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NUCLEAR MAGNETIC RESONANCE SPECTRA
OF
TWOFOLD SYMMETRIC MOLECULES.

by

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Nuclear Magnetic Resonance Spectra of Twofold Symmetric Molecules submitted by Alan R. Quirt in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

A new general method of calculating the high resolution NMR spectra of all molecules with twofold frame symmetry has been developed. Full use is made of all of the symmetry factoring of the Hamiltonian matrix resulting from the twofold frame symmetry, and from any magnetic equivalence.

Explicit formulas have been derived to allow the direct calculation, from spin quantum numbers, of all of the Hamiltonian matrix elements. The formulas are valid for molecules with or without magnetically equivalent groups of nuclei, including the important class of molecules containing symmetrically equivalent pairs of magnetically equivalent groups. For molecules without frame symmetry, the formulas reduce to those of the Composite Particle method. They are suitable both for hand calculations on small molecules and for computer calculations on large molecules.

A systematic three stage approach to the factoring of the Hamiltonian matrix has been described, in which this symmetry factoring, molecular total spin factoring, and species total spin factoring are applied in succession. It has been shown that this approach to factoring simplifies the derivation of transition selection rules, and leads directly to a description of the structure of an NMR spectrum in terms of subspectra.

A computer program, NUMAR, has been written to allow the application of the full three stage factoring scheme to the spectra of molecules too large for hand calculations. In addition to the usual energy level and transition lists, the program provides all of the quantum numbers necessary to define the structure of the calculated spectrum in terms of subspectra. The efficient design of the program permits calculations on many large symmetric molecules whose spectra previously could be calculated only by approximate methods, if at all.

The new factoring procedure has been applied in the analysis of the NMR spectra of several molecules with twofold frame symmetry, including the perfluoro-2-butenes, the 2,5-dimethyl-3-hexenes, and $[(F_3C)_2P]_2NH$. In each case, initial NMR parameters obtained from a partial or approximate analysis were refined with the aid of exact spectra calculated with the NUMAR computer program. The use of all of the factoring appropriate to each molecule simplified all the analyses; in the case of the 2,5-dimethyl-3-hexenes, it permitted accurate calculations on spin systems too large for previous computer programs.

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CHAPTER 1 INTRODUCTION

1.1. High Resolution NMR Spectra

In a Nuclear Magnetic Resonance experiment, a sample containing magnetic nuclei is placed in a strong, uniform polarizing magnetic field and a weak radiofrequency magnetic field is applied. For particular frequencies of the radiofrequency field, resonant absorption of energy occurs; the intensity of absorption as a function of frequency is the NMR spectrum of the sample. This Thesis is restricted to High Resolution NMR, where the sample is a mobile, isotropic fluid, and there are no strong couplings to paramagnetic or quadrupolar species. The spectrum then normally consists of sharp lines with a natural linewidth of 1 Hz. or less.[†]

Most High Resolution NMR spectra are obtained from nuclei of spin $I = \frac{1}{2}$. Because nuclei of spin $I = 0$ (such as ^{12}C and ^{16}O) have no magnetic moments, they

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[†] For general information on the nature of Nuclear Magnetic Resonance, see Pople, Schneider, and Bernstein (PSB)[1]. For a more mathematical treatment of the theoretical aspects of NMR, with proofs of many useful theorems, see Corio[2] especially Chapters 5 and 2. The notation used in this Thesis, an extension of Corio's, is described in Appendix A.

do not interact with magnetic fields, and have no NMR spectra. Nuclei of spin $I > \frac{1}{2}$ are normally coupled by their electric quadrupole moments to fluctuations in the local electric field gradients, resulting from molecular motions. As a result, the lifetimes of their spin states are short, and their NMR spectra have linewidths orders of magnitude too great to be considered high resolution. When a nucleus of spin ½ is strongly coupled to a quadrupolar nucleus such as ^{14}N, its lines may also be broadened (see PSB[1]). More often, nuclei of spin greater than ½ may be treated as non-magnetic, because they have no observable effect on the spectra of the spin ½ nuclei.

Nuclei with electric quadrupole moments are not excluded completely from this Thesis, because they may yield High Resolution NMR spectra when they are in environments of high symmetry. However, the main emphasis is on nuclei of spin ½.

The parameters of chemical interest which determine the High Resolution NMR spectrum of a molecule are one chemical shift ν_i for each magnetic nucleus and one coupling constant J_{ij} connecting each pair of nuclei. For n nuclei there are thus a total of $n(n+1)/2$ parameters. The chemical shifts vary linearly with the strength of the polarizing magnetic field, but the coupling constants are independent of field strength.

There is no practical general method of calculating the parameters directly from the observed spectrum. Instead, one must calculate the spectrum that corresponds to a set of trial parameters, and compare it with the observed one. If the observed and calculated spectra agree, the trial parameters are probably correct.[†]

In principle, the calculation of a High Resolution NMR spectrum is quite easy. The Hamiltonian[‡] has the simple form

$$\underline{H} = \sum_i \nu_i \underline{I}_z(i) + \sum_{i<j} J_{ij} \underline{\vec{I}}(i) \cdot \underline{\vec{I}}(j). \tag{1.1}$$

A suitable basis set consists of products of spin functions for the individual nuclei, of the form

$$\prod_i |I_i, m_i\rangle. \tag{1.2a}$$

[†] It is always possible to invert the signs of all of the coupling constants simultaneously without in any way affecting the appearance of the calculated spectrum (see Corio[2], p. 167); often the spectrum is also insensitive to the relative signs of many of the coupling constants. One method of determining the relative signs of coupling constants is described in §3.3.2. The absolute signs of some coupling constants have been determined from spectra of partially oriented molecules in anisotropic media.[3]

[‡] Throughout this Thesis only nuclear spin Hamiltonians are used. The nuclear spin operators such as $\underline{\vec{I}}$ and $\underline{I}_z$ are dimensionless. See Appendix A for definitions of all operators, eigenvalues, and basis kets.

Since each nucleus has 2I+1 m-values ranging from +I to -I, there are

$$\prod_i (2I_i+1) \qquad (1.2b)$$

basis functions in the set.

A matrix representation of the Hamiltonian (1.1) in the basis (1.2a) is constructed; its dimension is given by (1.2b). When the Hamiltonian matrix has been diagonalized, differences between its eigenvalues give the transition frequencies. The corresponding relative intensities are given by the absolute squares of the matrix elements of the transition operator[†]

$$\underline{X} = \sum_i \underline{I}_x(i). \qquad (1.3)$$

The matrix elements of $\underline{X}$ are most easily calculated in the simple product basis (1.2). The matrix elements of $\underline{X}$ in the basis in which $\underline{H}$ is diagonal can be obtained from them using the unitary transformation that relates the bases. The total spectral intensity that is

---

[†] This equation is an approximation which introduces an error far smaller than the usual uncertainty in experimental intensities. See Corio[2] p. 164.

obtained using (1.3) is[2]

$$\frac{2}{3}\left\{ \prod_i (2I_i+1) \right\}\cdot\left\{ \sum_i I_i(I_i+1) \right\} \tag{1.4a}$$

which for n nuclei of spin ½ reduces to the simple form

$$n2^{n-1} \tag{1.4b}$$

The method of calculation described above is valid for all spin systems, but practical only for small ones. For example, each of the perfluoro-2-butenes (§5.1) has eight nuclei of spin ½. The 256×256 Hamiltonian matrix has 32896 distinct matrix elements (many of which are, in fact, zero). There could be as many as 11440 transitions. If thousands of distinct transitions were visible in the experimental spectrum, there would be little hope of recognizing patterns helpful in estimating the parameters. Trial and error calculations, with thirty-six independent parameters, would also be unlikely to yield a correct solution, even if reasonable values for some of the parameters could be estimated from previous work with related compounds.

The observed spectrum of each of the perfluoro-2-butenes contains only about 100 distinct lines of significant intensity, largely as a result of the high symmetry of the molecules.

For each isomer, the six $-CF_3$ fluorines have one chemical shift, and the two =C-F fluorines have a second chemical shift. Each spectrum consists of two multiplets, one centred on each chemical shift. The relative chemical shifts can be varied by using a variety of polarizing field strengths. For typical field strengths (over 10 kgauss), the two multiplets are far enough apart that the appearance of each multiplet is independent of the relative chemical shifts. Thus none of the eight chemical shift parameters need be determined in order to calculate the pattern of lines in the multiplets.[†]

The symmetry of the molecule also reduces the number of independent coupling constant parameters from 28 to four (F_3C-C=C-CF_3, F-C=C-F, F-C(=)-CF_3, F-C=C-CF_3). Thus only four parameters, rather than 36, need be found in order to completely analyze the spectrum. Quite generally, the complexity of an NMR spectrum is more closely related to the number of independent parameters than to the number of nuclei.

The major goal of this Thesis is to outline a method of calculating NMR spectra, such that the same factors that simplify the observed spectrum also simplify the calculation.

[†] As each multiplet is symmetrical about its chemical shift, the two chemical shifts can in fact be obtained by inspection.

1.2. Factoring the Hamiltonian Matrix

The NMR spectra of the perfluoro-2-butenes, and other molecules, are simplified by two molecular properties: symmetry, and large chemical shift separations. As a result of these molecular properties, certain symmetry operators and spin operators commute with the Hamiltonian. This in turn leads to the simplified method of calculation that is the goal of this Thesis.

If two operators commute, there exists a set of vectors which are simultaneous eigenvectors of both operators. This implies that if a basis for the Hamiltonian has been constructed out of eigenfunctions of any operator $\underline{O}$ which commutes with the Hamiltonian, there can be no off-diagonal matrix elements of the Hamiltonian between basis functions belonging to different eigenvalues of $\underline{O}$. The complete Hamiltonian matrix, before diagonalization, can be reduced to block diagonal form, with each block corresponding to a different eigenvalue of $\underline{O}$. If there is an additional operator that commutes with both $\underline{H}$ and $\underline{O}$, these blocks (submatrices) can themselves be factored into blocks along the main diagonal, and so on. Each block is labelled by a unique set of eigenvalues of the operators that commute with $\underline{H}$.

In an NMR calculation, this factoring process can be viewed as taking place in three stages, each stage being associated with a different kind of operator that commutes with $\underline{H}$ and with the other such operators.

The first stage, which is discussed in Chapter 2, is associated with symmetry operators. Because the symmetry operators commute with the transition operator $\underline{X}$, as well as with $\underline{H}$, every transition must connect states in the same symmetry submatrix. Thus each symmetry submatrix of $\underline{H}$ can be treated as a separate calculation.

The remaining two stages of factoring, which are associated with two kinds of total spin operator, are discussed in Chapter 3. With a suitable choice of basis, they can be applied as readily to each symmetry submatrix as to the complete Hamiltonian matrix of a molecule without symmetry.

The practical result of the factoring is that a single large, difficult calculation, involving the complete Hamiltonian matrix, is replaced by a series of smaller, easier calculations, involving the submatrix blocks along the main diagonal. In the example already used, the perfluoro-2-butenes, no block larger than 4×4 need be diagonalized after all three stages of factoring have been applied. The total number of Hamiltonian matrix elements to be evaluated is 32896 without factoring, and 168 with full use of all three stages of factoring.

CHAPTER 2. SYMMETRY FACTORING

This Chapter presents a new method of calculating the NMR spectra of all molecules with twofold symmetry. The spin Hamiltonian used is valid for all combinations of magnetic equivalence and twofold symmetry, including symmetrically equivalent pairs of magnetically equivalent groups. Expressions for all Hamiltonian matrix elements and transition intensities are given in a form suitable for computer calculations.

2.1. The NMR Symmetry Group

The symmetry properties of the NMR Hamiltonian were first used to simplify calculation of the NMR spectra of small, rigid molecules, such as 1,1-difluoroethylene.[1-4] The symmetry of these molecules can be adequately represented by a conventional point group (C_2 for 1,1-difluoroethylene), but there is usually no suitable point group for nonrigid molecules such as those with free rotation about a skeletal single bond.

Longuet-Higgins[5] has developed a more general approach to symmetry to describe the infrared spectra of nonrigid molecules, and Woodman[6] has shown that it can readily be adapted to NMR. Woodman's NMR Symmetry

Group (NMRSG) contains all permutations, of isotopically identical magnetic nuclei, that do not alter chemical shifts or coupling constants. The symmetry (or lack of symmetry) of non-magnetic nuclei is relevant only to the extent that it affects the environment of the magnetic nuclei.

The correct NMRSG for a nonrigid molecule cannot always be predicted from the structural formula. Many chemical shifts and coupling constants vary with the conformation of the molecule. If the molecule changes conformation rapidly,[†] the chemical shifts and coupling constants for the observed spectrum will be population-weighted averages over the values for the individual conformations. As a result, the NMRSG will often contain symmetry elements that are not present in any single molecular conformation. When the populations of the different conformations are not known, the NMRSG can be determined only by comparing the observed spectrum with trial spectra calculated for various possible symmetries.

[†] A nonrigid molecule's conformation is changing rapidly if its spectrum shows no effects that depend on the average lifetime of the conformations. In the other extreme, a conformation whose lifetime is much longer than the lifetime of a nuclear spin state is in effect a rigid molecule with its own spectrum. Conformation lifetimes between these extremes are beyond the scope of this thesis; see, for example, PSB[1], Chapter 10.

The symmetry operations of the NMRSG can be separated into two subgroups, either or both of which may include only the identity. The first of these subgroups includes only permutations within fully equivalent groups[†] of nuclei. The nuclei in a fully equivalent group must have:

i) equal chemical shifts,
ii) equal coupling constants to any nucleus outside the group,
iii) equal coupling constants within the group.

When these three conditions are satisfied, the Hamiltonian is invariant to any permutation of the fully equivalent nuclei. The subgroup of the NMRSG that describes the local symmetry of fully equivalent groups of nuclei can then be written as the direct product of symmetric[7] permutation groups, P_n.

The first two conditions for full equivalence are the necessary and sufficient conditions for the conservation of the square of the total spin[‡] of the group of nuclei. Every fully equivalent group is thus, by definition, a magnetically equivalent group.[8,9] It

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[†] The word 'group' is used throughout this thesis both for collections of nuclei and for groups (in the mathematical sense) of symmetry operations. It should be obvious from the context which meaning applies.

[‡] See §2.2 and Appendix A.

can be shown (see Corio[2] p. 175) that coupling constants within a magnetically equivalent group have no effect on transition frequencies or intensities. It will therefore be assumed throughout this thesis that all coupling constants within a magnetically equivalent group are effectively zero, and no distinction will be made between a magnetically equivalent group and a fully equivalent group of nuclei. The NMRSG, in this thesis, is the same as Woodman's Effective NMR Symmetry Group.[7]

The second ('frame'[7]) subgroup of the NMRSG permutes entire magnetically equivalent groups of nuclei. Magnetically equivalent groups interchanged by frame symmetry operations form a symmetrically equivalent set. Symmetrically equivalent sets of single nuclei are included in this definition, since a single nucleus can be considered a magnetically equivalent group of one. For example, in the perfluoro-2-butenes the single element of frame symmetry interchanges the two CF_3 groups and simultaneously interchanges the two olefinic fluorines. The frame subgroup is normally isomorphic with one of the geometrical point groups (C_2, C_s, or C_i in the example). This makes it convenient to borrow the notation of an appropriate geometrical point group, but it should not be assumed that any likely conformation has the geometry appropriate to the point group used. All that can be said is that the average values of the chemical shifts and coupling constants make the Hamiltonian invariant to particular permutations of nuclei.

Although the NMRSG of a molecule can usually best be described in terms of permutations, other approaches may lead to simpler calculations. For example, it is perfectly valid to classify the spin functions of a magnetically equivalent group according to the irreducible representations of the appropriate symmetric permutation group P_n. Since the character tables of all symmetric permutation groups useful in NMR are readily available,[10] in principle there is no difficulty in constructing a basis with the proper symmetry. However, in order to calculate Hamiltonian matrix elements and transition intensities, it is necessary to expand each basis function in terms of the original basis (1.2). For the larger magnetically equivalent groups this would involve a vast amount of unnecessary calculation. The composite particle method, described in §2.2, provides identical results without requiring any explicit expansion of the symmetrized basis.

2.2 Magnetic Equivalence[†]

In the composite particle approach to magnetic[8] equivalence, a total spin operator $\vec{\underline{F}}$ is defined for each magnetically equivalent group:

$$\vec{\underline{F}}(r) = \sum_{i \text{ in } r} \vec{\underline{I}}(i). \tag{2.1}$$

Any single nuclei are considered to be magnetically equivalent groups of one, with $\vec{\underline{F}} \equiv \vec{\underline{I}}$. The spin Hamiltonian (1.1) is rewritten in terms of these total spin operators:

$$\underline{H} = \sum_{r} \nu_r \underline{F}_z(r) + \sum_{r<s} J_{rs} \vec{\underline{F}}(r) \cdot \vec{\underline{F}}(s). \tag{2.2}$$

The conditions for magnetic equivalence are the necessary and sufficient conditions for $\underline{F}^2$ to commute with $\underline{H}$ and with the transition operator $\underline{X}$ of Eq. (1.3). As a result, it can be shown[2] that the terms involving coupling constants within magnetically equivalent groups, which have been omitted from the Hamiltonian (2.2), can have no effect on the high-resolution NMR spectrum.

Comparing (1.1) and (2.2), it is apparent that a magnetically equivalent group, when in a state with

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[†] This section presents only a brief summary of the useful results of the composite particle method. For a more detailed account with proofs, see §5.4 of Corio[2].

spin F, can be treated as a composite particle of spin I = F. A magnetically equivalent group of n nuclei of spin I takes on all non-negative F values in the sequence F = nI, nI-1, nI-2, ...

To take advantage of the commutation properties of the $\underline{F}^2$ operators, the basis for the system should be constructed from their eigenfunctions. A simple product form similar to (1.2) is suitable:

$$\prod_r |F_r,m_r>. \tag{2.3}$$

When these basis functions are correlated with the unsymmetrized basis functions (1.2), it is apparent that for each group all F values except the highest are degenerate, with degeneracy g_F. An index $s = 1,2,\ldots,g_F$ can be introduced; the basis vectors satisfy the orthogonality relationships[2]

$$<F_i,m_i;s_i|F_j,m_j;s_j> = \delta_{F_iF_j}\delta_{m_im_j}\delta_{s_is_j} \tag{2.4}$$

The indices i and j are used here for a magnetically equivalent group in two basis functions.

Since $\underline{F}^2$ for each magnetically equivalent group commutes with the Hamiltonian (2.2), the Hamiltonian matrix can be reduced to block-diagonal form with each block (submatrix) labelled by a unique set of F and s values.

Because $\underline{F}^2$ also commutes with the transition operator $\underline{X}$, every transition must connect energy levels in the same block.

The Hamiltonian (2.2) is written in terms of $\vec{\underline{F}}$ and $\underline{F}_z$ operators only; thus blocks whose basis functions have identical F and m values, but different s values, must yield identical Hamiltonian matrix elements. Similarly, the transitions in these blocks must be identical. The spectrum corresponding to each unique set of F values need be calculated only once, and its intensities multiplied by the statistical weight $\prod_i g_{F_i}$ (the index i running over magnetically equivalent groups), which can be calculated without reference to the original $|I,m>$ basis (see Corio[2] p. 120). These partial spectra for all sets of F values are then superimposed to give the complete spectrum of the spin system.

The same total spin properties of a magnetically equivalent group that provide useful factoring of the Hamiltonian matrix also lead to the new form (2.2) for the Hamiltonian. Matrix elements for an entire magnetically equivalent group can be found as easily as those of a single nucleus. In contrast, the permutation symmetry of the same magnetically equivalent group does not lead to a usefully simplified Hamiltonian. Instead, the original Hamiltonian (1.1) must be used to evaluate the complicated expressions for matrix elements in the symmetrized basis.

As the two approaches yield identical factoring,[†] the composite particle method will be used throughout the remainder of this thesis. A particular set of F values for all magnetically equivalent groups will be treated as defining a unique block (submatrix) of the Hamiltonian, with the implicit assumption that an appropriate statistical weight must be applied to all of its transition intensities.

C. W. Haigh has proposed (private communication) an excellent notation for symmetric spin systems, which is used throughout this Thesis.

As usual,[1] letters close together in the alphabet (A,B,...) are used for magnetically equivalent groups with similar chemical shifts, and other letters far from them in the alphabet (W,X,...) are used for groups widely separated in chemical shift from the A,B,... groups. The number of nuclei in each magnetically equivalent group

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[†] For magnetically equivalent groups of nuclei of spin 1/2, there is a one-to-one correspondence between total spin and irreducible representation in P_n. But for groups of three or more nuclei of spin $I > \frac{1}{2}$, blocks of basis functions degenerate with respect to F may belong to different irreducible representations of P_n. This yields no extra factoring, and is in any event unimportant; such groups are seldom significantly coupled to the other magnetic nuclei in the molecule. See Diehl, Harris, and Jones,[11] p.34, and their references.

is indicated by a subscript. Thus the spin ½ nuclei in monochloroethane form an A_2X_3 spin system.

An n-fold element of frame symmetry is indicated by $[...]_n$ enclosing the notation for a typical member of each symmetrically equivalent set. Thus 1,3,5-trifluorobenzene is an $[AX]_3$ spin system, and either of the perfluoro-2-butenes is an $[AX_3]_2$ spin system. Groups invariant to the symmetry operation are placed outside the brackets. Thus p-fluorotoluene could be described as $A_3[KL]_2X$.

The extension of the notation to molecules with more than one element of frame symmetry involves the use of more than one set of brackets. It will not be described here, because such molecules are outside the scope of this Thesis.

2.3. Twofold Frame Symmetry

2.3.1. The Spin Hamiltonian

The composite particle method has greatly simplified calculations involving magnetically equivalent groups,[8] but only conventional group theory has previously been used to deal with frame symmetry. It is shown below that for molecules with twofold frame symmetry it is useful to apply two general principles of the composite particle method: the basis is constructed from eigenfunctions of group total spin operators, and the Hamiltonian is written in terms of spin operators that embody all the symmetry of the spin system.

When there is twofold frame symmetry, the Hamiltonian (2.2) can be rearranged as follows

$$\left.\begin{aligned}
\underline{H} = {} & \sum_i \nu_i \underline{F}_z(i) + \sum_{i<j} J_{ij} \underline{\vec{F}}(i)\cdot\underline{\vec{F}}(j) \\
& + \sum_{ip}\sum J_{ip}[\underline{\vec{F}}(i)\cdot\underline{\vec{F}}(p)+\underline{\vec{F}}(i)\cdot\underline{\vec{F}}(p')] \\
& + \sum_p \nu_p[\underline{F}_z(p)+\underline{F}_z(p')] + \sum_p J_{pp'}\underline{\vec{F}}(p)\cdot\underline{\vec{F}}(p') \\
& + \sum_{p<q} J_{pq}[\underline{\vec{F}}(p)\cdot\underline{\vec{F}}(q)+\underline{\vec{F}}(p')\cdot\underline{\vec{F}}(q')] \\
& + \sum_{p<q} J_{qp}[\underline{\vec{F}}(p)\cdot\underline{\vec{F}}(q')+\underline{\vec{F}}(p')\cdot\vec{F}(q)]\,.
\end{aligned}\right\} \tag{2.5}$$

In (2.5), magnetically equivalent groups which are transformed into themselves by the frame symmetry (invariant groups) are labelled i,j,.... All other groups must appear in pairs, labelled p,q,..., such that the frame symmetry element interchanges the primed and unprimed members of each pair. The two distinct coupling constants (usually cis and trans) connecting pairs p and q are written J_{pq} and J_{qp}. The coupling constants connecting the two members of a pair to any invariant group must be equal or the symmetry is destroyed. As a result it is pointless to use frame symmetry unless there are at least two pairs in addition to any invariant groups. A single pair, as in 1,3-dichloro-benzene, meets the conditions for magnetic equivalence and is better treated by the usual composite particle method.

The actual nature of the twofold symmetry operation is irrelevant as long as the Hamiltonian can be written in the symmetrical form (2.5). In practice the NMR symmetry is usually the result of a plane or twofold axis of symmetry in the molecule, taking the conformation as an average over an NMR time scale. For convenience, the notation of the group C_2 will be used below, but this should not be considered a restriction to molecules with that symmetry.

A total spin operator $\underline{\vec{A}}$ is defined for each symmetrically equivalent pair of groups

$$\underline{\vec{A}}(p) = \underline{\vec{F}}(p) + \underline{\vec{F}}(p'), \qquad (2.6)$$

and a new basis is constructed which diagonalizes $\underline{A}^2$ and $\underline{A}_z$ for each pair.[†] In terms of the basis (2.3), the new basis for each pair may be written

$$|A,M\rangle = \sum_{\kappa} (F,F',\kappa,M-\kappa|F,F',A,M)\ |F,\kappa\rangle|F',M-\kappa\rangle. \quad (2.7a)$$

The Clebsch-Gordan coefficients[‡] (and the $|A,M\rangle$) exist only for values of A satisfying the triangle inequalities

$$|F-F'| \le A \le F+F' \quad (2.7b)$$

The basis for the entire spin system then consists of a product of magnetic equivalence functions for all invariant groups and pair total spin functions for all symmetrically equivalent pairs of groups

$$\prod_i |F_i,m_i\rangle \cdot \prod_p |A_p,M_p\rangle. \quad (2.8)$$

The symmetry properties of this basis are discussed in §2.3.3.

[†] It should be emphasized that, by definition, none of the $\underline{A}^2(p)$ commute with the Hamiltonian. If $\underline{A}^2$ for any pair of groups does commute with $\underline{H}$, all the nuclei in the pair of groups form a single magnetically equivalent group.[2]

[‡] The notation of Condon and Shortley[12] is used for the Clebsch-Gordan coefficients $(F,F',\kappa,M-\kappa|F,F',A,M)$.

One can now rewrite the Hamiltonian (2.5) using the symmetric spin operators $\vec{\underline{A}}(p)$ and the complementary antisymmetric operators

$$\vec{\underline{B}}(p) = \vec{\underline{F}}(p) - \vec{\underline{F}}(p'), \tag{2.9}$$

obtaining

$$\left.\begin{aligned} \underline{H} = {} & \sum_i \nu_i \underline{F}_z(i) + \sum_{i<j} J_{ij} \vec{\underline{F}}(i) \cdot \vec{\underline{F}}(j) \\ & + \sum_i \sum_p J_{ip} \vec{\underline{F}}(i) \cdot \vec{\underline{A}}(p) \\ & + \sum_p \nu_p \underline{A}_z(p) + \sum_p J_{pp'} \vec{\underline{F}}(p) \cdot \vec{\underline{F}}(p') \\ & + \tfrac{1}{2} \sum_{p<q} (J_{pq} + J_{qp}) \vec{\underline{A}}(p) \cdot \vec{\underline{A}}(q) \\ & + \tfrac{1}{2} \sum_{p<q} (J_{pq} - J_{qp}) \vec{\underline{B}}(p) \cdot \vec{\underline{B}}(q). \end{aligned}\right\} \tag{2.10}$$

The transition operator is now written

$$\underline{X} = \sum_i \underline{F}_x(i) + \sum_p \underline{A}_x(p). \tag{2.11}$$

2.3.2. Matrix Elements in the Symmetrized Basis

Many of the matrix elements appearing in (2.10) are easy to evaluate. $\underline{F}_z$ and $\underline{A}_z$ can contribute only to diagonal matrix elements, since the basis is constructed from their eigenfunctions. $\underline{\vec{F}}\cdot\underline{\vec{F}}'$, which commutes with both $\underline{A}^2$ and $\underline{A}_z$, also contributes only diagonal matrix elements. The first formula $12^3 2$ of Condon and Shortley[12] becomes, in the present notation,

$$\langle A,M|\underline{\vec{F}}\cdot\underline{\vec{F}}'|A,M\rangle = \tfrac{1}{2}[A(A+1)-F(F+1)-F'(F'+1)]. \qquad (2.12)$$

The remaining terms in (2.10) can contribute to either diagonal or off-diagonal matrix elements. Their dot-product form permits the separate evaluation of the two halves of each product. Each half is a matrix element such as $\langle A,M|\underline{\vec{A}}|A',M'\rangle$, whose vector character is shown in the following equations by the use of the Cartesian unit vectors $\vec{i},\vec{j},\vec{k}$.

The matrix elements of $\underline{\vec{F}}$ for the invariant groups are well known.[2] Those of $\underline{\vec{A}}$ and $\underline{\vec{B}}$ for the pairs can be found from the equations for matrix elements of $\underline{\vec{F}}$ and $\underline{\vec{F}}'$ in an $|A,M\rangle$ basis, given in pages 56-73 of Condon and Shortley.[12] The matrix elements of $\underline{\vec{A}}$ in the $|A,M\rangle$ basis are, of course, similar to those of $\underline{\vec{F}}$ in the $|F,m\rangle$ basis. Since $\underline{\vec{A}}$ commutes with $\underline{A}^2$, $\Delta A=0$ for all its nonzero matrix elements:

$$\left.\begin{aligned} \langle A,M|\vec{\underline{A}}|A,M\rangle &= M\,\vec{k} \\ \langle A,M|\vec{\underline{A}}|A,M\pm1\rangle &= [(A\mp M)(A\pm M+1)]^{\frac{1}{2}}\,\frac{\vec{i}\pm i\vec{j}}{2}. \end{aligned}\right\} \qquad (2.13)$$

The commutation rules for $\vec{\underline{B}}$ with respect to $\vec{\underline{A}}$ follow the common pattern

$$\begin{array}{lll} [\underline{A}_x,\underline{B}_x] = 0 & [\underline{A}_x,\underline{B}_y] = i\underline{B}_z & [\underline{A}_y,\underline{B}_x] = -i\underline{B}_z \\ [\underline{A}_y,\underline{B}_y] = 0 & [\underline{A}_y,\underline{B}_z] = i\underline{B}_x & [\underline{A}_z,\underline{B}_y] = -i\underline{B}_x \\ [\underline{A}_z,\underline{B}_z] = 0 & [\underline{A}_z,\underline{B}_x] = i\underline{B}_y & [\underline{A}_x,\underline{B}_z] = -i\underline{B}_y. \end{array}$$

As a result,

$$\langle A,M|\vec{\underline{B}}|A\pm\Delta A,M\pm\Delta M\rangle = 0 \quad \text{unless} \quad \Delta A=0,1;\Delta M=0,1. \qquad (2.14)$$

Nonzero matrix elements of $\vec{\underline{B}}$ allowed by (2.14) are

$$\left.\begin{aligned} \langle A,M|\vec{\underline{B}}|A-1,M\rangle &= f(F,F',A)\,[A^2-M^2]^{\frac{1}{2}}\,\vec{k} \\ \langle A,M|\vec{\underline{B}}|A-1,M\pm1\rangle &= f(F,F',A)\,[(A\mp M)(A\mp M-1)]^{\frac{1}{2}}\,\frac{\vec{i}\pm i\vec{j}}{2} \\ \langle A,M|\vec{\underline{B}}|A,M\pm1\rangle &= g(F,F',A)\,[(A\mp M)(A\pm M+1)]^{\frac{1}{2}}\,\frac{\vec{i}\pm i\vec{j}}{2} \\ \langle A,M|\vec{\underline{B}}|A,M\rangle &= g(F,F',A)M\,\vec{k}, \end{aligned}\right\} \qquad (2.15)$$

where

$$\left.\begin{aligned} f(F,F',A) &= \left[\frac{[A^2-(F-F')^2][(F+F'+1)^2-A^2]}{A^2(4A^2-1)} \right]^{1/2} \\ g(F,F',A) &= \frac{F(F+1)\ -\ F'(F'+1)}{A(A+1)}. \end{aligned}\right\} \qquad (2.16)$$

Note that when F=F′, $g(F,F',A)$ vanishes, giving the stronger condition $\Delta A=\pm 1$ for nonzero matrix elements of $\underline{\vec{B}}$. The expression for $f(F,F',A)$ then reduces to the simpler form

$$f(F,F',A) = \left[\frac{(2F+1)^2-A^2}{4A^2-1} \right]^{1/2}. \qquad (2.17)$$

As an aid to hand calculations, the squares of the factors in (2.16) are given in Table 2-1 for all combinations of F, F′, and A that occur for pairs of groups with spin up to 3/2.

TABLE 2-1

Squares of Factors[†] $\mathcal{f}(F,F',A)$ and $g(F,F',A)$

of $<A,M|\underline{\vec{B}}|A',M'>$

F	F′	A	A′ = 2	A′ = 1	A′ = 0
3/2	3/2	3	1/5	0	0
		2	0	4/5	0
		1	4/5	0	5
3/2	1/2	2	1/4	1/4	—
		1	1/4	9/4	—
1	1	2	0	1/3	0
		1	1/3	0	8/3
1	0	1	—	1	—
1/2	1/2	1	—	0	1

[†] See equations (2.15) and (2.16). Primes on A and M are used only to distinguish between bra and ket values.

2.3.3. Symmetry Properties of the |A,M> Basis

When the molecular twofold symmetry operator $\underline{C}_2$ is applied to the basis (2.8), the basis function (2.7) for each symmetrically equivalent pair becomes

$$\underline{C}_2|A,M\rangle = \sum_{\kappa}(F,F',\kappa,M-\kappa|F,F',A,M)|F',M-\kappa\rangle|F,\kappa\rangle \qquad (2.18)$$

The resulting basis function clearly belongs to a submatrix of the Hamiltonian related to the original submatrix by the interchange of all primed and unprimed groups. There are two possible cases: when for every pair $F=F'$, the new and old basis functions are the same; otherwise, $\underline{C}_2$ relates basis functions in different submatrices.

Thus when $F \neq F'$ for at least one pair, the product functions (2.8) are not eigenfunctions of $\underline{C}_2$, and the magnetic equivalence submatrix cannot be further factored on symmetry. However, from the symmetry of (2.5) it is obvious that the two submatrices related by $\underline{C}_2$ are degenerate. Energy levels and transition intensities need be found for only one member of each such pair of submatrices, giving it double the usual statistical weight.

When for all pairs $F=F'$, the redundant prime in (2.18) can be dropped. Substituting $m=M-\kappa$ and reversing the order of summation, one obtains from (2.18)

$$\underline{C}_2|A,M\rangle = \sum_{m}(F,F,M-m,m|F,F,A,M)|F,m\rangle|F,M-m\rangle \qquad (2.19)$$

Interchanging the two F values, along with the corresponding m values, at most changes the sign of a Clebsch-Gordan coefficient.† Thus (2.19) becomes

$$\left.\begin{aligned}\underline{C}_2|A,M\rangle &= \sum_m (-1)^{2F-A}(F,F,m,M-m|F,F,A,M)|F,m\rangle|F,M-m\rangle \\ &= (-1)^{2F-A}|A,M\rangle\end{aligned}\right\} \quad (2.20)$$

For each pair, |A,M> belongs to one of the irreducible representations of C_2. The state of highest spin belongs to the A representation, and those of lower spin are alternately B and A. The complete product function (2.8) will have B symmetry if an odd number of the individual pair functions have B symmetry; otherwise it will have A symmetry. The invariant groups, which always have A symmetry, cannot affect the symmetry of the product function.

Every submatrix in which all F=F′ may now be separated into two submatrices containing the symmetric (A) and antisymmetric (B) basis functions respectively. Because $\underline{C}_2$ commutes with both the Hamiltonian and the transition operator, these submatrices are completely independent of one another, just as they are independent of all magnetic equivalence submatrices with different F values.

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† $(j_1 j_2 m_1 m_2|j_1 j_2 J\ M) = (-1)^{j_1+j_2-J}(j_2 j_1 m_2 m_1|j_2 j_1 J\ M)$. See Condon and Shortley[12] p. 78.

2.3.4. Transitions

Transition intensities are calculated from the matrix elements of the transition operator $\underline{X}$ (see Eq. 2.11). Transitions involving invariant groups have intensities proportional to

$$| <F,m|\underline{F}_x|F,m-1> |^2, \qquad (2.21a)$$

and those involving symmetrically equivalent pairs have intensities proportional to

$$| <A,M|\underline{A}_x|A,M-1> |^2. \qquad (2.21b)$$

All $\underline{F}^2$ commute with $\underline{X}$, giving the selection rule $\Delta F=0$. Similarly, for those magnetic equivalence submatrices in which all $F=F'$, there is the additional selection rule that the symmetry must not change. Both of these selection rules are taken care of implicitly by treating each submatrix as an independent calculation. It must be remembered that all transition intensities for any submatrix are multiplied by the appropriate statistical weight to account for any degeneracy.

Since all $\underline{A}^2$ commute with $\underline{X}$, there is the additional selection rule within each submatrix that $\Delta A=0$ for every symmetrically equivalent pair.

2.3.5. Discussion

The form of the symmetrized Hamiltonian, Eq. (2.10), was chosen to show its derivation clearly, and as a result it appears unnecessarily complicated. It can be simplified by redefining some of its terms. The definition of the total spin operator $\underline{\vec{A}}$ can be extended to include $\underline{\vec{F}}$ for all invariant groups, just as $\underline{\vec{F}}$ includes $\underline{\vec{I}}$ for all single nuclei. Sums over i,j... now include both invariant groups and symmetrically equivalent pairs; sums restricted to the pairs now use the indices ℓ,m,.... In each case a symmetrically equivalent pair is considered to be a single entity, represented by a single index; primed indices such as ℓ',m$'$ are used only where the two halves of the pair must be distinguished. The two coupling constants J_{pq} and J_{qp} are combined to give the symmetrized couplings

$$\left.\begin{aligned} J_{\ell m} &= \tfrac{1}{2}(J_{pq} + J_{qp}) \\ J_{m\ell} &= \tfrac{1}{2}(J_{pq} - J_{qp}). \end{aligned}\right\} \qquad (2.22)$$

With these changes, the symmetrized Hamiltonian (2.10) can be replaced by

$$\left.\begin{aligned} \underline{H} = \sum_{i} \nu_i \underline{A}_z(i) &+ \sum_{\ell} J_{\ell\ell'} \underline{\vec{F}}(\ell)\cdot\underline{\vec{F}}(\ell') \\ &+ \sum_{i<j} J_{ij} \underline{\vec{A}}(i)\cdot\underline{\vec{A}}(j) \\ &+ \sum_{\ell<m} J_{m\ell} \underline{\vec{B}}(\ell)\cdot\underline{\vec{B}}(m); \end{aligned}\right| \tag{2.23}$$

the basis (2.8) reduces to

$$\prod_{i} \mid A_i, M_i>, \tag{2.24}$$

and (2.21a) is no longer needed. It must be remembered that the two F values for each symmetrically equivalent pair are essential to the definition of the basis, and appear in the equations for many of the matrix elements.

Equation (2.23) shows more clearly the distinction between a symmetrically equivalent pair and an invariant group. All matrix elements of $\underline{\vec{A}}$ for a pair are identical to those that would be found for an invariant group consisting of all the nuclei in the pair. The coupling constant $J_{\ell m}$ that appears in $\underline{\vec{A}}$ matrix elements connecting two pairs is just the average of the near and far couplings. But since the difference coupling $J_{m\ell}$ is not zero, matrix elements of $\underline{\vec{B}}$ can mix basis functions where a pair has different A values. This in turn allows the coupling $J_{\ell\ell'}$ within the pair to affect the appearance of the spectrum.

Frame symmetry does not factor all of the magnetic equivalence submatrices when there are symmetrically equivalent pairs of magnetically equivalent groups. However the largest submatrix, the one in which every group has its maximum F value, can always be separated into symmetric and antisymmetric parts. In these and all other symmetry-factored submatrices, $F = F'$ for every pair. As a result, $\underline{\vec{B}}$ contributes to off-diagonal matrix elements ($\Delta A = \pm 1$) only, and the simpler equation (2.17) can always be used to calculate them. If (2.23) is used for the submatrices which are not factored by symmetry, the full equations (2.15) and (2.16) must be used for at least some $\underline{\vec{B}}$ matrix elements. No factoring is lost here if the unsymmetrized Hamiltonian (2.5) is used, but the advantage of simpler equations for the Hamiltonian matrix elements may be outweighed by the need to treat each pair as two groups.

The usefulness of the symmetrized Hamiltonian and basis derived in this Chapter, is significantly increased by its suitability for computer calculations. Two characteristics of the method are particularly important in this respect. First, the simple product form of the basis (2.24) is valid for molecules of arbitrary size. Second, because the two halves of each dot-product Hamiltonian matrix element in (2.23) are evaluated separately, the calculation of each such matrix element depends only on the characteristics of the two

3.1. The Hamiltonian Matrix

The NMR Symmetry Group provides only the first stage of factoring the spin Hamiltonian. To permit easy reference to each stage, a simple subscript notation[13] is used in the remainder of this Thesis. The complete spin Hamiltonian matrix, prior to any factoring, is referred to as the Hamiltonian matrix$_1$. Symmetry factoring yields matrices$_2$, which are factored by the z component of total spin, M, into matrices$_3$. When there are large chemical shift separations, each matrix$_3$ is X factored into matrices$_4$. If a particular form of factoring does not apply, some of these terms become synonymous. For example, if there is no symmetry factoring, the single matrix$_2$ includes the entire matrix$_1$.

It is convenient to extend this notation to include other quantities associated with the Hamiltonian matrix. Thus basis functions, eigenvalues, eigenvectors, and transitions are also referred to as belonging to particular matrices$_2$, matrices$_3$, and matrices$_4$.

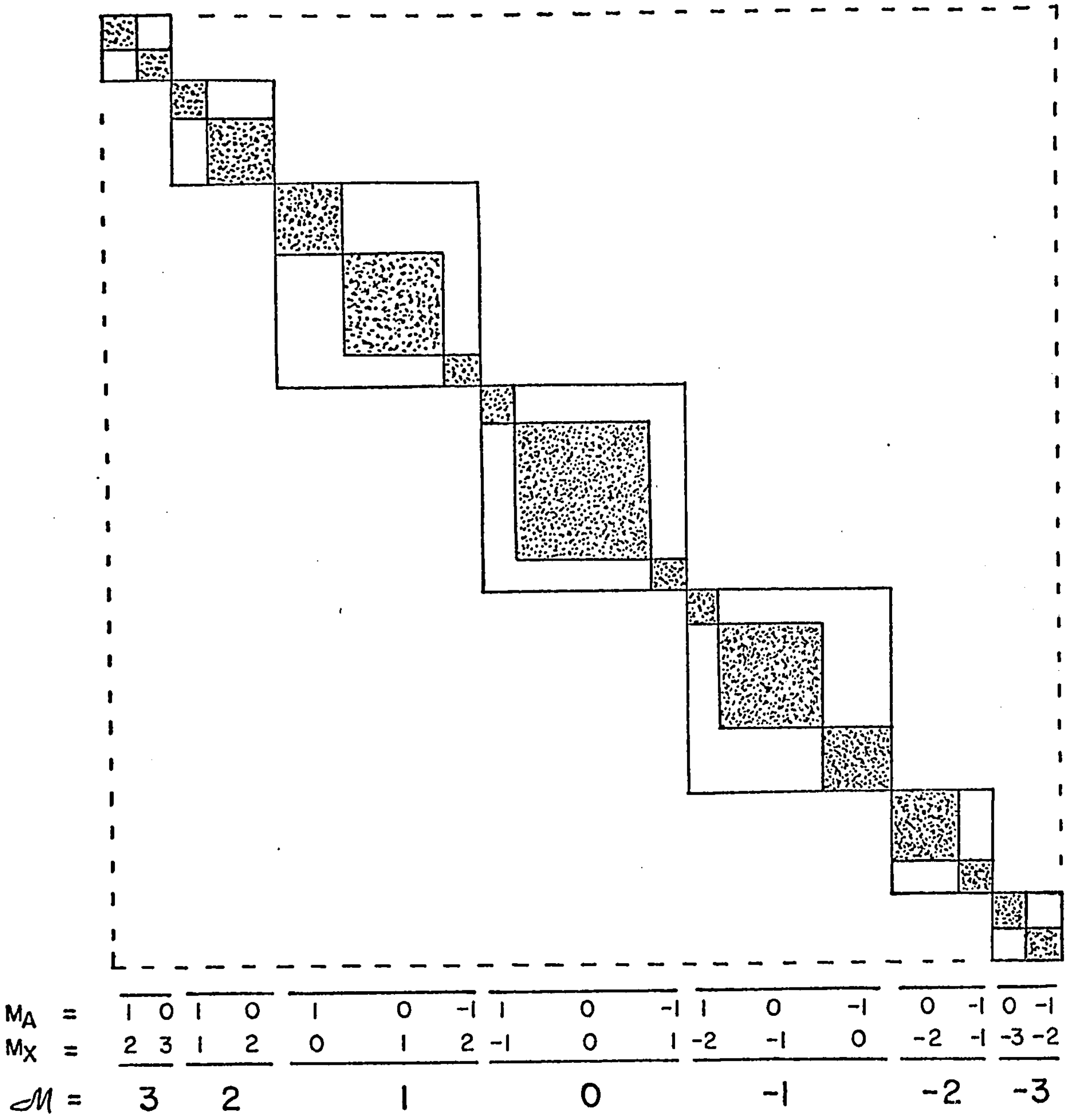
Only one kind of factoring always applies: every matrix$_2$ is factored into matrices$_3$, each labelled by a different eigenvalue M of the z component of molecular total spin. There are $2M_{max}+1$ matrices$_3$ in each matrix$_2$, with $M = M_{max}, M_{max}-1, \ldots, -M_{max}$; M_{max} is usually equal to the sum of the F values of all magnetically equivalent groups in the matrix$_2$. (When there is twofold frame symmetry, M_{max} in an antisymmetric matrix$_2$ is one less than M_{max} in the symmetric matrix$_2$ with the same set of F values.)

The size of each matrix$_3$ is determined by the number of possible basis functions with that M value. When all groups have $F = \frac{1}{2}$, with each basis function one of the 2^n possible combinations of α and β, these sizes go as the appropriate binomial coefficients. In general it can only be said that the matrices$_3$ with $M = \pm M_{max}$ are smallest, and those with M nearest zero are largest, within each matrix$_2$.

The third stage, X factoring, derives its name from the usual convention[1] for describing nuclear spin systems. Nuclei forming a set with similar chemical shifts are labelled A,B,...; those in a second set are labelled X,Y,... if all of the coupling constants J_{AX} connecting them to the first set are much smaller than the corresponding chemical shift separations Δ_{AX}. The concept can be generalized to allow any number of sets of nuclei, each of which meets these conditions with respect to every other set. Each such set of nuclei in a molecule is referred to here as a species.

The basic assumption of X factoring is that $\underline{A}_z(S)$, the z component of total spin for each species, commutes with the Hamiltonian. Each corresponding eigenvalue, M_S, is then a good quantum number. This approximation is valid only when all terms containing the first and higher powers of J_{AX}/Δ_{AX} can legitimately be dropped in a perturbation calculation (see Corio[2] Chapter 7). If the various species are in fact different isotropic species such as ^{19}F and ^{31}P, the chemical shift separation is many MHz at normal field strengths, compared with coupling constants of at most a few KHz. The X approximation is then essentially exact. Within proton spectra, coupling constants are usually small enough to allow X factoring when Δ_{AX} is only a few hundred Hz; for other nuclei, particularly ^{19}F, the wide range of chemical shifts makes X factoring even more common.

When all the M_S values are good quantum numbers, basis functions that differ in any M_S value cannot mix. An X factored matrix_3 reduces to a series of matrices_4, each of which is characterized by a unique set of M_S values whose sum is M for that matrix_3. Fig. 3-1 shows the resulting factoring of a matrix_2 from an $[AX_3]_2$ spin system (the antisymmetric matrix_2 with $F_A = F_{A'} = ½$, $F_X = F_{X'} = 3/2$). The two M_S values for each matrix_4 and the M value for each matrix_3 are given beside the matrices to which they belong. The matrix_3 boundaries show the amount of factoring that would be available if the two chemical shifts were too close together to



$[AX_3]_2$ ANTISYMMETRIC MATRIX$_2$:

$F_A = F_{A'} = 1/2$ $F_X = F_{X'} = 3/2$

FIG. 3-1. FULL FACTORING.

permit X factoring (i.e. for an $[AB_3]_2$ spin system).

The matrix sizes in Fig. 3-1 illustrate several typical points about X factoring. A large matrix_3 is generally factored into more matrices_4 than is a small matrix_3, but this does not prevent an increase in matrix_4 size as the matrix_3 size increases. Because some of the matrices_4 are quite small, the largest one in each matrix_3 may have a dimension only slightly smaller than the matrix_3. There is however a considerable saving in calculation. In the example, the three matrices_4 in the matrix_3 with $M = 0$ have sizes 1×1, 4×4, 1×1; there are, therefore, no more than 18 nonzero matrix elements compared with 36 for that matrix_3 without X factoring.

The basis functions in a matrix_2 can be paired, associating each one with its complement in which the signs of all the group M values are reversed. Since these basis functions have complementary M and M_S values, the pattern of matrix_3 and matrix_4 sizes is symmetrical about $M = 0$. In hand calculations, once the Hamiltonian matrix elements for each matrix_4 have been found, those for the complementary matrix_4 can be obtained much more quickly. Every term will be identical in magnitude to the corresponding term in the complementary matrix_4, but some terms will have the opposite sign.

The most extreme X factoring occurs for a molecule in which no two magnetically equivalent groups have closely spaced chemical shifts. Since each magnetically equivalent group is then a member of a different species, every group M is also an M_S. No two basis functions share the same set of F values and the same set of M_S values, so the Hamiltonian matrix can have no off-diagonal elements. The result is a simple spectrum of the type given in §5.2 of PSB[1]. Much of the popularity of NMR as an analytical tool results from the fact that the magnitude of every coupling constant can be taken directly from the separation of experimental lines when a spectrum meets these first order conditions.[2]

The spectrum of a molecule with frame symmetry is less easily analyzed, even when there is only one distinct chemical shift per species. The two or more magnetically equivalent groups in a symmetrically equivalent set have identical chemical shifts, and are therefore of the same species. Thus even the simplest of all spin systems with frame symmetry, $[AX]_2$, never yields a true first order spectrum.

One additional type of factoring, which has been applied by Harris[14] to some $[AX_n]_2$ spin systems, should be mentioned briefly. In strongly X factored spin systems, it may be possible to separate all the basis functions of a matrix_4 into groups, such that every off-diagonal matrix element between basis functions in different groups is some multiple of one coupling constant. If that coupling constant is zero, each of the groups of basis functions becomes a separate matrix$_5$. In hand calculations this extra factoring can yield additional easily solved 1×1 and 2×2 matrices. In computer calculations it is best ignored for two reasons: the matrices$_4$ that can be further factored are usually quite small, and there is no simple rule for sorting the basis functions into matrices$_5$.

Zero coupling constants produce additional factoring only if they appear in off-diagonal matrix elements. The basis that allows this may be different from the one that would normally be used when all coupling constants are nonzero. In the twofold frame symmetry basis of Chapter 2, both $J_{AA'}$ and $J_{XX'}$ appear only in diagonal matrix elements, and cannot affect the degree of factoring. There are 3×3 and 4×4 matrices$_4$ to diagonalize in an $[AX_3]_2$ system, and larger ones for larger $[AX_n]_2$ systems. However if a simple magnetic equivalence basis is used for any $[AX_n]_2$ system with $J_{XX'} = 0$, there is no matrix$_5$ larger than 2×2. When $J_{XX'}$ is nonzero but small, as in some molecules discussed in §5.3, Harris's[14] algebraic solution for $J_{XX'} = 0$ can still be applied to obtain a first approximation to the correct parameters.

3.2 Transitions

It was pointed out in Chapter 2 that the symmetry factoring of the Hamiltonian matrix is exactly matched by transition selection rules: each matrix_2 is a separate entity whose spectrum can be calculated without reference to the other matrices_2. Within each matrix_2, the factoring by M and M_S into matrices_3 and matrices_4 is also reflected in selection rules. These differ from the symmetry selection rules chiefly in that transitions occur not within a single matrix_3 or matrix_4, but rather between certain matrices_4 in adjacent matrices_3. It is shown below that these selection rules can be derived quite simply from the nature of the factoring described in §3.1.

The frequency of a transition is easily obtained from the algebraic difference in energy of the pair of states the transition connects. The corresponding intensity is obtained from the absolute square of the matrix element of $\underline{X}$ (see Eq. (2.21)) between these two states. This matrix element is best found indirectly. First, the readily calculated matrix elements of $\underline{X}$ in the original basis (2.3) are obtained. Each desired matrix element is then calculated from this initial representation of $\underline{X}$ using the unitary transformation that diagonalizes the Hamiltonian.

The transition selection rules in the basis representation are straightforward. There can be a nonzero matrix element of $\underline{X}$ between a pair of basis functions only if[2]

i) $\Delta F = 0$ for all magnetically equivalent groups

ii) $\Delta A = 0$ for all symmetrically equivalent pairs

iii) $\Delta M_i = \pm 1$ for some one (invariant) group or (symmetrically equivalent) pair

iv) $\Delta M_j = 0$ for all other groups and pairs.

Since, in the basis representation, the Hamiltonian matrix consists of matrix$_4$ blocks along the main diagonal, the unitary transformation that diagonalizes it can mix basis functions only within a matrix$_4$. Thus these selection rules operate at the matrix$_4$ level after the transformation.

Basis functions that meet the first two conditions must be in the same matrix$_2$. To meet the remaining two conditions, they must be in different matrices$_4$: if $\Delta M = \pm 1$ for group i, but not for any other group in the same species as group i, then the M_S values for that species differ by ±1. The fourth condition requires that $\Delta M_S = 0$ for every species other than the one containing group i. After transformation to the representation in which the Hamiltonian matrix is diagonal, it may no longer be possible to label any particular transition as belonging to group i, but all of the transitions connecting the pair of matrices$_4$ must still belong to the species whose M_S changes.

Matrices$_4$ that meet these conditions ($\Delta M_S = \pm 1$

for one species, $\Delta M_S = 0$ for all other species) are found in matrices$_3$ whose M values differ by ±1. If X factoring is not used, M_S for the only species is identical to M, and an argument similar to the one above leads to the usual selection rule[1] $\Delta M = \pm 1$. Transitions can then connect any pair of energy levels in adjacent matrices$_3$. Thus the additional selection rules introduced by the X approximation are a natural consequence of the additional factoring of the Hamiltonian matrix.

It was pointed out in §3.1 that X factoring is an approximate method in which all terms in J_{AX}/Δ_{AX} are assumed to be negligibly small. As in any perturbation method, eigenvectors are affected more than eigenvalues when the neglected terms begin to become important. In an NMR calculation, the eigenvectors are used only to transform the matrix elements of $\underline{X}$ (see Eq. (2.21)) to the representation in which the Hamiltonian is diagonal. Thus if a calculation is carried out using X factoring that is not quite justified by the chemical shifts and coupling constants, the intensities of the calculated lines may be somewhat distorted, but the frequencies will be very close to the true values. As a result, if the observed and calculated spectra are compared chiefly with respect to frequency, X factoring can be used to save time with little sacrifice in accuracy. A good example of the use of such borderline X factoring is given in

§5.2, in the analysis of the spectra of the 2,5-dimethyl-3-hexenes.

If the X-approximation is valid for a molecule, the transitions of each species are grouped together, far from the transitions of any other species. In calculations it is usually convenient to follow experimental practice, and give all chemical shifts for a species as displacements from a reference frequency in that species' region of the spectrum. Usually the reference for a calculation will be the same one used experimentally, but it is sometimes easier to use one of the chemical shifts in the molecule instead.

The chemical shift contribution to the Hamiltonian (2.23) can then be written in terms of the species reference frequencies ν_S and displacements $\bar{\nu}_i$ of each chemical shift from ν_S of its species:

$$\sum_i \nu_i \underline{A}_z(i) \equiv \sum_S \nu_S \underline{A}_z(S) + \sum_i \bar{\nu}_i \underline{A}_z(i). \tag{3.1}$$

The first sum on the right of (3.1), which contributes equally to every diagonal element of a matrix_4, contains all of the information about the actual separation between species. The selection rules described below allow transitions of species S only between matrices_4 where this sum differs by $\pm\nu_S$; thus each species' spectrum is unaffected by the ν_S values of the other species. Usually all ν_S values are set to zero, and $\overline{\nu}_i$ values are used for the chemical shifts. All calculated transition frequencies of a species are then displacements from ν_S rather than absolute transition frequencies.

3.3. The Structure of the Spectrum

3.3.1. Subspectra

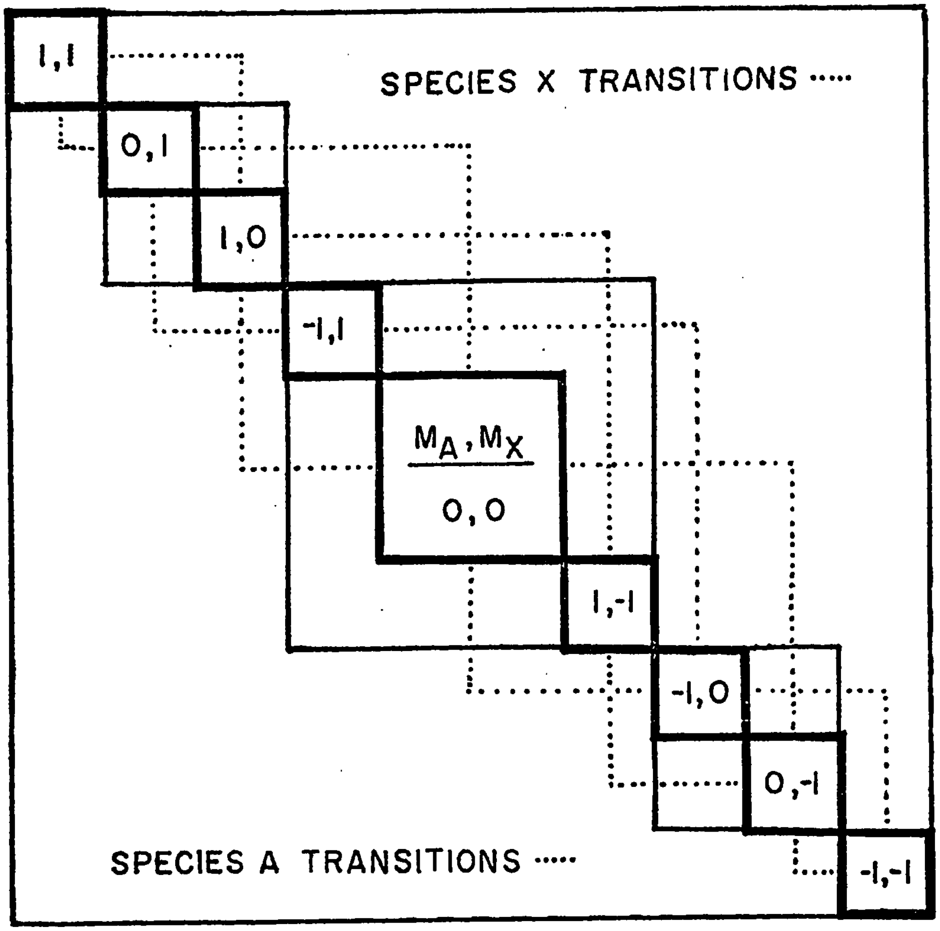
Together with symmetry factoring, X factoring breaks up the complete spectrum into smaller and more manageable groups of transitions. A particular matrix_2 yields a set of transitions that can be calculated without reference to the other matrices_2. When there is X factoring, these transitions can be separated according to species. Any single species' transitions can be further separated into sets each characterized by a particular set of M_S values for all other species. The factoring thus imposes a structure on the spectrum, making certain lines (not necessarily close together in frequency) members of natural groupings.

Each such natural grouping of lines, characterized by a particular set of quantum numbers, will be referred to as a subspectrum.[11] Though most references to subspectra will be to smaller groupings of lines, all of the lines belonging to a particular matrix_2 could also be called a subspectrum within this definition. The structure of the complete spectrum in terms of subspectra is independent of the chemical shifts and coupling constants, as long as the conditions for factoring are preserved.

Because a subspectrum is defined by a set of constant quantum numbers, its pattern of lines may be strongly affected by only a few of the chemical shifts and coupling constants. Often the functional relationship between these parameters and the line positions is simple enough to be directly useful in the analysis of complicated spectra. Many of the methods of Subspectral Analysis[11] are based on similarities between particular subspectra and the complete spectra of well known simple spin systems.

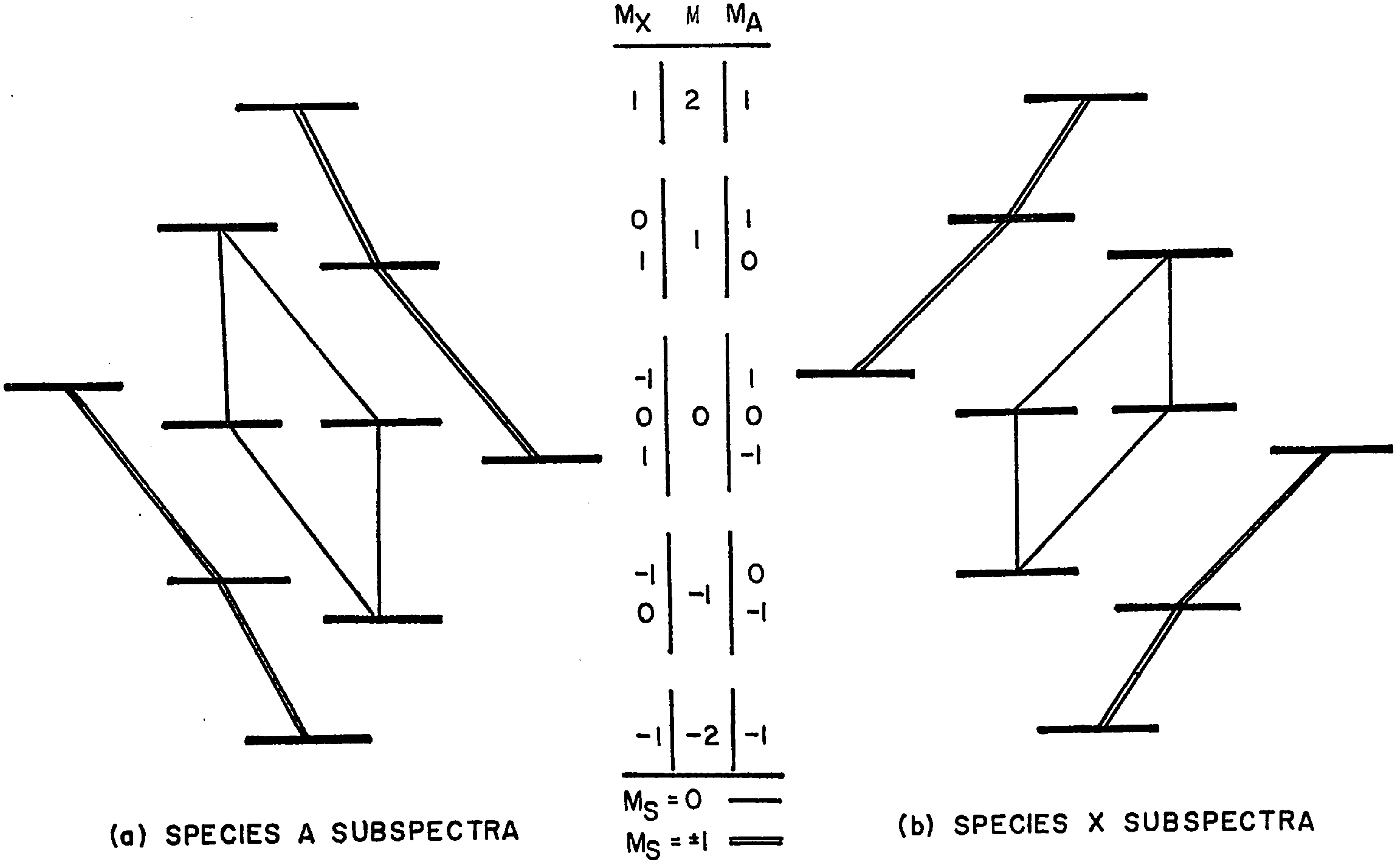
Fig. 3-2 shows the pattern of allowed transitions in the symmetric matrix$_2$ with all $F = \frac{1}{2}$ from an $[AX_3]_2$ system. This matrix$_2$, whose statistical weight is four, is identical in structure to the symmetric matrix$_2$ of an $[AX]_2$ spin system. The expressions for transition frequencies and intensities in an $[AX]_2$ spin system, given on p. 141 of PSB[1], are equally valid here. If the transitions of this subspectrum can be recognized in either the species A spectrum or the species X spectrum of the $[AX_3]_2$ system, all of the coupling constant combinations except $|J_{AA'}-J_{XX'}|$ can be calculated.

The species A transitions of this same matrix$_2$ are shown again in fig. 3-3(a), separated into subspectra. The simplest subspectra correspond to the extreme values for M_X; this is generally true in larger systems as well, partly because there are fewer basis functions with extreme M_S values than with M_S values near zero. In this case, the lines with $M_X = \pm 1$ form a strong, readily recognized



$[AX_3]_2$ SYMMETRIC MATRIX$_2$, ALL F=1/2, WEIGHT 4.

FIG. 3-2. ALLOWED TRANSITIONS.



(a) SPECIES A SUBSPECTRA

(b) SPECIES X SUBSPECTRA

FIG. 3-3. SUBSPECTRA IN THE MATRIX$_2$ OF FIG. 3-2.

doublet. The remaining four lines, whose total intensity is half that of the strong doublet, form the $M_X = 0$ subspectrum.

Within a particular species, the matrices$_4$, as well as the transitions, can be labelled as belonging to subspectra. This is true not only for this simple example, but for any X factored calculation. A transition of species A is allowed only if the M_S values of all other species are constant. Thus all transitions into or out of a matrix$_4$ are, by definition, members of the same subspectrum.

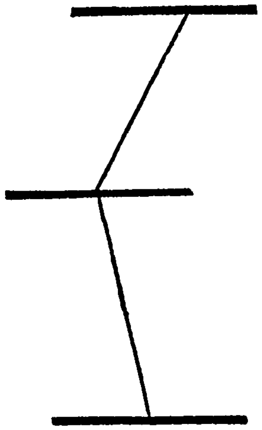
Because, in this matrix$_2$, species A and species X have the same number of groups, with the same F values, the species X subspectra in Fig. 3-3(b) follow a pattern identical to that of the species A subspectra just described. However, matrices$_4$ belonging to the same species A subspectrum never belong to the same species X subspectrum. This result can be generalized to any number of species. $\Delta M_A = \pm 1$ between matrices$_4$ connected by species A transitions. Thus these matrices$_4$ cannot belong to the same subspectrum for any other species.

3.3.2. Connected Transitions

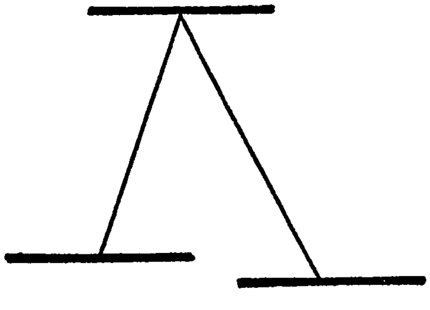
The algebraic relationship between the transition frequencies of a particular subspectrum, and unknown chemical shifts and coupling constants, is useful only if those transitions can be recognized in the experimental spectrum. Thus subspectral analysis can be applied only when the structure of the observed spectrum has already been determined. Often this requires special experimental techniques, such as the low power double resonance methods[15] described below.

In a spin tickling[15] or INDOR[16] experiment, a reasonably isolated transition (referred to below as transition *T*) is chosen. It is irradiated continuously while a second radiofrequency is swept slowly through the remainder of the spectrum. The resulting double resonance spectrum indicates which other transitions, in the region swept, share an energy level with *T*. All of these transitions (including *T*) form a set of connected transitions.[15]

Transitions can be connected in either of the two ways illustrated in Fig. 3-4. If the energy level common to the two transitions lies between the other two energy levels, as in Fig. 3-4(a), the transitions are said to be connected progressively; otherwise, as shown in Fig. 3-4(b), they are connected regressively.[15] With careful adjustment of experimental conditions, an INDOR spectrum



(a) PROGRESSIVE



(b) REGRESSIVE

FIG. 3-4. CONNECTED TRANSITION TYPES

can show clearly whether a particular transition is connected progressively or regressively to *T*; see §5.1 for examples. Tickling experiments can also give this information in some cases.[15]

Thus a double resonance spectrum can allow assignment of the relative positions of all of the energy levels belonging to transitions in the connected set. Further double resonance spectra, in which other transitions in the set are irradiated can extend the collection of energy levels and transitions whose structure is known.

The two approaches to the structure of a spectrum, in terms of subspectra, or in terms of sets of connected transitions, are complementary. Subspectral analysis[11] leads directly to values for unknown chemical shifts and coupling constants, but it requires a knowledge of the structure of the spectrum that often can be obtained only from double resonance experiments. The pattern of connected transitions, in addition to allowing assignment to subspectra, often provides direct confirmation of the signs of coupling constants in the many cases where these signs do not affect the appearance of an ordinary single-resonance spectrum.

It is seldom possible to work out the entire structure of a complicated spectrum from double resonance experiments. If other transitions T', T'', etc. are coincident in frequency with *T*, every transition connected to any of

T, *T*´, *T*´´, ... will appear, in the double resonance spectrum, to belong to a single connected set. Any additional double resonance spectra intended to resolve the problem may be equally ambiguous. One can, however, use whatever partial structure has already been determined, to assign transitions to subspectra. One then calculates a trial spectrum from parameters obtained by subspectral analysis. If the double resonance results were correctly interpreted, the experimental partial structure will fit into the calculated complete structure. The calculated structure will also suggest useful transitions *T* for additional unambiguous double resonance experiments.

The relationship between subspectra and sets of connected transitions is discussed again in §4.1 in connection with the design of a computer program for spectral calculations. The analysis of the spectrum of cis-perfluoro-2-butene, in §5.1, illustrates the use of INDOR to determine part of the structure of a complicated spectrum.

CHAPTER 4. COMPUTER CALCULATION OF SPECTRA

4.1. Objectives for a Computer Program

The usual goal in analyzing a high resolution NMR spectrum is to obtain all of the chemical shifts and coupling constants. Computer programs, generally based on either LAOCOON[17] or NMREN/NMRIT[18], have become an essential aid to the analysis of complicated spectra. Some of the limitations of existing programs can be avoided if a new program's design is derived from its intended uses, which vary according to the type of spectrum being analyzed.

The spectra of many molecules without frame symmetry contain several nearly first order multiplets well separated from each other. Spacings in these multiplets give reasonable approximations to the magnitudes of most or all of the coupling constants. The centre of gravity of each first order multiplet gives an approximate chemical shift. Frequently, particularly in proton spectra, there remain some chemical shifts close enough together that only rough estimates of their values can be obtained by inspection. To get more accurate values for these chemical shifts, and any remaining coupling constants, a series of trial spectra are calculated for various reasonable values of the parameters.

The essence of this type of analysis is obtaining a visual match to the observed spectrum. A good plotting routine is essential; other characteristics of the program become important only if they limit the size of problem that can be handled. When there are highly complex overlapping multiplets, a plot that simulates experimental lineshapes is necessary. Otherwise, a simple stick (bar) plot is adequate.

Visual matching of the observed and calculated spectra does not guarantee that the correct parameters have been found. A seemingly straightforward multiplet structure may be a deceptively simple limiting case of a more complicated type of spectrum.[19] Even when the spectrum is as simple as it appears to be, a first order analysis does not reveal the relative signs of coupling constants. These uncertainties can be resolved only by comparing the structure, as well as the appearance, of the observed and calculated spectra. This places heavier demands on a computer program than does trial-and-error visual matching. Thus the program features discussed below in connection with the analysis of complicated spectra are also useful in the full analysis of simple spectra.

Molecules whose NMR spectral parameters cannot be obtained by inspection fall into three classes. The first class includes the many common small spin systems, such as A_mB_n and $[AX]_2$, for which there are algebraic solutions, tables of examples, or both.[1,2] The second class includes those larger spin systems whose spectra are simplified by some combination of symmetry and X factoring. Their complicated complete spectra contain simpler subspectra[11] similar in form to the spectra of class 1 molecules; from these subspectra, the chemical shifts and coupling constants are calculated.

The third class, large molecules lacking both symmetry and X factoring, is of little concern here as it seldom yields spectra that can be analyzed. The positions of the strong lines do not correspond to chemical shifts, and the spacings (few of which are repeated) bear no simple relationship to the coupling constants. Double resonance experiments (see §3.3) may be of little value, as even the sharper lines are very often superpositions of several transitions.

Molecules in the second class, whose spectra can be analyzed, but only with difficulty, are the ones which most require a carefully designed computer program. Usually the most difficult stage in the analysis is the assignment of the observed lines to the various subspectra. Since the simpler subspectra usually originate in matrices_2 with high statistical weight, some of their lines may be intense enough to stand out clearly. Others will remain hidden among the lines belonging to other subspectra. The first step in the assignment is often the calculation of trial spectra for reasonable starting values of the parameters. If a trial spectrum bears any resemblance to the real spectrum, it will show which prominent lines in the real spectrum belong to useful subspectra.

To be useful in such subspectral analysis, a program must print enough information to allow the convenient tracing of calculated subspectra in two directions. Starting from a transition, one needs the quantum numbers that define its subspectrum; starting from a set of quantum numbers, one needs all of the transitions belonging to that subspectrum. The second requirement cannot be conveniently met by an ordinary transition table arranged by frequency, so the program must provide a second table arranged by subspectra.

The weaker transitions in the simple subspectra usually cannot be found without using double resonance methods, as described in §3.3. If one of the strong lines already assigned is sufficiently isolated from other lines, it should be chosen as the irradiated transition. INDOR can be used to particular advantage, as it reveals the frequencies of connected transitions even when they are weak components of strong, unresolved multiplets (see §5.1).

To aid the planning of double resonance experiments, and the interpretation of the results, a computer program must show the structure of the calculated spectrum in terms of sets of connected transitions. This can best be done by printing lists showing what transitions are connected to selected transitions chosen by the user. A table giving the transitions connected to every transition in the spectrum would be too large for convenient use.

It has been implicitly assumed above that the structure of the calculated spectrum is the same as that of the observed one. In a sense this is always true if correct parameters have been used in the calculation, but unless the program uses all of the factoring appropriate to each spin system, the structure of the calculated spectrum is not apparent to the user of the program. Since a program that ignores valid factoring does not have available all of the quantum numbers that define the observed subspectra, it provides little aid in a detailed analysis of the spectrum.

A computer program should be designed for the convenience of the user, even if this requires more work on the part of the programmer. The input data should be arranged logically, using a minimum number of different data card formats. Errors in the data should produce clear messages rather than a cryptic failure of the program. There should be a wide variety of output options to allow for the different types of analysis described above.

Observed and calculated spectra are more readily compared if the chemical shifts of each species can be given as displacements from the same reference frequency used experimentally. Each species' spectrum must then be given separately, to avoid confusion between numerically similar frequencies belonging to different species. This has the further advantage that each species' calculated spectrum is readily limited to a particular region of interest, or suppressed entirely.

Finally, a program should be capable of making calculations on large spin systems, and should be efficient enough to make such calculations economically feasible.

4.2. The Computer

The design of any computer program must take into account the limitations of generally available computer hardware. The most serious limitation is that a computer's fast main memory, in which all calculations take place, is small compared with the data storage requirements of an NMR program for large spin systems. Large calculations can be made only if, throughout the program, anything not relevant to the current step of the calculation is moved out into slower auxilliary storage. Most computers allow program instructions as well as data to be moved in and out of fast memory as needed.

An efficient NMR program thus consists of a series of steps, one of which is active in main memory at a time. Each step processes a string of data blocks, typically of matrix_4 size, in assembly-line fashion. The natural set of steps, which closely parallels the stages of a hand calculation, is given in §4.3.1.

There are two main kinds of auxilliary storage. Nearly all computers are equipped with sequential auxilliary storage, usually magnetic tape. In order to reach a particular piece of data, a sequential storage device must normally start at the beginning and read through all of the preceding data. Thus data items can be retrieved, conveniently, only in the same order in which they were stored.

Direct access auxilliary storage, such as magnetic disk, has become increasingly common. Data items can be retrieved in any order, but at the price of increased overhead time spent keeping track of where each piece of data has been stored. The overhead is reduced if a direct access device is divided (logically, not physically) into a number of regions. Any region can be chosen at random, but within a region only sequential access is allowed. This gives the programmer, in effect, dozens of fast sequential storage devices.

An NMR program with full factoring is sufficiently large and complicated that it is most often run on a large computer in the same general category as the IBM 360/67 at the University of Alberta. It is frequently more economical, with such a computer, to design a program to use a minimum of computing time, even if it then requires more main memory space. However, it is also desirable for an NMR program to be suitable for use with a small, fast computer of the kind now frequently part of an NMR spectrometer installation. The program described in §4.3 can be adapted to either kind of computer, but requires direct access auxilliary storage if it is to run efficiently on a small computer.

4.3. Some Aspects of Program Design

4.3.1. Introduction

The NUMAR[†] computer program, whose listing is given in Appendix B, has been designed to meet most of the requirements of §4.1. The present section provides a critical discussion of the methods of calculation used in NUMAR, and describes some alternative methods.

The basic structure of NUMAR is determined chiefly by the use of all possible factoring, to the matrix$_4$ level, throughout the program. This makes the program more complicated, but saves both main memory space and calculation time. The design has also been influenced by a decision to use only sequential auxilliary storage, making the program suitable for a wide variety of computers.

Although they may be combined in various ways, essentially the same set of program steps appears in all programs that calculate NMR spectra. Arranged in the order in which they appear in NUMAR, they are:

a Read and print the input data
b Construct the basis functions
c Generate the Hamiltonian matrix
d Diagonalize the Hamiltonian matrix
e Calculate the transition frequencies and intensities
f Order the transitions by frequency

[†] University of Alberta NMR

g Print the transition list
h Plot the spectrum (bar plot)
i Plot the spectrum (full lineshape simulation)

In the overall flow-chart for NUMAR, Fig. 4-1, the blocks are labelled according to this list, as well as by the names of the FORTRAN subroutines (see Appendix B). The use of full factoring has made most of these steps large enough to remain separate, but step *c* has been combined with *d*, and *f* with *g*.

The step whose data storage requirements limit problem size is TRANS. It must deal with a pair of matrices$_4$, compared with one matrix$_4$ for HAMIL. BASIS deals only with vectors of quantum numbers, rather than matrices, so its data storage requirements increase much more slowly with problem size. SPOUT also deals with vectors (of transition frequencies, etc.); its storage requirements increase only linearly with the number of transitions, but the number of transitions increases rapidly with problem size. For very large, highly factored, spin systems such as the 2,5-dimethyl-3-hexenes (§5.2), a species' transition list may require much more storage than that used for the matrices in TRANS. However this need not limit problem size; the transition list can be broken up into frequency regions before sorting without a drastic loss of efficiency.

Fig. 4-1 also shows an additional step, labelled ADJUST, for the iterative adjustment of chemical shifts

It is not part of the current NUMAR program, but could be added with few changes in the other steps. Possible designs for ADJUST are discussed in Appendix E.

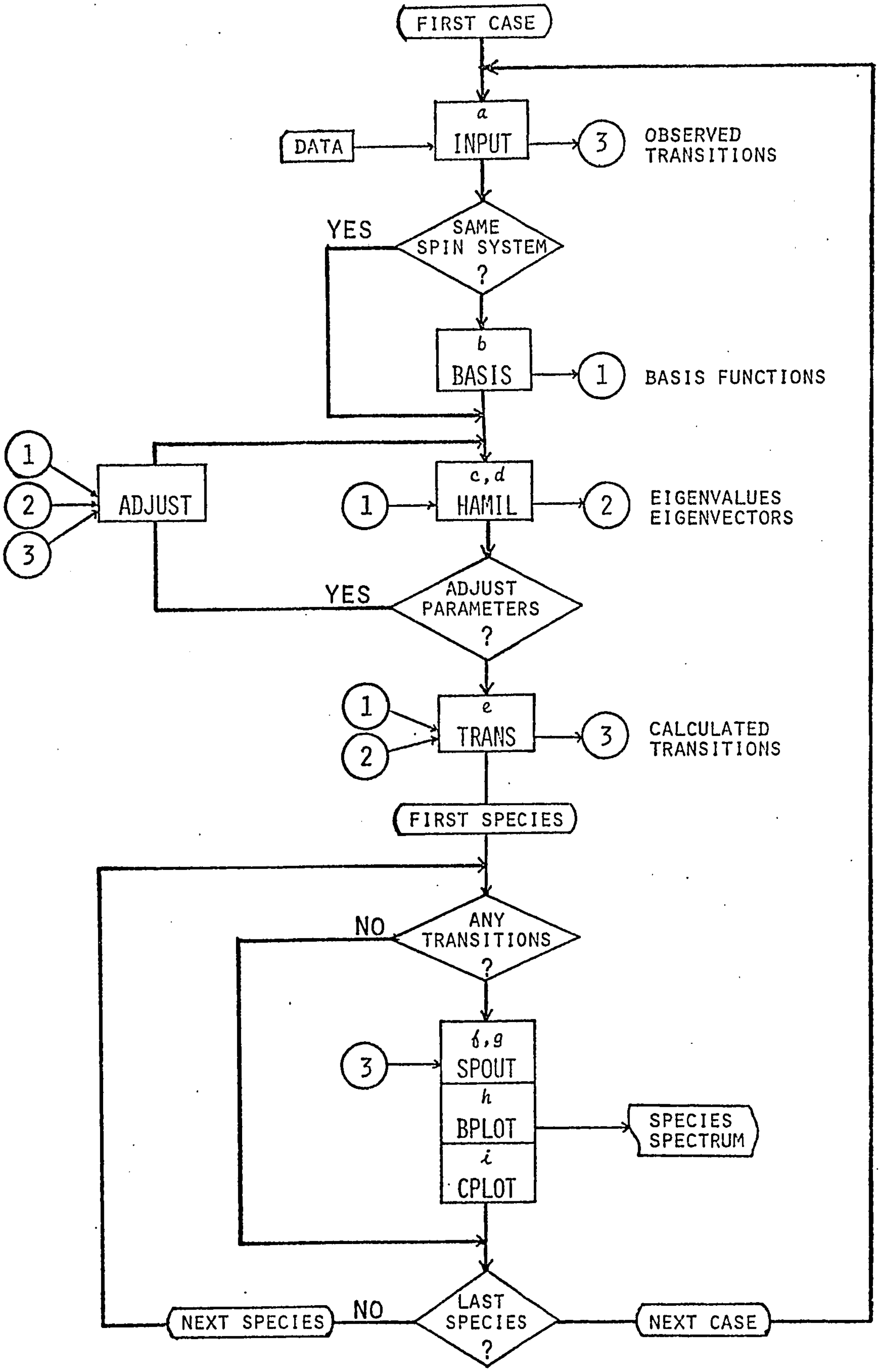


FIG. 4-1. NUMAR FLOW CHART.

4.3.2. Basis Functions

The choice of basis for an NMR program determines the degree of factoring of the Hamiltonian matrix, and consequently the kinds and sizes of spin systems that the program can handle. The 'basis functions' generated in the BASIS step of the NUMAR program are sets of quantum numbers that represent product functions of the form given by (2.24). In order to provide all three stages of factoring outlined in Chapter 3, these basis functions are grouped by symmetry into matrices_2, and within each matrix_2 by M and M_S into matrices_3 and matrices_4 respectively.

To fully define a basis function of the form given by (2.24), one must have the total spins F of all of the magnetically equivalent groups, in addition to the A and M values of all invariant groups and symmetrically equivalent pairs. For each group or pair each of these quantum numbers can take on any of a range of allowed values, in steps of 1. Each quantum number's range of allowed values is determined by the current value of another quantum number. This natural hierarchy of quantum numbers leads to a very straightforward procedure for generating all of the product functions.

All possible sets of valid F values for the magnetically equivalent groups are generated. For each magnetically equivalent group of n nuclei of spin I, the range of valid F values is given by

$$F = F_{max}, F_{max}-1, \ldots, +\tfrac{1}{2} \text{ or } 0; \; F_{max} = nI. \qquad (4.1)$$

For each of the sets of F values all possible combinations of A values for the invariant groups and symmetrically equivalent pairs are generated, subject to the constraints

$$F+F' \geq A \geq |F-F'| \qquad (4.2a)$$

for each pair, and

$$A \equiv F \qquad (4.2b)$$

for each invariant group. For each of the sets of A values, all possible combinations of M values are generated, subject to the constraints

$$A \geq M \geq -A \qquad (4.3)$$

for each pair or invariant group.

It is convenient to generate the basis functions for one matrix$_2$ at a time. All of the basis functions generated for a particular set of F values belong to one magnetic equivalence submatrix. If the molecule has no frame symmetry, or if $F \neq F'$ for any pair, they are the basis functions for one matrix_2.

When the molecule has twofold frame symmetry and $F = F'$ for all pairs, the magnetic equivalence submatrix is factored into symmetric and antisymmetric matrices_2. The basis functions generated according to (4.3) for a particular set of A values have a symmetry given by the product over all pairs

$$\prod_{\ell} (-1)^{2F(\ell)-A(\ell)} \tag{4.4}$$

When basis functions in a symmetric matrix_2 are being generated, the antisymmetric sets of A values generated according to (4.2) are skipped; when the basis functions in the corresponding antisymmetric matrix_2 are being generated, the sets of A values just used for the symmetric matrix_2 are skipped.

Successive basis functions produced by this generating procedure seldom belong to the same matrix_4 or even the same matrix_3. They must therefore be sorted by M into matrices_3 and, within each matrix_3, by all of the M_S values into matrices_4. To aid this sorting procedure, M and M_S values as well as A and M values are included as part of each basis function.

In the program, each of these spin quantum numbers is represented by an integer equal to twice its true value. Memory space is saved by 'packing' the integer representations of the M_S values of each basis function into a single integer, and those of the A values into another (see Appendix C). Because each possible set of M_S values within a matrix$_2$ has a unique packed representation, one need only check whether the packed M_S values are equal in order to determine whether two basis functions belong to the same matrix$_4$.

This allows grouping of the basis functions by matrices$_3$ and matrices$_4$ using a simple single-stage sorting routine. The basis functions are ordered by decreasing *M* value or, when *M* values are equal, by decreasing packed M_S value.

The sorted basis functions for the matrix$_2$ are then placed in auxilliary storage. For each matrix$_2$, the F values and the statistical weight are stored; for each matrix$_3$, the *M* value; for each matrix$_4$, the packed M_S value. The quantum numbers stored for each basis function within a matrix$_4$ are the packed A value, and the M values of all groups and pairs. These quantum numbers, for all matrices$_2$, are sufficient to define all following steps in the calculation.

The procedure used in the current NUMAR program differs in one major respect from the one just described. To simplify the calculation of some Hamiltonian matrix elements in those matrices$_2$ where $F = F'$ for all pairs (see HAMIL, §4.3.3), NUMAR reverts to a simple magnetic equivalence basis in the other matrices$_2$ where frame symmetry provides no additional factoring.

In all input to NUMAR each pair is treated as a single entity. This representation is then expanded internally (see Fig. 4-2) to give two magnetically equivalent groups in place of each pair. When $F \neq F'$ for any pair, these two groups are treated in the same way as any other magnetically equivalent groups. When $F = F'$ for all pairs, the first of the two groups (for each pair) is given the characteristics of the pair, and the second is given spin $F = 0$ in order to effectively remove it from the calculation.

The dual numbering system makes NUMAR considerably more difficult to understand and creates complications in HAMIL nearly as great as those it eliminates. The simpler approach described first, which always treats a pair as a single entity, is recommended for future programs.

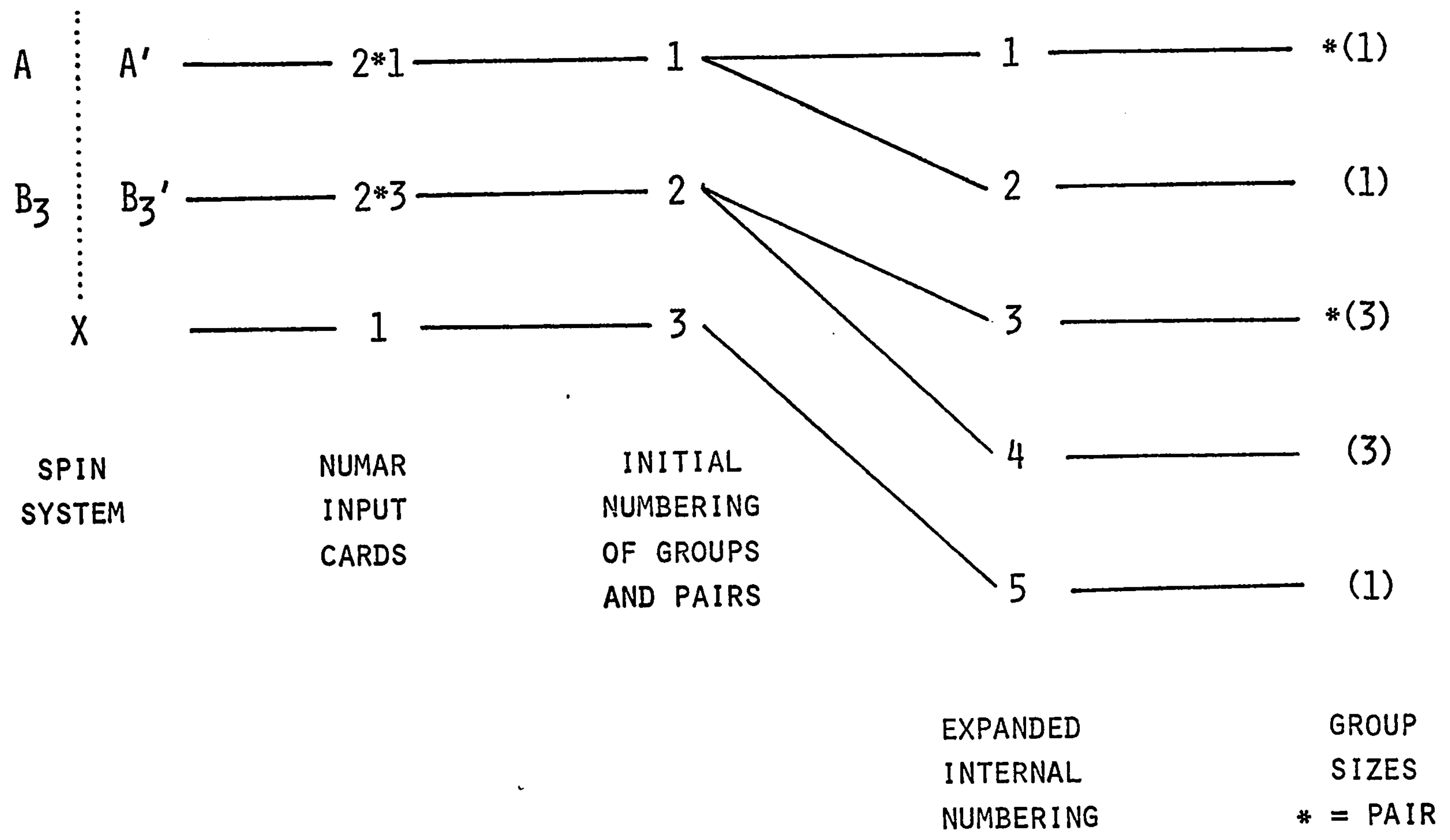


FIG. 4-2. REPRESENTATIONS OF AN $[AB_3]_2X$ SPIN SYSTEM IN NUMAR.

4.3.3. The Hamiltonian Matrix

The overall design of this step in the calculation is straightforward. The basis functions for one matrix_4 are brought into main memory, the matrix elements are calculated, the matrix is diagonalized, and the eigenvalues and eigenvectors are placed in auxilliary storage. When there is frame symmetry, some details of the calculation vary according to the procedure chosen for handling those matrices_2 that cannot be factored by frame symmetry. The recommended procedure is described first, followed by a brief summary of the ways in which the NUMAR procedure differs from it.

All Hamiltonian matrix elements are calculated using the Hamiltonian (2.23), which requires that the symmetrized combinations of coupling constants given by (2.22) be used in place of the actual coupling constants connecting symmetrically equivalent pairs. It is assumed that a coupling constant matrix containing these symmetrized coupling constants has been created in the input step. In this matrix, the only nonzero elements below the main diagonal are the difference couplings $J_{m\ell}$ between pairs, and the only nonzero elements on the main diagonal are the couplings $J_{\ell\ell'}$ between the two magnetically equivalent groups in a pair. Each symmetrically equivalent pair is treated, at all times, as a single entity; the size of the coupling constant matrix is given by the number of pairs plus the number of invariant groups.

Before any matrix elements are calculated in each matrix_2, its F values are brought into main memory. Two vectors are needed, the second containing only the F' values for the symmetrically equivalent pairs. Most matrix elements are calculated using only the A and M values of the individual basis functions ($A \equiv F$ only for invariant groups), but F and F' are used directly in calculating the matrix elements of $\underline{\vec{F}}\cdot\underline{\vec{F}}'$ and $\underline{\vec{B}}$ for the symmetrically equivalent pairs (see §2.3.2).

Rather than waste time evaluating $\underline{\vec{F}}\cdot\underline{\vec{F}}'$, and the expressions for $f(F,F',A)$ and $g(F,F',A)$ (see Eq. 2.16) every time they appear in a matrix element, one can calculate them, for each pair, at the beginning of each matrix_2 and store the values for use when needed. The values of $f(F,F',A)$ and $g(F,F',A)$ are stored in matrices, indexed by pair and by A value; the values of $\underline{\vec{F}}\cdot\underline{\vec{F}}'$ are stored in a vector indexed by pair. The rows, in the f and g matrices, corresponding to invariant groups can be set to zero, since they will never be used.

Basis functions for a matrix_4 are brought into main memory; each basis function consists of integers representing the M values of all pairs and invariant groups, and a single integer containing the corresponding A values in packed form. The Hamiltonian matrix elements

H_{ij} are then calculated, one row at a time.

The first step in calculating the matrix elements of row i is the unpacking of the A values of basis function i. The diagonal matrix element H_{ii} is then calculated; each diagonal element is a sum of terms contributed by all parts of (2.23).

Since the Hamiltonian matrix is real and hermitian (i.e. symmetric), one need calculate only those off-diagonal matrix elements H_{ij} that lie above the main diagonal. Only the last two sums in (2.23) can provide off-diagonal matrix elements. If the packed A values for basis functions i and j are identical, any nonzero off-diagonal element is a member of the $\underline{\vec{A}}$ sum; otherwise it is from the $\underline{\vec{B}}$ sum.

When the packed A_i and A_j values are not identical, the A values for basis function j must be unpacked. H_{ij} is zero unless the conditions (2.14) are met for two pairs, for example, pairs p and q. Combining these conditions with others inherent in the factoring into matrices$_2$ and matrices$_3$, one requires for a nonzero matrix element $J_{qp}\underline{\vec{B}}(p)\cdot\underline{\vec{B}}(q)$:

i) $\Delta A_p = \pm 1$; $\Delta A_q = \pm 1, \mp 1$;

ii) $\Delta M_p, \Delta M_q = 0$; or $\Delta M_p = \pm 1$, $\Delta M_q = \mp 1$.

iii) all other $\Delta A, \Delta M = 0$.

(In every case, ΔA or ΔM is between basis functions i and j.) If basis functions i and j meet these conditions, the matrix element H_{ij} is calculated using (2.15) and the stored values of $g(F,F',A)$.

When the packed A values are equal, there is no need to unpack the A values of basis function j. If conditions on ΔM similar to those above are satisfied, a matrix element $H_{ij} = J_{pq}\underline{\vec{A}}(p)\cdot\underline{\vec{A}}(q)$ is calculated using (2.13). Note that all nonzero off-diagonal matrix elements involving invariant groups (including those where p is an invariant group, and q is a pair) belong to the $\underline{\vec{A}}$ sum, not to the $\underline{\vec{B}}$ sum, of (2.23).

When the matrix elements in all rows of a matrix$_4$ have been calculated, the matrix is diagonalized. The diagonalization routine used in NUMAR, based on a new variant of Householder's method,[20] is particularly efficient in its use of memory space, very fast, and very accurate. It has already been pointed out that at least two matrices$_4$ must be present in main memory during the transition calculation. Thus the use of double precision arithmetic in the diagonalization does not increase the total amount of data storage used by the program. It has the advantage that the single precision eigenvalues and eigenvectors placed in auxilliary storage contain no rounding errors from the diagonalization.

The procedure used in the HAMIL subroutine of NUMAR for generating Hamiltonian matrix elements is generally similar to the one just described. All of the differences are the direct result of a decision to use the frame symmetry basis (2.24) only in those matrices_2 factored by frame symmetry.

In the symmetry factored matrices_2, a matrix of symmetrized coupling constants, similar to the one described above, is needed. However, in the other matrices_2, the coupling constants must be restored to a non-symmetrized form. In HAMIL, before any matrix elements of a matrix_2 are calculated, its coupling constant matrix is generated from a simple matrix of coupling constants created by the input routine. The generating process is complicated by NUMAR's expanded internal representation of a pair as two magnetically equivalent groups, which increases the size of the coupling constant matrix to the number of invariant groups plus twice the number of pairs. The relationships among the three forms of the coupling constant matrix are illustrated in Fig. 4-3.

In NUMAR, there is no need to generate values of $g(F,F',A)$, since they would all be zero in those matrices_2 for which all $F = F'$, and symmetry factoring is used. It is also unnecessary to generate $f(F,F',A)$ for each pair at the beginning of those matrices_2 in which it is used. A single matrix of values of $f(F,F',A)$, indexed by F ($\equiv F'$) and A, is used for all groups in those matrices_2 where it is needed. The values are calculated at the

	1	2	3
1	J_A	J_{CIS}	J_{AX}
2	J_{TRANS}	J_B	J_{BX}
3			

ORIGINAL MATRIX CONSTRUCTED
FROM INPUT DATA

	1	2	3	4	5
1		J_A	J_{CIS}	J_{TRANS}	J_{AX}
2			J_{TRANS}	J_{CIS}	J_{AX}
3				J_B	J_{BX}
4					J_{BX}
5					

EXPANDED COUPLING CONSTANT MATRIX FOR MATRICES$_2$
WITHOUT SYMMETRY FACTORING.

	1	2	3	4	5
1	J_A		J_{SYM}		J_{AX}
2					
3	J_{ANTI}		J_B		J_{BX}
4					
5					

EXPANDED COUPLING CONSTANT MATRIX FOR MATRICES$_2$
WITH SYMMETRY FACTORING.

$J_{SYM} = (J_{CIS} + J_{TRANS})/2$

$J_{ANTI} = (J_{CIS} - J_{TRANS})/2$

FIG. 4-3. COUPLING CONSTANT MATRICES IN NUMAR FOR THE $[AB_3]_2X$ SPIN SYSTEM OF FIG. 4-2 beginning of the program using (2.17).

Because $g(F,F',A)$ is zero, no provision is made in NUMAR for terms from the $\underline{\vec{B}}$ sum of (2.23) in diagonal matrix elements H_{ii}. Otherwise, the actual process of generating the Hamiltonian matrix elements is as described above. In the matrices$_2$ that are symmetry factored, the second position assigned to each symmetrically equivalent pair must be ignored. Because each such position has been set to M = A = F = 0, this requires no special action. Also, no special procedure is needed for matrices$_2$ that are not symmetry factored. Since each group always has A ≡ F, all the basis functions in each matrix$_2$ have identical packed A values. Thus the procedures for generating matrix elements from the $\underline{\vec{B}}$ sum of (2.23) are never used, and the calculation reduces to the usual magnetic equivalence form.[18]

4.3.4. Transitions

Transition calculations in NUMAR include essentially the same steps used in other programs.[17,18] However, X factoring creates some complications in the use of auxilliary storage devices. Three approaches are discussed below: one requiring direct-access storage, one for small computers without direct-access storage, and the one used in NUMAR.

Mathematically, the transition calculation is straightforward. The matrix elements of the transition operator $\underline{X}$ of Eq. (2.21) are calculated in the basis representation, using the selection rules discussed in §3.2. The $\underline{X}$ matrix is then transformed to the representation in which the Hamiltonian matrix is diagonal, using the eigenvector matrix U obtained previously in the diagonalization step. Since U is real and unitary, its transpose $\tilde{U}$ is equal to its inverse U^{-1}. The unweighted intensity I_{ij} of the transition connecting energy levels i and j is given by the square of the transformed matrix element:

$$I_{ij} = [(\tilde{U}\ \underline{X}\ U)_{ij}]^2 \tag{4.5}$$

This intensity must be multiplied by the statistical weight W_{ij} appropriate to the matrix$_2$ containing energy levels i and j. The corresponding frequency ν_{ij} is simply the algebraic difference in energy of the two eigenvalues:

$$\nu_{ij} = E_i - E_j \tag{4.6}$$

The NUMAR program follows the usual convention[1] of calculating the emission ($\Delta M = -1$) spectrum.

The nonzero elements of the $\underline{X}$ matrix are in blocks that do <u>not</u> fall along the main diagonal, but rather connect basis functions in matrices_4 that obey the selection rules in §3.2. Because the $\underline{X}$ matrix is symmetric, only the blocks above the main diagonal need be considered. The transformation matrix U is block-diagonal, with each block corresponding to a Hamiltonian matrix_4. Thus the transformation of a rectangular block $\underline{X}_{pq}$ of $\underline{X}$, connecting matrices_4 p and q, can be written:

$$\tilde{U}_p \, \underline{X}_{pq} \, U_q \tag{4.7}$$

Note that although $\underline{X}_{pq}$ is normally rectangular, as much memory space must be allotted to it as to the U matrices, because either matrix_4 p or matrix_4 q may be the larger.

This series of matrix multiplications is the critical step in limiting the size of problem that can be handled by an NMR program. Part of the available data storage space is used to hold a variety of small items such as the eigenvalues of the two matrices$_4$ p and q. Even using a minimum-storage method of matrix multiplication, the transformation of $\underline{X}_{pq}$ requires space for one other matrix of equal size. Thus the program can handle only those spin systems whose largest matrix$_4$ occupies less than half of the data storage space available for the transition calculation.

A transition calculation without X factoring is straightforward. For each matrix$_2$, the eigenvalues and eigenvectors of the matrices$_3$ with $M = M_{max}$ and $M = M_{max}-1$ are brought into main memory, and the transitions from M_{max} to $M_{max}-1$ are calculated, as described above. The eigenvalues and eigenvectors for $M = M_{max}$ are no longer needed, so their region of main memory is reused for the eigenvalues and eigenvectors of the matrix$_3$ with $M = M_{max}-2$. The transitions from $M_{max}-1$ to $M_{max}-2$ are then calculated. The procedure is repeated, with eigenvalues and eigenvectors of each matrix$_3$ serving first as the 'lower' then the 'upper' set. Each set is brought in from auxilliary storage only once, in the same order of decreasing M in which the matrices$_3$ were created and diagonalized in the previous step.

Referring to Fig. 3-3(a), one can see that in an X factored transition calculation, a procedure similar to the one just described can be used to calculate each complete species A subspectrum in turn. As each matrix$_4$

belongs to only one species A subspectrum, the only complication introduced is the need to bring the eigenvalues and eigenvectors into main storage in order of decreasing M_A, for each subspectrum in turn.

If only species A transitions are of interest, one can generate and diagonalize the Hamiltonian matrices_4 in the order needed for the transition calculation, and retrieve them from sequential auxilliary storage without difficulty. However, a completely different order of matrices_4 is required for calculations on each additional species (for example, see Fig. 3-3(b)). Three solutions to this problem are given below.

When direct access auxilliary storage is available, one can generate and diagonalize the Hamiltonian matrices_4 in any convenient order, then retrieve them in the order required for transition calculations on each species. Tables are kept showing the locations in auxilliary storage of the basis functions, eigenvalues, and eigenvectors that correspond to each set of M_S values. These tables can themselves be placed in auxilliary storage, so that main memory space need be reserved only for the entries for one matrix_2.

The majority of the data area in main memory is used for two regions each the size of the largest matrix_4 that the program can handle; they are referred to below as regions one and two.

Basis functions for the current pair of matrices$_4$, p and q, are brought into region one, and used to construct the matrix $\underline{X}_{pq}$ (see Eq. (4.7)) in region two. The eigenvalues of the two matrices$_4$ are also brought into main memory. The eigenvector matrix U_p is then brought into region one, and the matrix product $P = \tilde{U}_p\underline{X}_{pq}$ is formed as follows. The first column of $\underline{X}_{pq}$ is used to calculate the first column of P, which is stored as a vector. This P vector is next copied into the first column of $\underline{X}_{pq}$, and then is treated as the second column of P. At the end of the matrix multiplication, $\underline{X}_{pq}$ has been completely replaced by P. The second eigenvector matrix U_q is then brought into auxilliary storage, and used to calculate PU_q.

When each element of PU_q has been calculated, it is squared and multiplied by the statistical weight W to give a transition intensity. The frequency is calculated from the difference between the corresponding eigenvalues, and placed in auxilliary storage along with the intensity, subspectral quantum numbers, and an origin number to indicate which energy levels the transition connects.
It is convenient to edit the list of calculated transitions, placing in auxilliary storage only those whose intensity exceeds a minimum value specified as an input parameter. Frequency limits may also be imposed.

A procedure similar to the one just described can be used to calculate any one species' transitions when only sequential auxilliary storage is available. The basis functions, eigenvalues, and eigenvectors are placed in auxilliary storage in the same order in which they are needed in the transition calculation. (If a matrix$_4$ participates as both 'lower' and 'upper' in the transition calculation, its eigenvectors are placed in auxilliary storage twice in succession.) When all transitions of one species have been calculated, the entire program is repeated for each additional species.

The third method of calculation, used in NUMAR, is the fastest of the three, as it calculates the eigenvalues and eigenvectors of each matrix$_4$ only once, and brings them back into main memory only once. It does not require direct access auxilliary storage, but it does require far more main memory space than either of the first two methods.

The basis functions, eigenvalues and eigenvectors of all of the matrices$_4$ in an adjacent pair of matrices$_3$ are brought into main memory. A pair of matrices$_4$, p and q, connected by transitions of the first species, is selected, and the matrix $\underline{X}_{pq}$ is constructed. One row of the product matrix $P = \tilde{U}_p\underline{X}_{pq}$ is calculated, and stored as a vector. This row of P is used immediately to calculate, one at a time, the elements of the corresponding row of the product PU_q. These are used, as above, to calculate transition intensities, and the transitions of significant intensity are placed in auxilliary storage. The next row of P is then calculated (and stored in the same vector used for the first row), and so on.

All transitions of all species are calculated for this pair of matrices_3 before moving on to the next pair. Because the eigenvectors etc. of each matrix_4 are used again for each additional species, their storage space cannot be reused for another purpose. Thus space must be available for all of the eigenvectors, eigenvalues, and basis functions of two matrices_3, and for the matrix $\underline{X}_{pq}$. This is far more storage than is needed for the first two methods, but less than would be needed without X factoring. Taking the matrices_3 with $M = 1$ and $M = 0$ of Fig. 3-1 as an example, one would need 72 storage locations for the two 6×6 eigenvector matrices U_p and U_q if there were no X factoring. The eigenvectors for the six matrices_4 in these matrices_3 require only 32 storage locations. In addition, the matrix $\underline{X}_{pq}$ is the size of a matrix_4 rather than a matrix_3.

In the first two methods, all transitions of one species are calculated before any transitions of the next species. Within a species, all transitions of one subspectrum are calculated before any transitions of the next subspectrum. Thus one can readily print the transitions by species and by subspectrum in the output step. In the third method, the transitions must be sorted in a later step for this purpose. However, the third method is better suited to grouping together transitions of all species connected to a common transition.

Of the three methods of transition calculation discussed, the first clearly offers the best compromise between speed and efficient use of main memory, and should be used for those computers that have the necessary direct access storage. The second method should be used only when limitations of computer hardware make both of the other two impossible.

4.3.5. Input and Output

The input data cards[†] for NUMAR are designed to place logically related data items on the same card, and to minimize the number of different kinds of data card required. Where possible, the most important items are placed at the beginning of a card, and reasonable default values are provided if the remainder of the card is left blank. If an error is found in the data, the program prints a message and skips to the data for the next molecule. Chiefly because of the error checking, the input step is large enough to be kept separate.

The NUMAR output, much of which is optional, is printed throughout the program. The INPUT step (Fig. 4-2) prints chemical shifts, coupling constants, etc. on which the calculation is based. BASIS prints the total transition intensity, and the maximum possible number of transitions, for each species. HAMIL prints the energy levels, including in the table all of the quantum numbers necessary to define each matrix_2, matrix_3, and matrix_4. TRANS prints a Key, to show which energy levels are connected by each transition. SPOUT prints a transition list for each species, including all of the subspectral quantum numbers

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[†] The format of the data cards is fully described in Appendix D.

for each transition. Transitions are ordered by transition number in the Key and by frequency in the SPOUT list; both number and frequency appear in both lists to simplify cross reference.

This output does not fully meet the requirements of §4.1, as there is no provision for printing transitions by subspectra or by connected sets. However, it is quite easy to find all of the transitions in a subspectrum. One first finds in the Energy Level table the matrices_4 with the correct set of quantum numbers, then finds in the Key the transitions connecting those matrices_4. All transitions connecting a particular pair of matrices_4 appear in sequence. In contrast, transitions connected to a particular transition T are not in sequence; one must search a region of the Key, in both directions from T, for transitions of any species whose upper or lower energy level is the same as either of the energy levels connected by T.

In NUMAR, the transitions of all species are placed in a single sequential auxilliary storage unit as they are generated. In SPOUT, this entire list must be searched once for each species whose transitions are to be printed. If enough auxilliary storage units are available, it is more efficient to use a different storage unit for each species' transitions.

The number of transitions that can be sorted in SPOUT for each species is limited by the amount of main memory space available. Some large molecules (such as the 2,5-dimethyl-3-hexenes, §5.2) have many thousands of transitions of significant intensity within a single species. One can edit the transition list in TRANS, keeping only the transitions within a limited frequency range. This is an excellent solution when only a limited frequency range is of interest; it is inefficient when it requires repeat calculations to obtain the remainder of the spectrum. It would be better to calculate all the transitions of interest, separating them into frequency ranges in TRANS if necessary.

A bar plot, produced on the computer's output printer, may be more useful in preliminary calculations than either a transition list or a full lineshape plot, because it provides both frequencies and intensities for all the well-resolved lines in a convenient form. A useful feature of the NUMAR routine, BPLOT, is the option of plotting the entire spectrum of a species with any large regions of blank baseline automatically omitted.

A plot that simulates experimental lineshapes is better when one is attempting to fit a region of overlapping multiplets. The CPLOT routine in NUMAR provides a variety of lineshapes and scaling options to allow simulation of a variety of experimental conditions.

CHAPTER 5. NMR SPECTRA OF SOME SYMMETRIC MOLECULES

This Chapter presents analyses of the NMR spectra of a number of molecules containing symmetrically equivalent pairs of magnetically equivalent groups of nuclei. The full analysis of the spectra of the perfluoro-2-butenes (§5.1) illustrates most of the techniques of spectral analysis described in §3.3 and §4.1. The 2,5-dimethyl-3-hexenes (§5.2) and the trifluoromethyl phosphorus compounds (§5.3) are typical molecules of current interest whose spectra are not readily calculated except by using the NUMAR computer program (Appendix B).

5.1 The Perfluoro-2-butenes

5.1.1 Introduction

Fluorine coupling constants have remained a subject of interest for some years. A variety of evidence has been found[21] for a 'through-space' coupling mechanism, said to be responsible for large coupling constants between ^{19}F nuclei in close proximity spatially, but separated by many bonds. More recently, liquid crystal work[22] has shown that some ^{19}F-^{19}F indirect coupling constants are highly anisotropic.

Cis-perfluoro-2-butene was chosen as a small molecule of high symmetry, one of whose coupling constants might have a through-space contribution. Its spectrum (in an isotropic medium) was fully analyzed with the aid of the INDOR double-resonance technique. The spectrum of *trans*-perfluoro-2-butene, for which no through-space effects were anticipated, was also analyzed.

5.1.2. Experimental

A mixture of *cis*-and *trans*-perfluoro-2-butenes (Pierce Chemical Co., Rockford, Ill.) was introduced into a vacuum system and degassed by the freeze-pump-thaw method until the residual pressure at liquid nitrogen temperature was less than two microns.

Several attempts to separate the mixture by gas chromatography failed. Each column listed in Table 5-1 was used, at various temperatures from 25° C. to the maximum listed in the table, with helium carrier gas at flow rates from 30 to 300 ml./min. A Gow-Mac TR2-B thermal conductivity detector was used throughout. Under some conditions, small peaks indicative of trace impurities could be seen in the chromatogram, but the major components always gave a single, large peak.

Separation of these isomers has been reported.[23] However, column 3, used under conditions essentially the same as those of Bright and Matula,[23b] gave no better results than had been obtained with columns 1 and 2. Bright and Matula did, however, condition their column with 'three 250 torr samples of COF_2' before using it. No attempt was made to learn more details of this procedure, in order to repeat it, since the NMR spectra of both isomers could be obtained from the mixture.

All NMR spectra were obtained from a sample consisting

Table 5-1.

Gas Chromatography Columns[†]

Column Number	1	2	3
Length	20 ft.	10 ft.	10 ft.
Packing	10% TCP on 80-100 mesh Chromasorb W	Poly-Pak #2 Polymer Beads	Proapak T Polymer Beads
Maximum Temperature	50° C.	175° C.	150° C.

[†] All columns are spirals of 8 mm. O.D. glass tubing.

of 0.30 ml. of the perfluoro-2-butene mixture and 0.15 ml. of $CFCl_3$, both previously degassed, sealed into a 5 mm. O.D. medium wall NMR tube. Liquid volumes were measured at room temperature, in a calibrated tube on the vacuum rack, before distillation into the NMR tube.

^{19}F spectra used in the analysis were obtained at 14.092 kgauss (56.4 MHz.) on a Varian HA60I spectrometer, at 21.138 kgauss (84.7 MHz.) on a Bruker HFX-90 spectrometer, and at 23.487 kgauss (94.1 MHz.) on a Varian HA-100-12 spectrometer. ^{19}F INDOR spectra were obtained on the HA-60I and HFX-90 spectrometers. Modifications to the Varian spectrometers are described in Appendix E.

All spectra were obtained at ambient probe temperatures (300°-350° K) at a scale of 1.0 Hz/cm and a sweep rate of 0.02 Hz./sec. or slower. The spectra were calibrated as described in Appendix F.

Each observed multiplet is symmetrical about its chemical shift. Thus the mean of the frequencies of each pair of equivalent peaks on opposite sides of a multiplet is the centre frequency of the multiplet. (Because of the finite sweep rate, this value is slightly different from the true chemical shift.) For each multiplet, the RMS deviation of these values (from their mean) was less than 0.04 Hz., the larger deviations coming from the weaker peaks. This value can be taken as a reasonable estimate of the error in the observed frequencies.

5.1.3. Assignment and Analysis of Spectra

A preliminary spectrum of the mixture sample revealed four multiplets centred at -160.7, -143.5, -69.8, and -67.4 ppm from $CFCl_3$,[†] with relative intensities approximately 3:2:9:6. These intensities immediately suggested the assignment =C-F (isomer A), =C-F(B), $=C-CF_3(A)$, $=C-CF_3(B)$, respectively, for the four multiplets. Comparison of the chemical shifts with those of the 2-chloroheptafluoro-2-butenes [24] supported this assignment, and allowed tentative identification of isomer A as trans- and B as cis-perfluoro-2-butene. The coupling constants subsequently obtained from a full analysis of the spectra are consistent with this assignment of the multiplets.

No strong line in any multiplet is more than 40 Hz. from the chemical shift. At 14.1 kgauss, the two most closely spaced multiplets (those at -69.8 and -67.4 ppm.) are more than 135 Hz. apart; at the higher field strengths, the spacing is correspondingly greater. Thus the use of a sample containing both isomers does not interfere with the analysis.

[†] A positive chemical shift indicates a resonance frequency higher than that of the reference, at fixed magnetic field strength. A negative chemical shift indicates a resonance field strength higher than that of the reference, at fixed frequency. Spectra are presented with chemical shift decreasing algebraically from left to right, unless otherwise noted.

A few small impurity peaks were noted in a preliminary survey spectrum. One doublet of separation 3.95 Hz. is only 0.195 ppm. to high field of the cis-CF_3 chemical shift. It is weak (about 1% of the intensity of the cis-isomer), and does not interfere with the analysis because the lines it obscures at 14.1 kgauss are visible at 21.1 kgauss, and vice versa. The other impurity peaks, which are equally small, are far from any of the four multiplets of interest.

For each multiplet, spectra obtained at 14.1, 21.1, and 23.5 kgauss can be superimposed. This lack of effects dependent on relative chemical shift indicates that the =C-F and =C-CF_3 resonances are far enough apart, even at 14.1 kgauss, to be treated as separate species.

X factoring has therefore been used throughout the analysis below, with =C-F labelled species 1 and =C-CF_3 labelled species 2. A common criterion for the use of X factoring in a calculation is that the absolute value of the ratio J/Δ (see §3.1) between species be less than 0.1.[2] The largest $|J/\Delta|$ ratio in these molecules, in the worst case, (at 14.1 kgauss) is 0.002 for the cis-isomer, and 0.004 for the trans-isomer.

The structural formulae of the two isomers suggested that each should have twofold frame symmetry. Since the three fluorines of a CF_3 group are normally magnetically equivalent, both isomers were assumed to be $[AX_3]_2$ spin systems. Because each observed multiplet is symmetrical about its chemical shift, each chemical shift was chosen as the zero of frequency for its species. This left only the four possible coupling constants to be determined in the analysis of each spectrum.

These four coupling constants are labelled in a manner consistent with the input to the NUMAR computer program.(see Appendix D). For each isomer, the coupling constant between the two symmetrically equivalent olefinic fluorines is labelled J_{11}, and that between the two CF_3 groups J_{22}. The three bond coupling constant F-C(=)-CF_3 is J_{12}, and the four bond coupling constant F-C=C-CF_3 is J_{21}. It is convenient to use the combinations[1]

$$\left.\begin{array}{ll} K = J_{11}+J_{22} & L = J_{12}-J_{21} \\ \\ M = J_{11}-J_{22} & N = J_{12}+J_{21}. \end{array}\right\} \qquad (5.1)$$

The $[AX_3]_2$ spin system has a submatrix of statistical weight 4, with all composite particle spins $F = ½$. Its subspectra are identical to those of the $[AX]_2$ spin system, for which an algebraic solution is available (PSB[1], §6-7). The magnetic equivalence submatrix is factored by frame symmetry into symmetric and antisymmetric matrices_2, of dimensions 10 and 6 respectively. The symmetric matrix_2 has been discussed in §3.3; the antisymmetric matrix_2 has three matrices_3, all 2×2, with $M = 1, 0, -1$.

With X factoring, the matrices$_3$ with $M = \pm 1$ are further factored to 1×1 matrices$_4$, and the matrix$_3$ with $M = 0$ contains a single 2×2 matrix$_4$.

The subspectra belonging to these two matrices$_2$ are identical in the species A spectrum and the species X spectrum. The most prominent feature is a doublet of separation N which originates in the symmetric matrix$_2$. In the species A spectrum this doublet may not stand out among the lines from other subspectra. In the species X spectrum it is part of a doublet of separation N that contains half of the total species X intensity. This doublet, which includes all the lines from subspectra with $M_A = \pm 1$, is characteristic of the species X spectrum of all $[AX_n]_2$ spin systems.[25]

No coupling constant combinations other than N are available by inspection. However, analysis of the spectrum of the <u>trans</u>-isomer was made simple by the availability of literature values for coupling constants in a wide variety of related spin systems. A least-squares correlation of substituent effects on $J_{F-C=C-F}$ gave an estimate[26] $|J_{11}| = 139.4$ Hz. From the spectrum of <u>trans</u>-2-chloroheptafluoro-2-butene[24] $|J_{22}| = 1.3$ Hz., and $|J_{12}| = 5.45$ Hz. From various phenyl substituted perfluoroalkenes[27] $|J_{22}| = 1.5$ Hz., $|J_{12}| = 7$ to 10 Hz., and $|J_{21}| = 23$ to 28 Hz. Probable absolute signs are[28] $J_{11}{-}$, $J_{12}{-}$, $J_{21}{+}$.

Trial spectra were calculated using values from the above ranges, consistent with the experimental coupling constant sum $|N|$ = 12.80 Hz. A few trial calculations with the NUMAR computer program (Appendix B) yielded a good visual match to the observed spectra with parameters J_{11} = -140 Hz., J_{22} = +1.5 Hz., J_{12} = -9.2 Hz., and J_{21} = +21.9Hz. No good match to the observed spectrum could be obtained if J_{11} and J_{22} were given the same sign.

These values were used as initial parameters for an iterative calculation with the LAME† computer program. The final parameters in Table 5-2 give an RMS deviation of less than 0.05 Hz. between observed and calculated frequencies. Spectra calculated from these parameters, and the corresponding observed spectra, are shown in Fig. 5-1. The outer lines of the CF_3 region are omitted, as no satisfactory experimental spectrum is available.

An INDOR experiment which confirmed the relative signs of the coupling constants is described in connection with the analysis of the *cis*-compound.

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† The LAME computer program (LAOCOON with Magnetic Equivalence) was supplied by its author, C. W. Haigh of the University of Swansea, and modified by G. W. Stockton for use on the IBM 360/67 computer at the University of Alberta. It is similar to UEAITR.[17b]

TABLE 5-2

NMR PARAMETERS OF THE PERFLUORO-2-BUTENES

	cis	trans
Chemical Shifts		
(ppm. from $CFCl_3$)		
$=C-F$	-143.53	-160.65
$-CF_3$	-67.43	-69.80
Coupling Constants		
(Hz.)		
$J_{F-C=C-F}$	8.23	-139.87
$J_{F-C(=)-CF_3}$, $J_{F-C=C-CF_3}$	-9.56, 8.00	-9.10, 21.90
$J_{F_3C-C=C-CF_3}$	10.48	1.35

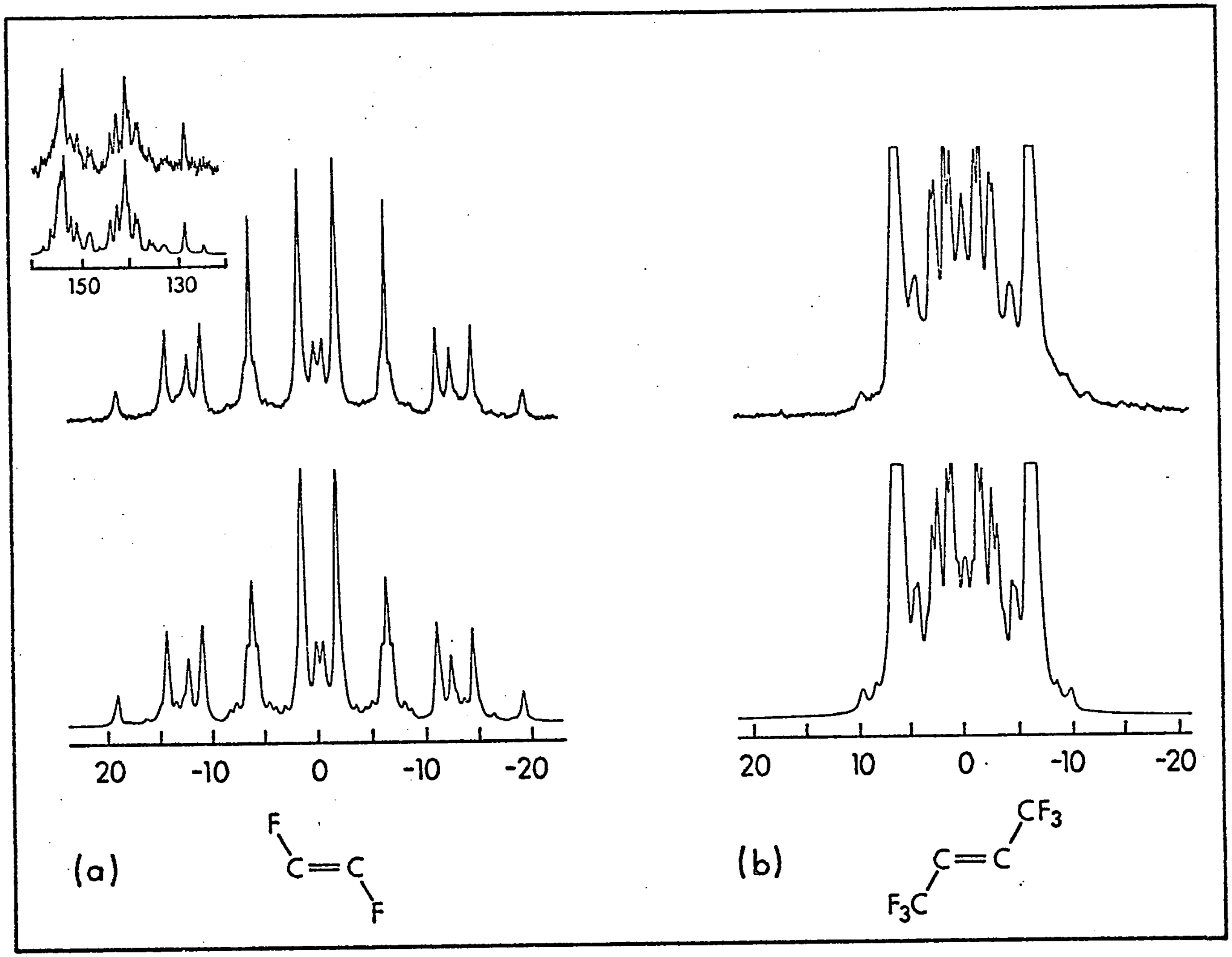

FIG. 5-1. OBSERVED AND CALCULATED SPECTRA.

Literature values for the probable coupling constants in cis-perfluoro-2-butene were less useful than they had been for the trans-isomer. Two of the coupling constants, J_{12} and J_{21}, were predicted with reasonable confidence to be in the ranges -7 to -13 Hz. and +8 to +12 Hz., respectively.[24,27-29] The absolute value of J_{22} was predicted to be 11-13 Hz.,[24] but no literature value for the sign was available. Values for $J_{F-C=C-F}$(cis) in trifluorovinyl compounds range from 24 to 65 Hz., with most in the range 30-40 Hz.[30] However, the table of additive substituent effects[26] which predicted the value of trans-J_{11} to within 0.5 Hz. gave 3.2 Hz. for cis-J_{11}. The sign of $J_{F-C=C-F}$(cis) is positive in most compounds,[28] but negative in cis-1,2-difluoroethylene.[26,31]

An attempt was made to visually match the observed spectrum using trial-and-error calculations with the NUMAR computer program. The magnitude and sign of J_{12} and J_{21} were fairly well known from the ranges given above, and the absolute value of their sum N was known (by inspection) to be 1.5 Hz. The magnitude of J_{22} was also well approximated; its sign was arbitrarily assumed to be positive.[†] However, the wide range of possible

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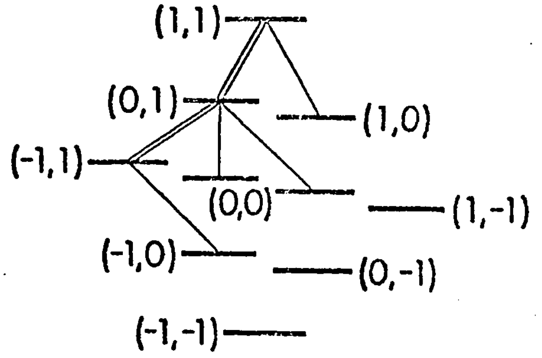
[†] The signs of J_{11} relative to J_{22} and of J_{12} relative to J_{21} affect the appearance of the spectrum, but the signs of J_{11} and J_{22} relative to J_{12} and J_{21} do not.[25]

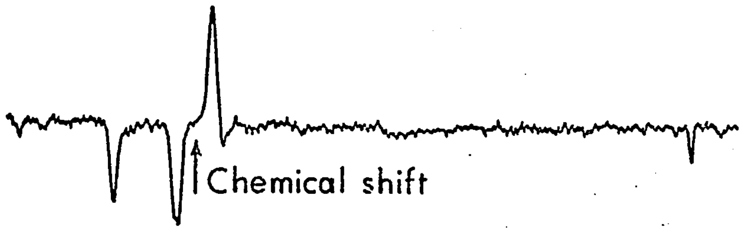
J_{11} values suggested that many trial calculations might be needed. It soon became apparent that most of the strong lines in the calculated spectra resulted from the accidental coincidence of unrelated transitions. Small changes in the coupling constants produced large changes in the appearance of the spectra, as various combinations of lines came into coincidence or separated throughout each multiplet. The trial-and-error approach was abandoned.

The only lines in the observed spectrum that could be assigned were those belonging to the doublets of spacing N = 1.5 Hz. The intense doublet in the CF_3 multiplet was known to consist of the superposition of many lines from various matrices_2, but the corresponding doublet in the =C-F multiplet seemed likely to contain only the lines originating in the symmetric matrix_2 with all spins F = ½.

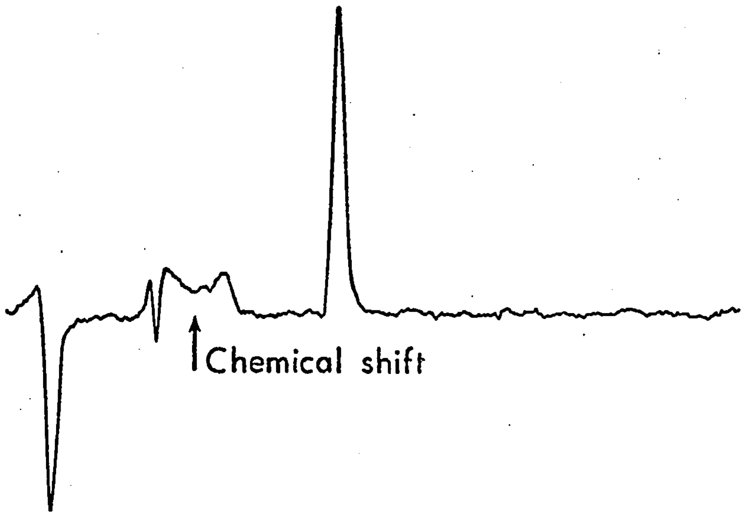
The low-field (frequency +0.75 Hz. from the =C-F chemical shift) member of this doublet was chosen as the transition *T* (see §3.3) to be irradiated in a double resonance experiment. It can be seen in Figs. 3-3 and 5-2 that there are four species X transitions connected to one or other of the two coincident species A transitions being irradiated. Two of these transitions are members of the species X doublet with spacing N, and the others are lines from the $M_A = 0$ subspectrum. Assuming that



(a) Connected Transitions: Irradiated ═
Indor —



(b) *cis* Isomer



(c) *trans* Isomer

FIG. 5-2. INDOR SPECTRA OF THE PERFLUORO-2-BUTENES.

the irradiated transitions *T* are those with frequency $+\frac{1}{2}N$, the frequencies of the two $M_A=0$ transitions are[1]

$$+\tfrac{1}{2}K \pm\tfrac{1}{2}(K^2+L^2)^{\frac{1}{2}} \qquad (5.2)$$

The INDOR double resonance technique[16] was chosen, because of the high probability that the connected transitions would be members of unresolved multiplets. INDOR spectra with a poor signal to noise ratio were obtained using a modified Varian HA-60I spectrometer (see §5.1.2). Comparison of a number of repeat spectra indicated that the two $M_A = 0$ transitions connected to *T* had frequencies of approximately +3.4 and -22.2 Hz., relative to the $-CF_3$ chemical shift.

These values were substituted in (5.2) to obtain the solution $K = \pm 18.8$ Hz., $L = \pm 17.4$ Hz. From L and N, J_{21} and J_{12} were calculated to be[†] ±8.0 and ∓9.5 Hz. A new series of trial spectra was then calculated, varying the one undetermined parameter, $M = J_{11}-J_{22}$. With $J_{11} = \pm 8.2$ Hz. and $J_{22} = \pm 10.5$ Hz., the calculated spectrum closely resembled the observed spectrum. Other values of J_{11} from -25 to +50 Hz. were used with appropriate values of J_{22}; none of these combinations gave a calculated

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[†] One cannot determine from the spectrum which of these values corresponds to J_{12} and which to J_{21}.

spectrum similar to the observed spectrum.

The INDOR results also provided the remaining relative signs of the coupling constants. Of the two INDOR lines given by (5.2), the one for which K and $(K^2+L^2)^{1/2}$ have the same sign is farther from the CF_3 chemical shift. If this sign were the same as the sign of N, the line would be on the low field side of the chemical shift (i.e. +22.2 Hz.). Since it is found at -22.2 Hz. from the CF_3 chemical shift, when observing at +0.78 Hz. from the =C-F chemical shift, K and N have opposite signs. The signs given above for the four coupling constants are consistent with this result.

The INDOR experiment was later repeated using a Bruker HFX-90 spectrometer. The resulting spectrum is shown in Fig. 5-2. The INDOR frequencies were individually measured under steady state conditions, and had the values -22.10, -0.85, +0.75, +3.47 Hz. from the $-CF_3$ chemical shift. These frequencies agree quite well with those measured in the single-resonance spectra, and confirm the original INDOR results. Curiously, the positive peak at -0.85 Hz., which was used to optimize the INDOR conditions, shows the largest discrepancy (about 0.08 Hz.) from the results of the single-resonance spectra.

The approximate parameters above, with the upper set of signs, were used as initial values for an iterative calculation with the LAME computer program. The RMS deviation of observed and calculated transitions was less than 0.09 Hz. for the parameters given in Table 5-2. Observed spectra, and spectra calculated from these parameters, are shown in Fig. 5-3.

An INDOR experiment was also performed (using the Bruker HFX-90) for the *trans*-isomer. As with the *cis*-isomer, the low field member of the N doublet in the =C-F region was observed while a second radiofrequency was swept through the $-CF_3$ region of the spectrum. The outermost peak, expected to be 140.23 Hz. from the chemical shift, was too weak to observe. The three central peaks, shown in Fig. 5-2, were as predicted by the previous analysis of the single-resonance spectrum. The inner peak of the pair given by (5.2) is to low field of the chemical shift; by the argument used above, this confirmed that K and N have opposite signs for the *trans*-isomer.

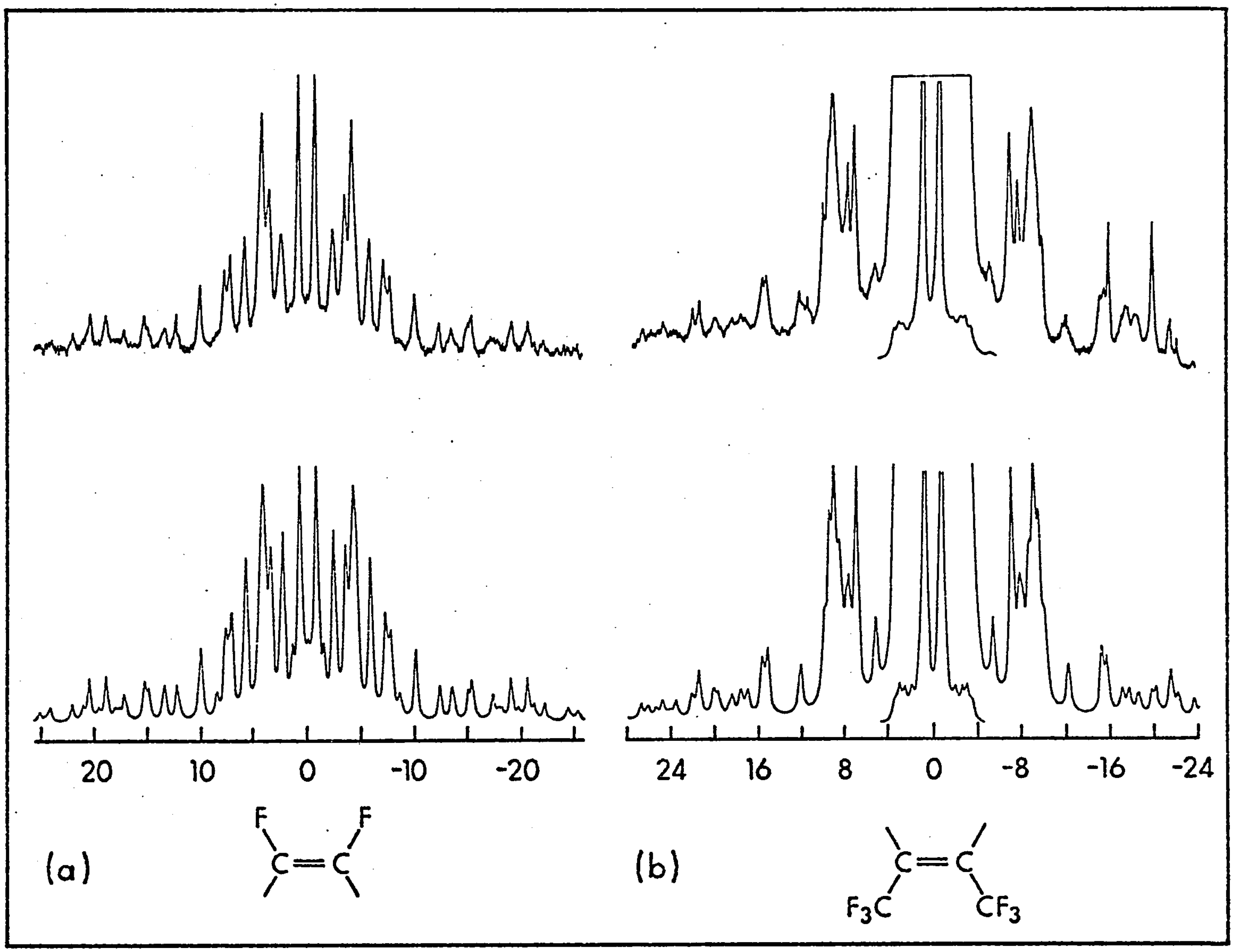

FIG. 5-3. OBSERVED AND CALCULATED SPECTRA.

5.1.4. Discussion

It was hoped that it would be possible to obtain the absolute signs, as well as the magnitudes, of all of the coupling constants in cis-perfluoro-2-butene. This has not been possible, because there is insufficient evidence to allow definite assignment of the two =C-F to $-CF_3$ coupling constants ±8.0 and ∓9.6 Hz.

The magnitude of each of these values is within the range expected for either the three bond $J_{F-C(=)-CF_3}$ or the four bond $J_{F-C=C-CF_3}$.[24,27,29] It is known that the three bond coupling constant J_{12} is negative, and the four bond coupling constant J_{21} is positive.[28] If $J_{12} = -9.6$ Hz., both J_{11} and J_{22} are positive; if $J_{12} = -8.0$ Hz., both J_{11} and J_{22} are negative.

Evidence from some 2-substituted heptafluoro-2-butenes[24,27] is conflicting. In each cis-isomer, $J_{F-C(=)-CF_3}$ is smaller in magnitude than $J_{F-C=C-CF_3}$. On this basis, $J_{12} = -8.0$ Hz. However, in these same studies, $J_{F-C(=)-CF_3}$ in each cis-isomer is at least as large (in magnitude) as the corresponding coupling constant in the trans-isomer. Since in trans-perfluoro-2-butene this coupling constant is -9.1 Hz., one is led to the assignment $J_{12} = -9.6$ Hz.

These results can be reconciled in any of three ways:

i) The coupling constants in the perfluoro-2-

butenes follow a different pattern from those in the heptafluoro-2-butenes.[24,27]

ii) The cis-and trans-isomers were incorrectly identified either in this study or in the previous ones.[24,27]

iii) The two CF_3 resonances were incorrectly assigned in either the cis-or trans-isomer, in both of the previous studies.[24,27]

The first possibility is quite likely the correct one, but is unimportant because it provides no useful information. The second can be ruled out immediately by the excellent agreement between J_{22} and J_{21} values for the trans-isomers in this study and the previous ones. The third possibility demands careful scrutiny, because, if it is correct, it leads to a clear assignment J_{12} = -9.6 Hz.

There is a variety of evidence[24] to show that in the trans-isomers $J_{F-C=C-CF_3}$ is near 25 Hz. Thus any misassignment must be in the cis-isomer. Andreades[27] bases his assignment on chemical shift evidence which he does not give. Tiers[24] finds chemical shifts of -64.8 and -68.4 ppm. from $CFCl_3$ for $C(1)F_3$ and $C(4)F_3$ respectively in trans-2-chloroheptafluoro-2-butene. He therefore assumes that the chemical shifts -62.2 and -66.3 ppm. in the cis-isomer belong to $C(1)F_3$ and $C(4)F_3$ respectively. This assignment appears to be entirely reasonable.

The small amount of literature evidence available tends to support positive signs for J_{11} and J_{22}. Additive substituent effects[26] predict J_{11} = +3.2 Hz. To the extent that J_{22} includes a through-space contribution, it may be expected to be positive.[32]

The weight of evidence seems to support the assignment given in Table 5-2. However, further studies to clarify the situation are indicated. It would be particularly interesting to study <u>cis</u>-perfluoro-2-butene in a liquid crystal medium, in order to determine the principle components of the J tensors, as well as the signs of the isotropic J values. The spectrum would be very complicated, but with the aid of the parameters obtained here for an isotropic medium, a full analysis might be possible.

5.2. The 2,5-Dimethyl-3-Hexenes

Full analysis of the spectra of cis- and trans-2,5-dimethyl-3-hexene was undertaken in cooperation with L. W. Kaslander and Dr. F.H.A. Rummens of the University of Saskatchewan, Regina, Saskatchewan. The chemical shifts and coupling constants, particularly of the methine protons, were of interest as part of a continuing study of conformations and NMR parameters of olefins.[33]

Cis- and trans-2,5,-dimethyl-3-hexene (Aldrich Chemical Co.) were degassed and sealed into 5 mm. O.D. thin wall NMR tubes, with 5% tetramethylsilane (TMS) added as an internal reference. The infrared spectrum (Beckman IR-8) of the cis-isomer had a band at 960 cm.$^{-1}$, indicating that a small amount of the trans-isomer was present; no impurities were noted in the infrared spectrum of the trans-isomer. The methyl region of the NMR spectrum of each isomer showed weak peaks corresponding to the intense methyl doublet of the other isomer. The amount of the other isomer present, about 2% in each case, was small enough not to interfere with the analysis.

Proton NMR spectra were obtained at 100.0 MHz. (23.487 kgauss) with a Varian HA-100-15 spectrometer in frequency sweep mode, locked to internal tetramethylsilane (TMS). A frequency synthesizer was used to obtain a more stable lock frequency (see Appendix E). The spectra were calibrated as described in Appendix F, yielding line positions estimated to be accurate to ±0.02 Hz. in the methine regions. It was noted that, for both isomers, when a peak was scanned first from the right and then from the left the two traces coincided.

The NMR spectrum of each isomer can be divided into three regions, approximately 5, 2.5, and 1 ppm. to low field of TMS, corresponding to olefinic, methine, and methyl protons respectively. As a first approximation, each kind of proton was treated as a separate species, and the two methyl groups of each isopropyl group were assumed to be a single magnetically equivalent group of six nuclei. With these assumptions, each isomer could be described as an $[AKX_6]_2$ spin system.

In the discussion below, the olefinic, methine, and methyl groups are labelled 1, 2, and 3 respectively. The coupling constant between the two olefinic protons is thus J_{11}. There are two coupling constants connecting, for example, the olefinic and methine protons. These are labelled J_{12} and J_{21}, with J_{12} (indices in increasing order) indicating the same-side (close range) coupling, and J_{21} the long-range coupling.

The general features of the spectra are similar for the two isomers. Each methyl region consists of an intense doublet with separation about 6.6 Hz., linewidth about 1 Hz., and no significant fine structure. Each olefinic region has four strong central lines and two weak outer lines, all with about 0.7 Hz. linewidth. Aside from a small intensity bias to high field, each olefinic spectrum is nearly symmetrical about its chemical shift. The methine regions are very complicated.

These features indicate that the methyl and olefinic protons both couple strongly to the methine protons, but weakly to each other. Each methyl (region 3) spectrum can be treated as the X region of a KX_6 spin system, with a doublet splitting equal to J_{KX}. The olefinic (region 1) spectrum is similar to the A region of an $[AK]_2$ spin system with $J_{KK'}$ small. In each case, the fine structure resulting from small coupling constants is unresolved.

When regions 1 and 3 were analyzed on this basis, using the $[AX]_2$ expressions of PSB[1], the approximate parameters obtained were:

	cis	trans
J_{11}	10.87	15.41
J_{12}, J_{21}	9.49, -1.04	6.77, -1.33
J_{13}	6.62	6.68

These values were used as the initial parameters for trial-and-error calculations on region 2 (methine) with the NUMAR computer program.

The overlapping multiplets of the observed methine spectra created some difficulties in comparing observed and calculated spectra. Preliminary calculations showed over two thousand transitions in the methine region. The peak positions in the observed spectrum had been measured very accurately but could not be assumed to be the same as the transition frequencies because of the influence of other nearby transitions.

For this reason, Calcomp plots that simulated the experimental lineshape were used throughout the analysis. It was found that a Lorentzian lineshape, with linewidth 0.14 Hz. for the cis-isomer and 0.32 Hz. for the trans-isomer, provided the best match between observed and calculated spectra. The plotter was found to be accurate enough that measurement of peak positions in the plots to ±0.01 cm. was justified.

Spectra calculated using the $[AKX_6]_2$ approximation gave a poor fit for the central part of each methine spectrum, but a reasonably good fit for the outer parts. The sign and approximate magnitude of J_{22} were determined, for both isomers, at this stage. $[ABX_6]_2$ spectra were calculated, but were not used because they were not significantly different from $[AKX_6]_2$ spectra calculated using the same parameters.

The final parameter adjustments were made treating the spin system as $[AXY_6]_2$ (i.e. olefin protons as one species, and methine and methyl together a second species). The previously determined parameters were changed very little. Peak positions in the methine regions, calculated from the final parameters in Table 5-3, nearly all agree with the observed peaks to within experimental error (±0.02 Hz.), and no deviation is greater than 0.1 Hz. Figures 5-4 and 5-5 show the observed methine spectra for the two isomers, and spectra calculated in the $[AXY_6]_2$ and $[AKX_6]_2$ approximations using the parameters of Table 5-3. Calculated spectra of the methyl and olefin regions (not shown) also agree well with the observed spectra.

The appearance of each spectral region is insensitive to small changes in the relative chemical shifts. Thus when the coupling constants had been determined, the chemical shift for each region was obtained very easily from the constant difference between observed and calculated transition frequencies. The methine chemical shifts are estimated to be accurate to ±0.02 Hz. (0.0002 ppm.). The broader observed lines in the olefinic and methyl regions did not allow such accurate determinations; the chemical shift errors are estimated to be ±0.05 Hz. (0.005 ppm.) and ±0.1 Hz. (0.0001 ppm.) respectively.

The spectra of the methine regions were surprisingly sensitive to both sign and magnitude of all of the coupling constants, including J_{13}. It is unlikely that the magnitude of any of the coupling constants is in error by more than ±0.05 Hz., and the excellent fit of the observed and calculated spectra suggests that most are accurate to ±0.03 Hz. The small coupling constants ($|J|<0.1$ Hz.)

TABLE 5-3

NMR PARAMETERS OF THE 2,5-DIMETHYL-3-HEXENES

		cis	trans
Chemical Shifts (ppm. from TMS)			
=CH	(1)	5.022	5.303
=C-CH	(2)	2.600	2.2005
$-(CH_3)_2$	(3)	0.932	0.950
Coupling Constants[†] (Hz.)			
J_{11}		10.80	15.40
J_{12}, J_{21}		9.47, -1.02	6.80, -1.30
J_{22}		0.40	0.60
J_{13}, J_{31}		0.20, 0.0	-1.08, 0.0
J_{23}, J_{32}		6.62, 0.0	6.72, 0.02

[†] In pairs such as J_{12} and J_{21}, J_{21} is the long range coupling constant.

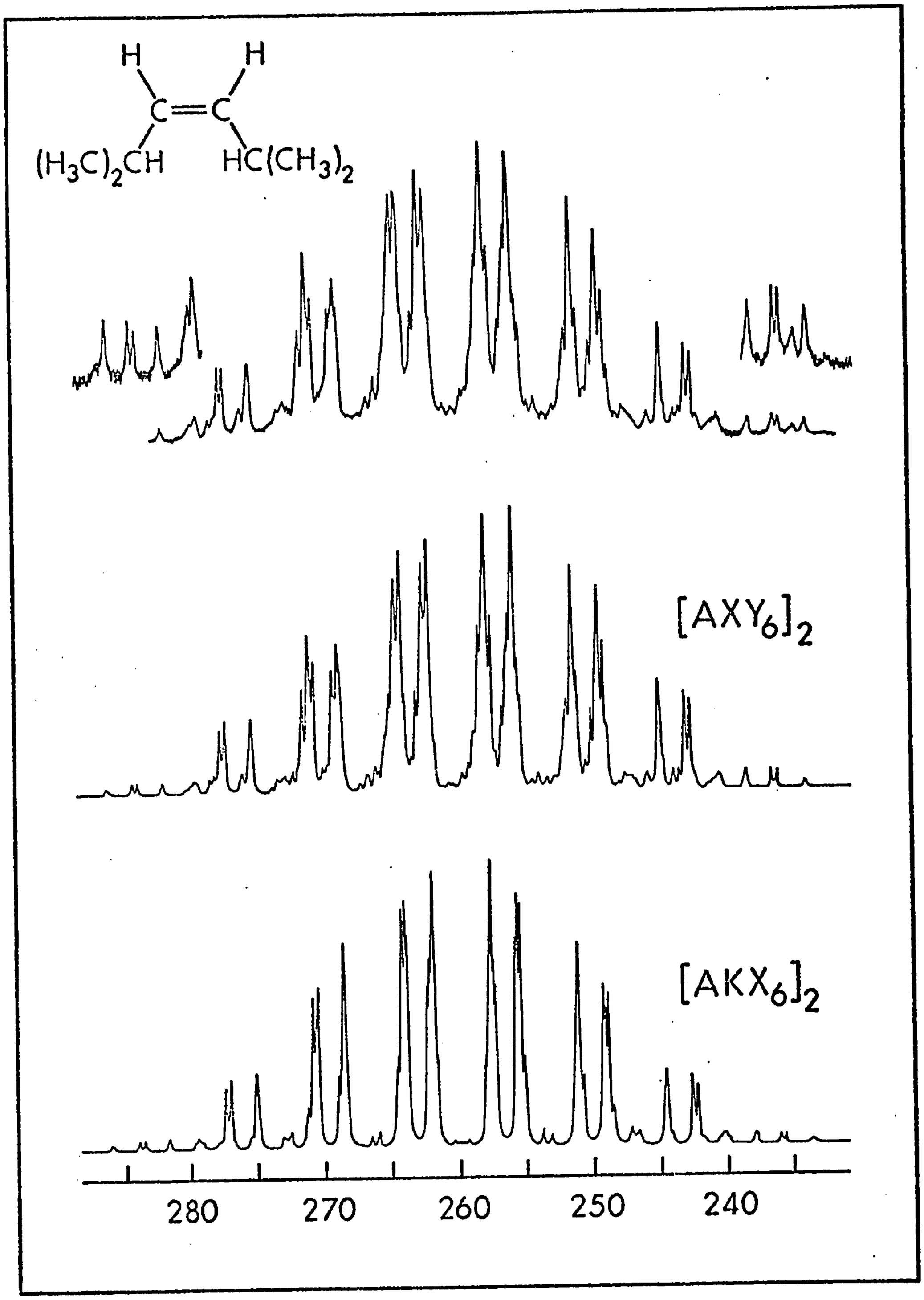

FIG. 5-4. OBSERVED AND CALCULATED SPECTRA.

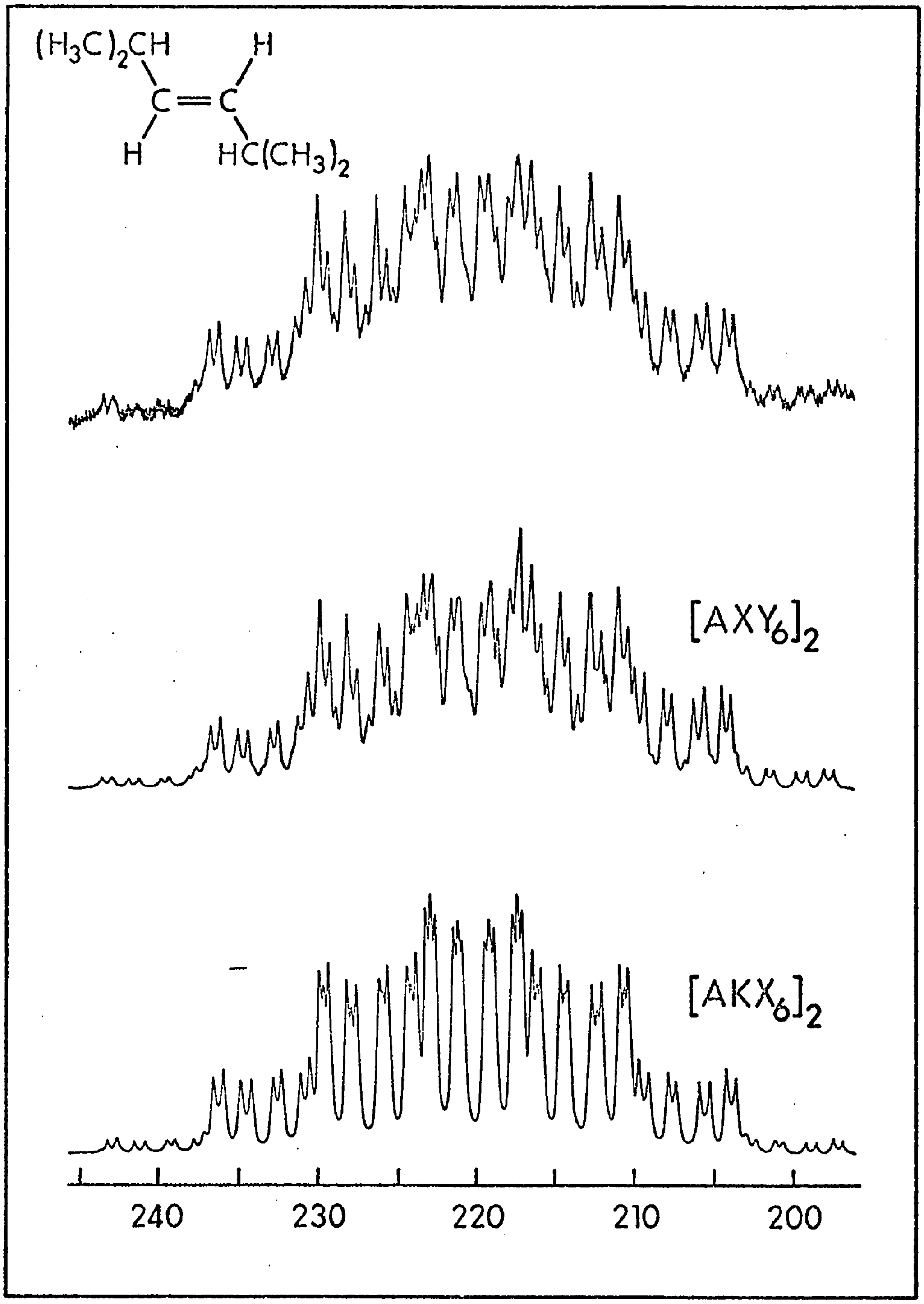

FIG. 5-5. OBSERVED AND CALCULATED SPECTRA.

were varied in smaller steps; their values are probably accurate to ±0.02 Hz. The six bond coupling constant J_{32} in the _trans_-isomer was varied from -0.1 to +0.1; the best agreement between observed and calculated intensities was obtained for $J_{32} = +0.02$. This value is so near zero that it may merely be compensating for higher order effects ignored in the $[AXY_6]_2$ calculation.

It is obvious that, for all practical purposes, the $[AXY_6]_2$ approximation adequately describes both of these spin systems. The few residual differences between observed and calculated spectra may equally likely be the result of small errors in the coupling constants or of the assumption that the olefin protons can be treated as a separate species. There is no evidence to suggest that the six methyl protons of each isopropyl group are not magnetically equivalent.

One puzzling minor observation should be noted. The linewidth needed to adequately match the spectrum of the _trans_-isomer is more than twice that needed for the _cis_-isomer. Higher-temperature spectra, which have not yet been fully analyzed, show noticeably sharper lines for the _trans_-isomer above 45°C. There is not sufficient evidence to indicate with any certainty the cause of the broadening, but it could perhaps be the result of high viscosity in the neat liquid at ambient temperatures.

5.3. Trifluoromethyl Phosphorus Compounds

The NMR spectra of a series of symmetric compounds containing $-P(CF_3)_2$ were analyzed as $[AX_6]_2$ spin systems, in cooperation with Drs. A. Pinkerton and R. G. Cavell of this University. The analysis for $(F_3C)_2P\text{-}NH\text{-}P\text{-}(CF_3)_2$, a typical member of the series, is presented briefly here as a further illustration of the ease with which the spectra of large, highly symmetrical spin systems can be calculated using the methods described in earlier Chapters of this Thesis.

The $[(CF_3)_2P]_2NH$ was prepared and purified by A. Pinkerton, using the usual procedure.[34] A sample was dissolved in CCl_4 with added $CFCl_3$ as an internal reference and sealed in a 5 mm. O.D. NMR sample tube. ^{19}F spectra were obtained using a Varian HA-100-12 spectrometer operating at 94.1 MHz. (23.487 kgauss). A frequency synthesizer was used to allow large offsets from the $CFCl_3$ lock (see Appendix E). ^{31}P spectra were not obtained.

Linewidths were somewhat greater than in the other compounds studied. This may have been the result of coupling either to ^{14}N, or to the NH proton. Since it produced no resolvable fine structure, the NH proton was ignored in the calculation.

The phosphorus and fluorine nuclei of this compound are labelled species 1 and species 2, and the three-bond and four-bond P-F coupling constants are labelled J_{12} and J_{21} respectively. One coupling constant combination, $N = J_{12}+J_{21} = 91.2$ Hz., is available by inspection from the separation of the intense doublet that dominates the ^{19}F spectrum (Fig. 5-6). The ^{19}F chemical shift is 3623 Hz. to high field of $CFCl_3$ (-38.51 ppm.)

Initial values of J_{11} and $L = J_{12}-J_{21}$ were obtained, with the assumption $J_{22} = 0$, using the procedure of Harris.[14] The separation of the innermost line outside the N doublet from the most intense line inside the N doublet on the same side gave $J_A = 228.0$ Hz. This value was then substituted in Harris' equation [5], which gives the separation of the innermost pair of lines as $(L^2+J_{11}{}^2)^{\frac{1}{2}}+|J_{11}|$. From the result, L = 82.2 Hz., and the known value of N, J_{12} and J_{21} were given as 86.7 and 4.5 Hz. respectively.

These values were used as starting parameters for trial-and-error calculations with the NUMAR computer program. The best visual match between observed and calculated spectra was obtained for (in Hz.)

J_{11}	228.0
J_{12}, J_{21}	86.9, 4.3
J_{22}	0.7

All of these coupling constants have estimated errors of ±0.1 Hz. The spectrum calculated using these values is shown in Fig. 5-6. Observed spectra are shown above the corresponding calculated spectra with the central lines and the outermost lines in an expanded scale. Frequency scales below the calculated spectra are in Hz. with an arbitrary zero.

The signs of J_{11} and J_{22} are the same, and the signs of J_{12} and J_{21} are the same; the signs of J_{11} and J_{22} relative to J_{12} and J_{21} do not affect the appearance of the spectrum.[25] The positive signs given are consistent with literature values,[35] but should be confirmed by a double resonance experiment.

Other compounds whose NMR spectra have been analyzed in a similar way include $[(CF_3)_2P(=S)]_2O$, $[(CF_3)_2P]_2O$, $[(CF_3)_2P]_2S$, and $[(CF_3)_2P(=S)S-]_2$. In most cases the spectra could have been calculated by perturbation methods,[25] but exact calculations with NUMAR program were much faster (ten seconds computer time, typically, on an IBM 360/67 computer), and provided plots that allowed a more accurate comparison of observed and calculated spectra.

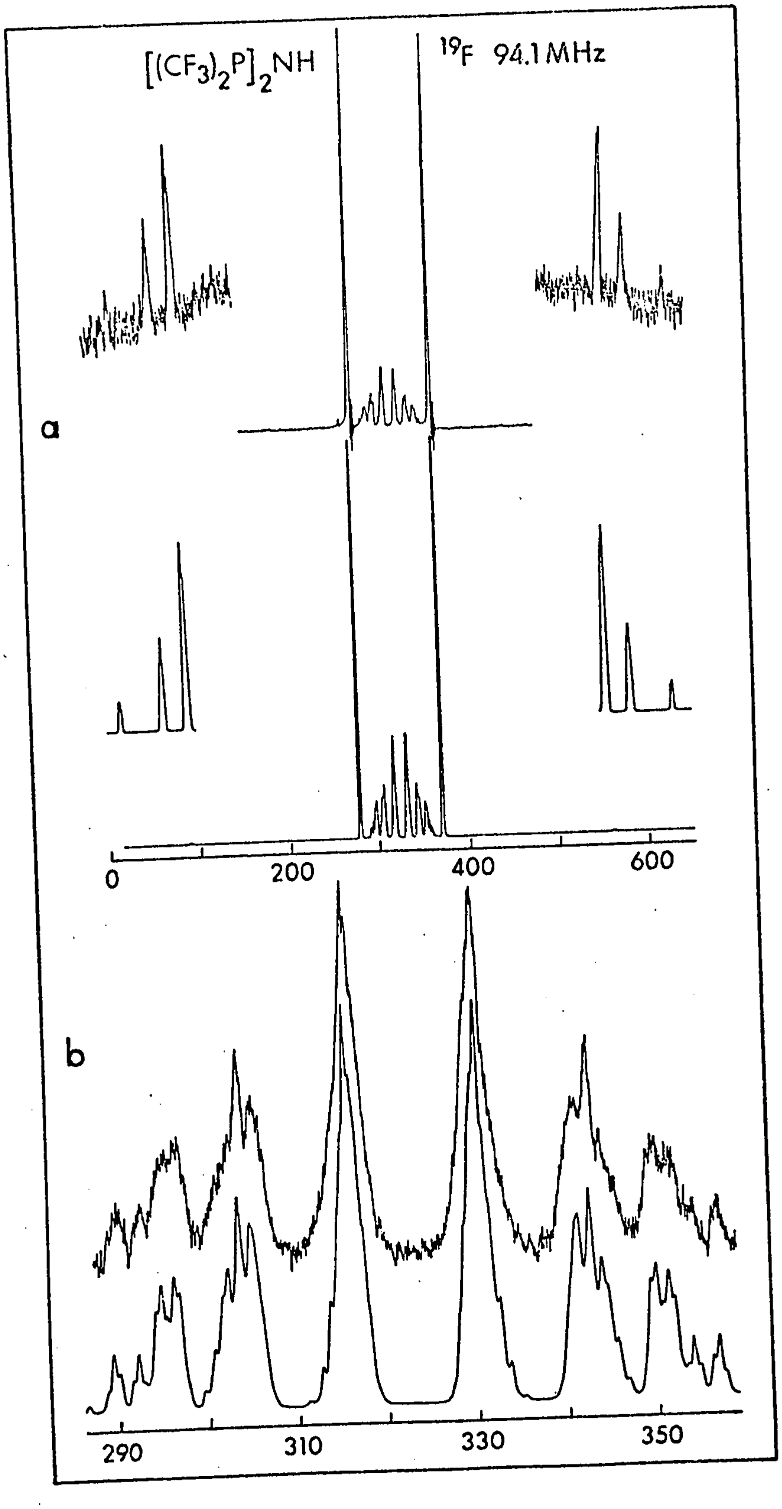

FIG. 5-6. OBSERVED AND CALCULATED SPECTRA.

CHAPTER 6 CONCLUSIONS

A new approach to the calculation of the NMR spectra of molecules with twofold frame symmetry has been developed. A total spin operator $\underline{\vec{A}}$ is defined for each symmetrically equivalent pair of magnetically equivalent groups

$$\underline{\vec{A}}\ (\text{pair } \ell) = \underline{\vec{F}}\ (\ell) + \underline{\vec{F}}\ (\ell'), \tag{6.1a}$$

and for each invariant magnetically equivalent group

$$\underline{\vec{A}}\ (\text{group } i) \equiv \underline{\vec{F}}\ (i). \tag{6.1b}$$

For each pair, an antisymmetric operator $\underline{\vec{B}}$ is also defined:

$$\underline{\vec{B}}\ (\text{pair } \ell) = \underline{\vec{F}}\ (\ell) - \underline{\vec{F}}\ (\ell'). \tag{6.2}$$

The two distinct coupling constants J_{near} and J_{far}, connecting the magnetically equivalent groups of pair ℓ to those of pair m, are replaced by the symmetric and antisymmetric combinations

$$\left.\begin{aligned} J_{\ell m} &= \tfrac{1}{2}\,(J_{near} + J_{far}) \\ J_{m\ell} &= \tfrac{1}{2}\,(J_{near} - J_{far}) \end{aligned}\right\} \tag{6.3}$$

The nuclear spin Hamiltonian for the molecule is then written

$$\left.\begin{aligned} \underline{H} = \sum_i \nu_i \underline{A}_z(i) &+ \sum_\ell J_{\ell\ell'} \underline{\vec{F}}(\ell)\cdot\underline{\vec{F}}(\ell') \\ &+ \sum_{i<j} J_{ij} \underline{\vec{A}}(i)\cdot\underline{\vec{A}}(j) \\ &+ \sum_{\ell<m} J_{m\ell} \underline{\vec{B}}(\ell)\cdot\underline{\vec{B}}(m), \end{aligned}\right] \qquad (6.4)$$

In (6.4), sums over i, j, ... include both invariant groups and pairs, while sums over ℓ, m, ... include only the pairs.

A suitable basis for this Hamiltonian is constructed from eigenfunctions of $\underline{A}^2$ and $\underline{A}_z$ for all the invariant groups and pairs:

$$\prod_i \mid A_i, M_i >. \qquad (6.5)$$

When $F \neq F'$ for any of the symmetrically equivalent pairs, these product functions are not eigenfunctions of the molecular twofold symmetry operator $\underline{C}_2$. When $F = F'$ for all pairs, the symmetry of each product function is given by

$$\underline{C}_2 \prod_i |A_i, M_i> = (\prod_\ell (-1)^{2F(\ell)-A(\ell)}) \prod_i |A_i, M_i>. \qquad (6.6)$$

The basis functions belonging to the symmetric (A) representation of $\underline{C}_2$ form one matrix$_2$, and those belonging to the antisymmetric (B) representation form another. Thus this basis yields all of the symmetry factoring that results from twofold frame symmetry as well as magnetic equivalence.

Explicit expressions have been derived for all of the matrix elements of the Hamiltonian (6.4) in the basis (6.5). Although these expressions can be used for hand calculations, their chief advantage is their suitability for use in a general computer program. Unlike previous expressions for molecules with frame symmetry,[1,2,6] they are valid for molecules of arbitrary size, with either no frame symmetry, or twofold frame symmetry. (For molecules without frame symmetry, (6.4) and (6.5) reduce to the corresponding equations of the Composite Particle method.[8])

This symmetry factoring has been combined with factoring by the z components of molecular total spin M, and species total spins M_S, to provide a systematic, three stage approach to the factoring of the Hamiltonian matrix. It has been shown that this approach to factoring leads in a particularly straightforward fashion to the selection rules governing transitions between Hamiltonian matrices$_4$ and to a description of each species' spectrum in terms of subspectra connecting separate series of matrices$_4$.

NUMAR, a flexible and efficient computer program, has been written to allow the use of all three stages of factoring for calculations on large spin systems. The user has the option of making quick initial calculations assuming a high degree of symmetry and X factoring, followed by more accurate calculations eliminating any factoring that has proved unjustified. Quantum numbers are printed with the energy levels and the transitions to simplify the identification of subspectra. Two plotting routines are included in the program. The one provides bar plots on the computer's printer for immediate use in the early stages of analysis. The other provides a variety of lineshape and scaling options to allow accurate comparison of the fine details of observed and calculated spectra.

The new factoring procedure has been applied in the analysis of the NMR spectra of a number of molecules with twofold frame symmetry. Preliminary parameters for the perfluoro-2-butenes were obtained from the literature, and from INDOR[16] spectra. Preliminary parameters for the 2,5-dimethyl-3-hexenes were obtained from approximate analyses of their methyl and olefin regions. Preliminary parameters for $[(F_3C)_2P]_2NH$ were obtained from Harris'[16] equations.[14] In each case, the preliminary parameters were refined by a series of trial and error calculations with the NUMAR computer program; the resulting final parameters gave calculated spectra that matched the observed spectra within experimental error.

The approach to NMR symmetry factoring developed in this Thesis is the most general presently available for calculations on large spin systems. It suggests several opportunities for future research, particularly the development of a similar procedure for molecules with C_{2v} or D_2 frame symmetry, and the extension of the equations and computer program to include partially oriented molecules in liquid crystal media.

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APPENDIX A. SYMBOLS AND NOTATION.

Spin Systems

A,B,...	Nuclei with similar chemical shifts; one species.
X,Y,...	Nuclei widely separated in chemical shift from A,B,...; another species.
A_n or X_n	Magnetically equivalent group of n nuclei.
$[...]_n$	Indicates an n-fold element of frame symmetry. The notation for a typical member of each set of nuclei (or of magnetically equivalent groups), related by the symmetry element, is enclosed in the brackets.

For example, *p*-fluorotoluene, at 24 kgauss, can be treated as an $A_3[KL]_2X$ spin system with three species. In the other commonly used notation, it would be called $A_3KK'LL'X$.

Chemical Shifts and Coupling Constants

ν_i	Absolute Chemical Shift, in Hz., of magnetically equivalent group, or pair, i.
ν_S	Absolute Chemical Shift, in Hz., of the reference for species S.

$\bar{\nu}_i$	Chemical Shift i, in Hz., relative to ν_S of the species containing group or pair i.
J_{ij}	Coupling Constant, in Hz., between magnetically equivalent groups or pairs.
J_{pq}, J_{qp}	The short range and long range coupling constants connecting pairs p and q.
$J_{\ell\ell'}$	The coupling constant between the two magnetically equivalent groups of pair ℓ.
$J_{\ell m}$, $J_{m\ell}$	Symmetrized coupling constants: $J_{\ell m} = \frac{1}{2} (J_{pq} + J_{qp})$ $J_{m\ell} = \frac{1}{2} (J_{pq} - J_{qp})$

Operators

All spin operators used in this Thesis are dimensionless.

$\underline{\quad}$	Operator
$\rightarrow$	Vector
$\underline{\vec{I}}$	Spin operator for a single nucleus.
$\underline{\vec{F}} = \sum\limits_{i \text{ in group}} \underline{\vec{I}}(i)$	Total Spin operator for a magnetically equivalent group of nuclei.
$\underline{\vec{A}} = \underline{\vec{F}} + \underline{\vec{F}}'$	Total spin operator for a symmetrically equivalent pair of magnetically

	equivalent groups of nuclei. Identical to $\vec{\underline{F}}$ for invariant groups.
$\underline{A}_z(S) = \sum_{i \text{ in } S} \underline{A}_z(i)$	Species S total spin operator (z component.
$\vec{\underline{B}} = \vec{\underline{F}} - \vec{\underline{F}}'$	Antisymmetric operator, complementary to $\vec{\underline{A}}$, for each symmetrically equivalent pair of magnetically equivalent groups. Not defined for invariant groups.
$\underline{\mathit{H}}$	Hamiltonian operator.
$\underline{X} = \sum_i \underline{I}_x(i)$	Molecular transition operator. Transition intensities are proportional to the absolute squares of its matrix elements.

Eigenvalues

The corresponding operator is given to the right of each eigenvalue.

$A(A+1)$	$\underline{A}^2$
E	$\underline{\mathit{H}}$
$F(F+1)$	$\underline{F}^2$
$I(I+1)$	$\underline{I}^2$
m	$\underline{I}_z$ or $\underline{F}_z$
M	$\underline{A}_z$
M_S	$\underline{A}_z(S)$
$\mathit{M} = \sum_S M_S$	Molecular total spin (z component)

Basis Functions

In kets of the form $|F,m\rangle$ the first eigenvalue always corresponds to the squared total spin operator $\underline{F}^2$, and the second to the corresponding z component operator $\underline{F}_z$:

$$\underline{F}^2 \, |F,m\rangle = F(F+1) \, |F,m\rangle$$

$$\underline{F}_z \, |F,m\rangle = m \, |F,m\rangle$$

The $|I,m\rangle$ and $|A,M\rangle$ kets also follow this convention.

APPENDIX B. THE NUMAR PROGRAM (FORTRAN LISTING).

NUMAR is written in FORTRAN IV at the level of the IBM FORTRAN G and FORTRAN H compilers. It has been tested on the IBM 360/67 computer at the University of Alberta under the OS/360 and MTS operating systems.

The routines TIME and CREPLY, used in INPUT and BPLOT, are specific to the MTS operating system. They may be omitted or replaced without significant effect on the remainder of the program.

Double-precision (REAL*8) arithmetic is used in HAMIL to reduce rounding errors, and half-precision (INTEGER*2) integers are used for some quantum numbers to save memory space. Neither of these choices is essential to the operation of the program.

NUMAR is designed for efficient operation as an overlay (or chained) program. The small main program, both Common blocks, and the FORTRAN library form the base segment. The single overlay region is used in turn for each subroutine called by the main program (and any subroutines it calls). NUMAR as presently dimensioned can execute in a storage region of less than 100K bytes (25000 words).

See also Appendix D, Instructions for NUMAR.

```
C     MAIN PROGRAM  ---  NUMAR  ---
C
C     REVISED DECEMBER 1971.
      COMMCN BAF(9.9).TITLE(24).IMCK.OLD.SYM.ITRAT.NCASE.NCPL.
     .LCSCC.AHALF(49).ABLANK.ANOT.ANTI.INFIN.ERIEF.NM2.OLDH.
     $LINE.INCATA.PUNCH.QUANT.TFI.EU.OTPL.
     . MAXF.MAXM43.MAXE4.MAXE3.MAXU3.MAXE2.MAXT.
     $MAXG.NG.SYMG(9).ISOG(9).NUCG(9).
     .NGS.SYMGS(9).IG(9).IMAXG(9).AGPB(9).
     $CC(9.9).JOINCC(9.9).CS(9).JGINCS(9).
     .MAXISO.NISO.TTLISO(3.9).IISC(9).MISOPA(9).MISOPB(9).NTISO(9).KM2P.
     .TIISO(9). OUTISO(9).WISO(9).TLISO(9).SFISO(9).FLISO(9).FUISO(9).
     $MAXREG.NREG.ISCREG(9).TTLREG(3.9).FLREG(9).FRREG(9).KREG(9).
     . HSREG(9). VSREG(9).CLWRCG(9).CRWREG(9)
      LOGICAL OLDH.     SYM.SYMG.SYMGS.ITRAT.LCSCC
      INTEGER FMAXG.AGPB.      PUNCH.QUANT.EU.TFI.OTPL
      REAL*8 BAF
C
      COMMON/ACOM/TFC(2501).TIC(2500).TNC(2500).TMISO(2500).SPACER(200)
      INTEGER*2 TMISO
      INTEGER TNC
C     THE FOLLOWING NUMBER IS THE LARGEST POSSIBLE POSITIVE INTEGER FOR
C     THE COMPUTER BEING USED.  IN GENERAL FOR A WORD LENGTH OF N BITS
C     INFIN SHOULD BE  (2**(N-1))-1 .
C     THE PROGRAM AS SUPPLIED USES 16 BIT INTEGERS FOR THE PACKED
C     QUANTUM NUMBERS WHERE INFIN IS USED.  IT SHOULD BE CHANGED FROM
C     32767 TO 2147483647 IF 32 BIT INTEGERS ARE USED.
      INFIN = 32767
C     PROVIDE UNIT NUMBERS FOR INPUT/OUTPUT DEVICES
C     CARD READER
      INDATA=5
C     LINE PRINTER
      LINE=6
C     CARD PUNCH
      PUNCH=7
C     INTERMEDIATE STORAGE DEVICES (TAPE OR SEQUENTIAL DISK FILES)
      QUANT=1
      EU=2
      TFI=3
      OTPL=4
C     SET LIMITS FOR ARRAYS TO AVOID OVERFLOWS.
      MAXISO=6
      MAXG=9
      MAXF=9
      MAXREG=9
      MAXE4=42
      MAXE3=150
      MAXE2=1200
      MAXM43=60
      MAXU3=2322
      MAXT=2500
C     INITIALIZE COUNTERS
      NCASE=0
      NCPL=0
      IMOK=-1
  100 CALL INPUT
      IF(IMOK.NE.1) GO TO 100
```

```
      IF(OLD.NE.ABLANK) GO TO 300
  200 CALL BASIS
      IF(IMOK.NE.1) GO TO 100
  300 IF(OLDH) GO TO 500
      CALL HAMIL
      IF(IMOK.NE.1) GO TO 100
  500 CALL TRANS
      ISO=0
  600 ISO=ISO+1
      IF(ISO.GT.NISO) GO TO 100
      IF(NTISO(ISO).LE.0) GO TO 600
      CALL SPCUT(ISO.NT)
      IF(IMOK) 100.600.610
  610 ISPC=1
      DO 650 JREG=1.NREG
      IF(ISOREG(JREG).NE.ISO) GO TO 650
      IF(KREG(JREG).EQ.0) ISPC=1
      WRITE(LINE.9000)ISPC.NCASE.TITLE.ISO.(TTLISO(I.ISO).I=1.3).
     1JREG.(TTLREG(I.JREG).I=1.3)
      IF(KREG(JREG).GT.0) GO TO 630
      CALL BPLOT(NT.    TFC.TIC.FLREG(JREG).FRREG(JREG). HSREG(JREG).
     1  VSREG(JREG).  TNC)
      GO TO 650
  630 CALL CPLOT(NT.JREG)
      ISPC=0
  650 CONTINUE
      GO TO 600
 9000 FORMAT(I1.'CASE'.I3.1X.24A4      /'0ISOTOPIC SPECIES'.I2.1X.3A4.
     1'     PLOT REGION'.I2.1X.3A4)
      END
```

```
      SUBROUTINE INPUT
C
C     REVISED DECEMBER 1971
C
C SUBROUTINE TO READ ALL INPUT DATA FROM CARDS AT THE START OF EACH CASE
C
C
C     DATA ITEM 1 IS READ AT STATEMENT 100 USING FORMAT 9001 AND ERRORS
C     FOUND ARE HANDLED AT STATEMENT 1510 WITH MESSAGE IN FORMAT 9510.
C     FOR ITEM 2 SIMILAR NUMBERS ARE 200,9002,1520,9520   ETC.
C
C     IF THERE ARE NO FATAL ERRORS, PARAMETERS ARE PRINTED AT 1000
C
C
      COMMON BAF(9,9),TITLE(24),IMOK,OLD,SYM,ITRAT,NCASE,NCPL,
     .LCSCC,AHALF(49),ABLANK,ANOT,ANTI,INFIN,BRIEF,NM2,OLDH,
     $LINE,INDATA,PUNCH,QUANT,TFI,EU,OTPL,
     . MAXF,MAXM43,MAXE4,MAXE3,MAXU3,MAXE2,MAXT,
     $MAXG,NG,SYMG(9),ISOG(9),NUCG(9),
     .NGS,SYMGS(9),IG(9),FMAXG(9),AGPB(9),
     $CC(9,9),JOINCC(9,9),CS(9),JOINCS(9),
     .MAXISO,NISO,TTLISO(3,9),IISO(9),MISOPA(9),MISOPB(9),NTISO(9),KM2P,
     .TIISO(9), OUTISO(9),WISO(9),TLISO(9),SFISO(9),FLISO(9),FUISO(9),
     $MAXREG,NREG,ISOREG(9),TTLREG(3,9),FLREG(9),FRREG(9),KREG(9),
     . HSREG(9), VSREG(9),CLWREG(9),CRWREG(9)
      LOGICAL OLDH,     SYM,SYMG,SYMGS,ITRAT,LCSCC
      INTEGER FMAXG,AGPB,      PUNCH,QUANT,EU,TFI,OTPL
      REAL*8 BAF,DENOM
C
      COMMON/ACOM/ TNO(1),TFO(1),TWT(1)
      INTEGER TNO
      REAL HALF(49) /'-12 ','-23/','-11','-21/','-10 ','-19/',' -9 ',
     *'-17/',' -8 ','-15/',' -7 ','-13/',' -6 ','-11/',' -5 ','-9/2',
     *' -4 ','-7/2',' -3 ','-5/2',' -2 ','-3/2',' -1 ','-1/2',
     *                ' 0 ',' 1/2',' 1 ',' 3/2',' 2 ',' 5/2',' 3 ',
     * ' 7/2',' 4 ',' 9/2',' 5 ','11/2',' 6 ','13/2',' 7 ','15/2',
     *' 8 ','17/2',' 9 ','19/2',' 10 ','21/2',' 11 ','23/2',' 12 '/
      REAL ERR30(2)/'SPEC','IES.'/, ERR40(4)/'CHEM','ICAL',' SHI',
     1'FTS.'/, ERR50(3)/'PLOT',' REG','IONS'/, ERR64(5)/'OBSE','RVED',
     2 ' TRA','NSIT','IONS'/
      INTEGER*2 TIME2(2),BLANK2
      DATA BLANK/'    '/,BNOT/'NOT '/,ANT/'ANTI'/,SYMBOL/'*   '/,
     1  SYMSYM/'2*  '/  ,PALPH/'P'/,FALPH/'F'/, BLANK2/' '/
      EQUIVALENCE                   (TIME2,TITLE(2))
C
      IF(NCASE.GT.0) GO TO 98
C     PUT DATE AND TIME OF DAY INTO FIRST 6 WORDS OF TITLE.
      CALL TIME(6,0,TITLE)
      TIME2(2)=BLANK2
      TITLE(6)=BLANK
      MAXTO=MAXT
      ABLANK=BLANK
      ANOT=BNOT
      ANTI=ANT
      DO 10 I=1,49
   10 AHALF(I)=HALF(I)
C     CALCULATE THE SQUARE OF THE J-INDEPENDENT PART OF THE
```

```
C     B-MATRIX ELEMENTS.
C     I IS '2F' VALUE AND J IS 'A' VALUE.
      DO 30 J=1,MAXF
      JJ=J*J
      DENOM=(4*JJ-1)*4
      DO 30 I=J,MAXF
         BAF(I,J)=DFLOAT((I+1)**2-JJ)/DENOM
   30 CONTINUE
      GO TO 99
   98 WRITE(LINE,9200)
C     SYSTEM DEPENDENT INTERVAL TIMING ROUTINE.  OMIT OR REPLACE.
      CALL TIME(1,1,TITLE)
   99 CALL TIME(0,1,TITLE)
C
C ITEM 1.   TITLE AND CONTROL CARD.
C
C     ANY NUMBER OF CARDS WILL BE READ UNTIL ONE IS FOUND WITH AN
C     ASTERISK IN COLUMN 1.  THIS ALLOWS SKIPPING TO THE NEXT CASE
C     WHEN AN ERROR IS FOUND.
C
C THE END= EXIT IS TAKEN AT THE END OF INPUT DATA.  IF THIS FEATURE IS
C   NOT AVAILABLE IN YOUR FORTRAN, CHECK FOR A NONBLANK CHARACTER IN
C   TITLE.  EACH RUN SHOULD THEN BE FOLLOWED BY A TITLE CARD BLANK
C   EXCEPT FOR THE ASTERISK IN COLUMN 1
C
  100 READ(INDATA,9001,END=999) A,OLD,BRIEF,C,D,E,(TITLE(I),I=7,24)
      IF(A.NE.SYMBOL) GO TO 100
      NCASE = NCASE + 1
      ITER=0
      ICONV=0
      LCSCC=.FALSE.
C     REMOVE NEXT FOUR  CARDS WHEN SETTING UP ITERATIVE VERSION..
      C=BLANK
      D=BLANK
      E=BLANK
      F=BLANK
C     PRINT A SUITABLE FIRST PAGE HEADING FOR ITERATIVE OR NON-ITERATIVE
      IF(C.EQ.BLANK) GO TO 110
      IF(D.NE.BLANK) LCSCC=.TRUE.
      ITRAT=.TRUE.
      A=BLANK
      GO TO 120
  110 ITRAT=.FALSE.
      A=ANOT
  120 WRITE(LINE,9111)       NCASE,TITLE,A
      IF(OLD.EQ.BLANK) GO TO 130
C     LIMITED SETTING OF INITIAL VALUES FOR AN 'OLD' CASE
      IF(IMOK.EQ.-1) GO TO 1510
      OLDH=.TRUE.
      IMOK=1
      LIMG=NG
      IF(OLD.EQ.PALPH) NREG=0
      DO 125 I=1,NISO
  125 OUTISO(I)=BRIEF
      GO TO 200
C     INITIALIZING OF VALUES FOR A 'NEW' CASE.
  130 NG=0
```

```
      OLDH=.FALSE.
      NGS=0
      NSYM=0
      NISO=0
      NREG=0
      NTO=0
      NTC=0
      IMOK=1
      LIMG=MAXG
      SYM=.FALSE.
      DO 140 J=1,MAXG
      ISOG(J)=0
      SYMG(J)=.FALSE.
      SYMGS(J)=.FALSE.
      DO 140 I=1,MAXG
      JOINCC(I,J)=0
  140 CC(I,J)=0.0
C
C ITEM 2.   COUPLING CONSTANT CARDS.  (FOR OLD CALCULATIONS, SHIFTS TOC
C
  200 READ(INDATA,9002,END=999) A,I,B,J,K,X,Y,Z,V,W
      IF(I.GT.LIMG .OR.J.GT.LIMG) GO TO 1520
      IF(J.NE.0) GO TO 210
      IF(I.EQ.0) GO TO 1520
      OLDH=.FALSE.
      CS(I)=X
      JOINCS(I)=K
      GO TO 250
  210 IF(I.NE.0) GO TO 240
      IF(B.NE.BLANK) OUTISO(J)=B
      IF(Y.NE.0.0) TLISO(J)=Y
      IF(Z.NE.0.0) SFISO(J)=Z
      IF(V-W) 220,250,230
  220 FLISO(J)=V
      FUISO(J)=W
      GO TO 250
  230 FLISO(J)=W
      FUISO(J)=V
      GO TO 250
  240 CC(I,J)=X
      JOINCC(I,J)=K
      OLDH=.FALSE.
  250 IF(A.EQ.BLANK) GO TO 200
      IF(OLD.NE.BLANK) GO TO 500
C
C ITEM 3     ISOTOPIC SPECIES CARDS.  ONE ITEM 3 CARD PRECEEDS THE ITEM
C              4, 5, AND 6 CARDS OF EACH ISOTOPIC SPECIES.
C
  300 NISO = NISO + 1
      IF(NISO.GT.MAXISO) GO TO 1530
      READ(INDATA,9003,END=999) A,IISO(NISO),OUTISO(NISO),E,F,
     1 (TTLISO(I,NISO),I=1,3),
     2 TLISO(NISO),SFISO(NISO),WISO(NISO),WTISO,FLISO(NISO),FUISO(NISO)
C     REMOVE NEXT CARD WHEN SETTING UP ITERATIVE VERSION.
      F=BLANK
      IF(OUTISO(NISO).EQ.BLANK) OUTISO(NISO)=BRIEF
      IF(OUTISO(NISO).EQ.FALPH) OUTISO(NISO)=BLANK
```

```
      IF(IISO(NISO).GT.MAXF) GO TO 1542
      IF( IISO(NISO).EQ.0)  IISO(NISO)=1
      IF(SFISO(NISO).EQ.0.0) SFISO(NISO)=60.0
      IF( WISO(NISO).EQ.0.0)  WISO(NISO)=-0.05
      IF(FLISO(NISO) -  FUISO(NISO))  400,310,320
  310 FLISO(NISO) = -999999.9
      FUISO(NISO) =  999999.9
      GO TO 400
  320 X=FLISO(NISO)
      FLISO(NISO)=FUISO(NISO)
      FUISO(NISO)=X
C
C ITEM 4.   GROUP CHEMICAL SHIFTS.
C
  400 NG = NG + 1
      NGS=NGS+1
      IF(NGS.GT.MAXG) GO TO 1540
      READ(INDATA,9004,END=999) B,C,NUCG(NG),JOINCS(NG),CS(NG)
      IF(NUCG(NG).GT.1.AND. IISO(NISO).GT.1)GO TO 1541
      IF(NUCG(NG).EQ.0) NUCG(NG)=1
      ISOG(NG)=NISO
      IG(NGS)=IISO(NISO)
      FMAXG(NGS)=IG(NGS)*NUCG(NG)
      IF(FMAXG(NGS).GT.MAXF) GO TO 1542
      IF(C.NE.SYMSYM) GO TO 410
      KSYM=NG
      NSYM=NSYM+1
      SYMG(NG)=.TRUE.
      SYMGS(NGS)=.TRUE.
      NGS=NGS+1
      IF(NGS.GT.MAXG) GO TO 1540
      IG(NGS)=IISO(NISO)
      FMAXG(NGS)=IG(NGS)*NUCG(NG)
  410 IF(B.EQ.BLANK) GO TO 400
C
C ITEM 5.   PLOT REGION CARDS.  OPTIONAL.
C
  500 IF(OLD.EQ.PALPH) GO TO 510
      IF(E.EQ.BLANK) GO TO 600
  510 NREG=NREG+1
      IF(NREG.GT.MAXREG) GO TO 1550
      READ(INDATA,9005,END=999) B,KREG(NREG),J,(TTLREG(I,NREG),I=1,3),
     1 FLREG(NREG),FRREG(NREG), HSREG(NREG), VSREG(NREG),
     2 CLWREG(NREG),CRWREG(NREG)
      IF(OLD.EQ.PALPH) GO TO 520
      ISOREG(NREG)=NISO
      GO TO 530
  520 ISOREG(NREG) = J
  530 IF(B.EQ.BLANK) GO TO 510
C
C ITEM 6.:  OBSERVED TRANSITION CARDS.  OPTIONAL.
C
  600 IF(F.EQ.BLANK) GO TO 700
      IF( NTO.EQ.MAXTO     .OR.(.NOT.ITRAT)) GO TO 1563
  610 NTO=NTO+1
      IF(NTO.GT.MAXTO) GO TO 1564
      READ(INDATA,9006,END=999) B,TNO(NTO),TFO(NTO),TWT(NTO)
```

```
      IF(TWT(NTO).EQ.0.0) TWT(NTO) = WTISO
      IF(B.EQ.BLANK) GO TO 610
  700 IF(A.EQ.BLANK) GO TO 300
C
C
      IF(ITRAT .AND. NTO.EQ.0 ) GO TO 1570
      IF(NSYM-1) 1000,1571,710
  710 SYM=.TRUE.
C     PRINTING OF CURRENT PARAMETERS.
C
      ENTRY CSCC
 1000 WRITE(LINE,9100)
      J=0
      DO 1040 I=1,NG
      IF(ISOG(I).EQ.J) GO TO 1010
      J=ISOG(I)
      A = AHALF(IISO(J)+25)
      WRITE(LINE,9101) J,  (TTLISO(K,J),K=1,3), A,SFISO(J)
 1010 IF(SYMG(I)) GO TO 1020
      A=BLANK
      GO TO 1030
 1020 A=SYMSYM
 1030 PPM=CS(I)/SFISO(J)
      WRITE(LINE,9102) I,A,NUCG(I),JOINCS(I),CS(I),PPM
 1040 CONTINUE
      WRITE(LINE,9103)
      DO 1080 I=1,NG
      WRITE(LINE,9104)
      IF(CC(I,I).EQ.0.0) GO TO 1050
      WRITE(LINE,9104) I,I,JOINCC(I,I),CC(I,I)
 1050 IF(I.EQ.NG) GO TO 1080
      K=I+1
      DO 1070 J=K,NG
      IF(SYMG(I).AND.SYMG(J)) GO TO 1060
      IF(CC(I,J).EQ.0.0) GO TO 1070
      WRITE(LINE,9104) I,J,JOINCC(I,J),CC(I,J)
      GO TO 1070
 1060 IF(CC(I,J).EQ.0.0 .AND. CC(J,I).EQ.0.0) GO TO 1070
      WRITE(LINE,9105) I,J,J,I,JOINCC(I,J),JOINCC(J,I),CC(I,J),CC(J,I)
 1070 CONTINUE
 1080 CONTINUE
      GO TO 2000
C
C     ERROR HANDLING ROUTINES TO PRINT MESSAGES AND TAKE APPROPRIATE
C     ACTION WHEN SIMPLE ERRORS IN INPUT DATA HAVE BEEN FOUND.
C
 1510 WRITE(LINE,9510)
      GO TO 2000
 1520 WRITE(LINE,9520) A,I,J,K,X
      IF(OLD.EQ.BLANK) GO TO 1999
      IMOK = 0
      GO TO 2000
 1530 WRITE(LINE,9500) MAXISO,ERR30
      GO TO 1999
 1540 WRITE(LINE,9500) MAXG,ERR40
      GO TO 1999
 1541 A = AHALF( IISO(NISO) + 25 )
```

```
      WRITE(LINE,9541)NG,NUCG(NG),A
      GO TO 1999
 1542 WRITE(LINE,9542)MAXF
      GO TO 1999
 1550 WRITE(LINE,9500) MAXREG,ERR50
      IF(A.EQ.BLANK.OR.F.NE.BLANK)  GO TO 1999
      GO TO 1000
 1560 READ(INDATA,9006,END=999) B
 1561 IF(B.EQ.BLANK) GO TO 1560
      GO TO 700
 1563 WRITE(LINE,9560) NISO
      GO TO 1561
 1564 WRITE(LINE,9500) MAXTO,ERR64
      NTO=NTO-1
      GO TO 1561
 1570 WRITE(LINE,9570)
      ITRAT=.FALSE.
      GO TO 1000
 1571 NSYM=2*NUCG(KSYM)
      WRITE(LINE,9571) KSYM,NSYM
      GO TO 710
C
C     NORMAL COMPLETION OF PROGRAM REACHED ON END OF DATA
C
  999 IF(NCPL.EQ.0) GO TO 1970
      WRITE(LINE,9200) NCPL
      CALL PLOT(0.,0.,999)
C     REMOVE THIS BIT OF SYSTEM DEPENDENT CODING UP TO JUST BEFORE 1980.
 1970 CALL CREPLY(&1980)
C     TERMINAL RUNS END WITH A CALL TO MTS.  THIS PERMITS MODIFYING
C     THE SHIFTS AND COUPLING CONSTANTS IN THE DATA TEMPORARY FILE, THEN
C     RESTARTING THE PROGRAM AFTER THE CALL TO MTS, USING $RESTART.
      CALL MTS
      REWIND INDATA
      IMOK=0
      GO TO  2000
C     BATCH RUNS END WITH A NORMAL STOP.
 1980 STOP
C
C     ERROR FLAG IS SET BY SEVERAL ERROR EXITS
 1999 IMOK=-1
C     NORMAL RETURN STATEMENT
 2000 RETURN
 9001 FORMAT(7A1,18A4)
 9002 FORMAT(A1,I1,A1,I1,1X,I2,2X,F10.3,2F5.5,10X,2F10.0)
 9003 FORMAT(A1,I1,A1,1X,2A1,1X,3A4,4F5.3,2F10.3)
 9004 FORMAT(A1,    A2,I1,1X,I2,2X,F10.3)
 9005 FORMAT(A1,I1,1X,I1,3X,3A4,2F10.3,4F5.3)
 9006 FORMAT(A1,I6,2X,2F10.3)
 9100 FORMAT('0SPECIES                SPIN   MHZ.  GROUP SYM,SIZE SET  CHEM.S
     1HIFT          PPM.')
 9101 FORMAT(I5,2X,3A4,1X,A4,F7.2)
 9102 FORMAT(32X,I4,5X,A2,I1,I6,F12.2,F12.3)
 9103 FORMAT('0 GROUPS  SETS   NONZERO COUPLINGS')
 9104 FORMAT(3X,I1,'-',I1,I7,F15.3)
 9105 FORMAT(1X,I1,'-',I1,',',I1,'-',I1,I3,',',I2,F10.3,',',F9.3)
 9111 FORMAT(         '1CASE',I3,2X, 24A4/'0',A4,'ITERATIVE'/)
```

```
DEC 15. 1971    18:56.30                    NAME=INPUT

9200 FORMAT('0',I3,' CALCOMP PLOTS COMPLETED')
9500 FORMAT('0*** LIMIT IS',I5,1X,10A4)
9510 FORMAT(' ***CANCELLED BY PREVIOUS ERROR')
9520 FORMAT(' ***GROUP INDEX ERROR /',A1,I1,1X,I1,1X,I2,2X,F10.3)
9541 FORMAT(' ***GROUP',I3,' HAS',I3,' NUCLEI OF SPIN',A4)
9542 FORMAT('0*** LIMIT IS SPIN',I2)
9550 FORMAT(' ***SPECIES',I3,' OBSERVED TRANSITIONS IGNORED')
9570 FORMAT('0***CHANGED TO NON-ITERATIVE (N) OBSERVED TRANSITIONS)')
9571 FORMAT('0*** PAIR',I3,' IS',I3,' MAGNETICALLY EQUIVALENT NUCLEI')
     END

 NUMBER OF CARDS READ:   352
18:5.32 .778 RC=0
```

```
DEC  6. 1971    23:40.02                    NAME=BASIS

      SUBROUTINE BASIS
C
C     REVISED DECEMBER 1971
C
C**********************************************************************
C
C     SUBROUTINE TO CREATE BASIS FUNCTIONS.
C     THE QUANTUM NUMBERS NECESSARY TO COMPLETELY DEFINE EACH BASIS
C     FUNCTION ARE WRITTEN ON AN INTERMEDIATE STORAGE DEVICE FOR LATER
C     USE IN HAMILTONIAN MATRIX GENERATION AND TRANSITION CALCULATIONS.
C
C**********************************************************************
C
C**********************************************************************
C
C**** IMPORTANT **************
C
C     ALL SPIN VARIABLES ARE REPRESENTED THROUGHOUT THIS SUBROUTINE BY
C     INTEGERS EQUAL TO TWICE THE ACTUAL VALUE OF THE QUANTUM NUMBERS.
C     FOR EXAMPLE, 1/2 IS REPRESENTED BY 1, AND -3 BY -6 .
C     IF 2 IS SUBTRACTED FROM SUCH A NUMBER IT CORRESPONDS TO A DECREASE
C     OF 1 IN THE ACTUAL QUANTUM NUMBER REPRESENTED.
C
C**********************************************************************
      COMMON BAF(9,9),TITLE(24),INOK,OLD,SYM,ITRAT,NCASE,NCPL,
     .LCSCC,AHALF(49),ABLANK,ANOT,ANTI,INFIN,BRIEF,NM2,OLDH,
     $LINE,INDATA,PUNCH,QUANT,TFI,EU,OTPL,
     . MAXF,MAXM43,MAXE4,MAXE3,MAXU3,MAXE2,MAXI,
     $MAXG,NG,SYMG(9),ISOG(9),NUCG(9),
     .NGS,SYMGS(9),IG(9),FMAXG(9),/GPB(9),
     $CC(9,9),JOINCC(9,9),CS(9),JOINCS(9),
     .MAXISO,NISO,TTLISO(3,9),IISO(9),MISOPA(9),MISOPB(9),NTISO(9),KM2P,
     .TIISO(9), OUTISO(9),NISO(9),TLISO(9),SFISO(9),FLISO(9),FUISO(9),
     $MAXREG,NREG,ISOREG(9),TTLREG(3,9),FLREG(9),FRREG(9),KREG(9),
     . HSREG(9), VSREG(9),CLWREG(9),CRWREG(9)
      LOGICAL OLDH,     SYM,SYMG,SYMGS,ITRAT,LCSCC
      INTEGER FMAXG,AGPB,      PUNCH,QUANT,EU,TFI,OTPL
      REAL*8 BAF
C
      COMMON/ACOM/  SG(9),F2G(9),AMAXG(9),AG(9),LGSISO(9),
     .LE43(60),MISO43(60),MP43A(60),NE43A(60),KTISO(9),
     .MG(9,1200),MTOT(1200),MISOP(1200),AGP(1200)
      LOGICAL SG,SYM2
      INTEGER APACK,F2G,AG,AMAXG,S2,SA
      INTEGER*2 MG,MTOT,MISOP,AGP,LE43,MISO43,MP43A,NE43A
      DIMENSION NFGW(5,7)
      DATA NFGW / 2,1,1,1,1, 2,3,1,1,1, 5,4,1,1,1, 5,9,5,1,1,
     *  14,14,6,1,1, 14,28,20,7,1, 42,48,27,8,1 /
C**********************************************************************
C
C     INITIALIZE PARAMETERS.
C
C**********************************************************************
      REWIND QUANT
      DO 20 ISO=1,NISO
   20 NTISO(ISO)=0
C
```

```
C     THE ORIGINAL GROUP NUMBERING USED FOR INPUT IS EXPANDED WITHIN
C     THE PROGRAM WHENEVER THERE ARE SYMMETRY-EQUIVALENT PAIRS.
C     EACH GROUP FLAGGED IN SYMG BECOMES AN ADJACENT PAIR OF GROUPS WITH
C     THE FIRST FLAGGED IN SYMGS.  WHERE THERE COULD BE CONFUSION THE
C     SUFFIX 'S' SHOWS A VALUE IN THE EXPANDED NUMBERING.  MOST QUANTUM
C     NUMBERS REFER ONLY TO THE EXPANDED SET OF GROUPS. SO HAVE NO 'S'.
C     IF THERE IS NO CHEMICAL EQUIVALENCE (TWOFOLD SYMMETRY) SPECIFIED.
C     THE EXPANDED NUMBERING IS THE SAME AS THE ORIGINAL NUMBERING.
C
C
C     CREATE VECTORS USED TO PACK AND UNPACK ISOTOPIC SPECIES TOTAL SPIN
C     IN A MULTI-BASE NUMBER SYSTEM.
C
      I=0
      J=0
      K=0
  210 I=I+1
      MISOPA(I)=0
  220 J=J+1
  230 K=K+1
      MISOPA(I)=MISOPA(I)+FMAXG(K)
      IF(SYMGS(K)) GO TO 230
      LGSISO(I)=K
      IF(J.GE.NG) GO TO 240
      IF(ISOG(J).EQ.ISOG(J+1)) GO TO 220
      GO TO 210
  240 N=1
      I=NISO
  250 MISOPB(I)=N
      J=1+2*MISOPA(I)
      IF(N.GT. INFIN/J) GO TO 8010
      N=N*J
      I=I-1
      IF(I.GT.0) GO TO 250
      KM2P=N
C
C     SIMILAR PACKING VECTORS FOR THE GROUP  A  VALUES.
C
      N=1
      I=NGS
  260 AGPB(I)=N
      J=1+FMAXG(I)
      IF(SYMGS(I))J=J+FMAXG(I)
      IF(N.GT. INFIN/J) GO TO 8010
      N=N*J
      I=I-1
      IF(I.GT.0) GO TO 260
      NM2=0
      DO 990 I=1.NGS
  990 F2G(I)=FMAXG(I)
      IF(IG(1).EQ.1) F2G(1)=F2G(1)+2
C***********************************************************************
C
C     START OF A NEW MATRIX(2) DEFINED BY A SET OF F VALUES.
C
C***********************************************************************
 1000 KF=1
```

```
 1010 IF(IG(KF).GT.1) GO TO 1015
      F2G(KF)=F2G(KF)-2
      IF(F2G(KF).GE.0) GO TO 1020
      F2G(KF)=FMAXG(KF)
 1015 KF=KF+1
      IF(KF.LE.NGS) GO TO 1010
C
C     NORMAL RETURN WHEN THE LAST MATRIX(2) IS COMPLETE.
C
      IF(KM2P.GT.INFIN/NM2) GO TO 8010
      IMOK=1
      GO TC 2000
C
C     IF BOTH MEMBERS OF EACH PAIR OF SYMMETRY EQUIVALENT GROUPS HAVE
C     THE SAME F VALUES. THIS 'MATRIX(2)' IS IN FACT A SYMMETRIC/ANTISYM
C     PAIR OF MATRICES(2) EACH OF WHICH WILL BE GENERATED SEPARATELY.
C     IF THE MOLECULE HAS SYMMETRY BUT THIS MATRIX(2) DOES NOT. IT MUST
C     BE CNE OF AN IDENTICAL PAIR CF MATRICES.  TO SAVE TIME THE FIRST
C     IS GIVEN DOUBLE WEIGHT IN THE TRANSITION CALCULATIONS AND THE
C     SECOND IS IGNORED.
C
 1020 SYM2=.FALSE.
      IF(.NOT.SYM) GO TO 1100
      I=-1
 1030 I=I+1
 1040 I=I+1
      IF(I.GT.NGS) GO TO 1060
      IF(.NOT.SYMGS(I)) GO TO 1040
      IF(F2G(I)-F2G(I+1)) 1050.1030.1000
 1050 KW=2
      GO TO 1110
 1060 SYM2=.TRUE.
C
C     CALCULATE THE WEIGHTING FACTCR FOR TRANSITIONS FROM THIS MATRIX(2)
C
 1100 KW=1
 1110 DO 1120 I=1.NGS
      IF(IG(I).GT.1) GO TO 1120
      J=FMAXG(I)-2
      IF(J.LE.0) GO TO 1120
      K=1+F2G(I)/2
      KW=KW*NFGW(K.J)
 1120 CCNTINUE
      W2=KW
      I=1
 1160 IF(SYM2.AND.SYMGS(I)) GO TO 1170
      AMAXG(I)=F2G(I)
      GO TO 1180
 1170 AMAXG(I)=2*F2G(I)
      I=I+1
      AMAXG(I)=0
 1180 I=I+1
      IF(I.LE.NGS) GO TO 1160
      S2=1
 1190 DO 1195 I=1.NGS
      AG(I)=AMAXG(I)
 1195 SG(I)=SYMGS(I)
```

```
      NE2=0
      N=1
      IF(SYM2) GO TO 1450
C*************************************************************************
C
C     CALCULATIONS BASED ON A SET OF A VALUES BEGIN HERE.  IF THIS
C     MATRIX(2) HAS NO SYMMETRY, THE A VALUES ARE IDENTICAL TO THE F
C     VALUES DEFINING THE MATRIX(2), SO REMAIN CONSTANT.
C     FOR A SYMMETRIC OR ANTISYMMETRIC MATRIX(2), THE A VALUE FOR EACH
C     SYMMETRY PAIR OF GROUPS IS KEPT IN THE FIRST GROUP POSITION, AND
C     CAN RANGE FROM THE SUM OF THE F VALUES TO ZERO.  THE A VALUE FOR
C     THE SECOND MEMBER OF EACH PAIR IS SET TO ZERO.
C     THE MG VALUES OF ANY GROUP ALWAYS RANGE FROM +AG TO -AG.
C
C*************************************************************************
C
C
C     CHECK THAT THIS MATRIX(2) IS NOT TOO LARGE.
C
 1200 K=1
      DO 1210 I=1.NGS
 1210 K=K*(AG(I)+1)
      IF(N+K.GT.MAXE2)  GO TO 8020
      APACK=0
      DO 1260 I=1.NGS
 1260 APACK=APACK+AG(I)*AGPB(I)
      DO 1280 I=1.NGS
 1280 MG(I.N)=AG(I)
C
C     PACK THE SPECIES TOTAL M VALUES FOR THIS BASIS FUNCTION, THEN TRY
C     TO GENERATE MORE BASIS FUNCTIONS WITHIN THE FSUM LIMITS.
C
 1300 NE2=N
      MPACK=0
      MTOT(NE2)=0
      K=1
      DO 1320 ISO=1,NISO
      L=LGSISC(ISO)
      M=0
      DO 1310 J=K.L
 1310 M=M+MG(J.NE2)
      MPACK=MPACK+MISOPB(ISO)*(M+MISOPA(ISO))
      MTOT(NE2)=MTOT(NE2)+M
      K=L+1
 1320 CONTINUE
      MISOP(NE2)=MPACK
      AGP(NE2)=APACK
      N=NE2+1
      DO 1330 I=1.NGS
      MG(I,N)=MG(I,NE2)
 1330 CONTINUE
      KM=1
 1340 MG(KM,N)=MG(KM,N)-2
      IF(MG(KM.N)+AG(KM).GE.0) GO TO 1300
      MG(KM.N)=AG(KM)
      KM=KM+1
      IF(KM.LE.NGS) GO TO 1340
```

```
      IF (.NOT.SYM2) GO TO 1500
C*************************************************************************
C
C     THIS SECTION IS USED ONLY WHEN A SYMMETRIC/ANTISYMMETRIC PAIR OF
C     MATRICES(2) IS BEING GENERATED.  EACH SYMMETRY-FLAGGED GROUP CAN
C     HAVE  A   VALUES DOWN TO ZERO, CORRESPONDING ALTERNATELY TO SYM.
C     AND ANTISYM. STATES FOR THAT GROUP.
C
C     S2 HAS BEEN SET TO +1 FOR THE SYMMETRIC MATRIX(2) OF THE PAIR, OR
C     -1 FOR THE ANTISYMMETRIC MATRIX.  THIS SET OF A VALUES BELONGS TO
C     THE CURRENT MATRIX(2) IF ITS SYMMETRY, REPRESENTED BY SA, MATCHES.
C
C*************************************************************************
 1400 K=0
 1410 K=K+1
      IF(K.GT.NGS) GO TO 1500
      IF(.NOT.SYMGS(K)) GO TO 1410
      AG(K)=AG(K)-2
      IF(AG(K).GE.0) GO TO 1420
      AG(K)=AMAXG(K)
      SG(K)=.TRUE.
      GO TO 1410
 1420 SG(K)=.NOT.SG(K)
 1450 SA=1
      DO 1460 I=1.NGS
      IF(SYMGS(I).AND.(.NOT.SG(I)))  SA=-SA
 1460 CONTINUE
      IF(SA.NE.S2) GO TO 1400
      N=NE2+1
      GO TO 1200
C*************************************************************************
C
C     ALL MATRICES(2) CONVERGE HERE TO BE SORTED FIRST ON TOTAL SPIN
C     INTO MATRICES(3) AND WITHIN THEM ON SPECIES TOTAL SPIN (PACKED)
C     INTO MATRICES(4).
C
C*************************************************************************
C
C     THIS IS A SINGLE STAGE SORT FOR MATRICES(3) AND MATRICES(4).
C     FIND A BASIS FUNCTION WITH THE LARGEST MTOT VALUE.  IF THERE ARE
C     SEVERAL, FIND THE ONE WITH THE LARGEST PACKED MISO VALUE.  IT AND
C     OTHERS LIKE IT ARE IN THE SAME MATRIX(4) OF THE SAME MATRIX(3).
C     BRING IT TO THE TOP, THEN REPEAT WITH WHAT REMAINS OF THE LIST.
C
 1500 KSTART=1
      KSTOP=NE2
      KA=KSTART
      NM32=0
      L=-10000
 1510 M=-10000
      DO 1540 I=KA,KSTOP
      IF(M-MTOT(I)) 1530,1520,1540
 1520 IF(MISOP(KB).GE.MISOP(I))GO TO 1540
 1530 KB=I
      M=MTOT(I)
 1540 CONTINUE
      IF(L.NE.M) NM32=NM32+1
```

```
      L=M
      IF(KB.EQ.KA) GC TO 1560
C
C     SWAP.  THE BASIS FUNCTION THAT BELONGS AT THE TOP OF THE REMAINING
C     LIST IS MOVED THERE. AND THE BASIS FUNCTION THAT WAS THERE IS
C     MOVED DCWN TO REPLACE IT.
C
      DO 1550 I=1.NGS
      M=MG(I.KA)
      MG(I.KA)=MG(I.KB)
      MG(I.KB)=M
 1550 CONTINUE
      M=MTOT(KA)
      MTOT(KA)=MTOT(KB)
      MTOT(KB)=M
      M=AGP(KA)
      AGP(KA)=AGP(KB)
      AGP(KB)=M
      M=MISOP(KA)
      MISOP(KA)=MISOP(KB)
      MISOF(KB)=M
C
C     SWAP CCMPLETE.
C
 1560 KA=KA+1
      IF(KA.LE.KSTOP) GO TO 1510
C
C     SORT COMPLETE.
C
C
C     THE SORTED MATRIX(2) IS WRITTEN ON THE INTERMEDIATE STORAGE DEVICE
C     IN MATRIX(3) BLCCKS.  THE VECTOR LE43 KEEPS TRACK OF MATRIX(4)
C     BCUNDARIES. AND MISO43 HOLDS THEIR PACKED SPECIES M TOTALS.
C
 1600 IF(NM32.LT.2) GC TO 1700
      NM2=NM2+1
      N=KSTOP-KSTART+1
      WRITE(QUANT) NM2.N.NM32.W2.SYM2.AMAXG
      MTOT (NE2+1)=-10000
      MISCP(NE2+1)=-10000
      K=KSTART
      MP=MISOP(K)
      NE4=1
      KM32=0
 1610 NE3=0
      NU3=0
      NM43=0
      M=MTCT(K)
      KA=K
 1620 NE3=NE3+1
      K=K+1
      IF(MP.EQ.MISOP(K)) GC TO 1640
      NM43=NM43+1
      IF(NM43.GT.MAXM43) GC TO 8030
      IF(NE4.GT.MAXE4) GO TO 8040
      LE43(NM43)=NE3
      NU3=NU3+NE4*NE4
```

```
      MISO43(NM43)=MP
      MP=MISOP(K)
      NE4=0
 1640 NE4=NE4+1
      IF(M.EQ.MTOT(K)) GO TO 1620
 1650 KM32=KM32+1
      IF(NU3.GT.MAXU3) GO TO 8050
      IF(NE3.GT.MAXE3) GO TO 8060
      KB=K-1
      WRITE(QUANT)KM32.M.NM43.NE3.(LE43(I).MISO43(I).I=1.NM43).
     1                           (AGP(J).J=KA.KB).((MG(I.J).I=1.NGS).J=KA.KB)
      IF(KM32.EQ.1) GC TO 1680
      J=0
      DO 1670 KB=1.NM43
      NE4B=LE43(KB)-J
      J=LE43(KB)
      MPB=MISO43(KB)
      DO 1670 ISO=1.NISO
      MPDIF=2*MISOPB(ISO)
      DO 1660 KA=1.NM43A
      IF(MP43A(KA)-MPB.EQ.MPDIF) NTISC(ISO)=NTISO(ISO)+NE43A(KA)*NE4B
 1660 CONTINUL
 1670 CONTINUE
 168C J=0
      NM43A=NM43
      DO 1690 KA=1.NM43A
      NE43A(KA)=LE43(KA)-J
      J=LE43(KA)
      MP43A(KA)=MISO43(KA)
 1690 CONTINUE
      IF(KM32.LT.NM32) GO TO 1610
 1700 IF(SYM2.AND.   S2.EQ.1) GO TO 1710
      GO TO 1000
C
C     AFTER THE SYMMETRIC MATRIX(2) OF A PAIR HAS BEEN WRITTEN THE
C     ANTISYMMETRIC ONE IS GIVEN THE SAME TREATMENT.
C
 1710 S2=-1
      GO TO 1190
C
C     PRINT THEORETICAL LIMITS ON TRANSITIONS.
C
 2000 N=0
      K=1
      KA=1
      DO 2050 ISO=1.NISO
      M=N+1
      N=LGSISO(ISO)
      I=IISO(ISO)
      KB=0
      DO 2030 L=M.N
      KA=KA*((I+1)**NUCG(K))
      KB=KB+NUCG(K)*I*(I+2)
      IF(SYMGS(L)) GO TO 2030
      K=K+1
 2030 CONTINUE
      KTISO(ISO)=KB
```

```
 2050 CONTINUE
      DO 2070 ISO=1.NISO
      KTISO(ISO)=(KTISO(ISO)*KA)/6
      IF(TLISO(ISO).EQ.0.0) TLISO(ISO)=0.0001*FLOAT(KTISO(ISO))
 2070 CONTINUE
      WRITE(LINE.9000) (ISO.NTISO(ISO).KTISO(ISO).ISO=1.NISO)
      GO TO 9999
C*********************************************************************
C
C     ERROR MESSAGE EXITS.
C
C*********************************************************************
C
C
C     UNLESS THE COMPUTER HAS A VERY SMALL INTEGER WORD LENGTH THE NEXT
C     EXIT SHOULD NEVER BE TAKEN.
C
 8010 WRITE(LINE.9510)
      GO TO 9998
 8020 K=2
      WRITE(LINE.9520)MAXE2.K
      GO TO 9998
 8030 WRITE(LINE.9530) MAXM43
      GO TO 9998
 8040 K=4
      WRITE(LINE.9520) MAXE4.K
      GO TO 9998
C
C     LATER IN THE PROGRAM THE EIGENVECTOR ELEMENTS FOR ALL THE
C     MATRICES(4) OF EACH MATRIX(3) ARE STORED AS A VECTOR.  THE SUM OF
C     SQUARES OF THE MATRIX(4) SIZES MUST NOT EXCEED THE VECTOR LENGTH.
C
 8050 WRITE(LINE.9550) MAXU3
      GO TO 9998
 8060 K=3
      WRITE(LINE.9520)MAXE3.K
 9998 IMOK=-1
 9999 RETURN
 9000 FORMAT('OSPECIES'.I2.'. UP TO'.I7.' TRANSITIONS. INTENSITY'.I7)
 9510 FORMAT('0*** INTERNAL PACKING OVERFLOW')
 9520 FORMAT('0*** LIMIT IS'.I5.' LEVELS IN A MATRIX('.I1.')')
 9530 FORMAT('0*** LIMIT IS'.I4.' MATRICES(4) IN A MATRIX(3)')
 9550 FORMAT('0*** LIMIT IS'.I5.' EIGENVECTOR ELEMENTS IN A MATRIX(3)')
      END
```

```
      SUBROUTINE HAMIL
C
C     REVISED DECEMBER 1971
C
C     GENERATES AND DIAGONALIZES THE HAMILTONIAN
      REAL*8 DBLE.DSQRT
      COMMON BAF(9.9).TITLE(24).IMCK.OLD.SYM.ITRAT.NCASE.NCPL.
     .LCSCC.AHALF(49).ABLANK.ANOT.ANTI.INFIN.BRIEF.NM2.OLDH.
     $LINE.INDATA.PUNCH.QUANT.TFI.EU.OTPL.
     . MAXF.MAXM43.MAXE4.MAXE3.MAXL3.MAXE2.MAXT.
     $MAXG.NG.SYMG(9).ISOG(9).NUCG(9).
     .NGS.SYMGS(9).IG(9).FMAXG(9).AGPB(9).
     $CC(9.9).JOINCC(9.9).CS(9).JOINCS(9).
     .MAXISO.NISO.TTLISO(3.9).IISO(9).MISOPA(9).MISOPB(9).NTISO(9).KM2P.
     .IIISO(9). OUIISO(9).WISO(9).TLISO(9).SFISO(9).FLISO(9).FUISO(9).
     $MAXREG.NREG.ISCREG(9).TTLREG(3.9).FLREG(9).FRREG(9).KREG(9).
     . HSREG(9). VSREG(9).CLWREG(9).CRWREG(9)
      LOGICAL OLDH.     SYM.SYMG.SYMGS.ITRAT.LCSCC
      INTEGER FMAXG.AGPB.      PUNCH.QUANT.EU.TFI.OTPL
      REAL*8 BAF
C
      COMMON/ACOM/ SHIFT(9).COUPLE(9.9).DJ(42).DK(42).DH(42.42).
     . AGJ(9).AMAXG(9).ALPHA(10).
     .LE43(60).MISO43(60).
     .AGP(150).MG(9.150).EJ(150).U3(2322)
      REAL*8 SHIFT.COUPLE.DJ.DK.DH.HH.DSIGN.DFACTS
      INTEGER APJ.AQJ.AA.AI.AQ.AR.AMAXG.AGJ
      INTEGER*2 MG.AGP.LE43.MISO43
      LOGICAL SYMCC.SYM2
      REAL EALPH/'E'/
      BRTEMP=BRIEF
      IF(BRIEF.EQ.EALPH)  BRIEF=ABLANK
      REWIND QUANT
      REWIND EU
      KTN=1
      K=MAXG+1
      DO 10 J=1.K
   10 ALPHA(J)=ABLANK
      J=0
      DO 100 I=1.NGS
      J=J+1
      SHIFT(I)=CS(J)
      IF(SYMGS(I)) J=J-1
      DO 90 L=1.NGS
   90 COUPLE(L.I)=0.D0
  100 CONTINUE
      J=0
      L=-1
  210 L=L+1
  220 J=J+1
      IF(J.GT.NG) GO TO 300
      L=L+1
      I=1
      K=0
      IF(SYMG(J)) GO TO 240
  230 K=K+1
      COUPLE(K.L)=CC(I.J)
```

```
      IF(SYMGS(K)) GO TO 230
      I=I+1
      IF(I.LT.J) GO TO 230
      GO TO 220
  240 IF(SYMG(I)) GO TO 270
  250 K=K+1
      COUPLE(K.L)=CC(I.J)
      COUPLE(K.L+1)=CC(I.J)
  260 I=I+1
      IF(I-J) 240.250.210
  270 IF(I.EQ.J) GO TO 250
      K=K+1
      COUPLE(L.K)=0.5D0*(DBLE(CC(I.J))-DBLE(CC(J.I)))
      COUPLE(K.L)=CC(I.J)
      COUPLE(K.L+1)=CC(J.I)
      K=K+1
      COUPLE(K.L)=CC(J.I)
      COUPLE(K.L+1)=CC(I.J)
      GO TO 260
  300 SYMCC=.FALSE.
      APJ=-1
 1000 READ(QUANT) KM2.NE2.NM32.W2.SYM2.AMAXG
      IF(SYM2) GO TO 1010
      ALPHA(1)=ANOT
      IF(SYMCC) GO TO 1030
      GO TO 1C80
 1010 IF(SYMCC) GO TO 1020
      ALPHA(1)=ABLANK
      GO TO 1C30
 1020 IF(ALPHA(1).EQ.ANTI) GO TO 1025
      ALPHA(1)=ANTI
      GO TO 1080
 1025 ALPHA(1)=ABLANK
      GO TC 1080
 1030 J=0
      DO 1070 L=1.NG
      J=J+1
      IF(.NOT.SYMG(L)) GO TO 107C
      I=0
      DO 1C60 K=1.L
      I=I+1
      IF(.NOT.SYMG(K)) GO TO 1060
      IF(I.EQ.J) GO TO 1050
      IF(SYM2) GO TO 1040
      COUPLE(I.J)=CC(K.L)
      GO TO 1050
 1040 COUPLE(I.J)=.5D0*(DBLE(CC(K.L))+DBLE(CC(L.K)))
 1050 I=I+1
 1060 CONTINUE
      J=J+1
 1070 CONTINUE
      SYMCC=.NOT.SYMCC
 1080 IF(BRIEF.NE.ABLANK) GO TO 1100
      J=1
      I=1
 1090 J=J+1
      ALPHA(J)=AHALF(AMAXG(I)+25)
```

```
      IF(SYM2.AND.SYMGS(I)) I=I+1
      I=I+1
      IF(I.LE.NGS) GO TO 1090
      WRITE(LINE.9000) KM2.ALPHA.W2.NCASE.TITLE
 1100 READ (QUANT)KM32.M.NM43.NE3.(LE43(I).MISO43(I).I=1.NM43).
     1                       (AGP(J).J=1.NE3).((MG(I.J).I=1.NGS).J=1.NE3)
      NU3=0
      KM43=1
      N=0
      IF(BRIEF.EQ.ABLANK) WRITE(LINE.9001) KM32
 1200 M=N+1
      N=LE43(KM43)
      JJ=0
      DO 2000 J=M.N
      JJ=JJ+1
      IF(APJ.EQ.AGP(J)) GO TO 1220
      APJ=AGP(J)
      AA=APJ
      DO 1210 KG=1.NGS
      AGJ(KG)=AA/AGPB(KG)
      AA=AA-AGJ(KG)*AGPB(KG)
 1210 CONTINUE
 1220 II=0
      DO 1950 I=M.J
      II=II+1
      HH=0.D0
      IF(I.EQ.J) GC TO 1800
      IF(AGP(I).NE.AGP(J)) GO TO 1400
      KDIF=-2
      DO 1330 KG=1.NGS
      MM=MG(KG.I)-MG(KG.J)
      IF(MM.EQ.0) GO TO 1330
      IF(IABS(MM).GT.2) GO TO 1900
      KDIF=KDIF+1
      IF(KDIF) 1310.1320.1900
 1310 KQ=KG
 1320 KR=KG
 1330 CONTINUE
      HH=(AGJ(KQ)*(AGJ(KQ)+2)-MG(KQ.I)*MG(KQ.J))
     1  *(AGJ(KR)*(AGJ(KR)+2)-MG(KR.I)*MG(KR.J))
      HH=0.125D0*DSQRT(HH)*COUPLE(KQ.KR)
      GO TC 1900
 1400 KDIF=-2
      AA=AGP(I)
      DO 1450 KG=1.NGS
      AI=AA/AGPB(KG)
      IF(AI.EQ.AGJ(KG)) GO TO 1430
      IF(IABS(AI-AGJ(KG)).GT.2) GO TO 1900
      MM=MG(KG.I)-MG(KG.J)
      IF(IABS(MM).GT.2) GO TO 1900
      KDIF=KDIF+1
      IF(KDIF) 1410.1420.1900
 1410 KQ=KG
      AQ=AI
      MQ=MG(KG.I)
      GO TC 1440
 1420 KR=KG
```

```
      AR=AI
      MR=MG(KG,I)
      GO TO 1440
1430 IF(MG(KG,I).NE.MG(KG,J)) GO TO 1900
1440 AA=AA-AI*AGPB(KG)
1450 CONTINUE
      DSIGN=0.5D0
      IF(AQ.GT.AGJ(KQ)) GO TO 1520
      AQ=AGJ(KQ)
      MQ=MG(KQ,J)
      IF(MM.LE.0) GO TO 1530
1510 DSIGN=-DSIGN
      MQ=-MQ
      GO TO 1530
1520 IF(MM.LT.0) GO TO 1510
1530 IF(AR.GT.AGJ(KR)) GO TO 1550
      AR=AGJ(KR)
      MR=MG(KF,J)
      IF(MM.GE.0) GO TO 1560
1540 DSIGN=-DSIGN
      MR=-MR
      GO TO 1560
1550 IF(MM.GT.0) GO TO 1540
1560 DFACTS=BAF(AMAXG(KC)/2,AQ/2)*BAF(AMAXG(KR)/2,AR/2)
      IF(MM.NE.0) GO TO 1570
      HH=(AQ*AC-MG*MQ)*(AR*AR-MR*MR)
      HH=DSQRT(HH*DFACTS)*COUPLE(KF,KQ)
      GO TO 1900
1570 HH=(AQ-MQ)*(AQ-MG-2)*(AR-MR)*(AR-MR-2)
      HH=DSIGN*DSQRT(HH*DFACTS)*CCUPLE(KR,KQ)
      GO TO 1900
1800 DO 1830 LG=1,NGS
      DO 1820 KG=1,LG
      IF(KG.NE.LG) GC TO 1810
      DFACTS=MG(LG,I)
      HH=HH+0.5D0*SHIFT(LG)*DFACTS
      IF(.NCT.(SYM2.AND.SYMGS(LG))) GO TO 1820
      DFACTS=AGJ(LG)*(AGJ(LG)+2)
      HH=HH+0.125D0*COUPLE(LG,LG)*DFACTS
      GO TO 1820
1810 DFACTS=MG(KG,I)*MG(LG,I)
      HH=HH+0.25D0*COUPLE(KG,LG)*DFACTS
1820 CONTINUE
1830 CONTINUE
1900 DH(II,JJ)=HH
      DH(JJ,II)=HH
1950 CONTINUE
2000 CONTINUE
      NE4=N-M+1
      CALL HSHLDR(MAXE4,NE4,DH,DJ,DK,IERR)
      IF(IERR.NE.0) GO TO 3000
      J=0
      DO 2010 I=M,N
      J=J+1
      E3(I)=DJ(J)
2010 CONTINUE
      DO 2030 J=1,NE4
```

```
      DO 2020 I=1,NE4
      NU3=NU3+1
      U3(NU3)=DH(I,J)
2020 CONTINUE
2030 CONTINUE
      IF(BRIEF.NE.ABLANK) GO TO 2100
      DO 2040 J=3,7
2040 ALPHA(J)=ABLANK
      L=MISO43(KM43)
      J=1
      DO 2050 I=1,NISO
      J=J+1
      K=L/MISOPB(I)
      ALPHA(J)=AHALF(K+25-MISOPA(I))
      L=L-K*MISOPB(I)
2050 CONTINUE
      WRITE(LINE,9002) KM43,(ALPHA(I),I=2,7),(E3(I),I=M,N)
2100 KM43=KM43+1
      IF(KM43.LE.NM43) GO TO 1200
      WRITE(CU)    NU3,(E3(I),I=1,NE3),(U3(I),I=1,NU3)
      IF(KM32.LT.NM32) GO TO 1100
      IF(KM2.LT.NM2) GO TO 1000
      IF(KTN.GT.INFIN) GO TO 3010
2999 BRIEF=BRTEMP
      RETURN
3000 WRITE(LINE,9500) KM2,KM32,KM43,IERR
      IMOK=-1
      GO TO 2999
3010 WRITE(LINE,9501) INFIN
      IMOK=-1
      GO TO 2999
9000 FORMAT('1MATRIX(2)',I3,',  ',A4,'SYMMETRIC.  GROUP  A  LIMITS',
    19A4,' WEIGHT',F4.0,      / '0CASE',I3,1X,24A4/
    2'0MATRIX(3) MATRIX(4) ISOTCPIC SPECIES Z-SPINS     ENERGY LEVELS')
9001 FORMAT('0',I5)
9002 FORMAT(I16,4X,6A5,5F11.3/(50X,5F11.3))
9500 FORMAT('0*** DIAGCNALIZATION FAILED.  M(2,3,4),LEVEL =',4I4)
9501 FORMAT('0*** TRANSITION NUMBER OVER',I8)
      END
```

```
      SUBROUTINE TRANS
C
C     REVISED DECEMBER 1971
C
C     CALCULATES TRANSITIONS FOR ALL SPECIES AND STORES THEM ON DISK.
      COMMON BAF(9.9).TITLE(24).INCK.OLD.SYM.ITRAT.NCASE.NCPL.
     .LCSCC.AHALF(49).ABLANK.ANOT.ANTI.INFIN.BRIEF.NM2.OLDH.
     $LINE.INDATA.PUNCH.QUANT.TFI.EU.OTPL.
     . MAXF.MAXM43.MAXE4.MAXE3.MAXU3.MAXE2.MAXT.
     $MAXG.NG.SYMG(9).ISOG(9).NUCG(9).
     .NGS.SYMGS(9).IG(9).FMAXG(9).AGPB(9).
     $CC(9.9).JOINCC(9.9).CS(9).JOINCS(9).
     .MAXISO.NISO.TTLISO(3.9).IISO(9).MISOPA(9).MISOPB(9).NTISO(9).KM2P.
     .TIISC(9). CUTISO(9).WISO(9).TLISC(9).SFISO(9).FLISO(9).FUISO(9).
     $MAXREG.NREG.ISOREG(9).TTLREG(3.9).FLREG(9).FRREG(9).KREG(9).
     . HSWEG(9). VSREG(9).CLWREG(9).CRWREG(9)
      LOGICAL OLDH.     SYM.SYNG.SYMGS.ITRAT.LCSCC
      INTEGER FMAXG.AGPB.      PUNCH.QUANT.EU.TFI.OTPL
      REAL*8 BAF
C
      COMMON/ACOM/ AG(9).MGA(9). MISO43(60.2).LE43(60.2).  T44(42).
     .TNC(100).TFC(100).TIC(100).TMISO(100).TKEYS(4.100).
     .E3(150.2).AGP(150.2).MG(9.150.2).U3(2322.2).TUB(42.42)
      INTEGER*2 LE43.MISO43.MG.AGP.MGA.AG.TMISO.    TKEYS
      INTEGER TNC
      INTEGER APACKA
      REAL KALPH/'K'/
      BRTEMP=BRIEF
      IF(BRIEF.EQ.KALPH) BRIEF = ABLANK
      REWIND QUANT
      REWIND EU
      REWIND TFI
      KZERO=0
      MAXNT=100
      NT=0
      KTN=0
      TITOT=0.0
      DO 10 ISO=1.MAXISO
      NTISC(ISO) = 0
      TIISC(ISO)=0.0
   10 CONTINUE
      IF(BRIEF.EQ.ABLANK) WRITE(LINE.9000) NCASE.TITLE
 1000 READ(QUANT) KM2.NE2.NM32.W2.SYM2.AMAXG
      IF(BRIEF.EQ.ABLANK) WRITE(LINE.9001) KM2
      WRITE(TFI) KZERO.KM2
      M3B=1
      GO TC 1110
 1100 M3A=M3B
      M3B=3-M3B
      NM43A=NM43B
      NE3A=NE3B
      NU3A=NU3B
 1110 READ(QUANT) KM32.M.NM43B.NE3B.
     1(LE43(I.M3B).MISO43(I.M3B).I=1.NM43B).(AGP(J.M3B).J=1.NE3B).
     2((MG(I.J.M3B).I=1.NGS).J=1.NE3B)
      READ(EU) NU3B.(E3(I.M3B).I=1.NE3B).(U3(I.M3B).I=1.NU3B)
      IF(KM32.EQ.1) GO TO 1100
```

```
      K=KM32-1
      IF(BRIEF.EQ.ABLANK) WRITE(LINE.9002) K.KM32
      DO 2000 ISO=1.NISO
      IF(TLISO(ISO).LT.0.0) GO TO 2000
      TIMIN=TLISC(ISO)
      TFL=FLISC(ISO)
      TFU=FUISC(ISO)
      MPDIF=2*MISOPB(ISO)
      KU3A=0
      JTN=KTN
      LA=0
      M4A=1
 1200 KA=LA+1
      LA=LE43(M4A.M3A)
      NE4A=1+LA-KA
      MPACKA=MISO43(M4A.M3A)
      KU3B=0
      LB=0
      M4B=1
 1250 KB=LB+1
      LB=LE43(M4B.M3B)
      NE4B=1+LB-KB
      IF(MPACKA-MISO43(M4B.M3B).EQ.MPDIF) GO TO 1300
      JTN=JTN+NE4A*NE4B
      GO TO 1500
 1300 JJA=0
      DO 1390 JA=KA.LA
      JJA=JJA+1
      APACKA=AGP(JA.M3A)
      KP=APACKA
      DO 1320 KG=1.NGS
      MGA(KG)=MG(KG.JA.M3A)
      AG(KG)=KP/AGPB(KG)
      KP=KP-AG(KG)*AGPB(KG)
 1320 CONTINUE
      KT=0
      DO 1350 JB=KB.LB
      KT=KT+1
      T=0.0
      IF(AGP(JB.M3B).NE.APACKA) GO TO 1340
      KDIF=0
      DO 1330 KG=1.NGS
      IF(MG(KG.JB.M3B).EQ.MGA(KG)) GO TO 1330
      KDIF=KDIF+1
      IF(KDIF.GT.1) GO TO 1340
      JG=KG
 1330 CONTINUE
      T=(AG(JG)+MGA(JG))*(2+AG(JG)-MGA(JG))
      T=0.5*SQRT(T)
 1340 T44(KT)=T
 1350 CONTINUE
      JU3B=KU3B
      DO 1380 JJB=1.NE4B
      T=0.0
      DO 1370 N=1.NE4B
      JU3B=JU3B+1
 1370 T=T+T44(N)*U3(JU3B.M3B)
```

```
DEC  6, 1971    23:40.02                    NAME=TRANS

1380 TUB(JJA,JJB)=T
1390 CONTINUE
     JB=KB
     JJB=0
1400 JJB=JJB+1
     JA=KA
     JJA=0
     JU3A=KL3A
1420 JJA=JJA+1
     JTN=JTN+1
     TI=0.0
     DO 1430 N=1.NE4A
     JU3A=JU3A+1
1430 TI=TI+U3(JU3A,M3A)*TUB(N.JJB)
     TI=TI*TI*W2
     TITOT=TITOT+TI
     IF(TI.LT.TIMIN) GO TO 1490
     TF=E3(JA.M3A)-E3(JB.M3B)
     IF(TF.GT.TFU .OR. TF.LT.TFL) GO TO 1490
     NT=NT+1
     TNC(NT)=JTN
     TFC(NT)=TF
     TIC(NT)=TI
     TMISO(NT)=MPACKA
     TKEYS(1.NT)=M4A
     TKEYS(2.NT)=JJA
     TKEYS(3.NT)=M4B
     TKEYS(4.NT)=JJB
     IF(NT.LT.MAXNT) GO TO 1490
1450 WRITE(TFI) ISO.NT
     WRITE(TFI) (TMISO(I).I=1.NT).(TNC(I).I=1.NT).
    1(TFC(I).I=1.NT).(TIC(I).I=1.NT)
     IF(BRIEF.EQ.ABLANK) WRITE(LINE.9C03)ISO.((TKEYS(I.J).I=1.4).
    1 TNC(J).TFC(J).J=1.NT)
     NTISO(ISO) = NTISO(ISO) + NT
     NT=0
1460 TIISC(ISO)=TIISC(ISO)+TITOT
     TITOT=0.0
     IF(M4A.GT.NM43A) GC TO 2000
1490 JA=JA+1
     IF(JA.LE.LA) GO TO 1420
     JB=JB+1
     IF(JB.LE.LB) GO TO 1400
1500 KU3E=KU3E+NE4B*NE4B
     M4B=M4B+1
     IF(M4B.LE.NM43B) GO TO 1250
     KU3A=KU3A+NE4A*NE4A
     M4A=M4A+1
     IF(M4A.LE.NM43A) GO TO 1200
     IF(NT.GT.0) GO TO 1450
     IF(TITCT.GT.0.0) GO TO 1460
2000 CONTINUE
     KTN=JTN
     IF(KM32.LT.NM32) GO TO 1100
     IF(KM2.LT.NM2) GO TO 1000
     WRITE(TFI) KZERO.KZERO
     BRIEF=BFTEMP
```

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DEC  6. 1971    23:40.02                    NAME=TRANS

     RETURN
9000 FORMAT('1KEY. ENERGY LEVELS AND TRANSITIONS'/
    1' CASE'.I3.1X.24A4        /'0MATRICES(3)'/
    2'0SPECIES:  MATRIX(4).LEVEL - MATRIX(4).LEVEL  NUMBER  MZ.  ....')
9001 FORMAT('-'.50X.'MATRIX(2)'.I3/)
9002 FORMAT(1X.2I3)
9003 FORMAT(I6.':'4I3.I7.F11.3.2(7X.4I3.I7.F11.3)/3(7X.4I3.I7.F11.3))
     END
```

```
DEC  6, 1971    23:40.02                    NAME=SPOUT

      SUBROUTINE SPOUT(ISG,NT)
C
C     MAJOR REVISION DECEMEER 1971.
C
C     READS IN ONE SPECIES' TRANSITIONS, SCRTS AND PRINTS THEM.
      COMMON BAF(9,9),TITLE(24),IMCK,CLD,SYM,ITRAT,NCASE,NCPL,
     .LCSCC,AHALF(49),ABLANK,ANOT,ANTI,INFIN,BRIEF,NM2,OLDH,
     $LINE,INDATA,PUNCH,QUANT,TFI,EU,OTPL,
     . MAXF,MAXM43,MAXE4,MAXE3,MAXU3,MAXE2,MAXT,
     $MAXG,NG,SYMG(9),ISOG(9),NLCG(9),
     .NGS,SYMGS(9),IG(9),FMAXG(9),AGPB(9),
     $CC(9,9),JOINCC(9,9),CS(9),JOINCS(9),
     .MAXISO,NISO,TTLISO(3,9),IISO(9),MISOPA(9),MISOPB(9),NTISO(9),KM2P,
     .TIISO(9), OUTISC(9),WISO(9),TLISO(9),SFISO(9),FLISO(9),FUISO(9),
     $MAXREG,NREG,ISCREG(9),TTLREC(3,9),FLREG(9),FRREG(9),KREG(9),
     . HSREG(9), VSREG(9),CLWREG(9),CRWREG(9)
      LOGICAL OLDH,    SYM,SYMG,SYMGS,ITRAT,LCSCC
      INTEGER FMAXG,AGPB,     PUNCH,QUANT,EU,TFI,OTPL
      REAL*8 BAF
C
      CCMMON/ACON/TFC(2501),TIC(2500),TNC(2500),TMISO(2500),SPACER(200)
      INTEGER*2         TMISO,DUMMY2
      INTEGER TNC
      DATA AXE/'X   '/
      REAL ALPHA(6)
      WRITE(LINE,8000) NCASE,     TITLE,ISO,(TTLISO(I,ISO),I=1,3)
     1,FUISO(ISO),FLISC(ISO),TLISO(ISO)
      REWIND TFI
      K=0
      NT=0
      TITOT=0.0
 1000 READ(TFI) ISCIN, NTIN
      IF(ISOIN.GT.0) GO TO 1100
      IF(NTIN.EQ.0) GO TO 2000
      KM2=NTIN
      KM2ADD=KM2*KM2P
      GC TC 1000
 1100 IF(ISOIN.EQ.ISO) GO TO 1200
      J=3*NTIN
      READ(TFI) (DUMMY2,I=1,NTIN),(DUMMY,I=1,J)
      GO TO 1000
 1200 J=K+1
      K=K+NTIN
      IF(K.LE.MAXT) GO TO 1210
      IMOK=0
      K=0
      GO TO 1200
 1210 READ(TFI) (TMISO  (I),I=J,K),(TNC(I),I=J,K),
     1(TFC(I),I=J,K),(TIC(I),I=J,K)
      DO 1220 I=J,K
      TITOT=TITOT+TIC(I)
      TMISO(I) = TMISO(I) + KM2ADD
 1220 CONTINUE
      NT=NT+NTIN
      GO TO 1000
 2000 IF(NT.EQ.0) IMOK=0
      IF(IMOK.NE.1) GO TO 4999
```

```
DEC  6, 1971    23:40.02                    NAME=SPOUT

      DO 2500 I=1,NT
      TFMAX=-1.E50
      DO 2100 J=I,NT
      IF(TFC(J).LT.TFMAX) GO TO 2100
      TFMAX=TFC(J)
      K=J
 2100 CONTINUE
      IF(K.EQ.I) GO TO 2500
      TFC(K)=TFC(I)
      TFC(I)=TFMAX
      X=TIC(K)
      TIC(K)=TIC(I)
      TIC(I)=X
      M=TNC(K)
      TNC(K)=TNC(I)
      TNC(I)=M
      M=TMISO(K)
      TMISC(K)=TMISO(I)
      TMISO(I)=M
 2500 CONTINUE
C
C     TRANSITION TABLES.
C
 3000 IF(OUTISO(NISO).EQ.AXE) GC TC 4999
      DIFF=ABS(WISO(ISO))
      GROUP=100.*DIFF
      GRPEND= 1.E50
      IF(OUTISO(NISO).EQ.ABLANK) GO TO 4000
C
C     CONDENSED TRANSITICN TABLE.
C
      WRITE(LINE,8001) DIFF
      KB=0
      TFC(NT+1)=-1.E50
 3100 KA=KB+1
      TFSUM=0.0
      TISUM=0.0
 3200 KB=KB+1
      TFSUM=TFSUM+TFC(KB)*TIC(KB)
      TISUM=TISUM+TIC(KB)
      IF(TFC(KB)-TFC(KB+1).LE.DIFF) GC TO 3200
      TFMEAN=TFSUM/TISUM
      WIDTH=TFC(KA)-TFC(KB)
      N=KB-KA+1
      IF(TFMEAN.GT.GRPEND) GO TO 3300
      WRITE(LINE,9001)
      GRPEND=TFMEAN-GROUP
 3300 WRITE(LINE,9001) TFMEAN,TISUM,N,WIDTH
      IF(KB.LT.NT) GO TO 3100
      GO TO 4999
C
C     FULL TRANSITION TABLE
C
 4000 WRITE(LINE,8002)(I,I=1,NISO)
      DO 4500 KT=1,NT
      M=TMISO(KT)
      KM2=M/KM2P
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DEC  6, 1971    23:40.02                    NAME=SPOUT

      M=M-KM2*KM2P
      DO 4100 KISO=1.NISO
      K=M/MISOPB(KISO)
      M=M-K*MISOPB(KISO)
      K=25+K-MISOPA(KISO)
      ALPHA(KISO)=AHALF(K)
 4100 CONTINUE
      IF(TFC(KT).GT.GHPEND) GO TO 4200
      WRITE(LINE.9001)
      GRPEND=TFC(KT)-GROUP
 4200 WRITE(LINE.9002) TFC(KT).TNC(KT).TIC(KT).KM2.(ALPHA(I).I=1.NISO)
 4500 CONTINUE
 4999 WRITE(LINE.8003) NT.TITOT.TIISC(ISO)
      IF(NT.GT.MAXT)WRITE(LINE.9500) MAXT
      RETURN
 8000 FORMAT('1CASE'.I3.1X.24A4        /'0TRANSITICNS OF ISCTOPIC SPECIES
     1'.I2.A5.2A4.' FRCM'.F11.1.' TO'.F10.1.' HZ.. MIN. INTENSITY'.F7.3)
 8001 FORMAT('CCONCENSED TRANSITICN TAELE.  LINES WITHIN'.F7.3.' HZ.'.
     1' GRCUPED TOGETHER.'/'0   FREQUENCY  INTENSITY  LINES  WIDTH')
 8002 FORMAT('0 WEIGHT'.11X.'FREQUENCIES'.11X.'NUMBER INTENSITY'
     1' MATRIX(2) ISOTOPIC SPECIES Z-SPINS'/12X.'OBSERVED  DIFF.'.
     2'  CALCULATED'.27X.6I5)
 8003 FORMAT('0'.I6.' TRANSITICNS WITH'.F13.3.' CUT OF'.F13.3.
     1' TOTAL INTENSITY')
 9001 FORMAT(1X.2F11.3.I7.F8.3)
 9002 FORMAT(1X.                        F38.3.I8.F10.3.I7.3X.6A5)
C     SUGGESTED FORMAT FOR PRINTING ASSIGNED LINES IN ITERATIVE RUNS.
C9003 FORMAT(1X.F7.3.F12.3.A1.F6.3.F12.3.I8.F10.3.I7.3X.6A5)
 9500 FORMAT('0*** LIMIT FCR SCRTING IS'.I5.' TRANSITIONS')
      END
```

```
DEC  6, 1971    23:40.02                    NAME=CPLOT

      SUBRCUTINE CPLOT(NT.JREG)
C
C     CALCCMP PLOTTING RCUTINE
C     REVISED DECEMBER 1971
C     CALLS ASSEMBLER RCUTINE PLOTBF TO GET PLCT BUFFER
C
      COMMCN BAF(9.9).TITLE(24).IMCK.CLD.SYM.ITRAT.NCASE.NCPL.
     .LCSCC.AHALF(49).ABLANK.ANOT.ANTI.INFIN.BRIEF.NM2.OLDH.
     $LINE.INDATA.PUNCH.QUANT.TFI.EU.OTPL.
     . MAXF.MAXM43.MAXE4.MAXE3.MAXU3.MAXE2.MAXT.
     $MAXG.NG.SYMG(9).ISCG(9).NUCG(9).
     .NGS.SYMGS(9).IG(9).FMAXG(9).AGPB(9).
     $CC(9.9).JOINCC(9.9).CS(9).JCINCS(9).
     .MAXISO.NISO.TTLISO(3.9).IISO(9).MISOPA(9).MISOPB(9).NTISO(9).KM2P.
     .TIISO(9). OUTISC(9).WISO(9).TLISO(9).SFISO(9).FLISO(9).FUISO(9).
     $MAXREG.NREG.ISOREG(9).TTLREG(3.9).FLREG(9).FRREG(9).KREG(9).
     . HSREG(9). VSREG(9).CLWREG(9).CRWREG(9)
      LOGICAL OLDH.    SYM.SYMG.SYMGS.ITRAT.LCSCC
      INTEGER FMAXG.AGPB.     PUNCH.QUANT.EU.TFI.OTPL
      REAL*8 BAF
      COMMCN/ACOM/TFC(2501).TIC(2500).TNC(2500).TMISO(2500).
     1XPLOT(100).YPLOT(100)
      INTEGER TNC
      INTEGER*2 TM2.TMISO
      DATA MAXXY/99/.             XTOP/C./.XBCT/0./.ORIGX/1.7/.ORIGY/2./
      REAL CMULT(5)/.04..1..25..4.2./
      LOGICAL TOP/.FALSE./.ZERO
      IF(NCPL.GT.0) GO TO 200
      CALL PLCTBF
      CALL XLIMIT(45.)
      CALL PLCT(0..-3..-3)
      CALL PLCT(0..0..-3)
      CALL FACTOR(0.3937)
C     SET UP PLOT DIRECTION AND LIMITS
  200 ISO=ISOREG(JREG)
      IBLAD=100+JREG+10*NCASE
      XINC=0.05
      WL=CLWREG(JREG)
      WR=CRWREG(JREG)
      IF(WL.LE.0.) WL=.15
      IF(WR.LE.0.) WR=.15
      TFL=FLREG(JREG)
      TFR=FRREG(JREG)
      IF(TFC(1)-TFC(NT)) 220.230.240
  220 REV=-1.
      GC TC 250
  230 WRITE(LINE.9500) TFC(1)
      GO TO 9999
  240 REV=1.
  250 IF(REV*(TFL-TFR)) 260.27C.290
  260 KSTEP=-1
      KSTART=NT
      KSTOP=1
      GO TO 300
  270 IF(REV*TFL.GT.0.) GO TO 280
      TFL=TFC(1)
      TFR=TFC(NT)
```

```
      GO TO 250
  280 TFL=TFC(NT)
      TFR=TFC(1)
      GO TO 250
  290 KSTEP=1
      KSTART=1
      KSTOP=NT
  300 REV=REV*FLOAT(KSTEP)
      IF(REV.GT.0.) GO TO 320
      TFL=-TFL
      TFR=-TFR
      DO 310 I=1,NT
  310 TFC(I)=-TFC(I)
  320 IF(HSREG(JREG)) 330,340,350
  330 XSCALE=(TFR-TFL)/HSREG(JREG)
      GO TO 360
  340 XSCALE=(TFL-TFR)/34.
      GO TO 370
  350 XSCALE= HSREG(JREG)
  360 IF((TFL-TFR)/XSCALE.LE.100.)GO TO 370
      XSCALE=(TFL-TFR)/100.
      WRITE(LINE,9502)
  370 FINC=XINC*XSCALE
      TFL=TFL+3.*WL
      TFR=TFR-3.*WR
C     CHECK FCR EMPTY REGION
      IF(TFC(KSTART).LT.TFR) GO TO 9998
      IF(TFC(KSTOP).GT.TFL) GO TO 9998
      REWIND OTPL
      NXY=0
      NBLOCK=1
      ZERO=.TRUE.
      X=0.
      YMAX=0.
      F=TFL+FINC
      K=KSTART
      KBS=KREG(JREG)-2
      IF(KBS.LT.0) GO TO 1300
C     CAUCHY (LORENTZ) TYPE LINESHAPES
      IF(VSREG(JREG)) 1010,1020,1030
 1010 Y=24000.
      GO TO 1040
 1020 Y=2400.
      GO TO 1040
 1030 Y=2400.*VSREG(JREG)
 1040 IF(KBS.GT.0) GO TO 1500
C
C     PURE CAUCHY (LORENTZ) LINESHAPE.
C
      CLIM=Y**.5
      ASSIGN 1150 TO IGC
 1050 FL=F+CLIM*WL
      FR=F-CLIM*WR
      AL=WL*WL
      AR=WR*WR
 1100 F=F-FINC
      IF(F.LT.TFR) GO TO 4500
```

```
      FL=FL-FINC
      FR=FR-FINC
      Y=0.
      X=X+XINC
 1110 IF(TFC(K).LE.FL) GO TO 1120
      IF(K.EQ.KSTOP) GO TO 4500
      K=K+KSTEP
      GO TO 1110
 1120 J=K
 1130 IF(TFC(J).LT.FR) GO TO 4000
      FDEL=TFC(J)-F
      GO TO IGC,(1150,1350,1550)
 1150 IF(FDEL)   1160,1370,1170
 1160 FDEL=FDEL*FDEL/AR
      GO TO 1180
 1170 FDEL=FDEL*FDEL/AL
 1180 Y=Y+TIC(J)/(1.0+FDEL)
 1190 IF(J.EQ.KSTOP) GO TO 4000
      J=J+KSTEP
      GO TO 1130
C
C     GAUSSIAN LINESHAPE
C     MUCH OF THE CODING IS SHARED WITH THE OTHER LINESHAPES.
C
 1300 FL=F+3.4*WL
      FR=F-3.4*WR
      AL=-.693/(WL*WL)
      AR=-.693/(WR*WR)
      ASSIGN 1350 TO IGC
      GO TO 1100
 1350 IF(FDEL) 1360,1370,1380
 1360 Y=Y+TIC(J)*EXP(AR*FDEL*FDEL)
      GO TO 1190
 1370 Y=Y+TIC(J)
      GO TO 1190
 1380 Y=Y+TIC(J)*EXP(AL*FDEL*FDEL)
      GO TO 1190
C
C     MODIFIED CAUCHY (LORENTZ) LINESHAPE WITH FOURTH POWER TERM
C     MUCH OF THE CODING IS SHARED WITH THE OTHER LINESHAPES.
C
 1500 IF(KBS.GT.5) KBS=2
      CM=CMULT(KBS)
      CN=1.+CM
      CLIM=(Y*CN/CM)**.25
      ASSIGN 1550 TO IGC
      GO TO 1050
 1550 IF(FDEL) 1560,1370,1570
 1560 FDEL=FDEL*FDEL/AR
      GO TO 1580
 1570 FDEL=FDEL*FDEL/AL
 1580 Y=Y+TIC(J)*CN/(CN+FDEL+CM*FDEL*FDEL)
      GO TO 1190
C
C     ACCUMULATE X,Y POINT PAIRS OF SPECTRUM.
C     ONLY BEGINNING AND END OF REGIONS OF BLANK BASELINE ARE SAVED.
C
```

```
 4000 IF(Y.GT.0.0005) GO TO 4010
      IF(ZERO) GO TO 1100
      ZERO=.TRUE.
      GO TC 4100
 4010 IF(.NOT.ZERO) GO TO 4100
      ZERO=.FALSE.
      NXY=NXY+1
      XPLOT(NXY)=X-XINC
      YPLOT(NXY)=0.
 4100 IF(Y.GT.YMAX) YMAX=Y
      NXY=NXY+1
      XPLOT(NXY)=X
      YPLOT(NXY)=Y
      IF(NXY.LT.MAXXY) GO TO 1100
      WRITE(OTFL) NXY,XPLOT,YFLOT
      NXY=0
      NBLOCK=NBLOCK+1
      GO TO 1100
 4500 IF(YMAX.LT.0.005) GO TO 9998
      NXY=NXY+1
      XPLCT(NXY)=(TFL-TFR)/XSCALE
      YPLOT(NXY)=0.
      WRITE(OTPL) NXY,XPLOT,YPLOT
      REWIND CTPL
C
C     SET VERTICAL SCALE
C
      IF( VSREG(JREG))4550,4560,4570
 4550 YSCALE=- VSREG(JREG)
      GO TC 5000
 4560 YSCALE=24.0/YMAX
      GO TC 5000
 4570 YSCALE= VSREG(JREG)*24./YMAX
C     WRITE REFERENCE ELOCK ADDRESS ON PLOT TAPE.
 5000 CALL PLCT(ORIGX,ORIGY,-IELAC)
      NCPL=NCPL+1
C
C     PLOT ACTUAL SPECTRUM AS STORED ON TEMPORARY FILE 'OTPL'
C
      DO 5100 I=1,NBLOCK
      READ(OTFL) NXY,XPLOT,YPLOT
      DO 5090 J=1,NXY
      Y=YPLCT(J)*YSCALE
      IF(Y.GT.24.) Y=24.
      CALL PLOT(XPLOT(J),Y,2)
 5090 CONTINUE
 5100 CCNTINUE
C     NOTE RIGHTHAND LIMIT OF PLOTTED SPECTRUM
      XR=XPLCT(NXY)
C     PLOT THE TITLE INFORMATICN VERTICALLY AT THE FAR RIGHT
      CALL SYMBOL(XR+.4,-.3,.21,TITLE,90.,96 )
      CALL SYMBCL(-.0,-.0,-.0,' SPECIES ',90.,9)
      CALL NUMBER(-.0,-.0,-.0,FLOAT(ISO),90.,-1)
      CALL SYMBOL(-.0,-.0,-.0,' ',90.,1)
      CALL SYMBOL(-.0,-.0,-.0,TTLISO(1,ISO),90.,12)
      CALL SYMBOL(-.0,-.0,-.0,' ',90.,1)
      CALL SYMBOL(-.0,-.0,-.0,TTLREG(1,JREG),90.,12)
```

```
      CALL SYMBOL(-.0,-.0,-.0,' ',90.,1)
      CALL NUMBER(-0.,-0.0,-0.0,FLCAT(IELAD),90.,0)
C     FIND INTERVAL FOR MARKING FREQUENCIES
      K= 5.0001*XSCALE
      IF(K.EQ.0) K=1
      IF(K.GT.10) K=10*(K/10)
      I=TFR
      J=K*(I/K)
      IF(J.LE.I) J=J+K
      F=J
      X=(F-TFR)/XSCALE
      FINC=K
      XINC=FINC/XSCALE
C     RETUFN FREQUENCIES TC NORMAL IF THEY HAVE BEEN NEGATED.
      IF(REV.GT.0) GO TO 5200
      DO 5150 I=1,NT
 5150 TFC(I)=-TFC(I)
      TFL=-TFL
      TFR=-TFR
      FINC=-FINC
      F=-F
C     PRINT IDENTIFYING INFORMATION ON LINE PRINTER.
 5200 WRITC(LINE,9000) IELAD,TFL,TFR,XSCALE,YSCALE,KREG(JREG),WL,WR
C     PLOT TOP OF SPECTRUM FRAME, COMPLETE WITH TIC MARKS.
      X=XR-X
      CALL PLOT(XR,24.5,3)
 5240 CALL PLOT(X,24.5,2)
      CALL SYMBOL(X,24.5,.2,13,0.,-1)
      X=X-XINC
      F=F+FINC
      IF(X.GT.0.) GO TO 5240
      CALL PLOT(0.,24.5,2)
C     CCRNER MARKS AND LEFT SIDE.
      CALL SYMBOL(-1.7,25.5,.15,3,0.,-1)
      CALL PLOT(0.,24.5,3)
      CALL PLOT(0.,-.5,2)
      CALL SYMBOL(-1.7,-2.0,.15,3,0.,-1)
C     BOTTOM WITH TIC MARKS AND FRECUENCY SCALE (HZ.)
      CALL PLOT(0.,-.5,3)
      GO TC 5270
 5260 CALL PLOT(X,-.5,2)
      CALL NUMBER(X-.3,-.9,.25,F,0.,-1)
      CALL SYMBOL(X,-.5,.2,13,0.,-1)
 5270 X=X+XINC
      F=F-FINC
      IF(X.LT.XR) GO TO 5260
      CALL PLOT(XR,-.5,2)
C     RIGHT SIDE AND CCRNEF MARKERS
      CALL SYMBOL(XR+.8,-2.0,.15,3,0.,-1)
      CALL PLCT(XR,-.5,3)
      CALL PLCT(XR,24.5,2)
      CALL SYMBOL(XR+.8,25.5,.15,3,0.,-1)
C     THIS PLCT IS NCW CCMPLETE.  RESET THE ORIGIN FOR THE NEXT PLOT.
      XR=XR+2.5
      IF(TOP) GO TO 5520
      IF(XTOP.LT.XR) GO TO 5510
      ORIGX=XR
```

```
      ORIGY=0.
      XTOP=XTOP-XR
      GO TO 9999
 5510 ORIGX=XTOP
      ORIGY=30.
      XBOT=XR-XTOP
      XTOP=0.
      TOP=.TRUE.
      GO TO 9999
 5520 IF(XBOT.LT.XR) GO TO 5530
      ORIGX=XR
      ORIGY=0.
      XBOT=XBOT-XR
      GO TO 9999
 5530 ORIGX=XBOT
      ORIGY=-30.
      XTOP=XR-XBOT
      XBOT=0.
      TOP=.FALSE.
      GO TO 9999
 9998 WRITE(LINE.9501)
 9999 RETURN
 9000 FORMAT('0CALCOMP PLOT'.I4.        ' FROM'.F9.2.' TO'.F9.2.' HZ.'/
     1        '  SCALES: HOR.'.F8.2.' HZ/CM.  VERT.'.F8.4.' CM/UNIT'    /
     2'  LINESHAPE'.I2.'  HALF HEIGHT PARTIAL WIDTHS'.2F6.2)
 9500 FORMAT('0*** CALCOMP PLOT CANCELLED. SINGLE LINE AT'.F10.3)
 9501 FORMAT('0*** CALCOMP PLOT CANCELLED.  EMPTY REGION')
 9502 FORMAT('0*** CALCOMP WIDTH REDUCED TO 100 CM.')
      END
```

```
      SUBROUTINE BPLOT(N.F.Y.VL.VR.VINC.SCALE.   LNUM)
C
C                                NMR BAR PLOTS
C
C     A. QUIRT. CHEMISTRY. UNIVERSITY OF ALBERTA. APRIL 1971.
C     USES TERMINAL PLOTTING ROUTINE TPLOT .
C
C     INPUT FREQUENCIES MUST HAVE BEEN SORTED IN EITHER INCREASING OR
C     DECREASING ORDER BEFORE BPLOT IS CALLED. IN EITHER CASE PLOTS CAN
C     BE IN EITHER DIRECTION. THE VERTICAL SCALE CAN BE EXPANDED TO SHOW
C     WEAK TRANSITIONS WITHOUT LOSING INFORMATION ON THE INTENSITY OF
C     THE STRONG TRANSITIONS.
C     THE INTENSITY-WEIGHTED MEAN FREQUENCY IS PRINTED WITH EACH BAR.
C
C
C.... REQUIRES 7 ARGUMENTS:
C.... N         NUMBER OF TRANSITIONS IN THE F AND Y VECTORS.
C.... F         VECTOR OF FREQUENCIES (HZ.) IN DECREASING ORDER
C.... Y         CORRESPONDING INTENSITIES
C.... FL.FR     LEFT AND RIGHT LIMITS OF PLOTTED FREQUENCY RANGE  (VL.VR)
C.... FINC      FREQUENCY INCREMENT (VINC)
C.... SCALE     FACTOR FOR VERTICAL SCALE EXPANSION.
C
C     ROOM HAS BEEN PROVIDED TO PRINT EXTRA INFORMATION ABOUT THE MOST
C     INTENSE TRANSITION IN EACH BAR.  IN THIS VERSION THE INFORMATION
C     CONSISTS OF THE LINE NUMBER.
C
C.... LNUM      LINE NUMBER OF CALCULATED TRANSITION.
C
      DIMENSION F(N).Y(N).LNUM(N)
C
C.... DICTIONARY OF OTHER VARIABLES.
C
C... BARL.BARR LEFT AND RIGHT FREQUENCY LIMITS OF ONE HISTOGRAM BAR.
C... BIGLIN    INTENSITY OF THE STRONGEST TRANSITION IN A BAR.
C... GAP       MAXIMUM RANGE OF BLANK BASELINE PRINTED. (100 LINES)
C... I         INDEX OF THE STRONGEST TRANSITION IN THIS BAR.
C... L         INDEX OVER TRANSITION LIST. (FROM 1 TO N)
C... LINES     NUMBER OF TRANSITIONS COMBINED IN ONE BAR.
C... LSTART    FIRST L VALUE.  (1 WHEN LSTEP IS 1)
C... LSTOP     1 EXCEPT -1 FOR A PLOT BEGINNING AT THE LAST TRANSITION
C... LSTOP     LAST L VALUE (1 WHEN LSTEP IS -1)
C... NBAR      NUMBER OF SYMBOLS FOR THIS BAR
C... PRIN      INTEGER VARIABLE REPRESENTING THE LINE PRINTER.
C... REV       1.0 EXCEPT -1.0 FOR A PLOT IN INCREASING FREQ. ORDER.
C... SYMBOL    CONTAINS THE LETTER X USED TO PRINT THE HISTOGRAM BARS.
C... X         TOTAL INTENSITY IN THE REGION PLOTTED.
C... X         BECOMES THE INTENSITY WEIGHTED MEAN FREQUENCY.
C... YSCL      INTENSITY SCALE FACTOR IN BAR SYMBOLS / INTENSITY UNIT.
C... ZMAX      INTENSITY OF THE LARGEST HISTOGRAM BAR.
C
C.... IT IS ASSUMED THAT A HEADING TO IDENTIFY THE PLOT HAS BEEN PRINTED
C.... BY THE CALLING PROGRAM.
C
      INTEGER*2 K.Q
      INTEGER PRIN
      DATA SYMBOL /1HX/
```

```
C
C**** ASSIGN UNIT NUMBER TO THE LINE PRINTER.
      PRIN = 6
C     ASSIGN DEFAULT VALUE TO FINC
      FINC=0.5
      IF (VINC.NE.0.0) FINC = ABS(VINC)
      GAP = 50.0 * FINC
C
C     DETERMINE PLOT DIRECTION FROM PLOT LIMITS.  IF THE LIMITS ARE
C     EQUAL THE DEFAULT IS THE COMPLETE SET OF TRANSITIONS.
C     IN THIS CASE EQUAL POSITIVE LIMITS INDICATE A PLOT WITH FREQUENCY
C     INCREASING FROM LEFT TO RIGHT. EQUAL NEGATIVE LIMITS GIVE A
C     DECREASING FREQUENCY PLOT.  FOR BOTH LIMITS ZERO, THE DIRECTION
C     IS THE SAME AS THE ORDER OF SORTING THE TRANSITIONS.
C
      FL=VL
      FR=VR
C     REV IS TEMPORARILY THE INDICATOR OF FREQUENCY SORT DIRECTION.
      IF ( F(1)-F(N) ) 5,10,15
    5 REV = -1.0
      GO TO 20
   10 WRITE(PRIN,9006) F(1)
      GO TO 999
   15 REV = 1.0
   20 IF( REV*(FL-FR) ) 25,30,40
   25 LSTEP=-1
      LSTART=N
      LSTOP=1
      GO TO 45
   30 IF( REV*FL .GT. 0.0 ) GO TO 35
      FL=F(1)
      FR=F(N)
      GO TO 20
   35 FL=F(N)
      FR=F(1)
      GO TO 20
   40 LSTEP=1
      LSTART=1
      LSTOP=N
C     THE DIRECTION OF STEPPING THROUGH THE FREQUENCY TABLE DEPENDS
C     ON WHETHER THE GIVEN LEFT AND RIGHT LIMITS INDICATE A PLOT IN THE
C     SAME ORDER THAT THE FREQUENCIES ARE SORTED OR THE REVERSE ORDER.
C     WHEN THIS HAS BEEN CHOSEN THE FREQUENCY MULTIPLIER REV IS MADE
C     1.0 OR -1.0 SO THAT THE SCAN IS ALWAYS IN THE DIRECTION OF
C     DECREASING APPARENT FREQUENCY.
   45 REV = REV*FLOAT(LSTEP)
      WRITE(PRIN,9000)FL,FR,FINC
C     IF REV IS NEGATIVE THE FREQUENCY TABLE IS TEMPORARILY REVERSED IN
C     SIGN SO THAT THE SEARCH WILL BE IN DECREASING ORDER.
      IF(REV.GT.0.0) GO TO 100
      FL=-FL
      FR=-FR
      DO 70 I=1,N
   70 F(I)=-F(I)
C.... IF THERE ARE NO TRANSITIONS IN THIS REGION, QUIT.
  100 IF(F(LSTART).LT.FR) GO TO 899
      IF(F(LSTOP).GT.FL) GO TO 899
```

```
C
C**** CHECK WHETHER SCALE IS NEGATIVE.
C     IF IT IS, ITS ABSOLUTE VALUE IS USED AS SYMBOLS/INTENSITY
C     AND THE FIRST PASS TO SET THE SCALE CAN BE SKIPPED.
C
      IF(SCALE.GE.0.0) GO TO 110
      YSCL=-SCALE
      GO TO 180
C**** FIND THE MOST INTENSE COMBINED LINE (HIGHEST HISTOGRAM BAR)
  110 Z = 0.0
      ZMAX=0.0
      BARR = FINC * AINT( FL/FINC )  + FINC
      L = LSTART
      GO TO 160
  120 IF(F(L).GT.BARL) GO TO 130
      Z = Y(L) + Z
      IF(L.NE.LSTOP) GO TO 130
      BARR = -1.E50
      GO TO 150
  130 L=L+LSTEP
  140 IF(F(L).GE.BARR) GO TO 120
      IF ( Z.GT.0.0 ) GO TO 150
      IF(BARR-F(L).LT.GAP) GO TO 160
      BARR= AINT(( F(L)      - BARR)/FINC)*FINC+FINC+BARR
      GO TO 160
  150 IF (ZMAX.LT.Z) ZMAX = Z
      Z=0.0
  160 BARL = BARR
      BARR = BARR - FINC
      IF ( BARL.GT.FR ) GO TO 140
C**** CALCULATE SCALE FACTOR FOR Y AXIS.
C.... DEFAULT SCALE IS 100 UNITS (FULL HEIGHT) FOR LARGEST LINE.
      IF(ZMAX.EQ.0.0) GO TO 899
      YSCL = 100.0 / ZMAX
      IF(SCALE.GT.0.0) YSCL = SCALE * YSCL
C     CHECK WHETHER THE PROGRAM IS BEING RUN FROM A TERMINAL
C     IF IT IS, USE A SPECIAL SHORT FORM PRINT ROUTINE
  180 CALL CREPLY(&190)
      CALL TPLOT(N,F,Y,FL,FR,FINC,REV,GAP,YSCL,LSTART,LSTOP,LSTEP)
      GO TO 900
  190 X=0.0
      DO 195 I=1,N
  195 X=X+Y(I)
C
C.... HEADING FOR ACTUAL HISTOGRAM.
      WRITE(PRIN,9001)X,YSCL
C
C**** THE REMAINDER IS THE ACTUAL PLOTTING OF THE HISTOGRAM.
      BARR = FINC * AINT( FL/FINC )  + FINC
      L=LSTART
      GO TO 260
  200 IF( F(L)      .GT. BARL ) GO TO 210
C.... ACCUMULATE INTENSITY FOR THIS HISTOGRAM BAR.
      LINES = 1 + LINES
      Z = Y(L) + Z
      X = F(L)*Y(L) + X
      IF(Y(L).LE.BIGLIN) GO TO 205
```

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DEC  6. 1971    23:40.02                     NAME=BPLOT

      BIGLIN = Y(L)
      I = L
  205 IF( L.NE.LSTOP) GO TO 210
      BARR = -1.E50
      GO TC 230
  210 L = L + LSTEP
  220 IF( F(L)      .GE. BARR ) GO TO 200
      IF (LINES.GT.0) GO TO 230
C.... WRITE A PIECE  BLANK BASELINE.  IF THERE IS A LARGE GAP BEFORE THE
C.... NEXT LINE IN THE TRANSITION TABLE. PRINT A MESSAGE TO SHOW THAT
C.... THE FLOT RESUMES JUST BEFORE THE NEXT LINE.
      WRITE(PRIN.9002)
      IF( BARR - F(L)      .LT. GAP) GO TO 270
      WRITE(PRIN.9003)
      BARR= AINT(( F(L)      - BARR)/FINC)*FINC+FINC+BARR
      GO TO 270
  230 NBAR = C.5 + YSCL*Z
      X = REV*X / Z
      IF (NBAR.GT.0) GC TO 240
C.... WRITE STATEMENT IF THE INTENSITY OF THIS BAR IS LESS THAN 1 SYMBOL
      WRITE(PRIN.9004) X.LNUM(I).LINES
      GO TO 260
  240 IF (NBAR.GT.100) GO TO 250
C.... WRITE STATEMENT FCR 1 TO 100 PLOT SYMBOLS.
      WRITE(PRIN.9004) X.LNUM(I).   LINES . (SYMBOL.J=1.NBAR)
      GO TO 260
C.... IF THE LINE IS OFF-SCALE. THE NUMBER OF SYMBOLS IS PRINTED.
  250 WRITE(PRIN.9005) X.LNUM(I).   LINES.NBAR
  260 LINES = 0
      X = 0.0
      Z = 0.0
      BIGLIN = 0.0
  270 BARL = BARR
      BARR = BARR - FINC
      IF ( BARL.GT.FR ) GO TO 220
      GO TO 900
C**** ERROR EXIT IF THIS REGION CONTAINS NO LINES TO PLOT.
  899 WRITE(PRIN.9003)
C**** NORMAL RETURN AFTER FLOTTING.
  900 IF(REV.GT.0.0) GO TO 999
      DO 910 I=1.N
  910 F(I)=-F(I)
  999 RETURN
 9000 FORMAT(16H0FREQUENCY RANGE.F10.3.4H TO .F10.3.15H HZ.. INCREMENT.
     1F8.3)
 9001 FORMAT(16H TOTAL INTENSITYF9.2.10H UNITS. ATF8.2.13H SYMBOLS/UNIT/
     124H-     MEAN   A LINE NO.OF  /
     239H  FREQUENCY NUMBER LINES        INTENSITY      /1H0)
 9002 FORMAT(1H9.23X.1H|)
 9003 FORMAT(1H-.27X.42H THIS REGION CONTAINS NO SIGNIFICANT LINES /1H0)
 9004 FORMAT(1H9.F10.3.I7.I5.'4 |.100A1)
 9005 FORMAT(1H9.F10.3.I7.I5.2H |.
     1 25H THIS LINE IS OFF SCALE (.I4.11H SYMBOLS ) .I5(4H0000) )
 9006 FORMAT('0SINGLE LINE AT'.F14.3)
      END
```

```
DEC  6. 1971    23:40.02                     NAME=TPLOT

      SUBROUTINE TPLOT(N.F.Y.FL.FR.FINC.REV.GAP.YSCL.LSTART.LSTOP.LSTEP)
C
C     SPECIAL SHORT FORM HISTOGRAM FOR TERMINALS
C     MAJOR REVISION AUGUST 1971
C
      INTEGER PRIN/6/
      DATA SYMBOL/'X'/.BLANK/' '/
      DATA BKSP/Z16161616/
      DIMENSION F(N).Y(N)
C
      X=0.0
      DO 195 I=1.N
  195 X=X+Y(I)
C
C.... HEADING FOR ACTUAL HISTOGRAM.
      WRITE(PRIN.9001)X.YSCL
C
C**** THE REMAINDER IS THE ACTUAL FLOTTING OF THE HISTOGRAM.
      BARR = FINC * AINT( FL/FINC )  + FINC
      L=LSTART
      GO TO 260
  200 IF( F(L)      .GT. BARL ) GO TO 210
C.... ACCUMULATE INTENSITY FOR THIS HISTOGRAM BAR.
      LINES = 1 + LINES
      Z = Y(L) + Z
      X = F(L)*Y(L) + X
  205 IF( L.NE.LSTOP) GO TO 210
      BARR = -1.E50
      GO TO 230
  210 L = L + LSTEP
  220 IF( F(L)      .GE. BARR ) GO TO 200
      IF (LINES.GT.0) GO TO 230
C.... WRITE A PIECE  BLANK BASELINE.  IF THERE IS A LARGE GAP BEFORE THE
C.... NEXT LINE IN THE TRANSITION TABLE. PRINT A MESSAGE TO SHOW THAT
C.... THE FLOT RESUMES JUST BEFORE THE NEXT LINE.
      WRITE(PRIN.9006)
      IF( BARR - F(L)      .LT. GAP) GO TO 270
      WRITE(PRIN.9003)
      BARR= AINT(( F(L)      - BARR)/FINC)*FINC+FINC+BARR
      GO TO 270
  230 NBAR = 0.5 + YSCL*Z
      X = REV*X / Z
      IF (NBAR.GT.0) GO TO 240
C.... WRITE STATEMENT IF THE INTENSITY OF THIS BAR IS LESS THAN 1 SYMBOL
      WRITE(PRIN.9002)
      GO TO 245
  240 IF (NBAR.GT.100) GO TO 250
C.... WRITE STATEMENT FOR 1 TO 100 PLOT SYMBOLS.
      WRITE(PRIN.9002)  (SYMBOL.J=1.NBAR)
  245 WRITE(PRIN.9004) X.BKSP
      GO TO 260
C.... IF THE LINE IS OFF-SCALE. THE NUMBER OF SYMBOLS IS PRINTED.
  250 WRITE(PRIN.9005) NBAR.X
  260 LINES = 0
      X = 0.0
      Z = 0.0
  270 BARL = BARR
```

```
DEC  6, 1971    23:40.02                  NAME=TPLOT

     BARR = BARR - FINC
     IF ( BARL.GT.FR ) GO TO 220
     RETURN
9001 FORMAT(16H TOTAL INTENSITYF8.2,10H UNITS, ATF8.2,13H SYMBOLS/UNIT/
    1'- INTENSITY,FREQUENCY'/'0')
9002 FORMAT('&|',100A1)
9003 FORMAT(1H-,    42H THIS REGION CONTAINS NO SIGNIFICANT LINES /1H0)
9004 FORMAT(' ',F14.2/'&',A4)
9005 FORMAT(' |',
    1 25H THIS LINE IS OFF SCALE (,I4,11H SYMBOLS ) ,15(4H0000),F10.2)
9006 FORMAT(' |')
     END
```

```
DEC  6, 1971    23:40.02                  NAME=HSHLDR

      SUBROUTINE HSHLDR(NDIM, NVAR, A, E, C, NOCONV)
C
C     EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC MATRIX.
C     BASED ON TRED2 (HOUSEHOLDER REDUCTION) AND TQL2 (QL METHOD)
C     RS MARTIN, C REINSCH, JH WILKINSON, NUMERISCHE MATHEMATIK 11, 181.
C     H.BOWDLER,R.S.MARTIN,C.REINSCH,J.H.WILKINSON, IBID, P 293.
C
C     DOUBLE PRECISION FORTRAN IV VERSION BY L.L. RINES & A.R. QUIRT.
C     CHEMISTRY DEPARTMENT, THE UNIVERSITY OF ALBERTA, EDMONTON CANADA.
C     REVISIED AUGUST 1971 (CORRECTED MACHINE DEPENDENT CONSTANTS)
C
C
C             THIS SUBROUTINE CALLS THE INTERNAL SUBROUTINES WHICH
C             TRIDIAGONALIZE THE INPUT MATRIX AND FIND THE EIGENVALUES
C             AND EIGENVECTORS.  IF A IS ALREADY IN TRIDIAGONAL FORM,
C             THE DIAGONALIZATION SUBROUTINE IS NOT CALLED.
C
C     THE ROUTINES HSHLDB AND HSHLDC CONTAIN MACHINE-DEPENDENT CONSTANTS
C     THEY ARE DEFINED AS FOLLOWS:
C     ETA   THE SMALLEST POSSIBLE POSITIVE NUMBER
C     ACH   THE SMALLEST NUMBER FOR WHICH 1+ACH IS GREATER THAN 1
C     (ACH IS THE SAME AS 'MACHEPS' IN THE REFERENCES)
C     TOL   ETA/ACH
C
C     THE VALUES OF THESE CONSTANTS FOR THE IBM /360, AS POWERS OF 16 :
C     ETA  16**-65  SINGLE OR DOUBLE PRECISION (NORMALIZED)
C     ACH  16**-5 (SINGLE PRECISION)   16**-13 (DOUBLE PRECISION)
C     TOL   16**-60 (SINGLE PRECISION)   16**-52 (DOUBLE PRECISION)
C     IN THE SUBROUTINES HEXADECIMAL CONSTANTS WITH THESES VALUES ARE
C     USED, SINCE THE NUMBERS ARE NOT EASY TO REPRESENT IN DECIMAL FORM.
C
C     FOR OTHER COMPUTERS THE VALUES WILL BE DIFFERENT.
C     USE THE DEFINITIONS TO CALCULATE THEM.
C
      REAL*8 A(NDIM,NDIM),B(NDIM),C(NDIM)
      NOCONV=0
C
C             CHECK FOR MATRIX ORDER OF 1 OR 2 .
C
      IF(NVAR-2) 1,15,5
    1 B(1) = A(1,1)
      A(1,1) = 1.D0
      GO TO 70
C
C             CHECK TO SEE IF A IS ALREADY IN TRI-DIAGONAL FORM.
    5 DO 10 I = 3, NVAR
      IM2 = I - 2
      DO 10 J = 1, IM2
      IF (A(I,J) .NE. 0.0D0 ) GO TO 50
   10 CONTINUE
C             STORAGE OF DIAGONAL, OFF-DIAGONAL  AND THE TRANSFORMATION
C             MATRIX (IDENTITY) OF THE TRIDIAGONAL INPUT MATRIX.
   15 NM1 = NVAR - 1
      DO 20 I = 1, NM1
      B(I) = A(I,I)
      C(I) = A(I+1,I)
   20 CONTINUE
```

```
DEC  6. 1971    23:40.02                 NAME=HSHLDR

      B(NVAR) = A(NVAR.NVAR)
      DO 40 J = 1. NVAR
      DO 30 I = 1. NVAR
   30 A(I.J) = 0.0D0
   40 A(J.J) = 1.0D0
      GO TO 60
C
C              TRIDIAGONALIZE A BY HOUSEHOLDER'S METHOD.
   50 CALL HSHLDB (NDIM.NVAR.A. E. C)
C
C              FIND EIGENVALUES AND EIGENVECTORS BY QL TRANSFORMATIONS.
   60 CALL HSHLDC (NDIM. NVAR. A. E. C. NOCONV)
C
   70 RETURN
      END
```

```
DEC  6. 1971    23:40.02                 NAME=HSHLDB

      SUBROUTINE HSHLCU (NDIM. NVAR. Z. D. E)
C
C
C             THIS SUBROUTINE REDUCES THE LOWER TRIANGLE OF A REAL*8
C             SYMMETRIC MATRIX Z. TO TRIDIAGCNAL FORM USING HOUSEHOLDER'
C             REDUCTION METHOC.  THE CIAGCNAL CF THE RESULTING MATRIX
C             IS STORED IN D(NVAR) AND THE CFF-DIAGONAL IN THE FIRST
C             NVAR-1 ELEMENTS OF E(NVAR).  Z IS USED FOR THE TRANSFORMAT
C             MATRIX AND THUS THE INFUT MATRIX IS NOT SAVED.
C
      IMPLICIT REAL*8 (A-H. O-Z)
      DIMENSION Z(NDIM.NDIM). C(NDIM). E(NDIM)
C     SEE THE COMMENTS IN HSHLDR (CALLING PROGRAM) FOR THE DEFINITION OF
C     THE FOLLGWING MACHINE-CEPENDENT CONSTANT.
      DATA TOL/Z0D100CC0C0CCC0C0/
C
C             MATRICES OF ORDER 1 AND 2 MUST BE HANDLED EXTERNALLY.
      I = NVAR
   10 IM1 = I - 1
      IM2 = I - 2
      G = C.0D0
      F = Z(I.IM1)
      DO 20 K = 1. IM2
   20 G = G + Z(I.K) * Z(I.K)
      H = G + F * F
      IF (G .GT. TOL) GO TO 30
      E(I) = F
      H = 0.0D0
      GO TO 65
C
   30 G = - DSIGN(DSQRT(H).F)
      E(I) = G
      H = H - F * G
      Z(I.IM1) = F - G
      F = C.0D0
C
      DO 50 J = 1. IM1
      Z(J.I) = Z(I.J) / H
      G = 0.0D0
C             FORM ELEMENT OF A * U
      DO 46 K = 1. IM1
      IF (K .GT. J) GC TO 42
      HH = Z(J.K)
      GO TO 44
   42 HH = Z(K.J)
   44 G = G + HH * Z(I.K)
   46 CONTINUE
C             FORM ELEMENT OF P
      E(J) = G / H
      F = F + G * Z(J.I)
   50 CONTINUE
C             FORM K
      HH = F / (H + H )
C             FORM RECUCED A
      DO 60 J = 1. IM1
      F = Z(I.J)
      E(J) = E(J) - HH * F
```

```
DEC  6, 1971    23:40.02                    NAME=HSHLDB

      G = E(J)
C
      DO 55 K = 1, J
   55 Z(J.K) = Z(J.K) - F * E(K)    - G * Z(I.K)
   60 CONTINUE
C
   65 D(I) = H
      IF (I .EQ. 3) GO TO 70
      I = I - 1
      GO TO 10
C
   70 CONTINUE
      D(1) = Z(1,1)
      D(2) = 0.0D0
      E(1) = 0.0D0
      E(2) = Z(2,1)
C             ACCUMULATION OF TRANSFORMATION MATRICES
      Z(1,1) = 1.0D0
      DO 80 I = 2, NVAR
      IM1 = I - 1
      IF (D(I) .EQ. 0.0D0) GO TO 78
      DO 76 J = 1, IM1
      G = 0.0D0
C
      DO 72 K = 1, IM1
   72 G = G + Z(I,K) * Z(K,J)
      DO 74 K = 1,IM1
   74 Z(K,J) = Z(K,J) - G * Z(K,I)
   76 CONTINUE
   78 D(I) = Z(I,I)
      E(I-1) = E(I)
      Z(I.I) = 1.0D0
      DO 79  J = 1, IM1
      Z(I.J) = 0.0D0
      Z(J.I) = 0.0D0
   79 CONTINUE
   80 CONTINUE
      E(NVAR) = 0.0D0
C
C
      RETURN
      END
```

```
DEC  6, 1971    23:40.02                    NAME=HSHLDC

      SUBROUTINE HSHLDC (NDIM, NVAR, Z, D, E, NCCONV)
C
C
C             THIS SUBROUTINE FINDS THE EIGENVALUES AND EIGENVECTORS FOR
C             TRIDIAGONAL MATRIX STORED WITH ITS DIAGONAL IN D AND THE
C             OFF-DIAGONAL IN THE FIRST N-1 ELEMENTS OF E.  Z CONTAINS
C             THE TRANSFORMATION MATRIX ON ENTRY AND RETURNS THE
C             EIGENVECTORS ON EXIT.  THE EIGENVALUES ARE RETURNED IN D.
C
      IMPLICIT REAL*8 (A-H.O-Z)
      DIMENSION Z(NDIM,NDIM), D(NDIM), E(NDIM)
C     SEE THE COMMENTS IN HSHLDR (CALLING PROGRAM) FOR THE DEFINITION OF
C     THE FOLLOWING MACHINE-DEPENDENT CONSTANT.
      DATA ACH/Z3410000000000000/
C
      B = 0.0D0
      E(NVAR) = 0.0D0
      F = 0.0D0
      DO 90 L = 1 , NVAR
      J = 0
      H = ACH * (DABS(D(L)) + DABS(E(L)))
      IF(B.LT.H) B = H
C             LOOK FOR SMALL SUBDIAGONAL ELEMENT.
      DO 10 M = L , NVAR
      IF (DABS(E(M)) .LE.B) GO TO 20
   10 CONTINUE
   20 IF(M.EQ.L) GO TO 80
   30 IF(J.EQ.30) GO TO 200
      J = J + 1
C             FORM SHIFT
      P = (D(L+1) - D(L))/(2.0D0 *E(L))
      R =DSQRT(P*P + 1.0D0)
      H = R
      IF(P.LT.0.0D0) H = - R
      H = D(L) - E(L)/(P + H)
      DO 40 I = L, NVAR
   40 D(I) = D(I) - H
      F = F + H
      P = D(M)
      C = 1.0D0
      S = 0.0D0
      I = M
   45  I = I - 1
       G = C*E(I)
       H = C*P
       IF (DABS(P) .LT. DABS(E(I))) GO TO 50
       C = E(I)/P
       R =DSQRT(C*C+1.0D0)
       E(I+1) = S*P*R
       S = C/R
       C = 1.0D0/R
       GO TO 60
   50 C = P/E(I)
       R =DSQRT(C*C + 1.0D0)
       E(I+1) = S*E(I)*R
       S = 1.0D0/R
       C = S*C
```

```
DEC  6, 1971    23:40.02                    NAME=HSHLDC

   60 P = C*D(I) - S*G
      D(I+1) = H + S*(C*G + S*D(I))
C               FORM VECTORS
      DO 70 K = 1 , NVAR
      H = Z(K,I+1)
      Z(K,I+1) = S*Z(K,I) + C*H
   70 Z(K,I) = C*Z(K,I) - S*H
      IF(I.NE.L) GO TO 45
      E(L) = S*P
      D(L) = C*P
      IF (DABS(E(L)) .GT. B) GO TO 30
  80  D(L) = D(L) + F
  90  CONTINUE
C               BEGIN SORT OF EIGENVALUES AND EIGENVECTORS
      NM1 = NVAR - 1
      DO 130 I = 1 , NM1
      K = I
      P = D(I)
      IP1 = I + 1
      DO 110 J = IP1 ,NVAR
      IF(D(J).LE.P) GO TO 100
      K = J
      P = D(J)
 100  CONTINUE
  110 CONTINUE
      IF(K.EQ.I) GO TO 130
      D(K) = D(I)
      D(I) = P
      DO 120 J = 1,NVAR
      P = Z(J,I)
      Z(J,I) = Z(J,K)
  120 Z(J,K) = P
  130 CONTINUE
  140 RETURN
C
 200  NOCONV = L
      GO TO 140
      END
```

APPENDIX C COMPUTER REPRESENTATIONS OF SPIN QUANTUM NUMBERS

Since spin quantum numbers are multiples of 0.5, it seems reasonable to represent them in a computer by floating point numbers.† Unfortunately, different sequences of floating point arithmetic operations that should yield the same result often do not because of rounding errors. Logic based on floating point quantum numbers is thus unreliable. A suitable internal representation for a spin quantum number is an integer equal to twice the true value. All equations for matrix elements must be modified accordingly.

Memory space can be saved by 'packing' a set of related quantum numbers, such as the A values of all groups. Each group's A value is multiplied by the corresponding element of a vector of multipliers derived from the maximum A values for the molecule; the sum is a unique integer representing the entire set.

Each multiplier, starting from the right, is the

---

† Non-integral numbers are normally represented in a computer by the product of a fractional part and an exponent, together known as a floating point number. The principle is the same as that of standard scientific notation, but base 2 rather than base 10 is normally used. Many numbers that are exact in scientific notation become endless fractions in floating point, causing unexpected rounding errors.

product:
(maximum A value next right, +1) × (multiplier next right)
For example, the maximum A values of an $A[BX_6]_2$ spin system are ½ 1 6, or, in internal representation, 1 2 12. This spin system's multiplier vector is 39 13 1, and the set of A values ½ 0 5 is packed as 49. To unpack, one reverses the packing process: 49÷39 = 1, remainder 10; 10÷13 = 0, ...

Unpacking is much more complicated if negative numbers are included in the set being unpacked. If M (or M_S) values are packed, they should first be made non-negative by adding to each a number equal to the largest possible absolute value of M (or M_S) for that group or species. In an $A_2B_2X_3$ system, the limits for M_S values of the two species are ±2 and ±3/2; in internal form, ±4 and ±3. Before packing, +4 and +3 respectively are added to the M_S values, giving ranges of 0 to 8, and 0 to 6. Thus the packed representation of M_S values of 2 and -½ is 58.

Packing is particularly advantageous when the packed representation of a set of quantum numbers can be used directly, without unpacking. As is pointed out in §4.3, basis functions can be sorted into matrices$_4$ by their packed M_S values, and packed A and M_S values can be used directly to determine transition selection rules. Since there is no direct use for packed group M values, they are best left unpacked.

APPENDIX D. INSTRUCTIONS FOR NUMAR[†]

NUMAR is a new program for the calculation of NMR spectra from chemical shifts and coupling constants. It makes full use of the factoring that results from magnetic equivalence, twofold symmetry, and large chemical shift differences.

SOME DEFINITIONS

SPECIES or ISOTOPIC SPECIES:

Usually this is just what it seems. Protons in a molecule are one species, ^{19}F nuclei another, and so on. Nuclei of the same isotopic species but far apart in chemical shift may also be entered as different species. For this "X-approximation" to be valid, all coupling constants between nuclei in different species must be much smaller than the chemical shift separations.

CASE:

The set of data cards necessary for calculations on a molecule is a CASE. Each computer run may include calculations on any number of cases.

[†] University of Alberta Nuclear Magnetic Resonance.

TYPE:

The cards making up a CASE may be grouped into several TYPES such as chemical shift cards, coupling constant cards, etc. Each TYPE has its own layout of columns for punching.

GROUP:

In these instructions a GROUP always refers to the collection of nuclei described by a single TYPE 4 card. A GROUP may consist of:

- a single nucleus of spin ½ up to 9/2.
- a magnetically equivalent group of up to 9 nuclei of spin ½.
- a chemically equivalent pair of either of the above.

The groups are numbered (for coupling constants etc.) sequentially from the first group of the first isotopic species to the last group of the last isotopic species. A chemically equivalent pair entered on one card counts as one group not two.

(There is just one time that you count two for a chemically equivalent pair. When adding up groups to see if the molecule will fit within the program limit of nine groups, each pair counts as two groups. This is the result of an internal requirement in the program and does not affect the *numbering* of the groups.)

ITEM:

An ITEM is the piece of data punched in any single region of a data card. For example, one data ITEM on a TYPE 4 card is the chemical shift, which is punched in card columns 10-19 (inclusive).

ORDER OF TYPES

A typical case includes up to six different TYPES of card:

1) One TITLE card.
2) One or more COUPLING CONSTANT cards.

For each species a set consisting of:

3) One ISOTOPIC SPECIES card.
4) One CHEMICAL SHIFT card for each group of nuclei in this isotopic species.
5) Zero or more PLOT cards <u>for this species</u>.

WHEN THERE ARE SEVERAL ISOTOPIC SPECIES the order of types is:

1,2,(3,4,[5]), [3,4,[5]], ...

Square brackets are used to show that some types, or sequences of types, will not appear in every CASE.

FORMAT OF DATA CARDS

In the detailed description of each TYPE only the main items on each card are included. For less common options see the separate sections at the end.

A format code letter and a card column range are given for each data item. Integer (I) values must be numbers with no decimal point, and must be punched as far right as possible in their column range. Floating point (F) numbers must have a decimal point. For both I and F, a blank and a punched zero are treated identically. Alphabetic (A) data may include any normal keypunch character.

Sometimes examples are included in parentheses.

In laying out the cards an attempt was made to have similar kinds of data appear in similar placed for each TYPE.

- the letter L in column 1 of a card always indicates the last member of a group of cards of the same type.
- every integer (I) number ends in column 2 or 4.
- every floating point (F) number occupies either 10 columns beginning in column 10, 20, etc. or 5 columns beginning in column 20, 25, 30, 35, etc.
- every title begins in column 8.

DEFAULT VALUES

A default value is assigned to many data items if nothing is punched in the card columns. For example, if column 2 of a TYPE 3 card is left blank, it is assumed that the isotopic species has spin ½.

When the item is one of a pair of frequencies that define a frequency range, the default value is assigned only if *both of the frequencies that define the range are equal.* This will be the case if both are left blank or 0.0 is punched for both. Equal positive or negative frequencies have a special meaning for some frequency ranges, as described on the following pages. Note that a frequency range of blank to 100.0 is treated as 0.0 to 100.0 and does not give a default value for the left hand limit.

NORMAL INPUT FOR NMR PROGRAM NUMAR

The most important items are indicated by → in the margin.

TYPE 1: TITLE

→	A 1	Must always be an asterisk *.
	A 2	Normally blank. Nonblank only if this case is one of a series with Short Form Input (see p.D-9)
	A 3	Normally blank. Master Output Control (see p.D12).
	A 8-79	Anything that you want for a title.

TYPE 2: COUPLING CONSTANTS

→	A 1	The letter L if this is the last coupling constant card for this case; otherwise blank.
→	I 2	The first group number.
→	I 4	The second group number (normally larger). (1 2) For the other (trans) coupling between two chemically equivalent pairs, reverse the order (2 1). Repeat the number (2 2) for the coupling between the two members of a pair.

TYPE 2: Continued

→	F 10-19	The coupling constant in Hz.

TYPE 3: ISOTOPIC SPECIES

→	A 1	The letter L if this is the last isotopic species for this case; otherwise blank.
	I 2	An integer equal to twice the nuclear spin of this species. The default (if left blank) is 1, meaning spin ½.
	A 3	Normally blank. Species Transition Table Control (see p. D-12).
→	A 5	Blank if no plots are to be made for this species. If any nonblank character is punched, one or more TYPE 5 cards (one per plot region) must follow the TYPE 4 cards for this species.
	A 8-19	A name for this species.
→	F 20-24	Lower intensity limit for keeping transitions calculated for this species. Default (if left blank) is 1/10000 of species total intensity. A negative value cancels all transition calculations for this species.
	F 25-29	Spectrometer frequency in MHz. (Used only to calculate ppm values for printing). Default 60.0 MHz.
	F 30-34	Grouping width. If a condensed frequency table has been selected for this species, this determines its resolution. In all transition tables a blank line is inserted at intervals of 100 times the grouping width. Default 0.05 Hz.
	F 40-49	Upper frequency limit for this species' transitions.
	F 50-59	Similar lower limit. Frequencies outside the range are not stored at all, so are missing from plots as well as tables. Default (if columns 30-49 are blank): no frequency limits for the species. Do not confuse this option with the plot frequency range on a TYPE 5 card, which affects only that plot.

TYPE 4: CHEMICAL SHIFTS

→	A 1	The letter L if this is the last chemical shift for this species; otherwise blank.
→	A 2-3	Normally blank. If this card is for a chemically equivalent pair of groups, the characters 2*.
→	I 4	The number of nuclei in the magnetically equivalent group. (A chemically equivalent pair of methyl groups would be entered as 2*3 in columns 2-4).
→	F 10-19	The chemical shift in Hz. from the species reference.

TYPE 5: PLOTS

→	A 1	The letter L if this is the last plot card for this species; otherwise blank.
→	I 2	Plot type. Blank or zero gives a line printer bar plot. Other values give Calcomp plots with different lineshape functions: 1, Gaussian; 2, Lorentzian; 3,4,5,6,7 modified Lorentzian with increasing fourth power contribution. For most Calcomp plots use 3.
	I 4	Ordinarily ignored by program. For plot cards in Short Form Input (p.D-9), the species.
	A 8-19	A title for this plot region.
→	F 20-29	The left frequency limit for this plot region.
→	F 30-39	The right limit. If the two limits are equal, all transitions of this species are included. Equal positive limits give a plot in increasing frequency order; equal negative (or zero) limits give decreasing order. In the bar plot, any large regions of blank baseline are skipped.
	F 40-44	Horizontal Scale. For bar plots, the width (Hz.) of each bar (default 0.5). For Calcomp plots: if positive, Hz/cm.; if negative, the absolute value is the plot width in cm.; default 20 cm. plot width.

TYPE 5:	Continued
F 45-49	Vertical Scale. For all plots, the default is full scale for the most intense line, and any positive value is used to multiply this scale. If the scale is negative, its absolute value is the scale factor in symbols (bar plot) or cm. (Calcomp plot) per intensity unit.
F 50-54	Left partial width at half height (Calcomp plot only).
F 55-59	Right partial width. Their sum is the line halfwidth. (Default 0.15 + 0.15 = 0.30).

SAMPLE DATA

The first thirty columns of a typical set of data for 1,1-difluoroethylene are shown. In this example the remaining columns (31-80) of all the cards would be blank. To the right of the vertical lines are card TYPE numbers and comments, none of which would appear on actual data cards.

*	1,1-DIFLUOROETHYLENE	1	Title	
1 1	4.8	2	J_{HH}	
1 2	0.7	2	J_{HF}	cis
2 1	33.9	2	J_{HF}	trans
L2 2	36.4	2	J_{FF}	
*	PROTON	3	Isotopic Species 1 (no plot, condensed table)	
L2*1	0.0	4	Chemical Shift of group 1	
L P	FLUORINE	3	Isotopic Species 2 (plots)	
L2*1	0.0	4	Chemical Shift of group 2	
L	COMPLETE	5	Plot region 1 (using defaults)	

SHORT FORM INPUT

Frequently several cases in a run are calculations on the same molecule with changes in chemical shifts, coupling constants, etc. The first case of each such series is exactly the same as it would be for a single separate calculation. For the others, a special short form of input is available in which only changes from the immediately preceding case are given.

Each case for which short form input is used begins with a TYPE 1 card that has a nonblank character in column 2. This is followed by one or more modified TYPE 2 cards. There are three kinds, labelled 2A, 2B, and 2C below; they may be intermixed in any order. Only the last TYPE 2 card, whether it is 2A, 2B, or 2C, has L in column 1. There are no TYPE 3 or TYPE 4 cards, but there can be modified TYPE 5 cards.

TYPE 2A. COUPLING CONSTANTS. Identical to a normal type 2 card.

TYPE 2B. CHEMICAL SHIFTS. Column 2: the group or pair number, in the same numbering scheme used for coupling constants. Column 4 must be blank. Columns 10-19: the chemical shift.

TYPE 2C. SPECIES DATA. Column 2 must be blank. Column 4: the species number. Columns 3 and 20-59: the same as the corresponding columns of a TYPE 3 card.

In each case with short form input, any coupling constant or chemical shift for which no new value is given remains as it was in the immediately preceding case. The default for an item left blank on a type 2C card is whatever value was in effect in the immediately preceding case, whether or not that value was itself a default.

Ordinarily all plot regions previously specified remain in effect for a case with short form input. Particularly when default frequency ranges have been used on the type 5 cards this is likely to be satisfactory. To set new plot ranges, use the letter P as the nonblank character in column 2 of the TYPE 1 card. *All previous plot ranges are then cancelled, and at least one TYPE 5 card must follow the type 2 cards of the case.* The number of the species to which the region belongs must be placed in column 4 of each of these type 5 cards. (If column 4 is left blank, the region belongs to the nonexistent species 0. A single species 0 card can be supplied when the intention is to cancel all plots for this case.) The new plot regions replace the previous ones as the default plot regions for following cases with short form input.

The sample short form data cards below could be used immediately after the cards on p. D-8 to cause two more calculations on 1,1-difluoroethylene. Fluorine transition calculations are cancelled, and the output is reduced to a condensed proton transition table (see Controlling Output).

```
*p*     1,1-DIFLUOROETHYLENE, CONTINUED.
 1 2      0.8
 2 1      33.7
L  2                -1.0
L
* *     1,1-DIFLUOROETHYLENE, STILL AGAIN.
L1 2      0.7
```

CONTROLLING OUTPUT

The printed output of NUMAR consists of a series of tables, most of which can be omitted if desired. The default is to print all tables:

INPUT DATA. Group sizes, chemical shifts, coupling constants, etc. This table is always printed.

SPECIES TRANSITION LIMITS. These few lines that follow the input data are not printed for cases with short form input.

ENERGY LEVELS. Includes quantum numbers useful in tracing subspectra. Optional.

KEY. Gives all transitions that appear in the following transition tables, arranged by transition number in groups. Shows which energy levels a transition connects. Optional.

TRANSITIONS. Each species has its own optional transition table. A full transition table includes the line number, frequency, intensity, and subspectral quantum numbers of all transitions of the species. In a condensed transition table, each series of transitions whose successive frequencies are separated by less than the Grouping Width (TYPE 3 card) is combined; only the intensity-weighted mean frequencies and the corresponding total intensities are printed.

The Master Output Control (TYPE 1 card) indicates which of the optional tables are to be printed. If it is blank, all tables are printed, including full transition tables for all species. Some nonblank characters, listed below, have special meanings; all others cancel the Energy Level and Key tables, and give condensed transition tables. The special control characters are:

E: Energy Level table, no Key; condensed transition tables.

K: Key, no Energy Level table; condensed transition tables.

F: Full transition tables; no Energy Level table or Key.

X: No Energy Level, Key, or transition tables. Used when only plots are of interest.

If the Species Transition Table Control (TYPE 3 card) is left blank, that species' transition table output is controlled by the Master Output Control as described above. If any nonblank character is punched it overrides the Master Output Control for that species only. A Species Transition Table Control has no effect on the Energy Level or Key tables, but otherwise different characters have the same meaning as above.

These Output Controls affect tables, but do not affect plots.

In cases with Short Form Input, the new Master Output Control on the TYPE 1 card overrides any Species Transition Table Control characters from the preceding cases. To override the Master Output Control, include a TYPE 2C card with a suitable nonblank character in column 3.

One can completely eliminate a species, or restrict its output to a limited frequency range; see columns 20-25 and 40-59 of the TYPE 3 card. These options affect plots as well as tables. If a species' transitions have been completely eliminated, any plot regions specified for it are ignored by the program.

HINTS

Since there is a separate transition table for each species, one has considerable freedom in entering chemical shifts. For example, when all the nuclei of a species have the same chemical shift, symmetries in the transition pattern can be made more obvious by using 0.0 as the shift.

Transition frequency calculations are made to seven significant figures. Ordinarily this lets you use the actual shifts from the species reference with accuracy of better than 0.01 Hz. However when all the shifts of a species are several kHz. to one side of the reference (as in many fluorine spectra) it is a good idea to add a constant to all the shifts of the species, reducing their absolute values. This amounts to a change of reference frequency.

Be especially careful about plot cards. There must be a nonblank symbol punched in column 5 of the TYPE 3 card if there are any plot (TYPE 5) cards for that species. Conversely, if column 5 of a TYPE 3 card is blank there must not be any plot cards for that species.

Some current limits: 9 groups, 9 plot cards, 6 species. There are several internal limits that depend on the number and size of groups. If you exceed one, greater use of the X-approximation (species factoring) may help. Maximum use of available factoring also saves considerable computer time.

Occasionally it is necessary to use the species frequency limits, and perhaps raise the minimum intensity. A very large molecule may excede the limit of 2500 transitions per species, making it impossible to sort them all. One must recalculate the spectrum with a small enough frequency range that under 2500 transitions are included.

The remaining transitions of interest are then calculated in the immediately following case or cases, using new frequency limits specified on TYPE 2C cards (see Short Form Input). The program saves considerable computer time by going straight to the transition calculations when it finds a case with Short Form Input and no changes in chemical shifts or coupling constants.

If fairly weak lines are of interest, one must be careful to specify a sufficiently low Minimum Intensity Limit on the Type 3 card. The default value may give a calculated spectrum in which some weak lines are missing, and others (which are superpositions of many weak transitions, some below the limit) have less than their correct relative intensity.

APPENDIX E. ITERATIVE ADJUSTMENT OF NMR PARAMETERS

Several methods of obtaining chemical shifts and coupling constants have been discussed above, particularly in §3.3 and §4.1. None of them yields exact values for the parameters. This is obvious when, for example, borderline X factoring is used deliberately to obtain approximate values. It is also true when parameters are obtained from the algebraic solution for a simple subspectrum, since the experimental frequencies used in the calculation are not known exactly. The influence of experimental error can be greatly reduced if the observed frequencies of other lines, in addition to the few that belong to simple subspectra, can be used to help determine the values of the NMR parameters.

Various least squares methods[17,18] have been developed in an attempt to obtain the best available parameter estimates. Each method uses a computer program, and involves a similar series of steps. The program calculates a spectrum from a set of starting parameters previously obtained. The analyst then matches up lines in this spectrum with their observed counterparts, so that whenever possible an observed frequency is assigned to each calculated transition. The program then adjusts the approximate chemical shifts and coupling constants to minimize the sum of the squares of the differences between observed and calculated frequencies.

As the relationship between the NMR parameters and the transition frequencies is not linear, the corrected parameters are themselves only approximations to the true least squares parameters. However, if the original assignment was correct, they will normally be closer to the least squares values than were the starting values. Thus after several repetitions of the adjustment step one obtains a set of parameters that represents the best available estimate of the experimental parameters consistent with the assignment made.

A useful byproduct of the iteration procedure in all of the common iterative programs [17,18] is an estimate of the probable error in each NMR parameter, derived from the residual differences between the observed and calculated spectra.

All of the programs mentioned above lead to similar values for the least squares parameter estimates, but they make use of two fundamentally different approaches to the calculation.

In the approach[18] based on the NMREN/NMRIT programs of Swalen and Reilly,[18a] attention is focussed on the pattern of energy levels of the spin system. Each observed transition that is correctly assigned provides information about the relative positions of two energy levels; collectively, all of the observed transitions assigned to a matrix$_2$

must provide information about the positions of all of the energy levels of the matrix_2. In the NMREN step, this information is used to provide a linear least squares solution for all of the 'observed' energy levels, E_{obs}, with each matrix_2 treated separately.

In the NMRIT step, an approximate Hamiltonian matrix $\mathcal{H}_{approx}$ is calculated (using the same starting parameters used previously when assigning the observed transitions to the energy level diagram) and diagonalized.

$$U^{-1}\,\mathcal{H}_{approx}\,U = E_{calc} \tag{E.1}$$

The transformation matrix U that relates the basis and diagonal representations of $\mathcal{H}_{approx}$ is used to generate from E_{obs} the diagonal matrix elements $\mathcal{H}_{ii}$ of an improved Hamiltonian matrix.

$$\mathcal{H}_{ii} = (U\,E_{obs}\,U^{-1})_{ii} \tag{E.2}$$

These diagonal matrix elements are used in a least squares solution for a new set of NMR parameters. An ingenious feature of this second least squares step is that no explicit matrix inversion is required, because the normal equations are diagonal.[18a] The new parameters are used to calculate a new $\mathcal{H}_{approx}$, and so on. NMRIT is repeated until additional iterations fail to reduce the residual errors in the $\mathcal{H}_{ii}$ values.

The NMREN/NMRIT approach is not well suited to calculations with full factoring. In the NMREN step, chains of transitions extending throughout a matrix_2 are needed to establish the relative positions of the energy levels. As a result, the least squares solution for E_{obs} of each matrix_2 requires the inversion of a large coefficient matrix equal in size to the matrix_2. Even if sufficient main storage is available for NMREN, other difficulties remain. Only the diagonal matrix elements are used in NMRIT to calculate new parameter estimates. If the frame symmetry basis (2.24) is used, the symmetrized coupling constants $J_{m\ell}$ of Eq. (2.22) do not appear in the diagonal matrix elements, so will not be adjusted.

The NMREN/NMRIT method of calculation also leads to considerable difficulty in calculating meaningful error estimates for the final parameters. Ferguson and Marquardt[18b] use a more elegant procedure than Swalen and Reilly,[18a] but both calculate only the contribution of the errors in E_{obs} to the errors in the parameters. They ignore the additional errors from the residual differences between H_{ii} obtained from (E.2), and the diagonal matrix elements of H_{approx} obtained with the final parameters. In principle, this error contribution could be included, but there is no obvious way to estimate the errors introduced by the deliberate exclusion of off-diagonal matrix elements from NMRIT.

All of these difficulties are avoided in the LAOCOON approach introduced by Castellano and Bothner-By,[17a] which focusses attention directly on the relationship between transition frequencies and parameters. In the trial spectrum used for the assignment step, each calculated transition is accompanied by a single origin number which unambiguously designates the energy levels connected by the transition. However, when the analyst assigns an observed transition frequency to an origin number, he need not know which energy levels the transition connects. There is no need to include sufficient transitions to produce a fully connected energy level diagram, because there is no step analogous to NMREN.

In the iterative step of LAOCOON,[17a] a matrix of partial derivatives, $\partial\nu_j/\partial p_i$, of the transition frequencies ν, with respect to the NMR parameters p (chemical shifts and coupling constants), is calculated. These partial derivatives are obtained from the differences between appropriate eigenvalues of an approximate Hamiltonian $\mathcal{H}_{approx}$ (see Eq. (E.1)).

$$\partial\nu_j/\partial p_i = \partial E_m/\partial p_i - \partial E_n/\partial p_i \qquad \text{(E.3)}$$

The partial derivatives of the eigenvalues have been shown[17a] to be identical to the diagonal elements of $U^{-1}(\partial\mathcal{H}_{approx}/\partial p_i)U$. Thus partial derivatives of both the diagonal and off-diagonal elements of H_{approx} are calculated in the basis representation, and transformed using the eigenvectors.

These partial derivatives are used to calculate corrections Δp to all of the parameters p being adjusted

$$\sum_i (\partial \nu_j/\partial p_i)\Delta p_i = (\nu_{\text{obs}}-\nu_{\text{calc}})_j \qquad \text{(E.4)}$$

The least squares solution to these equations gives the corrections to the parameters for use in calculating H_{approx} for the next iteration.

The LAOCOON method has been adapted for calculations using magnetic equivalence,[17b] and is quite suitable for a program, such as NUMAR, that uses full factoring.[†] The transformation of the partial derivatives from the basis representation is readily done one matrix_4 at a time, and the matrix of coefficients which must be inverted to obtain the Δp values is only as large as the number of parameters.

Because the LAOCOON least squares solution involves the entire Hamiltonian, and relates parameters to transitions directly, it produces far more reliable estimates of the errors in the parameters than does NMREN/NMRIT.

[†] C.W. Haigh (private communication) has adapted the LAOCOON method of iteration to a program LACX, which uses X factoring and limited twofold frame symmetry.

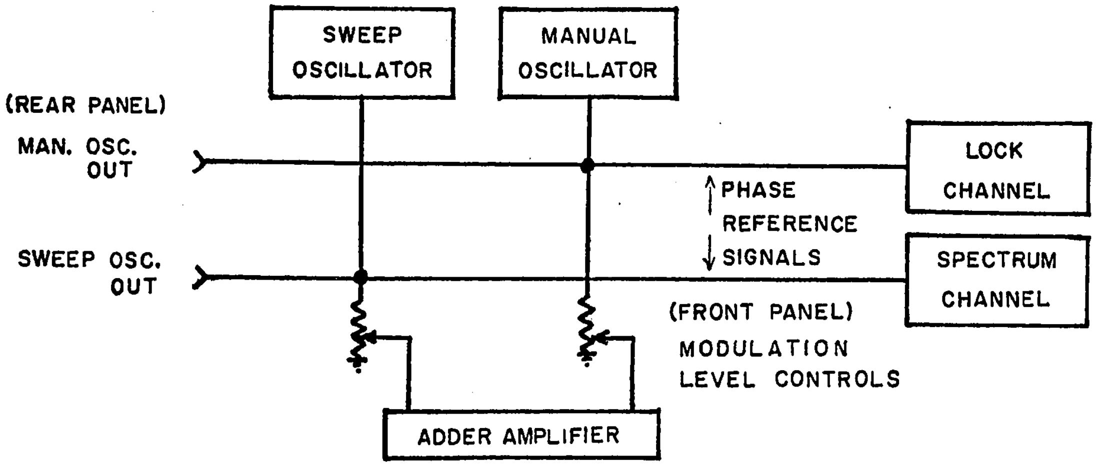
An iterative parameter adjustment step following the LAOCOON approach to iteration could be added to the NUMAR program with a minimum of difficulty. Most of the data required to calculate the parameter corrections (basis functions, eigenvalues, and eigenvectors) is already placed in auxilliary storage by the present program; observed transition frequencies, in order of line number, could readily be placed in auxilliary storage in the INPUT step.

One could therefore add the parameter adjustment step as a completely independent subroutine (ADJUST in Fig. 4-1) with negligible changes in existing subroutines. ADJUST would require main memory space for a matrix of coefficients as well as for eigenvector matrices for a transformation similar to that in TRANS. It would therefore become the step limiting problem size for an iterative calculation; one could, if necessary, allow larger matrices$_4$ for non-iterative calculations.

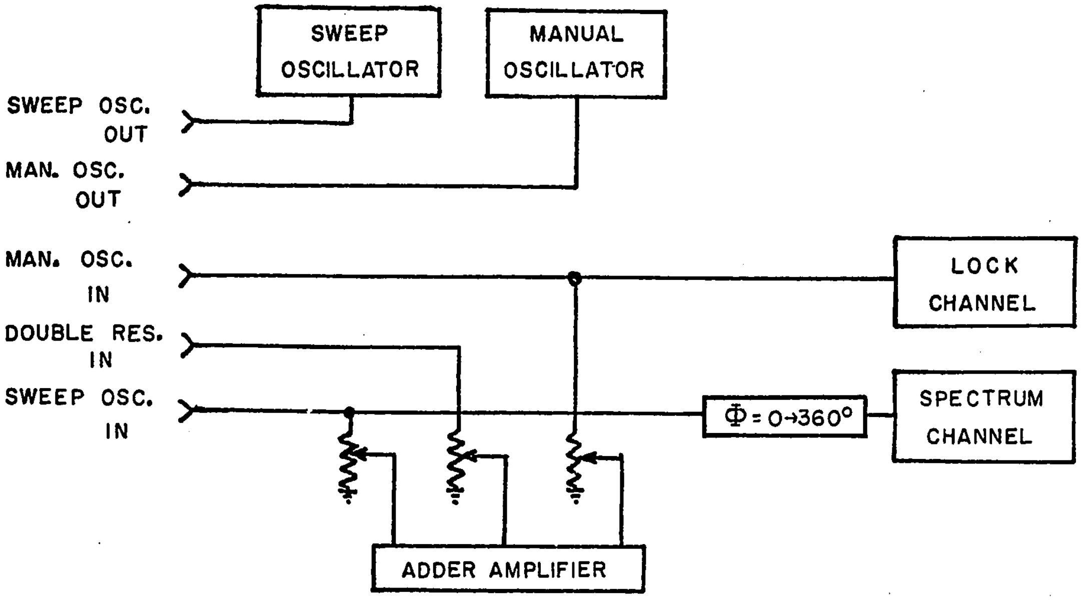
APPENDIX F. MODIFICATIONS TO VARIAN SPECTROMETERS; INDOR METHODS.

A Varian HA-60I spectrometer has been modified to permit INDOR spectroscopy [16] and to make large lock offsets more convenient. Varian HA-100-12 and HA-100-15 spectrometers have been slightly modified to permit more convenient use of large lock offsets. All modifications are in the V4354 Internal Reference Stabilized NMR Controllers, which provide audio frequency magnetic field modulation, and detect signals at the modulation frequencies. They are, therefore, effective for all radiofrequencies at which the spectrometers operate.

Figure F-1(a) shows a partial circuit diagram of the V4354 controller before modification. The Manual Oscillator can be set by hand to any frequency in the range 1500-3500 Hz., and the Sweep Oscillator, whose frequency is linked to recorder position, can sweep any of several frequency ranges all beginning at 2500 Hz., the widest extending to 3500 Hz. Sidebands of the basic radiofrequency (eg. 56.4 MHz. for ^{19}F) are obtained by modulating the magnetic field at the audiofrequencies produced by these two oscillators. In Frequency Sweep mode, the Manual Oscillator sideband corresponds to the resonance frequency of the reference compound, and the Sweep Oscillator sideband is swept through the frequency



(a) ORIGINAL CIRCUIT



(b) MODIFIED CIRCUIT

FIG. F-1. MODIFICATIONS TO VARIAN V-4354 CONTROLLER. (SIMPLIFIED PARTIAL CIRCUIT DIAGRAMS) region whose spectrum is of interest.

An audiofrequency phase shifter was inserted in the reference phase path of the spectrum phase detector, in both the HA-100-12 and HA-100-15 spectrometers. To offset the signal loss from the phase shifter the gain of the phase detector was increased. Otherwise, no wiring changes were made. When large lock offsets were used, the radiofrequency phase was adjusted for maximum lock signal, and the audiofrequency phase was adjusted to give an absorption mode spectrum.

For the spectra at 94.1 and 100.0 MHz. (Chapter 5), the internal manual oscillator of each spectrometer was disabled by the removal of its Oscillator Amplifier circuit card. The output of a Hewlett-Packard 5100B/5110B frequency synthesizer was fed in through the Man. Osc. Out jack (Fig. F-1(a)) to provide stable lock frequencies up to 16 kHz.

The more thoroughly modified circuit of Fig. F-1(b), used in the HA-60I, allows a wider variety of operating modes. An external oscillator for large lock offsets is simply connected to Man. Osc. In; the phase shifter (as described above) allows correct adjustment of both lock and observing phases. For normal operation, essentially as in Fig. F-1(a), Man. Osc. Out is connected to Man. Osc. In, and Sweep Osc. Out to Sweep Osc. In. The third modulation input simplifies low power double resonance experiments.[15] The use of the modified spectrometer for INDOR[16] is described below.

For all 56.4 MHz. ^{19}F spectra (§5.1), a Hewlett-Packard 5100B/5110B frequency synthesizer was connected to Man. Osc. In to provide stable lock frequencies up to 11 kHz.

For the 56.4 MHz. INDOR spectra of §5.1, the frequency synthesizer was set to 10640.00 Hz. With the internal sweep oscillator connected to Sweep Osc. In, a conventional spectrum of the =C-F region was obtained. The recorder was adjusted to bring the low field member of the central doublet into resonance, and the sweep oscillator frequency was measured using a Hewlett-Packard 5245L counter in period average mode. The internal Manual Oscillator was then adjusted to this same frequency (about 2540 Hz.), and connected to Sweep Osc. In. It was discovered that the Manual Oscillator had a short term stability of ±0.02 Hz. (measured at 5 second intervals) and would typically drift only about 0.05 Hz. in 1000 seconds. The modulation level for the observing channel was set to produce slight saturation.

The INDOR sweep frequency ν_2 was obtained by connecting a Data Royal F230B voltage controlled oscillator to the Double Resonance In jack. The oscillator was swept from 6800 to 6900 Hz. (i.e. through the $-CF_3$ resonances) in about 1000 seconds by its internal ramp generator, while the Varian recorder was swept across the chart paper on its 1000 second sweep time setting.

For ^{1}H homonuclear INDOR experiments no external INDOR sweep oscillator is needed. With a suitable choice of lock frequency, the INDOR sweep range can be made to coincide with the sweep range of the internal sweep oscillator. After initial setup similar to that above, Sweep Osc. Out is connected to Double Resonance In and Man. Osc. Out to Sweep Osc. In for the actual INDOR spectrum.

APPENDIX G

CALIBRATION OF SPECTRA

A basically similar procedure was followed in the calibration of all NMR spectra used in §5.1 and §5.2. At a number of calibration points across each spectrum, pen position was read to ±0.01 cm. from the chart paper grid, and sweep frequency was read to ±0.01 Hz. using a Hewlett-Packard 5245L counter in period average mode. These position/frequency pairs were used as input to a computer program which obtained a least-squares quadratic equation for frequency as a function of chart position. The frequencies of the spectral lines were then obtained from their chart positions, using the calibration equation.

Higher order polynomials were tried for some spectra, but in every case the estimated errors in the cubic and higher coefficients were much larger than the coefficients themselves. Fewer than five calibration points were available for some spectra; in these cases, a linear calibration equation was used.

For the ^{19}F single resonance spectra of §5.1, the calibration points were obtained by stopping the sweep between peaks while the spectrum was being recorded. The RMS deviation of the calibration points from the least squares curve was typically 0.05 Hz.

For the ^{19}F INDOR spectra at 56.4 MHz., the sweep could not be stopped during frequency measurements.

During that time when a frequency measurement was being taken, the recorder pen was lifted from the paper to mark the location. The resulting calibration was estimated to be accurate to ±0.1 Hz. Because of the poor signal to noise ratio in the INDOR spectra, the positions of the INDOR peaks were estimated to be accurate only to ±0.15 cm. (±0.3 Hz.); averages from several INDOR spectra were used to identify corresponding single resonance peaks whose frequencies were better known.

The methine proton spectra of the 2,5-dimethyl-3-hexenes were obtained without interrupting the sweep. A number of strong, well resolved peaks were then chosen as calibration points. Their frequencies were determined individually to 0.01 Hz., with the recorder stationary at the position of maximum pen deflection. Special care was taken to avoid saturation. At least two determinations, in which the peak was approached from opposite sides, were averaged for each calibration peak. This procedure nearly eliminated systematic errors resulting from the finite sweep rate in the original spectrum. The RMS deviation of calibration peaks from the least squares curve was typically ±0.03 Hz.

In the methyl and olefin regions of these molecules the frequency of every strong line was obtained directly, following the same procedure used for the methine calibration peaks.