NMR SPECTRA IN THE STRONG-COUPLING REGION

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A method of calculating high-resolution NMR spectra in the region of strong spin-spin coupling is described. It is shown that in the general case one can determine the number of spectral lines and the intensities of these lines. The forms of the spectra for which the calculation is carried out in analytical form are indicated. A_aB_b and ABC spectra are considered as examples.

This paper is a continuation of [1, 2]. The general formulation of the problem, the classification of spectra, and the terminology and notation are discussed in detail in [1]. In this paper we give the theory of NMR spectra for the condition $|J_{ij}| \gg |\nu_k - \nu_l|$. In accordance with the terminology used in [1] this region of variation of the parameters is called the strong-coupling region.

General method of calculation. In order to be able to use perturbation theory we will subtract from the Hamiltonian the operator $n^{-1}\sum_{i=1}^{n}\nu_i I_z$ (n is the number of groups of equivalent nuclei, and I_z is the projection operator of the total spin of all the nuclei of the system). This is equivalent to choosing the origin from which the frequencies are read at the point $n^{-1}\sum_{i=1}^{n}\nu_i$. As a result the Hamiltonian takes the form

$$\mathcal{H} = \sum_{i=1}^{n} f_i I_{iz} + \mathcal{H}_1$$
$$\mathcal{H}_1 = \sum_{i<k} J_{ik}\mathbf{I}_i\mathbf{I}_k, \qquad (1)$$

where $f_i = \nu_i - n^{-1}\sum_{i=1}^{n}\nu_i$, and I_i is the total spin operator of all the nuclei occurring in a group of equivalent nuclei with number i. In the strong-coupling region the first operator in (1) is the perturbation with respect to the operator $\mathcal{H}_1$.

Consider the subspectrum $\{I_1, I_2, \ldots, I_n\}$. We will denote the eigenvectors of the operator $\mathcal{H}_1$ by the symbol $|I, M, (k)\rangle$, where I is the total spin of the whole system, and M is the eigenvalue of the operator I_z, and the index (k) denotes different states pertaining to the specified values of I and M. The eigenvectors of the operator $\mathcal{H}_1$ are characterized by certain values of I, since $\mathcal{H}_1$ commutes with the operator I^2. The determination of the eigenvectors and the eigenvalues reduces to diagonalizing the matrix of the operator $\mathcal{H}_1$ calculated in any system of basis vectors. In particular, we can choose vectors obtained by sequential addition of the spins $\mathbf{I}_i$. We will denote these vectors by the symbol $|I, M, k\rangle$.

For example, if n = 2 (A_aB_b spectra), the basis vectors are given by the expression

$$|I, M\rangle = \sum_{M_1} C(I_1M_1, I_2M_2; IM)\,|I_1, M_1\rangle\,|I_2, M_2\rangle, \qquad (2)$$

where $C(I_1M_1, I_2M_2; IM)$ are the Clebsch-Gordan coefficients, and $M_2 = M - M_1$; $I = I_1 + I_2, I_1 + I_2 - 1, \ldots, |I_1 - I_2|$. In this case the index k takes one value and is therefore not written, and the ba-

sis vector (2) is identical with the eigenvector of the operator $\mathcal{H}_1$. If n = 3 ($A_a B_b C_c$ spectra), then initially two spins are combined, for example, I_2 and I_3. The spin I' thereby obtained is then combined with the spin I_1.

If a = 1, and consequently I_1 = 1/2, the specified total spin I can be obtained by two methods, by combining the spin I_1 = 1/2 with the spin I' = I - 1/2 where I' = I + 1/2. Hence, k = 1, 2, and to determine the eigenvectors and the eigenvalues one must diagonalize a second-order matrix. If a = 2 and I_1 = 1, the problem reduces to diagonalizing a third-order matrix, etc.

For the eigenvalues of the operator $\mathcal{H}_1$ we will introduce the notation $E^{(0)}_{I,M,(k)}$. It can be shown that it follows from the commutativity of the operators $\mathcal{H}_1$ and I_+ that

$$\langle I, M, k' | \mathcal{H}_1 | I, M, k \rangle = \langle I, M-1, k' | \mathcal{H}_1 | I, M-1, k \rangle.$$

As a result the matrix for determining the energies $E^{(0)}_{I,M,(k)}$ agrees with the matrix for determining the energies $E^{(0)}_{I,M-1,(k)}$. Consequently, $E^{(0)}_{I,M,(k)}$ does not depend on M. In exactly the same way the coefficients $d_{I,k,k'}$, which define the superposition

$$|I, M, (k)\rangle = \sum_{k'} d_{I,k,k'} |I, M, k'\rangle,$$

also do not depend on M. Hence, the total-spin operators translate the vectors $|I, M, (k)\rangle$ into the vectors $|I, M', (k)\rangle$ with the same value of (k). Consequently, $\langle I, M', (k') | I_x | I, M, (k)\rangle = 0$ for $k' \neq k$, and transitions between states with different (k) are forbidden. Hence, all the frequencies of the zero approximation for the resolved transitions $E^{(0)}_{I,M,(k)} - E^{(0)}_{I,M-1,(k)}$ are zero (in the chosen frequency frame of reference).

The first-order correction to the frequency is

$$\langle I, M, (k) | \sum_i f_i I_{iz} | I, M, (k)\rangle - \langle I, M-1, (k) | \sum_i f_i I_{iz} | I, M-1, (k)\rangle. \tag{3}$$

We will prove that it is independent of M

$$\begin{aligned} &\left\langle M \left| \sum_i f_i I_{iz} \right| M \right\rangle - \left\langle M-1 \left| \sum_i f_i I_{iz} \right| M-1 \right\rangle = \\ &= \left\langle M-1 \left| \sum_i f_i I_{iz} \right| M-1 \right\rangle - \left\langle M-2 \left| \sum_i f_i I_{iz} \right| M-2 \right\rangle. \end{aligned} \tag{4}$$

Here and henceforth the symbols I and (k) will be omitted from the vector notation for brevity. We will rewrite Eq. (4) in the following form

$$\begin{aligned} &\left\langle M \left| \sum_i f_i I_{iz} \right| M \right\rangle - 2 \left\langle M-1 \left| \sum_i f_i I_{iz} \right| M-1 \right\rangle + \\ &+ \left\langle M-2 \left| \sum_i f_i I_{iz} \right| M-2 \right\rangle = 0. \end{aligned} \tag{5}$$

It is easy to show that after multiplication by $a^2_M a^2_{M-1}$ ($a^2_M = I(I+1) - M(M-1)$) the left side of Eq. (5) becomes

$$\left\langle M \left| a^2_M a^2_{M-1} \sum_i f_i I^2_{iz} - 2a^2_{M-1} I_+ \sum_i f_i I_{iz} I_- + I^2_+ \sum_i f_i I_{iz} I^2_- \right| M \right\rangle.$$

Using the identities

$$I_+ \sum_i f_i I_{iz} = \sum_i f_i I_{iz} I_+ - \sum_i f_i I_{i+},$$

$$I^2_+ \sum_i f_i I_{iz} = \sum_i f_i I_{iz} I^2_+ - 2 \sum_i f_i I_{i+} I_+,$$

we convert this expression to the form

$$\left\langle M \left| \sum_i f_i I_{iz} \left(\alpha_M^2 \alpha_{M-1}^2 - 2\alpha_{M-1}^2 I_+ I_- + I_+^2 I_-^2\right) + \right.\right.$$
$$\left.\left. + 2\sum_i f_i I_{i+} \left(\alpha_{M-1}^2 - I_+ I_-\right) I_- \right| M \right\rangle. \qquad (6)$$

In view of the relations

$$\left(\alpha_M^2 \alpha_{M-1}^2 - 2\alpha_{M-1}^2 I_+ I_- + I_+^2 I_-^2\right)|M\rangle = 0 \text{ и } \left(\alpha_{M-1}^2 - I_+ I_-\right) I_-|M\rangle = 0$$

the matrix element (6) is identically equal to zero, and Eq. (4) is proved.

Hence, to a first approximation the number of lines of the subspectrum $\{I_1, I_2, \ldots, I_n\}$ is equal to the number of different sets of numbers I and k. The position of the lines is determined by calculation in each specific case, but the intensities in the zeroth approximation can be calculated in general form. Summing the intensities $4|\langle I, M|I_x|I, M-1\rangle|^2$ over all M we obtain, irrespective of the value of k

$$\frac{2}{3} I (I+1)(2I+1). \qquad (7)$$

We will consider some special types of spectra in more detail.

A_aB_b **spectra.** The Hamiltonian of the perturbation in this case has the form $\frac{1}{2}(\nu_1 - \nu_2)(I_{1z} - I_{2z})$. In view of the property proved above it is sufficient to carry out the calculation for M = I. Since the frequencies of the subspectrum $\{I_1, I_2\}$ in this case are characterized solely by the value of I, they can be denoted by the symbol $(I_1, I_2; I)$. We will represent the contribution to the frequency in the form

$$\frac{1}{2}(\nu_1 - \nu_2)\langle I, I|I_{1z} - I_{2z} - I_+ (I_{1z} - I_{2z}) I_-/2I|I, I\rangle, \qquad (8)$$

where $I_\pm = I_x \pm iI_y$. As a consequence of the identities $I_+(I_{1z} - I_{2z}) = (I_{1z} - I_{2z})I_+ - I_{1+} + I_{2-}$ and $(I_+I_-/2I)|I, I\rangle = |I, I\rangle$ the matrix element (8) is equal to the matrix element

$$(4I)^{-1}(\nu_1 - \nu_2)\langle I, I|(I_{1+} - I_{2+})(I_{1-} + I_{2-})|I, I\rangle. \qquad (9)$$

To calculate expression (9) we will use the expansion (2) and the equation for the Clebsch-Gordan coefficients. As a result we obtain the following expression for the frequency:

$$(I_1, I_2; I) = (\nu_1 - \nu_2) \frac{(I_1 + I_2 - I)!\,(2I+1)!}{(I + I_1 + I_2 + 1)!\,(I - I_1 + I_2)!\,(I + I_1 - I_2)!\,2I} \times$$
$$\times \sum_{M_1} \frac{(I_1 + M_1)!\,(I + I_2 - M_1)!}{(I_1 - M_1)!\,(I_2 - I + M_1)!} (2M_1 - I) \qquad (10)$$
$$(I_1 \geqslant M_1 \geqslant I - I_2).$$

The frequencies (10) are measured from the point $\frac{1}{2}(\nu_1 + \nu_2)$.

We will also give some special cases of Eq. (10):

$$(I_1, I_2; I_1 + I_2) = \frac{I_1 - I_2}{2(I_1 + I_2)}(\nu_1 - \nu_2), \qquad (11)$$

$$(I_1, I_2; I_1 + I_2 - 1) = \frac{(I_1 - I_2)(I_1 + I_2 + 1)}{2(I_1 + I_2)(I_1 + I_2 - 1)}(\nu_1 - \nu_2), \qquad (12)$$

$$(I_1, I_2; I_1 + I_2 - 2) = \frac{(I_1 - I_2)(I_1 + I_2 + 1)}{2(I_1 + I_2 - 1)(I_1 + I_2 - 2)}(\nu_1 - \nu_2). \qquad (13)$$

The energies of the zeroth approximation, which are compensated when calculating the frequency, have the value

$$E^0_{I,M} = \frac{1}{2} J_{12}[I(I+1) - I_1(I_1+1) - I_2(I_2+1)]. \qquad (14)$$

We will find the position of the frequencies obtained on the energy diagram. The en-

ergy diagram for the subspectrum $\left\{\frac{1}{2}, I_2\right\}$ is shown in Fig. 1a. (More detail is given of these energy diagrams in [3, 4]). To be specific we will choose the value $I_2 = 5/2$. We will assume that $\nu_1 > \nu_2$, $J_{12} > 0$. In the limit of weak coupling the energies on each horizontal of the diagram increase from left to right. Since one of the roots of the quadratic equation is greater than the other for all values of the constant field, in the limit of strong coupling the energies must also increase from left to right. Hence, it follows from expression (14) that the points corresponding to maximum I (in this case I = 3), are rotated to the right. Transitions, allowed in the limit of strong coupling, are denoted in Fig. 1a by double lines. The frequencies situated along each double line, straight or broken, are the same. The values of both frequencies of the subspectrum $\left\{\frac{1}{2}, \frac{5}{2}\right\}$ are determined by Eqs. (11) and (12).

In the case of the subspectra $\{1, I_2\}$ $(I_2 \geqslant 1)$ the expressions for the energy for arbitrary coupling are solutions of equations not higher than the third degree (see Fig. 1b). The three roots of the equation of the third degree, as a consequence of the inequalities

$$\cos\frac{\varphi}{3} \geqslant -\cos\frac{\varphi+\pi}{3} \geqslant -\cos\frac{\varphi-\pi}{3} \qquad (0 \leqslant \varphi \leqslant \pi) \tag{15}$$

preserve a certain sequence in order of decrease for all values of the constant magnetic field. Hence, as in the previous case, in the limit of strong coupling the value of I on each horizontal of the diagram increases from left to right. Permitted transitions in Fig. 1b are also distinguished by double lines.

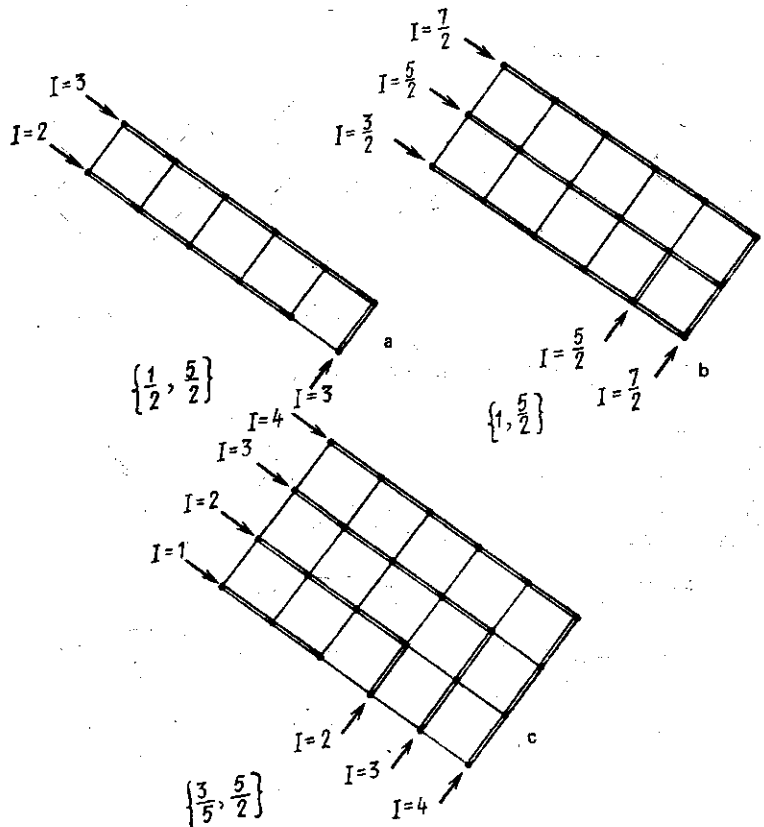

Fig. 1. Energy diagrams for the subspectra (I_1, I_2).
Correction. In Fig. 1b instead of three ordinary lines (see Fig. 1c), three double lines are incorrectly drawn.

This scheme can be generalized to the case of large values of I_1 (see, in particular, Fig. 1c), if the energies as a function of the field H_0 do not intersect. However, the problem of intersection can be eliminated if we assume that the continuation of the function which is large before intersection is a large function after intersection. Then the position scheme of the permitted transitions in the limit of strong coupling will always

be determined by diagrams of type 1c and by similar diagrams for large I_1.

The ABC spectrum. The energy diagram of an ABC system is shown in Fig. 2a, where the notation of the states relates to a system with arbitrary value of the coupling. As usual, α and β denote the z-projection of the spin ½ and -½. In accordance with the symbols used in [3, 4], $|(\beta\alpha\alpha)\rangle$ means the state which transfers in the limit of weak coupling into the pure state $|\beta\alpha\alpha\rangle$, etc.

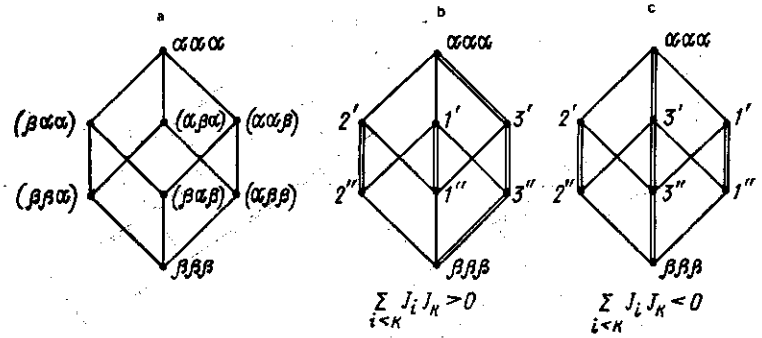

Fig. 2. Energy diagrams for the ABC spectrum.

We will give, without derivation, expressions for the energies in the limit of weak coupling up to the first approximation of perturbation theory. These expressions can be obtained by the method considered in the first section. For the state vectors $|I, M, (k)\rangle$ we will introduce a more abbreviated notation. Detailed expressions for the state vectors in terms of the basis vectors $|\alpha\rangle$ and $|\beta\rangle$ will not be given here

$$
\begin{aligned}
|\alpha\alpha\alpha\rangle &= \left|\tfrac{3}{2},\ \tfrac{3}{2}\right\rangle & E_{\alpha\alpha\alpha} &= \tfrac{1}{4}\sum_i J_i,\\
|1'\rangle &= \left|\tfrac{1}{2},\ \tfrac{1}{2},\ (1)\right\rangle & E_{1'} &= -\tfrac{1}{4}\sum_i J_i + D - \sum_i f_i J_i/4D,\\
|2'\rangle &= \left|\tfrac{1}{2},\ \tfrac{1}{2},\ (2)\right\rangle & E_{2'} &= -\tfrac{1}{4}\sum_i J_i - D + \sum_i f_i J_i/4D,\\
|3'\rangle &= \left|\tfrac{3}{2},\ \tfrac{1}{2}\right\rangle & E_{3'} &= \tfrac{1}{4}\sum_i J_i,\\
|1''\rangle &= \left|\tfrac{1}{2},\ -\tfrac{1}{2},\ (1)\right\rangle & E_{1''} &= -\tfrac{1}{4}\sum_i J_i + D + \sum_i f_i J_i/4D,\\
|2''\rangle &= \left|\tfrac{1}{2},\ -\tfrac{1}{2},\ (2)\right\rangle & E_{2''} &= -\tfrac{1}{4}\sum_i J_i - D - \sum_i f_i J_i/4D,\\
|3''\rangle &= \left|\tfrac{3}{2},\ -\tfrac{1}{2}\right\rangle & E_{3''} &= \tfrac{1}{4}\sum_i J_i,\\
|\beta\beta\beta\rangle &= \left|\tfrac{3}{2},\ -\tfrac{3}{2}\right\rangle & E_{\beta\beta\beta} &= \tfrac{1}{4}\sum_i J_i,
\end{aligned}
\qquad (16)
$$

$$
D = \tfrac{1}{2}\Big(\sum_i J_i^2 - \sum_{i<k} J_i J_k\Big)^{1/2},
$$

$$
J_1 = J_{23},\ J_2 = J_{13},\ J_3 = J_{12}.
$$

The frequencies and intensities of the permitted transitions have the following values:

$$
\begin{aligned}
&\beta\beta\beta \to 3'',\ 3'' \to 3',\ 3' \to \alpha\alpha\alpha && 0; && 10\\
&1'' \to 1' && -\sum_i f_i J_i/2D; && 1\\
&2'' \to 2' && \sum_i f_i J_i/2D; && 1
\end{aligned}
\qquad (17)
$$

The origin of the frequency frame of reference is at the point $\frac{1}{3}(\nu_1+\nu_2+\nu_3)$.

Without loss of generality we can assume that $\nu_1>\nu_2>\nu_3$. Then, as in the version of the previous section, it follows from inequalities (15) that the energies along each horizontal level of the energy diagram increase from left to right. On the other hand, the relation between the energies $E_{1'}, E_{2'}, E_{3'}$ depends on the sign of the quantity $\sum_{i<k} J_iJ_k$. We will conditionally assume that $\sum_i J_i>0$. Then for $\sum_{i<k} J_iJ_k>0$ the inequality $\frac{1}{2}\sum_i J_i>D$ is satisfied, and, consequently, $E_{3'}>E_{1'}>E_{2'}$. As a result these energies are identified with the energies of diagram 2a as follows:

$$E_{3'}=E_{(\alpha\alpha\beta)},\ E_{1'}=E_{(\alpha\beta\alpha)},\ E_{2'}=E_{(\beta\alpha\alpha)}.$$

Similarly

$$E_{3''}=E_{(\alpha\beta\beta)},\ E_{1''}=E_{(\beta\alpha\beta)},\ E_{2''}=E_{(\beta\beta\alpha)}.$$

This version is shown in Fig. 2b, the permitted transition being denoted by the double lines. The energy identification version for the case $\sum_{i<k} J_iJ_k<0$ is shown in Fig. 2c.

Conclusion. From the general theory considered in the first section it follows that the energies cannot in all cases be calculated in analytical form since higher-order equations may occur. However, for any spectrum we can determine the number of lines in the limit of strong coupling and the intensities of these lines.

As far as the practical application of this theory is concerned we can say the following. Spectra in the region of strong coupling contain a relatively small number of lines and are therefore more easily interpreted. But these spectra, generally speaking, gives less information on the parameters ν_i, J_{ik} than spectra in other regions. On the other hand, each form of spectrum in the region of strong coupling has its own characteristic structure, and these spectra can be used to recognize one form of spectrum or another if it was previously unknown. It is not difficult in principle to reach the region of strong coupling, for which one must observe resonance in relatively weak magnetic fields. But in order to obtain useful information one must be able to observe the fine structure of the spectrum, i.e., splitting of the order of $|\nu_i-\nu_j|$. Since one must at the same time satisfy the condition $|\nu_i-\nu_j|\ll|J_{kl}|$, this can only be achieved for fairly large values of $|J_{kl}|$, for example, in the case of resonance in heavy nuclei.

The results obtained have much greater practical applications not so much in the strong-coupling region, but in the regions close to it, or even in the medium-coupling region. Data on the nature of the spectrum in the strong-coupling region enable one to determine with some probability the movement of lines in intermediate regions when the constant magnetic field is reduced. In particular, one can establish which lines have a tendency to a reduction in intensity with simultaneous motion to the periphery of the spectrum, which lines increase in intensity and are grouped in the center of the spectrum, and which of these lines have a tendency to converge. All these results can be used with reference to spectral lines observed for a fixed value of constant field.

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