

Chapter 6 THE DENSITY MATRIX & PRODUCT OPERATORS

The system at the beginning of the experiment: $\Psi(0) = \sum c_i(0)u_i$

At the end of the NMR experiment: $\Psi(t) = \sum c_i(t)u_i$

Regardless of the change in the coefficients, it is possible to calculate the expectation value of any observable. For example, the signal detected in the real channel of the receiver, S_x , is given by:

$$\langle S_x \rangle = \langle \Psi | S_x | \Psi \rangle = \sum_{ij} c_i^*(t) c_j(t) \langle u_i | S_x | u_j \rangle$$

However, in most NMR experiments, the detected signal arises from an ensemble of N spins, therefore, the average expectation value of S_x is the actual observable:

$$\overline{\langle S_x \rangle} = \sum_N \sum_{ij} c_i^*(t) c_j(t) \langle u_i | S_x | u_j \rangle$$

This ensemble average can be obtained in one of two ways. The first method involves calculating the evolution of all N wavefunctions through the experiment and then averaging over all N spins. This procedure is very tedious. The second method uses density matrix approach, which is more concise and manipulatable.

The density matrix is a matrix whose elements contain information on the average probability of all possible states of the ensemble. Instead of following the evolution of the different wavefunctions through the experiment, the evolution of the density matrix is followed. At the end of the experiment, the average expectation values are obtained from the final density matrix. The close correspondence between the wavefunction and the density matrix is illustrated below:

$$\begin{array}{ccccccc} \Psi_o & \xrightarrow{\mathcal{H}} & \Psi(t) & \xrightarrow{R} & \Psi' & \xrightarrow{\mathcal{H}} & \Psi'(t) & S(t) = \langle \Psi'(t)^* | S_x | \Psi'(t) \rangle \\ \rho_o & \xrightarrow{\mathcal{H}} & \rho(t) & \xrightarrow{R} & \rho' & \xrightarrow{\mathcal{H}} & \rho'(t) & S(t) = \text{Trace}[\rho S_x] \end{array}$$

6.1 Introduction to the Density Matrix

The information on the ensemble average of a system is contained in the ensemble average of the pairwise products of the coefficient that are associated with the basis vectors, for example:

$$\overline{\langle S_x \rangle} = \sum_N \sum_{ij} c_i^*(t) c_j(t) \langle u_i | S_x | u_j \rangle = \sum_{ij} \overline{c_i^*(t) c_j(t)} \langle u_i | S_x | u_j \rangle$$

Therefore, if we specified the value of: $\overline{c_i^*(t) c_j(t)}$ for all possible values of i and j , then the properties of the system are completely determined. The density matrix, ρ , consists of all such products.

The m th, n th element of the density matrix (ρ_{mn}) for an arbitrary, time-dependent, wavefunction is obtained as follows:

$$\rho_{mn}(t) = \langle u_m | \psi(t) \rangle \langle \psi(t) | u_n \rangle = \langle u_m | \psi(t) \rangle c_n^*(t) = c_m(t) c_n^*(t)$$

For a system with two basis vectors the density matrix is: $\rho = \begin{bmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{bmatrix}$ (6.7)

The matrix elements of the density matrix, as defined by Eq. 6.6 are of the same form as the matrix elements of an operator. Hence the density matrix is an operator, and will be transformed by rotations with the same rules as any other operator: $\rho' = R \rho R^\dagger$

6.1.1 Calculation of Expectation Values From ρ

The expectation value for an observable:

$$\begin{aligned} A &= \langle \psi | A | \psi \rangle = \sum_{k,p} \langle c_k^* u_k | A | c_p u_p \rangle = \sum_{k,p} c_p c_k^* \langle u_k | A | u_p \rangle \\ &= \sum_{k,p} \rho_{pk} \langle u_k | A | u_p \rangle = \sum_{k,p} \langle u_p | \rho | u_k \rangle \langle u_k | A | u_p \rangle = \sum_p \rho_{pp} A_{pp} \\ &= \text{Trace}[\rho A] \end{aligned}$$

(The trace of a matrix is simply the sum of its diagonal elements)

→ IF we know the density matrix of the system at anytime we can easily calculate the expectation values of an operator from that density matrix. E.g. The signal detected for the real dat channel would be:

$$M_x = \text{Trace}(\rho S_x)$$

6.1.2 Density Matrix for a Statistical Mixture

For the case of a single isolated spin, representation of the system by either its wavefunction or density matrix are essentially equivalent and equally tedious. However, if there is a statistical mixture of states, such as the large number of molecules in a typical NMR sample, the density matrix is much more convenient. For an ensemble of spins, the total state of the system is given by:

$$\Psi = \sum_{k=0}^N p_k \psi_k$$

where p_k is the statistical probability of finding a spin in a particular state. p_k is the fraction of the k th mixed state or sub-system in the sample, and ψ_k corresponds to the wavefunction for that sub-system. Each ψ_k is a linear combination of the basis functions: $\psi_k = \sum_i c_i^k u_i$ where c_i^k are the normal quantum mechanical probabilities associated with finding the wavefunction in the i th state. The expectation value of any operator, A , for the k th sub-system is:

$$A_k = \langle \psi_k | A | \psi_k \rangle$$

The average value of this observable for the entire system is the expectation value associated with a particular state, multiplied by the statistical probability of that particular state.

$$\bar{A} = \sum_k p_k A_k$$

$$A_k = \text{Trace}(\rho^k A) = \sum_j \rho_{jj}^k A_{jj}$$

The expectation value of the system in the k th sub-state is:

Therefore, the average expectation value over the entire ensemble of sub-states is:

$$\begin{aligned} \bar{A} &= \sum_k p_k \text{Trace}(\rho^k A) = \sum_k p_k \sum_j \rho_{jj}^k A_{jj} = \sum_j \sum_k p_k \rho_{jj}^k A_{jj} \\ &= \sum_j \bar{\rho}_{jj} A_{jj} = \text{Trace}[\bar{\rho} A] \end{aligned}$$

The important result is that the average expectation value can be obtained from the average density matrix in exactly the same fashion as the expectation value of a single spin was obtained from its density matrix (see Eq. 6.9).

As an example consider the wavefunction for a spin that is oriented at an angle θ and ϕ in polar coordinates:

$$\Psi = \cos\left(\frac{\theta}{2}\right)e^{-i\phi/2}|u_{+1/2}\rangle + \sin\left(\frac{\theta}{2}\right)e^{i\phi/2}|u_{-1/2}\rangle$$

The density matrix for this state is:

$$\rho = \begin{bmatrix} \cos^2(\theta/2) & \cos(\theta/2)\sin(\theta/2)e^{-i\phi} \\ \cos(\theta/2)\sin(\theta/2)e^{+i\phi} & \sin^2(\theta/2) \end{bmatrix}$$

The expectation value for S_x is: $\langle S_x \rangle = \text{Trace}(\rho S_x)$

$$\begin{aligned} \rho S_x &= \begin{bmatrix} \cos^2(\theta/2) & \cos(\theta/2)\sin(\theta/2)e^{-i\phi} \\ \cos(\theta/2)\sin(\theta/2)e^{+i\phi} & \sin^2(\theta/2) \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ &= \frac{\hbar}{2} \begin{bmatrix} \cos(\theta/2)\sin(\theta/2)e^{-i\phi} & \cos^2(\theta/2) \\ \sin^2(\theta/2) & \cos(\theta/2)\sin(\theta/2)e^{+i\phi} \end{bmatrix} \\ \langle S_x \rangle &= \text{Trace}(\rho S_x) = \frac{\hbar}{2} \left[\cos\frac{\theta}{2}\sin\frac{\theta}{2}e^{-i\phi} + \cos\frac{\theta}{2}\sin\frac{\theta}{2}e^{+i\phi} \right] \\ &= \frac{\hbar}{2} 2 \cos\frac{\theta}{2}\sin\frac{\theta}{2} \left[\frac{e^{i\phi} + e^{-i\phi}}{2} \right] = \frac{\hbar}{2} 2 \cos\frac{\theta}{2}\sin\frac{\theta}{2}\cos\phi \end{aligned}$$

If the spin is oriented such that its magnetic moment is along the x-axis, then $\theta = 90$, and $\phi = 0$. The expectation value of S_x is then, $\langle S_x \rangle = \frac{\hbar}{2} 2 \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} = \frac{\hbar}{2}$ as expected:

Calculation of the expectation value of S_y for this example yields $\langle S_y \rangle = 0$.

6.2 One-pulse Experiment: Density Matrix Description

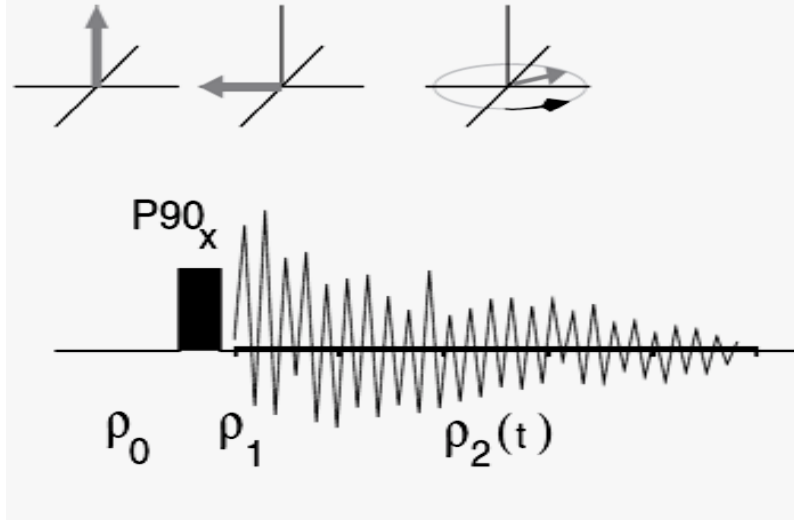


Figure 6.2 Density matrix description of the one-pulse experiment. The top part of the figure shows the classical description of a one-pulse NMR experiment. The density matrix ρ_0 defines the system prior to the pulse, ρ_1 is the system immediately after the pulse, and $\rho_2(t)$ defines the time evolution of the system during detection of the free induction decay.

The density matrix that describes an ensemble of spins at thermal equilibrium, or ρ_0 , is required. This density matrix should reflect the fact that the average value of $\langle S_x \rangle$ and $\langle S_y \rangle$ are zero, and it should also reflect the population difference between the ground and the excited state at thermal equilibrium.

The population difference at thermal equilibrium is given by the Boltzmann distribution:

$$\frac{e^{-E/kT}}{Z}$$

Using the Boltzmann distribution as an operator gives the desired form of the density matrix. A single element of the density matrix is:

$$\rho_{pn} = \langle u_p | \frac{e^{-\mathcal{H}/kT}}{Z} | u_n \rangle$$

And the entire density matrix is:

$$\begin{aligned} \rho &= \frac{1}{Z} \begin{bmatrix} \langle u_1 | e^{-\mathcal{H}/kT} | u_1 \rangle & \langle u_1 | e^{-\mathcal{H}/kT} | u_2 \rangle \\ \langle u_2 | e^{-\mathcal{H}/kT} | u_1 \rangle & \langle u_2 | e^{-\mathcal{H}/kT} | u_2 \rangle \end{bmatrix} = \frac{1}{Z} \begin{bmatrix} e^{-E_1/kT} \langle u_1 | u_1 \rangle & e^{-E_2/kT} \langle u_1 | u_2 \rangle \\ e^{-E_1/kT} \langle u_2 | u_1 \rangle & e^{-E_2/kT} \langle u_2 | u_2 \rangle \end{bmatrix} \\ &= \frac{1}{Z} \begin{bmatrix} e^{-E_1/kT} & 0 \\ 0 & e^{-E_2/kT} \end{bmatrix} = \frac{1}{Z} \begin{bmatrix} e^{+\hbar\omega_0/2kT} & 0 \\ 0 & e^{-\hbar\omega_0/2kT} \end{bmatrix} \end{aligned}$$

Expanding the exponential as a series and taking only the first term ($e^a \approx 1 + a$) we find:

$$\rho = \frac{1}{Z} \begin{bmatrix} 1 + \gamma & 0 \\ 0 & 1 - \gamma \end{bmatrix} = \frac{1}{Z} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{Z} \frac{\omega_o \hbar}{kT} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (6.28)$$

Where $\gamma = \hbar\omega_o/2kT$.

One can see that this matrix is composed of the unit matrix plus S_z . Since the unit matrix has no effect on any of the common observables we can ignore it 1. Furthermore, since we are only interested in the changes in the amplitudes and the time evolution of the individual elements of the density matrix, we can also ignore constants. Therefore, the density operator for a system under thermal equilibrium can be written:

$$\rho_0 = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = S_z$$

To simplify the calculations even further, can be removed from the expression using the following representation of angular momentum operators: Thus, ρ_0 is equal to the matrix I_z .

$$I_x = \frac{S_x}{\hbar} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad I_y = \frac{S_y}{\hbar} = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad I_z = \frac{S_z}{\hbar} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (6.30)$$

6.2.1 Effect of Pulses on the Density matrix

$$\rho_f = R\rho R^\dagger = e^{-iP}\rho e^{iP}$$

$$R_\phi(\alpha) = e^{-iP} = \begin{bmatrix} \cos(\frac{\alpha}{2}) & -i\sin(\frac{\alpha}{2})e^{-i\phi} \\ -i\sin(\frac{\alpha}{2})e^{i\phi} & \cos(\frac{\alpha}{2}) \end{bmatrix}$$

$$R_x(\pi/2) = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} \\ \frac{-i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix}$$

The density matrix after this pulse is given by:

$$\rho_1 = R_x I_z R_x^\dagger = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -I_y$$

If we calculate the expectation value of S_x , S_y , and S_z for this density matrix, we find:

$$\langle S_x \rangle = 0; \quad \langle S_y \rangle = -1; \quad \langle S_z \rangle = 0 \quad (6.34)$$

Note that the off-diagonal elements of the density matrix after the pulse are clearly non-zero. This implies that the ensemble average of this element of the density matrix is non-zero. Therefore, after the pulse, the distribution of the spins about the z-axis is no longer random - a preferred direction of the spins has been induced by the pulse. Specifically, the ensemble of spins has become coherent, with each spin having the same value of φ (compare to Eq. 6.24).

6.2.1.1 Free Precession: Time evolution of the Density Matrix

The time evolution of any wavefunction is defined by the evolution operator:

$$\Psi(t) = e^{-iHt/\hbar}\Psi(0) = e^{i\omega_s I_z t}\Psi(0)$$

Comparing this equation to the rotation operator for z-rotations: $R_z(\alpha) = e^{-i\frac{L_z}{\hbar}\alpha}$

shows that the evolution of the spins under free precession is equivalent to rotation of the system about the z-axis with a rotation angle equal to $\omega_s t$. The time evolution of the density matrix formed after the 90° x pulse is:

$$\rho_2(t) = e^{+i\omega_s t I_z} \rho_1 e^{-i\omega_s t I_z}$$

Conversion of $e^{i\omega_s t I_z}$ to its matrix form is simple since the basis vectors are eigenvalues of I_z . Therefore, we can directly write:

$$e^{+i\omega_s t I_z} = \begin{bmatrix} e^{+i\omega_s t/2} & 0 \\ 0 & e^{-i\omega_s t/2} \end{bmatrix}$$

$$\begin{aligned} \rho(t) &= \frac{1}{2} \begin{bmatrix} e^{+i\omega_s t/2} & 0 \\ 0 & e^{-i\omega_s t/2} \end{bmatrix} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \begin{bmatrix} e^{-i\omega_s t/2} & 0 \\ 0 & e^{+i\omega_s t/2} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & ie^{+i\omega_s t} \\ -ie^{-i\omega_s t} & 0 \end{bmatrix} \\ &= \begin{bmatrix} 0 & i[\cos(\omega_s t) + i\sin(\omega_s t)] \\ -i[\cos(\omega_s t) - i\sin(\omega_s t)] & 0 \end{bmatrix} \end{aligned}$$

$$= \begin{bmatrix} 0 & i \cos(\omega_s t) \\ -i \cos(\omega_s t) & 0 \end{bmatrix} + \begin{bmatrix} 0 & -\sin(\omega_s t) \\ -\sin(\omega_s t) & 0 \end{bmatrix} = \frac{1}{2} [-I_y \cos(\omega_s t) - I_x \sin(\omega_s t)]$$

This density matrix represents a spin precessing clockwise in the x-y plane at an angular velocity of ω_s , beginning from the minus y-axis.

6.2.1.2 Detection of the Signal

Quadrature detection of the FID is defined as measuring $I^+ = I_x + iI_y$. In matrix notation I^+ is:

$$I^+ = I_x + iI_y = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \frac{i}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

The expectation value of I^+ is given by the trace of $I^+ \rho$ (ignoring constants):

$$\langle I^+ \rangle = \text{Trace} \left(\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & i e^{+i\omega_s t} \\ -i e^{-i\omega_s t} & 0 \end{bmatrix} \right) = \text{Trace} \left(\begin{bmatrix} -i e^{-i\omega_s t} & 0 \\ 0 & 0 \end{bmatrix} \right) = -i e^{-i\omega_s t}$$

The Fourier transform of this function will give a dispersion lineshape found at ω_s . This result is completely consistent with a classical description of the effect of a 90° pulse applied along the x-axis, and detection such that the real channel is defined to be along the x-axis and the imaginary channel along the y-axis.

6.3 Product Operators

From the above analysis of a one-pulse experiment we see that it is possible to write ρ as a matrix that is proportional to one, or more, angular momentum operators:

- The initial density matrix, ρ_0 , is proportional to S_z .
- The density matrix after the pulse, ρ_1 , is proportional to S_y .
- The density matrix during detection is given by a combination of S_y and S_x .

This representation of the density matrix also provide a good deal of intuition to the quantum mechanical description of the system. For example, prior to the pulse, the bulk magnetization is aligned along the z-axis. After the 90° pulse on the x-axis, the magnetization is along the y-axis. During detection, the bulk magnetization will precess in the transverse plane. However, such representation can be quite cumbersome.

The use of Cartesian angular momentum operators to represent the density matrix is referred to as the product operator notation. The origin of this name will become apparent when two coupled spins are analyzed, as products of angular momentum operators will be required to describe the density matrix.

(Ref: O.W. Sorensen, G.W. Eich, M.H. Levitt, G. Bodenhausen, and R.R. Ernst. Product operator-formalism for the description of NMR pulse experiments. **Progress in Nuclear Magnetic Resonance Spectroscopy**, 16:163-192, 1983.)

For a single isolated spin, it is possible to represent any density matrix using a linear combination of the following four operators: $\tilde{1}$, I_x , I_y , I_z where $\tilde{1}$ is the identity operator.

Although the use of product operators provides a very convenient and concise algebraic representation of the density matrix, keep in mind that the various angular momentum operators simply represent the density matrix.

6.3.1 Transformation Properties of Product Operators

Since the density matrix can be represented by angular momentum operators, the effects of pulses and free precession on the density matrix can be determined by evaluating the effect of rotations on the angular momentum operators. In this context, pulses are represented by rotations about the x- or y-axis with a rotational angle equal to the flip angle of the pulse (β). Similarly, free precession is represented by a rotation about the z-axis with an angle ωt . The evolution of the density matrix due to rotations about the x-, y-, or z-axis are given in Table 6.1 and illustrated in Fig. 6.3.

These rotations follow the right-hand rule. In general, rotation of a product operator about an orthogonal axis gives the original product operator times $\cos\beta$ plus the other orthogonal product operator, times $\sin\beta$. For example, a z-rotation applied to $\rho = I_x$ generates the following:

$$I_x \xrightarrow{R_z(\beta)} I_x \cos\beta + I_y \sin\beta$$

These transformation laws are exactly as one would predict from the classical description of the system. For example, a 45° pulse applied along the y-axis would leave the bulk magnetic moment half-way between the z- and x-axis with a observed magnetic moment in the z-direction of $\cos(45^\circ)$ and the observed magnetic moment in the x-axis of $\sin(45^\circ)$.

Figure 6.3 Evolution of single-spin product operators. A graphical representation of the effect of chemical shift evolution (rotation about the z-axis) and pulses on the single-spin density matrix is shown.

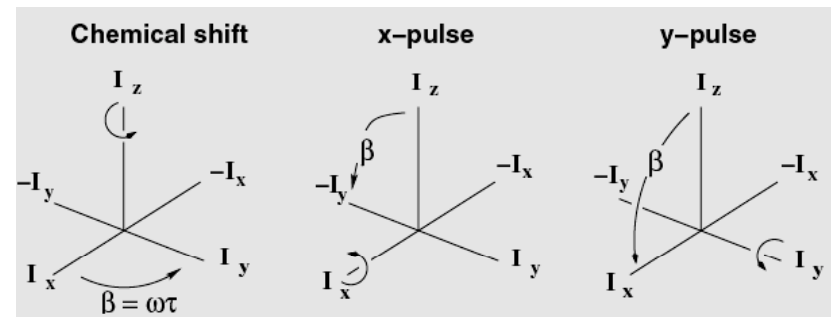


Table 6.1. Transformation of product operators for a single spin. Excitation pulses are represented as rotations about the x-axis (R_x) or the y-axis (R_y), with a flip angle of β . Evolution of the system under the static magnetic field, B_0 , is represented by a rotation about the z-axis (R_z), with an overall rotation angle of ωt . In all cases, a right-handed rotation is used. The actual direction of evolution can be either clockwise or counter-clockwise, depending on the sign of γ .

ρ_0	R_x	R_y	R_z
I_x	I_x	$I_x \cos(\beta) - I_z \sin(\beta)$	$I_x \cos(\omega t) + I_y \sin(\omega t)$
I_y	$I_y \cos(\beta) + I_z \sin(\beta)$	I_y	$I_y \cos(\omega t) - I_x \sin(\omega t)$
I_z	$I_z \cos(\beta) - I_y \sin(\beta)$	$I_z \cos(\beta) + I_x \sin(\beta)$	I_z

6.3.2 Description of the One-pulse Experiment

The product operator notation shown in Table 6.1 permits the rapid evaluation of the outcome of NMR experiments. The simple one-pulse experiment, consisting of a 90° degree pulse along the x-axis, is evaluated as follows:

$$I_z \xrightarrow{R_x(\pi/2)} -I_y \xrightarrow{R_z(\omega t)} -I_y \cos(\omega t) + I_x \sin(\omega t)$$

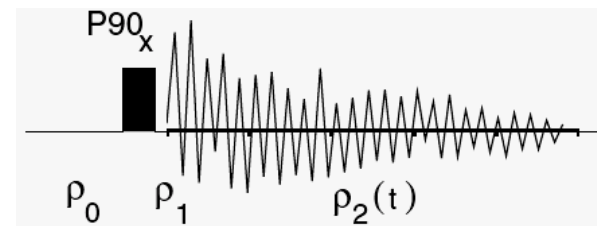
The observed signal is obtained in the usual fashion:

$$\text{Signal}(t) = \text{Trace}[I^+ \rho_2(t)] = \text{Trace}[I^+ (-I_y \cos(\omega t) + I_x \sin(\omega t))] = -ie^{i\omega t}$$

Figure 6.4. One-pulse expt, representation by the density matrix and product operators

$$\rho_0 = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \xrightarrow{R_x(\pi/2)} \rho_1 = \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \xrightarrow{R_z(\omega_s t)} \rho_2(t) = \frac{1}{2} \begin{bmatrix} 0 & ie^{+i\omega_s t} \\ -ie^{-i\omega_s t} & 0 \end{bmatrix}$$

$$I_z \quad \quad \quad -I_y \quad \quad \quad -I_y \cos(\omega_s t) + I_x \sin(\omega_s t)$$



6.3.3 Evaluation of Composite Pulses

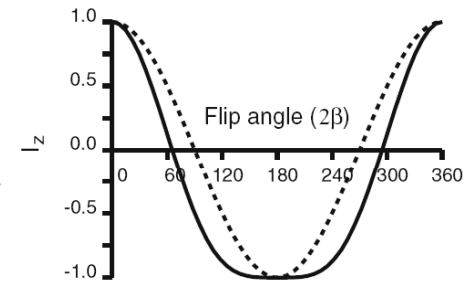
Composite pulses are a series of pulses whose overall effect is to produce a specific flip angle with reduced sensitivity to non-ideal pulse lengths or rotation angles. For example, a widely used composite 180° (π) pulse is:

$$\left[\frac{\pi}{2}\right]_x - [\pi]_y - \left[\frac{\pi}{2}\right]_x$$

The effect of this pulse on magnetization beginning along the z-axis (i.e. $\rho_0 = I_z$) is rapidly obtained as follows:

$$I_z \xrightarrow{\pi/2_x} -I_y \xrightarrow{\pi_y} -I_y \xrightarrow{\pi/2_x} -I_z$$

Figure 6.5 Excitation profile of 180° composite pulse. The effect of varying the flip angle of a single π pulse (dashed line) and a composite π pulse on the z-component of the magnetization are shown (solid line).



Now assume that the flip angles are set to $\beta < 90^\circ$, then the final density matrix after this pulse is:

$$\rho = I_z[\cos^2\beta \cos 2\beta - \sin^2\beta] - I_y[\cos\beta \sin\beta \cos 2\beta + \sin\beta \cos\beta] + I_x[\cos\beta \sin 2\beta]$$

- The composite pulse is capable of inverting the magnetization over a much wider range of flip angles and is thus less affected by pulse imperfection i.e. $\beta \neq 90^\circ$.
- It can be shown that the composite pulse is also less sensitive to these resonance offset effects and is able to invert the magnetization over a wider frequency range than a simple π pulse.

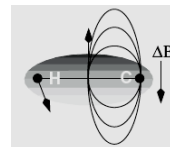
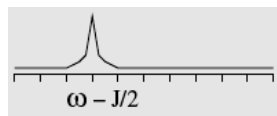
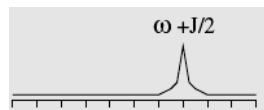
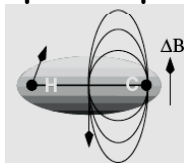
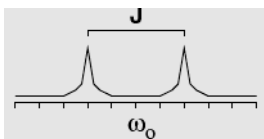
Chapter 7 SCALAR COUPLING

Scalar couplings arise from spin-spin interactions that occur via bonding electrons. Consequently, they provide information on the chemical connectivity between atoms. Therefore, these couplings can be utilized to correlate NMR signals of atoms that are chemically bonded to one another, providing chemical shift assignments if the molecular structure is known. In particular, the scalar coupling across the peptide bond permits the linkage of spins within one amino acid to those of its neighbors.

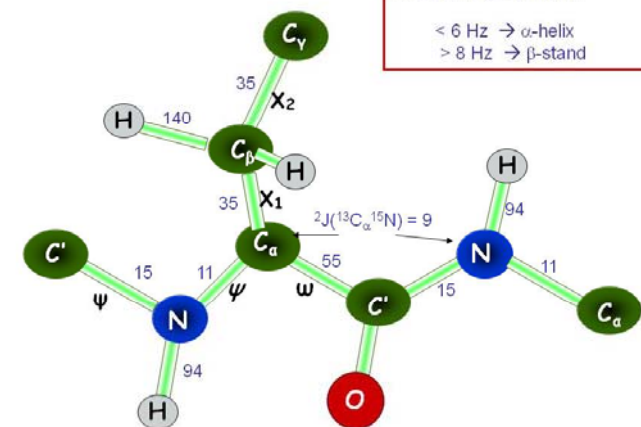
In addition to providing information on chemical connectivities, the sizes of three bond scalar couplings are sensitive to the electron distribution of the intervening bonds, consequently these couplings can provide information on the conformation of rotatable bonds in proteins.

Scalar, or J-coupling, occurs between nuclei which are connected by chemical bonds. This coupling causes splitting of the spectral lines for both coupled spins by an amount J , or the coupling constant. The nomenclature that is used to describe the coupling is as follows: ${}^nJ_{AB}$

where n refers to the number of intervening bonds, and A and B identify the two coupled spins. For example, the coupling constant between the amide nitrogen and the $C\beta$ carbon would be written as: ${}^2J_{NC\beta}$. The value of J is usually given in Hz and is the observed frequency separation between the split resonance lines of the coupled spins.



J-coupling of backbone nuclei (Hz)



The effect of J-coupling on the spectrum depends on the frequency separation of the coupled spins. If the two coupled spins differ greatly in their resonance frequencies ($\Delta\nu \gg J$), then the system is referred to as an **AX system**, where the X signifies the fact that the two chemical shifts are quite different. All coupling between different atom types, or heteronuclear spins, are AX couplings because of the large difference in the frequencies of coupled spins. Examples include, J_{NH} , J_{CH} , and J_{NC} . AX couplings can be analyzed using a classical analysis, similar to that depicted in Fig. 7.1. When two coupling spins have nearly equivalent resonance frequencies ($\Delta\nu \leq J$) then the system is referred to as an AB system. For example, the coupling between two H_β protons on an amino acid is an example of an AB system. Accurate analysis of **AB systems** require a detailed quantum mechanical treatment. **Lastly, when the coupled spins have the identical resonance frequencies, the observed coupling disappears entirely. This is most often seen when multiple protons have equivalent environments, such as the three protons on a methyl group.**

7.2 Basis of Scalar Coupling: Scalar coupling arises from the interaction of the nuclear magnetic moment with the electrons involved in the chemical bond. The nuclear spin polarization of one atom affects the polarization of the surrounding electrons. The electron polarization subsequently produces a change in the magnetic field that is sensed by the coupled spin..

Table 7.1. Homonuclear and heteronuclear coupling constants. The values are approximate; the coupling constants will also be affected by the electronic environment of the associated spins.

<i>Couplings Involving Heteronuclear (^{13}C or ^{15}N) Spins</i>		<i>Proton-Proton Couplings</i>	
C-N	14 Hz	H-C-H	-12 to -15 Hz
C-C	35 Hz	H-C-C-H	2-14 Hz
H-N	92 Hz	H-C=C-H	10 (cis)/17 (trans)
H-C	130 Hz	H-N-C-H	1-10 Hz
H-C-C	5 Hz (two bond coupling)		(3 Hz α -helix) (10 Hz β -strand)