

Theory for Dynamic Lineshapes of Strongly Correlated Two-Spin Systems

NIKOLAS P. BENETIS

*University of Linköping, Department of Physics and Measurement Technology,
IFM, 581 83 Linköping, Sweden*

AND

DAVID J. SCHNEIDER AND JACK H. FREED

Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York 14853

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The calculation of spectra of two coupled spin systems within the stochastic Liouville equation formalism is systematized by the use of the coupled multipole-operator representation. The Liouville superoperator of the system is easily calculated in this representation in a unified way for all interactions by using a generalized Wigner-Eckart theorem in operator space. The spectrum is defined as the Fourier-Laplace transform of a single generalized correlation function, which, besides the autocorrelation of the observed spin can also contain contributions of the unobserved spin degrees of freedom, as well as all counterrotating parts when needed. The expression for the spectrum, which is an average of the appropriate first-order multipoles, is the same irrespective of the particular system; i.e., the multiplicity of the spin system, its states, and the relevant transition probabilities are all treated implicitly. This definition of the spectrum also introduces, through the preparation stage of the spin system prior to the free induction decay, another first-order multipole which is important for the case of strongly correlated spins. Two spins are strongly correlated when the difference in their Zeeman resonance frequency is comparable to their broadening. Accordingly, strong correlation is most likely to be important in low field and/or slow motion. The present method imposes no limitations on the relative strength of the relevant interactions or the rate of their modulation and is consequently valid in the slow-motion regime. A fast matrix-tridiagonalization method, based on the Lanczos algorithm, is used to calculate the spectrum, working directly in the frequency domain. © 1989 Academic Press, Inc.

The relaxation theory appropriate for coupled spins is well known. For example, Pople (1) studied the collapse of the hyperfine multiplet structure of the spectrum of a spin I, interacting with another spin S, in the case when the spin S has an efficient relaxation mechanism of its own. Such pairs of spins are, for example, proton-¹⁴N and proton-^{10,11}B, which find important applications in structural and dynamical studies (2, 3). A number of approximations were involved in Pople's treatment: (i) The nonsecular part of the scalar interaction is neglected; (ii) the DD interaction is neglected; (iii) the S spin is assumed to be in the extreme-narrowing limit. In Pople's

theory, it is assumed that the source of broadening of the I spectrum is the spin-lattice relaxation processes of the S system. As long as the I multiplet is well separated, the width of its lines is proportional to the inverse lifetimes of the S states. For S-relaxation rates comparable to ω_{SC} (the scalar coupling) the multiplet has a complicated structure (involving both shift and superposition) due to the possibility of reencounters within the manifold of the S states.

When the S-relaxation rate becomes even faster, the I multiplet coalesces into a single line which narrows with faster S-relaxation rates. For S-relaxation rates on the order of magnitude of the shift difference, i.e., $|\omega_{0S} - \omega_{0I}|$, Pople's method is no longer adequate, since the scalar interaction becomes a relaxation mechanism which involves simultaneous flips of both spins. This case is treated separately by Redfield theory, viz., scalar interaction of the second kind. A further complication arises for comparable shift and scalar broadening (line overlap) for which the Redfield theory must be applied in a more general fashion (4, 5). These theories essentially disregard to a different extent the correlation in the dynamics of the two spins, an approximation which is legitimate as long as the mutual interaction of the two spins is not as strong as the interaction of the S spin with the lattice. In this case, e.g., if the S spin is strongly coupled to the lattice, then it can be considered to be in equilibrium within time scales of relevance to the I spin.

The above conditions are not always fulfilled, however, as in some recent low-field experiments in proteins (2). Winter and Kimmich (6) obtain a T_1 theory for a spin I coupled to another spin S by DD interaction, which relaxes the extreme narrowing conditions, and is valid even when the Larmor frequency, ω_{0S} , of the S spin is comparable in strength to its quadrupolar interaction, ω_Q (see under System for definition of ω_Q), i.e., for low field. They find, in particular, that when the condition $\omega_{0I} = \omega_Q$ is fulfilled, an extra enhancement for the T_1 relaxation rate is obtained due to relaxation transfer from spin S to spin I (7, 8). This phenomenon is known as the quadrupolar dip, due to the characteristic field dependence of the longitudinal relaxation rate, and can only be obtained when $\gamma_S < \gamma_I$, in addition to the slow-motion and low-field conditions (2, 6). The Winter and Kimmich theory is essentially restricted to a Redfield treatment of the quadrupolar nucleus S even though for the low-field case, i.e., $\omega_{0S} \ll \omega_Q$, the quadrupolar term is considered the main part of the interaction, while the Zeeman term is treated as a perturbation. Notice also that the intermediate case $\omega_{0S} \cong \omega_Q$ cannot be treated by their theory.

Thus there is no unified lineshape theory valid for an arbitrary combination of different relaxation mechanisms and an unrestricted set of parameters. The principal aim of this paper is the development of a general lineshape theory including both slow motions and low fields, for the case of strong correlation of the two spins, since those conditions are fulfilled in a number of experiments (2, 6).

Freed and co-workers (9) have calculated low-field ESR spectra, both field and frequency swept, of triplets in the slow-motion regime even beyond the relaxation theory limit. The modification of conventional relaxation theory for the calculation of the low-field spectrum was given, together with some characteristic lineshapes. Freed and co-workers describe the complications arising in the low-field case, which are also important for the calculation of the spectra in the present work. In another paper Meirovitch *et al.* (10) considered the theory for slow-motional lineshapes for

a two-spin ($S = \frac{1}{2}$, but arbitrary I) case that is valid for all values of the field. It was particularly designed for the ESR of spin probes. The calculations were performed by a method due to Moro and Freed (11) based upon the Lanczos algorithm which greatly speeds up the computations. The treatment employs an uncoupled representation of the S spin from the I (nuclear) spin as is appropriate for ESR. In the present work we use the computational methods of Moro and Freed, but we use a coupled representation.

Sanctuary's work (12), concerning the multipole decomposition of the spin density matrix for high angular momenta as well as for multispin systems, shows that the multipoles have a direct connection to the experimental observables. He used the multipole representation of the density operator to describe some pulsed NMR experiments in the absence of relaxation. We use a closely related multipole decomposition appropriate for coupled spins to both describe the pulse which prepares the system as well as in the calculation of the evolution of the system after the pulse. The preparation of the spin system is not treated to the same degree of accuracy as the free evolution of the spins in the present work. This is similar to a procedure followed by Schwartz *et al.* (13) in a treatment for a single slow-motional $I = 1$ spin with quadrupolar interaction.

SYSTEM

We consider a system consisting of two spins, S and I, which are coupled by the hyperfine interaction, i.e., the usual scalar coupling (SC) as well as the dipole-dipole (DD) interaction. Within the spin-Hamiltonian description, which we will use here, this interaction is represented by

$$\mathcal{H}^{\text{HYP}} = \mathbf{SAI}, \quad [1]$$

where $\text{tr}(\mathbf{A}/3)$ is identified with the strength of the SC interaction and the remaining traceless part \mathbf{A}' of the second-order tensor \mathbf{A} with the DD interaction (14). The DD interaction and the SC coupling of the two spins can be important as relaxation mechanisms. We are going to perform the calculations of the spectrum for such a system in the presence of some other interactions acting on one or both spins. The spins might be either nuclear or one nuclear (I) and one electronic (S). The Zeeman interaction of the electron spin with a dc field is described by the g tensor (14). For $S > \frac{1}{2}$ the unpaired electrons interact and give rise to the zero-field splitting (ZFS) with associated tensor \mathbf{D} . Thus we get

$$\mathcal{H}_{SR} = \mathcal{H}^{\text{ZEE}} + \mathcal{H}^{\text{ZFS}} = \mathbf{SgH} + \mathbf{SDS}, \quad [2]$$

where R refers to the reorientational degrees of freedom (see later in this section). For a nuclear spin, I, the relevant interactions are the chemical shift tensor and the quadrupolar tensor which are formally equivalent to the g tensor and the ZFS tensor, respectively. The quadrupolar interaction (QDR) can be written in standard spherical tensor representation as

$$\mathcal{H}_{IR}^{\text{QDR}} = C_Q \omega_Q \cdot \sum_r (-1)^r D_{0,-r}^{(2)}(\Omega) Q_r^{(2)}(I) \quad [3]$$

with

$$C_Q = \left(\frac{2}{3}\right)^{1/2} \frac{(I+1)(2I+1)}{4(2I-1)}$$

and

$$\omega_Q = \frac{e^2 q Q}{h} \quad \text{in s}^{-1},$$

where e is the electronic charge, q the electric field gradient, and Q the quadrupole coupling constant. The quantity ω_Q will depend on the given system. Explicit formulas for the remaining interactions which are used in this work can be found in Benetis (14).

All the interactions will be treated by the stochastic Liouville equation (SLE) formalism (15–17). The SLE does not require any restriction on the relative strength of the different interactions (18) such as imposed by perturbation or Redfield type theories. Note also that the complete interactions are retained here, e.g., both pseudosecular and nonsecular along with the secular terms are included. This allows the theory to be valid even near zero field. The molecular reorientation is treated classically, but it is allowed to be strongly coupled to the spin degrees of freedom, as it is in the case of slow reorientation (16, 19, 20).

In these calculations, it is assumed that all the tensorial interactions possess cylindrical symmetry and that their principal frames coincide (21). Furthermore, we are dealing only with intramolecular interactions. In addition, we treat only a single dynamical model for the modulation of the time-dependent interactions, viz., molecular tumbling, as the single source of relaxation. Any other type of broadening, such as inhomogeneous broadening or broadening due to faster processes than reorientation, can readily be incorporated in the present theory as a single parameter for each of the two spins (14, 16).

Strongly Correlated Two-Spin Systems. If the correlated spin dynamics of the two spins S and I is important (see later in this section), the two-spin density operator ρ_{SI} cannot be separated into a product; e.g., the equation

$$\rho_{SI}(t) = \rho_S(t) \cdot \rho_I(t) \quad [4]$$

is not valid (22–24). In this case, e.g., for strong correlation, the equation of motion of the full density matrix ρ_{SI} must be solved before the calculation of any macroscopic observables $\langle Q(S, I) \rangle$, according to

$$\langle Q(S, I) \rangle_t = \text{tr}_{SI} \{ Q(S, I) \rho_{SI}(t) \}. \quad [5]$$

The usual way to deal with this complication is to use the equation of motion of ρ_{SI} and Eq. [5], in order to obtain the equation of motion for one spin observable, but with the following approximation for operator products of different spin, when they occur:

$$\langle Q_1(S) Q_2(I) \rangle \cong \langle Q_1(S) \rangle \langle Q_2(I) \rangle. \quad [6]$$

This method has been used by Abragam (25) in the derivation of the equations for

the spin-lattice relaxation of two spin S and I coupled by DD interaction. In this manner, some correlation is retained in the equation of motion of the macroscopic quantities $\langle I_z \rangle$ and $\langle S_z \rangle$ represented by the time constants $T_{1,SI}$ and $T_{1,IS}$, e.g., the cross-relaxation times. This theory has been applied in interpreting the relaxation behavior of the HF molecule (25). For spin-spin relaxation, the correlation is not retained by Abragam, but Solomon (26) discusses the conditions for which it is important, and Vasavada and Kaplan (27) give the expression for the $T_{2,SI}$ and $T_{2,IS}$. The effects of correlation for the transverse magnetization are negligible in the fast-motional regime even when the Larmor frequencies of the two spins are comparable.

The simplest two-spin system where the coupling of the spin degrees of freedom is important is the case of scalar-coupled spins under the condition $|\omega_{SC}|/|\omega_{0S} - \omega_{0I}| \cong 1$, which is the condition for the usual AB spectrum. It can be shown, for example, that the cross-correlation function $\langle I_z^\dagger(0)S_z(t) \rangle$ does not vanish. On the other hand the same function of two weakly coupled spins in the AX system is always zero (see some more details for these systems under Results for Typical Cases). The scalar interaction in NMR is usually two orders of magnitude smaller than the DD interaction. The DD interaction is, however, time dependent and traceless, so for fast motion it can merely give a broadening. This is not the case in the slow-motional regime, especially for low fields, where the difference in the Zeeman terms, $|\omega_{0S} - \omega_{0I}|$, can easily be of the same order of magnitude as the DD interaction, and the two spins should be treated as strongly correlated. This is also suggested by considering the rigid-limit (powder) spectrum of such a system which has a width equal to the DD interaction. A similar effect, viz., the near equivalence of the Larmor frequencies ω_{0S} and ω_{0I} , of the two spins in relation to their mutual interaction, can be obtained if the spin with the smaller gyromagnetic ratio possesses another strong interaction, such as a quadrupolar interaction in addition to the hyperfine coupling. The pure quadrupole spectrum (28) for a single spin shows that in the slow-motion and low-field region the quadrupolar spin can overlap with the other one due to the considerable modification of its free Larmor frequency.

The usual definition of strongly coupled spins is limited to the AB spectra of spins coupled by scalar interactions. The above discussion indicates that a clear manner for defining strong correlation cannot be given before the dynamical features of the system have been taken into account. It is always the case, however, that slow-motional and low-field conditions lead to strong coupling. If the condition $|\omega_{0S} - \omega_{0I}| \gg \omega_{REL}^2 \cdot \tau_c$ (where ω_{REL} is the strength of the main relaxation source, viz., DD, QDR, ZFS, and τ_c the relevant correlation time) is not satisfied, the spin must be considered strongly correlated. For NMR in paramagnetic systems, the nucleus can be strongly correlated to the electron spin when the relationship $\omega_{0I} < \omega_{HYP}^2 \cdot \tau_R$ is valid.

In order to find out when these conditions are relevant and can give visible effects on experimental spectra, we review some orders of magnitude for NMR and ESR. The SC interaction for nuclei is of the order of kilohertz at most, the DD interaction of the order of 0.1 MHz at most, while the QDR interaction can be 10 MHz. If one of the spins is the electron spin, the above (and related) quantities scale up by about three orders of magnitude. Accordingly, the low-field condition is strongly system dependent. For example, in NMR studies of the peptide group in large proteins con-

taining the pair $^1\text{H} \ ^{14}\text{N}$, a dc field of 0.3 T is considered low (6), due to the large value of the quadrupolar interaction. In some cycling experiments on this system one goes down to fields corresponding to 10 kHz resonance frequency for the proton (2).

THE SPECTRUM OF A TWO-SPIN SYSTEM

In the case of a two-spin system all the dynamical information of the spins is contained in the quantity $\rho_{SI}(\Omega, t)$, the density matrix of the composite system, which is also explicitly dependent on the reorientational degree of freedom Ω . Accordingly, the macroscopic magnetization μ is in this case

$$\mu(t) = \hbar \langle \mathbf{M} \rangle = \hbar \langle \gamma_S \mathbf{S} + \gamma_I \mathbf{I} \rangle_t, \quad [7]$$

where \mathbf{M} is the total spin operator. The mean value $\langle Q(S, I) \rangle$ of the operator Q is defined by

$$\langle Q(S, I) \rangle_t = \text{tr}_S \text{tr}_I \int d\Omega \{ Q(S, I) \rho_{SI}(\Omega, t) \}. \quad [8]$$

The density operator $\rho_{SI}(\Omega, t)$ satisfies a stochastic Liouville equation (10, 11):

$$\frac{\partial \rho_{SI}(\Omega t)}{\partial t} = -i \mathcal{L}(\Omega) \rho_{SI}(\Omega, t). \quad [9]$$

The Liouville superoperator \mathcal{L} consists of two parts. The first part is due to the total Hamiltonian operator for the two spins, which is explicitly reorientation dependent, and the second is a Laplace operator with respect to the orientational degree of freedom; see (18) for example.

For the sake of simplicity in testing the implications of strong correlation, we shall simulate the absorption spectrum obtained by Fourier transforming the free induction decay signal after a single 90°_y pulse. Before the pulse the system is in equilibrium described by the appropriate time-independent density operator ρ^T at thermal equilibrium with a lattice with temperature T . We define also the deviation from the equilibrium density operator $\chi(t) = \rho(t) - \rho^T$, since we observe the deviation of the x magnetization from equilibrium and arrive at

$$\mu_x(t) = \hbar \langle (\gamma_S S_x + \gamma_I I_x) e^{-i \mathcal{L} t} \chi(0) \rangle, \quad [10]$$

where $\chi(0)$ can be calculated from a $\pi/2$ pulse. Notice that the spectrum in the present case is the Fourier-Laplace transform of a cross-correlation function, since the operator $\chi(0)$ depends on the nature of the pulse and is not necessarily proportional to $\gamma_S S_x + \gamma_I I_x$. This is in contrast to the usual definition of a spectrum as the Fourier transform of an autocorrelation function (25). Notice also that the above expressions allow for the possibility that, while observing one of the coupled spins, we might have an appreciable contribution from the spectral density of the other one.

The vector representation of the operator on the left side of the exponential in Eq. [10] shall contain the relative observing transition moment of the different spin operators. On the right side of the exponential $\chi(0)$ contain exciting transition moments of the different spin operators. We proceed by defining an appropriate operator basis set.

By using the basis set $\{|SM_S\rangle\langle SM_S|\}$ for one spin S we can generate the operator space $\{Q_\sigma^S(S)\}$, which constitutes an irreducible representation of the full rotation group (14, 24). Analogously the operators $Q_\xi^I(I)$ can be defined for the spin I . Now, by taking the external product of the above operator spaces for the spin S and I , we can generate the appropriate irreducible spherical operators $Q_\lambda^{(A)}(\Sigma, \Xi)$ (with $\Sigma + \Xi \equiv \Lambda \equiv |\Sigma - \Xi|$) of the combined spin system, or what we call the coupled spherical operators or multipole operators (12, 24). In general $(2S + 1)^2(2I + 1)^2$ coupled spherical operators $Q^{(A)}$ must be generated and be normalized with respect to all the spin degrees of freedom within Liouville space. We can express the density operator of the two-spin system in the following way,

$$\rho_{SI}(\Omega, t) = \sum_{\Lambda, \lambda, L, K, M} C_{\lambda, KM}^{\Lambda, L}(\Sigma, \Xi) Q_\lambda^{(A)}(\Sigma, \Xi) \Phi_{K, M}^L(\Omega), \quad [11]$$

where Φ are the normalized Wigner matrix elements $D(31)$. The reorientation averaged quantities

$$C_\lambda^{(A)}(\Sigma, \Xi) = \langle Q_\lambda^{(A)}(\Sigma, \Xi)^\dagger \rangle \quad [12]$$

which are obtained by using Eqs. [8] and [11] are observable polarizations (12) also called statistical tensors (24). In a standard one-pulse NMR experiment of isotropic liquids the first-order multipole of either spin is directly observed. Some higher-order multipoles are, however, observed in two-dimensional NMR, or multipulse NMR experiments such as the Jeener–Brochaert pulse sequence, or acoustic resonance; see examples in Sanctuary (12) and references therein. The time dependence of the multipole operators is the simplest possible in comparison to other observables due to their simple transformation properties under rotations. The definition of the “spectrum” of a given multipole $C_\lambda^{(A)}(\Sigma, \Xi)$ is given in general by the following expectation value:

$$\begin{aligned} \langle Q_\lambda^{(A)}(\Sigma, \Xi)^\dagger \rangle_{(\omega)} &= \int_0^\infty dt e^{-i\omega t} \langle Q_\lambda^{(A)}(\Sigma, \Xi) \rangle_{(t)} \\ &= \text{tr}_{\text{SIR}} \{ Q_\lambda^{(A)\dagger}(\Sigma, \Xi) [i(\mathcal{L} + \mathbf{1}_{\text{sup}}\omega)]^{-1} \chi(0) \}. \end{aligned} \quad [13]$$

The deviation density operator from equilibrium directly after the pulse $\chi(0)$ can also be expanded in the basis of the coupled multipole operators (12). The preparation of the spin system enters into the calculation of the lineshape by the initial condition $\chi(0)$ and is studied immediately.

Preparation of the two-spin system. The description of the general behavior of the system during a given RF pulse can be very complicated in the general case. For simplicity we disregard relaxation during the pulse. This is accurate provided the relevant relaxation times are long compared to the pulse width. The following calculations are thus limiting cases of real pulses. The main purpose of this section is to establish some reasonable values of the observing transition moment $\chi(0)$ in a fairly simple way. These values are used later in order to calculate carefully the relevant spectra in next section.

We approximate the equilibrium density matrix ρ^T by the following time-independent part of the total Hamiltonian \mathcal{H}_0

$$\rho^T = \rho_{SI}^T \cdot \rho_R^T = \frac{e^{-\hbar \mathcal{H}_0/kT}}{\text{tr}(1_{op})}, \quad [14]$$

where R denotes the reorientation degrees of freedom. In the high-temperature approximation we keep only linear terms in the exponential and accordingly we have for isotropic liquids

$$\rho^T \cong \{1_{op} - \hbar [\omega_{0S}S_z + \omega_{0I}I_z + \omega_{SC}\mathbf{S} \cdot \mathbf{I}]\} / (2S+1)(2I+1)8\pi^2. \quad [15]$$

Under typical conditions we apply a selective pulse to one spin, say I , and observe the spectrum of the same spin. For high fields, this corresponds approximately to the following deviation density matrix $\chi(0)$

$$\chi(0) = -\hbar \omega_{0I}I_x/kT. \quad [16]$$

The same initial conditions would be appropriate when irradiating the I spin while we observe the other one in a cross-polarization experiment (12).

For a nonselective pulse we would have on the other hand

$$\chi(0) \cong -\hbar (\omega_{0S}S_x + \omega_{0I}I_x)/kT. \quad [17]$$

It can be shown that in this case the multipole $Q_0^{(0)}(1, 1)$ is not affected at all by the RF pulse.

We now consider the low-field case in some detail. For a selective pulse, at low fields, it is very likely that, for certain ranges of the strength, duration, and RF frequency, some other mixed multipoles such as $Q_{-1}^{(1)}(1, 1)$ can be excited. This multipole can be expressed in terms of standard operators as

$$Q_{-1}^{(1)}(1, 1) \propto S_{-1}I_0 - S_0I_{-1}. \quad [18]$$

For example, we study the spectrum of a two-spin system after a selective 90°_y pulse leading approximately to the following initial deviation density operator (some irrelevant parts, such as, for example, z components have been disregarded)

$$\chi(0) \cong -\hbar [\omega_{0I}I_x + \omega_{SC}Q_x^{(1)}(1, 1)]/kT. \quad [19]$$

The multipole $Q_{-1}^{(1)}(1, 1)$ has one term which may be set to be exactly on resonance as can be seen in Eq. [18]. The contribution of this multipole to the observed magnetization should be a manifestation of the "lost identity" of the two spins, since $\chi(0)$ contains products of the two operator spaces. Usually the multipole $Q_{-1}^{(1)}(1, 1)$ cannot be excited by the RF field, unless the scalar coupling is comparable to the Zeeman terms and unless we can irradiate preferentially only one spin at the time. We find, in general, that the effect of this multipole on the spectrum is to enhance the "forbidden singlet-triplet" transitions of a two spin spectrum (see Results for Typical Cases).

Before describing the calculations of the spectra we consider two complications occurring in low field. Although, for high field, only one of the multipoles I_+ or I_- is in resonance, in the low-field case both of them can give comparable contributions to the spectrum. However, due to the relation $\langle I_+(-\omega) \rangle = \langle I_-(\omega) \rangle^*$ one does not need to calculate the different spectra separately. Instead, the calculation of one multipole (here I_-) is adequate, while the total spectrum, i.e., $\langle I_x \rangle = \langle I_- + I_+ \rangle / 2$, is obtained by folding the negative part of the frequency axis over to the positive and

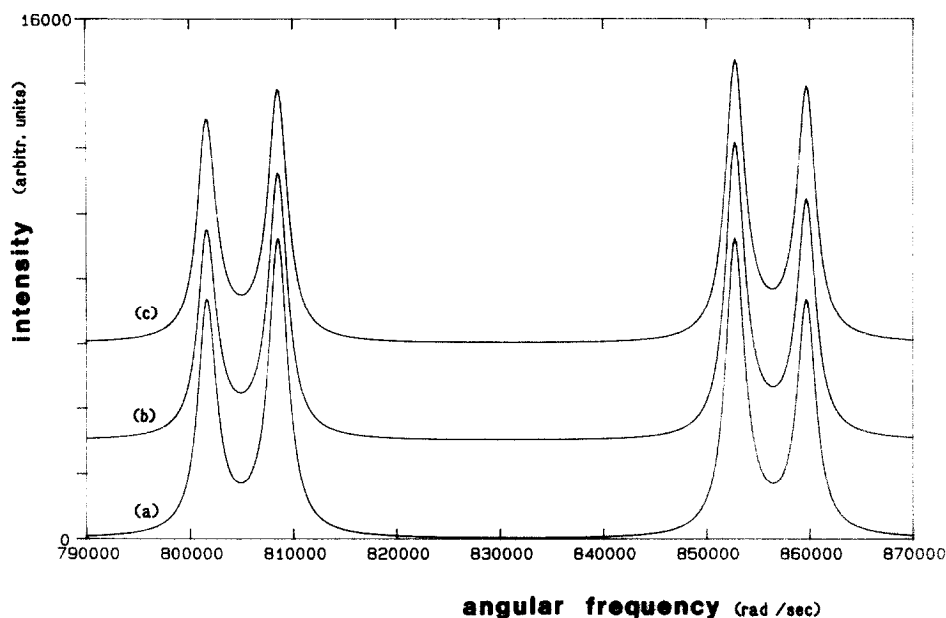


FIG. 1. H-F spectra for low field and slow motion. Spectrum (a) is equivalent to letting transition probabilities $P_{a,b} \propto |\langle a | J_x | b \rangle|^2$, whereas in (b) the difference in frequencies of the two species is taken into account (cf. text). The effect of the excitation of the multipole $Q^{(1)}(1, 1)$ is shown in (c). The parameters used are magnetic field, $H_0 = 3.2 \times 10^{-3}$ T, $\bar{g}_H = 2.0$, $\bar{g}_F = 2.0$, $\Delta g = g_{\parallel} - g_{\perp} = 1.0 \times 10^{-5}$ units for both H and F, $\omega_{SC} = 7.0 \times 10^3$ rad/s, $\omega_{DD}/\omega_{SC} = 30$. The isotropic rotational correlation time $\tau_R = 5.627 \times 10^{-8}$ s and additional line-broadening contributions $T_2' = 0.5 \times 10^{-3}$ s for both nuclei. In (a) the exciting and observing transition moments are taken as equal for H and F, whereas in (b) and (c) they are in the ratio 1:0.941, respectively; also in (c) $Q^{(1)}(1, 1)$ in the observing transition moment has nonzero relative weight of 0.082. The matrix dimension $N = 78$ based on an $L_{Max} = 10$, and 45 Lanczos steps were used.

taking the sum of both parts. This makes the total spectrum symmetric about the origin (9).

The CW absorption lineshape $L(\omega)$, which is equivalent to the spectra calculated in the present work, is defined by (9, 29)

$$L(\omega) = \chi''(\omega)/\omega, \quad [20]$$

where $\chi''(\omega)$ is the imaginary part of the complex susceptibility (cf. Eq. [1] in Ref. (9)) and is a scalar quantity if we assume that the sample is isotropic. Since, for a high-frequency narrow line, we can neglect the variation of the factor ω in Eq. [20] over its width, both the susceptibility and the absorption lineshape have a very similar frequency dependence for a high-field experiment, and consequently the shapes of both $\chi''(\omega)$ and $L(\omega)$ are the same. For a low-field experiment, however, the differences are significant (9). For example, no zero-frequency component (4) is expected for the susceptibility, while the absorption lineshape may have zero-frequency components (see later under Results for Typical Cases).

NUMERICAL METHOD

The calculation of the matrix elements of the Liouville superoperator in this work is simplified by using the coupled multipole representation and the Wigner-Eckart

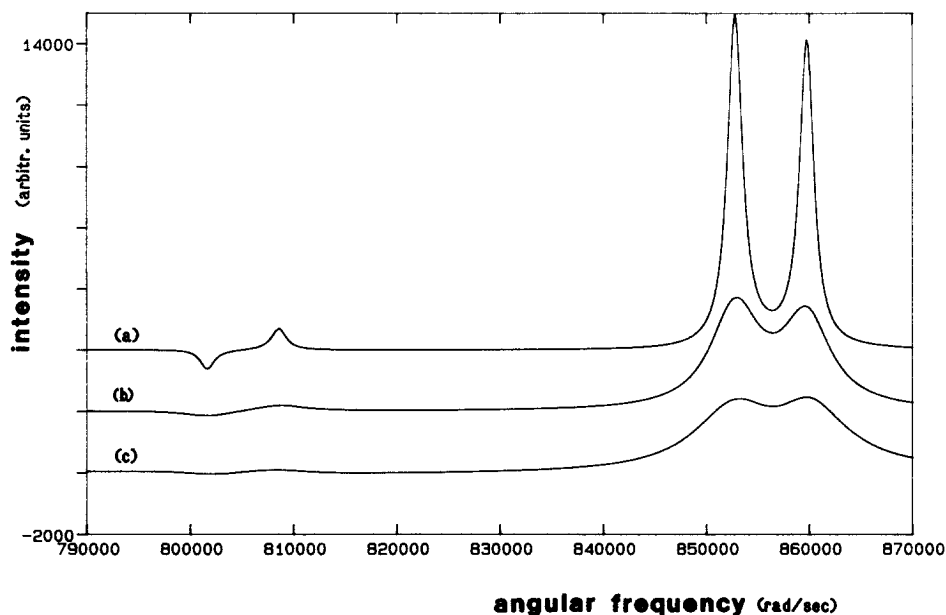


FIG. 2. The effect of selective irradiation of the proton while observing at the frequency of F is shown for a system similar to that of Fig. 1. All parameters are the same as those in Fig. 1 except that (a) and (c) $\omega_{DD}/\omega_{SC} = 30$, and (b) $\omega_{DD}/\omega_{SC} = 100$. In (c) a substantial independent exchange or cross-relaxation time $T_{ex} = 1 \times 10^{-4}$ s has been added in order to simulate the effect of water on the spectrum.

theorem in operator space (31). In this way, the matrix elements can be expressed in terms of only one reduced matrix element and the numerical calculations become more systematic, which also enhances the speed of the calculations. Furthermore, this makes it possible to use the same program in the calculation of the spectrum of arbitrary two-spin systems and even to calculate the spectra of one spin system as a limiting case by taking one spin equal to zero.

Two observations simplify the calculation of the spectrum. They both rely on the scalar property of the Liouville operator (14): (a) In the lineshape simulation we only need the multipoles with projection quantum number $|\lambda| = 1$ for the expansion of $\chi(0)$ (four for two spins $I = \frac{1}{2}$). (b) We only need the combinations $Q_{\lambda}^A \times \Phi_{K,M}^L$ with $|\lambda + M| = 1$ for the calculation of the transverse magnetization ($|\lambda + M| = 0$ for the longitudinal magnetization). The supermatrix elements of the Liouville operator are given in the Appendix and in references cited there.

However, the calculation of the matrix elements is the slowest part of the program because of the numerous couplings and the large dimensionality of the representation of the reorientational degrees of freedom. To make this part more efficient a symbolic matrix is first calculated for every interaction only once, and it is then used for different values of the strength of the interactions. The sparseness of the matrix is exploited here by saving only nontrivial element of the symbolic matrix in a one-dimensional array which has much smaller dimensions than the square of the matrix. Due to the structure of the Lanczos calculation of the spectrum, a huge speedup of the calculations is gained up to approximately 10^3 in some favorable cases when compared with

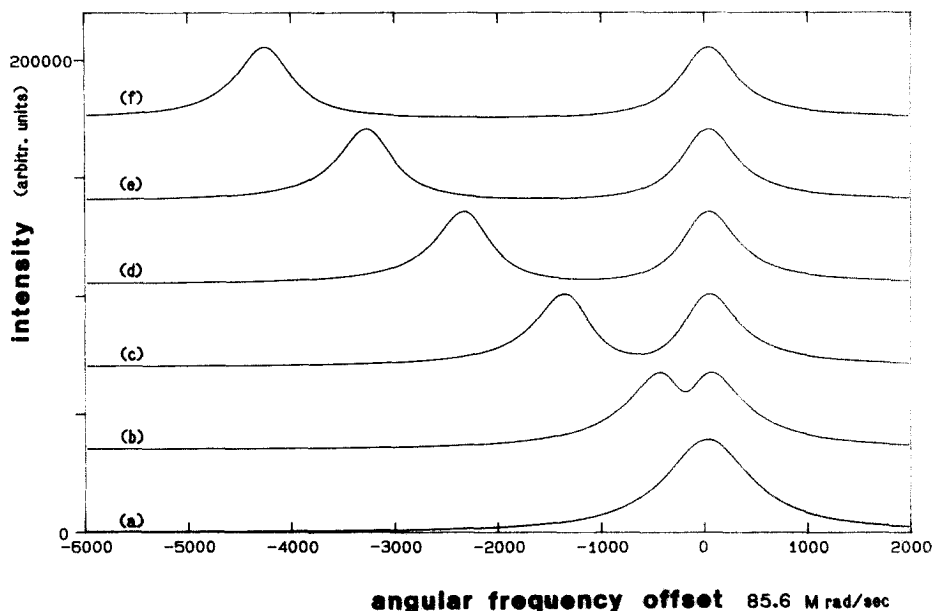


FIG. 3. The slow-motion spectrum of two protons with nearly equal chemical shifts and coupled with a dipole-dipole interaction. From (a) to (f) one of the protons has chemical shifts 2.000000, 1.999990, 1.999968, 1.999945, 1.999923, 1.999900, while the other proton's shift is retained at the value 2.000000. Spectrum (a) corresponds to the case of like spins of Abragam (25), while spectrum (f) almost corresponds to the case of unlike spins. The 3/2 effect of Abragam is also present in the figures, e.g., the width of the line in (a) is approximately 1.5 times broader than the width of either lines in spectrum (f). The other parameters are $H_0 = 3.2 \times 10^{-1}$ T, $\Delta g = 1 \times 10^{-5}$ for both protons, $\omega_{SC} = 0.23$ rad/s, $\omega_{DD}/\omega_{SC} = 1 \times 10^6$, $\tau_R = 6.00 \times 10^{-7}$ s, $T_2' = 1 \times 10^{-2}$ s with the same matrix size and convergence parameters as those in Fig. 1.

conventional algorithms for diagonalization (11, 32). This makes the simulation of high-spin spectra possible even for small computer facilities. For the systems calculated in this work the total time for a spectrum varied between 0.5 and 10 min of CPU time on a Prime computer.

As shown above, the calculation of the spectrum, i.e., the F - L transform of the cross-correlation function, reduces to essentially calculating the following off-diagonal elements of the resolvent matrix (33, 34)

$$L(\omega) = \langle u | [i(\mathcal{L} + \mathbf{1}_{op}\omega)]^{-1} | v \rangle, \tag{21}$$

where $|u\rangle$ and $|v\rangle$ are real column vectors well defined in the basis set $\{Q_k^\lambda(\Sigma, \Xi) \cdot (\Phi_{k,M}^\lambda)\}$. Since the Lanczos algorithm can only be used directly to calculate diagonal elements (autocorrelations), the calculation of Eq. [21] relies on the identity

$$\langle u + v | \mathbf{M}^{-1} | u + v \rangle = \langle u | \mathbf{M}^{-1} | u \rangle + \langle v | \mathbf{M}^{-1} | v \rangle + 2\langle u | \mathbf{M}^{-1} | v \rangle \tag{22}$$

assuming that the matrix \mathbf{M} is symmetric, which is the case here. The convergence of the spectrum is tested by choosing a larger L quantum number, e.g., by using a larger basis set to represent the reorientation subspace and by checking for the consistency

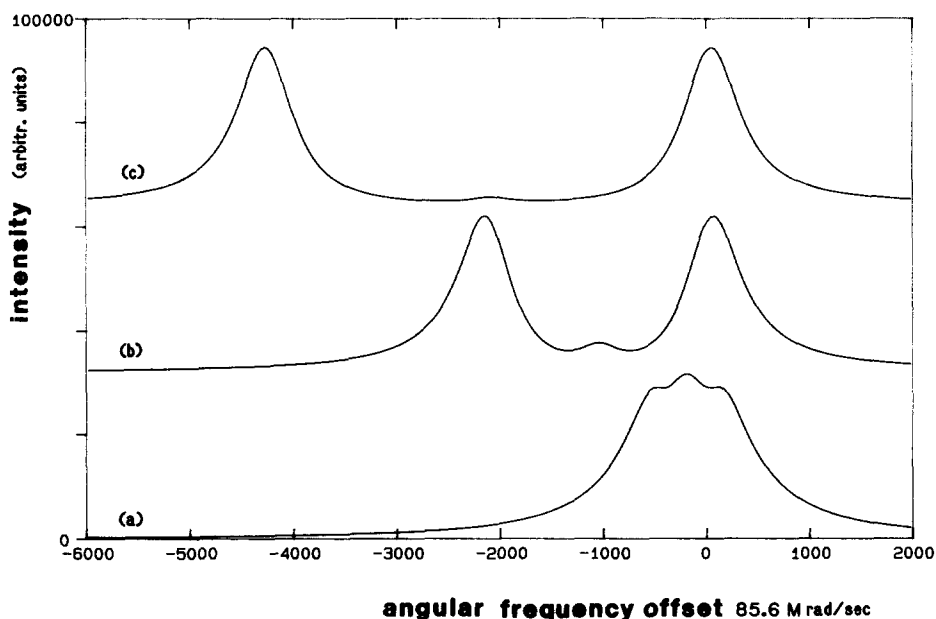


FIG. 4. Proton-proton spectrum showing the effects of a scalar interaction. One of the protons has chemical shift (a) 1.99999, (b) 1.99995, and (c) 1.99990, whereas the other is kept fixed at 2.000000. Observe that even though $\omega_{DD}/\omega_{SC} = 10^3$, ω_{SC} gives important effects. All other parameters are as in Fig. 3.

of the results for the different L . The slower the motion the larger the L_{\max} required for convergence. The second test for convergence in using the Lanczos algorithm is the number of iterative steps needed. For simple spin systems only a few steps are needed in fast motion (11). What we find here is that, even for fast motion, a large number of iterative steps are needed, suggesting that the coupling of the quantum-mechanical spin degrees of freedom is significant. Before using the program for the actual calculations some tests were made with well-studied systems in slow motion. Accordingly ESR nitroxide spectra were reproduced (16). Also the program was used to reproduce doublet and triplet ESR spectra in slow motion, e.g., the g tensor and/or ZFS interactions in a single-spin system (9, 16). Also higher spin NMR spectra were tested (25). Another test was to reproduce the low-field slow-motion spectra in triplets (9).

RESULTS FOR TYPICAL CASES

The Generalized AB Spectrum. The calculation of an AB spectrum is traditionally restricted to finding the relative transition probabilities with respect to the x component of the total angular momentum operator $J_x = S_x + I_x$ (30). This implies that the total magnetization is proportional to the total angular momentum which is accurate if the two nuclei are the same magnetic isotope, as, for example, two protons with slightly different chemical shifts. A corrected AB spectrum should correspond to calculating the magnetization μ defined by Eq. [7], and using the appropriate initial conditions, such as those discussed under The Spectrum of a Two-Spin System. The present formalism also allows for different preparation of the system as well as

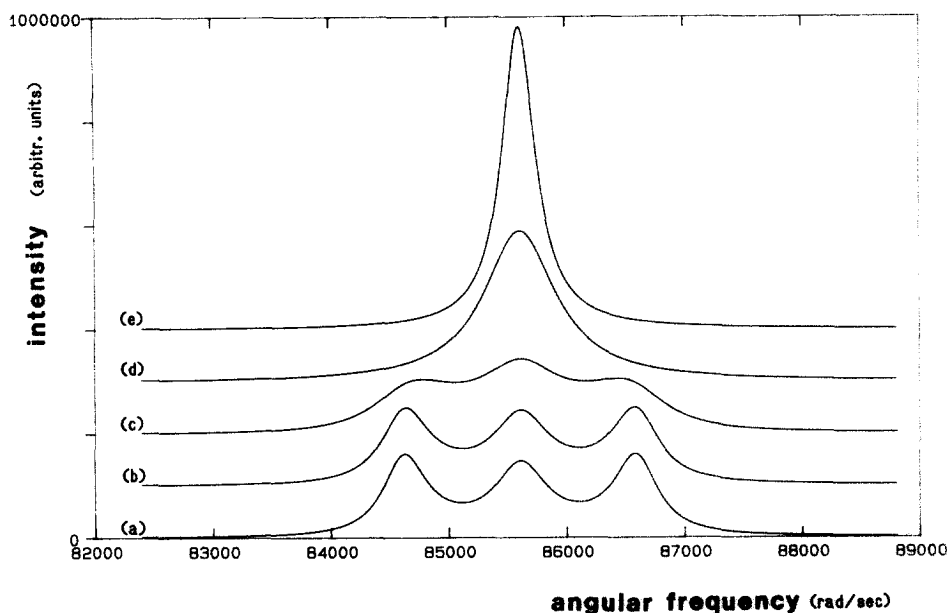


FIG. 5. Low-field proton spectrum coupled to nitrogen-14. The different spectra (a)–(e) have been obtained for different values of quadrupolar interaction of the nitrogen-14 nucleus. A comparison of spectra (a) and (c) illustrates the differences of the lineshapes of a strongly correlated spin system (a) and a weakly correlated spin system (c). The parameters used are $H_0 = 3.2 \times 10^{-4}$ T, $\bar{g}_H = 2.0$, $\bar{g}^{14N} = 2.0$, $\Delta g = 1.0 \times 10^{-5}$ for both ^{14}N and ^1H , $\omega_{SC} = 10^3$ rad/s, $\omega_{DD}/\omega_{SC} = 10^2$, $\tau_R = 6.0 \times 10^{-8}$ s, $T_2 = 1 \times 10^{-2}$ s for both nuclei. The values of the quadrupole splitting given as ω_Q/ω_{SC} are (a) 10, (b) 30, (c) 90, (d) 270, (e) 810. The exciting transition moments for H and ^{14}N are taken as 1.0 and 0.0722, respectively, whereas for observation they are taken as 1.0 and 0, respectively. The matrix dimension is 178 based on an $L_{\text{Max}} = 10$, and 100 Lanczos steps were used.

the calculation of cross-correlations while it reduces correctly to the usual AB spectrum for $\gamma_S \cong \gamma_I$. Using an initial condition $\chi(0) \propto \omega_{0S}S_x + \omega_{0I}I_x$, for example, the relative transition probability $P_{a,b} \propto |\langle a|J_x|b\rangle|^2$ should be replaced by $P_{a,b} \propto |\langle a|\omega_{0S}S_x + \omega_{0I}I_x|b\rangle|^2 = |\langle a|\gamma_J J_x + \gamma_K K_x|b\rangle|^2$, where $\gamma_J = (\gamma_S + \gamma_I)/2$, $\gamma_K = (\gamma_S - \gamma_I)/2$ and $\mathbf{K} = \mathbf{S} - \mathbf{I}$. This type of AB calculation would be reasonable for systems like HF in low enough fields that a single pulse could irradiate both nuclei. In addition to a field-independent overall relative increase of the signal of the species with the larger γ this expression also gives field-dependent corrections to the intensity of the “allowed” versus “forbidden” transitions, which is of great importance for the present work.

In general, the DD interaction between the A and B nuclei should be incorporated giving the appropriate broadening to the spectrum. Figure 1a shows a low-field, slow-motional HF spectrum where the correction due to the difference in γ is not taken into account. The DD interaction has been included (see legend for details). This figure is to be contrasted with Fig. 1b where the effect of the difference in the gyromagnetic ratios has been included in the calculation. In Fig. 1c the effect of the excitation of the multipole $Q_{-1}^{(1)}(1, 1)$ by the RF field has also been included in the calculation which enhances selectively the forbidden transitions. The effects of magnetization

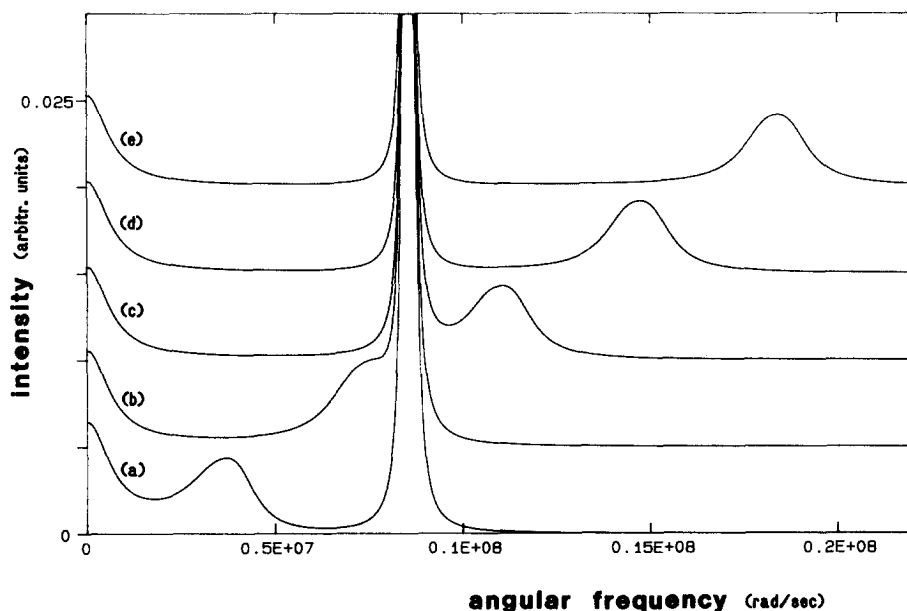


FIG. 6. Proton-nitrogen spectrum for the same system as that in Fig. 5 for very slow rotation ($\tau_R \cong 6 \times 10^{-6}$ s). The field is $H_0 = 3.2 \times 10^{-2}$ T. The values of ω_Q for ^{14}N are (a) 1.5, (b) 3.0, (c) 4.5, (d) 6.0, and (e) 7.5 Mrad/s. Observe that under the present conditions the nitrogen resonates at the frequency ω_Q instead of ω_{0S} (Zeeman). The other differences from Fig. 5 are that the exciting and observing transition moments are both taken as 1.0 and 0.0722 for H and ^{14}N , respectively, and the matrix dimension is 248 corresponding to $L_{\text{Max}} = 15$ with 180 Lanczos steps taken.

transfer are shown in Fig. 2. They are obtained by applying a pulse to one spin (proton) while observing the other one (fluorine). One effect here is an inversion of the forbidden singlet-triplet transition.

In the spectrum of two protons with very similar chemical shifts, we can immediately observe the effects of strong correlation. Figure 3 shows the two-proton spectrum for considerable DD interaction but negligibly small scalar interaction as a function of the chemical-shift difference. Notice the characteristic doublet with somewhat "burned" overlap which agrees with Ref. (27). This effect is due to the pseudosecular terms of the DD interaction. The pseudosecular terms can be shown not to induce any "singlet-triplet" transition. In Fig. 4 the effect of incorporating the scalar interaction is also shown. Figure 4 is drawn for a scalar interaction three orders of magnitude smaller than the DD interaction. Nevertheless, a new property appears which is not negligible. The present theory predicts that a transition with a resonance at the mean value of the two Larmor frequencies can be observed directly in the one-pulse one-dimensional spectrum. This signal is due to the superposition of the "triplet-triplet" transitions which broaden more than the remaining two transitions in the strongly correlated spin system but are still visible for the conditions chosen here.

The 3/2 effect discussed by Abragam is also shown in the same spectrum, viz., the width of the single line in Fig. 3a (like spins) is approximately 1.5 times the width of either line in Fig. 3f (unlike spins). As seen from the plots, however, the intermediate

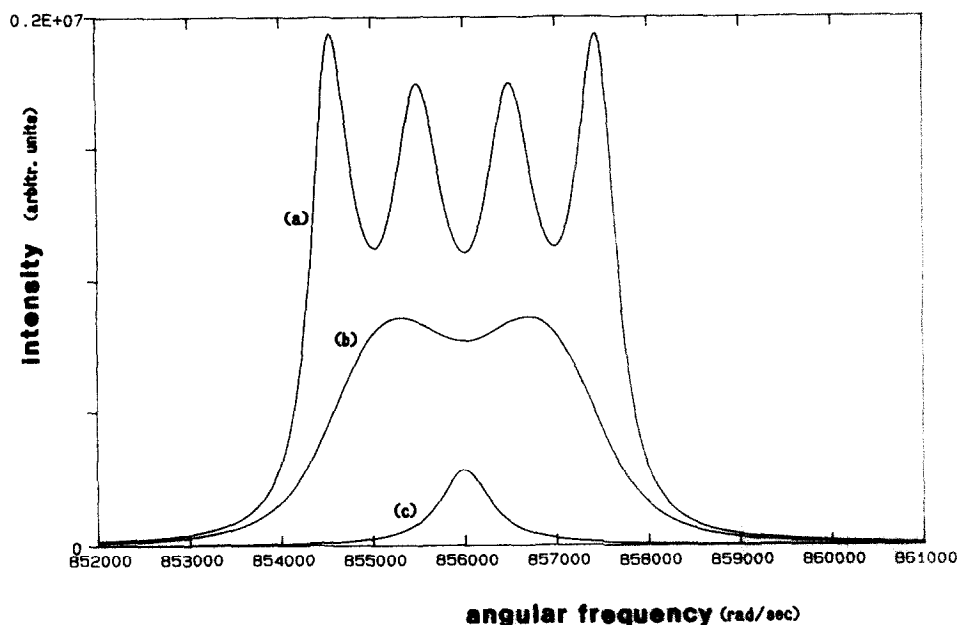


FIG. 7. The proton spectrum of the H-¹¹B system for strong correlation conditions. (The intensity axes of (b) and (c) are multiplied by 5 and 10, respectively.) Compare with Fig. 3 of Bushweller *et al.* (36). The parameters used are $H_0 = 3.2 \times 10^{-3}$ T, $\bar{g}_H = 2.0000$, $g_B = 2.0000$, $\Delta g = 1.0 \times 10^{-5}$ for both nuclei, $\omega_{SC} = 1.0 \times 10^3$ rad/s, $\omega_{DD}/\omega_{SC} = 10$, $\omega_Q = 1 \times 10^5$ rad/s. The values of τ_R are (a) 3.38 ns, (b) 33.8 ns, (c) 338 ns. Also $T_2' = 1 \times 10^{-2}$ s for both nuclei. The exciting transition moments are taken as 1.0 and 0.321 for H and ¹¹B, respectively, and the observing transition moments are taken as 1.0 and 0.0, respectively. For case (c) the matrix size is 186 corresponding to an $L_{max} = 6$, and 100 Lanczos steps were used.

cases, which cannot be treated by the formalism given by Abragam, can also be of interest. The experimental significance of this finding is that one can decide if two protons with similar chemical shifts are located geometrically close to each other in the same macromolecule, or not.

Proton Spectra Coupled to Quadrupolar Nuclei. For high fields and fast motion, the proton spectrum of an ¹H-¹⁴N pair is a triplet with the outer lines of equal width which is $\frac{3}{2}$ the width of the middle line. In this limit (1) the triplet coalesces for stronger quadrupole coupling constant (and sharpens with further increase quadrupole coupling constant). This was also observed with the present theory for a variety of the reorientational rates, e.g., even outside of the extreme narrowing regime for the quadrupole interaction, where Pople's theory is not applicable. Even for low field, the fast-motional spectrum with respect to the DD interaction is a resolved triplet due to the nonaveraged scalar interaction. The slow-motional spectrum of the whole system is totally different, however.

We discuss the fast-motional limit first, in the extreme-narrowing condition. For low field two regions are distinguished, with respect to the relative magnitude of the quadrupole (ω_Q) and the dipole-dipole (ω_{DD}) interactions, e.g., the low ω_Q and the high ω_Q regions. The high ω_Q region resembles three superimposed Lorentzians, which is very similar to the results of Pople valid for no appreciable cross-correlation.

In the superimposed triplet that is predicted, the outer lines are broader than the middle one and shifted toward the middle one. This is the area where the broadening of the proton triplet is due to the lifetime of the nitrogen spin states. This mechanism for broadening is not restrictive for the proton transitions and implies "reencounters" of the same S state; hence the early shift and the final triplet collapse for large ω_Q .

The low ω_Q spectra, where the multiplet broadens mainly by the hyperfine interaction, are characterized by "burned" overlap regions between the peaks, Figs. 5a, 5b, which is in contrast to Pople's predictions. There is also another difference with respect to Pople's theory, viz., the central peak appears to be broader than the outer peaks. The differences from the high ω_Q case are as follows: The lines are almost equally broadened, they do not show any shift, and they tend to separate.

The slow-motional spectrum of the same system is plotted next in Fig. 6 for higher field. The parameters are chosen, however, to be in the low-field area; e.g., the Zeeman interaction of the proton is comparable to the quadrupole interaction. In this spectrum the proton triplet has collapsed due to the fast relaxation of the ^{14}N spin. Another effect is observed in this spectrum. The resonance frequency of the ^{14}N is equal to ω_Q instead of the regular Larmor frequency $\omega_{0\text{N}}$, and can even be superimposed on the proton resonance for appropriate values of the parameters. The ^{14}N resonance is much broader, however, than the proton resonance, and consequently the experimentally expected effect in high-resolution NMR is at most a distortion of the baseline of the proton spectrum. A resonance at zero frequency is characteristic for a slow-reorientation low-field spectrum; this resonance is revealed in Fig. 6 because the absorption lineshape $L(\omega)$ is plotted here, not the imaginary part of the susceptibility. This resonance is due to the reorientational degree of freedom and has a width of the order of magnitude of the inverse reorientation correlation time τ_R . The ^{14}N resonance also has a broadening of the same order of magnitude. As the reorientation gets faster both the resonance at zero and ω_Q disappear.

The proton resonance of the ^1H - ^{11}B system is shown in Fig. 7. It is very similar to that for ^1H - ^{14}N , except for the spin quantum number of the quadrupolar nucleus, with $I = \frac{3}{2}$ for ^{11}B , and consequently we get a quartet instead of a triplet. Usually in the ^1H - ^{11}B system the ratio $\omega_{\text{DD}}/\omega_{\text{SC}}$ is also smaller. Pople's theory predicts equal broadening for all the elements of the proton quartet, which as seen by Fig. 7 is not always the case. The series of proton spectra for the system proton-boron obtained by Bushweller *et al.* (36) seems to be very similar to the spectral series obtained by the present theory. Note, for example, the earlier coalescence of the lines in pairs with one outer line in each pair.

NMR Spectra in Paramagnetic Systems. The proton spectrum in a solution of paramagnetic complexes is usually observed under conditions of fast exchange, since the pure spectrum of a proton on the complex is too broad to be observed. The same is also true for some other $I = \frac{1}{2}$ nuclei such as ^{13}C , ^{31}P , and ^{15}N . The directly coupled protons have been observed in some favorable cases (35).

To obtain the theory of the spectrum of exchanging protons, one first needs the spectrum of the protons attached to the complex. Usually the two spins on a complex molecule, the proton and the electron, are considered weakly coupled, and the electron is considered a part of the lattice (18, 37, 38). This simplification is legitimate when the electron is strongly coupled to the lattice, which is almost always true for S

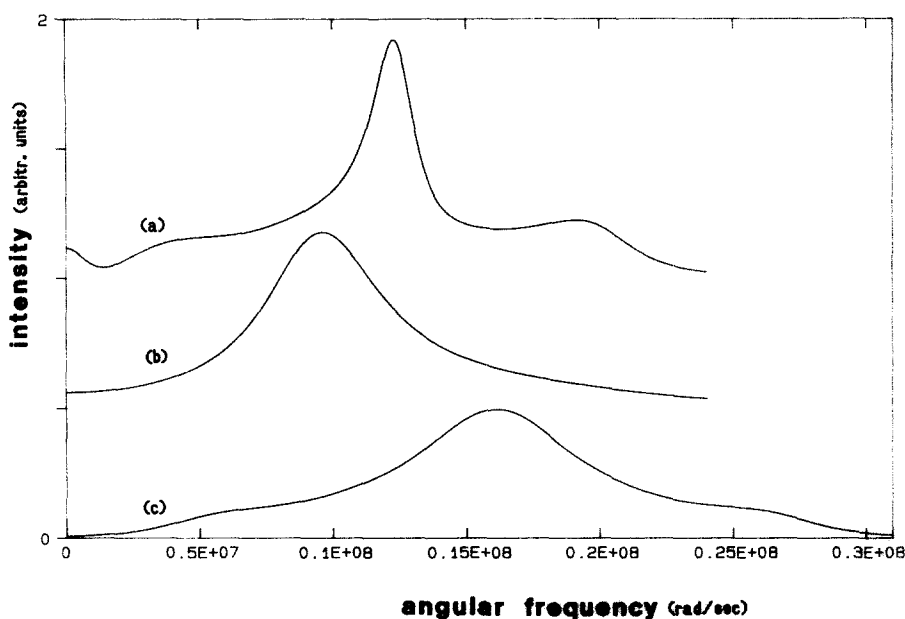


FIG. 8. The NMR spectrum of a proton in a paramagnetic complex ($S = \frac{1}{2}$) as a function of magnetic field in the slow-motional regime. The magnetic field is (a) and (b) 3.2×10^{-2} T, (c) 3.2 T (the same frequency axis is used in plotting (c) by taking an offset of 0.86×10^9 rad/s). Spectrum (b) differs from (a) in the magnitude of $T_{1,e}$ for the electron spin relaxation time; e.g., $T_{1,e} = 1.0 \times 10^{-7}$ s in (b) and $T_{1,e} = 1.0 \times 10^{-3}$ s in (a) and (c). The other parameters are $\bar{g} = 2.0000$ and $\Delta g = 0.2$ for the proton, $\tau_R = 3.376 \times 10^{-6}$ s, $\omega_{SC} = 3.0 \times 10^6$ rad/s, $\omega_{DD}/\omega_{SC} = 10$. The matrix dimension is $N = 183$ based on an $L_{max} = 25$, and 100 Lanczos steps were taken.

$> \frac{1}{2}$. A consequence of the above assumption is that the proton is in the Redfield limit due to the fast motion of the lattice. The Redfield theory predicts a Lorentzian line with $T_2^{-1} \propto \tau_R$. We can demonstrate that this is not true for low field and slow motion. In Fig. 8a we obtain a more complex lineshape, instead of a Lorentzian which broadens down to near zero frequency which is the natural frequency of the pure dissipative lattice (reorientations) we assume. When we impose a fast relaxation on the electron spin we get a Lorentzian, however, Fig. 8b. In Fig. 8c the same parameters as those in Figs. 8a and 8b are retained except that the dc field is taken to be much larger. The spectrum of the nuclear spin is now more similar to a Lorentzian but still has a more complex structure at the wings.

FURTHER COMMENTS

The effects of strong coupling are expected to be more important in studying two-dimensional spectra and multipulse experiments as well as in experiments that observe the same system in both low and high field (cycling). The present formalism can simplify the calculations very much in the above cases. ESR experiments can also be directly calculated by the present formalism, especially macromolecular systems with two coupled paramagnetic centers (39).

APPENDIX

In Appendix A of Benetis (14) the Wigner-Eckart theorem for the matrix elements of the Liouville superoperator was given, along with a general reduced matrix element $R_{\Lambda'PA}^{SK}$ appropriate for a coupled two-spin system. The matrix elements of different parts of the Liouville superoperator, along with some simple selection rules, were also given. Here we illustrate just the quadrupolar part of the Liouville operator which was not given there,

$$\begin{aligned} & (\Phi_{K'M'}^{L'} Q_{\lambda'}^{\Lambda'}(\Sigma' \Xi') | \mathbf{L}^{\text{QDR}} | \Phi_{KM}^L Q_{\lambda}^{\Lambda}(\Sigma \Xi)) = \delta_{K'K} \delta_{\lambda'+M', \lambda+M} \cdot (-1)^{K+\Lambda+M+\lambda'} \cdot C_Q \cdot \omega_Q \\ & \times [(2L' + 1)(2L + 1)(2\Lambda' + 1)]^{1/2} \cdot R_{\Lambda'2\Lambda}^{0}(\Sigma' \Xi'; 20; \Sigma \Xi) \\ & \times \begin{pmatrix} L' & 2 & L \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L' & 2 & L \\ -M & M-M & M \end{pmatrix} \begin{pmatrix} \Lambda & 2 & \Lambda' \\ \lambda & M-M' & M-\lambda-M \end{pmatrix}, \end{aligned}$$

where

$$C_Q = \left(\frac{2}{3}\right)^{1/2} \frac{(I+1)(2I+1)}{4(2I-1)}.$$

The matrix element yields the following selection rules:

$$\left\{ \begin{array}{l} \Sigma' = \Sigma \pm 1; \Xi' = \Xi \\ \Lambda' = \Lambda, \Lambda \pm 1, \Lambda \pm 2 \end{array} \right\}.$$

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