

The terms  $a_{rs}$  are the complex amplitudes of the spectral peaks. The peak frequencies are given by differences in the Hamiltonian eigenvalues:

$$\Omega_{rs} = -\Omega_r + \Omega_s$$

In order to complete the calculation of the NMR signal, we require the signal amplitudes  $a_{rs}$ . Here, we must be careful, since in strongly coupled systems the different  $(-1)$ -quantum coherences couple to the observable magnetization with different efficiencies. This may be seen by repeating the arguments in Appendix A.5 for the strongly coupled system. For example, Equation A.17 becomes

$$M_x \sim \langle \hat{I}_x \rangle = \text{Tr}\{\hat{\rho} \hat{I}_x\} = \sum_{r=1}^4 \sum_{s=1}^4 \langle r | \hat{\rho} | s \rangle \langle s | \hat{I}_x | r \rangle = \sum_{r=1}^4 \sum_{s=1}^4 \rho_{rs} \langle s | \hat{I}_x | r \rangle$$

which shows that a coherence  $\rho_{rs}$  couples to the observable magnetization with a factor  $\langle s | \hat{I}_x | r \rangle$ . The signal coupling efficiencies for the four  $(-1)$ -quantum coherences in the AB system are readily calculated to be

$$\begin{aligned} \langle 1 | \hat{I}_x | 2 \rangle &= \frac{1}{2} \left( \cos \frac{1}{2} \xi + \sin \frac{1}{2} \xi \right) & \langle 1 | \hat{I}_x | 3 \rangle &= \frac{1}{2} \left( \cos \frac{1}{2} \xi - \sin \frac{1}{2} \xi \right) \\ \langle 2 | \hat{I}_x | 4 \rangle &= \frac{1}{2} \left( \cos \frac{1}{2} \xi + \sin \frac{1}{2} \xi \right) & \langle 3 | \hat{I}_x | 4 \rangle &= \frac{1}{2} \left( \cos \frac{1}{2} \xi - \sin \frac{1}{2} \xi \right) \end{aligned}$$

In general, two of the four coherences provide stronger NMR signals than the other two. In the case of magnetic equivalence ( $\xi = \pi/2$ ), two of the coherences do not induce NMR signals at all.

Taking this into account, we get the following general expression for the quadrature-detected signal amplitude generated by the coherence  $\rho_{rs}$ :

$$a_{rs} = 2i\rho_{rs}(0) \langle r | \hat{I}_x | s \rangle \exp\{-i\phi_{\text{rec}}\} \quad (\text{A.32})$$

where  $\phi_{\text{rec}}$  is the receiver phase. This equation applies to any  $(-1)$ -quantum coherence in an arbitrary coupled system.

The above expressions may be combined to obtain the NMR signal obtained by applying a single  $\pi/2$  pulse to an ensemble of AB systems:

$$s(t) = a_{21} \exp\{[i\Omega_{21} - \lambda]t\} + a_{31} \exp\{[i\Omega_{31} - \lambda]t\} \\ + a_{42} \exp\{[i\Omega_{42} - \lambda]t\} + a_{43} \exp\{[i\Omega_{43} - \lambda]t\}$$

The signal frequencies are given by

$$\begin{aligned} \Omega_{21} &= \frac{1}{2} \Omega_{\Sigma} + \omega_{12}^A - \frac{1}{2} \sqrt{(\omega_{12}^B)^2 + \Omega_{\Delta}^2} \\ \Omega_{31} &= \frac{1}{2} \Omega_{\Sigma} + \omega_{12}^A + \frac{1}{2} \sqrt{(\omega_{12}^B)^2 + \Omega_{\Delta}^2} \\ \Omega_{42} &= \frac{1}{2} \Omega_{\Sigma} - \omega_{12}^A + \frac{1}{2} \sqrt{(\omega_{12}^B)^2 + \Omega_{\Delta}^2} \\ \Omega_{43} &= \frac{1}{2} \Omega_{\Sigma} - \omega_{12}^A - \frac{1}{2} \sqrt{(\omega_{12}^B)^2 + \Omega_{\Delta}^2} \end{aligned}$$

and the signal amplitudes after a single  $\pi/2$  pulse are

$$\begin{aligned} a_{21} &= \frac{1}{2} \left( \cos \frac{1}{2} \xi + \sin \frac{1}{2} \xi \right)^2 = \frac{1}{2} (1 + \sin \xi) & a_{31} &= \frac{1}{2} \left( \cos \frac{1}{2} \xi - \sin \frac{1}{2} \xi \right)^2 = \frac{1}{2} (1 - \sin \xi) \\ a_{42} &= \frac{1}{2} \left( \cos \frac{1}{2} \xi + \sin \frac{1}{2} \xi \right)^2 = \frac{1}{2} (1 + \sin \xi) & a_{43} &= \frac{1}{2} \left( \cos \frac{1}{2} \xi - \sin \frac{1}{2} \xi \right)^2 = \frac{1}{2} (1 - \sin \xi) \end{aligned}$$

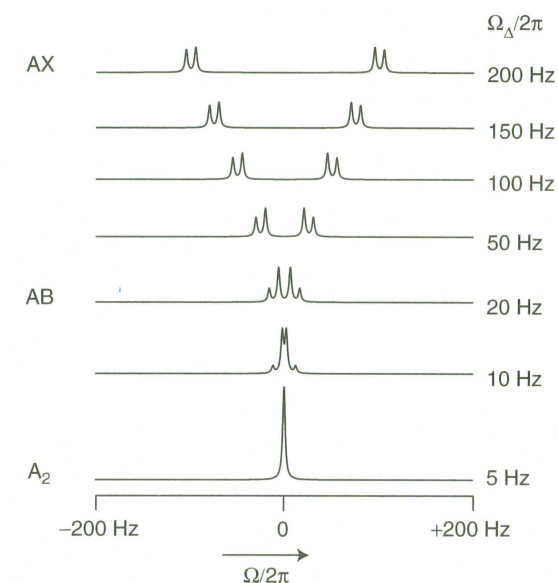
assuming  $\phi_{\text{rec}} = 0$ .

After FT, we get the following expression for the NMR spectrum:

$$S(\Omega) = a_{21} \mathcal{L}(\Omega; \Omega_{21}, \lambda) + a_{31} \mathcal{L}(\Omega; \Omega_{31}, \lambda) + a_{42} \mathcal{L}(\Omega; \Omega_{42}, \lambda) + a_{43} \mathcal{L}(\Omega; \Omega_{43}, \lambda)$$

displaying four peaks with different frequencies and amplitudes.

The simulations shown below illustrate the case with  $\Omega_{\Sigma} = 0$ , no dipole-dipole coupling ( $d_{jk} = 0$ ), a  $J$ -coupling of  $J_{jk} = 10$  Hz, and different values for the chemical shift frequency difference  $\Omega_{\Delta}$ :



**Figure A.7**

Spectra of spin-1/2 pairs, in the case of  $J_{jk} = 10$  Hz and zero dipole-dipole coupling.

In the limit of a large frequency difference  $\Omega_{\Delta}$ , the system is weakly coupled, and the spectrum displays the typical four-peak pattern of an AX spin system (although with small residual distortions in the relative peak amplitudes). As  $\Omega_{\Delta}$  is reduced, the outer peaks lose amplitude (these peaks correspond to the coherences  $\rho_{31}$  and  $\rho_{43}$ , which are weakly excited by the  $\pi/2$  pulse and which also couple poorly to the observable signal). At the same time, the inner peaks gain amplitude. In the case of a very small chemical shift difference, the outer peaks disappear and the inner peaks coalesce. In the limit of identical chemical shift frequencies, the system displays only a single spectral peak. This is the case of magnetic equivalence in the absence of  $J$ -coupling (see Figure 14.6a).

The simulation shown in Figure A.8 illustrates what happens if there is no  $J$ -coupling  $J_{jk} = 0$ , but there is a finite secular dipole-dipole coupling of  $d_{jk}/2\pi = 10$  Hz. The behaviour of the spin system is similar to the  $J$ -coupled case in the limit of large chemical shift difference: a four-peak AX pattern is observed, with a frequency splitting of  $2d_{jk}/2\pi = 20$  Hz between the doublet components. However, when  $\Omega_{\Delta}$  is reduced, it is the central peaks that lose amplitude in the dipolar-coupled case. At very small values of  $\Omega_{\Delta}$ , the central peaks vanish altogether, leaving a doublet with splitting  $3d_{jk}/2\pi = 30$  Hz.