37. *Composite Particle Technique for* AB_4 *Nuclear Resonance Systems.*

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By regarding each group of identical nuclei as a composite particle of fixed total-spin, spectra of the AB_4 nuclear resonance system have been readily calculated.

THE solution of the secular determinant for a nuclear magnetic system, arising from the usual spin Hamiltonian, is normally difficult when the number of nuclei involved increases above about three.[1] Where there are equivalent nuclei, however, simplifications are possible by using group theoretical techniques.[2] A further technique which is valuable for an A_mB_n system is that of the composite particle.[3] Here each group of identical nuclei is considered as a composite particle with fixed total spin. The advantage is that it is unnecessary to determine the explicit form of the zero-order eigen-functions. The method has been applied previously[3] to the A_2B_6 system and we have recently[4, 5] used it to calculate spectra for the AB_4 system. Here we now outline its application to the latter system and give values of energies and intensities. The feature of A_mB_n systems is that the spectrum depends only on the ratio $R = J_{AB}/\delta_{AB}$, where J_{AB} is the coupling constant between A and B groups and δ is their chemical-shift difference.

The basis of the composite-particle method lies in the fact that wave-functions do not mix if they have different eigen-value of $\mathbf{I}_A{}^2$ or of $\mathbf{I}_B{}^2$, where $\mathbf{I}$ is the total spin angular momentum operator of a group. States with eigen-values $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ of the total spin are designated *S*, *D*, *T*, *Q*, *Qt*, *Sx*, ... This refers to the $(2J + 1)$ possible values for the *z*-component of the spin of the composite particle. The possible overall spin states are the possible combinations of the separate spin states of the A and the B groups. The required matrix elements are obtained for given eigen-values of $\mathbf{I}_A{}^2$ and $\mathbf{I}_B{}^2$ from the general angular momentum matrices corresponding to these eigen-values. For a given state the secular determinant is

$$|\mathscr{H}_{mn} - \delta_{mn}E| = |-\nu_A\mathbf{I}_z{}^A \times \mathbf{I}^B - \nu_B\mathbf{I}^A \times \mathbf{I}_z{}^B + J_{AB}(\mathbf{I}_x{}^A \times \mathbf{I}_x{}^B + \mathbf{I}_y{}^A \times \mathbf{I}_y{}^B + \mathbf{I}_z{}^A \times \mathbf{I}_z{}^B) - E\mathbf{I}^A \times \mathbf{I}^B|$$

where $\mathbf{I}_x{}^A$, $\mathbf{I}_y{}^A$, and $\mathbf{I}_z{}^A$ are the Pauli matrices of the components of angular momentum corresponding to the eigen-value J. $\mathbf{I}^A$ and $\mathbf{I}^B$ are unit matrices of order $(2J + 1)$, and

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[1] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw Hill Book Co., New York, 1959.

[2] Waugh and Dobbs, *J. Chem. Phys.*, 1959, **31**, 1235.

[3] Pople and Schaeffer, *Mol. Phys.*, 1960, **3**, 547; Whitman, Onsager, Saunders, and Dubb, *J. Chem. Phys.*, 1960, **32**, 67.

[4] Harris and Packer, *J.*, 1961, 4736.

[5] Chapman, *J.*, in the press.

TABLE 1.

Submatrices for the AB_4 system.

Total I_z	Spin state	Diagonal element	Off-diagonal element	Total I_z	Spin state	Diagonal element	Off-diagonal element
$-\frac{1}{2}$	$D^{-\frac{1}{2}}S^{\circ}$	0		$-\frac{3}{2}$	$D^{\frac{1}{2}}Qt^{-2}$	$4 - 2R$	$2R$
$\frac{1}{2}$	$D^{\frac{1}{2}}S^{\circ}$	0		$-\frac{3}{2}$	$D^{-\frac{1}{2}}Qt^{-1}$	$2 + R$	
$-\frac{3}{2}$	$D^{-\frac{1}{2}}T^{-1}$	$2 + R$		$-\frac{1}{2}$	$D^{\frac{1}{2}}Qt^{-1}$	$2 - R$	$R\sqrt{6}$
$-\frac{1}{2}$	$D^{\frac{1}{2}}T^{-1}$	$2 - R$	$R\sqrt{2}$	$-\frac{1}{2}$	$D^{-\frac{1}{2}}Qt^{\circ}$	0	
$-\frac{1}{2}$	$D^{-\frac{1}{2}}T^{\circ}$	0		$\frac{1}{2}$	$D^{\frac{1}{2}}Qt^{\circ}$	0	$R\sqrt{6}$
$\frac{1}{2}$	$D^{\frac{1}{2}}T^{\circ}$	0	$R\sqrt{2}$	$\frac{1}{2}$	$D^{-\frac{1}{2}}Qt^{1}$	$-2 - R$	
$\frac{1}{2}$	$D^{-\frac{1}{2}}T^{1}$	$-2 - R$		$\frac{3}{2}$	$D^{\frac{1}{2}}Qt^{1}$	$-2 + R$	$2R$
$\frac{3}{2}$	$D^{\frac{1}{2}}T^{1}$	$-2 + R$		$\frac{3}{2}$	$D^{-\frac{1}{2}}Qt^{2}$	$-4 - 2R$	
$-\frac{5}{2}$	$D^{-\frac{1}{2}}Qt^{-2}$	$4 + 2R$		$\frac{5}{2}$	$D^{\frac{1}{2}}Qt^{2}$	$-4 + 2R$	

Note. The elements are given in multiples of half the chemical shift δ_{AB}. Diagonal terms leading to the appearance of ν_A in each transition energy have been omitted; this implies that ν_A has been taken as the arbitrary origin for the transitions.

TABLE 2.

Energies and intensities for AB_4 and AX_4 systems.

Spin state	AB_4 energy	AB_4 Relative intensity	AX4 relative intensity	Assign-ment	Line no.
DS	-4	1	2	A	1
DT	$P_1 - (2 - 3R)$	$\sqrt{2}\cos\theta_1 - \sin\theta_1$	6	B	2
	$-P_1 - (2 - 3R)$	$\cos\theta_1 + \sqrt{2}\sin\theta_1$	3	A	3
	$-(P_1 - P_2)$	$\sqrt{2}\cos\theta_1\cos\theta_2 - \cos\theta_1\sin\theta_2 + \sqrt{2}\sin\theta_1\sin\theta_2$	6	B	4
	$-(P_1 + P_2)$	$\cos\theta_1\cos\theta_2 + \sqrt{2}\cos\theta_1\sin\theta_2 - \sqrt{2}\sin\theta_1\cos\theta_2$	3	A	5
	$P_1 + P_2$	$-\sqrt{2}\cos\theta_1\sin\theta_2 + \sqrt{2}\sin\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2$	0	Comb	6
	$P_1 - P_2$	$\sqrt{2}\cos\theta_1\cos\theta_2 + \sin\theta_1\cos\theta_2 + \sqrt{2}\sin\theta_1\sin\theta_2$	6	B	7
	$-P_2 - (2 + 3R)$	$\cos\theta_2 - \sqrt{2}\sin\theta_2$	3	A	8
	$P_2 - (2 + 3R)$	$\sqrt{2}\cos\theta_2 + \sin\theta_2$	6	B	9
DQt	$P_3 - (2 - 5R)$	$2\cos\theta_3 - \sin\theta_3$	4	B	10
	$-P_3 - (2 - 5R)$	$\cos\theta_3 + 2\sin\theta_3$	1	A	11
	$-(P_3 - P_4)$	$\sqrt{6}\cos\theta_3\cos\theta_4 - \cos\theta_3\sin\theta_4 + 2\sin\theta_3\sin\theta_4$	6	B	12
	$-(P_3 + P_4)$	$\cos\theta_3\cos\theta_4 + \sqrt{6}\cos\theta_3\sin\theta_4 - 2\sin\theta_3\cos\theta_4$	1	A	13
	$P_3 + P_4$	$-2\cos\theta_3\sin\theta_4 + \sqrt{6}\sin\theta_3\cos\theta_4 - \sin\theta_3\sin\theta_4$	0	Comb	14
	$P_3 - P_4$	$2\cos\theta_3\cos\theta_4 + \sin\theta_3\cos\theta_4 + \sqrt{6}\sin\theta_3\sin\theta_4$	4	B	15
	$-(P_4 - P_5)$	$\sqrt{6}\cos\theta_4\cos\theta_5 - \cos\theta_4\sin\theta_5 + \sqrt{6}\sin\theta_4\sin\theta_5$	6	B	16
	$-(P_4 + P_5)$	$\cos\theta_4\cos\theta_5 + \sqrt{6}\cos\theta_4\sin\theta_5 - \sqrt{6}\sin\theta_4\cos\theta_5$	1	A	17
	$P_4 + P_5$	$-\sqrt{6}\cos\theta_4\sin\theta_5 + \sqrt{6}\sin\theta_4\cos\theta_5 - \sin\theta_4\sin\theta_5$	0	Comb	18
	$P_4 - P_5$	$\sqrt{6}\cos\theta_4\cos\theta_5 + \sin\theta_4\cos\theta_5 + \sqrt{6}\sin\theta_4\sin\theta_5$	6	B	19
	$-(P_5 - P_6)$	$2\cos\theta_5\cos\theta_6 - \cos\theta_5\sin\theta_6 + \sqrt{6}\sin\theta_5\sin\theta_6$	4	B	20
	$-(P_5 + P_6)$	$\cos\theta_5\cos\theta_6 + 2\cos\theta_5\sin\theta_6 - \sqrt{6}\sin\theta_5\cos\theta_6$	1	A	21
	$P_5 + P_6$	$-\sqrt{6}\cos\theta_5\sin\theta_6 + 2\sin\theta_5\cos\theta_6 - \sin\theta_5\sin\theta_6$	0	Comb	22
	$P_5 - P_6$	$\sqrt{6}\cos\theta_5\cos\theta_6 + \sin\theta_5\cos\theta_6 + 2\sin\theta_5\sin\theta_6$	6	B	23
	$-P_6 - (2 + 5R)$	$\cos\theta_6 - 2\sin\theta_6$	1	A	24
	$P_6 - (2 + 5R)$	$2\cos\theta_6 + \sin\theta_6$	4	B	25

The energies are given as $4(E/\delta_{AB} - 1)$ where E is the position of a given line relative to ν_A, in the same units as the chemical shift δ_{AB}; a positive term indicates a high-field shift.

The intensities in column 3 are given as $(Z/\gamma)^{\frac{1}{2}}$ where Z is the intensity relative to that of the *DS* line as 2, and γ is the degeneracy of the spin state (2 for *DS*; 3 for *DT*; 1 for *DQ*t). The various values of the parameters P and θ are as follows:

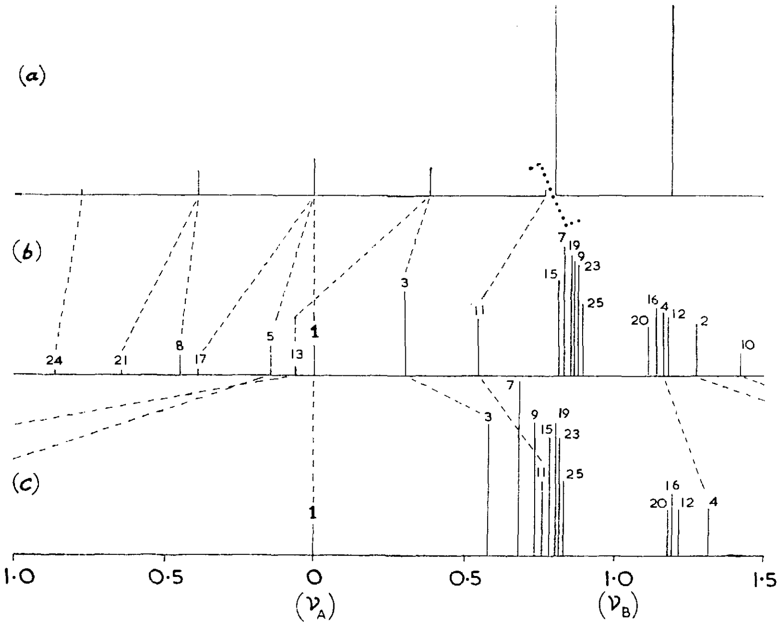
Subscript	P^2	$\tan 2\theta$	Subscript	P^2	$\tan 2\theta$
1	$(2 - R)^2 + 8R^2$	$R2\sqrt{2}/(2 - R)$	4	$P_1^2 + 16R^2$	$\sqrt{3}(\tan 2\theta_1)$
2	$(2 + R)^2 + 8R^2$	$R2\sqrt{2}/(2 + R)$	5	$P_2^2 + 16R^2$	$\sqrt{3}(\tan 2\theta_2)$
3	$(2 - 3R)^2 + 16R^2$	$4R/(2 - 3R)$	6	$(2 + 3R)^2 + 16R^2$	$4R/(2 + 3R)$

P is taken as $+\sqrt{P^2}$, and $\tan 2\theta$ between 0 and π. The line numbers are those used in the text.

ν_A and ν_B are the Larmor frequencies of the A and B nuclei. The superscripts denote the composite group.

The energies of the transitions are obtained after diagonalisations of the secular determinant.

Thus, with the AB_4 system the single proton forms a D particle with spin $\frac{1}{2}$, whilst the four equivalent protons form S, T, and Qt states of spin 0, 1, and 2. The overall spin states possible are then D_AS_B, D_AT_B, and D_AQt_B, with degeneracies 2, 3, and 1, respectively. In this way the D_AT_B state gives rise to a pair of two by two matrices and the D_AQt_B state gives four two-by-two matrices. The energy values can hence be obtained. The complete spectrum is a combination of the lines from these three states.



AB_4 spectra for differing values of R ($= J/\delta$).
(*a*) $R \rightarrow 0$ ($\delta \rightarrow \infty$). (*b*) $R \sim 0{\cdot}4$ (J as for *a*). (*c*) $R \sim 2{\cdot}0$ (δ as for *b*).
Intensity scale of (*b*) and (*c*) is $2\frac{1}{2}$ times that of (*a*). The greatest intensity of any line off scale in (*c*) is only one-tenth of that of line 1.
The horizontal scale of (*b*) and (*c*) is in units of δ_{AB}.

The relative transition probabilities can be estimated by the direct use of the angular momentum matrices.

If ϕ_p and ϕ_q are eigen-functions of states p and q, and if Z_{pq} is the relative transition probability between these states,

then
$$\phi_p = \sum_i C_{pi}(\phi_{Ai}\phi_{Bi}) \text{ and } \phi_q = \sum_j C_{qj}(\phi_{Aj}\phi_{Bj});$$
$$Z_{(pq)} = \{\sum_{ij} C_{pi}C_{qj}[(I_{Ax})_{ij}\delta_{ij}^{B} + \delta_{ij}^{A}(I_{Bx})_{ij}]\}^2$$
where $\delta_{ij}^B = 1$ if ϕ_{Bi} has the same eigen-value of $\boldsymbol{I}_z$ as ϕ_{Bj} and otherwise is zero; similarly for δ_{ij}^A.

From the energy levels of the spin system the coefficients of the corresponding eigenfunctions are obtained and used to determine the relative transition probabilities. The intensities have to be weighted depending upon the degeneracies of the spin states of A and B.

We show in Table 1 the sub-matrices with the diagonal and off-diagonal elements for the AB_4 system; in Table 2 are listed the explicit forms for the energies and intensities of the transition. A comparison with the AX_4 situation is also given.

There are some features of the AB_4 resonance spectra of interest: (*a*) The *DS* line (1) is constant in intensity and in the unshifted position at ν_A. (*b*) Lines marked 20 and 23, 16 and 19, 4 and 7, and 12 and 15 are symmetrically grouped about ν_B; the chemical shift may therefore be obtained by direct measurement after assignment of the spectrum, *e.g.*, $\delta_{AB} = (E_7 - E_1) + (E_4 - E_7)$. (*c*) The coupling constant may also be obtained by means of a relationship such as: $3|J_{AB}| = 2(E_3 - E_8) - (E_4 - E_7)$. This provides a simple and direct method for obtaining the coupling constant if there is sufficient resolution. It eliminates laborious fitting procedures. These direct calculations, however, depend upon the assignment of the lines, the values of R ($= J/\delta$) and the resolution of the lines.

As R increases so that perturbation from the AX_4 case occurs, it is more marked with the A than with the B group of lines (see Figure). As $R > 1$, lines 24, 21, 8, 17, 5, and 13 move away from the other lines and decrease to negligible intensity, whilst among the group lines 2 and 10 behave similarly. For $R = 2$ three distinct groups of lines occur: line 1 at ν_A and constant in intensity; lines 3 (A), 7 and 9 (B), 11 (A), and 15, 19, 23, and 25 (all B) of high intensity; and lines 20, 16, 12, and 4 (B) of lower intensity. As R approaches infinity, collapse into a single line occurs.

The contribution to the B lines from the *DQt* state is not always less intense than that from the *DT* state, although the degeneracy is less. The contribution to the A lines is usually less intense.

The expressions for line positions and intensities in Table 2 may be used for any other A_mB_n nuclear magnetic system in which the *DS*, *DT*, and *DQt* states are present, with the single alteration of the degeneracies used. This is particularly useful for systems where $m = 1$ and n is even.

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