

THEORETICAL DESCRIPTION OF NMR SPECTROSCOPY

A rigorous treatment of the dynamics of nuclear spin systems and NMR spectroscopy is afforded by the quantum mechanical representation known as the *density matrix formalism* (1, 2). Instead of following only the evolution of the bulk magnetization vector as in the Bloch model, the evolution of the density matrix provides a complete description of the state of a spin system at any point during an NMR experiment. The next few sections present a detailed overview of the development of the density matrix theory and its application in the simplest pulsed NMR experiments.

2.1 Postulates of Quantum Mechanics

A rather formal exposition of the mathematical concepts to be used through the remainder of the text is presented first. Commonly, in introductory quantum mechanics texts (3–5), quantum mechanical orbital angular momentum is introduced via the classical concepts of angular momentum. After establishing the relevant physics, the results are generalized to include the *intrinsic* angular momentum of electrons and nuclei. The intrinsic angular momentum does not have a classical analog; accordingly, in this text, orbital angular momentum will not be

discussed. Instead, the foundations of the theory of intrinsic angular momentum will be presented as postulates whose validity is established by comparison with experiment. NMR spectroscopy is a particularly powerful demonstration of the concepts.

2.1.1 THE SCHRÖDINGER EQUATION

The evolution in time of a quantum mechanical system is governed by the Schrödinger equation:

$$\frac{\partial \Psi(t)}{\partial t} = -\frac{i}{\hbar} \mathcal{H} \Psi(t). \quad [2.1]$$

The operator \mathcal{H} is termed the Hamiltonian of the system and incorporates the essential physics determining the evolution of the system. The Hamiltonian may be time dependent or time independent. Units in which $\hbar = 1$ will be assumed and factors of \hbar will not be written explicitly; thus,

$$\frac{\partial \Psi(t)}{\partial t} = -i \mathcal{H} \Psi(t). \quad [2.2]$$

When desired, necessary factors of \hbar can be reintroduced by dimensional analysis; equivalently, all energies are measured in angular frequency units with dimensions of s^{-1} . The solution of the Schrödinger equation is called the *wavefunction* for the system, $\Psi(t)$. The wavefunction contains *all* the knowable information about the state of the system and, consequently, is a function of the variables appropriate to the system of interest (e.g., spatial coordinates and spin coordinates). The probability density that the system is in the state described by $\Psi(t)$ at time t is given by

$$P(t) = \Psi^*(t) \Psi(t), \quad [2.3]$$

in which $\Psi^*(t)$ is the complex conjugate of $\Psi(t)$. If the wavefunction is known, then all the observable properties of the system can be deduced by performing the appropriate mathematical operations upon the wavefunction. Wavefunctions generally will be assumed to be normalized such that

$$\int \Psi^*(t) \Psi(t) d\tau = 1, \quad [2.4]$$

in which τ represents the generalized coordinates of the wavefunction (and may include sums over spin states). If necessary, wavefunctions can be normalized simply by defining

$$\Psi'(t) = \Psi(t) / \left[\int \Psi^*(t) \Psi(t) d\tau \right]^{1/2}. \quad [2.5]$$

If \mathcal{H} is time independent, then [2.2] can be solved by the method of separation of variables. Defining $\Psi(t) = \psi(\tau)\varphi(t)$, in which $\psi(\tau)$ contains the time-independent spatial and spin variables [for simplicity, $\psi(\tau)$ is frequently written as ψ] and $\varphi(t)$ contains time-dependent terms,

$$\begin{aligned}\frac{\partial \Psi(t)}{\partial t} &= -i\mathcal{H}\Psi(t), \\ \psi(\tau) \frac{d\varphi(t)}{dt} &= -i\mathcal{H}\psi(\tau)\varphi(t), \\ \int \psi^*(\tau)\psi(\tau) d\tau \frac{d\varphi(t)}{dt} &= -i\varphi(t) \int \psi^*(\tau)\mathcal{H}^*\psi(\tau) d\tau, \\ \frac{d\varphi(t)}{dt} &= -iE\varphi(t),\end{aligned}\tag{2.6}$$

in which the energy of the system is defined by

$$E = \int \psi^*(\tau)\mathcal{H}\psi(\tau) d\tau.\tag{2.7}$$

Solving [2.6] yields $\varphi(t) = C \exp(-iEt)$. Using this result gives

$$\Psi(t) = \psi(\tau) \exp(-iEt),\tag{2.8}$$

in which the integration constant C has been included in the normalization of $\psi(\tau)$. If \hbar is reintroduced explicitly, then

$$\Psi(t) = \psi(\tau) \exp(-iEt/\hbar) = \psi(\tau) \exp(-i\omega t),\tag{2.9}$$

in which $E = \hbar\omega$. As shown by [2.8] and [2.9], if \mathcal{H} is time independent, then the time dependence of the wavefunctions is limited to a phase factor; this factor cancels when calculating probability densities using [2.3].

2.1.2 EIGENVALUE EQUATIONS

The purpose of quantum mechanics, at least insofar as it is applied to NMR spectroscopy, is to calculate the results expected from experiments. In the language of quantum mechanics, every physically observable quantity, A , has associated with it a Hermitian operator \mathbf{A} , that satisfies the eigenvalue equation:

$$\mathbf{A}f(\tau) = \lambda f(\tau).\tag{2.10}$$

This equation defines a set of eigenfunctions, $f_i(\tau)$, and eigenvalues, λ_i , for $i = 1$ to N , that satisfy in turn

$$\mathbf{A}f_i(\tau) = \lambda_i f_i(\tau).\tag{2.11}$$

The number of eigenvalues and eigenfunctions, N , is determined by the system of interest and may be finite or infinite. The adjoint of an operator is defined by $\mathbf{A}^\dagger = \mathbf{A}^{T*}$, in which T indicates transposition and $*$ indicates complex conjugation. The adjoint operator satisfies the eigenvalue equation,

$$f^*(\tau)\mathbf{A}^\dagger = \lambda^* f^*(\tau). \quad [2.12]$$

Hermitian operators are self-adjoint, $\mathbf{A} = \mathbf{A}^\dagger$, and satisfy the relationship

$$\int f^*(\tau)\mathbf{A}g(\tau) d\tau = \left[\int g^*(\tau)\mathbf{A}f(\tau) d\tau \right]^* \quad [2.13]$$

for well-behaved functions $f(\tau)$ and $g(\tau)$. If $f(\tau)$ is a normalized eigenfunction of the operator \mathbf{A} with eigenvalue λ , then the following relationships are obtained from [2.10] and [2.12]:

$$\int f^*(\tau)\mathbf{A}f(\tau) d\tau = \lambda \int f^*(\tau)f(\tau) d\tau = \lambda, \quad [2.14]$$

$$\int f^*(\tau)\mathbf{A}^\dagger f(\tau) d\tau = \lambda^* \int f^*(\tau)f(\tau) d\tau = \lambda^*. \quad [2.15]$$

If the operator \mathbf{A} corresponds to an observable quantity, then the eigenvalues of \mathbf{A} must be real numbers. Thus, $\lambda = \lambda^*$ and equating [2.14] and [2.15] proves that $\mathbf{A} = \mathbf{A}^\dagger$ and \mathbf{A} is Hermitian. Consequently, operators corresponding to observable quantities in quantum mechanics must be Hermitian.

The eigenfunctions of a Hermitian operator form a complete orthonormal set. The orthonormality condition is

$$\int f_i^*(\tau)f_j(\tau) d\tau = \delta_{i,j}, \quad [2.16]$$

in which $\delta_{i,j}$ is the Kronecker delta with values

$$\delta_{i,j} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}. \quad [2.17]$$

Unnormalized eigenfunctions can be normalized as in [2.5]; if necessary, the wavefunctions can be orthogonalized using a procedure known as the Gram–Schmidt process (5). A *complete* set of orthonormal functions, ψ_n , constitutes a set of basis functions for a vector space of dimension N , called the Hilbert space. Therefore, an arbitrary function defined in the

vector space can be written as

$$\Psi(t) = \sum_{n=1}^N c_n \psi_n, \quad [2.18]$$

in which the c_n are complex numbers and may depend upon time.

The eigenvalue equation [2.11] leads to the following interpretation of the relationship between an operator and its associated observable: the result of making a measurement of A upon a system is one of the eigenvalues of \mathbf{A} . This statement illustrates the discrete nature of quantum mechanics: only a limited set of outcomes is possible for the measurement. In practice, however, the expectation value of \mathbf{A} is measured experimentally. The expectation value is defined as the average magnitude of a particular property obtained following a large number of measurements of that property carried out over an ensemble of identically prepared systems. The expectation value of some property, $\langle A \rangle$, is calculated mathematically as the scalar product of $\Psi(t)$ and $\mathbf{A}\Psi(t)$,

$$\langle A \rangle = \int \Psi^*(t) \mathbf{A} \Psi(t) d\tau. \quad [2.19]$$

If the wavefunction for the system is an eigenfunction of the operator, $\Psi(t) = \psi_n$, then

$$\langle A \rangle = \int \Psi^*(t) \mathbf{A} \Psi(t) d\tau = \int \psi_n^* \mathbf{A} \psi_n d\tau = \lambda_n \int \psi_n^* \psi_n d\tau = \lambda_n. \quad [2.20]$$

This result shows that if $\Psi(t)$ is an eigenfunction of the operator \mathbf{A} , then measuring A for each member of the ensemble yields the identical result λ_n . In general, the wavefunction for the system will not be an eigenfunction of \mathbf{A} , and [2.18] is used to express [2.19] in terms of the eigenfunctions of \mathbf{A} . The derivation of $\langle A \rangle$ proceeds as follows:

$$\begin{aligned} \langle A \rangle &= \int \Psi^*(t) \mathbf{A} \Psi(t) d\tau \\ &= \int \left[\sum_{i=1}^N c_i^* \psi_i \right]^* \mathbf{A} \left[\sum_{j=1}^N c_j \psi_j \right] d\tau = \int \left[\sum_{i=1}^N c_i^* \psi_i^* \right] \mathbf{A} \left[\sum_{j=1}^N c_j \psi_j \right] d\tau \\ &= \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j \int \psi_i^* \mathbf{A} \psi_j d\tau = \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j \lambda_j \int \psi_i^* \psi_j d\tau \\ &= \sum_{j=1}^N c_j^* c_j \lambda_j. \end{aligned} \quad [2.21]$$

In obtaining [2.21], the orthonormality condition [2.16] has been used. The resulting equation for $\langle A \rangle$ has the following interpretation. When A is measured for a single member of the ensemble, the result obtained is one of the eigenvalues of \mathbf{A} ; however, which eigenvalue is obtained cannot be specified in advance of the measurement. For the ensemble as a whole, the result λ_j is obtained in a proportion $c_j^* c_j$; that is, $c_j^* c_j$ is interpreted as the probability that the result λ_j is obtained in a single measurement. Consequently, although the allowed values of A must be members of the discrete set of eigenvalues of \mathbf{A} , the observable expectation value $\langle A \rangle$ can have any (continuous) value consistent with [2.21].

The time-independent Schrödinger equation is an eigenvalue equation for the Hamiltonian operator. Substitution of [2.8] into [2.2] yields

$$\begin{aligned}\frac{\partial \Psi(t)}{\partial t} &= -i\mathcal{H}\Psi(t), \\ \psi(\tau) \frac{d \exp[-iEt]}{dt} &= -i\mathcal{H}\psi(\tau) \exp[-iEt], \\ E\psi(\tau) &= \mathcal{H}\psi(\tau).\end{aligned}\tag{2.22}$$

The eigenvalues of this equation are the energies of the system and the eigenfunctions are termed the *stationary states* of the system.

2.1.3 SIMULTANEOUS EIGENFUNCTIONS

Next, quantum mechanical restrictions on measurement of different observable quantities are presented. Two operators, \mathbf{A} and \mathbf{B} , corresponding to observable properties A and B , are considered as an example. The eigenfunctions and eigenvalues of \mathbf{A} will be designated ψ and a ; the eigenfunctions and eigenvalues of \mathbf{B} will be designated φ and b . The operators are called compatible if the result of measuring A (or B) does not depend upon whether B (or A) is measured first. Compatible, or simultaneous, measurements of A and B are possible only if \mathbf{A} and \mathbf{B} have the same eigenfunctions (but not necessarily the same eigenvalues). An important theorem states that if $\mathbf{AB} = \mathbf{BA}$, then \mathbf{A} and \mathbf{B} have the same complete set of eigenfunctions. The proof of this statement is straightforward:

$$\begin{aligned}\mathbf{AB} &= \mathbf{BA}, \\ \mathbf{AB}\psi_i &= \mathbf{BA}\psi_i, \\ \mathbf{AB}\psi_i &= a_i \mathbf{B}\psi_i.\end{aligned}\tag{2.23}$$

Next, ψ_i is expanded in the eigenfunctions of **B**:

$$\begin{aligned}
 \mathbf{A}\mathbf{B}\psi_i &= a_i\mathbf{B}\psi_i, \\
 \mathbf{A}\mathbf{B} \sum_j c_{ij}\phi_j &= a_i\mathbf{B} \sum_j c_{ij}\phi_j, \\
 \sum_j c_{ij}b_j\mathbf{A}\phi_j &= a_i \sum_j c_{ij}b_j\phi_j, \\
 \sum_j c_{ij}b_j(\mathbf{A}\phi_j - a_i\phi_j) &= 0.
 \end{aligned} \tag{2.24}$$

By definition, $c_{ij} \neq 0$ for at least one value of $j=k$. Thus, the bracketed term in the last equation is zero for some ϕ_k :

$$\mathbf{A}\phi_k - a_i\phi_k = 0, \quad \mathbf{A}\phi_k = a_i\phi_k. \tag{2.25}$$

Thus, ϕ_k is an eigenfunction of **A** with eigenvalue a_i and must be identical to ψ_i (to within a constant of proportionality). This equality is satisfied for all members of the set of eigenfunctions, ψ and ϕ ; therefore, the general theorem must hold.

The commutator of **A** and **B** is defined as

$$[\mathbf{A}, \mathbf{B}] = \mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A}. \tag{2.26}$$

The earlier result can be restated: if the commutator of two operators vanishes, then the operators have the same eigenfunctions. If the commutator does not vanish, then a Heisenberg uncertainty relationship can be established for the two operators (5).

2.1.4 EXPECTATION VALUE OF THE MAGNETIC MOMENT

As should now be clear, each operator for an observable quantity defines a set of basis vectors. Any complete orthonormal set can be used to expand an arbitrary wavefunction; consequently, a basis set can be chosen for computational convenience. In no case can the expectation value of an operator depend upon the choice of the basis functions.

As an example of these ideas, the time-dependent expectation value of the magnetic moment $\boldsymbol{\mu} = \gamma\mathbf{I}$ of a single spin ($I=1/2$) will be calculated. Using [2.9] and [2.18], the wavefunction for the spin in the static magnetic field can be written as

$$\Psi = c_\alpha\psi_\alpha + c_\beta\psi_\beta = a \exp[-i\omega_\alpha t]\psi_\alpha + b \exp[-i\omega_\beta t]\psi_\beta, \tag{2.27}$$

in which ψ_α and ψ_β are the stationary states and $E_\alpha = \hbar\omega_\alpha$ and $E_\beta = \hbar\omega_\beta$ are the energies of the states with $m = 1/2$ and $m = -1/2$, respectively, and $a = |a| \exp[i\phi_a]$ and $b = |b| \exp[i\phi_b]$ are complex numbers satisfying the normalization relation $|a|^2 + |b|^2 = 1$. U γ sing [2.19] yields

$$\begin{aligned}
 \langle \mu_x \rangle &= \int \Psi^* \mu_x \Psi d\tau = \gamma \int \Psi^* I_x \Psi d\tau \\
 &= \gamma a^* a \int \psi_\alpha^* I_x \psi_\alpha d\tau + \gamma a^* b \exp[i(\omega_\alpha - \omega_\beta)t] \int \psi_\alpha^* I_x \psi_\beta d\tau \\
 &\quad + \gamma ab^* \exp[-i(\omega_\alpha - \omega_\beta)t] \int \psi_\beta^* I_x \psi_\alpha d\tau + \gamma b^* b \int \psi_\beta^* I_x \psi_\beta d\tau \\
 &= \frac{\gamma \hbar |a| |b|}{2} (\exp[i\{(\omega_\alpha - \omega_\beta)t + \phi\}] + \exp[-i\{(\omega_\alpha - \omega_\beta)t + \phi\}]) \\
 &= \gamma \hbar |a| |b| \cos[(\omega_\alpha - \omega_\beta)t + \phi] = \gamma \hbar |a| |b| \cos[\omega_0 t + \phi],
 \end{aligned} \tag{2.28}$$

$$\begin{aligned}
 \langle \mu_y \rangle &= \int \Psi^* \mu_y \Psi d\tau = \gamma \int \Psi^* I_y \Psi d\tau \\
 &= \gamma a^* a \int \psi_\alpha^* I_y \psi_\alpha d\tau + \gamma a^* b \exp[i(\omega_\alpha - \omega_\beta)t] \int \psi_\alpha^* I_y \psi_\beta d\tau \\
 &\quad + \gamma ab^* \exp[-i(\omega_\alpha - \omega_\beta)t] \int \psi_\beta^* I_y \psi_\alpha d\tau + \gamma b^* b \int \psi_\beta^* I_y \psi_\beta d\tau \\
 &= -i \frac{\gamma \hbar |a| |b|}{2} (\exp[i\{(\omega_\alpha - \omega_\beta)t + \phi\}] - \exp[-i\{(\omega_\alpha - \omega_\beta)t + \phi\}]) \\
 &= \gamma \hbar |a| |b| \sin[(\omega_\alpha - \omega_\beta)t + \phi] = \gamma \hbar |a| |b| \sin[\omega_0 t + \phi],
 \end{aligned} \tag{2.29}$$

$$\begin{aligned}
 \langle \mu_z \rangle &= \int \Psi^* \mu_z \Psi d\tau = \gamma \int \Psi^* I_z \Psi d\tau \\
 &= \gamma \int (a^* \exp[i\omega_\alpha t] \psi_\alpha^* + b^* \exp[i\omega_\beta t] \psi_\beta^*) I_z \\
 &\quad \times (a \exp[-i\omega_\alpha t] \psi_\alpha + b \exp[-i\omega_\beta t] \psi_\beta) d\tau \\
 &= \gamma a^* a \int \psi_\alpha^* I_z \psi_\alpha d\tau + \gamma a^* b \exp[i(\omega_\alpha - \omega_\beta)t] \int \psi_\alpha^* I_z \psi_\beta d\tau \\
 &\quad + \gamma ab^* \exp[-i(\omega_\alpha - \omega_\beta)t] \int \psi_\beta^* I_z \psi_\alpha d\tau + \gamma b^* b \int \psi_\beta^* I_z \psi_\beta d\tau, \\
 &= \frac{\gamma \hbar}{2} (|a|^2 - |b|^2),
 \end{aligned} \tag{2.30}$$

in which $\omega_0 = \omega_\alpha - \omega_\beta = -\gamma B_0$ is the Larmor frequency and $\phi = \phi_b - \phi_a$ is a phase angle. These results utilize the following equations for the angular momentum operators (note that only the equations for I_z are eigenvalue equations):

$$\begin{aligned} I_x \psi_\alpha &= \frac{\hbar}{2} \psi_\beta, & I_x \psi_\beta &= \frac{\hbar}{2} \psi_\alpha, \\ I_y \psi_\alpha &= \frac{i\hbar}{2} \psi_\beta, & I_y \psi_\beta &= -\frac{i\hbar}{2} \psi_\alpha, \\ I_z \psi_\alpha &= \frac{\hbar}{2} \psi_\alpha, & I_z \psi_\beta &= -\frac{\hbar}{2} \psi_\beta, \end{aligned} \quad [2.31]$$

together with the orthonormality of the wavefunctions. Equations [2.31] are derived from the Pauli spin matrices as shown in Section 2.2.5. The three equations, [2.29]–[2.30], represent a vector of constant magnitude precessing about the z -axis with an angular velocity ω_0 . This result is identical to the predicted motion of the magnetic moment obtained from the Bloch model.

2.2 The Density Matrix

Calculations of scalar products and expectation values are frequent operations in quantum mechanics. Such calculations are facilitated by a formulation of quantum mechanics that focuses on the *density matrix* rather than on the wavefunction for a system. Additionally, the symbolic manipulations required are simplified by using a notational system introduced into quantum mechanics by Dirac (6).

2.2.1 DIRAC NOTATION

The Dirac notation is a compact formalism for representing the scalar product. In this notation, a wavefunction, ψ , is represented by the *ket* function, $|\psi\rangle$, and the conjugate wavefunction, ψ^* , is represented by the *bra* function, $\langle\psi|$. In the Dirac notation, the scalar product of ψ and φ is written as the contraction of the bra $\langle\psi|$ and the ket $|\varphi\rangle$,

$$\langle\psi|\varphi\rangle \equiv \int \psi^* \varphi d\tau. \quad [2.32]$$

Using the Dirac notation, an arbitrary wavefunction, Ψ , can be written as a superposition of a set of orthonormal time-independent kets, known as eigenkets or basis kets,

$$|\Psi\rangle = \sum_{n=1}^N c_n |n\rangle, \quad [2.33]$$

where $|n\rangle$ are the basis kets (e.g., the α and β wavefunctions), c_n are complex numbers, and N is the dimensionality of the vector space. For example, the wavefunction for a system consisting of a single spin-1/2 nucleus can be described by the linear combination of the kets for the α and β states of that nucleus (which are the eigenfunctions of the angular momentum operator). The coefficients, c_n , can be regarded as amplitude factors that describe how much a particular basis ket contributes to the total wavefunction at any particular time. The basis kets are time independent; consequently, any time dependence in Ψ is contained in the complex coefficients. Premultiplying [2.33] by the bra, $\langle m|$, and applying the orthogonality condition yields,

$$c_m = \langle m | \Psi \rangle, \quad [2.34]$$

so that

$$|\Psi\rangle = \sum_{n=1}^N c_n |n\rangle = \sum_{n=1}^N \langle n | \Psi \rangle |n\rangle = \sum_{n=1}^N |n\rangle \langle n | \Psi \rangle. \quad [2.35]$$

The latter identity suggests that $|n\rangle \langle n|$ is an operator acting on Ψ such that

$$|n\rangle \langle n | \Psi \rangle = c_n |n\rangle. \quad [2.36]$$

Because [2.35] must hold for arbitrary Ψ , the useful Closure Theorem is obtained immediately,

$$\sum_{n=1}^N |n\rangle \langle n| = \mathbf{E}, \quad [2.37]$$

in which \mathbf{E} is the identity operator. The operator $|n\rangle \langle n|$ is called a projection operator because it “projects out” from Ψ the component ket $|n\rangle$.

The expectation value of some property, $\langle A \rangle$, can be written in Dirac notation as

$$\langle A \rangle = \int \Psi^* \mathbf{A} \Psi d\tau = \langle \Psi | \mathbf{A} | \Psi \rangle. \quad [2.38]$$

Now, using [2.33],

$$\langle A \rangle = \sum_{nm} c_m^* c_n \langle m | \mathbf{A} | n \rangle. \quad [2.39]$$

In contrast to [2.21], the kets $|n\rangle$ are not necessarily the eigenfunctions of \mathbf{A} ; therefore, the scalar products $\langle m | \mathbf{A} | n \rangle$ do not necessarily vanish for $m \neq n$. Equation [2.21] is a special case derived from [2.39] if the kets $|n\rangle$ are eigenfunctions of \mathbf{A} . For a given basis set, the terms $\langle m | \mathbf{A} | n \rangle$ are constants, and the value of the observable A for a particular state of the system is determined by the products of the coefficients $c_m^* c_n$. Once the coefficients $c_m^* c_n$ are known, the expectation value of any observable can be calculated. The term $A_{mn} = \langle m | \mathbf{A} | n \rangle$ is the (mn) th element of the $N \times N$ matrix representation of the operator \mathbf{A} in a given basis. The products $c_m^* c_n$ can be regarded as the elements of a matrix representation of an operator \mathbf{P} defined by

$$P_{nm} = \langle n | \mathbf{P} | m \rangle = c_m^* c_n. \quad [2.40]$$

Note that \mathbf{P} can be explicitly written as a projection operator, $\mathbf{P} = |\Psi\rangle\langle\Psi|$. Substituting [2.40] into [2.39] yields

$$\begin{aligned} \langle A \rangle &= \sum_{nm} c_n c_m^* \langle m | \mathbf{A} | n \rangle \\ &= \sum_{nm} \langle n | \mathbf{P} | m \rangle \langle m | \mathbf{A} | n \rangle = \sum_n \langle n | \mathbf{P} \mathbf{A} | n \rangle \\ &= \sum_{nm} P_{nm} A_{mn} = \sum_n (P \mathbf{A})_{nn} \\ &= \text{Tr}\{\mathbf{P} \mathbf{A}\}, \end{aligned} \quad [2.41]$$

where $\text{Tr}\{\}$ is the *trace* of a matrix defined as the sum of the diagonal elements of the matrix. The equality on line 2 of [2.41] is a consequence of the Closure Theorem [2.37]; the equality on line 3 results from the definition of matrix multiplication of the matrix representations of the operators. Equation [2.41] states that the expectation value of some observable of a system, say, for example, the amount of x -magnetization, is calculated as the trace of the product of \mathbf{P} and \mathbf{A} . \mathbf{P} is the operator that is defined by the coefficients $c_m^* c_n$ and so describes the state of the system at any particular point in time, and \mathbf{A} is the operator corresponding to the required observable. For the sake of completeness and formality, \mathbf{P} is a Hermitian operator such that

$$\langle n | \mathbf{P} | m \rangle = \langle m | \mathbf{P} | n \rangle^*. \quad [2.42]$$

The trace of a product of matrices is invariant to cyclic permutations of the matrices. Thus,

$$\text{Tr}\{\mathbf{ABC}\} = \text{Tr}\{\mathbf{CAB}\} = \text{Tr}\{\mathbf{BCA}\}. \quad [2.43]$$

A corollary of this theorem is that the trace of a commutator is zero:

$$\text{Tr}\{[\mathbf{A}, \mathbf{B}]\} = \text{Tr}\{\mathbf{AB} - \mathbf{BA}\} = \text{Tr}\{\mathbf{AB}\} - \text{Tr}\{\mathbf{BA}\} = 0. \quad [2.44]$$

2.2.2 QUANTUM STATISTICAL MECHANICS

The preceding analysis is applicable to a system in a so-called pure state in which the entire system is described by the same wavefunction. The wavefunction for a macromolecule in an NMR solution is an enormously complicated function of the degrees of freedom of the molecule and includes contributions from the spin, rotational, vibrational, electronic, and translational properties of the molecule. Determining the complete wavefunction for the molecule is both unfeasible and unnecessary because the properties of the nuclear spins are of primary interest in NMR spectroscopy. Accordingly, the system is divided into two components: the spin system and the surroundings (i.e., all other degrees of freedom). For historical reasons, the surroundings are termed the *lattice*. As a result of this division, the spin wavefunctions for different molecules in the NMR sample are no longer identical, but rather depend upon the “hidden” lattice variables. Such a system is called a *mixed state* and the effects of the lattice are incorporated by using statistical mechanics (2, 7). Each subensemble comprising the sample can be described by a wavefunction, Ψ , and a probability density, $\mathcal{P}(\Psi)$, that represents the contribution of the subensemble to the mixed state. The statistical value of the expectation value for a mixed state is then obtained by averaging over the probability distribution,

$$\begin{aligned} \langle \bar{A} \rangle &= \int \mathcal{P}(\Psi) \langle \Psi | \mathbf{A} | \Psi \rangle d\tau \\ &= \sum_{nm} \int \mathcal{P}(\Psi) c_n c_m^* d\tau \langle m | \mathbf{A} | n \rangle \\ &= \sum_{nm} \overline{c_n c_m^*} \langle m | \mathbf{A} | n \rangle. \end{aligned} \quad [2.45]$$

The factors $\overline{c_n c_m^*}$ will vary from system to system, but the matrix elements $\langle m | \mathbf{A} | n \rangle$ will not. An overbar has been used to denote the statistical ensemble average in [2.45].

The ensemble average of coefficients, $\overline{c_n c_m^*}$, forms a matrix that is referred to as the *density matrix*. The density matrix is the matrix representation of an operator σ , referred to as the *density operator*, such that

$$\overline{c_n c_m^*} = \overline{\langle n | \mathbf{P} | m \rangle} = \langle n | \sigma | m \rangle = \sigma_{nm}. \quad [2.46]$$

Because \mathbf{P} is a Hermitian operator, so is σ . An expression similar to [2.41] for the expectation value of the property A in an ensemble of spins in a mixed state can be written as

$$\langle \bar{A} \rangle = \text{Tr}\{\sigma \mathbf{A}\} = \text{Tr}\{\mathbf{A} \sigma\}. \quad [2.47]$$

The overbar will now be dropped for convenience, but an ensemble average is implied. To evaluate the expectation value of an observable, the matrix representation of the appropriate operator and, most importantly, the form of the density operator must be known. The time evolution of the system, say as it passes through a particular sequence of rf pulses and delays, is described by the time evolution of the density operator.

2.2.3 THE LIOUVILLE–VON NEUMANN EQUATION

A differential equation that describes the evolution in time of the density operator must be derived. Using the Dirac notation, the time-dependent Schrödinger equation [2.2] is written as

$$\sum_n \frac{dc_n(t)}{dt} |n\rangle = -i \sum_n c_n(t) \mathcal{H} |n\rangle. \quad [2.48]$$

Multiplying both sides by $\langle k |$ yields

$$\sum_n \frac{dc_n(t)}{dt} \langle k | n \rangle = -i \sum_n c_n(t) \langle k | \mathcal{H} | n \rangle. \quad [2.49]$$

The set of basis kets is orthonormal; therefore, $\langle k | n \rangle = 0$ unless $n = k$, and [2.49] reduces to

$$\frac{dc_k(t)}{dt} = -i \sum_n c_n(t) \langle k | \mathcal{H} | n \rangle. \quad [2.50]$$

Equation [2.50] can be used to find a differential equation for the matrix elements of the density operator,

$$\begin{aligned}
 \frac{d\langle k|\sigma|m\rangle}{dt} &= \overline{\frac{dc_k c_m^*}{dt}} = c_k \frac{dc_m^*}{dt} + \frac{dc_k}{dt} c_m^* \\
 &= i \sum_n \overline{c_k c_n^*} \langle n|\mathcal{H}|m\rangle - i \sum_n \overline{c_n c_m^*} \langle k|\mathcal{H}|n\rangle \\
 &= i \sum_n \langle k|\sigma|n\rangle \langle n|\mathcal{H}|m\rangle - i \sum_n \langle k|\mathcal{H}|n\rangle \langle n|\sigma|m\rangle \\
 &= i[\langle k|\sigma\mathcal{H}|m\rangle - \langle k|\mathcal{H}\sigma|m\rangle], \tag{2.51}
 \end{aligned}$$

in which \mathcal{H} is assumed to be identical for all members of the ensemble and the complex conjugate of [2.50] is written as

$$\begin{aligned}
 \frac{dc_k^*(t)}{dt} &= \left[-i \sum_n c_n(t) \langle k|\mathcal{H}|n\rangle \right]^* \\
 &= i \sum_n c_n^*(t) \langle k|\mathcal{H}|n\rangle^* \\
 &= i \sum_n c_n^*(t) \langle n|\mathcal{H}|k\rangle. \tag{2.52}
 \end{aligned}$$

The last line of [2.52] is obtained using the Hermitian property of \mathcal{H} [2.13]. Equation [2.51] is written in operator form as

$$\frac{d\sigma(t)}{dt} = -i[\mathcal{H}, \sigma(t)]. \tag{2.53}$$

This is known as the *Liouville–von Neumann* equation and describes the time evolution of the density operator.

The solution to [2.53] is straightforward if the Hamiltonian is time independent:

$$\sigma(t) = \exp(-i\mathcal{H}t)\sigma(0)\exp(i\mathcal{H}t). \tag{2.54}$$

The exponential operator $\exp(\mathbf{A})$ used in [2.54] is defined by its Taylor series expansion:

$$\exp(\mathbf{A}) = \sum_{k=0}^{\infty} \frac{1}{k!} \mathbf{A}^k = \mathbf{E} + \mathbf{A} + \frac{1}{2} \mathbf{A}\mathbf{A} + \cdots, \tag{2.55}$$

in which \mathbf{E} is the identity operator. The operators \mathbf{A} and $\exp(\mathbf{A})$ necessarily commute. Using these results, [2.54] can be shown to be a

solution to [2.53] by simple differentiation:

$$\begin{aligned}
 \frac{d\sigma(t)}{dt} &= -i\mathcal{H} \exp(-i\mathcal{H}t)\sigma(0) \exp(i\mathcal{H}t) + \exp(-i\mathcal{H}t)\sigma(0)i\mathcal{H} \exp(i\mathcal{H}t) \\
 &= i\{\exp(-i\mathcal{H}t)\sigma(0)\mathcal{H} \exp(i\mathcal{H}t) - \mathcal{H} \exp(-i\mathcal{H}t)\sigma(0) \exp(i\mathcal{H}t)\} \\
 &= i\{\sigma(t)\mathcal{H} - \mathcal{H}\sigma(t)\} = -i[\mathcal{H}, \sigma(t)].
 \end{aligned}
 \tag{2.56}$$

For completeness, some additional properties of the exponential operator are given here. First, in the eigenbase of \mathbf{A} , the matrix representation of the exponential operator is

$$\begin{aligned}
 \langle m | \exp(\mathbf{A}) | n \rangle &= \langle m | \mathbf{E} | n \rangle + \langle m | \mathbf{A} | n \rangle + (1/2)\langle m | \mathbf{A}\mathbf{A} | n \rangle + \dots \\
 &= \delta_{m,n} [1 + A_{mm} + (1/2)A_{mm}^2 + \dots] \\
 &= \delta_{m,n} \exp(A_{mm}) = \delta_{m,n} \exp(\lambda_m),
 \end{aligned}
 \tag{2.57}$$

in which $\lambda_m = A_{mm}$ are the eigenvalues of \mathbf{A} . Thus, the exponential matrix is diagonal in the eigenbase of \mathbf{A} and the diagonal elements are the exponentials of the eigenvalues of \mathbf{A} . Second, the Baker–Campbell–Hausdorff (BCH) relationship states that

$$\exp\{\mathbf{A}\} \exp\{\mathbf{B}\} = \exp\left\{\mathbf{A} + \mathbf{B} + \frac{1}{2}[\mathbf{B}, \mathbf{A}] + \frac{1}{12}([\mathbf{B}, [\mathbf{B}, \mathbf{A}]] + [[\mathbf{B}, \mathbf{A}], \mathbf{A}]) + \dots\right\}.
 \tag{2.58}$$

An extremely important corollary to this theorem states that $\exp(\mathbf{A}+\mathbf{B}) = \exp(\mathbf{A})\exp(\mathbf{B})$ if and only if $[\mathbf{A}, \mathbf{B}] = 0$ (5).

2.2.4 THE ROTATING FRAME TRANSFORMATION

The solution to the Liouville–von Neumann equation is straightforward if the Hamiltonian is time independent. A pulse sequence generally consists of two distinct parts: pulses (during which one or more rf fields are applied) and delays (during which no rf fields are present). For the present treatment, the time-dependent effects of the coupling between the spin system and the lattice will be neglected; these effects give rise to spin relaxation phenomena that will be discussed in Chapter 5. With this simplification, the Hamiltonian governing the delays is time independent; however, the rf fields comprising the pulses remain time-dependent perturbations. The simplest solution to this complication is to find a transformation that renders the rf Hamiltonian time independent and then apply [2.54]. The transformation that renders

\mathcal{H} time independent is the quantum mechanical equivalent of the rotating frame transformation in the Bloch picture.

A *similarity transformation* applied to the laboratory frame density operator σ generates a transformed density operator σ^r , such that

$$\sigma^r = \mathbf{U}\sigma\mathbf{U}^{-1}, \quad [2.59]$$

in which \mathbf{U} is an operator. A unitary operator is defined by the relationship $\mathbf{U}^{-1} = \mathbf{U}^\dagger$. If \mathbf{U} is a unitary operator, then [2.59] is called a unitary transformation. The equation of motion for σ^r is described by

$$\frac{d\sigma^r(t)}{dt} = -i[\mathcal{H}_e, \sigma^r(t)], \quad [2.60]$$

in which \mathcal{H}_e is a transformed Hamiltonian. The form of \mathcal{H}_e can be established as follows:

$$\begin{aligned} \frac{d\sigma^r}{dt} &= \frac{d(\mathbf{U}\sigma\mathbf{U}^{-1})}{dt} = \mathbf{U} \frac{d\sigma}{dt} \mathbf{U}^{-1} + \frac{d\mathbf{U}}{dt} \sigma \mathbf{U}^{-1} + \mathbf{U} \sigma \frac{d\mathbf{U}^{-1}}{dt} \\ &= i\mathbf{U}[\sigma, \mathcal{H}]\mathbf{U}^{-1} + \frac{d\mathbf{U}}{dt} \mathbf{U}^{-1} \mathbf{U} \sigma \mathbf{U}^{-1} + \mathbf{U} \sigma \mathbf{U}^{-1} \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} \\ &= i\mathbf{U}[\sigma, \mathcal{H}]\mathbf{U}^{-1} + \frac{d\mathbf{U}}{dt} \mathbf{U}^{-1} \sigma^r + \sigma^r \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt}. \end{aligned} \quad [2.61]$$

The common technique of inserting $\mathbf{E} = \mathbf{U}^{-1}\mathbf{U}$ has been utilized. To proceed, the following identities are established:

$$\frac{d\mathbf{E}}{dt} = \frac{d(\mathbf{U}\mathbf{U}^{-1})}{dt} = \frac{d\mathbf{U}}{dt} \mathbf{U}^{-1} + \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} = 0, \quad [2.62]$$

which yields

$$\frac{d\mathbf{U}}{dt} \mathbf{U}^{-1} = -\mathbf{U} \frac{d\mathbf{U}^{-1}}{dt}, \quad [2.63]$$

and

$$\begin{aligned} \mathbf{U}[\sigma, \mathcal{H}]\mathbf{U}^{-1} &= \mathbf{U}(\sigma\mathcal{H} - \mathcal{H}\sigma)\mathbf{U}^{-1} = \mathbf{U}\sigma\mathbf{U}^{-1}\mathbf{U}\mathcal{H}\mathbf{U}^{-1} - \mathbf{U}\mathcal{H}\mathbf{U}^{-1}\mathbf{U}\sigma\mathbf{U}^{-1} \\ &= [\sigma^r, \mathbf{U}\mathcal{H}\mathbf{U}^{-1}]. \end{aligned} \quad [2.64]$$

Substituting [2.63] and [2.64] into [2.61] yields

$$\begin{aligned}
 \frac{d\sigma^r}{dt} &= i\mathbf{U}[\sigma, \mathcal{H}]\mathbf{U}^{-1} + \frac{d\mathbf{U}}{dt} \mathbf{U}^{-1} \sigma^r + \sigma^r \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} \\
 &= i[\sigma^r, \mathbf{U}\mathcal{H}\mathbf{U}^{-1}] - \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} \sigma^r + \sigma^r \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} \\
 &= i[\sigma^r, \mathbf{U}\mathcal{H}\mathbf{U}^{-1}] + \left[\sigma^r, \mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} \right] \\
 &= i \left[\sigma^r, \mathbf{U}\mathcal{H}\mathbf{U}^{-1} - i\mathbf{U} \frac{d\mathbf{U}^{-1}}{dt} \right].
 \end{aligned} \tag{2.65}$$

This system obeys [2.60] if the effective Hamiltonian, \mathcal{H}_e , is written as

$$\mathcal{H}_e = \mathbf{U}\mathcal{H}\mathbf{U}^{-1} - i\mathbf{U} \frac{d\mathbf{U}^{-1}}{dt}. \tag{2.66}$$

If a unitary transformation can be found that renders \mathcal{H}_e time independent, then the solution to [2.60] can be obtained by straightforward adaptation of [2.54]:

$$\sigma^r(t) = \exp(-i\mathcal{H}_e t) \sigma^r(0) \exp(i\mathcal{H}_e t). \tag{2.67}$$

The general procedure for solving [2.53] is as follows: find a unitary transformation that renders \mathcal{H} time independent; transform $\sigma(0)$ and \mathcal{H} to $\sigma^r(0)$ and \mathcal{H}_e ; solve [2.60] for $\sigma^r(t)$; and, finally, transform $\sigma^r(t)$ back to $\sigma(t)$.

Spin operator calculations involving unitary transformations frequently involve propagator expressions of the general form

$$\mathbf{B}(\lambda) = \exp(-i\lambda\mathbf{A})\mathbf{B}\exp(i\lambda\mathbf{A}), \tag{2.68}$$

in which \mathbf{A} and \mathbf{B} are Hermitian operators and λ is a real parameter. A series representation of $\mathbf{B}(\lambda)$ is given by one form of the BCH formula:

$$\mathbf{B}(\lambda) = \sum_{k=0}^{\infty} \frac{(i\lambda)^k}{k!} \mathcal{A}^k\{\mathbf{B}\}, \tag{2.69}$$

in which $\mathcal{A}\{\} = [\mathbf{A}, \]$ is a commutation superoperator and $\mathcal{A}^0 := \mathbf{E}$. Thus, the propagator expression is evaluated as

$$\mathbf{B}(\lambda) = \mathbf{B} + i\lambda[\mathbf{A}, \mathbf{B}] + \frac{(i\lambda)^2}{2} [\mathbf{A}, [\mathbf{A}, \mathbf{B}]] + \dots \tag{2.70}$$

Although this expression is an infinite series of terms, a compact closed-form solution often can be obtained if recursive relationships can be identified after evaluating a small number of terms. For example, in evaluating the propagator $\exp(-i\theta I_z)I_x \exp(i\theta I_z)$ using the BCH formula, the series expansion can be separated into two parts that represent the series expansions of $\cos \theta$ and $\sin \theta$, leading to the compact solution $I_x \cos \theta + I_y \sin \theta$. The BCH formula provides an alternative approach to that outlined in Section 2.3 for determining the effects of propagators on the density operator.

2.2.5 MATRIX REPRESENTATIONS OF THE SPIN OPERATORS

To proceed, the matrix representation of the angular momentum operators that uses the $|\alpha\rangle$ and $|\beta\rangle$ states of the spin as basis functions must be presented. As shown by [1.1], the intrinsic spin angular momentum has units of \hbar . Consequently, the spin angular momentum operators also have units of \hbar , as shown directly by [2.31]. However, in the remainder of this text, the spin operators will be defined as dimensionless quantities by mapping $\mathbf{I} \rightarrow \mathbf{I}/\hbar$. The constant of proportionality \hbar will be reintroduced explicitly as necessary. As will be seen, a dimensionless set of spin angular momentum operators is particularly useful for analyzing the evolution of the density operator, which is itself dimensionless. The Pauli spin matrices form a complete basis set for a single spin-1/2 system (5):

$$I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad I_y = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad [2.71]$$

Each of these operators is Hermitian. The spin operators satisfy the commutation relation

$$[I_x, I_y] = iI_z \quad [2.72]$$

and any cyclic permutation of [2.72], i.e., $[I_z, I_x] = iI_y$ and $[I_y, I_z] = iI_x$. The eigenkets are represented by the 2×1 column vectors,

$$|\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad [2.73]$$

and the eigenbras are represented by the 1×2 row vectors,

$$\langle\alpha| = [1 \quad 0], \quad \langle\beta| = [0 \quad 1]. \quad [2.74]$$

Arbitrary kets and bras, expressed as a linear combination of the eigenkets or eigenbras, have the representations

$$\begin{aligned} |\Psi\rangle &= c_\alpha|\alpha\rangle + c_\beta|\beta\rangle = c_\alpha \begin{bmatrix} 1 \\ 0 \end{bmatrix} + c_\beta \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} c_\alpha \\ c_\beta \end{bmatrix}, \\ \langle\Psi| &= c_\alpha^*\langle\alpha| + c_\beta^*\langle\beta| = c_\alpha^* \begin{bmatrix} 1 & 0 \end{bmatrix} + c_\beta^* \begin{bmatrix} 0 & 1 \end{bmatrix} = \begin{bmatrix} c_\alpha^* & c_\beta^* \end{bmatrix}. \end{aligned} \quad [2.75]$$

Thus, the matrix representation of a ket is the column vector whose elements are the coefficients from the expansion in terms of basis kets. The results of operator manipulations can be expressed using matrix algebra. For example,

$$\begin{aligned} I_x|\alpha\rangle &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2}|\beta\rangle, & I_x|\beta\rangle &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}|\alpha\rangle, \\ I_y|\alpha\rangle &= \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 \\ i \end{bmatrix} = \frac{i}{2}|\beta\rangle, & I_y|\beta\rangle &= \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -i \\ 0 \end{bmatrix} = -\frac{i}{2}|\alpha\rangle, \\ I_z|\alpha\rangle &= \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}|\alpha\rangle, & I_z|\beta\rangle &= \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 \\ -1 \end{bmatrix} = -\frac{1}{2}|\beta\rangle, \end{aligned} \quad [2.76]$$

express the results of the Cartesian spin operators acting on the $|\alpha\rangle$ and $|\beta\rangle$ kets. These results should be compared with [2.31]. Similarly, the orthogonality relations are obtained as

$$\begin{aligned} \langle\alpha|\alpha\rangle &= \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 1, \\ \langle\alpha|\beta\rangle &= \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = 0, \\ \langle\beta|\alpha\rangle &= \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 0, \\ \langle\beta|\beta\rangle &= \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = 1. \end{aligned} \quad [2.77]$$

The matrix representations of operators and wavefunctions depend upon the particular basis set employed. Matrix representations using different basis sets can be interconverted using unitary transformations. If Ψ' is the representation of a wavefunction in one (primed) basis set and Ψ is the representation in another (unprimed basis), then

$$|\Psi'\rangle = \mathbf{U}|\Psi\rangle, \quad [2.78]$$

in which \mathbf{U} is a unitary operator with matrix elements in the unprimed basis given by

$$U_{ij} = \langle i | \mathbf{U} | j \rangle = \langle i | j' \rangle. \quad [2.79]$$

The representation of an operator in the two basis sets is then given by the similarity transformation

$$\mathbf{A}' = \mathbf{U} \mathbf{A} \mathbf{U}^{-1}. \quad [2.80]$$

Using these results, the expectation value of \mathbf{A}' is

$$\langle \Psi' | \mathbf{A}' | \Psi' \rangle = \langle \Psi | \mathbf{U}^{-1} \mathbf{U} \mathbf{A} \mathbf{U}^{-1} \mathbf{U} | \Psi \rangle = \langle \Psi | \mathbf{A} | \Psi \rangle, \quad [2.81]$$

which justifies earlier assertions that the results of calculating the expectation value of an operator do not depend on the choice of basis set.

In order to clarify these ideas, the transformation between a basis set consisting of the eigenfunctions of I_z and a basis set consisting of the eigenfunctions of I_x is presented. The eigenfunction equations for I_x are defined as

$$I_x |\phi_1\rangle = \frac{1}{2} |\phi_1\rangle, \quad I_x |\phi_2\rangle = -\frac{1}{2} |\phi_2\rangle, \quad [2.82]$$

in which ϕ_1 and ϕ_2 are the (as yet unspecified) eigenfunctions. An arbitrary wavefunction can be written as

$$\Psi = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle \quad [2.83]$$

in the basis functions of I_z and as

$$\Psi' = c_1 |\phi_1\rangle + c_2 |\phi_2\rangle \quad [2.84]$$

in the basis functions of I_x . Application of [2.78] yields the matrix equation

$$\begin{aligned} \Psi' &= \mathbf{U} \Psi, \\ \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} &= \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} \begin{bmatrix} c_\alpha \\ c_\beta \end{bmatrix}. \end{aligned} \quad [2.85]$$

Using [2.82] and [2.84],

$$I'_x \Psi' = \frac{1}{2} c_1 |\phi_1\rangle - \frac{1}{2} c_2 |\phi_2\rangle = \frac{1}{2} \begin{bmatrix} c_1 \\ -c_2 \end{bmatrix}, \quad [2.86]$$

in which the prime has been added to I_x to emphasize that the eigenbase of I_x is being utilized. Using [2.75] and [2.78],

$$\begin{aligned} I'_x \Psi' &= \mathbf{U} I_x \mathbf{U}^{-1} \mathbf{U} \Psi = \mathbf{U} (I_x \Psi) = \mathbf{U} \left(\frac{1}{2} c_\alpha |\beta\rangle + \frac{1}{2} c_\beta |\alpha\rangle \right) \\ &= \frac{1}{2} \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} \begin{bmatrix} c_\beta \\ c_\alpha \end{bmatrix}, \end{aligned} \quad [2.87]$$

in which the results in [2.76] have been used. Equating [2.86] and [2.87] yields

$$\begin{bmatrix} c_1 \\ -c_2 \end{bmatrix} = \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} \begin{bmatrix} c_\beta \\ c_\alpha \end{bmatrix}. \quad [2.88]$$

Satisfying the simultaneous system of equations in [2.85] and [2.88] requires that $U_{11} = U_{12}$ and $U_{21} = -U_{22}$. The columns of \mathbf{U} must be normalized and orthogonal, because \mathbf{U} is unitary. Thus, $U_{11}^2 + U_{22}^2 = 1$ and $U_{11}^2 - U_{22}^2 = 0$. Finally, the determinant of \mathbf{U} must equal +1, so that \mathbf{U} represents a proper rotation. Thus, $2U_{11}U_{22} = 1$. These additional constraints give

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}, \quad [2.89]$$

from which the explicit relationships are obtained:

$$\begin{aligned} |\varphi_1\rangle &= \frac{1}{\sqrt{2}} (|\alpha\rangle + |\beta\rangle), \\ |\varphi_2\rangle &= -\frac{1}{\sqrt{2}} (|\alpha\rangle - |\beta\rangle). \end{aligned} \quad [2.90]$$

Using [2.80], the operator, I_z for example, has a matrix representation in the basis set of the I_x eigenfunctions of

$$\begin{aligned} I'_z &= \mathbf{U} I_z \mathbf{U}^{-1} = \frac{1}{4} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} = \frac{1}{4} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} 1 & -1 \\ -1 & -1 \end{bmatrix} \\ &= -\frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \end{aligned} \quad [2.91]$$

In a particularly important application of these ideas, the matrix representation of the Hamiltonian operator, \mathcal{H} , is calculated in some convenient basis. The matrix \mathbf{U} is then determined such that the new

matrix representation of the operator, \mathcal{H}' , given by

$$\mathcal{H}' = \mathbf{U}\mathcal{H}\mathbf{U}^{-1}, \quad [2.92]$$

is a diagonal matrix. The transformed basis functions given by [2.78] then represent the eigenfunctions of the Hamiltonian operator and the diagonal elements of \mathcal{H}' are the energies associated with the stationary states of the system.

2.3 Pulses and Rotation Operators

The simple case of applying an rf pulse to a single spin-1/2 nucleus in a static field B_0 will be considered first. The pulse is applied as a linearly polarized transverse rf field with magnitude $2B_1$ and angular frequency ω_{rf} . Remembering from the Bloch approach that this field can be decomposed into two counter-rotating fields, only one of which has a significant effect on the spin, the Hamiltonian for the pulse is written as (8)

$$\begin{aligned} \mathcal{H} &= -\boldsymbol{\mu} \cdot \mathbf{B}(t) = \mathcal{H}_z + \mathcal{H}_{\text{rf}} \\ &= \omega_0 I_z + \omega_1 [I_x \cos(\omega_{\text{rf}}t + \phi) + I_y \sin(\omega_{\text{rf}}t + \phi)], \end{aligned} \quad [2.93]$$

where I_α is the spin angular momentum operator along the axis α , $\omega_0 = -\gamma B_0$, and $\omega_1 = -\gamma B_1$. The first term in [2.93] takes into account the precession of the spin under the influence of the static field, that is, the Zeeman Hamiltonian, and the second term represents the pulse.

The choice of \mathbf{U} that removes the time dependence from [2.93] is

$$\mathbf{U} = \exp(i\omega_{\text{rf}}I_z t). \quad [2.94]$$

Application of this unitary transformation, using [2.66], gives the effective Hamiltonian,

$$\begin{aligned} \mathcal{H}_e &= \omega_0 I_z + \omega_1 \exp(i\omega_{\text{rf}}I_z t) [I_x \cos(\omega_{\text{rf}}t + \phi) + I_y \sin(\omega_{\text{rf}}t + \phi)] \exp(-i\omega_{\text{rf}}I_z t) \\ &\quad + i \exp(i\omega_{\text{rf}}I_z t) i\omega_{\text{rf}}I_z \exp(-i\omega_{\text{rf}}I_z t). \end{aligned} \quad [2.95]$$

Using the rotation properties of the spin angular momentum operators presented in Table 2.1 (these properties will be derived later),

$$\begin{aligned} I_x \cos(\omega_{\text{rf}}t) + I_y \sin(\omega_{\text{rf}}t) &= \exp(-i\omega_{\text{rf}}I_z t) I_x \exp(i\omega_{\text{rf}}I_z t) \\ &\quad - I_x \sin(\omega_{\text{rf}}t) + I_y \cos(\omega_{\text{rf}}t) \\ &= \exp(-i\omega_{\text{rf}}I_z t) I_y \exp(i\omega_{\text{rf}}I_z t), \end{aligned} \quad [2.96]$$

TABLE 2.1
Rotation Properties of Angular Momentum Operators

u, v^a	x	y	z
x	I_x	$I_x \cos\theta - I_z \sin\theta$	$I_x \cos\theta + I_y \sin\theta$
y	$I_y \cos\theta + I_z \sin\theta$	I_y	$I_y \cos\theta - I_x \sin\theta$
z	$I_z \cos\theta - I_y \sin\theta$	$I_z \cos\theta + I_x \sin\theta$	I_z

^aThe table entries (u, v) are the results of the unitary transformation $\exp(-i\theta I_y)I_u \exp(i\theta I_y)$.

the second term in [2.95] is simplified to $\omega_1(I_x \cos\phi + I_y \sin\phi)$. The third term in [2.95] is simplified to $-\omega_{\text{rf}}I_z$ because an operator commutes with an exponential operator of itself. The effective Hamiltonian can be written as

$$\begin{aligned}
 \mathcal{H}_e &= \omega_0 I_z + \omega_1(I_x \cos\phi + I_y \sin\phi) - \omega_{\text{rf}}I_z \\
 &= (\omega_0 - \omega_{\text{rf}})I_z + \omega_1(I_x \cos\phi + I_y \sin\phi) \\
 &= \Omega I_z + \omega_1(I_x \cos\phi + I_y \sin\phi).
 \end{aligned} \tag{2.97}$$

This is now a *time-independent* effective Hamiltonian and the solution in the form of [2.67] describes evolution of the density operator in the rotating frame. Note the strong similarity between [2.97] and [1.18]. For completeness, the isotropic chemical shift Hamiltonian is given by

$$\mathcal{H} = -\sigma\omega_0 I_z, \tag{2.98}$$

in which σ is the isotropic shielding constant [1.48], rather than the density operator, and can be incorporated into the definition of $\Omega = \omega_0(1 - \sigma) - \omega_{\text{rf}}$.

If $\Omega = 0$ and $\phi = 0$, then the Hamiltonian for an on-resonance x -pulse becomes

$$\mathcal{H}_e = \omega_1 I_x \tag{2.99}$$

and, as follows from [2.67],

$$\begin{aligned}
 \sigma(\tau_p) &= \exp(-i\mathcal{H}_e \tau_p) \sigma(0) \exp(i\mathcal{H}_e \tau_p) \\
 &= \exp(-i\omega_1 I_x \tau_p) \sigma(0) \exp(i\omega_1 I_x \tau_p).
 \end{aligned} \tag{2.100}$$

For simplicity, the superscript has been omitted from the rotating frame density operator; in general, context is sufficient to establish whether a

rotating frame or laboratory frame density operator is intended. If $\alpha = \omega_1 \tau_p$, is defined to be the flip angle of the pulse of length τ_p , then

$$\sigma(\tau_p) = \exp(-i\alpha I_x) \sigma(0) \exp(i\alpha I_x). \quad [2.101]$$

The matrix representation of the exponential operators in [2.101] must be derived so that the effect on the density operator can be calculated. If the exponential rotation operators are defined as

$$\mathbf{R}_x(\alpha) = \exp(-i\alpha I_x), \quad [2.102]$$

then [2.101] becomes

$$\sigma(t) = \mathbf{R}_x(\alpha) \sigma(0) \mathbf{R}_x^{-1}(\alpha). \quad [2.103]$$

The rotation operators can be expanded as

$$\mathbf{R}_x^{-1}(\alpha) = E + i\alpha I_x - \frac{1}{2}\alpha^2 I_x^2 + \dots \quad [2.104]$$

Using the Pauli spin matrices given in [2.71], the following relationships are easily derived:

$$I_x^2 = I_y^2 = I_z^2 = \frac{1}{4} \mathbf{E}, \quad [2.105]$$

$$I_\eta^{2n} = \frac{1}{4^n} \mathbf{E}, \quad [2.106]$$

$$I_\eta^{2n+1} = \frac{1}{4^n} I_\eta. \quad [2.107]$$

Substituting the results contained in [2.105]–[2.107] into [2.104] and grouping together even and odd powers of iI_x yields

$$\begin{aligned} \mathbf{R}_x^{-1}(\alpha) &= \mathbf{E} \left(1 - \frac{\alpha^2}{2!2^2} + \frac{\alpha^4}{4!2^4} + \dots \right) + 2iI_x \left(\frac{\alpha}{2} - \frac{\alpha^3}{3!2^3} + \frac{\alpha^5}{5!2^5} + \dots \right) \\ &= \mathbf{E} \cos(\alpha/2) + 2iI_x \sin(\alpha/2). \end{aligned} \quad [2.108]$$

Expanding I_x in terms of the raising and lowering operators,

$$I^+ = I_x + iI_y, \quad I^- = I_x - iI_y, \quad [2.109]$$

yields

$$2I_x = (I^+ + I^-) \equiv \mathbf{T}. \quad [2.110]$$

\mathbf{T} is known as the inversion operator and has the effect of changing the spin quantum number from $+1/2$ to $-1/2$ and *vice versa*. This leads to

$$\mathbf{R}_x^{-1}(\alpha) = \mathbf{E} \cos(\alpha/2) + i\mathbf{T} \sin(\alpha/2). \quad [2.111]$$

By similar reasoning,

$$\mathbf{R}_x(\alpha) = \mathbf{E} \cos(\alpha/2) - i\mathbf{T} \sin(\alpha/2). \quad [2.112]$$

The rotation matrix corresponding to a pulse of flip angle, α , applied along the x -axis can now be calculated. The elements of the matrix representations of the pulse rotation operators $\mathbf{R}_x^{-1}(\alpha)$ and $\mathbf{R}_x(\alpha)$ are constructed from the basis eigenfunctions using the expressions

$$\begin{aligned} [\mathbf{R}_x^{-1}(\alpha)]_{rs} &= \langle r | \{ \mathbf{E} \cos(\alpha/2) + i\mathbf{T} \sin(\alpha/2) \} | s \rangle, \\ [\mathbf{R}_x(\alpha)]_{rs} &= \langle r | \{ \mathbf{E} \cos(\alpha/2) - i\mathbf{T} \sin(\alpha/2) \} | s \rangle. \end{aligned} \quad [2.113]$$

For example, if $\langle 1 | = \langle \alpha |$ and $| 2 \rangle = | \beta \rangle$, then matrix element $[\mathbf{R}_x^{-1}(\alpha)]_{12}$ is

$$[\mathbf{R}_x^{-1}(\alpha)]_{12} = \langle \alpha | \{ \mathbf{E} \cos(\alpha/2) + i\mathbf{T} \sin(\alpha/2) \} | \beta \rangle = i \sin(\alpha/2). \quad [2.114]$$

The matrix representations of the pulse operators are

$$\mathbf{R}_x^{-1}(\alpha) = \begin{bmatrix} c & is \\ is & c \end{bmatrix} \quad \text{and} \quad \mathbf{R}_x(\alpha) = \begin{bmatrix} c & -is \\ -is & c \end{bmatrix}, \quad [2.115]$$

where $c = \cos(\alpha/2)$ and $s = \sin(\alpha/2)$.

Similar analysis for a pulse with y -phase ($\phi = \pi/2$) generates a rotation matrix of the form

$$\mathbf{R}_y^{-1}(\alpha) = \begin{bmatrix} c & s \\ -s & c \end{bmatrix} \quad \text{and} \quad \mathbf{R}_y(\alpha) = \begin{bmatrix} c & -s \\ s & c \end{bmatrix}. \quad [2.116]$$

Finally a rotation about the z -axis (which in practice is difficult to achieve experimentally with rf pulses) has the matrix representation

$$\mathbf{R}_z^{-1}(\alpha) = \begin{bmatrix} c + is & 0 \\ 0 & c - is \end{bmatrix} \quad \text{and} \quad \mathbf{R}_z(\alpha) = \begin{bmatrix} c - is & 0 \\ 0 & c + is \end{bmatrix}. \quad [2.117]$$

The rotation induced by the general Hamiltonian given by [2.97], which includes off-resonance effects and arbitrary pulse phases, can be written as

$$\mathbf{R}_\phi(\alpha, \theta) = \exp(-i\alpha \mathbf{n} \cdot \mathbf{I}) = \mathbf{E} \cos(\alpha/2) - i2\mathbf{n} \cdot \mathbf{I} \sin(\alpha/2), \quad [2.118]$$

in which \mathbf{n} is a unit vector along the direction of the effective field in the rotating frame \mathbf{B}^f , given by [1.18], α is given by [1.23],

$$\mathbf{n} \cdot \mathbf{I} = I_x \cos\phi \sin\theta + I_y \sin\phi \sin\theta + I_z \cos\theta, \quad [2.119]$$

and θ is defined by [1.21]. Rather than derive a matrix representation of [2.118], the following identity will be established:

$$\mathbf{R}_\phi(\alpha, \theta) = \mathbf{R}_z(\phi) \mathbf{R}_y(\theta) \mathbf{R}_z(\alpha) \mathbf{R}_y^{-1}(\theta) \mathbf{R}_z^{-1}(\phi). \quad [2.120]$$

The proof of [2.120] depends upon the following useful relationship:

$$\mathbf{U} f(\mathbf{A}) \mathbf{U}^{-1} = f(\mathbf{U} \mathbf{A} \mathbf{U}^{-1}), \quad [2.121]$$

in which $f(\mathbf{A})$ is an arbitrary function acting on the operator \mathbf{A} . Equation [2.121] can be verified by expanding $f(\mathbf{U} \mathbf{A} \mathbf{U}^{-1})$ as a Taylor series. Using [2.121],

$$\begin{aligned} \mathbf{R}_\phi(\alpha, \theta) &= \mathbf{R}_z(\phi) \mathbf{R}_y(\theta) \mathbf{R}_z(\alpha) \mathbf{R}_y^{-1}(\theta) \mathbf{R}_z^{-1}(\phi) \\ &= \mathbf{R}_z(\phi) \exp[-i\alpha \mathbf{R}_y(\theta) I_z \mathbf{R}_y^{-1}(\theta)] \mathbf{R}_z^{-1}(\phi) \\ &= \mathbf{R}_z(\phi) \exp[-i\alpha (I_z \cos\theta + I_x \sin\theta)] \mathbf{R}_z^{-1}(\phi) \\ &= \exp[-i\alpha \mathbf{R}_z(\phi) (I_z \cos\theta + I_x \sin\theta) \mathbf{R}_z^{-1}(\phi)] \\ &= \exp[-i\alpha (I_z \cos\theta + I_x \cos\phi \sin\theta + I_y \sin\phi \sin\theta)] \\ &= \exp[-i\alpha \mathbf{n} \cdot \mathbf{I}], \end{aligned} \quad [2.122]$$

which completes the desired proof. Thus, the operator for rotation about an arbitrary angle can be represented as a series of rotations about the y and z axes. The five rotations used to represent $\mathbf{R}_\phi(\alpha, \theta)$ in [2.120] are not mutually independent; the rotation $\mathbf{R}_\phi(\alpha, \theta)$ can be reduced to three independent rotations using the Euler decomposition of the general three-dimensional rotation (8).

2.4 Quantum Mechanical NMR Spectroscopy

Theoretical analysis of an NMR experiment requires calculation of the signal observed following a sequence of rf pulses and delays. The initial state of the spin system is described by the *equilibrium density operator*. Evolution of the density operator through the sequence of pulses and delays is calculated using the Liouville–von Neumann equation [2.53]. The Hamiltonian consists of the appropriate spin interaction terms that govern evolution of the density operator.

In isotropic solution, the Zeeman, chemical shift, scalar coupling, and rf pulse terms are the dominant interactions. The expectation value of the observed signal at the desired time is calculated using [2.47] as the trace of the product of the density operator and the *observation operator* corresponding to the observable magnetization. The equilibrium density and observation operators are described in the following section.

2.4.1 EQUILIBRIUM AND OBSERVATION OPERATORS

The lattice is assumed to always be in thermal equilibrium at a temperature T (equivalently, the lattice is assumed to have infinite heat capacity). At thermodynamic equilibrium, the nuclear spin states are assumed to be in thermal equilibrium with the lattice. Consequently, the values of $\mathcal{P}(\Psi)$ (see Section 2.2.2) are constrained such that the populations of the stationary states (given by the diagonal elements of the density matrix) have a Boltzmann distribution. Furthermore, the density matrix is diagonal at equilibrium because the members of the different subensembles described by $\mathcal{P}(\Psi)$ are uncorrelated. The form of the equilibrium density operator that satisfies these requirements is

$$\sigma^{\text{eq}} = e^{-\mathcal{H}/k_{\text{B}}T} / \text{Tr}\{e^{-\mathcal{H}/k_{\text{B}}T}\}. \quad [2.123]$$

In the eigenbase of the Hamiltonian operator, the matrix elements of σ^{eq} are given by

$$\begin{aligned} \sigma_{mn}^{\text{eq}} &= \langle m | e^{-\mathcal{H}/k_{\text{B}}T} | n \rangle / \sum_{i=1}^N \langle i | e^{-\mathcal{H}/k_{\text{B}}T} | i \rangle \\ &= \delta_{m,n} e^{-E_n/k_{\text{B}}T} / \sum_{i=1}^N e^{-E_i/k_{\text{B}}T}, \end{aligned} \quad [2.124]$$

which is a diagonal matrix whose elements are the required Boltzmann probabilities. In the high-temperature approximation, $E_n \ll k_{\text{B}}T$ and the equilibrium density operator can be approximated by

$$\begin{aligned} \sigma^{\text{eq}} &= e^{-\mathcal{H}/k_{\text{B}}T} / \text{Tr}\{e^{-\mathcal{H}/k_{\text{B}}T}\} \\ &\approx \{\mathbf{E} - \mathcal{H}/k_{\text{B}}T\} / \text{Tr}\{\mathbf{E} - \mathcal{H}/k_{\text{B}}T\} \\ &\approx \{\mathbf{E} - \mathcal{H}/k_{\text{B}}T\} / \text{Tr}\{\mathbf{E}\} \\ &\approx \mathbf{E} / N - \mathcal{H} / (Nk_{\text{B}}T), \end{aligned} \quad [2.125]$$

in which N is the dimensionality of the Hilbert space and is equal to 2^M for M spin-1/2 nuclei (i.e., $M=2$ for an IS two-spin system). The term

\mathbf{E}/N is a constant that does not affect the NMR experiment; accordingly, this term is normally not written explicitly and the high-temperature approximation to the equilibrium density operator is simply written in terms of the Zeeman Hamiltonian as

$$\sigma^{\text{eq}} = -\mathcal{H}/(Nk_{\text{B}}T) = -\sum_{k=1}^M \frac{\hbar\omega_{0k}}{Nk_{\text{B}}T} I_{kz}, \quad [2.126]$$

in which \hbar has been included explicitly.

By convention, the complex magnetization recorded during the acquisition period of an NMR experiment is given by (2)

$$\langle M^+ \rangle(t) = \mathcal{N} \gamma \hbar \text{Tr} \{ \sigma(t) \mathbf{F}^+ \}, \quad [2.127]$$

in which \mathcal{N} is the number of spins per unit volume,

$$\mathbf{F}^+ = \sum_{k=1}^M I_k^+ = \sum_{k=1}^M (I_{kx} + iI_{ky}). \quad [2.128]$$

The operator \mathbf{F}^- could have been chosen as the observation operator equally well.

2.4.2 THE ONE-PULSE EXPERIMENT

The simplest NMR experiment consists of a single pulse followed by acquisition of the FID. For a single spin, [2.126] indicates that $\sigma^{\text{eq}} \propto I_z$. The effect of a pulse with x -phase and a rotation angle α pulse applied to I_z is calculated using [2.115] as

$$\begin{aligned} \mathbf{R}_x(\alpha) I_z \mathbf{R}_x^{-1}(\alpha) &= \frac{1}{2} \begin{bmatrix} c & -is \\ -is & c \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} c & is \\ is & c \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} c & is \\ -is & -c \end{bmatrix} \begin{bmatrix} c & is \\ is & c \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} c^2 - s^2 & 2ics \\ -2ics & s^2 - c^2 \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} \cos \alpha & i \sin \alpha \\ -i \sin \alpha & -\cos \alpha \end{bmatrix} \\ &= I_z \cos \alpha - I_y \sin \alpha, \end{aligned} \quad [2.129]$$

in which the last line is obtained by using the Pauli spin matrices, [2.71]. If $\alpha = 180^\circ$, the final matrix would be equal to

$$\mathbf{R}_x(\pi)I_z\mathbf{R}_x^{-1}(\pi) = \frac{1}{2}\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} = -\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = -I_z, \quad [2.130]$$

corresponding to population inversion. If $\alpha = 90^\circ$, then the final matrix becomes

$$\mathbf{R}_x(\pi/2)I_z\mathbf{R}_x^{-1}(\pi/2) = \frac{1}{2}\begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -\frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = -I_y. \quad [2.131]$$

Simply, a 90° pulse applied with x -phase to I_z magnetization generates $-I_y$ magnetization. These results are identical to the results obtained using the Bloch model. The $-I_y$ magnetization will evolve during acquisition under the Zeeman Hamiltonian (in the rotating frame) given as

$$\mathcal{H}_z = (\omega_0 - \omega_{\text{rf}})I_z = \Omega I_z. \quad [2.132]$$

This is a time-independent Hamiltonian; therefore,

$$\begin{aligned} \sigma(t) &= \exp(-i\mathcal{H}_z t)\sigma(0)\exp(i\mathcal{H}_z t) \\ &= \exp(-i\Omega I_z t)\sigma(0)\exp(i\Omega I_z t) \\ &= \mathbf{U}\sigma(0)\mathbf{U}^{-1} \end{aligned} \quad [2.133]$$

and

$$\mathbf{U} = \exp(-i\Omega t I_z) = \begin{bmatrix} \exp(-i\Omega t/2) & 0 \\ 0 & \exp(i\Omega t/2) \end{bmatrix}. \quad [2.134]$$

Performing the matrix manipulations for $\sigma(0) = -I_y$, yields

$$\begin{aligned} \sigma(t) &= \frac{1}{2}\begin{bmatrix} 0 & i \exp(-i\Omega t) \\ -i \exp(i\Omega t) & 0 \end{bmatrix} \\ &= \frac{1}{2}\begin{bmatrix} 0 & i[\cos(\Omega t) - i \sin(\Omega t)] \\ -i[\cos(\Omega t) + i \sin(\Omega t)] & 0 \end{bmatrix} \\ &= \frac{1}{2}\begin{bmatrix} 0 & i \cos(\Omega t) + \sin(\Omega t) \\ -i \cos(\Omega t) + \sin(\Omega t) & 0 \end{bmatrix} \\ &= \frac{1}{2}\begin{bmatrix} 0 & \sin(\Omega t) \\ \sin(\Omega t) & 0 \end{bmatrix} + \frac{i}{2}\begin{bmatrix} 0 & \cos(\Omega t) \\ -\cos(\Omega t) & 0 \end{bmatrix}. \end{aligned} \quad [2.135]$$

Using the Pauli spin matrices, [2.135] can be written as

$$\sigma(t) = \mathbf{U}\sigma(0)\mathbf{U}^{-1} = -\exp(-i\Omega t I_z) I_y \exp(i\Omega t I_z) = I_x \sin(\Omega t) - I_y \cos(\Omega t). \quad [2.136]$$

Note that at $t=0$, $\sigma(t) = -I_y$ and at $\Omega t = \pi/2$, $\sigma(t) = I_x$. Magnetization with a positive resonance offset in the rotating frame precesses in the sense $x \rightarrow y \rightarrow -x \rightarrow -y$.

The preceding results yield the form of the detectable magnetization for a one-pulse sequence for a single isolated spin:

$$\begin{aligned} \langle M^+ \rangle(t) &= \frac{\mathcal{N} \gamma \hbar^2 \omega_0}{2k_B T} \text{Tr} \{ [I_x \sin(\Omega t) - I_y \cos(\Omega t)] (I_x + iI_y) \} \\ &= \frac{\mathcal{N} \gamma \hbar^2 \omega_0}{2k_B T} [\text{Tr} \{ I_x^2 \} \sin(\Omega t) + i \text{Tr} \{ I_x I_y \} \sin(\Omega t) \\ &\quad - \text{Tr} \{ I_y I_x \} \cos(\Omega t) - i \text{Tr} \{ I_y^2 \} \cos(\Omega t)] \\ &= \frac{\mathcal{N} \gamma \hbar^2 \omega_0}{8k_B T} [\sin(\Omega t) - i \cos(\Omega t)] \\ &= \frac{\mathcal{N} \gamma \hbar^2 \omega_0}{8k_B T} \exp[i(\Omega t - \pi/2)], \end{aligned} \quad [2.137]$$

in which all constants have been reintroduced. This signal has the form expected from the analysis of the same system using the Bloch model in the absence of relaxation (the factor $\exp[-i\pi/2]$ is a time-independent phase factor).

2.5 Quantum Mechanics of Multispin Systems

In this section, the use of the density operator approach to perform calculations on larger, scalar coupled spin systems will be illustrated; as discussed in Chapter 1, Section 1.6, the Bloch model fails to properly account for the evolution of such spin systems. The problem is to establish the matrix representation of wavefunctions and operators in a two-spin (in general, N -spin) system and derive an appropriate operator algebra. The central results will be derived using the direct product basis; transformations to other basis sets can be performed using similarity transformations as described previously. Additional details can be found in the monograph by Corio (8).

2.5.1 DIRECT PRODUCT SPACES

The wavefunctions in the *product basis* are given by the *direct products* of the wavefunctions for individual spins:

$$\Psi_k = |m_1\rangle \otimes |m_2\rangle \otimes |m_N\rangle \equiv \bigotimes_{i=1}^N |m_i\rangle \equiv |m_1, m_2, \dots, m_N\rangle, \quad [2.138]$$

in which m_i takes on all possible values, yielding 2^N wavefunctions for spin-1/2 nuclei. The total magnetic quantum number associated with a wavefunction in the product basis is

$$M_k = \sum_{i=1}^N m_i. \quad [2.139]$$

The direct product of two matrices is given by (illustrated for two 2×2 matrices)

$$\begin{aligned} \mathbf{A} \otimes \mathbf{B} &= \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix} \otimes \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} = \begin{bmatrix} A_{11}\mathbf{B} & A_{12}\mathbf{B} \\ A_{21}\mathbf{B} & A_{22}\mathbf{B} \end{bmatrix} \\ &= \begin{bmatrix} A_{11}B_{11} & A_{11}B_{12} & A_{12}B_{11} & A_{12}B_{12} \\ A_{11}B_{21} & A_{11}B_{22} & A_{12}B_{21} & A_{12}B_{22} \\ A_{21}B_{11} & A_{21}B_{12} & A_{22}B_{11} & A_{22}B_{12} \\ A_{21}B_{21} & A_{21}B_{22} & A_{22}B_{21} & A_{22}B_{22} \end{bmatrix} \end{aligned} \quad [2.140]$$

Thus, for example, the four wavefunctions in the product basis of a two-spin system are

$$\begin{aligned} \psi_1 = |\alpha\alpha\rangle &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, & \psi_2 = |\alpha\beta\rangle &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \\ \psi_3 = |\beta\alpha\rangle &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, & \psi_4 = |\beta\beta\rangle &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \end{aligned} \quad [2.141]$$

Next, consider the operator corresponding to the sum of the components I_z and S_z in a two-spin system. Clearly, the matrix

representation of $I_z + S_z$ in a two-spin system must be a 4×4 matrix because the vector space is spanned by four wavefunctions; thus,

$$I_z + S_z \neq \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad [2.142]$$

A more formal analysis indicates that matrix representations of the operators in the two-spin system can be calculated from the direct product of the one-spin operators with the identity operator. The results for a two-spin system are

$$I_{\eta}^{(2\text{spin})} = I_{\eta}^{(1\text{spin})} \otimes \mathbf{E} \quad \text{and} \quad S_{\eta}^{(2\text{spin})} = \mathbf{E} \otimes S_{\eta}^{(1\text{spin})}, \quad [2.143]$$

where $\eta = x, y$, or z . In general, for an N -spin system, the representations of the angular momentum operators for the k th spin are given by

$$I_{k\eta}^{(N\text{spin})} = \mathbf{E}_1 \otimes \mathbf{E}_2 \otimes \cdots \otimes \mathbf{E}_{k-1} \otimes I_{k\eta}^{(1\text{spin})} \otimes \mathbf{E}_{k+1} \otimes \cdots \otimes \mathbf{E}_N. \quad [2.144]$$

Returning to the previous example,

$$I_z^{(2\text{spin})} = I_z^{(1\text{spin})} \otimes \mathbf{E} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}, \quad [2.145]$$

$$S_z^{(2\text{spin})} = \mathbf{E} \otimes S_z^{(1\text{spin})} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}. \quad [2.146]$$

The combination of $I_z^{(2\text{spin})} + S_z^{(2\text{spin})}$ gives the correct matrix representation:

$$I_z^{(2\text{spin})} + S_z^{(2\text{spin})} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}. \quad [2.147]$$

From now on, the (2spin) superscript will be implied. The fundamental rule of the operator algebra in direct product spaces is (as illustrated for

a two-spin system)

$$\mathbf{AB}|ij\rangle \equiv (\mathbf{A} \otimes \mathbf{B})(|i\rangle \otimes |j\rangle) = \mathbf{A}|i\rangle \otimes \mathbf{B}|j\rangle, \quad [2.148]$$

in which \mathbf{A} is an operator that acts on the i spin and \mathbf{B} is an operator that acts on the j spin. Also note that

$$\mathbf{AB} \equiv \mathbf{A} \otimes \mathbf{B} = (\mathbf{A} \otimes \mathbf{E})(\mathbf{E} \otimes \mathbf{B}). \quad [2.149]$$

Thus, for example,

$$I_z|\alpha\beta\rangle \equiv (I_z \otimes \mathbf{E})(|\alpha\rangle \otimes |\beta\rangle) = I_z|\alpha\rangle \otimes \mathbf{E}|\beta\rangle = \frac{1}{2}|\alpha\rangle \otimes |\beta\rangle = \frac{1}{2}|\alpha\beta\rangle. \quad [2.150]$$

As a second example,

$$\begin{aligned} 2I_zS_z|\alpha\beta\rangle &\equiv 2(I_z \otimes S_z)(|\alpha\rangle \otimes |\beta\rangle) = 2(I_z|\alpha\rangle \otimes S_z|\beta\rangle) \\ &= 2\left(\frac{1}{2}|\alpha\rangle \otimes -\frac{1}{2}|\beta\rangle\right) = -\frac{1}{2}|\alpha\beta\rangle. \end{aligned} \quad [2.151]$$

In matrix notation,

$$2I_zS_z \equiv 2I_z \otimes S_z = \frac{1}{2}\left(\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\right) = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad [2.152]$$

so that [2.151] also can be written as

$$2I_zS_z|\alpha\beta\rangle \equiv \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 \\ -1 \\ 0 \\ 0 \end{bmatrix} = -\frac{1}{2}|\alpha\beta\rangle. \quad [2.153]$$

As will be discussed in Section 2.7.1, the factor of 2 in the operator $2I_zS_z$ is introduced as a normalization factor.

2.5.2 SCALAR COUPLING HAMILTONIAN

The free-precession laboratory frame Hamiltonian for N scalar coupled spins is

$$\mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_J = \sum_{i=1}^N \omega_i I_{iz} + 2\pi \sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j, \quad [2.154]$$

in which ω_i is the Larmor frequency of the i th spin and J_{ij} is the scalar coupling constant between the i th and j th spins. The eigenfunctions of this Hamiltonian are used as the basis functions for the construction of the matrix representation of the density operator. For completeness, the effects of *strong coupling* must be taken into account. The product wavefunctions given by [2.138] are eigenfunctions of \mathcal{H} only if $2\pi J_{ij}/|\omega_i - \omega_j| \ll 1$; this condition is known as the *weak coupling* regime. If the weak coupling condition does not hold, then the spins are said to be strongly coupled. In the strong coupling regime, the wavefunctions in the product basis with the same total magnetic quantum number become mixed and are no longer completely independent. A proper basis set is obtained by taking linear combinations of the subset of wavefunctions with the same value of m . Construction of wavefunctions for strongly coupled spin systems with $N > 2$ is facilitated by use of group theoretical methods (8). Strong coupling effects are particularly important in the analysis of coherence transfer in isotropic mixing experiments; group theoretical analyses are also important for treatment of identical spins (such as the three protons in a methyl group).

To illustrate these ideas, a scalar coupled two-spin system, which was treated in the weak coupling limit in Chapter 1, Section 1.6, will be analyzed. The two spins will be labeled I and S . The free-precession Hamiltonian laboratory frame for the IS spin system is

$$\mathcal{H} = \omega_I I_z + \omega_S S_z + 2\pi J_{IS} \mathbf{I} \cdot \mathbf{S}, \quad [2.155]$$

in which the scalar coupling constant is J_{IS} . A system of two coupled spins has the following four eigenfunctions:

$$\begin{aligned} \Psi_1 &= |\alpha\alpha\rangle, & \Psi_2 &= \cos\theta|\alpha\beta\rangle + \sin\theta|\beta\alpha\rangle, \\ \Psi_3 &= \cos\theta|\beta\alpha\rangle - \sin\theta|\alpha\beta\rangle, & \Psi_4 &= |\beta\beta\rangle, \end{aligned} \quad [2.156]$$

where θ is known as the strong coupling parameter and is defined as

$$\tan(2\theta) = \frac{2\pi J_{IS}}{\omega_I - \omega_S} \quad [2.157]$$

for 2θ in the range 0 to π radians. If the spins have the same resonance frequency, then $\theta = \pi/4$ and the wavefunctions become

$$\begin{aligned} \Psi_1 &= |\alpha\alpha\rangle, & \Psi_2 &= 2^{-1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle), \\ \Psi_3 &= 2^{-1/2}(|\beta\alpha\rangle - |\alpha\beta\rangle), & \Psi_4 &= |\beta\beta\rangle. \end{aligned} \quad [2.158]$$

The wavefunctions of [2.158] are symmetric or antisymmetric under the exchange of identical particles, as is required by the postulates of quantum mechanics (5). The energies of the four eigenstates are

$$\begin{aligned} E_1 &= \frac{1}{2}\omega_I + \frac{1}{2}\omega_S + \frac{1}{2}\pi J_{IS}, & E_2 &= D - \frac{1}{2}\pi J_{IS}, \\ E_3 &= -D - \frac{1}{2}\pi J_{IS}, & E_4 &= -\frac{1}{2}\omega_I - \frac{1}{2}\omega_S + \frac{1}{2}\pi J_{IS}, \end{aligned} \quad [2.159]$$

where

$$D = \frac{1}{2}[(\omega_I - \omega_S)^2 + (2\pi J_{IS})^2]^{1/2}. \quad [2.160]$$

In the strongly coupled spectrum, the energies of the stationary states and the positions of the resonance signals in the spectrum are altered, compared to the weakly coupled spin system (see [1.56]). In addition, the intensities of the lines in the multiplet are no longer of equal intensity; specifically, the two outer lines reduce progressively in intensity as the strong coupling effect becomes more pronounced.

The results given in [2.156]–[2.160] are derived by diagonalizing the Hamiltonian matrix in the product basis; these results can be easily verified. For example, if Ψ_2 is an eigenfunction of \mathcal{H} , then

$$\begin{aligned} \mathcal{H}\Psi_2 &= E_2\Psi_2 \\ &= (\omega_I I_z + \omega_S S_z + 2\pi J_{IS} \mathbf{I} \cdot \mathbf{S})(\cos\theta|\alpha\beta\rangle + \sin\theta|\beta\alpha\rangle) \\ &= \frac{1}{2}\omega_I \cos\theta|\alpha\beta\rangle - \frac{1}{2}\omega_I \sin\theta|\beta\alpha\rangle - \frac{1}{2}\omega_S \cos\theta|\alpha\beta\rangle + \frac{1}{2}\omega_S \sin\theta|\beta\alpha\rangle \\ &\quad - \frac{1}{2}\pi J_{IS} \cos\theta|\alpha\beta\rangle - \frac{1}{2}\pi J_{IS} \sin\theta|\beta\alpha\rangle + \pi J_{IS} \cos\theta|\beta\alpha\rangle + \pi J_{IS} \sin\theta|\alpha\beta\rangle \\ &= \frac{1}{2}(\omega_I \cos\theta - \omega_S \cos\theta - \pi J_{IS} \cos\theta + 2\pi J_{IS} \sin\theta)|\alpha\beta\rangle \\ &\quad + \frac{1}{2}(-\omega_I \sin\theta + \omega_S \sin\theta - \pi J_{IS} \sin\theta + 2\pi J_{IS} \cos\theta)|\beta\alpha\rangle \\ &= \frac{1}{2}(\omega_I - \omega_S - \pi J_{IS} + 2\pi J_{IS} \tan\theta)\cos\theta|\alpha\beta\rangle \\ &\quad + \frac{1}{2}(-\omega_I + \omega_S - \pi J_{IS} + 2\pi J_{IS}/\tan\theta)\sin\theta|\beta\alpha\rangle. \end{aligned} \quad [2.161]$$

In order for Ψ_2 to be an eigenfunction, the two terms in parentheses following the last equal sign must be identical. Thus,

$$\begin{aligned}\omega_I - \omega_S - \pi J_{IS} + 2\pi J_{IS} \tan\theta &= -\omega_I + \omega_S - \pi J_{IS} + 2\pi J_{IS}/\tan\theta, \\ 2 \tan\theta(\omega_I - \omega_S) - 2\pi J_{IS}(1 - \tan^2\theta) &= 0, \\ \frac{2 \tan\theta}{1 - \tan^2\theta} &= \frac{2\pi J_{IS}}{(\omega_I - \omega_S)}, \\ \tan(2\theta) &= \frac{2\pi J_{IS}}{(\omega_I - \omega_S)},\end{aligned}\tag{2.162}$$

which completes the demonstration, because θ is defined according to [2.157]. By inspection,

$$E_2 = \frac{1}{2}(\omega_I - \omega_S - \pi J_{IS} + 2\pi J_{IS} \tan\theta),\tag{2.163}$$

which is easily shown to be equal to [2.159] by solving [2.157] for $\tan\theta$. By comparing [2.138] and [2.156], the transformation matrix \mathbf{U} that converts the product basis into the strong coupling basis (and diagonalizes the Hamiltonian) is given by

$$\mathbf{U} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\theta & \sin\theta & 0 \\ 0 & -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.\tag{2.164}$$

In the limit of weak scalar coupling, $\theta = 0$ and the wavefunctions of the two energy levels $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ are independent. The weak coupling Hamiltonian simplifies to

$$\mathcal{H} = \omega_I I_z + \omega_S S_z + 2\pi J_{IS} I_z S_z.\tag{2.165}$$

To calculate evolution of the density operator under the weak coupling Hamiltonian, the effect of the operation

$$\sigma(t) = \exp[-i\alpha 2I_z S_z] \sigma(0) \exp[i\alpha 2I_z S_z]\tag{2.166}$$

for $\alpha = \pi J_{IS} t$ must be calculated. The derivation is similar to the derivation of the rotation operators; thus,

$$\exp[i\alpha 2I_z S_z] = \mathbf{E} + i\alpha 2I_z S_z - \frac{1}{2}\alpha^2 (2I_z S_z)^2 + \dots\tag{2.167}$$

Using the matrix representation given in [2.152], the following relationship is easily derived

$$(2I_z S_z)^{2n} = \mathbf{E}. \quad [2.168]$$

Substituting the results contained in [2.168] into [2.167] and grouping together even and odd powers of $iI_z S_z$ yields

$$\begin{aligned} \exp(i\alpha 2I_z S_z) &= \mathbf{E} \left(1 - \frac{\alpha^2}{2!2^2} + \frac{\alpha^4}{4!2^4} + \right) + 4iI_z S_z \left(\frac{\alpha}{2} - \frac{\alpha^3}{3!2^3} + \frac{\alpha^5}{5!2^5} + \right) \\ &= \mathbf{E} \cos \frac{\alpha}{2} + 4iI_z S_z \sin \frac{\alpha}{2}. \end{aligned} \quad [2.169]$$

Again using [2.152], the matrix representation of the operator becomes

$$\exp[i\alpha 2I_z S_z] = \begin{bmatrix} c + is & 0 & 0 & 0 \\ 0 & c - is & 0 & 0 \\ 0 & 0 & c - is & 0 \\ 0 & 0 & 0 & c + is \end{bmatrix}, \quad [2.170]$$

where $c = \cos(\alpha/2)$ and $s = \sin(\alpha/2)$.

2.5.3 ROTATIONS IN PRODUCT SPACES

For a homonuclear system of N spins, the matrix representation of the pulse operator can be calculated from

$$\mathbf{R}_x^{-1}(\alpha) = \bigotimes_{j=1}^N \mathbf{R}_{jx}^{-1}(\alpha) = \bigotimes_{j=1}^N \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_j \right), \quad [2.171]$$

in which $\alpha = -\gamma B_1 \tau_p$. In [2.171], the effect of the scalar coupling term of the Hamiltonian has been ignored; this simplification requires that the length of the rf pulse, τ_p , satisfy $2\pi J_{ij} \tau_p \ll 1$. For a two-spin system,

$$\mathbf{R}_x^{-1}(\alpha) = \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_1 \right) \otimes \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_2 \right). \quad [2.172]$$

The elements of the matrix representation of \mathbf{R} are constructed from the basis eigenfunctions using the expressions

$$[\mathbf{R}_x^{-1}(\alpha)]_{rs} = \langle r | \bigotimes_{j=1}^N \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_j \right) | s \rangle. \quad [2.173]$$

For example, using the strong coupling eigenbasis [2.158], the matrix element $[\mathbf{R}_x^{-1}(\alpha)]_{12}$ is calculated as

$$\begin{aligned}
 [\mathbf{R}_x^{-1}(\alpha)]_{12} &= \langle \Psi_1 | \bigotimes_{j=1}^N \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_j \right) | \Psi_2 \rangle \\
 &= \langle \alpha\alpha | \bigotimes_{j=1}^N \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_j \right) (\cos\theta |\alpha\beta\rangle + \sin\theta |\beta\alpha\rangle) \\
 &= \langle \alpha\alpha | \left(\mathbf{E} \cos^2 \frac{\alpha}{2} + i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} \mathbf{T}_1 + i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} \mathbf{T}_2 - \sin^2 \frac{\alpha}{2} \mathbf{T}_1 \mathbf{T}_2 \right) \\
 &\quad \times (\cos\theta |\alpha\beta\rangle + \sin\theta |\beta\alpha\rangle) \\
 &= i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} \sin\theta + i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} \cos\theta \\
 &= i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} (\cos\theta + \sin\theta).
 \end{aligned} \tag{2.174}$$

This result is calculated using the property that the inversion operator \mathbf{T}_j changes the spin state of spin j from α to β and *vice versa*. As another example, $[\mathbf{R}_x^{-1}(\alpha)]_{14}$ is given by

$$\begin{aligned}
 [\mathbf{R}_x^{-1}(\alpha)]_{14} &= \langle \Psi_1 | \bigotimes_{j=1}^N \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_j \right) | \Psi_4 \rangle \\
 &= \langle \alpha\alpha | \bigotimes_{j=1}^N \left(\mathbf{E} \cos \frac{\alpha}{2} + i \sin \frac{\alpha}{2} \mathbf{T}_j \right) | \beta\beta \rangle \\
 &= \langle \alpha\alpha | \left(\mathbf{E} \cos^2 \frac{\alpha}{2} + i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} \mathbf{T}_1 + i \cos \frac{\alpha}{2} \sin \frac{\alpha}{2} \mathbf{T}_2 - \sin^2 \frac{\alpha}{2} \mathbf{T}_1 \mathbf{T}_2 \right) | \beta\beta \rangle \\
 &= -\sin^2 \frac{\alpha}{2}.
 \end{aligned} \tag{2.175}$$

Repeating these calculations for every element of the matrix representation of the pulse operator yields

$$\mathbf{R}_x^{-1}(\alpha) = \begin{bmatrix} c^2 & icsu & icsv & -s^2 \\ icsu & 1 - s^2 u^2 & -s^2 uv & icsu \\ icsv & -s^2 uv & 1 - s^2 v^2 & icsv \\ -s^2 & icsu & icsv & c^2 \end{bmatrix}, \tag{2.176}$$

where $c = \cos(\alpha/2)$, $s = \sin(\alpha/2)$, $u = \cos\theta + \sin\theta$, and $v = \cos\theta - \sin\theta$. Because the rotation operators are unitary, $\mathbf{R}_x(\alpha)$ is the adjoint

of $\mathbf{R}_x^{-1}(\alpha)$,

$$\mathbf{R}_x(\alpha) = \begin{bmatrix} c^2 & -icsu & -icsv & -s^2 \\ -icsu & 1 - s^2u^2 & -s^2uv & -icsu \\ -icsv & -s^2uv & 1 - s^2v^2 & -icsv \\ -s^2 & -icsu & -icsv & c^2 \end{bmatrix}. \quad [2.177]$$

The same calculation can be performed using rotation matrices that concentrate on each spin in the two-spin system individually rather than both at the same time. This approach can be particularly useful in heteronuclear NMR experiments. The matrix representations of the rotation operators are obtained from the direct products of the single-spin rotation operators derived previously in [2.115–2.117]. For example, for spin I ,

$$\mathbf{R}_x(\alpha)[I] = \mathbf{R}_x(\alpha) \otimes \mathbf{E} = \begin{bmatrix} c & -is \\ -is & c \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} c & 0 & -is & 0 \\ 0 & c & 0 & -is \\ -is & 0 & c & 0 \\ 0 & -is & 0 & c \end{bmatrix}, \quad [2.178]$$

$$\mathbf{R}_y(\alpha)[I] = \mathbf{R}_y(\alpha) \otimes \mathbf{E} = \begin{bmatrix} c & -s \\ s & c \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} c & 0 & -s & 0 \\ 0 & c & 0 & -s \\ s & 0 & c & 0 \\ 0 & s & 0 & c \end{bmatrix}, \quad [2.179]$$

and for spin S ,

$$\mathbf{R}_x(\alpha)[S] = \mathbf{E} \otimes \mathbf{R}_x(\alpha) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} c & -is \\ -is & c \end{bmatrix} = \begin{bmatrix} c & -is & 0 & 0 \\ -is & c & 0 & 0 \\ 0 & 0 & c & -is \\ 0 & 0 & -is & c \end{bmatrix}, \quad [2.180]$$

$$\mathbf{R}_y(\alpha)[S] = \mathbf{E} \otimes \mathbf{R}_y(\alpha) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} c & -s \\ s & c \end{bmatrix} = \begin{bmatrix} c & -s & 0 & 0 \\ s & c & 0 & 0 \\ 0 & 0 & c & -s \\ 0 & 0 & s & c \end{bmatrix}. \quad [2.181]$$

The result $\mathbf{R}_x(\alpha) = \mathbf{R}_x(\alpha)[I]\mathbf{R}_x(\alpha)[S]$ is obtained by matrix multiplication and agrees with [2.176] in the weak coupling limit where $\theta = 0$.

2.5.4 ONE-PULSE EXPERIMENT FOR A TWO-SPIN SYSTEM

To compute the observable magnetization following a pulse and subsequent free precession, the evolution of the density operator, beginning with the equilibrium matrix representation of the density operator for a two-spin system, must be determined. Using [2.125], the initial density matrix is written as

$$\sigma(0) \approx \omega_I I_z + \omega_S S_z = \frac{1}{2} \begin{bmatrix} \omega_I + \omega_S & 0 & 0 & 0 \\ 0 & \omega_I - \omega_S & 0 & 0 \\ 0 & 0 & -\omega_I + \omega_S & 0 \\ 0 & 0 & 0 & -\omega_I - \omega_S \end{bmatrix}, \quad [2.182]$$

in which a common divisor of $2k_B T$ has not been written for convenience and weak coupling has been assumed. A pulse α_x (with rotation angle α and x -phase) rotates an initial state of the density operator according to the now well-known general equation,

$$\sigma(t) = \mathbf{R}_x(\alpha) \sigma(0) \mathbf{R}_x^{-1}(\alpha). \quad [2.183]$$

For simplicity, an ideal 90° pulse with x -phase will be assumed. Using [2.182], [2.183], [2.176], and [2.177],

$$\begin{aligned} \sigma(t) &= \mathbf{R}_x(\pi/2) \sigma(0) \mathbf{R}_x^{-1}(\pi/2) \\ &= \frac{1}{8} \begin{bmatrix} 1 & -i & -i & -1 \\ -i & 1 & -1 & -i \\ -i & -1 & 1 & -i \\ -1 & -i & -i & 1 \end{bmatrix} \begin{bmatrix} \omega_I + \omega_S & 0 & 0 & 0 \\ 0 & \omega_I - \omega_S & 0 & 0 \\ 0 & 0 & -\omega_I + \omega_S & 0 \\ 0 & 0 & 0 & -\omega_I - \omega_S \end{bmatrix} \\ &\quad \times \begin{bmatrix} 1 & i & i & -1 \\ i & 1 & -1 & i \\ i & -1 & 1 & i \\ -1 & i & i & 1 \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} 0 & i\omega_S & i\omega_I & 0 \\ -i\omega_S & 0 & 0 & i\omega_I \\ -i\omega_I & 0 & 0 & i\omega_S \\ 0 & -i\omega_I & -i\omega_S & 0 \end{bmatrix} = -\omega_I I_y - \omega_S S_y \end{aligned} \quad [2.184]$$

because [2.143] yields the results that

$$I_y = \frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} \quad \text{and} \quad S_y = \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}. \quad [2.185]$$

This is exactly the expected result: each term in the initial density operator is transformed identically by the nonselective pulse. Following the pulse, the density operator evolves under the free-precession Hamiltonian. Combining [2.134] with [2.170] yields the matrix representation of the exponential operator,

$$\exp[i(\Omega_I I_z + \Omega_S S_z + 2\pi J_{IS} I_z S_z)t] = \begin{bmatrix} e^{i(\Omega_I + \Omega_S + \pi J_{IS})t/2} & 0 & 0 & 0 \\ 0 & e^{i(\Omega_I - \Omega_S - \pi J_{IS})t/2} & 0 & 0 \\ 0 & 0 & e^{i(-\Omega_I + \Omega_S - \pi J_{IS})t/2} & 0 \\ 0 & 0 & 0 & e^{i(-\Omega_I - \Omega_S + \pi J_{IS})t/2} \end{bmatrix}. \quad [2.186]$$

Performing the matrix multiplications yields

$$\exp[-i(\Omega_I I_z + \Omega_S S_z + 2\pi J_{IS} I_z S_z)t](-I_y - S_y)\exp[i(\Omega_I I_z + \Omega_S S_z + 2\pi J_{IS} I_z S_z)t] \\ = \frac{i}{2} \begin{bmatrix} 0 & e^{-i(\Omega_S + \pi J_{IS})t} & e^{-i(\Omega_I + \pi J_{IS})t} & 0 \\ -e^{i(\Omega_S + \pi J_{IS})t} & 0 & 0 & e^{-i(\Omega_I - \pi J_{IS})t} \\ -e^{i(\Omega_I + \pi J_{IS})t} & 0 & 0 & e^{-i(\Omega_S - \pi J_{IS})t} \\ 0 & -e^{i(\Omega_I - \pi J_{IS})t} & -e^{i(\Omega_S - \pi J_{IS})t} & 0 \end{bmatrix}. \quad [2.187]$$

This result is the final density operator $\sigma(t)$. The observable signal is found by forming the product with operator $\mathbf{F}^+ \propto I^+ + S^+$,

$$\frac{i}{2} \begin{bmatrix} 0 & e^{-i(\Omega_S + \pi J_{IS})t} & e^{-i(\Omega_I + \pi J_{IS})t} & 0 \\ -e^{i(\Omega_S + \pi J_{IS})t} & 0 & 0 & e^{-i(\Omega_I - \pi J_{IS})t} \\ -e^{i(\Omega_I + \pi J_{IS})t} & 0 & 0 & e^{-i(\Omega_S - \pi J_{IS})t} \\ 0 & -e^{i(\Omega_I - \pi J_{IS})t} & -e^{i(\Omega_S - \pi J_{IS})t} & 0 \end{bmatrix} \begin{bmatrix} 0 & -1 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \end{bmatrix} \\ = \frac{i}{2} \begin{bmatrix} 0 & 0 & 0 & -e^{-i(\Omega_I + \pi J_{IS})t} - e^{-i(\Omega_S + \pi J_{IS})t} \\ 0 & e^{i(\Omega_S + \pi J_{IS})t} & e^{i(\Omega_S + \pi J_{IS})t} & 0 \\ 0 & e^{i(\Omega_I + \pi J_{IS})t} & e^{i(\Omega_I + \pi J_{IS})t} & 0 \\ 0 & 0 & 0 & e^{i(\Omega_I - \pi J_{IS})t} + e^{i(\Omega_S - \pi J_{IS})t} \end{bmatrix}. \quad [2.188]$$

The trace of this matrix is proportional to the observed complex magnetization:

$$\langle M^+ \rangle(t) \propto e^{i(\Omega_I + \pi J_{IS})t} + e^{i(\Omega_I - \pi J_{IS})t} + e^{i(\Omega_S + \pi J_{IS})t} + e^{i(\Omega_S - \pi J_{IS})t}. \quad [2.189]$$

The spectrum consists of four signals arranged into two doublets. One doublet consists of the frequencies $\Omega_I \pm \pi J_{IS}$ and the other doublet consists of the frequencies $\Omega_S \pm \pi J_{IS}$.

2.6 Coherence

So far the density operator has been represented in terms of a Cartesian basis of the spin angular momentum operators I_x , I_y , and I_z . Product operators in the Cartesian basis will be used most often in this text because the Cartesian basis affords the simplest treatment of pulses during a pulse sequence (9–11). For a system of two spin-1/2 nuclei, 16 Cartesian product operator terms are required:

$$\begin{array}{cccccc} (1/2)\mathbf{E} & I_x & I_y & I_z & S_x & S_y & S_z \\ 2I_x S_z & 2I_y S_z & 2I_z S_z & 2I_z S_x & 2I_z S_y & & \\ 2I_x S_x & 2I_y S_y & 2I_x S_y & 2I_y S_x & & & \end{array} \quad [2.190]$$

The matrix representations of these two-spin product operators, derived using [2.149], are shown in Table 2.2.

The density operator also can be expressed in the shift operator basis, which provides additional insight into the density matrix theory. For a single spin-1/2 nucleus, the shift basis consists of the operators

$$\begin{aligned} I^+ &= I_x + iI_y = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, & I^- &= I_x - iI_y = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}, \\ I_0 &= \sqrt{2}I_z = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, & \frac{1}{\sqrt{2}}E &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \end{aligned} \quad [2.191]$$

formed by taking linear combinations of the Cartesian operators. As discussed in Section 2.7.1, the factors of $2^{-1/2}$ appearing in the matrix representations of the operators are normalization factors. Operators in the shift basis are transformed to the Cartesian basis by

$$I_x = -\frac{1}{2}(I^+ + I^-), \quad I_y = \frac{1}{2i}(I^+ - I^-), \quad I_z = \frac{1}{\sqrt{2}}I_0. \quad [2.192]$$

TABLE 2.2
Product Operators in the Cartesian Basis for a Two-Spin System

$\frac{1}{2}\mathbf{E} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$	$S_z = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$	$2I_zS_z = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$
$I_x = \frac{1}{2} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	$I_y = \frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}$	$2I_xS_z = \frac{1}{2} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$	$2I_yS_z = \frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix}$
$S_x = \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$S_y = \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}$	$2I_zS_x = \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix}$	$2I_zS_y = \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{bmatrix}$
$2I_xS_x = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$	$2I_yS_y = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}$	$2I_xS_y = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$	$2I_yS_x = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$

The 16 operators in the shift basis for a system of two spin-1/2 nuclei are

$$\begin{array}{cccccc}
 (1/2)\mathbf{E} & I^+ & I^- & I_0 & S^+ & S^- & S_0 \\
 I^+S_0 & I^-S_0 & I_0S_0 & I_0S^+ & I_0S^- & & \\
 I^+S^+ & 2I^-S^- & 2I^+S^- & 2I^-S^+ & & &
 \end{array} \quad [2.193]$$

The matrix representations of these operators are shown in Table 2.3. These operators are constructed from the direct products of the respective operators for each individual spin. For example,

$$\begin{aligned}
 I^- &= \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, & I^+S^+ &= \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \\
 I^+S^- &= \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}.
 \end{aligned} \quad [2.194]$$

The physical meaning of the shift operator basis is illustrated by examining the matrix representations in Table 2.3. First, consider the I^- operator. For illustration, the matrix is written in [2.195] with the spin states of the system along the side and top of the matrix to indicate the spin states connected by each matrix element,

$$I^- = \frac{1}{\sqrt{2}} \begin{array}{c|cccc} & \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ \hline \alpha\alpha & 0 & 0 & 0 & 0 \\ \alpha\beta & 0 & 0 & 0 & 0 \\ \beta\alpha & 1 & 0 & 0 & 0 \\ \beta\beta & 0 & 1 & 0 & 0 \end{array} \quad [2.195]$$

The only nonzero matrix elements present correspond to the transitions $\alpha\alpha \rightarrow \beta\alpha$ and $\alpha\beta \rightarrow \beta\beta$. The lowering operator, I^- , is associated with a change in the spin angular momentum quantum number of $\Delta m = -1$ and a change in the state of the I spin from $\alpha(+1/2) \rightarrow \beta(-1/2)$. In the case of the I^+S^+ operator, the only nonzero matrix element corresponds to $\Delta m = +2$ and a change in spin state from $|\beta\beta\rangle \rightarrow |\alpha\alpha\rangle$. In this instance, both the I spin and the S spin change state from β to α . Similarly for the I^+S^- operator, the nonzero matrix element corresponds to the transition $|\beta\alpha\rangle \rightarrow |\alpha\beta\rangle$ with $\Delta m = 0$. In this example, both spins change spin states in opposite senses.

TABLE 2.3
Product Operators in the Shift Basis for a Two-Spin System

$\frac{1}{2}\mathbf{E} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$I_0 = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$	$S_0 = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$	$I_0 S_0 = \frac{1}{4} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$
$I^+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$I^- = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	$I^+ S_0 = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$I^- S_0 = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$
$S^+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$S^- = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$I_0 S^+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$I_0 S^- = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{bmatrix}$
$I^+ S^+ = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$I^- S^+ = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$I^+ S^- = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	$I^- S^- = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$

The preceding examples illustrate the concept of *coherence*, which is one of the most fundamental aspects of NMR spectroscopy. As has been stated previously, a diagonal matrix element of the density operator, $\sigma_{nn} = \overline{c_n c_n^*}$, is a real, positive number that corresponds to the population of the state described by the basis function $|n\rangle$. Formally, an off-diagonal element of the density operator, σ_{nm} , represents coherence between eigenstates $|n\rangle$ and $|m\rangle$, in the sense that the time-dependent phase properties of the various members of the ensemble are correlated with respect to $|n\rangle$ and $|m\rangle$. Those matrix elements that denote $\Delta m = \pm 1$ are called *single-quantum coherence*; those denoting $\Delta m = \pm 2$ are called *double-quantum coherence* and, not surprisingly, those denoting $\Delta m = 0$ are called *zero-quantum coherence*.

To make these ideas more concrete, consider the following example. The coefficients c_n for the two-level system for a spin-1/2 can be written in polar notation in terms of an amplitude and a phase factor for the α and β states,

$$c_\alpha = |c_\alpha| \exp(i\phi_\alpha), \quad [2.196]$$

$$c_\beta = |c_\beta| \exp(i\phi_\beta). \quad [2.197]$$

Any wavefunction can be expressed as

$$\Psi = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle = |c_\alpha| \exp(i\phi_\alpha) |\alpha\rangle + |c_\beta| \exp(i\phi_\beta) |\beta\rangle, \quad [2.198]$$

thus, for a pure state, the matrix elements of the projection operator $\mathbf{P} = |\Psi\rangle\langle\Psi|$ are

$$\begin{aligned} \langle\alpha|\mathbf{P}|\alpha\rangle &= |c_\alpha|^2, & \langle\alpha|\mathbf{P}|\beta\rangle &= |c_\alpha| |c_\beta| \exp[i(\phi_\beta - \phi_\alpha)], \\ \langle\beta|\mathbf{P}|\beta\rangle &= |c_\beta|^2, & \langle\beta|\mathbf{P}|\alpha\rangle &= |c_\alpha| |c_\beta| \exp[i(\phi_\alpha - \phi_\beta)]. \end{aligned} \quad [2.199]$$

Because the state is pure, all members of the ensemble are identical and the terms $(\phi_\beta - \phi_\alpha)$ do not vary between members of the ensemble. For a mixed, macroscopic state, however,

$$\begin{aligned} \langle\alpha|\sigma|\alpha\rangle &= \overline{|c_\alpha|^2}, & \langle\alpha|\sigma|\beta\rangle &= \overline{|c_\alpha| |c_\beta| \cdot \exp[i(\phi_\beta - \phi_\alpha)]}, \\ \langle\beta|\sigma|\beta\rangle &= \overline{|c_\beta|^2}, & \langle\beta|\sigma|\alpha\rangle &= \overline{|c_\alpha| |c_\beta| \cdot \exp[i(\phi_\alpha - \phi_\beta)]}. \end{aligned} \quad [2.200]$$

If no relationship exists between the macroscopic phase properties of the α state (across the ensemble) and the phase properties of the β state (across the ensemble), then $(\phi_\alpha - \phi_\beta)$ takes on all values in the range 0 to 2π , and $\overline{\exp[i(\phi_\beta - \phi_\alpha)]} = \overline{\exp[i(\phi_\alpha - \phi_\beta)]} = 0$. In this case,

$\langle \alpha | \sigma | \beta \rangle = \langle \beta | \sigma | \alpha \rangle = 0$, and there is *no coherence between the two states*. Therefore, as has been stated previously, the equilibrium density matrix is diagonal.

The application of an rf pulse to the equilibrium density operator induces exchange of population (i.e., transitions) between stationary states for which $\Delta m = \pm 1$ and causes perturbations of the equilibrium population distribution. In the case of a spin-1/2 nucleus, an rf pulse that redistributes populations across the $\alpha \leftrightarrow \beta$ transition creates a phase relationship across that transition such that $\exp[i(\phi_\alpha - \phi_\beta)] \neq 0$ (averaged over the ensemble and assuming that the rotation angle is not a multiple of 180°). The density operator following the pulse is said to represent a coherent superposition between the two states; more commonly, this phenomenon is referred to simply as *coherence*. Coherence describes correlation of quantum mechanical phase relationships among a number of systems (separate nuclei) that persists even after the rf field is removed. Coherence is a phenomenon *associated* with an NMR transition and is not a transition itself; evolution of coherence does *not* change the populations of the spin states. Nonzero off-diagonal elements of the density matrix denote the existence of coherence.

Both shift and Cartesian basis operators are useful for describing NMR spectroscopy. The Cartesian operators are a convenient basis for describing the effects of rf pulses on the density operator, and the shift operators are a convenient basis for describing the evolution of coherence in an NMR experiment. Only two eigenstates, $|\alpha\rangle$ and $|\beta\rangle$, exist for a single spin-1/2 nucleus; consequently, coherences associated with the $|\alpha\rangle \leftrightarrow |\beta\rangle$ transitions with $\Delta m = \pm 1$ are conveniently represented by the raising and lowering operators I^+ and I^- . Four eigenstates exist for a two-spin system. Figure 2.1 illustrates the appearance of double- and zero-quantum coherence where eigenstates are connected in which $\Delta m = \pm 2$ and $\Delta m = 0$, respectively. Double-quantum coherence is associated with transitions in which the spin states can change from $\alpha\alpha \leftrightarrow \beta\beta$. The change in eigenstate is identical for both of the spins involved, and this is often called a “flip-flip” transition. On the other hand, zero-quantum coherence is associated with transitions in which the spin states change $\alpha\beta \leftrightarrow \beta\alpha$, i.e., in the opposite sense to each other; these are often called “flip-flop” terms.

The two-spin case will be seen to be the most commonly encountered as far as this text is concerned; however, spin systems consisting of three or more scalar coupled spins are evidently important and display additional features. Some of the salient features of larger spin systems will be briefly discussed using a weakly coupled three-spin system as an exemplar. In the two-spin case, each of the $\Delta m = \pm 1$ transitions involves

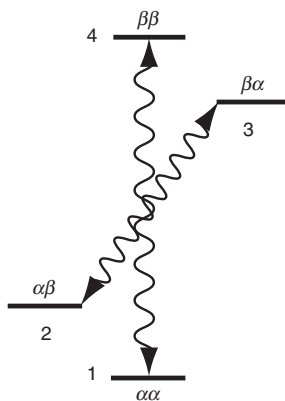


FIGURE 2.1 Multiple-quantum transitions for IS spin system. Shown are the zero-quantum flip-flop transitions between states $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ and the double-quantum flip-flop transitions between states $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$.

the spin state of one nucleus changing while the spin state of the other nucleus remains constant. The spectrum can be conveniently labeled with the spin states of the coupled spins as shown in Fig. 2.1. Similar considerations apply to the three-spin system, although the appearance of the spectrum is a little more complex. The three spins are denoted I , R , and S and have three scalar coupling constants, J_{IS} , J_{IR} , and J_{SR} . The wavefunctions for the scalar coupled three-spin system are denoted $|m_I, m_S, m_R\rangle$ in the product basis, and the energies of the *eight* levels can be calculated by generalizing [1.57] or by direct application of [2.154] and [2.7]. The energy level diagram for a three-spin system is shown in Fig. 2.2a. The single-quantum transitions that connect pairs of eigenstates in which the spin state of one of the three nuclei changes are represented as solid or dashed arrows. Each of the indicated transitions has $\Delta m = -1$ and, just as in the two-spin case, is associated with a resonance line of a specific multiplet (in this case the multiplets are *quartets*) in the one-dimensional NMR spectrum. Schematic NMR spectra are shown in Fig. 2.2b,c. As seen by comparing b and c in Fig. 2.2, the appearance of the spectrum depends on the relative chemical shifts of the I , S , and R spins and on the relative sizes of J_{IS} , J_{IR} , and J_{SR} ; however, Fig. 2.2a is sufficient for illustrative purposes. The two transitions 1–2 and 2–4 share a common eigenstate (2 in this case); consequently, these two transitions are referred to as *connected* transitions. The spin state of one of the three spins remains unchanged across connected transitions (e.g., the I spin state is $|\alpha\rangle$ for the connected

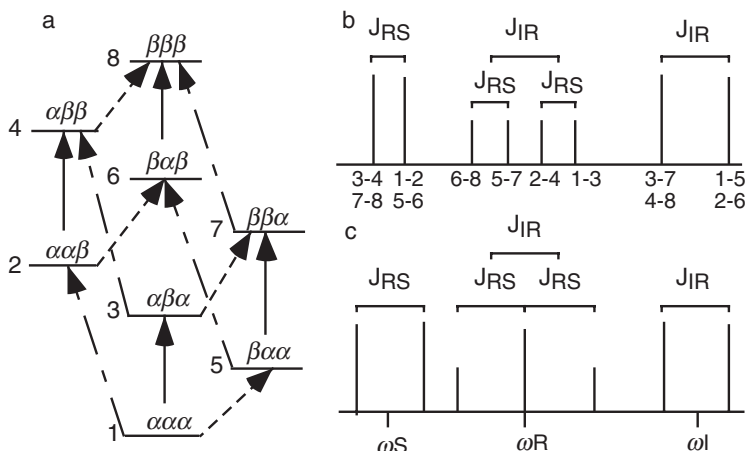


FIGURE 2.2 Spin states and spectrum for a three-spin IRS system. (a) The eight spin states and the allowed single-quantum transitions between states are shown. (---) Single-quantum transitions of the I spin, (—) single-quantum transitions of the R spin, and (····) single-quantum transitions of the S spin. (b) A schematic spectrum for an IRS spin system is shown for the special case that $J_{IR} < J_{RS}$ and $J_{IS} = 0$. (c) A schematic spectrum for an IRS spin system is shown for the special case that $J_{IR} = J_{RS}$ and $J_{IS} = 0$.

transitions 1–2 and 2–4). The values of m_i for the stationary states are $m_1 = +3/2$, $m_2 = +1/2$, and $m_4 = -1/2$. The states represented by m_1 and m_4 are at opposite ends of the transition pathway under discussion and differ in their value of m by 2. In this case, the two connected transitions are said to be *progressively* connected. On the other hand, levels 6 and 7 in the connected transitions 5–6 and 5–7 do not differ in their values of m (e.g., $m_6 = m_7 = -1/2$). In this instance, the transitions are said to be *regressively* connected. In contrast to the single- and two-spin systems, single-quantum transitions exist in three-spin systems for which all three nuclei change spin state. For example, the transition connecting eigenstate 2 with eigenfunction $|\alpha\alpha\beta\rangle$, and eigenstate 7 with eigenfunction $|\beta\beta\alpha\rangle$, has $\Delta m = -1/2 - 1/2 = -1$.

2.7 Product Operator Formalism

Although the density matrix theory provides a rigorous description of the evolution of a nuclear spin system, the requisite matrix calculations quickly become cumbersome as the number of spins and

eigenstates increases unless implemented numerically on a computer. Unfortunately as well, the density matrix formalism provides little physical insight into NMR experiments. The design of new experiments and the optimization of existing experiments are facilitated if the spectroscopist has an intuitive feel for the evolution of the important components of the density operator at each point in the experiment.

The aim of the theoretical analysis of NMR spectroscopy is prediction of the outcome of experiments. The Hamiltonian is an operator, and as has been stated previously, physically observable quantities such as energy, position, and angular momentum are represented in quantum mechanics by operators. Therefore, concentration on the operators themselves, rather than on the solutions to the Schrödinger equation, proves to be a powerful approach. As an illustration, the analysis of the one-pulse experiment in Section 2.4.2 indicates that the equilibrium density operator can be expressed in terms of the Cartesian I_z spin operator. This operator is partially converted into the I_y operator by a pulse with x -phase and rotation angle α ; subsequent evolution under the Zeeman Hamiltonian converts the I_y operator into a linear combination of I_x and I_y spin operators. In this case, the evolution of the density operator is represented by the interconversion of single spin operators. Increasingly, due to the continued development of stronger magnets, spin systems of interest in heteronuclear and ^1H NMR spectroscopy of proteins are weakly coupled. A simplified formalism, referred to as the *product operator formalism*, that treats each weakly coupled system independently can be used to analyze evolution of the density operator (9–11). The product operator formalism retains much of the rigor of the full density matrix treatment while facilitating manual computation and offering considerable insight into complex NMR experiments.

2.7.1 OPERATOR SPACES

In general, an arbitrary density operator can be represented as a linear combination of a complete set of orthogonal basis operators, \mathbf{B}_k :

$$\sigma(t) = \sum_{k=1}^K b_k(t) \mathbf{B}_k, \quad [2.201]$$

in which $b_k(t)$ are complex coefficients and K is the dimensionality of the Liouville operator space spanned by the basis operators. For a system of N spin-1/2 nuclei, $K=4^N$. *Liouville operator space*, and its attendant operator algebra, can be regarded as an elaboration of the ideas of the

Hilbert vector space and vector algebra (2, 12). The orthogonality condition is

$$\text{Tr}\{\mathbf{B}_j^\dagger \mathbf{B}_k\} = \langle \mathbf{B}_j | \mathbf{B}_k \rangle = \delta_{jk} \langle \mathbf{B}_k | \mathbf{B}_k \rangle. \quad [2.202]$$

Unnormalized basis operators, \mathbf{B}_k , can be normalized using

$$\mathbf{B}'_k = \mathbf{B}_k / \langle \mathbf{B}_k | \mathbf{B}_k \rangle^{1/2}. \quad [2.203]$$

The expectation value of an operator \mathbf{A} can be written, by substitution of [2.201] into [2.47],

$$\langle A \rangle(t) = \text{Tr}\{\sigma(t)\mathbf{A}\} = \text{Tr}\left\{\sum_{k=1}^K b_k(t)\mathbf{B}_k\mathbf{A}\right\} = \sum_{k=1}^K b_k(t) \text{Tr}\{\mathbf{B}_k\mathbf{A}\}. \quad [2.204]$$

Note that $\text{Tr}\{\mathbf{A}\mathbf{B}\}$ used in [2.204] and $\text{Tr}\{\mathbf{A}^\dagger\mathbf{B}\}$ used in [2.202] in general are not equal unless \mathbf{A} is a Hermitian operator. The time evolution of the density operator can be expressed, by substitution of [2.201] into [2.53] and [2.54], as

$$\frac{d\sigma(t)}{dt} = -i[\mathcal{H}, \sigma(t)] = -i \sum_{k=1}^K b_k(t)[\mathcal{H}, \mathbf{B}_k], \quad [2.205]$$

$$\sigma(t) = \exp\{-i\mathcal{H}t\}\sigma(0)\exp\{i\mathcal{H}t\} = \sum_{k=1}^K b_k(0)\exp\{-i\mathcal{H}t\}\mathbf{B}_k\exp\{i\mathcal{H}t\}. \quad [2.206]$$

The usefulness of [2.204]–[2.206] is that the evolution of the density operator and expectation values can be calculated from a limited number of trace operations $\text{Tr}\{\mathbf{B}_k\mathbf{B}_j\}$ and transformation rules for $\exp\{-i\mathcal{H}t\}\mathbf{B}_k\exp\{i\mathcal{H}t\}$.

A transformation of the density operator is formally described as a rotation of an initial density operator σ^1 to a new operator σ^2 under the effect of a particular Hamiltonian, \mathcal{H} . The notation to be employed has the form

$$\sigma^1 \xrightarrow{\mathcal{H}t} \sigma^2, \quad [2.207]$$

which represents the formal expression:

$$\sigma^2 = \exp\{-i\mathcal{H}t\}\sigma^1\exp\{i\mathcal{H}t\}. \quad [2.208]$$

If \mathcal{H} and σ are expressed in terms of the angular momentum operators, then the solutions to [2.208] are given by the expressions derived in

Section 2.3. These solutions can be applied as a recipe by using a simple set of rules, which are presented in Section 2.7.3. The Hamiltonians of most interest in solution NMR consist of one or more of four interactions: (1) rf pulse, (2) chemical shift, (3) scalar coupling, and (4) residual dipolar coupling. Most importantly, in the weak coupling regime, the chemical shift, scalar, and residual dipolar coupling interactions commute with each other. Note that throughout this analysis relaxation of the spins back to equilibrium is not considered.

2.7.2 BASIS OPERATORS

The choice of basis operators is determined by the problem at hand at any specific time. For example, the angular momentum operators I_x , I_y , and I_z , which represent the x -, y -, and z -components of the spin angular momentum of the system, are particularly useful for calculating the effects of rf pulses, whereas the shift operators, I^+ and I^- , are particularly suited to evaluating evolution under the free-precession Hamiltonian. For a *single spin*, the state of a magnetization vector can be specified by the amounts of x , y , and z magnetization. In the same way, the quantum mechanical state of the system can be described by specifying the magnitudes of the operators that are present at any time. Formally, the state of the system is specified by the density operator and the density operator is expressed as a linear combination of operators. In most cases, Cartesian basis operators ($\mathbf{E}/2, I_x, I_y, I_z$), will be employed. Other basis sets, such as the single-element ($I^\alpha, I^\beta, I^+, I^-$) basis operators, defined using the Dirac notation as

$$\begin{aligned} I^\alpha &= |\alpha\rangle\langle\alpha|, & I^+ &= |\alpha\rangle\langle\beta|, \\ I^\beta &= |\beta\rangle\langle\beta|, & I^- &= |\beta\rangle\langle\alpha|, \end{aligned} \quad [2.209]$$

and the shift basis operators ([2.191]), are also useful. The Cartesian and single-element basis sets are related by

$$\begin{aligned} I_z &= \frac{1}{2}(I^\alpha - I^\beta), & I_x &= \frac{1}{2}(I^+ + I^-), \\ I_y &= \frac{1}{2i}(I^+ - I^-), & \frac{1}{2}\mathbf{E} &= \frac{1}{2}(I^\alpha + I^\beta). \end{aligned} \quad [2.210]$$

Levitt notes that the three Cartesian operators form a three-dimensional space in which the density operator, represented by a vector \mathbf{I} , rotates at a frequency $|\boldsymbol{\omega}| = (\boldsymbol{\omega} \cdot \boldsymbol{\omega})^{1/2}$ about a vector $\boldsymbol{\omega}$, with Cartesian components

$$\omega_x = \omega_1 \cos\phi, \quad \omega_y = \omega_1 \sin\phi, \quad \omega_z = \Omega, \quad [2.211]$$

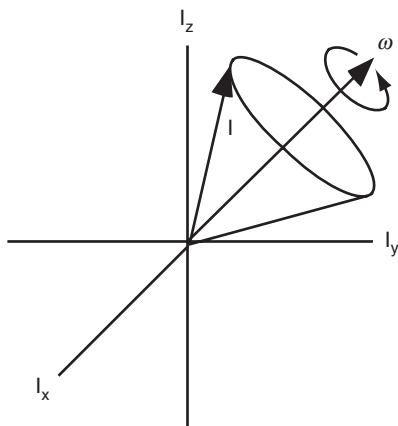


FIGURE 2.3 Geometrical representations of rotations in an operator space: precession of the angular momentum operator about the effective field direction in angular momentum operator space.

where Ω is the resonance offset, ϕ is the phase of an applied rf pulse, and $\omega_1 = -\gamma B_1$, and B_1 is the rf field strength (13). This geometrical interpretation of the Cartesian operator space is illustrated in Fig. 2.3. The identity operator \mathbf{E} is independent of rotation.

Single-transition shift operators can be defined in terms of the Cartesian components or as products of kets and bras,

$$\begin{aligned} I^+(rs) &= I_x(rs) + iI_y(rs) = |r\rangle\langle s|, \\ I^-(rs) &= I_x(rs) - iI_y(rs) = |s\rangle\langle r|. \end{aligned} \quad [2.212]$$

As noted by Ernst (2), the indices are ordered such that $M_r > M_s$, as defined by [2.139], to ensure that the raising and lowering operators increase and decrease the magnetic quantum numbers, respectively:

$$I^+(rs)|s\rangle = |r\rangle, \quad I^-(rs)|r\rangle = |s\rangle. \quad [2.213]$$

For the one-spin case, the eigenstates are $|\alpha\rangle$ and $|\beta\rangle$, and the density operator can be expanded in terms of the basis operators I^α , I^β , I^+ , and I^- . In this case, for example, $I^-|\alpha\rangle = |\beta\rangle\langle\alpha|\alpha\rangle = |\beta\rangle$ because the eigenstate $|\alpha\rangle$ is associated with $m=+1/2$ and $|\beta\rangle$ is associated with $m=-1/2$. Similarly $I^+|\beta\rangle = |\alpha\rangle\langle\beta|\beta\rangle = |\alpha\rangle$.

The potential of the product operator approach becomes evident in the case of two weakly scalar coupled spins. Each pair of spins has four

eigenstates, $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$, and $|\beta\beta\rangle$, where the first symbol in each represents the state of the I spin and the second symbol represents the S spin. The single-element operator basis set contains four so-called population terms:

$$\begin{aligned} |\alpha\alpha\rangle\langle\alpha\alpha| &= I^\alpha S^\alpha, & |\alpha\beta\rangle\langle\alpha\beta| &= I^\alpha S^\beta, \\ |\beta\alpha\rangle\langle\beta\alpha| &= I^\beta S^\alpha, & |\beta\beta\rangle\langle\beta\beta| &= I^\beta S^\beta. \end{aligned} \quad [2.214]$$

The basis set contains eight terms representing the *single-quantum transitions* associated with the two spins (remembering the definitions of [2.209]):

$$\begin{aligned} |\alpha\alpha\rangle\langle\alpha\beta| &= I^\alpha S^+, & |\alpha\beta\rangle\langle\alpha\alpha| &= I^\alpha S^-, \\ |\beta\alpha\rangle\langle\beta\beta| &= I^\beta S^+, & |\beta\beta\rangle\langle\beta\alpha| &= I^\beta S^-, \\ |\alpha\alpha\rangle\langle\beta\alpha| &= I^+ S^\alpha, & |\beta\alpha\rangle\langle\alpha\alpha| &= I^- S^\alpha, \\ |\alpha\beta\rangle\langle\beta\beta| &= I^+ S^\beta, & |\beta\beta\rangle\langle\alpha\beta| &= I^- S^\beta. \end{aligned} \quad [2.215]$$

In these cases, one spin remains “untouched” and the transition involves only the change in spin state of the other spin. These operators describe the *single-quantum coherences* associated with the single-quantum transitions. The basis set contains four terms representing transitions in which both spins change their spin state simultaneously. These coherences are classified as *double-quantum coherence* if both spins change spin states in the same sense,

$$|\alpha\alpha\rangle\langle\beta\beta| = I^+ S^+, \quad |\beta\beta\rangle\langle\alpha\alpha| = I^- S^-, \quad [2.216]$$

or *zero-quantum coherence* if both spins change spin states in the opposite sense,

$$|\alpha\beta\rangle\langle\beta\alpha| = I^+ S^-, \quad |\beta\alpha\rangle\langle\alpha\beta| = I^- S^+. \quad [2.217]$$

Each of these product operators has a simple interpretation in terms of energy levels and transitions shown in Fig. 2.4. For N scalar coupled spins-1/2, a full operator set contains 4^N elements.

The relationship between the Cartesian and single-element operators [2.210] can be seen as, for example,

$$\begin{aligned} I_z &= 2(I_z)(\tfrac{1}{2}\mathbf{E}) = \tfrac{1}{2}(I^\alpha - I^\beta)(S^\alpha + S^\beta), \\ S_x &= 2(\tfrac{1}{2}\mathbf{E})(S_x) = \tfrac{1}{2}(I^\alpha + I^\beta)(S^+ + S^-), \\ 2I_z S_y &= 2(I_z)(S_y) = \tfrac{1}{2i}(I^\alpha - I^\beta)(S^+ - S^-). \end{aligned} \quad [2.218]$$

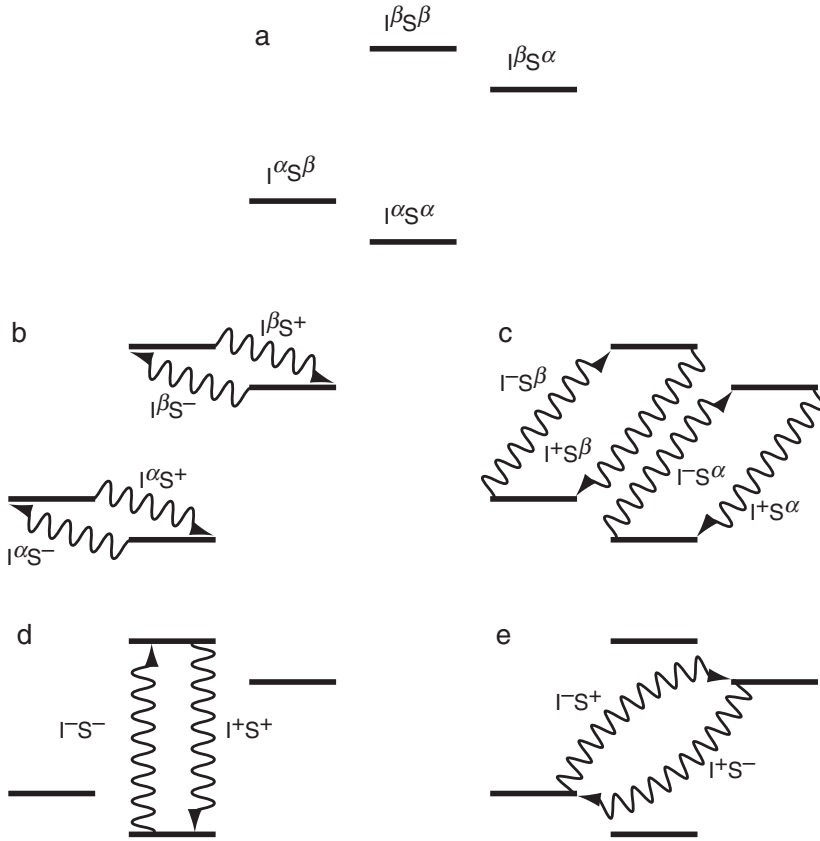


FIGURE 2.4 Single-transition-basis operators for IS spin system. (a) Populations, (b) S-spin and (c) I-spin single-quantum coherences, (d) double-quantum coherences, and (e) zero-quantum coherences.

The operators have physical interpretations; for example,

$$\mathbf{E} = I^{\alpha}S^{\alpha} + I^{\alpha}S^{\beta} + I^{\beta}S^{\alpha} + I^{\beta}S^{\beta} \quad [2.219]$$

denotes equal populations of all energy levels, and

$$I_z = \frac{1}{2} (I^{\alpha}S^{\alpha} + I^{\alpha}S^{\beta} - I^{\beta}S^{\alpha} - I^{\beta}S^{\beta}) \quad [2.220]$$

denotes equal polarization across the two single-quantum transitions of the I spin.

2.7.3 EVOLUTION IN THE PRODUCT OPERATOR FORMALISM

The goal of the product operator formalism is to derive the evolution of a spin system through a particular pulse sequence as conveniently as possible. Effects of pulses and delays in terms of Cartesian product operators are extremely simple, because each factor of the product is rotated independently. Rotation operator equations similar to [2.136] can be derived by the matrix derivations established previously; however, this approach is rather laborious. Instead, the rules for transformations of product operators can be established using the following useful theorem: if three operators satisfy the commutation relationship (and its cyclic permutations)

$$[\mathbf{A}, \mathbf{B}] = i\mathbf{C}, \quad [2.221]$$

then

$$\exp(-i\theta\mathbf{C})\mathbf{A}\exp(-i\theta\mathbf{C}) = \mathbf{A}\cos\theta + \mathbf{B}\sin\theta. \quad [2.222]$$

Equation [2.222] can be verified by differentiating $\exp(-i\theta\mathbf{C})\mathbf{A}\exp(i\theta\mathbf{C})$ twice with respect to θ , applying the commutation relations and solving the resulting harmonic differential equation. The evolution indicated by [2.222] can be illustrated succinctly by Fig. 2.5.

2.7.3.1 Free Precession During periods of free precession, the effects of chemical shift evolution and scalar coupling evolution must be considered. For a spin I , the chemical shift Hamiltonian has the form $\mathcal{H} = \Omega_I I_z$, where Ω_I is the offset of spin I . Evolution during a delay, t , is described by

$$I_x \xrightarrow{\Omega_I I_z t} I_x \cos(\Omega_I t) + I_y \sin(\Omega_I t), \quad [2.223]$$

$$I_y \xrightarrow{\Omega_I I_z t} I_y \cos(\Omega_I t) - I_x \sin(\Omega_I t), \quad [2.224]$$

$$I_z \xrightarrow{\Omega_I I_z t} I_z. \quad [2.225]$$

For a weakly coupled two-spin system, I and S , the scalar coupling Hamiltonian has the form $\mathcal{H} = 2\pi J_{IS} I_z S_z$, where J_{IS} is the scalar coupling constant. Evolution of the single-spin operators during a delay, t , is described by

$$I_x \xrightarrow{2\pi J_{IS} I_z S_z t} I_x \cos(2\pi J_{IS} t) + 2I_y S_z \sin(2\pi J_{IS} t), \quad [2.226]$$

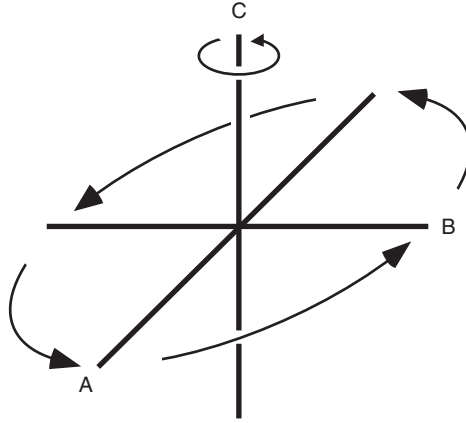


FIGURE 2.5 Operator rotations. The rotations induced by an operator C acting on an operator A are illustrated. The operators satisfy the commutation relationship [2.221] and the rotations are represented mathematically by [2.222].

$$I_y \xrightarrow{2\pi J_{IS} I_z S_z t} I_y \cos(2\pi J_{IS} t) - 2I_x S_z \sin(2\pi J_{IS} t), \quad [2.227]$$

$$I_z \xrightarrow{2\pi J_{IS} I_z S_z t} I_z. \quad [2.228]$$

Equations [2.226] and [2.227] demonstrate that single-spin operators evolve into two-spin operators under the influence of the scalar coupling interaction. The analogous evolution of the two-spin operators, $2I_\eta S_z$, is given by

$$2I_x S_z \xrightarrow{2\pi J_{IS} I_z S_z t} 2I_x S_z \cos(2\pi J_{IS} t) + I_y \sin(2\pi J_{IS} t), \quad [2.229]$$

$$2I_y S_z \xrightarrow{2\pi J_{IS} I_z S_z t} 2I_y S_z \cos(2\pi J_{IS} t) - I_x \sin(2\pi J_{IS} t), \quad [2.230]$$

$$2I_z S_z \xrightarrow{2\pi J_{IS} I_z S_z t} 2I_z S_z. \quad [2.231]$$

Evolution of the S_η and $2I_z S_\eta$ operators is obtained by exchanging the I and S labels in [2.223]–[2.231].

2.7.3.2 Pulses On-resonance rf pulses applied along a specific axis induce rotations in a plane orthogonal to that axis. The Hamiltonian

expression describing the pulses can be written as $\mathcal{H}t = \alpha I_x$ or αI_y , for an x -pulse or y -pulse, respectively, and α is the flip angle of the pulse. Pulses of arbitrary phase or that include the effects of resonance offset can be obtained using composite rotations as in [2.120]. The transformations for a pulse of phase $\pm x$ are given by

$$I_x \xrightarrow{\alpha I_{\pm x}} I_x, \quad [2.232]$$

$$I_y \xrightarrow{\alpha I_{\pm x}} I_y \cos \alpha \pm I_z \sin \alpha, \quad [2.233]$$

$$I_z \xrightarrow{\alpha I_{\pm x}} I_z \cos \alpha \mp I_y \sin \alpha, \quad [2.234]$$

and, for a pulse of phase $\pm y$,

$$I_x \xrightarrow{\alpha I_{\pm y}} I_x \cos \alpha \mp I_z \sin \alpha, \quad [2.235]$$

$$I_y \xrightarrow{\alpha I_{\pm y}} I_y, \quad [2.236]$$

$$I_z \xrightarrow{\alpha I_{\pm y}} I_z \cos \alpha \pm I_x \sin \alpha. \quad [2.237]$$

These transformations of the product operators are illustrated geometrically in Fig. 2.6.

2.7.3.3 Practical Points The preceding rules enable description of a wide variety of pulsed NMR experiments. Before examining some very useful specific examples, some formalities and practical points will be presented.

Cascades. During a period of free precession for the two-spin system I and S , the evolution of the density operator is represented as

$$\sigma^1 \xrightarrow{\Omega_I I_z t + \Omega_S S_z t + 2\pi J_{IS} I_z S_z t} \sigma^4. \quad [2.238]$$

Because each term in this Hamiltonian commutes with the others, the one evolution period can be divided into a series of rotations or a *cascade*,

$$\sigma^1 \xrightarrow{\Omega_I I_z t} \sigma^2 \xrightarrow{\Omega_S S_z t} \sigma^3 \xrightarrow{2\pi J_{IS} I_z S_z t} \sigma^4. \quad [2.239]$$

The order in which the rotations due to shift and coupling evolution are applied is unimportant. Likewise, the effect of a nonselective pulse applied to the I and S spins is written as

$$\sigma^1 \xrightarrow{\alpha(I_x + S_x)} \sigma^3. \quad [2.240]$$

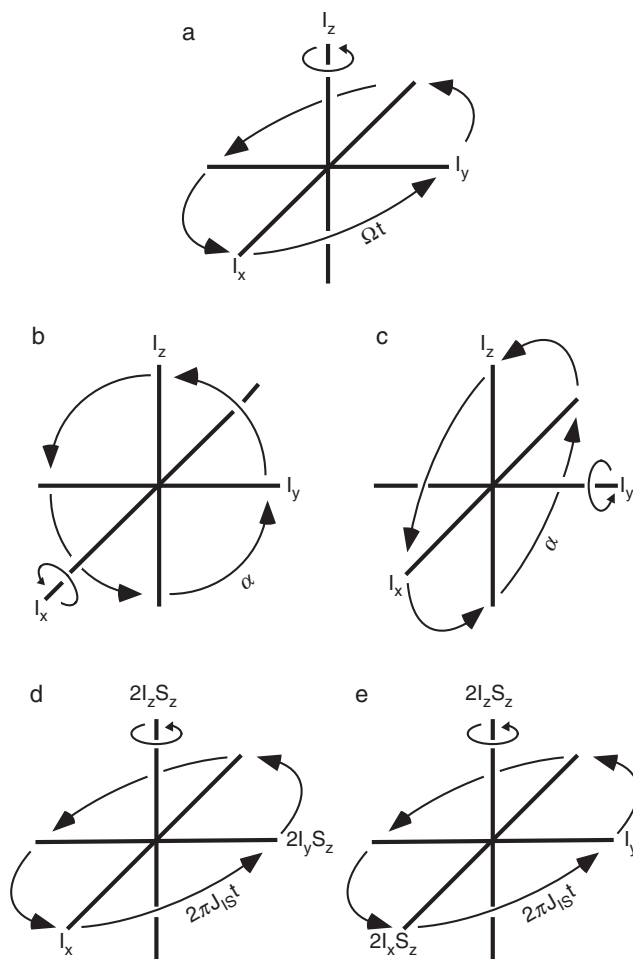


FIGURE 2.6 Transformations of product operators. The product operator transformations given in [2.225]–[2.237] are represented geometrically. (a) Transformations under the chemical shift Hamiltonian, (b) rotations induced by a pulse of x -phase, (c) rotations induced by a pulse of y -phase, and (c)–(d) transformations under the scalar coupling Hamiltonian.

Because I and S operators commute, a nonselective pulse can be represented by a pulse on I first, followed by a pulse on S (or by a pulse acting on S followed by a pulse acting on I),

$$\sigma^1 \xrightarrow{\alpha I_x} \sigma^2 \xrightarrow{\alpha S_x} \sigma^3. \quad [2.241]$$

Rotations of products. The effect of a pulse applied selectively to the S spin of a product term such as $2I_x S_z$ is obtained using the rule that rotations only affect operators of the same spin. In other words, the I_x part of the product operator remains untouched by the pulse to the S spin and the S_z term is rotated normally. The result obtained is

$$2I_x S_z \xrightarrow{\alpha S_x} 2I_x S_z \cos \alpha - 2I_x S_y \sin \alpha. \quad [2.242]$$

Rotations involving the same operator. Operators are unaffected by rotations about themselves because an operator and the exponential of an operator commute. For example,

$$I_x \xrightarrow{\alpha I_x} I_x, \quad [2.243]$$

$$2I_y S_z \xrightarrow{\Omega_S S_z t} 2I_y S_z. \quad [2.244]$$

2.7.4 SINGLE-QUANTUM COHERENCE AND OBSERVABLE OPERATORS

The single-quantum coherence term I_x can be expressed using [2.210] and [2.218] as

$$I_x = \frac{1}{2}(I^+ S^\alpha + I^- S^\alpha) + \frac{1}{2}(I^+ S^\beta + I^- S^\beta). \quad [2.245]$$

This operator, involving a transverse Cartesian component, results from the sum of the single-quantum transitions of the I spin. Evolution under the free-precession Hamiltonian yields

$$\begin{aligned} \exp\{-i\mathcal{H}t\} I_x \exp\{i\mathcal{H}t\} = & \frac{1}{2}(I^+ S^\alpha \exp[-i(\Omega_I + \pi J)t] \\ & + I^- S^\alpha \exp[i(\Omega_I + \pi J)t]) \\ & + \frac{1}{2}(I^+ S^\beta \exp[-i(\Omega_I - \pi J)t] \\ & + I^- S^\beta \exp[i(\Omega_I - \pi J)t]). \end{aligned} \quad [2.246]$$

The trace of this result with the observation operator, ignoring for convenience the constants of proportionality, yields

$$\text{Tr}\{\exp[-i\mathcal{H}t]I_x \exp[i\mathcal{H}t]\mathbf{F}^+\} = \frac{1}{2} \exp[i(\Omega_I + \pi J)t] + \frac{1}{2} \exp[i(\Omega_I - \pi J)t]. \quad [2.247]$$

Both terms comprising the detected signal are *positive*, indicating an *in-phase* component of the x -magnetization. The frequencies of the two components of the in-phase signal are separated by the scalar coupling between the two spins. *An operator with a single transverse Cartesian component is observable.* Another example of a single-quantum coherence operator is

$$2I_x S_z = \frac{1}{2}(I^+ S^\alpha + I^- S^\alpha) - \frac{1}{2}(I^+ S^\beta + I^- S^\beta). \quad [2.248]$$

Evolution under the free-precession Hamiltonian yields

$$\begin{aligned} \exp\{-i\mathcal{H}t\}2I_x S_z \exp\{i\mathcal{H}t\} &= \frac{1}{2}(I^+ S^\alpha \exp[-i(\Omega_I + \pi J)t] \\ &\quad + I^- S^\alpha \exp[i(\Omega_I + \pi J)t]) \\ &\quad - \frac{1}{2}(I^+ S^\beta \exp[-i(\Omega_I - \pi J)t] \\ &\quad + I^- S^\beta \exp[i(\Omega_I - \pi J)t]). \end{aligned} \quad [2.249]$$

The trace of this result with the observation operator yields

$$\begin{aligned} \text{Tr}\{\exp[-i\mathcal{H}t]2I_x S_z \exp[i\mathcal{H}t]\mathbf{F}^+\} \\ = \frac{1}{2} \exp[i(\Omega_I + \pi J)t] - \frac{1}{2} \exp[i(\Omega_I - \pi J)t]. \end{aligned} \quad [2.250]$$

In this case, the contributions from the S spin are of opposite sign, indicating an *antiphase* x -component of the magnetization on the I spin, in which the two components of the signal have opposite sign. Formally, the antiphase terms are not directly observable in the sense that, at a particular instant, a term such as $2I_x S_z$ does not contribute to the observed x -magnetization. However, antiphase operators will evolve under the influence of the scalar coupling interaction, provided that I and S have a nonzero scalar coupling constant, into an in-phase operator that is detectable. Analogous terms for the I spin product operator involving y -components are similar except that the phase of the magnetization is shifted by 90° .

The preceding detailed calculations are not necessary in practice, because the form of the observable signal can be determined by inspection of the coherences present at the start of the acquisition period. For a system of N spins, the operators I_{ix} and I_{iy} ($1 \leq i \leq N$) are

observable and generate in-phase resonance signals. Operators of the form $I_{1z} \dots I_{(i-1)z} I_{ix} I_{(i+1)z} \dots I_{kz}$ and $I_{1z} \dots I_{(i-1)z} I_{iy} I_{(i+1)z} \dots I_{kz}$ evolve into I_{ix} and I_{iy} and generate antiphase resonance signals if $J_{1i} \dots, J_{(i-1)i}, J_{(i+1)i} \dots, J_{ki}$ are all nonzero, for $k \leq N$. The resonance signals generated by operators containing I_{ix} and I_{iy} have a 90° relative phase difference. If the signals arising from I_{ix} are phased to have absorptive lineshapes, then the signals arising from I_{iy} will have dispersive lineshapes.

In spin systems with $N \geq 3$, single-quantum coherences with >1 transverse factors in their operator representations exist and are referred to as combination lines, combination operators, or N -spin ± 1 coherences (14, 15). For example, in an $N=3$ spin system, the single-quantum combination coherence $|\beta\beta\alpha\rangle\langle\alpha\alpha\beta|$ has $\Delta m = -1$ and is represented by the operator $I_1^- I_2^- I_3^+$. In the weak coupling limit, combination operators are orthogonal to the detection operator and consequently are not directly observable during the acquisition period. In the strong coupling limit, the product wavefunctions are not eigenfunctions of the Hamiltonian [2.154]; eigenfunctions are obtained by diagonalizing the Hamiltonian as described in Section 2.5.2. The appearance of combination lines in strongly coupled NMR spectra is discussed by Bain (16) and references therein.

2.7.5 MULTIPLE-QUANTUM COHERENCE

For a system of two spin-1/2 nuclei, multiple-quantum coherence states are represented by product operators in which both spins have transverse components. For example,

$$2I_x S_y = \frac{1}{2i}(I^+ S^+ - I^- S^-) - \frac{1}{2i}(I^+ S^- - I^- S^+). \quad [2.251]$$

The first term on the right-hand side, $(I^+ S^+ - I^- S^-)$, is pure double-quantum coherence ($|\Delta m| = 2$), whereas the second term, $(I^+ S^- - I^- S^+)$, is pure zero-quantum coherence ($\Delta m = 0$). The multiple-quantum coherence term $2I_x S_y$ is a superposition of both double- and zero-quantum coherence. Multiple-quantum coherences can be prepared by suitable combinations of pulses and free-precession periods. Such terms have more than one transverse operator component and are not observable directly; however, multiple-quantum coherences possess some unique properties of considerable utility.

Multiple-quantum coherences can be expressed conveniently in terms of Cartesian and/or shift operators. Pure double-quantum (DQ)

coherence is represented by suitable combinations of bilinear product operators,

$$\frac{1}{2}(I^+S^+ + I^-S^-) = \frac{1}{2}(2I_xS_x - 2I_yS_y) = DQ_x, \quad [2.252]$$

$$\frac{1}{2i}(I^+S^+ - I^-S^-) = \frac{1}{2}(2I_xS_y + 2I_yS_x) = DQ_y. \quad [2.253]$$

Pure double-quantum coherence precesses at the *sum* of the two chemical shifts involved, e.g., during a delay, t ,

$$DQ_x \xrightarrow{\Omega_I I_z t + \Omega_S S_z t} DQ_x \cos[(\Omega_I + \Omega_S)t] + DQ_y \sin[(\Omega_I + \Omega_S)t], \quad [2.254]$$

$$DQ_y \xrightarrow{\Omega_I I_z t + \Omega_S S_z t} DQ_y \cos[(\Omega_I + \Omega_S)t] - DQ_x \sin[(\Omega_I + \Omega_S)t]. \quad [2.255]$$

Similarly, pure zero-quantum (ZQ) coherence is represented by

$$\frac{1}{2}(I^+S^- + I^-S^+) = \frac{1}{2}(2I_xS_x + 2I_yS_y) = ZQ_x, \quad [2.256]$$

$$\frac{1}{2i}(I^+S^- - I^-S^+) = \frac{1}{2}(2I_yS_x - 2I_xS_y) = ZQ_y, \quad [2.257]$$

and evolution occurs at the *difference* of the chemical shifts of the spins involved,

$$ZQ_x \xrightarrow{\Omega_I I_z t + \Omega_S S_z t} ZQ_x \cos[(\Omega_I - \Omega_S)t] + ZQ_y \sin[(\Omega_I - \Omega_S)t], \quad [2.258]$$

$$ZQ_y \xrightarrow{\Omega_I I_z t + \Omega_S S_z t} ZQ_y \cos[(\Omega_I - \Omega_S)t] - ZQ_x \sin[(\Omega_I - \Omega_S)t]. \quad [2.259]$$

Two-spin multiple-quantum coherence such as that noted previously, *does not evolve under the influence of the scalar coupling of the two spins involved in the coherence (the active coupling)*. This principle can be rationalized using [1.57] and the energy level diagram of Fig. 1.7b. Double-quantum coherence connects the states $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$. The difference in energy between these two states does not depend on the active scalar coupling constant. Similar considerations are relevant for zero-quantum coherence that connects states $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$. However, multiple-quantum coherence can evolve under the influence of a scalar coupling to a third *passive* spin. For example, consider the three-spin system I , S , R , where the couplings present are J_{IS} , J_{IR} , and J_{SR} . A multiple-quantum coherence term can be identified by the appearance of more than one transverse Cartesian operator in the product; therefore, the operator, $4I_yS_xR_z$, is a multiple-quantum coherence with

respect to I and S . This operator evolves under the J_{IR} and J_{SR} scalar coupling interactions but not under the J_{IS} scalar coupling interaction. Evolution under the J_{IR} scalar coupling interaction is given by

$$4I_y S_x R_z \xrightarrow{2\pi J_{IR} I_z R_z} 4I_y S_x R_z \cos(\pi J_{IR} t) - 2I_x S_x \sin(\pi J_{IR} t). \quad [2.260]$$

Evolution of multiple-quantum coherences under the scalar coupling interaction proceeds at the sum and difference frequencies of the passive scalar coupling constants in a manner analogous to the chemical shift evolution. For example, consider the zero-quantum term $ZQ_y^{IS} = \frac{1}{2}(2I_y S_x - 2I_x S_y)$ evolving under the passive coupling effects J_{IR} and J_{SR} for a time t ,

$$ZQ_y^{IS} \xrightarrow{2\pi J_{IR} I_z R_z + 2\pi J_{SR} I_z R_z} ZQ_y^{IS} \cos(\pi K_{IS} t) - 2ZQ_x^{IS} R_z \sin(\pi K_{IS} t), \quad [2.261]$$

in which $K_{IS} = |J_{SR} - J_{IR}|$ is known as the *zero-quantum splitting*, and

$$2ZQ_x^{IS} R_z = \frac{1}{2}(2I_x S_x + 2I_y S_y) R_z. \quad [2.262]$$

2.7.6 COHERENCE TRANSFER AND GENERATION OF MULTIPLE-QUANTUM COHERENCE

Coherence transfer is a vital effect in multidimensional NMR spectroscopy, and, most notably, an effect that cannot be described in the Bloch model. Suppose that an antiphase component, $2I_x S_z$, of the density operator has been generated in some manner. As will be discussed later, antiphase operators can be produced by the use of a spin echo pulse sequence. The effect of applying a 90_y° pulse to both spins is

$$2I_x S_z \xrightarrow{\frac{\pi}{2} I_y} -2I_z S_z \xrightarrow{\frac{\pi}{2} S_y} 2I_z S_x. \quad [2.263]$$

The original antiphase coherence on the I spin (containing a single transverse operator) is converted to antiphase coherence on the S spin. *Coherence has been transferred from one spin to another under the influence of the rf pulse.*

In contrast, application of a 90_x° to both spins gives

$$2I_x S_z \xrightarrow{\frac{\pi}{2}(I_x + S_x)} -2I_x S_y. \quad [2.264]$$

This operator represents multiple-quantum coherence (containing more than one transverse operator). The same result would be obtained if a pulse is applied to the S spin alone,

$$2I_x S_z \xrightarrow{\frac{\pi}{2} S_x} -2I_x S_y. \quad [2.265]$$

The two examples represented by [2.264] and [2.265] represent the generation of multiple-quantum coherences in homonuclear and heteronuclear spin systems, respectively.

2.7.7 EXAMPLES OF PRODUCT OPERATOR CALCULATIONS

Some simple examples using product operators to follow evolution during spin echo and polarization transfer pulse sequences will be presented. Although these examples may appear trivial, each one plays an important part as a component of more complicated pulse sequences. These pulse sequence elements will be encountered in many of the multidimensional NMR experiments discussed in Chapters 6 and 7.

2.7.7.1 The Spin Echo The spin echo pulse sequence must be examined in three cases: (a) one spin, (b) two coupled spins of the same nuclear type (homonuclear case), and (c) two coupled spins of different nuclear types (heteronuclear case).

Starting from equilibrium magnetization proportional to I_z , an initial 90_x° pulse yields

$$I_z \xrightarrow{\frac{\pi}{2} I_x} -I_y. \quad [2.266]$$

The spin echo pulse sequence for an isolated spin is written as

$$-t - 180_x^\circ - t -. \quad [2.267]$$

Evolution during the period of free precession, t , yields

$$-I_y \xrightarrow{\Omega_I I_z t} -I_y \cos(\Omega_I t) + I_x \sin(\Omega_I t). \quad [2.268]$$

The 180_x° pulse converts this density operator to

$$-I_y \cos(\Omega_I t) + I_x \sin(\Omega_I t) \xrightarrow{\pi I_x} I_y \cos(\Omega_I t) + I_x \sin(\Omega_I t). \quad [2.269]$$

The 180_x° pulse inverts the I_y term but does not affect the I_x term. The final part of the spin echo sequence is another delay of

duration t ,

$$I_y \cos(\Omega_I t) + I_x \sin(\Omega_I t) \xrightarrow{\Omega_I I_z t} I_y \cos^2(\Omega_I t) - I_x \cos(\Omega_I t) \sin(\Omega_I t) \\ + I_x \sin(\Omega_I t) \cos(\Omega_I t) + I_y \sin^2(\Omega_I t). \quad [2.270]$$

Using the identity $\cos^2\theta + \sin^2\theta = 1$, [2.270] can be written as

$$I_y \cos(\Omega_I t) + I_x \sin(\Omega_I t) \xrightarrow{\Omega_I I_z t} I_y. \quad [2.271]$$

The overall effect of the spin echo segment, $-t - 180_x^\circ - t -$, is seen to take an initial state $-I_y$ and generate a final state I_y . Apart from a sign change, no net evolution of the chemical shift occurs during the spin echo sequence: *evolution under the chemical shift Hamiltonian is refocused*. If a 180_y° pulse had been used for refocusing, then the sign inversion would not have occurred.

The same result can be demonstrated more elegantly as follows. The density operator at the end of the pulse sequence is given by $\sigma(t) = \mathbf{U}\sigma(0)\mathbf{U}^{-1}$, with

$$\mathbf{U} = \exp[-i\Omega_I t I_z] \exp[-i\pi I_x] \exp[-i\Omega_I t I_z], \quad [2.272]$$

in which each factor in \mathbf{U} represents the propagator for one segment of the spin echo sequence. Applying the identity of [2.121] yields

$$\begin{aligned} \mathbf{U} &= \exp[-i\Omega_I t I_z] \exp[-i\pi I_x] \exp[-i\Omega_I t I_z] \\ &= \exp[-i\Omega_I t I_z] \exp[-i\pi I_x] \exp[-i\Omega_I t I_z] \exp[i\pi I_x] \exp[-i\pi I_x] \\ &= \exp[-i\Omega_I t I_z] \exp[-i\Omega_I t e^{-i\pi I_x} I_z e^{i\pi I_x}] \exp[-i\pi I_x] \\ &= \exp[-i\Omega_I t I_z] \exp[i\Omega_I t I_z] \exp[-i\pi I_x] \\ &= \exp[-i\pi I_x]. \end{aligned} \quad [2.273]$$

Therefore, the *net* evolution during the spin echo sequence is given by

$$-I_y \xrightarrow{\pi I_x} I_y, \quad [2.274]$$

in agreement with [2.271]. Considerable simplification of propagators for pulse sequences containing 180° pulses is often possible by use of [2.121].

The same spin echo pulse sequence can be applied to a homonuclear IS two-spin system. The pulses are assumed to be nonselective and affect both the I and the S spins equally. As for the isolated spin, the chemical shift evolution of the I and the S spins is refocused over the spin echo sequence and can be neglected. Therefore, evolution during the pulse

sequence is due to the scalar coupling interaction only. The initial 90_x° pulse generates the $-I_y$ operator from the equilibrium operator I_z (the similar S spin term is omitted for clarity). The coupling develops during t ,

$$-I_y \xrightarrow{2\pi J_{IS} I_z S_z t} -I_y \cos(\pi J_{IS} t) + 2I_x S_z \sin(\pi J_{IS} t). \quad [2.275]$$

The 180° pulse, regarded as a 180° pulse on one spin followed by a 180° pulse on the other spin, yields

$$\begin{aligned} -I_y \cos(\pi J_{IS} t) + 2I_x S_z \sin(\pi J_{IS} t) &\xrightarrow{\pi I_x} I_y \cos(\pi J_{IS} t) + 2I_x S_z \sin(\pi J_{IS} t) \\ &\xrightarrow{\pi S_x} I_y \cos(\pi J_{IS} t) - 2I_x S_z \sin(\pi J_{IS} t). \end{aligned} \quad [2.276]$$

The 180_x° pulse applied to the I spin does not affect the S spin and *vice versa*. Evolution during the second delay, t , yields

$$\begin{aligned} I_y \cos(\pi J_{IS} t) - 2I_x S_z \sin(\pi J_{IS} t) \\ \xrightarrow{2\pi J_{IS} I_z S_z t} I_y \cos^2(\pi J_{IS} t) - 2I_x S_z \sin(\pi J_{IS} t) \cos(\pi J_{IS} t) \\ - 2I_x S_z \cos(\pi J_{IS} t) \sin(\pi J_{IS} t) - I_y \sin^2(\pi J_{IS} t), \end{aligned} \quad [2.277]$$

which, using the identities $\cos(2\theta) = \cos^2\theta - \sin^2\theta$ and $\sin(2\theta) = 2\sin\theta\cos\theta$, reduces to

$$\begin{aligned} I_y \cos(\pi J_{IS} t) - 2I_x S_z \sin(\pi J_{IS} t) \\ \xrightarrow{2\pi J_{IS} I_z S_z t} I_y \cos(2\pi J_{IS} t) - 2I_x S_z \sin(2\pi J_{IS} t). \end{aligned} \quad [2.278]$$

The overall effect of the $-t - 180_x^\circ - t$ pulse sequence on the initial $-I_y$ magnetization is given by

$$-I_y \xrightarrow{t - \pi(I_x + S_x) - t} I_y \cos(2\pi J_{IS} t) - 2I_x S_z \sin(2\pi J_{IS} t). \quad [2.279]$$

The density operator has evolved under the scalar coupling Hamiltonian for the entire spin echo period, $2t$. The result obtained for initial S_z magnetization is obtained by exchanging I and S operators in [2.279]. Setting the delay, t , to be equal to $1/(4J_{IS})$ generates the purely anti-phase term $2I_x S_z$, while having $t = 1/(2J_{IS})$ serves to produce $-I_y$. The generation of an antiphase state by this method is a common feature in many pulse sequences.

If the two scalar coupled spins belong to different nuclear species, or if sufficiently selective rf pulses can be obtained (see Chapter 3,

Section 3.4.4), then the rf pulses in the spin echo sequence can be applied to *only one* of the scalar coupled spins (the I spins in the following example). For example, the spin echo sequence can be applied selectively to the proton spins in an ^1H – ^{15}N scalar coupled spin system. Again, I spin chemical shift is refocused and can be ignored. As before, following the 90_x° pulse on the I spin, evolution occurs as follows:

$$\begin{aligned} -I_y &\xrightarrow{2\pi J_{IS}I_zS_zt} -I_y \cos(\pi J_{IS}t) + 2I_xS_z \sin(\pi J_{IS}t) \\ &\xrightarrow{\pi I_x} I_y \cos(\pi J_{IS}t) + 2I_xS_z \sin(\pi J_{IS}t). \end{aligned} \quad [2.280]$$

Only the I_y term is inverted by the 180_x° pulse; the S spin is unaffected. The second delay generates

$$\begin{aligned} &I_y \cos(\pi J_{IS}t) + 2I_xS_z \sin(\pi J_{IS}t) \\ &\xrightarrow{2\pi J_{IS}I_zS_zt} I_y \cos^2(\pi J_{IS}t) - 2I_xS_z \sin(\pi J_{IS}t) \cos(\pi J_{IS}t) \\ &\quad + 2I_xS_z \cos(\pi J_{IS}t) \sin(\pi J_{IS}t) + I_y \sin^2(\pi J_{IS}t), \end{aligned} \quad [2.281]$$

which reduces to

$$I_y \cos(\pi J_{IS}t) + 2I_xS_z \sin(\pi J_{IS}t) \xrightarrow{2\pi J_{IS}I_zS_zt} I_y. \quad [2.282]$$

So, for the heteronuclear spin echo,

$$-I_y \xrightarrow{-t - \pi I_x - t} I_y \quad [2.283]$$

and *both* the chemical shift and the heteronuclear coupling are refocused. In essence, the S spins have been decoupled from the I spins by use of the echo sequence.

The scalar coupling interaction evolves over the entire duration of the spin echo sequence in a *homonuclear spin echo* because the 180° echo pulse affects both the I and the S spins equally. By analogy, the heteronuclear scalar coupling interaction evolves over the duration of a spin echo sequence if *180° pulses are applied to both the I and the S spins simultaneously* (usually using two rf transmitter channels). The overall effect of the $-t - 180_x^\circ(I, S) - t$ pulse sequence on initial $-I_y$ magnetization is given by

$$-I_y \xrightarrow{t - \pi I_x, \pi S_x - t} I_y \cos(2\pi J_{IS}t) - 2I_xS_z \sin(2\pi J_{IS}t). \quad [2.284]$$

2.7.7.2 Insensitive Nuclei Enhanced by Polarization Transfer Pulse sequence elements can be combined to produce more complex sequences

designed to perform specific tasks. An important experiment that takes advantage of the basic schemes is the INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) sequence (17). The INEPT sequence is a crucial component of many multidimensional NMR experiments. The aim of the INEPT sequence is to transfer magnetization from a sensitive nucleus with a high magnetogyric ratio (usually protons) to a less sensitive nucleus with a lower magnetogyric ratio (e.g., nitrogen or carbon) by means of the scalar coupling interaction. By doing this, the detected signal from the heteronucleus will be increased. The INEPT sequence is written:

$$\begin{array}{llll} I \text{ spin:} & 90_x^\circ - t - & 180_x^\circ - t - & 90_y^\circ, \\ S \text{ spin:} & & 180_x^\circ & 90_x^\circ - \text{acquire}. \end{array} \quad [2.285]$$

Up to the final pair of 90° pulses, the sequence is a spin echo in which both spins have been affected by 180_x° pulses, so that chemical shift is refocused during the echo, but scalar coupling evolves fully. Beginning with equilibrium magnetization $K_I I_z$, in which $K_I = \hbar\omega_I/(4k_B T)$ [2.126],

$$K_I I_z \xrightarrow{\frac{\pi}{2} I_x - t - \pi(I_x + S_x) - t} K_I \{I_y \cos(2\pi J_{IS}t) - 2I_x S_z \sin(2\pi J_{IS}t)\}. \quad [2.286]$$

A 90_y° pulse is applied to the I spin, and a 90_x° pulse is applied to the S spin,

$$\begin{aligned} & K_I \{I_y \cos(2\pi J_{IS}t) - 2I_x S_z \sin(2\pi J_{IS}t)\} \\ & \xrightarrow{\frac{\pi}{2}(I_y + S_x)} K_I \{I_y \cos(2\pi J_{IS}t) - 2I_z S_y \sin(2\pi J_{IS}t)\}. \end{aligned} \quad [2.287]$$

If the delay $t = 1/(4J_{IS})$, then the final signal is given by $-[\hbar\omega_I/(4k_B T)]2I_z S_y$. The antiphase I spin magnetization has been transferred to the S spin. The antiphase term is scaled by a factor of $\hbar\omega_I/(4k_B T)$. This is an important advantage over simply recording a spectrum on the S spin following the application of a simple 90° pulse. In this case, after a 90_x° pulse is applied to the S spin, the observable magnetization is given by $-[\hbar\omega_S/(4k_B T)]S_y$, which is an in-phase doublet. The intensity ratio between the INEPT and conventional experiment is given by

$$\frac{\text{INEPT}}{\text{Conventional}} = \frac{\gamma_I}{\gamma_S} \quad [2.288]$$

The advantage of performing the INEPT experiment becomes enormous as the magnetogyric ratio of the S spin decreases. INEPT procedures are used with great effect in multidimensional heteronuclear NMR

experiments. An additional advantage of the INEPT experiment, sometimes overlooked, is that the repetition rate of the experiment is set by the relaxation time constants of the I spin rather than the S spin. Typically, the I spin is proton, and the time constants can be notably shorter than the relaxation time constants are for the S spins (see Chapter 5).

2.7.7.3 Refocused INEPT NMR spectroscopy is a relatively insensitive technique because, as has been noted in Chapter 1 (Section 1.1), the differences in populations between stationary states of a nuclear spin are very small numbers. Maximizing the sensitivity of NMR experiments consequently is a major concern. The amplitudes of the resonance signals in a scalar coupled heteronuclear spin system can be increased dramatically by *decoupling* the spins involved in the scalar coupling interaction. Decoupling reduces the effect of the scalar coupling constant with the result that the signal normally observed as a multiplet is collapsed into a singlet resonance at the Larmor frequency of the unperturbed spin. Sensitivity is increased because the amplitude of the singlet is given by the sum of the amplitudes of the multiplet components. As will be discussed in Chapter 3 (Section 3.5), decoupling can be achieved by the application of a suitable rf field on one of the spins in a heteronuclear scalar coupled spin system.

As the following example indicates, increased sensitivity is not obtained necessarily by application of a decoupling field to an arbitrary coherence. If a decoupling field is applied to the I spins during detection of the S spins following the INEPT sequence introduced in the previous section, the resonance signal disappears completely. Following the INEPT sequence, the density operator is proportional to $2I_zS_y$. Decoupling prevents evolution of this operator into observable in-phase single-quantum S_x coherence under the influence of the scalar coupling Hamiltonian (Section 2.7.4). Viewed another way, the $2I_zS_y$ operator represents an *antiphase* doublet, in which one multiplet component of the doublet is *positive* and the other component is *negative*. Collapsing the doublet by decoupling the I spins results in the mutual cancellation of the doublet components of opposite sign. Constructive interference between multiplet components is obtained only if the decoupling field is applied to an in-phase operator (with respect to the decoupled spin).

Re-examination of the INEPT experiment indicates that the antiphase coherence $2I_zS_y$ can be converted into in-phase coherence by an appropriate extension to the INEPT pulse sequence. The ensuing

refocused INEPT experiment (18) can now be written as

$$\begin{array}{lllll} I \text{ spin:} & 90_x^\circ - t - & 180_x^\circ - t - & 90_y^\circ - \tau - & 180_x^\circ - \tau - \text{decouple,} \\ S \text{ spin:} & & 180_x^\circ & 90_x^\circ & 180_x^\circ \text{ acquire.} \end{array} \quad [2.289]$$

By setting $\tau = 1/(4J_{IS})$, the final echo component of the sequence yields

$$-K_I 2I_z S_y \xrightarrow{\tau - \pi(I_x + S_x) - \tau} K_I S_x. \quad [2.290]$$

This is an in-phase doublet and can now be decoupled to give enhanced sensitivity in the spectrum. As will be discussed in Chapter 7 (Section 7.1.1.3), the value of τ required for optimal sensitivity in a refocused INEPT sequence depends upon the nature of the spin system and must be adjusted appropriately for spin systems other than the two-spin system considered in this example.

The S_x operator obtained following the refocused INEPT sequence can be converted to an S_z operator by application of a 90_y° pulse to the S spin:

$$K_I S_x \xrightarrow{\frac{\pi}{2} S_{-y}} K_I S_z. \quad [2.291]$$

The equilibrium magnetization for the S spin is proportional to $K_S S_z$; therefore, the remarkable result is obtained that the Boltzmann population difference for the I spin has been transferred to the S spin by the refocused INEPT pulse sequence.

2.7.7.4 Spin-State Selective Polarization Transfer Numerous modern NMR experiments, including Transverse Relaxation Optimized Spectroscopy (TROSY; Chapter 7) and measurements of scalar and residual dipolar coupling constants (Chapter 7), utilize pulse sequence elements that transfer polarization between operators in the single-element basis, corresponding to transfer of coherence between individual transitions or between spin states. Although useful in their own right, these methods also provide additional insights into the behavior of spin systems that continue to lead to new applications. For example, the pulse sequence element

$$\begin{array}{llll} I \text{ spin:} & & 180_x^\circ & 180_x^\circ, \\ S \text{ spin:} & 90_x^\circ - t - & 180_x^\circ - t - & 90_y^\circ, \end{array} \quad [2.292]$$

with $t = 1/(4J_{IS})$, is called the spin-state-selective coherence transfer (S^3CT) sequence element (19). The propagator corresponding to this sequence is given by

$$\begin{aligned}
 U &= \exp\left(-i\frac{\pi}{2}S_y\right) \exp(-i\pi I_x) \exp(-i\mathcal{H}t) \exp[-i\pi(I_x + S_x)] \\
 &\quad \times \exp(-i\mathcal{H}t) \exp\left(-i\frac{\pi}{2}S_x\right) \\
 &= \exp\left(-i\frac{\pi}{2}S_y\right) \exp(-i\pi S_x) \exp\left(-i\frac{\pi}{2}2I_zS_z\right) \exp\left(-i\frac{\pi}{2}S_x\right) \\
 &= \exp\left(-i\frac{\pi}{2}S_y\right) \exp\left(i\frac{\pi}{2}S_x\right) \exp\left(i\frac{\pi}{2}S_x\right) \exp\left(-i\frac{\pi}{2}2I_zS_z\right) \exp\left(-i\frac{\pi}{2}S_x\right) \\
 &= \exp\left(-i\frac{\pi}{2}S_y\right) \exp\left(i\frac{\pi}{2}S_x\right) \exp\left(-i\frac{\pi}{2}2I_zS_y\right) \\
 &= \exp\left(-i\frac{\pi}{2}S_z\right) \exp\left(-i\frac{\pi}{2}S_y\right) \exp\left(-i\frac{\pi}{2}2I_zS_y\right).
 \end{aligned}
 \tag{2.293}$$

This propagator can be expressed using single transition basis operators as

$$\begin{aligned}
 U &= \exp\left(-i\frac{\pi}{2}S_z\right) \exp\left(-i\frac{\pi}{2}S_y\right) \exp\left(-i\frac{\pi}{2}2I_zS_y\right) \\
 &= \exp\left(-i\frac{\pi}{2}S_z\right) \exp\left[-i\pi\frac{1}{2}(S_y + 2I_zS_y)\right] \\
 &= \exp\left(-i\frac{\pi}{2}S_z\right) \exp(-i\pi I^\alpha S_y).
 \end{aligned}
 \tag{2.294}$$

Ignoring the z -rotation, which can be compensated by phase shifting subsequent pulses in an actual experiment, the propagator corresponds to a selective inversion across the $|\alpha\alpha\rangle \leftrightarrow |\alpha\beta\rangle$ transition in the two-spin energy level system (Fig. 2.4). In contrast, a conventional 180° pulse corresponds to simultaneous inversion across both the $|\alpha\alpha\rangle \leftrightarrow |\alpha\beta\rangle$ and the $|\beta\alpha\rangle \leftrightarrow |\beta\beta\rangle$ transitions. The effect of this sequence element on the S_z operator can be described in either the Cartesian or the single-transition operator bases by

$$\begin{aligned}
 S_z &\xrightarrow{\pi I^\alpha S_y} -2I_zS_z, \\
 (I^\alpha + I^\beta)S_z &\xrightarrow{\pi I^\alpha S_y} (-I^\alpha + I^\beta)S_z.
 \end{aligned}
 \tag{2.295}$$

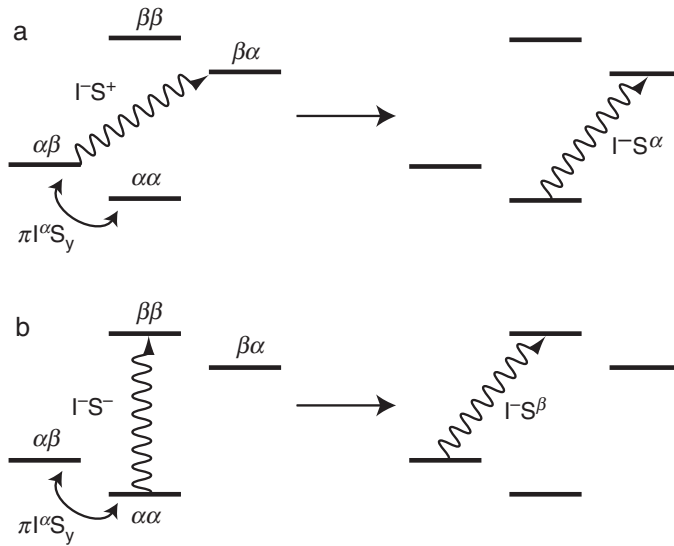


FIGURE 2.7 Energy level diagram for S³CT pulse sequence. The S³CT pulse sequence element is equivalent to a selective inversion across the $|\alpha\alpha\rangle \leftrightarrow |\alpha\beta\rangle$ transition, as indicated by the curved arrows. (a) The S³CT sequence converts zero-quantum coherence to single-quantum coherence I^-S^α . (b) The S³CT sequence converts double-quantum coherence to single-quantum coherence I^-S^β .

The second line shows that the S³CT sequence selectively inverts the component of S_z magnetization that is coupled to an I spin in the α state. A pictorial representation of the effect of the S³CT sequence on coherences is illustrated using zero-quantum and double-quantum coherences as an example in Fig. 2.7. The selective inversion is seen to transfer I^-S^+ coherence into I^-S^α coherence and I^-S^- coherence into I^-S^β coherence. An explicit calculation yields

$$\begin{aligned} I^-S^+ &\xrightarrow{\pi I^\alpha S_y} -I^-S^\alpha, \\ I^-S^- &\xrightarrow{\pi I^\alpha S_y} I^-S^\beta, \end{aligned} \quad [2.296]$$

which is necessary to obtain the correct signs of the operators. For completeness, the corresponding selective inversion across the

$|\beta\alpha\rangle \leftrightarrow |\beta\beta\rangle$ transition is obtained by inverting the phase of the final y -pulse. The propagator $\mathbf{U} = \exp(-i\pi I^\alpha S_x)$ is obtained by shifting the phases of all pulses by $-\pi/2$.

2.8 Averaging of the Spin Hamiltonians and Residual Interactions

The presentations in the preceding sections of this chapter have focused on evolution of the density operator under the isotropic components of the nuclear spin Hamiltonian. At this point, a more formal analysis is presented of the nuclear spin Hamiltonian and the effects of isotropic and nonisotropic averaging in solution. The nuclear spin Hamiltonians important in NMR spectroscopy of diamagnetic molecules are described most generally in the form

$$\mathcal{H} = \mathbf{u}^T \mathbf{C} \mathbf{v}, \quad [2.297]$$

in which \mathbf{u} and \mathbf{v} are vectors, the superscript T indicates the transpose, and \mathbf{C} is a general second-rank Cartesian tensor. The Cartesian tensor \mathbf{C} is represented by a 3×3 matrix and can be decomposed into the sum of irreducible tensors of rank 0, 1, and 2:

$$\mathbf{C} = \mathbf{C}^{(0)} + \mathbf{C}^{(1)} + \mathbf{C}^{(2)}, \quad [2.298]$$

in which $\mathbf{C}^{(0)} = \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{E}$, $\mathbf{C}^{(1)} = (\mathbf{C} - \mathbf{C}^T)/2$ is traceless and anti-symmetric, and $\mathbf{C}^{(2)} = (\mathbf{C} + \mathbf{C}^T)/2 - \mathbf{C}^{(0)}$ is traceless and symmetric. The vector \mathbf{u} normally will be an angular momentum operator, the vector \mathbf{v} will be an angular momentum operator or a magnetic field vector, and \mathbf{C} will depend on the particular magnetic spin interaction being considered. For example, the chemical shielding Hamiltonian (introduced in Chapter 1, Section 1.5) is described, in the laboratory reference frame, by $\mathbf{u}^T = (I_x, I_y, I_z)$, $\mathbf{v} = (0, 0, \gamma B_0)^T$, and $\mathbf{C} = \boldsymbol{\sigma}$, in which

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad [2.299]$$

is the Cartesian nuclear shielding tensor for the I spin (which should not be confused with the density operator in this context).

The observation that the nuclear spin Hamiltonian must be invariant to rotation has profound consequences for NMR spectroscopy because this constraint limits the types of interactions that can couple to the nuclear spin angular momentum operators. The antisymmetric tensor

does not affect the energy levels of the nuclear spin systems and consequently does not contribute to the observed resonance frequencies. This component of the nuclear spin Hamiltonian will not be considered further in this text. The Hamiltonian can then be written as

$$\mathcal{H} = \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \mathbf{u}^T \mathbf{C}^{(2)} \mathbf{v}. \quad [2.300]$$

In the principal axis reference frame of the tensor, $\mathbf{C}^{(2)}$ is diagonal with elements $d_k = C_{kk} - \text{Tr}\{\mathbf{C}\}/3$, in which C_{kk} for $k = \{x, y, z\}$ are the principal values of \mathbf{C} . In this frame,

$$\mathbf{u}^T \mathbf{C}^{(2)} \mathbf{v} = d_x u_x v_x + d_y u_y v_y + d_z u_z v_z. \quad [2.301]$$

Equation [2.301] is expressed in terms of the Cartesian components of \mathbf{u} , \mathbf{v} , and $\mathbf{C}^{(2)}$, which facilitates a physical interpretation of spin interactions. However, the effects of rotation are more easily considered by expressing the Hamiltonian using spherical, rather than Cartesian, tensors. Thus, [2.301] can be reformulated as

$$\mathbf{u}^T \mathbf{C}^{(2)} \mathbf{v} = \sqrt{3/2} d_z \mathbf{A}_2^0 + \frac{1}{2} d_z \eta (\mathbf{A}_2^2 + \mathbf{A}_2^{-2}), \quad [2.302]$$

in which $\eta = (d_x - d_y)/d_z$, \mathbf{A}_2^q are the $2q + 1$ components of the irreducible spherical tensor operator of second rank:

$$\begin{aligned} \mathbf{A}_2^0 &= \frac{1}{\sqrt{6}} (3u_z v_z - \mathbf{u} \cdot \mathbf{v}), \\ \mathbf{A}_2^{\pm 1} &= \mp \frac{1}{2} (u^{\pm} v_z + u_z v^{\pm}), \\ \mathbf{A}_2^{\pm 2} &= \frac{1}{2} u^{\pm} v^{\pm}, \end{aligned} \quad [2.303]$$

$u^{\pm} = u_x \pm i u_y$ and $v^{\pm} = v_x \pm i v_y$, and \mathbf{u} and \mathbf{v} are expressed in the principal axis frame. In obtaining [2.302], the relationship $d_z = -(d_x + d_y)$ has been invoked because the tensor $\mathbf{C}^{(2)}$ is traceless. For the chemical shielding tensor, $d_z = \frac{2}{3} \Delta\sigma$ [1.49]. The expression [2.302] can be written equivalently in the form

$$\mathbf{u}^T \mathbf{C}^{(2)} \mathbf{v} = \sum_{q=-2}^2 (-1)^q F_2^{-q} \mathbf{A}_2^q \quad [2.304]$$

by making the identifications

$$\begin{aligned} F_2^0 &= \sqrt{3/2} d_z, \\ F_2^{\pm 1} &= 0, \\ F_2^{\pm 2} &= \frac{1}{2} d_z \eta = \frac{1}{2} (d_x - d_y). \end{aligned} \quad [2.305]$$

The F_2^q also are the $2q + 1$ components of an irreducible spherical tensor of second rank. With these definitions, the nuclear spin Hamiltonian is given by

$$\mathcal{H} = \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \sum_{q=-2}^2 (-1)^q F_2^{-q} \mathbf{A}_2^q. \quad [2.306]$$

The advantage of writing the Hamiltonian in this form is that [2.306] is valid in any reference frame provided that the tensors are expressed in the suitable frame of interest. Thus, the Hamiltonian in the principal axis frame is obtained by using \mathbf{A}_2^q and F_2^q expressed in the principal axis frame, and the Hamiltonian in the laboratory frame is obtained by using \mathbf{A}_2^q and F_2^q expressed in the laboratory reference frame. The tensors $F_2^{q(\text{lab})}$ are obtained in the laboratory frame from the tensors $F_2^{q(\text{PAS})}$ in the principal axis frame by using the transformation properties of the irreducible spherical tensors (20):

$$F_2^{q(\text{lab})} = \sum_{k=-2}^2 D_{kq}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, \gamma_{\text{LP}}) F_2^{k(\text{PAS})}, \quad [2.307]$$

in which $D_{mn}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, \gamma_{\text{LP}})$ are the Wigner rotation matrices, given in Table 2.4 and $\{\alpha_{\text{LP}}, \beta_{\text{LP}}, \gamma_{\text{LP}}\}$ are the Euler angles specifying the relative orientation of the laboratory and principal axis reference frames. Using this relationship, the nuclear spin Hamiltonian is expressed in the laboratory reference frame as

$$\mathcal{H} = \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \sum_{q=-2}^2 (-1)^q \mathbf{A}_2^q \sum_{k=-2}^2 D_{kq}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, \gamma_{\text{LP}}) F_2^{k(\text{PAS})}, \quad [2.308]$$

in which the vectors \mathbf{u} and \mathbf{v} and the tensors \mathbf{A}_2^q are understood to be expressed in the laboratory reference frame. This equation makes use of the observation that \mathbf{u} , \mathbf{v} , and \mathbf{A}_2^q usually are much simpler to express in the laboratory reference frame but the tensors F_2^q have their simplest form in the principal axis system of the interaction.

The full form of the Hamiltonian in [2.308] is important for the development of nuclear spin relaxation theory, and is discussed in Chapter 5. For the consideration of first-order spectra—that is, of resonance frequencies and intensities—the nuclear spin Hamiltonian can be treated as a weak perturbation to the Zeeman Hamiltonian. As a result, only the components of [2.308] that commute with the Zeeman Hamiltonian need to be retained. This simplification is called truncation

TABLE 2.4
Reduced Rotation Matrices $d_{mn}^2(\beta)$

m, n^a	-2	-1	0	1	2
-2	$\cos^4(\beta/2)$	$\frac{1}{2} \sin\beta(\cos\beta + 1)$	$\sqrt{3/8} \sin^2\beta$	$-\frac{1}{2} \sin\beta(\cos\beta - 1)$	$\sin^4(\beta/2)$
-1	$-\frac{1}{2} \sin\beta(\cos\beta + 1)$	$\frac{1}{2}(2 \cos\beta - 1)(\cos\beta + 1)$	$\sqrt{3/2} \sin\beta \cos\beta$	$-\frac{1}{2}(2 \cos\beta - 1)(\cos\beta - 1)$	$-\frac{1}{2} \sin\beta(\cos\beta - 1)$
0	$\sqrt{3/8} \sin^2\beta$	$-\sqrt{3/2} \sin\beta \cos\beta$	$\frac{1}{2}(3 \cos^2\beta - 1)$	$\sqrt{3/2} \sin\beta \cos\beta$	$\sqrt{3/8} \sin^2\beta$
1	$\frac{1}{2} \sin\beta(\cos\beta - 1)$	$-\frac{1}{2}(2 \cos\beta - 1)(\cos\beta - 1)$	$-\sqrt{3/2} \sin\beta \cos\beta$	$\frac{1}{2}(2 \cos\beta - 1)(\cos\beta + 1)$	$\frac{1}{2} \sin\beta(\cos\beta + 1)$
2	$\sin^4(\beta/2)$	$\frac{1}{2} \sin\beta(\cos\beta - 1)$	$\sqrt{3/8} \sin^2\beta$	$-\frac{1}{2} \sin\beta(\cos\beta + 1)$	$\cos^4(\beta/2)$

^aThe Wigner rotation matrices are given by $D_{mn}^2(\alpha, \beta, \gamma) = d_{mn}^2(\beta) \exp(-im\alpha - in\gamma)$.

of the Hamiltonian, with the result

$$\begin{aligned}
 \mathcal{H} &= \frac{1}{3}\text{Tr}\{\mathbf{C}\}\mathbf{u}\cdot\mathbf{v} + \mathbf{A}_2^0 F_2^{0(\text{lab})} \\
 &= \frac{1}{3}\text{Tr}\{\mathbf{C}\}\mathbf{u}\cdot\mathbf{v} + \mathbf{A}_2^0 \sum_{k=-2}^2 D_{k0}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, 0) F_2^{k(\text{PAS})} \\
 &= \frac{1}{3}\text{Tr}\{\mathbf{C}\}\mathbf{u}\cdot\mathbf{v} + \mathbf{A}_2^0 \sqrt{\frac{3}{2}} d_z \left\{ D_{00}^2(0, \beta_{\text{LP}}, 0) \right. \\
 &\quad \left. + \frac{1}{\sqrt{6}} \eta [D_{20}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, 0) + D_{-20}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, 0)] \right\}. \quad [2.309]
 \end{aligned}$$

The third Euler angle γ is unnecessary for determining the truncated Hamiltonian, and has been arbitrarily set to zero, because only $D_{m0}^2(\alpha, \beta, \gamma)$ are required to obtain $F_2^{0(\text{lab})}$ using [2.307]. This simplification results because the truncated Hamiltonian commutes with the Zeeman Hamiltonian and consequently is unaffected by a rotation around the z -axis of the laboratory reference frame. Also,

$$\begin{aligned}
 D_{m0}^2(\alpha, \beta, 0) &= Y_2^m(\beta, -\alpha), \\
 D_{0m}^2(0, \beta, \gamma) &= Y_2^m(\beta, -\gamma),
 \end{aligned} \quad [2.310]$$

in which $Y_2^m(\theta, \phi)$ are the modified spherical harmonic functions used in Chapter 5 (20). If operators of the form u^+v^- and u^-v^+ commute with the Zeeman Hamiltonian, then \mathbf{A}_2^0 is given in [2.303]. If operators of the form u^+v^- and u^-v^+ do not commute with the Zeeman Hamiltonian, then these are truncated as well and

$$\mathbf{A}_2^0 = \sqrt{2/3} u_z v_z. \quad [2.311]$$

For example, this simplified expression for \mathbf{A}_2^0 is obtained if $u=I$ and $v=S$ refer to different heteronuclear spins.

In solution NMR spectroscopy, the Hamiltonians given in [2.308] and [2.309] must be averaged over the rotational distribution of molecules in solution. The angular dependence of the Hamiltonian is expressed by the angular dependence of the Wigner rotation matrices. This means that the $D_{mn}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, \gamma_{\text{LP}})$ in [2.308] and [2.309] must be replaced by average values $\langle D_{kq}^2(\alpha_{\text{LP}}, \beta_{\text{LP}}, \gamma_{\text{LP}}) \rangle$. The rotational average of $D_{mn}^l(\alpha, \beta, \gamma)$ is defined in general by

$$\langle D_{mn}^l(\alpha, \beta, \gamma) \rangle = \int D_{mn}^l(\alpha, \beta, \gamma) p(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma, \quad [2.312]$$

in which $p(\alpha, \beta, \gamma)$ is the probability distribution for the set of Euler angles $\{\alpha, \beta, \gamma\}$. In isotropic solution, all molecular orientations are equally likely. Consequently, $p(\alpha, \beta, \gamma) = 1/(8\pi^2)$ and $\langle D_{mn}^l(\alpha, \beta, \gamma) \rangle = 0$. Therefore, the second term in [2.308] and [2.309], depending on the traceless tensor $\mathbf{C}^{(2)}$, is zero as a result of averaging over the random distribution of molecular orientations. The first term is a scalar product and is invariant to rotation. The rotationally averaged nuclear spin Hamiltonian in isotropic phase is given by

$$\mathcal{H} = \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v}. \quad [2.313]$$

This is the form of the nuclear spin Hamiltonians considered thus far in this text. For example, the chemical shift Hamiltonian [2.98] has the form of [2.313] with $\mathbf{u} \cdot \mathbf{v} = \gamma B_0 I_z$ and $\frac{1}{3} \text{Tr}\{\sigma\} = \sigma$ is the isotropic chemical shielding. The strong scalar coupling Hamiltonian [2.154] has the form of [2.313] with $\mathbf{u} = (I_x, I_y, I_z)^T$; $\mathbf{v} = (S_x, S_y, S_z)^T$; $\mathbf{C} = \mathbf{J}$, where \mathbf{J} is the scalar coupling tensor; and $\frac{1}{3} \text{Tr}\{\mathbf{J}\} = 2\pi J_{IS}$. The dipole-dipole and quadrupole tensors are traceless and consequently do not contribute to the rotationally averaged nuclear spin Hamiltonian in isotropic phase.

The isotropy of a solution of molecules is destroyed if the molecules are subject to a potential of mean force, $W(\alpha, \beta, \gamma)$, that depends on the orientation of a molecular fixed frame, relative to the laboratory reference frame. The time-dependent Euler angles $\{\alpha, \beta, \gamma\}$ describe the relative orientation of these two frames of reference. The probability distribution is given by the Boltzmann equation:

$$\begin{aligned} p(\alpha, \beta, \gamma) &= \frac{\exp[-W(\alpha, \beta, \gamma)/k_B T]}{\int \exp[-W(\alpha, \beta, \gamma)/k_B T] \sin\beta \, d\alpha \, d\beta \, d\gamma} \\ &\approx \left(\frac{1}{8\pi^2} \right) (1 - W(\alpha, \beta, \gamma)/k_B T). \end{aligned} \quad [2.314]$$

The second equality is obtained by assuming that the potential of mean force is weak and that

$$\int W(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma = 0. \quad [2.315]$$

Because the probability $p(\alpha, \beta, \gamma)$ is unaffected by adding a constant to $W(\alpha, \beta, \gamma)$, the zero of potential energy always can be chosen to satisfy this constraint. The Wigner rotation matrices form a complete set; therefore, the probability density also can be expressed as (20)

$$p(\alpha, \beta, \gamma) = \frac{1}{8\pi^2} \sum_l (2l+1) \sum_{m,n=-l}^l \langle D_{mn}^l(\alpha, \beta, \gamma)^* \rangle D_{mn}^l(\alpha, \beta, \gamma). \quad [2.316]$$

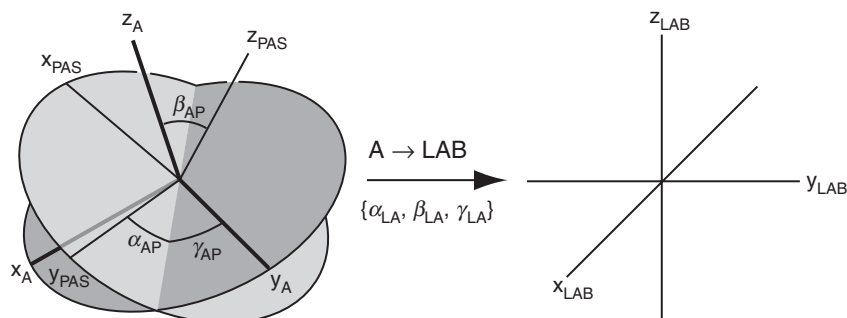


FIGURE 2.8 Coordinate transformations. The principal axis system (PAS) of the nuclear spin interaction is oriented with fixed angles $\{\theta, \phi\}$ with respect to the molecule-fixed alignment reference frame, A . The alignment frame is oriented with respect to the laboratory (LAB) reference frame by time-dependent Euler angles $\{\alpha_{LA}, \beta_{LA}, \gamma_{LA}\}$.

In order to perform the averaging over the probability distribution, the principal axis system of the spin Hamiltonian must first be transformed to the molecule-fixed frame, which will be referred to as the alignment frame, and then the alignment frame must be transformed to the laboratory reference frame. The principal axis system is oriented with time-independent Euler angles $\{\alpha_{AP}, \beta_{AP}, \gamma_{AP}\}$ with respect to the alignment frame. The alignment frame is oriented with time-dependent Euler angles $\{\alpha_{LA}, \beta_{LA}, \gamma_{LA}\}$ with respect to the laboratory frame. The relationships between the three frames are illustrated in Fig. 2.8. Thus, [2.307] is generalized to

$$F_2^{q(\text{lab})} = \sum_{j=-2}^2 \sum_{k=-2}^2 D_{jq}^2(\alpha_{LA}, \beta_{LA}, \gamma_{LA}) D_{kj}^2(\alpha_{AP}, \beta_{AP}, \gamma_{AP}) F_2^{k(\text{PAS})} \quad [2.317]$$

and the rotationally averaged truncated nuclear spin Hamiltonian becomes, by extension of [2.309] (2I),

$$\begin{aligned} \mathcal{H} &= \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \mathbf{A}_2^0 \sum_{j=-2}^2 \sum_{k=-2}^2 \langle D_{j0}^2(\alpha_{LA}, \beta_{LA}, 0) \rangle D_{kj}^2(\alpha_{AP}, \beta_{AP}, \gamma_{AP}) F_2^{k(\text{PAS})} \\ &= \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \mathbf{A}_2^0 \sum_{j=-2}^2 \sum_{k=-2}^2 S_j^* D_{kj}^2(\alpha_{AP}, \beta_{AP}, \gamma_{AP}) F_2^{k(\text{PAS})}, \end{aligned} \quad [2.318]$$

in which the order parameters S_m are defined as

$$\begin{aligned} S_m^* &= \langle D_{m0}^2(\alpha_{\text{LA}}, \beta_{\text{LA}}, 0) \rangle, \\ S_m &= -1^m S_{-m}^*. \end{aligned} \quad [2.319]$$

The order parameters in [2.319] are identical to the corresponding coefficients in the expansion of the probability density [2.316].

The set of five order parameters in [2.318] transform under rotation like a second-rank tensor and constitute the irreducible representation of the 3×3 Saupe order matrix defined by (22)

$$S_{ij} = \frac{3}{2} \langle \cos \alpha_i \cos \alpha_j \rangle - \delta_{ij}/2, \quad [2.320]$$

in which α_k , for $k = \{x, y, z\}$, is the angle between the k th axis of the alignment frame and the z -axis of the laboratory frame. The spherical and Saupe order parameters are related by

$$\begin{aligned} S_0 &= S_{zz}, \\ S_{\pm 1} &= \pm \sqrt{2/3} (S_{xz} \mp i S_{yz}), \\ S_{\pm 2} &= \sqrt{1/6} (S_{xx} - S_{yy}) \mp i \sqrt{2/3} S_{xy}. \end{aligned} \quad [2.321]$$

The Saupe order matrix is a traceless, real, and symmetric Cartesian tensor of rank 2. Consequently, the alignment frame always can be defined such that the order matrix is diagonal with principal values S_{xx} , S_{yy} , and S_{zz} . In this frame, $S_{\pm 1} = 0$ and

$$\begin{aligned} \mathcal{H} = & \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \mathbf{A}_2^0 \left\{ S_{zz} \sum_{k=-2}^2 D_{k0}^2(\alpha_{\text{AP}}, \beta_{\text{AP}}) F_2^{k(\text{PAS})} \right. \\ & \left. + \sqrt{\frac{1}{6}} (S_{xx} - S_{yy}) \sum_{k=-2}^2 [D_{k2}^2(\alpha_{\text{AP}}, \beta_{\text{AP}}, \gamma_{\text{AP}}) + D_{k-2}^2(\alpha_{\text{AP}}, \beta_{\text{AP}}, \gamma_{\text{AP}})] F_2^{k(\text{PAS})} \right\}. \end{aligned} \quad [2.322]$$

This expression is frequently expressed as (23)

$$\begin{aligned} \mathcal{H} = & \frac{1}{3} \text{Tr}\{\mathbf{C}\} \mathbf{u} \cdot \mathbf{v} + \mathbf{A}_2^0 \left\{ A_a \sum_{k=-2}^2 D_{k0}^2(\alpha_{\text{AP}}, \beta_{\text{AP}}) F_2^{k(\text{PAS})} \right. \\ & \left. + \sqrt{\frac{3}{8}} A_r \sum_{k=-2}^2 [D_{k2}^2(\alpha_{\text{AP}}, \beta_{\text{AP}}, \gamma_{\text{AP}}) + D_{k-2}^2(\alpha_{\text{AP}}, \beta_{\text{AP}}, \gamma_{\text{AP}})] F_2^{k(\text{PAS})} \right\}, \end{aligned} \quad [2.323]$$

in which $A_{kk} = (2/3)S_{kk}$ are the principal values of the alignment tensor, $A_a = (3/2)A_{zz}$ is the axial component of the tensor, and $A_r = A_{xx} - A_{yy}$ is the rhombic component of the tensor. If the Hamiltonian is axially symmetric with $\eta = 0$, then the above expression simplifies to

$$\mathcal{H} = \frac{1}{3}\text{Tr}\{\mathbf{C}\}\mathbf{u} \cdot \mathbf{v} + \mathbf{A}_2^0 \sqrt{3/2} \delta_z \left\{ A_a \frac{1}{2} (3 \cos^2 \theta - 1) + \frac{3}{4} A_r \sin^2 \theta \cos 2\phi \right\}, \quad [2.324]$$

in which $\{\alpha_{\text{AP}}, \beta_{\text{AP}}, \gamma_{\text{AP}}\} = \{\theta, \phi\}$ and $\{\theta, \phi\}$ are the polar angles describing the orientation of the z -axis of the principal axis system of the Hamiltonian with respect to the alignment frame.

As an explicit example, the Hamiltonian for the dipole-dipole Hamiltonian is traceless and symmetric, with $d_z = -2(\mu_0/4\pi)\gamma_I\gamma_S\hbar r_{IS}^{-3}$. Consequently, [2.322] is given by

$$\mathcal{H} = \pi D_{IS}(3I_z S_z - \mathbf{I} \cdot \mathbf{S}), \quad [2.325]$$

in which

$$\begin{aligned} D_{IS} &= D_{IS}^{\max} \left\{ S_{zz} \frac{1}{2} (3 \cos^2 \theta - 1) + (S_{xx} - S_{yy}) \frac{1}{2} \sin^2 \theta \cos 2\phi \right\} \\ &= D_{IS}^{\max} \left\{ A_a \frac{1}{2} (3 \cos^2 \theta - 1) + \frac{3}{4} A_r \sin^2 \theta \cos 2\phi \right\} \end{aligned} \quad [2.326]$$

is the residual dipolar coupling constant (RDC), measured in units of Hertz, and

$$D_{IS}^{\max} = -\frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi^2 r_{IS}^3}. \quad [2.327]$$

If the residual dipole coupling is weak, $2\pi D_{IS}/|\omega_I - \omega_S| \ll 1$, then the Hamiltonian is further truncated to

$$\mathcal{H} = 2\pi D_{IS} I_z S_z. \quad [2.328]$$

This Hamiltonian has the same functional form as does the weak scalar coupling Hamiltonian. As a consequence, if alignment occurs, then the apparent scalar coupling constant observed experimentally is given by $J_{IS} + D_{IS}$.

The alignment of a molecule with an anisotropic magnetic susceptibility tensor in the presence of a static magnetic field is a simple, easily calculable example of the effects of an orienting potential. A molecule in a magnetic field, \mathbf{B} , has an induced magnetic dipole moment that is proportional to the magnetic susceptibility tensor χ .

The potential energy function is (24)

$$W = -\frac{1}{2\mu_0} \mathbf{B}^T \chi \mathbf{B}. \quad [2.329]$$

Using similar derivations as used for the nuclear spin Hamiltonians yields for the traceless symmetric component of the potential

$$W(\alpha_{\text{LA}}, \beta_{\text{LA}}, \gamma_{\text{LA}}) = -\frac{B_0^2}{\mu_0 \sqrt{6}} \sum_{k=-2}^2 D_{k0}^2(\alpha_{\text{LA}}, \beta_{\text{LA}}, \gamma_{\text{LA}}) \chi_2^k, \quad [2.330]$$

in which $\chi_0^2 = \sqrt{2/3} \Delta\chi$, $\chi_{\pm 2}^2 = (\chi_{yy} - \chi_{xx})/2$, $\Delta\chi = \chi_{zz} - (\chi_{xx} + \chi_{yy})/2$, and $\{\chi_{xx}, \chi_{yy}, \chi_{zz}\}$ are the principle values of χ . The isotropic component of the potential does not contribute to the probability density, as noted previously, and has not been included in [2.330]. Thus, a molecule in solution has a preferential orientation with respect to the static magnetic field. Integration of [2.312] using [2.314] and [2.330] gives

$$\langle D_{00}^2 \rangle = \frac{B_0^2 \Delta\chi}{15\mu_0 k_B T}, \quad [2.331]$$

$$\langle D_{0-2}^2 \rangle = \langle D_{02}^2 \rangle = \frac{B_0^2 (\chi_{xx} - \chi_{yy})}{10\sqrt{6}\mu_0 k_B T},$$

from which

$$S_{zz} = \frac{B_0^2 \Delta\chi}{15\mu_0 k_B T}, \quad [2.332]$$

$$S_{xx} - S_{yy} = \frac{B_0^2 (\chi_{xx} - \chi_{yy})}{10\mu_0 k_B T},$$

The resulting residual dipolar coupling constant is

$$D_{IS} = -\left(\frac{\gamma_I \gamma_S \hbar B_0^2}{60\pi^2 k_B T r_{IS}^3} \right) \left\{ \Delta\chi \frac{1}{2} (3 \cos^2 \theta - 1) + \frac{3}{4} (\chi_{xx} - \chi_{yy}) \sin^2 \theta \cos 2\phi \right\}. \quad [2.333]$$

For diamagnetic molecules, the achievable alignment is weak because χ is very small. For example, a benzene molecule has $\Delta\chi = -1.3 \times 10^{-33} \text{ m}^3$ and $\chi_{xx} - \chi_{yy} = 0$. For $B_0 = 18.8 \text{ T}$ (800 MHz), $T = 300 \text{ K}$, a C-H bond length of 0.11 nm, and $D_{\text{CH}}^{\text{max}} = -45.1 \text{ kHz}$, a maximum value of $D_{\text{CH}} = 0.26 \text{ Hz}$ is obtained when $\theta = 0$, and a minimum value of $D_{\text{CH}} = -0.13 \text{ Hz}$ is obtained when $\theta = \pi/2$. In this case, $S_{zz} = 5.9 \times 10^{-6}$,

which is indicative of a very small net alignment. The dependence of D_{IS} on B_0^2 can be used to separate D_{IS} from the scalar coupling constant J_{IS} .

The effects of partial alignment of small molecules have been observed for the chemical shift, dipole–dipole, and quadrupole nuclear spin Hamiltonians (25). Alignment has been obtained using electric fields, magnetic fields, thermotropic liquid crystals, and lyotropic liquid crystals. Applications to proteins and other biological macromolecules, including the use of liquid crystalline and other media to obtain larger degrees of alignment (23), are discussed in Chapter 7.

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