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The Direct Method

NMDR in an AB System

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A superoperator formalism is used to calculate the theoretical nuclear magnetic double resonance spectra for an AB spin system. Transition frequencies and intensities are derived for the cases of tickling, spin decoupling and perturbation of the double quantum transition.

1. INTRODUCTION

Nuclear magnetic resonance spectra are normally calculated from a spin Hamiltonian H. The eigenvalues of H give the energy levels of the system, and the transition frequencies are found from the differences between these energy levels.

Another method of finding transition frequencies has been described by Banwell and Primas.[1] In this so called direct method the transition frequencies are found directly as the eigenvalues of a derivation superoperator Λ° generated by the normal Hamilton operator. When Λ° operates on a spin operator X the commutator of H and X is formed

$$\Lambda^\circ X = [H, X] = HX - XH \tag{1}$$

If the dimension of H is $n \times n$, the dimension of the Λ° matrix is $n^2 \times n^2$. The solution of the eigenvalue problem in this formalism involves the construction of n^2 linearly independent basis operators, and the evaluation of the commutators between the basis operators and H. The superoperator matrix is then diagonalized. The advantage of this method is that no energy levels need to be constructed and the observable quantities, *i.e.* the transition frequencies, are directly given by the eigenvalues of the matrix.

The derivation superoperator matrix can be constructed without explicit use of eqn. (1). In this "basis function representation"[2] the superoperator matrix elements are found directly from the Hamiltonian matrix elements as [2,3]

$$\Lambda^\circ{}_{jklm} = \delta_{km}H_{jl} - \delta_{jl}H_{km} \tag{2}$$

where j,k$\cdots$ are the basis functions of H. The basis operators R_{jk} of the Λ° matrix need not be known in explicit form when this representation is used. Eqn. (2) ensures that they will be "shift operators" with the property of changing one basis function k of H into another j.

The "direct method" has been used to calculate single and multiple quantum spectra of a few multispin systems.[1,3-5] The "direct method" is also applicable to double resonance spectra if a transformation to the rotating frame is made. NMDR in an AX spin system has been studied in a basis operator formalism.[6,7]

In this paper the "direct method" is applied to NMDR in an AB system. The "basis function representation" will be used here as it offers the simpler way of calculating the superoperator matrix elements.

2. THE AB SYSTEM

The double resonance Hamiltonian of an AB system in the rotating frame is given by (in frequency units)

$$V = -(\nu_A - \nu_2)I_A{}^z - (\nu_B - \nu_2)I_B{}^z + J\mathbf{I}_A \cdot \mathbf{I}_B - \frac{\gamma H_2}{2\pi}(I_A{}^x + I_B{}^x) \tag{3}$$

where ν_2 is the frequency of the irradiating rf field H_2, ν_A and ν_B are the Larmor frequencies of nuclei A and B, J the spin-spin coupling between the nuclei, and γ their gyromagnetic ratio.

It is well known that the single resonance Hamiltonian H° of an AB system is diagonalized by choosing the basis functions

$$\begin{aligned} \psi_1 &= \beta\beta & \psi_2 &= \beta\alpha\cos\theta + \alpha\beta\sin\theta \\ \psi_3 &= -\beta\alpha\sin\theta + \alpha\beta\cos\theta & \psi_4 &= \alpha\alpha \end{aligned} \tag{4}$$

Table 1. Matrix elements of the rotating frame Hamiltonian V for the AB system.

Basis function	ψ_1	ψ_2	ψ_3	ψ_4
ψ_1	$(\nu_A + \nu_B)/2 - \nu_2 + J/4$	$-\frac{\nu}{2}(\cos\theta + \sin\theta)$	$-\frac{\nu}{2}(\cos)\theta - \sin\theta)$	0
ψ_2	$-\frac{\nu}{2}(\cos\theta + \sin\theta)$	$C - J/4$	0	$-\frac{\nu}{2}(\cos\theta + \sin\theta)$
ψ_3	$-\frac{\nu}{2}(\cos\theta - \sin\theta)$	0	$-C - J/4$	$-\frac{\nu}{2}(\cos\theta - \sin\theta)$
ψ_4	0	$-\frac{\nu}{2}(\cos\theta + \sin\theta)$	$-\frac{\nu}{2}(\cos\theta - \sin\theta)$	$-(\nu_A + \nu_B)/2 + \nu_2 + J/4$

$\nu = \frac{\gamma H_2}{2\pi}$ $\quad \tan 2\theta = J/(\nu_A - \nu_B)$

$C = \frac{1}{2}[(\nu_A - \nu_B)^2 + J^2]^{1/2}$

Table 2. Matrix elements of the rotating frame derivation superoperator Λ for the AB system.

Basis operator	R_{14}	R_{12}	R_{13}	R_{24}	R_{34}	R_{11}	R_{22}	R_{23}	R_{32}	R_{33}	R_{44}	R_{21}	R_{31}	R_{42}	R_{43}	R_{41}
R_{14}	$2\nu_d - 2\nu_2$	$-\frac{v}{2}(+)$	$-\frac{v}{2}(-)$	$\frac{v}{2}(+)$	$\frac{v}{2}(-)$	0	0	0	0	0	0	0	0	0	0	0
R_{12}		$\nu_d - \nu_2 - C + J/2$	0	0	0	$-\frac{v}{2}(+)$	$\frac{v}{2}(+)$	0	$\frac{v}{2}(-)$	0	0	0	0	0	0	
R_{13}			$\nu_d - \nu_2 + C + J/2$	0	0	$-\frac{v}{2}(-)$	0	$\frac{v}{2}(+)$	0	$\frac{v}{2}(-)$	0	0	0	0		
R_{24}				$\nu_d - \nu_2 + C - J/2$	0	0	$-\frac{v}{2}(+)$	$-\frac{v}{2}(-)$	0	0	$\frac{v}{2}(+)$	0	0			
R_{34}					$\nu_d - \nu_2 - C - J/2$	0	0	0	$-\frac{v}{2}(+)$	$-\frac{v}{2}(-)$	$\frac{v}{2}(-)$	0				
R_{11}						0	0	0	0	0	0					
R_{22}							0	0	0	0						
R_{23}								2C	0							

The matrix is symmetric about the principal diagonal. It is also symmetric about the secondary diagonal but for a sign reversal of ν_d, ν_2, C and $\sin\theta$. The following abbreviations are used:

$$\nu_d = \frac{\nu_A + \nu_B}{2}; \quad \frac{v}{2}(+) = \frac{\gamma H_2}{4\pi}(\cos\theta + \sin\theta); \quad \frac{v}{2}(-) = \frac{\gamma H_2}{4\pi}(\cos\theta - \sin\theta); \quad C = \tfrac{1}{2}[(\nu_A - \nu_B)^2 + J^2]^{1/2}.$$

where $\tan 2\theta = J/(\nu_A - \nu_B)$. The matrix elements of the rotating frame Hamiltonian V in this set of basis functions is given in Table 1. In analogy with eqn. (2) we can calculate the derivation superoperator Λ, corresponding to the rotating frame Hamiltonian V from

$$\Lambda_{jklm} = \delta_{km} V_{jl} - \delta_{jl} V_{km} \tag{5}$$

This matrix is given in Table 2.

The basis operators of Table 2 are eigenoperators to the derivation superoperator Λ^z, which is generated by the spin operator I^z, with eigenvalues $\mu = 0, \pm 1, \pm 2$. The matrix has been arranged according to these μ values.

This matrix can in the general case not be diagonalized, but can be handled in the practically important cases of spin tickling and spin decoupling.

2a. THE SINGLE RESONANCE SPECTRUM

The single resonance spectrum can be found from the derivation superoperator matrix in a coordinate system rotating with the frequency ν_1 of the observing rf field H_1. This matrix is obtained if ν_2 and H_2 of eqn. (3) and Table 2 are replaced by ν_1 and H_1. For weak observing fields all off-diagonal elements in the Λ matrix can be neglected. The transition frequencies are given by the frequencies ν_1 at which the frequency-dependent diagonal elements become equal to zero.[2] The ν_1 frequencies which make the $\mu = -1$ elements Λ_{1212}, Λ_{1313}, Λ_{2424}, and Λ_{3434} zero constitute the four single quantum transition frequencies of the AB spectrum (transitions A2, B2, B1, and A1, respectively).

The intensity L of a transition corresponding to an eigenoperator X in the rotating frame is given by [1]

$$L \propto |\,\mathrm{Tr}\left\{\sum_i I_i^+ X\right\}|^2 \tag{6}$$

In application of eqn. (6) to the eigenoperators obtained from Table 2, it can be noticed that only basis operators from the $\mu = -1$ block will contribute to the intensities.[2]

In the AB single resonance case, the off-diagonal elements in Table 2 are negligible and the eigenoperators are the same as the basis operators. Then

$$L_{jk} \propto |\,\mathrm{Tr}\,\{(I_A^+ + I_B^+)R_{jk}\}|^2 \tag{7}$$

Using the annihilating property [2] of the shift operators R_{jk} this is reduced to

$$L_{jk} \propto |\,\langle\psi_j|\,I_A^+ + I_B^+\,|\psi_k\rangle\,|^2 \tag{8}$$

which is the same expression as obtained in the indirect method. The intensities in the single resonance spectrum become

$$\begin{aligned} L_{12} = L_{24} &\propto (\cos\theta + \sin\theta)^2 \\ L_{13} = L_{34} &\propto (\cos\theta - \sin\theta)^2 \end{aligned} \tag{9}$$

2b. IRRADIATION OF A SINGLE QUANTUM TRANSITION (TICKLING)

The perturbing rf field H_2 is now centered on one of the single quantum transitions. The Λ matrix in the coordinate system rotating with frequency ν_2 is given by Table 2. The transition frequencies in the rotating frame will

be given by the eigenvalues of the matrix, and the corresponding transition frequencies in the laboratory frame are obtained by adding the frequency of the irradiating field ν_2 to these values. In tickling experiments the H_2 field is assumed to perturb only one transition and the influence on other transitions is neglected. Consider the case when the line A1 (corresponding to shift operator R_{34}) is irradiated. This means that the element Λ_{3434} in Table 2 is set to zero, *i.e.* $\nu_2 = (\nu_A + \nu_B)/2 - C - J/2$. When this value of ν_2 is introduced into the other frequency dependent matrix elements, two pairs of degenerate diagonal elements will appear ($\Lambda_{1414} = \Lambda_{1313}$ and $\Lambda_{2323} = \Lambda_{2424}$). The non-negligible off-diagonal elements Λ_{1314} and Λ_{2324} will ensure complete mixing of the corresponding basis operators, on diagonalization of the matrix. These 2×2 matrices are diagonalized by the transformations

$$\begin{aligned} R'_{13} &= (R_{13} + R_{14})/\sqrt{2} & R'_{23} &= (R_{23} + R_{24})/\sqrt{2} \\ R'_{14} &= (-R_{13} + R_{14})/\sqrt{2} & R'_{24} &= (-R_{23} + R_{24})/\sqrt{2} \end{aligned} \tag{10}$$

which gives the eigenvalues

$$\begin{aligned} \Lambda'_{1313} &= 2C + J - \frac{v}{2}(\cos\theta - \sin\theta) & \Lambda'_{2323} &= 2C - \frac{v}{2}(\cos\theta - \sin\theta) \\ \Lambda'_{1414} &= 2C + J + \frac{v}{2}(\cos\theta - \sin\theta) & \Lambda'_{2424} &= 2C + \frac{v}{2}(\cos\theta - \sin\theta) \end{aligned} \tag{11}$$

This means that the lines B1 and B2 are split into doublets with splittings $S = v(\cos\theta - \sin\theta)$.

When A2 is irradiated, the splittings in B1 and B2 turn out to be $v(\cos\theta + \sin\theta)$. Corresponding expressions are obtained for the splittings of the A lines when one of the B lines is irradiated.

Thus the results of a tickling experiment is obtained in this formalism by selecting the proper ν_2 and considering the diagonal elements of the Λ matrix. The off-diagonal elements connecting the doubly degenerate elements give the magnitudes of the corresponding splittings. The difference between progressive and regressive transitions [8] also appears in the formalism. In the progressive case a $\mu = -1$ transition is degenerate with a $\mu = -2$ transition but in the regressive case it is degenerate with a transition in the $\mu = 0$ block.

In tickling experiments the amplitude of the H_2 field should be small and only one transition be perturbed. The intensities of the unperturbed transitions remain approximately unchanged. When A1 is irradiated the intensities in the B1 doublet will be given by

$$\begin{aligned} L'_{13} &\propto |\mathrm{Tr}\{(I_A^+ + I_B^+) R'_{13}\}|^2 = \tfrac{1}{2}|\mathrm{Tr}\{(I_A^+ + I_B^+)(R_{13} + R_{14})\}|^2 \\ L'_{14} &\propto |\mathrm{Tr}\{(I_A^+ + I_B^+) R'_{14}\}|^2 = \tfrac{1}{2}|\mathrm{Tr}\{(I_A^+ + I_B^+)(-R_{13} + R_{14})|^2 \end{aligned} \tag{12}$$

Only the shift operators R_{13} and R_{24} belonging to the $\mu = -1$ block have to be accounted for.

Thus

$$\begin{aligned} L'_{13} &\propto |\mathrm{Tr}\{(I_A^+ + I_B^+) R'_{13}\}|^2 = \\ &= \tfrac{1}{2}|\mathrm{Tr}\{(I_A^+ + I_B^+) R_{13}\}|^2 = \tfrac{1}{2}(\cos\theta - \sin\theta)^2 \end{aligned} \tag{13}$$

and $$L'_{14} \propto |\mathrm{Tr}\{(I_A^+ + I_B^+) R'_{14}\}|^2 = \\ = \tfrac{1}{2}|\mathrm{Tr}\{(I_A^+ + I_B^+) R_{13}\}|^2 = \tfrac{1}{2}(\cos\theta - \sin\theta)^2 \quad (14)$$

In the same way

$$L'_{23} = L'_{24} \propto \tfrac{1}{2}(\cos\theta + \sin\theta)^2 \quad (15)$$

This means that the lines B1 (corresponding to operator 24) and B2 (corresponding to operator 13) are split into symmetrical doublets, when the irradiating field is exactly centered on transition A1. This is the same result as obtained from the indirect method.[8]

2c. IRRADIATION OF THE DQ TRANSITION

If the rf field H_2 is centered on the double quantum transition, second-order splittings can be shown to appear in the spectral lines.[9,10] Irradiation of the DQ transition corresponds to setting Λ_{1414} (and Λ_{4141}) = 0, *i.e.* $\nu_2 = (\nu_A + \nu_B)/2$. When this value of ν_2 is introduced into the other frequency dependent elements of the Λ matrix, it is seen that each of the four diagonal elements in the $\mu = -1$ block will be degenerate with one diagonal element from the $\mu = +1$ block [*e.g.* $\Lambda_{1212} = \Lambda_{4242} = -C + J/2$]. Contrary to the "tickling" case there will be no first-order splittings of the degenerate lines as there are no off-diagonal elements between the $\mu = -1$ and $\mu = +1$ blocks. The basis operators involved are, however, indirectly connected by non-zero off-diagonal elements to the $\mu = 0$ block. The diagonalization of the matrix can be done with a form of perturbation theory [11,12] which introduces a new non-zero non-diagonal element between indirectly connected basis operators, as well as a second-order correction to the diagonal elements. The new elements are given by

$$\Lambda_{ijkl} = \Lambda_{ijkl} + \tfrac{1}{2}\sum_{\substack{m,n \\ \neq j,k}} \Lambda_{ijmn}\Lambda_{mnkl}\left(\frac{1}{\Lambda_{ijij} - \Lambda_{mnmn}} + \frac{1}{\Lambda_{klkl} - \Lambda_{mnmn}}\right) \quad (16)$$

From eqn. (16) and from Table 2 one finds that the new off-diagonal element which connects the four pairs of degenerate diagonal elements will be the same for all four pairs and given by

$$\Lambda_{ijkl} = \tfrac{1}{2}\left\{\frac{(\nu^2/2)(\cos\theta + \sin\theta)^2}{-C + J/2} + \frac{(\nu^2/2)(\cos\theta - \sin\theta)^2}{C + J/2}\right\} \quad (17)$$

The second order contributions to the diagonal elements are pairwise identical, *i.e.* we get the same correction in the $\mu = +1$ as in the $\mu = -1$ block. We can therefore use the same transformation as in the preceding section to diagonalize the 2 × 2 matrices and we find that the eigenvalues will be separated by

$$S = \tfrac{1}{2}\left(\frac{\gamma H_2}{2\pi}\right)^2 \left\{\frac{(\cos\theta + \sin\theta)^2}{-C + J/2} + \frac{(\cos\theta - \sin\theta)^2}{C + J/2}\right\} \quad (18)$$

This expression then gives the splitting of the four single quantum transitions on irradiation of the double quantum transition. This is in agreement with the results from the indirect method.[10]

In evaluation of the intensities, the first-order eigenoperators should be used. The perturbation expansion introduces the following corrections to the zeroth order operators.

$$R^{(1)}_{ij} = R_{ij} + \sum_{\substack{kl \\ \neq ij}} R_{kl} \frac{\Lambda_{ijkl}}{\Lambda_{ijij} - \Lambda_{klkl}} \tag{19}$$

The first-order corrections to the eigenoperators will, however, *not* contribute to the intensity since only operators from the $\mu = 0$ or $\mu = \pm 2$ blocks are added in the perturbation expansion.

The 2×2 diagonalizations lead to complete mixing of the pairwise degenerate operator states from the $\mu = -1$ and $\mu = +1$ blocks analogous to eqn. (10). As the $\mu = +1$ basis operators not contribute to the intensities we find that the intensities of the two lines in the doublets will be pairwise equal, we get symmetrical doublets.

3a. THE AX CASE. SELECTIVE DECOUPLING

NMDR in an AX system has been studied in the "direct method"[6,7] with a superoperator matrix obtained from explicit basis operators using the commutator relationship of eqn. (1). The solution is simpler, however, when carried out in the "basis function" formalism.

In the AX limit, the AB superoperator matrix of Table 2 can be simplified. When $\nu_A - \nu_B \gg J$ one obtains

$$\sin\theta = 0 \qquad \cos\theta = 1$$
$$C = \tfrac{1}{2}(\nu_A - \nu_B)$$

We rename nucleus B and call it X, and consider the case when the irradiating H_2 field is applied somewhere in the region of the ν_X frequency. Then the off-diagonal elements can be neglected when the difference between corresponding diagonal elements are of the order $\nu_2 - \nu_A$.

When these simplifications are carried out, the resulting Λ matrix for the AX system can be made blockwise diagonal by a rearrangement of the basis operators. The resulting four 4×4 submatrices are given in Table 3. Although the matrices are of high order, the eigenvalue problem can be solved in analytical form.

The A submatrix has the eigenvalues

$$\lambda_{1,2} = \nu_A - \nu_2 \pm \tfrac{1}{2}\{[(\nu_x - \nu_2 + J/2)^2 + v^2]^{1/2} + [(\nu_x - \nu_2 - J/2)^2 + v^2]^{1/2}\}$$
$$\lambda_{3,4} = \nu_A - \nu_2 \pm \tfrac{1}{2}\{[(\nu_x - \nu_2 + J/2)^2 + v^2]^{1/2} - [(\nu_x - \nu_2 - J/2)^2 + v^2]^{1/2}\} \tag{20}$$

The transition frequencies in the laboratory system are found by adding ν_2 to these λ values. The transitions are symmetric around ν_A and represent the A part of the spectrum when the X resonance is irradiated.

The eigenvalues of the B matrix are found to be

$$\lambda_{5,6} = 0 \text{ and } \lambda_{7,8} = \pm [(\nu_x - \nu_2 + J/2)^2 + v^2]^{1/2} \tag{21}$$

The C matrix is equal to the B matrix if $-J/2$ replaces $J/2$ and gives the eigenvalues

$$\lambda_{9,10} = 0 \text{ and } \lambda_{11,12} = \pm [(\nu_x - \nu_2 - J/2)^2 + v^2]^{1/2} \tag{22}$$

Table 3. The Λ matrix for the AX system.

Submatrix A

Basis operator	R_{14}	R_{13}	R_{24}	R_{23}
R_{14}	$\nu_A + \nu_X - 2\nu_2$	$-\frac{v}{2}$	$\frac{v}{2}$	0
R_{13}	$-\frac{v}{2}$	$\nu_A - \nu_2 + J/2$	0	$\frac{v}{2}$
R_{24}	$\frac{v}{2}$	0	$\nu_A - \nu_2 - J/2$	$-\frac{v}{2}$
R_{23}	0	$\frac{v}{2}$	$-\frac{v}{2}$	$\nu_A - \nu_X$

Submatrix B

Basis operator	R_{12}	R_{11}	R_{22}	R_{21}
R_{12}	$\nu_X - \nu_2 + J/2$	$-\frac{v}{2}$	$\frac{v}{2}$	0
R_{11}	$-\frac{v}{2}$	0	0	$\frac{v}{2}$
R_{22}	$\frac{v}{2}$	0	0	$-\frac{v}{2}$
R_{21}	0	$\frac{v}{2}$	$-\frac{v}{2}$	$\nu_2 - \nu_X - J/2$

Submatrix C

Basis operator	R_{34}	R_{33}	R_{44}	R_{43}
R_{34}	$\nu_X - \nu_2 - J/2$	$-\frac{v}{2}$	$\frac{v}{2}$	0
R_{33}	$-\frac{v}{2}$	0	0	$\frac{v}{2}$
R_{44}	$\frac{v}{2}$	0	0	$-\frac{v}{2}$
R_{43}	0	$\frac{v}{2}$	$-\frac{v}{2}$	$\nu_2 - \nu_X + J/2$

Submatrix D

Basis operator	R_{41}	R_{31}	R_{42}	R_{32}
R_{41}	$2\nu_2 - \nu_A - \nu_X$	$\frac{v}{2}$	$-\frac{v}{2}$	0
R_{31}	$\frac{v}{2}$	$\nu_2 - \nu_A - J/2$	0	$-\frac{v}{2}$
R_{42}	$-\frac{v}{2}$	0	$\nu_2 - \nu_A + J/2$	$\frac{v}{2}$
R_{32}	0	$-\frac{v}{2}$	$\frac{v}{2}$	$\nu_X - \nu_A$

The transition frequencies in eqns. (21) – (22) are symmetric around the origin (*i.e.* the ν_2 frequency in the laboratory system) and represent the irradiated X part of the spectrum.

The D matrix finally is the negative of A and gives transition frequencies that are the negatives of those in eqn. (20), centered around $\nu_2 - \nu_A$ ($2\nu_2 - \nu_A$ in the laboratory system).

The intensities of the transitions can be found from eqn. (6). The eigenoperators of the Λ matrix will contain different amounts of the basis operators after the diagonalization. Only the basis operators from the $\mu = -1$ block contribute to the intensities.

The intensity of a transition in the A matrix is given by

$$L = |a_{13} + a_{24}|^2 \tag{23}$$

where a_{13} and a_{24} are the amounts of the basis operators R_{13} and R_{24} contained in the corresponding eigenoperator R

$$R = a_{14}R_{14} + a_{13}R_{13} + a_{24}R_{24} + a_{23}R_{23} \tag{24}$$

The a_{ij} coefficients are found from the diagonalization of the A matrix and it is found that the intensities of the $\lambda_{1,2,3,4}$ transitions can be expressed as

$$L_{1,2} \propto \sin^2 \frac{\theta^+ - \theta^-}{2} \quad L_{3,4} \propto \cos^2 \frac{\theta^+ - \theta^-}{2} \tag{25}$$

where the angles θ^+ and θ^- are defined as

$$\cos\theta^{\pm} = \frac{\nu_x - \nu_2 \pm J/2}{[(\nu_x - \nu_2 \pm J/2)^2 + v^2]^{1/2}} \tag{26}$$

In the B matrix the intensities are given by $L = |b_{12}|^2$ where b_{12} gives the coefficient of the R_{12} operator in the eigenoperators. This gives for the $\lambda_{7,8}$ transitions the intensities

$$L_{7,8} \propto \frac{(\nu_x - \nu_2 + J/2)^2 + v^2/2 \pm (\nu_x - \nu_2 + J/2)\,[(\nu_x - \nu_2 + J/2)^2 + v^2]^{1/2}}{2(\nu_x - \nu_2 + J/2)^2 + 2v^2} \tag{27}$$

It is convenient to make a transformation of the B matrix to determine the intensity of the $\lambda = 0$ transitions. A rotation of the basis operators R_{22} and R_{11} through the angle $\pi/4$ will leave one row with only zero elements which is factored out of the matrix. The intensity of the $\lambda = 0$ transitions is found to be

$$L_{4,5} \propto \frac{v^2}{(\nu_x - \nu_2 + J/2)^2 + v^2} \tag{28}$$

The C matrix is identical with the B matrix on a substitution $J/2 \rightarrow -J/2$ and the intensities are

$$L_{11,12} \propto \frac{(\nu_x - \nu_2 - J/2)^2 + v^2/2 \pm (\nu_x - \nu_2 - J/2)\,[(\nu_x - \nu_2 - J/2)^2 + v^2]^{1/2}}{2(\nu_x - \nu_2 - J/2)^2 + 2v^2} \tag{29}$$

and

$$L_{9,10} = \frac{v^2}{(\nu_x - \nu_2 - J/2)^2 + v^2} \tag{30}$$

No basis operators from the $\mu = -1$ block are contained in the D matrix, and the four D matrix transitions have zero intensities.

3b. INTERPRETATION OF AX FREQUENCIES AND INTENSITIES

In eqns. (20) and (25) we have from the "A" matrix obtained expressions for transitions and intensities in the A part of the spectrum when nucleus X is irradiated. These agree with those obtained by the indirect method.[13]

Eqns. (21), (22), (27), and (29) describe the irradiated X part of the spectrum. These equations have the same form as if we regard the two single

resonance transitions X1 and X2 as two single spins $\frac{1}{2}$, an interpretation already discussed in Ref. 7.

According to the analogy with "single spin $\frac{1}{2}$" we could expect one of the peaks in eqns. (27) and (29) to be inverted. This negative intensity cannot be accounted for in the present formalism, nor in the indirect method without recourse to a full density matrix treatment. The D matrix transition frequencies are the mirror image of those from the A matrix but have zero intensity. This is a direct consequence of the AX approximation.

The transitions $\lambda = 0$ are the resonances due to the H_2 field itself. Eqns. (26) and (28) represent the effect of the finite amplitude of the H_2 field at the two X line positions. This results in absorption of quanta from the H_2 field at the ν_2 frequency.

4. CONCLUSIONS

Although the "direct" method may appear complicated, the use of "the basis function representation" makes it as easy to handle as the normal "indirect" method. It is seen that various types of double resonance spectra in AB spin systems can be derived in the superoperator formalism. The direct method even has a few advantages over the indirect method. The derivation superoperator gives us in a natural way the appearance of the complete NMDR spectrum including the irradiated nuclei and as an additional feature gives the resonance due to the H_2 field itself.

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