5. Relaxation

Relaxation is the process by which the spins in the sample come to equilibrium with the surroundings. At a practical level, the rate of relaxation determines how fast an experiment can be repeated, so it is important to understand how relaxation rates can be measured and the factors that influence their values. The rate of relaxation is influenced by the physical properties of the molecule and the sample, so a study of relaxation phenomena can lead to information on these properties. Perhaps the most often used and important of these phenomena in the nuclear Overhauser effect (NOE) which can be used to probe internuclear distances in a molecule. Another example is the use of data on relaxation rates to probe the internal motions of macromolecules.

In many kinds of spectroscopy relaxation is very fast, making it difficult to study. However, in NMR relaxation is rather slow, typically measured on a timescale of seconds, and so it is much easier to study and exploit. The reason that NMR relaxation is so slow is that molecular collisions, which are responsible for the efficient relaxation of electronic, vibrational and rotational energy levels, have little or no effect on the nuclei. The interactions responsible for relaxation in NMR are rather weak and involve, not surprisingly, magnetic interactions with the nuclei.

To understand the microscopic origin of relaxation it is necessary to use quantum mechanics to consider the details of the motions of individual spins in the sample. At the most basic level, these motions are identical in origin to those encountered in normal pulsed NMR. However, the difference is that the magnetic fields which affect the spins are not applied by the spectrometer *e.g.* as a pulse, but appear due to interactions with other molecules in the sample. These interactions are modulated by molecular motion and so are time dependent and random. Working out the effect of such random fields will require some extra quantum mechanical tools not needed in the normal description of pulsed NMR. It will also be seen that the random nature of these interactions is what drives the spins towards equilibrium.

5.1 Describing relaxation

In this section the language and concepts used to describe relaxation will be introduced and illustrated. At this stage it will simply be taken for granted that there are processes which give rise to relaxation; the relaxation rate constants will simply be treated as parameters. In the subsequent sections it will be seen how relaxation arises and how the values of the rate constants can be calculated.

5.1.1 What is relaxation?

Relaxation is the process by which the spins return to *equilibrium.* Equilibrium is the state in which (a) the populations of the energy levels are those predicted by the Boltzmann distribution and (b) there are no coherences present in the system.

Both of the criteria (a) and (b) refer to a system in which there are many

spins present, that is an *ensemble*. As was seen in Section 1.6, a coherence arises when there is a special relationship between the phases of the wavefunctions of the spins in the sample; observable transverse magnetization is an example of such a coherence. The concept of populations – that is the number of spins occupying a particular energy level – is one which only makes sense when there are many spins present. Relaxation as an approach to equilibrium is therefore a concept which is associated with the behaviour of large numbers of spins – a macroscopic sample. It is not possible to talk about a single spin returning to equilibrium.

One of the features of a system at equilibrium is that it should not display any time dependence (*e.g.* a mechanical system at equilibrium does not move and the concentrations of species which have come to chemical equilibrium do not change with time). The presence of coherences is therefore incompatible with equilibrium as coherences are time dependent. For example, transverse magnetization, which is a coherence, precesses in the *xy*-plane giving rise to oscillating *x*- and *y*-components which can be detected.

5.1.1.1 Populations

The NMR sample consists of a large number of identical molecules. Due to the rapid isotropic motion in a liquid, it is a very good approximation to assume that the spins in different molecules are not interacting with one another. Even within the same molecule some of the interactions between the spins are also averaged to zero by the motion of the liquid, typically leaving just the scalar coupling. The set of interacting spins in a molecule is called the *spin system*. Thus, the sample can be thought of as an ensemble of identical spin systems.

It will be seen that relaxation arises from these interactions both between and in spin systems. However, relaxation phenomena are such a weak perturbation on the system that it is an excellent approximation to assume in the first instance that the sample consists of an ensemble of non-interacting spin systems.

Each member of the ensemble has the same spin system and so has the same set of quantized energy levels. Different members of the ensemble will find themselves in different energy levels, so that taking the sample as a whole it is possible to talk about the population of a particular energy level. By population, it is meant the number of members of the ensemble which are to be found in a particular energy level.

At equilibrium, the number, n_i, in energy level i with energy ε_i is given by the Boltzmann distribution:

$$n_i = \frac{g_i N}{Z} \exp\left(\frac{-\varepsilon_i}{kT}\right)$$

where g_i is the degeneracy of the ith level, k is Boltzmann's constant, T is the temperature and N is the number of systems in the ensemble. Z is the partition function, defined as

$$Z = \sum_j g_j \exp\left(\frac{-\varepsilon_j}{kT}\right)$$

where the sum is over all energy levels of the spin system.

In words, the Boltzmann distribution says that as the energy of a level goes up, its population goes down. It also says that only levels with energies of the order of kT or less (measured from the ground state) are significantly populated.

For a system consisting of one spin in a magnetic field, there are just two energy levels (α and β) with energies $\pm\frac{1}{2}\hbar\omega_0$, where ω_0 is the Larmor frequency in rad s^{-1} (Section 1.4); the levels are not degenerate. The partition function is therefore

$$Z = \exp\left(\frac{\hbar\omega_0}{2kT}\right) + \exp\left(\frac{-\hbar\omega_0}{2kT}\right)$$

For typical NMR frequencies, $\hbar\omega_0 << kT$, so the argument of the exponential is a small number and the approximation $\exp(x) \approx 1 + x$ can be used. So

$$Z \approx \left(1 + \frac{\hbar\omega_0}{2kT}\right) + \left(1 - \frac{\hbar\omega_0}{2kT}\right) \approx 2$$

The population of the two spin states is therefore

$$n_{\alpha/\beta} = \frac{N}{2}\exp\left(\frac{\pm\hbar\omega_0}{2kT}\right) \qquad [1]$$

The population difference is therefore

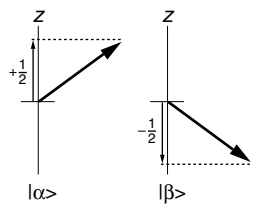
$$n_\alpha - n_\beta = \frac{N}{2}\left[\exp\left(\frac{\hbar\omega_0}{2kT}\right) - \exp\left(\frac{-\hbar\omega_0}{2kT}\right)\right]$$

$$\approx \frac{N}{2}\left[\left(1 + \frac{\hbar\omega_0}{2kT}\right) - \left(1 - \frac{\hbar\omega_0}{2kT}\right)\right] \approx \frac{N}{2}\frac{\hbar\omega_0}{kT}$$

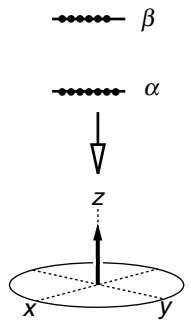
where, as before, the approximation for $\exp(x)$ has been used. For spins with a Larmor frequency of 500 MHz this difference is of the order of 4×10^{-5} N at room temperature. In words, as the two energy levels are so closely spaced in energy compared to kT their populations are almost equal. It is this very small population difference which ultimately leads to an observable signal in NMR.

5.1.1.2 Longitudinal magnetization

When an NMR sample is placed in a static magnetic field and allowed to come to equilibrium it is found that a net magnetization of the sample along the direction of the applied field (traditionally the z-axis) is developed. Magnetization parallel to the applied field is termed longitudinal.



Vector representation of the two possible spin states of a spin-half nucleus.



A population difference gives rise to net magnetization along the *z*-axis.

This equilibrium magnetization arises from the unequal population of the two energy levels. The argument is that the state α has a magnetic quantum number $+\frac{1}{2}$ and therefore is represented by a vector with a projection of $+\frac{1}{2}$ along the field direction; likewise β has a projection of $-\frac{1}{2}$. If the number of spins in the two states were equal the individual z-components would cancel, leaving no resultant. However, the α state is slightly more populated so the cancellation is not complete resulting in a net contribution along the field direction. This is the origin of the equilibrium magnetization.

The z-magnetization, M_z, is proportional to the population difference

$$M_z \propto \left(n_\alpha - n_\beta\right)$$

where n_α and n_β are the populations of the two corresponding energy levels. Ultimately, the constant of proportion just determines the absolute size of the signal we will observe. As we are generally interested in the *relative* size of magnetizations and signals we may just as well write

$$M_z = \left(n_\alpha - n_\beta\right) \qquad [2]$$

5.1.1.3 Transverse magnetization and coherence

Transverse magnetization or, more generally, coherence, cannot be described using populations. A detailed discussion of the phenomenon of coherence was given in Section 1.6; the main points will be reviewed here.

The wavefunction for a single spin can be written as a superposition state

$$\left|\psi(t)\right\rangle = c_\alpha(t)\left|\alpha\right\rangle + c_\beta(t)\left|\beta\right\rangle \qquad [3]$$

where $c_\alpha(t)$ and $c_\beta(t)$ are complex coefficients which depend on time. The expectation value of the operator, I_x, $\langle I_x \rangle$ is

$$\langle I_x \rangle = \tfrac{1}{2}\left(c_\beta^* c_\alpha + c_\alpha^* c_\beta\right)$$

where, for brevity, the time dependence has not been indicated explicitly. This expectation value is the value of x-component of the angular momentum, averaged over many measurements of the same system.

It is convenient to write the coefficients c_α *etc.* in the r/ϕ format

$$c_\alpha = r_\alpha \exp\left(i\phi_\alpha\right) \qquad c_\beta = r_\alpha \exp\left(i\phi_\beta\right)$$

Using these $\langle I_x \rangle$ is

$$\langle I_x \rangle = r_\alpha r_\beta \cos\left(\phi_\alpha - \phi_\beta\right)$$

All of this refers to a single spin. However, in a sample there are many spins, so to find the total angular momentum along the x-direction, which gives the x-magnetization from the sample, it is necessary to add up the contributions from each spin in the sample

$$
\begin{aligned}
\overline{\langle I_x \rangle} &= \langle I_x \rangle_1 + \langle I_x \rangle_2 + \langle I_x \rangle_3 + \ldots \\
&= \tfrac{1}{2}\left(c_\beta^* c_\alpha + c_\beta^* c_\alpha\right)_1 + \tfrac{1}{2}\left(c_\beta^* c_\alpha + c_\beta^* c_\alpha\right)_2 + \tfrac{1}{2}\left(c_\beta^* c_\alpha + c_\beta^* c_\alpha\right)_3 + \ldots \\
&= \tfrac{1}{2}\left(\overline{c_\beta^* c_\alpha} + \overline{c_\beta^* c_\alpha}\right) \\
&= \overline{r_\alpha r_\beta \cos\left(\phi_\alpha - \phi_\beta\right)}
\end{aligned}
$$

where $\langle I_x \rangle_i$ is the contribution from the ith spin in the sample. This process is called ensemble averaging and indicated by the overbar.

The contribution from each spin depends on the values of r and ϕ. It is supposed that at equilibrium the phases ϕ are distributed randomly, and as a result the average of the cosine term in the last line above is zero. The *hypothesis of random phases* predicts that there is no x-magnetization at equilibrium, which is consistent with observation.

It was also shown in Section 1.6 that a radio-frequency pulse can cause the coefficients c_α and c_β to vary in such a way that the ensemble average

$$\overline{c_\beta^* c_\alpha}$$

is no longer zero. This situation is referred to as a *coherence*, and it is clear from the above relations that it will give rise to an ensemble average for I_x which is non zero *i.e.* net x-magnetization. In this situation, the phases are no longer random.

It therefore follows that the loss of net x-magnetization results from a progressive randomization of the phases of the individual spins which contribute to the ensemble. When the phases are completely randomized once more, equilibrium will be reached and there will be no transverse magnetization.

5.1.1.4 Populations again

For the superposition state of Eq. [3] the expectation value of the z-component of angular momentum is

$$\langle I_z \rangle = \tfrac{1}{2}\left(c_\alpha c_\alpha^* - c_\beta c_\beta^*\right) = \tfrac{1}{2}\left(r_\alpha^2 - r_\beta^2\right)$$

and the ensemble average is

$$\overline{\langle I_z \rangle} = \tfrac{1}{2}\left(\overline{c_\alpha c_\alpha^*} - \overline{c_\beta c_\beta^*}\right) = \tfrac{1}{2}\left(\overline{r_\alpha^2} - \overline{r_\beta^2}\right) \qquad [4]$$

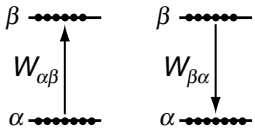
Note that, in contrast to the case of $\langle I_x \rangle$ the phases do not come into this expression, so the ensemble is not necessarily zero at equilibrium.

In quantum mechanics the product $c_\alpha c_\alpha^*$ is identified at the probability of finding the spin in the α state, and so its ensemble average can be identified with the population of this state. So, Eq. [4] says that the ensemble average of the x-component of the angular momentum, that is the net x-magnetization, is proportional to the population difference between the α and β states, just as was stated in Section 5.1.1.1 .

5.1.2 Rate equations and rate constants

The populations of energy levels are in many ways analogous to

concentrations in chemical kinetics, and many of the same techniques that are used to describe the rates of chemical reactions can also be used to describe the dynamics of populations. This will lead to a description of the dynamics of the z-magnetization but not, as has been seen from Section 5.1.1.3, of the transverse magnetization.



Suppose that the populations of the α and β states at time t are n_α and n_β, respectively. If these are not the equilibrium values, then for the system to reach equilibrium the population of one level must increase and that of the other must decrease. This implies that there must be *transitions* between the two levels *i.e.* something must happen which causes a spin to move from the α state to the β state or *vice versa*.

The simplest assumption is that the rate of transitions from α to β is proportional to the population of the α state (*i.e.* a first order process):

$$\begin{aligned}\text{rate from } \alpha \text{ to } \beta &\propto n_\alpha \\ &= W_{\alpha\beta} n_\alpha\end{aligned}$$

where $W_{\alpha\beta}$ is the rate constant for transitions from α to β. Likewise the rate of transitions from β to α is written

$$\text{rate from } \beta \text{ to } \alpha = W_{\beta\alpha} n_\beta$$

So, the overall rate of change of the populations of the two states are

$$\frac{\mathrm{d}n_\alpha}{\mathrm{d}t} = W_{\beta\alpha} n_\beta - W_{\alpha\beta} n_\alpha \qquad \frac{\mathrm{d}n_\beta}{\mathrm{d}t} = W_{\alpha\beta} n_\alpha - W_{\beta\alpha} n_\beta \qquad [5]$$

In these differential equations the positive terms represent a gain in population, and the negative ones a loss.

The z-magnetization just depends on the population difference (Eq. [2]), so using Eqs. [5] it is possible to find a differential equation for M_z

$$\begin{aligned}\frac{\mathrm{d}M_z}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\left(n_\alpha - n_\beta\right) = \frac{\mathrm{d}n_\alpha}{\mathrm{d}t} - \frac{\mathrm{d}n_\beta}{\mathrm{d}t} \\ &= W_{\beta\alpha} n_\beta - W_{\alpha\beta} n_\alpha - W_{\alpha\beta} n_\alpha + W_{\beta\alpha} n_\beta \\ &= -2W_{\alpha\beta} n_\alpha + 2W_{\beta\alpha} n_\beta\end{aligned}$$

Not surprisingly, the rate of change of M_z depends on both the transition rates.

At equilibrium the z-magnetization must not be changing, so

$$\begin{aligned}\left.\frac{\mathrm{d}M_z}{\mathrm{d}t}\right|_{\mathrm{eq}} &= -2W_{\alpha\beta} n_\alpha^0 + 2W_{\beta\alpha} n_\beta^0 = 0 \\ \text{hence } \frac{n_\alpha^0}{n_\beta^0} &= \frac{W_{\beta\alpha}}{W_{\alpha\beta}}\end{aligned} \qquad [6]$$

where n_α^0 is the equilibrium population of the α state, and likewise for β.

At equilibrium, the lower energy state (α) is the more populated, so it follows that $W_{\beta\alpha}$ must be larger than $W_{\alpha\beta}$. In other words, the *probability of a spin going from the higher energy state to the lower one is higher than that for the reverse process.*

The extent to which these rates are different can be calculated from by

using the Boltzmann distribution to find n_α^0/n_β^0. From Eq. [1]

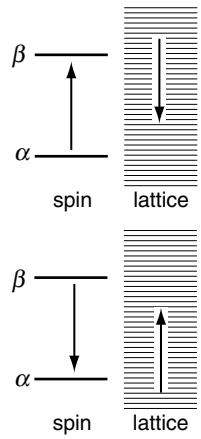
$$\frac{W_{\beta\alpha}}{W_{\alpha\beta}} = \frac{n_\alpha^0}{n_\beta^0} = \frac{\exp\left(\dfrac{\hbar\omega_0}{2kT}\right)}{\exp\left(\dfrac{-\hbar\omega_0}{2kT}\right)} = \exp\left(\frac{\hbar\omega_0}{kT}\right)$$

5.1.2.1 The lattice

Why is it that the transition rate constants for the $\alpha\rightarrow\beta$ and $\beta\rightarrow\alpha$ processes are different? The key lies in understanding the details of the energy flow between the spin and the surroundings. If the spin goes from the lower to the upper state it requires energy which must come from somewhere; likewise, if the spin drops from the higher to the lower energy level the energy given out must be taken up elsewhere.

This sink or source of energy is traditionally called the *lattice.* This name really implies the surroundings in general, rather than a particular kind of surroundings such as a crystalline lattice; it is simply a historical accident that the surroundings have been termed the lattice.

When the spin moves up in energy, the lattice must experience a corresponding drop in energy – that is, there must be a transition in the lattice from a higher to a lower energy level. Likewise, when the spin gives up energy as it falls to the lower state there must be a corresponding transition in the lattice which takes it to a higher level.



The amounts of energy involved in NMR transitions are so tiny and the lattice (the surroundings) are so large that it is safe to assume that there will always be a transition in the lattice whose energy matches that of the spin. Put another way, the density of quantum states in the lattice is so high that they form a virtual continuum.

If the lattice is at equilibrium, its energy levels are populated in a way which is predicted by the Boltzmann distribution; the populations of the lattice levels decrease as they go up in energy. Therefore, it is "easier" for the lattice to take in energy than for it to give out energy as in taking in energy the transition in the lattice starts from a more populated level. In contrast, to give out energy, the lattice has to start in a higher energy level which is less populated.

The probability that the lattice will be able to take in energy is thus higher than the probability that it will be able to give out the same amount of energy. In terms of the two rate constants, this implies that $W_{\beta\alpha} > W_{\alpha\beta}$, which is what is required for the spins to come to equilibrium with the lattice. A detailed discussion of the population distribution of the lattice shows that these two rate constants are expected to be in precisely the ratio given by Eq. [6].

This simple example illustrates what turns out to be a more general point which is that to obtain a correct description of NMR relaxation it is important to consider *both* the spins and the lattice as quantum objects. Unfortunately, this considerably complicates the theory needed to predict relaxation rate constants. However, there is neat way of side-stepping this

problem, which is described in the next section.

5.1.2.2 Equilibrium

It will turn out that if the quantum nature of the lattice is ignored, any theory about the transition rate constant will predict that $W_{\beta\alpha} = W_{\alpha\beta}$ (= W). If this is the case, the equilibrium situation, described by Eq. [6], becomes

$$\left.\frac{\mathrm{d}M_z}{\mathrm{d}t}\right|_{\mathrm{eq}} = -2Wn_\alpha^0 + 2Wn_\beta^0 = 0$$

$$\text{hence } n_\alpha^0 = n_\beta^0 \quad \text{and} \quad M_z^0 = n_\alpha^0 - n_\beta^0 = 0$$

where M_z^0 is the equilibrium z-magnetization. In other words, the assumption that the two transition rate constants are equal results in a prediction of zero equilibrium z-magnetization, which is certainly not correct.

The situation can be retrieved by modifying the rate equations given in Eq. [5] so that rather than the rates depending on the populations they depend on the *difference of the populations* from their equilibrium values. So

$$\frac{\mathrm{d}n_\alpha}{\mathrm{d}t} = W_{\beta\alpha}n_\beta - W_{\alpha\beta}n_\alpha \qquad \frac{\mathrm{d}n_\beta}{\mathrm{d}t} = W_{\alpha\beta}n_\alpha - W_{\beta\alpha}n_\beta \qquad [5]$$

become

$$\frac{\mathrm{d}n_\alpha}{\mathrm{d}t} = W\left(n_\beta - n_\beta^0\right) - W\left(n_\alpha - n_\alpha^0\right) \qquad \frac{\mathrm{d}n_\beta}{\mathrm{d}t} = W\left(n_\alpha - n_\alpha^0\right) - W\left(n_\beta - n_\beta^0\right)$$

With this assumption, the equation for the z-magnetization is

$$\begin{aligned}\frac{\mathrm{d}M_z}{\mathrm{d}t} &= \frac{\mathrm{d}n_\alpha}{\mathrm{d}t} - \frac{\mathrm{d}n_\beta}{\mathrm{d}t} \\ &= W\left(n_\beta - n_\beta^0\right) - W\left(n_\alpha - n_\alpha^0\right) - W\left(n_\alpha - n_\alpha^0\right) + W\left(n_\beta - n_\beta^0\right) \\ &= -2W\left(n_\alpha - n_\beta\right) + 2W\left(n_\alpha^0 - n_\beta^0\right) \\ &= -2W\left(M_z - M_z^0\right)\end{aligned}$$

At equilibrium, $\mathrm{d}M_z/\mathrm{d}t = 0$, and so the last line gives the correct result that $M_z = M^0{}_z$ at equilibrium.

In fact, provided that we replace the populations by their deviations from their equilibrium values (or, equivalently, magnetizations by deviations from their equilibrium values) it is possible to use the simpler theory for calculating transition rate constants. Quantum effects from the lattice need not be considered.

5.1.2.3 Differential equations for magnetizations and operators

The discussion in the previous section led to a differential equation describing the motion of the z-magnetization

$$\frac{\mathrm{d}M_z(t)}{\mathrm{d}t} = -R_z\left(M_z(t) - M_z^0\right) \qquad [7]$$

where the rate constant, $R_z = 2W$ and M_z has been written explicitly as a

function of time, $M_z(t)$. This equation can easily be integrated:

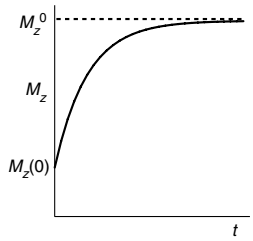
$$\int \frac{\mathrm{d}M_z(t)}{\left(M_z(t) - M_z^0\right)} = \int -R_z \mathrm{d}t$$

$$\ln\left(M_z(t) - M_z^0\right) = -R_z t + \text{const.}$$

If, at time zero, the magnetization is $M_z(0)$, the constant of integration can be determined. Hence

$$\ln\left(M_z(t) - M_z^0\right) = -R_z t + \ln\left(M_z(0) - M_z^0\right)$$

$$\text{or} \quad M_z(t) = \left[M_z(0) - M_z^0\right]\exp\left(-R_z t\right) + M_z^0$$



In words, this says that the z-magnetization returns from $M_z(0)$ to the equilibrium value following an exponential law. The time constant of the exponential is $1/R_z$. This time constant is the familiar T_1 from the Bloch equations.

The z-magnetization is proportional to the ensemble average of the expectation value of the operator for the z-component of spin angular momentum:

$$M_z \propto \overline{\langle I_z \rangle}.$$

Therefore Eq. [7] can be written

$$\frac{\mathrm{d}\overline{\langle I_z \rangle}(t)}{\mathrm{d}t} = -R_z\left(\overline{\langle I_z \rangle}(t) - \overline{\langle I_z \rangle}^0\right) \qquad [8]$$

It is particularly convenient to express relaxation behaviour in terms of operators as multiple-pulse sequences are often analysed using operators. It is common to write Eq. [8] as

$$\frac{\mathrm{d}I_z(t)}{\mathrm{d}t} = -R_z\left(I_z(t) - I_z^0\right)$$

where the expectation value and the ensemble average is implied; as it stands this last equation seems to imply that the operators change with time, which is not what is meant. What is changing is the wavefunctions and populations of the spin system.

5.1.3 Solomon equations

The idea of writing differential equations for the populations, and then transcribing these into magnetizations, is a particularly convenient way of describing relaxation, especially in more complex system. This will be illustrated in this section.

Consider a sample consisting of molecules which contain two spins, I and S; the spins are not coupled. As was seen in Section 1.4, the two spins have between them four energy levels, which can be labelled according to the spin states of the two spins.

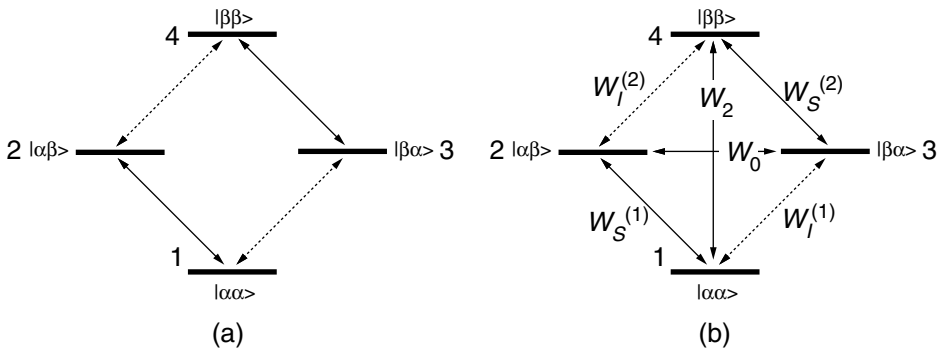


Diagram (a) shows the energy levels of a two spin system; the levels are labelled with the spin of I first and the spin of S second. The dashed arrows indicate allowed transitions of the I spin, and the solid arrows indicate allowed transitions of the S spin. Diagram (b) shows the relaxation induced transitions which are possible amongst the same set of levels.

It turns out that in such a system it is possible to have relaxation induced transitions between *all* possible pairs of energy levels, even those transitions which are forbidden in normal spectroscopy; why this is so will be seen in detail below. The rate constants for the two allowed I spin transitions will be denoted $W_I^{(1)}$ and $W_I^{(2)}$, and likewise for the spin S transitions. The rate constant for the transition between the $\alpha\alpha$ and $\beta\beta$ states is denoted W_2, the "2" indicating that it is a double quantum transition. Finally, the rate constant for the transition between the $\alpha\beta$ and $\beta\alpha$ states is denoted W_0, the "0" indicating that it is a double quantum transition.

Just in the same was as was done in Section 5.1.2, rate equations can be written for the flow of population from any of the levels. For example, for level 1

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -W_S^{(1)}n_1 - W_I^{(1)}n_1 - W_2 n_1 + W_S^{(1)}n_2 + W_I^{(1)}n_3 + W_2 n_4$$

The negative terms are rates which lead to a loss of population of level 1 and the positive terms are ones that lead to a gain in its population. As was discussed in Section 5.1.2.2 the populations ought to be written as deviations from their equilibrium values, $\left(n_i - n_i^{\upsilon}\right)$. However, to do this results in unnecessary complexity; rather, the calculation will be carried forward as written and then at the last stage the populations will be replaced by their deviations from equilibrium.

The corresponding equations for the other populations are

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = -W_S^{(1)}n_2 - W_I^{(2)}n_2 - W_0 n_2 + W_S^{(1)}n_1 + W_I^{(2)}n_4 + W_0 n_3$$

$$\frac{\mathrm{d}n_3}{\mathrm{d}t} = -W_I^{(1)}n_3 - W_S^{(2)}n_3 - W_0 n_3 + W_I^{(1)}n_1 + W_S^{(2)}n_4 + W_0 n_2$$

$$\frac{\mathrm{d}n_4}{\mathrm{d}t} = -W_S^{(2)}n_4 - W_I^{(2)}n_4 - W_2 n_4 + W_S^{(2)}n_3 + W_I^{(2)}n_2 + W_2 n_1$$

All of this can be expressed in a more compact way if we introduce the I and S spin z-magnetizations, just as was done in Section 5.1.1.2 . The I spin magnetization is equal to the population difference across the two I spin transitions, 1–3 and 2–4

$$I_z = n_1 - n_3 + n_2 - n_4 \qquad [9]$$

As discussed above, the magnetization has been represented as the

corresponding operator, I_z. Likewise for the S-spin magnetization

$$S_z = n_1 - n_2 + n_3 - n_4 \qquad [10]$$

A fourth combination of populations will be needed, which is represented by the operator $2I_zS_z$

$$2I_zS_z = n_1 - n_3 - n_2 + n_4 \qquad [11]$$

Comparing this with Eq. [9] reveals that $2I_zS_z$ represents the *difference* in population differences across the two I-spin transitions; likewise, comparison with Eq. [10] shows that the same operator also represents the difference in population differences across the two S-spin transitions.

Taking the derivative of Eq. [9] and then substituting for the derivatives of the populations gives

$$\begin{aligned}
\frac{\mathrm{d}I_z}{\mathrm{d}t} &= \frac{\mathrm{d}n_1}{\mathrm{d}t} - \frac{\mathrm{d}n_3}{\mathrm{d}t} + \frac{\mathrm{d}n_2}{\mathrm{d}t} - \frac{\mathrm{d}n_4}{\mathrm{d}t} \\
&= -W_S^{(1)}n_1 - W_I^{(1)}n_1 - W_2n_1 + W_S^{(1)}n_2 + W_I^{(1)}n_3 + W_2n_4 \\
&+W_I^{(1)}n_3 + W_S^{(2)}n_3 + W_0n_3 - W_I^{(1)}n_1 - W_S^{(2)}n_4 - W_0n_2 \\
&-W_S^{(1)}n_2 - W_I^{(2)}n_2 - W_0n_2 + W_S^{(1)}n_1 + W_I^{(2)}n_4 + W_0n_3 \\
&+W_S^{(2)}n_4 + W_I^{(2)}n_4 + W_2n_4 - W_S^{(2)}n_3 - W_I^{(2)}n_2 - W_2n_1
\end{aligned} \qquad [12]$$

This unpromising looking equation can be expressed in terms of I_z, S_z *etc.* by first introducing one more operator E, which is essentially the identity or unit operator

$$E = n_1 + n_2 + n_3 + n_4 \qquad [13]$$

and then realizing that the populations, n_i, can be written in terms of E, I_z, S_z, and $2I_z\,S_z$:

$$\begin{aligned}
n_1 &= \tfrac{1}{4}\left(E + I_z + S_z + 2I_zS_z\right) \\
n_2 &= \tfrac{1}{4}\left(E + I_z - S_z - 2I_zS_z\right) \\
n_3 &= \tfrac{1}{4}\left(E - I_z + S_z - 2I_zS_z\right) \\
n_4 &= \tfrac{1}{4}\left(E - I_z - S_z + 2I_zS_z\right)
\end{aligned}$$

where these relationships can easily be verified by substituting back in the definitions of the operators in terms of populations, Eqs. [9] – [13].

After some tedious algebra, the following differential equation is found for I_z

$$\begin{aligned}
\frac{\mathrm{d}I_z}{\mathrm{d}t} &= -\left(W_I^{(1)} + W_I^{(2)} + W_2 + W_0\right)I_z \\
&\quad -\left(W_2 - W_0\right)S_z - \left(W_I^{(1)} - W_I^{(2)}\right)2I_zS_z
\end{aligned} \qquad [14]$$

Similar algebra gives the following differential equations for the other operators

$$\frac{\mathrm{d}S_z}{\mathrm{d}t} = -\left(W_2 - W_0\right)I_z - \left(W_S^{(1)} + W_S^{(2)} + W_2 + W_0\right)S_z - \left(W_S^{(1)} - W_S^{(2)}\right)2I_zS_z$$

$$\frac{\mathrm{d}2I_zS_z}{\mathrm{d}t} = -\left(W_I^{(1)} - W_I^{(2)}\right)I_z - \left(W_S^{(1)} - W_S^{(2)}\right)S_z$$
$$-\left(W_I^{(1)} + W_I^{(2)} + W_S^{(1)} + W_S^{(2)}\right)2I_zS_z$$

As expected, the total population, represented by E, does not change with time. These three differential equations are known as the *Solomon equations*.

It must be remembered that the populations used to derive these equations are really the deviation of the populations from their equilibrium values. As a result, the I and S spin magnetizations should properly be their deviations from their equilibrium values, I_z^0 and S_z^0; the equilibrium value of $2I_zS_z$ is easily shown, from its definition, to be zero. For example, Eq. [14] becomes

$$\frac{\mathrm{d}\left(I_z - I_z^0\right)}{\mathrm{d}t} = -\left(W_I^{(1)} + W_I^{(2)} + W_2 + W_0\right)\left(I_z - I_z^0\right)$$
$$-\left(W_2 - W_0\right)\left(S_z - S_z^0\right) - \left(W_I^{(1)} - W_I^{(2)}\right)2I_zS_z$$

5.1.3.1 Interpreting the Solomon equations

What the Solomon equations predict is, for example, that the rate of change of I_z depends not only on $I_z - I_z^0$, but also on $S_z - S_z^0$ and $2I_zS_z$. In other words the way in which the magnetization on the I spin varies with time depends on what is happening to the S spin – the two magnetizations are connected. This phenomena, by which the magnetizations of the two different spins are connected, is called *cross relaxation*.

The rate at which S magnetization is transferred to I magnetization is given by the term

$$\left(W_2 - W_0\right)\left(S_z - S_z^0\right)$$

in Eq. [14]; $(W_2–W_0)$ is called the cross-relaxation rate constant, and is sometimes given the symbol σ_{IS}. It is clear that in the absence of the relaxation pathways between the $\alpha\alpha$ and $\beta\beta$ states (W_2), or between the $\alpha\beta$ and $\beta\alpha$ states (W_0), there will be no cross relaxation. This term is described as giving rise to transfer from S to I as it says that the rate of change of the I spin magnetization is proportional to the deviation of the S spin magnetization from its equilibrium value. Thus, if the S spin is not at equilibrium the I spin magnetization is perturbed.

In Eq. [14] the term

$$\left(W_I^{(1)} + W_I^{(2)} + W_2 + W_0\right)\left(I_z - I_z^0\right)$$

describes the relaxation of I spin magnetization on its own; this is sometimes called the self relaxation. Even if W_2 and W_0 are absent, self relaxation still occurs. The self relaxation rate constant, given in the previous equation as a sum of W values, is sometimes given the symbol R_I or ρ_I.

Finally, the term

$$\left(W_I^{(1)} - W_I^{(2)}\right)2I_zS_z$$

in Eq. [14] describes the transfer of I_zS_z into I spin magnetization. Recall that $W_I^{(1)}$ and $W_I^{(2)}$ are the relaxation induced rate constants for the two allowed transitions of the I spin (1–3 and 2–4). Only if these two rate constants are different will there be transfer from $2I_zS_z$ into I spin magnetization. It will be seen later in Section 6.2.6 that such a situation arises when there is cross-correlation between different relaxation mechanisms. The rate constants for this transfer will be written

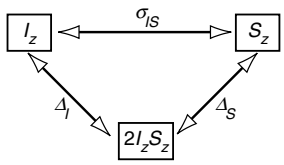
$$\Delta_I = \left(W_I^{(1)} - W_I^{(2)}\right) \qquad \Delta_S = \left(W_S^{(1)} - W_S^{(2)}\right)$$

According to the final Solomon equation, the operator $2I_zS_z$ shows self relaxation with a rate constant

$$R_{IS} = \left(W_I^{(1)} + W_I^{(2)} + W_S^{(1)} + W_S^{(2)}\right)$$

Note that the W_2 and W_0 pathways do not contribute to this. This rate combined constant will be denoted R_{IS}.

Using these combined rate constants, the Solomon equations can be written



$$\begin{aligned}
\frac{\mathrm{d}\left(I_z - I_z^0\right)}{\mathrm{d}t} &= -R_I\left(I_z - I_z^0\right) - \sigma_{IS}\left(S_z - S_z^0\right) - \Delta_I 2I_zS_z \\
\frac{\mathrm{d}\left(S_z - S_z^0\right)}{\mathrm{d}t} &= -\sigma_{IS}\left(I_z - I_z^0\right) - R_S\left(S_z - S_z^0\right) - \Delta_S 2I_zS_z \qquad [15] \\
\frac{\mathrm{d}2I_zS_z}{\mathrm{d}t} &= -\Delta_I\left(I_z - I_z^0\right) - \Delta_S\left(S_z - S_z^0\right) - R_{IS}2I_zS_z
\end{aligned}$$

The pathways between the different magnetization are visualized in the diagram opposite. Note that as $\mathrm{d}I_z^0/\mathrm{d}t = 0$ (the equilibrium magnetization is a constant), the derivatives on the left-hand side of these equations can equally well be written $\mathrm{d}I_z/\mathrm{d}t$ and $\mathrm{d}S_z/\mathrm{d}t$.

It is important to realize that in such a system I_z and S_z do not relax with a simple exponentials. They only do this if the differential equation is of the form

$$\frac{\mathrm{d}I_z}{\mathrm{d}t} = -R_z\left(I_z - I_z^0\right)$$

which is plainly not the case here. For such a two-spin system, therefore, it is not proper to talk of a "T_1" relaxation time constant.

5.1.4 Nuclear Overhauser effect

The Solomon equations are an excellent way of understanding and analysing experiments used to measure the nuclear Overhauser effect. Before embarking on this discussion it is important to realize that although the states represented by operators such as I_z and S_z cannot be observed directly, they can be made observable by the application of a radiofrequency pulse, ideally a 90° pulse

$$aI_z \xrightarrow{(\pi/2)I_x} -aI_y$$

The subsequent recording of the free induction signal due to the evolution of the operator I_y will give, after Fourier transformation, a spectrum with a peak of size $-a$ at frequency Ω_I. In effect, by computing the value of the coefficient a, the appearance of the subsequently observed spectrum is predicted.

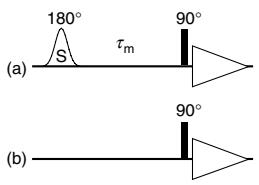
The basis of the nuclear Overhauser effect can readily be seen from the Solomon equation (for simplicity, it is assumed in this section that $\Delta_I = \Delta_S = 0$)

$$\frac{\mathrm{d}\left(I_z - I_z^0\right)}{\mathrm{d}t} = -R_I\left(I_z - I_z^0\right) - \sigma_{IS}\left(S_z - S_z^0\right)$$

What this says is that if the S spin magnetization deviates from equilibrium there will be a change in the I spin magnetization at a rate proportional to (a) the cross-relaxation rate, σ_{IS} and (b) the extent of the deviation of the S spin from equilibrium. This change in the I spin magnetization will manifest itself as a change in the intensity in the corresponding spectrum, and it is this change in intensity of the I spin when the S spin is perturbed which is termed the nuclear Overhauser effect.

Plainly, there will be no such effect unless σ_{IS} is non-zero, which requires the presence of the W_2 and W_0 relaxation pathways. It will be seen in Section 6.2.4 that such pathways are only present when there is dipolar relaxation between the two spins and that the resulting cross-relaxation rate constants have a strong dependence on the distance between the two spins. The observation of a nuclear Overhauser effect is therefore diagnostic of dipolar relaxation and hence the proximity of pairs of spins. The effect is of enormous value, therefore, in structure determination by NMR.

5.1.4.1 Transient experiments



Pulse sequence for recording transient NOE enhancements. Sequence (a) involves selective inversion of the S spin – shown here using a shaped pulse. Sequence (b) is used to record the reference spectrum in which the intensities are unperturbed.

A simple experiment which reveals the NOE is to invert just the S spin by applying a selective 180° pulse to its resonance. The S spin is then not at equilibrium so magnetization is transferred to the I spin by cross-relaxation. After a suitable period, called the mixing time, τ_m, a non-selective 90° pulse is applied and the spectrum recorded.

After the selective pulse the situation is

$$I_z(0) = I_z^0 \qquad S_z(0) = -S_z^0 \qquad [16]$$

where I_z has been written as $I_z(t)$ to emphasize that it depends on time and likewise for S. To work out what will happen during the mixing time the differential equations

$$\frac{\mathrm{d}I_z(t)}{\mathrm{d}t} = -R_I\left(I_z(t) - I_z^0\right) - \sigma_{IS}\left(S_z(t) - S_z^0\right)$$

$$\frac{\mathrm{d}S_z(t)}{\mathrm{d}t} = -\sigma_{IS}\left(I_z(t) - I_z^0\right) - R_S\left(S_z(t) - S_z^0\right)$$

need to be solved (integrated) with this initial condition. One simple way to do this is to use the *initial rate approximation*. This involves assuming that the mixing time is sufficiently short that, on the *right-hand side* of the

equations, it can be assumed that the initial conditions set out in Eq. [16] apply, so, for the first equation

$$\left.\frac{\mathrm{d}I_z(t)}{\mathrm{d}t}\right|_{\text{init}} = -R_I\left(I_z^0 - I_z^0\right) - \sigma_{IS}\left(-S_z^0 - S_z^0\right)$$
$$= 2\sigma_{IS}S_z^0$$

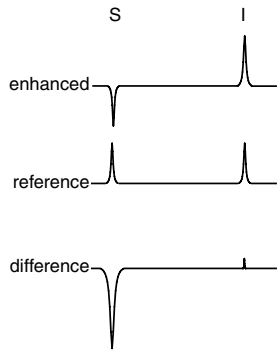
This is now easy to integrate as the right-hand side has no dependence on $I_z(t)$

$$\int_0^{\tau_\mathrm{m}} \mathrm{d}I_z(t) = \int_0^{\tau_\mathrm{m}} 2\sigma_{IS}S_z^0\,\mathrm{d}t$$
$$I_z(\tau_\mathrm{m}) - I_z(0) = 2\sigma_{IS}\tau_\mathrm{m}S_z^0$$
$$I_z(\tau_\mathrm{m}) = 2\sigma_{IS}\tau_\mathrm{m}S_z^0 + I_z^0$$

This says that for zero mixing time the I magnetization is equal to its equilibrium value, but that as the mixing time increases the I magnetization has an additional contribution which is proportional to the mixing time and the cross-relaxation rate, σ_{IS}. This latter term results in a change in the intensity of the I spin signal, and this change is called an *NOE enhancement*.

The normal procedure for visualizing these enhancements is to record a reference spectrum in which the intensities are unperturbed. In terms of z-magnetizations this means that $I_{z,\mathrm{ref}} = I_z^0$. The difference spectrum, defined as (perturbed spectrum – unperturbed spectrum) corresponds to the difference

$$I_z(\tau_\mathrm{m}) - I_{z,\mathrm{ref}} = 2\sigma_{IS}\tau_\mathrm{m}S_z^0 + I_z^0 - I_z^0$$
$$= 2\sigma_{IS}\tau_\mathrm{m}S_z^0$$



Visualization of how an NOE difference spectrum is recorded. The enhancement is assumed to be positive.

The NOE enhancement factor, η, is defined as

$$\eta = \frac{\text{intensity in enhanced spectrum - intensity in reference spectrum}}{\text{intensity in reference spectrum}}$$

so in this case η is

$$\eta(\tau_\mathrm{m}) = \frac{I_z(\tau_\mathrm{m}) - I_{z,\mathrm{ref}}}{I_{z,\mathrm{ref}}} = \frac{2\sigma_{IS}\tau_\mathrm{m}S_z^0}{I_z^0}$$

and if I and S are of the same nuclear species (*e.g.* both proton), their equilibrium magnetizations are equal so that

$$\eta(\tau_\mathrm{m}) = 2\sigma_{IS}\tau_\mathrm{m}$$

Hence a plot of η against mixing time will give a straight line of slope σ_{IS}; this is a method used for measuring the cross-relaxation rate constant. A single experiment for one value of the mixing time will reveal the presence of NOE enhancements.

This initial rate approximation is valid provided that

$$\sigma_{IS}\tau_\mathrm{m} << 1 \text{ and } R_S\tau_\mathrm{m} << 1$$

the first condition means that there is little transfer of magnetization from S to I, and the second means that the S spin remains very close to complete inversion.

Longer mixing times

At longer mixing times the differential equations are a little more difficult to solve, but they can be integrated using standard methods (symbolic mathematical programmes such as *Mathematica* are particularly useful for this). Using the initial conditions given in Eq. [16] and, assuming for simplicity that $I_z^0 = S_z^0$ the following solutions are found

$$\frac{I_z(\tau_\mathrm{m})}{I_z^0} = \frac{2\sigma_{IS}}{R}\left[\exp(-\lambda_2\tau_\mathrm{m}) - \exp(-\lambda_1\tau_\mathrm{m})\right] + 1$$

$$\frac{S_z(\tau_\mathrm{m})}{I_z^0} = \left[\frac{R_I - R_S}{R}\right]\left[\exp(-\lambda_1\tau_\mathrm{m}) - \exp(-\lambda_2\tau_\mathrm{m})\right] + 1 - \exp(-\lambda_1\tau_\mathrm{m}) + \exp(-\lambda_2\tau_\mathrm{m})$$

where

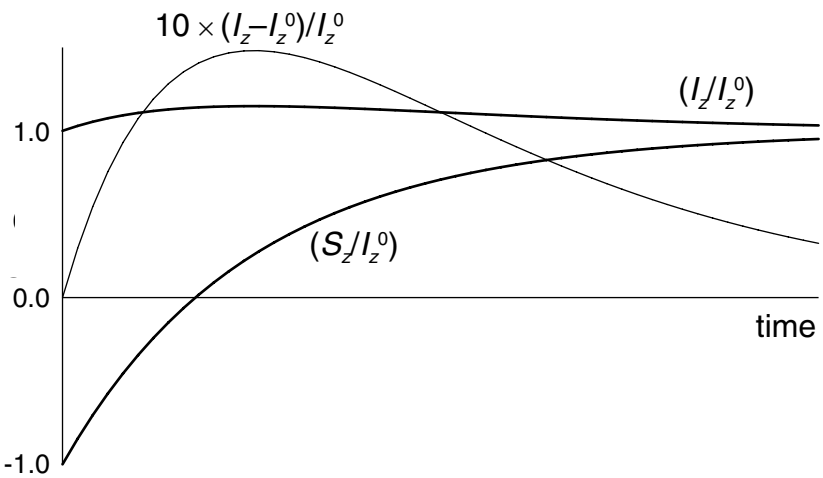
$$R = \sqrt{R_I^2 - 2R_IR_S + R_S^2 + 4\sigma_{IS}^2}$$

$$\lambda_1 = \tfrac{1}{2}\left[R_I + R_S + R\right] \qquad \lambda_2 = \tfrac{1}{2}\left[R_I + R_S - R\right]$$

These definitions ensure that $\lambda_1 > \lambda_2$. If R_I and R_S are not too dissimilar, R is of the order of σ_{IS}, and so the two rate constants λ_1 and λ_2 differ by a quantity of the order of σ_{IS}.

As expected for these two coupled differential equations, integration gives a time dependence which is the sum of two exponentials with different time constants.

The figure below shows the typical behaviour predicted by these equations (the parameters are $R_I = R_S = 5\sigma_{IS}$)



The S spin magnetization returns to its equilibrium value with what appears to be an exponential curve; in fact it is the sum of two exponentials but their time constants are not sufficiently different for this to be discerned. The I spin magnetization grows towards a maximum and then drops off back towards the equilibrium value. The NOE enhancement is more easily visualized by plotting the difference magnetization, $(I_z - I_z^0)/I_z^0$, on an expanded scale; the plot now shows the positive NOE enhancement reaching a maximum of about 15%.

Differentiation of the expression for I_z as a function of τ_m shows that the

maximum enhancement is reached at time

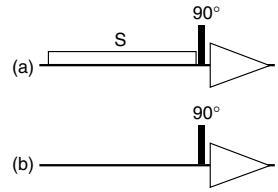
$$\tau_{\mathrm{m,max}} = \frac{1}{\lambda_1 - \lambda_2} \ln \frac{\lambda_1}{\lambda_2}$$

and that the maximum enhancement is

$$\frac{I_z(\tau_{\mathrm{m,max}}) - I_z^0}{I_z^0} = \frac{2\sigma_{IS}}{R}\left[\left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{-\lambda_1}{R}} - \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{-\lambda_2}{R}}\right]$$

5.1.4.2 Steady state experiments

The steady-state NOE experiment involves irradiating the S spin with a radiofrequency field which is sufficiently weak that the I spin is not affected. The irradiation is applied for long enough that the S spin is saturated, meaning $S_z = 0$, and that the steady state has been reached, which means that none of the magnetizations are changing, *i.e.* $(\mathrm{d}I_z/\mathrm{d}t) = 0$.



Pulse sequence for recording steady state NOE enhancements. Sequence (a) involves selective irradiation of the S spin leading to saturation. Sequence (b) is used to record the reference spectrum in which the intensities are unperturbed.

Under these conditions the first of Eqs. [15] can be written

$$\left.\frac{\mathrm{d}(I_z - I_z^0)}{\mathrm{d}t}\right|_{\mathrm{SS}} = -R_I(I_{z,\mathrm{SS}} - I_z^0) - \sigma_{IS}(0 - S_z^0) = 0$$

therefore

$$I_{z,\mathrm{SS}} = \frac{\sigma_{IS}}{R_I} S_z^0 + I_z^0$$

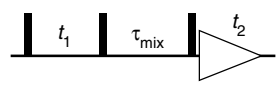
As in the transient experiment, the NOE enhancement is revealed by subtracting a reference spectrum which has equilibrium intensities. The NOE enhancement, as defined above, will be

$$\eta_{\mathrm{SS}} = \frac{I_{z,\mathrm{SS}} - I_{z,\mathrm{ref}}}{I_{z,\mathrm{ref}}} = \frac{\sigma_{IS}}{R_I}\frac{S_z^0}{I_z^0}$$

In contrast to the transient experiment, the steady state enhancement only depends on the relaxation of the receiving spin (here I); the relaxation rate of the S spin does not enter into the relationship simply because this spin is held saturated during the experiment.

5.1.4.3 NOESY

The dynamics of the NOE in NOESY are very similar to those for the transient NOE experiment. The key difference is that instead of the magnetization of the S spin being inverted at the start of the mixing time, the magnetization has an amplitude label which depends on the evolution during t_1.



Pulse sequence for NOESY.

Starting with equilibrium magnetization on the I and S spins, the *z*-magnetizations present at the start of the mixing time are (other magnetization will be rejected by appropriate phase cycling)

$$S_z(0) = -\cos\Omega_S t_1 S_z^0 \qquad I_z(0) = -\cos\Omega_I t_1 I_z^0$$

The equation of motion for S_z is

$$\frac{\mathrm{d}S_z(t)}{\mathrm{d}t} = -\sigma_{IS}\left(I_z(t) - I_z^0\right) - R_S\left(S_z(t) - S_z^0\right)$$

As before, the initial rate approximation will be used:

$$\left.\frac{\mathrm{d}S_z(\tau_\mathrm{m})}{\mathrm{d}t}\right|_{\mathrm{init}} = -\sigma_{IS}\left(-\cos\Omega_I t_1 I_z^0 - I_z^0\right) - R_S\left(-\cos\Omega_S t_1 S_z^0 - S_z^0\right)$$

$$= \sigma_{IS}\left(\cos\Omega_I t_1 + 1\right)I_z^0 + R_S\left(\cos\Omega_S t_1 + 1\right)S_z^0$$

Integrating gives

$$\int_0^{\tau_\mathrm{m}} \mathrm{d}S_z(t) = \int_0^{\tau_\mathrm{m}} \sigma_{IS}\left(\cos\Omega_I t_1 + 1\right)I_z^0 + R_S\left(\cos\Omega_S t_1 + 1\right)S_z^0\,\mathrm{d}t$$

$$S_z(\tau_\mathrm{m}) - S_z(0) = \sigma_{IS}\tau_\mathrm{m}\left(\cos\Omega_I t_1 + 1\right)I_z^0 + R_S\tau_\mathrm{m}\left(\cos\Omega_S t_1 + 1\right)S_z^0$$

$$S_z(\tau_\mathrm{m}) = \sigma_{IS}\tau_\mathrm{m}\left(\cos\Omega_I t_1 + 1\right)I_z^0 + R_S\tau_\mathrm{m}\left(\cos\Omega_S t_1 + 1\right)S_z^0 - \cos\Omega_S t_1 S_z^0$$

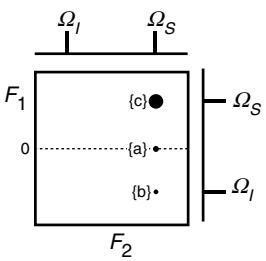
$$= \sigma_{IS}\tau_\mathrm{m} I_z^0 + R_S\tau_\mathrm{m} S_z^0 \qquad \{\mathrm{a}\}$$

$$+\cos\Omega_I t_1\left[\sigma_{IS}\tau_\mathrm{m}\right]I_z^0 \qquad \{\mathrm{b}\}$$

$$+\cos\Omega_S t_1\left[R_S\tau_\mathrm{m} - 1\right]S_z^0 \qquad \{\mathrm{c}\}$$

After the end of the mixing time, this z-magnetization on spin S is rendered observable by the final 90° pulse; the magnetization is on spin S, and so will precess at Ω_S during t_2.

The three terms {a}, {b} and {c} all represent different peaks in the NOESY spectrum.



Term {a} has no evolution as a function of t_1 and so will appear at $F_1 = 0$; in t_2 it evolves at Ω_S. This is therefore an *axial peak* at $\{F_1,F_2\} = \{0, \Omega_S\}$. This peak arises from z-magnetization which has recovered during the mixing time. In this initial rate limit, it is seen that the axial peak is zero for zero mixing time and then grows linearly depending on R_S and σ_{IS}.

Term {b} evolves at Ω_I during t_1 and Ω_S during t_2; it is therefore a cross peak at $\{\Omega_I, \Omega_S\}$. The intensity of the cross peak grows linearly with the mixing time and also depends on σ_{IS}; this is analogous to the transient NOE experiment.

Term {c} evolves at Ω_S during t_1 and Ω_S during t_2; it is therefore a diagonal peak at $\{\Omega_S, \Omega_S\}$ and as $R_s\tau_\mathrm{m} << 1$ in the initial rate, this peak is negative. The intensity of the peak grows back towards zero linearly with the mixing time and at a rate depending on R_S. This peak arises from S spin magnetization which remains on S during the mixing time, decaying during that time at a rate determined by R_S.

If the calculation is repeated using the differential equation for I_z a complimentary set of peaks at $\{0, \Omega_I\}$, $\{\Omega_S, \Omega_I\}$ and $\{\Omega_I, \Omega_I\}$ are found.

It will be seen later that whereas R_I and R_S are positive, σ_{IS} can be either positive or negative. If σ_{IS} is positive, the diagonal and cross peaks will be of opposite sign, whereas if σ_{IS} is negative all the peaks will have the same sign.

5.2 Theory of transition rates

In the previous sections it has been seen that populations can be related to longitudinal magnetization and as a result the return of such magnetization to its equilibrium value is brought about by transitions between the spin energy levels. In this section the details of how these transitions come about are explored and a theory is developed which relates the transition rate for a macroscopic sample to the physical properties of the sample. In particular, it will be seen that the *correlation time*, which is characteristic of molecular motion, plays an important part in determining the rate of relaxation.

The theory will, of course, be based on quantum mechanics and will use many of the techniques and ideas which were introduced in Section 1 for dealing with the case of a spin subject to longitudinal and transverse magnetic fields. As was previously the case, it will be important to consider both the behaviour of individual spins as well as the behaviour of the overall sample *i.e.* the ensemble.

Anticipating the final result, what will be found is that transitions between the spin states are promoted by transverse magnetic fields (that is, fields in the *xy*-plane) which have components oscillating at frequencies close to the Larmor frequency. This is not a surprising outcome, as such an oscillating magnetic field is precisely that supplied by a resonant radiofrequency pulse. Longitudinal magnetic fields, where oscillating or not, do not cause transitions.

In relaxation, the magnetic fields which cause these transitions acquire their time dependence from molecular motion. Such motion is very complex but, when its effect is averaged over a macroscopic sample, it turns out that it can be characterised by just a few parameters.

To simplify matters as much as possible, this section will consider the simplest possible case which is a sample consisting of molecules each of which contains just a single spin-half nucleus. It will be assumed that there is a source of time varying magnetic fields in the sample – for example, this might be due to the presence of a dissolved paramagnetic species whose unpaired electrons give rise to local magnetic fields.

Before embarking on the calculation, some background material concerning quantum mechanics and correlation functions will be introduced.

5.2.1 Quantum mechanical background

Further details of the ideas which are briefly reviewed in this Section are to be found in Lecture 1.

The wavefunction for each spin in the sample is written as a superposition state

$$\psi(t) = c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle \qquad [3]$$

where $c_\alpha(t)$ and $c_\beta(t)$ are complex coefficients. Note that the spin is neither in the α state, nor the β state, but has a probability $c_\alpha c_\alpha^*$ of being found in the α state, and $c_\beta c_\beta^*$ of being in β.

The wavefunction evolves in time according to the time-dependent

Schrödinger equation

$$\frac{\mathrm{d}\psi(t)}{\mathrm{d}t} = -iH\psi(t)$$

where H is the relevant hamiltonian. For a spin in a static magnetic field (of strength B_0) along the z-axis, the hamiltonian (called the static hamiltonian, H_0) is

$$H_0 = \omega_0 I_z$$

where $\omega_0 = \gamma B_0$, the Larmor frequency. The functions $|\alpha\rangle$ and $|\beta\rangle$ are eigenfunctions of H_0

$$H_0|\alpha\rangle = \tfrac{1}{2}\omega_0|\alpha\rangle \qquad H_0|\beta\rangle = -\tfrac{1}{2}\omega_0|\beta\rangle$$

with eigenvalues $\pm\frac{1}{2}\omega_0$ It is easy to solve the time-dependent Schrödinger equation to find how the coefficients c_α and c_β vary with time; the result is

$$c_\alpha(t) = c_\alpha(0)\exp\left(-\tfrac{1}{2}i\omega_0 t\right) \qquad c_\beta(t) = c_\beta(0)\exp\left(\tfrac{1}{2}i\omega_0 t\right)$$

In words, this says that the phase of each wavefunction oscillates at a frequency characteristic of its energy. Note, however, that there is no mixing between the α and β states – $c_\alpha c_\alpha^*$ and $c_\beta c_\beta^*$ remain constant under this evolution

$$c_\alpha(t)c_\alpha^*(t) = c_\alpha(0)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\left[c_\alpha(0)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\right]^* = c_\alpha(0)c_\alpha^*(0)$$

An alternative way of writing the super-position state, Eq. [3], is to include the phase oscillation due to evolution under H_0 ($= \omega_0 I_z$) explicitly

$$\psi(t) = c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle + c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle \qquad [17]$$

It is easy to show that, if the wavefunction is written in this way, the coefficients $c_\alpha(t)$ and $c_\beta(t)$ do not vary with time during evolution under the hamiltonian $H_0 = \omega_0 I_z$.

5.2.2 Correlation functions

In this section some of the properties of random functions will be described as these play a crucial role in the development of the theory of relaxation rates.

To make the discussion concrete, suppose that a spin in a sample experiences a magnetic field due to a dissolved paramagnetic species. The size of the magnetic field will depend on the relative orientation of the spin and the paramagnetic species, and as both are subject to random thermal motion, this orientation will vary randomly with time (it is said to be a random function of time), and so the magnetic field will be a random function of time. Let the field experienced by this first spin be $F_1(t)$.

Now consider a second spin in the sample. This also experiences a random magnetic field, $F_2(t)$, due to the interaction with the paramagnetic species. At any instant, this random field will not be the same as that experienced by the first spin.

For a macroscopic sample, each spin experiences a different random field, $F_i(t)$. There is no way that a detailed knowledge of each of these random fields can be obtained, but in some cases it is possible to

characterise the *overall* behaviour of the system quite simply.

The average field experienced by the spins is found by taking the ensemble average – that is adding up the fields for all members of the ensemble (*i.e.* all spins in the system)

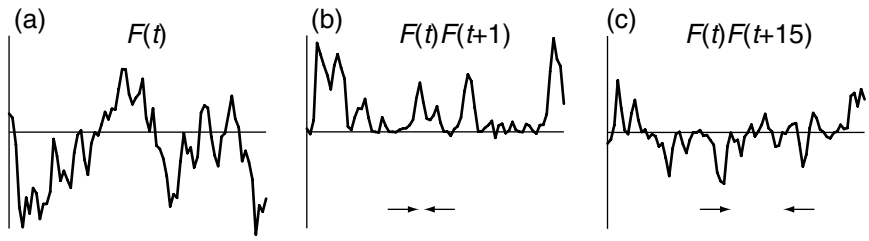
$$\overline{F(t)} = F_1(t) + F_2(t) + F_3(t) + \ldots$$

For random thermal motion, this ensemble average turns out to be independent of the time; this is a property of *stationary* random functions. Typically, the $F_i(t)$ are signed quantities, randomly distributed about zero, so this ensemble average will be zero.

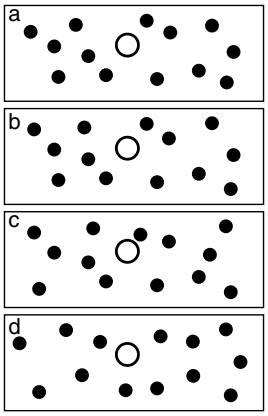
An important property of random functions is the *correlation function*, $G(t,\tau)$, defined as

$$\begin{aligned} G(t,\tau) &= F_1(t)F_1^*(t+\tau) + F_2(t)F_2^*(t+\tau) + F_3(t)F_3^*(t+\tau) + \ldots \\ &= \overline{F(t)F^*(t+\tau)} \end{aligned}$$

$F_1(t)$ is the field experienced by spin 1 at time t, and $F_1(t+\tau)$ is the field experienced at a time τ later. If the time τ is short the spins will not have moved very much and so $F_1(t+\tau)$ will be very little different from $F_1(t)$. As a result, the product $F_1(t)F_1^*(t+\tau)$ will be positive. This is illustrated in the figure below, plot (b).



(a) is a plot of the random function $F(t)$ against time; there are about 100 separate time points. (b) is a plot of the value of F multiplied by its value one data point later – *i.e.* one data point to the right; all possible pairs are plotted. (c) is the same as (b) but for a time interval of 15 data points. The two arrows indicate the spacing over which the correlation is calculated.



Visualization of the different timescales for random motion. (a) is the starting position: the black dots are spins and the open circle represents a paramagnetic species. (b) is a snap shot a very short time after (a); hardly any of the spins have moved. (c) is a snapshot at a longer time; more spins have moved, but part of the original pattern is still discernible. (d) is after a long time, all the spins have moved and the original pattern is lost.

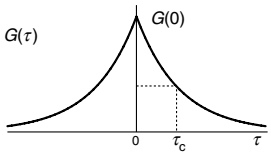
The same is true for all of the other members of then ensemble, so when the $F_i(t)F_i^*(t+\tau)$ are added together for a particular time, t, – that is, the ensemble average is taken – the result will be for them to reinforce one another and hence give a finite value for $G(t,\tau)$.

As τ gets longer, the spin will have had more chance of moving and so $F_1(t+\tau)$ will differ more and more from $F_1(t)$; the product $F_1(t)F_1^*(t+\tau)$ need not necessarily be positive. This is illustrated in plot (c) above. The ensemble average of all these $F_i(t)F_i^*(t+\tau)$ is thus less than it was when τ was shorter. In the limit, once τ becomes sufficiently long, the $F_i(t)F_i^*(t+\tau)$ are randomly distributed and their ensemble average, $G(t,\tau)$, goes to zero. Clearly, from its definition, $G(t,\tau)$ has its maximum value at $\tau = 0$.

For stationary random functions, the correlation function is independent of the time t; it will therefore be written $G(\tau)$. In addition, for such random functions averaging over the ensemble is equivalent to averaging over the time t. So, for example, the value of $G(\tau)$ can be found by taking the average of the values plotted in (b) or (c) above. It is clear that for the data

in plot (c) the average will be much less than for that in plot (b).

The correlation function, $G(\tau)$, is thus a function which characterises the memory that the system has of a particular arrangement of spins in the sample. For times τ which are much less than the time it takes for the system to rearrange itself $G(\tau)$ will be close to its maximum value. As time proceeds, the initial arrangement becomes more and more disturbed, and $G(\tau)$ falls. For sufficiently long times, $G(\tau)$ tends to zero.



The simplest form for $G(\tau)$ is

$$G(\tau) = G(0)\exp\left(-|\tau|/\tau_c\right) \qquad [18]$$

the variable τ appears as the modulus, resulting in the same value of $G(\tau)$ for positive and negative values of τ. This means that the correlation is the same with time τ before and time τ after the present time.

τ_c is called the *correlation time*. For times much less than the correlation time the spins have not moved much and the correlation function is close to its original value; when the time is of the order of τ_c significant rearrangements have taken place and the correlation function has fallen to about half its initial value. For times much longer than τ_c the spins have moved to completely new positions and the correlation function has fallen close to zero.

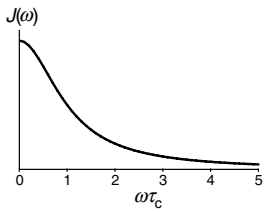
5.2.3 Spectral densities

The correlation function is a function of time, just like a free induction decay. So, it can be Fourier transformed to give a function of frequency. The resulting frequency domain function is called the *spectral density*; as the name implies, the spectral density gives a measure of the amount of motion present at different frequencies. The spectral density is usually denoted $J(\omega)$

$$G(\tau) \xrightarrow{\text{Fourier Transform}} J(\omega)$$

If the spins were executing a well ordered motion, such as oscillating back and forth about a mean position, the spectral density would show a peak at that frequency. However, the spins are subject to random motions with a range of different periods, so the spectral density shows a range of frequencies rather than having peaks at discreet frequencies.

Generally, for random motion characterised by a correlation time τ_c, frequencies from zero up to about $1/\tau_c$ are present. The amount of higher frequencies then begins to tail off quite rapidly, so that the amount of motion with frequency much greater than $1/\tau_c$ is quite low.

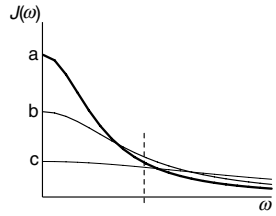


Plot of the spectral density as a function of the dimensionless variable $\omega\tau_c$. The curve is a lorentzian

For a simple exponential correlation function, given in Eq. [18], the corresponding spectral density is a lorentzian

$$\exp\left(-|\tau|/\tau_c\right) \xrightarrow{\text{Fourier Transform}} \frac{2\tau_c}{1+\omega^2\tau_c^2}$$

This function is plotted in the margin; note how it drops off significantly once the product $\omega\tau_c$ begins to exceed ~1.



The plot opposite compares the spectral densities for three different correlation times; curve *a* is the longest, *b* an intermediate value and *c* the shortest. Note that as the correlation time decreases the spectral density moves out to higher frequencies. However, the area under the plot remains the same, so the contribution at lower frequencies is decreased. In particular, at the frequency indicated by the dashed line the contribution at correlation time *b* is greater than that for either correlation times *a* or *c*.

For this spectral density function, the maximum contribution at frequency ω is found when τ_c is $1/\omega$. This will turn out to be important later on.

5.2.4 Calculation of the transition rate

5.2.4.1 General approach

The transition rate constant between the β and α states will be computed using the following method:

(a) At time zero it will be assumed that the spins are in the β state.

(b) The evolution of the spins under the influence of a time dependent random hamiltonian, $H_1(t)$, will then be calculated; $H_1(t)$ represents the random fields which are acting on the spins.

(c) After time t each spin will have evolved from the state $|\beta\rangle$ to the superposition state $c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle$; the population of the α state is therefore $c_\alpha(t)c_\alpha^*(t)$.

(d) As the spins started in the β state, the rate of change of the population of the α state is equal to the transition rate constant for $\beta \to \alpha$.

5.2.4.2 Equation of motion

As was discussed in Section 5.2.1, the superposition state can be written as

$$\psi(t) = c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle + c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle \qquad [17]$$

where the phase oscillation due to evolution under the static Hamiltonian H_0 (= $\omega_0 I_z$) is included explicitly; the coefficients $c_\alpha(t)$ and $c_\beta(t)$ do not vary with time when the evolution is just under H_0.

The evolution under the combined effects of the static hamiltonian, H_0, and the random hamiltonian $H_1(t)$ can be found from the time dependent Schrödinger equation:

$$\frac{\mathrm{d}\psi(t)}{\mathrm{d}t} = -i\{H_0 + H_1(t)\}\psi(t) \qquad [19]$$

Inserting $\psi(t)$ from Eq. [17] into the left-hand side of [19] gives

$$\begin{aligned}\frac{\mathrm{d}\psi(t)}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\left[c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle + c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle\right] \\ &= -\tfrac{1}{2}i\omega_0 c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle + \frac{\mathrm{d}c_\alpha(t)}{\mathrm{d}t}\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle \\ &\quad + \tfrac{1}{2}i\omega_0 c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle + \frac{\mathrm{d}c_\beta(t)}{\mathrm{d}t}\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle\end{aligned}$$

Likewise with the right-hand side

$$
\begin{aligned}
&-i\{H_0 + H_1(t)\}\psi(t) \\
&= -i\{H_0 + H_1(t)\}\left[c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle + c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle\right] \\
&= -ic_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)H_1(t)|\alpha\rangle - ic_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)H_1(t)|\beta\rangle \\
&\quad -ic_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)H_0|\alpha\rangle - ic_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)H_0|\beta\rangle \\
&= -ic_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)H_1(t)|\alpha\rangle - ic_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)H_1(t)|\beta\rangle \\
&\quad -\tfrac{1}{2}i\omega_0 c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)|\alpha\rangle + \tfrac{1}{2}i\omega_0 c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)|\beta\rangle
\end{aligned}
$$

where to get to the last line the fact that $|\alpha\rangle$ and $|\beta\rangle$ are eigenfunctions of H_0 has been used (Section 1.4.1.1)

$$H_0|\alpha\rangle = \omega_0 I_z|\alpha\rangle = \tfrac{1}{2}\omega_0|\alpha\rangle \qquad H_0|\beta\rangle = -\tfrac{1}{2}\omega_0|\beta\rangle$$

Equating the left and right hand sides and multiplying from the left by $\langle\alpha|$ gives

$$
\begin{aligned}
&-\tfrac{1}{2}i\omega_0 c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|\alpha\rangle + \frac{\mathrm{d}c_\alpha(t)}{\mathrm{d}t}\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|\alpha\rangle \\
&+\tfrac{1}{2}i\omega_0 c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|\beta\rangle + \frac{\mathrm{d}c_\beta(t)}{\mathrm{d}t}\exp\left(\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|\beta\rangle \\
&= -ic_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|H_1(t)|\alpha\rangle - ic_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|H_1(t)|\beta\rangle \\
&\quad -\tfrac{1}{2}i\omega_0 c_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|\alpha\rangle + \tfrac{1}{2}i\omega_0 c_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|\beta\rangle
\end{aligned}
$$

The functions $|\alpha\rangle$ and $|\beta\rangle$ are orthonormal (Section 1.3.2)

$$\langle\alpha|\alpha\rangle = 1 \quad \langle\alpha|\beta\rangle = 0$$

So, using this and cancelling common terms, the previous equation simplifies to

$$
\begin{aligned}
&\frac{\mathrm{d}c_\alpha(t)}{\mathrm{d}t}\exp\left(-\tfrac{1}{2}i\omega_0 t\right) \\
&= -ic_\alpha(t)\exp\left(-\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|H_1(t)|\alpha\rangle - ic_\beta(t)\exp\left(\tfrac{1}{2}i\omega_0 t\right)\langle\alpha|H_1(t)|\beta\rangle
\end{aligned}
$$

Finally, multiplying both sides by $\exp\left(\tfrac{1}{2}i\omega_0 t\right)$ and defining

$$H_{\alpha\alpha}(t) = \langle\alpha|H_1(t)|\alpha\rangle \qquad H_{\alpha\beta}(t) = \langle\alpha|H_1(t)|\beta\rangle$$

gives

$$\frac{\mathrm{d}c_\alpha(t)}{\mathrm{d}t} = -ic_\alpha(t)H_{\alpha\alpha}(t) - ic_\beta(t)\exp\left(i\omega_0 t\right)H_{\alpha\beta}(t) \qquad [20]$$

The interpretation of this equation is that $H_{\alpha\beta}$ is a measure of the "ability" of the random hamiltonian to transform the spin from state β to state α. For example if H_1 is of the form cI_x then

$$H_{\alpha\beta} = \langle\alpha|cI_x|\beta\rangle = \tfrac{1}{2}\langle\alpha|\{c|\beta\rangle + c|\alpha\rangle\} = \tfrac{1}{2}c$$

but if H_1 is of the form cI_z

$$H_{\alpha\beta} = \langle\alpha|cI_z|\beta\rangle = \langle\alpha|\{-\tfrac{1}{2}|\beta\rangle\} = 0$$

So it is clear that to cause transitions from β to α the random hamiltonian needs to have transverse operators in it *i.e.* there must be transverse magnetic fields present.

In contrast, the term $H_{\alpha\alpha}$ is a measure of the extent to which the random hamiltonian leaves the initial state unperturbed; this term does not represent transitions between the two states.

The exponential term, $\exp(i\omega_0 t)$, arises from the phase oscillation of the two states α and β. Recall that these states have a phase oscillation at $(\mp\frac{1}{2}\omega_0 t)$ respectively. The term in Eq. [20] thus represents their relative phase oscillation.

5.2.4.3 Integration in the initial rate

Starting from the equation of motion, Eq. [20], it is assumed that

(1) At time zero the spin is entirely in the β state, so that $c_\alpha(0) = 0$ and $c_\beta(0) = 1$.

(2) The initial rate approximation may be applied, so that $c_\alpha(t)$ and $c_\beta(t)$ on the right hand side of Eq. [20] can be replaced by their values at time 0

With these assumptions the equation can be integrated

$$\left.\frac{\mathrm{d}c_\alpha(t)}{\mathrm{d}t}\right|_{\text{init}} = -i\exp(i\omega_0 t)H_{\alpha\beta}(t)$$

$$\int_0^t \mathrm{d}c_\alpha(t) = -i\int_0^t \exp(i\omega_0 t')H_{\alpha\beta}(t')\,\mathrm{d}t'$$

$$c_\alpha(t) = -i\int_0^t \exp(i\omega_0 t')H_{\alpha\beta}(t')\,\mathrm{d}t' \qquad [21]$$

As the initial rate assumption has been made, this relationship will only be valid for short times, such that the coefficients have not deviated too much from their initial values.

Interpretation – constant field

Suppose that a constant magnetic field is applied along the x direction; $H_1(t)$ is εI_x and so $H_{\alpha\beta} = \frac{1}{2}\varepsilon$. The integral in Eq. [21] is then straightforward

$$c_\alpha(t) = -\tfrac{1}{2}\varepsilon i\int_0^t \exp(i\omega_0 t')\,\mathrm{d}t' = -\tfrac{1}{2}\varepsilon i\left[\exp(i\omega_0 t) - 1\right]$$

It appears that there is a contribution to the coefficient $c_\alpha(t)$. However, this contribution simply oscillates back and forth at the Larmor frequency, ω_0, and so averaged over time there is no net change in $c_\alpha(t)$. Recall that the Larmor frequency is typically hundreds of MHz, so on the timescale of relaxation, an enormous number of Larmor periods will have elapsed.

Thus it is concluded that a constant transverse magnetic field causes no net transfer from β to α.

Interpretation – oscillating field

Suppose that an oscillating magnetic field is applied along the x direction; $H_1(t)$ is $\varepsilon\cos(\omega t)I_x$ and so $H_{\alpha\beta} = \frac{1}{2}\varepsilon\cos(\omega t)I_x$. The integral in Eq. [21] is then straightforward

$$c_\alpha(t) = -i\tfrac{1}{2}\varepsilon\int_0^t \exp(i\omega_0 t')\cos(\omega t')\,\mathrm{d}t'$$

$$= -i\tfrac{1}{2}\varepsilon\int_0^t \cos(\omega_0 t')\cos(\omega t')\,\mathrm{d}t' + \tfrac{1}{2}\varepsilon\int_0^t \sin(\omega_0 t')\cos(\omega t')\,\mathrm{d}t'$$

The second term on the right always averages to zero when considered over many Larmor periods. The first term on the right can be written

$$-i\tfrac{1}{2}\varepsilon\int_0^t \cos(\omega_0 t')\cos(\omega t')\,\mathrm{d}t'$$

$$= -i\tfrac{1}{4}\varepsilon\left[\int_0^t \cos(\omega_0 t' + \omega t')\,\mathrm{d}t' + \int_0^t \cos(\omega_0 t' - \omega t')\,\mathrm{d}t'\right]$$

Both of these terms are integrals of oscillating functions, and so will average to zero over time except in the case where $\omega = \omega_0$. The cosine term on the right is then 1 and the integral becomes $-i\tfrac{1}{4}\varepsilon t$.

This is precisely as expected, only if the transverse field is oscillating at or near the Larmor frequency will there be any significant probability of driving the spins from one state to another.

5.2.4.4 Piecewise approximation

The two special cases considered at the end of the previous section are useful in understanding what Eq. [21] means, but they are not representative of the problem in hand which is the case where $H_{\alpha\beta}(t)$ is a random function. One way to approach this is to imagine that for a sufficiently short period, δ, $H_{\alpha\beta}(t)$ is constant between time t and time $t + \delta$. During this period, it will be possible to integrate Eq. [21].

In detail, the approach is to imagine that time is divided into small periods of length δ. Between time $n\delta$ and $(n + 1)\delta$ it is supposed that $H_{\alpha\beta}(t)$ is constant with value H_n. The integral in Eq. [21] is then evaluated between time $n\delta$ and $(n + 1)\delta$

$$\int_{n\delta}^{(n+1)\delta} \mathrm{d}c_\alpha(t) = -i\int_{n\delta}^{(n+1)\delta} \exp(i\omega_0 t')H_n\,\mathrm{d}t'$$

$$c_\alpha^{(n+1)} - c_\alpha^{(n)} = \frac{-iH_n}{i\omega_0}\left[\exp(i\omega_0(n+1)\delta) - \exp(i\omega_0 n\delta)\right]$$

$$= \frac{-H_n}{\omega_0}\exp(i\omega_0 n\delta)\left[\exp(i\omega_0\delta) - 1\right]$$

$$= \frac{-H_n}{\omega_0}\exp(i\omega_0 n\delta)\left[1 + i\omega_0\delta - 1\right]$$

$$= -iH_n\delta\exp(i\omega_0 n\delta)$$

where on the fourth line it has been assumed that $\omega_0\delta$ is small so that the approximation $\exp(x) \approx 1 + x$ can be used. The value of the coefficient c_α at time $n\delta$ has been written $c_\alpha^{(n)}$.

To find the value of this coefficient after N steps, all that is required is to add up the differences:

$$c_\alpha^{(N)} = \left\{c_\alpha^{(1)} - c_\alpha^{(0)}\right\} + \left\{c_\alpha^{(2)} - c_\alpha^{(1)}\right\} + \left\{c_\alpha^{(3)} - c_\alpha^{(2)}\right\} + \ldots$$
$$= -i\delta \sum_{n=0}^{N} H_n \exp\left(in\omega_0\delta\right)$$

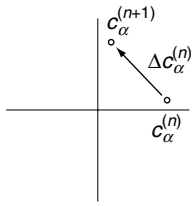
Defining the differences as $\Delta c_\alpha^{(n)} = c_\alpha^{(n+1)} - c_\alpha^{(n)}$, this last relationship can be expressed as

$$c_\alpha^{(N)} = \sum_{n=0}^{N} \Delta c_\alpha^{(n)}$$

where, from the above

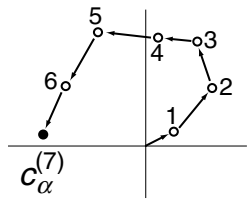
$$\Delta c_\alpha^{(n)} = -iH_n\delta \exp\left(i\omega_0 n\delta\right)$$

Graphical interpretation



The coefficient c_α is complex, so each of the $c_\alpha^{(n)}$ can be imagined as being a point on the complex plane, where the *x*- and *y*-coordinates are the real and imaginary parts of $c_\alpha^{(n)}$. The difference, $\Delta c_\alpha^{(n)}$, can therefore be thought of as a vector joining the points $c_\alpha^{(n)}$ and $c_\alpha^{(n+1)}$. This is illustrated opposite.

The overall motion can thus be thought of as a series of small steps, each represented by one of the $\Delta c_\alpha^{(n)}$. The final value of $c_\alpha^{(N)}$ depends on the vector sum of these small steps. This is illustrated opposite for the case of seven steps; note that as the coefficient c_α starts at zero, so does the first vector.



There are two factors which influence the length and direction of each of the vectors which represent the $\Delta c_\alpha^{(n)}$, given by

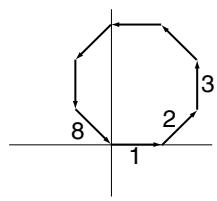
$$\Delta c_\alpha^{(n)} = -iH_n\delta \exp\left(i\omega_0 n\delta\right)$$

The length is given by the square modulus of $\Delta c_\alpha^{(n)}$:

$$\left|\Delta c_\alpha^{(n)}\right|^2 = \left|H_n\right|^2 \delta^2$$

This varies as for different n the size of the random fields (which are represented by H_n) vary.

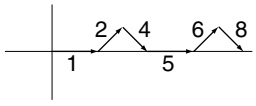
The direction of the vector is given by the phase of $\Delta c_\alpha^{(n)}$. As H_n may be complex, the phase has two parts: one from H_n and one of size $\omega_0 n\delta$ from the exponential term. The latter part of the phase increments regularly as time (the index n) increases; note that for the nth step, the phase is that acquired during the time from zero up until the time $n\delta$.



To see the effect of these two phases, consider first a case where H_n is constant, and the delay δ is chosen so that $\omega_0\delta = \pi/4$. Each vector representing $\Delta c_\alpha^{(n)}$ thus differs in phase by 45° from the previous one, but the vectors are all of the same length. The diagram opposite shows the motion during 8 steps.

Clearly, after 8 steps the coefficient c_α returns to zero. In fact further steps will just take the coefficient round and round this approximate circle, never deviating far from zero. One complete circuit is completed each Larmor period. This situation is exactly that described in Section 5.2.4.3; a constant transverse field does not, when averaged over many Larmor periods, lead to a significant transfer from one spin state to the other.

It is clear looking at the diagram that for the coefficient c_α to move steadily away from zero the arrows representing the $\Delta c_\alpha^{(n)}$ need to lie in more or less the same direction on each step. The phase term $\omega_0 n\delta$ naturally turns successive vectors away from one another, so to keep them aligned the term H_n (the random hamiltonian) must provide a phase which cancels out that due to $\omega_0 n\delta$.



An example would be if H_n were of the form

$$\cos(\omega_0 n\delta)$$

i.e. a field which is oscillating at the Larmor frequency. The H_n would then be, for the 8 steps, 1, $1/\sqrt{2}$, 0, $-1/\sqrt{2}$, -1, $-1/\sqrt{2}$, 0, $1/\sqrt{2}$. The diagram opposite shows the effect that these factors have on the motion of the vectors. Now, rather than the sum of the vectors returning to the origin, the final position has moved away from the starting position. Further steps will continue to move it away. This is the same result as in Section 5.2.4.3; a transverse field which is oscillating at the Larmor frequency will drive the spin from the β to the α state.

If the H_n are random, it is clear that the situation will be intermediate between the two extremes discussed here. It may be anticipated that the component of the motion of H_n which is at the Larmor frequency will be that part which is effective at driving the spin from the β to the α state. The details of how this comes about will be seen in the next section.

5.2.4.5 Ensemble average

The results obtained in the previous sections are just for a single spin. In order to translate these into the observed behaviour of a macroscopic NMR sample it is necessary to take the ensemble average. This is done in the usual way by adding up the contribution from each member of the ensemble.

The first thing to establish is that this motion under a random hamiltonian does not generate any coherences. As was seen in Section 1.6, coherences arise when the ensemble average of products such as $c_\alpha c_\beta^*$ are non zero. From Section 5.2.4.4 it was shown that c_α at time $N\delta$ is given by

$$c_\alpha^{(N)} = -i\delta\sum_{n=0}^{N} H_n \exp(in\omega_0\delta)$$

and, as the initial rate has been assumed, c_β is still very close to 1. Therefore the ensemble average of $c_\alpha c_\beta^*$ is

$$\overline{c_\alpha^{(N)} c_\beta^*} = -i\delta\sum_{n=0}^{N} H_n^{(1)} \exp(in\omega_0\delta) - i\delta\sum_{n=0}^{N} H_n^{(2)} \exp(in\omega_0\delta) - \ldots$$

where $H_n^{(i)}$ are the values of H_n for the ith member of the ensemble. This average can be written

$$\overline{c_\alpha^{(N)} c_\beta^*} = -i\delta\sum_{n=0}^{N} \overline{H_n} \exp(in\omega_0\delta)$$

where $\overline{H_n}$ is the ensemble average of the H_n. It is usually the case that the random fields which cause relaxation have zero mean (or, they are defined

as such), so this ensemble average is zero. In words, no coherences are generated by the action of this random hamiltonian.

The probability of finding the spin in the α level is $c_\alpha c_\alpha^*$

$$\begin{aligned} c_\alpha^{(N)} c_\alpha^{(N)*} &= \left[-i\delta \sum_{n=0}^{N} H_n \exp(in\omega_0\delta) \right] \left[-i\delta \sum_{m=0}^{N} H_m \exp(im\omega_0\delta) \right]^* \\ &= \left[-i\delta \sum_{n=0}^{N} H_n \exp(in\omega_0\delta) \right] \left[i\delta \sum_{m=0}^{N} H_m^* \exp(-im\omega_0\delta) \right] \\ &= \delta^2 \sum_{n=0}^{N} \sum_{m=0}^{N} H_n H_m^* \exp(i(n-m)\omega_0\delta) \end{aligned}$$

and this can be used to give the population of the α level, P_α, by taking the ensemble average. As before, it is just the $H_n H_m^*$ term which is averaged

$$P_\alpha^{(N)} = \overline{c_\alpha^{(N)} c_\alpha^{(N)*}} = \delta^2 \sum_{n=0}^{N} \sum_{m=0}^{N} \overline{H_n H_m^*} \exp(i(n-m)\omega_0\delta) \qquad [22]$$

The ensemble average of $H_n H_m^*$ is just the correlation function. Recall from Section 5.2.2 that the correlation function of a function F(t) is defined as

$$G(\tau) = \overline{F(t) F^*(t+\tau)}$$

Here H_n corresponds to time $n\delta$ and H_m to time $m\delta$, so τ is $(m - n)\delta$. So, defining

$$G((m-n)\delta) = \overline{H_n H_m^*}$$

Eq. [22] can be written

$$P_\alpha^{(N)} = \delta^2 \sum_{n=0}^{N} \sum_{m=0}^{N} G((m-n)\delta) \exp(i(n-m)\omega_0\delta)$$

Interpretation

Another way of writing $c_\alpha^{(N)} c_\alpha^{(N)*}$ is to use

$$c_\alpha^{(N)} = \sum_{n=0}^{N} \Delta c_\alpha^{(n)}$$

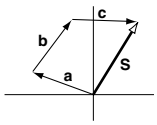
so that

$$\begin{aligned} c_\alpha^{(N)} c_\alpha^{(N)*} &= \left[\sum_{n=0}^{N} \Delta c_\alpha^{(n)} \right] \left[\sum_{m=0}^{N} \Delta c_\alpha^{(m)} \right]^* \\ &= \sum_{m=0}^{N} \sum_{n=0}^{N} \Delta c_\alpha^{(n)} \Delta c_\alpha^{(m)*} \end{aligned}$$

If the vector picture for the $c_\alpha^{(n)}$ and $\Delta c_\alpha^{(n)}$ is used, then $c_\alpha^{(N)} c_\alpha^{(N)*}$ is interpreted as the square of the length of the vector $c_\alpha^{(N)}$; $c_\alpha^{(N)} c_\alpha^{(N)*}$ is like the dot-product of a vector with itself, which is how the length of a vector is computed.

Recall that $c_\alpha^{(N)}$ gives the final position of the coefficient after N steps. However, of interest is just the probability of the spin being in state α, not the actual coefficient c_α. Thus it is the length (or magnitude) of the vector representing $c_\alpha^{(N)}$ that is needed; its phase is irrelevant.

The vector $c_\alpha^{(N)}$ is seen as the sum of the individual vectors $\Delta c_\alpha^{(n)}$. Consider the case where there are just three vectors contribution to the sum, and let these vectors be **a**, **b** and **c** representing $\Delta c_\alpha^{(0)}$, $\Delta c_\alpha^{(1)}$ and $\Delta c_\alpha^{(2)}$; let the sum be the vector **S**, representing $c_\alpha^{(2)}$.



In vector notation, **S** is

$$\mathbf{S} = \mathbf{a} + \mathbf{b} + \mathbf{c}$$

the square of the length of **S**, $|\mathbf{S}|^2$, is

$$\begin{aligned}|\mathbf{S}|^2 &= \mathbf{S}\cdot\mathbf{S} = (\mathbf{a}+\mathbf{b}+\mathbf{c})\cdot(\mathbf{a}+\mathbf{b}+\mathbf{c}) \\ &= \mathbf{a}\cdot\mathbf{a}+\mathbf{b}\cdot\mathbf{b}+\mathbf{c}\cdot\mathbf{c}+\mathbf{a}\cdot\mathbf{b}+\mathbf{a}\cdot\mathbf{c}+\mathbf{b}\cdot\mathbf{a}+\mathbf{b}\cdot\mathbf{c}+\mathbf{c}\cdot\mathbf{a}+\mathbf{c}\cdot\mathbf{b}\end{aligned}$$

So, it is seen that the length of the resultant vector **S** depends on all possible dot products between its constituent vectors, **a**, **b** and **c**. As these vectors correspond to different times, it is implied that the final result depends on the correlation between events at different times, which is precisely the result found above.

5.2.4.6 Computation of the transition rate

The population of the state α is expected to obey the differential equation

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = W_{\beta\alpha}P_\beta - W_{\alpha\beta}P_\alpha$$

However, in this case it has been supposed that the initial rate limit applies and that at time zero all the spins are in the β state. So, on the right hand side, $P_\beta = 1$ and $P_\alpha = 0$. Therefore

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = W_{\beta\alpha}$$

Using the piecewise approximation the derivative is found by taking the difference between successive values of P_α

$$\frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \frac{P_\alpha^{(N+1)} - P_\alpha^{(N)}}{\delta}$$

Using Eq. [22] for the $P_\alpha^{(N)}$, and after some careful algebra it is found that

$$W_{\beta\alpha} = \delta^2 \sum_{p=0}^{N} G(p\delta)\exp(ip\omega_0\delta)$$

The sum can be recognized as the Fourier coefficient at ω_0 of the correlation function $G(p\delta)$. In words, the transition rate constant depends on the spectral density at the Larmor frequency. It has been seen earlier in a qualitative way that it is only if the random hamiltonian has components at the Larmor frequency that there is a significant probability of driving the spin from one state to another. This conclusion has now been put onto a firm foundation.

5.2.4.7 Integral form

The piecewise approximation introduced in Section 5.2.4.4 is convenient for trying to understand the nature of relaxation, but it is not really very convenient for making further calculations. To make further progress it is

best to use the integral rather than the discrete sum. The start is Eq. [21]

$$c_\alpha(t) = -i\int_0^t \exp(i\omega_0 t')H_{\alpha\beta}(t')\,\mathrm{d}t' \qquad [21]$$

As was shown in Section 5.2.4.6, the rate of change of P_α gives $W_{\beta\alpha}$,

$$W_{\beta\alpha} = \frac{\mathrm{d}P_\alpha}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(c_\alpha c_\alpha^*\right)$$

$$= c_\alpha \frac{\mathrm{d}c_\alpha^*}{\mathrm{d}t} + c_\alpha^* \frac{\mathrm{d}c_\alpha}{\mathrm{d}t}$$

Equation [21] gives a value for c_α, and its derivative can be found simply by removing the integration from Eq. [21]

$$W_{\beta\alpha} = \left[-i\int_0^t \exp(i\omega_0 t')H_{\alpha\beta}(t')\,\mathrm{d}t'\right]\left[i\exp(-i\omega_0 t)H_{\alpha\beta}^*(t)\right] +$$

$$\left[i\int_0^t \exp(-i\omega_0 t')H_{\alpha\beta}^*(t')\,\mathrm{d}t'\right]\left[-i\exp(i\omega_0 t)H_{\alpha\beta}(t)\right]$$

$$= \int_0^t \exp(i\omega_0(t'-t))H_{\alpha\beta}(t')H_{\alpha\beta}^*(t)\,\mathrm{d}t'$$

$$+\int_0^t \exp(-i\omega_0(t'-t))H_{\alpha\beta}^*(t')H_{\alpha\beta}(t)\,\mathrm{d}t'$$

The ensemble average of the right-hand side has to be computed. The two relevant parts are

$$G_{\alpha\beta}(t'-t) = \overline{H_{\alpha\beta}(t')H_{\alpha\beta}^*(t)} \quad \text{and} \quad G_{\alpha\beta}^*(t'-t) = \overline{H_{\alpha\beta}^*(t')H_{\alpha\beta}(t)}$$

If it is assumed that the random processes are stationary, then the correlation function $G_{\alpha\beta}$ will only depend on the difference $(t - t') = \tau$. So the two integrals become

$$W_{\beta\alpha} = \int_0^t \exp(i\omega_0(t'-t))G_{\alpha\beta}(\tau)\,\mathrm{d}t' + \int_0^t \exp(-i\omega_0(t'-t))G_{\alpha\beta}^*(\tau)\,\mathrm{d}t'$$

Changing the variable of integration from t to τ gives

$$W_{\beta\alpha} = \int_0^t \exp(-i\omega_0\tau)G_{\alpha\beta}(\tau)\,\mathrm{d}\tau + \int_0^t \exp(i\omega_0\tau)G_{\alpha\beta}^*(\tau)\,\mathrm{d}\tau$$

The argument now goes that once τ significantly exceeds the correlation time the correlation function $G(\tau)$ falls very close to zero. As a result, provided that the theory is only used to predict the rate of transitions for periods much greater than the correlation time (which is easily satisfied), the upper limit of the integral can be extended to infinity.

To further simplify matters it will be assumed that the correlation function is real. Then it follows that

$$W_{\beta\alpha} = \int_0^\infty \left[\exp(-i\omega_0\tau) + \exp(i\omega_0\tau)\right] G_{\alpha\beta}(\tau)\,\mathrm{d}\tau$$

$$= 2\int_0^\infty \cos(\omega_0\tau) G_{\alpha\beta}(\tau)\,\mathrm{d}\tau$$

The integral is recognized as the Fourier coefficient of $G_{\alpha\beta}(\tau)$ at the Larmor frequency ω_0. If the spectral density, $J_{\alpha\beta}(\omega)$, is defined as

$$J_{\beta\alpha}(\omega) = \int_0^\infty \cos(\omega\tau) G_{\alpha\beta}(\tau)\,\mathrm{d}\tau$$

then

$$W_{\beta\alpha} = 2J_{\beta\alpha}(\omega_0)$$

This is the final result. It says that the transition rate depends on the spectral density of the Larmor frequency, and this in turn depends on the correlation function. If a model exists for the correlation function, then it is possible to predict the value of $W_{\beta\alpha}$.

5.2.4.8 Correlation functions again

In Section 5.2.2 the idea of a correlation function was introduced, with the definition

$$G(\tau) = \overline{F(t)F^*(t+\tau)}$$

In the calculation carried out in the previous Sections, the random function $F(t)$ is $H_{\alpha\beta}(t)$ where

$$H_{\alpha\beta}(t) = \langle\alpha|H_1(t)|\beta\rangle$$

The hamiltonian, $H_1(t)$, often consists of a time dependent part, $Y(t)$, multiplied by a spin operator, A. In this case

$$H_{\alpha\beta}(t) = \langle\alpha|H_1(t)|\beta\rangle$$

$$= \langle\alpha|Y(t)A|\beta\rangle = Y(t)A_{\alpha\beta}$$

where $A_{\alpha\beta} = \langle\alpha|A|\beta\rangle$. The correlation function is thus

$$G(\tau)_{\alpha\beta} = \overline{H_1(t)H_1^*(t+\tau)}$$

$$= \overline{Y(t)Y^*(t+\tau)}\ A_{\alpha\beta}A_{\alpha\beta}^*$$

$$= \overline{Y(t)Y^*(t+\tau)}\ \left|A_{\alpha\beta}\right|^2$$

The value of $\overline{Y(t)Y^*(t+\tau)}$ is clearly a maximum when $\tau = 0$, so defining

$$\overline{Y(t)Y^*(t+0)} = \overline{Y^2}$$

The correlation function, $G_{\alpha\beta}(\tau)$ can be written

$$G_{\alpha\beta}(\tau) = \left|A_{\alpha\beta}\right|^2\ \overline{Y^2}\ g(\tau)$$

where $g(\tau)$ is a *reduced correlation function* which takes the value 1 when $\tau = 0$.

The corresponding spectral density function, $J_{\alpha\beta}(\omega)$, is

$$J_{\alpha\beta}(\omega) = \left|A_{\alpha\beta}\right|^2 \overline{Y^2}\ j(\omega)$$

where $j(\omega)$ is the Fourier transform of $g(\tau)$.

Using this, the transition rate calculated in the previous section can be written

$$\begin{aligned} W_{\beta\alpha} &= 2J_{\beta\alpha}(\omega_0) \\ &= 2\left|A_{\alpha\beta}\right|^2 \overline{Y^2}\ j(\omega_0) \end{aligned} \qquad [23]$$

This form emphasises that there are three contributing parts to the transition rate. (1) A spin part, $\left|A_{\alpha\beta}\right|$, which is a measure of the extent to which the spin operators present in the random hamiltonian are capable of transforming the β state into the α state. (2) A size factor, $\overline{Y^2}$, which gives the absolute magnitude of the interaction causing the transition. (3) The spectral density at the Larmor frequency, which gives the amount of energy available at the Larmor frequency. This separation is a very useful way of thinking about the contributions to the relaxation rate constant.

5.2.5 Example calculation

Suppose that the spin experiences a randomly fluctuating field which has components in the x, y and z directions. The random hamiltonian can be written as

$$H_1(t) = \omega_x(t)I_x + \omega_y(t)I_y + \omega_z(t)I_z \qquad [24]$$

where $\omega_x(t)$ gives the size of the field (in angular frequency units) in the x direction and so on for y and z. Each term will be considered separately to start with; why this is so will be considered later. Taking just the x component, the random hamiltonian is thus

$$H_1(t) = \omega_x(t)I_x \equiv Y(t)A$$

So

$$\overline{Y^2} = \overline{\omega_x(t)\omega_x^*(t+0)} = \overline{\omega_x^2}$$

where the quantity on the extreme right is the ensemble average of the square of the field in the x direction.

For the spin part

$$A_{\alpha\beta} = \langle\alpha|A|\beta\rangle = \langle\alpha|I_x|\beta\rangle = \tfrac{1}{2}$$

so $\left|A_{\alpha\beta}\right|^2 = \frac{1}{4}$. The transition rate constant is therefore, according to Eq. [23]

$$\begin{aligned} W_{\beta\alpha} &= 2\left|A_{\alpha\beta}\right|^2 \overline{Y^2}\ j(\omega_0) \\ &= 2\,\tfrac{1}{4}\,\overline{\omega_x^2}\ j(\omega_0) = \tfrac{1}{2}\,\overline{\omega_x^2}\ j(\omega_0) \end{aligned}$$

A similar calculation shows that the contribution from the field in the y direction is similar

$$W_{\beta\alpha} = \tfrac{1}{2}\,\overline{\omega_y^2}\ j(\omega_0)$$

The z component makes no contribution to the transition rate constant as the matrix element $A_{\alpha\beta}$ is zero

$$A_{\alpha\beta} = \langle \alpha | I_z | \beta \rangle = 0$$

The total transition rate constant is

$$W_{\beta\alpha} = \tfrac{1}{2}\,\overline{\omega_x^2}\; j(\omega_0) + \tfrac{1}{2}\,\overline{\omega_y^2}\; j(\omega_0)$$

The rate constant for longitudinal relaxation, R_z, in such a system was shown to be $2W$ (Section 5.1.2.2, assuming $W_{\alpha\beta} = W_{\beta\alpha}$), so, assuming that the random fields in the x and y directions have the same magnitude, $\overline{\omega^2}$

$$R_z = 2\,\overline{\omega^2}\; j(\omega_0)$$

5.2.6 Cross Correlation

Returning to the random hamiltonian of the previous section,

$$H_1(t) = \omega_x(t) I_x + \omega_y(t) I_y + \omega_z(t) I_z \qquad [24]$$

the question arises as to whether it is valid to consider each term separately. This idea will be explored by following through the calculation without this assumption so as to highlight the differences.

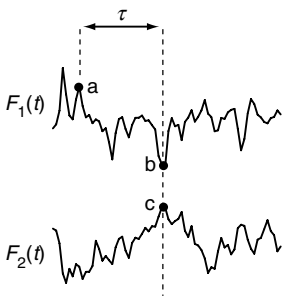
The matrix element $H_{\alpha\beta}(t)$ is

$$H_{\alpha\beta}(t) = \omega_x(t)\langle \alpha | I_x | \beta \rangle + \omega_y(t)\langle \alpha | I_y | \beta \rangle = \tfrac{1}{2}\omega_x(t) - \tfrac{1}{2} i\omega_y(t)$$

So the correlation function is

$$\begin{aligned} G_{\alpha\beta}(\tau) &= \overline{\left\{\tfrac{1}{2}\omega_x(t) - \tfrac{1}{2} i\omega_y(t)\right\}\left\{\tfrac{1}{2}\omega_x(t+\tau) - \tfrac{1}{2} i\omega_y(t+\tau)\right\}^*} \\ &= \tfrac{1}{4}\overline{\omega_x(t)\omega_x(t+\tau)} + \tfrac{1}{4}\overline{\omega_y(t)\omega_y(t+\tau)} \\ &\quad + \tfrac{1}{4} i\overline{\omega_x(t)\omega_y(t+\tau)} - \tfrac{1}{4} i\overline{\omega_y(t)\omega_x(t+\tau)} \end{aligned}$$

where for simplicity it has been assumed that ω_x and ω_y are real. The first two terms are precisely those encountered in Section 5.2.5 in which the terms in the hamiltonian were considered separately. The remaining two terms are new: they are called cross correlation terms as they involve two different terms of the hamiltonian.



Computation of the correlation function involves comparing points a and b which are separated by time but from the same random function. The cross correlation function involves comparing points a and c, which are from different random functions.

One interpretation of these cross correlation terms is that they are associated with transitions in which the variation of the magnetic field between time t and time $(t + \tau)$ is not due to the variation in one of the sources of magnetic fields but due to the variation *between* two different sources.

In the case described here, it is very likely that the two extra terms will cancel one another out as physical intuition implies that

$$\overline{\omega_x(t)\omega_y(t+\tau)} = \overline{\omega_y(t)\omega_x(t+\tau)}$$

i.e. the correlation of the x with the y field is identical to that of the y with the x field. The analysis in which the terms in the random hamiltonian were considered separately is thus likely to be valid.

However, a situation where cross correlation does have an effect is when there are two different sources of the same transverse component.

$$H_1(t) = \omega_x^{(1)}(t) I_x + \omega_x^{(2)}(t) I_x$$

In this case the correlation function is

$$G_{\alpha\beta}(\tau) = \overline{\left\{\tfrac{1}{2}\omega_x^{(1)}(t) + \tfrac{1}{2}\omega_x^{(2)}(t)\right\}\left\{\tfrac{1}{2}\omega_x^{(1)}(t+\tau) + \tfrac{1}{2}\omega_x^{(2)}(t+\tau)\right\}^*}$$
$$= \tfrac{1}{4}\overline{\omega_x^{(1)}(t)\omega_x^{(1)}(t+\tau)} + \tfrac{1}{4}\overline{\omega_x^{(2)}(t)\omega_x^{(2)}(t+\tau)}$$
$$+ \tfrac{1}{4}\overline{\omega_x^{(1)}(t)\omega_x^{(2)}(t+\tau)} + \tfrac{1}{4}\overline{\omega_x^{(2)}(t)\omega_x^{(1)}(t+\tau)}$$

Again, the first two terms are just those expected from ignoring cross correlation. The second two describe a situation where the variation in the magnetic field is due, as above, to the difference between the two different sources of the magnetic field.

Assuming that

$$\overline{\omega_x^{(1)}(t)\omega_x^{(2)}(t+\tau)} = \overline{\omega_x^{(2)}(t)\omega_x^{(1)}(t+\tau)} = \overline{\omega_x^{(2)}\omega_x^{(1)}}\, g^{(1,2)}(\tau)$$

where $g^{(1,2)}(\tau)$ is the reduced cross-correlation spectral density, the contribution to the transition rate constant is

$$W_{\beta\alpha}^{\text{cross}} = \overline{\omega_x^{(2)}\omega_x^{(1)}}\; j^{(1,2)}(\omega_0)$$

where $j^{(1,2)}(\omega)$ is the Fourier transform of $g^{(1,2)}(\tau)$.

Cross correlation arises when the same physical motion gives rise to the varying magnetic fields from different sources. It is often encountered when the two sources of magnetic fields are in the same molecule; in such a case, as the molecule tumbles the variation in the two fields is necessarily correlated. Further details are considered in Section 6.2.6 .

5.3 Relaxation mechanisms

So far, the source of the magnetic fields which give rise to relaxation and the origin of their time dependence have not been considered. Each such source is referred to as a *relaxation mechanism*. There are quite a range of different mechanisms that can act, but of these only two are really important for spin half nuclei.

5.3.1 The dipolar mechanism

Each spin has associated with it a magnetic moment, and this is turn gives rise to a magnetic field which can interact with other spins. Two spins are thus required for this interaction, one to "create" the field and one to "experience" it. However, their roles are reversible, in the sense that the second spin creates a field which is experienced by the first. So, the overall interaction is a property of the pair of nuclei.

The size of the interaction depends on the inverse cube of the distance between the two nuclei and the direction of the vector joining the two nuclei, measured relative to that of the applied magnetic field. As a molecule tumbles in solution the direction of this vector changes and so the magnetic field changes. Changes in the distance between the nuclei also result in a change in the magnetic field. However, molecular vibrations, which do give such changes, are generally at far too high frequencies to give significant spectral density at the Larmor frequency. As a result, it is generally changes in orientation which are responsible for relaxation.

The pair of interacting nuclei can be in the same or different molecules,

leading to intra- and inter-molecular relaxation. Generally, however, nuclei in the same molecule can approach much more closely than those in different molecules so that intra-molecular relaxation is dominant.

The size of the dipolar interaction depends on the product of the gyromagnetic ratios of the two nuclei involved, and the resulting relaxation rate constants depends on the square of this. Thus, pairs of nuclei with high gyromagnetic ratios are most efficient at promoting relaxation. For example, every thing else being equal, a proton-proton pair will relax 16 times faster than a carbon-13 proton pair.

It is important to realize that in dipolar relaxation the effect is not primarily to distribute the energy from one of the spins to the other. This would not, on its own, bring the spins to equilibrium. Rather, the dipolar interaction provides a path by which energy can be transferred between the lattice and the spins. In this case, the lattice is the molecular motion. Essentially, the dipole-dipole interaction turns molecular motion into an oscillating magnetic field which can cause transitions of the spins.

In a molecule in which there are more than two spins, cross-correlation between different dipolar interactions is likely to occur. This is because the same molecular motion affects the internuclear vectors of all possible spin pairs in the molecule. Some correlation between their motions is therefore inevitable.

5.3.2 The chemical shift anisotropy mechanism

The chemical shift arises because, due to the effect of the electrons in a molecule, the magnetic field experienced by a nucleus is different to that applied to the sample. In liquids, all that is observable is the average chemical shift, which results from the molecule rapidly experiencing all possible orientations by rapid molecular tumbling.

At a more detailed level, the magnetic field experienced by the nucleus depends on the orientation of the molecule relative to the applied magnetic field. This is called chemical shift anisotropy (CSA). In addition, it is not only the magnitude of the field which is altered but also its *direction*. The changes are very small, but sufficient to be detectable in the spectrum and to give rise to relaxation.

One convenient way of imagining the effect of CSA is to say that due to it there are small additional fields created at the nucleus – in general in all three directions. These fields vary in size as the molecule reorients, and so they have the necessary time variation to cause relaxation. As has already been discussed, it is the transverse fields which will give rise to changes in population.

The size of the CSA is specified by a tensor, which is a mathematical object represented by a three by three matrix.

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

The element σ_{xz} gives the size of the extra field in the x-direction which results from a field being applied in the z-direction; likewise, σ_{yz} gives the extra field in the y-direction and σ_{zz} that in the z-direction. These elements depend on the electronic properties of the molecule and the orientation of the molecule with respect to the magnetic field.

Cross correlation between dipolar interactions and CSA is likely when the spins are all in the same molecule as both interactions are modulated by the same molecular motion.