ABSTRACT

QUANTUM MECHANICAL ANALYSIS OF HIGH-RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA

by Yuh Kang Pan

The quantum mechanical and algebraic procedures involved in the analysis of high-resolution nuclear magnetic resonance spectra were investigated. The formulation of the quantum mechanical problem for analysis of high-resolution nuclear magnetic resonance spectra was first discussed. Particular attention has been given to developing a convenient computer program for calculating matrix elements of the high-resolution nuclear magnetic resonance spin-coupling Hamiltonian.

The derivations of general equations for the chemical shifts and spin coupling constants of a number of systems of nuclei with spin 1/2 in terms of the values of the experimental energy levels have been developed and presented. A computer technique for assigning the observed spectral lines to transitions within the energy-level diagram in a manner consistent with equal-spacing and intensity-sum rules has been described. It has been shown that the analysis of many complex NMR spectra can be reduced to the problem of assigning observed spectral lines to the appropriate transitions within schematic energy level diagrams, followed by direct calculation of the desired spin parameters. This computer assignment technique was then applied to examples of two, three, four and five-spin systems to illustrate the procedure.

QUANTUM MECHANICAL ANALYSIS OF HIGH-RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA

By

Yuh-Kang Pan

A THESIS

Submitted to
Michigan State University
in partial fulfullment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1966

9-13-67

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor Max T. Rogers for his counsel and encouragement throughout this work. The author also wishes to thank Professor D. Whitman of the Case Institute of Technology and Professor Y. N. Chiu of the Catholic University of America for helpful discussions.

Thanks are also expressed to the staff of the computer Laboratory of Michigan State University for their valuable cooperation.

He also wishes to express his gratitude to the National Science Foundation and the Atomic Energy Comission for research assistantships and to the Department of Chemistry, Michigan State University for the teaching assistantships.

Special thanks are also due to my wife for her help in some of the calculations and for her encouragement.

****

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

I. PRINCIPLES OF HIGH-RESOLUTION NMR SPECTROSCOPY

I. A. Introduction

The introduction of the molecular beam resonance method (1), which permits a direct measurement of nuclear gyromagnetic ratios, was the first successful application of the nuclear magnetic resonance technique, but it was pointed out at an early stage that it should be possible to observe resonance absorption in other forms of matter (2). The phenomenon of nuclear resonance was first discovered in the condensed phase in 1945 by Purcell, Torrey and Pound (3) at Harvard University and by Bloch, Hansen and Packard (4) at Stanford University. The growth and scope of this new field has been enormous, its uses now extend into many fundamental research branches of physics and chemistry including the structure of solids, study of large local magnetic fields in single crystals, the internal structure of molecules in the liquid and gaseous states, the intermolecular structure of liquids and associated electric and magnetic field effects, chemical kinetics and still others, and its use as an analytical tool has been extensive. This research will investigate the quantum mechanical and algebraic procedures involved in the analysis of high-resolution NMR spectra. The computer assignment technique and the direct calculation method for analysis of NMR spectra will be discussed.

In this chapter an attempt is made to give a very brief discussion of the terminology and principles of nuclear magnetic resonance spectroscopy which will be important in following chapters. For further details on any point, a number of excellent references are available which have covered general theoretical and experimental advances in detail (5-26).

I. B. Nuclear Magnetic Moments

In order to explain the hyperfine structure of some optical spectra, Pauli (27) suggested in 1924 that some nuclei possess an intrinsic angular momentum and magnetic moment. It has been found that only the atomic nuclei with odd atomic number or odd mass number or with both odd atomic number and odd mass number have a nuclear spin and these have integral or odd half-integral spin quantum number. Nuclei with even mass number and even atomic number such as ^{12}C or ^{16}O do not have a nuclear spin so the spin quantum number $I=0$. The spin angular momentum $\vec{p}$ of an atomic nucleus may be characterized by a spin quantum number I, such that the angular momentum is $\vec{I}$ in units $\hbar$. The spin of the positively charged nucleus confers on it a magnetic moment $\vec{\mu}$, which is proportional (28) to $\vec{I}$, and the proportionality constant is γ, the nuclear gyromagnetic ratio (or nuclear magnetogyric ratio):

$$\vec{\mu} = \gamma \vec{I} \hbar = \gamma \vec{p} \qquad (I.\ 1)$$

For a simple particle of mass M and charge e, the value of γ is $g_{\circ} \dfrac{e}{2Mc}$

nance spectroscopy which will be important in following chapters. For further details on any point, a number of excellent references are available which have covered general theoretical and experimental advances in detail (5-26).

I. B. Nuclear Magnetic Moments

In order to explain the hyperfine structure of some optical spectra, Pauli (27) suggested in 1924 that some nuclei possess an intrinsic angular momentum and magnetic moment. It has been found that only the atomic nuclei with odd atomic number or odd mass number or with both odd atomic number and odd mass number have a nuclear spin and these have integral or odd half-integral spin quantum number. Nuclei with even mass number and even atomic number such as ^{12}C or ^{16}O do not have a nuclear spin so the spin quantum number $I=0$. The spin angular momentum $\vec{p}$ of an atomic nucleus may be characterized by a spin quantum number I, such that the angular momentum is $\vec{I}$ in units $\hbar$. The spin of the positively charged nucleus confers on it a magnetic moment $\vec{\mu}$, which is proportional (28) to $\vec{I}$, and the proportionality constant is γ, the nuclear gyromagnetic ratio (or nuclear magnetogyric ratio):

$$\vec{\mu} = \gamma \vec{I} \hbar = \gamma \vec{p} \qquad (I.\ 1)$$

For a simple particle of mass M and charge e, the value of γ is $g \cdot \frac{e}{2Mc}$

and $$\vec{\mu} = g \cdot \frac{e}{2Mc} \cdot \hbar \vec{I} \tag{I. 2}$$

where g is called the nuclear g factor.

From the theory of quantum mechanics (28) we know that $\vec{I}$ has the magnitude $[\, I\,(I+1)]^{\frac{1}{2}}$ but that the only measurable values of this vector are given by the magnetic quantum number m, which may take on any of the (2I+1) values: -I, -(I-1), -(I-2),.....,+(I-1),...., +I. The maximum observable value of $\vec{\mu}$ is , therefore:

$$g \cdot \frac{e\hbar}{2Mc} \cdot I = \mu = g\,\beta_N \cdot I \tag{I. 3}$$

where $\beta_N = e\hbar/2Mc$, and is known as the nuclear magneton. It has the value 5.050×10^{-24} ergs/gauss. The maximum observable value of $\vec{\mu}$ (the above equation) is called "the magnetic moment" of the nucleus and is denoted by the letter μ .

I. C. The Nucleus in a Magnetic Field

In the absence of a magnetic field, all orientations of a nuclear magnet possess the same energy. But when a strong magnetic field, H_o, is supplied, this degeneracy is removed. The energy of a nucleus of magnetic moment $\vec{\mu}$, in the magnetic field H_o is

$$\begin{aligned} E_m &= -\vec{\mu} \cdot \vec{H}_o \\ &= -H_o \times \text{component of } \vec{\mu} \text{ along } H_o \\ &= -H_o \cdot mg\beta_N \end{aligned} \tag{I. 4}$$

There are (2I+1) energy levels, corresponding to the (2I+1) values of m. These energy levels are illustrated in Fig. 1 for the cases of $I = \frac{1}{2}$ and $I = 1$.

The selection rule for transitions among these nuclear energy levels is $m = \pm 1$, so that a quantum of radiation could induce a transition if $$E_{m+1,m} = h\,\nu_0 = E_{m+1} - E_m = g\,H_o\,\beta_N = \frac{\mu H_o}{I} \qquad (I.5)$$

or using the definition of the magnetogyric ratio of equation (I.1),

$$h\,\nu_0 = \gamma\,\hbar\,H_o \quad \text{or} \quad \nu_0 = \frac{\gamma\,H_o}{2\pi} \qquad (I.6)$$

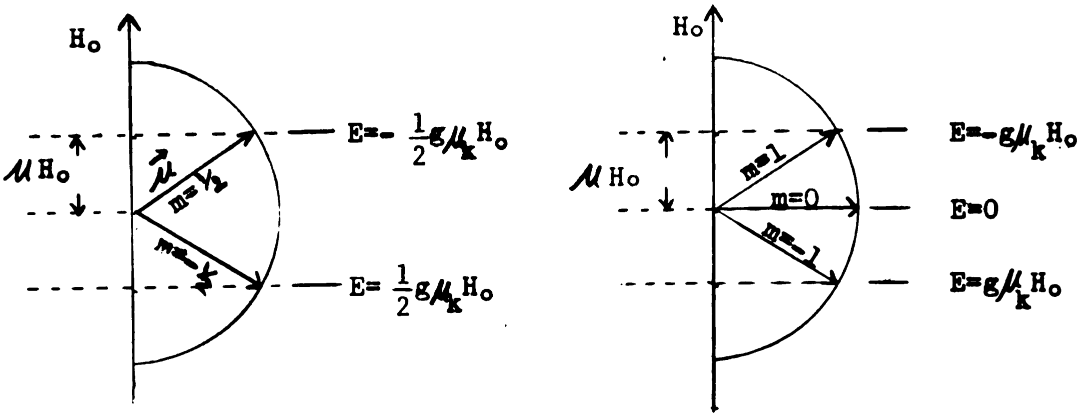


Fig. 1. Energy levels for nuclei with $I=\frac{1}{2}$ and I=1 in the magnetic field.

When transitions are induced between energy levels of this kind, the phenomenon is known as nuclear resonance. If more nuclei are excited from the lower level to the upper than the reverse, then a net amount of energy is absorbed and an NMR spectrum may be observed. From equation (I.6) we note that the frequency is proportional to the applied field. For $H_o = 10^4$ gauss, typical values of ν_0 are given in Table I. The frequencies lie in the radiofrequency region of the spectrum; the experimental procedure is discussed in section (I.E).

The theory of transition probabilities shows that the Einstein transition probability coefficient for the absorption of energy is equal to the probability coefficient for stimulated emission (29). For this reason, any detectable net absorption of energy in a bulk sample

Table I. Typical Values of ν_0 for $H_0 = 10^4$ gauss

Nucleus	I	μ	ν_0 Mc/sec. when $H_0=10^4$ gauss
^1H	$\frac{1}{2}$	2.79270	42.577
^2H	1	0.85738	6.536
^{12}C	0	0.00000	---
^{13}C	$\frac{1}{2}$	0.70216	10.705
^{14}N	1	0.40357	3.076
^{16}O	0	0.00000	---
^{17}O	$\frac{5}{2}$	-1.8930	5.772
^{19}F	$\frac{1}{2}$	2.6273	40.055

requires the existence of a population difference between adjacent energy levels. If there is weak coupling among a group of identical nuclei, and between the nuclei and the remainder of the system, the "lattice", thermal equilibrium may exist, and the energy levels will be populated according to the Boltzmann factor. That is, the ratio of the population of a lower energy level to that of the next higher level will be the factor $e^{\gamma \hbar H_o/kT_s}$ where T_s is the temperature of the spin system. As a typical example, we consider the proton, the ratio of the population of a low energy level $m = \frac{1}{2}$ to that of the next higher level $m = -\frac{1}{2}$ at temperature 27°C and $H_o = 10{,}000$ gauss is $\frac{N_{m=+\frac{1}{2}}}{N_{m=-\frac{1}{2}}} = e^{2\mu H_o/kT_s} \simeq \frac{2\mu H_o}{kT} + 1 \simeq 1.000007$. So, under typical conditions the fractional excess in the lower energy state will be only about 10^{-5}, but it is this small excess which gives rise to an observable net absorption of energy.

As a transition-inducing electromagnetic radiation is applied to a system of nuclear magnetic moments at thermal equilibrium, net absorption will occur, and the excess population in the lower energy levels will rapidly diminish. The net absorption will then disappear, unless some mechanism exists by which nuclei "relax" from the higher to the lower energy levels, thus maintaining thermal equilibrium and the Boltzmann distribution of populations.

I. D. Relaxation

If there is to be a net absorption of energy in the nuclear magnetic resonance experiment, then some mechanisms must exist to promote thermal equilibrium between the populations of the energy levels and the surrounding matter (the lattice) which may be liquid, solid or gas. There exist various possibilities for radiationless transitions by means of which the nuclei can exchange energy with their environment and it can be shown (6) that such transitions are more likely to occur from an upper to a lower state than in the reverse direction. We therefore have the situation in which the applied radiofrequency field is trying to equalize the spin-state equilibrium while radiationless transitions are counteracting this process. In the type of systems of interest to us a steady state is usually reached such that the original Boltzmann excess of nuclei in the lower states is somewhat decreased but not to zero so that a net absorption can still be registered. The various types of radiationless transitions, by means of which nuclei in an upper spin state return to a lower state, are called relaxation processes. We may divide relaxation processes into two categories, namely, spin-lattice relaxation and spin-spin relaxation.

Spin-lattice relaxation (30) is sometimes called longitudinal relaxation (31). This process is responsible for the establishment and maintenance of the absorption condition. The magnetic nuclei are usually part of an assembly of molecules which constitute a sample under investigation and the entire molecular system is referred to as the lattice irrespective of the physical state of the sample. For the moment we will confine our attention to liquids and gases in which the atoms and molecules constituting the lattice will be undergoing random translational and rotational motion. Since some or all of these atoms and molecules contain the magnetic nuclei such motions will be associated with fluctuating magnetic fields. Now, any given magnetic nucleus will be precessing about the direction of the applied field H_o and at the same time it will experience the fluctuating magnetic fields associated with nearby lattice components. The fluctuating lattice fields can be regarded as being built up of a number of oscillating components so that there will be a component which will just match the precessional frequency of the magnetic nuclei. In other words, the lattice motions, by virtue of the magnetic nuclei contained in the lattice, can from time to time generate in the neighborhood of a nucleus in an excited spin state, a field, which like the applied radiofrequency field H_1, is correctly oriented and phased to induce spin-state transitions. In these circumstances a nucleus in an upper spin state can relax to the lower state and the energy lost is given to the lattice as extra translational or rotational energy. The same process is responsible for producing the Boltzmann excess of nuclei in lower states when the sample is first placed in the magnetic field. Since the exchange of energy between nuclei and lattice leaves the total energy of the sample unchanged,it follows that the process must always operate so as to establish the most probable distribution of energy or, in other words, so as to establish the Boltzmann excess of nuclei in lower states. The so called spin-lattice relaxation time T_1 is a measure of the rate at which the spin system comes into thermal equilibrium with the other degree of freedom. It, in effect, is the half-life required for a perturbed system of nuclei to reach an equilibrium condition. The value of T_1 will depend on the magnetogyric ratio (or ratios) of nuclei in the lattice and on the nature and rapidity of the molecular motions which produce the fluctuating fields. Because of the great restriction of molecular motions in the crystal lattice, most highly purified solids exhibit very long spin-lattice relaxation times, often of the order of hours. For liquids the value of T_1 usually lies between 10^{-2} and 10^{2} sec., although in the presence of paramagnetic ions it may be as low as 10^{-4} second.

Spin-spin relaxation or transverse relaxation (3), is a process in which a nucleus in its upper state transfers its energy to a neighbouring nucleus of the same isotope by a mutual exchange of spin. This relaxation process therefore does nothing to offset the equalizing of the spin state populations caused by radiofrequency absorption and is not directly responsible for maintaining the absorption condition.

This relaxation process occurs with a characteristic time T_2 called the spin-spin relaxation time or transverse relaxation time. Both spin-lattice relaxation and spin-spin relaxation processes may control the natural line width of a spectral line.

We have seen that adequate spin-lattice relaxation is a necessary condition for the continued observation of radiofrequency absorption. In practice this condition is not always fulfilled and in such circumstances the observed absorption signal diminishes with time and may, in extreme cases vanish. For example, if the relaxation process is a slow one, or if the perturbing radiofrequency field is strong, the observed absorption signal may vanish. This behaviour is called saturation. This occurs when the populations of all the energy levels are nearly equal, in which case no net absorption of energy occurs.

I. E. The Nuclear Magnetic Resonance Experiment

The apparatus for observing nuclear magnetic resonance absorption of energy consists essentially of four parts:

(1) A magnet capable of producing a very strong homogeneous field.

(2) A means of continuously varying the magnetic field over a very small range.

(3) A radiofrequency oscillator.

(4) A radiofrequency receiver.

The magnet is necessary to produce the condition for the absorption of radiofrequency radiation. The remaining components then have analogues in other method of absorption spectroscopy. Thus the radiofrequency oscillator is the source of radiant energy. The device for varying the magnetic field over a small range corresponds to a prism or grating in as much as it permits us to scan the spectrum and determine the positions of absorption lines in terms of frequency or field strength. The radiofrequency receiver is the device which tell us when energy from the source is being absorbed by the sample.

A sample containing nuclei which possess magnetic moments is placed between the poles of a magnet of magnetic field strength H_o. The magnetic moments of the nuclei in the sample tend to orient in the direction of the field, giving rise to a resultant macroscopic magnetic moment. The effect of the magnetic field is to cause a precession of the macroscopic moment about the direction of the field with an angular frequency γH_o. If now a small coil, connected to an rf signal generator, is wound around the sample so that the axis of the coil is at right angles to the direction of the applied field, there is introduced a small alternating magnetic field of strength H_1 which rotates about the H_o direction with the particular radio frequency used. The field H_1 tends to tilt the direction of the macroscopic moment away from the H_o direction as the radiofrequency approaches the precession frequency; at the resonant frequency, transitions are induced between the nuclear Zeeman levels. These transitions correspond to some of the nuclear magnets changing their orientation in the field. The energy absorbed in this process produces a drop in rf voltage in the tuned circuit containing the transmitter coil; the voltage drop may be detected, amplified, and fed into the vertical deflection plates of an oscilloscope. In practice, the radio frequency of the signal generator is usually fixed and the applied field H_o is varied near the value at which resonance occurs. This is accomplished by mounting, on the pole faces of the magnet, coils which can be used to sweep the field with an amplitude of a few gauss at some low frequency (about 50 cps). The same sweep signal can be fed into the horizontal deflection plates an oscilloscope, and the recurring absorption signal is displayed on the screen.

I. F. Chemical Shift

The nuclear resonance frequency of a particular nucleus occurs at different values of a given applied magnetic field, according to the nature of the chemical compound containing the nucleus. These frequency differences have therefore been called "chemical shifts". In equation (I.5), H_o refers to the magnetic field actually experienced by the nucleus and this is not equal to the applied magnetic field, H, when the nucleus is present in a chemical compound. The reason is that when any chemical substance is placed in a magnetic field, weak currents are induced in the electron clouds surrounding the nuclei. These induced currents flow according to Lenz's law in such a way as to set up a magnetic moment which opposes the applied fields, and it is this effect which is responsible for the bulk diamagnetism of all matter. These weak induced diamagnetic moments reduce the field experienced by the nucleus to a value smaller than the applied field, and it is usual to express this effect as

$$H_o = H (1 - \sigma) \qquad (I.7)$$

where σ represents the factor by which H is modified by the induced diamagnetism. Equation (I.5) is then written ;

$$h\nu_0 = \frac{\mu H}{I} (1 - \sigma) \qquad (I.8)$$

and the parameter σ is known as the "chemical shift" or magnetic shielding constant. The chemical shift is dependent upon the externally applied field, becoming larger with increasing field strength.

I. G. Spin-Spin Interactions

In NMR spectra the absorption lines are usually affected by interactions between the nuclei and between the nuclei and their environment. These interactions can be classified as dipole-dipole interactions, electric quadrupole coupling, and electron coupled spin-spin interactions.

Dipole-dipole interactions between neighboring nuclear magnetic moments are dependent upon separation and relative orientations of the nuclear moments. Thus, instead of all nuclei experiencing the same uniform magnetic field H_o, different nuclei in a specimen will experience various fields spread over a range of frequencies and the spectral line will be broadened. These considerations are effective, however, only if the nuclei maintain the same orientation relative to one another and to the external field, as in solids. In liquids and gases, where the molecules are rotating and tumbling about rapidly, the magnetic field at any one nucleus due to the others effectively averages out to zero. The cause of the magnetic dipole broadening (dipole-dipole interaction) is removed by this averaging and the resonance signals become much sharper. In solids, since nuclei for which $I = \frac{1}{2}$ have no electric quadrupole moment, the dipole-dipole coupling is usually the dominant mechanism for line broadening. In a solid containing nuclei ($I = \frac{1}{2}$) grouped in relatively isolated pairs, each nucleus experiences a magnetic field whose direction is taken as the z-axis $H_o \pm H_{local}$, where H_{local} is the local magnetic field set up by one nuclear magnet in the region of the other. For dipoles of moment μ at a distance r apart and with the internuclear vector making an angle θ with H_o (which is parallel to the z-axis)

$$H_{local} = \frac{\mu}{r^3}(3 \cos^2\theta - 1) \qquad (I.9)$$

so that $H = H_o \pm \frac{\mu}{r^3} (3 \cos^2\theta - 1).$ (I.10)

The nuclear resonance spectrum would therefore be expected to be a pair of lines at frequencies separated by

$$\frac{2\mu}{r^3} (3 \cos^2\theta - 1). \qquad (I.11)$$

In fact, however, there is an additional quantum mechanical interaction which in this case leads to a pair of lines separated by

$\frac{3\mu}{r^3} (3 \cos^2\theta - 1)$, for pairs of identical nuclei. (I.12)

The detailed shape of this pair of lines has been obtained by Pake (32) by a simple quantum mechanical perturbation calculation using the dipole-dipole interaction Hamiltonian:

$$\mathcal{H} = r^{-3}[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3r^{-2} (\vec{\mu}_1 \cdot \vec{r}) (\vec{\mu}_2 \cdot \vec{r})], \qquad (I.13)$$

where r is the internuclear distance and $\vec{r}$ is the unit vector. For two protons at a distance of 1Å, the doublet separation is of the order of 10 gauss or 42 kc/sec at 10,000 gauss field. If the pair of nuclei are not identical the line separation is then

$$\frac{2\mu}{r^3} (3 \cos^2\theta - 1). \qquad (I.14)$$

In a single crystal containing pairs of nuclei with the internuclear vectors all pointing in the same direction, the doublet separation varies from $\frac{3\mu}{r^3}$ when θ is $\frac{\pi}{2}$ to $\frac{6\mu}{r^3}$ when $\theta = 0$. From the variation of the doublet separation with the orientation of the crystal in the magnetic field, the directions of the H-H vectors in the crystal can be found, and from the spacing of the doublet r can be deduced. When the nuclei are grouped in a crystal in more complicated arrangements than those described above, the absorption line is often a broad and shapeless hump. Van Vleck (33) showed that useful information can still be derived. Rigorous expressions were obtained for the second and fourth moments of the absorption line in terms of the internuclear distances in the crystals.

Nuclei for which $I > \frac{1}{2}$ usually have an electric quadrupole moment (7). This is a measure of the deviation from spherical symmetry of the electric charge distribution within the nucleus. If the positive charge is spread over a prolate spheroid, the quadrupole moment is said to be positive; if the charge is spread over an oblate spheroid, the quadrupole moment is taken to be negative. Nuclei with $I = \frac{1}{2}$ have no electric quadrupole moment, therefore NMR experiments on these nuclei are not complicated by direct interactions of the nuclear spin with the electrical environment.

When a number of liquids were examined by NMR spectroscopy, it was found that certain substances showed more lines than could be explained by means of the chemical shift alone. For example, Gutowsky, McCall and Slichter (34) found that the fluorine resonance spectrum of $POCl_2F$ consists of two lines of equal intensity, although there is only one fluorine atom in the molecule. Other molecules gave symmetrical multiplet signals. These multiplicities were attributed by Gutowsky, McCall and Slichter (34), and by Hahn and Maxwell (35), to an interaction between the nuclear spins which is proportional to the scalar product $\vec{I}_i \cdot \vec{I}_j$ where $\vec{I}_i$ and $\vec{I}_j$ are the nuclear spin vectors. Unlike the direct interaction of magnetic dipoles (dipole-dipole interaction) an energy of this sort does not average to zero when the molecules are in rapid random motion, so its effect is still observable in the spectra of liquids and solutions. Furthermore, the splitting of the lines which results from this interaction is independent of the applied magnetic field, in contrast to the separation of chemically shifted lines which is proportional to it. The interpretation of these interactions was first given by Ramsey and Purcell (36) and by Ramsey (37). They showed that they arise from an indirect coupling mechanism via the electrons in the molecule. Thus a nuclear spin tends to orient the spins of the electrons and consequently spins of other nuclei. The magnitudes of the spin-interaction energies are usually expressed in cycles per second (cps). Observed interaction energies vary from about 1,000 cps to small values at the limit of experimental detection (<1 cps).

The way in which the spin-spin coupling affects the NMR spectrum can be seen easily for the simple case of a pair of unlike nuclei, A and B, coupled together. From equations (I.1) and (I.4) the energy of interaction of the nucleus with the strong field H_0, taken to be along the z-axis, is $-\hbar \cdot \gamma \cdot m H_0(1- \sigma)$ (I.15)

For a system of two particles with no spin coupling, the Hamiltonian for interaction with a static field H_0 in the z-direction is therefore

$$\mathcal{H} = -\hbar[\gamma_A H_0(1-\sigma_A)\, I_{zA} + \gamma_B H_0(1-\sigma_B)\, I_{zB}\ . \qquad (I.16)$$

If we take ν_0 as the mean of the two resonance frequencies, and δ as an interaction between the nuclear spins which is proportional to the scalar product $\vec{I}_i \cdot \vec{I}_j$ where $\vec{I}_i$ and $\vec{I}_j$ are the nuclear spin vectors. Unlike the direct interaction of magnetic dipoles (dipole-dipole interaction) an energy of this sort does not average to zero when the molecules are in rapid random motion, so its effect is still observable in the spectra of liquids and solutions. Furthermore, the splitting of the lines which results from this interaction is independent of the applied magnetic field, in contrast to the separation of chemically shifted lines which is proportional to it. The interpretation of these interactions was first given by Ramsey and Purcell (36) and by Ramsey (37). They showed that they arise from an indirect coupling mechanism via the electrons in the molecule. Thus a nuclear spin tends to orient the spins of the electrons and consequently spins of other nuclei. The magnitudes of the spin-interaction energies are usually expressed in cycles per second (cps). Observed interaction energies vary from about 1,000 cps to small values at the limit of experimental detection (<1 cps).

The way in which the spin-spin coupling affects the NMR spectrum can be seen easily for the simple case of a pair of unlike nuclei, A and B, coupled together. From equations (I.1) and (I.4) the energy of interaction of the nucleus with the strong field H_o, taken to be along the z-axis, is $-\hbar \cdot \gamma \cdot m H_o(1- \sigma)$ (I.15)

For a system of two particles with no spin coupling, the Hamiltonian for interaction with a static field H_o in the z-direction is therefore

$$\mathcal{H} = -\hbar[\gamma_A H_o(1- \sigma_A)\, I_{zA} + \gamma_B H_o(1- \sigma_B)\, I_{zB} \,. \qquad (I.16)$$

If we take ν_o as the mean of the two resonance frequencies, and δ as an interaction between the nuclear spins which is proportional to the scalar product $\vec{I}_i \cdot \vec{I}_j$ where $\vec{I}_i$ and $\vec{I}_j$ are the nuclear spin vectors. Unlike the direct interaction of magnetic dipoles (dipole-dipole interaction) an energy of this sort does not average to zero when the molecules are in rapid random motion, so its effect is still observable in the spectra of liquids and solutions. Furthermore, the splitting of the lines which results from this interaction is independent of the applied magnetic field, in contrast to the separation of chemically shifted lines which is proportional to it. The interpretation of these interactions was first given by Ramsey and Purcell (36) and by Ramsey (37). They showed that they arise from an indirect coupling mechanism via the electrons in the molecule. Thus a nuclear spin tends to orient the spins of the electrons and consequently spins of other nuclei. The magnitudes of the spin-interaction energies are usually expressed in cycles per second (cps). Observed interaction energies vary from about 1,000 cps to small values at the limit of experimental detection (<1 cps).

The way in which the spin-spin coupling affects the NMR spectrum can be seen easily for the simple case of a pair of unlike nuclei, A and B, coupled together. From equations (I.1) and (I.4) the energy of interaction of the nucleus with the strong field H_o, taken to be along the z-axis, is $-\hbar \cdot \gamma \circ m H_o (1- \sigma)$ (I.15)

For a system of two particles with no spin coupling, the Hamiltonian for interaction with a static field H_o in the z-direction is therefore

$$\mathcal{H} = -\hbar[\gamma_A H_o(1- \sigma_A)\, I_{zA} + \gamma_B H_o(1- \sigma_B)\, I_{zB} \, . \qquad (I.16)$$

If we take ν_o as the mean of the two resonance frequencies, and δ as the chemical shift between them, this can be re-written:

$$\mathcal{H} = -\hbar[(\nu_o - \frac{1}{2}\delta) I_{zA} + (\nu_o + \frac{1}{2}\delta) I_{zB}] . \qquad (I.17)$$

The energy levels are therefore,

$$E_{m_A m_B} = -\hbar[(\nu_o - \frac{1}{2}\delta) m_A + (\nu_o + \frac{1}{2}\delta) m_B] . \qquad (I.18)$$

The energy levels are shown in Fig. 2 (a), and if the allowed transitions are $\Delta m_A = 1$ and $\Delta m_B = 1$, we obtain two lines in the spectrum, separated by the chemical shift δ , each of the two lines being doubly degenerate.

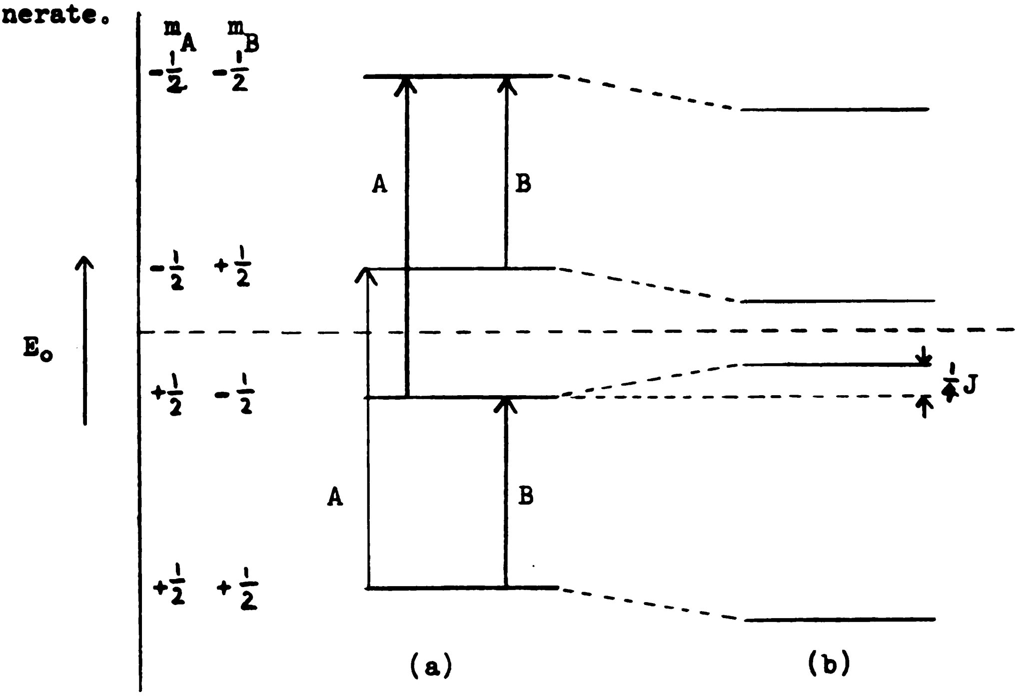


Fig. 2.

If the two nuclei are coupled together, the Hamiltonian now becomes:

$$\mathcal{H} = -\hbar[(\nu_o - \frac{1}{2}\delta) I_{zA} + (\nu_o + \frac{1}{2}\delta) I_{zB}] - \hbar J \vec{I}_A \cdot \vec{I}_B \qquad (I.19)$$

where J is the coupling constant in cps. If J is very much smaller than δ , the last term in equation (I.19) can be treated as a small perturbation on $\mathcal{H}$, so that m_A and m_B remain good quantum numbers, and we can write

$$E = -h[(\nu_o - \frac{1}{2}\delta) m_A + (\nu_o + \frac{1}{2}\delta) m_B + J m_A m_B] \qquad (I.20)$$

The energy levels are now as in Fig. 2 (b) and transitions of nuclei A and

B give energy changes of $\Delta E_A = h(\nu_o - \frac{1}{2}\delta + Jm_B)$ and $\Delta E_B = h(\nu_o + \frac{1}{2}\delta + Jm_A)$, respectively. The perturbation has lifted the degeneracy of the two lines which are split by J cps. Note that the resonance due to the A nuclei is split according to the values m_B of the B nuclei and vice-versa.

If the two nuclei A and B are entirely equivalent ($\delta = 0$), then no splitting of the lines can be observed and only a single resonance occurs. This is because the now indistinguishable nuclei must be described by writing wave functions which are either symmetric or antisymmetric in the spin, as in describing the ortho and para states of hydrogen. The singlet state with $I = 0$ has no magnetic sublevels and the triplet state has $m = +1$, 0 and -1. However, all the sublevels of the triplet have $\vec{I}_A \cdot \vec{I}_B = +\frac{1}{4}$, so that the interaction shifts them all equally and produces no observable splitting.

In the case of the proton resonance spectrum of acetaldehyde (CH_3CHO), there are two sets of equivalent nuclei, one in the CHO group (A) and the other in the CH_3 group (B). Since the protons of the CH_3 group are indistinguishable we must treat them as a group with $M_B = \Sigma m_B$. The energy changes are then found to be:

CHO group: $\Delta E_A = h(\nu_o - \frac{1}{2}\delta + JM_B)$; CH_3 group: $\Delta E_B = h(\nu_o + \frac{1}{2}\delta + Jm_A)$. Now m_A can take on the values $\pm\frac{1}{2}$, so that the CH_3 resonance is a doublet, and since the two values of m_A are equally probable, the two components of the doublet are of equal intensity. M_B can take on the values $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$ by combination of the three B spins:

$$
\begin{array}{llll}
+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}, & +\frac{1}{2}+\frac{1}{2}-\frac{1}{2}, & +\frac{1}{2}-\frac{1}{2}-\frac{1}{2}, & -\frac{1}{2}-\frac{1}{2}-\frac{1}{2} \\
 & +\frac{1}{2}-\frac{1}{2}+\frac{1}{2}, & -\frac{1}{2}+\frac{1}{2}-\frac{1}{2}, & \\
 & -\frac{1}{2}+\frac{1}{2}+\frac{1}{2}, & -\frac{1}{2}-\frac{1}{2}+\frac{1}{2}, &
\end{array}
$$

The CHO resonance is therefore a quartet, and since the values $+\frac{1}{2}$ and $-\frac{1}{2}$ of M_B can be achieved in three times as many ways as the values $+\frac{3}{2}$ and $-\frac{3}{2}$, the intensities of the quartet lines are in the ratio 1:3:3:1. In the general case for a set of N_A equivalent nuclei of type A interacting with N_X equivalent nuclei of type X, the A signal has $2N_XI_X + 1$ components and the X signal has $2N_AI_A + 1$ components. The relative intensities of each group of signals are in the ratio of the corresponding binomial coefficients. The A and X nuclei may belong to different species, or they may be of the same species if the chemical shift between their resonance signals is large. When the value of J is not small compared with δ, then it can no longer be considered as a simple perturbation and an exact calculation must be made. The methods for the analysis of complex spectra will be discussed in Chapters III and IV.

I. H. Classification of Nuclear Groups

It is convenient to introduce a notation for typical groups of nuclei which may appear in molecules and which will possess characteristic NMR spectra. First of all we should distinguish between isochronous nuclei and equivalent nuclei (38). Isochronous nuclei are those which have exactly the same chemical shift; while equivalent nuclei not only have the same chemical shift but are also identically coupled to all other nuclei in the system. A pair of nuclei can be equivalent only if they are isochronous. There is a well known theorem stating that scalar couplings between equivalent nuclei are unobservable in an NMR experiment (18, 23). The proof of this theorem does not depend on symmetry in any way. The importance of the distinction between isochronous and equivalent nuclei lies in the fact that the total spin angular momentum of a group of equivalent nuclei is a good quantum number. As a consequence, the NMR spectrum of a molecule containing a group of equivalent nuclei consists of a superposition of spectra arising from the various "spin particles" formed by the equivalent nuclei. This observation makes direct analysis of spectra of this type much simpler, once assignment of spectral lines to the corresponding transitions within the appropriate energy-level diagrams is accomplished. We shall use the symbols A, B, ··· for nonequivalent nuclei of the same species whose relative chemical shifts are of the same order of magnitudes as the spin couplings between them. X, Y, ··· will be used for another such set whose signals are not close to those of the set A, B, ··· The nuclei in the set X, Y, ··· may or may not be of the same species as those in the set A, B, ···, the only feature that is important in the theory is that the chemical shift between the groups A, B, ··· and X, Y, ··· is large compared with any of the spin couplings. Equivalent nuclei will be described by the same symbol. Thus, 1,1,1-trifluoroethane (CH_3CF_3) is an example of an A_3X_3 system since the carbon nuclei have no magnetic moment and may be ignored. The protons in 1-bromoethane (CH_3CH_2Br) form two groups of equivalent protons and are described as an A_3B_2 system, for the chemical shift between the three protons in CH_3-group and the two protons in CH_2-group is observed to be relatively small. o-Dichlorobenzene protons, on the other hand, constitute a system of two groups of isochronous protons and would be represented as AA'BB'. Here we notice that the primes on A and B are used to describe nuclei that are isochronous but not equivalent.

II. FORMULATION OF THE QUANTUM-MECHANICAL PROBLEM

The fundamental procedure involved in the analysis of NMR spectra consists of finding the energies and transition intensities corresponding to the stationary states of the nuclear spin system. The basic quantum-mechanical method of finding expressions for the nuclear energy levels of the system of interest, together with expressions for the relative transition probabilities between these levels, is quite similar to the methods that have been extensively employed in other field of spectroscopy (e.g., infrared, ultraviolet etc.). This requires deriving or hypothesizing a satisfactory Hamiltonian for the system of nuclear magnetic moments in magnetic field and solving the Schrödinger equation for the eigenvalues of this Hamiltonian, which are the desired levels of the system. Usually, the exact Hamiltonian for the energy of a molecule is simplified in some way so as to give an approximate Hamiltonian; the approximate Hamiltonian is chosen to be as accurate as possible and, at the same time, to be such that the Schrödinger equation can be solved exactly and conveniently. The zero-order energies and wavefunctions thus obtained are then used as a starting point for a more accurate calculation of energies and wave functions using, in so far as possible, a complete exact Hamiltonian. This latter calculation is, in many cases, greatly simplified by selecting the zero-order wave functions to be eigenfunctions of all those molecular properties that commute with the complete Hamiltonian. Molecular symmetry and spin or rotational angular momenta are typical of such molecular properties. The exact wave functions and energies are also commonly classified according to such molecular properties inasmuch as the spectroscopic selection rules are generally conveniently formulated in terms of such classifications. Also the classification of energy states according to these molecular properties often enables one to predict how transition energies and intensities will behave under specified perturbations.

II. A. Hamiltonian

It has been well established that high-resolution NMR spectra (omitting relaxation effects) are fully accounted for by the following spin Hamiltonian (18, 34, 36, 37):

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} . \tag{II.1}$$

$\mathcal{H}^{(0)}$, the external-field Hamiltonian, corresponds to the interaction of the nuclear moments with the external field. If the direction of the strong magnetic field H is the "negative" z-direction, the energy of a nucleus in this field will be $\gamma\hbar H I_z$, measured in ergs if H is measured in gauss. The more convenient unit for measurement will be cps. With this unit, the interaction becomes $\gamma H I_z/2\pi$. For a set of nuclei with magnetogyric ratios γ_i and acted on by field H_i, the external-field Hamiltonian will be

$$\mathcal{H}^{(0)} = (2\pi)^{-1} \sum_i \gamma_i H_i I_z(i) . \tag{II.2}$$

Where γ_i will depend only on the species of nucleus and $I_z(i)$ is the angular momentum component in the z-direction (in units of $\frac{h}{2\pi}$). For nuclei of spin $\frac{1}{2}$, $I_z(i)$ can take values $+\frac{1}{2}$ or $-\frac{1}{2}$. The sign convention is such that the external field is in the negative z-direction so that nuclei with positive spins have high energies. The magnetic field H_i will differ from the external field H_0 because of electronic screening. Thus, we write $H_i = H_0(1-\sigma_i)$, where σ_i is the appropriate screening constant. Because the theoretical presentation is simpler, we shall discuss the set of energy levels when the external field H_0 is held constant although, as we have already mentioned, the experiment is usually performed by varying H_0 to get the resonance at a fixed frequency.

The other part of the Hamiltonian corresponds to the indirect spin coupling and can be written:

$$\mathcal{H}^{(1)} = \sum_{i>j} J_{ij} \vec{I}(i)\cdot\vec{I}(j) \qquad (\text{II.3})$$

where $\vec{I}(i)$ is the spin angular momentum vector (in units $\frac{h}{2\pi}$) and J_{ij} is the coupling constant between nuclei i and j and will have the dimensions of energy (cps).

In the presence of a perturbing rf field, $H_x = 2H_1 \cos \omega t$, along the x-axis, it is necessary to include a third term in the Hamiltonian:

$$\mathcal{H}^{(2)} = -\frac{\gamma h}{2\pi} \sum_{i=1}^{n} \vec{I}(i) \vec{H}_x \qquad (\text{II.4})$$

However, to avoid saturation H_x is kept very small in practice and this term may be neglected in the complete spin Hamiltonian. So the complete spin Hamiltonian is:

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

$$= (2\pi)^{-1} \sum_i \gamma_i H_i I_z(i) + \sum_{i>j} J_{ij} \vec{I}(i)\cdot\vec{I}(j) \qquad (\text{II.5})$$

II. B. Spin Functions, Basic Product Functions and Basic State Wavefunctions

We write α for the spin function of the nuclei with spin quantum number $\frac{1}{2}$ and β for nuclei with spin quantum number $-\frac{1}{2}$. If the system contains N nuclei (all with spin $\frac{1}{2}$), there will be a total of 2^N

possible spin states. The simplest set of functions describing this many-spin system would be the 2^N basic product functions such as $\psi_n = \alpha(1)\ \beta(2)\alpha(3)\ \ldots\ldots\ \beta(N)$. This product will usually be shortened to $\alpha\beta\alpha\ \ldots\ldots\ \beta$, it being implied that the r^{th} symbol applies to the r^{th} nucleus. If the nuclei were actually independent, the basic product functions would themselves be stationary-state wavefunctions (or basic state wavefunctions) in the presence of the external magnetic field. The only constant of the motion in this case is I_z, the total z-component of spin. However, the spin-coupling Hamiltonian $\mathcal{H}^{(1)}$ may cause mixing between different product functions. Since the various basic product functions ψ_n are all orthogonal to one another, the correct basic state wavefunctions are the linear combinations of the basic product functions which diagonalize the matrix of the complete spin Hamiltonian. The coefficients in the linear combinations of the basic product functions may be obtained from the secular equations by substituting the roots and normalizing. It often happens that in a molecule there are several equivalent nuclei as far as equation (I.5) is concerned. These are treated as groups of equivalent nuclei κ, λ,... having resultant angular momenta $\vec{K} = \Sigma \vec{I}_i.(\kappa)$ etc., and having the coupling constants $J_{\kappa\lambda\ldots}$ between groups and the couplings $J_{ij}(\kappa)$ between nuclei in the same group. We can then write

$$\mathcal{H} = (2\pi)^{-1} \sum_i \gamma_i H_i I_z(i) + J_{\kappa\lambda}\, \vec{K}(\kappa)\cdot\vec{L}(\lambda) + \sum_{\substack{ij\\(\kappa)}} J_{ij}\vec{I}(i)\cdot\vec{I}(j) + \sum_{\substack{i,j\\(\lambda)}} J_{ij}\vec{I}(i)\cdot\vec{I}(j) \quad \text{(II.6)}$$

Now it can be shown (18) that a selection rule on the resultant spins of the group prevents any effects of the intra-group couplings from being manifested in the spectrum. Therefore all these couplings may be set equal to zero for simplicity. The remainder of $\mathcal{H}$ in equation (II.6) is then seen to be identical to equation (II.5) if we treat $\vec{K}$ and $\vec{L}$ in the same way as the spins of individual nuclei. We can then take advantage of the spin groups in evaluation of matrix elements and obtain a significantly better factorization of the secular equation if we use basic functions which are eigenfunctions of K^2, K_z ......, just as the spin functions α and β are eigenfunctions of $I^2(i)$, $I_z(i)$ for individual nuclei. The basic product functions are eigenfunctions of K_z but not K^2. Linear combinations of them which satisfy this additional requirement can be constructed using the projection operators proposed by Löwdin (39, 40, 41):

$$\mathcal{O}_{km} = (2k+1)\frac{(k+m)!}{(k-m)!}\sum_{\nu=0}^{k_{max}-k}(-1)^{\nu}\frac{M_-^{k-m+\nu}\;M_+^{k-m+\nu}}{\nu!\,(2k+\nu+1)!}\,, \tag{II.7}$$

where k and m are quantum numbers which go with K^2 and K_z, and k_{max} is the maximum value of k consistent with group of spin κ. The raising and lowering operators M_+ and $M-$ may be symmetrically expanded in terms of the individual I_{+i}, whose matrix elements are known, by the multinomial theorem. The operator $\mathcal{O}_{k,m}$ operating on a product function of known m turns it into a simultaneous eigenfunction of K^2. For example, if $\mathcal{O}_{k,m}$ operate on $\alpha\alpha\alpha\beta$, $k_{max} = \frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2} = 2$, $k = 1$, $m_k = 1$, thus:

$$\mathcal{O}_{11} = 3\cdot 2!\sum_{\nu=0}^{2-1}(-1)^{\nu}\frac{M_-^{\nu}\;M_+^{\nu}}{\nu!(\nu+3)!} = 3!\left(\frac{1}{3!}+\frac{M_-\;M_+}{1!\;4!}\right)$$

$$\mathcal{O}_{11}\alpha\alpha\alpha\beta = 3!\left[\frac{\alpha\alpha\alpha\beta}{3!}+\frac{(-1)M_-M_+}{4!}\alpha\alpha\alpha\beta\right] = 3!\left[\frac{\alpha\alpha\alpha\beta}{3!}-\frac{M_-}{4!}(\alpha\alpha\alpha\beta)\right]$$

$$= 3!\left[\frac{\alpha\alpha\alpha\beta}{3!}-\frac{1}{4!}(\beta\alpha\alpha\alpha+\alpha\beta\alpha\alpha+\alpha\alpha\beta\alpha+\alpha\alpha\alpha\beta)\right]$$

$$= \frac{1}{4}(3\alpha\alpha\alpha\beta-\beta\alpha\alpha\alpha-\alpha\beta\alpha\alpha-\alpha\alpha\beta\alpha)$$

When degeneracies arise, the degenerate functions may be orthogonalized by standard methods (40, 41). When the number of spins in a group is large it may become awkward to handle the basic functions described above. It very often happens that several nuclei in a molecule have the same chemical shift but each nucleus does not identically couple to all other nuclei in the system (i.e., isochronous nuclei, see section I. H.). For example, in $CH_2 = CF_2$ both protons must have the same chemical shift, but each is in a different relation to the F^{19} nuclei individually. Under such circumstances the H-H spin coupling cannot be ignored and the above simplification is not valid. In this case nothing is necessarily gained by using the basic spin wavefunctions which are eigenfunctions of the squared-group angular momenta. It is profitable, however, to make them eigenfunctions of the symmetry operations of the molecular point group; that is, use is made of sets of basic spin wavefunctions that belong to the irreducible representations of the symmetry group. Methods for setting up the desired basic functions are discussed by McConnell et al. (42), by Pople et al. (18) and in detail, by Wilson(43). As an example, the three hydrogen atoms (numbered 1, 2, 3) in sym-trifluorobenzene can interact through the terms

$$\mathcal{H}_H^{(1)} = J_H[\, \vec{I}(1)\cdot\vec{I}(2) + \vec{I}(2)\cdot\vec{I}(3) + \vec{I}(3)\cdot\vec{I}(1)] . \qquad \text{(II.8)}$$

Consider the three product functions for these H nuclei, for the case $m_H = \frac{1}{2}$, i.e, $\beta\alpha\alpha$,$\alpha\beta\alpha$,$\alpha\alpha\beta$. These can be combined to form one A_1 combination and one pair in E [A_1 is one-dimensional group representation; while E is two-dimensional group representation (46)]. To construct the actual linear combinations (symmetry basic spin wavefunctions) it is convenient to use the formula (44):

$$\psi^{(\gamma)} = \eta\sum_P \chi P^{(\gamma)} P\, \phi_1 \qquad \text{(II.9)}$$

in which $\psi^{(\gamma)}$ is a symmetry combination of species Γ_γ , η is a normalizing factor, $\chi P^{(\gamma)}$ is the character for the permutation P and species Γ_γ [available in tables (44)], ϕ_1 is one of the product functions (here $\beta\alpha\alpha$ for the H nuclei), and $P\,\phi_1$ is the function formed from ϕ_1 by applying the permutation P. The sum is over the whole group. In the present case there results for the three hydrogen nuclei:

$$\psi_H^{(A1)} = \left(\frac{1}{3}\right)^{\frac{1}{2}} (\beta_1\alpha_2\alpha_3 + \alpha_1\beta_2\alpha_3 + \alpha_1\alpha_2\beta_3)$$

$$\psi_H^{(E_a)} = \left(\frac{1}{6}\right)^{\frac{1}{2}} (2\beta_1\alpha_2\alpha_3 - \alpha_1\beta_2\alpha_3 - \alpha_1\alpha_2\beta_3) = h_a . \qquad \text{(II.10)}$$

It is often not necessary to construct the other member of the degenerate E pair (abbreviated notation h_b), but in case it is, it can be done by applying the same formula but using ϕ_2 ($= \alpha_1\beta_2\alpha_3$) instead of ϕ_1($= \beta_1\alpha_2\alpha_3$), then forming the linear combination of the resulting function with $\psi_H^{(E_a)}$ in the foregoing so as to obtain a function orthogonal to $\psi_H^{(E_a)}$. The result is

$$\psi_H^{(E_b)} = \left(\frac{1}{2}\right)^{\frac{1}{2}} (\alpha_1\beta_2\alpha_3 - \alpha_1\alpha_2\beta_3) = h_b . \qquad \text{(II.11)}$$

II. C. Matrix Elements

The calculation of matrix elements of the NMR spin Hamiltonian (equation II.5) between basic state wavefunctions (or basic symmetry state wavefunctions) is one of the preliminary steps for the detailed analysis of high resolution NMR spectra. Since each basic product function is itself an eigenfunction of each term in the external-field Hamiltonian, the diagonal matrix elements of this part are simply obtained by replacing $I_z(i)$ in this part by $\pm \frac{1}{2}$ according to whether the corresponding spin function is α or β; and there are no off-diagonal matrix elements of external-field Hamiltonian between the basic product functions. There will, however, be both diagonal and off-diagonal matrix elements of the spin coupling Hamiltonian between the basic product functions. McConnell et al. (42) have shown some relatively simple rules that can be used in the evaluation of non-zero matrix elements involving spin-spin interactions, i.e., the matrix elements of the spin coupling Hamiltonian between basic (symmetry) wavefunctions. In the evaluation of a matrix element of the type

$$< \Phi_m^o | \sum_{i<j} J_{ij}\vec{I}(i)\cdot\vec{I}(j) | \Phi_n^o >$$

there occur many terms of the type

$$< \psi_p | \sum_{i<j} J_{ij}\vec{I}(i)\cdot\vec{I}(j) | \psi_q >$$

where the ψ_p and ψ_q are single products of spin functions such as $\alpha\beta\alpha\alpha$ ......(basic product functions). These integrals are easily evaluated by the equations

$$< \psi_p | \sum_{i<j} J_{ij}\vec{I}(i)\cdot\vec{I}(j) | \psi_p > = \frac{1}{4} \sum_{i<j} J_{ij}T_{ij} \qquad \text{(II.12)}$$

where $T_{ij} = +1$ if spins i and j are parallel, and $T_{ij} = -1$ if spins i and j are antiparallel, and

$$< \psi_p | \sum_{i<j} J_{ij}\vec{I}(i)\cdot\vec{I}(j) | \psi_q > = \frac{1}{2} UJ_{ij} \qquad \text{(II.13)}$$

where U = 1 if ψ_p only differs from ψ_q in the permutation of spins i and j, and U = 0 in all other cases. If the basic set consists of some linear combinations of products, corresponding matrix elements are easily evaluated by expansion. The evaluation of these matrix elements of the spin-coupling Hamiltonian is a relatively simple problem with but three or four nuclei; with five or more spins, however there is considerable labor and tedious work involved. Corio (45) has proposed a method to simplify the calculations, but the calculation still must be done manually. A new method which employs a digital computer to evaluate the matrix elements of the spin-coupling Hamiltonian is proposed in the following sections.

II. C-a. Glossary of Definition and Notations

J: The number of basic state wavefunctions, e.g., the two spin system has four states ($2^2 = 4$), so the maximum value of J is 4. $\psi_1 = \alpha\alpha$, $J = 1$; $\psi_2 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$, $J = 2$;...etc.

K: The number of basic product functions in a basic state wavefunction due to degeneracy. $K = 1, \ldots, M(J)$, e.g., in $\psi_2 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$, $(\frac{1}{\sqrt{2}})\alpha\beta$ has $J = 2$, $K = 1$; $(\frac{1}{\sqrt{2}})\beta\alpha$ has $J = 2$, $K = 2$.

L: The number of spin functions, $L = 1, \ldots, N$ in a basic product function. e.g., in $\psi_2 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$ the spin function α in the first term of the right side of the equation has $J = 2$, $K = 1$, $L = 1$.

I: The total number of states (or basic state wavefunctions), e.g., two spin system has a total of four states ($2^2 = 4$) (or four basic state wavefunctions); $J = 1, 2, \ldots, I$.

N: The total number of spins; e.g., for the two spin system, $N = 2$.

M(J): The total number of basic product functions in the state J; e.g., for the two spin system in state $J = 1$, ψ_1 has only one basic product function $\alpha\alpha$, so $M(J) = M(1) = 1$; while in state $J = 2$, ψ_2 has two basic product functions, namely, $(\frac{1}{\sqrt{2}})\alpha\beta$ and $(\frac{1}{\sqrt{2}})\beta\alpha$, so $M(J) = M(2) = 2$, and $(\frac{1}{\sqrt{2}})\alpha\beta$ is the first basic product function in state $J = 2$ for which $K = 1$ while $(\frac{1}{\sqrt{2}})\beta\alpha$ is the second basic product function in state $J = 2$ for which $K = 2$; $K = 1, 2, \ldots, M(J)$.

CD(J, K):	The coefficient for each of the basic product wavefunctions; e.g., $\psi_2 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$, CD(2, 1) = CD(2, 2) = $\frac{1}{\sqrt{2}}$.
CJ(K, L):	Coefficients for the coupling constants between nuclei K and L.
JL:	The number of the last basic state wavefunction in the system.
JF:	Label for final basic state wavefunction in the matrix element of $\mathcal{H}^{(1)}$ connecting initial and final states as: $<$ final state $\lvert\mathcal{H}^{(1)}\rvert$ initial state $>$.
JI:	Label for initial basic state wavefunction in the matrix element of $\mathcal{H}^{(1)}$ under computation, e.g., $<\psi_1\lvert\mathcal{H}^{(1)}\rvert\psi_3>$, JF = 1, JI = 3.
KF:	Final basic product function.
KI:	Initial basic product function.
LS:	Comparing two basic product functions the first pair of different spin is labeled LS.
LT:	The second pair of different spin.
LI:	Label for the LI^th spin under consideration.
MD:	The total number of pairs of different spins.

The definitions of ND(S), ND(t), NABS, NDD, NSUM, ... etc. are given in Table III. Other variables in the flow chart are dummy variables.

From the above definitions and notations, we can use a three-dimension array ID(J, K, L) to denote spin functions, basic product functions and basic state wavefunctions, e.g., in a two spin system, ID(1, 1, 1) means the first spin function in the first product function of the first state wavefunction. Thus, x. ID(2, 2, 1) means the first

CD(J, K): The coefficient for each of the basic product wavefunctions; e.g., $\psi_2 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$, CD(2, 1) = CD(2, 2) = $\frac{1}{\sqrt{2}}$.

CJ(K, L): Coefficients for the coupling constants between nuclei K and L.

JL: The number of the last basic state wavefunction in the system.

JF: Label for final basic state wavefunction in the matrix element of $\mathcal{H}^{(1)}$ connecting initial and final states as: $<$ final state $|\mathcal{H}^{(1)}|$ initial state $>$.

JI: Label for initial basic state wavefunction in the matrix element of $\mathcal{H}^{(1)}$ under computation, e.g., $<\psi_1|\mathcal{H}^{(1)}|\psi_3>$, JF = 1, JI = 3.

KF: Final basic product function.

KI: Initial basic product function.

LS: Comparing two basic product functions the first pair of different spin is labeled LS.

LT: The second pair of different spin.

LI: Label for the LIth spin under consideration.

MD: The total number of pairs of different spins.

The definitions of ND(S), ND(t), NABS, NDD, NSUM, ... etc. are given in Table III. Other variables in the flow chart are dummy variables.

From the above definitions and notations, we can use a three-dimension array ID(J, K, L) to denote <u>spin functions</u>, <u>basic product functions</u> and <u>basic state wavefunctions</u>, e.g., in a two spin system, ID(1, 1, 1) means the first spin function in the first product function of the first state wavefunction. Thus, α. ID(2, 2, 1) means the first

CD(J, K): The coefficient for each of the basic product wavefunctions; e.g., $\psi_2 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$, CD(2, 1) = CD(2, 2) = $\frac{1}{\sqrt{2}}$.

CJ(K, L): Coefficients for the coupling constants between nuclei K and L.

JL: The number of the last basic state wavefunction in the system.

JF: Label for final basic state wavefunction in the matrix element of $\mathcal{H}^{(1)}$ connecting initial and final states as: $<$ final state $|\mathcal{H}^{(1)}|$ initial state $>$.

JI: Label for initial basic state wavefunction in the matrix element of $\mathcal{H}^{(1)}$ under computation, e.g., $<\psi_1|\mathcal{H}^{(1)}|\psi_3>$, JF = 1, JI = 3.

KF: Final basic product function.

KI: Initial basic product function.

LS: Comparing two basic product functions the first pair of different spin is labeled LS.

LT: The second pair of different spin.

LI: Label for the LI$^{\text{th}}$ spin under consideration.

MD: The total number of pairs of different spins.

The definitions of ND(S), ND(t), NABS, NDD, NSUM, ... etc. are given in Table III. Other variables in the flow chart are dummy variables.

From the above definitions and notations, we can use a three-dimension array ID(J, K, L) to denote *spin functions*, *basic product functions* and *basic state wavefunctions*, e.g., in a two spin system, ID(1, 1, 1) means the first spin function in the first product function of the first state wavefunction. Thus, ID(2, 2, 1) means the first spin function in the second product function of the second state wave function; i.e., β . So in the two spin system, $\psi_1 = \alpha\alpha$ can be represented by $\psi_1 = ID(1, 1, 1)\ ID(1, 1, 2)$; $\psi_2 = (\frac{1}{\sqrt{2}})(\alpha\beta + \beta\alpha)$ by $\psi_2 = \frac{1}{\sqrt{2}}\{ID(2, 1, 1)\ ID(2, 1, 2) + ID(2, 2, 1)\ ID(2, 2, 2)\}$,....etc. The coefficients are introduced as CD(J, K).

II. C-b. Logical Argument of the Computer Program

From the last section and the simple rules for evaluating the matrix elements (42), we know that matrix elements of

$$\vec{I}_s \cdot \vec{I}_t = I_{sx} \cdot I_{tx} + I_{sy} \cdot I_{ty} + I_{sz} \cdot I_{tz}$$

exist only when the two basic product functions ID(J, K, L), L = 1, ..., N; i.e., $(ID_{JK1} ID_{JK2} \ldots\ldots ID_{JKN})$ and ID(J', K', L'), L' = 1, ..., N; i.e., $(ID_{J'K'1} ID_{J'K'2} \ldots\ldots ID_{J'K'N})$ differ by no more than two of the ID's. For computer calculation, we let these ID's have numerical values 1 or 2 according as ID's are α or β spins; e.g., if a basic product function is $(ID_{JK1} ID_{JK2} ID_{JK3} ID_{JK4}) = \alpha\beta\alpha\beta$, then it has the numerical value 1212. If another basic product function is $(ID_{J'K'1} ID_{J'K'2} ID_{J'K'3} ID_{J'K'4}) = \alpha\alpha\beta\alpha$, then it has the numerical value 1121. These two wavefunctions differ by three of the ID's ($ID_{JK2} \neq ID_{J'K'2}$; $ID_{JK3} \neq ID_{J'K'3}$; $ID_{JK4} \neq ID_{J'K'4}$) so there are no matrix elements between these two product functions. Also, if the two product functions differ by one of the ID's only, there are still no matrix elements between them; e.g., $(ID_{JK1} ID_{JK2} ID_{JK3} ID_{JK4}) = \alpha\beta\alpha\beta = 1212$, and $(ID_{J'K'1} ID_{J'K'2} ID_{J'K'3} ID_{J'K'4})$ $\alpha\beta\alpha\alpha = 1211$ differ by one ID only ($ID_{JK4} \neq ID_{J'K'4}$), the other ID's in these two product functions are the same , so there are no matrix elements between them. Matrix elements exist between two wavefunctions for even differences up to two (namely zero and two) of the spin functions, e.g., $(ID_{JK1}ID_{JK2}ID_{JK3}ID_{JK4}) = \alpha\beta\alpha\beta = 1212$ and $(ID_{J'K'1}ID_{J'K'2}ID_{J'K'3}ID_{J'K'4}) = \alpha\beta\alpha\beta = 1212$ have zero difference, so matrix elements exist between them. $(ID_{JK1}ID_{JK2}ID_{JK3}ID_{JK4}) = \alpha\beta\alpha\beta = 1212$ and $(ID_{J'K'1}ID_{J'K'2}ID_{J'K'3}ID_{J'K'4}) = \alpha\beta\beta\alpha = 1221$ differ by two ID's ($ID_{JK3} \neq ID_{J'K'3}$ and $ID_{JK4} \neq ID_{J'K'4}$), so matrix elements also exist between these two basic product functions.

From the above, we know that the typical term of the matrix elements of the spin coupling Hamiltonian is $J_{ij}\vec{I}(i)\cdot\vec{I}(j)$, in which only two nuclei are involved. So when we calculate the matrix elements, we need only consider two nuclei each time and Table II can be easily obtained. Using the numerical characteristics of each two pairs of spin functions, Table III can be constructed. Based on Table III, the flow chart and the Fortran computer program MATREL have been written for the Control Data 3600 computer (see Appendix I).

Table II.

$(ID_{JKS}ID_{JKt})$	$(ID_{J'K'S}ID_{J'K't})$	Coeff. for $J_{st}I_{sx}I_{tx}$	Coeff. for $+J_{st}I_{sy}I_{ty}$	Coeff. for $+J_{st}I_{sz}I_{tz}$	Total coeff. for $= J_{st}\vec{I}_s\cdot\vec{I}_t$
α α	α α	0	+ 0	+ 1/4	= 1/4
α β	α β	0	+ 0	+ (-1/4)	= -1/4
β α	β α	0	+ 0	+ (-1/4)	= -1/4
β β	β β	0	+ 0	+ 1/4	= 1/4
α α	β β	1/4	+ (-1/4)	+ 0	= 0
β β	α α	1/4	+ (-1/4)	+ 0	= 0
α β	β α	1/4	+ 1/4	+ 0	= 1/2
β α	α β	1/4	+ 1/4	+ 0	= 1/2

tions, e.g., $(ID_{JK1}ID_{JK2}ID_{JK3}ID_{JK4}) = \alpha\beta\alpha\beta = 1212$ and $(ID_{J'K'1}ID_{J'K'2}ID_{J'K'3}ID_{J'K'4}) = \alpha\beta\alpha\beta = 1212$ have zero difference, so matrix elements exist between them. $(ID_{JK1}ID_{JK2}ID_{JK3}ID_{JK4}) = \alpha\beta\alpha\beta = 1212$ and $(ID_{J'K'1}ID_{J'K'2}ID_{J'K'3}ID_{J'K'4}) = \alpha\beta\beta\alpha = 1221$ differ by two ID's ($ID_{JK3} \neq ID_{J'K'3}$ and $ID_{JK4} \neq ID_{J'K'4}$), so matrix elements also exist between these two basic product functions.

From the above, we know that the typical term of the matrix elements of the spin coupling Hamiltonian is $J_{ij}\vec{I}(i)\cdot\vec{I}(j)$, in which only two nuclei are involved. So when we calculate the matrix elements, we need only consider two nuclei each time and Table II can be easily obtained. Using the numerical characteristics of each two pairs of spin functions, Table III can be constructed. Based on Table III, the flow chart and the Fortran computer program MATREL have been written for the Control Data 3600 computer (see Appendix I).

Table II.

$(ID_{JKs}ID_{JKt})$	$(ID_{J'K's}ID_{J'K't})$	Coeff. for $J_{st}I_{sx}I_{tx}$		Coeff. for $+J_{st}I_{sy}I_{ty}$		Coeff. for $+J_{st}I_{sz}I_{tz}$		Total coeff. for $= J_{st}\vec{I}_s\cdot\vec{I}_t$
α α	α α	0	+	0	+	1/4	=	1/4
α β	α β	0	+	0	+	(-1/4)	=	-1/4
β α	β α	0	+	0	+	(-1/4)	=	-1/4
β β	β β	0	+	0	+	1/4	=	1/4
α α	β β	1/4	+	(-1/4)	+	0	=	0
β β	α α	1/4	+	(-1/4)	+	0	=	0
α β	β α	1/4	+	1/4	+	0	=	1/2
β α	α β	1/4	+	1/4	+	0	=	1/2

Table III.

Case	Coeff. for J_{st}	$ID_{JKS}ID_{JKt}$	$ID_{J'K'S}ID_{J'K't}$	ND(S)= ID_{JKS}- $ID_{J'K'S}$	ND(t)= ID_{JKt}- $ID_{J'K't}$	NABS= $\lvert ND(s)\rvert + \lvert ND(t)\rvert$	NDD ND(s)-ND(t)	NSUM= ND(s)+ND(t)	ID_{JKS} $-ID_{JKt}$	Both Pairs
I_a	1/4	$\alpha\ \alpha$	$\alpha\ \alpha$	1-1=0	1-1=0	0	0	0	0	same
I_b	-1/4	$\alpha\ \beta$	$\alpha\ \beta$	1-1=0	2-2=0	0	0	0	-1	same
I_c	-1/4	$\beta\ \alpha$	$\beta\ \alpha$	2-2=0	1-1=0	0	0	0	1	same
I_d	1/4	$\beta\ \beta$	$\beta\ \beta$	2-2=0	2-2=0	0	0	0	0	same
O_a	0	$\alpha\ \alpha$	$\beta\ \beta$	1-2=-1	1-2=-1	2	0	-2	0	diff.
O_b	0	$\beta\ \beta$	$\alpha\ \alpha$	2-1=1	2-1=1	2	0	2	0	diff.
II_a	1/2	$\alpha\ \beta$	$\beta\ \alpha$	1-2=-1	2-1=1	2	-2	0	-1	diff.
II_b	1/2	$\beta\ \alpha$	$\alpha\ \beta$	2-1=1	1-2=-1	2	2	0	1	diff.

II. C-c. Description of the Program

The program used for calculation of spin-coupling Hamiltonian matrix elements is quite straightforward. The basic state wavefunctions, the basic product functions and the spin functions are numbered by J's, K's and L's respectively. The program steps systematically through all of the basic wavefunctions, attempting to calculate the matrix element between each different pair of the basic state wavefunctions. First, it calculates the matrix element between ψ_1 and ψ_1, then ψ_1 and ψ_2, then ψ_1 and ψ_3,....to ψ_{JL} which is the last of the basic state wavefunctions; then it comes back to calculate ψ_2 and ψ_1, ψ_2 and ψ_2, and so forth. The computer picks up two basic state wavefunctions ψ_1 and ψ_1, then compares the basic product functions in the basic state wavefunctions. (e.g., it compares the basic product function of J = 1, K = 1 with that of J = 1, K = 1; then J = 1, K = 1 with J = 1, K = 2; then J = 1, K = 2 with J = 1, K = 1; then J = 1, K = 2 with J = 1, K = 2). If these two basic product wavefunctions have matrix elements between them, then the computer goes further to pick up each different pair of spin functions and performs various tests as listed in Table III, classifies it into one of the eight cases in Table III, and gives a value for the coefficient of the spin coupling constant of these two nuclei. If these two basic product wavefunctions do not differ (i.e., have the same spin wavefunction) the computer also assigns a value according to Table III for the coefficients of the spin coupling constants of any two nuclei. If these two basic products do not have matrix elements, then the computer picks up another basic product function for comparison. These procedures go on and on until it has calculated all the possible matrix elements. The output will be all the coefficients of all the spin coupling constants, e.g., in five-spin systems, the matrix element between ψ_1 and ψ_1 will be represented by coefficients of J_{ij} in J_{11} J_{12} J_{13} J_{14} J_{15}, J_{21} ....J_{25}, J_{31} ....J_{35}, J_{41} ....J_{45}, J_{51} ....J_{55}. Here obviously, we know that J_{11}, J_{22}, J_{33}, ...etc. are zero and that $J_{13} = J_{31}$, $J_{12} = J_{21}$, ...etc., so from the output we can easily obtain the matrix elements between any two basic state wavefunctions.

In order to handle larger spin systems, the input basic state wavefunctions of a system can be broken down into many subgroups, and each time we may take one subgroup as the input basic state wavefunctions; e.g., in a five-spin system, there are a total of thirty-two basic state wavefunctions; each time we can take eight or sixteen basic state wavefunctions as input. The size of the subgroup (the total number of basic state wavefunctions of the subgroup) depends entirely on the size of the system (total number of nuclei) and the capacity of the computer. One can also use the basic state functions with the same projection of spin angular momentum M_s whichever is more convenient for the computer.

II. D. The Secular Equation

We let Φ_i and Φ_i^{o} be the stationary state eigenfunctions of $\mathcal{H}$ and $\mathcal{H}^{(0)}$, respectively, and let E_i and $E_i^{(0)}$ be the corresponding eigenenergies. Our quantum mechanical problem will then be to solve the secular equation

$$|\mathcal{H}_{mn} - E\,\delta_{mn}| = 0 \qquad \text{(II.14)}$$

for the energies, where $\mathcal{H}_{mn} = \langle\Phi_m^{o}|\mathcal{H}|\,\Phi_n^{o}\rangle$ (II.15)

and $\delta_{mn} = 1$ if $m = n$ and $\delta_{mn} = 0$ if $m \neq n$. The exact eigenfunctions of the complete Hamiltonian are expressed in terms of the Φ_n^{o} by the equations

$$\Phi_m = \sum_{n=1}^{P} a_{mn}\,\Phi_n^{o}\,, \qquad \text{(II.16)}$$

where the a_{mn} are obtained from the solutions of the P simultaneous equations

$$\sum_{n=1}^{P}\,[\mathcal{H}_{mn} - \delta_{mn}\,E_m]\,a_{mn} = 0 \qquad \text{(II.17)}$$

The order of secular equation (II.14) is 2^N, where N is the total number of nuclei in the molecule with spin $\frac{1}{2}$. This $2^N x 2^N$ secular determinant can only be useful for obtaining the energies E_n for molecules with $N \geqslant 5$ when it is easily factored. It will be very important to obtain any possible factorization of the secular determinant. The secular equation (II.14) can be factorized into a number of equations of lower degree in E if we classify the basic state wavefunctions by total spin and symmetry i.e., we make use of the following mixing rules:

(1) There is no mixing between states of different total spin F_z,

where $$F_z = \sum_i I_z(i) \qquad \text{(II.18)}$$

(2) There is no mixing between states of different symmetry.

The factorization of the secular equation arises because there are no off-diagonal matrix elements of the Hamiltonian between the basic product functions corresponding to different values of F_z, and there are no matrix elements of the Hamiltonian between functions belonging to different irreducible representations. This is because the operator F_z commutes with the Hamiltonian $\mathcal{H}$ and the Hamiltonian is totally symmetric with respect to permutations of equivalent nuclei. As a result we can divide the basic state wavefunctions into classes according to their values of F_z and their symmetries, and then it is only necessary to evaluate the submatrices of functions in one such class. In other words, for these cases, the basic symmetry functions are themselves stationary-state functions. The set of functions $\alpha\alpha$, $\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)$, $\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)$, $\beta\beta$, for example, all differ from one another either in spin or symmetry. There is no mixing and these are the correct stationary state wavefunctions for the symmetrical two-nuclear system A_2.

II. E. Selection Rules and Intensities of Transitions

The probability $P(m\rightarrow n)$(in $\sec^{-1}$) that a nuclear system undergoes the transition $m\rightarrow n$ (i.e., $\Phi_m\rightarrow\Phi_n$) is given (46) by the equation:

$$P_{(m\rightarrow n)} = \frac{8\pi^3}{h^2}(M_x)^2_{mn}\,\rho_\nu \qquad \text{(II.20)}$$

where $$M_x = \sum_i \gamma_i I_x(i) \qquad \text{(II.21)}$$

and $$(M_x)_{mn} = (\Phi_m|\,\mu_x|\,\Phi_n)\;; \qquad \text{(II.22)}$$

M_x is the x-component of the magnetic moment operator and ρ_ν is the energy density per unit frequency range arising from the oscillatory radiofrequency field in the x-direction and Φ_m and Φ_n are the stationary state wavefunctions. McConnell et al. (42) derive the following two selection rules:

(1) In any allowed transition, the change of total spin is

$$\Delta F = \pm 1 \tag{II.23}$$

(2) All allowed transitions must be between two states of the same symmetry.

So $(M_x)_{mn}$, the transition moment, in equation (II.22) is different from zero only when these two selection rules are obeyed and the intensity of the transition between two states m and n is proportional to the square of the transition moment.

III. A SURVEY OF THE VARIOUS METHODS CURRENTLY USED FOR ANALYSIS OF NMR SPECTRA

In analysis of simple high-resolution NMR spectra, in which the spin-spin couplings are much smaller than the difference between the chemical shifts, the simple rules based on a simple interaction Hamiltonian and first-order perturbation theory can be generally used (34, 42, 47). The NMR spectra become complicated in substances where there are nonequivalent nuclei of the same species whose relative chemical shifts are of the same order of magnitude as the splittings due to spin coupling. If the chemical shifts are still moderately large, higher order perturbation methods can be used with some success (48, 49), but eventually individual multiplets become merged in a general mixed group of lines which may have few features of regularity. One is then faced with the problem of interpreting such a band system, assigning each line to a definite transition, and finally extracting numerical values for the chemical shifts and spin-coupling constants. A spectrum is considered analyzed when the chemical shifts δ_i and the spin coupling constants J_{ij} of the system have been completely determined. Various methods have been proposed for the analysis of complex NMR spectra. These methods can be roughly classified into three different approaches, namely, the iterative approach (50-78), the subspectral analysis approach (79-102) and the direct calculation approach (103-113).

III. A. <u>Iterative Approach</u>

Analysis of complex spectra has most often been performed using the iterative approach. In iterative procedures, judicious estimates of chemical shifts and spin coupling constants are inserted into the spin Hamiltonian and the eigenspectrum problem is solved to obtain transition energies and relative transition probabilities which can be used to plot a calculated line spectrum. This calculated spectrum is compared with the experimental spectrum and any differences are used as a basis for readjustment of the initial estimates of the chemical shifts and spin coupling constants. The initial estimates of the chemical shifts and spin coupling constants can frequently be obtained from known values in similar cases or sometimes by use of the moment method of Anderson and McConnell or by use of double resonance techniques. Swalen and Reilly's, Hoffman's, Arata, Shimizu and Fujiwara's and Castellano and Bothner-By's methods are all based on the iterative principle.

In Swalen and Reilly's method (50-54), the experimental energy levels are derived from the observed spectrum by making use of the trace invariance property of the Hamiltonian matrix. They use derived levels for iterative purposes. An approximate Hamiltonian $\mathcal{H}^{\circ}$ is chosen and is brought into diagonal form by a similarity transformation $S^{-1}\mathcal{H}^{\circ}S = \Lambda^{\circ}$. From the experimental spectrum an energy level scheme is constructed, and the reverse similarity transformation is then applied to the experimental energy level matrix to obtain an improved Hamiltonian $S\Lambda_{\mathrm{exptl}}S^{-1} = \mathcal{H}_{\mathrm{imp}}$. From $\mathcal{H}_{\mathrm{imp}}$ new values of δ_i and J_{ij} are deduced, and the process repeated until a consistent set emerges. Two Fortran computer programs based on this method have been written. These two programs are used in three stages in the analysis of a given spectrum. Systems up to and including eight nuclei of spin $\frac{1}{2}$ can be analyzed. Recently, Ferguson and Marquardt use magnetic equivalence factoring as a means of removing cal shifts and spin coupling constants are inserted into the spin Hamiltonian and the eigenspectrum problem is solved to obtain transition energies and relative transition probabilities which can be used to plot a calculated line spectrum. This calculated spectrum is compared with the experimental spectrum and any differences are used as a basis for readjustment of the initial estimates of the chemical shifts and spin coupling constants. The initial estimates of the chemical shifts and spin coupling constants can frequently be obtained from known values in similar cases or sometimes by use of the moment method of Anderson and McConnell or by use of double resonance techniques. Swalen and Reilly's, Hoffman's, Arata, Shimizu and Fujiwara's and Castellano and Bothner-By's methods are all based on the iterative principle.

In Swalen and Reilly's method (50-54), the experimental energy levels are derived from the observed spectrum by making use of the trace invariance property of the Hamiltonian matrix. They use derived levels for iterative purposes. An approximate Hamiltonian $\mathcal{H}^{o}$ is chosen and is brought into diagonal form by a similarity transformation $S^{-1}\mathcal{H}^{o}S = \Lambda^{o}$. From the experimental spectrum an energy level scheme is constructed, and the reverse similarity transformation is then applied to the experimental energy level matrix to obtain an improved Hamiltonian $S\Lambda_{exptl}S^{-1} = \mathcal{H}_{imp}$. From $\mathcal{H}_{imp}$ new values of δ_i and J_{ij} are deduced, and the process repeated until a consistent set emerges. Two Fortran computer programs based on this method have been written. These two programs are used in three stages in the analysis of a given spectrum. Systems up to and including eight nuclei of spin $\frac{1}{2}$ can be analyzed. Recently, Ferguson and Marquardt use magnetic equivalence factoring as a means of removing the eight spin limitation of Swalen and Reilly's method and have worked out the case of ten nuclei of spin $\frac{1}{2}$.

Arata, Shimizu and Fujiwara (59) use the observed frequencies and relative intensities simultaneously for the iterative procedures. Both frequencies and intensities are reduced to a dimensionless representation. The appropriate differentials are found by equating terms in the power series expansion of the correct parameters in terms of the dimensionless trial constants with the corresponding terms in the perturbation expansion of the Hamiltonian and I_x matrices.

In Hoffman's method (56, 57), first order perturbation theory is used to determine the correction to an approximate set of parameters fitted to the observed line positions. The line positions instead of the derived experimental energy levels are used for iterative purposes. An approximate Hamiltonian matrix is diagonalized. For selected experimental transition frequencies, the approximation eigenvectors $(S^{-1}\mathcal{H}'S)_{mm} - (S^{-1}\mathcal{H}'S)_{nn} = \nu'_{mn} = \overset{o}{\nu}_{mn} - (\nu_{exptl})_{mn}$ are evaluated, using the approximate eigenvectors S. $\mathcal{H}'$ is an estimate of the correction to the approximate Hamiltonian. If it is expressed algebraically as an array of linear functions of the fundamental parameters, the set of approximations is obtained in the form of a set of linear simultaneous equations in the corrections to the parameters. These may be solved by various methods to yield the corrections and the iteration may be repeated until a consistent set is obtained. Castellano and Bothner-By's method (61, 62, 67, 68) is very closely related to that of Hoffman. This method is applicable even if not all lines are assignable, is not affected by symmetry in the Hamiltonian, yields an estimate of the ellipsoid of error, and converges relatively rapidly to a predetermined assignment. A Fortran computer program based on this method has been written systems up to and including seven nuclei of spin $\frac{1}{2}$ are acceptable.

The most serious disadvantage of the iterative procedures is that they are unsystemmatic and tedious where there are more than one or two variables. In addition, these procedures still require identification of the corresponding experimental and calculated spectral lines with one another. For spectra containing many lines or with some closely-spaced lines, such an assignment is particularly difficult. As a consequence ambiguity may exist in the derived values for the chemical shifts δ_i and spin-spin coupling constants J_{ij} and these procedures do not always give unique results. If only the transition frequencies (or experimental energy levels) are used as the criteria for satisfactory agreement between calculated and experimental spectra ambiguities always exist since more than one set of parameters give results consistent with the experimental data (104).

The iterative approach is unsatisfactory for the reasons mentioned above; but once an approximate set of the NMR parameters is given, this method can then be applied to any general spin system up to eight nuclei of spin $\frac{1}{2}$.

III. B. Sub-spectral Analysis Approach

The composite "particle" method of Waugh and Dobbs (80) and Whitman, Onsager, Saunders and Dubb (79) is a special case of the subspectral analysis approach. This method has been applied to complex systems made up of a number of groups of magnetically equivalent nuclei. The spectra of such complex systems have been attributed to the superposition of simpler spectra. The method considers each group of identical nuclei as a composite "particle" with fixed total spin. When the symmetry of the Hamiltonian (but not necessarily of the molecule) is very high, it is often possible to handle the entire problem without any explicit reference to the zero-order spin eigenfunctions, thereby greatly simplifying the mechanical details of calculation. This method offers no particular advantages in dealing with cases of high molecular symmetry but low symmetry of the Hamiltonian, several examples of which have been previously discussed (5, 6).

A more recent and powerful method is the effective frequencies method which also can be considered as a special case of sub-spectral analysis. Alexander (60) first recognized that complicated spectra can be considered as being composed of two or more simpler spectra when one interacting group is greatly chemically shifted from the other nuclei (or is of different nuclear species). This is the concept of "effective frequencies". This concept has been first used by Narasimhan and Rogers (81, 82) in the interpretation of the proton portion (i.e., the ethyl group portion) of the spectra of some organometallic compounds. The use of effective frequencies was first put on firm theoretical ground and applied to the calculations of ABR_3X and AB_2X_q type spectra by Pople and Schaefer (83) and Diehl and Pople (84). In Pople, Schaefer and Diehl's effective frequencies method, if a group of n magnetically equivalent nuclei, X_n, are greatly chemically shifted from any group of strongly coupled nuclei, for example, ABC, then $ABCX_n$ spectrum can be considered to be composed of n+1 ABC type subspectra. They define ν_A, ν_B, ν_C as the chemical shifts that the A, B and C nuclei would have in the absence of spin coupling to the X_n group and they define $x = F_z(X_n)$ as the z-component of the total spin of the group X_n. Then the apparent "internal chemical shifts" or "effective Larmor frequencies" for each ABC subspectrum, $\nu_A{}^*(x)$, $\nu_B{}^*(x)$ and $\nu_C{}^*(x)$ are given by the equations:

$$
\begin{aligned}
\nu_A{}^*(x) &= \nu_A + x\,J_{AX} \\
\nu_B{}^*(x) &= \nu_B + x\,J_{BX} \\
\nu_C{}^*(x) &= \nu_C + x\,J_{CX} \qquad \text{(III.1)}
\end{aligned}
$$

The statistical weights of the various subspectra are given by the binomial coefficients of n.

Each ABC subspectrum must have the same value of J_{AB}, J_{AC} and J_{BC}, but will have different internal chemical shifts (if $J_{AX} \neq J_{BX} \neq J_{CX}$). Hence frequency and intensity sum rules are directly applicable to the job of dividing the ABC transitions into their appropriate subspectra. ABC subspectra are then solved by previously developed methods, and equation (III.1) gives directly the magnitudes of J_{AX}, J_{BX} and J_{CX}, and their signs relative to each other, but not relative to the couplings within the ABC group. This method has been limited to the analysis of spectra of the type $AA'....BB'....R_p....X_q$ where the prime symbol denotes magnetic non-equivalence. In those case it leads to an impressive simplification of the analysis, and it has been possible to derive all the coupling constants and chemical shift data from the analysis of the subspectra of the system.

Diehl, et. al. and Bernstein (85, 87, 88) expanded the effective frequencies method and proposed a sub-spectral analysis which is applicable to all possible combinations of magnetically equivalent and non-equivalent, strongly and weakly coupled, groups of nuclei and includes the special case of the composite particle model as well as the effective frequency method. In this method, the number and type of sub-spectra can be obtained without knowledge of the Hamiltonian simply from group theory and good quantum numbers. In order to derive the relations between the parameters of the complex problem and the parameters of the simple sub-spectra it is necessary, however, to compare corresponding parts of the Hamiltonian and to find transformations which leave transitions unchanged. As these transitions may be non-analytical in terms of the molecular NMR parameters the transformations have to be obtained by a study of invariants. Diehl et al. (87) have given the rules for the general breakdown of NMR spectra into simpler sub-spectral problems as follows:

(1) Construct the basic local symmetry wave functions for the chemically equivalent groups.

(2) Determine the total molecular symmetry.

(3) Reclassify the basic local symmetry functions according to their transformation properties under the covering operations of the total molecular symmetry and rewrite them in the abbreviated notation.

(4) Construct the 2^n (n is number of nuclei in the system. We consider only systems of spin $\frac{1}{2}$ nuclei here) molecular basic symmetry product wave functions. Use these to form the 2^n possible basic group symmetry functions.

(5) Derive the symmetry species of the products of basic group symmetry functions.

(6) Regroup the molecular wave functions into the molecular symmetry species.

strongly and weakly coupled, groups of nuclei and includes the special case of the composite particle model as well as the effective frequency method. In this method, the number and type of sub-spectra can be obtained without knowledge of the Hamiltonian simply from group theory and good quantum numbers. In order to derive the relations between the parameters of the complex problem and the parameters of the simple sub-spectra it is necessary, however, to compare corresponding parts of the Hamiltonian and to find transformations which leave transitions unchanged. As these transitions may be non-analytical in terms of the molecular NMR parameters the transformations have to be obtained by a study of invariants. Diehl et al. (87) have given the rules for the general breakdown of NMR spectra into simpler sub-spectral problems as follows:

(1) Construct the basic local symmetry wave functions for the chemically equivalent groups.

(2) Determine the total molecular symmetry.

(3) Reclassify the basic local symmetry functions according to their transformation properties under the covering operations of the total molecular symmetry and rewrite them in the abbreviated notation.

(4) Construct the 2^n (n is number of nuclei in the system. We consider only systems of spin $\frac{1}{2}$ nuclei here) molecular basic symmetry product wave functions. Use these to form the 2^n possible basic group symmetry functions.

(5) Derive the symmetry species of the products of basic group symmetry functions.

(6) Regroup the molecular wave functions into the molecular symmetry species.

(7) Sort out the transitions of the contributing species (e.g., ABB' transitions of ABB'XX' : $\Delta F_z(XX') = 0$; $\Delta F_z(ABB') = \pm 1$).

(8) Isolate the sub-spectral patterns and analyze them.

(9) Using the sub-spectra of maximum $|F_z|$ derive the parameters of the strongly coupled parts.

(10) In those cases where the Hamiltonian matrix elements of the NMR problem are given in the literature in detail, steps 1 to 5 can be deleted and step 7 can be performed on the existing tables.

In general, sub-spectral transformations considerably simplify the treatment of complex systems containing at least one pair of weakly coupled nuclei and help the analysis. However, in sorting out of sub-spectra, one needs a lot of experience and possibly the help of double resonance experiments or tickling techniques. If the structure of a given system is not very well known, it is difficult to sort out sub-spectra. Sometimes, even if the sorting out of sub-spectra can be easily achieved, the sub-spectra may be still very complicated. If we use the conventional methods to analyze these sub-spectra, sometimes clear cut solutions can not be obtained. So this method also has the disadvantages of the conventional methods as mentioned previously.

III. C. Direct Calculation Approach

The moment method was worked out by Anderson and McConnell (103) on a basis laid down by Van Vleck (115) and makes use of the experimentally determined moments of the spectrum. This method provides a technique for direct calculation of chemical shifts and spin coupling constants from the observed line positions and intensities of the experimental spectra in principle, but it is seriously handicapped in practice by its sensitivity to the relatively large errors present in most intensity measurements. Considering this point, Castellano and Waugh (104) have developed a new method for calculating the chemical shifts and spin-spin coupling constants directly from the observed spectrum which does not suffer from this limitation. Their method consists in assigning each experimental spectral line to one of the possible transitions between spin energy levels, utilizing the trace invariance property of the Hamiltonian matrix and its square in a manner similar to that of Swalen and Reilly (54), of Alexander (60) and of Banwell and Sheppard (70). The use of experimental intensities is kept separate from that of experimental frequencies, and the former may be omitted entirely when experimental values of sufficient accuracy are not available by using intensity rules for transitions. In this method, trial-and-error adjustment of the chemical shifts and spin-spin coupling constants is avoided entirely, and the values of these parameters obtained are exactly consistent with the input information. From the theoretical point of view this method is an ideal one. In order to apply this method completely, however, one needs considerable practice and one must be able to resolve and measure most of the lines that are theoretically present. This presents practical difficulties when the lines overlap each other or the line intensity is very weak. In addition, the amount of manual labor involved is such as to make exhaustion of all possibilities impractical in many cases. In practice this method can be applied only to an analysis of the nonequivalent three spin system.

Whitman (107) has developed a similar technique for calculating NMR spectra. He uses frequency sum rules and intensity sum rules to obtain an assignment of spectral lines to an energy-level diagram for the system. He instructs the computer to construct all possible energy-level diagrams consistent with the sum rules and a set of estimated experimental errors. When a satisfactory spectral line assignment has been found, it is used to calculate the experimental eigenvalues of the spin Hamiltonian. Whitman (108) also has developed the general equations for chemical shifts and spin coupling constants of a number of proton systems in terms of the experimental energy eigenvalues. In many cases formulas explicit in the NMR parameters are obtained while in other cases the equations are implicit and must be solved numerically.So the chemical shifts and spin coupling constants can then be derived from the observed experimental energy eigenvalues. This method has the advantage of eliminating any bias, but requires considerable computer time trying the many possibilities. The assignment technique is limited by the resolution of the experimental spectrum. If two real lines are unresolved in an experimental spectrum,then any assignment based on this pair considered as a single line is doomed to failure. Unfortunately, the more complex the spectrum, the greater the probability of unresolved pairs of lines. However, this shortcoming can be overcome by examining high-resolution spectra at two different frequencies and by choosing a relatively large validity limit on the intensity sum rules in the assignment program. Hence, this method is a very promising one.

Primas and Banwell (109, 110) have developed another method for direct calculation of NMR spectra which gives the resonance frequencies and intensities directly as solutions of a new eigenvalue problem, involving the derivation superoperator of the Hamiltonian. From this direct method the more elegant and compact correlation function method is developed, yielding the complete spectrum as a single entity. The two-nucleus AB system has been worked out by this method. It seems very promising. However, its applicability to larger spin systems is still unknown.

By starting from the energy diagram of the spectrum and without guessing initial values, the perturbation method proposed by Granger (114) yields an iterative procedure leading to δ and J. The ABC system is worked out as an example. However, this method can not handle large spin systems.

III. D. Miscellaneous Approaches

There are many miscellaneous methods (116-158). Some of the methods have combined different approaches. Some methods are proposed for special systems. However, there is still no general perfect method. All the methods proposed for calculating NMR spectra have their advantages and disadvantages. It is suggested that by combining different methods for special systems, when appropriate, better results could be obtained.

IV. COMPUTER ASSIGNMENT TECHNIQUE FOR ANALYSIS OF NMR SPECTRA

The present method is based on that of Whitman for the direct analysis of spectra. The aim of the present work is to utilize more fully the computer and more general computer language in order to handle bigger spin systems.

This investigation consists of two parts, namely, the derivations of general equations for the chemical shifts and spin coupling constants, and the computer assignment of experimental spectral lines to transitions between spin-energy levels. The first part gives the general equations for the chemical shifts and spin coupling constants of a number of nuclei with spin $\frac{1}{2}$ systems in terms of the values of the experimental energy levels. From the second part we can obtain the unambiguous experimental eigenvalues. When the experimental eigenvalues are inserted into those equations derived in the first part, they can be solved numerically for the chemical shifts and the spin coupling constants. Thus, the calculation of these NMR parameters from the experimental spectrum is reduced in the most general case to the solution of a system of nonlinear simultaneous equations.

IV. A. General Equations for the Chemical Shifts and Spin Coupling Constants

The method of derivation of equations for the calculation of chemical shifts and spin coupling constants of a molecule directly from the spin energy levels derived from its experimental nuclear magnetic resonance spectrum (nuclei with $\frac{1}{2}$ spin) consists of several essential steps. First of all, we have to write out the Hamiltonian for the system and obtain the basic state wavefunctions for the system, then evaluate diagonal and off-diagonal matrix elements of the Hamiltonian between the basic state wavefunctions. We reduce the original forms of the matrix elements into standardized forms by choosing the center of gravity of the spectrum as the origin for measuring the transition energies and choosing the energy of the state with the highest spin quantum number as zero energy level. The secular determinant obtained with the Hamiltonian, using basic product functions or basic state wavefunctions as a basis set, factor into subdeterminants corresponding to the different eigenvalues of I_z. If the nuclear system is symmetric or if groups of equivalent nuclei exist, additional factoring results. The factoring of the analytical secular determinants necessarily corresponds with the factoring of experimentally-observed energy eigenvalue diagrams. Thus, the secular subdeterminants in analytical form must be isomorphic with the experimentally-observed subdeterminants in diagonal form. Exploitation of this equivalence permits derivation of equations for the spin-coupling constants and the chemical shifts in terms of observed energy eigenvalues. The eigenvalue problem is essentially worked "backwards" by a method similar to the one proposed by Parker and Brown (159). The five spin ABB'CC' system will be discussed in detail as an illustrative example. The spin Hamiltonian of the ABB'CC' system is

$$\begin{aligned}\mathcal{H} = {} & 2\nu_B I_{BZ}(1) + 2\nu_C I_{CZ}(3) + \nu_A I_{AZ}(5) + J_{BB'} I_B(1) I_{B'}(2) + \\ & J_{CC'} I_C(4) I_{C'}(3) + 2J_{AB} I_A(5) I_B(1) + 2J_{AC} I_A(5) I_C(4) + \\ & 2J_{BC} I_B(1) I_C(4) + 2J_{BC'} I_B(1) I_{C'}(3) \qquad \text{(IV.1)}\end{aligned}$$

After we obtain the basic state wavefunctions by the method described in section II. B, the diagonal and off-diagonal matrix elements of the Hamiltonian (equation IV. 1) between the basic state wavefunctions can be evaluated easily by the proposed computer program MATREL (see section II. C-a to II. C-d). In Table IV, the basic state wavefunctions, the diagonal matrix elements and their standardized forms (last column in the table) are given. In Table V, the off-diagonal matrix elements and their standardized forms are shown. Following Pople, Schneider and Bernstein's notations (18), we can use the following convenient variables: $K=J_{BC}+J_{BC'}$; $L = J_{BC} - J_{BC'}$; $M = J_{AC} + J_{AB}$; $N = J_{AC} - J_{AB}$; $P = J_{CC'} + J_{BB'}$; $-Q=J_{BB}-J_{CC'}$

Reducing the diagonal and off-diagonal matrix elements into standardized forms is a rather important step. It will be illustrated in the following examples. As mentioned before, the transition energies can be measured relative to any desired origin, but for the present purposes it is most convenient to choose the center of gravity of the spectrum as the origin. In the ABB'CC' system this corresponds to setting $\nu_B+\nu_C+\frac{1}{2}\nu_A = 0$ in the analytical form of the matrix elements. A plane of symmetry exists in this system and consequently the basic state wavefunctions can be chosen to be either symmetric or antisymmetric. The symmetric functions lead to secular subdeterminants of orders 1, 3, 6, 6, 3 and 1 corresponding to the values $+\frac{5}{2}$, $+\frac{3}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$ and $-\frac{5}{2}$ for I_z, respectively. The antisymmetric functions yield secular subdeterminants of orders 2, 4, 4 and 2 corresponding to $I_z = +\frac{3}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$ and $-\frac{3}{2}$. We identify experimental energy eigenvalues by a subscript indicating twice the corresponding I_z value and a superscript s or a indicating symmetric or antisymmetric. So, when we reduce the matrix elements into standardized forms, besides setting $\nu_B + \nu_C + \frac{1}{2}\nu_A = 0$, we also set $E^s_5=0$ and $E^a_3=0$; i.e., $\frac{1}{2} K+\frac{1}{4}P+\frac{1}{2}M$ is substracted from each of the diagonal elements of the symmetric state, making $E^s_5=E^s_{-5}=0$,

Table IV. Basic Functions and Diagonal Matrix Elements of the Hamiltonian for ABB'CC'

I_z	Function		Diagonal Matrix Elements	Standardized forms
	A	BB'CC'		
$S_{\frac{5}{2}}$	α	$\alpha\alpha\alpha\alpha$	$H_{11}=\nu_B+\nu_C+\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}+J_{23}+J_{15}+J_{35})+\frac{1}{4}(J_{12}+J_{34})=\nu_B+\nu_C+\frac{1}{2}\nu_A+\frac{1}{2}K+\frac{1}{4}P+\frac{1}{2}M\rightarrow$	0
$1S_{\frac{3}{2}}$	α	$\frac{1}{\sqrt{2}}\alpha\alpha(\alpha\beta+\beta\alpha)$	$H_{22}=\nu_B+\frac{1}{2}\nu_A+\frac{1}{2}J_{15}+\frac{1}{4}(J_{12}+J_{34})=\nu_B+\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{4}(M-N)\rightarrow$	$-\frac{2}{5}\delta_B+\frac{3}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}(M+N)$
$2S_{\frac{3}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)\alpha\alpha$	$H_{33}=\nu_C+\frac{1}{2}\nu_A+\frac{1}{2}J_{35}+\frac{1}{4}(J_{12}+J_{34})=\nu_C+\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{4}(M+N)\rightarrow$	$\frac{3}{5}\delta_B-\frac{2}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}(M-N)$
$3S_{\frac{3}{2}}$	β	$\alpha\alpha\alpha\alpha$	$H_{44}=\nu_B+\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}+J_{23}-J_{15}-J_{35})+\frac{1}{4}(J_{12}+J_{34})=\nu_B+\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}K+\frac{1}{4}P-\frac{1}{2}M\rightarrow$	$-\frac{2}{5}(\delta_B+\delta_C)-M$
$1S_{\frac{1}{2}}$	α	$\alpha\alpha\beta\beta$	$H_{55}=\nu_B-\nu_C+\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}-J_{23}+J_{15}-J_{35})+\frac{1}{4}(J_{12}+J_{34})=\nu_B+\nu_C+\frac{1}{2}\nu_A-\frac{1}{2}K-\frac{1}{2}N+\frac{1}{4}P\rightarrow$	$\frac{4}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}N-\frac{1}{2}M$
$2S_{\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)$	$H_{66}=\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}-J_{23})-\frac{1}{4}(J_{12}+J_{34})=\frac{1}{2}\nu_A-\frac{1}{2}L-\frac{1}{4}P\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}L-\frac{1}{2}P-\frac{1}{2}K-\frac{1}{2}M$
$3S_{\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)$	$H_{77}=\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}+J_{23})-\frac{1}{4}(J_{12}+J_{34})=\frac{1}{2}\nu_A+\frac{1}{2}L-\frac{1}{4}P\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C+\frac{1}{2}L-\frac{1}{2}P-\frac{1}{2}K-\frac{1}{2}M$
$4S_{\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}\alpha\alpha(\alpha\beta+\beta\alpha)$	$H_{88}=-\frac{1}{2}\nu_A+\nu_B-\frac{1}{2}J_{15}+\frac{1}{4}(J_{12}+J_{34})=\nu_B-\frac{1}{2}\nu_A+\frac{1}{4}P-\frac{1}{4}(M-N)\rightarrow$	$-\frac{4}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}M+\frac{1}{4}N$
$5S_{\frac{1}{2}}$	α	$\beta\beta\alpha\alpha$	$H_{99}=\frac{1}{2}\nu_A-\nu_B+\nu_C+\frac{1}{2}(-J_{13}-J_{23}-J_{15}+J_{35})+\frac{1}{4}(J_{12}+J_{34})=-\nu_B+\nu_C+\frac{1}{2}\nu_A-\frac{1}{2}K+\frac{1}{2}N+\frac{1}{4}P\rightarrow$	$\frac{6}{5}\delta_B-\frac{4}{5}\delta_C-K+\frac{1}{2}N-\frac{1}{2}M$
$6S_{\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)\alpha\alpha$	$H_{1010}=-\frac{1}{2}\nu_A+\nu_C-J_{35}+\frac{1}{4}(J_{12}+J_{34})=\nu_C-\frac{1}{2}\nu_A+\frac{1}{4}P-\frac{1}{4}(M-N)\rightarrow$	$\frac{1}{5}\delta_B-\frac{4}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}M+\frac{1}{4}N$
$1S_{-\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)\beta\beta$	$H_{1111}=-\nu_C+\frac{1}{2}\nu_A-\frac{1}{2}J_{35}+\frac{1}{4}(J_{12}+J_{34})=-\nu_C+\frac{1}{2}\nu_A+\frac{1}{4}P-\frac{1}{4}(M+N)\rightarrow$	$\frac{1}{5}\delta_B-\frac{4}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}M-\frac{1}{4}N$
$2S_{-\frac{1}{2}}$	β	$\alpha\alpha\beta\beta$	$H_{1212}=\nu_B-\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}-J_{23}-J_{15}+J_{35})+\frac{1}{4}(J_{12}+J_{34})=\nu_B-\nu_C-\frac{1}{2}\nu_A-\frac{1}{2}K+\frac{1}{4}P+\frac{1}{2}N\rightarrow$	$\frac{6}{5}\delta_B-\frac{4}{5}\delta_C-K-\frac{1}{2}M+\frac{1}{2}N$
$3S_{-\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}\beta\beta(\alpha\beta+\beta\alpha)$	$H_{1313}=-\nu_B+\frac{1}{2}\nu_A-\frac{1}{2}J_{15}+\frac{1}{4}(J_{12}+J_{34})=-\nu_B+\frac{1}{2}\nu_A+\frac{1}{4}P-\frac{1}{4}(M-N)\rightarrow$	$-\frac{2}{5}\delta_B+\frac{3}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}N+\frac{1}{4}M$
$4S_{-\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)$	$H_{1414}=-\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}+J_{23})-\frac{1}{2}(J_{12}+J_{34})=-\frac{1}{2}\nu_A+\frac{1}{2}L-\frac{1}{4}P\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{1}{2}P+\frac{1}{2}L-\frac{1}{2}M$
$5S_{-\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)$	$H_{1515}=-\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}-J_{23})-\frac{1}{2}(J_{12}+J_{34})=-\frac{1}{2}\nu_A-\frac{1}{2}L-\frac{1}{4}P\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{1}{2}P-\frac{1}{2}L-\frac{1}{2}M$
$6S_{-\frac{1}{2}}$	β	$\beta\beta\alpha\alpha$	$H_{1616}=-\nu_B+\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}-J_{23}+J_{15}-J_{35})+\frac{1}{4}(J_{12}+J_{34})=-\nu_B+\nu_C-\frac{1}{2}\nu_A-\frac{1}{2}K+\frac{1}{4}P-\frac{1}{2}N\rightarrow$	$-\frac{4}{5}\delta_B+\frac{6}{5}\delta_C-K-\frac{1}{2}(M+N)$
$1S_{-\frac{3}{2}}$	α	$\beta\beta\beta\beta$	$H_{1717}=-\nu_B-\nu_C+\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}+J_{23}-J_{15}-J_{35})+\frac{1}{4}(J_{12}+J_{34})=-\nu_B-\nu_C+\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{2}K-\frac{1}{2}M\rightarrow$	$\frac{2}{5}\delta_B+\frac{2}{5}\delta_C-M$
$2S_{-\frac{3}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)\beta\beta$	$H_{1818}=-\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}J_{35}+\frac{1}{4}(J_{12}+J_{34})=-\nu_C-\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{4}(M+N)\rightarrow$	$-\frac{1}{5}\delta_B+\frac{2}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}(M-N)$

Continued

Table IV- Continued

I_z	Function		Diagonal Matrix Elements	Standardized Forms
	A	BB'CC'		
$3S_{-\frac{3}{2}}$	β	$\frac{1}{\sqrt{2}}\beta\beta(\alpha\beta+\beta\alpha)$	$H_{1919}=-\nu_B-\frac{1}{2}\nu_A+\frac{1}{2}J_{15}+\frac{1}{4}(J_{12}+J_{34})=-\nu_B-\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{4}(M-N)\rightarrow$	$\frac{2}{5}\delta_B-\frac{3}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}(M+N)$
$S_{-\frac{5}{2}}$	β	$\beta\beta\beta\beta$	$H_{2020}=-\nu_B-\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}+J_{23}+J_{15}+J_{35})+\frac{1}{4}(J_{12}+J_{34})$	
			$=-\nu_B-\nu_C-\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{2}K+\frac{1}{2}M\rightarrow$	$\frac{4}{5}\delta_B+\frac{6}{5}\delta_C$
$1a_{\frac{3}{2}}$	α	$\frac{1}{\sqrt{2}}\alpha\alpha(\alpha\beta-\beta\alpha)$	$H_{2121}=\nu_B+\frac{1}{2}\nu_A+\frac{1}{2}J_{15}+\frac{1}{4}J_{12}-\frac{3}{4}J_{34}=\nu_B+\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{2}Q+\frac{1}{4}(M-N)\rightarrow$	$-\frac{2}{5}\delta_B+\frac{3}{5}\delta_C-\frac{1}{2}P-\frac{1}{2}Q-\frac{1}{4}(M+N)-\frac{1}{2}K$
$2a_{\frac{3}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)\alpha\alpha$	$H_{2222}=\nu_C+\frac{1}{2}\nu_A+\frac{1}{2}J_{35}-\frac{3}{4}J_{12}+\frac{1}{4}J_{34}=\nu_C+\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{2}Q+\frac{1}{4}(M+N)\rightarrow$	$\frac{3}{5}\delta_B-\frac{2}{5}\delta_C-\frac{1}{2}P+\frac{1}{2}Q-\frac{1}{4}(M-N)-\frac{1}{2}K$
$1a_{\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta-\beta\alpha\beta\alpha)$	$H_{2323}=\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}-J_{23})-\frac{1}{4}(J_{12}+J_{34})=\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{2}Q-\frac{1}{2}L\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C$
$2a_{\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)$	$H_{2424}=\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}+J_{23})-\frac{1}{4}(J_{12}+J_{34})=\frac{1}{2}\nu_A+\frac{1}{4}P+\frac{1}{2}Q+\frac{1}{2}L\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}P+\frac{1}{2}L$
$3a_{\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}\alpha\alpha(\alpha\beta-\beta\alpha)$	$H_{2525}=\nu_B-\frac{1}{2}\nu_A-\frac{1}{2}J_{15}+\frac{1}{4}J_{12}-\frac{3}{4}J_{34}=\nu_B-\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{2}Q-\frac{1}{4}(M-N)\rightarrow$	$-\frac{4}{5}\delta_B+\frac{1}{5}\delta_C-\frac{3}{4}P-\frac{1}{4}M+\frac{1}{2}N$
$4a_{\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)$	$H_{2626}=\nu_C-\frac{1}{2}\nu_A-\frac{1}{2}J_{35}-\frac{3}{4}J_{12}+\frac{1}{4}J_{34}=\nu_C-\frac{1}{2}\nu_A-\frac{1}{4}P+\frac{1}{2}Q-\frac{1}{4}(M+N)\rightarrow$	$\frac{1}{5}\delta_B-\frac{4}{5}\delta_C-\frac{3}{4}P-\frac{1}{2}K-\frac{3}{4}M-\frac{1}{2}N$
$1a_{-\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)\beta\beta$	$H_{2727}=-\nu_C+\frac{1}{2}\nu_A-\frac{1}{2}J_{35}-\frac{3}{4}J_{12}+\frac{1}{4}J_{34}=-\nu_C+\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{4}(M+N)+\frac{1}{2}Q\rightarrow$	$\frac{1}{5}\delta_B-\frac{4}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}P-\frac{3}{4}M-\frac{1}{2}N$
$2a_{-\frac{1}{2}}$	α	$\frac{1}{\sqrt{2}}\beta\beta(\alpha\beta-\beta\alpha)$	$H_{2828}=-\nu_B+\frac{1}{2}\nu_A-\frac{1}{2}J_{15}+\frac{1}{4}J_{12}-\frac{3}{4}J_{34}=-\nu_B+\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{2}Q-\frac{1}{4}(M-N)\rightarrow$	$\frac{4}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}M+\frac{1}{2}N$
$3a_{-\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)$	$H_{2929}=-\frac{1}{2}\nu_A+\frac{1}{2}(-J_{13}+J_{23})-\frac{1}{4}(J_{12}+J_{34})=-\frac{1}{2}\nu_A-\frac{1}{4}P+\frac{1}{2}Q+\frac{1}{2}L\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}P+\frac{1}{2}L-\frac{1}{2}M$
$4a_{-\frac{1}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta-\beta\alpha\beta\alpha)$	$H_{3030}=-\frac{1}{2}\nu_A+\frac{1}{2}(J_{13}-J_{23})-\frac{1}{4}(J_{12}+J_{34})=-\frac{1}{2}\nu_A-\frac{1}{4}P-\frac{1}{2}L-\frac{1}{2}Q\rightarrow$	$\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}P-\frac{1}{2}L-\frac{1}{2}M$
$1a_{-\frac{3}{2}}$	β	$\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)\beta\beta$	$H_{3131}=-\nu_C-\frac{1}{2}\nu_A+\frac{1}{2}J_{35}-\frac{3}{4}J_{12}+\frac{1}{4}J_{34}=-\nu_C-\frac{1}{2}\nu_A-\frac{1}{4}P+\frac{1}{4}(M+N)+\frac{1}{2}Q\rightarrow$	$-\frac{3}{5}\delta_B+\frac{2}{5}\delta_C-\frac{1}{2}K-\frac{1}{2}P+\frac{1}{2}Q-\frac{1}{4}(M-N)$
$2a_{-\frac{3}{2}}$	β	$\frac{1}{\sqrt{2}}\beta\beta(\alpha\beta-\beta\alpha)$	$H_{3232}=-\nu_B-\frac{1}{2}\nu_A+\frac{1}{2}J_{15}+\frac{1}{4}J_{12}-\frac{3}{4}J_{34}=-\nu_B-\frac{1}{2}\nu_A-\frac{1}{4}(M-N)-\frac{1}{2}Q\rightarrow$	$\frac{2}{5}\delta_B-\frac{3}{5}\delta_C-\frac{1}{2}K-\frac{1}{2}P-\frac{1}{2}Q-\frac{1}{4}(M+N)$

Table V. Off-diagonal matrix elements of the Hamiltonian for ABB'CC'

$$H_{2,3} = \frac{1}{2}K = \frac{1}{2}(J_{23}+J_{13})$$

$$H_{2,4} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(M+N) = \frac{1}{\sqrt{2}}(J_{35})$$

$$H_{3,4} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(M-N) = \frac{1}{\sqrt{2}}(J_{15})$$

$$H_{5,6} = H_{6,9} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(L+K) = \frac{1}{\sqrt{2}}(J_{23})$$

$$H_{5,7} = H_{7,9} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(K-L) = \frac{1}{\sqrt{2}}(J_{13})$$

$$H_{5,8} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(M+N) = \frac{1}{\sqrt{2}}(J_{35})$$

$$H_{5,9} = H_{5,10} = H_{8,9} = 0$$

$$H_{6,7} = \frac{1}{2}P = J_{12}$$

$$H_{6,8} = H_{7,8} = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(M-N) = \frac{1}{2}(J_{15})$$

$$H_{6,10} = H_{7,10} = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(M+N) = \frac{1}{2}(J_{35})$$

$$H_{8,10} = \frac{1}{2}K = \frac{1}{2}(J_{23}+J_{13})$$

$$H_{9,10} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(M-N) = \frac{1}{\sqrt{2}}(J_{15})$$

$$H_{11,12} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(M-N) = \frac{1}{\sqrt{2}}(J_{15})$$

$$H_{11,13} = \frac{1}{2}K = \frac{1}{2}(J_{23}+J_{13})$$

$$H_{11,14} = H_{11,15} = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(M+N) = \frac{1}{2}(J_{35})$$

$$H_{11,16} = H_{12,13} = H_{12,16} = 0$$

$$H_{12,14} = H_{14,16} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(K-L) = \left(\frac{1}{\sqrt{2}}\right)(J_{13})$$

$$H_{12,15} = H_{15,16} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(K+L) = \left(\frac{1}{\sqrt{2}}\right)(J_{23})$$

$$H_{13,14} = H_{13,15} = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(M-N) = \frac{1}{2}(J_{15})$$

$$H_{13,16} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right)(M+N) = \left(\frac{1}{\sqrt{2}}\right)(J_{35})$$

$$H_{14,15} = \frac{1}{2}P = J_{12}$$

Continued

Table V- Continued

$$H_{17,18} = (\frac{1}{\sqrt{2}})(\frac{1}{2})(M-N) = (\frac{1}{\sqrt{2}})(J_{15})$$

$$H_{17,19} = (\frac{1}{\sqrt{2}})(\frac{1}{2})(M+N) = (\frac{1}{\sqrt{2}})(J_{35})$$

$$H_{18,19} = \frac{1}{2}K = \frac{1}{2}(J_{23}+J_{13})$$

$$H_{21,22} = \frac{1}{2}L = \frac{1}{2}(J_{23}-J_{13})$$

$$H_{23,24} = -\frac{1}{2}Q = \frac{1}{2}(J_{12}-J_{34})$$

$$H_{23,25} = H_{24,25} = (\frac{1}{2})(\frac{1}{2})(M-N) = \frac{1}{2}(J_{15})$$

$$-H_{23,26} = H_{24,26} = -(\frac{1}{2})(\frac{1}{2})(M+N) = -(\frac{1}{2})(J_{35})$$

$$H_{25,26} = -\frac{1}{2}L = -(\frac{1}{2})(J_{23}-J_{13})$$

$$H_{27,28} = \frac{1}{2}L = (\frac{1}{2})(J_{23}-J_{13})$$

$$-H_{27,29} = H_{27,30} = (-\frac{1}{2})(\frac{1}{2})(M+N) = -(\frac{1}{2})(J_{35})$$

$$H_{28,29} = H_{28,30} = (-\frac{1}{2})(\frac{1}{2})(M-N) = -(\frac{1}{2})(J_{15})$$

$$H_{29,30} = -(\frac{1}{2})\,Q = \frac{1}{2}(J_{12}-J_{34})$$

$$H_{31,32} = -(\frac{1}{2})\,L = -(\frac{1}{2})(J_{23}-J_{13})$$

while $-P-Q-\frac{1}{2}(M+N)-K$ is subtracted from each of the diagonal elements of the antisymmetric states to make $E_3^{a}=0$. Throughout this chapter we will measure the chemical shifts relative to that of the group of A nuclei in each molecule. Thus, $\delta_B = \nu_A - \nu_B$, $\delta_C = \nu_A - \nu_C$, etc. For example:

$H_{11} = \nu_B + \nu_C + \frac{1}{2}\nu_A + \frac{1}{2}K + \frac{1}{4}P + \frac{1}{2}M = 0$. To reduce $H_{2\;2}$, $H_{19\;19}$, $H_{21\;21}$ and $H_{32\;32}$, we let $(\nu_B + \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = (\frac{3}{2}k + \frac{1}{2})(\nu_A - \nu_B) - k(\nu_A - \nu_C)$;

$(\frac{1}{2}k + \frac{1}{2})\nu_A + (k+1)\nu_B + k\nu_C = (\frac{3}{2}k - k + \frac{1}{2})\nu_A - (\frac{3}{2}k + \frac{1}{2})\nu_B + k\nu_C$;

$(k+1)\nu_B = (-\frac{3}{2}k - \frac{1}{2})\nu_B$; $\frac{5}{2}k = -\frac{3}{2}$, $k = -\frac{3}{5}$

$\frac{3}{2}k + \frac{1}{2} = -\frac{3}{2}\cdot\frac{3}{2} + \frac{1}{2} = -\frac{9}{10} + \frac{5}{10} = -\frac{4}{10} = -\frac{2}{5}$; therefore,

$(\nu_B + \frac{1}{2}\nu_A) = -\frac{2}{5}\delta_B + \frac{3}{5}\delta_C$. To reduce $H_{3\;3}$, $H_{18\;18}$, $H_{22\;22}$ and $H_{31\;31}$, we let $(\nu_C + \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = -k(\nu_A - \nu_B) + (\frac{3}{2}k + \frac{1}{2})(\nu_A - \nu_C)$;

$(\frac{1}{2}k + \frac{1}{2})\nu_A + k\nu_B + (k+1)\nu_C = (\frac{3}{2}k - k + \frac{1}{2})\nu_A + k\nu_B - (\frac{3}{2}k + \frac{1}{2})\nu_C$;

$(k+1)\nu_C = -(\frac{3}{2}k + \frac{1}{2})\nu_C$; $\frac{5}{2}k = -\frac{3}{2}$, $k = -\frac{3}{5}$;

therefore, $(\nu_C + \frac{1}{2}\nu_A) = \frac{3}{5}\delta_B - \frac{2}{5}\delta_C$. To reduce $H_{4\;4}$ and $H_{17\;17}$

we let $(\nu_B + \nu_C - \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = (\frac{1}{4}k - \frac{1}{4})(\nu_A - \nu_B) + (\frac{1}{4}k - \frac{1}{4})(\nu_A - \nu_C)$;

$(k+1)(\nu_B + \nu_C) = -(\frac{1}{4}k - \frac{1}{4})(\nu_B + \nu_C)$; $\frac{5}{4}k = -\frac{3}{4}$, $k = -\frac{3}{5}$;

or we let $(\nu_B + \nu_C - \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = (\frac{3}{2}k + \frac{1}{2})(\nu_A - \nu_B) - (k+1)(\nu_A - \nu_C)$;

$(k+1)\nu_B = -(\frac{3}{2}k + \frac{1}{2})\nu_B$; $\frac{5}{2}k = -\frac{3}{2}$, $k = -\frac{3}{5}$,

therefore, $\nu_B + \nu_C - \frac{1}{2}\nu_A = -\frac{2}{5}\delta_B - \frac{2}{5}\delta_C$. To reduce $H_{5\;5}$ and $H_{16\;16}$

we let $(\nu_B - \nu_C + \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = (\frac{3}{2}k - \frac{1}{2})(\nu_A - \nu_B) - (k-1)(\nu_A - \nu_C)$;

$(k+1)\nu_B = (-\frac{3}{2}k + \frac{1}{2})\nu_B$; $\frac{5}{2}k = -\frac{1}{2}$, $k = -\frac{1}{5}$,

therefore, $\nu_B - \nu_C + \frac{1}{2}\nu_A = -\frac{4}{5}\delta_B + \frac{6}{5}\delta_C$. To reduce $H_{6\;6}$, $H_{7\;7}$, $H_{14\;14}$ and $H_{15\;15}$, we let $\frac{1}{2}\nu_A + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = -k(\nu_A - \nu_B) - k(\nu_A - \nu_C)$;

$(\frac{1}{2}k + \frac{1}{2})\nu_A = -2k\nu_A$; $\frac{5}{2}k = -\frac{1}{2}$, $k = -\frac{1}{5}$,

therefore, $\frac{1}{2}\nu_A = \frac{1}{5}\delta_B + \frac{1}{5}\delta_C$. To reduce $H_{10\;10}$, $H_{11\;11}$, $H_{26\;26}$

and $H_{27\ 27}$, we let $(\nu_C - \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = -k(\nu_A - \nu_B) + (\frac{3}{2}k - \frac{1}{2})(\nu_A - \nu_C)$;

$$(k+1)\nu_C = (-\frac{3}{2}k + \frac{1}{2})\nu_C;\ \frac{5}{2}k = -\frac{1}{2},\quad k = -\frac{1}{5},$$

therefore, $(\nu_C - \frac{1}{2}\nu_A) = \frac{1}{5}\delta_B - \frac{4}{5}\delta_C$. To reduce $H_{8\ 8}$, $H_{13\ 13}$, $H_{25\ 25}$ and $H_{28\ 28}$, we let $(\nu_B - \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = (\frac{3}{2}k - \frac{1}{2})(\nu_A - \nu_B) - k(\nu_A - \nu_C)$;

$$(k+1)\nu_B = (-\frac{3}{2}k + \frac{1}{2})\nu_B;\ \frac{5}{2}k = -\frac{1}{2},\quad k = -\frac{1}{5},$$

therefore, $(\nu_B - \frac{1}{2}\nu_A) = -\frac{4}{5}\delta_B + \frac{1}{5}\delta_C$. To reduce $H_{9\ 9}$ and $H_{12\ 12}$, we let $(-\nu_B + \nu_C + \frac{1}{2}\nu_A) + k(\nu_B + \nu_C + \frac{1}{2}\nu_A) = (\frac{3}{2}k + \frac{3}{2})(\nu_A - \nu_B) - (k+1)(\nu_A - \nu_C)$;

$$(k-1)\nu_B = -(\frac{3}{2}k + \frac{3}{2})\nu_B;\ \frac{5}{2}k = -\frac{1}{2},\quad k = -\frac{1}{5},$$

therefore, $-\nu_B + \nu_C + \frac{1}{5}\nu_A = \frac{6}{5}\delta_B - \frac{4}{5}\delta_C$.

After we reduce all these matrix elements into standardized forms, the 32x32 secular determinant can be obtained. This secular determinant can be factorized into subdeterminants corresponding to the experimentally-observed subdeterminants in diagonal form. Exploitation of this equivalence permits derivation of equations for spin coupling constants and chemical shifts in terms of the observed energy eigenvalues. Thus, if $I_z = \frac{3}{2}$,

$$\begin{vmatrix} -\frac{2}{5}\delta_B + \frac{3}{5}\delta_C - \frac{1}{2}K - \frac{1}{4}(M+N) - E & \frac{1}{2}K & \frac{1}{2\sqrt{2}}(M+N) \\ \frac{1}{2}K & \frac{3}{5}\delta_B - \frac{2}{5}\delta_C - \frac{1}{2}K - \frac{1}{4}(M-N) - E & \frac{1}{2\sqrt{2}}(M-N) \\ \frac{1}{2\sqrt{2}}(M+N) & \frac{1}{2\sqrt{2}}(M-N) & -\frac{2}{5}\delta_B - \frac{2}{5}\delta_C - M - E \end{vmatrix} = \begin{vmatrix} E^s_{31} - E & 0 & 0 \\ 0 & E^s_{32} - E & 0 \\ 0 & 0 & E^s_{33} - E \end{vmatrix}$$

$$\begin{aligned}
&-E^3 - E^2(-\tfrac{1}{5}\delta_B - \tfrac{1}{5}\delta_C - K - \tfrac{3}{2}M) - E\{[-\tfrac{2}{5}(\delta_B + \delta_C) - M][-\tfrac{2}{5}(\delta_B - \delta_C) + \tfrac{1}{5}\delta_C - \tfrac{1}{2}K - \tfrac{1}{4}(M+N) + \tfrac{2}{5}(\delta_B - \delta_C) + \\
&\tfrac{1}{5}\delta_B - \tfrac{1}{2}K - \tfrac{1}{4}(M-N)] + [-\tfrac{2}{5}(\delta_B - \delta_C) + \tfrac{1}{5}\delta_C - \tfrac{1}{2}K - \tfrac{1}{4}(M+N)][\tfrac{2}{5}(\delta_B - \delta_C) + \tfrac{1}{5}\delta_B - \tfrac{1}{2}K - \tfrac{1}{4}(M-N)] + \\
&\tfrac{1}{8}(M-N)^2 + \tfrac{1}{4}K^2 + \tfrac{1}{8}(M+N)^2\} + \{[-\tfrac{2}{5}(\delta_B - \delta_C) - M][-\tfrac{2}{5}(\delta_B - \delta_C) + \tfrac{1}{5}\delta_C - \tfrac{1}{2}K - \tfrac{1}{4}(M+N)][\tfrac{2}{5}(\delta_B - \\
&\delta_C) + \tfrac{1}{5}\delta_B - \tfrac{1}{2}K - \tfrac{1}{4}(M-N)] + \tfrac{1}{8}(M^2 - N^2)K - \tfrac{1}{8}(M-N)^2[-\tfrac{2}{5}(\delta_B - \delta_C) + \tfrac{1}{5}\delta_C - \tfrac{1}{2}K - \tfrac{1}{4}(M+N)] - \\
&\tfrac{1}{4}K^2[-\tfrac{2}{5}(\delta_B + \delta_C) - M] - \tfrac{1}{8}(M+N)^2[\tfrac{2}{5}(\delta_B - \delta_C) + \tfrac{1}{5}\delta_B - \tfrac{1}{2}K - \tfrac{1}{4}(M-N)]\} = -E^3 + E^2(E^s_{31} + E^s_{32} + \\
&E^s_{33}) - E(E^s_{31}E^s_{32} + E^s_{31}E^s_{33} + E^s_{32}E^s_{33}) + E^s_{31}E^s_{32}E^s_{33} \qquad \text{(IV.2)}
\end{aligned}$$

If $I_z = -\frac{3}{2}$, then

$$\begin{vmatrix} \frac{2}{5}\delta_B+\frac{2}{5}\delta_C-M-E & \frac{1}{2}K & \frac{1}{2\sqrt{2}}(M+N) \\ \frac{1}{2}K & -\frac{3}{5}\delta_B+\frac{2}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}(M-N)-E & \frac{1}{2\sqrt{2}}(M-N) \\ \frac{1}{2\sqrt{2}}(M+N) & \frac{1}{2\sqrt{2}}(M-N) & \frac{2}{5}\delta_B-\frac{3}{5}\delta_C-\frac{1}{2}K-\frac{1}{4}(M+N)-E \end{vmatrix} = \begin{vmatrix} E^s_{-31}-E & 0 & 0 \\ 0 & E^s_{-32}-E & 0 \\ 0 & 0 & E^s_{-33}-E \end{vmatrix}$$

$$-E^3+E^2\left(\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-K-\frac{3}{2}M\right)-E\{[\tfrac{2}{5}(\delta_B+\delta_C)-M][\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_C-\tfrac{1}{2}K-\tfrac{1}{4}(M+N)-\tfrac{2}{5}(\delta_B-$$
$$\delta_C)-\tfrac{1}{5}\delta_B-\tfrac{1}{2}K-\tfrac{1}{4}(M-N)]+[\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_C-\tfrac{1}{2}K-\tfrac{1}{4}(M+N)][-\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_B-\tfrac{1}{2}K-\tfrac{1}{4}(M-N)]+$$
$$\tfrac{1}{8}(M-N)^2+\tfrac{1}{4}K^2+\tfrac{1}{8}(M+N)^2\}+\{[\tfrac{2}{5}(\delta_B+\delta_C)-M][\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_C-\tfrac{1}{2}K-\tfrac{1}{4}(M+N)][-\tfrac{2}{5}(\delta_B-\delta_C)-$$
$$\tfrac{1}{5}\delta_B-\tfrac{1}{2}K-\tfrac{1}{4}(M-N)]+\tfrac{1}{8}K(M^2-N^2)-\tfrac{1}{8}(M-N)^2[\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_C-\tfrac{1}{2}K-\tfrac{1}{4}(M+N)]-\tfrac{1}{4}K^2[\tfrac{2}{5}(\delta_B+$$
$$\delta_C)-M]-\tfrac{1}{8}(M+N)^2[-\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_B-\tfrac{1}{2}K-\tfrac{1}{4}(M-N)]\} = E^3+E^2(E^s_{-31}+E^s_{-32}+E^s_{-33})-$$
$$E(E^s_{-31}E^s_{-32}+E^s_{-31}E^s_{-33}+E^s_{-32}E^s_{-33})+E^s_{-31}E^s_{-32}E^s_{-33} \qquad \text{(IV.3)}$$

Adding the coefficients of E^2 on both sides of equations (IV. 3) and (IV.2),

we have $-\frac{1}{5}\delta_B-\frac{1}{5}\delta_C-K-\frac{3}{2}M+\frac{1}{5}\delta_B+\frac{1}{5}\delta_C-K-\frac{3}{2}M = -2K-3M = E^s_{31}+E^s_{32}+E^s_{33}+E^s_{-31}+$ $E^s_{-32}+E^s_{-33}$ or $K = -\frac{3}{2}M-\frac{1}{2}(E^s_{31}+E^s_{32}+E^s_{33}+E^s_{-31}+E^s_{-32}+E^s_{-33})$ (IV.4)

Substracting the coefficients of E on both sides of equations (IV.2) and (IV.3)

we have

$$\{-2M[\tfrac{1}{5}(\delta_B+\delta_C)]-\tfrac{4}{5}(\delta_B+\delta_C)[-K-\tfrac{1}{2}M]-\tfrac{2}{5}(\delta_B-\delta_C)[-K-\tfrac{1}{2}(M-N)]+\tfrac{1}{5}\delta_C[-K-$$
$$\tfrac{1}{2}(M-N)]-[\tfrac{1}{2}K+\tfrac{1}{4}(M+N)][\tfrac{4}{5}(\delta_B-\delta_C)+\tfrac{2}{5}\delta_B]\} = (\delta_B+\delta_C)[\tfrac{2}{5}M+\tfrac{4}{5}K+\tfrac{2}{5}M+\tfrac{1}{5}(-K-\tfrac{1}{2}M)]+$$
$$N[-\tfrac{1}{5}(\delta_B-\delta_C)-\tfrac{1}{10}\delta_B-\tfrac{2}{5}(\delta_B-\delta_C)+\tfrac{1}{10}\delta_C] = (\delta_B+\delta_C)[\tfrac{3}{5}K-\tfrac{1}{10}M]+[\delta_B-\delta_C][0]+N[-\tfrac{5}{10}(\delta_B-\delta_C)] =$$
$$(E^s_{31}E^s_{32}+E^s_{31}E^s_{33}+E^s_{32}E^s_{33}-E^s_{-31}E^s_{-32}-E^s_{-31}E^s_{-33}-E^s_{-32}E^s_{-33})$$

$$\text{or } N = \frac{(6K-M)(\delta_B+\delta_C)}{5(\delta_B-\delta_C)} + \{2(E^s_{31}E^s_{32}+E^s_{31}E^s_{33}+E^s_{32}E^s_{33}-E^s_{-31}E^s_{-32}-E^s_{-31}E^s_{-33}-E^s_{-32}E^s_{-33})/(\delta_B-\delta_C$$

(IV.5)

Subtracting the coefficients of E° (the constant term) on both sides of equations (IV. 2) and (IV. 3) we consider the first term:

$$[-\tfrac{2}{5}(\delta_B+\delta_C)-M][-\tfrac{2}{5}(\delta_B-\delta_C)+\tfrac{1}{5}\delta_C-\tfrac{1}{2}K-\tfrac{1}{4}(M+N)][\tfrac{2}{5}(\delta_B-\delta_C)+\tfrac{1}{5}\delta_B-\tfrac{1}{2}K-\tfrac{1}{4}(M-N)]-[\tfrac{2}{5}(\delta_B+$$
$$\delta_C)-M][\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_C-\tfrac{1}{2}K-\tfrac{1}{4}(M+N)][-\tfrac{2}{5}(\delta_B-\delta_C)-\tfrac{1}{5}\delta_B-\tfrac{1}{2}K-\tfrac{1}{4}(M-N)] =$$

$$2\cdot\left(\frac{2}{5}\right)^3(\delta_B+\delta_C)(\delta_B-\delta_C)^2+2\left(\frac{2}{5}\right)^2(\delta_B-\delta_C)\left(\frac{1}{5}\right)\delta_B-2\cdot\left(\frac{2}{5}\right)^2(\delta_B^2-\delta_C^2)\left(\frac{1}{5}\right)\delta_C-$$
$$2\cdot\left(\frac{2}{5}\right)(\delta_B+\delta_C)\left(\frac{1}{5}\right)^2\delta_B\delta_C-2\circ\left(\frac{2}{5}\right)(\delta_B+\delta_C)\left[-\frac{1}{2}K-\frac{1}{4}(M+N)\right]\left[-\frac{1}{2}K-\frac{1}{4}(M-N)\right]-$$
$$2M\left(\frac{2}{5}\right)(\delta_B-\delta_C)\left[-\frac{1}{2}K-\frac{1}{4}(M-N)\right]-2M\left[-\frac{1}{2}K-\frac{1}{4}(M+N)\right]\left[\frac{2}{5}(\delta_B-\delta_C)+\frac{1}{5}\delta_B\right] \qquad \text{(IV.6)}$$

To the above equation (IV.6), add the following terms:

$$-2\cdot\frac{1}{8}(M-N)^2\left[-\frac{2}{5}(\delta_B-\delta_C)+\frac{1}{5}\delta_C\right]-2\circ\frac{1}{4}K^2\left[-\frac{2}{5}(\delta_B+\delta_C)\right]-2\cdot\frac{1}{8}(M+N)^2\left[-\frac{2}{5}(\delta_B-\delta_C)-\frac{1}{5}\delta_B\right]$$

therefore, the total $= E^s_{31}E^s_{32}E^s_{33} - E^s_{-31}E^s_{-32}E^s_{-33}$

Then this is reduced to the following form:

$$(\delta_B-\delta_C)^2=\frac{(\delta_B+\delta_C)^2}{25}+\frac{5(E^s_{31}E^s_{32}E^s_{33}-E^s_{-31}E^s_{-32}E^s_{-33})}{(\delta_B+\delta_C)} \qquad \text{(IV.7)}$$

When $I_z = \frac{1}{2}$

$$\begin{vmatrix} H_{5\,5}-E & 0 & 0 & 0 & 0 & 0 \\ 0 & H_{6\,6}-E & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{7\,7}-E & 0 & 0 & 0 \\ 0 & 0 & 0 & H_{8\,8}-E & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{9\,9}-E & 0 \\ 0 & 0 & 0 & 0 & & H_{10\,10}-E \end{vmatrix} = \begin{vmatrix} E^s_{11}-E & 0 & 0 & 0 & 0 & 0 \\ 0 & E^s_{12}-E & 0 & 0 & 0 & 0 \\ 0 & 0 & E^s_{13}-E & 0 & 0 & 0 \\ 0 & 0 & 0 & E^s_{14}-E & 0 & 0 \\ 0 & 0 & 0 & 0 & E^s_{15}-E & 0 \\ 0 & 0 & 0 & 0 & 0 & E^s_{16}-E \end{vmatrix}$$

$$E^6-E^5\left(-\frac{4}{5}\delta_B+\frac{1}{5}\delta_C-\frac{1}{2}K-\frac{3}{4}M+\frac{1}{4}N+\frac{1}{5}\delta_B-\frac{4}{5}\delta_C-\frac{1}{2}K+\dots\dots\dots\right)=E^6-E^5(E^s_{11}+E^s_{12}+\dots+E^s_{15}+E^s_{16})$$

therefore, $-4K-\frac{7}{2}M-P=(E^s_{11}+\dots\dots+E^s_{15}+E^s_{16})$

$$P=-4K-\frac{7}{2}M-(E^s_{11}+E^s_{12}+E^s_{13}+E^s_{14}+E^s_{15}+E^s_{16}) \qquad \text{(IV.8)}$$

For the antisymmetric case, when $I_z = \frac{1}{2}$,

$$\begin{vmatrix} H_{23\,23}-E & 0 & 0 & 0 \\ 0 & H_{24\,24}-E & 0 & 0 \\ 0 & 0 & H_{25\,25}-E & 0 \\ 0 & 0 & 0 & H_{26\,26}-E \end{vmatrix} = \begin{vmatrix} E^a_{11}-E & 0 & 0 & 0 \\ 0 & E^a_{12}-E & 0 & 0 \\ 0 & 0 & E^a_{13}-E & 0 \\ 0 & 0 & 0 & E^a_{14}-E \end{vmatrix}$$

$$\sum_{i=23}^{26} H_{ii}=\nu_B+\nu_C-P-\frac{1}{2}M-\frac{1}{2}\nu_A-P-\frac{1}{2}M=E^a_{11}+E^a_{12}+E^a_{13}+E^a_{14} \qquad \text{(IV.9)}$$

When $I_z = -\frac{1}{2}$ for the antisymmetric case,

$$\begin{vmatrix} H_{27\,27}-E & 0 & 0 & 0 \\ 0 & H_{28\,28}-E & 0 & 0 \\ 0 & 0 & H_{29\,29}-E & 0 \\ 0 & 0 & 0 & H_{30\,30}-E \end{vmatrix} = \begin{vmatrix} E^a_{-11}-E & 0 & 0 & 0 \\ 0 & E^a_{-12}-E & 0 & 0 \\ 0 & 0 & E^a_{-13}-E & 0 \\ 0 & 0 & 0 & E^a_{-14}-E \end{vmatrix}$$

$$\sum_{i=27}^{30} H_{ii} = -\nu_B-\nu_C-P-\frac{1}{2}M = E^a_{-11}+E^a_{-12}+E^a_{-13}+E^a_{-14} \qquad \text{(IV.10)}$$

Adding equations (IV.9) and (IV.10) and using the results given in equations (IV.4) and (IV.8) for K and P, we have:

$$M = -\frac{1}{3}(E^a_{11}+E^a_{12}+E^a_{13}+E^a_{14}+E^a_{-11}+E^a_{-12}+E^a_{-13}+E^a_{-14}) \qquad \text{(IV.11)}$$

Subtracting equation (IV.10) from equation (IV.9) and using the results given in equations (IV.4) and (IV.8), we have:

$$\delta_B+\delta_C = -\frac{5}{6}(E^a_{11}+E^a_{12}+E^a_{13}+E^a_{14}-E^a_{-11}-E^a_{-12}-E^a_{-13}-E^a_{-14}) \qquad \text{(IV.12)}$$

When $I_z = \frac{3}{2}$ and $I_z = -\frac{3}{2}$ in the anti-symmetric case:

$$\begin{vmatrix} H_{21\,21}-E & H_{21\,22} \\ H_{22\,21} & H_{22\,22}-E \end{vmatrix} = \begin{vmatrix} -\frac{3}{5}\delta_B+\frac{3}{5}\delta_C-\frac{1}{2}P-\frac{1}{2}K-\frac{1}{2}Q-\frac{1}{4}(M+N)-E & \frac{1}{2}L \\ \frac{1}{2}L & \frac{3}{5}\delta_B-\frac{2}{5}\delta_C-\frac{1}{2}P-\frac{1}{2}K+\frac{1}{2}Q-\frac{1}{4}(M-N)-E \end{vmatrix} = \begin{vmatrix} E^a_{31}-E & 0 \\ 0 & E^a_{32}-E \end{vmatrix} \qquad \text{(IV.13)}$$

$$\begin{vmatrix} H_{31\,31}-E & H_{31\,32} \\ H_{32\,31} & H_{32\,32}-E \end{vmatrix} = \begin{vmatrix} -\frac{3}{5}\delta_B+\frac{2}{5}\delta_C-\frac{1}{2}P-\frac{1}{2}K+\frac{3}{2}Q-\frac{1}{4}(M-N)-E & -\frac{1}{2}L \\ -\frac{1}{2}L & \frac{2}{5}\delta_B-\frac{3}{5}\delta_C-\frac{1}{2}P-\frac{1}{2}K-\frac{1}{2}Q-\frac{1}{4}(M+N)-E \end{vmatrix} = \begin{vmatrix} E^a_{-31}-E & 0 \\ 0 & E^a_{-32}-E \end{vmatrix} \qquad \text{(IV.14)}$$

Multiplying out the above two equations (IV.13) and (IV,14), and simplifying we have:

$$Q = -\frac{1}{2}N - [(E^a_{31}E^a_{32} - E^a_{-31}E^a_{-32})/(\delta_B - \delta_C)] \qquad \text{(IV.15)}$$

and

$$L^2 = -(\delta_B - \delta_C)^2 - \frac{1}{4}(N+2Q)^2 - 2(E^a_{31}E^a_{32} + E^a_{-31}E^a_{-32}) \qquad \text{(IV.16)}$$

By successive use of equations (IV.4), (IV.5), (IV.7), (IV.8), (IV.11), (IV.12), (IV.15) and (IV.16) it is possible to solve directly for both of the chemical shifts and all of the spin coupling constants of this five-spin system in terms of the experimental energy values obtained from the observed spectrum.

Using similar procedures to those described above, the general equations for the chemical shifts and the spin coupling constants for other spin systems can be derived. The equations for AB, AB_2, A_2B_2, AA'BB', A_2BC, ABC and ABCD are given by Whitman (108).

IV. B. The Computer Assignment Technique

The most difficult step in any analysis of a complex NMR spectrum is usually that of making an assignment of the observed lines to the many possible energy transitions. The proper assignment must be sorted out from many thousands of possibilities. For example, in the general five-spin system a total of 210 transitions which obey the selection rule $\Delta F_z = -1$ are possible, while a typical high-resolution spectrum might contain about 40 lines. The total number of ways of distributing 40 lines among 210 transitions is about $\frac{210!}{\quad}$. So, all possibilities can be exhausted only by the utilization of the speed of modern computers. A correct assignment of experimental spectral lines to the permitted transitions within the energy-level diagram must be consistent with two sets of rules, namely, the intensity sum rules and the line spacing rules.

Multiplying out the above two equations (IV.13) ~~and (IV,14),~~ and simplifying we have:

$$Q = -\frac{1}{2}N - [(E^a_{31}E^a_{32} - E^a_{-31}E^a_{-32})/(\delta_B - \delta_C)] \qquad \text{(IV.15)}$$

and

$$L^2 = -(\delta_B - \delta_C)^2 - \frac{1}{4}(N+2Q)^2 - 2(E^a_{31}E^a_{32} + E^a_{-31}E^a_{-32}) \qquad \text{(IV.16)}$$

By successive use of equations (IV.4), (IV.5), (IV.7), (IV.8), (IV.11), (IV.12), (IV.15) and (IV.16) it is possible to solve directly for both of the chemical shifts and all of the spin coupling constants of this five-spin system in terms of the experimental energy values obtained from the observed spectrum.

Using similar procedures to those described above, the general equations for the chemical shifts and the spin coupling constants for other spin systems can be derived. The equations for AB, AB_2, A_2B_2, AA'BB', A_2BC, ABC and ABCD are given by Whitman (108).

IV. B. The Computer Assignment Technique

The most difficult step in any analysis of a complex NMR spectrum is usually that of making an assignment of the observed lines to the many possible energy transitions. The proper assignment must be sorted out from many thousands of possibilities. For example, in the general five-spin system a total of 210 transitions which obey the selection rule $\Delta F_z = -1$ are possible, while a typical high-resolution spectrum might contain about 40 lines. The total number of ways of distributing 40 lines among 210 transitions is about $\frac{210!}{\ }$. So, all possibilities can be exhausted only by the utilization of the speed of modern computers. A correct assignment of experimental spectral lines to the permitted transitions within the energy-level diagram must be consistent with two sets of rules, namely, the intensity sum rules and the line spacing rules.

Multiplying out the above two equations (IV.13) and (IV.14), and simplifying we have:

$$Q = -\frac{1}{2}N - [(E^a_{31}E^a_{32} - E^a_{\underline{3}1}E^a_{\underline{3}2})/(\delta_B - \delta_C)] \qquad \text{(IV.15)}$$

and

$$L^2 = -(\delta_B - \delta_C)^2 - \frac{1}{4}(N+2Q)^2 - 2(E^a_{31}E^a_{32} + E^a_{\underline{3}1}E^a_{\underline{3}2}) \qquad \text{(IV.16)}$$

By successive use of equations (IV.4), (IV.5), (IV.7), (IV.8), (IV.11), (IV.12), (IV.15) and (IV.16) it is possible to solve directly for both of the chemical shifts and all of the spin coupling constants of this five-spin system in terms of the experimental energy values obtained from the observed spectrum.

Using similar procedures to those described above, the general equations for the chemical shifts and the spin coupling constants for other spin systems can be derived. The equations for AB, AB_2, A_2B_2, AA'BB', A_2BC, ABC and ABCD are given by Whitman (108).

IV. B. The Computer Assignment Technique

The most difficult step in any analysis of a complex NMR spectrum is usually that of making an assignment of the observed lines to the many possible energy transitions. The proper assignment must be sorted out from many thousands of possibilities. For example, in the general five-spin system a total of 210 transitions which obey the selection rule $\Delta F_z = -1$ are possible, while a typical high-resolution spectrum might contain about 40 lines. The total number of ways of distributing 40 lines among 210 transitions is about $\frac{210!}{\quad}$. So, all possibilities can be exhausted only by the utilization of the speed of modern computers. A correct assignment of experimental spectral lines to the permitted transitions within the energy-level diagram must be consistent with two sets of rules, namely, the intensity sum rules and the line spacing rules.

IV. B-a. Intensity Sum Rules

The principle of spectroscopic stability states that the sum of the intensities of all the transitions between two sets of nearly degenerate energy levels is independent of the strength of a perturbation. This principle was originally applied to multiplet structures in atomic and molecular spectra. It applies in the NMR case even more rigorously. When a small perturbation is applied to a system so as to break up a line into a number of components, the sum of the intensities must be equal to the intensity of the unsplit line. In NMR spectroscopy the small perturbations are the various chemical shift differences and the spin-spin coupling constants. These perturbations are clearly small when compared with a resonant frequency in the megacycle-per-second range. Castellano and Waugh (104) have derived the intensity-sum rules for a three proton system. If the total spectral intensity is normalized to $N2^{N-1}$, then a general sum rule of this sort for an N-spin system is:

$$\sum_k I_{jk} = \sum_i I_{ij} + 2F_z(j) \qquad \text{(IV.17)}$$

for any level j (j is the upper level on the left of equation (IV.17) and the lower one on the right). The rule states that the sum of the intensities of all transitions <u>from</u> a given energy level is simply related to the sum of the intensities of all transitions <u>to</u> that level. The proof of this general rule as stated above has been given by Gioumousis and Swalen (160) and by Whitman (107). The considerable experimental error involved in measurements of intensities of spectral lines means that it is futile to require of the proper assignment exact adherence to the intensity sum rules. It is necessary to introduce some validity limit on intensity sums by which the correct assignment may differ from exact agreement with the intensity sum rules. This parameter is an estimate of the experimental error in intensity measurements.

IV. B-b. Line Spacing Rules

The line spacing rules (or the equal-spacing rules) are entirely equivalent to those derived from the trace invariance properties of the Hamiltonian. However, Whitman (107) first used the rules in a form which is more convenient for computer programming and somewhat more obvious physically. Examination of the schematic energy-level diagram in Fig. 3

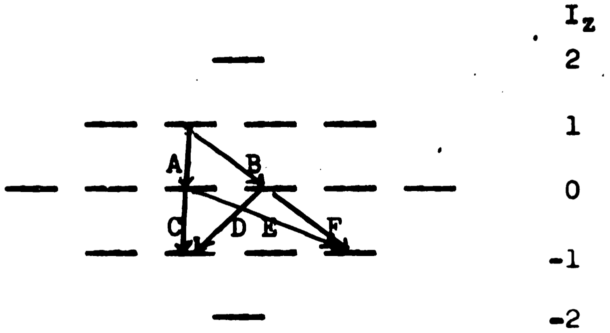


Fig. 3. Schem~~m~~etic energy-level diagram for a general four-spin system, illustrating equal-spacing conditions.

shows that the two transitions A and B with a common origin differ in energy by the spacing between the energy levels which form their terminations. Similarly, the transitions D and C with a common terminal state differ by this same spacing. Thus, after assigning two spectral lines to the transitions A and B, we must seek two lines with identical spacing to assign to the transitions D and C, Similarly, the lines assigned to the transitions F and E must have this same spacing. Such equalities of spacing occur throughout the energy-level diagram, and impose severe restrictions upon the possible assignments of spectral lines to transitions between energy levels. Because of the experimental error it is again futile to require that the correct assignment of the observed spectral lines obey the equal-spacing rules exactly. Therefore it is necessary to introduce some validity limit on equal line spacings in such a way that two energy spacings are taken as equal if they differ by no more than this limit. The magnitude chosen for this quantity will depend upon the accuracy of the experimental spectrum. The number of experimental spectral lines is usually much smaller than the number of possible transitions. For this reason an actual transition diagram will contain many incomplete transition "loops", and many of the equal-spacing rules will not be applicable.

IV. B-c. Description of the Computer Program

As mentioned before, a correct assignment of the experimental spectral lines to the permitted transitions within the energy-level diagram must be consistent with the intensity-sum rules and the line-spacing rules. So we use these two sets of rules as the criteria for the computer assignment program. Because of the considerable experimental errors involved in the measurements of the intensities and the positions of spectral lines, the proper choice of the permitted limits of validity of the line-spacing and intensity-sum rules is of considerable importance. If these limits are chosen so small as to be less than the experimental errors, then even the correct assignment will be excluded as unsatisfactory. On the other hand, if these limits are too large a great number of assignments may be found which are apparently equally satisfactory. In addition, if the validity checks are not sharp, the program running time may be considerably lengthened. The optimal technique is to choose the validity limits to be about equal to a liberal estimate of the experimental errors and to remember that the line positions are normally known with far greater accuracy than are the line intensities, so the validity limit on line spacings the equal-spacing rules exactly. Therefore it is necessary to introduce some validity limit on equal line spacings in such a way that two energy spacings are taken as equal if they differ by no more than this limit. The magnitude chosen for this quantity will depend upon the accuracy of the experimental spectrum. The number of experimental spectral lines is usually much smaller than the number of possible transitions. For this reason an actual transition diagram will contain many incomplete transition "loops", and many of the equal-spacing rules will not be applicable.

IV. B-c. Description of the Computer Program

As mentioned before, a correct assignment of the experimental spectral lines to the permitted transitions within the energy-level diagram must be consistent with the intensity-sum rules and the line-spacing rules. So we use these two sets of rules as the criteria for the computer assignment program. Because of the considerable experimental errors involved in the measurements of the intensities and the positions of spectral lines, the proper choice of the permitted limits of validity of the line-spacing and intensity-sum rules is of considerable importance. If these limits are chosen so small as to be less than the experimental errors, then even the correct assignment will be excluded as unsatisfactory. On the other hand, if these limits are too large a great number of assignments may be found which are apparently equally satisfactory. In addition, if the validity checks are not sharp, the program running time may be considerably lengthened. The optimal technique is to choose the validity limits to be about equal to a liberal estimate of the experimental errors and to remember that the line positions are normally known with far greater accuracy than are the line intensities, so the validity limit on line spacings will be chosen relatively much smaller than the validity limit on intensity sums. If no satisfactory assignment is obtained, the limits are increased and the assignment procedure is repeated. Or, if a number of different satisfactory assignments are obtained, the assignment program is rerun with the reduced validity limits until only one satisfactory assignment is obtained, or at most several. If a single basic spectral line assignment is distinctly better than any other, this assignment is used to determine the best set (or sets) of the chemical shifts and spin coupling constants by the method described in section IV. A. However, if several almost equally satisfactory assignments are obtained, it is desirable to use each of these assignments to calculate a set of chemcal shifts and spin coupling constants. A priori estimates of some parameters can then be used to immediately exclude some of these sets from further consideration.

The input data for the computer program are the number of experimental (observed) spectral lines, the number of possible transitions, the number of nuclei in the system, the number of energy levels, the permissible error in intensities, the permissible error in positions, the positions of observed spectral lines in order of decreasing intensities and the normalized intensities of lines in decreasing order. After the data have been read into the computer, the binomial coefficients of the number of nuclei in the system, the lowest numbered transition from each energy level, the total number of possible transitions from each energy level, the normalized intensity factor by which intensities of transitions <u>from</u> a level exceed those <u>to</u> the level, the energy level numbers <u>from</u> which transitions occur [e.g., K(29) = 6 means the

29th transition is from the energy level 6] and the energy level numbers to which transitions occur [e.g., L(24) = 7 means the 24th transition is to the energy level 7] are calculated, then the size of the energy-level diagram is determined.

The observed spectral lines are numbered in order of decreasing intensity and the program steps systematically through all of the possible transitions, attempting to assign to each transition the most intense spectral line available. The most intense line available is assigned into the first possible transition. The intensity sum for the level involved is constructed; the line is either accepted or rejected by this test. If it is rejected, the next most intense line is tried and the testing begins anew, and so on until finally a zero-intensity (or unobserved) line is used. If some line should pass the first test, ~~the~~ program then constructs the line spacing test when applicable (or possible). If it is not possible to construct this test, as is the case for transitions 1, 2 and 3 for the two-spin system, and 1, 2, 3, 4, 5, 6 and 13 for the three-spin system, or if some number of this test has been assigned a zero intensity transition, the tentative assignment will be accepted and the program will proceed to the assignment of the next level. If a zero-intensity (or unobserved) line is used, and it still fails both the intensity-sum test and the line-spacing test, then the program backs up and reassigns to the preceding transition an unused, less intense line. A proper assignment has been obtained when every spectral line has been assigned to some transition in such a way that all of the spacing and intensity-sum rules are obeyed.

Computer time can be saved by taking advantage of the equivalent nuclei and (or) the molecular symmetry. For example, a plane of symmetry exists in the ABB'CC' system. Choosing the basic functions which are either symmetric or antisymmetric enables the secular determinant to be factored into noncombining symmetric and antisymmetric portions. The symmetric functions lead to secular subdeterminants of order 1, 3, 6, 6, 3 and 1 corresponding to the values $+\frac{5}{2}$, $+\frac{3}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$ and $-\frac{5}{2}$ for I_z, respectively. The antisymmetric functions yield secular subdeterminants of orders 2, 4, 4 and 2 corresponding to $I_z = +\frac{3}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$ and $-\frac{3}{2}$. The schematic energy-level diagram is shown in Fig. 4.

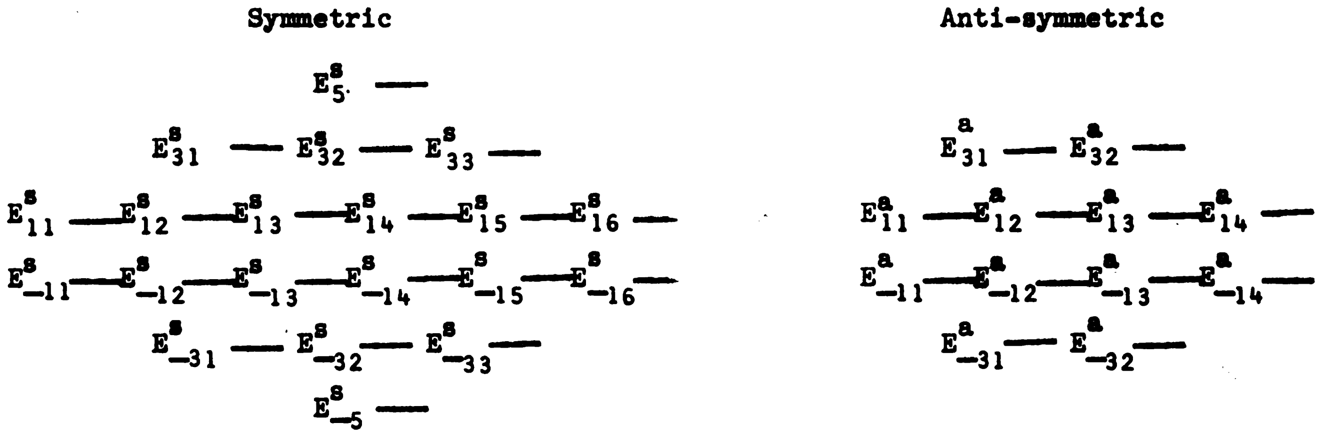


Fig. 4. The schematic energy-level diagram of AA'BB'C system

As mentioned before, we identify the experimental energy eigenvalues by a subscript indicating twice the corresponding I_z value and a superscript s or a indicating symmetric or antisymmetric. The schematic energy-level diagram consists of two sets of levels between which no transitions occur: an antisymmetric set of two levels for $I_z = \frac{3}{2}$; four levels for $I_z = \frac{1}{2}$; four levels for $I_z = -\frac{1}{2}$ and two levels for $I_z = -\frac{3}{2}$, and the remaining set of symmetric levels.

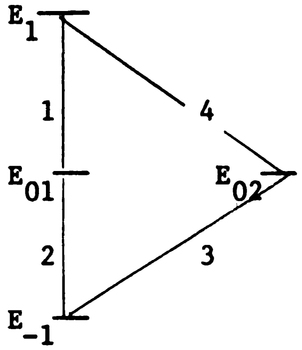
There are a total of 32 possible transitions within the antisymmetric levels and 178 possible transitions within the symmetric levels. The assignment procedure can be done in two segments. In this case, if we have 40 observed spectral lines, the 32 antisymmetric transitions were first assigned from among the total of 40 observed lines and then the remaining observed lines were assigned to symmetric transitions. When we assign the antisymmetric portion we consider that the 178 transitions within the symmetric levels are forbidden. In this case, besides the data mentioned previously, two other sets of data should be read in. The extra two sets of data are the number of unassignable (or forbidden) transitions and the set of values (-1 or 0) assigned to the transitions, e.g., KD(4) = -1 means the transition 4 is forbidden or unassignable; KD(5) = 0 means the transition 5 is available to be assigned. So we give values of -1 to the transitions which are forbidden or unassignable, while we give values of 0 to the transitions which are available to be assigned before the computer starts to make the assignments. This set of values (either -1 or 0) is read into the computer. When the computer starts to make the assignments, it will skip the transitions which have values of -1 and only try to assign the observed spectral lines to the transitions which have values of 0. For the symmetric portion, a similar procedure can be applied. A lot of computer time can be saved in this way.

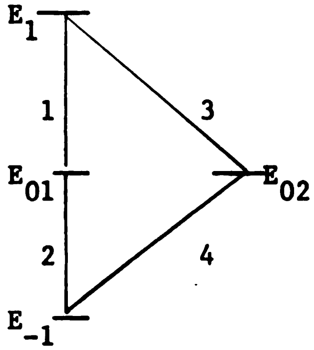
IV. C. Examples

The technique described above is now applied to the study of the spectrum of cyclopropyl cyanide, a five-spin ABB'CC' system. The spectra of 2-bromo-5-chlorothiophene (two-spin AB system), styrene oxide (three-spin ABC system) and o-dichlorobenzene (four-spin AA'BB' system) are also treated here for sake of completeness and to illustrate the procedure.

IV. C-a. Two-spin System

2-Bromo-5 chlorothiophene has been studied by the pertubation method (48). It belongs to the two-spin AB system. In this case, the number of observed spectral lines is four (N=4), the number of possible transitions is four (NA=4), the number of proton is two (NB=2), and the number of energy levels is four ($NW=2^{NB}=2^2=4$). The permissible error of intensities is chosen to be 160, about 10% of the intensity of the strongest line. The permissible error in position is selected as 5 which usually is about twice the observed fluctuation in position of the center of gravity of corresponding lines in the symmetrical spectrum. In this case, we set both the number of unassignable transitions (ND) and the number of the last initially assigned transition (NT) equal to zero for the first run. The experimental spectrum is taken from Anderson's paper (48). For convenience of computer calculation the experimental values of relative intensities are initially normalized to $1000 \cdot NB \cdot 2^{(NB-1)} = 1000 \cdot 2 \cdot 2 = 4000$, and the experimental values of the positions are converted to fixed point values and referenced to the center of gravity of the spectrum as the origin. This corresponds to setting $\nu_A + \nu_B = 0$ in the analytical form of the matrix elements. After these manipulations, we arrange the positions of the experimental lines in order of their decreasing intensities and arrange the normalized intensities of the experimental lines in decreasing order. That is, KA (1, 2, ···· N + 1) are -11, 11, -50 and 0, while KB (1, 2, ···· N + 1) are 1680,1680,320,320, and 0. All the values mentioned above are the input data. We then put these input data into Program "Assign" and obtained two possible assignments as follows:





The first assignment gives the following values of the energy levels: $E_1 = 0$ cps, $E_{01} = -5.0$ cps, $E_{02} = 1.1$ cps and $E_{-1} = 0$ cps. These values of the energy levels are substituted into the following equations which have been derived for AB systems (108):

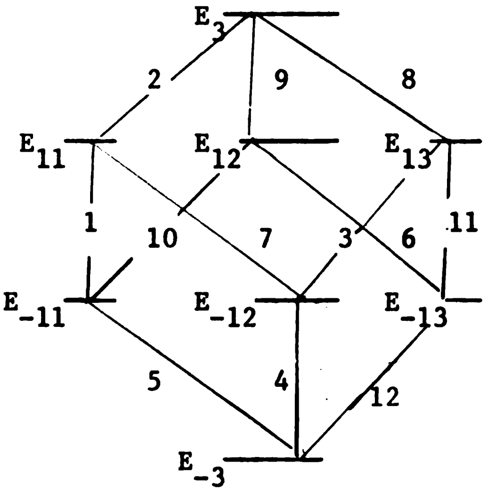
$$J = -(E_{01} + E_{02}) \tag{IV-18}$$

$$\delta^2 = -4\, E_{01}E_{02} \tag{IV-19}$$

These give $J = 3.9$ cps and $\delta = 4.7$ cps which agree with Anderson's results. From the second assignment, we have $E_1 = 0$ cps, $E_{01} = 5.0$ cps, $E_{02} = 1.1$ cps, and $E_{-1} = 0$ cps. We substitute these values into (IV-18) and (IV-19) and get $J = -6.6$ cps and $\delta = 4.7$icps. The second solution is excluded since it is physically impossible.

IV. C-b. Three-Spin System

Reilly and Swalen have analyzed the 40-MHz proton resonance spectrum of styrene oxide by using the iterative method (50). In the computer assignment technique, we have the following input data for this spectrum: $N = 12$, $NA = 15$, $NB = 3$, $NW = 2^{NB} = 2^3 = 8$, $NPEI = 160$, $NPEP = 190$, KA(1, 2, ··· N + 1) = -655, -1423, -1729, -1061, -2254, 2508, 2652, 2902, -95, -2047, -496, -2306 and 0; and KB (1, 2, ···· N + 1) = 1521, 1456, 1324, 1248, 1141, 1088, 956, 812, 696 648, 564, 536 and 0. The best assignment we obtained is:



These lead to the energy levels $E_3 = 0$ cps, $E_{11} = -14.25$ cps, $E_{12} = -95$ cps, $E_{13} = 29.02$ cps, $E_{-11} = -21.38$ cps, $E_{-12} = 11.69$ cps, $E_{-13} = 24.06$ cps, and $E_{-3} = 0$ cps. These values are then substituted into the following equations (108):

$$J_{AB} + J_{AC} + J_{BC} = -(E_{11} + E_{12} + E_{13}) = -(E_{-11} + E_{-12} + E_{-13}) \qquad \text{(IV-20)}$$

$$J_{AB}(\delta_B-2\delta_C) + J_{AC}(\delta_C-2\delta_B) + J_{BC}(\delta_B + \delta_C) = 3(E_{11}E_{12} + E_{11}E_{13} + E_{12}E_{13} + E_{12}E_{13} - E_{-11}E_{-12} - E_{-11}E_{-13} - E_{-12}E_{-13}) \qquad \text{(IV-21)}$$

$$2/3\ \delta_B^2 + 2/3\ \delta_C^2 - 2/3\ \delta_B\delta_C - 3/2\ (J_{AB}J_{AC} + J_{AB}J_{BC} + J_{AC}J_{BC}) = -(E_{11}E_{12} + E_{11}E_{13} + E_{12}E_{13} + E_{-11}E_{-12} + E_{-11}E_{-12} + E_{-11}E_{-13} + E_{-12}E_{-13}) \qquad \text{(IV-22)}$$

$$J_{AB}\ (\delta_B - 2\delta_C)^2 + J_{AC}(\delta_C - 2\delta_B)^2 + J_{BC}(\delta_B + \delta_C)^2 = 9\ (E_{11}E_{12}E_{13} + E_{-11}E_{-12}E_{-13}) \qquad \text{(IV-23)}$$

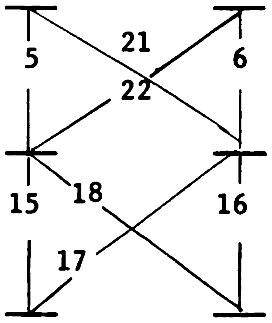
$$2(\delta_B - 2\delta_C)\ (\delta_C - 2\delta_B)\ (\delta_B + \delta_C) = -27(E_{11}E_{12}E_{13} - E_{-11}E_{-12}E_{-13}) \qquad \text{(IV-24)}$$

and the above equations solved numerically to obtain $J_{AB} = 5.63$ cps. $J_{AC} = 2.47$ cps, $J_{BC} = 4.08$ cps, $\delta_B = 11.95$ cps, and $\delta_C = 43.87$ cps which are in good agreement with Reilly and Swalen's results.

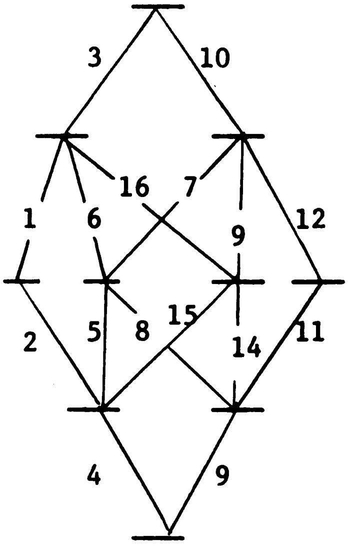
IV. C-c. Four-Spin System

The 40 MHz proton resonance spectrum of o-dichlorobenzene has been analyzed by Pople et al.,(122) using the conventional methods and has been analyzed by Whitman (107) using the computer assignment method. It is included here for the sake of illustration and to compare different versions of the assignment program.

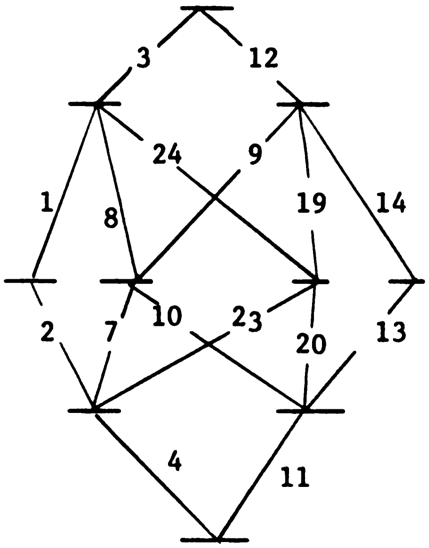
Since the molecule of o-dichlorobenzene contains a plane of symmetry the spin-energy-level diagram consists of two sets of levels between which no transitions occur — an antisymmetric set of two levels each for m = +1, 0, and -1, and the remaining set of symmetric levels. There are a total of eight permitted transitions within the antisymmetric levels and 20 transitions within the symmetric levels. In order to save computer time, the assignment procedure can be done in two segments. First the eight antisymmetric transitions are assigned from among the total of 24 observed lines, and then the remaining observed lines are assigned to symmetric transitions. The input data for the first segment of the assignment are N=24, NA=56, NB=4, NW=16, NPEI=250, NPEP=28, ND=48, NT=0, KA(1,2, ···N + 1) = 353, -353, 416, -416, 680, -680, 843, -843, 967, -967, 1394, -1394, 1340, -1340, 1006, -1006, 41, -41, 72, -72, 1645, -1645, 1738, -1738 and 0, KB(1,2, ···N + 1) = 3651, 3651, 3081, 3081, 1896, 1896, 1341, 1341, 1288, 1288, 1145, 1145, 959, 959, 919, 919, 855, 855, 669, 669, 104, 104, 90, 90 and 0. To save computer time, another set of data KD(1,2, ··· NA) should be read in, i.e. KD(1,2, ··· NA) = -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 0, 0, -1, -1, -1, -1, 0, 0, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 0, 0, -1, -1, 0, 0, -1, -1, -1, -1. From the above input, we obtain the best assignment for the antisymmetric portion as follows:



For the second segment of the assignment, N=16, ND=36, KA(1,2,···N + 1) = 353, -353, 416, -416, 843, -843, 967, -967, 1394, -1394, 1340, -1340, 72, -72, 1738, -1738, 0; KB(1,2, ··· N + 1) = 3651, 3651, 3081, 3081, 1341, 1341, 1288, 1288, 1145, 1145, 959, 959, 919, 919, 669, 669, 90, 90, 0. KD(1,2, ··· NA) = 0, 0, -1, -1, 0, 0, 0, 0, -1, -1, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 0, 0, -1, -1, 0, 0, -1, -1, -1, 0, 0, -1, -1, 0, 0, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 0, 0. -1, -1. All the other input data are the same as the first segments of the assignment. The best output for the symmetric portion is as follows:



The lines are now renumbered to the order of the input KA (1,2···N + 1) of the first segment assignment, which leads to the following assignment:



The experimental values of the energy levels obtained from the experimental spectrum using this assignment are $E_2^S = 0$, $E_{+11}^S = 4.16$, $E_{+12}^S = -13.94$, $E_{0S}^S = 7.69$, $E_{02}^S = -4.27$, $E_{03}^S = -13.22$, $E_{04}^S = -27.34$, $E_{-11}^S = 4.16$, $E_{-12}^S = -13.94$, $E_{-2}^0 = 0$, $E_{+11}^a = 11.62$, $E_{-11}^a = +\ 5.24$, $E_{-12}^a = 5.24$. The transition energies are measured relative to the average of the energies of the transitions 1, 2, 3, and 4, and the energy of the state m = +2 is chosen as zero. Since the antisymmetric levels are not joined by transitions to the symmetric levels an additional zero of energy is needed for the antisymmetric levels. This has been chosen such that the sums of the antisymmetric energies for a given m value is zero. The values of the energy levels are then substituted in the following equations (107) and solved,

$$N = -(E_{11}^S + E_{12}^S) = J_{AB} + J_{AB'} \qquad \text{(IV-25)}$$

$$K=3(E_{11}^S + E_{12}^S)-(E_{01}^S + E_{02}^S + E_{03}^S + E_{04}^S) = J_{BB'} + J_{AA'} \qquad \text{(IV-26)}$$

$$M=(E_{-11}^aE_{-12}^a-E_{11}^aE_{12}^a)/(-4E_{11}^SE_{12}^S)^{1/2} = J_{BB'} - J_{AA'} \qquad \text{(IV-27)}$$

$$L^2=[(E_{-11}^aE_{-12}^a-E_{11}^aE_{12}^a)^2/4E_{11}^SE_{12}^S] - 4E_{01}^aE_{02}^a=(J_{AB}-J_{AB'})^2 \qquad \text{(IV-28)}$$

$$\delta^2= -4E_{11}^SE_{12}^S=4E_{01}^aE_{02}^a - 2(E_{11}^aE_{12}^a + E_{-11}^aE_{-12}^a) \qquad \text{(IV-29)}$$

This leads to $\delta=\nu_B-\nu_A = 15.23$ cps, $J_{AB} = 8.17$ cps, $J_{AB'} = 1.01$ cps, $J_{BB'} = 7.44$ cps, and $J_{AA'} = 0.36$ cps, which are in excellent agreement with Whitman's results.

The experimental values of the energy levels obtained from the experimental spectrum using this assignment are $E_2^S = 0$, $E_{+11}^S = 4.16$, $E_{+12}^S = -13.94$, $E_{0S}^S = 7.69$, $E_{02}^S = -4.27$, $E_{03}^S = -13.22$, $E_{04}^S = -27.34$, $E_{-11}^S = 4.16$, $E_{-12}^S = -13.94$, $E_{-2}^0 = 0$, $E_{+11}^a = 11.62$, $E_{-11}^a = +5.24$, $E_{-12}^a = 5.24$. The transition energies are measured relative to the average of the energies of the transitions 1, 2, 3, and 4, and the energy of the state $m = +2$ is chosen as zero. Since the antisymmetric levels are not joined by transitions to the symmetric levels an additional zero of energy is needed for the antisymmetric levels. This has been chosen such that the sums of the antisymmetric energies for a given m value is zero. The values of the energy levels are then substituted in the following equations (107) and solved,

$$N = -(E_{11}^S + E_{12}^S) = J_{AB} + J_{AB'} \tag{IV-25}$$

$$K=3(E_{11}^S + E_{12}^S)-(E_{01}^S + E_{02}^S + E_{03}^S + E_{04}^S) = J_{BB'} + J_{AA'} \tag{IV-26}$$

$$M=(E_{-11}^aE_{-12}^a-E_{11}^aE_{12}^a)/(-4E_{11}^SE_{12}^S)^{1/2} = J_{BB'} -J_{AA'} \tag{IV-27}$$

$$L^2=[(E_{-11}^aE_{-12}^a-E_{11}^aE_{12}^a)^2/4E_{11}^SE_{12}^S] - 4E_{01}^aE_{02}^a=(J_{AB}-J_{AB'})^2 \tag{IV-28}$$

$$\delta^2= -4E_{11}^SE_{12}^S=4E_{01}^aE_{02}^a - 2(E_{11}^aE_{12}^a + E_{-11}^aE_{-12}^a) \tag{IV-29}$$

This leads to $\delta=\nu_B-\nu_A = 15.23$ cps, $J_{AB} = 8.17$ cps, $J_{AB'} = 1.01$ cps, $J_{BB'} = 7.44$ cps, and $J_{AA'} = 0.36$ cps, which are in excellent agreement with Whitman's results.

IV. C-d. Five-Spin System

The proton resonance spectrum of cyclopropyl cyanide belongs to the five-spin ABB'CC' system. As mentioned before, the ABB'CC' is one of the most general system of five-spin spectra since the A_2B_3 , A_2B_2X , ··· etc. systems can be considered as special cases of ABB'CC'. The experimental 60 MHz proton spectrum was taken by Dr. Myra Gordon with a Varian A-60 spectrometer. Since a plane of symmetry exists in these systems the spin-energy-level diagram also consists of two sets of levels between which no transitions occur. The assignment procedure can also be done in two segments. First, the 32 antisymmetric transitions are assigned from among the total of 40 observed lines, and then the remaining observed lines are assigned to the 78 symmetric transitions, or vice versa. However, in this case, the best assignment can be obtained by assigning 40 observed spectral lines among 110 possible transitions, since from the spin-energy-level diagram we know there are 100 unassignable or forbidden transitions in this system. The input data for this spectrum are: N=40, NA=210, NB=5, NW=32, NPEI=900, NPEP=35, ND=100, NT=0, KA(1,2, ··· N + 1) = 356, 349, 346, 342, 276, 340, 293, 286, 520, 469, 296, 281, 576, 302, 594, 384, 991, 310, 246, 507, 313, 377, 392, 539, 652, 649, 600, 657, 534, 548, 620, 743, 644, 0, 612, 694, 712, 721, 640, 727, 0; KB(1,2, ··· N + 1) = 11693, 9517, 8346, 5496, 5479, 4733, 3800, 3200, 3147, 2681, 2600, 2215, 1982, 1632, 1426, 1372, 1201, 1066, 933, 816, 799, 779, 610, 583, 579, 535, 439, 401, 350, 233, 233, 233, 148, 116, 116, 116, 93, 93, 85, 47, 0, KD(1,2, ··· N + 1) = 0, 0, 0, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0,

IV. C-d. Five-Spin System

The proton resonance spectrum of cyclopropyl cyanide belongs to the five-spin ABB'CC' system. As mentioned before, the ABB'CC' is one of the most general system of five-spin spectra since the A_2B_3 , A_2B_2X , ··· etc. systems can be considered as special cases of ABB'CC'. The experimental 60 MHz proton spectrum was taken by Dr. Myra Gordon with a Varian A-60 spectrometer. Since a plane of symmetry exists in these systems the spin-energy-level diagram also consists of two sets of levels between which no transitions occur. The assignment procedure can also be done in two segments. First, the 32 antisymmetric transitions are assigned from among the total of 40 observed lines, and then the remaining observed lines are assigned to the 78 symmetric transitions, or vice versa. However, in this case, the best assignment can be obtained by assigning 40 observed spectral lines among 110 possible transitions, since from the spin-energy-level diagram we know there are 100 unassignable or forbidden transitions in this system. The input data for this spectrum are: N=40, NA=210, NB=5, NW=32, NPEI=900, NPEP=35, ND=100, NT=0, KA(1,2, ··· N + 1) = 356, 349, 346, 342, 276, 340, 293, 286, 520, 469, 296, 281, 576, 302, 594, 384, 991, 310, 246, 507, 313, 377, 392, 539, 652, 649, 600, 657, 534, 548, 620, 743, 644, 0, 612, 694, 712, 721, 640, 727, 0; KB(1,2, ··· N + 1) = 11693, 9517, 8346, 5496, 5479, 4733, 3800, 3200, 3147, 2681, 2600, 2215, 1982, 1632, 1426, 1372, 1201, 1066, 933, 816, 799, 779, 610, 583, 579, 535, 439, 401, 350, 233, 233, 233, 148, 116, 116, 116, 93, 93, 85, 47, 0, KD(1,2, ··· N + 1) = 0, 0, 0, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, 0, 0, 0, 0, -1, -1, -1, -1, -1, -1, 0, 0, 0, 0, 0, 0, 0, -1, -1, 0, 0, 0, -1, -1, 0, 0, 0, -1, -1, 0, 0, 0, -1, -1, 0, 0, 0, -1, -1, 0, 0, 0, -1, -1, -1, -1, -1, 0, 0, -1, -1, -1, 0, 0, -1, -1, -1, 0, 0, -1, -1, -1, 0, 0, 0, 0, 0, -1, -1. The output of the assignment 4, 28, 41, -1, -1, 3, 19, 34, 41, 41, 41, -1, -1, -1, -1, 41, 41, 41, 7, 27, 40, -1, -1, -1, -1, 8, 41, 41, 24, 41, 41, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 9, 23, 35, 41, -1, -1, -1, -1, -1, -1, 10, 18, 41, 33, 1, 14, 36, 41, 41, 41, -1, -1, -1, -1, 41, 16, 41, 15, 41, 41, -1, -1, -1, -1, 37, 25, 41, 41, 17, 38, -1, -1, -1, -1, 41, 41, 41, 41, 22, 41, -1, -1, -1, -1, 41, 41, 41, 41, 41, 41, -1, -1, -1, -1, 41, 41, 41, 41, 41, 41, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, 5, 12, 41, 41, -1, -1, -1, -1, -1, -1, 41, 41, 11, 41, -1, -1, -1, -1, -1, -1, 41, 41, 41, 13, -1, -1, -1, -1, -1, -1, 41, 41, 41, 20, 2, 21, 30, -1, -1, 41, 41, 41, -1, -1, 26, 31, 41, -1, -1, 29, 41, 32, -1, -1, 41, 41, 41, -1, -1, 41, 39, 41, -1, -1, -1, -1, -1, 41, 41, -1, -1, -1, 41, 41, -1, -1, -1, 41, 41, -1, -1, -1, 6, 41, 41, 41, 41, 41, -1, -1. Before we evaluate all the values of the energy levels, we rewrite all the positions of the observed spectral levels relative to the center of gravity of the spectrum as the origin. So we have KA(1,2, ··· N + 1) = -130, -137, -140, -144,

-210, -146, -193, -200, 34, -17, -190, -205, 90, -184, 108, -102, 505, -176, -240, 21, -173, -109, -94, 53, 166, 163, 114, 171, 48, 62, 134, 257, 158, -486, 126, 208, 226, 235, 154, 241, and 0. The energy of state m = +5 is chosen as zero and for the antisymmetric energy levels the sum of the antisymmetric energies for m = 3 is chosen as an additional zero as in the four-spin case. From this assignment, we obtain the following "experimental" values of energy levels: $E_5^S = 0$ cps, $E_{31}^S = -14.4$ cps, $E_{32}^S = 17.1$ cps, $E_{33}^S = 3.1$ cps, $E_{31}^a = 4.1$ cps, $E_{32}^a = -4.1$ cps, $E_{11}^S = -28.4$ cps, $E_{12}^S = 38.4$ cps, $E_{13}^S = 53.0$ cps, $E_{14}^S = 2.2$ cps, $E_{15}^S = 14.5$ cps, $E_{16}^S = 32.5$ cps, $E_{11}^a = 7.5$ cps, $E_{12}^a = 5.3$ cps, $E_{13}^a = 16.7$ cps, $E_{14}^a = 15.8$ cps, $E_{-11}^S = -41.4$ cps, $E_{-12}^S = -18.4$ cps, $E_{-13}^S = -7.6$ cps, $E_{-14}^S = -27.8$ cps, $E_{-15}^S = 0.9$ cps, $E_{-16}^S = -17.2$ cps, $E_{-11}^a = -13.5$ cps, $E_{-12}^a = -13.0$ cps, $E_{-13}^a = -24.3$ cps, $E_{-14}^a = 24.8$ cps, $E_{-31}^S = 17.7$ cps, E_{-32}^S 29.1 cps, $E_{-33}^S = 17.4$ cps, $E_{-34}^S = 18.7$ cps, $E_{-5}^S = 0$, $E_{-31}^a = 7.3$ cps, and $E_{-32} = -7.3$ cps. Substituting these values into equations (IV-4) to (IV-16) gives $\delta_B = 48.0$cps, $\delta_C = 42.2$ cps, $J_{12} = 7.6$ cps, $J_{13} = 4.1$ cps, $J_{14} = 7.6$ cps, $J_{15} = 4.1$ cps, $J_{23} = -5.6$, $J_{24} = 10.4$, $J_{25} = 7.1$, $J_{34} = 7.1$, $J_{35} = 10.1$, $J_{45} = -5.6$.

IV. C-e. Conclusions

The computer assignment method described here has considerable applicability. If the high-resolution spectrum to be analized is well resolved, the present method always gives a clean-cut solution without guessing initially any parameters. For spectra for which we cannot estimate a set of good parameters for the iterative methods, the present method thus has advantages. The major limitation of the computer assignment method is the resolution of the experimental spectrum, as mentioned in a previous section. Also, this method usually needs more computer time than other methods do, especially if we cannot choose sharp validity limits on the line-spacing rules and on the intensity-sum rules; the computer time required may then be considerably lengthened.

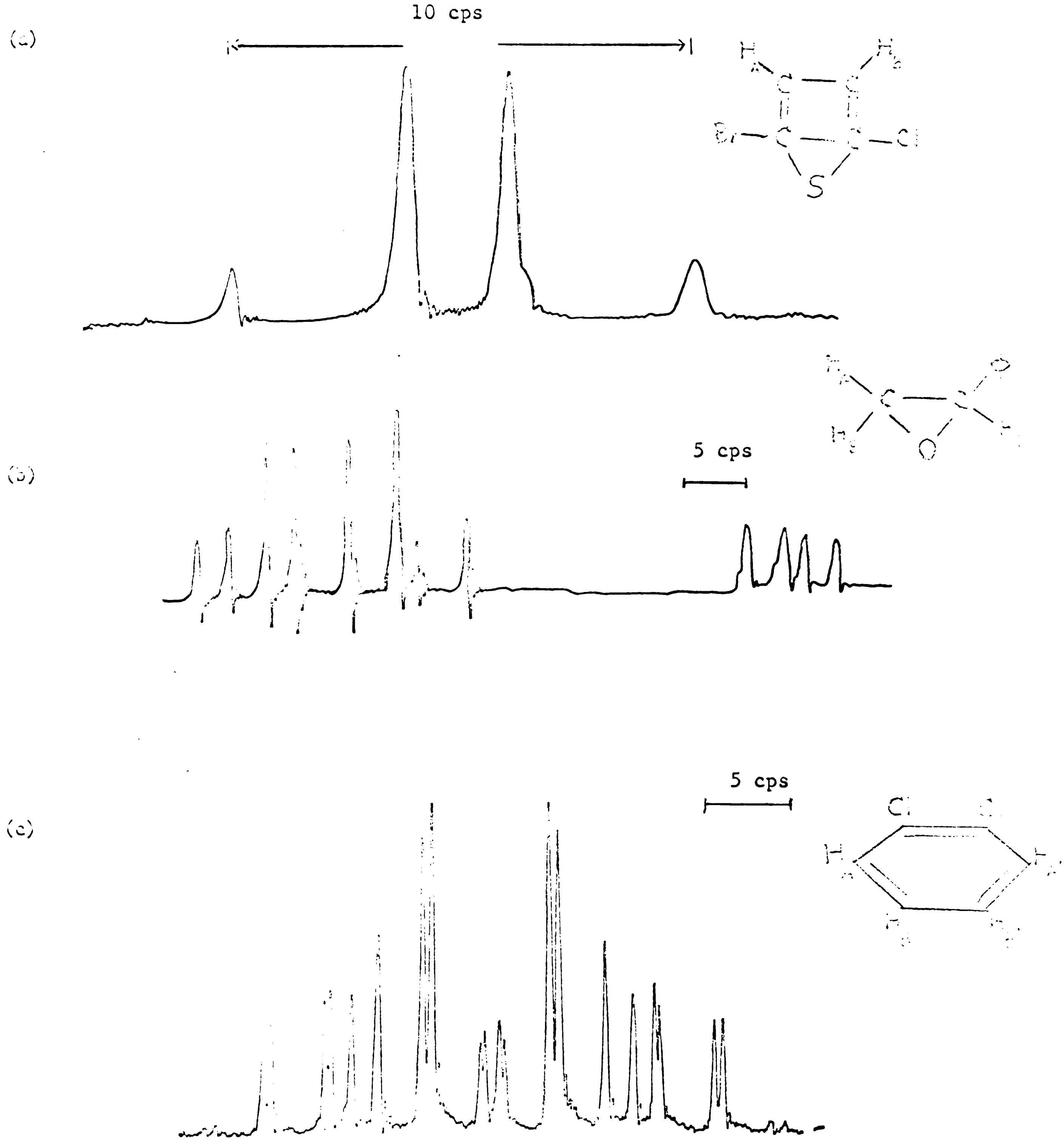
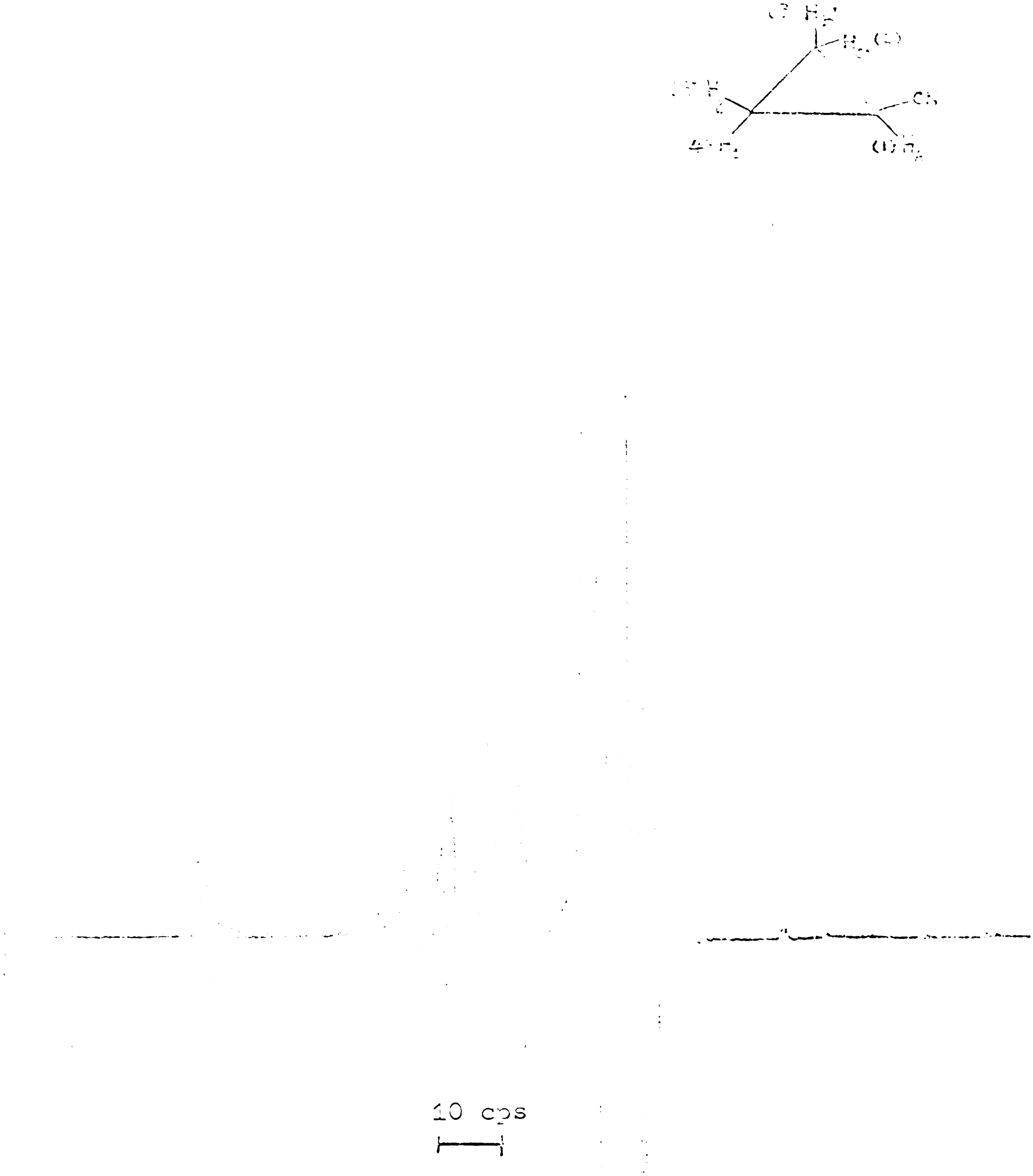


Figure 4 (a) Spectrum of 2-bromo-5-chlorothiophene
(b) Spectrum of Styrene Oxide
(c) Spectrum of O-dichlorobenzene

Figure 5 Spectrum of Cyclopropyl Cyanide



BIBLIOGRAPHY

(1) I. I. Rabi, S. Millman, P. Kusch and J. R. Zacharias, Phys. Rev. 55, 526 (1939).

(2) C. J. Gorter, Physica 3, 995 (1936).

(3) E. M. Purcell, H. C. Torrey and R. V. Pound, Phys. Rev. 69, 37 (1946).

(4) F. Bloch, W. W. Hansen and M. E. Packard, Phys. Rev. 69, 127 (1946).

(5) N. Bloembergen, Nuclear Magnetic Relaxation (W. A. Benjamin, Inc., New York, 1948).

(6) G. E. Pake, Am. J. Phys. 18, 438, 473 (1950).

(7) N. F. Ramsey, Nuclear Moments (Wiley, New York, 1953).

(8) E. R. Andrew, Nuclear Magnetic Resonance (Cambridge University Press, London, 1955).

(9) P. Grivet, La Résonance Paramagnétique Nucléaire (C. N. R. S., Paris, 1955).

(10) J. E. Wertz, Chem. Revs. 55, 829 (1955).

(11) G. E. Pake, Solid State Physics, Vol. II (Academic Press, New York, 1956).

(12) W. D. Knight, ibid. (Academic Press, New York, 1956).

(13) H. S. Gutowsky, Physical Method in Chemical Analysis, Vol. III (Academic Press, New York, 1956).

(14) A. K. Saha and T. P. Das, Theory and Applications of Nuclear Induction (Saha Institute of Nuclear Physics, Calcutta, India, 1957)

(15) A. Losche, Kerninduktion (Verb. deut. Verlag Wiss., Berlin, 1957).

(16) G. Lankien, Handbuch der Physik-- Encyclopedia of Physics (S. Flügge, ed.), Vol. 38, Part 1, p. 120, Springer, Berlin (1958).

(17) H. Kopfermann , Nuclear Moments (Academic Press, New York, 1958).

(18) J. A. Pople, W. G. Schneider and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance (McGraw-Hill, New York, 1959).

(19) L. Jackman, Applications of NMR in Organic Chemistry (Pergamon, London, 1959).

(20) J. D. Roberts, Nuclear Magnetic Resonance Applications to Organic Chemistry (McGraw-Hill, New York, 1959).

(21) J. G. Powles, Rept . Progr. Phys. 22, 33 (1959).

(22) Varian Associates, N. M. R. and E. P. R. Spectroscopy (Pergamon, New York, 1960).

(23) A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press, London, 1961).

(24) H. Strehlow, Magnetische Kernesonanz und Chemische Struktur (Dr. Dietrich Steinkopff Verlag, Damstat, 1962).

(25) E. Fluck, Die Kernmagnetische Resonanz und Ihre Anwendung in der Anorganischen Chemie (Springer, Berlin, 1963).

(26) C. P. Slichter, Principles of Magnetic Resonance (Harper & Row, New York, 1963).

(27) W. Pauli, Naturwiss, 12, 741 (1924).

(28) E. Feenberg and G. E. Pake, Notes on the Quantum Theory of Angular Momentum (Addison-Wesley Publ. Co., Cambridge, Mass., 1953).

(29) E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, London, 1953).

(30) N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 679 (1948).

(31) F. Bloch, Phys. Rev., 70, 460 (1946).

(32) G. E. Pake, J. Chem. Phys. 16, 327 (1948).

(33) J. H. Van Vleck, Phys. Rev. 74, 1184 (1948).

(34) H. S. Gutowsky, D. W. McCall and C. P. Slichter, J. Chem. Phys. 21, 279 (1953).

(35) E. L. Hahn and D. E. Maxwell, Phys. Rev. 84, 1286 (1951).

(36) N. F. Ramsey and E. M. Purcell, ibid. 85, 143 (1952).

(37) N. F. Ramsey, Phys. Rev. 91, 303 (1953).

(38) Note: Whitman calls isochronous nuclei equivalent nuclei and equivalent nuclei identical nuclei (see reference 108).

(39) P. O. Löwdin, Rev. Mod. Phys. 36, 966 (1964).

(40) P. O. Löwdin, Phys. Rev. 97, 1509 (1955).

(41) P. O. Löwdin, Adv. Physics 5, 1 (1956).

(42) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 24, 479 (1956).

(43) E. B. Wilson,Jr., J. Chem. Phys. 27, 60 (1957).

(44) E. B. Wilson,Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1958).

(45) P. L. Corio, J. Chem. Phys. 29, 682 (1958).

(46) H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944).

(47) E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

(48) W. A. Anderson, Phys. Rev. 102, 151 (1956).

(49) J. T. Arnold, Phys. Rev. 102, 136 (1956).

(50) C. A. Reilly and J. D. Swalen, J. Chem. Phys. 32, 1378 (1960).

(51) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 34, 2122 (1961).

(52) C. A. Reilly and J. D. Swalen, J. Chem Phys. 34, 980 (1961).

(53) R. Freeman, N. S. Bhacca and C. A. Reilly, J. Chem. Phys. 38, 293 (1963).

(54) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21 (1962).

(55) R. C. Ferguson and D. W. Marquardt, J. Chem. Phys. 41, 2087 (1964).

(56) R. A. Hoffman and S. Gronowitz, Arkiv Kemi. 15, 45 (1959).

(57) R. A. Hoffman, J. Chem. Phys. 33, 1256 (1960).

(58) B. Mathiasson, Acta Chem. Scand. 17, 2133 (1963).

(59) Y. Arata, H. Shimizu and S. Fujiwara, J. Chem. Phys. 36, 1951 (1962).

(60) S. Alexander, J. Chem. Phys. 32, 1700 (1960).

(61) S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964).

(62) S. Castellano and J. Lorenc, J. Chem. Phys. 69, 3552 (1965).

(63) V. J. Kowalewski and D. G. DeKowalewski, J. Chem. Phys. 36, 266 (1962).

(64) V. J. Kowalewski and D. G. DeKowalewski, ibid. 33, 1794 (1960).

(41) P. O. Löwdin, Adv. Physics 5, 1 (1956).

(42) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 24, 479 (1956).

(43) E. B. Wilson,Jr., J. Chem. Phys. 27, 60 (1957).

(44) E. B. Wilson,Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1958).

(45) P. L. Corio, J. Chem. Phys. 29, 682 (1958).

(46) H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944).

(47) E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

(48) W. A. Anderson, Phys. Rev. 102, 151 (1956).

(49) J. T. Arnold, Phys. Rev. 102, 136 (1956).

(50) C. A. Reilly and J. D. Swalen, J. Chem. Phys. 32, 1378 (1960).

(51) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 34, 2122 (1961).

(52) C. A. Reilly and J. D. Swalen, J. Chem Phys. 34, 980 (1961).

(53) R. Freeman, N. S. Bhacca and C. A. Reilly, J. Chem. Phys. 38, 293 (1963).

(54) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21 (1962).

(55) R. C. Ferguson and D. W. Marquardt, J. Chem. Phys. 41, 2087 (1964).

(56) R. A. Hoffman and S. Gronowitz, Arkiv Kemi. 15, 45 (1959).

(57) R. A. Hoffman, J. Chem. Phys. 33, 1256 (1960).

(58) B. Mathiasson, Acta Chem. Scand. 17, 2133 (1963).

(59) Y. Arata, H. Shimizu and S. Fujiwara, J. Chem. Phys. 36, 1951 (1962).

(60) S. Alexander, J. Chem. Phys. 32, 1700 (1960).

(61) S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964).

(62) S. Castellano and J. Lorenc, J. Chem. Phys. 69, 3552 (1965).

(63) V. J. Kowalewski and D. G. DeKowalewski, J. Chem. Phys. 36, 266 (1962).

(64) V. J. Kowalewski and D. G. DeKowalewski, ibid. 33, 1794 (1960).

(41) P. O. Löwdin, Adv. Physics 5, 1 (1956).

(42) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 24, 479 (1956).

(43) E. B. Wilson,Jr., J. Chem. Phys. 27, 60 (1957).

(44) E. B. Wilson,Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1958).

(45) P. L. Corio, J. Chem. Phys. 29, 682 (1958).

(46) H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944).

(47) E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

(48) W. A. Anderson, Phys. Rev. 102, 151 (1956).

(49) J. T. Arnold, Phys. Rev. 102, 136 (1956).

(50) C. A. Reilly and J. D. Swalen, J. Chem. Phys. 32, 1378 (1960).

(51) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 34, 2122 (1961).

(52) C. A. Reilly and J. D. Swalen, J. Chem Phys. 34, 980 (1961).

(53) R. Freeman, N. S. Bhacca and C. A. Reilly, J. Chem. Phys. 38, 293 (1963).

(54) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21 (1962).

(55) R. C. Ferguson and D. W. Marquardt, J. Chem. Phys. 41, 2087 (1964).

(56) R. A. Hoffman and S. Gronowitz, Arkiv Kemi. 15, 45 (1959).

(57) R. A. Hoffman, J. Chem. Phys. 33, 1256 (1960).

(58) B. Mathiasson, Acta Chem. Scand. 17, 2133 (1963).

(59) Y. Arata, H. Shimizu and S. Fujiwara, J. Chem. Phys. 36, 1951 (1962).

(60) S. Alexander, J. Chem. Phys. 32, 1700 (1960).

(61) S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964).

(62) S. Castellano and J. Lorenc, J. Chem. Phys. 69, 3552 (1965).

(63) V. J. Kowalewski and D. G. DeKowalewski, J. Chem. Phys. 36, 266 (1962).

(64) V. J. Kowalewski and D. G. DeKowalewski, ibid. 33, 1794 (1960).

(41) P. O. Löwdin, Adv. Physics 5, 1 (1956).

(42) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 24, 479 (1956).

(43) E. B. Wilson,Jr., J. Chem. Phys. 27, 60 (1957).

(44) E. B. Wilson,Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1958).

(45) P. L. Corio, J. Chem. Phys. 29, 682 (1958).

(46) H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944).

(47) E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

(48) W. A. Anderson, Phys. Rev. 102, 151 (1956).

(49) J. T. Arnold, Phys. Rev. 102, 136 (1956).

(50) C. A. Reilly and J. D. Swalen, J. Chem. Phys. 32, 1378 (1960).

(51) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 34, 2122 (1961).

(52) C. A. Reilly and J. D. Swalen, J. Chem Phys. 34, 980 (1961).

(53) R. Freeman, N. S. Bhacca and C. A. Reilly, J. Chem. Phys. 38, 293 (1963).

(54) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21 (1962).

(55) R. C. Ferguson and D. W. Marquardt, J. Chem. Phys. 41, 2087 (1964).

(56) R. A. Hoffman and S. Gronowitz, Arkiv Kemi. 15, 45 (1959).

(57) R. A. Hoffman, J. Chem. Phys. 33, 1256 (1960).

(58) B. Mathiasson, Acta Chem. Scand. 17, 2133 (1963).

(59) Y. Arata, H. Shimizu and S. Fujiwara, J. Chem. Phys. 36, 1951 (1962).

(60) S. Alexander, J. Chem. Phys. 32, 1700 (1960).

(61) S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964).

(62) S. Castellano and J. Lorenc, J. Chem. Phys. 69, 3552 (1965).

(63) V. J. Kowalewski and D. G. DeKowalewski, J. Chem. Phys. 36, 266 (1962).

(64) V. J. Kowalewski and D. G. DeKowalewski, ibid. 33, 1794 (1960).

(41) P. O. Löwdin, Adv. Physics 5, 1 (1956).

(42) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 24, 479 (1956).

(43) E. B. Wilson, Jr., J. Chem. Phys. 27, 60 (1957).

(44) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1958).

(45) P. L. Corio, J. Chem. Phys. 29, 682 (1958).

(46) H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944).

(47) E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

(48) W. A. Anderson, Phys. Rev. 102, 151 (1956).

(49) J. T. Arnold, Phys. Rev. 102, 136 (1956).

(50) C. A. Reilly and J. D. Swalen, J. Chem. Phys. 32, 1378 (1960).

(51) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 34, 2122 (1961).

(52) C. A. Reilly and J. D. Swalen, J. Chem Phys. 34, 980 (1961).

(53) R. Freeman, N. S. Bhacca and C. A. Reilly, J. Chem. Phys. 38, 293 (1963).

(54) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21 (1962).

(55) R. C. Ferguson and D. W. Marquardt, J. Chem. Phys. 41, 2087 (1964).

(56) R. A. Hoffman and S. Gronowitz, Arkiv Kemi. 15, 45 (1959).

(57) R. A. Hoffman, J. Chem. Phys. 33, 1256 (1960).

(58) B. Mathiasson, Acta Chem. Scand. 17, 2133 (1963).

(59) Y. Arata, H. Shimizu and S. Fujiwara, J. Chem. Phys. 36, 1951 (1962).

(60) S. Alexander, J. Chem. Phys. 32, 1700 (1960).

(61) S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964).

(62) S. Castellano and J. Lorenc, J. Chem. Phys. 69, 3552 (1965).

(63) V. J. Kowalewski and D. G. DeKowalewski, J. Chem. Phys. 36, 266 (1962).

(64) V. J. Kowalewski and D. G. DeKowalewski, ibid. 33, 1794 (1960).

(65) K. B. Wiberg and B. J. Nist, J. Am. Chem. Soc. 85, 2788 (1963).

(66) R. W. Fessenden and J. S. Waugh, J. Chem. Phys. 31, 996 (1959).

(67) A. A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc. 84, 743 (1962).

(68) A. A. Bothner-By and R. K. Harris, ibid. 87, 3445 (1965).

(69) E. O. Bishop and R. E. Richards, Mol. Phys. 3, 114 (1960).

(70) C. N. Banwell and N. Sheppard, ibid. 3, 351 (1960).

(71) N. Sheppard and J. J. Turner, ibid. 3, 168 (1960).

(72) C. N. Banwell, N. Sheppard and J. J. Turner, Spectrochim. Acta, 794 (1960).

(73) P. J. Black and M. L. Heffernan, Australian J. Chem 16, 1051 (1963).

(74) P. J. Black and M. L. Heffernan, ibid. 17, 558 (1964).

(75) T. J. Batterham, L. Tsai and H. Ziffer, ibid. 17, 163 (1964).

(76) M. I. Levenberg and J. H. Richards, J. Am. Chem. Soc. 86, 2634 (1964).

(77) P. J. Black and M. L. Heffernan, Australian J. Chem. 18, 353 (1965).

(78) P. J. Black and M. L. Heffernan, ibid. 18, 707 (1965).

(79) D. R. Whitman, L. Onsager, M. Saunders and H. E. Dubb, J. Chem. Phys. 32, 67 (1960).

(80) J. S. Waugh and F. Dobbs, ibid. 31, 1235 (1959).

(81) P. T. Narasimhan and M. T. Rogers, ibid. 31, 1430 (1959).

(82) P. T. Narasimhan and M. T. Rogers, ibid. 34, 1049 (1961).

(83) J. A. Pople and T. Schaefer, Mol. Phys. 3, 547 (1960).

(84) P. Diehl and J. A. Pople, ibid. 3, 557 (1960).

(85) R. C. Hirst, Thesis (University of Utah, 1963).

(86) J. Ranft, Ann. Physik. 10, 1 (1962).

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

(88) R. G. Jones, R. C. Hirst and H. J. Bernstein, ibid. 43, 683 (1965).

(89) T. Schaefer, Can. J. Chem. 40, 1678 (1962).

(90) T. Schaefer, ibid. 40, 431 (1962).

(91) H. M. Hutton and T. Schaefer, ibid. 41, 2774 (1963).

(92) R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. (London) A269, 385 (1962).

(93) R. M. Lynden-Bell, Trans. Faraday Soc. 57, 888 (1961).

(94) R. M. Lynden-Bell, Mol. Phys. 6, 601 (1963).

(95) D. Chapman and R. K. Harris, J. Chem. Soc. (London), 237 (1963).

(96) R. K. Harris and K. J. Packer, ibid. 3077 (1962).

(97) R. K. Harris and K. J. Packer, ibid. 4736 (1961).

(98) D. Chapman, ibid. 131 (1963).

(99) P. L. Corio, J. Mol. Spect. 8, 193 (1962).

(100) P. Diehl and I. Grünacher, J. Chem Phys. 34, 1846 (1961).

(101) C. N. Banwell and N. Sheppard, Proc. Roy. Soc (London) A263, 136 (1961).

(102) F. A. L. Anet, J. Am. Chem. Soc. 84, 747 (1962).

(103) W. A. Anderson and H. M. McConnell, J. Chem. Phys. 26, 1496 (1957).

(104) S. Castellano and J. S. Waugh, ibid. 34, 295 (1961).

(105) W. Brügel, T. Ankel and F. Krückeberg, Z. Elektrochem. 64, 1121 (1960).

(106) B. R. McGarvey and G. Slomp, Jr., J. Chem. Phys. 30, 1586 (1959).

(107) D. R. Whitman, ibid. 36, 2085 (1962).

(108) D. R. Whitman, Mol. Spect. 10, 250 (1963).

(109) H. Primas, Spectrochim. Acta 14, 17 (1959).

(110) H. Primas and H. H. Gunthard, Helv. Phys. Acta 31, 413 (1958).

(111) C. N. Banwell and H. Primas, Mol. Phys. 6, 225 (1963).

(112) B. Dischler and W. Maier, Z. Naturfusch. 16a, 318 (1961).

(113) B. Dischler and G. Englert, ibid. 16a, 1180 (1961).

(114) P. Granger, J. Chem. Phys. 62, 594 (1965).

(115) J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

(116) N. K. Bannerjee, T. P. Das and A. K. Saha, Proc. Roy. Soc. (London) A226, 490 (1954).

(117) P. L. Corio, Chem. Revs. 60, 363 (1960).

(118) K. B. Wiberg and J. Nist, Interpretation of NMR Spectra (W. A. Benjamin, Inc., New York, 1962).

(119) H. S. Gutowsky, Ann. N. Y. Acad. Sci. 70, 786 (1958).

(120) J. D. Roberts, An Introduction to the Analysis of Spin-Spin Splitting in Nuclear Magnetic Resonance (W. A. Benjamin Inc., New York, 1961).

(121) H. J. Bernstein, J. A. Pople and W. G. Schneider, Can. J. Chem. 35, 65 (1957).

(122) J. A. Pople, W. G. Schneider and H. J. Bernstein, Can. J. Chem. 35, 1060 (1957).

(123) W. G. Schneider, H. J. Bernstein and J. A. Pople, ibid. 35, 1487 (1957).

(124) R. J. Abraham, J. A. Pople and H. J. Bernstein, ibid. 36, 1302 (1958).

(125) R. J. Abraham and H. J. Bernstein, ibid. 39, 216 (1961).

(126) R. J. Abraham and H. J. Bernstein, ibid. 39, 905 (1961).

(127) A. D. Cohen and N. Sheppard, Proc. Roy. Soc. A252, 488 (1959).

(128) N. Sheppard and J. J. Turner, Proc. Roy. Soc. A252, 506 (1959).

(129) R. E. Richards and T. Schaefer, ibid. A246, 429 (1958).

(130) R. J. Abraham and K. G. R. Pachler, Mol. Phys. 7, 165 (1963).

(131) T. Schaefer, Can. J. Chem. 37, 882 (1959).

(132) R. J. Abraham, E. O. Bishop and R. E. Richards, J. Mol. Phys. 3, 485 (1960).

(133) R. E. Richards and T. Schaefer, Mol. Phys. 1, 331 (1958).

(134) F. S. Mortimer, J. Mol. Spect. 3, 335 (1959).

(135) R. E. Richards and T. Schaefer, Trans. Faraday Soc. 54, 1280 (1958).

(136) D. M. Grant, R. C. Hirst and H. S. Gutowsky, J. Chem. Phys. 38, 470 (1963).

(137) R. C. Hirst and D. M. Grant, ibid. 40, 1909 (1964).

(138) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, J. Am. Chem. Soc. 79, 4596 (1957).

(139) G. A. Williams and H. S. Gutowsky, J. Chem. Phys. 25, 1288 (1956).

(140) W. G. Schneider, H. J. Bernstein and J. A. Pople, Ann. N. Y. Acad. Sci. 70, 806 (1958).

(141) B. Gestblom, R. A. Hoffman and S. Rodmar, Mol. Phys. 8, 425 (1964).

(142) V. I. Glazkov, Opt. Spect. (USSR) 9, 217 (1960).

(143) R. S. Berry, R. Dehl and W. R. Vaughan, J. Chem. Phys. 34, 1460 (1961).

(144) J. V. Acrivos, Mol. Phys. 5, 1 (1962).

(145) R. W. Fessenden and J. S. Waugh, J. Chem. Phys. 30, 944 (1959).

(146) R. R. Fraser, Can. J. Chem. 38, 2226 (1960).

(147) J. Martin and B. P. Dailey, J. Chem. Phys. 37, 2594 (1962).

(148) H. S. Gutowsky, M. Karplus and D. M. Grant, ibid. 31, 1278 (1959).

(149) H. M. Hutton and T. Schaefer, Can. J. Chem. 40, 875 (1962).

(150) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 23, 1152 (1955).

(151) H. M. Hutton and T. Schaefer, Can. J. Chem. 41, 2429 (1963).

(152) B. Sunners, L. H. Piette and W. G. Schneider, Can. J. Chem. 38, 581 (1960).

(153) R. K. Harris, ibid. 42, 2275 (1964).

(154) R. K. Harris, ibid. 42, 2282 (1964).

(155) P. L. Corio, Chem. Rev. 60, 363 (1960).

(156) B. D. Rao and P. Venkateswaran, Proc. Indian Acad. Sci. 54A, 1 (1961).

(136) D. M. Grant, R. C. Hirst and H. S. Gutowsky, J. Chem. Phys. 38, 470 (1963).

(137) R. C. Hirst and D. M. Grant, ibid. 40, 1909 (1964).

(138) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, J. Am. Chem. Soc. 79, 4596 (1957).

(139) G. A. Williams and H. S. Gutowsky, J. Chem. Phys. 25, 1288 (1956).

(140) W. G. Schneider, H. J. Bernstein and J. A. Pople, Ann. N. Y. Acad. Sci. 70, 806 (1958).

(141) B. Gestblom, R. A. Hoffman and S. Rodmar, Mol. Phys. 8, 425 (1964).

(142) V. I. Glazkov, Opt. Spect. (USSR) 9, 217 (1960).

(143) R. S. Berry, R. Dehl and W. R. Vaughan, J. Chem. Phys. 34, 1460 (1961).

(144) J. V. Acrivos, Mol. Phys. 5, 1 (1962).

(145) R. W. Fessenden and J. S. Waugh, J. Chem. Phys. 30, 944 (1959).

(146) R. R. Fraser, Can. J. Chem. 38, 2226 (1960).

(147) J. Martin and B. P. Dailey, J. Chem. Phys. 37, 2594 (1962).

(148) H. S. Gutowsky, M. Karplus and D. M. Grant, ibid. 31, 1278 (1959).

(149) H. M. Hutton and T. Schaefer, Can. J. Chem. 40, 875 (1962).

(150) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys. 23, 1152 (1955).

(151) H. M. Hutton and T. Schaefer, Can. J. Chem. 41, 2429 (1963).

(152) B. Sunners, L. H. Piette and W. G. Schneider, Can. J. Chem. 38, 581 (1960).

(153) R. K. Harris, ibid. 42, 2275 (1964).

(154) R. K. Harris, ibid. 42, 2282 (1964).

(155) P. L. Corio, Chem. Rev. 60, 363 (1960).

(156) B. D. Rao and P. Venkateswaran, Proc. Indian Acad. Sci. 54A, 1 (1961).

(157) D. M. Grant and H. S. Gutowsky, J. Chem. Phys. 34, 699 (1961).

(158) B. Bak, J. N. Shoolery and G. A. Williams, J. Mol. Spect. 2, 525 (1958).

(159) P. M. Parker and L. C. Brown, J. Am. Phys. 27, 509 (1959).

(160) G. Gioumousis and J. D. Swalen, J. Chem. Phys. 36, 2077 (1962).

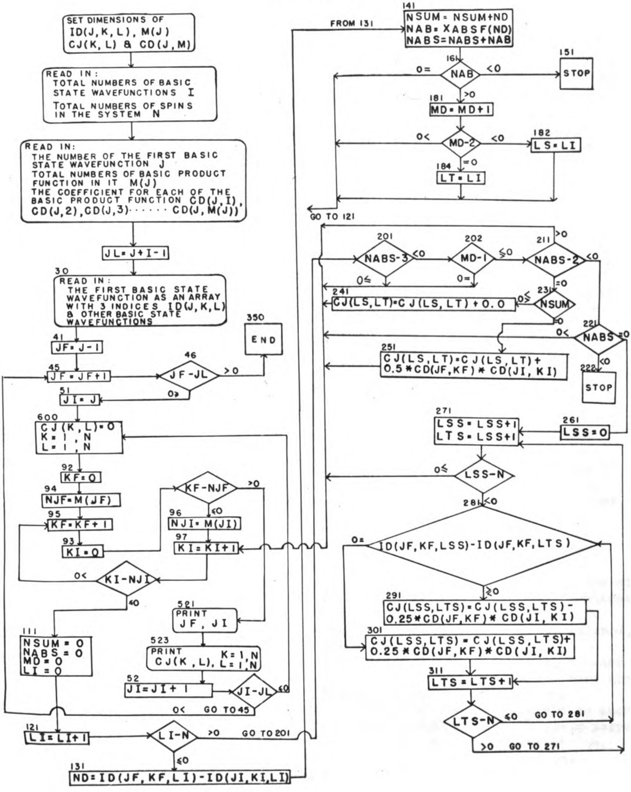
APPENDIX I PROGRAM 'MATRELE'

```
      PROGRAM MATRELE
      DIMENSION ID(32,4,5),CJ(5,5),N(32),CD(32,4)
      READ 10,I,NN
   10 FORMAT(2I5)
      READ 15,J
   15 FORMAT(I2)
      JL=J+I-1
      READ 20,(N(K),K=J,JL)
   20 FORMAT(32I2)
      PRINT 20,(N(K),K=J,JL)
      DO 27 K=J,JL
      NK=N(K)
      DO 27 NCD=1,NK
   25 READ 26,CD(K,NCD)
   26 FORMAT(F10.7)
   27 PRINT 28,CD(K,NCD)
   28 FORMAT(1H ,F10.7)
      DO 32 JK=J,JL
      NK=N(JK)
      DO 32 KN=1,NK
   30 READ 31,(ID(JK,KN,LN),LN=1,NN)
   31 FORMAT(5I1)
   32 PRINT 33, (ID(JK,KN,LN),LN=1,NN)
   33 FORMAT(1H ,5I1)
   41 JF=J-1
   45 JF=JF+1
   46 IF(JF-JL)51,51,350
   51 JI=J
  600 DO 601 K=1,NN
      DO 601 L=1,NN
  601 CJ(K,L)=0
   92 KF=0
   94 NJF=N(JF)
   95 KF=KF+1
   93 KI=0
      IF(KF-NJF)96,96,521
   96 NJI=N(JI)
   97 KI=KI+1
      IF(KI-NJI)111,111,95
  521 PRINT 522, JF,JI
  522 FORMAT(2I5)
      PRINT 523, ((CJ(K,L), K=1,NN), L=1,NN)
  523 FORMAT(12F10.6//)
   52 JI=JI+1
      IF(JI-JL)600,600,45
```

```
111  NSUM=0
     NABS=0
     MD=0
     LI=0
121  LI=LI+1
122  IF(LI-NN)131,131,201
131  ND=ID(JF,KF,LI)-ID(JI,KI,LI)
141  NSUM=NSUM+ND
     NAB=XABSF(ND)
     NABS=NABS+NAB
161  IF(NAB)151,121,181
151  STOP
181  MD=MD+1
     IF(MD-2)182,184,121
182  LS=LI
     GO TO 121
184  LT=LI
     GO TO 121
201  IF(NABS-3)202,97,97
202  IF(MD-1)211,97,211
211  IF(NABS-2)221,231,97
221  IF(NABS)222,261,97
222  STOP
231  IF(NSUM)241,251,241
241  CJ(LS,LT)=CJ(LS,LT)+0.0
     GO TO 97
251  CJ(LS,LT)=CJ(LS,LT)+0.5*CD(JF,KF)*CD(JI,KI)
     GO TO 97
261  LSS=0
271  LSS=LSS+1
     LTS=LSS+1
     IF(LSS-NN)281,97,97
281  IF(ID(JF,KF,LSS)-ID(JF,KF,LTS))291,301,291
291  CJ(LSS,LTS)=CJ(LSS,LTS)-0.25*CD(JF,KF)*CD(JI,KI)
     GO TO 311
301  CJ(LSS,LTS)=CJ(LSS,LTS)+0.25*CD(JF,KF)*CD(JI,KI)
311  LTS=LTS+1
321  IF(LTS-NN)281,281,271
350  END
```

Program "Matrele"

FLOW CHART



APPENDIX II. PROGRAM "ASSIGN"

VARIABLES, NAMES AND ARRAYS

N	Number of observed spectral lines (input).
NA	Number of possible transitions (input).
NB	Number of nuclei with spin ½ (input).
ND	Number of unassignable (forbidden) transitions (input).
NN	Number of times zero-intensity (unobserved) spectral line has been used.
NT	Number of last initially assigned transition (input).
IP	Next available location in KH array, initially IP = 1.
NPEI	Permissible error of intensities (input).
NPEP	Permissible error of positions (input).
IQ	Next available network number, initially IQ = 5.
IR	Next available index of I and J arrays.
IS	Number of energy level from which current transition occurs.
ISSS	Index to avoid meaningless permutations of equivalent energy levels. If ISSS = 0, try the first spectral line in the list for the next transition. If ISSS = 1, try the next spectral line in the list for the next transition.
IT	Number of energy level to which current transition occurs.
IU	Number of spectral line being considered.
IV	Number of transition currently to be assigned.
NW	Number of energy levels, 2^{NB} (input).

IX, IY, IZ, IYY and IZZ are dummy variables.

KA(1,2,...,N+1)	Positions of lines in order of decreasing intensities. KA(N+1) = 0 (input).
LAB(1,2,...,NW)	Normalized intensity factor by which intensities of transitions <u>from</u> a level exceed those <u>to</u> the
KB(1,2,...,N+1)	Normalized intensities of lines in decreasing order. KB(N+1) = 0 (input).
IBC(1,2,...,NB+1)	Binomial coefficients of NB.
KC(1,2,...,N)	Transition assignments of lines. 0 = unassigned,
KD(1,2,...,NA)	Numbers of lines assigned to transitions; e.g., KD(4)=7 means line 7 has been assigned to transition 4, KD(5)=-1 means transition 5 is forbidden.
KE(1,2,...,NW)	Energies of energy levels, relative to KE(1) = 0.
KF(1,2,...,NW)	Network assignments of energy levels. 0 = unassigned, 1 = network 1, etc.
KG(1,2,...,NA)	Number of energy levels assigned to networks by each transition. KG(12)=3 means three levels were assigned to a new network by the 12th transition.
KH(1,2,...)	Numbers of energy levels assigned to networks by each transition, stored consecutively. KG array keeps track of how many are due to each transition.
I(1,2,...)	Network numbers of levels before IV transition assignment , indexed by IR.

J(1,2,....)	Amount added to network to bring it into correlation with another network, through transition V.
K(1,2,...,NA)	Energy level numbers from which transitions occur. e.g, K(29)=6 means the 29th transition is from level 6.
L(1,2,...,NA)	Energy level numbers to which transitions occur.
M(1,2,...,NW)	Lowest numbered transition from each energy level.
MA(1,2,...NW)	Total number of possible transitions from each energy level.
MB(1,2,...NW)	Accumulated intensities of transitions to each energy level.
MC(1,2,...NW)	Accumulated intensities of transitions from each energy level.

NOTES

All data are introduced as integers and all calculations are fixed point.

Intensities are initially normalized to 1000 $NB \cdot 2^{(NB-1)}$.

Networks identify the possibility of non-interacting sets of levels, e.g., symmetric and antisymmetric.

```
      PROGRAM ASSIGN
      DIMENSION KA(50),KB(50),KC(50),KD(3003),KE(128),KF(128),KG(3003),
     1KH(400),I(200),J(200),K(3003),L(3003),M(128),MA(128),MB(128),
     2MC(128),LAB(128),IBC(9)
  100 READ 101, N,NA,NB,NW,NPEI,NPEP,ND,NT
  101 FORMAT(8I5)
      NEE=N+1
      READ 104, (KA(IX), IX=1,NEE)
  104 FORMAT(13I6)
      READ 104, (KB(JX),JX=1,NEE)
      READ 2100,(KD(JX),JX=1,NA)
 2100 FORMAT(40I2)
      IZ=1
      NBV=NB+1
      DO 102 IX=1,NBV
      IBC(IX)=IZ
      IZ=IZ*(NB-IX+1)/IX
  102 PRINT 103, (IBC(IX))
  103 FORMAT (I4)
      IV=1
      IYY=0
      IZZ=1
      DO 106 JX=1,NB
      IBCE=IBC(JX)
      DO 116 IY=1,IBCE
      MX=IY+IYY
      M(MX)=IV
      JXA=JX+1
      MA(MX)=IBC(JXA)
      LAB(MX)=1000*(NB+2-2*JX)
      IBCV=IBC(JXA)
      DO 116 IZ=1,IBCV
      K(IV)=IY+IYY
      L(IV)=IZ+IZZ
      PRINT 8, (K(IV), L(IV))
    8 FORMAT(2I5)
  116 IV=IV+1
      IYY=IYY+IBC(JX)
      KX=JX+1
  106 IZZ=IZZ+IBC(KX)
  200 DO 201 IX=1,N
  201 KC(IX)=0
      DO 202 JX=1,NW
      KE(JX)=0
      KF(JX)=0
      MB(JX)=0
  202 MC(JX)=0
```

```
      IP=1
      IQ=5
      IR=1
      KF(1)=1
      IV=1
      NN=0
      KAN=0
      KBN=0
      KCN=0
      KDN=0
      KEN=0
      KFN=0
      KGN=0
      KHN=0
      KIN=0
      KJN=0
      KKN=0
      KLN=0
      KMN=0
      KNN=0
      KON=0
      KPN=0
      PRINT 204, N,NA,NB,NW,NPEI,NPEP,ND,NT
  204 FORMAT(8I5)
      NE=N+1
      PRINT 205,(KA(IX),IX=1,NE)
  205 FORMAT(13I6)
      PRINT 206, (KB(JX),JX=1,NE)
  206 FORMAT(13I6)
      IF(NT-1)300,999,999
  999 DO 2201 LX=1,NT
      IF(KD(LX))300,300,2202
 2201 CONTINUE
 2202 DO 2222 NX=1,NT
      IY=KD(NX)
      KC(IY)=NX
      IS=K(NX)
      IT=L(NX)
      KE(IT)=KE(IS)+KA(IY)
      KF(IT)=KF(IS)
      KG(NX)=1
      KH(IP)=IT
      IP=IP+1
      MC(IS)=MC(IS)+KB(IY)
      MB(IT)=MB(IT)+KB(IY)
 2222 IV=NT+1
```

```
  300 IF(KD(IV))301,400,400
  301 IV=IV+1
      GO TO 300
  400 ISSS=0
      IU=1
  500 IF(IU-(N+1))511,501,1800
  511 IF(KC(IU))600,501,600
  501 IS=K(IV)
      IT=L(IV)
      IF((MC(IS)+KB(IU))-(MB(IS)+LAB(IS)+NPEI))503,503,502
  502 IF(IU-(N+1))600,1800,1800
  503 IX=M(IS)+MA(IS)-IV
      IF(ISSS-1)504,700,504
  504 IF(IX-1)701,700,701
  700 IF((MC(IS)+IX*KB(IU))-(MB(IS)+LAB(IS)-NPEI))1800,701,701
  701 IF(IU-(N+1))704,702,702
  702 IF(NN-(NA-N-ND))703,1800,1800
  703 NN=NN+1
      KG(IV)=0
      GO TO 800
  704 KFS=KF(IS)
      KFT=KF(IT)
      IF(KFS-KFT)900,705,900
  705 IF(KFS)706,1000,706
  706 IF(KE(IT)-(KE(IS)+KA(IU)+NPEP))707,707,600
  707 IF(KE(IT)-(KE(IS)+KA(IU)-NPEP))600,708,708
  708 KG(IV)=0
 1100 KC(IU)=IV
      MB(IT)=MB(IT)+KB(IU)
      MC(IS)=MC(IS)+KB(IU)
  800 KD(IV)=IU
      IF(IV-26)1400,810,880
  810 KAN=KAN+1
      IF(KAN-5)801,801,1400
  880 IF(IV-31)1400,811,881
  811 KBN=KBN+1
      IF(KBN-5)801,801,1400
  881 IF(IV-45)1400,812,882
  812 KCN=KCN+1
      IF(KCN-5)801,801,1400
  882 IF(IV-55)1400,813,883
  813 KDN=KDN+1
      IF(KDN-5)801,801,1400
  883 IF(IV-58)1400,814,884
  814 KEN=KEN+1
      IF(KEN-5)801,801,1400
  884 IF(IV-61)1400,815,885
  815 KFN=KFN+1
```

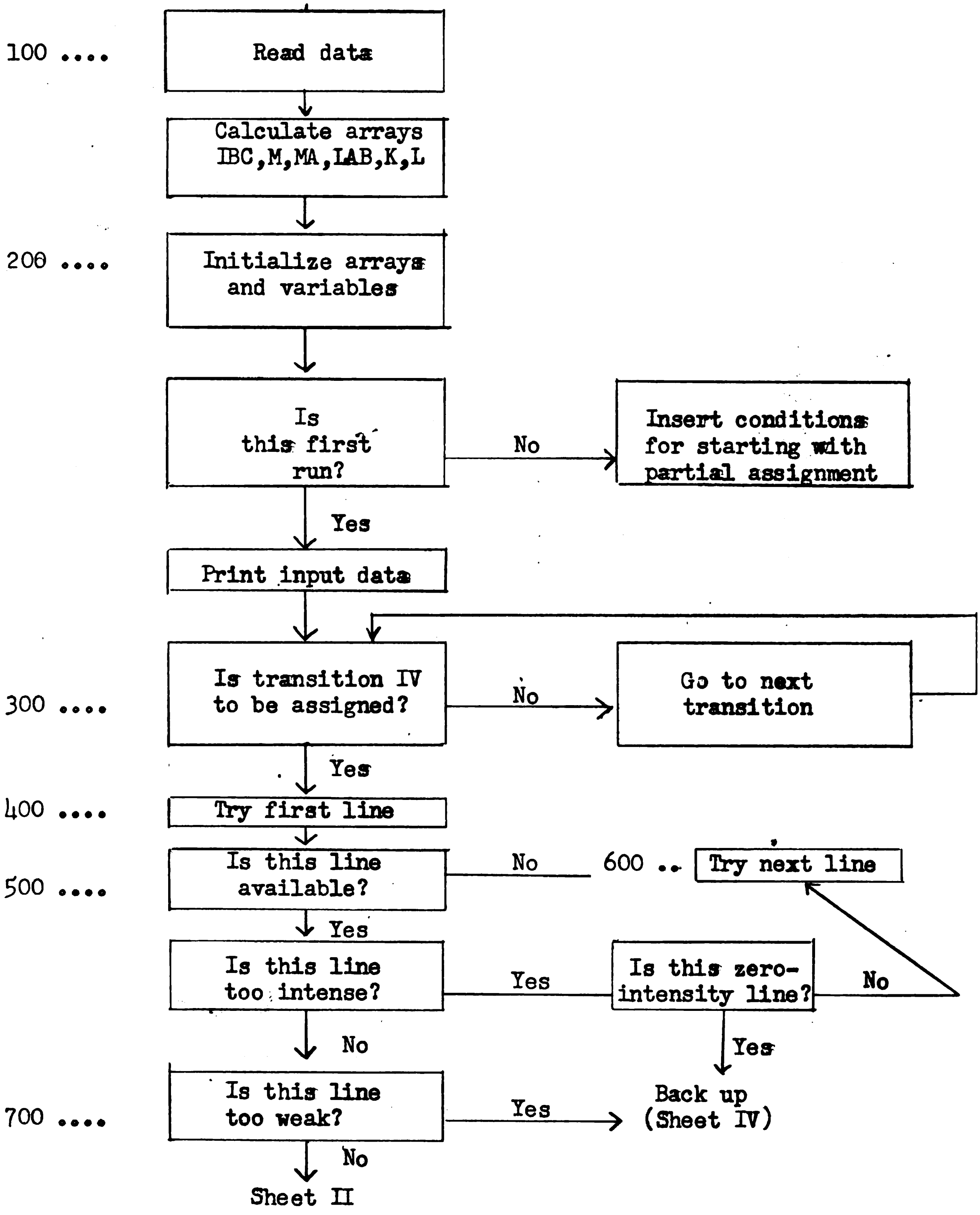
```
      IF(KFN-5)801,801,1400
  885 IF(IV-68)1400,816,886
  816 KGN=KGN+1
      IF(KGN-5)801,801,1400
  886 IF(IV-71)1400,817,887
  817 KHN=KHN+1
      IF(KHN-5)801,801,1400
  887 IF(IV-78)1400,818,888
  818 KIN=KIN+1
      IF(KIN-5)801,801,1400
  888 IF(IV-81)1400,819,889
  819 KJN=KJN+1
      IF(KJN-5)801,801,1400
  889 IF(IV-105)1400,820,890
  820 KKN=KKN+1
      IF(KKN-5)801,801,1400
  890 IF(IV-145)1400,821,891
  821 KLN=KLN+1
      IF(KLN-5)801,801,1400
  891 IF(IV-163)1400,822,892
  822 KMN=KMN+1
      IF(KMN-5)801,801,1400
  892 IF(IV-180)1400,823,893
  823 KNN=KNN+1
      IF(KNN-5)801,801,1400
  893 IF(IV-190)1400,824,894
  824 KON=KON+1
      IF(KON-5)801,801,1400
  894 IF (IV-200) 1400,825,825
  825 KPN=KPN+1
      IF(KPN-5)801,801,1400
  801 PRINT 1151,(KD(IX), IX=1,NA)
 1151 FORMAT(30I4)
 1400 IF(IV-NA)1401,1150,1150
 1401 IV=IV+1
      IF(KD(IV))1400,1402,1402
 1402 IF(IS-K(IV))400,1600,400
 1600 IT=L(IV)
      IF(KF(IT))400,1601,400
 1601 IF(IS-1)1602,1700,1602
 1602 IF(IS-2)1603,1700,1603
 1603 IF(IS-(NB+2))1604,1700,1604
 1604 IF(ISSS-1)1605,1700,1605
 1605 ISSS=1
      IU=1
      GO TO 500
 1700 ISSS=1
```

```
      IF(IU-(N+1))600,500,500
 600  IU=IU+1
1701  GO TO 500
1000  KF(IS)=IQ
      IQ=IQ+1
      KG(IV)=2
      KH(IP)=IS
      IPV=IP+1
      KH(IPV)=IT
      I(IR)=0
      KE(IS)=0
      J(IR)=0
      IP=IP+2
      IR=IR+1
1200  KF(IT)=KF(IS)
      KE(IT)=KE(IS)+KA(IU)
      GO TO 1100
 900  IF(KFT)902,901,902
 901  KG(IV)=1
      KH(IP)=IT
      IP=IP+1
      GO TO 1200
 902  IF(KFS)904,903,904
 903  KG(IV)=1
      KH(IP)=IS
      IP=IP+1
      KF(IS)=KF(IT)
      KE(IS)=KE(IT)-KA(IU)
      GO TO 1100
 904  IF(KFS-XMINOF(KFS,KFT))908,907,908
 907  I(IR)=KFT
      J(IR)=KE(IS)+KA(IU)-KE(IT)
      GO TO 1300
 908  I(IR)=KFS
      J(IR)=KE(IT)-KE(IS)-KA(IU)
1300  KG(IV)=0
      DO 1307 IX=1,NW
      IF(KF(IX)-XMAXOF(KFS,KFT))1308,1304,1308
1304  KF(IX)=XMINOF(KFS,KFT)
1306  KE(IX)=KE(IX)+J(IR)
      KG(IV)=KG(IV)+1
      KH(IP)=IX
1307  IP=IP+1
1308  IR=IR+1
      GO TO 1100
1800  IV=IV-1
      IF(IV)1801,1801,1500
```

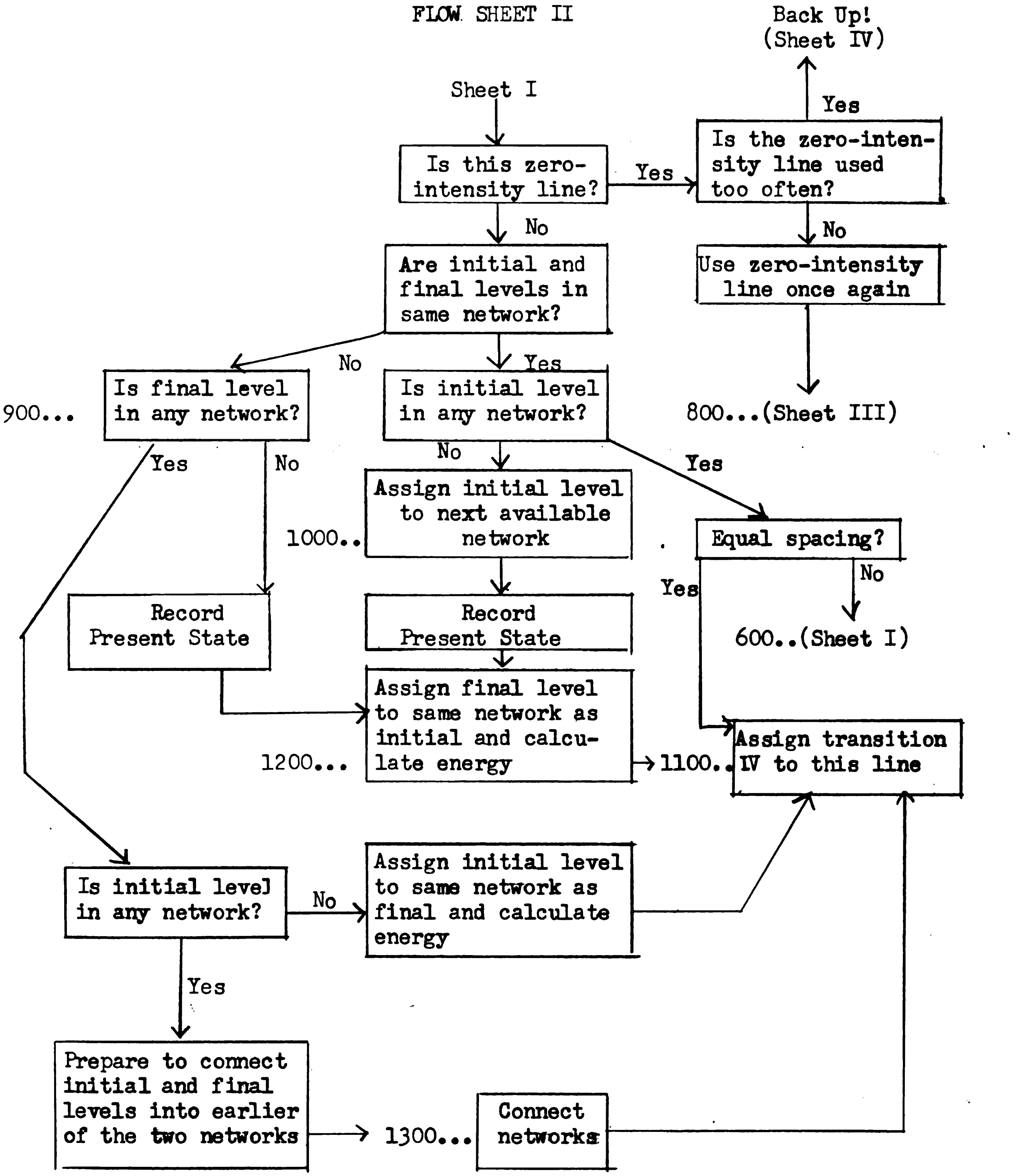
```
1801 NPEI=2*NPEI
     NPEP=2*NPEP
     IF(NPEP-100)200,200,1888
1888 STOP
1500 IF(KD(IV))1800,1501,1501
1501 IU=KD(IV)
     KC(IU)=0
     KD(IV)=0
     IF(IU-(N+1))1503,1502,1502
1502 NN=NN-1
     GO TO 1800
1503 IS=K(IV)
     IT=L(IV)
     MB(IT)=MB(IT)-KB(IU)
     MC(IS)=MC(IS)-KB(IU)
     IF(KG(IV))1504,1900,1504
1504 IF(KG(IV)-1)1506,1505,1506
1505 IP=IP-1
     IX=KH(IP)
     KF(IX)=0
     IF(IX-IT)1900,1700,1900
1506 IR=IR-1
     KGV=KG(IV)
     DO 1507 IX=1,KGV
     IP=IP-1
     IY=KH(IP)
     KF(IY)=I(IP)
1507 KE(IY)=KE(IY)-J(IR)
1900 ISSS=0
     GO TO 600
1150 PRINT 1151, (KD(IX), IX=1,NA)
     GO TO 1500
2000 END
```

PROGRAM "ASSIGN"

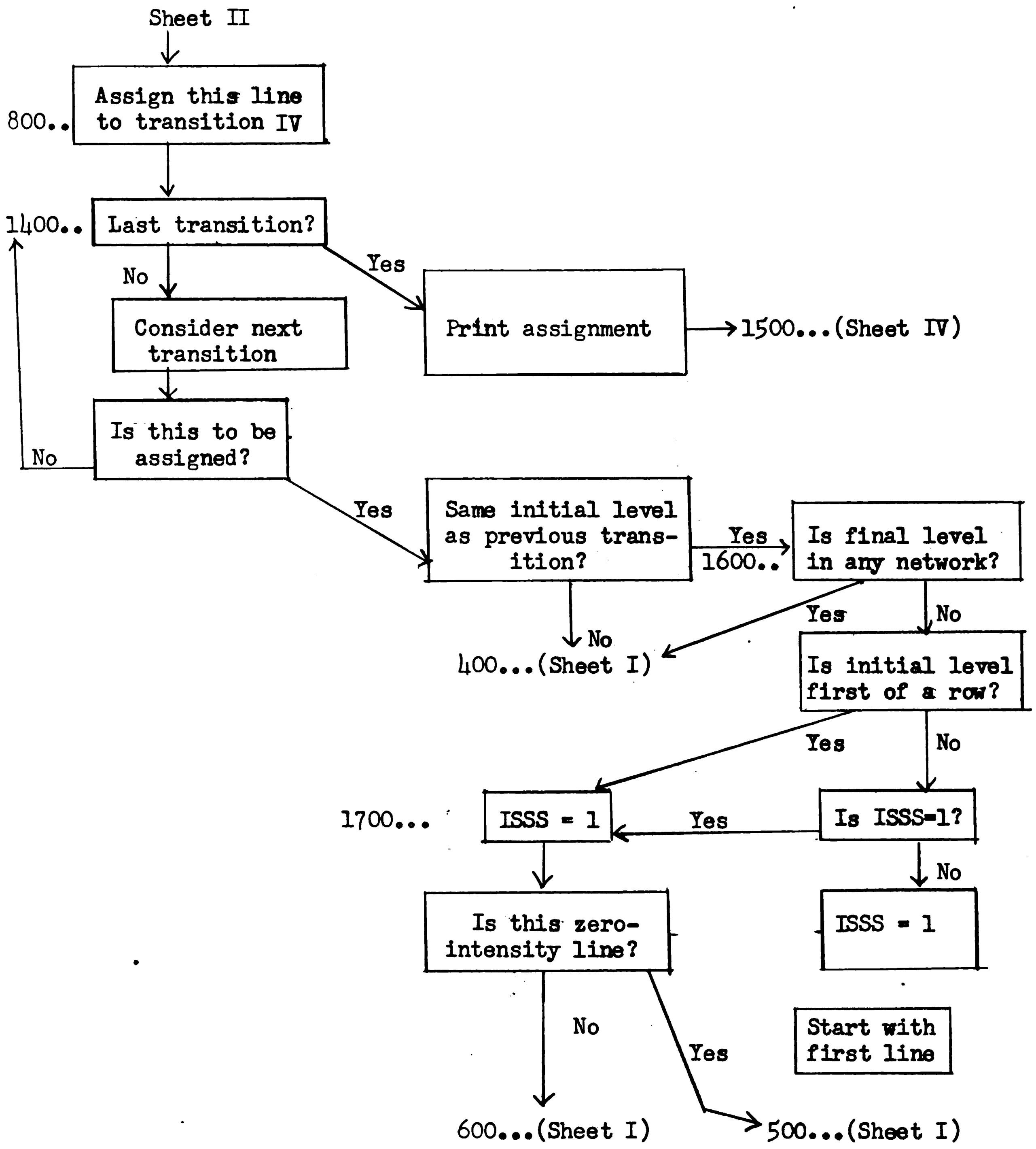
FLOW SHEET I



FLOW SHEET II



FLOW SHEET III



FLOW SHEET IV