CHAPTER 3

THEORY

This chapter is divided into three sections. In the first section we apply the method developed by Anderson and Ramsey (AND 66) for the symmetrization of the hyperfine and Zeeman Hamiltonian to symmetric rotors of the $XY_3$-type. The second section contains the discussion of the Zeeman effect of the asymmetric rotor. In the last section the Zeeman Hamiltonian for an internal rotor is derived.

3.1 Symmetric top molecules

The advantage of symmetrization of the hyperfine Hamiltonian has first been recognized by Anderson and Ramsey (AND 66) for tetrahedral molecules. This theory has been extended and generalized by Yi, Ozier and Anderson (YI 68) and by Ozier Crapo and Lee (OZI 68). The method however was only applied to spherical top molecules. In some special cases the theory was used for $C_{3v}$ molecules (WOF 70).

In this section the method of symmetrization of the hyperfine and Zeeman Hamiltonian is applied to general $C_{3v}$ type molecules of the form $XY_3$ or $XAY_3$, where $A$ denotes a nucleus with zero magnetic moment on the symmetry axis.

The geometry of the $XAY_3$-molecule is given in Fig. 3.1.

The $AX$-axis is a threefold symmetry axis and each $XAY$ plane is a plane of symmetry. We call the $AX$ axis the $c$-axis and choose the $b$-axis perpendicular to the $c$-axis in one of the symmetry planes. The $a$-axis is chosen such that the $abc$-reference system is a right handed one. We call this system the molecule fixed reference system.

The invariance group of the molecule is now

$$C_{3v} = \{1, C_{3c}, C_{3c}', \sigma_a, \sigma_a C_{3c}, \sigma_a C_{3c}', \sigma_a^2 \} \quad (3.1)$$

where $C_{3c}$ is an (active) rotation about the $c$-axis over $2\pi/3$, and $\sigma_a$ a reflection in the $bc$-plane. It is easy to see that
the elements of the $C_{3v}$ set constitute a group.

The symmetry operations of the $C_{3v}$ group permute the identical Y-nuclei. There is a one to one correspondence between the permutations of the Y-nuclei and the symmetry operations. For the situation of Fig. 3.1 we have

$$C_{3c}: Y_1 \rightarrow Y_3; Y_2 \rightarrow Y_1; Y_3 \rightarrow Y_2$$

in short (132)

$$\sigma_a : (23) \quad (3.2)$$

The group of permutations of the three Y-nuclei is called the symmetric group of order three $S_3$. In total

$$S_3 = \{1, (132), (123), (23), (13), (12)\} \quad (3.3)$$

### 3.1.1 The wavefunction

The molecular wavefunction $u$ is a function of the electronic and nuclear spatial and spin coordinates. In the Born-Oppenheimer approximation the function $u$ can be written as

$$u = \Psi_{\text{el}} \Psi_{\text{nucl}}' \quad (3.4)$$

where $\Psi_{\text{el}}$ and $\Psi_{\text{nucl}}$ is the electronic and nuclear part of the total wavefunction respectively. We assume that the electronic function is known. The nuclear wavefunction can be written as

$$\Psi_{\text{nucl}} = \Psi_{\text{vib}} \Psi_{\text{rot}} \chi' \quad (3.5)$$

where $\Psi_{\text{rot}}$ is the rotational, $\Psi_{\text{vib}}$ the vibrational and $\chi$ is the nuclear spin wavefunction. This decoupling into a vibrational and rotational part of the nuclear function is only valid in the absence of vibration rotation coupling. Assuming that the molecule is in the vibrational ground state we only consider the function

$$\Psi = \Psi_{\text{rot}} \chi \quad (3.6)$$

(a) The rotational wavefunction

Symmetry shows that the moments of inertia for the XAY$_3$ molecule about the a and b-axes are equal. Consequently the rotational hamiltonian is

$$H_{\text{rot}} = A J^2 + (C-A) K^2 \quad (3.7)$$

where $J=M+\frac{1}{2}$ is the total angular momentum of the molecule, $M$ is the nuclear and $\frac{1}{2}$ the electronic contribution to it; $A$ and $C$ is the rotational constant about the a and c-axis respectively. We assume that the molecule is in the electronic ground state in which case $<L^2> = 0$ and hence (in zeroth order) $<N> = <J>$.

The hamiltonian of Eq.(3.7) is invariant under any rotation about the molecular symmetry axis and under a rotation over $\pi$ about an axis perpendicular to the symmetry axis. The invariance group is the $D_{3h}$ group. The solutions of the Schrödinger equation

$$H_{\text{rot}} \Psi_{\text{rot}} = E_{\text{rot}} \Psi_{\text{rot}}$$

are the well known symmetric top eigenfunctions. If $\psi, \theta$ and $\phi$ are the Euler angles of the molecule, then we have in the convention of Edmonds (EDM 57)

$$\Psi_{\text{rot}}(\psi, \theta, \phi) = \frac{(2J+1)}{8\pi^2} S^{(J)}_{MK}(\psi, \theta, \phi) \quad (3.8a)$$

$$E_{\text{rot}} = A J(J+1) + (C-A) K^2 \quad (3.8b)$$

$$J = 0, 1, 2, \ldots \quad (3.8c)$$

$$K = J, J-1, \ldots, 0 \quad (3.8d)$$

$$M = \pm J, \pm (J-1), \ldots, 0 \quad (3.8e)$$
In Eq. (3.8a) the $c_{MN}^{(J)}$ are the matrix elements of the J-th irreducible representation of the three-dimensional rotation group $SO(3)$ on the basis of the spherical harmonic functions. For a given rotational energy $E_{\text{rot}}$ we have $2(2J+1)$ rotational wavefunctions. The Hamiltonian of Eq. (3.7) is not only invariant under the $D_\infty$-group but also under inversion at the origin. The inversion operator $J$, commutes with any rotation, and from the parity of the spherical harmonics follows

$$J c_{MK}^{(J)} (\psi\varphi) = (-1)^J c_{MK}^{(J)} (\psi\varphi) \quad (3.9)$$

The factor $(-1)^J$ is the parity of the $c_{MK}^{(J)}$ function.

(b) The spin function

Let $I_K$ be the angular momentum associated with the K-th nucleus and

$$I_{23} = I_2 + I_3 \quad (3.10)$$

then the basis functions can be written as

$$x_{I_{23}} (I_T^M) = (i^T) I_{23} I_T I_M \quad (3.11)$$

i.e. eigenfunctions of the $I_2^2, I_3^2, I_{23}^2, I_T^2$ and $I_T$ operators; $I_1 = I_2 = I_3 = I_T$ is the spin of the Y-nucleus.

For a given $I_T$ and $M_T$ there will in general be a number of possible basis functions depending on $I_{23}$. Let $V$ be the space spanned by these functions. Under the permutations in Eq. (3.3) the vector $I_T$ always transforms into itself. So $I_T$ and $M_T$ are conserved under $S_3$. The permutations therefore cause a one to one mapping of the space $V$ onto itself. The so formed representation of $S_3$ is in general reducible. The characters of the irreducible representations of $S_3$ are given in Table 3.1, and from the basis functions in Eq. (3.11) linear combinations can be formed, which transform under $S_3$ as one of the irreducible representations. The new basis functions are defined as

$$\Gamma_{I_1}^{\Gamma} (I_T^M) = \sum_{I_{23}} C_{I_{23}}^{I_1 I_T} x_{I_{23}} (I_T^M) \quad (j=1, \ldots, n_{\Gamma}) \quad (3.12)$$

where $\Gamma$ can be $A_1, A_2$ or $E$; $\xi$ is one for the $A_1$ and $A_2$ representations and can take the values 1 and 2 for the $E$-type representation; $n_{\Gamma}$ can be zero.

<table>
<thead>
<tr>
<th>$S_3$</th>
<th>1</th>
<th>(123)</th>
<th>(23)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.1 Character table of $S_3$.

We note that the coefficients $c_{I_{23}}^{I_1 I_T}$ do not depend upon $M_T$ as can be seen by applying the $I_T$ operators. The matrix of the $c_{I_{23}}^{I_1 I_T}$ is unitary.

From Table 3-1 we see that for all $\rho\in S_3$

$$\rho x_{I_1} = x_{j} \quad \rho x_{j} = \pm x_{j} \quad (3.13a)$$

where $\rho$ is zero or one depending on whether $\rho$ is even or odd respectively. On the two dimensional \(\{x_j^{E,1}, x_j^{E,2}\}\)

$$\begin{pmatrix} e^{2\pi i/3} & 0 \\ 0 & e^{-2\pi i/3} \end{pmatrix} \quad (23) \rightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (3.13c)$$
The representation of the other permutations on this basis can be found by expressing them as a product of these two basic operations. The coefficients \( c^i_{j,K} \) are discussed in Appendix I.

(a) The total wavefunction

The total wavefunction must obey the Pauli exclusion principle under an interchange of two identical Y-nuclei. Consider a \((J,J)\) rotational level. First assume \( K \neq 0 \). Without loss of generality we may take \( K > 0 \).

The spin function can belong to \( A_1 \), \( A_2 \) or \( E \) symmetry. We shall treat these cases here separately.

I. Spin function of \( A_1 \) symmetry

For a given \( I \) and \( M \) we have the basis functions

\[
\{|JKM> \text{ and } |J-KM>\}
\]

where \( M = -J, \ldots, J \) and \( j=1, \ldots, \eta \). The two independent symmetry operations of the \( C_3 \)-group are \( C_3 \) and \( \sigma_a \). Expressed in the Euler angles \( \psi, \theta \) and \( \varphi \) we have

\[
C_3: \psi \to \psi, \theta \to \theta, \varphi \to \varphi + 2\pi/3
\]

However \( \sigma_a \) is not a rotation, but a reflection. We have

\[
\sigma_a = J C_2 a
\]

\[
C_2 a: \psi \to \psi + \pi, \theta \to \pi - \theta, \varphi \to 2\pi - \varphi
\]

Because of the properties of the \( \delta_{MK}^{(J)}(\psi \varphi) \) we have

\[
C_3 c \delta_{MK}^{(J)}(\psi \varphi) = e^{2\pi iK/3} \delta_{MK}^{(J)}(\psi \varphi)
\]

(3.15a)

\[
C_2 a \delta_{MK}^{(J)}(\psi \varphi) = (-1)^J \delta_{MK}^{(J)}(\psi \varphi)
\]

(3.15b)

So on the basis of (3.14) we get

\[
c_3 = (132) \begin{pmatrix}
0 & e^{2\pi iK/3} \\
0 & e^{-2\pi iK/3}
\end{pmatrix}
\]

(3.16a)

\[
\sigma_a = J C_2 a = (23) \begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}
\]

(3.16b)

The first operation represents an even permutation of the Y-nuclei. The Pauli principle states that for both bosons and fermions the wavefunction should be invariant. This can only be satisfied if \( K = 3n \), where \( n \) is an integer.

The second operation is an odd permutation of the Y-nuclei. The appropriate wavefunction obeying the Pauli principle should be symmetric (antisymmetric) under this operation if the Y-nuclei are bosons (fermions). Consequently the following linear combinations must be taken

\[
\{|JKM> + (-1)^{J+\gamma} |J-KM>\}
\]

(3.17)

where \( \gamma \) can take the values zero or one. The factor \((-1)^J\) is introduced for calculation purposes only. Operating with \( \sigma_a \) on this wavefunction yields

\[
\sigma_a |\psi_j> = (-1)^{J+\gamma} |\psi_j>
\]

(3.18)
So for bosons $\gamma = J(\text{mod.2})$ and for fermions $\gamma = J+1(\text{mod.2})$

II. Spin function of $A_2$-symmetry

The procedure of deriving the total wavefunction for this case is the same as above. The matrix for $C_3^c$ is identical with the one of Eq(3.16a) while the matrix of $\sigma_a$ is the negative of the matrix in Eq(3.17b). Again $K$ must be a multiple of three, and the wavefunctions become

$$|\psi_j^A\rangle = \frac{1}{\sqrt{2}} \left( |JM\rangle + (-1)^{J+\gamma} |J-KM\rangle \right) X_j^A$$

where again $\gamma$ can be zero or one. Furthermore

$$\sigma_a |\psi_j^A\rangle = (-1)^{J+\gamma+1} |\psi_j^A\rangle$$

So for bosons $\gamma = J(\text{mod.2})$, and for fermions $\gamma = J+1(\text{mod.2})$

III. Spin function of $E$-symmetry

In this case the basis functions for a given $I, M$, and $M$ are

$$\{|JM\rangle, |JM\rangle, |J-KM\rangle, |J-KM\rangle\}$$

where $j=1, \ldots, n$. On this basis we obtain for the two independent $C_3^v$-operators using Eqs(3.16) and (3.13c)

$$C_3^c \rightarrow \begin{pmatrix}
2\pi i (K+1)/3 & 0 & 0 & 1 \\
0 & 2\pi i (K-1)/3 & 0 & 0 \\
0 & 0 & 2\pi i (-K+1)/3 & 0 \\
0 & 0 & 0 & 2\pi i (-K-1)/3
\end{pmatrix}$$

As for the spin functions of $A$-symmetry the first operator should leave the wavefunctions invariant, which leads to $K+1 = 3n$, or $K = 3n - 1$, where $n$ is an integer. Then the appropriate linear combinations are

$$|\psi_j^{E,1}\rangle = \frac{1}{\sqrt{2}} \left( |JM\rangle + (-1)^{J+\gamma} |J-KM\rangle \right) K=3n-1$$

$$|\psi_j^{E,2}\rangle = \frac{1}{\sqrt{2}} \left( |JM\rangle + (-1)^{J+\gamma} |J-KM\rangle \right) K=3n+1$$

Again $\gamma$ can take the values zero or one. For both functions

$$\sigma_a |\psi_j^{E,\gamma}\rangle = (-1)^{J+\gamma} |\psi_j^{E,\gamma}\rangle$$

So $\gamma = J(\text{mod.2})$ for bosons and $\gamma = J+1(\text{mod.2})$ for fermions.

So far we assumed the case $K>0$. In case $K=0$ the wavefunctions are simpler because there is no $K$-degeneracy for the rotational level. For a spin function of $A_1$-symmetry the basis functions are the $|JM\rangle X_j\rangle$,

where $M$ and $j$ can take the same values as the corresponding symbols in Eq(3.14). On this basis both $C_3^c$ and $\sigma_a$ are the unit matrix, hence the appropriate function for $K=0$ is

$$|\psi_j^{A_1}\rangle = (-1)^{J+\gamma} |JM\rangle X_j\rangle$$

where $\gamma = J(\text{mod.2})$ for bosons and $\gamma = J+1(\text{mod.2})$ for fermions.
Analogously for $A_2^-$-type spin functions we get for $K=0$.

$$|\Psi_0^A> = (-1)^{J+Y} |JOMX>$$

with now $Y = J+1 (\mod. 2)$ for bosons, and $Y = J (\mod. 2)$ for fermions.

For $E$-type spin functions it is clear from Eq(3.22a) that for $K=0$ $C_{3v}$ does not have the eigenvalue one, and hence no valid wavefunction can be constructed.

The results for the total wavefunction, excluding the spin of the $X$-nucleus, are summarized in Table 3.2.

<table>
<thead>
<tr>
<th>$K$</th>
<th>symm. spin f.</th>
<th>Total wavefunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$A_1$</td>
<td>$(-1)^{J+Y}</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>$(-1)^{J+Y}</td>
</tr>
<tr>
<td>3n</td>
<td>$A_1$</td>
<td>$\sqrt{\frac{1}{2}}</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>$\sqrt{\frac{1}{2}}</td>
</tr>
<tr>
<td>3n-1</td>
<td>$E$</td>
<td>$\sqrt{\frac{1}{2}}</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>$\sqrt{\frac{1}{2}}</td>
</tr>
</tbody>
</table>

Table 3.2. The total wavefunction in a $XY^-_m$-molecule excluding the nuclear spin of the $X$-nucleus.

The complete wavefunction can be found by multiplying the appropriate function of Table 3.2 with the spin function of the $X$-nuclear spin $|I_X^M>$. This function is of $A_1$-symmetry under the $C_{3v}$-operators and does not affect the symmetry of the product function. If $|\Psi_E>$ is one of the functions of Table 3.2 then the complete wavefunction is

$$|\Psi_0 = |\Psi_E> |I_X^M>$$

3.1.2 The Hamiltonian

The general hyperfine and Zeeman hamiltonian $K_{\text{hyp}}$ is discussed by many authors (ESH 52, GOR 55, FLY 64, FLY 70). An expression applicable, in principle to any $E$-molecule in the absence of external electric fields can be found e.g. in (VER 69). For the symmetric top molecule $XY_3$ in the ground electronic and vibrational state the hamiltonian including all relevant contributions can be written as

$$K_{\text{hyp}} = \gamma X Q_X + \sum_{K=1}^3 \frac{3}{K} I_X^M X^K + I_X^M I_X^M J + \frac{3}{K=1} I_X^M X^K J +$$

$$\frac{3}{K=1} I_X^M D_{XX} I_X^M K + \frac{3}{K=1} I_X^M D_{KL} I_X^M L +$$

$$- \mu \sum_{N} H_{YH} J - \frac{1}{2} \sum_{N} H_{XH} - q_{X} \sum_{N} (1-\sigma_{X}^N) I_{X} H +$$

$$- q_{Y} \sum_{N} \frac{3}{K=1} (1-\sigma_{X}^N) I_{K} H +$$

$$+ q_{X} \sum_{N} I_{K} (1-\sigma_{X}^N) H + q_{Y} \sum_{N} I_{K} (1-\sigma_{X}^N) H$$

$$+ q_{X} \sum_{N} I_{K} (1-\sigma_{X}^N) H + q_{Y} \sum_{N} I_{K} (1-\sigma_{X}^N) H$$

$$+ q_{X} \sum_{N} I_{K} (1-\sigma_{X}^N) H + q_{Y} \sum_{N} I_{K} (1-\sigma_{X}^N) H$$

(3.25)

(3.26)
In this expression $H$ is the magnetic field, $X$ stands for the $X$-nucleus and $K=1,2$ and 3 for the respective $Y$-nuclei. All tensors in the hamiltonian (indicated by $\equiv$) are second rank Cartesian tensors. $V^K$ is the gradient tensor of the electric field at the $K$-th nucleus, while $Q^K$ is the quadrupole tensor of this nucleus, $M^K$ is the spin-rotation tensor $D_{KL}$ the spin-spin interaction tensor, $G$ is the molecular magnetic moment tensor, $X$ is the molecular magnetic susceptibility tensor, $g^K$ is the "$g$"-factor of the $K$-th nucleus, $\mu_N$ is the nuclear magneton, and $\sigma^K$ is the nuclear shielding tensor:

$$\sigma^K \equiv (\sigma^K_{aa} + \sigma^K_{bb} + \sigma^K_{cc})/3.$$  

All tensors appearing in $K_{\text{hyp}}$ depend upon the electronic and nuclear positions and momenta in the molecule. Expressions for the cartesian components of these tensors are given in Table 5.1.

The symmetry of the molecule has implications upon the tensors appearing in $K_{\text{hyp}}$. The symmetry operations only affect the $Y$-nuclei. So all tensors in the hamiltonian that do not belong to these nuclei must be invariant under the $C_3v$ operations. Let $T$ be a general tensor not belonging to one of the $Y$-nuclei. Then in the molecular frame of reference shown in Fig. 3.1 $T$ has the form

$$T = \begin{pmatrix} T_{aa} & 0 & 0 \\ 0 & T_{bb} & 0 \\ 0 & 0 & T_{cc} \end{pmatrix}.$$

Then by applying the relations (3.28) we get for $T_1$ and $T_3$

$$T_1 = \begin{pmatrix} T_{aa}^V & 0 & 0 \\ 0 & T_{bb}^V & 0 \\ 0 & 0 & T_{cc}^V \end{pmatrix},$$

$$T_3 = \begin{pmatrix} (T_{aa}^V + 3T_{bb}^V)/4 & \sqrt{3} (T_{aa}^V - T_{bb}^V)/4 & T_{bc}^V \\ \sqrt{3} (T_{aa}^V - T_{bb}^V)/4 & (3T_{aa}^V + T_{bb}^V)/4 & -T_{bc}^V \\ T_{bc}^V & -T_{bc}^V & T_{cc}^V \end{pmatrix}.$$  

The + sign holds for $T_3$ and the − sign for $T_2$.

In the absence of external fields, i.e. when $H=0$, the hamiltonian $K_{\text{hyp}}$ is invariant under $0(3) \times C_{3v}$, where $0(3)$ is the
group of orthogonal transformations in threedimensional space. The symbol $\times$ means a direct product. Because the full invariance group of $\mathcal{K}_{\text{hyp}}$ is a direct product, the hamiltonian can separately be reduced over $C_{3v}$ and $O(3)$. If $H \neq 0$ then the invariance group becomes $SO(2) \times C_{3v}$.

First we shall discuss the reduction of $\mathcal{K}_{\text{hyp}}$ over $C_{3v}$. The tensors of the type of Eq. (3.27) transform as a scalar under the $C_{3v}$ operations, and are therefore of $A_1$ symmetry. The tensors $\mathcal{T}_h$ transform under $S_3$ as vectors, as can be seen by applying the $C_{3v}$ operator to the matrices in Eq (3.29).

Therefore we define

$$T_{\text{X}} = \frac{1}{3}(T_{aa} + T_{bb} + T_{cc})$$

$$T_{\text{X}}^{E,1} = \frac{1}{6}(2T_{aa} - T_{bb} - T_{cc})$$

$$T_{\text{X}}^{E,2} = \frac{1}{2}(T_{aa}^2 - T_{bb}^2)$$

The first tensor is an $A_1$-symmetric tensor $S_3$. The remaining tensors are of $E$-symmetry. In the molecular reference frame we obtain

$$\mathcal{T}_h^{A_1} = \begin{pmatrix} T_{aa}^Y & 0 & 0 \\ 0 & T_{bb}^Y & 0 \\ 0 & 0 & T_{cc}^Y \end{pmatrix}$$

$$\mathcal{T}_h^{E,1} = \begin{pmatrix} (T_{aa}^Y - T_{bb}^Y)/4 & 0 & 0 \\ 0 & -(T_{aa}^Y - T_{bb}^Y)/4 & 0 \\ 0 & 0 & T_{bc}^Y \end{pmatrix}$$

$$\mathcal{T}_h^{E,2} = \begin{pmatrix} 0 & -\sqrt{3}(T_{aa}^Y - T_{bb}^Y)/4 & -\sqrt{3}T_{bc}^Y \\ -\sqrt{3}(T_{aa}^Y - T_{bb}^Y)/4 & 0 & 0 \\ -\sqrt{3}T_{bc}^Y & 0 & 0 \end{pmatrix}$$

Let furthermore

$$\mathcal{T}_h^{A_1} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$$

$$\mathcal{T}_h^{E,1} = \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix}$$

$$\mathcal{T}_h^{E,2} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$$

The $\mathcal{T}_h^{E}$-tensors are second rank cartesian tensors, the tensor $\mathcal{T}_h^{E}$ is a tensorial product of the vectors $\mathcal{T}_h^{E}$.

Substituting in $\mathcal{K}_{\text{hyp}}$ we get

$$\mathcal{K}_{\text{hyp}} = \mathcal{K}_h^{A_1} + \mathcal{K}_h^{E_1}$$

with

$$\mathcal{K}_h^{A_1} = \sum_{X,Y} \mathcal{T}_h^{E,1} \mathcal{T}_h^{E,1} \mathcal{T}_h^{E,2} + \sum_{X,Y} \mathcal{T}_h^{E,2} \mathcal{T}_h^{E,2} \mathcal{T}_h^{E,1}$$

$$\mathcal{K}_h^{E_1} = \sum_{X,Y} \mathcal{T}_h^{A_1} \mathcal{T}_h^{A_1} \mathcal{T}_h^{A_1} + \sum_{X,Y} \mathcal{T}_h^{E_1} \mathcal{T}_h^{E_1} \mathcal{T}_h^{E_1}$$

$$\mathcal{K}_h^{E_2} = \sum_{X,Y} \mathcal{T}_h^{E_2} \mathcal{T}_h^{E_2} \mathcal{T}_h^{E_2}$$

The $\mathcal{T}_h^{E}$-tensors are second rank cartesian tensors.
The terms in $\mathcal{V}^A_{\text{hyp}}$ are products of A-type tensors, while $\mathcal{V}^E_{\text{hyp}}$ contains E-type tensors.

So far we reduced $\mathcal{V}^E_{\text{hyp}}$ over $S_3$, yielding tensors which belong to the irreducible representations of this group. The next step is to reduce the hamiltonian over $O(3)$. The irreducible tensors in $O(3)$ are tensors that transform like the spherical harmonics. The way in which irreducible tensors can be constructed from Cartesian tensors can e.g. be found in (FAN 59). For a hermitian second rank Cartesian tensor $T$, we have

$$T_0 = -\frac{(T_{aa} + T_{bb} + T_{cc})}{3}$$
$$T_0 = \sqrt{2} \frac{T_{ab} + T_{ba}}{\sqrt{6}}$$
$$T_{+1} = \left[ \frac{2}{3} (T_{aa} + T_{bb} - T_{cc}) \right]$$
$$T_{+2} = \left[ \frac{2}{3} (T_{aa} - T_{bb}) \right]$$

For a tensor of the type of Eq(3.27) we have in the molecular frame of reference

$$T_{0} = -\frac{(T_{aa} + T_{bb} + T_{cc})}{3}$$
$$T_{0} = \frac{2}{3} (T_{ab} + T_{ba})$$
$$T_{+1} = \left[ \frac{2}{3} (T_{aa} + T_{bb} - T_{cc}) \right]$$
$$T_{+2} = \left[ \frac{2}{3} (T_{aa} - T_{bb}) \right]$$

For the tensor $T_{12}$ of Eq(3.1a) the components $T_{0}$ and $T_{0}$ are identical to the corresponding components in Eq(3.34), for $q \neq 0$ we have

$$T_{0} = 0$$

For the tensors $T_{12}^E$ and $T_{12}^E$, we get using Eqs(3.31b) and (3.31c)

$$T_{12}^E = \left[ \frac{2}{3} (T_{aa} + T_{bb} - T_{cc}) \right]$$
$$T_{12}^E = \left[ \frac{2}{3} (T_{aa} - T_{bb}) \right]$$

All spherical tensors thus far have been defined in the molecular frame of reference. The wavefunction, however is defined in the space fixed frame. The spherical tensors transform like the spherical harmonic functions under a rotation. In the convention of Edmonds (EDM 57) the components of a tensor in the space fixed frame $(T_{q})$ are thereby related to the components of the tensor in the molecule fixed system $(T_{q})$ by

$$T_{q} = \frac{1}{\sqrt{2}} (T_{q} + T_{q})$$
$$T_{q} = \frac{1}{\sqrt{2}} (T_{q} - T_{q})$$

and the inverse transformation

$$T_{q} = \frac{1}{\sqrt{2}} (T_{q} + T_{q})$$
$$T_{q} = \frac{1}{\sqrt{2}} (T_{q} - T_{q})$$

In the hamiltonian of Eq(3.33) products appear of the type $A_T B$, where $A$ and $B$ are cartesian vectors and $T$ is a second rank cartesian tensor. This cartesian product can be expressed as a product of spherical tensors (HUI 66)
For a hermitian cartesian tensor $T \equiv \nabla$ can only take the values zero and two. The right hand side of Eq(3.38) can be written out in the components of the irreducible tensors and vectors in the usual way (EDM 57) using spherical tensor techniques. The other type of interactions appearing in Eq(3.33) are of the form $T \cdot \overline{u}$, where $T$ and $\overline{u}$ are traceless hermitian cartesian tensors. In that case

$$T \cdot \overline{u} = \sum_{q=0}^{2} (-1)^q T^{(2)} \overline{u}^{(2)}$$

(3.38b)
as can be found in (JUD 63).

3.1.3 The matrix elements of $\mathcal{H}_{\text{hyp}}$

i. General considerations

The matrix elements of the symmetrized hamiltonian of Eq(3.33) can be calculated in the representation of Eq(3.25) using the spherical tensor formulae in Eq(3.35) through (3.38). The general matrix element is

$$<\Psi|\mathcal{H}_{\text{hyp}}|\Psi'> = <\Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta} | \mathcal{H}_{\text{hyp}} | \Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta}>$$

(3.39)

where $\Gamma$ indicates the irreducible representation to which the spin function of the $Y$-nuclei belongs under $S_3$.

Before calculating the matrix elements we examine the implications of the symmetry of wavefunction and hamiltonian in order to avoid unnecessary calculations. As in the derivation of the total wavefunction we consider the matrix elements for the different irreducible representations of $S_3$ separately.

(a) Spin function of $A_1$ symmetry

With the aid of the functions in Table 3.2 we obtain for the matrix elements for $K$ and $K'$ positive

$$<\Psi|\mathcal{H}_{\text{hyp}}|\Psi'> = \sum_{\Gamma_{\text{hyp}}}^{A_1} <\Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta} | \mathcal{H}_{\text{hyp}} | \Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta}>$$

$$+ (-1)^{J+I+\gamma} \sum_{\Gamma_{\text{hyp}}}^{A_1} <\Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta} | \mathcal{H}_{\text{hyp}} | \Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta}>$$

(3.40)

Because the spin functions are of $A_1$-symmetry, the spin operator in $\mathcal{H}_{\text{hyp}}$ giving non-zero matrix elements must also be of $A_1$-symmetry, consequently the $I_{E,1}$ and $I_{E,2}$ operators in Eq(3.33) do not contribute to this matrix element. Let $R_c(\varphi_0)$ be a rotation over an angle $\varphi_0$ about the c-axis. We know from Eq(3.8a) that $|\Gamma_{\text{hyp}}\chi_{\alpha} \chi_{\beta}> = e^{i\varphi_0} \mathcal{A}_{MK}^{(j)}(\varphi_0 \varphi)$, and we have

$$R_c(\varphi_0) \mathcal{A}_{MK}^{(j)}(\varphi_0 \varphi) = e^{ik\varphi} \mathcal{A}_{MK}^{(j)}(\varphi_0 \varphi)$$

(3.41)

The $A_1$ symmetric tensors given in Eq(3.27) and (3.31a) remain unchanged under $R_c(\varphi_0)$. Since the matrix element (3.40) must be of $A_1$-symmetry under this operation and both $K$ and $K'$ are positive, the last two terms must be zero and furthermore $K=K'$. Operating with the operator $\sigma_a$ using Eq(3.16b) gives both for bosons and for fermions...
The matrix element on the left hand side must be of $A_1$ symmetry, and therefore remain unchanged under $\sigma_a$, thus the first two terms in Eq(3.40) must be equal. So we finally have

$$<\psi_{KL} | A_1 | \psi'_{KL}> = (-1)^{J+\gamma}(\gamma) A_1^{(KL)} A_1^{(KL')} | J'K'M'X^1 (I'_{T' T}) I'_{M' M} >$$

In the case $K=0$ the invariance of the $A_1$-symmetric tensors under a rotation about the $c$-axis requires (as for the case that $K\neq 0$) that $K'$ must also be zero. The operator $\sigma_a$ gives $J+\gamma = J'+\gamma'$, therefore the resulting matrix element is identical to that in Eq(3.42).

The matrix elements for spin functions of $A_1$-symmetry are identical to those for $A_2$-symmetric spin functions.

(b) Spin function of $E$-symmetry

In the case $K=3n+1$ the matrix element becomes

$$<\psi_{KL} | E_1 | \psi'_{KL}> = (-1)^{J+\gamma} A_1^{(KL)} A_1^{(KL')} | J'K'M'X^1 (I'_{T' T}) I'_{M' M} >$$

The tensors in $K^h_{xyz}$ of $A_1$-symmetry only contribute to the first terms in Eq(3.43) as can be seen from the same argument as under (a). The operator $R_c(\phi_0)$ gives $K=K'$, and the operator $\sigma_a$ gives $J+\gamma = J'+\gamma'$.

The tensors in $K^h_{xyz}$ of $E$-symmetry are not invariant under an arbitrary rotation about the $c$-axis, because from Eqs(3.36) it is seen that the non-zero components transform like $Y_2^{(1)}$ and $Y_2^{(2)}$. We have

$$R_c(\phi_0) Y_q^{(2)} = e^{i\phi_0} Y_q^{(2)}, q = 0, 1, 2$$

In order the matrix element to be of $A_1$-symmetry, Eq(3.44) requires that for the first two terms in Eq(3.43) $K'$ must be equal to $K+q$ and for the third and fourth term $K'=-K+q$. For the first two terms, however, the matrix element of the spin operator is zero as we shall see in part ii of this section, so that the $E$-type tensors only contribute for the last two terms of Eq(3.43). If we require that $K>0$, only the matrix elements for $K=K'=1$ and $q=2$ are non zero ones. So we have

$$<\psi_{KL} | E_1 | \psi'_{KL}> = (-1)^{J+\gamma} A_1^{(KL)} A_1^{(KL')} | J'K'M'X^1 (I'_{T' T}) I'_{M' M} >$$

For $K$ and $K'$ equal to $3n-1$ the matrix element is similar to Eq(3.43). For the $A_1$-type tensors in $K^h_{xyz}$ the result is identical to Eq(3.45), while for the $E$-type tensors the relation $K'=K_0$ has no solutions for this case.
(c) Matrix elements off-diagonal in $\Gamma$

Because of the absence of $A_2$-type spin operators in $K_{hyp}$ we have

$$<\Psi_1^A | K_{hyp} | \Psi_2^A> = 0$$

(3.46)

The only operators that can couple states with different $\Gamma$ are the $E$-type tensors. The transformation of these tensors under a rotation about the symmetry axis given in Eq(3.44) yield the following "selection" rules

$$K' = K + 2$$

(3.47a)

$$K' = K + 1$$

(3.47b)

In addition the $E$-type spin operators can in principle couple from a spin state with a certain symmetry to a state with $E$-symmetry.

It is seen from Eq(3.47) and (3.36) that the $\Delta K=1$ coupling is established by the off-diagonal tensor component $T_{bc}$, while the $\Delta K=2$ originates from the difference $\nabla_{aa} \cdot \nabla_{bb}$. So far we discussed only the selection rules for $\gamma$ and $K$. The rules for $J$ and $I_T$ follow from spherical tensor techniques. For all tensors in $K_{hyp}$ we have $J'=J+2, J+1$ and $J$, for the first rank spin operators of $E$-type $I_T^1 = I_T^{1+1}, I_T^1$; and for the second rank spin operators $I_T^1 = I_T^{1+2}, I_T^{1+1}$, and $I_T$.

ii. The angular momentum operators

The symmetrized angular momentum operators $I_X, I_Y, I_Z, I_T^1$ and $I_T^{1+2}$ appear in the expressions for the matrix elements. The spin functions $|I_M\rangle$ are eigenfunctions of the $I_X^2$ and $I_Z^2$ operators. The functions $|D_{I_T}(I_M)\rangle$ are eigenfunctions of the operators $I_T^1$ and $I_T^{1+2}$. Therefore these operators are diagonal in $I_T$. The $E$-type operators, however, can have non zero matrix elements off-diagonal in $I_T$. If we are only interested in $\Delta K=0$ matrix elements, which will be discussed from now on, then the $E$-type spin operators only act on $E$-type spin functions as is clear from Eq(3.45), and we have for the reduced matrix element

$$<X, I_T^1 | E, I_T^1 | Y, I_T^1> = 3 <X, I_T^1 | E, I_T^1 | I_T^1>$$

(3.48)

The reduced matrix elements of the above type are given in Table 3.3 for $I_T$ up to 3/2.

The reduced matrix element of the $I_T^{1+2}$ operator can be expressed in the matrix element of Eq(3.48). If the operator (132) is applied to the left hand side of (3.48), we get using Eq(3.13c)

$$<X, I_T^1 | E, I_T^1 | I_T^{1+2} | Y, I_T^1> =$$

$$e^{2\pi i/3} <X, I_T^1 | E, I_T^1 | I_T^{1+2} | I_T^1>$$

From Eqs(3.32b,c) this can be written as
Table 3.3. The matrix elements $<E^{1,1}(\bar{I})||I^{E,2}(I')||I^{E}(\bar{I})>$ for Y nuclear spin $\frac{1}{2}$, 1 and $\frac{3}{2}$.

It is seen from Eq (3.42) and (3.45) that it appears in matrix elements of the type

$$
<\chi^{\Gamma_{E}}(I_{T})||(\Pi^{A})^{(2)}||\chi^{\Gamma_{E}}(I'_{T})>
$$

By applying the symmetry operators (123) and (132) to this matrix element we see that the last three operators in $\Pi^{A}$ must give the same contribution. Consequently

$$
<\chi^{\Gamma_{E}}(I_{T})||I^{A}_{2}(2)||\chi^{\Gamma_{E}}(I'_{T})> = 3 \sum_{I} c_{I_{T}}^{T} c_{I'_{T}}^{T} c_{I_{T}}^{T} c_{I'_{T}}^{T}
$$

For the $\Pi^{A}$-operator we must calculate

$$
<\chi^{E,1}(I_{T})||(\Pi^{A})^{(2)}||\chi^{E,2}(I'_{T})>
$$

The A-type tensor gives no contribution to this matrix element, because then the matrix element is not invariant under (132). So we get

$$
(\Pi^{A}) = \frac{1}{2} (I_{2} \otimes I_{-2} - I_{1} \otimes I_{1} - I_{2} \otimes I_{-2} - I_{3} \otimes I_{3})
$$
\[ \langle \chi^1 \parallel (I_q)^{(2)} \parallel \chi^2 \rangle = 3 \langle \chi^1 \parallel (I_q)^{(2)} \parallel \chi^2 \rangle = \sum_{I_{23}} \left( \begin{array}{c} I_{23}^+ \parallel I_{23}^+ \parallel I_{23}^+ \parallel I_{23}^{(2)} \parallel I_{23} \parallel \chi^2 \rangle \right) \]

\[ = \frac{1}{3 \sqrt{5}} \left[ (2I_{23}+1) (2I_{23}+1) \right] \]

iii. Calculation of the matrix elements

In the calculation of the matrix elements we shall only take into account the terms diagonal in \( K \). The general expressions for these elements are given in Eqs. (3.42) and (3.45).

(a) Quadrupole interaction \( X \)-nucleus

The operator for the \( X \)-quadrupole is \( V_x Q_x \). It is a product of A-type tensors. The transformation to irreducible spherical tensors is given in Eq. (3.38b). Because the tensors in this interaction are A-type we have from Eqs. (3.42) and (3.45)

\[ \langle V_x Q_x \parallel \psi \parallel \rangle = \delta_{KM} \delta_{I} \delta_{ T} (-1)^{q} \langle J \parallel Q_x \parallel J \parallel \rangle \langle \chi \parallel \psi \parallel \chi \parallel \rangle \]

Substituting Eqs. (3.57) and (3.58) into Eq. (3.56) we obtain

\[ \langle \chi \parallel V_x Q_x \parallel \psi \parallel \rangle = \frac{\delta_{KM} \delta_{I} \delta_{ T} (-1)^{q} \langle J \parallel Q_x \parallel J \parallel \rangle \langle \chi \parallel \psi \parallel \chi \parallel \rangle}{4 \delta_{KM} \delta_{I} \delta_{ T} (-1)^{q} \langle J \parallel Q_x \parallel J \parallel \rangle \langle \chi \parallel \psi \parallel \chi \parallel \rangle} \]

The first reduced matrix element can be evaluated with the aid of the Wigner-Eckart theorem; the tensor components are then transformed to the molecular frame using Eq. (3.37b)

\[ \langle J \parallel V_x Q_x \parallel J' \rangle = \frac{\langle J \parallel Q_x \parallel J' \rangle}{\sqrt{2} (J+1)} \]

This matrix element is an integral over three \( \delta \)-functions yielding

\[ \langle J \parallel Q_x \parallel J' \rangle = \frac{\langle J \parallel Q_x \parallel J' \rangle}{\sqrt{2} (J+1)} \]

The trace of \( V_x \) must be zero, and hence \( Q_x = -\psi \parallel \parallel \psi \parallel \parallel \psi \parallel \parallel \rho \parallel \parallel \)

The reduced matrix element in Eq. (3.56) for the \( X \)-quadrupole moment is usually written as

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]

Substituting Eqs. (3.57) and (3.58) into Eq. (3.56) we obtain

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]

The trace of \( V_x \) must be zero, and hence \( Q_x = -\psi \parallel \parallel \psi \parallel \parallel \rho \parallel \parallel \)

The reduced matrix element in Eq. (3.56) for the \( X \)-quadrupole moment is usually written as

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]

Substituting Eqs. (3.57) and (3.58) into Eq. (3.56) we obtain

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]

The trace of \( V_x \) must be zero, and hence \( Q_x = -\psi \parallel \parallel \psi \parallel \parallel \rho \parallel \parallel \)

The reduced matrix element in Eq. (3.56) for the \( X \)-quadrupole moment is usually written as

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]

Substituting Eqs. (3.57) and (3.58) into Eq. (3.56) we obtain

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]

The trace of \( V_x \) must be zero, and hence \( Q_x = -\psi \parallel \parallel \psi \parallel \parallel \rho \parallel \parallel \)

The reduced matrix element in Eq. (3.56) for the \( X \)-quadrupole moment is usually written as

\[ \langle I_x Q_x \parallel \parallel \rangle = \frac{\langle I_x Q_x \parallel \parallel \rangle}{\sqrt{2} (J+1)} \]
and for the contribution diagonal in $J$

$$
<\Phi|\mathcal{V}_x|\Phi> = (-1)^{J-M+I_x-M_x} \frac{eq_{M_X}}{4} \frac{[1 - \frac{J^2}{J(J+1)}]}{[J(J+1)(2J+1)(2I_x+1)(2I_x+2)(2I_x+3)]^{\frac{1}{2}}} \delta_{\frac{K}{K_T}} \delta_{\frac{I}{I_T}} \delta_{\frac{M}{M_T}} \frac{J(J+1)}{(2I_x+1)(2I_x)} (-1)^{\frac{M}{M_T}} \frac{J}{J_T} \frac{I}{I_T} \frac{M}{M_T}.
$$

Substituting the 6j-symbol in the above expression for the possible $v$-values zero and two, and transforming $M_X^{(v)}$ to the molecular frame the following result is obtained.

(b) Spin rotation $X$-nucleus

We shall calculate only the matrix element diagonal in $J$, because off diagonal matrix elements give energy corrections less than 1 Hz. Using Eq(3.38a) and the fact that the spin-rotation interaction of the $X$-nucleus belongs to $X^A$, the matrix element for this interaction is

$$
<\Phi|\mathcal{V}_x|\Phi> = \sum_v \sum_q (-1)^{v+q+1} \sqrt{\frac{2v+1}{3}} \frac{\delta_{\frac{I}{I_T}} \delta_{\frac{M}{M_T}} \frac{J}{J_T} \frac{I}{I_T} \frac{M}{M_T}}{J(J+1)(2J+1)(2I_x+1)(2I_x+2)(2I_x+3)}.
$$

Substituting the 6j-symbol in the above expression for the possible $v$-values zero and two, and transforming $M_X^{(v)}$ to the molecular frame the following result is obtained.

(c) Quadrupole interaction $Y$-nuclei

It is seen from Eq(3.33b) and (3.33c) that part of this interaction belongs to $X^A$ and part to $X^E$. For the part belonging to $X^A$ we have

$$
<\Phi|\mathcal{V}_y|\Phi'> = \sum_q (-1)^q <\Phi|\mathcal{V}_y|\Phi'> q
$$

Substituting the 6j-symbol in the above expression for the possible $v$-values zero and two, and transforming $M_X^{(v)}$ to the molecular frame the following result is obtained.

The first reduced matrix element can be treated as in Eq(3.57), but now $q_y = v_y + V_y - 2V^2_y$. For the second reduced matrix element the expansion given in Eq(3.12) has to be used for further evaluation. If we define $Q_y$ analogously to $Q_X$ in Eq(3.58) then
The part of the quadrupole interaction belonging to \( K' \) only contributes for \( K=1 \) terms as was shown in Sect. 3.1.3(i) Eq (3.45). The matrix element becomes

\[
\langle \psi_{\Gamma E}' | Q Y, E | \psi_{\Gamma E} \rangle = \frac{3e_{Q Y}}{4} \frac{\delta_{KK} \delta_{MM'}}{2I(I+1)} \sum_{-M}^{M} \left( \begin{array}{ccc} I & 2 & I' \\ -M & 2 & M' \end{array} \right). 
\]

The part of the quadrupole interaction belonging to \( K_{BP} \) only contributes for \( K=1 \) terms as was shown in Sect. 3.1.3(i), Eq (3.45). The matrix element becomes

\[
\langle \psi_{\Gamma E}' | Q_{Y}, E_{1} | \psi_{\Gamma E} \rangle + \langle \psi_{\Gamma E}' | Q_{Y}, E_{2} | \psi_{\Gamma E} \rangle = 
\]

\[\sum_{q} (-1)^{q} \frac{q+J-M+1-M'}{q-M} \left( \begin{array}{ccc} I & 2 & I' \\ -M & 2 & M' \end{array} \right). \]

In Eq(3.50) we obtained a relation between the matrix elements of the \( E_{1} \) and \( E_{2} \) operator. Because the definition of the \( E \)-type quadrupole operators is basically the same as for the

\[\langle \psi_{\Gamma E}' | Q_{Y}, E_{1} | \psi_{\Gamma E} \rangle + \langle \psi_{\Gamma E}' | Q_{Y}, E_{2} | \psi_{\Gamma E} \rangle = 
\]

\[
\frac{3e_{Q Y}}{4} \frac{\delta_{KK} \delta_{MM'}}{2I(I+1)} \sum_{-M}^{M} \left( \begin{array}{ccc} I & 2 & I' \\ -M & 2 & M' \end{array} \right). 
\]

(d) Spin-rotation \( Y \)-nuclei

As in the case of the spin-rotation of the \( X \)-nucleus only the contribution diagonal in \( J \) and \( K \) is considered. The transformation from the cartesian tensors to the spherical tensors is given in Eq(3.38a). For the \( M_{T} \)-tensor we find

\[
\langle \psi_{\Gamma E}' | Q_{Y}, E_{1} | \psi_{\Gamma E} \rangle = 
\]

\[\sum_{q} (-1)^{q+1} \frac{q+1}{3} \langle \psi_{\Gamma E}' | Q_{Y}, E_{1} | \psi_{\Gamma E} \rangle. \]

In Eq(3.50) we obtained a relation between the matrix elements of the \( E_{1} \) and \( E_{2} \) operator. Because the definition of the \( E \)-type quadrupole operators is basically the same as for the

\[\langle \psi_{\Gamma E}' | Q_{Y}, E_{1} | \psi_{\Gamma E} \rangle + \langle \psi_{\Gamma E}' | Q_{Y}, E_{2} | \psi_{\Gamma E} \rangle = 
\]

\[
\frac{3e_{Q Y}}{4} \frac{\delta_{KK} \delta_{MM'}}{2I(I+1)} \sum_{-M}^{M} \left( \begin{array}{ccc} I & 2 & I' \\ -M & 2 & M' \end{array} \right). 
\]

In Eq(3.50) we obtained a relation between the matrix elements of the \( E_{1} \) and \( E_{2} \) operator. Because the definition of the \( E \)-type quadrupole operators is basically the same as for the
Note that this term is diagonal in \( I_T \). The E-type tensors are not diagonal in \( I_T \) and we get
\[
\langle \psi^E_1 | J_{\text{XY}}, E, 1 \rangle \langle E, 1 | \psi^E_2 \rangle + \langle \psi^E_1 | J_{\text{XY}}, E, 2 \rangle \langle E, 2 | \psi^E_2 \rangle =
\sum_q (-1)^{q+J+M+I_T-M_T} \frac{q^2}{J(J+1)(2J+1)\Gamma^2}
\times \left( \begin{array}{ccc} J & 1 & J \\ -M & -q & M' \\ -M_T & q & M_T' \end{array} \right)
\]
\[
\left[ J(J+1)(2J+1) \right]^{1/2} \times \begin{bmatrix} J & J & J \\ -M & -q & -M' \end{bmatrix}
\begin{bmatrix} E_1 \langle I_T \rangle \| E_1 \| E_2 \langle I_T \rangle \end{bmatrix}
\]
\[
\times \langle E_1 \langle I_T \rangle \| E_2 \rangle + (-1)^{J+Y} \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle + \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle \langle E_2 \rangle \langle I_T \rangle \rangle
\]
\]
\[
The relation (3.50) for the reduced matrix elements of the spin operators, and the transformation of \( E^Y_X \) to the molecular frame of reference yield for this matrix element
\[
\langle \psi^E_1 | J_{\text{XY}}, E, 1 \rangle \langle E, 1 | \psi^E_2 \rangle + \langle \psi^E_1 | J_{\text{XY}}, E, 2 \rangle \langle E, 2 | \psi^E_2 \rangle
\]
\[
\sum_q (-1)^{q+J+M+I_T-M_T} \frac{q^2}{J(J+1)(2J+1)\Gamma^2}
\times \left( \begin{array}{ccc} J & 1 & J \\ -M & -q & M' \\ -M_T & q & M_T' \end{array} \right)
\]
\[
\left[ J(J+1)(2J+1) \right]^{1/2} \times \begin{bmatrix} J & J & J \\ -M & -q & -M' \end{bmatrix}
\begin{bmatrix} E_1 \langle I_T \rangle \| E_1 \| E_2 \langle I_T \rangle \end{bmatrix}
\]
\[
\times \langle E_1 \langle I_T \rangle \| E_2 \rangle + (-1)^{J+Y} \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle + \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle \langle E_2 \rangle \langle I_T \rangle \rangle
\]
\]
\[
The reduced matrix element in Eq(3.63b) is given in Table (3.4).

It is seen from this Table that for \( I_Y=4 \) the operator is diagonal in \( I_T \) if only one rotational level is considered. For higher values of \( I_Y \) also off-diagonal matrix elements in \( I_T \) appear.

(e) Spin-spin interaction X-Y

The direct spin-spin interaction can be calculated from the molecular geometry. The tensor components are given in Table 5.1. If \( \phi_0 \) is the angle between the XY-bond and the symmetry axis and \( r_{XY} \) the distance between the X-nucleus and the Y-nucleus, then, since the \( D_{XY} \)-tensors are traceless, we have for the \( A_1 \)-tensor using Eq(3.38a)
\[
\frac{A_1}{I_T} \frac{D_{XY}}{I_T} = \frac{1}{\sqrt{5}} \{ \frac{1}{I_X} \{ D_{XY} I_X \} (1) \} (0) = \frac{1}{\sqrt{5}} \{ (I_X I_T) (2) \} D_{XY} \}
\]
\[
= \sum_{q_1 q_2} \frac{A_1}{I_T} \frac{D_{XY}}{I_T} \cdot \begin{bmatrix} 1 & 1 & 2 \\ q_1 & q_2 & q \end{bmatrix}
\]
\[
\left[ J(J+1)(2J+1) \right]^{1/2} \times \begin{bmatrix} J & J & J \\ -M & -q & -M' \end{bmatrix}
\begin{bmatrix} E_1 \langle I_T \rangle \| E_1 \| E_2 \langle I_T \rangle \end{bmatrix}
\]
\[
\times \langle E_1 \langle I_T \rangle \| E_2 \rangle + (-1)^{J+Y} \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle + \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle \langle E_2 \rangle \langle I_T \rangle \rangle
\]
\]
\[
The same expansion holds for the E-type tensors.

Now the matrix elements become
\[
\langle \psi^E_1 | J_{\text{XY}}, E, 1 \rangle \langle E, 1 | \psi^E_2 \rangle + \langle \psi^E_1 | J_{\text{XY}}, E, 2 \rangle \langle E, 2 | \psi^E_2 \rangle
\]
\[
\sum_q (-1)^{q+J+M+I_T-M_T} \frac{q^2}{J(J+1)(2J+1)\Gamma^2}
\times \left( \begin{array}{ccc} J & 1 & J \\ -M & -q & M' \\ -M_T & q & M_T' \end{array} \right)
\]
\[
\left[ J(J+1)(2J+1) \right]^{1/2} \times \begin{bmatrix} J & J & J \\ -M & -q & -M' \end{bmatrix}
\begin{bmatrix} E_1 \langle I_T \rangle \| E_1 \| E_2 \langle I_T \rangle \end{bmatrix}
\]
\[
\times \langle E_1 \langle I_T \rangle \| E_2 \rangle + (-1)^{J+Y} \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle + \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle \langle E_2 \rangle \langle I_T \rangle \rangle
\]
\[
\left[ J(J+1)(2J+1) \right]^{1/2} \times \begin{bmatrix} J & J & J \\ -M & -q & -M' \end{bmatrix}
\begin{bmatrix} E_1 \langle I_T \rangle \| E_1 \| E_2 \langle I_T \rangle \end{bmatrix}
\]
\[
\times \langle E_1 \langle I_T \rangle \| E_2 \rangle + (-1)^{J+Y} \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle + \langle \psi^E_Y, 2 \rangle \langle E_1 \langle I_T \rangle \| E_2 \rangle \langle E_2 \rangle \langle I_T \rangle \rangle
\]
The reduced matrix elements can be expressed in \( \vartheta \) and \( r_{XY} \) using

the Wigner-Eckart theorem, and transforming the tensor components to the molecular frame. The result is

\[
<\psi|E| \xi> = \frac{\mu}{dN} \frac{g_Y g_X}{4 \pi r_{XY}^3} (-1)^{J-M+I} \delta_{X^+X} \delta_{I^+I} (\frac{J}{2}) \frac{\sin^2 \vartheta}{\vartheta} \delta_{K^+K} \frac{1}{I_T} \frac{1}{I_{T+1}} \frac{1}{(2I_{T+1} + 1)^{\frac{1}{2}}} \]

\[
\sum_{q\ell} (J \quad 2 \quad J) (I_T \quad 1 \quad I_T) (I_X \quad 1 \quad I_X) (M - q \quad M') (-M\chi \quad q_1 \quad M^\prime\chi') (q_2 \quad q_2 \quad -q) \]

(3.64)

(1) Spin-spin interaction Y-Y

The direct spin-spin interaction between the Y-nuclei can be

expressed in spherical tensor components using Eq(3.38b). Sub-

stituted in the matrix element gives

\[
<\psi|E| \xi> = \frac{\mu}{dN} \frac{g_Y g_X}{4 \pi r_{XY}^3} (-1)^{J-M+I} \delta_{X^+X} \delta_{I^+I} (\frac{J}{2}) \frac{\sin^2 \vartheta}{\vartheta} \delta_{K^+K} \frac{1}{I_T} \frac{1}{I_{T+1}} \frac{1}{(2I_{T+1} + 1)^{\frac{1}{2}}} \]

\[
\sum_{q\ell} (J \quad 2 \quad J) (I_T \quad 1 \quad I_T) (I_X \quad 1 \quad I_X) (M - q \quad M') (-M\chi \quad q_1 \quad M^\prime\chi') (q_2 \quad q_2 \quad -q) \]

(3.65)

For \( I_Y = \frac{1}{2} \) the spin of the E-type levels is \( I_T = \frac{1}{2} \), hence the second

\( 3j \)-symbol in Eq(3.65) is zero, and the interaction vanishes for

these states.

(g) Molecular magnetic moment and susceptibility

These interactions involve \( A_1 \)-type tensors and hence can be

treated in essentially the same way as the spin-rotation inter-

action of the X-nucleus. If in the space fixed frame the quant-

ization axis is chosen along \( H \) then the matrix elements dia-

gonal in \( J \) are

\[
<\psi|E| J> = \frac{\mu}{dN} \frac{g_Y g_X}{4 \pi r_{XY}^3} (-1)^{J-M+I} \delta_{X^+X} \delta_{I^+I} (\frac{J}{2}) \frac{\sin^2 \vartheta}{\vartheta} \delta_{K^+K} \frac{1}{I_T} \frac{1}{I_{T+1}} \frac{1}{(2I_{T+1} + 1)^{\frac{1}{2}}} \]

\[
\sum_{q\ell} (J \quad 2 \quad J) (I_T \quad 1 \quad I_T) (I_X \quad 1 \quad I_X) (M - q \quad M') (-M\chi \quad q_1 \quad M^\prime\chi') (q_2 \quad q_2 \quad -q) \]

(3.66)
(h) Nuclear magnetic moment of the X-nucleus

It is seen in Eq(3.33b) that the operators in this interaction belong to \( J^\text{hyp} \). Let

\[
\sigma^X_\text{av} = \frac{1}{3} (\sigma^X_{\text{aa}} + \sigma^X_{bb} + \sigma^X_{cc}) = \frac{2}{3} \sigma^X_1 + \frac{1}{3} \sigma^X_3
\]

then the matrix elements of the scalar interaction

\[
-\mu N^X I X \cdot \hat{H} (1 - \sigma^X_\text{av}) \text{ are}
\]

\[
\left\langle \Psi | J^\text{TE} \right| -\mu N^X I X \cdot \hat{H} (1 - \sigma^X_\text{av}) | \Psi, J^\text{TE} \rangle = -\delta_{MM'} \delta_{T'T''} \delta_{M' M''} \delta_{M'' M'''} \mu N^X (1 - \sigma^X_\text{av}) M_X
\]

The remaining interaction is the anisotropic nuclear shielding, which involves an irreducible tensor of rank two:

\[
-\mu N^X I X \cdot \hat{H} (1 - \sigma^X_\text{av}) \text{ is}
\]

\[
\text{This cartesian tensor product can be written as a product of irreducible tensors using Eq(3.38a), which in turn can be expressed in the spherical tensor components. In total}
\]

\[
I_X \sigma^X_\text{an} \cdot \hat{H} = \sqrt{5} H \sum \sigma^X_{\text{av}, -q} I_X (2 1 1) \]

Herewith the matrix elements become

\[
\left\langle \Psi | J^\text{TE} \right| I^Y I^X (2I^Y + 1) \left| J^\text{TE} \right\rangle = \sum_q (-1)^q \begin{pmatrix} J \quad \text{and} \quad 2 \quad 1 \quad 1 \end{pmatrix} \begin{pmatrix} \text{odd} \quad \text{and} \quad \text{odd} \end{pmatrix} \]

As for the X-nucleus we define the average shielding as

\[
\sigma^X_\text{av} = \frac{1}{3} (\sigma^X_{\text{aa}} + \sigma^X_{bb} + \sigma^X_{cc})
\]

and

\[
\sigma^X_\text{an} = \sigma^X_{\text{av}}
\]

The \( E \)-type tensors have zero trace and so they are already second rank irreducible tensors. Proceeding in the same way as for the X-nucleus we obtain

\[
\left\langle \Psi | J^\text{TE} \right| g^X \sigma^X \cdot \hat{H} (1 - \sigma^X_\text{av}) | \Psi, J^\text{TE} \rangle = -\delta_{MM'} \delta_{T'T''} \delta_{M' M''} \delta_{M'' M'''} g^X \sigma^X \cdot \hat{H}
\]

The reduced matrix element can be evaluated with the aid of the Wigner Eckart theorem and then transformed to the molecular frame of reference. The result is

\[
\left\langle \Psi \left| J^\text{TE} \right| g^X \sigma^X \cdot \hat{H} | \Psi, J^\text{TE} \rangle = \mu N^X g^X \cdot \hat{H} \left(1 - \frac{J^2}{(J+1)^2}\right) \cdot \left[ \begin{pmatrix} I^X \times 1 \end{pmatrix} \sum \begin{pmatrix} J \quad J \quad 2 \quad 2 \quad 1 \quad 1 \end{pmatrix} \begin{pmatrix} I^X \quad 1 \quad I^X \end{pmatrix} \begin{pmatrix} \text{odd} \quad \text{even} \quad \text{odd} \end{pmatrix} \right]
\]

(i) Magnetic moment of the Y-nuclei

\[
\text{As for the X-nucleus we define the average shielding as}
\]

\[
\sigma^Y_\text{av} = \frac{1}{3} (\sigma^Y_{\text{aa}} + \sigma^Y_{bb} + \sigma^Y_{cc})
\]

and

\[
\sigma^Y_\text{an} = \sigma^Y_{\text{av}}
\]

The \( E \)-type tensors have zero trace and so they are already second rank irreducible tensors. Proceeding in the same way as for the X-nucleus we obtain

\[
\left\langle \Psi \left| J^\text{TE} \right| g^Y \sigma^Y \cdot \hat{H} | \Psi, J^\text{TE} \rangle = -\delta_{MM'} \delta_{T'T''} \delta_{M' M''} \delta_{M'' M'''} g^Y \sigma^Y \cdot \hat{H}
\]

\[
= g^Y \sigma^Y \cdot \hat{H} \left(1 - \frac{J^2}{(J+1)^2}\right) \cdot \left[ \begin{pmatrix} I^Y \times 1 \end{pmatrix} \sum \begin{pmatrix} J \quad J \quad 2 \quad 2 \quad 1 \quad 1 \end{pmatrix} \begin{pmatrix} I^Y \quad 1 \quad I^Y \end{pmatrix} \begin{pmatrix} \text{odd} \quad \text{even} \quad \text{odd} \end{pmatrix} \right]
\]
The coupling constants

In a rotational transition the tensor components $T_{aa}$, $T_{bb}$ and $T_{cc}$ cannot be measured directly. What can be determined are the so called coupling constants. They are certain linear combinations of the tensor components. From the derived formulae for the matrix elements it is obvious how the coupling constants could be defined. For a general tensor $T$ we therefore introduce a coupling constant $t_{JK}$ which is given by

$$t_{JK} = \frac{\hbar}{T_{aa} + T_{bb}} + \frac{K^2}{3(J+1)} (T_{cc} - \frac{1}{2}(T_{aa} + T_{bb})) +$$

$$\frac{(-1)^J}{4} \delta_{Kl}(T_{aa} - T_{bb}) \frac{\langle E_1^{(L)}(I^L) \parallel E_1^{(L)} \parallel E_2^{(L)}(I^L) \rangle}{[I^L(I^L+1)(2I^L+1)]^{1/2}}$$

(3.69)

For the $A_1$-type tensors of Eq(3.27) the last term in (3.69) vanishes because $T_{aa} = T_{bb}$ for these tensors. For the traceless tensors in $K_{hyp}$ we have $T_{aa} + T_{bb} + T_{cc} = 0$.

There are two interactions in the hamiltonian of Eq(3.33) whose coupling constants cannot be described by this formula. The coupling constant is defined diagonal in $J,K$ and $I^L$.

These interactions are the Y-quadrupole interaction and the spin-spin interaction between the Y-nuclei. For the quadrupole it is obvious from Eqs(3.62a) and (3.62b) to define (diagonal in $J,K$ and $I^L$)

$$d_{JK}^Y = \frac{3K^2}{J(J+1)} \frac{\hbar}{(T_{aa} - T_{bb})} \frac{\langle E_1^{(L)} (I^L) \parallel E_1^{(L)} \parallel E_2^{(L)}(I^L) \rangle}{[I^L(I^L+1)(2I^L+1)]^{1/2}}$$

$$\sum_{I_{23}} \left| c_{I_{23}}^{E_1^{(L)}}(I^L) \right|^2 (-1)^J \frac{2I_T}{4} \left\{ I_T 2 I_T \right\} \left\{ I_Y 2 I_Y \right\} (3.70)$$

and for the YY-spin-spin interaction from Eq(3.65)

$$d_{JK}^{YY} = \frac{2}{4\pi \gamma_{YY}} \left[ \langle E_1^{(L)} (I^L) \parallel E_1^{(L)} \parallel E_2^{(L)}(I^L) \rangle \right] \frac{3K^2}{J(J+1)} \frac{\hbar}{(T_{aa} - T_{bb})}$$

$$\sum_{I_{23}} \left| c_{I_{23}}^{E_1^{(L)}}(I^L) \right|^2 (-1)^J \frac{2I_T}{4} \left\{ I_T 2 I_T \right\} \left\{ I_Y 2 I_Y \right\} \left\{ I_{23}^2 \right\} \left\{ I_Y 2 I_Y \right\} \left\{ I_{23}^2 \right\} \left\{ I_Y 2 I_Y \right\} (3.71)$$

The coupling constants for $I_{23} = \frac{3}{2}$ are given in Appendix II.

5.2 THE ASYMMETRIC ROTOR

An asymmetric rotor molecule is a molecule which has three different inertial moments in the principal axis system. Measurements have been performed on two asymmetric rotor molecules, $D_2O$ and $SO_2$. The hamiltonian for the first molecule contains the same interactions as $K_{hyp}$ in Eq(3.26). The matrix elements in the case of $D_2O$ are calculated by Verhoeven (VER 69).

The hamiltonian of $SO_2$ is very simple because of the absence of nuclear spins. In the electronic and vibrational ground state of the molecule, and in external magnetic field $B$ the
(Zeeman) Hamiltonian $H_z$ is

$$H_z = -\mu \cdot \mathbf{H} \cdot J - \frac{1}{2} \gamma \mathbf{H} \cdot \mathbf{H}$$

The magnetic coupling constants ($g_{Jr}$ and $\chi_{Jr}$) for an asymmetric top molecule in a rotational state $J_r$ are usually defined as

$$g_{Jr} = \frac{\sum_a (\gamma_{aa} - \gamma_{av}) <J^2_a>}{\sum_a (\gamma_{aa} - \gamma_{av})}$$

and

$$\chi_{Jr} = \frac{\sum_a (\gamma_{aa} - \gamma_{av})}{\sum_a (\gamma_{aa} - \gamma_{av})} (<J^2_a> - \chi_{av})$$

where the sum over $a$ runs over the principle axes of the molecule and $<J^2_a>$ is the expectation value of $J_a^2$ in the state $J_r$.

The matrix elements can be written as

$$<J_M|H_z|J_{M'}> = \delta_{MM'} \left[ -\gamma g_{Jr} J_H^2 - \frac{3J(J+1)}{2J+1} (\chi_{Jr} H^2) \right]$$

3.3 THE INTERNAL ROTOR

3.3.1 The hyperfine and Zeeman Hamiltonian

The hyperfine Hamiltonian for an internal rotor with one degree of freedom for the field free case and in the absence of nuclear vibrations has been developed by Heuvel (HEU 72). The main difference between a rigid rotor and an internal rotor is that in the latter case the velocity $\dot{x}_K$ of a nucleus $K$ depends not only upon the overall velocity of the nuclear frame but also upon the internal angular velocity $\dot{a}$, where $a$ is the angle between the two parts of the molecule rotating with respect to each other. For a molecule with only one degree of freedom an axis $a$ and for each nucleus a vector $\mathbf{g}_K$ can be found such that $\mathbf{g}_K \cdot a = 0$ and $\dot{x}_K = \omega \times r_K + \dot{a} \times \mathbf{g}_K$.

In this equation $\omega$ is the overall angular velocity and $r_K$ the position of the $K$-th nucleus with respect to the center of mass of the molecule. Let $m_K$ be the mass of the $K$-th nucleus then the overall inertia tensor of the molecule is

$$I_{gg'} = \sum_K m_K \left( r_K^2 \delta_{gg'} - r_K \cdot r_K \right)$$

This tensor is called $I_{gg'}$ in (HEU 72). The quantities $F$, $P$, and $\rho$ defined by Heuvel can be written as

$$\Lambda = \frac{1}{2} (I_{gg'})^{-1}$$

$$\rho = 2 \frac{\Lambda}{F} m_K \left( \sigma_K \times \lambda \right) \cdot r_K$$

$$\frac{1}{F} = \frac{1}{2} m_K \frac{\sigma_K^2}{F} + 2 \rho \cdot \rho$$

The equations (3.77b) and (3.77c) follow from the definitions of Heuvel by substituting therein the various inertia tensors. Furthermore it is customary to define an effective rotational tensor via

$$\Lambda_{eff}^{gg'} = \Lambda_{gg'} + F P \rho$$

Then the rotational hamiltonian in Eq(8) of (HEU 72) is equal to

$$H_{rot} = R \cdot \Lambda_{eff}^{gg'} \cdot R + P^2 + 2F \rho \cdot R + V(a)$$

where $R$ is the nuclear contribution to the overall angular momentum and $P$ the nuclear contribution to the internal angular momentum, $V(a)$ is the hindering potential. The advantage of Eq(3.78) above Eq(8) of (HEU 72) is that the coupling between $R$ and $P$ is more obvious, but moreover the calculation of the hyperfine operators is easier.
For the overall angular velocity $\omega$ and the internal angular velocity $\delta$ we obtain

$$\omega = 2 A^\text{eff} \cdot R + 2 F \cdot P \quad (3.79b)$$

$$\delta = 2 F \cdot P \cdot R + 2 F \cdot P \quad (3.79b)$$

The angular momentum $R$ is the difference of the total angular momentum $J$ and the electronic angular momentum $L$. We get for $K^\text{rot}$

$$K^\text{rot} = J \cdot A^\text{eff} \cdot J + F \cdot P \cdot J - 2L \cdot A^\text{eff} \cdot J - 2F \cdot P \cdot L +$$

$$+ V(a) + L \cdot A^\text{eff} \cdot L \quad (3.80)$$

For $^1\Sigma$-molecules $\langle L \rangle = 0$ and we approximate

$$\omega = 2 A^\text{eff} \cdot J + 2P \cdot P \quad (3.81a)$$

$$\delta = 2 F \cdot P \cdot J + 2F \cdot P \quad (3.81b)$$

The last term in $K^\text{rot}$ shifts all rotational energy levels in a certain electronic state by the same amount and is therefore not observable in rotational transitions. The fourth and fifth term in Eq (3.80) are zero in first order in $^1\Sigma$-molecules. The second order contributions of these terms, however are not negligible. The hamiltonian can therefore be written as

$$K^\text{rot} = K^1 + K^2 + V(a) \quad (3.82a)$$

$$K^1 = J \cdot A^\text{eff} \cdot J + 2F \cdot P \cdot J + F \cdot P \quad (3.82b)$$

$$K^2 = -2L \cdot A^\text{eff} \cdot J - 2F \cdot P \cdot L \quad (3.82c)$$

The spin-rotation and spin-spin interaction are discussed by Heuvel. Therefore we treat only the magnetic interactions. The important magnetic interactions are discussed by many authors. For the present treatment we shall follow Verhoeven (VER 69).

The relevant interactions are

$$h_1 = -\frac{e^2}{4} \sum_{K} Z_K H \cdot r_K \times r_K^\text{L} + \frac{e^2}{4} \sum_{K} H \cdot r_K \times r_K^\text{L} \quad (3.83a)$$

$$h_2 = e \frac{2}{8m} \sum_{K} (\vec{H} \times r_K)^a \cdot (\vec{H} \times r_K) \quad (3.83b)$$

$$h_3 = \frac{\mu_o}{4\pi} \sum_{K} \frac{e^2}{2m} \sum_{K} (\vec{H} \times r_K)^a \cdot \frac{g_K^\text{N} \cdot r_K \times r_K^\text{L}}{r_{1K}^3} \quad (3.83c)$$

$$h_4 = \frac{\mu_o}{4\pi} \sum_{i,K} \frac{e^2}{2m} \sum_{i,K} \frac{r_{iK} \times (v_i^a - \gamma_K r_i^a) \cdot \vec{r}_{1K}}{r_{iK}^3}$$

$$- \sum_{L,K} \frac{e^2}{2m} \sum_{L,K} \frac{g_K^\text{L} \cdot r_{iK} \times (v_i^a - \gamma_{K-L} r_i^a)}{r_{iK}^3} \quad (3.83d)$$

In these equations $Z_K, g_K, I_K, r_K$ and $r_K^\text{L}$ are the number of protons, the nuclear g-factor, the nuclear spin, position in the CM system and velocity of the K-th nucleus respectively, $-e, m, v_i^a$ and $v_i^a$ the charge, mass, position in the CM-system and velocity of the i-th electron respectively, $u_N$ is the nuclear magneton, and $\vec{H}$ the magnetic field. The sum over $K$ and $L$ runs over all nuclei, the sum over $i$ runs over all electrons.

The first term describes the interaction of the magnetic field $\vec{H}$ with the rotating charges of nuclei and electrons in the molecule. The second term represents the interaction of the magnetic field with the induced magnetic moment; this term also has a nuclear contribution, but this contribution is negligible. The term $h_4$ gives the interaction of the magnetic moment of the K-th nucleus with the molecular charge distribution disturbed by the external field. Again the nuclear part of
this interaction is neglected. The last term is simply the interaction of the nuclear magnetic moment with the magnetic field produced by the rotating charges in the molecule.

The terms in \( h_1, h_2, h_3, \) and \( h_4 \) can be worked out using the equations for \( \tilde{z}_K, \tilde{p} \) and \( \tilde{d} \).

For the first term we get

\[
h_1 = -\mu_N \tilde{z}_K \left( \frac{1}{7} - \frac{1}{n} \right) \tilde{p} + \mu_N \tilde{z}_K \tilde{d} \tag{3.84}
\]

where \( \tilde{z}_K \) is the nuclear contribution to the \( G \)-tensor due to the overall rotation of the molecule, and \( \tilde{d} \) the contribution to the \( g \)-vector due to the internal rotation. We have

\[
g^{(n)}_{gg'} = \frac{e}{2\mu_N} \sum K \left[ \left( \frac{1}{8} \right) g^{(n)}_K \delta_{gg'} - \frac{1}{3} g_{xK} g_{yK} \right] \lambda_{gg'}^{\text{eff}} + \left( \frac{1}{3} \right) \tilde{d}_K \tilde{p} \tilde{d}_K \tilde{d}_K^* \tag{3.85}
\]

\[
\tilde{d}^{(n)} = \frac{e}{2\mu_N} \sum K \left[ \tilde{d}_K \tilde{d}_K \tilde{d}_K^* \right] \tag{3.86}
\]

The third term in \( h_4 \) is zero in first order for \( 1^1 \) molecules, however the second order contribution of this term to the hyperfine energy is important.

The interaction \( h_2 \) of Eq(3.83b) is of purely electronic origin. If \( |\phi> \) denotes the electronic \( 1^1 \) state then the first order contribution of this term to the energy is

\[
<\phi| h_2 |\phi> = -\frac{1}{2} H_2 \chi^{(d)} \tag{3.87}
\]

where the cartesian components of the diamagnetic susceptibility tensor \( \chi^{(d)} \) are given by

\[
\chi^{(d)}_{gg'} = \frac{2}{4m} <\phi| \tilde{z}_L \tilde{z}_L^* \delta_{gg'} |\phi> \tag{3.88}
\]

The higher order contributions of \( h_2 \) may be neglected.
So far we discussed only the operators that give first order electronic contributions. The terms in the total Hamiltonian giving important second order contributions can be taken from Eq. (3.82c), (3.84) and (3.91). They are $X$ and $Y$.

The second order contributions are of the form

$$Z \left[ \langle \psi | H | \psi \rangle + \langle \psi | H | \psi \rangle^{\ast} \right]$$

where $H_1$ and $H_2$ are two of the operators of Eq. (3.82c), (3.85) or (3.95). The summation runs over all excited electronic states $| \psi \rangle$ with energy $E_\psi$. The second term in the Eq. (3.97) is the complex conjugate, abbreviated as c.c., of the first term.

The paramagnetic susceptibility $\chi^{(p)}$ originates in the second order effect of $H_1$. The cartesian components are given by

$$\chi_{pq}^{(p)} = 2B \frac{2}{3} \sum_{n} \langle \psi | L_p | \psi \rangle \langle \psi | L_q | \psi \rangle^{\ast}$$

The paramagnetic nuclear shielding of the $K$-th nucleus is due to the effect of $h_1^{(2)}$ and $h_4^{(2)}$. Here the cartesian components are

$$\sigma_{Kgg}^{(e2)} = 2B \frac{2}{3} \sum_{n} \langle \psi | L_g | \psi \rangle \langle \psi | L_g | \psi \rangle^{\ast}$$
term of $\mathcal{H}_2$ combined with $h_4^{(2)}$. The cartesian components for this tensor are

$$m_{K\ell g} = -\frac{e\mu_B^4}{2\pi^2} \sum_{n} \langle 0| \hat{r}_K \sum_{\ell} \frac{\mu_{\ell} e^{i\ell \varphi}}{n} |0\rangle + \text{c.c.}$$

The second term in $\mathcal{H}_2$ combined with $h_4^{(2)}$ gives the second order contribution to the spin-internal rotation vector

$$m_{K\ell g} = \frac{e\mu_B^4}{2\pi^2} \sum_{n} \langle 0| \hat{r}_K \sum_{\ell} \frac{\mu_{\ell} e^{i\ell \varphi}}{n} |0\rangle + \text{c.c.}$$

The last term in Eq (3.98) is the so-called electron coupled spin-spin interaction, due to the second order effect of $h_4^{(2)}$. For this tensor we have

$$D_{K\ell g}^{(e)} = \frac{e\mu_B^4}{16\pi^2} \sum_{n} \langle 0| \hat{r}_K \sum_{\ell} \frac{\mu_{\ell} e^{i\ell \varphi}}{n} |0\rangle + \text{c.c.}$$

This term is usually negligible, except for large nuclei. A more important contribution to the spin-spin interaction is via the contact interaction. This interaction, however, will not be discussed here.

The interactions in Eqs (3.83) do not completely describe the Zeeman and hyperfine structure of the molecule. If no nuclear quadrupoles are present, then the additional terms to the Zeeman and hyperfine interactions are the direct spin-spin interaction between the nuclear magnetic moments, and the interactions of the nuclear magnetic moments with the external field. These interactions can be written as

$$h_6 = \sum_{K \ell L} \frac{1}{K} \mathcal{H}^{(n)}_{K\ell L} \cdot I_{K\ell L}$$

$$h_7 = \sum_{K} -\frac{1}{K} \mathcal{H}^{(c)}_{K}$$

The spin-spin interaction tensor $\mathcal{H}_{KL}^{(n)}$ is given in Table 5.1. The total hyperfine and Zeeman hamiltonian due to $h_1$ through $h_7$ can be written as

$$\mathcal{H}_{\text{hyp}} = \frac{1}{K} \sum_{KL} \mathcal{H}^{(n)}_{KL} \cdot I_{KL}$$

In this equation the vectors and tensors are defined as

$$M_K = M_{K}^{(n)} + M_{K}^{(e1)} + M_{K}^{(e2)}$$

$$D_{K\ell g} = D_{K\ell g}^{(n)} + D_{K\ell g}^{(e)}$$

$$G = G^{(n)} + G^{(e)}$$

$$g = g^{(n)} + g^{(e)}$$

$$\sigma = \sigma^{(d)} + \sigma^{(p)}$$

The hamiltonian $\mathcal{H}_{\text{hyp}}$ differs from the hamiltonian for a rigid rotor, as can be seen by comparison of Eq (3.26) and (3.108). Apart from the fact that the tensors in Eq (3.108) are functions of $\alpha$, there are two additional terms in the hamiltonian caused by the internal rotation, e.g., the vectors in Eq (3.109b) and (3.109g).
methyl alcohol. The $\text{H}_2\text{O}_2$ -molecule has a twofold potential barrier shown in Fig. 3.3, and $\text{CH}_3\text{OH}$ a threefold barrier. Both molecules, however, can be described (in first order) by symmetric top wave functions (HUN 64, HEU 72) such that the matrix elements are basically the same as for the symmetric rotor.

The methyl alcohol molecule is discussed in detail by Heuvel in zero field. Expressions for the matrix elements and the coupling constants can be found in (HEU 72). In this chapter we shall restrict ourselves to hydrogen peroxyde.

### 3.3.2 Hydrogen peroxyde

![Diagram of the hydrogen peroxyde molecule](image)

The geometry of the molecule is shown in Fig. (3.2). The molecule fixed c-axis is chosen along the O-O bond. The a-axis is defined as the bissectrix of the projection of the OH bars on a plane perpendicular to the c-axis through the center of mass of the molecule.

The b-axis is chosen so that the system abc becomes right-handed.

The internal rotation in $\text{H}_2\text{O}_2$ is due to the relative motion of the OH-bars with respect to each other. This rotation is hindered by two interactions: the repulsion of the dipole moments of the OH bars and the interaction with the two non-bonding pairs of p-electrons associated with the oxygen atoms. The potential energy $V(\alpha)$ is given in Fig. 3.3 as a function of $\alpha$, the angle between the projection of the OH-bars in the bc-plane. The situation when $\alpha=\pi$ is called the trans-position, while for $\alpha=0$ the molecule is in the cis-position. The corresponding barrier heights in the potential are $V\text{trans}$ and $V\text{cis}$. They have been determined by Hunt et al (HUN 64), while the angle $\alpha_e$, where the potential reaches its minimum, was obtained by Oelfke and Gordy (OEL 69).

$$V\text{trans} = 386 \text{ cm}^{-1}$$

$$V\text{cis} = 2460 \text{ cm}^{-1}$$

$$\alpha_e = 118^\circ 4'$$

*) This value is the average value of $\alpha_e$ in the states $\tau=1,2$ and $\tau=3,4$.
In the abc-frame there is a coupling in the rotational hamiltonian between the internal rotation and the overall rotation (HUN 64). This coupling can be removed by applying a small rotation about the a-axis. Then the Hamiltonian becomes (HUN 64)

\[ H = H_{\text{rot}} + H_{\text{int}} \]

\[ H_{\text{rot}} = A(\omega)J_a^2 + C(\omega)J_c^2 + B(\omega)(J_a^2J_b^2) + D(\omega)(J_bJ_c - J_aJ_d) \]

\[ H_{\text{int}} = f(\omega)\mathbf{p}^2 + V(\omega) \]

The rotational constants A, B, C, and D all are functions of \( \omega \). The constants B and D are very sensitive to \( \omega \). Fortunately the dominant terms in the expression for \( H_{\text{rot}} \) are A(\( \omega \)) and C(\( \omega \)), which are in first order independent of \( \omega \). Consequently the zeroth order basis functions of \( H_{\text{rot}} \) are the functions \( |JKM> \) discussed in Sect. 3.1.1. The basis functions for the overall plus internal rotation are then the \(|jKM_M(\omega)\), where \( M(\omega) \) is a solution of the equation

\[ K_{\text{int}} M(\omega) = E_{\text{int}} N(\omega) \]

The Hamiltonian \( H_{\text{int}} \) is invariant under a reflection in the trans plane \( \sigma(\text{trans}) \) and under a reflection in the cis-plane \( \sigma(\text{cis}) \). These reflections can be expressed in \( \omega \):

\[ \sigma(\text{trans}) : \omega \rightarrow -2\pi - \omega \]

\[ \sigma(\text{cis}) : \omega \rightarrow -\omega \]

In addition the molecule is invariant if one of the two OH-bars is rotated over \( 2\pi \), while the other one is fixed. If \( \psi, \theta, \varphi \) are the Euler angles of the molecule then the operation that describes this is given by (ELL 75)

\[ C_2^c: \psi + \varphi + (n_1 + n_2)\pi \]

\[ \alpha \rightarrow \alpha + (n_1 - n_2)2\pi \]

Here one of the OH bars is rotated over \( n_12\pi \), while the other one is rotated over \( n_22\pi \). Because the molecule is invariant under this transformation, the total wavefunction has to be invariant too. The transformation of the \(|JKM>\) under \( C_2^c \) (see Sect. 3.1.1) then requires for the internal rotor function \( M(\omega) \)

\[ M(\omega) = e^{-iK\pi/2}N(\omega) \]

where \( N \) is a function of \( \omega \) with period \( 2\pi \). The operations \( \alpha(\text{trans}) \) and \( \alpha(\text{cis}) \) leave \( H_{\text{int}} \) invariant and therefore complex numbers \( c_t \) and \( c_c \) can be found with \(|c_t|^2 = |c_c|^2 = 1\) and

\[ \sigma(\text{trans}) M(\omega) = c_t M(\omega) \]

\[ \sigma(\text{cis}) M(\omega) = c_c M(\omega) \]

Furthermore

\[ \sigma(\text{trans})^2 = \sigma(\text{cis})^2 = 1 : \omega \rightarrow \omega \]

\[ \sigma(\text{trans})\sigma(\text{cis}) : \omega \rightarrow \omega - 2\pi \]

So

\[ c_t = \pm 1 \]

\[ c_c = \pm 1 \]

\[ c_t c_c = (-1)^\tau \]

The wavefunctions for the internal rotation can now be classified according to their symmetry under these operations. The quantum number \( \tau \) which describes this symmetry is given in Table 3.4. The states with a certain \( \tau \) are ordered by the principal quantum number \( n \) (\( n=0 \) for the ground state and can further take integral values \( 1, 2, \ldots \) ordered in ascending energy). All measurements were performed in the \( n=0 \) state.
In addition to the symmetry operations described above, the molecule is invariant under a rotation about the a-axis over π. This interaction interchanges the two protons in the molecule, and the Pauli principle then implies that the wavefunction is antisymmetric under this operation. The antisymmetric spin function corresponds with total proton spin zero, while the symmetric spin function has total spin one. The total hydrogen spin in a particular state is given in Table 3.4.

<table>
<thead>
<tr>
<th>J</th>
<th>Overall rot. state</th>
<th>int. rot. state</th>
<th>total spin</th>
<th>hydr.nucl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>( \Psi_{JK^+} )</td>
<td>( \tau = 1,2 )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Psi_{JK^-} )</td>
<td>( \tau = 1,2 )</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Psi_{JK^+} )</td>
<td>( \tau = 3,4 )</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Psi_{JK^-} )</td>
<td>( \tau = 3,4 )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>odd</td>
<td>( \Psi_{JK^+} )</td>
<td>( \tau = 1,2 )</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Psi_{JK^-} )</td>
<td>( \tau = 1,2 )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Psi_{JK^+} )</td>
<td>( \tau = 3,4 )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Psi_{JK^-} )</td>
<td>( \tau = 3,4 )</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. The \( H_2O_2 \) wavefunction and its spin symmetry.

More details about the wavefunction can be found in (HUN 64, ELL 75).

We mentioned in the beginning of this section that the coupling between J and P in \( H_2O_2 \) can be removed by a small rotation about the a-axis. This rotation is called a contact transformation. In the present notation this contact transformation implies that the term

\[
\sum_K m_K (a_{K\lambda}) x_K = I \cdot P
\]

(3.113)
given in Eq (3.77b) becomes zero in the new reference frame, as is shown in Appendix III. This causes severe implications upon the hyperfine hamiltonian of Eq (3.108). If we substitute zero for the term in Eq (3.113) in the tensors derived in Sect. 3.3.1 we have from Eq (3.100)

\[ g^{(e)} = 0 \]

and from Eq (3.86)

\[
\sum_K \frac{eF}{2\mu_N} \sum_K Z_K (a_{K\lambda}) x_K
\]

Under the inversion operator the vector \( g^{(n)} \) transforms into \( -g^{(n)} \). Hence the first order contribution due to this term is zero, and the term \( H \cdot g \cdot P \) in Eq (3.108) vanishes in first order.

The matrix elements of \( K_{hyp} \) and the coupling constants are given in (ELL 75).