line width on the number of spins and thus the size of the sample, on frequency and r.f. power is thus predicted.

3 Second-order equivalent Hamiltonian

We consider the interaction

$$\mathcal{H}' = \sum_{qj} A_{qj} (I_j^+ b_q - I_j^+ b_{-q}^\dagger + I_j^- b_q - I_j^- b_{-q}^\dagger). \tag{10}$$

The second-order energy of the many-body state $|m\, n_k\rangle$ is given by a virtual process and a real process. The contribution of the real process to the self energy is

$$\sum_2^{(1)} = \sum_{qi} |A_{qi}|^2 \left(\frac{\langle m, n_k | I_i^+ b_k^\dagger | m-1, n_k-1 \rangle \langle m-1, n_k-1 | I_i^- b_k | m, n_k \rangle}{\hbar\Omega_s - \hbar\omega_k} + \frac{\langle m, n_k | I_j^- b_k | m+1, n_k+1 \rangle \langle m+1, n_k+1 | I_i^+ b_k^\dagger | m, n_k \rangle}{-\hbar\Omega_s + \hbar\omega_k} \right)$$

$$= \sum_{qi} |A_{qi}|^2 \left[-I(I+1) + m^2 + m(2n_k+1) \right] / (\hbar\Omega_s - \hbar\omega_k), \tag{11}$$

where we have noted that in nuclei $|m-1\rangle$ is a higher energy state compared with the state $|m\rangle$ and therefore we have taken $E(m-1) - E(m) = \hbar\Omega_s$. In terms of the usual approach towards an equivalent Hamiltonian, the above gives

$$\mathcal{H}_{\text{eff}}^{(1)} = -\sum_{qi} \frac{|A_{qi}|^2}{\hbar\Omega_s - \hbar\omega_k} \{I_i (I_i+1) - I_{zi}^2\} + \sum_{qi} \frac{|A_{qi}|^2 (2n_k+1)}{\hbar\Omega_s - \hbar\omega_k} I_{zi}. \tag{12}$$

Similarly the second-order self-energy due to the virtual process is given by

$$\sum_2^{(2)} = \sum_{qi} |A_{qi}|^2 \left(\frac{\langle m, n_k | I_i^- b_k^+ | m+1, n_k-1 \rangle \langle m+1, n_k-1 | b_k I_i^+ | m, n_k \rangle}{-\hbar\Omega_s - \hbar\omega_k} + \frac{\langle m, n_k | I_i^+ b_k | m-1, n_k+1 \rangle \langle m-1, n_k+1 | I_i^- b_k^\dagger | m, n_k}{\hbar\Omega_s + \hbar\omega_k} \right)$$

$$= \sum_{qi} |A_{qi}|^2 \left[I(I+1) - m^2 + m(2n_k+1) \right] / (\hbar\Omega_s + \hbar\omega_k), \tag{13}$$

which corresponds to the equivalent Hamiltonian of

$$\mathcal{H}_{\text{eff}}^{(2)} = \sum_{qj} |A_{qj}|^2 \frac{I_j(I_j+1)-I_{zj}^2}{\hbar\Omega_s+\hbar\omega_k} + \sum_{qj} |A_{qj}|^2 \frac{(2n_k+1)}{\hbar\Omega_s+\hbar\omega_k} I_{zj}. \tag{14}$$

At resonance $\hbar\Omega_s = \hbar\omega_k = \hbar\omega_0$ so the evaluation of (13) is straightforward. However in (11) the denominator tends to zero and therefore its real and imaginary parts must be separated using Dirac's identity,

$$\lim_{\epsilon\to 0} \frac{1}{x\pm i\epsilon} = \frac{P}{x} \mp i\pi\delta(x), \tag{15}$$

where P stands for Cauchy's principal value. Thus in the equivalent Hamiltonians (12) and (14), terms containing I_z and I_z^2 occur.

4. The line shift

The real part of (11) is

$$\triangle E^{(1)} = \gamma^2 \hbar^2 \omega_0^3 N (4\pi c^3)^{-1} \{-I(I+1) + m^2 + m(2n_0+1)\}. \tag{16}$$

Similarly from (13),

$$\triangle E^{(2)} = \gamma^2 \hbar^2 \pi N (4L^3) \{I(I+1) - m^2 + m(2n_0+1)\}, \tag{17}$$

so that the total shift is

$$\triangle E = m(2n_0+1)\gamma^2\hbar^2(2\pi\hbar\omega_0) N \left(\frac{1}{8\hbar\omega_0 L^3} + \frac{\omega_0^2}{8\hbar\pi^2 c^3}\right)$$

$$+ \{I(I+1) - m^2\} \gamma^2 \hbar^2 (2\pi\hbar\omega_0) N \left(\frac{1}{8\hbar\omega_0 L^3} - \frac{\omega_0^2}{8\hbar\pi^2 c^3}\right). \tag{18}$$

For $\gamma = 1{\cdot}3376 \times 10^4$, $N = 10^{22}$, $m = 1/2$, $L^3 = 1$ cm^3, $\omega_0 = 9{\cdot}36 \times 10^7$ Hz at $H = 7000$ G for protons the various terms are of the order of,

$$m\pi\gamma^2\hbar^2 N/4L^3 = 0{\cdot}118 \text{ kHz}, \tag{18a}$$

$$m\gamma^2\hbar^2\omega_0^3 N/(4\pi c^3) = 10^{-6} \text{ Hz (negligible)}, \tag{18b}$$

$$\{I(I+1) - m^2\}\gamma^2\hbar^2\pi N/4L^3 = 0{\cdot}24 \text{ kHz}, \tag{18c}$$

$$\{I(I+1) - m^2\}\gamma^2\hbar^2\omega_0^3 N/4\pi c^3 = 10^{-6} \text{ Hz (negligible)}. \tag{18d}$$

At 1 mW power, the power dependent term is

$$mn_0\, \gamma^2\, \hbar^2\, \pi\, N/2\, L^3 = 240 \text{ kHz}. \tag{18e}$$

This last term is within observable range and ought to be accounted for in accurate experiments which claim to obtain measurement of the ratio of magnetic moment of the electron to that of proton. Perhaps water is not a good choice for the observation of radiation effects. Benzene has sharper proton resonance. Besides, nuclei with larger value of γ and larger mass densities, so that N/L^3 is large, may be more desirable.

From the first term of (18) there is a correction to γ so that the new value of γ is

$$\gamma' = \gamma[1+\pi N\hbar\,(2n_0+1)/4HL^3] \simeq \gamma\,[1+\pi M_0(2n_0+1)/4\gamma H], \tag{19}$$

apart from a negligible term. Our correction depends on the r.f. power and on the number of atoms per unit volume or on the saturation magnetisation and inversely on the d.c. field. This effect is much bigger than the Bloch-Siegert (1940) effect.

5. Lifetime

The lifetime is determined from the imaginary part of the self energy as

$$1/\tau_2 = -(2/\hbar)\,\text{Im}\,\Sigma, \tag{20}$$

as (13) is purely real, the contributions arise only from (11), as

$$\frac{2\pi}{\hbar}\sum_{qi} |A_{qi}|^2\,[-I(I+1)+m^2+m(2n_q+1)]\,\delta(\hbar\,\Omega_s-\hbar\omega_q)$$

$$= \hbar\gamma^2\,\omega_0^3\,N\,\{I(I+1)+m^2+m(2n_0+1)\}/2c^3. \tag{21}$$

This lifetime is of the same order of magnitude as (9). In the experiment only the average value will be recorded,

$$1/\tau = 1/\tau_1+1/\tau_2, \tag{22}$$

however, one or the other term can also be measured separately.

6. Spin-spin coupling

If we write the interaction (4) in the positive definite form, the Hamiltonian of interest can be described as

$$\mathcal{H} = \sum_q \hbar\omega_q\, b_q^\dagger\, b_q + \sum_{iq} 2\,|A_q|\,I_{xi}\,(b_q + b_q^\dagger), \tag{23}$$

where the first term represents the photon field. Upon the transformation

$$c_k^\dagger = b_k^\dagger + \frac{2\,A_k}{\hbar\omega_k} I_{xj},$$

$$c_k = b_k + \frac{2\,A_k^*}{\hbar\omega_k} I_{xj}, \tag{24}$$

the reduced Hamiltonian appears as

$$\tilde{\mathcal{H}} = \sum_k \hbar\omega_k\, c_k^\dagger\, c_k - \sum_{kij}{}' J_{kij}\, I_{xi}\, I_{xj} \exp\{i\,(r_i - r_j)\,k\}. \tag{25}$$

where the sum $\langle ij \rangle$ is over $N/2$ pairs. So it appears that the energy is reduced and there appears a nuclear spin-spin coupling of amount

$$NJ_{ij}/2 = N(2A_k)^2/(2\hbar\omega_k) \simeq 3{\cdot}8 \text{ kHz}. \tag{26}$$

Had we considered an spin-spin coupling of the form $B_{ij}\, I_i \cdot I_j$ such as is ordinarily present in organic liquids, it would appear that an anisotropy has been introduced by the electromagnetic radiation by reducing the x-component. What happens is that the photons emitted at one site are later absorbed at another site and the single spin absorption of the r.f. wave does not occur. This effect will reduce the intensity of the magnetic resonance and the incident r.f. power would be transmitted after a large number of processes in which the photons are continually absorbed and re-emitted and later reabsorbed and emitted by another atom and so on and so forth. From the second moment formula of van Vleck the line width caused from this coupling is determined to be about 4 kHz. In a pulse propagation experiment only $N^{1/3}$ number of atoms may be effective so that the pulse delay will be of the order of 10^{-8} sec. The effect can be regarded as a ' nuclear self-induced transparency '. This nuclear effect is being discussed here for the first time although its electronic analog is known (McCall and Hahn 1969).

7. Conclusions

The relaxation time and the life-time which occur in our calculation are important particularly at low temperatures. We also find corrective terms of the type I_z and I_z^2 which may be thought to give corrections to the effective value of γ and to the quadrupole interaction. We have presented the first quantum theory of the radiation damping in nuclear magnetic resonance. At least one new shift has been predicted which does not seem to have been indicated in the literature. The number of atoms N occurring in our results can be written as

$$N = M_0\, V/\gamma\hbar,$$

where V is the sample volume and the magnetisation is

$$M_0 = \chi_0 H_0 = [N_0 \gamma^2 \hbar^2 I(I+1)/3k_B T] H_0.$$

Therefore a temperature dependence can be incorporated through the temperature-dependence of the magnetisation. Otherwise our effect is independent of temperature. The effect of the radio-frequency is to produce a 'superradiant' state which naturally decays into radiation. However, the construction of the super-radiant state itself is dependent upon radiation and in our relaxation time both processes matter. There is a frequency shift caused by both the construction as well as the decay of the super-radiant state. We have also considered a virtual process in which the super-radiant state is created by the emission rather than the absorption of radiation. Thus it is quite obvious that we find '*quantum effects*' not recognised by Bloembergen and Pound (1954). Through a transformation we predict a nuclear self-induced transparency in which the incident pulse emerges after a time delay.

We have not considered the possibility of a pseudo scalar coupling like $\hbar \overleftarrow{\Gamma} \mathbf{h} \times \mathbf{I}$ in addition to (4) and the possible deviation of $\mathbf{h}$ from the x-direction, which may have interesting consequences. It may be remarked that although some authors do refer to Suryan's original work, most authors using the Suryan's broadening do not appear to know about Suryan's letter.

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