

**Analysis of the Microwave Spectrum of bis-Trifluoromethyl Nitroxide**

by

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(ABSTRACT)

The microwave spectrum of the stable free radical bis-trifluoromethyl nitroxide was analyzed in the 20 to 26.5 GHz region. 39 transitions have been assigned. The rigid rotor rotational constants determined by calculation of the hypothetical unsplit rotational transitions are  $A = 2256.94$  MHz,  $B = 1056.08$  MHz, and  $C = 971.51$  MHz.  $k = -0.868$

A program to calculate the fine and hyperfine splitting patterns was written which reproduced the experimentally observed splittings. The spin-rotation coupling constants are  $\epsilon_{aa} = -3597.7$  MHz,  $\epsilon_{bb} = -1121.4$  MHz, and  $\epsilon_{cc} = 29.8$  MHz. The magnitude of  $\epsilon_{cc}$  indicates that the unpaired electron is in an orbital extending perpendicularly to the molecular plane. The determined magnetic hyperfine coupling constants are  $T_{aa} = -183.74$  MHz,  $T_{bb} = -177.77$  MHz,  $T_{cc} = 361.51$  MHz, and  $a_F = 22.8$  MHz. The spin density on the fluorine atom is 11.9% which is estimated from the value of  $T_{cc}$ . The value of the Fermi coupling constant  $a_F$  indicates that the unpaired electron occupies an unhybridized p orbital. An insufficient number of unsplit rotational transitions were assigned to allow a centrifugal distortion analysis to be performed.

Since isotopic substitution was not feasible an  $r_0$  structure was determined by doing a least squares fit of the three moments of inertia. The following parameters were not allowed to vary during the least squares fit:  $r_{CF} = 1.32\text{\AA}$ ,  $r_{CN} = 1.441\text{\AA}$ ,  $F - C - F = 109.8^\circ$ . The calculated structure gave a N-O bond length of  $1.212\text{\AA}$ , a C-N-O angle of  $116.9^\circ$ , a C-N-C angle of  $126.2^\circ$ , and an angle which measures the deviation of the O atom from the CNC plane of  $0^\circ$ .

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# Chapter I

## Introduction

The purpose of this work was to investigate the microwave spectrum of bis-trifluoromethyl nitroxide. This is the first compound in which there is fine and hyperfine structure due to six coupled nuclei to be investigated by microwave spectroscopy. Therefore the primary emphasis of this study was to develop the theoretical basis for analysis of the microwave spectrum.

From the analysis of the fine and hyperfine splittings of several transitions between low rotational energy levels the diagonal elements of the fine and hyperfine coupling constants and the Fermi contact constant can be determined. Using these values the hypothetical unsplit rotational transitions can be calculated and the principal moments of inertia determined. From the three moments three of the eight bond lengths/angles of the molecular structure can be determined. The position of the orbital, relative to the molecular plane, in which the unpaired electron resides can be examined by considering the relative magnitudes of the spin-rotation interaction constants. The spin density on the fluorine atoms can be estimated from the magnitudes of the dipolar coupling constants. The magnitude of the Fermi contact term will give some insight into the hybridization of the F orbitals.

Because of the unusual stability of this radical it was possible to construct and test a spectrometer designed specifically to observe the microwave spectra of paramagnetic species. A semi-confocal Fabry-Perot resonant microwave cavity spectrometer was chosen because of its simplicity of construction and high sensitivity. The construction and implementation of this system has provided valuable information relative to the construction of another cavity system which will be used to obtain the microwave spectra of transient free radicals.

# Chapter II

## Review of Prior Research

This chapter is composed of three parts. The first is a brief historical background on the development of high resolution spectroscopy of free radicals. The second section details the previous structural and EPR studies of bis-trifluoromethyl nitroxide,  $(\text{CF}_3)_2\text{NO}$ . The final section discusses the microwave study of the trifluoromethyl,  $\text{CF}_3$  radical.

According to Herzberg<sup>19</sup>, the concept of the free radical dates back to the 19<sup>th</sup> century. The chemically stable triphenylmethyl,  $(\text{C}_6\text{H}_5)_3\text{C}$ , radical was identified in the early 20<sup>th</sup> century<sup>20</sup>. This proof that free radicals existed prompted heightened interest in the study of free radicals. However, because of the transient nature of most free radicals, characterization remained a formidable task. The first transient radicals identified, primarily diatomics, were found in flames and electric discharges through analysis of their emission spectra. The development of quantum mechanics provided the spectroscopist with the theoretical basis to interpret the spectra of many diatomic free radicals in the 1920's and 30's.

Development of radar techniques during World War II led to new spectroscopic techniques, in particular electron paramagnetic resonance (EPR) and zero field microwave spectroscopy. EPR has been successfully applied to a number of free radicals, both those trapped in inert matrices and

the gas phase. The hyperfine coupling constants and g factors give information about the electronic environment of the molecule which is not available from optical spectroscopy. Microwave spectroscopy improved the precision in the determination of molecular parameters but it wasn't until 1955 that the first free radical, OH, was detected by Townes and co-workers<sup>21</sup>. Nine years would pass before the second radical, SO, was observed<sup>22</sup> using microwave techniques. In the two decades since that time many other techniques have been developed to record the spectra of transient species, in addition to improvements in EPR and microwave instrumentation, to the point that the main limitation now is the generation of the radicals themselves and the theoretical basis for the analysis of spectra obtained from studies of molecules with a large number of coupling nuclei.

Bis-trifluoromethyl nitroxide was first ~~first~~ synthesized, isolated, and characterized by Blackley and Reinhard<sup>23</sup> in 1964. At room temperature it is a purple gas. On cooling it condenses to a reddish-brown liquid and solidifies to a yellow solid. It was found to be chemically inert to water, aqueous sodium hydroxide, air, stainless steel, copper, glass, fluorotrichloromethane, and benzene. The infrared spectrum of the radical exhibited absorptions at 728, 995, and 1200-1300  $\text{cm}^{-1}$  which are characteristic of the  $(\text{CF}_3)_2\text{N}$  group. A comparison of the  $^{19}\text{F}$  NMR spectrum with the NMR data for several related compounds indicated the six fluorine atoms are equivalent. The intensity ratio of the nine lines observed in the EPR spectrum agreed well with the theoretical predictions for six equivalent fluorine atoms of two trifluoromethyl groups. Analysis of the EPR spectrum as a function of temperature showed that the change in color corresponded to a decrease in radical concentration upon cooling.

Scheidler and Bolton<sup>24</sup> examined the EPR spectrum of  $(\text{CF}_3)_2\text{NO}$  in  $\text{CFCl}_3$  in the temperature range from  $-163$  to  $297\text{K}$ . The temperature dependence of the fluorine Fermi interaction constant was determined to obey the relationship

$$a_F = 9.327 - 0.0036T \quad [2.1]$$

where  $a_F$  is in gauss and T in Kelvin. This temperature dependence was postulated to be due to partial conjugation of the fluorine p orbitals with the nitrogen  $2p_z$  orbital. At lower temperatures

the fluorine nuclei are still equivalent but configurations favorable to conjugation could be more heavily weighted. This would lead to a larger transfer of spin to the fluorine atoms at lower temperatures.

Morokuma<sup>25</sup> advanced a molecular orbital interpretation of the results obtained by Scheidler and Bolton. The calculations were performed using the unrestricted SCF method in the INDO approximation. Through comparison of calculations and EPR data for the isoelectronic molecule hexafluoroacetone ketyl,  $[\text{OC}(\text{CF}_3)_2]^-$ , which does not exhibit any temperature dependence in its EPR spectrum, he found that the barrier to rotation of the  $\text{CF}_3$  group was higher in bistrifluoromethyl nitroxide than in hexafluoroacetone ketyl. However, this difference could not adequately explain the observed temperature dependence or why  $[\text{OC}(\text{CF}_3)_2]^-$  does not exhibit this dependence.

A detailed theoretical analysis of the temperature dependence of the EPR spectrum was reported by Underwood and Vogel<sup>26</sup>. The calculations were again performed using the SCF method in the INDO approximation. The initial geometry was assumed to be planar except for the F atoms and the remaining parameters were varied to determine the structure of lowest energy. Then, using this geometry, the structure was allowed to deviate from planarity at the N atom. The lowest energy corresponded to the NO bond being  $10^\circ$  out of the CNC plane. The calculated geometry is listed in Table 1. The energy required for deformation of up to  $30^\circ$  from planarity was calculated to be about 600 cal. and had an inversion barrier of 53 cal. They concluded that deviation from planarity is the only possible molecular distortion which could reasonably account for the temperature dependence.

The EPR spectrum of the gas was examined by Schaafsma and Kivelson<sup>27</sup> in 1968. They determined the Fermi Contact interaction to be  $1.46 \times 10^8$  rad/sec. The root-mean-square spin rotational constant,  $C^2$ , was determined to be  $6.5 \times 10^7$  rad/sec. Unfortunately, insufficient data was reported to determine the spin rotational constants which are required for the present analysis.

The molecular structure was determined via electron diffraction (ED) by Glidewell<sup>28</sup> and co-workers. They assumed that all CF bond lengths were identical, the two CN bond lengths are equal, and that the oxygen atom is equidistant from the carbon atoms. The vibrational amplitudes

Table 1. Molecular Structure Derived from SCF Calculation

NO	$1.26 \pm 0.01\text{\AA}$
NC	$1.41 \pm 0.01\text{\AA}$
CF	$1.34 \pm 0.01\text{\AA}$
ONC	$117 \pm 1^\circ$
NCF	$111 \pm 1^\circ$
$\Delta$	$10 \pm 1^\circ$

---

were also constrained to specific values. The structure determined is given in Table 2. It was determined that the  $\text{CF}_3$  group appears to be staggered with respect to the opposing CN bond. The calculated structure was found to be somewhat sensitive to the choice of vibrational amplitude of the NF distance. The deviation from planarity was explained through comparison of the structure of  $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ . The argument was essentially that since oxygen is smaller than nitrogen a greater deviation from planarity was possible.

The most recent study reported on bis-trifluoromethyl nitroxide was by Compton<sup>29</sup> and co-workers on the infrared and Raman spectra. If the estimation of vibrational amplitudes in the ED study were incorrect then a planar or quasi-planar structure could give results indicative of a non-planar structure. For bis-trifluoromethyl hydroxylamine,  $(\text{CF}_3)_2\text{NOH}$ , the angle measuring the deviation from planarity was determined by ED<sup>30</sup> to be  $43^\circ$ . If the nitrogen had tetrahedral geometry this angle would be  $55^\circ$ . The smaller angle was hypothesized to be a result of conjugative delocalization of the unpaired electron from oxygen to nitrogen which increases the polarity and decreases the length of the bond. These factors favor planarity at the N atom. The Raman spectrum of the radical contained only seven polarized bands. If the molecule had  $\text{C}_s$  symmetry thirteen are expected and if  $\text{C}_{2v}$  symmetry, only eight. The authors felt that the probability of six polarized lines being too weak to be observed was quite small and therefore concluded that the molecule was planar.

A full Hartree-Fock calculation was performed by Dr. Michael Palmer<sup>31</sup>, using the structure derived from the ED study, in order to determine the electron populations of the constituent atoms. Approximately 65% of the unpaired electron resides on the oxygen, 24% on the nitrogen, 10% on the six fluorines and approximately 1% on the C atoms.

**Table 2. Molecular Parameters Derived From Electron Diffraction**

	1.26(3)Å
NO	1.441(8)Å
CN	1.320(4)Å
CF	109.8(2)°
FCF	120.9(2)°
CNC	117.2(0.6)°
ONC	21.9(3)°
Δ	

---

The microwave spectrum of the trifluoromethyl radical in the ground vibrational state was analysed by Endo<sup>32</sup> and co-workers. The theory for the hyperfine structure due to three identical nuclei in a  $^2A_1$  vibronic state was examined in detail from which an expression for the matrix elements was derived. In the analysis of the microwave spectrum, the matrix elements off-diagonal in  $K$  were neglected. The difference in observed and calculated frequency showed no systematic dependence on the  $K$  values thus justifying consideration of only those matrix elements diagonal in  $K$ . The matrix element diagonal in  $K$  is identical to that for a single nucleus<sup>33</sup> with spin 3/2. Table 3 lists the molecular constants determined from the study. The spin density on one fluorine nucleus was found to be 12.3%. The very small value of  $\epsilon_{cc}$  was explained on the basis of orbital symmetry. The very large value of  $a_F$  is due to the fact that the unpaired electron resides in an orbital which is considerably  $sp$  hybridized.

**Table 3. Molecular Constants for the Trifluoromethyl Radical**

$B_0$	10900.9118(52)
$D_N$	0.013882(87)
$D_{NK}$	-0.02343(17)
$\epsilon_{bb}$	-36.500(42)
$\epsilon_{cc}$	3.35(15)
$a_F$	408.5(16)
$T_{cc}$	320.01(20)
$ T_{aa} - T_{bb} $	40.1(49)

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# Chapter III

## Review of Theoretical Concepts

### *Angular Momentum*

#### Group Theoretical Background

The principle of conservation of angular momentum is of fundamental importance in the quantum mechanics of a many-particle system. First, the relevance of conservation of angular momentum in a classical system will be discussed. Next it will be shown how it is related to the symmetry of the Hamiltonian. A constant of the motion is a function which does not change with time. In classical mechanics a knowledge of all the constants of the motion amounts to a solution of the equations of motion. For any time independent function,  $u$ , of the canonical variables the commutator of  $u$  with the Hamiltonian is zero.

$$\frac{du}{dt} = [u, H] = 0 \quad [3.1]$$

An infinitesimal transformation is defined as a transformation which changes the canonical variables  $q_i, p_i$  ( $i = 1, 2, \dots, n$ ) by an infinitesimal amount:

$$q_i \rightarrow q'_i = q_i + \delta q_i \quad [3.2]$$

$$p_i \rightarrow p'_i = p_i + \delta p_i \quad [3.3]$$

The generating function  $F$  of the infinitesimal transformation<sup>1</sup> differs only infinitesimally from the generating function of the identity transformation,  $\sum_i q_i p'_i$ . Therefore

$$F = \sum_i q_i p'_i + \varepsilon G(q, p') \quad [3.4]$$

where  $\varepsilon$  is an infinitesimal parameter.  $G(q, p')$  is also called the generating function of the infinitesimal transformation. The change in  $u$  due to this transformation is

$$\delta u = \varepsilon [u, G] \quad [3.5]$$

Since  $u$  and  $H$  commute we have

$$\delta H = \varepsilon [H, G] \quad [3.6]$$

Therefore the constants of the motion are the generating functions of the infinitesimal transformations which leave  $H$  invariant.

In particular the components of angular momentum are the generating functions of the infinitesimal rotations about the corresponding axes of the frame of reference. The group of transformations which leave  $H$  invariant, denoted as the group of the Hamiltonian, contains the group  $SO(3)$  of rotations in three dimensional space. The Wigner-Eckart theorem<sup>2,3</sup> states that if  $T$  is an element of the arbitrary group  $G_H$  of the Hamiltonian  $H$ , and if  $u$  is an eigenvector of  $H$ , then  $Tu$  is also an eigenvector of  $H$  with the same eigenvalue. Therefore, all eigenvectors of  $H$  belonging to a given irreducible representation of  $G_H$  are degenerate in energy.

For a system with rotational symmetry, the theorem implies that the angular momentum eigenvectors are eigenvectors of the energy and that the set of states with the same total angular

momentum and different values of the z-component are degenerate. Let us now define some of the terms in the preceding paragraph.

The concept of a group is a generalization of the properties of a mathematical system of interest. An abstract group is defined without reference to any particular physical or mathematical system. It is a set of elements among which a law of composition is defined such that the composition of any two elements  $a$  and  $b$  of the group taken in this order and denoted by  $ba$  ( $ba$  is not necessarily equal to  $ab$ ) is an element of the set.

The following conditions must be added to this property: 1)  $c(ba) = (cb)a$ , 2) there exists a unit element  $1$ , such that  $1a = a1 = a$ , and 3) to each element  $a$  there exists a corresponding inverse  $a^{-1}$  such that  $aa^{-1} = a^{-1}a = 1$ .

The order of a group, the number of elements, may be finite, or denumerably or nondenumerably infinite. A subgroup  $h$  of a group  $g$  is a set of elements of  $g$  which itself fulfills the group conditions. Therefore, the unit element must belong to  $h$ , and if  $a$  and  $b$  both belong to  $h$ , then so do  $a^{-1}$  and  $ba$ .

Only those groups which are nondenumerably infinite will be considered further. Consider the set of all linear homogeneous transformations on an  $n$ -dimensional vector space. This set forms a group with respect to matrix multiplication and is known as the full linear group  $GL(n)$ . The subgroup of  $GL(n)$  which has as its elements only unitary transformations is denoted by  $U(n)$ . We restrict  $U(n)$  even further to only those unitary matrices which are unimodular, that is have a determinant equal to  $+1$ . This group is called the special unitary group  $SU(n)$ . Finally, the group of all real linear homogeneous transformations on an  $n$ -dimensional space which preserves the distance between two points, the rotations and reflections about the origin, is called the orthogonal group  $O(n)$ . It corresponds to the set of all real  $n \times n$  matrices. We will be particularly interested with rotations in 3-space, the unimodular orthogonal group  $SO(3)$ .

How are the elements of  $GL(n)$  and its subgroups labelled? For  $GL(n)$   $n^2$  complex numbers would be necessary since the elements are independent. Imposition of restrictions will reduce the number of independent quantities. For the rotation group  $SO(3)$  only three real numbers are needed. These three numbers are most usefully defined in terms of the Euler angles.

The displacement of a rigid body about a fixed point may be obtained by performing three rotations about two of three mutually perpendicular axes fixed in the body. A right-handed frame of axes is assumed with a positive rotation about a given axis being one which would carry a right handed screw in the positive direction along that axis. These assumptions define the phases of matrix elements of finite rotations. The rotations are to be performed successively in the order (see Figure 1):

1) A rotation  $\alpha$  ( $0 \leq \alpha \leq 2\pi$ ) about the z-axis, bringing the axis from the initial position S into the position S'.

This is the vertical axis of rotation.

2) A rotation  $\beta$  ( $0 \leq \beta \leq \pi$ ) about the y-axis of the frame.

S' is called the line of nodes. The resulting position is symbolized by S''.

3) A rotation  $\gamma$  ( $0 \leq \gamma \leq 2\pi$ ) about the z-axis of the frame

S'', called the figure axis. The position of this axis depends on  $\alpha$  and  $\beta$ . The final position of the frame is symbolized by S'''.

A rotation  $\theta$  about an axis  $\zeta$  is represented by the operator  $D_{\zeta}(\theta)$ . Operators corresponding to successive rotations are ordered from right to left. It can be shown that

$$D_{z''}(\gamma)D_{y'}(\beta)D_z(\alpha) \equiv D_z(\alpha)D_y(\beta)D_z(\gamma) \quad [3.7]$$

A very important part of the theory of groups is concerned with the representation of the elements of a group by linear transformations. A representation of degree n of a group G means that to every element a of G is assigned a linear transformation T(a) on a vector space  $R_n$  of dimension n in such a way that these linear transformations obey the law of composition

$$T(a) \cdot T(b) = T(ab) \quad [3.8]$$

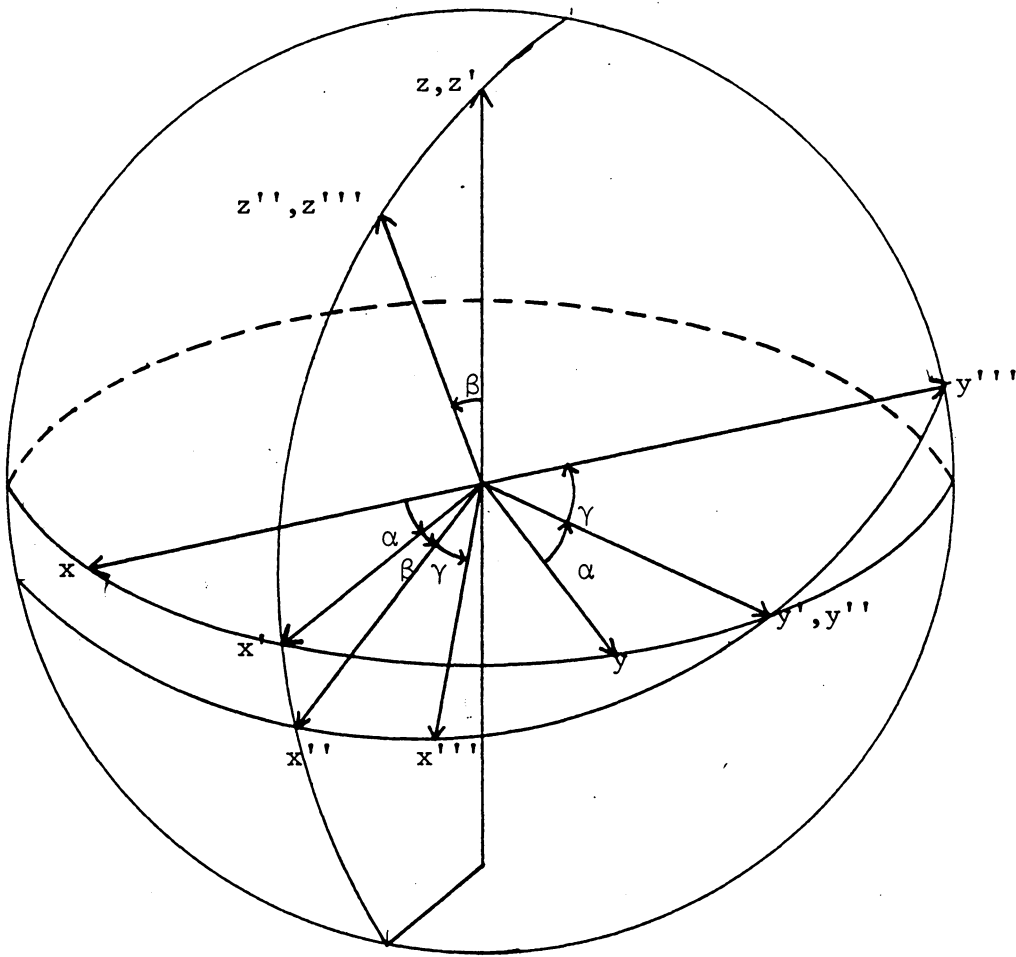


Figure 1. Euler's Angles of Rotation

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A faithful representation is the case in which to each group element corresponds a distinct transformation. By choosing the identity transformation for every transformation Eqn 3.8 is always satisfied.

When a definite coordinate system is chosen in  $R_n$  each  $T(a)$  corresponds to a square nonsingular matrix. The orthogonal unit vectors which establish this coordinate system are called the basis of the representation. If the coordinate system is replaced with another through a transformation  $S$ ,  $a$  will be represented by the transformation  $ST(a)S^{-1}$ . This also is a representation of  $G$ , and is said to be equivalent to the former representation.

Consider a subspace  $R'$  of  $R$  such that all vectors lying in this subspace are transformed by a transformation  $T$  into vectors of  $R'$ . The subspace  $R'$  is invariant under the transformation  $T$ . If  $R'$  is invariant under all transformations  $T(a)$  representing the group  $G$ , the transformations  $T'(a)$  which are induced in  $R'$  also give a representation of  $G$ . Consider the transformations as matrices. It is possible to choose a basis set such that all the representation matrices in a given representation take the form shown in Figure 2. The submatrix  $P$  corresponds to transformations on the subspace  $R'$ . A representation based on a space  $R$  is called irreducible if  $R$  contains no subspace other than itself and the null space which is invariant under  $T(a)$  representing the group  $G$ .

The spherical harmonics of a given order  $l$  are an example of an irreducible representation. A spherical harmonic  $Y_{lm}$  is transformed by rotation of the frame of reference into a function expressible as a sum of the spherical harmonics with the same  $l$  and with  $m$  ranging over  $-l \leq m \leq l$ , each multiplied by a coefficient. The coefficients are the matrix elements of the representation. Since any  $Y_{lm}$  may be transformed by some rotation into a function containing any other with the same  $l$ , the representation of degree  $2l + 1$  is irreducible.

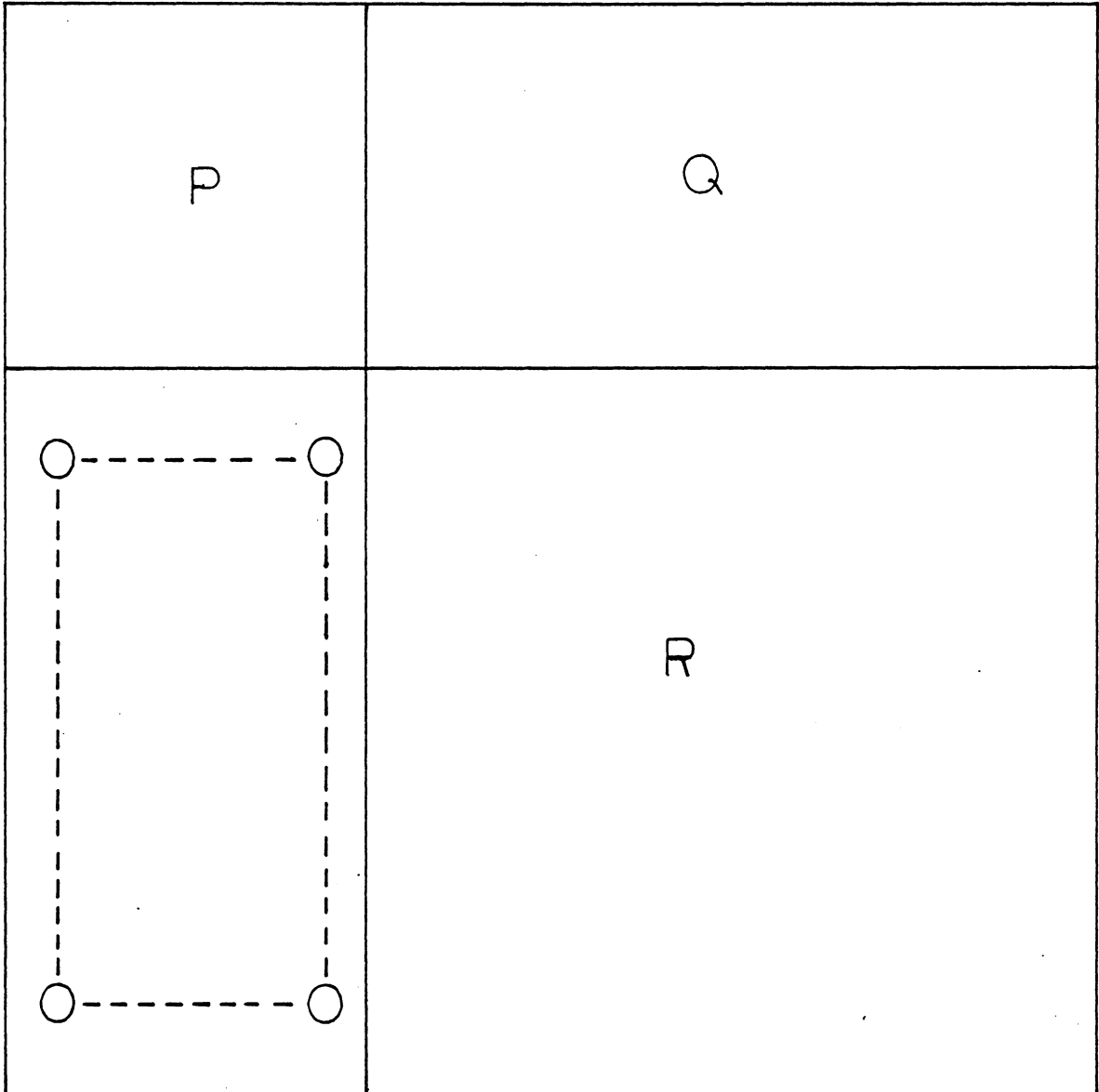


Figure 2. Desired Form of the Representation Matrices.

## Basic Theory of Angular Momentum

The classical definition of angular momentum is

$$\mathbf{L} = \sum_i (\mathbf{r}_i \times \mathbf{p}_i) \quad [3.9]$$

where the summation is over all particles  $i$ ,  $\mathbf{r}_i$  is the position vector of the  $i^{\text{th}}$  particle and  $\mathbf{p}_i$  its respective linear momentum. If there are no external forces present  $L_x$ ,  $L_y$ , and  $L_z$  are constants of the motion.

The components of  $\mathbf{r}$  and  $\mathbf{p}$  obey the commutation relations

$$[r_i, p_j] = \frac{i\hbar\delta_{ij}}{2\pi} \quad [3.10]$$

$$[r_i, r_j] = 0 \quad [3.11]$$

$$[p_i, p_j] = 0 \quad [3.12]$$

where  $i, j = x, y, z$ . Application of these relations gives for the commutators of the components of angular momentum

$$\begin{aligned} [L_x, L_y] &= (yp_z - zp_y)(zp_x - xp_z) - (zp_x - xp_z)(yp_z - zp_y) \\ &= yp_x(p_z z - zp_z) + xp_y(zp_z - p_z z) \\ &= \frac{i\hbar}{2\pi}(xp_y - yp_x) \\ &= \frac{i\hbar L_z}{2\pi} \end{aligned} \quad [3.13]$$

$$[L_y, L_z] = \frac{i\hbar L_x}{2\pi} \quad [3.14]$$

and



$$[L_z, L_x] = \frac{i\hbar L_y}{2\pi} \quad [3.15]$$

Taking  $p_x = \frac{-i\hbar}{2\pi}(\partial/\partial x)$ , etc.<sup>4</sup> the operators of angular momentum may be expressed as

$$L_x = \frac{-i\hbar}{2\pi} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad [3.16]$$

$$L_y = \frac{-i\hbar}{2\pi} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad [3.17]$$

$$L_z = \frac{-i\hbar}{2\pi} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad [3.18]$$

In spherical polar coordinates they may be written as

$$L_x = \frac{i\hbar}{2\pi} \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \quad [3.19]$$

$$L_y = \frac{i\hbar}{2\pi} \left( -\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \quad [3.20]$$

$$L_z = \frac{-i\hbar}{2\pi} \frac{\partial}{\partial \varphi} \quad [3.21]$$

The angular momentum operators are proportional to the infinitesimal rotation operators<sup>5</sup>.

The square of the angular momentum given by

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2 \quad [3.22]$$

commutes with  $L_x$ ,  $L_y$ , and  $L_z$ . In spherical polar coordinates it is written as

$$\mathbf{L}^2 = \frac{-\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \quad [3.23]$$

Eqn. 3.9 may also be expressed as

$$\mathbf{L} = \sum_{i=1}^n \mathbf{L}_i \quad [3.24]$$

where  $\mathbf{L}_i$  is the angular momentum of the  $i^{\text{th}}$  particle. Since the quantum mechanical operators relating to different particles commute, this definition applies in quantum mechanics with the knowledge that the components  $L_x$ ,  $L_y$ , and  $L_z$  obey the same commutation rules as the components of the angular momenta  $\mathbf{L}_i$ .

A number of invariants, quantities whose values are unchanged by rotation of the frame of reference, may be constructed from the  $3n$  coordinates of a system of  $n$  particles. There are the  $n$  lengths  $r_i$  of the position vectors. There are also the scalar products of the vectors taken two at a time. Consider the two vectors,  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , whose scalar product  $(\mathbf{r}_1 \cdot \mathbf{r}_2)$  is specified. Each of the remaining  $n - 2$  vectors is fixed by specifying the values of two scalar products. There are thus  $2n - 3$  independent scalar products. The total number of independent invariants is  $3n - 3$ . The three remaining independent quantities are the three Euler angles (Figure 1) of a moving frame of reference which is associated with the motion of the  $n$  particles. If the  $3n - 3$  invariants are constants of the motion we have the case of the rotation of a rigid body with the moving frame fixed in the body. If the motion is not rigid and  $n > 2$  specification of the Euler angles is not straightforward, but there is no ambiguity in their specification in terms of the coordinates since there are only three independent quantities with which they may be identified.

To determine the expression for the total angular momentum in terms of the Euler angles the operators of infinitesimal rotations about the vertical, the line of nodes, and the figure axes are first expressed in terms of the infinitesimal rotations about the fixed  $x, y$ , and  $z$  axes. These infinitesimal rotations may be compounded as vectors. Therefore the operator of infinitesimal rotation about the line of nodes is given by

$$\frac{\partial}{\partial \beta} = -\sin \alpha \frac{\partial}{\partial \alpha_x} + \cos \alpha \frac{\partial}{\partial \alpha_y} \quad [3.25]$$

where  $\alpha_x$  and  $\alpha_y$  are angles measured about the fixed  $x$  and  $y$  axes respectively. The infinitesimal rotation about the figure axis is

$$\frac{\partial}{\partial \gamma} = \cos \alpha \sin \beta \frac{\partial}{\partial \alpha_z} + \sin \alpha \sin \beta \frac{\partial}{\partial \alpha_y} + \cos \beta \frac{\partial}{\partial \alpha} \quad [3.26]$$

In analogy with  $L_z = \frac{-i\hbar}{2\pi}(\partial/\partial\alpha)$

$$L_x = \frac{-i\hbar}{2\pi} \frac{\partial}{\partial \alpha_x} \quad [3.27]$$

$$L_y = \frac{-i\hbar}{2\pi} \frac{\partial}{\partial \alpha_y} \quad [3.28]$$

The equations for  $\partial/\partial\alpha$ ,  $\partial/\partial\beta$ ,  $\partial/\partial\gamma$  may be inverted to obtain

$$L_x = \frac{-i\hbar}{2\pi} \left[ -\cos \alpha \cot \beta \frac{\partial}{\partial \alpha} - \sin \alpha \frac{\partial}{\partial \beta} + \frac{\cos \alpha}{\sin \beta} \frac{\partial}{\partial \gamma} \right] \quad [3.29]$$

$$L_y = \frac{-i\hbar}{2\pi} \left[ -\sin \alpha \cot \beta \frac{\partial}{\partial \alpha} + \cos \alpha \frac{\partial}{\partial \beta} + \frac{\sin \alpha}{\sin \beta} \frac{\partial}{\partial \gamma} \right] \quad [3.30]$$

$$L_z = \frac{-i\hbar}{2\pi} \frac{\partial}{\partial \alpha} \quad [3.31]$$

The square of the total angular momentum is given by Eqns. 3.22 and 29-31 as

$$L^2 = \frac{\hbar^2}{4\pi^2} \left[ -\frac{\partial^2}{\partial \beta^2} - \cot \beta \frac{\partial}{\partial \beta} - \frac{1}{\sin^2 \beta} \left( \frac{\partial^2}{\partial \alpha^2} + \frac{\partial^2}{\partial \gamma^2} \right) + \frac{2 \cos \beta}{\sin^2 \beta} \frac{\partial^2}{\partial \alpha \partial \gamma} \right] \quad [3.32]$$

In deriving the matrix representations of the operators in Eqns. 3.13-15 it is convenient to assume that the operators are defined by these commutation relations. If all angular properties were expressed in terms of differential operators spin could not exist, since there is no classical analog of spin. This redefinition permits the eigenvalues of angular momentum to take half-integer values as will be seen shortly.  $L$  will be reserved specifically for orbital angular momentum and  $J$  will symbolize a general angular momentum.

The operators  $J_+$  and  $J_-$  are defined by

$$J_+ = J_x + iJ_y \quad [3.33]$$

$$\mathbf{J}_- = \mathbf{J}_x - i\mathbf{J}_y \quad [3.34]$$

and obey the following commutation relations.

$$[\mathbf{J}^2, \mathbf{J}_\pm] = 0 \quad [3.35]$$

$$[\mathbf{J}_+, \mathbf{J}_-] = \frac{2\hbar\mathbf{J}_z}{2\pi} \quad [3.36]$$

$$[\mathbf{J}_z, \mathbf{J}_+] = \frac{\hbar\mathbf{J}_+}{2\pi} \quad [3.37]$$

$$[\mathbf{J}_z, \mathbf{J}_-] = \frac{\hbar\mathbf{J}_-}{2\pi} \quad [3.38]$$

To determine the eigenvalues of  $\mathbf{J}^2$  and one of the components of  $\mathbf{J}$ , normally  $\mathbf{J}_z$ , one takes as a basis set the set of simultaneous normalized eigenvectors of  $\mathbf{J}^2$  and  $\mathbf{J}_z$ . The indices  $j, m$  in the eigenvector notation  $u(j, m)$  are related to the distinct eigenvalues  $\lambda_j$  and  $\lambda_m$  of  $\mathbf{J}^2$  and  $\mathbf{J}_z$  respectively. That is, eigenvectors with different values of  $j$  or  $m$  are orthogonal<sup>7</sup>. All the elements of the basis set are supposed to possess the same eigenvalues with respect to those operators  $\Gamma$  which, together with  $\mathbf{J}^2$  and  $\mathbf{J}_z$  form a complete set for the system.

The matrix element of any operator in this representation is given by

$$\mathbf{O}u(j, m) = \sum_{j' m'} u(j', m') \langle j' m' | \mathbf{O} | j m \rangle \quad [3.39]$$

$$\langle j' m' | \mathbf{O} | j m \rangle = (u(j', m'), \mathbf{O}u(j, m)) \quad [3.40]$$

The basis functions are orthonormal  $\langle j' m' | j m \rangle = \delta_{j'j} \delta_{m'm}$ . The eigenvalue of  $\mathbf{J}_z$  operating on  $u(j, m)$  is

$$\mathbf{J}_z u(j, m) = \frac{m\hbar}{2\pi} u(j, m) \quad [3.41]$$

Since  $J_x$ ,  $J_y$ , and  $J_z$  commute with  $J^2$  we may write

$$J^2 J_i u(j m) = J_i J^2 u(j m) = \lambda_j J_i u(j m) \quad [3.42]$$

where  $i = x, y, z$  and  $\lambda_j$  is as yet the undetermined eigenvalue of  $J^2$  for a particular value of  $j$ . This restricts the analysis to a set of eigenvectors with the same  $j$  but different values for  $m$ . Consider the matrix component of

$$J_z J_+ - J_+ J_z$$

between  $j' m'$  and  $j m$ . From Eqns. 3.38 and 41 we get

$$\frac{\hbar}{2\pi} (m' - m) \langle j m' | J_+ | j m \rangle = \frac{\hbar}{2\pi} \langle j m' | J_+ | j m \rangle \quad [3.43]$$

This is nonvanishing only when  $m' - m = 1$ . Application of  $J_+$  to  $u(j m)$  has the effect

$$J_+ u(j m) = \frac{x_m \hbar}{2\pi} u(j m + 1) \quad [3.44]$$

where  $x_m$  is the eigenvalue. The value of  $m$  has been increased by one. Application of  $J_-$  will decrease the value of  $m$  by one, thus the terms raising and lowering operators. Operation on  $u(j m + 1)$  by  $J_-$  gives

$$J_- u(j m + 1) = \frac{x'_{m+1} \hbar}{2\pi} u(j m) \quad [3.45]$$

where  $x'_{m+1}$  is the eigenvalue of  $J_-$ . From the definition of  $J_+$  and  $J_-$  and the fact that  $J_x$  and  $J_y$  are Hermitian, it follows that

$$x'_{m+1} = x_m^* \quad [3.46]$$

The commutation relation  $[J_+, J_-] = \frac{2\hbar J_z}{2\pi}$  implies that

$$|x_{m-1}|^2 - |x_m|^2 = 2m \quad [3.47]$$

where  $|x|^2 = xx^*$ . The general solution is

$$|x_m|^2 = C - m(m + 1) \quad [3.48]$$

where  $C$  is an arbitrary constant. For any finite value of  $C$  the right hand side of Eqn. 3.48 is negative for large enough values of  $m$ ; but,  $|x_m|^2$  must be positive. Eqn. 3.43 is true for any values of  $m$  if the matrix element of  $J_+$  is zero, that is, when  $|x_m| = 0$ . Therefore  $|x_m|^2$  is nonzero only over a restricted range of  $m$ :

$$m = m_l + 1, m_l + 2, \dots, m_u - 2, m_u - 1 \quad [3.49]$$

where  $m_u$  and  $m_l$  are the upper and lower bounds respectively of  $m$  and differ by an integer. These bounds are determined by setting  $|x_m|^2$  to zero and solving the resulting quadratic equation to obtain

$$C = m_u(m_u + 1) \quad [3.50]$$

$$m_l = -m_u - 1 \quad [3.51]$$

Since  $m_u$  and  $m_l$  differ by an integer  $2m_u$  is a positive integer and  $m_u$  may take the values  $0, 1/2, 1, 3/2, \dots$

$J^2$  is given in terms of  $J_+, J_-$ , and  $J_z$  by

$$J^2 = 1/2(J_+J_- + J_-J_+) + J_z^2 \quad [3.52]$$

The eigenvalues of  $J^2$  are determined by making use of the preceding results giving

$$J^2 u(j, m) = \lambda_j u(j, m) \quad [3.53]$$

$$\begin{aligned} \lambda_j &= \frac{\hbar}{2\pi} (|x_{m-1}|^2 + |x_m|^2) + m^2 \left( \frac{\hbar}{2\pi} \right)^2 \\ &= \frac{\hbar}{4\pi} [m_u(m_u + 1) - (m - 1)m + m_u(m_u + 1) - m(m + 1)] + \left( \frac{m\hbar}{2\pi} \right)^2 \\ &= m_u(m_u + 1) \left( \frac{\hbar}{2\pi} \right)^2 \end{aligned} \quad [3.54]$$

$$\lambda_j = m_u(m_u + 1) \quad [3.55]$$

which is independent of  $m$ .  $m_u$  is identified with the symbol  $j$ . In summary, the eigenvalues of  $\mathbf{J}^2$  and  $\mathbf{J}_z$  are  $j(j+1)$  and  $m$ , respectively, where  $J$  may take the values  $0, 1/2, 1, 3/2, \dots$  and  $m$  ranges from  $-j, -j+1, \dots, j-1, j$ .

The  $(2j+1)$ -dimensional representation whose basis is given by the eigenvectors  $u(j-j)$ ,  $u(j-j+1)$ , ...,  $u(j+j)$  is symbolized by  $D^{(j)}$ . By successive use of  $\mathbf{J}_+$  and  $\mathbf{J}_-$  any vector in this set may be transformed into any other.  $D^{(j)}$  is in the group theoretical sense irreducible.

The matrix elements of  $\mathbf{J}_+$  and  $\mathbf{J}_-$  are given by Eqns. 3.56 and 57 where the phase follows the convention of Condon and Shortley<sup>7</sup>

$$\mathbf{J}_+ u(j, m) = \frac{\hbar[(j-m)(j+m+1)]^{1/2}}{2\pi} u(j, m+1) \quad [3.56]$$

$$\mathbf{J}_- u(j, m) = \frac{\hbar[(j+m)(j-m+1)]^{1/2}}{2\pi} u(j, m-1) \quad [3.57]$$

The nonzero matrix elements of  $\mathbf{J}_x$ , and  $\mathbf{J}_y$  are

$$\langle j, m+1 | \mathbf{J}_x | j, m \rangle = \frac{\hbar}{4\pi} [(j-m)(j+m+1)]^{1/2} \quad [3.58]$$

$$\langle j, m-1 | \mathbf{J}_x | j, m \rangle = \frac{\hbar}{4\pi} [(j+m)(j-m+1)]^{1/2} \quad [3.59]$$

$$\langle j, m+1 | \mathbf{J}_y | j, m \rangle = \frac{-i\hbar}{4\pi} [(j-m)(j+m+1)]^{1/2} \quad [3.60]$$

$$\langle j, m-1 | \mathbf{J}_y | j, m \rangle = \frac{i\hbar}{4\pi} [(j+m)(j-m+1)]^{1/2} \quad [3.61]$$

The matrices of the angular momentum operators when  $j = 1/2$  are

$$\langle 1/2m' | J_x | 1/2m \rangle$$

	$m$	
$m'$	$+1/2$	$-1/2$
$+1/2$	$0$	$\frac{\hbar}{4\pi}$
$-1/2$	$\frac{\hbar}{4\pi}$	$0$

[3.62]

$$\langle 1/2m' | J_y | 1/2m \rangle$$

	$m$	
$m'$	$+1/2$	$-1/2$
$+1/2$	$0$	$\frac{-i\hbar}{4\pi}$
$-1/2$	$\frac{i\hbar}{4\pi}$	$0$

[3.63]

$$\langle 1/2m' | J_z | 1/2m \rangle$$

	$m$	
$m'$	$+1/2$	$-1/2$
$+1/2$	$\frac{\hbar}{4\pi}$	$0$
$-1/2$	$0$	$\frac{-\hbar}{4\pi}$

[3.64]

These are the Pauli spin matrices<sup>8</sup> and are frequently written  $(\hbar/4\pi)\sigma_x$ ,  $(\hbar/4\pi)\sigma_y$ , and  $(\hbar/4\pi)\sigma_z$  where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad [3.65]$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad [3.66]$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad [3.67]$$

With quantization of the angular momentum of a system the components no longer commute. The uncertainty principle makes it impossible to determine more than one component of the angular momentum at any given time. The rule for the minimum uncertainties  $\Delta A$  and  $\Delta B$  of any two operators **A** and **B** is



$$\overline{(\Delta A)^2} \cdot \overline{(\Delta B)^2} \geq \left\{ \frac{i}{2} [A, B] \right\}^2 \quad [3.68]$$

where the bars imply expectation values. If we choose to measure the z-component, which is equal to  $\frac{\hbar m}{2\pi}$ , then for the minimum uncertainties of  $J_x$  and  $J_y$  we have

$$\overline{(\Delta J_x)^2} \cdot \overline{(\Delta J_y)^2} \geq \frac{\hbar^2}{8\pi^2} \overline{J_z^2} = \frac{m^2 \hbar^2}{8\pi^2} \quad [3.69]$$

Another feature of quantization is the fact that the measured values of total angular momentum and of its component in a given direction can take only the values,  $\frac{\hbar^2}{4\pi^2} j(j+1)$  and  $\frac{\hbar}{2\pi} m$  ( $m = -j, -j+1, \dots, j$ ). The eigenvalue  $j(j+1)$  for the square of the length of the angular momentum vector initially was empirically discovered<sup>9</sup>. The maximum value of  $m$  is  $j$  while the length of the vector is  $\frac{\hbar}{2\pi} \sqrt{j(j+1)}$ . The angular momentum vector can never point exactly in the direction of  $z$ . This is due to the uncertainty in measurement of the  $x$  and  $y$  components. The final feature of quantization is the possibility of half-integer values of the eigenvalues of angular momentum. This is attributable to the generalization of the concept of angular momentum, e.g. the redefinition of the angular momentum operators. A more accurate measure of the uncertainty in  $J_x$  and  $J_y$  can be shown to be<sup>1</sup>

$$\overline{(\Delta J_x)^2} + \overline{(\Delta J_y)^2} = \frac{\hbar^2}{4\pi^2} (j^2 + j - m^2) \quad [3.70]$$

The minimum uncertainty in the measurements of  $J_x$  and  $J_y$  occurs for  $|m| = j$ . However, when the total angular momentum is zero all three components of the angular momentum are well defined.

We now turn our attention to determination of the eigenvectors of angular momentum. Consider the orbital angular momentum eigenvectors  $L^2$  and  $L_z$ . We need to determine the  $u(j, m)$  in the  $r$  representation. The solution of the equation

$$L_z \psi(\theta, \varphi) = -\frac{i\hbar}{2\pi} \frac{\partial}{\partial \varphi} \psi(\theta, \varphi) = \lambda \psi(\theta, \varphi) \quad [3.71]$$

is  $2\pi\lambda/h = m = 0, \pm 1, \pm 2, \dots$  and  $\psi(\theta, \varphi) = a(\theta) \exp im\varphi$ .  $m$  is restricted to integer values since  $\psi$  must be a single valued function of  $\varphi$ . Assume now that  $\psi(\theta, \varphi)$  is an eigenfunction of  $L^2$  with eigenvalue  $\frac{\hbar^2}{4\pi^2}l(l+1)$  and of  $L_z$  with eigenvalue  $\frac{\hbar}{2\pi}m$ ,  $|m| \leq l$  and write it as

$$\psi_{lm}(\theta) \exp im\varphi$$

The eigenfunction  $\psi_{l,-l}(\theta)$  and all the other  $\psi_{l,-l+1}(\theta), \dots$  may be constructed by application of the raising and lowering operators

$$L_+ = L_x + iL_y = \frac{\hbar}{2\pi} \exp i\varphi \left( -\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\varphi} \right) \quad [3.72]$$

$$L_- = L_x - iL_y = \frac{\hbar}{2\pi} \exp -i\varphi \left( \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\varphi} \right) \quad [3.73]$$

These equations give

$$\frac{\partial}{\partial\theta} \psi_{l,-l}(\theta) - l \cot\theta \psi_{l,-l}(\theta) = 0 \quad [3.74]$$

$$\log \psi_{l,-l}(\theta) = \log \sin\theta + C \quad [3.75]$$

$$\psi_{l,-l}(\theta) = a(\sin\theta)^l \quad [3.76]$$

where  $a$  is independent of  $\theta$  and  $\varphi$ .

We have also

$$\begin{aligned} L_+ \psi_{lm}(\theta) \exp im\varphi &= \frac{\hbar}{2\pi} \left( \frac{\partial}{\partial\theta} - m \cot\theta \right) \psi_{lm}(\theta) \exp i(m+1)\varphi \\ &= \frac{\hbar}{2\pi} [(l-m)(l+m+1)]^{1/2} \psi_{l,m+1}(\theta) \exp i(m+1)\varphi \end{aligned} \quad [3.77]$$

$$\psi_{l,m+1}(\theta) = [(l-m)(l+m+1)]^{-1/2} \left( \frac{d}{d\theta} - m \cot\theta \right) \psi_{lm}(\theta) \quad [3.78]$$

After application of the raising operator to the known  $\psi_{l,-l}(\theta)$  one obtains the unnormalized wave equation

$$\psi_{lm}(\theta) = (-1)^{l+m} a \left[ \frac{(l-m)!}{(2l)!(l+m)!} \right]^{1/2} (\sin \theta)^m \left( \frac{d}{d \cos \theta} \right)^{l+m} (\sin \theta)^{2l} \quad [3.79]$$

This function is normalized if the integral of the probability over the sphere is unity. For the eigenfunction  $\psi_{l, -l}$

$$\int_0^{2\pi} \int_0^\pi \psi_{l, -l}^*(\theta, \varphi) \psi_{l, -l}(\theta, \varphi) \sin \theta d\theta d\varphi = 1 \quad [3.80]$$

$$2\pi a^2 \int_0^\pi (\sin \theta)^{2l+1} d\theta = 1 \quad [3.81]$$

Therefore

$$a = \frac{1}{2^l l!} \left[ \frac{(2l+1)!}{4\pi} \right]^{1/2} \quad [3.82]$$

The  $Y_{lm}(\theta, \varphi)$  are now defined as the normalized eigenfunctions and we have

$$\int_0^{2\pi} \int_0^\pi Y_{lm}^*(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \sin \theta d\theta d\varphi = \delta_{ll'} \delta_{mm'} \quad [3.83]$$

where

$$Y_{lm}(\theta, \varphi) = \frac{(-1)^{l+m}}{2^l l!} \left[ (2l+1) \frac{(l-m)!}{4\pi(l+m)!} \right]^{1/2} (\sin \theta)^m \left[ \frac{\partial}{\partial(\cos \theta)} \right]^{l+m} (\sin \theta)^{2l} \exp im\varphi \quad [3.84]$$

The  $Y_{lm}(\theta, \varphi)$  may also be expressed in terms of the associated Legendre functions. The  $Y_{lm}(\theta, \varphi)$  have been assumed to be solutions of the eigenvalue equation  $L^2\psi = \frac{\hbar^2}{4\pi^2}\lambda\psi$ , that is

$$-\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \psi = \frac{\hbar^2}{4\pi^2} \lambda \psi \quad [3.85]$$

Taking  $\psi = \psi_m(\theta) \exp im\varphi$  one obtains

$$-\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} \right] \psi_m(\theta) = \frac{\hbar^2}{4\pi^2} \lambda \psi_m(\theta) \quad [3.86]$$

The same equation appears when either the Laplace equation or the wave equation in spherical coordinates are separated

$$(\Delta + k^2)\psi \equiv \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + k^2 \right] \psi = 0 \quad [3.87]$$

having the solution  $\psi = R(r)\Theta(\theta)\Phi(\phi)$  and the separation constants  $m^2$  and  $\lambda$ . The  $Y_{lm}(\theta, \phi)$  are therefore the spherical harmonics.

If  $\cos \theta = x$  and  $\lambda = l(l + 1)$  Legendre's differential equation is obtained

$$(1 - x^2) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + [l(l + 1) - \frac{m^2}{1 - x^2}] y = 0 \quad [3.88]$$

For  $x$  real and  $-1 \leq x \leq +1$  this equation has single valued continuous solutions for  $l$  and  $m$  integers.  $l$  is assumed to be positive. The solution, which is finite at all points in the restricted range of  $x$ , is nonzero only for  $|m| \leq l$ . The equation is satisfied by the associated Legendre functions of the first and second kinds,

$$P_l^m(x) = (1 - x^2)^{m/2} \frac{d^m P_l(x)}{dx^m} \quad [3.89]$$

$$Q_l^m(x) = (1 - x^2)^{m/2} \frac{d^m Q_l(x)}{dx^m} \quad [3.90]$$

where  $m$  is a positive integer and  $P_l(x), Q_l(x)$  are the Legendre functions. The second solution  $Q$  is not finite at all points in the range of  $x$  and will not be considered further. The definition for  $P$  is that for a real argument  $x$ .

The Legendre polynomials  $P_l(x)$  are defined by the generating function

$$(1 - 2xh + h^2)^{-1/2} = P_0(x) + hP_1(x) + h^2P_2(x) + \dots \quad [3.91]$$

or more generally

$$P_l(x) = \sum_{r=0}^{\nu} (-1)^r \frac{(2l-2r)! x^{l-2r}}{2^l r! (l-r)! (l-2r)!} \quad [3.92]$$

where  $\nu = l/2$  or  $(l-1)/2$  whichever is an integer. The polynomials are given by the Rodrigues formula

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \quad [3.93]$$

and satisfy the differential equation

$$(1-x^2) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + l(l+1)y = 0 \quad [3.94]$$

The Legendre polynomials are orthogonal

$$\int_{-1}^{+1} P_k(x) P_l(x) dx = \frac{2\delta_{kl}}{2k+1} \quad [3.95]$$

The associated Legendre function  $P_l^m(x)$  needs to be generalized to include negative values for  $m$ . Eqns. 3.88 and 93 are combined to give

$$P_l^m(x) = \frac{(1-x^2)^{m/2}}{2^l l!} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l \quad [3.96]$$

This equation defines the Legendre polynomials when  $m$  is negative.

Comparison of the definition of the  $Y_{lm}(\theta, \varphi)$  and the Rodrigues formula for the  $P_l^m(\cos \theta)$  shows the functions are related by

$$Y_{lm}(\theta, \varphi) = (-1)^m \left[ \frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{1/2} P_l^m(\cos \theta) \exp im\varphi \quad [3.97]$$

A notation which will be convenient in the discussion of tensor operators is that of Racah<sup>10</sup>

$$C_q^{(k)} = \left[ \frac{4\pi}{2k+1} \right]^{1/2} Y_{kq}(\theta, \varphi) \quad [3.98]$$

It has been shown that representations of the angular momentum operators exist for half integer values of  $j$  and  $m$ . The basis vectors  $u(j, m)$  for these representations may not be expressed in terms of single-valued functions on a sphere. However, they may be considered as quantities which have certain transformation properties under infinitesimal rotations and which are normalized. The scalar product of the eigenvectors is no longer associated with an integration over configuration space.

A useful notation for these eigenvectors is to write them as column vectors. Consider an arbitrary linear combination  $v$  of a set of  $2j+1$  eigenvectors  $u(j, m)$  which form the basis of a representation  $D^{(j)}$

$$v = \sum_m u(j, m) \langle m | v \rangle \quad [3.99]$$

If  $\mathbf{J}$  is an angular momentum operator

$$v' = \mathbf{J}v = \sum_{mm'} u(j, m') \langle j, m' | \mathbf{J} | j, m \rangle \langle m | v \rangle \quad [3.100]$$

The new coefficients  $\langle m | v' \rangle$  are given by

$$\langle m | v' \rangle = \sum_m \langle j, m' | \mathbf{J} | j, m \rangle \langle m | v \rangle \quad [3.101]$$

The coefficients transform contragrediently to the eigenvectors  $u(j, m)$ . That is, if a vector set transforms according to a unitary matrix  $D$ , then its contragredient set is defined to transform according to  $D^*$ . The set of coefficients  $\langle m | v' \rangle$  may be represented from the point of view of matrix multiplication. An eigenvector  $u(j, m)$  will appear as

$$\begin{bmatrix} \delta_{j,m} \\ \delta_{j-1,m} \\ \cdot \\ \cdot \\ \cdot \\ \delta_{-j,m} \end{bmatrix}$$

This assumes that the  $m$  values labeling rows and columns decreases from left to right and top to bottom. The eigenvectors  $u(1/2 \ 1/2)$  and  $u(1/2 \ -1/2)$  are denoted by

$$u(1/2 \ 1/2) \sim \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad [3.102]$$

$$u(1/2 \ -1/2) \sim \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad [3.103]$$

and a general spin vector as

$$\begin{pmatrix} \psi_+(\mathbf{r}) \\ \psi_-(\mathbf{r}) \end{pmatrix}$$

if the spin is a function of position where

$$\int \{ |\psi_+(\mathbf{r})|^2 + |\psi_-(\mathbf{r})|^2 \} d\mathbf{r} = 1 \quad [3.104]$$

Thus a spin 1/2 particle may be described by a pair of functions on the configuration space.

$u(1/2 \ 1/2)$  and  $u(1/2 \ -1/2)$  define a linear unitary space of two dimensions, called the spin space. The transformations corresponding to the matrices Eqns. 3.62-64 are considered to be equivalent to certain differential operators in this space. For brevity

$$u(1/2 \ 1/2) \equiv \chi_+ \quad [3.105]$$

$$u(1/2 \ -1/2) \equiv \chi_- \quad [3.106]$$

and the differential operators

$$\frac{\partial}{\partial \chi_+} \equiv \partial_+ \quad [3.107]$$

$$\frac{\partial}{\partial \chi_-} \equiv \partial_- \quad [3.108]$$

In the  $D^{(1/2)}$  representation the angular momentum operators may be equated with linear differential operators in the following way:

$$\mathbf{J}_x \sim \frac{\hbar}{4\pi}(\chi_- \partial_+ + \chi_+ \partial_-) \quad [3.109]$$

$$\mathbf{J}_y \sim \frac{i\hbar}{4\pi}(\chi_- \partial_+ - \chi_+ \partial_-) \quad [3.110]$$

$$\mathbf{J}_z \sim \frac{\hbar}{4\pi}(\chi_+ \partial_+ + \chi_- \partial_-) \quad [3.111]$$

$$\mathbf{J}_+ \sim \frac{\hbar}{2\pi} \chi_+ \partial_- \quad [3.112]$$

$$\mathbf{J}_- \sim \frac{\hbar}{2\pi} \chi_- \partial_+ \quad [3.113]$$

The square of the total angular momentum operator is given by

$$\begin{aligned} \mathbf{J}^2 &= \mathbf{J}_z(\mathbf{J}_z - 1) + \mathbf{J}_+ \mathbf{J}_- \\ &= \frac{\hbar^2}{16\pi^2}(\chi_+ \chi_+ \partial_+ \partial_+ + \chi_- \chi_- \partial_- \partial_- + 2\chi_+ \chi_- \partial_+ \partial_- + 3\chi_+ \partial_+ + 3\chi_- \partial_-) \\ &= \frac{\hbar^2}{4\pi^2} k(k + 1) \end{aligned} \quad [3.114]$$

where  $k = 1/2(\chi_+ \partial_+ + \chi_- \partial_-)$

These spinor differential operator expressions lead to a way of representing the angular momentum eigenvectors. Consider the monomial  $\chi_+^k \chi_-^{k'}$ . It is a simultaneous eigenvector of



$J_z$  and  $J^2$  when they are expressed as in Eqns. 3.109-114. The eigenvalues are  $\frac{\hbar}{4\pi}(x - y)$  and  $\frac{\hbar^2}{4\pi^2}\left(\frac{x + y}{2}\right)\left(\frac{x + y}{2} + 1\right)$  respectively. Operation with  $J_+$  or  $J_-$  changes the values of  $x$  and  $y$  but leaves the degree,  $x + y$ , unchanged. Therefore the set of  $2j + 1$  monomials  $\chi_+^{j+m}\chi_-^{j-m}$  where  $m$  may take the values identified several times before, form a basis for the  $D(j)$  representation of the angular momentum operators. The normalized monomials are

$$u(j, m) \equiv \frac{\chi_+^{j+m}\chi_-^{j-m}}{[(j + m)!(j - m)!]^{1/2}} \quad [3.115]$$

Their behavior under application of the angular momentum operators in Eqns 3.109-113 follows exactly that of the  $u(j, m)$  in Eqns. 3.53 and 56-57.

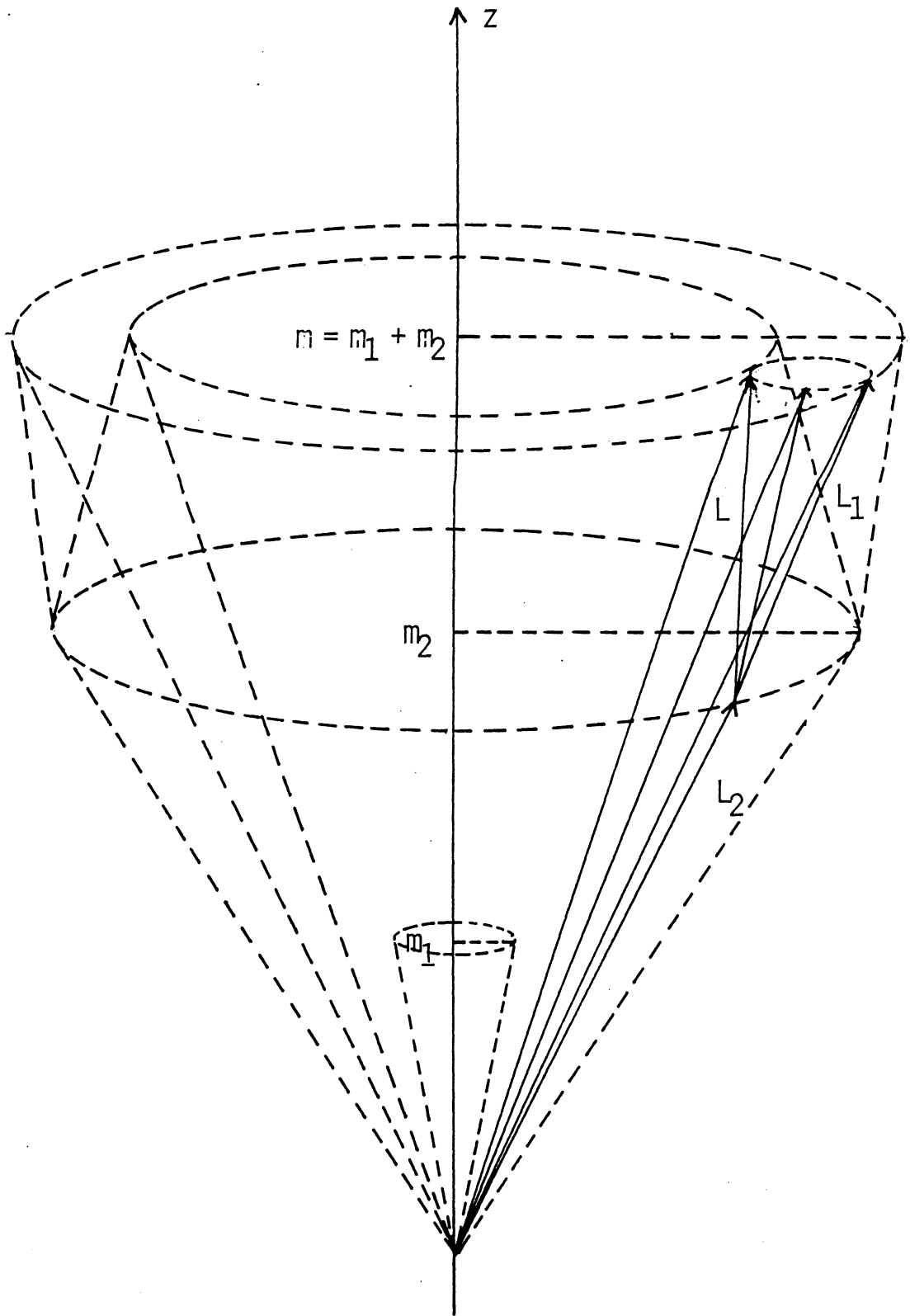
## Coupling of Angular Momenta

The total angular momentum of a classical system composed of two parts,  $L_1$  and  $L_2$ , each having a well defined magnitude and direction is obtained by vector addition of  $L_1$  and  $L_2$ . However, in quantum mechanics the direction of the angular momentum vectors are undefined. Only the magnitude of the vector and its projection on the  $z$ -axis is known. Consider a classical system of two noninteracting angular momentum vectors  $L_1$  and  $L_2$  whose lengths  $l_1$  and  $l_2$  and their corresponding projections on the  $z$ -axis are fixed but whose directions are undefined.  $L$  therefore has a range of lengths and orientations. Figure 3 shows that the projection  $m$  on the  $z$ -axis is fixed to the value  $m_1 + m_2$ . The length  $l$  falls within a range whose bounds depend on  $m_1$  and  $m_2$  but must meet the requirements that

$$|l_1 - l_2| \leq l \leq l_1 + l_2. \quad [3.116]$$

The angle between  $L$  and the  $z$ -axis may take any value between 0 and  $2\pi$ .

The probability that the length of  $L$  lies between  $l$  and  $l + dl$  is called  $P(l)dl$ . Assuming  $L_2$  rotates at a constant rate about the  $z$ -axis relative to  $L_1$ ,  $P(l)$  is inversely proportional to  $dl/dt$  and



**Figure 3. Two Classical non-Interacting Angular Momentum Vectors**

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$$l^2 = m^2 + l_1^2 \sin^2 \theta_1 + l_2^2 \sin^2 \theta_2 - l_1 l_2 \sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2) \quad [3.117]$$

where  $\theta_1$  and  $\theta_2$  are the angles between  $L_1$  and  $L_2$  respectively with the z-axis. Therefore

$$P(l) \sim \left( \frac{dl}{dt} \right)^{-1} \sim 2l [l^2(m^2 + l_1^2 \sin^2 \theta_1 + l_2^2 \sin^2 \theta_2) - l^4 - m^4 - l_1^4 \sin^4 \theta_1 - l_2^4 \sin^4 \theta_2 - m_1^2 l_1^2 \sin^2 \theta_1 - m_2^2 l_2^2 \sin^2 \theta_2]^{-1/2} \quad [3.118]$$

$P(l)$  becomes infinite at the bounding values of  $l$  and varies smoothly between them.

In quantum mechanics the continuously varying probability density is replaced by the squares of the coefficients in the series of terms obtained by analysis of a state specified by the quantum numbers  $j_1, m_1; j_2, m_2$  into states specified by the quantum numbers  $j, m$  of total angular momentum. Aside from the angular momenta taking discrete values the behavior of the squares of these coefficients is similar to  $P(l)$ .

If an interaction between  $L_1$  and  $L_2$  is introduced the total angular momentum  $L$  will be unaltered but  $L_1$  and  $L_2$  will precess about the axis of  $L$  as shown in Figure 4. This corresponds to the values of  $m_1$  and  $m_2$  varying over a certain range with  $m$  remaining constant. This interaction connects states of different  $m_1$  and  $m_2$  which are no longer good quantum numbers.

As in the previous section  $J$  will be used for a general angular momentum operator and  $L$  will be reserved for orbital angular momentum. The quantum mechanical approach is based on the relation

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \quad [3.119]$$

$\mathbf{J}_1$  and  $\mathbf{J}_2$  commute since they are independent momenta. Therefore,  $\mathbf{J}$  obeys the previously defined commutation relations.

$\mathbf{J}_z$  is given by Eqn. 3.119

$$\mathbf{J}_z = \mathbf{J}_{1z} + \mathbf{J}_{2z} \quad [3.120]$$

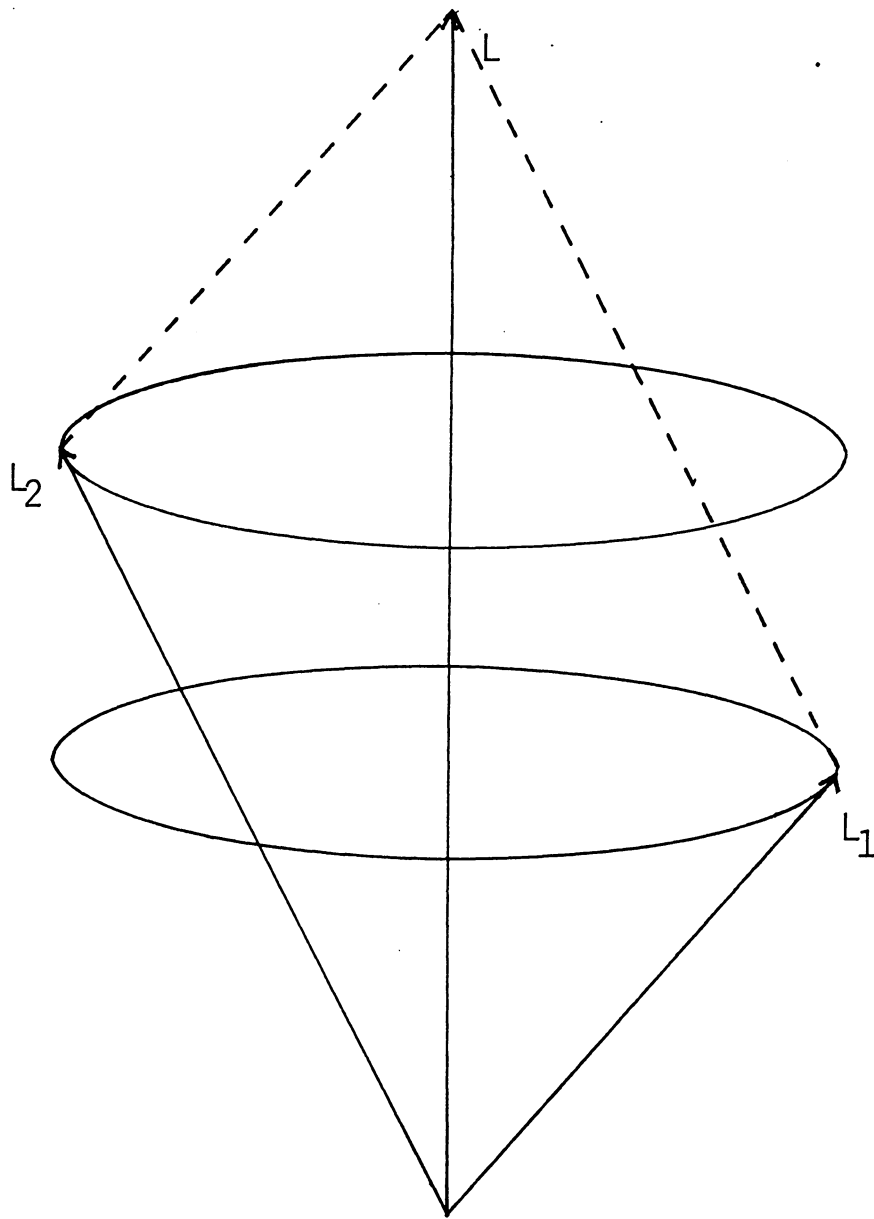


Figure 4. Two Interacting Angular Momentum Vectors

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and from Eqn. 3.41

$$m = m_1 + m_2 \quad [3.121]$$

To determine the allowed values of  $j$  for particular values of  $j_1$  and  $j_2$  consider  $\mathbf{J}^2$  in terms of the original operators

$$\begin{aligned} \mathbf{J}^2 &= (\mathbf{J}_{1x} + \mathbf{J}_{2x})^2 + (\mathbf{J}_{1y} + \mathbf{J}_{2y})^2 + (\mathbf{J}_{1z} + \mathbf{J}_{2z})^2 \\ &= \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2(\mathbf{J}_1 \cdot \mathbf{J}_2) \\ &= \mathbf{J}_1^2 + \mathbf{J}_2^2 + \mathbf{J}_{1+}\mathbf{J}_{2-} + \mathbf{J}_{1-}\mathbf{J}_{2+} + 2\mathbf{J}_{1z}\mathbf{J}_{2z} \end{aligned} \quad [3.122]$$

The states in the coupled system will be expressed by  $\nu(j_1 m_1 j_2 m_2)$ . Consider the state where  $m_1 = j_1$  and  $m_2 = j_2$ , the maximum values for  $m_1$  and  $m_2$ . This state is an eigenstate of  $\mathbf{J}^2$  with eigenvalue

$$\begin{aligned} \frac{\hbar^2}{4\pi^2} j(j+1) &= \frac{\hbar^2}{2\pi} [j_1(j_1+1) + j_2(j_2+1) + 2j_1j_2] \\ &= \frac{\hbar^2}{2\pi} (j_1 + j_2)(j_1 + j_2 + 1) \end{aligned} \quad [3.123]$$

i.e.

$$j = j_1 + j_2 \quad [3.124]$$

and

$$\nu(j_1 j_1 j_2 j_2) = e^{i\delta} w(j_1 j_2 j_1 + j_2 j_1 + j_2) \quad [3.125]$$

where  $w(j_1 j_2 j m)$  is an eigenvector of  $\mathbf{J}_1^2$ ,  $\mathbf{J}_2^2$ ,  $\mathbf{J}^2$ , and  $\mathbf{J}_z$ . The factor  $e^{i\delta}$  is a phase factor and will be discussed shortly. Now consider the states where  $m_1$  and  $m_2$  are decreased by one,  $\nu(j_1 j_1 - 1 j_2 j_2)$  and  $\nu(j_1 j_1 j_2 j_2 - 1)$ . A linear combination of these states corresponds to the state  $w(j_1 j_2 j_1 + j_2 j_1 + j_2 - 1)$ . From Eqn. 3.46 and 3.125

$$\begin{aligned}
e^{i\delta} \mathbf{J}_- w(j_1 j_2 j_1 + j_2 j_1 + j_2) &= \frac{\hbar}{2\pi} (2j_1 + 2j_2)^{1/2} w(j_1 j_2 j_1 + j_2 j_1 + j_2 - 1) \\
&= (\mathbf{J}_{1-} + \mathbf{J}_{2-}) v(j_1 j_1 j_2 j_2) \\
&= \frac{\hbar}{2\pi} [(2j_1)^{1/2} v(j_1 j_1 - 1 j_2 j_2) + (2j_2)^{1/2} v(j_1 j_1 j_2 j_2 - 1)]
\end{aligned} \tag{3.126}$$

This eigenvector has the same value of  $j, j_1 + j_2$ , however it is possible to construct a state which is orthogonal to this one,

$$(2j_2)^{1/2} v(j_1 j_1 - 1 j_2 j_2) - (2j_1)^{1/2} v(j_1 j_1 j_2 j_2 - 1).$$

Application of Eqn. 3.55 shows this state to be an eigenstate of  $\mathbf{J}^2$  with an eigenvalue  $\frac{\hbar^2}{4\pi^2} (j_1 + j_2)(j_1 + j_2 - 1)$  or

$$j = j_1 + j_2 - 1 \tag{3.127}$$

One continues this process reducing  $m$  by one until either  $m_1 = -j_1$  or  $m_2 = -j_2$ . The resulting values for  $j$  and  $m$  are

$$j = j_1 + j_2, j_1 + j_2 - 1, j_1 + j_2 - 2, \dots, |j_1 - j_2| + 1, |j_1 - j_2| \tag{3.128}$$

$$m = j, j - 1, j - 2, \dots, j \tag{3.129}$$

The number of states in the two representations must be the same

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \tag{3.130}$$

This was determined empirically by spectroscopists before the advent of quantum mechanics and is called the addition rule for angular momenta.

If two angular momenta commute they must refer to different particles or different properties of the same particle. A state vector such as  $v(j_1 m_1 j_2 m_2)$  may be split into a sum of products of factors relating the separate parts of the system

$$v(j_1 m_1 j_2 m_2) = \sum_{\alpha_1, \alpha_2} v_1(\alpha_1 j_1 m_1) v_2(\alpha_2 j_2 m_2) \quad [3.131]$$

State vectors of this type are linear combinations of the basis elements of the product representation  $D(j_1) \times D(j_2)$ . This representation of dimension  $(2j_1 + 1)(2j_2 + 1)$  is reducible. The representation space is split into a number of invariant irreducible subspaces each of which corresponds to a particular value of  $j$ . It is this result which allows one to consider the nuclear spins of a set of identical nuclei to be the sum of the individual spins. For two spin 3/2 nuclei, or six spin 1/2 nuclei, the allowed values for  $I$ , corresponding to  $j$  in the above discussion, are 3, 2, 1 and 0.

The commutation relations involving the components of  $J$  may be determined by substitution of these components according to Eqn. 3.119 and remembering that  $J_1$  and  $J_2$  commute.

$$[J_x, J_y] = \frac{i\hbar}{2\pi} J_z \quad [3.132]$$

$$[J_z, J_x] = \frac{i\hbar}{2\pi} J_y \quad [3.133]$$

$$[J_y, J_z] = \frac{i\hbar}{2\pi} J_x \quad [3.134]$$

The following relations also hold when  $J_2$  is substituted for  $J_1$ .

$$[J_x, J_{1x}] = 0 \quad [3.135]$$

$$[J_y, J_{1y}] = 0 \quad [3.136]$$

$$[J_z, J_{1z}] = 0 \quad [3.137]$$

$$[J_x, J_{1y}] = \frac{i\hbar}{2\pi} J_{1z} \quad [3.138]$$

$$[J_y, J_{1z}] = \frac{i\hbar}{2\pi} J_{1x} \quad [3.139]$$

$$[\mathbf{J}_z, \mathbf{J}_{1x}] = \frac{i\hbar}{2\pi} \mathbf{J}_{1y} \quad [3.140]$$

$$[\mathbf{J}_x, \mathbf{J}_{1z}] = \frac{-i\hbar}{2\pi} \mathbf{J}_{1y} \quad [3.141]$$

$$[\mathbf{J}_y, \mathbf{J}_{1x}] = \frac{-i\hbar}{2\pi} \mathbf{J}_{1z} \quad [3.142]$$

$$[\mathbf{J}_z, \mathbf{J}_{1y}] = \frac{-i\hbar}{2\pi} \mathbf{J}_{1x} \quad [3.143]$$

These relations may be rewritten using the raising and lowering operators

$$\mathbf{J}_+ = \mathbf{J}_x + i\mathbf{J}_y \quad [3.144]$$

$$\mathbf{J}_- = \mathbf{J}_x - i\mathbf{J}_y \quad [3.145]$$

$$\mathbf{J}_{1+} = \mathbf{J}_{1x} + i\mathbf{J}_{1y} \quad [3.146]$$

$$\mathbf{J}_{1-} = \mathbf{J}_{1x} - i\mathbf{J}_{1y} \quad [3.147]$$

$$[\mathbf{J}_\pm, \mathbf{J}_{1\pm}] = 0 \quad [3.148]$$

$$[\mathbf{J}_\pm, \mathbf{J}_{1\mp}] = \pm \frac{2\hbar}{2\pi} \mathbf{J}_{1z} \quad [3.149]$$

$$[\mathbf{J}_\pm, \mathbf{J}_{1z}] = \mp \frac{\hbar}{2\pi} \mathbf{J}_{1\pm} \quad [3.150]$$

$$[\mathbf{J}_z, \mathbf{J}_{1\pm}] = \pm \frac{\hbar}{2\pi} \mathbf{J}_{1\pm} \quad [3.151]$$

The commutation relations given above imply certain selection rules on the matrix elements of  $\mathbf{J}_1$  in the  $(j_1 j_2 j m)$  representation. Again, the same relations hold for  $\mathbf{J}_2$ .

The matrix elements of  $\mathbf{J}_{1z}$  are diagonal in  $m$ . From Eqn. 3.137



$$m' \langle j' m' | J_{1z} | j m \rangle - \langle j' m' | J_{1z} | j m \rangle m = 0 \quad [3.152]$$

Therefore the matrix element is zero unless  $m' - m = 0$

The operator  $J_{1+}$  increases  $m$  by one and  $J_{1-}$  decreases  $m$  by one. From Eqn. 3.151

$$m' \langle j' m' | J_{1\pm} | j m \rangle - \langle j' m' | J_{1\pm} | j m \rangle m = \pm \langle j' m' | J_{1\pm} | j m \rangle \quad [3.153]$$

Therefore  $m' - m = \pm 1$  is necessary if the matrix element is to be nonzero.

The matrix elements of the components of  $J_1$  are zero if  $|j' - j| > 1$ . Suppose that  $j' = j + 1 + \lambda, \lambda > 0$ . Then  $\langle j' m' | J_+ | j m \rangle = 0$  for  $m' > j + 1$ . But  $[J_+, J_{1+}] = 0$ . Therefore

$$\begin{aligned} \langle j' m' | J_+ | j' m' - 1 \rangle \langle j' m' - 1 | J_{1+} | j m \rangle - \langle j' m' | J_{1+} | j m + 1 \rangle \\ \times \langle j m + 1 | J_+ | j m \rangle = 0 \end{aligned} \quad [3.154]$$

and  $\langle j' m' | J_{1+} | j m \rangle$  is zero for all  $m, m'$ . It is obvious from Eqns. 3.148 and 150 that all the matrix elements of  $J_1$  between  $j' = j + 1 + \lambda$  and  $j$  must be zero. A similar selection rule can be proven for  $j' < j - 1$ .

Returning to the question of the phase of the eigenvectors of  $J^2, J_z$  the reader is referred to Edmonds<sup>1</sup> or Condon and Shortley<sup>7</sup>. The result, which is quite arbitrary is: All matrix elements of  $J_{1z}$  which are nondiagonal in  $j$  are real and nonnegative.

The eigenvectors of  $J^2, J_z$  are given in terms of the states  $v(j_1 m_1 j_2 m_2)$  by<sup>1</sup>

$$w(j_1 j_2 j m) = \sum_{m_1, m_2} v(j_1 m_1 j_2 m_2) \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle \quad [3.155]$$

The second term on the right hand side of this equation is called the vector-coupling, Wigner, or Clebsch-Gordon coefficient. These coefficients form unitary matrices of dimension  $(2j_1 + 1)(2j_2 + 1)$  with rows and columns labeled by the pairs  $m_1, m_2$  and  $j, m$  respectively. Eqns. 3.124 and 21 indicate the coefficients are zero unless these conditions on  $j$  and  $m$  are satisfied. Using the phase choice just described these coefficients are real quantities. Because of some of the un-

symmetric properties<sup>1</sup> of these coefficients it is convenient to introduce a new quantity called the Wigner 3-j symbol.

The unitary properties of the coefficient matrix for given  $j_1, j_2$  are expressed by

$$\sum_{jm} \langle j_1 m'_1 j_2 m'_2 | j_1 j_2 j m \rangle \langle j_1 j_2 j m | j_1 m_1 j_2 m_2 \rangle = \delta_{m'_1 m_1} \delta_{m'_2 m_2} \quad [3.156]$$

$$\sum_{m_1 m_2} \langle j_1 j_2 j' m' | j_1 m_1 j_2 m_2 \rangle \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle = \delta_{j' j} \delta_{m' m} \delta_{\langle j_1 j_2 j \rangle} \quad [3.157]$$

where  $\delta_{\langle j_1 j_2 j \rangle} = 1$  if  $j$  satisfies Eqn. 3.128 and is zero otherwise.

Since  $m = m_1 + m_2$  is a good quantum number on both sides of the transformation, this square matrix may be divided into submatrices, each corresponding to a given value of  $m$ . Each is unitary, and we have

$$\sum_j \langle j_1 m'_1 j_2 m - m'_1 | j_1 j_2 j m \rangle \langle j_1 j_2 j m | j_1 m_1 j_2 m - m_1 \rangle = \delta_{m'_1 m_1} \quad [3.158]$$

$$\sum_{m_1} \langle j_1 j_2 j' m | j_1 m_1 j_2 m - m_1 \rangle \langle j_1 m_1 j_2 m - m_1 | j_1 j_2 j m \rangle = \delta_{j' j} \delta_{\langle j_1 j_2 j \rangle} \quad [3.159]$$

When dealing with the coupling of two angular momenta, say  $\mathbf{J}_a$  and  $\mathbf{J}_b$ , which of the two is associated with  $\mathbf{J}_1$  in the preceding arguments is important. This is important because of the phase convention chosen, namely that all matrix elements of  $\mathbf{J}_{1z}$  nondiagonal in  $j$  are nonnegative. This implies that the corresponding matrix elements of  $\mathbf{J}_{2z}$  are nonpositive. Therefore the matrix elements of  $\mathbf{J}_{az}$  in the schemes  $(j_a j_b j m)$  and  $(j_b j_a j m)$  have opposite signs.  $\mathbf{J}_{az}$  connects only those states whose  $j$ 's differ by one or zero. For successive values of  $j$  the eigenvectors  $w(j_a j_b j m)$  and  $w(j_b j_a j m)$  will change their relative phase. When  $j = j_a + j_b$  the eigenvectors will have the same phase, for the convention  $w(j_1 j_2 j_1 + j_2 j_1 + j_2) \equiv v(j_1 j_1 j_2 j_2)$  implies that the states  $w(j_a j_b j_a + j_b j_a + j_b)$  and  $w(j_b j_a j_b + j_a j_b + j_a)$  are identical. The states with other values of  $m$  may be obtained by application of the lowering operator a sufficient number of times. For a general value of  $j$  we must have

$$w(j_a j_b j m) = (-1)^{j_a + j_b - j} w(j_b j_a j m) \quad [3.160]$$

The vector coupling coefficients are related by

$$\langle j_a m_a j_b m_b | j_a j_b j m \rangle = (-1)^{j_a + j_b - j} \langle j_b m_b | j_b j_a j m \rangle \quad [3.161]$$

Edmonds<sup>1</sup> gives several symmetry relations between vector coupling coefficients.

The Wigner 3-j symbol is obtained by considering the coupling of  $j_1, j_2$  and  $j$  to produce a zero resultant, i.e. the coupling of three angular momenta. This gives

$$\sum_m u_1(jm) u_2(j - m) (-1)^{j - m} = (2j + 1) v(jj 0 0) \quad [3.162]$$

Since the right hand side is invariant under rotations the quantities  $(-1)^{j - m} u(j - m)$  transform under rotation contragrediently to the  $u(jm)$ . Following Wigner<sup>11</sup> a quantity is introduced

$$\begin{pmatrix} j \\ m \ m' \end{pmatrix} \equiv (-1)^{j + m} \delta_{m, -m'} \quad [3.163]$$

That is

$$\sum_{mm'} u(j m) u(j m') \begin{pmatrix} j \\ m \ m' \end{pmatrix}$$

is an invariant quantity. These properties of the angular momentum eigenvectors are associated with their behavior under rotation of the frame of reference through  $180^\circ$  about the y-axis.

The concept of contragredient quantities indicates that the vector coupling coefficients are components of mixed tensors which explains some of their unsymmetric properties. A more symmetric quantity is the Wigner 3-j symbol defined by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3} (2j_3 + 1)^{-1/2} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j_3 - m_3 \rangle \quad [3.164]$$

An even permutation of the columns leaves the numerical value unchanged while an odd permutation also leaves the absolute value unchanged but the sign changes by  $(-1)^{j_1 + j_2 + j_3}$ . The orthogonality properties of the 3-j symbols are

$$\sum_{j_3 m_3} (2j_3 + 1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m_3 \end{pmatrix} = \delta_{m_1 m'_1} \delta_{m_2 m'_2} \quad [3.165]$$

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = (2j_3 + 1)^{-1} \delta_{j_3 j'_3} \delta_{m_3 m'_3} \delta(j_1 j_2 j_3) \quad [3.166]$$

where  $\delta(j_1 j_2 j_3) = 1$  if  $j_1, j_2, j_3$  satisfy the triangular condition and is zero otherwise.

The 3-j symbol is useful in the numerical evaluation of vector-coupling coefficients but its primary application is in the discussion of the 6-j and 9-j symbols. These symbols will be discussed shortly.

## Representations of Finite Rotations

The  $2j + 1$  angular momentum eigenvectors  $u(j m)$  form a basis for an irreducible representation of the angular momentum operators. These operators are proportional to the infinitesimal rotations. Finite rotations are obtained by iteration of the infinitesimal rotations, and the eigenvectors mentioned above form a basis for a representation of finite rotations. For the integer representations, the  $u(l m)$  in the  $r$  representation are the spherical harmonics  $Y_{lm}(\theta, \varphi)$ . Although the angular momentum operators in the half integer representations cannot be expressed as differential operators in configuration space, in a way, representations of finite rotations are given by the corresponding transformations of the  $u(j m)$ .

The term rotation will be interpreted as a rotation of the frame of reference about the origin with the physical system assumed fixed. Each point of three dimensional space is given new coordinates which are a function of the old coordinates and the Euler angles. This rotation will be described as outlined in the section on group theory.

Consider the effect of such a rotation upon the description of a field variable. A field variable is a quantity which can be described by a function of coordinates. At each point of space this field variable takes a numerical value which may be expressed by a function of the coordinates of the point in question. A point with coordinates  $r, \theta, \varphi$  with respect to frame S will have a value  $f = f(r, \theta, \varphi)$  of the field variable. The value of  $f$  at a point with the coordinates  $r, \theta, \varphi$  in  $S''''$  will in general no longer be  $f(r, \theta, \varphi)$  but some other function  $f'(r, \theta, \varphi)$ . The point with coordinates  $r, \theta, \varphi$  in  $S''''$  will have in general different coordinates in S, say  $r, \theta', \varphi'$ .

$f'(r, \theta, \varphi)$  is given by

$$f'(r, \theta, \varphi) = f(r, \theta', \varphi') \quad [3.167]$$

The effect of this rotation of the frame of reference upon the representation of a field variable may be expressed by the operator equation

$$D(\alpha \beta \gamma)f(r, \theta, \varphi) = f'(r, \theta, \varphi) = f(r, \theta', \varphi') \quad [3.168]$$

$f'$  may be computed by expressing  $\theta'$  and  $\varphi'$  as functions of  $\theta, \varphi; \alpha, \beta, \gamma$  in Eqn. 3.167

$$f'(r, \theta, \varphi) = f(r, \theta'(\theta, \varphi; \alpha, \beta, \gamma), \varphi'(\theta, \varphi; \alpha, \beta, \gamma)) \quad [3.169]$$

Assume that the function  $f$  is an eigenfunction of the operator of orbital angular momentum  $L^2$ .  $L^2$  is invariant under rotation of the frame of reference. Therefore, in  $S''''$  the function  $f'$  is still an eigenfunction of  $L^2$  which has the same eigenvalue, that is, the same value of  $l$ . The  $Y_{lm}(\theta, \varphi)$  of angular momentum transform according to the scheme

$$\begin{aligned} D(\alpha \beta \gamma)Y_{lm}(\theta, \varphi) &= Y_{lm}(\theta', \varphi') \\ &= \sum_{m'=-l}^l Y_{lm'}(\theta, \varphi) \langle l m' | D(\alpha \beta \gamma) | l m \rangle \end{aligned} \quad [3.170]$$

A relation of this kind is also valid for half integer angular momentum even though the  $u(j m)$  are not expressible as functions of  $\theta$  and  $\varphi$

$$D(\alpha\beta\gamma)u(j m) = \sum_{m'=-j}^j u(j m') \langle j m' | D(\alpha \beta \gamma) | j m \rangle \quad [3.171]$$

The relationship between the operators  $D(\alpha\beta\gamma)$  associated with finite rotations of the frame of reference to the operators of infinitesimal rotations will now be shown. Consider a positive rotation  $\gamma$  about the z-axis ( $0 0 \gamma$ ). A point P with coordinate  $\varphi$  in  $S'$  will correspond to a point with coordinate  $\varphi' = \varphi + \gamma$  in  $S$ . That is,  $f'(\theta, \varphi) = f(\theta, \varphi')$ . This leads to

$$\frac{\partial}{\partial \gamma} D(\alpha \beta \gamma) f(\theta, \varphi) = D(\alpha \beta \gamma) \frac{\partial}{\partial \varphi} f(\theta, \varphi) \quad [3.172]$$

Since  $L_z = \frac{-i\hbar}{2\pi} \left( \frac{\partial}{\partial \varphi} \right)$  we may write

$$D(\alpha \beta \gamma) f(\theta, \varphi) = D(\alpha \beta \gamma) \frac{2\pi i}{\hbar} L_z f(\theta, \varphi) \quad [3.173]$$

Solution of this equation for  $D(\alpha\beta\gamma)$  is

$$D(\alpha\beta\gamma) = c(\alpha\beta) \exp \frac{2\pi i \gamma}{\hbar} L_z \quad [3.174]$$

where the exponential is considered as a formal operator series. A rotation  $\beta$  about the y-axis is found to correspond to

$$\exp \frac{2\pi i \beta}{\hbar} L_y$$

Yielding

$$D(\alpha\beta\gamma) = \exp \frac{2\pi i \alpha}{\hbar} L_z \exp \frac{2\pi i \beta}{\hbar} L_y \exp \frac{2\pi i \gamma}{\hbar} L_z \quad [3.175]$$

The properties of the  $D(\alpha\beta\gamma)$  are determined by the commutation relations between  $L_x, L_y,$  and  $L_z$  or, more generally,  $J_x, J_y,$  and  $J_z$  when  $J$  is substituted for  $L$  in the above derivation.

The matrix elements of  $D(\alpha\beta\gamma)$  are denoted by

$$\langle j m' | D(\alpha\beta\gamma) | j m \rangle \equiv D_{m'm}^{(j)}(\alpha\beta\gamma) \equiv D_{m'm}^{(j)}(\omega) \quad [3.176]$$

The matrix of  $D(\alpha\beta\gamma)$  in the representation  $D^{(j)}$  will be symbolized by  $D^{(j)}(\omega)$ . Finally, for a single rotation about a given axis, in this case  $\beta$

$$D_{m'm}^{(j)}(0\beta 0) = d_{m'm}^{(j)}(\beta) \quad [3.177]$$

Since the representations under consideration have matrices which are diagonal in  $J_z$

$$D_{m'm}^{(j)}(\alpha\beta\gamma) = \exp(im'\gamma) d_{m'm}^{(j)}(\beta) \exp ima \quad [3.178]$$

and only the quantities

$$d_{m'm}^{(j)}(\beta) = \langle j m' | \exp \frac{2\pi i \beta}{h} J_y | j m \rangle \quad [3.179]$$

needs to be evaluated.

Consider the spin representation  $j = 1/2$ . Eqns. 3.62-64 shows that the  $2 \times 2$  unitary matrix  $\exp \frac{2\pi i \beta}{h} J_y$  is equal to  $\exp M$  where

$$M = \frac{\beta}{2} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad [3.180]$$

$$M^{2n} = (-1)^n (\beta/2)^{2n} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad [3.181]$$

$$M^{2n+1} = (-1)^n (\beta/2)^{2n+1} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad [3.182]$$

where  $n$  is an integer. Since

$$\exp M = 1 + M + \frac{M^2}{2} + \frac{M^3}{3!} + \dots \quad [3.183]$$

one obtains

$$\exp \frac{2\pi i\beta}{h} \mathbf{J}_y = \begin{array}{c|cc} & \mathbf{m} & \\ \hline \mathbf{m}' & + 1/2 & - 1/2 \\ + 1/2 & \cos \beta/2 & \sin \beta/2 \\ - 1/2 & - \sin \beta/2 & \cos \beta/2 \end{array} \quad [3.184]$$

This result along with Eqn. 3.178 gives the transformation properties of the spinors under coordinate rotations. Since the spin matrices Eqns 3.62-64 are proportional to the angular momentum operators in the  $D^{(1/2)}$  representation they transform under rotations like the components of a vector.

A generating function for the  $d_{m'm}^{(j)}(\beta)$  for general  $j$  may be constructed by using the representation of the  $u(j\ m)$  in terms of Eqn. 3.115.

$$\begin{aligned} D(\alpha\beta\gamma)u(j\ m) &= \frac{(\chi_+)^{j+m}(\chi_-)^{j-m}}{[(j+m)!(j-m)!]^{1/2}} \\ &= \sum_{m'} u(j\ m') D_{m'm}^{(j)}(\alpha\beta\gamma) \end{aligned} \quad [3.185]$$

From Eqn 3.184

$$D(0\beta 0)u(j\ m) = \sum_{m'} \frac{\chi_+^{j+m'} \chi_-^{j-m'}}{m' [(j+m')!(j-m')!]^{1/2}} d_{m'm}^{(j)}(\beta) \quad [3.186]$$

The function  $d_{m'm}^{(j)}(\beta)$  can be expressed in terms of the Jacobi polynomial. The notation<sup>12</sup>  $P_n^{(\alpha, \beta)}(x)$  is used for the normalized orthogonal polynomials defined by

$$(\varphi_n, \varphi_m) \equiv \int_{-1}^1 (1-x)^\alpha (1+x)^\beta \varphi_n(x) \varphi_m(x) dx \quad [3.187]$$

$\alpha$  and  $\beta$  which are real, should not be negative in order to integrate this equation but most of the relations derived here are valid without this restriction.



The  $P_n^{(\alpha, \beta)}(x)$  are normalized so that

$$P_n^{(\alpha, \beta)}(1) = \left(\frac{n + \alpha}{n}\right) \quad [3.188]$$

They satisfy the Rodrigues formula

$$P_n^{(\alpha, \beta)}(x) = \frac{(-1)^n}{2^n n!} (1-x)^{-\alpha} (1+x)^{-\beta} \frac{d^n}{dx^n} [(1-x)^{\alpha+n} (1+x)^{\beta+n}] \quad [3.189]$$

from which the series expansion is obtained

$$P_n^{(\alpha, \beta)}(x) = 2^{-n} \sum_{v=0}^n \binom{n+\alpha}{v} \binom{n+\beta}{n-v} (x-1)^{n-v} (x+1)^v \quad [3.190]$$

$d_{m' m}^{(j)}(\beta)$  in terms of the Jacobi polynomial is

$$d_{m' m}^{(j)}(\beta) = \left[ \frac{(j+m')!(j-m)!}{(j+m)!(j-m)!} \right]^{1/2} (\cos \beta/2)^{m'+m} (\sin \beta/2)^{m'-m} P_{j-m}^{(m'-m, m'+m)}(\cos \beta) \quad [3.191]$$

Again all results derived from this expression are correct even though  $m' - m$  and  $m' + m$  should be positive for the matrix to be valid.

We turn our attention now to products of the complete matrix elements  $D_{m'_1 m_1}^{(j_1)}(\alpha\beta\gamma) D_{m'_2 m_2}^{(j_2)}(\alpha\beta\gamma)$ . The values of the Euler angles in the two matrix elements are equal. These products are the matrix elements of the transformation of products of angular momentum eigenvectors of the type  $u(j_1 m_1)u(j_2 m_2)$ . The reduction of products of the  $u(j m)$  by use of the vector coupling coefficients corresponds to a similarity transformation for the corresponding matrix elements.

$$D_{m'_1 m_1}^{(j_1)}(\omega) D_{m'_2 m_2}^{(j_2)}(\omega) = \sum_j \langle j_1 m'_1 j_2 m'_2 | j_1 j_2 j m \rangle D_{m'_1 + m'_2 m_1 + m_2}^{(j)}(\omega) \quad [3.192]$$

$$\langle j_1 j_2 j m_1 + m_2 | j_1 m_1 j_2 m_2 \rangle$$

where the values of  $j$  are given by Eqn 3.128. Substitution of the 3-j symbols for the vector coupling coefficients gives

$$D_{m'_1 m_1}^{(j_1)}(\omega) D_{m'_2 m_2}^{(j_2)}(\omega) = \sum_{jm'm} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m'_1 & m'_2 & m' \end{pmatrix} D_{m'm}^{(j)*}(\omega) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \quad [3.193]$$

which, as a result of the unitary property of the matrices, leads to

$$\sum_{m'_1 m'_2 m'_3} D_{m'_1 m_1}^{(j_1)}(\omega) D_{m'_2 m_2}^{(j_2)}(\omega) D_{m'_3 m_3}^{(j_3)}(\omega) \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m'_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad [3.194]$$

The inverse transformation is given by

$$\sum_{m'_1 m'_2 m_1 m_2} \begin{pmatrix} j_1 & j_2 & j \\ m'_1 & m'_2 & m' \end{pmatrix} D_{m'_1 m_1}^{(j_1)}(\omega) D_{m'_2 m_2}^{(j_2)}(\omega) \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m \end{pmatrix} = \frac{\delta_{j'j}}{2j+1} D_{m'm}^{(j)}(\omega) \quad [3.195]$$

We return now to the consideration of the differential properties of finite rotation operators with respect to variation of the Euler angles. It has already been shown that

$$\frac{\partial}{\partial \alpha} D(\alpha\beta\gamma) = D(\alpha\beta\gamma) \frac{\partial}{\partial \varphi} \quad [3.196]$$

$$\frac{\partial}{\partial \beta} D(\alpha\beta\gamma) = D(\alpha\beta\gamma) \frac{\partial}{\partial \varphi_\beta} \quad [3.197]$$

$$\frac{\partial}{\partial \gamma} D(\alpha\beta\gamma) = D(\alpha\beta\gamma) \frac{\partial}{\partial \varphi_\gamma} \quad [3.198]$$

where  $\varphi_\beta$  is the angle coordinate of a point in the frame of reference measured about the line of nodes and  $\varphi_\gamma$  is the angle about the figure axis. To each differential operation  $x$  on the  $D(\omega)$  with respect to  $\alpha, \beta, \gamma$  corresponds a differential operation  $\zeta$  on a function defined in coordinate space.

The result of a succession of operations  $x_1, x_2, x_3, \dots$  may be written as

$$\dots x_3 x_2 x_1 D(\alpha\beta\gamma) \dots \zeta_3 \zeta_2 \zeta_1$$

The angles  $\varphi, \varphi_\beta,$  and  $\varphi_\gamma$  were used to emphasize that the differential operators on the right hand side of Eqns. 3.196-198, and work upon functions defined in coordinate space. They are

identical to  $\alpha$ ,  $\beta$ , and  $\gamma$  respectively. From these equations it is obvious that the representation given by the  $D$ 's corresponds to that given by the angular momentum eigenvectors.

By use of Eqn. 3.16-18 one may write

$$\mathbf{L}_x D(\alpha\beta\gamma) = D(\alpha\beta\gamma) \mathbf{L}_x \quad [3.199]$$

$$\mathbf{L}_y D(\alpha\beta\gamma) = D(\alpha\beta\gamma) \mathbf{L}_y \quad [3.200]$$

$$\mathbf{L}_z D(\alpha\beta\gamma) = D(\alpha\beta\gamma) \mathbf{L}_z \quad [3.201]$$

and

$$\begin{aligned} \mathbf{L}^2 D(\alpha\beta\gamma) &= \frac{\hbar^2}{4\pi^2} \left[ -\frac{\partial^2}{\partial\beta^2} - \cot\beta \frac{\partial}{\partial\beta} - \frac{1}{\sin^2\beta} \left( \frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\gamma^2} - 2\cos\beta \frac{\partial^2}{\partial\alpha\partial\gamma} \right) \right] D(\alpha\beta\gamma) \\ &= D(\alpha\beta\gamma) \mathbf{L}^2 \end{aligned} \quad [3.202]$$

Remembering that the eigenvalue of  $\mathbf{L}^2$  is  $\frac{\hbar^2}{4\pi^2} l(l+1)$  it is obvious that Eqn. 3.202 is an eigenvalue equation for  $\mathbf{L}^2$ . The matrix elements of  $D(\alpha\beta\gamma)$  are the eigenfunctions of  $\mathbf{L}^2$  and  $\mathbf{L}_z$ . Eqn. 3.202 may be rewritten as

$$\left[ \frac{\partial^2}{\partial\beta^2} + \cot\beta \frac{\partial}{\partial\beta} + \frac{1}{\sin^2\beta} \left( \frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\gamma^2} - 2\cos\beta \frac{\partial^2}{\partial\alpha\partial\gamma} \right) + l(l+1) \right] D_{mk}^{(l)}(\omega) = 0 \quad [3.203]$$

where the  $lm;lk$  matrix component of the operator equation was chosen.  $D_{mk}^{(l)}(\omega)$  is the eigenfunction of  $\mathbf{L}^2$  with eigenvalue  $\frac{\hbar^2}{4\pi^2} l(l+1)$  and also of  $\mathbf{L}_z$  with eigenvalue  $\frac{\hbar}{2\pi} m$ . It is simultaneously an eigenfunction of the angular momentum operator  $\frac{-i\hbar}{2\pi} (\partial/\partial\gamma)$  with eigenvalue  $\frac{\hbar}{2\pi} k$ . This operator is analogous to  $\mathbf{L}_z$  in the moving coordinate system and commutes with  $\mathbf{L}^2$  and  $\mathbf{L}_z$ .

## Spherical Tensors and Tensor Operators

The coordinates  $(x,y,z)$  of a point in a given orthogonal axis system are related to the coordinates  $(x',y',z')$  in a rotated orthogonal axis system by

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad [3.204]$$

where the matrix  $||\mathbf{a}||$  is real and orthogonal.

A vector is a set of three entities which, under coordinate rotations, transform as the coordinates of a fixed point, such as  $(x,y,z)$  in Eqn. 3.204 Consider the set of all possible products of the kind  $x^2, xy, yx, \dots$  constructed from  $(x,y,z)$ . There are nine and they span the direct product  $(x,y,z) \times (x,y,z)$ . Under coordinate rotations they will be transformed into the set of nine products  $x'^2, x'y', y'z', \dots$ , with a  $9 \times 9$  transformation matrix which is the direct product matrix  $a \times a$ . A second rank Cartesian tensor is a set of nine entities which transform under rotations according to the matrix  $a \times a$  where  $||\mathbf{a}||$  is defined by Eqn. 3.204.

The definition of higher rank Cartesian tensors is an obvious generalization of these concepts. The set of 27 possible triple products needs a  $27 \times 27$  matrix  $a \times a \times a$  to describe its transformations. This is a third rank Cartesian tensor. A vector is therefore a first rank Cartesian tensor.

The matrix  $a$  is technically equivalent to  $D^{(1)}$ . It follows that the matrix  $a \times a$  must be equivalent to  $D^{(1)} \times D^{(1)}$ . The latter direct product can be reduced to  $D^{(2)} + D^{(1)} + D^{(0)}$ , and it follows that  $a \times a$  can be reduced to the same matrices by a suitable transformation of the basis functions.

A set of  $(2k+1)$  entities that span  $D^{(k)}$  will be termed an irreducible spherical tensor of rank  $k$ . The transformation under rotations is given by

$$D(\alpha\beta\gamma)T_q^k = \sum_{q'} T_{q'}^k D_{q'q}^{(k)}(\alpha\beta\gamma) \quad [3.205]$$

The fact that  $T_q^k$  spans an irreducible representation guarantees that under rotations the set itself is irreducible, that is, only the  $(2k+1)$  functions are needed to describe all their transformations. The superscript  $k$  gives the rank of the tensor, while the subscript  $q$  ranges from  $-k$  to  $k$ .

An  $n^{\text{th}}$  rank Cartesian tensor has  $3^n$  components so a zero rank tensor has only one component. Its transformations are described by a  $1 \times 1$  matrix, and therefore does not mix with other quantities under coordinate rotations. This invariance is what characterizes a zero rank tensor. The term scalar is used to denote a zero rank tensor, the classic example being the scalar or dot product  $\mathbf{A} \cdot \mathbf{B}$  of two vectors.

Now that some of the terms have been defined we shall examine the properties of Cartesian tensors in three dimensions when they are subjected not to the whole group of linear nonsingular transformations but to the subgroup of orthogonal transformations. In this case a tensor which is otherwise irreducible may be reduced. A typical tensor component is

$$T_{ik} = x_i y_k (i, k = 1, 2, 3). \quad [3.206]$$

$T_{ik}$  may be split into symmetric and antisymmetric tensors

$$S_{ik} = 1/2(T_{ik} + T_{ki}) \quad [3.207]$$

$$A_{ik} = 1/2(T_{ik} - T_{ki}). \quad [3.208]$$

Under orthogonal transformations the scalar product  $\mathbf{x} \cdot \mathbf{y} = \sum_i x_i y_i$  is invariant and the symmetric tensor may therefore be reduced by subtracting the invariant quantity to obtain

$$S_{ik} = 1/2(x_i y_k + x_k y_i - 2/3(\mathbf{x} \cdot \mathbf{y})\delta_{ik}) \quad [3.209]$$

It is possible in principle to build up irreducible tensors of any rank from the components of the basic vectors by subtracting all quantities which are invariant under orthogonal transformations. If these tensors are constructed from a single vector  $\mathbf{r}$ , then they are identical with the normalized harmonic polynomials  $Y_{lm}(\mathbf{r})$  except for constant factors.

A harmonic polynomial  $H_l(\mathbf{r})$  is a homogeneous polynomial of degree  $l$  in the components of  $\mathbf{r}$ , and satisfies Laplace's equation

$$\Delta H_l(\mathbf{r}) = 0 \quad [3.210]$$

The harmonic polynomials may be generated as follows. Consider a vector  $\mathbf{v}$  of zero amplitude ( $\mathbf{v} \cdot \mathbf{v} = 0$ )

$$\mathbf{v} = (-2t, 1 - t^2, i(1 + t^2)) \quad [3.211]$$

$$\Delta(\mathbf{r} \cdot \mathbf{a})^l = l(l-1)(\mathbf{a} \cdot \mathbf{a})(\mathbf{r} \cdot \mathbf{a})^{l-2} \quad [3.212]$$

where  $\mathbf{a} = \text{constant}$ . Therefore  $\Delta(\mathbf{r} \cdot \mathbf{v})^l = 0$  and the coefficients of the powers of  $t$  in  $\mathbf{r} \cdot \mathbf{v}^l = [y + iz - 2xt - (y - iz)t^2]^l$  are themselves harmonic polynomials. We have the generating function

$$[y + iz - 2xt - (y - iz)t^2]^l = t^l \sum_{m=-l}^l H_{lm}(\mathbf{r}) t^m \quad [3.213]$$

There are then  $(2l+1)$  independent harmonic polynomials of a given degree  $l$ . The functions  $r^{-l}H_{lm}(\mathbf{r})$  are single valued continuous functions on the unit sphere which are solutions of the Laplace equation. Therefore the  $2l+1$  functions  $r^{-l}H_{lm}(\mathbf{r})$  ( $m = 0, \pm 1, \pm 2, \dots, \pm l$ ) are linear combinations of the  $2l+1$  spherical harmonics  $Y_{lm}(\theta, \varphi)$ . The normalized harmonic polynomial or solid harmonic is defined

$$Y_{lm}(\mathbf{r}) = r^l Y_{lm}(\theta, \varphi) \quad [3.214]$$

A few of the  $Y_{lm}(\mathbf{r})$  are listed in Appendix A.

The spherical components of  $\mathbf{r}$  are defined as

$$r_{\pm} = \mp 1/\sqrt{2} (x \pm iy); r_0 = z \quad [3.215]$$

$$r_0 = z \quad [3.216]$$

and the solid harmonic  $Y_{lm}(\mathbf{r})$  in this notation is

$$Y_{lm}(\mathbf{r}) = (3/4\pi)^{1/2} r_m (m = 0, \pm 1) \quad [3.217]$$

$$Y_{lm}(\mathbf{r}) = (3/4\pi)^{1/2} r^l (m = 0, \pm 1) \quad [3.217]$$

It is possible to construct similar expressions for any quantity which transforms like a vector under rotations. Using this convention and the vector coupling methods described in the previous section one may construct spherical tensors of any rank from the spherical components of a given set of vector quantities. Hence

$$T(lm) = \sum_{m_1 m_2} T(l_1 m_1) T(l_2 m_2) \langle l_1 m_1 l_2 m_2 | l_1 l_2 l m \rangle \quad [3.218]$$

where  $T(l_1 m_1), \dots$  are the components of any spherical tensors which transform under rotations in the same way as the  $Y_{lm}, \dots$  respectively. The product of two spherical harmonics is<sup>1</sup>

$$Y_{l_1 m_1}(\mathbf{r}) Y_{l_2 m_2}(\mathbf{r}) = \sum_{lm} \left[ \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)} \right]^{1/2} \langle l_1 m_1 l_2 m_2 | l_1 l_2 l m \rangle \langle l_1 0 l_2 0 | l_1 l_2 l 0 \rangle r^{l_1 + l_2 - l} Y_{lm}(\mathbf{r}) \quad [3.219]$$

The relationship of a tensor operator  $T(lm)$  formed from two solid harmonics  $Y_{l_1 m_1}(\mathbf{r}), Y_{l_2 m_2}(\mathbf{r})$  to  $Y_{lm}(\mathbf{r})$  is shown by use of the unitary properties<sup>1</sup> of the vector-coupling coefficients and Eqn. 3.219

$$T(lm) = \left[ \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)} \right]^{1/2} \langle l_1 0 l_2 0 | l_1 l_2 l 0 \rangle r^{l_1 + l_2 - l} Y_{lm}(\mathbf{r}) \quad [3.220]$$

The inverse transformation of  $T(lm)$  to  $T(l_1 m_1) T(l_2 m_2)$  is given by the orthogonality of the vector-coupling coefficients

$$T(l_1 m_1) T(l_2 m_2) = \sum_{lm} T(lm) \langle l_1 l_2 l m | l_1 m_1 l_2 m_2 \rangle \quad [3.221]$$

Let us turn our attention now to tensor operators in quantum mechanics. A finite rotation of the frame of reference of a quantum mechanical system about the origin induces a canonical transformation<sup>6</sup> on the coordinates and momenta, and a corresponding unitary transformation on

all operators relating to the system. Each unitary transformation  $D(\alpha \beta \gamma) \equiv D(\omega)$  corresponds to a rotation  $(\alpha \beta \gamma) \equiv (\omega)$  and for any operator  $Q$

$$Q \rightarrow Q' = D(\omega)QD^{-1}(\omega) \quad [3.222]$$

The concept of spherical tensor can be extended to that of an irreducible tensor operator  $T(k)$  which is a set of the  $2k+1$  operators  $T(k q)$  and which transforms under rotations like the components of the spherical tensor  $Y_{kq}$

$$D(\omega)T(k q)D^{-1}(\omega) = \sum_{q'=-k}^k T(k q')D_{q'q}^{(k)}(\omega) \quad [3.223]$$

In Racah's original work on irreducible tensors<sup>10</sup>, he defined them by the relationships

$$[J_{\pm}, T_q^k] = T_{q \pm 1}^k [(k \mp q)(k \pm q + 1)]^{1/2} \quad [3.224]$$

$$[J_z, T_q^k] = qT_q^k \quad [3.225]$$

These definitions are equivalent to Eqn. 3.223. Take the operator in Eqn. 3.223 to be that for an infinitesimal rotation. The rotation operator can be given by  $1 + i\delta\alpha J_n$  where  $n$  labels the axis about which the rotation  $d\alpha$  is made. Then

$$(1 + i\delta\alpha J_n)T_q^k(1 - i\delta\alpha J_n) = \sum_{q'} T_{q'q}^k D_{q'q}^{(k)}(\delta\alpha_n) \quad [3.226]$$

From Eqn. 3.176

$$D_{q'q}^{(k)}(\delta\alpha_n) = \langle k q' | 1 + i\delta\alpha J_n | k q \rangle = \delta_{q'q} + i\delta\alpha \langle k q' | J_n | k q \rangle \quad [3.227]$$

From Eqns. 3.226-227, expanding and neglecting quantities of the order of  $(\delta\alpha)^2$ , we obtain

$$T(k q) - i\delta\alpha T(k q)J_n + i\delta\alpha J_n T(k q) = \sum_{q'} [\delta_{q'q} + i\delta\alpha \langle k q' | J_n | k q \rangle] T(k q') \quad [3.228]$$



which gives

$$\mathbf{J}_n T(k q) - T(k q) \mathbf{J}_n = \sum_{q'} T(k q')(k q' | \mathbf{J}_n | k q) \quad [3.229]$$

Substituting  $\mathbf{J}_z$  or  $\mathbf{J}_\pm$  for  $\mathbf{J}_n$  one obtains Eqns. 3.224-225. Expressed in a more compact form one has

$$[\mathbf{J}, \cdot [\mathbf{J}, T(k q)]] = \frac{\hbar^2}{4\pi^2} k(k+1) T(k q) \quad [3.230]$$

$$[\mathbf{J}_0, T(k q)] = \frac{\hbar}{2\pi} q T(k q) \quad [3.231]$$

The scalar product of two tensors of the same rank is

$$(\mathbf{T} \cdot \mathbf{U}) = \sum_q (-1)^q T(k q) U(k q) \quad [3.232]$$

The spherical tensor formalism, along with the 6- and 9-j symbols greatly simplifies calculations for quantities which may be expressed as scalar or tensor products. This simplification arises from the factorization of the matrix elements and is often called the Wigner-Eckart theorem<sup>3,13</sup>.

Consider the component  $T(k q)$  of a tensor operator acting on a state vector  $u(j m)$  of a system where  $u(j m)$  is an eigenvector of the operators  $\mathbf{J}^2, \mathbf{J}_z$ . The effect of a finite rotation  $\omega$  of the coordinate system on the quantity  $T(k q)u(j m)$  will be examined.

$$\begin{aligned} D(\omega)[T(k q)u(j m)] &= [D(\omega)T(k q)D^{-1}(\omega)]D(\omega)u(j m) \\ &= \sum_{q'm'} T(k q)u(j m') D_{q'q}^{(k)}(\omega) D_{m'm}^{(j)}(\omega) \end{aligned} \quad [3.233]$$

from Eqn. 3.223. The vector  $T(k q)u(j m)$  is transformed according to the product representation  $D^{(k)} \times D^{(j)}$  of the rotation group and may be expressed by use of vector-coupling coefficients as a linear combination of quantities each of which is transformed according to an irreducible representation.

Thus

$$T(k q)u(j m) = \sum_{j' m'} \langle k q j m | k j' m' \rangle \Phi(j' m') \quad [3.234]$$

where

$$\Phi(j' m') = \sum_q T(k q)u(j m) \langle k q j m | k j' m' \rangle \quad [3.235]$$

due to the orthogonality of the vector-coupling coefficients.  $\Phi(j' m')$  are eigenvectors of  $J^2$ ,  $J_z$  with eigenvalues  $j'$  and  $m'$  respectively.

The matrix element of  $T(k q)$

$$\langle j' m' | T(k q) | j m \rangle \equiv (u(j' m'), T(k q)u(j m)) \quad [3.236]$$

is, since the  $u(j m)$  are assumed to be orthogonal, equal to

$$(u(j' m'), \Phi(j' m') \langle k q j m | k j' m' \rangle)$$

Following is the proof of the Wigner-Eckart theorem: **THEOREM.** Consider the transformation

$$v(\alpha j m) = \sum_{\beta} w(\beta j m) \langle \beta j m + 1 | \alpha j m \rangle \quad [3.237]$$

Then (supposing  $m < j$ ),

$$v(\alpha j m + 1) = \sum_{\beta} w(\beta j m + 1) \langle \beta j m + 1 | \alpha j m + 1 \rangle \quad [3.238]$$

But

$$\begin{aligned} v(\alpha j m + 1) &= \frac{2\pi J_+}{[(j - m)(j + m + 1)]^{1/2}} v(\alpha j m) \\ &= \sum_{\beta} w(\beta j m + 1) \langle \beta j m | \alpha j m \rangle \end{aligned} \quad [3.239]$$

from the original expression. Hence

$$\langle \beta j m + 1 | \alpha j m + 1 \rangle = \langle \beta j m | \alpha j m \rangle \quad [3.240]$$

and the transformation coefficients  $(\beta j m | \alpha j m)$  are independent of  $m$ .

Thus the left hand factor in Eqn. 3.240 is independent of  $m$ ; that is, it does not depend on the frame of reference but only on the physical properties of the operator and the system.

A scalar quantity which differs slightly from the left hand term in Eqn. 3.77 is defined. The symmetry of the 3-j symbol with an even permutation is used to replace the vector coupling coefficient with a more symmetrical coefficient in  $j, j'$  and  $m, m'$ . The reduced or double bar matrix elements are defined as

$$\begin{aligned} \langle j' m' | T(k q) | j m \rangle &= (-1)^{j'-m} \frac{\langle j' m' j - m | j' j k q \rangle}{(2k + 1)^{1/2}} \langle j' || T(k) || j \rangle \\ &= (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle j' || T(k) || j \rangle \\ &= (-1)^{k-j+j'} \frac{\langle k q j m | k j j' m' \rangle}{(2j' + 1)^{1/2}} \langle j' || T(k) || j \rangle \end{aligned} \quad [3.241]$$

The phase convention is that chosen by Racah.<sup>10</sup>

Because of the orthogonality of the vector-coupling coefficients one obtains

$$\begin{aligned} \delta_{kk'} \delta_{qq'} \langle j' || T(k) || j \rangle &= (2k + 1)^{1/2} \sum_{mm'} (-1)^{j'-m} \langle j' j k' q' | j' m' j - m \rangle \langle j' m' | T(k q) | j m \rangle \\ &= (2k + 1) \sum_{mm'} (-1)^{j'-m'} \begin{pmatrix} j' & k' j \\ -m' q' m \end{pmatrix} \langle j' m' | T(k q) | j m \rangle \\ &= \sum_{mm'q} (-1)^{j'-m'} \begin{pmatrix} j' & k' j \\ -m' q' m \end{pmatrix} \langle j' m' | T(k q) | j m \rangle \end{aligned} \quad [3.242]$$

### ***Coupling of Three or Four Angular Momenta***

Consider the coupling of three angular momenta  $j_1, j_2$ , and  $j_3$  to form a resultant  $J$ . There is no unique way to carry out this coupling. The order of coupling determines the phase of the resulting state vector.

In general there are several values of intermediate angular momentum (say  $j_{12}$ ) which gives a particular value of  $J$  once a definite way to carry out the coupling has been chosen. Let  $j_1 = 1$  and  $j_2 = 2$ . The possible values of  $j_{12}$  are 1, 2, and 3. Now, if  $j_3 = 1$  and we require that  $J = 3$ , either  $j_{12} = 2$  or 3 will give this resultant when coupled to  $j_3$ . The states with particular  $J$  and  $M$  but different values of the intermediate angular momentum are independent. They must be distinguished by the intermediate  $j$  values and the mode of coupling. For a given  $JM$  there is in general a system of states which are represented in different ways by different modes of coupling. There exists a unitary transformation connecting two such representations.

For a coupling given by  $j_1$  and  $j_2$  to form  $j_{12}$  which is then coupled to  $j_3$  to form  $J$ , the state vector is denoted by  $v((j_1 j_2) j_{12} j_3, JM)$ . The state vector  $(j_1, (j_2 j_3) j_{23}, JM)$  arises from  $j_1$  being coupled to  $j_{23}$  to form the resultant  $J$ . These vectors are given by

$$\begin{aligned} w((j_1 j_2) j_{12} j_3, JM) &= \sum_{m_{12} m_3} v(j_1 j_2 j_{12} m_{12}) u(j_3 m_3) \langle j_{12} m_{12} j_3 m_3 | j_{12} j_3 J M \rangle \\ &= \sum_{m_1 m_2 m_3 m_{12}} u(j_1 m_1) u(j_2 m_2) u(j_3 m_3) \langle j_1 m_1 j_2 m_2 | j_1 j_2 j_{12} m_{12} \rangle \langle j_{12} m_{12} j_3 m_3 | j_{12} j_3 J M \rangle \end{aligned} \quad [3.243]$$

and

$$\begin{aligned} w(j_1, (j_2 j_3) j_{23}, JM) &= \sum_{m_1 m_2 m_3 m_{23}} u(j_1 m_1) u(j_2 m_2) u(j_3 m_3) \langle j_2 m_2 j_3 m_3 | j_2 j_3 j_{23} m_{23} \rangle \\ &\quad \times \langle j_1 m_1 j_{23} m_{23} | j_1 j_{23} J M \rangle \end{aligned} \quad [3.244]$$

The unitary transformation connecting these two representations is given by

$$w(j_1, (j_2 j_3) j_{23}, JM) = \sum_{j_{12}} w((j_1 j_2) j_{12} j_3, JM) \langle (j_1 j_2) j_{12} j_3 J M | j_1 (j_2 j_3) j_{23} J M \rangle \quad [3.245]$$

Making use of the orthogonality of the vector coupling coefficients, Eqns. 3.156-157 one obtains

$$\begin{aligned} \langle (j_1 j_2) j_{12} j_3 J | j_1 (j_2 j_3) j_{23} J \rangle &= \sum_{m_1 m_2 m_3 m_{12} m_{23}} \langle j_{12} j_3 J M | j_{12} m_{12} j_3 m_3 \rangle \langle j_1 j_2 j_{12} m_{12} | j_1 m_1 j_2 m_2 \rangle \\ &\quad \times \langle j_2 m_2 j_3 m_3 | j_2 j_3 j_{23} m_{23} \rangle \langle j_1 m_1 j_{23} m_{23} | j_1 j_{23} J M \rangle \end{aligned} \quad [3.246]$$

where the argument  $M$  in the transformation coefficient has been dropped as a result of the Wigner-Eckart theorem. The  $M$  in the vector coupling coefficients ranges from  $-J$  to  $J$ .

The vector coupling coefficients are not invariant under rotations of the frame of reference, while the energies to be computed from them are scalars, and therefore, invariant. The transformation coefficient just derived is a scalar quantity but evaluation of this coefficient would be very tedious due to the large numbers of vector coupling coefficients involved. It is possible, however, to evaluate scalar quantities such as this transformation coefficient directly.

A quantity associated with such transformations between coupling schemes of three angular momenta, the 6-j symbol, is now defined<sup>11</sup>. It is normalized such that the symbol has maximum symmetry with respect to its arguments. It is defined as

$$\left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{matrix} \right\} = [(2j_{12} + 1)(2j_{23} + 1)]^{-1/2} (-1)^{j_1 + j_2 + j_{23} + J} \langle (j_1 j_2) j_{12} j_3 J | j_1 (j_2 j_3) j_{23} J \rangle$$

$$[(2j_{12} + 1)(2j_{23} + 1)]^{-1/2} (-1)^{j_1 + j_2 + j_3 + J} \quad [3.247]$$

$$\sum_{m_1 m_2} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j_{12} m_1 + m_2 \rangle \langle j_{12} m_1 + m_2 j_3 M - m_1 - m_2 | j_{12} j_3 J M \rangle$$

$$\langle j_2 m_2 j_3 M - m_1 - m_2 | j_2 j_3 j_{23} M - m_1 \rangle \langle j_1 m_1 j_{23} M - m_1 | j_1 j_{23} J M \rangle$$

where the number of indices of summation have been reduced because of the rule  $m_1 + m_2 = M$ .

The 6-j symbol is important in all situations involving recoupling of angular momenta. Even when more than three angular momenta are being coupled the recoupling coefficients may be expressed in terms of the 6-j symbols.

The symmetry properties of the 6-j symbol are best determined by use of the 3-j symbol instead of the vector coupling coefficient. The 3-j symbol is associated with the coupling of three angular momenta to give zero resultant. The expression

$$\sum_{m_1 m_2 m_3} u(j_1 m_1) u(j_2 m_2) u(j_3 m_3) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

is a scalar. The set of  $(2j_1 + 1)(2j_2 + 1)(2j_3 + 1)$  3-j symbols with given values of  $j_1, j_2$ , and  $j_3$  and all possible corresponding values of  $m_1, m_2$ , and  $m_3$  may be regarded as a tensor which transforms under rotations contragrediently to the set of products  $u(j_1 m_1) u(j_2 m_2) u(j_3 m_3)$ . A quantity such as

$\begin{pmatrix} j \\ m \ m' \end{pmatrix}$  has been previously defined, Eqn. 3.163. A corresponding contraction process may also be defined. Contraction of the indices (the  $m$ 's) in products of 3- $j$  symbols will be carried out. The contractions may only occur between 3- $j$  symbols which have the same  $j$  values. The basic contraction process is exemplified by

$$\sum_{m_3 m'_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_4 & j_3 & j_5 \\ m_4 & m'_3 & m_5 \end{pmatrix} \begin{pmatrix} j_3 \\ m_3 \ m'_3 \end{pmatrix}$$

Once a definite convention for carrying out the contraction process is chosen<sup>1</sup>, and remembering both that the metric tensor is skew symmetric for half-integer  $j$  and the symmetry properties of the 3- $j$  symbols, one obtains

$$\left. \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{matrix} \right\} = \sum_{\text{all } m} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_5 & j_6 \\ m'_1 & m'_5 & m'_6 \end{pmatrix} \begin{pmatrix} j_4 & j_2 & j_6 \\ m'_4 & m'_2 & m'_6 \end{pmatrix} \\ \begin{pmatrix} j_4 & j_5 & j_3 \\ m_4 & m'_5 & m'_3 \end{pmatrix} \begin{pmatrix} j_1 \\ m_1 \ m'_1 \end{pmatrix} \begin{pmatrix} j_2 \\ m_2 \ m'_2 \end{pmatrix} \begin{pmatrix} j_3 \\ m_3 \ m'_3 \end{pmatrix} \\ \begin{pmatrix} j_4 \\ m_4 \ m'_4 \end{pmatrix} \begin{pmatrix} j_5 \\ m_5 \ m'_5 \end{pmatrix} \begin{pmatrix} j_6 \\ m_6 \ m'_6 \end{pmatrix} \quad [3.248]$$

From the symmetries of the 3- $j$  symbols<sup>1</sup>, the symmetries of the 6- $j$  symbol are derived. It is left invariant by any permutation of the columns. It is also invariant against any interchange of the upper and lower arguments in each of any two columns.

Relationships between the 6- $j$  symbol and the vector coupling coefficients are obtained by use of the orthogonal properties of the vector coupling coefficients<sup>1</sup>.

The known unitary nature of the recoupling transformations implies that the real 6- $j$  symbols have the property

$$\sum_j \Sigma_j (2j+1)(2j''+1) \left\{ \begin{matrix} j_1 & j_2 & j' \\ j_3 & j_4 & j \end{matrix} \right\} \left\{ \begin{matrix} j_3 & j_2 & j \\ j_1 & j_4 & j'' \end{matrix} \right\} = \delta_{j'j''} \quad [3.249]$$

That is

$$[(2j+1)(2j'+1)]^{1/2} \left\{ \begin{matrix} j_1 & j_2 & j \\ j_3 & j_4 & j' \end{matrix} \right\}$$

forms a real orthogonal matrix, rows and columns labelled by  $j$  and  $j'$  respectively.

Composition of recoupling transformations yields another relation for the 6- $j$  symbols

$$\sum_{j_{23}} \langle (j_1 j_2) j_{12} j_3 j | j_1 (j_2 j_3) j_{23} j \rangle \langle j_1 (j_2 j_3) j_{23} j | j_2 (j_3 j_1) j_{31} j \rangle = \langle (j_1 j_2) j_{12} j_3 j | j_2 (j_3 j_1) j_{31} j \rangle [3.250]$$

which gives

$$\sum_{j_{23}} (-1)^{j_{23} + j_{31} + j_{12}} (2j_{23} + 1) \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} \begin{Bmatrix} j_2 & j_3 & j_{23} \\ j_1 & j & j_{31} \end{Bmatrix} = \begin{Bmatrix} j_3 & j_1 & j_{31} \\ j_2 & j & j_{12} \end{Bmatrix} [3.251]$$

The sum rule of Biedenharn<sup>14</sup> and Elliott<sup>15</sup> is given by a similar consideration of the recoupling of four angular momenta. Consider the transformation

$$\langle (j_1 j_2) j_{12} j_3 j_{123} j_4 j | (j_2 j_3) j_{23} (j_1 j_4) j_{14} j \rangle$$

This is equivalent to the product of two successive recouplings of three angular momenta:

$$\langle (j_1 j_2) j_{12} j_3 j_{123} j | (j_2 j_3) j_{23} j_1 j_4 j \rangle \langle (j_2 j_3) j_{23} j_1 j_{123} j_4 j | (j_2 j_3) j_{23} (j_1 j_4) j_{14} j \rangle$$

Alternatively the recoupling may be carried out in three stages

$$\sum_{j_{124}} \langle (j_1 j_2) j_{12} j_3 j_{123} j | (j_1 j_2) j_{12} j_4 j_{124} j \rangle \langle (j_1 j_2) j_{12} j_4 j_{124} j | (j_1 j_4) j_{14} j_2 j_{124} j_3 j \rangle \langle (j_1 j_4) j_{14} j_2 j_{124} j_3 j | (j_2 j_3) j_{23} (j_1 j_4) j_{14} j \rangle$$

Substitution of 6- $j$  symbols into these two expressions gives

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_{123} & j_{23} \end{Bmatrix} \begin{Bmatrix} j_{23} & j_1 & j_{123} \\ j_4 & j & j_{14} \end{Bmatrix} = \sum_{j_{124}} (-1)^{j_1 + j_2 + j_3 + j_4 + j_{12} + j_{23} + j_{14} + j_{123} + j_{124}} (2j_{124} + 1) \times \begin{Bmatrix} j_3 & j_2 & j_{23} \\ j_{14} & j & j_{124} \end{Bmatrix} \begin{Bmatrix} j_2 & j_1 & j_{12} \\ j_4 & j_{124} & j_{14} \end{Bmatrix} \begin{Bmatrix} j_3 & j_{12} & j_{123} \\ j_4 & j & j_{124} \end{Bmatrix} [3.252]$$

We now turn our attention to the 9- $j$  symbol. One case of transformation between two coupling schemes of four angular momenta gave rise to the Elliott-Biedenharn sum rule, Eqn. 3.252 for 6- $j$  symbols. A transformation of more general interest is one in which the transformation coefficient may not be expressed as a simple product of two transformations of the type given by Eqn. 3.249. The two state vectors which are constructed from the four basic vectors

$u(j_1 m_1), u(j_2 m_2), u(j_3 m_3)$ , and  $u(j_4 m_4)$  are  $w((j_1 j_2) j_{12} (j_3 j_4) j_{34} j m)$  and  $w((j_1 j_3) j_{13} (j_2 j_4) j_{24} j m)$ . The transformation

$$\langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j m | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j m \rangle$$

which connects these schemes may be performed in three steps. In each step recoupling of only three angular momenta is carried out. The transformation coefficient may therefore be expressed in terms of 6-j symbols.

$$\begin{aligned} \langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j \rangle &= \sum_{j'} \langle (j_1 j_2) j_{12} j_{34} j | j_1 (j_2 j_3) j' j \rangle \langle j_2 (j_3 j_4) j_{34} j' | j_3 (j_2 j_4) j_{24} j' \rangle \\ &\times \langle j_1 (j_3 j_4) j' j | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j \rangle \\ &= [(2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)]^{1/2} \sum_{j'} (-1)^{2j'} [3.253] \\ &\times (2j' + 1) \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ & j_3 & j & j' \end{matrix} \right\} \left\{ \begin{matrix} j_3 & j_4 & j_{34} \\ & j_2 & j' & j_{24} \end{matrix} \right\} \left\{ \begin{matrix} j_{13} & j_{24} & j \\ & j' & j_1 & j_3 \end{matrix} \right\} \end{aligned}$$

This recoupling scheme leads to another rotational invariant called the 9-j symbol.

The 9-j symbol<sup>1</sup> is defined by the relation

$$\begin{aligned} \langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j \rangle &= [(2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)]^{1/2} \\ &\left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ & j_3 & j_4 & j_{34} \\ & & j_{13} & j_{24} & j \end{matrix} \right\} \quad [3.254] \end{aligned}$$

Choosing a symmetrical set of labels for the  $j$ 's

$$\left\{ \begin{matrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{matrix} \right\} = \sum_{\kappa} (-1)^{2\kappa} (2\kappa + 1) \left\{ \begin{matrix} j_{11} & j_{21} & j_{31} \\ & j_{32} & j_{33} & \kappa \end{matrix} \right\} \left\{ \begin{matrix} j_{12} & j_{22} & j_{32} \\ & j_{21} & \kappa & j_{23} \end{matrix} \right\} \left\{ \begin{matrix} j_{13} & j_{23} & j_{33} \\ & \kappa & j_{11} & j_{12} \end{matrix} \right\} \quad [3.255]$$

Replacing the 6-j symbols by appropriate 3-j symbols and making use of their orthogonality properties one obtains the symmetric expression



$$\left\{ \begin{matrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{matrix} \right\} = \sum_{\text{all } m} \begin{pmatrix} j_{11} & j_{12} & j_{13} \\ m_{11} & m_{12} & m_{13} \end{pmatrix} \begin{pmatrix} j_{21} & j_{22} & j_{23} \\ m_{21} & m_{22} & m_{23} \end{pmatrix} \begin{pmatrix} j_{31} & j_{32} & j_{33} \\ m_{31} & m_{32} & m_{33} \end{pmatrix} \quad [3.256]$$

$$\begin{pmatrix} j_{11} & j_{21} & j_{31} \\ m_{11} & m_{21} & m_{31} \end{pmatrix} \begin{pmatrix} j_{12} & j_{22} & j_{32} \\ m_{12} & m_{22} & m_{32} \end{pmatrix} \begin{pmatrix} j_{13} & j_{23} & j_{33} \\ m_{13} & m_{23} & m_{33} \end{pmatrix}$$

The rows or columns in the matrix forming the 9-j symbol may be permuted, or the matrix itself may be transposed, producing no more than a change of sign in the numerical value. An odd permutation of the rows produces an odd permutation of the  $j$ 's in each of the last three 3-j symbols in the above equation leaving the first three unchanged. An odd permutation of the columns has the opposite effect on the  $j$ 's in the 3-j symbols. Transposition simply changes the ordering of the 3-j symbols. The symmetry properties of the 3-j symbols, shows that an odd permutation of rows or columns produces a sign change of

$$(-1)^{j_{11} + j_{12} + j_{13} + j_{21} + j_{22} + j_{23} + j_{31} + j_{32} + j_{33}}$$

An even permutation or transposition leaves the sign unchanged.

The orthogonality and sum rules for the 9-j symbol are derived in the same way as the 6-j symbol. We have

$$\sum_{j_{12} j_{24}} (2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1) \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{matrix} \right\} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j'_{13} & j'_{24} & j \end{matrix} \right\} = \delta_{j_{13} j'_{13}} \delta_{j_{24} j'_{24}} \quad [3.257]$$

from the unitary property of the recoupling transformation on four angular momenta. The multiplicative property of the transformations

$$\sum_{j_{13} j_{24}} \langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j \rangle \langle (j_1 j_3) j_{13} (j_2 j_4) j_{24} j | (j_1 j_4) j_{14} (j_2 j_3) j_{23} j \rangle$$

$$= \langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j | (j_1 j_4) j_{14} (j_2 j_3) j_{23} j \rangle \quad [3.258]$$

gives the sum rule

$$\begin{aligned}
 & \sum_{j_{13}j_{24}} (-1)^{2j_2 + j_{24} + j_{23} - j_{34}} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \end{Bmatrix} \begin{Bmatrix} j_1 & j_3 & j_{13} \\ j_4 & j_2 & j_{24} \end{Bmatrix} (2j_{13} + 1)(2j_{24} + 1) \\
 & \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_{13} & j_{24} & j \end{Bmatrix} \begin{Bmatrix} j_1 & j_3 & j_{13} \\ j_{14} & j_{23} & j \end{Bmatrix} \\
 & = \begin{Bmatrix} j_4 & j_3 & j_{34} \\ j_{14} & j_{23} & j \end{Bmatrix}
 \end{aligned} \tag{3.259}$$

Relations linking the 6-j symbol and 9-j symbols are obtained by making use of the orthogonality properties of the 6-j symbols or by composition of recoupling transformations<sup>1</sup>.

Two different recoupling coefficients associated with four angular momenta have been given in terms of a product of two 6-j symbols and a sum of products of three 6-j symbols, the 9-j symbol. It may be shown that every coefficient associated with a recoupling of four angular momenta which is not a recoupling of three of the four may be expressed in one or the other of the above ways.

## *The Rigid Asymmetric Rotor*

If none of the principal moments of inertia are equal or zero the molecule is classified as an asymmetric top. The energy levels cannot be expressed by closed algebraic expressions but can be readily solved using matrix mechanical techniques. A brief description of the notation employed in the energy levels will clarify the discussion of the solution of the asymmetric rotor Hamiltonian.

In the derivation of the energy levels of a symmetric top<sup>16</sup> one internal component of the angular momentum is a constant of the motion and is characterized by the quantum number K. In the asymmetric rotor there is no component of the angular momentum which is a constant of the motion and therefore K is no longer a good quantum number. King et al.<sup>17</sup> devised a double

subscript system for the labeling of energy levels where the subscripts are pseudo-quantum numbers. The asymmetry of the molecule is measured by the value of  $\kappa$  where

$$\kappa = \frac{2B - A - C}{A - C}. \quad [3.260]$$

A, B, C are the rotational constants corresponding to the a, b, c axes and defined by

$$A = \frac{\hbar^2}{8\pi^2 I_a} = \frac{\hbar^2}{8\pi^2 I_c} \quad [3.261]$$

$$B = \frac{\hbar^2}{8\pi^2 I_b} = \frac{\hbar^2}{8\pi^2 I_c} \quad [3.262]$$

$$C = \frac{\hbar^2}{8\pi^2 I_c} \quad [3.263]$$

For a prolate symmetric top  $B=C$  and  $\kappa = -1$  and for an oblate symmetric top  $A=B$  and  $\kappa = +1$ . In an asymmetric rotor the  $-K$  and  $+K$  degeneracy is removed and there are  $(2J+1)$  energy levels for each value of  $J$ .

The Hamiltonian for the rigid asymmetric rotor is given by

$$H = AP_a^2 + BP_b^2 + CP_c^2 \quad [3.264]$$

where  $A = \frac{\hbar^2}{8\pi^2 I_a}$  and B, C are similarly defined. Rearrangement of this equation yields

$$H = \frac{(A + C)P^2}{2} + \frac{(A - C)H(\kappa)}{2} \quad [3.265]$$

$$H(\kappa) = P_a^2 + \kappa P_b^2 - P_c^2 \quad [3.266]$$

where  $P^2 = P_a^2 + P_b^2 + P_c^2$ .

The Schrödinger equation

$$H\psi = E\psi \quad [3.267]$$

cannot be solved directly to yield a closed algebraic expression. The general approach for obtaining values for the energy levels is to assume that the eigenfunctions of the asymmetric top can be written as a linear combination of symmetric top wave functions

$$\psi = \sum_n c_n \psi_n \quad [3.268]$$

where  $\psi_n$  is a member of a normalized set of orthogonal symmetric top wave functions. Substitution of Eq 3.260 into Eq. 3.268 yields

$$\sum_n c_n H \psi_n = E \sum_n c_n \psi_n \quad [3.269]$$

Multiplication by  $\psi_m^*$  and integration gives

$$\sum_n c_n \int \psi_m^* H \psi_n d\tau = E \sum_n c_n \int \psi_m^* \psi_n d\tau \quad [3.270]$$

Since the symmetric top wave functions are orthogonal  $\int \psi_m^* \psi_n d\tau = \delta_{mn}$ . The secular equation thus obtained is

$$|(m|H|n) - E\delta_{m,n}| = 0 \quad [3.271]$$

where  $(m|H|n) = \int \psi_m^* H \psi_n d\tau$ . It is therefore possible to solve for the energy levels of the asymmetric top if the matrix elements  $(m|H|n)$  are known. The nonvanishing matrix elements in the symmetric rotor representation are shown in Table 4.

From Table 4 one can see that the matrix is diagonal in J and off diagonal in K by 2. The matrix is also Hermitian, that is  $H_{K,K} = H_{-K,-K}$ ,  $H_{K,K+2} = H_{K+2,K} = H_{-K,-K-2} = H_{-K-2,-K}$ , which is required in order for the eigenvalues, the solutions to the secular equations, to be real. Because the matrix is diagonal in J it may be factored into J blocks and solved separately as shown in Figure 5. The general K structure associated with each value of J is shown in Figure 6. J can have values of 0,1,2,3,... with K values from

**Table 4. Nonvanishing Matrix Elements in Symmetric Rotor Representation**

$$(J, K, M | P_z | J, K, M) = K$$

$$(J, K, M | P^2 | J, K, M) = J(J + 1)$$

$$(J, K, M | P_z^2 | J, K, M) = K^2$$

$$(J, K, M | P_y^2 | J, K, M) = (J, K, M | P_x^2 | J, K, M) = \frac{1}{2}[J(J + 1) - K^2]$$

$$(J, K, M | P_y^2 | J, K \pm 2, M) = \frac{1}{4} (J, K, M | P_x^2 | J, K \pm 2, M) \\ = \frac{1}{4} \{ [J(J + 1) - K(K \pm 1)][J(J + 1) - (K \pm 1)(K \pm 2)] \}^{1/2}$$

$-J, -J + 1, \dots, J$ . There are  $2J + 1$  eigenvalues for a particular value of  $J$ . Details on these calculations appear in a variety of different sources<sup>16</sup>.

## Symmetry Properties of the Asymmetric Rotor Wave Functions

Classification of the total wave function based on its behavior, change or no change in sign, toward inversion through the origin is indicated as parity. The total wave function is represented by

$$\Psi_T = \Psi_e \Psi_v \Psi_r \Psi_n \quad [3.272]$$

where  $e, v, r, n$  denote electronic, vibrational, rotational, and nuclear functions respectively. Inversion of the coordinates of a nonplanar polyatomic molecule leads to a configuration which cannot be achieved by a simple combination of rotations. These two configurations lead to a doubling of all rotational levels but this doubling is not resolved if the barrier to inversion is sufficiently high. Exchange of identical nuclei due to a rotation about a symmetry axis is crucial to the classification of the energy levels.

The asymmetric rotor wave functions are classified according to their behavior when subjected to the symmetry operations  $C_2^e$ ,  $C_2^v$ , and  $C_2^r$ . Only two of these operations need be considered since

		J				
		0	1	2	3	...
J'	0					
	1					
	2					
	3					
	4					
	⋮					

**Figure 5. General J Matrix**

		K			
	-J	-J+1	...	J+1	J
-J					
-J+1					
⋮					
J+1					
J					

Figure 6. K Structure for a Value of J

the third is a combination of the other two, normally a and c. There are four different types of rotational levels: ++, +-, -+, and --. The first sign is the behavior of the wave function with respect to c and the second is the behavior upon rotation about the a axis<sup>18</sup>.

For a  $C_{2v}$  molecule, if the b axis is the  $C_2(z)$  axis and the c axis is parallel to the x axis, reflection through the yz plane will determine the behavior for a rotation of  $180^\circ$  about the c axis. The behavior under  $C_2$  is determined by rotation about the b axis. The possible combinations are shown in Table 5<sup>18</sup>. In an  $A_1$  vibronic state the ++ levels are  $A_1$ , the +- levels are  $B_2$ , the -+ levels are  $B_1$ , and the -- levels are  $A_2$ . Figure 7 shows the energy level diagram up to  $J = 3$  including symmetry classification for a totally symmetric,  $A_1$ , vibronic state.

The symmetry of the total wave function is also affected by I, the nuclear spin quantum number. For two identical nuclei if I is an integer the total wave function obeys Bose-Einstein statistics and must be symmetric with respect to rotation about the symmetry axis. If I is half-integer then the wave function obeys Fermi-Dirac statistics and must be antisymmetric with respect to rotation.

For two identical nuclei there are  $(2I + 1)^2$  spin functions.  $(I + 1)(2I + 1)$  are symmetric and the remaining  $I(2I + 1)$  are antisymmetric. For two spin 3/2 nuclei, which obey Fermi-Dirac statistics, the symmetric spin functions will combine with antisymmetric rotational levels and vice-versa for a totally symmetric vibronic state.

## *Moments of Inertia*

The classical angular momentum of a rigid body is given by the expression

$$\mathbf{P} = \mathbf{I} \cdot \boldsymbol{\omega} \quad [3.273]$$

where  $\boldsymbol{\omega}$  is the angular velocity and  $\mathbf{I}$  is the moment of inertia tensor. The nine components of the moment of inertia tensor are given by



**Table 5. Rovibronic Species of a  $C_{2v}$  Asymmetric Top Molecule**

Asymmetric rotator designation	( $C_2 = b = z,$ $x = c$ ) $A_1 A_2 B_1 B_2$
++	$A_1 A_2 B_1 B_2$
+ -	$B_2 B_1 A_2 A_1$
- +	$B_1 B_2 A_1 A_2$
--	$A_2 A_1 B_2 B_1$

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2) \quad [3.274]$$

$$I_{yy} = \sum_i m_i (z_i^2 + x_i^2) \quad [3.275]$$

$$I_{zz} = \sum_i m_i (x_i^2 + y_i^2) \quad [3.276]$$

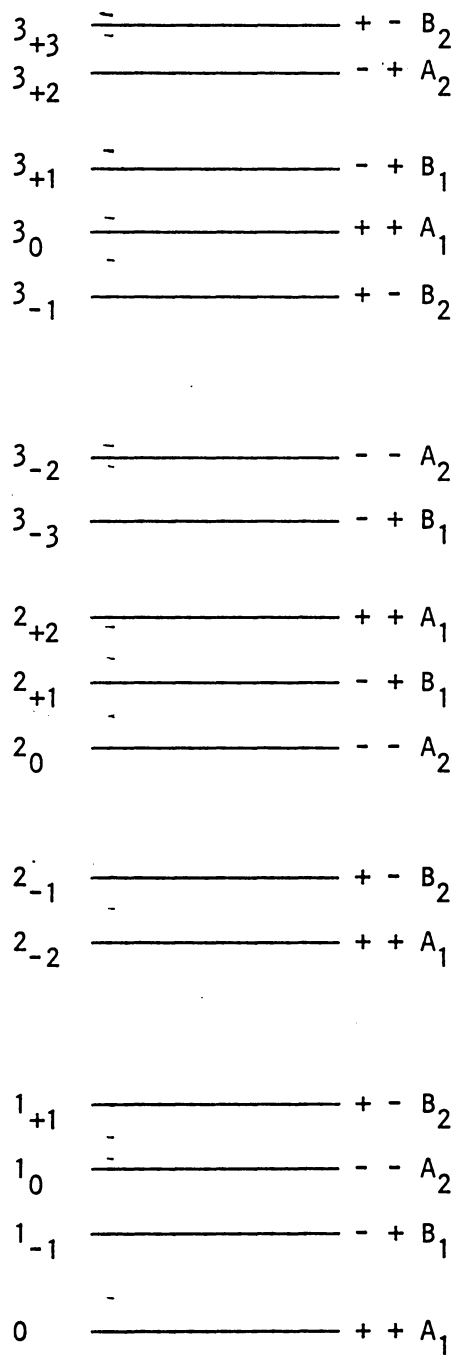
$$I_{xy} = I_{yx} = - \sum_i m_i x_i y_i \quad [3.277]$$

$$I_{zx} = I_{xz} = - \sum_i m_i z_i x_i \quad [3.278]$$

$$I_{yz} = I_{zy} = - \sum_i m_i y_i z_i \quad [3.279]$$

where  $m_i$  is the mass of each particle located at  $x_i, y_i, z_i$  relative to a fixed coordinate system whose origin is the center of mass of the molecule. One may always find a coordinate system such that only the diagonal elements are nonvanishing. These elements are called the principal moments of inertia and are designated  $I_a, I_b,$  and  $I_c$  where a,b,c are the principal axes. The principal moments are the roots of the cubic equation

$$\begin{vmatrix} I_{xx} - I & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} - I & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} - I \end{vmatrix} = 0 \quad [3.280]$$



**Figure 7. Asymmetric top and rovibronic species for  $C_{2v}$  molecule in an  $A_1$  vibronic state**

# Chapter IV

## Matrix Elements of the Hamiltonian

The analysis of the microwave spectrum of a compound with six coupled nuclei has never been reported. This section gives a description of the Hamiltonian which was employed in the assignment of the microwave spectrum of  $(\text{CF}_3)_2\text{NO}$ . The starting point in the study was the analysis of the spectrum of the trifluoromethyl radical<sup>32</sup>. The major postulate of this research was that the  $\text{CF}_3$  group in bis-trifluoromethyl nitroxide could be analysed using the same Hamiltonian and matrix elements used in the study of the  $\text{CF}_3$  radical. The analysis of the trifluoromethyl radical was based on the matrix elements derived for a  $\text{C}_{3v}$  symmetric top molecule with three coupling nuclei. The assumption was made and then verified that the matrix elements off diagonal in  $K$  could be neglected. This assumption reduced the matrix elements to those for a single nucleus with spin  $3/2$ . The analysis of the microwave spectrum of bis-trifluoromethyl nitroxide will require the evaluation of the matrix elements for two identical spin  $3/2$  nuclei. As the results of the section on angular momentum showed, the matrix elements for two identical nuclei are the same. Instead of  $I$  being that for the single nucleus the vector sum is taken and  $I$  will range from  $0, 1, \dots$  to  $\sum_i I_i$ .

When a molecule has one or more unpaired electrons the rotational structure of its spectrum shows splittings referred to as the fine and hyperfine interaction. For an asymmetric top molecule with a single unpaired electron the electron spin angular momentum  $S$  couples with the molecular rotation producing the fine structure in the spectrum. If the molecule contains at least one nucleus with non-zero spin the nuclear spin angular momentum  $I$  couples with  $J$  to produce the hyperfine structure in the microwave spectrum.

Hund proposed five extreme cases of coupling of angular momenta. Two of these are most often observed. In Hund's case (a) both the orbital and spin angular momenta are strongly coupled to the molecular axis. This coupling is applicable mainly to diatomic and linear polyatomic molecules. Most nonlinear molecules closely approximate Hund's case (b). In this case the electron spin is not coupled with the molecular axis. The orbital angular momentum couples with the rotational angular momentum to form the resultant  $N$ , which is then combined with  $S$  to give the total angular momentum minus the nuclear spin,  $J$ .

The  $CF_3$  radical was analysed using Hund's case (b) coupling scheme. The Hamiltonian employed was

$$H = H_{rot} + H_{sr} + H_{hf} \quad [4.1]$$

where the terms on the right are the Hamiltonians for rotation, spin-rotation, and hyperfine respectively. The second and third terms in Eqn. 4.1 will now be discussed, the asymmetric top Hamiltonian has already been presented.

## *Spin-Rotation*

An unpaired electron induces two kinds of interactions. When the electronic orbital angular momentum is not quenched, the spin-orbit interaction is the most important. This interaction is given by

$$H_{so} = A_{so} \mathbf{N} \cdot \mathbf{S} \quad [4.2]$$

The second interaction is called the spin rotation interaction and is given by

$$H_{sr} = (1/2) \sum_{\alpha, \beta} \epsilon_{\alpha\beta} (\mathbf{N}_\alpha \mathbf{S}_\beta + \mathbf{S}_\beta \mathbf{N}_\alpha) \quad [4.3]$$

where  $\alpha, \beta = x, y, z$ . This interaction is a result of the coupling of the weak magnetic field generated by the molecular rotation and the unpaired electron's spin magnetic moment. However, this classical mechanism is outweighed by the second order term generated by a combination of the spin orbit interaction and the electronic Coriolis interaction given by<sup>34</sup>

$$\mathbf{N}_+ \mathbf{L}_- + \mathbf{N}_- \mathbf{L}_+$$

In Hund's case (b) the spin rotation interaction is the most important. The matrix elements are readily obtained using the spherical irreducible tensor method outlined in the previous section on angular momenta. A derivation of the matrix elements of tensor operators is in Appendix F. The derivation of the spin-rotation matrix elements have been reported in many different places (Cook and DeLucia<sup>35</sup> is one of the better) and only a general outline of the procedure will be presented here.

The spin rotational Hamiltonian, Eqn. 4.3, is rewritten in terms of spherical tensors as

$$H_{sr} = (1/2) \sum_{k=0}^2 [T^k(\epsilon) T^k(\mathbf{N}, \mathbf{S}) + T^k(\mathbf{N}, \mathbf{S}) T^k(\epsilon)] \quad [4.4]$$

where

$$T_p^k(\mathbf{N}, \mathbf{S}) = (-1)^p (2k + 1)^{1/2} \sum_{p_1, p_2} T_{p_1}^1(\mathbf{N}) T_{p_2}^1(\mathbf{S}) \begin{pmatrix} 1 & 1 & k \\ p_1 & p_2 & -p \end{pmatrix} \quad [4.5]$$

and  $T^k(\epsilon)$  represents an irreducible tensor of rank  $k$  of the spin rotation coupling constants. The spin rotation interaction tensor consists of nine components but only six are independent even in

a molecule with no symmetry<sup>36</sup>. The number of independent components is reduced as the symmetry increases. Only the diagonal elements remain for a molecule with  $C_{2v}$  symmetry.

The matrix elements are evaluated using Hund's case (b) as a basis set, that is  $NKSJM_J$ . The rotational part of this function is the symmetric top wave function which diagonalizes  $N^2$  and  $N_z$  and is expressed by the rotation matrix of rank  $N$

$$\left[ \frac{(2N+1)}{8\pi} \right]^{1/2} D_{mk}^{(N)*}(\omega)$$

The anomalous sign which appears between the commutation relations of the angular momentum operators in the space-fixed and body fixed axis systems<sup>37</sup> is a problem in dealing with operators expressed in the body fixed axis system as in Eqn. 4.3. This may be avoided by transformation of the molecule-fixed axis components  $q$  of the angular momenta to the space fixed components  $p$ . Using the rotation matrix this transformation is

$$T_p^k(\epsilon) = \sum_q D_{pq}^{(k)*}(\omega) T_q^k(\epsilon) \quad [4.6]$$

The matrix elements of  $H_{sr}$  are given by

$$\begin{aligned} (N'K'SJ'M'_J | H_{sr} | NKSJM_J) &= \delta_{J'J} \delta_{M'_J M_J} \sum_{k=0}^2 (2k+1)^{1/2} [S(S+1)(2S+1)(2N+1)(2N'+1)]^{1/2} \\ &\times \left\{ \begin{matrix} 1 & 1 & k \\ N' & N & N \end{matrix} \right\} (-1)^{J+S+N(1/2)} \left\{ (-1)^k [N(N+1)(2N+1)]^{1/2} \left\{ \begin{matrix} 1 & 1 & k \\ N' & N & N \end{matrix} \right\} \right\} \\ &\times \sum_q (-1)^{N'-K'} \begin{pmatrix} N' & k & N \\ -K' & q & K \end{pmatrix} T_q^k(\epsilon) \end{aligned} \quad [4.7]$$

The spin-rotation Hamiltonian has nonvanishing matrix elements for  $\Delta N = 0, \pm 1$  and  $\Delta K = 0, \pm 1, \pm 2$ . For a molecule with  $C_{2v}$  or higher symmetry the  $\Delta K = \pm 1$  vanish. Explicit expressions for the matrix elements evaluated using Appendices B and C are given in Table 6.

Table 6. Matrix Elements of the Spin-Rotation Interaction

$$\begin{aligned}
 (NKSJ|H_{sr}|NKSJ) &= - \left[ \frac{N(N+1) + S(S+1) - J(J+1)}{2N(N+1)} \right] \{ \epsilon_{aa} K^2 + (\epsilon_{bb} + \epsilon_{cc}) [N(N+1) - K^2] / 2 \} \\
 (N \begin{smallmatrix} \pm \\ \mp \end{smallmatrix} 2SJ|H_{sr}|NKSJ) &= - \left[ \frac{N(N+1) + S(S+1) - J(J+1)}{4N(N+1)} \right] \\
 &\quad \times \{ [N(N+1) - K(K \pm 1)] [N(N+1) - (K \pm 1)(K \pm 2)] \}^{1/2} (\epsilon_{bb} - \epsilon_{cc}) / 2 \\
 (N - \begin{smallmatrix} \mp \\ \pm \end{smallmatrix} KSJ|H_{sr}|NKSJ) &= - [(N - J + S)(N + J + S + 1)(S + J - N + 1) \frac{(N + J - S)}{(2N + 1)} (2N - 1)]^{1/2} \\
 &\quad \times (K/2N)(N^2 - K^2)^{1/2} [\epsilon_{aa} - (\epsilon_{bb} + \epsilon_{cc})] \\
 (N - \begin{smallmatrix} \mp \\ \pm \end{smallmatrix} K \pm 2SJ|H_{sr}|NKSJ) &= \\
 &= - [(N - S + J)(N + J + S + 1)(S + J - N + 1) \frac{(N + J - S)}{4N} (2N + 1)(2N - 1)]^{1/2} \\
 &\quad [(N \pm K)(N \pm K - 1)(N \pm K - 2)(N \pm K + 1)]^{1/2} \{ \pm (\epsilon_{bb} - \epsilon_{cc}) / 2 \}
 \end{aligned}$$

## *Hyperfine Interaction*

All interactions involving the nuclear spin angular momentum  $I$  are called the hyperfine interaction. The splittings caused by this interaction are usually small and therefore only spectroscopic methods with resolution better than a few MHz, such as microwave, can resolve the splittings. The most important hyperfine interaction in open-shell molecules is magnetic, caused by coupling between the unpaired electron and the nuclear spins in the molecule. The nuclear electric quadrupole interaction splits the rotational transitions in both free radicals and closed-shell molecules. All nuclei with a spin quantum number greater than zero are involved in the magnetic hyperfine interaction. The nuclear spin-rotation interaction is orders of magnitude smaller and may be neglected in most microwave investigations.

There are two different types of magnetic interactions. One is between the electron orbital angular momentum  $L$  and  $I$ , and the other between the electron spin  $S$  and  $I$ . Nonlinear molecules do not exhibit the first interaction and this interaction will not be discussed further. The second interaction is divided into two parts, the Fermi contact interaction  $H_F$  and the dipole-dipole interaction  $H_{DD}$

$$H_F = a_F \mathbf{S} \cdot \mathbf{I} \quad [4.8]$$

$$H_{DD} = \mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I} \quad [4.9]$$

where  $T$  denotes a second rank traceless tensor, the sum of the diagonal components is zero. This tensor has only five independent components. The expression for the nuclear quadrupole interaction is identical to that for a closed shell molecule. The nuclear spin-rotation interaction Hamiltonian is identical to that for the electron spin-rotation, Eqn. 4.3, except  $S$  is replaced by  $I$  and  $\epsilon$  by  $C$ .



For molecules which do not involve heavy atoms, the hyperfine energy is much smaller than others. Therefore, in the absence of an external magnetic field the nuclear spin angular momentum is coupled to the angular momentum  $\mathbf{J} = \mathbf{N} + \mathbf{S}$  to form the total angular momentum  $\mathbf{F}$ :

$$\mathbf{F} = \mathbf{J} + \mathbf{I} \quad [4.10]$$

This coupling scheme is referred to as case (a) <sub>$\beta$</sub>  or case (b) <sub>$\beta$</sub> <sup>9</sup>. The basis function is  $w(NKSJIFM_F)$ . The derivation of the matrix elements of the hyperfine Hamiltonians have apparently not been reported in the literature. Following is a detailed description of the derivation of the matrix elements for both the Fermi and dipole-dipole interaction using the irreducible spherical tensor techniques. Pertinent results from the preceding section on Angular Momenta are summarized in Appendix F.

The Fermi contact constant  $a_F$  is proportional to the expectation value of the unpaired electron orbital at the nucleus considered,  $|\psi(0)|^2$ , that is, it represents the s character of the orbital and may be written

$$a_F = (8\pi/3)g_s g_N \beta \beta_N |\psi(0)|^2 \quad [4.11]$$

Consider now only the  $\mathbf{S} \cdot \mathbf{I}$  term in the Hamiltonian. This is a magnetic interaction between the electron and the nucleus. The operators have the form  $g_s \beta \mathbf{S}$  and  $g_N \beta_N \mathbf{I}$  where  $g$  is the nuclear  $g$  factor and  $\beta$  the magnetic moment expressed in Bohr magnetons.  $\mathbf{S}$  and  $\mathbf{I}$  are vector operators and may be written in spherical tensor notation as  $T^1(\mathbf{S})$  and  $T^1(\mathbf{I})$ . The matrix elements are expressed as

$$(N'K'SJ'I'F'M'_F | T^1(\mathbf{S}) \cdot T^1(\mathbf{I}) | NKSJIFM_F)$$

The dot product of two vectors is a scalar quantity.  $\mathbf{I}$  and  $\mathbf{S}$  commute since they refer to different parts of the system. Therefore, the results of the section on the scalar product of two commuting vectors in Appendix F is applicable.

The quantum numbers shown in the above representation of the matrix indicates that it is possible to have matrix elements off-diagonal in  $\mathbf{I}$ . As long as no accidental near degeneracies exist

for the energy levels identified by the same quantum numbers  $NKSJFM_F$  and different values of  $I$  the restriction that the matrix is diagonal in  $I$  is appropriate<sup>38</sup>.

Setting  $j_1 = J, j_2 = I, T(k) = T^1(S), U(k) = T^1(I), k = 1, J = F$  and  $M = M_F$  in F.5 we have

$$(N'K'SJ'IFM'_F | T^1(s) \cdot T^1(I) | NKSJIFM_F) = (-1)^{J+I+F} \delta_{F'F} \delta_{M'_F M_F} \begin{Bmatrix} f & I & J \\ 1 & J & I \end{Bmatrix} \sum_{N''K''} (N'K'SJ' || T^1(S) || N''K''SJ)(N''K''I || T^1(I) || NKI) \quad [4.12]$$

The second reduced matrix element is zero unless  $N'' = N$  and  $K'' = K$ . Since  $I$  does not operate on  $N$  or  $K$  this reduced matrix element may be rewritten as

$$(N'K'I || T^1(I) || NKI) \equiv (I || T^1(I) || I) \delta_{N'N} \delta_{K'K} \quad [4.13]$$

which is equal to<sup>1</sup>

$$(I || T^1(I) || I) = [I(I+1)(2I+1)]^{1/2} \quad [4.14]$$

The other reduced matrix element involves a tensor operator working on only part two of a coupled scheme. The appropriate substitutions in Eqn. F.6 are  $j_1 = S, j_2 = N, J = J, k = 1$ , and  $T(k) = T^1(S)$

$$(K'N'SJ' || T^1(S) || KNSJ) = (-1)^{N+S+J'+1} [(2J+1)(2J'+1)]^{1/2} \begin{Bmatrix} S & J' & N \\ J & S & 1 \end{Bmatrix} \times (K'N'S || T^1(S) || KNS) \quad [4.15]$$

$$(K'N'S || T^1(S) || KNS) = [S(S+1)(2S+1)]^{1/2} \quad [4.16]$$

Combination of Eqns. 4.12, 14, 15, and 16 yield the matrix element expression for the Fermi contact interaction

$$\begin{aligned}
(N'K'SJ'IDF'M'_F|H_F|NKSJIFM_F) &= \delta_{F'F}\delta_{M'_F M_F}\delta_{N'N}\delta_{K'K}(-1)^{J+I+F}(-1)^{N+S+J'+1} \\
&[(2J+1)(2J'+1)I(I+1)(2I+1)S(S+1)(2S+1)]^{1/2} \\
&\left\{ \begin{matrix} F & I & J' \\ 1 & J & I \end{matrix} \right\} \left\{ \begin{matrix} S & J' & N \\ J & S & 1 \end{matrix} \right\} a_F
\end{aligned} \tag{4.17}$$

The dipole-dipole interaction is slightly more complex.  $\mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I}$  may be rewritten<sup>39</sup> as

$$H_{DD} = -r^{-3}\sqrt{10} [T^1(\mathbf{I}) \cdot T^1(\mathbf{S}, C)] \tag{4.18}$$

The operator portion of this equation may be expressed by<sup>39</sup>

$$T^1(\mathbf{I}) \cdot T^1(\mathbf{S}, C^2) = -\sum_{p,q} \begin{pmatrix} 1 & 1 & 2 \\ p & q-p & -q \end{pmatrix} T_p^1(\mathbf{I}) T_{q-p}^1(\mathbf{S}) C_{-q}^2(\theta, \varphi) r^{-3} \tag{4.19}$$

Just as in the spin-rotation interaction the components of the angular momentum are transformed from the molecule-fixed coordinates,  $p$ , to the space fixed coordinates,  $q$ .

$$T_p^k(\mathbf{A}) = \sum_q D_{p-q}^{(k)*}(\theta, \varphi) T_{-q}^k(\mathbf{A}) \tag{4.20}$$

Upon transformation of the operators in Eqn. 4.19 we have

$$T^1(\mathbf{I}) \cdot T^1(\mathbf{S}, C^2) = -T^1(\mathbf{I}) \cdot [T^1(\mathbf{S}) \sum_q C_q^2(\theta, \varphi) r^{-3} D_q^2(\theta, \varphi)] \tag{4.21}$$

The matrix element is now written as

$$(N'K'SJ'IDF'M'_F|T^1(\mathbf{I}) \cdot [T^1(\mathbf{S}) \sum_q C_q^2(\theta, \varphi) r^{-3} D_q^{(k)*}(\theta, \varphi)]|NKSJIFM_F)$$

$C_q^2$  is related to the second rank spherical harmonics as<sup>39</sup>

$$C_q^2(\theta, \varphi) = (4\pi/5)^{1/2} Y_{2q}(\theta, \varphi) \tag{4.22}$$

This harmonic is related only to which orbital the unpaired electron resides on the F atom, that is, it is a function only of the electronic state of the molecule. The coupling constant is now defined as

$$T_q^2(C) = (n | C_q^2(\theta, \varphi) | n) \quad [4.23]$$

where  $n$  (the vibronic state has been implicitly assumed throughout) is the quantum number defining the electronic state of the molecule.

The remaining operator corresponds to the case of a scalar product of two tensors. In the same manner as was done for the Fermi interaction we have

$$\begin{aligned} (N'K'SJ'IFM'_F | T^1(\mathbf{I}) \cdot T^1(\mathbf{S}) \sum_q D_q^2(\theta, \varphi) | NKSJIFM_F) &= \delta_{F'F} \delta_{M'_F M_F} (-1)^{J+I+F} \\ &\left\{ \begin{matrix} F & I & J' \\ 1 & J & I \end{matrix} \right\} (N'K'SJ' | | T^1(\mathbf{S}) \sum_q D_q^2(\theta, \varphi) | | NKSJ)(I | | T^1(\mathbf{I}) | | I) \end{aligned} \quad [4.24]$$

The first reduced matrix element in this equation corresponds to the case of tensors operating on different systems. From F.6 we have

$$\begin{aligned} (N'K'SJ' | | T^1(\mathbf{S}) \sum_q D_q^2(\theta, \varphi) | | NKSJ) &= (N'K' | | \sum_q D_q^2(\theta, \varphi) | | NK)(S | | T^1(\mathbf{S}) | | S) [(2J' + 1)(2J + 1)]^{1/2} \\ &\left\{ \begin{matrix} N' & N & 1 \\ S & S & 1 \\ J' & J & 2 \end{matrix} \right\} \end{aligned} \quad [4.25]$$

The matrix element of the rotation operator is given by<sup>34</sup>

$$(N'K' | | D_q^2(\theta, \varphi) | | NK) = [(2N' + 1)(2N + 1)]^{1/2} (-1)^{N'-K'} \begin{pmatrix} n' & 2 & N \\ -k' & q & K \end{pmatrix} \quad [4.26]$$

This completes the analysis of the dipole-dipole interaction. Combination of Eqns. 4.17 and 23-26 and picking up the negative sign which was left off after Eqn. 4.21 we have

$$\begin{aligned}
(N'K'SJIFM'_F|H_{DD}|NKSJIFM_F) &= -\sqrt{30} g_S g_N \beta_N (-1)^{N+S+J'+1} (-1)^{J+I+F} \\
&\times [I(I+1)(2I+1)S(S+1)(2S+1)(2N'+1)(2N+1)]^{1/2} \begin{Bmatrix} F & I & J' \\ 1 & J & I \end{Bmatrix} \cdot (2S+1)(2J'+1) \\
&\begin{Bmatrix} N' & N & 1 \\ S & S & 1 \\ J' & J & 2 \end{Bmatrix} \sum_q (-1)^{N'-K'} \begin{pmatrix} N' & 2 & N \\ -k' & q & K \end{pmatrix} T_q^2(C)
\end{aligned} \tag{4.27}$$

The components of the tensor in the molecule fixed axis system are

$$g_S g_N \beta_N T_0^2(C) = \frac{T_{zz}}{2} = -\frac{(T_{yy} + T_{xx})}{2} \tag{4.28}$$

$$g_S g_N \beta_N T_{\pm 1}^2(C) = \mp (1/\sqrt{6})(T_{xz} \pm iT_{yz}) \tag{4.29}$$

$$g_S g_N \beta_N T_{\pm 2}^2(C) = (1/\sqrt{24})(T_{xx} - T_{yy} \pm 2iT_{xy}) \tag{4.30}$$

Combination of Eqns. 4.7 and 27 give the expression for the matrix elements of the hyperfine interaction matrix elements. Making use of Appendices B and C the nonvanishing matrix elements are evaluated. The hyperfine matrix elements are given in Table 7. The selection rules are  $\Delta N = 0, \pm 2$ ;  $\Delta K = 0, \pm 2$ ; and  $\Delta J = 0, \pm 1$ .

A Fortran77 program was written which calculates the splitting of the b-type rotational transitions. The spin-rotation and hyperfine constants as well as the minimum and maximum values of N are read in as data. The program calls subroutine FINE which calculates all matrix elements for a given value of J. This subroutine then calls HDIAG, a subroutine written by Robert A. Beaudet, which diagonalizes a Hermitian matrix using the Jacobi method. Subroutine XORDER orders the diagonalized matrix elements, the eigenvalues, in ascending order. The eigenvalues are assigned to specific values of the quantum numbers N, K, and J in subroutine JASSIN. The same sequence of events is then repeated for the hyperfine matrix elements. Subroutine ELEVEL combines the values of the spin-rotation and hyperfine energy levels for each value of I (greater than zero) and F with the same J, N, K. Subroutine FREQP then takes the appropriate differences

**Table 7. Hyperfine Interaction Matrix Elements**

$$\begin{aligned}
 (NKSJIF|H_{hf}|NKSJIF) &= \frac{[F(F+1) - I(I+1) - J(J+1)]}{4J(J+1)} a_F [S(S+1) + J(J+1) - N(N+1)] \\
 &+ 3T_{cc} \frac{[N(N+1) - 3K^2]}{2N} (N+1)(2N-1)(2N+3) \\
 &[N(N+1) + S(S+1) - J(J+1)][N(N+1) + J(J+1) - S(S+1)] \\
 &+ (2/3)N(N+1)[S(S+1) + J(J+1) - N(N+1)] \\
 (NK \pm 2SJIF|H_{hf}|NKSJIF) &= 3(T_{bb} - T_{aa}) \frac{[F(F+1) - I(I+1) - J(J+1)]}{16J(J+1)N(N+1)(2N-1)(2N+3)} \\
 &[(N \pm K - 1)(N \pm K + 1)(N \pm K + 1)(N \pm K + 2)]^{1/2} \\
 &[N(N+1) + S(S+1) - J(J+1)][N(N+1) + J(J+1) - S(S+1)] \\
 &+ (2/3)N(N+1)[S(S+1) + J(J+1) - N(N+1)] \\
 (NKSJ - 1IF|H_{hf}|NKSJIF) &= \\
 &\frac{1}{4J}(F+I+J+1)(I+J-F)(F+J-I)(F+I-J+1) \\
 &(N+S+J+1)(S+J-N)(N+J-S) \frac{(N+S-J+1)}{(2J-1)} (2J+1)^{1/2} \\
 a_F + T_{cc} \frac{[N(N+1) - 3K^2]}{4N^2(N+1)^2(2N+3)} &[S(S+1) + N(N+1) - J(J+1)](2N+3) \\
 + \frac{N^2(N+S+J+2)(N-S+J+1)}{(2N+1)} & \\
 (NK \pm 2J - 1IF|H_{hf}|NKSJIF) &= \frac{(T_{bb} - T_{aa})}{32JN^2(N+1)^2(2N+3)} (F+I+J+1)(I+J-F)(F+I-J+ \\
 &(N-S+J)(N+S-J+1)(-N+S+J)(N+S+J+1)(N \pm K - 1)(N \pm K) \\
 &(N \pm K + 1) \frac{(N \pm K + 2)}{(2J-1)} (2J+1)^{1/2} \\
 (N - 2KSJ - 1IF|H_{hf}|NKSJIF) &= \frac{T_{cc}}{16JN} (N-1)(I+J+F+1)(J+F-I)(I-J+F+1)(I+J \\
 &(J+S+N-1)(J+S+N)(J-S+N-2)(J-S+N-1)[(N-1)^2 - K^2](N^2 - K^2)^{1/2}
 \end{aligned}$$


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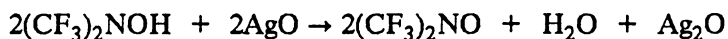
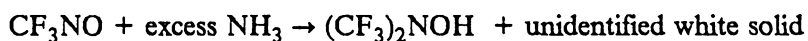
between the energy levels according to the selection rules

$$\Delta N = \Delta J = \Delta F = 1, \Delta I = 0, \text{ and } \Delta K_{-1} = \pm 1, \pm 3, \Delta K_1 = \pm 1, \pm 3.$$

# Chapter V

## Experimental

The bis-trifluoromethyl nitroxide used for this study was synthesized using a published procedure<sup>ref</sup>. The synthetic route



gives a yield of 100% conversion of  $(\text{CF}_3)_2\text{NOH}$  to radical. The water was removed by vacuum distillation. The purity of the product was determined from its infrared spectrum. Not all water was removed since an absorption at 22,235 MHz was observed. This corresponds to the 5(2,5) – 6(1,6) rotational transition. It was easily identified and posed no problem in the assignment of the microwave spectrum.

Although one of the reported properties of this radical is its unusual stability<sup>23</sup>, during the course of this investigation, the sample had to be replenished daily due to some unknown reaction forming products which gave no observable microwave spectrum.

A conventional Stark modulated microwave spectrometer was used for recording the microwave spectrum from 18 to 26.5 GHz. A Hewlett-Packard 8690B microwave sweeper employing a



backward wave oscillator phase locked to a HP8466A reference oscillator was the microwave radiation source. The gaseous radical was introduced into the Stark cell via the vacuum manifold. The Stark cell consisted of a ten foot length of X-band waveguide sealed with mica windows. A nickel plated phosphor bronze septum was supported by Teflon insulators and ran the length of the waveguide. A 33 KHz zero based square wave, the potential of which could be varied from 0- 750 volts, was applied between the septum and the waveguide. This arrangement modulates the resonance frequency through the Stark effect.

The microwave spectrum of bis-trifluoromethyl nitroxide was recorded at dry ice temperature and a sample pressure of approximately 25 microns. To ensure that each line was fully modulated the spectrum was recorded at Stark voltages of 500 and 750 volts. The frequencies of the rotational transitions were recorded using frequency markers of 1 and/or 10 MHz.

Because of the unpaired electron  $(CF_3)_2NO$  is paramagnetic. It is therefore possible to modulate the rotational resonance frequencies via the Zeeman effect, that is, magnetic field modulation. A microwave spectrometer system employing a semi-confocal Fabry-Perot resonant cavity was constructed. The modulating magnetic field was produced by a solenoidal winding of copper wire around the glass walls of the cavity and passing a current square wave through the winding. Zener diodes were placed in the modulating circuit to clamp the current to zero when switched off. These diodes were necessary to make the current waveform a sharply rising and falling square wave. Because of the high inductance of the coil a current spike is created as the current switches off. This produced a source of modulation pickup which effectively buries the signal because of its intensity. This problem could not be overcome during the time frame of this research.

The HP8673B microwave source did not generate sufficient microwave power to be useful. A complete description of this system is given in Appendix E. Once these two problems are overcome, by redesign of the modulation circuit and acquisition of a microwave amplifier, the cavity system should work as expected.

# Chapter VI

## Microwave Spectrum and Molecular Structure of Bis-trifluoromethyl Nitroxide

The most obvious feature of the microwave spectrum of bis-trifluoromethyl nitroxide is an abundance of peaks. Large molecules have small rotational constants resulting in closely spaced energy levels leading to many transitions in the microwave region. The spectrum was analysed between 18 and 26.5 GHz. Flexible molecules also have low-lying vibrational states with significant populations even at low temperatures. Add to this the effects of the interactions between the unpaired electron and the molecular rotation and nuclear spins and the reasons for the congestion becomes obvious.

The presence of so many lines poses a problem in the assignment of the spectrum. Ideally, rotational transitions are assigned by the number of Stark components. Due to the high density of lines these components are not resolved. One must therefore assume a model structure, and in this case, reasonable estimates of the hyperfine and spin-rotation coupling constants, and correlate positions and intensities with that predicted from the model.

The spectrum was assigned in four stages. A rigid rotor spectrum was calculated to determine approximately where the unsplit transitions might be observed. The hyperfine structure will be absent for  $I=0$  leaving only the spin-rotation interaction. Assignment of these components allows determination of  $\epsilon_{aa}$ ,  $\epsilon_{bb}$ , and  $\epsilon_{cc}$ . The hyperfine structure is then analysed to determine  $T_{aa}$ ,  $T_{bb}$ ,  $T_{cc}$ , and  $a_F$ . From the calculated splitting due to the spin-rotation and hyperfine interactions a theoretical unsplit rotational transition is determined. From the series of rotational transitions assigned in this manner the molecular structure can be determined.

The initial values of the rotational constants A, B, and C, were determined from the structure derived in the electron diffraction study<sup>28</sup> except the CNCO framework was assumed to be planar<sup>29</sup>. The Moment of Inertia program, see Appendix G, was used to calculate the rotational constants based on this structure, shown in Figure 8. Transition frequencies and relative intensities were calculated based on these constants and an assumed dipole moment component,  $\mu_b = 1.0D$ , by the Rigid Asymmetric Rotor program, Appendix G. The rigid rotor spectrum predicted rotational transitions occurring in pairs. That is, transitions with the same rotational quantum number and pseudo-quantum number  $K_{-1}$  but  $K_{+1}$  differing by 1 occurred at approximately the same frequency. Normally, unless centrifugal distortion effects removes this degeneracy only one member of each pair may be assigned until the analysis is completed. This is done to prevent locking the rotational constants down too quickly. The presence of the hyperfine structure allows the assignment of the components of these pairs since the splitting for the two are not equal.

For a  $C_{2v}$  symmetry molecule in an  $A_1$  ground vibronic state it was shown that the  $K_{-1}K_1$  which are ee or oo are symmetric and those with eo or oe are antisymmetric. Since the nuclei obey Fermi-Dirac statistics, only symmetric spin functions ( $I=1,3$ ) may exist with antisymmetric rotational states. For  $I=0,2$ , only those vibronic states which are antisymmetric may exist. Analysis of the rotational levels with  $K_{-1}K_1 = ee$  or  $oo$  for  $I=0$  allows determination of the spin-rotation coupling constants. The second order expression for  $\epsilon_{\alpha\beta}$  is<sup>40</sup>

$$\epsilon_{\alpha\beta} = - \frac{2h^2 R_e \langle 0 | \mu_{\alpha\alpha} L_{\alpha} | n \rangle \langle n | A_{SO} L_{\beta} | 0 \rangle}{4\pi^2 (E_0 - E_n)} \quad [6.1]$$

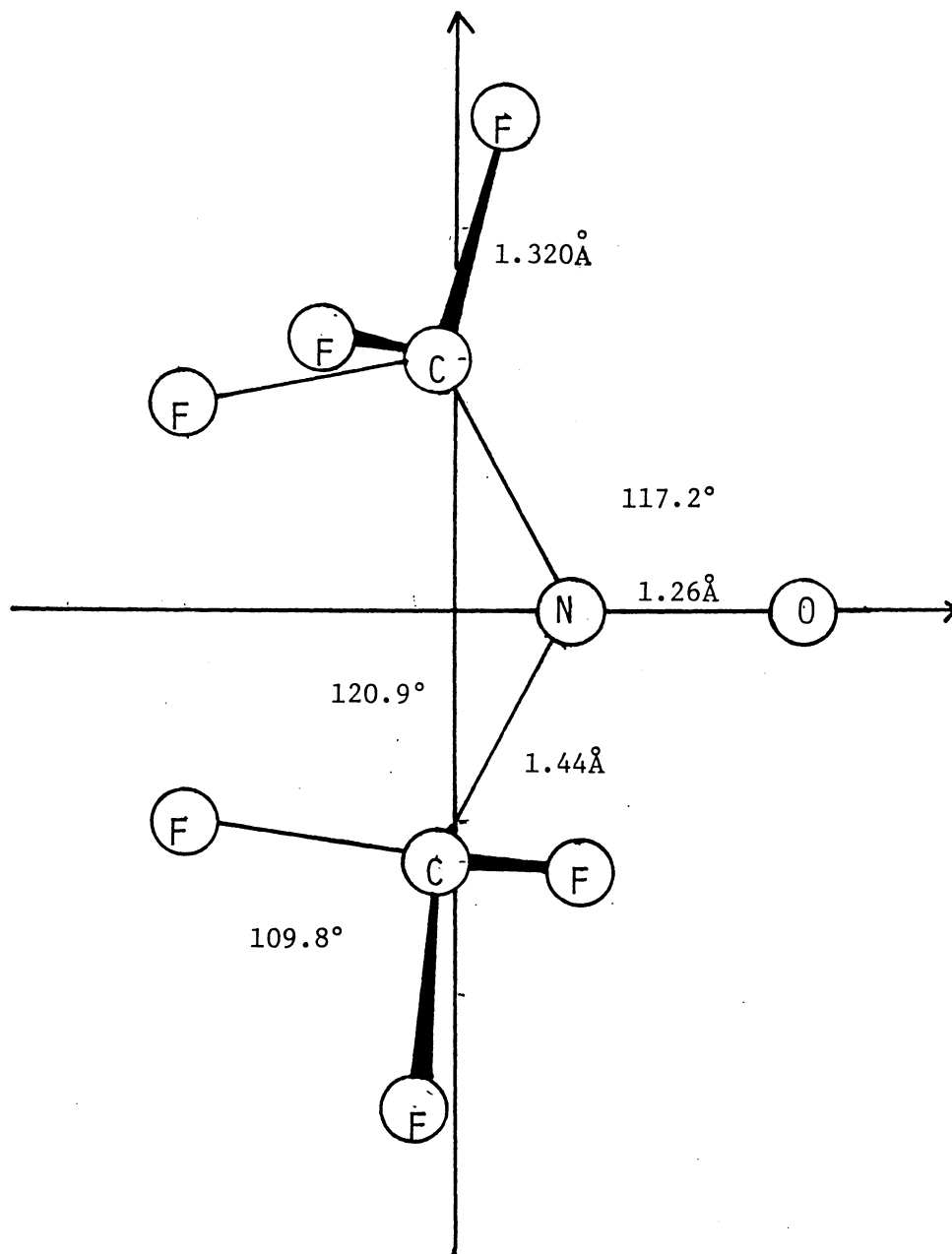


Figure 8. Initial Molecular Structure Taken From Electron Diffraction

where  $\mu_{\alpha\alpha}$  denotes the  $\alpha\alpha$  component of the inverse inertia tensor. This indicates that the spin-rotation interaction is proportional to the rotational constant. Table 8 shows the normalized spin rotation constants for a variety of different molecules. An initial estimate for the three spin rotation constants was taken as the average value of the constants for the molecules with  $C_{2v}$  symmetry.

The  $\epsilon$  values were then systematically varied, both positive and negative, to determine their effect on the splitting. The 4(3,1)-5(4,2), 5(5,1)-6(6,0), and the 6(2,4)-7(3,5) rotational transitions were used to determine the spin-rotation constants. Each of these transitions is split into a doublet. Using the frequencies determined from the rigid rotor calculation and the splittings calculated using the average values three transitions were assigned. Rather than attempt to fit to actual frequencies the constants were varied to reproduce the differences between the N=4-5, J=3.5-4.5 and N=5-6, J=5.5-6.5; the N=4-5, J=3.5-4.5 and N=6-7, J=5.5-6.5; and the N=5-6, J=5.5-6.5 and N=6-7, J=5.5,6.5. Once these values were determined the hyperfine splitting could be analysed.

For the hyperfine interaction more information was available on which the initial estimates could be based. The initial value of the Fermi contact constant of 8.31G (23.3 MHz) was taken from the EPR study<sup>27</sup> By assuming<sup>34</sup>

$$T_{cc} = (4/5)g_s g_n \beta \beta_n \langle r^{-3} \rangle \quad [6.2]$$

and using the spin density on the fluorine atoms calculated by Palmer<sup>31</sup> of 11% the initial value of  $T_{cc}$  could be determined.

The magnetic interaction is normally determined in reference to the principal axis system of the molecule. When one of the inertial axes coincides with the axis of the unpaired electron p orbital, the magnetic dipolar interaction tensor (T) has diagonal components that approximately satisfy the ratios 4/5: -2/5: -2/5<sup>34</sup>, where the first number applies to the axial component and the second and third to the perpendicular components. For a molecule with an unpaired electron in an out of plane p-orbital,  $T_{cc} = -2T_{aa} = -2T_{bb}$ . Therefore  $T_{aa}$  and  $T_{bb}$  are estimated from the calculated spin density. Then using the same technique just described to determine the values of the spin rotation constants and concentrating on 4 of the 9 hyperfine transitions which were cal-

Table 8. Normalized spin-rotation constants in Mhz

	$\epsilon_{aa}/A$	$\epsilon_{bb}/B$	$\epsilon_{cc}/C$	
HO <sub>2</sub>	-8.1228	-1.2613	0.0272	[41]
HSO	-3.4613	-2.0808	0.0012	[42]
FO <sub>2</sub>	-1.0473	-	-	[43]
FSO	-0.8774	0.3736	0.0248	[44]
NH <sub>2</sub>	-1.3046	-0.3488	0.0049	[45]
PH <sub>2</sub>	-3.0782	-1.0145	-0.0056	[46]
NF <sub>2</sub>	-1.3501	-0.7822	0.0443	[47]
ClO <sub>2</sub>	-2.6654	-2.1794	0.0552	[48]
CH <sub>2</sub> F	-0.4057	-0.6003	0.0051	[49]
CH <sub>2</sub> Cl	-1.1478	-1.4900	0.0785	[50]
HCO	1.5938	0.0423	-0.4906	[51]
FCO	0.9576	-	-	[52]
NO <sub>2</sub>	2.2536	0.0593	-0.7742	[53]
CH <sub>3</sub>	-	-0.1219	-	[54]
CF <sub>3</sub>	-	-0.3348	-	[32]

culated to be well resolved for the 4(4,0)-5(5,1) rotational transition the hyperfine constants were determined.

Kirchoff<sup>55</sup> has developed a spectral fitting program which fits the observed rotational transitions to 13 spectral constants. Three of these are the rotational constants and the remaining ten are centrifugal distortion constants. The program allows fitting to any combination of these constants the user wishes. Using the calculated splittings and the observed transitions theoretical unsplit rotational frequencies were determined. These hypothetical transitions were then fit to a rigid rotor model. In this manner 39 transitions were assigned yielding 7 hypothetical unsplit transitions between N=4 and 7. The results of this fit are given in Table 9. In Table 10, the spectroscopic constants derived from this fit are presented.

There are four types of structures which may be determined experimentally. An equilibrium structure,  $r_e$ , is determined by analysis of the microwave spectrum in several different vibrational states. Although this is the most useful structure to obtain it is also the most difficult. The average structure,  $\langle r \rangle$ , represents the structure where the nuclear positions have been averaged over the vibrational motion. Knowledge of the harmonic part of the vibrational potential function is necessary in order to determine this type of structure. If isotopic substitution is possible then by use of Costain's<sup>56</sup> method, which employs Kraitchman's equations<sup>57</sup>, a substitution structure,  $r_s$ , may

Table 9. Rigid Rotor Assignment

$N(K_{-1}, K_1) \rightarrow N'(K'_{-1}, K_1)$	$J \rightarrow J'$	$F \rightarrow F'$	Obs.	O-C
4(3,1)-5(4,2) 18840.965	3.5-4.5	1.5-2.5	20623.24	1.55
		2.5-3.5	20617.56	1.05
		3.5-4.5	20650.00	-0.60
		4.5-5.5	unresolved	
		5.5-6.5	unresolved	
		6.5-7.5	unresolved	
4(3,2)-5(4,1)	3.5-4.5	2.5-3.5	unresolved	
		3.5-4.5	unresolved	
		4.5-5.5	20630.45	-0.61
		0.5-1.5	unresolved	
		1.5-2.5	20717.94	1.97
		2.5-3.5	20710.59	0.55
		3.5-4.5	20559.54	-0.77
		4.5-5.4	20678.33	-0.85
		5.5-6.5	unresolved	
		6.5-7.5	unresolved	
4(4,0)-5(5,1)	4.5-5.5	2.5-3.5	unresolved	
		3.5-4.5	20460.31	-1.35
		4.5-5.5	20472.78	-0.96
		5.5-6.5	unresolved	
		6.5-7.5	20487.42	-1.51
		7.5-8.5	20480.00	0.29
4(4,1)-5(5,0)	3.5-4.5	2.5-3.5	unresolved	
		3.5-4.5	unresolved	
		4.5-5.5	23130.74	0.44
		0.5-1.5	23112.25	-0.20
		1.5-2.5	23216.34	1.66
		2.5-3.5	23172.04	1.48
		3.5-4.5	23061.50	-1.62
		4.5-5.5	23176.82	-0.89
		5.5-6.5	unresolved	
		6.5-7.5	unresolved	
		7.5-8.5	unresolved	

Table 9. Rigid Rotor Fit (continued)

$N(K_{-1}, K_1) \rightarrow N'(K'_{-1}, K'_1)$	$J \rightarrow J'$	$F \rightarrow F'$	Obs.	O-C
4(4,1)-5(5,0)	4.5-5.5	3.5-4.5	21619.35	-2.36
		4.5-5.5	unresolved	
		5.5-6.5	unresolved	
		1.5-2.5	21677.42	-0.58
		2.5-3.5	21570.00	0.50
		3.5-4.5	21596.92	-1.37
		4.5-5.5	21635.00	-2.33
		5.5-6.5	21656.22	1.14
		6.5-7.5	21630.00	-1.22
		7.5-8.5	21743.33	0.83
5(5,1)-6(6,0) 25840.675	5.5-6.5	3.5-4.5	25982.35	0.69
		4.5-5.5	unresolved	
		4.5-5.5	26009.79	0.77
		5.5-6.5	25987.06	0.15
		6.5-7.5	unresolved	
	4.5-5.5	7.5-8.5	25974.58	-1.45
		4.5-5.5	25126.88	0.93
		5.5-6.5	unresolved	
		6.5-7.5	unresolved	
		2.5-3.5	24902.81	-0.01
6(4,2)-7(5,3) 25384.279	6.5-7.5	3.5-4.5	25216.33	-0.15
		4.5-5.5	25156.25	2.60
		5.5-6.5	25142.94	-1.36
		6.5-7.5	unresolved	
		7.5-8.5	unresolved	
		8.5-9.5	25114.64	1.19
		4.5-5.5	23722.5	-1.45
		5.5-6.5	unresolved	
5.5-6.5	23712.93	0.78		
6.5-7.5	unresolved			
7.5-8.5	23718.54	0.73		
8.5-9.5	not assigned			



Table 10. Spectroscopic Constants (MHz)

A	$2256.94 \pm 0.04$
B	$1056 \pm 1.2$
C	$971 \pm 1.2$
$\epsilon_{aa}$	$-3597.7 \pm .5$
$\epsilon_{bb}$	$-1121.4 \pm .5$
$\epsilon_{cc}$	$29.8 \pm .5$
$T_{aa}$	$-183.74 \pm .05$
$T_{bb}$	$-177.77 \pm .05$
$T_{cc}$	$361.51 \pm 0.05$
$a_F$	$22.8 \pm 0.2$

be determined. For a complete  $r_s$  structure each atom in the molecule must be isotopically substituted. The type of structure determined in this study is the effective structure,  $r_0$ . This structure represents the average structure over the ground vibrational state.

The molecular structure of bis-trifluoromethyl nitroxide which reproduces the experimentally determined moments of inertia was obtained using the structural fitting program ~~program~~ developed by Schwendeman<sup>58f</sup> called STRFTQ. This program adjusts bond distances and angles to fit the observed moments of inertia through a least squares reduction scheme, see Appendix G.

Nine independent parameters;  $r_{NO}$ ,  $r_{CN}$ ,  $r_{CF}$ ,  $ONC$ ,  $CNC$ ,  $NCF$ ,  $FCF$  and two dihedral angles must be determined to obtain a complete  $r_0$  structure. The three moments determined from a single isotopic species does not allow determination of more than three parameters. Several assumptions will therefore have to be made about the structure. Some of the more interesting questions about the structures of nitroxide radicals deal with the nature of the structure at the N atom. As pointed out earlier there are conflicting reports about the planarity of the molecule at the N atom. The effect of the unpaired electron on the NO bond length is also of some interest.

Two different sets of three parameters were considered. They were variation of the NO bond length, the  $ONC$  angle, and either the  $CNC$  angle or the dihedral angle measuring the nonplanarity of the two  $CF_3$  groups relative to the NO bond. The remaining parameters were held fixed to the values determined from the the electron diffraction study<sup>28</sup>. The CF bond lengths were assumed to be  $r_{CF} = 1.32\text{\AA}$ . The FCF angles were also assumed to be  $FCF = 109.8^\circ$ . The six NCF angles

were also assumed to be identical and the values used were those determined by Underwood and Vogel<sup>26</sup> The two CN bond lengths were each fixed at 1.441Å.

An attempt was made to determine the nonplanarity at the nitrogen atom by fixing the CNC angle to 120.9° which was derived from the ED study. ~~(No reasonable value for the NO bond length or dihedral angle could be obtained.)~~ <sup>c, γ, α</sup> The dihedral value was then fixed to give the deviation from planarity of 21.9°. No reasonable values could be obtained for either the NO bond length or the CNC angle. This result was the same even when the various parameters held fixed were changed within reasonable limits. However, by fixing the structure in a planar configuration, a structure which agrees well with all parameters other than the nonplanarity at the nitrogen determined by electron diffraction is obtained. Table 11 presents the parameters of several nitroxide radical including this work and the electron diffraction study. The derived structure is shown in Figure 9. A comparison of the experimental moments and those derived from the calculated molecular structure are presented in Table 12. Because most of the bonding parameters had to be assumed and no isotopic species were assigned, the reported structure is not unique. However, since no reasonable structure could be obtained for the structure with a nonplanar framework, the nonplanar configuration is felt to be incorrect for (CF<sub>3</sub>)<sub>2</sub>NO.

## Discussion

The present result is the first assignment of the hyperfine structure for a molecule with six identical coupled nuclei. The hyperfine Hamiltonian employed in this work, based upon a theory developed by Hougen<sup>38</sup> and ultimately by Bowater et al.<sup>33</sup>, explains well the observed spectrum of (CF<sub>3</sub>)<sub>2</sub>NO up to N=7.

The hyperfine structure is absent when I=0. If the molecule was in a vibronic state other than A<sub>1</sub> the rotational energy levels which exist with the symmetric and antisymmetric spin functions would be different<sup>18</sup>. Since most of the radicals reported to date have been in a B<sub>1</sub> vibronic

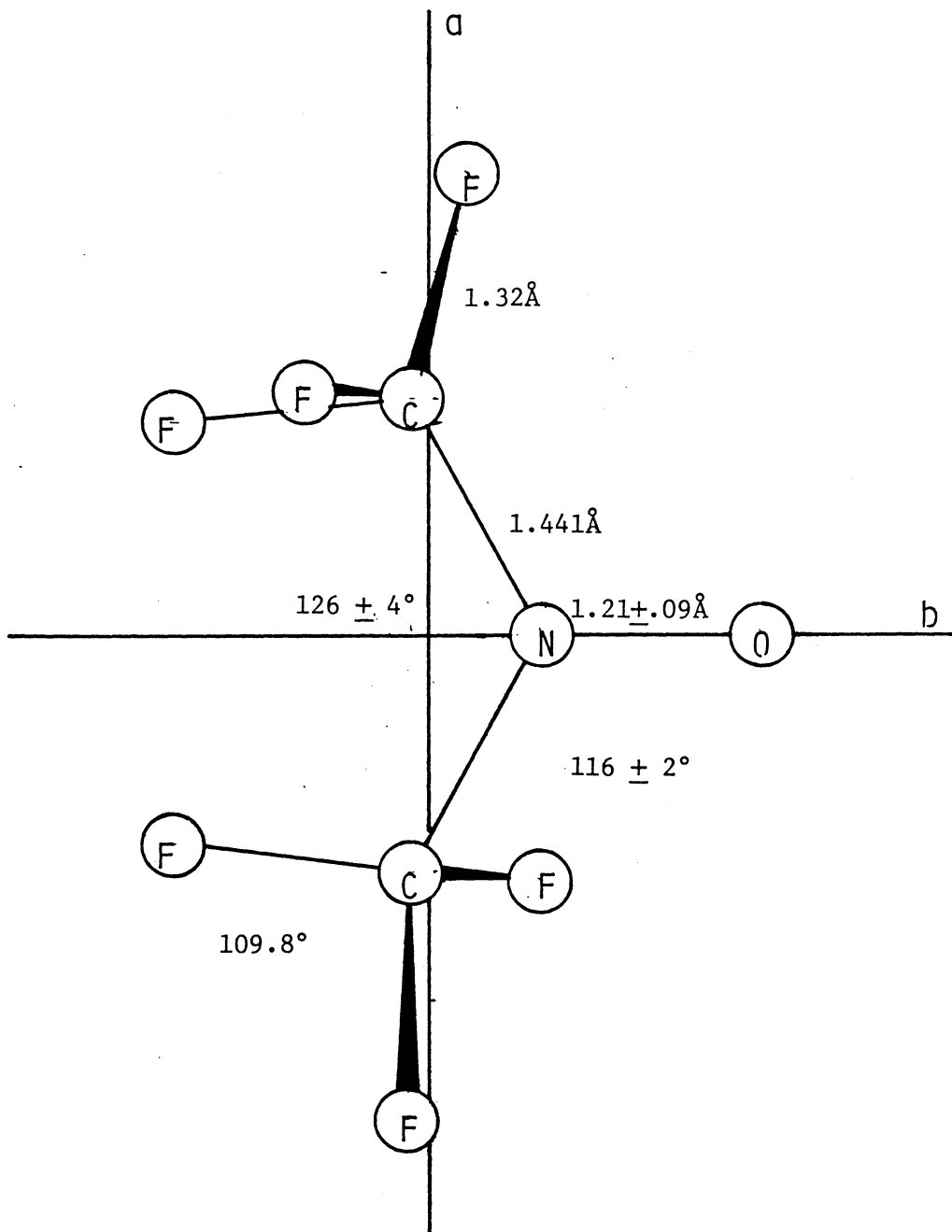
Table 11. Comparison of Distances and Angles in Nitroxides

	(N-O)	C-N-C	C-N-O	$\Delta$
bis-trifluoromethyl nitroxide	1.212	126.2	116.9	0
bis-trifluoromethyl nitroxide <sup>28</sup>	<i>r</i> 1.26	120.9	117.2	21.9
bis-( <i>t</i> -butyl) nitroxide <sup>59</sup>	1.28	136	112.2	0
di-( <i>p</i> -methoxybenzyl) nitroxide <sup>60</sup>	1.23	124	124	0

state<sup>34</sup>, an attempt was made to assign the  $I=0$  components of the hyperfine structure to the  $B_1$  ground state. By using the same procedure as that previously described, reasonable values for the spin-rotation constants could not be obtained. The ground vibrational state of a  $C_{2v}$  symmetry molecule is  $A_1$ . The stability of the  $(CF_3)_2NO$  radical permits thermal equilibrium to be established. Based on a Boltzman distribution of populations only the ground electronic state would be expected to have a significant population. Because of the complexity inherent in determination of ground electronic states<sup>18</sup> a comparison could not be made. The results do, however, indicate a symmetric ground electronic state.

The observed rotational constants do not allow determination of a unique molecular structure. Table 11 lists the molecular parameters determined in this study for several nitroxide radicals. The NO bond length of 1.212Å agrees well with that determined by ED. The CNC angle of 126.2° is larger than that determined by electron diffraction but less than the angle of 136° found for the *t*-butyl analog. The trend in all of the nitroxide radicals appears to be that the CNC angle is a function of steric hindrance. The determined CNO angle of <sup>116.9</sup>109° again agrees well with that determined by electron diffraction. The deviation from planarity has already been discussed and both of the other nitroxide radicals which have been reported are planar around the N atom.

It is possible that the determined rotational constants were biased towards a planar structure. The procedure used to fit the spectrum to the assumed planar structure allowed determination of reasonable spin-rotation and hyperfine interactions. A consistent fit could not, however, be obtained when the initial structure included the nonplanarity determined by ED. The basis for a consistent fit was the number of transitions which could be fit and the value of the T test determined by the rigid rotor fit. The T test is determined by deleting the transition from the fit and then



**Figure 9. Molecular Structure of Bis-trifluoromethyl Nitroxide**

Table 12. Comparison of Observed and Calculated Moments

Observed Moments	Calculated Moments	Obs. - Calc.
223.92 ± .01	221.27	2.65
478.5 ± .1	475.8	2.65
520.2 ± .1	522.8	-2.65

recalculating the spectrum. The observed frequency is then compared to the new calculated value. If the transition does not agree well the value of the T test will be large. The standard deviation of the fit using the assumed planar structure was 0.630 MHz. The corresponding deviation using the nonplanar structure was 5.217 MHz. The planar structure determined agrees well with the conclusions drawn from the infrared study<sup>29</sup>. It was suggested in this article that an error in estimation of vibrational amplitudes in the ED work could lead to a nonplanar structure.

The Fermi contact constant obtained here agrees well with that determined by EPR. Table 13 lists the F hyperfine coupling constants for several radicals. The Fermi contact constants are much smaller than the corresponding atomic value for fluorine of 443 MHz<sup>61</sup>. This is to be expected since all but the CF<sub>3</sub> radical are π radicals. The CF<sub>3</sub> radical is a σ radical with the unpaired electron orbital considerably s-p hybridized. Eqn. 4.11 indicates that a<sub>F</sub> is a measure of the s character of the orbital. This equation alone is not sufficient to interpret the Fermi interaction constant. When a diatomic molecule is in a <sup>2</sup>Π, <sup>3</sup>Σ, or <sup>1</sup>Δ state the unpaired electron orbital has a node on a line connecting the two nuclei<sup>34</sup>. In this case the Fermi interaction constant should vanish but does not. This was explained by spin polarization of a p<sub>σ</sub> orbital, caused by the unpaired electron in a p<sub>π</sub> orbital. The part of p<sub>σ</sub> near the nucleus will be polarized parallel to the spin of the unpaired electron. The part of p<sub>σ</sub> far from the nucleus is antiparallel. This results in small positive Fermi contact constants for all nuclei other than protons and small negative a<sub>F</sub> for protons. The Fermi term for F seems to be proportional to the spin density which suggests that the constant is caused by spin polarization. The very small value of a<sub>F</sub> for (CF<sub>3</sub>)<sub>2</sub>NO indicates that the s-p hybridization is relatively unimportant. It was postulated that there is a 1-3 conjugation between the unpaired electron orbital on the F atom and the p<sub>z</sub> orbital of the N atom. This would tend to reduce the s character of the electron orbital therefore reducing the value of the Fermi contact term.

Table 13. Fluorine Magnetic Hyperfine Coupling Constants (in MHz)

	$a_F$	$T_{aa}$	$T_{bb}$	$T_{cc}$	density
FSO	67.23	-118.16	-117.06	235.22	6.7
NF <sub>2</sub>	164.39	-241.75	-226.48	468.22	13.3
CH <sub>2</sub> F	184.10	-255.21	-212.31	467.52	13.3
CF <sub>3</sub>	408.50	$ T_{aa} - T_{bb}  = 40.1$		320.01	10.6
(CF <sub>3</sub> ) <sub>2</sub> NO	22.8	-183.74	-177.77	361.51	11.9

The dipolar coupling constants, the T tensor, are determined in the present work for the first time. From Table 13 the relationship  $T_{aa} \cong T_{bb} \cong -1/2T_{cc}$  holds. This indicates that around the fluorine nuclei the unpaired electron occupies a  $p_\pi$  orbital which is out of the molecular plane. Due to the tetrahedral structure of the C atoms none of the F  $p_\pi$  orbitals should lie in the molecular plane and this result is therefore not surprising. By comparing  $T_{cc}$  with that of atomic fluorine<sup>61</sup> (3030 MHz) a spin density of 11.9 is calculated. This agrees well with that predicted by Palmer<sup>31</sup> as well as those determined experimentally for the radicals in Table 13. The anisotropic hyperfine interaction constants were not determined in the EPR work and a direct comparison between techniques cannot be made.

The spin rotation splitting was found to be much larger than the corresponding hyperfine splitting in agreement with prediction. Table 10 lists the spin-rotation constants for a number of radicals. Care must be exercised in drawing any conclusions from the comparison of the different scaled values. The initial values of the spin-rotation constants were the least well defined based on evidence from other sources. Also, interpretation of these constants is fraught with assumptions about other electronic constants and contributions from excited states<sup>34</sup>. The general trend that  $\epsilon_{aa} < \epsilon_{bb} < \epsilon_{cc}$  was found to hold. The electron occupies mainly the  $p_z$  orbital<sup>31</sup> on N which extends perpendicularly to the plane of the molecule. In this case, no one electron excitation can produce the cc component and  $\epsilon_{cc}$  is very small<sup>34</sup>. The determined value of  $\epsilon_{cc}$  is in agreement with this statement.

## *Conclusion*

The molecular constants and structure were discussed and compared to other experimental evidence. All of these results were found to be satisfactorily explained or compared favorably with prior research.

A spectral fitting program for the determination of the spin-rotation and hyperfine interactions is essential to a thorough investigation of the complex microwave spectrum of this molecule. The program should include all possible matrix elements so that no a priori assumptions about the molecular structure need be made.

The effects of centrifugal distortion also needs to be included both in the fitting of the calculated unsplit frequencies and the spin-rotation interaction. The hyperfine interaction is so small that centrifugal distortion effects may be neglected in the calculation of the splittings. These changes will facilitate a more accurate fit and improved spectral constants.

The improvement in the rotational constants will not lead to a better determined molecular structure unless isotopic substitution is possible. Due to the difficulty of handling fluorine isotopes and the low natural abundance of isotopes of nitrogen and oxygen a complete  $r_0$  structure will be difficult to obtain.

The high resolution spectroscopy of transient species has just begun. If it follows the development of microwave spectroscopy on closed shell molecules the information being derived from the studies of small molecules today will lead to improvements in techniques and methodologies for the study of larger more complex molecules. This research has shown that such studies are in fact feasible.

# Appendix A

## Harmonic Polynomials and Spherical Harmonics

$$Y_{lm}(\mathbf{r}) = r^l Y_{lm}(\theta, \varphi)$$



$l$	$m$	$Y_{lm}(r)$	$Y_{lm}(\theta, \varphi)$
0	0	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}z$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	$\pm 1$	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}(x \pm iy)$	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\varphi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(2z^2 - x^2 - y^2)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(2\cos^2\theta - \sin^2\theta)$
2	$\pm 1$	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}z(x \pm iy)$	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta e^{\pm i\varphi}$
2	$\pm 2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}(x \pm iy)^2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\varphi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(2z^2 - 3x^2 - 3y^2)z$	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(2\cos^2\theta - 3\cos\theta\sin^2\theta)$
3	$\pm 1$	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}(4z^2 - x^2 - y^2)(x \pm iy)$	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}(4\cos^2\theta\sin\theta - \sin^3\theta)e^{\pm i\varphi}$
3	$\pm 2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}z(x \pm iy)^2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cos\theta\sin^2\theta e^{\pm 2i\varphi}$
3	$\pm 3$	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}(x \pm iy)^3$	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta e^{\pm 3i\varphi}$

## Appendix B

### Selected Wigner 3-j Symbols

$$\begin{pmatrix} J+1 & J & 1 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M-1} \left[ \frac{(J-M)(J-M+1)}{(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M-1} \left[ \frac{(J+M+1)(J-M+1)2}{(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M} \left[ \frac{(J-M)(J+M+1)2}{(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \frac{M}{[(2J+1)(J+1)]^{1/2}}$$

$$\begin{pmatrix} J+2 & J & 2 \\ M & -M-2 & 2 \end{pmatrix} = (-1)^{J-M} \left[ \frac{(J-M-1)(J-M)(J-M+1)(J-M+2)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+2 & J & 2 \\ M & -M-1 & 1 \end{pmatrix} = 2(-1)^{J-M} \left[ \frac{(J+M+2)(J-M+2)(J-M+1)(J-M)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+2 & J & 2 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \left[ \frac{6(J+M+2)(J+M+1)(J-M+2)(J-M+1)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 2 \\ M & -M-2 & 2 \end{pmatrix} = 2(-1)^{J-M+1} \left[ \frac{(J-M-1)(J-M)(J-M+1)(J+M+2)}{(2J+4)(2J+3)(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 2 \\ M & -M & 1 \end{pmatrix} (-1)^{J-M+1} 2(J+2M+2) \left[ \frac{(J-M+1)(J-M)}{(2J+4)(2J+3)(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 2 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M+1} 2M \left[ \frac{6(J+M+1)(J-M+1)}{(2J+4)(2J+3)(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 2 \\ M & -M-2 & 2 \end{pmatrix} = (-1)^{J-M} \left[ \frac{6(J-M-1)(J-M)(J+M+1)(J+M+2)}{(2J+3)(2J+2)(2J+1)2J(2J-1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 2 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M} (1+2M) \left[ \frac{6(J+M+1)(J-M)}{(2J+3)(2J+2)(2J+1)2J(2J-1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 2 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \frac{2[3M^2 - J(J+1)]}{[(2J+3)(2J+2)(2J+1)2J(2J-1)]^{1/2}}$$

## Appendix C

### Selected Wigner 6-j Symbols

$$s = a + b + c$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b-1 \end{matrix} \right\} = (-1)^s \left[ \frac{s(s+1)(s-2a-1)(s-2a)}{(2b-1)2b(2b+1)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b \end{matrix} \right\} = (-1)^s \left[ \frac{2(s+1)(s-2a)(s-2b)(s-2c+1)}{2b(2b+1)(2b+2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b+1 \end{matrix} \right\} = (-1)^s \left[ \frac{(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)}{(2b+1)(2b+2)(2b+3)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c & b \end{matrix} \right\} = (-1)^{s+1} 2 \frac{[b(b+1) + c(c+1) - a(a+1)]}{[2b(2b+1)(2b+2)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b-2 \end{matrix} \right\} = (-1)^s \left[ \frac{(s-2)(s-1)s(s+1)(s-2a-3)(s-2a-2)(s-2a-1)(s-2a)}{(2b-3)(2b-2)(2b-1)2b(2b+1)(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b-1 \end{matrix} \right\} = (-1)^s 2 \left[ \frac{(s-1)s(s+1)(s-2a-2)(s-2a-1)(s-2a)(s-2b)(s-2c+1)}{(2b-2)(2b-1)2b(2b+1)(2b+2)(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b \end{matrix} \right\} = (-1)^s \left[ \frac{6s(s+1)(s-2a-1)(s-2b-1)(s-2a)(s-2b)(s-2c+1)(s-2c+2)}{(2b-1)2b(2b+1)(2b+2)(2b+3)(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b+1 \end{matrix} \right\} = (-1)^s 2 \left[ \frac{(s+1)(s-2a)(s-2b-2)(s-2b-1)(s-2b)}{2b(2b+1)(2b+2)(2b+3)(2b+4)} \right] \left[ \frac{(s-2c+1)(s-2c+2)(s-2c+3)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b+2 \end{matrix} \right\} = (-1)^s \left[ \frac{(s-2b-3)(s-2b-2)(s-2b-1)(s-2b)}{(2b+1)(2b+2)(2b+3)(2b+4)(2b+5)} \right]^{1/2} \left[ \frac{(s-2c+1)(s-2c+2)(s-2c+3)(s-2c+4)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 2c-1 & b-1 & \end{matrix} \right\} = (-1)^s \frac{4[(a+b)(a-b+1) - (c-1)(c-b+1)][s(s+1)(s-2a-1)(s-2a)]}{[(2b-2)(2b-1)2b(2b+1)(2b+2)(2c-2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-1 & b \end{matrix} \right\} = (-1)^s \frac{2[(a+b+1)(a-b) - c^2 + 1][6(s+1)(s-2a)(s-2b)(s-2c+1)]^{1/2}}{[(2b-1)2b(2b+1)(2b+2)(2b+3)(2c-2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-1 & b+1 \end{matrix} \right\} = (-1)^s \frac{4[(a+b+2)(a-b-1) - (c-1)(b+c+2)]}{[(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)]^{1/2} [2b(2b+1)(2b+2)(2b+3)(2b+4)(2c-2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

$$X = b(b+1) + c(c+1) - a(a+1)$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c & b \end{matrix} \right\} = (-1)^s \frac{2[3X(X-1) - 4b(b+1)c(c+1)]}{[(2b-1)2b(2b+1)(2b+2)(2b+3)(2c-1)2c(2c+1)(2c+2)(2c+3)]^{1/2}}$$

## Appendix D

### Selected Wigner 9-j Symbols

$$\Gamma(abc) = a(a+1) + b(b+1) - c(c+1)$$

$$\left\{ \begin{matrix} N & N & 2 \\ S & S & 1 \\ J & J & 1 \end{matrix} \right\} = \frac{\sqrt{3} [\Gamma(NSJ)\Gamma(NJS) + (2/3)N(N+1)\Gamma(SJN)]}{[40N(N+1)(2N-1)(2N+3)S(S+1)(2S+1)J(J+1)(2J+1)]^{1/2}}$$

$$\left\{ \begin{matrix} N & N & 2 \\ S & S & 1 \\ J-1 & J & 1 \end{matrix} \right\} = \frac{1}{4N(N+1)} \left[ \frac{(N-S+J)(N+S-J+1)(-N+S+J)(N+S+J+1)}{30N(N+1)(2N-1)(2N+1)(2N+3)S(S+1)(2S+1)J(2J-1)(2J+1)} \right]^{1/2}$$

$$\left\{ \Gamma(SNJ)(2N-1)(2N+3) + \frac{1}{2N+1} [N^2(2N-1)(N+S+J+2)(N-S+J+1) - (N+1)^2(2N+3)(N+S-J)(-N+S+J+1)] \right\}$$

$$\left\{ \begin{matrix} N-2 & N & 2 \\ S & S & 1 \\ J+1 & J & 1 \end{matrix} \right\} = - \left[ \frac{(J+S+N+1)(-J+S+N)(J-S+N)(J+S-N+1)}{16(N-1)N(2N-3)(2N-1)(2N+1)S(S+1)(2S+1)} \right]^{1/2}$$

$$\left[ \frac{(-J+S+N-2)(-J+S+N-1)(J+S-N+2)(J+S-N+3)}{(J+1)(2J+1)(2J+3)} \right]^{1/2}$$

$$\left\{ \begin{matrix} N-2 & N & 2 \\ S & S & 1 \\ J & J & 1 \end{matrix} \right\} = - \left[ \frac{(J+S+N+1)(-J+S+N)(J-S+N)(J+S-N+1)}{16(N-1)N(2N-3)(2N-1)(2N+1)S(S+1)(2S+1)} \right]^{1/2} \\ \left[ \frac{(J+S+N)(J-S+N-1)(-J+S+N-1)(J+S-N+2)}{J(2J-1)(2J+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} N-2 & N & 2 \\ S & S & 1 \\ J-1 & J & 1 \end{matrix} \right\} = - \left[ \frac{(J+S+N+1)(-J+S+N)(J-S+N)(J+S-N+1)}{16(N-1)N(2N-3)(2N-1)(2N+1)S(S+1)(2S+1)} \right]^{1/2} \\ \left[ \frac{(J+S+N-1)(J+S+N)(J-S+N-2)(J-S+N-1)}{J(2J-1)(2J+1)} \right]^{1/2}$$

# Appendix E

## Semi-confocal Fabry-Perot Microwave Cavity Spectrometer System

A cavity resonator is defined as a dielectric region in which electromagnetic energy can be stored for intervals that are long relative to the period of oscillation of the electromagnetic fields<sup>62</sup>. The resonance condition exists because the stored electrical energy equals the stored magnetic energy. At some instant in the periodic cycle the energy resides completely in the electric field, while a quarter cycle later, it resides entirely in the magnetic field. For a cavity of given shape and dimensions, the resonant configurations are called normal modes and are characterized by a certain number of standing waves between the conducting walls. There are an infinite set of such modes and a corresponding infinite set of resonant frequencies.

It is desirable to obtain very sharp resonances or, equivalently, very high quality factors (Q) in a resonator cavity. The Q of a cavity is at a maximum when the conductive and diffractive losses are at a minimum. The conductive losses occur due to the electrical characteristics of the cavity itself<sup>62</sup>. The diffractive losses are due to the coupling into and out of the cavity.



A quasi-optical technique is used to minimize these losses. Resonant modes at microwave frequencies may be obtained in an open cavity made up of two opposed circular mirrors at a given separation similar to a Fabry-Perot interferometer. The microwave energy is coupled into and out of the cavity through an iris hole in the launching mirror, see Figure 10. A curved reflecting mirror produces less diffraction of the microwave energy.

For a semi-confocal resonator whose curved mirror has a radius of curvature  $b$ , and whose mirror separation is  $d < b$ , the resonant frequencies are<sup>62</sup>

$$\nu = \frac{c}{8d} \left\{ 2q + (1 + m + n) \left[ 1 - \frac{2}{\pi} \tan^{-1} \left( \frac{2d - b}{2\sqrt{d(b-d)}} \right) \right] \right\} \quad [E.1]$$

which reduces to

$$\nu = \frac{c}{4b} [2q + (1 + m + n)] \quad [E.2]$$

if  $d = b/2$ .  $\nu$  is the resonant frequency,  $c$  is the speed of light, and  $m, n$ , and  $q$  are integers corresponding to the mode denoted by  $TEM_{mnq}$ . Because one of the mirrors is flat  $q$  is restricted to even integers and denotes the actual number of half-wavelengths between the two mirrors at resonance.

It can be shown that the quality factor may be expressed by<sup>63</sup>

$$Q \cong \left( \frac{2\pi d}{\lambda \alpha} \right) \quad [E.3]$$

where  $\lambda$  = wavelength at resonance and  $\alpha$  is the fractional power lost per reflection.  $Q$  increases with spacing to a maximum value when diffraction losses become large enough to cause  $Q$  to decrease. For a given mirror separation,  $Q$  should increase at higher frequencies.

Resonant cavities have been used by many authors<sup>64-70</sup> in microwave spectrometers for molecular studies. At resonance the cavity has a very large effective path length. The cavity is compact and has a high volume to surface ratio. It is tunable over fairly wide bandwidths. The cavity response to a swept input frequency permits stabilization of the source oscillator.

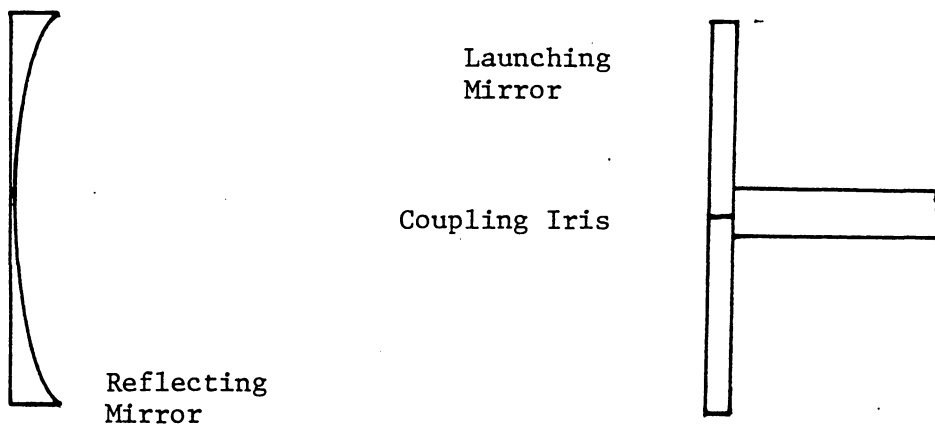


Figure 10. Semi-confocal Mirror Arrangement

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Hrubesh<sup>62</sup> shows that the response of the cavity at a given mirror separation to a swept input frequency can be described by Figure 11. The dotted lines is the response curve for an empty cavity. The solid line is the response curve of the cavity with a gas whose absorption frequency corresponds to the resonant frequency of the cavity. This indicates that power is reflected from the cavity rather than absorbed by it at the peak of a gas resonance. This accounts for the high sensitivity of a resonator absorption spectrometer.

The electronic system for an effective free radical spectrometer must offer good long- and short-term frequency stability. It must also provide frequency sweep capability and provide sensitive detection, amplification, and presentation of weak absorption signals.

A resonant cavity is the ideal absorption cell because, besides a very long effective path length, the cavity itself may be used as a means to control the mirror position to keep the cavity on resonance as the input frequency is swept. The sharp attenuation in power shown in Figure 11 is accompanied by a phase shift in the modulation frequency. Near the resonant frequency the phase angle changes quickly, depending on the Q value, from a positive angle to a negative one. At exactly the resonant frequency the phase angle is zero, see Figure 12. A dc error signal proportional to the phase change near resonance is derived and applied to the motor control circuitry to move the mirror in the direction required to bring the cavity on resonance.

A change in the physical dimensions of the cavity changes its resonant frequency. The motor control circuit tracks the cavity resonance. The frequency may be changed at any rate, limited only by the response time or maximum speed of the servo-motor.

The fractional change in voltage caused by an absorption as weak as that in a microwave experiment is so small that it is impossible to control fluctuations in output power to the required accuracy. There are two general types of modulating procedures used in microwave rotational spectroscopy. Source modulation is a technique in which the microwave signal is electronically modulated at a frequency of approximately 10 KHz. Absorption of the microwave radiation causes a phase shift in the carrier frequency. A phase sensitive technique with narrow band ac amplification, such as a lock-in amplifier, can be used to detect a weak absorption.

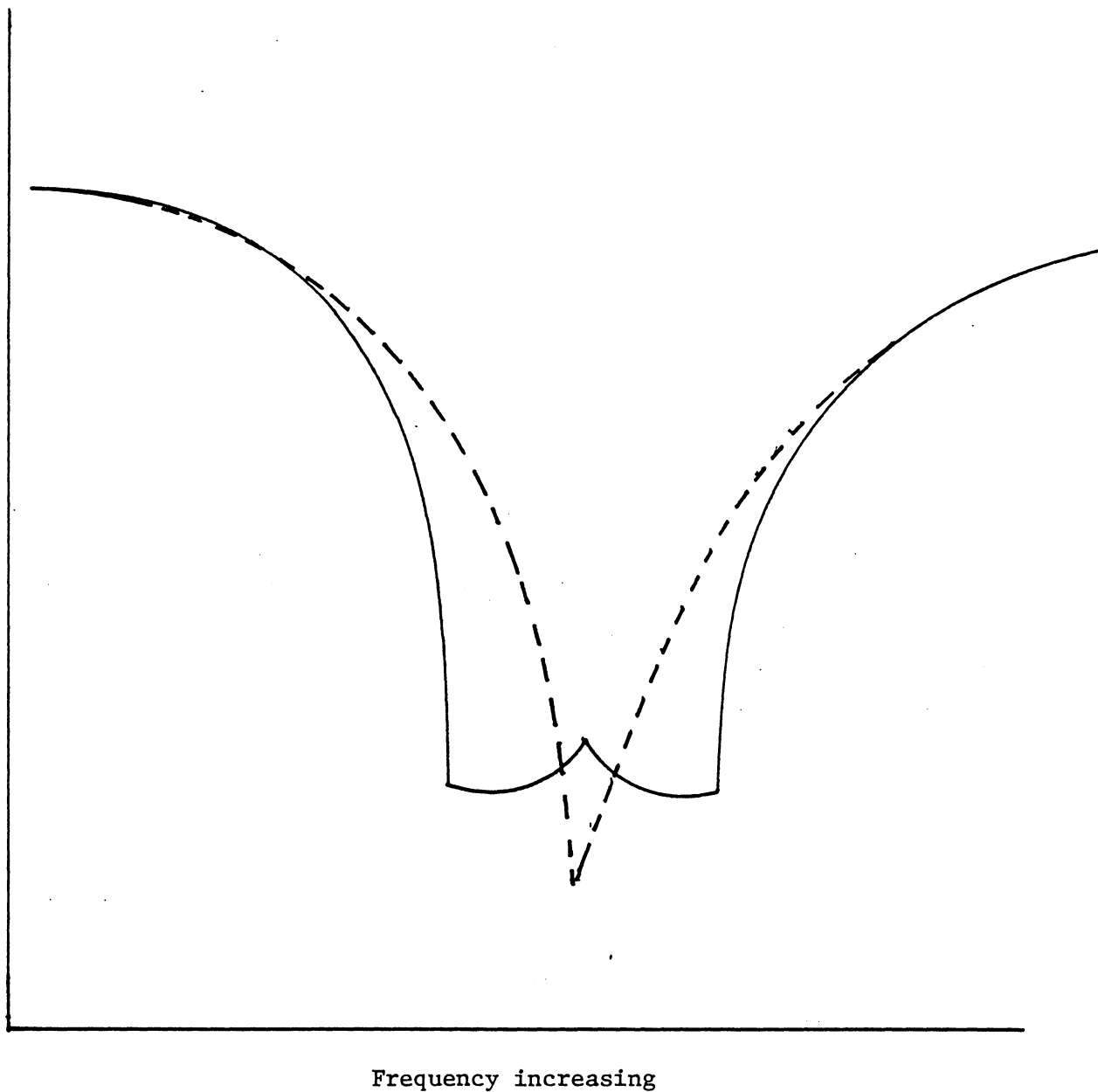


Figure 11. Power Absorbed vs. Frequency Curve

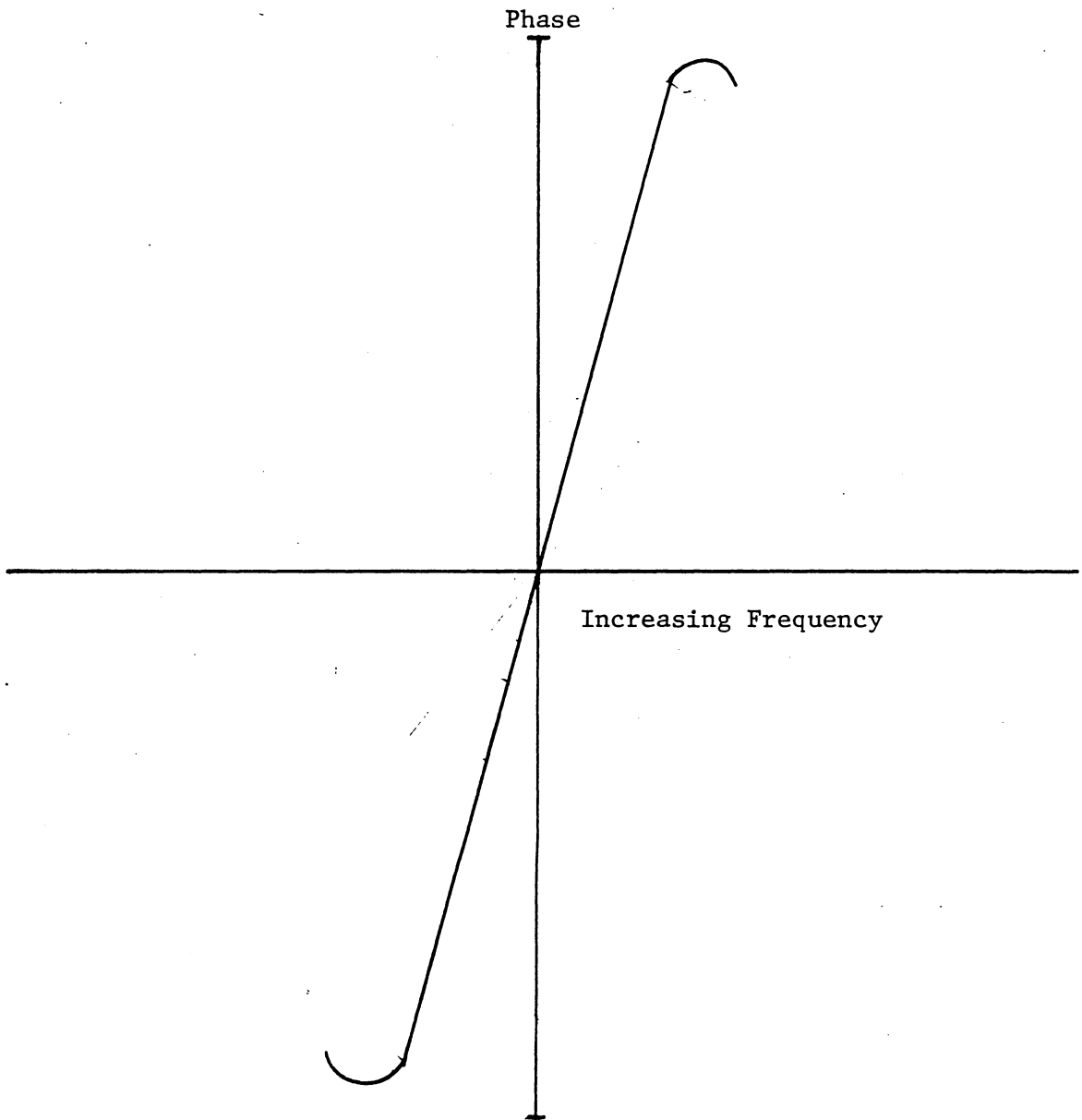


Figure 12. Phase Angle vs. Frequency Curve

Sample modulation is the most common technique in microwave spectroscopy. Use is made of the interaction of an electric or magnetic field with a rotating molecule. This interaction causes a splitting in the molecular energy levels. When a molecule is paramagnetic a magnetic field can couple to the magnetic dipole. Splitting of the energy levels via application of an external magnetic field is called the Zeeman effect. Amplitude modulation of the absorption signal results from the application of a field which is turned on and off at an appropriate rate. When the field is on, the intensity of the absorption is decreased due to the removal of the degeneracy in the energy levels, when off, the unsplit line is at full intensity. This technique also requires ac amplification and phase sensitive detection techniques.

The modulating magnetic field is produced by a solenoidal coil wrapped around the vacuum enclosure. To obtain the sharpest possible absorption lineshape the magnetic field must be zero based and must be switched from off to on in the fastest possible time. The current through the windings should approximate a square waveform. Because of the high inductance inherent in windings the modulation frequency is limited to a maximum value of 10 KHz.

Lock-in detection allows extremely narrow bandwidth selectivity and raises the frequency of amplification. These functions minimize noise effects. The input signal is preamplified in a tuned amplifier. Its frequency is then compared to a stable reference frequency. If the input signal frequency is not identical to the reference frequency, no output signal is generated. If the frequencies are the same the phases of the two signals are compared and a dc signal proportional to the phase difference and relative input signal strength is produced as the output of the lock-in amplifier.

Figure 13 contains a block diagram of the spectrometer system constructed. Following is a brief description of the components and their function.

1)HP8673B-This is a synthesized signal generator capable of producing microwave radiation from 12-26.5 GHz and couples the microwave energy into the external waveguide.

2)Isolator-A two port waveguide device which allows microwave radiation to pass in one direction and highly attenuates the radiation in the reverse direction.

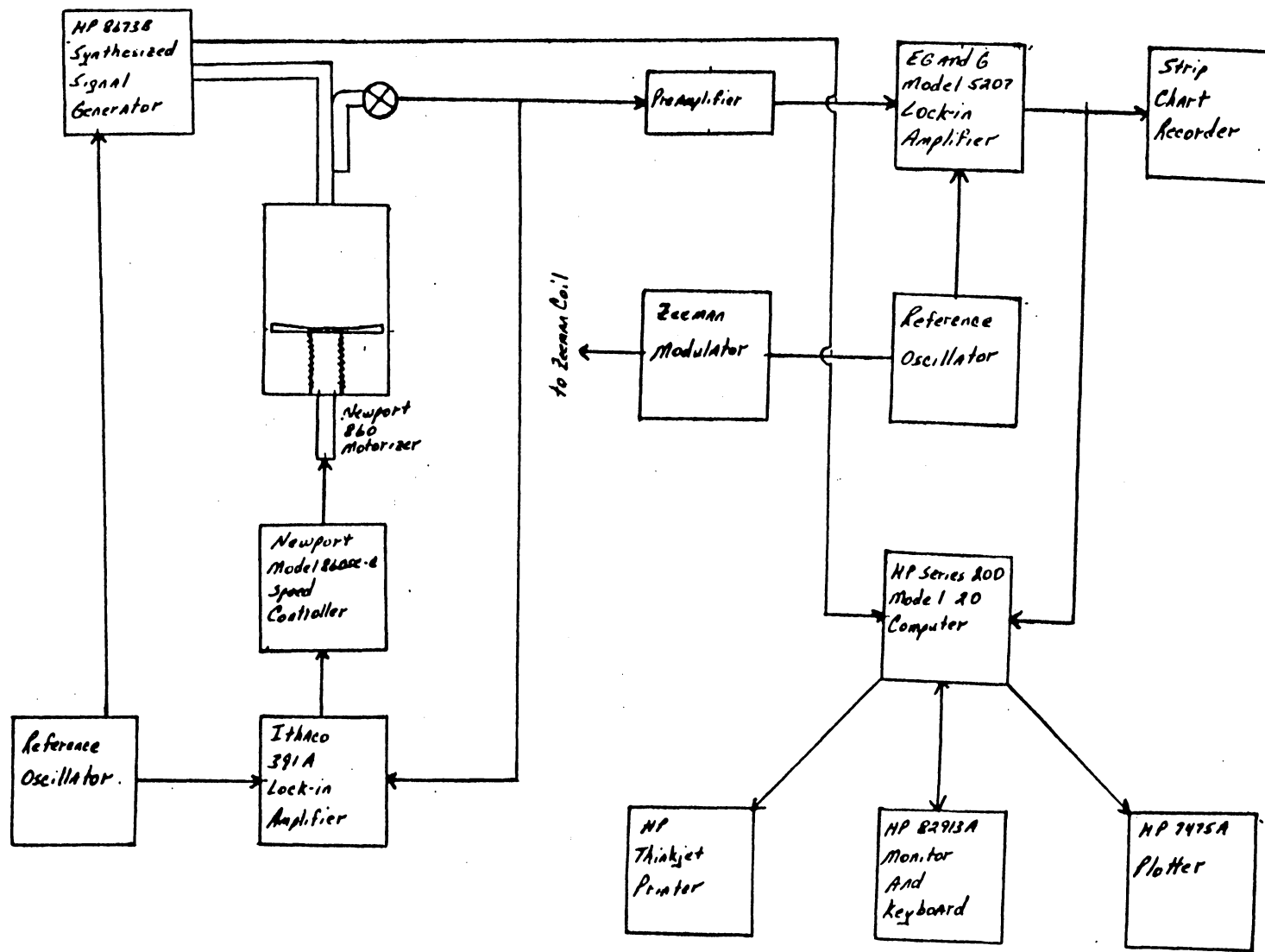


Figure 13. Block Diagram of the Microwave Spectrometer System.

3) Fabry-Perot resonant cavity-Absorbs most of the microwave energy if a resonant condition exists. It provides a phase shift of the microwave modulation frequency near the resonant frequency. The resonant frequency of the cavity is a function of mirror separation.

4) Crystal detector-Rectifies microwave frequencies to produce a dc output signal proportional to the incident power. Demodulates the microwave carrier frequency and couples the modulating frequency to the external circuitry.

5) Lock-in amplifier-A very narrow bandwidth amplifier that accepts from a crystal detector or preamplifier only a signal of the same frequency as that of a reference oscillator, compares phases, and provides a dc output proportional to the phase shift and relative intensity. 6) Zeeman Modulator-The square current waveform generated by the modulation circuit is applied to the coils to produce a magnetic field inside the cavity.

7) Preamplifier-Amplifies the ac part of the signal from the crystal detector. This amplified signal is then supplied to the lock-in amplifier.

8) Reference oscillator-Provides a very stable frequency used by the lock-in amplifier and modulation circuit.

9) Servo-motor-The motor control accepts a dc signal from the lock-in amplifier and outputs the appropriate signal to the motor to move the mirror in the required direction. A negative voltage causes the mirror separation to decrease. The speed of the motion is proportional to the value of the voltage.

10) HP computer system-The computer controls the HP8673B generator. The operator enters all sweep parameters from here. The computer then controls the sweep and acquires both intensity and frequency information. This data may then be plotted on any of the devices the operator desires.

11) Chart recorder-Gives an instantaneous hard-copy of the spectrum.



## Appendix F

# Matrix Elements of the Tensor Product of Two Tensor Operators

The tensor operators  $T(k_1)$  and  $U(k_2)$  are assumed to work on parts 1 and 2 of the system respectively. An expression for the reduced matrix element of the tensor product in the coupled scheme in terms of the reduced matrix elements in the uncoupled scheme will be derived. The quantum numbers  $j_1, m_1, j_2, m_2$  and  $J M$  refer to parts 1 and 2 and the whole system respectively.

By use of Eqn. 3.245 and the symmetry properties of the vector coupling coefficients<sup>1</sup> an expression for the reduced matrix element of the tensor product,  $X(K)$ , in the the coupled scheme ( $j_1 j_2 J M$ ) in terms of the matrix element in the uncoupled scheme ( $j_1 m_1 j_2 m_2$ ) is obtained:

$$\begin{aligned} \langle j'_1 j'_2 J' || X(K) || j_1 j_2 J \rangle (2K + 1)^{-1/2} = & \sum_{Q M M' m_1 m_2 m'_1 m'_2} \langle J' M' J M | J' J K Q \rangle \langle j_1 m_1 j_2 m_2 | j_1 j_2 J M \rangle \\ & \langle j'_1 m'_1 j'_2 m'_2 | j'_1 j'_2 J' M' \rangle (-1)^{j_1 + j_2 + m_1 + m_2} \quad [F.1] \\ & \langle j'_1 m'_1 j'_2 m'_2 | X(K Q) | j_1 - m_1 j_2 - m_2 \rangle \end{aligned}$$

The reduced matrix element of the simple product of  $T(k_1 q_1)$  and  $U(k_2 q_2)$  may be expressed in terms of the same matrix element of  $X(K Q)$ . By use of Eqn. 3.245 and 3.223 one obtains

$$\begin{aligned}
& \langle j'_1 j'_2 | | \mathbf{T}(k_1) \mathbf{U}(k_2) | | j_1 j_2 \rangle [(2k_1 + 1)(2k_2 + 1)]^{-1/2} \\
& = \langle j'_1 j'_2 | | \mathbf{T}(k_1) | | j_1 j'_2 \rangle \langle j_1 j'_2 | | \mathbf{U}(k_2) | | j_1 j_2 \rangle \\
& [(2k_1 + 1)(2k_2 + 1)]^{-1/2} \\
& = \sum_{m_1 m'_1 m_2 m'_2 p r_2 q_1 q_2 Q} \langle j'_1 m'_1 j_1 m_1 | j'_1 j_1 k_1 q_1 \rangle \langle j'_2 m'_2 j_2 m_2 | j'_2 j_2 k_2 q_2 \rangle \\
& \langle k_1 q_1 k_2 q_2 | k_1 k_2 K Q \rangle (-1)^{j_1 + j_2 + m_1 + m_2} \\
& \langle j'_1 m'_1 j'_2 m'_2 | x(K Q) | j_1 - m_1 j_2 - m_2 \rangle
\end{aligned} \tag{F.2}$$

These two expressions are associated with different coupling schemes for the angular momenta  $j'_1, j_1, j'_2, j_2$  and the left hand sides are related by the corresponding transformation coefficient

$$\begin{aligned}
\langle j'_1 j'_2 J' | | \mathbf{X}(K) | | j_1 j_2 J \rangle (2K + 1)^{-1/2} & = \langle j'_1 | | \mathbf{T}(k_1) | | j_1 \rangle \\
& \langle j'_2 | | \mathbf{U}(k_2) | | j_2 \rangle [(2k_1 + 1)(2k_2 + 1)]^{-1/2} \tag{F.3} \\
& \langle (j'_1 j_1) k_1, (j'_2 j_2) k_2, K | (j'_1 j'_2) J', (j_1 j_2) J, K \rangle
\end{aligned}$$

Eqn. 3.257 gives the desired relation involving the 9-j symbol

$$\begin{aligned}
\langle j'_1 j'_2 J' | | \mathbf{X}(K) | | j_1 j_2 J \rangle & = \langle j'_1 | | \mathbf{T}(k_1) | | j_1 \rangle \langle j'_2 | | \mathbf{U}(k_2) | | j_2 \rangle \\
& [(2J + 1)(2J' + 1)(2K + 1)]^{1/2} \left\{ \begin{matrix} j'_1 & j_1 & k_1 \\ j'_2 & j_2 & k_2 \\ J' & J & K \end{matrix} \right\} \tag{F.4}
\end{aligned}$$

The matrix element of the scalar product  $\mathbf{T}(k) \cdot \mathbf{U}(k)$  in the coupled scheme is derived by setting  $K=0$  and  $k_1 = k_2 = k$  in Eqn. F.4.

$$\begin{aligned}
\langle j'_1 j'_2 J' M' | \mathbf{T}(k) \cdot \mathbf{U}(k) | j_1 j_2 J M \rangle & = (-1)^{j_1 + j_2 + J} \delta_{J' J} \delta_{M' M} \left\{ \begin{matrix} J & j'_2 & j'_1 \\ k & j_1 & j_2 \end{matrix} \right\} \tag{F.5} \\
& \langle j'_1 | | \mathbf{T}(k) | | j_1 \rangle \langle j'_2 | | \mathbf{U}(k) | | j_2 \rangle
\end{aligned}$$

The reduced matrix element of a tensor operator  $\mathbf{T}$  operating only on part 1 in the coupled scheme is obtained by putting  $k_2 = 0$  and substituting  $\mathbf{U}(k) = 1$

$$\begin{aligned}
\langle j'_1 j_2 J' || \mathbf{T}(k) || j_1 j_2 J \rangle &= (-1)^{j'_1 + j_2 + J + k} [(2J + 1)(2J' + 1)]^{1/2} \left\{ \begin{matrix} j'_1 & J' & j_2 \\ J & j_1 & k \end{matrix} \right\} \\
&\quad \langle j'_1 || \mathbf{T}(k) || j_1 \rangle
\end{aligned} \tag{F.6}$$

# Appendix G

## Computer Programs

### *Moment of Inertia*

The moment of inertia program, developed by R. A. Beudet and W. R. Pauly, calculates the principal moments of inertia of a molecule from the atomic masses, bond lengths, and bond angles. The bond lengths and angles are read in as data. They are referenced to three arbitrary atoms: atom 1 is the origin, atom 2 defines the positive x direction, and atom 3 defines the positive xy quadrant. The center of mass is computed which then becomes the origin of the coordinate system. The center of mass coordinates for each atom may then be computed. The center of mass coordinate system is then transformed to the principal axis coordinate system. From the coordinates of the atoms in this axis system the principal moments of inertia may be calculated.

## *Rigid Rotor*

The Rigid Rotor program, written by R. A. Beaudet, calculates for any asymmetric rotor the rotational energy levels from  $J=1$  to 40. The transition frequencies are then determined by taking the appropriate differences in the energy levels based on the input dipole selection rules. Line strengths and relative intensities may be requested by selecting this option and inputting a value for the dipole moment of the molecule. The data read in is : rotational constants, dipole selection rules, magnitude of the dipole moment components, frequency limits, and the limits on  $J$ .

## *STRFTQ*

The program STRFTQ<sup>58</sup> adjusts internal coordinates to fit the experimentally determined moments of inertia and assumed constraints in bond angles or lengths by an iterative least squares procedure. The program computes the final values of the coordinates, moments of inertia, planar second moments, and rotational constants. The final values of the coordinates are used to determine the bond lengths and angles.

Required input data is: trial set of internal coordinates, atomic masses, experimental rotational constants, and the experimental parameters to be fit. These parameters include the moments of inertia, distances, angles, sums and differences of these values.

# Hyperfine

The basic logic flow has already been discussed. The program listing, sample data file, and sample output are included here. The required input data are the limits on N ( $N < 8$ ), and the values of the spin-rotation and hyperfine coupling constants.

## Program Listing

```
IMPLICIT REAL (A-H,O-Z)
REAL J1,J
INTEGER ARANK,FM
CHARACTER*4 IDENT(20)
C THIS PORTION OF THE PROGRAM IS THE MAIN PROGRAM WHICH CONTROLS
C EXECUTION OF THE SUBROUTINES AND READS IN ALL DATA
DIMENSION EJ(3:7,4:7,0:7,0:7),EF(0:10,3:7,4:7,0:7,0:7)
C THE DATA IS NOW READ IN. THE FIRST CARD IS AN IDENTIFICATION CARD
C WHICH MAY HAVE ANY INFORMATION THE USER WISHES TO USE TO LABEL THE
C OUTPUT. FORMAT IS 18A4. THE SECOND CARD CONTAINS THE MINIMUM AND
C MAXIMUM VALUES OVER WHICH N, THE ROTATIONAL QUANTUM NUMBER, VARIES
C FORMAT IS 2I5. THE THIRD CARD CONTAINS THE SPIN ROTATION COUPLING
C CONSTANTS IN MHZ. THE FORMAT IS 2F10.2. THE FINAL CARD CONTAINS
C THE HYPERFINE INTERACTION CONSTANTS IN MHZ. THE FORMAT IS 4F10.2.
READ (7,10) (IDENT(I),I= 1,18)
10 FORMAT (18A4)
WRITE (6,10) (IDENT(I),I= 1,18)
READ (7,20) NMIN,NMAX
20 FORMAT (2I5)
READ (7,30) EAA,EBB,ECC
30 FORMAT (4F10.2)
READ (7,30) TAA,TBB,TCC,AF
C THE FINE STRUCTURE ENERGY LEVELS ARE CALCULATED FIRST. THE LOOP
C OVER J IS BEGUN AT JMIN AND GOES TO JMAX.
DO 50 J= ABS(NMIN-0.5),NMAX + 0.5
ARANK = 2*(2*J + 1)
NM= ABS(J-0.5)
NP= J + 0.5
CALL FINE (ARANK,J,EAA,EBB,ECC,NM,NP,EJ,NMIN,NMAX)
50 CONTINUE
C THE HYPERFINE ENERGY LEVELS ARE NOW CALCULATED. THE LOOP IS OVER
C ALL VALUES OF I SINCE THE TRANSITION SPLITTINGS ARE CALCULATED IN
C THIS LOOP. THE LOOP OVER F IS BEGUN AT FMIN AND GOES TO FMAX.
DO 80 I= 0,3
DO 70 F= ABS(ABS(NMIN-0.5)-I),NMAX + 0.5 + I
```

```

FM = F-0.5
CALL HYPER(F,I,ARANK,TAA,TBB,TCC,AF,NMIN,NMAX,EF,NM,NP,NM1,FM)
CALL ELEVEL (I,NM1,NP,NMIN,NMAX,F,FM,NM,EF,EJ)
70 CONTINUE
CALL FREQP(NMIN,NMAX,I,EJ,EF)
80 CONTINUE
END
SUBROUTINE FINE (ARANK,J,EAA,EBB,ECC,NM,NP,E,NMIN,NMAX)
IMPLICIT REAL (A-H,O-Z)
REAL J
C THIS SUBROUTINE CALCULATES THE MATRIX ELEMENTS FOR THE SPIN
C ROTATION INTERACTION. THE RANK OF THE MATRIX IS 2*(NM+NP+1) WHERE
C NM=J-.5 AND NP=J+.5. THE MATRIX ELEMENTS ARE STORED IN THE ARRAY
C NAMED A. THE DIAGONALIZED MATRIX ELEMENTS WHICH ARE THE ENERGY
C LEVELS ARE ASSIGNED TO ENERGY LEVELS USING J,N,KP,KO AS THE
C INDICES AND ARE STORED IN THE ARRAY LABELED EJ.
INTEGER DK,ARANK
DIMENSION A(350,350),E(3:7,4:7,0:7,0:7)
DO 10 L = 1,2*(NM+NP+1)
DO 10 M = 1,2*(NM+NP+1)
A(L,M) = 0.0
10 CONTINUE
L = 0
DO 150 NPRIME = NM,NP
DO 150 KPRIME = -NPRIME,NPRIME
M = 0
L = L + 1
DO 150 N = NM,NP
NPN = NPRIME - N
IF (NPN) 20,20,140
20 DO 150 K = -N,N
KM = KPRIME - K
M = M + 1
IF (M.LT.L) GOTO 150
IF (N) 30,120,30
30 DK = ABS(KPRIME - K)
IF (DK .GT. 2) GOTO 120
IF (DK .EQ. 1) GOTO 120
C SINCE THE MATRIX IS HERMITIAN ONLY THOSE MATRIX ELEMENTS TO THE
C RIGHT OF THE MAIN DIAGONAL ARE CALCULATED. THE NEXT LINE
C DETERMINES IF THE CHANGE IN N IS POSITIVE (NOT CALCULATED), ZERO
C OR NEGATIVE AND DIRECTS THE PROGRAM TO THE APPROPRIATE STATEMENT
C STATEMENT.
IF (NPN) 40,80,150
C THE CHANGE IN K IS NOW DETERMINED AND THE APPROPRIATE MATRIX
C ELEMENT IS CALCULATED.
40 IF (KM) 50,60,70
50 B = (N+K)*(N+K-1)*(N+K-2)*(N-K+1)
A(L,M) = (EBB-ECC)*SQRT(B)/(8*N)
GOTO 130
60 B = N*N-K*K
A(L,M) = ((EBB + ECC)/2.0-EAA)*K*SQRT(B)/(2*N)
GOTO 130
70 B = (N-K)*(N-K-1)*(N-K-2)*(N+K+1)
A(L,M) = (ECC-EBB)*SQRT(B)/(8*N)
GOTO 130

```

```

80 IF (KM) 90,100,110
90 B=(N*(N+1)-K*(K-1))*(N*(N+1)-(K-1)*(K-2))
  A(L,M)=(ECC-EBB)*(N*(N+1)+0.75-J*(J+1))*SQRT(B)/(8*N*(N+1))
  GOTO 130
100 A(L,M)=(EAA*K*K+(EBB+ECC)*(N*(N+1)-K*K)/2.0)*(J*(J+1)-N*(N+1)
  1-0.75)/(2.0*N*(N+1))
  GOTO 130
110 B=(N*(N+1)-K*(K+1))*(N*(N+1)-(K+1)*(K+2))
  A(L,M)=(ECC-EBB)*(N*(N+1)+0.75-J*(J+1))*SQRT(B)/(8*N*(N+1))
  GOTO 130
120 A(L,M)=0.0
130 A(M,L)=A(L,M)
  GOTO 150
140 M=2*N+1
150 CONTINUE
  CALL HDIAG(A,L,1,L)
  CALL XORDER(A,L,L)
  CALL JASSIN(NM,NP,A,L,E,NMIN,NMAX)
  RETURN
  END
SUBROUTINE HDIAG(H,N,IEGEN,NX)
C THIS SUBROUTINE WAS TAKEN FROM THE ASYMMETRIC ROTOR PROGRAM
C WRITTEN BY ROBERT A. BEAUDET. MIHDI3, FORTRAN II DIAGONALIZATION
C OF A REAL SYMMETRIC MATRIX BY THE JACOBI METHOD. MAY 19, 1959
C CALLING SEQUENCE FOR DIAGONALIZATION. CALL HDIAG(H,N,IEGEN,U,NR)
C WHERE H IS THE ARRAY TO BE DIAGONALIZED. N IS THE ORDER OF THE
C MATRIX, H. U IS THE UNITARY MATRIX USED FOR FORMATION OF THE
C EIGENVECTORS. NR IS THE NUMBER OF ROTATIONS. IEGEN MUST BE SET
C UNEQUAL TO ZERO IF ONLY EIGENVALUES ARE TO BE COMPUTED. IEGEN
C MUST BE SET EQUAL TO ZERO IF EIGENVALUES AND EIGENVECTORS ARE TO
C BE COMPUTED. SUBROUTINE PLACES COMPUTER IN FLOATING TRAP MODE.
C THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE
C RIGHT OF THE MAIN DIAGONAL. THUS, ONLY A TRIANGULAR SECTION NEED
C BE STORED IN THE ARRAY H.
  IMPLICIT REAL (A-H,O-Z)
  DIMENSION H(350,350),X(350),IQ(350)
  IF (IEGEN) 15,10,15
10 DO 14 I=1,N
  DO 14 J=1,N
  IF (I-J) 12,11,12
11 CONTINUE
  GOTO 14
12 CONTINUE
14 CONTINUE
15 NR=0
  IF (N-1) 1000,1000,17
C SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW. X(I) CONTAINS
C LARGEST ELEMENT IN ITH ROW. IQ(I) HOLDS SECOND SUBSCRIPT DEFINING
C POSITION OF ELEMENT.
17 NMII=N-1
  DO 30 I=1,NMII
  X(I)=0.0
  IPL1=I+1
  DO 30 J=IPL1,N
  IF (X(I)-ABS(H(I,J))) 20,20,30
20 X(I)=ABS(H(I,J))

```



```

      IQ(I)=J
30 CONTINUE
C   SET INDICATOR FOR SHUTOFF. RAP=2**-27, NR=NO. OF ROTATIONS
      RAP=0.745058059D-08
      HDTEST=1.0D38
C   FIND MAXIMUM OF X(I)S FOR PIVOT ELEMENT AND TEST FOR END OF
C   PROBLEM.
40 DO 70 I=1,NM1
      IF (I-1) 60,60,45
45 IF (XMAX-X(I)) 60,70,70
60 XMAX=X(I)
      IPIV=I
      JPIV=IQ(I)
70 CONTINUE
C   IF MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST, REVISE HDTEST
      IF (XMAX) 1000,1000,80
80 IF (HDTEST) 90,90,85
85 IF (XMAX-HDTEST) 90,90,148
90 HDIMIN=ABS(H(1,1))
      DO 110 I=2,N
      IF (HDIMIN-ABS(H(I,I))) 110,110,100
100 HDIMIN=ABS(H(I,I))
110 CONTINUE
      HDTEST=HDIMIN*RAP
C   RETURN IF MAX. H(I,J) LESS THAN (2**-27)*ABS(H(K,K)-MIN)
      IF (HDTEST-XMAX) 148,1000,1000
148 NR=NR+1
C   COMPUTE TANGENT SINE AND COSINE, H(I,I), H(J,J)
150 TANG=SIGN(2.,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/(ABS
1(H(IPIV,IPIV)-H(JPIV,JPIV))+SQRT((H(IPIV,IPIV)-H(JPIV,JPIV))
2**2+4.0*H(IPIV,JPIV)**2))
      COSINE=1.0/SQRT(1.0+TANG**2)
      SINE=TANG*COSINE
      HII=H(IPIV,IPIV)
      H(IPIV,IPIV)=COSINE**2*(HII+TANG*(2.0*H(IPIV,JPIV)+TANG*H(JPIV,
1PIV)))
      H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.0*H(IPIV,JPIV)-TANG
1*HII))
      H(IPIV,JPIV)=0.0
C   PSEUDO RANK THE EIGENVALUES. ADJUST SINE AND COS FOR COMPUTATION
C   OF H(IK) AND U(IK).
      IF (H(IPIV,IPIV)-H(JPIV,JPIV)) 152,153,153
152 HTEMP=H(IPIV,IPIV)
      H(IPIV,IPIV)=H(JPIV,JPIV)
      H(JPIV,JPIV)=HTEMP
C   RECOMPUTE SINE AND COS
      HTEMP=SIGN(1.0,-SINE)*COSINE
      COSINE=ABS(SINE)
      SINE=HTEMP
153 CONTINUE
C   INSPECT THE IQS BETWEEN I+1 AND N-1 TO DETERMINE WHETHER A NEW
C   MAXIMUM VALUE SHOULD BE COMPUTED SINCE THE PRESENT MAXIMUM IS
C   IN THE I OR J ROW.
      DO 350 I=1,NM1
      IF (I-IPIV) 210,350,200
200 IF (I-JPIV) 210,350,210

```

```

210 IF (IQ(I)-IPIV)230,240,230
230 IF (IQ(I)-JPIV)350,240,350
240 K = IQ(I)
250 HTEMP = H(I,K)
    H(I,K) = 0.0
    IPL1 = I + 1
    X(I) = 0.0
C   SEARCH IN DEPLETED ROW FOR NEW MAXIMUM
    DO 320 J = IPL1,N
    IF (X(I)-ABS(H(I,J)))300,300,320
300 X(I) = ABS(H(I,J))
    IQ(I) = J
320 CONTINUE
    H(I,K) = HTEMP
350 CONTINUE
    X(IPIV) = 0.0
    X(JPIV) = 0.0
C   CHANGE THE OTHER ELEMENTS OF H.
    DO 530 I = 1,N
    IF (I-IPIV)370,530,420
370 HTEMP = H(I,IPIV)
    H(I,IPIV) = COSINE*HTEMP + SINE*H(I,JPIV)
    IF (X(I)-ABS(H(I,IPIV)))380,390,390
380 X(I) = ABS(H(I,IPIV))
    IQ(I) = IPIV
390 H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)
    IF (X(I)-ABS(H(I,JPIV)))400,530,530
400 X(I) = ABS(H(I,JPIV))
    IQ(I) = JPIV
    GOTO 530
420 IF (I-JPIV)430,530,480
430 HTEMP = H(IPIV,I)
    H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)
    IF (X(IPIV)-ABS(H(IPIV,I)))440,450,450
440 X(IPIV) = ABS(H(IPIV,I))
    IQ(IPIV) = I
450 H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)
    IF (X(I)-ABS(H(I,JPIV)))400,530,530
480 HTEMP = H(IPIV,I)
    H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)
    IF (X(IPIV)-ABS(H(IPIV,I)))490,500,500
490 X(IPIV) = ABS(H(IPIV,I))
    IQ(IPIV) = I
500 H(JPIV,I) = -SINE*HTEMP + COSINE*H(JPIV,I)
    IF (X(JPIV)-ABS(H(JPIV,I))) 510,530,530
510 X(JPIV) = ABS(H(JPIV,I))
    IQ(JPIV) = I
530 CONTINUE
C   TEST FOR COMPUTATION OF EIGENVECTORS.
    IF (IEGEN) 40,540,40
540 DO 550 I = 1,N
550 CONTINUE
    GOTO 40
1000 RETURN
END

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SUBROUTINE XORDER(ARRAY,LIMIT,NX)
C THIS SUBROUTINE IN ADDITION TO HDIAG WERE TAKEN FROM THE
C ASYMMETRIC ROTOR PROGRAM WRITTEN BY ROBERT A. BEAUDET.
IMPLICIT REAL (A-H,O-Z)
C ROBERT A. BEUDET AI06 ENERGY DIAGONALIZATION
C THIS SUBROUTINE ARRANGES THE EIGENVALUES AND EIGENVECTORS
C IN INCREASING ORDER. HDIAG IS NOT DEPENDABLE IN DOING THIS.
DIMENSION ARRAY(350,350)
30 IF (LIMIT-1) 220,220,40
40 DO 210 KTEST = 2,LIMIT
50 DO 200 JTEST = 2,KTEST
ITEST = KTEST + 2-JTEST
ITESTM = ITEST-1
IF (ARRAY(ITEST,ITEST)-ARRAY(ITESTM,ITESTM)) 60,210,210
60 XCHAN = ARRAY(ITEST,ITEST)
ARRAY(ITEST,ITEST) = ARRAY(ITESTM,ITESTM)
ARRAY(ITESTM,ITESTM) = XCHAN
DO 70 L = 1,LIMIT
70 CONTINUE
200 CONTINUE
210 CONTINUE
220 RETURN
END
SUBROUTINE JASSIN(NM,NP,D,L,C,NMIN,NMAX)
C THIS SUBROUTINE ASSIGNS THE ORDERED EIGENVALUES TO ENERGY LEVELS
C USING THE VALUES OF J,N,KP,KO AS SUBSCRIPTS AND STORES THEM IN
C THE ARRAY EJ.
IMPLICIT REAL (A-H,O-Z)
DIMENSION D(350,350),C(3:7,4:7,0:7,0:7)
LINDEX = 1
DO 10 N = NM,NP
IF (N .LT. NMIN) GOTO 5
IF (N .GT. NMAX) GOTO 5
DO 10 K = 0,N
KO = N-K
C(NM,N,K,KO) = D(LINDEX,LINDEX)
LINDEX = LINDEX + 1
IF (K .EQ. N) GOTO 10
KP = K + 1
C(NM,N,KP,KO) = D(LINDEX,LINDEX)
LINDEX = LINDEX + 1
GOTO 10
5 LINDEX = 2*N + 1 + LINDEX
10 CONTINUE
RETURN
END
SUBROUTINE HYPER(F,I,ARANK,TAA,TBB,TCC,AF,NMIN,NMAX,P,NM,NP,NM1,FM
1)
C THIS SUBROUTINE CALCULATES THE HYPERFINE MATRIX ELEMENTS. HDIAG
C IS THEN CALLED WHICH DIAGONALIZES THE MATRIX. XORDER ORDERS THE
C DIAGONALIZED MATRIX A AND FASSIGN THEN ASSIGNS THESE EIGENVALUES
C TO THE ARRAY EF USING I,F,J,N,KP,KO AS THE ASSIGNMENT INDICES.
IMPLICIT REAL (A-H,O-Z)
REAL JPRIME,J,J1,MULT,KM,KP
INTEGER DJ,DNMAX,DN,DFIJ,ADK,ARANK,FM
DIMENSION A(350,350),P(0:10,3:7,4:7,0:7,0:7)

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IF (I) 10,310,10
10 L=0
DO 300 JPRIME = ABS(F-I),F + I
DO 300 NPRIME = ABS(JPRIME-0.5),JPRIME + 0.5
DO 300 KPRIME = -NPRIME,NPRIME
M=0
L=L+1
DO 300 J = ABS(F-I),F + I
DJ = ABS(JPRIME-J)
DNMAX = DJ + 1
IF (DNMAX .EQ. 2) DNMAX = 3
IF (JM) 20,20,280
20 IJF = (I+J+F+1)*(-I+J+F)*(I-J+F+1)*(I+J-F)
FIJ = F*(F+1)-I*(I+1)-J*(J+1)
DO 300 N = ABS(J-0.5),J + 0.5
DN = ABS(NPRIME-N)
NPN = NPRIME-N
IF (DN .GT. DNMAX) GOTO 300
IF (NPN) 30,30,290
30 NSJ = (N+J-0.5)*(N-J+1.5)*(J-N+0.5)*(N+J+1.5)
NSQ = N*N*(N+1)*(N+1)*(2*N+3)
NFAC = N*(N+1)*(2*N-1)*(2*N+3)
NSJ1 = N*(N+1)+0.75-J*(J+1)
NJS = N*(N+1)+J*(J+1)-0.75
SJN = 0.75+J*(J+1)-N*(N+1)
IF (JM) 40,40,50
40 IF (DN .EQ. 2) GOTO 300
50 DO 300 K = -N,N
DK = KPRIME-K
ADK = ABS(DK)
M = M + 1
IF (M .LT. L) GOTO 300
IF (DN .EQ. DNMAX) GOTO 260
IF (DN .EQ. 1) GOTO 260
IF (DN .GT. 2) GOTO 260
IF (DJ .GT. 1) GOTO 260
IF (ADK .GT. 2) GOTO 260
IF (ADK .EQ. 1) GOTO 260
KM = (N+K-1)*(N+K)*(N-K+1)*(N-K+2)
KSQ = N*(N+1)-3*K*K
KP = (N-K-1)*(N-K)*(N+K+1)*(N+K+2)
C THE MATRIX ELEMENTS ARE NOW CALCULATED. THE CHANGE IN J AND N
C CONTROL WHERE THE PROGRAM BRANCHES TO CALCULATE THE APPROPRIATE
C MATRIX ELEMENTS FOR THE VARIOUS VALUES OF K.
IF (JM) 60,170,300
60 IF (NPN) 70,90,300
70 IF (DK) 260,80,260
80 B = IJF*(J+N-0.5)*(J+N+0.5)*(J+N-2.5)*(J+N-1.5)*((N-1)*(N-1)-K*K)*(N
1*N-K*K)/((2*J-1)*(2*J+1)*(2*N-1)*(2*N-3))
A(L,M) = TCC*SQRT(B)/(16*J*(N-1)*N)
GOTO 270
90 IF (DK) 100,120,150
100 IF (N) 110,260,110
110 B = IJF*NSJ*KM/((2*J-1)*(2*J+1))
A(L,M) = (TBB-TAA)/(32*J*NSQ)*SQRT(B)
GOTO 270

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120 B = IJF*NSJ/((2*J-1)*(2*J + 1))
    MULT = SQRT(B)/(4*J)
    IF (N) 130,80,130
130 A(L,M) = MULT*(AF + TCC*KSQ/(4*NSQ)*(NSJ1*(2*N + 3) + N*N*(N + J + 2.5)*
    1(N + J + 0.5)/(2*N + 1)))
    GOTO 270
140 A(L,M) = MULT*AF
    GOTO 270
150 IF (N) 160,260,160
160 B = IJF*NSJ*KP/((2*J-1)*(2*J + 1))
    A(L,M) = (TBB-TAA)*SQRT(B)/(32*J*NSQ)
    GOTO 270
170 IF (NPN) 260,180,300
180 IF (DK) 190,210,240
190 IF (N) 200,260,200
200 A(L,M) = 3*(TBB-TAA)*FIJ*SQRT(KM)/(16*J*(J + 1)*NFAC)
    GOTO 270
210 MULT = FIJ/(4*J*(J + 1))
    IF (N) 220,230,220
220 A(L,M) = MULT*(AF*SJN + 3*TCC*KSQ/(2*NFAC)*(NSJ1*NJS + 2*N*(N + 1)*SJN/3))
    GOTO 270
230 A(L,M) = MULT*AF*SJN
    GOTO 270
240 IF (N) 250,260,250
250 A(L,M) = 3*(TBB-TAA)*FIJ*SQRT(KP)/(16*J*(J + 1)*NFAC)
    GOTO 270
260 A(L,M) = 0.0
270 A(M,L) = A(L,M)
    GOTO 300
280 M = 4*J + 2
    GOTO 300
290 M = 2*N + 1 + M
300 CONTINUE
    CALL HDIAG(A,L,1,L)
    CALL XORDER(A,L,L)
    FM = F-0.5
    CALL FASSIN(I,NMIN,NMAX,F,NM1,NM,NP,L,A,P)
310 RETURN
    END
SUBROUTINE FASSIN(I,NMIN,NMAX,F,NM1,NM,NP,L,D,G)
C THIS SUBROUTINE ASSIGNS THE DIAGONALIZED MATRIX ELEMENTS TO
C THE VARIOUS VALUES OF I,F,J,N,KP,KO. IF I=0 THEN THIS SUBROUTINE
C IS BYPASSED. THE ENERGY LEVELS ARE STORED IN A MATRIX NAMED EF.
    IMPLICIT REAL (A-H,O-Z)
    REAL J
    INTEGER FM
    DIMENSION D(350,350),G(0:10,3:7,4:7,0:7,0:7)
    IF (I) 30,30,10
10 FM = F-0.5
    LINDEX = 1
    DO 20 J = ABS(F-I),F + I
    JM = J-0.5
    DO 20 N = ABS(J-0.5),J + 0.5
    IF (N .LT. NMIN) GOTO 15
    IF (N .GT. NMAX) GOTO 15
    DO 20 K = 0,N

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```

KO = N-K
KP = K + 1
G(FM,JM,N,K,KO) = D(LINDEX,LINDEX)
LINDEX = LINDEX + 1
IF (K .EQ. N) GOTO 20
G(FM,JM,N,KP,KO) = D(LINDEX,LINDEX)
LINDEX = LINDEX + 1
GOTO 20
15 LINDEX = LINDEX + 2*N + 1
20 CONTINUE
30 RETURN
END
SUBROUTINE ELEVEL(I,NM1,NP,NMIN,NMAX,F,FM,NM,P,E)
C THIS SUBROUTINE COMBINES THE ENERGY LEVELS DETERMINED FROM
C SUBROUTINES HYPER AND FINE AND STORES THEM IN ARRAY EF.
IMPLICIT REAL (A-H,O-Z)
INTEGER*4 FM
REAL J
DIMENSION P(0:10,3:7,4:7,0:7,0:7),E(3:7,4:7,0:7,0:7)
IF (I) 30,30,10
10 FM = F-0.5
DO 20 J = ABS(F-I),F + I
JM = J-0.5
DO 20 N = ABS(J-.5),J + .5
IF (N .LT. NMIN) GOTO 20
IF (N .GT. NMAX) GOTO 20
DO 20 K = 0,N
KO = N-K
KP = K + 1
P(FM,JM,N,K,KO) = P(FM,JM,N,K,KO) + E(JM,N,K,KO)
IF (K .EQ. N) GOTO 20
P(FM,JM,N,KP,KO) = P(FM,JM,N,KP,KO) + E(JM,N,KP,KO)
20 CONTINUE
30 RETURN
END
SUBROUTINE FREQP(NMIN,NMAX,I,E,P)
IMPLICIT REAL (A-H,O-Z)
INTEGER DKP,DKO,FM,FMP
REAL J,JP
DIMENSION E(3:7,4:7,0:7,0:7),P(0:10,3:7,4:7,0:7,0:7)
WRITE (6,120) NMIN,NMAX,I
DO 110 N = NMIN,NMAX-1
NP = N + 1
DO 110 K = 0,N
KO = N-K
DO 110 DKP = -3,3,2
KD = K + DKP
IF (KD .GT. (N + 1)) GOTO 110
10 DO 110 DKO = -3,3,2
KOD = KO + DKO
IF (KOD .GT. (N + 1)) GOTO 110
IF (KOD) 110,20,20
20 DO 110 J = ABS(N-.5),N + .5
JP = J + 1
JM = J-.5
JMP = JM + 1

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```

      IF (J) 110,30,30
30 IF (I) 150,35,65
35 KP = K
      KA = IABS(K-KO)
      DAK = KA/2.0
      IKA = INT(DAK)
      DIKA = DAK-IKA
40 IF (DIKA .GT. 0.1) KP = K + 1
      KPD = KP + DKP
      IF (KPD) 110,45,45
45 KSUM = KOD + KPD
50 IF (KP .GT. N) GOTO 110
55 IF (KSUM .GT. (N + 2)) GOTO 110
      IF (KSUM .LT. (N + 1)) GOTO 110
60 FREQ = E(JMP,NP,KPD,KOD)-E(JM,N,KP,KO)
      WRITE (6,130) NP,KPD,KOD,N,KP,KO,JP,J,FREQ
      GOTO 110
65 DO 110 F = ABS(J-I),J + I
      FP = F + 1
      FM = F - 0.5
      FMP = FM + 1
      IF (I .NE. 2) GOTO 75
      KP = K
      KA = IABS(K-KO)
      DAK = KA/2.0
      IKA = INT(DAK)
      DIKA = DAK-IKA
      IF (DIKA .GT. 0.1) KP = K + 1
      KPD = KP + DKP
      IF (KPD) 110,66,66
66 KSUM = KOD + KPD
70 IF (KP .GT. N) GOTO 110
72 IF (KSUM .GT. (N + 2)) GOTO 110
      IF (KSUM .LT. (N + 1)) GOTO 110
      GOTO 100
75 KP = K
80 KA = IABS(K-KO)
      DAK = KA/2.0
      IKA = INT(DAK)
      DIKA = DAK-IKA
      IF (DIKA .LT. 0.4) KP = K + 1
      KPD = KP + DKP
      IF (KPD) 110,85,85
85 KSUM = KPD + KOD
90 IF (KP .GT. N) GOTO 110
95 IF (KSUM .GT. (N + 2)) GOTO 110
      IF (KSUM .LT. (N + 1)) GOTO 110
100 FREQ = P(FMP,JMP,NP,KPD,KOD)-P(FM,JM,N,KP,KO)
      WRITE (6,140) NP,KPD,KOD,N,KP,KO,JP,J,FP,F,FREQ
110 CONTINUE
120 FORMAT(43HTHESE ARE THE B-TYPE TRANSITIONS FROM NMIN = ,I2,9H TO NMA
      IX = ,I2,7H FOR I = ,I1/91H. THE ORDER OF THE QUANTUM NUMBERS ARE FROM
      2 LEFT TO RIGHT, N',KP',KO'-N,KP,KO; J'-J, F'-F.)
130 FORMAT(I2,1H(I2,1H,,I2,2H)-,I2,1H(I2,1H,,I2,1H),5X,F4.1,1H-,F4.1
      1,10X,F10.3)
140 FORMAT (I2,1H(I2,1H,,I2,2H)-,I2,1H(I2,1H,,I2,1H),5X,F4.1,1H-,F4.

```

11,5X,F4.1,1H-,F4.1,10X,F10.3)  
 150 RETURN  
 END

## Data File

RUN #6 CF32NO AA = -183.74BB = -177.77CC = 361.51AF = 22.8

4 7

-3597.7 -1121.4 29.8

-183.74 -177.77 361.51 22.8

## Sample Output

RUN #6 CF32NO AA = -183.74BB = -177.77CC = 361.51AF = 22.8  
 THESE ARE THE B-TYPE TRANSITIONS FROM NMIN = 4 TO NMAX = 7 FOR I = 0  
 THE ORDER OF THE QUANTUM NUMBERS ARE FROM LEFT TO RIGHT, N',KP',KO'-N,KP  
 J'-J; F'-F.

5( 1, 5)- 4( 0, 4)	4.5- 3.5	242.855
5( 1, 5)- 4( 0, 4)	5.5- 4.5	-1797.805
5( 3, 3)- 4( 0, 4)	4.5- 3.5	5050.539
5( 3, 3)- 4( 0, 4)	5.5- 4.5	1541.723
5( 2, 4)- 4( 1, 3)	4.5- 3.5	992.148
5( 2, 4)- 4( 1, 3)	5.5- 4.5	-1790.906
5( 4, 2)- 4( 1, 3)	4.5- 3.5	4209.988
5( 4, 2)- 4( 1, 3)	5.5- 4.5	1443.853
5( 1, 5)- 4( 2, 2)	4.5- 3.5	-3185.913
5( 1, 5)- 4( 2, 2)	5.5- 4.5	-5095.469
5( 3, 3)- 4( 2, 2)	4.5- 3.5	1621.773
5( 3, 3)- 4( 2, 2)	5.5- 4.5	-1755.945
5( 5, 1)- 4( 2, 2)	4.5- 3.5	4926.227
5( 5, 1)- 4( 2, 2)	5.5- 4.5	1408.531
5( 2, 4)- 4( 3, 1)	4.5- 3.5	-1437.250
5( 2, 4)- 4( 3, 1)	5.5- 4.5	-4744.930
5( 4, 2)- 4( 3, 1)	4.5- 3.5	1780.594
5( 4, 2)- 4( 3, 1)	5.5- 4.5	-1510.173
5( 3, 3)- 4( 4, 0)	4.5- 3.5	-1507.520
5( 3, 3)- 4( 4, 0)	5.5- 4.5	-4008.438
5( 5, 1)- 4( 4, 0)	4.5- 3.5	1796.934
5( 5, 1)- 4( 4, 0)	5.5- 4.5	-843.962
6( 0, 6)- 5( 1, 5)	5.5- 4.5	-166.550



6( 0, 6)- 5( 1, 5)	6.5- 5.5	-1798.191
6( 2, 4)- 5( 1, 5)	5.5- 4.5	3843.194
6( 2, 4)- 5( 1, 5)	6.5- 5.5	1559.648
6( 4, 2)- 5( 1, 5)	5.5- 4.5	6574.680
6( 4, 2)- 5( 1, 5)	6.5- 5.5	4651.465
6( 1, 5)- 5( 2, 4)	5.5- 4.5	-263.219
6( 1, 5)- 5( 2, 4)	6.5- 5.5	-1794.047
6( 3, 3)- 5( 2, 4)	5.5- 4.5	1812.203
6( 3, 3)- 5( 2, 4)	6.5- 5.5	1486.164
6( 5, 1)- 5( 2, 4)	5.5- 4.5	5008.336
6( 5, 1)- 5( 2, 4)	6.5- 5.5	4030.830
6( 0, 6)- 5( 3, 3)	5.5- 4.5	-4974.234
6( 0, 6)- 5( 3, 3)	6.5- 5.5	-5137.719
6( 2, 4)- 5( 3, 3)	5.5- 4.5	-964.492
6( 2, 4)- 5( 3, 3)	6.5- 5.5	-1779.879
6( 4, 2)- 5( 3, 3)	5.5- 4.5	1766.996
6( 4, 2)- 5( 3, 3)	6.5- 5.5	1311.937
6( 6, 0)- 5( 3, 3)	5.5- 4.5	5102.195
6( 6, 0)- 5( 3, 3)	6.5- 5.5	3305.266
6( 1, 5)- 5( 4, 2)	5.5- 4.5	-3481.062
6( 1, 5)- 5( 4, 2)	6.5- 5.5	-5028.805
6( 3, 3)- 5( 4, 2)	5.5- 4.5	-1405.641
6( 3, 3)- 5( 4, 2)	6.5- 5.5	-1748.595
6( 5, 1)- 5( 4, 2)	5.5- 4.5	1790.492
6( 5, 1)- 5( 4, 2)	6.5- 5.5	796.071
6( 2, 4)- 5( 5, 1)	5.5- 4.5	-4268.945
6( 2, 4)- 5( 5, 1)	6.5- 5.5	-4944.352
6( 4, 2)- 5( 5, 1)	5.5- 4.5	-1537.457
6( 4, 2)- 5( 5, 1)	6.5- 5.5	-1852.538
6( 6, 0)- 5( 5, 1)	5.5- 4.5	1797.742
6( 6, 0)- 5( 5, 1)	6.5- 5.5	140.791
7( 1, 7)- 6( 0, 6)	6.5- 5.5	72.367
7( 1, 7)- 6( 0, 6)	7.5- 6.5	-1798.336
7( 3, 5)- 6( 0, 6)	6.5- 5.5	5372.504
7( 3, 5)- 6( 0, 6)	7.5- 6.5	1571.012
7( 2, 6)- 6( 1, 5)	6.5- 5.5	683.707
7( 2, 6)- 6( 1, 5)	7.5- 6.5	-1795.609
7( 4, 4)- 6( 1, 5)	6.5- 5.5	3787.613
7( 4, 4)- 6( 1, 5)	7.5- 6.5	1518.340
7( 1, 7)- 6( 2, 4)	6.5- 5.5	-3937.377
7( 1, 7)- 6( 2, 4)	7.5- 6.5	-5156.176
7( 3, 5)- 6( 2, 4)	6.5- 5.5	1362.762
7( 3, 5)- 6( 2, 4)	7.5- 6.5	-1786.828
7( 5, 3)- 6( 2, 4)	6.5- 5.5	4509.586
7( 5, 3)- 6( 2, 4)	7.5- 6.5	1431.867
7( 2, 6)- 6( 3, 3)	6.5- 5.5	-1391.715
7( 2, 6)- 6( 3, 3)	7.5- 6.5	-5075.820
7( 4, 4)- 6( 3, 3)	6.5- 5.5	1712.191
7( 4, 4)- 6( 3, 3)	7.5- 6.5	-1761.871
7( 6, 2)- 6( 3, 3)	6.5- 5.5	4989.805
7( 6, 2)- 6( 3, 3)	7.5- 6.5	1312.785
7( 3, 5)- 6( 4, 2)	6.5- 5.5	-1368.727
7( 3, 5)- 6( 4, 2)	7.5- 6.5	-4878.645
7( 5, 3)- 6( 4, 2)	6.5- 5.5	1778.098
7( 5, 3)- 6( 4, 2)	7.5- 6.5	-1659.949
7( 7, 1)- 6( 4, 2)	6.5- 5.5	5133.316

7( 7, 1)- 6( 4, 2)	7.5- 6.5	1422.395
7( 4, 4)- 6( 5, 1)	6.5- 5.5	-1483.941
7( 4, 4)- 6( 5, 1)	7.5- 6.5	-4306.535
7( 6, 2)- 6( 5, 1)	6.5- 5.5	1793.672
7( 6, 2)- 6( 5, 1)	7.5- 6.5	-1231.881
7( 5, 3)- 6( 6, 0)	6.5- 5.5	-1557.102
7( 5, 3)- 6( 6, 0)	7.5- 6.5	-3653.278
7( 7, 1)- 6( 6, 0)	6.5- 5.5	1798.117
7( 7, 1)- 6( 6, 0)	7.5- 6.5	-570.934

THESE ARE THE B-TYPE TRANSITIONS FROM NMIN= 4 TO NMAX= 7 FOR I=1

THE ORDER OF THE QUANTUM NUMBERS ARE FROM LEFT TO RIGHT, N',KP',KO'-N

5( 0, 5)- 4( 1, 4)	4.5- 3.5	3.5- 2.5	-265.548
5( 0, 5)- 4( 1, 4)	4.5- 3.5	4.5- 3.5	-266.563
5( 0, 5)- 4( 1, 4)	4.5- 3.5	5.5- 4.5	-253.007
5( 0, 5)- 4( 1, 4)	5.5- 4.5	4.5- 3.5	-1798.031
5( 0, 5)- 4( 1, 4)	5.5- 4.5	5.5- 4.5	-1808.473
5( 0, 5)- 4( 1, 4)	5.5- 4.5	6.5- 5.5	-1808.047
5( 2, 3)- 4( 1, 4)	4.5- 3.5	3.5- 2.5	3434.389
5( 2, 3)- 4( 1, 4)	4.5- 3.5	4.5- 3.5	3431.993
5( 2, 3)- 4( 1, 4)	4.5- 3.5	5.5- 4.5	3454.810
5( 2, 3)- 4( 1, 4)	5.5- 4.5	4.5- 3.5	1561.129
5( 2, 3)- 4( 1, 4)	5.5- 4.5	5.5- 4.5	1538.070
5( 2, 3)- 4( 1, 4)	5.5- 4.5	6.5- 5.5	1623.184
5( 4, 1)- 4( 1, 4)	4.5- 3.5	3.5- 2.5	6398.266
5( 4, 1)- 4( 1, 4)	4.5- 3.5	4.5- 3.5	6374.871
5( 4, 1)- 4( 1, 4)	4.5- 3.5	5.5- 4.5	6401.238
5( 4, 1)- 4( 1, 4)	5.5- 4.5	4.5- 3.5	4335.246
5( 4, 1)- 4( 1, 4)	5.5- 4.5	5.5- 4.5	4310.586
5( 4, 1)- 4( 1, 4)	5.5- 4.5	6.5- 5.5	4424.898
5( 1, 4)- 4( 2, 3)	4.5- 3.5	3.5- 2.5	-443.052
5( 1, 4)- 4( 2, 3)	4.5- 3.5	4.5- 3.5	-429.094
5( 1, 4)- 4( 2, 3)	4.5- 3.5	5.5- 4.5	-432.030
5( 1, 4)- 4( 2, 3)	5.5- 4.5	4.5- 3.5	-1790.566
5( 1, 4)- 4( 2, 3)	5.5- 4.5	5.5- 4.5	-1800.070
5( 1, 4)- 4( 2, 3)	5.5- 4.5	6.5- 5.5	-1795.797
5( 3, 2)- 4( 2, 3)	4.5- 3.5	3.5- 2.5	1804.320
5( 3, 2)- 4( 2, 3)	4.5- 3.5	4.5- 3.5	1809.121
5( 3, 2)- 4( 2, 3)	4.5- 3.5	5.5- 4.5	1816.293
5( 3, 2)- 4( 2, 3)	5.5- 4.5	4.5- 3.5	1435.958
5( 3, 2)- 4( 2, 3)	5.5- 4.5	5.5- 4.5	1425.753
5( 3, 2)- 4( 2, 3)	5.5- 4.5	6.5- 5.5	1476.512
5( 5, 0)- 4( 2, 3)	4.5- 3.5	3.5- 2.5	5187.121
5( 5, 0)- 4( 2, 3)	4.5- 3.5	4.5- 3.5	5107.945
5( 5, 0)- 4( 2, 3)	4.5- 3.5	5.5- 4.5	5114.180
5( 5, 0)- 4( 2, 3)	5.5- 4.5	4.5- 3.5	3559.937
5( 5, 0)- 4( 2, 3)	5.5- 4.5	5.5- 4.5	3526.097
5( 5, 0)- 4( 2, 3)	5.5- 4.5	6.5- 5.5	3582.196
5( 0, 5)- 4( 3, 2)	4.5- 3.5	3.5- 2.5	-4879.812
5( 0, 5)- 4( 3, 2)	4.5- 3.5	4.5- 3.5	-4846.770
5( 0, 5)- 4( 3, 2)	4.5- 3.5	5.5- 4.5	-4865.281
5( 0, 5)- 4( 3, 2)	5.5- 4.5	4.5- 3.5	-5131.691
5( 0, 5)- 4( 3, 2)	5.5- 4.5	5.5- 4.5	-5122.469
5( 0, 5)- 4( 3, 2)	5.5- 4.5	6.5- 5.5	-5220.395
5( 2, 3)- 4( 3, 2)	4.5- 3.5	3.5- 2.5	-1179.879
5( 2, 3)- 4( 3, 2)	4.5- 3.5	4.5- 3.5	-1148.215
5( 2, 3)- 4( 3, 2)	4.5- 3.5	5.5- 4.5	-1157.465

5( 2, 3)- 4( 3, 2)	5.5- 4.5	4.5- 3.5	-1772.533
5( 2, 3)- 4( 3, 2)	5.5- 4.5	5.5- 4.5	-1775.929
5( 2, 3)- 4( 3, 2)	5.5- 4.5	6.5- 5.5	-1789.166
5( 4, 1)- 4( 3, 2)	4.5- 3.5	3.5- 2.5	1784.000
5( 4, 1)- 4( 3, 2)	4.5- 3.5	4.5- 3.5	1794.664
5( 4, 1)- 4( 3, 2)	4.5- 3.5	5.5- 4.5	1788.965
5( 4, 1)- 4( 3, 2)	5.5- 4.5	4.5- 3.5	1001.587
5( 4, 1)- 4( 3, 2)	5.5- 4.5	5.5- 4.5	996.589
5( 4, 1)- 4( 3, 2)	5.5- 4.5	6.5- 5.5	1012.550
5( 1, 4)- 4( 4, 1)	4.5- 3.5	3.5- 2.5	-3833.220
5( 1, 4)- 4( 4, 1)	4.5- 3.5	4.5- 3.5	-3729.156
5( 1, 4)- 4( 4, 1)	4.5- 3.5	5.5- 4.5	-3744.881
5( 1, 4)- 4( 4, 1)	5.5- 4.5	4.5- 3.5	-5053.770
5( 1, 4)- 4( 4, 1)	5.5- 4.5	5.5- 4.5	-5039.066
5( 1, 4)- 4( 4, 1)	5.5- 4.5	6.5- 5.5	-5089.809
5( 3, 2)- 4( 4, 1)	4.5- 3.5	3.5- 2.5	-1585.848
5( 3, 2)- 4( 4, 1)	4.5- 3.5	4.5- 3.5	-1490.941
5( 3, 2)- 4( 4, 1)	4.5- 3.5	5.5- 4.5	-1496.559
5( 3, 2)- 4( 4, 1)	5.5- 4.5	4.5- 3.5	-1827.248
5( 3, 2)- 4( 4, 1)	5.5- 4.5	5.5- 4.5	-1813.246
5( 3, 2)- 4( 4, 1)	5.5- 4.5	6.5- 5.5	-1817.500
5( 5, 0)- 4( 4, 1)	4.5- 3.5	3.5- 2.5	1796.953
5( 5, 0)- 4( 4, 1)	4.5- 3.5	4.5- 3.5	1807.883
5( 5, 0)- 4( 4, 1)	4.5- 3.5	5.5- 4.5	1803.328
5( 5, 0)- 4( 4, 1)	5.5- 4.5	4.5- 3.5	294.731
5( 5, 0)- 4( 4, 1)	5.5- 4.5	5.5- 4.5	287.097
5( 5, 0)- 4( 4, 1)	5.5- 4.5	6.5- 5.5	288.184
6( 1, 6)- 5( 0, 5)	5.5- 4.5	4.5- 3.5	152.447
6( 1, 6)- 5( 0, 5)	5.5- 4.5	5.5- 4.5	137.018
6( 1, 6)- 5( 0, 5)	5.5- 4.5	6.5- 5.5	133.612
6( 1, 6)- 5( 0, 5)	6.5- 5.5	5.5- 4.5	-1790.934
6( 1, 6)- 5( 0, 5)	6.5- 5.5	6.5- 5.5	-1784.043
6( 1, 6)- 5( 0, 5)	6.5- 5.5	7.5- 6.5	-1806.242
6( 3, 4)- 5( 0, 5)	5.5- 4.5	4.5- 3.5	5209.465
6( 3, 4)- 5( 0, 5)	5.5- 4.5	5.5- 4.5	5194.266
6( 3, 4)- 5( 0, 5)	5.5- 4.5	6.5- 5.5	5206.531
6( 3, 4)- 5( 0, 5)	6.5- 5.5	5.5- 4.5	1582.684
6( 3, 4)- 5( 0, 5)	6.5- 5.5	6.5- 5.5	1580.055
6( 3, 4)- 5( 0, 5)	6.5- 5.5	7.5- 6.5	1635.547
6( 2, 5)- 5( 1, 4)	5.5- 4.5	4.5- 3.5	839.435
6( 2, 5)- 5( 1, 4)	5.5- 4.5	5.5- 4.5	830.340
6( 2, 5)- 5( 1, 4)	5.5- 4.5	6.5- 5.5	833.264
6( 2, 5)- 5( 1, 4)	6.5- 5.5	5.5- 4.5	-1796.098
6( 2, 5)- 5( 1, 4)	6.5- 5.5	6.5- 5.5	-1779.340
6( 2, 5)- 5( 1, 4)	6.5- 5.5	7.5- 6.5	-1797.504
6( 4, 3)- 5( 1, 4)	5.5- 4.5	4.5- 3.5	4001.657
6( 4, 3)- 5( 1, 4)	5.5- 4.5	5.5- 4.5	3989.531
6( 4, 3)- 5( 1, 4)	5.5- 4.5	6.5- 5.5	3998.549
6( 4, 3)- 5( 1, 4)	6.5- 5.5	5.5- 4.5	1509.578
6( 4, 3)- 5( 1, 4)	6.5- 5.5	6.5- 5.5	1504.141
6( 4, 3)- 5( 1, 4)	6.5- 5.5	7.5- 6.5	1552.719
6( 1, 6)- 5( 2, 3)	5.5- 4.5	4.5- 3.5	-3547.490
6( 1, 6)- 5( 2, 3)	5.5- 4.5	5.5- 4.5	-3561.539
6( 1, 6)- 5( 2, 3)	5.5- 4.5	6.5- 5.5	-3574.205
6( 1, 6)- 5( 2, 3)	6.5- 5.5	5.5- 4.5	-5150.094
6( 1, 6)- 5( 2, 3)	6.5- 5.5	6.5- 5.5	-5130.586

6( 1, 6)- 5( 2, 3)	6.5- 5.5	7.5- 6.5	-5237.473
6( 3, 4)- 5( 2, 3)	5.5- 4.5	4.5- 3.5	1509.531
6( 3, 4)- 5( 2, 3)	5.5- 4.5	5.5- 4.5	1495.711
6( 3, 4)- 5( 2, 3)	5.5- 4.5	6.5- 5.5	1498.715
6( 3, 4)- 5( 2, 3)	6.5- 5.5	5.5- 4.5	-1776.477
6( 3, 4)- 5( 2, 3)	6.5- 5.5	6.5- 5.5	-1766.488
6( 3, 4)- 5( 2, 3)	6.5- 5.5	7.5- 6.5	-1795.684
6( 5, 2)- 5( 2, 3)	5.5- 4.5	4.5- 3.5	4754.516
6( 5, 2)- 5( 2, 3)	5.5- 4.5	5.5- 4.5	4729.598
6( 5, 2)- 5( 2, 3)	5.5- 4.5	6.5- 5.5	4731.793
6( 5, 2)- 5( 2, 3)	6.5- 5.5	5.5- 4.5	1394.688
6( 5, 2)- 5( 2, 3)	6.5- 5.5	6.5- 5.5	1395.967
6( 5, 2)- 5( 2, 3)	6.5- 5.5	7.5- 6.5	1428.125
6( 2, 5)- 5( 3, 2)	5.5- 4.5	4.5- 3.5	-1407.937
6( 2, 5)- 5( 3, 2)	5.5- 4.5	5.5- 4.5	-1407.875
6( 2, 5)- 5( 3, 2)	5.5- 4.5	6.5- 5.5	-1415.059
6( 2, 5)- 5( 3, 2)	6.5- 5.5	5.5- 4.5	-5022.621
6( 2, 5)- 5( 3, 2)	6.5- 5.5	6.5- 5.5	-5005.160
6( 2, 5)- 5( 3, 2)	6.5- 5.5	7.5- 6.5	-5069.812
6( 4, 3)- 5( 3, 2)	5.5- 4.5	4.5- 3.5	1754.285
6( 4, 3)- 5( 3, 2)	5.5- 4.5	5.5- 4.5	1751.316
6( 4, 3)- 5( 3, 2)	5.5- 4.5	6.5- 5.5	1750.227
6( 4, 3)- 5( 3, 2)	6.5- 5.5	5.5- 4.5	-1716.947
6( 4, 3)- 5( 3, 2)	6.5- 5.5	6.5- 5.5	-1721.683
6( 4, 3)- 5( 3, 2)	6.5- 5.5	7.5- 6.5	-1719.590
6( 6, 1)- 5( 3, 2)	5.5- 4.5	4.5- 3.5	5180.539
6( 6, 1)- 5( 3, 2)	5.5- 4.5	5.5- 4.5	5094.375
6( 6, 1)- 5( 3, 2)	5.5- 4.5	6.5- 5.5	5089.488
6( 6, 1)- 5( 3, 2)	6.5- 5.5	5.5- 4.5	1409.052
6( 6, 1)- 5( 3, 2)	6.5- 5.5	6.5- 5.5	1407.727
6( 6, 1)- 5( 3, 2)	6.5- 5.5	7.5- 6.5	1408.595
6( 3, 4)- 5( 4, 1)	5.5- 4.5	4.5- 3.5	-1454.348
6( 3, 4)- 5( 4, 1)	5.5- 4.5	5.5- 4.5	-1447.168
6( 3, 4)- 5( 4, 1)	5.5- 4.5	6.5- 5.5	-1447.715
6( 3, 4)- 5( 4, 1)	6.5- 5.5	5.5- 4.5	-4550.594
6( 3, 4)- 5( 4, 1)	6.5- 5.5	6.5- 5.5	-4539.004
6( 3, 4)- 5( 4, 1)	6.5- 5.5	7.5- 6.5	-4597.398
6( 5, 2)- 5( 4, 1)	5.5- 4.5	4.5- 3.5	1790.637
6( 5, 2)- 5( 4, 1)	5.5- 4.5	5.5- 4.5	1786.719
6( 5, 2)- 5( 4, 1)	5.5- 4.5	6.5- 5.5	1785.363
6( 5, 2)- 5( 4, 1)	6.5- 5.5	5.5- 4.5	-1379.432
6( 5, 2)- 5( 4, 1)	6.5- 5.5	6.5- 5.5	-1376.551
6( 5, 2)- 5( 4, 1)	6.5- 5.5	7.5- 6.5	-1373.591
6( 4, 3)- 5( 5, 0)	5.5- 4.5	4.5- 3.5	-1628.516
6( 4, 3)- 5( 5, 0)	5.5- 4.5	5.5- 4.5	-1547.508
6( 4, 3)- 5( 5, 0)	5.5- 4.5	6.5- 5.5	-1547.660
6( 4, 3)- 5( 5, 0)	6.5- 5.5	5.5- 4.5	-3840.925
6( 4, 3)- 5( 5, 0)	6.5- 5.5	6.5- 5.5	-3822.026
6( 4, 3)- 5( 5, 0)	6.5- 5.5	7.5- 6.5	-3825.274
6( 6, 1)- 5( 5, 0)	5.5- 4.5	4.5- 3.5	1797.738
6( 6, 1)- 5( 5, 0)	5.5- 4.5	5.5- 4.5	1795.551
6( 6, 1)- 5( 5, 0)	5.5- 4.5	6.5- 5.5	1791.602
6( 6, 1)- 5( 5, 0)	6.5- 5.5	5.5- 4.5	-714.927
6( 6, 1)- 5( 5, 0)	6.5- 5.5	6.5- 5.5	-692.616
6( 6, 1)- 5( 5, 0)	6.5- 5.5	7.5- 6.5	-697.089
7( 0, 7)- 6( 1, 6)	6.5- 5.5	5.5- 4.5	-116.780

7( 0, 7)- 6( 1, 6)	6.5- 5.5	6.5- 5.5	-97.101
7( 0, 7)- 6( 1, 6)	6.5- 5.5	7.5- 6.5	-104.181
7( 0, 7)- 6( 1, 6)	7.5- 6.5	6.5- 5.5	-1801.074
7( 0, 7)- 6( 1, 6)	7.5- 6.5	7.5- 6.5	-1808.266
7( 0, 7)- 6( 1, 6)	7.5- 6.5	8.5- 7.5	-1804.832
7( 2, 5)- 6( 1, 6)	6.5- 5.5	5.5- 4.5	4285.680
7( 2, 5)- 6( 1, 6)	6.5- 5.5	6.5- 5.5	4280.363
7( 2, 5)- 6( 1, 6)	6.5- 5.5	7.5- 6.5	4290.184
7( 2, 5)- 6( 1, 6)	7.5- 6.5	6.5- 5.5	1582.855
7( 2, 5)- 6( 1, 6)	7.5- 6.5	7.5- 6.5	1571.449
7( 2, 5)- 6( 1, 6)	7.5- 6.5	8.5- 7.5	1643.797
7( 4, 3)- 6( 1, 6)	6.5- 5.5	5.5- 4.5	6819.332
7( 4, 3)- 6( 1, 6)	6.5- 5.5	6.5- 5.5	6809.000
7( 4, 3)- 6( 1, 6)	6.5- 5.5	7.5- 6.5	6824.887
7( 4, 3)- 6( 1, 6)	7.5- 6.5	6.5- 5.5	4818.633
7( 4, 3)- 6( 1, 6)	7.5- 6.5	7.5- 6.5	4798.910
7( 4, 3)- 6( 1, 6)	7.5- 6.5	8.5- 7.5	4922.293
7( 1, 6)- 6( 2, 5)	6.5- 5.5	5.5- 4.5	-137.957
7( 1, 6)- 6( 2, 5)	6.5- 5.5	6.5- 5.5	-122.359
7( 1, 6)- 6( 2, 5)	6.5- 5.5	7.5- 6.5	-122.773
7( 1, 6)- 6( 2, 5)	7.5- 6.5	6.5- 5.5	-1796.055
7( 1, 6)- 6( 2, 5)	7.5- 6.5	7.5- 6.5	-1809.082
7( 1, 6)- 6( 2, 5)	7.5- 6.5	8.5- 7.5	-1800.730
7( 3, 4)- 6( 2, 5)	6.5- 5.5	5.5- 4.5	1861.359
7( 3, 4)- 6( 2, 5)	6.5- 5.5	6.5- 5.5	1857.781
7( 3, 4)- 6( 2, 5)	6.5- 5.5	7.5- 6.5	1861.039
7( 3, 4)- 6( 2, 5)	7.5- 6.5	6.5- 5.5	1540.633
7( 3, 4)- 6( 2, 5)	7.5- 6.5	7.5- 6.5	1517.125
7( 3, 4)- 6( 2, 5)	7.5- 6.5	8.5- 7.5	1575.941
7( 5, 2)- 6( 2, 5)	6.5- 5.5	5.5- 4.5	4950.320
7( 5, 2)- 6( 2, 5)	6.5- 5.5	6.5- 5.5	4942.578
7( 5, 2)- 6( 2, 5)	6.5- 5.5	7.5- 6.5	4954.883
7( 5, 2)- 6( 2, 5)	7.5- 6.5	6.5- 5.5	4513.320
7( 5, 2)- 6( 2, 5)	7.5- 6.5	7.5- 6.5	4488.836
7( 5, 2)- 6( 2, 5)	7.5- 6.5	8.5- 7.5	4553.855
7( 0, 7)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	-5173.801
7( 0, 7)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	-5154.348
7( 0, 7)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	-5177.098
7( 0, 7)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	-5174.691
7( 0, 7)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	-5172.363
7( 0, 7)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	-5246.621
7( 2, 5)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	-771.340
7( 2, 5)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	-776.883
7( 2, 5)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	-782.734
7( 2, 5)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	-1790.762
7( 2, 5)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	-1792.648
7( 2, 5)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	-1797.992
7( 4, 3)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	1762.312
7( 4, 3)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	1751.754
7( 4, 3)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	1751.969
7( 4, 3)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	1445.016
7( 4, 3)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	1434.812
7( 4, 3)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	1480.504
7( 6, 1)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	5042.832
7( 6, 1)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	5030.309
7( 6, 1)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	5035.148

7( 6, 1)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	3804.296
7( 6, 1)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	3785.359
7( 6, 1)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	3842.804
7( 1, 6)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	-3300.180
7( 1, 6)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	-3281.551
7( 1, 6)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	-3288.059
7( 1, 6)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	-5101.730
7( 1, 6)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	-5092.562
7( 1, 6)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	-5150.953
7( 3, 4)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	-1300.863
7( 3, 4)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	-1301.410
7( 3, 4)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	-1304.246
7( 3, 4)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	-1765.043
7( 3, 4)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	-1766.355
7( 3, 4)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	-1774.281
7( 5, 2)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	1788.098
7( 5, 2)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	1783.387
7( 5, 2)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	1789.598
7( 5, 2)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	1207.645
7( 5, 2)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	1205.355
7( 5, 2)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	1203.633
7( 7, 0)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	5224.375
7( 7, 0)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	5141.352
7( 7, 0)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	5147.750
7( 7, 0)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	3163.915
7( 7, 0)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	3159.495
7( 7, 0)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	3164.219
7( 2, 5)- 6( 5, 2)	6.5- 5.5	5.5- 4.5	-4016.324
7( 2, 5)- 6( 5, 2)	6.5- 5.5	6.5- 5.5	-4010.770
7( 2, 5)- 6( 5, 2)	6.5- 5.5	7.5- 6.5	-4015.812
7( 2, 5)- 6( 5, 2)	7.5- 6.5	6.5- 5.5	-4961.926
7( 2, 5)- 6( 5, 2)	7.5- 6.5	7.5- 6.5	-4955.102
7( 2, 5)- 6( 5, 2)	7.5- 6.5	8.5- 7.5	-5021.801
7( 4, 3)- 6( 5, 2)	6.5- 5.5	5.5- 4.5	-1482.672
7( 4, 3)- 6( 5, 2)	6.5- 5.5	6.5- 5.5	-1482.133
7( 4, 3)- 6( 5, 2)	6.5- 5.5	7.5- 6.5	-1481.109
7( 4, 3)- 6( 5, 2)	7.5- 6.5	6.5- 5.5	-1726.149
7( 4, 3)- 6( 5, 2)	7.5- 6.5	7.5- 6.5	-1727.642
7( 4, 3)- 6( 5, 2)	7.5- 6.5	8.5- 7.5	-1743.305
7( 6, 1)- 6( 5, 2)	6.5- 5.5	5.5- 4.5	1797.848
7( 6, 1)- 6( 5, 2)	6.5- 5.5	6.5- 5.5	1796.422
7( 6, 1)- 6( 5, 2)	6.5- 5.5	7.5- 6.5	1802.070
7( 6, 1)- 6( 5, 2)	7.5- 6.5	6.5- 5.5	633.132
7( 6, 1)- 6( 5, 2)	7.5- 6.5	7.5- 6.5	622.905
7( 6, 1)- 6( 5, 2)	7.5- 6.5	8.5- 7.5	618.996
7( 3, 4)- 6( 6, 1)	6.5- 5.5	5.5- 4.5	-4727.117
7( 3, 4)- 6( 6, 1)	6.5- 5.5	6.5- 5.5	-4644.469
7( 3, 4)- 6( 6, 1)	6.5- 5.5	7.5- 6.5	-4643.508
7( 3, 4)- 6( 6, 1)	7.5- 6.5	6.5- 5.5	-4891.039
7( 3, 4)- 6( 6, 1)	7.5- 6.5	7.5- 6.5	-4895.762
7( 3, 4)- 6( 6, 1)	7.5- 6.5	8.5- 7.5	-4902.465
7( 5, 2)- 6( 6, 1)	6.5- 5.5	5.5- 4.5	-1638.156
7( 5, 2)- 6( 6, 1)	6.5- 5.5	6.5- 5.5	-1559.672
7( 5, 2)- 6( 6, 1)	6.5- 5.5	7.5- 6.5	-1549.664
7( 5, 2)- 6( 6, 1)	7.5- 6.5	6.5- 5.5	-1918.354
7( 5, 2)- 6( 6, 1)	7.5- 6.5	7.5- 6.5	-1924.054

7( 5, 2)- 6( 6, 1)	7.5- 6.5	8.5- 7.5	-1924.552
7( 7, 0)- 6( 6, 1)	6.5- 5.5	5.5- 4.5	1798.121
7( 7, 0)- 6( 6, 1)	6.5- 5.5	6.5- 5.5	1798.293
7( 7, 0)- 6( 6, 1)	6.5- 5.5	7.5- 6.5	1808.488
7( 7, 0)- 6( 6, 1)	7.5- 6.5	6.5- 5.5	37.917
7( 7, 0)- 6( 6, 1)	7.5- 6.5	7.5- 6.5	30.085
7( 7, 0)- 6( 6, 1)	7.5- 6.5	8.5- 7.5	36.034

THESE ARE THE B-TYPE TRANSITIONS FROM NMIN= 4 TO NMAX= 7 FOR I=2

THE ORDER OF THE QUANTUM NUMBERS ARE FROM LEFT TO RIGHT, N',KP',KO'-N

5( 1, 5)- 4( 0, 4)	4.5- 3.5	2.5- 1.5	242.763
5( 1, 5)- 4( 0, 4)	4.5- 3.5	3.5- 2.5	271.201
5( 1, 5)- 4( 0, 4)	4.5- 3.5	4.5- 3.5	269.365
5( 1, 5)- 4( 0, 4)	4.5- 3.5	5.5- 4.5	276.204
5( 1, 5)- 4( 0, 4)	4.5- 3.5	6.5- 5.5	323.979
5( 1, 5)- 4( 0, 4)	5.5- 4.5	3.5- 2.5	-1803.746
5( 1, 5)- 4( 0, 4)	5.5- 4.5	4.5- 3.5	-1787.766
5( 1, 5)- 4( 0, 4)	5.5- 4.5	5.5- 4.5	-1787.535
5( 1, 5)- 4( 0, 4)	5.5- 4.5	6.5- 5.5	-1796.297
5( 1, 5)- 4( 0, 4)	5.5- 4.5	7.5- 6.5	-1810.148
5( 3, 3)- 4( 0, 4)	4.5- 3.5	2.5- 1.5	5113.918
5( 3, 3)- 4( 0, 4)	4.5- 3.5	3.5- 2.5	5103.168
5( 3, 3)- 4( 0, 4)	4.5- 3.5	4.5- 3.5	5084.207
5( 3, 3)- 4( 0, 4)	4.5- 3.5	5.5- 4.5	5097.133
5( 3, 3)- 4( 0, 4)	4.5- 3.5	6.5- 5.5	5143.191
5( 3, 3)- 4( 0, 4)	5.5- 4.5	3.5- 2.5	1570.840
5( 3, 3)- 4( 0, 4)	5.5- 4.5	4.5- 3.5	1552.359
5( 3, 3)- 4( 0, 4)	5.5- 4.5	5.5- 4.5	1565.324
5( 3, 3)- 4( 0, 4)	5.5- 4.5	6.5- 5.5	1549.180
5( 3, 3)- 4( 0, 4)	5.5- 4.5	7.5- 6.5	1670.418
5( 2, 4)- 4( 1, 3)	4.5- 3.5	2.5- 1.5	968.917
5( 2, 4)- 4( 1, 3)	4.5- 3.5	3.5- 2.5	1006.435
5( 2, 4)- 4( 1, 3)	4.5- 3.5	4.5- 3.5	1011.611
5( 2, 4)- 4( 1, 3)	4.5- 3.5	5.5- 4.5	1023.031
5( 2, 4)- 4( 1, 3)	4.5- 3.5	6.5- 5.5	1005.398
5( 2, 4)- 4( 1, 3)	5.5- 4.5	3.5- 2.5	-1772.273
5( 2, 4)- 4( 1, 3)	5.5- 4.5	4.5- 3.5	-1786.340
5( 2, 4)- 4( 1, 3)	5.5- 4.5	5.5- 4.5	-1797.531
5( 2, 4)- 4( 1, 3)	5.5- 4.5	6.5- 5.5	-1792.273
5( 2, 4)- 4( 1, 3)	5.5- 4.5	7.5- 6.5	-1805.613
5( 4, 2)- 4( 1, 3)	4.5- 3.5	2.5- 1.5	4382.715
5( 4, 2)- 4( 1, 3)	4.5- 3.5	3.5- 2.5	4245.133
5( 4, 2)- 4( 1, 3)	4.5- 3.5	4.5- 3.5	4235.590
5( 4, 2)- 4( 1, 3)	4.5- 3.5	5.5- 4.5	4248.090
5( 4, 2)- 4( 1, 3)	4.5- 3.5	6.5- 5.5	4236.613
5( 4, 2)- 4( 1, 3)	5.5- 4.5	3.5- 2.5	1473.811
5( 4, 2)- 4( 1, 3)	5.5- 4.5	4.5- 3.5	1449.316
5( 4, 2)- 4( 1, 3)	5.5- 4.5	5.5- 4.5	1450.396
5( 4, 2)- 4( 1, 3)	5.5- 4.5	6.5- 5.5	1459.839
5( 4, 2)- 4( 1, 3)	5.5- 4.5	7.5- 6.5	1485.855
5( 1, 5)- 4( 2, 2)	4.5- 3.5	2.5- 1.5	-3295.384
5( 1, 5)- 4( 2, 2)	4.5- 3.5	3.5- 2.5	-3181.664
5( 1, 5)- 4( 2, 2)	4.5- 3.5	4.5- 3.5	-3191.639
5( 1, 5)- 4( 2, 2)	4.5- 3.5	5.5- 4.5	-3191.210
5( 1, 5)- 4( 2, 2)	4.5- 3.5	6.5- 5.5	-3183.612
5( 1, 5)- 4( 2, 2)	5.5- 4.5	3.5- 2.5	-5116.848
5( 1, 5)- 4( 2, 2)	5.5- 4.5	4.5- 3.5	-5098.824

5( 1, 5)- 4( 2, 2)	5.5- 4.5	5.5- 4.5	-5106.477
5( 1, 5)- 4( 2, 2)	5.5- 4.5	6.5- 5.5	-5104.602
5( 1, 5)- 4( 2, 2)	5.5- 4.5	7.5- 6.5	-5261.711
5( 3, 3)- 4( 2, 2)	4.5- 3.5	2.5- 1.5	1575.773
5( 3, 3)- 4( 2, 2)	4.5- 3.5	3.5- 2.5	1650.305
5( 3, 3)- 4( 2, 2)	4.5- 3.5	4.5- 3.5	1623.203
5( 3, 3)- 4( 2, 2)	4.5- 3.5	5.5- 4.5	1629.723
5( 3, 3)- 4( 2, 2)	4.5- 3.5	6.5- 5.5	1635.602
5( 3, 3)- 4( 2, 2)	5.5- 4.5	3.5- 2.5	-1742.265
5( 3, 3)- 4( 2, 2)	5.5- 4.5	4.5- 3.5	-1758.702
5( 3, 3)- 4( 2, 2)	5.5- 4.5	5.5- 4.5	-1753.617
5( 3, 3)- 4( 2, 2)	5.5- 4.5	6.5- 5.5	-1759.127
5( 3, 3)- 4( 2, 2)	5.5- 4.5	7.5- 6.5	-1781.146
5( 5, 1)- 4( 2, 2)	4.5- 3.5	2.5- 1.5	5033.660
5( 5, 1)- 4( 2, 2)	4.5- 3.5	3.5- 2.5	4962.020
5( 5, 1)- 4( 2, 2)	4.5- 3.5	4.5- 3.5	4934.508
5( 5, 1)- 4( 2, 2)	4.5- 3.5	5.5- 4.5	4951.031
5( 5, 1)- 4( 2, 2)	4.5- 3.5	6.5- 5.5	4950.270
5( 5, 1)- 4( 2, 2)	5.5- 4.5	3.5- 2.5	1452.373
5( 5, 1)- 4( 2, 2)	5.5- 4.5	4.5- 3.5	1407.638
5( 5, 1)- 4( 2, 2)	5.5- 4.5	5.5- 4.5	1432.278
5( 5, 1)- 4( 2, 2)	5.5- 4.5	6.5- 5.5	1443.158
5( 5, 1)- 4( 2, 2)	5.5- 4.5	7.5- 6.5	1507.773
5( 2, 4)- 4( 3, 1)	4.5- 3.5	2.5- 1.5	-1638.344
5( 2, 4)- 4( 3, 1)	4.5- 3.5	3.5- 2.5	-1427.203
5( 2, 4)- 4( 3, 1)	4.5- 3.5	4.5- 3.5	-1438.320
5( 2, 4)- 4( 3, 1)	4.5- 3.5	5.5- 4.5	-1438.645
5( 2, 4)- 4( 3, 1)	4.5- 3.5	6.5- 5.5	-1435.520
5( 2, 4)- 4( 3, 1)	5.5- 4.5	3.5- 2.5	-4767.082
5( 2, 4)- 4( 3, 1)	5.5- 4.5	4.5- 3.5	-4749.199
5( 2, 4)- 4( 3, 1)	5.5- 4.5	5.5- 4.5	-4762.434
5( 2, 4)- 4( 3, 1)	5.5- 4.5	6.5- 5.5	-4767.551
5( 2, 4)- 4( 3, 1)	5.5- 4.5	7.5- 6.5	-4806.395
5( 4, 2)- 4( 3, 1)	4.5- 3.5	2.5- 1.5	1775.457
5( 4, 2)- 4( 3, 1)	4.5- 3.5	3.5- 2.5	1809.496
5( 4, 2)- 4( 3, 1)	4.5- 3.5	4.5- 3.5	1785.660
5( 4, 2)- 4( 3, 1)	4.5- 3.5	5.5- 4.5	1786.418
5( 4, 2)- 4( 3, 1)	4.5- 3.5	6.5- 5.5	1795.695
5( 4, 2)- 4( 3, 1)	5.5- 4.5	3.5- 2.5	-1520.998
5( 4, 2)- 4( 3, 1)	5.5- 4.5	4.5- 3.5	-1513.544
5( 4, 2)- 4( 3, 1)	5.5- 4.5	5.5- 4.5	-1514.508
5( 4, 2)- 4( 3, 1)	5.5- 4.5	6.5- 5.5	-1515.441
5( 4, 2)- 4( 3, 1)	5.5- 4.5	7.5- 6.5	-1514.929
5( 3, 3)- 4( 4, 0)	4.5- 3.5	2.5- 1.5	-1660.953
5( 3, 3)- 4( 4, 0)	4.5- 3.5	3.5- 2.5	-1504.984
5( 3, 3)- 4( 4, 0)	4.5- 3.5	4.5- 3.5	-1514.832
5( 3, 3)- 4( 4, 0)	4.5- 3.5	5.5- 4.5	-1511.488
5( 3, 3)- 4( 4, 0)	4.5- 3.5	6.5- 5.5	-1520.801
5( 3, 3)- 4( 4, 0)	5.5- 4.5	3.5- 2.5	-4057.948
5( 3, 3)- 4( 4, 0)	5.5- 4.5	4.5- 3.5	-4019.570
5( 3, 3)- 4( 4, 0)	5.5- 4.5	5.5- 4.5	-4029.033
5( 3, 3)- 4( 4, 0)	5.5- 4.5	6.5- 5.5	-4038.328
5( 3, 3)- 4( 4, 0)	5.5- 4.5	7.5- 6.5	-4138.176
5( 5, 1)- 4( 4, 0)	4.5- 3.5	2.5- 1.5	1796.934
5( 5, 1)- 4( 4, 0)	4.5- 3.5	3.5- 2.5	1806.730
5( 5, 1)- 4( 4, 0)	4.5- 3.5	4.5- 3.5	1796.473



5( 5, 1)- 4( 4, 0)	4.5- 3.5	5.5- 4.5	1809.820
5( 5, 1)- 4( 4, 0)	4.5- 3.5	6.5- 5.5	1793.867
5( 5, 1)- 4( 4, 0)	5.5- 4.5	3.5- 2.5	-865.310
5( 5, 1)- 4( 4, 0)	5.5- 4.5	4.5- 3.5	-853.230
5( 5, 1)- 4( 4, 0)	5.5- 4.5	5.5- 4.5	-843.137
5( 5, 1)- 4( 4, 0)	5.5- 4.5	6.5- 5.5	-838.043
5( 5, 1)- 4( 4, 0)	5.5- 4.5	7.5- 6.5	-847.260
6( 0, 6)- 5( 1, 5)	5.5- 4.5	3.5- 2.5	-166.099
6( 0, 6)- 5( 1, 5)	5.5- 4.5	4.5- 3.5	-187.637
6( 0, 6)- 5( 1, 5)	5.5- 4.5	5.5- 4.5	-167.194
6( 0, 6)- 5( 1, 5)	5.5- 4.5	6.5- 5.5	-157.797
6( 0, 6)- 5( 1, 5)	5.5- 4.5	7.5- 6.5	-171.461
6( 0, 6)- 5( 1, 5)	6.5- 5.5	4.5- 3.5	-1788.887
6( 0, 6)- 5( 1, 5)	6.5- 5.5	5.5- 4.5	-1800.805
6( 0, 6)- 5( 1, 5)	6.5- 5.5	6.5- 5.5	-1783.559
6( 0, 6)- 5( 1, 5)	6.5- 5.5	7.5- 6.5	-1795.137
6( 0, 6)- 5( 1, 5)	6.5- 5.5	8.5- 7.5	-1808.375
6( 2, 4)- 5( 1, 5)	5.5- 4.5	3.5- 2.5	3879.322
6( 2, 4)- 5( 1, 5)	5.5- 4.5	4.5- 3.5	3857.679
6( 2, 4)- 5( 1, 5)	5.5- 4.5	5.5- 4.5	3856.959
6( 2, 4)- 5( 1, 5)	5.5- 4.5	6.5- 5.5	3861.249
6( 2, 4)- 5( 1, 5)	5.5- 4.5	7.5- 6.5	3845.171
6( 2, 4)- 5( 1, 5)	6.5- 5.5	4.5- 3.5	1593.254
6( 2, 4)- 5( 1, 5)	6.5- 5.5	5.5- 4.5	1562.777
6( 2, 4)- 5( 1, 5)	6.5- 5.5	6.5- 5.5	1579.324
6( 2, 4)- 5( 1, 5)	6.5- 5.5	7.5- 6.5	1589.891
6( 2, 4)- 5( 1, 5)	6.5- 5.5	8.5- 7.5	1679.547
6( 4, 2)- 5( 1, 5)	5.5- 4.5	3.5- 2.5	6613.793
6( 4, 2)- 5( 1, 5)	5.5- 4.5	4.5- 3.5	6606.988
6( 4, 2)- 5( 1, 5)	5.5- 4.5	5.5- 4.5	6593.484
6( 4, 2)- 5( 1, 5)	5.5- 4.5	6.5- 5.5	6595.668
6( 4, 2)- 5( 1, 5)	5.5- 4.5	7.5- 6.5	6584.051
6( 4, 2)- 5( 1, 5)	6.5- 5.5	4.5- 3.5	4712.875
6( 4, 2)- 5( 1, 5)	6.5- 5.5	5.5- 4.5	4672.352
6( 4, 2)- 5( 1, 5)	6.5- 5.5	6.5- 5.5	4676.715
6( 4, 2)- 5( 1, 5)	6.5- 5.5	7.5- 6.5	4697.547
6( 4, 2)- 5( 1, 5)	6.5- 5.5	8.5- 7.5	4887.754
6( 1, 5)- 5( 2, 4)	5.5- 4.5	3.5- 2.5	-276.582
6( 1, 5)- 5( 2, 4)	5.5- 4.5	4.5- 3.5	-276.277
6( 1, 5)- 5( 2, 4)	5.5- 4.5	5.5- 4.5	-256.828
6( 1, 5)- 5( 2, 4)	5.5- 4.5	6.5- 5.5	-256.786
6( 1, 5)- 5( 2, 4)	5.5- 4.5	7.5- 6.5	-270.316
6( 1, 5)- 5( 2, 4)	6.5- 5.5	4.5- 3.5	-1803.027
6( 1, 5)- 5( 2, 4)	6.5- 5.5	5.5- 4.5	-1793.922
6( 1, 5)- 5( 2, 4)	6.5- 5.5	6.5- 5.5	-1776.219
6( 1, 5)- 5( 2, 4)	6.5- 5.5	7.5- 6.5	-1785.758
6( 1, 5)- 5( 2, 4)	6.5- 5.5	8.5- 7.5	-1805.363
6( 3, 3)- 5( 2, 4)	5.5- 4.5	3.5- 2.5	1832.965
6( 3, 3)- 5( 2, 4)	5.5- 4.5	4.5- 3.5	1823.687
6( 3, 3)- 5( 2, 4)	5.5- 4.5	5.5- 4.5	1823.215
6( 3, 3)- 5( 2, 4)	5.5- 4.5	6.5- 5.5	1825.320
6( 3, 3)- 5( 2, 4)	5.5- 4.5	7.5- 6.5	1806.801
6( 3, 3)- 5( 2, 4)	6.5- 5.5	4.5- 3.5	1507.480
6( 3, 3)- 5( 2, 4)	6.5- 5.5	5.5- 4.5	1491.523
6( 3, 3)- 5( 2, 4)	6.5- 5.5	6.5- 5.5	1509.648
6( 3, 3)- 5( 2, 4)	6.5- 5.5	7.5- 6.5	1513.332

6( 3, 3)- 5( 2, 4)	6.5- 5.5	8.5- 7.5	1539.293
6( 5, 1)- 5( 2, 4)	5.5- 4.5	3.5- 2.5	5202.520
6( 5, 1)- 5( 2, 4)	5.5- 4.5	4.5- 3.5	5034.430
6( 5, 1)- 5( 2, 4)	5.5- 4.5	5.5- 4.5	5021.848
6( 5, 1)- 5( 2, 4)	5.5- 4.5	6.5- 5.5	5023.230
6( 5, 1)- 5( 2, 4)	5.5- 4.5	7.5- 6.5	5019.543
6( 5, 1)- 5( 2, 4)	6.5- 5.5	4.5- 3.5	4067.446
6( 5, 1)- 5( 2, 4)	6.5- 5.5	5.5- 4.5	4052.036
6( 5, 1)- 5( 2, 4)	6.5- 5.5	6.5- 5.5	4062.476
6( 5, 1)- 5( 2, 4)	6.5- 5.5	7.5- 6.5	4071.908
6( 5, 1)- 5( 2, 4)	6.5- 5.5	8.5- 7.5	4161.793
6( 0, 6)- 5( 3, 3)	5.5- 4.5	3.5- 2.5	-5037.254
6( 0, 6)- 5( 3, 3)	5.5- 4.5	4.5- 3.5	-5019.605
6( 0, 6)- 5( 3, 3)	5.5- 4.5	5.5- 4.5	-4982.035
6( 0, 6)- 5( 3, 3)	5.5- 4.5	6.5- 5.5	-4978.727
6( 0, 6)- 5( 3, 3)	5.5- 4.5	7.5- 6.5	-4990.672
6( 0, 6)- 5( 3, 3)	6.5- 5.5	4.5- 3.5	-5163.473
6( 0, 6)- 5( 3, 3)	6.5- 5.5	5.5- 4.5	-5140.930
6( 0, 6)- 5( 3, 3)	6.5- 5.5	6.5- 5.5	-5136.418
6( 0, 6)- 5( 3, 3)	6.5- 5.5	7.5- 6.5	-5140.613
6( 0, 6)- 5( 3, 3)	6.5- 5.5	8.5- 7.5	-5288.941
6( 2, 4)- 5( 3, 3)	5.5- 4.5	3.5- 2.5	-991.836
6( 2, 4)- 5( 3, 3)	5.5- 4.5	4.5- 3.5	-974.289
6( 2, 4)- 5( 3, 3)	5.5- 4.5	5.5- 4.5	-957.883
6( 2, 4)- 5( 3, 3)	5.5- 4.5	6.5- 5.5	-959.684
6( 2, 4)- 5( 3, 3)	5.5- 4.5	7.5- 6.5	-974.043
6( 2, 4)- 5( 3, 3)	6.5- 5.5	4.5- 3.5	-1781.332
6( 2, 4)- 5( 3, 3)	6.5- 5.5	5.5- 4.5	-1777.348
6( 2, 4)- 5( 3, 3)	6.5- 5.5	6.5- 5.5	-1773.535
6( 2, 4)- 5( 3, 3)	6.5- 5.5	7.5- 6.5	-1755.586
6( 2, 4)- 5( 3, 3)	6.5- 5.5	8.5- 7.5	-1801.020
6( 4, 2)- 5( 3, 3)	5.5- 4.5	3.5- 2.5	1742.637
6( 4, 2)- 5( 3, 3)	5.5- 4.5	4.5- 3.5	1775.023
6( 4, 2)- 5( 3, 3)	5.5- 4.5	5.5- 4.5	1778.645
6( 4, 2)- 5( 3, 3)	5.5- 4.5	6.5- 5.5	1774.738
6( 4, 2)- 5( 3, 3)	5.5- 4.5	7.5- 6.5	1764.840
6( 4, 2)- 5( 3, 3)	6.5- 5.5	4.5- 3.5	1338.292
6( 4, 2)- 5( 3, 3)	6.5- 5.5	5.5- 4.5	1332.230
6( 4, 2)- 5( 3, 3)	6.5- 5.5	6.5- 5.5	1323.855
6( 4, 2)- 5( 3, 3)	6.5- 5.5	7.5- 6.5	1352.070
6( 4, 2)- 5( 3, 3)	6.5- 5.5	8.5- 7.5	1407.187
6( 6, 0)- 5( 3, 3)	5.5- 4.5	3.5- 2.5	5255.629
6( 6, 0)- 5( 3, 3)	5.5- 4.5	4.5- 3.5	5119.301
6( 6, 0)- 5( 3, 3)	5.5- 4.5	5.5- 4.5	5116.945
6( 6, 0)- 5( 3, 3)	5.5- 4.5	6.5- 5.5	5122.777
6( 6, 0)- 5( 3, 3)	5.5- 4.5	7.5- 6.5	5120.676
6( 6, 0)- 5( 3, 3)	6.5- 5.5	4.5- 3.5	3345.509
6( 6, 0)- 5( 3, 3)	6.5- 5.5	5.5- 4.5	3332.488
6( 6, 0)- 5( 3, 3)	6.5- 5.5	6.5- 5.5	3331.928
6( 6, 0)- 5( 3, 3)	6.5- 5.5	7.5- 6.5	3352.756
6( 6, 0)- 5( 3, 3)	6.5- 5.5	8.5- 7.5	3424.073
6( 1, 5)- 5( 4, 2)	5.5- 4.5	3.5- 2.5	-3690.383
6( 1, 5)- 5( 4, 2)	5.5- 4.5	4.5- 3.5	-3514.977
6( 1, 5)- 5( 4, 2)	5.5- 4.5	5.5- 4.5	-3480.809
6( 1, 5)- 5( 4, 2)	5.5- 4.5	6.5- 5.5	-3481.849
6( 1, 5)- 5( 4, 2)	5.5- 4.5	7.5- 6.5	-3501.531

6( 1, 5)- 5( 4, 2)	6.5- 5.5	4.5- 3.5	-5049.109
6( 1, 5)- 5( 4, 2)	6.5- 5.5	5.5- 4.5	-5029.578
6( 1, 5)- 5( 4, 2)	6.5- 5.5	6.5- 5.5	-5024.145
6( 1, 5)- 5( 4, 2)	6.5- 5.5	7.5- 6.5	-5037.867
6( 1, 5)- 5( 4, 2)	6.5- 5.5	8.5- 7.5	-5096.832
6( 3, 3)- 5( 4, 2)	5.5- 4.5	3.5- 2.5	-1580.836
6( 3, 3)- 5( 4, 2)	5.5- 4.5	4.5- 3.5	-1415.012
6( 3, 3)- 5( 4, 2)	5.5- 4.5	5.5- 4.5	-1400.766
6( 3, 3)- 5( 4, 2)	5.5- 4.5	6.5- 5.5	-1399.742
6( 3, 3)- 5( 4, 2)	5.5- 4.5	7.5- 6.5	-1424.414
6( 3, 3)- 5( 4, 2)	6.5- 5.5	4.5- 3.5	-1738.604
6( 3, 3)- 5( 4, 2)	6.5- 5.5	5.5- 4.5	-1744.133
6( 3, 3)- 5( 4, 2)	6.5- 5.5	6.5- 5.5	-1738.278
6( 3, 3)- 5( 4, 2)	6.5- 5.5	7.5- 6.5	-1738.780
6( 3, 3)- 5( 4, 2)	6.5- 5.5	8.5- 7.5	-1752.176
6( 5, 1)- 5( 4, 2)	5.5- 4.5	3.5- 2.5	1788.719
6( 5, 1)- 5( 4, 2)	5.5- 4.5	4.5- 3.5	1795.730
6( 5, 1)- 5( 4, 2)	5.5- 4.5	5.5- 4.5	1797.867
6( 5, 1)- 5( 4, 2)	5.5- 4.5	6.5- 5.5	1798.168
6( 5, 1)- 5( 4, 2)	5.5- 4.5	7.5- 6.5	1788.328
6( 5, 1)- 5( 4, 2)	6.5- 5.5	4.5- 3.5	821.361
6( 5, 1)- 5( 4, 2)	6.5- 5.5	5.5- 4.5	816.380
6( 5, 1)- 5( 4, 2)	6.5- 5.5	6.5- 5.5	814.550
6( 5, 1)- 5( 4, 2)	6.5- 5.5	7.5- 6.5	819.796
6( 5, 1)- 5( 4, 2)	6.5- 5.5	8.5- 7.5	870.327
6( 2, 4)- 5( 5, 1)	5.5- 4.5	3.5- 2.5	-4449.723
6( 2, 4)- 5( 5, 1)	5.5- 4.5	4.5- 3.5	-4286.004
6( 2, 4)- 5( 5, 1)	5.5- 4.5	5.5- 4.5	-4269.187
6( 2, 4)- 5( 5, 1)	5.5- 4.5	6.5- 5.5	-4280.992
6( 2, 4)- 5( 5, 1)	5.5- 4.5	7.5- 6.5	-4288.711
6( 2, 4)- 5( 5, 1)	6.5- 5.5	4.5- 3.5	-4975.969
6( 2, 4)- 5( 5, 1)	6.5- 5.5	5.5- 4.5	-4943.687
6( 2, 4)- 5( 5, 1)	6.5- 5.5	6.5- 5.5	-4959.430
6( 2, 4)- 5( 5, 1)	6.5- 5.5	7.5- 6.5	-4957.871
6( 2, 4)- 5( 5, 1)	6.5- 5.5	8.5- 7.5	-5089.937
6( 4, 2)- 5( 5, 1)	5.5- 4.5	3.5- 2.5	-1715.250
6( 4, 2)- 5( 5, 1)	5.5- 4.5	4.5- 3.5	-1536.691
6( 4, 2)- 5( 5, 1)	5.5- 4.5	5.5- 4.5	-1532.660
6( 4, 2)- 5( 5, 1)	5.5- 4.5	6.5- 5.5	-1546.570
6( 4, 2)- 5( 5, 1)	5.5- 4.5	7.5- 6.5	-1549.828
6( 4, 2)- 5( 5, 1)	6.5- 5.5	4.5- 3.5	-1856.346
6( 4, 2)- 5( 5, 1)	6.5- 5.5	5.5- 4.5	-1834.110
6( 4, 2)- 5( 5, 1)	6.5- 5.5	6.5- 5.5	-1862.040
6( 4, 2)- 5( 5, 1)	6.5- 5.5	7.5- 6.5	-1850.215
6( 4, 2)- 5( 5, 1)	6.5- 5.5	8.5- 7.5	-1881.731
6( 6, 0)- 5( 5, 1)	5.5- 4.5	3.5- 2.5	1797.742
6( 6, 0)- 5( 5, 1)	5.5- 4.5	4.5- 3.5	1807.586
6( 6, 0)- 5( 5, 1)	5.5- 4.5	5.5- 4.5	1805.641
6( 6, 0)- 5( 5, 1)	5.5- 4.5	6.5- 5.5	1801.469
6( 6, 0)- 5( 5, 1)	5.5- 4.5	7.5- 6.5	1806.008
6( 6, 0)- 5( 5, 1)	6.5- 5.5	4.5- 3.5	150.871
6( 6, 0)- 5( 5, 1)	6.5- 5.5	5.5- 4.5	168.147
6( 6, 0)- 5( 5, 1)	6.5- 5.5	6.5- 5.5	146.033
6( 6, 0)- 5( 5, 1)	6.5- 5.5	7.5- 6.5	150.471
6( 6, 0)- 5( 5, 1)	6.5- 5.5	8.5- 7.5	135.155
7( 1, 7)- 6( 0, 6)	6.5- 5.5	4.5- 3.5	86.978

7( 1, 7)- 6( 0, 6)	6.5- 5.5	5.5- 4.5	97.423
7( 1, 7)- 6( 0, 6)	6.5- 5.5	6.5- 5.5	73.662
7( 1, 7)- 6( 0, 6)	6.5- 5.5	7.5- 6.5	73.765
7( 1, 7)- 6( 0, 6)	6.5- 5.5	8.5- 7.5	76.267
7( 1, 7)- 6( 0, 6)	7.5- 6.5	5.5- 4.5	-1784.727
7( 1, 7)- 6( 0, 6)	7.5- 6.5	6.5- 5.5	-1794.059
7( 1, 7)- 6( 0, 6)	7.5- 6.5	7.5- 6.5	-1795.910
7( 1, 7)- 6( 0, 6)	7.5- 6.5	8.5- 7.5	-1780.527
7( 1, 7)- 6( 0, 6)	7.5- 6.5	9.5- 8.5	-1806.879
7( 3, 5)- 6( 0, 6)	6.5- 5.5	4.5- 3.5	5396.992
7( 3, 5)- 6( 0, 6)	6.5- 5.5	5.5- 4.5	5406.102
7( 3, 5)- 6( 0, 6)	6.5- 5.5	6.5- 5.5	5383.496
7( 3, 5)- 6( 0, 6)	6.5- 5.5	7.5- 6.5	5385.309
7( 3, 5)- 6( 0, 6)	6.5- 5.5	8.5- 7.5	5388.043
7( 3, 5)- 6( 0, 6)	7.5- 6.5	5.5- 4.5	1596.988
7( 3, 5)- 6( 0, 6)	7.5- 6.5	6.5- 5.5	1579.449
7( 3, 5)- 6( 0, 6)	7.5- 6.5	7.5- 6.5	1575.418
7( 3, 5)- 6( 0, 6)	7.5- 6.5	8.5- 7.5	1594.914
7( 3, 5)- 6( 0, 6)	7.5- 6.5	9.5- 8.5	1683.125
7( 2, 6)- 6( 1, 5)	6.5- 5.5	4.5- 3.5	705.477
7( 2, 6)- 6( 1, 5)	6.5- 5.5	5.5- 4.5	693.793
7( 2, 6)- 6( 1, 5)	6.5- 5.5	6.5- 5.5	676.164
7( 2, 6)- 6( 1, 5)	6.5- 5.5	7.5- 6.5	681.302
7( 2, 6)- 6( 1, 5)	6.5- 5.5	8.5- 7.5	686.593
7( 2, 6)- 6( 1, 5)	7.5- 6.5	5.5- 4.5	-1784.004
7( 2, 6)- 6( 1, 5)	7.5- 6.5	6.5- 5.5	-1792.414
7( 2, 6)- 6( 1, 5)	7.5- 6.5	7.5- 6.5	-1797.312
7( 2, 6)- 6( 1, 5)	7.5- 6.5	8.5- 7.5	-1782.988
7( 2, 6)- 6( 1, 5)	7.5- 6.5	9.5- 8.5	-1804.598
7( 4, 4)- 6( 1, 5)	6.5- 5.5	4.5- 3.5	3820.207
7( 4, 4)- 6( 1, 5)	6.5- 5.5	5.5- 4.5	3829.418
7( 4, 4)- 6( 1, 5)	6.5- 5.5	6.5- 5.5	3789.008
7( 4, 4)- 6( 1, 5)	6.5- 5.5	7.5- 6.5	3802.290
7( 4, 4)- 6( 1, 5)	6.5- 5.5	8.5- 7.5	3804.581
7( 4, 4)- 6( 1, 5)	7.5- 6.5	5.5- 4.5	1554.086
7( 4, 4)- 6( 1, 5)	7.5- 6.5	6.5- 5.5	1526.426
7( 4, 4)- 6( 1, 5)	7.5- 6.5	7.5- 6.5	1523.441
7( 4, 4)- 6( 1, 5)	7.5- 6.5	8.5- 7.5	1541.984
7( 4, 4)- 6( 1, 5)	7.5- 6.5	9.5- 8.5	1580.016
7( 1, 7)- 6( 2, 4)	6.5- 5.5	4.5- 3.5	-3958.442
7( 1, 7)- 6( 2, 4)	6.5- 5.5	5.5- 4.5	-3947.894
7( 1, 7)- 6( 2, 4)	6.5- 5.5	6.5- 5.5	-3950.491
7( 1, 7)- 6( 2, 4)	6.5- 5.5	7.5- 6.5	-3945.281
7( 1, 7)- 6( 2, 4)	6.5- 5.5	8.5- 7.5	-3940.365
7( 1, 7)- 6( 2, 4)	7.5- 6.5	5.5- 4.5	-5166.867
7( 1, 7)- 6( 2, 4)	7.5- 6.5	6.5- 5.5	-5157.641
7( 1, 7)- 6( 2, 4)	7.5- 6.5	7.5- 6.5	-5158.793
7( 1, 7)- 6( 2, 4)	7.5- 6.5	8.5- 7.5	-5165.555
7( 1, 7)- 6( 2, 4)	7.5- 6.5	9.5- 8.5	-5294.801
7( 3, 5)- 6( 2, 4)	6.5- 5.5	4.5- 3.5	1351.574
7( 3, 5)- 6( 2, 4)	6.5- 5.5	5.5- 4.5	1360.785
7( 3, 5)- 6( 2, 4)	6.5- 5.5	6.5- 5.5	1359.344
7( 3, 5)- 6( 2, 4)	6.5- 5.5	7.5- 6.5	1366.266
7( 3, 5)- 6( 2, 4)	6.5- 5.5	8.5- 7.5	1371.414
7( 3, 5)- 6( 2, 4)	7.5- 6.5	5.5- 4.5	-1785.152
7( 3, 5)- 6( 2, 4)	7.5- 6.5	6.5- 5.5	-1784.133

7( 3, 5)- 6( 2, 4)	7.5- 6.5	7.5- 6.5	-1787.465
7( 3, 5)- 6( 2, 4)	7.5- 6.5	8.5- 7.5	-1790.113
7( 3, 5)- 6( 2, 4)	7.5- 6.5	9.5- 8.5	-1804.797
7( 5, 3)- 6( 2, 4)	6.5- 5.5	4.5- 3.5	4535.430
7( 5, 3)- 6( 2, 4)	6.5- 5.5	5.5- 4.5	4533.129
7( 5, 3)- 6( 2, 4)	6.5- 5.5	6.5- 5.5	4516.242
7( 5, 3)- 6( 2, 4)	6.5- 5.5	7.5- 6.5	4524.652
7( 5, 3)- 6( 2, 4)	6.5- 5.5	8.5- 7.5	4534.883
7( 5, 3)- 6( 2, 4)	7.5- 6.5	5.5- 4.5	1464.840
7( 5, 3)- 6( 2, 4)	7.5- 6.5	6.5- 5.5	1437.828
7( 5, 3)- 6( 2, 4)	7.5- 6.5	7.5- 6.5	1442.082
7( 5, 3)- 6( 2, 4)	7.5- 6.5	8.5- 7.5	1441.574
7( 5, 3)- 6( 2, 4)	7.5- 6.5	9.5- 8.5	1523.066
7( 2, 6)- 6( 3, 3)	6.5- 5.5	4.5- 3.5	-1404.070
7( 2, 6)- 6( 3, 3)	6.5- 5.5	5.5- 4.5	-1406.172
7( 2, 6)- 6( 3, 3)	6.5- 5.5	6.5- 5.5	-1403.879
7( 2, 6)- 6( 3, 3)	6.5- 5.5	7.5- 6.5	-1400.805
7( 2, 6)- 6( 3, 3)	6.5- 5.5	8.5- 7.5	-1390.523
7( 2, 6)- 6( 3, 3)	7.5- 6.5	5.5- 4.5	-5094.512
7( 2, 6)- 6( 3, 3)	7.5- 6.5	6.5- 5.5	-5077.859
7( 2, 6)- 6( 3, 3)	7.5- 6.5	7.5- 6.5	-5083.180
7( 2, 6)- 6( 3, 3)	7.5- 6.5	8.5- 7.5	-5082.078
7( 2, 6)- 6( 3, 3)	7.5- 6.5	9.5- 8.5	-5149.254
7( 4, 4)- 6( 3, 3)	6.5- 5.5	4.5- 3.5	1710.660
7( 4, 4)- 6( 3, 3)	6.5- 5.5	5.5- 4.5	1729.453
7( 4, 4)- 6( 3, 3)	6.5- 5.5	6.5- 5.5	1708.965
7( 4, 4)- 6( 3, 3)	6.5- 5.5	7.5- 6.5	1720.184
7( 4, 4)- 6( 3, 3)	6.5- 5.5	8.5- 7.5	1727.465
7( 4, 4)- 6( 3, 3)	7.5- 6.5	5.5- 4.5	-1756.422
7( 4, 4)- 6( 3, 3)	7.5- 6.5	6.5- 5.5	-1759.020
7( 4, 4)- 6( 3, 3)	7.5- 6.5	7.5- 6.5	-1762.426
7( 4, 4)- 6( 3, 3)	7.5- 6.5	8.5- 7.5	-1757.105
7( 4, 4)- 6( 3, 3)	7.5- 6.5	9.5- 8.5	-1764.641
7( 6, 2)- 6( 3, 3)	6.5- 5.5	4.5- 3.5	5162.699
7( 6, 2)- 6( 3, 3)	6.5- 5.5	5.5- 4.5	5010.000
7( 6, 2)- 6( 3, 3)	6.5- 5.5	6.5- 5.5	4993.973
7( 6, 2)- 6( 3, 3)	6.5- 5.5	7.5- 6.5	5007.395
7( 6, 2)- 6( 3, 3)	6.5- 5.5	8.5- 7.5	5021.809
7( 6, 2)- 6( 3, 3)	7.5- 6.5	5.5- 4.5	1329.555
7( 6, 2)- 6( 3, 3)	7.5- 6.5	6.5- 5.5	1325.281
7( 6, 2)- 6( 3, 3)	7.5- 6.5	7.5- 6.5	1320.254
7( 6, 2)- 6( 3, 3)	7.5- 6.5	8.5- 7.5	1332.645
7( 6, 2)- 6( 3, 3)	7.5- 6.5	9.5- 8.5	1367.031
7( 3, 5)- 6( 4, 2)	6.5- 5.5	4.5- 3.5	-1382.898
7( 3, 5)- 6( 4, 2)	6.5- 5.5	5.5- 4.5	-1388.527
7( 3, 5)- 6( 4, 2)	6.5- 5.5	6.5- 5.5	-1377.184
7( 3, 5)- 6( 4, 2)	6.5- 5.5	7.5- 6.5	-1368.156
7( 3, 5)- 6( 4, 2)	6.5- 5.5	8.5- 7.5	-1367.469
7( 3, 5)- 6( 4, 2)	7.5- 6.5	5.5- 4.5	-4904.773
7( 3, 5)- 6( 4, 2)	7.5- 6.5	6.5- 5.5	-4893.707
7( 3, 5)- 6( 4, 2)	7.5- 6.5	7.5- 6.5	-4884.855
7( 3, 5)- 6( 4, 2)	7.5- 6.5	8.5- 7.5	-4897.770
7( 3, 5)- 6( 4, 2)	7.5- 6.5	9.5- 8.5	-5013.004
7( 5, 3)- 6( 4, 2)	6.5- 5.5	4.5- 3.5	1800.957
7( 5, 3)- 6( 4, 2)	6.5- 5.5	5.5- 4.5	1783.816
7( 5, 3)- 6( 4, 2)	6.5- 5.5	6.5- 5.5	1779.715

7( 5, 3)- 6( 4, 2)	6.5- 5.5	7.5- 6.5	1790.230
7( 5, 3)- 6( 4, 2)	6.5- 5.5	8.5- 7.5	1796.000
7( 5, 3)- 6( 4, 2)	7.5- 6.5	5.5- 4.5	-1654.784
7( 5, 3)- 6( 4, 2)	7.5- 6.5	6.5- 5.5	-1671.750
7( 5, 3)- 6( 4, 2)	7.5- 6.5	7.5- 6.5	-1655.309
7( 5, 3)- 6( 4, 2)	7.5- 6.5	8.5- 7.5	-1666.082
7( 5, 3)- 6( 4, 2)	7.5- 6.5	9.5- 8.5	-1685.141
7( 7, 1)- 6( 4, 2)	6.5- 5.5	4.5- 3.5	5311.109
7( 7, 1)- 6( 4, 2)	6.5- 5.5	5.5- 4.5	5147.547
7( 7, 1)- 6( 4, 2)	6.5- 5.5	6.5- 5.5	5136.484
7( 7, 1)- 6( 4, 2)	6.5- 5.5	7.5- 6.5	5159.480
7( 7, 1)- 6( 4, 2)	6.5- 5.5	8.5- 7.5	5165.187
7( 7, 1)- 6( 4, 2)	7.5- 6.5	5.5- 4.5	1448.799
7( 7, 1)- 6( 4, 2)	7.5- 6.5	6.5- 5.5	1435.269
7( 7, 1)- 6( 4, 2)	7.5- 6.5	7.5- 6.5	1437.298
7( 7, 1)- 6( 4, 2)	7.5- 6.5	8.5- 7.5	1433.628
7( 7, 1)- 6( 4, 2)	7.5- 6.5	9.5- 8.5	1435.282
7( 4, 4)- 6( 5, 1)	6.5- 5.5	4.5- 3.5	-1658.895
7( 4, 4)- 6( 5, 1)	6.5- 5.5	5.5- 4.5	-1481.289
7( 4, 4)- 6( 5, 1)	6.5- 5.5	6.5- 5.5	-1489.668
7( 4, 4)- 6( 5, 1)	6.5- 5.5	7.5- 6.5	-1477.727
7( 4, 4)- 6( 5, 1)	6.5- 5.5	8.5- 7.5	-1485.277
7( 4, 4)- 6( 5, 1)	7.5- 6.5	5.5- 4.5	-4316.387
7( 4, 4)- 6( 5, 1)	7.5- 6.5	6.5- 5.5	-4319.531
7( 4, 4)- 6( 5, 1)	7.5- 6.5	7.5- 6.5	-4315.250
7( 4, 4)- 6( 5, 1)	7.5- 6.5	8.5- 7.5	-4315.680
7( 4, 4)- 6( 5, 1)	7.5- 6.5	9.5- 8.5	-4387.141
7( 6, 2)- 6( 5, 1)	6.5- 5.5	4.5- 3.5	1793.145
7( 6, 2)- 6( 5, 1)	6.5- 5.5	5.5- 4.5	1799.258
7( 6, 2)- 6( 5, 1)	6.5- 5.5	6.5- 5.5	1795.340
7( 6, 2)- 6( 5, 1)	6.5- 5.5	7.5- 6.5	1809.484
7( 6, 2)- 6( 5, 1)	6.5- 5.5	8.5- 7.5	1809.066
7( 6, 2)- 6( 5, 1)	7.5- 6.5	5.5- 4.5	-1230.411
7( 6, 2)- 6( 5, 1)	7.5- 6.5	6.5- 5.5	-1235.231
7( 6, 2)- 6( 5, 1)	7.5- 6.5	7.5- 6.5	-1232.574
7( 6, 2)- 6( 5, 1)	7.5- 6.5	8.5- 7.5	-1225.931
7( 6, 2)- 6( 5, 1)	7.5- 6.5	9.5- 8.5	-1255.472
7( 5, 3)- 6( 6, 0)	6.5- 5.5	4.5- 3.5	-1712.035
7( 5, 3)- 6( 6, 0)	6.5- 5.5	5.5- 4.5	-1560.461
7( 5, 3)- 6( 6, 0)	6.5- 5.5	6.5- 5.5	-1558.586
7( 5, 3)- 6( 6, 0)	6.5- 5.5	7.5- 6.5	-1557.809
7( 5, 3)- 6( 6, 0)	6.5- 5.5	8.5- 7.5	-1559.836
7( 5, 3)- 6( 6, 0)	7.5- 6.5	5.5- 4.5	-3662.001
7( 5, 3)- 6( 6, 0)	7.5- 6.5	6.5- 5.5	-3672.007
7( 5, 3)- 6( 6, 0)	7.5- 6.5	7.5- 6.5	-3663.381
7( 5, 3)- 6( 6, 0)	7.5- 6.5	8.5- 7.5	-3666.768
7( 5, 3)- 6( 6, 0)	7.5- 6.5	9.5- 8.5	-3702.027
7( 7, 1)- 6( 6, 0)	6.5- 5.5	4.5- 3.5	1798.117
7( 7, 1)- 6( 6, 0)	6.5- 5.5	5.5- 4.5	1803.270
7( 7, 1)- 6( 6, 0)	6.5- 5.5	6.5- 5.5	1798.184
7( 7, 1)- 6( 6, 0)	6.5- 5.5	7.5- 6.5	1811.441
7( 7, 1)- 6( 6, 0)	6.5- 5.5	8.5- 7.5	1809.352
7( 7, 1)- 6( 6, 0)	7.5- 6.5	5.5- 4.5	-558.419
7( 7, 1)- 6( 6, 0)	7.5- 6.5	6.5- 5.5	-564.989
7( 7, 1)- 6( 6, 0)	7.5- 6.5	7.5- 6.5	-570.775
7( 7, 1)- 6( 6, 0)	7.5- 6.5	8.5- 7.5	-567.058

7( 7, 1)- 6( 6, 0)	7.5- 6.5	9.5- 8.5	-581.604
THESE ARE THE B-TYPE TRANSITIONS FROM NMIN= 4 TO NMAX= 7 FOR I=3			
THE ORDER OF THE QUANTUM NUMBERS ARE FROM LEFT TO RIGHT, N',KP',KO'			
5( 0, 5)- 4( 1, 4)	4.5- 3.5	1.5- 0.5	-189.812
5( 0, 5)- 4( 1, 4)	4.5- 3.5	2.5- 1.5	-209.434
5( 0, 5)- 4( 1, 4)	4.5- 3.5	3.5- 2.5	-173.754
5( 0, 5)- 4( 1, 4)	4.5- 3.5	4.5- 3.5	-358.206
5( 0, 5)- 4( 1, 4)	4.5- 3.5	5.5- 4.5	-266.814
5( 0, 5)- 4( 1, 4)	4.5- 3.5	6.5- 5.5	-244.951
5( 0, 5)- 4( 1, 4)	4.5- 3.5	7.5- 6.5	-283.759
5( 0, 5)- 4( 1, 4)	5.5- 4.5	2.5- 1.5	-1786.293
5( 0, 5)- 4( 1, 4)	5.5- 4.5	3.5- 2.5	-1770.820
5( 0, 5)- 4( 1, 4)	5.5- 4.5	4.5- 3.5	-1832.055
5( 0, 5)- 4( 1, 4)	5.5- 4.5	5.5- 4.5	-1753.773
5( 0, 5)- 4( 1, 4)	5.5- 4.5	6.5- 5.5	-1797.336
5( 0, 5)- 4( 1, 4)	5.5- 4.5	7.5- 6.5	-1785.703
5( 0, 5)- 4( 1, 4)	5.5- 4.5	8.5- 7.5	-1810.402
5( 2, 3)- 4( 1, 4)	4.5- 3.5	1.5- 0.5	3769.624
5( 2, 3)- 4( 1, 4)	4.5- 3.5	2.5- 1.5	3500.127
5( 2, 3)- 4( 1, 4)	4.5- 3.5	3.5- 2.5	3513.342
5( 2, 3)- 4( 1, 4)	4.5- 3.5	4.5- 3.5	3341.426
5( 2, 3)- 4( 1, 4)	4.5- 3.5	5.5- 4.5	3451.248
5( 2, 3)- 4( 1, 4)	4.5- 3.5	6.5- 5.5	3446.803
5( 2, 3)- 4( 1, 4)	4.5- 3.5	7.5- 6.5	3436.328
5( 2, 3)- 4( 1, 4)	5.5- 4.5	2.5- 1.5	1619.406
5( 2, 3)- 4( 1, 4)	5.5- 4.5	3.5- 2.5	1568.055
5( 2, 3)- 4( 1, 4)	5.5- 4.5	4.5- 3.5	1520.547
5( 2, 3)- 4( 1, 4)	5.5- 4.5	5.5- 4.5	1599.687
5( 2, 3)- 4( 1, 4)	5.5- 4.5	6.5- 5.5	1549.937
5( 2, 3)- 4( 1, 4)	5.5- 4.5	7.5- 6.5	1581.211
5( 2, 3)- 4( 1, 4)	5.5- 4.5	8.5- 7.5	1703.535
5( 4, 1)- 4( 1, 4)	4.5- 3.5	1.5- 0.5	6759.992
5( 4, 1)- 4( 1, 4)	4.5- 3.5	2.5- 1.5	6499.844
5( 4, 1)- 4( 1, 4)	4.5- 3.5	3.5- 2.5	6451.695
5( 4, 1)- 4( 1, 4)	4.5- 3.5	4.5- 3.5	6285.652
5( 4, 1)- 4( 1, 4)	4.5- 3.5	5.5- 4.5	6414.605
5( 4, 1)- 4( 1, 4)	4.5- 3.5	6.5- 5.5	6391.594
5( 4, 1)- 4( 1, 4)	4.5- 3.5	7.5- 6.5	6427.090
5( 4, 1)- 4( 1, 4)	5.5- 4.5	2.5- 1.5	4412.312
5( 4, 1)- 4( 1, 4)	5.5- 4.5	3.5- 2.5	4318.668
5( 4, 1)- 4( 1, 4)	5.5- 4.5	4.5- 3.5	4280.305
5( 4, 1)- 4( 1, 4)	5.5- 4.5	5.5- 4.5	4371.148
5( 4, 1)- 4( 1, 4)	5.5- 4.5	6.5- 5.5	4340.383
5( 4, 1)- 4( 1, 4)	5.5- 4.5	7.5- 6.5	4346.238
5( 4, 1)- 4( 1, 4)	5.5- 4.5	8.5- 7.5	4600.000
5( 1, 4)- 4( 2, 3)	4.5- 3.5	1.5- 0.5	-335.063
5( 1, 4)- 4( 2, 3)	4.5- 3.5	2.5- 1.5	-414.431
5( 1, 4)- 4( 2, 3)	4.5- 3.5	3.5- 2.5	-344.720
5( 1, 4)- 4( 2, 3)	4.5- 3.5	4.5- 3.5	-506.016
5( 1, 4)- 4( 2, 3)	4.5- 3.5	5.5- 4.5	-410.841
5( 1, 4)- 4( 2, 3)	4.5- 3.5	6.5- 5.5	-410.191
5( 1, 4)- 4( 2, 3)	4.5- 3.5	7.5- 6.5	-445.423
5( 1, 4)- 4( 2, 3)	5.5- 4.5	2.5- 1.5	-1773.562
5( 1, 4)- 4( 2, 3)	5.5- 4.5	3.5- 2.5	-1798.629
5( 1, 4)- 4( 2, 3)	5.5- 4.5	4.5- 3.5	-1812.746
5( 1, 4)- 4( 2, 3)	5.5- 4.5	5.5- 4.5	-1743.742

5( 1, 4)- 4( 2, 3)	5.5- 4.5	6.5- 5.5	-1786.680
5( 1, 4)- 4( 2, 3)	5.5- 4.5	7.5- 6.5	-1767.379
5( 1, 4)- 4( 2, 3)	5.5- 4.5	8.5- 7.5	-1807.641
5( 3, 2)- 4( 2, 3)	4.5- 3.5	1.5- 0.5	2195.148
5( 3, 2)- 4( 2, 3)	4.5- 3.5	2.5- 1.5	1871.512
5( 3, 2)- 4( 2, 3)	4.5- 3.5	3.5- 2.5	1884.230
5( 3, 2)- 4( 2, 3)	4.5- 3.5	4.5- 3.5	1727.539
5( 3, 2)- 4( 2, 3)	4.5- 3.5	5.5- 4.5	1830.173
5( 3, 2)- 4( 2, 3)	4.5- 3.5	6.5- 5.5	1828.237
5( 3, 2)- 4( 2, 3)	4.5- 3.5	7.5- 6.5	1837.621
5( 3, 2)- 4( 2, 3)	5.5- 4.5	2.5- 1.5	1491.756
5( 3, 2)- 4( 2, 3)	5.5- 4.5	3.5- 2.5	1405.608
5( 3, 2)- 4( 2, 3)	5.5- 4.5	4.5- 3.5	1398.921
5( 3, 2)- 4( 2, 3)	5.5- 4.5	5.5- 4.5	1483.637
5( 3, 2)- 4( 2, 3)	5.5- 4.5	6.5- 5.5	1459.084
5( 3, 2)- 4( 2, 3)	5.5- 4.5	7.5- 6.5	1454.367
5( 3, 2)- 4( 2, 3)	5.5- 4.5	8.5- 7.5	1408.902
5( 5, 0)- 4( 2, 3)	4.5- 3.5	1.5- 0.5	5570.004
5( 5, 0)- 4( 2, 3)	4.5- 3.5	2.5- 1.5	5204.234
5( 5, 0)- 4( 2, 3)	4.5- 3.5	3.5- 2.5	5177.934
5( 5, 0)- 4( 2, 3)	4.5- 3.5	4.5- 3.5	5027.082
5( 5, 0)- 4( 2, 3)	4.5- 3.5	5.5- 4.5	5150.984
5( 5, 0)- 4( 2, 3)	4.5- 3.5	6.5- 5.5	5133.164
5( 5, 0)- 4( 2, 3)	4.5- 3.5	7.5- 6.5	5156.895
5( 5, 0)- 4( 2, 3)	5.5- 4.5	2.5- 1.5	3627.580
5( 5, 0)- 4( 2, 3)	5.5- 4.5	3.5- 2.5	3501.787
5( 5, 0)- 4( 2, 3)	5.5- 4.5	4.5- 3.5	3498.811
5( 5, 0)- 4( 2, 3)	5.5- 4.5	5.5- 4.5	3594.147
5( 5, 0)- 4( 2, 3)	5.5- 4.5	6.5- 5.5	3566.184
5( 5, 0)- 4( 2, 3)	5.5- 4.5	7.5- 6.5	3559.421
5( 5, 0)- 4( 2, 3)	5.5- 4.5	8.5- 7.5	3665.138
5( 0, 5)- 4( 3, 2)	4.5- 3.5	1.5- 0.5	-5165.219
5( 0, 5)- 4( 3, 2)	4.5- 3.5	2.5- 1.5	-4837.402
5( 0, 5)- 4( 3, 2)	4.5- 3.5	3.5- 2.5	-4757.512
5( 0, 5)- 4( 3, 2)	4.5- 3.5	4.5- 3.5	-4925.648
5( 0, 5)- 4( 3, 2)	4.5- 3.5	5.5- 4.5	-4842.336
5( 0, 5)- 4( 3, 2)	4.5- 3.5	6.5- 5.5	-4818.441
5( 0, 5)- 4( 3, 2)	4.5- 3.5	7.5- 6.5	-4891.469
5( 0, 5)- 4( 3, 2)	5.5- 4.5	2.5- 1.5	-5145.379
5( 0, 5)- 4( 3, 2)	5.5- 4.5	3.5- 2.5	-5140.922
5( 0, 5)- 4( 3, 2)	5.5- 4.5	4.5- 3.5	-5141.934
5( 0, 5)- 4( 3, 2)	5.5- 4.5	5.5- 4.5	-5088.562
5( 0, 5)- 4( 3, 2)	5.5- 4.5	6.5- 5.5	-5117.398
5( 0, 5)- 4( 3, 2)	5.5- 4.5	7.5- 6.5	-5112.094
5( 0, 5)- 4( 3, 2)	5.5- 4.5	8.5- 7.5	-5297.488
5( 2, 3)- 4( 3, 2)	4.5- 3.5	1.5- 0.5	-1205.785
5( 2, 3)- 4( 3, 2)	4.5- 3.5	2.5- 1.5	-1127.844
5( 2, 3)- 4( 3, 2)	4.5- 3.5	3.5- 2.5	-1070.418
5( 2, 3)- 4( 3, 2)	4.5- 3.5	4.5- 3.5	-1226.020
5( 2, 3)- 4( 3, 2)	4.5- 3.5	5.5- 4.5	-1124.277
5( 2, 3)- 4( 3, 2)	4.5- 3.5	6.5- 5.5	-1126.687
5( 2, 3)- 4( 3, 2)	4.5- 3.5	7.5- 6.5	-1171.383
5( 2, 3)- 4( 3, 2)	5.5- 4.5	2.5- 1.5	-1739.682
5( 2, 3)- 4( 3, 2)	5.5- 4.5	3.5- 2.5	-1802.050
5( 2, 3)- 4( 3, 2)	5.5- 4.5	4.5- 3.5	-1789.332
5( 2, 3)- 4( 3, 2)	5.5- 4.5	5.5- 4.5	-1735.104



5( 2, 3)- 4( 3, 2)	5.5- 4.5	6.5- 5.5	-1770.125
5( 2, 3)- 4( 3, 2)	5.5- 4.5	7.5- 6.5	-1745.181
5( 2, 3)- 4( 3, 2)	5.5- 4.5	8.5- 7.5	-1783.551
5( 4, 1)- 4( 3, 2)	4.5- 3.5	1.5- 0.5	1784.586
5( 4, 1)- 4( 3, 2)	4.5- 3.5	2.5- 1.5	1873.875
5( 4, 1)- 4( 3, 2)	4.5- 3.5	3.5- 2.5	1867.937
5( 4, 1)- 4( 3, 2)	4.5- 3.5	4.5- 3.5	1718.211
5( 4, 1)- 4( 3, 2)	4.5- 3.5	5.5- 4.5	1837.082
5( 4, 1)- 4( 3, 2)	4.5- 3.5	6.5- 5.5	1818.105
5( 4, 1)- 4( 3, 2)	4.5- 3.5	7.5- 6.5	1819.379
5( 4, 1)- 4( 3, 2)	5.5- 4.5	2.5- 1.5	1053.226
5( 4, 1)- 4( 3, 2)	5.5- 4.5	3.5- 2.5	948.567
5( 4, 1)- 4( 3, 2)	5.5- 4.5	4.5- 3.5	970.429
5( 4, 1)- 4( 3, 2)	5.5- 4.5	5.5- 4.5	1036.360
5( 4, 1)- 4( 3, 2)	5.5- 4.5	6.5- 5.5	1020.324
5( 4, 1)- 4( 3, 2)	5.5- 4.5	7.5- 6.5	1019.848
5( 4, 1)- 4( 3, 2)	5.5- 4.5	8.5- 7.5	1112.915
5( 1, 4)- 4( 4, 1)	4.5- 3.5	1.5- 0.5	-4117.590
5( 1, 4)- 4( 4, 1)	4.5- 3.5	2.5- 1.5	-3730.962
5( 1, 4)- 4( 4, 1)	4.5- 3.5	3.5- 2.5	-3679.068
5( 1, 4)- 4( 4, 1)	4.5- 3.5	4.5- 3.5	-3796.958
5( 1, 4)- 4( 4, 1)	4.5- 3.5	5.5- 4.5	-3711.088
5( 1, 4)- 4( 4, 1)	4.5- 3.5	6.5- 5.5	-3715.568
5( 1, 4)- 4( 4, 1)	4.5- 3.5	7.5- 6.5	-3775.337
5( 1, 4)- 4( 4, 1)	5.5- 4.5	2.5- 1.5	-5050.117
5( 1, 4)- 4( 4, 1)	5.5- 4.5	3.5- 2.5	-5059.895
5( 1, 4)- 4( 4, 1)	5.5- 4.5	4.5- 3.5	-5040.238
5( 1, 4)- 4( 4, 1)	5.5- 4.5	5.5- 4.5	-5025.535
5( 1, 4)- 4( 4, 1)	5.5- 4.5	6.5- 5.5	-5024.754
5( 1, 4)- 4( 4, 1)	5.5- 4.5	7.5- 6.5	-5020.555
5( 1, 4)- 4( 4, 1)	5.5- 4.5	8.5- 7.5	-5057.258
5( 3, 2)- 4( 4, 1)	4.5- 3.5	1.5- 0.5	-1587.379
5( 3, 2)- 4( 4, 1)	4.5- 3.5	2.5- 1.5	-1445.020
5( 3, 2)- 4( 4, 1)	4.5- 3.5	3.5- 2.5	-1450.117
5( 3, 2)- 4( 4, 1)	4.5- 3.5	4.5- 3.5	-1563.402
5( 3, 2)- 4( 4, 1)	4.5- 3.5	5.5- 4.5	-1470.074
5( 3, 2)- 4( 4, 1)	4.5- 3.5	6.5- 5.5	-1477.141
5( 3, 2)- 4( 4, 1)	4.5- 3.5	7.5- 6.5	-1492.293
5( 3, 2)- 4( 4, 1)	5.5- 4.5	2.5- 1.5	-1784.799
5( 3, 2)- 4( 4, 1)	5.5- 4.5	3.5- 2.5	-1855.661
5( 3, 2)- 4( 4, 1)	5.5- 4.5	4.5- 3.5	-1828.572
5( 3, 2)- 4( 4, 1)	5.5- 4.5	5.5- 4.5	-1798.157
5( 3, 2)- 4( 4, 1)	5.5- 4.5	6.5- 5.5	-1778.992
5( 3, 2)- 4( 4, 1)	5.5- 4.5	7.5- 6.5	-1798.812
5( 3, 2)- 4( 4, 1)	5.5- 4.5	8.5- 7.5	-1840.716
5( 5, 0)- 4( 4, 1)	4.5- 3.5	1.5- 0.5	1785.477
5( 5, 0)- 4( 4, 1)	4.5- 3.5	2.5- 1.5	1887.703
5( 5, 0)- 4( 4, 1)	4.5- 3.5	3.5- 2.5	1843.586
5( 5, 0)- 4( 4, 1)	4.5- 3.5	4.5- 3.5	1736.141
5( 5, 0)- 4( 4, 1)	4.5- 3.5	5.5- 4.5	1850.738
5( 5, 0)- 4( 4, 1)	4.5- 3.5	6.5- 5.5	1827.789
5( 5, 0)- 4( 4, 1)	4.5- 3.5	7.5- 6.5	1826.980
5( 5, 0)- 4( 4, 1)	5.5- 4.5	2.5- 1.5	351.025
5( 5, 0)- 4( 4, 1)	5.5- 4.5	3.5- 2.5	242.519
5( 5, 0)- 4( 4, 1)	5.5- 4.5	4.5- 3.5	271.317
5( 5, 0)- 4( 4, 1)	5.5- 4.5	5.5- 4.5	310.353

5( 5, 0)- 4( 4, 1)	5.5- 4.5	6.5- 5.5	328.107
5( 5, 0)- 4( 4, 1)	5.5- 4.5	7.5- 6.5	304.242
5( 5, 0)- 4( 4, 1)	5.5- 4.5	8.5- 7.5	415.520
6( 1, 6)- 5( 0, 5)	5.5- 4.5	2.5- 1.5	190.818
6( 1, 6)- 5( 0, 5)	5.5- 4.5	3.5- 2.5	76.560
6( 1, 6)- 5( 0, 5)	5.5- 4.5	4.5- 3.5	126.938
6( 1, 6)- 5( 0, 5)	5.5- 4.5	5.5- 4.5	172.767
6( 1, 6)- 5( 0, 5)	5.5- 4.5	6.5- 5.5	179.295
6( 1, 6)- 5( 0, 5)	5.5- 4.5	7.5- 6.5	131.323
6( 1, 6)- 5( 0, 5)	5.5- 4.5	8.5- 7.5	149.376
6( 1, 6)- 5( 0, 5)	6.5- 5.5	3.5- 2.5	-1959.238
6( 1, 6)- 5( 0, 5)	6.5- 5.5	4.5- 3.5	-1756.551
6( 1, 6)- 5( 0, 5)	6.5- 5.5	5.5- 4.5	-1787.473
6( 1, 6)- 5( 0, 5)	6.5- 5.5	6.5- 5.5	-1789.605
6( 1, 6)- 5( 0, 5)	6.5- 5.5	7.5- 6.5	-1770.195
6( 1, 6)- 5( 0, 5)	6.5- 5.5	8.5- 7.5	-1793.105
6( 1, 6)- 5( 0, 5)	6.5- 5.5	9.5- 8.5	-1808.910
6( 3, 4)- 5( 0, 5)	5.5- 4.5	2.5- 1.5	5350.445
6( 3, 4)- 5( 0, 5)	5.5- 4.5	3.5- 2.5	5126.883
6( 3, 4)- 5( 0, 5)	5.5- 4.5	4.5- 3.5	5187.168
6( 3, 4)- 5( 0, 5)	5.5- 4.5	5.5- 4.5	5229.199
6( 3, 4)- 5( 0, 5)	5.5- 4.5	6.5- 5.5	5234.426
6( 3, 4)- 5( 0, 5)	5.5- 4.5	7.5- 6.5	5189.418
6( 3, 4)- 5( 0, 5)	5.5- 4.5	8.5- 7.5	5254.891
6( 3, 4)- 5( 0, 5)	6.5- 5.5	3.5- 2.5	1415.883
6( 3, 4)- 5( 0, 5)	6.5- 5.5	4.5- 3.5	1613.484
6( 3, 4)- 5( 0, 5)	6.5- 5.5	5.5- 4.5	1584.258
6( 3, 4)- 5( 0, 5)	6.5- 5.5	6.5- 5.5	1579.051
6( 3, 4)- 5( 0, 5)	6.5- 5.5	7.5- 6.5	1597.230
6( 3, 4)- 5( 0, 5)	6.5- 5.5	8.5- 7.5	1578.598
6( 3, 4)- 5( 0, 5)	6.5- 5.5	9.5- 8.5	1713.883
6( 2, 5)- 5( 1, 4)	5.5- 4.5	2.5- 1.5	879.079
6( 2, 5)- 5( 1, 4)	5.5- 4.5	3.5- 2.5	765.689
6( 2, 5)- 5( 1, 4)	5.5- 4.5	4.5- 3.5	827.880
6( 2, 5)- 5( 1, 4)	5.5- 4.5	5.5- 4.5	856.481
6( 2, 5)- 5( 1, 4)	5.5- 4.5	6.5- 5.5	848.033
6( 2, 5)- 5( 1, 4)	5.5- 4.5	7.5- 6.5	825.033
6( 2, 5)- 5( 1, 4)	5.5- 4.5	8.5- 7.5	877.083
6( 2, 5)- 5( 1, 4)	6.5- 5.5	3.5- 2.5	-1979.879
6( 2, 5)- 5( 1, 4)	6.5- 5.5	4.5- 3.5	-1747.277
6( 2, 5)- 5( 1, 4)	6.5- 5.5	5.5- 4.5	-1790.316
6( 2, 5)- 5( 1, 4)	6.5- 5.5	6.5- 5.5	-1786.359
6( 2, 5)- 5( 1, 4)	6.5- 5.5	7.5- 6.5	-1772.320
6( 2, 5)- 5( 1, 4)	6.5- 5.5	8.5- 7.5	-1798.129
6( 2, 5)- 5( 1, 4)	6.5- 5.5	9.5- 8.5	-1813.500
6( 4, 3)- 5( 1, 4)	5.5- 4.5	2.5- 1.5	4242.602
6( 4, 3)- 5( 1, 4)	5.5- 4.5	3.5- 2.5	3919.478
6( 4, 3)- 5( 1, 4)	5.5- 4.5	4.5- 3.5	3988.755
6( 4, 3)- 5( 1, 4)	5.5- 4.5	5.5- 4.5	4013.594
6( 4, 3)- 5( 1, 4)	5.5- 4.5	6.5- 5.5	4008.428
6( 4, 3)- 5( 1, 4)	5.5- 4.5	7.5- 6.5	3987.104
6( 4, 3)- 5( 1, 4)	5.5- 4.5	8.5- 7.5	4046.309
6( 4, 3)- 5( 1, 4)	6.5- 5.5	3.5- 2.5	1324.711
6( 4, 3)- 5( 1, 4)	6.5- 5.5	4.5- 3.5	1544.023
6( 4, 3)- 5( 1, 4)	6.5- 5.5	5.5- 4.5	1502.781
6( 4, 3)- 5( 1, 4)	6.5- 5.5	6.5- 5.5	1516.516

6( 4, 3)- 5( 1, 4)	6.5- 5.5	7.5- 6.5	1530.137
6( 4, 3)- 5( 1, 4)	6.5- 5.5	8.5- 7.5	1493.473
6( 4, 3)- 5( 1, 4)	6.5- 5.5	9.5- 8.5	1493.797
6( 1, 6)- 5( 2, 3)	5.5- 4.5	2.5- 1.5	-3768.618
6( 1, 6)- 5( 2, 3)	5.5- 4.5	3.5- 2.5	-3633.001
6( 1, 6)- 5( 2, 3)	5.5- 4.5	4.5- 3.5	-3560.158
6( 1, 6)- 5( 2, 3)	5.5- 4.5	5.5- 4.5	-3526.864
6( 1, 6)- 5( 2, 3)	5.5- 4.5	6.5- 5.5	-3538.767
6( 1, 6)- 5( 2, 3)	5.5- 4.5	7.5- 6.5	-3560.431
6( 1, 6)- 5( 2, 3)	5.5- 4.5	8.5- 7.5	-3570.711
6( 1, 6)- 5( 2, 3)	6.5- 5.5	3.5- 2.5	-5364.937
6( 1, 6)- 5( 2, 3)	6.5- 5.5	4.5- 3.5	-5095.426
6( 1, 6)- 5( 2, 3)	6.5- 5.5	5.5- 4.5	-5140.074
6( 1, 6)- 5( 2, 3)	6.5- 5.5	6.5- 5.5	-5143.066
6( 1, 6)- 5( 2, 3)	6.5- 5.5	7.5- 6.5	-5117.469
6( 1, 6)- 5( 2, 3)	6.5- 5.5	8.5- 7.5	-5160.020
6( 1, 6)- 5( 2, 3)	6.5- 5.5	9.5- 8.5	-5322.848
6( 3, 4)- 5( 2, 3)	5.5- 4.5	2.5- 1.5	1391.012
6( 3, 4)- 5( 2, 3)	5.5- 4.5	3.5- 2.5	1417.324
6( 3, 4)- 5( 2, 3)	5.5- 4.5	4.5- 3.5	1500.074
6( 3, 4)- 5( 2, 3)	5.5- 4.5	5.5- 4.5	1529.570
6( 3, 4)- 5( 2, 3)	5.5- 4.5	6.5- 5.5	1516.367
6( 3, 4)- 5( 2, 3)	5.5- 4.5	7.5- 6.5	1497.664
6( 3, 4)- 5( 2, 3)	5.5- 4.5	8.5- 7.5	1534.805
6( 3, 4)- 5( 2, 3)	6.5- 5.5	3.5- 2.5	-1989.816
6( 3, 4)- 5( 2, 3)	6.5- 5.5	4.5- 3.5	-1725.391
6( 3, 4)- 5( 2, 3)	6.5- 5.5	5.5- 4.5	-1768.344
6( 3, 4)- 5( 2, 3)	6.5- 5.5	6.5- 5.5	-1774.410
6( 3, 4)- 5( 2, 3)	6.5- 5.5	7.5- 6.5	-1750.043
6( 3, 4)- 5( 2, 3)	6.5- 5.5	8.5- 7.5	-1788.316
6( 3, 4)- 5( 2, 3)	6.5- 5.5	9.5- 8.5	-1800.055
6( 5, 2)- 5( 2, 3)	5.5- 4.5	2.5- 1.5	4780.699
6( 5, 2)- 5( 2, 3)	5.5- 4.5	3.5- 2.5	4645.184
6( 5, 2)- 5( 2, 3)	5.5- 4.5	4.5- 3.5	4738.562
6( 5, 2)- 5( 2, 3)	5.5- 4.5	5.5- 4.5	4760.934
6( 5, 2)- 5( 2, 3)	5.5- 4.5	6.5- 5.5	4764.219
6( 5, 2)- 5( 2, 3)	5.5- 4.5	7.5- 6.5	4753.559
6( 5, 2)- 5( 2, 3)	5.5- 4.5	8.5- 7.5	4786.176
6( 5, 2)- 5( 2, 3)	6.5- 5.5	3.5- 2.5	1181.200
6( 5, 2)- 5( 2, 3)	6.5- 5.5	4.5- 3.5	1434.938
6( 5, 2)- 5( 2, 3)	6.5- 5.5	5.5- 4.5	1389.520
6( 5, 2)- 5( 2, 3)	6.5- 5.5	6.5- 5.5	1401.918
6( 5, 2)- 5( 2, 3)	6.5- 5.5	7.5- 6.5	1425.062
6( 5, 2)- 5( 2, 3)	6.5- 5.5	8.5- 7.5	1384.074
6( 5, 2)- 5( 2, 3)	6.5- 5.5	9.5- 8.5	1505.051
6( 2, 5)- 5( 3, 2)	5.5- 4.5	2.5- 1.5	-1651.133
6( 2, 5)- 5( 3, 2)	5.5- 4.5	3.5- 2.5	-1520.254
6( 2, 5)- 5( 3, 2)	5.5- 4.5	4.5- 3.5	-1401.070
6( 2, 5)- 5( 3, 2)	5.5- 4.5	5.5- 4.5	-1377.074
6( 2, 5)- 5( 3, 2)	5.5- 4.5	6.5- 5.5	-1392.980
6( 2, 5)- 5( 3, 2)	5.5- 4.5	7.5- 6.5	-1413.395
6( 2, 5)- 5( 3, 2)	5.5- 4.5	8.5- 7.5	-1405.961
6( 2, 5)- 5( 3, 2)	6.5- 5.5	3.5- 2.5	-5245.195
6( 2, 5)- 5( 3, 2)	6.5- 5.5	4.5- 3.5	-4951.512
6( 2, 5)- 5( 3, 2)	6.5- 5.5	5.5- 4.5	-5001.980
6( 2, 5)- 5( 3, 2)	6.5- 5.5	6.5- 5.5	-5013.738

6( 2, 5)- 5( 3, 2)	6.5- 5.5	7.5- 6.5	-5018.082
6( 2, 5)- 5( 3, 2)	6.5- 5.5	8.5- 7.5	-5019.875
6( 2, 5)- 5( 3, 2)	6.5- 5.5	9.5- 8.5	-5030.043
6( 4, 3)- 5( 3, 2)	5.5- 4.5	2.5- 1.5	1712.391
6( 4, 3)- 5( 3, 2)	5.5- 4.5	3.5- 2.5	1633.535
6( 4, 3)- 5( 3, 2)	5.5- 4.5	4.5- 3.5	1759.805
6( 4, 3)- 5( 3, 2)	5.5- 4.5	5.5- 4.5	1780.039
6( 4, 3)- 5( 3, 2)	5.5- 4.5	6.5- 5.5	1767.414
6( 4, 3)- 5( 3, 2)	5.5- 4.5	7.5- 6.5	1748.676
6( 4, 3)- 5( 3, 2)	5.5- 4.5	8.5- 7.5	1763.266
6( 4, 3)- 5( 3, 2)	6.5- 5.5	3.5- 2.5	-1940.608
6( 4, 3)- 5( 3, 2)	6.5- 5.5	4.5- 3.5	-1660.213
6( 4, 3)- 5( 3, 2)	6.5- 5.5	5.5- 4.5	-1708.886
6( 4, 3)- 5( 3, 2)	6.5- 5.5	6.5- 5.5	-1710.863
6( 4, 3)- 5( 3, 2)	6.5- 5.5	7.5- 6.5	-1715.627
6( 4, 3)- 5( 3, 2)	6.5- 5.5	8.5- 7.5	-1728.273
6( 4, 3)- 5( 3, 2)	6.5- 5.5	9.5- 8.5	-1722.746
6( 6, 1)- 5( 3, 2)	5.5- 4.5	2.5- 1.5	5168.801
6( 6, 1)- 5( 3, 2)	5.5- 4.5	3.5- 2.5	4969.414
6( 6, 1)- 5( 3, 2)	5.5- 4.5	4.5- 3.5	5119.566
6( 6, 1)- 5( 3, 2)	5.5- 4.5	5.5- 4.5	5120.156
6( 6, 1)- 5( 3, 2)	5.5- 4.5	6.5- 5.5	5123.539
6( 6, 1)- 5( 3, 2)	5.5- 4.5	7.5- 6.5	5110.379
6( 6, 1)- 5( 3, 2)	5.5- 4.5	8.5- 7.5	5119.230
6( 6, 1)- 5( 3, 2)	6.5- 5.5	3.5- 2.5	1197.773
6( 6, 1)- 5( 3, 2)	6.5- 5.5	4.5- 3.5	1473.792
6( 6, 1)- 5( 3, 2)	6.5- 5.5	5.5- 4.5	1410.672
6( 6, 1)- 5( 3, 2)	6.5- 5.5	6.5- 5.5	1415.939
6( 6, 1)- 5( 3, 2)	6.5- 5.5	7.5- 6.5	1415.105
6( 6, 1)- 5( 3, 2)	6.5- 5.5	8.5- 7.5	1406.084
6( 6, 1)- 5( 3, 2)	6.5- 5.5	9.5- 8.5	1526.815
6( 3, 4)- 5( 4, 1)	5.5- 4.5	2.5- 1.5	-1599.359
6( 3, 4)- 5( 4, 1)	5.5- 4.5	3.5- 2.5	-1582.395
6( 3, 4)- 5( 4, 1)	5.5- 4.5	4.5- 3.5	-1438.281
6( 3, 4)- 5( 4, 1)	5.5- 4.5	5.5- 4.5	-1414.660
6( 3, 4)- 5( 4, 1)	5.5- 4.5	6.5- 5.5	-1446.992
6( 3, 4)- 5( 4, 1)	5.5- 4.5	7.5- 6.5	-1447.129
6( 3, 4)- 5( 4, 1)	5.5- 4.5	8.5- 7.5	-1455.957
6( 3, 4)- 5( 4, 1)	6.5- 5.5	3.5- 2.5	-4782.723
6( 3, 4)- 5( 4, 1)	6.5- 5.5	4.5- 3.5	-4476.004
6( 3, 4)- 5( 4, 1)	6.5- 5.5	5.5- 4.5	-4528.102
6( 3, 4)- 5( 4, 1)	6.5- 5.5	6.5- 5.5	-4545.871
6( 3, 4)- 5( 4, 1)	6.5- 5.5	7.5- 6.5	-4540.488
6( 3, 4)- 5( 4, 1)	6.5- 5.5	8.5- 7.5	-4553.344
6( 3, 4)- 5( 4, 1)	6.5- 5.5	9.5- 8.5	-4696.520
6( 5, 2)- 5( 4, 1)	5.5- 4.5	2.5- 1.5	1790.328
6( 5, 2)- 5( 4, 1)	5.5- 4.5	3.5- 2.5	1645.465
6( 5, 2)- 5( 4, 1)	5.5- 4.5	4.5- 3.5	1800.207
6( 5, 2)- 5( 4, 1)	5.5- 4.5	5.5- 4.5	1816.703
6( 5, 2)- 5( 4, 1)	5.5- 4.5	6.5- 5.5	1800.859
6( 5, 2)- 5( 4, 1)	5.5- 4.5	7.5- 6.5	1808.766
6( 5, 2)- 5( 4, 1)	5.5- 4.5	8.5- 7.5	1795.414
6( 5, 2)- 5( 4, 1)	6.5- 5.5	3.5- 2.5	-1611.707
6( 5, 2)- 5( 4, 1)	6.5- 5.5	4.5- 3.5	-1315.678
6( 5, 2)- 5( 4, 1)	6.5- 5.5	5.5- 4.5	-1370.242
6( 5, 2)- 5( 4, 1)	6.5- 5.5	6.5- 5.5	-1369.545

6( 5, 2)- 5( 4, 1)	6.5- 5.5	7.5- 6.5	-1365.386
6( 5, 2)- 5( 4, 1)	6.5- 5.5	8.5- 7.5	-1380.955
6( 5, 2)- 5( 4, 1)	6.5- 5.5	9.5- 8.5	-1391.415
6( 4, 3)- 5( 5, 0)	5.5- 4.5	2.5- 1.5	-1662.465
6( 4, 3)- 5( 5, 0)	5.5- 4.5	3.5- 2.5	-1699.187
6( 4, 3)- 5( 5, 0)	5.5- 4.5	4.5- 3.5	-1533.898
6( 4, 3)- 5( 5, 0)	5.5- 4.5	5.5- 4.5	-1519.504
6( 4, 3)- 5( 5, 0)	5.5- 4.5	6.5- 5.5	-1553.398
6( 4, 3)- 5( 5, 0)	5.5- 4.5	7.5- 6.5	-1556.254
6( 4, 3)- 5( 5, 0)	5.5- 4.5	8.5- 7.5	-1556.008
6( 4, 3)- 5( 5, 0)	6.5- 5.5	3.5- 2.5	-4076.432
6( 4, 3)- 5( 5, 0)	6.5- 5.5	4.5- 3.5	-3756.393
6( 4, 3)- 5( 5, 0)	6.5- 5.5	5.5- 4.5	-3808.775
6( 4, 3)- 5( 5, 0)	6.5- 5.5	6.5- 5.5	-3821.373
6( 4, 3)- 5( 5, 0)	6.5- 5.5	7.5- 6.5	-3822.727
6( 4, 3)- 5( 5, 0)	6.5- 5.5	8.5- 7.5	-3833.327
6( 4, 3)- 5( 5, 0)	6.5- 5.5	9.5- 8.5	-3978.982
6( 6, 1)- 5( 5, 0)	5.5- 4.5	2.5- 1.5	1793.945
6( 6, 1)- 5( 5, 0)	5.5- 4.5	3.5- 2.5	1636.691
6( 6, 1)- 5( 5, 0)	5.5- 4.5	4.5- 3.5	1825.863
6( 6, 1)- 5( 5, 0)	5.5- 4.5	5.5- 4.5	1820.613
6( 6, 1)- 5( 5, 0)	5.5- 4.5	6.5- 5.5	1802.727
6( 6, 1)- 5( 5, 0)	5.5- 4.5	7.5- 6.5	1805.449
6( 6, 1)- 5( 5, 0)	5.5- 4.5	8.5- 7.5	1799.957
6( 6, 1)- 5( 5, 0)	6.5- 5.5	3.5- 2.5	-938.051
6( 6, 1)- 5( 5, 0)	6.5- 5.5	4.5- 3.5	-624.388
6( 6, 1)- 5( 5, 0)	6.5- 5.5	5.5- 4.5	-687.218
6( 6, 1)- 5( 5, 0)	6.5- 5.5	6.5- 5.5	-696.571
6( 6, 1)- 5( 5, 0)	6.5- 5.5	7.5- 6.5	-691.995
6( 6, 1)- 5( 5, 0)	6.5- 5.5	8.5- 7.5	-698.969
6( 6, 1)- 5( 5, 0)	6.5- 5.5	9.5- 8.5	-727.421
7( 0, 7)- 6( 1, 6)	6.5- 5.5	3.5- 2.5	-327.431
7( 0, 7)- 6( 1, 6)	6.5- 5.5	4.5- 3.5	-15.519
7( 0, 7)- 6( 1, 6)	6.5- 5.5	5.5- 4.5	-93.118
7( 0, 7)- 6( 1, 6)	6.5- 5.5	6.5- 5.5	-107.147
7( 0, 7)- 6( 1, 6)	6.5- 5.5	7.5- 6.5	-99.210
7( 0, 7)- 6( 1, 6)	6.5- 5.5	8.5- 7.5	-101.607
7( 0, 7)- 6( 1, 6)	6.5- 5.5	9.5- 8.5	-101.141
7( 0, 7)- 6( 1, 6)	7.5- 6.5	4.5- 3.5	-1647.875
7( 0, 7)- 6( 1, 6)	7.5- 6.5	5.5- 4.5	-1799.570
7( 0, 7)- 6( 1, 6)	7.5- 6.5	6.5- 5.5	-1780.422
7( 0, 7)- 6( 1, 6)	7.5- 6.5	7.5- 6.5	-1785.461
7( 0, 7)- 6( 1, 6)	7.5- 6.5	8.5- 7.5	-1788.867
7( 0, 7)- 6( 1, 6)	7.5- 6.5	9.5- 8.5	-1797.754
7( 0, 7)- 6( 1, 6)	7.5- 6.5	10.5- 9.5	-1807.570
7( 2, 5)- 6( 1, 6)	6.5- 5.5	3.5- 2.5	4109.828
7( 2, 5)- 6( 1, 6)	6.5- 5.5	4.5- 3.5	4360.301
7( 2, 5)- 6( 1, 6)	6.5- 5.5	5.5- 4.5	4285.715
7( 2, 5)- 6( 1, 6)	6.5- 5.5	6.5- 5.5	4289.656
7( 2, 5)- 6( 1, 6)	6.5- 5.5	7.5- 6.5	4289.695
7( 2, 5)- 6( 1, 6)	6.5- 5.5	8.5- 7.5	4307.484
7( 2, 5)- 6( 1, 6)	6.5- 5.5	9.5- 8.5	4329.109
7( 2, 5)- 6( 1, 6)	7.5- 6.5	4.5- 3.5	1740.562
7( 2, 5)- 6( 1, 6)	7.5- 6.5	5.5- 4.5	1580.430
7( 2, 5)- 6( 1, 6)	7.5- 6.5	6.5- 5.5	1591.281
7( 2, 5)- 6( 1, 6)	7.5- 6.5	7.5- 6.5	1600.937

7( 2, 5)- 6( 1, 6)	7.5- 6.5	8.5- 7.5	1586.105
7( 2, 5)- 6( 1, 6)	7.5- 6.5	9.5- 8.5	1584.117
7( 2, 5)- 6( 1, 6)	7.5- 6.5	10.5- 9.5	1716.211
7( 4, 3)- 6( 1, 6)	6.5- 5.5	3.5- 2.5	6724.863
7( 4, 3)- 6( 1, 6)	6.5- 5.5	4.5- 3.5	6923.391
7( 4, 3)- 6( 1, 6)	6.5- 5.5	5.5- 4.5	6812.766
7( 4, 3)- 6( 1, 6)	6.5- 5.5	6.5- 5.5	6823.836
7( 4, 3)- 6( 1, 6)	6.5- 5.5	7.5- 6.5	6825.766
7( 4, 3)- 6( 1, 6)	6.5- 5.5	8.5- 7.5	6839.723
7( 4, 3)- 6( 1, 6)	6.5- 5.5	9.5- 8.5	6868.309
7( 4, 3)- 6( 1, 6)	7.5- 6.5	4.5- 3.5	4980.062
7( 4, 3)- 6( 1, 6)	7.5- 6.5	5.5- 4.5	4806.227
7( 4, 3)- 6( 1, 6)	7.5- 6.5	6.5- 5.5	4807.988
7( 4, 3)- 6( 1, 6)	7.5- 6.5	7.5- 6.5	4831.441
7( 4, 3)- 6( 1, 6)	7.5- 6.5	8.5- 7.5	4822.223
7( 4, 3)- 6( 1, 6)	7.5- 6.5	9.5- 8.5	4822.312
7( 4, 3)- 6( 1, 6)	7.5- 6.5	10.5- 9.5	5071.457
7( 1, 6)- 6( 2, 5)	6.5- 5.5	3.5- 2.5	-326.223
7( 1, 6)- 6( 2, 5)	6.5- 5.5	4.5- 3.5	-37.898
7( 1, 6)- 6( 2, 5)	6.5- 5.5	5.5- 4.5	-121.812
7( 1, 6)- 6( 2, 5)	6.5- 5.5	6.5- 5.5	-132.574
7( 1, 6)- 6( 2, 5)	6.5- 5.5	7.5- 6.5	-112.387
7( 1, 6)- 6( 2, 5)	6.5- 5.5	8.5- 7.5	-112.277
7( 1, 6)- 6( 2, 5)	6.5- 5.5	9.5- 8.5	-157.348
7( 1, 6)- 6( 2, 5)	7.5- 6.5	4.5- 3.5	-1640.949
7( 1, 6)- 6( 2, 5)	7.5- 6.5	5.5- 4.5	-1797.711
7( 1, 6)- 6( 2, 5)	7.5- 6.5	6.5- 5.5	-1781.496
7( 1, 6)- 6( 2, 5)	7.5- 6.5	7.5- 6.5	-1773.000
7( 1, 6)- 6( 2, 5)	7.5- 6.5	8.5- 7.5	-1784.391
7( 1, 6)- 6( 2, 5)	7.5- 6.5	9.5- 8.5	-1795.844
7( 1, 6)- 6( 2, 5)	7.5- 6.5	10.5- 9.5	-1811.113
7( 3, 4)- 6( 2, 5)	6.5- 5.5	3.5- 2.5	1739.000
7( 3, 4)- 6( 2, 5)	6.5- 5.5	4.5- 3.5	1958.348
7( 3, 4)- 6( 2, 5)	6.5- 5.5	5.5- 4.5	1857.777
7( 3, 4)- 6( 2, 5)	6.5- 5.5	6.5- 5.5	1871.199
7( 3, 4)- 6( 2, 5)	6.5- 5.5	7.5- 6.5	1875.695
7( 3, 4)- 6( 2, 5)	6.5- 5.5	8.5- 7.5	1890.672
7( 3, 4)- 6( 2, 5)	6.5- 5.5	9.5- 8.5	1872.344
7( 3, 4)- 6( 2, 5)	7.5- 6.5	4.5- 3.5	1689.453
7( 3, 4)- 6( 2, 5)	7.5- 6.5	5.5- 4.5	1529.953
7( 3, 4)- 6( 2, 5)	7.5- 6.5	6.5- 5.5	1534.320
7( 3, 4)- 6( 2, 5)	7.5- 6.5	7.5- 6.5	1556.113
7( 3, 4)- 6( 2, 5)	7.5- 6.5	8.5- 7.5	1544.758
7( 3, 4)- 6( 2, 5)	7.5- 6.5	9.5- 8.5	1530.059
7( 3, 4)- 6( 2, 5)	7.5- 6.5	10.5- 9.5	1539.148
7( 5, 2)- 6( 2, 5)	6.5- 5.5	3.5- 2.5	4881.891
7( 5, 2)- 6( 2, 5)	6.5- 5.5	4.5- 3.5	5065.594
7( 5, 2)- 6( 2, 5)	6.5- 5.5	5.5- 4.5	4951.562
7( 5, 2)- 6( 2, 5)	6.5- 5.5	6.5- 5.5	4960.008
7( 5, 2)- 6( 2, 5)	6.5- 5.5	7.5- 6.5	4961.828
7( 5, 2)- 6( 2, 5)	6.5- 5.5	8.5- 7.5	4973.437
7( 5, 2)- 6( 2, 5)	6.5- 5.5	9.5- 8.5	4961.949
7( 5, 2)- 6( 2, 5)	7.5- 6.5	4.5- 3.5	4693.738
7( 5, 2)- 6( 2, 5)	7.5- 6.5	5.5- 4.5	4518.457
7( 5, 2)- 6( 2, 5)	7.5- 6.5	6.5- 5.5	4497.594
7( 5, 2)- 6( 2, 5)	7.5- 6.5	7.5- 6.5	4521.930

7( 5, 2)- 6( 2, 5)	7.5- 6.5	8.5- 7.5	4524.687
7( 5, 2)- 6( 2, 5)	7.5- 6.5	9.5- 8.5	4524.230
7( 5, 2)- 6( 2, 5)	7.5- 6.5	10.5- 9.5	4623.527
7( 0, 7)- 6( 3, 4)	6.5- 5.5	3.5- 2.5	-5487.059
7( 0, 7)- 6( 3, 4)	6.5- 5.5	4.5- 3.5	-5065.844
7( 0, 7)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	-5153.348
7( 0, 7)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	-5163.582
7( 0, 7)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	-5154.344
7( 0, 7)- 6( 3, 4)	6.5- 5.5	8.5- 7.5	-5159.699
7( 0, 7)- 6( 3, 4)	6.5- 5.5	9.5- 8.5	-5206.656
7( 0, 7)- 6( 3, 4)	7.5- 6.5	4.5- 3.5	-5022.996
7( 0, 7)- 6( 3, 4)	7.5- 6.5	5.5- 4.5	-5169.605
7( 0, 7)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	-5152.152
7( 0, 7)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	-5154.117
7( 0, 7)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	-5156.293
7( 0, 7)- 6( 3, 4)	7.5- 6.5	9.5- 8.5	-5169.457
7( 0, 7)- 6( 3, 4)	7.5- 6.5	10.5- 9.5	-5330.363
7( 2, 5)- 6( 3, 4)	6.5- 5.5	3.5- 2.5	-1049.801
7( 2, 5)- 6( 3, 4)	6.5- 5.5	4.5- 3.5	-690.023
7( 2, 5)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	-774.516
7( 2, 5)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	-766.777
7( 2, 5)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	-765.437
7( 2, 5)- 6( 3, 4)	6.5- 5.5	8.5- 7.5	-750.609
7( 2, 5)- 6( 3, 4)	6.5- 5.5	9.5- 8.5	-776.406
7( 2, 5)- 6( 3, 4)	7.5- 6.5	4.5- 3.5	-1634.559
7( 2, 5)- 6( 3, 4)	7.5- 6.5	5.5- 4.5	-1789.605
7( 2, 5)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	-1780.449
7( 2, 5)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	-1767.719
7( 2, 5)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	-1781.320
7( 2, 5)- 6( 3, 4)	7.5- 6.5	9.5- 8.5	-1787.586
7( 2, 5)- 6( 3, 4)	7.5- 6.5	10.5- 9.5	-1806.582
7( 4, 3)- 6( 3, 4)	6.5- 5.5	3.5- 2.5	1565.234
7( 4, 3)- 6( 3, 4)	6.5- 5.5	4.5- 3.5	1873.066
7( 4, 3)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	1752.535
7( 4, 3)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	1767.402
7( 4, 3)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	1770.633
7( 4, 3)- 6( 3, 4)	6.5- 5.5	8.5- 7.5	1781.629
7( 4, 3)- 6( 3, 4)	6.5- 5.5	9.5- 8.5	1762.793
7( 4, 3)- 6( 3, 4)	7.5- 6.5	4.5- 3.5	1604.941
7( 4, 3)- 6( 3, 4)	7.5- 6.5	5.5- 4.5	1436.191
7( 4, 3)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	1436.258
7( 4, 3)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	1462.785
7( 4, 3)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	1454.797
7( 4, 3)- 6( 3, 4)	7.5- 6.5	9.5- 8.5	1450.609
7( 4, 3)- 6( 3, 4)	7.5- 6.5	10.5- 9.5	1548.664
7( 6, 1)- 6( 3, 4)	6.5- 5.5	3.5- 2.5	4950.980
7( 6, 1)- 6( 3, 4)	6.5- 5.5	4.5- 3.5	5160.918
7( 6, 1)- 6( 3, 4)	6.5- 5.5	5.5- 4.5	5058.152
7( 6, 1)- 6( 3, 4)	6.5- 5.5	6.5- 5.5	5050.215
7( 6, 1)- 6( 3, 4)	6.5- 5.5	7.5- 6.5	5047.734
7( 6, 1)- 6( 3, 4)	6.5- 5.5	8.5- 7.5	5059.473
7( 6, 1)- 6( 3, 4)	6.5- 5.5	9.5- 8.5	5046.176
7( 6, 1)- 6( 3, 4)	7.5- 6.5	4.5- 3.5	3978.064
7( 6, 1)- 6( 3, 4)	7.5- 6.5	5.5- 4.5	3806.268
7( 6, 1)- 6( 3, 4)	7.5- 6.5	6.5- 5.5	3784.729
7( 6, 1)- 6( 3, 4)	7.5- 6.5	7.5- 6.5	3815.351

7( 6, 1)- 6( 3, 4)	7.5- 6.5	8.5- 7.5	3810.751
7( 6, 1)- 6( 3, 4)	7.5- 6.5	9.5- 8.5	3821.285
7( 6, 1)- 6( 3, 4)	7.5- 6.5	10.5- 9.5	3949.865
7( 1, 6)- 6( 4, 3)	6.5- 5.5	3.5- 2.5	-3689.746
7( 1, 6)- 6( 4, 3)	6.5- 5.5	4.5- 3.5	-3191.687
7( 1, 6)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	-3282.687
7( 1, 6)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	-3289.687
7( 1, 6)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	-3272.781
7( 1, 6)- 6( 4, 3)	6.5- 5.5	8.5- 7.5	-3274.348
7( 1, 6)- 6( 4, 3)	6.5- 5.5	9.5- 8.5	-3326.574
7( 1, 6)- 6( 4, 3)	7.5- 6.5	4.5- 3.5	-4945.539
7( 1, 6)- 6( 4, 3)	7.5- 6.5	5.5- 4.5	-5089.012
7( 1, 6)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	-5074.594
7( 1, 6)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	-5075.875
7( 1, 6)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	-5086.848
7( 1, 6)- 6( 4, 3)	7.5- 6.5	9.5- 8.5	-5087.445
7( 1, 6)- 6( 4, 3)	7.5- 6.5	10.5- 9.5	-5118.410
7( 3, 4)- 6( 4, 3)	6.5- 5.5	3.5- 2.5	-1624.523
7( 3, 4)- 6( 4, 3)	6.5- 5.5	4.5- 3.5	-1195.441
7( 3, 4)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	-1303.098
7( 3, 4)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	-1285.914
7( 3, 4)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	-1284.699
7( 3, 4)- 6( 4, 3)	6.5- 5.5	8.5- 7.5	-1271.398
7( 3, 4)- 6( 4, 3)	6.5- 5.5	9.5- 8.5	-1296.883
7( 3, 4)- 6( 4, 3)	7.5- 6.5	4.5- 3.5	-1615.137
7( 3, 4)- 6( 4, 3)	7.5- 6.5	5.5- 4.5	-1761.348
7( 3, 4)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	-1758.777
7( 3, 4)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	-1746.762
7( 3, 4)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	-1757.699
7( 3, 4)- 6( 4, 3)	7.5- 6.5	9.5- 8.5	-1761.543
7( 3, 4)- 6( 4, 3)	7.5- 6.5	10.5- 9.5	-1768.148
7( 5, 2)- 6( 4, 3)	6.5- 5.5	3.5- 2.5	1518.367
7( 5, 2)- 6( 4, 3)	6.5- 5.5	4.5- 3.5	1911.805
7( 5, 2)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	1790.687
7( 5, 2)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	1802.895
7( 5, 2)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	1801.434
7( 5, 2)- 6( 4, 3)	6.5- 5.5	8.5- 7.5	1811.367
7( 5, 2)- 6( 4, 3)	6.5- 5.5	9.5- 8.5	1792.723
7( 5, 2)- 6( 4, 3)	7.5- 6.5	4.5- 3.5	1389.148
7( 5, 2)- 6( 4, 3)	7.5- 6.5	5.5- 4.5	1227.156
7( 5, 2)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	1204.496
7( 5, 2)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	1219.055
7( 5, 2)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	1222.230
7( 5, 2)- 6( 4, 3)	7.5- 6.5	9.5- 8.5	1232.629
7( 5, 2)- 6( 4, 3)	7.5- 6.5	10.5- 9.5	1316.230
7( 7, 0)- 6( 4, 3)	6.5- 5.5	3.5- 2.5	4956.559
7( 7, 0)- 6( 4, 3)	6.5- 5.5	4.5- 3.5	5276.145
7( 7, 0)- 6( 4, 3)	6.5- 5.5	5.5- 4.5	5168.031
7( 7, 0)- 6( 4, 3)	6.5- 5.5	6.5- 5.5	5170.562
7( 7, 0)- 6( 4, 3)	6.5- 5.5	7.5- 6.5	5164.344
7( 7, 0)- 6( 4, 3)	6.5- 5.5	8.5- 7.5	5186.258
7( 7, 0)- 6( 4, 3)	6.5- 5.5	9.5- 8.5	5156.027
7( 7, 0)- 6( 4, 3)	7.5- 6.5	4.5- 3.5	3381.702
7( 7, 0)- 6( 4, 3)	7.5- 6.5	5.5- 4.5	3179.466
7( 7, 0)- 6( 4, 3)	7.5- 6.5	6.5- 5.5	3158.613
7( 7, 0)- 6( 4, 3)	7.5- 6.5	7.5- 6.5	3178.828



7( 7, 0)- 6( 4, 3)	7.5- 6.5	8.5- 7.5	3179.865
7( 7, 0)- 6( 4, 3)	7.5- 6.5	9.5- 8.5	3193.872
7( 7, 0)- 6( 4, 3)	7.5- 6.5	10.5- 9.5	3331.606
7( 2, 5)- 6( 5, 2)	6.5- 5.5	3.5- 2.5	-4439.488
7( 2, 5)- 6( 5, 2)	6.5- 5.5	4.5- 3.5	-3917.883
7( 2, 5)- 6( 5, 2)	6.5- 5.5	5.5- 4.5	-4013.004
7( 2, 5)- 6( 5, 2)	6.5- 5.5	6.5- 5.5	-3998.141
7( 2, 5)- 6( 5, 2)	6.5- 5.5	7.5- 6.5	-4013.289
7( 2, 5)- 6( 5, 2)	6.5- 5.5	8.5- 7.5	-4006.504
7( 2, 5)- 6( 5, 2)	6.5- 5.5	9.5- 8.5	-4027.777
7( 2, 5)- 6( 5, 2)	7.5- 6.5	4.5- 3.5	-4805.574
7( 2, 5)- 6( 5, 2)	7.5- 6.5	5.5- 4.5	-4949.934
7( 2, 5)- 6( 5, 2)	7.5- 6.5	6.5- 5.5	-4938.312
7( 2, 5)- 6( 5, 2)	7.5- 6.5	7.5- 6.5	-4944.047
7( 2, 5)- 6( 5, 2)	7.5- 6.5	8.5- 7.5	-4956.426
7( 2, 5)- 6( 5, 2)	7.5- 6.5	9.5- 8.5	-4959.977
7( 2, 5)- 6( 5, 2)	7.5- 6.5	10.5- 9.5	-5111.687
7( 4, 3)- 6( 5, 2)	6.5- 5.5	3.5- 2.5	-1824.453
7( 4, 3)- 6( 5, 2)	6.5- 5.5	4.5- 3.5	-1354.793
7( 4, 3)- 6( 5, 2)	6.5- 5.5	5.5- 4.5	-1485.953
7( 4, 3)- 6( 5, 2)	6.5- 5.5	6.5- 5.5	-1463.961
7( 4, 3)- 6( 5, 2)	6.5- 5.5	7.5- 6.5	-1477.219
7( 4, 3)- 6( 5, 2)	6.5- 5.5	8.5- 7.5	-1474.266
7( 4, 3)- 6( 5, 2)	6.5- 5.5	9.5- 8.5	-1488.578
7( 4, 3)- 6( 5, 2)	7.5- 6.5	4.5- 3.5	-1566.075
7( 4, 3)- 6( 5, 2)	7.5- 6.5	5.5- 4.5	-1724.137
7( 4, 3)- 6( 5, 2)	7.5- 6.5	6.5- 5.5	-1721.605
7( 4, 3)- 6( 5, 2)	7.5- 6.5	7.5- 6.5	-1713.543
7( 4, 3)- 6( 5, 2)	7.5- 6.5	8.5- 7.5	-1720.309
7( 4, 3)- 6( 5, 2)	7.5- 6.5	9.5- 8.5	-1721.781
7( 4, 3)- 6( 5, 2)	7.5- 6.5	10.5- 9.5	-1756.441
7( 6, 1)- 6( 5, 2)	6.5- 5.5	3.5- 2.5	1561.293
7( 6, 1)- 6( 5, 2)	6.5- 5.5	4.5- 3.5	1933.059
7( 6, 1)- 6( 5, 2)	6.5- 5.5	5.5- 4.5	1819.664
7( 6, 1)- 6( 5, 2)	6.5- 5.5	6.5- 5.5	1818.852
7( 6, 1)- 6( 5, 2)	6.5- 5.5	7.5- 6.5	1799.883
7( 6, 1)- 6( 5, 2)	6.5- 5.5	8.5- 7.5	1803.578
7( 6, 1)- 6( 5, 2)	6.5- 5.5	9.5- 8.5	1794.805
7( 6, 1)- 6( 5, 2)	7.5- 6.5	4.5- 3.5	807.047
7( 6, 1)- 6( 5, 2)	7.5- 6.5	5.5- 4.5	645.939
7( 6, 1)- 6( 5, 2)	7.5- 6.5	6.5- 5.5	626.866
7( 6, 1)- 6( 5, 2)	7.5- 6.5	7.5- 6.5	639.022
7( 6, 1)- 6( 5, 2)	7.5- 6.5	8.5- 7.5	635.645
7( 6, 1)- 6( 5, 2)	7.5- 6.5	9.5- 8.5	648.894
7( 6, 1)- 6( 5, 2)	7.5- 6.5	10.5- 9.5	644.759
7( 3, 4)- 6( 6, 1)	6.5- 5.5	3.5- 2.5	-5080.934
7( 3, 4)- 6( 6, 1)	6.5- 5.5	4.5- 3.5	-4531.320
7( 3, 4)- 6( 6, 1)	6.5- 5.5	5.5- 4.5	-4662.859
7( 3, 4)- 6( 6, 1)	6.5- 5.5	6.5- 5.5	-4626.031
7( 3, 4)- 6( 6, 1)	6.5- 5.5	7.5- 6.5	-4640.824
7( 3, 4)- 6( 6, 1)	6.5- 5.5	8.5- 7.5	-4633.102
7( 3, 4)- 6( 6, 1)	6.5- 5.5	9.5- 8.5	-4652.848
7( 3, 4)- 6( 6, 1)	7.5- 6.5	4.5- 3.5	-4753.516
7( 3, 4)- 6( 6, 1)	7.5- 6.5	5.5- 4.5	-4895.352
7( 3, 4)- 6( 6, 1)	7.5- 6.5	6.5- 5.5	-4878.332
7( 3, 4)- 6( 6, 1)	7.5- 6.5	7.5- 6.5	-4873.562

7( 3, 4)- 6( 6, 1)	7.5- 6.5	8.5- 7.5	-4888.430
7( 3, 4)- 6( 6, 1)	7.5- 6.5	9.5- 8.5	-4895.898
7( 3, 4)- 6( 6, 1)	7.5- 6.5	10.5- 9.5	-5017.707
7( 5, 2)- 6( 6, 1)	6.5- 5.5	3.5- 2.5	-1938.043
7( 5, 2)- 6( 6, 1)	6.5- 5.5	4.5- 3.5	-1424.074
7( 5, 2)- 6( 6, 1)	6.5- 5.5	5.5- 4.5	-1569.074
7( 5, 2)- 6( 6, 1)	6.5- 5.5	6.5- 5.5	-1537.223
7( 5, 2)- 6( 6, 1)	6.5- 5.5	7.5- 6.5	-1554.691
7( 5, 2)- 6( 6, 1)	6.5- 5.5	8.5- 7.5	-1550.336
7( 5, 2)- 6( 6, 1)	6.5- 5.5	9.5- 8.5	-1563.242
7( 5, 2)- 6( 6, 1)	7.5- 6.5	4.5- 3.5	-1749.232
7( 5, 2)- 6( 6, 1)	7.5- 6.5	5.5- 4.5	-1906.848
7( 5, 2)- 6( 6, 1)	7.5- 6.5	6.5- 5.5	-1915.062
7( 5, 2)- 6( 6, 1)	7.5- 6.5	7.5- 6.5	-1907.748
7( 5, 2)- 6( 6, 1)	7.5- 6.5	8.5- 7.5	-1908.501
7( 5, 2)- 6( 6, 1)	7.5- 6.5	9.5- 8.5	-1901.729
7( 5, 2)- 6( 6, 1)	7.5- 6.5	10.5- 9.5	-1933.330
7( 7, 0)- 6( 6, 1)	6.5- 5.5	3.5- 2.5	1500.148
7( 7, 0)- 6( 6, 1)	6.5- 5.5	4.5- 3.5	1940.266
7( 7, 0)- 6( 6, 1)	6.5- 5.5	5.5- 4.5	1808.270
7( 7, 0)- 6( 6, 1)	6.5- 5.5	6.5- 5.5	1830.445
7( 7, 0)- 6( 6, 1)	6.5- 5.5	7.5- 6.5	1808.219
7( 7, 0)- 6( 6, 1)	6.5- 5.5	8.5- 7.5	1824.555
7( 7, 0)- 6( 6, 1)	6.5- 5.5	9.5- 8.5	1800.062
7( 7, 0)- 6( 6, 1)	7.5- 6.5	4.5- 3.5	243.322
7( 7, 0)- 6( 6, 1)	7.5- 6.5	5.5- 4.5	45.461
7( 7, 0)- 6( 6, 1)	7.5- 6.5	6.5- 5.5	39.055
7( 7, 0)- 6( 6, 1)	7.5- 6.5	7.5- 6.5	52.026
7( 7, 0)- 6( 6, 1)	7.5- 6.5	8.5- 7.5	49.134
7( 7, 0)- 6( 6, 1)	7.5- 6.5	9.5- 8.5	59.514
7( 7, 0)- 6( 6, 1)	7.5- 6.5	10.5- 9.5	82.045

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