# NMR Group meeting lecture notes

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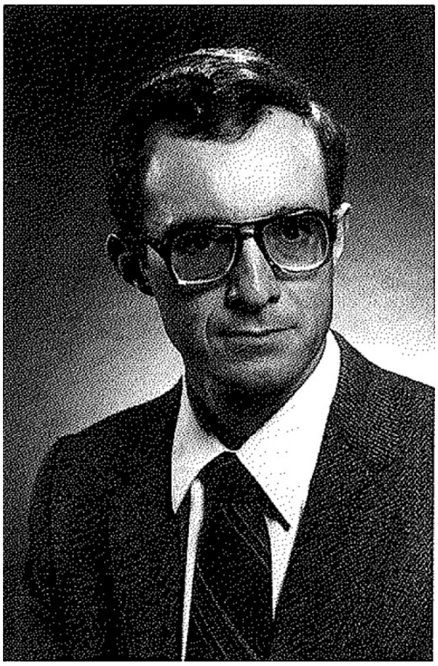

**University of Alberta**

**Department of Chemistry**

**1983-1984**

# Master Contents Page

**Angular Momentum Theory**



**Density Matrix Theory**




**Course taken by Ranjith Muhandirum, pHD student**



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ANGULAR MOMENTUM THEORY

Angular Momentum Theory

References: * 1. M. E. Rose, "Elementary Theory of Angular Momentum" (Wiley, 1957). Chapters I-V. 

2. A. R. Edmonds, "Angular Momentum in Quantum Mechanics" (Princeton, 1957). Chapters I-V.

 *3. D. M. Brink and G. R. Satchler "Angular Momentum" 2nd Ed. (Oxford, 1968). Chapters I-IV.

16.09.83



# I. Review of Basic Principles

## 1. Hermitian Operators

We assume that the scalar product of two functions $\chi$ and $\xi$ is defined and has the properties:

If $\chi$ & $\xi$ are f^ns of space coordinate, then $\langle\chi|\xi\rangle = \int_{space} \chi^* \xi \, d\tau$.

(i) $$\langle\chi|\xi\rangle = \langle\xi|\chi\rangle^*$$

(ii) $$\langle\chi|c\xi\rangle = c\langle\chi|\xi\rangle \qquad c \text{ complex no.}$$

(iii) $$\langle\chi\{|\xi_1\rangle + |\xi_2\rangle\} = \langle\chi|\xi_1\rangle + \langle\chi|\xi_2\rangle$$

(iv) $$\{\langle\chi_1| + \langle\chi_2|\}|\xi\rangle = \langle\chi_1|\xi\rangle + \langle\chi_2|\xi\rangle$$

Here * denotes complex conjugation and c is a complex number.

The Hermitian adjoint, $\hat{\Omega}^\dagger$, of an operator $\hat{\Omega}$, is defined by the property

$$\langle\hat{\Omega}^\dagger\chi|\xi\rangle = \langle\chi|\hat{\Omega}\xi\rangle = \langle\chi|\hat{\Omega}|\xi\rangle$$

A <u>Hermitian or self-adjoint operator</u> is <u>its own adjoint</u>: *

$$\hat{\Omega}^\dagger = \hat{\Omega}$$

Hence for a Hermitian operator

$$\langle\chi|\hat{\Omega}|\xi\rangle = \langle\hat{\Omega}^\dagger\chi|\xi\rangle = \langle\xi|\hat{\Omega}^\dagger\chi\rangle^*$$
$$= \langle\xi|\hat{\Omega}|\chi\rangle^*$$

Thus the matrix representation of a Hermitian operator has real diagonal elements and the off-diagonal elements are the complex conjugates of the transpose matrix.

Important properties of Hermitian operators:

(a) have real eigenvalues $\hat{\Omega}|f\rangle = \omega|f\rangle$ $\quad\omega$ - eigen value.

(b) eigenfunctions form a <u>complete orthonormal</u> set $\langle\psi_n|\psi_{n'}\rangle = \delta_{n,n'}$ so that any function $|f\rangle$ can be expanded as $|f\rangle = \sum_n |\psi_n\rangle\langle\psi_n|f\rangle$

(Close: a reasonably behaved f^ns) coeff. $\langle\psi_n|f\rangle$

The representation of a general function as a column vector

$$|f\rangle = \begin{pmatrix} \langle\psi_1|f\rangle \\ \langle\psi_2|f\rangle \\ \vdots \\ \langle\psi_N|f\rangle \end{pmatrix}$$

is convenient since one can work with the function as a physical vector rather than an abstract function. In the same way, representation of operators as matrices

$$\hat{\Omega} = \begin{pmatrix} \langle\psi_1|\hat{\Omega}|\psi_1\rangle & \langle\psi_1|\hat{\Omega}|\psi_2\rangle & \cdots & \langle\psi_1|\hat{\Omega}|\psi_N\rangle \\ \langle\psi_2|\hat{\Omega}|\psi_1\rangle & \langle\psi_2|\hat{\Omega}|\psi_2\rangle & \cdots & \langle\psi_2|\hat{\Omega}|\psi_N\rangle \\ \vdots & \vdots & & \vdots \\ \langle\psi_N|\hat{\Omega}|\psi_1\rangle & \langle\psi_N|\hat{\Omega}|\psi_2\rangle & \cdots & \langle\psi_N|\hat{\Omega}|\psi_N\rangle \end{pmatrix}$$

will be convenient.

## 2. Unitary Transformations

A unitary transformation is a linear homogeneous transformation which preserves "lengths" and "angles", i.e. scalar products are invariant under unitary transformations.

If $\hat{U}$ is an operator (matrix) which generates a unitary transformation of the basis functions $\{|\psi_n\rangle\}$, then the scalar products $\langle\psi_n|\psi_{n'}\rangle$ must be invariant:
Let $|\phi_n\rangle = \hat{U}|\psi_n\rangle$ and $|\phi_{n'}\rangle = \hat{U}|\psi_{n'}\rangle$. Then $\langle\phi_n|\phi_{n'}\rangle = \langle\psi_n|\psi_{n'}\rangle$ is required. Hence

$$\langle\phi_n|\phi_{n'}\rangle = \langle\hat{U}\psi_n|\hat{U}\psi_{n'}\rangle = \langle\psi_n|\hat{U}^\dagger\hat{U}|\psi_{n'}\rangle$$

( The inverse of a unitary matrix is equal to its Hermitian conjugate ).

and $\hat{U}^{\dagger}\ \hat{U} = \hat{1}$

i.e. $\hat{U}^{\dagger} = \hat{U}^{-1}$.

In terms of matrix elements

$U_{mn}$ = m,n elt. of the matrix rep. of the operator $\hat{U}$.

$$|\phi_n\rangle = \hat{U}|\psi_n\rangle = \sum_m |\psi_m\rangle\langle\psi_m|\hat{U}|\psi_n\rangle = \sum_m |\psi_m\rangle U_{mn}$$

$$= \sum_m |\psi_m\rangle\langle\psi_m|\phi_n\rangle$$

Hence $U_{mn} = \langle\psi_m|\phi_n\rangle = \langle\psi_m|\hat{U}|\psi_n\rangle$

Now unitarity requires $\hat{U}^{\dagger}\hat{U} = 1$ so that

$$\Sigma\{|\psi_m\rangle\langle\psi_m|\hat{U}^{\dagger}|\psi_n\rangle\langle\psi_n|\}\{|\psi_{m'}\rangle\langle\psi_{m'}|\hat{U}|\psi_{n'}\rangle\langle\psi_{n'}|\} \quad *$$
$$= \sum_m |\psi_m\rangle\langle\psi_m|$$

and $\sum_n \langle\psi_m|U^{\dagger}|\psi_n\rangle\langle\psi_n|U|\psi_{n'}\rangle = \delta_{m,n'}$

or $\sum_n U^*_{nm}U_{nn'} = \delta_{m,n'}$

Thus if we view the columns of $\underset{\sim}{U}$ as a collection of column vectors, these column vectors form an orthonormal set. Similarly, one can show that the rows of $\underset{\sim}{U}$ can be viewed as a collection of orthonormal row vectors.

Note: I differ from Rose in my representation of the transformation operator. His $\hat{C}$ corresponds to my $\hat{U}^{\dagger}$.

The transformation of the matrix representation $\underset{\sim}{\Omega}_{\psi}$ of the operator $\hat{\Omega}$ in the $\{|\psi_n\rangle\}$ basis to the matrix representation $\underset{\sim}{\Omega}_{\phi}$ in the $\{|\phi_n\rangle\}$ is straightforward:

$$\langle\phi_i|\hat{\Omega}|\phi_j\rangle = \Sigma\{|\psi_m\rangle U_{mi}\}^*\hat{\Omega}\{|\psi_n\rangle U_{nj}\}$$
$$= \Sigma U^{\dagger}_{im}\langle\psi_m|\hat{\Omega}|\psi_n\rangle U_{nj}$$

and

$$\underset{\sim}{\Omega}_{\phi} = \underset{\sim}{U}^{\dagger}\underset{\sim}{\Omega}_{\psi}\underset{\sim}{U}$$

## 3. Diagonalization of Operators

Suppose that the representation $\underset{\sim}{\Omega}_{\psi}$ of the operator $\hat{\Omega}$ in the $\{|\psi_n>\}$ basis is not diagonal. How does one find the unitary transformation $\hat{U}$ to a basis $\{|\phi_i>\}$ in which the representation $\underset{\sim}{\Omega}_{\phi}$ is diagonal?

$$|\phi_i> = \Sigma|\psi_n>U_{ni}$$

$$\hat{\Omega}|\phi_i> = \omega_i|\phi_i> \quad \text{(requirement for diagonal representation)}$$

$$\text{LHS} = \Sigma\hat{\Omega}|\psi_n>U_{ni}$$

$$= \sum_{n,m}|\psi_m><\psi_m|\hat{\Omega}|\psi_n>U_{ni}$$

$$\text{RHS} = \omega_i\sum_m|\psi_m>U_{mi}$$

Since the $|\psi_m>$ are a set of linearly independent functions

$$\sum_n\{<\psi_m|\hat{\Omega}|\psi_n> - \omega_i\delta_{mn}\}U_{ni} = 0$$

This set of linear homogeneous equations has nontrivial solution if and only if $|\underset{\sim}{\Omega}_{\psi} - \omega_i\underset{\sim}{1}| = 0$. This determinantal equation furnishes the algebraic equation from which the allowed eigenvalues $\{\omega_i\}$ are determined, and back substitution into the set of linear equations gives the elements of $\underset{\sim}{U}$ within an arbitrary constant. The arbitrary constant is determined by requiring $\underset{\sim}{U}$ to be unitary, and one is left with only arbitrary phases of exp($i\eta$) on each column of $\underset{\sim}{U}$.

## 4. Exponential Form of Unitary Operators

An exponential operator exp($\hat{A}$) is defined as the McLaurin series:

McLaurin Series:
$f(x) = f(0) + f'(0)(x) + \frac{f''(0).x^2}{2!} + \frac{f'''(0)x^3}{3!} + \ldots$
$= \sum_{n=0}^{\infty} \frac{f^n(0).x^n}{n!}$

$$\exp(\hat{A}) = \sum_{n=0}^{\infty} \hat{A}^n/n!$$

Note that for two operators $\hat{A}$ and $\hat{B}$,

$$\exp(\hat{A} + \hat{B}) = \exp(\hat{A}) \exp(\hat{B})$$

IF and ONLY IF $\hat{A}$ and $\hat{B}$ commute.

Note also that $[\exp(\hat{A})]^{-1} = \exp(-\hat{A})$

since $\hat{A}$ and $-\hat{A}$ do commute.

Theorem: If $\hat{S}$ is Hermitian, the operator $\exp(i\hat{S})$ is unitary.

Proof: $\hat{U} = \exp(i\hat{S})$

$$\begin{aligned}
\hat{U}^\dagger &= [\Sigma(iS)^n/n!]^\dagger \\
&= \Sigma([i\hat{S}]^\dagger)^n/n! \\
&= \Sigma(-i\hat{S}^\dagger)^n/n! \\
&= \exp(-i\hat{S}^\dagger) \\
&= \exp(-i\hat{S}) \\
&= \hat{U}^{-1}
\end{aligned}$$

Hence $\hat{U}$ is unitary.

Example: Rotation in One Dimension

The Schroedinger equation for rotation of a diatomic rotor in a plane is

$$\frac{-\hbar^2}{2\mu r^2} \frac{\partial^2\psi}{\partial\phi^2} = E\psi$$

with solutions $\psi_n(\phi) = A \exp in\phi$ $\quad n = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots$

and eigenvalues $E_n = \dfrac{\hbar^2 n^2}{2\mu r^2}$

If the coordinate axes are rotated by angle $\alpha$ so that the rotor remains in the plane, the transformed wavefunction is $\psi_n'(\phi) = \psi_n(\phi - \alpha) = \exp(-in\alpha)\psi_n(\phi)$

But $\exp(-in\alpha)$ is just the matrix representation of the operator $\exp(-i\hat{L}_Z\alpha)$, where $\hat{L}_Z = -i\partial/\partial\phi$ is the dimensionless orbital angular momentum operator. Hence the rotational transformation is unitary and the Hermitian operator $\hat{S}$ in this case is just $-\alpha\hat{L}_Z$.

Addendum

It is useful to look at this problem in another way:

$\psi'(\phi) = \psi(\phi-\alpha)$

We can express $\psi(\phi-\alpha)$ as a Taylor series

$$\psi(\phi-\alpha) = \psi(\phi) - \alpha\frac{d\psi}{d\phi} + \frac{(-\alpha)^2}{2!}\frac{d^2\psi}{d\psi^2} + \frac{(-\alpha)^3}{3!}\frac{d^3\psi}{d\phi^3} + \ldots$$

$$= \psi + (-\alpha\frac{d}{d\phi})\psi + \frac{1}{2!}(-\alpha\frac{d}{d\phi})^2\psi + \frac{1}{3!}(-\alpha\frac{d}{d\phi})^3\psi + \ldots$$

$$= \exp(-\alpha\frac{d}{d\phi})\ \psi(\phi)$$

In quantum mechanics, the dimensionless z-component angular momentum operator is $-i\frac{d}{d\phi}$, hence $\hat{L}_Z = -i\,d/d\phi$

$\psi' = \exp(-i\alpha\hat{L}_z)\psi$.

This derivation is probably more instructive than that given above which was taken directly from Rose's book.

## II. The Angular Momentum Operators

### 5. Definition of Angular Momentum Operators

From the observational point of view, the physical quantity to which the term angular momentum refers is usually the result of a rather indirect measurement. In the theory, this appears as a quantity related to the eigenvalue of an operator having to do with the rotational properties of the physical system. In classical mechanics, orbital angular momentum is conserved if the classical Hamiltonian is invariant under rotations, and in quantum mechanics, this would correspond to the statement that $\hat{H}$ commutes with the angular momentum operators. In classical mechanics all 3 components of orbital angular momentum can be constants of the motion, but only one component operator can be a constant in the quantal system because the component angular momentum operators, although they commute with $\hat{H}$, do not commute with each other. Another very important difference between classical and quantal angular momenta is that only orbital angular momentum is possible in classical mechanics, whereas one very often finds intrinsic spin angular momenta as well as orbital angular momentum in quantum mechanical systems. We shall define angular momentum operators in a more general manner and show that orbital angular momentum operators fit into the general scheme.

To define the angular momentum operators, we generalize the simple example of section 4. Consider a rotation of the coordinate system by angle $\theta$ about an axis defined by the direction of the unit vector $\vec{n}$. The wavefunction $\psi$ in the original coordinate system is related to the wavefunction $\psi'$ in the rotated system by a unitary transformation $\hat{R}(\vec{n},\theta)$:

$$\psi' \equiv \hat{R}(\vec{n},\theta)\psi$$

In the limit $\theta \to 0$ $\hat{R} \to \hat{1}$ and it is convenient to express $\hat{R}$ as

$$\hat{R}(\vec{n},\theta) = \exp[-i\hat{S}(\vec{n},\theta)] \tag{2.2}$$

where $\hat{S}$ is a Hermitian operator whose identity is yet to be specified. Clearly $\hat{S} \to 0$ as $\theta \to 0$.

It is useful to look at <u>infinitesimal</u> rotations:

$$\hat{R}(\vec{n},\theta) = \hat{1} - i\hat{S}(n,\theta) \quad + (\ldots \text{higher order terms neglected})$$

$$\hat{R}\psi = (\hat{1} - i\hat{S})\psi \text{ or } \hat{R}\psi - \psi = -i\hat{S}\psi$$

For an infinitesimal rotation about the z-axis, it is clear (section 4) $(\hat{J}_z = \hat{L}_z)$ that

$$\hat{R}_z\psi - \psi = -i\theta\hat{J}_z\psi \qquad \left[\text{In a general context: } \hat{R}_z(\theta_z) = \exp(-i\theta\hat{J}_z)\right]$$

where $\hat{J}_z$ is the z-component of the angular momentum operator. Similarly infinitesimal rotations about the x, or y axes are described by

$$\hat{R}_x\psi - \psi = -i\theta\hat{J}_x\psi$$

and

$$\hat{R}_y\psi - \psi = -i\theta\hat{J}_y\psi.$$

The operators $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$ are the operators for the three components of the total angular momentum of the system and generate infinitesimal rotations of the coordinate system about the x, y, z directions. They are complete in that any infinitesimal rotation about a general direction can be represented as a linear combination of these primitive rotations. For infinitesimal rotation by $\theta$ about $\vec{n}$:

$$\hat{R}(\vec{n},\theta)\psi - \psi = -i\theta\vec{n}\cdot\hat{\vec{J}}\psi \qquad \Rightarrow \hat{R}(\vec{n},\theta)\psi = \underline{(1 + (-)i\theta\vec{n}\cdot\hat{\vec{J}})}\psi = \exp(-i\theta\vec{n}\cdot\hat{\vec{J}})\psi$$

Thus the operator $\hat{S}$ in (2.2) above must be given by

$$\hat{S} = \theta\vec{n}\cdot\hat{\vec{J}}$$

and the unitary transformation is

$$\underline{\underline{\hat{R} = \exp(-i\theta\vec{n}\cdot\hat{\vec{J}})}}$$

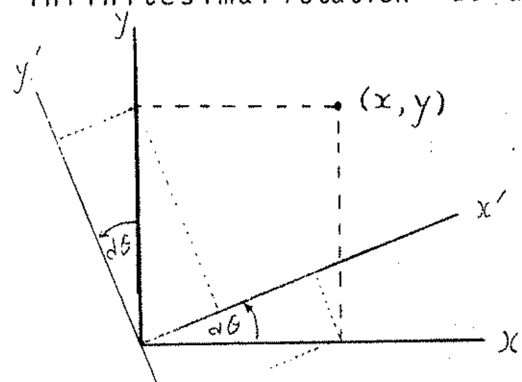
Thus the angular momentum determines the transformation properties * of the system under rotations of coordinates. Conversely, the angular momentum operator $\hat{\vec{J}}$ can be determined from the transformation properties of the system. This is the essence of our definition * of angular momentum.

6. Orbital Angular Momentum

As an illustration of the ideas developed above, let us consider the case of a function $\psi_{(x,y,z)}$ of the space coordinates, and let us apply a rotation of the coordinate system so that the point (x,y,z) in the original frame corresponds to coordinates (x',y',z') in the rotated frame. Thus

$$\psi_{(x',y',z')} = \hat{R}\psi_{(x,y,z)}$$

Let us consider an infinitesimal rotation $d\theta$ about the z-axis




For an infinitesimal θ
sinθ → θ
cosθ → 1.

$$x' = x\cos(d\theta) + y\sin(d\theta) = x + yd\theta$$

$$y' = -x\sin(d\theta) + y\cos(d\theta) = y - xd\theta$$

$$z' = z$$

Then we make a Taylor expansion of $\psi_{(x',y',x')}$ about (x,y,z) =

$$\psi_{(x',y',z')} = \psi_{(x,y,z)} + \left(\frac{\partial\psi}{\partial x}\right)(x'-x) + \left(\frac{\partial\psi}{\partial y}\right)(y'-y) + \left(\frac{\partial\psi}{\partial z}\right)(z'-z) + \ldots$$

Since we are considering only an infinitesimal rotation, higher order terms can be neglected, hence

$$\psi_{(x',y',z')} = \psi_{(x,y,z)} + d\theta\ (y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y})\psi_{(x,y,z)}$$

Recall that, by definition,

$$\hat{R}\psi_{(x,y,z)} = (1 - id\theta\hat{J}_z)\psi_{(x,y,z)}$$

for an infinitesimal rotation. Hence we make the identification

$$\hat{J}_z = -i(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) \equiv \hat{L}_z$$

In an analogous fashion, one can show that

$$\hat{L}_x = -i(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$$

and

$$\hat{L}_y = -i(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}).$$

It is straightforward to derive the commutation relations among the orbital angular momentum operators:

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

$$= -(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) + (z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$$

$$= -y\frac{\partial}{\partial x} - yz\frac{\partial^2}{\partial z\partial x} + xy\frac{\partial^2}{\partial z^2} + z^2\frac{\partial^2}{\partial y\partial x} - xz\frac{\partial^2}{\partial y\partial z} + yz\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y}$$

$$-xy\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}$$

$$= x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}$$

$$= i\hat{L}_z$$

By cyclic permutation of indices, we obtain

$$[\hat{L}_y, \hat{L}_z] = i\hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hat{L}_y$$

or

$$\hat{\vec{L}} \times \hat{\vec{L}} = i\hat{\vec{L}}$$

x y z + i

$[\hat{L}_x, \hat{L}_y] = i\hat{L}_z$

$[\hat{L}_y, \hat{L}_z] = i\hat{L}_x$

$[\hat{L}_z, \hat{L}_x] = i\hat{L}_y$

## 7. Commutation Rules for Angular Momentum Operators

We now wish to show that our general definition of angular momentum operators in terms of transformation properties implies the commutator relations $\hat{\vec{J}} \times \hat{\vec{J}} = i\hat{\vec{J}}$ for a general angular momentum. We apply two infinitesimal rotations to the coordinate system $\exp(-id\theta_x \hat{J}_x)$ and $\exp(-id\theta_y \hat{J}_y)$ and find the difference which arises when the operations are applied in different order. The rotation matrix for a rotation about the x-axis is

Recall that for $R_z(\theta)$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\hat{R}_x(\theta_x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_x & \sin\theta_x \\ 0 & -\sin\theta_x & \cos\theta_x \end{pmatrix}$$

and for a rotation about the y-axis

$$\hat{R}_y(\theta_y) = \begin{pmatrix} \cos\theta_y & 0 & -\sin\theta_y \\ 0 & 1 & 0 \\ \sin\theta_y & 0 & \cos\theta_y \end{pmatrix}$$

and for infinitesimal rotations

$$\hat{R}_x(d\theta_x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & d\theta_x \\ 0 & -d\theta_x & 1 \end{pmatrix}$$

$$\hat{R}_y(d\theta_y) = \begin{pmatrix} 1 & 0 & -d\theta_y \\ 0 & 1 & 0 \\ d\theta_y & 0 & 1 \end{pmatrix}$$

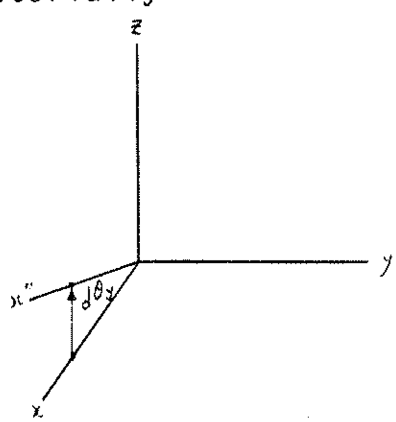
Let us concentrate our attention on the point (1,0,0) to see how it is transformed by the operations $\hat{R}_x(d\theta_x)$ followed by $\hat{R}_y(d\theta_y)$ and by the operations $\hat{R}_y(d\theta_y)$ followed by $\hat{R}_x(d\theta_x)$

$$\hat{R}_y(d\theta_y)\ \hat{R}_x(d\theta_x) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ d\theta y \end{pmatrix}$$

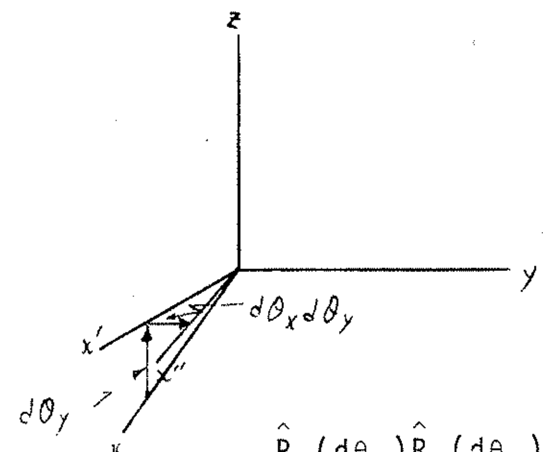
and

$$\hat{R}_x(d\theta_x)\ \hat{R}_y(d\theta_y) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ d\theta_x d\theta_y \\ d\theta_y \end{pmatrix}$$

Pictorially




$\hat{R}_y(d\theta_y)\ \hat{R}_x(d\theta_x)$




$\hat{R}_x(d\theta_x)\hat{R}_y(d\theta_y)$

Thus $\hat{R}_x(d\theta_x)\hat{R}_y(d\theta_y) - \hat{R}_y(d\theta_y)\hat{R}_x(d\theta_x)$ corresponds to rotation of magnitude $d\theta_x d\theta_y$ about the z-axis.

Equating the net changes in the vector (1,0,0), we have

$$\exp(-id\theta_x\hat{J}_x)\exp(-id\theta_y\hat{J}_y) - \exp(-id\theta_y\hat{J}_y)\exp(-id\theta_x\hat{J}_x)$$
$$= \exp(-id\theta_x d\theta_y \hat{J}_z) - 1$$

Expanding to second order in infinitesimals, we obtain

$$[1-id\theta_x\hat{J}_x - (d\theta_x)^2\hat{J}_x{}^2][1-id\theta_y\hat{J}_y - (d\theta_y)^2\hat{J}_y{}^2]$$
$$- [1-id\theta_y\hat{J}_y - (d\theta_y)^2\hat{J}_y{}^2][1-id\theta_x\hat{J}_x - (d\theta_x)^2\hat{J}_x{}^2]$$
$$= [1-id\theta_x d\theta_y\hat{J}_z] - 1$$

and

$$1 - id\theta_x\hat{J}_x - id\theta_y\hat{J}_y - (d\theta_x)^2\hat{J}_x{}^2 - (d\theta_y)^2\hat{J}_y{}^2 - d\theta_x d\theta_y\hat{J}_x\hat{J}_y$$

$$- [1-id\theta_x\hat{J}_x-id\theta_y\hat{J}_y-(d\theta_x)^2\hat{J}_x{}^2-(d\theta_y)^2\hat{J}_y{}^2 - d\theta_x d\theta_y\hat{J}_y\hat{J}_x]$$

$$= -id\theta_x d\theta_y\hat{J}_z$$

or $-d\theta_x d\theta_y(\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x) = -id\theta_y d\theta_y\hat{J}_z$

Thus we find the usual commutator relation *

$$[\hat{J}_x,\hat{J}_y] = i\hat{J}_z \, .$$ for general angular momentum $\hat{\vec{J}}$

## 8. Eigenvalues of the Angular Momentum Operators

Let us consider a single system (one molecule say) with total angular momentum j. In a large number of physical problems, one finds that the Hamiltonian operator commutes with the operator for a rotation about the k-axis: $\hat{H}$ is invariant under a rot'n about the k axis.

$$\exp(-i\hat{J}_k\theta)\hat{H}\exp(i\hat{J}_k\theta) = \hat{H}$$

or
$$[\hat{H},\exp(i\hat{J}_k\theta)] = 0.$$

If we expand $\exp(i\hat{J}_k\theta)$ in its McLaurin series representation, the coefficient of each term in the $\theta^n$ series must be independently zero. Hence we conclude that

$$[H,J_k{}^n] = 0$$

i.e. $\hat{H}$ commutes with any power of $\hat{J}_k$. Of course the condition that $[\hat{H},\hat{J}_k] = 0$ is sufficient to prove that $\hat{H}$ commutes with all powers of $\hat{J}_k$.

In some cases, $\hat{H}$ commutes with $\hat{J}_x,\hat{J}_y$ and $\hat{J}_z$ (spectroscopic experiments in the absence of large static electric or magnetic fields), while in others $\hat{H}$ commutes only with $\hat{J}_z$ (experiments with static field along z-axis). In both of these cases $\hat{H}$ commutes with $\hat{J}^2 = \hat{J}_x{}^2 + \hat{J}_y{}^2 + \hat{J}_z{}^2$. Thus, we generally have the conditions

In general $[\hat{H}, \hat{J}_z] = 0$
$[\hat{H}, \hat{J}^2] = 0$

$[\hat{J}^2, \hat{J}_z] = 0$
$[\hat{J}^2, \hat{J}_y] = 0$
$\hat{J}_x$

$$[\hat{H},\hat{J}_z] = 0 \quad * \quad \text{in general.}$$

and $$[\hat{H},\hat{J}^2] = 0$$

In addition $[\hat{J}^2,\hat{J}_z] = 0$, $[\hat{J}^2,\hat{J}_y] = 0$, and $[\hat{J}^2,\hat{J}_x] = 0$. This implies that the eigenfunctions of the Hamiltonian are simultaneously eigenfunctions of $\hat{J}_z$ and $\hat{J}^2$. Let us designate these eigenfunctions $|jm\rangle$ and define their eigenvalues by

$$\hat{J}_z|jm\rangle = m|jm\rangle \qquad |jm\rangle = \psi_{jm}$$
$$\hat{J}^2|jm\rangle = a_j|jm\rangle$$

We now proceed with the determination of the eigenvalues m and $a_j$ of these angular momentum operators. At this point, j is simply an index to distinguish one eigenvalue of $\hat{J}^2$ from another. Now the operator $\hat{J}_x{}^2 + \hat{J}_y{}^2 = \hat{J}^2 - \hat{J}_z{}^2$ will have eigenvalue $(a_j - m^2)$ for $|jm\rangle$. The eigenvalue of the square of a Hermitian operator is necessarily positive:

$$\langle jm|\hat{J}_x{}^2|jm\rangle = \sum_{j'm'}\langle jm|\hat{J}_x|j'm'\rangle\langle j'm'|\hat{J}_x|jm\rangle$$

$$= \sum_{j'm'}|\langle jm|\hat{J}_x|j'm'\rangle|^2 \geq 0$$

This implies that $a_j \geq 0$ and that $a_j - m^2 \geq 0$ and that for a given j, m will be bounded $-\sqrt{a_j} \leq m \leq +\sqrt{a_j}$. We shall find presently the precise values of these bounds and the allowed values of $a_j$.

It is useful to introduce the <u>ladder operators</u>

$$\underline{\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y}$$

They obey the commutator relationships

$$[\hat{J}_z,\hat{J}_+] = [\hat{J}_z,\hat{J}_x] + i[\hat{J}_z,\hat{J}_y] = i\hat{J}_y + i(-i\hat{J}_x)$$
$$= \hat{J}_+$$

$\therefore [\hat{J}_z, \hat{J}_\pm] = \pm \hat{J}_\pm$

$[\hat{J}_+, \hat{J}_-] = 2\hat{J}_z$

$[\hat{J}^2, \hat{J}_\pm] = 0$

$$[\hat{J}_z,\hat{J}_-] = [\hat{J}_z,\hat{J}_x] - i[\hat{J}_z,\hat{J}_y] = i\hat{J}_y - i(-i\hat{J}_x)$$
$$= -\hat{J}_-$$

$$[\hat{J}_+,\hat{J}_-] = [\hat{J}_x + i\hat{J}_y, \hat{J}_x - i\hat{J}_y] = i[\hat{J}_y,\hat{J}_x] - i[\hat{J}_x,\hat{J}_y]$$
$$= 2\hat{J}_z$$

It is useful to recognize that

$$[\hat{J}^2,\hat{J}_\pm] = 0$$

and that

$$\hat{J}^2 = \hat{J}_x{}^2 + \hat{J}_y{}^2 + \hat{J}_z{}^2 = [\tfrac{1}{2}(\hat{J}_+ + \hat{J}_-)]^2 + [-\tfrac{i}{2}(\hat{J}_+ - \hat{J}_-)]^2 + \hat{J}_z{}^2$$

$$= \tfrac{1}{4}[\hat{J}_+{}^2 + \hat{J}_-{}^2 + \hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+] - \tfrac{1}{4}[\hat{J}_+{}^2 + \hat{J}_-{}^2 - \hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+] + \hat{J}_z{}^2$$

$$= \tfrac{1}{2}(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+) + \hat{J}_z{}^2 \quad .$$

Since

$$\hat{J}_+\hat{J}_- = \hat{J}_-\hat{J}_+ + 2\hat{J}_z \qquad [\because [\hat{J}_+, \hat{J}_-] = 2\hat{J}_z]$$

we obtain

$$\hat{J}^2 = \hat{J}_z{}^2 + \hat{J}_z + \hat{J}_-\hat{J}_+ \quad \text{or} \quad \hat{J}_-\hat{J}_+ = \hat{J}^2 - \hat{J}_z{}^2 - \hat{J}_z$$

and

$$\hat{J}^2 = \hat{J}_z{}^2 - \hat{J}_z + \hat{J}_+\hat{J}_- \quad \text{or} \quad \hat{J}_+\hat{J}_- = \hat{J}^2 - \hat{J}_z{}^2 + \hat{J}_z$$

Suppose that one of the eigenfunctions $|jm>$ is known. We operate on it with the commutator

$$[\hat{J}_z,\hat{J}_\pm] = \pm\hat{J}_\pm$$

to obtain

$$\hat{J}_z(\hat{J}_\pm|jm>) - \hat{J}_\pm(\hat{J}_z|jm>) = \pm(\hat{J}_\pm|jm>)$$

or

$$\hat{J}_z(\hat{J}_\pm|jm>) = (m \pm 1)(\hat{J}_\pm|jm>)$$

Note that $\hat{J}^2$ commutes with $\hat{J}_+$ and with $\hat{J}_-$ so that

$$\hat{J}^2(\hat{J}_{\pm}|jm\rangle) = \hat{J}_{\pm}(J^2|jm\rangle) = a_j(\hat{J}_{\pm}|jm\rangle)$$

Thus the functions $\hat{J}_{\pm}|jm\rangle$ are simultaneous eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$ with eigenvalues $a_j$ and $m \pm 1$. Hence

$$\hat{J}_{\pm}|jm\rangle = \Gamma_{\pm}|jm \pm 1\rangle$$

where the proportionality constant $\Gamma_{\pm}$ may depend on both j and ~~x~~ m and may be zero in some cases.

We have shown above that the eigenvalue m has both lower and upper bounds so there must exist an eigenvalue $m = m_1$ which corresponds to the lowest allowed m, and an eigenvalue $m = m_2$ which corresponds to the highest allowed m for a given j (and $a_j$). Thus we must require

$$\hat{J}_-|jm_1\rangle = 0$$

and

$$\hat{J}_+|jm_2\rangle = 0$$

Otherwise there would be eigenfunctions $|jm\rangle$ with $m > m_2$ or $m < m_1$ contrary to the bounds already established. Now

$$\hat{J}_+\hat{J}_- = \hat{J}^2 - \hat{J}_z^{\,2} + \hat{J}_z$$

hence

$$\begin{aligned} \hat{J}_+(\hat{J}_-|jm_1\rangle) &= 0 \\ &= (\hat{J}^2 - \hat{J}_z^{\,2} + \hat{J}_z)|jm_1\rangle \\ &= (a_j - m_1^{\,2} + m_1)|jm_1\rangle \end{aligned}$$

Therefore $a_j - m_1^{\,2} + m_1 = 0$

Similarly, since $\hat{J}_-\hat{J}_+ = \hat{J}^2 - \hat{J}_z^{\,2} - \hat{J}_z$

$$\begin{aligned} \hat{J}_-(\hat{J}_+|jm_2\rangle) &= 0 \\ &= (\hat{J}^2 - \hat{J}_z^{\,2} - \hat{J}_z)|jm_2\rangle \\ &= (a_j - m_2^{\,2} - m_2)|jm_2\rangle \end{aligned}$$

we find that

$$a_j - m_2^2 - m_2 = 0$$

Hence $$m_1^2 - m_1 = m_2^2 + m_2$$

which has solutions

$$m_1 = -m_2$$

and $$m_1 = m_2 + 1$$

Since $m_1 \leq m_2$, we disregard the latter and conclude that $m_1 = -m_2$ i.e. the upper and lower bounds on m have the same magnitude but are opposite in sign.

Now

$$|jm_2> \ \alpha\ (J_+)^n |jm_1>$$

where n is a non-negative integer. Thus

$$m_2 = m_1 + n$$

or $$m_2 = -m_2 + n$$

and $$n = 2m_2 \quad \text{or} \quad m_2 = n/2$$

The upper bound on m was shown above to depend on $a_j$ and hence upon the index j. It is useful at this time to identify the index j with the largest allowed m i.e.

$$j = n/2 = m_2 = -m_1.$$

j can therefore take on values 0, 1/2, 1, 3/2, 2, ....

Thus $m_2 = j$, $m_1 = -j$ and the allowed values of m for a given j are $-j, -j+1, -j+2, \ldots, j-2, j-1, j$. There are $2j+1$ allowed values of m. The eigenvalue $a_j = j(j+1)$. In summary

$$\hat{J}^2|jm> = j(j+1)|jm> \qquad j \text{ - integer or half integer}$$

$$\hat{J}_z|jm> = m|jm> \qquad m = -j, -j+1, \ldots, j$$

The quantum number j is the total angular momentum in units of $\hbar$. In the classical limit where $j \to \infty$, the eigenvalue of $J^2$ is $j^2$. We recognize that the maximum and minimum eigenvalues of $\pm j$ are, in the classical limit, the situations where the angular momentum points in the $\pm z$ directions. The extra term in the exact eigenvalue of $\hat{J}^2$, i.e. $j(j+1) = j^2(1+1/j)$ is a quantum-mechanical effect which arises from the noncommutability of the angular momentum operators. It is seen therefore to arise from the impossibility of precisely defining the direction and magnitude of the angular momentum vector simultaneously as required by the Heisenberg uncertainty principle.

We must now determine the matrix elements of $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_\pm$ in the basis functions $|jm\rangle$ which diagonalize $\hat{J}_z$ and $\hat{J}^2$. We have shown above that

$$\hat{J}_\pm|jm\rangle = \Gamma_\pm|jm\pm 1\rangle$$

Hence

$$\begin{aligned}(\hat{J}_\pm|jm\rangle)^*(\hat{J}_\pm|jm\rangle) &= \langle jm\pm 1|\Gamma_\pm^*)(\Gamma_\pm|jm\pm 1\rangle \\ &= |\Gamma_\pm|^2\langle jm\pm 1|jm\pm 1\rangle \\ &= |\Gamma_\pm|^2\end{aligned}$$

Now $(\hat{J}_\pm|jm\rangle)^* = \langle jm|\hat{J}_\pm^\dagger$

so that $\langle jm|\hat{J}_\pm^\dagger\hat{J}_\pm|jm\rangle = |\Gamma_\pm|^2$

But $\hat{J}_\pm^\dagger = \hat{J}_\mp$

and $\hat{J}_\mp\hat{J}_\pm = \hat{J}^2 - \hat{J}_z^2 \mp \hat{J}_z$

Hence $|\Gamma_\pm|^2 = j(j+1) - m(m\pm 1)$

We take the square root and choose the phase so that

$$\Gamma_\pm = [j(j+1) - m(m\pm 1)]^{\frac{1}{2}}$$

This is often called the Condon and Shortley phase convention.

Thus we have shown that the matrix representations of the angular momentum operators are given by:

$$\langle j'm'|\hat{J}^2|jm\rangle = j(j+1)\delta_{j',j}\delta_{m',m}$$

$$\langle j'm'|\hat{J}_z|jm\rangle = m\delta_{j',j}\delta_{m',m}$$

$$\langle j'm'|\hat{J}_{\pm}|jm\rangle = [j(j+1) - m(m\pm 1)]^{\frac{1}{2}}\delta_{j',j}\delta_{m',m\pm 1}$$

$$\langle j'm'|\hat{J}_x|jm\rangle = \frac{1}{2}[j(j+1) - m(m+1)]^{\frac{1}{2}}\delta_{j',j}\delta_{m',m+1} + \frac{1}{2}[j(j+1) - m(m-1)]^{\frac{1}{2}}\delta_{j',j}\delta_{m',m-1}$$

$$\langle j'm'|\hat{J}_y|jm\rangle = -\frac{i}{2}[j(j+1) - m(m+1)1^{\frac{1}{2}}\delta_{j',j}\delta_{m'm+1} + \frac{i}{2}[j(j+1) - m(m-1)]^{\frac{1}{2}}\delta_{j',j}\delta_{m',m-1}$$

<u>The Functions |LM> and Angular Parts of Hydrogenic Wavefunctions</u>

In Cartesian coordinates the orbital angular momentum operators are:

$$\hat{L}_x = -i\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$\hat{L}_y = -i\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$\hat{L}_z = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

It is useful to represent these operators in spherical polar coordinates:

$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}} \qquad x = r\sin\theta\cos\phi$$
$$\theta = \arccos(z/r) \qquad y = r\sin\theta\sin\phi$$
$$\phi = \arctan(y/x) \qquad z = r\cos\theta$$

The transformation of differential operators is effected by recognizing that

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta} \qquad \text{(chain rule)}$$

$$= \sin\theta\cos\phi\frac{\partial}{\partial r} + r^{-1}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - r^{-1}\csc\theta\sin\phi\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + r^{-1}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + r^{-1}\csc\theta\cos\phi\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - r^{-1}\sin\theta\frac{\partial}{\partial\theta}$$

Then $\hat{L}_x = i(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi})$

$$\hat{L}_y = i(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi})$$

$$\hat{L}_z = -i\frac{\partial}{\partial\phi}$$

and $\hat{L}_{\pm} = \pm\exp(\pm i\phi)(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi})$

Now let us derive the functional forms of the functions $|LM\rangle$ which are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues $L(L+1)$ and $M$ respectively.

$$\hat{L}_z|LM\rangle = M|LM\rangle$$

Hence

$$-i\frac{\partial}{\partial\phi}|LM\rangle = M|LM\rangle$$

or

$$\frac{\partial}{\partial\phi}|LM\rangle = iM|LM\rangle$$

with solution

$$|LM\rangle = f_{L,M}(\theta)\exp(iM\phi)$$

Since $\phi$ corresponds to a real angle, the function $|LM\rangle$ for $\phi' = \phi + 2\pi$ must be identical to the function $|LM\rangle$ at $\phi' = \phi$. *
This requires that M, and hence L, must be integral for orbital angular momenta.

In the previous section, we recognized that $\hat{j}_+|jj\rangle = 0$ so we now take

$$\hat{L}_+|LL\rangle = \exp(i\phi)(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}|LL\rangle = 0$$

(But $i\frac{\partial}{\partial\phi}|LL\rangle = -L|LL\rangle$ ?)

so that

$$\frac{\partial}{\partial\theta}|LL\rangle - L\cot\theta|LL\rangle = 0$$

If we introduce the change of variable

$$q = \sin\theta$$

so that

$$\frac{\partial}{\partial\theta} = \frac{\partial q}{\partial\theta}\frac{\partial}{\partial q} = \cos\theta\frac{\partial}{\partial q}$$

and

$$\cot\theta = \cos\theta/q$$

the differential equation becomes

$$\frac{d}{dq}f_{L,L} - \frac{L}{q}f_{L,L} = 0$$

which has solution

$$f_{L,L} = q^L = (\sin\theta)^L$$

Hence

$$|L,L\rangle = A_L(\sin\theta)^L\exp(iL\phi)$$

where $A_L$ is a normalization constant.

The other functions $|L,L-1\rangle$, $|L,L-2\rangle$, ---, $|L,-L\rangle$ are obtained by operating on $|L,L\rangle$ with the operator $\hat{L}_-$.

<u>Example: THe L = 2 Eigenfunctions</u>

$$|22\rangle = A_2\sin^2\theta\exp(+2i\phi)$$

$$\hat{L}_-|22\rangle = [2(2+1) - 2(2-1)]^{\frac{1}{2}}|2\ 1\rangle = 2|2\ 1\rangle$$

$$\hat{L}_-|22\rangle = -\exp(-i\phi)[\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}]\{A_2\sin^2\theta\exp(+2i\phi)\}$$

$$= -4A_2\sin\theta\cos\theta\exp(+i\phi)$$

$$\therefore |2\ 1\rangle = -2A_2\sin\theta\cos\theta\exp(+i\phi)$$

$$\hat{L}_-|2\ 1\rangle = [2(2+1) - 1(1-1)]^{\frac{1}{2}}|2\ 0\rangle = (6)^{\frac{1}{2}}|2\ 0\rangle$$

$$\hat{L}_-|2\ 1\rangle = -\exp(-i\phi)[\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}]\{-2A_2\sin\theta\cos\theta\exp(+i\phi)\}$$
$$= 2A_2(3\cos^2\theta-1)$$

$$\therefore |2\ 0\rangle = 2(6)^{-\frac{1}{2}}A_2(3\cos^2\theta-1)$$

$$\hat{L}_-|2\ 0\rangle = [2(2+1) - 0(0-1)]^{\frac{1}{2}}|2-1\rangle = (6)^{\frac{1}{2}}|2-1\rangle$$

$$\hat{L}_-|2\ 0\rangle = -\exp(-i\phi)[\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}]\{2(6)^{-\frac{1}{2}}A_2(3\cos^2\theta-1)\}$$
$$= 2(6)^{\frac{1}{2}}A_2\sin\theta\cos\theta\exp(-i\phi)$$

$$\therefore |2-1\rangle = 2A_2\sin\theta\cos\theta\exp(-i\phi)$$

$$\hat{L}_-|2-1\rangle = [2(2+1) - (-1)(-1-1)]^{\frac{1}{2}}|2-1\rangle = 2|2-1\rangle$$

$$\hat{L}_-|2-1\rangle = -\exp(-i\phi)[\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}]\{2A_2\sin\theta\cos\theta\exp(-i\phi)\}$$
$$= 2A_2\sin^2\theta\exp(-2i\phi)$$

$$\therefore |2-2\rangle = A_2\sin^2\theta\exp(-2i\phi)$$

Note that $\hat{L}_-|2-2\rangle = 0$ as it should. The functions $|LM\rangle$ have the property

$$|LM\rangle^* = (-1)^M|L-M\rangle.$$

## 9. Physical Interpretation of Angular Momentum

In this section of Rose's book, he is preoccupied with the nuclear physicsts view of angular momentum so we shall ignore this section.

# III Coupling of Two Angular Momenta

In many spectroscopic and other physical problems, more than one angular momentum will be present: in atomic spectroscopy we have the orbital and spin angular momenta, in magnetic resonance we have any number of spin angular momenta from the electrons and nuclei in the system. In virtually every case where two or more angular momenta are present, the Hamiltonian for the system will contain terms representing the interaction between the different angular momenta. For example, the spin Hamiltonian for a molecular fragment with two equivalent protons in a magnetic field is

$$\hat{H} = -h\nu_o(\hat{I}_{1z} + \hat{I}_{2z}) + hJ\hat{\vec{I}}_1\cdot\hat{\vec{I}}_2$$

where $\nu_o$ is the Larmour frequence for the protons, J is the scalar coupling between the nuclear spins, h is Planck's constant and $\hat{\vec{I}}_1$ and $\hat{\vec{I}}_2$ are the nuclear spin angular momentum operators for the two protons. It should be noted that $\hat{I}_{1z}$ and $\hat{I}_{2z}$ do not comute with $\hat{H}$, whereas the operator $\hat{I}_{1z} + \hat{I}_{2z}$ does commute with $\hat{H}$. One finds, in fact, that the set of operators $\hat{I}_{1z} + \hat{I}_{2z}$, $(\hat{\vec{I}}_1 + \hat{\vec{I}}_2)^2$, $\hat{I}_1{}^2$, $\hat{I}_2{}^2$, $\hat{H}$ simultaneously commute with all members of the set so the eigenfunctions of $\hat{H}$ can be defined in terms of the eigenvalues of the z-component of the total angular momentum, the square of the total angular momentum, and the squares of the individual spin angular momenta. The objective of this chapter is to relate the coupled functions (the eigenfunctions of $\hat{I}_{1z} + \hat{I}_{2z}$, $(\hat{\vec{I}}_1 + \hat{\vec{I}}_2)^2$ $\hat{I}_1{}^2$ and $\hat{I}_2{}^2$) to the uncoupled functions (the eigenfunctions of $\hat{I}_{1z}$, $\hat{I}_1{}^2$, $\hat{I}_{2z}$, $\hat{I}_2{}^2$).

## 10. Definition of the Clebsch-Gordan Coefficients

Let the eigenfunctions for the angular momenta $j_1$ and $j_2$ be $|j_1m_1\rangle$ and $|j_2m_2\rangle$ respectively with the properties

$$\hat{J}_{1z}|j_1m_1\rangle = m_1|j_1m_1\rangle$$

$$\hat{J}_1{}^2|j_1m_1\rangle = j_1(j_1+1)|j_1m_1\rangle$$

$$\hat{J}_{2z}|j_2m_2\rangle = m_2|j_2m_2\rangle$$

$$\hat{J}_2{}^2|j_2m_2\rangle = j_2(j_2+1)|j_2m_2\rangle$$

It must be remembered that although we use the same notation for the wavefunctions $|j_1m_1\rangle$ and $|j_2m_2\rangle$, these functions refer to completely different spaces and depend on completely different variables. The direct product functions $|j_1m_1\rangle|j_2m_2\rangle$ are usually called the "uncoupled" representation, and the operators $\hat{J}_{1z}$, $\hat{J}_{2z}$, $\hat{J}_1{}^2$ and $\hat{J}_2{}^2$ are diagonal in this representation.

The total angular momentum vector operator is defined by

$$\hat{\vec{J}} = \hat{\vec{J}}_1 + \hat{\vec{J}}_2$$

It is easily shown that the sum of two angular momenta is itself an angular momentum since $\hat{\vec{J}} \times \hat{\vec{J}} = i\hat{\vec{J}}$ can be derived by recognizing that $\hat{\vec{J}}_1 \times \hat{\vec{J}}_2 = 0$ since these angular momentum operators operate in different spaces. We seek a set of functions $|jm\rangle$ or $|j_1j_2jm\rangle$ which have the properties

$$\hat{J}^2|j_1j_2jm\rangle = j(j+1)|j_1j_2jm\rangle$$

$$\hat{J}_z|j_1j_2jm\rangle = m|j_1j_2j_m\rangle$$

$$\hat{J}_1{}^2|j_1j_2jm\rangle = j_1(j_1+1)|j_1j_2jm\rangle$$

$$\hat{J}_2{}^2|j_1j_2jm\rangle = j_2(j_2+1)|j_1j_2jm\rangle$$

where
$$\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$$
and
$$\hat{J}^2 = (\hat{\vec{J}}_1 + \hat{\vec{J}}_2)^2$$

This coupled representation $|jm\rangle$ is connected to the uncoupled representation $|j_1m_1\rangle|j_2m_2\rangle$ by a unitary transformation

$$|jm\rangle = \sum_{m_1,m_2} C(j_1j_2j;\ m_1m_2m)|j_1m_1\rangle|j_2m_2\rangle \qquad (3.4) \ *$$

where the elements of the transformation, $C(j_1j_2j;\ m_1m_2m)$, are the Clebsch-Gordan coefficients, Wigner coefficients, C-coefficients, or vector-coupling coefficients.

Let us apply $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$ to (3.4)

$$\hat{J}_z|jm\rangle = m|jm\rangle = \sum_{m_1,m_2} m\,C(j_1j_2j;\ m_1m_2m)|j_1m_1\rangle|j_2m_2\rangle$$

$$(\hat{J}_{1z} + \hat{J}_{2z})\sum_{m_1,m_2} C(j_1j_2j;\ m_1m_2m)|j_1m_1\rangle|j_2m_2\rangle$$

$$= \sum_{m_1m_2} (m_1 + m_2)C(j_1j_2j;\ m_1m_2m)|j_1m_1\rangle|j_2m_2\rangle.$$

Clearly

$$(m-m_1-m_2)C(j_1j_2j;\ m_1m_2m) = 0$$

and $C(j_1j_2j;\ m_1m_2m)$ must be zero unless $m = m_1 + m_2$. Hence we can collapse the summation over $m_2$ in (3.4) since only a single non-zero term survives:

$$|jm\rangle = \sum_{m_1} C(j_1j_2j;m_1,\ m-m_1)|j_1m_1\rangle|j_2,\ m-m_1\rangle \qquad (3.6) \ *$$

where we have suppressed the third m label in the C-coefficient since it is superfluous.

Since the C-coefficients are the elements of a unitary transformation, they must satisfy certain orthogonality relations. We begin by recognizing that

$$<j'm'|jm> = \delta_{j',j}\delta_{m'm}$$

Then, from (3.6),

$$<j'm'|jm> = \sum_{m_1,m_1'} C^*(j_1j_2j';\ m_1',m' - m_1')C(j_1j_2j;\ m_1,m - m_1)$$

$$\times <j_2,m' - m_1'|<j_1m_1'|j_1m_1>|j_2,m - m_1>$$

$$= \delta_{j',j}\delta_{m',m}$$

or $$\sum_{m_1} C^*(j_1j_2j';\ m_1,m - m_1)C(j_1j_2j;\ m_1,m - m_1) = \delta_{j',j} \quad *$$

With this orthogonality relation, we can derive the inverse transformation

$$|j_1m_1>|j_2m - m_1> = \sum_{j'}|j'm>B(j_1j_2\ j';\ m_1,\ m - m_1)$$

We multiply this equation by $C(j_1j_2j;\ m_1,m - m_1)$ and sum over $m_1$ so that

$$\text{LHS} = \sum_{m_1} C(j_1j_2j;\ m_1,\ m - m_1)|j_1m_1>|j_2m - m_1>$$

$$= |jm>$$

and

$$\text{RHS} = \sum_{j'}|j'm>\sum_{m_1} C(j_1j_2j;\ m_1,\ m - m_1)B(j_1j_2j';\ m_1,\ m - m_1)$$

This requires that

$$\sum_{m_1} C(j_1 j_2 j;\ m_1, m-m_1) B(j_1 j_2 j';\ m_1, m-m_1) = \delta_{j',j}$$

and therefore

$$B(j_1 j_2 j';\ m_1,\ m-m_1) = C^*(j_1 j_2 j';\ m_1,\ m-m_1)$$

Therefore

$$|j_1 m_1\rangle |j_2 m-m_1\rangle = \sum_{j'} C^*(j_1 j_2 j';\ m_1,\ m-m_1)|j'm\rangle$$

or

$$|j_1 m_1\rangle |j_2 m_2\rangle = \sum_{j} C^*(j_1 j_2 j;\ m_1,\ m_2)|j\ m_1+m_2\rangle \qquad (3.8) \quad *$$

Now we can derive another othrogonality relation for the C-coefficients:

$$\langle j_2 m'_2|\langle j_1 m'_1|j_1 m_1\rangle|j_2 m_2\rangle = \delta_{m'_1,m_1},\ \delta_{m'_2,m_2}.$$

But, with (3.8), we have

$$\langle j_2 m'_2|\langle j_1 m'_1|j_1 m_1\rangle|j_2 m_2\rangle$$

$$= \sum_{j,j'} C(j_1 j_2 j';\ m'_1, m'_2) C^*(j_1 j_2 j;\ m_1, m_2)\langle j', m'_1+m'_2|j, m_1+m_2\rangle$$

$$= \sum_{j} C(j_1 j_2 j;\ m'_1, m'_2) C^*(j_1 j_2 j'\ m_1, m_2)\delta_{m'_1+m'_2,\ m_1+m_2}$$

$$= \delta_{m'_1,m_1}\delta_{m'_2,m_2}$$

column ortho. ~~cond~~ relation

$$\text{or} \sum_{j} C(j_1 j_2 j;\ m'_1,\ m'-m'_1) C^*(j_1 j_2 j;\ m_1,\ m-m_1) = \delta_{m'_1,m_1}\delta_{m',m}$$

We now wish to investigate the allowed ranges of j and m.

Quite generally, we know that $-j \leq m \leq j$. Since $m = m_1 + m_2$ and the maximum values of $m_1$ and $m_2$ are $j_1$ and $j_2$ respectively, the maximum value of $m = j_1 + j_2$ and, of course this must be the maximum allowed value of j.

$$j_{max} = j_1 + j_2$$

For the case of $j = m = j_1 + j_2$, the sum in Eq. (3.4) reduces to a single term and

$$|j_1 + j_2,\ j_1 + j_2> = C(j_1, j_2, j_1 + j_2; j_1, j_2)|j_1 j_1>|j_2 j_2>$$

By the normalization requirement $|C(j_1, j_2, j_1 + j_2; j_1, j_2)|$ must be 1. By convention, the phases of the C-coefficients are chosen so that all of the C-coefficients are real. Hence

$$C(j_1, j_2, j_1 + j_2;\ j_1, j_2) = 1$$

The next smaller value of $m = j_1 + j_2 - 1$ and corresponds to linear combinations of the uncoupled states $|j_1, j_1 - 1>|j_2, j_2>$ and $|j_1, j_1>|j_2, j_2 - 1>$. One combination must correspond to the coupled state $|j_1 + j_2,\ j_1 + j_2 - 1>$ and the other to the coupled state $|j_1 + j_2 - 1,\ j_1 + j_2 - 1>$ where $j = m = j_1 + j_2 - 1$. Similarly the next lowest $m = j_1 + j_2 - 2$ will have linear combinations of the uncoupled functions $|j_1, j_1 - 2>|j_2, j_2>$, $|j_1, j_1 - 1>|j_2, j_2 - 1>$ and $|j_1, j_1>|j_2, j_2 - 2>$ which correspond to the coupled states $|j_1 + j_2,\ j_1 + j_2 - 2>$, $|j_1 + j_2 - 1,\ j_1 + j_2 - 2>$ and $|j_1 + j_2 - 2,\ j_1 + j_2 - 2>$, where the last state has $j = m = j_1 + j_2 - 2$. This procedure can be carried out by stepping down the m values, but eventually the procedure will end when the number of generated coupled states is equal to the number of uncoupled states. This limit will be reached for a particular value of $j = j_{min}$. Then

$$\sum_{j_{min}}^{j_{max}} (2j + 1) = (2j_1 + 1)(2j_2 + 1)$$

We recognize that $\sum j$ is simply an arithmetic progression with sum

$$\sum_{b}^{a} j = \tfrac{1}{2}(b - a + 1)(a + b) = \tfrac{1}{2}[b(b + 1) - a(a - 1)]$$

Hence

$[(j_1 + j_2)(j_1 + j_2 + 1) - j_{min}(j_{min} - 1)] + [j_1 + j_2 - j_{min} + 1] = (2j_1 + 1)(2j_2 + 1)$ and $(j_{min})^2 = (j_1 - j_2)^2$

Since $j_{min} \geq 0$, we obtain

$$j_{min} = |j_1 - j_2|.$$

Hence the allowed values of j are $j_1 + j_2$, $j_1 + j_2 - 1$, ..., $|j_1 - j_2|$. The numbers $j_1$, $j_2$ and j are said to satisfy a triangular relationship, often denoted $\Delta(j_1, j_2, j)$ and it is symmetric with respect to the three angular momenta. The C-coefficients will vanish unless this triangular condition is satisfied.

$j_1 + j_2 \geq j \geq |j_1 - j_2|$

In summary,

$$C(j_1 j_2 j;\, m_1, m - m_1) = 0$$

unless $\Delta(j_1, j_2, j)$,

$$|m_1| \leq j_1,$$
$$|m| \leq j,$$

and $|m - m_1| \leq j_2$.

*

## 11. Symmetry Relations of the Clebsch-Gordan Coefficients

In the previous section we considered the relationships between the functions $|j_1m_1\rangle|j_2m_2\rangle$ and $|jm\rangle$. In order to emphasize the symmetry properties, we now replace $|jm\rangle$ by $|j_3m_3\rangle$. Clearly there is a certain symmetry among the three number pairs $j_1,m_1$; $j_2,m_2$; $j_3,m_3$ in that $m_3 = m_1 + m_2$ and there exists a triangular relationship between $j_1,j_2$ and $j_3$. We expect therefore some simple symmetry relations among the C-coefficients when the roles of the participating angular momenta are interchanged. In order to investigate the symmetry relations it is necessary to look at the explicit expression for the C-coefficients derived by Racah [Phys. Rev. 62, 438 (1942)]:

$$
\begin{aligned}
C(j_1j_2j_3;m_1m_2m_3) &= \delta_{m_3,m_1+m_2} \\
&\times [(2j_3+1)(j_1+j_2-j_3)!(j_3+j_1-j_2)!(j_3+j_2-j_1)!/(j_1+j_2+j_3+1)!]^{\frac{1}{2}} \\
&\times [(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j_3+m_3)!(j_3-m_3)!]^{\frac{1}{2}} \\
&\times \sum_\nu (-1)^\nu [\nu!(j_1+j_2-j_3-\nu)!(j_1-m_1-\nu)!(j_2+m_2-\nu)! \\
&\qquad \times (j_3-j_2+m_1+\nu)!(j_3-j_1-m_2+\nu)!]^{-1}
\end{aligned}
\tag{3.19}
$$

Here the integral index $\nu$ assumes all values for which the factorial arguments are not negative.

(a) Relation between $C(j_1j_2j_3;m_1m_2m_3)$ and $C(j_1j_2j_3;-m_1,-m_2,-m_3)$:

Inverting the signs of the m's changes only the denominator in the sum over $\nu$ in (3.19) and changes it to

$$\nu!(j_1+j_2-j_3-\nu)!(j_1+m_1-\nu)!(j_2-m_2-\nu)!(j_3-j_2-m_1+\nu)!(j_3-j_1+m_2+\nu)$$

If we introduce a change of variables

$$\nu = j_1 + j_2 - j_3 - \nu' \quad .$$

this denominator becomes

$$(j_1+j_2-j_3-\nu')!(\nu')\ (j_3-j_2+m_1+\nu')\ (j_3-j_1-m_2+\nu')\ (j_1-m_1-\nu')\ (j_2+m_2-\nu')!$$

Thus

$$C(j_1j_2j_3;-m_1,-m_2,-m_3) = (-1)^{j_1+j_2-j_3}C(j_1j_2j_3;m_1,m_2,m_3)$$

(b) Relation between $C(j_1j_2j_3;m_1m_2m_3)$ and $C(j_2j_1j_3;m_2m_1m_3)$:

Interchanging the index pairs $j_1,m_1$ and $j_2,m_2$ causes only a change in the denominator in the sum over $\nu$ in (3.19) and changes it to

$$\nu!(j_1+j_2-j_3-\nu)!(j_2-m_2-\nu)!(j_1+m_1-\nu)!(j_3-j_1+m_2+\nu)!(j_3-j_2-m_1+\nu)!$$

which is exactly the denominator obtained when $m_1$, $m_2$, $m_3$ were replaced by $-m_1$, $-m_2$, $-m_3$ above. Hence

$$C(j_2j_1j_3,m_2m_1m_3) = (-1)^{j_1+j_2-j_3}C(j_1j_2j_3;m_1m_2m_3)$$

(c) Relation between $C(j_1j_2j_3;m_1m_2m_3)$ and $C(j_1j_3j_2;m_1,-m_3,-m_2)$

Performing the replacements $(j_2,m_2) \to (j_3,-m_3)$ and $(j_3,m_3) \to (j_2,-m_2)$, we change the $(2j_3+1)^{\frac{1}{2}}$ factor to $(2j_2+1)^{\frac{1}{2}}$ and we change the denominator in the $\nu$ summation in (3.19) to

$$\nu!(j_1+j_3-j_2-\nu)!(j_1-m_1-\nu)!(j_3-m_3-\nu)!(j_2-j_3+m_1+\nu)!(j_2-j_1+m_3+\nu)$$

Introducing a change of variables

$$\nu = j_1 - m_1 - \nu'$$

we obtain the denominator

$$(j_1-m_1-\nu')!(j_3-j_2+m_1+\nu')!(\nu)!(j_3-j_1-m_3+m_1+\nu')!(j_1+j_2-j_3-\nu')(j_2+m_3-m_1-\nu'$$

Recognizing that $-m_3+m_1 = -m_2$ and that $m_3-m_1 = m_2$, this denominator is shown to be identical to that in (3.19). Hence

$$C(j_1j_3j_2;m_1,-m_3,-m_2) = (-1)^{j_1-m_1}[(2j_2+1)/(2j_3+1)]^{\frac{1}{2}}C(j_1j_2j_3;m_1m_2m_3)$$

From these three basic symmetry relations, others may be derived:

$$C(j_3j_2j_1;-m_3,m_2,-m_1) = (-1)^{j_2+m_2}[(2j_2+1)/)2j_3+1)]^{\frac{1}{2}}C(j_1j_2j_3;m_1m_2m_3)$$

$$C(j_3 j_1 j_2; m_3, -m_1, m_2) = (-1)^{j_1 - m_1}[(2j_2 + 1)/2j_3 + 1)]^{\frac{1}{2}} C(j_1 j_2 j_3; m_1 m_2 m_3)$$

$$C(j_2 j_3 j_1; -m_2, m_3, m_1) = (-1)^{j_2 + m_2}[(2j_1 + 1)/2j_3 + 1)]^{\frac{1}{2}} C(j_1 j_2 j_3; m_1 m_2 m_3).$$

Symmetrized vector coupling coefficients have been defined by a number of workers. These coefficients display a greater symmetry than the C-coefficients. We consider two examples:

<u>Racah's V-Coefficients</u>

$$V(j_1 j_2 j_3; m_1, m_2, m_3) = (-1)^{j_3 - m_3}(2j_3 + 1)^{-\frac{1}{2}} C(j_1 j_2 j_3; m_1, m_2, -m_3)$$ ← both

which have symmetry relations

$$V(j_1 j_2 j_3; -m_1, -m_2, -m_3) = (-1)^{j_1 + j_2 + j_3} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

$$V(j_2 j_1 j_3; m_2 m_1 m_3) = (-1)^{j_1 + j_2 - j_3} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

$$V(j_1 j_3 j_2; m_1 m_3 m_2) = (-1)^{j_1 + j_2 + j_3} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

$$V(j_3 j_2 j_1; m_3 m_2 m_1) = (-1)^{j_1 - j_2 + j_3} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

$$V(j_3 j_1 j_2; m_3 m_1 m_2) = (-1)^{2j_2} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

$$V(j_2 j_3 j_1; m_2 m_3 m_1) = (-1)^{2j_3} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

and orthogonality relations

$$\sum_{m_1} V(j_1 j_2 j'; m_1, m_2, -m_3) V(j_1 j_2 j; m_1, m_2, -m_3) = \delta_{j,j'}(2j + 1)^{-1}$$

$$\sum_{j} V(j_1 j_2 j; m_1, m_2, -m_3) V(j_1 j_2 j; m_1', m_2', -m_3) = \delta_{m_1', m_1} \delta_{m_2', m_2}$$

<u>Wigner's 3j Symbols</u>

$$\begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3}(2j_3 + 1)^{-\frac{1}{2}} C(j_1 j_2 j_3; m_1, m_2, -m_3)$$ based on

$$= (-1)^{j_2 + j_3 - j_1} V(j_1 j_2 j_3; m_1 m_2 m_3)$$

Note that the 3j-symbol is invariant under cyclic permutation of the indices 1,2,3.

There are two useful properties of the C-coefficients which may be deduced from the symmetry properties:

$C(\ell_1\ell_2\ell_3;000) = 0$ unless $\ell_1 + \ell_2 + \ell_3$ is even

[$\ell_1, \ell_2, \ell_3$ are orbital (i.e. integral) angular momenta].

and

$C(j_1 0 j_3; m_1 0 m_3) = \delta_{j_1,j_3}\delta_{m_1,m_3}$

## 12. Evaluation of Clebsch-Gordan Coefficients

Rose derives a number of recurrence relations among the C-coefficients at this point, but I have never found this very useful. Instead I find it more instructive to consider two examples where the C-coefficients are computed:

### (a) Coupling of Two Spin 1/2 Angular Momenta

Consider two magnetically equivalent nuclear spins of 1/2 in a static field. The Hamiltonian is $\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z}) + J\hat{\vec{I}}_1\cdot\hat{\vec{I}}_2$ (in units of Hz). We have the uncoupled basis $|I_1M_1\rangle|I_2M_2\rangle$ with both $I_1$ and $I_2$ equal to ½, and we wish to construct the functions $|IM\rangle$ which are eigenfunctions of $(\hat{\vec{I}}_1 + \hat{\vec{I}}_2)^2$ and $\hat{I}_z = \hat{I}_{1z} + \hat{I}_{2z}$.

$$|IM\rangle = \sum_{M_1,M_2} C(I_1I_2I;M_1,M_2,M)|I_1M_1\rangle|I_2M_2\rangle$$

$$= \sum_{M_1} C(\tfrac{1}{2}\tfrac{1}{2}I;M_1,M-M_1)|\tfrac{1}{2}M_1\rangle|\tfrac{1}{2}M_2\rangle$$

Clearly (Section 10), the largest I = 1 and

$$C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2},\tfrac{1}{2},1) = 1$$

i.e. $|1,1\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle$

We can obtain the other members of the set $|1M\rangle$ by applying the operator $\hat{I}_- = \hat{I}_{1-} + \hat{I}_{2-}$ to the function $|11\rangle$:

$$\hat{I}_-|11\rangle = [1(1+1) - 1(1-1)]^{\frac{1}{2}}|10\rangle = \sqrt{2}|10\rangle$$

$$(\hat{I}_{1-} + \hat{I}_{2-})|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle = [\tfrac{1}{2}(\tfrac{1}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}-1)]^{\frac{1}{2}}\{|\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle + |\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle\}$$

$$= |\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle + |\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Thus $|10\rangle = (2)^{-\frac{1}{2}}\{|\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle + |\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle\}$

Now we apply $\hat{I}_-$ to $|10\rangle$:

$$\hat{I}_-|10\rangle = [1(1+1) - 0(0-1)]|1,-1\rangle = \sqrt{2}|1,-1\rangle$$

$$(\hat{I}_{1-} + \hat{I}_{2-})(2)^{-\frac{1}{2}}\{|\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle + |\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle\}$$

$$= (2)^{-\frac{1}{2}}(2)|\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Hence $\quad |1,-1\rangle = |\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$

Thus we have determined the set of coupled function $|1M\rangle$.

Now the value of I takes on all integral values between $|\tfrac{1}{2}-\tfrac{1}{2}| = 0$ and $\tfrac{1}{2} + \tfrac{1}{2} = 1$, so we must now determine the coupled function $|00\rangle$. We know that $|00\rangle$ must be a linear combination of $|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$ and $|\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle$ which is orthogonal to the coupled function $|10\rangle$. $|00\rangle$ is most easily determined by using the <u>projection operator $|00\rangle\langle 00|$.</u> We know that

$$\hat{1} = \sum_{I,M}|I,M\rangle\langle I,M| \quad ,$$ ※

so that $|0,0\rangle\langle 0,0| = 1 - \sum_{M}|1M\rangle\langle 1M|$

Applying this projection operator to the uncoupled function $|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$, we obtain

$$|0,0\rangle\langle 0,0|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

$$-\tfrac{1}{2}(|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle + |\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle)$$

$$= \tfrac{1}{2}(|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle - |\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle)$$

This is not normalized so we normalize it and obtain

$$|0,0\rangle = (2)^{-\frac{1}{2}}\{|\tfrac{1}{2},\tfrac{1}{2}\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle - |\tfrac{1}{2},-\tfrac{1}{2}\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle\}$$

We have determined the C-coefficients:

$$C(\tfrac{1}{2},\tfrac{1}{2},1;\tfrac{1}{2},\tfrac{1}{2},1) = 1$$

$$C(\tfrac{1}{2},\tfrac{1}{2},1;\tfrac{1}{2},-\tfrac{1}{2},0) = C(\tfrac{1}{2},\tfrac{1}{2},1;-\tfrac{1}{2},\tfrac{1}{2},0) = (2)^{-\frac{1}{2}}$$

$$C(\tfrac{1}{2},\tfrac{1}{2},1;-\tfrac{1}{2},-\tfrac{1}{2},-1) = 1$$

$$C(\tfrac{1}{2},\tfrac{1}{2},0;\tfrac{1}{2},-\tfrac{1}{2},0) = -C(\tfrac{1}{2},\tfrac{1}{2},0;-\tfrac{1}{2},\tfrac{1}{2},0) = (2)^{-\frac{1}{2}}$$

In this basis set, the Hamiltonian operator has a diagonal matrix representation with eigenvalues

$$\varepsilon_{1,M} = -M\nu_o + J/4 \quad ,$$

$$\varepsilon_{0,M} = -3J/4 \quad .$$

The allowed transitions in an NMR experiment on this system are $|1,1\rangle \rightarrow |1,0\rangle$, $|1,0\rangle \rightarrow |1,-1\rangle$ and these both occur at frequency $\nu_o$. Hence two magnetically equivalent nuclei do not "split each other" in the NMR spectrum.

(b) Coupling of Two Spin 1 Nuclei

We wish to construct the functions

$$|IM\rangle = \sum_{M_1} C(11I;M_1,M-M_1)\,|1,M_1\rangle|1,M-M_1\rangle$$

We know that the maximum value of $I = I_1 + I_2 = 2$, and its minimum value is $I = |I_1 - I_2| = 0$, so we should find states with $I = 0,1,2$. We start with

$$|2,2\rangle = |1,1\rangle|1,1\rangle \quad ,$$

and apply $\hat{I}_- = \hat{I}_{1-} + \hat{I}_{2-}$ to obtain

$$|2,1\rangle = (2)^{\frac{1}{2}}\{|1,1\rangle|1,0\rangle + |1,0\rangle|1,1\rangle\}.$$

Applying $\hat{I}_-$ to $|21\rangle$ gives

$$|2,0\rangle = (6)^{-\frac{1}{2}}\{|1,1\rangle|1,-1\rangle + 2|1,0\rangle|1,0\rangle + |1,-1\rangle|1,1\rangle\}$$

In the same way

$$|2,-1\rangle = (2)^{-\frac{1}{2}}\{|1,0\rangle|1,-1\rangle + |1,-1\rangle|1,0\rangle\}$$

and

$$|2,-2\rangle = |1,-1\rangle|1,-1\rangle$$

To start the coupled $|1,M\rangle$ manifold, we use the projection operator

$$|1,1\rangle\langle 1,1| = \hat{1} - \sum_{M}|2,M\rangle\langle 2,M| - \sum_{M\neq 1}|1,M\rangle\langle 1,M| - |0,0\rangle\langle 0,0|$$

on the uncoupled function $|11\rangle|10\rangle$:

$$|1,1\rangle\langle 1,1|(|1,1\rangle|1,0\rangle) = |1,1\rangle|1,0\rangle - |2,1\rangle\langle 2,1|(|1,1\rangle|1,0\rangle)$$

$$= |11\rangle|10\rangle - |2,1\rangle(2)^{-\frac{1}{2}}\{\langle 1,1|\langle 1,0| + \langle 1,0|\langle 1,1|\}|1,1\rangle|1,0\rangle$$

$$= \tfrac{1}{2}|1,1\rangle|1,0\rangle - \tfrac{1}{2}|1,0\rangle|1,1\rangle$$

The normalized function is

$$|1,1\rangle = (2)^{-\frac{1}{2}}\{|1,1\rangle|1,0\rangle - |1,0\rangle|1,1\rangle\}$$

Applying $\hat{I}_-$ to this function, we obtain

$$|1,0\rangle = (2)^{-\frac{1}{2}}\{|1,1\rangle|1,-1\rangle - |1,-1\rangle|1,1\rangle\}$$

and

$$|1,-1\rangle = (2)^{-\frac{1}{2}}\{|1,0\rangle|1,-1\rangle - |1,-1\rangle|1,0\rangle\}$$

To obtain $|0,0\rangle$ we use the projection

$$|0,0\rangle\langle 0,0| = \hat{1} - \sum_{I,M\neq 0}|I,M\rangle\langle I,M| - |2,0\rangle\langle 2,0| - |1,0\rangle\langle 1,0|$$

on the funcion $|1,1\rangle|1,-1\rangle$:

$$|0,0\rangle\langle 0,0|(|1,1\rangle|1,-1\rangle) = |1,1\rangle|1,-1\rangle - |2,0\rangle\langle 2,0|(|1,1\rangle|1,-1\rangle)$$

$$- |1,0\rangle\langle 1,0|(|1,1\rangle|1,-1\rangle)$$

$$= |1,1\rangle|1,-1\rangle - (6)^{-\frac{1}{2}}|2,0\rangle - (2)^{-\frac{1}{2}}|1,0\rangle$$

$$= \frac{1}{3}\{|1,1\rangle|1,-1\rangle - |1,0\rangle|1,0\rangle + |1,-1\rangle|1,1\rangle\}$$

and the normalized coupled function is

$$|0,0\rangle = (3)^{-\frac{1}{2}}\{|1,1\rangle|1,-1\rangle - |1,0\rangle|1,0\rangle + |1,-1\rangle|1,1\rangle|$$

We have determined the C-coefficients

$C(112;1,1,2) = 1$

$C(112;1,0,1) = C(112;0,1,1) = (2)^{-\frac{1}{2}}$

$C(112;1,-1,0) = C(112;-1,1,0) = (6)^{-\frac{1}{2}}$

$C(112;0,0,0) = 2/(6)^{\frac{1}{2}}$

$C(112;0,-1,-1) = C(112;-1,0,-1) = (2)^{-\frac{1}{2}}$

$C(112;-1,-1,-2) = 1$

$C(111;1,0,1) = -C(111;0,1,1) = (2)^{-\frac{1}{2}}$

$C(111;1,-1,0) = -C(111;-1,1,0) = (2)^{-\frac{1}{2}}$

$C(111;000) = 0$

$C(111;0,-1,-1) = -C(111;-1,0,-1) = (2)^{-\frac{1}{2}}$

$C(110;1,-1,0) = -C(110;0,0,0) = C(110;-1,1,0) = (3)^{-\frac{1}{2}}$

In many cases, it is easier to evaluate the C-coefficients explicitly as we have done above rather than work them out with Racah's formula. Tables of some of the frequently encountered C-coefficients are given below: (from Abramowitz and Stegun, Handbook of Mathematical Functions)

**Table 27.9.1**

$(j_1\, \frac{1}{2}\, m_1\, m_2 \,|\, j_1\, \frac{1}{2}\, j\, m)$

| $j=$ | $m_2=\frac{1}{2}$ | $m_2=-\frac{1}{2}$ |
|---|---|---|
| $j_1+\frac{1}{2}$ | $\sqrt{\frac{j_1+m+\frac{1}{2}}{2j_1+1}}$ | $\sqrt{\frac{j_1-m+\frac{1}{2}}{2j_1+1}}$ |
| $j_1-\frac{1}{2}$ | $-\sqrt{\frac{j_1-m+\frac{1}{2}}{2j_1+1}}$ | $\sqrt{\frac{j_1+m+\frac{1}{2}}{2j_1+1}}$ |

Notation:

$$(j_1 j_2 m_1 m_2 | j_1 j_2 j m) = C(j_1 j_2 j; m_1 m_2)$$

**Table 27.9.2** $(j_1\ 1\ m_1\ m_2|j_1\ 1\ j\ m)$

| $j=$ | $m_2=1$ | $m_2=0$ | $m_2=-1$ |
|---|---|---|---|
| $j_1+1$ | $\sqrt{\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}}$ | $\sqrt{\frac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}}$ | $\sqrt{\frac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}}$ |
| $j_1$ | $-\sqrt{\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}}$ | $\frac{m}{\sqrt{j_1(j_1+1)}}$ | $\sqrt{\frac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}}$ |
| $j_1-1$ | $\sqrt{\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}}$ | $-\sqrt{\frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}}$ | $\sqrt{\frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)}}$ |

**Table 27.9.3** $(j_1\ \tfrac{3}{2}\ m_1\ m_2|j_1\ \tfrac{3}{2}\ j\ m)$

| $j=$ | $m_2=\tfrac{3}{2}$ | $m_2=\tfrac{1}{2}$ |
|---|---|---|
| $j_1+\tfrac{3}{2}$ | $\sqrt{\frac{(j_1+m-\frac{1}{2})(j_1+m+\frac{1}{2})(j_1+m+\frac{3}{2})}{(2j_1+1)(2j_1+2)(2j_1+3)}}$ | $\sqrt{\frac{3(j_1+m+\frac{1}{2})(j_1+m+\frac{3}{2})(j_1-m+\frac{3}{2})}{(2j_1+1)(2j_1+2)(2j_1+3)}}$ |
| $j_1+\tfrac{1}{2}$ | $-\sqrt{\frac{3(j_1+m-\frac{1}{2})(j_1+m+\frac{1}{2})(j_1-m+\frac{3}{2})}{2j_1(2j_1+1)(2j_1+3)}}$ | $-(j_1-3m+\tfrac{3}{2})\sqrt{\frac{j_1+m+\frac{1}{2}}{2j_1(2j_1+1)(2j_1+3)}}$ |
| $j_1-\tfrac{1}{2}$ | $\sqrt{\frac{3(j_1+m-\frac{1}{2})(j_1-m+\frac{1}{2})(j_1-m+\frac{3}{2})}{(2j_1-1)(2j_1+1)(2j_1+2)}}$ | $-(j_1+3m-\tfrac{1}{2})\sqrt{\frac{j_1-m+\frac{1}{2}}{(2j_1-1)(2j_1+1)(2j_1+2)}}$ |
| $j_1-\tfrac{3}{2}$ | $-\sqrt{\frac{(j_1-m-\frac{1}{2})(j_1-m+\frac{1}{2})(j_1-m+\frac{3}{2})}{2j_1(2j_1-1)(2j_1+1)}}$ | $\sqrt{\frac{3(j_1+m-\frac{1}{2})(j_1-m-\frac{1}{2})(j_1-m+\frac{1}{2})}{2j_1(2j_1-1)(2j_1+1)}}$ |

| $j=$ | $m_2=-\tfrac{1}{2}$ | $m_2=-\tfrac{3}{2}$ |
|---|---|---|
| $j_1+\tfrac{3}{2}$ | $\sqrt{\frac{3(j_1+m+\frac{3}{2})(j_1-m+\frac{1}{2})(j_1-m+\frac{3}{2})}{(2j_1+1)(2j_1+2)(2j_1+3)}}$ | $\sqrt{\frac{(j_1-m-\frac{1}{2})(j_1-m+\frac{1}{2})(j_1-m+\frac{3}{2})}{(2j_1+1)(2j_1+2)(2j_1+3)}}$ |
| $j_1+\tfrac{1}{2}$ | $(j_1+3m+\tfrac{3}{2})\sqrt{\frac{j_1-m+\frac{1}{2}}{2j_1(2j_1+1)(2j_1+3)}}$ | $\sqrt{\frac{3(j_1+m+\frac{3}{2})(j_1-m-\frac{1}{2})(j_1-m+\frac{1}{2})}{2j_1(2j_1+1)(2j_1+3)}}$ |
| $j_1-\tfrac{1}{2}$ | $-(j_1-3m-\tfrac{1}{2})\sqrt{\frac{j_1+m+\frac{1}{2}}{(2j_1-1)(2j_1+1)(2j_1+2)}}$ | $\sqrt{\frac{3(j_1+m+\frac{1}{2})(j_1+m+\frac{3}{2})(j_1-m-\frac{1}{2})}{(2j_1-1)(2j_1+1)(2j_1+2)}}$ |
| $j_1-\tfrac{3}{2}$ | $-\sqrt{\frac{3(j_1+m-\frac{1}{2})(j_1+m+\frac{1}{2})(j_1-m-\frac{1}{2})}{2j_1(2j_1-1)(2j_1+1)}}$ | $\sqrt{\frac{(j_1+m-\frac{1}{2})(j_1+m+\frac{1}{2})(j_1+m+\frac{3}{2})}{2j_1(2j_1-1)(2j_1+1)}}$ |

**Table 27.9.4** $(j_1\ 2\ m_1\ m_2|j_1\ 2\ j\ m)$

| $j=$ | $m_2=2$ | $m_2=1$ | $m_2=0$ |
|---|---|---|---|
| $j_1+2$ | $\sqrt{\frac{(j_1+m-1)(j_1+m)(j_1+m+1)(j_1+m+2)}{(2j_1+1)(2j_1+2)(2j_1+3)(2j_1+4)}}$ | $\sqrt{\frac{(j_1-m+2)(j_1+m+2)(j_1+m+1)(j_1+m)}{(2j_1+1)(j_1+1)(2j_1+3)(j_1+2)}}$ | $\sqrt{\frac{3(j_1-m+2)(j_1-m+1)(j_1+m+2)(j_1+m+1)}{(2j_1+1)(2j_1+2)(2j_1+3)(j_1+2)}}$ |
| $j_1+1$ | $-\sqrt{\frac{(j_1+m-1)(j_1+m)(j_1+m+1)(j_1-m+2)}{2j_1(j_1+1)(j_1+2)(2j_1+1)}}$ | $-(j_1-2m+2)\sqrt{\frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)(j_1+1)(j_1+2)}}$ | $m\sqrt{\frac{3(j_1-m+1)(j_1+m+1)}{j_1(2j_1+1)(j_1+1)(j_1+2)}}$ |
| $j_1$ | $\sqrt{\frac{3(j_1+m-1)(j_1+m)(j_1-m+1)(j_1-m+2)}{(2j_1-1)2j_1(j_1+1)(2j_1+3)}}$ | $(1-2m)\sqrt{\frac{3(j_1-m+1)(j_1+m)}{(2j_1-1)j_1(2j_1+2)(2j_1+3)}}$ | $\frac{3m^2-j_1(j_1+1)}{\sqrt{(2j_1-1)j_1(j_1+1)(2j_1+3)}}$ |
| $j_1-1$ | $-\sqrt{\frac{(j_1+m-1)(j_1-m)(j_1-m+1)(j_1-m+2)}{2(j_1-1)j_1(j_1+1)(2j_1+1)}}$ | $(j_1+2m-1)\sqrt{\frac{(j_1-m+1)(j_1-m)}{(j_1-1)j_1(2j_1+1)(2j_1+2)}}$ | $-m\sqrt{\frac{3(j_1-m)(j_1+m)}{(j_1-1)j_1(2j_1+1)(j_1+1)}}$ |
| $j_1-2$ | $\sqrt{\frac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1-m+2)}{(2j_1-2)(2j_1-1)2j_1(2j_1+1)}}$ | $-\sqrt{\frac{(j_1-m+1)(j_1-m)(j_1-m-1)(j_1+m-1)}{(j_1-1)(2j_1-1)j_1(2j_1+1)}}$ | $\sqrt{\frac{3(j_1-m)(j_1-m-1)(j_1+m)(j_1+m-1)}{(2j_1-2)(2j_1-1)j_1(2j_1+1)}}$ |

| $j=$ | $m_2=-1$ | $m_2=-2$ |
|---|---|---|
| $j_1+2$ | $\sqrt{\frac{(j_1-m+2)(j_1-m+1)(j_1-m)(j_1+m+2)}{(2j_1+1)(j_1+1)(2j_1+3)(j_1+2)}}$ | $\sqrt{\frac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1-m+2)}{(2j_1+1)(2j_1+2)(2j_1+3)(2j_1+4)}}$ |
| $j_1+1$ | $(j_1+2m+2)\sqrt{\frac{(j_1-m+1)(j_1-m)}{j_1(2j_1+1)(2j_1+2)(j_1+2)}}$ | $\sqrt{\frac{(j_1-m-1)(j_1-m)(j_1-m+1)(j_1+m+2)}{j_1(2j_1+1)(j_1+1)(2j_1+4)}}$ |
| $j_1$ | $(2m+1)\sqrt{\frac{3(j_1-m)(j_1+m+1)}{(2j_1-1)j_1(2j_1+2)(2j_1+3)}}$ | $\sqrt{\frac{3(j_1-m-1)(j_1-m)(j_1+m+1)(j_1+m+2)}{(2j_1-1)j_1(2j_1+2)(2j_1+3)}}$ |
| $j_1-1$ | $-(j_1-2m-1)\sqrt{\frac{(j_1+m+1)(j_1+m)}{(j_1-1)j_1(2j_1+1)(2j_1+2)}}$ | $\sqrt{\frac{(j_1-m-1)(j_1+m)(j_1+m+1)(j_1+m+2)}{(j_1-1)j_1(2j_1+1)(2j_1+2)}}$ |
| $j_1-2$ | $-\sqrt{\frac{(j_1-m-1)(j_1+m+1)(j_1+m)(j_1+m-1)}{(j_1-1)(2j_1-1)j_1(2j_1+1)}}$ | $\sqrt{\frac{(j_1+m-1)(j_1+m)(j_1+m+1)(j_1+m+2)}{(2j_1-2)(2j_1-1)2j_1(2j_1+1)}}$ |

## IV. Transformation Properties Under Rotations

### 13. Matrix Representations of the Rotation Operators

The functions $|jm\rangle$, which we have discussed at length in the previous sections, presuppose a definite choice of the axis of quantization since $|jm\rangle$ is an eigenfunction of $\hat{J}_z$. It is necessary, particularly in molecular spectroscopy, to consider angular momentum operators referred to different coordinate systems, so it is essential to look at the transformation properties of the functions $|jm\rangle$ under coordinate rotations. These properties lead to a very important classifiaction of the operators which represent interactions in quantum mechanics.

We are interested in determining the nature of the function which results when the rotation operator $\hat{R} = \exp(-i\theta\vec{n}.\hat{\vec{J}})$ is applied to the function $|jm\rangle$:

$$\hat{R}|jm\rangle = \exp(-i\theta\vec{n}.\hat{\vec{J}})|jm\rangle$$

First we recognize that $\hat{J}^2$ commutes with the rotation operator $\hat{R}$:

$$[\hat{J}^2,\exp-i\theta(\vec{n}.\hat{\vec{J}})] = \sum_{P=0}^{\infty} (P!)^{-1}(-i\theta)^P[\hat{J}^2,(\vec{n}.\hat{\vec{J}})^P] = 0$$

Hence

$$\hat{J}^2\hat{R}|jm\rangle = \hat{R}\hat{J}^2|jm\rangle$$
$$= j(j+1)\hat{R}|jm\rangle$$

so the eigenvalue of $\hat{J}^2$ is unchanged by coordinate rotations and we can confine our interest to the effects of rotations within a particular j-manifold:

$$\hat{R}|jm\rangle = \sum_{m'} |jm'\rangle\langle jm'|\hat{R}|jm\rangle$$

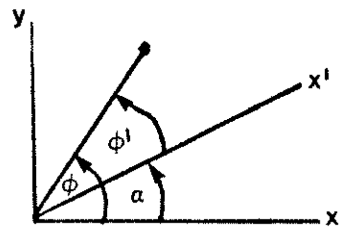
One very simple example is the case where a rotation by angle $\alpha$ about the z-axis of quantization is made:

$$\hat{R}|jm\rangle = \exp(-i\alpha\hat{J}_z)|jm\rangle \quad = \exp(-im\alpha)|jm\rangle$$

As we have seen in our considerations of orbital angular momentum, the function $|jm\rangle$ is a function of the angles $\theta$ and $\phi$ in spherical polar coordinates:

$$|jm\rangle = F_{jm}(\theta)\exp(im\phi)$$

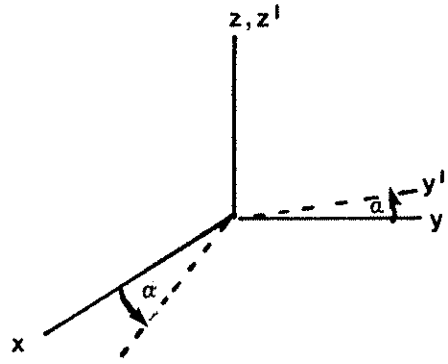
A rotation of the coordinates by angle $\alpha$ about the z-axis changes $\phi$ to $\phi-\alpha$ in the new coordinate system and leaves $\theta$ unchanged.



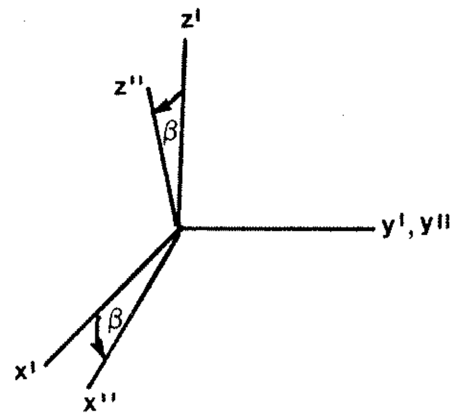

Hence
$$\begin{aligned}\hat{R}|jm\rangle &= F_{jm}(\theta')\exp(im\phi')\\ &= F_{jm}(\theta)\exp[im(\phi-\alpha)]\\ &= \exp(-im\alpha)|jm\rangle\end{aligned}$$

In general, the relationship between the function in the rotated coordinates and the function in the original coordinates will be more complicated since rotations about axes other than the axis of quantization must be considered. We shall define a general rotation in terms of the Euler angles $\alpha,\beta,\gamma$ which uniquely define the orientation of the rotated frame $(x''',y''',z''')$ with respect to the original frame $(x,y,z)$. The transformation of the coordinate axis is defined as:

(i) a rotation about the z-axis by angle $\alpha$ in the right-handed sense to give new coordinates $(x',y',z')$ so that the $z'''$ axis lies in the $x'$-$z'$ plane.



(ii) a rotation about the y'-axis by angle $\beta$ in the right-handed sense to give new coordinates $(x'',y'',z'')$ such that the z''-axis lies along the z'''-axis.




(iii) a rotation about the z''-axis by angle $\gamma$ in the right-handed sense to give the coordinates $(x''',y''',z''')$ which represent the final rotated coordinate system.

The rotation operator $\hat{R}$ is clearly the product of 3 operators:

$$\hat{R} = \exp(-i\theta\vec{n}.\vec{\hat{J}}) = \hat{R}_{z''}(\gamma)\hat{R}_{y'}(\beta)\hat{R}_{z}(\alpha)$$
$$= \exp(-i\gamma\hat{J}_{z''})\exp(-i\beta\hat{J}_{y'})\exp(-i\alpha\hat{J}_{z})$$

Note that the second and third rotations are with respect to rotated axes not the original set of axes. It is more convenient to express the rotation operator in terms of rotations about the axes in the original (or final) coordinate system. To do this, we return to the discussion of section 2 and consider the behaviour of the operator $\hat{O}$ under a unitary transformation $\hat{U}$. Suppose that

$$|\psi\rangle = \hat{U}|\phi\rangle \text{ and } |\psi'\rangle = \hat{U}|\phi'\rangle$$

Then $\langle\phi|\hat{O}|\phi'\rangle = \langle\hat{U}^{-1}\psi|\hat{O}|\hat{U}^{-1}\psi'\rangle$

$$= \langle\psi|\hat{U}\hat{O}\hat{U}^{\dagger}|\psi'\rangle$$

Hence the transformed operator is

$$\hat{O}_{\text{transformed}} = \hat{U}\hat{O}\hat{U}^{\dagger}$$

Using this idea, $\hat{R}_{y'}(\beta)$ is the transform of $\hat{R}_{y}(\beta)$ under the unitary transformation $\hat{U} = \exp(-i\alpha\hat{J}_z) = R_z(\alpha)$ so that

$$\begin{aligned}\hat{R}_y(\beta) &= \exp(-i\alpha\hat{J}_z)\hat{R}_y(\beta)\exp(+i\alpha\hat{J}_z)\\ &= \hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}_z{}^{\dagger}(\alpha)\end{aligned}$$

Similarly $\hat{R}_{z''}(\gamma)$ is the transform of $\hat{R}_{z'}(\gamma)$ under the unitary transformation $\hat{U} = \exp(-i\beta\hat{J}_{y'}) = \hat{R}_{y'}(\beta)$ and

$$\begin{aligned}\hat{R}_{z''}(\alpha) &= \hat{R}_{y'}(\beta)\exp(-i\alpha\hat{J}_{z'})R^{\dagger}_{y'}(\beta)\\ &= \hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}^{\dagger}_z(\alpha)\left\{\hat{R}_z(\alpha)\hat{R}_z(\gamma)R^{\dagger}_z(\alpha)\right\}\{\hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}^{\dagger}_z(\alpha)\}^{\dagger}\\ &= \hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}_z(\gamma)\hat{R}^{\dagger}_z(\alpha)\left\{\hat{R}_z(\alpha)\hat{R}^{\dagger}_y(\beta)\hat{R}^{\dagger}_z(\alpha)\right\}\\ &= \hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}_z(\gamma)\hat{R}^{\dagger}_y(\beta)\hat{R}^{\dagger}_z(\alpha)\end{aligned}$$

Hence the rotation operator $\hat{R}$ is given by

$$\begin{aligned}\hat{R} &= \left\{\hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}_z(\gamma)\hat{R}^{\dagger}_y(\beta)\hat{R}^{\dagger}_z(\alpha)\right\}\left\{\hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}^{\dagger}_z(\alpha)\right\}\left\{\hat{R}_z(\alpha)\right\}\\ &= \hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}_z(\gamma)\end{aligned}$$

or

$$\hat{R} = \exp(-i\alpha\hat{J}_z)\exp(-i\beta\hat{J}_y)\exp(-i\gamma\hat{J}_z)$$

This implies that the rotation described by the Euler angles $\alpha,\beta,\gamma$ can be viewed as (i) a rotation by $\gamma$ about the z-axis followed by (ii) a rotation by $\beta$ about the original y-axis followed by (iii) a rotation by $\alpha$ about the original z-axis. Note that the order of the rotations taken about the original fixed set of axes is the reverse of the order of rotations taken about the successive rotated sets of axes. It may be shown that (an exercise for the reader!)

$$\hat{R} = \exp(-i\alpha\hat{J}_{z'''})\exp(-i\beta\hat{J}_{y'''})\exp(-i\gamma\hat{J}_{z'''})$$

so that whether one choses to do all the rotations about the laboratory axes (x,y,x) or the molecular axes $(x''',y''',z''')$, the order and direction of the rotational steps is the same.

We are now equipped to write down the matrix representation of the general rotation operator:

$$\hat{R}|jm\rangle = \sum_{m'} |jm'\rangle\langle jm'|\hat{R}|jm\rangle$$

$$= \sum_{m'} |jm'\rangle \mathcal{D}^{(j)}_{m',m}[\Omega]$$

where the Wigner rotation matrix $\mathcal{D}^{(j)}$ has elements

$$\mathcal{D}^{(j)}_{m',m}[\Omega] = \langle jm'|\exp(-i\alpha\hat{J}_z)\exp(-i\beta\hat{J}_y)\exp(-i\gamma\hat{J}_z)|jm\rangle$$

$$= \exp(-im'\alpha)\langle jm'|\exp(-i\beta\hat{J}_y)|jm\rangle\exp(-im\gamma)$$

$$= \exp(-im'\alpha)d^{j}_{m',m}[\beta]\exp(-im\gamma)$$

and the functions $d^{j}_{m',m}[\beta]$ are related to the Jacobi polynomials and have the finite series expansion:

$$d^{j}_{m',m}[\beta] = [(j+m)!(j-m)!(j+m')!(j-m')!]^{\frac{1}{2}}$$

$$\times\sum_{\nu} \frac{(-1)^{\nu}(\cos\frac{\beta}{2})^{2j+m-m'-2\nu}(-\sin\frac{\beta}{2})^{m'-m+2\nu}}{(\nu)!(j-m'-\nu')!(j+m-\nu)!(m'-m+\nu)!} \qquad (4.13)$$

where the index $\nu$ takes on all integer values for which the factional arguments are non-negative. Rose derives the result in his Appendix II, but I shall bypass the derivation.

From (4.13), it is evident that

$$d^{j}_{m,m'}(\beta) = d^{j}_{m',m}(-\beta)$$

which follows directly from the unitary properties of $\exp(-i\beta J_y)$:

$$\hat{U} = \exp\left\{-i\beta\hat{J}_y\right\}$$

$$\hat{U}^{-1} = \hat{U}^{\dagger} = \exp\left\{+i\beta\hat{J}^{\dagger}_y\right\} = \exp\left\{+i\beta\hat{J}y\right\}$$

i.e. the inverse of a rotation by $+\beta$ about the y-axis is simply a rotation by $-\beta$ about the y-axis. Since

$$U_{m',m} = (U^{-1})^{*}_{m,m'} \quad ,$$

$$d^{j}_{m',m}[\beta] = d^{j}_{m,m'}[-\beta]$$ (symmetric about diagonal)

where we have recognized that the d-matrices have only real elements. We note from (4.13) that

$$d^{j}_{m',m}[-\beta] = (-1)^{m'-m} d^{j}_{m',m}[\beta]$$

and therefore

$$d^{j}_{m,m'}[\beta] = (-1)^{m'-m} d^{j}_{m',m}[\beta]$$

Now we consider the relationship between $d^{j}_{-m',-m}[\beta]$ and $d^{j}_{m',m}[\beta]$: From (4.13), we recognize that

$$d^{j}_{-m,-m'}[\beta] = d^{j}_{m',m}[\beta]$$ (sym. about anti-diagonal)

Hence we obtain

$$d^{j}_{-m',-m}[\beta] = (-1)^{m'-m} d^{j}_{m',m}[\beta] = d^{j}_{m,m'}[\beta]$$
$$= (-1)^{m'-m} d^{j}_{-m,-m'}[\beta]$$

which describes the symmetry of the d-matrix about the diagonal and antidiagonal.

It is useful to look at the symmetry of the $\mathcal{D}$-matrices as well: We recognize that

$$\hat{R}^{-1} = \exp(+i\gamma J_z)\exp(+i\beta\hat{J}_y)\exp(+i\alpha\hat{J}_z)$$

and hence

$$\langle jm'|\hat{R}^{-1}|jm\rangle = \mathcal{D}^{(j)}_{m,m'}[-\gamma,-\beta,-\alpha]$$
$$= \langle jm|\hat{R}|jm'\rangle^{*}$$
$$= \mathcal{D}^{(j)*}_{m',m}[\alpha,\beta,\gamma]$$

One can also recognize that

$$\mathcal{D}^{(j)*}_{m',m}[\alpha,\beta,\gamma] = \exp(+im'\alpha)d^{j}_{m',m}[\beta]\exp(+im\gamma)$$
$$= \exp(+im'\alpha)\left\{(-1)^{m'-m} d^{j}_{-m',-m}[\beta]\right\}\exp(+im'\alpha)$$
$$= (-1)^{m'-m}\mathcal{D}^{(j)}_{-m',-m}[\alpha,\beta,\gamma]$$

or $$\mathcal{D}^{(j)}_{-m',-m}[\alpha,\beta,\gamma] = (-1)^{m'-m}\mathcal{D}^{(j)*}_{m',m}[\alpha,\beta,\gamma]$$

The rotation matrices $\underset{\sim}{\mathcal{D}}^{(j)}[\alpha,\beta,\gamma]$ are related to the eigenfunctions of the symmetric top rigid rotor Hamltonian

$$\hat{H} = (\hbar^2/2I_x)(\hat{L}^2_{x'''} + \hat{L}^2_{y'''}) + (\hbar^2/2I_z)\hat{L}^2_{z'''} \quad .$$

$$|JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^{(J)}_{-M,-K}[\alpha,\beta,\gamma]$$

is an eigenfunction of $\hat{H}$ with eigenvalue $(\hbar^2/2I_x)J(J+1) + (\hbar^2/2I_z - \hbar^2/2I_x)K^2$ and is an eigenfunction of $\hat{J}_z$ (laboratory frame) with eigenvalue M and of $\hat{J}_{z'''}$ (molecular frame) with eigenvalue K. We shall look into this further when we have constructed more of the apparatus of angular momentum operators and rotations. The rotation matrices $\underset{\sim}{\mathcal{D}}^{(j)}$ can be shown to form (2j+1)-dimensional irreducible representations of the 3-dimensional rotation group. For the present, we shall not get too involved with the group theoretic nature of the rotation problem.

## 14. The Clebsch-Gordan Series for the $\mathcal{D}$-Matrices

Recall that

$$|jm\rangle = \sum_{m_1} C(j_1 j_2 j; m_1, m-m_1)|j_1, m_1\rangle|j_2, m-m_1\rangle$$

and $$|j_1 m_1\rangle|j_2 m-m_1\rangle = \sum_{j} C(j_1 j_2 j; m_1, m-m_1)|jm\rangle$$

If we apply a general rotation operator to the first of these equations, we obtain

$$\sum_{\mu} |j\mu\rangle\mathcal{D}^{(j)}_{\mu m} = \sum_{\mu_1,\mu_2,m_1} \left\{ C(j_1 j_2 j; m_1, m-m_1)|j_1\mu_1\rangle|j_2\mu_2\rangle \times \mathcal{D}^{(j_1)}_{\mu_1 m_1}\mathcal{D}^{(j_2)}_{\mu_2 m-m_1} \right\}$$

(arguments of all $\mathcal{D}$-matrices are equal to $\Omega = \alpha,\beta,\gamma$ as above).

Now we use the inverse Clebsch-Gordan series to obtain

$$\sum_{\mu} |j\mu\rangle \mathcal{D}^{(j)}_{\mu m} = \sum_{\mu_1,\mu_2,m_1,j'} \Big\{ C(j_1 j_2 j; m_1, m-m_1) C(j_1 j_2 j'; \mu_1 \mu_2) \times |j', \mu_1+\mu_2\rangle \mathcal{D}^{(j_1)}_{\mu_1 m_1} \mathcal{D}^{(j_2)}_{\mu_2, m-m_1} \Big\}$$

Since the functions $|j\mu\rangle$ are linearly independent, the coefficients of $|j\mu\rangle$ on both sides of the equation must be equal and

$$\mathcal{D}^{(j)}_{\mu m} = \sum_{\mu_1, m_1} C(j_1 j_2 j; m_1, m-m_1)\, C(j_1 j_2 j; \mu_1, \mu-\mu_1) \mathcal{D}^{(j_1)}_{\mu_1 m_1} \mathcal{D}^{(j_2)}_{\mu-\mu_1, m-m_1} \tag{4.26}$$

This is the inverse Clebsch-Gordan series for $\mathcal{D}$-matrices.

Similarly, if we apply the general rotation operator to the inverse Clebsch-Gordan series, we find

$$\sum_{\mu_1,\mu_2} |j_1\mu_1\rangle |j_2\mu_2\rangle \mathcal{D}^{(j_1)}_{\mu_1, m_1} \mathcal{D}^{(j_2)}_{\mu_2, m-m_1} = \sum_{\mu, j} |j\mu\rangle \mathcal{D}^{(j)}_{\mu m} C(j_1 j_2 j; m_1, m-m_1)$$

We use the C-G series to obtain

$$\sum_{\mu_1,\mu_2} |j_1\mu_1\rangle |j_2\mu_2\rangle \mathcal{D}^{(j_1)}_{\mu_1 m_1} \mathcal{D}^{(j_2)}_{\mu_2 m_2} = \sum_{\mu, j, \mu_1} C(j_1 j_2 j; \mu_1, \mu-\mu_1) |j_1, \mu_1\rangle |j_2, \mu-\mu_1\rangle \mathcal{D}^{(j)}_{\mu m} \quad C(j_1 j_2 j; m_1, m-m_1)$$

and conclude from linear independence arguments that

$$\mathcal{D}^{(j_1)}_{\mu_1 m_1} \mathcal{D}^{(j_2)}_{\mu_2 m_2} = \sum_{j} C(j_1 j_2 j; \mu_1 \mu_2) C(j_1 j_2 j; m_1 m_2) \mathcal{D}^{(j)}_{\mu_1+\mu_2, m_1+m_2} \tag{4.25}$$

This is the Clebsch-Gordan series for $\mathcal{D}$-matrices.

## 14a. Relations Between $\mathcal{D}$-matrices and Spherical Harmonics

The eigenfunctions of the orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ are often called the spherical harmonics and denoted $Y_{\ell m}(\theta,\phi)$. The function $Y_{\ell m}(\theta,\phi)$ are just the functions $|LM\rangle$ which we discussed in detail in Section 8 . Hence the spherical harmonics transform under rotations as

$$\hat{R}Y_{\ell m}(\theta,\phi) = Y_{\ell m}(\theta',\phi')$$

$$= \sum_{m'} Y_{\ell m'}(\theta,\phi)\mathcal{D}^{(\ell)}_{m'm}[\Omega]$$

Consider the quantity

$$I = \sum_m Y^*_{\ell m}(\theta_1,\phi_1)Y_{\ell m}(\theta_2,\phi_2)$$

where $(\theta_1,\phi_1)$ and $(\theta_2,\phi_2)$ define the orientations of any two arbitrary vectors in 3-D coordinates. If we apply a rotation to the coordinate system

$$\hat{R}I = \sum_m Y^*_{\ell m}(\theta_1',\phi_1')Y_{\ell m}(\theta_2',\phi_2')$$

$$= \sum_m \left\{\hat{R}Y_{\ell m}(\theta_1,\phi_1)\right\}^* \left\{\hat{R}Y_{\ell m}(\theta_2,\phi_2)\right\}$$

$$= \sum_{m,m_1,m_2} \left\{Y_{\ell m_1}(\theta_1,\phi_1)\mathcal{D}^{(\ell)}_{m_1 m}[\Omega]\right\}^*\left\{Y_{\ell m_2}(\theta_2,\phi_2)\mathcal{D}^{(\ell)}_{m_2 m}[\Omega]\right\}$$

Now

$$\sum_m \mathcal{D}^{(\ell)*}_{m_1 m}[\Omega]\mathcal{D}^{(\ell)}_{m_2 m}[\Omega] = \sum_m \mathcal{D}^{(\ell)}_{m_2 m}[\Omega]\mathcal{D}^{(\ell)^{-1}}_{m m_1}[\Omega] = \delta_{m_1,m_2},$$

hence

$$\hat{R}I = \sum_{m_1} Y^*_{\ell m_1}(\theta_1,\phi_1)Y_{\ell m_1}(\theta_2,\phi_2)$$

and we conclude that $I$ is invariant under rotations. This is not too unexpected since $I$ represents a generalized scalar product which we anticipate as invariant. One can evaluate $I$ in any convenient coordinate system and we choose $\theta_1 = 0$ (first vector along z-axis), $\theta_2 = \theta$ and $\phi_2 = 0$ (second vector in xz-plane with angle $\theta$ between the two vectors). Since

$$Y_{\ell m}(0,\phi_1) = \delta_{m,0}\left(\frac{2\ell+1}{4\pi}\right)^{\frac{1}{2}} ,$$

$$I = \left(\frac{2\ell+1}{4\pi}\right)^{\frac{1}{2}} Y_{\ell 0}(\theta,0)$$

and we obtain the well-known spherical harmonic addition theorem

$$Y_{\ell 0}(\theta,0) = \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} \sum_m Y^*_{\ell m}(\theta_1,\phi_1)Y_{\ell m}(\theta_2,\phi_2) \qquad . \qquad *$$

The connection of this addition theorem to the $\mathcal{D}$-matrices must now be made. We recall from above that

$$Y_{\ell m}(\theta',\phi') = \sum_{m'} Y_{\ell m'}(\theta,\phi)\mathcal{D}^{(\ell)}_{m'm}[\alpha,\beta,\gamma]$$

Now if we set $\gamma = 0$ and recognize that the angles $\alpha,\beta$ simply define the orientation of the rotated z-axis with respect to the original coordinate axes, and relabel $\alpha,\beta$ as $\phi_1,\theta_1$, and relabel $\theta,\phi$ as $\theta_2,\phi_2$, we obtain

$$Y_{\ell m}(\theta',\phi') = \sum_{m'} \mathcal{D}^{(\ell)}_{m'm}[\phi_1,\theta_1,0]Y_{\ell m'}(\theta_2,\phi_2)$$

Then for the case $\phi' = 0$ (rotation $\phi_1,\theta_1$ such that the vector with orientation $\theta_2,\phi_2$ is rotated so that it lies in the xz-plane), and $m = 0$,

$$Y_{\ell 0}(\theta',0) = \sum_{m'} \mathcal{D}^{(\ell)}_{m'0}[\phi_1,\theta_1,0]Y_{\ell m'}[\theta_2,\phi_2).$$

Hence

$$\mathcal{D}^{(\ell)}_{m'0}[\phi_1,\theta_1,0] = \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} Y^*_{\ell m'}(\theta_1,\phi_1) \qquad *$$

This connection between the $Y_{\ell m}$ and $\mathcal{D}^{(\ell)}_{m0}$ can be used to derive the relationship between $Y_{\ell,m}$ and $Y_{\ell,-m}$:

$$Y_{\ell,-m} = \left(\frac{2\ell+1}{4\pi}\right)^{\frac{1}{2}} \mathcal{D}^{(\ell)*}_{-m,0} = (-1)^m \left(\frac{2\ell+1}{4\pi}\right)^{\frac{1}{2}} \mathcal{D}^{(\ell)}_{m,0}$$

$$= (-1)^m Y^*_{\ell,m}$$

One can use the connection between Wigner rotation matrices and spherical harmonics to derive a Clebsch-Gordan series for the spherical harmonics:

$$Y_{\ell_1 m_1}(\theta,\phi) Y_{\ell_2 m_2}(\theta,\phi) = [(2\ell_1+1)(2\ell_2+1)]^{\frac{1}{2}}/(4\pi) \mathcal{D}^{(\ell_1)^*}_{m_1 0}[\phi,\theta,0] \mathcal{D}^{(\ell_2)^*}_{m_2 0}[\phi,\theta,0]$$

$$= [(2\ell_1+1)(2\ell_2+1)]^{\frac{1}{2}}/(4\pi) \sum_{\ell} \mathcal{D}^{(\ell)^*}_{m_1+m_2,0}[\phi,\theta,0] C(\ell_1\ell_2\ell;m_1m_2) \times C(\ell_1\ell_2\ell;00)$$

$$= \sum \left\{(2\ell_1+1)(2\ell_2+1)/[4\pi(2\ell+1)]\right\}^{\frac{1}{2}} Y_{\ell,m_1+m_2}(\theta,\phi) C(\ell_1\ell_2\ell;m_1m_2) \times C(\ell_1\ell_2\ell;00)$$

Here the arguments of both spherical harmonics are the same.

This result must not be confused with the usual Clebsch-Gordan series discussed in Chapter III which describes the coupling of two independent angular momenta which have disjoint spaces. For this latter case, the corresponding series would be

whereas in the previous case, the ~~arg~~ arguments ~~of~~ are different.

$$Y_{\ell_1 m_1}(\zeta,\eta) Y_{\ell_2 m_2}(\alpha,\beta) = \sum_{\ell} |\ell m_1+m_2\rangle C(\ell_1\ell_2\ell;m_1m_2)$$

where the eigenfunction $|\ell m_1+m_2\rangle$ is a function of all four angles $\zeta,\eta,\alpha$, and $\beta$, and is not a spherical harmonic at all.

The C-G coupling series for spherical harmonics can be used for the evaluation of the multipole transition element which arises in the spectroscopy of linear molecules:

$$\langle \ell_3 m_3 | Y_{\ell_2 m_2}(\theta,\phi) | \ell_1 m_1 \rangle = \int d\phi \int \sin\theta \, d\theta \, Y^*_{\ell_3 m_3}(\theta,\phi) Y_{\ell_2 m_2}(\theta,\phi) Y_{\ell_1 m_1}(\theta,\phi)$$

$$= \sum_{\ell} \left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell+1)}\right]^{\frac{1}{2}} C(\ell_1 \ell_2 \ell; m_1 m_2) C(\ell_1 \ell_2 \ell; 00)$$

$$\times \int d\phi \int \sin\theta d\theta Y^*_{\ell_3 m_3}(\theta,\phi) Y_{\ell m_1+m_2}(\theta,\phi)$$

$$= \left[\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}\right]^{\frac{1}{2}} C(\ell_1 \ell_2 \ell_3; m_1 m_2) C(\ell_1 \ell_2 \ell_3; 00) \, \delta_{m_3, m_1+m_2} \quad *$$

(triangular rel$^{n}$ of $l_1, l_2, l_3$)

For the special case $\ell_2=1$, this matrix element is the familiar electric transition dipole moment matrix element which is related to the transition probability for the spectroscopic transition $|\ell_1 m_1\rangle \to |\ell_3 m_3\rangle$ when an oscillating electric field (electromagnetic radiation) is applied. In this case

(allowed values of $m_2 = -1, 0, 1$.)

$$\langle \ell_3 m_3 | Y_{1 m_2} | \ell_1 m_1 \rangle \propto C(\ell_1 1 \ell_3; m_1 m_2) C(\ell_1 1 \; \ell_3; 00) \, \delta_{m_3, m_1+m_2}$$

so that only transitions with $\ell_3 = \ell_1 \pm 1$ (R- and P-branches) and $m_3 = m_1, m_1 \pm 1$ are allowed. It is clear that the selection rules are contained in the C-G coefficients which arise in the transition moment matrix element. We shall see later that the corresponding transition moment matrix element for non-linear molecules also involves a product of C-G coefficients.

## 15. Determination of the $\mathcal{D}$ Rotation Matrices

In this section, we shall demonstrate the determination of $\underset{\sim}{\mathcal{D}}^{(1)}[\alpha,\beta,\gamma]$ in two ways. The first involves only trigonometric considerations, while the second approach begins with the determination of $\underset{\sim}{\mathcal{D}}^{(\frac{1}{2})}[\alpha,\beta,\gamma]$ and building up to form $\underset{\sim}{\mathcal{D}}^{(1)}[\alpha,\beta,\gamma]$ with the

C-G series for $\underset{\sim}{\mathcal{D}}$-matrices.

The rotation matrix $\underset{\sim}{\mathcal{D}}^{(1)}$ can be determined by investigating the transformation properties of any j=1 angular momentum eigenfunctions under rotations. We could, for example, follow the $\ell$=1 spherical harmonics or a spinor with spin 1. We shall investigate the $\ell$=1 spherical harmonics.

$$Y_{11}(\theta,\phi) = -(3/8\pi)^{\frac{1}{2}}\sin\theta\exp(i\phi) = (3/4\pi)^{\frac{1}{2}}r^{-1}[-(x+iy)/\sqrt{2}]$$

$$Y_{10}(\theta,\phi) = (3/4\pi)^{\frac{1}{2}}\cos\theta \qquad = (3/4\pi)^{\frac{1}{2}}r^{-1}[z]$$

$$Y_{1-1}(\theta,\phi) = (3/8\pi)^{\frac{1}{2}}\sin\theta\exp(-i\phi) = (3/4\pi)^{\frac{1}{2}}r^{-1}[(x-iy)/\sqrt{2}]$$

The factor $(3/4\pi)^{\frac{1}{2}}/r$ is invariant under rotations, so that transformation properties of the $Y_{1m}$ are completely determined by the transformation properties of the Carestian coordinates x,y,z (or linear combinations). We shall therefore follow the transformation of the vector r = (x,y,z) as it is transformed by the general rotation described by Euler angles $\alpha,\beta,\gamma$ into $\vec{r}''' = x''',y''',z'''$ ).

Note that

$$\vec{Y}_1(\theta,\phi) = (3/4\pi)^{\frac{1}{2}}r^{-1}\overset{(x,y,z)}{\vec{r}}.\underset{\sim}{U}$$

and that

$$\vec{Y}_1(\theta'',\phi') = (3/4\pi)^{\frac{1}{2}}r^{-1}\vec{r}'''.\underset{\sim}{U}$$

where

$$\underset{\sim}{U} = \begin{pmatrix} -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ -i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & 1 & 0 \end{pmatrix}$$

is the unitary transformation from Cartesian to spherical variables, and $\vec{Y}_1 = (Y_{11},Y_{10},Y_{1-1})$.

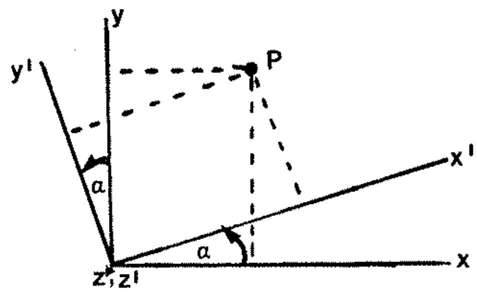
We shall now construct the transformation matrix $\underset{\sim}{M}$ which represents the transformation of $\vec{r}$ into $\vec{r}'''$ :

$$\vec{r}''' = \vec{r}.\underset{\sim}{M}(\alpha,\beta,\gamma)$$

by recognizing that

$$\underset{\sim}{M}(\alpha,\beta,\gamma) = \underset{\sim}{M}_z(\alpha)\underset{\sim}{M}_{y'}(\beta)\underset{\sim}{M}_{z''}(\gamma)$$

where $\underset{\sim}{M}_v(\zeta)$ is transformation matrix for a rotation of the coordinates by angle $\zeta$ about the v-axis. Consider first the rotation by $\alpha$ about the z-axis:




The point P has coordinates (x,y,z) in the original frame, and coordinates (x',y',z') in the rotated frame. Geometrical considerations show that

$$x' = x\cos\alpha + y\sin\alpha$$
$$y' = -x\sin\alpha + y\cos\alpha$$
$$z' = z$$

$\underline{M}_z(\alpha)$

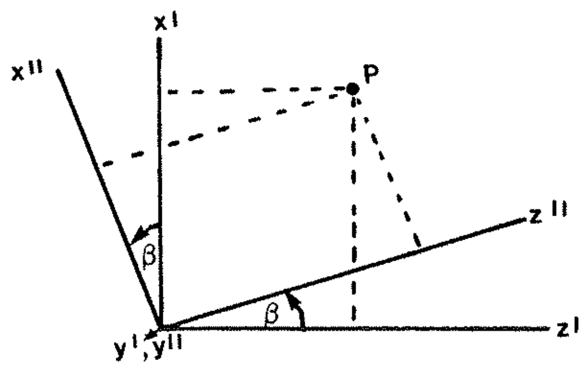
or

$$(x',y',z') = (x,y,z)\begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which is really the equation

$$\vec{r}' = \vec{r}\cdot\underset{\sim}{M}_z(\alpha)$$

Next we consider the rotation of the coordinates by angle $\beta$ above the y'-axis:




The point P has coordinates (x',y',z') in the first frame and coordinates (x",y",z") in the second, and the coordinates are related by:

$$x'' = x'\cos\beta - z'\sin\beta$$

$$y'' = y'$$

$$z'' = x'\sin\beta + z'\cos\beta$$

Hence $\vec{r}'' = \vec{r}'\cdot\underset{\sim}{M}_{y'}(\beta)$

with

$$\underset{\sim}{M}_{y'}(\beta) = \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix}$$

The final rotation about the z"-axis by angle $\gamma$ is handled in exactly the same way as the earlier rotation by $\alpha$ about the z-axis, and one obtains

$$\vec{r}''' = \vec{r}''\cdot\underset{\sim}{M}_{z''}(\gamma)$$

with

$$\underset{\sim}{M}_{z''}(\gamma) = \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Hence the full transformation of $\vec{r}$ to $\vec{r}'''$ is described by

$$\underset{\sim}{M}(\alpha,\beta,\gamma) = \underset{\sim}{M}_z(\alpha)\,\underset{\sim}{M}_{y'}(\beta)\underset{\sim}{M}_{z''}(\gamma)$$

$$= \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma & -\cos\alpha\cos\beta\sin\gamma-\sin\alpha\cos\gamma & \cos\alpha\sin\beta \\ \sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma & -\sin\alpha\cos\beta\sin\gamma+\cos\alpha\cos\gamma & \sin\alpha\sin\beta \\ -\sin\beta\cos\gamma & \sin\beta\sin\gamma & \cos\beta \end{pmatrix}$$

Now

$$\vec{Y}_1(\theta',\phi') = (3/4\pi)^{\frac{1}{2}} r^{-1}\vec{r}'''\,\underset{\sim}{U} = \underbrace{(3/4\pi)^{\frac{1}{2}} r^{-1}\vec{r}\underset{\sim}{M}}_{\vec{Y}_1(\theta,\phi)\underset{\sim}{U}^\dagger}\underset{\sim}{U}$$

$$= \vec{Y}_1(\theta,\phi)\underset{\sim}{U}^\dagger\underset{\sim}{M}\underset{\sim}{U}$$

$$= \vec{Y}_1(\theta,\phi)\underset{\sim}{\mathcal{D}}^{(1)}$$

Hence $\underset{\sim}{\mathcal{D}}^{(1)} = \underset{\sim}{U}^\dagger\underset{\sim}{M}\underset{\sim}{U}$

$$\underset{\sim}{\mathcal{D}}^{(1)} = \begin{pmatrix} e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)e^{-i\gamma} & -e^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)e^{i\gamma} \\ \frac{\sin\beta}{\sqrt{2}}\,e^{-i\gamma} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}}\,e^{i\gamma} \\ e^{i\alpha}\left(\frac{1-\cos\beta}{2}\right)e^{-i\gamma} & e^{i\alpha}\,\frac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\frac{(1+\cos\beta)}{2}e^{i\gamma} \end{pmatrix}$$

ie $\mathcal{D}^{(1)}_{11}$ $e^{-i\gamma}$ throughout the column since keeping m constant.

no $\gamma$ dependence (2nd index 0.)

Now we turn to building up $\underset{\sim}{\mathcal{D}}^{(1)}[\Omega]$ from $\underset{\sim}{\mathcal{D}}^{(\frac{1}{2})}[\Omega]$, the rotation matrix for $j = \frac{1}{2}$. The eigenfunctions of the matrix representation of $\hat{J}_z$:

$$\underset{\sim}{J}_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

are the two component spinors

$$|\tfrac{1}{2}\tfrac{1}{2}> = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\tfrac{1}{2}\,-\tfrac{1}{2}> = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{for which} \quad \underset{\sim}{J}_z|\tfrac{1}{2} \pm \tfrac{1}{2}> = \pm\tfrac{1}{2}|\tfrac{1}{2} \pm \tfrac{1}{2}>.$$

The functions $|\chi m>$ which diagonalize some other component $\hat{J}_k$ are obtained with the rotation matrices. If $|\chi m>$ diagonalizes the matrix representation $\underset{\sim}{J}_k$, the function $|\chi m>$ is related to the original functions $|\frac{1}{2}m'>$ by the transformation

$$|\chi m> = \sum_{m'} |\tfrac{1}{2},m'>\mathcal{D}^{(\frac{1}{2})}_{m'm}[\alpha\beta\gamma],$$

where the Euler angles take the original z-axis into the k-direction of interest. We shall determine the $|\chi m>$ by requiring that

$$\hat{J}_k|\chi,\pm\tfrac{1}{2}> = \pm\tfrac{1}{2}|\chi,\pm\tfrac{1}{2}> .$$

Since we already know the $\alpha$- and $\gamma$-dependence of $\underset{\sim}{\mathcal{D}}^{(j)}[\Omega]$, it is sufficient here to consider only a rotation about the y-axis by angle $\beta$ i.e. to determine $\underset{\sim}{d}^{(\frac{1}{2})}(\beta)$.

Much of the required information about $\underset{\sim}{d}^{(\frac{1}{2})}(\beta)$ can be inferred from its unitarity and the fact that its determinant must be +1. We define the general form as

$$\underset{\sim}{d}^{(\frac{1}{2})}(\beta) = \begin{pmatrix} A & B \\ C & D \end{pmatrix}$$

Since this matrix is unitary,

$$\underset{\sim}{d}^{(\frac{1}{2})-1}(\beta) = \begin{pmatrix} A^* & C^* \\ B^* & D^* \end{pmatrix}$$

and $\underset{\sim}{d}^{(\frac{1}{2})}(\beta)\underset{\sim}{d}^{(\frac{1}{2})-1}(\beta) = \begin{pmatrix} |A|^2 + |B|^2 & AC^* + BD^* \\ A^*C + B^*D & |C|^2 + |D|^2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

Hence $|A|^2 + |B|^2 = |C|^2 + |D|^2 = 1$

and $\frac{A}{B} = -\frac{D^*}{C^*}$ or $\frac{|A|^2}{|B|^2} = \frac{|D|^2}{|C|^2}$

Therefore $|A|^2 + |B|^2 = |B|^2|D|^2/|C|^2 + |B|^2 = |B|^2(|C|^2 + |D|^2)/|C|^2 =$

and $|B|^2 = |C|^2$, so that $|A|^2 = |D|^2$. The most general form which satisfies these conditions is

$$\underset{\sim}{d}^{(\frac{1}{2})}(\beta) = \begin{pmatrix} a \exp(i\xi) & b \exp(i\eta) \\ b \exp(i\zeta) & a \exp(i\lambda) \end{pmatrix}$$

with $b = (1-a^2)^{\frac{1}{2}}$

and $\frac{A}{B} = -\frac{D^*}{C^*}$ requires $\exp[i(\xi-\eta)] = -\exp[i(\lambda-\zeta)]^*$

or $\exp[i(\xi+\lambda)] = -\exp[i(\eta+\zeta)]$

Recognizing that the determinant of $\underset{\sim}{d}^{(\frac{1}{2})}$ must be +1, we obtain

$$\det|\underset{\sim}{d}^{(\frac{1}{2})}| = AD - BC = a^2 \exp[i(\xi+\lambda)] - b^2 \exp[i(\eta+\zeta)] = 1$$

and $(a^2 + b^2)\exp[i(\xi+\lambda)] = 1$ so that

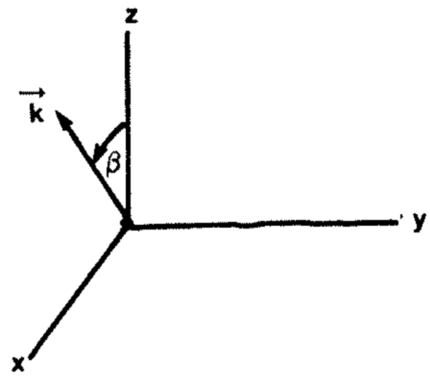
$$\exp(i\xi) = \exp(-i\lambda)$$

and
$$\exp(i\zeta) = -\exp(-i\eta)$$

Thus we have the general form

$$\underset{\sim}{d}^{(\frac{1}{2})}(\beta) = \begin{pmatrix} a \exp(-i\lambda) & -b \exp(-i\zeta) \\ b \exp(i\zeta) & a \exp(i\lambda) \end{pmatrix}$$

Now we consider $\beta$ to be the rotation which takes the z-axis onto the k-axis which is in the zx-plane:




Thus $\hat{J}_k = \hat{J}_z \cos\beta + \hat{J}_x \sin\beta$

with matrix representation

$$\hat{\underset{\sim}{J}}_k = \begin{pmatrix} \frac{1}{2}\cos\beta & \frac{1}{2}\sin\beta \\ \frac{1}{2}\sin\beta & -\frac{1}{2}\cos\beta \end{pmatrix}$$

in the original $|\frac{1}{2},\pm\frac{1}{2}>$ basis. We now require

$$\underset{\sim}{J}_k|\chi,\pm\tfrac{1}{2}> = \pm\tfrac{1}{2}|\chi,\pm\tfrac{1}{2}>$$

$$\tfrac{1}{2}\begin{pmatrix} \cos\beta & \sin\beta \\ \sin\beta & -\cos\beta \end{pmatrix}\begin{pmatrix} a\exp(-i\lambda) & -b\exp(-i\zeta) \\ b\exp(i\zeta) & a\exp(i\lambda) \end{pmatrix} = \begin{pmatrix} a\exp(-i\lambda) & -b\exp(-i\zeta) \\ b\exp(i\zeta) & a\exp(i\lambda) \end{pmatrix}\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

from which

$$a\exp(-i\lambda)\cos\beta + b\exp(i\zeta)\sin\beta = a\exp(-i\lambda) \quad (1)$$

$$a\exp(-i\lambda)\sin\beta - b\exp(i\zeta)\cos\beta = b\exp(i\zeta) \quad (2)$$

$$-b\exp(-i\zeta)\cos\beta + a\exp(i\lambda)\sin\beta = b\exp(-i\zeta) \quad (3)$$

$$-b\exp(-i\zeta)\sin\beta - a\exp(i\lambda)\cos\beta = -a\exp(i\lambda) \quad (4)$$

and from (2)

$$a\exp(-i\lambda)\sin\beta = b\exp(i\zeta)[1+\cos\beta]$$

or $$b = a\exp[-i(\lambda+\zeta)]\sin\beta / [1+\cos\beta].$$

Introducing the trigonometric functions for $\beta/2$:

$$\sin\beta = 2\sin(\beta/2)\cos(\beta/2)$$

$$\cos\beta = 2\cos^2(\beta/2) - 1$$

we obtain

$$b = a\exp[-i(\lambda+\zeta)]\sin(\beta/2)/\cos(\beta/2)$$

This result (or its complex conjugate) is also obtained from equations 1, 3 and 4

We note that a and b are real and conclude that the phase factor $\exp[-i(\lambda+\zeta)]$ must be real:

$$\exp[-i(\lambda+\zeta)] = \pm 1$$

and we choose the possibility with + sign, and choose the arbitrary phase angle $\lambda$ (and hence $\zeta$) to be zero so that

$$d^{(\frac{1}{2})}[\beta] = \begin{pmatrix} a & -b \\ b & a \end{pmatrix}$$

with $b = \sqrt{1-a^2}$ and $b = a\sin(\beta/2)/\cos(\beta/2)$

Hence

$$1 - a^2 = a^2\sin^2(\tfrac{\beta}{2})/\cos^2(\beta/2)$$

and $a^2 = \cos^2\beta/2$

or $a = \pm\cos(\beta/2)$

We choose the + sign here and have

$a = \cos\beta/2 \qquad b = \sin\beta/2$

Furthermore the arbitrary phase factor $\exp(i\eta) = \exp(i\lambda)$ is taken to be unity so that

$$\underset{\sim}{d}^{(\frac{1}{2})}(\beta) = \begin{pmatrix} \cos\beta/2 & -\sin\beta/2 \\ \sin\beta/2 & \cos\beta/2 \end{pmatrix}$$

We now have devised the matrix $\underset{\sim}{d}^{(\frac{1}{2})}(\beta)$, from which we obtain

$$\underset{\sim}{\mathcal{D}}^{(\frac{1}{2})}[\alpha\beta\gamma] = \begin{pmatrix} \exp(-i\alpha/a)\cos(\beta/2)\exp(-i\gamma/2) & -\exp(-i\alpha/2)\sin(\beta/2)\exp(+i\gamma/2) \\ \exp(+i\alpha/2)\sin(\beta/2)\exp(-i\gamma/2) & \exp(+i\alpha/2)\cos(\beta/2)\exp(+i\gamma/2) \end{pmatrix} .$$

The matrix element $\mathcal{D}^{(1)}_{\mu m}[\Omega]$ is given by the inverse Clebsch-Gordan series:

$$\mathcal{D}^{(1)}_{\mu m} = \sum_{\mu_1, m_1} \mathcal{D}^{(\frac{1}{2})}_{\mu_1 m_1} \; \mathcal{D}^{(\frac{1}{2})}_{\mu-\mu_1, m-m_1} \quad C(\tfrac{1}{2}\tfrac{1}{2}1;\mu_1\mu-\mu_1)C(\tfrac{1}{2}\tfrac{1}{2}1;m_1,m-m_1)$$

or

$$d^{(1)}_{\mu m}[\beta] = \sum_{\mu_1, m_1} d^{(\frac{1}{2})}_{\mu_1 m_1}[\beta] d^{(\frac{1}{2})}_{\mu-\mu_1, m-m_1}[\beta] \; C(\tfrac{1}{2}\tfrac{1}{2}1;\mu_1,\mu-\mu_1)$$

$$\times\; C(\tfrac{1}{2}\tfrac{1}{2}1;m_1,m-m_1)$$

From the table of C-G coefficients (pg. 37),

$$C(\tfrac{1}{2}\tfrac{1}{2}1;\pm\tfrac{1}{2},m\mp\tfrac{1}{2}) = [(1\pm m)/2]^{\frac{1}{2}}$$

so that

$$d^{(1)}_{11}[\beta] = d^{(\frac{1}{2})}_{\frac{1}{2}\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{\frac{1}{2}\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1,\tfrac{1}{2}\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2}\tfrac{1}{2})$$

$$= \cos^2\beta/2 = (1+\cos\beta)/2$$

$$d^{(1)}_{01}[\beta] = d^{(\frac{1}{2})}_{\frac{1}{2}\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{-\frac{1}{2}\frac{1}{2}}[\beta] \; C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2},-\tfrac{1}{2}) \; C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2}\tfrac{1}{2})$$

$$+ d_{-\frac{1}{2}\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{\frac{1}{2}\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2}\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;-\tfrac{1}{2},\tfrac{1}{2})$$

$$= 2\cos(\beta/2)\sin(\beta/2)(1)(1/\sqrt{2}) = \sin\beta/\sqrt{2}$$

$$d^{(1)}_{-11}[\beta] = d^{(\frac{1}{2})}_{-\frac{1}{2}\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{-\frac{1}{2}\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1;-\tfrac{1}{2},-\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2}\tfrac{1}{2})$$

$$= \sin^2(\beta/2) = (1-\cos\beta)/2$$

$$d^{(1)}_{00}[\beta] = d^{(\frac{1}{2})}_{\frac{1}{2}\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{-\frac{1}{2},-\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2},-\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2},-\tfrac{1}{2})$$

$$+ d^{(\frac{1}{2})}_{-\frac{1}{2},-\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{\frac{1}{2}\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1;-\tfrac{1}{2},\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;-\tfrac{1}{2},\tfrac{1}{2})$$

$$+ d^{(\frac{1}{2})}_{\frac{1}{2},-\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{-\frac{1}{2},\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2},-\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;-\tfrac{1}{2},\tfrac{1}{2})$$

$$+ d^{(\frac{1}{2})}_{-\frac{1}{2},\frac{1}{2}}[\beta] d^{(\frac{1}{2})}_{\frac{1}{2},-\frac{1}{2}}[\beta] C(\tfrac{1}{2}\tfrac{1}{2}1;-\tfrac{1}{2},\tfrac{1}{2}) C(\tfrac{1}{2}\tfrac{1}{2}1;\tfrac{1}{2},-\tfrac{1}{2});-\tfrac{1}{2},-\tfrac{1}{2})$$

$$= 2\cos^2(\beta/2)(1/\sqrt{2})^2 + 2[-\sin^2(\beta/2)](1/\sqrt{2})^2$$

$$= \cos\beta$$

Thus

$$d^{(1)}[\beta] = \begin{pmatrix} (1+\cos\beta)/2 & -\sin\beta/\sqrt{2} & (1-\cos\beta)/2 \\ \sin\beta/\sqrt{2} & \cos\beta & -\sin\beta/\sqrt{2} \\ (1-\cos\beta)/2 & \sin\beta/\sqrt{2} & (1+\cos\beta)/2 \end{pmatrix}$$

just as we found previously (pg. 54) by considering the transformation properties of the Cartesian coordinate axes.

## 16. Orthogonality of the $\mathcal{D}$-Matrices and Integrals of Products of $\mathcal{D}$-Matrices

Since the $\mathcal{D}$-matrices are unitary,

$$\sum_m \mathcal{D}^{(j)*}_{m',m}[\Omega]\mathcal{D}^{(j)}_{m'',m}[\Omega] = \delta_{m',m''} ,$$

and

$$\sum_m \mathcal{D}^{(j)*}_{m,m'}[\Omega]\mathcal{D}^{(j)}_{m,m''}[\Omega] = \delta_{m',m''} .$$

Now let us show the orthogonality of the $\mathcal{D}$-matrices in a very different sense by considering the integral

$$K(j_1j_2;\mu_1\mu_2;m_1m_2) = \int d\Omega\mathcal{D}^{(j_1)^*}_{\mu_1m_1}[\Omega]\mathcal{D}^{(j_2)}_{\mu_2m_2}[\Omega]$$

where

$$\int d\Omega = \int_0^{2\pi} d\alpha\int_0^{\pi}\sin\beta d\beta\int_0^{2\pi} d\gamma$$

First we recognize that

$$\mathcal{D}^{(j_1)^*}_{\mu_1m_1}[\Omega] = (-1)^{\mu_1-m_1}\mathcal{D}^{(j_1)}_{-\mu_1,-m_1}[\Omega]$$

and use the inverse C-G series for the $\mathcal{D}$-matrices to write

$$K(j_1j_2;\mu_1\mu_2;m_1m_2) = (-1)^{\mu_1-m_1}\sum_j C(j_1j_2j;-\mu_1,\mu_2)C(j_1j_2j;-m_1,m_2)$$
$$\times\int d\Omega\mathcal{D}^{(j)}_{\mu_2-\mu_1,m_2-m_1}[\Omega]$$

Note that

$$\int d\Omega \mathcal{D}^{(j)}_{\mu_2-\mu_1,m_2-m_1}[\Omega] = \int_0^{2\pi} d\alpha \exp[-i(\mu_2-\mu_1)\alpha] \int_0^{\pi} \sin\beta d\beta d^j_{\mu_2-\mu_1,m_2-m_1}[\beta]$$

$$\times \int_0^{2\pi} d\gamma \exp[-i(m_2-m_1)\gamma]$$

$$= (2\pi)^2 \delta_{\mu_1,\mu_2} \delta_{m_1,m_2} \int_0^{\pi} \sin\beta d\beta d^j_{00}[\beta]$$

The $d^j_{00}[\beta]$ are just the Legendre polynomials $P_j[\cos\beta]$ which are orthogonal so the only non-vanishing integral occurs for $j=0$. Hence

$$K(j_1 j_2;\mu_1\mu_2;m_1m_2) = (-1)^{\mu_1-m_1} 8\pi^2 \delta_{\mu_1,\mu_2} \delta_{m_1,m_2}$$

$$\times C(j_1j_20;-\mu_1,\mu_1)C(j_1j_20;-m_1,m_1)$$

We recall the symmetry relation

$$C(j_1j_20;-\mu_1,\mu_1) = (1)^{j_1+\mu_1} \left(\frac{2(0)+1}{2j_2+1}\right)^{\frac{1}{2}} C(j_1 0 j_2;-\mu_1,0)$$

and the value

$$C(j_1 0 j_2;-\mu_1,0) = \delta_{j_1,j_2}$$

so that

$$K(j_1j_2;\mu_1\mu_2;m_1m_2) = (-1)^{\mu_1-m_1} 8\pi^2 \delta_{\mu_1,\mu_2} \delta_{m_1,m_2} (-1)^{j_1+\mu_1} (2j_2+1)^{-\frac{1}{2}} \delta_{j_1,j_2}$$

$$\times (-1)^{j_1+m_1} (2j_2+1)^{-\frac{1}{2}} \delta_{j_1,j_2}$$

$$= 8\pi^2/2j_1+1)\delta_{j_1,j_2} \delta_{\mu_1,\mu_2} \delta_{m_1,m_2}$$

Thus the $\mathcal{D}$-matrix elements form a complete orthogonal set of functions with orthogonality relation

$$\int d\Omega \mathcal{D}^{(j_1)*}_{m_1 m_2}[\Omega]\mathcal{D}^{(j_2)}_{\mu_1\mu_2}[\Omega] = 8\pi^2/(2j_1+1)\delta_{j_1,j_2}\delta_{m_1,m_2}\delta_{\mu_1,\mu_2}$$

It is useful to consider the transition moment integral

$$\int d\Omega \mathcal{D}^{(j_3)*}_{\mu_3,m_3}[\Omega]\mathcal{D}^{(j_2)}_{\mu_2,m_2}[\Omega]\mathcal{D}^{(j_1)}_{\mu_1,m_1}[\Omega]$$

$$= \sum_j \int d\Omega \mathcal{D}^{(j_3)*}_{\mu_3,m_3}[\Omega]\mathcal{D}^{(j)}_{\mu_1+\mu_2,m_1+m_2}[\Omega]\ C(j_1j_2j;\mu_1,\mu_2)\ C(j_1j_2j;m_1,m_2)$$

$$= 8\pi^2/(2j_3+1)C(j_1j_2j_3;\mu_1,\mu_2,\mu_3)\ C(j_1j_2j_3;m_1,m_2,m_3)$$

This integral arises in the intensities of spectroscopic transitions for polyatomic symmetric top molecules where the intensity of a transition from state $|J_1K_1M_1\rangle$ to state $|J_3K_3M_3\rangle$ induced by the generalized direction cosine element $\mathcal{D}^{(j_2)}_{m,k}[\Omega]$ is proportional to

$$\langle J_3K_3M_3|\mathcal{D}^{(j_2)}_{m,k}[\Omega]|J_1K_1M_1\rangle$$

$$= (2J_3+1)^{1/2}(2J_1+1)^{1/2}/(8\pi^2)\int d\Omega \mathcal{D}^{(J_3)*}_{-M_3,-K_3}[\Omega]\mathcal{D}^{(j_2)}_{m,k}[\Omega]\mathcal{D}^{(J_1)}_{-M_1,-K_1}[\Omega]$$

$$= [(2J_1+1)/(2J_3+1)]^{1/2}C(J_1j_2J_3;-K_1,k,-K_3)C(J_1j_2J_3;-M_1,m,-M_3)$$

Hence we have the selection rules $K_3 = K_1-k$, $M_3 = M_1-m$, $\Delta(J_1j_2J_3)$. For electric dipole transitions $j_2 = 1$ and k, m take on values -1,0,+1 so our selection rules are

$J_3 = J_1-1,\ J_1,\ J_1+1$ (P, Q, R branches)

$K_3 = K_1,\ K_1 \pm 1$

$M_3 = M_1,\ M_1 \pm 1$

with randomly polarized incident radiation. Note that the index k refers to the direction of the dipole in the molecular coordinate system. In pure rotational spectroscopy, the dipole of interest is the permanent dipole moment of the molecule and must be directed along the molecular z-axis. Hence k = 0 and the selection rules for pure rotational absorption are governed by $C(J_1 1 J_3; -K_1, C, -K_3)$ which requires $K_3 = K_1$ and, for absorption, $J_3 = J_1+1$. In rotation-vibration spectroscopy, the vibrating dipole moment may be along the molecular z-axis (parallel bands) or perpendicular to the z-axis (perpendicular bands). Parallel bands are therefore governed by a $K_3 = K_1$ selection rule and perpendicular bands by $K_3 = K_1 \pm 1$. In both cases P, Q, R branches occur.

## V. Irreducible Tensors

### 17. Definition of Irreducible Tensor Operators

The subject of irreducible tensor operators is very important in the applications of angular momentum theory and was first introduced by Racah and by Wigner. A tensor is defined by its tranformation properties under rotations of the coordinate system. The more familiar Cartesian tensors are not suitable here because they usually appear in reducible form. For example, the general second rank Cartesian tensor

$$\underset{\sim}{A} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix}$$

can be reduced into three irreducible parts:

$$T = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$$

which is a scalar (rank zero tensor),

$$\vec{A}' = \begin{pmatrix} \frac{1}{2}(A_{yz} - A_{zy}) \\ \frac{1}{2}(A_{zx} - A_{xz}) \\ \frac{1}{2}A_{xy} - A_{yx}) \end{pmatrix}$$

which is an antisymmetric tensor of rank one, and

$$\underset{\sim}{S} = \begin{pmatrix} A_{xx} - T & \frac{1}{2}(A_{xy} + A_{yx}) & \frac{1}{2}(A_{xz} + A_{zx}) \\ \frac{1}{2}(A_{xy} + A_{yx}) & A_{yy} - T & \frac{1}{2}(A_{yz} + A_{zy}) \\ \frac{1}{2}(A_{xz} + A_{zx}) & \frac{1}{2}(A_{yz} + A_{zy}) & A_{zz} - T \end{pmatrix}$$

which is a symmetric tensor of second rank. We can write

$$A_{ij} = T + A'_k + S_{ij}$$

where ijk is a cyclic permutation of x, y, z. It turns out that $T$, $\vec{A}'$ and $\underset{\sim}{S}$ transform under rotations like spherical harmonics of orders 0, 1 and 2 respectively, but this representation is not very useful because the components $\{A'_x, A'_y, A'_z\}$, $\{S_{xx}, S_{xy}, S_{xz}, S_{yy}, S_{yz}, S_{zz}\}$ do not correspond to definite projection quantum numbers m and their transformation rules under rotations are rather awkward. For example, x, y, and z are the components of an irreducible tensor of first rank, but the transformation law for the general rotation is very complicated. On the other hand, the linear combinations $-(x+iy)/\sqrt{2}$, $z$, $(x-iy)/\sqrt{2}$ are proportional to the first order spherical harmonics $Y_{1m}(\theta,\phi)$[$m = +1,0,-1$ respectively] and the transformation law is simply

$$[-(x''' + iy''')/\sqrt{2}, z, (x''' - iy''')/\sqrt{2}] = [-(x+iy)/\sqrt{2}, z, (x-iy)/\sqrt{2}]\mathcal{D}^{(1)}[\Omega]$$

It is therefore more convenient to discuss irreducible tensors in the spherical coordinate representation. Such tensors are usually called irreducible spherical tensors.

An irreducible tensor of rank L will be defined as a set of $2L + 1$ operators $\hat{T}_{LM}$($M = -L, -L+1, ---, L-1, L$) which transform under the $(2L + 1)$-dimensional representation of the rotation group

$$\hat{R}\,\hat{T}_{LM}\,\hat{R}^{-1} = \sum_{M'} \hat{T}_{LM'}\mathcal{D}^{(L)}_{M',M}[\Omega]$$

where $\hat{R}$ is the rotation operator for Euler angles $\Omega$. This definition of spherical tensor operators simply classifies them as operators which transform like the spherical harmonics. In this definition, the linear combinations $-(V_x + iV_y)/\sqrt{2}$, $V_z$, $(V_x - iV_y)/\sqrt{2}$ of the Cartesian components $V_x$, $V_y$, $V_z$ of any vector $\vec{V}$ transform like the first order spherical harmonics and are therefore a set of irreducible tensor operators of rank 1.

The algebra of spherical tensors has analogies to the algebra of Cartesian tensors, and some of the ideas may be clearest if the Cartesian tensors are studied first. Suppose that we define a Cartesian tensor T by the transformation law

$$T'_{ijk\ldots} = \sum_{\ell mn\ldots} a_{i\ell}a_{jm}a_{kn}\cdots T_{\ell mn\ldots}$$

where $a_{ij}$ is the ij-th element of an orthogonal 3 x 3 matrix which describes the rotation of the coordinate axes, and T' means the components in the rotated coordinate system. The rank of the tensor T is the number of subscripts ijk... needed to uniquely specify the components. The sum of two tensors of a given rank is another tensor of the same rank. For example

$$T_{ijk} + U_{ijk} = V_{ijk}$$

for a third rank tensor. A Cartesian tensor can always be written as the sum of tensors which are symmetric and antisymmetric with respect to the interchange of a particular pair of indices:

$$T_{ijk} = \tfrac{1}{2}(T_{ijk} + T_{jik}) + \tfrac{1}{2}(T_{ijk} - T_{jik})$$

The product of two tensors is a tensor whose rank is the sum of their ranks. For example

$$W_{ijk\ell m} = T_{ijk}S_{\ell m}$$

The final property of Cartesian tensors which we wish to discuss is the idea of a contraction. The rank of a tensor may be reduced by two units by equating a particular pair of indices and summing over all possible values of this index. For example, suppose that the second rank tensor T is constructed as a product of two first rank tensors U and V, then

$$T_{ij} = U_i V_j$$

The contraction of T results in the scalar (rank zero tensor)

$$t = \sum_i T_{ii} = \sum_i U_i V_i$$

which we recognize as the scalar product of vectors $\vec{U}$ and $\vec{V}$. In general, one may form contractions of a third order tensor in 3 ways:

$$\sum_i T_{iij} \quad , \sum_i T_{iji} \quad , \sum_j T_{ijj}$$

Now let us consider the addition, multiplication and contraction of spherical tensors. Let $T_{L_1M_1}(A_1)$ and $T_{L_2M_2}(A_2)$ be two spherical tensors of ranks $L_1$ and $L_2$. The symbols $A_1$ and $A_2$ represent all the other variables, besides $M_1$ or $M_2$, upon which the tensor depends.The addition of two spherical tensors of the same rank L is another tensor $T_{LM}(A_1) + T_{LM}(A_2)$ just as one finds for Cartesian tensors. This follows directly from the linearity of the rotational transformation.

Multiplication and contraction of spherical tensors are somewhat different than for Cartesian tensors: The tensor formed by the product of the components $\hat{T}_{L_1M_1}(A_1)\ \hat{T}_{L_2M_2}(A_2)$ transforms under rotations as

$$\hat{R}\hat{T}_{L_1M_1}(A_1)\hat{T}_{L_2M_2}(A_2)\hat{R}^{-1}$$

$$= \left\{\hat{R}\hat{T}_{L_1M_1}(A_1)\hat{R}^{-1}\right\}\left\{\hat{R}\hat{T}_{L_2M_2}(A_2)\hat{R}^{-1}\right\}$$

$$= \sum_{M_1',M_2'} T_{L_1M_1'}(A_1)\mathcal{D}^{(L_1)}_{M_1'M_1}[\Omega]T_{L_2M_2'}(A_2)\mathcal{D}^{(L_2)}_{M_2'M_2}[\Omega]$$

$$= \sum_{M_1',M_2'} \hat{T}_{L_1M_1'}\hat{T}_{L_2M_2'}\sum_{L}\mathcal{D}^{(L)}_{M_1'+M_2',M_1+M_2}[\Omega]$$

$$\times\ C(L_1L_2L;M_1',M_2')C(L_1L_2L;M_1M_2)$$

and is seen to be reducible into a number of irreducible spherical tensors of rank L with $L = |L_1-L_2|,\ |L_1-L_2| + 1,\ldots,\ L_1 + L_2$ since $L_1, L_2, L$ must satisfy the triangle condition discussed on pg. 29. The rank L of the irreducible tensor $\hat{T}_{LM}(A_1,A_2)$ obtained from the product of $\hat{T}_{L_1M_1}(A_1)$ and $\hat{T}_{L_2M_2}(A_2)$ must be a linear combination of simple products of the type $\hat{T}_{L_1M_1}(A_1)\ \hat{T}_{L_2,M-M_1}(A_2)$. The form of the above equation suggests that we investigate the linear combination

$$\hat{W}_{LM}(A_1,A_2) = \sum_{M_1}\hat{T}_{L_1M_1}(A_1)\hat{T}_{L_2,M-M_2}(A_2)C(L_1L_2L;M_1,M-M_1)$$

to see if it does transform as a spherical tensor of rank L.

$$\hat{R}\hat{W}_{LM}\hat{R}^{-1} = \sum_{M_1,M_1',M_2'}\hat{T}_{L_1M_1'}(A_1)\hat{T}_{L_2M_2'}(A_2)\sum_{L'}\mathcal{D}^{(L')}_{M_1'+M_2',M}[\Omega]$$
$$\times\ C(L_1L_2L';M_1',M_2')C(L_1L_2L';M_1,M-M_1)C(L_1L_2L;M_1,M-M_1)$$

Recognizing that (see pg. 26)

$$\sum_{M_1} C(L_1L_2L';M_1,M-M_1)C(L_1L_2L;M_1,M-M_1) = \delta_{L',L} ,$$

we have

$$\hat{R}\hat{W}_{LM}\hat{R}^{-1} = \sum_{M_1',M_2'} \hat{T}_{L_1M_1'}(A_1)\hat{T}_{L_2M_2'}(A_2)C(L_1L_2L;M_1',M_2')$$
$$\times \mathcal{D}^{(L)}_{M_1'+M_2',M}[\Omega]$$

$$= \sum_{M'} \left\{ \sum_{M_1'} \hat{T}_{L_1M_1'}(A_1)\hat{T}_{L_2M_2'}(A_2)C(L_1L_2L;M_1',M'-M_1') \right\}$$
$$\times \mathcal{D}^{(L)}_{M',M}[\Omega]$$

$$= \sum_{M'} \hat{W}_{LM'}(A_1,A_2)\mathcal{D}^{(L)}_{M',M}[\Omega]$$

Hence the linear combination $W_{LM}$ defined above is indeed a spherical tensor of rank L.

It is clear that the multiplication law

$$\hat{T}_{LM}(A_1,A_2) = \sum_{M_1} \hat{T}_{L_1M_1}(A_1)\hat{T}_{L_2,M-M_1}(A_2)C(L_1L_2L;M_1,M-M_1)$$

explicitly contains contractions of the product of two spherical tensors. If $L_1 = L_2$, it is possible to construct an invariant (a tensor of rank zero which is invariant to rotations).

$$\hat{T}_{00}(A_1,A_2) = \sum_{M_1} \hat{T}_{L_1M_1}(A_1)\hat{T}_{L_1,-M_1}(A_2)C(L_1L_10;M_1,-M_1)$$

Since

$$C(L_1L_10;M_1,-M_1) = (-1)^{L_1-M_1}(2L_1+1)^{-\frac{1}{2}}C(L_10L_1;M_1,0)$$
$$= (-1)^{L_1-M_1}(2L_1+1)^{\frac{1}{2}},$$

(see pgs. 31-32)

$$\hat{T}_{00}(A_1,A_2) = (-1)^{L_1}(2L_1+1)^{-\frac{1}{2}}\sum_{M_1}(-1)^{M_1}\hat{T}_{L_1M_1}(A_1)\hat{T}_{L_1,-M_1}(A_2).$$

Ignoring the constant factor $(-1)^{L_1}(2L_1+1)^{-\frac{1}{2}}$, we have an invariant

$$\hat{I} = \sum_{M}(-1)^{M}\hat{T}_{LM}(A_1)\hat{T}_{L,-M}(A_2)$$

and this is often referred to as the scalar product of two tensors. The Cartesian analog of these invariants are

$$I = \sum_{ijk\ldots} U^{*}_{ijk\ldots}V_{ijk\ldots}$$

where the * represents complex conjugation. This complex conjugate feature arises because

$$\hat{T}^{*}_{L,-M} = (-1)^{M}\hat{T}_{L,M}$$

Vector operators - Tensors of Rank 1

In classical mechanics, one is continually dealing with vectors - the position vector $\vec{r}$, the angular momentum vector $\vec{L}$, the force vector $\vec{F}$, the gradient vector $\vec{\nabla}$, etc. These classical vectors become vector operators in a quantum mechanical description. The classical vectors and the corresponding vector operators transform under rotations of the coordinate system as

$$(V'_x,\ V'_y,\ V'_z) = (V_x,\ V_y,\ V_z)\begin{pmatrix} M_{xx} & M_{xy} & M_{xz} \\ M_{yx} & M_{yy} & M_{yz} \\ M_{zx} & M_{zy} & M_{zz} \end{pmatrix}$$

where $\underset{\sim}{M}$ is the unitary matrix for the general rotation of coordinates by Euler angles $\alpha,\beta,\gamma$ (see pg. 54 for explicit expressions for the elements of $\underset{\sim}{M}$). Any collection of 3 operators $(\hat{O}_x,\ \hat{O}_y,\ \hat{O}_z)$ which transform under rotations like the vector $\vec{V}$ above is called a vector operator. As we have seen (pg. 54), the transformation matrix $\underset{\sim}{M}$

is a complicated function of the angles $\alpha,\beta,\delta$, but the transformation matrix $\underset{\sim}{\mathcal{D}}^{(1)}[\alpha,\beta,\gamma]$ for the spherical components $-(V_x + V_y)/\sqrt{2}$, $V_z$, $(V_x - iV_y)/\sqrt{2}$ has elements which are products of simple functions of $\alpha$, $\beta$, and $\delta$. It is therefore useful, and convenient, to use the spherical components of vector operators. In the jargon of tensors, the spherical component $\hat{O}_M$, of a vector operator form an irreducible spherical tensor of rank 1 since the tensor components $\hat{O}_M$ transform under rotations according to

$$\hat{R}\hat{O}_M\hat{R}^{-1} = \sum_{M'} \hat{O}_{M'}\mathcal{D}^{(1)}_{M'M}[\alpha,\beta,\gamma]$$

In the previous section, products of two tensor operators were considered, and a rule for the decomposition of the general product into irreducible tensors of various ranks was devised. It is very useful to consider some examples of tensor products in some detail so that these ideas are made clear.

Example 1. Product of $\vec{r}$ and $\vec{\nabla}$.

Consider the vector operators

$$\hat{\vec{V}} = (x,\ y,\ z) \qquad \text{(the Cartesian position vector operator)}$$

and

$$\hat{\vec{W}} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \qquad \text{(the Cartesian gradient operator)}$$

We wish to construct the product tensor operator $\hat{\vec{V}} \otimes \hat{\vec{W}}$ and investigate its irreducible components. First we convert $\hat{\vec{V}}$ and $\hat{\vec{W}}$ into spherical components

$$\hat{\vec{V}} = [-(x+iy)/\sqrt{2},\quad z,\ (x-iy)/\sqrt{2})]$$

and

$$\hat{\vec{W}} = [-(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y})\ ,\ \frac{\partial}{\partial z}\ ,\ (\frac{\partial}{\partial x} - i\frac{\partial}{\partial y})]$$

and recall that one can construct a spherical tensor operator $\hat{T}_{LM}$ of rank L from tensor operators $\hat{T}_{L_1,M_1}$ and $\hat{T}_{L_2,M_2}$ by

$$\hat{T}_{LM} = \sum_{M_1} \hat{T}_{L_1M_1}\hat{T}_{L_2,M-M_1}\, C(L_1L_2L;M_1,M-M_1,M)$$

For our case

$$\hat{T}_{LM} = \sum_{M_1} \hat{V}_{M_1}\hat{W}_{M-M_1} C(11L;M_1,M-M_1,M)$$

and the C-G coefficients vanish except for L = 0,1,2.

L = 0 Case

$$\hat{T}_{00} = \sum_{M_1} \hat{V}_{M_1}\hat{W}_{-M_1} C(110;M_1,-M_1,0)$$

$$= V_1W_{-1}(1/\sqrt{3}) + V_0W_0(-1/\sqrt{3}) + V_{-1}W_1(1/\sqrt{3})$$

$$= \left\{[-(x+iy)][\tfrac{\partial}{\partial x} - i\tfrac{\partial}{\partial y})]/2 + (z)(\tfrac{\partial}{\partial z})(-1) + [(x-iy)][-(\tfrac{\partial}{\partial x} + i\tfrac{\partial}{\partial y})]/2\right\}/\sqrt{3}$$

$$= -(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z})/\sqrt{3}$$

$$= -(1/\sqrt{3})\hat{\vec{V}}\cdot\hat{\vec{W}}$$ (the familiar scalar product of two vectors)

L = 1 Case

$$\hat{T}_{1M} = \sum_{M_1} \hat{V}_{M_1}\hat{W}_{M-M_1} C(111;M_1,M-M_1,M)$$

$$\hat{T}_{11} = \hat{V}_1\hat{W}_0 C(111;101) + \hat{V}_0\hat{W}_1 C(111;011)$$

$$= [-(x+iy)/\sqrt{2}][\tfrac{\partial}{\partial z}][1/\sqrt{2}] + [z][-(\tfrac{\partial}{\partial x} + i\tfrac{\partial}{\partial y})/\sqrt{2}][-1/\sqrt{2}]$$

$$= (\tfrac{1}{2})[-x\frac{\partial}{\partial z} + z\frac{\partial}{\partial x} - iy\frac{\partial}{\partial z} + iz\frac{\partial}{\partial y}]$$

$$= (\tfrac{1}{2})[\hat{L}_x + i\hat{L}_y] = -1/\sqrt{2}\hat{L}_{+1}$$

$$\hat{T}_{10} = \hat{V}_1\hat{W}_{-1} C(111;1,-1,0) + \hat{V}_0\hat{W}_0 C(111;000) + \hat{V}_{-1}\hat{W}_1 C(111;-1,1,0)$$

$$= [-(x+iy)/\sqrt{2}][(\tfrac{\partial}{\partial x} - i\tfrac{\partial}{\partial y})/\sqrt{2}][1/\sqrt{2}] + [z][\tfrac{\partial}{\partial z}][0]$$

$$+[(x-iy)/\sqrt{2}][-(\tfrac{\partial}{\partial x} + i\tfrac{\partial}{\partial y})/\sqrt{2}][-1/\sqrt{2}]$$

$$= (1/\sqrt{2})[-iy\frac{\partial}{\partial x} + ix\frac{\partial}{\partial y}]$$

$$= -(1/\sqrt{2})\hat{L}_z = -1/\sqrt{2}\hat{L}_0$$

$$\hat{T}_{1,-1} = \hat{V}_0\hat{W}_{-1}C(111;0,-1,-1) + \hat{V}_{-1}\hat{W}_0C(111;-1,0,-1)$$

$$= [z][(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y})/\sqrt{2}][1/\sqrt{2}] + [(x-iy)/\sqrt{2}][\frac{\partial}{\partial z}][-1/\sqrt{2}]$$

$$= (\tfrac{1}{2})[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} + iy\frac{\partial}{\partial z} - iz\frac{\partial}{\partial y}]$$

$$= (\tfrac{1}{2})[i\hat{L}_y - \hat{L}_x] = -(1/\sqrt{2})\hat{L}_{-1}$$

Hence the first rank tensor from the product of $\vec{r}$ and $\hat{\vec{\nabla}}$ is just the angular momentum vector operator in spherical component form.

L = 2 Case

$$\hat{T}_{22} = \hat{V}_1\hat{W}_1C(112;112)$$

$$= [-(x+iy)/\sqrt{2}][-(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y})/\sqrt{2}][1]$$

$$= (\tfrac{1}{2})[x\frac{\partial}{\partial x} - y\frac{\partial}{\partial y} + iy\frac{\partial}{\partial x} + ix\frac{\partial}{\partial y}]$$

$$\hat{T}_{21} = \hat{V}_1\hat{W}_0C(112;101) + \hat{V}_0\hat{W}_1C(112;011)$$

$$= [-(x+iy)/\sqrt{2}][\frac{\partial}{\partial z}][1/\sqrt{2}] + [z][-(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y})/\sqrt{2}][1/\sqrt{2}]$$

$$= (\tfrac{1}{2})[-x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x} - iy\frac{\partial}{\partial z} - iz\frac{\partial}{\partial y}]$$

$$\hat{T}_{20} = \hat{V}_1\hat{W}_{-1}C(112;1,-1,0) + \hat{V}_0\hat{W}_0C(112;000) + \hat{V}_{-1}\hat{W}_1C(112;-110)$$

$$= [-(x+iy)/\sqrt{2}][(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y})/\sqrt{2}][1/\sqrt{6}] + [z][\frac{\partial}{\partial z}][2/\sqrt{6}]$$

$$+ [(x-iy)/\sqrt{2}][-(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y})/\sqrt{2}][1/\sqrt{6}]$$

$$= (-x\frac{\partial}{\partial x} - y\frac{\partial}{\partial y} + 2z\frac{\partial}{\partial z})/\sqrt{6}$$

$$\hat{T}_{2,-1} = \hat{V}_0\hat{W}_{-1}C(112;0,-1,-1) + \hat{V}_{-1}\hat{W}_0C(112;-1,0,-1)$$

$$= [z][(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y})/\sqrt{2}][1/\sqrt{2}] + [(x - iy)/\sqrt{2}][\frac{\partial}{\partial z}][1/\sqrt{2}]$$

$$= (\tfrac{1}{2})[z\frac{\partial}{\partial x} + x\frac{\partial}{\partial z} - iz\frac{\partial}{\partial y} - iy\frac{\partial}{\partial z}]$$

$$\hat{T}_{2,-2} = \hat{V}_{-1}\hat{W}_{-1}C(112;-1,-1,-2)$$
$$= [(x - iy)/\sqrt{2}][(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y})/\sqrt{2}][1]$$
$$+ (\tfrac{1}{2})[x\frac{\partial}{\partial x} - y\frac{\partial}{\partial y} - ix\frac{\partial}{\partial y} - iy\frac{\partial}{\partial x}]$$

This second rank tensor does not correspond to anything which we commonly encounter in quantum mechanics.

Example 2. The Product of $\hat{\vec{I}}$ and $\hat{\vec{S}}$

Consider the spin angular momentum vector operators $\hat{\vec{I}}$ and $\hat{\vec{S}}$ for two distinct particles (e.g. a nucleus and an electron). We wish to investigate the irreducible tensor operators generated from the product $\hat{\vec{I}} \otimes \hat{\vec{S}}$. As in example 1, we have two rank 1 spherical tensors with components

$$[\hat{I}_1, \hat{I}_0, \hat{I}_{-1}] = [-(\hat{I}_x + i\hat{I}_y)/\sqrt{2}, \hat{I}_z, (\hat{I}_x - i\hat{I}_y)/\sqrt{2}]$$

and

$$[\hat{S}_1, \hat{S}_0, \hat{S}_{-1}] = [-(\hat{S}_x + i\hat{S}_y)/\sqrt{2}, \hat{S}_z, (\hat{S}_x - i\hat{S}_y)/\sqrt{2}]$$

There are spherical tensors $T_L$ of rank L = 0, 1, and 2 as before.

L = 0 Case

$$\hat{T}_{00} = \hat{I}_1\hat{S}_{-1}C(110;1,-1,0) + \hat{I}_0\hat{S}_0C(110;000) + \hat{I}_{-1}\hat{S}_1\ C(110;-110)$$
$$= (1/\sqrt{3})[\hat{I}_1\hat{S}_{-1} - \hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_1] = -1/\sqrt{3}[\hat{I}_z\hat{S}_z + (\tfrac{1}{2})(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+)]$$
$$= -(1/\sqrt{3})\hat{\vec{I}}\cdot\hat{\vec{S}}$$

As before $\hat{T}_{00}$ is proportional to the scalar product of the vectors.

L = 1 Case

$$\hat{T}_{11} = \hat{I}_1\hat{S}_0 C(111;101) + \hat{I}_0\hat{S}_1 C(111;011)$$
$$= (\hat{I}_1\hat{S}_0 - \hat{I}_0\hat{S}_1)/\sqrt{2}$$
$$\hat{T}_{10} = \hat{I}_1\hat{S}_{-1} C(111;1,-1,0) + \hat{I}_0\hat{S}_0 C(111;000) + \hat{I}_{-1}\hat{S}_1 C(111;-1,1,0)$$
$$= (\hat{I}_1\hat{S}_{-1} - \hat{I}_{-1}\hat{S}_1)/\sqrt{2}$$
$$\hat{T}_{1,-1} = \hat{I}_0\hat{S}_{-1} C(111;0,-1,-1) + \hat{I}_{-1}\hat{S}_0 C(111;-1,0,-1)$$
$$= (\hat{I}_0\hat{S}_{-1} - \hat{I}_{-1}\hat{S}_0)/\sqrt{2}$$

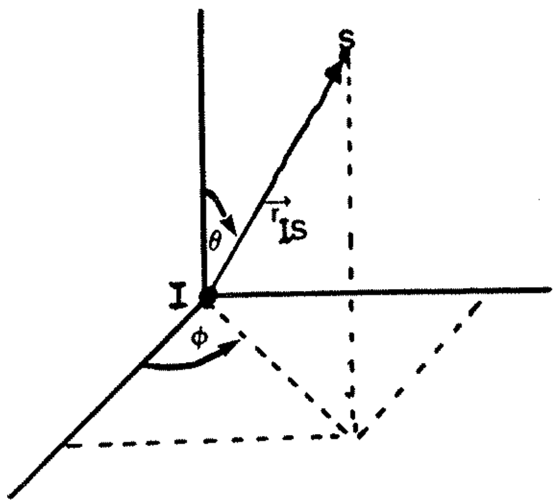
The L = 1 tensor operators are not commonly encountered in magnetic resonance.

L = 2 Case

$$\hat{T}_{22} = \hat{I}_1\hat{S}_1 C(112;112) = \hat{I}_1\hat{S}_1 = I_+S_+/2$$
$$\hat{T}_{21} = \hat{I}_1\hat{S}_0 C(112;101) + \hat{I}_0\hat{S}_1 C(112;011)$$
$$= (\hat{I}_1\hat{S}_0 + \hat{I}_0\hat{S}_1)/\sqrt{2} = -(\hat{I}_+\hat{S}_z + \hat{I}_z\hat{S}_+)/2$$
$$\hat{T}_{20} = \hat{I}_1\hat{S}_{-1} C(112;1,-1,0) + \hat{I}_0\hat{S}_0 C(112;000) + \hat{I}_{-1}\hat{S}_1 C(112;-110)$$
$$= (\hat{I}_1\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_1)/\sqrt{6} = [2\hat{I}_z\hat{S}_z - (\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+)/2]/\sqrt{6}$$
$$= [2\hat{I}_z\hat{S}_z - (\hat{\vec{I}}\cdot\hat{\vec{S}} - \hat{I}_z\hat{S}_z)]/\sqrt{6} = [3\hat{I}_z\hat{S}_z - (\hat{I}\cdot\hat{S})]/\sqrt{6}$$
$$\hat{T}_{2,-1} = \hat{I}_0\hat{S}_{-1} C(112;0,-1,-1) + \hat{I}_{-1}\hat{S}_0 \hat{C}(112;-1,0,-1)$$
$$= (\hat{I}_0\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_0)/\sqrt{2} = (\hat{I}_z\hat{S}_- + \hat{I}_-\hat{S}_z)/2$$
$$\hat{T}_{2.-2} = \hat{I}_{-1}\hat{S}_{-1} C(112;-1,-1,-2) = \hat{I}_{-1}\hat{S}_{-1} = \hat{I}_-\hat{S}_-/2$$

As we shall see in the next example, these operators are the ones which occur in the dipolar interaction between spin I and spin S.

## Example 3. The Magnetic Dipolar Interaction Between $\hat{\vec{I}}$ and $\hat{\vec{S}}$.




The dipolar interaction between the magnetic moment $\gamma_I \hbar \hat{\vec{I}}$ and the magnetic moment $\gamma_S \hbar \hat{\vec{S}}$ is given by (Slichter chapter 3).

$$\hat{H}_{dd} = \gamma_I \gamma_S \hbar^2 (\hat{\vec{I}} \cdot \hat{\vec{S}})/r_{IS}^3 - 3\gamma_I \gamma_S \hbar^2 (\hat{\vec{I}} \cdot \vec{r}_{IS})(\hat{\vec{S}} \cdot \vec{r}_{IS})/r_{IS}^5$$

where $\vec{r}_{IS}$ is the vector from the nucleus I to the nucleus S.

Let us look at the basic interaction as

$$\hat{H}' = (\hat{\vec{I}} \cdot \hat{\vec{S}}) - 3(\hat{\vec{I}} \cdot \vec{r}_{IS}/r_{IS})(\hat{\vec{S}} \cdot \vec{r}_{IS}/r_{IS})$$

From the figure above,

$$\vec{r}_{IS}/r_{IS} = (\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$$

Hence

$$\hat{H}' = (\hat{\vec{I}} \cdot \hat{\vec{S}}) - 3[\hat{I}_x \sin\phi\cos\phi + \hat{I}_y \sin\theta\sin\phi + \hat{I}_z \cos\theta]$$

$$\times\ [\hat{S}_x \sin\theta\cos\phi + \hat{S}_y \sin\theta\sin\phi + \hat{S}_z \cos\theta]$$

$$= \hat{I}_x \hat{S}_x (1-3\sin^2\theta\cos^2\phi) + \hat{I}_y \hat{S}_y (1-3\sin^2\theta\sin^2\phi) + \hat{I}_z \hat{S}_z (1-3\cos^2\theta)$$

$$-3(I_x S_y + I_y S_x)(\sin^2\theta\sin\phi\cos\phi)$$

$$-3(I_x S_z + I_z S_x)(\sin\theta\cos\theta\cos\phi)$$

$$-3(I_y S_z + I_z S_y)(\sin\theta\cos\theta\sin\phi)$$

Introducing the spherical tensor components of $\hat{\vec{I}}$ and $\hat{\vec{S}}$

$$\hat{I}_x = (-\hat{I}_{+1} + \hat{I}_{-1})/\sqrt{2} \qquad \hat{S}_x = (-\hat{S}_{+1} + \hat{S}_{-1})/\sqrt{2}$$
$$\hat{I}_y = i(\hat{I}_{+1} + \hat{I}_{-1})/\sqrt{2} \qquad \hat{S}_y = i(\hat{S}_{+1} + \hat{S}_{-1})/\sqrt{2}$$
$$\hat{I}_z = \hat{I}_0 \qquad \hat{S}_z = \hat{S}_0$$

We can rewrite the dipolar interaction as

$$\begin{aligned}
\hat{H}' = {} & (\tfrac{1}{2})(\hat{I}_{+1}\hat{S}_{+1} + \hat{I}_{-1}\hat{S}_{-1} - \hat{I}_{+1}\hat{S}_{-1} - \hat{I}_{-1}\hat{S}_{+1})(1-3\sin^2\theta\cos^2\phi) \\
& -(\tfrac{1}{2})(\hat{I}_{+1}\hat{S}_{+1} + \hat{I}_{-1}\hat{S}_{-1} + \hat{I}_{+1}\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_{+1})(1-3\sin^2\theta\sin^2\phi) \\
& +\hat{I}_0\hat{S}_0(1-3\cos^2\theta) \\
& -3i(-\hat{I}_{+1}\hat{S}_{+1} + \hat{I}_{-1}\hat{S}_{-1})(\sin^2\theta\sin\phi\cos\phi) \\
& -(3/\sqrt{2})(-\hat{I}_{+1}\hat{S}_0 + \hat{I}_{-1}\hat{S}_0 - \hat{I}_0\hat{S}_{+1} + \hat{I}_0\hat{S}_{-1})(\sin\theta\cos\theta\cos\phi) \\
& -(3i/\sqrt{2})(\hat{I}_{+1}\hat{S}_0 + \hat{I}_{-1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1} + \hat{I}_0\hat{S}_{-1})(\sin\theta\cos\theta\sin\phi) \\
= {} & \hat{I}_{+1}\hat{S}_{+1}[-(3/2)\sin^2\theta(\cos^2\phi-\sin^2\phi) + 3i\sin^2\theta(\sin\ \cos\phi)] \\
& +(\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})[(3/\sqrt{2})\sin\theta\cos\theta\cos\phi-(3i/\sqrt{2})\sin\theta\cos\theta\sin\phi] \\
& +(\hat{I}_{+1}\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_{+1})[-1+(3/2)\sin^2\theta] \ + \hat{I}_0\hat{S}_0[1-3\cos^2\theta] \\
& +(\hat{I}_0\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_0)[-(3/\sqrt{2})\sin\theta\cos\theta\cos\phi - (3i/\sqrt{2})\sin\theta\cos\theta\sin\phi] \\
& +\hat{I}_{-1}\hat{S}_{-1}[-(3/2)\sin^2\theta(\cos^2\phi-\sin^2\phi) - 3i\sin^2\theta(\sin\phi\cos\phi)] \\
= {} & \hat{I}_{+1}\hat{S}_{+1}[-(3/2)\sin^2\theta\exp(-2i\phi)] \\
& +(\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})[(3/\sqrt{2})\sin\theta\cos\theta\exp(-i\phi)] \\
& +(\hat{I}_{+1}\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + I_{-1}S_{+1})[(\tfrac{1}{2})(1-3\cos^2\theta)] \\
& +(\hat{I}_0\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_0)[-(3/\sqrt{2})\sin\theta\cos\theta\exp(+i\phi)] \\
& +\hat{I}_{-1}\hat{S}_{-1}[-(3/2)\sin^2\theta\exp(+2i\phi)] \\
= {} & \hat{T}_{2,2}[-(3/2)\sin^2\theta\exp(-2i\phi)] \\
& +\hat{T}_{2,1}[3\sin\theta\cos\theta\exp(-i\phi)] \\
& +\hat{T}_{2,0}[(\sqrt{6}/2)(1-3\cos^2\theta)] \\
& +\hat{T}_{2,-1}[-3\sin\theta\cos\theta\exp(+i\phi)] \\
& +\hat{T}_{2,-2}[-(3/2)\sin^2\theta\exp(+2i\phi)]
\end{aligned}$$

where the $\hat{T}_{2M}$ are the components of the second rank spherical tensor obtained from the product of $\hat{\vec{I}}$ and $\hat{\vec{S}}$ in Example 2 above.

We note that (see pg. 21-22) that the coefficients of $\hat{T}_{2M}$ in $\hat{H}'$ are proportional to the second order spherical harmonics:

$$Y_{2,2}(\theta,\phi) = (15/32\pi)^{\frac{1}{2}}\sin^2\theta\exp(+2i\phi)$$
$$Y_{2,1}(\theta,\phi) = -(15/8\pi)^{\frac{1}{2}}\sin\theta\cos\theta\exp(+i\phi)$$
$$Y_{2,0}(\theta,\phi) = (5/16\pi)^{\frac{1}{2}}(3\cos^2\theta-1)$$
$$Y_{2,-1}(\theta,\phi) = (15/8\pi)^{\frac{1}{2}}\sin\theta\cos\theta\exp(-i\phi)$$
$$Y_{2,-2}(\theta,\phi) = (15/32\pi)^{\frac{1}{2}}\sin^2\theta\exp(-2i\phi)$$

Hence

$$\hat{H}' = -(24\pi/5)^{\frac{1}{2}}[\hat{T}_{2,2}Y_{2,-2}-\hat{T}_{2,1}Y_{2,-1} + \hat{T}_{2,0}Y_{2,0}-\hat{T}_{2,-1}Y_{2,1} + \hat{T}_{2,-2}Y_{2,2}]$$
$$= -(24\pi/5)^{\frac{1}{2}} \sum_M (-1)^M \hat{T}_{2,M}Y_{2,-M}$$

Note that this corresponds to a scalar (a spherical tensor of rank zero) which is obtained from the product of the second rank tensors $\hat{T}$ and $Y$. This reflects the invariance of the dipolar interaction under rotations of the coordinate system. Finally we write

$$\hat{H}_{dd} = -(24\pi/5)^{\frac{1}{2}}(\gamma_I\gamma_S\hbar^2/r_{IS}) \sum_M (-1)^M\hat{T}_{2M}(IS)Y_{2,-M}(\theta,\phi)$$

where the second rank tensor T(IS) has components

$$\hat{T}_{2,2}(IS) = \hat{I}_{+1}\hat{S}_{+1}$$
$$\hat{T}_{2,1}(IS) = (\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})/\sqrt{2}$$
$$\hat{T}_{2,0}(IS) = (\hat{I}_{+1}\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_{+1})/\sqrt{6}$$
$$\hat{T}_{2,-1}(IS) = (\hat{I}_0\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_0)/\sqrt{2}$$
$$\hat{T}_{2,-2}(IS) = \hat{I}_{-1}\hat{S}_{-1}$$

## 18. Racah's Definition of Irreducible Tensor Operators

Racah has defined an irreducible tensor of rank L to be a set of operators $\hat{T}_{LM}$ (M = -L, -L+1 , ..., L) which satisfy the commutator relations

$$[\hat{J}_+, \hat{T}_{LM}] = \left\{L(L+1) - M(M+1)\right\}^{\frac{1}{2}} \hat{T}_{L,M+1}$$
$$[\hat{J}_-, \hat{T}_{LM}] = \left\{L(L+1) - M(M-1)\right\}^{\frac{1}{2}} \hat{T}_{L,M-1}$$
$$[\hat{J}_z, \hat{T}_{LM}] = M\hat{T}_{LM}$$

We must now show that this definition is consistent with the previous definition which required the $\hat{T}_{LM}$ to have certain transformation properties under rotations:

$$\hat{R}\hat{T}_{LM}\hat{R}^{-1} = \sum_{M'} \hat{T}_{LM'}\mathcal{D}^{(L)}_{M'M}[\alpha,\beta,\gamma] \qquad (5.2)$$

First let us investigate the case of an infinitesimal rotation by angle $\delta\theta$ about the z-axis. The Left right hand side of (5.2) will be

$$\hat{R}\hat{T}_{LM}\hat{R}^{-1} = \exp(-i\delta\theta\hat{J}_z)\hat{T}_{LM}\exp(i\delta\theta\hat{J}_z)$$
$$= (1 - i\delta\theta\hat{J}_z)\hat{T}_{LM}(1 + i\delta\theta\hat{J}_z)$$
$$= \hat{T}_{LM} - i\delta\theta[\hat{J}_z, \hat{T}_{LM}],$$

and the Right left hand side will be

$$\sum_{M'}\hat{T}_{LM'}\mathcal{D}^{(L)}_{M'M}[\delta\theta,0,0] = \sum_{M'}\hat{T}_{LM'}\exp(-i\delta\theta M')\delta_{M'M}$$
$$= \hat{T}_{LM}(1 - i\delta\theta M)$$
$$= \hat{T}_{LM} - i\delta\theta M\hat{T}_{LM}$$

Hence $[\hat{J}_z, \hat{T}_{LM}] = M\hat{T}_{LM}$ as Racah's definition requires.

Now we consider a rotation by $\delta\theta$ about the y-axis:

$$\hat{R}\hat{T}_{LM}\hat{R}^{-1} = \exp(-i\delta\theta\hat{J}_y)\hat{T}_{LM}\exp(i\delta\theta\hat{J}_y)$$
$$= \hat{T}_{LM} - i\delta\theta[\hat{J}_y, \hat{T}_{LM}]$$

and

$$\sum_{M'} \hat{T}_{LM'}\mathcal{D}^{(L)}_{M'M}[0,\delta\theta,0] = \sum_{M'} \hat{T}_{LM'}\langle LM'|\exp(-i\delta\theta\hat{J}_y)|LM\rangle$$
$$= \sum_{M'} \hat{T}_{LM'}\langle LM'|1 - i\delta\theta\hat{J}_y|LM\rangle$$
$$= \sum_{M'} \hat{T}_{LM}\left\{\delta_{M',M} - i\delta\theta\langle LM'|\hat{J}_y|LM\rangle\right\}$$
$$= \hat{T}_{LM} - i\delta\theta\sum_{M'} \hat{T}_{LM'}\langle LM'|\hat{J}_y|LM\rangle$$

Hence

$$[\hat{J}_y, \hat{T}_{LM}] = \sum_{M'} \hat{T}_{LM'}\langle LM'|\hat{J}_y|LM\rangle$$

To perform an infinitesimal rotation about the x-axis, we rotate by $-\pi/2$ about the z-axis, rotate by $\delta\theta$ about the new y-axis (identical to the old x-axis), then rotate by $+\pi/2$ about the z-axis. Hence

$$\hat{R}\hat{T}_{LM}\hat{R}^{-1} = \exp(-i\delta\theta\hat{J}_x)\hat{T}_{LM}\exp(i\delta\theta\hat{J}_x)$$
$$= \hat{T}_{LM} - i\delta\theta[\hat{J}_x, \hat{T}_{LM}]$$

and

$$\sum_{M'} \hat{T}_{LM'}\mathcal{D}^{(L)}_{M'M}[-\pi/2,\delta\theta, +\pi/2]$$

$$= \sum_{M'} \hat{T}_{LM'}\exp(+iM'\pi/2)\langle LM'|\exp(-i\delta\theta\hat{J}_y)|LM\rangle\exp(-iM\pi/2)$$

$$= \sum_{M'} \hat{T}_{LM'}\langle LM'|1-i\delta\theta\hat{J}_y|LM\rangle[\exp(i\pi/2)]^{M'-M}$$

$$= \sum_{M'} \hat{T}_{LM'}(\delta_{M',M} - i\delta\theta\langle LM'|\hat{J}_y|LM\rangle)(i)^{M'-M}$$

$$= \hat{T}_{LM} - i\delta\theta \sum_{M'} \hat{T}_{LM'}(i)^{M'-M}\langle LM'|\hat{J}_y|LM\rangle$$

so that

$$[J_x, \hat{T}_{LM}] = \sum_{M'} \hat{T}_{LM}'(i)^{M'-M}\langle LM'|J_y|LM\rangle$$

Therefore

$$[\hat{J}_x \pm i\hat{J}_y, \hat{T}_{LM}] = \sum_{M'} T_{LM'}\left\{ (i)^{M'-M} \pm i\right\} \langle LM'|\hat{J}_y|LM\rangle$$

$$= \sum_{M'} T_{LM'}\left\{ (i)^{M'-M} \pm i\right\}\left\{(2i)^{-1} \left[[(L(L+1) - M(M+1))]^{\frac{1}{2}}\delta_{M',M+1} - [(L(L+1) - M(M-1))]^{\frac{1}{2}}\delta_{M',M-1}\right]\right\}$$

and

$$[\hat{J}_x + i\hat{J}_y, \hat{T}_{LM}] = T_{L,M+1}\left\{L(L+1) - M(M+1)\right\}^{\frac{1}{2}}$$
$$[\hat{J}_x - i\hat{J}_y, \hat{T}_{LM}] = T_{L,M-1}\left\{L(L+1) - M(M-1)\right\}^{\frac{1}{2}}$$

exactly as the Racah definition requires.

A familiar example of a set of tensor operators which satisfy these commutator relations is the set of spherical components of the angular momentum operators themselves:

$$\hat{J}_{+1} = -[\hat{J}_x + i\hat{J}_y]/\sqrt{2} = -\hat{J}_+/\sqrt{2}$$
$$\hat{J}_0 = \hat{J}_z$$
$$\hat{J}_{-1} = +\hat{J}_x - i\hat{J}_y]/\sqrt{2} = +\hat{J}_-/\sqrt{2}$$

Recall that the angular momentum operators satisfy the commutator relations

$$[\hat{J}_z, \hat{J}_\pm] = \pm\hat{J}_\pm \quad \text{and} \quad [\hat{J}_+, \hat{J}_-] = 2\hat{J}_z$$

We note that

$$[\hat{J}_+,\hat{J}_{+1}] = [\hat{J}_+,-\hat{J}_+/\sqrt{2}] = 0 = \{1(1+1) - 1(1+1)\}^{\frac{1}{2}}\hat{J}_{+2}$$

$$[\hat{J}_+,\hat{J}_0] = [\hat{J}_+,\hat{J}_z] = -\hat{J}_+ = \sqrt{2}J_{+1} = \{1(1+1) - 0(0+1)\}^{\frac{1}{2}}J_{+1}$$

$$[\hat{J}_+,\hat{J}_{-1}\hat{]} = [\hat{J}_+,\hat{J}_-/\sqrt{2}] = \sqrt{2}\hat{J}_z = \sqrt{2}\hat{J}_0 = \{1(1+1) - (-1)(-1+1)\}^{\frac{1}{2}}\hat{J}_0$$

$$[\hat{J}_z,\hat{J}_{+1}] = [\hat{J}_z, -\hat{J}_+/\sqrt{2}] = -\hat{J}_+/\sqrt{2} = \hat{J}_{+1} = (+1)\hat{J}_{+1}$$

$$[\hat{J}_z,\hat{J}_0] = [\hat{J}_z,\hat{J}_z] = 0 = (0)\hat{J}_0$$

$$[\hat{J}_z,\hat{J}_{-1}] = [\hat{J}_z,\hat{J}_-/\sqrt{2}] = -\hat{J}_-/\sqrt{2} = -\hat{J}_{-1} = (-1)\hat{J}_{-1}$$

$$[\hat{J}_-,\hat{J}_{+1}] = [\hat{J}_-,-\hat{J}_+/\sqrt{2}] = \sqrt{2}\hat{J}_z = \{1(1+1) - 1(1-1)\}^{\frac{1}{2}}\hat{J}_0$$

$$[\hat{J}_-,\hat{J}_0] = [\hat{J}_-,\hat{J}_z] = \hat{J}_- = \sqrt{2}\hat{J}_{-1} = \{1(1+1) - 0(0-1)\}^{\frac{1}{2}}\hat{J}_{-1}$$

$$[\hat{J}_-,\hat{J}_{-1}] = [\hat{J}_-,\hat{J}_-/\sqrt{2}] = 0 = \{1(1+1) - (-1)(-1-1)\}^{\frac{1}{2}}\hat{J}_{-2}$$

and conclude that the operators $\hat{J}_\mu$, $\mu = -1, 0, 1$ form a tensor operator of rank one.

It is useful to write the commutator relations for the $\hat{T}_{LM}$ in terms of spherical components of the angular momentum operators:

$$[\hat{J}_{+1},\hat{T}_{LM}] = -\{[L(L+1) - M(M+1)]/2\}^{\frac{1}{2}}T_{L,M+1}$$

$$[\hat{J}_0,\hat{T}_{LM}] = M\ T_{L,M}$$

$$[\hat{J}_{-1},\hat{T}_{LM}] = \{[L(L+1) - M(M-1)]/2\}^{\frac{1}{2}}T_{L,M-1}$$

Referring to the table of C-G coefficients on pg. 38, we find

$$C(L1L;M+1,-1) = \{[L(L+1) - M(M+1)]/[2(L)(L+1)]\}^{\frac{1}{2}}$$

$$C(L1L;M,0) = M/\{L(L+1)\}^{\frac{1}{2}}$$

$$C(L1L;M-1,1) = -\{[L(L+1) - M(M-1)]/[2L(L+1)]\}^{\frac{1}{2}}$$

so that we may write the commutator relations as

$$[\hat{J}_\mu,\hat{T}_{LM}] = (-1)^\mu\{L(L+1)\}^{\frac{1}{2}}C(C1L;M+\mu,-\mu)\hat{T}_{L,M+\mu}.$$

In an exactly analogous way, we can express the matrix elements of the spherical tensor components of the angular momentum operators by

$$\langle j'm'|\hat{J}_\mu|jm\rangle = \delta_{j',j}\delta_{m',m+\mu}(-1)^\mu\{j(j+1)\}^{\frac{1}{2}}C(j1j;m+\mu,-\mu).$$

## 19. The Wigner-Eckart Theorem

Having defined the components $\hat{T}_{LM}$ of the irreducible spherical tensor of rank L by their transformation properties under rotations, and by their commutation relations with the angular momentum operators, we are now in a position to investigate the matrix elements of $\hat{T}_{LM}$ between angular momentum states: $\langle j'm'|\hat{T}_{LM}|jm\rangle$. The Wigner-Eckart theorem states that the dependence of the matrix element $\langle j'm'|\hat{T}_{LM}|jm\rangle$ on the quantum numbers m', M and m is entirely contained in the Clebsch-Gordan coefficient $C(jLj';mMm')$ so that

$$\langle j'm'|\hat{T}_{LM}|jm\rangle = \langle j'||\hat{T}_L||j\rangle C(jLj';mMm')$$

where the "double bar" matrix element $\langle j'||\hat{T}_L||j\rangle$ depends only on the quantum numbers j', L and j, not on m', M and m. Sometimes $\langle j'||\hat{T}_L||j\rangle$ is called the reduced matrix element of the set of operators $\hat{T}_{LM}$ between angular momentum state j and j'.

The proof of the Wigner-Eckart theorem relies on the commutator relations for the spherical tensor operators with the angular momentum operators. We begin with

$$[\hat{J}_z,\hat{T}_{LM}] = M\,\hat{T}_{LM}$$

and take the matrix element of this equation:

$$\langle j'm'|\hat{J}_z\hat{T}_{LM}|jm\rangle - \langle j'm'|\hat{T}_{LM}\hat{J}_z|jm\rangle = M\langle j'm'|\hat{T}_{LM}|jm\rangle$$

Now

$$\langle j'm'|\hat{J}_z\hat{T}_{LM}|jm\rangle = \sum_{j'',m''}\langle j'm'|\hat{J}_z|j''m''\rangle\langle j''m''|\hat{T}_{LM}|jm\rangle$$

$$= \sum_{j'',m''} m''\delta_{m'',m'}\delta_{j'',j'}\langle j''m''|\hat{T}_{LM}|jm\rangle$$

$$= m'\langle j'm'|\hat{T}_{LM}|jm\rangle \quad ,$$

and

$$\langle j'm'|\hat{T}_{LM}\hat{J}_z|jm\rangle = m\langle j'm'|\hat{T}_{LM}|jm\rangle \quad ,$$

therefore

$$(m' - m - M)\langle j'm'|\hat{T}_{LM}|jm\rangle = 0$$

which requires $\langle j'm'|\hat{T}_{LM}|jm\rangle = 0$ unless $m' = m+M$. This relation between m', m and M is, of course, contained in the C-G coefficient $C(jLj';\ mMm')$.

Next we consider the commutators

$$[\hat{J}_{\pm},\hat{T}_{LM}] = [L(L+1) - M(M\pm 1)]^{\frac{1}{2}}\hat{T}_{LM\pm 1}$$

and the matrix element of this equation:

$$\langle j'm'|\hat{J}_{\pm}\hat{T}_{LM}|jm\rangle - \langle j'm'|\hat{T}_{LM}\hat{J}_{\pm}|jm\rangle$$
$$= [L(L+1) - M(M\pm 1)]^{\frac{1}{2}}\langle j'm'|\hat{T}_{LM\pm 1}|jm\rangle$$

$$\langle j'm'|\hat{J}_{\pm}\hat{T}_{LM}|jm\rangle = \sum_{j''m''} \langle j'm'|\hat{J}_{\pm}|j''m''\rangle\langle j''m''|\hat{T}_{LM}|jm\rangle$$

$$= \sum_{j''m''} \delta_{m',m''\pm 1}\delta_{j',j''}[j'(j'+1) - m''(m''\pm 1)]^{\frac{1}{2}}\langle j''m''|\hat{T}_{LM}|jm\rangle$$

$$= [j'(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}}\langle j'm'\mp 1|\hat{T}_{LM}|jm\rangle$$

$$\langle j'm'|\hat{T}_{LM}\hat{J}_{\pm}|jm\rangle = [j(j+1) - m(m\pm 1)]^{\frac{1}{2}}\langle j'm'|\hat{T}_{LM}|jm\pm 1\rangle$$

Hence

$$[j'(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}}\langle j'm'\mp 1|\hat{T}_{LM}|jm\rangle$$
$$-[j(j+1) - m(m\pm 1)]^{\frac{1}{2}}\langle j'm'|\hat{T}_{LM}|jm\pm 1\rangle$$

$$= [L(L+1) - M(M\pm 1)]^{\frac{1}{2}} \langle j'm'|\hat{T}_{LM\pm 1}|jm\rangle$$

Now we know that each term in this equation will vanish unless $m' = m + M \pm 1$, but to understand this further, we must look back at the coupling of two angular momenta:

$$|j'm'\rangle = \sum_{m,M} |jm\rangle|LM\rangle C(jLj';mMm')$$

where $|jm\rangle$ are eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$, $|LM\rangle$ are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, and $|j'm'\rangle$ are eigenfunctions of $(\vec{\hat{J}}+\vec{\hat{L}})^2$, $\hat{J}_z + \hat{L}_z$. If we operate on $|j'm'\rangle$ with $\hat{J}_{\mp} + \hat{L}_{\mp}$, we obtain

$$(\hat{J}_{\mp} + \hat{L}_{\mp})|j'm'\rangle = [j'(j'+1) - m'(m\mp 1)]^{\frac{1}{2}}|j'm'\mp 1\rangle$$

from the LHS, and

$$(\hat{J}_{\mp} + \hat{L}_{\mp})|j'm'\rangle = \sum_{m,M} \Big\{[j(j+1) - m(m\mp 1)]^{\frac{1}{2}}|jm\mp 1\rangle|LM\rangle + [L(L+1) - M(M\mp 1)]^{\frac{1}{2}}|jm\rangle|LM\mp 1\rangle\Big\} \times C(jLj';mMm')$$

on the RHS. We use the C-G series to eliminate $|j'm'\mp 1\rangle$ on the LHS and obtain

$$\sum_{\mu,\lambda} |j\mu\rangle|L\lambda\rangle C(jLj';\mu\lambda m'\mp 1)[j(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}}$$
$$= \sum_{m,M} [L(L+1) - M(M\mp 1)]^{\frac{1}{2}}|jm\rangle|LM\mp 1\rangle C(jLj';mMm') + \sum_{m,M} [j(j+1) - m(m\mp 1)]^{\frac{1}{2}}|jm\mp 1\rangle|LM\rangle C(jLj';mMm')$$

or

$$\sum_{\mu,\lambda} |j\mu\rangle|L\lambda\rangle C(jLj';\mu\lambda m'\mp 1)[j'(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}}$$
$$= \sum_{\mu,\lambda} |j\mu\rangle|L\lambda\rangle[j(j+1) - \mu(\mu\pm 1)]^{\frac{1}{2}} C(jLj';\mu\pm 1,\lambda,m')$$
$$+ \sum_{\mu,\lambda} |j\mu\rangle|L\lambda\rangle[L(L+1) - \lambda(\lambda\pm 1)]^{\frac{1}{2}} C(jLj';\mu,\lambda\pm 1,m')$$

Hence

$$[j'(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}} C(jLj';\mu\lambda m'\mp 1)$$

$$- [j(j+1) - \mu(\mu\pm 1)]^{\frac{1}{2}} C(jLj';\mu\pm 1,\lambda,m')$$

$$= [L(L+1) - \lambda(\lambda\pm 1)]^{\frac{1}{2}} C(jLj';\mu,\lambda\pm 1,m')$$

Setting $\lambda = M$ and $\mu = m$, we have

$$[j'(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}} C(jLj';m,M,m'\mp 1)$$

$$-[j(j+1) - m(m\pm 1)]^{\frac{1}{2}} C(jLj';m\pm 1,M,m')$$

$$= [L(L+1) - M(M\pm 1)]^{\frac{1}{2}} C(jLj';m,M\pm 1,m')$$

which is to be compared with our previous equation for the matrix elements of $\hat{T}_{LM}$:

$$[j'(j'+1) - m'(m'\mp 1)]^{\frac{1}{2}} \langle j'm'\mp 1|\hat{T}_{LM}|jm\rangle$$

$$- [j(j+1) - m(m\pm 1)]^{\frac{1}{2}} \langle j'm'|\hat{T}_{LM}|jm\pm 1\rangle$$

$$= [L(L+1) - M(M\pm 1)]^{\frac{1}{2}} \langle j'm'|\hat{T}_{LM\pm 1}|jm\rangle$$

These equations imply that, for given values of j, L, j',

$$\langle j'm'|\hat{T}_{LM}|jm\rangle = f(j,L,j')C(jLj';mMm')$$

or

$$\langle j'm'|\hat{T}_{LM}|jm\rangle = C(jLj';mMm')\langle j'||\hat{T}_L||j\rangle$$

which proves the Wigner-Eckart theorem.

The Quadrupole Interaction

Let us now look at the electrostatic interaction between the electrons in an atom or molecule and the charges within a particular nucleus. It is easiest to investigate this problem if we take our origin of coordinates to be at the centre of the nucleus of interest. We then recognize that the electrons in the atom or molecule generate an electric potential $V(x,y,z)$ at the point $(x,y,z)$ and, if the density of nuclear charge is $\rho(x,y,z)$ at this point, the interaction between the electronic and nuclear charges is simply

$$\hat{H}_{int} = \iiint \rho(x,y,z)V(x,y,z)dxdydz$$

where the integration is over the total volume of the nucleus. Now $V(x,y,z)$ does not vary strongly over the nuclear volume so one expects the McLaurin expansion

$$V(x,y,z) = V_0 + x\left(\frac{\partial V}{\partial x}\right)_0 + y\left(\frac{\partial V}{\partial y}\right)_0 + z\left(\frac{\partial V}{\partial z}\right)_0 + \tfrac{1}{2}x^2\left(\frac{\partial^2 V}{\partial x^2}\right) + xy\left(\frac{\partial^2 V}{\partial x\partial y}\right)_0$$
$$+ xz\left(\frac{\partial^2 V}{\partial x\partial z}\right)_0 + \tfrac{1}{2}y^2\left(\frac{\partial^2 V}{\partial y^2}\right)_0 + yz\left(\frac{\partial^2 V}{\partial y\partial z}\right)_0 + \tfrac{1}{2}z^2\left(\frac{\partial^2 V}{\partial z^2}\right)_0 + \ldots ,$$

(where the subscript zero means that V or its derivative is to be evaluated at the origin of coordinates) is expected to converge rapidly. If we truncate the expansion at second order terms, the interaction can be written as

$$\hat{H}_{int} = ZeV_0 + \mu_x\left(\frac{\partial V}{\partial x}\right)_0 + \mu_y\left(\frac{\partial V}{\partial y}\right)_0 + \mu_z\left(\frac{\partial V}{\partial z}\right)_0 + \tfrac{1}{2}Q_{xx}\left(\frac{\partial^2 V}{\partial x^2}\right)_0$$
$$+ Q_{xy}\left(\frac{\partial^2 V}{\partial x\partial y}\right)_0 + Q_{xz}\left(\frac{\partial^2 V}{\partial x\partial z}\right)_0 + \tfrac{1}{2}Q_{yy}\left(\frac{\partial^2 V}{\partial y^2}\right)_0 + Q_{yz}\left(\frac{\partial^2 V}{\partial y\partial z}\right)_0$$
$$+ \tfrac{1}{2}Q_{zz}\left(\frac{\partial^2 V}{\partial z^2}\right)_0$$

where Ze is just the total nuclear charge, $\vec{\mu}$ is the electric dipole moment with components

$$\mu_\alpha = \iiint dxdydz\rho(x,y,z)\alpha \qquad , \alpha = x,y,z$$

and $\underset{\sim}{Q}$ is the quadrupole moment tensor for the nucleus with elements

$$Q_{\alpha\beta} = \iiint dxdydz\rho(x,y,\ )\alpha\beta \quad , \quad \alpha,\beta = x,y,z \quad .$$

In general, nuclei do not have electric dipole moments so $\mu_\alpha = 0$. We are interested particularly in the terms in the interaction associated with the quadrupole moment tensor of the nucleus and its interaction with the electric field gradients at the nucleus

$$\hat{H}_Q = \tfrac{1}{2}Q_{xx}V_{xx} + Q_{xy}V_{xy} + Q_{xz}V_{xz} + \tfrac{1}{2}Q_{yy}V_{yy} + Q_{yz}V_{yz} + \tfrac{1}{2}Q_{zz}V_{zz}$$

$$= \tfrac{1}{2}\sum_{\alpha,\beta} Q_{\alpha\beta}V_{\alpha\beta}$$

where

$$V_{\alpha\beta} = \left(\frac{\partial^2 V}{\partial\alpha\partial\beta}\right)_0 \qquad , \quad \alpha,\beta = x,y,z \ .$$

Now the elements $Q_{\alpha\beta}$ form a symmetric Cartesian tensor of second rank as do the elements $V_{\alpha\beta}$ of the electric field gradient. It is clear that $\hat{H}_Q$ is the contraction of the product of $\underset{\sim}{Q}$ and $\underset{\sim}{V}$ which is the invariant zero rank tensor (scalar).

In order to use angular momentum theory and the Wigner-Eckart theorem, we must convert the Cartesian tensors to irreducible spherical tensors. The tensor $\underset{\sim}{Q}$ is built up from the product of $\vec{r}$ with $\vec{r}$ integrated over all space with weighting function $\rho(x,y,z)$. Hence the relation between the spherical components of $\underset{\sim}{Q}$ and its Cartesian components can be inferred from the relationships between the diadic $\vec{r}\,\vec{r}$ in Cartesian components and the irreducible spherical tensor components. In Cartesian coordinates

$$\vec{r}\,\vec{r} = \begin{pmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zx & z^2 \end{pmatrix}$$

$\vec{r}$ has spherical components

$$r_{+1} = -(x + iy)/\sqrt{2}$$
$$r_0 = z$$
$$r_{-1} = (x - iy)/\sqrt{2}$$

and the inverse transformation is

$$x = (-r_{+1} + r_{-1})/\sqrt{2}$$
$$y = i(r_{+1} + r_{-1})/\sqrt{2}$$
$$z = 0$$

so that

$$x^2 = (r_{+1}^2 + r_{-1}^2 - 2r_{+1}r_{-1})/2$$
$$xy = i(-r_{+1}^2 + r_{-1}^2)/2$$
$$xz = (-r_{+1}r_0 + r_0r_{-1})/\sqrt{2}$$
$$y^2 = (-r_{+1}^2 - r_{-1}^2 - 2r_{+1}r_{-1})/2$$
$$yz = i(r_{+1}r_0 + r_0r_{-1})/\sqrt{2}$$
$$z^2 = r_0^2$$

The irreducible tensor components of $\vec{r} \otimes \vec{r}$ are

$$R_{L,M} = \sum_m r_m r_{M-m} C(11L;m,M-m,M)$$

with L = 0, 1 and 2 allowed.

L = 0 Case

$$R_{0,0} = r_{+1}r_{-1}C(110;1,-1,0) + r_0^2C(110;000) + r_{-1}r_{+1}C(110;-110)$$

$$= r_{+1}r_{-1}(1/\sqrt{3}) - r_0^2(-1/\sqrt{3}) + r_{-1}r_{+1}(1/\sqrt{3}) = (2r_{+1}r_{-1} - r_0^2)/\sqrt{3}$$

$$= -(x^2 + y^2 + z^2)/\sqrt{3}$$

L = 1 Case

$$R_{1,1} = r_{+1}r_0C(111;101) + r_0r_{+1}C(111;011) = r_{+1}r_0(1/\sqrt{2} - 1/\sqrt{2})$$

$$= 0$$

$$R_{1,0} = r_{+1}r_{-1}C(111;1,-1,0) + r_0^2C(111;000) + r_{-1}r_{+1}C(111;-110)$$

$$= r_{+1}r_{-1}(1/\sqrt{2} - 1/\sqrt{2}) + r_0^2(0) = 0$$

$$R_{1,-1} = r_0r_{-1}C(111;0-1-1) + r_{-1}r_0C(111;-10-1) = r_0r_{-1}(1/\sqrt{2} - 1/\sqrt{2})$$

$$= 0$$

It is not surprising that the first rank tensor vanishes since it is essentially the vector cross-product of $\vec{r}$ with $\vec{r}$ which we know is zero.

L = 2 Case

$$R_{2,2} = r_{+1}^2$$

$$R_{2,1} = r_{+1}r_0C(112;101) + r_0r_{+1}C(112;011) = r_{+1}r_0(1/\sqrt{2} + 1/\sqrt{2})$$

$$= \sqrt{2}r_{+1}r_0$$

$$R_{2,0} = r_{+1}r_{-1}C(112;1,-1,0) + r_0^2C(112;000) + r_{-1}r_{+1}C(112;-1,1,0)$$

$$= r_{+1}r_{-1}(1/\sqrt{6} + 1/\sqrt{6}) + r_0^2(2/\sqrt{6}) = (2/\sqrt{6})(r_{+1}r_{-1} + r_0^2)$$

$$R_{2,-1} = r_0r_{-1}C(112;0,-1,-1) + r_{-1}r_0C(112;-1,0,-1)$$

$$= r_0r_{-1}(1/\sqrt{2} + 1/\sqrt{2}) = \sqrt{2}r_0r_{-1}$$

$$R_{2,-2} = r_{-1}^2$$

Hence the products of the spherical tensor components of $\vec{r}$ are related to the irreducible tensor components $R_{LM}$ by

$$r_{+1}^2 = R_{2,2}$$

$$r_{+1}r_0 = R_{2,1}/\sqrt{2}$$

$$r_{+1}r_{-1} = R_{2,0}/\sqrt{6} + R_{0,0}/\sqrt{3}$$
$$r_0^2 = 2R_{2,0}/\sqrt{6} - R_{0,0}/\sqrt{3}$$

$$r_0r_{-1} = R_{2,-1}/\sqrt{2}$$
$$r_{-1}^2 = R_{2,-2}$$

and the Cartesian components are given by

$$x^2 = R_{2,2}/2 + R_{2,-2}/2 - R_{2,0}/\sqrt{6} - R_{0,0}/\sqrt{3}$$

$$xy = -iR_{2,2}/2 + iR_{2,-2}/2$$
$$xz = -R_{2,1}/2 + R_{2,-1}/2$$
$$y^2 = -R_{2,2}/2 - R_{2,-2}/2 - R_{2,0}/\sqrt{6} - R_{0,0}/\sqrt{3}$$
$$yz = iR_{2,1}/2 + iR_{2,-1}/2$$
$$z^2 = 2R_{2,0}/\sqrt{6} - R_{0,0}/\sqrt{3}$$

Therefore

$$Q_{xx} = Q_{2,2}/2 + Q_{2,-2}/2 - Q_{2,0}/\sqrt{6} - Q_{0,0}/\sqrt{3}$$
$$Qxy = -iQ_{2,2}/2 + iQ_{2,-2}/2$$
$$Qxz = -Q_{2,1}/2 + Q_{2,-1}/2$$
$$Q_{yy} = -Q_{2,2}/2 - Q_{2,-2}/2 - Q_{2,0}/\sqrt{6} - Q_{0,0}/\sqrt{3}$$
$$Q_{yz} = iQ_{2,1}/2 + iQ_{2,-1}/2$$
$$Q_{zz} = 2Q_{2,0}/\sqrt{6} - Q_{0,0}/\sqrt{3}$$

with the spherical tensor components of the nuclear quadrupole tensor given by

$$Q_{0,0} = -(Q_{xx} + Q_{yy} + Q_{zz})/\sqrt{3} = -Tr(Q)/\sqrt{3}$$
$$Q_{2,2} = (Q_{xx} - Q_{yy})/2 + iQ_{xy}$$
$$Q_{2,1} = -Q_{xz} - iQ_{yz}$$
$$Q_{2,0} = [3Q_{zz} - Tr(\underset{\sim}{Q})]/\sqrt{6}$$
$$Q_{2,-1} = Q_{xz} - iQ_{yz}$$
$$Q_{2,-2} = (Q_{xx} - Q_{yy})/2 - iQ_{xy}$$

In an exactly analogous fashion, the electric field gradient tensor $\underset{\sim}{V}$ can be reduced to its spherical tensor components

$$V_{xx} = V_{2,2}/2 + V_{2,-2}/2 - V_{2,0}/\sqrt{6} - V_{0,0}/\sqrt{3}$$
$$V_{xy} = -iV_{2,2}/2 + iV_{2,-2}/2$$
$$V_{xz} = -V_{2,1}/2 + V_{2,-1}/2$$
$$V_{yy} = -V_{2,2}/2 - V_{2,-2}/2 - V_{2,0}/\sqrt{6} - V_{0,0}/\sqrt{3}$$
$$V_{yz} = iV_{2,1}/2 + iV_{2,-1}/2$$
$$V_{zz} = 2V_{2,0}/\sqrt{6} - V_{0,0}/\sqrt{3}$$

where

$$V_{0,0} = -\mathrm{Tr}(\underset{\sim}{V})/\sqrt{3}$$
$$V_{2,2} = (V_{xx} - V_{yy})/2 + iV_{xy}$$
$$V_{2,1} = -V_{xz} - iV_{yz}$$
$$V_{2,0} = [3V_{zz} - \mathrm{Tr}(\underset{\sim}{V})]/\sqrt{6}$$
$$V_{2,-1} = V_{xz} - iV_{yz}$$
$$V_{2,-2} = (V_{xx} - V_{yy})/2 - iV_{xy}$$

The quadrupole interaction can now be written as

$$\hat{H}_Q = \tfrac{1}{2}Q_{0,0}V_{0,0} + \tfrac{1}{2}\sum_{m=-2}^{+2} (-1)^m Q_{2,m}V_{2,-m}$$

Now all we know about the nucleus is that it has spin angular momentum I and angular momentum eigenfunctions $|IM\rangle$. In this basis, the quadrupole interaction has representation

$$\langle IM'|\hat{H}_Q|IM\rangle = \tfrac{1}{2}\langle IM'|\hat{Q}_{0,0}|IM\rangle V_{0,0} + \tfrac{1}{2}\sum_m (-1)^m \langle IM'|\hat{Q}_{2,m}|IM\rangle V_{2,-m}$$

The first term will have only diagonal elements and gives rise to a small shift in the energies of all states. It is the second term which is correctly referred to as the quadrupole interaction. In order to proceed further, we must evaluate the matrix elements $\langle IM'|\hat{Q}_{2,m}|IM\rangle$ using the Wigner-Eckart theorem:

$$\langle IM'|\hat{Q}_{2,m}|IM\rangle = C(I2I;M,m,M')\langle I||\hat{Q}_2||I\rangle$$

The measured quadrupole moment of a nucleus is defined as

$$eQ = \langle II|\sqrt{6}\hat{Q}_{2,0}|II\rangle = \sqrt{6}C(I2I;I0I)\langle I||\hat{Q}_2||I\rangle$$

The C-G coefficient is given on pg. 38 and we find

$$eQ = \sqrt{6}[3I^2 - I(I+1)]/[2I-1)I(I+1)(2I+3)]^{\frac{1}{2}}\langle I||\hat{Q}_2||I\rangle$$

$$= \sqrt{6}\left\{I(2I-1)/[(I+1)(2I+3)]\right\}^{\frac{1}{2}}\langle I||\hat{Q}_2||I\rangle$$

This shows clearly that $eQ = 0$ for $I = 0$ and $I = 1/2$. The reason why nuclei with spin less than 1 cannot have electric quadrupole moments is seen to evolve from the transformation properties of the quadrupole interaction under rotations.

The matrix element of $\hat{Q}_{2m}$ is now given by

$$\langle IM'|\hat{Q}_{2m}|IM\rangle = eQC(I2I;MmM')\left\{(I+1)(2I+3)/[6I(2I-1)]\right\}^{\frac{1}{2}}$$

It is useful at this point to recognize that the matrix elements of the second rank tensor $\hat{T}_2$ constructed from the product $\hat{\vec{I}} \otimes \hat{\vec{I}}$ of the spherical components of the spin angular momentum operators, with

$$\hat{T}_{2,2} = (\hat{I}_{+1})^2 = (\hat{I}_x^2 - \hat{I}_y^2)/2 + i(\hat{I}_x\hat{I}_y + \hat{I}_y\hat{I}_x)/2$$
$$\hat{T}_{2,1} = (\hat{I}_{+1}\hat{I}_0 + \hat{I}_0\hat{I}_{+1})\sqrt{2}$$
$$\hat{T}_{2,0} = (\hat{I}_{+1}\hat{I}_{-1} + 2\hat{I}_0^2 + \hat{I}_{-1}\hat{I}_{+1})/\sqrt{6} = (-\hat{I}_x^2 - \hat{I}_y^2 + 2\hat{I}_z^2)/\sqrt{6} = (3\hat{I}_z^2 - \hat{I}^2)/\sqrt{6}$$
$$\hat{T}_{2,-1} = (\hat{I}_0\hat{I}_{-1} + \hat{I}_{-1}\hat{I}_0)/\sqrt{2}$$
$$\hat{T}_{2,-2} = (\hat{I}_{-1})^2 = (\hat{I}_x^2 - \hat{I}_y^2)/2 - i(\hat{I}_x\hat{I}_y + \hat{I}_y\hat{I}_x)/2$$

has matrix elements

$$\langle IM'|\hat{T}_{2,m}|IM\rangle = C(I2I;MmM')\langle I||\hat{T}_2||I\rangle$$

The reduced matrix element $\langle I||\hat{T}_2||I\rangle$ is evaluated by taking the case $M = M' = I$, $m = 0$, for which

$$\langle II|\hat{T}_{2,0}|II\rangle = \langle II|(3\hat{I}_z^2 - \hat{I}^2)/\sqrt{6}|II\rangle = [3I^2 - I(I+1)]/\sqrt{6}$$

and

$$C(I2I;I0I) = [3I^2 - I(I+1)]/[(2I-1)I(I+1)(2I+3)]^{\frac{1}{2}}$$

Hence

$$<I||\hat{T}_2||I> = [(2I-1)I(I+1)(2I+3)]^{\frac{1}{2}}/\sqrt{6}$$

and we can write

$$C(I2I;MmM') = <IM'|\hat{T}_{2,m}|IM>\sqrt{6}/[(2I-1)I(I+1)(2I+3)]^{\frac{1}{2}}$$

Therefore the matrix element of $\hat{Q}_{2,m}$ can be written as

$$\begin{aligned} <IM'|\hat{Q}_{2,m}|IM> &= eQ\left\{(I+1)(2I+3)/[I(2I-1)]\right\}^{\frac{1}{2}} \\ &\quad \times \left\{(2I-1)I(I+1)(2I+3)\right\}^{-\frac{1}{2}}<IM'|\hat{T}_{2,m}|IM> \\ &= eQ[I(2I-1)]^{-1}<IM'|\hat{T}_{2,m}|IM> \end{aligned}$$

This implies that, for all intents and purposes,

$$\hat{Q}_{2,m} = eQ[I(2I-1)]^{-1}\hat{T}_{2,m}$$

and we can replace the operators $\hat{Q}_{2,m}$ in $\hat{H}_Q$ with the operators $\hat{T}_{2m}$ within a particular I manifold. Therefore

$$\hat{H}_Q = \left\{eQ/[2I(2I-1)]\right\}\sum_m (-1)^m\hat{T}_{2,m}V_{2,-m}$$

Now $\underset{\sim}{V}_2$ is the electric field gradient tensor and its elements reflect the symmetry of the electron distribution in the atom or molecule. We shall assume that the coordinate system is chosen so that the derivatives $(\partial^2V/\partial x\partial y)_0$, $(\partial^2V/\partial y\partial z)$ and $(\partial^2V/\partial z\partial x)_0$ vanish i.e. the Cartesian tensor $\underset{\sim}{V}$ is diagonal. Then only $V_{xx}$, $V_{yy}$, $V_{zz}$ are non-zero and the spherical tensor components of $\underset{\sim}{V}_2$ are

$$V_{2,2} = (V_{xx} - V_{yy})/2$$

$$V_{2,1} = 0$$

$$V_{2,0} = [2V_{zz} - (V_{xx} + V_{yy})]/\sqrt{6}$$

$$V_{2,-1} = 0$$

$$V_{2,-2} = (V_{xx} - V_{yy})/2$$

and the only surviving terms in the sum over m in $\hat{H}_Q$ are

$$\hat{T}_{2,2}\hat{V}_{2,-2} + \hat{T}_{2,0}\hat{V}_{2,0} + \hat{T}_{2,-2}\hat{V}_{2,2}$$

$$=[(\hat{I}_x^2 - \hat{I}_y^2)/2 + i(\hat{I}_x\hat{I}_y + \hat{I}_y\hat{I}_x)/2][(V_{xx} - V_{yy})/2]$$

$$+ [(3\hat{I}_z^2 - \hat{I}^2)/\sqrt{6}][(2V_{zz} - V_{xx} - V_{yy})/\sqrt{6}]$$

$$+ [(\hat{I}_x^2 - \hat{I}_y^2)/2 - i(\hat{I}_x\hat{I}_y + \hat{I}_y\hat{I}_x)/2][(V_{xx} - V_{yy})/2]$$

$$= (3I_z^2 - I^2)[2V_{zz} - V_{xx} - V_{yy})/6] + (I_x^2 - I_y^2)](V_{xx} - V_{yy})/2]$$

Therefore

$$\hat{H}_Q = \Big\{eQ/[2I(2I-1)]\Big\}\Big\{[(2V_{zz} - V_{xx} - V_{yy})/6](3\hat{I}_z^2 - \hat{I}^2) + [(V_{xx} - V_{yy})/2](I_x^2 - I_y^2)\Big\}$$

Now $\underset{\sim}{V}_2$ must be traceless (we have ignored the scalar $Q_{0,0}V_{0,0}$ term in $\hat{H}_Q$) so that

$$V_{xx} + V_{yy} + V_{zz} = 0$$

Furthermore, we define

$eq = V_{zz}$ (often called the field gradient at the nucleus)

and $\eta = (V_{xx} - V_{yy})/V_{zz}$ (the asymmetry of the field gradient)

so that

$$\hat{H}_Q = \frac{e^2qQ}{4I(2I-1)}\Big\{(3\hat{I}_z^2 - \hat{I}^2) = \eta(\hat{I}_x^2 - \hat{I}_y^2)\Big\}$$

which is the usual form of the quadrupole interaction (see, for example, Abragam).

## 20. The Projection Theorem for First-Rank Tensors

In connection with the electric quadrupole interactions, we used an operator replacement to obtain the final form for the Hamiltonian operator. The use of operator replacements is very important in atomic spectroscopy and crystal field theory. In a formal sense one should be much more precise about operator replacements than I have been above. In this section we want to investigate the matrix elements of an arbitrary first-rank tensor $\hat{T}_1$. We can view the rank zero contraction of $\hat{T}_1$ and the angular momentum vector $\hat{J}$

$$\hat{\vec{J}} \cdot \hat{\vec{T}}_1 = \sum_{\mu} (-1)^{\mu} \hat{J}_{\mu} \hat{T}_{1,-\mu}$$

as a projection of $\hat{\vec{T}}_1$ on $\hat{\vec{J}}$. Actually the projection is $[j(j+1)]^{-\frac{1}{2}}(\hat{\vec{J}} \cdot \hat{\vec{T}}_1)$. There are three theorems which deserve mention:

I. Decomposition Theorem of the First Kind

$$\langle j'm'|\hat{T}_{1M}|jm\rangle = \frac{\langle jm'|\hat{J}_M(\hat{\vec{J}} \cdot \hat{\vec{T}}_1)|jm\rangle}{j(j+1)} \delta_{j',j}$$

II. Factorization Theorem

$$\langle j'm'|\hat{J}_M(\hat{\vec{J}} \cdot \hat{\vec{T}}_1)|jm\rangle = \langle jm'|\hat{J}_M|jm\rangle \langle j||\hat{\vec{J}} \cdot \hat{\vec{T}}_1||j\rangle \delta_{j',j}$$

III. Decomposition Theorem of the Second Kind

$$\langle jm'|\hat{T}_{1M}|jm\rangle = \langle jm'|\hat{J}_M|jm\rangle \langle j||\hat{\vec{J}} \cdot \hat{\vec{T}}_1||j\rangle / j(j+1)$$

The last expression is really the operator replacement theorem in that it implies that, <u>within a given j manifold</u>,

$$\hat{T}_{1M} = \hat{J}_M \langle j||\hat{\vec{J}} \cdot \hat{\vec{T}}_1||j\rangle / j(j+1)$$

**STANDARD PROTON PARAMETERS**
**OBSERVE H1**
**FREQUENCY 499.843 MHz**
**SPECTRAL WIDTH 8000.0 Hz**
**2D SPECTRAL WIDTH 8000.0 Hz**
**ACQUISITION TIME 0.500 sec**
**RELAXATION DELAY 1.500 sec**
**MIXING TIME 0.050 sec**
**PULSE WIDTH 26.5 usec**
**TEMPERATURE 30.0 deg. C.**
**NO. REPETITIONS 1**
**NO. INCREMENTS 1**
**DECOUPLE H1**
**HIGH POWER 0**
**DECOUPLER GATED OFF DURING ACQUISITION**
**DECOUPLER GATED ON DURING DELAY**
**SINGLE FREQUENCY**
**DOUBLE PRECISION ACQUISITION**
**DATA PROCESSING**
**FT SIZE 8192**
**F1 DATA PROCESSING**
**LINE BROADENING 0.3 Hz**
**FT SIZE 1024**
**TOTAL ACQUISITION TIME 1 minutes**

Density Matrix Theory of Magnetic (Relaxation / Resonance.)

A. Introduction.

B. Equation of motion for the Density matrix.

C. The Interaction representation and Time-Dependent Perturbation-Theory.

   1. An Introductory example - Transition rates under a random perturbation.

*  2. A ~~comb~~ concrete example - Relaxation rate due to a simple chemical exchange.

D. The Master equation of motion for the Density Matrix.

E. Derivation of Bloch equations.

F. The Interactions which produce Relaxation - Origins of Time Dependence

   1. Anisotropic chemical shift Interaction.
   2. Electric Quadrupole Interactions.
   3. The Intramolecular Dipole-Dipole Interaction.

# Density Matrix Theory of Magnetic Relaxation

## A. Introduction

In high resolution NMR, one is predominantly concerned with the average spin Hamiltonian which accurately predicts and accounts for the positions and intensities of the lines in the observed NMR spectra. However, the Hamiltonian for a spin system is really time-dependent (even in the absence of applied rf fields) due to the interactions between spins on different molecules or between spins on the same molecule due to the rotational and translational motion of the molecules. Usually the time dependence is very high frequency (molecules rotate and translate rapidly) so that the effects of the time-dependent interactions appear only in the widths of spectral lines. In a more general sense, these time-dependent interactions give rise to magnetic relaxation so that studies of magnetic relaxation can give information about the molecular motions which govern the time-dependent interactions.

We shall use the density matrix as a convenient vehicle in the computation of relaxation rates from molecular motional modulation of magnetic interactions. Hence a brief review on the density matrix description of magnetic systems is in order. In standard quantum mechanics, one always describes the state of a single system by the wavefunction $|\Psi(t)\rangle$ which satisfies the Schroedinger Equation

$$\hat{\mathcal{H}}|\Psi\rangle = i\hbar \frac{\partial|\Psi\rangle}{\partial t}$$

It is usually convenient to represent $|\Psi\rangle$ in a basis set of functions $\{|n\rangle\}$ (these are most often the eigenfunctions of the time-independent part of $\hat{\mathcal{H}}$, <u>but not necessarily so</u>); hence

$$|\Psi\rangle = \sum_n C_n(t)\,|n\rangle$$

where all of the time-dependence of $|\Psi(t)\rangle$ is contained in the coefficients $C_n(t)$. Now if we make a measurement of some property of this single system at time t, quantum mechanics tells us that the expectation value M is given by

$$M(t) = \langle\Psi(t)|\hat{\mathcal{M}}|\Psi(t)\rangle$$
$$= \sum_{m,n} C_m^*(t)\,C_n(t)\,\langle m|\hat{\mathcal{M}}|n\rangle$$

where $\hat{\mathcal{M}}$ is the Hermitian operator which corresponds to physical property M. When one performs a real measurement of the property M, one usually measures to average property $\langle M\rangle$ or $\overline{M}$ for a large number of systems. Hence

$$\overline{M}(t) = \sum_{m,n} \overline{C_m^*(t)\,C_n(t)}\,\langle m|\hat{\mathcal{M}}|n\rangle = \sum_{m,n} \rho_{nm}^{(t)}\langle m|\hat{\mathcal{M}}|n\rangle$$

where $\rho_{nm}(t) = \overline{C_n(t)\,C_m^*(t)}$

is the $n,m$ density matrix element for the ensemble. It is also convenient to define a density operator $\hat{\rho}$ which has matrix representation $\underset{\sim}{\rho}$, i.e.

$$\hat{\rho}|n\rangle = \sum_m |m\rangle\langle m|\hat{\rho}|n\rangle = \sum_m |m\rangle\rho_{mn}.$$

It should be noted that all of the time-dependence of $\overline{M}(t)$ is contained in the matrix elements $\rho_{nm}(t)$ so that a knowledge of $\underset{\sim}{\rho}(t)$ allows us to compute the values of <u>all</u> physical observables at time $t$.

## B. Equation of Motion for the Density Matrix

Given that $\rho_{nm}(t) = \overline{C_n(t)\, C_m^*(t)}$

$$\frac{d\rho_{nm}}{dt} = \overline{\frac{dc_n}{dt} C_m^*} + \overline{c_n \frac{dC_m^*}{dt}}$$

Now $|\Psi\rangle = \sum_n C_n(t)|n\rangle$

and $|\Psi\rangle$ satisfies the time-dependent Schroedinger equation

$$\hat{\mathcal{H}}|\Psi\rangle = i\hbar \frac{\partial}{\partial t}|\Psi\rangle$$

$$\therefore \sum_n c_n(t)\, \hat{\mathcal{H}}|n\rangle = \sum_n i\hbar \frac{dC_n}{dt}|n\rangle$$

Premultiplying by $\langle m|$, we obtain

$$i\hbar \frac{dC_m}{dt} = \sum_n C_n \langle m|\hat{\mathcal{H}}|n\rangle$$

with complex conjugate

$$-i\hbar \frac{dc_m^*}{dt} = \sum_n C_n^* \langle n|\hat{\mathcal{H}}|m\rangle$$

Hence

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar}\overline{\sum_p C_p \langle n|\hat{\mathcal{H}}|p\rangle C_m^*} + \frac{i}{\hbar}\overline{C_n \sum_p C_p^* \langle p|\hat{\mathcal{H}}|m\rangle}$$

$$= -\frac{i}{\hbar}\sum_p \langle n|\hat{\mathcal{H}}|p\rangle \rho_{pm} + \frac{i}{\hbar}\sum_p \rho_{np}\langle p|\hat{\mathcal{H}}|m\rangle$$

$$= \frac{i}{\hbar}\langle n|[\hat{\rho}, \hat{\mathcal{H}}]|m\rangle$$

i.e. $$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}]$$

is the equation of motion for the density operator.

Much of our effort will be devoted to the solution of this equation of motion for $\hat{\rho}(t)$ since, once we have $\hat{\rho}(t)$, everything else will be a matter of algebra.

## C. The Interaction Representation and Time-Dependent Perturbation Theory

Suppose that the Hamiltonian for our system can be written as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1(t)$$

where $\hat{\mathcal{H}}_0$ has no explicit time-dependence. The equation of motion for $\hat{\rho}$ is

$$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1(t)] = \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}_0] + \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}_1]$$

Now this equation can be simplified if we define the <u>interaction representation</u> of the operators:

$$\hat{\rho}^*(t) = \exp(+i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\rho}(t)\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

$$\hat{\mathcal{H}}_1^*(t) = \exp(+i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\mathcal{H}}_1(t)\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

$$\mathcal{H}_0^*(t) = \exp(+i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\mathcal{H}}_0(t)\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar) = \hat{\mathcal{H}}_0(t)$$

$\frac{i}{\hbar}\mathcal{H}_0\hat{\rho} + \frac{d\hat{\rho}}{dt} - \frac{i}{\hbar}\hat{\rho}\mathcal{H}_0$
$= -\frac{i}{\hbar}[\hat{\rho}, \mathcal{H}_0] + \frac{i}{\hbar}[\hat{\rho}, \mathcal{H}_0] + \frac{i}{\hbar}[\hat{\rho}, \mathcal{H}_1]$
$= \frac{i}{\hbar}[\hat{\rho}, \mathcal{H}_1]$

$$\frac{d\hat{\rho}^*}{dt} = \exp(+i\mathcal{H}_0 t/\hbar)\left\{+\frac{i\hat{\mathcal{H}}_0}{\hbar}\hat{\rho}\right\}\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

$$+ \exp(+i\mathcal{H}_0 t/\hbar)\left\{\frac{d\hat{\rho}}{dt}\right\}\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

$$+ \exp(+i\mathcal{H}_0 t/\hbar)\left\{\hat{\rho}\left(-\frac{i\hat{\mathcal{H}}_0}{\hbar}\right)\right\}\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

$$= \exp(+i\hat{\mathcal{H}}_0 t/\hbar)\left\{-\frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}_0] + \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}_0] + \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}_1]\right\}\exp(-i\mathcal{H}_0 t/\hbar)$$

$$= \exp(i\hat{\mathcal{H}}_0 t/\hbar)\left\{\frac{i}{\hbar}[\rho, \hat{\mathcal{H}}_1]\right\}\exp(-i\mathcal{H}_0 t/\hbar)$$

$$= \frac{i}{\hbar}\left\{\exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\rho}\,\hat{\mathcal{H}}_1\exp(-i\hat{\mathcal{H}}_0 t/\hbar) - \exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\mathcal{H}}_1\,\hat{\rho}\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)\right\}$$

$$= \frac{i}{\hbar}\Big\{\exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\rho}\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)\exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\mathcal{H}}_1\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

$$- \exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\mathcal{H}}_1\exp(-i\hat{\mathcal{H}}_0 t/\hbar)\exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\rho}\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)\Big\}$$

$$= \frac{i}{\hbar}\left\{\hat{\rho}^*\hat{\mathcal{H}}_1^* - \hat{\mathcal{H}}_1^*\hat{\rho}^*\right\}$$

$$= \frac{i}{\hbar}[\hat{\rho}^*, \hat{\mathcal{H}}_1^*]$$

← Equation of motion of the density matrix in the interaction representation.

In a rather formal sense, one can integrate this differential equation to obtain

$$\hat{\rho}^*(t) = \hat{\rho}^*(0) + \frac{i}{\hbar}\int_0^t [\hat{\rho}^*(t'), \mathcal{H}_1^*(t')]\, dt'$$

or, substituting this expression for $\hat{\rho}(t')$ in the commutator,

$$\hat{\rho}^*(t) = \hat{\rho}^*(0) + \frac{i}{\hbar}\int_0^t [\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t')]\, dt' - \frac{1}{\hbar^2}\int_0^t \int_0^{t'} [[\hat{\rho}^*(t''), \mathcal{H}_1^*(t'')], \mathcal{H}_1^*(t')]\, dt'' dt'$$

This iterative substitution procedure can be carried on indefinitely to obtain

$$\hat{\rho}^*(t) = \hat{\rho}^*(0) + \frac{i}{\hbar}\int_0^t dt' [\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t')] \cancel{dt'} - \frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' [[\hat{\rho}^*(0), \mathcal{H}_1^*(t'')], \hat{\mathcal{H}}_1^*(t')]$$

$$+ \cdots$$

This amounts to a power series expansion of $\hat{\rho}(t)$ in the time-dependent interaction $\hat{\mathcal{H}}_1^*$. Provided that $\hat{\mathcal{H}}_1^*$ represents a weak perturbation, the series converges rapidly, and one obtains a good approximation for $\hat{\rho}^*(t)$ with only the first ~~two~~ terms:

$$\hat{\rho}^*(t) \cong \hat{\rho}(0) + \frac{i}{\hbar}\int_0^t dt' [\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t')] \cancel{dt'} - \frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' [[\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t'')], \hat{\mathcal{H}}_1^*(t')]$$

In equation of motion form, we can then write

$$\frac{d\hat{\rho}^*}{dt} \cong \frac{i}{\hbar}[\hat{\rho}^*, \hat{\mathcal{H}}_1^*(t)] - \frac{1}{\hbar^2}\int_0^t dt'' [[\hat{\rho}^*(0), \mathcal{H}_1^*(t'')], \hat{\mathcal{H}}_1^*(t)]$$

## 1. An Introductory Example - Transition Rates Under a Random Perturbation

Suppose that we have an ensemble at time zero where only state $|k\rangle$ is occuppied. (This is not really a necessary assumption, but it makes the analysis very clear). Then

$$\langle n|\hat{\rho}^*(0)|m\rangle = \delta_{n,k}\,\delta_{m,k}$$ (i.e. all the states are of 0 pop'n except $k$)

i.e. only the $k,k$ element of $\hat{\rho}^*(0)$ is non-zero. Then the equation of motion for the $m,m$ matrix element of $\hat{\rho}^*(t)$ [the population of the m-th state] is

$$\frac{d}{dt}\langle m|\hat{\rho}^*|m\rangle = \frac{i}{\hbar}\sum_n \langle m|\hat{\rho}^*(0)|n\rangle\langle n|\hat{\mathcal{H}}_1^*(t)|m\rangle$$

$$-\frac{1}{\hbar^2}\int_0^t dt'' \sum_{n,p}\{\langle m|\hat{\rho}^*(0)|n\rangle\langle n|\hat{\mathcal{H}}_1^*(t'')|p\rangle\langle p|\hat{\mathcal{H}}_1^*(t)|m\rangle$$

$$-\langle m|\hat{\mathcal{H}}_1^*(t)|n\rangle\langle n|\hat{\rho}^*(0)|p\rangle\langle p|\hat{\mathcal{H}}_1^*(t'')|m\rangle$$

$$-\langle m|\hat{\mathcal{H}}_1^*(t'')|n\rangle\langle n|\hat{\rho}^*(0)|p\rangle\langle p|\hat{\mathcal{H}}_1^*(t)|m\rangle$$

$$+\langle m|\hat{\mathcal{H}}_1^*(t)|n\rangle\langle n|\hat{\mathcal{H}}_1^*(t'')|p\rangle\langle p|\hat{\rho}^*(0)|m\rangle\}$$

We are interested in the case $k \neq m$ so that we are considering a transition from $|k\rangle \to |m\rangle$ during the time $t$. Then

$$\frac{d\langle m|\hat{\rho}^*|m\rangle}{dt} = \frac{1}{\hbar^2}\int_0^t dt''\{\langle m|\hat{\mathcal{H}}_1^*(t)|k\rangle\langle k|\hat{\mathcal{H}}_1^*(t'')|m\rangle$$

$$+\langle m|\hat{\mathcal{H}}_1^*(t'')|k\rangle\langle k|\hat{\mathcal{H}}_1^*(t)|m\rangle\}$$

Now we recall that

$$\hat{\mathcal{H}}_1^*(t) = \exp(+i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\mathcal{H}}_1(t)\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

and recognize that the functions $|m\rangle$ and $|k\rangle$ above are just eigenfunctions of $\hat{\mathcal{H}}_0$ so that

$$\langle m|\hat{\mathcal{H}}_1^*(t)|k\rangle = \langle m|\exp(+i\hat{\mathcal{H}}_0 t/\hbar)|m\rangle\langle m|\hat{\mathcal{H}}_1(t)|n\rangle\langle n|\exp(-i\hat{\mathcal{H}}_0 t/\hbar)|n\rangle$$

$$= \langle m|\hat{\mathcal{H}}_1(t)|n\rangle\exp[i(E_m - E_n)t/\hbar]$$

$$= \langle m|\hat{\mathcal{H}}_1(t)|n\rangle\exp(i\omega_{nm}t)$$

where $\omega_{nm} = E_m - E_n$ is the frequency (radians/sec) of the transition from state $|n\rangle \to |m\rangle$. Hence our equation of motion for $\rho_{m,m}$ becomes

$$\frac{d\langle m|\rho^*|m\rangle}{dt} = \frac{1}{\hbar^2}\int_0^t dt''\{\langle m|\hat{\mathcal{H}}_1(t)|k\rangle\langle k|\hat{\mathcal{H}}_1(t'')|m\rangle\exp[i\omega_{km}(t-t'')]$$

$$+\langle m|\hat{\mathcal{H}}_1(t'')|k\rangle\langle k|\hat{\mathcal{H}}_1(t)|m\rangle\exp[-i\omega_{km}(t-t'')]\}$$

Furthermore, since $\hat{\rho}^*(t) = \exp(i\hat{\mathcal{H}}_0 t/\hbar)\,\hat{\rho}(t)\,\exp(-i\hat{\mathcal{H}}_0 t/\hbar)$

$$\langle m|\rho^*(t)|m\rangle = \langle m|\exp(i\mathcal{H}_1 t/\hbar)|m\rangle\langle m|\rho(t)|m\rangle\langle m|\exp(-i\mathcal{H}_0 t/\hbar)|m\rangle$$
$$= \langle m|\rho(t)|m\rangle$$

Hence

$$\frac{d\langle m|\hat{\rho}|m\rangle}{dt} = \frac{1}{\hbar^2}\int_0^t dt'' \left\{ \begin{array}{l} \langle m|\hat{\mathcal{H}}_1(t)|k\rangle\langle k|\hat{\mathcal{H}}_1(t'')|m\rangle \exp[i\omega_{km}(t-t'')] \\ +\langle m|\hat{\mathcal{H}}_1(t'')|k\rangle\langle k|\hat{\mathcal{H}}_1(t)|m\rangle \exp[-i\omega_{km}(t-t'')] \end{array}\right\}$$

Up to this point we have made no reference to the nature of $\hat{\mathcal{H}}_1(t)$ and its time-dependence. The above equation of motion is valid for any weak perturbation $\hat{\mathcal{H}}_1(t)$, but we are interested in the particular case of a perturbation with random time-dependence. Now what we mean by random time-dependence is that $\hat{\mathcal{H}}_1(t)$ varies from one point to another in the ensemble and that the variation of $\hat{\mathcal{H}}_1(t)$ at a given site with time is so complicated that, for all intents and purposes, it must be viewed as a random function of time $t$. We will therefore perform an ensemble average to obtain

$$\frac{d\langle m|\hat{\rho}|m\rangle}{dt} = \frac{1}{\hbar^2}\int_0^t dt'' \left\{ \begin{array}{l} \overline{\langle m|\hat{\mathcal{H}}_1(t)|k\rangle\langle k|\hat{\mathcal{H}}_1(t'')|m\rangle} \exp[i\omega_{km}(t-t'')] \\ + \overline{\langle m|\hat{\mathcal{H}}_1(t'')|k\rangle\langle k|\hat{\mathcal{H}}_1(t)|m\rangle} \exp[-i\omega_{km}(t-t'')] \end{array}\right\}$$

If the time-dependence of $\hat{\mathcal{H}}_1(t)$ is so chaotic that we cannot describe it in an analytical way, how can we proceed further? To answer this question, we must delve into the lore of stochastic (i.e. random) processes: We consider $\hat{\mathcal{H}}_1(t)$ to follow a stationary random process so that

$$\overline{\langle m|\hat{\mathcal{H}}_1(t)|k\rangle} = 0 \qquad (\text{for all values of } t)$$

and that the ensemble average $\overline{\langle m|\hat{\mathcal{H}}_1(t)|k\rangle\langle k|\hat{\mathcal{H}}_1(t'')|m\rangle}$ depends on $|t-t''|$ not on $t$ and $t''$ independently. In the jargon of stochastic processes, this ensemble average is called a correlation function:

$$G_{mk}(t-t'') = \overline{\langle m|\hat{\mathcal{H}}_1(t)|k\rangle\langle k|\hat{\mathcal{H}}_1(t'')|m\rangle}$$

Since the time-dependence of $\hat{\mathcal{H}}_1(t)$ follows a stationary random process,

$$\overline{\langle m|\hat{\mathcal{H}}_1(t)|k\rangle\langle k|\hat{\mathcal{H}}_1(t'')|m\rangle} = \overline{\langle m|\hat{\mathcal{H}}_1(t-t'')|k\rangle\langle k|\hat{\mathcal{H}}_1(0)|m\rangle}$$
$$= \overline{\langle m|\hat{\mathcal{H}}_1(0)|k\rangle\langle k|\hat{\mathcal{H}}_1(t''-t)|m\rangle}$$

moving back in time by $(t-t'')$

which implies that

$= G^{*}_{mk}(-t+t'')$

$= G_{km}$ ([illegible])

$$G_{mk}(\tau) = \overline{\langle m|\hat{\mathcal{H}}_1(\tau)|k\rangle\langle k|\hat{\mathcal{H}}_1(0)|m\rangle}$$
$$= \overline{\langle m|\hat{\mathcal{H}}_1(0)|k\rangle\langle k|\hat{\mathcal{H}}_1(-\tau)|m\rangle}$$

characterized by $\tau_c$

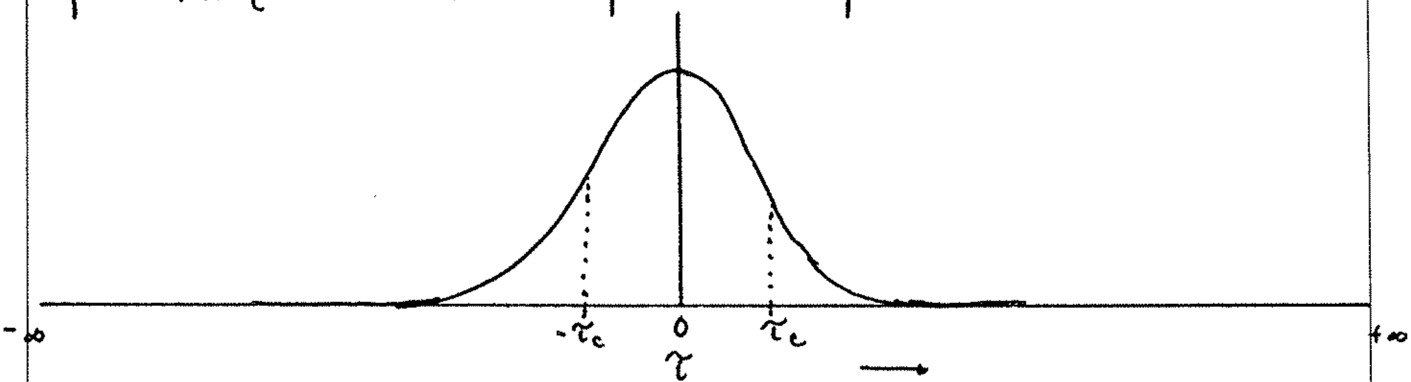
$$= G_{km}(-\tau)$$

$G_{mk}(\tau)$ is called a correlation function because it serves as a quantitative measure of the correlation between the value of $\hat{\mathcal{H}}_1(0)$ and its value $\hat{\mathcal{H}}_1(\tau)$ at a time $\tau$ later. If $\tau$ is very short compared to the average time for $\hat{\mathcal{H}}_1$ to change its value significantly, $\hat{\mathcal{H}}_1(0)$ and $\hat{\mathcal{H}}_1(\tau)$ will be strongly correlated and $G_{mk}(\tau) \cong \overline{|\langle m|\hat{\mathcal{H}}_1(0)|k\rangle|^2}$. However if $\tau$ is very long compared to the average time for $\hat{\mathcal{H}}_1$ to change significantly, our knowledge of the value of $\hat{\mathcal{H}}_1$ at time zero will be of very little value in predicting the value of $\hat{\mathcal{H}}_1$ at time $\tau$ since the system will have undergone a large number of fluctuations on the interval $(0, \tau)$. Hence for very long $\tau$, $G_{mk}(\tau) \cong \overline{\langle m|\hat{\mathcal{H}}_1(0)|k\rangle}\ \overline{\langle k|\hat{\mathcal{H}}_1(\tau)|m\rangle} = 0$ since $\hat{\mathcal{H}}_1(0)$ and $\hat{\mathcal{H}}_1(\tau)$ are essentially independent and to ensemble averages may be taken independently. This "time for $\hat{\mathcal{H}}_1$ to change significantly" referred to above is called the correlation time for $\hat{\mathcal{H}}_1$ and will be denoted by $\tau_c$. The qualitative discussion above can be summarized in the equations

$$G_{mk}(\tau) \cong G_{mk}(0) \quad \text{for } \tau \ll \tau_c$$

$$G_{mk}(\tau) \cong 0 \quad \text{for } \tau \gg \tau_c$$

Typically $G_{mk}(\tau)$ will have time-dependence like $\exp(-|\tau|/\tau_c)$, $\exp(-\tau^2/2\tau_c^2)$ or more complecated dependence.




Now back to our perturbation calculation:

$\tau = t - t''$ ?

$$\frac{d\langle m|\rho|m\rangle}{dt} = \frac{1}{\hbar^2}\int_{t''=0}^{t} dt'' \Big\{ G_{mk}(t-t'')\exp[i\omega_{km}(t-t'')] + G_{mk}(t''-t)\exp[-i\omega_{km}(t-t'')]\Big\}$$

$\tau = t'' - t$

$$= \frac{1}{\hbar^2}\int_{\tau=0}^{t} d\tau\, G_{mk}(\tau)\exp(i\omega_{km}\tau) + \frac{1}{\hbar^2}\int_{\tau=-t}^{0} d\tau\, G_{mk}(\tau)\exp[i\omega_{km}(\tau)]$$

$$= \frac{1}{\hbar^2}\int_{-t}^{t} d\tau\, G_{mk}(\tau)\exp(i\omega_{km}\tau)$$

We are of course only interested in the time-dependence of the system at times $t$ which are much longer than the correlation time $\tau_c$. Hence we can replace the limits on the above integral with $\pm\infty$ and obtain

$$\frac{d\langle m|\rho|m\rangle}{dt} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} d\tau\, G_{mk}(\tau)\exp(i\omega_{km}\tau)$$

for the transition rate from state $|k\rangle$ to state $|m\rangle$ under the action of $\mathcal{H}_1$.

This is of course just a Fourier integral and we define the spectral density

$$J_{mk}(\omega) = \int_{-\infty}^{\infty} d\tau\, G_{mk}(\tau)\, \exp(i\omega\tau)$$

with the inverse Fourier relationship

$$G_{mk}(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, J_{mk}(\omega)\, \exp(-i\omega\tau)$$

Typically $J_{mk}(\omega)$ will have frequency dependence

$$J_{mk}(\omega) = \frac{\tau_c}{1+\omega^2\tau_c^2} \quad \text{(Lorentzian form)} \quad \text{for} \quad G_{mk}(\tau) = \frac{1}{2}\exp -|\tau|/\tau_c$$

$$J_{mk}(\omega) = \tau_c \exp\left(-\frac{\omega^2\tau_c^2}{2}\right) \quad \text{(Gaussian line shape)} \quad \text{for} \quad G_{mk}(\tau) = \sqrt{\frac{2}{\pi}}\, \exp(-t^2/2\tau_c^2)$$

but it may be much more complicated. For these simple analytical forms $J_{mk}(\omega) \cong J_{mk}(0)$ for $\omega < 1/\tau_c$ and the transition rate

$$W_{k\to m} = \frac{J_{mk}(\omega_{km})}{\hbar^2} \cong \frac{J_{mk}(0)}{\hbar^2}$$

This limit is often realized in magnetic resonance in liquids. It is clear from the simple forms above that $J_{mk}(\omega) \propto \tau_c$ so we conclude that $W_{km} \propto \tau_c$ as well. This means that the transition rate induced by the random time-dependence of $\hat{\mathcal{H}}_1(t)$ increases as $\tau_c$ increases.

## 2. A Concrete Example - Relaxation Rate Due to a Simple Chemical Exchange

In the previous section we have dealt with time-dependent perturbation theory for random functions of time in a fairly general way. Now I want to be much more specific and deal with a relaxation perturbation of the form

$$\hat{\mathcal{H}}_1(t) = \overbrace{-\gamma\hbar H_x(t)\,\hat{I}_x - \gamma\hbar H_y(t)\,\hat{I}_y - \gamma\hbar H_z(t)\,\hat{I}_z}^{\text{A fluctuating field}} = -\gamma\hbar \sum_q H_q(t)\,\hat{I}_q$$

for a single spin ½ system with time-independent Hamiltonian

$$\hat{\mathcal{H}}_0 = -\gamma\hbar H_0 \hat{I}_z = -\hbar\omega_0 \hat{I}_z$$

The random fields $H_x(t)$, $H_y(t)$, $H_z(t)$ will ultimately be fields due to scalar coupling of nucleus I to another spin ½ nucleus which is exchanging, but for now, I will keep them as general fluctuating magnetic fields.

We have shown above that the transition rate between state $|k\rangle$ and state $|m\rangle$ is given by

freq. of the transition

$$W_{k\to m} = \frac{d\langle m|\rho|m\rangle}{dt} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} d\tau\; G_{mk}(\tau)\, \exp(i\omega_{km}\tau)$$

$$\text{Now}\quad G_{mk}(\tau) = \overline{\langle m|\hat{\mathcal{H}}_1(\tau)|k\rangle\langle k|\hat{\mathcal{H}}_1(0)|m\rangle}$$

$$= \sum_{q,q'} \gamma^2\hbar^2\, \overline{H_q(\tau) H_{q'}(0)}\; \langle m|I_q|k\rangle\langle k|I_{q'}|m\rangle$$

Hence the objects of interest here are the correlation functions for the fluctuating fields

$$g_{q,q'}(\tau) = \overline{H_q(\tau) H_{q'}(0)}$$

Now we shall assume that the fluctuating fields along different axes are uncorrelated, i.e.

$$g_{q,q'}(\tau) = \delta_{q,q'}\; g_{q,q}(\tau)$$

since the correlation functions for $q \neq q'$ vanish at $\tau = 0$, and for most known motional modulations never have significant amplitude.

Therefore

$$G_{mk}(\tau) = \sum_q \gamma^2\hbar^2\, \overset{\overline{H_q(\tau)H_q(0)}}{g_{q,q}(\tau)}\, |\langle m|\hat{I}_q|k\rangle|^2$$

Suppose that we take a very simple fluctuation for $H_q(\tau)$: $H_q$ can have values $+h$ and $-h$ only, and since it follows a stationary random process, the two possibilities are equiprobable. Following Slichter (appendix C in both editions), we determine the correlation function for $H_q(\tau)$:

$$g_{qq}(\tau) = H_q(\tau)\,H_q(0)$$
$$= \{+h\}\{\tfrac{1}{2}\}\{(+h)P_{++}(\tau) + (-h)P_{+-}(\tau)\}$$
$$+ \{-h\}\{\tfrac{1}{2}\}\{(+h)P_{-+}(\tau) + (-h)P_{--}(\tau)\}$$
$$= \frac{h^2}{2}\{P_{++}(\tau) + P_{--}(\tau) - P_{+-}(\tau) - P_{-+}(\tau)\}$$

where $P_{++}(\tau)$ is the probability that $H_q(\tau) = +h$ given that $H_q(0) = +h$, $P_{+-}(\tau)$ is the probability that $H_q(\tau) = -h$ given that $H_q(0) = +h$, etc. We expect the populations $p_+(t)$ and $p_-(t)$ to follow differential equations of the form $\frac{dp_+}{dt} = k(p_- - p_+)$ and $\frac{dp_-}{dt} = k(p_+ - p_-)$
where $k$ is the "rate constant" for exchange between the $+h$ and $-h$ states. These equations can be combined to the forms

$$\frac{d(p_+ + p_-)}{dt} = 0 \quad \text{and} \quad \frac{d(p_+ - p_-)}{dt} = -2k(p_+ - p_-)$$

with solutions $p_+(t) + p_-(t) = 1$ (using a normalized population).
and $p_+(t) - p_-(t) = [p_+(0) - p_-(0)]\exp(-2kt)$
These results imply that

$$P_{++}(\tau) + P_{+-}(\tau) = 1$$
$$P_{++}(\tau) - P_{+-}(\tau) = [P_{++}(0) - P_{+-}(0)]\exp(-2k\tau) = \exp(-2k\tau)$$
or $P_{++}(\tau) = \frac{1}{2} + \frac{1}{2}\exp(-2k\tau)$ , $P_{+-}(\tau) = \frac{1}{2} - \frac{1}{2}\exp(-2k\tau)$

and
$$P_{-+}(\tau) + P_{--}(\tau) = 1$$
$$P_{-+}(\tau) - P_{--}(\tau) = [P_{-+}(0) - P_{--}(0)]\exp(-2k\tau) = -\exp(-2k\tau)$$
or $P_{-+}(\tau) = \frac{1}{2} - \frac{1}{2}\exp(-2k\tau)$ , $P_{--}(\tau) = \frac{1}{2} + \frac{1}{2}\exp(-2k\tau)$

Hence

$$g_{qq}(\tau) = \frac{h^2}{2}\{1 + \exp(-2k\tau) - [1 - \exp(-2k\tau)]\}$$
$$= h^2\exp(-2k\tau) = h^2\exp(-|\tau|/\tau_c)$$
where the correlation time $\tau_c = 1/2k$.

This relationship between $\tau_c$ and $k$ makes sense if we view $\tau_c$ as the mean time between fluctuations in $H_q$. On the average, every $\tau_c/2$ seconds, the field becomes $+h$ or $-h$ with probabilities of ½ and ½ irrespective of the previous value of $H_q$. Hence the rate of transitions from $+h$ to $-h$ is $\frac{P_+}{2\tau_c}$ not $\frac{P_+}{\tau_c}$ because only ½ of the exchanges result in the opposite value of $H_q$.

The transition probability per unit time for transitions from the $|+\frac{1}{2}\rangle$ state to the $|-\frac{1}{2}\rangle$ state is

$$W_{+\frac{1}{2}\rightarrow-\frac{1}{2}} = \frac{d\langle -\frac{1}{2}|\hat{\rho}|-\frac{1}{2}\rangle}{dt} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} d\tau \left(\sum_q \gamma^2\hbar^2 h^2 \exp(-|\tau|/\tau_c)\right)\exp\left(i(E_{-\frac{1}{2}}-E_{+\frac{1}{2}})\tau/\hbar\right) |\langle -\tfrac{1}{2}|\hat{I}_q|+\tfrac{1}{2}\rangle|^2$$

$$= \gamma^2 h^2 \int_{-\infty}^{\infty} d\tau \exp -\frac{|\tau|}{\tau_c} \exp i\omega_0\tau \sum_q |\langle -\tfrac{1}{2}|\hat{I}_q|+\tfrac{1}{2}\rangle|^2$$

$$= \frac{2\gamma^2 h^2 \tau_c}{1+\omega_0^2\tau_c^2}\left\{|\langle -\tfrac{1}{2}|\hat{I}_x|\tfrac{1}{2}\rangle|^2 + |\langle -\tfrac{1}{2}|\hat{I}_y|\tfrac{1}{2}\rangle|^2 + |\langle -\tfrac{1}{2}|\hat{I}_z|\tfrac{1}{2}\rangle|^2\right\}$$

$$= \frac{2\gamma^2 h^2 \tau_c}{1+\omega_0^2\tau_c^2}\left\{\frac{1}{4}+\frac{1}{4}\right\} = \frac{\gamma^2 h^2 \tau_c}{1+\omega_0^2\tau_c^2}$$

Now it is easily shown (Slichter, Chapter 1) that

$$\frac{1}{T_1} = W_{+\frac{1}{2}\rightarrow-\frac{1}{2}} + W_{-\frac{1}{2}\rightarrow+\frac{1}{2}}$$

so, for our simple case

$$\frac{1}{T_1} = \frac{2\gamma^2 h^2 \tau_c}{1+\omega_0^2\tau_c^2}$$

If $h$ is the field due to a scalar interaction to another spin ½ nucleus, then

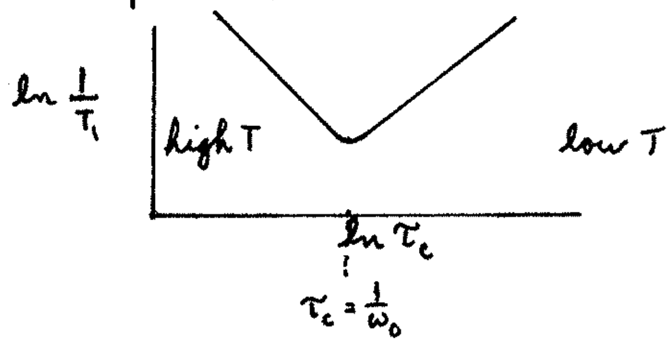
$$\gamma h = J/2$$

where $J$ is the spin-spin coupling constant (in rad/sec), and

$$\frac{1}{T_1} = \frac{J^2\tau_c}{2(1+\omega_0^2\tau_c^2)}$$

(This agrees with Abragam's Eq. (121), pg 309 for relaxation by Scalar relaxation of the first kind).

If we view $\tau_c$ as a time which gets longer at lower temperatures, then we expect $1/T_1$ to exhibit a minimum when $\tau_c \sim \frac{1}{\omega_0}$.




At low T, we have two distinct resonances due to the +h and −h fields. At high T, we have a single resonance line at $\omega_0$.

We shall find that $1/T_2$ does not show this behaviour.

## D. The Master Equation of Motion for the Density Matrix

On pg. 5, we developed the second order perturbation result

$$\frac{d\hat{\rho}^*}{dt} = \frac{i}{\hbar}\left[\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t)\right] - \frac{1}{\hbar^2}\int_0^t dt' \left[\left[\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t')\right], \hat{\mathcal{H}}_1^*(t)\right]$$

If $\hat{\mathcal{H}}_1(t)$ is a stationary random perturbation, then we must perform an ensemble average over this random motion and obtain

$$\frac{d\hat{\rho}^*}{dt} = \frac{i}{\hbar}\left[\rho^*(0), \overline{\hat{\mathcal{H}}_1^*(t)}\right] - \frac{1}{\hbar^2}\int_0^t dt' \,\overline{\left[\left[\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t')\right], \hat{\mathcal{H}}_1^*(t)\right]}$$

But $\overline{\hat{\mathcal{H}}_1^*(t)} = 0$ and

$$\overline{\mathcal{H}_1^*(t')\,\mathcal{H}_1^*(t)} = \overline{\mathcal{H}_1^*(0)\,\mathcal{H}_1^*(t-t')}$$

so that

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^t d\tau \,\overline{\left[\left[\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(0)\right], \mathcal{H}_1^*(\tau)\right]}$$

Now, provided that times t of interest (the time scale of magnetic relaxation) are much longer than the times $\tau$ where the correlation function $\overline{\mathcal{H}_1^*(0)\,\mathcal{H}_1^*(\tau)}$ has significant amplitude (the time scale of the correlation time $\tau_c$), we can extend the limit of the integration to $+\infty$. Then

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \,\overline{\left[\left[\hat{\rho}^*(0), \mathcal{H}_1^*(t)\right], \mathcal{H}_1^*(t+\tau)\right]}$$

One further assumption must be introduced: that it is permissible to replace $\hat{\rho}^*(0)$ in the above equation of motion by $\hat{\rho}^*(t)$. This can be justified by recognizing that our equation of motion is really a perturbation theory result and will only be valid if $\hat{\rho}^*(t) \cong \hat{\rho}^*(0)$. This implies that the time element $dt$ is short compared to the relaxation time of the system. One can show this by considering the time $t$ axis to be divided up into segment of length $\Delta t$. $\Delta t$ is chosen to be short enough that the 2nd order perturbation theory equation of motion describes the change in $\rho^*$ over the time interval $\Delta t$. Then

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \, \overline{[[\hat{\rho}^*(0), \hat{\mathcal{H}}_1^*(t)], \hat{\mathcal{H}}_1^*(t+\tau)]} \qquad \text{for } 0 \le t \le \Delta t$$

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \, \overline{[[\hat{\rho}^*(\Delta t), \hat{\mathcal{H}}_1^*(t)], \hat{\mathcal{H}}_1^*(t+\tau)]} \qquad \text{for } \Delta t \le t \le 2\Delta t$$

$$\vdots$$

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \, \overline{[[\hat{\rho}^*(n\Delta t), \hat{\mathcal{H}}_1^*(t)], \hat{\mathcal{H}}_1^*(t+\tau)]} \qquad \text{for } n\Delta t \le t \le (n+1)\Delta t$$

Provided $\rho^*$ does not change very much during time period $\Delta t$

$$\hat{\rho}^*(n\Delta t) \cong \hat{\rho}^*[(n+1)\Delta t] \quad \text{and}$$

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \, \overline{[[\hat{\rho}^*(t), \hat{\mathcal{H}}_1^*(t)], \hat{\mathcal{H}}_1^*(t+\tau)]}$$

should be valid for all $t$ long compared to $\tau_c$. Note that this analysis implicitly assumes the existence of an interval $\Delta t$ which satisfies the simultaneous inequalities

$$T_1, T_2 \gg \Delta t \gg \tau_c$$

This condition is usually fulfilled for relaxation in liquids where $\tau_c \sim 10^{-9}$ to $10^{-11}$ and $T_1, T_2 \sim 1$.

We are now in a position to specify $\mathcal{H}_1(t)$ in terms of spherical tensor operators $\hat{A}_{\ell m}$ in the spin space and functions $F_{\ell m}(t)$ of the "lattice" variables (rotations, translations, ...). I will choose to write

$$\hat{\mathcal{H}}_1(t) = \hbar \sum_m (-1)^m F_{\ell,-m}(t)\ \hat{A}_{\ell,m}$$

as we have shown to be the appropriate contraction of two tensors of rank $\ell$ in our discussions of the quantum mechanics of angular momenta. *

In terms of the $\hat{A}_{\ell,m}$ operators:

$$\frac{d\hat{\rho}^*}{dt} = -\sum_{m,m'} (-1)^{m+m'} \int_0^\infty \overline{F_{\ell,-m}(t)\, F_{\ell,-m'}(t+\tau)}\ \left[\left[\hat{\rho}^*(t), \hat{A}^*_{\ell,m}(t)\right], \hat{A}^*_{\ell,m'}(t+\tau)\right] d\tau \quad \cdots$$

For most types of motional modulation

$$\begin{aligned}\overline{F_{\ell,-m}(t)\quad F_{\ell,-m'}(t+\tau)} &= (-1)^m\ \overline{\underbrace{F^*_{\ell,m}}_{\text{complex conjugate}}(t)\ F_{\ell,-m'}(t+\tau)} \\ &= \delta_{m',-m}\ (-1)^m\ \overline{F^*_{\ell,m}(t)\ F_{\ell,m}(t+\tau)} \\ &= (-1)^m g_m(\tau)\ \delta_{m',-m}\end{aligned}$$

$$\frac{d\hat{\rho}^*}{dt} = -\sum_m (-1)^m \int_0^\infty g_m(\tau)\ \left[\left[\hat{\rho}^*(t), \hat{A}^*_{\ell,m}(t)\right], \hat{A}^*_{\ell,-m}(t+\tau)\right] d\tau$$

Now, since the operators $\hat{A}_{\ell,m}$ are spherical tensor operators, they have "very selective" non-zero matrix elements in the basis of eigenfunctions of $\mathcal{H}^0$. For example, the $\ell = 1$ spin operators $\hat{I}_{+1}, \hat{I}_0, \hat{I}_{-1}$ (for a system with $\mathcal{H}_0 = -\gamma\hbar H_0 \hat{I}_z$) will have matrix elements:

$\langle I\ M{+}1 | \hat{I}_{+1} | I\ M\rangle$, $\langle I\ M | \hat{I}_0 | I\ M\rangle$ and $\langle I\ M{-}1 | \hat{I}_{-1} | I\ M\rangle$ only.

The matrix elements of the $\hat{A}^*_{\ell,m}$ for this case will be

$$\begin{aligned}\langle I\ M' | \hat{I}^*_{+1}(t) | I\ M\rangle &= \langle I\ M' | \exp(+i\hat{\mathcal{H}}_0 t/\hbar)\ \hat{I}_{+1}\ \exp(-i\hat{\mathcal{H}}_0 t/\hbar) | I\ M\rangle \\ &= \delta_{M',M+1}\ \exp{\mp i\omega_0 t}\ \langle I\ M{+}1 | \hat{I}_{+1} | I\ M\rangle \\ &= \langle I\ M' | \hat{I}_{+1}\, e^{\mp i\omega_0 t} | I\ M\rangle,\end{aligned}$$

$$\langle I, M' | \hat{I}_z^*(t) | I, M\rangle = \langle I, M' | \exp(i\hat{\mathcal{H}}_0 t/\hbar)\ \hat{I}_z \exp(-i\hat{\mathcal{H}}_0 t/\hbar) | I, M\rangle$$
$$= \langle I, M' |\ \hat{I}_z\ | I, M\rangle ,$$

and

$$\langle I, M' | \hat{I}_{-1}^*(t) | I, M\rangle = \langle I, M' | \exp(i\hat{\mathcal{H}}_0 t/\hbar)\ \hat{I}_{-1} \exp(-i\hat{\mathcal{H}}_0 t/\hbar) | I, M\rangle$$
$$= \delta_{M', M-1} \exp +i\omega_0 t \langle I, M-1 | \hat{I}_{-1} | I, M\rangle$$
$$= \langle I, M' |\ \hat{I}_{-1} \exp(+i\omega_0 t) | I, M\rangle .$$

Thus, we can write

$$\underline{\hat{A}^*_{l,m}(t) = \hat{A}_{lm} \exp i\omega_m t}$$

where $\omega_m$ is the energy separation (in rad/sec) of states connected by the operator $\hat{A}_{lm}$. For certain cases, we will find it necessary to modify this statement to make it more general.

Our equation of motion can therefore be written as

$$\frac{d\hat{\rho}^*}{dt} = -\sum_m (-1)^m \int_0^\infty d\tau\ \underbrace{g_m(\tau) \exp(-i\omega_m \tau)}\ [[\hat{\rho}^*(t), \hat{A}_{l,m}], \hat{A}_{l,-m}]$$

The spectral density $J_m(\omega)$ is defined as

$$J_m(\omega) = \int_{-\infty}^{\infty} g_m(\tau) \exp(-i\omega\tau) d\tau$$

from which

$$\int_0^\infty g_m(\tau) \exp(-i\omega_m\tau)\, d\tau = \frac{1}{2} J_m(\omega_m) - i \int_0^\infty g_m(\tau) \sin(\omega_m\tau)\ d\tau$$
$$= \frac{1}{2} J_m(\omega_m) - i\, k_m(\omega_m)$$

where $k_m(\omega_m)$ corresponds to a small frequency shift and will be ignored.

$$\boxed{\frac{d\hat{\rho}^*}{dt} = -\frac{1}{2}\sum_m (-1)^m J_m(\omega_m) [[\hat{\rho}^*(t), \hat{A}_{l,m}], \hat{A}_{l,-m}]}$$

is called the Master Equation of Motion.

## E. "Derivation" of Bloch Equations

In magnetic relaxation, we are interested in the time dependence of the magnetizations of a system. Let us consider the simple single spin ½ system with

$$\hat{\mathcal{H}}_0 = -\gamma\hbar H_0 \hat{I}_z = -\hbar\omega_0 \hat{I}_z = -\hbar\omega_0 \hat{I}_0$$

and

$$\hat{\mathcal{H}}_1(t) = -\gamma\hbar \sum_m (-1)^m H_m(t)\, \hat{I}_m$$

Now we wish to find equations of motion for $\langle M_x(t)\rangle$, $\langle M_y(t)\rangle$ and $\langle M_z(t)\rangle$. By definition

$$\langle M_x(t)\rangle = \text{Trace}\{\hat{M}_x \hat{\rho}(t)\} = -\gamma\hbar\, \text{Tr}\{\hat{I}_x \hat{\rho}(t)\}$$

Then

$$\frac{d\langle M_x(t)\rangle}{dt} = -\gamma\hbar\, \text{Tr}\left\{\hat{I}_x \frac{d\hat{\rho}}{dt}\right\}$$

Hence if we can derive equations of motion for $\hat{I}_{+1}$, $\hat{I}_0$, $\hat{I}_{-1}$ the eqns of motion for $M_x$, $M_y$, $M_z$ are easily obtained.

Our first problem is that our master equation is an equation for $\hat{\rho}^*$ not for $\hat{\rho}$. Recognize that

$$\hat{\rho}^*(t) = \exp(i\hat{\mathcal{H}}_0 t/\hbar)\, \hat{\rho}(t) \exp(-i\hat{\mathcal{H}}_0 t/\hbar)$$

and

$$\hat{\rho}(t) = \exp(-i\hat{\mathcal{H}}_0 t/\hbar)\, \hat{\rho}^*(t) \exp(i\hat{\mathcal{H}}_0 t/\hbar)$$

$$\therefore \frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{\mathcal{H}}_0, \hat{\rho}] + \exp(-i\hat{\mathcal{H}}_0 t/\hbar)\frac{d\hat{\rho}^*}{dt}\exp(i\hat{\mathcal{H}}_0 t/\hbar)$$

$$\frac{d\langle \hat{I}_q\rangle}{dt} = \text{Tr}\left\{\hat{I}_q \frac{d\hat{\rho}}{dt}\right\} = -\frac{i}{\hbar}\text{Tr}\left\{\hat{I}_q[\hat{\mathcal{H}}_0, \hat{\rho}]\right\}$$

$$+ \text{Tr}\left\{\hat{I}_q \exp\left(-\frac{i\hat{\mathcal{H}}_0 t}{\hbar}\right)\frac{d\hat{\rho}^*}{dt}\exp\left(\frac{i\hat{\mathcal{H}}_0 t}{\hbar}\right)\right\}$$

Since a trace is invariant under the cyclic permutation of operators it will usually be possible to take care of the $\exp(\pm i\hat{\mathcal{H}}_0 t/\hbar)$ terms without difficulty:

$$\text{Tr}\left\{\hat{I}_q \exp\left(-\frac{i\hat{\mathcal{H}}_0 t}{\hbar}\right)\frac{d\hat{\rho}^*}{dt}\exp\left(+\frac{i\hat{\mathcal{H}}_0 t}{\hbar}\right)\right\} = \text{Tr}\left\{e^{(i\mathcal{H}_0 t/\hbar)}\,\hat{I}_q\, e^{(-i\mathcal{H}_0 t/\hbar)}\frac{d\hat{\rho}^*}{dt}\right\}$$

Of course $\hat{I}_q$ has non-zero matrix elements only between states differing by $q\hbar\omega_0$ in energy. Hence this term reduces to

$$\mathrm{Tr}\left\{\hat{I}_q \exp\left(-\frac{i\hat{\mathcal{H}}_0 t}{\hbar}\right)\frac{d\hat{\rho}^*}{dt}\exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right)\right\} = \mathrm{Tr}\left\{\hat{I}_q \frac{d\hat{\rho}^*}{dt}\right\}\exp(+i\omega_q t)$$
$$= \mathrm{Tr}\left\{\hat{I}_q \frac{d\hat{\rho}^*}{dt}\right\}\exp(\cancel{+}-iq\omega_0 t)$$

Hence

$$\frac{d\langle\hat{I}_q\rangle}{dt} = -\frac{i}{\hbar}\mathrm{Tr}\left\{\hat{I}_q[\hat{\mathcal{H}}_0,\hat{\rho}]\right\}$$
$$-\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\,\mathrm{Tr}\left\{I_q[[\hat{\rho}^*(t),\hat{I}_m]\,\hat{I}_{-m}]\right\}\exp(-iq\omega_0 t)$$

Before proceeding to the details which are specific to our choice of $\mathcal{H}_1(t)$, let us look carefully at the terms involving the traces in the above equation:

$$\mathrm{Tr}\{\hat{I}_q[\hat{\mathcal{H}}_0,\hat{\rho}(t)]\} = \mathrm{Tr}\{\hat{I}_q\mathcal{H}_0\hat{\rho}(t) - \hat{I}_q\hat{\rho}(t)\hat{\mathcal{H}}_0\}$$
$$= \mathrm{Tr}\{\hat{I}_q\mathcal{H}_0\hat{\rho}(t) - \mathcal{H}_0\hat{I}_q\hat{\rho}(t)\}$$
$$= \mathrm{Tr}\{[\hat{I}_q,\mathcal{H}_0]\hat{\rho}(t)\}$$

$$\mathrm{Tr}\{\hat{I}_q[[\hat{\rho}^*(t),\hat{I}_m],\hat{I}_{-m}]\}$$
$$= \mathrm{Tr}\{\hat{I}_q\hat{\rho}^*(t)\hat{I}_m\hat{I}_{-m} - \hat{I}_q\hat{I}_{-m}\hat{\rho}^*(t)\hat{I}_m - \hat{I}_q\hat{I}_m\hat{\rho}^*(t)\hat{I}_{-m} + \hat{I}_q\hat{I}_{-m}\hat{I}_m\hat{\rho}^*(t)\}$$
$$= \mathrm{Tr}\{\hat{I}_m\hat{I}_{-m}\hat{I}_q - \hat{I}_m\hat{I}_q\hat{I}_{-m} - \hat{I}_{-m}\hat{I}_q\hat{I}_m + \hat{I}_q\hat{I}_{-m}\hat{I}_m)\hat{\rho}^*(t)\}$$
$$= \mathrm{Tr}\{([\hat{I}_q,\hat{I}_{-m}]\hat{I}_m - \hat{I}_m[\hat{I}_q,\hat{I}_{-m}])\hat{\rho}^*(t)\}$$
$$= \mathrm{Tr}\{[[\hat{I}_q,\hat{I}_{-m}],\hat{I}_m]\,\hat{\rho}^*(t)\}$$

Futhermore, it should be recognized that the only non-zero elements of $[[\hat{I}_q,\hat{I}_m],\hat{I}_m]$ will be $\langle I, M+q|[[\hat{I}_q,\hat{I}_m],\hat{I}_m]|I,M\rangle$ so that the only elements of $\hat{\rho}^*(t)$ which come into the Trace are $\langle I,M|\hat{\rho}^*(t)|I,M+q\rangle$ which is just

$$\langle I,M|\exp(i\mathcal{H}_0 t/\hbar)\,\hat{\rho}(t)\exp(-i\mathcal{H}_0 t/\hbar)|I,M+q\rangle = \langle I,M|\hat{\rho}(t)|I,M+q\rangle\exp(-i\omega_q t)$$
$$= \langle I,M|\hat{\rho}(t)|I,M+q\rangle\exp(+iq\omega_0 t)$$

Hence we have the general equation of motion for the ensemble average of $\hat{I}_q$:

$$\frac{d\langle \hat{I}_q\rangle}{dt} = -\frac{i}{\hbar} \mathrm{Tr}\left\{[\hat{I}_q, \hat{\mathcal{H}}_0]\hat{\rho}(t)\right\}$$
$$- \frac{1}{2}\sum_m (-1)^m J_m(\omega_m) \mathrm{Tr}\left\{[[\hat{I}_q, \hat{I}_{-m}], \hat{I}_m]\hat{\rho}(t)\right\}$$

For $q = 0$ ($\langle \hat{I}_z\rangle$, $\langle M_z\rangle$ and longitudinal relaxation)

$$\frac{d\langle \hat{I}_0\rangle}{dt} = -\frac{i}{\hbar} \mathrm{Tr}\left\{[\hat{I}_0, \hat{\mathcal{H}}_0]\hat{\rho}(t)\right\}$$
$$- \frac{1}{2}\sum_m (-1)^m J_m(\omega_m) \mathrm{Tr}\left\{[[\hat{I}_0, \hat{I}_{-m}], \hat{I}_m]\hat{\rho}(t)\right\}$$

$$[\hat{I}_0, \hat{\mathcal{H}}_0] = [\hat{I}_z, -\hbar\omega_0 \hat{I}_z] = 0$$
$$[\hat{I}_0, \hat{I}_{-m}] = [\hat{I}_z, \hat{I}_{-m}] = -m\,\hat{I}_{-m}$$
$$[[I_0, I_{-m}], I_m] = -m\,[I_{-m}, I_m]$$

For $m = -1$ $\quad [[I_0, I_{+1}], I_{-1}] = -(-1)[I_{+1}, I_{-1}] = \left[-\frac{1}{\sqrt{2}}I_+, \frac{1}{\sqrt{2}}I_-\right] = -\hat{I}_z$

For $m = 0$ $\quad [[I_0, I_0], I_0] = 0$

For $m = +1$ $\quad [[I_0, I_{-1}], I_{+1}] = -(1)[I_{-1}, I_{+1}] = -I_z$

$$\therefore \frac{d\langle \hat{I}_0\rangle}{dt} = -\frac{1}{2}\left[(-1)^1 J_1(\omega_1)\mathrm{Tr}\left\{-\hat{I}_0\hat{\rho}(t)\right\} + (-1)^{-1} J_{-1}(\omega_{-1})\mathrm{Tr}\left\{-\hat{I}_0\hat{\rho}(t)\right\}\right]$$
$$= -\frac{[J_1(\omega_1) + J_{-1}(\omega_{-1})]}{2}\langle \hat{I}_0\rangle$$

which should be compared to

$$\frac{dM_z}{dt} = -\frac{1}{T_1} M_z \qquad \text{(where } M_0 \text{ term is ignored!)}$$

Then
$$\frac{1}{T_1} = \frac{J_1(\omega_1) + J_{-1}(\omega_{-1})}{2}$$

$$J_1(\omega_0) = \int_{-\infty}^{\infty} g_1(\tau)\,\exp(-i\omega_0\tau)\,d\tau = J_{-1}(\omega_0)$$

$$g_1(\tau) = \overline{\gamma H_1^*(t)\gamma H_1(t+\tau)}$$
$$= \overline{\gamma^2\left(-\frac{1}{\sqrt{2}}\right)\left(H_x(t) - iH_y(t)\right)\left(-\frac{1}{\sqrt{2}}\right)\left(H_x(t+\tau) + iH_y(t+\tau)\right)}$$
$$= \frac{\gamma^2}{2}\left[\overline{H_x(t)H_x(t+\tau)} + \overline{H_y(t)H_y(t+\tau)}\right] \quad \text{since fields along } x \,\&\, y \text{ are uncorrelated.}$$
$$= \gamma^2 |H_x(t)|^2 \exp -|\tau|/\tau_c$$

$$J_1(\omega_0) = \frac{2\tau_c}{1+\omega_0^2\tau_c^2}\left(\gamma^2|H_x(t)|^2\right)$$

$$\therefore \frac{1}{T_1} = \frac{\tau_c}{1+\omega_0^2\tau_c^2}\gamma^2\left(|H_x(t)|^2 + |H_y(t)|^2\right)$$

For $q=+1$ (Transverse Relaxation $M_x$ & $M_y$) $\quad \frac{d\langle I_1\rangle}{dt} = -\frac{1}{\sqrt{2}}\frac{d\langle I_x + i I_y\rangle}{dt}$

$$d\langle \hat{I}_{+1}\rangle = -\frac{i}{\hbar}\,\mathrm{Tr}\{[\hat{I}_{+1},\hat{\mathcal{H}}_0]\hat{\rho}(t)\}$$
$$-\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\,\mathrm{Tr}\{[[\hat{I}_{+1},\hat{I}_{-m}],\hat{I}_m]\hat{\rho}(t)\}$$

$$[\hat{I}_{+1},\hat{\mathcal{H}}_0] = -\frac{1}{\sqrt{2}}[\hat{I}_+, -\hbar\omega_0 I_z] = -\frac{\hbar\omega_0}{\sqrt{2}}[\hat{I}_z,\hat{I}_+] = -\frac{\hbar\omega_0}{\sqrt{2}}\hat{I}_+$$
$$= \hbar\omega_0\hat{I}_{+1}$$

$$[\hat{I}_{+1},\hat{I}_{-m}] = -\frac{1}{\sqrt{2}}[\hat{I}_+,\hat{I}_{-m}] = -\frac{1}{\sqrt{2}}\sqrt{1(1+1)-(-m)(-m+1)}\;\hat{I}_{-m+1}$$
$$= -\sqrt{\frac{2-m(m-1)}{2}}\;\hat{I}_{-m+1}$$

$m=+1 \quad [\hat{I}_{+1},\hat{I}_{-1}] = -\hat{I}_0$

$\quad [[I_{+1},I_{-1}],I_{+1}] = -[\hat{I}_0,\hat{I}_{+1}] = -\hat{I}_{+1}$

$m=0 \quad [\hat{I}_{+1},\hat{I}_0] = -\hat{I}_{+1}$

$\quad [[\hat{I}_{+1},\hat{I}_0],\hat{I}_0] = -[\hat{I}_{+1},\hat{I}_0] = +\hat{I}_{+1}$

$m=-1 \quad [\hat{I}_{+1},\hat{I}_{+1}] = 0$

Note $\omega_0$ and $(\omega_0)$ are different.

$$\therefore \frac{d\langle\hat{I}_{+1}\rangle}{dt} = -\frac{i}{\hbar}(\hbar\omega_0)\,\mathrm{Tr}\{\hat{I}_{+1}\rho(t)\}$$
$$-\frac{1}{2}\left[(-1)^1 J_1(\omega_1)\,\mathrm{Tr}\{(-\hat{I}_{+1})\hat{\rho}(t)\} + (-1)^0 J_0(\omega_0)\,\mathrm{Tr}\{\hat{I}_{+1}\hat{\rho}(t)\}\right]$$
$$= -i\omega_0\langle\hat{I}_{+1}\rangle - \frac{1}{2}\left\{J_1(\omega_0) + J_0(0)\right\}\langle\hat{I}_{+1}\rangle$$

or $-\frac{1}{\sqrt{2}}\frac{d\langle\hat{I}_x\rangle}{dt} - \frac{i}{\sqrt{2}}\frac{d\langle\hat{I}_y\rangle}{dt} = -i\omega_0\left(-\frac{1}{\sqrt{2}}\langle I_x\rangle - \frac{i}{\sqrt{2}}\langle I_y\rangle\right) - \frac{1}{T_2}\left\{-\frac{1}{\sqrt{2}}\langle I_x\rangle - \frac{i}{\sqrt{2}}\langle I_y\rangle\right\}$

and $\frac{d\langle\hat{I}_x\rangle}{dt} = +\omega_0\langle\hat{I}_y\rangle - \frac{\langle\hat{I}_x\rangle}{T_2}$ ; $\frac{d\langle\hat{I}_y\rangle}{dt} = -\omega_0\langle\hat{I}_x\rangle - \frac{\langle I_y\rangle}{T_2}$

where

$$\frac{1}{T_2} = \frac{1}{2}(J_1(\omega_0) + J_0(0))$$

$$= \frac{1}{2}\left(\gamma^2|H_x(0)|^2 + \gamma^2|H_y(0)|^2\right)\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \gamma^2|H_z(0)|^2\tau_c$$

Here we find that fluctuating fields in the z-direction cause relaxation because x- and y- components of the magnetization experience torques $\gamma\vec{M}\times\vec{H}$ due to these fields. The spectral density for the z-components enters with zero frequency, because no energy transfer between lattice and spin-system occurs due to fluctuations in z-component.

It is interesting to note that our result for $1/T_2$ can be written as

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'}$$

The $\frac{1}{2T_1}$ contribution is often called the non-secular or lifetime broadening since it arises due to terms in $\hat{\mathcal{H}}_1$ which do not commute with $\mathcal{H}_0$ (by definition non-secular part of $\mathcal{H}_1$) and it is these terms which give rise to longitudinal relaxation which in turn determines the "lifetime" of the population of a nuclear state. The $1/T_2'$ term is called the secular broadening since it is produced by terms in $\hat{\mathcal{H}}_1$ which commute with $\hat{\mathcal{H}}_0$. It is essentially the dephasing of the transverse components due to the fluctuating z-components of the magnetic field experienced by the nuclei in the sample.

The approach which we have used to derive expressions for $1/T_1$ and $1/T_2$ above is the standard approach I wish to follow in the discussion of other relaxation mechanisms. We shall find it necessary to investigate the interactions $\hat{\mathcal{H}}_1(t)$ which are important in spin-relaxation before proceeding with the calculation of $1/T_1$ and $1/T_2$ for each.

## F. The Interactions which Produce Relaxation – Origins of Time Dependence

Abragam (Chapter VIII) gives a very comprehensive treatment of the relaxation mechanisms which are important in liquids. His treatment is, however, rather more complicated than necessary since he does not look at the origin of the time-dependence in $\hat{\mathcal{H}}_1(t)$ before going off to determine the relaxation rates. At this point, I want to look at the interactions – intramolecular dipole-dipole, electric quadrupolar, and anisotropic chemical shift – whose time-dependence arises solely from the rotation of the molecule in the liquid. Later I will deal with spin-rotation and intermolecular dipole-dipole interactions. All of the interactions which are important in magnetic relaxation are of the form

$$\hat{\mathcal{H}}_1(t) = \sum_m (-1)^m F_{-m}(t)\, \hat{A}_m$$

where $\hat{A}_m$ is a spin operator and $F_{-m}(t)$ is an appropriate lattice operator. Unfortunately, it is not always obvious just what $F_{-m}(t)$ is or how you should get at it. For intramolecular dipolar, quadrupole and chemical shift anisotropy interactions, the specification of $F_{-m}(t)$ can be particularly ambiguous unless one looks at the problem as a molecular rotation problem. The ambiguity really arises because we are so used to working with isotropic interactions that we forget about the ~~importance~~ difference between ~~of~~ the coordinate system in which we apply the magnetic field and the coordinate system in which we write the magnetic interaction in its simplest possible form.

### 1. Anisotropic Chemical Shift Interaction

In the molecular coordinate system, the total Zeeman interation is:

$$\hat{\mathcal{H}}_{Zeeman} = -\gamma\hbar\left[(1-\sigma_{xx})h_x\hat{I}_x + (1-\sigma_{yy})h_y\hat{I}_y + (1-\sigma_{zz})h_z\hat{I}_z\right]$$

where $\vec{h}$ is the applied field referred to molecular (rotating) axes $\hat{\vec{I}}$ is the nuclear spin angular momentum operator in molecular coordinates and $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ are the elements of the chemical shielding tensor which is diagonalized in the molecular frame. It is useful to define

$$\sigma_{ave} = \frac{1}{3}(\sigma_{xx}+\sigma_{yy}+\sigma_{zz}) \qquad \sigma_{zz} = \sigma_{ave} + 2\Delta\sigma$$

$$\Delta\sigma = \frac{1}{3}\left[\sigma_{zz} - \frac{1}{2}(\sigma_{xx}+\sigma_{yy})\right] \qquad \sigma_{xx} = \sigma_{ave} - \Delta\sigma + \delta\sigma$$

$$\sigma_{yy} = \sigma_{ave} - \Delta\sigma - \delta\sigma$$

and

$$\delta\sigma = \frac{1}{2}(\sigma_{xx}-\sigma_{yy})$$

and the spherical tensor components of $\vec{h}$ and $\hat{\vec{I}}$:

$$h_x = -\frac{1}{\sqrt{2}}h_{+1} + \frac{1}{\sqrt{2}}h_{-1} \qquad \hat{I}_x = -\frac{1}{\sqrt{2}}\hat{I}_{+1} + \frac{1}{\sqrt{2}}\hat{I}_{-1}$$

$$h_y = \frac{i}{\sqrt{2}}h_{+1} + \frac{i}{\sqrt{2}}h_{-1} \qquad \hat{I}_y = \frac{i}{\sqrt{2}}\hat{I}_{+1} + \frac{i}{\sqrt{2}}\hat{I}_{-1}$$

$$h_z = h_0 \qquad \hat{I}_z = \hat{I}_0$$

Then

$$\hat{\mathcal{H}}_{zeeman} = -\gamma\hbar\Big[(1-\sigma_{ave}+\Delta\sigma-\delta\sigma)(\tfrac{1}{2})(h_{+1}\hat{I}_{+1} + h_{-1}\hat{I}_{-1} - h_{-1}\hat{I}_{+1} - h_{+1}\hat{I}_{-1})$$
$$+ (1-\sigma_{ave}+\Delta\sigma+\delta\sigma)(-\tfrac{1}{2})(h_{+1}\hat{I}_{+1} + h_{-1}\hat{I}_{-1} + h_{-1}\hat{I}_{+1} + h_{+1}\hat{I}_{-1})$$
$$+ (1-\sigma_{ave}-2\Delta\sigma)(h_0\hat{I}_0)\Big]$$

$$= -\gamma\hbar(1-\sigma_{ave})\{-h_{-1}\hat{I}_{+1} + h_0\hat{I}_0 - h_{+1}\hat{I}_{-1}\}$$ ← scalar product of the tensors.

$$-\gamma\hbar\Delta\sigma\{-h_{-1}\hat{I}_{+1} - h_{+1}\hat{I}_{-1} - 2h_0\hat{I}_0\}$$

$$-\gamma\hbar\delta\sigma\{-h_{+1}\hat{I}_{+1} - h_{-1}\hat{I}_{-1}\}$$

2nd rank tensor.

$$= -\gamma\hbar(1-\sigma_{ave})\vec{h}\cdot\hat{\vec{I}} + \sqrt{6}\gamma\hbar\Delta\sigma\hat{a}^{(2)}_0 + \gamma\hbar\delta\sigma(\hat{a}_{+2}+\hat{a}_{-2})$$

where $\hat{a}_0 = \frac{1}{\sqrt{6}}(h_{-1}\hat{I}_{+1} + h_{+1}\hat{I}_{-1} + 2h_0\hat{I}_0)$ and $\hat{a}_{\pm 2} = h_{\pm 1}\hat{I}_{\pm 1}$ are components of a second rank tensor operator in the

(See pg. 77 of angular momentum notes).

molecular coordinate system, The first term in the Zeeman interaction is just the isotropic chemical shift interaction

$$\hat{\mathcal{H}}_0 = -\gamma\hbar(1-\sigma_{ave})\vec{h}\cdot\hat{\vec{I}}$$

and the last 2 terms are the anisotropic chemical shift interaction:

$$\mathcal{H}_{ACS} = \gamma\hbar\Delta\sigma\sqrt{6}\hat{a}_0 + \gamma\hbar\delta\sigma(\hat{a}_{+2}+\hat{a}_{-2})$$

Now $\vec{h}$ is the applied magnetic ~~charge~~ field with components referred to the molecular coordinate system. In a magnetic resonance experiment, we apply $\vec{H}_0$ along the laboratory z-axis. Hence it is important to transform $\vec{h}$ and $\hat{\vec{I}}$ to their components in the laboratory frame:

$$\hat{\mathcal{H}}_0 = -\gamma\hbar(1-\sigma_{ave})H_0\hat{I}_z$$

Since $\hat{a}$ is a 2nd rank spherical tensor

2nd rank tensor molecular component k

$$\hat{a}_k = \sum_m \hat{A}_m \mathcal{D}^{(2)}_{mk}[\Omega(t)]$$

(lab frame m)

where $\hat{A}_m$ are the components of this (2nd rank) spherical tensor in the laboratory frame and $\underset{\sim}{\mathcal{D}}^{(2)}$ is the Wigner rotation matrix for tensors of second rank. $\Omega$ represents the Euler angles for the transformation from the Laboratory to the Molecular Coordinates. Clearly $\Omega$ is Time-dependent.

Now

$$\hat{\mathcal{H}}_{ACS} = \sqrt{6}\gamma\hbar\Delta\sigma\sum_m \hat{A}_m\mathcal{D}^{(2)}_{m0}[\Omega] + \gamma\hbar\delta\sigma\sum_m \hat{A}_m\left(\mathcal{D}^{(2)}_{m2}[\Omega] + \mathcal{D}^{(2)}_{m,-2}[\Omega]\right)$$

But $\hat{A}_{\pm2} = H_{\pm1}\hat{I}_{\pm1} = \frac{1}{2}[H_x \pm iH_y][\hat{I}_x \pm \hat{I}_y] = 0$ because $\vec{H}_0$ is along the z-axis, ($H_{\pm1} = 0$, $H_0 = H_0$) ( $\because$ $\vec{H_0} = H_0\hat{z}$)

$$\hat{A}_{\pm1} = \frac{1}{\sqrt{2}}(H_0\hat{I}_{\pm1} + H_{\pm1}\hat{I}_0) = \frac{H_0}{\sqrt{2}}\hat{I}_{\pm1}$$

and $\hat{A}_0 = \frac{1}{\sqrt{6}}\left(H_{-1}\hat{I}_{+1} + H_{+1}\hat{I}_{-1} + 2H_0\hat{I}_0\right) = \sqrt{\frac{2}{3}}\, H_0\hat{I}_0 .$

Hence

$$\begin{aligned}
\hat{\mathcal{H}}_{ACS} &= \sqrt{6}\,\gamma\hbar\,\Delta\sigma\, H_0\left\{\frac{1}{\sqrt{2}}\hat{I}_{+1}\mathcal{D}^{(2)}_{1,0}[\Omega] + \frac{1}{\sqrt{2}}\hat{I}_{-1}\mathcal{D}^{(2)}_{-1,0}[\Omega] + \sqrt{\frac{2}{3}}\,\hat{I}_0\,\mathcal{D}^{(2)}_{0,0}[\Omega]\right\} \\
&\quad + \gamma\hbar\,\delta\sigma\, H_0\left\{\frac{1}{\sqrt{2}}\hat{I}_{+1}\left(\mathcal{D}^{(2)}_{1,2}[\Omega] + \mathcal{D}^{(2)}_{1,-2}[\Omega]\right) + \frac{1}{\sqrt{2}}\hat{I}_{-1}\left(\mathcal{D}^{(2)}_{-1,2}[\Omega] + \mathcal{D}^{(2)}_{-1,-2}[\Omega]\right)\right. \\
&\qquad\qquad \left. + \sqrt{\frac{2}{3}}\,\hat{I}_0\left(\mathcal{D}^{(2)}_{0,2}[\Omega] + \mathcal{D}^{(2)}_{0,-2}[\Omega]\right)\right\}
\end{aligned}$$

$$\begin{aligned}
&= \hbar(-1)^{1}\hat{I}_{+1}\left\{-\gamma H_0\right\}\left\{\sqrt{3}\,\Delta\sigma\,\mathcal{D}^{(2)}_{10}[\Omega] + \frac{1}{\sqrt{2}}\delta\sigma\left(\mathcal{D}^{(2)}_{12}[\Omega] + \mathcal{D}^{(2)}_{1,-2}[\Omega]\right)\right\} \\
&\quad + \hbar(-1)^{0}\hat{I}_0\left\{\gamma H_0\right\}\left\{2\,\Delta\sigma\,\mathcal{D}^{(2)}_{00}[\Omega] + \sqrt{\frac{2}{3}}\,\delta\sigma\left(\mathcal{D}^{(2)}_{02}[\Omega] + \mathcal{D}^{(2)}_{0,-2}[\Omega]\right)\right\} \\
&\quad + \hbar(-1)^{-1}\hat{I}_{-1}\left\{-\gamma H_0\right\}\left\{\sqrt{3}\,\Delta\sigma\,\mathcal{D}^{(2)}_{-1,0}[\Omega] + \frac{1}{\sqrt{2}}\delta\sigma\left(\mathcal{D}^{(2)}_{-1,2}[\Omega] + \mathcal{D}^{(2)}_{-1,-2}[\Omega]\right)\right\}
\end{aligned}$$

$$= \hbar\sum_m (-1)^m F_{-m}(t)\,\hat{I}_m$$ (see pg. 16)

with

$$\begin{aligned}
F_{-1}(t) &= -\gamma H_0\left\{\sqrt{3}\,\Delta\sigma\,\mathcal{D}^{(2)}_{10}[\Omega(t)] + \frac{1}{\sqrt{2}}\delta\sigma\left(\mathcal{D}^{(2)}_{12}[\Omega(t)] + \mathcal{D}^{(2)}_{1,-2}[\Omega(t)]\right)\right\} \\
F_0(t) &= \frac{2}{\sqrt{3}}\gamma H_0\left\{\sqrt{3}\,\Delta\sigma\,\mathcal{D}^{(2)}_{00}[\Omega(t)] + \frac{1}{\sqrt{2}}\delta\sigma\left(\mathcal{D}^{(2)}_{02}[\Omega(t)] + \mathcal{D}^{(2)}_{0,-2}[\Omega(t)]\right)\right\} \\
F_{+1}(t) &= -\gamma H_0\left\{\sqrt{3}\,\Delta\sigma\,\mathcal{D}^{(2)}_{-1,0}[\Omega(t)] + \frac{1}{\sqrt{2}}\delta\sigma\left(\mathcal{D}^{(2)}_{-1,2}[\Omega(t)] + \mathcal{D}^{(2)}_{-1,-2}[\Omega(t)]\right)\right\}.
\end{aligned}$$

The correlation functions for the Wigner matrix elements are (in the rotational diffusion model)

$$\begin{aligned}
\overline{\mathcal{D}^{(2)*}_{k',m'}[\Omega(t)]\;\mathcal{D}^{(2)}_{k,m}[\Omega(t+\tau)]} &= \delta_{k',k}\,\delta_{m',m}\,\overline{\left|\mathcal{D}^{(2)}_{k,m}[\Omega(t)]\right|^2}\,\exp\left[-|\tau|/\tau_\theta^{(2,k)}\right] \\
&= \delta_{k',k}\,\delta_{m',m}\,\frac{\exp\left[-|\tau|/\tau_\theta^{(2,k)}\right]}{5}
\end{aligned}$$

Hence

$$\overline{F_{\pm1}^*(t)\,F_{\pm1}(t+\tau)} = \gamma^2 H_0^2 \left\{ \frac{3}{5}\Delta\sigma^2 \exp\left(-|\tau|/\tau_\theta^{(2,0)}\right) + \frac{1}{5}\delta\sigma^2 \exp\left(-|\tau|/\tau_\theta^{(2,2)}\right)\right\},$$

and

$$\overline{F_0^*(t)\,F_0(t+\tau)} = \frac{4}{3}\gamma^2 H_0^2 \left\{ \frac{3}{5}\Delta\sigma^2 \exp\left(-|\tau|/\tau_\theta^{(2,0)}\right) + \frac{1}{5}\delta\sigma^2 \exp\left(-|\tau|/\tau_\theta^{(2,2)}\right)\right\}$$

where we have assumed that $\tau_\theta^{(2,-2)} = \tau_\theta^{(2,2)}$ which is true for a symmetric top or molecule of higher symmetry.

2. <u>Electric Quadrupole Interactions</u>

In the molecular coordinate system (see Angular Momentum notes, pg. 94), the quadrupole interaction is

$$\hat{\mathcal{H}}_Q = \frac{e^2 q Q}{4I(2I-1)} \left\{ (3\hat{\mathcal{I}}_z^2 - \hat{\mathcal{I}}^2) + \eta\,(\hat{\mathcal{I}}_x^2 - \hat{\mathcal{I}}_y^2) \right\}$$ ← $x, y, z$ indicate that these are in some ~~frame~~ coord. sys.

where $eq = \left(\frac{\partial^2 V}{\partial z^2}\right)_0$ and $\eta = \left[\left(\frac{\partial^2 V}{\partial x^2}\right)_0 - \left(\frac{\partial^2 V}{\partial y^2}\right)_0\right] \Big/ \left(\frac{\partial^2 V}{\partial z^2}\right)_0$ are the components of the electric field gradient tensor. Clearly $eq$ and $\eta$ are defined in a molecular frame because they reflect the symmetry of the electron distribution in the molecule. Note that this molecular frame in which the electric field gradient tensor is diagonal may not be the molecular coordinate system in which the rotational diffusion tensor or the inertia tensor of the molecule is diagonalized. For example, in the $CD_3CN$ molecule, the coordinate system in which the C–D bond lies along the z-axis will be the coordinate system in which the electric field gradient tensor is diagonal. However, the rotation of the molecule is best described if the molecular coordinate system in which the C–C≡N direction defines the z-axis. The CD bond direction is tilted at an angle $\theta$ with respect to the $C_3$ rotation axis of the molecule so we must transform $\hat{\mathcal{H}}_Q$ from axes where the C–D bond lies along the z-axis to axes where the C–C≡N axis defines the z-axis.

We first recognize that the second rank tensor $\hat{a}'$ formed from the nuclear spin angular momentum operators (pg. 92 of the Notes on Angular Momentum) has components

$$\hat{a}'_{\pm 2} = (\hat{\mathcal{I}}_{\pm 1})^2 \;, \quad \hat{a}'_{\pm 1} = \frac{1}{\sqrt{2}}(\hat{\mathcal{I}}_{\pm 1}\hat{\mathcal{I}}_0 + \hat{\mathcal{I}}_0\hat{\mathcal{I}}_{\pm 1})$$

and $\hat{a}'_0 = \frac{1}{\sqrt{6}}(\hat{\mathcal{I}}_{+1}\hat{\mathcal{I}}_{-1} + 2\hat{\mathcal{I}}_0^2 + \hat{\mathcal{I}}_{-1}\hat{\mathcal{I}}_{+1})$ so that we can write

$$\hat{\mathcal{H}}_Q = \frac{e^2qQ}{4I(2I-1)}\left\{\sqrt{6}\,\hat{a}'_0 + \eta(\hat{a}'_{+2} + \hat{a}'_{-2})\right\}$$

Now the tensor operator $\hat{a}$ in the "true" molecular frame has components

$$\hat{a}'_k = \sum_{\ell} \hat{a}_\ell\, \mathcal{D}^{(2)}_{\ell k}[0,\theta,0]$$

where $\theta$ is the angle between the axis of symmetry of the electric field gradient tensor and the ~~principal~~ molecular symmetry axis. Therefore

$$\hat{\mathcal{H}}_Q = \frac{e^2qQ}{4I(2I-1)}\sum_{\ell}\left\{\sqrt{6}\,\hat{a}_\ell\,\mathcal{D}^{(2)}_{\ell 0}[0,\theta,0] + \eta\,\hat{a}_\ell\,\mathcal{D}^{(2)}_{\ell,2}[0,\theta,0] + \eta\,\hat{a}_\ell\,\mathcal{D}^{(2)}_{\ell,-2}[0,\theta,0]\right\}$$

It must be recognized that the nuclear spin angular momentum is quantized along the direction of the applied magnetic field which lies along the laboratory z-axis. Hence we must transform our tensor operator $\hat{a}$ into its laboratory components $\hat{A}$ by

$$\hat{a}_\ell = \sum_m \hat{A}_m\, \mathcal{D}^{(2)}_{m\ell}[\Omega]$$

where $\Omega$ is the set of Euler angles which rotates the laboratory axes into the molecular axes at time t. Then

$$\hat{\mathcal{H}}_Q = \frac{e^2qQ}{4I(2I-1)} \sum_m A_m \sum_l \sqrt{6}\, \mathcal{D}^{(2)}_{ml}[\Omega] \left\{ \mathcal{D}^{(2)}_{l0}[0,\theta,0] + \eta \left( \hat{\mathcal{D}}^{(2)}_{ml}[\Omega]\, \mathcal{D}^{(2)}_{l,2}[0,\theta,0] + \mathcal{D}^{(2)}_{ml}[\Omega]\, \mathcal{D}^{(2)}_{l,-2}[0,\theta,0] \right) \right\}$$

$$= \hbar \sum_m (-1)^m F_{-m}(t)\, \hat{A}_m \qquad \text{(see pg. 16)}$$

with

time dependent part.

$$F_{-m}(t) = \frac{e^2qQ(-1)^m}{4I(2I-1)\hbar} \sum_l \mathcal{D}^{(2)}_{ml}[\Omega] \left\{ \sqrt{6}\, \mathcal{D}^{(2)}_{l0}[0,\theta,0] + \eta\, \mathcal{D}^{(2)}_{l,2}[0,\theta,0] + \eta\, \mathcal{D}^{(2)}_{l,-2}[0,\theta,0] \right\}$$

Note that

$$\sqrt{6}\, \mathcal{D}^{(2)}_{20}[0,\theta,0] + \eta\left(\mathcal{D}^{(2)}_{22}[0,\theta,0] + \mathcal{D}^{(2)}_{2,-2}[0,\theta,0]\right) = \frac{3}{2}\sin^2\theta + \frac{\eta}{2}(1+\cos^2\theta) = f_2(\theta) \quad (l=+2)$$

$$\sqrt{6}\, \mathcal{D}^{(2)}_{10}[0,\theta,0] + \eta\left(\mathcal{D}^{(2)}_{12}[0,\theta,0] + \mathcal{D}^{(2)}_{1,-2}[0,\theta,0]\right) = -3\sin\theta\cos\theta + \eta\sin\theta\cos\theta = f_1(\theta) \quad (l=+1)$$

$$\sqrt{6}\, \mathcal{D}^{(2)}_{00}[0,\theta,0] + \eta\left(\mathcal{D}^{(2)}_{02}[0,\theta,0] + \mathcal{D}^{(2)}_{0,-2}[0,\theta,0]\right) = \sqrt{\tfrac{3}{2}}(3\cos^2\theta-1) + \sqrt{\tfrac{3}{2}}\,\eta\sin^2\theta = f_0(\theta) \quad (l=0)$$

$$\sqrt{6}\, \mathcal{D}^{(2)}_{-10}[0,\theta,0] + \eta\left(\mathcal{D}^{(2)}_{-1,2}[0,\theta,0] + \mathcal{D}^{(2)}_{-1,-2}[0,\theta,0]\right) = 3\sin\theta\cos\theta - \eta\sin\theta\cos\theta = f_{-1}(\theta) \quad (l=-1)$$

$$\sqrt{6}\, \mathcal{D}^{(2)}_{-20}[0,\theta,0] + \eta\left(\mathcal{D}^{(2)}_{-2,2}[0,\theta,0] + \mathcal{D}^{(2)}_{-2,-2}[0,\theta,0]\right) = \frac{3}{2}\sin^2\theta + \frac{\eta}{2}(1+\cos^2\theta) = f_{-2}(\theta) \quad (l=-2)$$

The correlation functions are

$$\overline{F^*_m(t)\, F_m(t+\tau)} = \left[\frac{e^2qQ}{4I(2I-1)\hbar}\right]^2 \overline{\sum_{l',l} \mathcal{D}^{(2)*}_{ml'}[\Omega(t)]\, \mathcal{D}^{(2)}_{ml}[\Omega(t+\tau)]}\; f_l(\theta)\, f_{l'}(\theta)$$

$$= \left[\frac{e^2qQ}{4I(2I-1)\hbar}\right]^2 \sum_l \frac{\exp[-|\tau|/\tau_\theta^{(2,l)}]}{5} \left|f_l(\theta)\right|^2$$

$$= \frac{(e^2qQ/\hbar)^2}{80\, I^2(2I-1)^2} \left\{ \left[\frac{3}{2}\sin^2\theta + \frac{\eta}{2}(1+\cos^2\theta)\right]^2 \exp(-|\tau|/\tau_\theta^{(2,2)}) + 2\left[-3\sin\theta\cos\theta + \eta\sin\theta\cos\theta\right]^2 \exp[-|\tau|/\tau_\theta^{(2,1)}] + \frac{3}{2}\left[3\cos^2\theta - 1 + \eta\sin^2\theta\right]^2 \exp[-|\tau|/\tau_\theta^{(2,0)}] \right\}$$

(independent of m).

3. The Intramolecular Dipole-Dipole Interaction

In our discussions of angular momentum theory, we showed that the dipolar interaction between spins I and S (Angular Momentum Notes pp 75-77)

$$\hat{\mathcal{H}}_{dipolar} = \gamma_I \gamma_S \hbar^2 \left[ \frac{\hat{\vec{I}}\cdot\hat{\vec{S}}}{r_{IS}^3} - 3\frac{(\hat{\vec{I}}\cdot\vec{r}_{IS})(\hat{\vec{S}}\cdot\vec{r}_{IS})}{r_{IS}^5} \right]$$

could be written in terms of the spherical tensor operators $\hat{a}_{\pm 2} = \hat{I}_{\pm 1}\hat{S}_{\pm 1}$, $\hat{a}_{\pm 1} = 1/\sqrt{2}\,(\hat{I}_{\pm 1}\hat{S}_0 + \hat{I}_0\hat{S}_{\pm 1})$ and $\hat{a}_0 = 1/\sqrt{6}\,(\hat{I}_{+1}\hat{S}_{-1} + \hat{I}_{-1}\hat{S}_{+1} + 2\hat{I}_0\hat{S}_0)$. For consistency with the above discussions of relaxation theory, I'm using $\hat{a}$ here rather than $\hat{T}$ as I did in the Angular Momentum Theory. Furthermore, I wish to redefine the other second rank spherical tensor which appears in the dipolar interaction to be

$$\mathcal{Y}_2(\theta,\varphi) = -\left(\frac{24\pi}{5}\right)^{1/2} Y_{2,2}(\theta,\varphi) = -\frac{3}{2}\sin^2\theta\, e^{2i\varphi}$$

$$\mathcal{Y}_1(\theta,\varphi) = -\left(\frac{24\pi}{5}\right)^{1/2} Y_{2,1}(\theta,\varphi) = 3\sin\theta\cos\theta\, e^{i\varphi}$$

$$\mathcal{Y}_0(\theta,\varphi) = -\left(\frac{24\pi}{5}\right)^{1/2} Y_{2,0}(\theta,\varphi) = -\sqrt{\frac{3}{2}}\,(3\cos^2\theta - 1)$$

$$\mathcal{Y}_{-1}(\theta,\varphi) = -\left(\frac{24\pi}{5}\right)^{1/2} Y_{2,-1}(\theta,\varphi) = -3\sin\theta\cos\theta\, e^{-i\varphi}$$

$$\mathcal{Y}_{-2}(\theta,\varphi) = -\left(\frac{24\pi}{5}\right)^{1/2} Y_{2,-2}(\theta,\varphi) = -\frac{3}{2}\sin^2\theta\, e^{-2i\varphi}$$

Now

curly y's.

$$\mathcal{H}_{dipolar} = \frac{\gamma_I \gamma_S \hbar^2}{r_{IS}^3} \sum_k (-1)^k \mathcal{Y}_{-k}(\theta,\varphi)\, \hat{a}_k$$

Of course we must transform the $\hat{a}_k$ into their laboratory frame counterparts $\hat{A}_m$ by

$$\hat{a}_k = \sum_m \hat{A}_m \mathcal{D}^{(2)}_{mk}[\Omega(t)]$$

Hence

$$\mathcal{H}_{dipolar} = \frac{\gamma_I \gamma_S \hbar^2}{r_{IS}^3} \sum_m \hat{A}_m \sum_k (-1)^k \mathcal{D}^{(2)}_{mk}[\Omega(t)]\, Y_{-k}(\theta,\varphi)$$

$$= \hbar \sum_m (-1)^m F_{-m}(t)\, \hat{A}_m$$

(see page 16)

with

$$F_{-m}(t) = (-1)^m \frac{\gamma_I \gamma_S \hbar}{r_{IS}^3} \sum_k (-1)^k \mathcal{D}^{(2)}_{mk}[\Omega(t)]\, Y_{-k}(\theta,\varphi)$$

The correlation functions are

$$\overline{F^*_m(t)\; F_m(t+\tau)} = \frac{(\gamma_I \gamma_S \hbar)^2}{r_{IS}^6} \sum_{k,k'} \overline{\mathcal{D}^{(2)*}_{mk}[\Omega(t)]\, \mathcal{D}^{(2)}_{mk'}[\Omega(t+\tau)]}\; Y^*_{-k}(\theta,\varphi)\, Y_{k'}(\theta,\varphi)$$

$$= \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \sum_k \frac{\exp[-|\tau|/\tau_\theta^{(2,k)}]}{5}\, |Y_{-k}|^2$$

$$= \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{5\, r_{IS}^6} \Big\{ 2\left(-\tfrac{3}{2}\sin^2\theta\right)^2 \exp-[|\tau|/\tau_\theta^{(2,2)}] + 2\left(3\sin\theta\cos\theta\right)^2 \exp[-|\tau|/\tau_\theta^{(2,1)}] + \tfrac{3}{2}(3\cos^2\theta - 1)^2 \exp[-|\tau|/\tau_\theta^{(2,0)}] \Big\}$$

$$= \frac{6\gamma_I^2 \gamma_S^2 \hbar^2}{5\, r_{IS}^6} \Big\{ \left(\frac{3\cos^2\theta - 1}{2}\right)^2 \exp[-|\tau|/\tau_\theta^{(2,0)}] + \left(3\sin^2\theta\cos^2\theta\right) \exp[-|\tau|/\tau_\theta^{(2,1)}] + \left(\tfrac{3}{4}\sin^4\theta\right) \exp[-|\tau|/\tau_\theta^{(2,2)}] \Big\}$$

again independent of m.

## Commutators for Dipolar Interactions

We will need the commutators $[[\hat{I}_q+\hat{S}_q, \hat{A}_m], \hat{A}_m]$ for "like" spins and $[[\hat{I}_q, \hat{A}_{-m}], \hat{A}_m]$ for "unlike" spins. It will be useful therefore to ~~perform~~ evaluate the commutators $[[\hat{I}_q, \hat{A}_{-m}], \hat{A}_m]$ and $[[\hat{S}_q, \hat{A}_{-m}], \hat{A}_m]$ so that we can handle both cases

### (a) $[[\hat{I}_z, \hat{A}_{-m}], \hat{A}_m]$

$\underline{m=+2}$

$$[\hat{I}_z, \hat{A}_{-2}] = [I_z, I_{-1}S_{-1}] = -I_{-1}S_{-1}$$

$$[[\hat{I}_z, \hat{A}_{-2}], \hat{A}_{+2}] = -[\hat{I}_{-1}\hat{S}_{-1}, \hat{A}_{+2}] = -\tfrac{1}{2}[\hat{I}_-\hat{S}_-, \hat{I}_{+1}\hat{S}_{+1}]$$

$$= -\tfrac{1}{2}\hat{I}_-(\sqrt{2}\,\hat{I}_{+1}\hat{S}_0) - \tfrac{1}{2}(\sqrt{2}\,\hat{I}_0\hat{S}_{+1})\hat{S}_-$$

$$= \tfrac{1}{2}(\hat{I}_-\hat{I}_+)\hat{S}_z + \tfrac{1}{2}\hat{I}_z(\hat{S}_+\hat{S}_-)$$

$\underline{m=+1}$

$$[\hat{I}_z, \hat{A}_{-1}] = [\hat{I}_z, \tfrac{1}{\sqrt{2}}(\hat{I}_{-1}\hat{S}_0 + \hat{I}_0\hat{S}_{-1})] = -\tfrac{1}{\sqrt{2}}\hat{I}_{-1}\hat{S}_0 = -\tfrac{1}{2}\hat{I}_-\hat{S}_z$$

$$[[\hat{I}_z, \hat{A}_{-1}], \hat{A}_{+1}] = -\tfrac{1}{2}[\hat{I}_-\hat{S}_z, \tfrac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})]$$

$$= -\tfrac{1}{2\sqrt{2}}\hat{I}_-(0 + \hat{I}_0\hat{S}_{+1}) - \tfrac{1}{2\sqrt{2}}(\sqrt{2}\,\hat{I}_0\hat{S}_0 + \sqrt{2}\,\hat{I}_{-1}\hat{S}_{+1})\hat{S}_z$$

$$= \tfrac{1}{4}(\hat{I}_-\hat{S}_+)\hat{I}_z - \tfrac{1}{2}(S_z^2)\hat{I}_z + \tfrac{1}{4}(\hat{I}_-\hat{S}_+)\hat{S}_z$$

$\underline{m=0}$

$$[\hat{I}_z, \hat{A}_0] = [\hat{I}_z, \tfrac{1}{\sqrt{6}}(\hat{I}_{+1}\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_{+1})] = \tfrac{1}{\sqrt{6}}(I_{+1}S_{-1} - I_{-1}S_{+1})$$

$$= +\tfrac{1}{2\sqrt{6}}(\hat{I}_-\hat{S}_+ - \hat{I}_+\hat{S}_-)$$

$$[[\hat{I}_z, \hat{A}_0], \hat{A}_0] = \tfrac{1}{2\sqrt{6}}[\hat{I}_-\hat{S}_+ - \hat{I}_+\hat{S}_-, \tfrac{1}{\sqrt{6}}(\hat{I}_{+1}\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_{+1})]$$

$$= \tfrac{1}{12}\hat{I}_-(\sqrt{2}\,\hat{I}_{+1}\hat{S}_0 + 2\sqrt{2}\,\hat{I}_0\hat{S}_{+1} + 0) + \tfrac{1}{12}(\sqrt{2}\,\hat{I}_0\hat{S}_{-1} + 2\sqrt{2}\,\hat{I}_{-1}\hat{S}_0 + 0)\hat{S}_+$$

$$-\tfrac{1}{12}\hat{I}_+(0 + 2\sqrt{2}\,\hat{I}_0\hat{S}_{-1} + \sqrt{2}\,\hat{I}_{-1}\hat{S}_0) - \tfrac{1}{12}(0 + 2\sqrt{2}\,\hat{I}_{+1}\hat{S}_0 + \sqrt{2}\,\hat{I}_0\hat{S}_{+1})\hat{S}_-$$

$$= \tfrac{1}{12}\{-\hat{I}_-\hat{I}_+\hat{S}_z - 2\hat{I}_-\hat{S}_+\hat{I}_z + \hat{I}_z\hat{S}_-\hat{S}_+ + 2\hat{S}_z\hat{I}_-\hat{S}_+ - 2\hat{I}_+\hat{S}_-\hat{I}_z - \hat{I}_+\hat{I}_-\hat{S}_z$$

$$+ 2\hat{S}_z\hat{I}_+\hat{S}_- + \hat{I}_z\hat{S}_+\hat{S}_-\}$$

$$[[\hat{I}_z, \hat{A}_0], \hat{A}_0] = \frac{1}{12}\hat{S}_z\{-\hat{I}_-\hat{I}_+ + 2\hat{I}_-\hat{S}_+ - \hat{I}_+\hat{I}_- + 2\hat{I}_+\hat{S}_-\} + \frac{1}{12}\{\hat{S}_-\hat{S}_+ - 2\hat{I}_+\hat{S}_- + \hat{S}_+\hat{S}_- - 2\hat{I}_-\hat{S}_+\}\hat{I}_z$$

$$= \frac{1}{12}\hat{S}_z\{2(\hat{I}_-\hat{S}_+ + \hat{I}_+\hat{S}_-) - (\hat{I}_+\hat{I}_- + \hat{I}_-\hat{I}_+)\} - \frac{1}{12}\{2(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) - (\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+)\}\hat{I}_z$$

$m = -1$

$$[\hat{I}_z, \hat{A}_{+1}] = [\hat{I}_z, \tfrac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})] = \frac{1}{\sqrt{2}}\hat{I}_{+1}\hat{S}_0 = -\frac{1}{2}\hat{I}_+\hat{S}_z$$

$$[[I_z, \hat{A}_{+1}], \hat{A}_{-1}] = -\frac{1}{2}[I_+S_z, \tfrac{1}{\sqrt{2}}(\hat{I}_{-1}\hat{S}_0 + \hat{I}_0\hat{S}_{-1})]$$

$$= -\frac{1}{2\sqrt{2}}\hat{I}_+(0 - \hat{I}_0\hat{S}_{-1}) - \frac{1}{2\sqrt{2}}(\sqrt{2}\hat{I}_0\hat{S}_0 + \sqrt{2}\hat{I}_{+1}\hat{S}_{-1})\hat{S}_z$$

$$= \frac{1}{4}(\hat{I}_+\hat{S}_-)\hat{I}_z - \frac{1}{2}(\hat{I}_z\hat{S}_z)\hat{S}_z + \frac{1}{4}(\hat{I}_+\hat{S}_-)\hat{S}_z$$

$$= \frac{1}{4}(\hat{I}_+\hat{S}_-)\hat{S}_z - \frac{1}{2}(S_z^2)\hat{I}_z + \frac{1}{4}(\hat{I}_+\hat{S}_-)\hat{I}_z$$

$m = -2$

$$[\hat{I}_z, \hat{A}_{+2}] = [I_z, I_{+1}S_{+1}] = I_{+1}S_{+1} = \frac{1}{2}\hat{I}_+\hat{S}_+$$

$$[[\hat{I}_z, \hat{A}_{+2}], \hat{A}_{-2}] = \frac{1}{2}[\hat{I}_+\hat{S}_+, \hat{I}_{-1}\hat{S}_{-1}]$$

$$= \frac{1}{2}I_+(\sqrt{2}\hat{I}_{-1}\hat{S}_0) + \frac{1}{2}(\sqrt{2}\hat{I}_0\hat{S}_{-1})\hat{S}_+$$

$$= \frac{1}{2}(\hat{I}_+\hat{I}_-)\hat{S}_z + \frac{1}{2}\hat{I}_z(\hat{S}_-\hat{S}_+)$$

(b) $[[\hat{I}_z + \hat{S}_z, \hat{A}_{-m}], \hat{A}_m]$

$m = +2$

$$[[\hat{I}_z + \hat{S}_z, \hat{A}_{-2}], \hat{A}_2] = \frac{1}{2}(\hat{I}_-\hat{I}_+)\hat{S}_z + \frac{1}{2}\hat{I}_z(\hat{S}_+\hat{S}_-) + \frac{1}{2}(\hat{S}_-\hat{S}_+)\hat{I}_z + \frac{1}{2}\hat{S}_z(\hat{I}_+\hat{I}_-)$$

$$= \frac{1}{2}\hat{S}_z(\hat{I}_-\hat{I}_+ + \hat{I}_+\hat{I}_-) + \frac{1}{2}\hat{I}_z(\hat{S}_-\hat{S}_+ + \hat{S}_+\hat{S}_-)$$

$m = +1$

$$[[\hat{I}_z + \hat{S}_z, \hat{A}_{-1}], \hat{A}_1] = (\tfrac{1}{4}\hat{I}_-\hat{S}_+ - \tfrac{1}{2}\hat{S}_z^2)\hat{I}_z + (\tfrac{1}{4}\hat{I}_-\hat{S}_+)\hat{S}_z + (\tfrac{1}{4}\hat{S}_-\hat{I}_+ - \tfrac{1}{2}\hat{I}_z^2)\hat{S}_z + (\tfrac{1}{4}\hat{S}_-\hat{I}_+)\hat{I}_z$$

$$= \left[\tfrac{1}{4}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) - \tfrac{1}{2}\hat{S}_z^2\right]\hat{I}_z + \left[\tfrac{1}{4}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) - \tfrac{1}{2}\hat{I}_z^2\right]\hat{S}_z$$

<u>m = 0</u>

$$[[\hat{I}_z + \hat{S}_z, \hat{A}_0], \hat{A}_0] = 0$$

<u>m = -1</u>

$$[[\hat{I}_z + \hat{S}_z, \hat{A}_{-1}], \hat{A}_{+1}] = \tfrac{1}{4}(\hat{I}_+\hat{S}_-)\hat{S}_z + \left(\tfrac{1}{4}\hat{I}_+\hat{S}_- - \tfrac{1}{2}\hat{S}_z^2\right)\hat{I}_z$$

$$+ \tfrac{1}{4}(\hat{S}_+\hat{I}_-)\hat{I}_z + \left(\tfrac{1}{4}\hat{S}_+\hat{I}_- - \tfrac{1}{2}\hat{I}_z^2\right)\hat{S}_z$$

$$= \left\{\tfrac{1}{4}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) - \tfrac{1}{2} I_z^2\right\}\hat{S}_z + \left\{\tfrac{1}{4}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) - \tfrac{1}{2}\hat{S}_z^2\right\}\hat{I}_z$$

<u>m = -2</u>

$$[[\hat{I}_z + \hat{S}_z, \hat{A}_{-2}], \hat{A}_{+2}] = \tfrac{1}{2}(\hat{I}_+\hat{I}_-)\hat{S}_z + \tfrac{1}{2}(\hat{S}_-\hat{S}_+)\hat{I}_z + \tfrac{1}{2}(\hat{S}_+\hat{S}_-)\hat{I}_z + \tfrac{1}{2}(\hat{I}_-\hat{I}_+)\hat{S}_z$$

$$= \tfrac{1}{2}(\hat{I}_+\hat{I}_- + \hat{I}_-\hat{I}_+)\hat{S}_z + \tfrac{1}{2}(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+)\hat{I}_z$$

## (c) $[[\hat{I}_+, \hat{A}_{-m}], \hat{A}_{+m}]$

<u>m = +2</u>

$$[\hat{I}_+, \hat{A}_{-2}] = [\hat{I}_+, \hat{I}_{-1}\hat{S}_{-1}] = \sqrt{2}\,\hat{I}_0\hat{S}_{-1} = \hat{I}_z\hat{S}_-$$

$$[[\hat{I}_+, \hat{A}_{-2}], \hat{A}_{+2}] = [\hat{I}_z\hat{S}_-, \hat{I}_{+1}\hat{S}_{+1}]$$

$$= \hat{I}_z(\sqrt{2}\,\hat{I}_{+1}\hat{S}_0) + (\hat{I}_{+1}\hat{S}_{+1})\hat{S}_- = -(\hat{I}_z\hat{S}_z)\hat{I}_+ + \tfrac{1}{2} I_+(\hat{S}_+\hat{S}_-)$$

$$= \left(\tfrac{1}{2}\hat{S}_+\hat{S}_- - \hat{I}_z\hat{S}_z\right)\hat{I}_+$$

<u>m = +1</u>

$$[\hat{I}_+, \hat{A}_{-1}] = [\hat{I}_+, \tfrac{1}{\sqrt{2}}(\hat{I}_{-1}\hat{S}_0 + \hat{I}_0\hat{S}_{-1})] = \tfrac{1}{\sqrt{2}}(\sqrt{2}\hat{I}_0\hat{S}_0) + \tfrac{1}{\sqrt{2}}(\sqrt{2}\,\hat{I}_{+1}\hat{S}_{-1}) = \hat{I}_z\hat{S}_z - \tfrac{1}{2}\hat{I}_+\hat{S}_-$$

$$[[\hat{I}_+, \hat{A}_{-1}], \hat{A}_{+1}] = [\hat{I}_z\hat{S}_z - \tfrac{1}{2}\hat{I}_+\hat{S}_-, \tfrac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})]$$

$$= \tfrac{1}{\sqrt{2}} I_z(0 + \hat{I}_0\hat{S}_{+1}) + \tfrac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{S}_0 + 0)\hat{S}_z - \tfrac{1}{2\sqrt{2}}\hat{I}_+(\sqrt{2}\,\hat{I}_{+1}\hat{S}_{-1} + \sqrt{2}\,\hat{I}_0\hat{S}_0)$$

$$- \tfrac{1}{2\sqrt{2}}(0 + \sqrt{2}\,\hat{I}_{+1}\hat{S}_{+1})\hat{S}_-$$

$$= -\tfrac{1}{2}\hat{I}_z^2\hat{S}_+ - \tfrac{1}{2}\hat{I}_+\hat{S}_z^2 + \tfrac{1}{4}\hat{I}_+(\hat{I}_+\hat{S}_-) - \tfrac{1}{2}\hat{I}_+(\hat{I}_z\hat{S}_z) - \tfrac{1}{4}\hat{I}_+(\hat{S}_+\hat{S}_-)$$

$$= \left(-\tfrac{1}{2}\hat{I}_z^2\right)\hat{S}_+ + \hat{I}_+\left(\tfrac{1}{4}\hat{I}_+\hat{S}_- - \tfrac{1}{2}\hat{S}_z^2 - \tfrac{1}{2}\hat{I}_z\hat{S}_z - \tfrac{1}{4}\hat{S}_+\hat{S}_-\right)$$

m = 0

$$[\hat{I}_+, \hat{A}_0] = \frac{1}{\sqrt{6}}[\hat{I}_+, \hat{I}_{+1}\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_{+1}] = \frac{1}{\sqrt{6}}(0 + 2\sqrt{2}\,\hat{I}_{+1}\hat{S}_0 + \sqrt{2}\,\hat{I}_0\hat{S}_{+1})$$

$$= -\frac{1}{\sqrt{6}}(2\hat{I}_+\hat{S}_z + \hat{I}_z\hat{S}_+)$$

$$[[\hat{I}_+, \hat{A}_0], \hat{A}_0] = -\frac{1}{\sqrt{6}}[2\hat{I}_+\hat{S}_z + \hat{I}_z\hat{S}_+, \frac{1}{\sqrt{6}}(\hat{I}_{+1}\hat{S}_{-1} + 2\hat{I}_0\hat{S}_0 + \hat{I}_{-1}\hat{S}_{+1})]$$

$$= -\frac{1}{6}\{2\hat{I}_+(-\hat{I}_{+1}\hat{S}_{-1} + 0 + \hat{I}_{-1}\hat{S}_{+1}) + 2(0 + 2\sqrt{2}\,\hat{I}_{+1}\hat{S}_0 + \sqrt{2}\,\hat{I}_0\hat{S}_{+1})\hat{S}_z$$
$$+ \hat{I}_z(\sqrt{2}\,\hat{I}_{+1}\hat{S}_0 + 2\sqrt{2}\,\hat{I}_0\hat{S}_{+1} + 0) + (\hat{I}_{+1}\hat{S}_{-1} + 0 - \hat{I}_{-1}\hat{S}_{+1})\hat{S}_+\}$$

$$= -\frac{1}{6}\{\hat{I}_+(\hat{I}_+\hat{S}_-) - (\hat{I}_+\hat{I}_-)\hat{S}_+ - 4\hat{I}_+\hat{S}_z^2 - 2\hat{S}_+(\hat{I}_z\hat{S}_z) - (\hat{I}_z\hat{S}_z)\hat{I}_+ - 2\hat{I}_z^2\hat{S}_+$$
$$- \frac{1}{2}\hat{I}_+(\hat{S}_-\hat{S}_+) + \frac{1}{2}(\hat{I}_-\hat{S}_+)\hat{S}_+\}$$

$$= -\frac{1}{6}\{\hat{I}_+(\hat{I}_+\hat{S}_- - 4\hat{S}_z^2 - \frac{1}{2}\hat{S}_-\hat{S}_+ - \hat{I}_z\hat{S}_z) + \hat{S}_+(-\hat{I}_+\hat{I}_- - 2\hat{I}_z\hat{S}_z - 2\hat{I}_z^2 + \frac{1}{2}\hat{I}_-\hat{S}_+)\}$$

m = −1

$$[\hat{I}_+, \hat{A}_{+1}] = [\hat{I}_+, \frac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{S}_0 + \hat{I}_0\hat{S}_{+1})] = \frac{1}{\sqrt{2}}(\sqrt{2}\,\hat{I}_{+1}\hat{S}_{+1}) = \frac{1}{2}\hat{I}_+\hat{S}_+$$

$$[[\hat{I}_+, \hat{A}_{+1}], \hat{A}_{-1}] = \frac{1}{2}[\hat{I}_+\hat{S}_+, \frac{1}{\sqrt{2}}(\hat{I}_{-1}\hat{S}_0 + \hat{I}_0\hat{S}_{-1})]$$

$$= \frac{1}{2\sqrt{2}}\hat{I}_+(\sqrt{2}\,\hat{I}_{-1}\hat{S}_{+1} + \sqrt{2}\,\hat{I}_0\hat{S}_0) + \frac{1}{2\sqrt{2}}(\sqrt{2}\,\hat{I}_0\hat{S}_0 + \sqrt{2}\,\hat{I}_{+1}\hat{S}_{-1})\hat{S}_+$$

$$= \frac{1}{2}\hat{I}_+(-\frac{1}{2}\hat{I}_-\hat{S}_+ + \hat{I}_z\hat{S}_z) + \frac{1}{2}(\hat{I}_z\hat{S}_z - \frac{1}{2}\hat{I}_+\hat{S}_-)\hat{S}_+$$

$$= \hat{I}_+(\frac{1}{2}\hat{I}_z\hat{S}_z - \frac{1}{4}\hat{S}_-\hat{S}_+) + (\frac{1}{2}\hat{I}_z\hat{S}_z - \frac{1}{4}\hat{I}_+\hat{I}_-)\hat{S}_+$$

m = −2

$$[\hat{I}_+, \hat{A}_{+2}] = [\hat{I}_+, \hat{I}_{+1}\hat{S}_{+1}] = 0$$

$$[[\hat{I}_+, \hat{A}_{+2}], \hat{A}_{-2}] = 0$$

## (d) $[[\hat{I}_+ + \hat{S}_+, \hat{A}_{-m}], \hat{A}_m]$

m = +2

$$[[\hat{I}_+ + \hat{S}_+, \hat{A}_{-2}], \hat{A}_{+2}] = (\frac{1}{2}\hat{S}_+\hat{S}_- - \hat{I}_z\hat{S}_z)\hat{I}_+ + (\frac{1}{2}\hat{I}_+\hat{I}_- - \hat{I}_z\hat{S}_z)\hat{S}_+$$

m = +1

$$[[\hat{I}_+ + \hat{S}_+, \hat{A}_{-1}], \hat{A}_{+1}] = (-\frac{1}{2}\hat{I}_z^2)\hat{S}_+ + \hat{I}_+(\frac{1}{4}\hat{I}_+\hat{S}_- - \frac{1}{2}\hat{S}_z^2 - \frac{1}{2}\hat{I}_z\hat{S}_z - \frac{1}{4}\hat{S}_+\hat{S}_-)$$
$$+ (-\frac{1}{2}\hat{S}_z^2)\hat{I}_+ + \hat{S}_+(\frac{1}{4}\hat{S}_+\hat{I}_- - \frac{1}{2}\hat{I}_z^2 - \frac{1}{2}\hat{I}_z\hat{S}_z - \frac{1}{4}\hat{I}_+\hat{I}_-)$$

$$= \hat{S}_+\{\frac{1}{4}\hat{S}_+\hat{I}_- - \hat{I}_z^2 - \frac{1}{2}\hat{I}_z\hat{S}_z - \frac{1}{4}\hat{I}_+\hat{I}_-\} + \hat{I}_+\{\frac{1}{4}\hat{I}_+\hat{S}_- - \hat{S}_z^2 - \frac{1}{2}\hat{I}_z\hat{S}_z - \frac{1}{4}\hat{S}_+\hat{S}_-\}$$

$\underline{m=0}$

$$[[\hat I_+ + \hat S_+ , \hat A_0], A_0] = -\tfrac{1}{6}\hat I_+ (\hat I_+ \hat S_- - 4\hat S_z^2 - \tfrac12 \hat S_- \hat S_+ - \hat I_z \hat S_z)$$
$$-\tfrac16 \hat S_+ (-\hat I_+ \hat I_- - 2 I_z^2 + \tfrac12 \hat I_- \hat S_+ - 2\hat I_z \hat S_z)$$
$$-\tfrac16 \hat S_+ (\hat S_+ \hat I_- - 4 I_z^2 - \tfrac12 \hat S_- \hat I_+ - \hat I_z \hat S_z)$$
$$-\tfrac16 \hat I_+ (-\hat S_+ \hat S_- - 2 S_z^2 + \tfrac12 \hat S_- \hat I_+ - 2\hat I_z \hat S_z)$$
$$= -\tfrac16 \hat I_+ (\hat I_+ \hat S_- - \hat S_+ \hat S_- - \tfrac12 \hat S_- \hat S_+ - 6\hat S_z^2 - 3\hat I_z \hat S_z + \tfrac12 \hat S_- \hat I_+)$$
$$-\tfrac16 \hat S_+ (\hat S_+ \hat I_- - \hat I_+ \hat I_- - \tfrac12 \hat I_- \hat I_+ - 6\hat I_z^2 - 3\hat I_z \hat S_z + \tfrac12 \hat I_- \hat S_+)$$

$\underline{m=-1}$

$$[[\hat I_{+1} + \hat S_{+1}, \hat A_{+1}]\hat A_{-1}] = \hat I_+ (\tfrac12 \hat I_z \hat S_z - \tfrac14 \hat S_- \hat S_+) + (\tfrac12 \hat I_z \hat S_z - \tfrac14 \hat I_+ \hat I_-)\hat S_+$$
$$+ \hat S_+ (\tfrac12 \hat I_z \hat S_z - \tfrac14 I_- I_+) + (\tfrac12 \hat I_z \hat S_z - \tfrac14 \hat S_+ \hat S_-)\hat I_+$$
$$= \hat I_+ [\hat I_z \hat S_z - \tfrac14 (\hat S_+ \hat S_- + \hat S_- \hat S_+)] + \hat S_+ [\hat I_z \hat S_z - \tfrac14 (I_- I_+ + I_+ I_-)]$$

$\underline{m=-2}$

$$[[\hat I_+ + \hat S_+, \hat A_{+2}], \hat A_{-2}] = 0$$

## Ensemble Averages for Dipolar Interactions

(i) $\langle [[\hat I_z + \hat S_z, \hat A_{-m}], \hat A_m] \rangle$

$\underline{m=+2}$

$$\langle [[\hat I_z + \hat S_z, \hat A_{-2}], \hat A_{+2}] \rangle = \tfrac12 \langle \hat S_z (\hat I_- \hat I_+ + \hat I_+ \hat I_-)\rangle + \tfrac12 \langle \hat I_z (\hat S_- \hat S_+ + \hat S_+ \hat S_-)\rangle$$

We have a problem here because our ensemble averaged quantities are not simply $\hat S_z$ and $\hat I_z$. Abragam gets over this difficulty as follows:

"In the approximation for high temperatures where $\hat\rho - \hat\rho_{eq}$ is an infinitely small quantity of the first order, quantities such as $\langle I_x \rangle$, $\langle I_y \rangle$, $\langle I_z \rangle$ are also small quantities of the first order, and to the same approximation

$$\langle I_z S_x^2 \rangle = \langle I_z S_y^2 \rangle = \langle I_z S_z^2 \rangle \cong \frac{S(S+1)}{3} \langle I_z \rangle$$
$$\langle I_z S_x \rangle = \langle I_z S_y \rangle = \langle I_z S_z \rangle \cong 0 \text{"}$$

I'm afraid that I cannot illuminate this approximation any further. It is clearly exact for spin ½ particles which are of greatest importance, but I have not delved deeper into it.

We recognize that

$$\hat{I}_+\hat{I}_- = I(I+1) - \hat{I}_z^2 + \hat{I}_z \qquad \hat{S}_+\hat{S}_- = S(S+1) - \hat{S}_z^2 + \hat{S}_z$$

$$\hat{I}_-\hat{I}_+ = I(I+1) - \hat{I}_z^2 - \hat{I}_z \qquad \hat{S}_-\hat{S}_+ = S(S+1) - \hat{S}_z^2 - \hat{S}_z$$

$$\langle [[\hat{I}_z+\hat{S}_z, \hat{A}_{-2}], \hat{A}_2] \rangle = \langle \hat{S}_z [I(I+1) - I_z^2] \rangle + \langle \hat{I}_z [S(S+1) - S_z^2] \rangle$$

$$= \frac{2I(I+1)}{3}\langle \hat{S}_z \rangle + \frac{2S(S+1)}{3}\langle \hat{I}_z \rangle$$

$$= \frac{2I(I+1)}{3}\langle \hat{I}_z + \hat{S}_z \rangle \qquad (\text{since } I = S \text{ for identical spins})$$

<u>$m = +1$</u>

$$\langle [[\hat{I}_z+\hat{S}_z, \hat{A}_{-1}], A_{+1}] \rangle = \tfrac{1}{4}\langle \hat{I}_z(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) \rangle + \tfrac{1}{4}\langle \hat{S}_z(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) \rangle$$
$$- \tfrac{1}{2}\langle \hat{I}_z \hat{S}_z^2 \rangle - \tfrac{1}{2}\langle \hat{S}_z \hat{I}_z^2 \rangle$$

$$= -\frac{1}{2}\left(\frac{S(S+1)}{3}\right)\langle \hat{I}_z \rangle - \frac{1}{2}\left(\frac{S(S+1)}{3}\right)\langle \hat{S}_z \rangle$$

$$= -\frac{I(I+1)}{6}\langle \hat{I}_z + \hat{S}_z \rangle$$

<u>$m = 0$</u>

$$\langle [[\hat{I}_z+\hat{S}_z, \hat{A}_0], \hat{A}_0] \rangle = 0$$

<u>$m = -1$</u>

$$\langle [[\hat{I}_z+\hat{S}_z, \hat{A}_{+1}], \hat{A}_{-1}] \rangle = \tfrac{1}{4}\langle \hat{S}_z(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) \rangle + \tfrac{1}{4}\langle \hat{I}_z(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+) \rangle$$
$$- \tfrac{1}{2}\langle I_z^2 S_z \rangle - \tfrac{1}{2}\langle I_z S_z^2 \rangle$$

$$= -\frac{I(I+1)}{6}\langle \hat{I}_z + \hat{S}_z \rangle$$

$m=-2$

$$\langle[[\hat{I}_z+\hat{S}_z,\hat{A}_{+2}],\hat{A}_{-2}]\rangle = \tfrac{1}{2}\langle\hat{S}_z(\hat{I}_+\hat{I}_- + \hat{I}_-\hat{I}_+)\rangle + \tfrac{1}{2}\langle\hat{I}_z(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+)\rangle$$

$$= 2\frac{I(I+1)}{3}\langle\hat{I}_z+\hat{S}_z\rangle$$

(ii) $\langle[[\hat{I}_+ + \hat{S}_+,\hat{A}_{-m}],\hat{A}_m\rangle$

$m=+2$

$$\langle[[\hat{I}_+ + \hat{S}_+,\hat{A}_{-2}],\hat{A}_{+2}]\rangle = \tfrac{1}{2}\langle\hat{I}_+(\hat{S}_+\hat{S}_-)\rangle + \tfrac{1}{2}\langle\hat{S}_+(\hat{I}_+\hat{I}_-)\rangle - \langle\hat{I}_+\hat{I}_z\hat{S}_z\rangle - \langle\hat{S}_+\hat{I}_z\hat{S}_z\rangle$$

$$= \tfrac{1}{2}\langle\hat{I}_+[S(S+1)-\hat{S}_z^2+\hat{S}_z]\rangle + \tfrac{1}{2}\langle\hat{S}_+[I(I+1)-\hat{I}_z^2-\hat{I}_z]\rangle$$

$$= \langle I_+\rangle\left(\tfrac{1}{2}\right)\left(\frac{2S(S+1)}{3}\right) + \langle S_+\rangle\left(\tfrac{1}{2}\right)\left(\frac{2I(I+1)}{3}\right)$$

$$= \frac{I(I+1)}{3}\langle\hat{I}_+ + \hat{S}_+\rangle$$

$m=+1$

$$\langle[[\hat{I}_+ + \hat{S}_+,\hat{A}_{-1}],\hat{A}_{+1}]\rangle = \langle\hat{S}_+(-\hat{I}_z^2 - \tfrac{1}{4}\hat{I}_+\hat{I}_- + \tfrac{1}{4}\hat{S}_+\hat{I}_- - \tfrac{1}{2}\hat{I}_z\hat{S}_z\rangle + \langle\hat{I}_+(-\hat{S}_z^2 - \tfrac{1}{4}\hat{S}_+\hat{S}_- + \tfrac{1}{4}\hat{I}_+\hat{S}_- - \tfrac{1}{2}\hat{I}_z\hat{S}_z\rangle$$

$$= \langle\hat{S}_+\rangle\left\{-\frac{I(I+1)}{3} - \frac{1}{4}\left(\frac{2I(I+1)}{3}\right)\right\} + \langle\hat{I}_+\rangle\left\{-\frac{S(S+1)}{3} - \frac{1}{4}\left(\frac{2S(S+1)}{3}\right)\right\}$$

$$= -\frac{I(I+1)}{2}\langle\hat{I}_+ + \hat{S}_+\rangle$$

$m=0$

$$\langle[[\hat{I}_+ + \hat{S}_+,\hat{A}_0],\hat{A}_0]\rangle = -\tfrac{1}{6}\langle\hat{I}_+\rangle\left\{-\frac{2S(S+1)}{3} - \frac{1}{2}\left(\frac{2S(S+1)}{3}\right) - 6\left(\frac{S(S+1)}{3}\right)\right\} - \tfrac{1}{6}\langle\hat{S}_+\rangle\left\{-\frac{2I(I+1)}{3} - \frac{1}{2}\left(\frac{2I(I+1)}{3}\right) - 6\left(\frac{I(I+1)}{3}\right)\right\}$$

$$= \frac{I(I+1)}{2}\langle\hat{I}_+ + \hat{S}_+\rangle$$

$m=-1$

$$\langle[[\hat{I}_+ + \hat{S}_+,\hat{A}_{+1}],\hat{A}_{-1}]\rangle = \langle\hat{I}_+\rangle\left\{-\frac{1}{4}\left(\frac{2S(S+1)}{3} + \frac{2S(S+1)}{3}\right)\right\} + \langle\hat{S}_+\rangle\left\{-\frac{1}{4}\left(\frac{2I(I+1)}{3} + \frac{2I(I+1)}{3}\right.\right.$$

$$= -\frac{I(I+1)}{3}\langle\hat{I}_+ + \hat{S}_+\rangle$$

$\underline{m=-2}$

$$\langle [[\hat{I}_+ + \hat{S}_+ , \hat{A}_{+2}], \hat{A}_{-2}] \rangle = 0$$

(iii) $\langle [[\hat{I}_z , \hat{A}_{-m}], \hat{A}_m] \rangle$

$\underline{m=+2}$

$$\langle [[\hat{I}_z , \hat{A}_{-2}], \hat{A}_{+2}] \rangle = \frac{1}{2} \langle \hat{S}_z (\hat{I}_- \hat{I}_+) \rangle + \frac{1}{2} \langle \hat{I}_z (\hat{S}_+ \hat{S}_-) \rangle$$

$$= \frac{1}{2}\left(2\frac{I(I+1)}{3}\right) \langle \hat{S}_z \rangle + \frac{1}{2}\left(\frac{2S(S+1)}{3}\right) \langle \hat{I}_z \rangle$$

$$= \frac{I(I+1)}{3} \langle \hat{S}_z \rangle + \frac{S(S+1)}{3} \langle \hat{I}_z \rangle$$

$\underline{m=+1}$

$$\langle [[\hat{I}_z , \hat{A}_{-1}], \hat{A}_{+1}] \rangle = \frac{1}{4} \langle (\hat{I}_- \hat{S}_+) \hat{I}_z \rangle - \frac{1}{2} \langle \hat{I}_z (\hat{S}_z^2) \rangle + \frac{1}{4} \langle (\hat{I}_- \hat{S}_+) \hat{S}_z \rangle$$

$$= - \frac{S(S+1)}{6} \langle \hat{I}_z \rangle$$

$\underline{m=0}$

$$\langle [[\hat{I}_z , \hat{A}_0], \hat{A}_0] \rangle = \frac{1}{12} \langle \hat{S}_z [2(\hat{I}_- \hat{S}_+ + \hat{I}_+ \hat{S}_-) - (\hat{I}_+ \hat{I}_- + \hat{I}_- \hat{I}_+)] \rangle$$

$$- \frac{1}{12} \langle \hat{I}_z [2(\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+) - (\hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+)] \rangle$$

$$= \frac{1}{12} \langle \hat{S}_z \rangle \left\{ -\frac{4I(I+1)}{3} \right\} + \frac{1}{12} \langle \hat{I}_z \rangle \left\{ \frac{4S(S+1)}{3} \right\}$$

$$= \frac{S(S+1)}{9} \langle \hat{I}_z \rangle - \frac{I(I+1)}{9} \langle \hat{S}_z \rangle$$

$\underline{m=-1}$

$$\langle [[\hat{I}_z , \hat{A}_{+1}], \hat{A}_{-1}] \rangle = \frac{1}{4} \langle (\hat{I}_+ \hat{S}_-) \hat{S}_z \rangle - \frac{1}{2} \langle \hat{I}_z (\hat{S}_z^2) \rangle + \frac{1}{4} \langle \hat{I}_z (\hat{I}_+ \hat{S}_-) \rangle$$

$$= - \frac{S(S+1)}{6} \langle \hat{I}_z \rangle$$

$\underline{m=-2}$

$$\langle [[\hat{I}_z , \hat{A}_{+2}], \hat{A}_{-2}] \rangle = \frac{1}{2} \langle (\hat{I}_+ \hat{I}_-) \hat{S}_z \rangle + \frac{1}{2} \langle \hat{I}_z (\hat{S}_- \hat{S}_+) \rangle$$

$$= \frac{S(S+1)}{3} \langle I_z \rangle + \frac{I(I+1)}{3} \langle S_z \rangle$$

(iv) $\langle[[\hat{I}_+,\hat{A}_{-m}],\hat{A}_m]\rangle$

m = +2

$$\langle[[\hat{I}_+,\hat{A}_{-2}],\hat{A}_{+2}]\rangle = \tfrac{1}{2}\langle\hat{S}_+\hat{S}_-\hat{I}_+\rangle - \langle\hat{I}_z\hat{S}_z\hat{I}_+\rangle$$
$$= \frac{S(S+1)}{3}\langle\hat{I}_+\rangle$$

m = +1

$$\langle[[\hat{I}_+,\hat{A}_{-1}],\hat{A}_{+1}]\rangle = -\tfrac{1}{2}\langle\hat{I}_z^2\hat{S}_+\rangle - \tfrac{1}{2}\langle\hat{S}_z^2\hat{I}_+\rangle - \tfrac{1}{4}\langle\hat{S}_+\hat{S}_-\hat{I}_+\rangle$$
$$= -\frac{S(S+1)}{3}\langle\hat{I}_+\rangle - \frac{I(I+1)}{6}\langle\hat{S}_+\rangle$$

m = 0

$$\langle[[\hat{I}_+,\hat{A}_0],\hat{A}_0]\rangle = -\tfrac{1}{6}\langle\hat{I}_+(-4\hat{S}_z^2 - \tfrac{1}{2}\hat{S}_-\hat{S}_+)\rangle - \tfrac{1}{6}\langle\hat{S}_+(-2\hat{I}_z^2 - \hat{I}_+\hat{I}_-)\rangle$$
$$= \frac{5}{18}S(S+1)\langle\hat{I}_+\rangle + \frac{2}{9}I(I+1)\langle\hat{S}_+\rangle$$

m = −1

$$\langle[[\hat{I}_+,\hat{A}_{+1}],\hat{A}_{-1}]\rangle = -\tfrac{1}{4}\langle\hat{I}_+\hat{S}_-\hat{S}_+\rangle - \tfrac{1}{4}\langle\hat{I}_+\hat{I}_-\hat{S}_+\rangle$$
$$= -\frac{S(S+1)}{6}\langle\hat{I}_+\rangle - \frac{I(I+1)}{6}\langle\hat{S}_+\rangle$$

m = −2

$$\langle[[\hat{I}_+,\hat{A}_{+2}],\hat{A}_{-2}]\rangle = 0$$

## Dipolar Relaxation - Like Spins

### $T_1$

$$\frac{d\langle \hat{I}_z+\hat{S}_z\rangle}{dt} = -\frac{i}{\hbar}\left\langle\left[\hat{I}_z\hat{S}_z\mathcal{H}_0\right]\right\rangle - \frac{1}{2}\sum_m(-1)^m J_m(\omega_m)\left\langle\left[\left[\hat{I}_z+\hat{S}_z\,,\hat{A}_{-m}\right],\hat{A}_m\right]\right\rangle$$

$$= -\frac{1}{2}\Big\{(-1)^2 J_2(2\omega_0)\left(\frac{2I(I+1)}{3}\langle\hat{I}_z+\hat{S}_z\rangle\right)$$

$$+(-1)^1 J_1(\omega_0)\left(-\frac{I(I+1)}{6}\langle\hat{I}_z+\hat{S}_z\rangle\right)$$

$$+(-1)^0 J_0(0)\,(0)$$

$$+(-1)^{-1} J_1(\omega_0)\left(-\frac{I(I+1)}{6}\langle\hat{I}_z+\hat{S}_z\rangle\right)$$

$$+(-1)^2 J_2(2\omega_0)\left(\frac{2I(I+1)}{3}\langle\hat{I}_z+\hat{S}_z\rangle\right)\Big\}$$

$$= -\langle\hat{I}_z+\hat{S}_z\rangle\left\{\frac{2I(I+1)}{3}J_2(2\omega_0) + \frac{I(I+1)}{6}J_1(\omega_0)\right\} \quad - *$$

Hence

$$\frac{1}{T_1} = \frac{I(I+1)}{6}\left\{4J_2(2\omega_0) + J_1(\omega_0)\right\}$$

$$= \frac{I(I+1)}{6}\left\{4\left[\frac{6\gamma_I^4\hbar^2}{5r_{IS}^6}\frac{(2\tau_{\theta eff})}{1+4\omega_0^2\tau_{\theta eff}^2}\right] + \frac{6\gamma_I^4\hbar^2}{5r_{IS}^6}\left[\frac{(2\tau_{\theta eff})}{1+\omega_0^2\tau_{\theta eff}^2}\right]\right\}$$

$$= \frac{2I(I+1)\gamma_I^4\hbar^2}{5r_{IS}^6}\left\{4\frac{\tau_{\theta eff}}{1+4\omega_0^2\tau_{\theta eff}^2} + \frac{\tau_{\theta eff}}{1+\omega_0^2\tau_{\theta eff}^2}\right\}$$

Abragam gives the result

$$\frac{1}{T_1} = \frac{3}{2}\gamma_I^4\hbar^2 I(I+1)\left\{J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)\right\} \qquad [\text{Eq. (76), pg 291}]$$

with $J^{(1)}(\omega_I) = \frac{4}{15r_{IS}^6}\frac{\tau_2}{1+\omega_I^2\tau_2^2}$, $J^{(2)}(2\omega_I) = \frac{16}{15r_{IS}^6}\frac{\tau_2}{1+4\omega_I^2\tau_2^2}$

[Eq (104), pg 300]

and therefore

$$\frac{1}{T_1} = \frac{2I(I+1)\gamma_I^4\hbar^2}{5r_{IS}^6}\left\{\frac{4\tau_2}{1+4\omega_I^2\tau_2^2} + \frac{\tau_2}{1+\omega_I^2\tau_2^2}\right\}$$

in agreement with our result.

$T_2$

$$\left(\frac{d\langle \hat{I}_+ + \hat{S}_+\rangle}{dt}\right)_{relaxation} = -\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\left\langle \left[\left[\hat{I}_+ + \hat{S}_+ , \hat{A}_{-m}\right], \hat{A}_m\right]\right\rangle$$

$$= -\frac{1}{2}\Big\{ (-1)^2 J_2(2\omega_0)\, \frac{I(I+1)}{3}\langle \hat{I}_+ + \hat{S}_+\rangle$$
$$+(-1)^1 J_1(\omega_0)\left(-\frac{I(I+1)}{2}\right)\langle \hat{I}_+ + \hat{S}_+\rangle$$
$$+(-1)^0 J_0(0)\left(\frac{I(I+1)}{2}\right)\langle \hat{I}_+ + \hat{S}_+\rangle$$
$$+(-1)^{-1} J_1(\omega_0)\left(-\frac{I(I+1)}{3}\right)\langle \hat{I}_+ + \hat{S}_+\rangle\Big\}$$

$$= -\langle \hat{I}_+ + \hat{S}_+\rangle\left\{\frac{I(I+1)}{6}J_2(2\omega_0) + \frac{5I(I+1)}{12}J_1(\omega_0) + \frac{I(I+1)}{4}J_0(0)\right\}$$

$$\therefore \frac{1}{T_2} = \frac{I(I+1)}{12}\left\{2J_2(2\omega_0) + 5J_1(\omega_0) + 3J_0(0)\right\}$$

$$= \frac{I(I+1)}{12}\Big\{2\left(\frac{6\gamma_I^4\hbar^2}{5r_{IS}^6}\right)\left(\frac{2\tau_{\theta eff}}{1+4\omega_0^2\tau_{\theta eff}^2}\right) + 5\left(\frac{6\gamma_I^4\hbar^2}{5r_{IS}^6}\right)\left(\frac{2\tau_{\theta eff}}{1+\omega_0^2\tau_{\theta eff}^2}\right)$$
$$+ 3\left(\frac{6\gamma_I^4\hbar^2}{5r_{IS}^6}\right)\left(2\tau_{\theta eff}\right)\Big\}$$

$$= \frac{I(I+1)\gamma_I^4\hbar^2}{5r_{IS}^6}\left\{2\left(\frac{\tau_{\theta eff}}{1+4\omega_0^2\tau_{\theta eff}^2}\right) + 5\left(\frac{\tau_{\theta eff}}{1+\omega_0^2\tau_{\theta eff}^2}\right) + 3\left(\tau_{\theta eff}\right)\right\}$$

Abragam gives the result

$$\frac{1}{T_2} = \gamma_I^4\hbar^2 I(I+1)\left\{\frac{3}{8}J^{(2)}(2\omega_0) + \frac{15}{4}J^{(1)}(\omega_0) + \frac{3}{8}J^{(0)}(0)\right\}$$ [Eq (79), pg 292]

where $J^{(2)}(2\omega_0) = \frac{16}{15r_{IS}^6}\frac{\tau_2}{1+4\omega_0^2\tau_2^2}$, $J^{(1)}(\omega_0) = \frac{4}{15r_{IS}^6}\frac{\tau_2}{1+\omega_0^2\tau_2^2}$, $J^{(0)}(0) = \frac{8}{5r_{IS}^6}\tau_2$

and

$$\frac{1}{T_2} = \frac{\gamma_I^4\hbar^2 I(I+1)}{r_{IS}^6}\left\{\left(\frac{3}{8}\right)\left(\frac{16}{15}\right)\left(\frac{\tau_2}{1+4\omega_0^2\tau_2^2}\right) + \left(\frac{15}{4}\right)\left(\frac{4}{15}\right)\left(\frac{\tau_2}{1+\omega_0^2\tau_2^2}\right) + \left(\frac{3}{8}\right)\left(\frac{8}{5}\right)(\tau_2)\right\}$$

$$= \frac{\gamma_I^4\hbar^2 I(I+1)}{5r_{IS}^6}\left\{2\left(\frac{\tau_2}{1+4\omega_0^2\tau_2^2}\right) + 5\left(\frac{\tau_2}{1+\omega_0^2\tau_2^2}\right) + 3(\tau_2)\right\}$$

in agreement with our result above.

## Limit of Extreme Motional Narrowing

For $\omega_0^2 \tau_{\theta_{eff}}^2 << 1$

$$\frac{1}{T_1} = \frac{2\,I(I+1)\,\gamma_I^4 \hbar^2}{r_{IS}^6}\,\tau_{\theta_{eff}}$$

"like" Spins

and

$$\frac{1}{T_2} = \frac{2\,I(I+1)\,\gamma_I^4 \hbar^2}{r_{IS}^6}\,\tau_{\theta_{eff}}$$

## Dipolar Relaxation - Unlike Spins

I will consider only $T_1$ here since the computation of $T_2$ would require considerable "backtracking" in order to take into account the distinct frequency dependence of each of the terms in $\hat{A}_0^*(t)$ and $\hat{A}_{\pm 1}^*(t)$.

$$\frac{d\langle \hat{I}_z\rangle}{dt} = -\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\,\langle [[\hat{I}_z, \hat{A}_{-m}], \hat{A}_m]\rangle$$

$$= -\frac{1}{2}\Big\{(-1)^2 J_2(\omega_I+\omega_S)\left(\frac{S(S+1)}{3}\langle \hat{I}_z\rangle + \frac{I(I+1)}{3}\langle \hat{S}_z\rangle\right)$$

$$+ (-1)^1 J_1(\omega_I)\left(-\frac{S(S+1)}{6}\langle \hat{I}_z\rangle\right)$$

$$+ (-1)^0 J_0(\omega_I-\omega_S)\left(\frac{S(S+1)}{9}\langle \hat{I}_z\rangle - \frac{I(I+1)}{9}\langle \hat{S}_z\rangle\right)$$

$$+ (-1)^{-1} J_1(\omega_I)\left(-\frac{S(S+1)}{6}\langle \hat{I}_z\rangle\right)$$

$$+ (-1)^2 J_2(\omega_I+\omega_S)\left(\frac{S(S+1)}{3}\langle \hat{I}_z\rangle + \frac{I(I+1)}{3}\langle \hat{S}_z\rangle\right)\Big\}$$

$$= -\langle \hat{I}_z\rangle\left\{\left(\frac{S(S+1)}{3}\right)J_2(\omega_I+\omega_S) + \frac{S(S+1)}{6}J_1(\omega_I) + \frac{S(S+1)}{18}J_0(\omega_I-\omega_S)\right\}$$

$$-\langle \hat{S}_z\rangle\left\{\left(\frac{I(I+1)}{3}\right)J_2(\omega_I+\omega_S) - \frac{I(I+1)}{18}J_0(\omega_I-\omega_S)\right\}$$

Hence we have coupled equations of the form

$$\frac{d\langle I_z\rangle}{dt} = -\frac{\langle I_z\rangle}{T_1^{II}} - \frac{\langle S_z\rangle}{T_1^{IS}}$$

and

$$\frac{d\langle\hat{S}_z\rangle}{dt} = -\frac{\langle\hat{S}_z\rangle}{T_1^{SS}} - \frac{\langle\hat{I}_z\rangle}{T_1^{SI}}$$

where

$$\frac{1}{T_1^{II}} = \frac{S(S+1)}{18}\left\{6J_2(\omega_I+\omega_S) + 3J_1(\omega_I) + J_0(\omega_I-\omega_S)\right\}$$

$$= \frac{S(S+1)}{18}\left\{6\left(\frac{6\gamma_I^2\gamma_S^2\hbar^2}{5r_{IS}^6}\right)\frac{2\tau_{\theta eff}}{1+(\omega_I+\omega_S)^2\tau_{\theta eff}^2} + 3\left(\frac{6\gamma_I^2\gamma_S^2\hbar^2}{5r_{IS}^6}\right)\left(\frac{2\tau_{\theta eff}}{1+\omega_I^2\tau_{\theta eff}^2}\right) + \left(\frac{6\gamma_I^2\gamma_S^2\hbar^2}{5r_{IS}^6}\right)\left(\frac{2\tau_{\theta eff}}{1+(\omega_I-\omega_S)^2\tau_{\theta eff}^2}\right)\right.$$

$$= \frac{2S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r_{IS}^6}\left\{\frac{6\tau_{\theta eff}}{1+(\omega_I+\omega_S)^2\tau_{\theta eff}^2} + \frac{3\tau_{\theta eff}}{1+\omega_I^2\tau_{\theta eff}^2} + \frac{\tau_{\theta eff}}{1+(\omega_I-\omega_S)^2\tau_{\theta eff}^2}\right.$$

and

$$\frac{1}{T_1^{IS}} = \frac{I(I+1)}{18}\left\{6J_2(\omega_I+\omega_S) - J_0(\omega_I-\omega_S)\right\}$$

$$= \frac{2I(I+1)\gamma_I^2\gamma_S^2\hbar^2}{15r_{IS}^6}\left\{\frac{6\tau_{\theta eff}}{1+(\omega_I+\omega_S)^2\tau_{\theta eff}^2} - \frac{\tau_{\theta eff}}{1+(\omega_I-\omega_S)^2\tau_{\theta eff}^2}\right\}$$

Abragam gives the results

$$\frac{1}{T_1^{II}} = \gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left\{\frac{1}{12}J^{(0)}(\omega_I-\omega_S) + \frac{3}{2}J^{(1)}(\omega_I) + \frac{3}{4}J^{(2)}(\omega_I+\omega_S)\right\}$$ [Eq (88) pg 295

$$= \frac{\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{r_{IS}^6}\left\{\frac{1}{12}\left(\frac{8}{5}\frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2^2}\right) + \frac{3}{2}\left(\frac{4\tau_2}{15(1+\omega_I^2\tau_2^2)}\right) + \frac{3}{4}\left(\frac{16}{15}\frac{\tau_2}{1+(\omega_I+\omega_S)^2\tau_2^2}\right)\right\}$$

$$= \frac{2S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r_{IS}^6}\left\{\frac{6\tau_2}{1+(\omega_I+\omega_S)^2\tau_2^2} + \frac{3\tau_2}{1+\omega_I^2\tau_2^2} + \frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2^2}\right\}$$

and

$$\frac{1}{T_1^{IS}} = \gamma_I^2\gamma_S^2\hbar^2 I(I+1)\left\{-\frac{1}{12}J^{(0)}(\omega_I-\omega_S) + \frac{3}{4}J^{(2)}(\omega_I+\omega_S)\right\}$$ [Eq (88), pg 295

$$= \frac{2I(I+1)\gamma_I^2\gamma_S^2\hbar^2}{15r_{IS}^6}\left\{\frac{6\tau_2}{1+(\omega_I+\omega_S)^2\tau_2^2} - \frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2^2}\right\}$$

which agree with our results.

The coupling of $\langle I_z \rangle$ and $\langle S_z \rangle$ in the relaxation equation corresponds to "cross" relaxation and has been the subject of a number of papers by D. Grant in recent years. The cross relaxation effect will be important when one uses a non-selective pulse to study $T_1$ for all protons (or $^{13}C$) in a molecule. Use of a selective pulse will make cross-relaxation unimportant because, our relaxation equation really should be

$$\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1^{II}}\left(\langle I_z \rangle - \langle I_z \rangle_0\right) - \frac{1}{T_1^{IS}}\left(\langle S_z \rangle - \langle S_z \rangle_0\right)$$

where $\langle\,\rangle_0$ means equilibrium value. A selective pulse which shifts $\langle I_z \rangle$ away from $\langle I_z \rangle_0$ but not $\langle S_z \rangle$ from $\langle S_z \rangle_0$ will therefore only (in lowest order at least) has the dominant $\frac{1}{T_1^{II}}\left(\langle I_z \rangle - \langle I_z \rangle_0\right)$ term in the decay law for $d\langle I_z \rangle$.

# Commutators for Electric Quadrupole Interaction

1. $[[\hat{I}_0, \hat{A}_{-m}], \hat{A}_m]$

$$= -m[\hat{A}_{-m}, \hat{A}_m]$$

(a) $m = +2$

$$[\hat{A}_{-2}, \hat{A}_{+2}] = \frac{1}{2}[\hat{I}_-^2, \hat{A}_{+2}] = \frac{1}{2}\hat{I}_-[\hat{I}_-, \hat{A}_{+2}] + \frac{1}{2}[\hat{I}_-, \hat{A}_{+2}]\hat{I}_-$$

$$= \hat{I}_-\hat{A}_{+1} + \hat{A}_{+1}\hat{I}_-$$

$$= \frac{1}{\sqrt{2}}(\hat{I}_-\hat{I}_{+1}\hat{I}_0 + \hat{I}_-\hat{I}_0\hat{I}_{+1}) + \frac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{I}_0\hat{I}_- + \hat{I}_0\hat{I}_{+1}\hat{I}_-)$$

$$= -\frac{1}{2}(\hat{I}_-\hat{I}_+\hat{I}_z + \hat{I}_-\hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z\hat{I}_- + \hat{I}_z\hat{I}_+\hat{I}_-)$$

$$= -\frac{1}{2}(\hat{I}_-\hat{I}_+\hat{I}_z + \hat{I}_-\hat{I}_+\hat{I}_z + \hat{I}_-[\hat{I}_z, \hat{I}_+] + \hat{I}_z\hat{I}_+\hat{I}_- + [\hat{I}_+, \hat{I}_z]\hat{I}_- + \hat{I}_z\hat{I}_+\hat{I}_-)$$

$$= -\hat{I}_-\hat{I}_+\hat{I}_z - \hat{I}_z\hat{I}_+\hat{I}_- - \frac{1}{2}(\hat{I}_-\hat{I}_+ - \hat{I}_+\hat{I}_-)$$

$$= -(\hat{I}^2 - \hat{I}_z^2 - \hat{I}_z)\hat{I}_z - \hat{I}_z(\hat{I}^2 - \hat{I}_z^2 + \hat{I}_z) - \frac{1}{2}(\hat{I}^2 - \hat{I}_z^2 - \hat{I}_z - \hat{I}^2 + \hat{I}_z^2 - \hat{I}_z)$$

$$= (-2\hat{I}^2 + 1)\hat{I}_z + 2\hat{I}_z^3$$

$$[[\hat{I}_0, \hat{A}_{-2}], \hat{A}_{+2}] = -2\{(-2\hat{I}^2 + 1)\hat{I}_z + 2\hat{I}_z^3\}$$

$$= (4I(I+1) - 2)\hat{I}_z - 4\hat{I}_z^3$$

(b) $m = +1$

$$[\hat{A}_{-1}, \hat{A}_{+1}] = [\frac{1}{\sqrt{2}}(\hat{I}_{-1}\hat{I}_0 + \hat{I}_0\hat{I}_{-1}), \hat{A}_{+1}] = \frac{1}{2}[\hat{I}_-\hat{I}_z + \hat{I}_z\hat{I}_-, \hat{A}_{+1}]$$

$$= \frac{1}{2}(\hat{I}_-[\hat{I}_z, \hat{A}_{+1}] + [\hat{I}_-, \hat{A}_{+1}]\hat{I}_z + \hat{I}_z[\hat{I}_-, \hat{A}_{+1}] + [\hat{I}_z, \hat{A}_{+1}]\hat{I}_-)$$

$$= \frac{1}{2}(\hat{I}_-\hat{A}_{+1} + \hat{A}_{+1}\hat{I}_- + \sqrt{6}\hat{A}_0\hat{I}_z + \sqrt{6}\hat{I}_z\hat{A}_0)$$

$$= \frac{1}{2}(\hat{I}_-\hat{A}_{+1} + \hat{A}_{+1}\hat{I}_-) + \sqrt{6}\hat{A}_0\hat{I}_z \qquad \text{since } [\hat{I}_z, \hat{A}_0] = 0$$

$$= \frac{1}{2}\{(-2\hat{I}^2 + 1)\hat{I}_z + 2\hat{I}_z^3\} + \sqrt{6}\left(\frac{1}{\sqrt{6}}\right)(I_{+1}I_{-1} + 2I_0^2 + I_{-1}I_{+1})\hat{I}_z$$

$$= \frac{1}{2}\{(-2\hat{I}^2 + 1)\hat{I}_z + 2\hat{I}_z^3\} + \cancel{2}(-\frac{1}{2}\hat{I}_+\hat{I}_- + 2\hat{I}_z^2 - \frac{1}{2}\hat{I}_-\hat{I}_+)\hat{I}_z$$

$$= \frac{1}{2}\{(-2\hat{I}^2 + 1)\hat{I}_z + 2\hat{I}_z^3\} + [-\frac{1}{2}(\hat{I}^2 - \hat{I}_z^2 - \hat{I}_z + \hat{I}^2 - \hat{I}_z^2 + \hat{I}_z) + 2\hat{I}_z^2]\hat{I}_z$$

$$= \frac{1}{2}\{(-2\hat{I}^2 + 1)\hat{I}_z + 2\hat{I}_z^3\} + [-\hat{I}^2 + 3\hat{I}_z^2]\hat{I}_z$$

$$= (-2I^2 + \frac{1}{2})\hat{I}_z + 4\hat{I}_z^3$$

$$[[\hat{I}_0, \hat{A}_{-1}], \hat{A}_{+1}] = -\left\{(-2\hat{I}^2 + \tfrac{1}{2})\hat{I}_z + 4\hat{I}_z^3\right\}$$
$$= \left\{2I(I+1) - \tfrac{1}{2}\right\}\hat{I}_z - 4\hat{I}_z^3$$

(c) $m = 0$

$$[[\hat{I}_0, \hat{A}_0], \hat{A}_0] = 0$$

(d) $m = -1$

$$[[\hat{I}_0, \hat{A}_{+1}], \hat{A}_{-1}] = [\hat{A}_{+1}, \hat{A}_{-1}] = -[\hat{A}_{-1}, \hat{A}_{+1}]$$
$$= \left\{2I(I+1) - \tfrac{1}{2}\right\}\hat{I}_z - 4\hat{I}_z^3$$

(e) $m = -2$

$$[[\hat{I}_0, \hat{A}_{+2}], \hat{A}_{-2}] = 2[\hat{A}_{+2}, \hat{A}_{-2}] = -2[\hat{A}_{-2}, \hat{A}_{+2}]$$
$$= \left\{4I(I+1) - 2\right\}\hat{I}_z - 4\hat{I}_z^3$$

2. $[[\hat{I}_{+1}, \hat{A}_{-m}], \hat{A}_m]$

$$= -\frac{1}{\sqrt{2}}[[\hat{I}_+, \hat{A}_{-m}], \hat{A}_m]$$
$$= -\sqrt{\frac{6 - m(m-1)}{2}}\,[\hat{A}_{-m+1}, \hat{A}_m]$$

(a) $m = +2$

$$[\hat{A}_{-1}, \hat{A}_{+2}] = \tfrac{1}{2}[\hat{I}_-\hat{I}_z + \hat{I}_z\hat{I}_-, \hat{A}_{+2}] =$$
$$= \tfrac{1}{2}\left(\hat{I}_-[\hat{I}_z, \hat{A}_{+2}] + [\hat{I}_-, \hat{A}_{+2}]\hat{I}_z + \hat{I}_z[\hat{I}_-, \hat{A}_{+2}] + [\hat{I}_z, \hat{A}_{+2}]\hat{I}_-\right)$$
$$= \tfrac{1}{2}\left(2\hat{I}_-\hat{A}_{+2} + 2\hat{A}_{+1}\hat{I}_z + 2\hat{I}_z\hat{A}_{+1} + 2\hat{A}_{+2}\hat{I}_-\right)$$
$$= \tfrac{1}{2}\hat{I}_-\hat{I}_+^2 + \tfrac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{I}_0 + \hat{I}_0\hat{I}_{+1})\hat{I}_z + \frac{\hat{I}_z}{\sqrt{2}}(\hat{I}_{+1}\hat{I}_0 + \hat{I}_0\hat{I}_{+1}) + \tfrac{1}{2}I_+^2 I_-$$
$$= \tfrac{1}{2}\hat{I}_-\hat{I}_+^2 + \tfrac{1}{2}\hat{I}_+^2\hat{I}_- - \tfrac{1}{2}(\hat{I}_+\hat{I}_z^2 + 2\hat{I}_z\hat{I}_+\hat{I}_z + \hat{I}_z^2\hat{I}_+)$$
$$= \tfrac{1}{2}(\hat{I}^2 - \hat{I}_z^2 - \hat{I}_z)\hat{I}_+ + \tfrac{1}{2}\hat{I}_+(\hat{I}^2 - \hat{I}_z^2 + \hat{I}_z) - \tfrac{1}{2}(\hat{I}_+\hat{I}_z^2 + \hat{I}_z^2\hat{I}_+)$$
$$- \tfrac{1}{2}\left(\hat{I}_+\hat{I}_z^2 + [\hat{I}_z, \hat{I}_+]\hat{I}_z + \hat{I}_z^2\hat{I}_+ - \hat{I}_z[\hat{I}_z, \hat{I}_+]\right)$$
$$= \hat{I}^2\hat{I}_+ - \tfrac{1}{2}(\hat{I}_z^2\hat{I}_+ + \hat{I}_+\hat{I}_z^2) - \tfrac{1}{2}(\hat{I}_z\hat{I}_+ - \hat{I}_+\hat{I}_z) - \tfrac{1}{2}(\hat{I}_+\hat{I}_z^2 + \hat{I}_z^2\hat{I}_+)$$
$$- \tfrac{1}{2}(\hat{I}_+\hat{I}_z^2 + \hat{I}_z^2\hat{I}_+) - \tfrac{1}{2}(I_+I_z - I_zI_+)$$

$$[\hat{A}_{-1}, \hat{A}_{+2}] = \hat{I}^2 \hat{I}_+ - \frac{3}{2}(\hat{I}_+\hat{I}_z^2 + \hat{I}_z^2\hat{I}_+)$$

$$\begin{aligned}
\hat{I}_z^2 \hat{I}_+ &= \hat{I}_+ \hat{I}_z^2 + [\hat{I}_z^2, \hat{I}_+] \\
&= \hat{I}_+ \hat{I}_z^2 + \hat{I}_z[\hat{I}_z, \hat{I}_+] + [\hat{I}_z, \hat{I}_+]\hat{I}_z \\
&= \hat{I}_+\hat{I}_z^2 + \hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z \\
&= \hat{I}_+\hat{I}_z^2 + \hat{I}_+\hat{I}_z + [\hat{I}_z, \hat{I}_+] + \hat{I}_+\hat{I}_z \\
&= \hat{I}_+\hat{I}_z^2 + 2\hat{I}_+\hat{I}_z + \hat{I}_+
\end{aligned}$$

$$[\hat{A}_{-1}, \hat{A}_{+2}] = \hat{I}_+ \left\{ \hat{I}^2 - 3\hat{I}_z^2 - 3\hat{I}_z - \frac{3}{2} \right\}$$

$$\begin{aligned}
[[\hat{I}_{+1}, \hat{A}_{-2}], \hat{A}_{+2}] &= -\sqrt{\frac{6-2}{2}}\, \hat{I}_+ \left\{ \hat{I}^2 - 3\hat{I}_z^2 - 3\hat{I}_z - \frac{3}{2} \right\} \\
&= \hat{I}_{+1} \left\{ 2\hat{I}^2 - 6\hat{I}_z^2 - 6\hat{I}_z - 3 \right\}
\end{aligned}$$

(b) $m = +1$

$$\begin{aligned}
[\hat{A}_0, \hat{A}_{+1}] &= -[\hat{A}_{+1}, \hat{A}_0] = -\left[\tfrac{1}{\sqrt{2}}(\hat{I}_{+1}\hat{I}_0 + \hat{I}_0\hat{I}_{+1}), \hat{A}_0\right] \\
&= \frac{1}{2}[\hat{I}_+\hat{I}_z + \hat{I}_z\hat{I}_+, \hat{A}_0] \\
&= \frac{1}{2}\left([\hat{I}_+, \hat{A}_0]\hat{I}_z + \hat{I}_+[\hat{I}_z, \hat{A}_0] + [\hat{I}_z, \hat{A}_0]\hat{I}_+ + \hat{I}_z[\hat{I}_+, \hat{A}_0]\right) \\
&= \frac{\sqrt{6}}{2}\hat{A}_{+1}\hat{I}_z + 0 + 0 + \frac{\sqrt{6}}{2}\hat{I}_z\hat{A}_{+1} \\
&= \frac{\sqrt{6}}{2}\left(\frac{-1}{\sqrt{2}}\right)\left(\hat{I}_+\hat{I}_z^2 + \hat{I}_z\hat{I}_+\hat{I}_z + \hat{I}_z\hat{I}_+\hat{I}_z + \hat{I}_z^2\hat{I}_+\right) \\
&= -\frac{\sqrt{3}}{2}\left(\hat{I}_+\hat{I}_z^2 + 2\hat{I}_+\hat{I}_z^2 + 2[\hat{I}_z, \hat{I}_+]\hat{I}_z + \hat{I}_+\hat{I}_z^2 + [\hat{I}_z^2, \hat{I}_+]\right) \\
&= -\frac{\sqrt{3}}{2}\left(4\hat{I}_+\hat{I}_z^2 + 2\hat{I}_+\hat{I}_z + \hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z\right) \\
&= -\frac{\sqrt{3}}{2}\left(4\hat{I}_+\hat{I}_z^2 + 4\hat{I}_+\hat{I}_z + [\hat{I}_z, \hat{I}_+]\right) \\
&= -\frac{\sqrt{3}}{2}\hat{I}_+\left(4\hat{I}_z^2 + 4\hat{I}_z + 1\right) \\
&= +\frac{\sqrt{3}}{2}\hat{I}_{+1}\left(4\hat{I}_z^2 + 4\hat{I}_z + 1\right)
\end{aligned}$$

$$\begin{aligned}
[[\hat{I}_{+1}, \hat{A}_{-1}], \hat{A}_{+1}] &= -\sqrt{\frac{6}{2}}\,[\hat{A}_0, \hat{A}_{+1}] \\
&= -\frac{3}{2}\hat{I}_{+1}\left(4\hat{I}_z^2 + 4\hat{I}_z + 1\right) = -\hat{I}_{+1}\left\{6\hat{I}_z^2 + 6\hat{I}_z + \frac{3}{2}\right\}
\end{aligned}$$

(c) $m = 0$

$$[\hat{A}_{+1}, \hat{A}_0] = -[\hat{A}_0, \hat{A}_{+1}] = -\frac{\sqrt{3}}{2}\,\hat{I}_{+1}\,(4 I_z^2 + 4 I_z + 1)$$

$$[[\hat{I}_{+1}, \hat{A}_0], \hat{A}_0] = -\sqrt{\frac{6}{2}}\,[\hat{A}_{+1}, \hat{A}_0]$$
$$= +\,\hat{I}_{+1}\left\{6\hat{I}_z^2 + 6\hat{I}_z + \frac{3}{2}\right\}$$

(d) $m = -1$

$$[\hat{A}_{+2}, \hat{A}_{-1}] = -[\hat{A}_{-1}, \hat{A}_{+2}] = -\hat{I}_+\left\{\hat{I}^2 - 3\hat{I}_z^2 - 3\hat{I}_z - \frac{3}{2}\right\}$$

$$[[\hat{I}_{+1}, \hat{A}_{+1}], \hat{A}_{-1}] = -\sqrt{\frac{6-2}{2}}\,[\hat{A}_{+2}, \hat{A}_{-1}]$$
$$= -\hat{I}_{+1}\left\{2I(I+1) - 6\hat{I}_z^2 - 6\hat{I}_z - 3\right\}$$

(e) $m = -2$

$$[[\hat{I}_{+1}, \hat{A}_{+2}], \hat{A}_{-2}] = 0$$

## Calculation of Relaxation Rates for Quadrupolar Interactions

(a) $1/T_1$

$$\frac{d\langle I_0\rangle}{dt} = -\frac{i}{\hbar}\,\mathrm{Tr}\left\{[\hat{I}_0, \hat{\mathcal{H}}_0]\hat{\rho}(t)\right\}$$
$$-\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\,\mathrm{Tr}\left\{[[\hat{I}_0, \hat{A}_{-m}], \hat{A}_{+m}]\hat{\rho}(t)\right\}$$

The second term is the relaxation term:

$$-\frac{1}{2}\Big[J_0(0)\,\mathrm{Tr}\left\{[[\hat{I}_0, \hat{A}_0], \hat{A}_0]\hat{\rho}(t)\right\} - J_1(\omega_0)\,\mathrm{Tr}\left\{[[\hat{I}_0, \hat{A}_{-1}], \hat{A}_{+1}]\hat{\rho}(t)\right\}$$
$$- J_1(\omega_0)\,\mathrm{Tr}\left\{[[\hat{I}_0, \hat{A}_{+1}], \hat{A}_{-1}]\hat{\rho}\right\} + J_2(2\omega_0)\,\mathrm{Tr}\left\{[[\hat{I}_0, \hat{A}_{-2}], \hat{A}_{+2}]\hat{\rho}(t)\right\}$$
$$+ J_2(2\omega_0)\,\mathrm{Tr}\left\{[[\hat{I}_0, \hat{A}_{+2}], \hat{A}_{+2}]\hat{\rho}(t)\right\}\Big]$$

$$= -\frac{1}{2}\Big\{J_0(0)\,(0) - J_1(\omega_0)\Big([4I(I+1) - 1]\,\mathrm{Tr}\{\hat{I}_0\hat{\rho}(t)\} - 8\,\mathrm{Tr}\{\hat{I}_z^3\hat{\rho}(t)\}\Big)$$
$$+ J_2(2\omega_0)\Big([8I(I+1) - 4]\,\mathrm{Tr}\{\hat{I}_0\hat{\rho}(t)\} - 8\,\mathrm{Tr}\{\hat{I}_z^3\hat{\rho}(t)\}\Big)$$

$$= -\frac{1}{2}\langle I_0\rangle\Big\{[8I(I+1) - 4]\,J_2(2\omega_0) - [4I(I+1) - 1]\,J_1(\omega_0)\Big\}$$
$$-4\langle I_0^3\rangle\Big\{J_1(\omega_0) - J_2(2\omega_0)\Big\}$$

Clearly, unless we are in the limit of extreme narrowing where $J_m(\omega_m) \equiv J_0(0)$, we do not obtain a Bloch equation for $\hat{I}_z$. In the limit of extreme narrowing

$$\frac{1}{T_1} = \{[4I(I+1)-2] - [2I(I+1)-\tfrac{1}{2}]\} J_0(0)$$

$$= [2I(I+1) - 3/2] J_0(0) = \tfrac{1}{2}[\cancel{4}I^2 + \cancel{4}I - 3] J_0(0)$$

$$= \tfrac{1}{2}(2I-1)(2I+3) J_0(0)$$ (see pg 29 for $J_m(\omega)$)

$$= \frac{(e^2qQ/\hbar)^2 (2I+3)}{160\ I^2(2I-1)} \Big\{ 2\left[\tfrac{3}{2}\sin^2\theta + \tfrac{\eta}{2}(1+\cos^2\theta)\right]^2 (2\tau_\theta^{(2,2)}) + 2\left[-3\sin\theta\cos\theta + \eta\sin\theta\cos\theta\right]^2 (2\tau_\theta^{(2,1)}) + \tfrac{3}{2}\left[3\cos^2\theta - 1 + \eta\sin^2\theta\right]^2 (2\tau_\theta^{(2,0)}) \Big\}$$

$$= \frac{3(e^2qQ/\hbar)^2(2I+3)}{40\ I^2(2I-1)} \Big\{ \tfrac{3}{4}\left[\sin^2\theta + \tfrac{\eta}{3}(1+\cos^2\theta)\right]^2 \tau_\theta^{(2,2)} + 3\left[-\sin\theta\cos\theta + \tfrac{\eta}{3}\sin\theta\cos\theta\right]^2 \tau_\theta^{(2,1)} + \tfrac{1}{4}\left[3\cos^2\theta - 1 + \eta\sin^2\theta\right]^2 \tau_\theta^{(2,0)} \Big\}$$

For isotropic reorientation where

$$\tau_\theta^{(2,k)} = \tau_\theta \quad \text{for } k = 0, 1, 2$$

$$\frac{1}{T_1} = \frac{3(e^2qQ/\hbar)^2(2I+3)}{40\ I^2(2I-1)}\ \tau_\theta\ (1 + \eta^2/3)$$

which is Abragam's Eq (137), pg. 314.

Note that, for the special case $I = 1$,

$$\hat{I}_z^3 = \hat{I}_z$$

(i.e. $\hat{I}_z^3$ has the same matrix representation as $\hat{I}_z$ does), hence we do observe a Bloch decay even in the slow motion limit.

Here

$$\left(\frac{1}{T_1}\right)_{I=1} = \frac{1}{2}\left\{[8(1)(1+1)-4]\,J_2(2\omega_0) - [4I(I+1)-1]\,J_1(\omega_0)\right\} + 4\left\{J_1(\omega_0) - J_2(2\omega_0)\right\}$$

$$= 2J_2(2\omega_0) + \tfrac{1}{2}J_1(\omega_0)$$

Now
$$J_m(\omega) = \frac{[e^2qQ/\hbar]^2}{80I^2(2I-1)^2}\left\{2\left[\tfrac{3}{2}\sin^2\theta + \tfrac{\eta}{2}(1+\cos^2\theta)\right]^2 \frac{2\tau_\theta^{(2,2)}}{1+\omega^2[\tau_\theta^{(2,2)}]^2} + 2\left[-3\sin\theta\cos\theta + \eta\sin\theta\cos\theta\right]^2 \frac{2\tau_\theta^{(2,1)}}{1+\omega^2[\tau_\theta^{(2,1)}]^2} + \frac{3}{2}\left[3\cos^2\theta - 1 + \eta\sin^2\theta\right]^2 \frac{2\tau_\theta^{(2,0)}}{1+\omega^2[\tau_\theta^{(2,0)}]^2}\right\}$$

$$= \frac{3[e^2qQ/\hbar]^2}{40I^2(2I-1)^2}\left\{\frac{3}{4}\left[\sin^2\theta + \frac{\eta}{3}(1+\cos^2\theta)\right]^2 \frac{2\tau_\theta^{(2,2)}}{1+\omega^2[\tau_\theta^{(2,2)}]^2} + 3\left[\sin\theta\cos\theta - \frac{\eta}{3}\sin\theta\cos\theta\right]^2 \frac{2\tau_\theta^{(2,1)}}{1+\omega^2[\tau_\theta^{(2,1)}]^2} + \frac{1}{4}\left[3\cos^2\theta - 1 + \eta\sin^2\theta\right]^2 \frac{2\tau_\theta^{(2,0)}}{1+\omega^2[\tau_\theta^{(2,0)}]^2}\right\}$$

$$= \frac{3[e^2qQ/\hbar]^2}{40}\,\mathcal{J}(\omega)$$

Then
$$\left(\frac{1}{T_1}\right)_{I=1} = \frac{3[e^2qQ/\hbar]^2}{80}\left\{4\mathcal{J}(2\omega_0) + \mathcal{J}(\omega_0)\right\}$$

This is essentially Abragam's Eq. (136), pg 314.

(b) $1/T_2$

$$\frac{d\langle I_{+1}\rangle}{dt} = -\frac{i}{\hbar}\,\mathrm{Tr}\left\{[\hat{I}_{+1},\hat{\mathcal{H}}_0]\,\rho(t)\right\} - \frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\,\mathrm{Tr}\left\{[[\hat{I}_{+1},\hat{A}_{-m}],\hat{A}_m]\,\hat{\rho}(t)\right\}$$

The relaxation term is

$$-\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)\,\mathrm{Tr}\left\{[[\hat{I}_{+1},\hat{A}_{-m}],\hat{A}_{+m}]\,\hat{\rho}(t)\right\}$$

$$= -\frac{1}{2}\Big[(-1)^2 J_2(2\omega_0)\,\mathrm{Tr}\left\{\hat{I}_{+1}\left(2I(I+1)-6\hat{I}_z^2-6\hat{I}_z-3\right)\hat{\rho}(t)\right\}$$
$$+ (-1)^1 J_1(\omega_0)\,\mathrm{Tr}\left\{-\hat{I}_{+1}\left(6I_z^2+6\hat{I}_z+\tfrac{3}{2}\right)\hat{\rho}(t)\right\}$$
$$+ (-1)^0 J_0(0)\,\mathrm{Tr}\left\{\hat{I}_{+1}\left(6\hat{I}_z^2+6\hat{I}_z+\tfrac{3}{2}\right)\hat{\rho}(t)\right\}$$
$$+ (-1)^1 J_1(\omega_0)\,\mathrm{Tr}\left\{-\hat{I}_{+1}\left(2I(I+1)-6\hat{I}_z^2-6\hat{I}_z-3\right)\hat{\rho}(t)\right\}\Big]$$

$$= -\frac{1}{2}\Big[\langle\hat{I}_{+1}\rangle\Big([2I(I+1)-3]J_2(2\omega_0)+\tfrac{3}{2}J_1(\omega_0)+\tfrac{3}{2}J_0(0) + [2I(I+1)-3]J_1(\omega_0)\Big)$$
$$+ \langle\hat{I}_{+1}\hat{I}_z^2\rangle\Big(-6J_2(2\omega_0)+6J_1(\omega_0)+6J_0(0)-6J_1(\omega_0)\Big)$$
$$+ \langle\hat{I}_{+1}\hat{I}_z\rangle\Big(-6J_2(2\omega_0)+6J_1(\omega_0)+6J_0(0)-6J_1(\omega_0)\Big)\Big]$$

Clearly one does not in general have Bloch decays, but in the extreme narrowing limit where $J_m(\omega) \equiv J_0(0)$

$$\frac{1}{T_2} = \tfrac{1}{2}\left[2I(I+1)-3+\tfrac{3}{2}\right]J_0(0) = \frac{1}{2}\left[4I^2+4I-3\right]J_0(0)$$
$$= \frac{1}{2}(2I-1)(2I+3)\,J_0(0)$$
$$\equiv \frac{1}{T_1} \quad \text{as one might expect!!}$$

For the <u>special case of $I=1$</u>

$$\underset{\sim}{I}_+ = \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \quad \underset{\sim}{I}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \hat{I}_z^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\underset{\sim}{I}_+ \underset{\sim}{I}_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \hat{I}_+ \hat{I}_z^2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}$$

so one obtains Bloch decay even in the slow motion cases

and

$$\left(\frac{1}{T_2}\right)_{I=1} = \frac{1}{2}\Big[\big(2(1)(1+1)-3\big) J_2(2\omega_0) + \big(2(1)(1+1)-3+\tfrac{3}{2}\big) J_1(\omega_0) + \tfrac{3}{2} J_0(0)\Big]$$

$$= \frac{1}{2}\Big[J_2(2\omega_0) + \frac{5}{2} J_1(\omega_0) + \frac{3}{2} J_0(0)\Big]$$

$$= \frac{1}{4}\Big[2 J_2(2\omega_0) + 5 J_1(\omega_0) + 3 J_0(0)\Big]$$

$$= \frac{3\,[e^2 qQ/\hbar]^2}{160}\Big[2\, \mathcal{J}(2\omega_0) + 5\, \mathcal{J}(\omega_0) + 3\, \mathcal{J}(0)\Big]$$

which is Abragam's Eqn (139), pg 315.

In high resolution NMR,

(A) Hamiltonian $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1(t)$

time independent (~~tensor~~ high resolution) ; time-dependent (relaxation).

Time dependence is due to rotation & translation.

(In an inhomogeneous field), due to translation, Larmor freq. changes. – time-dependence.)

page ②. $\hat{\mathcal{H}}|\Psi\rangle = i\hbar \frac{\partial}{\partial t}|\Psi\rangle$

$|\Psi(t)\rangle = \sum_n c_n(t)|n\rangle$ time dependence in the coefficients ie $= \Sigma\, |n\rangle\langle n|\Psi(t)\rangle$

Ensemble average of an observable.

$$\bar{M}(t) = \sum_{m,n} \overline{c_m^*(t)c_n(t)}\, \langle m|\hat{M}|n\rangle$$

(usually eigen fns (states) of the time independent $\mathcal{H}_0$ – 99% of the is the case).

we define $\hat{\rho}_{n,m}(t) = \overline{c_m(t)\,c_n^*(t)}$ & this leads to

$$\bar{M}(t) = \sum_{n,m} \langle n|\hat{\rho}(t)|m\rangle\langle m|\hat{M}|n\rangle$$

$$= \sum_n \langle n|\hat{\rho}(t)\hat{M}|n\rangle = \text{Trace}(\underset{\sim}{\rho}(t)\,\underset{\sim}{M})$$

$$= \sum_n \langle n|\hat{M}\hat{\rho}(t)|n\rangle = \text{Trace}(\underset{\sim}{M}\,\underset{\sim}{\rho}(t))$$

5/6/7

$W_{k\to m} = \dfrac{d\langle m|\hat\rho|m\rangle}{dt}$ which is just the rate of $|k\rangle \to |m\rangle$ transitions.

$$\langle m|\hat\rho^*(t)|m\rangle = \langle m|\underbrace{e^{\frac{i\mathcal{H}_0 t}{\hbar}}}_{\text{a op.}}\,\hat\rho(t)\, e^{-\frac{i\hat{\mathcal{H}}_0 t}{\hbar}}|m\rangle$$

$$= \langle m|\cancel{e^{\frac{iE_m t}{\hbar}}}\,\hat\rho(t)\,\cancel{e^{-\frac{iE_m t}{\hbar}}}|m\rangle$$

$$= \langle m|\hat\rho(t)|m\rangle.$$

In general

$\Rightarrow$ Always $\langle n|\hat\rho^*(0)|m\rangle \equiv \langle n|\hat\rho(0)|m\rangle = \delta_{k,n}\delta_{k,m}$.

$\hat{\mathcal{H}}_1(t)$ is a random fn of time.

Page ⑦ - In the time scale of the perturbation. $\rho$ changes ~~slow~~ slowly (& fairly smoothly) ~~but~~ but at the same time $\hat{\mathcal{H}}_1(t)$ is changing very ~~fastly~~ rapidly ~~&~~ randomly.

Hence we are going to take an average value of $\hat{\mathcal{H}}_1(t)$ - i.e. ensemble average of $\hat{\mathcal{H}}_1(t)$

Under Stationary Random Process

$$\overline{\hat{\mathcal{H}}_1(t)} = 0 \quad \text{for all } t.$$

(if $\neq 0$, then separation of $\hat{\mathcal{H}}$ into time dependent & time independent parts is incorrect.)

⑧: For $\tau \ll \tau_c$ $\quad G_{mk}(\tau) \cong \overline{|\langle m|\hat{\mathcal{H}}_1(0)|k\rangle|^2}$

For $\tau \gg \tau_c$ $\quad G_{mk}(\tau) \cong \overline{\langle m|\hat{\mathcal{H}}_1(\tau)|k\rangle}\;\overline{\langle k|\hat{\mathcal{H}}_1(0)|m\rangle}$

(two averages are completely independent).

09.03.04.

$$\hat{\mathcal{H}}_1(t) = -\gamma\hbar \sum_q H_q(t)\, \hat{I}_q \quad \text{~ fluctuating field.}$$

$$\hat{\mathcal{H}}_0 = -\gamma\hbar\, \omega_0 \hat{I}_z$$

transition probability,

$$W_{k\to m} = \frac{dp_{mm}}{dt} = \gamma^2 \int_{-\infty}^{\infty} d\tau\, \overline{\sum_{q,q'} H_q(0)\, H_{q'}(\tau)} \, \langle k|\hat{I}_q|m\rangle\langle m|\hat{I}_{q'}|k\rangle\, e^{-i\,\text{system time}}$$

Assume $H_x, H_y, H_z$ are uncorrelated.

$$= \gamma^2 \sum_q \int_{-\infty}^{\infty} d\tau\, \overline{H_q(0)\, H_{q'}(\tau)}\; |\langle k|\hat{I}_q|m\rangle|^2.$$

restricting $H$ to values of $+q$ & $-q$,

$H_q$
$+h \quad P_+(0) = 1/2$
$-h \quad P_-(0) = 1/2$

$$g_{qq}(\tau) = \overline{H_q(0)\, H_q(\tau)}$$

Conditional probability that a given site had that time 0 & $+h$ at time $\tau$.

$$= (+h)(P_+(0))\{(+h)P_{++}(\tau) + (-h)P_{+-}(\tau)\}$$

$$(-h)(P_-(0))\{(+h)P_{-+}(\tau) + (-h)P_{--}(\tau)\}$$

$\approx 1/2$

$$= \frac{h^2}{2}\{P_{++}(\tau) + P_{--}(\tau) - P_{+-}(\tau) - P_{-+}(\tau)\}$$

We going to look at the problem as a "kinetics" problem at time t we expect $\frac{d}{dt} P_+(t) = -k P_+ + k P_-$

$$\frac{d}{dt} P_-(t) = -k P_- + k P_+$$

$\frac{d}{dt}(P_+(t) + P_-(t)) = 0$ $\Rightarrow$ $P_+(t) + P_-(t)$ constant.

$\therefore$ $P_+(t) + P_-(t) = P_+(0) + P_-(0) = 1$ ← normalized ~~constants~~ population.

Sub. $\frac{d(P_+ - P_-)}{dt} = -2k(P_+ - P_-)$

$\therefore$ $P_+ - P_- = (P_+(0) - P_-(0))\, e^{-2kt}$

For a system initially in the "+" state

$P_+(0) = 1 \quad P_-(0) = 0$

$P_+(t) \equiv P_{++}(t)$ and $P_-(t) = P_{+-}(t)$.

$\therefore$ $P_{++}(t) = \frac{1}{2} + \frac{1}{2} e^{-k\tau}$ at long times $\to \frac{1}{2}$.

Doing that the same analysis at initial "−" state $P_{--}(t)$ and $P_{-+}(t)$ can be found.

$\therefore$ $g_{qq}(\tau) = h^2 e^{-2k\tau}$.

correlation time $g_{qq}(\tau) = \langle h^2\rangle e^{-\tau/\tau_c}$ $\tau_c = \frac{1}{2k}$.

This leads to,

$$w_{k\to m} = \frac{2h^2\tau_c}{1+\omega_{km}^2\tau_c^2}\sum_q |\langle m|\hat{S}_q|k\rangle|^2$$

$$\therefore \frac{1}{T_1} = 2\,w_{\frac{1}{2}\to-\frac{1}{2}}$$

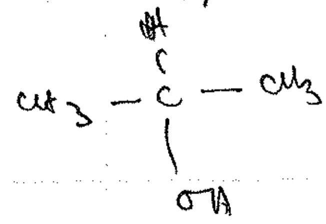
(for $\frac{1}{2}, -\frac{1}{2}$ case)

$$w_{\frac{1}{2}\to-\frac{1}{2}} = w_{-\frac{1}{2}\to\frac{1}{2}}$$

our spin I

I experiencing a field. $\frac{J\vec{S}}{\gamma}$ have values $\pm\frac{1}{2}\frac{J}{\gamma}$

eg



exchangeable $^1H$

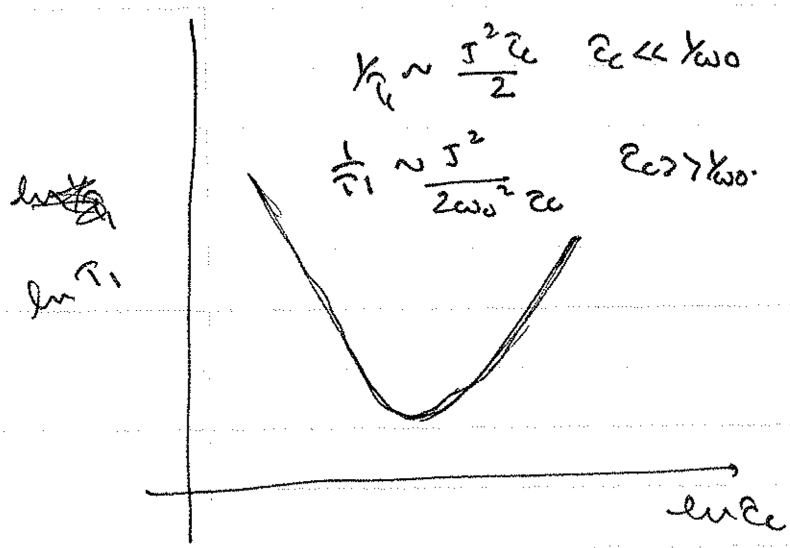
to convert radians $s^{-1}$ to Gauss.

$h = J/2\gamma$

Then.

$$w_{\frac{1}{2}\to-\frac{1}{2}} = \frac{J^2\tau_c}{4(1+\omega_0^2\tau_c^2)}.$$

$$\therefore 1/T_1 = \frac{J^2\tau_c}{2(1+\omega_0^2\tau_c^2)}$$




$1/T_1 \sim \frac{J^2\tau_c}{2}$ $\quad \tau_c \ll 1/\omega_0$

$\frac{1}{T_1} \sim \frac{J^2}{2\omega_0^2\tau_c}$ $\quad \tau_c \gg 1/\omega_0$.

This type of exchange relaxation is valid for $T_1 \gg \Delta t \gg \tau_c$

Before page 05/. suppose 2nd order eqn (P. Kners) holds for $0 \le t \le \Delta t$.

---

Refer spherical Tensor operators.

03.8A. page (16). $\hat{A}_{lm}$ spin operators (like $I_0$, $\hat{I}_{\pm 1}$, $I_z$
or dipolar interaction $T_{2,2} = I_{+1}^2$
$T_{2,1} = I_{+1}I_0 + I_0 I_{+1}$

($\hbar$ in front to remove $1/\hbar^2$ in $d\rho^*/dt$).

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \sum_m \sum_{m'} \overline{[[\hat{\rho}^*(t), (-1)^m \hbar f_{l,m}(t)\hat{A}^*_{l,m}(t)], (-1)^{m'}\hbar f_{l,-m}(t+\tau)\hat{A}^*_{l,m'}(t+\tau)]}$$

$\Rightarrow$ ($\hbar$) inside.

In general $\langle p | A^*_{l,m}(t) | q\rangle = \langle p | \exp(+i\frac{\mathcal{H}_0 t}{\hbar})\hat{A}_{lm}\exp(-i\frac{\mathcal{H}_0 t}{\hbar}) | q\rangle$

$$= \exp\frac{iE_p t}{\hbar}\langle p|\hat{A}_{lm}|q\rangle \exp -\frac{iE_q t}{\hbar}$$

$$= \langle p|\hat{A}_{lm}|q\rangle \exp i\omega_{qp}t \qquad \omega_{qp} = (E_p - E_q)/\hbar$$

$$= \delta_{p,q+m}\langle q+m|\hat{A}_{lm}|q\rangle \exp i\frac{(E_{q+m} - E_q)}{\hbar}t$$

$$= \langle p|\hat{A}_{lm}|q\rangle \exp(i\omega_m t)$$

$$\frac{d\rho^*}{dt} = -\int_0^\infty d\tau \sum_m (-1)^m g_m(\tau)\exp(i\omega_m t)\exp(-i\omega_m t) \times [[\hat{\rho}^*(t), \hat{A}_{lm}], \hat{A}_{l,-m}]$$

from $-m$ $\frac{E_{q-m} - E_q}{\hbar}$.

$$J_m(\omega_m) = \frac{1}{2}\int_{-\infty}^{\infty} g_m(\tau)\exp(-i\omega_m\tau)\,d\tau$$

$$\boxed{\frac{d\rho^*}{dt} = -\frac{1}{2}\sum_m (-1)^m J_m(\omega_m)[[\hat{\rho}^*(t), \hat{A}_{l,m}], \hat{A}_{l,-m}]}$$

A. Master equation - of motion.

Bloch eqns: $\frac{d\langle M_x\rangle}{dt} = \omega_0\langle M_y\rangle - \langle M_x\rangle/T_2$

$$\frac{d\langle M_y\rangle}{dt} = -\omega_0\langle M_x\rangle - \langle M_y\rangle/T_2.$$

$$\frac{d\langle M_z\rangle}{dt} = -\left(\langle M_z\rangle - M_0\right)/T_1$$

page (19)

Simple case: $\hat{\mathcal{H}}_0 = -\hbar\omega_0\hat{I}_z = -\hbar\omega_0\hat{I}_0$

$\hat{\mathcal{H}}_{(t)}(t) = -\gamma\hbar\sum_m(-1)^m \underline{H}_{-m}(t)\,\hat{I}_m.$ $\qquad$ $H_{-m}(t)$ are random functions of time.

consider eqn of motion of $\langle\hat{I}_0\rangle$ ie $\langle I_z\rangle \equiv \langle M_z\rangle/-\gamma\hbar$

$$\frac{d\langle I_0\rangle}{dt} = -\frac{i}{\hbar}\,\mathrm{Tr}\left\{\hat{I}_0[\hat{\mathcal{H}}_0,\rho]\right\} - \frac{1}{2}\sum_m(-1)^m\ldots \quad (q=0)$$

making a 1-1 correspondence between $A_{lm} \equiv I_m \quad (l=1).$

ie $F^{(t)}_{lqm} \equiv -\gamma H^{(t)}_m$

---

$J_1(\omega_0)$ in note page (20)

$\therefore \frac{d\langle\hat{I}_0\rangle}{dt} = -J_1\omega_0\langle\hat{I}_0\rangle$

ie. $\frac{d\langle M_z\rangle}{dt} = -J_1(\omega_0)\,M_z.$

ie $\frac{1}{T_1} = J_1(\omega_0)$

bottom p(24)

$$\frac{d\langle I_{+1}\rangle}{dt} = \left(-i\omega_0 - 1/T_2\right)\langle I_{+1}\rangle$$

where $\frac{1}{T_2} = \frac{1}{2}\left\{J_1(\omega_0) + J_0(0)\right\}$

$$-i\omega_0\langle I_{+1}\rangle = -i\omega_0\left\{-\frac{1}{\sqrt{2}}\langle I_x\rangle - \frac{i}{\sqrt{2}}\langle I_y\rangle\right\}$$

$$= -\frac{\omega_0}{\sqrt{2}}\langle I_y\rangle + \frac{i\omega_0}{\sqrt{2}}\langle I_x\rangle$$

$$-\frac{1}{\sqrt{2}}\frac{d\langle I_x\rangle}{dt} - \frac{i}{\sqrt{2}}\frac{d\langle I_y\rangle}{dt} = -\frac{\omega_0}{\sqrt{2}}\langle I_y\rangle + \frac{i\omega_0}{\sqrt{2}}\langle I_x\rangle + \frac{1}{\sqrt{2}T_2}\langle I_x\rangle + \frac{i}{\sqrt{2}}\frac{1}{T_2}\langle I_y\rangle$$

$$\frac{d\langle I_x\rangle}{dt} = \omega_0\langle I_y\rangle - \frac{1}{T_2}\langle I_x\rangle$$

$$\frac{d\langle I_y\rangle}{dt} = -\omega_0\langle I_x\rangle - \frac{1}{T_2}\langle I_y\rangle$$

compare w.

$$\frac{dM_x}{dt} = \omega_0 M_y - M_x/T_2$$

$$\frac{dM_y}{dt} = -\omega_0 M_x - M_y/T_2.$$

$$\frac{1}{T_1} = J_1(\omega_0) \qquad J_q(\omega) = \int_{-\infty}^{\infty} \overline{\gamma H^*_q(0)\,\gamma H_q(\tau)}\, e^{-i\omega\tau}\, d\tau.$$

$$\frac{1}{T_2} = \frac{1}{2}\left(J_1(\omega_0) + J_0(0)\right)$$

In cartesian component

$$J_1(\omega_0) = \gamma^2 \int_{-\infty}^{\infty} \overline{\left\{-\frac{1}{\sqrt{2}}\left[H_x(0) + i\,H_y(0)\right]^*\right\}\left\{-\frac{1}{\sqrt{2}}\left[H_x(\tau) + i H_y(\tau)\right]\right\}}\, e^{-i\omega_0\tau}\, d\tau.$$

$$= \frac{\gamma^2}{2}\int_{-\infty}^{\infty}\left\{\overline{H_x(0)H_x(\tau)} + \overline{H_y(0)H_y(\tau)} - \overline{i H_y(0)H_x(\tau)} + \overline{i H_x(0)H_y(\tau)}\right\} e^{-i\omega_0\tau}\, d\tau$$

($x, y$ axis independent $\approx 0$.)

$$= \frac{\gamma^2}{2}\int_{-\infty}^{\infty}\left\{|H_x(0)|^2 e^{-|\tau|/\tau_c} + |H_y(0)|^2 e^{-|\tau|/\tau_c}\right\} e^{-i\omega_0\tau}\, d\tau$$

$$= \gamma^2\left[|H_x(0)|^2 + |H_y(0)|^2\right] \tau_c/(1+\omega_0^2\tau_c^2).$$

22/.

$$J_0(0) = \int_{-\infty}^{\infty} d\tau \, \gamma H_z(0) \, \gamma H_z(\tau) = 2\gamma^2 |H_z(0)|^2 \tau_c$$

$$1/T_2 = \frac{k}{2}\left(\frac{1}{T_1}\right) + \frac{1}{T_2'}$$ ~ secular broadening.

non-secular or lifetime broadening

terms in $[\hat{H}_1, \hat{H}_0] = 0$ secular

terms $[\hat{H}_1, H_0] \neq 0$ which, non-secular.

---

(28)

$$\overline{D^{(2)*}_{mk'}[\Omega(t)] \, D^{(2)}_{mk}[\Omega(t+\tau)]} = \delta_{k'k} \, \delta_{m',m} \, \frac{e^{-|\tau|/\tau_\Theta^{(2,k)}}}{5}$$

$$= \overline{D^{(2)*}_{m'k'}[\Omega(0)] \, D^{(2)}_{mk}[\Omega(0)]} \; e^{-|\tau|/\tau_\Theta^{(2,k)}}$$ (uncorrelated exponential)

$$= \frac{1}{8\pi^2} \int d\Omega \, D^{(2)*}_{m'k'}[\Omega] \, D^{(2)}_{mk}[\Omega] \, e^{-|\tau|/\tau_\Theta^{(2,k)}}$$

$$= \frac{1}{8\pi^2} \, \frac{8\pi^2}{(5)} \, \delta_{m',m} \, \delta_{k',k} \quad \text{''}.$$ ← (Refer page 62 Ang. theory).

---

$$\overline{F^*_m(t) \, F_m(t+\tau)} = \left\{ \sqrt{6}\, \gamma \, \Delta\sigma \, D^{(2)*}_{m0}[\Omega(t)] + \gamma \, \delta\sigma \left( D^{(2)*}_{m2}[\Omega(t)] + D^{(2)}_{m,-2}[\Omega(t)] \right) \right\}$$

$$\times \left\{ \sqrt{6}\, \gamma \, \Delta\sigma \, D^{(2)}_{m0}[\Omega(t+\tau)] + \gamma \, \delta\sigma \left( D^{(2)}_{m2}[\Omega(t+\tau)] + D^{2}_{m-2}[\Omega(t+\tau)] \right) \right\}$$

$$= 6\gamma^2 \Delta\sigma^2 \frac{e^{-|\tau|/\tau_\Theta^{(2,0)}}}{5} + \gamma^2 \delta\sigma^2 e^{-\frac{|\tau|}{\tau_\Theta}(2,2)} + \gamma^2 \delta_\sigma^2 \frac{e^{-\frac{|\tau|}{\tau_\Theta}(2-2)}}{5}$$

$$\tau_\Theta^{(2,2)} = \tau_\Theta^{(2,-2)}$$ for symm. tops.

$$= \frac{2\gamma^2}{5}\left(3\Delta\sigma^2 \, e^{\frac{-|\tau|}{\tau_\theta^{(2,0)}}} + \delta\sigma^2 e^{-|\tau|/\tau_\theta^{(2,2)}}\right).$$

---

Calculation of $T_1$, $T_2$

$$\hat{\mathcal{H}}_1(t) = \hbar \sum_m (-1)^m F_m(t)\, \hat{I}_m$$

correlation f'ns.

$$F_{-1}(t) = \frac{-\gamma H_0}{\sqrt{2}}\left\{\left(\sqrt{6}\,\Delta\sigma\, \mathcal{D}^{(2)}_{+1\,0} + \delta\sigma\left(\mathcal{D}^{(2)}_{+1,2} + \mathcal{D}^{(2)}_{+1,-2}\right)\right\}\right.$$

$$F_0(t) = \gamma H_0\sqrt{\frac{2}{3}}\left\{\sqrt{6}\,\Delta\sigma\,\mathcal{D}^{(2)}_{00} + \delta\sigma\left(\mathcal{D}^{(2)}_{02} + \mathcal{D}^{(2)}_{0-2}\right)\right\}$$

$$F_{+1}(t) = \frac{-\gamma H_0}{\sqrt{2}}\left\{\sqrt{6}\,\Delta\sigma\,\mathcal{D}^{(2)}_{-1\,0} + \delta\sigma\left(\mathcal{D}^{(2)}_{-1\,2} + \mathcal{D}^{(2)}_{-1,-2}\right)\right\}$$

correlation functions.

$$\overline{F^*_{\mp1}(t)\, F_{\mp1}(t+\tau)} = \frac{\gamma^2 H_0^2}{2}\left\{\frac{6}{5}\Delta\sigma^2 \exp -|\tau|/\tau_\theta^{(2,0)} + \frac{2}{5}\delta\sigma^2 \exp -|\tau|/\tau_\theta^{(2,2)}\right.$$

$$\overline{F^*_0(t)\, F_0(t+\tau)} = \frac{2\gamma^2 H_0^2}{3}\left\{\frac{6\Delta\sigma^2}{5} e^{-|\tau|/\tau_\theta^{(2,0)}} + \frac{2}{5}\delta\sigma^2 e^{-|\tau|/\tau_\theta^{(2,2)}}\right\}$$

$$1/T_1 = J_1(\omega_0) \qquad 1/T_2 = \frac{1}{2}\left\{J_1(\omega_0) + J_0(0)\right\}$$

$$J_1(\omega_0) = \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau}\left\{C^{\gamma H_0}\right\}\left\{3\Delta\sigma^2 e^{-|\tau|/\tau_\theta^{(2,0)}} + \delta\sigma^2 e^{-|\tau|/\tau_\theta^{(3,2)}}\right\}$$

$$= \{\;\}\left\{3\Delta\sigma^2 \cdot \frac{2\tau_\theta^{(2,0)}}{1+\omega_0^2\tau_\theta^{(2,0)\,2}} + \delta\sigma^2 \cdot \frac{2\tau_\theta^{(2,2)}}{1+\omega_0^2\tau_\theta^{(2,2)\,2}}\right\}$$

$$\therefore \frac{1}{T_1} = 2\left(\frac{\gamma^2 H_0^2}{5}\right)\left\{ 3\Delta\sigma^2 \frac{\tau_\theta^{(2,0)}}{1+\omega_0^2\tau_\theta^{(2,0)^2}} + \delta\sigma^2 \frac{\tau_\theta^{(2,2)}}{1+\omega_0^2\tau_\theta^{(2,2)^2}} \right\}$$

$$\frac{1}{T_2} = \frac{\gamma^2 H_0^2}{5}\left\{ 3\Delta\sigma^2 \frac{\tau_\theta^{(2,0)}}{1+\omega_0^2\tau_\theta^{(2,0)^2}} + \delta\sigma^2 \frac{\tau_\theta^{(2,2)}}{1+\omega_0^2\tau_\theta^{(2,2)^2}} \right\}$$

$$+ \frac{4}{15}\gamma^2 H_0^2 \left\{ 3\Delta\sigma^2 \frac{\tau_\theta^{(2,0)}}{1} + \delta\sigma^2 \tau_\theta^{(2,2)} \right\}$$

0 freq ⇒ deno = 1

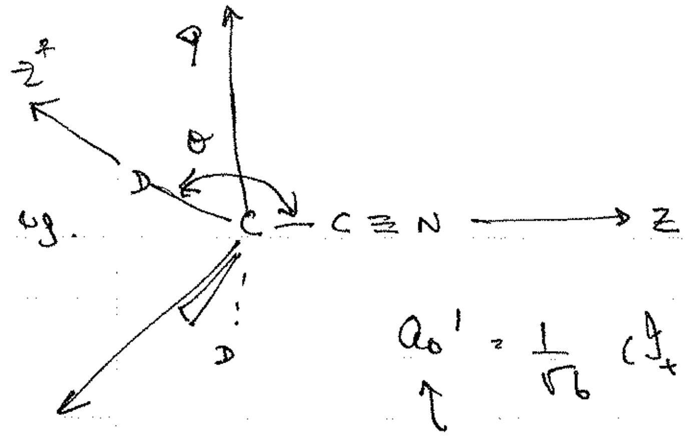
Extremely narrowing limit, $\omega_0^2 \tau_\theta^{(2,k)^2} << 1$

$$\frac{1}{T_1} = \frac{2\gamma^2 H_0^2}{5}\left\{ 3\Delta\sigma^2 \tau_\theta^{(2,0)} + \delta\sigma^2 \tau_\theta^{(2,2)} \right\}$$

$$\frac{1}{T_2} = \frac{7}{15}\gamma^2 H_0^2 \left( 3\Delta\sigma^2 \tau_\theta^{(2,0)} + \delta\sigma^2 \tau_\theta^{(2,2)} \right).$$

$$\therefore \frac{T_1}{T_2} \approx \frac{7}{6}$$

e.g.




$$a_0' = \frac{1}{\sqrt{6}}\left(f_+ f_{-1} + 2 f_0^2 + f_{-1} f_{+1}\right)$$

(in the tilted z coord-system).

Transfer ~~this~~ to the principal molecular coordinate system,

$$\hat{a}'_m = \sum_l \hat{a}_l \, D^{(2)}_{lm}[0,\theta,0]$$

$$\therefore \hat{\mathcal{H}}_Q = \frac{e^2 q Q}{4I(2I-1)} \left\{ \sqrt{6}\, a_0' + \eta\left(\hat{a}'_{+2} + \hat{a}'_{-2}\right) \right\}$$

$$= \frac{e^2 q Q}{4I(2I-1)} \sum_l \hat{a}_l \left\{ \sqrt{6}\, D^{(2)}_{l,0}[0,\theta,0] + \eta\, D^{(2)}_{l+2}[0,\theta,\theta] + \eta\, D^{(2)}_{l-2}[0,\theta,0] \right\}$$

Since the operator $\hat{a}_l$ is time dependent (only time dependence here);

Laboratory ← molecular transformation,

$$\hat{a}_l^{(t)} = \sum_{m} \hat{A}_m \, D^{(2)}_{ml}[\Omega(t)]$$

{ $\hat{A}_m$ – time independent – an operator which is quantized & its eigen f'ns are described in the laboratory).

$\Omega(t)$ = Euler angles which relate molecular to laboratory coord. at time t.

$$\therefore \doteq \frac{e^2 q Q}{4I(2I-1)}$$ (top of page 29)

From last line of p 29

if $\eta = 0$, (Spin

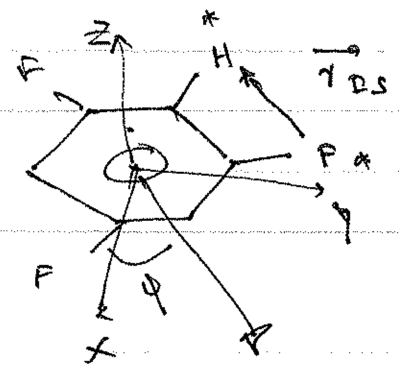
{ these results for $j$ is independent of $m$, but this is not so in chemical shift anisotropy.

$$\int_{-\infty}^{\infty} F_m^*(t)\, F_m(t+\tau)\, d\Omega = 2.(\ \ )\Big\{ \tfrac{9}{2} \sin^4\theta\, \tau_\theta^{(2,2)} + 18 \sin^2\theta \cos^2\theta\, \tau_\theta^{(2,1)} + \tfrac{3}{2}(3\cos^2\theta - 1)^2\, \tau_\theta^{(2,0)} \Big\}$$

$$= 6 \Big\{ \tfrac{3}{4} \sin^2\theta\, \tau_\theta^{(2,2)} + 3 \sin^2\theta \cos^2\theta\, \tau_\theta^{(2,1)} + \left(\frac{3\cos^2\theta - 1}{2}\right)^2 \tau_\theta^{(2,0)} \Big\}$$

$\{ \tau_{CH}$ in Wo's seminar.

Dipolar interactions




corr$^n$ fn.

$$F_{-m}^*(t)\, F_{-m}(t+\tau) = (\ \ ) \sum_{k,k'} (-1)^{k+k'}\, D_{mk}^{(2)*}[\Omega(t)]\, D_{mk'}^{(2)}[\Omega(t+\tau)] \times Y_{-k}^{(2)*}(\theta,\phi)\, Y_{-k'}^{(2)}(\theta,\phi).$$

Spectral Densities.

$$J_m(0) = \frac{2\gamma_I^2 \gamma_S^2 \hbar^2}{5 r_{IS}^6} \Big\{ \tau_\theta^{(2,0)} \left\{ \tfrac{3}{2} (3\cos^2\theta - 1)^2 \right\}$$

$$+ 2\tau_\theta^{(2,1)} \left\{ (3 \sin\theta \cdot \cos\theta)^2 \right\} \quad (\text{same for } -2, -1)$$

$$+ 2\tau_\theta^{(2,2)} \left\{ \left(-3/2 \sin^2\theta\right)^2 \right\}$$

$$= \frac{12 \gamma_I^2 \gamma_S^2 \hbar^2}{5 r_{IS}^6} \Big\{ (3\cos^2\theta - 1)^2 \tau_\theta^{(2,0)} + 3\sin^2\theta \cos^2\theta \, \tau_\theta^{(2,1)} + 3/4 \sin^4\theta \, \tau_\theta^{(2,2)} \Big\}$$

$\tau$ effective.

---

$\underline{q=0}$ For quadrupolar interactions.

$$[[\hat{I}_0, \hat{A}_{-m}], \hat{A}_m] = [-m\hat{A}_{-m}, \hat{A}_m] = -m [\hat{A}_{-m}, \hat{A}_m]$$

evaluate for $m = 2, 1, 0$

$\underline{m = +2}$

$$[\hat{A}_{-2}, \hat{A}_{+2}] = [\hat{I}_{-1}^2, \hat{A}_{+2}] = [\tfrac{1}{2} \hat{I}_-, \hat{A}_{+2}]$$

$$= \frac{1}{2} \hat{I}_- [\hat{I}_-, \hat{A}_{+2}] + \frac{1}{2} [\hat{I}_-, \hat{A}_{+2}] \hat{I}_-$$

$$= \frac{1}{2} \hat{I}_- \sqrt{2(3) - 2(1)} \, \hat{A}_{+1}$$

from the commutation rel$^n$

$$[\hat{I}_-, A_m^{(l)}] = \sqrt{l(l+1) - m(m-1)} \, A_{m-1}^{(l)} \quad (\text{Racah's def}^n)$$

$$= \hat{I}_- \hat{A}_{+1} + \hat{A}_{+1} \hat{I}_-$$

~~using I~~ Recall

$$\hat{I}_-\hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hat{I}_z$$

$$\hat{I}_+\hat{I}_- = \hat{I}^2 - \hat{I}_z^2 + \hat{I}_z$$

$$\hat{I}_-\hat{I}_z\hat{I}_+ = I_z I_- I_+ + [I_-, I_z] I_+$$

$$= I_z I_- I_+ - [I_z, I_-] I_+$$

$$= I_z I_- I_+ - (-I_-) I_+$$

$$= I_z I_- I_+ + I_- I_+$$

$$\hat{I}_+ I_z I_- = I_+ I_- I_z + I_+ [I_z, I_-]$$

$$= I_+ I_- I_z - I_+ I_-$$

Addenda. P(A).

$$I_{+1} I_{+1} |I\ M\rangle \Rightarrow |I\ \ M+2\rangle$$

for $m = 2$ $\quad J_2(\omega_2) = J_2(\omega_2) = J_2(2\omega_0) = J_2(2 \times$ larmor frequency$)$

Extreme narrowing. can $J_m(m\omega) = J_0(0)$

$$\frac{d\langle I_z\rangle}{dt} = 0 - \{2I(I+1) - 3/2\} J_0(0) \langle I_z\rangle$$

$$\therefore \frac{1}{T_1} = (2I(I+1) - 3/2) J_0(0)$$

$$= \frac{1}{2}[4I^2 + 4I - 3] J_0(0)$$

$$= \frac{1}{2}(2I-1)(2I+3) J_0(0)$$

06/04. (P 7)

$$\left.\begin{array}{l}\frac{d\langle I_q\rangle}{dt}\text{relax} \\ (1/T_2)_{relax}\end{array}\right\} = -\frac{1}{2}\sum_m (-1)^m J_m(\omega_m) \langle [\underbrace{[\hat{I}_q, \hat{A}_{-m}]}, \hat{A}_m] \rangle$$

$$\downarrow$$

$$-\frac{1}{T_2}\langle I_q\rangle$$

For dipolar interaction. (p. 9)-onwards.

"like" spins $[[I_z + S_z, A_{-m}], A_m]$

"unlike" $[[I_z, A_{-m}], A_m]$ — P21 {Add together after flipping I & S}

In unlike case $A_0 = \frac{1}{\sqrt{6}}\left\{I_{+1}S_{-1} + 2I_0S_0 + I_{-1}S_{+}\right\}$

$\downarrow$ connects states. $(\omega_I - \omega_S)$ $\quad$ 0 $\quad$ $(\omega_S - \omega_I)$ $\quad$ and ~~sim~~ silly in $A_1$ & so on

(1.14 → middle of p.12 — it is not very important).

p.(13) taking ensemble averages:

$$\langle [[\hat{I}_z + \hat{S}_z, \hat{A}_2], \hat{A}_2] \rangle = \frac{1}{2}\langle \hat{S}_z(\hat{I}_-\hat{I}_+ + \hat{I}_+\hat{I}_-)\rangle + \frac{1}{2}\langle \hat{I}_z(\hat{S}_-\hat{S}_+ + \hat{S}_+\hat{S}_-)\rangle$$

now use Abragam's approximation.

(18) Like spins $\omega_I = \omega_S = \omega_0 \Rightarrow J_2(2\omega_0)$.

In last term ⊗ remind that it is really

$$= -\frac{1}{T_1}\left\{\langle I_z + S_z\rangle - \langle I_z + S_z\rangle_0\right\}$$

density matrix at thermal equilibrium.

(note:- In Abragam book $A_m$ is not same as ours)

p. 20 unlike-spins.

$$\langle [[I_z, A_{-2}] A_{+2}] \rangle = \left( \frac{S(S+1)}{3} \langle \hat{I}_z \rangle + \frac{I(I+1)}{3} \langle \hat{S}_z \rangle \right)$$

i.e. magnetization transfer from I to S spin.

– nuclear overhauser effect.

at bottom p. 20

it should be. $-\frac{1}{T_1^{II}} \left( \langle I_z \rangle - \langle I_z \rangle_0 \right) - \frac{1}{T_1^{IS}} \left( \langle S_z \rangle - \langle S_z \rangle_0 \right)$

cross relaxation terms.

---

* I, S both spin ½ case. (from bott of p 20 – B.'s equations).

$$\frac{1}{T_1^{II}} = \frac{1}{T_1^{SS}} \qquad \frac{1}{T_1^{IS}} = \frac{1}{T_1^{SI}} = \frac{1}{2}\frac{1}{T_1^{II}}$$

$$= \frac{1}{\tau} \text{ (say)} \qquad\qquad = \frac{1}{2\tau}$$

$$\frac{d\langle I_z \rangle}{dt} = -\frac{1}{\tau} \langle I_z \rangle - \frac{1}{2\tau} \langle S_z \rangle$$

$$\frac{d\langle S_z \rangle}{dt} = -\frac{1}{2\tau} \langle I_z \rangle - \frac{1}{\tau} \langle S_z \rangle$$

$$\therefore \frac{d\vec{M}}{dt} = -\frac{1}{\tau} \begin{pmatrix} 1 & 1/2 \\ 1/2 & 1 \end{pmatrix} \vec{M}$$

now let $\vec{M} = \underset{\sim}{U}\,\vec{m}$

$$\frac{d\vec{M}}{dt} = \underset{\sim}{U}\,\frac{d\vec{m}}{dt}$$

~~$\frac{d\vec{m}}{dt} = -\frac{1}{\tau}\{U^{-1}$~~ $\qquad \frac{d\vec{m}}{dt} = \underset{\sim}{U}^{-1}\,\frac{d\vec{M}}{dt}$

$$\frac{d\vec{m}}{dt} = -\frac{1}{\tau}\left\{ U^{-1}\begin{pmatrix} 1 & 1/2 \\ 1/2 & 1 \end{pmatrix}\underset{\sim}{U} \right\}\vec{m}.$$

$$U = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \qquad U^{-1}\begin{pmatrix} 1 & 1/2 \\ 1/2 & 1 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2}\,3/2 & 1/\sqrt{2}(3/2) \\ \frac{1}{\sqrt{2}}(1/2) & 1/\sqrt{2}(-1/2) \end{pmatrix}$$

$$U^{-1} = \underset{\sim}{U}. \qquad\qquad = \begin{pmatrix} 3/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

$$\therefore \quad \frac{d}{dt}\langle I_z + S_z\rangle = -\frac{3}{2\tau}\langle I_z + S_z\rangle$$

$$+ \quad \frac{d}{dt}\langle I_z - S_z\rangle = -\frac{1}{2\tau}\langle I_z - S_z\rangle.$$

$$\therefore \langle I_z(t)\rangle + \langle S_z(t)\rangle = (\langle I_z(0)\rangle + \langle S_z(0)\rangle)\, e^{-3t/2\tau}$$

$$\underline{\quad " \;\; - \;\; " \quad} = \quad " \;\; - \;\; " \;\;)\, e^{-t/2\tau}$$

)

$+\ \langle I_z(t)\rangle$

$-\ \langle S_z(t)\rangle$

but this is not a purely exponential decay.

$\vec{F}$:

<u>spin-Rot$^n$</u>

$$\mathcal{H}_{SR} = \hbar \vec{J} \cdot \underset{\sim}{C} \cdot \hat{S}$$ (cartesians - molec. frame)

$$= \hbar\left(J_x C_{xx} S_x + J_y C_{yy} S_y + J_z C_{zz} S_z\right)$$

transform into spherical tensors: $\rightarrow$ $= \hbar \sum_k (JC)_{-k} S_k (-1)^k$ (k - molec. frame)

$$= \hbar \sum_m \sum_k (JC)_{-k} \hat{S}_m \mathcal{D}^{(1)}_{mk}[\Omega(t)](-1)^k$$ in lab fr.

$$= \hbar \sum_m (-1)^m F_{-m}(t) \hat{S}_m .$$

Ang$^r$. $\left\langle (JC)^{*}_{-k}(t)\, \mathcal{D}^{(1)*}_{mk}[\Omega(t)]\, (J_{\tau}C)_{-k'}\, \mathcal{D}^{(1)}_{mk'}[\Omega(t+\tau)] \right\rangle$

$$= \frac{1}{3} \langle I k T \rangle\, e^{-\tau/\tau_J}$$

moment of inertia.

Refer Hubbards also: $\left( \ldots e^{-\tau/\tau_J} \cdot e^{-\tau/\tau_{\theta}^{(1)}} \right)$.