

What follows are scanned pages of the Note

Linewidths in High-Resolution NMR Spectra. Homogeneous Broadening due to Intramolecular Dipolar Relaxation.

by Stanislav Sykora

which appeared in

Journal of Chemical Physics, Volume 52, p 4818-4825 (1970)

For other works by Stan Sykora, please visit www.ebyte.it.

Abstract

The theory of energy-level widths in coupled nuclear systems is discussed, and a detailed study of the intramolecular dipolar relaxations based on it is presented. The restrictions of the theory and all the approximations made are carefully discussed. The nuclear system coupling structure enters the formulas through relatively simple functionals defined over the unperturbed eigenvectors of the system. On the other hand, the spectral density functions, which appear as coefficients of these functional, depend only on molecular geometry and motions. Both groups of parameters are thus to a great extent separated. In order to show the effectiveness as well as the limits of the method, the structure and the linewidths of resonance transitions of several simple systems (AB, A₂, ABX, A₂X, A₃, and A₃X) are studied in detail.

Keywords: NMR, NMR spectroscopy, HR-NMR, Linewidth, Relaxation, Coupled system

Erratum: The coefficient $18 C^M/45\pi$ in Eq.(28) should be $4 C^M/45\pi$

This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

Original URL: <http://link.aip.org/link/JCPSA6/v52/i9/p004818>

Linewidths in High-Resolution NMR Spectra. Homogeneous Broadening Due to the Intramolecular Dipolar Relaxation

STANISLAV SÝKORA

Istituto di Chimica Industriale del Politecnico, Piazza Leonardo da Vinci 32, Milano, Italy*

(Received 18 September 1969)

The theory of energy-level widths in coupled nuclear systems is discussed, and a detailed study of the intramolecular dipolar relaxations based on it is presented. The restrictions of the theory and all the approximations made are carefully discussed. The nuclear system coupling structure enters the formulas through relatively simple functionals defined over the unperturbed eigenvectors of the system. On the other hand, the spectral density functions, which appear as coefficients of these functionals, depend only on molecular geometry and motions. Both groups of parameters are thus to a great extent separated. In order to show the effectiveness as well as the limits of the method, the structure and the linewidths of resonance transitions of several simple systems (AB , A_2 , ABX , A_2X , A_3 , and A_3X) are studied in detail.

If the high-resolution NMR spectrum of a molecular system has to be calculated in detail, i.e., including the line shapes as well as the frequencies and integral intensities of the transitions, extreme difficulties arise. In many cases, however, the properties of the system enable one to determine the energy level widths and to draw from them some semiquantitative conclusions about the linewidths. The general theory of the energy level widths is still quite complex, but as will be shown, very general assumptions about the type of the relaxation mechanism and about the energy level structure of the systems studied lead directly to extensive simplification.

In this paper the influence of the dipolar relaxations has been studied in more detail. The underlying theory, however, is adequate to deal with any other of the relaxation mechanisms.

I. BASIC THEORY

In this discussion the nuclear system is defined by the set of eigenvectors $|i\rangle$ and corresponding energies ν_i for each of its eigenstates i . Any perturbation $H'(t)$ which is a stationary random function of time will lead to transitions from the eigenstate r to the eigenstate s , the probability \mathfrak{W}_{rs} of which is known to be

$$\mathfrak{W}_{rs} = J_{rs}(\omega_{rs}), \quad \omega_{rs} = \nu_r - \nu_s. \quad (1)$$

Here $J_{rs}(\omega)$ is the spectral density function of the perturbation matrix element $\langle r | H'(t) | s \rangle$, i.e.,

$$J_{rs}(\omega) = L_\omega A_\sigma g_{rs}(t, \tau),$$

$$g_{rs}(t, \tau) = \langle r | H'(t) | s \rangle \langle s | H'(t+\tau) | r \rangle, \quad (2)$$

with A_σ denoting the statistical-averaging operator and L_ω the Fourier transform operator:

$$L_\omega f(\tau) = \int_{-\infty}^{+\infty} f(\tau) \exp(-i\omega\tau) d\tau. \quad (3)$$

Because of the stationary nature of the perturbation operator $H'(t)$,

$$A_\sigma g_{rs}(t, \tau) = A_\sigma g_{rs}(0, \tau). \quad (4)$$

In almost all the physically significant cases the perturbation $H'(t)$ can be written in the form

$$H'(t) = \sum_i W^i f_i(t), \quad (5)$$

where W^i are time-independent operators and $f_i(t)$ are stationary random functions. Then

$$\mathfrak{W}_{rs} = \sum_i \sum_k J_{ik}(\omega_{rs}) W_{rs}^i W_{sr}^k, \quad (6)$$

where

$$J_{ik}(\omega_{rs}) = L_\omega A_\sigma \{ f_i(t) f_k(t+\tau) \}, \quad W_{rs}^i \equiv \langle r | W^i | s \rangle.$$

The total probability $\Gamma(r)$ that the state r will be changed by the influence of the perturbation $H'(t)$ now becomes

$$\Gamma(r) = \sum'_s \mathfrak{W}_{rs} = \sum'_i \sum_k \sum'_s J_{ik}(\omega_{rs}) W_{rs}^i W_{sr}^k. \quad (7)$$

The single prime in Eq. (7) denotes that the summation extends over all the states s with the exception of the state r .

With respect to the uncertainty relations, the width δ_r of the r th energy level is approximately given by $\Gamma(r)$, i.e., $\delta_r = g\Gamma(r)$, where $g \simeq 1$ depends upon the particular shape of the density function $g_r(\nu)$ of the r th energy level. It is further supposed that the density functions $g_r(\nu)$ are approximately of the same shape for all levels on account of the statistical nature of the relaxation processes. The linewidth Δ_{rs} of the transition $r \rightarrow s$ will then be approximately determined by the relation

$$\Delta_{rs}^2 = g' \{ \Gamma^2(r) + \Gamma^2(s) \}, \quad g' \simeq 1. \quad (8)$$

To compare Eq. (8) with the experimental results the natural linewidths must be measured; experimentally these are seldom obtained. A short discussion of this problem is given in the Appendix.

II. RESTRICTIONS OF THE THEORY

The relation (1) is in fact the result of a perturbation expansion of the density matrix into the powers of H' . As a consequence, it is necessary for its validity that

the unperturbed Hamiltonian of the system is not degenerate. More precisely, if $\omega_{rs} \gg A_{\sigma} g_{rs}(0, 0)$ the eigenstates r and s retain their authenticity, at least from the point of view of the statistical average. On the other hand, if $\omega_{rs} \ll A_{\sigma} g_{rs}(0, 0)$ the perturbation H' causes time-dependent rotations of the base in the manifold M_{rs} generated by the vectors $|r\rangle$ and $|s\rangle$, the amplitudes of which can be large enough to change completely the statistical parameters of the resulting distribution of the base.

For any base $|r'\rangle, |s'\rangle$ of the manifold M_{rs} it is still true that

$$\mathcal{W}_{mr'} + \mathcal{W}_{ms'} = \mathcal{W}_{mr} + \mathcal{W}_{ms}.$$

Consequently, the relation (7) remains valid even in a degenerate case for any $\Gamma(m)$ as long as m is not identical with one of the degenerate states r and s .

A special situation occurs if $\langle r | H'(t) | s \rangle = 0$ identically. Then, despite the degeneracy of the states r and s , the relations (1)–(7) remain valid.

The relation (8) can be used only under the condition that there is no phase correlation between the states r and s . This condition is not fulfilled, for example, if the whole system is composed of two (or more) mutually noninteracting parts. The allowed transitions inside one of the subsystems then occur only between those eigenstates of the whole system in which the states of the second subsystem are identical. But the random processes acting in the second subsystem cause exactly the same and, hence, in-phase changes in both levels.

As soon as the subsystems are in mutual interaction the phase correlation between both levels disappears and, if caused artificially, decays with a characteristic time given by the magnitude of the energy change of the second subsystem caused by the interaction. The relation (8) can be used if the interactions are considerably stronger than the energy level widths.

III. APPLICATION TO THE NUCLEAR SYSTEM UNDER HIGH-RESOLUTION CONDITIONS

The most important relaxation mechanisms in a system of nuclear spins are (a) the dipolar interactions of the nuclear magnetic moments, (b) the interactions of the nuclear magnetic moments with the magnetic moments of the unpaired electrons, (c) the interactions of the nuclear electric quadrupole moments with the electric multipoles of the molecule, and (d) the interaction of the nuclear system of the molecule with its internal rotations through the chemical shifts and indirect coupling constants. In the first three cases it is further possible to distinguish between intramolecular and intermolecular interactions.

Under certain experimental conditions (diamagnetic samples which do not contain any nuclei with nonzero quadrupole moments and from which all paramagnetic impurities are removed) the relaxations through the

nuclear dipolar interactions remain dominant. With respect to the strong dependence of the latter on inter-nuclear distances, one expects intramolecular rather than intermolecular interactions to be of major importance. By a suitable choice of experimental conditions (dilute solutions in solvents free of magnetic nuclei), these intramolecular interactions will assume even more importance.

Since there is hardly any correlation between intra- and intermolecular interactions, their contributions to the energy level widths may be studied independently and summed in additive manner. This could break down only if there were strong correlations between the positions and movements of the adjacent molecules in the sample.

Such an additive independence of relaxation mechanisms will not hold for two different types of interactions between two molecules or inside the same molecule. In such a way there arises a whole series of different crossterms in the relation (7).

IV. THE PURE NUCLEAR DIPOLAR INTERACTIONS

The dipolar interaction between the nuclei i and j contributes to the perturbation Hamiltonian $H'(t)$ through a term whose form is

$$H_{ij}' = \alpha_{ij} [(F_{ij} + F_{i,j^0} + F_{j,i^0}) f_{ij}^0(t) + (T_{i,j^+} + T_{j,i^+}) \times f_{ij}^{+1}(t) + (T_{i,j^-} + T_{j,i^-}) f_{ij}^{-1}(t) + D_{ij}^+ f_{ij}^{+2}(t) + D_{ij}^- f_{ij}^{-2}(t)], \quad (9)$$

where

$$\begin{aligned} F_{ij} &= -K_i K_j, \\ F_{i,j^0} &= I_i^+ I_j^-, \\ T_{i,j^\pm} &= K_i I_j^\pm, \\ D_{ij^\pm} &= I_i^\pm I_j^\pm, \end{aligned} \quad (10)$$

and

$$\begin{aligned} f_{ij}^0(t) &= (\frac{1}{3} - \cos^2 \theta_{ij}) / r_{ij}^3, \\ f_{ij}^{\pm 1}(t) &= \sin \theta_{ij} \cos \theta_{ij} \exp(\mp \phi_{ij}) / r_{ij}^3, \\ f_{ij}^{\pm 2}(t) &= \sin^2 \theta_{ij} \exp(\mp 2\phi_{ij}) / r_{ij}^3, \end{aligned}$$

and $K_i = 2I_i^z$, $\alpha_{ij} = -(3/4)\gamma_i \gamma_j$, γ_i being the gyromagnetic ratio of the nucleus i (the convention $\hbar = 1$ is adopted). The usual notation is used for the spin operators I_i^z and I_i^\pm acting on the spin variables of the nucleus i and for the spherical coordinates r_{ij} , θ_{ij} , and ϕ_{ij} of the vector $(\vec{r}_j - \vec{r}_i)$.

The operators (10), which will be denoted generally by W , change the value I^z of the z component of the total spin by $\epsilon(W)$. Here $\epsilon(W)$ equals: 0 for the phase-shift operators F and the flip-flop operators F^0 ; ± 1 for the transition operators T^\pm ; and ± 2 for the double-quantum transition operators D^\pm . Because I^z is invariant, for any two operators W^I and W^{II} and for any two

eigenstates r and s it immediately follows that

$$W_{rs}^I W_{sr}^{II} = 0 \quad \text{if} \quad \epsilon(W^I) + \epsilon(W^{II}) \neq 0$$

and

$$W_{rr}^I = 0 \quad \text{if} \quad \epsilon(W^I) \neq 0. \quad (11)$$

In a heteronuclear system (or in a system composed of several very weakly interacting subsystems) the linear space in which the W operate can be decomposed into a direct product of subspaces, each one being the configurational space for one nuclear species (or for one of the weakly coupled subsystems). I^z now has to be invariant inside each of these subspaces; this can be used to further extend the rules (11). For this sake it is convenient to define the symbol e_{ij} the value of which is either 0 if the nuclei i and j belong to different nuclear species or 1 if these two nuclei are of the same kind. Thus, the additional rules are

$$(F_{ij})_{rs}(F_{k,l}^0)_{sr} \neq 0 \quad \text{only if} \quad e_{kl} \neq 0, \quad (12a)$$

$$(T_{i,j}^\pm)_{rs}(T_{k,l}^\mp)_{sr} \neq 0 \quad \text{only if} \quad e_{ik}e_{jl} \neq 0, \quad (12b)$$

$$(D_{ij}^\pm)_{rs}(D_{kl}^\mp)_{sr} \neq 0 \quad \text{only if} \quad (e_{ik}e_{jl} + e_{il}e_{jk} - e_{ik}e_{il}) \neq 0. \quad (12c)$$

From the relations (11) and (12) it follows that the coefficients of the nonzero terms $W_{rs}^I W_{sr}^{II}$ in Eq. (7) may always be expressed in the form $J_{I,II}(\Omega_{I,II} + \mu_{rs}^{I,II})$. $\Omega_{I,II}$ is dependent only on the given pair of operators W^I and W^{II} while $\mu_{rs}^{I,II}$ depends also on the eigenstates r and s . The value of $\Omega_{I,II}$ is determined by the type of the nonzero terms (12a)–(12c) to which the product $W_{rs}^I W_{sr}^{II}$ belongs. Thus, denoting the fundamental resonance frequency of the nuclear species to which the nucleus k belongs by Φ_k , $\Omega_{I,II}$ equals either 0 or $\pm\Phi_j$ or $\pm(\Phi_i + \Phi_j)$ for (12a)–(12c), respectively.

The values $\mu_{rs}^{I,II}$ do not exceed the range of the NMR spectrum, and at the usual high intensities of magnetic fields, the differences between the $\Omega_{I,II}$ parameters are greater than the $\mu_{rs}^{I,II}$ values by several orders of magnitude. Under the relatively rapid reorientation of the molecules, the spectral densities $J_{I,II}(\omega)$ are very smooth functions of frequency. If the reorientation frequencies are much greater than the $\mu_{rs}^{I,II}$, then

$$J_{I,II}(\Omega_{I,II} + \mu_{rs}^{I,II}) = J_{I,II}(\Omega_{I,II}). \quad (13)$$

In this case the expression (7) is considerably simplified. The contribution of the $W_{rs}^I W_{sr}^{II}$ terms to $\Gamma(r)$ becomes

$$\begin{aligned} \Gamma_{I,II}(r) &= \sum_s' J_{I,II}(\Omega_{I,II}) W_{rs}^I W_{sr}^{II} \\ &= J_{I,II}(\Omega_{I,II}) [(W^I W^{II})_{rr} - W_{rr}^I W_{rr}^{II}]. \end{aligned} \quad (14)$$

This statement shows that the energy level is now given by means of a functional; it depends only on the eigenvector of the given state and not on the properties of the other states.

A rather more detailed notation for the required cor-

relation functions and spectral densities is now given:

$$g_{ij,kl}^M(\tau) = A_\sigma [f_{ij}^M(t) f_{kl}^{-M}(t+\tau)];$$

$$J_{ij,kl}^M(\omega) = L_\omega g_{ij,kl}^M(\tau), \quad (15)$$

where $M=0, \pm 1, \pm 2$. Note that $J_{ij,kl}^M(-\omega)$ is the complex conjugate of $J_{ij,kl}^{-M}(\omega)$. From Eq. (14) the cross term $\Gamma_{ij,kl}^d(r)$ arising from the dipolar interactions within each of the nuclear pairs (i, j) and (k, l) is

$$\begin{aligned} \Gamma_{ij,kl}^d(r) / \alpha_{ij} \alpha_{kl} &= J_{ij,kl}^0(0) G_{ij,kl}(r) + J_{ij,kl}^0(\Phi_i - \Phi_j) \\ &\times G_{ij,kl}^0(r) + 2 \operatorname{Re} [J_{ij,kl}^1(\Phi_i) G_{ij,kl}^1(r) + J_{ij,kl}^1(\Phi_j) \\ &\times G_{ij,kl}^1(r) + J_{ij,kl}^2(\Phi_i + \Phi_j) G_{ij,kl}^2(r)], \end{aligned} \quad (16)$$

where the functionals G have the form

$$\begin{aligned} G_{ij,kl}(r) &= (F_{ij} F_{kl} + e_{kl} F_{ij} (F_{k,l}^0 + F_{l,k}^0)) \\ &+ e_{ij} (F_{i,j}^0 + F_{j,i}^0) F_{kl} - (F_{ij})_{rr} (F_{kl})_{rr} - e_{kl} (F_{ij})_{rr} \\ &\times (F_{k,l}^0 + F_{l,k}^0)_{rr} - e_{ij} (F_{i,j}^0 + F_{j,i}^0)_{rr} (F_{kl})_{rr}, \\ G_{ij,kl}^0(r) &= e_{il} e_{jk} [(F_{i,j}^0 F_{k,l}^0 + F_{j,i}^0 F_{l,k}^0)_{rr} \\ &- (F_{i,j}^0)_{rr} (F_{k,l}^0)_{rr} - (F_{j,i}^0)_{rr} (F_{l,k}^0)_{rr}] \\ &+ e_{ik} e_{jl} [(F_{i,j}^0 F_{l,k}^0 + F_{j,i}^0 F_{k,l}^0)_{rr} \\ &- (F_{i,j}^0)_{rr} (F_{l,k}^0)_{rr} - (F_{j,i}^0)_{rr} (F_{k,l}^0)_{rr}], \\ G_{ij,kl}^1(r) &= e_{ik} e_{jl} (T_{i,j}^+ T_{k,l}^-)_{rr} + e_{il} e_{jk} (T_{i,j}^+ T_{l,k}^-)_{rr}, \\ G_{ij,kl}^2(r) &= (e_{ik} e_{jl} + e_{il} e_{jk} - e_{ik} e_{il}) (D_{ij}^+ D_{kl}^-)_{rr}. \end{aligned} \quad (17)$$

The purely dipolar interaction contribution to the line-widths $\Gamma^d(r)$ is thus

$$\Gamma^d(r) = \sum_{(i,j)} \sum_{(k,l)} \Gamma_{ij,kl}^d(r). \quad (18)$$

With respect to the simple structure of the operators (10), the calculation of the values of the functionals G is not complicated and, as will be shown below, can be further simplified.

The fundamental importance of expression (16) does not consist, however, in the special form of the functionals but in the fact that the energy level widths can be expressed as a sum of products of two terms, one of which depends only on the molecular geometry and motions while the other is given only by the parameters of the spin system specifying the given energy level.

V. HOMONUCLEAR SYSTEMS

For any two nuclei i and j of an homonuclear system it holds that $e_{ij} = 1$, $\alpha_{ij} = a$, and $\Phi_i = \Phi_j$, as follows from the definition of these parameters. The following notation for the spectral densities is used:

$$Y_{ij,kl}(\omega) = Y_{kl,ij}(\omega) = \operatorname{Re} J_{ij,kl}(\omega),$$

$$Z_{ij,kl}(\omega) = -Z_{kl,ij}(\omega) = \operatorname{Im} J_{ij,kl}(\omega). \quad (19)$$

Similarly, the simplified functionals are introduced:

$$\begin{aligned} Q^0_{ij,kl}(r) &= (\mathcal{F}_{ij}\mathcal{F}_{kl})_{rr} - (\mathcal{F}_{ij})_{rr}(\mathcal{F}_{kl})_{rr}, \\ Q^1_{ij,kl}(r) &= (\mathcal{D}_{ij}^+\mathcal{D}_{kl}^- + \mathcal{D}_{ij}^-\mathcal{D}_{kl}^+)_{rr}, \\ q^1_{ij,kl}(r) &= (\mathcal{D}_{ij}^+\mathcal{D}_{kl}^- - \mathcal{D}_{ij}^-\mathcal{D}_{kl}^+)_{rr}, \\ Q^2_{ij,kl}(r) &= (\mathcal{D}_{ij}^+\mathcal{D}_{kl}^- + \mathcal{D}_{ij}^-\mathcal{D}_{kl}^+)_{rr}, \\ q^2_{ij,kl}(r) &= (\mathcal{D}_{ij}^+\mathcal{D}_{kl}^- - \mathcal{D}_{ij}^-\mathcal{D}_{kl}^+)_{rr}, \end{aligned} \quad (20)$$

where

$$\begin{aligned} \mathcal{F}_{ij} &= I_i^+ I_j^- + I_i^- I_j^+ - K_i K_j, \\ \mathcal{D}_{ij}^\pm &= K_i I_j^\pm + K_j I_i^\pm, \\ \mathcal{D}_{ij}^\pm &= I_i^\pm I_j^\pm. \end{aligned}$$

The expression (16) now reduces to

$$\begin{aligned} \frac{\Gamma^2_{ij,kl}(r)}{a^2} &= \sum_{M=0}^2 Y^M_{ij,kl}(M\Phi) Q^M_{ij,kl}(r) \\ &+ \sum_{M=1}^2 Z^M_{ij,kl}(M\Phi) q^M_{ij,kl}(r). \end{aligned} \quad (21)$$

The terms (21) can be divided into three groups: four-particle terms if $i, j, k,$ and l are different; three-particle terms if $i=k$ but $j \neq l$; and two-particle terms if $i=k$ and $j=l$. It is convenient to use a shortened notation for the three-particle terms, defined by

$$\begin{aligned} Y^M_{i,k,l} &\equiv Y^M_{ik,il}; & Z^M_{i,k,l} &\equiv Z^M_{ik,il}; \\ Q^M_{i,k,l} &\equiv Q^M_{ik,il}; & q^M_{i,k,l} &\equiv q^M_{ik,il}, \end{aligned} \quad (22)$$

and a similar notation for the two-particle terms:

$$Y^M_{ij} \equiv Y^M_{ij,ij}; \quad Q^M_{ij} \equiv Q^M_{ij,ij}. \quad (23)$$

As a result of (19), it may be noted that $Z^M_{ij,ij}(\omega) = 0$ identically, which simplifies the two-particle terms. Further, with respect to (19), the quantities

$$\begin{aligned} Q^M_{i,(kl)} &\equiv Q^M_{i,kl} + Q^M_{i,lk}, & q^M_{i,(kl)} &\equiv q^M_{i,kl} - q^M_{i,lk}, \\ Q^M_{(ij),kl} &\equiv Q^M_{ij,kl} + Q^M_{kl,ij}, & q^M_{(ij),kl} &\equiv q^M_{ij,kl} - q^M_{kl,ij} \end{aligned} \quad (24)$$

are quite convenient for the summation process (18) and will be used in proceeding paragraphs.

VI. SPECTRAL DENSITY FUNCTIONS FOR THE INTRAMOLECULAR DIPOLAR RELAXATION

As stated previously, in many cases the intramolecular interactions represent the dominant relaxation mechanism and, under suitable experimental conditions, can determine the linewidth. In these cases it is sufficient to take into account only one isolated molecule; this approach to the problem will be called the single-molecule approximation (SMA).

The intramolecular terms in (21) can be reduced and many of their properties investigated without any further assumptions about the detailed molecular structure.

First of all, from (10) and (15) it is clear that there is a strong dependence of the dipolar relaxations on the internuclear distances. In rigid molecules, where the distances R_{ij} between the nuclei are constant, the spectral densities are

$$J^M_{ij,kl}(\omega) = \Theta^M_{ij,kl}(\omega) / R_{ij}^3 R_{kl}^3, \quad (25)$$

where $\Theta^M_{ij,kl}$ depends only on the type of molecular movements and on the mutual orientation of the vectors \bar{r}_{ij} and \bar{r}_{kl} . In nonrigid molecules it is often possible, at least as a first approximation, to consider the vibrational and torsional movements as being independent of the over-all rotations of the molecule. This holds particularly for the vibrations and free internal rotations, the frequencies of which are much greater than the over-all rotation frequency. In these cases the statistical averaging in (15) can be done separately for both types of movements. If, moreover, the molecule can exist in n different stable forms, then

$$J^M_{ij,kl}(\omega) = \Theta^M_{ij,kl}(\omega) \sum_{\alpha} \sum_{\beta} \frac{C_{\alpha} C_{\beta}}{R_{ij}^3(\alpha) R_{kl}^3(\beta)}, \quad (26)$$

where C_{α} denotes the concentration of the form α and $R_{ij}(\alpha)$ is the distance between nuclei i and j in the same form α .

In many molecules the minimum distance between the nuclei is considerably smaller than any other internuclear distance. The relaxations in the nuclear system of such a molecule will take place mainly through the pair interactions connected with the minimum distance. Neglecting all the other relaxation mechanisms, an approximation results for these molecules which may be called the one-pair approximation.

The one-pair approximation cannot be used, of course, if there are more pairs of nuclei in the molecule with internuclear distances equal or near to the minimum one. Especially, if $R_{ij} = R_{kl}$ and the vectors \bar{r}_{ij} and \bar{r}_{kl} are collinear then $Y^M_{ij} = Y^M_{kl} = J^M_{ij,kl}$, i.e., the four-particle term is equal to the corresponding two-particle terms and can never be neglected.

The exact theory of the spectral densities is very complicated and necessarily involves all the dynamical parameters of the molecule. For practical purposes it is found¹ that a crude approximation is sufficient which substitutes all the reduced correlation functions $\bar{g}^M_{ij,kl}(\tau)$,

$$\bar{g}^M_{ij,kl}(\tau) = g^M_{ij,kl}(\tau) / g^M_{ij,kl}(0), \quad (27)$$

by a unique function of the shape $\exp(-|\tau|/\tau_c)$, where τ_c is called the correlation time of the reorientation process. In this approximation $\Theta^M_{ij,kl}(\omega)$ in Eq. (25) is real and, as shown by the direct calculation of $g^M_{ij,kl}(0)$,

$$\begin{aligned} \Theta^M_{ij,kl}(\omega) &= (18C^M/45\pi) (3 \cos^2 \gamma_{kl}^{ij} - 1) \\ &\times [\tau_c / (1 + \omega^2 \tau_c^2)], \end{aligned} \quad (28)$$

where $C^0 = 1$, $C^1 = 3/2$, $C^2 = 6$, and γ_{kl}^{ij} is the angle between the vectors \bar{r}_{ij} and \bar{r}_{kl} .

TABLE I. The values of Q functionals in the AB system.^a

r	$ \mathbf{r}\rangle$	$Q_{AB}^0(r)$	$Q_{AB}^1(r)$	$Q_{AB}^2(r)$	$G^d(r)$ in FRL ^b
1	$ \alpha\alpha\rangle$	0	2	1	9
2	$\cos\phi \alpha\beta\rangle + \sin\phi \beta\alpha\rangle$	pq	$2p$	0	$(3+q)p$
3	$\cos\phi \beta\alpha\rangle - \sin\phi \alpha\beta\rangle$	pq	$2q$	0	$(3+p)q$
4	$ \beta\beta\rangle$	0	2	1	9

^a $p = 1 + \sin 2\phi$; $q = 1 - \sin 2\phi$; $\tan 2\phi = J/\delta$; $G^d(r) = \Gamma^d(r)/[a^2 Y_{AB}^0(0)]$.

^b FRL means fast-reorientation limit.

Equations (25) and (28) now determine uniquely all the $J_{ij,kl}^M(\omega)$ by means of the molecular geometry and of only one additional parameter τ_c .

In the approximation (27) $Z_{ij,kl}^M(\omega) = 0$ and the expressions (16) and (21) are further simplified. In particular, the dipolar relaxation terms for homonuclear systems become (with $Y_{ij,kl}^M = J_{ij,kl}^M$):

$$\frac{\Gamma_{ij,kl}^d(\mathbf{r})}{a^2} = \sum_{M=0}^2 Y_{ij,kl}^M(M\Phi) Q_{ij,kl}^M(\mathbf{r}), \quad (29)$$

which, together with the relations (25) and (28), are already quite practical expressions.

In the following paragraphs, two extreme cases will be distinguished. In the first case $\Phi\tau_c \gg 1$, and consequently, the values of $J_{ij,kl}^M(\Phi)$ and $J_{ij,kl}^M(2\phi)$ will be negligible in comparison with $J_{ij,kl}^M(0)$. Such a situation is usually referred to as the slow-reorientation limit (SRL). In the other case, called the fast-reorientation limit (FRL), $\Phi\tau_c \ll 1$ which leads to the equalities

$$J_{ij,kl}^M(2\Phi) = J_{ij,kl}^M(\Phi) = J_{ij,kl}^M(0).$$

In order to give a qualitative description of the linewidths in both of these limits, the explicit calculation of the spectral densities is not necessary. Instead, the $J_{ij,kl}^0(0)$ may be used as parameters, taking into account that $J_{ij,kl}^1(0) = \frac{3}{2}J_{ij,kl}^0(0)$ and $J_{ij,kl}^2(0) = 6J_{ij,kl}^0(0)$, as follows from (28).

VII. Q FUNCTIONALS FOR THE SYSTEMS OF SPIN $\frac{1}{2}$ NUCLEI

The operators Λ_{ij} , ξ_{ij} , and χ_{ij} are defined giving their influence on the fundamental product vectors $|\phi\rangle$:

If the nuclei i and j are in the same spin states in $|\phi\rangle$, then

$$\Lambda_{ij}|\phi\rangle = 0, \quad \xi_{ij}|\phi\rangle = |\phi\rangle, \quad \chi_{ij}|\phi\rangle = |\phi\rangle. \quad (30a)$$

If, on the other hand, the spin states of the nuclei i and j are opposite,

$$\Lambda_{ij}|\phi\rangle = |\Phi\rangle, \quad \xi_{ij}|\phi\rangle = -|\phi\rangle, \quad \chi_{ij}|\phi\rangle = 0, \quad (30b)$$

where the vectors $|\phi\rangle$ and $|\Phi\rangle$ differ only by the permutation of the spin states of the nuclei i and j .

It is now easy to show that the Q functionals defined previously can be expressed by means of these extremely

simple operators as follows:

$$Q_{ij}^1(\mathbf{r}) = 2 + 2(\Lambda_{ij})_{rr}; \quad Q_{ij}^2(\mathbf{r}) = (\chi_{ij})_{rr};$$

$$Q_{ij}^0(\mathbf{r}) = Q_{ij}^1(\mathbf{r}) - Q_{ij}^2(\mathbf{r}) - (\Lambda_{ij} - \xi_{ij})_{rr}^2, \quad (31a)$$

$$Q_{i,(kl)}^1(\mathbf{r}) = 2(\Lambda_{kl} + \xi_{kl})_{rr}; \quad Q_{i,(kl)}^2(\mathbf{r}) = (\Lambda_{kl})_{rr};$$

$$Q_{i,(kl)}^0(\mathbf{r}) = Q_{i,(kl)}^1(\mathbf{r}) - 2(\Lambda_{ik} - \xi_{ik})_{rr}(\Lambda_{il} - \xi_{il})_{rr}, \quad (31b)$$

$$Q_{(ij,kl)}^1(\mathbf{r}) = 2(\xi_{ik}\Lambda_{jl} + \xi_{il}\Lambda_{jk} + \xi_{jk}\Lambda_{il} + \xi_{jl}\Lambda_{ik})_{rr};$$

$$Q_{(ij,kl)}^2(\mathbf{r}) = 2(\chi_{ij}\chi_{kl}\Lambda_{ik}\Lambda_{jl})_{rr};$$

$$Q_{(ij,kl)}^0(\mathbf{r}) = 2\{[(\Lambda_{ij} - \xi_{ij})(\Lambda_{kl} - \xi_{kl})]_{rr} - (\Lambda_{ij} - \xi_{ij})_{rr}(\Lambda_{kl} - \xi_{kl})_{rr}\}. \quad (31c)$$

VIII. SOME APPLICATIONS WITHIN THE SINGLE-MOLECULE APPROXIMATION

A. AB System

Defining the AB system by the chemical shift δ and the coupling constant J , its eigenstates and eigenvectors may be written down and the corresponding relaxational parameters calculated. The results, summed in Table I, provide the following qualitative picture.

In SRL the levels with spin ± 1 are considerably narrower than the levels with spin 0. With increasing influence of the T and D processes [see expression (10)] at shorter correlation times the situation is reversed and in FRL the spin ± 1 levels are much broader.

If the interaction is weak ($J/\delta \ll 1$), both levels with spin 0 have the same widths, and consequently, all the four lines of the AB quartet have the same linewidths. At stronger interactions the widths of the levels 2 and 3 become different in such a way that the more intensive central transitions of the AB quartet become broader than the weaker ones. The ratio of the linewidths of both types of transitions can assume distinct values only for strongly interacting systems in the SRL. In FRL this effect is not very pronounced.

B. A_2 Group

Although this system is degenerate (the symmetric state 2 and the antisymmetric state 3 have the same energy), the values in Table I remain valid because the dipolar interaction between the nuclei preserves the symmetry of the group. As a result, the energy level width of the antisymmetric state 3 will be zero in the single-molecule approximation.

TABLE II. The eigenfunctions and the values of Q functionals for the ABX system.^a

Subsystem	I				II			
	1	2	3	4	5	6	7	8
	α				β			
State $ X\rangle$								
$ AB\rangle$	$\alpha\alpha$	$V\alpha\beta+W\beta\alpha$	$V\beta\alpha-W\alpha\beta$	$\beta\beta$	$\alpha\alpha$	$\bar{V}\alpha\beta+\bar{W}\beta\alpha$	$\bar{V}\beta\alpha-\bar{W}\alpha\beta$	$\beta\beta$
Q_{AB}^0	0	pq	pq	0	0	$\bar{p}\bar{q}$	$\bar{p}\bar{q}$	0
Q_{AB}^1	2	$2p$	$2q$	2	2	$2\bar{p}$	$2\bar{q}$	2
Q_{AB}^2	1	0	0	1	1	0	0	1
Q_{AX}^0	0	$r+t$	$s+t$	1	1	$\bar{s}+\bar{t}$	$\bar{r}+\bar{t}$	0
Q_{AX}^1	2	2	2	2	2	2	2	2
Q_{AX}^2	1	s	r	0	0	\bar{r}	\bar{s}	1
$Q_{X,(AB)}^0$	0	$2(u-q)$	$2(u-p)$	0	0	$2(\bar{u}-\bar{q})$	$2(\bar{u}-\bar{p})$	0
$Q_{X,(AB)}^1$	2	$-2q$	$-2p$	2	2	$-2\bar{q}$	$-2\bar{p}$	2
$Q_{X,(AB)}^2$	0	$1-q$	$1-p$	0	0	$1-\bar{q}$	$1-\bar{p}$	0
$Q_{A,(BX)}^0$	0	$-2p$	$-2q$	0	0	$-2\bar{q}$	$-2\bar{p}$	0
$Q_{A,(BX)}^1$	2	$2(r-s)$	$2(s-r)$	-2	-2	$2(\bar{s}-\bar{r})$	$2(\bar{r}-\bar{s})$	2
$Q_{A,(BX)}^2$	0	0	0	0	0	0	0	0

^a $V=\cos\phi$, $W=\sin\phi$, $p=1+\sin 2\phi$, $q=1-\sin 2\phi$, $r=\sin^2\phi$, $s=\cos^2\phi$, $t=\sin^2 2\phi$, $u=\cos^2 2\phi$; the barred quantities result from this formulas if ϕ is substituted by ϕ' . If the couples of quantities (r, s) and (\bar{r}, \bar{s}) are simul-

taneously permuted, the Q_{BX}^M and $Q_{B,(AX)}^M$ values result instead of the Q_{AX}^M and $Q_{A,(BX)}^M$, respectively.

C. ABX System

An ABX system can be specified by means of four parameters J , δ , b , and d defined by the relations

$$J=J_{AB}, \quad \delta=\nu_A-\nu_B, \quad (32)$$

$$b=(J_{AX}-J_{BX})/2, \quad d=(J_{AX}+J_{BX})/2. \quad (32)$$

It is also convenient to involve the angles ϕ , ϕ' which satisfy the conditions

$$\tan 2\phi=J/(\delta+b); \quad \tan 2\phi'=J/(\delta-b). \quad (33)$$

The eigenvectors, calculated by the method of effective chemical shifts,² are given in Table II together with the accepted numbering of the eigenstates.

The X part of the spectrum involves two pairs of transitions, each centered symmetrically with respect to the center of the band. The first pair involves the transitions 1 \rightarrow 5 and 4 \rightarrow 8, the splitting between them being equal to $2|d|$, while the second pair, composed of the transitions 2 \rightarrow 6 and 3 \rightarrow 7, is characterized by the splitting $2|b(\cos 2\phi - \cos 2\phi')|$.

In the AB part of the spectrum there are two quartets corresponding to the effective chemical shifts $\delta_1=\delta+b$, $\delta_2=\delta-b$ and the common coupling constant J . The frequency difference between the centers of these quartets is $|d|$. The quartet with the greater absolute value of the effective chemical shift is located at higher field if the sign of $(\delta b d)$ is positive; this is the only information about the signs of the parameters (32) which can be obtained from the resonance frequency values. As indicated in Table II, the energy level diagram may be

decomposed into two subsystems with respect to the state of the nucleus X .

The values of the Q functionals for the individual energy levels are explicitly given in Table II. On the basis of these many qualitative features of the system can be discussed.

(a) If the AB relaxation is dominant, the linewidths of the AB -part transitions are the same as they would be in two independent AB quartets with chemical shifts δ_1 , δ_2 and coupling constant J . Consequently, this part of the spectrum is not very interesting. The situation in the X part of the spectrum is quite different. In the first pair of transitions, both components have always the same width; they are infinitely sharp in SRL but with decreasing values of τ_c rapidly become the broadest lines of the group. The components of the second pair, broadened even in SRL by the influence of the F processes, have at shorter correlation times different linewidths due to the T processes. If $|b|$ is known, the order of the lines in the field determines the sign of $(\delta b J)$.

(b) If, on the other hand, the AX relaxation is dominant, then all the energy levels are equally broadened by the influence of T processes, and the differences between them arise only from the F and D processes. In the X part both lines of the first pair are of identical width while the transitions of the second pair may differ. This difference may become particularly distinct only if ϕ and ϕ' are considerably different; this will occur in the region $|b| \simeq |\delta|$. The most interesting effects can now be expected in the AB part. In general, all the lines of both AB quartets have different linewidths. The

TABLE III. The eigenvectors and the values of Q functionals for the A_3 group.^a

Symmetry	r	$ r\rangle$	Energy	Q^0	Q^1	Q^2	G^d in FRL
A	1	$\alpha\alpha\alpha$	$3s+3i$	0	3	3	45
	2	$(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/3^{1/2}$	$s+3i$	6	9	1	51
	3	$(\alpha\beta\beta+\beta\alpha\beta+\beta\beta\alpha)/3^{1/2}$	$-s+3i$	6	9	1	51
	4	$\beta\beta\beta$	$-3s+3i$	0	3	3	45
E	5	$(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)/6^{1/2}$	$s-5i$	1	1	1	17
	6	$(\alpha\beta\alpha-\beta\alpha\alpha)/2^{1/2}$	$s-5i$	3	3	1	27
	7	$(2\alpha\beta\beta-\beta\alpha\beta-\beta\beta\alpha)/6^{1/2}$	$-s-5i$	1	1	1	17
	8	$(\beta\alpha\beta-\beta\beta\alpha)/2^{1/2}$	$-s-5i$	3	3	1	27

^a $s = \frac{1}{2}\Phi$; $i = \frac{1}{4}J$; $Q^M = Q^{M_{12}}(r) + Q^{M_{13}}(r) + Q^{M_{23}}(r)$; $G^d = 2\Gamma^d(r) / [\sigma^2 Y_{10}^d(0)]$.

order of the lines in the field, determined according to the increasing linewidth, reverses during the transition from SRL to FRL. In the more common case of FRL the D processes are the most important [see Eq. (29)]. The order of the lines is then completely determined by the J , δ , and b and may be used as additional information about the signs of these parameters (although this is not sufficient to remove the ambiguity completely).

(c) It can be deduced from the values in Table II that the simultaneous influence of the AB , AX (and/or BX) relaxations will tend to smear out the above-mentioned differences between the various linewidths. Furthermore, the influence of the three-particle terms has the same effect as soon as they become important.

D. A_2X System

The transition from the ABX to the A_2X system leads to degeneracies of the levels 2, 3 and 6, 7; in this situation the validity of Eq. (1) becomes doubtful.

Providing the dominant relaxation mechanism arises from the A_2 -nuclei interaction, the perturbation element preserves the symmetry of the system (compare with the A_2 system) and does not mix the levels with different symmetries. Consequently, Eq. (1) can still be used, and the values given in Table II are valid. Inspecting them, it follows that both of the A_2 -part lines are composed of two completely equivalent transitions, while in the X -part triplet there are two broad outer lines and a central line which is composed of the infinitely sharp antisymmetrical component overlapped by the broader symmetrical component.

When the AX interactions dominate, the situation is considerably different. $H'(t)$ is no longer symmetrical and the problems connected with degeneracy can not be avoided. But, as can easily be proved, the $Q_{AX}(r)$ values are the same for all vectors from the subspaces generated by eigenvectors $|2\rangle$, $|3\rangle$ or $|6\rangle$, $|7\rangle$. If the three-particle terms are negligible [e.g., if $3\cos^2(AXA) \ll 1$], then the widths of the degenerate energy levels will be the same and equal to the values given in Table II regardless of how the interactions

redistribute the bases of both subspaces. From this it follows that in such a case all the X -triplet transitions are of almost the same linewidth (both coinciding central lines being slightly broader than the side lines as a consequence of F processes). But each of the A_2 transitions will now be composed of two lines with different linewidths.

If the three-particle terms become important or if the AA and AX two-particle terms become comparable, the degeneracy can not be avoided and the theory based on Eq. (1) is not applicable.

E. A_3 Group

Because of the symmetry of this system, the form of its eigenvectors does not depend on the coupling constant. The eigenvectors, their symmetry, and the corresponding energies are given in Table III.

There are two pairs of degenerate states, numbered 5, 6 and 7, 8, respectively. Instead of the eigenvectors $|5\rangle$ and $|6\rangle$ given in Table III it is possible to choose, without any change of the results, any other orthonormalized pair of vectors which generates the same manifold as $|5\rangle$ and $|6\rangle$; the same applies to the vectors $|7\rangle$ and $|8\rangle$.

This was true if relaxations did not take place. In the presence of relaxations the symmetry of the system is perturbed by the terms (9). As long as the coupling constant J is much greater than the linewidth, the relaxation interaction between the different symmetry states is negligible. But there still remain the interactions between the degenerate states, which cannot be neglected *a priori*. The bases of the subspaces M_{56} and M_{78} (i.e., the manifolds generated by the eigenvectors $|5\rangle$, $|6\rangle$ and $|7\rangle$, $|8\rangle$, respectively) will no longer be arbitrary and the solution of this problem could be quite difficult. Fortunately, in this case such bases can be found which remain the eigenbases of the random perturbation $H'(t)$ independently of time. As is easily proved, the interaction terms $\langle 5|H'(t)|6\rangle$ and $\langle 7|H'(t)|8\rangle$ for H' given by (9) are identically zero. Thus, the vectors $|5\rangle$, $|6\rangle$ and $|7\rangle$, $|8\rangle$ given in Table III are already those stable vector which are invariant

under the perturbation and, consequently, allow the perturbation theory to be used.

The angle between any two sides of the A_3 triangle equals 60° and, following Eqs. (25) and (28), the coefficients of the three-particle terms will be almost one order of magnitude smaller than the two-particle coefficients. For a qualitative description of the results these three-particle terms can thus be neglected.

The resulting values of the Q functionals are given in Table III. It appears that the A_3 -group resonance line consists of four transitions with different linewidths. Although the quantitative relations between the linewidths change on passing from the SRL to the FRL, the qualitative picture remains unchanged. The narrowest component is the $E(-\frac{1}{2}, +\frac{1}{2})$ transition 5 \rightarrow 7, followed by the $E'(-\frac{1}{2}, +\frac{1}{2})$ transition 6 \rightarrow 8. The relative intensity of each of these transitions is $\frac{1}{12}$. Within the generally broader A -symmetry transitions there are two distinct components: the narrower which has a relative intensity $\frac{1}{2}$ is formed by the transitions $A(-\frac{3}{2}, -\frac{1}{2})$ and $A(\frac{1}{2}, \frac{3}{2})$ (i.e., 3 \rightarrow 4 and 1 \rightarrow 2, respectively), the broader with a relative intensity of $\frac{1}{3}$ corresponds to the $A(-\frac{1}{2}, +\frac{1}{2})$ transition 2 \rightarrow 3. The ratio of the linewidths of the narrowest and the broadest components ranges from 6 in SRL to 3 in FRL.

F. A_3X System with Relaxations in the A_3 Group Only

Like in the cases of the ABX and A_2X systems, a weak interaction of the A_3 group with a nucleus X (but still sufficient to produce a clearly resolved X quartet) allows the possibility of measuring the A_3 -group energy level widths directly as the linewidths of the X transitions.

While each of the sideband components of the X quartet is composed of only one transition (transitions corresponding to the A_3 -group energy levels 1 and 4, respectively), the central components are each composed of three transitions with different linewidths, which correspond to the A_3 -group levels 2, 5, 6 in one case and 3, 7, 8 in the other case. Quantitative values of the linewidths follow straightforwardly from the parameters given in Table III.

IX. CONCLUSIONS

The proposed theory leaves a broad field open to further investigations. Intramolecular interactions other than the dipolar ones may be studied without any change in the basic scheme. There are good reasons for hoping that the intermolecular interactions could also be involved without drastic changes to the structure of

the theory. The difficulties arising from the degenerate systems can sometimes be avoided as was shown above in several examples. This does not solve the problem of the degenerate and roughly degenerate systems in general, of course, and new theoretical ways must be found to deal with these cases.

This study, at least for the case of dipolar intramolecular relaxation, leads to two basic conclusions:

(a) The different spectral lines of the coupled nuclear systems should have different natural linewidths; this difference can remain even if the transitions coincide in frequency as long as some other of their parameters (symmetry type, spin values, etc.) are different.

(b) The differences in the linewidths, as well as their absolute values, depend not only on the type of the nuclei involved and on the molecular reorientation processes but also on the geometry of the molecule and on the coupling constant and chemical shifts characterizing the nuclear system.

APPENDIX

The measurement of the natural linewidths is, at the present state of development, highly complicated by such factors as the field inhomogeneity, the insufficiently slow sweep, the saturation effects, the over-all time constant of the low-frequency part of the signal path (recorder system), the nonlinearity of the high-frequency path of the signal, and, occasionally, some other effects (e.g., the instability of the axis of the rotating sample tube).

Because of all these difficulties, new experimental techniques are being developed from which the transition probabilities \mathcal{W}_{ij} can be more directly obtained. High selectivity is the basic condition for the application of these methods to the studies of the behavior of individual lines. The most important of these methods are the progressive saturation technique,^{3,4} the saturation-recovery technique,⁵ and the selective pulse-recovery technique.^{6,7}

* Supported by the "Consiglio Nazionale delle Ricerche."

¹ A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961).

² P. Diehl, R. G. Jones, and H. J. Bernstein, *Can. J. Chem.* **43**, 81 (1965).

³ E. G. Finner and R. K. Harris, *Chem. Commun.* **1969**, 42.

⁴ R. Freeman and B. Gestblom, *J. Chem. Phys.* **48**, 5008 (1968).

⁵ J. H. Noggle, *J. Chem. Phys.* **43**, 3304 (1965).

⁶ R. Freeman and S. Wittekoek, *J. Magn. Resonance* **1**, 238 (1969).

⁷ I am grateful to Dr. R. Freeman for sending me a preprint concerning recent encouraging studies of some AB systems by this technique.