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Effect of chemical shift and J-coupling on nuclear resonance line-shape

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The splitting up of nuclear resonance lines due to J-coupling has been dealt with in detail for both the cases $J \sim \delta$ and $J \ll \delta$. It is shown that for $J \sim \delta$, appreciable departures occur from Gutowsky's rule in both the intensities and frequencies of the components, particularly the former. The exact line-patterns in several important cases are given.

Introduction

The J-splitting of nuclear magnetic resonance lines has been the subject of extensive experiments by a number of observers, e.g. Gutowsky, McCall & Slichter (1953) using the slow-passage technique and Hahn & Maxwell (1952) using the transient spin-echo technique. This splitting has been found by Gutowsky *et al.* (1953) to have the following distinctive features which distinguish it from the splittings due to spin-spin interaction and chemical shift:

(1) The splitting does not depend upon the temperature and state of aggregation of the sample under study. (Thus it is unaltered both in the gaseous and liquid states, as observed by Gutowsky *et al.* with PF_5.)

(2) The splitting is independent of the applied field.

(3) It appears only when there are two non-equivalent groups of magnetic nuclei in the molecule, where, by non-equivalent, we mean either different nuclei or same nuclei in structurally different positions so that there is a chemical shift between them.

(4) If there are n_A and n_B nuclei respectively in the two interacting groups A and B, and if the spins of the individual nuclei in A and B be I_A and I_B respectively, so that they have maximum spin-values $n_A I_A$ and $n_B I_B$ respectively, then it is found that

(a) The total number of fine components in the resonance pattern due to B is $2n_A I_A + 1$ and in A it is $2n_B I_B + 1$.

(b) The intensity pattern for each group is symmetrical about the centre, falling off outwards, and if the components be numbered from one extreme of the pattern, then the intensities of the different components is proportional to the binomial coefficients $\binom{n_B}{r-1}$ for A and $\binom{n_A}{r-1}$ for B.

(c) The frequency separations between the fine components of each group are equal and in units of magnetic field for two groups A and B these are in the ratio given by

$$\frac{\delta H_A}{\delta H_B} = \frac{\gamma_B}{\gamma_A}. \tag{1}$$

When we consider J-coupling between similar nuclei in different structural environments, $\gamma_B = \gamma_A$ and we have

$$\delta H_A = \delta H_B. \tag{2}$$

Gutowsky *et al.* (1953) have explained these experimental observations using a first-order perturbation treatment. This treatment is valid for J-coupling between dissimilar nuclei, and between similar nuclei, only when it is weak compared to the chemical shift between them. We have shown in this paper that a more vigorous treatment is possible for J-coupling between like nuclei, which holds even when it is comparable with the chemical shift. In the special case when the J-coupling is weak, our results reduce to those of Gutowsky *et al.* We shall first outline briefly the treatment of Gutowsky *et al.* before passing on to ours.

Outline of previous theoretical treatments

Gutowsky *et al.* explained their experimental observations by assuming a 'dot' coupling interaction-Hamiltonian between the interacting groups of nuclei giving rise to the pattern observed. Such a form for the interaction-Hamiltonian was suggested first by Hahn *et al.* (1951) and later justified by Ramsey & Purcell (1952, 1953). Thus, the Hamiltonian of the spin system consisting of the two groups can be written as

$$\mathscr{H} = -\hbar[\gamma_A S_{Az}(H_z + h_A) + \gamma_B S_{Bz}(H_z + h_B)] - J\hbar \mathbf{S}_A . \mathbf{S}_B, \tag{3}$$

where γ_A refers to the magnetogyric ratio of the nuclei in group A and γ_B to the magnetogyric ratio of the nuclei in B, h_A and h_B referring to the local fields at A and B respectively. Here S_A and S_B can take up all the values $n_A I_A, n_A I_A - 1, \ldots,$ $\frac{1}{2}$ or 0 and $n_B I_B, n_B I_B - 1, \ldots, \frac{1}{2}$ or 0 respectively. But Gutowsky's treatment was mainly confined to a coupling between dissimilar nuclei. He pointed out that in these cases, as also for the cases of coupling between similar nuclei in non-equivalent positions where $J \ll \gamma(h_A - h_B)$, we could neglect the part $J(S_{Ax}S_{Bx} + S_{Ay}S_{By})$ of the dot-coupling interaction-Hamiltonian as far as the first-order perturbation approximation was concerned. With this restriction he found agreement between the theory and his experimental results to the order for accuracy that he could attain with his apparatus (viz. 3 % for intensity measurements and about 10 cycles for the splitting frequencies).

But Hahn & Maxwell (1952), in their paper dealing with spin-echo modulations due to chemical shift and J-coupling, have pointed out the necessity of retaining the term

$$J(S_{Ax}S_{Bx} + S_{Ay}S_{By})$$

for coupling between two groups where $\gamma_A = \gamma_B$, and he has given the Zeeman level diagram and frequencies to be expected for a coupling between two groups of nuclei A and B where $n_A = 2$ and $n_B = 1$, and shows that a serious departure from Gutowsky's rule occurs in the case, when $J \sim \delta$ with regard to the splittings, intensity and the number of fine lines in each split-up component. His treatment for deducing the frequencies and intensities of the lines is not very clear from his paper, as it deals with the effects of J-coupling on spin-echoes. It is presumably as follows. He neglects the J-coupling and the chemical shift in the presence of the *rf*-field. The zero-order states are now the eigen-states of the Hamiltonian

$$\mathscr{H}_0 = -\hbar\gamma(S_{Az}H_z + S_{Bz}H_z) = -\hbar\gamma H_z S_z, \tag{4}$$

where $$S_z = S_{Az} + S_{Bz}.$$

The eigen-states are now the rotational group states (i.e. eigen-states of $\mathbf{S}^2$ and $\mathbf{S}_z$), where

$$\mathbf{S} = \mathbf{S}_A + \mathbf{S}_B. \tag{5}$$

These we shall call the J-states.* The Rabi–Bloch (1945) coefficients for transitions between these states (given by his equation (5) for $S_A = S_B = \frac{1}{2}$), may be denoted by $R^S_{MM'}$. He now takes into account the fact that the zero-order states are not actually the J-states but a mixture of these, being eigen-kets of the total Hamiltonian

$$\mathscr{H}_{J\delta} = -\gamma\hbar[S_{Az}(H_z + h_A) + S_{Bz}(H_z + h_B)] - J\hbar\mathbf{S}_A.\mathbf{S}_B. \tag{6}$$

Using the variation principle we obtain the eigen-states of the total $\mathscr{H}_{J\delta}$ as a mixture of the J-states, the matrix causing the mixing being denoted by A. Thus, the transformed matrix giving the transition probabilities between the δJ-states is easily seen to be given by

$$AR^S A^{-1}.$$

But even in following this procedure for the calculation of the transition probabilities for $n_A = 1$ and $n_B = 1$, we find a discrepancy between our results and Hahn's in the intensities of the different lines that will be observed in the 'slow-passage' experiment. This point will be clear when our Zeeman level diagram and the splittings of the resonance lines in this case are subsequently presented.

In our treatment we use the products of the rotational group kets $|S_A m_A\rangle|S_B m_B\rangle$ for the two groups as our basis. These will be seen later to correspond to the eigen-kets of the Hamiltonian corresponding to the form to which $\mathscr{H}_{J\delta}$ reduces when $J = 0$, viz.

$$\mathscr{H}_{\delta} = -\gamma\hbar[S_{Az}(H_z + h_A) + S_{Bz}(H_z + h_B)]. \tag{7}$$

This method has certain advantages which will be evident as we discuss our procedure. We have given a general method of handling the case of n_A nuclei in group A and n_B in group B, and have also given explicit generalized expressions for the Zeeman level energies and eigen-kets ($J\delta$ kets) of the total Hamiltonian for $n_B = 1$ and n_A = any value. This enables us to write down generalized expressions for the frequencies and intensities of the different lines to be expected for both $J \sim \delta$ and $J \ll \delta$. We shall now discuss our procedure.

Our treatment: general case—n_A and n_B arbitrary

The Hamiltonian (6) can be written in the alternative form

$$\mathscr{H}_{J\delta} = -\hbar\{(\omega + \tfrac{1}{2}\delta)S_z + J\mathbf{S}_A.\mathbf{S}_B - \delta S_{Bz}\}, \tag{8}$$

where

$$\left.\begin{aligned} \omega &= \gamma\left(H_z + \frac{h_A + h_B}{2}\right) = \frac{\omega_A + \omega_B}{2}, \\ \delta &= \gamma(h_A - h_B), \\ S_z &= S_{Az} + S_{Bz}, \end{aligned}\right\} \tag{9}$$

and

$$\left.\begin{aligned} \omega_A &= \omega + \tfrac{1}{2}\delta = \gamma(H_z + h_A), \\ \omega_B &= \omega - \tfrac{1}{2}\delta = \gamma(H_z + h_B). \end{aligned}\right\}$$

* This terminology is used because these are also the eigen-states in the presence of J-coupling alone, without chemical shift, i.e. of the Hamiltonian

$$\mathscr{H}_J = -\hbar\gamma H_z S_z - \hbar J\mathbf{S}_A.\mathbf{S}_B.$$

The Hamiltonian is composed of two parts which commute with each other, viz.

$$(a) \quad S_z, \text{ with eigen-value } M = m_A + m_B,$$

$$(b) \quad \Sigma = J\mathbf{S}_A.\mathbf{S}_B - \delta S_{Bz},$$

whose eigen-value may be denoted by σ.

The eigen-kets of $\mathscr{H}_{J\delta}$ may therefore be labelled by two eigen-values M and σ, i.e. $|M\sigma\rangle$, and will be called the $J\delta$-kets. When J-coupling is absent, the total system is composed of two non-interacting groups A and B. The eigen-kets are then simply the products of the eigen-kets $|S_A m_A\rangle$ of group A and $|S_B m_B\rangle$ of group B. Of course, if there are n_A spins in group A and n_B in group B as mentioned before, the different possible values of S_A that may occur are $n_A I_A, n_A I_A - 1, \ldots, \frac{1}{2}$ or 0 and of S_B are $n_B I_B, n_B I_B - 1, \ldots, \frac{1}{2}$ or 0. Also it can be shown from group-theoretical considerations that the number of ways in which a spin-value S may be realized out of an assembly of N spins $\frac{1}{2}$ is

$$\nu(S) = \binom{N}{\frac{1}{2}N - S} - \binom{N}{\frac{1}{2}N - S - 1}. \tag{10}$$

But we shall first make generalized considerations for specific values of S_A and S_B, then take into account the different possible values of S_A and S_B and the corresponding weight factors $\nu(S_A)$ and $\nu(S_B)$ in calculating the frequencies and intensities involved in the different transitions. The product kets $|S_A m_A\rangle |S_B m_B\rangle$ may then be denoted by $|M, m_B\rangle$ (S_z being diagonal also in the product space), S_A and S_B being now omitted for brevity. These kets will be termed the δ-kets. As S_z is diagonal in both the systems, the $J\delta$ kets $|M\sigma\rangle$ will, in general, be linear combinations of the different δ-kets $|Mm_B\rangle$. The general unitary transformation matrix

$$A = \| \langle Mm_B | M\sigma \rangle \|$$

will have the following structure: there will be square submatrices placed along the principal diagonal, each of these being associated with a particular value of M; the other elements of A will be zero. The total number of possible M-values is $2(S_A + S_B) + 1$, M varying from $(S_A + S_B)$ to $-(S_A + S_B)$. Regarding the dimensions $p_{|M|}$ of the submatrices we have

$$|M| \geqslant |S_A - S_B|, \quad p_{|M|} = S_A + S_B - |M| + 1,$$

$$|M| < |S_A - S_B|, \quad p_{|M|} = 2S_B + 1.$$

The submatrices for the extremal M-values, viz. $(S_A + S_B)$ and $-(S_A + S_B)$, will thus be of dimension unity, the $J\delta$-kets corresponding to these being simply equal to the corresponding δ-kets. The matrix elements $\langle M\sigma | M, m_B\rangle$ can be determined as a solution of the set of equations

$$\sum_{m_{B'}} \langle M, m_{B'} | M\sigma \rangle \{ \langle Mm_B | \mathscr{H} | Mm_{B'} \rangle - E\delta_{m_B, m_{B'}} \} = 0, \tag{12}$$

together with the unitary property of matrix A. In order that (12) may have non-trivial solutions, the equation

$$\det \{ \langle Mm_B | \mathscr{H} - E | Mm_{B'} \rangle = 0 \tag{13}$$

must be satisfied. This equation yields the energy-values E corresponding to the $J\delta$-states. The explicit expression for $\langle Mm_B \mid \mathscr{H}-E \mid Mm_{B'}\rangle$ is

$$\langle Mm_B \mid \mathscr{H}-E \mid Mm_{B'}\rangle = [-\hbar\{(\omega+\tfrac{1}{2}\delta)M+Jm_B(M-m_B)-\delta m_B\}-E]\,\delta_{m_Bm_{B'}} - J\hbar[(S_B+\tfrac{1}{2})^2-(m_{B'}\pm\tfrac{1}{2})^2]^{\frac{1}{2}}[(S_A+\tfrac{1}{2})^2-(M-m_{B'}\pm\tfrac{1}{2})^2]^{\frac{1}{2}}\,\delta_{m_B,m_{B'}\pm1}. \quad (14)$$

Using the energy-values obtained by a solution of (13), we get from (12) the elements $\langle Mm_B \mid M\sigma\rangle$ of the matrix A. In most of the usual cases, $J \ll \delta$, i.e. the J-coupling is weak and the $J\delta$-kets are very close to the δ-kets; reducing exactly to the δ-kets in the limit $J \to 0$; this one of the advantages of our method over Hahn's.

When S_A and S_B are greater than $\frac{1}{2}$, the determinantal equations are of the pth degree with $p > 2$ and become too difficult to solve. But when either S_A or $S_B = \frac{1}{2}$, the determinantal equations are just of the second degree and are amenable to further simplification. We shall now consider these in some detail.

Case of $n_B = 1$. The subdeterminant equation (13) for a certain M-value now reduces to

$$\begin{vmatrix} -\hbar\left\{(\omega+\tfrac{1}{2}\delta)M+\tfrac{1}{2}J(M-\tfrac{1}{2})-\tfrac{1}{2}\delta+\dfrac{E}{\hbar}\right\} & -\tfrac{1}{2}J\hbar[(S_A+\tfrac{1}{2})^2-M^2]^{\frac{1}{2}} \\ -\tfrac{1}{2}J\hbar[(S_A+\tfrac{1}{2})^2-M^2]^{\frac{1}{2}} & -\hbar\left\{(\omega+\tfrac{1}{2}\delta)M-\tfrac{1}{2}J(M+\tfrac{1}{2})+\tfrac{1}{2}\delta+\dfrac{E}{\hbar}\right\} \end{vmatrix} = 0, \quad (15)$$

from which we get

$$E_M = \hbar[-M(\omega+\tfrac{1}{2}\delta)+\tfrac{1}{4}J \pm \tfrac{1}{2}\sqrt{(\delta_M^2+J_M^2)}], \quad (16)$$

where
$$\delta_M = \delta - JM,$$
and
$$J_M = J[(S_A+\tfrac{1}{2})^2-M^2]^{\frac{1}{2}}. \quad (17)$$

Thus, the eigen-values σ of Σ are given by

$$\sigma = \tfrac{1}{4}J\hbar \pm \tfrac{1}{2}\hbar[\delta_M^2+J_M^2]^{\frac{1}{2}}. \quad (18)$$

It is now convenient to introduce the parameter λ which distinguishes the above two eigen-values σ of Σ. λ can take the values ± 1, so that we can characterize the $J\delta$-kets also by $\mid M\lambda\rangle$. We thus get

$$E_{M,\lambda} = -\hbar M(\omega+\tfrac{1}{2}\delta)+\tfrac{1}{4}J\hbar+\tfrac{1}{2}\lambda\hbar[\delta_M^2+J_M^2]^{\frac{1}{2}}, \quad (19)$$

and from (12) we then get the matrix elements of A connecting δ-kets with the $J\delta$-kets as

$$\langle M, m_B \mid M, \lambda\rangle = \frac{1-2m_BQ(M,\lambda)}{[2\{1+Q^2(M,\lambda)\}]^{\frac{1}{2}}},$$
where
$$Q(M,\lambda) = \frac{-J_M-\lambda[\delta_M^2+J_M^2]^{\frac{1}{2}}}{\delta_M}. \quad (20)$$

The unitary property follows from the relations

$$Q(M,1)\,Q(M,-1) = -1$$
and
$$\frac{Q^n(M,1)}{1+Q^2(M,1)}+\frac{Q^n(M,-1)}{1+Q^2(M,-1)} = \frac{1+(-)^n}{2}. \quad (21)$$

The general expression for the frequency of the line $(M, \lambda \rightarrow M+1, \lambda')$ is

$$\omega_{M,\lambda,\lambda'} = \omega + \tfrac{1}{2}\delta + \tfrac{1}{2}\{\lambda \sqrt{(\delta_M^2 + J_M^2)} - \lambda' \sqrt{(\delta_{M+1}^2 + J_{M+1}^2)}\}. \tag{22}$$

Regarding the number of lines, it may be seen that between each pair of $M\lambda$ levels corresponding to two successive values (in keeping with selection rule $\Delta M = \pm 1$) there can be four transitions corresponding to $(\lambda = \pm 1) \rightarrow (\lambda' = \pm 1)$; but for the extremal M-values, viz. $|M| = S_A + \frac{1}{2}$, it may be shown that $J_M = 0$, as a consequence of which it may be seen from (20) that there is only one level corresponding to each of these extremal values. This is also evident from the fact that the dimension of the submatrix of A, corresponding to this value of $|M|$, viz. $p_{|M|=S_A+\frac{1}{2}} = 1$. Thus there can only be two transitions from these extremal levels, so that for a particular value the total number of lines is easily seen to be

$$4(2S_A - 1) + 4 = 8S_A. \tag{23}$$

The different possible values of S_A for n_A spin $\frac{1}{2}$ nuclei in group is $n_{\frac{1}{2}A}, n_{\frac{1}{2}A} - 1, \ldots, 0$ or $\frac{1}{2}$ according as n_A is even or odd, the total number of lines that will be obtained with $n_B = 1$ and n_A some finite value is therefore

$$N = (n_A + 1)^2. \tag{24}$$

This is justified because, from (22), the frequency of a line is seen to depend both on M, λ, λ' as well as S_A, so that the lines from different S_A-values are distinct. Thus, there is a complete violation of the Gutowsky rule regarding the number of lines. Regarding the intensity of a certain $M, \lambda \rightarrow M+1, \lambda'$ line, it is seen that the intensity is proportional to the square of the matrix elements of

$$A(R^{S_A} \times R^{\frac{1}{2}})\, A^{-1} \tag{25}$$

(cf. Appendix), i.e. to

$$\Sigma \langle M+1, \lambda' | M+1, m_B \rangle \langle M+1-m_B | R^{S_A} | M-m_{B'} \rangle \langle m_B | R^{\frac{1}{2}} | m_{B'} \rangle \langle M, m_{B'} | M, \lambda \rangle, \tag{26}$$

where the matrices R are those defined by Schwinger (1937) and Rabi & Bloch (1945), but in which the terms higher than the first order in $\phi = t_\omega \omega_1$ are neglected. Of course, remembering that in a group of n_A spins $\frac{1}{2}$ the number of ways of realizing S_A is given by (10), the intensity of each line will further have to be weighted by the factor $\nu(S_A)$ depending on the value from which it arises.

It is thus clear that there is complete violation in number of lines, frequency and intensity from the Gutowsky experimental rules for $J \sim \delta$. To emphasize the departures we have plotted in figure 8 the different lines and their intensity for

$$n_A = 2, \quad n_B = 1 \quad \text{with} \quad J \sim \tfrac{1}{2}\delta \sim 20 \text{ c/s}.$$

But in most cases $J/\delta < 0{\cdot}1$, and the nature of splitting and intensity pattern in such cases is considered in the subsequent section.

Case of $J \ll \delta$. This case corresponds more closely to that dealt with by Gutowsky *et al.* (1953), but although there is fairly close agreement with the Gutowsky rule

(1951) now for the number and splitting of the lines, the intensities will be still seen to need some correction.

In the extreme case, viz. $J = 0$, the δJ-kets are seen from (20) to coincide with the δ-kets which are characterized by $|M, m_B\rangle$, i.e. $|M, \pm\frac{1}{2}\rangle$, there being two δ-kets for each value of M characterized by the two possible values of $m_B = \pm\frac{1}{2}$. Now when we are close to the limit, i.e. $J \ll \delta$, we have from (20),

$$\left.\begin{aligned} \langle M, m_B \,|\, M, \lambda = 2m_B\rangle &\sim 1, \\ \langle M, m_B \,|\, M, \lambda = -2m_B\rangle &\sim m_B \frac{J_M}{\delta}, \end{aligned}\right\} \tag{27}$$

i.e. the contribution from the $|M, -\frac{1}{2}\lambda\rangle$ state is proportional to J_M/δ. So, we can say that the $J\delta$-kets in this condition are still nearly characterized by the two possible values of m_B. This idea is very useful in the following considerations.

From figure 1 we see that the transitions in λ given by a, b, c and d have in this approximation the following correspondence with the transitions in m_B, viz.

transition in λ	line	transition in m_B and m_A
$\Delta\lambda = 0$	(a) and (b)	$\Delta m_B = 0$, $\Delta m_A = 1$
$\Delta\lambda = 2$	(c)	$\Delta m_B = 1$, $\Delta m_A = 0$
$\Delta\lambda = -2$	(d)	$\Delta m_B = -1$, $\Delta m_A = 2$

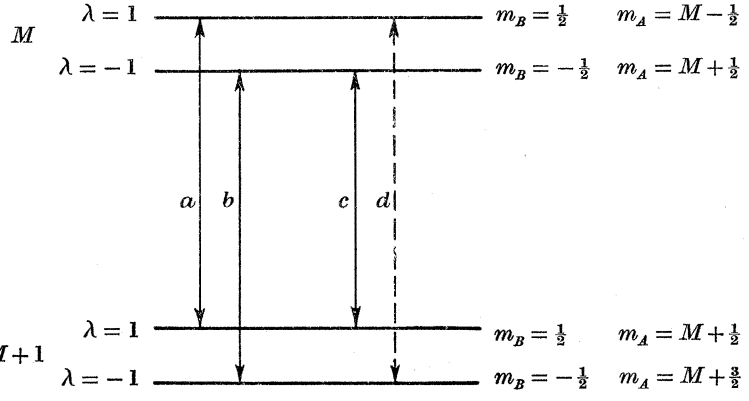


FIGURE 1. Lines originating from transitions between two adjacent M levels.

From (22) we have the frequencies of the lines under the approximation $J \ll \delta$ given by (denoting $\lambda' - \lambda$ by $\Delta\lambda$),

$$\omega_{M,\lambda\lambda'} = \omega + \tfrac{1}{2}\delta(1 - \Delta\lambda) + \tfrac{1}{2}J[\Delta\lambda(M+1) + \lambda]. \tag{28}$$

For $\Delta\lambda = 0$, the lines are

$$\omega_{M,\lambda,\lambda} = \omega + \tfrac{1}{2}\delta + \tfrac{1}{2}J[\lambda + 2(M+1)] = \omega - \tfrac{1}{2}\delta + m_A J, \tag{29}$$

giving a doublet at $\omega+\frac{1}{2}\delta$, corresponding to $m_B=\pm\frac{1}{2}$ and for $\Delta\lambda=2$, the lines are

$$\omega_{M,\lambda,\lambda+2}=\omega-\tfrac{1}{2}\delta+\tfrac{1}{2}J[[\lambda+2(M+1)]=\omega-\tfrac{1}{2}\delta+m_AJ, \tag{30}$$

giving a multiplet at $\omega-\frac{1}{2}\delta$ corresponding to the $2S_A+1$ values of m_A. Remembering that $\omega_A=\omega+\frac{1}{2}\delta$ and $\omega_B=\omega-\frac{1}{2}\delta$, these frequencies are seen to agree with those deduced by Gutowsky from simplified considerations depending only on the m-values of the other group. But as we shall see presently the intensities still need a correction. For $\Delta\lambda=-2$, the lines are

$$\omega_{M,\lambda,\lambda-2}=\omega+\tfrac{3}{2}\delta+\tfrac{1}{2}J[\lambda-2(M+1)], \tag{31}$$

leading to a group of lines at $\omega+\frac{3}{2}\delta$. The intensities of these lines will presently be shown to be small in the approximation $J\ll\delta$.

Thus, we have for either of the lines (a), (b), (c) and (d) illustrated in figure 2, the general expression

$$\sum_{S_A}\nu(S_A)\sum_{M}|\langle M+1,\lambda'\,|\,A(R^{S_A}\times R^{\frac{1}{2}})\,A^{-1}\,|\,M\lambda\rangle|^2, \tag{32}$$

$\nu(S_A)$ being given by equation (10), the summations over S_A and M extending over all their possible values which can contribute to the intensity of the line in question. Using this relation and (20), we have for the doublets (a) and (b), at $\omega+\frac{1}{2}\delta$, retaining only the first power of ϕ in the Rabi–Bloch matrix elements, and the first power of J/δ:

$$I_{(a)}=\sum_{S_A=0\text{ or }\frac{1}{2}}^{n_{\frac{1}{2}A}}\nu(S_A)\sum_{M=-(S_A-\frac{1}{2})}^{S_A-\frac{1}{2}}\left|\langle M+\tfrac{1}{2},\tfrac{1}{2}\,|\,R\,|\,M-\tfrac{1}{2},\tfrac{1}{2}\rangle-\frac{J_M}{2\delta}\langle M+\tfrac{1}{2},\tfrac{1}{2}\,|\,R\,|\,M+\tfrac{1}{2},-\tfrac{1}{2}\rangle\right|^2, \tag{33}$$

$$I_{(b)}=\sum_{S_A=0\text{ or }\frac{1}{2}}^{n_{\frac{1}{2}A}}\nu(S_A)\sum_{M=-(S_A+\frac{1}{2})}^{S_A-\frac{3}{2}}\left|\langle M+\tfrac{3}{2},-\tfrac{1}{2}\,|\,R\,|\,M+\tfrac{1}{2},-\tfrac{1}{2}\rangle+\frac{J_{M+1}}{2\delta}\langle M+\tfrac{1}{2},\tfrac{1}{2}\,|\,R\,|\,M+\tfrac{1}{2},-\tfrac{1}{2}\rangle\right|^2, \tag{34}$$

the kets now referring to the δ-kets. Remembering that R in this case is given by the direct product

$$R^{S_A}\times R^{\frac{1}{2}},$$

so that

$$\langle m_{A'}m_{B'}\,|\,R\,|\,m_Am_B\rangle=-\mathrm{i}[\sqrt{\{(S_A\mp m_A)\,(S_A\pm m_A+1)\}}\,\delta_{m_{A'},m_A\pm1}\,\delta_{m_{B'},m_B}+\delta_{m_{B'},m_B\pm1}\,\delta_{m_{A'}m_A}]\,\tfrac{1}{2}\phi, \tag{35}$$

we obtain

$$I_{(a),(b)}=\frac{\phi^2}{2}(1\mp J/\delta)\sum_{m_A=0\text{ or }\frac{1}{2}}^{n_{\frac{1}{2}A}}m_A^2\binom{n_A}{\frac{1}{2}n_A-m_A} \tag{36}$$

$$=\phi^2n_A.\,2^{n_A-3}(1\mp J/\delta).$$

For line (c) we have

$$I_{(c)}=\sum_{S_A=m_A}^{n_{A\frac{1}{2}}}\nu(S_A)\left|\langle m_A,\tfrac{1}{2}\,|\,R\,|\,m_A,-\tfrac{1}{2}\rangle+\frac{J_{m_A+\frac{1}{2}}}{2\delta}\langle m_A+1,-\tfrac{1}{2}\,|\,R\,|\,m_A,-\tfrac{1}{2}\rangle-\frac{J_{m_A+\frac{3}{2}}}{2\delta}\langle m_A+2,-\tfrac{1}{2}\,|\,R\,|\,m_A+1,-\tfrac{1}{2}\rangle\right|^2\tfrac{1}{4}\phi^2, \tag{37}$$

there being now no summation over M as a certain value of m_A occurs only once in each S_A; the lower limit of summation over S_A is also m_A as only values of S_A greater than m_A can contribute to $I_{(c)}$. We thus have

$$I_{(c)} = \sum_{S_A=m_A}^{n_{\frac{1}{2}A}} \nu(S_A)\{(m_A+\tfrac{1}{2})^2-(m_A-\tfrac{1}{2})^2\}\tfrac{1}{4}\phi^2,$$

i.e.
$$I_{(c)} = \binom{n_A}{\frac{1}{2}n_A - m_A}(1+2m_A J/\delta)\tfrac{1}{4}\phi^2. \tag{38}$$

For $I_{(d)}$ we have, using as before only terms up to the first power in ϕ in the Rabi–Bloch matrix,

$$I_{(d)} = \sum_{S_A=m_A}^{n_{\frac{1}{2}A}} \nu(S_A)\left|\frac{J_{m_A+\frac{1}{2}}}{2\delta}\langle m_A-1,\tfrac{1}{2}\,|\,R\,|\,m_A-2,\tfrac{1}{2}\rangle+\frac{J_{m_A-\frac{1}{2}}}{2\delta}\langle m_A,-\tfrac{1}{2}\,|\,R\,|\,m_A-1,\tfrac{1}{2}\rangle\right|^2\tfrac{1}{4}\phi^2,$$

$$\approx\frac{J^2}{\delta^2}\tfrac{1}{4}\phi^2, \tag{39}$$

so that it is rather small compared to the intensity of lines like $I_{(a),(b)}$ and $I_{(c)}$. These results enable us to write down the following table for the frequencies and intensities of the lines of group A and group B, in the approximation $J \ll \delta$:

	group A	group B
frequency:	$\omega+\frac{1}{2}\delta\pm\frac{1}{2}J$	$\omega-\frac{1}{2}\delta+m_A J$
intensity:	$\frac{1}{4}\phi^2 n_A 2^{n_A-1}(1\mp J/\delta)$	$\frac{1}{4}\phi^2\binom{n_A}{\frac{1}{2}n_A-m_A}(1+2m_A J/\delta)$

These expressions for intensities can be also deduced from the following simple considerations. For a line of group B, the only particle present in group B must undergo a transition, the intensity due to this process being in general proportional to

$$|-i\sin\tfrac{1}{2}\phi\,|^2.$$

If the line corresponding to this transition be associated with the magnetic sublevel m_A, then there will be an additional factor $\binom{n_A}{\frac{1}{2}n_A-m_A}$ of realizing the m_A-value in group A. Further as the basic kets are not pure δ-kets, but $J\delta$-kets, there will be an additional factor $1+2m_A J/\delta$ due to the mixing up of the δ-kets corresponding to a certain M-value, to give the $J\delta$-kets. For the lines of group A, the corresponding factor $\binom{n_B}{\frac{1}{2}n_B-m_B}$ is unity and $(1-2m_B J/\delta)$ is $(1\mp J/\delta)$, but there will be the additional factor $n_A 2^{n_A-1}$, as any one of the n_A particles in group A can undergo a transition, the others having their spins either 'up' or down, i.e. parallel or anti-parallel to the field.

In tables 1, 2, 3, 4 and figures 2 to 5 we present the Zeeman level diagrams for $S_B=\frac{1}{2}$ and $S_A=\frac{1}{2},1,\frac{3}{2}$ and 2 respectively. Using these tables the different lines and their intensities to be expected, for $n_A=4,3,2$ and 1 with $n_B=1$, can be explicitly obtained. We have presented the results for $n_A=2$ and 4 in figures 6 and 7. The upper pattern represents on an arbitrary scale, the frequencies to be expected for $J\sim\frac{1}{2}\delta$ while the lower gives the frequencies and intensities of the lines to be expected for $J\ll\delta$.

TABLE 1. ENERGY LEVELS FOR $S_A = \frac{1}{2}$, $S_B = \frac{1}{2}$

	$J = 0, \delta \neq 0$		$J \sim \delta$		$J \ll \delta$		$\delta = 0, J \neq 0$	
level	energy-values	eigen-kets (δ-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets (J-kets)
1	$-\frac{1}{2}\hbar.2\omega$	$\xi\alpha$	$-\frac{1}{2}\hbar(2\omega+\frac{1}{2}J)$	$\xi\alpha$	$-\frac{1}{2}\hbar(2\omega+\frac{1}{2}J)$	$\xi\alpha$	$-\frac{1}{2}\hbar(2\omega+\frac{1}{2}J)$	ψ_1^1
2	$\frac{1}{2}\hbar.2\omega$	$\eta\beta$	$\frac{1}{2}\hbar(2\omega-\frac{1}{2}J)$	$\eta\beta$	$\frac{1}{2}\hbar(2\omega-\frac{1}{2}J)$	$\eta\beta$	$-\frac{1}{2}\hbar.\frac{1}{2}J$	ψ_0^1
3	$-\frac{1}{2}\hbar\delta$	$\xi\beta$	$\hbar(\frac{1}{2}J-Z)$	$\dfrac{\xi\beta(1+Q')+\eta\alpha(1-Q')}{\sqrt{\{2(1+Q'^2)\}}}$	$\frac{1}{2}\hbar(\frac{1}{2}J-\delta)$	$\dfrac{\xi\beta(1+q')+\eta\alpha(1-q')}{\sqrt{\{2(1+q'^2)\}}}$	$-\frac{1}{2}\hbar.3J$	ψ_0^0
4	$\frac{1}{2}\hbar\delta$	$\eta\alpha$	$\hbar(\frac{1}{2}J+Z)$	$\dfrac{\xi\beta(1+Q)+\eta\alpha(1-Q)}{\sqrt{\{2(1+Q^2)\}}}$	$\frac{1}{2}\hbar(\frac{1}{2}J+\delta)$	$\dfrac{\xi\beta(1+q)+\eta\alpha(1-q)}{\sqrt{\{2(1+q^2)\}}}$	$\frac{1}{2}\hbar(2\omega-\frac{1}{2}J)$	ψ_{-1}^1

$$Q = -\frac{J-Z}{\delta}, \quad Q' = -\frac{J+Z}{\delta}; \qquad q = -(1+J/\delta), \quad q' = (1-J/\delta); \qquad Z = \sqrt{(J^2+\delta^2)}.$$

ξ and η are the rotational group states for group A for $m_A = \frac{1}{2}, -\frac{1}{2}$ respectively, and α and β are the rotational group states for group B for $m_B = \frac{1}{2}, -\frac{1}{2}$ respectively. ψ_m^1 and ψ_0^0 are the rotational group states for spin 1.

TABLE 2. ENERGY LEVELS FOR $S_A = 1$, $S_B = \frac{1}{2}$

	$J = 0, \delta \neq 0$		$J \sim \delta$		$J \ll \delta$		$\delta = 0, J \neq 0$	
level	energy-values	eigen-kets (δ-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets (J-kets)
1	$\frac{1}{2}\hbar(-3\omega-\frac{1}{2}\delta)$	$\xi\alpha$	$\frac{1}{2}\hbar(-3\omega-\frac{1}{2}\delta-J)$	$\xi\alpha$	$\frac{1}{2}\hbar(-3\omega-\frac{1}{2}\delta-J)$	$\xi\alpha$	$\frac{1}{2}\hbar(-3\omega-J)$	$\psi^{\frac{3}{2}}_{\frac{3}{2}}$
2	$\frac{1}{2}\hbar(3\omega+\frac{1}{2}\delta)$	$\zeta\beta$	$\frac{1}{2}\hbar(3\omega+\frac{1}{2}\delta-J)$	$\zeta\beta$	$\frac{1}{2}\hbar(3\omega+\frac{1}{2}\delta-J)$	$\zeta\beta$	$\frac{1}{2}\hbar(3\omega-J)$	$\psi^{\frac{3}{2}}_{-\frac{3}{2}}$
3	$\frac{1}{2}\hbar(-\omega-\frac{3}{2}\delta)$	$\xi\beta$	$\frac{1}{2}\hbar(-\omega-\frac{1}{2}\delta+\frac{1}{2}J-X)$	$\dfrac{\xi\beta(1+Q_1')+\eta\alpha(1-Q_1')}{\sqrt{\{2(1+Q_1'^2)\}}}$	$\frac{1}{2}\hbar(-\omega-\frac{3}{2}\delta+J)$	$\dfrac{\xi\beta(1+q_1')+\eta\alpha(1-q_1')}{\sqrt{\{2(1+q_1'^2)\}}}$	$\frac{1}{2}\hbar(-\omega-J)$	$\psi^{\frac{3}{2}}_{\frac{1}{2}}$
4	$\frac{1}{2}\hbar(-\omega+\frac{1}{2}\delta)$	$\eta\alpha$	$\frac{1}{2}\hbar(-\omega-\frac{1}{2}\delta+\frac{1}{2}J+X)$	$\dfrac{\xi\beta(1+Q_1)+\eta\alpha(1-Q_1)}{\sqrt{\{2(1+Q_1^2)\}}}$	$\frac{1}{2}\hbar(-\omega+\frac{1}{2}\delta)$	$\dfrac{\xi\beta(1+q_1)+\eta\alpha(1-q_1)}{\sqrt{\{2(1+q_1^2)\}}}$	$\frac{1}{2}\hbar(-\omega+2J)$	$\psi^{\frac{1}{2}}_{\frac{1}{2}}$
5	$\frac{1}{2}\hbar(\omega-\frac{1}{2}\delta)$	$\eta\beta$	$\frac{1}{2}\hbar(\omega+\frac{1}{2}\delta+\frac{1}{2}J-Y)$	$\dfrac{\eta\beta(1+Q_2')+\zeta\alpha(1-Q_2')}{\sqrt{\{2(1+Q_2'^2)\}}}$	$\frac{1}{2}\hbar(\omega-\frac{1}{2}\delta)$	$\dfrac{\eta\beta(1+q_2')+\zeta\alpha(1-q_2')}{\sqrt{\{2(1+q_2'^2)\}}}$	$\frac{1}{2}\hbar(\omega-J)$	$\psi^{\frac{3}{2}}_{-\frac{1}{2}}$
6	$\frac{1}{2}\hbar(\omega+\frac{3}{2}\delta)$	$\zeta\alpha$	$\frac{1}{2}\hbar(\omega+\frac{1}{2}\delta+\frac{1}{2}J+Y)$	$\dfrac{\eta\beta(1+Q_2)+\zeta\alpha(1-Q_2)}{\sqrt{\{2(1+Q_2^2)\}}}$	$\frac{1}{2}\hbar(\omega+\frac{3}{2}\delta+J)$	$\dfrac{\eta\beta(1+q_2)+\zeta\alpha(1-q_2)}{\sqrt{\{2(1+q_2^2)\}}}$	$\frac{1}{2}\hbar(\omega+2J)$	$\psi^{\frac{1}{2}}_{-\frac{1}{2}}$

$$Q_1 = \frac{-\sqrt{2}J-X}{(\delta-\frac{1}{2}J)}, \quad Q_1' = \frac{-\sqrt{2}J+X}{(\delta-\frac{1}{2}J)}; \qquad q_1 = -\left(1+\frac{\sqrt{2}J}{\delta}\right), \quad q_1' = \left(1-\frac{\sqrt{2}J}{\delta}\right); \qquad X = \sqrt{\{(\delta-\tfrac{1}{2}J)^2+(\sqrt{2}J)^2\}}$$

$$Q_2 = \frac{-\sqrt{2}J-Y}{(\delta+\frac{1}{2}J)}, \quad Q_2' = \frac{-\sqrt{2}J+Y}{(\delta+\frac{1}{2}J)}; \qquad q_2 = -\left(1+\frac{\sqrt{2}J}{\delta}\right), \quad q_2' = \left(1-\frac{\sqrt{2}J}{\delta}\right); \qquad Y = \sqrt{\{(\delta+\tfrac{1}{2}J)^2+(\sqrt{2}J)^2\}}$$

ξ, η, ζ represent the rotational group states for $S_A = 1, m_A = 1, 0, -1$ respectively; α and β represent the rotational group states for $S_B = \frac{1}{2}$, $m_B = \frac{1}{2}, -\frac{1}{2}$ respectively. $\psi^{\frac{3}{2}}_{m}$ and $\psi^{\frac{1}{2}}_{m}$ are the rotational group states for $I = \frac{3}{2}$ and $\frac{1}{2}$ respectively.

TABLE 3. ENERGY LEVELS FOR $S_A = \frac{3}{2}$, $S_B = \frac{1}{2}$

	$J = 0, \delta \neq 0$		$J \sim \delta$		$J \ll \delta$		$\delta = 0, J \neq 0$	
level	energy-values	eigen-kets (δ-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets (J-kets)
E_1	$\frac{1}{2}\hbar(-4\omega-\delta)$	$\zeta\alpha$	$-\frac{1}{2}\hbar(4\omega+\delta+\frac{3}{2}J)$	$\xi\alpha$	$-\frac{1}{2}\hbar(4\omega+\delta+\frac{3}{2}J)$	$\xi\alpha$	$-\frac{1}{2}\hbar(4\omega+\frac{3}{2}J)$	ψ^2_2
E_2	$\frac{1}{2}\hbar(4\omega+\delta)$	$\lambda\beta$	$\frac{1}{2}\hbar(4\omega+\delta-\frac{3}{2}J)$	$\lambda\beta$	$\frac{1}{2}\hbar(4\omega+\delta-\frac{3}{2}J)$	$\lambda\beta$	$\frac{1}{2}\hbar(4\omega-\frac{3}{2}J)$	ψ^2_{-2}
E_3	$\frac{1}{2}\hbar(-2\omega-2\delta)$	$\xi\beta$	$\frac{1}{2}\hbar[(-2\omega-\delta+\frac{1}{2}J)-E]$	$\dfrac{\xi\beta(1+Q_1')+\eta\alpha(1-Q_1')}{\sqrt{\{2(1+Q_1'^2)\}}}$	$\frac{1}{2}\hbar(-2\omega-2\delta+\frac{3}{2}J)$	$\dfrac{\xi\beta(1+q_1')+\eta\alpha(1-q_2')}{\sqrt{\{2(1+q_1'^2)\}}}$	$\frac{1}{2}\hbar(-2\omega-\frac{3}{2}J)$	ψ^2_1
E_4	$-\frac{1}{2}\hbar.2\omega$	$\eta\alpha$	$\frac{1}{2}\hbar[(-2\omega-\delta+\frac{1}{2}J)+E]$	$\dfrac{\xi\beta(1+Q_1)+\eta\alpha(1-Q_1)}{\sqrt{\{2(1+Q_1^2)\}}}$	$\frac{1}{2}\hbar(-2\omega-\frac{1}{2}J)$	$\dfrac{\xi\beta(1+q_1)+\eta\alpha(1-q_1)}{\sqrt{\{2(1+q_1^2)\}}}$	$\frac{1}{2}\hbar(-2\omega+\frac{5}{2}J)$	ψ^1_1
E_5	$-\frac{1}{2}\hbar.\delta$	$\eta\beta$	$\frac{1}{2}\hbar(\frac{1}{2}J-F)$	$\dfrac{\eta\beta(1+Q_2')+\zeta\alpha(1-Q_2')}{\sqrt{\{2(1+Q_2'^2)\}}}$	$\frac{1}{2}\hbar(-\delta+\frac{1}{2}J)$	$\dfrac{\eta\beta(1+q_2')+\zeta\alpha(1-q_2')}{\sqrt{\{2(1+q_2'^2)\}}}$	$-\frac{1}{2}\hbar.\frac{3}{2}J$	ψ^2_0
E_6	$\frac{1}{2}\hbar.\delta$	$\zeta\alpha$	$\frac{1}{2}\hbar(\frac{1}{2}J+F)$	$\dfrac{\eta\beta(1+Q_2)+\zeta\alpha(1-Q_2)}{\sqrt{\{2(1+Q_2^2)\}}}$	$\frac{1}{2}\hbar(\delta+\frac{1}{2}J)$	$\dfrac{\eta\beta(1+q_2)+\zeta\alpha(1-q_2)}{\sqrt{\{2(1+q_2^2)\}}}$	$+\frac{1}{2}\hbar.\frac{5}{2}J$	ψ^1_0
E_7	$\frac{1}{2}\hbar.2\omega$	$\zeta\beta$	$\frac{1}{2}\hbar[2\omega+\delta+\frac{1}{2}J-G]$	$\dfrac{\zeta\beta(1+Q_3')+\lambda\alpha(1-Q_3')}{\sqrt{\{2(1+Q_3'^2)\}}}$	$\frac{1}{2}\hbar(2\omega-\frac{1}{2}J)$	$\dfrac{\zeta\beta(1+q_3')+\lambda\alpha(1-q_3')}{\sqrt{\{2(1+q_3'^2)\}}}$	$\frac{1}{2}\hbar(2\omega-\frac{3}{2}J)$	ψ^2_{-1}
E_8	$\frac{1}{2}\hbar(2\omega+2\delta)$	$\lambda\alpha$	$\frac{1}{2}\hbar[2\omega+\delta+\frac{1}{2}J+G]$	$\dfrac{\zeta\beta(1+Q_3)+\lambda\alpha(1-Q_3)}{\sqrt{\{2(1+Q_3^2)\}}}$	$\frac{1}{2}\hbar(2\omega+2\delta+\frac{3}{2}J)$	$\dfrac{\zeta\beta(1+q_3)+\lambda\alpha(1-q_3)}{\sqrt{\{2(1+q_3^2)\}}}$	$\frac{1}{2}\hbar(2\omega+\frac{5}{2}J)$	ψ^1_{-1}

$$Q_1 = \frac{-\sqrt{3}J-E}{\delta-J}, \quad Q_1' = \frac{-\sqrt{3}J+E}{\delta-J} \qquad q_1 = -\left(1+\frac{\sqrt{3}J}{\delta}\right), \quad q_1' = \left(1-\frac{\sqrt{3}J}{\delta}\right) \qquad E = \sqrt{\{(\delta-J)^2+(\sqrt{3}J)^2\}}$$

$$Q_2 = \frac{-2J-F}{\delta}, \quad Q_2' = \frac{-2J+F}{\delta} \qquad q_2 = -\left(1+\frac{2J}{\delta}\right), \quad q_2' = \left(1-\frac{2J}{\delta}\right) \qquad F = \sqrt{\{\delta^2+(2J)^2\}}$$

$$Q_3 = \frac{-\sqrt{3}J-G}{\delta+J}, \quad Q_3' = \frac{-\sqrt{3}J+G}{\delta+J} \qquad q_3 = -\left(1+\frac{\sqrt{3}J}{\delta}\right), \quad q_3' = \left(1-\frac{\sqrt{3}J}{\delta}\right) \qquad G = \sqrt{\{(\delta+J)^2+(\sqrt{3}J)^2\}}$$

ξ, η, ζ and λ now correspond to the rotational group eigen-kets $|S_A, m_A\rangle$ of group A for $S_A = \frac{3}{2}$, $m_A = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ respectively, and α and β to those of group B for $S_B = \frac{1}{2}$, $m_B = +\frac{1}{2}, -\frac{1}{2}$ respectively. ψ^2_m and ψ^1_m are rotational group states for spins 2 and 1.

TABLE 4. ENERGY LEVELS FOR $S_A = 2$, $S_B = \frac{1}{2}$

	$J = 0, \delta \neq 0$		$J \sim \delta$		$J \ll \delta$		$J \neq 0, \delta = 0$	
level	energy-values	eigen-kets (δ-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets ($J\delta$-kets)	energy-values	eigen-kets (J-kets)
E_1	$\frac{1}{2}\hbar(-5\omega-\frac{3}{2}\delta)$	$\xi\alpha$	$\frac{1}{2}\hbar(-5\omega-\frac{3}{2}\delta-2J)$	$\xi\alpha$	$\frac{1}{2}\hbar(-5\omega-\frac{3}{2}\delta-2J)$	$\xi\alpha$	$\frac{1}{2}\hbar(-5\omega-2J)$	$\psi^{\frac{5}{2}}_{\frac{5}{2}}$
E_2	$\frac{1}{2}\hbar(5\omega+\frac{3}{2}\delta)$	$\mu\beta$	$\frac{1}{2}\hbar(5\omega+\frac{3}{2}\delta-2J)$	$\mu\beta$	$\frac{1}{2}\hbar(5\omega+\frac{3}{2}\delta-2J)$	$\mu\beta$	$\frac{1}{2}\hbar(5\omega-2J)$	$\psi^{\frac{5}{2}}_{-\frac{3}{2}}$
E_3	$\frac{1}{2}\hbar(-3\omega-\frac{5}{2}\delta)$	$\xi\beta$	$\frac{1}{2}\hbar(-3\omega-\frac{3}{2}\delta+\frac{1}{2}J-A)$	$\dfrac{\xi\beta(1+Q_1')+\eta\alpha(1-Q_1')}{\sqrt{\{2(1+Q_1'^2)\}}}$	$\frac{1}{2}\hbar(-3\omega-\frac{5}{2}\delta+2J)$	$\dfrac{\xi\beta(1+q_1')+\eta\alpha(1-q_1')}{\sqrt{\{2(1+q_1'^2)\}}}$	$\frac{1}{2}\hbar(-3\omega-2J)$	$\psi^{\frac{5}{2}}_{\frac{1}{2}}$
E_4	$\frac{1}{2}\hbar(-3\omega-\frac{1}{2}\delta)$	$\eta\alpha$	$\frac{1}{2}\hbar(-3\omega-\frac{3}{2}\delta+\frac{1}{2}J+A)$	$\dfrac{\xi\beta(1+Q_1)+\eta\alpha(1-Q_1)}{\sqrt{\{2(1+Q_1^2)\}}}$	$\frac{1}{2}\hbar(-3\omega-\frac{1}{2}\delta-J)$	$\dfrac{\xi\beta(1+q_1)+\eta\alpha(1-q_1)}{\sqrt{\{2(1+q_1^2)\}}}$	$\frac{1}{2}\hbar(-3\omega+3J)$	$\psi^{\frac{5}{2}}_{\frac{5}{2}}$
E_5	$\frac{1}{2}\hbar(-\omega-\frac{3}{2}\delta)$	$\eta\beta$	$\frac{1}{2}\hbar(-\omega-\frac{1}{2}\delta+\frac{1}{2}J-B)$	$\dfrac{\eta\beta(1+Q_2')+\zeta\alpha(1-Q_2')}{\sqrt{\{2(1+Q_2'^2)\}}}$	$\frac{1}{2}\hbar(-\omega-\frac{3}{2}\delta+J)$	$\dfrac{\eta\beta(1+q_2')+\zeta\alpha(1-q_2')}{\sqrt{\{2(1+q_2'^2)\}}}$	$\frac{1}{2}\hbar(-\omega-2J)$	$\psi^{\frac{5}{2}}_{\frac{3}{2}}$
E_6	$\frac{1}{2}\hbar(-\omega+\frac{1}{2}\delta)$	$\zeta\alpha$	$\frac{1}{2}\hbar(-\omega-\frac{1}{2}\delta+\frac{1}{2}J+B)$	$\dfrac{\eta\beta(1+Q_2)+\zeta\alpha(1-Q_2)}{\sqrt{\{2(1+Q_2^2)\}}}$	$\frac{1}{2}\hbar(-\omega+\frac{1}{2}\delta)$	$\dfrac{\eta\beta(1+q_2)+\zeta\alpha(1-q_2)}{\sqrt{\{2(1+q_2^2)\}}}$	$\frac{1}{2}\hbar(-\omega+3J)$	$\psi^{\frac{5}{2}}_{\frac{3}{2}}$
E_7	$\frac{1}{2}\hbar(\omega-\frac{1}{2}\delta)$	$\zeta\beta$	$\frac{1}{2}\hbar(\omega+\frac{1}{2}\delta+\frac{1}{2}J-C)$	$\dfrac{\zeta\beta(1+Q_3')+\lambda\alpha(1-Q_3')}{\sqrt{\{2(1+Q_3'^2)\}}}$	$\frac{1}{2}\hbar(\omega-\frac{1}{2}\delta)$	$\dfrac{\zeta\beta(1+q_3')+\lambda\alpha(1-q_3')}{\sqrt{\{2(1+q_3'^2)\}}}$	$\frac{1}{2}\hbar(\omega-2J)$	$\psi^{\frac{5}{2}}_{-\frac{1}{2}}$
E_8	$\frac{1}{2}\hbar(\omega+\frac{3}{2}\delta)$	$\lambda\alpha$	$\frac{1}{2}\hbar(\omega+\frac{1}{2}\delta+\frac{1}{2}J+C)$	$\dfrac{\zeta\beta(1+Q_3)+\lambda\alpha(1-Q_3)}{\sqrt{\{2(1+Q_3^2)\}}}$	$\frac{1}{2}\hbar(\omega+\frac{3}{2}\delta+J)$	$\dfrac{\zeta\beta(1+q_3)+\lambda\alpha(1-q_3)}{\sqrt{\{2(1+q_3^2)\}}}$	$\frac{1}{2}\hbar(\omega+3J)$	$\psi^{\frac{5}{2}}_{-\frac{3}{2}}$
E_9	$\frac{1}{2}\hbar(3\omega+\frac{1}{2}\delta)$	$\lambda\beta$	$\frac{1}{2}\hbar(3\omega+\frac{3}{2}\delta+\frac{1}{2}J-D)$	$\dfrac{\lambda\beta(1+Q_4')+\mu\alpha(1-Q_4')}{\sqrt{\{2(1+Q_4'^2)\}}}$	$\frac{1}{2}\hbar(3\omega+\frac{1}{2}\delta-J)$	$\dfrac{\lambda\beta(1+q_4')+\eta\alpha(1-q_4')}{\sqrt{\{2(1+q_4'^2)\}}}$	$\frac{1}{2}\hbar(3\omega-2J)$	$\psi^{\frac{5}{2}}_{-\frac{5}{2}}$
E_{10}	$\frac{1}{2}\hbar(3\omega+\frac{5}{2}\delta)$	$\mu\alpha$	$\frac{1}{2}\hbar(3\omega+\frac{3}{2}\delta+\frac{1}{2}J+D)$	$\dfrac{\lambda\beta(1+Q_4)+\mu\alpha(1-Q_4)}{\sqrt{\{2(1+Q_4^2)\}}}$	$\frac{1}{2}\hbar(3\omega+\frac{5}{2}\delta+2J)$	$\dfrac{\lambda\beta(1+q_4)+\mu\alpha(1-q_4)}{\sqrt{\{2(1+q_4^2)\}}}$	$\frac{1}{2}\hbar(3\omega+3J)$	$\psi^{\frac{5}{2}}_{\frac{3}{2}}$

$$Q_1 = \frac{-2J-A}{\delta-\frac{3}{2}J}, \quad Q_1' = \frac{-2J+A}{\delta-\frac{3}{2}J}; \quad q_1 = -\left(1+\frac{2J}{\delta}\right), \quad q_1' = \left(1-\frac{2J}{\delta}\right); \quad A = \sqrt{\{(\delta-\tfrac{3}{2}J)^2+(2J)^2\}}$$

$$Q_2 = \frac{-\sqrt{6}J-B}{\delta-\frac{1}{2}J}, \quad Q_2' = \frac{-\sqrt{6}J+B}{\delta-\frac{1}{2}J}; \quad q_2 = -\left(1+\frac{\sqrt{6}J}{\delta}\right), \quad q_2' = \left(1-\frac{\sqrt{6}J}{\delta}\right); \quad B = \sqrt{\{(\delta-\tfrac{1}{2}J)^2+(\sqrt{6}J)^2\}}$$

$$Q_3 = \frac{-\sqrt{6}J-C}{\delta+\frac{1}{2}J}, \quad Q_3' = \frac{-\sqrt{6}J+C}{\delta+\frac{1}{2}J}; \quad q_3 = -\left(1+\frac{\sqrt{6}}{\delta}\right), \quad q_3' = \left(1-\frac{\sqrt{6}J}{\delta}\right); \quad C = \sqrt{\{(\delta+\tfrac{1}{2}J)^2+(\sqrt{6}J)^2\}}$$

$$Q_4 = \frac{-2J-D}{\delta+\frac{3}{2}J}, \quad Q_4' = \frac{-2J+D}{\delta+\frac{3}{2}J}; \quad q_4 = -\left(1+\frac{2J}{\delta}\right), \quad q_4' = \left(1-\frac{2J}{\delta}\right); \quad D = \sqrt{\{(\delta+\tfrac{3}{2}J)^2+(2J)^2\}}$$

$\xi, \eta, \zeta, \lambda, \mu$ represent the rotational group states for group A for $S_A = 2$, $m_A = 2, 1, 0, -1, -2$ respectively, and α, β for group B for $S_B = \frac{1}{2}$, $m_B = \frac{1}{2}, -\frac{1}{2}$ respectively. $\psi^{\frac{5}{2}}_{m}$ and $\psi^{\frac{3}{2}}_{m}$ represent the rotational group states for spins $\frac{5}{2}$ and $\frac{3}{2}$ respectively.

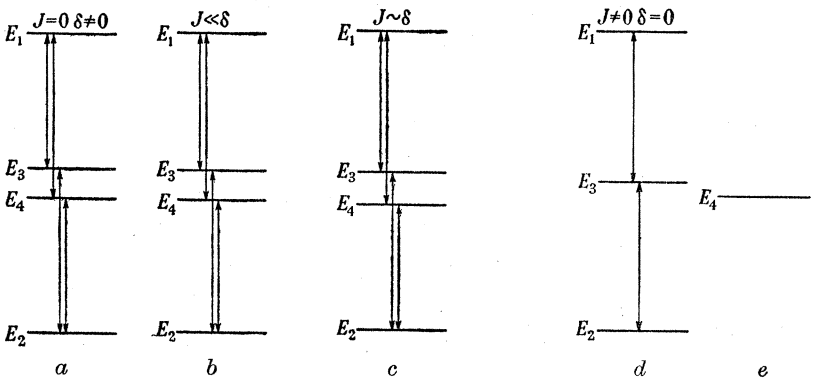


FIGURE 2. Energy-level diagrams and transitions for $S_A = \frac{1}{2}$, $S_B = \frac{1}{2}$ (cf. table 1).

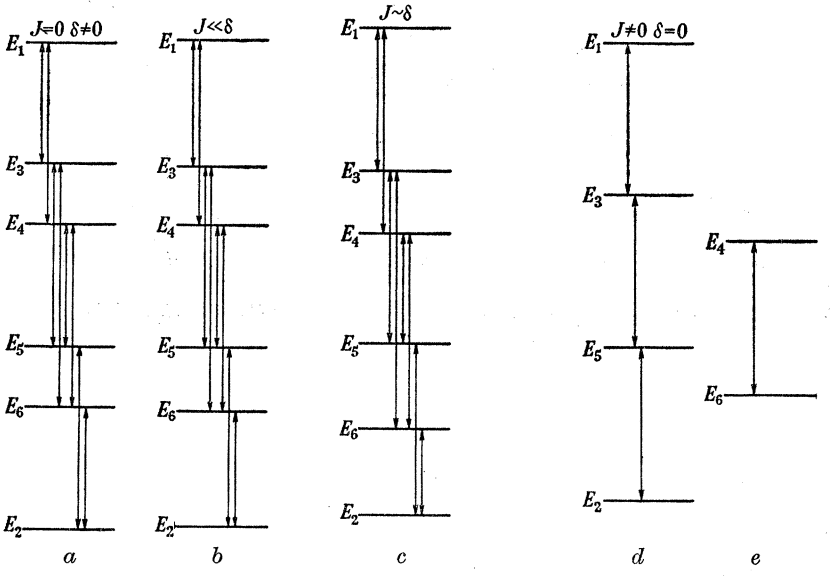


FIGURE 3. Energy-level diagrams and transitions for $S_A = 1$, $S_B = \frac{1}{2}$ (cf. table 2).

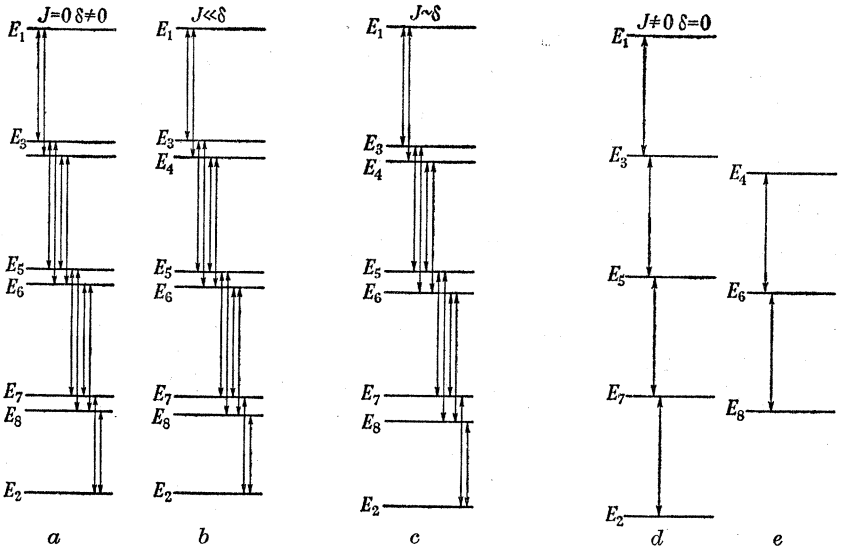


FIGURE 4. Energy-level diagrams and transitions for $S_A = \frac{3}{2}$, $S_B = \frac{1}{2}$ (cf. table 3).

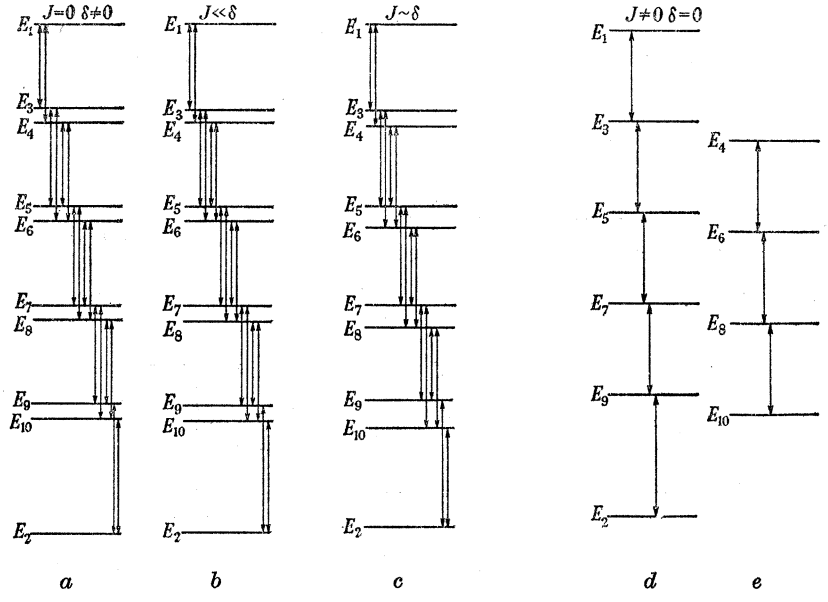


FIGURE 5. Energy-level diagrams and transitions for $S_A = 2$, $S_B = \frac{1}{2}$ (cf. table 4).

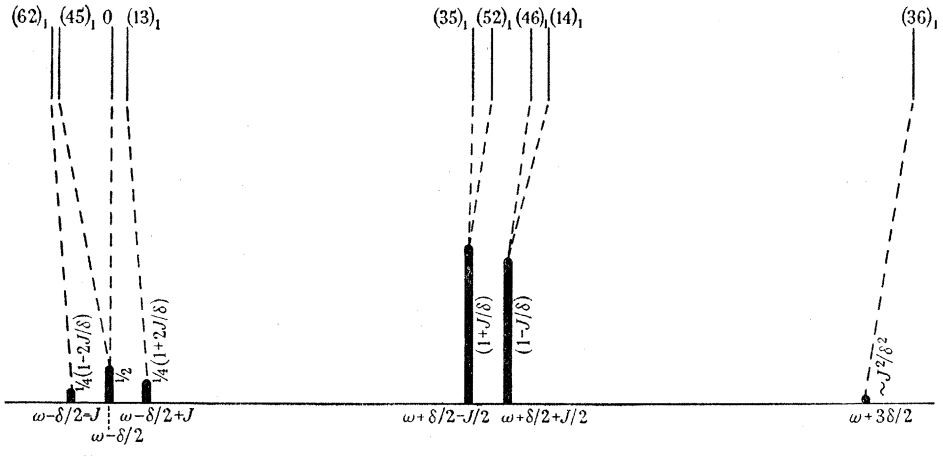


FIGURE 6. Resonance line splittings for $n_A = 2$, $n_B = 1$. The lower dark lines indicate the pattern for $J/\delta \sim \frac{1}{10}$, the unit being ϕ^2, where $\phi = \omega_r t_w$, t_w being the time of passage through resonance. The upper lines represent the pattern for $J \sim \delta$ in an arbitrary scale. The symbols $(pq)_r$ represent the transition between levels E_p and E_q for $S_A = r$ and $S_B = \frac{1}{2}$.

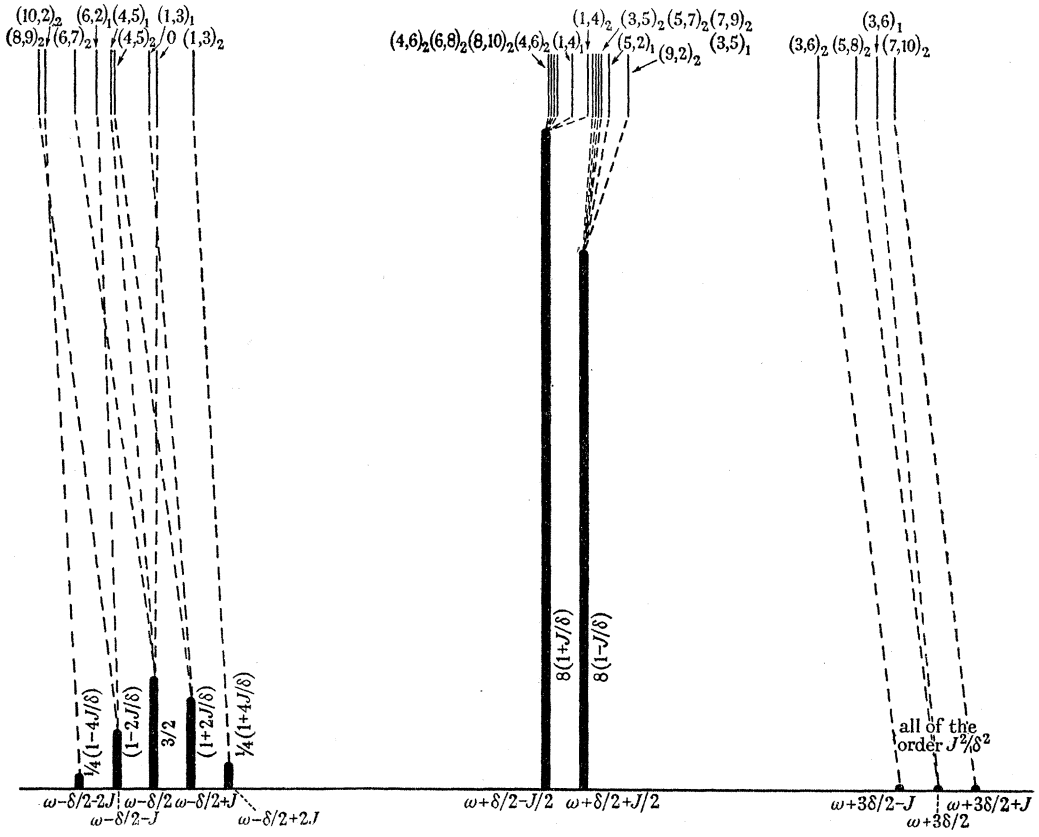
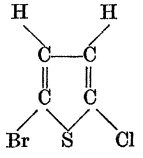


FIGURE 7. Resonance line splittings for $n_A = 4$, $n_B = 1$, the lower pattern representing the case $J/\delta \sim \frac{1}{10}$ and the upper for $J \sim \delta$ as in figure 6.

DISCUSSION

(i) The investigation yields a general method of handling the J-coupling between non-equivalent groups of nuclei. The case of $n_B = \frac{1}{2}$ is specially simple and leads to explicit expressions for the energy-values and eigen-kets to be expected.

(ii) As a result of the investigation we see clearly that for $J \sim \delta$, a serious departure occurs from the Gutowsky rule (1951) both in intensity and frequency. A special feature of these departures is in the appearance of lines at frequencies close to $\omega + \frac{3}{2}\delta$, which for $J \sim \delta$ are by no means of very small intensity, as shown in figure 8 for $n_A = n_B = 1$ and $J \sim \frac{1}{2}\delta \sim 20$ c/s. Of course, these lines become of very low intensity for $J \ll \delta$ (proportional to J^2/δ^2). But even when $J \sim \frac{1}{10}\delta$, although departure from the Gutowsky rule in regard to the splittings is not so marked, the departure in the intensity is evident from the asymmetry of the patterns at $\omega + \frac{1}{2}\delta$ and $\omega - \frac{1}{2}\delta$ due to groups A and B respectively. It therefore becomes necessary to repeat these experiments with compounds where the condition $J \sim \delta$ is true as, for example, in



to test the correctness of our theory.

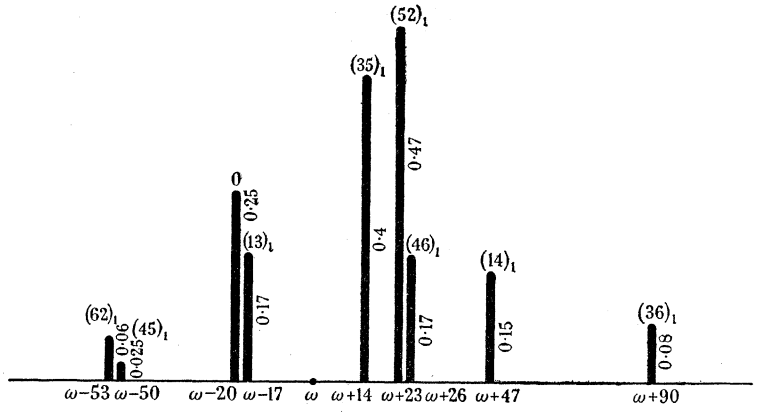


FIGURE 8. Resonance line splittings for $n_A = 2$, $n_B = 1$ for $J \sim \frac{1}{2}\delta \sim 20$ c/s, the quantities added to ω represent frequency shifts from ω in c/s. The units of intensity are again $\frac{1}{4}\phi^2$.

APPENDIX

The matrix used for calculating the transition probabilities for the different transitions in the $J\delta$-states, viz.

$$B = A(R^{S_A} \times R^{\frac{1}{2}})\, A^{-1}, \tag{40}$$

follows from the definition of direct product of matrices. But it has to be remembered that the Rabi-Bloch transformation matrix obtained by forming direct product

$$R = R^{S_A} \times R^{\frac{1}{2}}$$

gives the law of transformation with time of the δ-kets. This is rigorous when the Hamiltonian of the system is given by $\mathscr{H}_\delta$. If we retain the Hamiltonian and make a change of basis to $J\delta$-kets, then the law of transformation with time would be given by

$$B = ARA^{-1}.$$

But the proper Hamiltonian is not $\mathscr{H}_\delta$ but $\mathscr{H}_{J\delta}$, and we shall prove now, using Dirac's method of dealing with time-dependent Hamiltonians, that up to a first order of approximation B still gives the proper law of transformation.

Thus, if we consider the two particular spin-values S_A and S_B of the groups A and B respectively, then the Hamiltonian for these two coupled systems may be written for convenience as

$$\mathscr{H}_{J\delta} = -\hbar(\omega_z S_z + \tfrac{1}{2}\delta K_z + J\mathbf{S}_A.\mathbf{S}_B), \tag{6}$$

where

$$\left.\begin{aligned} &\omega_z = \gamma H_z, \quad \delta = \gamma(h_1 - h_2), \\ &K_z = S_{Az} - S_{Bz} \quad \text{and} \quad S_z = S_{Az} + S_{Bz}. \end{aligned}\right\} \tag{41}$$

Now, the Hamiltonian for the interaction of the two systems with the rf-field is given by

$$V = -\tfrac{1}{2}\omega_1\hbar(S_+ \mathrm{e}^{(-)^r \mathrm{i}\omega t} + S_- \mathrm{e}^{(-)^{r+1}\mathrm{i}\omega t}), \tag{42}$$

where

$$\omega = \gamma H_r, \quad S_\pm = (S_x \pm \mathrm{i}S_y), \tag{43}$$

H_r being the amplitude of the rotating field, and $r = 1, 2$ referring respectively to anti-clockwise and clockwise rotating fields. The problem is to find the transformation matrix T connecting the initial and final states, viz.

$$|P, t\rangle = T(t)\,|P, 0\rangle. \tag{44}$$

To do this, we employ the usual transformations

$$\left.\begin{aligned} V' &= \mathrm{e}^{\mathrm{i}\mathscr{H}_0 t/\hbar} V \mathrm{e}^{-\mathrm{i}\mathscr{H}_0 t/\hbar}, \\ T' &= \mathrm{e}^{\mathrm{i}\mathscr{H}_0 t/\hbar} T, \end{aligned}\right\} \tag{45}$$

it may then be shown that T' then satisfies the equation

$$\frac{\mathrm{d}T'}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar} V'T'. \tag{46}$$

Now it is to be noted that if A and B are two operators then $\mathrm{e}^{(A+B)}$ is defined by the series

$$\mathrm{e}^{(A+B)} = \sum_{n=0}^{\infty} \frac{(A+B)^n}{n!}. \tag{47}$$

However, we cannot deduce the properties of this exponential series, viz.

$$\mathrm{e}^{A+B} = \mathrm{e}^{A}.\mathrm{e}^{B} \tag{48}$$

from this expansion, if A and B do not commute, because anti-commutators will complicate the issue. This property is of particular importance in the following consideration. Thus, K_z and $\mathbf{S}_A.\mathbf{S}_B$ do not commute so they cannot be interchanged in the exponential, but S_z commutes with the rest, and also possesses convenient commutation rules with respect to S_+ and S_-, hence we can simplify to the following form, viz.

$$\begin{aligned} V' = -\frac{\omega_1\hbar}{2}[\exp\{-\mathrm{i}(\tfrac{1}{2}\delta K_z + J\mathbf{S}_A.\mathbf{S}_B)\,t\}]\,[S_+ \exp\{\mathrm{i}[\omega - (-)^r\omega_z]\,t\} \\ + S_- \exp\{-\mathrm{i}[\omega - (-)^r\omega_z]\,t\}]\,[\exp\{\mathrm{i}(\tfrac{1}{2}\delta K_z + \mathbf{S}_A.\mathbf{S}_B)\,t\}]. \end{aligned} \tag{49}$$

It is seen easily that for γ positive, ω_z is positive, and only $r = 2$ gives the feasible resonance condition $\omega = \omega_z$. Similarly for γ negative only $r = 1$ gives the resonance condition. In any case, we have at resonance

$$\omega - (-)^r\omega_z = 0. \tag{50}$$

Further simplification is not possible if we retain the exponential form, as K_z does not commute with $\mathbf{S}_A.\mathbf{S}_B$. We therefore expand the exponentials, retaining only the terms of first degree in δt and Jt. This is justified if we have the approximation

$$(\delta t)^2, \quad (Jt)^2 \ll 1,$$

a condition nearly always satisfied in 'slow-passage' experiments. Using the resonance condition (50) we then obtain

$$V' = U' + \frac{\mathrm{i}\omega_1\hbar\,\delta t}{4}(K_+ - K_-), \tag{51}$$

where

$$U' = -\frac{\omega_1\hbar}{2}(S_+ + S_-). \tag{52}$$

If it had been possible to obtain the matrix elements of $\exp\left\{-\frac{\mathrm{i}}{\hbar}\int_0^{t_w} V'\,\mathrm{d}t\right\}$, then we could have obtained a rigorous solution of (46).

We could also have applied the first-order perturbation theory here, but as we want to use the transformation matrix for calculations on the effect of J-coupling on spin-echo in another paper, we have applied the following method which gives us the transformation matrix as a combination of the Rabi–Bloch matrix together with a small correction. But, in the steady experiment where ϕ is small, we shall use only the first power of ϕ in the Rabi–Bloch matrix, which is in effect equivalent to a first-order perturbation calculation. Thus we define

$$T' = \exp\left(-\frac{\mathrm{i}}{\hbar}\int U'\,\mathrm{d}t\right) T'', \tag{53}$$

when we get

$$\frac{\mathrm{d}T''}{\mathrm{d}t} = vT'', \tag{54}$$

where

$$v = \omega_1 t \tfrac{1}{4}\delta \exp\left\{\frac{\mathrm{i}}{\hbar}\int U'\,\mathrm{d}t\right\}(K_+ - K_-)\exp\left\{-\frac{\mathrm{i}}{\hbar}\int U'\,\mathrm{d}t\right\}. \tag{55}$$

We now solve (54) for spins $\frac{1}{2}$ of the two groups by applying Dirac's perturbation theory and retaining only terms up to the first order, when we get

$$T'' = \exp\left\{-\frac{\mathrm{i}}{\hbar}\int_0^{t_w} U'\,\mathrm{d}t\right\}\left(1+\int_0^{t_w} v\,\mathrm{d}t\right), \tag{56}$$

t_ω being the time of passage through the resonance width. We then obtain on simplification

$$\left.\begin{aligned} T' &= C + \frac{\delta}{4\omega_1}\{[K_+ - K_-, C] + \phi CD\}, \\ \text{where}\quad C &= \exp\left\{-\frac{\mathrm{i}}{\hbar}\int_0^{t_w} U'\,\mathrm{d}t\right\}. \end{aligned}\right\} \tag{57}$$

The matrix D is obtained from

$$B^\dagger(K_+ - K_-)B \tag{58}$$

by substituting $\phi + \frac{1}{2}\pi$ in place of ϕ ($B^\dagger$ referring to the Hermitian conjugate of B). C corresponds to the Rabi–Bloch matrix in whatever basis we choose. With the J-states as basis, it corresponds to the Rabi–Bloch matrix used by Hahn (1952) (equation (5)); with the δ-states, it corresponds to the direct product $R^{S_A} \times R^{S_B}$ and with the $J\delta$-states as basis it corresponds to B. The other term, $\delta/4\omega_1$, gives a small correction to it. On making explicit calculations, we find that this term gives a correction of the order $J\sqrt{(J^2+\delta^2)}\,t_\omega$ which is usually less than 0·01 % for 'slow-passage' experiments with most compounds. But, as t_ω is comparatively larger in spin-echo experiments where resonance condition lasts for the interval determined by the width of the pulse, we expect such a term to be comparatively more important.

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