JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 94, NUMBER 9 MAY 3, 1972

Effect of Molecular Reorganization on Nuclear Magnetic Resonance Line Shapes. Permutation of Indices Method

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Abstract: The density matrix equations describing nmr in chemically exchanging systems have been generalized to include the reaction $AB + CD \rightleftharpoons AC + BD$, where the chemical species are labeled in terms of their exchanging parts. The calculation is first derived in terms of an integral representation and then, by differentiation, a Bloch-like set of differential equations is obtained. A great simplification (which is called the permutation of indices method) is then made in the algebraic evaluation of the molecular reorganization which bypasses the previous need to define the "*R*" matrices. An explicit catalog of all possible interactions is then displayed as well as the form of the density matrix equation in the low rf power domain. A generalization of the relaxation operator $(\dot{\rho})_{\text{relaxation}} = \rho/\tau$ used in the main part of the paper is given in Appendix II.

Starting with the work of Gutowsky,[1] the effect of exchange processes on nmr spectra has been the subject of extensive theoretical and experimental investigation. The subject has been widely reviewed.[2–5] It is one of the few techniques which can be used to measure the rate of an exchange process in a system at thermodynamic equilibrium and has been applied to a variety of intramolecular reorganizations such as hindered rotation, configurational inversion, ring inversion, certain molecular rearrangements, as well as different kinds of proton transfer processes.[2–5]

The experimentally measured quantity, the magnetization, is obtained from the relation

$$M_{\text{total}} = \sum_i (\text{concentration } i)\ \mathrm{Tr}\rho^i\mathbf{M}^i$$

where $\mathbf{M}^i$ is the magnetization matrix and ρ^i is the density matrix of molecule "*i*."

In principle the density matrix formalism for nmr line shapes, due to Kaplan[6,7] and elaborated by Alexander,[8] applies to all cases of inter- and intramolecular reorganization processes in diamagnetic systems. Binsch[9] has derived explicitly a density matrix formalism in Liouville space to describe the general case of intra- and intermolecular exchange. However, the notation and algebra in all these methods are of such complexity that they do not lend themselves to a simple physical understanding. Several approximate treatments, involving modified Bloch equations,[10] have appeared but these mainly apply to first-order systems, weakly coupled.[11–17]

It is the purpose of this article to reexamine the basic assumptions of the density matrix formalism and to show how, within this theoretical framework, a simple unified treatment may be easily derived to treat all intra- and intermolecular exchanging systems. The procedures are simple enough that they allow derivation of the density matrix equations without recourse to computer techniques. We believe that it is instructive to see displayed the principle features of these equations, features which are concealed by the black box character of computer algebraic calculations.

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[2] A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Phys. Chem.*, **67**, 280 (1963).

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[4] C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

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[7] J. I. Kaplan, *ibid.*, **28**, 462 (1958).

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In section I we derive the basic equations for nuclear magnetic resonance in reorganizing systems (NMRIRS) from a kinetic theory point of view (*i.e.*, integral equation formulation) and then reexpress these results in an equivalent Bloch formulation (differential equation formulation).[10] It is then shown, in section II, that if the basis representation is used the exchange operator becomes a permutation matrix which acts only to rearrange the order of the individual spin functions. Simplifications of the density matrix equations appropriate to low rf power are made in section III. Then in section IV a general prescription for applying the method is presented and several examples are worked out.

Appendices I and II treat respectively the equilibrium matrix and a more general theory of nuclear relaxation, and in Appendix III there are some remarks on the relationship of the preexchange lifetimes to rate constants and concentrations of species. It is our hope that with the simplified methods of writing down the density matrix equations that nmr line shape analysis will become a truly standard technique for kinetic studies of fast exchange in equilibrium systems.

I. General Results

Consider the general reaction

$$\mathrm{AB} + \mathrm{CD} \rightleftarrows \mathrm{AC} + \mathrm{BD} \tag{1}$$

where the chemical species have been described in terms of their exchanging parts. The nuclear spin Hamiltonian[4] is of the general form

$$\mathcal{H}_{\mathrm{AB}} = \sum_i \omega_{0_i} I_i^{\gamma} + \sum_{i>j} J_{ij} I_i \cdot I_j + \sum_i (\omega_{1_i} \cos \omega t I_i^{x} - \omega_{1_i} \sin \omega t I_i^{y}) = \mathcal{H}^0 + \mathcal{H}(t) \tag{2}$$

where $\omega_{0_i} = \gamma_i H^z$, $\omega_{1_i} = \gamma_i H_1$, and H^z and H_1 are respectively the static applied field in the z direction and the magnitude of the circularly polarized radio frequency field in the x,y plane.

If any one of the reacting species in (1) were isolated, it would obey the density matrix equation

$$\dot{\rho}^{\mathrm{AB}} = \frac{i}{\hbar}[\rho^{\mathrm{AB}}, \mathcal{H}_{\mathrm{AB}}] - \frac{\rho^{\mathrm{AB}}}{T_{\mathrm{OD}}{}^{\mathrm{AB}}} - \frac{(\rho_{\mathrm{D}}{}^{\mathrm{AB}} - \rho_{\mathrm{O}}{}^{\mathrm{AB}})}{T_{\mathrm{D}}{}^{\mathrm{AB}}} \tag{3}$$

where T_{OD} refers to the off-diagonal elements of the density matrix ρ^{AB} and T_{D} to the diagonal components. $\rho_{\mathrm{O}}{}^{\mathrm{AB}}$ is the equilibrium density matrix for the isolated spin system. In this article we only consider the low power solution for NMRIRS. This implies that the diagonal elements of ρ^{AB} will never be far from equilibrium which allows us to ignore $(\rho_{\mathrm{D}}{}^{\mathrm{AB}} - \rho_{\mathrm{O}}{}^{\mathrm{AB}})/T_{\mathrm{D}}{}^{\mathrm{AB}}$. Further with low power we obtain off-diagonal elements of the density matrix linear in the rf field and diagonal elements zero order in H_1.[6,7] In this way (3) is rewritten as

$$\dot{\rho}^{\mathrm{AB}} = \frac{i}{\hbar}[\rho^{\mathrm{AB}}, \mathcal{H}^{\mathrm{AB}}] - \rho^{\mathrm{AB}}/T_{\mathrm{AB}} \tag{4}$$

A more general discussion of the "equilibrium density matrix" is given in Appendix I, and in Appendix II a generalization of the relaxation operator $\rho^{\mathrm{AB}}/T_{\mathrm{AB}}$ is derived.

Making the substitution (5) into (4)

$$\rho^{\mathrm{AB}} = \hat{\rho}^{\mathrm{AB}} e^{-t/T_{\mathrm{AB}}} \tag{5}$$

one obtains

$$\dot{\hat{\rho}}^{\mathrm{AB}} = \frac{i}{\hbar}[\hat{\rho}^{\mathrm{AB}}, \mathcal{H}^{\mathrm{AB}}] \tag{6}$$

with the solution

$$\hat{\rho}^{\mathrm{AB}}(t) = \mathcal{S}^{\mathrm{AB}}(t,t')\hat{\rho}^{\mathrm{AB}}(t')(\mathcal{S}^{\mathrm{AB}}(t,t'))^{-1}$$

or (7)

$$\rho^{\mathrm{AB}}(t) = e^{-(t-t')/T_{\mathrm{AB}}}\mathcal{S}^{\mathrm{AB}}(t,t')\rho^{\mathrm{AB}}(t')(\mathcal{S}^{\mathrm{AB}}(t,t'))^{-1}$$

For $\mathcal{H}_{\mathrm{AB}}$ independent of time it can be shown that

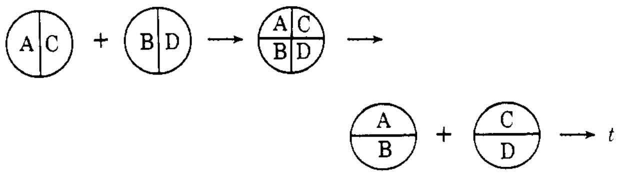
$$\mathcal{S}^{\mathrm{AB}}(t,t') = e^{-i\mathcal{H}_{\mathrm{AB}}(t-t')/\hbar} \tag{8}$$

and in general for any $\mathcal{H}_{\mathrm{AB}}$ one can show that

$$\begin{aligned} \dot{\mathcal{S}}^{\mathrm{AB}} &= \frac{i}{\hbar}\mathcal{H}_{\mathrm{AB}}\mathcal{S}^{\mathrm{AB}} \\ (\dot{\mathcal{S}}^{\mathrm{AB}})^{-1} &= \frac{i}{\hbar}(\mathcal{S}^{\mathrm{AB}})^{-1}\mathcal{H}_{\mathrm{AB}} \end{aligned} \tag{9}$$

We are now in a position to obtain the density matrix for species AB in the exchanging system (1). Consider this reaction as shown in Scheme I, with the time increasing from left to right. At time t' molecules AC and BD collide. After collision but just before they interact their density matrix will be a product

Scheme I



$$\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}} \tag{10}$$

just as the wave functions of the two independent systems are given as a product.[6,7] One can obtain the density matrix of AB from product 10 by noting that

$$\mathrm{Tr}_{\mathrm{BD}}\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}} = \rho^{\mathrm{AC}}\mathrm{Tr}_{\mathrm{BD}}\rho^{\mathrm{BD}} = \rho^{\mathrm{AC}} \tag{11}$$

using the relation $\mathrm{Tr}\rho = 1$.

After formation of the collision complex a rearrangement takes place and AB and CD emerge as products. We assume this happens so quickly that the individual nuclear spins remain unchanged during the time of the collision; *i.e.*, *the Hamiltonians of the molecules have changed while the wave functions have not.* This is the so-called "sudden approximation."[18]

The reorganization operator in an arbitrary representation is defined as

$$R\psi_{\mathrm{AC}}\psi_{\mathrm{BD}} = \sum C_{nm}\psi_{\mathrm{AB}}{}^{n}\psi_{\mathrm{CD}}{}^{m} \tag{12}$$

The system described by $\rho^{\mathrm{AB}} \times \rho^{\mathrm{CD}}$ after reorganization but before separation of products becomes[19]

$$\rho^{\mathrm{AB}}(t') \times \rho^{\mathrm{CD}}(t') \longrightarrow R\rho^{\mathrm{AC}}(t') \times \rho^{\mathrm{BD}}(t')R^{-1} \tag{13}$$

To bring about separation of $\rho^{\mathrm{AB}}(t')$ (after exchange) from the right-hand side of (13), it is necessary to take

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(18) L. I. Schiff, "Quantum Mechanics," McGraw-Hill, New York, N. Y., 1949, p 211.

(19) U. Fano, *Rev. Modern Phys.*, **29**, 74 (1957).

the trace over CD, *i.e.*, that portion which is diagonal in CD (eq 14) (*e.g.*, see eq 11).

$$\rho^{\mathrm{AB}}(t')(\text{after exchange}) = \mathrm{Tr}_{\mathrm{CD}}[R\rho^{\mathrm{AC}}(t') \times \rho^{\mathrm{BD}}(t')R^{-1}] \quad (14)$$

To obtain ρ^{AB} at time t we make use of eq 7.

$$\rho^{\mathrm{AB}}(t) = e^{-(t-t')/T_{\mathrm{AB}}}\mathcal{S}^{\mathrm{AB}}(t,t') \times \mathrm{Tr}_{\mathrm{CD}}[R\rho^{\mathrm{AC}}(t') \times \rho^{\mathrm{BD}}(t')R^{-1}](\mathcal{S}^{\mathrm{AB}}(t,t'))^{-1} \quad (15)$$

Now, the probability of a $\rho^{\mathrm{AB}}(t')$ which was formed at t' to survive to time t is

$$\frac{e^{-(t-t')/\tau_{\mathrm{AB}}}}{\tau_{\mathrm{AB}}} \quad (16)$$

so the value of ρ^{AB} at time t is given as the weighted probability of molecules AB being created at time t' and lasting until time t or

$$\rho^{\mathrm{AB}}(t) = \int_0^t \frac{e^{-(t-t')/\tau_{\mathrm{AB}}}}{\tau_{\mathrm{AB}}} e^{-(t-t')/T^{\mathrm{AB}}}\mathcal{S}^{\mathrm{AB}}(t,t')\,\mathrm{Tr}_{\mathrm{CD}}[R\rho^{\mathrm{AC}}(t') \times \rho^{\mathrm{BC}}(t')R^{-1}](\mathcal{S}^{\mathrm{AB}}(t,t'))^{-1}\,\mathrm{d}t' \quad (17)$$

The time averaging used here is equivalent to eq 38 in the paper by Gutowsky, McCall, and Slichter.[1]

A more useful form of eq 17 is obtained by differentiating (17) with respect to "t" and using eq 9. The result is

$$\dot{\rho}^{\mathrm{AB}}(t) = \frac{i}{\hbar}[\rho^{\mathrm{AB}}, \mathcal{H}_{\mathrm{AB}}] + \frac{1}{\tau_{\mathrm{AB}}} \times [\mathrm{Tr}_{\mathrm{CD}}R\rho^{\mathrm{AC}}\rho^{\mathrm{BD}}R^{-1} - \rho^{\mathrm{AB}}] - \frac{\rho^{\mathrm{AB}}}{T_{\mathrm{AB}}} \quad (18)$$

One should think of the second term on the right-hand side of eq 18 as

$$\frac{1}{\tau_{\mathrm{AB}}}[\rho^{\mathrm{AB}}\,(\text{after exchange}) - \rho^{\mathrm{AB}}\,(\text{before exchange})] \quad (19)$$

II. Evaluation of ρ (After Exchange). Permutation of Indices

In this section we derive a procedure for obtaining ρ^{AB} (after exchange) without the previous necessity of deriving the reorganization matrix. When the eigenfunction representation is used the matrix elements of R are complicated functions of the nmr parameters for the different species undergoing the exchange process. Note however that these equations can be expressed in any representation. By use of *product basis functions*, defined as $\psi_{\mathrm{B}} = |\pi_i m_i\rangle$ and $I_i^z|m_i\rangle = m_i|m_i\rangle$, R becomes a permutation matrix P, symmetric about the diagonal and with all elements either 1 or 0. Using R in the basis representation greatly simplifies the evaluation of ρ (after exchange).

It is convenient to factor the basis functions for the individual species according to the parts which exchange. Thus for AB a and b are basis functions of A and B, respectively, and ψ_{AB} is given by

$$\psi_{\mathrm{AB}} = ab \quad (20)$$

and corresponding expressions apply to the other species

$$\begin{array}{lcccccc} & \mathrm{AB} & + & \mathrm{CD} \rightleftarrows & \mathrm{AC} & + & \mathrm{BD} \\ \text{states} & ab & & cd & ac & & bd \end{array} \quad (21)$$

To evaluate ρ^{AB} (after exchange)

$$\rho^{\mathrm{AB}}{}_{ab,a'b'}\,(\text{after exchange}) = [\mathrm{Tr}_{\mathrm{CD}}R\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}}R^{-1}]_{ab,a'b'} \quad (22)$$

for an arbitrary representation, it is necessary to perform the matrix multiplication and collect all terms diagonal in the states of CD. Using basis functions, the right-hand side eq 21 may be evaluated in an alternative manner. Before exchange a matrix element of ρ^{AB} is given by

$$\begin{aligned}\rho^{\mathrm{AB}}{}_{ab,a'b'} &= \rho^{\mathrm{AB}}{}_{ab,a'b'}\mathrm{Tr}\rho^{\mathrm{CD}} \\ &= \sum_{cd}\rho^{\mathrm{AB}}{}_{ab,a'b'}\rho^{\mathrm{CD}}{}_{cd,cd}\end{aligned} \quad (23)$$

After exchange (23) becomes

$$\rho^{\mathrm{AB}}{}_{ab,a'b'}\,(\text{after exchange}) = \sum_{cd}\rho^{\mathrm{AC}}{}_{ac,a'c}\rho^{\mathrm{BD}}{}_{bd,b'd} \quad (24)$$

Equation 24 is obtained from eq 23 by permutation of the basis function indices and relabeling of the ρ's according to the chemical and basis function description of the reorganization process (21). The permutation of indices method, PI method, allows one to evaluate ρ (after exchange) without explicitly considering the form of the reorganization matrix and entirely avoids the matrix multiplication procedure indicated in (22). The PI method applies in all cases of intra- and intermolecular reorganization and its application will henceforth be indicated by P.

Proof of the validity of the PI method is obtained as follows. The rows and columns of a product density matrix $\rho^{\mathrm{AB}} \times \rho^{\mathrm{CD}}$, of the system in eq 21, are labeled by the appropriate products of basis functions of species, $abcd$ and $a'b'c'd'$, respectively. Recall, too, that in the basis function representation $R = P$ is a symmetrical (about the diagonal) permutation matrix, with all elements either 0 or 1 and with $P = P^{-1}$. A typical nonzero matrix element of $[P\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}}P^{-1}]$ is given by

$$[P\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}}P^{-1}]_{abcd,a'b'c'd'} = \langle abcd|P|acbd\rangle\langle acbd|\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}}|a'c'b'd'\rangle\langle a'c'b'd'|P|a'b'c'd'\rangle \quad (25)$$

Since after exchange ρ^{AB} is given as

$$\rho^{\mathrm{AB}}{}_{ab,a'b'}\,(\text{after exchange}) = [\mathrm{Tr}_{\mathrm{CD}}P\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}}P^{-1}]_{ab,a'b'} \quad (26)$$

we must sum the right-hand side of (25) over the diagonal states of CD, cd. Performing this summation and labeling the individual ρ matrix elements, we obtain the remaining nonzero terms of (26), as

$$\sum_{cd}\langle abcd|P|acbd\rangle\langle acbd|\rho^{\mathrm{AC}} \times \rho^{\mathrm{BD}}|a'cb'd\rangle\langle a'cb'd|P|a'b'cd\rangle \quad (26a)$$

which becomes after noting that $\langle abcd|P|acbd\rangle = 1$, etc.

$$\rho^{\mathrm{AB}}{}_{ab,a'b'}\,(\text{after exchange}) = \sum_{cd}\rho^{\mathrm{AC}}{}_{ac,a'c}\rho^{\mathrm{BD}}{}_{bd,b'd} \quad (27)$$

which is identical with (23).

III. Linear Response and High-Temperature Approximation

In this section we obtain simplifications of eq 18 which result from the high-temperature approximation and from the use of low power. These allow the removal of the rf driving term from the commutator and the dropping of terms in ρ (after exchange) which are products of off-diagonal density matrix elements.

First, a unitary transformation on ρ^{AB}

$$\rho^{AB} = e^{-i\omega I^z{}_{AB}t}\bar{\rho}^{AB}e^{i\omega I^z{}_{AB}t} \tag{28}$$

where

$$I^z{}_{AB} = \sum_i I_i^z \tag{29}$$

takes one into the rotating coordinating system.[20] Substitution of (28) into (18) gives

$$\dot{\bar{\rho}}^{AB}(t) = \frac{i}{h}[\bar{\rho}^{AB}, \bar{\mathcal{H}}_{AB}] - \frac{1}{\tau_{AB}}[\mathrm{Tr}_{CD}P\bar{\rho}^{AC}\bar{\rho}^{BD}P^{-1} - \bar{\rho}^{AB}] - \bar{\rho}^{AB}/T_{AB} \tag{30}$$

where $\bar{\mathcal{H}}_{AB}$ is given as

$$\bar{\mathcal{H}}_{AB} = e^{i\omega I^z{}_{AB}t}\mathcal{H}_{AB}e^{-i\omega I^z{}_{AB}t} = \sum_i^{AB}(\omega_{0_i} - \omega)I_i^z + \sum_{i>j}^{AB}J_{ij}I_iI_j + \sum_i^{AB}\omega_{1_i}I_i^x \tag{31}$$

and the shift and driving frequencies are ω_{0_i} and ω_{1_i}, respectively. The last term in the right-hand side of (31) is called $\bar{\mathcal{H}}^1{}_{AB}$ and

$$\bar{\mathcal{H}}_{AB} = \bar{\mathcal{H}}^0{}_{AB} + \bar{\mathcal{H}}^1{}_{AB} \tag{32}$$

Several simplifications of eq 30 now follow. Because the Hamiltonian is time independent, the steadystate solution of (28) will also be time independent which implies that $\dot{\bar{\rho}}^{AB} = 0$. Since we are assuming low rf power we can treat $\sum_i \omega_{1_i}I_{0_i}^x$ as a small perturbation so that

$$\bar{\rho}^{AB} \simeq \bar{\rho}_0{}^{AB}(\omega_1 = 0) + \omega_1\bar{\rho}_1{}^{AB}$$

Lastly we make use of the inequalities

$$kT \gg h\omega_{0_i} \tag{33}$$

$$\omega_{0_i} \gg J_{ij} \tag{34}$$

and the experimental fact that only the position of the resonance peaks can be obtained accurately and not the absolute area under each peak. Thus, any time we deal with the amplitude of the peaks and not their position we can set $\omega_{0_i} = \omega_0$ and $\omega_{1_i} = \omega_1$. We will refer to this as the amplitude approximation (AA).

Substitution of (32) into the commutator in (30) leads to

$$[\bar{\rho}^{AB}, \bar{\mathcal{H}}_{AB}] = [\bar{\rho}^{AB}, \bar{\mathcal{H}}^0{}_{AB}] + [\bar{\rho}^{AB}, \sum_i^{AB}\omega_{1_i}I_i^x] \tag{35}$$

We show in Appendix I that at equilibrium

$$\rho^{AB} = \bar{\rho}^{AB} \simeq \frac{e^{-\omega_0 I^z{}_{AB}/kT}}{\mathrm{Tr}e^{-\omega_0 I^z{}_{AB}/kT}} \tag{36}$$

Using eq 33 and keeping only terms linear in ω_1, the second commutator on the right-hand side of eq 35 becomes

$$[(\mathcal{I}^{AB} - \omega_0 I^z{}_{AB}/kT), \omega_1 I^x{}_{AB}]/\mathrm{Tr}\mathcal{I}_{AB} = \frac{-\omega_0\omega_1}{kT}\left[\sum_i I_i^z, \sum_i I_i^x\right]\bigg/\mathrm{Tr}\mathcal{I}_{AB} = \frac{-i\omega_0\omega_1}{kTn_{AB}}\left[\sum_i I_i^y\right] \tag{37}$$

where $\mathcal{I}^{AB}$ is the identity matrix in the space AB and $n_{AB} = \mathrm{Tr}\mathcal{I}^{AB}$.

A second simplification of eq 18 involves the term ρ (after exchange) (27). The use of low rf power allows neglect of all terms in (27) which will be quadratic in ω_1, that is, all products of off-diagonal matrix elements. Also due to inequality (33) and eq 36 all diagonal density matrix elements $\rho_{k,k}{}^{AB}$ are given by

$$\rho_{k,k}{}^{AB} \simeq \langle k|\rho_0{}^{AB}|k\rangle \simeq \frac{1}{n_{AB}} \tag{38}$$

Equation 27 then becomes

$$\rho^{AB}{}_{ab,a'b'}\text{ (after exchange)} = \sum_d \delta(a,a')\frac{n_C}{n_{AC}}\bar{\rho}^{BD}{}_{bd,b'd} + \sum_c \delta(b,b')\frac{n_D}{n_{BD}}\bar{\rho}^{AC}{}_{ac,a'c} \tag{39}$$

Finally the result of applying all the simplifications discussed in this section together with the steady state condition

$$\dot{\bar{\rho}} = 0$$

gives in the product basis representation the density matrix equation for the exchanging system

$$AB + CD \rightleftarrows AC + BD$$

$$\frac{i}{\hbar}\langle ab|[\bar{\rho}^{AB}, \mathcal{H}^0{}_{AB}]|a'b'\rangle + \frac{1}{\tau_{AB}}\left[\sum_d \delta(a,a')\frac{n_C}{n_{AC}}\bar{\rho}^{BD}{}_{bd,b'd} + \sum_c \delta(b,b')\frac{n_D}{n_{BD}}\bar{\rho}^{AC}{}_{ac,a'c'} - \bar{\rho}^{AB}{}_{ab,a'b'}\right] - \bar{\rho}^{AB}{}_{ab,a'b'}/T_{AB}\ \frac{-\omega_0\omega_1}{kTn_{AB}}\left[\sum_i^{AB}I_i^y\right]_{ab,a'b'} \tag{40}$$

or

$$\dot{\bar{\rho}}^{AB}{}_{\text{static}} + \dot{\bar{\rho}}^{AB}{}_{\text{exchange}} + \dot{\bar{\rho}}^{AB}{}_{\text{relaxation}} = \frac{-\omega_0\omega_1}{kTn_{AB}}\sum_i^{AB}I_i^y \tag{41}$$

In eq 40 and 41 $\bar{\rho}$ and $\mathcal{H}_{AB}$ are in the rotating frame. $\mathcal{H}^0{}_{AB}$ does not contain the driving frequency term. Equation 41 as written applies only when *basis functions are used.*

The set of inhomogeneous linear equations (eq 40) is constructed for all off-diagonal matrix elements between the states $|m_\alpha\rangle$ and $|m_\alpha - 1\rangle$ for which $I_\alpha{}^z|m_\alpha\rangle = m_\alpha|m_\alpha\rangle$ where α = AB, CD, AC, BD. The set of such equations can be written as

$$[\omega I + A]\begin{pmatrix}\bar{\rho}_{AB}{}^{col}\\ \bar{\rho}_{CD}{}^{col}\\ \bar{\rho}_{AC}{}^{col}\\ \bar{\rho}_{BD}{}^{col}\end{pmatrix} = \begin{pmatrix}B_{AB}{}^{col}\\ B_{CD}{}^{col}\\ B_{AC}{}^{col}\\ B_{BD}{}^{col}\end{pmatrix} \tag{42}$$

where $\bar{\rho}_\alpha{}^{col}$ is a column vector with elements $\langle m_\alpha|\bar{\rho}_\alpha|m_\alpha - 1\rangle$ and $B_\alpha{}^{col}$ is a column vector with elements $(i\omega_1\omega_0\hbar/kTn_\alpha)\langle m_\alpha|I_\alpha{}^y|m_\alpha - 1\rangle$. The absorption (the magnetization transverse to the rf field in the rotating coordinate system) is given as

$$Ab \sim \sum_\alpha(\text{concentration }\alpha)\ \mathrm{Tr}\bar{\rho}_\alpha I_\alpha{}^y \tag{43}$$

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[20] C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963, p 26.

In terms of $\hat{\rho}_\alpha{}^c$ this can be written as

$$Ab \sim \sum_\alpha (\text{concentration } \alpha) \text{ Imag } (\hat{\rho}_\alpha{}^{\text{col}} \cdot I_\alpha{}^{\text{col}}) \tag{44}$$

where $\hat{\rho}_\alpha{}^{\text{col}} \cdot I_\alpha{}^{\text{col}}$ is the scalar product of the vectors $\hat{\rho}_\alpha{}^{\text{col}}$ and the identity vector $I_\alpha{}^c$ and "Imag" means to take the imaginary part.

Equation 42 is solved[9,17,21] by writing

$$A = UgU^{-1} \tag{45}$$

where g is a diagonal matrix, and substituting this expression for A into eq 42, one then obtains

$$\bar{\rho}^c = U(\omega + g)^{-1}U^{-1}B^c \tag{46}$$

We next multiply eq 46 on the left by the diagonal matrix c, where the diagonal elements spanning the same column elements occupied by $\bar{\rho}^c{}_{\mathrm{AB}}$ in $\bar{\rho}^c$ are concentration (AB), etc. The absorption is then given as the imaginary part of the scalar product of the vectors

$$CU(\omega + g)^{-1}U^{-1}B^c \text{ and } I^c \tag{47}$$

i.e.

$$Ab \sim \text{Imag}(CU(\omega + g)^{-1}U^{-1}B^c) \cdot (I^c) \tag{48}$$

IV. Examples of Procedure

Since matrix elements of nuclear spin Hamiltonians are straightforward to evaluate and well described in the literature, we restrict this section to the evaluation of ρ (after exchange) for different exchanging systems using the PI method of permuting labels and basis function indices. Several examples follow.

Mutual exchange of fragments

$$\mathrm{AB} + \mathrm{CD} \rightleftharpoons \mathrm{AC} + \mathrm{BD} \tag{49}$$

$$\begin{array}{lllll} \text{states} & ab & cd & ac & bd \\ & a'b' & c'd' & a'c' & b'd' \end{array}$$

$$\bar{\rho}^{\mathrm{CD}}{}_{cd,c'd'} \text{ (after)} = \sum_{ab} \bar{\rho}^{\mathrm{AC}}{}_{ac,ac'} \bar{\rho}^{\mathrm{BD}}{}_{bd,bd'} \tag{50}$$

$$\bar{\rho}^{\mathrm{AC}}{}_{ac,a'c'} \text{ (after)} = \sum_{bd} \bar{\rho}^{\mathrm{AB}}{}_{ab,a'b} \bar{\rho}^{\mathrm{CD}}{}_{cd,c'd} \tag{51}$$

$$\bar{\rho}^{\mathrm{BD}}{}_{bd,b'd'} \text{ (after)} = \sum_{ac} \bar{\rho}^{\mathrm{AB}}{}_{ab,ab'} \bar{\rho}^{\mathrm{CD}}{}_{cd,cd'} \tag{52}$$

$$\rho^{\mathrm{AB}}{}_{ab,a'b'} \text{ (after)} = \sum_{cd} \rho^{\mathrm{AC}}{}_{ac,a'c} \rho^{\mathrm{BD}}{}_{bd.b'd} \tag{53}$$

$$\mathrm{AB} + \mathrm{B} \rightleftharpoons \mathrm{AB} + \mathrm{B} \tag{54}$$

$$\begin{array}{lllll} \text{states} & ab & c & ac & b \\ & a'b' & c' & a'c' & b' \end{array}$$

$$\bar{\rho}^{\mathrm{AB}}{}_{ab,a'b'} \text{ (after)} = \sum_{c} \bar{\rho}^{\mathrm{AB}}{}_{ac,a'c} \bar{\rho}^{\mathrm{B}}{}_{b.b'} \tag{55}$$

$$\bar{\rho}^{\mathrm{B}}{}_{c,c'} \text{ (after)} = \sum_{ab} \bar{\rho}^{\mathrm{AB}}{}_{ac,ac'} \bar{\rho}^{\mathrm{B}}{}_{b,b} = \sum_{a} \bar{\rho}^{\mathrm{AB}}{}_{ac,ac'} \tag{56}$$

using $\sum_b \rho^{\mathrm{B}}{}_{b.b} = 1$.

Group transfer

$$\mathrm{AB} + \mathrm{CD} \rightleftharpoons \mathrm{ABC} + \mathrm{D} \tag{57}$$

$$\begin{array}{lllll} \text{states} & ab & cd & abc & d \\ & a'b' & c'd' & a'b'c' & d' \end{array}$$

$$\bar{\rho}^{\mathrm{AB}}{}_{ab,a'b'} \text{ (after)} = \sum_{cd} \bar{\rho}^{\mathrm{ABC}}{}_{abc,ab'c'} \bar{\rho}^{\mathrm{D}}{}_{d,d} \tag{58}$$

$$\bar{\rho}^{\mathrm{CD}}{}_{cd,c'd'} \text{ (after)} = \sum_{ab} \bar{\rho}^{\mathrm{ABC}}{}_{abc,abc'} \bar{\rho}^{\mathrm{D}}{}_{d,d'} \tag{59}$$

$$\bar{\rho}^{\mathrm{ABC}}{}_{abc,a'b'c'} \text{ (after)} = \sum_{d} \bar{\rho}^{\mathrm{AB}}{}_{ab,a'b'} \bar{\rho}^{\mathrm{CD}}{}_{cd,c'd} \tag{60}$$

$$\bar{\rho}^{\mathrm{D}}{}_{d,d'} \text{ (after)} = \sum_{abc} \bar{\rho}^{\mathrm{AB}}{}_{ab,ab} \bar{\rho}^{\mathrm{CD}}{}_{cd,cd'} \tag{61}$$

Dissociation recombination

$$\mathrm{AB} \rightleftharpoons \mathrm{A} + \mathrm{B} \tag{62}$$

$$\begin{array}{llll} \text{states} & ab & a & b \\ & a'b' & a' & b' \end{array}$$

$$\bar{\rho}^{\mathrm{AB}}{}_{ab,a'b'} \text{ (after)} = \bar{\rho}^{\mathrm{A}}{}_{a,a'} \rho^{\mathrm{B}}{}_{b,b'} \tag{63}$$

$$\bar{\rho}^{\mathrm{A}}{}_{a,a'} \text{ (after)} = \sum_{b} \bar{\rho}^{\mathrm{AB}}{}_{ab,a'b} \tag{64}$$

$$\bar{\rho}^{\mathrm{B}}{}_{b,b'} \text{ (after)} = \sum_{a} \rho^{\mathrm{AB}}{}_{ab,ab'} \tag{65}$$

Unimolecular conversion, includes hindered rotation

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{66}$$

$$\begin{array}{lll} \text{states} & a & a \\ & a' & a' \end{array}$$

$$\bar{\rho}^{\mathrm{A}}{}_{a,a'} \text{ (after)} = \bar{\rho}^{\mathrm{B}}{}_{a,a'} \tag{67}$$

Unimolecular mutual exchange

$$\mathrm{A} \rightleftharpoons \mathrm{A} \tag{68}$$

$$\begin{array}{lll} \text{states} & ab & ba \\ & a'b' & b'a' \end{array}$$

$$\bar{\rho}^{\mathrm{A}}{}_{ab,a'b'} \text{ (after)} = \bar{\rho}^{\mathrm{A}}{}_{ba,b'a'} \tag{69}$$

The contraction of these sums making use of the low rf power condition follows the method outlined in the previous section.

General Conclusions

We have shown how, by use of basis function factoring in conjunction with the low power and high-temperature approximations, respectively, density matrix equations for exchanging systems may be obtained in compact form. The product basis function representation is especially useful in that the exchange part can be concisely derived by direct reference to the chemistry of the exchange process and without explicitly writing down the exchange matrix. Our results, as described in eq 17–19 and 24, are true for all rf power levels. In this paper we have only obtained in detail the low rf (linear response) approximation. Equations for exchange under conditions of high rf in general will be nonlinear in ρ. Nonlinear response will be the subject of a future paper. Computer programs for calculating nmr line shapes for exchanging systems, using the procedures of this paper, are being developed. These methods constitute a powerful tool for the investigation of fast reaction kinetics in equilibrium systems and vastly expand the scope of the nmr line shape method as it has been employed heretofore.

Appendix I. Equilibrium Density Matrix

For an isolated system defined by the Hamiltonian $\mathcal{H}_{\mathrm{AB}}$ the density matrix is given as

$$\bar{\rho}_{\mathrm{AB}} = \rho_0{}^{\mathrm{AB}} = \frac{e^{-\mathcal{H}_{\mathrm{AB}}/kT}}{\mathrm{Tr}e^{-\mathcal{H}_{\mathrm{AB}}/kT}} \tag{A1}$$

Using the condition defined by eq 34 and the (AA)

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(21) R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.*, **49**, 2455 (1968).

approximation, eq A1 simplifies as

$$\rho_0{}^{\mathrm{AB}} \simeq \frac{e^{-\omega_0 I^z{}_{\mathrm{AB}}/kT}}{\mathrm{Tr}e^{-\omega_0 I^z{}_{\mathrm{AB}}/kT}} \tag{A2}$$

which is just eq 36.

We now must investigate the form of $\rho_0{}^{\mathrm{AB}}$ when it is not isolated, *i.e.*, when it "exchanges" with other systems. To do this most simply consider two systems A and B each consisting of a single spin. The diagonal component of the density matrix for the A and B systems is given as[11]

$$\begin{aligned} \dot{\rho}^{\mathrm{A}}{}_{\alpha\alpha} &= \frac{1}{\tau_{\mathrm{A}}}(\rho^{\mathrm{B}}{}_{\alpha\alpha} - \rho^{\mathrm{A}}{}_{\alpha\alpha}) - \frac{1}{\tau_{1\mathrm{A}}}(\rho^{\mathrm{A}}{}_{\alpha\alpha} + \rho^{\mathrm{A}}{}_{0\alpha\alpha}) \\ \dot{\rho}^{\mathrm{B}}{}_{\alpha\alpha} &= \frac{1}{\tau_{\mathrm{B}}}(\rho^{\mathrm{A}}{}_{\alpha\alpha} - \rho^{\mathrm{B}}{}_{\alpha\alpha}) - \frac{1}{\tau_{1\mathrm{B}}}(\rho^{\mathrm{B}}{}_{\alpha\alpha} - \rho^{\mathrm{B}}{}_{0\alpha\alpha}) \end{aligned} \tag{A3}$$

where

$$\rho^{\mathrm{A}}{}_{0\alpha\alpha} = \langle\alpha|\rho_0{}^{\mathrm{A}}|\alpha\rangle = \frac{\langle\alpha|e^{-\omega_0{}^{\mathrm{A}} I_{\mathrm{A}^z}/kT}|\alpha\rangle}{\mathrm{Tr}e^{-\omega_0{}^{\mathrm{A}} I_{\mathrm{A}^z}/kT}} \tag{A4}$$

and similarly for $\rho^{\mathrm{B}}{}_{0\alpha\alpha}$. In the steady state (*i.e.*, $\dot{\rho}^{\mathrm{A}}{}_{\alpha\alpha} = \dot{\rho}^{\mathrm{B}}{}_{\alpha\alpha} = 0$) one solves eq 3 and obtains

$$\rho^{\mathrm{A}}{}_{\alpha\alpha} = \frac{\rho^{\mathrm{A}}{}_{0\alpha\alpha} T_{1\mathrm{A}}{}^{-1}(1/\tau_{\mathrm{B}} + 1/\tau_{1\mathrm{B}}) + \rho^{\mathrm{B}}{}_{0\alpha\alpha} T_{1\mathrm{B}}{}^{-1}\tau_{\mathrm{A}}{}^{-1}}{(1/\tau_{\mathrm{A}} + 1/T_{1\mathrm{A}})(1/\tau_{\mathrm{B}} + 1/T_{1\mathrm{B}}) - 1/\tau_{\mathrm{A}}\tau_{\mathrm{B}}} \tag{A5}$$

Applying condition (AA), which is equivalent to setting

$$\omega_0{}^{\mathrm{A}} = \omega_0{}^{\mathrm{B}} = \omega_0 \tag{A6}$$

or

$$\rho^{\mathrm{A}}{}_{0\alpha\alpha} = \rho^{\mathrm{B}}{}_{0\alpha\alpha} = \rho_{0\alpha\alpha} = \frac{\langle\alpha|e^{-\omega_0 I_{\mathrm{A}^z}/kT}|\alpha\rangle}{\mathrm{Tr}e^{-\omega_0 I_{\mathrm{A}^z}/kT}} \tag{A7}$$

one obtains

$$\rho^{\mathrm{A}}{}_{\alpha\alpha} = \rho^{\mathrm{A}}{}_{0\alpha\alpha} \tag{A8}$$

Appendix II. Generalization of the Relaxation Operator

In eq 4 we used for our relaxation form

$$(\dot{\rho})_{\mathrm{relaxation}} = -\rho/\tau \tag{A9}$$

This usually will be sufficient, but for a more detailed theory one can use the relaxation matrix as derived from the Wangness–Bloch,[9] Redfield theory.[22] This as discussed in ref 20 is given in the energy eigenvalue representation $|\alpha\rangle$ as

$$\langle\alpha|\dot{\rho}|\alpha'\rangle_{\mathrm{relaxation}} = \sum_{\beta\beta'} R_{\alpha\alpha',\beta\beta'}\rho_{\beta\beta'} \tag{A10}$$

We wish to show that by making certain assumptions and approximations we can introduce ($\dot{\rho}$) relaxation which is sort of intermediate between eq A9 and A10.

Our assumption is that each spin interacts with its environment *via* a classical random magnetic field,[20] *i.e.*

$$\mathcal{H}_{\mathrm{int}} = \sum_{i\alpha} H_{i\alpha}(t) I_i{}^{\alpha} \qquad \alpha = 1, 2, 3 \tag{A11}$$

and that the correlation function for the H's is given as

$$\langle H_{i\alpha}(t) H_{j\beta}(t')\rangle = \delta_{ij}\delta_{\alpha\beta}g(|t - t'|) \tag{A12}$$

The approximation we use is that as

$$\omega_{0_i} \gg J_{ij} \tag{A13}$$

the Zeeman energy alone is used explicitly in evaluating $R_{\alpha\alpha',\beta\beta'}$.

The result is that we are able to express eq A10 in the operator form as

$$\begin{aligned} (\dot{\rho})_{\mathrm{relaxation}} = -\sum_i [1/\tau_{i_1}\{[[\rho, I_i{}^x], I_i{}^x] + \\ [[\rho, I_i{}^y], I_i{}^y]\} + 1/\tau_{i_2}[[\rho, I_i{}^z], I_i{}^z]] \end{aligned} \tag{A14}$$

A simple example of the use of eq A14 is to calculate $\dot{M}_x$ for a single spin, *i.e.*

$$\begin{aligned} \dot{M}_x = -\mathrm{Tr}I^x[1/\tau_1\{[[\rho, I^x], I^x] + [[\rho, I^y], I^y]\} + \\ 1/\tau_2[[\rho, I^z], I^z]] = -(1/\tau_1 + 1/\tau_2)M_x \end{aligned} \tag{A15}$$

Appendix III. Rate Constants

It is desirable to point out that the mean preexchange lifetimes for the different species are simply related to the rate constants. These relationships are illustrated for the exchanging system

$$\mathrm{AB} + \mathrm{CD} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} \mathrm{AC} + \mathrm{BD} \tag{21}$$

Noting that the τ's are defined by eq A16 according to Grunwald, Loewenstein, and Meiboom,[23] the other mean lifetimes are given by eq A17–A20.

$$\frac{1}{\tau_{\mathrm{AB}}} = \frac{\text{total rate of exchange}}{(\mathrm{AB})} \tag{A16}$$

$$\frac{1}{\tau_{\mathrm{AB}}} = k_{\mathrm{f}}(\mathrm{CD}) \tag{A17}$$

$$\frac{1}{\tau_{\mathrm{CD}}} = k_{\mathrm{f}}(\mathrm{AB}) \tag{A18}$$

$$\frac{1}{\tau_{\mathrm{AC}}} = k_{\mathrm{r}}(\mathrm{BD}) \tag{A19}$$

$$\frac{1}{\tau_{\mathrm{BD}}} = k_{\mathrm{r}}(\mathrm{AC}) \tag{A20}$$

Equivalent treatments apply to other systems.

Acknowledgment. This research was supported by the National Science Foundation Grants No. 8567 7326 and the Office of Naval Research Contract No. N00014-69-C-0218. We express our appreciation to Dr. Robert Carter, Lund Institute of Technology, for stimulating discussions.

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