

## Proton Magnetic Resonance of Symmetrical Molecules

### IV. The Analysis of $A_2B_2X$ Spectra by Perturbation Methods

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In the analysis of  $A_2B_2X$  spectra the  $A_2B_2$  part is conveniently analysed as two superimposed simple  $A_2B_2$  multiplets. These can in favourable cases be analysed by perturbation methods, which can also be extended to the X part of the spectrum. In this paper the  $A_2R_2X$ ,  $(AR)_2X$  and  $(AB)_2X$  approximations are discussed. In the  $A_2R_2X$  approximation the  $A_2B_2$  part is considered as two almost independent  $A_2$  and  $R_2$  systems, in the  $(AR)_2X$  approximation as two almost independent AR systems and in the  $(AB)_2X$  approximation as two almost independent AB systems. Expressions are given for the X transitions to first and second order in these approximations. As examples spectra of *p*-bromofluorobenzene, *p*-chlorofluorobenzene and 4,4'-difluorodiphenyl are studied. The spectrum of *p*-fluoroanisole is also analysed by exact methods.

#### 1. INTRODUCTION

The analysis of an NMR spectrum can be simplified to a large extent if the molecule shows symmetry properties. The Hamiltonian matrix can then, in addition to the factorization according to different eigenvalues of  $F_z$ , be further factorized according to the symmetries of the molecule. A recurring example is the  $A_2B_2$  system where the general  $16 \times 16$  matrix is reduced to two  $1 \times 1$ , five  $2 \times 2$  matrices, and one  $4 \times 4$  matrix. Although this is a considerable reduction of the secular equation, this  $4 \times 4$  matrix cannot be transformed to diagonal form in the general case, and the expressions for all transition frequencies and intensities cannot be obtained in analytical form. Thus the  $4 \times 4$  matrix must be handled by other methods, the conventional one being numerical diagonalization.

In some  $A_2B_2$  cases the Hamiltonian matrix can be treated by perturbation methods in which a suitable choice of the zeroth order functions leads to the approximate diagonalization of the troublesome  $4 \times 4$  matrix. In the foregoing papers of this series\* we have discussed the analysis of  $A_2B_2$  spectra by the

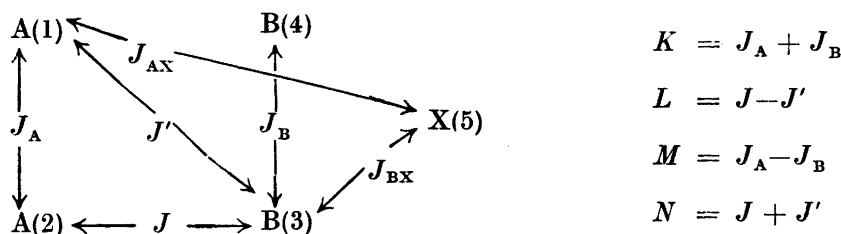
\* Paper I: see Ref.<sup>1</sup> Paper II: see Ref.<sup>2</sup> Paper III: see Ref.<sup>3</sup>

so-called  $A_2B_2$ ,  $(AR)_2$  and  $(AB)_2$  approximations and applied them to several examples.\*

These perturbation methods may be extended and applied to somewhat more complicated systems like the  $A_2B_2X$  case. The  $A_2B_2$  part of such a spectrum can be regarded as two overlapping  $A_2B_2$  patterns, each of which may possibly be treated by one of these perturbation methods. An analysis of the ring-proton spectrum of *p*-nitrobenzaldehyde along these lines has been reported in paper III of this series. However, the X part of the spectrum may also be simply calculated by these approximations, from which tractable expressions for the transition frequencies and intensities can be derived.

## 2. THEORY

In the  $A_2B_2X$  case we define the parameters in the following way:



where the quantities  $K$ ,  $L$ ,  $M$ , and  $N$  are those conventionally introduced in the  $A_2B_2$  case.<sup>4-6</sup>

The couplings  $J_{AX}$  and  $J_{BX}$  are assumed to be very small compared to the corresponding relative shifts, *i.e.* we have a strict  $A_2B_2X$  case. Then  $F_x$  of the X nucleus will be a good quantum number, *i.e.* terms in the Hamiltonian containing the other spin components of X can be neglected. As has been discussed by Pople *et al.*,<sup>7,8</sup> the Hamiltonian can then be rewritten in such a way that new "effective" Larmor frequencies

$$\nu_A^* = \nu_A + x \times J_{AX}; \quad \nu_B^* = \nu_B + x \times J_{BX}$$

are introduced for the A and B nuclei.

The A and B nuclei will thus experience an additional magnetic field from the X nucleus, the value of which depends upon the quantum number  $F_x(X) = x$  of the X nucleus.

From the selection rules for the  $A_2B_2$  transitions,  $\Delta F_x(A_2B_2) = \pm 1$ ,  $\Delta x = 0$ , one then realizes that the  $A_2B_2$  part of the spectrum will consist of two simple overlapping  $A_2B_2$  patterns belonging to the two different eigenvalues of  $F_x(X)$ , *i.e.* one belongs to spin  $\alpha$  of the X nucleus and the other to spin  $\beta$ .

\* The large-shift  $A_2B_2$  approximations were then actually denoted  $A_2X_2$  and  $(AX)_2$ . We change notation in this paper, however, in order to avoid confusion with the X nucleus in the  $A_2B_2X$  system to be discussed.

The different effective Larmor frequencies are then obtained from the analysis of these patterns.

For the X transitions we have the selection rules  $\Delta x = \pm 1$  and  $\Delta F_x(A_2B_2) = 0$ . The X part of the spectrum can thus be calculated from a knowledge of the eigenvalues and eigenfunctions of these two  $A_2B_2$  patterns with different effective Larmor frequencies.

The two simple  $A_2B_2$  multiplets will have the apparent relative shifts

$$\delta\nu^+ = \nu_A - \nu_B + \frac{1}{2}(J_{AX} - J_{BX})$$

$$\delta\nu^- = \nu_A - \nu_B - \frac{1}{2}(J_{AX} - J_{BX})$$

corresponding to spin state  $\alpha$  or  $\beta$ , respectively, of the X nucleus. It is also seen that the two symmetrical  $A_2B_2$  multiplets will be centered upon  $(\nu_A + \nu_B)/2 + (J_{AX} + J_{BX})/4$  and  $(\nu_A + \nu_B)/2 - (J_{AX} + J_{BX})/4$ , respectively, giving two symmetry points that should easily be identified in the experimental spectrum.

Most of the information needed to evaluate the parameters characterizing the spectrum can be obtained from the  $A_2B_2$  part. The analysis of the two  $A_2B_2$  patterns gives  $K$ ,  $L$ ,  $M$ , and  $N$  twice over as well as the difference of the X couplings, while the separation of the centers of these patterns gives the sum of the X couplings. However, to differentiate between the possible X couplings, and to determine the signs of these couplings relative to any  $A_2B_2$  coupling one also has to study the X part of the spectrum.

The analysis of the  $A_2B_2$  part of the spectrum has thus been reduced to the simpler problem of analysing two  $A_2B_2$  multiplets. In several cases these can be treated by the perturbation methods that have been discussed in detail in the previous papers of this series. Formulae pertinent to the large-shift  $A_2R_2$  and  $(AR)_2$  approximations can be found in paper II, while the  $(AB)_2$  approximation is developed in paper III.

These perturbation treatments can now be extended to the X part of the  $A_2B_2X$  spectrum. In general, to calculate the X spectrum, it is necessary to know the eigenvalues and eigenfunctions of the two discussed  $A_2B_2$  patterns of the spectrum, and use the selection rules  $\Delta x = \pm 1$ ,  $\Delta F_x(A_2B_2) = 0$ . The approximate eigenfunctions of the  $A_2R_2$ ,  $(AR)_2$  and  $(AB)_2$  approximations and their energies to first and second order can then evidently be applied to calculate the transition frequencies and intensities in the X part of the spectrum. The diagonalizations of the two  $4 \times 4$  matrices which are necessary in the general case can thus be circumvented.

In the  $A_2R_2$  approximation, it is assumed that the relative shift  $\nu_A - \nu_B$  is much larger than the related coupling constants, *i.e.* the  $A_2B_2$  system is regarded as two almost independent  $A_2$  and  $R_2$  systems, where the couplings are introduced as perturbations. If this assumption is valid it is clear that the X part of the  $A_2B_2X$  spectrum will consist of a triplet of triplets, the splittings of the triplets simply being  $J_{AX}$  and  $J_{BX}$ . This result is also obtained by using the first order terms for the energies of an  $A_2B_2$  system in this approximation given in Tables 1 and 2 of paper II. The transition frequencies are collected in Table 1. The intensities obtained from the zeroth order basis functions are constant. The transitions, *e.g.*  $1s_1(\beta) \rightarrow 1s_1(\alpha)$ , are labelled by the corresponding

Table 1. Transition frequencies  $\nu$  for the X transitions in the  $A_2R_2X$  and  $(AR)_2X$  approximations to first and second order.<sup>b</sup>

Transition No. Assignment	$A_2R_2X$ and $(AR)_2X$ First order	$(AR)_2X$ Second order corrections	Transition frequency relative $\nu_X$		$A_2R_2X$ Generalized second order corrections
			$A_2R_2X$ Restricted second order corrections	$(AR)_2X$ Second order corrections	
1 $s_2(\beta) \rightarrow s_2(\alpha)$	$J_{AX} + J_{BX}$				
2 $1s_1(\beta) \rightarrow 1s_1(\alpha)$	$J_{BX}$	$-\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$-\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$-\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	
3 $2s_1(\beta) \rightarrow 2s_1(\alpha)$	$J_{AX}$	$+\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$+\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$+\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	
4 $1s_0(\beta) \rightarrow 1s_0(\alpha)$	$-J_{AX} + J_{BX}$	$-\frac{(N+L)^2}{8} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$-\frac{N^2 + L^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$-\frac{1}{2}(L\cos\theta_s + N\sin\theta_s)^2 \left[ \frac{1}{2\delta\nu + N - 2K - L\tan\theta_s} \right]_{\delta\nu^-}$ $-\frac{1}{2}(L\sin\theta_s - N\cos\theta_s)^2 \left[ \frac{1}{2\delta\nu + N + L\tan\theta_s} \right]_{\delta\nu^-}$	
5 $2s_0(\beta) \rightarrow 2s_0(\alpha)$	$J_{AX} - J_{BX}$	$+\frac{(N+L)^2}{8} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$+\frac{N^2 + L^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	$+\frac{1}{2}(L\cos\theta_s + N\sin\theta_s)^2 \left[ \frac{1}{2\delta\nu - N + 2K + L\tan\theta_s} \right]_{\delta\nu^-}$ $+\frac{1}{2}(L\sin\theta_s - N\cos\theta_s)^2 \left[ \frac{1}{2\delta\nu - N - L\tan\theta_s} \right]_{\delta\nu^-}$	
6 $3s_0'(\beta) \rightarrow 3s_0'(\alpha)$	0			$+\frac{1}{2}(L\cos\theta_s + N\sin\theta_s)^2 \left[ \frac{1}{2\delta\nu + N - 2K - L\tan\theta_s} \right]_{\delta\nu^-}$ $-\frac{1}{2\delta\nu - N + 2K + L\tan\theta_s} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	
7 $4s_0'(\beta) \rightarrow 4s_0'(\alpha)$	0			$+\frac{1}{2}(L\sin\theta_s - N\cos\theta_s)^2 \left[ \frac{1}{2\delta\nu + N + L\tan\theta_s} \right]_{\delta\nu^-}$ $-\frac{1}{2\delta\nu - N - L\tan\theta_s} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-}$	

8	$1s_{-1}(\beta) \rightarrow 1s_{-1}(\alpha)$	$-J_{\text{BX}}$	$+\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$+\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$	$+\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$+\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$
9	$2s_{-1}(\beta) \rightarrow 2s_{-1}(\alpha)$	$-J_{\text{AX}}$	$-\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$-\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$	$-\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$-\frac{N^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$
10	$s_{-2}(\beta) \rightarrow s_{-2}(\alpha)$	$-J_{\text{AX}} - J_{\text{BX}}$				
11	$1a_1(\beta) \rightarrow 1a_1(\alpha)$	$J_{\text{BX}}$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu+M}\right]\delta\nu^+$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu+M}\right]\delta\nu^-$
12	$2a_1(\beta) \rightarrow 2a_1(\alpha)$	$J_{\text{AX}}$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu+M}\right]\delta\nu^+$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu+M}\right]\delta\nu^-$
13	$1a_0'(\beta) \rightarrow 1a_0'(\alpha)$	0				
14	$2a_0'(\beta) \rightarrow 2a_0'(\alpha)$	0				
15	$1a_{-1}(\beta) \rightarrow 1a_{-1}(\alpha)$	$-J_{\text{BX}}$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu-M}\right]\delta\nu^+$	$+\frac{L^2}{4}\left[\frac{1}{\delta\nu-M}\right]\delta\nu^-$
16	$2a_{-1}(\beta) \rightarrow 2a_{-1}(\alpha)$	$-J_{\text{AX}}$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^+$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu}\right]\delta\nu^-$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu-M}\right]\delta\nu^+$	$-\frac{L^2}{4}\left[\frac{1}{\delta\nu-M}\right]\delta\nu^-$

<sup>a</sup> The relative intensities of all transitions to lowest order are equal.

<sup>b</sup> The angles are defined by  $\tan 2\theta_s = L/K$  and  $\tan 2\theta_e = L/M$ .

$A_2B_2$  eigenfunctions involved in the transition followed by the changing spin state of the X nucleus. Only the "allowed" transitions are considered; the "forbidden" transitions of type  $1s_1(\beta) \rightarrow 2s_1(\alpha)$ , in which the state function of the  $A_2B_2$  part is changed, have negligible intensity.

If the requirements underlying the  $A_2R_2$  approximation are not strictly fulfilled the perturbation treatment is easily extended to second order. The second order corrections to the eigenvalues can be obtained from Tables 1 and 2 in paper II. Two alternative sets of correction terms were discussed in that paper. In one scheme all couplings are considered small compared to  $\nu_A - \nu_B$  and are introduced as perturbations. The second order corrections to the X transitions calculated by ordinary second order perturbation theory under this assumption are given in Table 1 under the heading 'restricted second order corrections'. A specific notation is used for the second order corrections, *e.g.*

$$\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^+} \delta\nu^+$$

means that the expression inside the brackets should be calculated for  $\delta\nu = \delta\nu^+$  and  $\delta\nu = \delta\nu^-$  and the results subtracted from each other, *i.e.*

$$\frac{N^2}{4} \left[ \frac{1}{\delta\nu} \right]_{\delta\nu^-} \delta\nu^+ = \frac{N^2}{4\delta\nu^+} - \frac{N^2}{4\delta\nu^-}$$

The notation  $\cos^2[\vartheta]_{\delta\nu^+}^{\delta\nu^-}$  for the intensities correspondingly means  $\cos^2(\vartheta\delta\nu^+ - \vartheta\delta\nu^-)$ , where the angle  $\vartheta$  is calculated for the two apparent relative shifts  $\delta\nu^+$  and  $\delta\nu^-$ .

In the other scheme only the couplings  $J$  and  $J'$  are considered small in comparison with  $\nu_A - \nu_B$ . The second order corrections to the X transitions obtained by generalized second order perturbation theory<sup>9</sup> under this assumption are given in Table 1 under the heading 'general second order corrections'.

The second order corrections to the X transitions are thus obtained as the difference between correction terms which in the ideal case are small. An extension of the perturbation calculation to higher orders in the intensities shows that the first non-vanishing correction terms are of second order and therefore may usually be neglected, especially since relative intensities cannot be measured very accurately.

In the  $(AR)_2$  approximation it is assumed that the relative shift is much larger than the coupling constants, and furthermore that one of the AB couplings is much larger than the other coupling constants. The  $A_2B_2$  system can then be regarded as two almost independent AR systems, where the couplings are introduced as perturbations. If these conditions are fulfilled, it is again clear that the X part of the  $A_2B_2X$  spectrum will consist of a triplet of triplets having the splittings  $J_{AX}$  and  $J_{BX}$ . This is also obtained by using the first order energies for an  $A_2B_2$  system in this approximation as given in Tables 1 and 4 of paper II. The correction terms in the second order treatment obtained

Table 2. Transition frequencies for the X transitions in an  $A_2B_2X$  system.<sup>a</sup> The frequencies of the " $\nu_0$ " transitions were obtained by the  $(AB)_2X$  approximation to first and second order, while the remaining transitions are exactly treated.

Transition	Exact and $(AB)_2X$ to first order	Transition frequency relative $\nu_X$ $(AB)_2X$ Second order correction	Relative intensity
1 $\nu_0(\beta) \rightarrow \nu_0(\alpha)$	$J_{AX} + J_{BX}$		1
2 $1s_1'(\beta) \rightarrow 1s_1'(\alpha)$	$\frac{1}{2}(J_{AX} + J_{BX}) - \frac{1}{2}[(\delta\nu)^2 + N^2] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$
3 $2s_1'(\beta) \rightarrow 2s_1'(\alpha)$	$\frac{1}{2}(J_{AX} + J_{BX}) + \frac{1}{2}[(\delta\nu)^2 + N^2] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$
4 $1s_0(\beta) \rightarrow 1s_0(\alpha)$	$-\frac{1}{2}[(\delta\nu)^2 + J^2] \frac{\delta\nu^+}{\delta\nu^-} + \frac{(K-2J')}{4} [\cos^2 2\varphi] \frac{\delta\nu^+}{\delta\nu^-}$	$-\frac{(K-2J')^2}{32} \left[ \frac{(4-3\sin^2 2\varphi)\sin^2 2\varphi}{(\delta\nu^2 + J^2)^{\frac{1}{2}}} \right] \frac{\delta\nu^+}{\delta\nu^-}$	$\cos^4[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$
5 $2s_0(\beta) \rightarrow 2s_0(\alpha)$	$+\frac{1}{2}[(\delta\nu)^2 + J^2] \frac{\delta\nu^+}{\delta\nu^-} + \frac{(K-2J')}{4} [\cos^2 2\varphi] \frac{\delta\nu^+}{\delta\nu^-}$	$-\frac{1}{32} \left[ \frac{(K\sin 2\varphi - 2J')^2}{(\delta\nu^2 + J^2)^{\frac{1}{2}}} \right] \frac{\delta\nu^+}{\delta\nu^-}$ $+\frac{(K-2J')}{32} \left[ \frac{(4-3\sin^2 2\varphi)\sin^2 2\varphi}{(\delta\nu^2 + J^2)^{\frac{1}{2}}} \right] \frac{\delta\nu^+}{\delta\nu^-} + \cos^4[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$	
6 $3s_0(\beta) \rightarrow 3s_0(\alpha)$	$-\frac{(K-2J')}{2} [\cos^2 2\varphi] \frac{\delta\nu^+}{\delta\nu^-}$	$-\frac{K^2}{4J} [\cos^2 2\varphi] \frac{\delta\nu^+}{\delta\nu^-}$	$\cos^2 2[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$
7 $4s_0(\beta) \rightarrow 4s_0(\alpha)$	0	$+\frac{K^2}{4J} [\cos^2 2\varphi] \frac{\delta\nu^+}{\delta\nu^-} + \frac{1}{32} \left[ \frac{(K\sin 2\varphi - 2J')^2}{(\delta\nu^2 + J^2)^{\frac{1}{2}}} \right] \frac{\delta\nu^+}{\delta\nu^-}$	1
8 $1s_{-1}'(\beta) \rightarrow 1s_{-1}'(\alpha)$	$-\frac{1}{2}(J_{AX} + J_{BX}) + \frac{1}{2}[(\delta\nu)^2 + N^2] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$
9 $2s_{-1}'(\beta) \rightarrow 2s_{-1}'(\alpha)$	$-\frac{1}{2}(J_{AX} + J_{BX}) - \frac{1}{2}[(\delta\nu)^2 + N^2] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\varphi] \frac{\delta\nu^+}{\delta\nu^-}$
10 $s_{-2}(\beta) \rightarrow s_{-2}(\alpha)$	$-J_{AX} - \frac{L}{2} J_{BX}$		1
11 $1\alpha_1'(\beta) \rightarrow 1\alpha_1'(\alpha)$	$J_{BX} - \frac{L}{2} [\tan \psi_+ ] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\psi_+ ] \frac{\delta\nu^+}{\delta\nu^-}$
12 $2\alpha_1'(\beta) \rightarrow 2\alpha_1'(\alpha)$	$J_{AX} + \frac{L}{2} [\tan \psi_+ ] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\psi_+ ] \frac{\delta\nu^+}{\delta\nu^-}$
13 $1\alpha_0'(\beta) \rightarrow 1\alpha_0'(\alpha)$	0		1
14 $2\alpha_0'(\beta) \rightarrow 1\alpha_0'(\alpha)$	0		1
15 $1\alpha_{-1}'(\beta) \rightarrow 1\alpha_{-1}'(\alpha)$	$-J_{BX} + \frac{L}{2} [\tan \psi_- ] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\psi_- ] \frac{\delta\nu^+}{\delta\nu^-}$
16 $2\alpha_{-1}'(\beta) \rightarrow 2\alpha_{-1}'(\alpha)$	$-J_{AX} - \frac{L}{2} [\tan \psi_- ] \frac{\delta\nu^+}{\delta\nu^-}$		$\cos^2[\psi_- ] \frac{\delta\nu^+}{\delta\nu^-}$

<sup>a</sup> The angles are defined by  $\tan 2\varphi = J/\delta\nu$ ,  $\tan 2\psi_{\pm} = L/(\delta\nu \pm M)$ ,  $\tan 2\Phi = N/\delta\nu$ .

by generalized perturbation theory are also included in Table 1. In these formulae, terms of a magnitude smaller than  $K^2/J$  have been neglected.\*

In the  $(AB)_2$  approximation discussed in paper III it is assumed that the relative shift and one of the AB coupling constants are of similar magnitude, and much larger than the rest of the coupling constants. The molecule can then be treated as two almost independent AB systems where the smaller couplings are introduced as perturbations. If this approximation is valid, it is clear that the X part of the spectrum can be regarded as composed of a quartet from one AB group, each line of which is further split into a quartet by the presence of the other AB group. The X part will then consist of a triplet of triplets where the splittings are not simply given by  $J_{AX}$  and  $J_{BX}$  but can be obtained from the general expressions for the splittings in the X quartet of a simple ABX spectrum.

The perturbation expressions for the spin zero states of an  $A_2B_2$  system in this approximation, as given in Table 2 of paper III may now be adapted to calculate the X transition frequencies to first and second order.

These expressions are given in Table 2, listed as transitions 4–7, together with the intensities to lowest order. For the remaining transitions the exact expressions for the  $A_2B_2$  states as given in Table 1 of paper III are used since no simplification in the formulae of these transitions is obtained by extension of the  $A_2B_2$  approximation throughout the whole set of basis functions.

From the expressions for the transition frequencies it is evident that the X part of the spectrum is not symmetrical with respect to  $\nu_X$ , as might naively be expected.

From the analysis of the  $A_2B_2$  part it is not possible to distinguish between  $J$  and  $J'$  nor  $J_A$  and  $J_B$ . The signs of  $J_{AX}$  and  $J_{BX}$  can be determined relative to each other, in a way analogous to that used in the simpler ABX case. However, the mentioned asymmetry in the X spectrum will in the  $A_2B_2X$  case also give us the signs of  $J_{AX}$  and  $J_{BX}$  relative to the AB couplings, as first discussed by Bak *et al.*<sup>12</sup> This is realized by looking at the unsymmetrical expressions in Table 2 for the  $s_0(\beta) \rightarrow s_0(\alpha)$  transitions. The  $a_{\pm 1}(\beta) \rightarrow a_{\pm 1}(\alpha)$  transitions are also unsymmetrical with respect to  $\nu_X$  depending upon the sign of  $M (= J_A - J_B)$ . Thus, if this asymmetry can also be resolved, the sign of  $M$  may be determined.

### 3. ILLUSTRATIVE APPLICATIONS

We have applied the discussed perturbation methods to the analysis of the spectra of some  $p$ -disubstituted benzenes, namely  $p$ -bromofluorobenzene,  $p$ -chlorofluorobenzene, and 4,4'-difluorodiphenyl. The spectrum of  $p$ -fluoroanisole has also been analysed in detail using the exact treatment by numerical diagonalization.

\* The  $s_0$  functions used in the  $(AR)_2$  approximation have been given earlier by Richards and Schaefer<sup>10</sup> in the analysis of  $p$ -fluoroaniline but were not used as the basis for a perturbation treatment. Recently Aruldas and Venkateswarlu<sup>11</sup> have employed the same  $s_0$  functions as the basis for a perturbational analysis of some  $p$ -substituted fluorobenzenes.



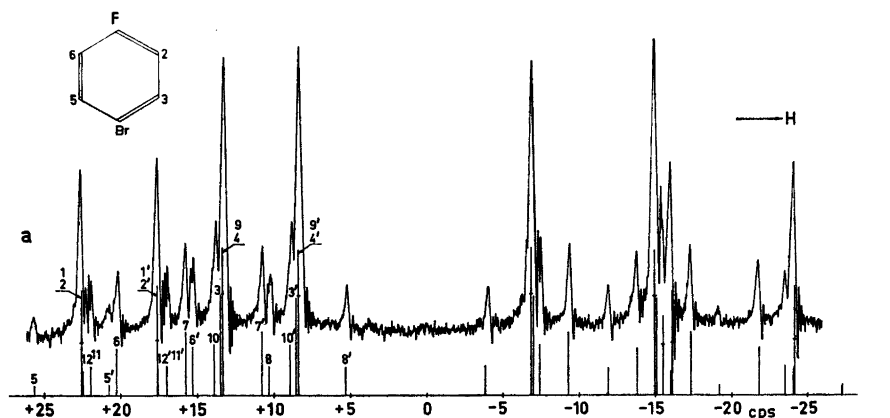
For the analysis of the  $A_2B_2$  patterns a program written for the IBM 1620 computer of this University was used, which adjusts the parameter set to a least squares fit of experimental and theoretical transition frequencies. Different approximations for the theoretical transition frequencies can be used in this program, including the exact treatment by numerical diagonalization.

### Experimental details

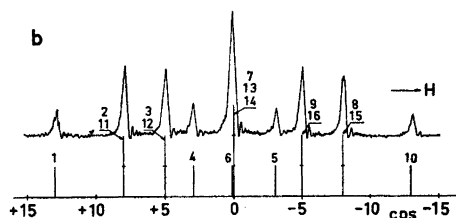
The *p*-substituted benzenes used in this investigation were commercial products of highest purity. To remove dissolved oxygen, argon was bubbled through the sample tubes before they were sealed off. The proton resonance spectra were recorded on a Varian A 60 spectrometer. The chemical shifts were either measured relative to TMS as internal reference or, in one case, relative to cyclohexane as internal reference. The sweep was calibrated with the side-band technique in which the powerline frequency of  $50.00 \pm 0.05$  cps was used as modulation frequency. At least five recordings were made of each sample and the uncertainty in the experimental line positions is estimated to be less than 0.10 cps.

The fluorine resonance spectra were recorded on a Varian Associates model V 4300 B high resolution spectrometer operating at 40.00 Mcps. For calibration of the sweep, sidebands were generated using the powerline frequency as modulation frequency. The fluorine resonance line positions are estimated to be correct within 0.15 cps.

For calibration of the fluorine resonance shift, 10 % *p*-difluorobenzene was added to the samples as internal reference, and the fluorine shift was then measured using the side-band technique. This addition of *p*-difluorobenzene was seen to slightly affect the



*Fig. 1.* Proton and fluorine resonance spectra of *p*-bromofluorobenzene in a 29 % solution in  $CS_2$ . The proton spectrum (a) was recorded at 60 Mcps, and the fluorine spectrum (b) at 40 Mcps. One proton line is displaced slightly outside the shown recording. The experimental proton spectrum is fitted by the parameters (in cps):  $\delta\nu^+ = 28.10$ ,  $\delta\nu^- = 31.35$ ,  $J = 8.80$ ,  $J' = 0.25$ ,  $J_A = 2.55$ ,  $J_B = 3.10$ ,  $J_{AX} = 4.90$  and  $J_{BX} = 8.15$ , and the fluorine spectrum by  $\delta\nu^+ = 19.45$  and  $\delta\nu^- = 22.80$  and the same coupling constants.



relative shifts in the proton spectrum in some compounds. Thus, in the accurate measurement of the fluorine part of the spectrum, side-bands were created from the fluorine multiplet itself, as described above.

### *p*-Bromofluorobenzene

The proton and fluorine resonance spectra of a 29 % solution of *p*-bromofluorobenzene in CS<sub>2</sub> are shown in Fig. 1.

In the proton resonance spectrum most of the theoretical 48 lines are well resolved. It is then an easy task to pick out the two overlapping A<sub>2</sub>B<sub>2</sub> patterns, the first step being to find the symmetry lines of these patterns. The assignment of a line to one of the two A<sub>2</sub>B<sub>2</sub> multiplets is then checked by a reflection in the symmetry lines where its mirror transition should be found. In this case the complete set of lines of both A<sub>2</sub>B<sub>2</sub> multiplets could be picked out unambiguously, and the two parts could readily be analysed separately.

As the relative shift  $\nu_A - \nu_B$  is fairly large, the large shift A<sub>2</sub>R<sub>2</sub> approximation could be applied in the analysis. In the benzene ring  $J_{ortho}$  is much larger than  $J_{meta}$  or  $J_{para}$ , and consequently the simpler (AR)<sub>2</sub> analysis could also be used. Then of course the (AB)<sub>2</sub> approximation is also applicable. The parameter sets obtained from the least squares fit procedure for these different approximations and the exact treatment are collected in Table 3. Here only the results from the perturbation treatments to second order are given, the first order terms give less accurate results. The least squares fit procedure was accomplished for both A<sub>2</sub>B<sub>2</sub> multiplets independently, giving consistent sets of parameters. The two sets of coupling constants agree within 0.05 cps. The coupling constants given are the mean values of the results derived from the two separate A<sub>2</sub>B<sub>2</sub> analyses, rounded off to the nearest 0.05 cps, a precision in keeping with the experimental accuracy. The root mean square deviations of the total A<sub>2</sub>B<sub>2</sub> spectrum obtained with these parameters are also included.

Table 3. Parameter sets (in cps) obtained for *p*-bromofluorobenzene from the proton multiplet using various A<sub>2</sub>B<sub>2</sub> approximations in addition to the exact treatment.

	Exact treatment	(AB) <sub>2</sub> approximation second order	A <sub>2</sub> R <sub>2</sub> approximation		(AR) <sub>2</sub> approximation Second order
			Restricted second order	General second order	
$\delta\nu^+$	28.10	28.10	28.10	28.10	28.10
$\delta\nu^-$	31.35	31.35	31.35	31.35	31.35
$J$	8.80	8.80	8.80	8.80	8.80
$J'$	0.25	0.25	0.35	0.25	0.35
$J_A$	2.55	2.55	2.40	2.55	2.40
$J_B$	3.10	3.10	3.00	3.15	2.95
Root mean square deviation					
	0.05	0.05	0.06	0.04	0.10
$J_{AX}^a$	4.90	4.90	4.90	4.90	4.90
$J_{BX}^a$	8.15	8.15	8.15	8.15	8.15

<sup>a</sup> Derived from the separation of symmetry points  $(J_{AX} + J_{BX})/2 = 6.50$ .

Table 4. The experimental fluorine transition frequencies (in cps) of *p*-bromofluorobenzene relative  $\nu_F$ , and the theoretical ones calculated from various approximations in addition to the exact treatment using the parameters of Table 3.<sup>a</sup>

Transition number	$A_2R_2X$ and $(AR)_2X$ approximations		$A_2R_2X$ approximation		$(AB)_2X$ approximation		Exact treatment	Experimental
	First order	Second order	Restricted second order	General second order	First order	Second order		
1	13.05	13.05		13.05		13.05		13.05
2	8.15	8.00		8.00		8.02		8.05
3	4.90	5.05		5.05		5.03		5.05
4	3.25	2.96	2.95	2.86	2.95	2.94	2.93	2.97
5	3.25	2.96	2.95	3.00	3.05	3.01	3.03	3.08
6	0.00	0.00	—	0.18	0.10	0.14	0.13	0.00 <sup>b</sup>
7	0.00	0.00	—	0.05	0.00	0.06	—	0.00 <sup>b</sup>
8	8.15	8.00	—	8.00	—	8.02	—	8.05
9	4.90	5.05	—	5.05	—	5.03	—	5.05
10	13.05	13.05	—	13.05	—	13.05	—	13.05
11	8.02	8.02	8.01	8.01	—	8.02	—	8.05
12	5.03	5.03	5.04	5.04	—	5.03	—	5.05
13	0.00	0.00	0.00	0.00	—	0.00	—	0.00
14	0.00	0.00	0.00	0.00	—	0.00	—	0.00
15	8.02	8.02	—	8.01	—	8.04	—	8.05
16	5.03	5.03	—	5.03	—	5.01	—	5.05

<sup>a</sup> Calculated with the apparent relative shifts at 42.52 Mcps:  $\delta\nu^+ = 19.45$  and  $\delta\nu^- = 22.70$ .

<sup>b</sup> Overlapping lines.

As seen from the table all three approximations reproduce the exact solution well, except that in the  $(AR)_2$  approximation  $J_A + J_B$  is slightly outside the uncertainty.

The fluorine coupling constants  $J_{AX}$  and  $J_{BX}$  are now immediately obtained, and are included in Table 3. The fluorine spectrum was then calculated with these parameter sets for the different approximations to first and second order with use of the expressions of Tables 1 and 2 as well as by the exact treatment with numerical diagonalization.

The results are given in Table 4 together with the experimental frequencies. In order not to interlard the table with unnecessary data, those transition frequencies which are equal by definition in the various treatments are only included once. The  $(AB)_2X$  approximation to first order reproduces the exactly calculated spectrum very well and the small asymmetry in the  $s_0$  transitions is well reproduced. The extension of the approximation to second order in this case leads only to an improvement of a few hundredths of a cps in the line positions.

The large-shift approximations to first order deviate appreciably in some of the inner lines, and may be extended to second order to obtain almost complete agreement with the exact solution. Only in the general  $A_2R_2X$

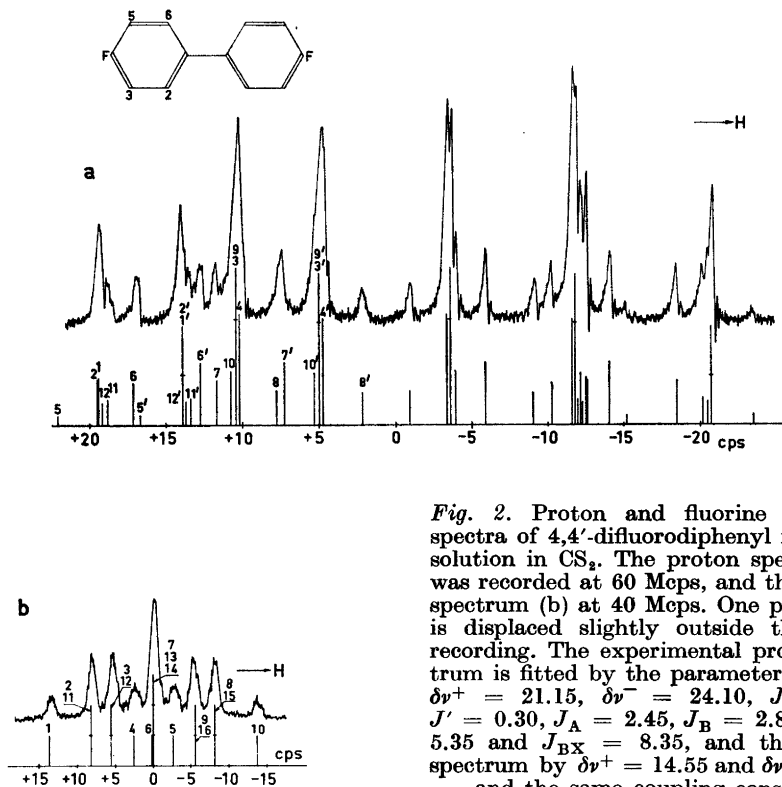


Fig. 2. Proton and fluorine resonance spectra of 4,4'-difluorodiphenyl in a 21% solution in  $CS_2$ . The proton spectrum (a) was recorded at 60 Mcps, and the fluorine spectrum (b) at 40 Mcps. One proton line is displaced slightly outside the shown recording. The experimental proton spectrum is fitted by the parameters (in cps):  $\delta\nu^+ = 21.15$ ,  $\delta\nu^- = 24.10$ ,  $J = 8.65$ ,  $J' = 0.30$ ,  $J_A = 2.45$ ,  $J_B = 2.80$ ,  $J_{AX} = 5.35$  and  $J_{BX} = 8.35$ , and the fluorine spectrum by  $\delta\nu^+ = 14.55$  and  $\delta\nu^- = 17.50$  and the same coupling constants.

approximation can the asymmetry in the  $s_0$  transitions be noticed. It should be noted that the fluorine spectra are calculated for a smaller relative shift  $\nu_A - \nu_B$  than the proton resonance spectrum, since the fluorine resonance was measured at 40 Mcps. The conditions for the large shift approximations are then less well fulfilled, but they still perform remarkably well in the X part of the spectrum.

The asymmetry in the  $a_{\pm 1}$  transitions cannot be detected in the spectrum in this case due to the small value of  $M$  in  $p$ -disubstituted benzenes, giving an asymmetry of only a few hundredths of a cps.

The theoretical proton and fluorine resonance spectra calculated by use of the parameters of the exact solution in Table 3 are included in Fig. 1.

#### 4,4'-Difluorodiphenyl

The proton and fluorine resonance spectra of a 21 % solution of 4,4'-difluorodiphenyl in  $CS_2$  are shown in Fig. 2. The proton resonance spectral

Table 5. Parameter sets (in cps) obtained for 4,4'-difluorodiphenyl from the proton multiplet using various  $A_2B_2$  approximations in addition to the exact treatment.

	Exact treatment	$(AB)_2$ approximation		$A_2B_2$ approximation	
		Second order	Restricted second order	General second order	$(AR)_2$ approximation Second order
$\delta\nu^+$	21.15	21.15	21.10	21.05	21.10
$\delta\nu^-$	24.10	24.10	24.05	24.05	24.05
$J$	8.65	8.65	8.60	8.65	8.60
$J'$	0.30	0.30	0.40	0.30	0.45
$J_A$	2.45	2.40	2.25	2.45	2.25
$J_B$	2.80	2.80	2.60	2.85	2.60
Root mean square deviation	0.06	0.06	0.12	0.05	0.14
$J_{AX}^a$	5.35	5.35	5.35	5.35	5.35
$J_{BX}^a$	8.35	8.35	8.35	8.35	8.35

<sup>a</sup> Derived from the separation of symmetry points  $(J_{AX} + J_{BX})/2 = 6.85$ .

lines of the low field multiplet are slightly broadened, probably due to an unresolved coupling to the other ring. However, the high-field multiplet is well resolved, and it is also simple to pick out the two overlapping  $A_2B_2$  patterns in this case. The fluorine resonance lines are also broadened in this compound, probably due to the suggested coupling to the other ring.

The apparent relative chemical shifts of these patterns are smaller in this case, but the large shift approximations to second order should still be successfully applicable. The approximations almost reproduce the exact solution, as seen from Table 5, where the results of the least squares fits are collected. These parameters and the obtained fluorine coupling constants were then used to calculate the fluorine spectrum, using the different approximations and the exact treatment. The calculated spectra are given in Table 6 together with the experimental transition frequencies. The measured asymmetry in the

Table 6. The experimental fluorine transition frequencies (in cps) of 4,4'-difluorodiphenyl relative  $\nu_F$ , and the theoretical ones calculated from various approximations in addition to the exact treatment using the parameters <sup>a</sup> of Table 5.

Transition number	A <sub>1</sub> R <sub>2</sub> X and (AR) <sub>2</sub> X approximations		A <sub>1</sub> R <sub>2</sub> X approximation		(AB) <sub>2</sub> X approximation		Exact treatment	Experimental
	First order	Second order	Restricted second order	General second order	First order	Second order		
1	13.70		13.70	13.70		13.70		13.61
2	8.35		8.12	8.12		8.14		8.12
3	5.35		5.58	5.58		5.56		5.41
4	3.00	2.57		2.37	2.52	2.50	2.50	2.62
5	-3.00	-2.57		-2.60	-2.67	-2.60	-2.62	2.67
6	0.00		0.00		0.15			0.00 <sup>b</sup>
7	0.00		0.00		0.00			0.00 <sup>b</sup>
8	-8.35		-8.12	-8.12		-8.14		8.12
9	-5.35		-5.58	-5.58		-5.56		5.41
10	-13.70		-13.70	-13.70		-13.70		-13.61
11	8.35		8.16	8.14		8.17		8.12
12	5.35		5.44	5.56		5.54		5.41
13	0.00		0.00	0.00		0.00		0.00
14	0.00		0.00	0.00		0.00		0.00
15	-8.35		-8.16	-8.14		-8.19		8.12
16	-5.35		-5.44	-5.54		-5.51		5.41

<sup>a</sup> With apparent relative shifts reduced to a proton resonance frequency of 42.52 Mcps, for example  $\delta\nu^+ = 14.55$ ,  $\delta\nu^- = 17.50$ .

<sup>b</sup> Overlapping lines.

$s_0$  transitions is hardly significant in this case, due to the difficulties in accurately measuring the positions of the broadened lines.

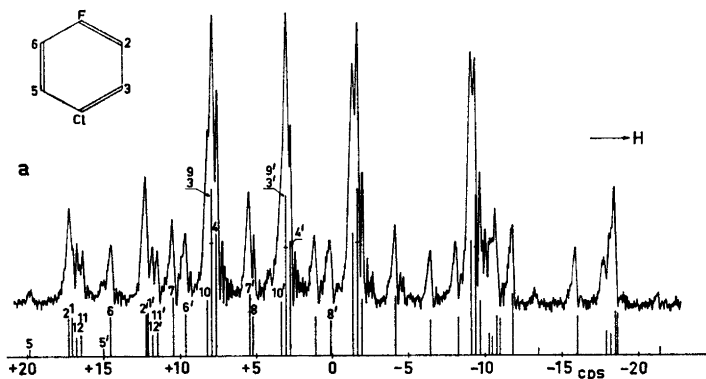
The theoretical spectrum calculated by the  $(AB)_2$  approximation to first order reproduces that of the exact solution very well, and only a slight improvement is achieved by extending the treatment to second order. The theoretical asymmetry of the spin zero transitions is well reproduced in this approximation. It is also noted that for this smaller shift the  $s_{\pm 1}$  and  $a_{\pm 1}$  transitions separate. The separation is, however, too small to be resolved.

The large shift approximations to first order give a much worse reproduction of the exact solution; however, inclusion of the second order corrections leads to a considerable improvement. The fit obtained for these approximations is remarkably good, considering that the apparent relative shift  $\delta\nu^+$  (14.55) is much less than twice the largest AB coupling constants in this fluorine spectrum. Only the general second order  $A_2R_2X$  terms reveal the discussed asymmetry, which becomes somewhat exaggerated in this approximation model, however.

The proton and fluorine resonance spectra calculated with the parameters of the exact solution are included in Fig. 2.

### *p*-Chlorofluorobenzene

The proton and fluorine resonance spectra of a 24 % solution of *p*-chlorofluorobenzene in  $CS_2$  are shown in Fig. 3.



*Fig. 3.* Proton and fluorine resonance spectra of *p*-chlorofluorobenzene in a 24 % solution in  $CS_2$ . The proton spectrum (a) was recorded at 60 Mcps, and the fluorine spectrum (b) at 40 Mcps. The experimental proton spectrum is fitted by the parameters (in cps):  $\delta\nu^+ = 16.35$ ,  $\delta\nu^- = 19.45$ ,  $J = 8.80$ ,  $J' = 0.30$ ,  $J_A = 2.70$ ,  $J_B = 3.05$ ,  $J_{AX} = 4.80$  and  $J_{BX} = 7.90$ , and the fluorine spectrum by  $\delta\nu^+ = 11.10$  and  $\delta\nu^- = 14.20$  and the same coupling constants.

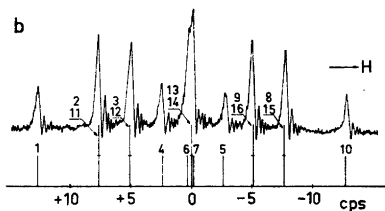


Table 7. Parameter sets (in cps) obtained for *p*-chlorofluorobenzene from the proton multiplet using various  $A_2B_2$  approximations in addition to the exact treatment.

	Exact treatment	(AB) <sub>2</sub> approximation Second order	A <sub>2</sub> R <sub>2</sub> approximation Restricted second order	General second order	(AR) <sub>2</sub> approximation Second order
$\delta\nu^+$	16.35	16.30	16.20	16.15	16.25
$\delta\nu^-$	19.45	19.45	19.40	19.35	19.40
<i>J</i>	8.80	8.80	8.75	8.75	8.75
<i>J'</i>	0.30	0.30	0.45	0.25	0.45
<i>J<sub>A</sub></i>	2.70	2.70	2.40	2.85	2.40
<i>J<sub>B</sub></i>	3.05	3.05	2.75	3.20	2.65
Root mean square deviation	0.05	0.06	0.15	0.09	0.18
<i>J<sub>AX</sub></i> <sup>a</sup>	4.80	4.80	4.75	4.75	4.75
<i>J<sub>BX</sub></i> <sup>a</sup>	7.90	7.90	7.95	7.95	7.95

<sup>a</sup> Derived from the separation of the symmetry points  $(J_{AX} + J_{BX})/2 = 6.35$ .

The proton resonance spectrum is extraordinarily well resolved, almost all of the 48 theoretical lines are individually resolved. It is then easy to pick out the two overlapping  $A_2B_2$  patterns. For this compound the apparent relative chemical shifts of these patterns are only twice the largest AB coupling constant. However the large-shift approximations reproduce the exact solution fairly well as seen in Table 7 where the results of the least squares fits are collected. The  $(AB)_2$  approximation and the exact solution agree completely.

The fluorine resonance spectra calculated with these parameters and the derived fluorine couplings are given in Table 8 together with the experimental frequencies.

As seen from the experimental spectrum the asymmetry is now more pronounced: the central peak is split and one  $s_0$  transition is almost resolved on its low field side. Thus in this case the signs of the fluorine couplings relative to the proton-proton couplings may be unambiguously obtained.

It is seen that the  $(AB)_2$  approximation to first order reproduces the exact solution fairly well, and no essential improvement is achieved by the second order corrections. The first order terms in the large shift approximations are quite insufficient in this case. The second order corrections lead to a certain improvement but the frequencies of the fluorine  $s_0$  transitions calculated by the large shift approximations deviate from the observed ones far outside the experimental errors, in particular in the generalized  $A_2R_2X$  approximation. This behaviour is not unexpected in this case, considering that the apparent relative shifts ( $\delta\nu^+ = 11.1$  and  $\delta\nu^- = 14.2$  cps) are only slightly larger than *N* (9.1 cps) and *L* (8.5 cps) and only twice as large as *K* (5.75 cps). The correction terms for the  $s_0$  transitions are then obtained as the difference between terms that are no longer small ( $\gg 1$  cps), leading to the slow convergence of the perturbation treatments in these approximations. It is thus seen that the large shift approximations become gradually insufficient as the apparent



Table 8. The experimental fluorine transition frequencies (in cps) of *p*-chlorofluorobenzene relative  $\nu_F$  and the theoretical ones calculated from various approximations in addition to the exact treatment using the parameters  $\alpha$  of Table 7.

Transition number	$A_2R_2X$ and $(AR)_2X$ approximations		$A_2R_2X$ approximation		$(AB)_2X$ approximation		Exact treatment	Experimental
	First order	Second order	Restricted second order	General second order	First order	Second order		
1	12.70		12.70		12.70		12.70	12.72
2	7.95		7.52		7.53		7.61	7.69
3	4.75		5.18		5.17		5.09	5.00
4	3.20	2.42		2.41	1.72	2.40	2.36	2.46
5	-3.20	-2.42		-2.41	-2.37	-2.68	-2.47	-2.65
6	0.00		0.00		1.03	0.27	0.38	0.30
7	0.00		0.00		-0.38	0.00	-0.28	0.00 <sup>b</sup>
8	-7.95		-7.52		-7.53		-7.61	-7.69
9	-4.75		-5.18		-5.17		-5.09	-5.00
10	-12.70		-12.70		-12.70		-12.70	-12.70
11	7.95		7.60		7.56		7.62	7.69
12	4.75		5.10		5.14		5.08	5.00
13	0.00		0.00		0.00		0.00	0.00
14	0.00		0.00		0.00		0.00	0.00
15	-7.95		-7.60		-7.56		-7.64	-7.69
16	-4.75		-5.10		-5.10		-5.05	-5.00

<sup>a</sup> With apparent relative shifts reduced to a proton resonance frequency of 42.62 Mcps, for example  $\delta\nu^+ = 11.10$  and  $\delta\nu^- = 14.20$ .

<sup>b</sup> Overlapping line.

relative shifts become smaller\* and the X part of the spectrum in the case discussed is most favourably treated by the  $(AB)_2X$  approximation.

The theoretical proton and fluorine resonance spectra calculated with the parameters of the exact solution of Table 7 are included in Fig. 3.

### *p*-Fluoroanisole

As an example of a case with small relative chemical shift we have chosen *p*-fluoroanisole. The proton and fluorine resonance spectra of a 28 % solution of *p*-fluoroanisole in  $CS_2$  are shown in Fig. 4.

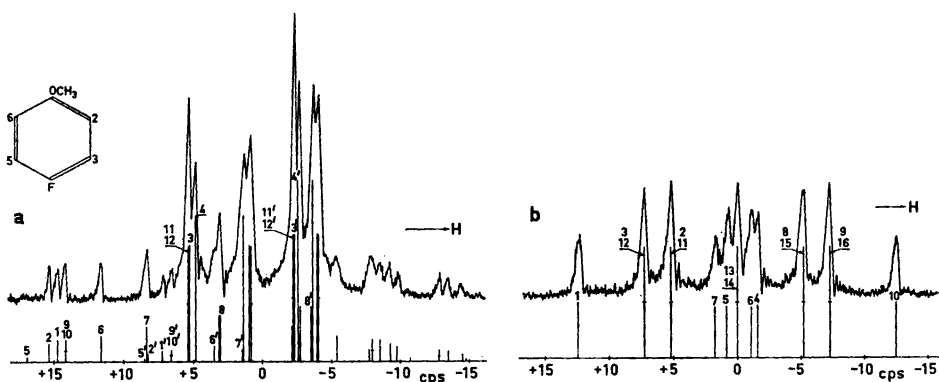


Fig. 4. Proton and fluorine resonance spectra of *p*-fluoroanisole in a 28 % solution in  $CS_2$ . The proton spectrum (a) was recorded at 60 Mcps, and the fluorine spectrum (b) at 40 Mcps. The experimental proton spectrum is fitted by the parameters (in cps):  $\delta\nu^+ = 10.00$ ,  $\delta\nu^- = 6.00$ ,  $J = 9.15$ ,  $J' = 0.35$ ,  $J_A = 3.20$ ,  $J_B = 3.20$ ,  $J_{AX} = 8.25$  and  $J_{BX} = 4.25$ , and the fluorine spectrum by  $\delta\nu^+ = 7.65$  and  $\delta\nu^- = 3.65$  and the same coupling constants.

The high field multiplet of the proton resonance spectrum is broadened due to an unresolved coupling to the methoxyl group.<sup>13</sup> The two  $A_2B_2$  patterns are readily picked out. All lines necessary for an assignment of the low field one are well resolved, while the high field pattern shows stronger overlapping of lines.

The  $A_2B_2$  pattern with largest apparent shift was analysed by the  $(AB)_2$  analysis scheme, and also fitted by the exact diagonalization procedure. The result of this analysis is given in Table 9. The  $A_2B_2$  pattern with the smaller apparent shift is, however, not suitably analysed by the  $(AB)_2$  scheme because the apparent relative chemical shift becomes too small, leading to strong mixing of states as discussed in paper III.

However, by calculating the exact  $A_2B_2$  spectrum using the couplings obtained in Table 9 with successively smaller shift until complete fit was

\* It was somewhat unexpected, however, that this insufficiency should be most manifest in the generalized  $A_2R_2X$  treatment.

Table 9. Parameter sets (in cps) obtained for the  $A_2B_2$  pattern with largest relative shift in *p*-fluoroanisole using the  $(AB)_2$  approximation and the exact treatment.

	Exact treatment	$(AB)_2$ approximation Second order
$\delta\nu^+$	10.00	9.95
$J$	9.15	9.25
$J'$	0.35	0.30
$J_A$	3.20	2.95
$J_B$	3.20	2.95
Root mean square deviation	0.05	0.12

<sup>a</sup> From the other multiplet  $\delta\nu^- = 6.00$  is obtained. The separation of the symmetry points  $(J_{AX} + J_{BX})/2 = 6.25$  then leads to  $J_{AX} = 8.25$  and  $J_{BX} = 4.25$ .

obtained in all resolved lines, this  $A_2B_2$  part could also be identified and all transitions accounted for. The  $(AB)_2X$  approximation is insufficient to calculate the fluorine spectrum. This has been done by exact diagonalization and the result is given in Table 10 together with the experimental transition frequencies. The agreement is seen to be very good, which confirms the assignment of parameters obtained from the analysis of the  $A_2B_2$  part.

As the basis for the diagonalization, the  $s_0$  functions generally given in the  $A_2B_2$  analysis were applied.<sup>4-6</sup> Due to the small relative shift, strong

Table 10. Experimental and theoretical fluorine transition frequencies (in cps) of *p*-fluoroanisole relative  $\nu_F$ . The theoretical spectrum is calculated from the parameters of Table 9, using exact diagonalization.<sup>a</sup>

Transition Number	Assignment	Exact treatment	Experimental
1	$s_2(\beta) \rightarrow s_2(\alpha)$	12.50	12.40
2	$1s_1'(\beta) \rightarrow 1s_1'(\alpha)$	5.24	5.20
3	$2s_1'(\beta) \rightarrow 2s_1'(\alpha)$	7.26	7.21
4	$2s_0'(\beta) \rightarrow 1s_0'(\alpha)$	- 1.59	- 1.59
5	$2s_0'(\beta) \rightarrow 4s_0'(\alpha)$	0.89	0.79
6	$3s_0'(\beta) \rightarrow 3s_0'(\alpha)$	- 1.09	- 1.15
7	$4s_0'(\beta) \rightarrow 2s_0'(\alpha)$	1.79	1.68
8	$1s_{-1}'(\beta) \rightarrow 1s_{-1}'(\alpha)$	- 5.24	- 5.20
9	$2s_{-1}'(\beta) \rightarrow 2s_{-1}'(\alpha)$	- 7.26	- 7.21
10	$s_{-2}(\beta) \rightarrow s_{-1}(\alpha)$	-12.50	-12.40
11	$1a_1'(\beta) \rightarrow 1a_1'(\alpha)$	5.19	5.20
12	$2a_1'(\beta) \rightarrow 2a_1'(\alpha)$	7.31	7.21
13	$1a_0'(\beta) \rightarrow 1a_0'(\alpha)$	0.00	0.00
14	$2a_0'(\beta) \rightarrow 2a_0'(\alpha)$	0.00	0.00
15	$1a_{-1}'(\beta) \rightarrow 1a_{-1}'(\alpha)$	- 5.19	- 5.20
16	$2a_{-1}'(\beta) \rightarrow 2a_{-1}'(\alpha)$	- 7.31	- 7.21

<sup>a</sup> Calculated with the apparent relative shift at 42.52 Mcps:  $\delta\nu^+ = 7.65$  and  $\delta\nu^- = 3.65$ .

mixing of these basis functions appears in the eigenfunctions. Some of the X transitions can then be assigned to "combination" transitions, provided that the assignment is based on correspondence with the limit of vanishing off-diagonal elements (*cf.* Table 10). Only the strongest transitions are included, the rest having too low intensity to be detected in the experimental spectrum in this case. In this strong coupling case the relative intensities are no longer constant, but the deviations from the large shift values are at most 10 % and can not be accurately measured.

The theoretical proton and fluorine resonance spectra are included in Fig. 4.

### Structural assignments

From the analysis of the  $A_2B_2$  part of the spectrum, it is not possible to distinguish between  $J$  and  $J'$  or  $J_A$  and  $J_B$ . In benzenes, however, the relations  $J_{ortho} > J_{meta} > J_{para}$  immediately give the assignment of  $J$  as well as that of  $J'$ . It has not been possible in the cases studied here to get a determination of the sign of  $M$  from the X part of the spectrum, due to the smallness of  $M$  in  $p$ -substituted benzenes.  $J_{AX}$  and  $J_{BX}$  are found to be of the same sign from the analysis, consistent with direct verifications by double resonance experiments performed in other fluorobenzenes.<sup>14,15</sup> They are also found to be of the same sign as the proton-proton couplings from the asymmetry in the  $s_0(\beta) \rightarrow s_0(\alpha)$  transitions of the X part, which is unambiguously resolved in the  $p$ -chlorofluorobenzene and  $p$ -fluoroanisole cases with the smallest relative shift  $\nu_A - \nu_B$ . The ring proton couplings in benzene have in turn been found positive in sign by other methods.<sup>16</sup>

In  $p$ -bromofluorobenzene the protons *ortho* to the bromo substituent are expected to be shifted downfield.<sup>17</sup> The smallest proton-proton *meta* coupling is tentatively assigned to the protons *ortho* to the bromo substituent. This value is similar to those obtained for other  $p$ -substituted bromobenzenes.<sup>2,3,18-21</sup> Thus we suggest the following parameter assignment:

$$\begin{aligned} \nu_A - \nu_B &= \nu_3 - \nu_2 = \nu_5 - \nu_6 = 29.75 \text{ cps (0.496 ppm)} \\ J &= J_{23} = J_{56} = 8.80 \text{ cps} \\ J' &= J_{25} = J_{36} = 0.25 \text{ cps} \\ J_A &= J_{35} = 2.55 \text{ cps} \\ J_B &= J_{26} = 3.10 \text{ cps} \\ J_{AX} &= J_{13} = J_{15} = 4.90 \text{ cps} \\ J_{BX} &= J_{12} = J_{16} = 8.15 \text{ cps} \end{aligned}$$

The uncertainty in these values is estimated to be 0.10 cps. The proton shift relative to TMS as internal reference is  $(\nu_A + \nu_B)/2 = 7.08$  ppm while the fluorine shift relative to  $p$ -difluorobenzene (10 %) as internal reference is 4.23 ppm.

In 4,4'-difluorodiphenyl the protons *meta* to the fluoro substituent are assigned to the low field multiplet due to the broadening of these lines, which probably depends upon an unresolved coupling with the other ring. In analogy with the previous case the *meta* coupling across the fluoro substituent is considered the largest. The other *meta* coupling is then similar to that obtained from the analysis of 4,4'-dichlorodiphenyl.<sup>21</sup>

We thus obtain the following assignment:

$$\begin{aligned} \nu_A - \nu_B &= \nu_2 - \nu_3 = \nu_6 - \nu_5 = 22.60 \text{ cps (0.377 ppm)} \\ J &= J_{23} = J_{56} = 8.65 \text{ cps} \\ J' &= J_{25} = J_{36} = 0.30 \text{ cps} \\ J_A &= J_{26} = 2.45 \text{ cps} \\ J_B &= J_{35} = 2.80 \text{ cps} \\ J_{AX} &= J_{24} = J_{46} = 5.35 \text{ cps} \\ J_{BX} &= J_{34} = J_{45} = 8.35 \text{ cps} \end{aligned}$$

The uncertainty is estimated to be 0.10 cps. The proton shift relative to TMS as internal reference is  $(\nu_A + \nu_B)/2 = 7.14$  ppm, while the fluorine shift relative to *p*-difluorobenzene (10 %) as internal reference is 3.99 ppm.

In *p*-chlorofluorobenzene the protons *ortho* to the chloro substituent are expected to be shifted to lower field.<sup>17</sup> The largest *meta* coupling is assigned to the coupling across the fluoro substituent in this case as well. Then the *meta* coupling across the chloro substituent is of a magnitude similar to those found for other *p*-substituted chlorobenzenes.<sup>3,18-21</sup>

We suggest the following assignment:

$$\begin{aligned} \nu_A - \nu_B &= \nu_3 - \nu_2 = \nu_5 - \nu_6 = 17.90 \text{ cps (0.298 ppm)} \\ J &= J_{23} = J_{56} = 8.80 \text{ cps} \\ J' &= J_{25} = J_{36} = 0.30 \text{ cps} \\ J_A &= J_{35} = 2.70 \text{ cps} \\ J_B &= J_{26} = 3.05 \text{ cps} \\ J_{AX} &= J_{13} = J_{15} = 4.80 \text{ cps} \\ J_{BX} &= J_{12} = J_{16} = 7.90 \text{ cps} \end{aligned}$$

The uncertainty is estimated to be 0.10 cps.

The proton shift was measured relative to cyclohexane as internal reference. Using a cyclohexane shift of 1.43 ppm we obtain the shift relative to TMS as  $(\nu_A + \nu_B)/2 = 7.02$  ppm, while the fluorine shift relative to *p*-difluorobenzene (10 %) as internal reference is 3.46 ppm.

In *p*-fluoroanisole the protons *ortho* to the methoxyl group may be expected to give the high field multiplet.<sup>17</sup> This is also seen from the spectrum, in which the high field lines are broadened due to an unresolved coupling to the methoxyl group.<sup>13</sup>

The *meta* couplings are both equal in this case. We thus suggest the following assignment:

$$\begin{aligned} \nu_A - \nu_B &= \nu_3 - \nu_2 = \nu_5 - \nu_6 = 8.00 \text{ cps (0.133 ppm)} \\ J &= J_{23} = J_{56} = 9.15 \text{ cps} \\ J' &= J_{25} = J_{36} = 0.35 \text{ cps} \\ J_A &= J_B = J_{35} = J_{26} = 3.20 \text{ cps} \\ J_{AX} &= J_{34} = J_{45} = 8.25 \text{ cps} \\ J_{BX} &= J_{24} = J_{46} = 4.25 \text{ cps} \end{aligned}$$

The uncertainty is estimated to be 0.10 cps.

The shift relative to TMS as internal reference is  $(\nu_A + \nu_B)/2 = 6.74$  ppm while the fluorine shift relative to 10 % *p*-difluorobenzene as internal reference

is  $-4.87$  ppm, *i.e.* the fluorine resonance is shifted to the high-field side of *p*-fluorobenzene, revealing the strong electron-donating properties of the methoxyl group.

#### 4. CONCLUSIONS

The analysis of  $A_2B_2X$  spectra is conveniently performed stepwise, since the  $A_2B_2$  part of the spectrum can be subdivided into two overlapping  $A_2B_2$  multiplets, which should be analysed separately. The analysis of a general  $A_2B_2$  spectrum is quite tedious, and much computational labour can be saved if perturbation methods can be applied. Then the X part of the spectrum may also be calculated by use of the same approximate eigenfunctions and eigenvalues as in the  $A_2B_2$  analysis.

In the present paper the  $A_2R_2X$ ,  $(AR)_2X$  and  $(AB)_2X$  approximations have been discussed. As seen from the *p*-substituted benzenes studied the large shift  $A_2R_2$  approximation can be used with success in the  $A_2B_2$  part even for cases where the relative shift  $\nu_A - \nu_B$  is only twice the largest AB coupling constant, especially if the general second order treatment is applied. In these compounds the conditions for the  $(AR)_2$  approximation were also fairly well fulfilled and this approximation could also be successfully applied in the  $A_2B_2$  analysis. The  $(AB)_2$  approximation should be more extensively applicable to the analysis of the spectra of *p*-substituted benzenes, as is seen in the examples studied here in which the parameter sets obtained were in almost complete agreement with those of the exact treatment. The proton spectrum of *p*-fluoroanisole could, however, only be partly analysed by this scheme because one multiplet showed too small a relative shift for this approximation to be applicable. This illustrates that different approximations can conveniently be used for the analysis of the two separate  $A_2B_2$  multiplets, *e.g.* the  $(AB)_2$  and  $(AR)_2$  schemes should sometimes be applicable together.

All  $A_2B_2$  couplings are obtained from the  $A_2B_2$  analysis, and since two separate  $A_2B_2$  spectra are analysed, a good mean value of these couplings can be obtained. In the cases studied here very good agreement between the parameter sets was obtained, the deviation being less than 0.10 cps.

To separate between the different  $J_{AX}$  and  $J_{BX}$  possibilities derived from the  $A_2B_2$  part, the X part must also be calculated, which will in addition give a good check of the  $A_2B_2$  couplings.

The large-shift approximations to first order simply give the X part of the spectrum as a triplet of triplets. Extension to second order gives corrections which lead to a better reproduction of the experimental spectrum. These approximations work successfully as illustrated here, even for cases where the apparent relative shift is only twice the largest AB coupling, but for smaller shifts appreciable deviations are obtained. Only the general second order  $A_2R_2X$  scheme reveals the asymmetry around  $\nu_X$  in some of the transitions, which makes possible the determination of the signs of  $J_{AX}$  and  $J_{BX}$  relative to the  $A_2B_2$  couplings. In the cases studied here this asymmetry did not become observable until the large shift approximations began to break down. As the deterioration was most pronounced in the generalized  $A_2R_2X$  approximation, it seems that this somewhat cumbersome treatment is of little

advantage in the analysis of *fluorine* spectra from *para* substituted fluorobenzenes. It is recommended that, for this particular class of spectra, the restricted  $A_2R_2X$  approximation be always used, as long as it is applicable ( $\delta\nu^\pm > 15$  cps, say).

The  $(AR)_2X$  approximation is a special case of the more general  $A_2R_2X$  treatment, giving very simple expressions for the  $A_2B_2$  transitions. However, the second order terms for the X transitions are no simpler than the restricted second order  $A_2R_2X$  corrections, which can thus just as well be used for the X part of the spectrum.

The  $(AB)_2X$  approximation is obviously the most exact one in the cases studied. Even the first order terms reproduce the exact solution closely and the asymmetry around  $\nu_X$  is well accounted for. The second order corrections gave no essential improvement in the cases studied here.

It is clear that these perturbation analyses may be extended to more general systems like  $A_2B_2X_n$  and  $A_2B_2P_nX_m$  etc., where the  $A_2B_2$  part will consist of a number of simple  $A_2B_2$  patterns <sup>7,8</sup> which may be analysed by one of the methods described above.

The proton-proton couplings found in this investigation agree well with those found in other *p*-substituted benzenes.<sup>2,3,21-24</sup> One of the *meta* couplings is slightly larger than in nonfluorinated compounds and has been attributed to the *meta* coupling across the fluorine substituent. The fluorine-hydrogen couplings are of the same magnitude as those found in other *p*-substituted fluorobenzenes.<sup>10-12,22-24</sup> Though these couplings, especially  $J_{meta}^{HF}$ , show a fairly large variation depending upon the substituent, no simple correlation of the couplings with the electron-donating and -attracting properties of the substituents has been noticed.

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