Further relaxation

6.1 Introduction

As presented so far, the theory is capable of predicting the rate of transitions between energy levels *i.e.* it is concerned with populations. The theory is thus perfectly acceptable for predicting the rate constants for relaxation of longitudinal magnetization ("T_1"), but is incapable of dealing with transverse magnetization ("T_2"). To do this, it is necessary to consider the evolution of coherences under the random hamiltonian.

A convenient way of proceeding is to look at the relaxation behaviour of operators. This fits in well with the Solomon equations, an approach already used for discussing the dynamics of z-magnetization and populations. The operator method is less well suited to discussing the relaxation behaviour of individual lines, but it will be seen that with some modifications is can be adapted to this use.

This Section starts with a brief revision of the properties of operators.

6.2 Properties of operators

6.2.1 Matrix representations

Operators were introduced in Section 1.2 as the way in which observable quantities are represented in quantum mechanics. It is sometimes convenient to think of operators as matrices, and the matrix representation of an operator can be formed in a particular basis set of wavefunctions (Sections 1.2.4 and 1.7.1).

The *ij*th element (meaning the element in row i and column j) of the matrix representation of an operator A is A_{ij}, given by

$$A_{ij} = \int \phi_i^* A \phi_j \, \mathrm{d}\tau \equiv \left\langle \phi_i \left| A \right| \phi_j \right\rangle$$

where ϕ_i is a basis function. The same operator will have different matrix representations in different sets of basis functions.

If a matrix has the property that

$$A_{ji} = A_{ij}^*$$

the matrix is said to be *hermetian*. Operators whose matrix representations are hermetian are called *hermetian operators*. Examples of such operators are the familiar angular momentum operators I_x, I_y and I_z.

The *adjoint* of an operator A, $A^\dagger$, is defined in the following way

$$\left(A^\dagger \right)_{ij} = A_{ji}^*$$

Hermetian operators, such as I_x, are self adjoint, meaning that the adjoint of the operator is equal to the operator. This follows as $A_{ji}^* = A_{ij}$ for a hermetian operator and so $A^\dagger{}_{ij} = A_{ij}$.

The raising and lowering operators, I_+ and I_-, are not hermetian, a fact that can readily be appreciated from the matrix representations:

$$I_+ = I_x + iI_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad I_- = I_x - iI_y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

These operators are the adjoints of one another:

$$I_+^\dagger = I_- \qquad I_-^\dagger = I_+$$

Again, this is readily appreciated from the matrix representations.

The *trace* of an operator is equal to the sum of its diagonal elements

$$\mathrm{Tr}\{A\} = \sum_i A_{ii}$$

6.1.2 Basis sets of operators

The density operator, σ, can be expanded in a basis of operators, B_i:

$$\sigma = b_1 B_1 + b_2 B_2 + \ldots = \sum_i b_i B_i$$

where the b_i are numerical coefficients. A basis set of wavefunctions can be described as being orthonormal (Section 1.2.4), which means that they have the properties

$$\langle \phi_i | \phi_j \rangle = 0 \ \text{ if } i \neq j; \quad \text{and} \ = 1 \text{ if } i = j$$

For operators, orthogonality is defined using the trace. Two operators B_i and B_j are orthogonal if

$$\mathrm{Tr}\{B_i^\dagger B_j\} = 0$$

To compute the trace, it would be necessary to find the matrix representations of $B_i^\dagger$ and B_j, multiply these together to give another matrix and then add up the diagonal elements of the resulting matrix. The operators I_x, I_y and I_z are all orthogonal to one another.

Normalization also involves computation of the trace of the adjoint of an operator with itself

$$\mathrm{Tr}\{B_i^\dagger B_i\} = \beta_i$$

Sometimes a basis set of operators are chosen so that $\beta_i = 1$, and sometimes the operators are chosen so that β_i is the same for each operator, but not necessarily $= 1$. For example:

$$\mathrm{Tr}\{I_x I_x\} = \mathrm{Tr}\{I_y I_y\} = \mathrm{Tr}\{I_z I_z\} = \tfrac{1}{2}.$$

The set of product operators for two spins (I_{1x}, $2\,I_{1x}I_{2z}$ etc.) all have $\beta_i = 1$; the factor of 2 in the operator products with two spin operators is needed to keep the β_i the same for all the operators.

6.1.3 Commutators

The *commutator* of two operators is written [A,B] and defined as follows

$$[A,B] = AB - BA$$

If A and B are numbers or simple functions, then the order in which they appear does not matter. For example $2\times3 = 3\times2$ and $x \times y^2 = y^2 \times x$. Such simple functions are said to *commute*; the commutator between them is zero

$$\left[x, y^2\right] = xy^2 - y^2x = 0$$

However, not all operators are simple functions and so they do not necessarily commute with one another. In particular, the angular momentum operators obey the following commutation relations I_x, I_y and I_z.

$$\left[I_x, I_y\right] = iI_z \quad \left[I_y, I_z\right] = iI_x \quad \left[I_z, I_x\right] = iI_y$$

The second commutator can be found from the first by cyclic permutation of the indices: $x \rightarrow y$, $y \rightarrow z$, $z \rightarrow x$; likewise the third can be found from the second by further cyclic permutation.

Using these relationships and the definitions of I_+ and I_- the following can be derived

$$\left[I_+, I_z\right] = I_+ \quad \left[I_-, I_z\right] = I_- \quad \left[I_+, I_-\right] = 2I_z$$

Operators for different spins always commute with one another, and an operator always commutes with itself. For example

$$\left[I_{1x}, I_{2z}\right] = 0 \quad \left[4I_{1x}I_{2z}I_{3z}, 4I_{1x}I_{2z}I_{3z}\right] = 0$$

6.1.1.1 Commutator relations

The following properties are often useful

$$[A, B] = -[B, A]$$
$$[PA, B] = P[A, B] \quad \text{if P commutes with } A \text{ and } B$$
$$[A + B, C] = [A, C] + [B, C]$$

6.1.1.2 Operator products

The commutator relations given in Section 6.1.3 for I_x, I_y and I_z apply for any spin. For spin $\frac{1}{2}$ *only* the following relationships also apply

$$I_xI_y = \tfrac{1}{2}iI_z \quad I_yI_x = -\tfrac{1}{2}iI_z \quad \text{and for cyclic permutations of } x, y \text{ and } z$$

$$I_x^2 = I_y^2 = I_z^2 = \tfrac{1}{4}E \quad \text{where } E \text{ is the unit operator or matrix}$$

There are also similar special relationships for the raising and lowering operators.

$$I_+^2 = I_-^2 = 0 \qquad I_+I_- = \tfrac{1}{2}\left(1 + 2I_z\right) \qquad I_-I_+ = \tfrac{1}{2}\left(1 - 2I_z\right)$$

Since $\left[I_x, I_y\right] = iI_z$ and $I_xI_y = \tfrac{1}{2}iI_z$, it follows that

$$I_xI_y = \tfrac{1}{2}\left[I_x, I_y\right] \quad I_yI_x = \tfrac{1}{2}\left[I_y, I_x\right]$$

These relationships are also valid for cyclic permutations of x, y and z.

If these relationships apply (*i.e.* for spin half) then it follows that

$$[AP, BQ] = 0 \text{ if } A \text{ and } B \text{ both commute with } P \text{ and } Q$$

An example of the latter is when A and B are operators of spin 1 and P and Q are operators of spin 2

$$\left[I_{1x}I_{2y}, I_{1y}I_{2z}\right] = 0$$

Another special case which will be of use is

$$[AP, AQ] = A^2[P,Q] = \tfrac{1}{4}[P,Q] \qquad A = I_x, I_y \text{ or } I_z$$

provided A commutes with P and Q.

6.2 Operator equations

The time evolution of coherences is conveniently handled using the density matrix introduced in Section 1.7 . Further, it is useful to make an operator expansion of this density matrix as this fits in well with the product operator approach (Section 3) used to described many multiple pulse experiments. In addition, this operator approach is closely related to the Solomon equations introduced in Section 5.1.3.

The starting point is the equation of motion of the density matrix (or operator)

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = -i[H, \sigma(t)]$$

where the square bracket indicates the commutator

$$[A, B] = AB - BA$$

As before, the hamiltonian consists of a static part, H_0, and a random time dependent part, $H_1(t)$

$$H = H_0 + H_1(t)$$

A transformed density operator, σ^{T}, and transformed time dependent hamiltonian, $H_1^{\mathrm{T}}(t)$, are defined as

$$\sigma^{\mathrm{T}}(t) = \exp(iH_0 t)\sigma(t)\exp(-iH_0 t) \quad H_1^{\mathrm{T}}(t) = \exp(iH_0 t)H_1(t)\exp(-iH_0 t)$$

It can be shown that the equation of motion of σ^{T} is

$$\frac{\mathrm{d}\sigma^{\mathrm{T}}(t)}{\mathrm{d}t} = -i[H_1^{\mathrm{T}}(t), \sigma^{\mathrm{T}}(t)] \tag{1}$$

This transformed representation is called the *interaction representation*. It is useful as σ^{T} just evolves under the action of the random hamiltonian; the evolution due to the large static hamiltonian has been factored out. It will be seen that the influence of H_0 appears as a simple phase evolution of $H_1^{\mathrm{T}}(t)$.

Equation [1] can be solved to second order in the perturbation represented by the random hamiltonian to give

$$\frac{\mathrm{d}\sigma^{\mathrm{T}}(t)}{\mathrm{d}t} = -\int_0^\infty \overline{\left[H_1^{\mathrm{T}}(t), \left[H_1^{\mathrm{T}}(t-\tau), \sigma^{\mathrm{T}}(t)\right]\right]} \, \mathrm{d}\tau \tag{2}$$

There are various approximations involved in this derivation, all of which rely on the fact that the random hamiltonian represents a small perturbation and that the theory is to be used for times longer than the correlation time, τ_c. Equation [2] is the master equation for the motion of the density operator.

However, this equation has one defect: it predicts that at long times the density operator goes to zero. This is incorrect – at long times the density operator must go to its equilibrium value, which is not zero but corresponds to the equilibrium population distribution. The reason for this defect is

identical to that discussed in Section 5.1.2 – it comes from the failure to treat the lattice as a quantum object. The solution to this problem is either to treat that lattice properly (which will be rather complex), or simply to replace σ^{T} by $(\sigma^{\mathrm{T}} - \sigma_{\mathrm{eq}})$, where σ_{eq} is the equilibrium density operator. In all that follows it will be assumed that this replacement is made at the end of the calculation.

6.2.1 Operator expansion

To develop Eq. [2] into a useful form, $H_1(t)$ is expanded according to

$$H_1(t) = \sum_q F^{(q)}(t) A^{(q)}$$

where the $F^{(q)}(t)$ are spatial functions and the $A^{(q)}$ are spin operators. This expansion allows for the possibility that there are several different terms, with different spatial factors, in the random hamiltonian. Since collisions cause the molecule to randomly change its orientation, the spatial functions become random functions of time.

The operators $A^{(q)}$ are chosen so that they evolve under the static hamiltonian according to

$$\exp(iH_0t)A^{(q)}\exp(-iH_0t) = \exp\left(i\omega^{(q)}t\right)A^{(q)} \qquad [3]$$

where the frequency $\omega^{(q)}$ is characteristic of the operator $A^{(q)}$. For example, in the case of a single spin, for which $H_0 = \omega_0 I_z$, the operator I_+ evolves in the way given by Eq. [3]:

$$\exp(iH_0t)I_+\exp(-iH_0t) = \exp(-i\omega_0t)I_+$$

with $\omega^{(q)} = -\omega_0$. Likewise, I_- and I_z evolve at frequencies $+\omega_0$ and 0, respectively.

In more complex cases it may be that $A^{(q)}$ is a sum of operators, all of which have the same spatial function $F^{(q)}(t)$, but all of which do not evolve at the same frequency under the transformation represented by Eq. [3].

For example, in the dipolar interaction there is a set of operators

$$I_z S_z, I^+S^-, I^-S^+$$

which all have the same spatial dependence, but which, under the static hamiltonian $H_0 = \omega_I I_z + \omega_S S_z$, evolve at frequencies 0, $-\omega_I + \omega_S$ and $\omega_I - \omega_S$ respectively. To cope with situation such as these, Eq. [3] is modified to

$$\exp(iH_0t)A^{(q)}\exp(-iH_0t) = \sum_p \exp\left(i\omega_p^{(q)}t\right)A_p^{(q)} \qquad [4]$$

where the sum over p allows for the possibility that the $A^{(q)}$ is a sum of operators $A_p^{(q)}$ each with its own associated frequency $\omega_p^{(q)}$.

The hamiltonian must be hermetian, so it follows that for each operator with a positive index q there must be one with a negative index, with the two operators being related by

$$\left[A^{(q)}\right]^\dagger = A^{(-q)} \qquad [5]$$

where the dagger (†) indicates the adjoint. For example

$$\left[I^+\right]^\dagger = I^- \qquad \left[I_z\right]^\dagger = I_z$$

Likewise for each $F^{(q)}$ there is an associated $F^{(-q)}$, related by $F^{(-q)} = F^{(q)*}$. It follows from these definitions that $\omega_p^{(-q)} = -\omega_p^{(q)}$.

Substituting the expansion of Eq. [4] into the master equation (Eq. [2]) gives, after considerable manipulation,

$$\frac{d\sigma^{\mathrm{T}}(t)}{dt} = -\tfrac{1}{2} \sum_{p,q,p',q'} \left[A_p^{(q)}, \left[A_{p'}^{(q')}, \sigma^{\mathrm{T}}(t)\right]\right] J_{q,-q'}\left(\omega_{p'}^{(q')}\right) \exp\left(i\left(\omega_p^{(q)} + \omega_{p'}^{(q')}\right)t\right) \quad [6]$$

where $J_{q,-q'}(\omega)$ is the Fourier transform of the correlation function $G_{q,-q'}(\tau)$

$$J_{q,-q'}(\omega) = \int_{-\infty}^{\infty} G_{q,-q'}(\tau) \exp(-i\omega\tau)\,d\tau$$

and where the correlation function is defined as

$$G_{q,-q'}(\tau) = \overline{F^{(q)}(t)F^{(q')}(t-\tau)} \qquad\qquad [7]$$

6.2.2 Simplification by neglecting cross correlation and non-secular terms

The relaxation behaviour predicted by Eq. [6] depends on the correlation function between all possible interactions *i.e.* all possible pairs q,q'. However, as has been seen above, it is often the case – or can be assumed to be the case – that there is no correlation between the fluctuations of different terms in the random hamiltonian; in other words, cross correlation can be ignored.

If cross correlation is indeed ignored, then the only non-zero correlation functions are ones with the same index q for both functions, *i.e.*

$$\overline{F^{(q)}(t)F^{(q)*}(t-\tau)}$$

By definition, $F^{(-q)} = F^{(q)*}$, this non zero correlation function can be written

$$\overline{F^{(q)}(t)F^{(-q)}(t-\tau)}$$

which, from Eq. [7] is $G_{q,-q'}$ with $q' = -q$, *i.e.* $G_{q,q}$

In Eq. [6] there is a complex exponential which causes a phase oscillation

$$\exp\left(i\left(\omega_p^{(q)} + \omega_{p'}^{(q')}\right)t\right)$$

If cross correlation is ignored, $q' = -q$, and as $\omega_p^{(-q)} = -\omega_p^{(q)}$ this term becomes

$$\exp\left(i\left(\omega_p^{(q)} + \omega_{p'}^{(-q)}\right)t\right) = \exp\left(i\left(\omega_p^{(q)} - \omega_{p'}^{(q)}\right)t\right)$$

If $\omega_p^{(q)}$ and $\omega_{p'}^{(q)}$ differ significantly, then this terms causes a rapid phase oscillation so the term will not contribute to relaxation, simply as it is constantly changing sign. The terms which will contribute are those with $\omega_p^{(q)} = \omega_{p'}^{(q)}$, for which there is no phase oscillation. This condition is only met if $p = p'$.

Terms which satisfy this restriction are termed secular contributions (as opposed to the remainder which are non-secular). Thus, retaining only the secular terms and ignoring cross correlation simplifies Eq. [6] to

$$\frac{d\sigma^{T}(t)}{dt} = -\tfrac{1}{2}\sum_{p,q}\left[A_{p}^{(q)},\left[A_{p'}^{(-q)},\sigma^{T}(t)\right]\right]J_{q,q}\!\left(\omega_{p}^{(q)}\right) \qquad\qquad [8]$$

6.2.3 Relaxation of individual operators

As was described in Section 6.1.2, it is common to expand the density operator is expanded in terms of a basis of operators, B_i,

$$\sigma(t)=\sum_{i}b_{i}(t)B_{i}$$

where the coefficients b_i carry the time dependence.

Evolution under pulses and delays causes the operators to transform into one another. It would be useful to have a similar way of handling the effect of relaxation on the operators. In such an approach, each operator would relax in a characteristic way, perhaps being transferred to other operators. The theory would predict these rate constants for self relaxation and for transfer to other operators.

Such a way of treating the motion of operators under the influence of relaxation has already been introduced as the Solomon equations. For example the equation

$$\frac{d\left(I_{z}-I_{z}^{0}\right)}{dt}=-R_{I}\left(I_{z}-I_{z}^{0}\right)-\sigma_{IS}\left(S_{z}-S_{z}^{0}\right)$$

says that I_z relaxes with a rate constant R_I and that S_z is transferred to I_z with a rate constant σ_{IS}. The aim is to use the master equation, Eq. [8], to produce similar equations for any operator, B_i.

Suppose that the density operator just contains a single operator, B_1, with coefficient $b_1(t)$. To use Eq. [8] the density operator has to be transformed to the interaction representation

$$\sigma^{T}(t)=\exp(iH_{0}t)\sigma(t)\exp(-iH_{0}t)$$
$$=\exp(iH_{0}t)b_{1}(t)B_{1}\exp(-iH_{0}t)$$
$$=b_{1}(t)B_{1}\exp(i\omega_{1}t)$$

where it has been assumed that under this transformation the operator B_1 acquires a phase modulation at a characteristic frequency ω_1. The exponential term can be merged into the coefficient by defining

$$b_{1}'(t)=b_{1}(t)\exp(i\omega_{1}t)$$

so that

$$\sigma^{T}(t)=b_{1}'(t)B_{1}$$

The right-hand side of Eq. [8] becomes

$$-\tfrac{1}{2}\sum_{p,q}\left[A_{p}^{(q)},\left[A_{p'}^{(-q)},b_{1}'(t)B_{1}\right]\right]J_{q,q}\!\left(\omega_{p}^{(q)}\right)$$

The effect of the double commutator will, in general, be to transform the operator B_1 into other operators; there will be some coefficient for this transfer, depending on the details of the operators and the spectral densities. In general, the result can be written

$$c_{11}b_1'(t)B_1 + c_{12}b_1'(t)B_2 + c_{13}b_1'(t)B_3 + \dots$$

where c_{1j} is the coefficient for the transfer of operator 1 to operator j.

So Eq. [8] becomes

$$\frac{d}{dt}\big(b_1'(t)B_1\big) = c_{11}b_1'(t)B_1 + c_{12}b_1'(t)B_2 + c_{13}b_1'(t)B_3 + \dots$$

$$= \sum_j c_{1j}b_1'(t)B_j$$

However, in general the density operator will not start out as just consisting of a single operator B_1, but will be a sum of many operators

$$\sigma^T(t) = b_1'(t)B_1 + b_2'(t)B_2 + b_3'(t)B_3 \dots$$

$$= \sum_i b_i'(t)B_i$$

Each of these operators can be transformed into any other operator by the action of the double commutators, and if, as above, the coefficient for transfer of operator B_j into operator B_i is c_{ji} the result is

$$\frac{d}{dt}\left(\sum_i b_i'(t)B_i\right) = c_{11}b_1'(t)B_1 + c_{12}b_1'(t)B_2 + c_{13}b_1'(t)B_3 + \dots$$

$$+ c_{21}b_2'(t)B_1 + c_{22}b_2'(t)B_2 + c_{23}b_1'(t)B_3 + \dots$$

$$+ c_{31}b_3'(t)B_1 + c_{32}b_3'(t)B_2 + c_{33}b_3'(t)B_3 + \dots$$

$$= \sum_{i,j} c_{ji}b_j'(t)B_i$$

This begins to look like a Solomon equation, but is rather complex as it has a sum of derivatives on the left. To pick out just one of these, say that of the operator B_k, both left and right hand sides are multiplied by the operator $B_k^\dagger$ and the trace taken

$$\frac{d}{dt}\left(\sum_j b_j'(t)\mathrm{Tr}\big\{B_k^\dagger B_j\big\}\right) = \sum_{i,j} c_{ji}b_j'(t)\mathrm{Tr}\big\{B_k^\dagger B_i\big\}$$

The operators are assumed to be orthogonal and to have a constant normalization factor, β:

$$\mathrm{Tr}\big\{B_p^\dagger B_q\big\} = 0 \quad \text{if } p \neq q \quad = \beta \text{ if } p = q$$

The β cancel and so the differential equation becomes

$$\frac{d}{dt}\big(b_k'(t)\big) = \sum_j c_{jk}b_j'(t) \qquad\qquad [9]$$

This is a Solomon-type equation. What it says is that if the rate of change of the "amount" of operator B_k, $b_k(t)$, depends on the amounts of all other operators B_j, $b_j(t)$, present. The rate constant for transfer of operator B_j into operator B_k is given c_{jk}.

The rate constant c_{jk} is simply found by computing

$$c_{jk} = \frac{1}{\beta}\mathrm{Tr}\left\{\big(B_k^{\;\dagger}\big)\left(-\tfrac{1}{2}\sum_{p,q}\big[A_p^{(q)},\big[A_{p'}^{(-q)},B_j\big]\big]J_{q,q}\big(\omega_p^{(q)}\big)\right)\right\} \qquad [10]$$

In words, what this means that starting with a single operator B_j it is seen how this operator is transformed into other operators by the double commutators; from the resulting set of operators, just the component of B_k is picked out.

A knowledge of the c_{jk} rate constants gives a complete set of Solomon equations and so a complete description of the relaxation behaviour of the set of operators. In practice, therefore, the theory is used to calculate these c_{jk} rather than the relaxation of an arbitrary density operator.

6.2.3.1 Time dependence

Equation [9] is written in the interaction representation, with the coefficients $b_i'(t)$ having a phase oscillation due to the evolution of the operators under the static hamiltonian.

$$b_i'(t) = b_i(t)\exp(i\omega_i t) \qquad [11]$$

The aim is now to separate the evolution due to relaxation from that due to evolution under the static hamiltonian. Starting from Eq. [9] the coefficients $b_i'(t)$ are replaced by those from Eq. [11]

$$\frac{\mathrm{d}}{\mathrm{d}t}\big(b_k'(t)\big) = \sum_j c_{jk} b_j'(t)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\big(b_k(t)\exp(i\omega_k t)\big) = \sum_j c_{jk} b_j(t)\exp(i\omega_j t)$$

$$\frac{\mathrm{d}b_k(t)}{\mathrm{d}t}\exp(i\omega_k t) + b_k(t)i\omega_k\exp(i\omega_k t) = \sum_j c_{jk} b_j(t)\exp(i\omega_j t)$$

$$\frac{\mathrm{d}b_k(t)}{\mathrm{d}t} = -b_k(t)i\omega_k + \sum_j c_{jk} b_j(t)\exp\big(i(\omega_j - \omega_k)t\big) \qquad [12]$$

Equation [12] can be interpreted in the following way. The first term on the right describes the phase evolution of the operator B_k due to the static hamiltonian; it has nothing to do with relaxation. The sum of terms on the right gives the rate of relaxation-induced transfer from operator B_j to B_k, with rate constant c_{jk}. However, each term on the right includes a phase oscillation at $(\omega_j - \omega_k)$; such terms will not be effective at transferring B_j to B_k unless $(\omega_j - \omega_k) = 0$ so that this phase oscillation goes away. Unless this is the case, the sign of the relaxation terms will change rapidly (much more rapidly than the rather slow rate of relaxation) and so the net effect will be zero.

For example, suppose that the two operators involved are I_+ and S_+; the characteristic frequencies are therefore ω_I and ω_S (the two Larmor frequencies), and as these are not the same any relaxation induced transfer between the two operators which in principle might take place will actually have no net effect. In contrast the two operators I_z and S_z which both have characteristic frequencies of zero can have relaxation induced transfer between them (just as has been seen in the Solomon equations).

So, Eq. [12] can be written

$$\frac{\mathrm{d}b_k(t)}{\mathrm{d}t} = -b_k(t)i\omega_k + \sum_{j'} c_{j'k}b_{j'}(t) \qquad [13]$$

where the sum over j' is taken to include only those terms for which $\omega_{j'} = \omega_k$. Concentrating on just the relaxation parts of the equation it is possible to write Eq. [13] in terms of the operators, rather than their coefficients, as was done in the case of the Solomon equations

$$\frac{\mathrm{d}B_k}{\mathrm{d}t} = \sum_{j'} c_{j'k}B_{j'}$$

As before, it is important to remember that this equation is just a short hand – it is not the operators that are changing with time, but their contributions to the density operator.

6.2.4 Superoperators

Often, it is acceptable to think of relaxation and evolution under the static hamiltonian as being separate, even though in reality they are clearly taking place at the same time. However, there are occasions on which it is essential to consider the two processes acting at the same time. Essentially, this is what a complete set of equations like Eq. [13] (for all operators B_k) will do.

A convenient way of expressing such equations is to use the idea of superoperators. The starting point is the equation of motion of the density operator:

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = -i[H,\sigma(t)]$$

For such an equation, it is usual to think of σ and H as being matrices expressed in some basis of wavefunctions. However, if σ is expressed as a linear combination of operators, as in the product operator formalism, it is then natural to think of σ as a (column) vector of the coefficients the individual operators.

The equation of motion is then written

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = -i\hat{\hat{H}}\sigma(t) \qquad [14]$$

where $\hat{\hat{H}}$ is the hamiltonian *superoperator*; this can be thought of as a matrix. Formally, the superoperator is defined as a commutator:

$$\hat{\hat{H}}\sigma = [H,\sigma] = H\sigma - \sigma H$$

If H is time independent the solution to Eq. [14] is

$$\sigma(t) = \exp\left(-i\hat{\hat{H}}t\right)\sigma(0)$$

Relaxation can be added to Eq. [14] by introducing a relaxation superoperator $\hat{\hat{\Gamma}}$

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = -i\hat{\hat{H}}\sigma(t) - \hat{\hat{\Gamma}}\left\{\sigma(t) - \sigma_{\mathrm{eq}}\right\}$$

where $\hat{\hat{\Gamma}}$ is defined via

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$$\hat{\hat{\Gamma}}\sigma^{\mathrm{T}}(t) = \tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},\sigma^{\mathrm{T}}(t)\right]\right]J_{q,q}\left(\omega_p^{(q)}\right)$$

In the case that σ is written as a vector of operators, $\hat{\hat{\Gamma}}$ will be a matrix with the elements c_{jk} given by Eq. [10].

6.3 Example calculations

6.3.1 One spin with random field

The simplest case to consider is a single spin experiencing a random field in the x, y and z directions given by the hamiltonian

$$H_1(t) = \omega_x(t)I_x + \omega_y(t)I_y + \omega_z(t)I_z$$

It will be convenient to re-express the I_x and I_y operators in terms of the raising and lowering operators, to give

$$H_1(t) = \omega_x(t)\tfrac{1}{2}\left[I^+ + I^-\right] + \omega_y(t)\tfrac{1}{2i}\left[I^+ - I^-\right] + \omega_z(t)I_z$$

$$= I^+\left[\tfrac{1}{2}\omega_x(t) - \tfrac{1}{2}i\omega_y(t)\right] + I^-\left[\tfrac{1}{2}\omega_x(t) + \tfrac{1}{2}i\omega_y(t)\right] + \omega_z(t)I_z$$

From this, three separate terms are identified

q	$A^{(q)}$	$F^{(q)}(t)$	$\omega^{(q)}$
0	I_z	$\omega_z(t)$	0
1	I_+	$\tfrac{1}{2}\omega_x(t) - \tfrac{1}{2}i\omega_y(t)$	$-\omega_I$
−1	I_-	$\tfrac{1}{2}\omega_x(t) + \tfrac{1}{2}i\omega_y(t)$	$+\omega_I$

where the static hamiltonian, H_0, has been taken as $\omega_I I_z$, so that

$$\exp(iH_0 t)I_{\pm}\exp(-iH_0 t) = \exp(\mp i\omega_I t)I_{\pm} \qquad \exp(iH_0 t)I_z\exp(-iH_0 t) = I_z$$

For each value of q there is just one term, so the index p in Eq. [8] is not needed.

The correlation function $G_{11}(\tau)$ is

$$G_{11}(\tau) = \overline{F^{(1)}(t)F^{(-1)}(t+\tau)}$$

$$= \overline{\left[\tfrac{1}{2}\omega_x(t) - \tfrac{1}{2}i\omega_y(t)\right]\left[\tfrac{1}{2}\omega_x(t+\tau) + \tfrac{1}{2}i\omega_y(t+\tau)\right]}$$

$$= \tfrac{1}{4}\overline{\left[\omega_x(t)\omega_x(t+\tau) + i\omega_x(t)\omega_y(t+\tau) - i\omega_y(t)\omega_x(t+\tau) + \omega_y(t)\omega_y(t+\tau)\right]}$$

If cross correlation between the x and y components is ignored, then the ensemble averages of the second and third terms is zero. The first and second terms will be written

$$\overline{\omega_x(t)\omega_x(t+\tau)} = \overline{\omega_x^2}\,g(\tau) \qquad \overline{\omega_y(t)\omega_y(t+\tau)} = \overline{\omega_y^2}\,g(\tau)$$

So that

$$G_{11}(\tau) = \tfrac{1}{4}\left[\overline{\omega_x^2} + \overline{\omega_y^2}\right]g(\tau)$$

The corresponding spectral density is

$$J_{11}(\omega) = \tfrac{1}{4}\left[\overline{\omega_x^2} + \overline{\omega_y^2}\right]j(\omega)$$

The correlation function $G_{-1,-1}(\tau)$ is the same as $G_{11}(\tau)$.

$G_{00}(\tau)$ is similarly given by

$$\begin{aligned} G_{00}(\tau) &= \overline{F^{(0)}(t)F^{(0)}(t+\tau)} \\ &= \overline{\omega_z(t)\omega_z(t+\tau)} \\ &= \overline{\omega_z^2}\, g(\tau) \end{aligned}$$

and so $J_{00}(\omega) = \overline{\omega_z^2}\, j(\omega)$.

The approach will be to start with Eq. [10]

$$c_{jk} = \frac{1}{\beta}\mathrm{Tr}\left\{\left(B_k^{\dagger}\right)\left(-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},B_j\right]\right]J_{q,q}\left(\omega_p^{(q)}\right)\right)\right\} \qquad [10]$$

and to put each operator B_j in turn into this relationship. To start with, just the part in the round brackets will be evaluated

Motion of I_z

The term to calculate is

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},I_z\right]\right]J_{q,q}\left(\omega_p^{(q)}\right)$$

where $q = 0, +1, -1$; the index p is not used. The following terms are found

$$q = 0 \;:\; \left[I_z,\left[I_z,I_z\right]\right]J_{00}(0) = \left[I_z,0\right]J_{00}(0) = 0$$

$$q = 1 \;:\; \left[I^-,\left[I^+,I_z\right]\right]J_{11}(-\omega_I) = \left[I^-,-I^+\right]J_{11}(-\omega_I) = 2I_z J_{11}(-\omega_I)$$

$$q = -1 \;:\; \left[I^+,\left[I^-,I_z\right]\right]J_{-1-1}(\omega_I) = \left[I^+,I^-\right]J_{-1-1}(\omega_I) = 2I_z J_{-1-1}(\omega_I)$$

The double commutators generate no new operators, so all that happens is that I_z relaxes on its own. It is not therefore necessary to go through the formal calculation of the trace. Rather, the coefficient c_{00} can be picked out as:

$$\begin{aligned} c_{00} &= -\tfrac{1}{2}\left\{2J_{11}(-\omega_I) + 2J_{-1-1}(\omega_I)\right\} \\ &= -J_{11}(\omega_I) - J_{11}(\omega_I) \\ &= -\tfrac{1}{4}\left[\overline{\omega_x^2} + \overline{\omega_y^2}\right]j(\omega_I) - \tfrac{1}{4}\left[\overline{\omega_x^2} + \overline{\omega_y^2}\right]j(\omega_I) \\ &= -\tfrac{1}{2}\left[\overline{\omega_x^2} + \overline{\omega_y^2}\right]j(\omega_I) \end{aligned}$$

where is has been assumed that the spectral densities at $\pm\omega_0$ are the same. The Solomon equation is therefore

$$\begin{aligned} \frac{dI_z}{dt} &= c_{00}I_z \\ &= -R_z I_z \end{aligned}$$

where R_z, the longitudinal relaxation rate constant is

$$R_z = \tfrac{1}{2}\left[\overline{\omega_x^2} + \overline{\omega_y^2}\right]j(\omega_I)$$

As expected, the rate of longitudinal relaxation depends on the size of transverse fields and the spectral density at the Larmor frequency.

6–12

Motion of I_+

The term to calculate this time is

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},I_+\right]\right]J_{q,q}\left(\omega_p^{(q)}\right)$$

where $q = 0, +1, -1$; the index p is not used. The following terms are found

$$q = 0 \;:\; \left[I_z,[I_z,I_+]\right]J_{00}(0)=\left[I_z,-I_+\right]J_{00}(0)=J_{00}(0)I_+$$

$$q = 1 \;:\; \left[I^-,[I_+,I_+]\right]J_{11}(-\omega_I)=\left[I_-,0\right]=0$$

$$q = -1 \;:\; \left[I_+,[I_-,I_+]\right]J_{-1-1}(\omega_I)=\left[I_+,-2I_z\right]J_{-1-1}(\omega_I)=2I_+J_{-1-1}(\omega_I)$$

The double commutators generate no new operators, so as before all that happens is that I_+ relaxes on its own. The coefficient, that is the rate constant for this process, can be extracted by inspection as

$$c_{11} = -\tfrac{1}{2}\left[J_{00}(0)+2J_{-1-1}(\omega_I)\right]$$

$$= -\tfrac{1}{2}\overline{\omega_z^2}\,j(0)-\tfrac{1}{4}\left[\overline{\omega_x^2}+\overline{\omega_y^2}\right]j(\omega_I)$$

The Solomon-type equation is therefore

$$\frac{\mathrm{d}I_+}{\mathrm{d}t}=c_{11}I_+ = -R_tI_+$$

where R_t, the transverse relaxation rate constant is

$$R_t = \tfrac{1}{2}\overline{\omega_z^2}\,j(0)+\tfrac{1}{4}\left[\overline{\omega_x^2}+\overline{\omega_y^2}\right]j(\omega_I)$$

6.3.1.1 Interpretation

It is interesting to compare the longitudinal and transverse relaxation rate constants

$$R_z = \tfrac{1}{2}\left[\overline{\omega_x^2}+\overline{\omega_y^2}\right]j(\omega_0)$$

$$R_t = \tfrac{1}{2}\overline{\omega_z^2}\,j(0)+\tfrac{1}{4}\left[\overline{\omega_x^2}+\overline{\omega_y^2}\right]j(\omega_0)=\tfrac{1}{2}\overline{\omega_z^2}\,j(0)+\tfrac{1}{2}R_z$$

Longitudinal relaxation only depends on the spectral density at the Larmor frequency, but transverse relaxation depends on the spectral density both at the Larmor frequency *and* at zero frequency.

The two contributions to transverse relaxation are quite distinct. Longitudinal random fields give a contribution which depends on the spectral density at zero frequency; this is called the *secular* contribution as no energy change is involved. Transverse random fields give a contribution which depends on the spectral density at the Larmor frequency; this is called the *non-secular* contribution as changes of energy are involved as the spins flip.

Furthermore, longitudinal relaxation is only brought about by transverse magnetic fields, but both transverse and longitudinal magnetic fields give rise to transverse relaxation. The longitudinal fields are associated with the spectral density at zero frequency.

The secular part of transverse relaxation

Recall that transverse magnetization is due to the presence of a coherence in the system; this coherence has a phase oscillation at the Larmor frequency and this in turn is what gives rise to the measured precession of transverse magnetization at the Larmor frequency. Each spin experiences the applied magnetic field along the z-direction plus any local random field, $\omega_z(t)$. As a result, the frequency of the phase oscillation of the contribution to the coherence from each spin has a spread of values across the sample. As time proceeds, therefore, these individual contributions get out of phase with one another and so the coherence (and hence the transverse magnetization) decays.

For such a mechanism to be effective at dephasing coherence it is not necessary for there to be any time variation in the fields along the z-direction, all that is required is that there is a distribution of fields across the sample. However, the dephasing caused by a completely static distribution of fields is *not* classed as relaxation since the dephasing could be reversed by the application of a 180° refocusing pulse. Indeed, this kind of dephasing is exactly that which occurs when a field gradient pulse is applied. Relaxation is a dissipative irreversible process whose effects *cannot* be undone with pulses.

So, for a distribution of fields in the z-direction to be effective at causing transverse relaxation these fields must be time dependent so that their effect cannot be reversed by a refocusing pulse. The time dependence has a different role in transverse and longitudinal relaxation. In the latter, the time dependence is needed to cause transitions – in the former, it is needed to inhibit refocusing.

The secular part of transverse relaxation depends on $j(0)$ which $= 2\tau_c$. So, as the correlation time gets shorter the rate of transverse relaxation decreases. To understand why this is it is useful to imagine first that the spins are frozen and not moving. The distribution of fields across the sample will give rise to a range of different Larmor frequencies and as a result the line observed in the spectrum will be broad.

Now suppose that the spins start to move; they will jump from position to position, experiencing a different field each time (just like chemical exchange, but between very many sites). As the jumping rate becomes comparable with the original linewidth, the line will start to narrow (again, just like exchange narrowing). What is happening is that there are now so many jumps that all the spins are beginning to see the same average frequency. As the jumps become much faster than the original linewidth the line is narrowed drastically; however, there is still a residual width which depends on the rate of jumping and the original linewidth for the static arrangement.

For typical NMR samples the linewidth of the frozen sample would be rather large (tens of kHz, or more). However, typical correlation times for liquids are in the ps to ns range; these times are an indication of the time between jumps. With such fast motion compared to the frozen linewidth, the line observed in the liquid is very much narrower than in the frozen sample. Nevertheless, the extent of narrowing depends on the rate of

jumping, and this is why the relaxation rate constant is proportional to $2\tau_c$. The smaller τ_c, the faster the jumping and the narrower the line.

The non-secular part of transverse relaxation

Longitudinal relaxation is associated with changes in populations, and hence transitions between spin states. Such processes involve a transfer of energy between the spins and the lattice. It is also clear that a transition from one spin state to another will cause an interruption in the phase of the contribution of a particular spin to the overall coherences. Thus, such transitions also lead to transverse relaxation.

The non-secular contribution to the transverse rate constant is $\frac{1}{2}R_z$. The half arises because one spin flipping causes the population difference, and hence the z-magnetization, to change by two units. Spin flips are thus *twice* as effective at causing longitudinal relaxation as they are at causing transverse relaxation.

6.3.2 Variation with correlation times

For simplicity, it will be assumed that

$$\overline{\omega_x^2} = \overline{\omega_y^2} = \overline{\omega_z^2} = \omega_R^2$$

In which case

$$R_z = \omega_R^2 \, j(\omega_I) \qquad R_t = \tfrac{1}{2}\omega_R^2 \, j(0) + \tfrac{1}{2}\omega_R^2 \, j(\omega_I)$$

The simplest model is to assume that the correlation function is exponential, $g(t) = \exp(-\tau/\tau_c)$; this gives a lorentzian spectral density

$$j(\omega) = \frac{2\tau_c}{1 + \omega^2 \tau_c^2}$$

The relaxation rate constants are therefore

$$R_z = \frac{2\tau_c \omega_R^2}{1 + \omega_I^2 \tau_c^2} \qquad R_t = \omega_R^2 \left[\tau_c + \frac{\tau_c}{1 + \omega_I^2 \tau_c^2} \right]$$

Several important points can be drawn from these relationships.

The first is that the rate of transverse relaxation is always greater than or equal to that of longitudinal relaxation. This follows as the difference

$$R_t - R_z = \frac{\tau_c \omega_R^2 \omega_I^2 \tau_c^2}{1 + \omega_I^2 \tau_c^2} \qquad\qquad [15]$$

is clearly always positive.

6.3.2.1 *Extreme narrowing*

The *extreme narrowing* or *fast motion limit* is when the correlation time is so short that $\omega_0 \tau_c \ll 1$. If this is the case then $1 + \omega_0^2 \tau_c^2 \approx 1$, and the spectral density is just $2\tau_c$ at all frequencies. The rate constants for longitudinal and transverse relaxation are equal in this limit:

$$R_t^{\text{ex. narrow}} = R_z^{\text{ex. narrow}} = 2\tau_c \omega_R^2$$

As the correlation time increases out of the extreme narrowing limit, the transverse relaxation rate constant becomes greater than the longitudinal

rate constant, as can be seen from Eq. [15].

For a 500 MHz spectrometer, the extreme narrowing limit implies a correlation time of much less than 300 ps. A small molecule in a non-viscous solvent might have a correlation time of 10 ps or less, which would place the molecule easily in the extreme narrowing limit.

6.3.2.2 Spin diffusion

The spin diffusion or slow motion limit is when $\omega_0 \tau_c \gg 1$ so that the spectral density at zero frequency is much larger that that at the Larmor frequency. In such a case the transverse relaxation rate constant is dominated by the term which depends on $j(0)$

$$R_t^{\text{spin diff.}} = \omega_R^2 \tau_c$$

The longitudinal rate constant goes on getting smaller and smaller as the correlation time increases, in principle becoming vanishingly small in the limit $\omega_0 \tau_c \gg 1$. There is thus a strong contrast in the behaviour of the longitudinal and transverse rates.

This difference comes about because longitudinal relaxation requires motion at the Larmor frequency but transverse relaxation can be caused either by motion at zero frequency or at the Larmor frequency.

As was noted in Section 5.2.3, for a given frequency the spectral density is a maximum when $\omega_0 \tau_c \approx 1$. Therefore the longitudinal relaxation rate constant is a maximum when the correlation time is such that $\omega_0 \tau_c \approx 1$.
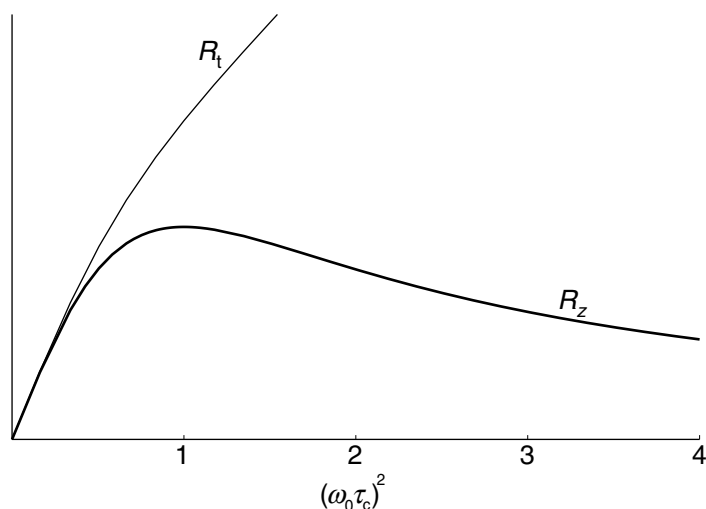
The longitudinal and transverse relaxation rate constants as a function of the correlation time for fixed Larmor frequency. For short correlation times the two rate constants are equal, but as the correlation time increases the longitudinal rate constant goes through a maximum and then falls away. In contrast, the transverse rate constant continues to increase.

6.3.3 More than one spin with random field

Suppose that there are two spins, each experiencing a random field so that the hamiltonian is

$$H_1(t) = \omega_{I,x}(t)I_x + \omega_{I,y}(t)I_y + \omega_{I,z}(t)I_z + \omega_{S,x}(t)S_x + \omega_{S,y}(t)S_y + \omega_{S,z}(t)S_z$$

which can be written

$$H_1(t) = I^+ F_I^{(1)} + I^- F_I^{(-1)} + F_I^{(0)}I_z + S^+ F_S^{(1)} + S^- F_S^{(-1)} + F_S^{(0)}S_z$$

where

$$F_{I,S}^{(0)} = \omega_z^{(I,S)}(t) \qquad F_{I,S}^{(\pm 1)} = \left[\tfrac{1}{2}\omega_x^{(I,S)}(t) \mp \tfrac{1}{2}i\omega_y^{(I,S)}(t)\right]$$

The I spin operators in the hamiltonian are the only ones which can affect I spins operators in the density operator and likewise for S spin operators. So, the set of double commutators

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)}, I_\alpha S_\beta\right]\right] J_{q,q}\left(\omega_p^{(q)}\right),$$

where I_α and S_β are any I and S spin operators, can be separated into two parts

$$\left(S_\beta\right)\left(-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(I,q)},\left[A_{p'}^{(I,-q)}, I_\alpha\right]\right] J_{I,q,q}\left(\omega_p^{(I,q)}\right)\right)$$

$$+\left(I_\alpha\right)\left(-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(S,q)},\left[A_{p'}^{(S,-q)}, S_\beta\right]\right] J_{S,q,q}\left(\omega_p^{(S,q)}\right)\right) \qquad [16]$$

The sub and superscript labels I and S on the operators, spectral densities and frequencies distinguish those for the I spins from those for the S spins.

As an example of using this separation, suppose that the relaxation behaviour of the operator product I^+S_z is required. From Eq. [16]

$$\left(S_z\right)\left(-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(I,q)},\left[A_{p'}^{(I,-q)}, I^+\right]\right] J_{I,q,q}\left(\omega_p^{(I,q)}\right)\right)$$

$$+\left(I^+\right)\left(-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(S,q)},\left[A_{p'}^{(S,-q)}, S_z\right]\right] J_{S,q,q}\left(\omega_p^{(S,q)}\right)\right)$$

The first bracket has already been calculated in the previous section when the relaxation of I^+ was considered; likewise the second bracket was also calculated above when the relaxation of S_z was considered. So, the relaxation rate constants for I^+S_z is just the sum of these two terms

$$R(I^+S_z) = R(I^+) + R(S_z)$$

$$= \left\{\tfrac{1}{2}\overline{\left(\omega_z^{(I)}\right)^2}j(0) + \tfrac{1}{4}\left[\overline{\left(\omega_x^{(I)}\right)^2} + \overline{\left(\omega_y^{(I)}\right)^2}\right]j(\omega_I)\right\} + \left\{\tfrac{1}{2}\left[\overline{\left(\omega_x^{(S)}\right)^2} + \overline{\left(\omega_y^{(S)}\right)^2}\right]j(\omega_S)\right\}$$

In fact, this approach will work for any operator with any number of terms in it. The overall relaxation rate constant will be the sum of the rate constants for each individual operator. Note that, with an operator such as I^+S_z, the result is a mixture of longitudinal and transverse relaxation rates.

A second example is a double quantum coherence: I^+S^+

$$R(I^+S^+) = R(I^+) + R(S^+)$$

$$= \left\{\tfrac{1}{2}\overline{\left(\omega_z^{(I)}\right)^2}j(0) + \tfrac{1}{4}\left[\overline{\left(\omega_x^{(I)}\right)^2} + \overline{\left(\omega_y^{(I)}\right)^2}\right]j(\omega_I)\right\}$$

$$+\left\{\tfrac{1}{2}\overline{\left(\omega_z^{(S)}\right)^2}j(0) + \tfrac{1}{4}\left[\overline{\left(\omega_x^{(S)}\right)^2} + \overline{\left(\omega_y^{(S)}\right)^2}\right]j(\omega_S)\right\}$$

The relaxation does *not* depend on the spectral density at the sum of the Larmor frequencies of I and S.
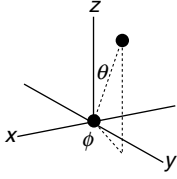
The dipole interaction depends on the angles θ and ϕ which are made by the vector joining the two nuclei. The static magnetic field is assumed to be along the z-axis.

6.3.4 Two spins with dipolar interaction

The dipole relaxation mechanism was described in Section 5.3.1; essentially, one spin gives rise to a magnetic field at a second spin due to the magnetic dipole that the former possesses. The interaction depends on the distance between the two spins, r, and the angles that the vector between them makes to the direction of the applied magnetic field. These angles are the usual θ and ϕ used in spherical polar coordinates and illustrated opposite.

The dipole hamiltonian can be separated into five terms with index $q = 0$, $\pm 1, \pm 2$

q	$A^{(q)}$	$F^{(q)}$
0	$I_z S_z - \tfrac{1}{4}\left(I_+ S_- + I_- S_+\right)$	$b\left(1 - 3\cos^2\theta\right)$
± 1	$I_z S_\pm + I_\pm S_z$	$-\tfrac{3}{2}b\left[\sin\theta\cos\theta\exp(\mp i\phi)\right]$
± 2	$I_\pm S_\pm$	$-\tfrac{3}{4}b\left[\sin^2\theta\exp(\mp 2i\phi)\right]$

where

$$b = \frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r^3}$$

in which γ_I and γ_S are the gyromagnetic ratios. The angles and the distance can, in principle, all change randomly with time; it will be assumed that r is fixed and that the angles change due to molecular tumbling. It is clear from the presence of operators such as I_z and I_+ that the hamiltonian will give rise to longitudinal and transverse relaxation. However, as will be seen, the really important thing about the dipole interaction is that it gives rise to *cross relaxation* as was described in Section 5.1.3 . The details of how this comes about will be seen in this section.

The operators $A^{(q)}$ evolve under the influence of the static hamiltonian at characteristic frequencies, as given in Eq. [4].

$$\exp(iH_0 t)A^{(q)}\exp(-iH_0 t) = \sum_p \exp\left(i\omega_p^{(q)}t\right)A_p^{(q)} \qquad [4]$$

Taking the static hamiltonian to be $\omega_I I_z + \omega_S S_z$ the operators $A^{(q)}$ separate out into the $A_p^{(q)}$, each with its associated frequency $\omega_p^{(q)}$, according to

q	p	$A_p^{(q)}$	$\omega_p^{(q)}$
0	0	$I_z S_z$	0
+0	1	$-\tfrac{1}{4}I_+ S_-$	$-\omega_I + \omega_S$
−0	1	$-\tfrac{1}{4}I_- S_+$	$\omega_I - \omega_S$
± 1	1	$I_z S_\pm$	$\pm\omega_S$
± 1	2	$I_\pm S_z$	$\pm\omega_I$

±2	$I_\pm S_\pm$	$\mp(\omega_I + \omega_S)$

The notation $q = \pm0$ is used to indicate that the operator with $q = +0$ is the adjoint of the one with $q = -0$, as required by Eq. [5]. The operators with $q = 2$ evolve at only one frequency, so the index p is not required for these; likewise for $q = -2$.

6.3.4.1 Correlation functions

If the calculation is restricted to secular contributions (Section 6.2.2), the required correlation functions are

$$G_{q,q}(\tau) = \overline{F^{(q)}(t)F^{(-q)}(t-\tau)}$$

and these will be written as

$$G_{q,q}(\tau) = \overline{F^{(q)}(t)F^{(-q)}(t)}\, g(\tau) = \overline{F^{(q)^2}}\, g(\tau)$$

where $g(\tau)$ is the reduced correlation function. The average of the square of $F^{(q)}$ is computed by averaging over the ensemble. If it is assumed that all angles are equally likely, *i.e.* all orientations are equally probable, then this averaging is equivalent to integrating over all angles θ and ϕ

$$\overline{F^{(q)^2}} = \frac{1}{4\pi}\int\limits_{\theta=0}^{\pi}\int\limits_{\phi=0}^{2\pi} F^{(q)}F^{(-q)}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

where $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is the volume element in spherical polar co-ordinates. The division by 4π is needed for normalization as

$$\int\limits_{\theta=0}^{\pi}\int\limits_{\phi=0}^{2\pi}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = 4\pi$$

For $q = 0$ the integral is

$$\overline{F^{(0)^2}} = \frac{1}{4\pi}\int\limits_{\theta=0}^{\pi}\int\limits_{\phi=0}^{2\pi} b\left(1-3\cos^2\theta\right)b\left(1-3\cos^2\theta\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= \tfrac{4}{5}b^2$$

The integral is tedious to evaluate by hand – *Mathematica* or some similar program makes short work of it, though.

Similar calculations give the following results for the correlation functions and spectral densities.

q	$\overline{F^{(q)^2}}$	$J_{q,q}(\omega)$
0	$\frac{4}{5}b^2$	$\frac{4}{5}b^2 j(\omega)$
±1	$\frac{3}{10}b^2$	$\frac{3}{10}b^2 j(\omega)$
±2	$\frac{3}{10}b^2$	$\frac{3}{10}b^2 j(\omega)$

From now on, for brevity, the spectral densities $J_{q,q}(\omega)$ will be written as $J_q(\omega)$.

6.3.4.2 Relaxation of I_z

The relaxation behaviour of the I_z operator is determined by evaluating

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},I_z\right]\right]J_q\!\left(\omega_p^{(q)}\right)$$

where the restriction to secular terms has been assumed. The spectral densities $J_q(\omega)$ have been computed in the previous section, so the problem reduces to evaluating the double commutator for all the relevant operators.

In evaluating the commutators the results given in Section 6.2.3 will be useful. In addition, the following commutators will be needed:

$$\left[I_+S_-,I_-S_+\right]=I_z-S_z \quad \left[I_+S_+,I_-S_-\right]=I_z+S_z$$

The following table shows the evaluation of all the double commutators

q	p	$\left[A_p^{(q)},\left[A_{p'}^{(-q)},I_z\right]\right]$	$\left[A_p^{(q)},Q\right]$	result
0	0	$\left[I_zS_z,\left[I_zS_z,I_z\right]\right]$	$\left[I_zS_z,0\right]$	0
+0	1	$\tfrac{1}{16}\left[I_+S_-,\left[I_-S_+,I_z\right]\right]$	$\tfrac{1}{16}\left[I_+S_-,I_-S_+\right]$	$\tfrac{1}{16}\left(I_z-S_z\right)$
−0	1	$\tfrac{1}{16}\left[I_-S_+,\left[I_+S_-,I_z\right]\right]$	$-\tfrac{1}{16}\left[I_-S_+,I_+S_-\right]$	$-\tfrac{1}{16}\left(-I_z+S_z\right)$
1	1	$\left[I_zS_+,\left[I_zS_-,I_z\right]\right]$	$\left[I_zS_+,0\right]$	0
1	2	$\left[I_+S_z,\left[I_-S_z,I_z\right]\right]$	$\left[I_+S_z,I_-S_z\right]$	$\tfrac{1}{2}I_z$
−1	1	$\left[I_zS_-,\left[I_zS_+,I_z\right]\right]$	$\left[I_zS_-,0\right]$	0
−1	2	$\left[I_-S_z,\left[I_+S_z,I_z\right]\right]$	$-\left[I_-S_z,I_+S_z\right]$	$\tfrac{1}{2}I_z$
2		$\left[I_+S_+,\left[I_-S_-,I_z\right]\right]$	$\left[I_+S_+,I_-S_-\right]$	$\left(I_z+S_z\right)$
−2		$\left[I_-S_-,\left[I_+S_+,I_z\right]\right]$	$-\left[I_-S_-,I_+S_+\right]$	$\left(I_z+S_z\right)$

The final result is therefore

$$-\tfrac{1}{2}\left\{\begin{array}{l}\tfrac{1}{16}\left(I_z-S_z\right)J_{+0,+0}\!\left(-\omega_I+\omega_S\right)+\tfrac{1}{16}\left(I_z-S_z\right)J_{-0,-0}\!\left(+\omega_I-\omega_S\right)\\[4pt]+\tfrac{1}{2}I_zJ_{1,1}\!\left(\omega_I\right)+\tfrac{1}{2}I_zJ_{-1,-1}\!\left(-\omega_I\right)\\[4pt]+\left(I_z+S_z\right)J_{2,2}\!\left(\omega_I+\omega_S\right)+\left(I_z+S_z\right)J_{-2,-2}\!\left(-\omega_I-\omega_S\right)\end{array}\right\}$$

where the appropriate spectral densities have been inserted. Assuming that

$$J_q(\omega)=J_{q,q}(\pm\omega)=J_{-q,-q}(\pm\omega)$$

gives

$$-I_z\left\{\tfrac{1}{16}J_0\!\left(\omega_I-\omega_S\right)+\tfrac{1}{2}J_1\!\left(\omega_I\right)+J_2\!\left(\omega_I+\omega_S\right)\right\}$$

$$-S_z\left\{J_2\!\left(\omega_I+\omega_S\right)-\tfrac{1}{16}J_0\!\left(\omega_I-\omega_S\right)\right\}$$

Inserting the explicit expressions for the spectral densities, this gives

$$-I_z\left\{\tfrac{1}{16}\tfrac{4}{5}j(\omega_I-\omega_S)+\tfrac{1}{2}\tfrac{3}{10}j(\omega_I)+\tfrac{3}{10}j(\omega_I+\omega_S)\right\}$$

$$-S_z\left\{\tfrac{3}{10}j(\omega_I+\omega_S)-\tfrac{1}{16}\tfrac{4}{5}j(\omega_I-\omega_S)\right\}$$

$$=-I_z\left\{\tfrac{1}{20}j(\omega_I-\omega_S)+\tfrac{3}{20}j(\omega_I)+\tfrac{3}{10}j(\omega_I+\omega_S)\right\}b^2$$

$$-S_z\left\{\tfrac{3}{10}j(\omega_I+\omega_S)-\tfrac{1}{20}j(\omega_I-\omega_S)\right\}b^2 \qquad [17]$$

An exactly analogous calculation for the operator S_z gives

$$-S_z\left\{\tfrac{1}{20}j(\omega_I-\omega_S)+\tfrac{3}{20}j(\omega_S)+\tfrac{3}{10}j(\omega_I+\omega_S)\right\}b^2$$

$$-I_z\left\{\tfrac{3}{10}j(\omega_I+\omega_S)-\tfrac{1}{20}j(\omega_I-\omega_S)\right\}b^2 \qquad [18]$$

which is easily obtained by swapping the indices I and S.

From Eq. [17] it is clear that the term multiplying I_z is the relaxation rate constant for I_z and the term multiplying S_z is the rate constant for transfer from S_z to I_z. Likewise in Eq. [18] the first term is the relaxation rate constant for S_z and the second is the term for transfer of I_z to S_z. These equations imply that I_z and S_z both relax on their own and are interconverted by relaxation according to the pair of differential equations

$$\frac{dI_z}{dt}=-R_I I_z-\sigma_{IS}S_z \qquad\qquad \frac{dS_z}{dt}=-R_S S_z-\sigma_{IS}I_z$$

where

$$R_S=\left\{\tfrac{1}{20}j(\omega_I-\omega_S)+\tfrac{3}{20}j(\omega_S)+\tfrac{3}{10}j(\omega_I+\omega_S)\right\}b^2$$

$$R_I=\left\{\tfrac{1}{20}j(\omega_I-\omega_S)+\tfrac{3}{20}j(\omega_I)+\tfrac{3}{10}j(\omega_I+\omega_S)\right\}b^2$$

$$\sigma_{IS}=\left\{\tfrac{3}{10}j(\omega_I+\omega_S)-\tfrac{1}{20}j(\omega_I-\omega_S)\right\}b^2$$

These are precisely the Solomon equations found in Section 5.1.3 . The difference is that it now it has been possible to identify the contributions to the self and cross relaxation rate constants.

Alternatively, these equations can be written in terms of the $J_q(\omega)$ as

$$R_I=\left\{\tfrac{1}{16}J_0(\omega_I-\omega_S)+\tfrac{1}{2}J_1(\omega_I)+J_2(\omega_I+\omega_S)\right\}$$

$$R_S=\left\{\tfrac{1}{16}J_0(\omega_I-\omega_S)+\tfrac{1}{2}J_1(\omega_S)+J_2(\omega_I+\omega_S)\right\} \qquad [19]$$

$$\sigma_{IS}=\left\{J_2(\omega_I+\omega_S)-\tfrac{1}{16}J_0(\omega_I-\omega_S)\right\}$$

Interpretation

Referring to Eq. [19] it is seen that the spectral densities $J_1(\omega_{I,S})$, $J_0(\omega_I-\omega_S)$, and $J_2(\omega_I+\omega_S)$ all contribute to the self relaxation of the I and S spin. However, only the latter two spectral densities contribute to the cross relaxation rate constant. These two spectral densities are associated with the terms in the hamiltonian $I_\pm S_\mp$, called the *flip-flop* terms as one spin flips one way and the other flips the other, and the terms $I_\pm S_\pm$, called the *flip-flip* and *flop-flop* terms. Dipole relaxation is almost unique in having these terms present and hence giving rise to cross relaxation. This is the reason why the presence of a nuclear Overhauser effect, which requires there to be cross relaxation, can almost always be associated with dipolar relaxation.

Writing in the simplest spectral density function gives the following expression for σ_{IS}

$$\sigma_{IS} = \left\{ \frac{3}{10} \frac{2\tau_c}{1 + (\omega_I + \omega_S)^2 \tau_c^2} - \frac{1}{20} \frac{2\tau_c}{1 + (\omega_I - \omega_S)^2 \tau_c^2} \right\} \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2}{r^6}$$

If I and S are both the same nuclear species, say protons, it is safe to assume that $(\omega_I + \omega_S) = 2\omega_I$ and $(\omega_I - \omega_S) = 0$, giving the simpler expression

$$\sigma_{IS} = \left\{ \frac{3}{10} \frac{2\tau_c}{1 + 4\omega_I^2 \tau_c^2} - \frac{1}{10} \tau_c \right\} \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2}{r^6}$$

The first thing to notice about this is that the cross-relaxation rate constant is proportional to $1/r^6$. Transient NOE experiments can be used to measure the cross-relaxation rate constant (see Section 5.1.4) and so provided the correlation time is known it is possible to determine the distance. Typically the correlation time is found from independent experiments, such as the measurement of the carbon-13 relaxation times and NOE enhancements. Alternatively, relative distances in the same molecule can simply be determined from the ratio of cross-relaxation rate constants

$$\frac{\sigma_{IS}}{\sigma_{PQ}} = \frac{r_{PQ}^6}{r_{IS}^6}$$

This will work provided it is valid to assume that the motion of both spin pairs I–S and P–Q can be modelled by a single correlation time (*i.e.* a rigid molecule). Note that as only dipolar relaxation contributes to the cross-relaxation rate constant it does not matter if other mechanisms are acting. These will alter the self relaxation rate constants, but not the cross-relaxation rate constants.

In the extreme narrowing limit $\omega_{I,S}\tau_c \ll 1$ and so σ_{IS} simplifies to

$$\sigma_{IS}^{\text{ext. narrow}} = \left\{ \frac{3}{10} 2\tau_c - \frac{1}{10} \tau_c \right\} \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2}{r^6} = \frac{1}{2} \tau_c \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2}{r^6}$$

This is positive, resulting in a positive NOE enhancement *i.e.* the spin receiving the enhancement will have its magnetization increased above the equilibrium value. This is typical of the NOE in small molecules.

In the spin diffusion limit the spectral density at $2\omega_I$ becomes negligible and so

$$\sigma_{IS}^{\text{spin diff.}} = \left\{ -\frac{1}{10} \tau_c \right\} \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2}{r^6}$$

This is negative, giving rise to negative NOE enhancements *i.e.* the spin receiving the enhancement will have its magnetization reduced when compared to the equilibrium value.

The self relaxation rate is

$$R_I = \left\{ \frac{1}{20} 2\tau_c + \frac{3}{20} \frac{2\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{3}{10} \frac{2\tau_c}{1 + (\omega_I + \omega_S)^2 \tau_c^2} \right\} \left(\frac{\mu_0 \hbar}{4\pi} \right)^2 \frac{\gamma_I^2 \gamma_S^2}{r^6}$$

which simplifies in the two limits to:

$$R_I^{\text{extr. narrow}} = \{\tau_c\}\left(\frac{\mu_0\hbar}{4\pi}\right)^2\frac{\gamma_I^2\gamma_S^2}{r^6}$$

$$R_I^{\text{spin diff.}} = \left\{\frac{1}{10}\tau_c\right\}\left(\frac{\mu_0\hbar}{4\pi}\right)^2\frac{\gamma_I^2\gamma_S^2}{r^6}$$

In Section 5.1.4.2 it was shown that the steady-state NOE enhancement is

$$\eta_{\text{SS}} = \frac{\sigma_{IS}}{R_I}$$

If the relaxation is purely due to the dipole interaction between I and S, then this enhancement is $+\frac{1}{2}$ in the extreme narrowing limit and -1 in the spin diffusion limit.

Somewhere in between the NOE enhancement goes to zero when the two terms in the cross-relaxation rate constant and equal *i.e.*

$$\sigma_{IS} = \left\{\frac{3}{10}\frac{2\tau_c}{1+4\omega_I^2\tau_c^2} - \frac{1}{10}\tau_c\right\}\left(\frac{\mu_0\hbar}{4\pi}\right)^2\frac{\gamma_I^2\gamma_S^2}{r^6}$$

which is zero when $\dfrac{6\tau_c}{1+4\omega_I^2\tau_c^2} = \tau_c$ *i.e.* $\omega_I^2\tau_c^2 = \dfrac{5}{4}$

At a Larmor frequency of 500 MHz this zero crossing corresponds to a correlation time of about 0.35 ns. Such a correlation time is characteristic of a medium-sized molecule such as a short peptide or oligo-saccharide dissolved in water.

6.3.4.3 Relaxation of $2I_zS_z$

As in the previous section, the process starts by evaluating

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},2I_zS_z\right]\right]J_q\left(\omega_p^{(q)}\right)$$

Following through the same procedure as before gives

$$-2I_zS_z\left\{\tfrac{1}{2}J_1(\omega_S)+\tfrac{1}{2}J_1(\omega_I)\right\}$$

there is no transfer to I_z or S_z. The differential equation is thus

$$\frac{d(2I_zS_z)}{dt} = -R_{IS}(2I_zS_z)$$

where

$$R_{IS} = \left\{\tfrac{1}{2}J_1(\omega_S)+\tfrac{1}{2}J_1(\omega_I)\right\}$$

$$= \left\{\tfrac{3}{20}j(\omega_S)+\tfrac{3}{20}j(\omega_I)\right\}b^2$$

$$= \left\{\frac{3}{20}\frac{2\tau_c}{1+\omega_S^2\tau_c^2}+\frac{3}{20}\frac{2\tau_c}{1+\omega_I^2\tau_c^2}\right\}\left(\frac{\mu_0\hbar}{4\pi}\right)^2\frac{\gamma_I^2\gamma_S^2}{r^6}$$

Note that in the spin diffusion limit this rate tends to zero.

6.3.4.4 Relaxation of I_+

Evaluating

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},I_+\right]\right]J_q\left(\omega_p^{(q)}\right)$$

gives

$$-I_+\left\{\tfrac{1}{8}J_0(0)+\tfrac{1}{2}J_1(\omega_S)+\tfrac{1}{32}J_0(\omega_I-\omega_S)+\tfrac{1}{4}J_1(\omega_I)+\tfrac{1}{2}J_2(\omega_I+\omega_S)\right\}$$

There are no transfer terms to other operators. The differential equation is thus

$$\frac{\mathrm{d}I_+}{\mathrm{d}t}=-R_I^t I_+$$

where

$$
\begin{aligned}
R_I^t &= \left\{\tfrac{1}{8}J_0(0)+\tfrac{1}{2}J_1(\omega_S)+\tfrac{1}{32}J_0(\omega_I-\omega_S)+\tfrac{1}{4}J_1(\omega_I)+\tfrac{1}{2}J_2(\omega_I+\omega_S)\right\} \\
&= \left\{\tfrac{1}{8}J_0(0)+\tfrac{1}{2}J_1(\omega_S)\right\}+\tfrac{1}{2}\left\{\tfrac{1}{16}J_0(\omega_I-\omega_S)+\tfrac{1}{2}J_1(\omega_I)+J_2(\omega_I+\omega_S)\right\} \\
&= \left\{\tfrac{1}{8}J_0(0)+\tfrac{1}{2}J_1(\omega_S)\right\}+\tfrac{1}{2}R_I
\end{aligned}
$$

Just as in the random field case, the transverse relaxation rate constant separates into two parts. The second part is just half of the longitudinal rate constant, R_I. The first part has a term which depends on the spectral density at zero frequency and a term which depends on the spectral density at the Larmor frequency of spin S.

This latter term is a little unusual. It says that the relaxation of transverse magnetization of spin I is affected by the spectral density at the *Larmor frequency of spin S*. The interpretation of this is that this latter spectral density is associated with processes which involve the flipping of spin S (terms such as $I_zS_\pm$). As I is (dipolar) coupled to S, when the spin state of S changes the field seen by the I spin changes, and so the precession frequency of the I spin coherence changes. These spin flips thus give rise to a constantly varying local field at spin I which causes loss of phase coherence amongst the spins which are contributing to the coherence. The term is secular from the point of view of the I spin as no energy is transferred to or from it.

In terms of the reduce spectral densities the relaxation rate constant is

$$R_I^t=\left\{\tfrac{1}{10}j(0)+\tfrac{3}{20}j(\omega_S)+\tfrac{1}{40}j(\omega_I-\omega_S)+\tfrac{3}{40}j(\omega_I)+\tfrac{3}{20}j(\omega_I+\omega_S)\right\}b^2$$

6.3.4.5 Transverse cross relaxation

In contrast to the relaxation behaviour of I_z and S_z, there is no cross relaxation transfer between I_+ and S_+; *i.e.* no transverse cross relaxation. Such a transfer would come about through the following double commutators

$$q=0\ :\ -\tfrac{1}{4}\left[I_zS_z,\left[I_-S_+,I_+\right]\right]=-\tfrac{1}{4}\left[I_zS_z,-2I_zS_+\right]=\tfrac{1}{8}S_+$$

$$-\tfrac{1}{4}\left[I_-S_+,\left[I_zS_z,I_+\right]\right]=-\tfrac{1}{4}\left[I_zS_z,I_+S_z\right]=\tfrac{1}{8}S_+$$

$$q=\pm1\ :\ \left[I_-S_z,\left[I_zS_+,I_+\right]\right]=\left[I_-S_z,I_+S_+\right]=\tfrac{1}{2}S_+$$

$$\left[I_zS_+,\left[I_-S_z,I_+\right]\right]=\left[I_zS_+,-2I_zS_z\right]=\tfrac{1}{2}S_+$$

However, none of these terms contribute as they are non-secular. For

example, in the first commutator the frequency associated with $I_z S_z$ is 0, whereas that associated with $I_- S_+$ is $(-\omega_I + \omega_S)$. The resulting term is therefore rapidly oscillating and thus ineffective at causing relaxation.

There are two cases in which these terms become secular. Firstly, when $\omega_I = \omega_S$ *i.e.* when the two spins are degenerate. Secondly, when it *appears* that the two spins have the same Larmor frequency. The first case is not of much interest as it would be impossible to detect the transfer of magnetization between degenerate spins. The latter case is important as it is possible to make it appear that two spins have the same Larmor frequency by spin locking their magnetization.

The simplest spin locking experiment involves a non-selective 90° pulse about the *y*-axis followed by a period during which a strong radiofrequency field is applied along the *x*-axis. The field is sufficiently strong that for both spins (which have different offsets) the effective field lies very close to the *x*-axis. The magnetization which is along the axis of the applied radiofrequency field (here *x*) experiences no rotation from that field; viewed in the laboratory frame the magnetization is precessing at the same rate as the rotating field. In the rotating frame, both appear static. The magnetization is said to be spin locked.

Since the magnetization from the two spins does not diverge while the spin-locking field is on, it appears as if they have the same offset or Larmor frequency. Thus, transverse cross-relaxation can take place. The results of the cross relaxation can be observed by removing the spin-locking field and then observing the FID in the usual way.

The experiments used to observe such transverse NOE enhancements, as they are called, are generally referred to as ROESY experiments (or sometime CAMELSPIN). Both one- and two-dimensional versions of the experiment are available.

Using the above double commutators, the cross-relaxation rate constant is computed as

$$\sigma_{IS}^{\text{tr}} = \left\{ \tfrac{1}{2} J_1(\omega_I) + \tfrac{1}{8} J_0(0) \right\}$$

or, in terms of the reduced spectral densities

$$\sigma_{IS}^{\text{tr}} = \left\{ \tfrac{3}{20} j(\omega_I) + \tfrac{1}{10} j(0) \right\} b^2$$

The important point about this rate constant is that for all values of the correlation time it is *always positive*. Therefore the NOE enhancements are always positive and there is no range of correlation times for which the enhancement crosses zero. ROESY has therefore proved to be a useful technique for obtaining distance information on molecules for which, because of their correlation times, the conventional NOE is close to zero.
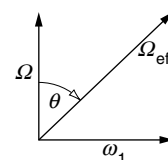
Off-resonance ROESY

In practice it is difficult to use a sufficiently strong spin locking field that the spin locking axis is in the transverse plane. Rather, the axis will by tilted up into the *xz*-plane. The tile angle of the effective field, θ, depends on the offset, Ω, and the radio frequency field strength ω_1.
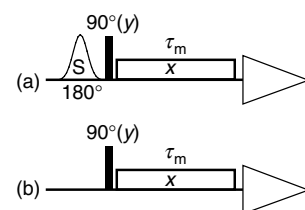
One-dimensional ROESY experiment. The combination of the selective 180° pulse and the 90° pulse in (a) generates a state in which the I spin is along *x* and the S spin is along −*x*. During the period of spin locking transverse cross relaxation can take place. Sequence (b) generates the reference spectrum without cross relaxation; it is subtracted from (a) to give the usual difference spectrum.
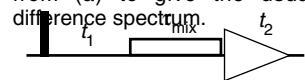
Two-dimensional ROESY experiment which uses a period of spin locking during the mixing time.


6–25

$$\tan\theta = \frac{\omega_1}{\Omega} \quad \sin\theta = \frac{\omega_1}{\Omega_{\text{eff}}} \quad \cos\theta = \frac{\Omega}{\Omega_{\text{eff}}} \quad \Omega_{\text{eff}}^2 = \omega_1^2 + \Omega^2$$

When the spin locking field is applied, components of the magnetization which are not parallel to the field are quickly dephased and lost. Only the part along the spin lock axis need be considered.

Magnetization which is spin locked about an axis tilted at angle θ will have a transverse component proportional to $\sin\theta$ – this relaxes at the appropriate rate for transverse magnetization, and a longitudinal component proportional to $\cos\theta$ – this relaxes at the longitudinal rate. The rate constant for the relaxation of spin locked magnetization thus depends on the rate constants for both transverse and longitudinal magnetization and the angle θ.

In an ROE experiment, the two spins which are cross-relaxing one another will have different offsets, and thus have different tilt angles, θ_I and θ_S. It is the transverse components which undergo transverse cross relaxation and the longitudinal components which undergo normal cross relaxation. To work out the effective cross relaxation rate of the spin locked magnetization it is thus necessary to consider the two components separately.
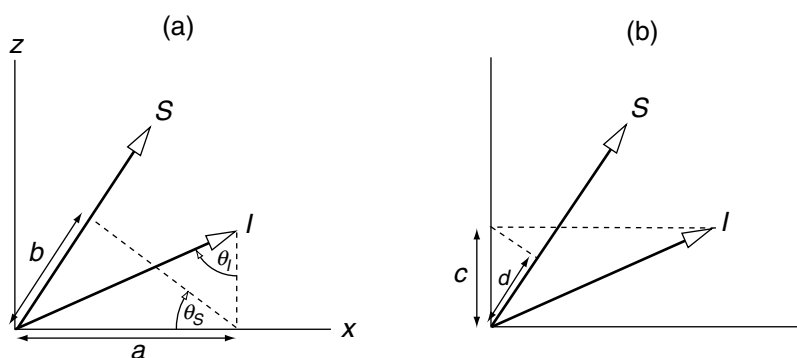
Geometric constructions for the case where the spin locking axes of *I* and *S* are tilted to different extents. Case (a) is for transverse and (b) for longitudinal relaxation.

Referring to diagram (a), the transverse component of I, labelled a, is proportional to $\sin\theta_I$; this component cross relaxes with S with a rate constant σ_t. Any S magnetization generated in this process appears along the x-axis, but only the component along the spin locking axis *of S* will survive. This component, labelled b, is proportional to $\sin\theta_S$. The effective transverse cross relaxation rate is thus $\sin\theta_I \sin\theta_S \, \sigma_t$.

Diagram (b) shows the longitudinal components. c is the longitudinal component of the I magnetization, and is proportional to $\cos\theta_I$. This component cross relaxes with rate constant σ_l to give S magnetization. The component of this magnetization along the S spin lock axis, d, is proportional to $\cos\theta_S$. The effective longitudinal cross relaxation rate constant is thus $\cos\theta_I \cos\theta_S \, \sigma_l$.

Overall, therefore, the cross relaxation rate constant of the spin locked magnetization is given by

$$\sigma_{\text{tilted}} = \sin\theta_I \sin\theta_S \, \sigma_t + \cos\theta_I \cos\theta_S \, \sigma_l$$

Using a similar geometric construction it is possible to show that the self

relaxation rate constant is

$$R_{\text{tilted},I} = \sin^2\theta_I \, R_{\text{t},I} + \cos^2\theta_I \, R_{1,I}$$

and likewise for S.

6.3.4.6 Relaxation of $2I_+S_z$

Evaluating

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},2I_+S_z\right]\right]J_q\left(\omega_p^{(q)}\right)$$

gives

$$-2I_+S_z\left\{\tfrac{1}{8}J_0(0)+\tfrac{1}{32}J_0(\omega_I-\omega_S)+\tfrac{1}{4}J_1(\omega_I)+\tfrac{1}{2}J_2(\omega_I+\omega_S)\right\}$$

there is no transfer to other terms. The differential equation is thus

$$\frac{\mathrm{d}2I_+S_z}{\mathrm{d}t}=-R_{I_+S_z}2I_+S_z$$

where

$$
\begin{aligned}
R_{I_+S_z} &= \left\{\tfrac{1}{8}J_0(0)+\tfrac{1}{32}J_0(\omega_I-\omega_S)+\tfrac{1}{4}J_1(\omega_I)+\tfrac{1}{2}J_2(\omega_I+\omega_S)\right\}\\
&= \left\{\tfrac{1}{10}j(0)+\tfrac{1}{40}j(\omega_I-\omega_S)+\tfrac{3}{40}j(\omega_I)+\tfrac{3}{20}j(\omega_I+\omega_S)\right\}b^2
\end{aligned}
$$

It is interesting to compare this with the relaxation time constant for I_+

$$R_I^{\text{t}}=\left\{\tfrac{1}{8}J_0(0)+\underline{\tfrac{1}{2}J_1(\omega_S)}+\tfrac{1}{32}J_0(\omega_I-\omega_S)+\tfrac{1}{4}J_1(\omega_I)+\tfrac{1}{2}J_2(\omega_I+\omega_S)\right\}$$

It is immediately clear that the antiphase term relaxes *more slowly* than the inphase term; the difference is the term $\tfrac{1}{2}J_1(\omega_S)$ which does not contribute to the relaxation of the antiphase term. The effect of this term was commented on in the previous section.

There is another important feature of the difference between the relaxation of inphase and antiphase terms. For the antiphase term, any additional *longitudinal* relaxation of the S spin, $R_S^{\text{addn.}}$, contributes directly to the relaxation of the operator product $2I_+S_z$; the reasons for this were discussed in Section 6.3.3.

$$R_{I_+S_z} = R_{I_+S_z}{}^{\text{dipole}} + R_S{}^{\text{addn.}}$$

Such longitudinal relaxation of spin S does not contribute to the relaxation of I_+. As such extra relaxation of S is often found, in practice it is usually the case that antiphase terms relax more quickly than inphase terms.

6.3.4.7 Relaxation of multiple quantum terms

Double quantum

Evaluating

$$-\tfrac{1}{2}\sum_{p,q}\left[A_p^{(q)},\left[A_{p'}^{(-q)},2I_+S_+\right]\right]J_q\left(\omega_p^{(q)}\right)$$

gives

$$-2I_+S_+\left\{\tfrac{1}{4}J_1(\omega_S)+\tfrac{1}{4}J_1(\omega_I)+J_2(\omega_I+\omega_S)\right\}$$

there is no transfer to other terms. The differential equation is thus

$$\frac{\mathrm{d}2I_+S_+}{\mathrm{d}t} = -R_{I_+S_+}2I_+S_+$$

where

$$R_{I_+S_+} = \left\{\tfrac{1}{4}J_1(\omega_S) + \tfrac{1}{4}J_1(\omega_I) + J_2(\omega_I + \omega_S)\right\}$$
$$= \left\{\tfrac{3}{40}j(\omega_S) + \tfrac{3}{40}j(\omega_I) + \tfrac{3}{10}j(\omega_I + \omega_S)\right\}b^2$$

The rate constant depends on the spectral density at the Larmor frequencies, and at the sum of these (in contrast to the random field case). In the spin diffusion limit, this rate constant becomes vanishingly small. However, other mechanisms which cause transverse relaxation of I or S will contribute directly to the rate constant for the double quantum coherence.

Zero quantum

The rate constant is

$$R_{I_+S_-} = \left\{\tfrac{1}{16}J_0(\omega_I - \omega_S) + \tfrac{1}{4}J_1(\omega_S) + \tfrac{1}{4}J_1(\omega_I)\right\}$$
$$= \left\{\tfrac{1}{20}j(\omega_I - \omega_S) + \tfrac{3}{40}j(\omega_S) + \tfrac{3}{40}j(\omega_I)\right\}b^2$$

6.3.5 Chemical shift anisotropy

As discussed in Section 5.3.2 the anisotropy of the chemical shift is a source of fluctuating fields in all three directions. The hamiltonian describing this anisotropic shift is

$$H = -\gamma\mathbf{I}(1 - \underline{\sigma})\mathbf{B}$$

where **I** is the vector of the three spin angular momentum operators and likewise **B** is a vector giving the components of the applied field in the three orthogonal directions

$$\mathbf{I} = \{I_x, I_y, I_z\} \qquad \mathbf{B} = \{B_x, B_y, B_z\}$$

If the applied field is just along the z direction, then only the B_z component of **B** is non-zero.

The chemical shift is described by the tensor $\underline{\sigma}$, which can be thought of as a 3×3 matrix with components σ_{xx}, σ_{xy} *etc.*

$$\underline{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

The interpretation of this tensor is that the element $\sigma_{\alpha\beta}$ gives how a magnetic field along the α direction is translated by the anisotropic shift into a field along the β direction. The size of these elements depends on the electronic structure (the factor that affects the "chemical shift"); they vary with time as the molecule tumbles in solution. It turns out that the shift tensor is usually symmetric: $\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$.

There exists a set of axes, called the principal axis system (PAS), in which the tensor is diagonal. These axes are at some fixed orientation with respect to the molecular framework.

$$\underline{\sigma}^{\mathrm{PAS}} = \begin{pmatrix} \sigma_{xx}^{\mathrm{PAS}} & 0 & 0 \\ 0 & \sigma_{yy}^{\mathrm{PAS}} & 0 \\ 0 & 0 & \sigma_{zz}^{\mathrm{PAS}} \end{pmatrix}$$

The shift tensor is specified completely by these three principal components $\sigma_{\alpha\alpha}^{\mathrm{PAS}}$. However, it is usual to define a number of other parameters related to these principal components:

$$\sigma_{\mathrm{iso}} = \tfrac{1}{3}\mathrm{Tr}\{\underline{\sigma}^{\mathrm{PAS}}\} = \tfrac{1}{3}\left(\sigma_{xx}^{\mathrm{PAS}} + \sigma_{yy}^{\mathrm{PAS}} + \sigma_{zz}^{\mathrm{PAS}}\right)$$

$$\sigma_{\|} = \sigma_{zz}^{\mathrm{PAS}} \quad \Delta = \sigma_{zz}^{\mathrm{PAS}} - \tfrac{1}{2}\left(\sigma_{xx}^{\mathrm{PAS}} + \sigma_{yy}^{\mathrm{PAS}}\right) \quad \eta = 3\left(\sigma_{xx}^{\mathrm{PAS}} + \sigma_{yy}^{\mathrm{PAS}}\right)\big/2\Delta$$

σ_{iso} is the isotropic chemical shift (dimensionless) which is observed in solution; η is called the *asymmetry parameter*. An *axially symmetric* shift tensor has

$$\sigma_{yy}^{\mathrm{PAS}} = \sigma_{xx}^{\mathrm{PAS}} = \sigma_{\perp}$$

and so $\eta = 0$. It then follows that

$$\Delta = \sigma_{\|} - \sigma_{\perp}$$

Δ is loosely called "the shift anisotropy". It is a dimensionless quantity, usually quoted in parts per million, ppm.

It is often a good approximation to assume that shift tensors are axially symmetric as they are frequently associated with chemical bonds which inherently have this symmetry.

The term in the hamiltonian which depends on σ_{iso} is time independent and forms the static hamiltonian. The remaining time dependent terms are

q	$A^{(q)}$	$F^{(q)}$	$\omega_p^{(q)}$
0	I_z	$\frac{\sqrt{5}}{3}\omega_I\Delta\left(3\cos^2\theta - 1\right)$	0
± 1	$I_{\pm}$	$\frac{\sqrt{5}}{4}\omega_I\Delta\sin 2\theta\exp(\mp i\phi)$	$\mp\omega_I$

where ω_I is the Larmor frequency, and θ and ϕ are the usual polar angles describing the orientation of the CSA tensor with respect to the z direction; these angles change with time as the molecule tumbles. The index p is not needed.

6.3.5.1 Correlation functions

The required correlation functions are

$$G_{q,q}(\tau) = \overline{F^{(q)}(t)F^{(-q)}(t-\tau)}$$

and, as before, these will be written as

$$G_{q,q}(\tau) = \overline{F^{(q)}(t)F^{(-q)}(t)}\,g(\tau) = \overline{F^{(q)^2}}\,g(\tau)$$

where $g(\tau)$ is the reduced correlation function. The average of the square of $F^{(q)}$ is computed by averaging over the ensemble, which is equivalent to averaging over all angles θ and ϕ. For example, for $q = 0$

$$\overline{F^{(0)2}} = \frac{1}{4\pi}\int\limits_{\theta=0}^{\pi}\int\limits_{\phi=0}^{2\pi}\tfrac{\sqrt{5}}{3}\omega_I\Delta\left(3\cos^2\theta-1\right)\tfrac{\sqrt{5}}{3}\omega_I\Delta\left(3\cos^2\theta-1\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= \tfrac{4}{9}\Delta^2\omega_I^2$$

In summary

q	$\overline{F^{(q)2}}$	$J_{q,-q}(\omega)=J_q(\omega)$
0	$\tfrac{4}{9}\Delta^2\omega_I^2$	$\tfrac{4}{9}\Delta^2\omega_I^2 j(\omega)$
± 1	$\tfrac{1}{6}\Delta^2\omega_I^2$	$\tfrac{1}{6}\Delta^2\omega_I^2 j(\omega)$

In fact, this is identical to the case of relaxation by a random field discussed in Section 6.3.1 . The relaxation rate constants found there were

$$R_z = 2J_1(\omega_I) \qquad R_t = \tfrac{1}{2}J_0(0)+J_1(\omega_I)$$

so, using the values from the table for the spectral densities, it is found for CSA relaxation that

$$R_z = \tfrac{1}{3}\Delta^2\omega_I^2 j(\omega_I) \qquad R_t = \left\{\tfrac{2}{9}j(0)+\tfrac{1}{6}j(\omega_I)\right\}\Delta^2\omega_I^2$$

These have a familiar form, with there being a contribution of $\tfrac{1}{2}R_z$ to the transverse rate constant, and also a contribution depending on the spectral density at zero frequency.

The CSA induced relaxation rate goes as the square of the Larmor frequency and the square of the shift anisotropy. It is thus rather unimportant for nuclei such as protons which have very small shift anisotropies, but it is very important for heteronuclei, such as ^{31}P, and some transition metals, at high magnetic fields. Note, however, that if the nucleus is at a site of cubic symmetry it has no shift anisotropy and thus there is no CSA relaxation.

In the extreme narrowing limit it can be shown that (for an axially symmetric CSA tensor)

$$\frac{R_t^{\text{ext. narrow}}}{R_z^{\text{ext. narrow}}} = \frac{7}{6}$$

This is in contrast to the case of dipolar relaxation where these two rates are equal in this limit.

6.3.6 CSA-Dipolar cross correlation

As was commented on in Section 5.3.2, cross correlation between the dipolar and CSA mechanisms is common, especially for directly bonded pairs of nuclei such as ^{15}N–^{1}H and ^{13}C–^{1}H in which the heteroatom has a significant CSA. The two hamiltonians have a variety of terms, and these are summarised in the table below. For convenience, operators with the associated frequencies, $\omega_p^{(q)}$, are placed on the same line. It is assumed that only the I spin has a significant CSA.

Dipolar hamiltonian	CSA hamiltonian	

q	p	$A_{p,\mathrm{D}}^{(q)}$	$F_{\mathrm{D}}^{(q)}$	$A_{\mathrm{CSA}}^{(q)}$	$F_{\mathrm{CSA}}^{(q)}$	$\omega_p^{(q)}$
0	0	I_zS_z	$b\left(1-3\cos^2\theta\right)$	I_z	$\frac{\sqrt5}{3}\omega_I\Delta\left(3\cos^2\theta-1\right)$	0
+0	1	$-\frac14 I_+S_-$	"			$-\omega_I+\omega_S$
-0	1	$-\frac14 I_-S_+$	"			$\omega_I-\omega_S$
±1	1	$I_zS_\pm$	$-\frac32 b\left[\sin\theta\cos\theta\exp(\mp i\phi)\right]$			$\pm\omega_S$
±1	2	$I_\pm S_z$	"	$I_\pm$	$\frac{\sqrt5}{4}\omega_I\Delta\sin2\theta\exp(\mp i\phi)$	$\pm\omega_I$
±2		$I_\pm S_\pm$	$-\frac34 b\left[\sin^2\theta\exp(\mp2i\phi)\right]$			$\mp(\omega_I+\omega_S)$

Only those terms appearing on the same line will be effective at inducing relaxation, as only these terms will be secular. Thus, there are in fact only three terms to consider: those involving the operators I_z, I_zS_+ and I_zS_-.

As described in Section 5.2.6, the key point about cross correlation is that two different interactions are involved *i.e.* in the master equation:

$$\frac{\mathrm{d}\sigma^{\mathrm{T}}(t)}{\mathrm{d}t} = -\frac12 \sum_{p,q,p',q'} \left[A_p^{(q)},\left[A_{p'}^{(q')},\sigma^{\mathrm{T}}(t)\right]\right] J_{q,-q'}\left(\omega_{p'}^{(q')}\right)\exp\left(i\left(\omega_p^{(q)}+\omega_{p'}^{(q')}\right)t\right)$$

$A_p^{(q)}$ and $A_{p'}^{(q')}$ are operators from different interactions, in this case one representing the dipole interaction and one representing the CSA interaction. As has already been noted, only those terms for which $\omega_p^{(q)}+\omega_{p'}^{(q')}=0$ need be considered.

6.3.6.1 Correlation functions

The first correlation function that is needed is

$$G_{00}^{\text{D-CSA}}(\tau) = \overline{F_{\mathrm{D}}^{(0)}(t)F_{\mathrm{CSA}}^{(0)}(t)}\, g(\tau) = \overline{F_{\text{D-CSA}}^{(0)}}^2\, g(\tau)$$

As before, the ensemble average of the interaction will be computed by averaging over all angles

$$\overline{F_{\text{D-CSA}}^{(0)}}^2 = \frac{1}{4\pi}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} b\left(1-3\cos^2\theta\right)\frac{\sqrt5}{3}\omega_I\Delta\left(3\cos^2\theta-1\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= -\tfrac{4}{3\sqrt5}b\omega_I\Delta$$

However, this calculation assumes that the CSA tensor and the dipole vector are aligned. Generally this is not the case, and so the average needs to be modified to

$$\overline{F_{\text{D-CSA}}^{(0)}}^2 = -\tfrac{4}{3\sqrt5}b\omega_I\Delta\times\tfrac12\left(3\cos^2\theta_{\mathrm{R}}-1\right)$$

$$= -\tfrac{4}{3\sqrt5}b\omega_I\Delta P_2\left(\cos\theta_{\mathrm{R}}\right)$$

where θ_{R} is the angle between the CSA tensor and the dipolar vector. The factor $P_2\left(\cos\theta_{\mathrm{R}}\right)$, has a maximum of 1 when $\theta_{\mathrm{R}} = 0$, $\pm\pi$ and goes to zero when θ_{R} is the magic angle, 54.7°.

The other correlation function is

$$G_{11}^{\text{D-CSA}}(\tau) = \overline{F_{\text{D}}^{(1)}(t)F_{\text{CSA}}^{(1)}(t)}\, g(\tau) = \overline{F_{\text{D-CSA}}^{(1)}}^{2}\, g(\tau)$$

$$\overline{F_{\text{D-CSA}}^{(1)}}^{2} = -\tfrac{1}{2\sqrt{5}}\, b\omega_I \Delta P_2\!\left(\cos\theta_{\text{R}}\right)$$

The correlation functions for CSA-D are the same as for D-CSA interactions.

6.3.6.2 Relaxation of longitudinal terms

Working through the double commutators reveals that the presence of CSA-D cross correlation leads to a transfer between I_z and $2I_zS_z$. The Solomon type equations become

$$\frac{dI_z}{dt} = -R_I I_z - \sigma_{IS}S_z - R_{I-IS}\,2I_zS_z \qquad \frac{d2I_zS_z}{dt} = -R_{IS}\,2I_zS_z - R_{I-IS}I_z$$

where the relaxation rate constants R_I, σ_{IS}, and R_{IS} have contributions from CSA and dipole relaxation as given above, and the rate constant R_{I-IS} is solely due to cross correlation and is given by

$$R_{I-IS} = 2J_1^{\text{D-CSA}}(\omega_I)$$
$$= -\tfrac{1}{\sqrt{5}}\, b\omega_I \Delta P_2\!\left(\cos\theta_{\text{R}}\right) j(\omega_I) \tag{20}$$

where $J_1^{\text{D-CSA}}(\omega)$ is the Fourier transform of $G_{11}^{\text{D-CSA}}(\tau)$. Note that as it has been assumed that only the I spin has a CSA, there is no relaxation induced transfer from S_z to $2I_zS_z$. It should also be recalled from Section 6.2.4.3 that in the presence of pure dipole relaxation, there is no transfer between I_z and $2I_zS_z$.

In practice, what this means is that during the mixing time of an NOE experiment there will be a gradual build up of the antiphase term $2I_zS_z$. For this to be observable in homonuclear systems a small flip angle pulse needs to be applied at the end of the mixing time – if a 90° pulse is used, the term is converted into multiple quantum coherence. In a heteronuclear system, the pulse at the end of the mixing time is applied to just one spin, so the antiphase term is detectable even for a 90° pulse.

In either case, it is necessary for there to be a resolved coupling between I and S for the antiphase term to be observable. As this term is accompanied by an inphase term, the result will be that the two lines of the doublet will have different intensities. Observation of such an unsymmetrical doublet is diagnostic of the presence of antiphase terms.

In Section 5.1.3 the rate constant for the transfer of $2I_zS_z$ to S_z was given as

$$\Delta_I = \tfrac{1}{2}\left(W_I^{(1)} - W_I^{(2)}\right)$$

where $W_I^{(1)}$ and $W_I^{(2)}$ are the transition rates for the two I spin transitions. As was commented on in that Section, what is required for there to be transfer to $2I_zS_z$ is that the two lines of the I spin doublet should relax at different rates. Cross correlation between dipole and CSA relaxation provides just this differential rate.

This connection leads to an physical interpretation of the effect of cross correlation. The two lines of the I spin doublet are associated with the two

different spin states of the S spin. These two lines relax at different rates, and so it follows that the relaxation of the I spin is affected by the *spin state* of the S spin. One picture is that the relaxation of the I spin depends on the CSA derived field and the field arising from the dipole of the S spin. The direction of this latter field depends on the spin state of the S spin. When the spin is one way, the dipolar field may add to the CSA derived field and hence promote relaxation. When the spin is the other way, the dipolar field may detract from the CSA derived field and so reduce the rate of relaxation. The two lines thus relax at different rates.

The expression given in Eq. [20] for the rate constant $R_{I\text{-}IS}$ shows that this can be positive or negative, depending on the sign of the CSA parameter Δ. Thus, which of the two lines of the I spin is the one which relaxes most quickly is depends on the sign of Δ.

6.3.6.3 Relaxation of transverse terms

Working through the double commutators reveals that the presence of CSA-D cross correlation leads to a transfer between I_+ and $2I_+S_z$. The Solomon type equations become

$$\frac{\mathrm{d}\,I_+}{\mathrm{d}t} = -R_I^{\mathrm{t}} I_+ - R_{I_+ - I_+ S_z} 2I_+ S_z \qquad \frac{\mathrm{d}\,2I_+ S_z}{\mathrm{d}t} = -R_{I_+ S_z} 2I_+ S_z - R_{I_+ - I_+ S_z} I_+ \quad [21]$$

where the relaxation rate constants R_I^{t} and $R_{I_+ S_z}$ have contributions from CSA and dipolar relaxation as given above. The rate constant $R_{I_+ - I_+ S_z}$ is solely due to cross correlation and is given by

$$R_{I_+ - I_+ S_z} = \tfrac{1}{2} J_0^{\text{D-CSA}}(0) + J_1^{\text{D-CSA}}(\omega_I)$$

$$= -\left\{ \tfrac{3}{2\sqrt{5}} j(0) + \tfrac{1}{2\sqrt{5}} j(\omega_I) \right\} b \omega_I \Delta P_2(\cos\theta_{\mathrm{R}})$$

where $J_q^{\text{D-CSA}}(\omega)$ is the Fourier transform of $G_{qq}^{\text{D-CSA}}(\tau)$.

As in the longitudinal case, this result implies that the two lines of the I spin doublet relax at different rates, and this would be observed in the form of different linewidths of the two components.

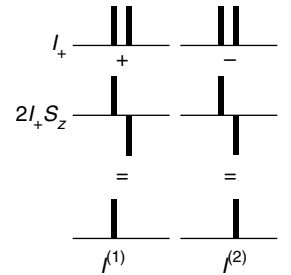### 6.3.6.4 Differential relaxation of the two lines of the doublet

In order to find out the width of the two individual lines of the I spin doublet it is necessary to convert the relaxation rates of individual operators into those of individual lines. This is readily done in this simple case once it is realized that the operator I_+ represents a situation in which the two lines of the I spin doublet are in-phase, whereas $2I_+S_z$ represents the two lines being out of phase. Therefore, the following operator combinations, $I^{(1)}$ and $I^{(2)}$ represent the individual lines of the multiplet

$$I^{(1)} = \tfrac{1}{2}\left(I_+ + 2I_+ S_z\right) \qquad I^{(2)} = \tfrac{1}{2}\left(I_+ - 2I_+ S_z\right)$$

The equation of motion for $I^{(1)}$ is simply found by adding Eqs. [21]

$$\frac{\mathrm{d}\,I^{(1)}}{\mathrm{d}t} = \tfrac{1}{2}\left[\frac{\mathrm{d}\,I_+}{\mathrm{d}t} + \frac{\mathrm{d}\,2I_+ S_z}{\mathrm{d}t}\right]$$

$$= \tfrac{1}{2}\left[-R_I^{\mathrm{t}} I_+ - R_{I_+ - I_+ S_z} 2I_+ S_z - R_{I_+ S_z} 2I_+ S_z - R_{I_+ - I_+ S_z} I_+\right]$$

The right-hand side is expressed in terms of $I^{(1)}$ and $I^{(2)}$ by noting that

$$I_+ = I^{(1)} + I^{(2)} \qquad 2I_+S_z = I^{(1)} - I^{(2)}$$

and so

$$\frac{\mathrm{d}\,I^{(1)}}{\mathrm{d}t} = \tfrac{1}{2}\begin{bmatrix} -R_I^t\left\{I^{(1)} + I^{(2)}\right\} - R_{I_+ - I_+S_z}\left\{I^{(1)} - I^{(2)}\right\} \\ -R_{I_+S_z}\left\{I^{(1)} - I^{(2)}\right\} - R_{I_+ - I_+S_z}\left\{I^{(1)} + I^{(2)}\right\} \end{bmatrix} \qquad [22]$$

$$= -\tfrac{1}{2}\left[R_I^t + 2R_{I_+ - I_+S_z} + R_{I_+S_z}\right]I^{(1)} + \tfrac{1}{2}\left[-R_I^t + R_{I_+ - I_+S_z} + R_{I_+S_z}\right]I^{(2)}$$

The operators $I^{(1)}$ and $I^{(2)}$ represent lines which differ in frequency by the coupling constant. If it is assumed that the lines are sufficiently narrow that the coupling is still well resolved, then the second term on the right on Eq. [22] can be ignored as the oscillation of $I^{(2)}$ relative to $I^{(1)}$ will be faster than the time dependence due to relaxation. This term will therefore be non-secular and so can be ignored.

A similar calculation for $I^{(2)}$ can be followed through to give the following rate constants for $I^{(1)}$ and $I^{(2)}$

$$\text{for } I^{(1)}: \quad R_{I^{(1)}} = \tfrac{1}{2}\left[R_I^t + 2R_{I_+ - I_+S_z} + R_{I_+S_z}\right]$$

$$\text{for } I^{(2)}: \quad R_{I^{(2)}} = \tfrac{1}{2}\left[R_I^t - 2R_{I_+ - I_+S_z} + R_{I_+S_z}\right]$$

As was calculated above, the rate constant $R_{I_+ - I_+S_z}$ is

$$R_{I_+ - I_+S_z} = -\left\{\tfrac{2}{3\sqrt{5}}j(0) + \tfrac{1}{2\sqrt{5}}j(\omega_I)\right\}b\omega_I \Delta P_2(\cos\theta_R)$$

The sign of $R_{I_+ - I_+S_z}$ depends on the relative signs of the gyromagnetic ratios γ_I and γ_S (these appear in b), and on the sign of the chemical shift anisotropy, Δ. If $R_{I_+ - I_+S_z}$ is positive, then the line represented by $I^{(2)}$ will relax more slowly than $I^{(1)}$ and so will be narrower. The opposite is the case if $R_{I_+ - I_+S_z}$ is negative.

The contribution made by $R_{I_+ - I_+S_z}$ turns out to be rather small in the extreme narrowing limit, but as the correlation time gets longer and longer the term becomes more significant compared to $R_I^t + R_{I_+S_z}$.

In the spin diffusion limit it is possible for the rate constant $R_{I_+ - I_+S_z}$ to be so large that it cancels out the other terms and thus leads to one of the components of the doublet being infinitely sharp as the associated operator does not relax at all. This cancellation takes place when

$$\frac{\omega_I \Delta}{b} = \frac{3}{2\sqrt{5}} \approx .67$$

Essentially, this condition is that the dipolar and CSA derived random fields cancel.

In practice there will always be other sources of relaxation present so that the line is not infinitely sharp. However, the attached proton is the dominant source of relaxation, so the line narrowing is very significant.

A typical ^{15}N–^{1}H spin pair in a protein has $\Delta_N = -160$ ppm and $r = 1.01$ Å. At a field of 18.8 T (800 MHz for proton), and with a correlation time of 10 ns, the relaxation rate constants for the two lines of the ^{15}N doublet are 77 and 4 s^{-1}. If the correlation time rises to 30 ns, the rate constants are 230 and 13 s^{-1}. There is more than an order of magnitude difference between the

linewidths. With these parameters, the narrowing is a maximum at a field of about 11.5 T.

The proton has a much smaller CSA than ^{15}N, but the proton Larmor frequency is about ten times higher than that for ^{15}N so that the effect of a given CSA is much greater. A typical ^{15}N–^{1}H spin pair in a protein has Δ_H = -16 ppm which, taking into account the Larmor frequency of proton, is significant. As a result, the two lines of the proton doublet also have different linewidths. For the parameters described in the previous section the rate constants are 75 and 4 s^{-1} for τ_c = 10 ns, and 226 and 13 s^{-1} for τ_c = 30 ns. Thus, the effect on the proton and ^{15}N doublets is much the same.

An important consequence of these observations is the development of the TROSY experiment.