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Learning Objectives

- Fundamental aspects of spin dynamics
- Density matrix description
- Product operator formalism to understand NMR experiments

5.1 Introduction

In the Fourier transform NMR experiment described in Chap. 3, the data was collected after the application of an RF pulse to a spin system, which was in equilibrium. Thus, the information that is obtained is essentially steady-state information. Much more information about the spin system, energy level diagrams, cross-relaxation pathways, etc. can be obtained by monitoring transient effects following a perturbation to the spin system. For this, it is necessary to create a nonequilibrium

state prior to the application of the observe RF pulse so that the transient phenomena are reflected in the data that will be collected thereafter. Now, a nonequilibrium state of the spin system can be created in different ways, depending upon what the specific interest is. The design of proper experimental schemes suitable for the purpose in mind requires proper knowledge of the behavior of spins under the influence of various perturbing forces that may be used. Such an understanding can be most appropriately obtained by using the most fundamental “density matrix” formalism. It is impossible to obtain correct and predictable information from vector representations, as was done in the steady-state case. In this chapter, the focus will be on developing this “density matrix” formalism from the NMR point of view.

Sections 5.2, 5.3, 5.4, and 5.5 give a formal description of the theory of density matrix. This involves a fair amount of quantum mechanics and mathematical rigor. Section 5.6 onward, the product operator formalism provides a convenient tool for the evaluation of density matrices and density operators applicable to weakly coupled spin systems. Students who find the initial sections hard to grasp due to insufficient background can skip to Sect. 5.6 and continue to familiarize themselves with calculation of evolution of magnetization components through given pulse sequences. Chapter 6 makes use of these in an extensive manner.

5.2 Density Matrix

We have seen in Chap. 1 that the state of spin can be represented by a wave function which is of the form

$$\Psi(t) = \sum_m C_m(t) U_{m,I} \quad (5.1)$$

$U_{m,I}$ constitutes an orthonormal set of basis functions. We also know that in quantum mechanics, when we make a measurement of an observable of the spin system, we observe the time average or equivalently the ensemble average of its value, and this average value of the observable of the spin system is described by the *expectation value* of the corresponding operator. The expectation value of operator A is defined as

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle \quad (5.2)$$

$$= \int \Psi^* A \Psi \, d\tau \quad (5.3)$$

For example, the expectation value of M_x , the operator for x-component of the magnetization, in terms of the functions $U_{m,I}$, is given by

$$\langle \Psi | M_x | \Psi \rangle = \sum_m \sum_n C_m(t)^* C_n(t) \langle U_{m,I} | M_x | U_{n,I} \rangle \quad (5.4)$$

Or, briefly,

$$\langle \Psi | M_x | \Psi \rangle = \sum_m \sum_n C_m(t)^* C_n(t) \langle m | M_x | n \rangle \quad (5.5)$$

Since $\langle m | M_x | n \rangle$ are constants, any variation of M_x results essentially from the changes in the coefficients. These products of coefficients, $C_m(t)^* C_n(t)$, can be conveniently arranged in the form of a matrix. It is useful to treat this matrix as made-up of matrix elements of a time-dependent operator, $P(t)$, operating on the basis set of functions.

$$\langle n | P(t) | m \rangle = C_n(t) C_m(t)^* \quad (5.6)$$

In this notation,

$$\langle \Psi | M_x | \Psi \rangle = \sum_m \sum_n \langle n | P(t) | m \rangle \langle m | M_x | n \rangle \quad (5.7)$$

Noting that, in general,

$$\sum_m \langle m | \langle m | = 1 \quad (5.8)$$

Equation 5.7 reduces to

$$\langle \Psi | M_x | \Psi \rangle = \sum_m \sum_n \langle n | P(t) M_x | n \rangle \quad (5.9)$$

$$= \text{Tr} \{ P M_x \} \quad (5.10)$$

In other words, the expectation value of M_x is given by the trace of the product of the matrix representations of P and M_x .

It is also easy to prove that P is a Hermitian operator:

$$\langle n | P(t) | m \rangle = \langle m | P(t) | n \rangle^* \quad (5.11)$$

When we are dealing with an ensemble of spins, different spins will have different wave functions in the sense that the coefficients C_n 's will be different for the individual spins. In such a case, one will have to take an ensemble average of these products to derive an average expectation value of the operator.

$$\langle \overline{M_x} \rangle = \sum_m \sum_n \overline{C_m(t)^* C_n(t)} \langle m | M_x | n \rangle \quad (5.12)$$

The matrix formed by the ensemble averages of the products $C_m(t)^* C_n(t)$ is represented by another operator, ρ , which is defined as

$$\langle n | \rho(t) | m \rangle = \overline{C_m(t)^* C_n(t)} \quad (5.13)$$

This operator ρ is called as the “density operator.”

5.3 Elements of Density Matrix

Matrix element ρ_{nm} is as given by Eq. 5.13.

$$\rho_{nm} = \overline{C_n(t) C_m(t)^*} \quad (5.14)$$

The coefficients C_n 's are complex quantities, and hence an ensemble average can also be written as follows

$$\overline{C_n(t) C_m(t)^*} = |C_m| |C_n| e^{-i(\alpha_n - \alpha_m)} \quad (5.15)$$

where the α s represent phases and the $|C_m|$ represents amplitudes.

At thermal equilibrium, by the hypothesis of random phases, all values of α in the range 0° – 360° are equally probable, and hence the ensemble average vanishes for $m \neq n$, that is, all off-diagonal elements vanish. Nonvanishing of off-diagonal elements implies the existence of phase coherence between states. The diagonal elements $|C_m|^2$ represent the probabilities (populations) given by Boltzmann's distribution.

Thus,

$$\rho_{mn} = \frac{\delta_{mn} e^{(-\frac{E_n}{kT})}}{Z} \quad (5.16)$$

where Z is the partition function given by

$$Z = \sum_{n=1}^N e^{-\frac{E_n}{kT}} \\ = \sum_{n=1}^N \left[1 - \frac{E_n}{kT} + \frac{1}{2!} \left(\frac{E_n}{kT} \right)^2 - \dots \dots \dots \right] \quad (5.17)$$

where N is the number of states. Under high-temperature approximation, $(\frac{E_n}{kT}) \ll 1$, Z can be approximated ignoring the higher-order terms as

$$Z = \sum_{n=1}^N \left[1 - \frac{E_n}{kT} \right] \quad (5.18)$$

$$= \sum_{n=1}^N 1 - \frac{1}{kT} \sum_{n=1}^N E_n \quad (5.19)$$

For Zeeman interaction, $\sum_{n=1}^N E_n = 0$

Therefore,

$$Z = \sum_{n=1}^N 1 = N \tag{5.20}$$

If \mathcal{H} is the Hamiltonian and $|i\rangle$ are the eigenstates with eigenvalues λ_i

$$\mathcal{H}|i\rangle = \lambda_i|i\rangle \tag{5.21}$$

and

$$e^{\mathcal{H}}|i\rangle = e^{\lambda_i}|i\rangle \tag{5.22}$$

Therefore

$$\langle j | e^{\mathcal{H}} | i \rangle = \langle j | e^{\lambda_i} | i \rangle = \delta_{ij} e^{\lambda_i} \tag{5.23}$$

Thus, Eq. 5.16 can be rewritten as

$$\begin{aligned} \rho_{mn} &= \frac{1}{N} \langle m | e^{-En/kT} | n \rangle \\ &= \frac{1}{N} \langle m | e^{-\frac{\mathcal{H}}{kT}} | n \rangle \end{aligned} \tag{5.24}$$

Thus,

$$\rho = \frac{1}{N} e^{-\frac{\mathcal{H}}{kT}} \tag{5.25}$$

Expanding this in power series, it becomes

$$\rho = \frac{1}{N} \left\{ 1 - \frac{\mathcal{H}}{kT} + \frac{1}{2!} \left(\frac{\mathcal{H}}{kT} \right)^2 - \dots \dots \dots \right\} \tag{5.26}$$

Under high-temperature approximation

$$\rho = \frac{1}{N} \left\{ 1 - \frac{\mathcal{H}}{kT} \right\} \tag{5.27}$$

For one spin

$$\mathcal{H} = -\gamma \hbar H_0 I_z \tag{5.28}$$

For $I = 1/2$,

$$\rho = \frac{1}{2} \left(1 + \frac{\gamma \hbar H_0 I_z}{kT} \right) \tag{5.29}$$

Calculating the matrix element of the operator I_z , the matrix elements of ρ will be

$$\rho_{\alpha\alpha} = \frac{1}{2} \left(1 + \frac{\gamma\hbar H_0}{2kT} \right); \rho_{\beta\beta} = \frac{1}{2} \left(1 - \frac{\gamma\hbar H_0}{2kT} \right); \rho_{\alpha\beta} = \rho_{\beta\alpha} = 0 \quad (5.30)$$

Thus,

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\gamma\hbar H_0}{4kT} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (5.31)$$

For multi-spin systems, the Hamiltonian will be

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_J \quad (5.32)$$

where \mathcal{H}_z represents the Zeeman interaction and \mathcal{H}_J represents the J-coupling interaction. Under high-field approximation, the contribution from \mathcal{H}_J will be very small compared to that from \mathcal{H}_z , and then the J-coupling can be dropped for the evaluation of the elements of the density matrix.

Explicitly for the two-spin system AX,

$$\rho = \frac{1}{(2I+1)_A(2I+1)_X} \left(1 + \frac{\gamma\hbar H_0 I_z}{kT} \right) \quad (5.33)$$

with $I_z = I_z(A) + I_z(X)$

The eigenstates of the spin system are $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. With these states, the matrix elements of ρ will be

$$\rho_{\alpha\alpha,\alpha\alpha} = \frac{1}{4} \left(1 + \frac{\gamma\hbar H_0}{kT} \right); \rho_{\beta\beta,\beta\beta} = \frac{1}{4} \left(1 - \frac{\gamma\hbar H_0}{kT} \right); \rho_{\alpha\beta,\alpha\beta} = \rho_{\beta\alpha,\beta\alpha} = \frac{1}{4} \quad (5.34)$$

All the remaining elements will be zero.

Thus,

$$\rho = \frac{1}{4} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} + \frac{\gamma\hbar H_0}{4kT} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad (5.35)$$

In general,

$$\rho = \frac{1}{Z} + \left(\frac{K}{Z} \right) I_z \quad (5.36)$$

where $K = \frac{\gamma\hbar H_0}{kT}$

5.4 Time Evolution of Density Operator ρ

An explicit understanding of the performance and characteristic features of an experiment is derived from the knowledge of the time evolution of the density operator through the experiment. To calculate this, we start from the relevant time-dependent Schrödinger equation:

$$\frac{-\hbar}{i} \frac{d\psi}{dt} = \mathcal{H}\psi \quad (5.37)$$

writing

$$\psi = \sum_n c_n(t) u_n \quad (5.38)$$

where $\{u_n\}$ s constitute the orthonormal basis set of eigenstates.

Substituting Eq. 5.38 in Eq. 5.37, one obtains

$$\frac{-\hbar}{i} \sum_n \frac{dc_n(t)}{dt} u_n = \mathcal{H} \sum_n c_n(t) u_n \quad (5.39)$$

Taking the matrix elements with the state u_k , one obtains

$$\frac{-\hbar}{i} \langle k | \sum_n \frac{dc_n(t)}{dt} | n \rangle = \langle k | \sum_n \mathcal{H} | c_n(t) | n \rangle \quad (5.40)$$

$$= \sum_n c_n(t) \langle k | \mathcal{H} | n \rangle \quad (5.41)$$

$$= \sum_n c_n(t) \mathcal{H}_{kn} \quad (5.42)$$

On the left-hand side, the only nonzero term will be $\frac{dc_k}{dt}$
Therefore,

$$\frac{-\hbar}{i} \frac{dc_k}{dt} = \sum_n c_n(t) \mathcal{H}_{kn} \quad (5.43)$$

Now,

$$\frac{d}{dt} \langle k | \rho | m \rangle = \frac{d}{dt} (c_k c_m^*) \quad (5.44)$$

The ensemble average for the coefficients is implicit in this equation.

$$= c_k \frac{dc_m^*}{dt} + c_m^* \frac{dc_k}{dt} \quad (5.45)$$

From Eq. 5.43

$$\frac{dc_m^*}{dt} = \frac{i}{\hbar} \sum_n c_n^* \mathcal{H}_{nm} \quad (5.46)$$

Thus, Eq. 5.45 reduces to

$$\frac{d}{dt} \langle k|\rho|m \rangle = \frac{i}{\hbar} \sum_n c_k c_n^* \mathcal{H}_{nm} - \frac{i}{\hbar} \sum_n c_m^* c_n \mathcal{H}_{kn} \quad (5.47)$$

$$= \frac{i}{\hbar} \sum_n \{ \langle k|\rho|n \rangle \langle n|\mathcal{H}|m \rangle - \langle k|\mathcal{H}|n \rangle \langle n|\rho|m \rangle \} \quad (5.48)$$

$$= \frac{i}{\hbar} \langle k|\rho\mathcal{H} - \mathcal{H}\rho|m \rangle \quad (5.49)$$

$$= \frac{i}{\hbar} \langle k | [\rho, \mathcal{H}] | m \rangle \quad (5.50)$$

Thus,

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}] \quad (5.51)$$

This is known as Liouville-von Neumann equation of motion for the density operator.

If the Hamiltonian is explicitly independent of time, then the solution of Eq. 5.51 is given as

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}t} \rho(o) e^{\frac{i}{\hbar}\mathcal{H}t} \quad (5.52)$$

This can be verified by explicit differentiation. Using Eq. 5.52, the off-diagonal elements of the density matrix can now be explicitly calculated.

$$\langle m|\rho(t)|n \rangle = \langle m| e^{-\frac{i}{\hbar}\mathcal{H}t} \rho(o) e^{\frac{i}{\hbar}\mathcal{H}t} |n \rangle \quad (5.53)$$

$$\rho_{mn} = e^{\frac{i}{\hbar}(E_n - E_m)t} \langle m|\rho(o)|n \rangle \quad (5.54)$$

Substituting $E_m = hv_m$, $E_n = hv_n$, and $\omega_{mn} = 2\pi(v_m - v_n)$, we get

$$\rho_{mn} = e^{i\omega_{mn}t} \langle m|\rho(o)|n \rangle \quad (5.55)$$

Now, we also have from Eq. 5.14

$$\langle m|\rho|n \rangle = \overline{c_m c_n^*} \quad (5.56)$$

$$= |c_m| |c_n| e^{i(\alpha_m - \alpha_n)} \quad (5.57)$$

where the α s represent the phases and c s represent the amplitudes, which are independent of each other. Therefore, the no-vanishing of ρ_{mn} implies the existence of phase coherence between the spins in the states $|m\rangle$ and $|n\rangle$ in the ensemble. At thermal equilibrium, all phases occur with equal probability which implies that

$$\overline{c_m c_n^*} = 0 \quad (5.58)$$

Then comparing this with Eq. 5.54,

$$e^{\frac{i}{\hbar}(E_n - E_m)t} \langle m | \rho(o) | n \rangle = 0 \quad (5.59)$$

Since the energy-dependent term which is oscillatory in time cannot be zero, it follows that

$$\langle m | \rho(o) | n \rangle = 0 \quad (5.60)$$

Therefore, all off-diagonal elements of the density matrix vanish at all times. Any nonvanishing off-diagonal element implies a nonequilibrium state.

Summarizing, the density matrix in the most general case,

$$\rho = \begin{bmatrix} P_1 & c_{12}e^{i\omega_{12}t} & c_{13}e^{i\omega_{13}t} & \cdots & \cdots & \cdots & c_{1n}e^{i\omega_{1n}t} \\ c_{21}e^{i\omega_{21}t} & P_2 & c_{23}e^{i\omega_{23}t} & \cdots & \cdots & \cdots & c_{2n}e^{i\omega_{2n}t} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ c_{n1}e^{i\omega_{n1}t} & c_{n2}e^{i\omega_{n2}t} & \cdots & \cdots & \cdots & \cdots & P_n \end{bmatrix} \quad (5.61)$$

The measured signal in an NMR experiment is given by the expectation value of the relevant operator M_x , M_y , or M_{\pm} .

For example, for M_x ,

$$\langle M_x \rangle = \text{Tr}(\rho M_x) = \text{Tr}(M_x \rho) \quad (5.62)$$

For a single spin $\frac{1}{2}$ system, if ρ at the start of data collection has some phase coherence between the two-spin states α and β and the populations are not equilibrium populations, we can write

$$\rho(t) = \begin{bmatrix} P_1 & e^{i\omega_{12}t} \\ e^{-i\omega_{12}t} & P_2 \end{bmatrix} \quad (5.63)$$

Here we have assumed identical coefficients for the off-diagonal elements. Therefore,

$$Tr(M_x \rho) = Tr \left\{ \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} P_1 & e^{i\omega_{12}t} \\ e^{-i\omega_{12}t} & P_2 \end{bmatrix} \right\} \quad (5.64)$$

$$= tr \left\{ \frac{1}{2} \begin{bmatrix} e^{-i\omega_{12}t} & P_2 \\ P_1 & e^{i\omega_{12}t} \end{bmatrix} \right\} \quad (5.65)$$

$$= \cos(\omega_{12}t) \quad (5.66)$$

Including transverse relaxation, Eq. 5.66 will become

$$\langle M_x \rangle = \cos(\omega_{12}t) e^{-t/T_2}$$

This oscillating function of time represents the frequency component of the time domain signal or the FID.

Extending to two spins,

$$M_x = M_{1x} + M_{2x}, \text{ and using the eigenstates } 1 = |\alpha\alpha\rangle, 2 = |\alpha\beta\rangle, 3 = |\beta\alpha\rangle, 4 = |\beta\beta\rangle$$

The matrix representation of M_x is

$$M_x = \frac{1}{2} \begin{bmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{bmatrix} \quad (5.67)$$

Assuming a nonequilibrium density operator of the form,

$$\rho(t) = \begin{bmatrix} P_1 & e^{i\omega_{12}t} & e^{i\omega_{13}t} & e^{i\omega_{14}t} \\ e^{-i\omega_{12}t} & P_2 & e^{i\omega_{23}t} & e^{i\omega_{24}t} \\ e^{-i\omega_{13}t} & e^{-i\omega_{23}t} & P_3 & e^{i\omega_{34}t} \\ e^{-i\omega_{14}t} & e^{-i\omega_{24}t} & e^{-i\omega_{34}t} & P_4 \end{bmatrix} \quad (5.68)$$

Here, ω_{12} , ω_{13} , ω_{24} , and ω_{34} represent the single-quantum coherences; ω_{14} and ω_{23} represent double-quantum and zero-quantum coherences, respectively.

The expectation value of M_x as per Eq. 5.62 is

$$\begin{aligned}
\langle M_x \rangle &= \text{Tr}(\rho M_x) \\
&= \text{Tr} \left\{ \frac{1}{2} \begin{bmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{bmatrix} \begin{bmatrix} P_1 & e^{i\omega_{12}t} & e^{i\omega_{13}t} & e^{i\omega_{14}t} \\ e^{-i\omega_{12}t} & P_2 & e^{i\omega_{23}t} & e^{i\omega_{24}t} \\ e^{-i\omega_{13}t} & e^{-i\omega_{23}t} & P_3 & e^{i\omega_{34}t} \\ e^{-i\omega_{14}t} & e^{-i\omega_{24}t} & e^{-i\omega_{34}t} & P_4 \end{bmatrix} \right\} \quad (5.69) \\
&= \cos(\omega_{12}t) + \cos(\omega_{13}t) + \cos(\omega_{24}t) + \cos(\omega_{34}t) \quad (5.70)
\end{aligned}$$

Clearly, the off-diagonal elements representing single-quantum coherences are selected, and this constitutes the frequency component of the free induction decay—the detected signal. Of course, transverse relaxation causes decay of the signal. The double-quantum and zero-quantum coherences, even though they are present in the density operator, are not detected. These constitute a non-observable magnetization.

5.5 Matrix Representations of RF Pulses

We begin with the Liouville equation (5.51) with the Hamiltonian, including the radio frequency (RF) pulse explicitly:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t) \quad (5.71)$$

where \mathcal{H}_0 is the time-independent part of the Hamiltonian and $\mathcal{H}_1(t)$, which is time-dependent, represents the RF pulse.

Substituting Eq. 5.71 in Eq. 5.51, we get

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}] = \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1(t)] \quad (5.72)$$

If \mathcal{H}_1 were nonexistent, the solution would have been

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}_0t} \rho(0) e^{\frac{i}{\hbar}\mathcal{H}_0t} \quad (5.73)$$

Now we define and quantify ρ^* such that

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}_0t} \rho^*(t) e^{\frac{i}{\hbar}\mathcal{H}_0t} \quad (5.74)$$

Such a solution satisfies the condition that at $t = 0$, ρ and ρ^* are identical. Differentiating equation (5.74) with respect to time, we get

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [\mathcal{H}_0, \rho] + e^{-\frac{i}{\hbar}\mathcal{H}_0t} \frac{d\rho^*}{dt} e^{\frac{i}{\hbar}\mathcal{H}_0t} \quad (5.75)$$

$$= \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1] \quad (5.76)$$

From this we get

$$\frac{d\rho^*}{dt} = \frac{i}{\hbar} e^{\frac{i\mathcal{H}_0 t}{\hbar}} [\rho, \mathcal{H}_1] e^{-\frac{i\mathcal{H}_0 t}{\hbar}} \quad (5.77)$$

$$= \frac{i}{\hbar} e^{\frac{i\mathcal{H}_0 t}{\hbar}} (\rho \mathcal{H}_1 - \mathcal{H}_1 \rho) e^{-\frac{i\mathcal{H}_0 t}{\hbar}} \quad (5.78)$$

$$= \frac{i}{\hbar} \{ e^{\frac{i\mathcal{H}_0 t}{\hbar}} \rho e^{-\frac{i\mathcal{H}_0 t}{\hbar}} e^{\frac{i\mathcal{H}_0 t}{\hbar}} \mathcal{H}_1 e^{-\frac{i\mathcal{H}_0 t}{\hbar}} - e^{\frac{i\mathcal{H}_0 t}{\hbar}} \mathcal{H}_1 e^{-\frac{i\mathcal{H}_0 t}{\hbar}} e^{\frac{i\mathcal{H}_0 t}{\hbar}} \rho e^{-\frac{i\mathcal{H}_0 t}{\hbar}} \} \quad (5.79)$$

$$= \frac{i}{\hbar} [\rho^*, \mathcal{H}_1^*] \quad (5.80)$$

where

$$\mathcal{H}_1^* = e^{\frac{i\mathcal{H}_0 t}{\hbar}} \mathcal{H}_1 e^{-\frac{i\mathcal{H}_0 t}{\hbar}} \quad (5.81)$$

At $t = 0$, $\mathcal{H}_1^* = \mathcal{H}_1$

The transformation operator $e^{\frac{i\mathcal{H}_0 t}{\hbar}}$ represents the rotation about the static field axis and thus represents the transformation into the rotating frame. Such a representation is also called the interaction representation. Under resonance condition the evolution under \mathcal{H}_0 will be negligible. Thus, as we will show, during the high-power short-duration pulse, the Hamiltonian \mathcal{H}_1^* will be identical to \mathcal{H}_1 . Similarly, ρ^* will also become identical to ρ during the pulse.

We now calculate the matrix elements of \mathcal{H}_1^* :

$$\langle k | \mathcal{H}_1^* | m \rangle = \langle k | e^{\frac{i\mathcal{H}_0 t}{\hbar}} \mathcal{H}_1 e^{-\frac{i\mathcal{H}_0 t}{\hbar}} | m \rangle \quad (5.82)$$

$$= e^{\frac{i}{\hbar} (E_k - E_m) t} \langle k | \mathcal{H}_1 | m \rangle \quad (5.83)$$

If $\mathcal{H}_1 = \mathcal{H}_1(0) e^{-i\omega_{\text{RF}} t}$, which represents the RF pulse, then

$$\langle k | \mathcal{H}_1^* | m \rangle = e^{\frac{i}{\hbar} (E_k - E_m - \hbar\omega_{\text{RF}}) t} \langle k | \mathcal{H}_1(0) | m \rangle \quad (5.84)$$

Now, $(E_k - E_m - \hbar\omega_{\text{RF}})$ is in the kHz range if “ P ” is in the μs range as in an RF pulse; the time-dependent term in (5.84) will be extremely slowly varying during the pulse and hence can be effectively considered to be constant. Thus, the matrix element $\langle k | \mathcal{H}_1^* | m \rangle$ can be assumed to be independent of time; in fact, under resonance condition, $(E_k - E_m - \hbar\omega_{\text{RF}})$ will be zero, and there will be no time dependence at all. In other words, during the time of the pulse, \mathcal{H}_1^* can be assumed to be time-independent and is equal to the amplitude of \mathcal{H}_1 .

Under this condition, the solution of Eq. 5.80 can be written as

$$\rho^*(t) = e^{-\frac{i}{\hbar}\mathcal{H}_1 t} \rho^*(0) e^{\frac{i}{\hbar}\mathcal{H}_1 t} \tag{5.85}$$

And since $\rho^*(0) = \rho(0)$, Eq. 5.85 becomes

$$\rho^*(t) = e^{-\frac{i}{\hbar}\mathcal{H}_1 t} \rho(0) e^{\frac{i}{\hbar}\mathcal{H}_1 t} \tag{5.86a}$$

Following the discussion above, under resonance condition, note that for high-power pulse, resonance condition can be considered to be satisfied for all the frequencies in the spectrum at the same time; the effective field will be equal to the RF amplitude; the field along the z-axis will be zero; and thus evolution under the Hamiltonian \mathcal{H}_0 will be negligible. Thus, looking at Eq. 5.74, we can also replace $\rho^*(t)$ by $\rho(t)$ in Eq. 5.86a. Thus, the density operator transformation by the RF pulse can be described by

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}_1 t} \rho(0) e^{\frac{i}{\hbar}\mathcal{H}_1 t} \tag{5.86b}$$

If the RF is applied along the x-axis,

$$\widehat{\mathcal{H}}_1 = \vec{\mu} \cdot \vec{H}_1 = \gamma \hbar H_1 \widehat{I}_x \tag{5.87}$$

The transformation operator $e^{-\frac{i}{\hbar}\mathcal{H}_1 t}$ thus becomes $e^{-i\beta \widehat{I}_x}$, where $\beta = \gamma H_1 t$ represents the rotation about the x-axis by angle β (flip-angle of the RF pulse). Thus, depending upon the length of the pulse, different rotation angles can be obtained.

For one spin, the I_q ($q = x, y, z$) operator can be written as $\frac{1}{2}\sigma_q$, where σ_s are the Pauli spin matrices given as

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}; \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{5.88}$$

The Pauli matrices satisfy the condition:

$$\sigma_z^2 = \sigma_y^2 = \sigma_x^2 = 1 \tag{5.89}$$

Using this notation, the operator $e^{-i\beta \widehat{I}_x}$ can be expanded as a series:

$$\begin{aligned} e^{-i\beta \widehat{I}_x} &= e^{-\frac{i\beta}{2}\sigma_x} \\ &= 1 - \frac{i\beta}{2}\sigma_x + \frac{1}{2!} \left(\frac{i\beta}{2}\right)^2 - \frac{1}{3!} \left(\frac{i\beta}{2}\right)^3 \sigma_x + \frac{1}{4!} \left(\frac{i\beta}{2}\right)^4 \\ &\quad - \dots \end{aligned} \tag{5.90}$$

Regrouping the terms,

$$e^{-i\beta\hat{I}_x} = \left(1 - \frac{1}{2!} \left(\frac{\beta}{2}\right)^2 + \frac{1}{4!} \left(\frac{\beta}{2}\right)^4 - \dots\right) - i \left(\frac{\beta}{2} - \frac{1}{3!} \left(\frac{\beta}{2}\right)^3 - \dots\right) \sigma_x \quad (5.91)$$

$$= \cos\left(\frac{\beta}{2}\right) - i\sigma_x \sin\left(\frac{\beta}{2}\right) \quad (5.92)$$

$$= \cos\left(\frac{\beta}{2}\right) - 2iI_x \sin\left(\frac{\beta}{2}\right)$$

Putting in matrix notation,

$$e^{-i\beta I_x} = \cos\left(\frac{\beta}{2}\right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - i \sin\left(\frac{\beta}{2}\right) \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (5.93)$$

Thus, for one spin, a 90° x -pulse ($\beta = \frac{\pi}{2}$), the matrix representation becomes

$$R_x\left(\frac{\pi}{2}\right) = e^{-i\frac{\pi}{2}I_x} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \quad (5.94)$$

Similarly, for a 90° y -pulse, we get

$$R_y\left(\frac{\pi}{2}\right) = e^{-i\frac{\pi}{2}I_y} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \quad (5.95)$$

The matrices for π pulses turn out to be

$$R_x(\pi) = e^{-i\pi I_x} = \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}; R_y(\pi) = e^{-i\pi I_y} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \quad (5.96)$$

The effect of these pulses on the density operator can be explicitly calculated using the matrix representations. For example, for a density operator represented by \hat{I}_z , the transformation under $R_x(\frac{\pi}{2})$ will be

$$\rho = R_x\left(\frac{\pi}{2}\right) \hat{I}_z R_x^{-1}\left(\frac{\pi}{2}\right) \quad (5.97)$$

$$= \frac{1}{4} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \quad (5.98)$$

$$= \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \quad (5.99)$$

$$= -\hat{I}_y \quad (5.100)$$

So clearly, the z-magnetization is rotated onto the negative y-axis, when we apply a $(\frac{\pi}{2})_x$ pulse.

Similarly, the transformation under $R_y(\frac{\pi}{2})$ on density operator represented by \hat{I}_z is given in Box 5.1.

Box 5.1: Density Operator Transformation for the Effect of a $(\frac{\pi}{2})_y$ Pulse on the \hat{I}_z Operator

For $R_y(\frac{\pi}{2})$ pulse, the \hat{I}_z operator will transform as

$$\begin{aligned}\rho &= R_y\left(\frac{\pi}{2}\right)\hat{I}_z R_y^{-1}\left(\frac{\pi}{2}\right) \\ &= \frac{1}{4} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ &= \hat{I}_x\end{aligned}$$

So clearly, the z-magnetization is rotated onto the positive x-axis, when we apply a $(\frac{\pi}{2})_y$ pulse.

For a two-spin system, the matrix representations of the operators are calculated by direct products (Box 5.2).

$$R_x\left(\frac{\pi}{2}\right)(\text{non-selective}) = \frac{1}{2} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \quad (5.101)$$

$$= \frac{1}{2} \begin{bmatrix} 1 & -i & -i & -1 \\ -i & 1 & -1 & -i \\ -i & -1 & 1 & -i \\ -1 & -i & -i & 1 \end{bmatrix} \quad (5.102)$$

Similarly,

$$R_y\left(\frac{\pi}{2}\right)(\text{non-selective}) = \frac{1}{2} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \quad (5.103)$$

$$= \frac{1}{2} \begin{bmatrix} 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 \end{bmatrix} \quad (5.104)$$

Box 5.2: The Calculation of the Direct Product Between Two 2×2 Matrices

The direct product between two matrices P and Q can be represented as

$$P = \begin{bmatrix} a & b \\ c & d \end{bmatrix}, Q = \begin{bmatrix} A & B \\ C & D \end{bmatrix}$$

$$P \otimes Q = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \otimes \begin{bmatrix} A & B \\ C & D \end{bmatrix}$$

$$= \begin{bmatrix} a \begin{bmatrix} A & B \\ C & D \end{bmatrix} & b \begin{bmatrix} A & B \\ C & D \end{bmatrix} \\ c \begin{bmatrix} A & B \\ C & D \end{bmatrix} & d \begin{bmatrix} A & B \\ C & D \end{bmatrix} \end{bmatrix}$$

Using these matrix representations for the pulses and the density operator, the evolution of the density operator through a multi-pulse experiment can be calculated.

5.6 Product Operator Formalism

In a generalized pulse sequence, as indicated in Fig. 5.1, the density operator evolution can be calculated as

$$\rho(t) = P_4 e^{-\frac{i}{\hbar} \mathcal{H}_3 \tau_3} P_3 e^{-\frac{i}{\hbar} \mathcal{H}_2 \tau_2} P_2 e^{-\frac{i}{\hbar} \mathcal{H}_1 \tau_1} P_1 \rho(0) P_1^{-1} e^{\frac{i}{\hbar} \mathcal{H}_1 \tau_1} P_2^{-1} e^{\frac{i}{\hbar} \mathcal{H}_2 \tau_2} P_3^{-1} e^{\frac{i}{\hbar} \mathcal{H}_3 \tau_3} P_4^{-1} \quad (5.105)$$

This can be essentially broken into two types of transformations occurring successively.

$$\rho' = e^{-\frac{i}{\hbar} \mathcal{H} t} \rho e^{\frac{i}{\hbar} \mathcal{H} t} \text{ [for free evolution]} \quad (5.106)$$

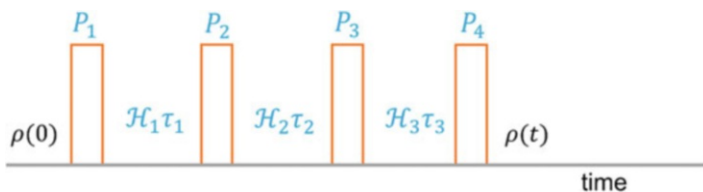


Fig. 5.1 A schematic of a multi-pulse sequence, which is used to calculate the density operator evolutions at different time points. P_s refer to the pulses, H_s refer to the Hamiltonians, and τ_s refer to the time for which the Hamiltonian is operative

and

$$\rho'' = P\rho P^{-1} \text{ [for pulses]} \quad (5.107)$$

To simplify this calculation, the product operator formalism has been developed for weakly coupled spin systems. The density operator is expressed as a linear combination of some basis operators, which constitute a complete set:

$$\rho(t) = \sum b_s(t) B_s \quad (5.108)$$

Thus,

$$\rho' = \sum b_s e^{-\frac{i}{\hbar} H t} B_s e^{\frac{i}{\hbar} H t} \text{ [for free evolution]} \quad (5.109)$$

$$\rho'' = \sum b_s P B_s P^{-1} \text{ [for pulses]} \quad (5.110)$$

In these two equations, ρ is the density operator at any particular instance in an experimental sequence. Thus, it is necessary to understand the transformational properties of individual B_s operators.

5.6.1 Basis Operator Sets

The basis operators can be defined in many ways: (i) Cartesian operators, (ii) single-element basis operators (polarization operators), and (iii) shift basis operators. The number of basis operator will depend on the number of coupled spins. For one spin, it will have four operators, which form a complete basis set. These are

Cartesian space; $\frac{E}{2}$, I_x , I_y , and I_z

Single-element operator space; I_α , I_β , I^+ , I^-

Shift operator space; $\frac{E}{\sqrt{2}}$, I^+ , I^- , I_0 ; $I_0 = \sqrt{2}I_z$

The corresponding matrix representations of various one-spin operators are given in Box 5.3.

Box 5.3: Matrix Representations of the Operators $I_z, I_x, I_y, I^+, I^-, I_\alpha$ and I_β for the Case of One Spin $\frac{1}{2}$

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

$$I^- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

$$I_\alpha = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}; I_\beta = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$$

For n spins, in a coupled network, there will be 4^n elements in the basis operator sets. For example, for 2 spins, there will be a total of 16 operators. For the Cartesian space, these are

E

$$I_{1x}, I_{1y}, I_{1z}, I_{2x}, I_{2y}, I_{2z}$$

$$2I_{1x}I_{2x}, 2I_{1x}I_{2y}, 2I_{1x}I_{2z}$$

$$2I_{1y}I_{2x}, 2I_{1y}I_{2y}, 2I_{1y}I_{2z}$$

$$2I_{1z}I_{2x}, 2I_{1z}I_{2y}, 2I_{1z}I_{2z}$$

For three spins, labeled as AMQ, the Cartesian operator sets would be

E

$$I_{Ap}, I_{Mp}, I_{Qp} \quad p = x, y, z \quad (\text{a total of 9 operators})$$

$$2I_{Ap}I_{Mr}, 2I_{Mp}I_{Qr}, 2I_{Ap}I_{Qr} \quad p, r = x, y, z \quad (\text{a total of 27 operators})$$

$$4I_{Ap}I_{Mr}I_{Qs} \quad p, r, s = x, y, z \quad (\text{a total of 27 operators})$$

Similar products can be written for other types of basis sets as well.

Matrix representations for all these operators can be derived, and these are explicitly listed in Table 5.1.

For one spin, the Cartesian space representations are

$$E = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}; I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; I_y = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (5.111)$$

For two spins, k and l ,

$$E = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Table 5.1 Matrix representations of product operators for a two-spin system

$I_E = \frac{1}{2}$	$I_{kz} = \frac{1}{2}$	$I_{lz} = \frac{1}{2}$	$I_{kz}I_{lz} = \frac{1}{2}$	$I_{kz}I_{lz} = \frac{1}{2}$	$2I_{kz}I_{lz} = \frac{1}{2}$
$I_{kx} = \frac{1}{2}$	$I_{ky} = \frac{1}{2}$	$I_{lx} = \frac{1}{2}$	$I_{ky}I_{lx} = \frac{1}{2}$	$2I_{ky}I_{lx} = \frac{1}{2}$	$2I_{ky}I_{lx} = \frac{1}{2}$
$I_{lx} = \frac{1}{2}$	$I_{ly} = \frac{1}{2}$	$I_{kx} = \frac{1}{2}$	$I_{ly}I_{kx} = \frac{1}{2}$	$2I_{ly}I_{kx} = \frac{1}{2}$	$2I_{ly}I_{kx} = \frac{1}{2}$
$2I_{kx}I_{lx} = \frac{1}{2}$	$2I_{ky}I_{ly} = \frac{1}{2}$	$2I_{kz}I_{lz} = \frac{1}{2}$	$2I_{lx}I_{ly} = \frac{1}{2}$	$2I_{kx}I_{ly} = \frac{1}{2}$	$2I_{ky}I_{lx} = \frac{1}{2}$

$$I_{kx} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$I_{lx} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$I_{ky} = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$I_{ly} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$I_{kz} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$I_{lz} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Similarly, for two spin products, for example, $2I_{kx}I_{ly}$, the matrix representation can be calculated as

$$2I_{kx}I_{ly} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

The complete list of matrix representations for two spins is given in Table 5.1. By examining the matrix representations, the following points become evident.

1. I_z operator represents the populations and the z-magnetizations.
2. I_x and I_y operators in a multi-spin system represent in-phase single-quantum coherences along the x- and y-axes, respectively.
3. $2I_{kx}I_{lz}$ and $2I_{ky}I_{lz}$ represent single-quantum coherences of k spin antiphase with respect to l along the x- and y-axes, respectively. Similar interpretations hold good for the l spin single-quantum coherences.
4. $2I_{kx}I_{ly}$, $2I_{ky}I_{lx}$, $2I_{kx}I_{lx}$, and $2I_{ky}I_{ly}$ represent mixtures of double-quantum and zero-quantum coherences, and suitable combinations of these represent pure double-quantum and single-quantum coherences.

$2I_{kx}I_{lx} + 2I_{ky}I_{ly}$ represents the x-component of zero-quantum coherence.

$2I_{kx}I_{ly} - 2I_{ky}I_{lx}$ represents the y-component of zero-quantum coherence.

$2I_{kx}I_{lx} - 2I_{ky}I_{ly}$ represents the x-component of double-quantum coherence

$2I_{kx}I_{ly} + 2I_{ky}I_{lx}$ represents the y-component of double-quantum coherence.

5. $2I_{kz}I_{lz}$ represents two-spin zz -order.

A pictorial representation of these coherences on the energy level diagram of a two-spin system is shown in Fig. 5.2.

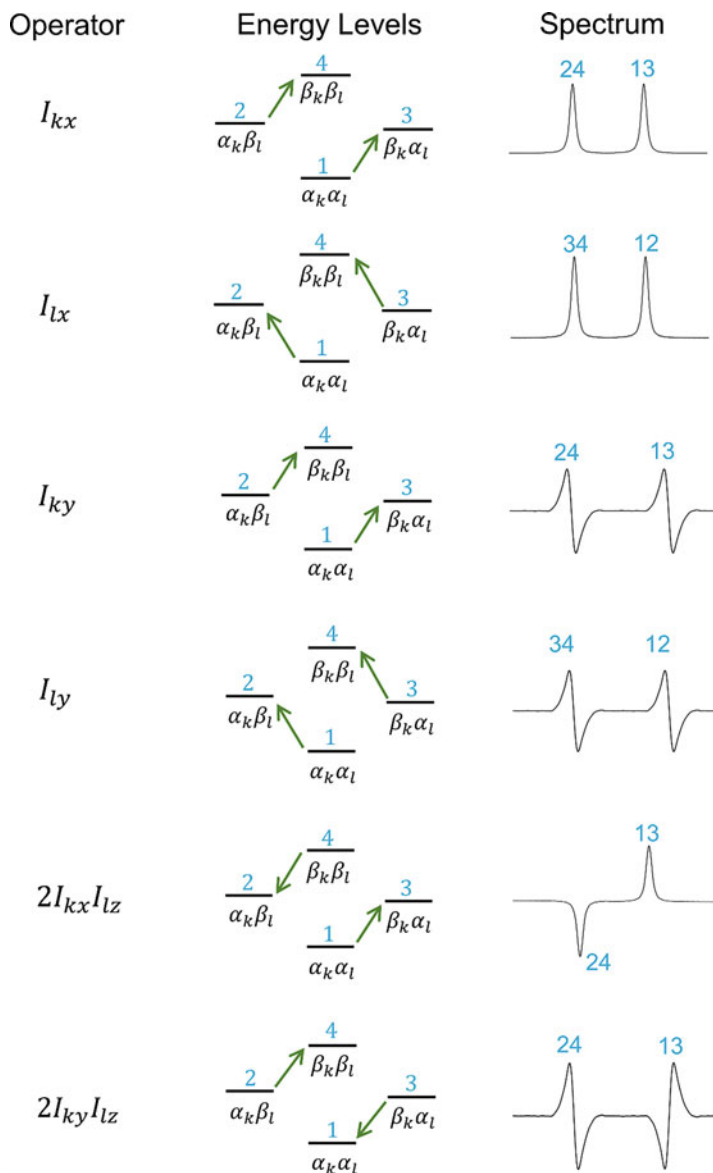


Fig. 5.2 Schematic drawings on the energy levels in a two-spin system (middle) to indicate the transitions represented by the individual operators on the left, and the corresponding spectra for different operators are shown on the right. Upward arrows indicate positive signals, and downward arrows indicate negative signals

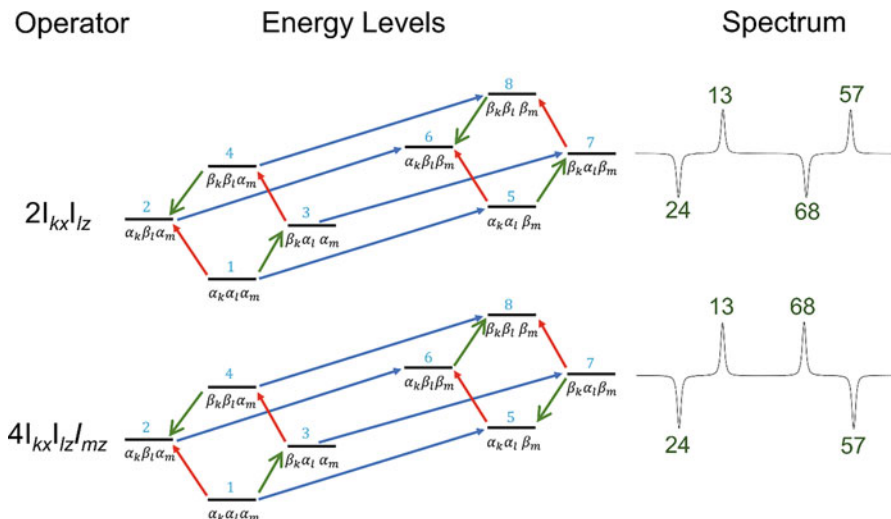


Fig. 5.3 Pictorial representations of the transitions represented by two-spin and three-spin product operators in a three-spin system (k, l, m) on the energy level diagram. In both cases, the operators represent the magnetization of k spin, and the spectrum on the right shows these four transitions. Upward arrows in the energy level diagram indicate positive signal, and downward arrows indicate negative signals. Different color codes are used to represent transitions belonging to the three spins. Note that arrows have been drawn for l and m spins as well for completeness, but the operators do not represent these transitions in any manner

Similar interpretations will hold good for two-spin and three-spin products in three-spin systems and other higher spin systems.

For example, a basis operator of type $4I_{Ax}I_{Mz}I_{Qz}$ represents a single-quantum coherence of A spin along the x -axis antiphase with respect to both M and Q spins.

Pictorial representations of a two-spin product in a three-spin system and a three-spin product in the three-spin system are shown in Fig. 5.3.

5.6.2 Time Evolution of Cartesian Basis Operators

5.6.2.1 Free Evolution Under the Influence of the Hamiltonian

The isotropic Hamiltonian for weakly coupled spin systems in liquids in units of \hbar is

$$\mathcal{H} = \sum_k \omega_k I_{zk} + \sum_{k < l} 2\pi J_{kl} I_{zk} I_{zl} \quad (5.112)$$

The first term represents the chemical shifts, and the second term represents the scalar couplings.

For a basis operator B_s , the evolution under the Hamiltonian is given by

$$B'_S = e^{-i\mathcal{H}t} B_S e^{i\mathcal{H}t} \quad (5.113)$$

$$= e^{-i \left(\sum_k \omega_k I_{zk} + \sum_{k<l} 2\pi J_{kl} I_{zk} I_{zl} \right) t} B_S e^{i \left(\sum_k \omega_k I_{zk} + \sum_{k<l} 2\pi J_{kl} I_{zk} I_{zl} \right) t} \quad (5.114)$$

Since the two parts of the Hamiltonian commute with each other, the terms in Eq. 5.114 can be shuffled without affecting the results.

$$B'_S = e^{-i \left(\sum_{k<l} 2\pi J_{kl} I_{zk} I_{zl} \right) t} \left(e^{-i \sum_k \omega_k I_{zk} t} B_S e^{i \sum_k \omega_k I_{zk} t} \right) e^{i \left(\sum_{k<l} 2\pi J_{kl} I_{zk} I_{zl} \right) t} \quad (5.115)$$

The central portion inside the bracket represents the evolution under chemical shift, and the outer terms represent the evolution under coupling. The two can be handled separately. One may also note that this order of evolutions can be interchanged because the two parts of the Hamiltonian commute with each other.

5.6.2.2 Chemical Shift Evolution

As an example, let us consider the evolution of the basis operator $B_S = I_{kx}$ representing the k spin magnetization.

So,

$$B'_S = e^{-i\omega_k I_{zk} t} I_{kx} e^{i\omega_k I_{zk} t} \quad (5.116)$$

From Eq. 5.92, this turns out to be

$$B'_S = \left\{ \cos \left(\frac{\omega_k t}{2} \right) - 2i \sin \left(\frac{\omega_k t}{2} \right) I_{kz} \right\} I_{kx} \left\{ \cos \left(\frac{\omega_k t}{2} \right) - 2i \sin \left(\frac{\omega_k t}{2} \right) I_{kz} \right\} \quad (5.117)$$

$$= \cos^2 \left(\frac{\omega_k t}{2} \right) I_{kx} + 4 \sin^2 \left(\frac{\omega_k t}{2} \right) I_{kz} I_{kx} I_{kz} - i \sin(\omega_k t) [I_{kz}, I_{kx}] \quad (5.118)$$

The product $I_{kz} I_{kx} I_{kz}$ can be evaluated by individual matrix multiplication and turns out to be

$$I_{kz} I_{kx} I_{kz} = \frac{1}{8} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \frac{1}{8} \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix} = -\frac{1}{4} I_{kx} \quad (5.119)$$

Thus, Eq. 5.118 reduces to

$$B'_S = \cos^2 \left(\frac{\omega_k t}{2} \right) I_{kx} - \sin^2 \left(\frac{\omega_k t}{2} \right) I_{kx} + \sin(\omega_k t) I_{ky} \quad (5.120)$$

$$= \cos(\omega_k t) I_{kx} + \sin(\omega_k t) I_{ky} \quad (5.121)$$

5.6.2.3 Scalar Coupling Evolution

For the basis operator I_{kx} , the evolution can be written as

$$B_S'' = e^{-i2\pi J_{kl}I_{kz}I_{lz}t} I_{kx} e^{i2\pi J_{kl}I_{kz}I_{lz}t} \quad (5.122)$$

As shown in Box 5.4,

$$e^{-i2\pi J_{kl}I_{kz}I_{lz}t} = \cos\left(\frac{\pi J_{kl}t}{2}\right) - 4i \sin\left(\frac{\pi J_{kl}t}{2}\right) I_{kz}I_{lz} \quad (5.123)$$

Box 5.4: Explicit Derivation of Eq. 5.123

Let $I_{kz}I_{lz} = \frac{1}{4}A$ and $2\pi J_{kl}t = \beta$

$$A = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$A^2 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$e^{-i2\pi J_{kl}(A/4)t} = 1 - \frac{i\beta}{4}A + \left(\frac{i\beta}{4}\right)^2 \frac{A^2}{2!} - \left(\frac{i\beta}{4}\right)^3 \frac{A^3}{3!} + \dots$$

$$= 1 - \frac{i\beta}{4}A + \left(\frac{i\beta}{4}\right)^2 \frac{1}{2!} - \left(\frac{i\beta}{4}\right)^3 \frac{A}{3!} + \dots$$

$$= \cos\left(\frac{\pi J_{kl}t}{2}\right) - 4i \sin\left(\frac{\pi J_{kl}t}{2}\right) I_{kz}I_{lz}$$

Substituting Eq. 5.123 into Eq. 5.122,

$$B_S'' = \left\{ \cos\left(\frac{\pi J_{kl}t}{2}\right) - 4i \sin\left(\frac{\pi J_{kl}t}{2}\right) I_{kz}I_{lz} \right\} I_{kx} \left\{ \cos\left(\frac{\pi J_{kl}t}{2}\right) + 4i \sin\left(\frac{\pi J_{kl}t}{2}\right) I_{kz}I_{lz} \right\} \quad (5.124)$$

After some algebra (Box 5.5) similar to that in the calculation of shift evolution (5.119),

$$B_S'' = I_{kx} \cos(\pi J_{kl}t) + 2I_{ky}I_{lz} \sin(\pi J_{kl}t) \quad (5.125)$$

Box 5.5: Explicit Derivation of Eq. 5.125

$$\begin{aligned} B_S'' &= \left\{ \cos\left(\frac{\pi J_{kl}t}{2}\right) - 4i \sin\left(\frac{\pi J_{kl}t}{2}\right) I_{kz}I_{lz} \right\} I_{kx} \left\{ \cos\left(\frac{\pi J_{kl}t}{2}\right) + 4i \sin\left(\frac{\pi J_{kl}t}{2}\right) I_{kz}I_{lz} \right\} \\ &= \left(\cos^2\left(\frac{\pi J_{kl}t}{2}\right) I_{kx} - \sin^2\left(\frac{\pi J_{kl}t}{2}\right) I_{kx} \right) - 2i \sin(\pi J_{kl}t) [I_{kz}, I_{kx}] I_{lz} \\ B_S'' &= I_{kx} \cos(\pi J_{kl}t) + 2I_{ky}I_{lz} \sin(\pi J_{kl}t) \end{aligned}$$

Similar calculations starting with other basis operators reveal that they form rotation groups, as indicated in Fig. 5.4. In Fig. 5.4a, operators I_x , I_y , and I_z form a group, which means they transform among themselves. For example, I_x and I_y interconvert under the influence of free evolution (I_z operator). In Fig. 5.4b, operator terms $2I_{kz}I_{lz}$, $2I_{ky}I_{lz}$, and I_{kx} form a rotation group under J-coupling evolution ($2I_{kz}I_{lz}$ operator). I_{kx} and $2I_{ky}I_{lz}$ interconvert among themselves under the influence of J-coupling evolution. Similarly, $2I_{kz}I_{lz}$, $2I_{kx}I_{lz}$, and I_{ky} form a rotation group under J-coupling evolution ($2I_{kz}I_{lz}$ operator). I_{ky} and $2I_{kx}I_{lz}$ interconvert among themselves under the influence of J-coupling evolution.

For example,

$$\begin{aligned} I_{kx} &\xrightarrow{J\text{-coupling evolution}} I_{kx} \cos(\pi J_{kl}t) + 2I_{ky}I_{lz} \sin(\pi J_{kl}t) \\ I_{ky} &\xrightarrow{J\text{-coupling evolution}} I_{ky} \cos(\pi J_{kl}t) - 2I_{kx}I_{lz} \sin(\pi J_{kl}t) \\ 2I_{kx}I_{lz} &\xrightarrow{J\text{-coupling evolution}} 2I_{kx}I_{lz} \cos(\pi J_{kl}t) + I_{ky} \sin(\pi J_{kl}t) \\ 2I_{ky}I_{lz} &\xrightarrow{J\text{-coupling evolution}} 2I_{ky}I_{lz} \cos(\pi J_{kl}t) - I_{kx} \sin(\pi J_{kl}t) \end{aligned} \quad (5.126)$$

5.6.2.4 Rotation by Pulses

This is represented by the transformation:

$$R_q B_s R_q^{-1} \quad q = x, y \quad (5.127)$$

We describe here a few cases:

- (i) $B_s = I_z$

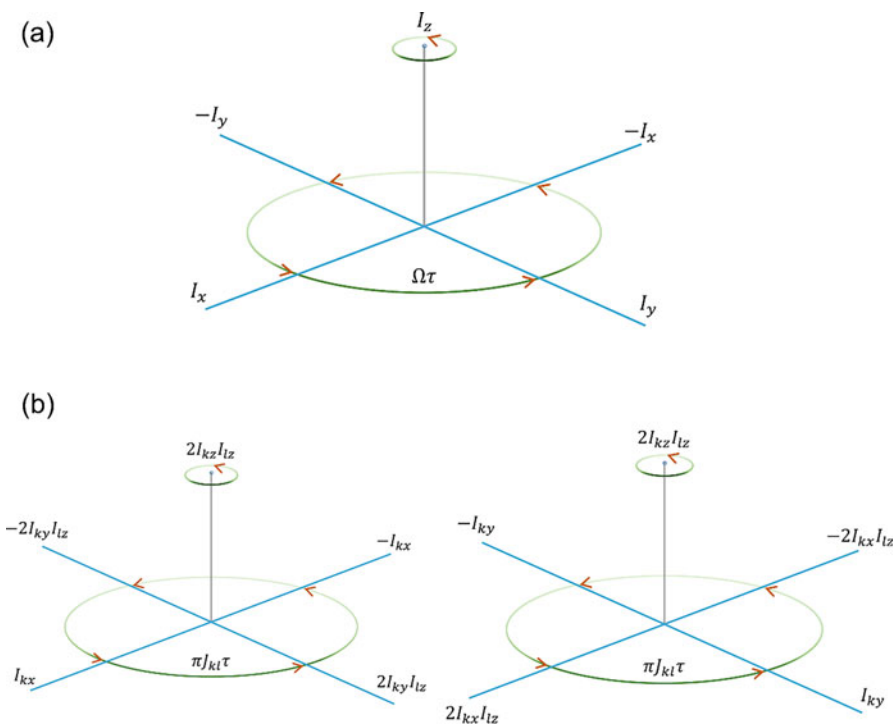


Fig. 5.4 (a) The free evolution of magnetization under Zeeman Hamiltonian (chemical shift evolution) and (b) scalar coupling evolutions. In either case, the Hamiltonian is represented along the z-axis, and the x- and y-axes represent the operators resulting from the respective evolutions. In each figure, the operators involved form rotation groups. See text for explicit transformations

For a 90_x pulse, the transformation will be

$$R_x\left(\frac{\pi}{2}\right)I_z R_x^{-1}\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -I_y$$

Thus,

$$I_z \xrightarrow{90_x} -I_y \quad (5.128)$$

(ii) $B_s = I_y$

For a 90_x pulse, the transformation will be

$$R_x\left(\frac{\pi}{2}\right)I_y R_x^{-1}\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = I_z$$

Thus,

$$I_y \xrightarrow{90_x} I_z \quad (5.129)$$

(iii) $B_S = I_x$

For a 90_x pulse, the transformation will be

$$R_x\left(\frac{\pi}{2}\right)I_x R_x^{-1}\left(\frac{\pi}{2}\right) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = I_x$$

Thus, I_x is invariant under R_x pulse.

For multi-spin basis operators, the effects of pulses can be applied to individual spins.

For example,

$$2I_{kx}I_{lz} \xrightarrow{90_x(k)+90_x(l)} -2I_{kx}I_{ly} \quad (5.130)$$

This represents the conversion of antiphase x-magnetization of k spin into a mixture of zero- and double-quantum coherences.

$$2I_{ky}I_{lz} \xrightarrow{90_x(k)+90_x(l)} -2I_{kz}I_{ly} \quad (5.131)$$

This represents the conversion of antiphase y-magnetization of k spin into antiphase y-magnetization spin l. This is referred to as the coherence transfer from spin k to spin l. In general, it is seen that the application of RF pulses to antiphase magnetization in multi-spin systems causes coherence transfer among the spins. This forms the basis of many multi-pulse experiments in homo- and heteronuclear multi-spin systems.

The effects of various transformations under the influence of pulses are schematically shown in Fig. 5.5.

5.6.2.5 Calculation of the Spectrum of a J-Coupled Two-Spin System

In this section, we illustrate the calculation of the spectrum of a simple two-spin system, kl , in the standard FTNMR experiment (Fig. 5.6), using the product operator formalism.

To begin with the system is in equilibrium, and this is represented by the equilibrium density operator, ρ (see Eq. 5.36), which is proportional to I_z operator.

$$\rho \propto I_z = I_{kz} + I_{lz} \quad (5.132)$$

This represents magnetization along the z-axis. On application of a 90_x pulse, the magnetization rotates to $-y$ -axis (see Fig. 5.5).

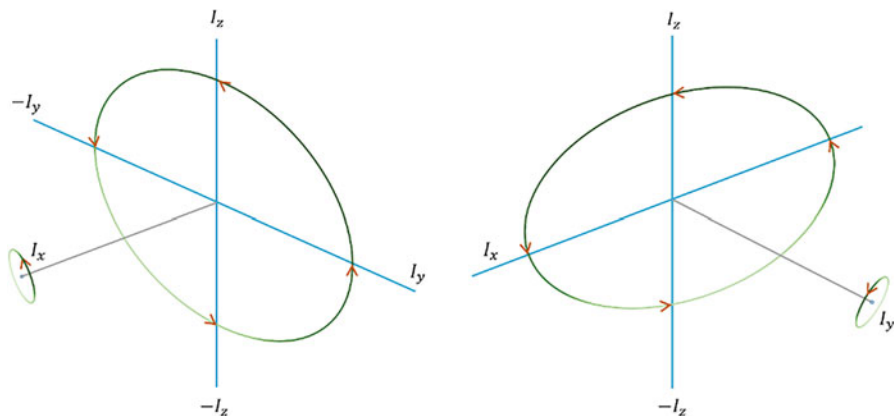
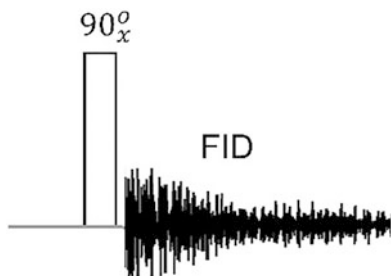


Fig. 5.5 The effect of 90°_x and 90°_y pulses on different magnetization components. The bigger circle indicates the rotation of magnetization components, while the smaller circle indicates the axis along which the pulse is applied

Fig. 5.6 One pulse FT-NMR experiment



$$-I_y = -(I_{ky} + I_{ly}) \quad (5.133)$$

This will then evolve under chemical shift and J-coupling Hamiltonians. Both the spins evolve independently and can thus be treated independently. Considering the k spin, chemical shift evolution for time t leads to (ignoring the negative sign in the beginning) (see Fig. 5.4a)

$$I_{ky} \rightarrow I_{ky} \cos(\omega_k t) - I_{kx} \sin(\omega_k t) \quad (5.134)$$

Under J-coupling Hamiltonian, $2I_{kz}I_{lz}$ (see Fig. 5.4b and Eq. 5.126), the I_{ky} and I_{kx} operators evolve, leading to

$$\{ [I_{ky} \cos \pi J_{kl} t - 2I_{kx} I_{lz} \sin \pi J_{kl} t] \cos \omega_k t - [I_{kx} \cos \pi J_{kl} t + 2I_{ky} I_{lz} \sin \pi J_{kl} t] \sin \omega_k t \} \quad (5.135)$$

As discussed earlier only the first term and the third terms in Eq. 5.135 are observable and contribute to the spectrum. If we observe only the y-magnetization,

then we need to consider the first term only. After taking the trace with I_{ky} , the signal (FID) will be represented by the time-dependent coefficients of this term. This is given by

$$\text{signal} = \cos(\omega_k t) \cos(\pi J_{kl} t) \quad (5.136)$$

Including transverse relaxation in the FID, the signal will be

$$\text{signal} = \cos(\omega_k t) \cos(\pi J_{kl} t) e^{-t/T_{2k}} \quad (5.137)$$

Substituting, $\omega_k = 2\pi\nu_k$

$$\text{signal} = \cos(2\pi\nu_k t) \cos(\pi J_{kl} t) e^{-t/T_{2k}} \quad (5.138)$$

$$\text{signal} = \frac{1}{2} \{ \cos(2\pi\nu_k t + \pi J_{kl} t) + \cos(2\pi\nu_k t - \pi J_{kl} t) \} e^{-t/T_{2k}} \quad (5.139)$$

After the real (or cosine) Fourier transformation, this leads to absorptive spectral lines at $(\nu_k + \frac{J_{kl}}{2})$ and $(\nu_k - \frac{J_{kl}}{2})$.

Similarly, starting from the z-magnetization of the l spin, the final signal will be

$$\text{signal} = \cos(2\pi\nu_l t) \cos(\pi J_{kl} t) e^{-t/T_{2l}} \quad (5.140)$$

$$\text{signal} = \frac{1}{2} \{ \cos(2\pi\nu_l t + \pi J_{kl} t) + \cos(2\pi\nu_l t - \pi J_{kl} t) \} e^{-t/T_{2l}} \quad (5.141)$$

Thus, for spin l , we will obtain absorptive signals at $(\nu_l + \frac{J_{kl}}{2})$ and $(\nu_l - \frac{J_{kl}}{2})$.

Thus, in the final spectrum (Fig. 5.7), we will get the doublets of k and l spins.

$$\text{Spectral lines} : (\nu_k + \frac{J_{kl}}{2}) \text{ and } (\nu_k - \frac{J_{kl}}{2}); (\nu_l + \frac{J_{kl}}{2}) \text{ and } (\nu_l - \frac{J_{kl}}{2}) \quad (5.142)$$

If we choose to observe the x-component of the signal in Eq. 5.135 and perform the same cosine transformation, we get the same four signals but with dispersive line shapes.



Fig. 5.7 A schematic of the J-coupled spectrum for a two-spin system, where ν_k and ν_l are the frequencies of k and l spins, respectively, and J_{kl} is the J-coupling between k and l spins

5.7 Summary

- The concept of density matrix description of NMR is described with some mathematical rigor.
- The product operator formalism which provides a simple and easy-to-handle description of density operator calculations for NMR pulse sequences is presented.
- A simple calculation for a two-spin system is presented as an illustration.

5.8 Further Reading

- Principles of Magnetic Resonance, C. P. Slichter, 3rd ed., Springer, 1990
- Principles of NMR in one and two dimensions, R. R. Ernst, G. Bodenhausen, A. Wokaun, Oxford, 1987
- Spin Dynamics, M. H. Levitt, 2nd ed., Wiley 2008
- Understanding NMR Spectroscopy, J. Keeler, Wiley, 2005
- Protein NMR Spectroscopy, J. Cavanagh, N. Skelton, W. Fairbrother, M. Rance, A. Palmer III, 2nd ed., Elsevier, 2006

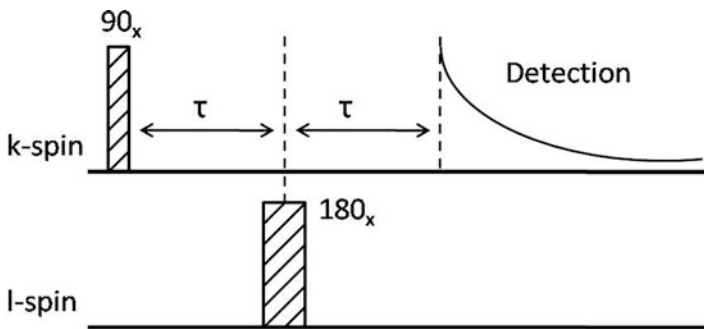
5.9 Exercises

- 5.1 For a three-spin system ($I = 1/2$), the density operator has
 - (a) 9 elements
 - (b) 6 elements
 - (c) 64 elements
 - (d) 3 elements
- 5.2 If ρ is the density operator, the expectation value of M_x operator is given by
 - (a) $Tr(M_x)$
 - (b) $Tr(M_x)^2$
 - (c) $Tr(M_x\rho)$
 - (d) $Tr\{(M_x)^2\rho\}$
- 5.3 Equilibrium density operator
 - (a) is related to I_z operator
 - (b) is related to I_x operator
 - (c) is related to I_y operator
 - (d) has no relation to angular momentum operators
- 5.4 The hypothesis of random phases leads to the following in the equilibrium density operator.
 - (a) Diagonal elements in the density operator become zero.
 - (b) Off-diagonal elements in the density operator become zero.
 - (c) Both diagonal and off-diagonal elements become zero.
 - (d) It has no effect on the diagonal and off-diagonal elements of the density operator.

- 5.5 For a two-spin system ($I = 1/2$), which of the following is true?
- $I_z | \alpha\alpha \rangle = | \alpha\alpha \rangle$
 - $I_x | \alpha\alpha \rangle = | \alpha\alpha \rangle$
 - $I_y | \alpha\alpha \rangle = | \alpha\alpha \rangle$
 - $I_z | \alpha\alpha \rangle = | \alpha\beta \rangle$
- 5.6 For a spin with $I = 5/2$, the partition function is
- $5/2$
 - $3/2$
 - 6
 - 4
- 5.7 An FID arises from
- diagonal elements of a density operators
 - single-quantum coherences in the density operators
 - zero-quantum coherences in the density operators
 - multiple-quantum coherences in the density operators
- 5.8 The off-diagonal elements of the density matrix represent
- the time evolution of isolated spins in the energy levels
 - deviations from equilibrium populations
 - the phase coherence of the spins in different energy levels
 - the populations of the spins in individual energy levels
- 5.9 An RF pulse with a flip angle β applied along the x-axis is represented by
- βI_x
 - $e^{-i\beta I_x}$
 - $\beta(I_x)^2$
 - $\beta^2(I_x)^2$
- 5.10 For a spin with precessional frequency ω_i , the field along z-axis in the rotating frame under resonance condition is
- H_0
 - 0
 - $\frac{\omega_i}{\gamma}$
 - H_1
- 5.11 For a single spin ($I = 1/2$), the matrix representation of π pulse along the y-axis is given by
- $\begin{bmatrix} 0 & -1 \\ -i & 0 \end{bmatrix}$
 - $\begin{bmatrix} 1 & -1 \\ -i & 1 \end{bmatrix}$
 - $\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$
 - $\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$

- 5.12 The basis operator $2I_{kx}I_{lz}$ represents
- in-phase magnetization of l spin
 - x-magnetization of k spin anti phase with respect to l spin
 - in-phase magnetization of k spin
 - z-magnetization of l spin
- 5.13 $(2I_{kx}I_{ly} + 2I_{ky}I_{lx})$ represents
- zero-quantum coherence of spin k and l
 - double-quantum coherence of spin k and l
 - mixture of double-quantum and zero-quantum coherences
 - total k spin magnetization
- 5.14 For a system of three spins ($I = 1/2$), the total number of basis operator is
- 9
 - 27
 - 64
 - 81
- 5.15 In a three-spin system ($I = 1/2$), the operator term $I_{kx}I_{lz}I_{mz}$ represents
- z-magnetization of l spin
 - z-magnetization of m spin
 - in-phase x-magnetization of k spin
 - x-magnetization of k spin antiphase to m and l spins
- 5.16 In a two-spin system k, l , the I_{kx} operator evolves under the J -coupling Hamiltonian for a time t to produce
- y-magnetization of k spin
 - y-magnetization of k spin antiphase to l spin
 - x-magnetization of k spin antiphase to l spin
 - double-quantum coherence between k and l spin
- 5.17 Which combination of the operators form a rotation group?
- $I_{kx}, I_{ky}, 2I_{kx}I_{lz}$
 - $I_{kx}, 2I_{ky}I_{lz}, 2I_{kz}I_{lz}$
 - $I_{kx}, 2I_{kx}I_{lz}, 2I_{ky}I_{lz}$
 - $I_{kx}, I_{lz}, 2I_{ky}I_{lz}$
- 5.18 The coherence transfer from k spin to l spin occurs due to
- evolution under chemical shift
 - evolution under J-coupling
 - application of RF pulse along the y-axis to k spin
 - application of RF pulse to anti phase magnetization of k spin
- 5.19 An RF pulse applied along the x-axis causes
- magnetization to align along the x-axis
 - rotation of the magnetization in the x-z plane
 - rotation of the magnetization in the y-z plane
 - rotation of the magnetization in the x-y plane
- 5.20 Which combination of the operators form a rotation group?
- I_{kx}, I_{ky}, I_{kz}
 - $I_{kx}, I_{ky}, 2I_{kz}I_{lz}$
 - I_{kz}, I_{lz}, I_{ky}
 - $2I_{kx}I_{lz}, 2I_{ky}I_{lz}, 2I_{kz}I_{lz}$

- 5.21 Which of the following statement is true?
- $2I_{kx}I_{ly}$ represents a pure double-quantum coherence.
 - $2I_{kx}I_{lz}$ is an observable operator.
 - $2I_{ky}I_{lz}$ evolves under coupling to produce $2I_{kx}I_{lz}$.
 - I_{kx} and I_{ky} are observable operators.
- 5.22 A spin echo arises because of
- refocusing of chemical shifts
 - refocusing of coupling constants
 - inhomogeneity in the main field
 - inaccuracy in RF pulses
- 5.23 In a spin echo experiment, refocusing of coupling evolution occurs when
- the spin echo period is equal to $1/4J$
 - the spin echo period is equal to $1/2J$
 - the spin echo period is equal to $1/J$
 - the spin echo period is equal to $1/3J$
- 5.24 In the given pulse sequence, at the beginning of the detection, which of the following statement is true?



- Coupling between k and l spins is effectively refocused.
 - Chemical shift evolution of l spin is refocused.
 - Chemical shift evolution of k spin is refocused.
 - Magnetization of k spin is inverted.
- 5.25 In a C-H INEPT experiment, magnetization is transferred from proton to carbon, which of the following operator transformation is valid?
- $H_x \rightarrow H_z C_y$
 - $H_x \rightarrow H_x C_y$
 - $H_x \rightarrow H_z C_z$
 - $H_x \rightarrow H_x C_z$
- 5.26 Calculate the matrix representations of the operators, $2I_x S_y$ and $2I_z S_z$, in the eigenbasis of the weak coupling Hamiltonian.
- 5.27 Prove the commutator relationship: $[2I_\alpha S_{\alpha'}, 2I_\beta S_{\beta'}] = 0$, if $\alpha \neq \alpha'$ and $\beta \neq \beta'$ simultaneously. α, α' and β, β' can be x, y, or z.
- 5.28 Calculate the effect of (a) $R_x(\pi)$ and (b) $R_y(\pi)$ pulses on the density operator represented by \hat{I}_z using matrix representations.