THEORETICAL NUCLEAR MAGNETIC RESONANCE LINE SHAPES OF TWO SPIN-1/2 AND SOME SIMPLE THREE SPIN-1/2 SYSTEMS UNDERGOING INTRAMOLECULAR EXCHANGE

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TO MY PARENTS AND GRANDPARENTS

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ABSTRACT

The density matrix technique is discussed for intramolecular exchange processes with respect to their effect on high-resolution nuclear magnetic resonance spectra. The theory has been developed in detail for the line shape of an ABX spin-½ system in which the A and B nuclei (assumed to be of the same nuclear species) are undergoing intramolecular exchange with an average pre-exchange lifetime τ, and an analytical expression is obtained for the region of transitions of the A and B nuclei. The expression is valid for arbitrary coupling constants and for an arbitrary chemical shift between the A and B nuclei, and reduces to simplier three spin-½ and all two spin-½ systems.

Computer programs have been written to plot the calculated spectra as a function of the lifetime τ, the natural line width, the chemical shift (between the A and B nuclei) and the coupling constants; and to calculate the peak positions and their half-height line widths for the computed spectra. Several plots are presented; in particular plots are given which have been used to correlate the lifetime with temperature for a compound reported elsewhere (34) with a temperature-dependent spectrum due to internal hindered rotation (equivalent in this case to an intramolecular exchange process).

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Chapter I

INTRODUCTION TO THE PROBLEM

The application of high-resolution nuclear magnetic resonance (n.m.r.) spectroscopy to chemical rate processes in liquids and gases is based on the study of the line shapes (number of peaks, their positions and their widths) as a function of the rate of exchange of atoms which possess a nuclear magnetic moment (1-3, 27-29). For example, the effect on the n.m.r. spectra of exchange of two uncoupled protons with differing chemical shifts may be described qualitatively as follows:

(a). When the exchange rate is slow (i.e. rate $<<$ shift), the spectrum consists of two sharp peaks separated by the chemical shift.

(b). When the exchange rate is fast (i.e. rate $>>$ shift), a single peak is observed at the midpoint of the peaks in (a).

(c). At intermediate exchange rates (i.e. rate $=$ shift), broadened doublets occur with a separation less than the chemical shift. These doublets sharpen as the rate decreases, and coalesce into a singlet as the rate increases.

The purpose of the ensuing discussion is to derive a general expression, using density matrix techniques, for the line shape of an ABX[†] spin-½ system as a function of τ, the inverse of the intramolecular exchange rate of the A and B nuclei, and to write a computer program to calculate the line shape. The expression derived is also valid for other

---

[†] In n.m.r. nomenclature, the notation ABX implies a system containing three spinning nuclei, two of which (the A and B nuclei) have a chemical shift of the same order of magnitude as the coupling between them, and one of which (the X nucleus) has a large chemical shift compared to the coupling with either of the A and B nuclei. See for example reference (1), page 98.

simple three spin-½ and two spin-½ systems (eg. A_2, AX, AB, A_2X, AMX) in which the two exchanging nuclei (for three spin systems, the first two nuclei are assumed to be exchanging) are of the same nuclear species. Several examples of calculated spectra are presented in Chapter VI; in particular the expression obtained has been used to correlate the exchange rate with temperature for a compound reported elsewhere (34) which is undergoing hindered rotation (in this case, the hindered rotation is equivalent to intramolecular exchange). Examples of the fitted spectra are also given in Chapter VI.

Chapter II is concerned with a brief outline of the n.m.r. experiment. The high-resolution n.m.r. Hamiltonian is discussed in Chapter III, and the density matrix technique in Chapter IV. The derivation of the general line shape expression for exchanging nuclei is outlined in Chapter V, and the AB part of the ABX line shape is deduced in detail. The computer programs and calculated spectra are presented in Chapter VI.

Chapter II

THE NUCLEAR MAGNETIC RESONANCE EXPERIMENT

1. Introduction[†]

The phenomenon of n.m.r. is concerned with the intrinsic spin and associated spin angular momentum of the nucleus. It has been well established that certain nuclei possess angular momentum and a magnetic moment, and it follows from the quantum mechanical theory of angular momentum that the measurement along any reference direction of a component of the angular momentum yields certain discrete values. For a nucleus with an angular momentum there are a total of (2I+1) of these quantized values, where I is known as the spin quantum number (or spin number) and is a characteristic of the nucleus in question. In general the spin number cannot be predicted; however several qualitative rules, deriving from experiment, may be set forth:

(a) the spin number is a multiple of ½ (i.e. 0, ½, 1, ...).

(b) nuclei with an even number of protons and an even number of neutrons have a spin number equal to zero (eg. $^{4}He_{2}$, $^{12}C_{6}$, $^{16}O_{8}$).

(c) nuclei with an odd number of protons and an odd number of neutrons have integral spin numbers (eg. $^{2}H_{1}$, $^{14}N_{7}$, $^{10}B_{5}$).

(d) nuclei with an even (odd) number of protons and an odd (even) number of neutrons have half-integral spin numbers (eg. $^{1}H_{1}$, $^{13}C_{6}$, $^{15}N_{7}$).

The discrete values taken by a measurement of a component of the spin angular momentum vector $\underline{P}$ are of the form ($m\hbar$) where $\hbar$ is the modified

---

[†] The succeeding discussion is a brief outline of the theory of the n.m.r. experiment. More detailed discourses may be found in a number of standard texts (1-6).

Planck's constant, and m is known as the magnetic quantum number with the range of values:

$$(1) \qquad m = -I, -I+1, \ldots\ldots, I-1, I\ .$$

Further, the magnitude of the spin angular momentum vector is given by the following expression:

$$(2) \qquad |\underline{P}| = \hbar \{I(I+1)\}^{\frac{1}{2}}$$

for a nucleus with spin number I.

Nuclei with a non-zero spin angular momentum are found to possess a nuclear magnetic moment (nuclei with spin number greater than ½ also possess a nuclear quadrupole moment arising from a non-spherical charge distribution. Since this discussion is concerned with spin-½ nuclei, this theory is not discussed here). Using the classical concept of a spinning nucleus with a charge Q and a mass M, the expression for the magnetic moment $\underline{\mu}$ (in e.m.u.) is given by (2,5):

$$(3) \qquad \underline{\mu} = \frac{Q}{2Mc} \underline{P}$$

where c is the speed of light, and the magnetic moment vector is colinear with the angular momentum vector $\underline{P}$. This result is inconsistent with experiment, and equation (3) is usually written as:

$$(4) \qquad \underline{\mu} = g_n \frac{e\hbar}{2M_p c} \frac{\underline{P}}{\hbar}$$

$$= g_n \beta_n \frac{\underline{P}}{\hbar}$$

where g_n is known as the nuclear g factor, and where β_n is the nuclear magneton, and e and M_p are the charge and mass respectively of the proton (this equation allows the neutron to have a magnetic moment, whereas equation (3) incorrectly predicts a vanishing magnetic moment since the charge of the neutron is zero). Since β_n is a constant (5.05×10^{-24}

ergs/gauss), the magnetic moments of different nuclei are characterized by their nuclear g factor and their spin angular momentum vector $\underline{P}$.

It is convenient at this point to introduce the vector $\underline{I}$, defined by the equation:

$$(5) \qquad \underline{I} = \frac{\underline{P}}{\hbar}$$

which corresponds to the measurement of $\underline{P}$ in units of $\hbar$. Equation (4) is now expressed in the form:

$$(6) \qquad \underline{\mu} = g_n \beta_n \underline{I}$$
$$= \gamma\hbar \, \underline{I}$$

where $\gamma (= g_n \beta_n / h)$ is known as the gyromagnetic ratio and is characteristic of the nucleus under consideration (for example, $\gamma = 2.67519 \times 10^4$ rad./sec./gauss for a proton).

It follows from the definition of $\underline{I}$ that its components along any reference direction are quantized, and take on values of the form (m). From equation (6) it can then be deduced that $\underline{\mu}$ is quantized, taking on values of the form ($\gamma\hbar m$) where m has the range of values in equation (1).

2. The Nuclear Zeeman Effect

The (2I+1) different values of a component of $\underline{\mu}$ give rise to the same number of different spin levels or spin states which are degenerate in free space. The degeneracy may be lifted by the application of an external magnetic field through an interaction between the magnetic moment and the magnetic field. This interaction is known as the nuclear Zeeman effect or the nuclear Zeeman splitting.

Classically, the energy of interaction of a magnetic moment with an external magnetic field is given by the vector dot product $\underline{\mu}\cdot\underline{H}$. For example, in a static magnetic field $\underline{H}_o$ the energy of interaction with a nuclear magnetic moment is:

$$(7) \qquad E_o = -\underline{\mu}\cdot\underline{H}_o = \mu_z H_o$$

where the n.m.r. convention is used whereby $\underline{H}_o$ defines the negative z direction. Substituting from equation (6), equation (7) is put into the form:

$$(8) \qquad E_o = \gamma\hbar\, I_z H_o$$

and the subsequent splitting in energy between two adjacent spin states (i.e. $\Delta m=1$) is given by:

$$(9) \qquad \Delta E_0 = \gamma\hbar\, \Delta m\, H_o = \gamma\hbar\, H_o = g_n\beta_n\, H_o\,.$$

The case for a nucleus with spin number I=1 is shown in figure (1). The observable in the n.m.r. experiment is related to the energy absorbed when a nucleus undergoes a transition from a lower spin state to a higher spin state (i.e. m(final) - m(initial) = +1), with an absorption of energy given by equation (9).

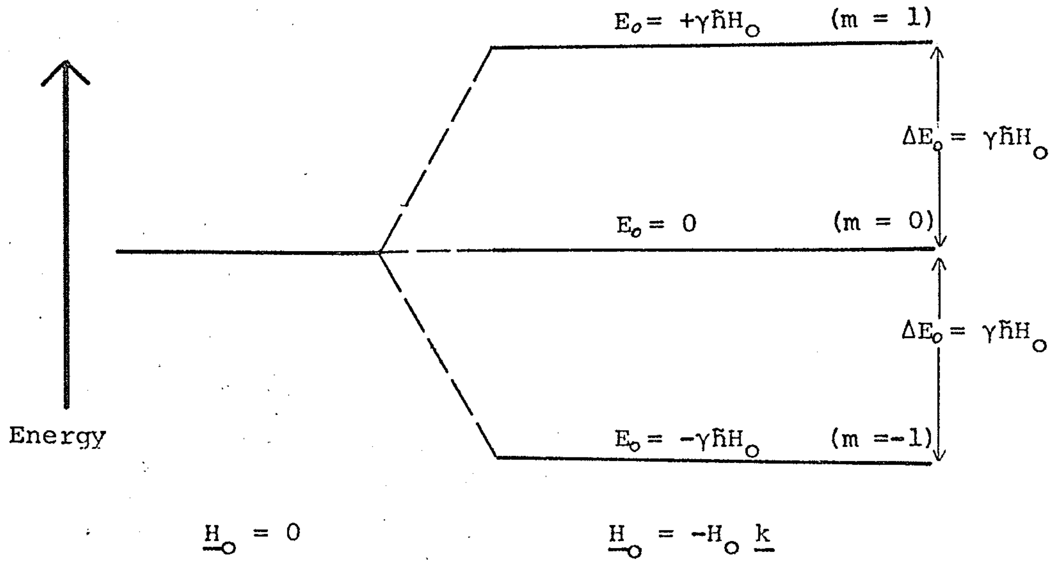

FIGURE (1). The nuclear Zeeman Splitting for a nucleus with spin number I = 1.

3. The Resonance Condition

Transitions between spin states is achieved in n.m.r. by the presence of a small rf field $\underline{H}_p(t)$ applied perpendicularily to a static magnetic field $\underline{H}_0$ (where small means $|\underline{H}_p(t)| << |\underline{H}_o|$). The classical equation of motion of the nuclear magnetic moment (ignoring for the present $\underline{H}_p(t)$) is given by (1-6):

$$(10) \qquad \dot{\underline{\mu}} = \gamma\,(\underline{\mu} \times \underline{H}_o) = \underline{\mu} \times \underline{\omega}_o$$

where $\underline{\omega}_o = \gamma \underline{H}_o$. This equation corresponds to the precession of $\underline{\mu}$ about $\underline{H}_o$ with an angular velocity $\omega_o = |\underline{\omega}_o|$ called the nuclear Larmour precessional velocity. For example, in a field of 10,000 gauss, the Larmour velocity of the proton is 6.77×10^6 rad./sec.

Considering now the presence of $\underline{H}_p(t)$ rotating about $\underline{H}_o$ with an angular velocity $\underline{\omega}_1$, the effect will be to produce on the magnetic moment a torque which varies direction rapidly. Consequently the magnetic moment is perturbed, and for $\underline{\omega}_1 \neq \underline{\omega}_o$ it will wobble slightly in its steady precessional motion about $\underline{H}_o$. At $\underline{\omega}_1 = \underline{\omega}_o$, the torque will be 'in phase' and effectively act in the same direction (relative to a coordinate system rotating at $-\underline{\omega}_o$) causing large oscillations which tend to change the orientation of $\underline{\mu}$; i.e. to change the spin level of the nucleus.

The semi-classical model on which this theory is based therefore predicts a transition between spin states at the resonance condition:

$$(11) \qquad \underline{\omega}_1 = \underline{\omega}_o = \gamma \underline{H}_o$$

and although it is useful in providing a geometrical description of the resonance phenomenon, it incorrectly predicts a continuous absorption of energy. For a more consistent explanation of the experiment, a quantum mechanical description must be employed. Qualitatively this description is relatively straight-forward: the small rf field $\underline{H}_p(t)$ interacts with the magnetic moment vector, producing a perturbation represented by the Hamiltonian $\hat{H}_p(t)$ where:

$$(12) \qquad \hat{H}_p(t) = - \underline{\mu} \cdot \underline{H}_p(t) \quad .$$

From time-dependent perturbation theory, taken to first order, it follows that the transition probability between adjacent spin states (to first order it also follows that only this type of transition is allowed) is given by an expression of the form (1-4,6):

$$(13) \qquad W_{i \rightarrow f} = | \langle \Phi_f(t) | \hat{H}_p(t) | \Phi_i(t) \rangle |^2 \ \delta(\omega_o, \omega_1)$$

where $W_{i \rightarrow f}$ represents the probability of a transition between the initial spin state $|\Phi_i(t)\rangle$ and the final state $|\Phi_f(t)\rangle$ and where $\delta(\omega_o, \omega_1)$ is the Dirac delta function. The nature of the Dirac delta function is such that a transition and an absorption of energy occurs only at the resonance condition given in equation (11) (this simple-minded approach ignores the various broadening processes operative in n.m.r.) . The quantum mechanical treatment of spin angular momentum and the n.m.r. experiment is discussed in more detail in the following chapter.

Chapter III

THE HIGH-RESOLUTION N.M.R. HAMILTONIAN

1. Introduction to the N.M.R. Hamiltonian

The spin angular momentum of a nucleus possesses no classical analogue, and consequently the usual construction of the corresponding quantum mechanical operators cannot be followed (7, 8). In section 2 of this chapter, an outline of the usual treatment of the spin angular momentum (following the method of Dirac) is presented.

In sections 3-5, the various elements of the high-resolution n.m.r. Hamiltonian are discussed[†]: the nuclear Zeeman interaction, the chemical shift, and the spin-spin coupling. This so-called 'high-resolution' Hamiltonian is valid for the n.m.r. of liquids and gases where it is assumed that intermolecular interactions can be ignored through a process of random averaging over all molecular orientations (1-6). It should also be pointed out that this Hamiltonian derives largely from a phenomenological approach rather than a theoretical approach to the n.m.r. experiment, and that an approximation similar to the Born-Oppenheimer approximation has been made:

$$(14) \qquad \Psi_{\text{molecular}} = \Psi_{\text{spacial}} \cdot \Psi_{\text{nuclear}}$$

so that a nuclear spin Hamiltonian may be separated out of the molecular Hamiltonian, and so that reference may be made to a nuclear spin state.

Section 6 deals with the unitary transformation corresponding to a transformation to a rotating coordinate system which is of some importance in the discussion to follow. Finally, in section 7, the various relaxation processes in spin-½ n.m.r. are discussed.

[†] Detailed monographs on the n.m.r. Hamiltonian may be found in references (1) to (6).

2. The Quantum Mechanical Treatment of Spin Angular Momentum Operators

The usual treatment of spin angular momentum (6-9), validated by its agreement with experiment, involves the assumption that the spinning nucleus can be described by equations similar to the orbital angular momentum of electrons in an atom. Hence the nuclear system is represented by a spin angular momentum vector operator $\underline{I} = (I_x, I_y, I_z)$ which corresponds to the orbital angular momentum vector operator. The commutation relationships are also similar:

$$\begin{aligned} \{I^2, I_r\} &= I^2 I_r - I_r I^2 = 0 \qquad (r = x, y, z) \\ \{I_x, I_y\} &= i\, I_z \\ \{I_y, I_z\} &= i\, I_x \\ \{I_z, I_x\} &= i\, I_y \end{aligned} \tag{15}$$

where i is the imaginary number $\sqrt{-1}$, $I^2 = \underline{I} \cdot \underline{I} = (I_x^2 + I_y^2 + I_z^2)$, and the spin angular momentum is measured in units of $\hbar$ (cf. equation (5)).

From this set of commutators and the theory of quantum mechanics it follows that (10) I^2 and only one of the components of $\underline{I}$ possess a complete set of simultaneous eigenvectors. Conventionally, for the n.m.r. experiment this set of eigenvectors is chosen to be the eigenvectors of I_z and I^2, so that only I_z and I^2 have discrete values, whereas I_x and I_y are given by expectation values. Designating any such eigenvector by the ket vector $|a, b\rangle$, where a is the eigenvalue of I^2 and b the eigenvalue of I_z, then the eigenvalue equations are:

$$I^2 \,|a, b\rangle = a \,|a, b\rangle , \tag{16a}$$

$$I_z \,|a, b\rangle = b \,|a, b\rangle . \tag{16b}$$

The properties of these eigenvalue equations are generally deduced using the raising and lowering operators, designated by I_+ and I_- respectively, and defined by the equations:

(17) $$I_{\pm} = I_x \pm i\, I_y \,.$$

The following commutation relations may be deduced from equations (15) and the definition (17):

(18) $$\begin{aligned} \{I^2, I_{\pm}\} &= 0 \\ \{I_z, I_{\pm}\} &= \pm I_{\pm} \\ \{I_+, I_-\} &= 2\, I_z \,. \end{aligned}$$

For these operators it can be shown that (6-9):

(19) $$I_{\pm} \,|a, b\rangle = \{(a-b)(a\pm b+1)\}^{\frac{1}{2}} \,|a, b\pm 1\rangle$$

and that $a = I(I+1)$ and $b = m$, where I is the spin quantum number and m the magnetic quantum number. The eigenvalue equations (16) therefore are written as:

(20) $$I^2 \,|I, m\rangle = I(I+1) \,|I, m\rangle$$

and (21) $$I_z \,|I, m\rangle = m \,|I, m\rangle \,.$$

Using equation (19) a set of (2I+1) eigenvectors corresponding to each spin state may be generated; it can be shown that the set is complete and orthonormal, i.e.:

(22) $$\langle I, m|I, m'\rangle = \delta_{m,m'}$$

(where $\delta_{m,m'}$ is the Kronecker delta function) and that it serves as a basis for a spin space of order (2I+1). For example, the spin space of a system with spin number $I = \frac{1}{2}$ is of order 2, and it is spanned by two independent eigenvectors denoted by $|\frac{1}{2}, +\frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ or more commonly by α and β respectively.

It is often very convenient to represent the spin operators in matrix form relative to this basis set of eigenvectors. The elements of the matrix corresponding to some spin operator R are given by the definition:

(23) $$R_{jk} = \langle I, m_j|R|I, m_k\rangle \,.$$

For example it follows from the orthonormality relations (22) and from equations (19)-(21) that the matrix representations of I^2, I_z and I_+ (note that I_- is the adjoint of I_+ ; i.e. $(I_-)_{jk} = (I_+)^*_{kj}$) relative to the basis set of eigenvectors of I^2 and I_z are:

$$(24) \qquad I^2 = I(I+1)\begin{bmatrix} 1 & 0 & 0 & \cdot\cdot & 0 \\ 0 & 1 & 0 & \cdot\cdot & 0 \\ 0 & 0 & 1 & \cdot\cdot & 0 \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ 0 & 0 & 0 & \cdot\cdot & 1 \end{bmatrix}$$

$$(25) \qquad I_z = \begin{bmatrix} I & 0 & 0 & \cdot\cdot & 0 \\ 0 & I-1 & 0 & \cdot\cdot & 0 \\ 0 & 0 & I-2 & \cdot\cdot & 0 \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ 0 & 0 & 0 & \cdot\cdot & -I \end{bmatrix}$$

$$(26) \qquad I_+ = \begin{bmatrix} 0 & \{1\cdot(2I)\}^{\frac{1}{2}} & 0 & \cdot\cdot & 0 \\ 0 & 0 & \{2\cdot(2I-1)\}^{\frac{1}{2}} & \cdot\cdot & 0 \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ 0 & 0 & 0 & \cdot\cdot & \{(2I)\cdot 1\}^{\frac{1}{2}} \\ 0 & 0 & 0 & \cdot\cdot & 0 \end{bmatrix}$$

Note that the matrices are square $(2I+1) \times (2I+1)$ matrices.

The description of the angular momentum of a system with more than one spinning nucleus is given by the vector addition of the spin angular momentum of each spinning nucleus. Designating the total angular momentum by $\underline{I}$ and the angular momentum of the j^{th} nucleus by $\underline{I}_j$, then:

$$(27)\qquad \begin{aligned} \underline{I} &= (I_x, I_y, I_z) = \sum_j \underline{I}_j \\ I_r &= \sum_j I_{jr} \qquad (r = x, y, z) \\ I^2 &= \underline{I}\cdot\underline{I} = I_x^{\,2} + I_y^{\,2} + I_z^{\,2} = \sum_j \underline{I}_j^{\,2} + 2\sum_{j<k}\sum \underline{I}_j\cdot\underline{I}_k \\ I_\pm &= I_x \pm i\,I_y = \sum_j I_{jx} \pm i\sum_j I_{jy} \end{aligned}$$

and the vectors $\underline{I}$ and each of the $\underline{I}_j$'s satisfy the commutation relations (15) and the following relationships (9):

$$(28)\qquad \begin{aligned} \{I_r, I_{jr}\} &= 0 \qquad (r = x, y, z, +, -) \\ \{I_x, I_{jy}\} &= i\,I_{jz} = \{I_{jx}, I_y\} \\ \{I_y, I_{jz}\} &= i\,I_{jx} = \{I_{jy}, I_z\} \\ \{I_z, I_{jx}\} &= i\,I_{jy} = \{I_{jz}, I_x\} \\ \{I_\pm, I_{jz}\} &= \mp\, I_\pm = \{I_{j\pm}, I_z\} \\ \{I_\pm, I_{j\mp}\} &= \pm\, 2\, I_{jz} \end{aligned}$$

The spin space of the system is given by the tensor product of the spin space of each nucleus, and the basis vectors by the tensor product of the basis vectors for each nucleus; i.e. all products of the form:

$$(29)\qquad \prod_j |I_j, m_j\rangle = |I_1, m_1; I_2, m_2; \cdots ; I_k, m_k; \cdots \rangle$$

where the subscripts refer to a particular nucleus, and where the basis set for a given nucleus is chosen to be the set of eigenvectors of I_j^2 and I_{jz} (in this particular case).

The discussion is somewhat simplified if it is assumed that all the nuclei have a spin quantum number of ½ (this is true for example in proton magnetic resonance). In this case a system containing n nuclei will have a total of 2^n basis product vectors (we define "basis product vectors" by equation (29), the tensor product of the eigenvectors of $I_j^{\,2}$ and I_{jz} for each nucleus 'j'), represented by the products of the states $\alpha(j)$ and $\beta(j)$

(corresponding to the eigenvalues of $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively of I_{jz}) of each of the nuclei in the system. This basis set consists of eigenvectors of I_z but not of I^2; however a simultaneous set of eigenvectors may be found by taking suitable linear combinations of the basis product vectors (since I^2 and I_z commute (10)). In table (1), the eight basis product vectors of a three spin-$\frac{1}{2}$ system are collected, and in table (2) linear combinations of the basis product vectors have been taken to produce a simultaneous set of eigenvectors of I^2 and I_z (this latter set is not unique).

The matrix representation of the total angular momentum operators is given by the tensor products of each appropriate nuclear spin operator or by using equations (19)-(22) and equation (27) for some set of basis vectors. For example, a three spin-$\frac{1}{2}$ system has the following definitions and matrix representations (relative to the basis product vectors given in table (1)) for the spin operators I^2, I_z and I_+ (as before I_- is the adjoint of I_+, and the operators I_x and I_y may be computed from I_+ and I_- using equation (27)):

$$(30) \qquad I^2 = I_1{}^2 + I_2{}^2 + I_3{}^2 + 2\,(\underline{I}_1\cdot\underline{I}_2 + \underline{I}_1\cdot\underline{I}_3 + \underline{I}_2\cdot\underline{I}_3)$$

(for the evaluation of the elements of I^2, it is useful to introduce the vector identity:

$$(30a) \qquad \underline{I}_j\cdot\underline{I}_k = I_{jz}\,I_{kz} + \tfrac{1}{2}\,(I_{j+}\,I_{k-} + I_{j-}\,I_{k+}) \quad);$$

$$(31) \qquad I_z = I_{1z} + I_{2z} + I_{3z}\ ;$$

and

$$(32) \qquad I_+ = I_{1+} + I_{2+} + I_{3+}\ .$$

TABLE (1)

Basis product vectors and eigenvalues of I_z for a system of three spin-½ nuclei (the designation number of the eigenstate is arbitrary; however it will prove convenient for the ABX system to be considered later). The numbering of each nuclear spin state is implicitly assumed by the position of the spin state (i.e. $\alpha(1)\beta(2)\alpha(3) = \alpha\beta\alpha$).

Designation	Basis Product Vector	Eigenvalue of I_z
$\|\Psi_1>$	$\alpha\alpha\alpha$	3/2
$\|\Psi_2>$	$\alpha\beta\alpha$	1/2
$\|\Psi_3>$	$\beta\alpha\alpha$	1/2
$\|\Psi_4>$	$\beta\beta\alpha$	-1/2
$\|\Psi_5>$	$\alpha\alpha\beta$	1/2
$\|\Psi_6>$	$\alpha\beta\beta$	-1/2
$\|\Psi_7>$	$\beta\alpha\beta$	-1/2
$\|\Psi_8>$	$\beta\beta\beta$	-3/2

TABLE (2)

A set of simultaneous eigenvectors and their corresponding eigenvalues of the spin operators I^2 and I_z for a system with three spin-½ nuclei.

Eigenvector	Eigenvalue	
	I^2	I_z
$\alpha\alpha\alpha$	15/4	3/2
$1/\sqrt{3}\ (\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$	15/4	1/2
$1/\sqrt{3}\ (\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha)$	15/4	-1/2
$\beta\beta\beta$	15/4	-3/2
$1/\sqrt{6}\ (\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$	3/4	1/2
$1/\sqrt{6}\ (2\alpha\beta\beta - \beta\alpha\beta - \beta\beta\alpha)$	3/4	-1/2
$1/\sqrt{2}\ (\alpha\alpha\beta - \alpha\beta\alpha)$	3/4	1/2
$1/\sqrt{2}\ (\beta\alpha\beta - \beta\beta\alpha)$	3/4	-1/2

$$I^2 = \begin{bmatrix} 15/4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 7/4 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 7/4 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 7/4 & 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 & 7/4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 7/4 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 7/4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 15/4 \end{bmatrix} \tag{33}$$

$$I_z = \begin{bmatrix} 3/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3/2 \end{bmatrix} \tag{34}$$

$$I_+ = \begin{bmatrix} 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} . \tag{35}$$

Since the Hamiltonian for the n.m.r. system (ignoring the driving term $\hat{H}_p(t)$; see the following section) commutes with I^2 and I_z (1-6), a set of simultaneous eigenvectors exists for the Hamiltonian, I^2, and I_z. The analysis of an n.m.r. spectrum is then simplified by a choice of basis in which as many as possible of the spin operators are diagonalized.

3. The Nuclear Zeeman Interaction

The Hamiltonian operator $\hat{H}(t)$ for a nuclear magnetic moment in a magnetic field $\underline{H}$ is given by equating $\hbar\,\hat{H}(t)$ to the classical energy of interaction and replacing the vector $\underline{\mu}$ by the quantum mechanical spin operator $\gamma\hbar\,\underline{I}$ (3,6,10); i.e.

$$(36) \qquad \hat{H}(t) = -\gamma\,\underline{I}\cdot\underline{H}\,.$$

In the n.m.r. experiment, the expression for H is given by (1-3,5,6,10):

$$(37) \qquad \underline{H} = \underline{H}_o + \underline{H}_p(t)$$

where $\underline{H}_o$ is a static magnetic field defining the negative z direction, and $\underline{H}_p(t)$ is a small rf field defining the negative x direction (in the analysis of high resolution n.m.r. spectra, the driving term $\underline{H}_p(t)$ is generally ignored because it is very small; however it will be included in this discussion). The latter field is given by:

$$(38) \qquad \underline{H}_p(t) = (-2H_p\cos\omega t;\ \ 0;\ \ 0)$$

where ω is the angular velocity of the oscillation and $2H_p$ the amplitude. Since $2H_p \ll |\underline{H}_0|$, the expression for $\underline{H}_p(t)$ may be decomposed into two circularily polarized components (3,13) and put into the form:

$$(39) \qquad \underline{H}_p(t) = (-H_p\cos\omega t;\ H_p\sin\omega t;\ \ 0).$$

Substituting equations (37) and (39) into equation (36), the Hamiltonian may be rewritten as:

$$\begin{aligned}(40) \qquad \hat{H}(t) &= -\gamma\underline{I}\cdot(\underline{H}_o + \underline{H}_p(t)) \\ &= \gamma H_o\, I_z + \gamma H_p\, I_x \cos\omega t + \gamma H_p\, I_y \sin\omega t \\ &= \gamma H_o\, I_z + \tfrac{1}{2}\gamma H_p\, (I_+ e^{-i\omega t} + I_- e^{i\omega t})\end{aligned}$$

(where $H_o = |\underline{H}_o|$). The last step in equation (40) uses the definitions of the raising and lowering operators (equation (17)) and the identity $e^{\pm i\omega t} = \cos\omega t \pm i\sin\omega t$. This equation is the quantum mechanical equivalent of the classical equation for the nuclear Zeeman interaction for the n.m.r. experiment.

For a system of n spinning nuclei, ignoring internal interactions, this equation is replaced by a summation over the nuclei:

$$(41)\quad \hat{H}(t) = \sum_{j=1}^{n} \{\gamma_j H_o I_{jz} + \gamma_j H_p (I_{j+} e^{-i\omega t} + I_{j-} e^{i\omega t})\}.$$

Each nucleus is characterized by its gyromagnetic ratio γ_j and its spin operator I_{jr} $(r = z, +, -)$. The internal interactions are included in an empirical manner in section 5 of this chapter.

4. The Chemical Shift

Experimentally it is well known that the resonance position of a nucleus depends on its particular chemical environment (1-6). These resonance shifts have been attributed to a partial screening of the nucleus from the applied field $\underline{H}$ due to an induced magnetic field set up by the precession of the electrons about $\underline{H}$. It has been found that this secondary field is antiparallel and proportional to the applied field, so that the local field $\underline{H}'$ experienced by the nucleus is given by:

$$(42) \qquad \begin{aligned} \underline{H}' &= \underline{H} - \sigma \underline{H} \\ &= \{\underline{H}_o + \underline{H}_p(t)\} \times (1-\sigma) \\ &\simeq \underline{H}_o(1-\sigma) + \underline{H}_p(t) \qquad (\text{since } |\underline{H}_p(t)| << |\underline{H}_0| \text{ and } \sigma<<1) \end{aligned}$$

where the proportionality constant σ, known as the shielding constant, is a function of the chemical environment of the nucleus (for solids, σ is a tensor quantity; for liquids and gases it may be treated as a scalar due to an averaging by molecular motions). The environmental dependency is carried into the Hamiltonian of equation (40) by substituting $\underline{H}'$ for $\underline{H}$. A similar argument for equation (41) yields the expression:

$$(43) \qquad H(t) = \sum_j \{\gamma_j H_o(1-\sigma_j)\, I_{jz} + \tfrac{1}{2}\gamma_j H_p\, (I_{j+} e^{-i\omega t} + I_{j-} e^{i\omega t})\}$$

where σ_j refers to the screening constant of the j^{th} nucleus.

It follows from equation (43) that the energy levels of the spinning nuclei, and therefore also the transition frequencies, are dependent on the chemical environment of the nucleus. For example, since $\sigma_j > o$, it follows that the resonance frequency of a bare nucleus is smaller than the resonance frequency of the same nucleus in an atom or molecule (using the fixed field-swept rf field mode). This difference in the resonance frequency between the bare nucleus and the shielded nucleus is known as the chemical shift.

Since most applications of n.m.r. do not require knowledge of the absolute chemical shift, it is convenient to express the shift relative to some reference compound. Generally the shift is specified in terms of the dimensionless parameter δ_{rs} in units of parts per million where δ_{rs} is defined by (1-6):

$$\delta_{rs} = \sigma_r - \sigma_s \qquad (44)$$

where the reference nucleus r and the sample nucleus are of the same nuclear species (i.e. $\gamma_r = \gamma_s$). An intramolecular chemical shift is also defined using equation (44), where "r" and "s" refer to nuclei (usually of the same species) in a molecule.

5. The Spin-Spin Interaction

Under conditions of high resolution, the n.m.r. spectra of chemically shifted peaks of liquids and gases show hyperfine structure for some systems (1-6). The properties of these multiplets has led to the conclusion that there is an intramolecular interaction, the spin-spin interaction, between each pair of nuclear magnetic moments. A variety of mechanisms have been proposed for this interaction; for example it is thought that the most important mechanism for a proton with only a single 1s electron involves polarization of the spins of the internuclear electrons (11).

The Hamiltonian of scalar interaction between two magnetic moments, designated by $\hat{H}_{jk}$, is given by the expression:

$$\hat{H}_{jk} = J_{jk}\, \underline{I}_j \cdot \underline{I}_k \tag{45}$$

where J_{jk} is known as the coupling constant between nuclei j and k which are characterized by spin operators $\underline{I}_j$ and $\underline{I}_k$ respectively. The Hamiltonian of a molecule $\hat{H}(t)$ is then given by equation (43) appended by a summation of terms of the form of equation (45) for all pairs of magnetic moments:

$$\hat{H}(t) = \hat{H}_o + \hat{H}_1 + \hat{H}_p(t) \tag{46a}$$

where:

$$\hat{H}_o = \sum_j \gamma_j H_o (1-\sigma_j)\, I_{jz} \tag{46b}$$

$$\hat{H}_1 = \sum_{j<k}\sum J_{jk}\, \underline{I}_j \cdot \underline{I}_k \tag{46c}$$

and

$$\hat{H}_p(t) = \sum_j \tfrac{1}{2}\gamma_j H_p (I_{j+} e^{-i\omega t} + I_{j-} e^{i\omega t}) \quad . \tag{46d}$$

This Hamiltonian is known as the high resolution n.m.r. Hamiltonian, and it has been found to be adequate for the analysis of the n.m.r. spectra of liquids and gases.

As a specific example, the Hamiltonian for a molecule with ABX spin-½ nuclei is given by:

$$(47a)\quad \hat{H}_o = \gamma H_o(1-\sigma_1)\, I_{1z} + \gamma H_o(1-\sigma_2)\, I_{2z} + \gamma_3 H_o(1-\sigma_3) I_{3z}$$

$$(47b)\quad \hat{H}_1 = J_{12}\, \underline{I}_1 \cdot \underline{I}_2 + J_{13}\, \underline{I}_1 \cdot \underline{I}_3 + J_{23}\, \underline{I}_2 \cdot \underline{I}_3$$

$$(47c)\quad \hat{H}_p(t) = \tfrac{1}{2}\gamma H_p \{ \sum_{j=1}^{2} (I_{j+} e^{-i\omega t} + I_{j-} e^{i\omega t}) \} + \tfrac{1}{2}\gamma_3 H_p (I_{3+} e^{-i\omega t} + I_{3-} e^{i\omega t})$$

where the subscripts 1, 2, and 3 refer respectively to the A, B, and X nuclei, and where it is assumed that the A and B nuclei are of the same nuclear species (i.e. $\gamma_1 = \gamma_2 = \gamma$).

6. The Rotating Coordinate System

If a quantum mechanical state vector of a system with interacting spinning nuclei is denoted by $|\Psi(t)>$, then solutions of equation (46) for the energy are found by solving the Schödinger equation:

$$(48) \qquad i \frac{d}{dt} |\Psi(t)> = \hat{H}(t) \, |\Psi(t)> \; .$$

The time-dependence of the Hamiltonian may be removed by means of the unitary transformation $e^{-i\omega t I_z}$ (12) where ω is the angular frequency of the rf field $\underline{H}_p(t)$. This transformation corresponds to a change from a fixed to a rotating coordinate system.

The effect of the transformation on the state vector $|\psi(t)>$ is given by the expression:

$$(49) \qquad |\phi(t)> = e^{-i\omega t I_z} \, |\psi(t)>$$

where $|\Phi(t)>$ is the transformed state vector; i.e. the state vector in the new coordinate frame. It can be shown that (13, 14) the Schrödinger equation in the new frame is:

$$(50) \qquad i \frac{d}{dt} |\Phi(t)> = \hat{H}^{\omega} \, |\Phi(t)>$$

where:

$$(51a) \qquad \hat{H}^{\omega} = \hat{H}_o' + \hat{H}_1' + \hat{H}_p'$$

$$(51b) \qquad \hat{H}_o' = \sum_j \{\gamma_j H_o(1-\sigma_j) - \omega\} I_{jz}$$

$$(51c) \qquad \hat{H}_1' = H_1 = \sum_{j<k}\sum J_{jk} \, \underline{I}_j \cdot \underline{I}_k$$

and $$(51d) \qquad \hat{H}_p' = \sum_j \gamma_j H_p \, I_{jx} \; .$$

The physical significance of this change of coordinates is that the small oscillating rf field $\underline{H}_p(t)$ appears as a stationary vector directed along the x axis, and each nucleus precesses about the z axis (ignoring the small rf field) with an angular velocity equal to the difference between its Larmour velocity (modified by the shielding constant) and the velocity of rotation ω of the new coordinate system (and the rf field $\underline{H}_p(t)$).

This new coordinate system also lends itself to a simple deduction of transition probabilities. The equation of motion of $|\Phi(t)\rangle$ follows from equation (50) since $\hat{H}^{\omega}$ is time-independent (13-15):

(52) $$|\Phi(t)\rangle = e^{i\hat{H}^{\omega}t}\,|\Phi(0)\rangle$$

where $|\Phi(0)\rangle = |\Psi(0)\rangle$ is the state vector when $t = 0$ (or $\underline{H}_p(t) = 0$). The probability of a transition from a state $|\Phi_i(t)\rangle$ to a state $|\Phi_f(t)\rangle$ is then given by (14,15):

(53) $$W_{i\to f} = \left|\,\langle\Phi_f(t)|\; e^{i\hat{H}^{\omega}t}\;|\,\Phi_i(t)\rangle\,\right|^2$$

which reduces in first order perturbation theory to equation (13) for one nucleus, and to (14,15):

(54) $$W_{i\to f} = \frac{e^{i(E_f - E_i)t}}{E_f - E_i}\;\left|\,\langle\Phi_f(t)|\,\sum_j \gamma_j H_p I_{jx}\,|\Phi_i(t)\rangle\,\right|^2$$

for a system with more than one (spinning) nucleus.

From equation (27), I_{jx} may be written as a sum of I_{j+} and I_{j-}, and an argument similar to the derivation of equation (19) shows that I_{j+} corresponds to an absorption of energy, while I_{j-} corresponds to an emission of energy. It may also be shown that there is a selection rule operative, namely $\Delta m_j = \Delta m = \pm 1$ (where m_j and m are respectively the eigenvalues of the z components of $\underline{I}_j$ and $\underline{I}$).

7. Relaxation Processes and Line Broadening

The theory of n.m.r. outlined thus far describes a process by which nuclei are excited from a lower energy spin state to a higher energy spin state through interaction with a perturbing rf field. The energy absorbed in a transition is given by the difference in energy between two states, and the transition probability is given by equation (53). The signal intensity observed in practice is related to the rate at which energy is absorbed from the rf field, and it is necessary to include in the theory the relative populations of the spin states, and the means by which the system returns to the ground or unexcited state.

Considering a macroscopic sample of N_o spins per unit volume, the number of states N_m with energy E_m is given by the Boltzmann distribution:

$$(55) \qquad N_m = \frac{N_o \, e^{-\hbar E_m/kT}}{\sum_j e^{-\hbar E_m/kT}}$$

where T is the absolute temperature of the sample and k the Boltzmann constant. The rate of absorption of energy between two states with energies E_m and $E_{m'}$ is then (14):

$$(56) \qquad \left(\frac{\partial E}{\partial t}\right)_{m \to m'} = W_{m \to m'} \, (E_{m'} - E_m) \times (N_m - N_{m'})$$

since to first order $W_{m \to m'} = W_{m' \to m}$ (15). In this equation, the term involving $N_{m'}$ represents the rate at which energy is emitted by stimulated emission (spontaneous emission is negligible in magnetic resonance (5)), and the term in N_m represents the rate at which the same amount of energy is absorbed. The condition that $N_m = N_{m'}$ gives rise to the phenomenon known as saturation, at which time the rate of absorption of energy and the signal intensity will disappear. Hence a n.m.r. spectrum should diminish in intensity as the lower spin states are excited upwards.

Since this is not the case observed in most n.m.r. spectra, some mechanism must be occurring which tends to remove the excess spin energy of the system. One such process is known as the spin-lattice relaxation (1-6), whereby non-radiative downward transitions occur through a redistribution of the spin energy with the "lattice" or other degrees of freedom of the system. Denoting the rate of relaxation by $1/T_1$, where T_1 is known as the spin-lattice relaxation time, then it can be shown that equation (56) is altered to the form (3):

$$(57) \qquad \left(\frac{\partial E}{\partial t}\right)_{m\to m'} = \frac{W_{m\to m'}\ (E_{m'} - E_m) \times (N_m - N_{m'})}{1 + 2W_{m\to m'}\ T_1} \ .$$

When $2W_{m\to m'} << 1$, saturation is easily avoided; experimentally this is achieved by using a small rf field since $W_{m\to m'} \propto |\underline{H}_p(t)|^2$

Spin-lattice relaxation also causes some broadening of the spectral peaks as a consequence of the uncertainty principle. Since

$$(58) \qquad \Delta E \cdot \Delta t \simeq \hbar$$

or

$$\Delta E = \hbar \Delta\omega \simeq \hbar/\Delta t$$

an uncertainty ΔE in the energy, corresponding to an uncertainty $\Delta\omega$ in the resonance frequency, is inversely proportional to Δt which may be taken as the lifetime of a state. Hence the line width of a transition will be of the order of $1/T_1$, since the lifetime of an excited spin state is of the order of T_1.

Another relaxation process of importance in n.m.r. is known as the spin-spin or transverse relaxation, whereby there is a sharing of excess spin energy between the nuclei. This process derives from inhomogeneous magnetic fields and local field variations due to neighbouring magnetic moments, and it is characterized by the spin-spin relaxation time T_2 (often

T_2 is separated into two terms T_2' and T_2^* which relate respectively to field inhomogeneity and to interaction with neighbouring magnetic moments). The line broadening resulting in this case is often included by replacing the Dirac delta functions, as in equation (13) for example, with a line shape function $g(\omega)$ (1-4,6). For the magnetic resonance of liquids, the Lorentz line shape is generally used:

$$(59) \qquad g(\omega) = \frac{T_2}{\pi} \quad \frac{1}{1 + T_2{}^2(\omega-\omega_o)^2}$$

where ω_o is the angular velocity of the rf field at resonance. It follows from (59) that the width of an absorption peak at half-height is $2/T_2$ (3).

Other broadening effects operating in n.m.r. spectroscopy may be attributed to exchange reactions or hindered rotations. These processes may be characterized by a rate $1/\tau$ where τ is of the order of the lifetime of a given state (before exchange or rotation). A broadening of the n.m.r. peaks is caused by the uncertainty in energy involved when the chemical environment of the nucleus is varied during exchange or hindered rotation processes. The effect of intramolecular exchange reactions (valid for certain hindered rotations in which the molecular symmetry is conserved) are considered in more detail in Chapter V.

Chapter IV

DESCRIPTION OF STATES — THE DENSITY MATRIX TECHNIQUE

1. Introduction

For a quantum mechanical system described by a normalized state vector $|\Psi_j\rangle$ the theory of quantum mechanics predicts that the expectation value $\langle Q\rangle_j$ of an observable corresponding to the linear Hermitian operator Q is given by (7):

$$(60) \qquad \langle Q\rangle_j = \langle\Psi_j|Q|\Psi_j\rangle \quad .$$

In many cases it is convenient to expand the state vector into a complete set of orthonormal time-independent vectors$\{|n\rangle\}$:

$$(61) \qquad |\Psi_j\rangle = \sum_n c_{jn} |n\rangle$$

with the time-dependence of the state vector carried in the expansion coefficients c_{jn}. Since $|\Psi_j\rangle$ is normalized and the basis set orthonormal, i.e.

$$(62) \qquad \langle\Psi_j|\Psi_j\rangle = 1 = \sum_n c_{jn}^* c_{jn} \quad ,$$

the expectation value of the observable may be expressed in the form:

$$(63) \qquad \langle Q\rangle_j = \sum_n \sum_{n'} c_{jn'}^* c_{jn} \langle n'|Q|n\rangle_j \quad .$$

This procedure is strictly valid only in the situation when the state of a system is completely known (16), that is when the system may be described fully by the state vector. For example, the analysis of high resolution n.m.r. spectra assumes that such a state vector exists which describes the nuclear spin state of a molecule. This state is known as a "pure" state (16) and is characterized by the existence of an experiment - in this case the determination of the energy - which gives a predictable result with certainty. On the other hand, determination of the signal intensity of an n.m.r. spectrum involves a deduction of the magnetization in the x-y plane of a macroscopic ensemble of molecules, and there is no pure state for the system since it is made up of an unspecified combination of pure states. One then resorts to the statement that the system has certain probabilities $p_1, p_2, \ldots, p_j, \ldots$ of being in the pure states $|\Psi_1\rangle, |\Psi_2\rangle, \ldots, |\Psi_j\rangle, \ldots$. In other words, the system is represented by a statistical mixture of state vectors (the $|\Psi_j\rangle$'s) with the statistical weights p_j, and the expectation value of an operator is given by a statistical distribution of its values for each of the state vectors.

It is especially convenient to describe a statistical mixture of states by means of the density matrix. This technique is a simple variation of time-dependent perturbation theory (17) and corresponds to the statistical matrix of classical statistical mechanics. The definition and some of the properties of the density matrix are given below in sections 2 and 3. In section 4 the density matrix is applied to a system of nuclei which possess spin angular momentum with the intent of deriving an expression for the line shape of a n.m.r. spectrum.

2. Definition of the Density Matrix[†]

As mentioned above, a macroscopic ensemble of states will be represented by a linear superposition of the pure states $|\Psi_1\rangle, |\Psi_2\rangle, \ldots$ with the statistical weights $p_1, p_2, \ldots$ (16). For each of these states there corresponds an expectation value $\langle Q\rangle_j$ of an observable, where $\langle Q\rangle_j$ is given by equations (60) or (63). The mean value of the observable, $\langle Q\rangle$, for the ensemble is given by the grand average (over each of the possible pure states of the system):

$$\langle Q\rangle = \sum_j p_j \langle Q\rangle_j \quad . \tag{64}$$

Substituting from equation (63), this average is recast into the form:

$$\begin{aligned}\langle Q\rangle &= \sum_j p_j \sum_n \sum_{n'} c^*_{jn'}\, c_{jn}\, Q_{n'n} \\ &= \sum_n \sum_{n'} Q_{n'n} \sum_j p_j\, c^*_{jn'}\, c_{jn}\end{aligned} \tag{65}$$

where $Q_{n'n}$ denotes the matrix element $\langle n'|Q|n\rangle$ of the operator Q.

The density matrix may be defined from the following equation for its elements[†]:

$$\rho_{nn'} = \sum_j p_j\, c^*_{jn'}\, c_{jn} \tag{66}$$

so that (65) reduces to:

$$\langle Q\rangle = \sum_n \sum_{n'} Q_{n'n}\, \rho_{nn'} = \mathrm{Tr}\,(Q\rho) = \mathrm{Tr}\,(\rho Q) \tag{67}$$

where $\mathrm{Tr}(A) = \sum_k A_{kk}$ indicates the trace of the matrix A. Hence the expec-

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[†] The definition and derivations of the properties of the density matrix presented here are after the method of Fano (16). Another equivalent definition used frequently ((17-19) for example) is given by:

$$\rho_{nn'} = \overline{c^*_{n'}\, c_n}$$

where the bar denotes an ensemble average.

tation value of an observable of a system consisting of a liner superposition of states is given by the trace of the matrix resulting from the matrix multiplication of the density matrix and the matrix of the operator corresponding to that observable. The operation of taking the trace of the product matrix is equivalent to taking the average of the expectation values of the observable for each pure state times the probability that the system is in that state.

It is instructive to note that the expectation values of different observables in the same system vary only as the matrix elements of their corresponding operators since ρ will be invariant for the same system. Alternatively, different systems will be represented by different density matrices, whereas the matrix of an operator is invariant from one system to another (assuming the same basis set $\{|n>\}$ is employed).

3. Interpretation and Properties of the Density Matrix

A physical interpretation of the diagonal elements of the density matrix is facilitated by considering the mean value of the operator $\delta_{jn}\delta_{jn'}$ (δ is the Kronecker delta function). From equation (67):

$$(68) \qquad \langle\delta_{jn}\ \delta_{jn'}\rangle = \mathrm{Tr}\ (\rho\ \delta_{jn}\ \delta_{jn'}) = \rho_{jj} = \rho_{nn} \ .$$

Since $\langle\delta_{jn}\ \delta_{jn'}\rangle$ represents the probability of finding the system in the basis state $|n\rangle$, the diagonal elements of ρ are then these same probabilities. This property is perhaps more obvious if a basis set is chosen such that ρ is diagonal, so that:

$$(69) \qquad \rho_{nn'} = \sum_j p_j\ c^*_{jn'}\ c_{jn}\ \delta_{nn'} \ .$$

A careful analysis of this equation then reveals that a diagonal element is given by the sum over each pure state $|\Psi_j\rangle$ of the probability p_j that the ensemble is in the state $|\Psi_j\rangle$ times the probability $c^*_{jn'}\ c_{jn}$ that $|\Psi_j\rangle$ is in one of the states of the basis vectors $|n\rangle$; i.e. one has the probability that the ensemble is in the basis state $|n\rangle$.

For a system in thermal equilibrium, these probabilities are given directly by the Boltzmann distribution factors (16,18,20) so that in the basis consisting of the eigenvectors of the Hamiltonian, the diagonal elements of the density matrix at thermal equilibrium (ρ^0) are:

$$(70) \qquad \rho^0_{nn} = \frac{e^{-E_n/kT}}{\sum_m e^{-E_m/kT}}$$

where E_m is the energy of the basis eigenvector $|m\rangle$. Also, since ρ^0 is diagonal in this basis (16,17), equation (70) may be put into operator notation:

$$(71) \qquad \rho^0 = \frac{e^{-H/kT}}{\mathrm{Tr}\ (e^{-H/kT})}$$

The interpretation of the off-diagonal elements of the density matrix is less clear. It follows from equation (67) that if the only non-zero element of an observable in some basis is Q_{jk}, then $\langle Q \rangle$ is proportional to ρ_{kj} (18). For example, in the discussion to follow, the signal intensity of an n.m.r. spectrum will be calculated using the raising operator I_+, and it is shown in section 4 of this chapter that the only elements of ρ appearing (when the basis product vectors are used as a basis) are some of the off-diagonals of ρ. One can then relate some off-diagonal ρ_{kj} with the element $(I_+)_{jk}$ which corresponds to the signal intensity of a transition from state $|j\rangle$ to state $|k\rangle$ ignoring the overlap of neighbouring transitions. Hence as an approximation, the off-diagonal elements of the density matrix are related to the probability of a transition between states, or more accurately it is proportional to the signal intensity of a transition when all other transitions are of zero intensity.

From the definition in equation (67) it is possible to deduce the following properties of the density matrix (see also (16-20)):

(a) The condition that $\langle Q \rangle$ be real for any observable corresponding to the Hermitian operator Q (7) requires that ρ be also Hermitian; i.e.

$$(72) \qquad \rho_{nn'} = \rho_{n'n}$$

(b) A special case of equation (67) where the operator Q is replaced by the identity or unit operator $\hat{1}$ requires that:

$$(73) \qquad \langle \hat{1} \rangle = \mathrm{Tr}\ (\hat{1}\rho) = \mathrm{Tr}\ (\rho) = 1 \ .$$

This property also follows from the properties of the statistical weights p_j (16):

$$(74) \qquad p_j \geq 0 \quad , \quad \sum_j p_j = 1$$

whence:

(75) $$\mathrm{Tr}\,(\rho) = \sum_n \sum_j p_j\, c_{jn}^* \, c_{jn}$$

$$= \sum_j p_j \sum_n c_{jn}^* \, c_{jn}$$

$$= \sum_j p_j = 1$$

using equation (62) in the last step.

(c) If the system can be described by a pure state vector $|\Psi_k>$ then $p_j = \delta_{jk}$, and therefore from equation (66):

(76a) $$\rho_{nn'} = \sum_j \delta_{jk}\, c_{jn'}^* \, c_{jn} = c_{kn'}^* \, c_{kn}$$

and (76b) $$(\rho)^2_{nn'} = \sum_l \rho_{nl}\, \rho_{ln'}$$

$$= \sum_l c_{kl}^* \, c_{kn}\, c_{kn'}^* \, c_{kl}$$

$$= c_{kn'}^* \, c_{kn} \sum_l c_{kl}^* \, c_{kl}$$

$$= c_{kn'}^* \, c_{kn} = \rho_{nn'}$$

Hence if the system is described by a pure state, the density matrix obeys the characteristic equation (16,18,20):

(77) $$\rho^2 = \rho \quad \text{or} \quad \mathrm{Tr}\,(\rho^2) = \mathrm{Tr}\,(\rho) = 1 \ .$$

In general it can be shown that (18):

(78) $$\mathrm{Tr}\,(\rho^2) \leq 1 \ .$$

(d) The equation of motion of the density matrix may be deduced from the definition (66):

(79) $$\frac{d}{dt}\rho_{nn'} = \frac{d}{dt}\Big(\sum_j p_j\, c_{jn'}^* \, c_{jn}\Big)$$

$$= \sum_j p_j \Big\{\Big(\frac{d}{dt} c_{jn'}^*\Big) c_{jn} + c_{jn'}^* \Big(\frac{d}{dt} c_{jn}\Big)\Big\}$$

since the statistical weights do not vary with time (20). An expression for the time dependence of the coefficients follows from equation (61) and the Schrödinger equation (49):

(80) $$i \sum_m \Big(\frac{d}{dt} c_{jm}\Big) |m> = \sum_m c_{jm}\, \hat{H} |m> \ .$$

Multiplying through by $|n>$ and integrating, the time derivative of c_{jn} is:

$$(81) \qquad i \frac{d}{dt} c_{jn} = \sum_m c_{jm} <n|\hat{H}|m> = \sum_m c_{jm} \hat{H}_{nm} .$$

The conjugate equation for c_{jn}^* is given by:

$$(82) \qquad -i \frac{d}{dt} c_{jn}^* = \sum_m \hat{H}_{mn} c_{jm}^* .$$

Substitution of the expressions (81) and (82) for the derivatives of c_{jn} and $c_{jn'}^*$ into equation (79) yields:

$$(83) \qquad \frac{d}{dt} \rho_{nn'} = \sum_j p_j (i \sum_m \hat{H}_{mn'} c_{jm}^* c_{jn} - i \sum_m c_{jn'}^* c_{jm} \hat{H}_{nm})$$

$$= i \sum_m (\hat{H}_{mn'} \sum_j p_j c_{jm}^* c_{jn} - \sum_j p_j c_{jm}^* c_{jn} \hat{H}_{nm})$$

$$= i \sum_m (\hat{H}_{mn'} \rho_{nm} - \rho_{mn'} \hat{H}_{nm})$$

$$= i <n|\rho\hat{H} - \hat{H}\rho|n'>$$

or in operator notation:

$$(84) \qquad \frac{d}{dt} \rho = i \{\rho, \hat{H}\}.$$

This derivation is based on the assumption that the Hamiltonian is identical for all the possible pure states of the system (16-18). It is similar to the Heisenberg equation of motion for an operator, differing in the sign of the commutator (20).

4. Application of the Density Matrix to N.M.R.

The application of the density matrix technique to n.m.r is straightforward: one uses equations (60) to (84) with the requirements that the basis set $\{|n\rangle\}$ consists of some suitable basis of nuclear spin states, and that the Hamiltonian is given by the appropriate n.m.r. Hamiltonian. The expectation value of an observable is then given by equation (67) for an ensemble of nuclear spin states. For example, as discussed in Chapter III, the quantity observed in n.m.r. is related to the absorption of energy as the rf field is swept. In fact it is well known that the signal intensity, or the line shape, is proportional to the expectation value of the raising operator I_+ (1-6,21) which corresponds to the transverse magnetization vector induced in the system as a result of the resonance absorption of energy from the rf field. Therefore from equation (67), since:

$$(85) \qquad \langle I_+\rangle = \mathrm{Tr}\,(\rho I_+) \;,$$

determination of the trace of ρ and I_+ will result in an expression for the line shape of an n.m.r. spectrum, where in this case, ρ is the spin density matrix.

It is often convenient to use the rotating coordinate system in n.m.r. In this case the observable I_+ is given by the transformed operator $e^{i\omega tI_z}\, I_+\, e^{-i\omega tI_z} = I_x = \frac{1}{2}(I_+ + I_-)$. As stated before, I_+ corresponds to the absorption process, so that the (absorption) line shape will again be proportional to the expectation value of I_+ in the new coordinate frame. The effect of the transformation on the spin density matrix is to take ρ to ρ^{ω} where (22,24):

$$(86) \qquad \rho^{\omega} = e^{i\omega tI_z}\, \rho\, e^{-i\omega tI_z}$$

so that equation (85) becomes:

$$(87) \qquad \langle I_+ \rangle \;=\; \mathrm{Tr}\,(\rho^{\omega} I_+) \quad .$$

This last equation describes the n.m.r. signal intensity (line shape) as a function of the angular velocity ω of the rf field. The real and imaginary parts of the equation refer respectively to the dispersion and the absorption modes of the signal (5,21).

If the basis product vectors of the spin operators I_j^2 and I_{jz} are chosen to be the basis set, it then follows that I_+ is a strictly upper triangular matrix. Consequently, from equation (67), the only terms of the spin density matrix appearing in the line shape expression are the off-diagonals (see Appendix I). Suitable expressions for the pertinent elements are found by solving equation (84), the equation of motion of ρ.

In order to include relaxation phenomena present in n.m.r. in the expression for the line shape, the equation of motion of the spin density matrix is altered to include the two rate processes. Since spin-lattice relaxation tends to take the system to thermal equilibrium (i.e. $\rho \rightarrow \rho^{o}$) at a rate of the order $1/T_1$, and spin-spin relaxation tends to take the transverse components of the magnetization to zero (which approximates taking the off-diagonal elements of the spin density matrix to zero) at a rate of the order $1/T_2$, one may write as an approximation (22,25,26, cf. Bloch's equations (24)):

$$(88) \qquad \left(\frac{\partial \rho^{\omega}}{\partial t}\right)_{\text{relaxation}} = \left(\frac{\rho^{o\omega} - \rho^{\omega}}{T_1}\right)_{d} + \left(\frac{-\rho^{\omega}}{T_2}\right)_{od}$$

where d and od refer respectively to the diagonal and off-diagonal elements, and where $\rho^{o\omega}$ refers to the transformed spin density matrix at thermal equilibrium; i.e. the system in the absence of $\underline{H}_p(t)$ and when a stationary state has been reached at the end of the spin-lattice relaxation. The elements of $\rho^{o\omega}$ are given by equation (71) where $\hat{H} = \hat{H}_o + \hat{H}_1$ (equation (46)) since $\rho o^{\omega} = e^{i\omega tI_z} \rho^o e^{-i\omega tI_z} = \rho^o$ (it can be shown than in general $\{I_z, \hat{H}_o' + \hat{H}_1'\} = 0$ (1,2,6) and that if $\{A, B\} = 0$, then $\{f(A), B\} = 0$ (10)); i.e. the spin density matrix at thermal equilibrium is the same in the fixed or in the rotating coordinate frame.

It should be pointed out that this inclusion of relaxation phenomena involves the assumption that the relaxation processes are exponential decay processes acting on deviations from equilibrium (24), and that its effect will be to introduce line broadening into the n.m.r. line shape (for example the term involving T_2 results in a shape function much the same as equation (59)).

The equation of motion of the spin density matrix is now altered to the form:

$$(89) \qquad \left(\frac{d\rho^{\omega}}{dt}\right) = \left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{relaxation}} + i\,\{\rho^{\omega}, \hat{H}^{\omega}\}$$

where equation (84) (transformed to the rotating system) has been appended by equation (88). The appropriate elements deriving from equation (87) are calculated using this equation.

A further simplification which may be made is to assume steady-state solutions of (89), corresponding to the slow passage condition in n.m.r., so that the lhs of (89) is equated to zero (22). Equation (89) then reduces to a set of linear homogeneous equations in the elements of the spin density matrix.

Chapter V

INTRAMOLECULAR EXCHANGE IN N.M.R.

1. Introduction

It is well known that exchange processes between spinning nuclei in different magnetic situations result in a modification of their n.m.r. spectra (1-3,22,23,25-31). It was shown in the previous chapter that the n.m.r. line shape may be calculated using density matrix techniques by evaluating the expectation value of I_+, the raising operator (corresponding to the transverse component of the induced magnetization). It is also possible to compute the line shape for the cases of exchanging nuclei by adding an appropriate exchange term to the equation of motion of ρ in the cases of intramolecular exchange. This term, devised by Kaplan (23a) and expanded by Alexander (22), is discussed in section 2.

In section 3, the detailed calculations of the line shape, following the method of Alexander (22) and extended by Whitesides (25), are carried out for a system of molecules with interacting ABX spin-½ nuclei, in which there is exchange of the (identical) AB nuclei. The application of the expression obtained to other spectra is discussed in section 4.

2. The Effect of Exchanging Nuclei on the Spin Density Matrix

When an exchange process occurs, the effect is to move a nuclear moment to a different magnetic surrounding. The following discussion will be concerned with intramolecular exchanges[†], so that it may be assumed that the spin Hamiltonian has the same form after exchange, differing from the pre-exchange Hamiltonian only in that some nonequivalent spins have changed their magnetic properties. In this case, the exchange process may be described by an exchange operator P (22) acting on the nuclear state vectors such that:

$$(90) \qquad |\Psi\rangle \rightarrow P\,|\Psi\rangle$$

whenever an exchange occurs. For example, choosing the basis product functions for three spin-½ nuclei (see Table 1) as the nuclear spin states, and assuming that nuclei 1 and 2 are undergoing an intramolecular exchange process, the effect of P is the following:

[†] In an intramolecular exchange process the nuclear species do not change, rather the magnetic properties of one nucleus are assumed by the other nucleus (for exchanging nuclei of the same species) and visa versa; i.e.

$$\text{nucleus } 1 \rightleftarrows \text{nucleus } 2$$

whenever an exchange occurs. Hence the Hamiltonian before exchange differs from the Hamiltonian after exchange only in the labelling of the exchanging nuclei.

The theory discussed here is also valid for numerous inversions of configuration (e.g. in cyclohexane when H(axial) ⇄ H(equatorial)) and internally hindered rotation when the molecular symmetry is conserved (see for example the following chapter) (26,27,29). For more complicated systems, other methods must be resorted to (22,23,27).

$$
\begin{aligned}
P\,|\Psi_1\rangle &= P\,\alpha\alpha\alpha = \alpha\alpha\alpha = |\Psi_1\rangle \\
P\,|\Psi_2\rangle &= P\,\alpha\beta\alpha = \beta\alpha\alpha = |\Psi_3\rangle \\
P\,|\Psi_3\rangle &= P\,\beta\alpha\alpha = \alpha\beta\alpha = |\Psi_2\rangle \\
P\,|\Psi_4\rangle &= P\,\beta\beta\alpha = \beta\beta\alpha = |\Psi_4\rangle \\
P\,|\Psi_5\rangle &= P\,\alpha\alpha\beta = \alpha\alpha\beta = |\Psi_5\rangle \\
P\,|\Psi_6\rangle &= P\,\alpha\beta\beta = \beta\alpha\beta = |\Psi_7\rangle \\
P\,|\Psi_7\rangle &= P\,\beta\alpha\beta = \alpha\beta\beta = |\Psi_6\rangle \\
P\,|\Psi_8\rangle &= P\,\beta\beta\beta = \beta\beta\beta = |\Psi_8\rangle \,.
\end{aligned}
\tag{91}
$$

From these relations it is seen that $|\Psi_1\rangle$, $|\Psi_4\rangle$, $|\Psi_5\rangle$ and $|\Psi_8\rangle$ are invariant during the exchange whereas $|\Psi_2\rangle$, $|\Psi_3\rangle$, $|\Psi_6\rangle$ and $|\Psi_7\rangle$ are altered.

The matrix representation of the operator P is given by operating on each of the state vectors and expressing the resultant vector in terms of the original set of basis vectors (it is convenient to use the basis product vectors because the matrix elements of P are then 0 or 1 (31)). For example, from equations (91), one has:

$$
\begin{aligned}
P\,|\Psi_1\rangle &= 1\,|\Psi_1\rangle + 0\,|\Psi_2\rangle + 0\,|\Psi_3\rangle + 0\,|\Psi_4\rangle \cdots \\
P\,|\Psi_2\rangle &= 0\,|\Psi_1\rangle + 0\,|\Psi_2\rangle + 1\,|\Psi_3\rangle + 0\,|\Psi_4\rangle \cdots
\end{aligned}
\tag{92}
$$

etc. The matrix representation of P (relative to the basis product vectors) for the above case is then:

$$
P = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{bmatrix} .
\tag{93}
$$

It follows from the definition that P is unitary, real, and symmetric so that:

$$(94) \qquad P^2 = \hat{1} \qquad \text{or} \qquad P^{-1} = P \; .$$

The effects of exchanging nuclei on the spin density matrix can be found by transforming the representation of ρ^{ω} to the new basis set given by $P\,|\Psi>$, which indicates that $\rho^{\omega} \rightarrow P^{-1}\,\rho^{\omega}\,P = P\,\rho^{\omega}\,P$ whenever an exchange occurs. If a random exchange process may be described by some correlation time τ (equivalent to the average lifetime of a state before an exchange occurs, if the time taken for the actual exchange may be ignored) then the equation of motion of the spin density is altered by the additive factor (22,23,25-27):

$$(95) \qquad \left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{exchange}} = \frac{P\,\rho^{\omega}\,P - \rho^{\omega}}{\tau}$$

so that equation (89) becomes:

$$(96) \qquad \left(\frac{d\rho^{\omega}}{dt}\right) = \left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{exchange}} + \left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{relaxation}} + i\,\{\rho^{\omega}, \hat{H}^{\omega}\}.$$

This equation is known as the Boltzmann equation and is used in conjunction with equation (87) to derive an analytical expression for the line shapes of the n.m.r. spectra when there is intramolecular exchange between two nuclei (for more than two exchanging nuclei, one correlation time may not be sufficient; see reference (31) for example).

A useful simplification that may be made is to assume steady-state solutions of equation (96). This corresponds experimentally with the slow passage condition and to the case when the correlation time is large (i.e. the exchange rate is slow) (cf. Alexander's paper (22)) although it has been found that at small correlation times relatively good fits with experimental spectra may be obtained (see Chapter VI or Whitesides (25) for some examples). This may result from the fact that the line shapes are dependent on the off-diagonal elements of the spin density matrix, which are much smaller than the diagonal elements.† Consequently it may be possible to approximate equation (96) by a series of linear homogeneous equations in the off-diagonals, and a series of linear inhomogeneous equations in the diagonals.

In the cases where this approximation is not valid, alternate methods have been proposed (22,23); for example Kaplan (23) derives an equation for $\rho(t)$ by calculating $\rho(0) = P\rho P$ and then allowing ρ to evolve according to equation (84). He then obtains an average density matrix by averaging $\rho(t)$ over the distribution of lifetimes (27).

---

† In the previous chapter, it was found that the off-diagonals are related to the transition probabilities, which are in turn proportional to the square of the rf field. Experimentally, a very small rf field is used, so that the off-diagonals are small. On the other hand, the diagonal elements are relatively large, of the order $1/(2^n)$ for n spin-½ nuclei (1-6,13).

3. AB Exchange in an ABX Spin-½ System

Using equation (35) for the matrix representation of I_+ relative to the basis product functions (Table 1) for a system of three spin-½ nuclei, equation (87) reduces to:

$$(97) \qquad \langle I_+ \rangle = \rho_{21} + \rho_{31} + \rho_{51} + \rho_{42} + \rho_{62} + \rho_{43} + \rho_{73} + \rho_{84} + \rho_{65} + \rho_{75} + \rho_{86} + \rho_{87}$$

where the superscript ω has been dropped for convenience of notation. Suitable expressions for these elements of the density matrix are found using equation (96) and assuming slow passage conditions (i.e. the lhs of (96) is equated to zero). In sections (a) to (c) below, each of the terms in equation (96) are calculated, and in section (d) the elements in equation (97) are solved for[†]. Finally in section (d) of this section a general expression for the line shape of the AB part of an ABX spectrum in which the AB nuclei are undergoing exchange has been derived.

[†] For the experimental system discussed in section 5 of the following chapter, it was only the AB part of the spectrum which was interesting because of its rapid variation of line shape with the exchange lifetime. For this particular region, it is necessary only to obtain expressions for the off-diagonal elements of ρ involving A or B transitions since the X transitions contribute negligibly to the intensity at the AB part of the spectrum. The line shape for the AB part of the spectrum is given by $\langle I_+ \rangle_{AB}$ where:

$$(98) \qquad \langle I_+ \rangle_{AB} = \rho_{21} + \rho_{31} + \rho_{42} + \rho_{43} + \rho_{65} + \rho_{75} + \rho_{86} + \rho_{87} .$$

Although an expression may be found to include the X transitions, the method involves tedious algebraic manipulation (for example, expansion of a 4x4 determinant) and the resultant line shape is relatively uninteresting.

(a). Evaluation of $\left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{exchange}}$.

The matrix representation of the exchange operator P for a three spin-½ system (relative to the basis product functions, Table 1) is given by equation (93) for the case where the first two nuclei are undergoing intramolecular exchange. From equation (94) it follows that:

$$(99) \qquad P^{-1}\rho^{\omega}P = \begin{bmatrix} \rho_{11} & \rho_{13} & \rho_{12} & \rho_{14} & \rho_{15} & \rho_{17} & \rho_{16} & \rho_{18} \\ \rho_{31} & \rho_{33} & \rho_{32} & \rho_{34} & \rho_{35} & \rho_{37} & \rho_{36} & \rho_{38} \\ \rho_{21} & \rho_{23} & \rho_{22} & \rho_{24} & \rho_{25} & \rho_{27} & \rho_{26} & \rho_{28} \\ \rho_{41} & \rho_{43} & \rho_{42} & \rho_{44} & \rho_{45} & \rho_{47} & \rho_{46} & \rho_{48} \\ \rho_{51} & \rho_{53} & \rho_{52} & \rho_{54} & \rho_{55} & \rho_{57} & \rho_{56} & \rho_{58} \\ \rho_{71} & \rho_{73} & \rho_{72} & \rho_{74} & \rho_{75} & \rho_{77} & \rho_{76} & \rho_{78} \\ \rho_{61} & \rho_{63} & \rho_{62} & \rho_{64} & \rho_{65} & \rho_{67} & \rho_{66} & \rho_{68} \\ \rho_{81} & \rho_{83} & \rho_{82} & \rho_{84} & \rho_{85} & \rho_{87} & \rho_{86} & \rho_{88} \end{bmatrix} .$$

Substituting the results of equation (99) into equation (95), the matrix representation of $\left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{exchange}}$ is the following:

$$(100) \qquad \frac{1}{\tau}\begin{bmatrix} 0 & \rho_{13}-\rho_{12} & \rho_{12}-\rho_{13} & 0 & 0 & \rho_{17}-\rho_{16} & \rho_{16}-\rho_{17} & 0 \\ \rho_{31}-\rho_{21} & \rho_{33}-\rho_{23} & \rho_{32}-\rho_{22} & \rho_{34}-\rho_{24} & \rho_{35}-\rho_{25} & \rho_{37}-\rho_{26} & \rho_{36}-\rho_{27} & \rho_{38}-\rho_{28} \\ \rho_{21}-\rho_{31} & \rho_{23}-\rho_{32} & \rho_{22}-\rho_{33} & \rho_{24}-\rho_{34} & \rho_{25}-\rho_{35} & \rho_{27}-\rho_{36} & \rho_{26}-\rho_{37} & \rho_{28}-\rho_{38} \\ 0 & \rho_{43}-\rho_{42} & \rho_{42}-\rho_{43} & 0 & 0 & \rho_{47}-\rho_{46} & \rho_{46}-\rho_{47} & 0 \\ \rho_{71}-\rho_{61} & \rho_{73}-\rho_{62} & \rho_{72}-\rho_{63} & \rho_{74}-\rho_{64} & \rho_{75}-\rho_{65} & \rho_{77}-\rho_{66} & \rho_{76}-\rho_{67} & \rho_{78}-\rho_{68} \\ \rho_{61}-\rho_{71} & \rho_{63}-\rho_{72} & \rho_{62}-\rho_{73} & \rho_{64}-\rho_{74} & \rho_{65}-\rho_{75} & \rho_{67}-\rho_{76} & \rho_{66}-\rho_{77} & \rho_{68}-\rho_{78} \\ 0 & \rho_{83}-\rho_{82} & \rho_{82}-\rho_{83} & 0 & 0 & \rho_{87}-\rho_{86} & \rho_{86}-\rho_{87} & 0 \end{bmatrix} .$$

(The superscript ω has been dropped for convenience in the above and in the following matrices.)

(b). Evaluation of $\left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{relaxation}}$.

Applying equation (88) to a three spin-½ system, one has immediately that the matrix representation of $\left(\frac{\partial\rho^{\omega}}{\partial t}\right)_{\text{relaxation}}$ is the following:

$$\begin{bmatrix}
\frac{(\rho^{o}-\rho)_{11}}{T_1} & \frac{-\rho_{12}}{T_2} & \frac{-\rho_{13}}{T_2} & \frac{-\rho_{14}}{T_2} & \frac{-\rho_{15}}{T_2} & \frac{-\rho_{16}}{T_2} & \frac{-\rho_{17}}{T_2} & \frac{-\rho_{18}}{T_2} \\
\frac{-\rho_{21}}{T_2} & \frac{(\rho^{o}-\rho)_{22}}{T_1} & \frac{-\rho_{23}}{T_2} & \frac{-\rho_{24}}{T_2} & \frac{-\rho_{25}}{T_2} & \frac{-\rho_{26}}{T_2} & \frac{-\rho_{27}}{T_2} & \frac{-\rho_{28}}{T_2} \\
\frac{-\rho_{31}}{T_2} & \frac{-\rho_{32}}{T_2} & \frac{(\rho^{o}-\rho)_{33}}{T_1} & \frac{-\rho_{34}}{T_2} & \frac{-\rho_{35}}{T_2} & \frac{-\rho_{36}}{T_2} & \frac{-\rho_{37}}{T_2} & \frac{-\rho_{38}}{T_2} \\
\frac{-\rho_{41}}{T_2} & \frac{-\rho_{42}}{T_2} & \frac{-\rho_{43}}{T_2} & \frac{(\rho^{o}-\rho)_{44}}{T_1} & \frac{-\rho_{45}}{T_2} & \frac{-\rho_{46}}{T_2} & \frac{-\rho_{47}}{T_2} & \frac{-\rho_{48}}{T_2} \\
\frac{-\rho_{51}}{T_2} & \frac{-\rho_{52}}{T_2} & \frac{-\rho_{53}}{T_2} & \frac{-\rho_{54}}{T_2} & \frac{(\rho^{o}-\rho)_{55}}{T_1} & \frac{-\rho_{56}}{T_2} & \frac{-\rho_{57}}{T_2} & \frac{-\rho_{58}}{T_2} \\
\frac{-\rho_{61}}{T_2} & \frac{-\rho_{62}}{T_2} & \frac{-\rho_{63}}{T_2} & \frac{-\rho_{64}}{T_2} & \frac{-\rho_{65}}{T_2} & \frac{(\rho^{o}-\rho)_{66}}{T_1} & \frac{-\rho_{67}}{T_2} & \frac{-\rho_{68}}{T_2} \\
\frac{-\rho_{71}}{T_2} & \frac{-\rho_{72}}{T_2} & \frac{-\rho_{73}}{T_2} & \frac{-\rho_{74}}{T_2} & \frac{-\rho_{75}}{T_2} & \frac{-\rho_{76}}{T_2} & \frac{(\rho^{o}-\rho)_{77}}{T_1} & \frac{-\rho_{78}}{T_2} \\
\frac{-\rho_{81}}{T_2} & \frac{-\rho_{82}}{T_2} & \frac{-\rho_{83}}{T_2} & \frac{-\rho_{84}}{T_2} & \frac{-\rho_{85}}{T_2} & \frac{-\rho_{86}}{T_2} & \frac{-\rho_{87}}{T_2} & \frac{(\rho^{o}-\rho)_{88}}{T_1}
\end{bmatrix} \tag{101}$$

(c). Evaluation of $\{\rho^{\omega}, \hat{H}^{\omega}\}$.

It is convenient to separate the commutator into the following:

$$(102) \qquad \{\rho^{\omega}, \hat{H}^{\omega}\} = \{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\} + \{\rho^{\omega}, \hat{H}'_p\}$$

for purposes of evaluation. From equations (50) and (51), the appropriate Hamiltonians (in the rotating frame) for a three spin-½ system are:

$$(103a) \qquad \hat{H}'_o + \hat{H}'_1 = \sum_{j=1}^{3} \{\gamma_j H_o(1-\sigma_j) - \omega\} I_{jz} + \sum_{j<k}\sum J_{jk} \underline{I}_j \cdot \underline{I}_k$$

$$= \sum_{j=1}^{3} (\omega_j - \omega) I_{jz} + \sum_{j<k}\sum J_{jk} \underline{I}_j \cdot \underline{I}_k$$

(where $\omega_j = \gamma_j H_o(1-\sigma_j)$)

and $$(103b) \qquad \hat{H}'_p = H_p \sum_{j=1}^{3} \gamma_j I_{jx} \quad .$$

It will be assumed at this point that nuclei 1 and 2 are of the same species, so that $\gamma_1 = \gamma_2 = \gamma$.

Relative to the basis product vectors (Table 1), the matrix representation of $H'_o + H'_1$ may be calculated using equations (30a) and (31). The elements of this part of the Hamiltonian have been compiled in Table 3.

For an ABX system, the simplification is made that the vectors $|\Psi_4\rangle$ and $|\Psi_5\rangle$ do not mix with the vectors $|\Psi_6\rangle$, $|\Psi_7\rangle$ and $|\Psi_2\rangle$, $|\Psi_3\rangle$ respectively, so that the off-diagonal elements joining these states may be set to zero (32). This approximation is particularly valid when the X nucleus is of a different species than the A and B nuclei.

The matrix elements resulting from taking the commutator of ρ^{ω} with $\hat{H}'_o + \hat{H}'_1$ are calculated directly from the results in Table 3 (with the ABX approximation). The significant elements arising in the evaluation of the elements of the spin density matrix appearing in equation (97) are given below (the 63 and 72 terms will be required at a later stage).

TABLE (3)

The matrix elements of $\hat{H}'_o + \hat{H}'_1$ relative to the basis product vectors for a three spin-½ system.

Basis Product Vector		Diagonal Elements: $(\hat{H}'_o + \hat{H}'_1)_{nn}$
$\|\Psi_1\rangle$	$\alpha\alpha\alpha$	$\frac{1}{2}(\omega_1+\omega_2+\omega_3-3\omega) + \frac{1}{4}(J_{12}+J_{13}+J_{23})$
$\|\Psi_2\rangle$	$\alpha\beta\alpha$	$\frac{1}{2}(\omega_1-\omega_2+\omega_3-\omega) - \frac{1}{4}(J_{12}-J_{13}+J_{23})$
$\|\Psi_3\rangle$	$\beta\alpha\alpha$	$\frac{1}{2}(-\omega_1+\omega_2+\omega_3-\omega) - \frac{1}{4}(J_{12}+J_{13}-J_{23})$
$\|\Psi_4\rangle$	$\beta\beta\alpha$	$\frac{1}{2}(-\omega_1-\omega_2+\omega_3+\omega) + \frac{1}{4}(J_{12}-J_{13}-J_{23})$
$\|\Psi_5\rangle$	$\alpha\alpha\beta$	$\frac{1}{2}(\omega_1+\omega_2-\omega_3-\omega) + \frac{1}{4}(J_{12}-J_{13}-J_{23})$
$\|\Psi_6\rangle$	$\alpha\beta\beta$	$\frac{1}{2}(\omega_1-\omega_2-\omega_3+\omega) - \frac{1}{4}(J_{12}+J_{13}-J_{23})$
$\|\Psi_7\rangle$	$\beta\alpha\beta$	$\frac{1}{2}(-\omega_1+\omega_2-\omega_3+\omega) - \frac{1}{4}(J_{12}-J_{13}+J_{23})$
$\|\Psi_8\rangle$	$\beta\beta\beta$	$\frac{1}{2}(-\omega_1-\omega_2-\omega_3+3\omega) + \frac{1}{4}(J_{12}+J_{13}+J_{23})$

Off-Diagonal elements:

$$(\hat{H}'_o + \hat{H}'_1)_{23} = (\hat{H}'_o + \hat{H}'_1)_{32} = \tfrac{1}{2} J_{12} = (\hat{H}'_0 + \hat{H}'_1)_{67} = (\hat{H}'_o + \hat{H}'_1)_{76}$$

$$(\hat{H}'_o + \hat{H}'_1)_{25} = (\hat{H}'_0 + \hat{H}'_1)_{52} = \tfrac{1}{2} J_{23} = (\hat{H}'_0 + \hat{H}'_1)_{47} = (\hat{H}'_o + \hat{H}'_1)_{74}$$

$$(\hat{H}'_o + \hat{H}'_1)_{35} = (\hat{H}'_0 + \hat{H}'_1)_{53} = \tfrac{1}{2} J_{13} = (\hat{H}'_0 + \hat{H}'_1)_{46} = (\hat{H}'_o + \hat{H}'_1)_{64}$$

ABX approximation: $J_{23} = J_{13} = 0$ for the off-diagonals.

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{21} &= \rho_{21}H_{11} - \rho_{21}H_{22} - \rho_{31}H_{23}\\ &= \rho_{21}(- \Delta - \delta + J_{12}/2) - \rho_{31} J_{12}/2\end{aligned}\tag{104a}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}' + \hat{H}'\}_{31} &= \rho_{31}H_{11} - \rho_{21}H_{32} - \rho_{31}H_{33}\\ &= \rho_{31}(- \Delta - \Sigma + J_{12}/2) - \rho_{21} J_{12}/2\end{aligned}\tag{104b}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{42} &= \rho_{42}H_{22} + \rho_{43}H_{32} - \rho_{42}H_{44}\\ &= \rho_{42}(- \Delta - \Sigma - J_{12}/2) + \rho_{43} J_{12}/2\end{aligned}\tag{104c}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{43} &= \rho_{42}H_{23} + \rho_{43}H_{33} - \rho_{43}H_{44}\\ &= \rho_{43}(- \Delta - \delta - J_{12}/2) + \rho_{42} J_{12}/2\end{aligned}\tag{104d}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{65} &= \rho_{65}H_{55} - \rho_{65}H_{66} - \rho_{75}H_{67}\\ &= \rho_{65}(- \Delta - \delta' + J_{12}/2) - \rho_{75} J_{12}/2\end{aligned}\tag{104e}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{75} &= \rho_{75}H_{55} - \rho_{65}H_{76} - \rho_{75}H_{77}\\ &= \rho_{75}(- \Delta - \Sigma' + J_{12}/2) - \rho_{65} J_{12}/2\end{aligned}\tag{104f}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{86} &= \rho_{86}H_{66} - \rho_{86}H_{88} + \rho_{87}H_{76}\\ &= \rho_{86}(- \Delta - \Sigma' - J_{12}/2) + \rho_{87} J_{12}/2\end{aligned}\tag{104g}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{87} &= \rho_{86}H_{67} + \rho_{87}H_{77} - \rho_{87}H_{88}\\ &= \rho_{87}(- \Delta - \delta' - J_{12}/2) + \rho_{86} J_{12}/2\end{aligned}\tag{104h}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{51} &= \rho_{51}H_{11} - \rho_{51}H_{55}\\ &= \rho_{51}\{ + \omega_3 - \omega + \tfrac{1}{2}(J_{13} + J_{23})\}\end{aligned}\tag{104i}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{62} &= \rho_{62}H_{22} + \rho_{63}H_{32} - \rho_{62}H_{66} - \rho_{72}H_{67}\\ &= \rho_{62}\{ + \omega_3 - \omega + \tfrac{1}{2}(J_{13} - J_{23})\} + \tfrac{1}{2}(\rho_{62} - \rho_{72})J_{12}\end{aligned}\tag{104j}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{73} &= \rho_{72}H_{23} + \rho_{73}H_{33} - \rho_{63}H_{76} - \rho_{73}H_{77}\\ &= \rho_{73}\{ + \omega_3 - \omega - \tfrac{1}{2}(J_{13} - J_{23})\} + \tfrac{1}{2}(\rho_{72} - \rho_{63})J_{12}\end{aligned}\tag{104k}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{84} &= \rho_{84}H_{44} - \rho_{84}H_{88}\\ &= \rho_{84}\{ + \omega_3 - \omega - \tfrac{1}{2}(J_{13} + J_{23})\}\end{aligned}\tag{104l}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{63} &= \rho_{62}H_{23} + \rho_{63}H_{33} - \rho_{63}H_{66} - \rho_{73}H_{76}\\ &= \rho_{63}\{ - \omega_1 + \omega_2 + \omega_3 - \omega \} + \tfrac{1}{2}(\rho_{62} - \rho_{73})J_{12}\end{aligned}\tag{104m}$$

$$\begin{aligned}\{\rho^{\omega}, \hat{H}'_o + \hat{H}'_1\}_{72} &= \rho_{72}H_{22} + \rho_{73}H_{32} - \rho_{62}H_{76} - \rho_{72}H_{77}\\ &= \rho_{72}\{ + \omega_1 - \omega_2 + \omega_3 - \omega \} + \tfrac{1}{2}(\rho_{73} - \rho_{62})J_{12}\end{aligned}\tag{104n}$$

Equations (104) have been derived using the substitutions:

(105) $\Delta = \omega - \frac{1}{2}(\omega_1 + \omega_2)$

(106a) $\delta = \frac{1}{2}(\omega_1 - \omega_2) - \frac{1}{2} J_{23}$

(106b) $\delta' = \frac{1}{2}(\omega_1 - \omega_2) + \frac{1}{2} J_{23}$

(106c) $\Sigma = \frac{1}{2}(\omega_2 - \omega_1) - \frac{1}{2} J_{13}$

(106d) $\Sigma' = \frac{1}{2}(\omega_2 - \omega_1) + \frac{1}{2} J_{13}$

which will result in considerable simplification of equation (96). The effect of the substitution for Δ is to shift the zero of the frequency of the rf field to the midpoint of the resonance frequencies of the A and B nuclei.

It is also instructive to note that equations (104a), (104d), (104e) and (104h) correspond to B-type transitions; equations (104b), (104c), (104f) and (104g) to A-type transitions; and equations (104i)-(104l) to X-type transitions (equations (104m) and (104n) correspond to multiple transitions which are forbidden in first order time-dependent perturbation theory). The last two equations, (104m) and (104n) will be required later to solve equation (96), since these elements occur in equations (104j) and (104k).

The matrix elements of $\hat{H}'_p$ are readily evaluated using equations (103b) and (35), and remembering that $I_x = \frac{1}{2}(I_+ + I_-)$ and that I_- is the adjoint of I_+ (in this case since I_+ is real, I_- is simply the transpose of I_+). The matrix representation of $\hat{H}'_p$, relative to the basis product vectors (Table 1) is then readily compiled from:

(107) $$\hat{H}'_p = \frac{1}{2} H_p \{ \sum_{j=1}^{3} \gamma_j (I_{j+} + I_{j+}^t) \}$$

where the superscript t indicates the transpose of the matrix. The matrix representation of $\hat{H}'_p$ is presented below.

$$(108) \qquad \hat{H}'_p = \tfrac{1}{2} H_p \begin{bmatrix} 0 & \gamma & \gamma & 0 & \gamma_3 & 0 & 0 & 0 \\ \gamma & 0 & 0 & \gamma & 0 & \gamma_3 & 0 & 0 \\ \gamma & 0 & 0 & \gamma & 0 & 0 & \gamma_3 & 0 \\ 0 & \gamma & \gamma & 0 & 0 & 0 & 0 & \gamma_3 \\ \gamma_3 & 0 & 0 & 0 & 0 & \gamma & \gamma & 0 \\ 0 & \gamma_3 & 0 & 0 & \gamma & 0 & 0 & \gamma \\ 0 & 0 & \gamma_3 & 0 & \gamma & 0 & 0 & \gamma \\ 0 & 0 & 0 & \gamma_3 & 0 & \gamma & \gamma & 0 \end{bmatrix}$$

(assuming $\gamma_1 = \gamma_2 = \gamma$).

Using the approximation that the perturbing rf field is small, the effect on the diagonal elements of the spin density matrix may be ignored, so that (effectively we set $\underline{H}_p(t) = 0$):

$$(109) \qquad \rho_{nn}{}^{\omega} = \rho_{nn} \simeq \rho^o_{nn}$$

where as before ρ^o_{nn} is the spin density matrix at thermal equilibrium. From equation (71), using $\hat{H}^{\omega} = \hat{H}'_o + \hat{H}'_1$,

$$(110) \qquad \rho^o_{nn} = \frac{\langle n|\, e^{-(\hat{H}'_o + \hat{H}'_1)/kT} \,|n\rangle}{\mathrm{Tr}\; e^{-(\hat{H}'_o + \hat{H}'_1)/kT}} \; .$$

Expanding to first order in the small quantity $(\hat{H}'_o + \hat{H}'_1)/kT$, and calling the denominator Z:

$$\begin{aligned} (111) \qquad \rho^o_{nn} &\simeq \{1 - (\hat{H}'_o + \hat{H}'_1)_{nn}/kT\} \,/Z \\ &\simeq \{1 - (\hat{H}'_o)_{nn}/kT\} \,/Z \\ &\simeq \{1 - \hbar H_o(\textstyle\sum_j \gamma_j\, I_{jz})/kT\} \,/Z \end{aligned}$$

where the Hamiltonian has been converted to energy units by the inclusion of $\hbar$. The last two steps in equation (111) involve the further approximation that the contribution to the total energy of the system by the shielding constants and the coupling constants are negligible compared to the nuclear Zeeman energy.

The off-diagonals of this approximation for the density matrix are ignored, since they are much smaller than the diagonal elements ((22,25); see also the footnote on page 46).

To these approximations, ρ^{ω} for a three spin-½ system is given by the following matrix (relative to the basis product vectors):

$$(112)\qquad \frac{1}{Z}\begin{bmatrix}
1-\kappa(\gamma+\frac{\gamma_3}{2}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1-\kappa\frac{\gamma_3}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1-\kappa\frac{\gamma_3}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1+\kappa(\gamma-\frac{\gamma_3}{2}) & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1-\kappa(\gamma-\frac{\gamma_3}{2}) & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1+\kappa\frac{\gamma_3}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1+\kappa\frac{\gamma_3}{2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1+\kappa(\gamma+\frac{\gamma_3}{2})
\end{bmatrix}$$

where $\kappa = \frac{\hbar H_o}{kT}$.

The matrix resulting from the commutator of ρ^{ω} with $\hat{H}_p'$ then follows directly from equations (108) and (112):

$$(113)\qquad \{\rho^{\omega}, \hat{H}_p'\} = C\begin{bmatrix}
0 & -\gamma^2 & -\gamma^2 & 0 & -\gamma_3{}^2 & 0 & 0 & 0 \\
\gamma^2 & 0 & 0 & \gamma^2 & 0 & -\gamma_3{}^2 & 0 & 0 \\
\gamma^2 & 0 & 0 & \gamma^2 & 0 & 0 & -\gamma_3{}^2 & 0 \\
0 & \gamma^2 & \gamma^2 & 0 & 0 & 0 & 0 & -\gamma_3{}^2 \\
\gamma_3{}^2 & 0 & 0 & 0 & 0 & -\gamma^2 & -\gamma^2 & 0 \\
0 & \gamma_3{}^2 & 0 & 0 & \gamma^2 & 0 & 0 & -\gamma^2 \\
0 & 0 & \gamma_3{}^2 & 0 & \gamma^2 & 0 & 0 & -\gamma^2 \\
0 & 0 & 0 & \gamma_3{}^2 & 0 & \gamma^2 & \gamma^2 & 0
\end{bmatrix}$$

where $C = \frac{\kappa H_p}{2Z} = \frac{\hbar H_o H_1}{2ZkT}$ (Alexander (22) has shown in general that $\langle\Psi_j|\ \{\rho^{\omega}, \hat{H}_p'\}\ |\Psi_k\rangle = \mp\ 2\gamma^2 C \langle\Psi_j|\ I_x\ |\Psi_k\rangle$ for $\Delta I_z = 1$, and 0 for $\Delta I_z = 0$;

assuming $\gamma_1 = \gamma_2 = \cdots = \gamma$).

(d). Evaluation of the elements of ρ.

The off-diagonal elements of the density matrix which are to be solved for are given in equation (97), Collecting the appropriate terms in equation (96), using the expressions found in equations (100), (101), (104) and (113), there result the following linearly dependent equations:

(114a) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{21} = \frac{\rho_{31}-\rho_{21}}{\tau} - \frac{\rho_{21}}{T_2} + i\,\{\rho_{21}\,(-\Delta-\delta+\tfrac{1}{2}J) - \tfrac{1}{2}\rho_{31}J + \gamma^2 C\}$$

(114b) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{31} = \frac{\rho_{21}-\rho_{31}}{\tau} - \frac{\rho_{31}}{T_2} + i\,\{\rho_{31}\,(-\Delta-\Sigma+\tfrac{1}{2}J) - \tfrac{1}{2}\rho_{21}J + \gamma^2 c\}$$

(114c) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{42} = \frac{\rho_{43}-\rho_{42}}{\tau} - \frac{\rho_{42}}{T_2} + i\,\{\rho_{42}\,(-\Delta-\Sigma-\tfrac{1}{2}J) + \tfrac{1}{2}\rho_{43}J + \gamma^2 c\}$$

(114d) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{43} = \frac{\rho_{42}-\rho_{43}}{\tau} - \frac{\rho_{43}}{T_2} + i\,\{\rho_{43}\,(-\Delta-\delta-\tfrac{1}{2}J) + \tfrac{1}{2}\rho_{42}J + \gamma^2 C\}$$

(114e) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{65} = \frac{\rho_{75}-\rho_{65}}{\tau} - \frac{\rho_{65}}{T_2} + i\,\{\rho_{65}\,(-\Delta-\delta'+\tfrac{1}{2}J) - \tfrac{1}{2}\rho_{75}J + \gamma^2 C\}$$

(114f) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{75} = \frac{\rho_{65}-\rho_{75}}{\tau} - \frac{\rho_{75}}{T_2} + i\,\{\rho_{65}\,(-\Delta-\Sigma'+\tfrac{1}{2}J) - \tfrac{1}{2}\rho_{65}J + \gamma^2 C\}$$

(114g) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{86} = \frac{\rho_{87}-\rho_{86}}{\tau} - \frac{\rho_{86}}{T_2} + i\,\{\rho_{86}\,(-\Delta-\Sigma'-\tfrac{1}{2}J) + \tfrac{1}{2}\rho_{87}J + \gamma^2 C\}$$

(114h) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{87} = \frac{\rho_{86}-\rho_{87}}{\tau} - \frac{\rho_{87}}{T_2} + i\,\{\rho_{87}\,(-\Delta-\delta'-\tfrac{1}{2}J) + \tfrac{1}{2}\rho_{86}J + \gamma^2 C\}$$

(114i) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{51} = -\frac{\rho_{51}}{T_2} + i\,\{\rho_{51}\,(\omega_3-\omega+\tfrac{1}{2}J_{13}+\tfrac{1}{2}J_{23}) + \gamma_3^2 C\}$$

(114j) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{62} = \frac{\rho_{73}-\rho_{62}}{\tau} - \frac{\rho_{62}}{T_2} + i\,\{\rho_{62}(\omega_3-\omega+\tfrac{1}{2}J_{13}-\tfrac{1}{2}J_{23}) + \tfrac{1}{2}(\rho_{63}-\rho_{72})J + \gamma_3{}^2C\}$$

(114k) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{73} = \frac{\rho_{62}-\rho_{73}}{\tau} - \frac{\rho_{73}}{T_2} + i\,\{\rho_{73}(\omega_3-\omega-\tfrac{1}{2}J_{13}+\tfrac{1}{2}J_{23}) + \tfrac{1}{2}(\rho_{72}-\rho_{63})J + \gamma_3{}^2C\}$$

(114l) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{84} = -\frac{\rho_{84}}{T_2} + i\,\{\rho_{84}(\omega_3-\omega-\tfrac{1}{2}J_{13}-\tfrac{1}{2}J_{23}) + \gamma_3{}^2C\}$$

(114m) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{63} = \frac{\rho_{72}-\rho_{63}}{\tau} - \frac{\rho_{63}}{T_2} + i\,\{\rho_{63}(-\omega_1+\omega_2+\omega_3-\omega) + \tfrac{1}{2}(\rho_{62}-\rho_{73})J\}$$

(114n) $$\left(\frac{d\rho^{\omega}}{dt}\right)_{72} = \frac{\rho_{63}-\rho_{72}}{\tau} - \frac{\rho_{72}}{T_2} + i\,\{\rho_{72}(+\omega_1-\omega_2+\omega_3-\omega) + \tfrac{1}{2}(\rho_{73}-\rho_{62})J\}$$

where J has been written for J_{12}. The last two equations do not enter into the equation for the line shape; however they are needed to calculate the off-diagonals ρ_{62} and ρ_{73}. Assuming now steady-state solutions (i.e. lhs = 0), these equations may be solved using Craemer's rule; for example the two linearly dependent equations (114a) and (114b) may be solved for the elements ρ_{21} and ρ_{31} by expanding the following determinants:

(115a) $$\rho_{21} = \frac{\begin{vmatrix} -i\gamma^2C & \frac{1}{\tau}-\tfrac{1}{2}J \\ -i\gamma^2C & -\frac{1}{\tau}-\frac{1}{T_2}+i(-\Delta-\Sigma+\tfrac{1}{2}J) \end{vmatrix}}{\begin{vmatrix} -\frac{1}{\tau}-\frac{1}{T_2}+i(-\Delta-\delta+\tfrac{1}{2}J) & \frac{1}{\tau}-\tfrac{1}{2}J \\ \frac{1}{\tau}-\tfrac{1}{2}J & -\frac{1}{\tau}-\frac{1}{T_2}+i(-\Delta-\Sigma+\tfrac{1}{2}J) \end{vmatrix}}$$

and:

$$(115b)\qquad \rho_{31} = \frac{\begin{vmatrix} -\frac{1}{\tau}-\frac{1}{T_2}+i(-\Delta-\delta+\frac{1}{2}J) & -i\gamma^2C \\ \frac{1}{\tau}-\frac{1}{2}J & -i\gamma^2C \end{vmatrix}}{\begin{vmatrix} -\frac{1}{\tau}-\frac{1}{T_2}+i(-\Delta-\delta+\frac{1}{2}J) & \frac{1}{\tau}-\frac{1}{2}J \\ \frac{1}{\tau}-\frac{1}{2}J & -\frac{1}{\tau}-\frac{1}{T_2}+i(-\Delta-\Sigma+\frac{1}{2}J) \end{vmatrix}}$$

Upon expanding (115a) and (115b), and putting into a form with a real denominator, one has the following:

$$(116)\qquad \left(\frac{\rho_{21}+\rho_{31}}{\gamma^2C}\right)_{im} = \frac{\begin{array}{l}\frac{\varepsilon^2}{\tau}-\frac{4\delta\Sigma}{\tau}+\frac{8}{\tau^2T_2}+\frac{8}{\tau T_2{}^2}+\frac{2\Delta^2}{T_2}-\frac{2\Delta\varepsilon}{T_2}-\frac{4\Delta J}{T_2} \\ \qquad -\frac{2\delta\Sigma}{T_2}+\frac{\varepsilon^2}{T_2}+\frac{2\varepsilon J}{T_2}+\frac{2J^2}{T_2}+\frac{2}{T_2{}^3}\end{array}}{\begin{array}{l}\Delta^4-2\Delta^3(\varepsilon+J)+\Delta^2(2\delta\Sigma+3\varepsilon J+\frac{4}{\tau T_2}+\frac{2}{T_2{}^2}+\varepsilon^2+J^2 \\ +\frac{4}{\tau^2})+\Delta(-2\varepsilon\delta\Sigma-\varepsilon^2J-\frac{2\varepsilon}{T_2{}^2}-2\delta\Sigma J-\varepsilon J^2-\frac{2J}{T_2{}^2}-\frac{4\varepsilon}{\tau^2}-\frac{4\varepsilon}{\tau T_2}) \\ +\delta^2\Sigma^2+\delta\Sigma\varepsilon J-\frac{4\delta\Sigma}{\tau T_2}-\frac{2\delta\Sigma}{T_2{}^2}+\frac{\varepsilon^2J^2}{4}+\frac{\varepsilon J}{T_2{}^2}+\frac{4}{\tau^2T_2{}^2}+\frac{4}{\tau T_2{}^3}+\frac{1}{T_2{}^4} \\ +\frac{\varepsilon^2}{\tau^2}+\frac{2\varepsilon^2}{\tau T_2}+\frac{\varepsilon^2}{T_2{}^2}+\frac{J^2}{T_2{}^2}\end{array}}$$

where im indicates that only the imaginary part of the expression has been retained (recall that the imaginary part describes the absorption mode of the n.m.r. spectrum), $J = J_{12}$, and where the substitution:

$$(117)\qquad \varepsilon = -\delta-\Sigma = \delta'+\Sigma' = \tfrac{1}{2}(J_{13}+J_{23})$$

has been used.

The usefulness of the substitutions (106) and (117) is now apparent: an expression similar to (116) exists for the elements ρ_{42} and ρ_{43}, solved for using equations (114c) and (114d), with the only difference that the sign of J $(= J_{12})$ is altered wherever it occurs in equation (116). Furthermore, similar expressions exist for the elements ρ_{65} and ρ_{75}, using δ' and Σ' instead of δ and Σ in equation (116) and (following from equation (117)) with the sign of ε changed; and for the elements ρ_{86} and ρ_{87} using δ' and Σ' in equation (116) and with the sign of ε and the sign of J altered wherever they occur. In other words, the paired elements ρ_{42} and ρ_{43}, ρ_{65} and ρ_{75}, and ρ_{86} and ρ_{87} may be expanded into an expression similar to equation (116) for the pair ρ_{21} and ρ_{31} with differences only in the signs of ε and J (and using δ' and Σ' for the latter two pairs).

The elements ρ_{62} and ρ_{73} may also be calculated using Craemer's rule; however in this case one must expand 4x4 determinants since the equations (114j) and (114k) are linearly dependent on the elements ρ_{63} and ρ_{72}, necessitating the use of equations (114m) and (114n) (see the footnote on page 47).

Equations (114i) and (114l) are each linearly independent so that onehas immediately the following expressions for ρ_{51} and ρ_{84}:

$$(118) \qquad \frac{\rho_{51}}{\gamma_3 2C} = \left\{ \frac{1}{T_2} - i \left(\omega_3 - \omega + \tfrac{1}{2}J_{13} + \tfrac{1}{2}J_{23} \right) \right\}^{-1}$$

and

$$(119) \qquad \frac{\rho_{84}}{\gamma_3 2C} = \left\{ \frac{1}{T_2} - i \left(\omega_3 - \omega - \tfrac{1}{2}J_{13} - \tfrac{1}{2}J_{23} \right) \right\}^{-1} .$$

(e). The AB part of the ABX line shape.

The line shape function for the AB part of the ABX spectrum is given by equation (98), and from the above discussion one has:

$$(120) \qquad \text{AB line shape} \propto \frac{\rho_{21}+\rho_{31}+\rho_{42}+\rho_{43}+\rho_{65}+\rho_{75}+\rho_{86}+\rho_{87}}{\gamma^2 C}$$

where the spin density matrix elements are given by expressions of the form of equation (116). This equation may be rewritten in the form:

$$(121) \qquad \text{AB line shape} \quad \propto \quad \Omega\ (J,\ \varepsilon;\ \frac{\rho_{21}+\rho_{31}}{\gamma^2 C})$$

where the function Ω indicates a summation over the permutations of the signs of ε and J of equation (116) for the elements ρ_{21} and ρ_{31} (it is understood that δ' and Σ' are to be used in the appropriate places).

Note that the units of measurement in equation (116) are radians/second for ε, δ, Σ, δ', Σ', J, J_{13}, J_{23}, and Δ. Conversion to the units of Hertz (also known as cycles/second) is made by use of the equation:

$$(122) \qquad \text{radians/second} \quad = \quad 2\pi \text{ Hertz}$$

so that equation (116) becomes:

$$(123) \qquad \left(\frac{\rho_{21}+\rho_{31}}{4\pi^2\gamma^2 C}\right)_{im} = \frac{\begin{array}{l} \frac{\varepsilon^2}{\tau} - \frac{4\delta\Sigma}{\tau} + \frac{2}{\pi 2\tau 2T_2} + \frac{2}{\pi^2\tau T_2{}^2} + \frac{2\Delta^2}{T_2} \\ - \frac{2\Delta\varepsilon}{T_2} - \frac{4\Delta J}{T_2} - \frac{2\delta\Sigma}{T_2} + \frac{\varepsilon^2}{T_2} + \frac{2\varepsilon J}{T_2} + \frac{2J^2}{T_2} + \frac{1}{2\pi^2 T_2{}^3} \end{array}}{\begin{array}{l} \Delta^4 - 2\Delta^3(\varepsilon + J) + \Delta^2(2\delta\Sigma + 3\varepsilon J + \frac{1}{\pi 2\tau T_2} \\ + \frac{1}{2\pi^2 T_2{}^2} + \varepsilon^2 + J^2 + \frac{1}{\pi 2\tau 2}) + \Delta(-2\varepsilon\delta\Sigma - \varepsilon^2 J - \frac{\varepsilon}{2\pi^2 T_2{}^2} \\ - 2\delta\Sigma J - \varepsilon J^2 - \frac{J}{2\pi 2T_2{}^2} - \frac{\varepsilon}{\pi 2\tau 2} - \frac{\varepsilon}{\pi^2\tau T_2}) + \delta^2\Sigma^2 + \delta\Sigma\varepsilon J \\ - \frac{\delta\Sigma}{\pi^2\tau T_2} - \frac{\delta\Sigma}{2\pi^2 T_2{}^2} + \frac{\varepsilon^2 J^2}{4} + \frac{\varepsilon J}{4\pi^2 T_2{}^2} + \frac{1}{4\pi^4\tau^2 T_2{}^2} + \frac{1}{4\pi^4\tau T_2{}^3} \\ + \frac{1}{16\pi^4 T_2{}^4} + \frac{\varepsilon^2}{4\pi^2\tau^2} + \frac{\varepsilon^2}{2\pi^2\tau T_2} + \frac{\varepsilon^2}{4\pi^2 T_2{}^2} + \frac{J^2}{4\pi^2 T_2{}^2} \end{array}}$$

Hence the function Ω in equation (121) refers to equation (116) if the parameters are in radians/second, and to equation (123) if the parameters are in Hertz. In the ensuing discussion, the latter units are assumed.

The proportionality constant in equation (121) is the factor $4\pi^2\gamma^2C$ appearing in equation (123). This term is a scaling factor, important only when signal intensities from different calculations are to be compared.

The positions of the extrema in equation (121) are found by solving the equation:

$$(124) \qquad \frac{\partial}{\partial\Delta}\left(\frac{\rho_{21}+\rho_{31}+\rho_{42}+\rho_{43}+\rho_{65}+\rho_{75}+\rho_{86}+\rho_{87}}{4\pi^2\gamma^2C}\right) = 0 \quad .$$

For each term of the form of equation (123), there exist at most five extrema: three minima and two maxima (peaks). Hence solution of equation (124) would yield at most eight peaks (two from each term) which is what would be expected for the AB part of an ABX spectrum. In general, an analytical expression for the position of the peaks can not be found; however in Chapter VI a program (ABXFIT) is presented which uses numerical methods to locate the peak positions (relative to the mid-point of the resonance frequency of the A and B nuclei; see equation (105)) as well as the width of the peaks at their half-height.

A case in which equation (124) may be solved is for the system when the three coupling constants are set to zero (in this case the four terms in equation (121) are identical, and the system is effectively an uncoupled AB system) and $1/T_2 = 0$. One then has:

$$(125) \qquad \Delta^3 - \Delta\left(\delta_{AB}^2 - \frac{1}{2\pi^2\tau^2}\right) = 0$$

where $\delta_{AB} = 2\delta = -2\Sigma$ is the chemical shift between the A and B nuclei (ie. nuclei 1 and 2 respectively). The roots of this equation are:

$$(126) \qquad \Delta = 0; \pm \frac{1}{2\pi\tau}\sqrt{4\pi^2\tau^2\delta^2_{AB} - 2} .$$

The non-zero roots correspond to the position of the peaks (the minima are at ± ∞ and 0) in the region of exchange rates up to the point at which the peaks coalesce, where the peak position is then at the zero point of the frequency. It is interesting to note that the separation between the peaks (before coalescence) is given by the expression:

$$(127) \qquad \frac{1}{\pi\tau}\sqrt{4\pi^2\tau^2\delta^2_{AB} - 2}$$

which is identical to the result obtained by Gutowsky and Holm (33), starting from the Bloch equations (see references (1-3),(24) for example), when the differences in definitions are taken into account.

4. Application of the ABX Equation to Other Systems

Equation (121) is also valid for all two spin-½ and many three spin-½ systems (assuming that the exchanging nuclei are of the same nuclear species). For example, if $J_{13} = J_{23} = 0$, the expression reduces to the (complete) line shape of a coupled AB system in which the two nuclei are exchanging (from the substitutions (106) and (117) one has that $\delta = -\Sigma$, and that $\varepsilon = 0$; further set $\rho_{jk} = 0$ for $j > 4$ and/or $k > 4$):

$$(128) \qquad \text{AB line shape} \propto \frac{\rho_{21} + \rho_{31} + \rho_{42} + \rho_{43}}{4\pi^2\gamma^2 C} =$$

$$\Omega\,(J) \left\{ \frac{\dfrac{4\delta^2}{\tau} + \dfrac{2}{\pi^2\tau^2 T_2} + \dfrac{2}{\pi^2\tau T_2{}^2} + \dfrac{2\Delta^2}{T_2} - \dfrac{4\Delta J}{T_2} + \dfrac{2\delta^2}{T_2} + \dfrac{2J^2}{T_2} + \dfrac{1}{2\pi^2 T_2{}^3}}{\begin{array}{l} \Delta^4 - 2\Delta^3 J + \Delta^2\left(-2\delta^2 + \dfrac{1}{\pi^2\tau T_2} + \dfrac{1}{2\pi^2 T_2{}^2} + J^2 + \dfrac{1}{\pi^2\tau^2}\right) \\ + \Delta\left(2\delta^2 J - \dfrac{-J}{2\pi^2 T_2{}^2}\right) + \delta^4 + \dfrac{\delta^2}{\pi^2\tau T_2} + \dfrac{\delta^2}{2\pi^2 T_2{}^2} + \dfrac{J}{4\pi^2 T_2{}^2} + \dfrac{1}{4\pi^4\tau^2 T_2{}^2} + \\ \qquad \dfrac{1}{4\pi^4\tau T_2{}^3} + \dfrac{1}{16\pi^4 T_2{}^4} + \dfrac{J^2}{4\pi^2 T_2{}^2} \end{array}} \right\}$$

where the function $\Omega\,(J)$ indicates permutation of the sign of J in the expression following, and where 'AB line shape' now refers to the entire line shape of an AB system. This expression is identical to equation (57) obtained by Whitesides (25) when it is assumed that $T_2 = \infty$ (i.e. the natural line width is negligible).

Equation (121) is also valid for an A_2 and an AX system, since these systems may be treated as special cases of the AB system. Similarly the equation is valid for an A_2X and an AMX system (it is assumed that nuclei 1 and 2 are exchanging), these being special cases of an ABX system. Finally, although the derivation is not valid for an ABC system[†], the equation may prove useful in the intermediate range between an ABX and an ABC system.

[†] The approximation for an ABX system was introduced for equation (104).

Chapter VI

COMPUTER PROGRAMS AND CALCULATED SPECTRA

1. Introduction

The plotting of equation (121) and the fitting of experimental spectra with calculated spectra has been greatly expedited by the use of computer programming. Section 2 of this chapter is concerned with a description and the specifications of several programs which have been written for the AB part of an ABX spectrum. As was mentioned in the previous chapter, the line shape expression (equation (121)) is valid for a number of other two and three spin-½ systems; these programs have the same range of validity.

In section 3, several plots of calculated spectra over a range of exchange (correlation) lifetimes for some of these different systems are presented. Examples of fitted experimental spectra, where the fitting has been achieved by the matching of line widths at half-height of the experimental and the calculated spectra, are shown in section 4.

2. Description of the Programs

The facilities at the University of Manitoba necessitated the writing of the following programs for the plotting of equation (121):

(a) ABXPUNCH: this program, written for an IBM-360, calculates the line shape for the AB part of the ABX spectrum (using equation (121)) and punches on cards the frequency and corresponding intensity over an input range of frequency.

(b) ABXPLOT: this program is written for an IBM-1620 computer with a Calcomp plotter utility. It reads in the punched cards from ABXPUNCH and plots the spectra.

The following programs were also written for the IBM-360:

(c) ABXGRAF: this program calculates and plots the spectra in the form of a rough step-type graph on the line printer.

(d) ABXFIT: this program is used to fit experimental spectra with calculated spectra. Output includes peak positions relative to the midpoint of the transitions of the A and B nuclei (i.e. solutions of equation (124)), and the widths of the peaks at their half-height.

(e) ABXGEN: a combination of ABXPUNCH, ABXGRAF and ABXFIT for multipurpose use.

The specifications and input requirements of these programs are given below (see Appendix II for a listing of the source deck and sample input and output).

(a). ABXPUNCH

Abstract: signal intensities are calculated using equation (121) (equation (123) is called four times, with the signs of J and ε permuted). Four values each of signal intensity and frequency are punched per card, and a variable step size is used; these features are used to minimize card-punching (and card-reading for ABXPLOT) while maintaining the requirements for a smooth plot. The signal intensity has been scaled so that the maximum peak has a height of 100 units.

Specifications: language: FORTRAN IV; library routines required: SQRT; storage required: approximately 6K; execution time: approximately 400 points/second or about 3 seconds/graph (the number of points vary from about 300 to about 2000 for a spectrum).

Input Parameters: card 1: J_{12}; J_{13}; J_{23}; AB shift; starting frequency; stopping frequency (the last two parameters may be set at (+shift) and (-shift) respectively; however it may be useful to decrease this range, since the number of points output increases as the range increases). The units for these parameters are Hz.

card 2: comment card.

card 3 to card n: lifetime (seconds); natural line width (seconds); height of plot required (in inches to the nearest tenth); scale (in Hz.) of the frequency axis. Defaults included set T_2 = 1.0 and/or scale = 1.0 if no values are specified.

card n+1: blank, denoting the end of this series of lifetimes with the parameters given in card 1.

card n+2: blank denoting the end of the job <u>or</u> a sequence of cards, starting from card 1 above, denoting a new series of calculations.

Output data: the input parameters and the number of cards punched are printed out. The following set of cards are punched for each spectra:

card 1: AB shift; J_{12}; J_{13}; J_{23}; lifetime; scale; starting frequency; stopping frequency.

card 2: height of plot, T_2.

card 3 to card m: signal intensities and frequencies, spaced alternately, and running from the starting frequency to the stopping frequency.

card m+1: blank, denoting the end of this spectrum. Further output is as above if more spectra are to be calculated.

(b). ABXPLOT

Abstract: reads in the cards directly from ABXPUNCH and plots the data on a Calcomp plotter. This program effectively uses the 1620 as a card reader. It may be easily converted to read and plot similar output from other programs.

Specifications: language: FORTRAN II; library routines required: CHAR and PLOT (used with the Calcomp); storage required: approximately 1K; execution time: about 1000 points/15 minutes, or about 10 minutes/spectrum (these limitations necessitated a minimizing of cards read in order that finite plot times would result).

Input Parameters: any set of output from ABXPUNCH, or any data set in the same sequence as the punched output from ABXPUNCH.

Output Data: prints out the parameters on cards 1 and

2, and plots the corresponding spectrum from the starting frequency to the stopping frequency (if the starting frequency is greater than the stopping frequency, the plot is from 'high field' to 'low field') with the scale and height (of the maximum peak) specified.

(c). ABXGRAF

Abstract: signal intensities are calculated using equation (121), and the spectrum plotted on the line printer. The density of the plot can be altered (by changing the scale parameter), and the signal intensities are scaled so that the maximum peak has a height of 100 units. This program is essentially the same as ABXPUNCH, except that the step-size is fixed for a spectrum and the output is printed rather than punched. Provision is also made for searches about a lifetime.

Specifications: as for ABXPUNCH.

Input Parameters: as for ABXPUNCH, except for cards 3-n. These cards have the lifetime; T_2; the scale in Hertz (assuming 6 lines/ inch on the line printer) of the graph (default options set scale = 1.0 Hz. if no value is specified); and the optional parameters of step-size and the number of steps which may be used for a search about the lifetime. For example, if step-size = 0.01 and number of steps = 10, ten spectra will be output with lifetimes ranging from (specified lifetime - 0.05 sec.) to (specified lifetime + 0.05 seconds).

Output Data: a rough step-type plot using the symbol '*'. Intensities have been scaled to give a maximum peak of 100 units and the intensities have been rounded off at the first decimal place.

(d). ABXFIT

Abstract: calculates the peak positions by searching equation (121) for maxima. A second pass is made through equation (121) to locate the positions of the half-heights of each peak (the half-height is found on both sides of the peak), and the half-height line width is calculated (on both sides of the peak; this eliminates errors due to the asymmetry resulting when there is overlap). Provision has been made for overlapping peaks, and all output intensities have been scaled so that the maximum peak has an intensity of 100 units.

Specifications: as for ABXPUNCH, except the storage required is approximately 23K and the execution time is about 1 second/ spectrum.

Input Parameters: as for ABXPUNCH with the search option of ABXGRAF.

Output Data: peak positions (relative to the midpoint of the transitions of the A and B nuclei); the half-height line widths of each peak (a line width of 0.0 indicates that the minimum on one of the sides of the peak is greater than the half-height; i.e. considerable overlap is occurring);the average half-height line width or the line width at the half-height of the lowest peak of two or more overlapping peaks.

(e). ABXGEN

Abstract: a conglomeration of ABXPUNCH, ABXGRAF, and ABXFIT. Output is either in the form of punched cards, or in the form of printed output.

Specifications: as for ABXPUNCH and ABXFIT, depending on the output. Storage required is about 26K.

Input Parameters: as for ABXPUNCH with the search option of ABXGRAF, and with the following changes: card 1 also specifies the type of output (printed data or punched cards) desired, and cards 3-n specifies the lifetime, T_2, scale (of the graph or of the punched cards for plotting), step-size, number of steps, and the height of the plot desired (for ABXPLOT only). Searches are not permitted for punched output.

Output Data: if punched output is specified, the output is the same as for ABXPUNCH; otherwise there will be output as from ABXFIT with a rough graph as from ABXGRAF for the lifetime specified (or the central lifetime specified in a search).

Detailed format instructions for the input parameters are included in the printed output of the source decks in Appendix II.

3. Calculated Spectra

The spectra presented in the following figures have been plotted by ABXPLOT using the data calculated and punched by ABXPUNCH. Several different systems have been done in order to test the range of validity of the theory and of the computer programs in calculating line shapes for these systems when there is intramolecular exchange.

For each system series of plots have been made for different correlation times (corresponding to the average lifetime of a state before exchange occurs), whichare equivalent to the inverses of the rates of exchange. Note that at a long lifetime (slow rate of exchange) the spectra resemble systems in which there is no exchange, and that at a short lifetime (fast rate of exchange) the spectra resemble systems in which the exchanging nuclei have the same chemical shift (and in general averaged coupling constants to other interacting nuclei): for example an AB system undergoing fast exchange resembles an A_2 system; similarly an ABX system resembles an A_2X system.

The references to a strongly coupled and a weakly coupled ABX system in Figures (5-8) mean that the ratios J_{AB}/(AB shift) are respectively large or small (1,2).

Figure (8) consists of only six peaks at a long lifetime because four of the peaks coincide.

Also note that in Figure (9) the peak at a very short lifetime is not split; this is because the effective coupling J_{AX} for the A_2X system is given by $\frac{1}{2}(J_{AX} + J_{BX}) \approx 0.26$ Hz., and this small splitting is not yet solved (cf. Figure (5): the effective coupling of 1.5 Hz. can be solved).

FIGURE (2a)

Calculated spectra for an AX spin-½ system in which the A and X nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AX shift = 10.00 Hz., J_{AX} = .5 Hz., T_2 = 1.00 sec.; scale: 1 division = 1 Hertz.

(A) Lifetime = 10. sec.

(B) Lifetime = 1. sec.

(C) Lifetime = .1 sec.

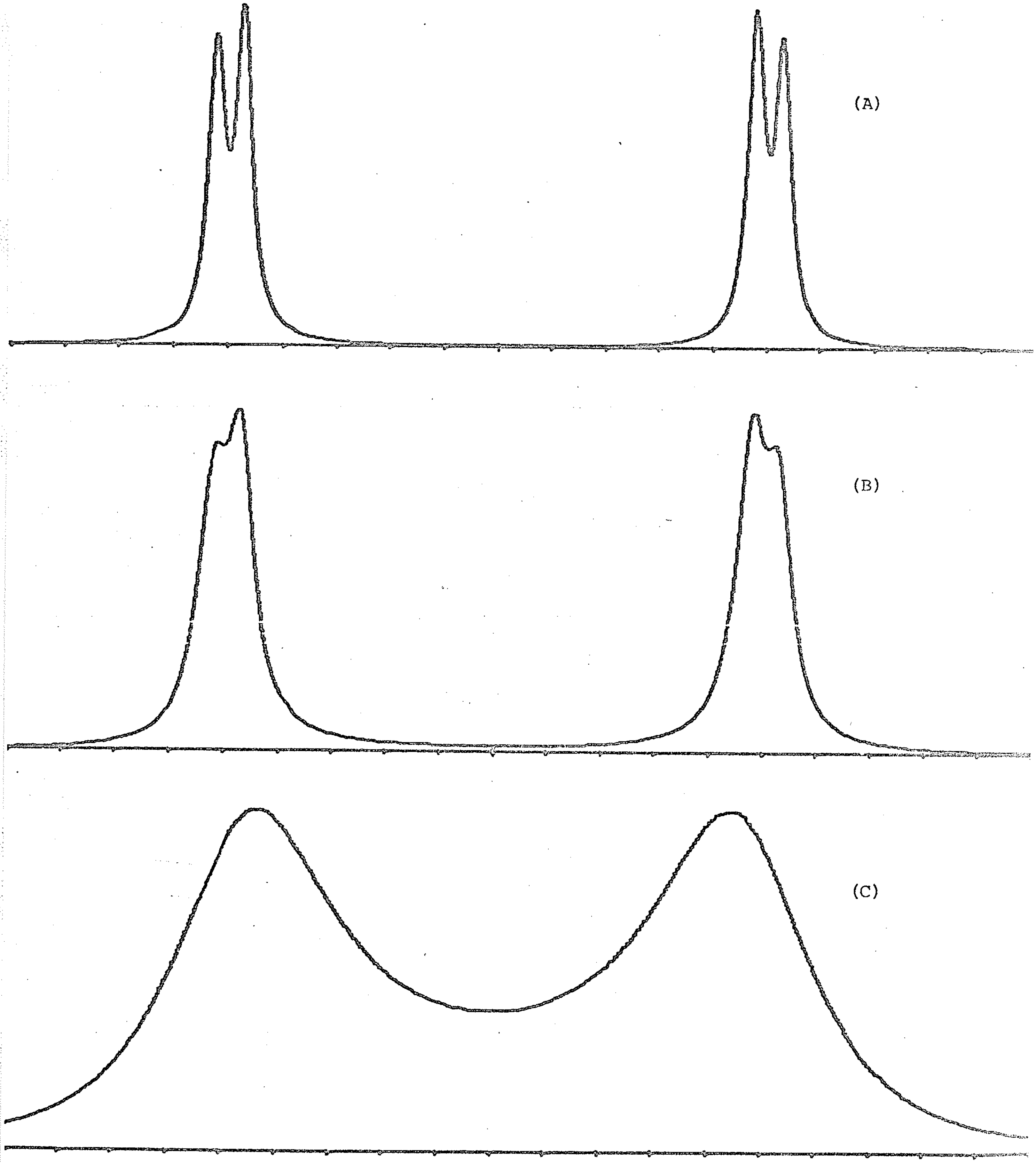

(A)
(B)
(C)

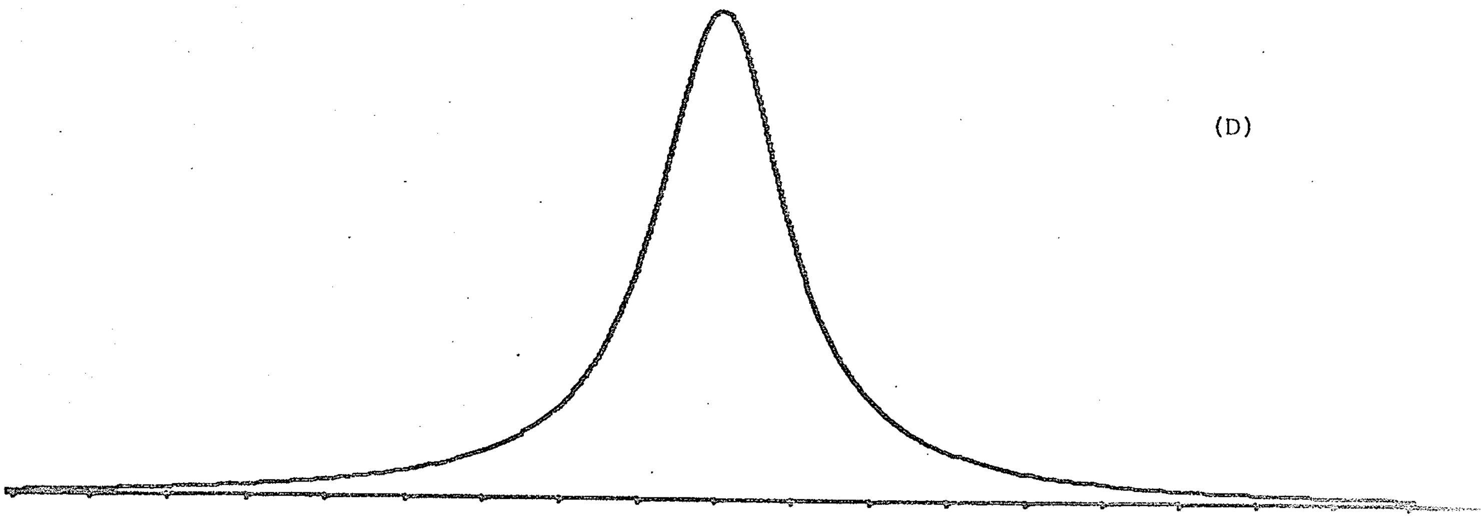
FIGURE (2b)

As for Figure (2a).

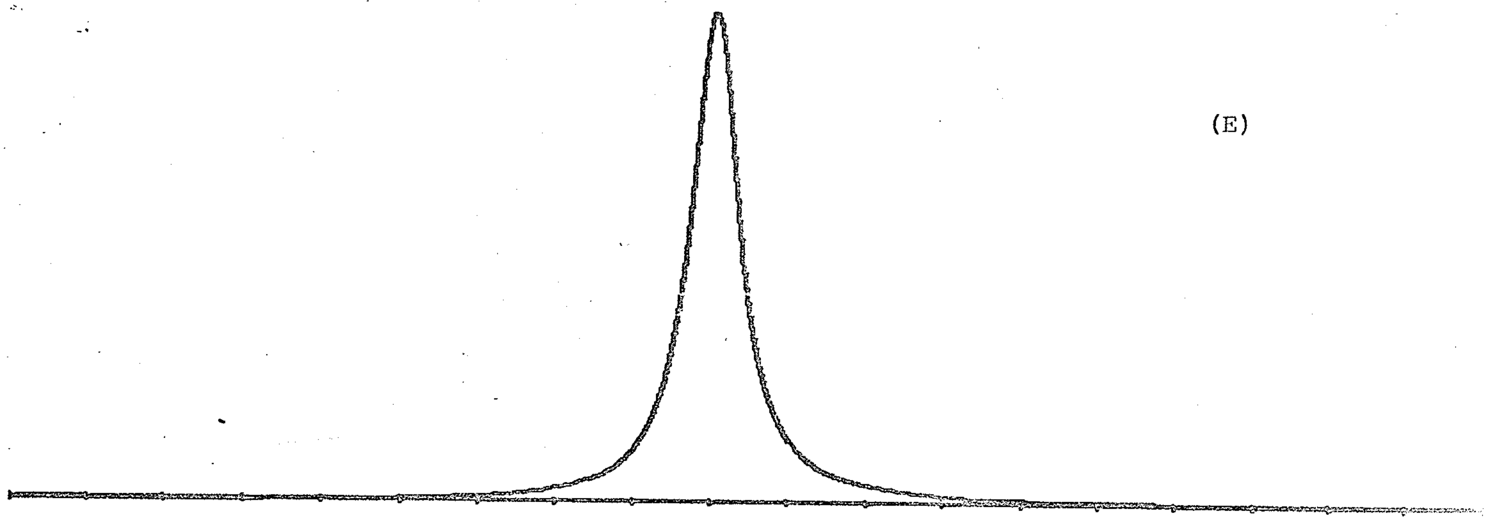
(D) Lifetime = 10^{-2} sec.

(E) Lifetime = 10^{-3} sec.

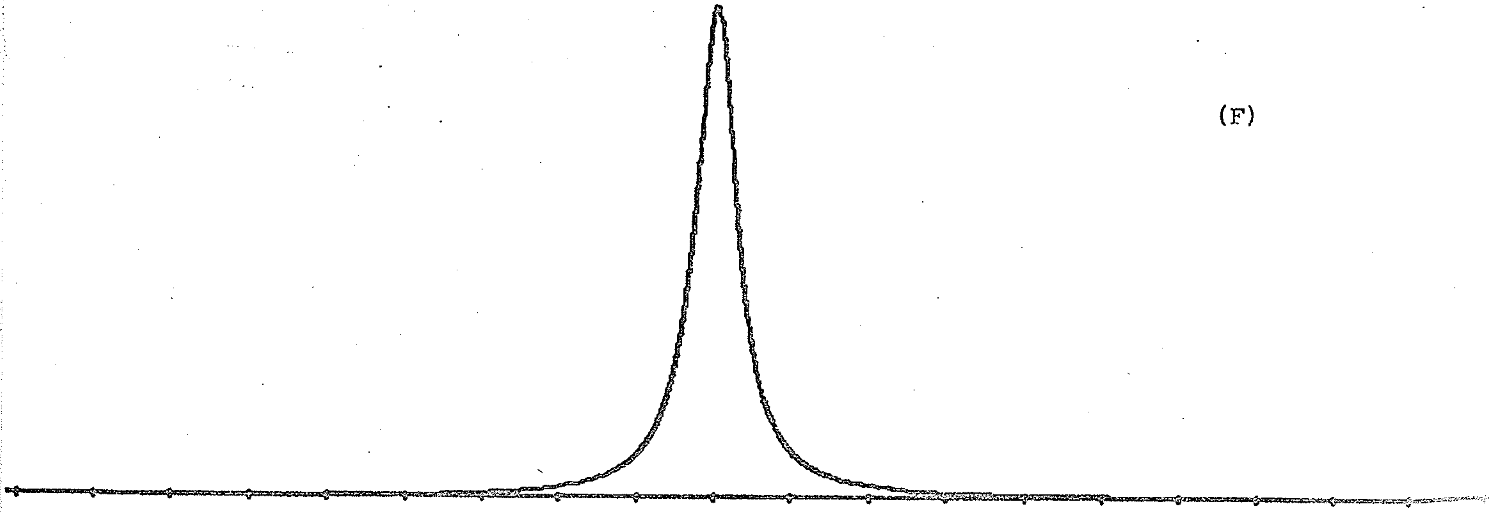
(F) Lifetime = 10^{-5} sec.



(D)



(E)



(F)

FIGURE (3a)

Calculated spectra for an AB spin-½ system in which the A and B nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AB shift = 10.00 Hz., J_{AB} = 2.00 Hz., T_2 = 1.00 seconds; scale: 1 division = 1 Hertz.

(A) Lifetime = 10. sec.

(B) Lifetime = 1. sec.

(C) Lifetime = .1 sec.

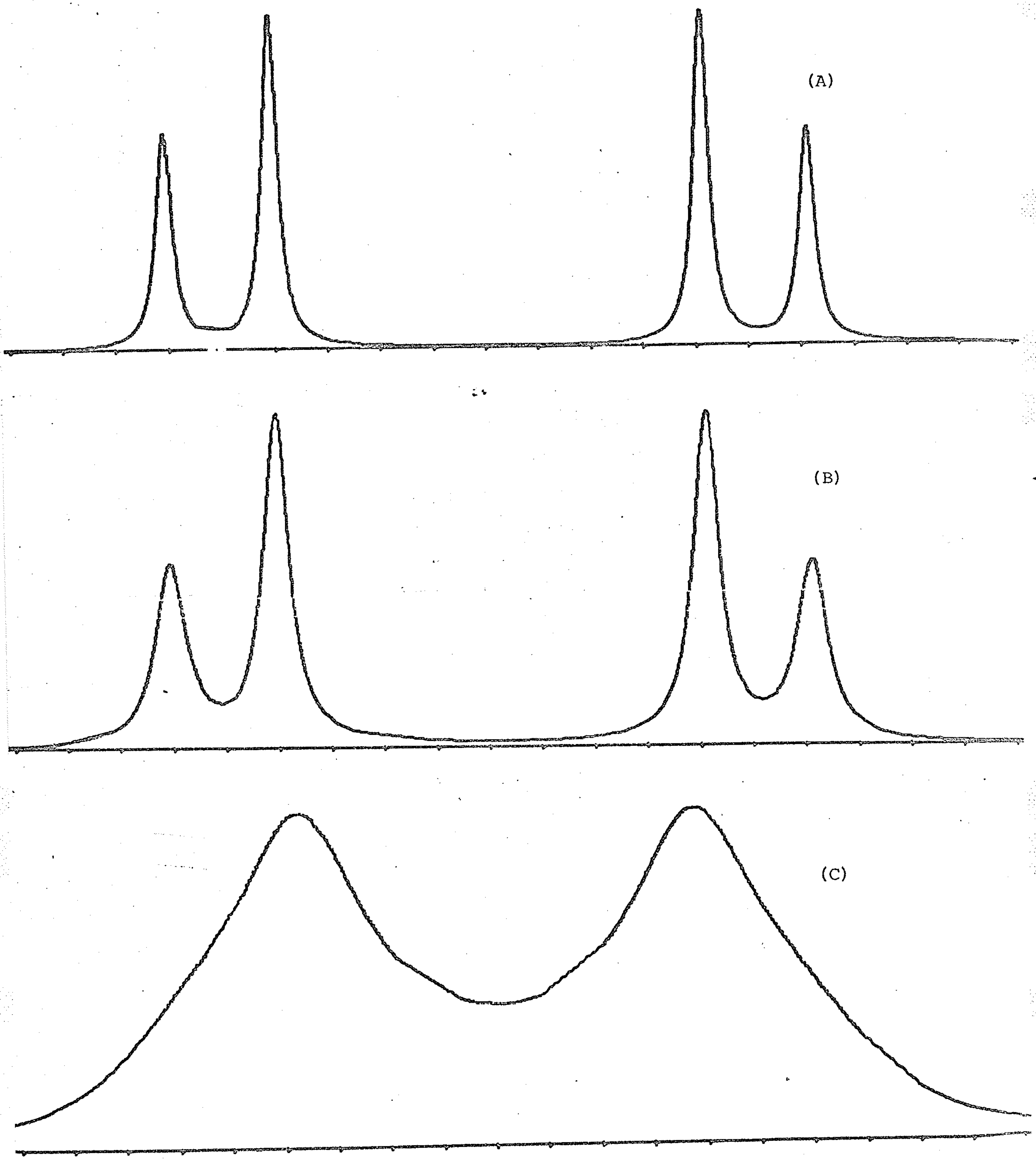

(A)
(B)
(C)

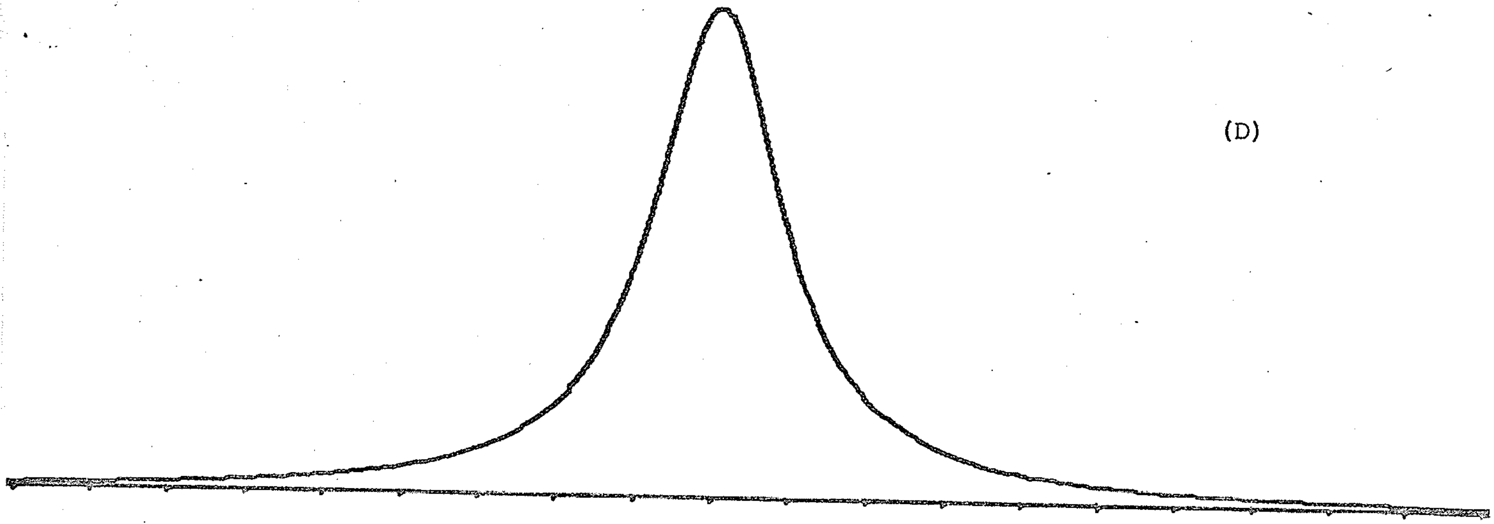
FIGURE (3b)

As for Figure (3a).

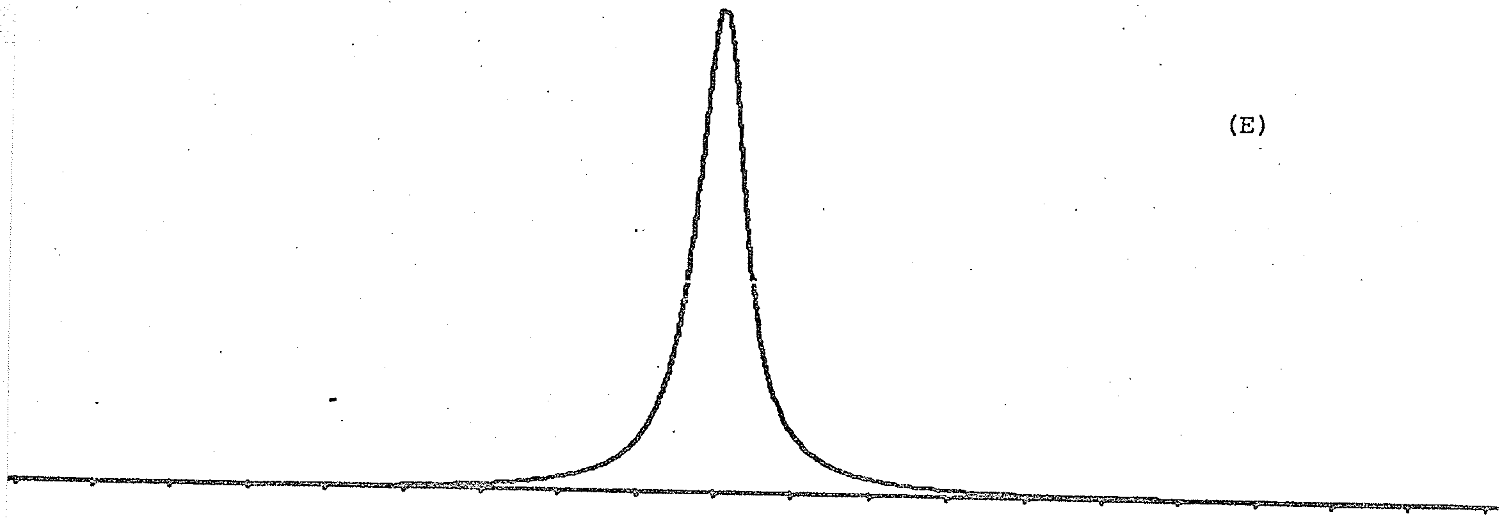
(D) Lifetime = 10^{-2} sec.

(E) Lifetime = 10^{-3} sec.

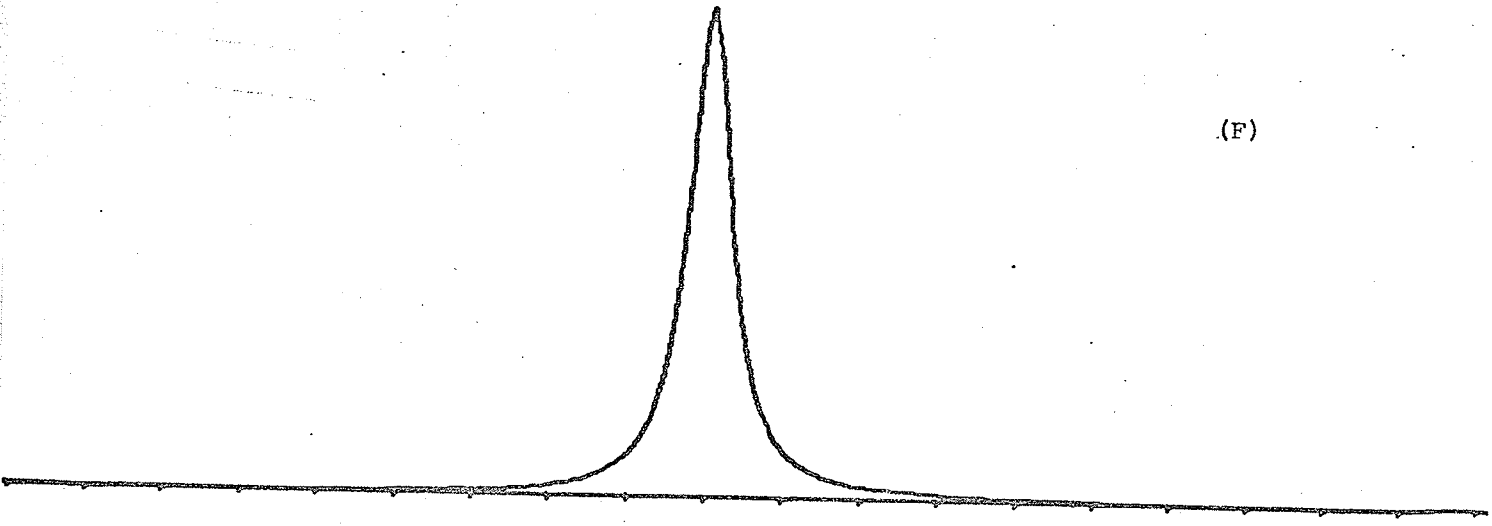
(F) Lifetime = 10^{-5} sec.



(D)



(E)



(F)

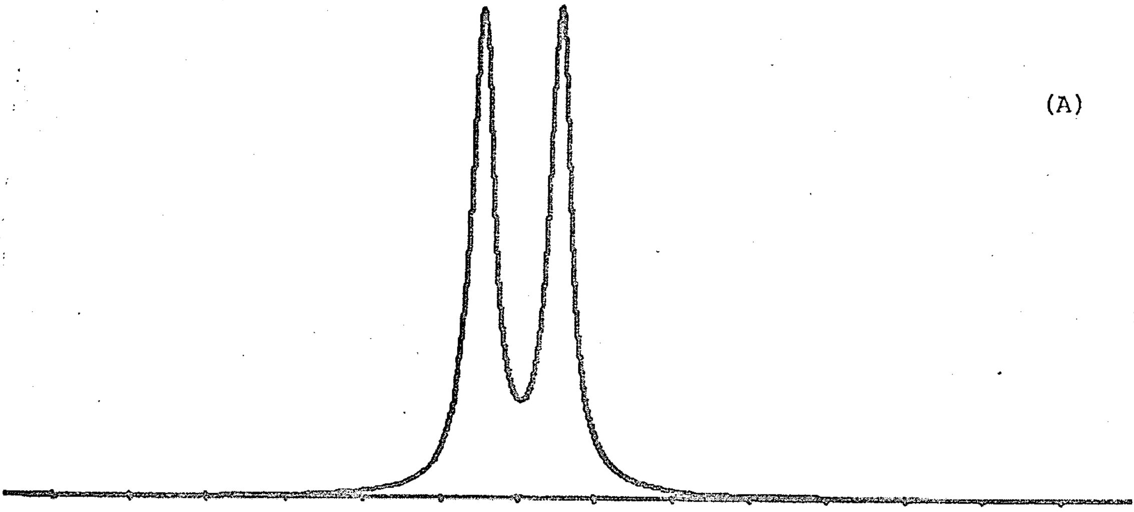
FIGURE (4)

Calculated spectra of the region of A-type transitions for an A_2X spin-½ system in which the two A nuclei are undergoing intramolecular exchange. Parameters for the spectra are: J_{AB} = 0 Hz., J_{AX} = J_{BX} = 1.00 Hz., T_2 = 1.00 sec.; scale: 1 division = 1 Hertz.

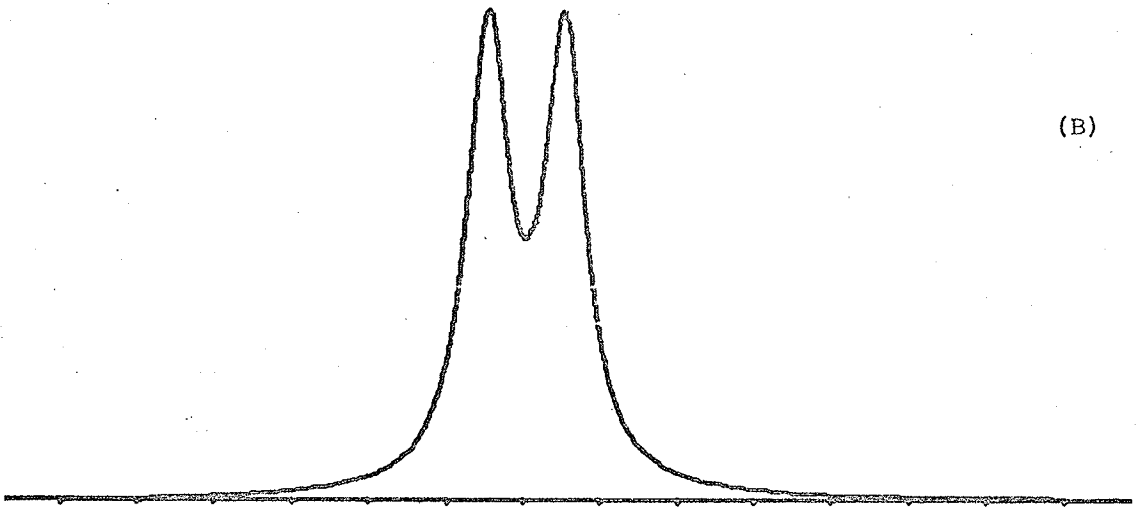
(A) Lifetime = 10^2 sec.

(B) Lifetime = .1 sec.

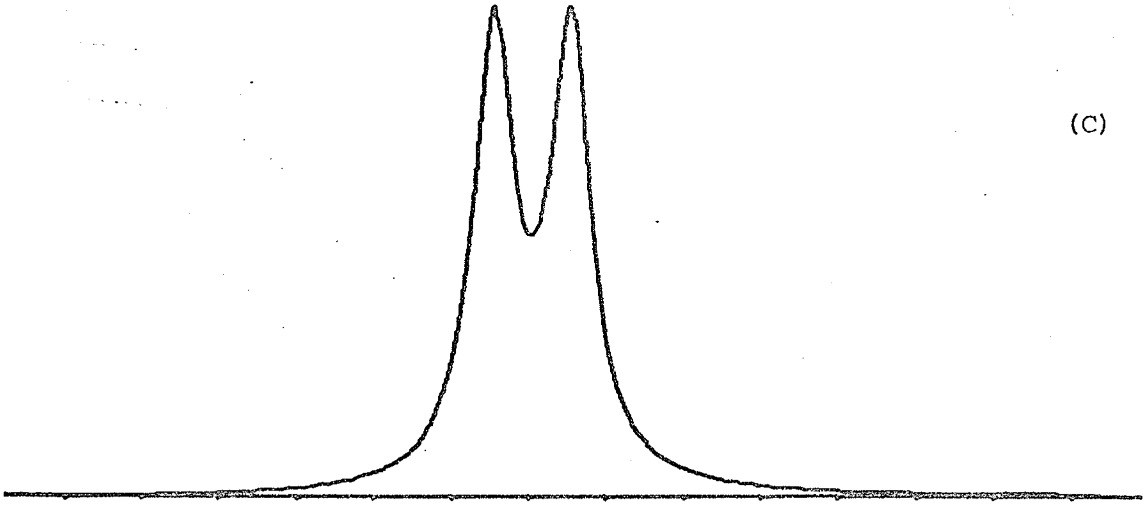
(C) Lifetime = 10^{-5} sec.



(A)



(B)



(C)

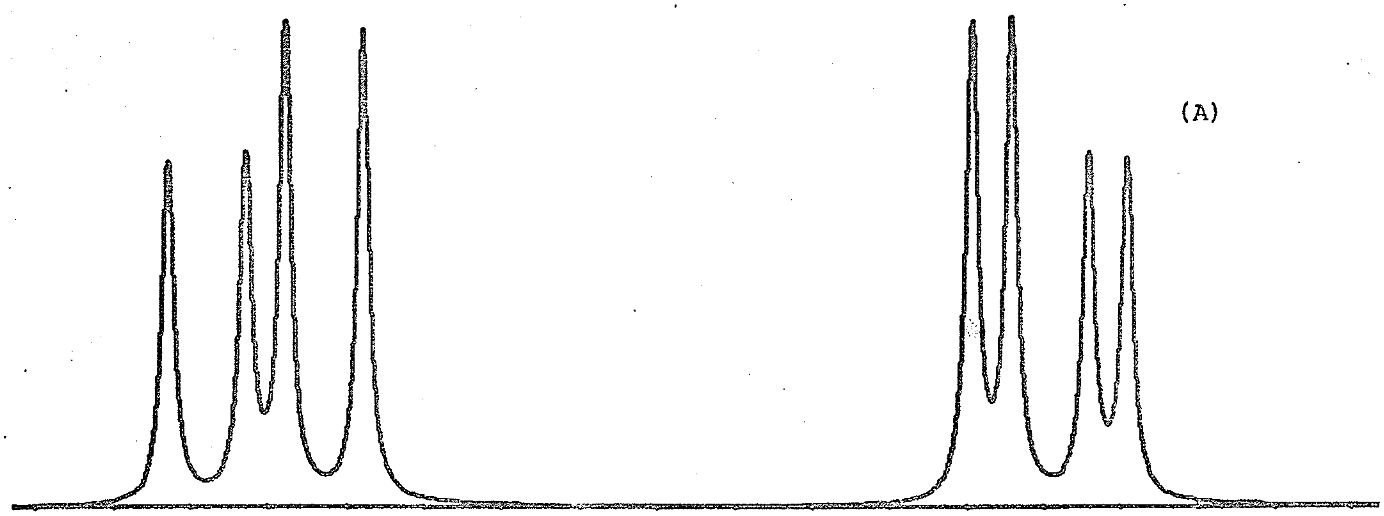
FIGURE (5a)

Calculated spectra for the region of A- and B-type transitions for a weakly coupled ABX spin-½ system in which the AB nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AB shift = 20.00 Hz., J_{AB} = 3.00 Hz., J_{AX} = 2.00 Hz., J_{BX} = 1.00 Hz., T_2 = 1.00 sec.; scale: 1 division = 2 Hertz.

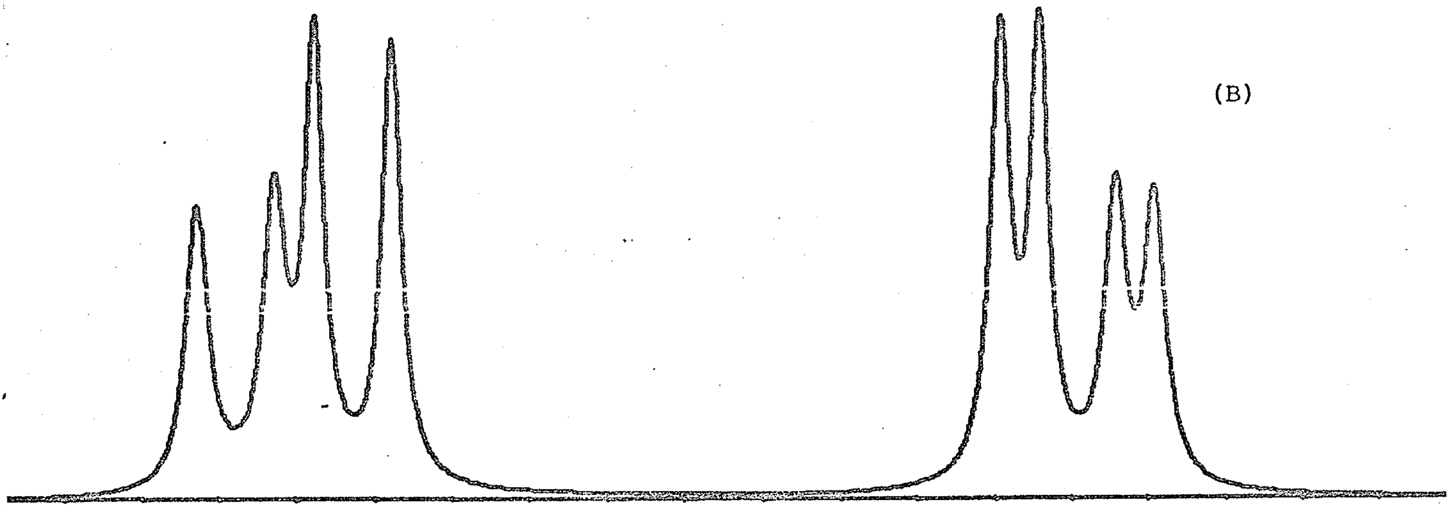
(A) Lifetime = 10. sec

(B) Lifetime = 1. sec.

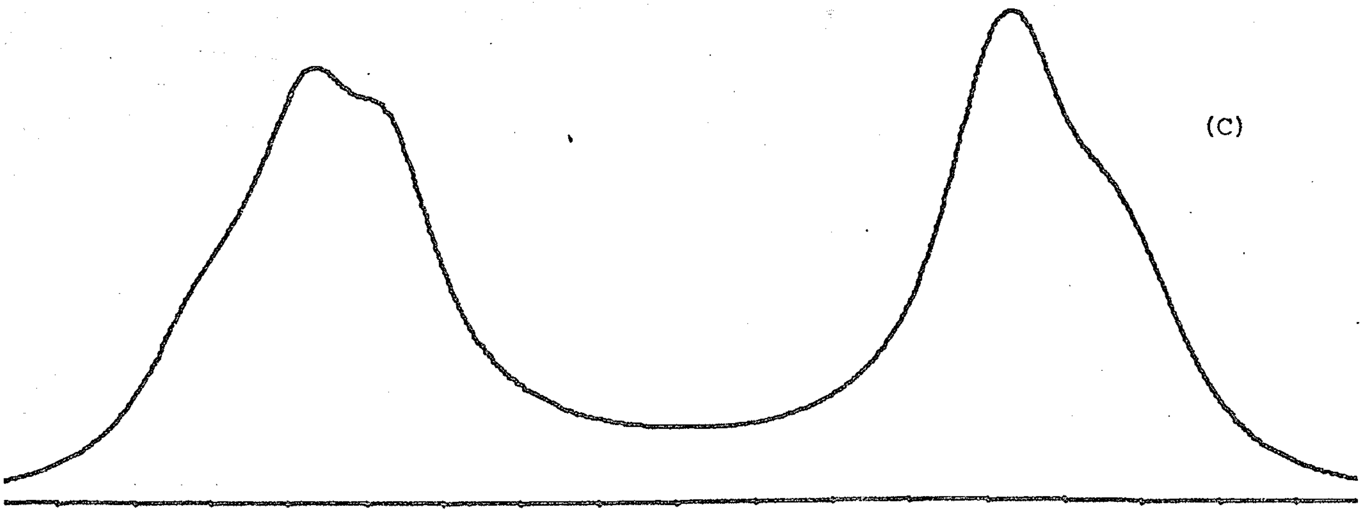
(C) Lifetime = .1 sec.



(A)



(B)



(C)

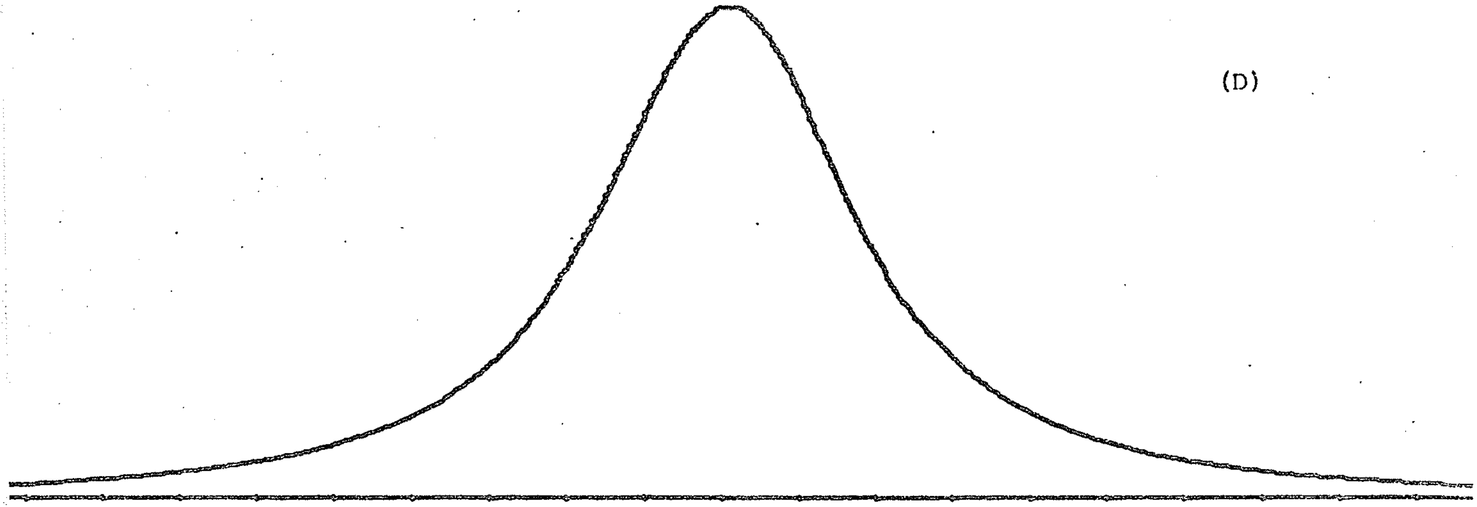
FIGURE (5b)

As for Figure (5a).

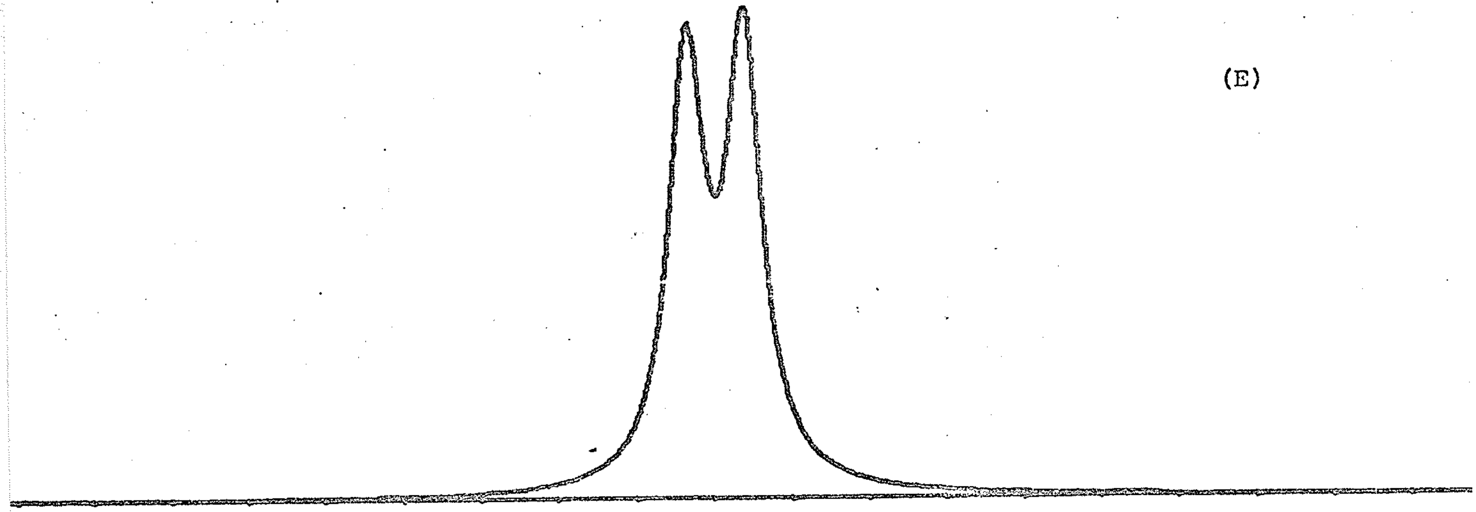
(D) Lifetime = 10^{-2} sec.

(E) Lifetime = 10^{-3} sec.

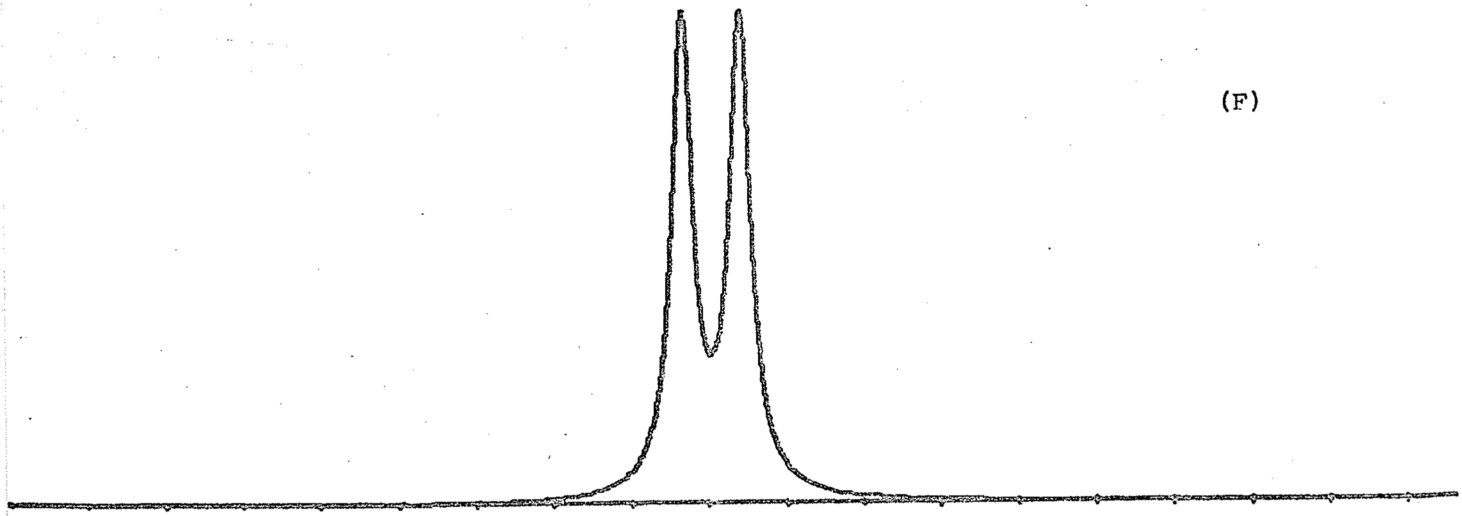
(F) Lifetime = 10^{-5} sec.



(D)



(E)



(F)

FIGURE (6a)

Calculated spectra for the region of A- and B-type transitions for a strongly coupled ABX spin-½ system in which the AB nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AB shift = 4.00 Hz., J_{AB} = 3.00 Hz., J_{AX} = 2.00 Hz., J_{BX} = 1.00 Hz., T_2 = 1.00 sec.; scale: 1 division = 1 Hertz.

(A) Lifetime = 10. sec.

(B) Lifetime = 1. sec.

(C) Lifetime = .1 sec.

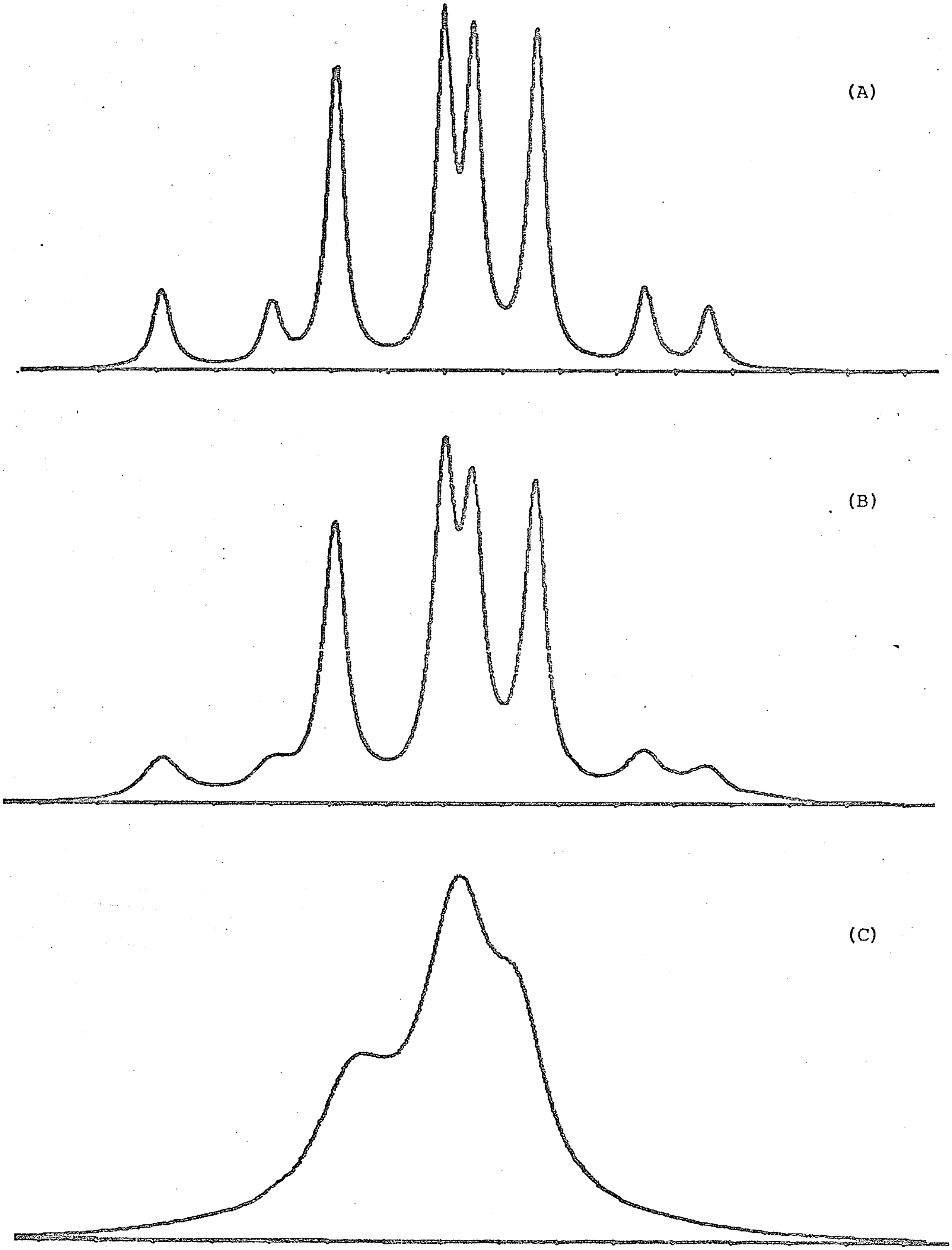

(A)
(B)
(C)

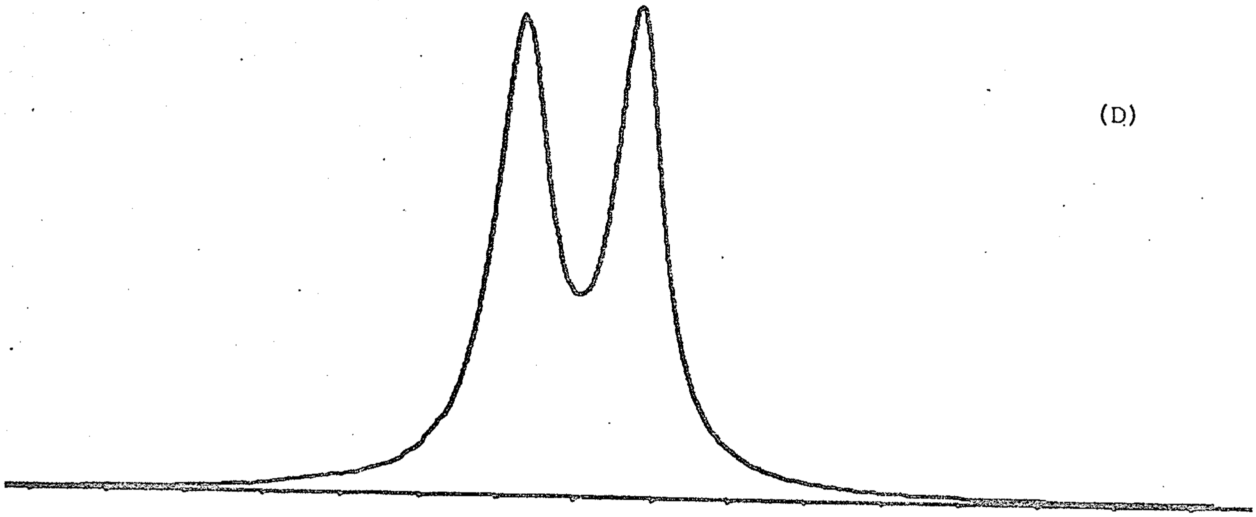
FIGURE (6b)

As for Figure (6a).

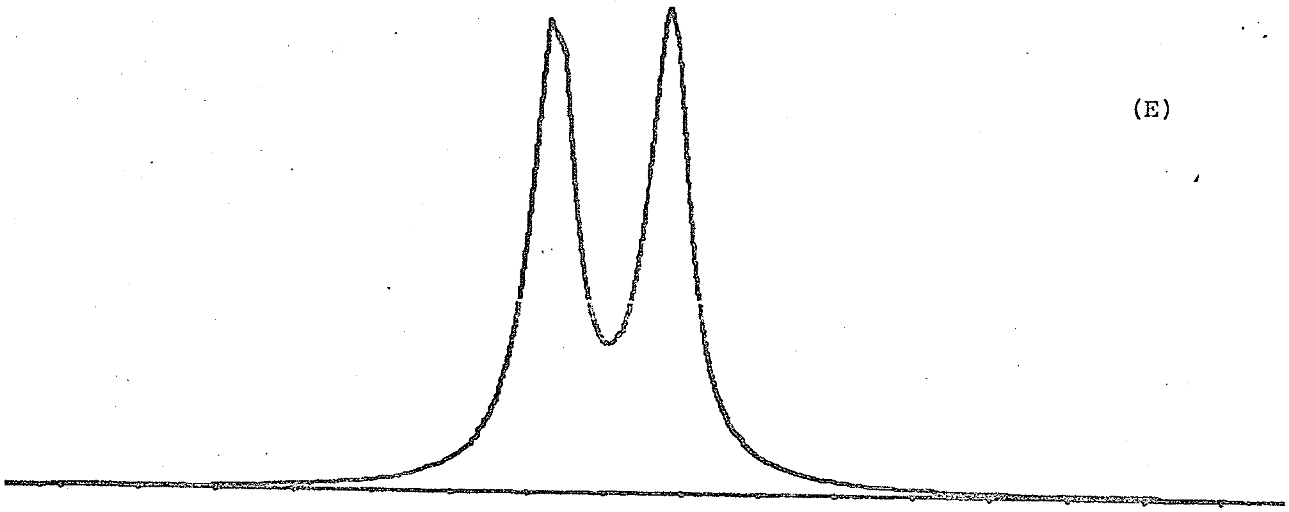
(D) Lifetime = 10^{-2} sec.

(E) Lifetime = 10^{-3} sec.

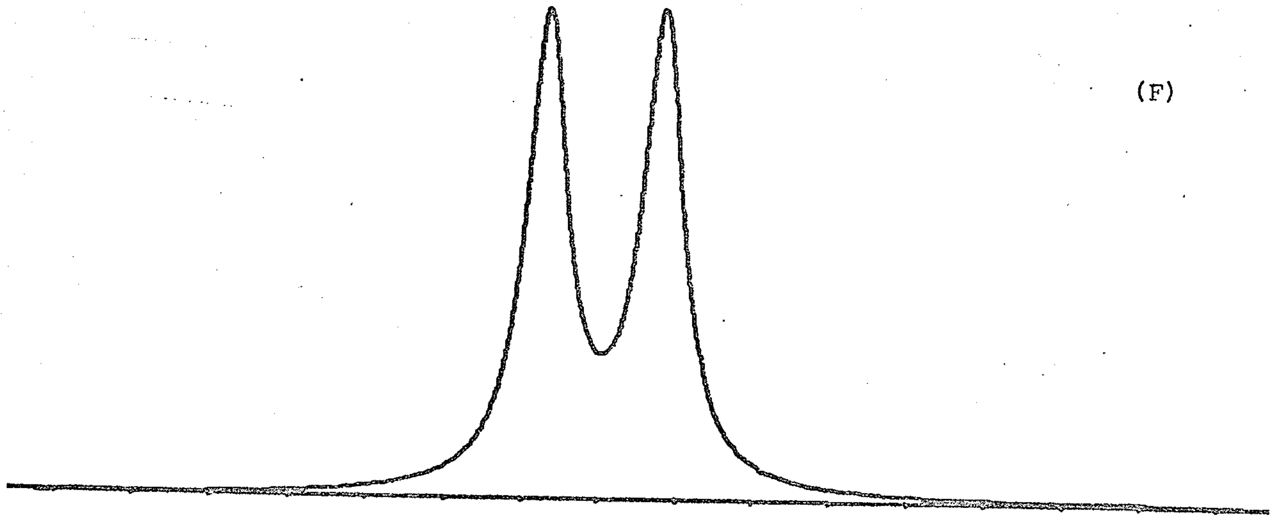
(F) Lifetime = 10^{-5} sec.



(D)



(E)



(F)

FIGURE (7a)

Calculated spectra of the region of A- and B-type transitions for a strongly coupled ABX spin-½ system in which the AB nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AB shift = 10.00 Hz., J_{AB} = 4.00 Hz., J_{AX} = 2.0 Hz., J_{AX} = 1.00 Hz., T_2 = 1.00 sec.; scale: 1 division = 1 Hertz.

(A) Lifetime = 10. sec.

(B) Lifetime = 1. sec.

(C) Lifetime = .1 sec.

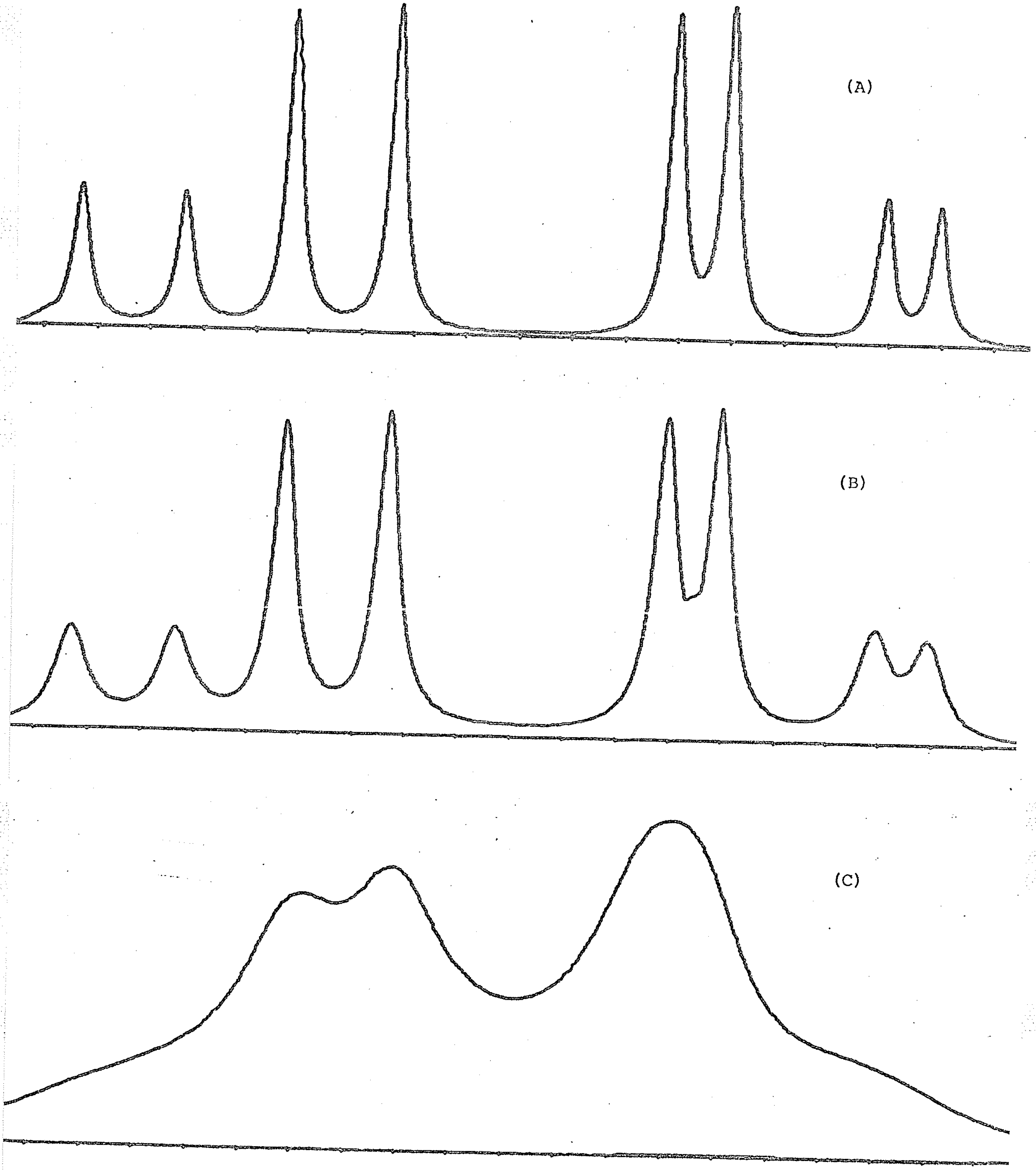

(A)
(B)
(C)

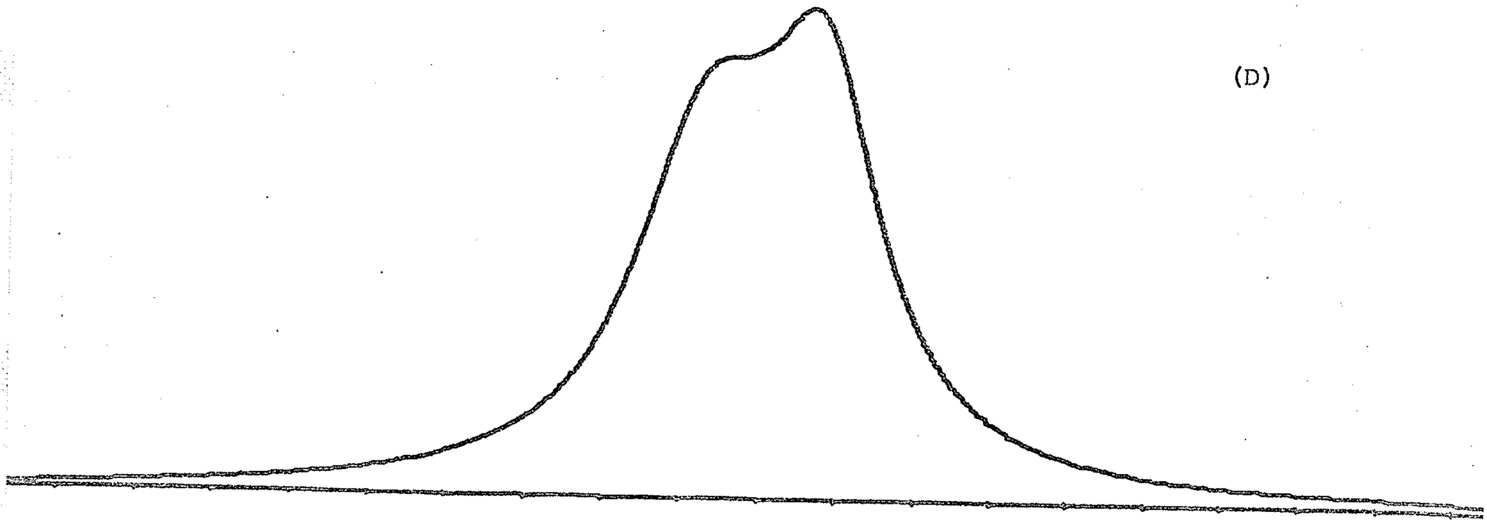
FIGURE (7b)

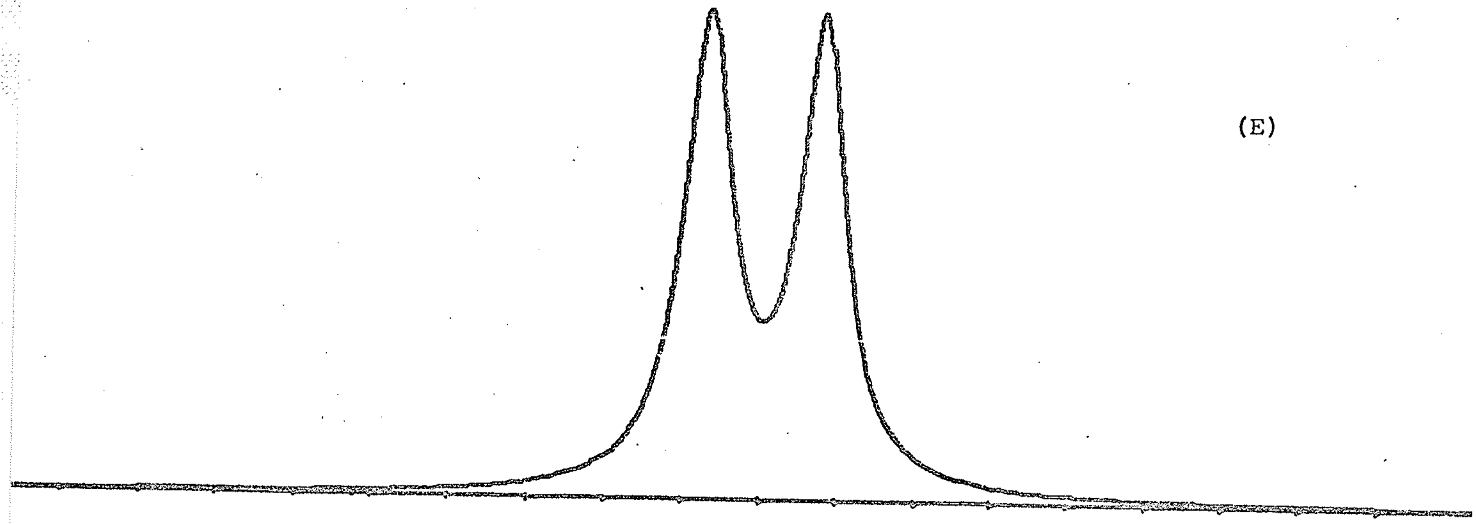
As for Figure (7a).

(D) Lifetime = 10^{-2} sec.

(E) Lifetime = 10^{-3} sec.

(F) Lifetime = 10^{-5} sec.


(D)


(E)

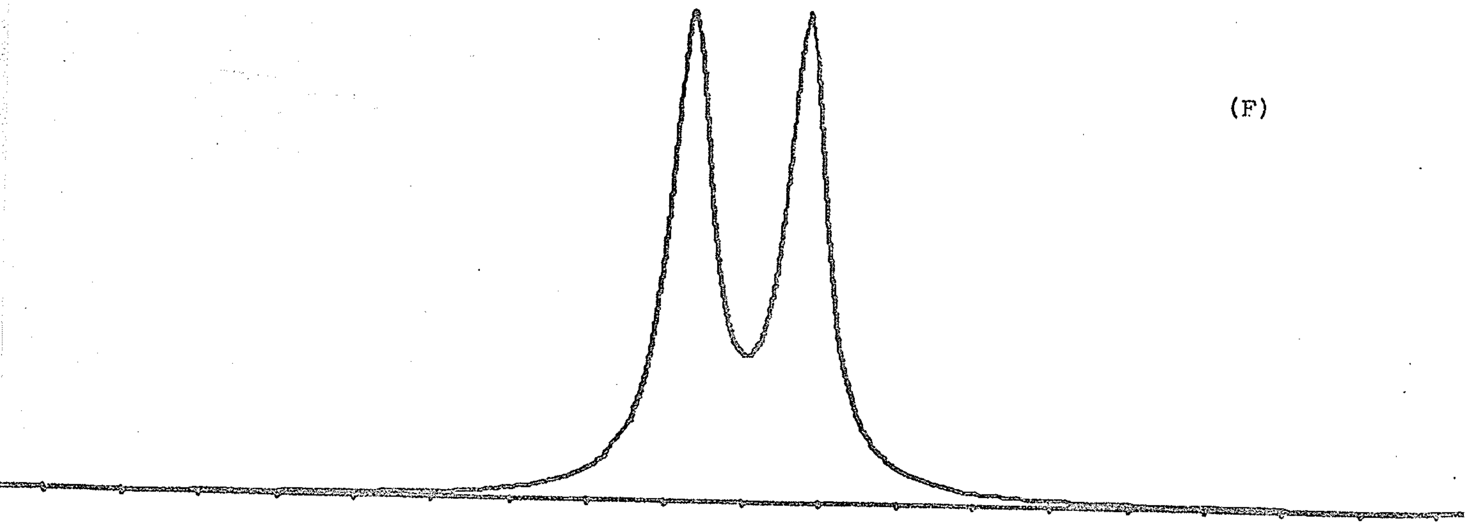

(F)

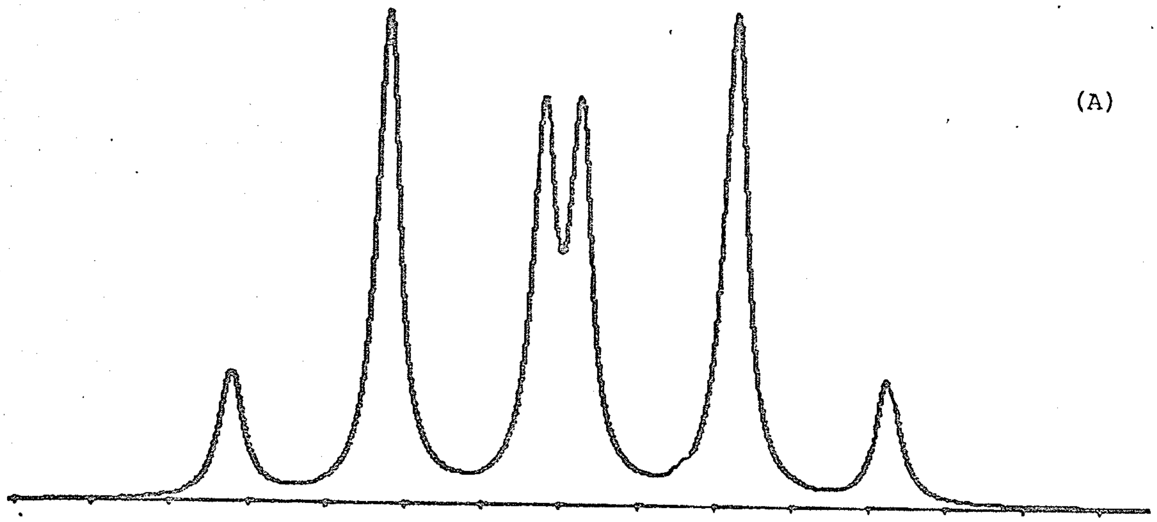
FIGURE (8)

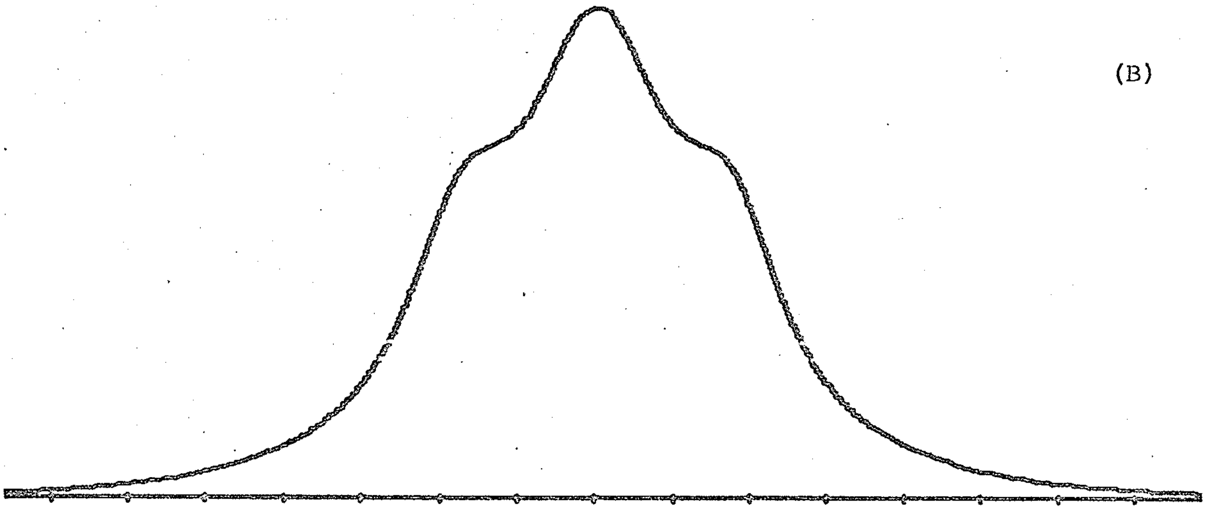
Calculated spectra for the region of A- and B-type transitions for a strongly coupled ABX spin-½ system in which the AB nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AB shift = 10.00 Hz., $J_{AB} = J_{AX} = J_{BX} = 2.00$ Hz., $T_2 = 1.00$ sec.; scale: 1 division = 1 Hertz.

(A) Lifetime = 10. sec.

(B) Lifetime = 1. sec.

(C) Lifetime = 10^{-5} sec.


(A)


(B)

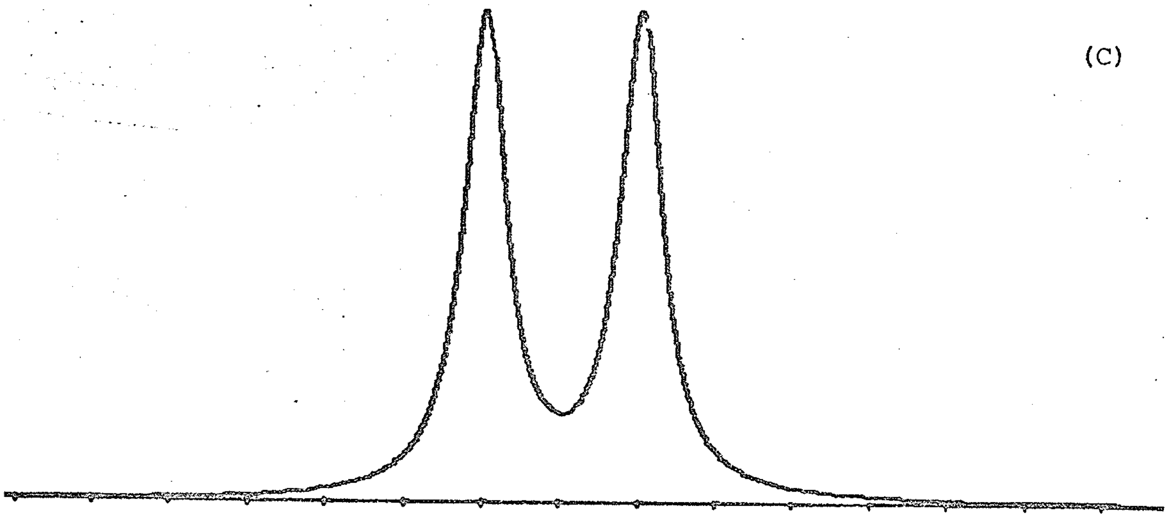

(C)

FIGURE (9a)

Calculated spectra for the region of A- and B-type transitions for an ABX spin-½ system in which the AB nuclei are undergoing intramolecular exchange. Parameters for the spectra are: AB shift = 15.00 Hz., J_{AB} = 2.14 Hz., J_{AX} = 0.50 Hz., J_{BX} = .01 Hz., T_2 = 1.00 sec.; scale: 1 division = 1 Hertz.

(A) Lifetime = 10. sec.

(B) Lifetime = 1. sec.

(C) Lifetime = .1 sec.

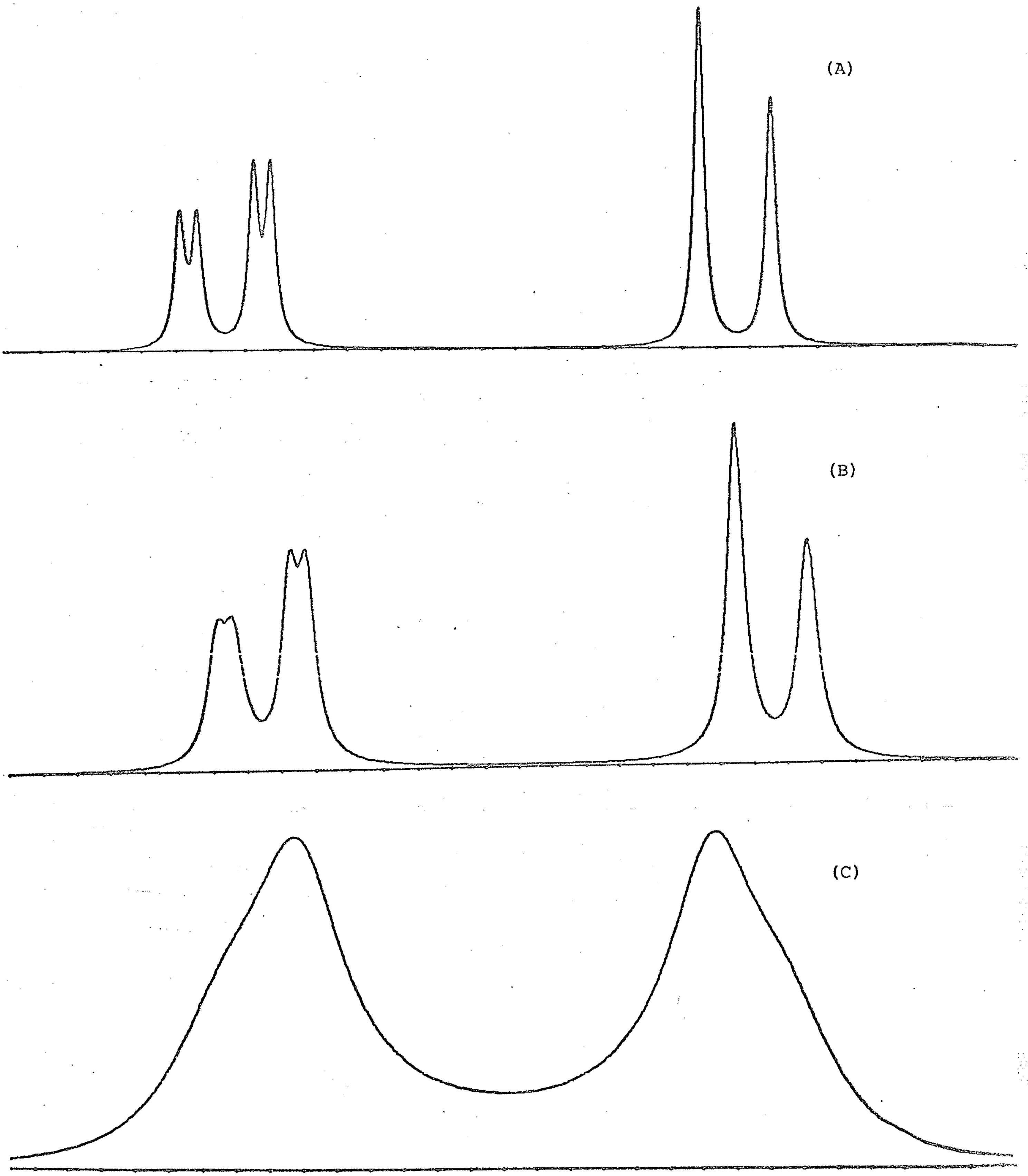
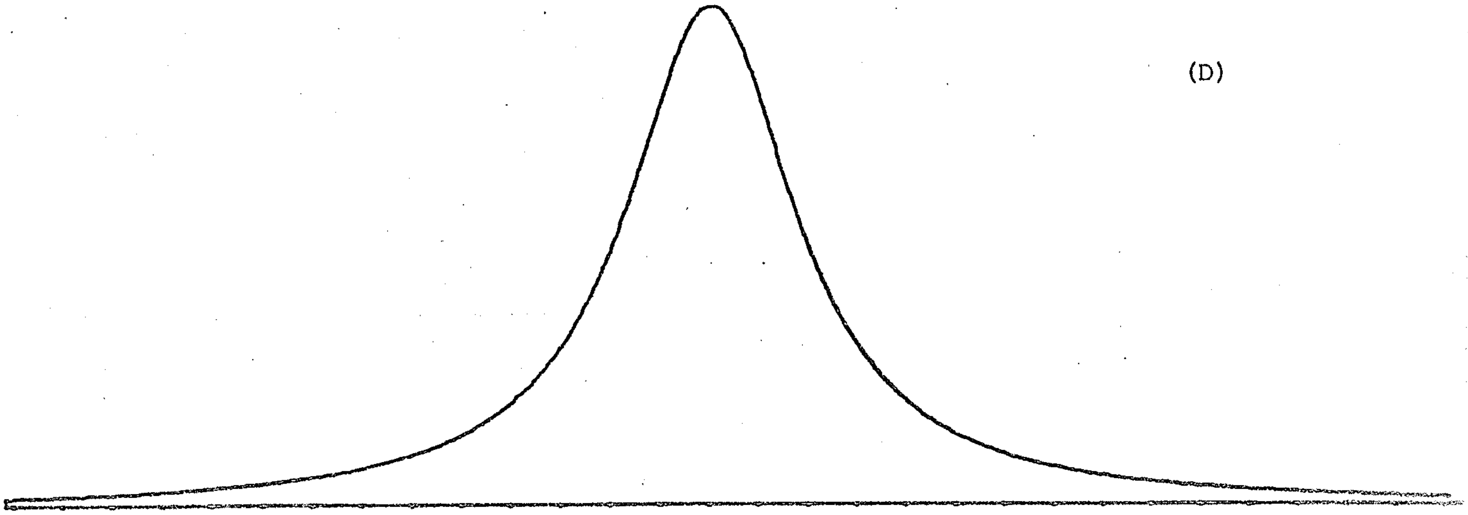

(A)
(B)
(C)

FIGURE (9b)

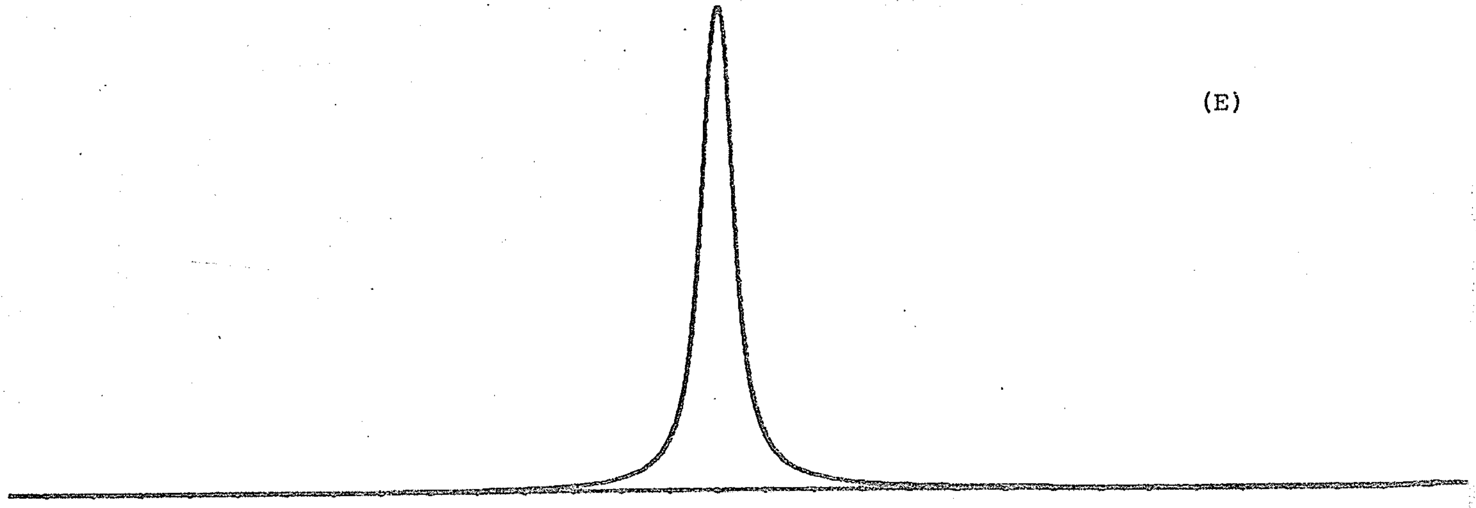
As for Figure (9a)

(D) Lifetime = 10^{-2} sec.

(E) Lifetime = 10^{-5} sec.



(D)



(E)

4. Fitted Experimental Spectra

Analysis of the hindered rotation in 2, 4, 6, α, α-pentachlorotoluene has been made possible by the use of a fit of calculated spectra with the experimental spectra (in the region of A and B transitions) (34). It was assumed that the molecule existed primarily in the two conformations below; in this case the hindered rotation is equivalent to an intramolecular exchange process because the molecular symmetry is conserved in the two conformations.

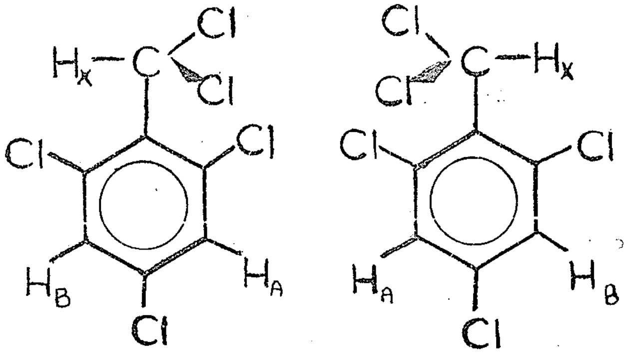


FIGURE (10). The two assumed molecular conformations of 2,4,6, α, α-pentachlorotoluene, arising due to hindered rotation.

In Table (4) there are presented the half-height line widths for the experimental spectra and the calculated spectra (using ABXFIT). These parameters were used to fit the spectra because there is an aromatic solvent induced shift (ASIS) which is temperature-dependent, and consequently the peak positions are not solely dependent on exchange phenomena.

Examples of some of the experimental spectra fitted to the calculated spectra are given in Figure (11). From the Arrhenius equation

$$(129) \qquad k = A\,e^{-E_a/RT} = 1/\tau$$

where k is the rate constant and R the gas constant, it has been calculated that the energy of activation, E_a, for the rotation is 15.2±1.3 kcal/mole for the compound in toluene-d_8 solution (34).

TABLE (4)

Half-height line widths of the experimental spectra of 2, 4, 6,α,α-pentachlorotoluene in toluene-d_8 solution, and of the calculated spectra (using ABXFIT) with the parameters: AB shift = 14.17 Hz.[†], J_{AB} = 2.14 Hz., J_{AX} = 0.52 Hz., J_{BX} = 0.01 Hz., and T_2 = 1.38 seconds (taken from Fuhr (34)).

Shift[†]	T(°C)	τ(sec.)	Calc. Widths[§]	Expt. Widths[§]
12.99	-8.8	.777	1.19 1.03 .52 .69	1.11 1.09 .62 .70
12.62	-3.2	.347	3.93 1.51 1.08 3.61	3.93 1.47 1.09 3.77
12.17	+2.7	.214	4.17 4.02	4.22 3.99
11.48	27.2	.0227	5.81	5.82
11.35	30.3	.0184	4.42	4.43
11.20	34.2	.0157	3.63	3.64
10.57	49.9	.00419	1.14	1.14
10.21	58.8	.00200	0.83	0.83
9.65	72.6	.00071	0.70	0.70

[†] Shift values for short lifetimes obtained by extrapolating a plot of temperature vs. shift (34).

[§] Width values are averages for the calculated widths, or the half-height line width of the smallest peak in a group of overlapping peaks, in Hertz.

FIGURE (11)

Experimental spectra of 2,4,6, α, α-pentachlorotoluene in toluene-d_8 solution fitted to the calculated spectra of an ABX spin-½ system with the parameters: AB shift = 14.17 Hz. (see footnote, Table (4)), J_{AB} = 2.14 Hz., J_{AX} = 0.52 Hz., J_{BX} = 0.01 Hz., and T_2 = 1.38 sec. (after Fuhr, (34)).

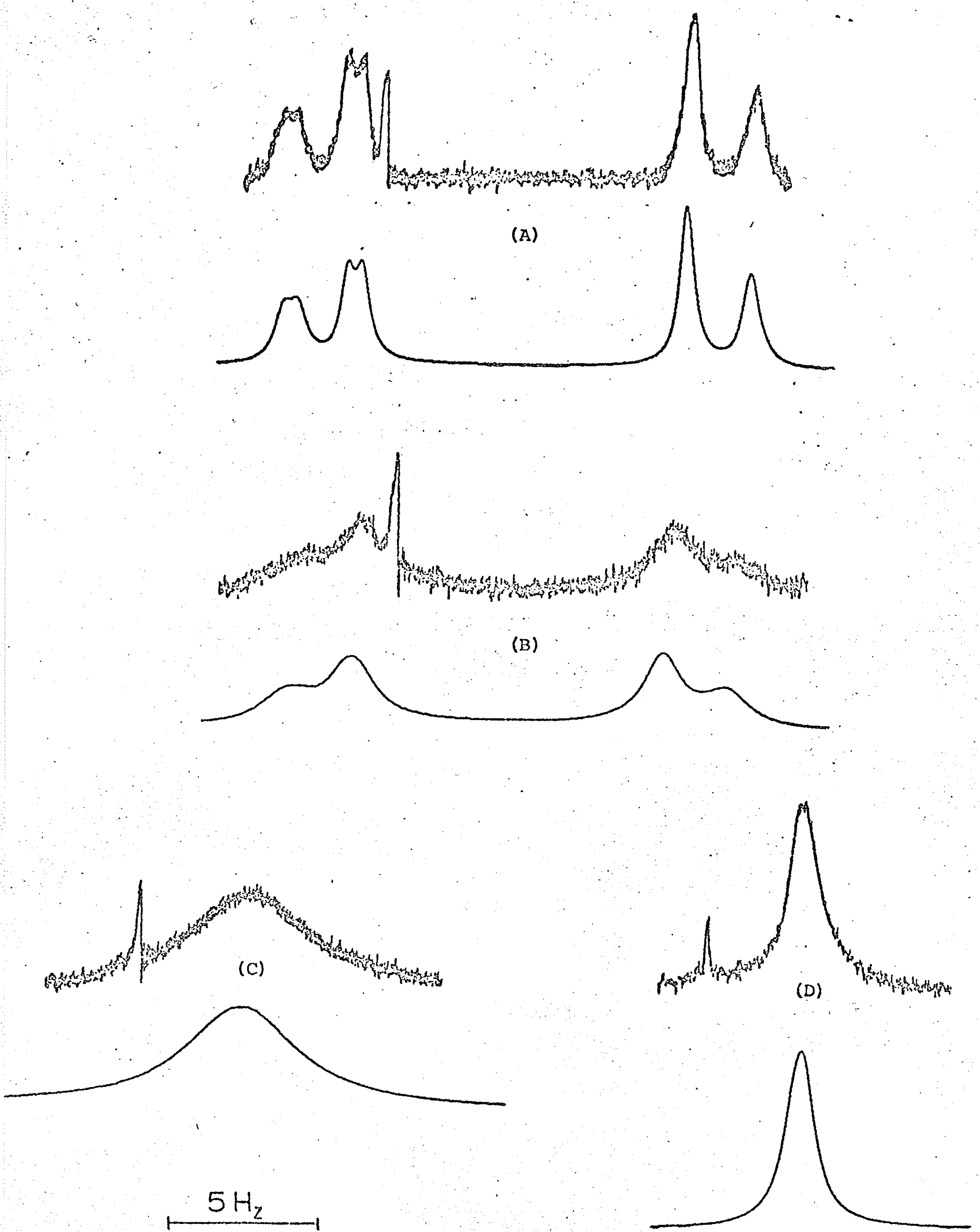
(A) Lifetime = .777 sec., T = -8.8 °C.

(B) Lifetime = .116 sec., T = 2.7 °C.

(C) Lifetime = .0184 sec., T = 30.3 °C.

(D) Lifetime = .00419 sec., T = 49.9°C.

(The sharp peak in all experimental spectra is due to an impurity in the sample).


(A)
(B)
(C)
(D)
5 Hz

Chapter VII

DISCUSSION AND CONCLUSIONS

It appears that the calculated spectra are at least qualitatively correct: at a long lifetime the spectra resemble systems in which there is no discernible exchange occurring[†], and at a short lifetime the spectra resemble systems in which the exchanging nuclei are identical[†] (eg. an AB system undergoing fast exchange resembles an A_2 system; similarly an ABX system resembles an A_2X system). The intermediate regions appear to be a resonable succession of plots from the long-lifetime limit to the short-lifetime limit.

Furthermore, because of the close similarity of an experimental ABX system to a calculated ABX system, it appears that the theory is also quantitatively accurate. It is this latter agreement which lends substantial proOf of the validity of the theory (explicitly for the ABX system, implicitly for the simpler systems discussed).

[†] The fast and slow exchange limits, relative to analysis by n.m.r. techniques, are of the order of 10^5 and 10^{-1} sec.$^{-1}$ respectively.

Chapter VIII

RECOMMENDATIONS FOR FUTURE RESEARCH

The application of density matrix techniques to the analysis of n.m.r. line shapes in the cases of chemical exchange is becoming very popular (22,23,25-31). Newmark and Sederholm (31) for example have applied the theory to, and written a program for an ABX system in which all three nuclei are undergoing intramolecular exchange. More recently, Binsch (35) has written a program which will handle an ABC system; his approach uses the 'Liouville' operator (31) and the density matrix technique. Applications to more complicated spectra are undoubtedly on the way.

Aside from the calculation of line shapes, the density matrix technique has potential in the analysis of high-resolution n.m.r. spectra. Starting from equations (84) and (85), and assuming a basis set consisting of the eigenvectors of the Hamiltonian, it might be possible to correlate a transition with a given element of the density matrix, and thereby determine the parameters of chemical shifts and coupling constants for a given spectrum. If one started from equation (89) instead of (84), the additional information of half-height line widths could be used as data for the analysis.

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APPENDIX I

THE ELEMENTS OF THE DENSITY MATRIX APPEARING IN THE LINE SHAPE EXPRESSIONS

Since I_+ is a strictly upper triangular matrix, one has:

(A1) $(I_+)_{jk} = 0$ for $j \geq k$.

The trace of the matrix product of I_+ with any matrix A is given by:

(A2) $\mathrm{Tr}\,(I_+A) = \sum_j \sum_k (I_+)_{jk}\, A_{kj}$.

The diagonal elements of A appearing in the trace of the product matrix are in terms of the form:

(A3) $(I_+)_{jj}\, A_{jj}$

which is zero because of (A1). Hence the only non-zero terms involving the density matrix appearing in equation (85) or in equation (87) must contain off-diagonal terms only.

APPENDIX II

LISTING OF THE COMPUTER PROGRAMS AND SAMPLE OUTPUT

```
   ABX PUNCH

   AUTHOR:  B.W.GOODWIN

   THIS PROGRAM IS A SUPPLIMENT TO THE MASTERS THESIS OF THE ABOVE
   AUTHOR.  IT WILL CALCULATE THE LINE SHAPE OF THE AB PART OF AN
   ABX SPIN-1/2  (OR SIMPLIER) SYSTEM WHEN (IDENTICAL) AB NUCLEI ARE
   UNDERGOING AN INTRAMOLECULAR EXHANGE AT A CHARACTERISTIC RATE
   1/TAU, USING EQUATION (123) OF THE THESIS.
   OUTPUT IS IN THE FORM OF PUNCHED CARDS WHICH WILL BE READ BY
   ANOTHER PROGRAM, AND PLOTTED ON A CALCOMP PLOTTER.  THE STEP SIZE
   ON THE FREQUENCY AXIS IS VARIABLE; THIS METHOD MINIMIZES PLOT TIME
   WHILE INSURING THAT THE PLOTS REMAIN SMOOTH.

   INPUT IS AS FOLLOWS:
      CARD 1:  J(12), J(13), J(23), SHIFT (12), STARTING FREQUENCY,
               STOPPING FREQUENCY (THESE LATTER TWO PARAMETERS MAY
               BE SET AT + SHIFT (12) AND -SHIFT(12) RESPECTIVELY).
               FORMAT:  6 F10.5  .
      CARD 2:  COMMENT CARD.
               FORMAT:  20 A4.
      CARD 3:  LIFETIME (TAU), NATURAL LINE WIDTH (T2), HEIGHT (IN
               INCHES TO THE NEAREST TENTH) OF THE PLOT REQUIRED,
               SCALE IN HERTZ OF THE PLOT REQUIRED.
               FORMAT:  4 F10.5 .
      CARD 4:  BLANK DENOTING THE END OF SPECTRA WITH THE PARAMETERS
               OF CARD 1, OR CARDS SIMILAR TO CARD 3, UNTIL THE END
               OF THIS SERIES OF SPECTRA.
      CARD 5:  BLANK, DENOTING THE END OF THE JOB, OR A SEQUENCE AS
               ABOVE FROM CARDS 1 TO 4 FOR A NEW SERIES OF SPECTRA.

   THIS ARITHMETIC STATEMENT IS THE GENERAL FORM OF EQUATION (123).
   ABX(A,B,C,D,E,F,G,H)=(A+H*(H*B+C))/(G+H*(F+H*(E+H*(-D+H))))
   DIMENSION D(4), AMP(4), NAME(20)
   INTEGER INDATA /5/, ONPRTR /6/, ONPUN /7/
   PI=3.14159
   PISQ=PI*PI
9 READ (INDATA, 100, END=128) CJAB, CJAX, CJBX, SHIFT, START, STOP
0 FORMAT (6F10.5)
   IF (START.EQ.STOP) GO TO 130
1 READ (INDATA, 102, END=128) NAME
2 FORMAT (20A4)
   THESE ARE THE SUBSTITUTIONS DEFINED IN EQUATION ((106) AND (117)
   EPSLON=0.5*(CJAX+CJBX)
   DEL1=0.25*(SHIFT-CJBX)*(-SHIFT-CJAX)
   DEL2=0.25*(SHIFT+CJBX)*(-SHIFT+CJAX)
3 READ (INDATA, 104, END=128) TAU, T2, YHGHT, SCALE
4 FORMAT (4F10.5)
   IF (TAU.LE.0.0) GO TO 99
5 IF (T2.LE.0.0) T2=1.00
   IF (SCALE.LE.0.0) SCALE=1.0
   THESE ARE THE CONSTANTS IN EQUATION (123)  THE PERMUTATIONS OF THE
   SIGNS OF EPSILON AND J(12) ARE CARRIED IN THESE CONSTANTS.
   FOR EXAMPLE, AA1 HAS J(12)>0, EPSLON>0; AA2 HAS J(12)>0,
   EPSLON<0;  AX1 HAS J(12)<0, EPSLON>0; AX2 HAS J(12)<0, EPSLON<0.
6 TEMP=(1.0/TAU)*(EPSLON*EPSLON+(2.0/(PISQ*T2))*(1.0/TAU+1.0/T2))+
  1(1.0/T2)*(EPSLON*EPSLCN+2.0*CJAB*CJAB+0.5/(PISQ*T2*T2))
   AA1=TEMP-2.0*DEL1*(2.0/TAU+1.0/T2)
```

```
      AA2=AA1-2.0*EPSLON*CJAB/T2
      AA1=AA1+2.0*EPSLON*CJAB/T2
      AX1=TEMP-2.0*DEL2*(2.0/TAU+1.0/T2)
      AX2=AX1+2.0*EPSLON*CJAB/T2
      AX1=AX1-2.0*EPSLON*CJAB/T2
      AB=2.0/T2
      CA1=(2.0/T2)*(-EPSLON-2.0*CJAB)
      CA2=(2.0/T2)*(-EPSLON+2.0*CJAB)
      DA1=2.0*(EPSLON+CJAB)
      DA2=2.0*(EPSLON-CJAB)
      TEMP=CJAB*CJAB     +EPSLON*EPSLON+(1.0/(PISQ*TAU))*(1.0/TAU+1.0/T2
     1)+0.5/(PISQ*T2*T2)
      EA1=TEMP+2.0*DEL1
      EA2=EA1-3.0*EPSLON*CJAB
      EA1=EA1+3.0*EPSLON*CJAB
      EX1=TEMP+2.0*DEL2
      EX2=EX1+3.0*EPSLON*CJAB
      EX1=EX1-3.0*EPSLON*CJAB
      FA1=-2.0*DEL1*EPSLON-EPSLON*CJAB*CJAB-(EPSLON/(PISQ*TAU))*(1.0/
     1TAU+1.0/T2)-0.5*EPSLON/(PISQ*T2*T2)
      FA2=FA1+CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
      FA1=FA1-CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
      FX1=2.0*DEL2*EPSLON+EPSLON*CJAB*CJAB+(EPSLON/(PISQ*TAU))*(1.0/
     1TAU+1.0/T2)+0.5*EPSLON/(PISQ*T2*T2)
      FX2=FX1+CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
      FX1=FX1-CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
      TEMP=EPSLON*EPSLON*(CJAB*CJAB/4.0+(1.0/PISQ)*(0.25/(TAU*TAU)+0.5
     1/(TAU*T2)+0.25/(T2*T2)))+1.0/(PISQ*PISQ*T2*T2)*(1.0/(TAU*TAU)+1.0
     2/(TAU*T2)+1.0/(16.0*T2*T2))+CJAB*CJAB*(0.25/(PISQ*T2*T2))
      GA1=TEMP+DEL1*(DEL1-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
      GA2=GA1-EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
      GA1=GA1+EPSLON*CJAB*(DEL1+C.25/(PISQ*T2*T2))
      GX1=TEMP+DEL2*(DEL2-(1.C/(PISQ*T2))*(1.C/TAU+0.5/T2))
      GX2=GX1+EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
      GX1=GX1-EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
      TMAX IS USED BELOW TO FIND THE HEIGHT OF THE HIGHEST PEAK IN ORDER
      TO SCALE THE PEAKS (THE LARGEST WILL BE 100 UNITS HIGH).  THE
      STEPSIZE IS INITIALIZED AT 0.01, AND THE FREQUENCY AT THE STARTING
      FREQUENCY.
      TMAX=-1.0E49
      STEP=0.01
      DELTA=START
      AMP1=-0.01
      AMP2=0.0
      NOTE THAT THE ARITHMETIC STATEMENT ABX IS CALLED FOUR TIMES:  ONCE
      FOR EACH PERMUTATION OF THE SIGNS OF J(12) AND EPSLON.
 )7   AMP3  =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
     1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
     2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
      IF (AMP2.GT.AMP3.AND.AMP2.GT.AMP1) GO TO 109
      IF A PEAK IS FOUND ROUGHLY, TRANSFER IS MADE TO  STATEMENT 109
 )8   DELTA=DELTA-STEP
      AMP1=AMP2
      AMP2=AMP3
      IF (STOP-DELTA) 107, 107, 116
      THIS PART OF THE PROGRAM LOCATES THE PEAK TO WITHIN AN ACCURACY
      OF 0.0001  HERTZ, AND CALCULATES THE HEIGHT AT THAT FREQUENCY.
```

```
09 IF (AMP1.LT.AMP3) GO TO 110
10 DELTA2=DELTA+STEP
   DELTA1=DELTA2+STEP
   GO TO 112
11 DELTA2=DELTA
   DELTA1=DELTA+STEP
12 PEAK=AMP2
13 IF (ABS(DELTA1-DELTA2).LE.0.0001) GO TO 1151
31 DELT=(DELTA1+DELTA2)/2.0
   TEMP  =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELT )
  1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELT )
  2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELT )
  3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELT )
   IF (PEAK.LT.TEMP) PEAK=TEMP
   DELT=DELT+0.00001
   TEMP2 =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELT )
  1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELT )
  2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELT )
  3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELT )
   IF (TEMP.LT.TEMP2) GO TO 115
14 DELTA1=DELT
   GO TO 113
15 DELTA2=DELT
   GO TO 113
51 IF (PEAK.GT.TMAX) TMAX=PEAK
   GO TO 108
   AT THIS POINT THE SCALING FACTOR FOR THE INTENSITIES
   IS COMPUTED.
16 TMULT=100./TMAX
   OUTPUT PARAMETERS FOR THIS RUN.
   WRITE (UNPRTR,117) NAME, SHIFT, CJAB, CJAX, CJBX, TAU, T2, SCALE,
  1 YHGHT
17 FORMAT (1H1,5X,47H COMPOUND UNDERGOING ABX LINESHAPE ANALYSIS IS
  1/1H ,8X,20A4,////,1H ,5X,18H INPUT PARAMETERS:  ,/1H ,8X,17H CHEMI
  2CAL SHIFT    ,F10.4,5H HTZ.   ,/1H ,8X,5H J12   ,F10.4,5H HTZ. ,/1H ,
  38X,5H J13   ,F10.4,5H HTZ. ,/1H ,8X,5H J23 ,F10.4,5H HTZ. ,/1H ,8X,
  410H LIFETIME   ,F10.6,5H SEC. ,/9X ,20H NATURAL LINE WIDTH   ,F10.4,
  55H SEC. ,/1H       ,8X, 7H SCALE   ,F10.4,9H HTZ./CM.    ,/1H ,8X,
  6 8H HEIGHT     ,F10.4,5H INS.    )
   WRITE (UNPUN,118) SHIFT, CJAB, CJAX, CJBX, TAU, SCALE, START, STOP
  1,YHGHT, T2
18 FORMAT (8F10.5)
   DELTA=START
   INDEX=1
   AMP1=0.0
   NOPUN=0
   CALCULATE AND OUTPUT ON CARDS THE INTENSITY OF THE SIGNAL AS A
   FUNCTION OF FREQUENCY.
19 AMP2  =ABX(AA1,AB,CA1,DA1,EA1,FA1,GA1,DELTA)
  1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
  2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
  3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
   VARIABLE STEP SIZE.  LIMITS 0.1 AND 0.0005 HTZ.
   STEP=ABS(STEP*0.2/(AMP2-AMP1))
   IF (STEP.GT.0.1) STEP =0.1
   IF (STEP.LT.0.0005) STEP =0.0005
   AMP1=AMP2
   D(INDEX)=DELTA
```

```
   AMP(INDEX) = AMP2*TMULT                                               PUNT 175
   INDEX=INDEX+1                                                         PUNT 176
   DELTA=DELTA-STEP                                                      PUNT 177
   IF (INDEX-4) 119, 119, 120                                            PUNT 178
20 WRITE (ONPUN,121) (AMP(INDEX), D(INDEX),INDEX=1,4)                    PUNT 179
21 FORMAT (8F10.5)                                                       PUNT 180
   INDEX=1                                                               PUNT 181
   NOPUN=NOPUN+1                                                         PUNT 182
   IF ((STOP-DELTA).LE.STEF) GO TO 119                                   PUNT 183
22 WRITE (ONPRTR, 123) NOPUN                                             PUNT 184
23 FORMAT (1H ,//,1H ,6X,'NUMBEP OF CARDS PUNCHED:',I5)                  PUNT 185
   WRITE (ONPRTR,124) NAME                                               PUNT 186
24 FORMAT (1H ,///,1H ,5X,30H END OF PUNCHING FOR COMFOUND  /,1H ,8X,PUNT 187
  120A4)                                                                 PUNT 188
   WRITE (ONPUN,125)                                                     PUNT 189
25 FORMAT (1H )                                                          PUNT 190
   GO TO 103                                                             PUNT 191
28 WRITE (ONPRTR, 129)                                                   PUNT 192
29 FORMAT (1H ,20H INPUT DATA BUNGLED     )                              PUNT 193
30 WRITE (ONPRTR, 131)                                                   PUNT 194
31 FORMAT (1H1,20H END OF THIS JOB***    )                               PUNT 195
   CALL EXIT                                                             PUNT 196
   END                                                                   PUNT 197
```

SAMPLE INPUT:

```
2.14      0.50      0.01      14.17     14.00     -14.00
TEST CASE; ABX-TYPE SPECTRA.
1.00      1.00      3.00      1.00
0.000001  1.00      3.00      1.00
```

```
    ABXPLOT

    AUTHOR  B.W.GOODWIN

    THIS PROGRAM READS IN CARDS PUNCHED BY ABXPUNCH AND PLOTS THEM
    ON A CALCOMP PLOTTER. IT IS WRITTEN FOR AN IBM-1620 IN FORTRAN II.
    TWO INTERNAL SUBROUTINES ARE REQUIRED, CHAR AND PLOT.  THEY ARE
    STANDARD SUBROUTINES SUPPLIED BY IBM FOR THE CALCOMP.

    EXCEPT FOR SCALE, START, STOP AND YHGHT THESE PARAMETERS WILL NOT
    BE USED IN ANY COMPUTATION.
 95 READ 96, SHIFT, CJAB, CJAX, CJBX, TAU, SCALE, START, STOP, YHGHT,
   1 T2
 96 FORMAT %5F10.5<
    BLANK CARDS TERMINATES JOB
    IF %TAU< 122, 122, 97
    YHGHT AND SCALE HAVE DEFAULTS OF 4.0 INCHES AND 1.0 HTZ PER CM.
 97 IF %YHGHT< 98, 98, 99
 98 YHGHT#4.0
 99 IF %SCALE< 100, 100, 101
100 SCALE#1.0
    OUTPUT PARAMETERS FOR THIS PLOT.
101 PRINT 102,SHIFT, CJAB, CJAX, CJBX, TAU, SCALE, START, STOP, YHGHT,
   1 T2
102 FORMAT %19H INPUT PARAMETERS.     /7H SHIFT   ,F10.5,/8H J%AB< #   ,
   1F10.5,/8H J%AX< # ,F10.5,/8H J%BX< # ,F10.5,/10H LIFETIME ,F10.5,
   2/8H SCALE # ,F10.5,/8H START # ,F10.5,/8H STOP #   ,F10.5,/8H HEIGH
   3T   ,F10.5,/4H T2# ,F10.5<
    CALCULATE PARAMETERS FOR SETTING UP THE PLOTTER.
    XMIN#- START-.2
    XMAX#-STOP
    XD#XMAX-XMIN
    XLGTH#XD/%2.54*SCALE<
    YHGHT#YHGHT*1.8
    CALL DOWN THE PLOTTER.
    CALL PLOT %201,XMIN,XMAX,XLGTH,XD,0.0,180.,YHGHT,180.0<
    OUTPUT SOME PARAMETERS ON THE GRAPH USING SUBROUTINE CHAR.
    CALL PLOT %9,-START&1.,180.<
    CALL CHAR %2,.1,0,TAU,T2<
104 FORMAT %26H SPECTRA FOR A LIFETIME OF    ,F8.5,27H SEC., AND A LINE
   1WIDTH OF      ,F6.3,5H SEC.   <
    CALL PLOT %9,-START&3.,165.<
    CALL CHAR % 4,.1,0,SHIFT,CJAB,CJAX,CJBX<
105 FORMAT %6H SHIFT    ,F6.2,5H C/S.  ,4H JAB ,F5.2,5H C/S.,4HJAX,F5.2
   1,5H C/S.,4H JBX,F5.2,5H C/S.    <
    CALL PLOT %9,-START&3.,150.<
    CALL CHAR %1,.1,0,SCALE<
106 FORMAT %8H SCALE #  ,F6.2,5H C/S.  <
    PUT IN FREQUENCY AXIS WITH MARKS EVERY SCALE UNITS.
    CALL PLOT %0,-START,0.<
    STEP#-START
107 STEP#STEP&SCALE
    CALL PLOT %0,STEP,0.0<
    IF %STEP& STOP<  107, 107, 108
108 CALL PLOT %99<
    BEGIN PLOTTING
```

```
109 READ 110, AMP1,D1,AMP2,D2,AMP3,D3,AMP4,D4
110 FORMAT %8F10.5<
    BLANK CARD DENOTES END OF THIS RUN.
    IF %D1-D4< 111, 112, 111
111 CALL PLOT %90,-D1,AMP1<
    CALL PLOT %90,-D2,AMP2<
    CALL PLOT %90,-D3,AMP3<
    CALL PLOT %90,-D4,AMP4<
    GO TO 109
112 PRINT 113
113 FORMAT %26H END OF PLOTTING THIS JOB  <
    THIS STATEMENT MOVES THE PEN 3 INCHES FURTHER DOWN THE PAPER IN
    PREPARATION FOR ANOTHER PLOT.
121 CALL PLOT %7<
    GO TO 95
122 PRINT 123
123 FORMAT %13H END OF JOB        <
    STOP
    END
```

```
 ABXGRAF

 AUTHOR:  B.W.GOODWIN

 THIS PROGRAM WILL CALCULATE THE LINE SHAPE OF THE AB PART OF AN
 ABX SPIN-1/2  (OR SIMPLIER) SYSTEM WHEN (IDENTICAL) AB NUCLEI ARE
 UNDERGOING AN INTRAMOLECULAR EXHANGE AT A CHARACTERISTIC RATE
 1/TAU, USING EQUATION (123).
 OUTPUT IS IN THE FORM OF A ROUGH GRAPH PRINTED ON THE 360 LINE
 PRINTER.

 INPUT IS AS FOLLOWS:
    CARD 1:  J(12), J(13), J(23), SHIFT (12), STARTING FREQUENCY,
             STOPPING FREQUENCY (THESE LATTER TWO PARAMETERS MAY
             BE SET AT + SHIFT (12) AND -SHIFT(12) RESPECTIVELY).
             FORMAT:  6 F10.5  .
    CARD 2:  COMMENT CARD.
             FORMAT:  20 A4.
    CARD 3:  LIFETIME (TAU), NATURAL LINE WIDTH (T2), SCALE, STEP
             SIZE OF A SERIES OF RUNS, NUMBER OF RUNS IN THE SERIES
             THE FIRST TWO PARAMETERS ARE IN SECONDS, THE THIRD IN
             HERTZ/CM.  THE LATTER TWO PARAMETERS MAY BE SET TO
             ZERO; OTHERWISE THE PROGRAM WILL OUTPUT A SERIES OF
             GRAPHS AROUND THE LIFETIME SPECIFIED, STARTING AT THE
             LIFETIME GIVEN BY  (LIFETIME-0.5*STEP SIZE) AND GOING
             IN STEPS OF STEP SIZE TO (LIFETIME + 0.5*STEP SIZE).
             FOR EXAMPLE, THE DATA 0.01,1.0,1.0,0.001,20 WIL RESULT
             IN 20 GRAPHS BEGINNING AT .001 AND GOING TO .02 IN
             STEPS OF 0.001 SECONDS.
             THE SCALE PARAMETER OUTPUTS IN HZ ASSUMING 6 LINES/IN
             OUTPUT OF THE LINE PRINTER..
             FORMAT: 3 F10.5, I3
    CARD 4:  BLANK DENOTING THE END OF SPECTRA WITH THE PARAMETERS
             OF CARD 1, OR CARDS SIMILAR TO CARD 3, UNTIL THE END
             OF THIS SERIES OF SPECTRA.
    CARD 5:  BLANK, DENOTING THE END OF THE JOB, OR A SEQUENCE AS
             ABOVE FROM CARDS 1 TO 4 FOR A NEW SERIES OF SPECTRA.
 THIS ARITHMETIC STATEMENT IS THE GENERAL FORM OF EQUATION (123).
 ABX(A,B,C,D,E,F,G,H)=(A+H*(H*B+C))/(G+H*(F+H*(E+H*(-D+H))))
 DIMENSION NAME (20), LINE (101)
 REAL TMAX, AMP, MAG
 INTEGER INDATA /5/, ONPRTR /6/, DOT /'.'/, BLANK /' '/, STAR /'*'/
 PI=3.14159
 PISQ=PI*PI
 LINE(1)=DOT
 DO 98 J=2,101
98 LINE(J)=BLANK
99 READ (INDATA, 100, END=128) CJAB, CJAX, CJBX, SHIFT, START, STOP
00 FORMAT (8F10.5)
 IF (START.EQ.STOP) GO TO 130
 READ (INDATA, 102, END=128) NAME
02 FORMAT (20A4)
 THESE ARE THE SUBSTITUTIONS DEFINED IN EQUATION ((106) AND (117)
 EPSLON=0.5*(CJAX+CJBX)
 DEL1=0.25*(SHIFT-CJBX)*(-SHIFT-CJAX)
 DEL2=0.25*(SHIFT+CJBX)*(-SHIFT+CJAX)
03 READ (INDATA, 104, END=128) TAU, T2, SCALE, STEP1, NCHOP
04 FORMAT (4F10.5,I3)
```

```
   IF (TAU.EQ.0.0) GO TO 99
05 IF (STEP1.LE.0.0) NOHOP=1
   IF (T2.LE.0.0) T2=1.0
   TEMP=(START-STOP)*6./(SCALE*2.54)
   STEP=(START-STOP)/TEMP
   NOSTEP=TEMP+1.5
   SET UP THE LIFETIME IF A SEARCH IS TO BE MADE.
   TAU=TAU-(NOHOP /2)*STEP1
   NO=0
50 IF (NO.GE.NOHOP) GO TO 103
51 TAU=TAU+STEP1
   IF A SEARCH IS TO BE MADE, CHECK THAT NON-POSITIVE VALUES OF THE
   LIFETIME WILL NOT BE ATTEMPTED.
   IF (TAU.GT.0.0) GO TO 106
   WRITE (ONPRTR,1052) TAU, T2, STEP1, NOHOP
52 FORMAT (1H1,22H***ERROR IN INPUT****   ,/5X,23HINPUT PARAMETERS ARE
  1    ,/8X,9HLIFETIME    ,F10.5,9H SECONDS   ,/8X,10HLINEWIDTH    ,F10.5
  2,9H SECONDS   ,/8X,10HSTEP SIZE    ,F10.5,/8X,16HNUMBER OF STEPS    ,
  3I4,//5X,20HREADING IN NEW DATA.     )
   GO TO 103
06 NO=NO+1
   THESE ARE THE CONSTANTS IN EQUATION (123)  THE PERMUTATIONS OF THE
   SIGNS OF EPSILON AND J(12) ARE CARRIED IN THESE CONSTANTS.
   TEMP=(1.0/TAU)*(EPSLON*EPSLON+(2.0/(PISQ*T2))*(1.0/TAU+1.0/T2))+
  1(1.0/T2)*(EPSLON*EPSLON+2.0*CJAB*CJAB+0.5/(PISQ*T2*T2))
   AA1=TEMP-2.0*DEL1*(2.0/TAU+1.0/T2)
   AA2=AA1-2.0*EPSLON*CJAB/T2
   AA1=AA1+2.0*EPSLON*CJAB/T2
   AX1=TEMP-2.0*DEL2*(2.0/TAU+1.0/T2)
   AX2=AX1+2.0*EPSLON*CJAB/T2
   AX1=AX1-2.0*EPSLON*CJAB/T2
   AB=2.0/T2
   CA1=(2.0/T2)*(-EPSLON-2.0*CJAB)
   CA2=(2.0/T2)*(-EPSLON+2.0*CJAB)
   DA1=2.0*(EPSLON+CJAB)
   DA2=2.0*(EPSLON-CJAB)
   TEMP=CJAB*CJAB     +EPSLON*EPSLON+(1.0/(PISQ*TAU))*(1.0/TAU+1.0/T2
  1)+0.5/(PISQ*T2*T2)
   EA1=TEMP+2.0*DEL1
   EA2=EA1-3.0*EPSLON*CJAB
   EA1=EA1+3.0*EPSLON*CJAB
   EX1=TEMP+2.0*DEL2
   EX2=EX1+3.0*EPSLON*CJAB
   EX1=EX1-3.0*EPSLON*CJAB
   FA1=-2.0*DEL1*EPSLON-EPSLON*CJAB*CJAB-(EPSLON/(PISQ*TAU))*(1.0/
  1TAU+1.0/T2)-0.5*EPSLON/(PISQ*T2*T2)
   FA2=FA1+CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
   FA1=FA1-CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
   FX1=2.0*DEL2*EPSLON+EPSLON*CJAB*CJAB+(EPSLON/(PISQ*TAU))*(1.0/
  1TAU+1.0/T2)+0.5*EPSLON/(PISQ*T2*T2)
   FX2=FX1+CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
   FX1=FX1-CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
   TEMP=EPSLON*EPSLON*(CJAB*CJAB/4.0+(1.0/PISQ)*(0.25/(TAU*TAU)+0.5
  1/(TAU*T2)+0.25/(T2*T2)))+1.0/(PISQ*PISQ*T2*T2)*(1.0/(TAU*TAU)+1.0
  2/(TAU*T2)+1.0/(16.0*T2*T2))+CJAB*CJAB*(0.25/(PISQ*T2*T2))
   GA1=TEMP+DEL1*(DEL1-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
   GA2=GA1-EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
   GA1=GA1+EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
```

```
   GX1=TEMP+DEL2*(DEL2-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
   GX2=GX1+EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
   GX1=GX1-EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
    MAX IS USED BELOW TO FIND THE HEIGHT OF THE HIGHEST PEAK IN ORDER
   TO SCALE THE PEAKS (THE LARGEST WILL BE 100 UNITS HIGH).  1
   MAX=-1.0E49
   DELTA=START
   DO 107 J=1,NOSTEP
   AMP   =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
  1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
  2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
  3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
   IF (AMP.GT.MAX) MAX=AMP
   IF (AMP.LT.MIN) MIN=AMP
   DELTA=DELTA-STEP
07 CONTINUE
   MAG IS THE SCALING FACTOR FOR THE INTENSITIES.
08 MAG=100./MAX
09 WRITE (ONPRTR,110) NAME
10 FORMAT (1H1,5X,18H NAME OF COUMPOUND    /,1H ,8X,20A4)
11 WRITE (ONPRTR,112) SHIFT, CJAB, CJAX, CJBX, TAU, T2, SCALE, MAG
12 FORMAT (1H ,8X, 43H INPUT PARAMETERS OF ABX LINE SHAPE GRAPH       ,
  1/1H ,8X,6HSHIFT ,F8.3,5H HTZ.,/1H ,8X,4HJ12  ,F7.3,5H HTZ. ,/1H ,
  28X,4HJ13 ,F7.3,5H HTZ. ,/1H ,8X,4HJ23  ,F7.3,5H HTZ. ,/1H ,8X,
  310HLIFETIME   ,F10.6,9H SECONDS    ,/1H ,8X,4HT2   ,F7.3,9H SECONDS
  4  ,/1H ,8X,6HSCALE  ,F10.5,6H HZ/CM  ,/1H ,8X, 26HINTENSITY SCALIN
  5G FACTOR      ,F15.7,//1H ,100X,10HINTENSITY  ,3X,6HDELTA   )
   CALCULATE AND GRAPH THE SPECTRUM
   DELTA=START
   DO 113 I=1,NOSTEP
   AMP   =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
  1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
  2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
  3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
   AMP=AMP*MAG
   IDIOT=AMP+1.5
   THE FOLLOWING ARE CHECKS FOR ERRORS.
   IF (IDIOT.LT.1) IDIOT=1
   IF (IDIOT.GT.101) IDIOT= 101
   LINE(IDIOT)=STAR
   WRITE (ONPRTR, 1131) (LINE(J),J=1,102), AMP, DELTA
31 FORMAT (1H ,102A1,F9.5,F9.4)
   LINE(IDIOT)=BLANK
   IF (IDIOT.EQ.1) LINE(IDIOT)=DOT
   DELTA=DELTA-STEP
 3 CONTINUE
   GO TO 1050
 8 WRITE (ONPRTR,129)
 9 FORMAT (1H ,15H DATA BUNGLED          )
 0 WRITE (ONPRTR, 131)
 1 FORMAT (1H1,22H **** END OF JOB ****      )
   CALL EXIT
   END
```

SAMPLE INPUT:

```
2.14      0.52      0.01      9.65      10.0      -10.0
ABX SPIN-1/2 SYSTEM.
.00071    1.38      2.0       0.00      0
(blank)
2.14      0.52      0.01      12.99     13.0      -13.0
ABX SPIN-1/2 SYSTEM.
.777      1.38      2.0       0.00      0
```

Sample output using these parameters is shown below (except for the printed values of intensity and frequency).

```
NAME OF COUMPOUND
  ABX SPIN-1/2 SYSTEM.
   INPUT PARAMETERS OF ABX LINE SHAPE GRAPH
  SHIFT     9.650 HTZ.
  J12   2.140 HTZ.
  J13   0.520 HTZ.
  J23   0.010 HTZ.
  LIFETIME    0.000710 SECONDS
  T2    1.380 SECONDS
  SCALE    2.00000 HZ/CM
  INTENSITY SCALING FACTOR         1.1363630
```

```
NAME OF COUMPOUND
   ABX SPIN-1/2 SYSTEM.
    INPUT PARAMETERS OF ABX LINE SHAPE GRAPH
   SHIFT   12.990 HTZ.
   J12   2.140 HTZ.
   J13   0.520 HTZ.
   J23   0.010 HTZ.
   LIFETIME    0.777000 SECONDS
   T2    1.380 SECONDS
   SCALE    2.00000 HZ/CM
   INTENSITY SCALING FACTOR        3.1250000
```

```
ABXFIT

AUTHOR:  D.W.GOODWIN

THIS PROGRAM IS A SUPPLIMENT TO THE MASTERS THESIS OF THE ABOVE
AUTHOR.  IT WILL CALCULATE THE PEAK POSITIONS AND THEIR HALF-
HEIGHT LINE WIDTHS FOR LATER USE IN FITTING EXPERIMENTAL AND
CLACULATED SPECTRA.
THIS PROGRAM MAY BE USED TO FIND THE PEAK POSITIONS AND HALF-
HEIGHT LINE WIDTHS OF AN ARBITRARY FUNCTION.  THE ONE USED HERE
IS DESIGNATED ABX AND GIVES THE LINE SHAPE OF THE AB PART OF AN
ABX N.M.R. SPECTRUM IN WHICH THE AB NUCLEI ARE UNDERGOING AN
EXCHANGE PROCESS .  A MAXIMUM OF TEN PEAKS IS ASSUMED;
HOWEVER CHANGE OF THE DIMENSION STATEMENT WILL INCREASE THIS
FACTOR.

    THE OUTLINE OF THE PROGRAM IS AS FOLLOWS;

  1. RUN THROUGH THE FUNCTION VARYING THE FREQUENCY OR 'X' VALUES
  IN RELATIVELY LARGE STEPS OF FREQUENCY, AND LOCATE THE EXTREMA.
  THE MINIMA ARE FOUND ONLY APPROXIMATELY, WHEREAS THE MAXIMA ARE
  LOCATED TO AN ACCURACY OF 0.001 FREQUENCY UNITS.  THE LOCATION
  OF THE EXTREMA AND THEIR RESPECTIVE HEIGHTS ARE STORED FOR
  LATER USAGE.  FINALLY THE MAXIMUM PEAK IS FOUND IN ORDER TO
  EVALUATE SCALE, A SCALING FACTOR TO BRING THE BIGGEST PEAK TO A
  HEIGHT OF 100.  THIS BRINGS THE PROGRAM TO STATEMENT NUMBER 124

  2. FOR EACH PEAK, THE HALF-HEIGHT IS FOUND ON BOTH SIDES OF THE
  PEAK USING A SERIES OF APPROXIMATIONS FROM THE MINIMA ON BOTH
  SIDES OF THE PEAK.  THE HALF-HEIGHT IS ACCURATE TO AT LEAST
  0.5%.  BOTH HALF-HEIGHT LINE WIDTHS AND THEIR AVERAGE ARE KEPT
  AND LATER OUTPUT.  IF IT HAPPENS THAT TWO OR MORE PEAKS OVER-
  LAP SUCH THAT THE HALF-HEIGHTS OF ONE OR MORE ARE NON-EXISTANT,
  THE HALF-HEIGHT LINE WIDTHS OF THE OVERLAPPING PEAKS IS THEN
  CALCULATED, AND THE HALF-HEIGHT LINE WIDTH(S) IS (ARE) SET
  EQUAL TO 0.0.  HENCE THE OCCURANCE OF A 0.0 FOR A HALF-HEIGHT
  LINE WIDTH IN THE OUTPUT DENOTES AN OVERLAPPING PEAK.  THIS
  SECTION OF THE PROGRAM OPERATES FROM STATEMENTS 1240 TO 137,
  AND THE ACTUAL LINE-WIDTH CALCULATIONS ARE CARRIED OUT IN THE
  AREA STATEMENTS 144 TO 152.

  3. THE HEIGHTS TO BE OUTPUT ARE SCALED BY THE SCALING FACTOR,
  AND THE VALUES FOR THE PEAKS, PEAK-HEIGHTS, BOTH HALF-HEIGHTS
  AND THEIR AVERAGE (IF BOTH HALF-HEIGHTS ARE GREATER THAN 0.0)
  AND THE OVERLAP HEIGHT AND LINE WIDTH  (IF GREATER THAN 0.0)
  ARE OUTPUT.  THIS PART OF THE PROGRAM IS FROM STATEMENTS 137 TO
  144.  CONTROL THEN RETURNS THE PROGRAM TO SEARCH FOR MORE INPUT
  DATA, AND THE PROCEDURE STARTS OVER AGAIN.
ABX(A,B,C,D,E,F,G,H)=(A+H*(H*3+C))/(G+H*(F+H*(E+H*(-D+H))))
REAL          PEAK(10), PEAKHT(10), MIN(10), MINHT(10),
1MEANWD(10), HAFHT1(10), HAFWD1(10), HAFWD2(10), HAFHT2(10),
2OVRLAP(10), OVRHT(10)
REAL MAX, MINI, HEIGHT, WIDTH, HALFHT, MINIHT
INTEGER INDATA /5/, ONPRTR /6/, NOSTEP, SWITCH, NOTRY, NAME(20)
PI=3.14159
PISQ=PI*PI
```

```
      READ IN THE FOLLOWING PARAMETERS: J(AB), J(AX), J(BX), CHEMICAL
     SHIFT BETWEEN THE A AND B PROTONS, AND THE STARTING AND STOPPING
     FREQUENCY THE SEARCH FOR PEAKS IS TO BE OVER.
     FORMAT FOR THIS STATEMENT IS 6F10.5

 99 READ (INDATA,100,END=154) CJAB, CJAX, CJBX, SHIFT, START, STOP
100 FORMAT (6F10.5)
    IF (START.EQ.STOP) GO TO 156

    READ IN SOME COMMENT CARD.
    FORMAT FOR THIS INPUT IS 60A1.
101 READ (INDATA,102,END=154) NAME
 02 FORMAT (20A4)
    WRITE OUT THE HEADING AND THE INPUT PARAMETERS.
    WRITE (UNPRTR,103) NAME, SHIFT, CJAB, CJAX, CJBX
 03 FORMAT (1H1,5X,54H COMPOUND UNDERGOING HALF HEIGHT PEAK WIDTH ANAL
   1YSIS      ,/1H ,9X,20A4,////1H ,5X,20H INPUT PARAMETERS:      ,/1H ,8X
   216H CHEMICAL SHIFT      ,F10.4, 5H C/S.   ,/1H ,8X,5H JAB   ,F10.5,
   35H C/S.   ,/1H ,8X,5H JAX   ,F10.5,5H C/S.  ,/1H ,8X,5H JBX   ,F10.5,
   45H C/S.   ,///)
    EVALUATE SOME OF THE CONSTANTS INVOLVED IN THE ABX EQUATION.
    EPSLON=0.5*(CJAX+CJBX)
    DEL1=0.25*(SHIFT-CJBX)*(-SHIFT-CJAX)
    DEL2=0.25*(SHIFT+CJBX)*(-SHIFT+CJAX)
    READ IN THE PARAMETERS TAU (LIFETIME) AND T2 (NATURAL LINE WIDTH).
    IF STEPSZ IS EQUAL TO ZERO, ONE RUN AT THIS LIFETIME WILL BE
    CARRIED OUT.  OTHERWISE A SEARCH OF LIFETIMES WILL BE MADE ON BOTH
    SIDES OF THE SPECIFIED LIFETIME IN STEPS OF STEPSZ, AND WITH
    NOSTEP/2 STEPS ON EACH SIDE.
    FOR EXAMPLE, A DATA CARD MIGHT SET TAU=.01, STEPSZ=.001 AND NOSTEP
    =20.  THIS WILL RESULT IN 10 SEARCHS ON EACH SIDE OF TAU, IN STEPS
    OF .001 SECONDS AND FROM .001 TO .02 SECONDS.  IT IS IMPORTANT
    THAT TAU NEVER BE NEGATIVE OR EQUAL TO ZERO:  THE COMPUTER WILL
    ASSUME AND ERROR IN THE INPUT AND IGNORE THE DATA.  HENCE IT IS
    ALSO IMPORTANT TO MAKE SURE THAT ANY SEARCH-LIFETIMES ARE GREATER
    THAN ZERO.  IF (TAU-STEPSZ*NOSTEP/2) IS GREATER THAN OR EQUAL TO
    ZERO, NO ERROR MESSAGE WILL OCCUR.  THE USE OF STEPSZ AND NOSTEP
    CAN BE USED EFFECTIVELY TO REDUCE THE NUMBER OF INPUT DATA CARDS,
    AND SAVE PUNCHING TIME.  FOR EXAMPLE TO MAKE A 'GENERAL' RUN OF
    LIFETIMES FROM 0.0001 TO 10 SECONDS, FOUR DATA CARDS WILL SUFFICE:
           1. TAU=.001, STEPSZ=.0001, NOSTEP=20
           2. TAU=.01, STEPSZ=.001, NOSTEP=20
           3. TAU=.1, STEPSZ=.01, NOSTEP=20
           4. TAU=1., STEPSZ=.1, NOSTEP=20.
    AFTER CARRYING OUT THE RUN OR RUNS INDICATED BY THIS DATA CARD,
    CONTROL WILL PASS AGIAIN TO THIS INPUT STATEMENT.  CONSEQUENTLY IF
    IT IS DESIRED TO RUN SEVERAL LIFETIMES (OR LIFETIME SEARCHS),
    SIMPLY INCLUDE THE NEXT DATA CARDS WITH LIFETIME ETC ON IT AS
    ABOVE.  AT THIS STAGE THE PROGRAM CAN BE TERMINATED WITH TWO BLANK
    CARDS OR , IF IT IS DESIRED, MORE RUNS CAN BE MADE WITH DIFFERENT
    VALUE(S) FOR J(AB), AND/OR J(AX), ETC, BY INSERTING ONE BLANK
    CARD AND PUTTING IN A NEW SET OF DATA CARDS AS DONE ABOVE IN
    STATEMENT NUMBER 99.
    FORMAT FOR THIS INPUT IS 3F10.5% I3
  4 READ (INDATA, 105, END=154) TAU, T2, STEPSZ, NOSTEP
```

```
05 FORMAT (3F10.4,I3)
   IF (TAU.LE.0.0) GO TO 99
06 IF (STEPSZ.LE.0.0) GO TO 99
   IF (T2.LE.0) T2=1.0
   SEARCH=0.0
   IF (NOSTEP.GT.1) SEARCH=TAU
   TAU=TAU-(NOSTEP/2)*STEPSZ
   NORUN=0
07 IF (NORUN.GE.NOSTEP) GO TO 104
08 TAU=TAU+STEPSZ
   IF (TAU.GT.0.0) GO TO 111
09 WRITE (UNPRTR,110) TAU, SEARCH, T2, STEPSZ, NOSTEP
10 FORMAT (1H ,40H ***ERROR IN INPUT, TAU NON-POSITIVE.     /1H ,5X,
  118H INPUT PARAMETERS:    ,/1H ,8X,9H LIFETIME  ,F10.5,5H SEC.,/1H ,
  28X, 18H ORIG&NAL L&FETIME  ,F10.5,5H SEC.,/1H ,
  38X,20H NATURAL LINE WIDTH   ,F10.5,5H SEC. /1H ,8X,20H STEP SIZE I
  4N SEARCH  ,F10.4,/1H ,8X,18H NOSTEPS IN SEARCH  ,I3,1H ,5X,21H REA
  5DING IN NEW DATA.    )
   GO TO 104
11 NORUN=NORUN+1
   CALCULATE CONSTANTS INVOLVED IN THE ABX EQUATION.
   TEMP=(1.0/TAU)*(EPSLON*EPSLON+(2.0/(PISQ*T2))*(1.0/TAU+1.0/T2))+
  1(1.0/T2)*(EPSLON*EPSLON+2.0*CJAB*CJAB+0.5/(PISQ*T2*T2))
   AA1=TEMP-2.0*DEL1*(2.0/TAU+1.0/T2)
   AA2=AA1-2.0*EPSLON*CJAB/T2
   AA1=AA1+2.0*EPSLON*CJAB/T2
   AX1=TEMP-2.0*DEL2*(2.0/TAU+1.0/T2)
   AX2=AX1+2.0*EPSLON*CJAB/T2
   AX1=AX1-2.0*EPSLON*CJAB/T2
   AB=2.0/T2
   CA1=(2.0/T2)*(-EPSLON-2.0*CJAB)
   CA2=(2.0/T2)*(-EPSLON+2.0*CJAB)
   DA1=2.0*(EPSLON+CJAB)
   DA2=2.0*(EPSLON-CJAB)
   TEMP=CJAB*CJAB     +EPSLON*EPSLON+(1.0/(PISQ*TAU))*(1.0/TAU+1.0/T2
  1)+0.5/(PISQ*T2*T2)
   EA1=TEMP+2.0*DEL1
   EA2=EA1-3.0*EPSLON*CJAB
   EA1=EA1+3.0*EPSLON*CJAB
   EX1=TEMP+2.0*DEL2
   EX2=EX1+3.0*EPSLON*CJAB
   EX1=EX1-3.0*EPSLON*CJAB
   FA1=-2.0*DEL1*EPSLON-EPSLON*CJAB*CJAB-(EPSLON/(PISQ*TAU))*(1.0/
  1TAU+1.0/T2)-0.5*EPSLON/(PISQ*T2*T2)
   FA2=FA1+CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
   FA1=FA1-CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
   FX1=2.0*DEL2*EPSLON+EPSLON*CJAB*CJAB+(EPSLON/(PISQ*TAU))*(1.0/
  1TAU+1.0/T2)+0.5*EPSLON/(PISQ*T2*T2)
   FX2=FX1+CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
   FX1=FX1-CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
   TEMP=EPSLON*EPSLON*(CJAB*CJAB/4.0+(1.0/PISQ)*(0.25/(TAU*TAU)+0.5
  1/(TAU*T2)+0.25/(T2*T2)))+1.0/(PISQ*PISQ*T2*T2)*(1.0/(TAU*TAU)+1.0
  2/(TAU*T2)+1.0/(16.0*T2*T2))+CJAB*CJAB*(0.25/(PISQ*T2*T2))
   GA1=TEMP+DEL1*(DEL1-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
   GA2=GA1-EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
   GA1=GA1+EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
```

```
    GX1=TEMP+DEL2*(DEL2-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
    GX2=GX1+EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
    GX1=GX1-EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
    TMAX=-1.0E49
    PEAK(1)=0.0
    PEAKHT(1)=0.0
    MIN(1)=START
    MINHT(1)=0.0
    MEANWD(1)=0.0
    BEGIN THE SEARCH FOR THE EXTREMA.
    STEP=0.05
    DELTA=START
    INDEX=1
    AMP1=-0.01
    AMP2=0.0
 12 AMP3  =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
   1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
   2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
   3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
    TEST FOR A PEAK.
    IF (AMP2.GT.AMP1.AND.AMP2.GT.AMP3) GO TO 116
    TEST FOR A MINIMUM.

 13 IF (AMP2.LT.AMP3.AND.AMP2.LT.AMP1) GO TO 115
 14 DELTA=DELTA-STEP
    AMP1=AMP2
    AMP2=AMP3
    IF (STOP-DELTA) 112, 112, 125
    STORE MINIMUM AND MIMIMUM HEIGHT.
 15 MIN(INDEX)=DELTA+STEP
    MINHT(INDEX)=AMP2
    GO TO 114
    FIND PEAK MORE EXACTLY, AND STORE PEAK AND PEAK HEIGHT.
 16 IF (AMP1.LE.AMP3) GO TO 118
 17 DELTA2=DELTA+STEP
    DELTA1=DELTA2+STEP
    GO TO 119
 18 DELTA2=DELTA
    DELTA1=DELTA+STEP
 19 PEEK=AMP2
    COORD=DELTA+STEP
    DELT1=1.0E49
 90 DELT=(DELTA1+DELTA2)/2.0
    TEST TO SEE IF PEAK IS DETERMINED WITHIN.001 UNITS.

    IF (ABS(DELT1-DELT).LT.0.0001) GO TO 1240
 91 DELT1=DELT
    TEMP=ABX(AA1,AB,CA1,DA1,EA1,FA1,GA1,DELT)
   1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELT )
   2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELT )
   3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELT )
    IF (PEEK.GT.TEMP) GO TO 121
 20 PEEK=TEMP
    COORD=DELT
 21 TEMP2 =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELT+.0001)
   1+ABX(AA2,AB,CA2,DA2,EA2,FA2,GA2,DELT+.0001)
```

```
  2+ABX(AX1,AB,-CA2,-DA2,EX1,FX1,GX1,DELT+.0001)                        FIT 225
  3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELT+.0001)                 FIT 226
   IF (TEMP.LT.TEMP2) GO TO 123                                         FIT 227
22 DELTA1=DELT                                                          FIT 228
   GO TO 1190                                                           FIT 229
23 DELTA2=DELT                                                          FIT 230
24 GO TO 1190                                                           FIT 231
40 PEAKHT(INDEX)=PEEK                                                   FIT 232
   PEAK(INDEX)=COORD                                                    FIT 233
   INDEX=INDEX+1                                                        FIT 234
   TEST TO OBTAIN THE LARGEST PEAK.                                     FIT 235
   IF (PEEK.GT.TMAX) TMAX=PEEK                                          FIT 236
   GO TO 114                                                            FIT 237
   AT THIS POINT ALL EXTREMA WITH THE LIMITS SET HAVE BEEN FOUND.       FIT 238
25 MIN(INDEX)=STOP                                                      FIT 239
   MINHT(INDEX)=0.0                                                     FIT 240
   EVALUATE THE SCALING FACTOR.                                         FIT 241
   SCALE=100./TMAX                                                      FIT 242
   NOPEAK=INDEX-1                                                       FIT 243
   J=0                                                                  FIT 244
   INDEX=1                                                              FIT 245
   BEGIN THE SEARCH FOR HALF-HEIGHT LINE WIDTHS.                        FIT 246
26 HALFHT=PEAKHT(INDEX)/2.0                                             FIT 247
   MAX=PEAK(INDEX)                                                      FIT 248
   SEARCH THE LEFT-HAND SIDE OF THE PEAK.                               FIT 249
   MINIHT=MINHT(INDEX)                                                  FIT 250
   MINI=MIN(INDEX)                                                      FIT 251
   SWITCH=1                                                             FIT 252
                                                                        FIT 253
   STATEMENTS 144 AND ON ARE INVLOLVED IN THE ACTUAL SEARCH FOR THE WFIT 254
                                                                        FIT 255
   GO TO 144                                                            FIT 256
27 HAFHT1(INDEX)=HEIGHT                                                 FIT 257
   HAFWD1(INDEX)=WIDTH                                                  FIT 258
   SEARCH THE RIGHT-HAND SIDE OF THE PEAK.                              FIT 259
28 MAX=PEAK(INDEX)                                                      FIT 260
   MINI=MIN(INDEX+1)                                                    FIT 261
   MINIHT=MINHT(INDEX+1)                                                FIT 262
   SWITCH=2                                                             FIT 263
   GO TO 144                                                            FIT 264
29 HAFHT2(INDEX)=HEIGHT                                                 FIT 265
   HAFWD2(INDEX)=WIDTH                                                  FIT 266
   CHECK LINE-WIDTHS.  IF ONE OR BOTH ARE ZERO, OVERLAP HAS OCCURED.    FIT 267
   IF (HAFWD1(INDEX).EQ.0.0.OR.HAFWD2(INDEX).EQ.0.0) GO TO 1302         FIT 268
   AVERAGE THE LINE-WIDTHS.                                             FIT 269
00 MEANWD(INDEX)=0.5*(HAFWD1(INDEX)+HAFWD2(INDEX))                      FIT 270
   OVRLAP(INDEX)=0.0                                                    FIT 271
   OVRHT(INDEX)=0.0                                                     FIT 272
   CHECK TO SEE IF A PREVIOUS PEAK HAS OVERLAPPED.  IF SO FIND THE      FIT 273
   TOTAL LINE WIDTH AT THE LOWER HALF-HEIGHT.                           FIT 274
   IF (J.GT.0.AND.MINHT(INDEX+1).LT.(HAFHT1(J)/2.0)) GO TO 1307         FIT 275
01 GO TO 136                                                            FIT 276
                                                                        FIT 277
   AT THIS POINT THERE HAS BEEN OVERLAP DETECTED.                       FIT 278
                                                                        FIT 279
02 MEANWD(INDEX)=0.0                                                    FIT 280
```

```
    IF (J.EQ.0) J=INDEX                                               FIT 281
    OVRHT(INDEX)=0.0                                                  FIT 282
    OVRLAP(INDEX)=0.0                                                 FIT 283
    CHECK TO SEE IF THE FINAL PEAK IN THE OVERLAP HAS BEEN ENCOUNTEREDFIT 284
 03 IF (HAFWD2(INDEX).EQ.0.0) GO TO 136                               FIT 285
    IF NOT, GO ON TO THE NEXT PEAK.  IF SO, CALCULATE THE OVERLAP     FIT 286
    WIDTH.                                                            FIT 287
 04 IF (J.NE.INDEX) GO TO 1307                                        FIT 288
 05 J=J-1                                                             FIT 289
    IF (MINHT(J).LT.(PEAKHT(INDEX)/2.0)) GO TO 1307                   FIT 290
 06 IF (J-1) 152, 152, 1305                                           FIT 291
    CHECK TO SEE WHICH OF THE OVERLAPPING PEAKS IS LOWEST, AND USE ITSFIT 292
    HALF-HEIGHT AT THE OTHER PEAK.                                    FIT 293
 07 IF (PEAKHT(J).GT.PEAKHT(INDEX)) GO TO 1331                        FIT 294
    THE FIRST PEAK IS LOWEST.                                         FIT 295
 21 MAX=PEAK(INDEX)                                                   FIT 296
    MINI=MIN(INDEX+1)                                                 FIT 297
    MINIHT=MINHT(INDEX+1)                                             FIT 298
 24 HALFHT=PEAKHT(J)/2.0                                              FIT 299
 25 SWITCH=3                                                          FIT 300
    GO TO 144                                                         FIT 301
 33 OVRHT(INDEX)=HEIGHT                                               FIT 302
    OVRLAP(INDEX)=WIDTH                                               FIT 303
    OVRLAP(INDEX)=0.5*(OVRLAP(INDEX)+HAFWD1(J))+ABS(PEAK(J)-          FIT 304
   1PEAK(INDEX))                                                      FIT 305
    GO TO 135                                                         FIT 306
    THE LAST PEAK IS LOWEST.                                          FIT 307
 31 MAX=PEAK(J)                                                       FIT 308
    MINI=MIN(J)                                                       FIT 309
    MINIHT=MINHT(J)                                                   FIT 310
    HALFHT=PEAKHT(INDEX)/2.0                                          FIT 311
    SWITCH=4                                                          FIT 312
    GO TO 144                                                         FIT 313
 34 OVRHT(INDEX)=HEIGHT                                               FIT 314
    OVRLAP(INDEX)=WIDTH                                               FIT 315
    OVRLAP(INDEX)=0.5*(OVRLAP(INDEX)+HAFWD2(INDEX))+ABS(PEAK(J)-      FIT 316
   1PEAK(INDEX))                                                      FIT 317
 35 J=0                                                               FIT 318
 36 INDEX=INDEX+1                                                     FIT 319
    CHECK TO SEE IF ALL THE PEAKS HAVE BEEN PROCESSED.                FIT 320
    IF (INDEX.LE.NOPEAK) GO TO 126                                    FIT 321
    SCALE ALL THE PEAKS.                                              FIT 322
 37 DO 138 J=1,NOPEAK                                                 FIT 323
    PEAKHT(J)=PEAKHT(J)*SCALE                                         FIT 324
    HAFHT1(J)=HAFHT1(J)*SCALE                                         FIT 325
    HAFHT2(J)=HAFHT2(J)*SCALE                                         FIT 326
    OVRHT(J)=OVRHT(J)*SCALE                                           FIT 327
 38 CONTINUE                                                          FIT 328
    OUTPUT LIFETIME, NATURAL LINE WIDTH AND HEADINGS.                 FIT 329
    WRITE (ONPRTR,1390)                                               FIT 330
 90 FORMAT (1H ,///)                                                  FIT 331
    IF (SEARCH.GT.0.0) WRITE (ONPRTR,1392) SEARCH                     FIT 332
 92 FORMAT (1H ,5X,'STEPPING AROUND TAU =',F15.7,' SEC.')             FIT 333
    WRITE (ONPRTR,1391) TAU, T2                                       FIT 334
 91 FORMAT (1H ,8X,'***TAU =',F15.7,' SEC.***',/1H ,8X,'NAT. LINE WIDTFIT 335
   1H =',F10.5,' SEC.', /                                             FIT 336
```

```
  2           1H ,15X,10H PEAK AT    ,6X,7H HEIGHT  ,12X,12H HALF HEIGFIT 337
  3HT   ,13X,6H WIDTH ,12X,14H AVERAGE WIDTH    )                     FIT 338
    DO 143 J=1,NOPEAK                                                 FIT 339
    OUTPUT PEAK LOCATION, PEAK HEIGHT, HALF-HEIGHT LINE WIDTHS AND    FIT 340
    HEIGHTS FROM BOTH SIDES OF THE PEAK.                              FIT 341
    WRITE (ONPRTR,140) PEAK(J), PEAKHT(J), HAFHT1(J), HAFWD1(J),      FIT 342
   1 HAFHT2(J), HAFWD2(J)                                             FIT 343
40 FORMAT (10X,F7.3,4H C/S ,8X,F7.3,17X,F7.3,8X,F7.3,4H C/S ,/        FIT 344
  153X,F7.3,8X,F7.3,4H C/S   )                                        FIT 345
                                                                      FIT 346
    OUTPUT AVERAGE OF HALF-HEIGHT LINE-WIDTHS IF IT EXISTS (IT IS 'NONFIT 347
    EXISTANT IF ONE OR BOTH LINE WIDTHS IS ZERO).                     FIT 348
                                                                      FIT 349
    IF (MEANWD(J).GT.0.0) WRITE (ONPRTR,141) MEANWD(J)                FIT 350
41 FORMAT (1H+,93X,F7.3,5H C/S.   )                                   FIT 351
    OUTPUT OVERLAP LINE WIDTH AND HEIGHT IF IT EXISTS.                FIT 352
    IF (OVRLAP(J).GT.0.0) WRITE (ONPRTR,142) OVRHT(J), OVRLAP(J)      FIT 353
42 FORMAT (1H ,15X,47H LINE WIDTH OF OVERLAPPING PEAKS AT A HEIGHT OFFIT 354
  1   ,F7.3,4H IS   ,F7.3,8H C/S.***    )                             FIT 355
43 CONTINUE                                                           FIT 356
    RETURN CONTROL TO EITHER CONTINUE SEARCH OR READ IN NEW LIFETIMES.FIT 357
    GO TO 107                                                         FIT 358
                                                                      FIT 359
                                                                      FIT 360
    THIS SECTION OF THE PROGRAM FINDS THE HALF-HEIGHTS LINE WIDTHS.   FIT 361
    CHECK TO SEE IF A HALF-HEIGHT EXISTS.  IF NOT, SET THE LINE WIDTH FIT 362
    EQUAL TO ZERO.                                                    FIT 363
44 IF (MINIHT.LT.HALFHT) GO TO 146                                    FIT 364
45 HEIGHT=0.0                                                         FIT 365
    WIDTH=0.0                                                         FIT 366
    GO TO (127, 129, 133, 134), SWITCH                                FIT 367
    THE HALF-HEIGHT IS FOUND TO WITHIN THIS ERROR, AT LEAST .5%.      FIT 368
46 ERROR=HALFHT/500.                                                  FIT 369
    NOTRY=0                                                           FIT 370
    DELTA1=MINI                                                       FIT 371
    DELTA2=MAX                                                        FIT 372
47 DELTA=(DELTA1+DELTA2)/2.0                                          FIT 373
    AMP    =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)               FIT 374
   1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)                     FIT 375
   2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)                   FIT 376
   3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)                   FIT 377
    CHECK TO SEE IF THE HALF-HEIGHT IS KNOWN WITHIN THE ERROR LIMITS. FIT 378
    IF (ABS(AMP-HALFHT).LT.ERROR) GO TO 151                           FIT 379
80 NOTRY=NOTRY+1                                                      FIT 380
    GIVE UP AFTER 250 TRIES IF A HALF-HEIGHT CANNOT BE FOUND.         FIT 381
    IF (NOTRY.GT.200) GO TO 152                                       FIT 382
81 IF (AMP.GT.HALFHT) GO TO 150                                       FIT 383
49 DELTA1=DELTA                                                       FIT 384
    GO TO 147                                                         FIT 385
50 DELTA2=DELTA                                                       FIT 386
    GO TO 147                                                         FIT 387
51 HEIGHT=AMP                                                         FIT 388
    WIDTH=ABS(DELTA-MAX)*2.0                                          FIT 389
    RETURN BACK TO THE MAIN SECTION OF THE PROGRAM.                   FIT 390
    GO TO (127, 129, 133, 134), SWITCH                                FIT 391
                                                                      FIT 392
```

```
                                                                                         FIT 393
                                                                                         FIT 394
   THIS SECTION CONTAINS SOME ERROR STATEMENTS                                           FIT 395
52 WRITE (UNPRTR,153)                                                                    FIT 396
53 FORMAT (1H ,//,1H ,12H***ERROR***    ,/1H ,5X,47H LARGE LOOP ENCOUNFIT 397
  1TERED IN HALF HEIGHT SEARCH.    /1H ,61H VALUES BELOW ARE INCORRECFIT 398
  2T; ERROR IS PROBABLY IN THE METHOD        )                                          FIT 399
   GO TO 151                                                                             FIT 400
54 WRITE (UNPRTR,155)                                                                    FIT 401
55 FORMAT (1H ,///1H ,14H ***WARNING***  /,1H ,5X,52H CHECK DATA: THEFIT 402
  1COMPUTOR IS LOOKING FOR MORE INPUT                         )                          FIT 403
56 WRITE (UNPRTR,157)                                                                    FIT 404
57 FORMAT (1H ,////,1H ,10X, 18H ***END OF JOB***       )                                FIT 405
   CALL EXIT                                                                             FIT 406
   END
```

```
      SAMPLE INPUT:

4         0.50      0.01       14.17       14.         -14.
T CASE; ABX-TYPE SPECTRA.
          1.         0.1       10
1         1.         0.001     10
```

Some of the output from these parameters are given below.

```
COMPOUND UNDERGOING HALF HEIGHT PEAK WIDTH ANALYSIS
   TEST CASE; ABX-TYPE SPECTRA.


INPUT PARAMETERS:
   CHEMICAL SHIFT    14.1700 C/S.
   JAB     2.14000 C/S.
   JAX     0.50000 C/S.
   JBX     0.01000 C/S.



STEPPING AROUND TAU =      1.0000000 SEC.
   ***TAU =       0.6000001 SEC.***
   NAT. LINE WIDTH =   1.00000 SEC.
         PEAK AT              HEIGHT                      HALF HEIGHT               WIDTH                 AVERAGE WIDTH
     8.137 C/S            49.112                       24.548           1.454 C/S
                                                       24.581           1.523 C/S                  1.489 C/S.
     6.225 C/S            72.132                       36.118           1.025 C/S
                                                        0.0             0.0   C/S
     5.952 C/S            72.304                        0.0             0.0   C/S
                                                       36.174           0.976 C/S
         LINE WIDTH OF OVERLAPPING PEAKS AT A HEIGHT OF 36.057 IS   1.275 C/S.***
    -6.087 C/S           100.000                       49.926           0.806 C/S
                                                       49.907           0.804 C/S                  0.805 C/S.
    -8.216 C/S            62.007                       30.975           1.064 C/S
                                                       30.976           0.935 C/S                  0.999 C/S.
```

```
STEPPING AROUND TAU =        1.0000000 SEC.
   ***TAU =        1.4999971 SEC.***
   NAT. LINE WIDTH =    1.00000 SEC.
          PEAK AT            HEIGHT                        HALF HEIGHT                WIDTH                         AVERAGE WIDTH
     8.464 C/S           41.701                              20.887            0.627 C/S
                                                               0.0             0.0   C/S
     8.019 C/S           42.402                                0.0             0.0   C/S
                                                             21.163            0.682 C/S
          LINE WIDTH OF OVERLAPPING PEAKS AT A HEIGHT OF 20.849 IS    1.084 C/S.***
     6.320 C/S           61.032                              30.552            0.560 C/S
                                                               0.0             0.0   C/S
     5.866 C/S           61.166                                0.0             0.0   C/S
                                                             30.537            0.550 C/S
          LINE WIDTH OF OVERLAPPING PEAKS AT A HEIGHT OF 30.537 IS    1.010 C/S.***
    -6.087 C/S          100.000                              50.000            0.496 C/S
                                                             50.074            0.517 C/S                    0.507 C/S.
    -8.225 C/S           66.060                              33.017            0.572 C/S
                                                             33.028            0.579 C/S                    0.576 C/S.



STEPPING AROUND TAU =        0.0100000 SEC.
   ***TAU =        0.0060000 SEC.***
   NAT. LINE WIDTH =    1.00000 SEC.
          PEAK AT            HEIGHT                        HALF HEIGHT                WIDTH                         AVERAGE WIDTH
    -0.013 C/S          100.000                              49.974            2.374 C/S
                                                             49.999            2.336 C/S                    2.355 C/S.



STEPPING AROUND TAU =        0.0100000 SEC.
   ***TAU =        0.0070000 SEC.***
   NAT. LINE WIDTH =    1.00000 SEC.
          PEAK AT            HEIGHT                        HALF HEIGHT                WIDTH                         AVERAGE WIDTH
    -0.011 C/S          100.000                              49.940            2.696 C/S
                                                             49.951            2.664 C/S                    2.680 C/S.
```

```
  ABXGEN

  ABX(A,B,C,D,E,F,G,H)=(A+H*(H*B+C))/(G+H*(F+H*(E+H*(-D+H))))
  REAL PEAK(10), PEAKHT(10), MIN(10), MINHT(10), D(4), AAA(4),
 1MEANWD(10), HAFHT1(10), HAFWD1(10), HAFWD2(10), HAFHT2(10),
 2OVRLAP(10), OVRHT(10), MAX, MINT, HEIGHT, WIDTH, HALFHT, MINIHT
  INTEGER LINE(101), DOT /'.'/, BLANK /' '/, STAR /'*'/, FIT /'F'/,
 1PUNCH /'P'/, INDATA  /5/, ONPRTR /6/, ONPUN /7/, I, J, SWITCH,
 2NOTRY, NOPTS, IDICT, OUTPUT, NAME(20)

  THIS PROGRAM IS A CONGLOMERATION OF ABXPUNCH, ABXGRAF, AND ABXFIT.

  LINE(1)=DOT
  DO 98 J=2,102
98 LINE(J)=BLANK
  PI=3.14159
  PISQ=PI*PI
  THE VARIABLE OUTPUT CONTAINS THE TYPE OF DESIRED OUTPUT:
  PUNCHED CARDS OR PRINTED DATA.  THE FIRST CARD WILL HAVE ON IT
  "F" FOR FITTING AND A "*" GRAPH OUTPUT, OR "P" FOR PUNCHED CARDS.
                                 THEREAFTER, INPUT IS MUCH THE
  SAME AS ABXFIT.
  READ IN THE PARAMETERS:  OUTPUT, J(12), J(13),, J(23), AB SHIFT,
  THE STARTING AND STOPPING FREQUENCIES THE RUN IS TO BE MADE OVER.
  IF THE STARTING AND STOPPING FREQUENCIES ARE EQUAL, THE RUN IS
  TERMINATED.
99 READ (INDATA, 100, END=174)  OUTPUT, CJAB, CJAX, CJBX, SHIFT,
 1 START, STOP
100 FORMAT (A1,9X,6F10.5)
  IF (START.EQ.STOP) GO TO 176
101 IF (SCALE1.LE.0.0) SCALE1=0.5
  IF (OUTPUT.EQ.BLANK) OUTPUT=FIT
  NOPTS=(START-STOP)*6.0/(SCALE1*2.54)
  STEP1=(START-STOP)/NOPTS
  READ IN SOME COMMENT
  FORMAT FOR THIS INPUT IS 60A1.
  READ (INDATA,102,END=174) NAME
102 FORMAT (20A4)
  WRITE OUT THE HEADING AND THE INPUT PARAMETERS.
  WRITE (ONPRTR,103) NAME, SHIFT, CJAB, CJAX, CJBX, OUTPUT
103 FORMAT (1H1,5X,54H COMPOUND UNDERGOING HALF HEIGHT PEAK WIDTH ANAL
 1YSIS    ,/1H ,8X,20A4,////1H ,5X,20H INPUT PARAMETERS:     ,/1H ,8X
 216H CHEMICAL SHIFT    ,F10.4, 5H C/S.  ,/1H ,8X,5H JAB  ,F10.5,
 35H C/S.  ,/1H ,8X,5H JAX  ,F10.5,5H C/S. ,/1H ,8X,5H JBX  ,F10.5,
 45H C/S.  ,/1H ,8X,9H OUTPUT:   ,A1)
  EVALUATE SOME OF THE CONSTANTS INVOLVED IN THE ABX EQUATION.
  EPSLON=0.5*(CJAX+CJBX)
  DEL1=0.25*(SHIFT-CJBX)*(-SHIFT-CJAX)
  DEL2=0.25*(SHIFT+CJBX)*(-SHIFT+CJAX)
  READ IN THE PARAMETERS TAU (LIFETIME), T2, SCALE (OF THE PLOT OR
  FOR THE GRAPH), STEP-SIZE AND NUMBER OF STEPS (THE LATTER
  PARAMETERS ARE USED FOR SEARCHING ABOUT A LIFETIME.), AND THE
  REQUIRED HEIGHT OF THE PLOTTED SPECTRA (IF PLOTS ARE TO BE MADE).
  IF STEPSZ IS EQUAL TO ZERO, ONE RUN AT THIS LIFETIME WILL BE
  CARRIED OUT.  OTHERWISE A SEARCH OF LIFETIMES WILL BE MADE ON BOTH
  SIDES OF THE SPECIFIED LIFETIME IN STEPS OF STEPSZ, AND WITH
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    NOSTEP/2 STEPS ON EACH SIDE.
    FO THE "F" TYPE OUTPUT A "*" GRAF WILL BE OUTPUT AT THE
    LIFETIME SPECIFIED, AND PEAK POSITIONS AND HALF-HEIGHT LINE WIDTHS
    OUTPUT FOR EACH LIFETIME THAT MAY BE RUNJ.
    FOR EXAMPLE, A DATA CARD MIGHT SET TAU=.01, STEPSZ=.001 AND NOSTEP
    =20.  THIS WILL RESULT IN 10 SEARCHS ON EACH SIDE OF TAU, IN STEPS
    OF .001 SECONDS FROM 0.001 TO 0.02 SECONDS.  IF THE OUTPUT TYPE IS
    "F" A GRAPH WILL BE PRINTED OUT AT A LIFETIME OF 0.01 SECONDS.
    TAU MUST NEVER BE NEGATIVE OR EQUAL TO ZERO:  THE COMPUTER WILL
    ASSUME AND ERROR IN THE INPUT AND IGNORE THE DATA.  HENCE IT IS
    ALSO IMPORTANT TO MAKE SURE THAT ANY SEARCH-LIFETIMES ARE GREATER
    THAN ZERO.  IF (TAU-STEPSZ*NOSTEP/2) IS GREATER THAN OR EQUAL TO
    ZERO, NO ERROR MESSAGE WILL OCCUR.  THE USE OF STEPSZ AND NOSTEP
    CAN BE USED EFFECTIVELY TO REDUCE THE NUMBER OF INPUT DATA CARDS,
    AND SAVE PUNCHING TIME.  FOR EXAMPLE TO MAKE A 'GENERAL' RUN OF
    LIFETIMES FROM 0.0001 TO 10 SECONDS, FOUR DATA CARDS WILL SUFFICE:
            1. TAU=.001, STEPSZ=.0001, NOSTEP=20
            2. TAU=.01, STEPSZ=.001, NOSTEP=20
            3. TAU=.1, STEPSZ=.01, NOSTEP=20
            4. TAU=1., STEPSZ=.1, NOSTEP=20.
    AFTER CARRYING OUT THE RUN OR RUNS INDICATED BY THIS DATA CARD,
    CONTROL WILL PASS AGIAIN TO THIS INPUT STATEMENT.  CONSEQUENTLY IF
    IT IS DESIRED TO RUN SEVERAL LIFETIMES (OR LIFETIME SEARCHS),
    SIMPLY INCLUDE THE NEXT DATA CARDS WITH LIFETIME ETC ON IT AS
    ABOVE.  AT THIS STAGE THE PROGRAM CAN BE TERMINATED WITH TWO BLANK
    CARDS OR , IF IT IS DESIRED, MORE RUNS CAN BE MADE WITH DIFFERENT
    VALUE(S) FOR J(AB), AND/OR J(AX), ETC, BY INSERTING ONE BLANK
    CARD AND PUTTING IN A NEW SET OF DATA CARDS AS DONE ABOVE IN
    STATEMENT NUMBER 99.
    YHGHT IS THE DESIRED HEIGHT FOR THE PLOTTED OUTPUT USING ABXPLOT.
    FORMAT FOR T IS INPUT IS 4F10.5, I3, 7X, F10.5   .
104 READ (INDATA, 105, END=174) TAU, T2, SCALE1, STEPSZ, NOSTEP, YHGHT
105 FORMAT (4F10.5,I3,7X,F10.5)
    IF (TAU.LE.0.0) GO TO 99
106 IF (STEPSZ.LE.0.0) NOSTEP=1
    IF (T2.LE.0.0) T2=1.0
    SEARCH=0.0
    IF (NOSTEP.GT.1) SEARCH=TAU
    TAU=TAU-(NOSTEP/2)*STEPSZ
    NORUN=0
107 IF (NORUN.GE.NOSTEP) GO TO 104
108 TAU=TAU+STEPSZ
    IF (TAU.GT.0.0) GO TO 111
    WRITE OUT AN ERROR MESSAGE IF TAU IS LESS THAN OR EQUAL TO ZERO, A
    READ IN NEW VALUES FOR TAU ETC.
109 WRITE (ONPRTR,110) TAU, SEARCH, T2, STEPSZ, NOSTEP
110 FORMAT (1H ,40H ****ERROR IN INPUT, TAU NON-POSITIVE.    /1H ,5X,
   116H INPUT PARAMETERS:    ,/1H ,8X,9H LIFETIME   ,F10.5,5H SEC.,/1H ,
   28X, 18H ORIGINAL LIFETIME   ,F10.5,5H SEC.,/1H ,
   38X,20H NATURAL LINE WIDTH    ,F10.5,5H SEC. /1H ,8X,20H STEP SIZE I
   4N SEARCH   ,F10.4,/1H ,8X,18H NOSTEPS IN SEARCH   ,I3,1H ,5X,21H REA
   5DING IN NEW DATA.    )
    GO TO 104
111 NORUN=NORUN+1
    CALCULATE CONSTANTS INVOLVED IN THE ABX EQUATION.
    TEMP=(1.0/TAU)*(EPSLON*EPSLON+(2.0/(PISQ*T2))*(1.0/TAU+1.0/T2))+
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     1(1.0/T2)*(EPSLON*EPSLON+2.0*CJAB*CJAB+0.5/(PISQ*T2*T2))
      AA1=TEMP-2.0*DEL1*(2.0/TAU+1.0/T2)
      AA2=AA1-2.0*EPSLON*CJAB/T2
      AA1=AA1+2.0*EPSLON*CJAB/T2
      AX1=TEMP-2.0*DEL2*(2.0/TAU+1.0/T2)
      AX2=AX1+2.0*EPSLON*CJAB/T2
      AX1=AX1-2.0*EPSLON*CJAB/T2
      AB=2.0/T2
      CA1=(2.0/T2)*(-EPSLON-2.0*CJAB)
      CA2=(2.0/T2)*(-EPSLON+2.0*CJAB)
      DA1=2.0*(EPSLON+CJAB)
      DA2=2.0*(EPSLON-CJAB)
      TEMP=CJAB*CJAB     +EPSLON*EPSLON+(1.0/(PISQ*TAU))*(1.0/TAU+1.0/T2
     1)+0.5/(PISQ*T2*T2)
      EA1=TEMP+2.0*DEL1
      EA2=EA1-3.0*EPSLON*CJAB
      EA1=EA1+3.0*EPSLON*CJAB
      EX1=TEMP+2.0*DEL2
      EX2=EX1+3.0*EPSLON*CJAB
      EX1=EX1-3.0*EPSLON*CJAB
      FA1=-2.0*DEL1*EPSLON-EPSLON*CJAB*CJAB-(EPSLON/(PISQ*TAU))*(1.0/
     1TAU+1.0/T2)-0.5*EPSLON/(PISQ*T2*T2)
      FA2=FA1+CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
      FA1=FA1-CJAB*(EPSLON*EPSLON+2.0*DEL1+0.5/(PISQ*T2*T2))
      FX1=2.0*DEL2*EPSLON+EPSLON*CJAB*CJAB+(EPSLON/(PISQ*TAU))*(1.0/
     1TAU+1.0/T2)+0.5*EPSLON/(PISQ*T2*T2)
      FX2=FX1+CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
      FX1=FX1-CJAB*(2.0*DEL2+EPSLON*EPSLON+0.5/(PISQ*T2*T2))
      TEMP=EPSLON*EPSLON*(CJAB*CJAB/4.0+(1.0/PISQ)*(0.25/(TAU*TAU)+0.5
     1/(TAU*T2)+0.25/(T2*T2)))+1.0/(PISQ*PISQ*T2*T2)*(1.0/(TAU*TAU)+1.0
     2/(TAU*T2)+1.0/(16.0*T2*T2))+CJAB*CJAB*(0.25/(PISQ*T2*T2))
      GA1=TEMP+DEL1*(DEL1-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
      GA2=GA1-EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
      GA1=GA1+EPSLON*CJAB*(DEL1+0.25/(PISQ*T2*T2))
      GX1=TEMP+DEL2*(DEL2-(1.0/(PISQ*T2))*(1.0/TAU+0.5/T2))
      GX2=GX1+EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
      GX1=GX1-EPSLON*CJAB*(DEL2+0.25/(PISQ*T2*T2))
      IF (OUTPUT.EQ.PUNCH) GO TO 117
1120  IF (NURUN-(NOSTEP/2))  117, 112, 117
 112  MAX=-1.0E49
      DELTA=START
      DO 113 J=1,NOPTS
      AMP   =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
     1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2,DELTA)
     2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1,DELTA)
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2,DELTA)
      IF (AMP.GT.MAX) MAX=AMP
      DELTA=DELTA-STEP1
 113  CONTINUE
      SCALE=100./MAX
      WRITE (ONPRTR,114) SHIFT, CJAB, CJAX, CJBX, TAU, T2, SCALE1, SCALE
 114  FORMAT (1H1,8X,'INPUT PARAMETERS OF ABX LINE SHAPE ANALYSIS'/1H ,
     18X,'SHIFT ',F8.3,' C/S.',/1H ,8X,'JAB ',F7.3,' C/S.',/1H ,8X,'JAX'
     2,F7.3,' C/S',/1H ,8X,'JBX ',F7.3,' C/S',/1H ,8X,'LIFETIME',F10.5,
     3'SECONDS',/1H ,8X,'LINEWIDTH ',F7.3,' SECONDS',/1H ,8X,'SCALE',
     4F10.5,' HZ/CM',/1H ,8X,'PEAKS MULTIPLIED BY A SCALE FACTOR OF',
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     5F15.7,//1H ,102X,'INTENSITY',3X,' DELTA')
      DELTA=START
      DO 116 J=1,NOPTS
      AMP   =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
     1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2,DELTA)
     2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1,DELTA)
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2,DELTA)
      IDIOT=AMP*SCALE+2.5
      IF (IDIOT.LT.2) IDIOT=2
      IF (IDIOT.GT.102) IDIOT=102
      LINE(IDIOT)=X
      WRITE (UNPRTR, 115) (LINE(I),I=1,102), AMP, DELTA
  115 FORMAT (1H ,102A1,F9.5,F9.4)
      LINE(IDIOT)=BLANK
      DELTA=DELTA-STEP1
  116 CONTINUE
  117 MAX=-1.0E49
      PEAK(1)=0.0
      PEAKHT(1)=0.0
      MIN(1)=START
      MINHT(1)=0.0
      MEANWD(1)=0.0
      BEGIN THE SEARCH FOR THE EXTREMA.
      STEP=0.05
      DELTA=START
      INDEX=1
      AMP1=-0.01
      AMP2=0.0
  118 AMP3  =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
     1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
     2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
      TEST FOR A PEAK.
      IF (AMP2.GT.AMP1.AND.AMP2.GT.AMP3) GO TO 122
      TEST FOR A MINIMUM.
  119 IF (AMP2.LT.AMP3.AND.AMP2.LT.AMP1) GO TO 121
  120 DELTA=DELTA-STEP
      AMP1=AMP2
      AMP2=AMP3
      IF (STOP-DELTA) 118, 118, 133
      STORE MINIMUM AND MIMIMUM HEIGHT.
  121 MIN(INDEX)=DELTA+STEP
      MINHT(INDEX)=AMP2
      GO TO 120
      FIND PEAK MORE EXACTLY, AND STORE PEAK AND PEAK HEIGHT.
  122 IF (AMP1.LE.AMP3) GO TO 124
  123 DELTA2=DELTA+STEP
      DELTA1=DELTA2+STEP
      GO TO 125
  124 DELTA2=DELTA
      DELTA1=DELTA+STEP
  125 PEEK=AMP2
      COORD=DELTA+STEP
      DELT1=1.0E49
  126 DELT=(DELTA1+DELTA2)/2.0
      TEST TO SEE IF PEAK IS DETERMINED WITHIN.001 UNITS.
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      IF (ABS(DELT1-DELT).LT.0.001) GO TO 132
  127 DELT1=DELT
      TEMP=ABX(AA1,AB,CA1,DA1,EA1,FA1,GA1,DELT)
     1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELT )
     2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELT )
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELT )
      IF (PEEK.GT.TEMP) GO TO 129
  128 PEEK=TEMP
      COORD=DELT
  129 TEMP2 =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELT+.0001)
     1+ABX(AA2,AB,CA2,DA2,EA2,FA2,GA2,DELT+.0001)
     2+ABX(AX1,AB,-CA2,-DA2,EX1,FX1,GX1,DELT+.0001)
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELT+.0001)
      IF (TEMP.LT.TEMP2) GO TO 131
  130 DELTA1=DELT
      GO TO 126
  131 DELTA2=DELT
      GO TO 126
  132 PEAKHT(INDEX)=PEEK
      PEAK(INDEX)=COORD
      INDEX=INDEX+1
      TEST TO OBTAIN THE LARGEST PEAK.
      IF (PEEK.GT.MAX) MAX=PEEK
      GO TO 120
      AT THIS POINT ALL EXTREMA WITH THE LIMITS SET HAVE BEEN FOUND.
  133 MIN(INDEX)=STOP
      MINHT(INDEX)=0.0
      EVALUATE THE SCALING FACTOR.
      SCALE = 100.00 / MAX
      IF (OUTPUT.EQ.PUNCH) GO TO 1711
 1330 NOPEAK=INDEX-1
      J=0
      INDEX=1
      BEGIN THE SEARCH FOR HALF-HEIGHT LINE WIDTHS.
  134 HALFHT=PEAKHT(INDEX)/2.0
      MAX=PEAK(INDEX)
      SEARCH THE LEFT-HAND SIDE OF THE PEAK.
      MINIHT=MINHT(INDEX)
      MINI=MIN(INDEX)
      SWITCH=1
      STATEMENTS 144 AND ON ARE INVLOLVED IN THE ACTUAL SEARCH FOR THE W
      GO TO 163
  135 HAFHT1(INDEX)=HEIGHT
      HAFWD1(INDEX)=WIDTH
      SEARCH THE RIGHT-HAND SIDE OF THE PEAK.
  136 MAX=PEAK(INDEX)
      MINI=MIN(INDEX+1)
      MINIHT=MINHT(INDEX+1)
      SWITCH=2
      GO TO 163
  137 HAFHT2(INDEX)=HEIGHT
      HAFWD2(INDEX)=WIDTH
      CHECK LINE-WIDTHS.  IF ONE OR BOTH ARE ZERO, OVEPLAP HAS OCCURED.
      IF (HAFWD1(INDEX).EQ.0.0.OR.HAFWD2(INDEX).EQ.0.0) GO TO 140
      AVERAGE THE LINE-WIDTHS.
  138 MEANWD(INDEX)=0.5*(HAFWD1(INDEX)+HAFWD2(INDEX))
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      OVRLAP(INDEX)=0.0                                                 GEN 281
      OVRHT(INDEX)=0.0                                                  GEN 282
      CHECK TO SEE IF A PREVIOUS PEAK HAS OVERLAPPED.  IF SO FIND THE TOGEN 283
      LINE WIDTH AT THE LOWER HALF-HEIGHT.                              GEN 284
      WRITE (6,27)                                                      GEN 285
      IF (J.GT.0.AND.MINHT(INDEX+1).LT.(HAFHT1(J)/2.0)) GO TO 145       GEN 286
      IF (J.LE.0) GO TO 139                                             GEN 287
1390  IF (MINHT(INDEX+1).LT.(HAFHT1(J)/2.0)) GO TO 145                  GEN 288
 139  CONTINUE                                                          GEN 289
      WRITE (6,27)                                                      GEN 290
  27  FORMAT (1H ,'CHECKING')                                           GEN 291
      GO TO 153                                                         GEN 292
      AT THIS POINT THERE HAS BEEN OVERLAP DETECTED.                    GEN 293
 140  MEANWD(INDEX)=0.0                                                 GEN 294
      IF (J.EQ.0) J=INDEX                                               GEN 295
      OVRHT(INDEX)=0.0                                                  GEN 296
      OVRLAP(INDEX)=0.0                                                 GEN 297
      CHECK TO SEE IF THE FINAL PEAK IN THE OVERLAP HAS BEEN ENCOUNTEREDGEN 298
 141  IF (HAFWD2(INDEX).EQ.0.0) GO TO 153                               GEN 299
      IF NOT, GO ON TO THE NEXT PEAK.  IF SO, CALCULATE THE OVERLAP WIDTGEN 300
 142  IF (J.NE.INDEX) GO TO 145                                         GEN 301
 143  J=J-1                                                             GEN 302
      IF (MINHT(J).LT.(PEAKHT(INDEX)/2.0)) GO TO 145                    GEN 303
 144  IF (J-1)  172, 172, 143                                           GEN 304
      CHECK TO SEE WHICH OF THE OVERLAPPING PEAKS IS LOWEST, AND USE ITSGEN 305
      HEIGHT AT THE OTHER PEAK.                                         GEN 306
 145  IF (PEAKHT(J).GT.PEAKHT(INDEX)) GO TO 150                         GEN 307
      THE FIRST PEAK IS LOWEST.                                         GEN 308
 146  MAX=PEAK(INDEX)                                                   GEN 309
      MINI=MIN(INDEX+1)                                                 GEN 310
      MINIHT=MINHT(INDEX+1)                                             GEN 311
 147  HALFHT=PEAKHT(J)/2.0                                              GEN 312
 148  SWITCH=3                                                          GEN 313
      GO TO 163                                                         GEN 314
 149  OVRHT(INDEX)=HEIGHT                                               GEN 315
      OVRLAP(INDEX)=WIDTH                                               GEN 316
      OVRLAP(INDEX)=0.5*(OVRLAP(INDEX)+HAFWD1(J))+ABS(PEAK(J)-          GEN 317
     1PEAK(INDEX))                                                      GEN 318
      GO TO 152                                                         GEN 319
      THE LAST PEAK IS LOWEST.                                          GEN 320
 150  MAX=PEAK(J)                                                       GEN 321
      MINI=MIN(J)                                                       GEN 322
      MINIHT=MINHT(J)                                                   GEN 323
      HALFHT=PEAKHT(INDEX)/2.0                                          GEN 324
      SWITCH=4                                                          GEN 325
      GO TO 163                                                         GEN 326
 151  OVRHT(INDEX)=HEIGHT                                               GEN 327
      OVRLAP(INDEX)=WIDTH                                               GEN 328
      OVRLAP(INDEX)=0.5*(OVRLAP(INDEX)+HAFWD2(INDEX))+ABS(PEAK(J)-      GEN 329
     1PEAK(INDEX))                                                      GEN 330
 152  J=0                                                               GEN 331
 153  INDEX=INDEX+1                                                     GEN 332
      CHECK TO SEE IF ALL THE PEAKS HAVE BEEN PROCESSED.                GEN 333
      IF (INDEX.LE.NOPEAK) GO TO 134                                    GEN 334
      SCALE ALL THE PEAKS.                                              GEN 335
 154  CONTINUE                                                          GEN 336
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    WRITE(6,23) OVRHT(J)
 23 FORMAT (1H ,/////,1H ,'HERE?',F15.7)
    DO 155 J=1,NOPEAK
    WRITE (6,34) J, NOPEAK
 34 FORMAT (1H ,'CHECKING J AND NOPEAK',I2,5X,I2)
    PEAKHT(J)=PEAKHT(J)*SCALE
    HAFHT1(J)=HAFHT1(J)*SCALE
    HAFHT2(J)=HAFHT2(J)*SCALE
    OVRHT(J)=OVRHT(J)*SCALE
155 CONTINUE
    OUTPUT LIFETIME, NATURAL LINE WIDTH AND HEADINGS.
    WRITE (ONPRTR,156) TAU, T2
156 FORMAT (1H ,///,1H ,8X,14H***LIFETIME = ,F10.5,12H SEC., T2 =    ,
   1F10.5,5H SEC. )
    IF (SEARCH.GT.0.0) WRITE (ONPRTR,157) SEARCH, STEPSZ
157 FORMAT (1H ,11X, 30H SEARCHING AROUND LIFETIME OF  ,F10.5,
   112H SECONDS, IN STEPS OF    ,F10.5,10H SECONDS.     )
    WRITE (ONPRTR,158)
158 FORMAT (1H ,/,1H ,15X,10H PEAK AT  ,6X,7H HEIGHT ,12X,12H HALF HEI
   1GHT  ,13X,6H WIDTH,12X,14H AVERAGE WIDTH  )
    DO 162 J=1,NOPEAK
    OUTPUT PEAK LOCATION, PEAK HEIGHT, HALF-HEIGHT LINE WIDTHS AND HEI
    FROM BOTHS SIDES OF THE PEAK.
    WRITE (ONPRTR,159) PEAK(J), PEAKHT(J), HAFHT1(J), HAFWD1(J),
   1 HAFHT2(J), HAFWD2(J)
159 FORMAT (10X,F10.5,4H C/S ,5X,F10.5,14X,F10.5,5X,F10.5,4H C/S ,/
   153X,F10.5,5X,F10.5,4H C/S  )
    OUTPUT AVERAGE OF HALF-HEIGHT LINE-WIDTHS IF IT EXISTS (IT IS 'NON
    TANT IF ONE OR BOTH LINE WIDTHS IS ZERO)
    IF (MEANWD(J).GT.0.0) WRITE (ONPRTR,160) MEANWD(J)
160 FORMAT (1H+,93X,F10.5,5H C/S.    )
    OUTPUT OVERLAP LINE WIDTH AND HEIGHT IF IT EXISTS.
    IF (OVRLAP(J).GT.0.0) WRITE (ONPRTR,161) OVRHT(J), OVRLAP(J)
161 FORMAT (1H ,15X,47H LINE WIDTH OF OVERLAPPING PEAKS AT A HEIGHT OF
   1  ,F10.5,4H IS  ,F10.5,8H C/S.***  )
162 CONTINUE
    RETURN CONTROL TO EITHER CONTINUE SEARCH OR READ IN NEW LIFETIMES.

    GO TO 107
    THIS SECTION OF THE PROGRAM FINDS THE HALF-HEIGHTS LINE WIDTHS.
    CHECK TO SEE IF A HALF-HEIGHT EXISTS.  IF NOT, SET THE LINE WIDTH
    TO ZERO.
163 IF (MINIHT.LT.HALFHT) GO TO 165
164 HEIGHT=0.0
    WIDTH=0.0
    GO TO (135, 137, 149, 151), SWITCH
    THE HALF-HEIGHT IS FOUND TO WITHIN THIS ERROR, AT LEAST .5%.
165 ERROR=HALFHT/500.
    NOTRY=0
    DELTA1=MINI
    DELTA2=MAX
166 DELTA=(DELTA1+DELTA2)/2.0
    AMP   =ABX(AA1,AB, CA1, DA1, EA1, FA1, GA1, DELTA)
   1+ABX(AA2, AB, CA2, DA2, EA2, FA2, GA2, DELTA)
   2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
   3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
```

```
      CHECK TO SEE IF THE HALF-HEIGHT IS KNOWN WITHIN THE ERROR LIMITS.
      IF (ABS(AMP-HALFHT).LT.ERROR) GO TO 171
  167 NOTRY=NOTRY+1
      GIVE UP AFTER 250 TRIES IF A HALF-HEIGHT CANNOT BE FOUND.
      IF (NOTRY.GT.200) GO TO 172
  168 IF (AMP.GT.HALFHT) GO TO 170
  169 DELTA1=DELTA
      GO TO 166
  170 DELTA2=DELTA
      GO TO 156
  171 HEIGHT=AMP
      WIDTH=ABS(DELTA-MAX)*2.0
      RETURN BACK TO THE MAIN SECTION OF THE PROGRAM.
      GO TO (135, 137, 149, 151), SWITCH
      THIS PART OF THE PROGRAM CONTAINS THE PUNCHING ROUTINE.
 1711 WRITE (ONPUN,1712) SHIFT, CJAB, CJAX, CJBX, TAU, SCALE1, START,
     1STOP, YHGHT, T2
 1712 FORMAT (8F10.5)
      DELTA=START
      INDEX=1
      AMP1=0.0
      NOPUN=0
      CALCULATE AND OUTPUT ON CARDS THE INTENSITY OF THE SIGNAL AS A
      FUNCTION OF FREQUENCY.
 1713 AMP2  =ABX(AA1,AB,CA1,DA1,EA1,FA1,GA1,DELTA)
     1+ABX(AA2, AB, CA2, DA2, EA2,.FA2, GA2, DELTA)
     2+ABX(AX1, AB, -CA2, -DA2, EX1, FX1, GX1, DELTA)
     3+ABX(AX2, AB, -CA1, -DA1, EX2, FX2, GX2, DELTA)
       VARIABLE STEP SIZE.  LIMITS 0.1 AND 0.0005 HTZ.
       STEP=ABS(STEP*0.2/(AMP2-AMP1))
       IF (STEP.GT.0.1) STEP =0.1
       IF (STEP.LT.0.0005) STEP =0.0005
       AMP1=AMP2
       D(INDEX)=DELTA
       AAA(INDEX) = AMP2*SCALE
       INDEX=INDEX+1
       DELTA=DELTA-STEP
       IF (INDEX-4) 1713, 1713, 1714
 1714 WRITE (ONPUN,1715)(AAA(INDEX), D(INDEX),INDEX=1,4)
 1715 FORMAT (8F10.5)
      INDEX=1
      NOPUN=NOPUN+1
      IF ((STOP-DELTA).LE.STEP) GO TO 1713
 1716 WRITE (ONPRTR,1717) NOPUN
 1717 FORMAT (1H ,//,1H ,6X,'NUMBER OF CARDS PUNCHED:',I5)
      WRITE (ONPRTR,1718) NAME
 1718 FORMAT (1H ,///,1H ,5X,30H END OF PUNCHINC FOR COMPOUND  /,1H ,8X,
     120A4)
      WRITE (ONPUN,1719)
 1719 FORMAT (1H )
      GO TO 107
      THIS SECTION CONTAINS SOME ERROR STATEMENTS
  172 WRITE (ONPRTR,173)
  173 FORMAT (1H ,//,1H ,12H***ERROR***    ,/1H ,5X,47H LARGE LOOP ENCCUN
     1TERED IN HALF HEIGHT SEARCH.    /1H ,61H VALUES BELOW ARE INCORREC
     2T; ERROR IS PROBABLY IN THE METHOD      )
```

```
      GO TO 171                                                         GEN 449
  174 WRITE (ONPRTR,175)                                                GEN 450
  175 FORMAT (1H ,///1H ,14H ***WARNING***  /,1H ,5X,52H CHECK DATA: THEGEN 451
     1COMPUTER IS LOOKING FOR MORE INPUT                   )            GEN 452
  176 WRITE (ONPRTR,177)                                                GEN 453
  177 FORMAT (1H ,////,1H ,10X, 18H ***END OF JOB***     )              GEN 454
      CALL EXIT                                                         GEN 455
      END                                                               GEN 456
```

SAMPLE INPUT:

(1). Punched output (as for ABXPUNCH).

```
P         2.14      0.50      0.01      14.17     14.00     -14.00
TEST CASE; ABX-TYPE SPECTRA
1.00      1.00      1.00      0.00       0        3.00
.000001   1.00      1.00      0.00       0        3.00
```

(2). Printed output (as for ABXFIT).

```
F         2.14      0.50      0.01      14.17     14.00     -14.00
TEST CASE; ABX-TYPE SPECTRA.
1.00      1.00      2.00      0.10      10        0.00
0.01      1.00      2.00      0.001     10        0.00
```

(any parameters of value 0.00 may be ommitted during punching; however it is essential that the numbers fall within the right range, especially the number of steps).