

NUCLEAR MAGNETIC RESONANCE SPECTRA FOR A SYSTEM ABC OF SPIN $\frac{1}{2}$ NUCLEI AND THEIR LINEWIDTHS

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1. INTRODUCTION

RECENTLY, very extensive work (Pople *et al.*, 1959) has been done to investigate the NMR spectra of groups of interacting nuclei in different molecules in the liquid state. Here, as in any other spectrum calculations, energies and stationary state wave functions for the system in the absence of a time-dependent r.f. field have first to be calculated. The problem starts with finding the eigenfunctions and eigenvalues of the spin-dependent Hamiltonian of the system given by

$$\begin{aligned} \frac{\mathcal{H}}{\hbar} &= E_0 = B + C \\ &= - \sum_r \gamma_r H_{0r} m_r^0 + \frac{1}{2} \sum_{r \neq s} J_{rs} (\vec{I}_r \cdot \vec{I}_s) \\ &= - \sum_r \omega_r m_r^0 + \frac{1}{2} \sum_{r \neq s} J_{rs} (m_r^0 m_s^0 + m_r^+ m_s^-) \end{aligned} \quad (1)$$

where the various groups of nuclei in the system are denoted by index r , the group r having the spin \vec{I}_r , γ_r is the gyromagnetic ratio of the nuclei and H_{0r} is a constant magnetic field effectively acting upon the group r in the z -direction. The notation

$$\begin{aligned} m_r^0 &= I_{zr} \\ m_r^\pm &= I_{xr} \pm i I_{yr}, \end{aligned}$$

where the operators I_{xr} , I_{yr} and I_{zr} represent the x , y and z components respectively of the spin vector \vec{I}_r has been used here following Bloch (1956). This paper will hereafter be referred to as II. In the Hamiltonian, a coupling invariant against rotation and bilinear in the spin operators has been assumed with coupling constants $J_{rs} = J_{sr}$, independent of the external field.

This spin-spin interaction is the most effective part of the interaction for groups of nuclei within a molecule in the liquid state. The other term 'dipole-dipole interaction' is zero due to rotational motions in liquid.

The case of two groups of nuclei, where the total spin of one group is $\frac{1}{2}$, the exact solution of the problem reduces essentially to a diagonalisation of matrices of maximum order 2×2 . The spectrum for this case has been worked out in detail by Banerjee *et al.* (1954). The two-group system is usually referred to as $A_m B_n$ system, if the groups contain m and n nuclei respectively of the same species, and as $A_m X_n$, if the nuclei in each group are of different kinds with quite different gyromagnetic ratios. For a system AB of two interacting spin $\frac{1}{2}$ nuclei, the widths of the resonance lines have been calculated in II in terms of the longitudinal and transverse relaxation times T_{1r} and T_{2r} respectively exhibited separately by the nuclei $r = s, t$, where s and t are the two groups under the conditions considered by Wangsness and Bloch (1953) in the paper hereafter referred to as I.

For arbitrary number of nuclear groups, but only with equivalent nuclei in each group, perturbation calculations have been done and applied to specific systems by Anderson (1956), Alexander (1958) and various other authors. As reported in Anderson's paper, higher order corrections beyond the second order perturbation calculations gave better agreement with the experiment for some specific cases. Fessenden and Waugh (1959) and Alexander (1960) have analysed the ABC type spectra of some compounds, but they did not derive an explicit expression for the intensities and the frequencies of the various transitions and had to resort to numerical computations to diagonalise the two 3×3 matrices involved in the solution of the present problem. They have, however, evolved certain useful relationships such as the intensity and frequency sum rules which can be applied unambiguously only to cases involving moderately strong coupling. The use of these relationships made in conjunction with the inspection of the observed spectrum for this type of molecules helps to reduce the number of independent parameters (J_s and δ_s) to be evaluated and makes possible the assignment of proper values to them. Further no attempt has been made by these workers to calculate the linewidths for such spectra. Therefore, it is thought worthwhile to find the exact solutions for simple cases of 3 groups of interacting nuclei. We report here the exact solution of the problem of ABC system, without any restriction on the magnitude of the spin coupling relative to chemical shifts.

The method for calculating the linewidths with only the external dipole relaxation, as in Sec. 5 of II, has also been considered for this system in terms

of longitudinal and transverse relaxation times of individual nuclei from the general expression derived in II with strong spin coupling compared to the r.f. field $\vec{H}_1(t)$ and to the effects of relaxation.

2. SPECTRUM CALCULATION

In the system ABC, we have three nuclei s , t and u of spin $\frac{1}{2}$, with Larmor frequencies ω_s , ω_t and ω_u respectively, so that

$$\begin{aligned} E_0 = & -(\omega_s m_s^0 + \omega_t m_t^0 + \omega_u m_u^0) + J_1 \{m_s^0 m_t^0 + \frac{1}{2}(m_s^+ m_t^- \\ & + m_t^+ m_s^-)\} + J_2 \{m_s^0 m_u^0 + \frac{1}{2}(m_s^+ m_u^- + m_u^+ m_s^-)\} \\ & + J_3 \{m_t^0 m_u^0 + \frac{1}{2}(m_t^+ m_u^- + m_u^+ m_t^-)\} \end{aligned} \quad (2)$$

with

$$J_{st} = J_{ts} = J_1$$

$$J_{su} = J_{us} = J_2$$

$$J_{tu} = J_{ut} = J_3$$

We take our initial complete set of kets as the product of eigen kets of individual nuclei without the interaction $|m_s\rangle |m_t\rangle |m_u\rangle$, in the representation where m_r^0 and I_r^2 are diagonal with eigenvalues of $m_r^0 = m_r$, ($r = s, t, u$). We label these kets in short as $|m_s m_t m_u\rangle$. The proper eigen kets for the Hamiltonian given by equation (2) will then be some linear combinations of $|m_s m_t m_u\rangle$ kets. Since here, $\sum m_r^0$ commutes with our total Hamiltonian \mathcal{H} , we can label the proper eigen kets of the system with a number M , the sum of the eigenvalues of m_s^0 , m_t^0 and m_u^0 .

It can be easily seen that the proper kets for $M = \pm 3/2$ can be only $|\frac{1}{2} \frac{1}{2} \frac{1}{2}\rangle$ and $|-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\rangle$ respectively. For $M = \pm \frac{1}{2}$, the eigen states will be linear combinations of the states $|\pm \frac{1}{2}, \pm \frac{1}{2}, \mp \frac{1}{2}\rangle$, $|\pm \frac{1}{2}, \mp \frac{1}{2}, \pm \frac{1}{2}\rangle$ and $|\mp \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}\rangle$. Now, if we write the eigen state

$$|g(M)\rangle = \sum_{m_s m_t m_u} \langle m_s m_t m_u | g(M)\rangle |m_s m_t m_u\rangle, \quad (3)$$

the transformation functions for $M = -3/2$ and $M = +3/2$ can be written as

$$\langle m_s m_t m_u | E(-\frac{3}{2})\rangle = \delta_{m_s, -\frac{1}{2}} \delta_{m_t, -\frac{1}{2}} \delta_{m_u, -\frac{1}{2}} \quad (4)$$

and

$$\langle m_s m_t m_u | E(\frac{3}{2})\rangle = \delta_{m_s, \frac{1}{2}} \delta_{m_t, \frac{1}{2}} \delta_{m_u, \frac{1}{2}} \quad (5)$$

respectively, with the corresponding values of energy in units of \hbar given by,

$$E\left(-\frac{\alpha}{2}\right) = \frac{\alpha}{2} \bar{\omega} + \frac{1}{4} (J_1 + J_2 + J_3) \quad (6)$$

and

$$E\left(\frac{\alpha}{2}\right) = -\frac{\alpha}{2} \omega + \frac{1}{4} (J_1 + J_2 + J_3). \quad (7)$$

Here ω is the average Larmor frequency

$$\frac{\omega_s + \omega_t + \omega_u}{3}$$

of the three nuclei.

For the states with $M = \pm \frac{1}{2}$, we can get the transformation functions by solving the corresponding sets of homogeneous equations

$$\sum_{m'_s m'_t m'_u} \langle m'_s m'_t m'_u | g(M) \rangle \{ \langle m_s m_t m_u | E_0 | m'_s m'_t m'_u \rangle - E \delta_{m_s m'_s} \delta_{m_t m'_t} \delta_{m_u m'_u} \} = 0. \quad (8)$$

Thus the secular determinants, to be solved for $M = \pm \frac{1}{2}$ for getting the eigenvalues E and the transformation functions, are

$$\begin{vmatrix} Y_{\pm} - \frac{J_1 + J_2 + J_3}{4} \mp \frac{\bar{\omega}}{2} - E & \frac{J_3}{2} & \frac{J_2}{2} \\ \frac{J_3}{2} & Y_{2\pm} - \frac{J_1 + J_2 + J_3}{4} \mp \frac{\bar{\omega}}{2} - E & \frac{J_1}{2} \\ \frac{J_2}{2} & \frac{J_1}{2} & Y_{3\pm} - \frac{J_1 + J_2 + J_3}{2} \mp \frac{\bar{\omega}}{2} - E \end{vmatrix} = 0 \quad (9)$$

with

$$\begin{aligned} Y_{1\pm} &= \frac{J_1}{2} \pm \frac{\delta_1 - 2\delta_2}{3} \\ Y_{2\pm} &= \frac{J_2}{2} \pm \frac{\delta_2 - 2\delta_1}{3} \\ Y_{3\pm} &= \frac{J_3}{2} \pm \frac{\delta_1 + \delta_2}{3} \end{aligned} \quad (10)$$

where the chemical shifts δ_1 and δ_2 are given by

$$\delta_1 = \omega_s - \omega_t$$

and

$$\delta_2 = \omega_s - \omega_u.$$

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These determinants are expanded so that the solutions of resulting cubic equations in E for $M = \pm \frac{1}{2}$ give the eigenvalues

$$E_i \left(\pm \frac{1}{2} \right) = \mp \frac{\bar{\omega}}{2} - \frac{1}{12} (J_1 + J_2 + J_3) - \frac{b^\pm}{a^\pm} f_i(\theta^\pm), \quad (11)$$

for $i = 1, 2, 3$. In equation (11),

$$\theta^\pm = \frac{(b^\pm)^2}{(a^\pm)^3}, \quad (12)$$

$$\left. \begin{aligned} f_1(\theta) &= \frac{\left[1 + \sqrt{\frac{4}{27\theta} + 1} \right]^{\frac{1}{3}} + \left[1 - \sqrt{\frac{4}{27\theta} + 1} \right]^{\frac{1}{3}}}{(2\theta)^{\frac{1}{3}}} \\ f_2(\theta) &= -\frac{f_1(\theta)}{2} + \sqrt{\frac{f_1^2(\theta)}{4} - \frac{1}{\theta f_1(\theta)}} \\ f_3(\theta) &= -\frac{f_1(\theta)}{2} - \sqrt{\frac{f_1^2(\theta)}{4} - \frac{1}{\theta f_1(\theta)}} \end{aligned} \right\} \quad (13)$$

with

$$\begin{aligned} a &= -\frac{1}{3} (Y_1^2 + Y_2^2 + Y_3^2 - Y_1 Y_2 - Y_1 Y_3 - Y_2 Y_3) \\ &\quad - \frac{1}{4} (J_1^2 + J_2^2 + J_3^2) \end{aligned} \quad (14)$$

and

$$\begin{aligned} b &= -\frac{2}{27} (Y_1 + Y_2 + Y_3)^3 + \frac{1}{4} (J_1^2 Y_1 + J_2^2 Y_2 + J_3^2 Y_3) \\ &\quad + \frac{1}{3} (Y_1 + Y_2 + Y_3) \{ Y_1 Y_2 + Y_1 Y_3 + Y_2 Y_3 \\ &\quad - \frac{1}{4} (J_1^2 + J_2^2 + J_3^2) \} - Y_1 Y_2 Y_3 - \frac{1}{4} J_1 J_2 J_3. \end{aligned} \quad (15)$$

The functions $f_1(\theta)$, $f_2(\theta)$ and $f_3(\theta)$ are tabulated for a wide range of θ by Salzer (1958). From the expression for 'a', one can easily see that for real values of J_1 , J_2 , J_3 , δ_1 and δ_2 , we will always get the value of 'a' negative and hence the value of θ will always be negative. Further, in our case, since all the roots will be real, θ will have the values such that

$$-\frac{4}{27} < \theta < 0.$$

The orthonormalised eigenvectors corresponding to the characteristic values $E_i (\pm \frac{1}{2})$ of the matrices

$$\begin{bmatrix} Y_1^\pm - \frac{J_1+J_2+J_3}{4} \mp \frac{\bar{\omega}}{2} & \frac{J_3}{2} & \frac{J_2}{2} \\ \frac{J_3}{2} & Y_2^\pm - \frac{J_1+J_2+J_3}{4} \mp \frac{\bar{\omega}}{2} & \frac{J_1}{2} \\ \frac{J_2}{2} & \frac{J_1}{2} & Y_3^\pm - \frac{J_1+J_2+J_3}{4} \mp \frac{\bar{\omega}}{2} \end{bmatrix}$$

can be denoted by

$$\begin{bmatrix} C_{i1}^\pm \\ C_{i2}^\pm \\ C_{i3}^\pm \end{bmatrix}.$$

The explicit values of these in our case are obtained as

$$\begin{bmatrix} C_{i1}^\pm \\ C_{i2}^\pm \\ C_{i3}^\pm \end{bmatrix} = \begin{bmatrix} \eta_{i1}^\pm \{(\eta_{i1}^\pm)^2 + (\eta_{i2}^\pm)^2 + (\eta_{i3}^\pm)^2\}^{-\frac{1}{2}} \\ \eta_{i2}^\pm \{(\eta_{i1}^\pm)^2 + (\eta_{i2}^\pm)^2 + (\eta_{i3}^\pm)^2\}^{-\frac{1}{2}} \\ \eta_{i3}^\pm \{(\eta_{i1}^\pm)^2 + (\eta_{i2}^\pm)^2 + (\eta_{i3}^\pm)^2\}^{-\frac{1}{2}} \end{bmatrix} \quad (16)$$

where

$$\begin{aligned} \eta_{i1}^\pm &= \frac{J_2}{2} \left\{ Y_2^\pm - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^\pm}{a^\pm} f_i(\theta^\pm) \right\} - \frac{J_1 J_3}{4} \\ \eta_{i2}^\pm &= \frac{J_1}{2} \left\{ Y_1^\pm - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^\pm}{a^\pm} f_i(\theta^\pm) \right\} - \frac{J_2 J_3}{4} \\ \eta_{i3}^\pm &= \frac{J_3^2}{4} - \left\{ Y_1^\pm - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^\pm}{a^\pm} f_i(\theta^\pm) \right\} \\ &\quad \times \left\{ Y_2^\pm - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^\pm}{a^\pm} f_i(\theta^\pm) \right\}. \end{aligned} \quad (17)$$

Now the transformation functions for the states with $E(\pm \frac{1}{2})$ can be easily written. They are

$$\begin{aligned} \langle m_s m_t m_u | E_i(+\frac{1}{2}) \rangle &= C_{i1}^+ \delta_{m_s \pm} \delta_{m_t \pm} \delta_{m_u \mp} + C_{i2}^+ \delta_{m_s \pm} \delta_{m_t \mp} \delta_{m_u \pm} \\ &\quad + C_{i3}^+ \delta_{m_s \mp} \delta_{m_t \pm} \delta_{m_u \pm} \end{aligned} \quad (18)$$

and

$$\begin{aligned} \langle m_s m_t m_u | E_i(-\frac{1}{2}) \rangle &= C_{i1}^- \delta_{m_s \mp} \delta_{m_t \mp} \delta_{m_u \pm} + C_{i2}^- \delta_{m_s \mp} \delta_{m_t \pm} \delta_{m_u \mp} \\ &\quad + C_{i3}^- \delta_{m_s \pm} \delta_{m_t \mp} \delta_{m_u \mp}. \end{aligned} \quad (19)$$

The magnetic dipole transitions due to a weak r.f. field are possible only between the states

$$|E(-\frac{3}{2})\rangle, |E_i(-\frac{1}{2})\rangle; |E_i(-\frac{1}{2})\rangle, |E_j(+\frac{1}{2})\rangle$$

and

$$|E_j(+\frac{1}{2})\rangle, |E(+\frac{3}{2})\rangle$$

where $i, j = 1, 2, 3$. The relative intensities of these 15 lines, for the transitions between different allowed pairs of states $|g\rangle, |g'\rangle$, can be calculated by evaluating the quantities

$$|g| \sum_r I_{xr} |g'\rangle|^2 \tag{20}$$

In Table I, we give the relative intensities for allowed transitions.

TABLE I

Transitions	No. of lines	Frequency ν , in cycles/sec.	Relative intensities
$E(-\frac{3}{2}) \rightarrow E_i(-\frac{1}{2})$ $i = 1, 2, 3$	3	$\frac{1}{2\pi} \left[\bar{\omega} + \frac{1}{3}(J_1 + J_2 + J_3) + \frac{b^-}{a^-} f_i(\theta^-) \right]$	$(C_{i1} + C_{i2} + C_{i3})^2$
$E_i(-\frac{1}{2}) \rightarrow E_j(\frac{1}{2})$ $i, j = 1, 2, 3$	9	$\frac{1}{2\pi} \left[\bar{\omega} - \frac{b^-}{a^-} f_i(\theta^-) + \frac{b^+}{a^+} f_j(\theta^+) \right]$	$(C_{j2}^+ C_{i1}^- + C_{j1}^+ C_{i2}^- + C_{j3}^+ C_{i1}^- + C_{j1}^+ C_{i3}^- + C_{j3}^+ C_{i2}^- + C_{j2}^+ C_{i3}^-)^2$
$E_j(\frac{1}{2}) \rightarrow E(\frac{3}{2})$ $j = 1, 2, 3$	3	$\frac{1}{2\pi} \left[\bar{\omega} - \frac{1}{3}(J_1 + J_2 + J_3) - \frac{b^+}{a^+} f_j(\theta^+) \right]$	$(C_{j1} + C_{j2} + C_{j3})^2$

3. LINEWIDTHS

Bloch has explicitly given the general expression for the linewidths in Sec. 5 of II, where he has assumed a spin-spin coupling term C strong in comparison to the r.f. field $\vec{H}_1(t)$ and to the effects of relaxation (considering only the external dipole relaxation). Following the same notations and assuming the isotropy of molecular surroundings, which is a good

approximation for molecules in liquid state, Bloch's expression for the linewidth for the transition between the stationary states b and a , is given by

$$\Gamma_{ab} = \sum_p \Gamma^p_{aa} + \Gamma^p_{bb} - 2\Gamma^0_{ab} \quad (21)$$

with

$$\begin{aligned} \Gamma^p_{gg'} = \sum_r \phi_r^p \{ & \langle g | I_r^0 | g+p \rangle \langle g'+p | I_r^0 | g' \rangle \\ & + \frac{1}{2} \langle g | I_r^{-1} | g+p \rangle \langle g'+p | I_r^{+1} | g' \rangle \\ & + \frac{1}{2} \langle g | I_r^{+1} | g+p \rangle \langle g'+p | I_r^{-1} | g' \rangle \} \end{aligned} \quad (22)$$

where

$$I_r^0 = m_r^0,$$

$$I_r^{\pm 1} = m_r^{\pm},$$

$|g\rangle$ is one of the stationary eigen kets for the system and the coefficients ϕ_r^p , characteristics of molecular surroundings, are given by equation (5.25) with (5.26) and (5.27) of II.

For calculating the linewidths of transition spectrum in our case, we neglect the slight variations of the coefficients ϕ_r^p due to chemical shifts and spin couplings, so that

$$\phi_r^{E_i(3/2)-E_i(-1/2)} = \phi_r^{E_i(-1/2)-E_i(+1/2)} = \phi_r^{E_i(1/2)-E_i(3/2)} = \phi_r^{\bar{\omega}}$$

and

$$\phi_r^{E_i(1/2)-E_i(1/2)} = \phi_r^{E_i(-1/2)-E_i(-1/2)} = \phi_r^0$$

for

$$i, j = 1, 2, 3.$$

Now, replacing $2\phi'_{11}$ and ϕ^0_{11} of equations (5.3) and (5.4) of I, by $\phi_r^{-\bar{\omega}}$ and ϕ_r^0 , we get

$$\phi_r^{-\bar{\omega}} = \frac{1}{(1 + e^{-K}) T_{1r}} \quad (23)$$

$$\phi_r^0 = \frac{1}{T_{2r}} - \frac{1}{2T_{1r}} \quad (24)$$

where

$$K = \frac{\hbar\bar{\omega}}{kT},$$

k being the Boltzmann constant and T the absolute temperature of the system. Since

$$\phi_r^{\bar{\omega}} = e^{-k\phi_r^{-\bar{\omega}}},$$

all the coefficients $\phi_r^{\mathcal{P}}$ for evaluating $\Gamma_{gg}^{\mathcal{P}}$ can be known approximately in terms of the longitudinal and transverse relaxation times T_{1r} and T_{2r} which are exhibited separately by the nuclei under the conditions considered in I.

We can easily verify that for our system, we have only the following non-zero matrix elements for I_r^0 and I_r^{\pm} :—

$$\begin{aligned} \langle E_i(-\frac{1}{2}) | I_s' | E(-\frac{3}{2}) \rangle &= \langle E(-\frac{3}{2}) | I_s^{-1} | E_i(-\frac{1}{2}) \rangle = C_{i3}^- \\ \langle E_i(-\frac{1}{2}) | I_t' | E(-\frac{3}{2}) \rangle &= \langle E(-\frac{3}{2}) | I_t^{-1} | E_i(-\frac{1}{2}) \rangle = C_{i2}^- \\ \langle E_i(-\frac{1}{2}) | I_u' | E(-\frac{3}{2}) \rangle &= \langle E(-\frac{3}{2}) | I_u^{-1} | E_i(-\frac{1}{2}) \rangle = C_{i1}^- \\ \langle E_i(-\frac{1}{2}) | I_s^{-1} | E_j(\frac{1}{2}) \rangle &= \langle E_j(\frac{1}{2}) | I_s^1 | E_i(-\frac{1}{2}) \rangle = C_{j2}^+ C_{i1}^- \\ &\quad + C_{j1}^+ C_{i2}^- \\ \langle E_i(-\frac{1}{2}) | I_t^{-1} | E_j(\frac{1}{2}) \rangle &= \langle E_j(\frac{1}{2}) | I_t^1 | E_i(-\frac{1}{2}) \rangle = C_{j3}^+ C_{i1}^- \\ &\quad + C_{j1}^+ C_{i2}^- \\ \langle E_i(-\frac{1}{2}) | I_u^{-1} | E_j(\frac{1}{2}) \rangle &= \langle E_j(\frac{1}{2}) | I_u^1 | E_i(-\frac{1}{2}) \rangle = C_{j3}^+ C_{i2} \\ &\quad + C_{j2}^+ C_{i3}^- \\ \langle E_j(\frac{1}{2}) | I_s^{-1} | E(\frac{3}{2}) \rangle &= \langle E(\frac{3}{2}) | I_s^1 | E_j(\frac{1}{2}) \rangle = C_{j3}^+ \\ \langle E_j(\frac{1}{2}) | I_t^{-1} | E(\frac{3}{2}) \rangle &= \langle E(\frac{3}{2}) | I_t^1 | E_j(\frac{1}{2}) \rangle = C_{j2}^+ \\ \langle E_j(\frac{1}{2}) | I_u^{-1} | E(\frac{3}{2}) \rangle &= \langle E(\frac{3}{2}) | I_u^1 | E_j(\frac{1}{2}) \rangle = C_{j1}^+ \\ \langle E(\frac{3}{2}) | I_r^0 | E(\frac{3}{2}) \rangle &= -\frac{1}{2}, \langle E(-\frac{3}{2}) | I_r^0 | E(-\frac{3}{2}) \rangle = \frac{1}{2} \\ &\quad \text{for } r = s, t, u \end{aligned}$$

$$\begin{aligned} \langle E_i(\pm \frac{1}{2}) | I_s^0 | E_j(\pm \frac{1}{2}) \rangle &= \pm \frac{1}{2} [C_{i1}^{\pm} C_{j1}^{\pm} + C_{i2}^{\pm} C_{j2}^{\pm} \\ &\quad \mp C_{i3}^{\pm} C_{j3}^{\pm}] \\ \langle E_i(\pm \frac{1}{2}) | I_t^0 | E_j(\pm \frac{1}{2}) \rangle &= \pm \frac{1}{2} [C_{i1}^{\pm} C_{j1}^{\pm} \mp C_{i2}^{\pm} C_{j2}^{\pm} + \\ &\quad C_{i3}^{\pm} C_{j3}^{\pm}] \\ \langle E_i(\pm \frac{1}{2}) | I_u^0 | E_j(\pm \frac{1}{2}) \rangle &= \pm \frac{1}{2} [\mp C_{i1}^{\pm} C_{j1}^{\pm} + C_{i2}^{\pm} C_{j2}^{\pm} \\ &\quad + C_{i3}^{\pm} C_{j3}^{\pm}]. \end{aligned}$$

With these expressions, $\Gamma_{gg}^{\mathcal{P}}$, and Γ_{gg}^0 , can be calculated for all g and g' from the equation (22). Finally equation (21) directly gives the linewidths for

the resonance lines. Since the analytical expressions for these are very complicated, they are not reported here, but it is clear that for any set of values for J_1 , J_2 , J_3 , δ_1 and δ_2 we can always calculate the linewidths by the procedure outlined above.

4. DISCUSSION

To analyse the experimental results of the system ABC, one has to proceed by a method of trial and error and assign some of the observed transitions to definite initial and final states by a clever guess, and then deduce from the values of their measured frequencies and intensities, the relevant constants J_1 , J_2 , J_3 , $\bar{\omega}$, δ_1 and δ_2 , using Table I. The relationships evolved by Fessenden and Waugh when used in conjunction with these calculations will reduce the number of independent parameters. From this set of values, one can find out the relative intensities and frequencies of all other transitions theoretically and try to see that all the transitions are described together in a self-consistent manner. Thus even if all the 15 lines are not well resolved in the experimental data it is possible to give unique solution for J_1 , J_2 , J_3 , $\bar{\omega}$, δ_1 and δ_2 .

There has so far been no attempt to verify the theoretical expressions for the linewidths even for the system AB of spin $\frac{1}{2}$ nuclei. This is probably due to the fact that the linewidths in question may be very small. It is hoped that as the precision in the experimental techniques of high resolution nuclear magnetic resonance spectroscopy increases, it may be possible to compare the results of linewidths for not only the system AB, but also for the more complicated system ABC and to get more information about the mechanism of relaxation.

The n.m.r. spectra of some trisubstituted benzenes have been analysed in our laboratory on the basis of these equations and the results will soon be communicated for publication.

SUMMARY

The exact solution for the splitting up of nuclear resonance lines due to J couplings of spins between three like nuclei of spin $\frac{1}{2}$ with relative chemical shifts is worked out. Here no specific assumption about the magnitude of the coupling constants compared to the chemical shifts is made. It is shown how the linewidths of all the resonance lines can be calculated for the present case from the general expressions derived in Bloch's dynamical theory of nuclear induction with external dipole relaxation mechanism.

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