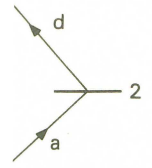

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As $|J|$ increases, θ increases and the functions are mixed. The energy levels are separated by more than if there were no mixing. The other extreme of the AB system is reached when $\nu_A = \nu_B$, the A_2 system. Now θ is 45° and there is maximum mixing to give one state symmetric with respect to exchange of nuclei, $2^{-1/2}(\alpha\beta + \beta\alpha)$, with energy $\frac{1}{4}J$ and an anti-symmetric state $2^{-1/2}(\alpha\beta - \beta\alpha)$ with energy $-\frac{3}{4}J$ (Problem 2-11).

For like nuclides (i.e. those with the same magnetogyric ratio) the relative intensities of the transitions in the spectrum are given by (cf. Eqn 2-46).

$$|\langle s|\,\hat{F}_-|r\rangle|^2 \qquad (2\text{-}72)$$

where $\hat{F}_-(=\hat{I}_{A-}+\hat{I}_{B-})$ lowers the value of m_T by one unit, giving a selection rule

$$\Delta m_T = -1 \qquad (2\text{-}73)$$

The AB system therefore has four allowed transitions which are shown in the energy-level diagram (Fig. 2-1). Their relative intensities are found by operating with $\hat{F}_-$ on the lower state. For example

$$\hat{F}_-|3\rangle = \cos\theta\,\hat{F}_-|\alpha\beta\rangle + \sin\theta\,\hat{F}_-|\beta\alpha\rangle \qquad (2\text{-}74)$$

but

$$\begin{aligned}\hat{F}_-|\alpha\beta\rangle &= \hat{I}_{A-}|\alpha\beta\rangle + \hat{I}_{B-}|\alpha\beta\rangle\\ &= |\beta\beta\rangle + 0\end{aligned} \qquad (2\text{-}75)$$

so

$$\langle 4|\,\hat{F}_-|3\rangle = (\cos\theta + \sin\theta) \qquad (2\text{-}76)$$

and the intensity of this transition is proportional to $(1+\sin 2\theta)$.

Table 2-3 shows the transition frequencies and intensities of the AB system. Figure 2-2 gives an example, and Fig. 2-3 shows the way in which the AB spectrum varies as θ increases. When $J/(\nu_B - \nu_A)$ is zero (the AX limit), the spectrum consists of four lines of equal intensity. Lines a and b arise from transitions in which the spin of the A nucleus changes and that of the X nucleus is unaltered. These can be described accurately as A lines, and are centred on ν_A and split by $|J|$. This is the first-order situation described in Chapter 1.

Table 2-3 NMR spectrum of the *AB* system

Transition	*Frequency*	*Relative intensity*
d $4\leftarrow 2$	$\frac{1}{2}(\nu_A+\nu_B)+\frac{1}{2}J+\frac{1}{2}D$	$1-\sin 2\theta$
b $4\leftarrow 3$	$\frac{1}{2}(\nu_A+\nu_B)+\frac{1}{2}J-\frac{1}{2}D$	$1+\sin 2\theta$
c $3\leftarrow 1$	$\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}J+\frac{1}{2}D$	$1+\sin 2\theta$
a $2\leftarrow 1$	$\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}J-\frac{1}{2}D$	$1-\sin 2\theta$

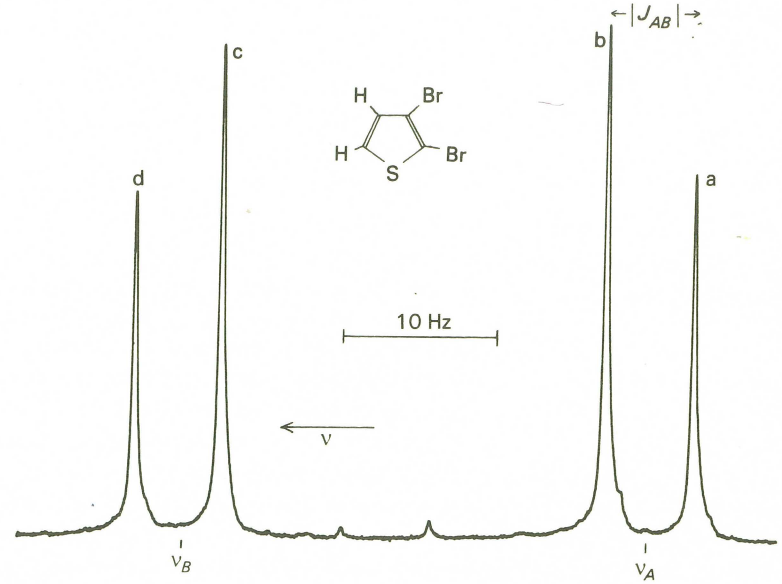

Fig. 2-2 The 100 MHz proton NMR spectrum of 2,3-dibromothiophene, an example of an *AB* spin system. The chemical shift difference $|\nu_A - \nu_B|$ is 30·5 Hz and the coupling constant is 5·7 Hz, giving a ratio of 5·3. The transitions are labelled in accordance with Fig. 2-1 and Table 2-3. The transition assignments (a, b, c and d) are made assuming *J* is positive.

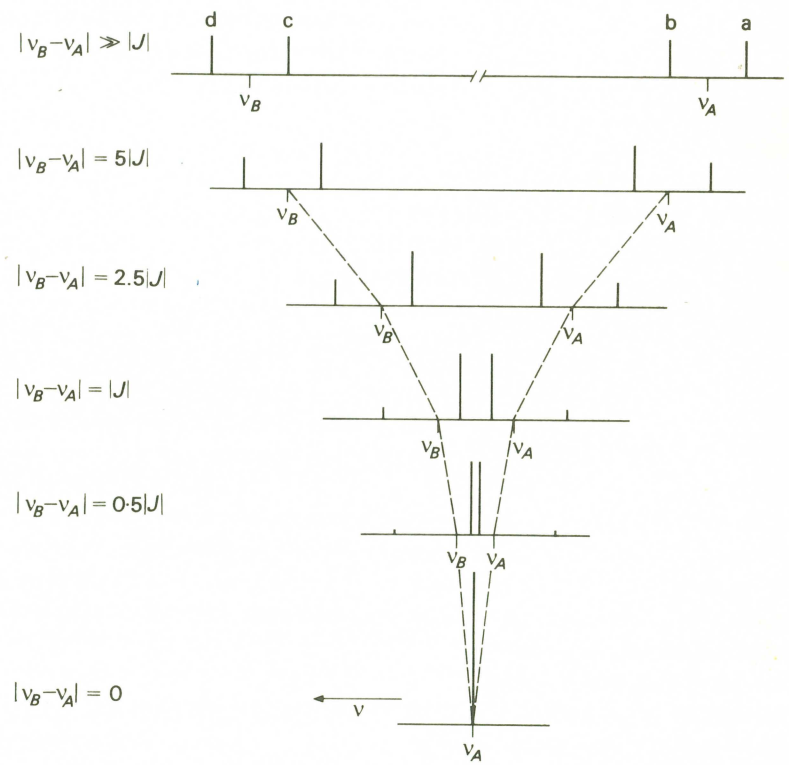

Fig. 2-3 *AB* spectra showing the effect of varying the ratio of the coupling constant to the difference in *A* and *B* resonance frequencies. The top spectrum is an *AX* type ($\theta = 0$) and the bottom is an A_2 type ($\theta = \pi/4$).