THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

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Received February 17, 1960

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I. INTRODUCTION

A. CHEMICAL SHIFTS

One of the principal objectives of high-resolution nuclear magnetic resonance studies of liquids is the evaluation of accurate chemical shift data. These data are of value not only for their characterization of specific molecules for analytical purposes, but also for their bearing on chemical phenomena in general. The term "chemical shift" or "chemical effect" was originally used to indicate that a given nucleus could exhibit different resonance fields (or frequencies) when contained in different molecules; the protons in water and benzene, for example. However, the subsequent production of magnetic fields of high homogeneity resulted in the frequent discrimination of several nuclear resonances within a given molecule. These multiple resonances result from internal or intramolecular chemical shifts, the classical example being the shifts of the methyl, methylene, and hydroxyl protons in ethyl alcohol (9).

Chemical shifts arise from a field-induced magnetic shielding of the nuclei by the molecular electrons, and

TABLE 1

Direction cosines for orthogonal transformations in terms of the Eulerian angles

	x	y	z
x'	$\cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi$	$\cos\psi\sin\phi + \cos\phi\cos\theta\sin\psi$	$\sin\psi\sin\theta$
y'	$-\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi$	$-\sin\psi\sin\phi + \cos\phi\cos\theta\cos\psi$	$\cos\psi\sin\theta$
z'	$\sin\theta\sin\phi$	$-\sin\theta\cos\phi$	$\cos\theta$

are quantitatively described by an appropriate shielding constant, σ_i, for each nucleus. Thus, in an applied field $\mathbf{H}_0$, the field in the immediate vicinity of a particular nucleus is given by

$$\mathbf{H}_i = (1 - \sigma_i)\mathbf{H}_0 \qquad (1)$$

The associated nuclear Larmor precession frequency is

$$\omega_i = \gamma_i \mathbf{H}_i = (1 - \sigma_i)\gamma_i \mathbf{H}_0 \qquad (2)$$

where γ_i is the gyromagnetic ratio for nucleus i. It should be noted that $|\omega_i| = \omega_i$ is in angular units (radians sec.$^{-1}$) and is related to the linear frequency by the equation

$$\omega_i = 2\pi\nu_i \qquad (3)$$

More generally, equation 1 is to be replaced by

$$\mathbf{H}_i^{(\lambda)} = \{\mathbf{1} - \boldsymbol{\sigma}_i^{(\lambda)}\}\mathbf{H}_0 \qquad (4)$$

where $\mathbf{1}$ is the second-rank unit tensor and $\boldsymbol{\sigma}_i^{(\lambda)}$ is the (second-rank) shielding tensor for nucleus i when the molecule has the orientation λ with respect to a set of space-fixed axes. The tensor form of magnetic shielding effects is appropriate when chemical shifts are observed in solids (49); in liquid systems, however, there are frequent changes in molecular orientations, so that equation 4 must be accordingly averaged. The rate of molecular reorientations in liquids is of the order of 10^{10} sec.$^{-1}$, which is about 1000 times faster than the usual nuclear Larmor precession frequencies (10^6–10^7 sec.$^{-1}$), so the assumption of complete averaging is normally a good one. The averaging is most conveniently carried out by considering a set of principal axes $(x'y'z')$ fixed in the molecule. The shielding tensor is diagonal in this coördinate system with the principal values $\sigma_{x'}$, $\sigma_{y'}$, and $\sigma_{z'}$ (the subscript i being dropped for the moment). The components of $\boldsymbol{\sigma}^{(\lambda)}$ relative to the space-fixed axes are related to those in the principal axes by the orthogonal transformation T (30)

$$\boldsymbol{\sigma}^{(\lambda)}(x, y, z) = \mathrm{T}\boldsymbol{\sigma}(x', y', z')\mathrm{T}^{-1} \qquad (5)$$

or, in component form,

$$\sigma_{rs}^{(\lambda)} = \sum_k \sigma_k T_{rk} T_{sk} \qquad \left.\begin{matrix} r, s = x, y, z \\ k = x', y', z' \end{matrix}\right\} \qquad (6)$$

The T_{rk} are the nine direction cosines between the (xyz) and $(x'y'z')$ axes and satisfy the orthogonality relations (29)

$$\sum_k T_{rk} T_{sk} = \delta_{rs} \qquad (7)$$

where δ_{rs} is the Kronecker delta

$$\delta_{rs} = \begin{cases} 0 \text{ for } r \neq s \\ 1 \text{ for } r = s \end{cases} \qquad (8)$$

The direction cosines are conveniently expressed in terms of Euler's angles θ, ϕ, χ, as in table 1 (29).

The characteristic values, σ_k, of the shielding tensor do not vary as the principal axes assume all possible orientations, so that

$$<\sigma_{rs}^{(\lambda)}>_{\text{av.}\lambda} = \frac{1}{8\pi^2}\sum_k \sigma_k \int_0^{2\pi} d\chi \int_0^{2\pi} d\phi \int_0^{\pi} T_{rk} T_{sk} \sin\theta \, d\theta \qquad (9)$$

Upon carrying out the integrations one obtains finally

$$<\boldsymbol{\sigma}_i^{(\lambda)}>_{\text{av.}\lambda} = \left(\frac{1}{3} Tr\boldsymbol{\sigma}_i\right)\mathbf{1} \qquad (10)$$

where $Tr\boldsymbol{\sigma}_i$ is the sum of the diagonal elements of the shielding tensor as determined *in any coördinate system.* Thus the averaging has the effect of diagonalizing $\boldsymbol{\sigma}_i$; but note, however, the degeneracy of the characteristic values of equation 10. Equation 4 can now be averaged with the result:

$$\begin{aligned} <\mathbf{H}_i^{(\lambda)}>_{\text{av.}\lambda} \equiv \mathbf{H}_i &= \{\mathbf{1} - <\boldsymbol{\sigma}_i^{(\lambda)}>_{\text{av.}\lambda}\}\mathbf{H}_0 \\ &= \left(1 - \frac{1}{3} Tr\boldsymbol{\sigma}_i\right)\mathbf{H}_0 \qquad (11) \end{aligned}$$

This result is identical with equation 1 if one defines

$$\sigma_i \equiv \left(\frac{1}{3} Tr\boldsymbol{\sigma}_i\right) \qquad (12)$$

The first theoretical calculations of shielding constants were couched in classical terms and restricted to atoms (48). The result of this work was the "Lamb diamagnetic correction"

$$\sigma = \frac{e}{3mc^2} V(0) \qquad (13)$$

where e and m are, respectively, the electronic charge and mass, c is the velocity of light, and $V(0)$ is the electric potential produced at the nucleus by the atomic electrons. For atomic hydrogen in a $1s$ state

$$V(0) = e<\frac{1}{r}>_{\text{av.}} = \frac{e}{a_0}$$

(a_0 is the first Bohr radius) and

$$\sigma_{1s}^{(\mathrm{H})} = \frac{e^2}{3mc^2a_0} = 1.76 \times 10^{-5} \tag{14}$$

For nuclei with large Z the Fermi–Thomas approximation yields (48):

$$\sigma = 3.19 \times 10^{-5}\, Z^{4/3} \tag{15}$$

Equation 15 is useful for estimating the magnitudes of chemical shifts. Fluorine ($Z = 9$) shifts, for example, are about thirty times greater than proton shifts.

A quantum-mechanical theory of molecular shielding (72, 73, 75, 77), based on second-order perturbation theory, leads to a term equivalent to the Lamb diamagnetic correction and an additional term that corresponds to an apparent paramagnetism of the molecular electrons. The paramagnetic term involves the energies and wave functions of excited states—quantities that are presently unavailable. The introduction of a mean electronic excitation energy, ΔE, reduces the correction term to one involving only the ground-state wave function, ψ_0. The (averaged) shielding constant is (73, 74)

$$\sigma = \frac{e}{3mc^2}V(0) - \frac{4}{3\Delta E} < \psi_0 \left| \sum_{j,k} \frac{\mathbf{m}_j^0 \cdot \mathbf{m}_k^0}{r_k^3} \right| \psi_0 > \tag{16}$$

where r_k is the distance of electron k from the shielded nucleus, $\mathbf{m}_j^0$ and $\mathbf{m}_k^0$ are the orbital angular momenta of the j^{th} and k^{th} electrons, and the angular brackets denote an integration over configuration space. Since $\mathbf{m}_j^0$ and $\mathbf{m}_k^0$ are differential operators in the quantum-mechanical sense, the second term of equation 16 involves a sum of second derivatives of the wave function. Thus the ground state must be known with considerable accuracy to avoid excessive accumulation of errors.

The lack of the required input data for this theory has forced a more simplified approach to the problem of molecular shielding. For example, the shielding constant may be considered as a sum of terms which represent the diamagnetic and paramagnetic contributions of various atoms (82). This method has been refined by coupling the atomic contributions by means of interatomic electronic currents (62). Other approaches have employed variational techniques (40, 54, 86), the molecular orbital approximation (2, 3, 51), and classical ideas (66). These calculations have provided useful qualitative results; at best, however, they are only semiquantitative and the burden of accurate determinations of chemical shifts rests almost exclusively with the experimentalist.[1]

The experimental evaluation of chemical shifts is not without its own peculiarities. Concentration-dependent shifts occur frequently (68, 69) and may be inter- or intramolecular in origin (14, 16). These effects do not hinder the analysis of a given spectrum, but corrections must be introduced whenever comparisons are made.

B. SPIN-SPIN COUPLINGS

High-resolution spectra frequently exhibit an abundance of hyperfine structure which, in contrast to the linear field dependence of chemical shifts, is independent of the applied field. This additional structure arises from an indirect coupling of the nuclear moments $\boldsymbol{\mu}_i$, which is transmitted from nucleus to nucleus by the paired electrons comprising the valence bonds. The effects of this interaction were first observed in the modulation of the echo envelope in pulse experiments (38, 39) and as simple multiplets in early high-resolution studies (35, 36, 37). From these experiments, it was concluded that the interaction between two spins i and j had the form

$$-K_{ij}\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \tag{17}$$

where K_{ij} is a constant depending upon the molecular electronic structure.[2] The scalar product form of the coupling guarantees rotational invariance, which must be the case since the multiplets survive the random averaging process characteristic of liquids.[3] Further, the interaction completely accounts for the fact that multiplets are not observed (*cf.* Section IV,A) for systems containing equivalent nuclei (35, 36, 37, 38, 39). For example, no multiplets are observed in the proton magnetic resonance spectra of benzene, water, methane, etc., and these results are predictable on the basis of equation 17. The fine structure predicted by the scalar product coupling has also been verified in a large number of cases.

The proportionality constant K_{ij} has the dimensions gauss^2 erg^{-1}; it is customary, however, to express spin couplings in frequency units (angular or linear). The magnetic moment of nucleus i is related to the spin vector $\mathbf{I}_i$ by the equation (26, 59)

$$\boldsymbol{\mu}_i = \gamma_i \hbar \mathbf{I}_i \tag{18}$$

where $\hbar$ is Planck's constant h divided by 2π. Thus

$$K_{ij}\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j = \gamma_i\gamma_j K_{ij}\hbar^2 \mathbf{I}_i \cdot \mathbf{I}_j \tag{19}$$

The spin-spin coupling constant (in angular units) for spins i and j is now defined as

$$J_{ij} = \gamma_i\gamma_j\hbar K_{ij} \tag{20}$$

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[1] Experimentally, one usually determines chemical shifts as diamagnetic or paramagnetic with respect to some reference compound, or simply the *relative* intramolecular shifts.

[2] The sign convention in equation 17 implies that for $K_{ij} > 0$ the coupling energy is lowest when the spins are parallel; if $K_{ij} < 0$, the minimum interaction energy is associated with antiparallel spins.

[3] Dipolar interactions, which produce fine structure in solids (60), cannot be effective in liquid systems, since they depend upon the angle θ between the applied field and the line joining a nuclear pair through the factor $(1 - 3\cos^2\theta)$, whose random average is

$$<(1 - 3\cos^2\theta)>_{\text{av.}} = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} (1 - 3\cos^2\theta)\sin\theta\, d\theta = 0$$

and the interaction energy becomes

$$-K_{ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j = -J_{ij}\hbar\mathbf{I}_i\cdot\mathbf{I}_j \tag{21}$$

In linear units the coupling constant is

$$A_{ij} = \frac{J_{ij}}{2\pi} \tag{22}$$

The indirect spin-spin coupling of magnetic nuclei has been justified quantum-theoretically (76, 78, 80) through consideration of a rather general molecular Hamiltonian plus a perturbation by the Fermi contact interaction (67). The Fermi interaction is, essentially, a coupling of nuclear and electron spins and its magnitude depends upon the probability that the electron is at the nucleus; hence the term "contact interaction." In the second order of pertubation one finds a scalar product coupling of the nuclei. Actually, the interaction has the form of a second-rank tensor which takes the dot product form upon averaging over all possible orientations.

Since the exchange coupling of the electrons is intimately involved in the interaction, the coupling mechanism is more properly described as a "nuclear spin–electron spin–electron spin–nuclear spin coupling"; for obvious reasons this is contracted to "spin-spin coupling" or simply "exchange coupling." For protons spin-spin coupling constants are small (0–20 sec.$^{-1}$) but may persist over five chemical bonds (22, 58). Other nuclei may couple to the extent of a kilocycle or more (67).

The theory is applied with some difficulty to the direct calculation of coupling constants, again owing to the lack of molecular energies and wave functions. Approximate calculations (50, 51, 52, 87) have provided qualitative and semiquantitative results of interest. More recently, valence bond theory has been used to calculate proton-proton coupling constants (42, 43, 44). The results are in good agreement with the experimental data and show an interesting relation with H—C—H bond angles (34). Although this method has only been applied to some simple molecules, the approach is very promising.

C. THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

In view of the possible interactions of a collection of nuclei in a magnetic field, a Hamiltonian operator may be constructed which involves the chemical shifts and coupling constants parametrically. With this Hamiltonian and the formalism of quantum mechanics, one seeks a set of chemical shifts and coupling constants which describe the experimental spectrum. This empirical approach is dictated by the lack of accurate theoretical values for the essential parameters and is quite common in molecular spectroscopy. The quantum-mechanical aspects of the problem lead to a formal identity with other branches of spectroscopy, but the analogy is somewhat sharper in the case of infrared with nuclear Larmor frequencies and coupling constants corresponding to fundamental frequencies and force constants, respectively.

The analysis of a high-resolution nuclear magnetic resonance spectrum is a relatively simple problem when only shielding effects are important and is closely related to the structure of the molecule under study. In such a case, there will be a single resonance associated with each distinct environment with an intensity proportional to the number of nuclei in the given environment. Measurement of the separations of the various resonances (in magnetic field or frequency units) gives the relative internal chemical shifts. The assignment of particular resonances to definite nuclei requires additional information obtained, for example, by isotopic substitution or reference to accumulated data (32, 64).

It frequently happens that nuclei which are structurally nonequivalent have nearly identical resonance frequencies and the associated line widths prevent their resolution. If the spectrum consists of more than one line, the intensity relations may be used to clarify this case.

The next order of approximation is obtained when the spin-spin coupling constants are small in comparison to the relative internal shifts. Simple multiplets occur in this situation and the spectrum can be interpreted without recourse to detailed calculations. The above-mentioned intensity rules remain valid in this "first-order case" when applied to the multiplets themselves. The multiplet structure may also be used to assist in the assignment of lines to individual nuclei.

When the coupling constants are comparable to the relative shifts, the simple rules no longer apply and detailed calculations must be made. If the molecule contains n (magnetic) nuclei there will be, at most, $n(n - 1)/2$ relative shifts (not all of these are independent) and an equal number of (independent) coupling constants. For $n > 2$ the general problem involves algebraic equations of degree ≥ 3, so that numerical techniques must be employed. There are many cases, however, where internal molecular motions result in an "effective symmetry" and the orders of the algebraic equations are accordingly reduced. Similar reductions occur when the molecule has group symmetry, thus allowing the use of group theoretical techniques (53, 93). Other methods of interpreting nuclear magnetic resonance spectra are: perturbation calculations of the second or third order (5, 9), moment calculations (7), and multiple irradiation experiments (12, 13). The latter is more of a "trick" than a general method of analysis, but its use can often simplify a complicated spectrum. All of these calculations lead to a delta function type of description; that is, the spectrum is given by a series of discrete lines of height P_{jk} located at frequency Ω_{jk}, where P_{jk} and Ω_{jk} are *constants* denoting, respectively, the transition probability and frequency associated with the transition from an initial quantum state k to the final state j. The calculations provide values of the P_{jk} and Ω_{jk}, and detailed descriptions of these calculations are given in the text. The inclusion of relaxation phenomena requires a quantum-statistical discussion and will not be considered here (13, 89). Discussions of elementary principles and the general theory of nuclear magnetic resonance may be found in review articles (32, 60, 61, 91) and texts (8, 64).

II. Elementary Theory

A. INTRINSIC SPIN ANGULAR MOMENTUM

1. *Spin theory for a single nucleus*

The magnetic moment operator $\boldsymbol{\mu}$, for a nucleus with nonvanishing spin, is related to the intrinsic spin vector **I** by the equation

$$\boldsymbol{\mu} = \gamma\hbar\mathbf{I} \tag{1}$$

where $\hbar$ is Planck's constant divided by 2π, and γ is a characteristic constant known as the gyromagnetic ratio. The spin vector $\mathbf{I} = (I_x, I_y, I_z)$ represents the angular momentum in units of $\hbar$ and its components satisfy the commutation rules (23, 26, 81)

$$\left.\begin{aligned} I_xI_y - I_yI_x &= iI_z \\ I_yI_z - I_zI_y &= iI_x \\ I_zI_x - I_xI_z &= iI_y \end{aligned}\right\} \tag{2}$$

where i is the imaginary unit. Equations 2 may be succinctly expressed as a symbolic vector cross product.

$$\mathbf{I} \times \mathbf{I} = i\mathbf{I} \tag{3}$$

In addition to these operators, the "square" of the spin vector

$$\mathbf{I}\cdot\mathbf{I} \equiv \mathbf{I}^2 = I_x^2 + I_y^2 + I_z^2 \tag{4}$$

and the so-called "raising" (+) and "lowering" (−) operators defined as

$$I^{\pm} = I_x \pm iI_y \tag{5}$$

are also of importance.

From equations 2 and 4 it is easily shown that $\mathbf{I}^2$ and I_z commute:

$$\mathbf{I}^2I_z - I_z\mathbf{I}^2 \equiv [\mathbf{I}^2, I_z] = 0 \tag{6}$$

The significance of this result follows from a general theorem which states that if a collection of operators commute with each other, then a set of functions exist which are simultaneously eigenfunctions of all the given operators (23). I_x and I_y also commute with $\mathbf{I}^2$, but in view of equation 2, only $\mathbf{I}^2$ and one of its components form a commuting set. It is customary to take $\mathbf{I}^2$ and I_z as the commuting set, and this choice defines the (space-fixed) z-axis as the axis of quantization.

Let $\Phi_{I,m}$ be a set of eigenfunctions of $\mathbf{I}^2$ and I_z. It can be shown (23) that

$$\mathbf{I}^2\Phi_{I,m} = I(I+1)\Phi_{I,m} \tag{7}$$

where $I \geq 0$ is the spin quantum number and is restricted to integral or half-odd integral values. The physical significance of I is that it is the maximum component of the spin vector in the z-direction. The eigenvalues of I_z are denoted by the letter m and are precisely $2I + 1$ in number

$$m = I, I-1, I-2, \cdots -I+1, -I \tag{8}$$

and the eigenvalue equation for I_z is

$$I_z\Phi_{I,m} = m\Phi_{I,m} \tag{9}$$

There are, therefore, $2I + 1$ independent spin functions which are characterized by the quantum number I, which is fixed, and the quantum number m, which may assume any of the values in equation 8.

The functions $\Phi_{I,m}$ are assumed to be an orthonormal set; i.e., the scalar product (26, 81) $(\Phi_{I,m},\Phi_{I,m'})$ satisfies the equation

$$(\Phi_{I,m}, \Phi_{I,m'}) = \delta_{mm'} \tag{10}$$

where $\delta_{mm'}$ is the Kronecker delta. The matrix elements of $\mathbf{I}^2$ and I_z are obtained by taking the scalar product of equations 7 and 9 with $\Phi_{I,m'}$:

$$(\Phi_{I,m'}, \mathbf{I}^2\Phi_{I,m}) \equiv \langle\Phi_{I,m'}|\mathbf{I}^2|\Phi_{I,m}\rangle = I(I+1)\delta_{m'm} \tag{11}$$

$$\langle\Phi_{I,m'}|I_z|\Phi_{I,m}\rangle = m\delta_{m'm} \tag{12}$$

Thus, relative to the basis $\Phi_{I,m}$, the matrix for $\mathbf{I}^2$ is $I(I + 1)$ times an identity matrix with $2I + 1$ rows and columns, and the I_z matrix is also diagonal with elements $I, I - 1, \cdots -I + 1, -I$.

The effects of I_x and I_y on the $\Phi_{I,m}$ can be evaluated but it is often more convenient to work with $I^{\pm}$ (23).

$$I^{\pm}\Phi_{I,m} = \sqrt{(I \mp m)(I \pm m + 1)}\ \Phi_{I,m\pm1} \tag{13}$$

The matrix elements of $I^{\pm}$ are:

$$\begin{aligned}\langle\Phi_{I,m'}|I^{\pm}|\Phi_{I,m}\rangle &= \sqrt{(I \mp m)(I \pm m + 1)} \text{ for } m' = m \pm 1 \\ &= 0 \text{ otherwise}\end{aligned} \tag{14}$$

From equation 5 it follows that

$$I_x\Phi_{I,m} = \frac{1}{2}(I^+ + I^-)\Phi_{I,m} \tag{15}$$

$$I_y\Phi_{I,m} = \frac{1}{2i}(I^+ - I^-)\Phi_{I,m} \tag{16}$$

which, when combined with equation 14, defines the matrix elements of I_x and I_y.

It should be noted that I_x, I_y, I_z, and $\mathbf{I}^2$ (but *not* $I^{\pm}$) are Hermitian operators; that is, if **A** represents any of these operators, then

$$(\Phi_{I,m'}, \mathbf{A}\Phi_{I,m}) = (\mathbf{A}\Phi_{I,m'}, \Phi_{I,m}) = (\Phi_{I,m}, \mathbf{A}\Phi_{I,m'})^* \tag{17}$$

where the asterisk denotes complex conjugation.

For the particular case of $I = 1/2$, $m = \pm 1/2$ and it is customary to introduce the definitions

$$\Phi_{1/2,1/2} = \alpha \tag{18}$$

$$\Phi_{1/2,-1/2} = \beta \tag{19}$$

α and β are often referred to as the "spin up" and "spin down" states, respectively. For this case, equations 7, 9, 10, and 13 yield the results:

$$\left.\begin{aligned} \mathbf{I}^2\alpha &= \frac{1}{2}\left(\frac{1}{2}+1\right)\alpha \\ \mathbf{I}^2\beta &= \frac{1}{2}\left(\frac{1}{2}+1\right)\beta \end{aligned}\right\} \tag{20}$$

$$\left.\begin{aligned} I_z\alpha &= \frac{1}{2}\alpha \\ I_z\beta &= -\frac{1}{2}\beta \end{aligned}\right\} \tag{21}$$

$$\left.\begin{aligned} I^+\alpha &= I^-\beta = 0 \\ I^+\beta &= \alpha \\ I^-\alpha &= \beta \end{aligned}\right\} \tag{22}$$

$$\left.\begin{aligned} (\alpha, \beta) &= (\beta, \alpha) = 0 \\ (\alpha, \alpha) &= (\beta, \beta) = 1 \end{aligned}\right\} \tag{23}$$

2. Spin theory for a collection of nuclei

The preceding results are applicable only to a single nucleus of spin I, while later problems will involve systems with n spins and operators such as

$$\mathbf{I} = \sum_{j=1}^{n} \mathbf{I}_j \tag{24}$$

$$I_s = \sum_{j=1}^{n} I_{sj} \quad (s = x, y, z) \tag{25}$$

$$\mathbf{I}^2 = \mathbf{I}\cdot\mathbf{I} = \sum_j \mathbf{I}_j^2 + \sum_j \sum_k \mathbf{I}_j\cdot\mathbf{I}_k \tag{26}$$

$$I^\pm = \sum_{j=1}^{n} I_j^\pm \tag{27}$$

The commutation rules for the components of $\mathbf{I}$ with each other and with $\mathbf{I}^2$ are (25, 26, 81)

$$\mathbf{I}_j \times \mathbf{I}_k = i\delta_{jk}\mathbf{I}_j \tag{28}$$

$$[\mathbf{I}^2, I_z] = 0 \tag{29}$$

Equation 28 states that the operators for independent nuclei commute, and equation 29 implies that a set of functions can be found which are simultaneous eigenfunctions of $\mathbf{I}^2$ and I_z. For the present the simpler, but useful, representation is considered in terms of products of the functions $\Phi_{I,m}$. In this scheme (83) each nucleus is represented by a function satisfying equations 7 and 9, and the entire spin system is described by products of the type

$$\Phi(m) \equiv \Phi(\cdots I_j m_j \cdots; m) = \prod_{j=1}^{n} \Phi_{I_j, m_j} \tag{30}$$

Since there are $2I_j + 1$ values of m_j, there will be

$$N = \prod_j (2I_j + 1) \tag{31}$$

such products. These product spin functions are eigenfunctions of I_z

$$I_z\Phi(m) = m\Phi(m) \tag{32}$$

where the quantum number

$$m = \sum_j m_j \tag{33}$$

takes the integrally spaced values

$$\left(\sum_j I_j\right), \left(\sum_j I_j\right) - 1, \cdots, -\left(\sum_j I_j\right) + 1, -\left(\sum_j I_j\right)$$

The functions $\Phi(m)$ are not, in general, eigenfunctions of $\mathbf{I}^2$, but it is possible to express these eigenfunctions as linear combinations of the $\Phi(m)$.

In high-resolution spectroscopy, particular interest focuses upon homogeneous spin systems with spin quantum number one-half. For such systems equation 31 shows that there are 2^n product functions. In writing these products explicitly, a serial order will be employed; i.e., $\alpha\beta\beta$ . . . means that nucleus 1 is described by the spin function α, nucleus 2 by β, etc. The possible values of m range from $n/2$ to $-n/2$ and it is easy to show that the number of spin functions with a given value of m is

$$\frac{n!}{\left(\frac{n}{2} - m\right)!\left(\frac{n}{2} + m\right)!} \tag{34}$$

It is to be noted that there are as many spin functions with the eigenvalue $-m$ as there are with the eigenvalue m. The products are given in table 2 for the case $n = 3$.

The problem of constructing spin eigenfunctions of the square and z-component of total angular momentum for n spin 1/2 particles is discussed in texts on quantum mechanicsand group theory (47, 83). It is shown that the total spin quantum I_T may assume the nonnegative values

$$I_T = \frac{n}{2}, \frac{n}{2} - 1, \frac{n}{2} - 2, \cdots \begin{cases} 0 \text{ for } n \text{ even} \\ 1/2 \text{ for } n \text{ odd} \end{cases} \tag{35}$$

TABLE 2

Product functions for three nuclei with spin 1/2

Spin Function	$m = m_1 + m_2 + m_3$	Abbreviation
$\alpha\alpha\alpha$	3/2	u_1
$\alpha\alpha\beta$	1/2	u_2
$\alpha\beta\alpha$	1/2	u_3
$\beta\alpha\alpha$	1/2	u_4
$\alpha\beta\beta$	−1/2	u_5
$\beta\alpha\beta$	−1/2	u_6
$\beta\beta\alpha$	−1/2	u_7
$\beta\beta\beta$	−3/2	u_8

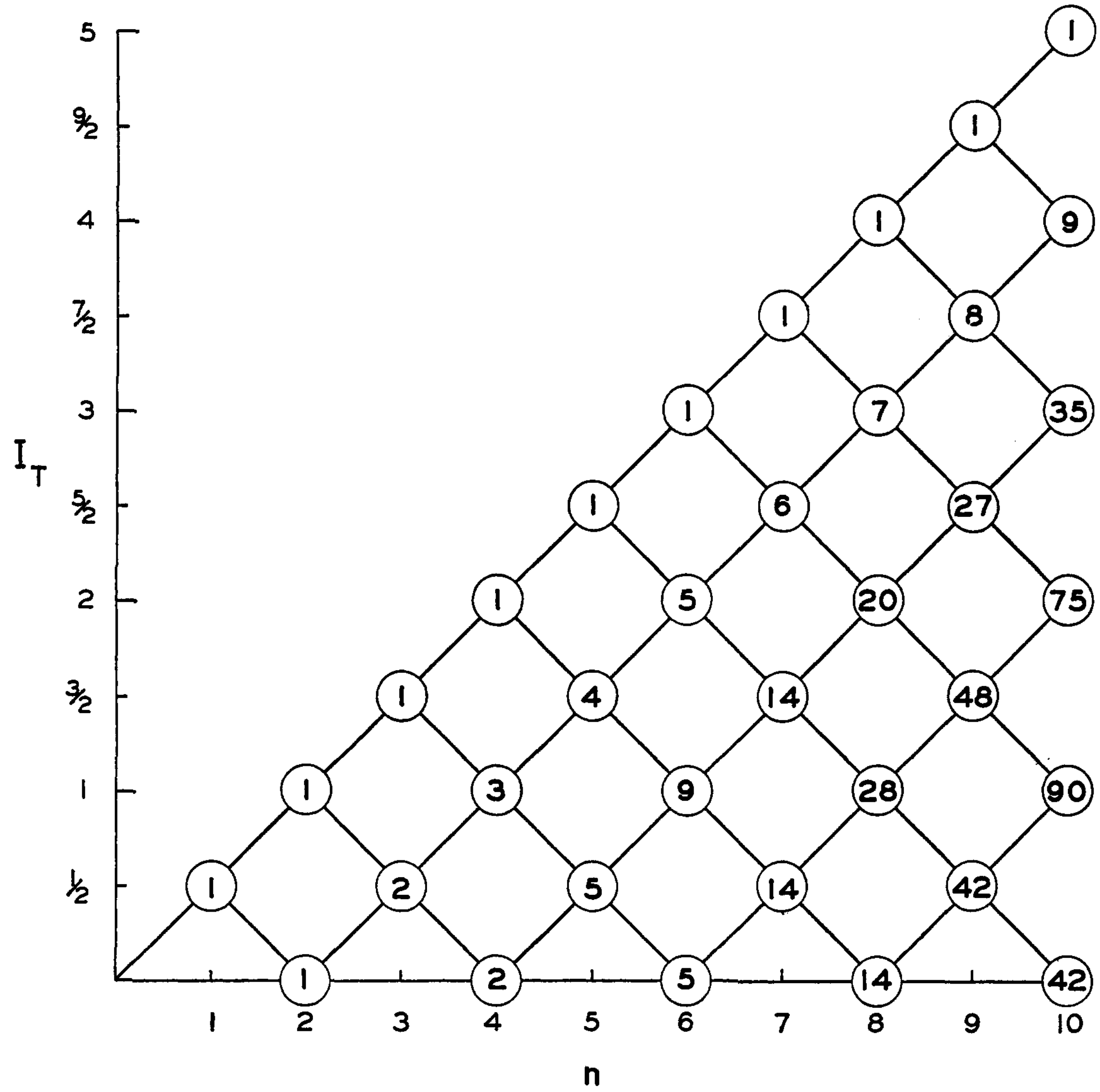

FIG. 1. Total spin quantum numbers and their statistical weights for n equivalent spin 1/2 nuclei.

For $n = 3$, $I_T = 3/2, 1/2$. Now the statistical weights g_{I_T} for spin functions with given I_T are not always unity except for $I_T = n/2$ (see tables 3, 4, and 5). In this case it is clear that $I_z(\max.) = n/2$ and this occurs only when all spins are up; hence

$$g_{I_T = \frac{n}{2}} = 1$$

If $I_T \neq n/2$, the g_{I_T} may be different from unity. Consider the case when $n = 3$. From equation 31 the total number of spin states is $2^3 = 8$. Therefore

$$\left(2 \cdot \frac{3}{2} + 1\right) g_{3/2} + \left(2 \cdot \frac{1}{2} + 1\right) g_{1/2} = 8$$

and since $g_{3/2} = 1$, $g_{1/2} = 2$. Thus, four of the eight spin functions correspond to $I_T = 3/2$ and the remaining four functions can be divided into two sets each corresponding to $I_T = 1/2$. Similarly, one can show that for $n = 2$ there are three spin functions for which $I_T = 1$ and one for $I_T = 0$.

These results can be extended by adding $\pm 1/2$ (for each additional spin) to the total spin quantum numbers already obtained and remembering that $I_T \geq 0$. In this way one can construct the branching diagram (46) shown in figure 1. The circled numbers give the statistical weights of the states with various values of I_T. For $n = 6$, $I_T = 3, 2, 1, 0$ with the statistical weights 1, 5, 9, and 5, respectively. In general, the statistical weights for total spin quantum number

$$I_T = \frac{n}{2} - k$$

are

$$g_{I_T} = g_{\frac{n}{2} - k} = \frac{n!(n - 2k + 1)}{(n - k + 1)!k!} \qquad (36)$$

where

$$k = \begin{cases} 0, 1, \cdots\cdots \frac{n}{2} \text{ for } n \text{ even} \\ 0, 1, \cdots\cdots \frac{n-1}{2} \text{ for } n \text{ odd} \end{cases}$$

TABLE 3

Spin eigenfunctions of $\mathbf{I}^2$ *and* I_z *for two spin 1/2 nuclei*

Spin Function	I_T	m	C_2 Symmetry
$\alpha\alpha$	1	1	$\mathcal{A}$
$\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$	1	0	$\mathcal{A}$
$\beta\beta$	1	−1	$\mathcal{A}$
$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$	0	0	$\mathcal{B}$

The spin functions for $n = 2$, 3, and 4 expressed as linear combinations of simple product functions are given in tables 3, 4, and 5.

B. FORMULATION OF THE QUANTUM-MECHANICAL PROBLEM

1. The Hamiltonian operator

Consider a molecule containing n nuclei with magnetic moments $\boldsymbol{\mu}_j = \gamma_j\hbar\mathbf{I}_j$ in a magnetic field $\mathbf{H}_0$. The actual field at a given nucleus is altered owing to intramolecular magnetic effects and intermolecular interactions. Assuming that all these shielding effects are described by a scalar shielding constant, the field at nucleus j can be expressed as

$$\mathbf{H}_j = (1 - \sigma_j)\mathbf{H}_0 \tag{37}$$

The interaction energy of nucleus j with the field $\mathbf{H}_j$ is obtained from the classical energy (59)

$$\begin{aligned} E = -\boldsymbol{\mu}\cdot\mathbf{H} &= \gamma_j\hbar(1 - \sigma_j)\mathbf{I}_j\cdot\mathbf{H}_0 \\ &= -\hbar\boldsymbol{\omega}_j\cdot\mathbf{I}_j \end{aligned} \tag{38}$$

where $\boldsymbol{\omega}_j = \gamma_j(1 - \sigma_j)\mathbf{H}_0$ is a vector parallel to $\mathbf{H}_0$ whose magnitude represents the Larmor frequency in the absence of spin-spin couplings. If nucleus j is indirectly coupled to the remaining nuclei there is, in addition, the spin-spin energy

$$-\sum_k K_{jk}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_k = -\hbar\sum_k J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k \tag{39}$$

The total energy for nucleus j is the sum of equations 38 and 39

$$-\hbar\left\{\boldsymbol{\omega}_j\cdot\mathbf{I}_j + \sum_k J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k\right\}$$

and the Hamiltonian operator, $\mathcal{H}$, for the entire spin system is obtained upon summing over j:

$$\mathcal{H} = -\hbar\left\{\sum_j \boldsymbol{\omega}_j\cdot\mathbf{I}_j + \sum_{j<}\sum_k J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k\right\} \tag{40}$$

It is to be noted that $|\boldsymbol{\omega}_j|$ and J_{jk} are in angular units and it is convenient to have the energies associated with $\mathcal{H}$ in these units also. This is easily done by choosing $\hbar$ for the unit of angular momentum as in the commutation rules (equations 2 in Section II,A,1). Further, the applied field $\mathbf{H}_0$ is usually taken to lie along the z-axis of a laboratory coördinate system

$$\mathbf{H}_0 = \mathrm{H}_0\mathbf{k} \tag{41}$$

and defining

$$|\boldsymbol{\omega}_j| = \omega_j \tag{42}$$

the time-independent Hamiltonian operator becomes

$$\mathcal{H} = -\left\{\sum_j \omega_j I_{zj} + \sum_{j<}\sum_k J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k\right\} \tag{43}$$

Equation 43 gives the Hamiltonian operator appropriate to the problem of determining the stationary states of a given spin system; i.e., a set of N spin functions, ψ_j, which are eigenfunctions of $\mathcal{H}$:

$$\mathcal{H}\psi_j = \Omega_j\psi_j \qquad j = 1, 2, \cdots N \tag{44}$$

(N is the total number of spin states and is determined by equation 31 in Section II,A,2.) Let u_j ($j = 1, 2, \cdots N$) be a set of zero-order initial spin functions. The u_k need not necessarily be pure product functions but they shall be required to be an orthonormal set which are eigenfunctions of I_z. Since the u_j form a basis, the ψ_j are expressible as linear combinations of these functions.

$$\psi_j = \sum_k a_{kj}u_k \tag{45}$$

Operating on ψ_j with $\mathcal{H}$ and using equation 44 yields:

$$\sum_k a_{kj}(\mathcal{H} - \Omega_j)u_k = 0 \tag{46}$$

TABLE 4

Spin eigenfunctions of $\mathbf{I}^2$ *and* I_z *for three spin 1/2 nuclei*

Spin Function	I_T	m	D_3 Symmetry
$\alpha\alpha\alpha$	3/2	3/2	$\mathcal{A}_1$
$\frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$	3/2	1/2	$\mathcal{A}_1$
$\frac{1}{\sqrt{3}}(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta)$	3/2	−1/2	$\mathcal{A}_1$
$\beta\beta\beta$	3/2	−3/2	$\mathcal{A}_1$
$\frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$	1/2	1/2	$\mathcal{E}$
$\frac{1}{\sqrt{6}}(\beta\beta\alpha + \beta\alpha\beta - 2\alpha\beta\beta)$	1/2	−1/2	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha)$	1/2	1/2	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\beta\beta\alpha - \beta\alpha\beta)$	1/2	−1/2	$\mathcal{E}$

TABLE 5

Spin eigenfunctions of $\mathbf{I}^2$ *and* I_z *for four spin 1/2 nuclei*

Spin Function	I_T	m	D_4 Symmetry
$\alpha\alpha\alpha\alpha$	2	2	$\mathcal{A}_1$
$\frac{1}{2}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)$	2	1	$\mathcal{A}_1$
$\frac{1}{\sqrt{6}}(\alpha\alpha\beta\beta + \beta\alpha\alpha\beta + \alpha\beta\beta\alpha + \beta\beta\alpha\alpha + \alpha\beta\alpha\beta + \beta\alpha\beta\alpha)$	2	0	$\mathcal{A}_1$
$\frac{1}{2}(\beta\beta\beta\alpha + \beta\beta\alpha\beta + \beta\alpha\beta\beta + \alpha\beta\beta\beta)$	2	−1	$\mathcal{A}_1$
$\beta\beta\beta\beta$	2	−2	$\mathcal{A}_1$
$\frac{1}{\sqrt{12}}(\alpha\alpha\beta\beta + \beta\alpha\alpha\beta + \alpha\beta\beta\alpha + \beta\beta\alpha\alpha - 2\alpha\beta\alpha\beta - 2\beta\alpha\beta\alpha)$	0	0	$\mathcal{A}_1$
$\frac{1}{2}(\alpha\alpha\beta\beta - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha + \beta\beta\alpha\alpha)$	0	0	$\mathcal{B}_1$
$\frac{1}{2}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	1	1	$\mathcal{B}_2$
$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)$	1	0	$\mathcal{B}_2$
$\frac{1}{2}(\beta\beta\beta\alpha - \beta\beta\alpha\beta + \beta\alpha\beta\beta - \alpha\beta\beta\beta)$	1	−1	$\mathcal{B}_2$
$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta - \alpha\beta\alpha\alpha)$	1	1	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)$	1	0	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\beta\beta\beta\alpha - \beta\alpha\beta\beta)$	1	−1	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\alpha\alpha\beta\alpha - \beta\alpha\alpha\alpha)$	1	1	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\beta\alpha\alpha\beta - \alpha\beta\beta\alpha)$	1	0	$\mathcal{E}$
$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta - \alpha\beta\beta\beta)$	1	−1	$\mathcal{E}$

Now the result of operating on u_k with $\mathcal{H}$ can always be expanded in terms of the orthonormal set $\{u_r\}$; that is,

$$u_k = \sum_r \mathcal{H}_{rk} u_r \tag{47}$$

where $\mathcal{H}_{rk} = \langle u_r | \mathcal{H} | u_k \rangle$. Substituting equation 47 into 46 and taking the scalar product with u_r gives, since the u_j are orthonormal,

$$\sum_k a_{kj}(\mathcal{H}_{rk} - \Omega_j \delta_{rk}) = 0 \qquad (k = 1, 2, \cdots N) \tag{48}$$

The N homogeneous equations for the a_{kj} have a non-trivial solution if and only if the determinant of the coefficients vanishes.

$$\det|\mathcal{H}_{rk} - \Omega_j \delta_{rk}| = 0 \tag{49}$$

Equation 49 is an algebraic equation of the N^{th} degree for the N characteristic roots Ω_j. Substituting any one of these, say Ω_j, into equation 48 leads to a set of equations for the a_{kj}. However, only $N - 1$ of these equations are linearly independent, so that one requires one more condition upon the a_{jk}. This condition is obtained by imposing the normalization requirements on the ψ_j. From equation 45 this requires that[4]

$$\sum_k a_{kj}^2 = 1 \tag{50}$$

Repetition of this procedure gives the set ψ_j and the corresponding eigenvalues Ω_j.

2. Some theorems on the matrix elements of the Hamiltonian

The determination of the eigenvalues and eigenfunctions of $\mathcal{H}$ requires the evaluation of the matrix elements

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[4] Note that neglecting arbitrary phase factors of unit modulus, the coefficient matrix (a_{ij}) is orthogonal and the Hamiltonian matrix real symmetric, $\mathcal{H}_{ij} = \mathcal{H}_{ji}$. These are special cases of the more general unitary and Hermitian matrices for (a_{ij}) and $\mathcal{H}$, respectively.

of $\mathcal{H}$ relative to some set of zero-order spin functions. The total number of matrix elements is

$$N^2 = \left\{\prod_{j=1}^{n} (2I_j + 1)\right\}^2$$

which can be rather large even for small n. (If all $I_j = 1/2$, $N^2 = 2^{2n}$.) Many of these matrix elements are zero, and useful relations can be established among the nonzero elements.

From the commutation rules it is readily demonstrated that

$$I_z = \sum_i I_{zi}$$

commutes with $\mathcal{H}$:

$$[I_z, \mathcal{H}] = 0 \tag{51}$$

This fact allows the use of an important theorem on the matrix elements of commuting operators (23). Suppose **A** and **B** commute and ψ_j and ψ_k are eigenfunctions of **A** with the eigenvalues a_j and a_k; then,

$$(\psi_j, \mathbf{AB}\psi_k) = (\psi_j, \mathbf{BA}\psi_k) = a_k(\psi_j, \mathbf{B}\psi_k) \tag{52}$$

If **A** is Hermitian,

$$(\psi_j, \mathbf{AB}\psi_k) = (\mathbf{A}\psi_j, \mathbf{B}\psi_k) = a_j(\psi_j, \mathbf{B}\psi_k) \tag{53}$$

Equating equations 52 and 53 leads to

$$(a_k - a_j)(\psi_j, \mathbf{B}\psi_k) = 0 \tag{54}$$

Therefore if $a_k \neq a_j$,

$$(\psi_j, \mathbf{B}\psi_k) = 0 \tag{55}$$

If the set of zero-order spin functions are taken to be eigenfunctions of I_z, then equation 55 (with $\mathbf{B} \equiv \mathcal{H}$) shows that the matrix elements of $\mathcal{H}$ are zero unless ψ_j and ψ_k have the same m-value. For the case of all $I_j = 1/2$, the number of spin functions with a specified value of m is given by the binomial coefficients n and the secular determinant factors accordingly. For example, with a three-spin system the secular equation factors into four subdeterminants of orders 1×1, 3×3, 3×3, and 1×1.

The relations between the nonzero matrix elements (18) are easily established by use of an operator, λ_i, for each individual spin function with the property

$$\lambda_i \Phi_{I_i, m_i} = \Phi_{I_i, -m_i} \tag{56}$$

By the definition of λ_i it follows that $\lambda_i^2 = 1$ (the unit operator) and from the commutation rules that

$$\lambda_i I_{zi} + I_{zi}\lambda_i = 0 \tag{57}$$

$$[\lambda_i, I_{xi}] = 0 \tag{58}$$

$$[\lambda_i, I_{yi}] = 0 \tag{59}$$

$$[\lambda_i, I_i^2] = 0 \tag{60}$$

For the complete spin system one employs the operator

$$\boldsymbol{\Lambda} = \prod_{i=1}^{n} \lambda_i \tag{61}$$

with properties analogous to those of the λ_i. For the Hamiltonian operator note that the first term

$$-\sum \omega_j I_{zj} \equiv \mathbf{A} \tag{62}$$

contributes only to the diagonal elements, while the coupling term

$$-\sum_{j}\sum_{<k} J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k \equiv \mathbf{B} \tag{63}$$

contributes to diagonal and off-diagonal elements. The diagonal elements of $\mathcal{H}$ corresponding to the $I_z = m$ states may therefore be written as

$$\begin{aligned} <\Phi(m)|\mathcal{H}|\Phi(m)> &= <\Phi(m)|\mathbf{A}|\Phi(m)> + <\Phi(m)|\mathbf{B}|\Phi(m)> \\ &= a_{mm} + b_{mm} \end{aligned} \tag{64}$$

The off-diagonal elements coming only from the second term are of the form

$$<\Phi(m')|\mathbf{B}|\Phi(m)> = b_{m'm} \tag{65}$$

Now the operator $\boldsymbol{\Lambda}$ commutes with the coupling operator **B**

$$[\mathbf{B}, \boldsymbol{\Lambda}] = 0 \tag{66}$$

and anticommutes with **A**,

$$\mathbf{A}\boldsymbol{\Lambda} + \boldsymbol{\Lambda}\mathbf{A} = 0 \tag{67}$$

From equations 66 and 67 **A** and **B** may be expressed as

$$\mathbf{B} = \boldsymbol{\Lambda}\mathbf{B}\boldsymbol{\Lambda} \tag{68}$$

$$\mathbf{A} = -\boldsymbol{\Lambda}\mathbf{A}\boldsymbol{\Lambda} \tag{69}$$

Substituting these expressions into equations 64 and 65 and noting that $\boldsymbol{\Lambda}$ is Hermitian, one obtains

$$<\Phi(-m)|\mathcal{H}|\Phi(-m)> = -a_{mm} + b_{mm} \tag{70}$$

$$<\Phi(-m')|\mathcal{H}|\Phi(-m)> = b_{m'm} \tag{71}$$

Therefore, if the matrix elements of $\mathcal{H}$ are calculated with respect to the states with $I_z = m$, equations 70 and 71 give the matrix elements for $I_z = -m$. In the case $m = 0$ there are two possibilities: (*1*) $\boldsymbol{\Lambda}$ permutes the several $\Phi(0)$ and the diagonal elements are related by equations 64 and 70; (*2*) $\boldsymbol{\Lambda}$ does not permute the $\Phi(0)$ and $a_{00} = 0$. Then the diagonal elements are just b_{00} (18). In general there will be a combination of these possibilities for $m = 0$.

The above theorems are general and hold for any *set* of spin functions which are eigenfunctions of I_z. The following results are restricted to the product representation and must be appropriately modified for more general spin functions. The derivation of the matrix elements in the product scheme (5) is facilitated by introducing the identity

$$\mathbf{I}_j \cdot \mathbf{I}_k = I_{zj}I_{zk} + \frac{1}{2}(I_j^+ I_k^- + I_j^- I_k^+) \tag{72}$$

into the Hamiltonian operator;

$$\mathcal{H} = -\Big\{\sum_j \omega_j I_{zj} + \sum_{j<}\sum_k J_{jk} I_{zj} I_{zk} + \frac{1}{2}\sum_{j<}\sum_k J_{jk}(I_j^+ I_k^- + I_j^- I_k^+)\Big\} \quad (73)$$

In the product representation, the spin functions have the form

$$\Phi(\cdots I_j m_j \cdots ; m) = \prod_{j=1}^{n} \Phi_{I_j, m_j} \quad (74)$$

The diagonal matrix elements are given by

$$<\Phi(\cdots I_j m_j \cdots ; m)|\mathcal{H}|\Phi(\cdots I_j m_j \cdots ; m)> = -\Big\{\sum_j \omega_j m_j + \sum_{j<}\sum_k J_{jk} m_j m_k\Big\} \quad (75)$$

and the off-diagonal elements are

$$<\Phi(\cdots I_j m_j + 1 \cdots I_k m_k - 1 \cdots ; m)|\mathcal{H}|\Phi(\cdots I_j m_j \cdots I_k m_k \cdots ; m)> = -\frac{1}{2} J_{jk}\{(I_j - m_j)(I_k + m_k)(I_j + m_j + 1)(I_k - m_k + 1)\}^{1/2} \quad (76)$$

In the special case where all $I_j = 1/2$, equations 75 and 76 become (53)

$$<\Phi|\mathcal{H}|\Phi> = -\frac{1}{2}\Big\{\sum_j S_j \omega_j + \frac{1}{2}\sum_{j<}\sum_k T_{jk} J_{jk}\Big\} \quad (77)$$

$$<\Phi'|\mathcal{H}|\Phi> = -\frac{1}{2} J_{jk} U \quad (78)$$

where $S_j = \pm 1$ accordingly as spin j is α or β, $T_{jk} = \pm 1$ accordingly as spin j and k are parallel or antiparallel, and $U = 1$ if Φ and Φ' differ by an interchange of spins j and k, and is zero otherwise.

In the following sections, the matrix elements of $\mathcal{H}$ will be computed for a variety of spin systems and the validity of the above formulae should be checked in detail, since they are of great value in expediting the calculations.

3. Transition probabilities

Once the eigenvalues and eigenfunctions of the Hamiltonian operator have been determined, there remains only the problem of calculating the probabilities of the transitions induced by the radiofrequency field

$$H_x' = 2H_1 \cos \omega t \quad (79)$$

It is convenient to decompose H_x into two contrarotating components confined to the xy-plane. For positive γ_j, only the component rotating in the negative sense is effective for resonance, and its x, y-components are

$$\left.\begin{aligned} H_x &= H_1 \cos \omega t \\ H_y &= -H_1 \sin \omega t \end{aligned}\right\} \quad (80)$$

The interaction of the nuclei with this field is

$$\mathcal{H}' = -\sum_k \gamma_k H_1 \{I_{xk} \cos \omega t - I_{yk} \sin \omega t\} \quad (81)$$

Shielding effects need not be considered here, since $H_1 \ll H_0$ in high-resolution experiments.

The complete time-dependent Hamiltonian is

$$\mathcal{H}(t) = -\Big\{\sum_j \omega_j I_{zj} + \sum_{j<}\sum_k J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k + \sum_k \gamma_k H_1 (I_{xk} \cos \omega t - I_{yk} \sin \omega t)\Big\} \quad (82)$$

and satisfies the time-dependent Schrodinger equation.

$$i \frac{\partial}{\partial t} \Psi(t) = \mathcal{H}(t) \Psi(t) \quad (83)$$

$\Psi(t)$ here represents a *state vector*; i.e., the components $c_m(t)$ of $\Psi(t)$ are the probability amplitudes for the stationary states of the time-independent Hamiltonian. The solution of equation 83 is facilitated by the substitution

$$\Psi(t) = e^{iI_z \omega t} \Psi_r(t) \quad (84)$$

which represents a transformation to a coördinate system rotating about the z-axis (71, 79, 85). $\Psi_r(t)$ satisfies an equation of Hamiltonian form:

$$i \frac{\partial}{\partial t} \Psi_r(t) = \{e^{-iI_z \omega t} \mathcal{H}(t) e^{iI_z \omega t} + \omega I_z\} \Psi_r(t) \quad (85)$$

In carrying out the transformation of $\mathcal{H}(t)$, it is helpful to note that I_{zj} commutes with I_z and that scalar products are invariant under rotations. Thus the first and second terms of equation 82 are unaltered by the transformation. The transformation of the remaining terms (85) is determined by equations 86:

$$\left.\begin{aligned} e^{-iI_z \omega t} I_x e^{iI_z \omega t} &= I_x \cos \omega t + I_y \sin \omega t \\ e^{-iI_z \omega t} I_y e^{iI \omega_z t} &= -I_x \sin \omega t + I_y \cos \omega t \end{aligned}\right\} \quad (86)$$

Carrying out the calculations gives:

$$e^{-iI_z \omega t} \mathcal{H}(t) e^{iI_z \omega t} = -\Big\{\sum_j \omega_j I_{zj} + \sum_{j<}\sum_k J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k + \sum_k \gamma_k H_1 I_{xk}\Big\} \quad (87)$$

The time-dependent equation for $\Psi_r(t)$ is, therefore,

$$i \frac{\partial}{\partial t} \Psi_r(t) = -\Big\{\sum_j (\omega_j - \omega) I_{zj} + \sum_{j<}\sum_k J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k + \sum_j \gamma_j H_1 I_{xj}\Big\} \Psi_r(t) \quad (88)$$

For convenience one writes equation 88 as

$$i \frac{\partial}{\partial t} \Psi_r(t) = -\{\alpha + \beta\} \Psi_r(t) \quad (89)$$

with

$$\beta = \sum_j \gamma_j H_1 I_{xj} \quad (90)$$

The eigenfunctions of α are identical with the eigenfunctions ψ_m of equation 43 in Section II, and the eigenvalues of α are just $\Omega_m + m\omega$.

Now α and β are independent of the time, so the solution of equation 89 in operator form is

$$\Psi_r(t) = e^{i(\alpha+\beta)t}\Psi_r(0) \tag{91}$$

and, since $\Psi(0) = \Psi_r(0)$,

$$\Psi(t) = e^{iI_z\omega t}e^{i(\alpha+\beta)t}\Psi(0) \tag{92}$$

If at $t = 0$, $|c_m|^2 = 1$ and $c_{m'} = 0$ for $m' \neq m$, then $\Psi(0) = \psi_m$ and

$$\Psi(t) = e^{iI_z\omega t}e^{i(\alpha+\beta)t}\psi_m \tag{93}$$

The probability that the system is in the state $\psi_{m'}$ at time t is

$$\begin{aligned} P_{mm'}(t) &= |(\psi_{m'}, \Psi(t))|^2 = |<\psi_{m'}|e^{iI_z\omega t}e^{i(\alpha+\beta)t}|\psi_m>|^2 \\ &= |<\psi_{m'}|e^{i(\alpha+\beta)t}|\psi_m>|^2 \end{aligned} \tag{94}$$

The last step follows from the fact that the ψ_m are eigenfunctions of $e^{iI_z\omega t}$. The term $e^{i(\alpha+\beta)t}$ cannot be further simplified, since α and β do not commute. In a representation which diagonalizes α the exponential may be easily expanded to yield:

$$\begin{aligned} [e^{i(\alpha+\beta)t}]_{m'm} &= e^{i\alpha_{m'}}\delta_{m'm} + \frac{e^{i\alpha_m} - e^{i\alpha_{m'}}}{\alpha_m - \alpha_{m'}}\beta_{m'm} \\ &+ \sum_k \frac{\beta_{m'k}\beta_{km}}{\alpha_k - \alpha_m}\left\{\frac{e^{i\alpha_k} - e^{i\alpha_m}}{\alpha_k - \alpha_{m'}} + \frac{e^{i\alpha_m} - e^{i\alpha_{m'}}}{\alpha_{m'} - \alpha_m}\right\} + \cdots \end{aligned} \tag{95}$$

Retaining only terms of the first order in β_{ij}, the absolute square of equation 95 gives

$$P_{mm'}(t) = \frac{2\{1 - \cos[\Omega_{m'} - \Omega_m + \omega(m' - m)]t\}}{[\Omega_{m'} - \Omega_m + (m' - m)\omega]^2}|\beta_{m'm}|^2 \tag{96}$$

From equation 96 it follows that $P_{m\to m'}$ will be zero unless $m' = m \pm 1$ (*cf.* equations 14 and 15 in Section II). For absorption the selection rule is $m' = m - 1$ and

$$P_{m,m-1}(t) = \frac{2\{1 - \cos(\Omega_{m-1} - \Omega_m - \omega)t\}}{(\Omega_{m-1} - \Omega_m - \omega)^2}|\beta_{m-1,m}|^2 \tag{97}$$

It is noted further that $P_{m\to m-1}$ will be large for

$$\omega = \Omega_{m-1} - \Omega_m \tag{98}$$

which is just the Bohr frequency rule in the system of units with $\hbar = 1$. Integrating equation 97 over a range of rf frequencies one finds that the *transition probability* (24) is proportional to

$$|\beta_{m-1,m}|^2 = |<\psi_{m-1}|\sum_j \gamma_j H_1 I_{xj}|\psi_m>|^2$$

Since the line intensities of nuclei with different γ_j are not ordinarily compared, there is no loss of generality in assuming all $\gamma_j = \gamma$. The relative intensities are then just proportional to

$$(\gamma H_1)^2|<\psi_{m-1}|I_x|\psi_m>|^2$$

The fact that transition probabilities are proportional to the matrix elements of I_x stems from the assumption that H_1 lies along the x-axis in the rotating frame. If H_1 were taken along the y-axis, I_y would replace I_x. Hence the transition probabilities are also proportional to the absolute square of the matrix elements of $\mathbf{I}^-$. Thus first-order time-dependent perturbation theory yields the selection rule

$$\Delta m = -1 \tag{100}$$

and relative intensities proportional to any of the following matrix elements:

$$\left.\begin{aligned} &|<m - 1|I_x|m>|^2 \\ &|<m - 1|I_y|m>|^2 \\ &|<m - 1|I^-|m>|^2 \end{aligned}\right\} \tag{101}$$

III. The Analysis of Some Simple Systems

A. THE TWO-SPIN SYSTEM AB

The simplest system that can be studied is one with two spin 1/2 nuclei A and B, having resonance frequencies ω_A and ω_B and coupling constant $J_{AB} = J_{BA} \equiv J$ (5, 10, 11, 39). For this case the Hamiltonian operator is

$$\mathcal{H} = -\left\{\omega_A I_{Az} + \omega_B I_{Bz} + JI_{Az}I_{Bz} + \frac{1}{2}J(I_A^+I_B^- + I_A^-I_B^+)\right\} \tag{1}$$

For a basis it is convenient to use the product functions $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$, whose m-values are 1, 0, 0, and -1, respectively. Operating on these spin functions with $\mathcal{H}$ gives:

$$\mathcal{H}\alpha\alpha = -\frac{1}{2}\left\{\omega_A + \omega_B + \frac{1}{2}J\right\}\alpha\alpha \tag{2}$$

$$\mathcal{H}\alpha\beta = -\frac{1}{2}\left\{\omega_A - \omega_B - \frac{1}{2}J\right\}\alpha\beta - \frac{1}{2}J\beta\alpha \tag{3}$$

$$\mathcal{H}\beta\alpha = -\frac{1}{2}\left\{-\omega_A + \omega_B - \frac{1}{2}J\right\}\beta\alpha - \frac{1}{2}J\alpha\beta \tag{4}$$

$$\mathcal{H}\beta\beta = -\frac{1}{2}\left\{-\omega_A - \omega_B + \frac{1}{2}J\right\}\beta\beta \tag{5}$$

Equations 2 and 5 show that $\alpha\alpha$ and $\beta\beta$ are eigenfunctions of $\mathcal{H}$, while equations 3 and 4 show that $\alpha\beta$ and $\beta\alpha$ are mixed by the spin coupling. This mixing is in agreement with the considerations of Section II,B, which showed that the secular equation is of order 2^n but factors according to the binomial coefficients of n (1:2:1 in this case). The 2 × 2 determinant is

$$\begin{vmatrix} <\alpha\beta|\mathcal{H}|\alpha\beta> - \Omega & <\beta\alpha|\mathcal{H}|\alpha\beta> \\ <\alpha\beta|\mathcal{H}|\beta\alpha> & <\beta\alpha|\mathcal{H}|\beta\alpha> - \Omega \end{vmatrix} = 0 \tag{6}$$

where

$$<\beta\alpha|\mathcal{H}|\alpha\beta> = <\alpha\beta|\mathcal{H}|\beta\alpha> = -\frac{1}{2}J$$

$$<\alpha\beta|\mathcal{H}|\alpha\beta> = -\frac{1}{2}\left\{\omega_A - \omega_B - \frac{1}{2}J\right\}$$

$$<\beta\alpha|\mathcal{H}|\beta\alpha> = -\frac{1}{2}\left\{-\omega_A + \omega_B - \frac{1}{2}J\right\}$$

Equation 6 is readily solved to give the eigenvalues

$$\Omega_2 = \frac{1}{2}\left\{\frac{1}{2}J - \sqrt{\delta^2 + J^2}\right\} \tag{7}$$

$$\Omega_3 = \frac{1}{2}\left\{\frac{1}{2}J + \sqrt{\delta^2 + J^2}\right\} \tag{8}$$

with

$$\delta = \omega_A - \omega_B \tag{9}$$

It can be assumed without loss of generality that $\delta > 0$. The eigenvalues Ω_2 and Ω_3 have the properties

$$\left.\begin{array}{l} \Omega_2 \rightarrow <\alpha\beta|\mathcal{H}|\alpha\beta> \\ \Omega_3 \rightarrow <\beta\alpha|\mathcal{H}|\beta\alpha> \end{array}\right\} \text{ as } J \rightarrow 0$$

The eigenfunctions corresponding to these eigenvalues are obtained by use of the equations

$$a_j\{<\alpha\beta|\mathcal{H}|\alpha\beta> - \Omega_j\} + b_j<\beta\alpha|\mathcal{H}|\alpha\beta> = 0 \tag{10}$$

$$a_j<\alpha\beta|\mathcal{H}|\beta\alpha> + b_j\{<\beta\alpha|\mathcal{H}|\beta\alpha> - \Omega_j\} = 0 \tag{11}$$

where a_j and b_j are, respectively, the coefficients of $\alpha\beta$ and $\beta\alpha$ in the mixed spin functions. Equations 10 and 11 are not independent, but either of these together with the normalization conditions

$$a_j^2 + b_j^2 = 1 \tag{12}$$

is sufficient to determine the a_j and b_j. The quadratic nature of equation 12 leads to several choices of sign, but the eigenfunctions thus obtained differ only by a factor of -1 so that no physical significance is to be attached to the various possibilities. Upon substituting the appropriate matrix elements and eigenvalues one obtains

$$\psi_2 = \frac{1}{\sqrt{1+Q^2}}\{\alpha\beta + Q\beta\alpha\} \tag{13}$$

$$\psi_3 = \frac{1}{\sqrt{1+Q^2}}\{Q\alpha\beta - \beta\alpha\} \tag{14}$$

which have the eigenvalues Ω_2 and Ω_3, respectively, and

$$Q = \frac{J}{\delta + \sqrt{\delta^2 + J^2}} \tag{15}$$

All of the eigenvalues and eigenfunctions are given in table 6.

To determine the transition probabilities the nonzero matrix elements of $I^- = I_A^- + I_B^-$ with respect to the eigenfunctions of $\mathcal{H}$ are required. Operating with I^- on the eigenfunctions yields

$$\begin{aligned} I^-\alpha\alpha &= \alpha\beta + \beta\alpha \\ &= \frac{1}{\sqrt{1+Q^2}}\{(1+Q)\psi_2 + (Q-1)\psi_3\} \end{aligned} \tag{16}$$

$$\begin{aligned} I^-\psi_2 &= \frac{1}{\sqrt{1+Q^2}}\{\beta\beta + Q\beta\beta\} \\ &= \frac{(1+Q)}{\sqrt{1+Q^2}}\beta\beta \end{aligned} \tag{17}$$

$$\begin{aligned} I^-\psi_3 &= \frac{1}{\sqrt{1+Q^2}}\{Q\beta\beta - \beta\beta\} \\ &= \frac{(Q-1)}{\sqrt{1+Q^2}}\beta\beta \end{aligned} \tag{18}$$

$$I^-\beta\beta = 0 \tag{19}$$

From equations 16, 17, and 18 the transition probabilities are:

$$|<\psi_2|I^-|\alpha\alpha>|^2 = \frac{(1+Q)^2}{1+Q^2} \tag{20}$$

$$|<\psi_3|I^-|\alpha\alpha>|^2 = \frac{(1-Q)^2}{1+Q^2} \tag{21}$$

$$|<\beta\beta|I^-|\psi_2>|^2 = \frac{(1+Q)^2}{1+Q^2} \tag{22}$$

$$|<\beta\beta|I^-|\psi_3>|^2 = \frac{(1-Q)^2}{1+Q^2} \tag{23}$$

By some elementary algebra one can show that

$$\frac{(1 \pm Q)^2}{1+Q^2} = 1 \pm \frac{J}{\sqrt{J^2 + \delta^2}} \tag{24}$$

The resonance frequencies corresponding to the above transitions are given by the Bohr formula:

$$\Omega_{j \leftarrow k} = \Omega_j - \Omega_k \tag{25}$$

These frequencies are given in table 7 along with relative line intensities (transition probabilities). The notation used for the transitions will be explained in Section IV.

From table 7 it is evident that the spectrum consists of four lines and is symmetrical with respect to the frequency $\frac{1}{2}(\omega_A + \omega_B)$. Theoretical spectra for several J/δ ratios are shown in figure 2 with $\frac{1}{2}(\omega_A + \omega_B)$ as the frequency origin. Figure 2a represents the case $J/\delta = 0$, which occurs when $J = 0$ or as $\delta \rightarrow \infty$. Only two lines are observed in this case, since the nuclei may "flip" independently (there is negligible coupling). A flip of nucleus A corresponds to absorption at ω_A and similarly at ω_B for B flips; the frequency separation is just $\omega_A - \omega_B = \delta$. Figure 2b illustrates the "first-order" case; that is, the off-diagonal elements of equation 6 are small compared to δ. The separations of the low- and high-frequency doublets are J (which is true for any J/δ ratio) and

$$\delta = \frac{1}{2}(S_1 + S_2)$$

TABLE 6

Eigenvalues and eigenfunctions for the two-spin system

Eigenfunction	Eigenvalue
$\alpha\alpha$	$-\frac{1}{2}(\omega_A + \omega_B) - \frac{1}{4}J$
$\frac{1}{\sqrt{1+Q^2}}\{\alpha\beta + Q\beta\alpha\}$	$\frac{1}{2}\{\frac{1}{2}J - \sqrt{\delta^2 + J^2}\}$
$\frac{1}{\sqrt{1+Q^2}}\{Q\alpha\beta - \beta\alpha\}$	$\frac{1}{2}\{\frac{1}{2}J + \sqrt{\delta^2 + J^2}\}$
$\beta\beta$	$\frac{1}{2}(\omega_A + \omega_B) - \frac{1}{4}J$

where S_1 and S_2 are the frequency separations of the extreme and central resonances. In figure 2c, $J/\delta = 1$ and the central resonances are of greater intensity than the extreme resonances. The coupling constant may be determined as in the first-order case, while δ is now obtained as the *geometric* mean of S_1 and S_2. When $J/\delta \gg 1$ (figure 2d) the extreme resonances are very weak (relative intensities $\simeq 0$) and are at

$$\simeq \pm\frac{1}{2}\left(J + \frac{1}{2} - \frac{\delta^2}{J}\right)$$

TABLE 7*

Resonance frequencies and relative intensities for the two-spin system

Transition in the Limit $J \rightarrow 0$	Relative Intensity	Frequency
$A_{1/2,1/2}B_{1/2,1/2} \rightarrow A_{1/2,-1/2}B_{1/2,1/2}$	$1 - \frac{J}{R}$	$\frac{1}{2}\{\omega_A + \omega_B + J + R\}$
$A_{1/2,1/2}B_{1/2,-1/2} \rightarrow A_{1/2,-1/2}B_{1/2,-1/2}$	$1 + \frac{J}{R}$	$\frac{1}{2}\{\omega_A + \omega_B - J + R\}$
$A_{1/2,1/2}B_{1/2,1/2} \rightarrow A_{1/2,1/2}B_{1,2,-1/2}$	$1 + \frac{J}{R}$	$\frac{1}{2}\{\omega_A + \omega_B + J - R\}$
$A_{1/2,-1/2}B_{1/2,1/2} \rightarrow A_{1/2,-1/2}B_{1/2,-1/2}$	$1 - \frac{J}{R}$	$\frac{1}{2}\{\omega_A + \omega_B - J - R\}$

* In this table $R = \sqrt{\delta^2 + J^2}$.

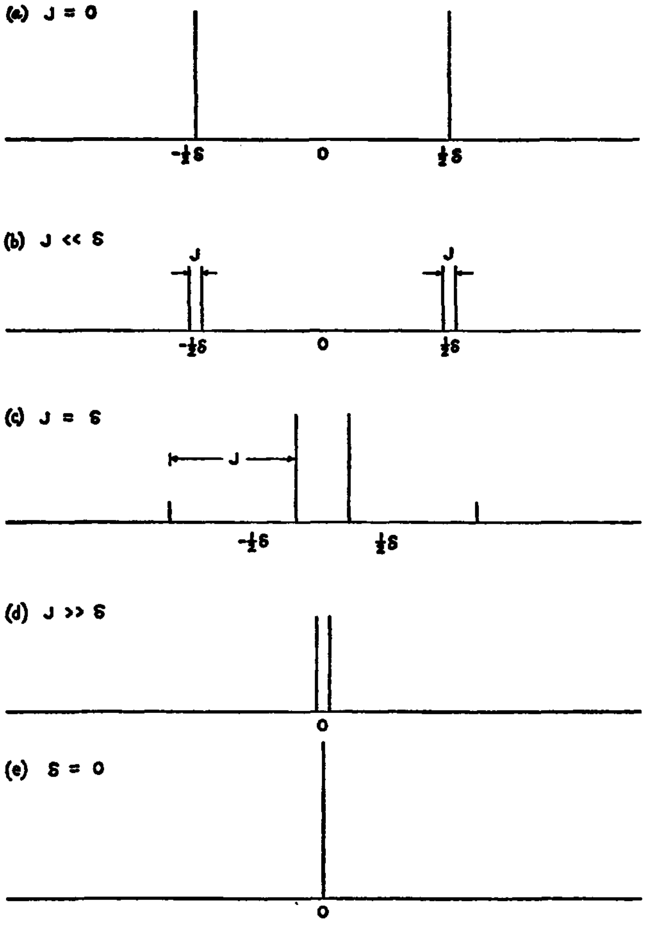


FIG. 2. Theoretical spectra for the two-spin system for various values of the J/δ ratio.

The central resonances are "peaked" towards the origin and have a residual splitting of order $\delta^2/2J$. The case $J/\delta = \infty$ (figure 2e), which occurs when $\delta = 0$ or as $J \rightarrow \infty$, leads to a single-line spectrum.

Zeeman energy-level diagrams corresponding to the spectra depicted in figure 2 are shown in figure 3. The separation of the extreme levels is actually much greater than that shown and is reduced only to facilitate the drawing. It should be noted that although there are four distinct energy levels, only three of these participate in the resonance in the case $\delta = 0$ (or $J \rightarrow \infty$). The spin functions for these levels are

$$\left.\begin{array}{r} \alpha\alpha \\ \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \\ \beta\beta \end{array}\right\} \qquad (26)$$

These functions make up the so-called "triplet state" (parallel spins), since they behave under the various spin operators like a single nucleus of spin 1 (83). The state which does not participate in the resonance as $\delta \rightarrow 0$ is described by the singlet state (antiparallel spins)

$$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \qquad (27)$$

and corresponds to zero spin. The proof of the fact that transitions to and from the singlet state are forbidden when $\delta = 0$ or $J = \infty$ is based upon the different symmetries of the singlet and triplet states under the operation P which interchanges spins A and B. Let ψ_S

denote any of the triplet-state functions and ψ_A the singlet state; then

$$P\psi_S = \psi_S \tag{28}$$

$$P\psi_A = -\psi_A \tag{29}$$

Thus the singlet state is described by an antisymmetric spin function and the triplet state by symmetric functions. Suppose now that a transition $\psi_A \rightarrow \psi_S$ is possible; then the line intensity will be proportional to the absolute square of

$$<\psi_A|I^-|\psi_S> \tag{30}$$

Now $I^- = I_1^- + I_2^-$ commutes with P

$$PI^- = I^-P \tag{31}$$

so that

$$\begin{aligned} <\psi_A|PI^-|\psi_S> &= <\psi_A|I^-P|\psi_S> \\ &= <\psi_A|I^-|\psi_S> \end{aligned} \tag{32}$$

and since P is Hermitian,

$$\begin{aligned} <\psi_A|PI^-|\psi_S> &= <P\psi_A|I^-|\psi_S> \\ &= -<\psi_A|I^-|\psi_S> \end{aligned} \tag{33}$$

From equations 32 and 33 it follows that

$$<\psi_A|I^-|\psi_S> = 0 \tag{34}$$

When $\delta > 0$ all four levels participate in the resonance because the spin functions are no longer purely symmetric or antisymmetric.

The experimental spectrum of the protons in 2,3-dibromothiophene (19b) is shown in figure 4. The theoretical spectrum for $J/\delta = 0.319$ is added for comparison. From the line spacings in the experimental trace the chemical shift and spin-spin coupling constant are determined to be

$$\frac{\delta}{2\pi} = 18.5 \pm 0.1 \text{ c.p.s. (c.p.s.} \equiv \text{sec.}^{-1})$$

$$\frac{J}{2\pi} = 5.9 \pm 0.1 \text{ c.p.s.}$$

Although the bromine nuclei have magnetic moments which could result in spin-spin multiplets, their quadrupole moments preclude the observation of additional fine structure (37).

B. A THREE-SPIN SYSTEM, A_2B

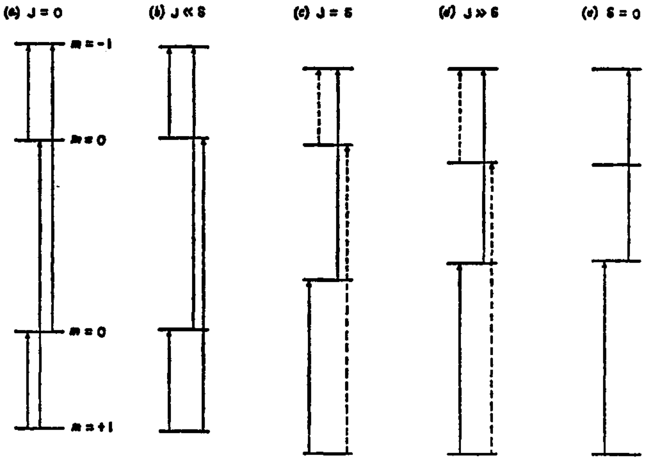


FIG. 3. Zeeman energy-level diagrams (schematic) for the theoretical spectra of figure 2. The more intense transitions are indicated with a solid line and the weaker transitions with a dashed line.

A three-spin system that frequently occurs in practice consists of two nuclei with identical Larmor frequencies, which are equally coupled to a third chemically shifted nucleus (5, 10, 11, 20, 39). An example of such a system is the substituted allene $H_2^AC{=}CH^BX$. It is assumed that the substituent X has negligible interactions with the H^A and H^B protons and that the equilibrium configuration of the molecule has a plane of symmetry passing through the carbon chain and perpendicular to the plane of the H^A nuclei. This spin system is actually more general than presently indicated, as will be seen in Section IV.

From the assumed symmetry it follows that

$$\omega_1 = \omega_2 \equiv \omega_A \tag{35}$$

$$J_{13}^{AB} = J_{23}^{AB} \equiv J \tag{36}$$

$$J_{12}^{A} = J_{21}^{A} \equiv J' \tag{37}$$

where the subscripts 1 and 2 refer to the two A-type nuclei and the subscript 3 to the nucleus B. The Hamiltonian for this system is

$$\begin{aligned} \mathcal{H} = -\Big\{ & \omega_A(I_{z1} + I_{z2}) + \omega_B I_{z3} + J(I_{z1} + I_{z2})I_{z3} + J'I_{z1}I_{z2} \\ & + \frac{1}{2}J[(I_1^+ + I_2^+)I_3^- + (I_1^- + I_2^-)I_3^+] \\ & + \frac{1}{2}J'(I_1^+I_2^- + I_2^-I_1^+)\Big\} \end{aligned} \tag{38}$$

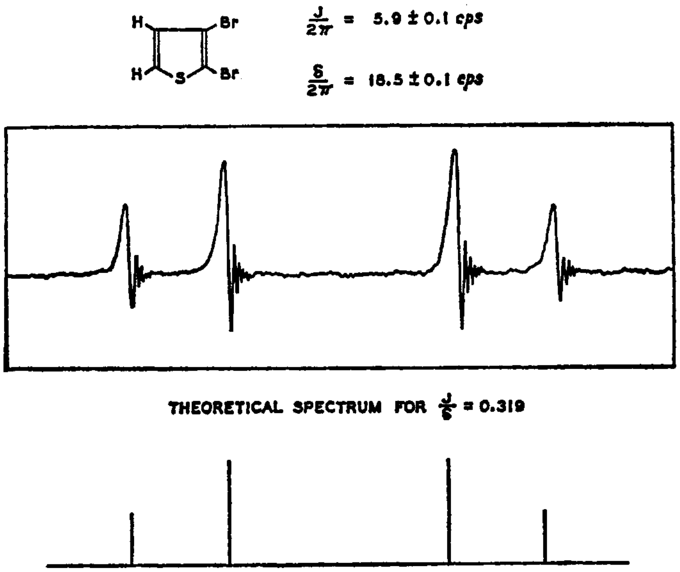


FIG. 4. Experimental and theoretical spectra of the protons in 2,3-dibromothiophene. The experimental trace is that of the pure liquid as observed at room temperature and 60 Mc./sec.

For zero-order spin functions the product functions given in table 2 may be used. However, since the molecule possesses a plane of symmetry, there are definite advantages if the initial spin functions reflect this symmetry. Since reflection in the plane of symmetry interchanges the A spins, the correct functions are eigenfunctions of the operator P; that is,

$$P\psi = c\psi$$

If ψ is normalized, then $(\psi, \psi) = 1$ and $(P\psi, P\psi) = (\psi, \psi) = 1 = (c\psi, c\psi) = c^2$, so that $c = \pm 1$. Thus spin functions with the proper symmetry are symmetric or antisymmetric under the operation P. To determine these functions operate on the product functions in table 2 with P:

$$Pu_1 = u_1 \tag{39}$$

$$Pu_2 = u_2 \tag{40}$$

$$Pu_3 = u_4 \tag{41}$$

$$Pu_4 = u_3 \tag{42}$$

$$Pu_5 = u_6 \tag{43}$$

$$Pu_6 = u_5 \tag{44}$$

$$Pu_7 = u_7 \tag{45}$$

$$Pu_8 = u_8 \tag{46}$$

Equations 39, 40, 45, and 46 show that u_1, u_2, u_7, and u_8 are symmetric functions, while equations 41, 42, 43, and 44 show that u_3, u_4, u_5, and u_6 do not possess definite symmetry under the operation P. However, if equations 41 and 42 are added and subtracted, it is found that the functions

$$\frac{1}{\sqrt{2}}(u_3 \pm u_4) \tag{47}$$

(the factor $2^{-1/2}$ is for normalization) are symmetric (+) and antisymmetric (−) with respect to P. Similarly, equations 43 and 44 provide the pair

$$\frac{1}{\sqrt{2}}(u_5 \pm u_6) \tag{48}$$

These are eight linearly independent spin functions of the required symmetry which can, therefore, be used as a basis. These functions are tabulated in table 8. It is of importance to note that the functions in table 8 consist of all possible products (i.e., the direct product) of the functions α and β for spin B with the singlet and triplet state spin functions (*cf.* table 3) for the A spins. The abbreviations for the spin functions have the general form $A_{I_A,m_A}B_{I_A,m_B}$, where I_A, I_B, m_A, and m_B are the total spins and z-components of angular momenta for the A and B nuclei, respectively. Since there are two spins of type A and one of type B, this system is conveniently abbreviated as A_2B (11).

TABLE 8

Symmetrized spin functions for the A_2B spin system

Spin Function	m	C_2 Symmetry	Notation
$\alpha\alpha\alpha$	3/2	$\mathcal{A}$	$A_{1,1}B_{1/2,1/2}$
$\alpha\alpha\beta$	1/2	$\mathcal{A}$	$A_{1,1}B_{1/2,-1/2}$
$\frac{1}{\sqrt{2}}(\alpha\beta\alpha + \beta\alpha\alpha)$	1/2	$\mathcal{A}$	$A_{1,0}B_{1/2,1/2}$
$\frac{1}{\sqrt{2}}(\alpha\beta\beta + \beta\alpha\beta)$	−1/2	$\mathcal{A}$	$A_{1,0}B_{1/2,-1/2}$
$\beta\beta\alpha$	−1/2	$\mathcal{A}$	$A_{1,-1}B_{1/2,1/2}$
$\beta\beta\beta$	−3/2	$\mathcal{A}$	$A_{1,-1}B_{1/2,-1/2}$
$\frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)$	1/2	$\mathcal{B}$	$A_{0,0}B_{1/2,1/2}$
$\frac{1}{\sqrt{2}}(\alpha\beta\beta - \beta\alpha\beta)$	−1/2	$\mathcal{B}$	$A_{0,0}B_{1/2,-1/2}$

Operating on these spin functions with $\mathcal{H}$ gives:

$$\mathcal{H}A_{1,1}B_{1/2,1/2} = -\frac{1}{2}\left\{2\omega_A + \omega_B + J + \frac{1}{2}J'\right\}A_{1,1}B_{1/2,1/2} \tag{49}$$

$$\mathcal{H}A_{1,1}B_{1/2,-1/2} = -\frac{1}{2}\left\{2\omega_A - \omega_B - J + \frac{1}{2}J'\right\}A_{1,1}B_{1/2,-1/2} - \frac{\sqrt{2}}{2}JA_{1,0}B_{1/2,1/2} \tag{50}$$

$$\mathcal{H}A_{1,0}B_{1/2,1/2} = -\frac{1}{2}\left\{\omega_B + \frac{1}{2}J'\right\}A_{1,0}B_{1/2,1/2} - \frac{\sqrt{2}}{2}JA_{1,1}B_{1/2,-1/2} \tag{51}$$

$$\mathcal{H}A_{1,0}B_{1/2,-1/2} = -\frac{1}{2}\left\{-\omega_B + \frac{1}{2}J'\right\}A_{1,0}B_{1/2,-1/2} - \frac{\sqrt{2}}{2}JA_{1,-1}B_{1/2,1/2} \tag{52}$$

$$\mathcal{H}A_{1,-1}B_{1/2,1/2} = -\frac{1}{2}\left\{-2\omega_A + \omega_B - J + \frac{1}{2}J'\right\}A_{1,-1}B_{1/2,1/2} - \frac{\sqrt{2}}{2}JA_{1,0}B_{1/2,-1/2} \tag{53}$$

$$\mathcal{H}A_{1,-1}B_{1/2,-1/2} = -\frac{1}{2}\left\{-2\omega_A - \omega_B + J + \frac{1}{2}J'\right\}A_{1,-1}B_{1/2,-1/2} \tag{54}$$

$$\mathcal{H}A_{1,0}B_{1/2,1/2} = -\frac{1}{2}\left\{\omega_B - \frac{3}{2}J'\right\}A_{1,0}B_{1/2,1/2} \tag{55}$$

$$\mathcal{H}A_{10,}B_{1/2,-1/2} = -\frac{1}{2}\left\{-\omega_B - \frac{3}{2}J'\right\}A_{1,0}B_{1/2,-1/2} \tag{56}$$

Equations 49, 54, 55, and 56 show that

$$A_{1,1}B_{1/2,1/2},\ A_{1,-1}B_{1/2,-1/2},\ A_{1,0}B_{1/2,1/2}, \text{ and } A_{1,0}B_{1/2,-1/2}$$

are eigenfunctions of $\mathcal{H}$, while equations 50 through 53 show that the remaining submatrices of $\mathcal{H}$ are 2 × 2, so that only quadratic equations are involved in the determination of the remaining eigenvalues and eigenfunctions. The calculations are identical with those

TABLE 9

Eigenvalues and eigenfunctions for the A_2B spin system

Eigenfunction	C_2 Symmetry	Eigenvalue
$A_{1,1}B_{1/2,1/2}$	$\mathcal{A}$	$-\frac{1}{2}\{2\omega_A + \omega_B + J + \frac{1}{2}J'\}$
$\frac{1}{\sqrt{1+Q^2}}\{A_{1,1}B_{1/2,-1/2} + QA_{1,0}B_{1/2,1/2}\}$	$\mathcal{A}$	$\frac{1}{2}\{-\omega_A + \frac{1}{2}(J - J') - R\}$
$\frac{1}{\sqrt{1+Q^2}}\{QA_{1,1}B_{1/2,-1/2} - A_{1,0}B_{1/2,1/2}\}$	$\mathcal{A}$	$\frac{1}{2}\{-\omega_A + \frac{1}{2}(J - J') + R\}$
$\frac{1}{\sqrt{1+Q'^2}}\{A_{1,-1}B_{1/2,1/2} - Q'A_{1,0}B_{1/2,-1/2}\}$	$\mathcal{A}$	$\frac{1}{2}\{\omega_A + \frac{1}{2}(J - J') + R'\}$
$\frac{1}{\sqrt{1+Q'^2}}\{Q'A_{1,-1}B_{1/2,1/2} + A_{1,0}B_{1/2,-1/2}\}$	$\mathcal{A}$	$\frac{1}{2}\{\omega_A + \frac{1}{2}(J - J') - R'\}$
$A_{1,-1}B_{1/2,-1/2}$	$\mathcal{A}$	$\frac{1}{2}\{2\omega_A + \omega_B - J - \frac{1}{2}J'\}$
$A_{0,0}B_{1/2,1/2}$	$\mathcal{B}$	$\frac{1}{2}\{-\omega_B + \frac{3}{2}J'\}$
$A_{0,0}B_{1/2,-1/2}$	$\mathcal{B}$	$\frac{1}{2}\{\omega_B + \frac{3}{2}J'\}$

of Section III,A and the results are given in table 9, where

$$R = \sqrt{\delta^2 - \delta J + 9J^2/4} \tag{57}$$

$$R' = \sqrt{\delta^2 + \delta J + 9J^2/4} \tag{58}$$

$$Q = \frac{2J}{\delta - \frac{1}{2}J + R} \tag{59}$$

$$Q' = \frac{2J}{\delta + \frac{1}{2}J + R'} \tag{60}$$

If the simple product functions had been used as a basis, the Hamiltonian matrix would have factored according to the binomial coefficients of 3; that is, 1:3:3:1. The two cubic equations could have been easily factored into pairs of linear and quadratic equations. In more complicated cases the factoring would not be so obvious. However, if spin functions of the proper symmetry are used, the factoring comes about *automatically* as in the present case. This is not the only advantage for, as table 9 shows, the symmetry properties are not destroyed by the perturbative effects of the spin couplings. This is to be contrasted with the case of the two-spin system where (excepting the limiting cases $\delta = 0$ or $J = \infty$) the symmetry properties of the singlet and triplet states are destroyed by the spin coupling. Since symmetry is preserved in this case, it follows from the discussion in Section III,A that transitions between states of different symmetry are forbidden. Only one antisymmetric transition is possible:

$$A_{1,0}B_{1/2,1/2} \rightarrow A_{1,0}B_{1/2,-1/2}$$

The intensity of this transition is proportional to the absolute square of

$$<A_{1,0}B_{1/2,-1/2}|I^-|A_{1,0}B_{1/2,1/2}>$$

where $I^- = I_1^- + I_2^- + I_3^-$. The matrix element is evaluated as in Section III,A with the result

$$|<A_{1,0}B_{1/2,-1/2}|I^-|A_{1,0}B_{1/2,1/2}>|^2 = 1$$

The frequency corresponding to this transition is

$$\frac{1}{2}\left\{\omega_B + \frac{3}{2}J'\right\} - \frac{1}{2}\left\{-\omega_B + \frac{3}{2}J'\right\} = \omega_B$$

Thus the antisymmetric transition is of unit intensity and results in a resonance undeviated by the coupling. Upon carrying out the calculations of line intensities and frequencies as before, one obtains the results given in table 10. In this table, ω_B has been taken as a new frequency origin, so that $\omega_A = \delta$. The transitions denoted as "group A" are such that the associated frequencies $\rightarrow \omega_A$ as $J \rightarrow 0$; similarly, "group B" transitions $\rightarrow \omega_B = 0$ as $J \rightarrow 0$. The remaining transition is an entirely different species, as its resonance frequency $\rightarrow 2\delta$ as $J \rightarrow 0$ and corresponds, in this limit, to a simultaneous flip of three spins: $\alpha\alpha\beta \rightarrow \beta\beta\alpha$. Since this transition involves flips of both A and B spins it is often called a "combination" or "forbidden" (because of its very low intensity) transition. The term "mixed" transition is used here, since it avoids complications in a notational scheme to be introduced later. An additional point of interest in table 10 is the fact that the resonance frequencies and line intensities are independent of the coupling constant J'. This result is not peculiar to the particular system considered but is in fact a general theorem for a number of spin systems. The proof of this theorem and a discussion of the systems for which it applies are given in the following section.

Theoretical spectra are given in figures 5, 6, and 7 for a number of J/δ ratios. The mixed transition is not shown in any of the figures, since its intensity is quite

TABLE 10

Resonance frequencies and relative intensities for the A_2B spin system

Transition in the Limit $J \to 0$	Intensity	Frequency
Transitions in group A		
1. $A_{1,1}B_{1/2,1/2} \to A_{1,0}B_{1/2,1/2}$	$\frac{(Q-\sqrt{2})^2}{1+Q^2}$	$\frac{1}{2}(\delta+\frac{3}{2}J+R)$
2. $A_{1,0}B_{1/2,-1/2} \to A_{1,-1}B_{1/2,-1/2}$	$\frac{(Q'+\sqrt{2})^2}{1+Q'^2}$	$\frac{1}{2}(\delta-\frac{3}{2}J+R')$
3. $A_{1,1}B_{1/2,-1/2} \to A_{1,0}B_{1/2,-1/2}$	$\frac{[Q(1+\sqrt{2}Q')+\sqrt{2}]^2}{(1+Q^2)(1+Q'^2)}$	$\delta+\frac{1}{2}(R-R')$
4. $A_{1,0}B_{1/2,1/2} \to A_{1,-1}B_{1/2,1/2}$	$\frac{[Q'(\sqrt{2}Q-1)+\sqrt{2}]^2}{(1+Q^2)(1+Q'^2)}$	$\delta+\frac{1}{2}(R'-R)$
Transitions in group B		
5. $A_{1,1}B_{1/2,1/2} \to A_{1,1}B_{1/2,-1/2}$	$\frac{(\sqrt{2}Q+1)^2}{1+Q^2}$	$\frac{1}{2}(\delta+\frac{3}{2}J-R)$
6. $A_{1,-1}B_{1/2,1/2} \to A_{1,-1}B_{1/2,-1/2}$	$\frac{(1-\sqrt{2}Q')^2}{1+Q'^2}$	$\frac{1}{2}(\delta-\frac{3}{2}J-R')$
7. $A_{0,0}B_{1/2,1/2} \to A_{0,0}B_{1/2,-1/2}$	$\frac{[\sqrt{2}(Q-Q')-1]^2}{(1+Q^2)(1+Q'^2)}$	$\delta-\frac{1}{2}(R+R')$
8. $A_{0,0}B_{1/2,1/2} \to A_{0,0}B_{1/2,-1/2}$	1	0
Mixed transition		
9. $A_{1,1}B_{1/2,-1/2} \to A_{1,-1}B_{1/2,1/2}$	$\frac{[Q(\sqrt{2}-Q')-\sqrt{2}Q']^2}{(1+Q^2)(1+Q'^2)}$	$\delta+\frac{1}{2}(R+R')$

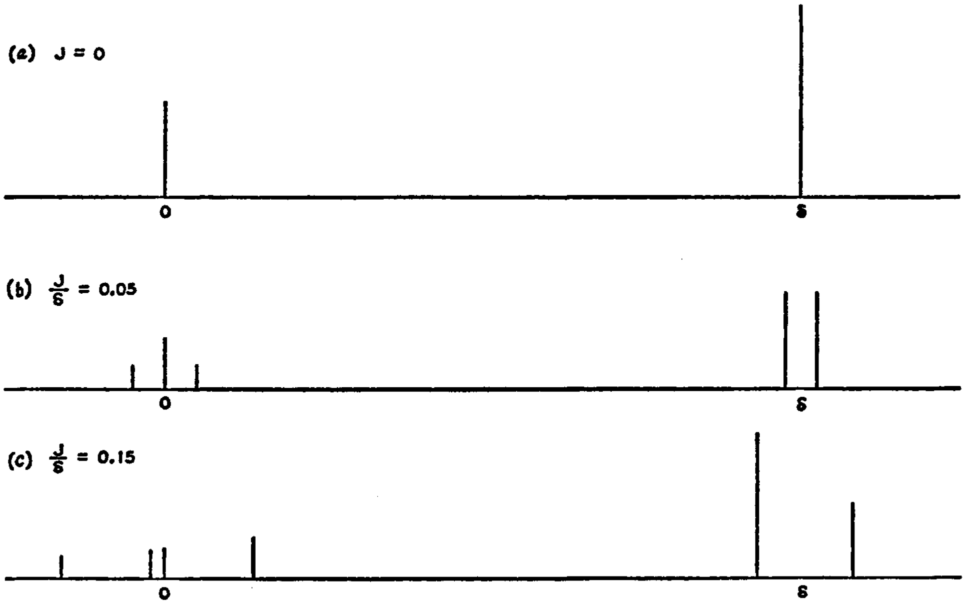


FIG. 5. Theoretical spectra for the A_2B spin system under conditions of weak coupling.

low (*cf.* the numerical data in the Appendix). The A transitions occur at the right in each drawing. The correspondence between the transitions shown in the figures and those in table 10 can be easily made by reference to the Appendix. It is interesting to note the symmetrical spectrum that results when $J \to \infty$ while δ is small but not zero (figure 7c). The lines of the triplet fall at 0, $\frac{2}{3}\delta$, and $\frac{4}{3}\delta$. If $\delta = 0$, the spectrum consists of a single line. For any J/δ ratio, the chemical shift is the mean of transitions 3 and 4 in table 10. The coupling constant may then be determined from any of several frequency differences derived from table 10.

The experimental and theoretical spectra of the —CH_2OH protons in benzyl alcohol (20) are shown in

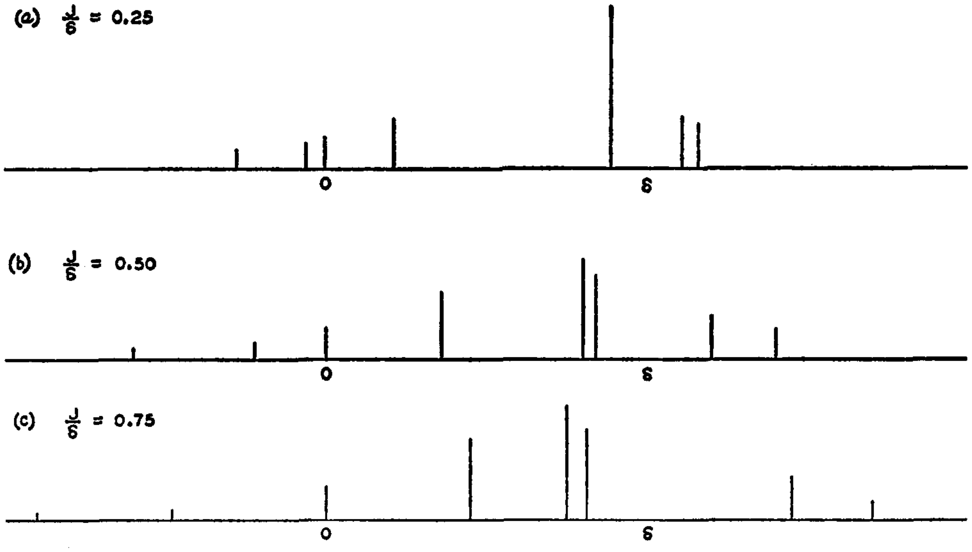


FIG. 6. Theoretical spectra for the A_2B spin system under conditions of intermediate coupling.

figure 8. The theoretical spectrum was calculated for $J/\delta = 0.370$, and the experimental data give

$$\frac{\delta}{2\pi} = 15.14 \pm 0.10 \text{ c.p.s.}$$

$$\frac{J}{2\pi} = 5.60 \pm 0.08 \text{ c.p.s.}$$

IV. GROUPS OF EQUIVALENT NUCLEI

A. DEFINITION OF EQUIVALENT NUCLEI

In Section II,B it was noted that the Hamiltonian operator

$$\mathcal{H} = -\left\{\sum_j \omega_j I_{zj} + \sum_{j<}\sum_k J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k\right\} \tag{1}$$

and the operator for the z-component of total spin angular momentum

$$I_z = \sum_j I_{zj} \tag{2}$$

commute. Let us now consider whether the square of the total angular momentum

$$\mathbf{I}^2 = \mathbf{I}\cdot\mathbf{I} = \sum_j \mathbf{I}_j^2 + 2\sum_{j<}\sum_k \mathbf{I}_j\cdot\mathbf{I}_k \tag{3}$$

commutes with $\mathcal{H}$. If this is the case, an additional constant of the motion results, since I_z and $\mathbf{I}^2$ commute. Evaluation of the commutator yields:

$$[\mathcal{H}, \mathbf{I}^2] = \sum_{j<}\sum_k 2i(\omega_j - \omega_k)(I_{xj}I_{yk} - I_{yj}I_{xk}) \tag{4}$$

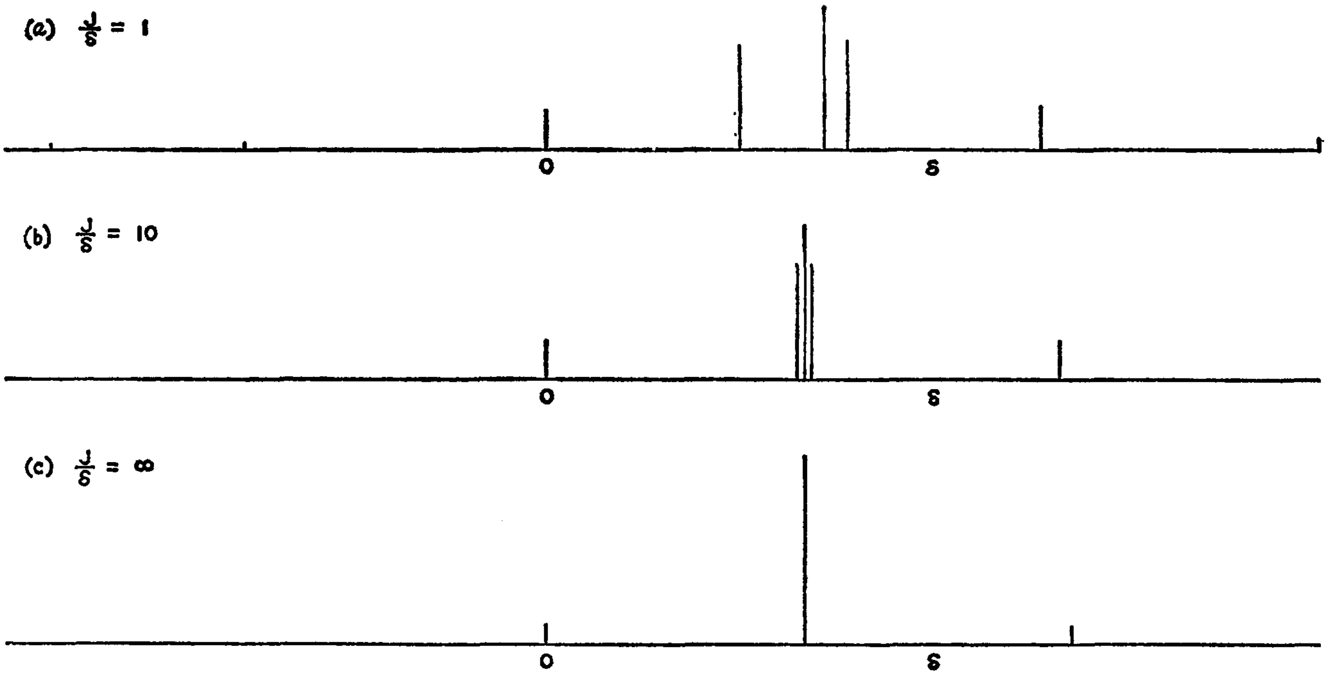


FIG. 7. Theoretical spectra for the A_2B spin system under conditions of strong coupling.

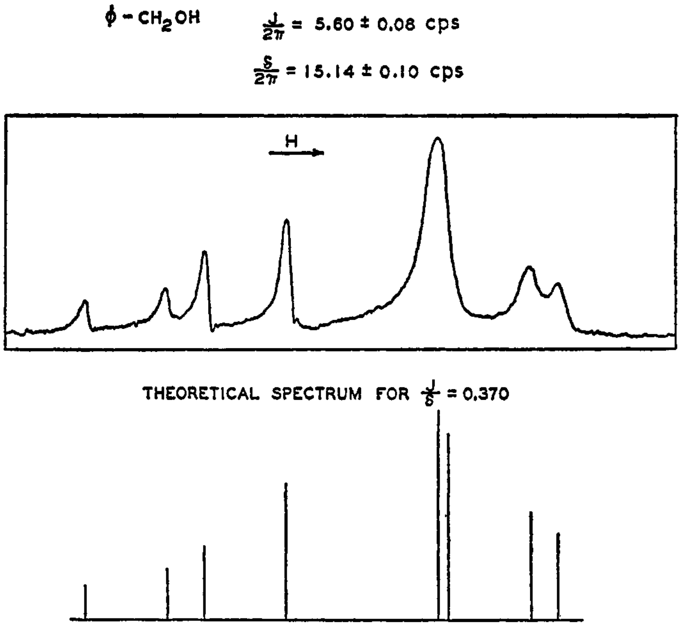


FIG. 8. Experimental and theoretical spectra of the —CH₂OH protons in benzyl alcohol. The experimental trace was observed with a solution of benzyl alcohol in acetone at mole fraction 0.5, room temperature, and 40 Mc./sec.

so that $\mathfrak{H}$ and $\mathbf{I}^2$ do not commute in general. If, however,

$$\omega_j = \omega_k \text{ for all } j,\ k \tag{5}$$

then $[\mathfrak{H}, \mathbf{I}^2] = 0$. In this circumstance, the Hamiltonian simplifies to

$$\mathfrak{H}_0 = -\left\{\omega I_z + \sum_{j<}\sum_{k} J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k\right\} \tag{6}$$

where ω is the common Larmor frequency of nuclei $j, k, \ldots$ and the second term is the coupling between these nuclei. Since I_z commutes with $\mathfrak{H}_0$, it follows that

$$[\mathfrak{H}_0, \sum_{j<}\sum_{k} J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k] = 0 \tag{7}$$

and the operators $\mathfrak{H}_0$, I_z, and

$$\sum_{j<}\sum_{k} J_{jk}\,\mathbf{I}_j\cdot\mathbf{I}_k$$

form a commuting set. If ψ_m and $\psi_{m'}$ are eigenfunctions of these operators, then

$$\mathfrak{H}_0\psi_m = -(m\omega + C_m)\psi_m = \Omega_m\psi_m \tag{8}$$

$$\mathfrak{H}_0\psi_{m'} = -(m'\omega + C_{m'})\psi_{m'} = \Omega_{m'}\psi_{m'} \tag{9}$$

where C_m and $C_{m'}$ are the eigenvalues of

$$\sum_{j<}\sum_{k} J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k$$

If $\psi_m \rightarrow \psi_{m'}$ is an allowed transition, then the observed frequency is

$$\Omega_{m'} - \Omega_m = (m - m')\omega + C_m - C_{m'} \tag{10}$$

Adding to $\mathfrak{H}_0$ the perturbing rf field (equation 80 in Section II) and using the transformation to rotating coördinates, one obtains

$$P_{mm'}(t) = |<\psi_{m'}|e^{i(\mathbf{C}+\gamma H_1 I_x)t}|\psi_m>|^2 \tag{11}$$

where

$$\mathbf{C} = \sum_{j<}\sum_{k} J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k \tag{12}$$

The term ωI_z does not occur in equation 11, since it vanishes if ω is also the frequency of the rotating field (*cf.* equation 88 in Section II). Now

$$[I_x, \mathbf{C}] = 0 \tag{13}$$

and the exponential $e^{i\mathbf{C}t}$ and $e^{i\gamma H_1 I_x t}$ operators commute. The matrix element in equation 11 may now be expressed as

$$\begin{aligned} <\psi_{m'}|e^{i(\mathbf{C}+\gamma H_1 I_x)t}|\psi_m> &= <e^{-i\mathbf{C}t}\psi_{m'}|e^{i\gamma H_1 I_x t}|\psi_m> \\ &= e^{iC_{m'}t}<\psi_{m'}|e^{i\gamma H_1 I_x t}|\psi_m> \end{aligned} \tag{14}$$

Therefore, the absolute square of this matrix element, and hence the transition probability, is independent of the spin couplings.

Equation 14 can also be written as

$$\begin{aligned} <\psi_{m'}|e^{i(\mathbf{C}+\gamma H_1 I_x)t}|\psi_m> &= <\psi_{m'}|e^{i\gamma H_1 I_x t}|e^{i\mathbf{C}t}\psi_m> \\ &= e^{iC_m t}<\psi_{m'}|e^{i\gamma H_1 I_x t}|\psi_m> \end{aligned} \tag{15}$$

If $\psi_m \rightarrow \psi_{m'}$ is an allowed transition, then

$$<\psi_{m'}|e^{\gamma H_1 I_x t}|\psi_m> \neq 0$$

and equations 14 and 15 give

$$e^{iC_m t} \equiv e^{iC_{m'}t}$$

which requires that

$$C_m = C_{m'} \tag{16}$$

From equations 10 and 16 it follows that the observed frequency is also independent of the spin couplings. The selection rule $m' = m - 1$ shows that

$$\Omega_{m'} - \Omega_m = \omega \tag{17}$$

that is, a molecule whose magnetic nuclei have identical Larmor frequencies exhibits resonance at one frequency only. It is to be emphasized that the proofs of the above theorems are not based on perturbation calculations or symmetry arguments. However, the circumstances under which $\omega_1 = \omega_2 = \ldots\ldots$ will frequently involve (but not require) molecular symmetry. For example, the protons in methane have $\omega_1 = \omega_2 = \omega_3 = \omega_4$ by symmetry, so the spectrum consists of a single line whose frequency and intensity are independent of the spin couplings.

Since the coupling term in $\mathfrak{H}_0$ does not result in observable effects it can be omitted from the Hamiltonian operator; that is,

$$\mathfrak{H}_0 = -\omega I_z$$

with the commutators $\mathbf{I}^2$ and I_z. Despite the trivial nature of this equation and its commutators, these results can be fruitfully generalized. Consider a molecule containing a collection of nuclei which can be decomposed into sets $G = A, B, C, \ldots$ such that the nuclei in each set have identical Larmor frequencies; i.e.,

$$\omega_{Gj} = \omega_{Gk} = \cdots \equiv \omega_G \tag{18}$$

where Gj means nucleus j in set G. Since the spin interactions within each set may be neglected, the Hamiltonian operator for such a system is

$$\mathcal{H} = -\left\{\sum_G \omega_G I_{Gz} + \sum_{\substack{Gj \\ G < G'}} \sum_{G'j'} J_{GjG'j'} \mathbf{I}_{Gj} \cdot \mathbf{I}_{G'j'}\right\} \tag{19}$$

where

$$I_{Gz} = \sum_j I_{Gjz} \tag{20}$$

and the spin-spin interactions are those between nuclei in different sets. The Hamiltonian $\mathcal{H}_0$ had as a commutator the square of the total angular momentum. The conditions for which the square of the total angular momentum of some set S commutes with the Hamiltonian (19) will now be determined.

$$\mathbf{I}_S^2 = \sum_{Sj} \mathbf{I}_{Sj}^2 + 2 \sum_{Sj} \sum_{< Sk} \mathbf{I}_{Sj} \cdot \mathbf{I}_{Sk} \tag{21}$$

and upon evaluating the commutator one finds:

$$\begin{aligned}[\mathcal{H}, \mathbf{I}_S^2] = 2i \sum_{G'j'} \sum_{Sj} \sum_{< Sk} & (J_{SjG'j'} - J_{SkG'j'}) \\ & \times \{I_{Skx}(I_{Sjy} I_{G'j'z} - I_{Sjz} I_{G'j'y}) \\ & \quad + I_{Sky}(I_{Sjz} I_{G'j'x} - I_{Sjx} I_{G'j'z}) \\ & \qquad + I_{Skz}(I_{Sjx} I_{G'j'y} - I_{Sjy} I_{G'j'x})\}\end{aligned} \tag{22}$$

Therefore, $\mathbf{I}_S^2$ commutes with equation 19 if

$$J_{SjG'j'} = J_{SkG'j'} \tag{23}$$

i.e., the nuclei Sj and Sk in set S are equally coupled to the nuclei in G' for all Sk, Sj, $G'j'$. The coupling of the set S to the remaining sets G' may therefore be described by coupling constants $J_{SG'}$, where $G' = A, B, \neq S$. These considerations lead to the following definition: *A set of nuclei G which satisfy equations 18 and 23 are said to be a group of equivalent nuclei* (5, 31, 37, 39, 53). If each set G is a group of equivalent nuclei, the Hamiltonian for equivalent nuclei is

$$\mathcal{H} = -\left\{\sum_G \omega_G I_{Gz} + \sum_G \sum_{< G'} J_{GG'} \mathbf{I}_G \cdot \mathbf{I}_{G'}\right\} \tag{24}$$

where $J_{GG'}$ is the coupling constant for groups G and G'. For this Hamiltonian, one has the commutators

$$[\mathcal{H}, I_z] = 0 \tag{25}$$

$$[\mathcal{H}, \mathbf{I}_G^2] = 0 \quad (\text{all } G) \tag{26}$$

where

$$I_z = \sum_G I_{Gz}$$

The eigenfunctions of the Hamiltonian operator for groups of equivalent nuclei are determined by the usual expansion in product spin functions. However, in the present case equations 25 and 26 show that the eigenfunctions of $\mathcal{H}$ can be chosen to be eigenfunctions of I_z and $\mathbf{I}_G^2$ as well. It follows that such an expansion of an eigenfunction of $\mathcal{H}$ contains only those products which (*a*) have the same z-component of angular momentum m and (*b*) have the same total spin quantum number, I_G, for each G. The selection rules for allowed transitions are

$$\Delta m = \sum_G \Delta m_G = -1 \tag{27}$$

$$\Delta I_G = 0 \tag{28}$$

$G = A, B, \ldots$. Equation 28 follows from the fact that $\mathbf{I}_G^2$ commutes with the operator

$$I^- = \sum_G I_G^- \text{ (or } I_z = \sum_G I_{Gz})$$

The selection rule $\Delta m = -1$ can be satisfied in several ways, and it is convenient to classify the various possibilities. Transitions for which

$$\Delta m_R = -1 \tag{29}$$

$$\Delta m_G = 0 \quad (G \neq R) \tag{30}$$

are said to be transitions in group R; transitions not satisfying these conditions are said to be "mixed" or "combination" transitions. Transitions which are associated with a given group R have the property that in the limit $J_{RG} \rightarrow 0$ $(G = A, B, \cdots \neq R)$ they approach the frequency ω_R. To illustrate these definitions consider the case of three spin 1/2 nuclei A, B, C. A transition in group A means $\Delta m_A = -1$, while $\Delta m_B = \Delta m_C = 0$. Thus spin A undergoes $1/2 \rightarrow -1/2$, while spins B and C remain unchanged; the latter may occur in four distinct ways so that there are four transitions (resonances) in group A. Similarly, there are four transitions in groups B and C. The mixed transitions have $\Delta m_A + \Delta m_B + \Delta m_C = -1$, for which there are three possibilities:

Δm_A	Δm_B	Δm_C
-1	-1	$+1$
-1	$+1$	-1
$+1$	-1	-1

In all, the three spin systems can exhibit fifteen lines, four in each group and three mixed transitions.

If a group G contains n_G spin 1/2 nuclei, the total spin quantum number I_G has the values

$$I_G = \frac{n_G}{2} - k_G \qquad k_G = \begin{cases} 0, 1 \cdots \dfrac{n_G}{2} \text{ for } n_G \text{ even} \\ 0, 1, \cdots \dfrac{n_G - 1}{2} \text{ for } n_G \text{ odd} \end{cases}$$

with the statistical weights

$$g_{I_G} = \frac{n_G! \, (n_G - 2k_G + 1)}{(n_G - k_G + 1)! \, k_G!}$$

The values of m_G are just

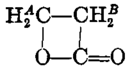
$$m_G = I_G, I_G - 1, \cdots, -I_G + 1, -I_G$$

When determining the various types of transitions one must be careful to take account of the different values of I_G and their statistical weights. Consider the case $n_A = 2$ and $n_B = 1$; here, $I_A = 1, 0$ and $I_B = 1/2$, all having statistical weights of unity. For transitions in group A one need only consider $I_A = 1$, since states with $I_A = 0$ have no magnetic sublevels and hence do not take part in the resonance; however, they must be considered when the transitions in *other groups* are calculated. For $I_A = 1$, $\Delta m_A = -1$ in two ways ($m_A = 1 \rightarrow 0$ or $m_A = 0 \rightarrow -1$) and $\Delta m_B = 0$ in $(2 \cdot \frac{1}{2} + 1) = 2$ ways; hence there are $2 \times 2 = 4$ transitions in group A. Similarly, $\Delta m_B = -1$ in one way $(\frac{1}{2} \rightarrow -\frac{1}{2})$, while $\Delta m_A = 0$ in $(2 \cdot 1 + 1) + (2 \cdot 0 + 1) = 4$ ways, resulting in four transitions in group B. By the same procedure one may show that there is only one "mixed" transition.

Groups of equivalent nuclei can result in several ways. Inherent molecular symmetry or effective molecular symmetry brought about by rapid internal motions is quite common. For example, in fluoromethane the symmetry of the molecule is such that the methyl protons have identical resonance frequencies and are equally coupled to the fluorine nucleus; they constitute a group of three equivalent nuclei. On the other hand, the methyl and methylene protons in CH_3CH_2X cannot be considered as two groups of equivalent nuclei unless the rotation about the carbon–carbon bond is sufficiently rapid so that intermediate configurations are accordingly averaged. In this event, the methyl and methylene protons possess an "effective symmetry" and are groups of equivalent nuclei. The coupling constant and chemical shift derived from such a case are, of course, averaged values. In general, if two sets of nuclei, G and G', are groups of equivalent nuclei because of the averaging effect of some internal molecular motion with frequency ν_0, then

$$\left.\begin{aligned} J_{GG'} &\ll 2\pi\nu_0 \\ |\omega_G - \omega_{G'}| \equiv |\omega_{GG'}| &\ll 2\pi\nu_0 \end{aligned}\right\} \tag{31}$$

The conditions for equivalent nuclei (equations 18 and 23) do not require any particular symmetries and can arise from accidental degeneracies. For example, in β-propiolactone (5)



there is no reason to expect that

$$J^{AB}_{\text{cis}} = J^{AB}_{\text{trans}}$$

Experimentally, however, these coupling constants are equal to an excellent approximation (5) and the A and B protons are groups of equivalent nuclei. A similar example is that of ethylene monothiocarbonate (19a; Section V,C).

Equation 23 is identically satisfied if the molecule contains only magnetic nuclei of the same Larmor frequency. Thus a molecule such as methane is to be considered as a single group of four equivalent nuclei. In general the spin couplings between these equivalent nuclei cannot be observed but isotopic substitution (e.g., deuterium for hydrogen) can be often used to determine the coupling constants (44). For example, the proton spectrum of CH_3D (31) is a 1:1:1 triplet with splitting equal to the J^{HD} coupling constant. Since isotopic substitution is not expected to alter the electronic structure significantly, one can write (*cf.* equation 20 in Section I):

$$J^{HH} = \frac{\gamma_H}{\gamma_D} J^{HD} \tag{32}$$

The concept of groups of equivalent nuclei can be generalized to groups of "groups of equivalent nuclei" with equations analogous to 18 and 23. It is much simpler, however, to consider these larger collections as a single group. Propane, for example, may be considered to consist of two groups with $n_A = 6$ and $n_B = 2$, provided, of course, that the internal motions are sufficiently rapid. Table 11 lists several molecules with groups of equivalent nuclei.

TABLE 11

Examples of molecules containing groups of equivalent nuclei

Molecule	Number of Groups	n_A	n_B	n_C
Benzene, C_6H_6	1	6		
Methane, CH_4	1	4		
Fluoromethane, CH_3F	2	1	3	
Difluoromethane, CH_2F_2	2	2	2	
Chloroethane, CH_3CH_2Cl*	2	3	2	
Propane, $(CH_3)_2CH_2$*	2	6	2	
Isobutane, $(CH_3)_3CH$*	2	9	1	
Vinyl chloride, $CH_2{=}CHCl$	3	1	1	1
Fluoroethane, CH_3CH_2F*	3	1	2	3

* Rapid internal rotation assumed.

B. NOTATION FOR EQUIVALENT NUCLEI

In future discussions of equivalent nuclei a specific notation will be used, some of which has already been defined. Groups will be denoted by capital letters A, B, C, . . . and the Larmor (angular) frequencies of these groups (in the absence of spin couplings) by ω_A, ω_B, ω_C, . . ., respectively. The spin functions of a group will be denoted by the appropriate capital letter for the group and subscripts giving the quantum numbers of total spin and z-component of angular momentum of the group. Thus the spin function for a group G is G_{I_G, m_G}. Independent spin functions having the same values of I_G and m_G will be distinguished by primes.

For example, in the case of three equivalent nuclei with spin 1/2 (*cf.* table 4):

$$\begin{array}{ll} A_{3/2,3/2} & A_{1/2,1/2} \\ A_{3/2,1/2} & A_{1/2,-1/2} \\ A_{3/2,-1/2} & A'_{1/2,1/2} \\ A_{3/2,-3/2} & A'_{1/2,-1/2} \end{array}$$

The designation of all the groups in a molecule will be made by a juxtaposition of the several capital letters with subscripts giving the number of nuclei in each group thus: $A_aB_bC_c$. . . . The simple two- and three-spin systems already discussed are thus described as AB and A_2B systems, respectively. Groups of equivalent nuclei that have large chemical shifts with respect to ω_A, ω_B, . . . will be denoted by X, Y, Z.

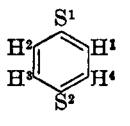
The product spin functions for the molecule are of the form

$$\Phi(\cdots I_Gm_G\cdots;m)=\prod_{G=A,B,\ldots}G_{I_G,m_G}$$

and the matrix elements of the Hamiltonian with respect to the product functions are given by equations 75 and 76 of Section II,B, with j and k replaced by G and G'. It is appropriate to mention at this point that when dealing with groups of equivalent nuclei it is not necessary to write a spin function explicitly. All that is required is the branching diagram (figure 1 for spin 1/2 nuclei) and a notation for the spin functions. The spin functions are completely determined by their quantum numbers, which are easily written down; hence there is no need to write products as $\alpha\alpha\beta\beta\alpha\beta\alpha$ . . . or linear combinations of these products.

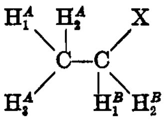
C. OTHER TYPES OF EQUIVALENCE

Before illustrating the preceding results by examples, some additional comments on equivalent nuclei are appropriate. In the literature one frequently encounters the phrases "chemically equivalent," "symmetrically equivalent" (93, 94), and "magnetically equivalent" (31). Of these, only "magnetically equivalent" is synonymous with the simpler term "equivalent nuclei" used here. The designations "chemically equivalent" and "symmetrically equivalent" have other connotations, which lead to ambiguities in the present connection. Consider, for example, the protons in a para-substituted benzene:



Protons 1 and 2 are chemically equivalent, as are protons 3 and 4. This is the classical definition of chemical equivalence made on the basis of additional substitution at the two distinct ring sites. In this case, $\omega_1 = \omega_2$ and $\omega_3 = \omega_4$. The sets (1,2) and (3,4), however, are not groups of (magnetically) equivalent nuclei, since more than one coupling constant ($J_{14} = J_{23}$, $J_{13} = J_{24}$) is required to describe the spin interactions between them. As $J_{13} \rightarrow J_{14}$, the two sets of protons approach magnetic equivalence. The sets (1,2) and (3,4) in this example are also symmetrically equivalent; i.e., under the operations of the molecular point group the nuclei in each set transform among themselves: $1 \rightleftarrows 2$, $3 \rightleftarrows 4$. From this example, it is seen that chemical and symmetrical equivalence imply identical Larmor frequencies of the nuclei in question.

As a second example, consider CH_3CH_2X. The description of the methyl and methylene protons as chemically equivalent means that the internal rotation is sufficiently rapid so that the rotation isomers cannot be resolved. If the conditions in equation 31 are satisfied, the methyl and methylene protons constitute groups of equivalent nuclei. These groups are, in effect, symmetrically equivalent under the group operations D_3 for the CH_3 group and C_2 for the CH_2 group. As the barrier to internal rotation increases, the number of nuclei with a specified type of equivalence decreases. To illustrate this, suppose that for high barriers the trans isomer is the stable form:



The protons H_1^A and H_2^A are chemically and symmetrically equivalent as are H_1^B and H_2^B, but they are not groups of equivalent nuclei except in the event of accidental degeneracy

$$(J_{11}^{AB} \equiv J_{22}^{AB} = J_{12}^{AB} \equiv J_{21}^{AB})$$

As a final example, consider the situation in fluoromethane, CH_3F. The protons are a group of equivalent nuclei and are chemically and symmetrically equivalent as well.

"Chemical" and "symmetrical" equivalence are thus closely related terms and may in fact be identical. Neither term, however, is generally synonymous with (magnetically) equivalent nuclei, and caution must be exercised in their use. In this study the term "equivalent nuclei" without additional modifiers will be used to indicate the validity of equations 18 and 23.

V. THE ANALYSIS OF TWO-GROUP SYSTEMS

A. THE A_3B SPIN SYSTEM

The Hamiltonian operator for two groups of equivalent nuclei is

$$\begin{aligned}\mathcal{H} &= -\left\{\omega_A I_{A_z} + \omega_B I_{B_z} + J\mathbf{I}_A\cdot\mathbf{I}_B\right\} \\ &= -\left\{\omega_A I_{A_z} + \omega_B I_{B_z} + JI_{A_z}I_{B_z} + \frac{1}{2}J(I_A^+I_B^- + I_A^-I_B^+)\right\} \qquad (1)\end{aligned}$$

where $J \equiv J_{AB} = J_{BA}$. The spin functions for group A are given in table 4, while those for group B are simply α and β. The product functions are therefore of the form:

$$A_{I_A,m_A}B_{1/2,1/2},\ A_{I_A,m_A}B_{1/2,-1/2}$$

where $I_A = 3/2$, $1/2$ and $g_{1/2} = 2$. Relative to this basis, the nonvanishing matrix elements of the operators in equation 1 are:

$$<I_G m_G I_G m_{G'}|I_{Gz}|I_G m_G I_{G'} m_{G'}> = m_G \qquad (2)$$

$$<I_G m_G I_{G'} m_{G'}|I_{Gz} I_{G'z}|I_G m_G I_G m_{G'}> = m_G m_{G'} \qquad (3)$$

$$<I_G m_G I_{G'} m_{G'}|I_G^+ I_{G'}^-|I_G m_G - 1,\ I_{G'} m_{G'} + 1>$$
$$= [(I_G + m_G)(I_G - m_G + 1)(I_{G'} - m_{G'})(I_{G'} + m_{G'} + 1)]^{1/2} \qquad (4)$$

where the subscripts G and $G' \neq G$ run over A and B. From the mixing rules (Section IV,A), or by direct evaluation of the matrix elements, one finds that the secular determinant (16 × 16) factors into six 1 × 1 and five 2 × 2 subdeterminants. The manner in which this factoring occurs is shown in table 12, where the spin functions are tabulated according to the orders of the subdeterminants they generate. The eigenvalues and eigenfunctions for this problem may thus be obtained through the solution of linear and quadratic equations. The algebra is lengthy but straightforward; the final results are given in table 13, where

$$R_1 = \sqrt{\delta^2 + J^2} \qquad (5)$$

$$R_2 = \sqrt{\delta^2 + 4J^2} \qquad (6)$$

$$R_3 = \sqrt{(\delta - J)^2 + 3J^2} \qquad (7)$$

$$R_4 = \sqrt{(\delta + J)^2 + 3J^2} \qquad (8)$$

$$Q_1 = \frac{J}{\delta - R_1} \qquad (9)$$

TABLE 12

Factoring of the secular determinant for the A_3B spin system

1 × 1	m	2 × 2	m
$A_{3/2,3/2}B_{1/2,1/2}$	2	$A_{3/2,1/2}B_{1/2,1/2}$	1
		$A_{3/2,3/2}B_{1/2,-1/2}$	
$A_{1/2,1/2}B_{1/2,1/2}$	1	$A_{3/2,1/2}B_{1/2,-1/2}$	0
$A'_{1/2,1/2}B_{1/2,1/2}$	1	$A_{3/2,-1/2}B_{1/2,1/2}$	
$A_{1/2,-1/2}B_{1/2,-1/2}$	−1	$A_{1/2,1/2}B_{1/2,-1/2}$	0
$A'_{1/2,-1/2}B_{1/2,-1/2}$	−1	$A_{1/2,-1/2}B_{1/2,1/2}$	
$A_{3/2,-3/2}B_{1/2,-1/2}$	−2	$A'_{1/2,1/2}B_{1/2,-1/2}$	0
		$A'_{1/2,-1/2}B_{1/2,1/2}$	
		$A_{3/2,-1/2}B_{1/2,-1/2}$	−1
		$A_{3/2,-3/2}B_{1/2,1/2}$	

TABLE 13

Eigenvalues and eigenfunctions for the A_3B spin system

Eigenfunction	Eigenvalue
$A_{3/2,3/2}B_{1/2,1/2}$	$-\frac{1}{2}(3\omega_A + \omega_B + \frac{3}{2}J)$
$(1 + Q_3^2)^{-1/2}\{A_{3/2,1/2}B_{1/2,1/2} + Q_3A_{3/2,3/2}B_{1/2,-1/2}\}$	$\frac{1}{2}(-2\omega_A + \frac{1}{2}J + R_3)$
$(1 + Q_3^2)^{-1/2}\{Q_3A_{3/2,1/2}B_{1/2,1/2} - A_{3/2,3/2}B_{1/2,-1/2}\}$	$\frac{1}{2}(-2\omega_A + \frac{1}{2}J - R_3)$
$A_{1/2,1/2}B_{1/2,1,2}$	$-\frac{1}{2}(\omega_A + \omega_B + \frac{1}{2}J)$
$A'_{1/2,1/2}B_{1/2,1/2}$	$-\frac{1}{2}(\omega_A + \omega_B + \frac{1}{2}J)$
$(1 + Q_2^2)^{-1/2}\{A_{3/2,1/2}B_{1/2,-1/2} + Q_2A_{3/2,-1/2}B_{1/2,1/2}\}$	$\frac{1}{2}(\frac{1}{2}J + R_2)$
$(1 + Q_2^2)^{-1/2}\{Q_2A_{3/2,1/2}B_{1/2\ -1/2} - A_{3/2,-1/2}B_{1/2,1/2}\}$	$\frac{1}{2}(\frac{1}{2}J - R_2)$
$(1 + Q_1^2)^{-1/2}\{A_{1/2,1/2}B_{1/2,-1/2} + Q_1A_{1/2,-1/2}B_{1/2,1/2}\}$	$\frac{1}{2}(\frac{1}{2}J + R_1)$
$(1 + Q_1^2)^{-1/2}\{Q_1A_{1/2,1/2}B_{1/2,-1/2} - A_{1/2,-1/2}B_{1/2,1/2}\}$	$\frac{1}{2}(\frac{1}{2}J - R_1)$
$(1 + Q_1^2)^{-1/2}\{A'_{1/2,1/2}B_{1/2,-1/2} + Q_1A'_{1/2,-1/2}B_{1/2,1/2}\}$	$\frac{1}{2}(\frac{1}{2}J + R_1)$
$(1 + Q_1^2)^{-1/2}\{Q_1A'_{1/2,1/2}B_{1/2,-1/2} - A'_{1/2,-1/2}B_{1/2,1/2}\}$	$\frac{1}{2}(\frac{1}{2}J - R_1)$
$(1 + Q_4^2)^{-1/2}\{A_{3/2,-1,2}B_{1/2,-1/2} + Q_4A_{3/2,-3/2}B_{1/2,1/2}\}$	$\frac{1}{2}(2\omega_A + \frac{1}{2}J + R_4)$
$(1 + Q_4^2)^{-1/2}\{Q_4A_{3/2,-1/2}B_{1/2,-1/2} - A_{3/2,-3/2}B_{1/2,1/2}\}$	$\frac{1}{2}(2\omega_A + \frac{1}{2}J - R_4)$
$A_{1/2,-1/2}B_{1/2,-1/2}$	$\frac{1}{2}(\omega_A + \omega_B - \frac{1}{2}J)$
$A'_{1/2,-1/2}B_{1/2,-1/2}$	$\frac{1}{2}(\omega_A + \omega_B - \frac{1}{2}J)$
$A_{3/2,-3/2}B_{1/2,-1/2}$	$\frac{1}{2}(3\omega_A + \omega_B - \frac{3}{2}J)$

$$Q_2 = \frac{2J}{\delta - R_2} \tag{10}$$

$$Q_3 = \frac{3J}{J - \delta - R_3} \tag{11}$$

$$Q_4 = \frac{3J}{J + \delta - R_4} \tag{12}$$

$$\delta = \omega_A - \omega_B \tag{13}$$

The line intensities and frequencies of the allowed transitions are calculated as before and are collected in table 14. From this table it is to be noted that the transitions 3 and 4 in group B (and the lines 3 and 4 in group A) are separated by the frequency J, so that if these lines are resolved J can be readily determined. This is not a fortuitous result and, as will be shown

TABLE 14

Resonance frequencies and relative intensities for the A_3B spin system

Transition in the Limit $J \rightarrow 0$	Relative Intensity	Frequency Relative to ω_B
Transitions in group A		
1. $A_{3/2,3/2}B_{1/2,1/2} \rightarrow A_{3/2,1/2}B_{1/2,1/2}$	$\frac{(\sqrt{3} + Q_3)^2}{1 + Q_3^2}$	$\frac{1}{2}(\delta + 2J + R_3)$
2. $A_{3/2,-1/2}B_{1/2,-1/2} \rightarrow A_{3/2,-3/2}B_{1/2,-1/2}$	$\frac{(\sqrt{3}Q_4 - 1)^2}{1 + Q_4^2}$	$\frac{1}{2}(\delta - 2J + R_4)$
3. $A_{1/2,1/2}B_{1/2,1/2} \rightarrow A_{1/2,-1/2}B_{1/2,1/2}$ $A'_{1/2,1/2}B_{1/2,1/2} \rightarrow A'_{1/2,-1/2}B_{1/2,1/2}$	$\frac{2(1 + Q_1)^2}{1 + Q_1^2}$	$\frac{1}{2}(\delta + J + R_1)$
4. $A_{1/2,1/2}B_{1/2,-1/2} \rightarrow A_{1/2,-1/2}B_{1/2,-1/2}$ $A'_{1/2,1/2}B_{1/2,-1/2} \rightarrow A'_{1/2,-1/2}B_{1/2,-1/2}$	$\frac{2(1 - Q_1)^2}{1 + Q_1^2}$	$\frac{1}{2}(\delta - J + R_1)$
5. $A_{3/2,1/2}B_{1/2,-1/2} \rightarrow A_{3/2,-1/2}B_{1/2,-1/2}$	$\frac{[(2Q_2 - 1)Q_4 + \sqrt{3}]^2}{(1 + Q_3^2)(1 + Q_4^2)}$	$\frac{1}{2}(2\delta + R_2 - R_4)$
6. $A_{3/2,-1/2}B_{1/2,1/2} \rightarrow A_{3/2,-3/2}B_{1/2,1/2}$	$\frac{[Q_2 + 2 + \sqrt{3}Q_2Q_4]^2}{(1 + Q_2^2)(1 + Q_4^2)}$	$\frac{1}{2}(2\delta + R_2 + R_4)$
7. $A_{3/2,3/2}B_{1/2,-1/2} \rightarrow A_{3/2,1/2}B_{1/2,-1/2}$	$\frac{[(Q_3 - \sqrt{3})Q_2 - 2Q_3]^2}{(1 + Q_3^2)(1 + Q_3^2)}$	$\frac{1}{2}(2\delta - R_2 + R_3)$
8. $A_{3/2,1/2}B_{1/2,1/2} \rightarrow A_{3/2,-1/2}B_{1/2,1/2}$	$\frac{[\sqrt{3}Q_3 + 2Q_2 + 1]^2}{(1 + Q_3^2)(1 + Q_2^2)}$	$\frac{1}{2}(2\delta + R_2 - R_3)$
Transitions in group B		
1. $A_{3/2,3/2}B_{1/2,1/2} \rightarrow A_{3/2,3/2}B_{1/2,-1/2}$	$\frac{(\sqrt{3}Q_3 - 1)^2}{1 + Q_3^2}$	$\frac{1}{2}(\delta + 2J - R_3)$
2. $A_{3/2,-3/2}B_{1/2,1/2} \rightarrow A_{3/2,-3/2}B_{1/2,-1/2}$	$\frac{(Q_4 + \sqrt{3})^2}{1 + Q_4^2}$	$\frac{1}{2}(\delta - 2J - R_4)$
3. $A_{1/2,1/2}B_{1/2,1/2} \rightarrow A_{1/2,1/2}B_{1/2,-1/2}$ $A'_{1/2,1/2}B_{1/2,1/2} \rightarrow A'_{1/2,1/2}B_{1/2,-1/2}$	$\frac{2(1 - Q_1)^2}{1 + Q_1^2}$	$\frac{1}{2}(\delta + J - R_1)$
4. $A_{1/2,-1/2}B_{1/2,1/2} \rightarrow A_{1/2,-1/2}B_{1/2,-1/2}$ $A'_{1/2,-1/2}B_{1/2,1/2} \rightarrow A'_{1/2,-1/2}B_{1/2,-1/2}$	$\frac{2(1 + Q_1)^2}{1 + Q_1^2}$	$\frac{1}{2}(\delta - J - R_1)$
5. $A_{3/2,-1/2}B_{1/2,1/2} \rightarrow A_{3/2,-1/2}B_{1/2,-1/2}$	$\frac{[Q_4(Q_2 + 2) - \sqrt{3}Q_2]^2}{(1 + Q_2^2)(1 + Q_4^2)}$	$\frac{1}{2}(2\delta - R_2 - R_4)$
6. $A_{3/2,1/2}B_{1/2,1/2} \rightarrow A_{3/2,1/2}B_{1/2,-1/2}$	$\frac{[(\sqrt{3}Q_3 + 1)Q_2 - 2]^2}{(1 + Q_3^2)(1 + Q_2^2)}$	$\frac{1}{2}(2\delta - R_2 - R_3)$
Mixed transitions		
1. $A_{3/2,1/2}B_{1/2,-1/2} \rightarrow A_{3/2,-3/2}B_{1/2,1/2}$	$\frac{(2Q_2 - 1 - \sqrt{3}Q_4)^2}{(1 + Q_2^2)(1 + Q_4^2)}$	$\frac{1}{2}(2\delta + R_2 + R_4)$
2. $A_{3/2,3/2}B_{1/2,-1/2} \rightarrow A_{3/2,-1/2}B_{1/2,1/2}$	$\frac{(2Q_3Q_2 + Q_3 - \sqrt{3})^2}{(1 + Q_3^2)(1 + Q_2^2)}$	$\frac{1}{2}(\delta + R_2 + R_3)$

below, occurs whenever group A contains an odd number of spin 1/2 nuclei and group B contains only one spin 1/2 nucleus. In general, however, the internal shift must be determined indirectly through the relations defined in table 14. In all, there are sixteen possible lines: eight in group A, six in group B, and two mixed transitions. These numbers could have been found without making any detailed calculations by using the procedure previously discussed and noting the degeneracy of the spin 1/2 states of group A.

In figures 9 to 11 the calculated spectra are given for weak, intermediate, and strong coupling. The mixed transitions are ordinarily too weak to observe and are not shown in these figures. The correspondence between the numbering of the transitions in table 14 and the figures may be easily made by reference to the numerical data in the Appendix.

An example of this system is that of CH_3SH (figure 12) for which

$$\frac{J}{2\pi} = 7.42 \pm 0.17 \text{ c.p.s.}$$

$$\frac{\delta}{2\pi} = 25.18 \pm 0.21 \text{ c.p.s.}$$

There are slight discrepancies of unknown origin between these values and those reported previously (1). Other examples of this system may be found in the literature (21, 45).

B. THE GENERAL $A_{n_A}B$ SYSTEM

The preceding spin systems have all been special cases of the $A_{n_A}B$ system, which will now be considered in detail. There are only two spin functions for group B, $B_{1/2,1/2}$ and $B_{1/2,-1/2}$. For group A there will be 2^{n_A} functions, some of which will be degenerate. The degree of degeneracy (i.e., the statistical weight) of a spin function with total spin I_A is given by equation 36 in Section II as

$$g_{I_A} = g_{\frac{n_A}{2}-k} = \frac{n_A!(n_A - 2k_A + 1)}{(n_A - k_A + 1)!k_A!} \tag{14}$$

where

$$k_A = \begin{cases} 0, 1 \cdots\cdots \frac{n_A}{2} \text{ for } n \text{ even} \\ 0, 1 \cdots\cdots \frac{n_A - 1}{2} \text{ for } n \text{ odd} \end{cases}$$

It is easy to show that for this system only linear and quadratic equations are involved (10, 19a, 90). To see this, note that for a given m_A

$$m = m_A + m_B = m_A \pm \frac{1}{2} \tag{15}$$

The only states that mix are those for which

$$m = m_A + \frac{1}{2} \text{ and } m = (m_A + 1) - \frac{1}{2}$$

i.e., the states with the same m-value:

$$A_{I_A,m_A}B_{1/2,1/2} \qquad m = m_A + \frac{1}{2}$$

$$A_{I_A,m_A+1}B_{1/2,-1/2} \qquad m = (m_A + 1) - \frac{1}{2} = m_A + \frac{1}{2}$$

The matrix elements for these states are

$$\langle A_{I_A,m_A}B_{1/2,1/2}|\mathcal{H}|A_{I_A,m_A}B_{1/2,1/2}\rangle = -\left\{m_A\omega_A + \frac{1}{2}\omega_B + \frac{1}{2}m_AJ\right\} \tag{16}$$

$$\langle A_{I_A,m_A+1}B_{1/2,-1/2}|\mathcal{H}|A_{I_A,m_A+1}B_{1/2,-1/2}\rangle = -\left\{(m_A + 1)\omega_A - \frac{1}{2}\omega_B - \frac{1}{2}(m_A + 1)J\right\} \tag{17}$$

$$\begin{aligned}\langle A_{I_A,m_A}B_{1/2,1/2}|\mathcal{H}|A_{I_A,m_A+1}B_{1/2,-1/2}\rangle &= \langle A_{I_A,m_A+1}B_{1/2,-1/2}|\mathcal{H}|A_{I_A,m_A}B_{1/2,1/2}\rangle \\ &= -\frac{1}{2}J\sqrt{(I_A - m_A)(I_A + m_A + 1)}\end{aligned} \tag{18}$$

With these matrix elements, the eigenvalues for the $m_A + 1/2$ states are easily calculated; the results are

$$-\frac{1}{2}\left\{(2m_A + 1)\omega_A - \frac{1}{2}J + R_{I_A,m_A}\right\} \tag{19}$$

$$-\frac{1}{2}\left\{(2m_A + 1)\omega_A - \frac{1}{2}J - R_{I_A,m_A}\right\} \tag{20}$$

where

$$R_{I_A,m_A} = \sqrt{\left[\delta - \frac{1}{2}(2m_A + 1)J\right]^2 + J^2(I_A - m_A)(I_A + m_A + 1)} \tag{21}$$

The corresponding eigenfunctions are

$$\frac{1}{\sqrt{1 + Q^2_{I_A,m_A}}}\{A_{I_A,m_A+1}B_{1/2,-1/2} + Q_{I_A,m_A}A_{I_A,m_A}B_{1/2,1/2}\} \tag{22}$$

$$\frac{1}{\sqrt{1 + Q^2_{I_A,m_A}}}\{Q_{I_A,m_A}A_{I_A,m_A+1}B_{1/2,-1/2} - A_{I_A,m_A}B_{1/2,1/2}\} \tag{23}$$

where

$$Q_{I_A,m_A} = \frac{J\sqrt{(I_A - m_A)(I_A + m_A + 1)}}{\delta + \frac{1}{2}(2m_A + 1)J + R_{I_A,m_A}} \tag{24}$$

There are two additional eigenfunctions which result when m_A and m_B have their maximum and minimum values for a given I_A; viz.,

$$A_{I_A,I_A}B_{1/2,1/2};\ m = I_A + \frac{1}{2} \tag{25}$$

$$A_{I_A,-I_A}B_{1/2,-1/2};\ m = -I_A - \frac{1}{2} \tag{26}$$

The eigenvalues are

$$-\left\{I_A\omega_A + \frac{1}{2}\omega_B + \frac{1}{2}I_AJ\right\} \tag{27}$$

$$-\left\{-I_A\omega_A - \frac{1}{2}\omega_B + \frac{1}{2}I_AJ\right\} \tag{28}$$

Note that equations 25, 26, 27, and 28 are special cases of equations 19, 20, 22, and 23.

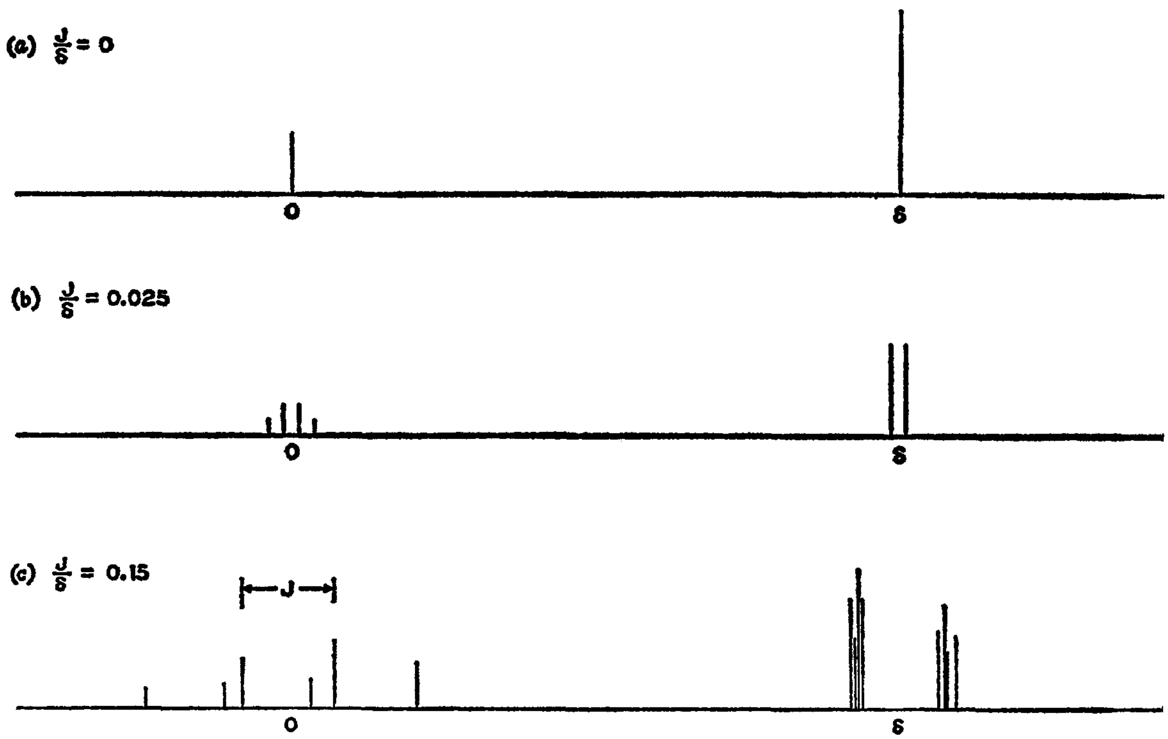


FIG. 9. Theoretical spectra for the A_2B spin system under conditions of weak coupling.

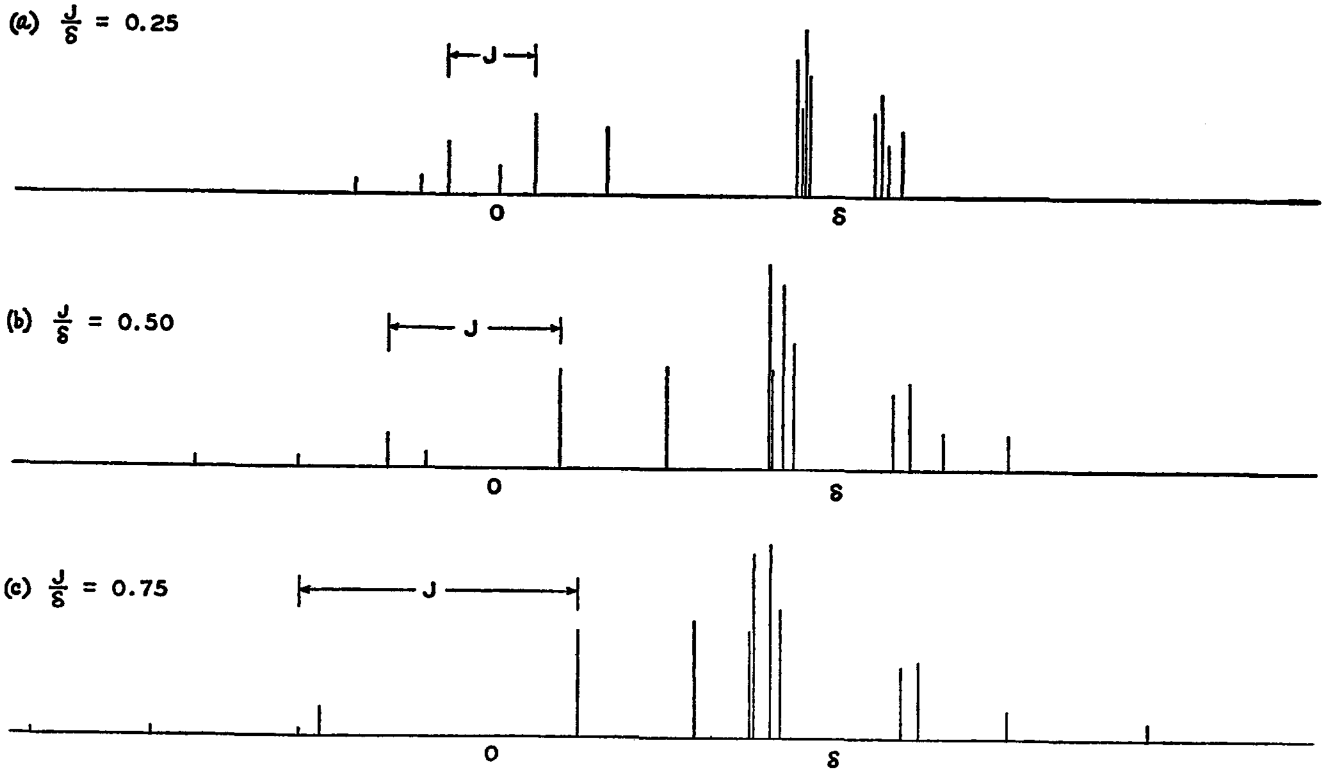


FIG. 10. Theoretical spectra for the A_2B spin system for intermediate coupling.

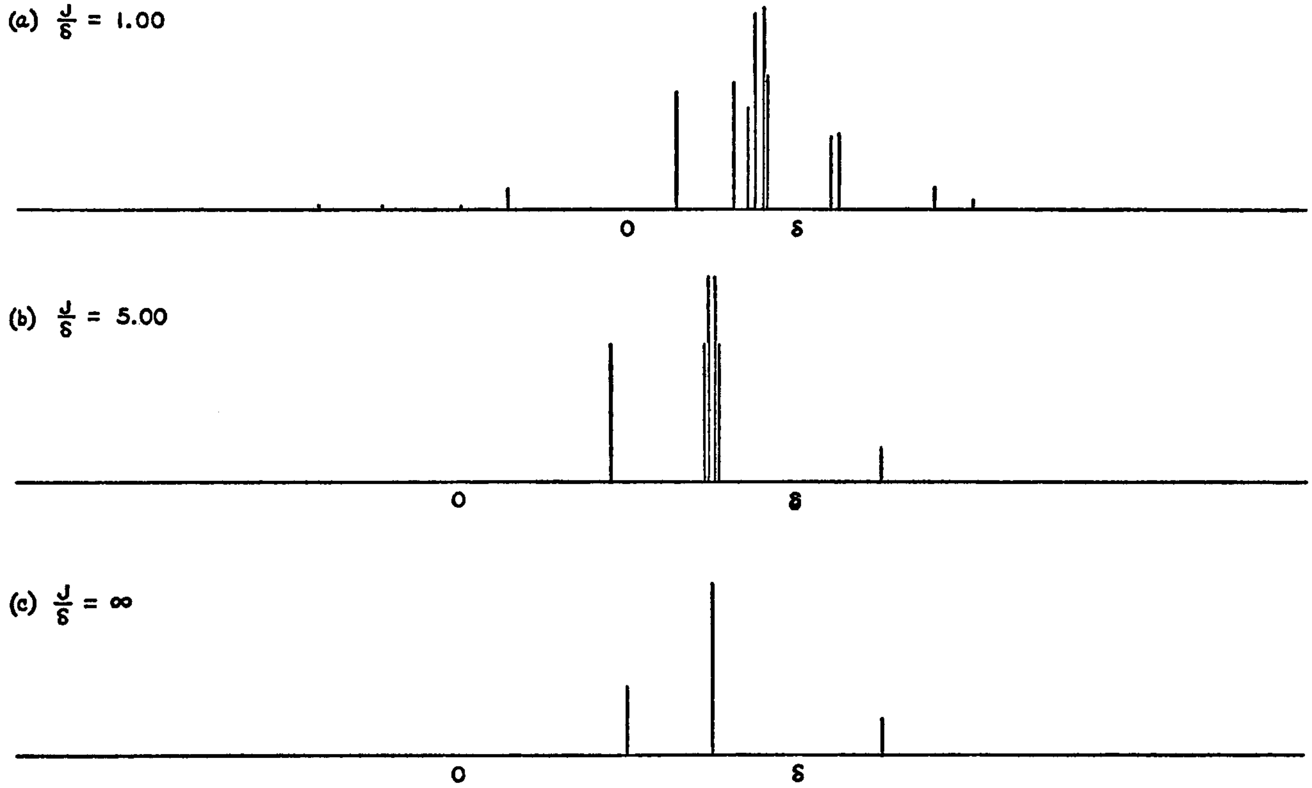


Fig. 11. Theoretical spectra for the A_3B spin system for strong coupling.

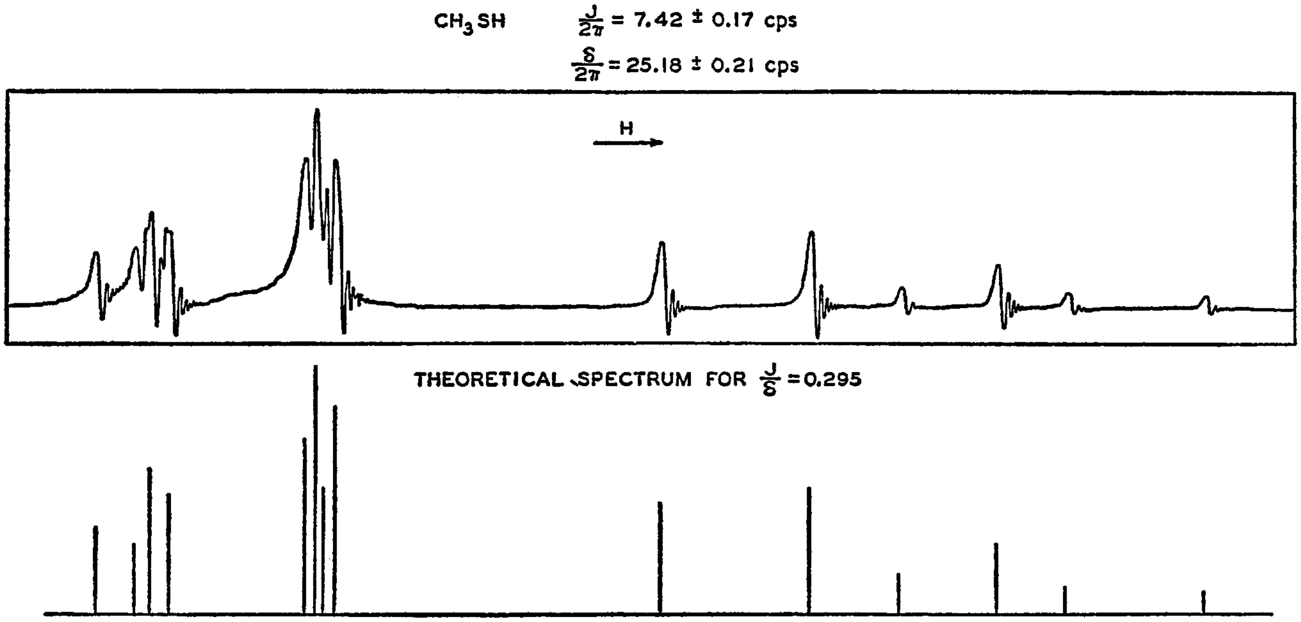


Fig. 12. Experimental and theoretical spectra of the protons in methyl mercaptan. The experimental trace is that of the pure liquid at room temperature and 40 Mc./sec.

With these eigenvalues and eigenfunctions it is easy to write recursive formulae for the line frequencies and relative intensities (19a). To see this, note that there can be transitions from the state

$$A_{I_A,I_A}B_{1/2,1/2}$$

to a pair of states with

$$m = \left(I_A + \frac{1}{2}\right) - 1 = I_A - 1/2$$

which are linear combinations of

$$A_{I_A,I_A-1}B_{1/2,1/2} \text{ and } A_{I_A,I_A}B_{1/2,-1/2}$$

Similarly the states which are linear combinations of

$$A_{I_A,-I_A+1}B_{1/2,-1/2} \text{ and } A_{I_A,-I_A}B_{1/2,1/2}$$

undergo transitions to

$$A_{I_A,-I_A}B_{1/2,-1/2}$$

Finally, there are transitions between states whose m-values differ by -1 and have the form given in equations 22 and 23. These calculations are illustrated by considering the transitions from the state

$$A_{I_A,I_A}B_{1/2,1/2}$$

Operating with $I_A^- + I_B^-$ one finds

$$\begin{aligned}(I_A^- + I_B^-)&A_{I_A,I_A}B_{1/2,1/2} \\ &= \sqrt{(I_A + m_A)(I_A - m_A + 1)}A_{I_A,I_A-1}B_{1/2,1/2} \\ &\qquad + A_{I_A,I_A}B_{1/2,-1/2} \qquad (28) \\ &= \sqrt{2I_A}\, A_{I_A,I_A-1}B_{1/2,1/2} + A_{I_A,I_A}B_{1/2,-1/2}\end{aligned}$$

since $m_A = I_A$. The eigenfunctions which are linear combinations of

$$A_{I_A,I_A-1}B_{1/2,1/2} \text{ and } A_{I_A,I_A}B_{1/2,-1/2}$$

and the corresponding eigenvalues, are obtained from equations 19 to 24 with $m_A = I_A - 1$. The products on the right of equation 28 can be expressed in terms of the eigenfunctions of $\mathcal{H}$ by applying the appropriate inverse transformation to equations 22 and 23. The matrix of the inverse transformation is just the transpose of the coefficient matrix of equations 22 and 23. Substituting these expressions for the products into equation 23 determines the transitions and frequencies. The other cases are determined in the same fashion and the results are given in table 15. The factor g_{I_A} accounts for the statistical weights of the group A spin states. Note, also, that the first and second group A transitions are special cases of the third and fourth transitions with m_A equal to I_A and $-I_A$, respectively. Similarly, the first pair of B transitions follow from the third with $m_A = I_A, -I_A$.

The theoretical spectrum of any $A_{n_A}B$ system follows from table 15 simply by substituting the appropriate values of I_A and g_{I_A}. Therefore, the general $A_{n_A}B$ spectrum consists of a superposition of all $A_{q_A}B$ spectra

$$q_A = \begin{cases} 1, 3, 5, \cdots n_A \text{ for } n_A \text{ odd} \\ 2, 4, 6, \cdots n_A \text{ for } n_A \text{ even} \end{cases}$$

with the intensities of the "subspectra" weighted by the g_{I_A}. Such a spectrum can be quite complex, but it should be rather easy to analyze with computer techniques.

The analysis can sometimes be facilitated by some properties of the general system. Consider the difference of the first pair of A transitions and B transitions

$$A\colon \quad J\left(I_A + \frac{1}{2}\right) + \frac{1}{2}(R_{I_A,I_A-1} - R_{I_A,-I_A})$$

$$B\colon \quad J\left(I_A + \frac{1}{2}\right) - \frac{1}{2}(R_{I_A,I_A-1} - R_{I_A,-I_A})$$

If $I_A = 1/2$, the terms in R cancel and there are pairs of A and B transitions whose separations are exactly J. States with $I_A = 1/2$ will occur whenever n_A is an odd integer and this proves the result mentioned previously. Hence, experiments at two values of the magnetic field may permit the direct evaluation of J, unless there is excessive overlapping of the resonances. If n_A is even, then $I_A = 0, \cdots n_A/2$, and it is seen that for $I_A = 0$, there is a transition in group B which is undeviated and of unit intensity. Further, for any $n_A > 1$ the mean of the third and fourth A transitions is just ω_A.

The number of lines in each group can be computed by considering the range of m_A. The third group A transition has $m_A + 1 \rightarrow m_A$ for spin I_A and, since $|m_A| \leq I_A$, m_A ranges from $I_A - 1$ to $-I_A$. Hence there are $2I_A$ lines for these transitions. Similarly, the fourth A transition yields $2I_A$ lines, so the total number of A transitions is

$$N_A = 4\Sigma I_A \quad \text{(all distinct } I_A) \tag{29}$$

The group B and mixed transitions are calculated in the same way with the results

$$N_B = \Sigma\{2I_A + 1\} \quad \text{(all distinct } I_A) \tag{30}$$

$$N_M = \Sigma\{2I_A - 1\} \quad \text{(all distinct } I_A \neq 0) \tag{31}$$

By writing $I_A = \dfrac{n_A}{2} - k$ these sums can be evaluated by elementary algebra:

$$N_A = \begin{cases} n_A\left(\dfrac{n_A}{2} + 1\right) & \text{for } n_A \text{ even} \\ \dfrac{1}{2}(n_A + 1)^2 & \text{for } n_A \text{ odd} \end{cases} \tag{32}$$

$$N_B = \begin{cases} \left(\dfrac{n_A}{2} + 1\right)^2 & \text{for } n_A \text{ even} \\ \dfrac{1}{4}(n_A + 1)(n_A + 3) & \text{for } n_A \text{ odd} \end{cases} \tag{33}$$

$$N_M = \begin{cases} n_A^2 & \text{for } n_A \text{ even} \\ \dfrac{1}{4}(n_A^2 - 1) & \text{for } n_A \text{ odd} \end{cases} \tag{34}$$

Summing these one finds that the total number of lines is $(n_A + 1)^2$ for odd or even n_A; that is, the total number of lines is just the square of the total number of

TABLE 15

Resonance frequencies and relative intensities for the $A_{n_A}B$ spin system

Transition in the Limit $J \to 0$	Intensity	Frequency
	Transitions in group A	
1. $A_{I_A,I_A}B_{1/2,1/2} \to A_{I_A,I_A-1}B_{1/2,1/2}$	$\dfrac{g_{I_A}(Q_{I_A,I_A-1} - \sqrt{2I_A})^2}{1 + Q^2_{I_A,I_A-1}}$	$\frac{1}{2}\{\omega_A + \omega_B + J(I_A + \frac{1}{2}) + R_{I_A,I_A-1}\}$
2. $A_{I_A,-I_A+1}B_{1/2,-1/2} \to A_{I_A,-I_A}B_{1/2,1/2}$	$\dfrac{g_{I_A}(Q_{I_A,-I_A} + \sqrt{2I_A})^2}{1 + Q^2_{I_A,-I_A}}$	$\frac{1}{2}\{\omega_A + \omega_B - J(I_A + \frac{1}{2}) + R_{I_A,-I_A}\}$
3. $A_{I_A,m_A}B_{1/2,1/2} \to A_{I_A,m_A-1}B_{1/2,1/2}$	$\dfrac{g_{I_A}\{Q_{I_A,m_A-1}[Q_{I_A,m_A}\sqrt{(I_A - m_A)(I_A + m_A + 1)} - 1] + \sqrt{(I_A + m_A)(I_A - m_A + 1)}\}^2}{(1 + Q^2_{I_A,m_A})(1 + Q^2_{I_A,m_A-1})}$	$\frac{1}{2}\{2\omega_A + R_{I_A,m_A-1} - R_{I_A,m_A}\}$
4. $A_{I_A,m_A+1}B_{1/2,-1/2} \to A_{I_A,m_A}B_{1/2,-1/2}$	$\dfrac{g_{I_A}\{\sqrt{(I_A - m_A)(I_A + m_A + 1)} + Q_{I_A,m_A}[1 + Q_{I_A,m_A-1}\sqrt{(I_A + m_A)(I_A - m_A + 1)}]\}^2}{(1 + Q^2_{I_A,m_A})(1 + Q^2_{I,m_A-1})}$	$\frac{1}{2}\{2\omega_A + R_{I_A,m_A} - R_{I_A,m_A-1}\}$
	Transitions in group B	
1. $A_{I_A,I_A}B_{1/2,1/2} \to A_{I_A,I_A}B_{1/2,-1/2}$	$\dfrac{g_{I_A}(\sqrt{2I_A}\,Q_{I_A,I_A-1} + 1)^2}{1 + Q^2_{I_A,I_A-1}}$	$\frac{1}{2}\{\omega_A + \omega_B + J(I_A + \frac{1}{2}) - R_{I_A,I_A-1}\}$
2. $A_{I_A,-I_A}B_{1/2,1/2} \to A_{I_A,-I_A}B_{1/2,-1/2}$	$\dfrac{g_{I_A}(\sqrt{2I_A}\,Q_{I_A,-I_A} - 1)^2}{1 + Q^2_{I_A,-I_A}}$	$\frac{1}{2}\{\omega_A + \omega_B - J(I_A + \frac{1}{2}) - R_{I_A,-I_A}\}$
3. $A_{I_A,m_A}B_{1/2,1/2} \to A_{I_A,m_A}B_{1/2,-1/2}$	$\dfrac{g_{I_A}\{Q_{I_A,m_A}\sqrt{(I_A - m_A)(I_A + m_A + 1)} - [1 + Q_{I_A,m_A-1}\sqrt{(I_A + m_A)(I_A - m_A + 1)}]^2\}}{(1 + Q^2_{I_A,m_A})(1 + Q^2_{I_A,m_A-1})}$	$\frac{1}{2}\{2\omega_A - R_{I_A,m_A-1} - R_{I_A,m_A}\}$
	Mixed transitions	
4. $A_{I_A,m_A+1}B_{1/2,-1/2} \to A_{I_A,m_A-1}B_{1/2,1/2}$	$\dfrac{g_{I_A}\{Q_{I_A,m_A-1}[\sqrt{(I_A - m_A)(I_A + m_A + 1)} + Q_{I_A,m_A}] - Q_{I_A,m_A}\sqrt{(I_A + m_A)(I_A - m_A + 1)}\}^2}{(1 + Q^2_{I_A,m_A})(1 + Q^2_{I_A,m_A-1})}$	$\frac{1}{2}\{2\omega_A + R_{I_A,m_A} + R_{I_A,m_A+1}\}$

TABLE 16

Factors of the secular determinant for the A_2B_2 spin system

1 × 1	m	2 × 2	m	3 × 3	m
$A_{1,1}B_{1,1}$	2	$A_{1,1}B_{1,0}$ $A_{1,0}B_{1,1}$	1	$A_{1,1}B_{1,-1}$ $A_{1,0}B_{1,0}$ $A_{1,-1}B_{1,1}$	0
$A_{1,1}B_{0,0}$	1				
$A_{0,0}B_{1,1}$	1				
$A_{1,0}B_{0,0}$	0	$A_{1,-1}B_{1,0}$ $A_{1,0}B_{1,-1}$	−1		
$A_{0,0}B_{1,0}$	0				
$A_{0,0}B_{0,0}$	0				
$A_{1,-1}B_{0,0}$	−1				
$A_{0,0}B_{1,-1}$	−1				
$A_{1,-1}B_{1,-1}$	−2				

spins. Of course, counting these lines is quite a different matter from resolving them.

C. THE A_2B_2 SPIN SYSTEM

The Hamiltonian operator for the A_2B_2 spin system (5, 19a) is given by equation 1, and its matrix elements, in the product scheme, are derived from equations 2 to 4 with I_A, I_B = 1, 0 (*cf.* table 3). Upon evaluating the matrix elements, one finds that the Hamiltonian matrix factors into one 3 × 3, two 2 × 2, and nine 1 × 1 submatrices. This factoring is indicated in table 16.

The 3 × 3 submatrix, which is generated by the product functions with $m = 0$, is

$$\mathbf{S} = \begin{pmatrix} (-\delta + J) & -J & 0 \\ -J & 0 & -J \\ 0 & -J & \delta + J \end{pmatrix} \tag{35}$$

Let $\Omega_1 < \Omega_2 < \Omega_3$ be the eigenvalues of S and $\mathbf{a} = (a_{ij})$ be the matrix whose normalized column vectors are the eigenvectors of S; that is,

$$\mathbf{aSa}^{-1} = (\Omega_i \delta_{jk}) \tag{36}$$

The elements of (a_{ij}) are just the expansion coefficients for the eigenfunctions of $\mathcal{H}$ in terms of the product functions with $m = 0$. In the limit as $J \rightarrow 0$ or $\delta \rightarrow \infty$, **a** is a 3 × 3 unit matrix and

$$\begin{aligned} \Omega_1 &= -\delta + J \\ \Omega_2 &= 0 \\ \Omega_3 &= \delta + J \end{aligned} \tag{37}$$

(The J's in equations 37 are the first-order corrections to Ω_1 and Ω_3.) For $J \rightarrow \infty$ or $\delta \rightarrow 0$, it is easily shown that

$$\begin{aligned} \Omega_1 &= -J \\ \Omega_2 &= J \\ \Omega_3 &= 2J \end{aligned} \tag{38}$$

$$\mathbf{a} = \begin{bmatrix} \sqrt{1/6} & \sqrt{1/2} & \sqrt{1/3} \\ \sqrt{2/3} & 0 & -\sqrt{1/3} \\ \sqrt{1/6} & -\sqrt{1/2} & \sqrt{1/3} \end{bmatrix} \tag{39}$$

Intermediate cases require the solution of the cubic equation

$$\det|S_{ij} - \Omega_i \delta_{ij}| = 0 \tag{40}$$

The calculation of the eigenvalues and eigenfunctions corresponding to the 1 × 1 and 2 × 2 determinants presents no difficulties. The algebra leading to these results will not be given here. All the algebra is summarized in table 17 in terms of the following definitions:

$$\delta = \omega_A - \omega_B \ (\omega_A \text{ assumed} > \omega_B) \tag{41}$$

$$R = \sqrt{\delta^2 + 4J^2} \tag{42}$$

$$Q = \frac{2J}{\delta - R} \tag{43}$$

In addition, the frequency origin has been taken at $\frac{1}{2}(\omega_A + \omega_B)$ so that

$$\begin{aligned} \omega_A &= \frac{1}{2}\delta \\ \omega_B &= -\frac{1}{2}\delta \end{aligned} \tag{44}$$

The resonance frequencies and relative intensities are determined in the usual manner, and the results are given in table 18. The spectrum is symmetrical with respect to the frequency $\frac{1}{2}(\omega_A + \omega_B) = 0$, so that only half of the lines are given. The spectrum thus consists of eighteen lines: seven in groups A and B and four mixed transitions. It is important to note that the mean separation of the lines $A7$ and $A2$ (also $B7$ and $B2$) is exactly J, and further, $A4 - B4 = \delta$. Thus, if these signals are resolved, J and δ may be determined without solving the cubic equation. The selection of these lines

TABLE 17

Eigenvalues and eigenfunctions for A_2B_2 spin system

Eigenfunction	Eigenvalue
$A_{1,1}B_{1,1}$	$-J$
$A_{1,-1}B_{1,-1}$	$-J$
$A_{1,1}B_{0,0}$	$-\frac{\delta}{2}$
$A_{0,0}B_{1,-1}$	$-\frac{\delta}{2}$
$A_{1,0}B_{0,0}$	0
$A_{0,0}B_{1,0}$	0
$A_{0,0}B_{0,0}$	0
$A_{0,0}B_{1,1}$	$\frac{\delta}{2}$
$A_{1,-1}B_{0,0}$	$\frac{\delta}{2}$
$(1+Q^2)^{-1/2}\{QA_{1,1}B_{1,0}-A_{1,0}B_{1,1}\}$	$-\frac{1}{2}R$
$(1+Q^2)^{-1/2}\{A_{1,-1}B_{1,0}+QA_{1,0}B_{1,-1}\}$	$-\frac{1}{2}R$
$(1+Q^2)^{-1/2}\{A_{1,1}B_{1,0}+QA_{1,0}B_{1,1}\}$	$\frac{1}{2}R$
$(1+Q^2)^{-1/2}\{QA_{1,-1}B_{1,0}-A_{1,0}B_{1,-1}\}$	$\frac{1}{2}R$
$a_{11}A_{1,1}B_{1,-1}+a_{21}A_{1,0}B_{1,0}+a_{31}A_{1,-1}B_{1,1}$	Ω_1
$a_{12}A_{1,1}B_{1,-1}+a_{22}A_{1,0}B_{1,0}+a_{32}A_{1,-1}B_{1,1}$	Ω_2
$a_{13}A_{1,1}B_{1,-1}+a_{23}A_{1,0}B_{1,0}+a_{33}A_{1,-1}B_{1,1}$	Ω_3

may be made by reference to the numerical data in the Appendix and can be confirmed by experiments at two field values.

Calculated spectra for the A_2B_2 system are presented in figures 13 to 15, and in figure 16 the experimental and theoretical spectra for ethylene monothiocarbonate are compared. As noted previously, the A_2B_2 system applies for this molecule because $J^{AB}_{\text{cis}} = J^{AB}_{\text{trans}}$ to an excellent approximation. The observed values of J and δ are

$$\frac{J}{2\pi} = 7.00 \pm 0.06 \text{ c.p.s.}$$

$$\frac{\delta}{2\pi} = 35.96 \pm 0.26 \text{ c.p.s.}$$

D. THE A_3B_2 SPIN SYSTEM

The Hamiltonian operator for the A_3B_2 spin system (5, 19a, 55) is given by equation 1 and its matrix elements are determined by equations 2 to 4 with $I_A = 3/2$, $1/2$ ($g_{1/2} = 2$), and $I_B = 1,0$ (*cf.* tables 3 and 4). Upon calculating the matrix elements, one finds that the matrix for $\mathcal{H}$ factors into fourteen 1 × 1, six 2 × 2, and two 3 × 3 submatrices; the manner in which this factoring occurs is indicated in table 19.

The two 3 × 3 matrices are

$$\mathcal{H}^{\pm} = \begin{vmatrix} \frac{3}{2}(\mp\delta + J) & -\sqrt{\frac{3}{2}}\,J & 0 \\ -\sqrt{\frac{3}{2}}\,J & \mp\frac{1}{2}\delta & -\sqrt{2}\,J \\ 0 & -\sqrt{2}\,J & \frac{1}{2}(\pm\delta + J) \end{vmatrix} \tag{45}$$

TABLE 18

Resonance frequencies and relative intensities for the A_2B_2 spin system

Transitions in group A and mixed transitions

Transition in the Limit as $J \to 0$	Relative Intensity	Frequency
1. $A_{1,1}B_{1,-1} \to A_{1,0}B_{1,-1}$	$\frac{2[a_{21}+a_{31}-Q(a_{11}+a_{21})]^2}{1+Q^2}$	$-\Omega_1 - \frac{1}{2}R$
2. $A_{1,0}B_{1,-1} \to A_{1,-1}B_{1,-1}$	$2\left(1+\frac{J}{R}\right)$	$-J + \frac{1}{2}R$
3. $A_{1,0}B_{1,0} \to A_{1,-1}B_{1,0}$	$\frac{2[a_{12}+a_{22}+Q(a_{22}+a_{32})]^2}{1+Q^2}$	$-\Omega_2 + \frac{1}{2}R$
4. $A_{1,1}B_{0,0} \to A_{1,0}B_{0,0}$ $A_{1,0}B_{0,0} \to A_{1,-1}B_{0,0}$	4	$\frac{1}{2}\delta$
5. $A_{1,0}B_{1,1} \to A_{1,-1}B_{1,1}$	$\frac{2[a_{13}+a_{23}+Q(a_{33}+a_{23})]^2}{1+Q^2}$	$\Omega_3 - \frac{1}{2}R$
6. $A_{1,1}B_{1,0} \to A_{1,0}B_{1,0}$	$\frac{2[Q(a_{22}+a_{12})-(a_{22}+a_{32})]^2}{1+Q^2}$	$\Omega_2 + \frac{1}{2}R$
7. $A_{1,1}B_{1,1} \to A_{1,0}B_{1,1}$	$2\left(1-\frac{2J}{R}\right)$	$J + \frac{1}{2}R$
M1. $A_{1,1}B_{1,-1} \to A_{1,-1}B_{1,0}$	$\frac{2[a_{11}+a_{21}+Q(a_{21}+a_{31})]^2}{1+Q^2}$	$-\Omega_1 + \frac{1}{2}R$
M2. $A_{1,1}B_{1,0} \to A_{1,-1}B_{1,1}$	$\frac{2[Q(a_{23}+a_{13})-(a_{23}+a_{33})]^2}{1+Q^2}$	$\Omega_3 + \frac{1}{2}R$

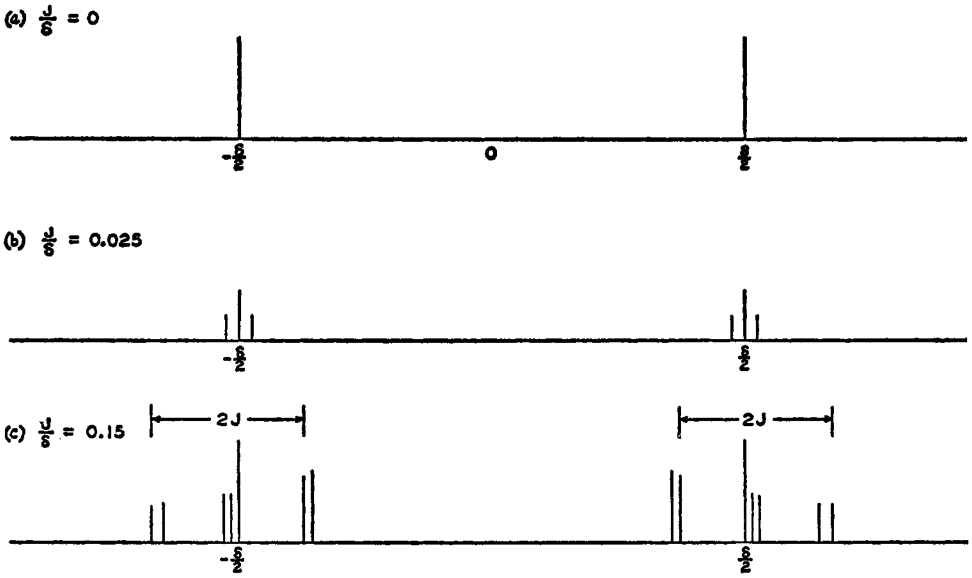


FIG. 13. Theoretical A_2B_2 spectra for the case of weak coupling.

These matrices are generated by the states with $m = \pm 1/2$ and $I_A = 3/2, I_B = 1$. Let $\Omega_1 < \Omega_2 < \Omega_3$ be the eigenvalues of $\mathcal{H}^+$ and $\mathbf{a} = (a_{ij})$ be the matrix whose normalized column vectors are the eigenvectors of $\mathcal{H}^+$; that is,

$$\mathbf{a}\mathcal{H}^+\mathbf{a}^{-1} = (\Omega_i\delta_{ij}) \tag{46}$$

Similarly, let $\Omega_1' < \Omega_2' < \Omega_3'$ and $\mathbf{b} = (b_{ij})$ be the corresponding quantities for $\mathcal{H}^-$. For $J/\delta \ll 1$ both $\mathbf{a}$ and $\mathbf{b}$ are 3×3 identity matrices and

$$\left.\begin{aligned} \Omega_1 &= \frac{3}{2}(-\delta + J) \\ \Omega_2 &= -\frac{\delta}{2} \\ \Omega_3 &= \frac{1}{2}(\delta + J) \end{aligned}\right\} \tag{47}$$

$$\left.\begin{aligned} \Omega_1' &= \frac{3}{2}(\delta + J) \\ \Omega_2' &= \frac{\delta}{2} \\ \Omega_3' &= \frac{1}{2}(-\delta + J) \end{aligned}\right\} \tag{48}$$

In the opposite limit, i.e., $J/\delta \gg 1$, it is easily shown that

$$\left.\begin{aligned} \Omega_1 &= \Omega_1' = -\frac{3}{2}J \\ \Omega_2 &= \Omega_2' = J \\ \Omega_3 &= \Omega_3' = \frac{5}{2}J \end{aligned}\right\} \tag{49}$$

(*Text continues on next page*)

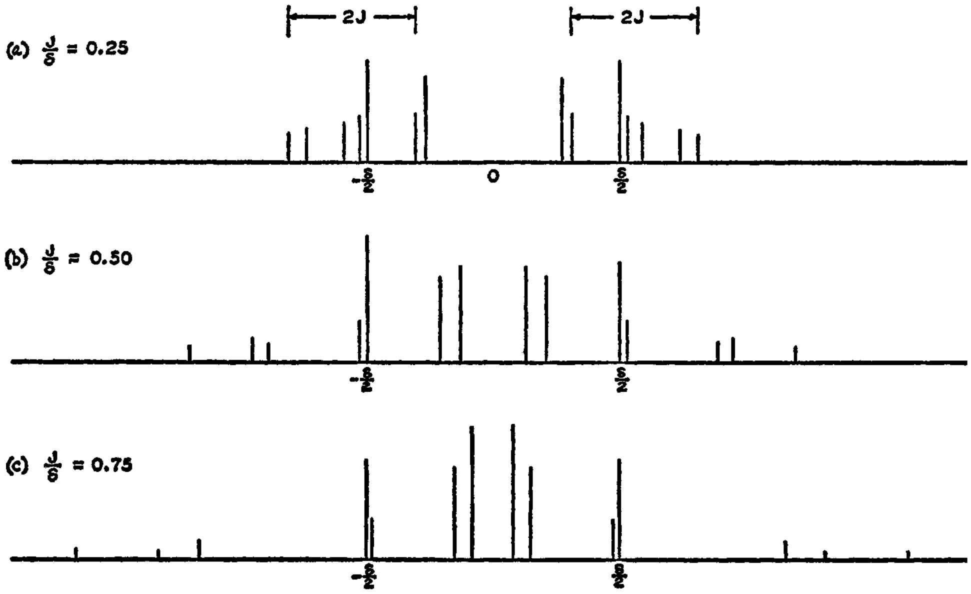


FIG. 14. Theoretical A_2B_2 spectra for the case of intermediate coupling.

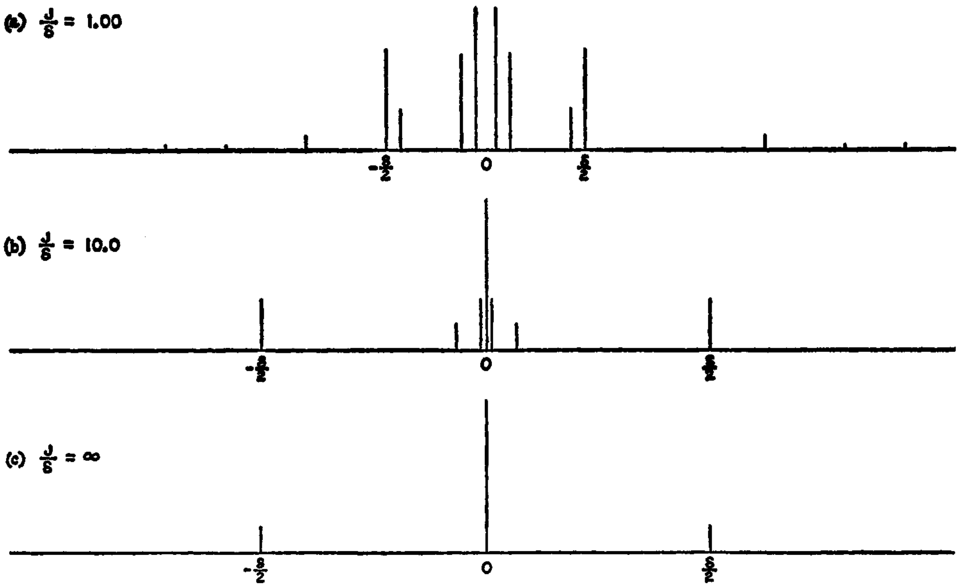


FIG. 15. Theoretical A_2B_2 spectra for the case of strong coupling.

$$\mathbf{a} = \begin{bmatrix} \sqrt{1/10} & \sqrt{2/5} & \sqrt{1/2} \\ \sqrt{3/5} & \sqrt{1/15} & -\sqrt{1/3} \\ \sqrt{3/10} & -\frac{2}{3}\sqrt{6/5} & \sqrt{1/6} \end{bmatrix} \tag{50}$$

$$\mathbf{b} = \begin{bmatrix} \sqrt{1/2} & \sqrt{2/5} & \sqrt{1/10} \\ -\sqrt{1/3} & \sqrt{1/15} & \sqrt{3/5} \\ \sqrt{1/6} & -\frac{2}{3}\sqrt{6/5} & \sqrt{3/10} \end{bmatrix} \tag{51}$$

For other values of J/δ one must solve a pair of cubic equations for the Ω's; this is most conveniently done numerically.

The eigenvalues and eigenfunctions for the remaining states offer no difficulty, since their determination requires only the solution of linear and quadratic equations. The rather extensive algebra leading to the eigenvalues and eigenfunctions will not be given here; instead, all the algebra is summarized in tables 20, 21, and 22, giving the allowed transitions, relative intensities, and line frequencies. In these tables the following abbreviations have been employed:

$$\left.\begin{aligned} R_1 &= \sqrt{\left(\delta - \frac{1}{2}J\right)^2 + 6J^2} \\ R_2 &= \sqrt{\left(\delta + \frac{1}{2}J\right)^2 + 6J^2} \\ R_3 &= \sqrt{\left(\delta + \frac{1}{2}J\right)^2 + 2J^2} \\ R_4 &= \sqrt{\left(\delta - \frac{1}{2}J\right)^2 + 2J^2} \end{aligned}\right\} \tag{52}$$

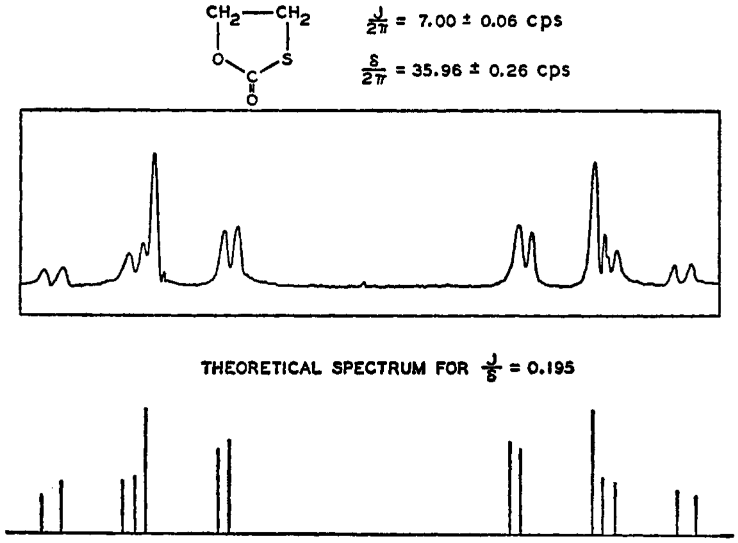


FIG. 16. Experimental and theoretical spectra for the protons in ethylene monothiocarbonate. The experimental trace is that of the pure liquid at room temperature and 40 Mc./sec.

TABLE 19

Factors of the secular determinant for the A_3B_2 *spin system*

1 × 1	m	2 × 2	m	3 × 3	m
$A_{3/2,3/2}B_{1,1}$	5/2	$A_{3/2,3/2}B_{1\ 0}$ $A_{3/2,1/2}B_{1,1}$	3/2	$A_{3/2,3/2}B_{1,-1}$ $A_{3/2,1/2}B_{1,0}$ $A_{3/2,-1/2}B_{1,1}$	1/2
$A_{3/2,3/2}B_{0,0}$	3/2	$A_{1/2,1/2}B_{1,0}$ $A_{1/2,-1/2}B_{1,1}$	1/2	$A_{3/2,-3/2}B_{1,1}$ $A_{3/2,-1/2}B_{1,0}$ $A_{3/2,1/2}B_{1,-1}$	−1/2
$A_{1/2,1/2}B_{1,1}$	3/2	$A'_{1/2,1/2}B_{1,0}$ $A'_{1/2,-1/2}B_{1,1}$	1/2		
$A'_{1/2,1/2}B_{1,1}$	3/2	$A_{1/2,1/2}B_{1,-1}$ $A_{1/2,-1/2}B_{1,0}$	−1/2		
$A_{3/2,1/2}B_{0,0}$	1/2	$A'_{1/2,1/2}B_{1,-1}$ $A'_{1/2,-1/2}B_{1,0}$	−1/2		
$A_{1/2,1/2}B_{0,0}$	1/2	$A_{3/2,-1/2}B_{1,-1}$ $A_{3/2,-3/2}B_{1,0}$	−3/2		
$A'_{1/2,1/2}B_{0,0}$	1/2				
$A_{1/2,-1/2}B_{0,0}$	−1/2				
$A'_{1/2,-1/2}B_{0,0}$	−1/2				
$A_{3/2,-1/2}B_{0,0}$	−1/2				
$A_{1/2,-1/2}B_{1,-1}$	−3/2				
$A'_{1/2,-1/2}B_{1,-1}$	−3/2				
$A_{3/2,-3/2}B_{0,0}$	−3/2				
$A_{3/2,-3/2}B_{1,-1}$	−5/2				

$$\left.\begin{aligned} Q_1 &= \frac{\sqrt{6}\,J}{\delta - \frac{1}{2}J - R_1} \\ Q_2 &= \frac{-\sqrt{6}\,J}{\delta + \frac{1}{2}J + R_2} \\ Q_3 &= \frac{\sqrt{2}\,J}{\delta + \frac{1}{2}J - R_3} \\ Q_4 &= \frac{-\sqrt{2}\,J}{\delta - \frac{1}{2}J + R_4} \end{aligned}\right\} \quad (53)$$

In addition, ω_B has been arbitrarily taken as the frequency origin, so that $\omega_A = \delta$.

From the tables, it is seen that the general A_3B_2 spectrum consists of thirty-four lines: thirteen in group A, twelve in group B, and nine mixed transitions. The most intense line in group A is undeviated from the position it would have in the absence of spin coupling. Further, the mean of lines 4 and 5 in group B gives the frequency origin exactly. Therefore the chemical shift can be exactly determined without solving the system in detail. The correct lines may be easily determined by reference to the numerical data in the Appendix. (If $\delta \simeq 0$, this procedure may be difficult to apply.) Once δ has been found, J can be determined from any of the line spacings involving R_1, R_2, R_3, and R_4.

Theoretical spectra for various J/δ ratios are given in figures 17, 18, and 19 (see the Appendix for the correspondence between the lines in these figures and the numbering in tables 20 and 21). The mixed transitions are not shown in any of these figures because of their low intensity.

The theoretical and experimental spectra for CH_3CH_2I (19a) are shown in figures 20 and 21. The chemical shift spin-spin coupling constants were found to be

$$\frac{J}{2\pi} = 7.5 \pm 0.3 \text{ c.p.s.}$$

$$\frac{\delta}{2\pi} = 54.13 \pm 0.20 \text{ c.p.s.}$$

E. THE GENERAL $A_{n_A}B_{n_B}$ SPIN SYSTEM

The general $A_{n_A}B_{n_B}$ spin system will involve determinantal equations of very high degree if both n_A and n_B are large. It is possible, however, to deduce a number of useful facts about the general case without solving the secular equations. Since the case $n_B = 1$ has been completely solved, it will be assumed that $n_A \geq n_B \geq 2$.

Let us first consider the orders of the secular equations. These are determined by the product functions $A_{I_A,m_A}B_{I_B,m_B}$, whose m_A and m_B values sum to a fixed m; that is,

$$m = m_A + m_B \tag{54}$$

Since $\mathbf{I}_A^2$ and $\mathbf{I}_B^2$ commute with $\mathcal{H}$, I_A and I_B are fixed, while

$$-I_A \leq m_A \leq I_A \tag{55}$$

$$-I_B \leq m_B \leq I_B \tag{56}$$

The largest value of m occurs when m_A and m_B have their maximum values I_A and I_B, so that

$$m_{\text{max.}} = I_A + I_B \tag{57}$$

TABLE 20

Transitions in group A

Transition in the Limit as $J \to 0$	Relative Intensity	Frequency
1. $A_{3/2,3/2}B_{1,1} \to A_{3/2,1/2}B_{1,1}$	$\frac{(\sqrt{2}+\sqrt{3}Q_1)^2}{1+Q_1^2}$	$\frac{1}{2}(\delta+\frac{5}{2}J+R_1)$
2. $A_{1/2,1/2}B_{1,1} \to A_{1/2,-1/2}B_{1,1}$ $A'_{1/2\ 1/2}B_{1,1} \to A'_{1/2,-1/2}B_{1,1}$	$\frac{2(Q_3+\sqrt{2})^2}{1+Q_3^2}$	$\frac{1}{2}(\delta+\frac{3}{2}J+R_3)$
3. $A_{3/2,-1/2}B_{1,-1} \to A_{3/2,-3/2}B_{1,-1}$	$\frac{(\sqrt{2}Q_2-\sqrt{3})^2}{1+Q_2^2}$	$\frac{1}{2}(\delta-\frac{5}{2}J+R_2)$
4. $A_{1/2,1/2}B_{1,0} \to A_{1/2,-1/2}B_{1,0}$ $A'_{1/2,1/2}B_{1,0} \to A'_{1/2,-1/2}B_{1,0}$	$\frac{2[Q_3+\sqrt{2}(Q_4Q_3-1)]^2}{(1+Q_3^2)(1+Q_4^2)}$	$\frac{1}{2}(R_3+R_4)$
5. $A_{1/2,1/2}B_{1,-1} \to A_{1/2,-1/2}B_{1,-1}$ $A'_{1/2,1/2}B_{1,-1} \to A'_{1/2,-1/2}B_{1,-1}$	$\frac{2(\sqrt{2}Q_4-1)^2}{1+Q_4^2}$	$\frac{1}{2}(\delta-\frac{3}{2}J+R_4)$
6. $A_{3/2,3/2}B_{0,0} \to A_{3/2,1/2}B_{0,0}$ $A_{3/2,1/2}B_{0,0} \to A_{3/2,-1/2}B_{0,0}$ $A_{3/2,-1/2}B_{0,0} \to A_{3/2,-3/2}B_{0,0}$ $A_{1/2,1/2}B_{0,0} \to A_{1/2,-1/2}B_{0,0}$ $A'_{1/2,1/2}B_{0,0} \to A'_{1/2,-1/2}B_{0,0}$	12	δ
7. $A_{3/2,1/2}B_{1,1} \to A_{3/2,-1/2}B_{1,1}$	$\frac{[\sqrt{2}a_{13}+(\sqrt{3}+\sqrt{2}Q_1)a_{23}+2Q_1a_{33}]^2}{1+Q_1^2}$	$\delta+\Omega_3+\frac{1}{4}J-\frac{1}{2}R_1$
8. $A_{3/2,3/2}B_{1\ 0} \to A_{3/2,1/2}B_{1,0}$	$\frac{[\sqrt{2}Q_1a_{12}+(\sqrt{3}Q_1-\sqrt{2})a_{22}-2a_{32}]^2}{1+Q_1^2}$	$\delta+\Omega_2+\frac{1}{4}J+\frac{1}{2}R_1$
9. $A_{3/2,3/2}B_{1,-1} \to A_{3/2,1/2}B_{1,-1}$	$[\sqrt{3}a_{31}b_{13}+(2a_{21}+\sqrt{2}a_{31})b_{23}+(\sqrt{3}a_{11}+\sqrt{2}a_{21})b_{33}]^2$	$\Omega'_3-\Omega_1$
10. $A_{3/2,1/2}B_{1,0} \to A_{3/2,-1/2}B_{1,0}$	$[\sqrt{3}a_{32}b_{12}+(2a_{22}+\sqrt{2}a_{32})b_{22}+(\sqrt{3}a_{12}+\sqrt{2}a_{22})b_{32}]^2$	$\Omega'_2-\Omega_2$
11. $A_{3/2,-1/2}B_{1,1} \to A_{3/2,-3/2}B_{1,1}$	$[\sqrt{3}a_{33}b_{11}+(2a_{23}+\sqrt{2}a_{33})b_{21}+(\sqrt{3}a_{13}+\sqrt{2}a_{23})b_{31}]^2$	$\Omega'_1-\Omega_3$
12. $A_{3/2,-1/2}B_{1,0} \to A_{3/2,-3/2}B_{1,0}$	$\frac{[\sqrt{2}b_{12}+(\sqrt{3}+\sqrt{2}Q_2)b_{22}+2Q_2b_{32}]^2}{1+Q_2^2}$	$\delta-\Omega'_2-\frac{1}{4}J+\frac{1}{2}R_2$
13. $A_{3/2,1/2}B_{1,-1} \to A_{3/2,-1/2}B_{1,-1}$	$\frac{[\sqrt{2}Q_2b_{13}+(\sqrt{3}Q_2-\sqrt{2})b_{23}-2b_{33}]^2}{1+Q_2^2}$	$\delta-\Omega'_3-\frac{1}{4}J-\frac{1}{2}R_2$

Clearly, there is only one such product function and it is an eigenfunction of $\mathcal{H}$. The next largest m-value is $m_{\max.} - 1$ and this occurs twice; once when $m_A = I_A$ while $m_B = I_B - 1$, and again when $m_A = I_A - 1$ while $m_B = I_B$. The eigenvalues for these states are obtained by solving quadratic equations. By continuing this process one obtains the $r + 1$ states

m_A	m_B
I_A	$I_B - r$
$I_A - 1$	$I_B - r + 1$
$\cdot$	$\cdot$
$\cdot$	$\cdot$
$\cdot$	$\cdot$
$I_A - r$	I_B

with $m = I_A + I_B - r$. If it is supposed that $I_B \leq I_A$, then $0 \leq r \leq 2I_B$; otherwise, m_B would exceed the lower limit demanded by equation 56. The greatest number of states with a given m occur when $r = 2I_B$ and this number is just $r + 1 = 2I_B + 1$. The m-value for all of these states is $m - I_A + I_B - r = I_A - I_B$. This process can also be started from $m_{\min.} = -I_A - I_B$ and continued up to the $2I_B + 1$ states with $m = -I_A + I_B$. However, this procedure *has not* accounted for all possible spin states, since

$$2\sum_{r=0}^{2I_B}(r+1) = 2(2I_B+1)(I_B+1) \qquad (58)$$

The correct number is, of course, $(2I_A + 1)(2I_B + 1)$, and the reason for the above shortage is that the states with

$$-I_A + I_B < m < I_A - I_B$$

have not been counted. To account for these states write the m_A and m_B values as follows,

$$\begin{array}{ll} m_A\colon & I_A \quad I_A-1 \quad I_A-2\cdots I_A-2I_B \\ & \qquad\qquad\qquad -1\cdots -I_A+1 \quad -I_A \\ m_B\colon & \quad -I_B \quad\; -I_B+1\cdots I_B \end{array}$$

TABLE 21

Transitions in group B

Transition in the Limit as $J \to 0$	Relative Intensity	Frequency
1. $A_{3/2,3/2}B_{1,1} \to A_{3/2,3/2}B_{1,0}$	$\dfrac{(\sqrt{2}Q_1 - \sqrt{3})^2}{1 + Q_1^2}$	$\frac{1}{2}(\delta + \frac{5}{2}J - R_1)$
2. $A_{1/2,1/2}B_{1,1} \to A_{1/2,1/2}B_{1,0}$ $A'_{1/2,1/2}B_{1,1} \to A'_{1/2,1/2}B_{1,0}$	$\dfrac{2(\sqrt{2}Q_3 - 1)^2}{1 + Q_3^2}$	$\frac{1}{2}(\delta + \frac{3}{2}J - R_3)$
3. $A_{3/2,-3/2}B_{1,0} \to A_{3/2,-3/2}B_{1,-1}$	$\dfrac{(\sqrt{2} + \sqrt{3}Q_2)^2}{1 + Q_2^2}$	$\frac{1}{2}(\delta - \frac{5}{2}J - R_2)$
4. $A_{1/2,-1/2}B_{1,1} \to A_{1/2,-1/2}B_{1,0}$ $A'_{1/2,-1/2}B_{1,1} \to A'_{1/2,-1/2}B_{1,0}$	$\dfrac{2[1 + \sqrt{2}(Q_3 + Q_4)]^2}{(1 + Q_3^2)(1 + Q_4^2)}$	$\frac{1}{2}(R_4 - R_3)$
5. $A_{1/2,1/2}B_{1,0} \to A_{1/2,1/2}B_{1,-1}$ $A'_{1/2,1/2}B_{1,0} \to A'_{1/2,1/2}B_{1,-1}$	$\dfrac{2[(Q_3 - \sqrt{2})Q_4 - \sqrt{2}Q_3]^2}{(1 + Q_3^2)(1 + Q_4^2)}$	$\frac{1}{2}(R_3 - R_4)$
6. $A_{1/2,-1/2}B_{1,0} \to A_{1/2,-1/2}B_{1,-1}$ $A'_{1/2,-1/2}B_{1,0} \to A'_{1/2\ -1/2}B_{1,-1}$	$\dfrac{2(Q_4 + \sqrt{2})^2}{1 + Q_4^2}$	$\frac{1}{2}(\delta - \frac{3}{2}J - R_4)$
7. $A_{3/2,3/2}B_{1,0} \to A_{3/2,3/2}B_{1,-1}$	$\dfrac{[\sqrt{2}Q_1a_{11} + (\sqrt{3}Q_1 - \sqrt{2})a_{21} - 2a_{31}]^2}{1 + Q_1^2}$	$\delta + \Omega_1 + \frac{1}{4}J + \frac{1}{2}R_1$
8. $A_{3/2,1/2}B_{1,1} \to A_{3/2,1/2}B_{1,0}$	$\dfrac{[\sqrt{2}a_{12} + (\sqrt{3} + \sqrt{2}Q_1)a_{22} + 2Q_1a_{32}]^2}{1 + Q_1^2}$	$\delta + \Omega_2 + \frac{1}{4}J - \frac{1}{2}R_1$
9. $A_{3/2,-3/2}B_{1,1} \to A_{3/2,-3/2}B_{1,0}$	$\dfrac{[\sqrt{2}b_{11} + (\sqrt{3} + \sqrt{2}Q_2)b_{21} + 2Q_2b_{31}]^2}{1 + Q_2^2}$	$\delta - \Omega'_1 - \frac{1}{4}J + \frac{1}{2}R_2$
10. $A_{3/2,-1/2}B_{1,0} \to A_{3/2,-1/2}B_{1,-1}$	$\dfrac{[\sqrt{2}Q_2b_{12} + (\sqrt{3}Q_2 - \sqrt{2})b_{22} - 2b_{32}]^2}{1 + Q_2^2}$	$\delta - \Omega'_2 - \frac{1}{4}J - \frac{1}{2}R_2$
11. $A_{3/2,-1/2}B_{1,0} \to A_{3/2,-1/2}B_{1,-1}$	$[\sqrt{3}a_{33}b_{12} + (2a_{23} + \sqrt{2}a_{33})b_{22} + (\sqrt{3}a_{13} + \sqrt{2}a_{23})b_{32}]^2$	$\Omega'_2 - \Omega_3$
12. $A_{3/2,1/2}B_{1,0} \to A_{3/2,1/2}B_{1,-1}$	$[\sqrt{3}a_{32}b_{13} + (2a_{22} + \sqrt{2}a_{32})b_{33} + (\sqrt{3}a_{12} + \sqrt{2}a_{22})b_{33}]^2$	$\Omega'_3 - \Omega_2$

TABLE 22

Mixed transitions

Transition in the Limit as $J \to 0$	Relative Intensity	Frequency
1. $A_{3/2,1/2}B_{1,1} \to A_{3/2,3/2}B_{1,-1}$	$\dfrac{[\sqrt{2}a_{11} + (\sqrt{3} + \sqrt{2}Q_1)a_{21} + 2Q_1a_{31}]^2}{1 + Q_1^2}$	$\delta + \Omega_1 + \frac{1}{4}J - \frac{1}{2}R_1$
2. $A_{3/2,3/2}B_{1,0} \to A_{3/2,-1/2}B_{1,1}$	$\dfrac{[\sqrt{2}Q_1a_{13} + (\sqrt{3}Q_1 - \sqrt{2})a_{23} - 2a_{33}]^2}{1 + Q_1^2}$	$\delta + \Omega_3 + \frac{1}{4}J + \frac{1}{2}R_1$
3. $A_{3/2,1/2}B_{1,-1} \to A_{3/2,-3/2}B_{1,0}$	$\dfrac{[\sqrt{2}b_{13} + (\sqrt{3} + \sqrt{2}Q_2)b_{23} + 2Q_2b_{33}]^2}{1 + Q_2^2}$	$\delta - \Omega'_3 - \frac{1}{4}J + \frac{1}{2}R_2$
4. $A_{3/2,-3/2}B_{1,1} \to A_{3/2,-1/2}B_{1,-1}$	$\dfrac{[\sqrt{2}Q_2b_{11} + (\sqrt{3}Q_2 - \sqrt{2})b_{21} - 2b_{31}]^2}{1 + Q_2^2}$	$\delta - \Omega'_1 - \frac{1}{4}J - \frac{1}{2}R_2$
5. $A_{3/2,3/2}B_{1,-1} \to A_{3/2,-3/2}B_{1,1}$	$[\sqrt{3}a_{31}b_{11} + (2a_{21} + \sqrt{2}a_{31})b_{21} + (\sqrt{3}a_{11} + \sqrt{2}a_{21})b_{31}]^2$	$\Omega'_1 - \Omega_1$
6. $A_{3/2,3/2}B_{1,-1} \to A_{3/2,-1/2}B_{1,0}$	$[\sqrt{3}a_{31}b_{12} + (2a_{21} + \sqrt{2}a_{31})b_{22} + (\sqrt{3}a_{11} + \sqrt{2}a_{21})b_{32}]^2$	$\Omega'_2 - \Omega_1$
7. $A_{3/2,1/2}B_{1,0} \to A_{3/2,-3/2}B_{1,1}$	$[\sqrt{3}a_{32}b_{11} + (2a_{22} + \sqrt{2}a_{32})b_{21} + (\sqrt{3}a_{12} + \sqrt{2}a_{22})b_{31}]^2$	$\Omega'_1 - \Omega_2$
8. $A_{3/2,-1/2}B_{1,1} \to A_{3/2,1/2}B_{1,-1}$	$[\sqrt{3}a_{33}b_{13} + (2a_{23} + \sqrt{2}a_{33})b_{23} + (\sqrt{3}a_{13} + \sqrt{2}a_{23})b_{33}]^2$	$\Omega'_3 - \Omega_3$
9. $A_{1/2,-1/2}B_{1,1} \to A_{1/2,1/2}B_{1,-1}$ $A'_{1/2,-1/2}B_{1,1} \to A'_{1/2,1/2}B_{1,-1}$	$\dfrac{2[(1 + \sqrt{2}Q_3)Q_4 - \sqrt{2}]^2}{(1 + Q_3^2)(1 + Q_4^2)}$	$-\frac{1}{2}(R_3 + R_4)$

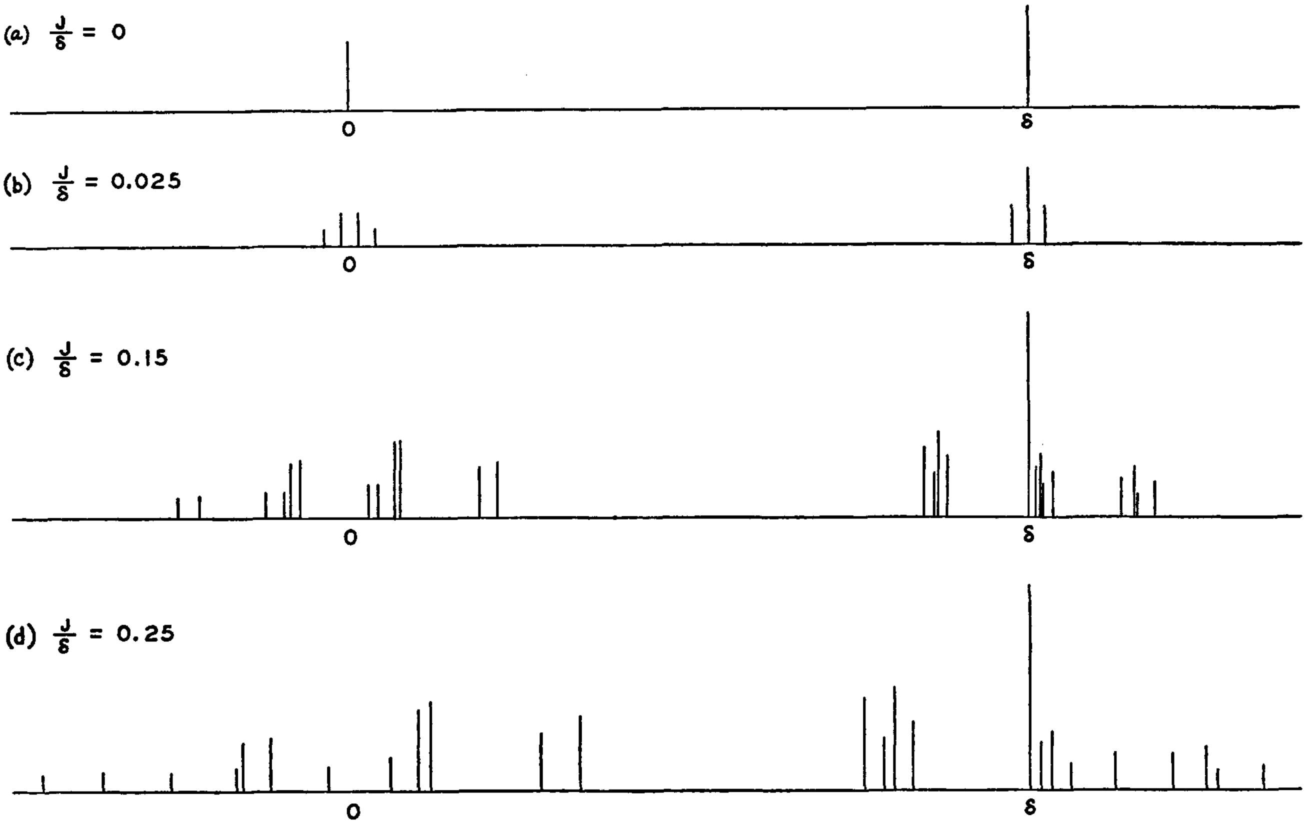


FIG. 17. Theoretical A_3B_2 spectra for the case of weak coupling.

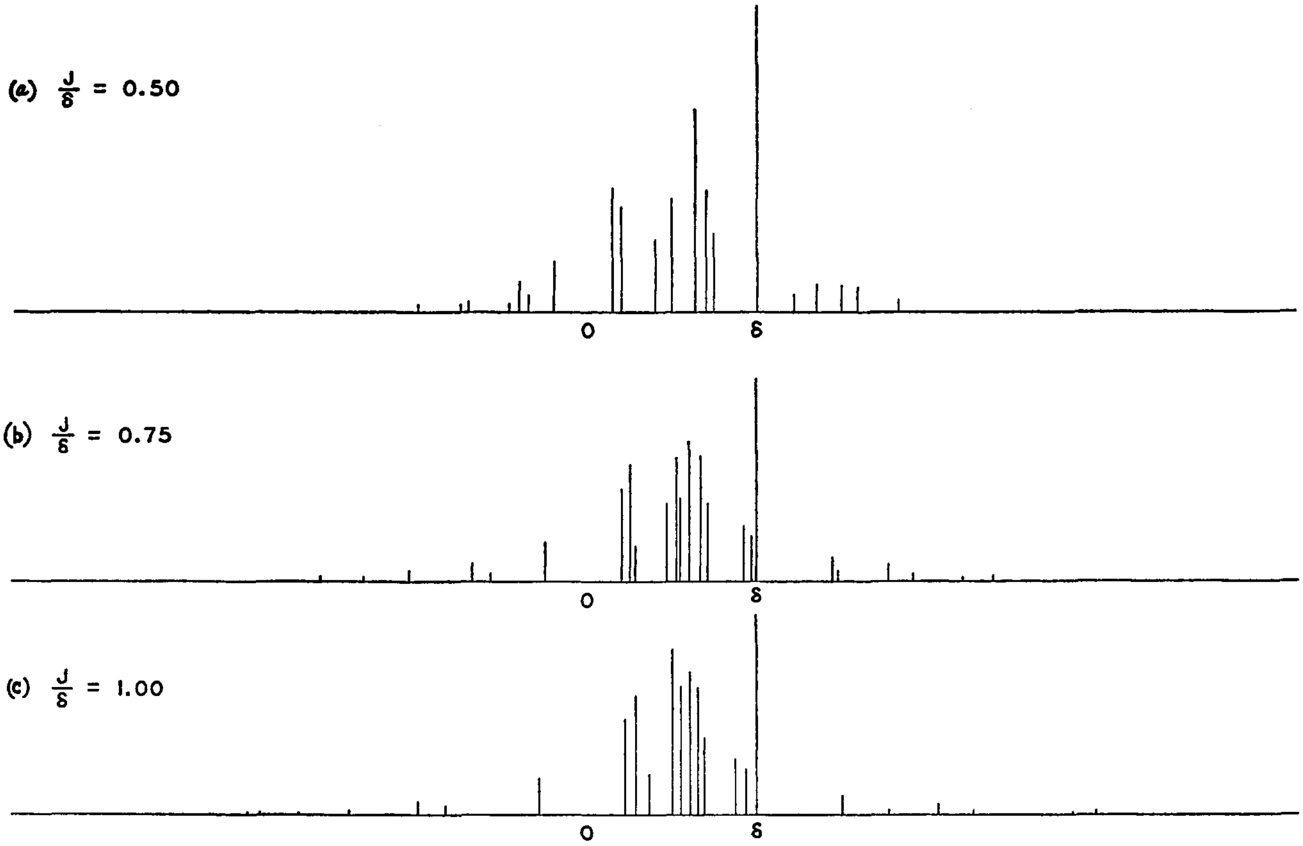


FIG. 18. Theoretical A_3B_2 spectra for the case of intermediate coupling.

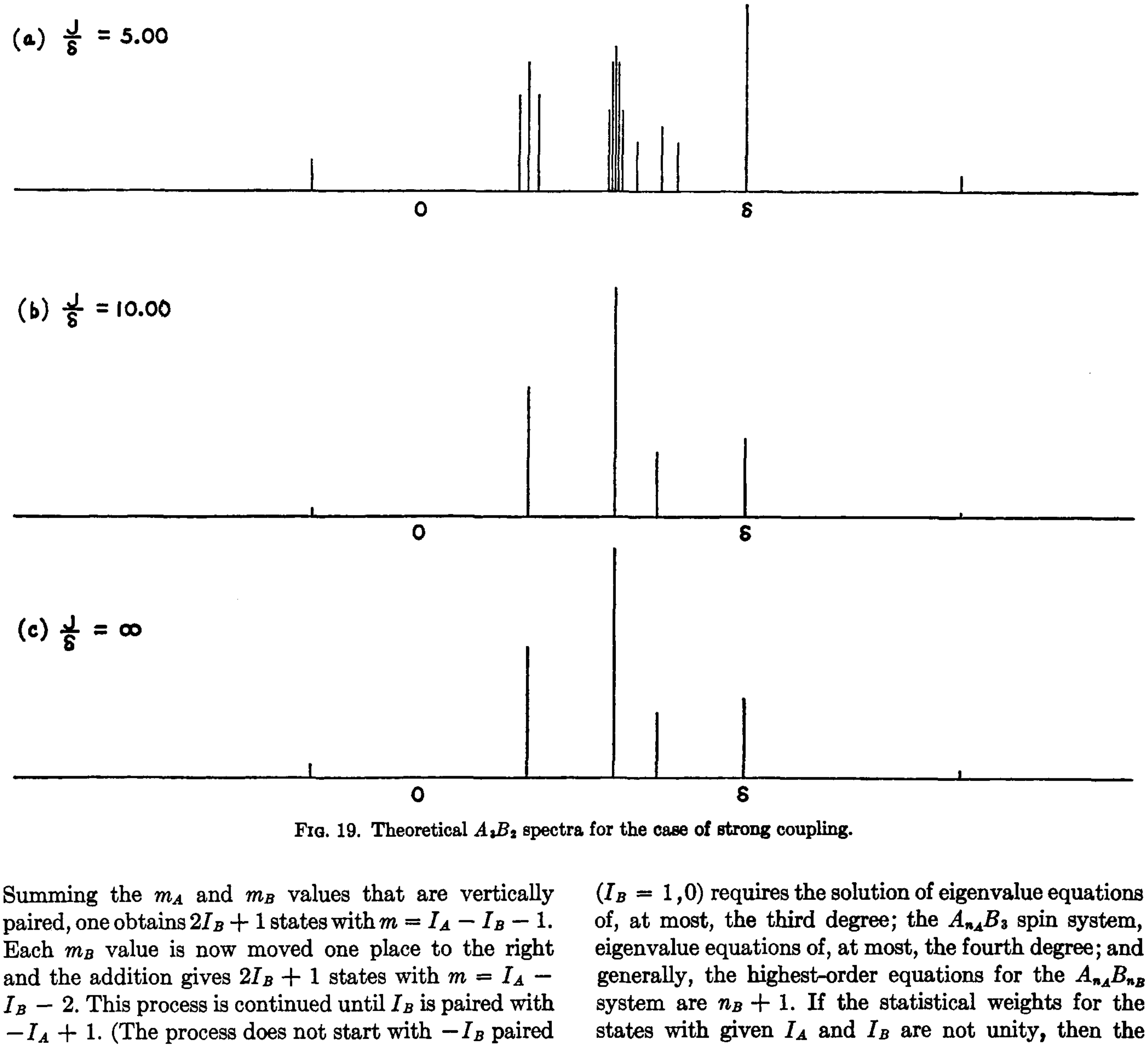


FIG. 19. Theoretical A_3B_2 spectra for the case of strong coupling.

Summing the m_A and m_B values that are vertically paired, one obtains $2I_B + 1$ states with $m = I_A - I_B - 1$. Each m_B value is now moved one place to the right and the addition gives $2I_B + 1$ states with $m = I_A - I_B - 2$. This process is continued until I_B is paired with $-I_A + 1$. (The process does not start with $-I_B$ paired with I_A nor end with I_B paired with $-I_A$, since the states with $m - I_A - I_B$, $-I_A + I_B$ have already been counted.) The total number of spin states determined by this process is

$$(2I_B + 1)[2(I_A - I_B) - 1]$$

which, when added to equation 58, gives $(2I_A + 1)(2I_B + 1)$, so that all possible states have now been counted. These results are summarized in table 23. The situation when $I_A < I_B$ is obtained by interchanging I_A and I_B in table 23.

From these results, it is seen that the interactions between states with spin quantum numbers $I_A > I_B$ generate secular equations of degree 1, 2, · · · · · $2I_B + 1$. The number of determinantal equations of degree $(2I_B + 1)$ is $2(I_A - I_B) + 1$ and there are two each of the 1×1, 2×2, · · · · and $(2I_B) \times (2I_B)$ determinants. It follows, then, that the $A_{n_A}B_2$ spin system ($I_B = 1, 0$) requires the solution of eigenvalue equations of, at most, the third degree; the $A_{n_A}B_3$ spin system, eigenvalue equations of, at most, the fourth degree; and generally, the highest-order equations for the $A_{n_A}B_{n_B}$ system are $n_B + 1$. If the statistical weights for the states with given I_A and I_B are not unity, then the energy levels will be $g_{I_A}g_{I_B}$-fold degenerate and the calculated intensities must be multiplied by the appropriate statistical weights.

The above considerations show also that the general $A_{n_A}B_{n_B}$ spectrum is a superposition of appropriately weighted $A_{q_A}A_{q_B}$ spectra, where q_A and q_B have the same parities (i.e., odd or even character) as n_A and n_B. It is, therefore, extremely important that the calculations for a given system be carefully indexed and stored for use in more complicated problems. It is for this reason that a completely detailed (but somewhat clumsy) notational scheme has been employed here.

Let us now consider the eigenvalue problem when $I_A > I_B = 0$. The highest-order secular equation is $2I_B + 1 = 1$; that is, $A_{I_A, m_A}B_{0,0}$ is an eigenfunction of $\mathcal{H}$ with the eigenvalue $m_A\omega_A$. A transition in group A leads to a resonance at

$$m_A\omega_A - (m_A - 1)\omega_A = \omega_A$$

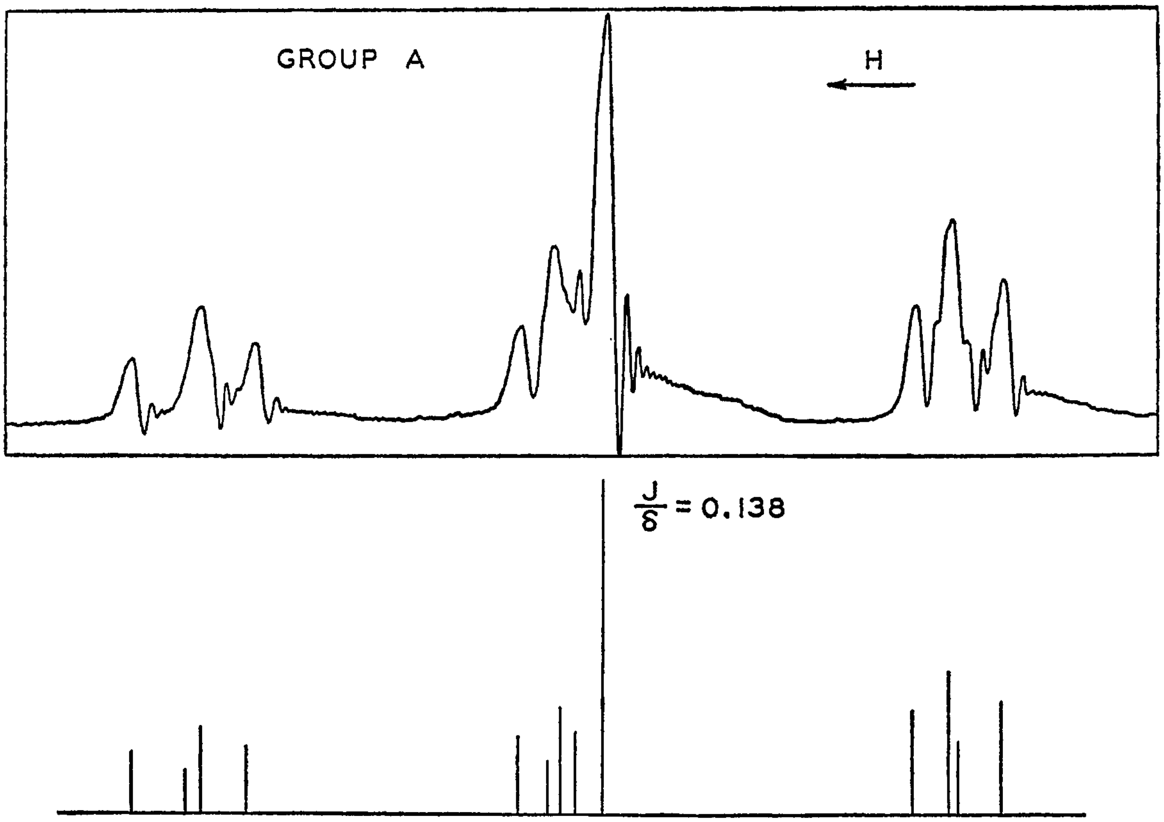


FIG. 20. Experimental and theoretical spectra of the methyl group protons in ethyl iodide. The experimental trace is that of the pure liquid at room temperature and 40 Mc./sec.

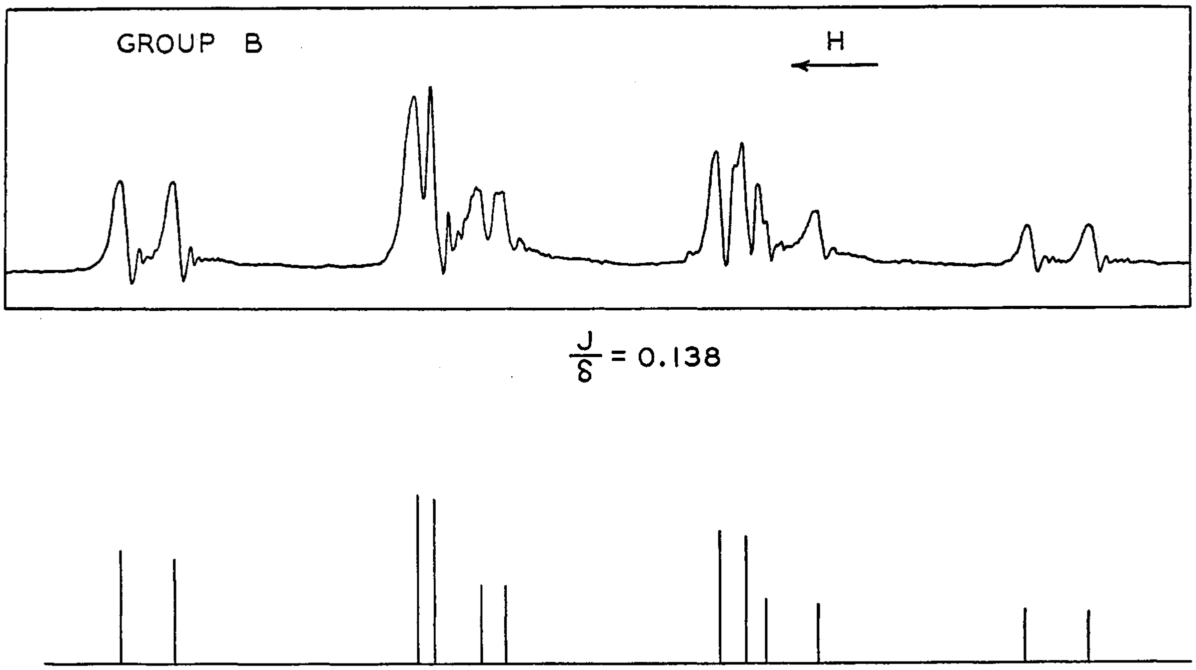


FIG. 21. Experimental and theoretical spectra of the methylene protons in ethyl iodide. Except for the rate of sweep, the experimental conditions are identical with those given for figure 20.

TABLE 23

Spin states for product functions with spin quantum numbers $I_A \leq I_B$

m_A	m_B	m	Number of States
I_A	I_B	$I_A + I_B$	1
I_A $I_A - 1$	$I_B - 1$ I_B	$I_A + I_B - 1$	2
....	....	....	....
I_A $I_A - 1$ .... $I_A - 2I_B$	$-I_B$ $-I_B + 1$ .... I_B	$I_A - I_B$	$2I_B + 1$
$I_A - 1$ .... $I_A - 2I_B - 1$	$-I_B$ .... I_B	$I_A - I_B - 1$	$2I_B + 1$
....	....	....	....
....	....	....	....
$-I_A + 2I_B + 1$ .... $-I_A + 1$	$-I_B$ .... I_B	$-I_A + I_B + 1$	$2I_B + 1$
$-I_A + 2I_B$ .... $-I_A + 1$ $-I_A$	$-I_B$ .... $I_B - 1$ I_B	$-I_A + I_B$	$2I_B + 1$
....	....	....	....
$-I_A + 1$ $-I_A$	$-I_B$ $-I_B + 1$	$-I_A - I_B + 1$	2
$-I_A$	$-I_B$	$-I_A - I_B$	1

of intensity

$$(I_A + m_A)(I_A - m_A + 1)$$

The total A intensity is then obtained by summing over I_A and m_A:

$$\sum_{I_A}\sum_{m_A} g_{I_A} < A_{I_A, m_A - 1} B_{0,0} \,|\, I_A^- \,|\, A_{I_A, m_A} B_{0,0} > \\ = \sum_{I_A}\sum_{m_A} g_{I_A}(I_A + m_A)(I_A - m_A + 1) \quad (59)$$

The summations are easily carried out (*cf.* Section VI) with the result

$$\sum_{I_A}\sum_{m_A} g_{I_A} < A_{I_A, m_A - 1} B_{0,0} \,|\, I_A^- \,|\, A_{I_A, m_A} B_{0,0} > = 2^{n_A - 1} n_A \quad (60)$$

Upon setting $n_A = 1, 2, 3$, one obtains the numbers 1, 2, and 12 which were found for the A_2B, A_2B_2, and A_3B_2 systems, respectively. Thus, if one of the groups has an even number of nuclei, the other group has an unshifted resonance whose intensity is given by equation 60. If both groups have an even number of equivalent nuclei, then there are a pair of lines whose separation is exactly $\delta = \omega_A - \omega_B$ and whose intensity ratio is

$$\frac{2^{n_A - 1}}{2^{n_B - 1}} \frac{n_A}{n_B}$$

Further, since the A_2B_2 system is included in the spectrum, there are A and B resonances separated by $2J$. Hence, experiments at two values of the magnetic field may permit the evaluation of J and δ without recourse to detailed calculations. An example of such a system is propane, for which $n_A = 6$, $n_B = 4$.

TABLE 24

Number of group A transitions for the $A_{n_A}B_{n_B}$ spin system

n_A	n_B	N_A
Odd	Odd	$\frac{(n_A + 1)^2(n_B + 1)(n_B + 3)}{16}$
Odd	Even	$\frac{n_B(n_B + 4)(n_A + 1)^2}{16} + 1$
Even	Odd	$\frac{n_A(n_A + 2)(n_B + 1)(n_B + 3)}{16}$
Even	Even	$\frac{n_A n_B(n_A + 2)(n_B + 4)}{16} + 1$

As in the $A_{n_A}B$ case it is possible to derive formulae for the number of transitions in groups A and B. These calculations are carried out as in the $A_{n_A}B$ case and the results are given in table 24. (The number of group B transitions are obtained from table 24 simply by interchanging n_A and n_B.) If in table 24 one sets $n_B = 1$, the results previously derived for the $A_{n_A}B$ system are obtained. Expressions can also be derived for the mixed transitions, but they will not be given here.

VI. Perturbation Calculations

When the ratios $J_{GG'}/\omega_{GG'}$ ($\omega_{GG'} \equiv \omega_G - \omega_{G'}$, $G \neq G'$) are less than unity, a perturbation calculation of the line frequencies and intensities may be appropriate (5). For this purpose, the Hamiltonian is written in the form

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}' \quad (1)$$

where

$$\mathcal{H}^{(0)} = -\sum_G \omega_G I_{Gz} \quad (2)$$

$$\mathcal{H}^{(1)} = -\sum_{G}\sum_{< G'} J_{GG'} I_{Gz} I_{G'z} \quad (3)$$

$$\mathcal{H}' = -\frac{1}{2}\sum_{G}\sum_{< G'} J_{GG'}(I_G^+ I_{G'}^- + I_G^- I_G^+) \quad (4)$$

$\mathcal{H}^{(0)}$ is the zero-order Hamiltonian; that is, $\mathcal{H}^{(0)}$ is applicable when the groups are uncoupled. $\mathcal{H}^{(1)}$ is the first-order correction to $\mathcal{H}^{(0)}$ when the groups are coupled and $\mathcal{H}'$ includes all corrections of higher order.

The eigenfunctions of $\mathcal{H}^{(0)}$ are the product spin functions

$$\Phi(\cdots I_G m_G \cdots; m) = \prod_G G_{I_G, m_G} \quad (5)$$

which are also eigenfunctions of I_z, I_{Gz}, and $\mathbf{I}_G^2$. Operating on Φ with $\mathcal{H}^{(0)}$ gives the zero-order energies

$$\Omega^{(0)}(\cdots m_G \cdots) = -\sum_G \omega_G m_G \quad (6)$$

which depend only upon the m_G.

For transitions in group G one has the selection rules

$$\left.\begin{aligned} \Delta m_G &= -1 \\ \Delta I_G = \Delta m_{G'} &= 0 \end{aligned}\right\} \quad (7)$$

and the associated frequency is

$$\Omega^{(0)}(\cdots m_G - 1 \cdots) - \Omega^{(0)}(\cdots m_G \cdots) = \omega_G$$

Thus, there is but one line for each group of equivalent nuclei. The relative line intensity for the transition $m_G \rightarrow m_G - 1$ is

$$\begin{aligned} |<\Phi(\cdots I_G m_G - 1, \cdots)|I_G^-|\Phi(\cdots I_G m_G \cdots)>|^2 \\ = (I_G + m_G)(I_G - m_G + 1) \end{aligned} \qquad (8)$$

Now all possible group G transitions result in a single resonance at ω_G independent of the total spin quantum numbers. Therefore, the total (relative) intensity of the group transitions is obtained by summing equation 8 over all m_G consistent with I_G, and then summing over all I_G:

$$\text{Group } G \text{ intensity} = 2^{N-n_G} \sum_{I_G} \sum_{m_G=-I_G}^{I_G} g_{I_G}(I_G + m_G)(I_G - m_G + 1) \qquad (9)$$

The statistical factor 2^{N-n_G} is the number of spin orientations of the remaining $N - n_G$ nuclei. The statistical weights g_{I_G} are given by the familiar equation

$$g_{I_G} = \frac{n_G!(n_G - 2k_G + 1)}{(n_G - k_G + 1)!k_G!} \qquad (10)$$

The sum over m_G is easily carried out for integral or half-off integral I_G, with the result

$$\text{Group } G \text{ intensity} = \frac{2^{N-n_G+1}}{3} \sum_{I_G} I_G(I_G + 1)(2I_G + 1) \qquad (11)$$

Substituting equation 10 into equation 11 and writing $I_G = \frac{n_G}{2} - k_G$, one finds:

$$\begin{aligned} \text{Group } G \text{ intensity} = \frac{2^{N-n_G+1}}{3} \sum_{k=0}^{\frac{n_G}{2} \text{ or } \frac{n_G-1}{2}} \times \\ \left\{\frac{n_G}{2}\left(\frac{n_G}{2} + 1\right) - k_G(n_G - k_G + 1)\right\} \frac{(n_G - 2k_G + 1)^2 n_G!}{(n_G - k_G + 1)!k_G!} \end{aligned} \qquad (12)$$

The summation may be evaluated with the aid of the identity (15)

$$\sum_{k=0}^{\frac{n}{2} \text{ or } \frac{n-1}{2}} \frac{n!(n - 2k + 1)^2}{(n - k + 1)!k!} = 2^n \qquad (13)$$

Using this result one finds:

$$\text{Group } G \text{ intensity} = 2^{N-1} n_G \qquad (14)$$

From this equation follows the familiar fact that the ratio of the intensities of group R and group S is equal to n_R/n_S. But note, however, that the proof is presently limited to the zero-order approximation. In this approximation

$$\text{Total intensity} = \sum_G 2^{N-1} n_G = 2^{N-1} N \qquad (15)$$

When the

$$\frac{J_{GG'}}{\omega_{GG'}} \ll 1$$

a first-order perturbation calculation is indicated with $\mathcal{H}^{(1)}$ as the perturbation. The product functions (6) are eigenfunctions of $\mathcal{H}^{(0)} + \mathcal{H}^{(1)}$, so that the first-order energy levels are

$$\Omega^{(1)}(\cdots m_G \cdots) = -\left\{\sum_G \omega_G m_G + \sum_{G<} \sum_{G'} J_{GG'} m_G m_{G'}\right\} \qquad (16)$$

From equation 16 and the selection rules the group G resonance frequencies are

$$\begin{aligned} \Omega^{(1)}(\cdots m_G - 1 \cdots) - \Omega^{(1)}(\cdots m_G \cdots) \\ = \omega_G + \sum_{G' \neq G} J_{GG'} m_{G'} \end{aligned} \qquad (17)$$

Since the first-order energies are independent of the spin quantum numbers, the correct number and frequencies of the group G resonances result if one takes $m_{G'} = I_{G'}(\text{max.}), I_{G'}(\text{max.}) - 1, \cdots\cdots -I_{G'}(\text{max.})$, where $I'_G(\text{max.}) = \frac{1}{2} n_{G'}$ is the maximum total spin quantum number of group G'. It follows from equation 17 that the coupling of group G with group G' results in $2I_{G'}(\text{max.}) + 1 = n'_G + 1$ resonances in group G. The intensity of a given line in the multiplet will depend upon the number of ways in which $m_{G'}$ can arise consistent with the total spin quantum numbers of group G'. If all the nuclei in G' have spin 1/2, then equation 34 of Section II gives the degeneracy of $m_{G'}$ as

$$\frac{n_{G'}!}{\left(\frac{n_{G'}}{2} - m_{G'}\right)!\left(\frac{n_{G'}}{2} + m_{G'}\right)!} \qquad (18)$$

From equations 17 and 18 it follows that there are $n_{G'} + 1$ group G resonances, which are symmetrically situated with respect to ω_G and whose intensities are given by the binomial coefficients of $n_{G'}$. If group G is further coupled to group G'', then each of the above lines is split into $n_{G''} + 1$ lines whose intensities are given by the degeneracies of the $m_{G''}$, etc. In all, there are

$$\prod_{G' \neq G} (n_{G'} + 1)$$

lines in group G. Since the $\Phi(\cdots I_G m_G \cdots; m)$ are eigenfunctions of $\mathcal{H}^{(0)} + \mathcal{H}^{(1)}$, the intensity relations in equations 14 and 15 are also valid in the first-order approximation.

If the conditions

$$\frac{J_{GG'}}{\omega_{GG'}} \ll 1$$

are not satisfied, second(or higher)-order perturbation theory may be used. In the case of ethyl alcohol (9),

$$\frac{J_{GG'}}{\omega_{GG'}} \simeq 0.1$$

and an accurate analysis requires a third-order calculation. The second-order correction to the energy levels is given by the standard expansion

$$\sum_j{}' \frac{|\mathcal{H}'_{ij}|^2}{\Omega_i^{(0)} - \Omega_j^{(0)}} \tag{19}$$

where i and j refer to all of the quantum numbers $(\cdots I_G m_G \cdots)$ of the unperturbed system and the prime indicates omission of the term for which $i = j$. The off-diagonal elements of $\mathcal{H}'$ are given by

$$\begin{aligned} &\langle \Phi(\cdots I_G m_G \cdots I_{G'} m_{G'} | \mathcal{H}' | \Phi(\cdots I_G m_G - 1, \cdots I_{G'} m_{G'} + 1) \rangle \\ &\qquad = -\frac{1}{2} J_{GG'} \{ (I_G - m_G + 1)(I_G + m_G)(I_{G'} - m_{G'})(I_{G'} + m_{G'} + 1) \}^{1/2} \end{aligned} \tag{20}$$

and, upon substitution into equation 19, lead to the second-order energy levels:

$$\Omega^{(2)}(\cdots I_G m_G \cdots) = -\sum_G \omega_G I_{Gz} - \sum_{G<}\sum_{G'} J_{GG'} m_G m_{G'} - \frac{1}{2}\sum_{G<}\sum_{G'} \frac{J_{GG'}^2}{\omega_G - \omega_{G'}} \{ m_G(I_{G'}^2 + I_{G'} - m_{G'}^2) - m_{G'}(I_G^2 + I_G - m_G^2) \} \tag{21}$$

The frequency of a transition in group G ($\Delta I_G = 0$, $\Delta m_G = -1$) is

$$\omega_G + \sum_{G' \neq G} J_{GG'} m_{G'} + \frac{1}{2} \sum_{G' \neq G} \frac{J_{GG'}^2}{\omega_G - \omega_{G'}} \{ I_{G'}(I_{G'} + 1) - m_{G'}(m_{G'} + 1) + 2 m_G m_{G'} \} \tag{22}$$

The significant point here is that the second-order frequencies for group G depend upon the total spin quantum numbers of all the remaining groups.

The calculation of the relative line intensities requires the first-order perturbed spin functions, which are given by equation 23:

$$\begin{aligned} \Psi(\cdots I_G m_G \cdots ; m) &= \Phi(\cdots I_G m_G \cdots ; m) \\ &\quad + \sum_{G'}{}' \frac{\langle \Phi(\cdots I_{G'} m_{G'} \cdots ; m) | \mathcal{H}' | \Phi(\cdots I_G m_G \cdots ; m) \rangle}{\Omega^0(\cdots m_G \cdots) - \Omega^0(\cdots m_{G'} \cdots)} \Phi(\cdots I_{G'} m_{G'} \cdots ; m) \end{aligned} \tag{23}$$

On substitution of the matrix elements obtained from equation 20, there results

$$\begin{aligned} \Psi(\cdots I_G m_G \cdots ; m) &= \Phi(\cdots I_G m_G \cdots ; m) - \frac{1}{2}\sum_{G<}\sum_{G'} \frac{J_{GG'}}{\omega_G - \omega_{G'}} \\ &\quad \times \{ F(m_{G'}) F(m_G + 1) \Phi(\cdots I_G m_G + 1, \cdots I_{G'} - 1, \cdots ; m) \\ &\quad - F(m_{G'} + 1) F(m_G) \Phi(\cdots I_G m_G - 1, \cdots I_{G'} m_{G'} + 1, \cdots ; m) \} \end{aligned} \tag{24}$$

where

$$F(m_G) = \sqrt{(I_G + m_G)(I_G - m_G + 1)}$$

The relative intensity of a transition

$$\Psi(\cdots I_G m_G \cdots) \rightarrow \Psi(\cdots I_G m_G - 1 \cdots)$$

is now obtained from

$$| \langle \Psi(\cdots I_G m_G \cdots) | I_G^- | \Psi(\cdots I_G m_G - 1 \cdots) \rangle |^2$$

Evaluating the matrix element and retaining only the first-order terms after squaring gives, for the relative intensity,

$$(I_G - m_G + 1)(I_G + m_G) \left\{ 1 - \sum_{G \neq G'} \frac{2 J_{GG'} m_{G'}}{\omega_G - \omega_{G'}} \right\} \tag{25}$$

From these second-order formulae two facts can be deduced that will be of value in later sections. First note that if $\omega_G - \omega_{G'} \gg J_{GG'}$, then the product spin functions are good approximations to the stationary states. Further, from equation 21 it follows that the interaction between a pair of widely separated unperturbed levels is negligible.

In the special case of two groups, A and B, with internal shift $\delta = \omega_A - \omega_B > 0$, equations 22 and 25 reduce to

$$\omega_A + J m_B + \frac{1}{2} \frac{J^2}{\delta} \{ I_B(I_B + 1) - m_B(m_B + 1) + 2 m_A m_B \} \tag{26}$$

and

$$(I_A - m_A + 1)(I_A + m_A) \left\{ 1 - \frac{2 J m_B}{\delta} \right\} \tag{27}$$

From equation 26 or 22 one notes that the second-order line spacings are of order $J^2/2\delta$ (unless $I_B = 0$) and from equation 27 that the intensities of the transitions in group A with $m_B < 0$ are greater than those with $m_B > 0$. From equation 26 it can be shown that the more intense lines are those which are closest to the frequency ω_B, while the weaker lines are those displaced away from ω_B in the direction of higher frequencies. Examples of perturbation calculations for two groups are given in figures 2, 5, 9, 13, and 17. Parts (a) and (b) are examples of zero-order and first-order perturbation calculations; part (c) of these figures roughly corresponds to second-order theory.

The perturbation formulae are actually seldom used, since the present trend in spectral analysis is towards exact diagonalization of $\mathcal{H}$. However, perturbation calculations can provide a convenient set of initial parameters for an exact analysis.

VII. Systems with Three Groups of Equivalent Nuclei

A. SIGNS OF THE COUPLING CONSTANTS

The extension of the preceding calculations to systems with three or more groups of equivalent nuclei is straightforward. There is one aspect of the analysis that has previously been ignored but now requires detailed consideration. This concerns the *relative* signs of the (two or more) coupling constants (4, 5, 34). The absolute signs of the coupling constants cannot (ordinarily) be determined from a high-resolution spectrum. In the cases already studied, one may see the validity of this theorem by writing $-J$ for $+J$ in the expressions for the line frequencies and intensities. This sign change does not alter the resonance spectrum and J may be given an arbitrary positive sign. This theorem can be demonstrated to hold for a set of nuclei with arbitrary spins (19a). To prove this, one uses the operator $\mathbf{\Lambda}$ defined in Section II,B. Let

$$\mathcal{H} = -\mathbf{A} - \mathbf{B} \tag{1}$$

where $-\mathbf{A}$ is the Zeeman energy and $-\mathbf{B}$ is the coupling energy. If the signs of *all* the coupling constants are changed ($J_{jk} \rightarrow -J_{jk}$), the Hamiltonian becomes

$$\mathcal{H}' = -\mathbf{A} + \mathbf{B} \tag{2}$$

Adding equations 2 and 3 gives:

$$\mathcal{H} + \mathcal{H}' = -2\mathbf{A} \tag{3}$$

Now

$$[\mathcal{H}, \mathbf{\Lambda}] = 2\mathbf{\Lambda}\mathbf{A}$$

hence

$$\mathbf{\Lambda}\mathcal{H}\mathbf{\Lambda} - \mathcal{H} = 2\mathbf{A} \tag{4}$$

Combining equations 3 and 4 gives a relation between $\mathcal{H}$ and $\mathcal{H}'$

$$\mathbf{\Lambda}\mathcal{H} = -\mathcal{H}'\mathbf{\Lambda} \tag{5}$$

Suppose now that $\{\phi_i\}$ is a set of eigenfunctions $\mathcal{H}$ and $\{\Omega_i\}$ the corresponding eigenvalues. From equation 5 it follows that

$$\mathbf{\Lambda}\mathcal{H}\phi_i = \Omega_i(\mathbf{\Lambda}\phi_i) = -\mathcal{H}'(\mathbf{\Lambda}\phi_i) \tag{6}$$

Therefore, the eigenfunctions of $\mathcal{H}'$ are $\{\mathbf{\Lambda}\phi_i\}$ and the eigenvalues are $\{-\Omega_i\}$. If the transition $\phi_i \rightarrow \phi_j$ is allowed, one can write

Transition	Intensity	Frequency
$\phi_i \rightarrow \phi_j$	$\left\lvert\left(\phi_j \middle\vert \sum_k \gamma_k I_{xk} \middle\vert \phi_i\right)\right\rvert^2$	$\Omega_j - \Omega_i$

But

$$\begin{aligned} \lvert <\phi_j\lvert\sum_k \gamma_k I_{xk}\rvert\phi_i>\rvert^2 &= \lvert <\phi_i\lvert\sum_k \gamma_k I_{xk}\rvert\phi_j>\rvert^2 \\ &= \lvert <\phi_i\lvert\sum_k \gamma_k I_{xk}\rvert\mathbf{\Lambda}^2\phi_j>\rvert^2 = \lvert <\mathbf{\Lambda}\phi_i\lvert\sum_k \gamma_k I_{xk}\rvert\mathbf{\Lambda}\phi_j>\rvert^2 \end{aligned} \tag{7}$$

upon recalling that $\mathbf{\Lambda}^2 = 1$ and $[\mathbf{\Lambda}, I_{xk}] = 0$. From equation 7 one can write for the spectrum defined by $\mathcal{H}'$

Transition	Intensity	Frequency
$\mathbf{\Lambda}\phi_j \rightarrow \mathbf{\Lambda}\phi_i$	$\left\lvert\left(\phi_j \middle\vert \sum_k \gamma_k I_{xk} \middle\vert \phi_i\right)\right\rvert^2$	$(-\Omega_i) - (-\Omega_j)$

which proves the theorem. The only assumption made in this proof is that the Boltzmann factors are so close to unity that they may be omitted in the calculation of relative intensities.

Since the absolute signs cannot be determined, only the relative signs require consideration. For example, with three coupling constants there are four sign possibilities: $(+\,+\,+)$, $(+\,+\,-)$, $(+\,-\,+)$, and $(-\,+\,+)$. In general, for n coupling constants there are 2^{n-1} sign possibilities.

B. THE ASYMMETRICAL THREE-SPIN SYSTEM (*ABC*)

The simplest system with three groups of equivalent nuclei has $n_A = n_B = n_C = 1$ (28, 34). The Hamiltonian operator is

$$\begin{aligned} \mathcal{H} = -\Big\{&\omega_A I_{Az} + \omega_B I_{Bz} + \omega_C I_{Cz} + J_{AB} I_{Az} I_{Bz} + J_{AC} I_{Az} I_{Cz} \\ &+ J_{BC} I_{Bz} I_{Cz} + \frac{1}{2} J_{AB}(I_A^+ I_B^- + I_A^- I_B^+) \\ &+ \frac{1}{2} J_{AC}(I_A^+ I_C^- + I_A^- I_C^+) + \frac{1}{2} J_{BC}(I_B^+ I_C^- + I_B^- I_C^+)\Big\} \end{aligned} \tag{8}$$

Since the problem has no symmetry, the simple product functions may be used as a basis. The functions $\alpha\alpha\alpha$ ($m = 3/2$) and $\beta\beta\beta$ ($m = -3/2$) are eigenfunctions of $\mathcal{H}$ with the eigenvalues

$$\begin{aligned} &<1/2, 1/2, 1/2\lvert\mathcal{H}\rvert 1/2, 1/2, 1/2> = \Omega_1 \\ &\qquad = -\frac{1}{2}\Big\{\omega_A + \omega_B + \omega_C + \frac{1}{2}(J_{AB} + J_{AC} + J_{BC})\Big\} \end{aligned} \tag{9}$$

$$\begin{aligned} &<-1/2, -1/2, -1/2\lvert\mathcal{H}\rvert -1/2, -1/2, -1/2> = \Omega_8 \\ &\qquad = -\frac{1}{2}\Big\{-\omega_A - \omega_B - \omega_C + \frac{1}{2}(J_{AB} + J_{AC} + J_{BC})\Big\} \end{aligned} \tag{10}$$

The quantum numbers in equations 9 and 10 refer to m_A, m_B, and m_C ($I_A = I_B = I_C = 1/2$). The states with $m = \pm 1/2$ generate 3×3 submatrices of $\mathcal{H}$ whose matrix elements are:

$$\begin{aligned} &<1/2, 1/2, -1/2\lvert\mathcal{H}\rvert 1/2, 1/2, -1/2> \\ &\qquad = -\frac{1}{2}\Big\{\omega_A + \omega_B - \omega_C + \frac{1}{2}(J_{AB} - J_{AC} - J_{BC})\Big\} \end{aligned} \tag{11}$$

$$\begin{aligned} &<1/2, -1/2, 1/2\lvert\mathcal{H}\rvert 1/2, -1/2, 1/2> \\ &\qquad = -\frac{1}{2}\Big\{\omega_A - \omega_B + \omega_C + \frac{1}{2}(-J_{AB} + J_{AC} - J_{BC})\Big\} \end{aligned} \tag{12}$$

$$\begin{aligned} &<-1/2, 1/2, 1/2\lvert\mathcal{H}\rvert -1/2, 1/2, 1/2> \\ &\qquad = -\frac{1}{2}\Big\{-\omega_A + \omega_B + \omega_C + \frac{1}{2}(-J_{AB} - J_{AC} + J_{BC})\Big\} \end{aligned} \tag{13}$$

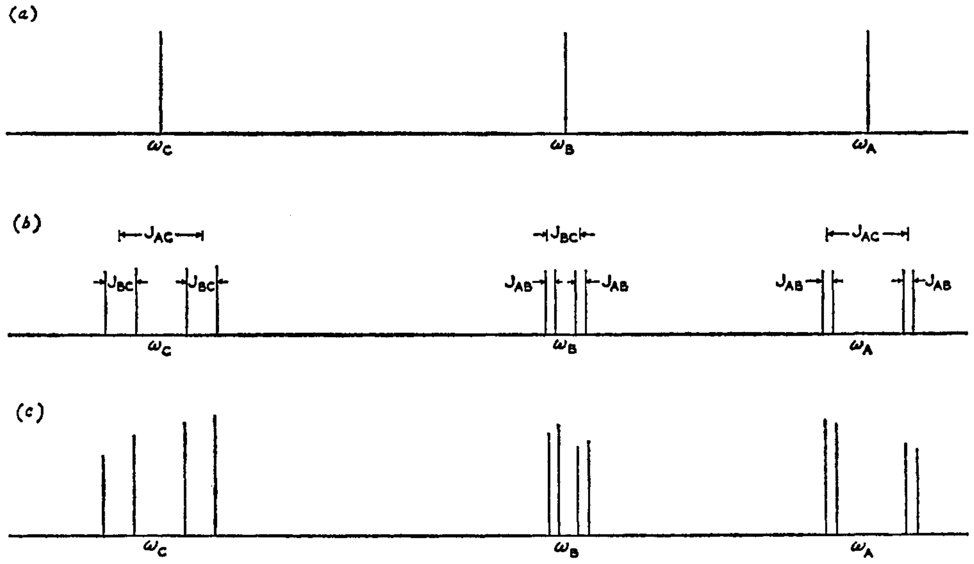


FIG. 22. The asymmetric three-spin system for (*a*) vanishingly small coupling, (*b*) first-order coupling effects, (*c*) second-order frequencies and first-order intensities.

$$<1/2,\ 1/2,\ -1/2|\mathcal{H}|1/2,\ -1/2,\ 1/2> \\ = <1/2,\ -1/2,\ 1/2|\mathcal{H}|1/2,\ 1/2,\ -1/2> = -\frac{1}{2}J_{BC} \quad (14)$$

$$<-1/2,\ 1/2,\ 1/2|\mathcal{H}|1/2,\ 1/2,\ -1/2> \\ = <1/2,\ 1/2,\ -1/2|\mathcal{H}|-1/2,\ 1/2,\ 1/2> = -\frac{1}{2}J_{AC} \quad (15)$$

$$<-1/2,\ 1/2,\ 1/2|\mathcal{H}|1/2,\ -1/2,\ 1/2> \\ = <1/2,\ -1/2,\ 1/2|\mathcal{H}|-1/2,\ 1/2,\ 1/2> = -\frac{1}{2}J_{AB} \quad (16)$$

$$<-1/2,\ -1/2,\ 1/2|\mathcal{H}|-1/2,\ -1/2,\ 1/2> \\ = -\frac{1}{2}\left\{-\omega_A - \omega_B + \omega_C + \frac{1}{2}(J_{AB} - J_{AC} - J_{BC})\right\} \quad (17)$$

$$<-1/2,\ 1/2,\ -1/2|\mathcal{H}|-1/2,\ 1/2,\ -1/2> \\ = -\frac{1}{2}\left\{-\omega_A + \omega_B - \omega_C + \frac{1}{2}(-J_{AB} + J_{AC} - J_{BC})\right\} \quad (18)$$

$$<1/2,\ -1/2,\ -1/2|\mathcal{H}|1/2,\ -1/2,\ -1/2> \\ = -\frac{1}{2}\left\{\omega_A - \omega_B - \omega_C + \frac{1}{2}(-J_{AB} - J_{AC} + J_{BC})\right\} \quad (19)$$

The remaining off-diagonal elements are obtained from equations 14 to 16 simply by changing the signs of m_A, m_B, and m_C. The eigenvalues for the $m = +1/2$ states will be denoted by Ω_2, Ω_3, and Ω_4; similarly Ω_5, Ω_6, and Ω_7 will be used to denote the eigenvalues for the $m = -1/2$ states. The relation between the transition types and the Ω's is shown in table 25. Since this system involves a pair of cubic equations containing six parameters and four choices of sign, numerical techniques are preferable to the (clumsy) closed form solution. Some insight into the structure of an *ABC* spectrum can be obtained by examining the results given by the perturbation formulae. In the absence of coupling there are only three lines, each occurring with equal intensity (figure 22a). In the first-order case (figure 22b), there are twelve lines (three quartets) and all lines are of equal intensity. It

TABLE 25

Transitions and frequencies for the ABC spin system

Transition in the Limit $J \to 0$	Frequency
Group *A*	
1. $A_{1/2,1/2}B_{1/2,1/2}C_{1/2,1/2} \to A_{1/2,-1/2}B_{1/2\ 1/2}C_{1/2,1/2}$	$\Omega_4 - \Omega_1$
2. $A_{1/2,1/2}B_{1/2,1/2}C_{1/2,-1/2} \to A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,-1/2}$	$\Omega_6 - \Omega_2$
3. $A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,1/2} \to A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,1/2}$	$\Omega_5 - \Omega_3$
4. $A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,-1/2} \to A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,-1/2}$	$\Omega_8 - \Omega_7$
Group *B*	
1. $A_{/12,1/2}B_{1/2,1/2}C_{1/2,1/2} \to A_{1/2\ 1/2}B_{1/2,-1/2}C_{1/2,1/2}$	$\Omega_3 - \Omega_1$
2. $A_{1/2,1/2}B_{1/2,1/2}C_{1/2,-1/2} \to A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,-1/2}$	$\Omega_7 - \Omega_2$
3. $A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,1/2} \to A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,1/2}$	$\Omega_5 - \Omega_4$
4. $A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,-1/2} \to A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,-1/2}$	$\Omega_8 - \Omega_6$
Group *C*	
1. $A_{1/2,1/2}B_{1/2,1/2}C_{1/2,1/2} \to A_{1/2,1/2}B_{1/2,1/2}C_{1/2,-1/2}$	$\Omega_2 - \Omega_1$
2. $A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,1/2} \to A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,-1/2}$	$\Omega_7 - \Omega_3$
3. $A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,1/2} \to A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,-1/2}$	$\Omega_6 - \Omega_4$
4. $A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,1/2} \to A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,-1/2}$	$\Omega_8 - \Omega_5$
Mixed transitions	
1. $A_{1/2,1/2}B_{1/2,1/2}C_{1/2,-1/2} \to A_{1/2,-1/2}B_{1/2,-1/2}C_{1/2,1/2}$	$\Omega_5 - \Omega_2$
2. $A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,1/2} \to A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,-1/2}$	$\Omega_6 - \Omega_3$
3. $A_{1/2,-1/2}B_{1/2,1/2}C_{1/2,1/2} \to A_{1/2,1/2}B_{1/2,-1/2}C_{1/2,-1/2}$	$\Omega_7 - \Omega_4$

TABLE 26*

Second-order frequencies and first-order intensities for the ABC system

Transition† in the Limit as $J \to 0$	Frequency	Intensity
1.	$\omega_A + \frac{1}{2}(J_{AB} + J_{AC}) + \frac{1}{4}\left\{\frac{J_{AB}^2}{\omega_A - \omega_B} + \frac{J_{AC}^2}{\omega_A - \omega_C}\right\}$	$1 - \frac{J_{AB}}{\omega_A - \omega_B} - \frac{J_{AC}}{\omega_A - \omega_C}$
2.	$\omega_A + \frac{1}{2}(J_{AB} - J_{AC}) + \frac{1}{4}\left\{\frac{J_{AB}^2}{\omega_A - \omega_B} + \frac{J_{AC}^2}{\omega_A - \omega_C}\right\}$	$1 - \frac{J_{AB}}{\omega_A - \omega_B} + \frac{J_{AC}}{\omega_A - \omega_C}$
3.	$\omega_A + \frac{1}{2}(-J_{AB} + J_{AC}) + \frac{1}{4}\left\{\frac{J_{AB}^2}{\omega_A - \omega_B} + \frac{J_{AC}^2}{\omega_A - \omega_C}\right\}$	$1 + \frac{J_{AB}}{\omega_A - \omega_B} - \frac{J_{AC}}{\omega_A - \omega_C}$
4.	$\omega_A - \frac{1}{2}(J_{AB} + J_{AC}) + \frac{1}{4}\left\{\frac{J_{AB}^2}{\omega_A - \omega_B} + \frac{J_{AC}^2}{\omega_A - \omega_C}\right\}$	$1 + \frac{J_{AB}}{\omega_A - \omega_B} + \frac{J_{AC}}{\omega_A - \omega_C}$

* The frequencies and intensities are for group A; the results for groups B and C are obtained by cyclical permutation of ABC.

† The numbering of the group A transitions corresponds to that given in table 25.

can be seen from figure 22b that in a given group G (i.e., a quartet) the first and second lines have the separation $J_{GG'}$, and the first and third lines have the separation $J_{GG''}$. If the signs of the coupling constants are changed in turn, the spectrum is unaltered and only the magnitudes of the J's can be obtained from a first-order spectrum. The second-order frequencies and first-order intensities are given in table 26 and are shown in figure 22c. Here it is seen that the intensities are different in the first-order approximation. (It is to be noted that by "first order" one means first order in $J_{GG'}/\omega_{GG'}$, not first order in I_z.) Further, from table 26 it is seen that the spectrum still has the property of constant spacings. In fact, the general ABC spectrum has this property. To see this, consider the following differences obtained from table 25:

$$\begin{aligned} A1 - A2 &= \Omega_4 - \Omega_1 - \Omega_6 + \Omega_2 = C1 - C3 = a \\ A3 - A4 &= \Omega_5 - \Omega_3 - \Omega_8 + \Omega_7 = C2 - C4 = a' \end{aligned} \tag{20}$$

These separations are in fact equal, for

$$a - a' = -\Omega_1 + (\Omega_2 + \Omega_3 + \Omega_4) - (\Omega_5 + \Omega_6 + \Omega_7) + \Omega_8$$

and the sums in parentheses are just the diagonal sums (i.e., the traces) of the 3 × 3 submatrices with $m = \pm 1/2$. From equations 11 to 13 and 17 to 18, one finds:

$$\begin{aligned} &\Omega_2 + \Omega_3 + \Omega_4 \\ &\qquad = \frac{1}{2}\left\{-\omega_A - \omega_B - \omega_C + \frac{1}{2}(J_{AB} + J_{AC} + J_{BC})\right\} \\ &\Omega_4 + \Omega_5 + \Omega_6 \\ &\qquad = \frac{1}{2}\left\{\omega_A + \omega_B + \omega_C + \frac{1}{2}(J_{AB} + J_{AC} + J_{BC})\right\} \end{aligned} \tag{21}$$

Substituting for Ω_1, Ω_8 and the traces, it follows that $a - a' = 0$. Similarly, one can show that

$$A1 - A3 = A2 - A4 = B1 - B3 = B2 - B4 = b \tag{22}$$

$$B1 - B2 = C2 - C1 = B3 - B4 = C4 - C3 = c \tag{23}$$

Thus, the groupings (AC), (AB), and (BC) have common characteristic splittings which, if observable, enable one to divide the spectrum into three quartets. The magnitudes of a, b, and c are useful approximations to the coupling constants ($a \simeq J_{AC}$, $b \simeq J_{AB}$, $c \simeq J_{BC}$). There are, however, exact sum rules (28) for the coupling constants which are easily derived from table 25 and equations 20 to 24. It is first noted that although a, b, and c are line spacings, a sign can be given to each of them. For example, if $\omega_{A1} > \omega_{A2}$, $a > 0$; and if $\omega_{A1} < \omega_{A2}$, then $a < 0$. Now if the sign of one of the J's is changed, the assignments of the corresponding lines (i.e., those lines with the associated characteristic splitting) are interchanged. Therefore,

$$|J_{AB} + J_{AC} + J_{BC}| = |a + b + c| \text{ if all } J_{GG'} > 0 \tag{24}$$

$$|J_{AB} + J_{AC} + J_{BC}| = |a + b - c| \text{ if } J_{BC} < 0 \tag{25}$$

$$|J_{AB} + J_{AC} + J_{BC}| = |a - b + c| \text{ if } J_{AB} < 0 \tag{26}$$

$$|J_{AB} + J_{AC} + J_{BC}| = |-a + b + c| \text{ if } J_{AC} < 0 \tag{27}$$

Thus, for a given assumption about the relative signs, one parameter can be eliminated from the problem. There is a similar sum rule for the chemical shifts which is obtained by summing all the frequencies in table 25:

$$\Sigma\Omega_{ij} = \omega_A + \omega_B + \omega_C$$

This sum depends upon the frequency origin but the difficulty can be removed by measuring all lines relative to some standard reference. The real problem with equation 27 is the observation of all the resonances. Another sum rule can be obtained (19) by summing only the frequencies in groups A, B, and C:

$$\sum_G \sum (\Omega_{ij}^G)_r = 4\{(\Delta\omega_A)_r + (\Delta\omega_B)_r + (\Delta\omega_C)_r\} \tag{28}$$

where $(\Delta X)_r$ indicates the measurement of the frequency X relative to some reference r. Now the twelve lines for groups A, B, and C are frequently resolved so that if two shifts relative to r are known or assumed, the third shift can be calculated from equation 28. In the case of protons, deuterium substitution can be very useful in this connection (19b).

TABLE 27

Eigenvalues and eigenfunctions for the ABX_{n_X} spin system

Eigenfunction	Eigenvalue
$A_{1/2,1/2}B_{1/2\ 1/2}X_{I_X,m_X}$	$-\frac{1}{2}\{\omega_A + \omega_B + 2m_X\omega_X + \frac{1}{2}J_{AB} + m_X(J_{AX} + J_{BX})\}$
$\frac{1}{\sqrt{1+Q_{m_X}^2}}\{A_{1/2,1/2}B_{1/2,-1/2} + Q_{I_X,m_X}A_{1/2,-1/2}B_{1/2,1/2}\}X_{I_X,m_X}$	$-\frac{1}{2}\{2m_X\omega_X - \frac{1}{2}J_{AB} + R_{m_X}\}$
$\frac{1}{\sqrt{1+Q_{m_X}^2}}\{Q_{I_X,m_X}A_{1/2,1/2}B_{1/2,-1/2} - A_{1/2,-1/2}B_{1/2,1/2}\}X_{I_X,m_X}$	$-\frac{1}{2}\{2m_X\omega_X - \frac{1}{2}J_{AB} - R_{m_X}\}$
$A_{1/2,-1/2}B_{1/2,-1/2}X_{I_X,m_X}$	$-\frac{1}{2}\{-\omega_A - \omega_B + 2m_X\omega_X + \frac{1}{2}J_{AB} - m_X(J_{AX} + J_{BX})\}$

C. THE ABX_{n_X} SPIN SYSTEM

Considerably more progress is possible with three-group systems if one of the groups has a chemical shift which is large compared to all other parameters; that is,

$$|\omega_X - \omega_A|,\ |\omega_X - \omega_B| \gg |\omega_A - \omega_B|,\ J_{AB},\ J_{AX},\ J_{BX} \quad (29)$$

In this case, the results of second-order perturbation theory show that only zero-order states of comparable energy (that is, states with the same values of m and m_X) can mix. Hence, those product functions which have different values of m_X are good approximations to the correct stationary states even if they have the same m-value. For $n_X = 1$, one has, for example, the case of two protons coupled to another proton (11) or a fluorine nucleus (33, 92). Solutions have also been given for small n_X (17, 27, 56). It is, however, very easy to write recursive formulae for the general case (19a), and this will be carried out here rather than discussing individual cases.

The spin functions for a particular value of m_X are

$$A_{1/2,1/2}B_{1/2,1/2}X_{I_X,m_X},\ A_{1/2,-1/2}B_{1/2,-1/2}X_{I_X,m_X},$$
$$A_{1/2,1/2}B_{1/2,-1/2}X_{I_X,m_X},\ A_{1/2,-1/2}B_{1/2,1/2}X_{I_X,m_X}$$

From the general mixing rules and the perturbation approximations only the last two functions mix. The algebra is straightforward and the results are given in table 27, where

$$R_{m_X} = \sqrt{[\delta + m_X(J_{AX} - J_{BX})]^2 + J_{AB}^2} \quad (30)$$

$$Q_{m_X} = \frac{J_{AB}}{\delta + m_X(J_{AX} - J_{BX}) + R_{m_X}} \quad (31)$$

Since there are $2I_X + 1$ values of m_X, it follows that table 27 gives $(n_X + 1)(n_X + 3)$ eigenvalues and eigenfunctions for n_X odd and $n_X^2 + 4n_X + 4$ for n_X even. The calculation of the relative intensities and frequencies for allowed transitions is carried out as in the $A_{n_A}B$ system and the results are given in table 28, where g_{I_X} is the statistical weight of I_X.

From table 28 one notes that if $I_X \equiv 0$ then the ABX_{n_X} system reduces to the simple AB system. For $I_X = 1/2$, $g_{I_X} = 1$, $m_X = \pm 1/2$ and the ABX system with fourteen lines results. If $I_X = 1$, $g_{I_X} = 1$, $m_X = 1, 0, -1$ and the system reduces, for example, to that of two protons and a deuteron. Other cases are obtained by substituting the appropriate values of I_X, m_X, and g_{I_X}.

The ABX system can often be useful in the analysis of ABC systems even if the conditions 29 are not strongly satisfied. This approximation will give better values for the coupling constants than the usual second-order perturbation theory and may even provide information about the relative signs of the coupling constants. The ABX system is most accurately applied when $\gamma_X \neq \gamma_A = \gamma_B$, as in the case of protons and fluorine, and has been extensively applied to substituted fluorobenzenes (33).

VIII. GROUP THEORETICAL TECHNIQUES

A. SYMMETRIZATION OF SPIN FUNCTIONS

In the discussion of the A_2B spin system it was noted that whenever the molecule under consideration is symmetrical, additional factoring of the Hamiltonian will occur if the zero-order spin functions are chosen properly. For the A_2B case, the correct spin functions were obtained by elementary considerations; in more complicated cases it is convenient to employ standard group theoretical techniques (47, 53, 93, 94). The procedure amounts to forming symmetrized linear combinations of product spin functions and classifying them according to the symmetry species (irreducible representations) of the group. One-dimensional representations are denoted by $\mathcal{A}$ and $\mathcal{B}$, while higher-dimensional representations are described by $\mathcal{E}$ (two-dimensional), $\mathcal{F}$ (three-dimensional), etc. The factoring of the Hamiltonian follows from the well-known group theoretical result (47, 94) that there is no mixing between states which "belong" to different symmetry species. Of course, in each symmetry species there is additional factoring according to z-components of total angular momentum.

The symmetrization of spin functions will be illustrated by considering three spin 1/2 nuclei situated at the vertices of an equilateral triangle. The point group

TABLE 28

Resonance frequencies and relative intensities for the ABX_{n_X} spin system

Transition in the Limit as All $J \to 0$	Intensity	Frequency
	***A* transitions**	
$A_{1/2,1/2}B_{1/2,1/2}X_{I_X,m_X} \to A_{1/2,-1/2}B_{1/2,1/2}X_{I_X,m_X}$	$\frac{g_{I_X}(1-Q_{m_X})^2}{1+Q^2_{m_X}}$	$\frac{1}{2}\{\omega_A+\omega_B+J_{AB}+m_X(J_{AX}+J_{BX})+R_{m_X}\}$
$A_{1/2,1/2}B_{1/2,-1/2}X_{I_X,m_X} \to A_{1/2,-1/2}B_{1/2,-1/2}X_{I_X,m_X}$	$\frac{g_{I_X}(1+Q_{m_X})^2}{1+Q^2_{m_X}}$	$\frac{1}{2}\{\omega_A+\omega_B-J_{AB}+m_X(J_{AX}+J_{BX})+R_{m_X}\}$
	***B* transitions**	
$A_{1/2,1/2}B_{1/2,1/2}X_{I_X,m_X} \to A_{1/2,1/2}B_{1/2,-1/2}X_{I_X,m_X}$	$\frac{g_{I_X}(1+Q_{m_X})^2}{1+Q^2_{m_X}}$	$\frac{1}{2}\{\omega_A+\omega_B+J_{AB}+m_X(J_{AX}+J_{BX})-R_{m_X}\}$
$A_{1/2,-1/2}B_{1/2,1/2}X_{I_X,m_X} \to A_{1/2,-1/2}B_{1/2,-1/2}X_{I_X,m_X}$	$\frac{g_{I_X}(1-Q_{m_X})^2}{1+Q^2_{m_X}}$	$\frac{1}{2}\{\omega_A+\omega_B-J_{AB}+m_X(J_{AX}+J_{BX})-R_{m_X}\}$
	***X* transitions**	
$A_{1/2,-1/2}B_{1/2,1/2}X_{I_X,m_X} \to A_{1/2,-1/2}B_{1/2,1/2}X_{I_Xm_X-1}$	$\frac{g_{I_X}(I_X+m_X)(I_X-m_X+1)(Q_{m_X}Q_{m_X-1}+1)^2}{(1+Q^2_{m_X})(1+Q^2_{m_X-1})}$	$\frac{1}{2}\{2\omega_X+R_{m_X-1}-R_{m_X}\}$
$A_{1/2,1/2}B_{1/2,-1/2}X_{I_Xm_X} \to A_{1/2,1/2}B_{1/2,-1/2}X_{I_X,m_X-1}$	$\frac{g_{I_X}(I_X+m_X)(I_X-m_X+1)(Q_{m_X}Q_{m_X-1}+1)^2}{(1+Q^2_{m_X})(1+Q^2_{m_X-1})}$	$\frac{1}{2}\{2\omega_X-R_{m_X-1}+R_{m_X}\}$
$A_{1/2,1/2}B_{1/2,1/2}X_{I_X,m_X} \to A_{1/2,1/2}B_{1/2,1/2}X_{I_X,m_X-1}$	$g_{I_X}(I_X+m_X)(I_X-m_X+1)$	$\frac{1}{2}\{2\omega_X+J_{AX}+J_{BX}\}$
$A_{1/2,-1/2}B_{1/2,-1/2}X_{I_X,m_X} \to A_{1/2,-1/2}B_{1/2,-1/2}X_{I_X,m_X-1}$	$g_{I_X}(I_X+m_X)(I_X-m_X+1)$	$\frac{1}{2}\{2\omega_X-J_{AX}-J_{BX}\}$
	***M* transitions**	
$A_{1/2\ 1/2}B_{1/2,-1/2}X_{I_Xm_X} \to A_{1/2,-1/2}B_{1/2,1/2}X_{I_X,m_X-1}$	$\frac{g_{I_X}(I_X+m_X)(I_X-m_X+1)(Q_{m_X}-Q_{m_X-1})^2}{(1+Q^2_{m_X})(1+Q^2_{m_X-1})}$	$\frac{1}{2}\{2\omega_X+R_{m_X-1}+R_{m_X}\}$
$A_{1/2,-1/2}B_{1/2,1/2}X_{I_X,m_X} \to A_{1/2,1/2}B_{1/2,-1/2}X_{I_X,m_X-1}$	$\frac{g_{I_X}(I_X+m_X)(I_X-m_X+1)(Q_{m_X}-Q_{m_X-1})^2}{(1+Q^2_{m_X})(1+Q^2_{m_X-1})}$	$\frac{1}{2}\{2\omega_X-R_{m_X-1}-R_{m_X}\}$

is D_3 and its symmetry elements (operators) are as follows:

E = the identity operator,
A, B, C = reflections in the planes passing through the three vertices and perpendicular to the sides opposite these vertices,
D = in the plane rotation by 120°, and
F = in the plane rotation by −120°.

Operating on the eight spin functions with the group elements one obtains the results given in table 29. (The abbreviations for the spin functions are those given in table 2.) From table 29 a matrix can be defined for each of the group elements. This matrix representation is reducible (47, 94), and its reduction can be expressed in terms of the irreducible representations of D_3. To do this, one requires the characters (i.e., the diagonal sums) of the group operators which are obtained from the formula

$$\chi(\mathrm{R}) = \sum_i \langle u_i|\mathrm{R}|u_i\rangle;\ \mathrm{R} = \mathrm{E}, \mathrm{A}, \cdots \tag{1}$$

From equation 1 and table 29 one obtains

$$\chi(\mathrm{E}) = 8;\ \chi(\mathrm{A}) = \chi(\mathrm{B}) = \chi(\mathrm{C}) = 4;\ \chi(\mathrm{D}) = \chi(\mathrm{F}) = 2$$

The characters of the irreducible representations of D_3 are given in table 30 (94), and the reduction of the product function representation is determined by the equation (47, 94)

$$n^{(\gamma)} = \frac{1}{g}\sum_{\mathrm{R}} \chi^{(\gamma)}(\mathrm{R})\chi(\mathrm{R}) \tag{2}$$

TABLE 29

Transformation properties of product spin functions for three spin 1/2 nuclei under the D_3 point group

	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8
E..............	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8
A..............	u_1	u_3	u_2	u_4	u_5	u_7	u_6	u_8
B..............	u_1	u_4	u_3	u_2	u_7	u_6	u_5	u_8
C..............	u_1	u_2	u_4	u_3	u_6	u_5	u_7	u_8
D..............	u_1	u_3	u_4	u_2	u_7	u_5	u_6	u_8
F..............	u_1	u_4	u_2	u_3	u_6	u_7	u_5	u_8

TABLE 30

Character table for the point group D_3

D_3	E	A	B	C	D	F
$\mathcal{A}_1$..........	1	1	1	1	1	1
$\mathcal{A}_2$..........	1	−1	−1	−1	1	1
$\mathcal{E}$..........	2	0	0	0	−1	−1

where $n^{(\gamma)}$ is the number of times the representation γ occurs, $\chi^{(\gamma)}(\mathrm{R})$ is the character of R in the (irreducible) representation γ, and g is the number of symmetry elements in the group. From the characters in the product representation and table 30 one finds

$$n^{(\mathcal{A}_1)} = \frac{1}{6}\{8 + 4 + 4 + 4 + 2 + 2\} = 4$$

$$n^{(\mathcal{A}_2)} = \frac{1}{6}\{8 - 4 - 4 - 4 + 2 + 2\} = 0$$

$$n^{(\mathcal{E})} = \frac{1}{6}\{16 - 2 - 2\} = 2$$

that is, the product representation, Γ, contains $\mathcal{A}_1$ four times and $\mathcal{E}$ twice. The reduction of a representation is often expressed in equation form as

$$\Gamma = \sum_{\gamma} n^{(\gamma)}\gamma \tag{3}$$

which, in the present case, is

$$\Gamma = 4\mathcal{A}_1 + 2\mathcal{E} \tag{4}$$

It should be noted that if d_γ is the dimension of γ, then

$$\sum_{\gamma} n^{(\gamma)}d_\gamma = \prod_{i}(2I_i + 1) \tag{5}$$

For the case under consideration this is easily checked, since $4 \times 1 + 2 \times 2 = (2\cdot\frac{1}{2} + 1)^3 = 8$.

The spin functions with the $\mathcal{A}_1$ and $\mathcal{E}$ symmetries are easily determined with the projection operator (47):

$$\eta_\gamma = \sum_{\mathrm{R}} \chi^{(\gamma)}(\mathrm{R})\mathrm{R} \tag{6}$$

The operator η_γ acting on a set of spin functions extracts sets of linear combinations with the symmetry of γ. Consider the operator

$$\eta_{\mathcal{A}_1} = \mathrm{E} + \mathrm{A} + \mathrm{B} + \mathrm{C} + \mathrm{D} + \mathrm{F} \tag{7}$$

Operating on the u_i with $\eta_{\mathcal{A}_1}$ one finds (omitting multiplicative factors) the following linear combinations:

$$\left.\begin{array}{l} u_1 \\ u_2 + u_3 + u_4 \\ u_5 + u_6 + u_7 \\ u_8 \end{array}\right\} \tag{8}$$

It is readily verified that these functions are symmetric with respect to all of the group operators. Similarly, the projection operator

$$\eta_{\mathcal{E}} = 2\mathrm{E} - \mathrm{D} - \mathrm{F} \tag{9}$$

yields the six functions:

$$\begin{array}{l} 2u_2 - u_3 - u_4 \\ 2u_3 - u_4 - u_2 \\ 2u_4 - u_2 - u_3 \\ 2u_5 - u_6 - u_7 \\ 2u_6 - u_5 - u_7 \\ 2u_7 - u_5 - u_6 \end{array}$$

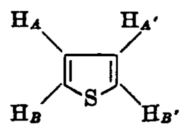
However, equation 4 states that only four functions "belong" to the symmetry species $\mathcal{E}$, so that the above functions are linearly dependent. By inspection, it is easily seen that the first three functions sum to zero and one may take any pair (or two linear combinations of any pair) as two of the functions with $\mathcal{E}$ symmetry. Similarly, the last three sum to zero and any pair of these may be taken for the remaining two $\mathcal{E}$ functions.

Since the three nuclei are equivalent, one could also require that the symmetrized functions be eigenfunctions of $\mathbf{I}^2$. This simply leads to the usual eigenvalue problem which, when solved, yields the (normalized) functions in table 4. In general, the 2^n spin functions which are eigenfunctions of I_z and $\mathbf{I}^2$ must also transform according to the symmetry species of D_n. The functions in table 5 ($n = 4$) were derived by this procedure and it will be found useful to carry out the detailed calculations.

Before considering a symmetrical spin system, it should be noted that the point groups required in nuclear magnetic resonance spectroscopy are usually simpler than those required for the same molecule in other connections. For example, the correct group for the normal vibrational modes of three equivalent nuclei is D_{3h}. In the nuclear magnetic resonance case only the equilibrium positions of the nuclei are really pertinent and the correct group is D_3. Strictly speaking, it would not be incorrect to use D_{3h}, but this group has twice the number of elements in D_3 and the calculations would be unnecessarily elaborate.

B. A FOUR-SPIN SYSTEM WITH C_2 SYMMETRY

Molecules whose equilibrium configurations have a twofold symmetry axis are described (for purposes of nuclear magnetic resonance) by the C_2 point group. Examples of such molecules are 1,1-difluoroethylene (53), thiophene (19b), furan, pyridine (84), o-dichlorobenzene (7, 63), etc. Consider the case of four spins, none of which lie on the C_2 axis. Using thiophene as a prototype system one has, by symmetry,



$$\begin{array}{l} \omega_A = \omega_{A'} \\ \omega_B = \omega_{B'} \\ J_{AB} = J_{A'B'} \equiv J \\ J_{AB'} = J_{A'B} \equiv J' \end{array} \tag{10}$$

From equations 10 the Hamiltonian operator is

$$
\begin{aligned}
\mathcal{H} = -\Big\{ & \omega_A(I_{Az} + I_{A'z}) + \omega_B(I_{Bz} + I_{B'z}) \\
& + J(I_{A'z}I_{B'z} + I_{Az}I_{Bz}) + J'(I_{A'z}I_{Bz} + I_{Az}I_{B'z}) \\
& + J_A I_{Az}I_{A'z} + J_B I_{Bz}I_{B'z} + \frac{1}{2}(J_A I_A^- + J' I_B^- + J I_{B'}^-)I_{A'}^+ \\
& + \frac{1}{2}(J I_B^- + J' I_{B'}^-)I_A^+ + \frac{1}{2}(J_A I_A^+ + J' I_B^+ + J I_{B'}^+)I_{A'}^- \\
& \quad + \frac{1}{2}(J I_B^+ + J' I_{B'}^+)I_A^- + \frac{1}{2}J_B(I_B^+ I_{B'}^- + I_B^- I_{B'}^+)\Big\} \qquad (11)
\end{aligned}
$$

where $J_A \equiv J_{AA'}$ and $J_B \equiv J_{BB'}$.

TABLE 31*

Symmetrized zero-order spin functions for four spin 1/2 nuclei with C_2 symmetry

Spin Functions	Symmetry
$\alpha\alpha\alpha\alpha$	$(\mathcal{A})_2$
$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha)$	$1(\mathcal{A})_1$
$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)$	$2(\mathcal{A})_1$
$\alpha\alpha\beta\beta$	$1(\mathcal{A})_0$
$\frac{1}{2}(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\beta\alpha + \beta\alpha\alpha\beta)$	$2(\mathcal{A})_0$
$\beta\beta\alpha\alpha$	$3(\mathcal{A})_0$
$\frac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta)$	$4(\mathcal{A})_0$
$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta + \beta\alpha\beta\beta)$	$1(\mathcal{A})_{-1}$
$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta + \beta\beta\beta\alpha)$	$2(\mathcal{A})_{-1}$
$\beta\beta\beta\beta$	$(\mathcal{A})_{-2}$
$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)$	$1(\mathcal{B})_1$
$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	$2(\mathcal{B})_1$
$\frac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha + \beta\alpha\alpha\beta)$	$1(\mathcal{B})_0$
$\frac{1}{2}(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \beta\alpha\alpha\beta)$	$2(\mathcal{B})_0$
$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta - \beta\alpha\beta\beta)$	$1(\mathcal{B})_{-1}$
$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta - \beta\beta\beta\alpha)$	$2(\mathcal{B})_{-1}$

* The product functions are ordered according to the scheme $A'ABB'$.

The symmetrized spin functions are derived as above. The group C_2 has only two elements E and C_2 and there are only two irreducible representations (94), $\mathcal{A}$ and $\mathcal{B}$. The required characters are

$$
\begin{aligned}
\chi_{\mathcal{A}}(\mathrm{E}) &= 1 \qquad \chi_{\mathcal{A}}(\mathrm{C}_2) = 1 \\
\chi_{\mathcal{B}}(\mathrm{E}) &= 1 \qquad \chi_{\mathcal{B}}(\mathrm{C}_2) = -1
\end{aligned} \qquad (12)
$$

and the projection operators are

$$
\begin{aligned}
\eta_{\mathcal{A}} &= \mathrm{E} + \mathrm{C}_2 \\
\eta_{\mathcal{B}} &= \mathrm{E} - \mathrm{C}_2
\end{aligned} \qquad (13)
$$

Upon calculating the characters for the product function representation, one finds that

$$\Gamma = 10\mathcal{A} + 6\mathcal{B} \qquad (14)$$

that is, ten of the symmetrized functions belong to the symmetric representation and six belong to the antisymmetric representation. The projection operators may be used to determine the functions explicitly and a symmetrized set is given in table 31. This set is not unique since, in a given representation, one may construct linear combinations of spin functions which also belong to the same symmetry species. The subscripts affixed to the symmetry species in table 31 give the m-values, and it is at once evident from these m-values that the Hamiltonian matrix factors into one 4×4 ($\mathcal{A}$ species), five 2×2 (two from $\mathcal{A}$, three from $\mathcal{B}$), and two 1×1 ($\mathcal{A}$) submatrices. The 4×4 submatrix is

$$
\begin{pmatrix}
\left\{-\delta + \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B)\right\} & -\frac{1}{2}(J + J') & 0 & -\frac{1}{2}(J - J') \\
-\frac{1}{2}(J + J') & -\frac{1}{4}(J_A + J_B) & -\frac{1}{2}(J + J') & \frac{1}{2}(J - J') \\
0 & -\frac{1}{2}(J + J') & \left\{\delta + \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B)\right\} & -\frac{1}{2}(J - J') \\
-\frac{1}{2}(J - J') & \frac{1}{2}(J - J') & -\frac{1}{2}(J - J') & \frac{3}{4}(J_A + J_B)
\end{pmatrix}
$$

As before, let Ω_1, Ω_2, Ω_3, and Ω_4 be the eigenvalues and $\mathbf{a} = (a_{kj})$ be the diagonalizing orthogonal matrix. The eigenvalues are such that

$$
\begin{aligned}
\Omega_1 &\to -\delta + \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B) \\
\Omega_2 &\to -\frac{1}{4}(J_A + J_B) \\
\Omega_3 &\to \delta + \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B) \\
\Omega_4 &\to \frac{3}{4}(J_A + J_B)
\end{aligned}
$$

as the off-diagonal elements of $\mathcal{H} \to 0$. The remaining eigenvalues and eigenfunctions require the solution of elementary equations and the results are given in table 32, where

$$
\begin{aligned}
\delta &= \omega_A - \omega_B > 0 \\
R_1 &= \sqrt{(\delta + J_A - J_B)^2 + (J - J')^2} \\
R_2 &= \sqrt{(J_A - J_B)^2 + (J - J')^2} \\
R_3 &= \sqrt{(\delta - J_A + J_B)^2 + (J - J')^2} \\
R_4 &= \sqrt{\delta^2 + (J + J')^2}
\end{aligned}
$$

TABLE 32

Eigenvalues and eigenfunctions for four spin 1/2 nuclei with C_2 symmetry

Eigenfunction	Eigenvalue
$(\mathcal{A})_2$	$-\{\omega_A + \omega_B + \frac{1}{2}(J + J') + \frac{1}{4}(J_A + J_B)\}$
$\frac{1}{\sqrt{1 + Q_4^2}}\{1(\mathcal{A})_1 + Q_4[2(\mathcal{A})_1]\}$	$-\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A + J_B) + R_4\}$
$\frac{1}{\sqrt{1 + Q_4^2}}\{Q_4[1(\mathcal{A})_1] - 2(\mathcal{A})_1\}$	$-\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A + J_B) - R_4\}$
$a_{11}[1(\mathcal{A})_0] + a_{21}[2(\mathcal{A})_0] + a_{31}[3(\mathcal{A})_0] + a_{41}[4(\mathcal{A})_0]$	Ω_1
$a_{12}[1(\mathcal{A})_0] + a_{22}[2(\mathcal{A})_0] + a_{32}[3(\mathcal{A})_0] + a_{42}[4(\mathcal{A})_0]$	Ω_2
$a_{13}[1(\mathcal{A})_0] + a_{23}[2(\mathcal{A})_0] + a_{33}[3(\mathcal{A})_0] + a_{43}[4(\mathcal{A})_0]$	Ω_3
$a_{14}[1(\mathcal{A})_0] + a_{24}[2(\mathcal{A})_0] + a_{34}[3(\mathcal{A})_0] + a_{44}[4(\mathcal{A})_0]$	Ω_4
$\frac{1}{\sqrt{1 + Q_4^2}}\{1(\mathcal{A})_{-1} + Q_4[2(\mathcal{A})_{-1}]\}$	$\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A + J_B) - R_4\}$
$\frac{1}{\sqrt{1 + Q_4^2}}\{Q_4[1(\mathcal{A})_{-1}] - 2(\mathcal{A})_{-1}\}$	$\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A + J_B) + R_4\}$
$(\mathcal{A})_{-2}$	$\omega_A + \omega_B - \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B)$
$\frac{1}{\sqrt{1 + Q_1^2}}\{1(\mathcal{B})_1 + Q_1[2(\mathcal{B})_1]\}$	$-\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A + J_B) + R_1\}$
$\frac{1}{\sqrt{1 + Q_1^2}}\{Q_1[1(\mathcal{B})_1] - 2(\mathcal{B})_1\}$	$-\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A + J_B) - R_1\}$
$\frac{1}{\sqrt{1 + Q_2^2}}\{1(\mathcal{B})_0 + Q_2[2(\mathcal{B})_0]\}$	$\frac{1}{2}\{\frac{1}{2}(J_A + J_B) - R_2\}$
$\frac{1}{\sqrt{1 + Q_2^2}}\{Q_2[1(\mathcal{B})_0] - 2(\mathcal{B})_0\}$	$\frac{1}{2}\{\frac{1}{2}(J_A + J_B) + R_2\}$
$\frac{1}{\sqrt{1 + Q_3^2}}\{1(\mathcal{B})_{-1} + Q_3[2(\mathcal{B})_{-1}]\}$	$\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A + J_B) - R_3\}$
$\frac{1}{\sqrt{1 + Q_3^2}}\{Q_3[1(\mathcal{B})_{-1}] - 2(\mathcal{B})_{-1}\}$	$\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A + J_B) + R_3\}$

$$Q_1 = \frac{J' - J}{\delta + J_A - J_B + R_1}$$

$$Q_2 = \frac{J' - J}{(J_A - J_B) + R_2}$$

$$Q_3 = \frac{J' - J}{\delta - J_A + J_B + R_3}$$

$$Q_4 = \frac{J + J'}{\delta + R_4}$$

The resonance frequencies and relative intensities are given in table 33. Since the spectrum is symmetrical about $\frac{1}{2}(\omega_A + \omega_B)$ only fourteen of the twenty-eight possible lines are given. (The $\mathcal{A}$ and $\mathcal{B}$ transitions in these tables refer, of course, to symmetry species, *not groups* of equivalent nuclei.)

From table 33 it is clear that the transitions 1, 2, and their images constitute a quartet which is similar to the AB spectrum except that J is replaced by $J + J'$. Hence if these lines can be identified, one may obtain δ and $|J + J'|$ exactly. The symmetrical nature of the spectrum may make the identification of these lines difficult and if $\delta \simeq 0$, the identification may be impossible. There are, however, eight $\mathcal{B}$ transitions involving R_1, R_2, R_3, Q_1, Q_2, and Q_3 whose intensities and frequencies are expressed in closed form and additional information may be obtainable. In general, it is best to "guess" a set of parameters and test them with the twelve explicitly known $\mathcal{A}$ and $\mathcal{B}$ lines, using the experimental data. If the fit is reasonable, the parameters can be used to diagonalize the 4 × 4 matrix and be checked in detail. If computers are available, the problem of fitting a spectrum is almost trivial.

In the special case where $J = J'$,

$$\Omega_4 = \frac{1}{2}(J_A + J_B)$$

and the system reduces to the A_2B_2 system already considered. Further, for J_A, J_B, $J' \rightarrow 0$, the system reduces to the superposition of two independent AB spin systems. Another special case of interest occurs

TABLE 33

Resonance frequencies and relative intensities for four spin 1/2 nuclei with C_2 symmetry

Transition in the Limit as All $J_{ij} \to 0$	Intensity	Frequency
$\mathcal{A}$ transitions		
1. $1(\mathcal{A})_{-1} \to (\mathcal{A})_{-2}$	$\frac{2(1+Q_4)^2}{1+Q_4^2}$	$\frac{1}{2}\{\omega_A + \omega_B - (J+J') + R_4\}$
2. $(\mathcal{A})_2 \to 2(\mathcal{A})_1$	$\frac{2(1-Q_4)^2}{1+Q_4^2}$	$\frac{1}{2}\{\omega_A + \omega_B + (J+J') + R_4\}$
3. $1(\mathcal{A})_0 \to 1(\mathcal{A})_{-1}$	$\frac{2}{1+Q_4^2}[a_{11} + (1+Q_4)a_{21} + Q_4a_{31}]^2$	$\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A+J_B) - R_4 - 2\Omega_1\}$
4. $1(\mathcal{A})_1 \to 2(\mathcal{A})_0$	$\frac{2}{1+Q_4^2}[a_{12} + (1+Q_4)a_{22} + Q_4a_{32}]^2$	$\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A+J_B) + R_4 + 2\Omega_2\}$
5. $1(\mathcal{A})_1 \to 3(\mathcal{A})_0$	$\frac{2}{1+Q_4^2}[a_{13} + (1+Q_4)a_{23} + Q_4a_{33}]^2$	$\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A+J_B) + R_4 + 2\Omega_3\}$
6. $1(\mathcal{A})_1 \to 4(\mathcal{A})_0$	$\frac{2}{1+Q_4^2}[a_{14} + (1+Q_4)a_{24} + Q_4a_{34}]^2$	$\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A+J_B) + R_4 + 2\Omega_4\}$
7. $1(\mathcal{A})_0 \to 2(\mathcal{A})_{-1}$	$\frac{2}{1+Q_4^2}[Q_4a_{11} + (Q_4-1)a_{21} - a_{31}]^2$	$\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A+J_B) + R_4 - 2\Omega_1\}$
8. $2(\mathcal{A})_0 \to 2(\mathcal{A})_{-1}$	$\frac{2}{1+Q_4^2}[Q_4a_{12} + (Q_4-1)a_{22} - a_{32}]^2$	$\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A+J_B) + R_4 - 2\Omega_2\}$
9. $2(\mathcal{A})_1 \to 3(\mathcal{A})_0$	$\frac{2}{1+Q_4^2}[Q_4a_{13} + (Q_4-1)a_{23} - a_{33}]^2$	$\frac{1}{2}\{\omega_A + \omega_B + \frac{1}{2}(J_A+J_B) - R_4 + 2\Omega_3\}$
10. $4(\mathcal{A})_0 \to 2(\mathcal{A})_{-1}$	$\frac{2}{1+Q_4^2}[Q_4a_{14} + (Q_4-1)a_{24} - a_{34}]^2$	$\frac{1}{2}\{\omega_A + \omega_B - \frac{1}{2}(J_A+J_B) + R_4 - 2\Omega_4\}$
$\mathcal{B}$ transitions		
11. $1(\mathcal{B})_1 \to 1(\mathcal{B})_0$	$\frac{2(1+Q_1Q_2)^2}{(1+Q_1^2)(1+Q_2^2)}$	$\frac{1}{2}\{\omega_A + \omega_B + R_1 - R_2\}$
12. $1(\mathcal{B})_1 \to 2(\mathcal{B})_0$	$\frac{2(Q_2-Q_1)^2}{(1+Q_1^2)(1+Q_2^2)}$	$\frac{1}{2}\{\omega_A + \omega_B + R_1 + R_2\}$
13. $2(\mathcal{B})_0 \to 2(\mathcal{B})_{-1}$	$\frac{2(Q_2+Q_3)^2}{(1+Q_2^2)(1+Q_3^2)}$	$\frac{1}{2}\{\omega_A + \omega_B + R_3 - R_2\}$
14. $1(\mathcal{B})_0 \to 2(\mathcal{B})_{-1}$	$\frac{2(1-Q_2Q_3)^2}{(1+Q_2^2)(1+Q_3^2)}$	$\frac{1}{2}\{\omega_A + \omega_B + R_3 + R_2\}$

when $\delta \to \infty$ as, for example, with 1,1-difluoroethylene (53). In this case, the only mixing of zero-order spin functions occurs between $2(\mathcal{A})_0$ and $4(\mathcal{A})_0$, and $1(\mathcal{B})_0$ and $2(\mathcal{B})_0$. The 4×4 factors into two 1×1 and one 2×2 submatrices and one finds the eigenvalues:

$$\Omega_1 = -\delta + \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B)$$

$$\Omega_2 = \frac{1}{4}(J_A + J_B) - \frac{1}{2}R_5$$

$$\Omega_3 = \delta + \frac{1}{2}(J + J') - \frac{1}{4}(J_A + J_B)$$

$$\Omega^4 = \frac{1}{4}(J_A + J_B) + \frac{1}{2}R_5$$

The corresponding eigenfunctions are

$1(\mathcal{A})_0$

$$\frac{1}{\sqrt{1+Q_5^2}}\{2(\mathcal{A})_0 + Q_5[4(\mathcal{A})_0]\}$$

$3(\mathcal{A})_0$

$$\frac{1}{\sqrt{1+Q_5^2}}\{Q_5[2(\mathcal{A})_0] - 4(\mathcal{A})_0\}$$

where

$$R_5 = \sqrt{(J_A + J_B)^2 + (J - J')^2}$$

$$Q_5 = \frac{J' - J}{J_A + J_B + R_5}$$

TABLE 34

Resonance frequencies and relative intensities for four spin 1/2 nuclei with C_2 symmetry as $\delta \rightarrow \infty$

Transition in the Limit as All $J_{ij} \rightarrow 0$	Intensity	Frequency
	$\mathcal{A}$ transitions	
1. $1(\mathcal{A})_{-1} \rightarrow (\mathcal{A})_{-2}$ $1(\mathcal{A})_0 \rightarrow 1(\mathcal{A})_{-1}$	4	$\frac{1}{2}\{2\omega_A - (J + J')\}$
2. $(\mathcal{A})_2 \rightarrow 2(\mathcal{A})_1$ $2(\mathcal{A})_1 \rightarrow 3(\mathcal{A})_0$	4	$\frac{1}{2}\{2\omega_A + (J + J')\}$
3. $1(\mathcal{A})_1 \rightarrow 2(\mathcal{A})_0$..........	$\frac{2}{1 + Q_5^2}$	$\frac{1}{2}\{2\omega_A + J_A + J_B - R_5\}$
4. $1(\mathcal{A})_1 \rightarrow 4(\mathcal{A})_0$..........	$\frac{2Q_5^2}{1 + Q_5^2}$	$\frac{1}{2}\{2\omega_A + J_A + J_B + R_5\}$
5. $2(\mathcal{A})_0 \rightarrow 2(\mathcal{A})_{-1}$.........	$\frac{2}{1 + Q_5^2}$	$\frac{1}{2}\{2\omega_A - (J_A + J_B) + R_5\}$
6. $4(\mathcal{A})_0 \rightarrow 2(\mathcal{A})_{-1}$.........	$\frac{2Q_5^2}{1 + Q_5^2}$	$\frac{1}{2}\{2\omega_A - (J_A + J_B) - R_5\}$
7. $1(\mathcal{A})_0 \rightarrow 2(\mathcal{A})_{-1}$.........	0	$\frac{1}{2}\{4\omega_A - 2\omega_B - J - J'\}$
8. $1(\mathcal{A})_1 \rightarrow 3(\mathcal{A})_0$..........	0	$\frac{1}{2}\{4\omega_A - 2\omega_B + J + J'\}$
	$\mathcal{B}$ transitions	
9. $1(\mathcal{B})_1 \rightarrow 1(\mathcal{B})_0$.........	$\frac{2}{1 + Q_2^2}$	$\frac{1}{2}\{2\omega_A + J_A - J_B - R_2\}$
10. $1(\mathcal{B})_1 \rightarrow 2(\mathcal{B})_0$.........	$\frac{2Q_2^2}{1 + Q_2^2}$	$\frac{1}{2}\{2\omega_A + J_A - J_B + R_2\}$
11. $2(\mathcal{B})_0 \rightarrow 2(\mathcal{B})_{-1}$........	$\frac{2Q_2^2}{1 + Q_2^2}$	$\frac{1}{2}\{2\omega_A - J_A + J_B - R_2\}$
12. $1(\mathcal{B})_0 \rightarrow 2(\mathcal{B})_{-1}$........	$\frac{2}{1 + Q_2^2}$	$\frac{1}{2}\{2\omega_A - J_A + J_B + R_2\}$

With these results, one finds the intensities and frequencies given in table 34.

C. GROUPS OF SYMMETRICALLY EQUIVALENT NUCLEI

Inspection of table 31 shows that the symmetrized spin functions for four spins with C_2 symmetry consist of all possible products (i.e., the direct product) of the singlet and triplet functions for the A nuclei with the singlet and triplet functions for the B nuclei. Further, the symmetry species of these products are given by the rules $\mathcal{A} \times \mathcal{A} = \mathcal{A}$, $\mathcal{A} \times \mathcal{B} = \mathcal{B}$, $\mathcal{B} \times \mathcal{B} = \mathcal{A}$. These results can be generalized and lead to the concept of groups of symmetrically equivalent nuclei (94); that is, a set of nuclei which are permuted under the operations of the appropriate point group. If the molecule can be divided into a number of such sets, then the spin functions for the molecule may be obtained by taking the direct products of the (symmetrized) functions for the various sets. The symmetry species of the molecular product functions may then be derived by standard rules (94). For example, 1,3,5-trifluorobenzene (94) may be considered as two sets of symmetrically equivalent nuclei: three protons with D_3 symmetry and three fluorine nuclei with D_3 symmetry. Thus, one has a systematic procedure for dealing with molecules of high symmetry. Since this procedure involves little that is essentially new, it will not be discussed further here. For full discussion and illustrations the reader is referred to the literature (57, 94).

IX. MOMENT ANALYSIS OF HIGH-RESOLUTION SPECTRA

The preceding calculations have been characterized by the fact that chemical shifts and coupling constants are obtained after the complete (or approximate) diagonalization of the Hamiltonian matrix. This procedure may require lengthy numerical computations—even in simple cases—and it is natural to seek more direct methods of analysis. Some simple rules, which can lead directly to coupling constants and chemical shifts in favorable cases, have already been discussed. There are, however, more general techniques (7, 70) and in this section moment calculations (7) will be discussed. This technique is, in principle, perfectly general, but practical considerations often impose severe restrictions and the method is of limited value. However, when the method is applicable, significant information is obtained which can lead to a complete solution of some problems or facilitate the solution of others.

The n^{th} moment of a spectrum is defined as

$$<\omega^n> = \frac{\sum_j \sum_k (\Omega_k - \Omega_j)^n |I_{kj}^-|^2}{\sum_j \sum_k |I_{jk}^-|^2} \qquad (1)$$

where $\Omega_k - \Omega_j$ is the resonance frequency associated with the transition $\psi_j \rightarrow \psi_k$ and $|I_{kj}^-|^2$ the corresponding relative intensity. $<\omega^n>$ is thus a weighting of each resonance line according to intensity; $<\omega>$ is the mean frequency of the spectrum, $<\omega^2>$ is the mean square frequency, etc. The denominator in equation 1 is the sum of the (relative) intensities of all resonances and can be rewritten in an alternative form as follows:

$$|I_{jk}^-|^2 = (I_{jk}^-)(I_{jk}^-)^* = (I_{jk}^-)\sum_{r=1}^{N}(I_{xr} - iI_{yr})_{jk}^* = I_{jk}^- I_{kj}^+$$

where N is the total number of number of nuclei and the Hermitian property for I_{xr} and I_{yr} has been used. Summing this result over j and k gives

$$\sum_k \sum_j |I_{jk}^-|^2 = \sum_k \sum_j I_{jk}^- I_{kj}^+ = \mathrm{Tr}\, I^- I^+ = \mathrm{Tr}\, I^+ I^-$$

where Tr denotes the diagonal sum or trace of the matrix product $I^- I^+$. Now $\Omega_k = \mathcal{H}_{kk}$ and $\Omega_j = \mathcal{H}_{jj}$, so that the numerator of equation 1 can be expressed as

$$\sum_k \sum_j (\mathcal{H}_{kk} - \mathcal{H}_{jj})^n I_{jk}^- I_{kj}^+$$

and

$$<\omega^n> = \frac{\sum_{k,j}(\mathcal{H}_{kk} - \mathcal{H}_{jj})^n I^-_{jk} I^+_{kj}}{\text{Tr } I^+I^-} \tag{2}$$

For $n = 1$,

$$\begin{aligned} <\omega> &= \frac{\sum_{k,j}(\mathcal{H}_{kk} - \mathcal{H}_{jj}) I^-_{jk} I^+_{kj}}{\text{Tr } I^+I^-} \\ &= \frac{\sum_{k,j}(\mathcal{H}_{kk} I^+_{kj} - I^+_{kj}\mathcal{H}_{jj}) I^-_{jk}}{\text{Tr } I^+I^-} \\ &= \frac{\sum_{k,j}[\mathcal{H}, I^+]_{kj} I^-_{jk}}{\text{Tr } I^+I^-} \\ &= \frac{\text{Tr}[\mathcal{H}, I^+]I^-}{\text{Tr } I^+I^-} \end{aligned} \tag{3}$$

Similarly, one can show that

$$<\omega^2> = \frac{\text{Tr}[\mathcal{H}, I^+][I^-, \mathcal{H}]}{\text{Tr } I^+I^-} \tag{4}$$

$$<\omega^3> = \frac{\text{Tr}[\mathcal{H}, [\mathcal{H}, I^+]][I^-, \mathcal{H}]}{\text{Tr } I^+I^-} \tag{5}$$

$$<\omega^4> = \frac{\text{Tr}[\mathcal{H}, [\mathcal{H}, I^+]][[I^-, \mathcal{H}], \mathcal{H}]}{\text{Tr } I^+I^-} \tag{6}$$

The rules of formation are now clear and the commutator form for $<\omega^n>$ can be written down immediately.

The distinguishing feature of these moment equations is that they are expressed in terms of traces of matrices and, since the trace is a matrix invariant, it is not necessary to solve a complicated eigenvalue problem in order to evaluate the moments; *any* convenient representation of the matrices involved will suffice. Consider, for example, the denominator Tr I^+I^-; expanding the product of I^+I^- one finds:

$$\begin{aligned} \text{Tr } I^+I^- &= \text{Tr}\Big(\sum_r I_{xr} + iI_{yr}\Big)\Big(\sum_s I_{xs} - iI_{ys}\Big) \\ &= \text{Tr}\Big\{\sum_r\sum_s I_{xr}I_{xs} + I_{yr}I_{ys} + i(I_{yr}I_{xs} - I_{xr}I_{ys})\Big\} \end{aligned} \tag{7}$$

Now in a matrix product of the type $I_{xr}I_{xs}$ $(r \neq s)$ both operators cannot make simultaneous contributions to the diagonal elements, since the spins are independent. These traces may be computed independently and, since Tr I_{xr} = Tr I_{yr} = Tr $I_{zr} = 0$, equation 7 reduces to

$$\begin{aligned} \text{Tr } I^+I^- &= \text{Tr} \sum_r (I^2_{xr} + I^2_{yr}) \\ &= 2\text{Tr} \sum_r I^2_{zr} \end{aligned} \tag{8}$$

The last equality in equation 8 results from the equivalence of the x-, y-, and z-components of angular momentum. The assumption that all nuclei have the same spin quantum number I simplifies equation 8 to

$$2N \text{ Tr } I^2_{zr} \tag{9}$$

In the product function representation, the matrix for I^2_{zr} is diagonal and may be expressed as the direct product of two matrices, one involving the coördinates of nucleus r alone and an identity matrix of dimension $(2I + 1)^{N-1}$. For a direct product $C = A \times B$ one has the result

$$\text{Tr } C = (\text{Tr } A)(\text{Tr } B) \tag{10}$$

Further, Tr I^2_{zr} over the coördinates of r alone is simply

$$\text{Tr } I^2_{zr} = \sum_{-I}^{+I} m^2_{zr} = \frac{1}{3}I(I + 1)(2I + 1) \tag{11}$$

Combining equations 9, 10, and 11 there results finally

$$\text{Tr } I^+I^- = \frac{2N}{3}I(I + 1)(2I + 1)^N \tag{12}$$

To proceed further, one must specify $\mathcal{H}$ and evaluate the required commutators and traces. For $\mathcal{H}$ one may use

$$\mathcal{H} = \sum_j \omega_j I_{zj} + \sum_{j<}\sum_k J_{jk}\mathbf{I}_j\cdot\mathbf{I}_k \tag{13}$$

(The minus sign that is usually prefixed to $\mathcal{H}$ is omitted here for convenience; this omission simply inverts the energy levels and does not alter the moments in any way.) From the commutation rules the following equations are readily verified:

$$[\mathcal{H}, I^+] = \sum_j \omega_j I^+_j \tag{14}$$

$$[I^-, \mathcal{H}] = \sum_j \omega_j I^-_j \tag{15}$$

$$[\mathcal{H}, [\mathcal{H}, I^+]] = \sum_j \omega^2_j I^+_j + \sum_j\sum_k J_{jk}(\omega_j - \omega_k) I^+_j I_{zk} \tag{16}$$

$$[[I^-, \mathcal{H}], \mathcal{H}] = \sum_j \omega^2_j I^-_j + \sum_j\sum_k J_{jk}(\omega_j - \omega_k) I^-_j I_{zk} \tag{17}$$

The evaluation of the requisite traces is straightforward and one obtains for the first four moments:

$$\sum_j \omega_j = N<\omega> \tag{18}$$

$$\sum_j \omega^2_j = N<\omega^2> \tag{19}$$

$$\sum_j \omega^3_j = N<\omega^3> \tag{20}$$

$$\sum_j \omega^4_j + \frac{1}{3}I(I + 1)(2I + 1)\sum_{j<}\sum_k J^2_{jk}(\omega_j - \omega_k)^2 = N<\omega^4> \tag{21}$$

From these equations, it is clear that the first three moments are independent of the spin quantum number and the coupling constants. The fourth moment (and higher moments) depends upon I and the J's. For the case $I = 1/2$ the fourth moment becomes

$$\sum_j \omega^4_j + \frac{1}{2}\sum_{j<}\sum_k J^2_{jk}(\omega_j - \omega_k)^2 = N<\omega^4> \tag{22}$$

It will be convenient to set $<\omega> = 0$ in subsequent calculations; that is, one evaluates $<\omega>$ from equation 18 and introduces a new reference system at the mean frequency from which all other moments are computed. Chemical shifts relative to this "center of gravity" will be denoted by $\Delta\omega_k$ and the moment equations 18 to 20 and 22 become

$$\sum_j \Delta\omega_j = 0 \tag{23}$$

$$\sum_j (\Delta\omega_j)^2 = N < (\Delta\omega)^2 > \tag{24}$$

$$\sum_j (\Delta\omega_j)^3 = N < (\Delta\omega)^3 > \tag{25}$$

$$\sum_j (\Delta\omega_j)^4 + \frac{1}{2}\sum_{j<}\sum_k J_{jk}^2 (\Delta\omega_j - \Delta\omega_k)^2 = N < (\Delta\omega)^4 > \tag{26}$$

where

$$\Delta\omega_j = \omega_j - <\omega>$$

Some simple cases of equations 23 to 26 will now be considered. If there are only two groups (A and B) of equivalent nuclei, the first four moments are

$$n_A(\Delta\omega_A) + n_B(\Delta\omega_B) = 0 \tag{27}$$

$$n_A(\Delta\omega_A)^2 + n_B(\Delta\omega_B)^2 = N < (\Delta\omega)^2 > \tag{28}$$

$$n_A(\Delta\omega_A)^3 + n_B(\Delta\omega_B)^3 = N < (\Delta\omega)^3 > \tag{29}$$

$$n_A(\Delta\omega_A)^4 + n_B(\Delta\omega_B)^4 + \frac{1}{2}(n_A n_B J^2 \delta^2) = N < (\Delta\omega)^4 > \tag{30}$$

where

$$n_A + n_B = N \tag{31}$$

$$\delta = \Delta\omega_A - \Delta\omega_B \tag{32}$$

From equations 27, 28, and 32 one obtains

$$\delta^2 = \frac{N^2}{n_A n_B} <(\Delta\omega)^2> \tag{33}$$

while equations 27, 28, 32, and 30 yield

$$J^2 = \frac{2}{N^2 < (\Delta\omega)^2 >} \left\{ N < (\Delta\omega)^4 > - \frac{n_A^3 + n_B^3}{n_A n_B} < (\Delta\omega)^2 >^2 \right\} \tag{34}$$

Equations 33 and 34 show that J and δ may be obtained from measurements of $< (\Delta\omega)^2 >$ and $> (\Delta\omega)^4 >$. Dividing equation 34 by equation 32 gives

$$\left(\frac{J}{\delta}\right)^2 = \frac{2n_A n_B}{N^4} \left\{ N \frac{< (\Delta\omega)^4 >}{< (\Delta\omega)^2 >^2} - \frac{(n_A^3 + n_B^3)}{n_A n_B} \right\} \tag{35}$$

so that the J/δ ratio may be obtained without the aid of a frequency measurement.

For the case of three groups, the first three moments provide the equations

$$\left.\begin{aligned} n_A\Delta\omega_A + n_B\Delta\omega_B + n_C\Delta\omega_C &= 0 \\ n_A(\Delta\omega_A)^2 + n_B(\Delta\omega_B)^2 + n_C(\Delta\omega_C)^2 &= N < (\Delta\omega)^2 > \\ n_A(\Delta\omega_A)^3 + n_B(\Delta\omega_B)^3 + n_C(\Delta\omega_C)^3 &= N < (\Delta\omega)^3 > \end{aligned}\right\} \tag{36}$$

Thus if $< (\Delta\omega) >$, $< (\Delta\omega)^2 >$, and $< (\Delta\omega)^3 >$ are measured, equations 36 provide simultaneous equations for the chemical shifts. If the coupling constants are desired by this method, the fourth, fifth, and sixth moments are required. This is not to be recommended in general, as the higher moments are quite sensitive to experimental errors (e.g., field and frequency drifts, saturation, etc.). Equations 36 are most conveniently solved by graphical methods (7). For this purpose, let

$$r = \frac{\Delta\omega_C}{\Delta\omega_B} \tag{37}$$

Then equations 36 become

$$\left.\begin{aligned} n_A\Delta\omega_A + (n_B + rn_C)\Delta\omega_B &= 0 \\ n_A(\Delta\omega_A)^2 + (n_B + r^2 n_C)(\Delta\omega_B)^2 &= N < (\Delta\omega)^2 > \\ n_A(\Delta\omega_A)^3 + (n_B + r^3 n_C)(\Delta\omega_B)^3 &= N < (\Delta\omega)^3 > \end{aligned}\right\} \tag{38}$$

The first of equations 38 gives:

$$\Delta\omega_A = -\frac{(n_B + rn_C)}{n_A}\Delta\omega_B \tag{39}$$

Substituting into the second and third of equations 38 yields:

$$\frac{(n_B + rn_C)^2}{n_A} + (n_B + r^2 n_C)(\Delta\omega_B)^2 = N < (\Delta\omega)^2 > \tag{40}$$

$$-\frac{(n_B + rn_C)^3}{n_A^2} + (n_B + r^3 n_C)(\Delta\omega_B)^3 = N < (\Delta\omega)^3 > \tag{41}$$

Taking the two-thirds power of equation 41 and dividing equation 40 by the result gives:

$$\frac{[(n_B + rn_C)^2 + n_A(n_B + r^2 n_C)]}{[-(n_B + rn_C)^3 + n_A^2(n_B + r^3 n_C)]^{2/3}} = \left(\frac{N}{n_A}\right)^{1/3} \frac{< (\Delta\omega)^2 >}{< (\Delta\omega)^3 >^{2/3}} \tag{42}$$

In equation 42 n_A, n_B, n_C, and N are assumed known, so that by assigning values to r $(-\infty \leq r \leq +\infty)$ values can be computed for the ratio

$$< (\Delta\omega)^2 > / < (\Delta\omega)^3 >^{2/3},$$

and plotted against r. From an experimental value of this ratio one may determine the value(s) of r. The quantity $\Delta\omega_B$ may be obtained from equations 40 and 41 as

$$\Delta\omega_B = \frac{(n_B + rn_C)^2 + n_A(n_B + r^2 n_C)}{-(n_B + rn_C)^3 + n_A^2(n_B + r^3 n_C)} \left\{ \frac{n_A < (\Delta\omega)^3 >}{< (\Delta\omega)^2 >} \right\} \tag{43}$$

Equation 39 then determines $\Delta\omega_A$ and, finally, equation 37 provides $\Delta\omega_C$.

The plot of equation 42 will generally provide several values for r (7) and, consequently, several sets of shifts. Some of these may be ruled out by a comparison with the experimental spectrum; other sets may require additional information for their elimination.

The experimental moments are calculated by means of the equation

$$<\omega^n> = \frac{\Sigma A_i(\omega^i)^n}{\Sigma A_i} \tag{44}$$

where A_i and (ω^i) are, respectively, the area and frequency of the i^{th} resonance. If all the resonances have the same width $\delta\omega$, then line heights may be used in place of the A_i. The widths of resonance lines frequently result in overlapping signals, so that one must decompose such a region into subareas and assign these to the appropriate resonances. This decomposition is somewhat arbitrary and can introduce large errors in the higher moments. Perhaps the most serious difficulty with the moment method is the assumption that all the resonance lines are observed. Hence weak or unresolved lines can lead to very large errors in the experimental moments. It is clear then, that before the moment technique is applied, there must be some consideration of the maximum number of lines, their intensities and frequencies. Ideally, one desires a well-resolved spectrum which is free from field and frequency drifts and saturation effects. Only a modest acquaintance with high-resolution work is required to know that this is almost impossible to realize. Except for the simplest cases, it is best to compromise and use the moment technique to obtain relations among the various parameters.

Equation 35 was applied to the spectrum of ethylene monothiocarbonate (figure 21) with the result $J/\delta = 0.198$, in excellent agreement with the value of 0.195 obtained directly from the spectrum. The use of moments in this particular case is really superfluous, since, as already noted, J and δ may be obtained very easily. The example does show, however, that with well-resolved spectra and with proper regard of instrumental drifts, excellent results may be obtained.

X. MISCELLANEOUS TECHNIQUES

A. DOUBLE RESONANCE EXPERIMENTS

A useful technique for removing the effects of an undesirable spin coupling is available in the double resonance experiment (5, 12, 13). The essential idea in this experiment is to observe the resonance of a particular group with a weak radiofrequency field and simultaneously irradiate a second (coupled) group with a strong radiofrequency field whose frequency is near the resonance value for the second group. In this way, the spins in the second group are constrained to undergo rapid transitions, which reduce the lifetime of states with a given value of m. If this lifetime is much less than J^{-1}, then the observed group is effectively decoupled. Actually, a residual splitting of order J^2/δ remains even for large amplitudes of the second radiofrequency field (12). This qualitative description is analogous to that used in discussions of exchange phenomena (9, 37, 39). An approximate treatment of the double resonance experiment has been given which is valid when $J \ll \delta$. A rigorous discussion requires statistical quantum mechanics (12).

From an experimental point of view, the method is most easily used when $\delta \gg J$. Hence, with one exception (5) the technique is usually applied to nuclei with different gyromagnetic ratios. Even with this restriction, the technique is useful in removing small couplings and line-broadening effects from nuclei such as nitrogen and deuterium.

B. MULTIPLE QUANTUM TRANSITIONS

From equation 95 in Section II it can be seen that the expansion of $[e^{i(\alpha+\beta)t}]_{mm'}$ to the second order in β involves terms of the type

$$\beta_{m'k}\beta_{km} = (\gamma H_1)^2 <m'|I_x|k> \; <k|I_x|m>$$

Terms of this type can result in multiple quantum transitions (6, 41, 95); that is, the spin system can absorb more than one quantum of energy. In the second order this occurs when the system absorbs a single quantum in the state m' and undergoes a transition to a virtual state k; a second quantum of energy is then absorbed which induces a transition to the final state m. In third order, triple quantum transitions can occur, etc. The observation of multiple quantum transitions involves large amplitudes of the radiofrequency field and detailed treatment of intensities requires statistical theory (95). However, if the stationary energies are known, the frequencies of transitions of higher order can be determined. Little has been done with multiple quantum transitions in analyzing high-resolution spectra.

The author wishes to thank Dr. W. A. Anderson, Professor B. P. Dailey, and Drs. C. D. Prater and J. Wei for reading the manuscript and for offering suggestions for its improvement.

The numerical data in the Appendix were computed at the Socony Mobil Oil Company Field Research Laboratory, Dallas, Texas, by Mrs. M. Nunn, Dr. M. Foster, and Mr. O. D. Ferris.

Finally, the author wishes to thank Mr. C. E. Urion for preparing the drawings, Mr. O. M. Epifanio and Mr. F. Heistermann for assisting with the measurements and calculations, and Mrs. A. H. Richman, who typed the entire manuscript.

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XII. INDEX OF SYMBOLS

A, B, C = groups of equivalent nuclei
$\mathcal{A}$ = symmetry species
A_{I_A,m_A}, B_{I_B,m_B} = spin functions for groups A and B with total spins I_A, I_B and z-components of angular momenta m_A, m_B
$\mathbf{A}$; A = Zeeman energy operator; group operator
$\mathcal{B}$ = symmetry species
$\mathbf{B}$; B = spin coupling operator; group operator
$\mathbf{C}$ = spin coupling operator
D = group operator
E = group identity element
$\mathcal{E}$ = symmetry species
F = group operator
G = generic group of equivalent nuclei
G_{I_G,m_G} = generic spin function for group of equivalent nuclei with total spin I_G and z-component of angular momentum m_G
$\mathbf{H}_0$ = applied magnetic field
$\mathbf{H}_i$ = field at nucleus i
$\mathbf{I}$ = spin vector
I_x, I_y, I_z = cartesian components of $\mathbf{I}$
$I^{\pm} = I_x \pm iI_y$ = "raising" (+) and "lowering" (−) operators
$\mathbf{I}^2 = \mathbf{I}\cdot\mathbf{I}$ = square of the spin vector
I_T = total spin quantum number
I_G = total spin quantum number for group G
J = spin-spin coupling constant in circular frequency units
$J_{GG'}$ = spin-spin coupling constant for groups G and G'
N = total number of nuclei, total number of spin functions
P = permutation operator
$P_{jk}(t)$ = probability of transition of state k to state j at time t
P_{jk} = transition probability
R = generic group operator
X, Y, Z = groups of equivalent nuclei with large chemical shifts

a = characteristic spacing for the ABC system
$\mathbf{a} = (a_{ij})$ = diagonalizing orthogonal matrix
b = characteristic spacing for the ABC system
$\mathbf{b} = (b_{ij})$ = diagonalizing orthogonal matrix
c = characteristic spacing for the ABC system
g_{I_G} = statistical weight for the spin function with total spin I_G
h = Planck's constant
$\hbar$ = Planck's constant divided by 2π
i, j, k = i^{th} spin, j^{th} spin, k^{th} spin
i, j, k = summation indices
i = imaginary unit
$m_A, m_B, m_C, \cdots$ = z-components of angular momentum for groups $A, B, C, \cdots$
m_G = generic z-component of angular momentum
$n_A, n_B, n_C, \cdots$ = number of nuclei in groups $A, B, C, \cdots$
n_G = number of nuclei in group G
r, s = summation indices
t = time
u_i = product spin function

α = spin function for spin 1/2 nucleus with $m = +1/2$
β = spin function for spin 1/2 nucleus with $m = -1/2$
γ = gyromagnetic ratio, generic symmetry species
γ = symmetry species
δ = relative internal shift
η_γ = projection operator for symmetry species
θ = Eulerian angle
λ_i = operator which transforms $m_i \rightarrow -m_i$
Λ = operator which transforms $m \rightarrow -m$
$\boldsymbol{\mu}_i$ = magnetic moment of nucleus i
ν = linear frequency
$\boldsymbol{\sigma}_i$ = shielding tensor for nucleus i
σ_i = averaged scalar shielding constant for nucleus i
ϕ, ψ = Eulerian angles
ϕ_i, ψ_i = eigenfunctions for the i^{th} quantum states
$\chi(\text{R})$ = character of the operator R
ω_i = uncoupled angular Larmor frequency for nucleus i
ω_G = uncoupled angular Larmor frequency for group G
ω = angular frequency of radiofrequency field
Ω_i = energy of i^{th} level in angular frequency

XIII. APPENDIX

Numerical tables of the line frequencies and relative intensities for some two-group systems

Tables 35, 36, 37, and 38 provide numerical data on the resonance frequencies and relative intensities for the systems: A_2B, A_3B, A_2B_2, and A_3B_2. All line frequencies are given in units of the relative internal shift $\delta = \omega_A - \omega_B$. The transitions in groups A and B are so labeled, while combination (mixed) transitions are prefixed with the letter "M". In the A_2B_2 case, the spectrum is symmetrical about $\frac{1}{2}(\omega_A + \omega_B)$, so that only one-half of the spectrum is given in the table. The center of symmetry is the frequency origin in this case, while in the other systems the origin is at ω_B(assumed $< \omega_A$). The numbering of the lines corresponds, in each case, to that given in the text. The frequencies and intensities are given as a function of the ratio J/δ, and for $0 \leq J/\delta \leq 1$, the usual interval of interest, the increments in this parameter are 0.05. Additional data are given for $J/\delta = 2, 3, 4, 5, 10$, and ∞.

TABLE 35

Line frequencies and relative intensities for the A_2B spin system

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1....	0.00	2.00000	1.00000	0.05	1.89640	1.02628	0.60	0.72727	1.50000	0.65	0.65603	1.55772
*A*2....		2.00000	1.00000		2.09615	0.97622		2.69169	0.82621		2.71695	0.81882
*A*3....		2.00000	1.00000		2.10361	0.97506		3.26433	0.77379		3.33436	0.76390
*A*4....		2.00000	1.00000		1.90386	1.02494		1.29991	1.22621		1.27345	1.23610
*B*1....		1.00000	0.00000		1.10361	0.04872		2.27273	0.40000		2.34397	0.41728
*B*2....		1.00000	0.00000		0.90386	−0.05122		0.30831	−0.72621		0.28306	−0.79382
*B*3....		1.00000	0.00000		0.99254	−0.00250		0.42737	−0.32621		0.38258	−0.37655
*B*4....		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....		0.00000	2.00000		0.00000	2.00250		0.00840	2.32621		0.00960	2.37655
*A*1....	0.10	1.78632	1.05523	0.15	1.67123	1.08701	0.70	0.59227	1.61714	0.75	0.53542	1.67805
*A*2....		2.18430	0.95474		2.26433	0.93537		2.73950	0.81203		2.75968	0.80578
*A*3....		2.21366	0.95049		2.32866	0.92664		3.39704	0.75510		3.45294	0.74728
*A*4....		1.81568	1.04951		1.73556	1.07336		1.24982	1.24490		1.22868	1.25272
*B*1		1.21368	0.09477		1.32877	0.13799		2.40773	0.43286		2.46458	0.44695
*B*2....		0.81570	−0.10474		0.73567	−0.16037		0.26050	−0.86203		0.24032	−0.93078
*B*3....		0.97064	−0.00997		0.93568	−0.02237		0.34245	−0.42917		0.30674	−0.48383
*B*4....		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....		0.00002	2.00997		0.00011	2.02237		0.01069	2.42917		0.01164	2.48383
*A*1....	0.20	1.55300	1.12170	0.25	1.43377	1.15936	0.80	0.48487	1.74031	0.85	0.43998	1.80376
*A*2....		2.33643	0.91789		2.40100	0.90212		2.77778	0.80000		2.79405	0.79465
*A*3....		2.44667	0.90381		2.56548	0.88224		3.50269	0.74031		3.54691	0.73411
*A*4....		1.66324	1.09619		1.59826	1.11776		1.20978	1.25969		1.19284	1.26589
*B*1....		1.44700	0.17830		1.56623	0.21564		2.51513	0.45969		2.56002	0.47124
*B*2....		0.66357	−0.21789		0.59900	−0.27712		0.22222	−1.00000		0.20595	−1.06965
*B*3....		0.88976	−0.03959		0.83552	−0.06149		0.27509	−0.54031		0.24714	−0.59841
*B*4....		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....		0.00034	2.03959		0.00074	2.06149		0.01245	2.54031		0.01311	2.59841
*A*1....	0.30	1.31579	1.20000	0.35	1.20117	1.24355	0.90	0.40014	1.86827	0.95	0.36477	1.93372
*A*2....		2.45859	0.88788		2.50981	0.87500		2.80871	0.78969		2.82196	0.78508
*A*3....		2.68284	0.86212		2.79660	0.84355		3.58623	0.72858		3.62120	0.72364
*A*4....		1.54004	1.13788		1.48796	1.15645		1.17766	1.27142		1.16401	1.27636
*B*1....		1.68421	0.25000		1.79883	0.28145		2.59986	0.48173		2.63523	0.49128
*B*2....		0.54141	−0.33788		0.49020	−0.40000		0.19129	−1.13969		0.17804	−1.21008
*B*3....		0.77575	−0.08788		0.71321	−0.11855		0.22249	−0.65796		0.20076	−0.71879
*B*4....		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....		0.00137	2.08788		0.00223	2.11855		0.01363	2.65796		0.01403	2.71879
*A*1....	0.40	1.09175	1.28990	0.45	0.98894	1.33890	1.00	0.33333	2.00000	2.00	0.08579	3.41421
*A*2....		2.55529	0.86332		2.59566	0.85272		2.83395	0.78078		2.94338	0.73205
*A*3....		2.90496	0.82657		3.00656	0.81118		3.65235	0.71922		3.90354	0.68216
*A*4....		1.44142	1.17343		1.39984	1.18882		1.15174	1.28078		1.04595	1.31784
*B*1....		1.90825	0.31010		2.01107	0.33610		2.66667	0.50000		2.91421	0.58579
*B*2....		0.44471	−0.46332		0.40434	−0.52772		0.16605	−1.28078		0.05662	−2.73205
*B*3....		0.65033	−0.15322		0.58910	−0.19163		0.18160	−0.78078		0.03984	−2.14626
*B*4....		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....		0.00329	2.15322		0.00450	2.19163		0.01432	2.78078		0.01067	4.14626
*A*1....	0.50	0.89366	1.39039	0.55	0.80641	1.44415	3.00	0.03699	4.88600	4.00	0.02034	6.37228
*A*2....		2.63151	0.84307		2.66335	0.83426		2.97225	0.71221		2.98365	0.70156
*A*3....		3.10054	0.79732		3.18647	0.78489		3.95651	0.67379		3.97543	0.67072
*A*4....		1.36270	1.20268		1.32953	1.21511		1.02125	1.32621		1.01212	1.32928
*B*1....		2.10634	0.35961		2.19359	0.38085		2.96302	0.61400		2.97966	0.62772
*B*2....		0.36850	−0.59307		0.33665	−0.65926		0.02775	−4.21221		0.01635	−5.70156
*B*3....		0.53097	−0.23346		0.47688	−0.27842		0.01574	−3.59822		0.00822	−5.07384
*B*4....		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....		0.00580	2.23346		0.00712	2.27842		0.00650	5.59822		0.00423	7.07384

TABLE 35—*Concluded*

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1....................	5.00	0.01281	7.86421	10.00	0.00309	15.34847	∞	0.00000	∞
*A*2....................		2.98925	0.69493		2.99717	0.68115		3.00000	0.66667
*A*3....................		3.98425	0.66927		3.99605	0.66732		4.00000	0.66667
*A*4....................		1.00781	1.33073		1.00197	1.33268		1.00000	1.33333
*B*1....................		2.98719	0.63579		2.99691	0.65153		3.00000	0.66667
*B*2....................		0.01075	−7.19493		0.00283	−14.68115		0.00000	— ∞
*B*3....................		0.00501	−6.55914		0.00112	−14.02961		0.00000	— ∞
*B*4....................		1.00000	0.00000		1.00000	0.00000		1.00000	0.00000
*M*1....................		0.00294	8.55914		0.00086	16.02961		0.00000	∞

TABLE 36

Line frequencies and relative intensities for the A_3B spin system

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1....	0.00	3.00000	1.00000	0.05	2.83863	1.02697	0.40	1.34535	1.35826	0.45	1.16137	1.42697
*A*2....		3.00000	1.00000		3.13899	0.97678		3.66448	0.88102		3.70088	0.87310
*A*3....		2.00000	1.00000		1.90012	1.02562		1.25722	1.23852		1.17927	1.27329
*A*4....		2.00000	1.00000		2.09988	0.97562		2.74278	0.83852		2.82073	0.82329
*A*5....		4.00000	1.00000		4.19900	0.97571		5.24658	0.85929		5.33451	0.84958
*A*6....		3.00000	1.00000		2.86104	1.02429		2.33271	1.14071		2.29570	1.15042
*A*7....		3.00000	1.00000		3.16141	0.97448		4.63898	0.81795		4.81807	0.80429
*A*8....		4.00000	1.00000		3.80099	1.02552		2.73493	1.18205		2.64151	1.19571
*B*1....		1.00000	0.00000		1.16137	0.07303		2.65465	0.44174		2.83863	0.47303
*B*2....		1.00000	0.00000		0.86101	−0.07678		0.33552	−0.68102		0.29912	−0.77310
*B*3....		2.00000	0.00000		2.09988	0.02438		2.74278	0.16148		2.82073	0.17671
*B*4....		2.00000	0.00000		1.90012	−0.02562		1.25722	−0.23852		1.17927	−0.27329
*B*5....		1.00000	0.00000		0.94000	−0.02928		0.41790	−0.42134		0.36637	−0.49579
*B*6....		1.00000	0.00000		1.03765	0.02054		0.61041	−0.09857		0.51986	−0.14965
*M*1....		0.00000	2.00000		0.00000	2.02928		0.00281	2.42134		0.00342	2.49579
*M*2....		0.00000	2.00000		0.00001	1.97946		0.01568	2.09857		0.02056	2.14965
*A*1....	0.10	2.65465	1.05826	0.15	2.45004	1.09441	0.50	1.00000	1.50000	0.55	0.86101	1.57678
*A*2....		3.25724	0.95678		3.35710	0.93949		3.73205	0.86603		3.75888	0.85967
*A*3....		1.80099	1.05249		1.70332	1.08059		1.10557	1.30902		1.03616	1.34564
*A*4....		2.19901	0.95249		2.29668	0.93059		2.89443	0.80902		2.96384	0.79564
*A*5....		4.39218	0.95313		4.57449	0.93252		5.41025	0.84108		5.47545	0.83363
*A*6....		2.74271	1.04687		2.64269	1.06748		2.26399	1.15892		2.23669	1.16637
*A*7....		3.34525	0.94836		3.54948	0.92239		4.97487	0.79289		5.10993	0.78348
*A*8....		3.60767	1.05164		3.42481	1.07761		2.56066	1.20711		2.49106	1.21652
*B*1....		1.34535	0.14174		1.54996	0.20559		3.00000	0.50000		3.13899	0.52322
*B*2....		0.74276	−0.15678		0.64290	−0.23949		0.26795	−0.86603		0.24112	−0.95967
*B*3....		2.19901	0.04751		2.29668	0.06941		2.89443	0.19098		2.96384	0.20436
*B*4....		1.80099	−0.05249		1.70332	−0.08059		1.10557	−0.30902		1.03616	−0.34564
*B*5....		0.86506	−0.06668		0.78262	−0.11151		0.32180	−0.57313		0.28343	−0.65297
*B*6....		1.04698	0.03184		1.02522	0.03358		0.43934	−0.20711		0.36995	−0.27009
*M*1....		0.00005	2.06668		0.00021	2.11151		0.00396	2.57313		0.00443	2.65297
*M*2....		0.00009	1.96816		0.00049	1.96643		0.02513	2.20711		0.02906	2.27009
*A*1....	0.20	2.22942	1.13589	0.25	2.00000	1.18301	0.60	0.74276	1.65678	0.65	0.64290	1.73949
*A*2....		3.44115	0.92450		3.51186	0.91144		3.78208	0.85394		3.80225	0.84875
*A*3....		1.60777	1.10990		1.51493	1.14039		0.97101	1.38310		0.91002	1.42134
*A*4....		2.39223	0.90990		2.48507	0.89039		3.02899	0.78310		3.08998	0.77134
*A*5....		4.74226	0.91402		4.89345	0.89758		5.53162	0.82709		5.58012	0.82131
*A*6....		2.55833	1.08598		2.48717	1.10242		2.21309	1.17291		2.19261	1.17869
*A*7....		3.76904	0.89737		3.99641	0.87400		5.22503	0.77575		5.32257	0.76943
*A*8....		3.25567	1.10263		3.10198	1.12600		2.43135	1.22425		2.38022	1.23057
*B*1....		1.77058	0.26411		2.00000	0.31699		3.25724	0.54322		3.35710	0.56051
*B*2....		0.55885	−0.32450		0.48814	−0.41144		0.21792	−1.05394		0.19775	−1.14875
*B*3....		2.39223	0.09010		2.48507	0.10961		3.02899	0.21690		3.08998	0.22866
*B*4....		1.60777	−0.10990		1.51493	−0.14039		0.97101	−0.38310		0.91002	−0.42134
*B*5....		0.69889	−0.16302		0.61841	−0.22045		0.25046	−0.73496		0.22214	−0.81881
*B*6....		0.97375	0.02559		0.89802	0.00797		0.31141	−0.33780		0.26268	−0.40955
*M*1....		0.00052	2.16302		0.00098	2.22045		0.00482	2.73496		0.00513	2.81881
*M*2....		0.00155	1.97441		0.00359	1.99203		0.03221	2.33780		0.03453	2.40955
*A*1....	0.30	1.77058	1.23589	0.35	1.54997	1.29441	0.70	0.55885	1.82450	0.75	0.48814	1.91144
*A*2....		3.57143	0.90000		3.62177	0.88993		3.81987	0.84403		3.83533	0.83972
*A*3....		1.42530	1.17202		1.33930	1.20474		0.85308	1.46033		0.80000	1.50000
*A*4....		2.57470	0.87202		2.66070	0.85474		3.14692	0.76033		3.20000	0.75000
*A*5....		5.02745	0.88310		5.14475	0.87040		5.62210	0.81620		5.65857	0.81166
*A*6....		2.42703	1.11690		2.37606	1.12960		2.17476	1.18380		2.15914	1.18834
*A*7....		4.22266	0.85279		4.43912	0.83408		5.40507	0.76427		5.47489	0.76005
*A*8....		2.96425	1.14721		2.84216	1.16592		2.33645	1.23573		2.29893	1.23995
*B*1....		2.22942	0.36411		2.45004	0.40559		3.44115	0.57550		3.51186	0.58856
*B*2....		0.42857	−0.50000		0.37823	−0.58993		0.18013	−1.24403		0.16467	−1.33972
*B*3....		2.57470	0.12798		2.66070	0.14526		3.14692	0.23967		3.20000	0.25000
*B*4....		1.42530	−0.17202		1.33930	−0.20474		0.85308	−0.46033		0.80000	−0.50000
*B*5....		0.54398	−0.28310		0.47702	−0.35026		0.19777	−0.90426		0.17676	−0.99111
*B*6....		0.80634	−0.01899		0.70780	−0.05474		0.22240	−0.48473		0.18921	−0.56283
*M*1....		0.00155	2.28310		0.00218	2.35026		0.00537	2.90426		0.00553	2.99111
*M*2....		0.00676	2.01899		0.01092	2.05474		0.03608	2.48473		0.03697	2.56283

TABLE 36—*Concluded*

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1....	0.80	0.42857	2.00000	0.85	0.37823	2.08993	3.00	0.02434	6.28388	4.00	0.01320	8.27492
*A*2....		3.84895	0.83578		3.86100	0.83216		3.98248	0.77872		3.98970	0.77200
*A*3....		0.75061	1.54031		0.70470	1.58122		0.10263	3.58114		0.05972	4.56155
*A*4....		3.24939	0.74031		3.29530	0.73122		3.89737	0.58114		3.94029	0.56155
*A*5....		5.69035	0.80762		5.71816	0.80400		5.97075	0.76266		5.98324	0.75913
*A*6....		2.14541	1.19238		2.13330	1.19600		2.01548	1.23734		2.00898	1.24087
*A*7....		5.53414	0.75660		5.58460	0.75378		5.96729	0.74250		5.98178	0.74379
*A*8....		2.26671	1.24340		2.23896	1.24622		2.01884	1.25750		2.01042	1.25621
*B*1....		3.57143	0.60000		3.62177	0.61007		3.97566	0.71612		3.98680	0.72508
*B*2....		0.15105	−1.43578		0.13900	−1.53216		0.01752	−5.77872		0.01030	−7.77200
*B*3....		3.24939	0.25969		3.29530	0.26878		3.89737	0.41886		3.94029	0.43845
*B*4....		0.75061	−0.54031		0.70470	−0.58122		0.10263	−2.58114		0.05972	−3.56155
*B*5....		0.15859	−1.07918		0.14284	−1.16831		0.01173	−5.32010		0.00646	−7.30313
*B*6....		0.16186	−0.64340		0.13927	−0.72609		0.00550	−4.82526		0.00278	−6.80605
*M*1....		0.00564	3.07918		0.00570	3.16831		0.00204	7.32010		0.00132	9.30313
*M*2....		0.03729	2.64340		0.03717	2.72609		0.00837	6.82526		0.00502	8.80605
*A*1....	0.90	0.33552	2.18102	0.95	0.29912	2.27310	5.00	0.00826	10.26970	10.00	0.00197	20.25961
*A*2....		3.87171	0.82882		3.88127	0.82574		3.99323	0.76783		3.99822	0.75914
*A*3....		0.66207	1.62268		0.62250	1.66466		0.03884	5.54951		0.00993	10.52494
*A*4....		3.33793	0.72268		3.37750	0.71466		3.96116	0.54951		3.99007	0.52494
*A*5....		5.74259	0.80074		5.76413	0.79781		5.98916	0.75711		5.99724	0.75335
*A*6....		2.12257	1.19926		2.11303	1.20219		2.00585	1.24289		2.00151	1.24665
*A*7....		5.62777	0.75146		5.66488	0.74956		5.98841	0.74476		5.99714	0.74712
*A*8....		2.21497	1.24854		2.19416	1.25044		2.00660	1.25524		2.00161	1.25288
*B*1....		3.66448	0.61898		3.70088	0.62690		3.99174	0.73030		3.99803	0.74039
*B*2....		0.12829	−1.62882		0.11873	−1.72574		0.00677	−9.76783		0.00178	−19.75914
*B*3....		3.33793	0.27732		3.37750	0.28534		3.96116	0.45049		3.99007	0.47506
*B*4....		0.66207	−0.62268		0.62250	−0.66466		0.03884	−4.54951		0.00993	−9.52494
*B*5....		0.12912	−1.25838		0.11714	−1.34928		0.00407	−9.29276		0.00098	−19.27163
*B*6....		0.12055	−0.81059		0.10496	−0.89665		0.00166	−8.79463		0.00036	−18.77210
*M*1....		0.00572	3.25838		0.00570	3.34928		0.00091	11.29276		0.00027	21.27163
*M*2....		0.03671	2.81059		0.03600	2.89665		0.00333	10.79463		0.00089	20.77210
*A*1....	1.00	0.26795	2.36603	2.00	0.05855	4.30278	∞	0.00000	∞			
*A*2....		3.88982	0.82288		3.96396	0.79129		4.00000	0.75000			
*A*3....		0.58579	1.70711		0.21115	2.61803		0.00000	∞			
*A*4....		3.41421	0.70711		3.78885	0.61803		4.00000	0.50000			
*A*5....		5.78319	0.79516		5.93683	0.77026		6.00000	0.75000			
*A*6....		2.10452	1.20484		2.03259	1.22974		2.00000	1.25000			
*A*7....		5.69694	0.74799		5.92525	0.74122		6.00000	0.75000			
*A*8....		2.17604	1.25201		2.04352	1.25878		2.00000	1.25000			
*B*1....		3.73205	0.63397		3.94145	0.69722		4.00000	0.75000			
*B*2....		0.11018	−1.82288		0.03604	−3.79129		0.00000	−∞			
*B*3....		3.41421	0.29289		3.78885	0.38197		4.00000	0.50000			
*B*4....		0.58579	−0.70711		0.21115	−1.61803		0.00000	−∞			
*B*5....		0.10663	−1.44091		0.02713	−3.35284		0.00000	−∞			
*B*6....		0.09191	−0.98406		0.01503	−2.86433		0.00000	−∞			
*M*1....		0.00566	3.44091		0.00345	5.35284		0.00000	∞			
*M*2....		0.03511	2.98406		0.01620	4.86433		0.00000	∞			

TABLE 37

Line frequencies and relative intensities for the A_2B_2 spin system

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1	0.00	2.00000	0.50000	0.05	2.21487	0.45013	0.70	5.26595	0.08474	0.75	5.35366	0.07701
*A*2		2.00000	0.50000		2.19901	0.45249		3.62747	0.16023		3.66410	0.15139
*A*3		2.00000	0.50000		1.98654	0.50224		1.59935	0.49322		1.60086	0.48270
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000
*A*5		2.00000	0.50000		1.81445	0.54988		0.74740	1.11773		0.70915	1.15833
*A*6		2.00000	0.50000		1.98413	0.50274		0.35985	1.22725		0.30881	1.32007
*A*7		2.00000	0.50000		1.80099	0.55249		0.37253	1.56023		0.33590	1.65139
*M*1		0.00000	1.50000		0.00000	1.45512		0.02579	1.80521		0.02588	1.87979
*M*2		0.00000	1.50000		0.00000	1.55487		0.00167	2.83819		0.00163	2.96110
*A*1	0.10	2.46251	0.40113	0.15	2.73999	0.35400	0.80	5.42746	0.07044	0.85	5.48990	0.06481
*A*2		2.39223	0.40990		2.57470	0.37202		3.69600	0.14340		3.72387	0.13615
*A*3		1.95243	0.50792		1.90650	0.51543		1.60483	0.47195		1.61071	0.46113
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000
*A*5		1.65527	0.59915		1.51843	0.64741		0.67356	1.19900		0.64034	1.23979
*A*6		1.92969	0.51188		1.83459	0.52860		0.26696	1.41484		0.23246	1.51118
*A*7		1.60777	0.60990		1.42530	0.67202		0.30400	1.74340		0.27613	1.83615
*M*1		0.00007	1.42094		0.00037	1.39803		0.02562	1.95724		0.02508	2.03712
*M*2		0.00003	1.61896		0.00012	1.69144		0.00158	3.08579		0.00151	3.21209
*A*1	0.20	3.04200	0.30975	0.25	3.35787	0.26928	0.90	5.54302	0.05996	0.95	5.58894	0.05574
*A*2		2.74278	0.33852		2.89443	0.30902		3.74831	0.12956		3.76984	0.12355
*A*3		1.85526	0.52322		1.80516	0.52998		1.61804	0.45033		1.62637	0.43965
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000
*A*5		1.40074	0.69445		1.29754	0.74024		0.60929	1.28072		0.58020	1.32184
*A*6		1.70049	0.55381		1.53606	0.58805		0.20386	1.60880		0.17954	1.70745
*A*7		1.25722	0.73852		1.10557	0.80902		0.25169	1.92956		0.23016	2.02355
*M*1		0.00122	1.38678		0.00288	1.38732		0.02436	2.11909		0.02359	2.20283
*M*2		0.00028	1.77148		0.00050	1.85828		0.00143	3.33985		0.00135	3.46893
*A*1	0.30	3.67373	0.23322	0.35	3.97544	0.20182	1.00	5.62808	0.05205	2.00	5.90634	0.02232
*A*2		3.02899	0.28310		3.14692	0.26033		3.78885	0.11803		3.94029	0.06155
*A*3		1.75801	0.53474		1.71648	0.53694		1.63556	0.42914		1.81161	0.27475
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000
*A*5		1.20752	0.78486		1.12774	0.82843		0.55292	1.36316		0.23917	2.23552
*A*6		1.35451	0.63145		1.17049	0.68371		0.15950	1.80693		0.03365	3.84835
*A*7		0.97101	0.88310		0.85308	0.96033		0.21115	2.11803		0.05972	4.06155
*M*1		0.00547	1.39941		0.00885	1.42247		0.02267	2.28812		0.00894	4.14542
*M*2		0.00075	1.95105		0.00099	2.04909		0.00127	3.59923		0.00029	6.35862
*A*1	0.40	4.25184	0.17500	0.45	4.49640	0.15242	3.00	5.95830	0.01434	4.00	5.97655	0.01061
*A*2		3.24939	0.24031		3.33793	0.22268		3.97279	0.04138		3.98456	0.03113
*A*3		1.68151	0.53644		1.65329	0.53340		1.89741	0.19571		1.93738	0.15066
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000
*A*5		1.05648	0.87113		0.99244	0.91313		0.12550	3.16867		0.07557	4.13014
*A*6		0.99634	0.74418		0.84015	0.81197		0.01441	5.88705		0.00797	7.91160
*A*7		0.75061	1.04031		0.66207	1.12268		0.02721	6.04138		0.01544	8.03113
*M*1		0.01262	1.45563		0.01634	1.49778		0.00431	6.09710		0.00250	8.07287
*M*2		0.00121	2.15176		0.00138	2.25850		0.00008	9.25143		0.00003	12.19240
*A*1	0.50	4.70725	0.13356	0.55	4.88597	0.11786	5.00	5.98500	0.00843	10.00	5.99625	0.00418
*A*2		3.41421	0.20711		3.47988	0.19330		3.99007	0.02494		3.99750	0.01249
*A*3		1.63173	0.52814		1.61632	0.52111		1.95828	0.12207		1.98897	0.06212
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000
*A*5		0.93449	0.95459		0.88162	0.99567		0.05002	5.10556		0.01311	10.05380
*A*6		0.70542	0.88607		0.59229	0.96550		0.00506	9.92780		0.00125	19.96286
*A*7		0.58579	1.20711		0.52012	1.29330		0.00993	10.02494		0.00250	20.01249
*M*1		0.01956	1.54777		0.02217	1.60447		0.00163	10.05831		0.00041	20.02916
*M*2		0.00154	2.36881		0.00162	2.48227		0.00001	15.15543		0.00000	30.07878
*A*1	0.60	5.03592	0.10480	0.65	5.16124	0.09390	∞	6.00000	0.00000			
*A*2		3.53644	0.18102		3.58525	0.17006		4.00000	0.00000			
*A*3		1.60632	0.51270		1.60092	0.50330		2.00000	0.00000			
*A*4		4.00000	0.50000		4.00000	0.50000		4.00000	0.50000			
*A*5		0.83322	1.03648		0.78863	1.07713		0.00000	∞			
*A*6		0.49884	1.04935		0.42232	1.13682		0.00000	∞			
*A*7		0.46356	1.38102		0.41475	1.47006		0.00000	∞			
*M*1		0.02402	1.66685		0.02520	1.73402		0.00000	∞			
*M*2		0.00168	2.59853		0.00169	2.71725		0.00000	∞			

TABLE 38

Line frequencies and relative intensities for the A_3B_2 spin system

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1....	0.00	3.00000	1.00000	0.05	2.69081	1.05383	0.20	1.76808	1.26235	0.25	1.50515	1.34650
*A*2....		2.00000	1.00000		1.80771	1.05122		1.32714	1.21789		1.19800	1.27712
*A*3....		3.00000	1.00000		3.28708	0.95365		3.95330	0.85208		4.11024	0.82793
*A*4....		2.00000	1.00000		1.98508	1.00250		1.77953	1.03959		1.67103	1.06149
*A*5....		2.00000	1.00000		2.20721	0.95128		2.89400	0.82170		3.13245	0.78436
*A*6....		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7....		4.00000	1.00000		3.61692	1.05103		2.69509	1.20794		2.45798	1.25940
*A*8....		3.00000	1.00000		2.97284	1.00301		2.38893	1.07329		2.03210	1.12573
*A*9....		3.00000	1.00000		3.33633	0.94894		4.83922	0.79765		5.45443	0.75560
*A*10...		4.00000	1.00000		3.97054	1.00244		3.64181	1.02684		3.51396	1.03278
*A*11...		3.00000	1.00000		2.73116	1.04862		2.19304	1.17551		2.07115	1.21162
*A*12...		3.00000	1.00000		2.98175	1.00202		2.85171	1.01431		2.81489	1.01593
*A*13...		4.00000	1.00000		4.41251	0.95147		5.65470	0.83149		6.00914	0.80158
*B*1....		2.00000	0.00000		2.30919	0.07117		3.23193	0.23765		3.49485	0.27850
*B*2....		4.00000	0.00000		4.19229	0.02378		4.67286	0.08211		4.80200	0.09788
*B*3....		2.00000	0.00000		1.71292	−0.07865		1.04671	−0.35208		0.88977	−0.45293
*B*4....		4.00000	0.00000		3.80771	−0.02494		3.32648	−0.09619		3.19652	−0.11776
*B*5....		4.00000	0.00000		4.20721	0.02494		4.89333	0.09619		5.13097	0.11776
*B*6....		4.00000	0.00000		3.79279	−0.02628		3.10600	−0.12170		2.86755	−0.15936
*B*7....		2.00000	0.00000		2.33634	0.07478		3.84190	0.28112		4.46083	0.33638
*B*8....		2.00000	0.00000		2.07388	0.02035		2.06969	0.04859		2.03914	0.05772
*B*9....		2.00000	0.00000		1.73116	−0.07484		1.19341	−0.29372		1.07188	−0.36458
*B*10...		2.00000	0.00000		1.87457	−0.03027		1.29841	−0.18985		1.10080	−0.26494
*B*11...		2.00000	0.00000		1.88577	−0.02824		1.50233	−0.13251		1.38730	−0.16890
*B*12...		2.00000	0.00000		2.07618	0.02071		1.81624	0.00549		1.55627	−0.03374
*M*1....		0.00000	−1.00000		0.00001	−0.90788		0.00329	−0.74357		0.00803	−0.73162
*M*2....		0.00000	2.00000		0.00001	2.03370		0.00110	2.23263		0.00192	2.32740
*M*3....		0.00000	2.00000		0.00001	1.98376		0.00159	2.03565		0.00300	2.08245
*M*4....		0.00000	−1.00000		0.00000	−1.10713		0.00019	−1.49787		0.00030	−1.64545
*M*5....		0.00000	3.00000		0.00000	3.00753		0.00000	3.12702		0.00000	3.20264
*M*6....		0.00000	2.00000		0.00001	1.93067		0.00597	1.81900		0.01443	1.82212
*M*7....		0.00000	2.00000		0.00001	2.07930		0.00057	2.33486		0.00102	2.41329
*M*8....		0.00000	−1.00000		0.00001	−1.00997		0.00082	−1.15385		0.00144	−1.23542
*M*9....		0.00000	−1.00000		0.00000	−1.00250		0.00067	−1.03959		0.00149	−1.06149
*A*1....	0.10	2.37259	1.11554	0.15	2.06044	1.18515	0.30	1.27627	1.43681	0.35	1.08169	1.53240
*A*2....		1.63141	1.10474		1.47134	1.16037		1.08283	1.33788		0.98039	1.40000
*A*3....		3.54341	0.91410		3.76534	0.88053		4.24027	0.80737		4.34769	0.78976
*A*4....		1.94128	1.00997		1.87135	1.02237		1.55150	1.08788		1.42642	1.11855
*A*5....		2.42736	0.90523		2.65754	0.86201		3.36842	0.75000		3.59766	0.71855
*A*6....		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7....		3.27099	1.10331		2.96460	1.15583		2.24844	1.31026		2.06194	1.36075
*A*8....		2.87275	1.01419		2.67892	1.03669		1.65864	1.19428		1.31588	1.27769
*A*9....		3.75441	0.89675		4.25941	0.84548		6.05064	0.72076		6.58156	0.69328
*A*10...		3.88909	1.00910		3.77276	1.01810		3.40196	1.03427		3.31352	1.03091
*A*11...		2.51488	1.09415		2.33849	1.13642		1.96723	1.24498		1.87783	1.27580
*A*12...		2.94153	1.00635		2.89540	1.01089		2.78667	1.01562		2.76641	1.01355
*A*13...		4.83939	0.90666		5.25994	0.86651		6.31618	0.77641		6.57539	0.75540
*B*1....		2.62741	0.13446		2.93957	0.18985		3.72374	0.31319		3.91831	0.34260
*B*2....		4.36860	0.04526		4.52866	0.06463		4.91717	0.11212		5.01961	0.12500
*B*3....		1.45659	−0.16410		1.23466	−0.25553		0.75974	−0.55737		0.65231	−0.66476
*B*4....		3.63136	−0.04951		3.47111	−0.07336		3.08008	−0.13788		2.97593	−0.15645
*B*5....		4.42732	0.04951		4.65731	0.07336		5.36568	0.13788		5.59319	0.15645
*B*6....		3.57264	−0.05523		3.34246	−0.08701		2.63158	−0.20000		2.40235	−0.24355
*B*7....		2.75454	0.14803		3.26018	0.21763		5.06234	0.38227		5.59901	0.41896
*B*8....		2.10145	0.03312		2.09490	0.04139		2.01299	0.07067		1.99743	0.08789
*B*9....		1.51492	−0.14891		1.33864	−0.22187		0.96842	−0.43467		0.87963	−0.50419
*B*10...		1.70399	−0.07185		1.50530	−0.12517		0.92371	−0.34911		0.77185	−0.44096
*B*11...		1.75615	−0.06110		1.62624	−0.09634		1.28190	−0.20532		1.18499	−0.24194
*B*12...		2.08504	0.03059		2.00081	0.02642		1.26810	−0.09126		0.99756	−0.16545
*M*1....		0.00015	−0.83304		0.00093	−0.77767		0.01483	−0.74134		0.02232	−0.77084
*M*2....		0.00012	2.08438		0.00046	2.15113		0.00276	2.43387		0.00342	2.55055
*M*3....		0.00014	1.98485		0.00062	2.00257		0.00464	2.14115		0.00627	2.20992
*M*4....		0.00003	−1.22710		0.00010	−1.35793		0.00038	−1.79940		0.00045	−1.95871
*M*5....		0.00000	3.03050		0.00000	3.06992		0.00001	3.29657		0.00002	3.40739
*M*6....		0.00028	1.87525		0.00170	1.83716		0.02652	1.84628		0.03976	1.88964
*M*7....		0.00007	2.16435		0.00025	2.25086		0.00157	2.48456		0.00222	2.54866
*M*8....		0.00008	−1.03960		0.00034	−1.08802		0.00207	−1.33084		0.00254	−1.43831
*M*9....		0.00005	−1.00997		0.00023	−1.02237		0.00275	−1.08788		0.00447	−1.11855

TABLE 38—*Continued*

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1....	0.40	0.91886	1.63246	0.45	0.78380	1.73623	0.60	0.50354	2.06394	0.65	0.43997	2.17717
*A*2....		0.88942	1.46332		0.80868	1.52772		0.61662	1.72621		0.56611	1.79382
*A*3....		4.43649	0.77460		4.51012	0.76146		4.66600	0.73107		4.70264	0.72319
*A*4....		1.30067	1.15322		1.17820	1.19163		0.85473	1.32621		0.76517	1.37655
*A*5....		3.81650	0.68990		4.02213	0.66390		4.54546	0.60000		4.68793	0.58272
*A*6....		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7....		1.89490	1.41118		1.74410	1.46185		1.36828	1.61775		1.26374	1.67155
*A*8....		1.03032	1.37367		0.80666	1.47960		0.41427	1.83505		0.34184	1.96085
*A*9....		7.02442	0.67235		7.37932	0.65669		8.04950	0.62972		8.18647	0.62468
*A*10...		3.25156	1.02335		3.21495	1.01267		3.21663	0.97215		3.24000	0.95812
*A*11...		1.80014	1.30430		1.73203	1.33064		1.57026	1.39813		1.52721	1.41720
*A*12...		2.75314	1.01004		2.74568	1.00541		2.74690	0.98781		2.75213	0.98140
*A*13...		6.79072	0.73790		6.96805	0.72330		7.33265	0.69201		7.41487	0.68453
*B*1....		4.08114	0.36754		4.21620	0.38877		4.49646	0.43606		4.56003	0.44783
*B*2....		5.11058	0.13668		5.19133	0.14728		5.38338	0.17379		5.43389	0.18118
*B*3....		0.56351	−0.77460		0.48989	−0.88646		0.33400	−1.23107		0.29736	−1.34819
*B*4....		2.88284	−0.17343		2.79967	−0.18882		2.59981	−0.22621		2.54690	−0.23610
*B*5....		5.80991	0.17343		6.01313	0.18882		6.52865	0.22621		6.66873	0.23610
*B*6....		2.18350	−0.28990		1.97787	−0.33890		1.45455	−0.50000		1.31207	−0.55772
*B*7....		6.04688	0.44761		6.40536	0.46977		7.07832	0.51114		7.21461	0.51978
*B*8....		1.99530	0.10876		2.00663	0.13215		2.10005	0.20717		2.14250	0.23150
*B*9....		0.80267	−0.57334		0.73541	−0.64226		0.57674	−0.84875		0.53484	−0.91773
*B*10...		0.64529	−0.53916		0.54154	−0.64250		0.33288	−0.97433		0.28730	−1.08999
*B*11...		1.09579	−0.27907		1.01323	−0.31703		0.79920	−0.43843		0.73766	−0.48192
*B*12...		0.77108	−0.25371		0.59450	−0.35314		0.29082	−0.69419		0.23635	−0.81639
*M*1....		0.02866	−0.81730		0.03307	−0.87768		0.03520	−1.11675		0.03373	−1.20957
*M*2....		0.00394	2.67609		0.00418	2.80930		0.00387	3.24564		0.00359	3.40089
*M*3....		0.00769	2.28709		0.00879	2.37122		0.01036	2.65415		0.01040	2.75591
*M*4....		0.00048	−2.12253		0.00052	−2.29017		0.00047	−2.81089		0.00046	−2.98911
*M*5....		0.00003	3.53278		0.00006	3.67016		0.00009	4.13263		0.00010	4.29832
*M*6....		0.05108	1.94941		0.05905	2.02250		0.06394	2.29607		0.06177	2.39919
*M*7....		0.00298	2.60672		0.00385	2.66034		0.00686	2.80871		0.00799	2.85725
*M*8....		0.00291	−1.55613		0.00302	−1.68283		0.00270	−2.10478		0.00245	−2.25644
*M*9....		0.00659	−1.15322		0.00901	−1.19163		0.01681	−1.32621		0.01921	−1.37655
*A*1....	0.50	0.67218	1.84307	0.55	0.57995	1.95246	0.70	0.38680	2.29186	0.75	0.34208	2.40776
*A*2....		0.73699	1.59307		0.67329	1.65926		0.52101	1.86203		0.48064	1.93078
*A*3....		4.57143	0.75000		4.62277	0.73995		4.73387	0.71616		4.76065	0.70985
*A*4....		1.06193	1.23346		0.95377	1.27842		0.68491	1.42917		0.61347	1.48383
*A*5....		4.21268	0.64039		4.38718	0.61915		4.81546	0.56714		4.92916	0.55305
*A*6....		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7....		1.60713	1.51304		1.48239	1.56495		1.16788	1.72640		1.07993	1.78234
*A*8....		0.63702	1.59307		0.50982	1.71207		0.28623	2.08859		0.24290	2.21766
*A*9....		7.65848	0.64503		7.87721	0.63631		8.29662	0.62076		8.38625	0.61767
*A*10...		3.20005	1.00000		3.20204	0.98627		3.26911	0.94448		3.30171	0.93141
*A*11...		1.67178	1.35496		1.61820	1.37742		1.48837	1.43476		1.45322	1.45091
*A*12...		2.74285	1.00000		2.74356	0.99406		2.75867	0.97494		2.76609	0.96853
*A*13...		7.11376	0.71107		7.23363	0.70076		7.48362	0.67808		7.54147	0.67248
*B*1....		4.32782	0.40693		4.42005	0.42255		4.61320	0.45814		4.65793	0.46724
*B*2....		5.26301	0.15693		5.32671	0.16574		5.47900	0.18797		5.51936	0.19422
*B*3....		0.42857	−1.00000		0.37724	−1.11495		0.26613	−1.46616		0.23935	−1.58485
*B*4....		2.72539	−0.20268		2.65905	−0.21511		2.49963	−0.24490		2.45737	−0.25272
*B*5....		6.20108	0.20268		6.37294	0.21511		6.79409	0.24490		6.90588	0.25272
*B*6....		1.78732	−0.39039		1.61282	−0.44415		1.18454	−0.61714		1.07084	−0.67805
*B*7....		6.68659	0.48696		6.90614	0.50043		7.32371	0.52686		7.41208	0.53276
*B*8....		2.02969	0.15693		2.06166	0.18216		2.18709	0.25488		2.23240	0.27714
*B*9....		0.67612	−0.71107		0.62358	−0.77988		0.49716	−0.98686		0.46315	−1.05617
*B*10...		0.45715	−0.75000		0.38863	−0.86083		0.24982	−1.20737		0.21879	−1.32616
*B*11...		0.93656	−0.35611		0.86541	−0.39652		0.68057	−0.52704		0.62769	−0.57379
*B*12...		0.46188	−0.46107		0.36363	−0.57533		0.19509	−0.94097		0.16336	−1.06723
*M*1....		0.03536	−0.94918		0.03590	−1.02948		0.03183	−1.30685		0.02974	−1.40776
*M*2....		0.00421	2.94918		0.00410	3.09486		0.00327	3.56011		0.00294	3.72286
*M*3....		0.00960	2.46107		0.01010	2.55566		0.01030	2.86039		0.01010	2.96717
*M*4....		0.00051	/ −2.46107		0.00050	−2.63477		0.00043	−3.16918		0.00039	−3.35086
*M*5....		0.00007	3.81718		0.00008	3.97185		0.00010	4.46801		0.00010	4.64101
*M*6....		0.06340	2.10611		0.06474	2.19791		0.05882	2.50621		0.05548	2.61631
*M*7....		0.00478	2.71107		0.00580	2.76021		0.00911	2.90628		0.01023	2.95611
*M*8....		0.00301	−1.81718		0.00288	−1.95812		0.00221	−2.41249		0.00197	−2.57243
*M*9....		0.01160	−1.23346		0.01424	−1.27842		0.02138	−1.42917		0.02328	−1.48383

TABLE 38—*Continued*

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1	0.80	0.30422	2.52470	0.85	0.27200	2.64250	1.00	0.20000	3.00000	2.00	0.05051	5.44949
*A*2		0.44444	2.00000		0.41190	2.06965		0.33211	2.28078		0.11325	3.73205
U3		4.78375	0.70416		4.80379	0.69901		4.85005	0.68614		4.95677	0.64575
U4		0.55019	1.54031		0.49428	1.59841		0.36319	1.78078		0.07967	3.14626
*A*5		5.03026	0.54031		5.12004	0.52876		5.33334	0.50000		5.82843	0.41421
*A*6		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7		0.99926	1.83936		0.92530	1.89745		0.73859	2.07772		0.21674	3.42349
*A*8		0.20864	2.34759		0.18117	2.47806		0.12515	2.87056		0.02886	5.44949
*A*9		8.46000	0.61521		8.52134	0.61322		8.65386	0.60911		8.91359	0.60202
*A*10		3.33609	0.91903		3.37101	0.90738		3.47168	0.87687		3.82280	0.78246
*A*11		1.42133	1.46576		1.39232	1.47940		1.31962	1.51402		1.10843	1.61552
*A*12		2.77405	0.96223		2.78228	0.95608		2.80704	0.93872		2.91365	0.86329
*A*13		7.59049	0.66758		7.63231	0.66328		7.72619	0.65302		7.92684	0.62521
*B*1		4.69578	0.47531		4.72800	0.48250		4.80000	0.50000		4.94949	0.55051
*B*2		5.55556	0.20000		5.58810	0.20535		5.66789	0.21922		5.88675	0.26795
*B*3		0.21625	−1.70416		0.19621	−1.82401		0.14995	−2.18614		0.04323	−4.64575
*B*4		2.41956	−0.25969		2.38569	−0.26589		2.30348	−0.28078		2.09190	−0.31784
*B*5		7.00537	0.25969		7.09382	0.26589		7.30470	0.28078		7.80708	0.31784
*B*6		0.96974	−0.74031		0.87997	−0.80376		0.66667	−1.00000		0.17157	−2.41421
*B*7		7.48451	0.53774		7.54450	0.54200		7.67326	0.55173		7.92048	0.57651
*B*8		2.27734	0.29820		2.32114	0.31805		2.44131	0.37056		2.82828	0.55051
*B*9		0.43238	−1.12566		0.40444	−1.19534		0.33453	−1.40560		0.12613	−2.84275
*B*10		0.19290	−1.44609		0.17115	−1.56694		0.12361	−1.93356		0.02989	−4.42822
*B*11		0.57883	−0.62213		0.53379	−0.67202		0.41955	−0.83030		0.10837	−2.09052
*B*12		0.13858	−1.19464		0.11894	−1.32284		0.07969	−1.70972		0.01661	−4.27096
*M*1		0.02762	−1.51165		0.02556	−1.61801		0.02010	−1.94827		0.00550	−4.32247
*M*2		0.00263	3.88875		0.00233	4.05745		0.00159	4.57772		0.00014	8.32247
*M*3		0.00982	3.07590		0.00949	3.18630		0.00838	3.52530		0.00345	5.91671
*M*4		0.00036	−3.53398		0.00034	−3.71836		0.00026	−4.27788		0.00005	−8.13425
*M*5		0.00010	4.81677		0.00009	4.99486		0.00008	5.54001		0.00002	9.36148
*M*6		0.05203	2.72888		0.04863	2.84344		0.03942	3.19570		0.01237	5.65545
*M*7		0.01132	3.00692		0.01236	3.05880		0.01508	3.22118		0.01773	4.48850
*M*8		0.00173	−2.73580		0.00152	−2.90224		0.00101	−3.41688		0.00008	−7.14395
*M*9		0.02489	−1.54031		0.02622	−1.59841		0.02863	−1.78078		0.02135	−3.14626
*A*1	0.90	0.24439	2.76106	0.95	0.22061	2.88025	3.00	0.02222	7.93273	4.00	0.01240	10.42443
*A*2		0.38258	2.13969		0.35609	2.21008		0.05550	5.21221		0.03270	6.70156
*A*3		4.82126	0.69433		4.83657	0.69005		4.98000	0.63104		4.98855	0.62348
*A*4		0.44497	1.65796		0.40151	1.71879		0.03148	4.59822		0.01644	6.07384
*A*5		5.19972	0.50827		5.27046	0.50872		5.92603	0.38600		5.95932	0.37228
*A*6		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7		0.85753	1.95657		0.79545	2.01667		0.09497	4.86824		0.05225	6.34128
*A*8		0.15884	2.60881		0.14046	2.73969		0.01272	7.98019		0.00715	10.49496
*A*9		8.57286	0.61159		8.61654	0.61024		8.96163	0.60087		8.97836	0.60049
*A*10		3.40561	0.89648		3.43928	0.88631		3.91785	0.75671		3.95328	0.74681
*A*11		1.36587	1.49193		1.34172	1.50344		1.05170	1.64241		1.02984	1.65270
*A*12		2.79061	0.95010		2.79889	0.94431		2.95387	0.82687		2.97172	0.80613
*A*13		7.66821	0.65946		7.69923	0.65606		7.96693	0.61651		7.98116	0.61228
*B*1		4.75561	0.48894		4.77940	0.49475		4.97778	0.56727		4.98760	0.57557
*B*2		5.61743	0.21031		5.64391	0.21492		5.94451	0.28779		5.96730	0.29844
*B*3		0.17874	−1.94433		0.16343	−2.06505		0.02000	−7.13104		0.01145	−9.62348
*B*4		2.35531	−0.27142		2.32803	−0.27636		2.04219	−0.32621		2.02424	−0.32928
*B*5		7.17245	0.27142		7.24240	0.27636		7.91303	0.32621		7.95087	0.32928
*B*6		0.80028	−0.86827		0.72954	−0.93372		0.07397	−3.88600		0.04068	−5.37228
*B*7		7.59471	0.54568		7.63713	0.54889		7.96503	0.58430		7.98044	0.58819
*B*8		2.36326	0.33670		2.40337	0.35418		2.92485	0.61473		2.95883	0.64610
*B*9		0.37900	−1.26523		0.35577	−1.33531		0.06437	−4.31234		0.03871	−5.79493
*B*10		0.15274	−1.68856		0.13706	−1.81080		0.01306	−6.93522		0.00738	−9.44082
*B*11		0.49238	−0.72339		0.45439	−0.77618		0.04329	−3.49680		0.02242	−4.94837
*B*12		0.10315	−1.45154		0.09029	−1.58055		0.00704	−6.79502		0.00382	−9.30628
*M*1		0.02360	−1.72643		0.02178	−1.83661		0.00239	−6.78116		0.00132	−9.26067
*M*2		0.00206	4.22868		0.00181	4.40218		0.00003	12.23370		0.00001	16.19014
*M*3		0.00913	3.29812		0.00876	3.41117		0.00176	8.37860		0.00103	10.85923
*M*4		0.00031	−3.90388		0.00028	−4.09042		0.00001	−12.07443		0.00000	−16.04188
*M*5		0.00009	5.17493		0.00008	5.35673		0.00001	13.29181		0.00000	17.25465
*M*6		0.04536	2.95961		0.04228	3.07711		0.00578	8.15260		0.00340	10.65358
*M*7		0.01334	3.11180		0.01425	3.16594		0.01268	5.89592		0.00888	7.34788
*M*8		0.00133	−3.07141		0.00116	−3.24304		0.00001	−11.04852		0.00000	−15.00146
*M*9		0.02727	−1.65796		0.02806	−1.71879		0.01301	−4.59822		0.00846	−6.07384

TABLE 38—*Concluded*

	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency	J/δ	Intensity	Frequency
*A*1	5.00	0.00789	12.91948	10.00	0.00195	25.40967	∞	0.00000	∞
*A*2		0.02150	8.19493		0.00566	15.68115		0.00000	∞
*A*3		4.99260	0.61887		4.99811	0.60952		5.00000	0.60000
*A*4		0.01001	7.55914		0.00224	15.02961		0.00000	∞
*A*5		5.97437	0.36421		5.99382	0.34847		6.00000	0.33333
*A*6		12.00000	1.00000		12.00000	1.00000		12.00000	1.00000
*A*7		0.03284	7.82550		0.00784	15.29514		0.00000	∞
*A*8		0.00458	13.00345		0.00115	25.51929		0.00000	∞
*A*9		8.98615	0.60031		8.99656	0.60008		9.00000	0.60000
*A*10		3.96996	0.74206		3.99243	0.73555		4.00000	0.73333
*A*11		1.01933	1.65763		1.00491	1.66437		1.00000	1.66667
*A*12		2.98097	0.79284		2.99477	0.76436		3.00000	0.73333
*A*13		7.98788	0.60977		7.99698	0.60484		8.00000	0.60000
*B*1		4.99211	0.58052		4.99805	0.59033		5.00000	0.60000
*B*2		5.97851	0.30507		5.99435	0.31885		6.00000	0.33333
*B*3		0.00741	−12.11887		0.00189	−24.60952		0.00000	−∞
*B*4		2.01562	−0.33073		2.00394	−0.33268		2.00000	−0.33333
*B*5		7.96850	0.33073		7.99211	0.33268		8.00000	0.33333
*B*6		0.02563	−6.86421		0.00618	−14.34847		0.00000	−∞
*B*7		7.98753	0.59053		7.99690	0.59524		8.00000	0.60000
*B*8		2.97422	0.66448		2.99390	0.69995		3.00000	0.73333
*B*9		0.02576	−7.28374		0.00693	−14.75966		0.00000	−∞
*B*10		0.00471	−11.94489		0.00113	−24.45469		0.00000	−∞
*B*11		0.01352	−6.41896		0.00293	−13.85965		0.00000	−∞
*B*12		0.00241	−11.81261		0.00061	−24.32398		0.00000	−∞
*M*1		0.00083	−11.74843		0.00020	−24.22411		0.00000	−∞
*M*2		0.00001	20.16446		0.00000	40.11449		0.00000	∞
*M*3		0.00068	13.34751		0.00019	25.82388		0.00000	−∞
*M*4		0.00000	−20.02148		0.00000	−39.97870		0.00000	−∞
*M*5		0.00000	21.23157		0.00000	41.18362		0.00000	∞
*M*6		0.00221	13.15498		0.00054	25.65960		0.00000	∞
*M*7		0.00643	8.81865		0.00202	16.25956		0.00000	∞
*M*8		0.00000	−18.97363		0.00000	−38.91917		0.00000	−∞
*M*9		0.00588	−7.55914		0.00172	−15.02961		0.00000	−∞