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Quantum description of nuclear ensembles

When the young Ernest Rutherford arrived at Cambridge University in 1897, his prospective PhD supervisor, John Joseph Thomson, had just discovered the electron, measured its charge and measured its mass. Rutherford had, the previous year, completed a Masters thesis at Canterbury College in New Zealand, developing a new and highly sensitive detector for Hertzian waves. Thomson was impressed with the talented New Zealander but suggested a new direction for his research, the elucidation of the radiation emanating from radium, the element recently extracted by Marie Curie. And so Rutherford discovered the alpha particle, measured its charge, and measured its mass [1]. That alpha particle of his PhD research became a fundamental tool in his subsequent life's work, but perhaps most remarkably in its use to determine atomic structure. At Manchester University in 1911, Ernest Rutherford and his students, Hans Geiger and Ernest Marsden, fired a collimated beam of alpha particles at a thin gold foil. The alpha scattering pattern led Rutherford to propose a model of the atom in which a dense, positively charged nucleus was surrounded by orbiting electrons.

Rutherford's picture of the atom presented a conundrum. Accelerated charges radiate electromagnetic radiation. How could orbiting electrons, with their consequent centripetal acceleration, remain in their orbits if they lost radiative energy? That question was boldly answered by Niels Bohr who was visiting Rutherford's Manchester Laboratory during the period of the famous experiments. In 1913 Bohr simply stated a rule whereby certain orbits of the electron would be allowed to exist without radiative loss, provided that their orbital path was an integral number of electron wavelengths. Given the dependence of the de Broglie wavelength on momentum, Bohr's rule corresponded to a quantisation of electron angular momentum. The quantisation rule fixed the energies of the allowed orbits such that the discrete changes in energy when electrons changed orbits, with energy released as photons of light, corresponded to the discrete nature of the spectral lines of atoms. The Rutherford–Bohr model of atomic structure, while essentially true, was limited in scope. It was, in what is now called 'old quantum theory', the precursor to the revolution in quantum mechanical description that followed Erwin Schrödinger's 1926 explanation of wave mechanics.

Those discoveries of the nucleus and of angular momentum quantisation had, in part, laid the foundations for the discovery of magnetic resonance half a century later. But two more insights were needed. In 1915, using a beautiful experiment in which a demagnetised iron bar suspended on a torsional pendulum was observed to rotate when magnetised along the suspension axis, Einstein and de Haas showed that angular

momentum and magnetism were intimately connected [2]. Electrons have a magnetic dipole moment proportional to their angular momentum. Then, in 1923, Wolfgang Pauli interpreted hyperfine structure in the spectra of atoms as evidence for nuclear angular momentum and nuclear magnetism [3]. Nuclear magnetic resonance and electron spin resonance were achieved in the two decades following.

When Rutherford discovered the atomic nucleus he could not have imagined that it might be a window to understanding molecular biology, seeing inside the human body, or revealing how the brain works. NMR has proven an essential tool in physics, it has revolutionised chemistry and biochemistry, it has made astonishing contributions to medicine, and is now making an impact in geophysics, chemical engineering, and food technology. It is even finding applications in new security technologies and in testing fundamental ideas concerning quantum computing.

In the next chapter, the ideas that underpin magnetic resonance are outlined. First, however, we cover some of the essential concepts that govern the quantum behaviour of ensembles of nuclear spins.

3.1 Quantum mechanics and nuclear spin

Nuclear magnetism is inherently quantum mechanical in nature, the fundamental quantity describing the nuclear spin being the angular momentum quantum number I . This fixed integer or half-integer quantity (sometimes called the ‘spin’) arises from the fundamental symmetry properties of nuclei and characterizes a nucleus in its stable ground state. For example, a proton or ^{13}C nucleus has $I = \frac{1}{2}$ while the deuteron has $I = 1$. Measurement of angular momentum always leads to the projection of one of its vector components along an axis defined by the observation, the most famous example being the Stern–Gerlach experiment [4], in which spin- $\frac{1}{2}$ electronic states were found in ‘up’ and ‘down’ projections labelled by $\frac{1}{2}$ and $-\frac{1}{2}$. In general these observational possibilities, defined by the component of angular momentum, m , as measured along some axis z , may be any one of a discrete set of integer or half-integer values in the range $-I, -I + 1, \dots, I - 1, I$. m is also known as the *azimuthal quantum number*. Note that the angular momentum is actually measured in units of $\hbar = h/2\pi$. We will only introduce this unit when it is specifically required.

Despite this underlying quantum behaviour, NMR is often described in semi-classical terms involving the interaction of a vector angular momentum and magnetic dipole moment with a magnetic field. How is this possible? The measurement of nuclear magnetism often involves vast numbers of nuclei, the states of which are statistically distributed in ensembles. When we average across ensembles, macroscopic effects appear continuous. Furthermore, in the case of independent spin- $\frac{1}{2}$ nuclei, the concern of much of this book, all states of the ensemble may be characterised by a simple vector quantity, referred to as the nuclear magnetisation and this vector description further justifies a classical description of the evolution of spin states. But delve a little deeper, allow the nuclear spins to interact with one another, or attempt to describe the time evolution of higher spin quantum number such as $I = 1$, and the underlying quantum mechanics becomes immediately apparent. Understanding those quantum mechanical principles is essential to any understanding of the magnetic resonance phenomenon.

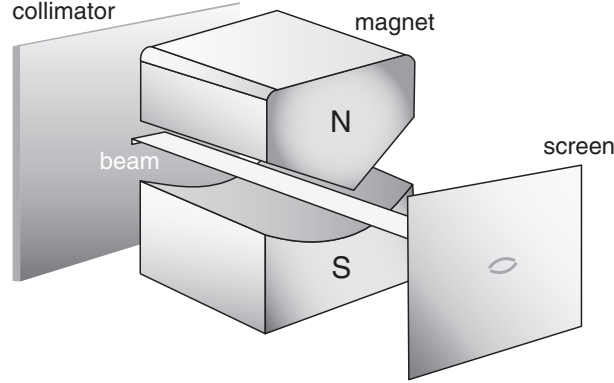


Fig. 3.1 Schematic of Stern–Gerlach apparatus, in which a beam of silver atoms is passed through a magnetic field gradient created by specially shaped magnetic pole pieces. On the screen the beam is found to split into ‘up’ and ‘down’ components.

3.1.1 Four key ideas in quantum mechanics

The quantum description of nuclear spin behaviour involves four underlying ideas. The first concerns the concept of a basis set of fundamental states that relate to the observational possibilities of quantum systems. The second relates these basis states to eigenvectors of a linear operator associated with measurement of a physical observable. The third involves a clear description of the measurement process and what that means for the quantum states. And the fourth tells us about dynamics—how quantum states evolve with time. We will deal with each idea in turn.

Before starting it is worth pointing out that, as straightforward as the rules of quantum mechanics may be in mathematical terms, they are deeply counterintuitive from a physical standpoint. Yet quantum mechanics has never failed a single experimental test. The science writer Simon Singh calls quantum mechanics ‘The most successful and utterly bizarre theory in the whole of physics’ [5]. Neils Bohr said ‘Anyone who is not shocked by quantum theory has not understood a single word’ [6], while, somewhat modestly, Richard Feynman expressed the mystery by saying ‘I think I can safely say that no one understands quantum mechanics’ [7].

The quantum states

These quantum states, labelled by α , form the basis of a vector space, $\{|\Psi\rangle\}$, such that any allowed state $|\Psi\rangle$ of a nuclear spin can be written as a linear superposition,

$$|\Psi\rangle = \sum_{\alpha} a_{\alpha} |\alpha\rangle \quad (3.1)$$

where α labels all the elements of the vector space basis set. A significant feature of this (Hilbert) vector space is that the coefficients or ‘amplitudes’, a_{α} , of the vector space are necessarily complex, causing the amplitudes to have phase δ_{α} as well as magnitude $|a_{\alpha}|$. In particular

$$a_{\alpha} = |a_{\alpha}| \exp(i\delta_{\alpha}) \quad (3.2)$$

For spins with angular momentum quantum number I , those basis states $|\alpha\rangle$ are labelled by the azimuthal quantum number m and

$$|\Psi\rangle = \sum_m a_m |m\rangle \quad (3.3)$$

where m ranges over all possible values from $-I$ to I . The inherent phase in the amplitudes a_m represents the most important property utilised in the descriptions of nuclear translational motion measurement throughout this book.

Eigenvalue equation and observables

The second idea, indeed the one that underlies the existence of the basis, concerns the so-called eigenvalue equation, in which all measurement possibilities are eigenvalues, α , of a linear operator, A , associated with this measurement—the so-called observable of interest.

$$A|\alpha\rangle = \alpha|\alpha\rangle \quad (3.4)$$

For example, the process of observation of the angular momentum component along the z -axis for a single nucleus in a basis state $|m\rangle$ is described by the eigenvalue equation,

$$I_z|m\rangle = m|m\rangle \quad (3.5)$$

In this example I_z is the ‘operator’ for angular momentum along the z -axis, while the eigenvalue m is the result of an observation. In general, the complete set, $\{|\alpha\rangle\}$, of eigenvector solutions to the eigenvalue equation provides a basis for describing any state $|\Psi\rangle$ of the system in terms of a superposition of basis states.

A property of all vector spaces concerns the ability to define an ‘inner product’, a number formed by the ordered pair of any two vectors. The inner product is essentially the projection of one vector onto the other, in our case denoted $\langle\Psi|\Psi'\rangle$, with the property $\langle\Psi|\Psi'\rangle = \langle\Psi'|\Psi\rangle^*$. This product is formed by an ordered multiplication of vectors $\langle\Psi|$ and $|\Psi'\rangle$, known respectively as ‘bras’ and ‘kets’. In that sense, given the existence of the set of ket vectors $\{|\Psi\rangle\}$, the inner product operation defines the set of bra vectors $\{\langle\Psi|\}$.

Physical measurements return real numbers, a consequence of which is that eigenvectors are necessarily orthogonal. By dividing each basis vector by its length, $\langle\alpha|\alpha\rangle$, also known as the ‘norm’, the vectors are said to be normalised. For such an orthonormal basis set the following relation applies

$$\langle\alpha|\alpha'\rangle = \delta_{\alpha\alpha'} \quad (3.6)$$

where $\delta_{\alpha\alpha'}$ is the Kronecker delta. Since we have a discrete set of orthonormal $|\alpha\rangle$ states, it is helpful to represent these using column vectors. For example, where $I = \frac{1}{2}$ we have the basis

$$|\tfrac{1}{2}\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |-\tfrac{1}{2}\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (3.7)$$

To fulfil the requirements of the inner product, the bra and ket vectors are each the complex conjugate transpose of the other, $\langle\alpha|$ being the row vector conjugate to column vector $|\alpha\rangle$. So

$$\left\langle \frac{1}{2} \right| = \begin{bmatrix} 1 & 0 \end{bmatrix}, \quad \left\langle -\frac{1}{2} \right| = \begin{bmatrix} 0 & 1 \end{bmatrix} \quad (3.8)$$

In this representation, the operator I_z becomes a matrix, namely

$$I_z = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \quad (3.9)$$

One of the consequences of the fact that the eigenvectors span the space of all possible state vectors is the ‘completeness relation’ $\sum_{\alpha} |\alpha\rangle\langle\alpha| = \underline{1}$ where $\underline{1}$ is the identity operator.

The measurement process

The third idea concerns interpretation of the measurement process. Of course, for a quantum system existing in an eigenstate $|\alpha\rangle$ of an observable A , the result of measurement of A follows directly by calculating $\langle\alpha|A|\alpha\rangle$. For example, a measurement of the I_z observable when the spin- $\frac{1}{2}$ system is in the definite ‘spin down’ state yields

$$\begin{aligned} \left\langle -\frac{1}{2} \right| I_z \left| -\frac{1}{2} \right\rangle &= \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ &= -\frac{1}{2} \end{aligned} \quad (3.10)$$

But what if the quantum system is not in an eigenstate of the observable but in some general superposition state $|\Psi\rangle$? This third postulate states that the result of measurement is given by $\langle\Psi|A|\Psi\rangle$. Again, we will illustrate for the case of a nuclear spin in an admixed state given by the superposition, $|\Psi\rangle = \sum_m a_m |m\rangle$. Then the result of a measurement, the so-called ‘expectation value’, is defined by

$$\begin{aligned} \langle\Psi|I_z|\Psi\rangle &= \sum_{m,m'} a_m^* a_{m'} \langle m'|I_z|m\rangle \\ &= \sum_{m,m'} a_m^* a_{m'} m \langle m'|m\rangle \end{aligned} \quad (3.11)$$

Because the basis vectors $\{|m\rangle\}$ are orthogonal we have the result

$$\langle\Psi|I_z|\Psi\rangle = \sum_m |a_m|^2 m \quad (3.12)$$

What is the meaning of this sum? For a large number of identically prepared nuclei it represents a mean of eigenvalue results weighted by the normalised probabilities $|a_m|^2$. For a single nucleus the interpretation is that the measurement will force the superposition state, $|\Psi\rangle$, into one of the eigenstates, $|m\rangle$, returning the result m . This mysterious ‘state reduction’ is a random process defined by a probability $|a_m|^2$.

Since we chose to represent our states as eigenvalues of I_z , the operator for I_z is diagonal. For measurement of angular momentum about other axes we find that the corresponding operators cannot be diagonal, reflecting the Heisenberg uncertainty principle whereby systems cannot simultaneously exist in definite states of certain pairs

of observables. Indeed, the observables I_x , I_y , and I_z are represented by operators that do not commute but follow the famous commutation relationship

$$[I_x, I_y] = I_x I_y - I_y I_x = iI_z \quad (3.13)$$

This relation arises from the fact that successive rotations about different axes do not commute and because the operator for rotation (for example about the z -axis) is related to the operator for angular momentum, I_z , by the rule

$$R_z(\phi) = \exp(i\phi I_z) \quad (3.14)$$

where the exponential function of the operator I_z is interpreted as the usual power series. Equation 3.13 is a fundamental algebra that underpins the behaviour of nuclear spins in magnetic resonance.

Dynamics and the Schrödinger equation

The fourth idea in quantum mechanics concerns dynamics—how quantum systems evolve with time. This is governed by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \mathcal{H} |\Psi(t)\rangle \quad (3.15)$$

where \mathcal{H} is the Hamiltonian (or energy) operator. Providing we express \mathcal{H} in angular frequency units, we may drop the \hbar in the Schrödinger equation and we will henceforth follow this convention. Note that this formulation (the Schrödinger picture) has the states as functions of time but the operators stationary. \mathcal{H} may have some explicit time-dependence if our quantum system is subjected to some fluctuating disturbance, but if \mathcal{H} is constant, then the Schrödinger equation yields the result

$$|\Psi(t)\rangle = U(t) |\Psi(0)\rangle \quad (3.16)$$

where

$$U(t) = \exp(-i\mathcal{H}t) \quad (3.17)$$

$U(t)$ is known as the evolution operator. Here we demonstrate its action in a simple example. To do so, we take as our Hamiltonian the interaction of the nuclear spin with an external magnetic field. This is known as the Zeeman interaction. Atomic nuclei have a magnetic dipole moment proportional to the angular momentum, the constant of proportionality being known as the gyromagnetic ratio, γ . The interaction energy of a magnetic dipole $\boldsymbol{\mu}$ in a magnetic field \mathbf{B}_0 is written classically and quantum mechanically as $-\boldsymbol{\mu} \cdot \mathbf{B}_0$ so that the Hamiltonian operator for the case of \mathbf{B}_0 oriented along the z -axis is

$$\mathcal{H} = -\gamma B_0 I_z \quad (3.18)$$

The energy levels associated with the eigenstates of the Zeeman Hamiltonian are shown in Fig. 3.2, the energy separation between adjacent levels being γB_0 for all spin quantum numbers I . Now consider the evolution of a nuclear spin quantum state $|\Psi\rangle$ under the influence of the magnetic field. The evolution operator,

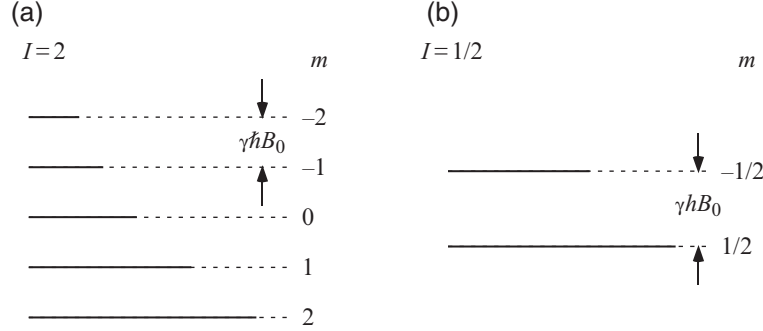


Fig. 3.2 Energy level diagram for spins experiencing a Zeeman interaction. In (a) $I = 2$, while in (b) $I = \frac{1}{2}$. The energy spacing for levels separated by $m = \pm 1$ is $\gamma\hbar B_0$, or in the frequency units adopted here, γB_0 . The bold line schematically represents the relative population in each state for an ensemble of spins in thermal equilibrium.

$U(t) = \exp(i\gamma B_0 I_z t)$, is identical to a clockwise rotation of the state about the z -axis by an angle $\gamma B_0 I_z t$. The existence of the field causes all states to precess at the Larmor frequency, ω_0 , given by

$$\omega_0 = \gamma B_0 \quad (3.19)$$

For protons ($\gamma = 2.75 \times 10^8$) in a typical superconductive magnet of $B_0 = 9.4$ T, the proton precession frequency, in cyclic frequency units, will be $\gamma B_0 / 2\pi = 400$ MHz, in the UHF part of the radiofrequency spectrum.

3.1.2 Representation of angular momentum

The starting point for any consideration of angular momentum is the classical orbital angular momentum vector, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, where \mathbf{p} is a translational momentum vector. By noting that in wave mechanics the operator for momentum is $\mathbf{p} = -i\hbar\nabla$, it may be easily shown that for a wavefunction $\Psi(\mathbf{r})$ whose position vector is rotated by an infinitesimal angle $\underline{\epsilon} = (\epsilon_x, \epsilon_y, \epsilon_z)$ to $\mathbf{r} + \underline{\epsilon} \times \mathbf{r}$, the rotation operator is $\exp((i/\hbar)\underline{\epsilon} \cdot \mathbf{L})$. The commutator relations $[L_x, L_y] = i\hbar L_z$ then follow by consideration of geometric non-commutation of classical rotations about orthogonal axes [8], a simple example being $R_x(\epsilon_x)R_y(\epsilon_y)R_x(-\epsilon_x)R_y(-\epsilon_y) = R_z(-\epsilon_x\epsilon_y)$, as shown in Fig. 3.3. Such orbital angular momentum may be shown to be quantised in units of \hbar .

Generalised angular momentum

If, instead of starting from rules for orbital motion, we take as our axiom the algebra of the commutator relations, then we find that the operators that obey this algebra belong to a wider class than orbital angular momentum alone. We have chosen to label this wider class I_x , I_y and I_z and conveniently non-dimensionalise them by dropping the explicit \hbar unit.

Using just the commutator relations alone and choosing I_z as our eigenoperator,¹ we find through simple algebraic manipulation the following rules. First, I_z and

¹Since I_x , I_y and I_z do not commute, only one can be an eigenoperator and hence represented by a diagonal matrix.

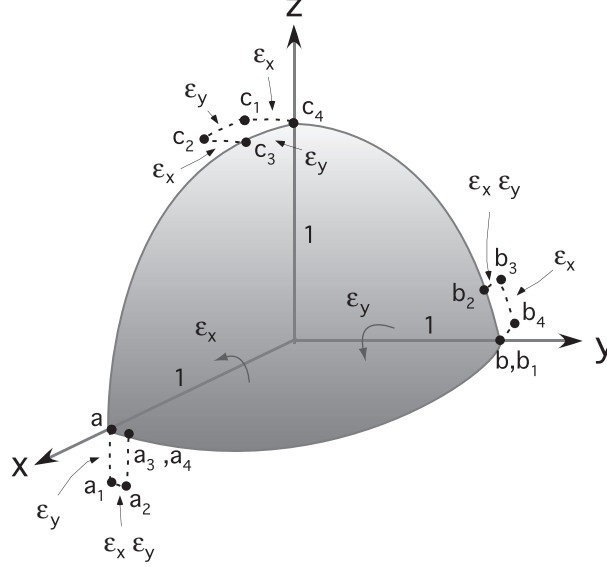


Fig. 3.3 Result of successive infinitesimal rotations on a unit sphere of $R_x(\epsilon_x)$, $R_y(\epsilon_y)$, $R_x(-\epsilon_x)$, and $R_y(-\epsilon_y)$, taking point a to a_1, a_2 , etc., and b to b_1, b_2 , etc. The final result is $R_z(-\epsilon_x \epsilon_y)$.

$\mathbf{I}^2 = I_x^2 + I_y^2 + I_z^2$ commute. Second, the eigenvalues of I_z range in unit steps between a minimum value $m = -I$, and maximum value $m = I$, where I is integer or half-integer. I is known as the angular momentum or ‘spin’ quantum number while m is called the azimuthal quantum number. Third, the eigenvalue of \mathbf{I}^2 is $I(I + 1)$. Because both I_z and \mathbf{I}^2 are diagonal operators, we sometimes call this basis the ‘ \mathbf{I}^2, I_z ’ representation. We could label our kets in this basis, $|Im\rangle$, or in shorthand, simply $|m\rangle$. Fourth, the operators $I_+ = I_x + iI_y$ and $I_- = I_x - iI_y$, known as raising and lowering operators, have the effect

$$I_+|m\rangle = \sqrt{I(I+1) - m(m+1)}|m+1\rangle \quad (3.20)$$

and

$$I_-|m\rangle = \sqrt{I(I+1) - m(m-1)}|m-1\rangle \quad (3.21)$$

The simplest non-trivial example of generalised angular momentum is the case of spin $I = \frac{1}{2}$, for which the I_z eigenstates are two-dimensional (2-D), and given by eqns 3.7. The raising and lowering operators have the effect of converting a $|\frac{1}{2}\rangle$ state into a $|\frac{1}{2}\rangle$ state and vice versa according to

$$I_+|-\frac{1}{2}\rangle = |\frac{1}{2}\rangle, \quad I_-|\frac{1}{2}\rangle = |-\frac{1}{2}\rangle \quad (3.22)$$

Rotation: active and passive view

Let us write down the rotation operator for spin- $\frac{1}{2}$ in the case of a rotation ϕ about the z -axis. First we need to establish the so-called ‘active and passive views’. A frame of reference rotation is termed ‘passive’ in quantum mechanics, and distinguished from

the ‘active view’ rotation of physical systems. Rotations of coordinate frames about a Cartesian axis, ζ , are represented by the operator, $\exp(i\theta I_\zeta)$, where a positive sign corresponds to an anticlockwise sense. The active- and passive-view operations are identical except for a sign change. For example, as shown in Fig. 3.4, rotating an object by 30° clockwise while keeping the reference frame constant leads to a measurement result identical to that which obtains when the object is held fixed while the reference frame is rotated 30° anticlockwise. Thus physical rotations of spins involve the same operator, $\exp(i\theta I_\zeta)$, but in the opposite sense.

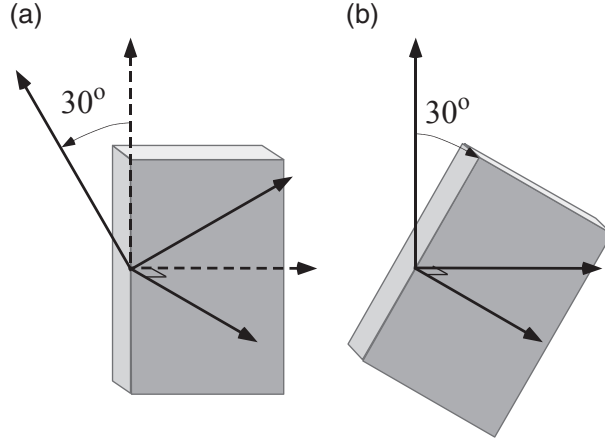


Fig. 3.4 Illustrating the relationship between the active and passive views. Rotating the axes by 30° anticlockwise, as shown in (a) results in the same relationship between axes and object as rotating the object by 30° clockwise, as shown in (b).

We have, for a rotation of axes,

$$R_z(\phi) \left| \frac{1}{2} \right\rangle = \begin{bmatrix} \exp(i\frac{1}{2}\phi) & 0 \\ 0 & \exp(-i\frac{1}{2}\phi) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \exp(i\frac{1}{2}\phi) \\ 0 \end{bmatrix} \quad (3.23)$$

and

$$R_z(\phi) \left| -\frac{1}{2} \right\rangle = \begin{bmatrix} \exp(i\frac{1}{2}\phi) & 0 \\ 0 & \exp(-i\frac{1}{2}\phi) \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ \exp(-i\frac{1}{2}\phi) \end{bmatrix} \quad (3.24)$$

Note the remarkable result that a rotation of 360° results in the transformation of $\left| \frac{1}{2} \right\rangle$ to $-\left| \frac{1}{2} \right\rangle$ and $\left| -\frac{1}{2} \right\rangle$ to $-\left| -\frac{1}{2} \right\rangle$. Spin- $\frac{1}{2}$ states, indeed all half-integral angular momentum states, are double-valued on rotation. A 720° rotation is needed to restore the ket to its original state. By contrast, integral angular momentum states (incorporating all orbital angular momentum) are single-valued under rotation. Take the case of spin-1. Here the rotation operator about the ‘eigen axis’ is

$$R_z(\phi) = \begin{bmatrix} \exp(i\phi) & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \exp(-i\phi) \end{bmatrix} \quad (3.25)$$

and the operator for a 360° rotation is clearly the identity.

What is spin?

It should now be abundantly clear that ‘spin’, at least in its half- integral form, has little to do with orbital motion. Spin is really a symmetry property, in the case of spin- $\frac{1}{2}$ associated with an ‘upness’ or ‘downness’ of the quantum system, in our case the atomic nucleus. But the fundamental definition of the spin property arises from the phase change observed when the quantum system rotates. Rotation may be of our axes, as we observe the quantum system by rotating our frame of reference around it (the passive view), or it may be of the system itself (active view), as we keep our observational axes fixed and the system physically rotates. The rotation operators are the same in the active and passive views but with opposite sign exponents.

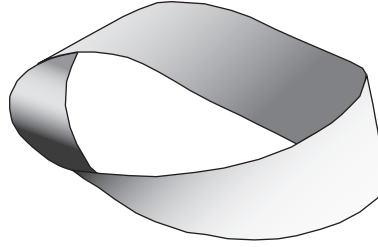


Fig. 3.5 The Möbius strip. Two 360° revolution circuits around the strip are needed to return to origin.

The curious nature of the need for 720° rotations to obtain an identity operator for half-integral spins has often been compared to the symmetry properties of the Möbius strip, where two orbits are needed to return to origin.

General rotations and irreducible representations

Suppose we wish to describe a general reorientation of coordinates. This could be done by specifying a succession of rotations about each of the three Cartesian axes. In fact, while three angles are needed in general, two rotation axes will suffice. These angles (α, β, γ) , are known as Euler angles and specify successive rotations α about z , followed by β about y , then γ about z , where the axes remain fixed. The rotation operator for the family of kets $\{|Im\rangle\}$ with angular momentum quantum number I is then the Wigner rotation matrix $D^{(I)}(\alpha, \beta, \gamma)$ [9, 10] where

$$D^{(I)}(\alpha, \beta, \gamma) = \exp(-i\gamma I_z) \exp(-i\beta I_y) \exp(-i\alpha I_z) \quad (3.26)$$

and

$$D^{(I)}|Im\rangle = \sum_{m'} D_{m'm}^{(I)}|Im'\rangle \quad (3.27)$$

$D_{m'm}^{(I)}$ being an element of the Wigner matrix. These matrix elements are well known and may be written in closed form [9, 10].

Equation 3.26 is the perspective appropriate for the active view, where the system itself is rotated. In the passive view, where the coordinates are rotated and the system remains fixed, we require the operator $D^{(I)\dagger}(\alpha, \beta, \gamma)$ and

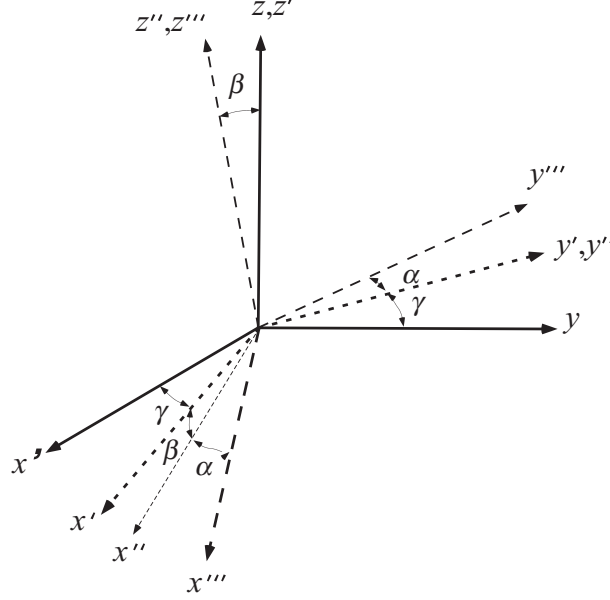


Fig. 3.6 Result of successive passive view Euler angle rotations in which successively rotated axes are used. Here the angle order is reversed from the active view, γ about z , followed by β about y' , then α about z'' .

$$D^{(I)\dagger}(\alpha, \beta, \gamma) = \exp(i\alpha I_z) \exp(i\beta I_y) \exp(i\gamma I_z) \quad (3.28)$$

Note the reversal of order of rotation as a result of the Hermitian conjugation operation, \dagger .

The particular matrix form of $D^{(I)}(\alpha, \beta, \gamma)$ depends on the angular momentum quantum number and hence the chosen basis set. In this sense we say that $D^{(I)}(\alpha, \beta, \gamma)$ is a ‘representation’ of the rotation for this particular basis. These Wigner matrices will be 2×2 , 3×3 or $(2I + 1) \times (2I + 1)$ for spin- $\frac{1}{2}$, spin-1, or spin- I systems, respectively. Most importantly, these Wigner matrices involve linear superpositions of all the m values of the ket space. And there is no unitary transformation on the kets which can change this fact, that is, to transform $D^{(I)}(\alpha, \beta, \gamma)$ into a block diagonal form involving mixing only within subsets of the m values. In other words, we say that the $D^{(I)}(\alpha, \beta, \gamma)$ are irreducible representations of the full rotation group in 3D.

In the next section we will see that it is possible to combine angular momenta to produce product states, and that these states themselves may be related to new total angular momentum states. Put in the language of group theory, we say that the rotation matrices for the product states may be ‘reduced’ to a sum of irreducible representations [11].

The product representation and the total angular momentum representation

Suppose that a system is characterised by two independent angular momenta, I_1 and I_2 . Here we will be concerned with two nuclear spins, but they might be, for example, the spin and orbital angular momentum of an electron, or the component proton and neutron angular momenta, which combine to form the intrinsic angular momentum of the deuteron. We will only consider the case of two such angular momenta but the argument can be generalised to more.

One important property of angular momentum operators in different spaces is that they commute. They operate in different ket spaces after all. The eigenkets in the ' \mathbf{I}^2, I_z ' representation for I_1 and I_2 , respectively, are $|I_1 m_1\rangle$ and $|I_2 m_2\rangle$. We can then define a combined system ket in which the operators in I_1 space have no effect on $|I_2 m_2\rangle$ and vice-versa. Clearly there are $(2I_1 + 1)$ eigenkets $|I_1 m_1\rangle$ and $(2I_2 + 1)$ eigenkets $|I_2 m_2\rangle$. We can write for a general system ket

$$|\psi\rangle_{\text{product}} = \sum_{m_1, m_2} |I_1 m_1\rangle |I_2 m_2\rangle \quad (3.29)$$

To write matrices in the product space, one forms an outer product \otimes . By way of illustration, here is the example where $I_1 = 1$, with three-dimensional kets and 3×3 , operators and $I_2 = \frac{1}{2}$, where the kets are 2-D and the operators 2×2 .

$$|I_1 m_1\rangle |I_2 m_2\rangle = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \otimes \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} a_1 \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} \\ a_2 \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} \\ a_3 \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} \end{bmatrix} = \begin{bmatrix} a_1 b_1 \\ a_1 b_2 \\ a_2 b_1 \\ a_2 b_2 \\ a_3 b_1 \\ a_3 b_2 \end{bmatrix} \quad (3.30)$$

The ket $|I_1 m_1\rangle |I_2 m_2\rangle = |1 \ -1\rangle |\frac{1}{2} \ \frac{1}{2}\rangle$ would correspond to $a_1 = a_2 = 0$, $a_3 = 1$, $b_1 = 1$, $b_2 = 0$.

Operator products are formed in a similar way

$$\begin{aligned} AB &= \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \otimes \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} \\ &= \begin{bmatrix} A_{11} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} & A_{12} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} & A_{13} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} \\ A_{21} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} & A_{22} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} & A_{23} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} \\ A_{31} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} & A_{32} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} & A_{33} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} \end{bmatrix} \quad (3.31) \end{aligned}$$

Using this rule we can see how to form a matrix to represent the Hamiltonian product operator $\mathbf{I}_1 \cdot \mathbf{I}_2$. But what do we do with operators that apparently involve only a single spin, such as I_{1z} ? In fact once we commit to the product representation, all operators

must be products involving each spin space. What this means for the apparently single-spin operator is that the corresponding operator in the other spin space is just the identity. Hence $I_{1z} = I_{1z} \otimes \underline{1}$ while $I_{2z} = \underline{1} \otimes I_{2z}$, the respective identity operator being of dimension appropriate to each space.

What is the general rotation operator in product space? It is simply the tensor product $D^{(I_1)} \otimes D^{(I_2)}$ [11]. Remarkably it may be shown that

$$D^{(I_1)} \otimes D^{(I_2)} = \sum_{I=|I_1-I_2|}^{I_1+I_2} D^{(I)} \quad (3.32)$$

which means that a unitary transformation U_{cg} exists such that

$$D^{(I_1)} \otimes D^{(I_2)} = U_{cg}^{-1} \begin{bmatrix} D^{(I_1+I_2)} & \underline{0} & \dots & \underline{0} \\ \underline{0} & D^{(I_1+I_2-1)} & \dots & \underline{0} \\ \vdots & \vdots & \ddots & \vdots \\ \underline{0} & \underline{0} & \dots & D^{(|I_1-I_2|)} \end{bmatrix} U_{cg} \quad (3.33)$$

Equation 3.33 shows that the product representation may be reduced to a block diagonal sum of irreducible representations. In other words the combined angular momenta I_1 and I_2 form new total angular momentum states with total angular momentum quantum numbers ranging from $I_1 + I_2$, $I_1 + I_2 - 1$, ..., to $|I_1 - I_2|$. The dimensionality of the product states $(2I_1 + 1)(2I_2 + 1)$ is identical to the sum of total angular momentum dimensions, $\sum_{I=|I_1-I_2|}^{I_1+I_2} (2I + 1)$. U_{cg} is known as a Clebsch–Gordon transformation and it connects the product and total angular momentum representations by

$$|\Psi\rangle_{total} = U_{cg} |\Psi\rangle_{product}. \quad (3.34)$$

The matrix elements of U_{cg} are known as Clebsch–Gordon coefficients [12], and are labelled by $\langle I_1 m_1 I_2 m_2 | I m \rangle$. The relationship between the product states $|I_1 m_1\rangle |I_2 m_2\rangle$ and the total angular momentum states $|I m\rangle$ is given by the Clebsch–Gordon transformation

$$|I m\rangle = \sum_{m_1} \langle I_1 m_1 I_2 m_2 | I m \rangle |I_1 m_1\rangle |I_2 m_2\rangle \quad (3.35)$$

with $m_1 + m_2 = m$.

3.2 Spin ensembles and the density matrix

So far the quantum description has been written in terms of the states $|\Psi\rangle$ of individual quantum particles. How do we describe the large ensembles of spins characteristic of macroscopic samples, allowing for the possibility that members of that ensemble may exist in a range of sub-ensembles, each labelled by a different quantum state? A schematic diagram of such a set is shown in Fig. 3.7. Note that the sub-ensemble is defined such that every quantum particle contained within it is in the same quantum state $|\Psi\rangle$. Those states may in fact be superpositions in some chosen basis. However, we start by describing an important set of sub-ensembles for which the best way to

represent the respective quantum particles is in terms of eigenstates of energy. This is the case of an ensemble in thermal equilibrium, a common starting point for most experiments!

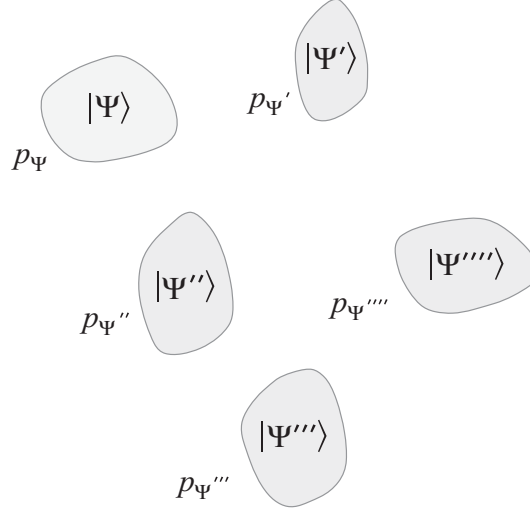


Fig. 3.7 Schematic for an ensemble of sub-ensembles, each a pure state containing quantum systems with common kets $|\Psi\rangle$, $|\Psi'\rangle$, etc., and with probability weightings p_Ψ , $p_{\Psi'}$, etc.

We choose as our example the case of atomic nuclei in thermal equilibrium in a magnetic field. In most condensed matter at physically accessible temperatures, the spacing between adjacent atomic nuclei will exceed the de Broglie wavelength and so Boltzmann statistics will apply. Under the Zeeman Hamiltonian, the Boltzmann distribution will dictate that the probability of occupancy of the quantum state $|\Psi\rangle = |m\rangle$ will be²

$$p_m = \frac{\exp(-\gamma B_0 m \hbar / k_B T)}{\sum_m \exp(-\gamma B_0 m \hbar / k_B T)} \quad (3.36)$$

These relative populations are shown in Fig. 3.2. Our question concerning the appropriate description is answered by classical statistical mechanics. The result of a measurement A for a statistical ensemble of quantum states $\{|\Psi\rangle\}$ with normalised probabilities p_Ψ is simply the weighted average

$$\begin{aligned} \overline{\langle A \rangle} &= \overline{\langle \Psi | A | \Psi \rangle} \\ &= \sum_{\Psi} p_{\Psi} \langle \Psi | A | \Psi \rangle \end{aligned} \quad (3.37)$$

where the bar over a quantity is taken to represent the classical statistical averaging over sub-ensembles while the angular brackets $\langle \dots \rangle$ represent the quantum mechanical expectation value, the quantum statistical process known as state reduction.

²Note the need to reintroduce \hbar so as to write the energy in units of Joules.

3.2.1 Spin- $\frac{1}{2}$ ensembles

Let us illustrate, using the simplest possible non-trivial example of a system in quantum mechanics, the case of a spin with $I = \frac{1}{2}$. In NMR the dominant interaction of a spin with its environment is always via the Zeeman interaction of eqn 3.18. This means that the ‘natural’ eigenstates are those whose quantum numbers are eigenvalues of I_z , namely $|\frac{1}{2}\rangle$ and $|\frac{1}{2}\rangle$. In general, therefore, we express any state of a particular sub-ensemble in this basis and write

$$|\Psi\rangle = a_{1/2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + a_{-1/2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (3.38)$$

Given the operator for I_z of eqn 3.9

$$\begin{aligned} \overline{\langle \Psi | I_z | \Psi \rangle} &= \overline{\left(a_{1/2}^* \begin{bmatrix} 1 & 0 \end{bmatrix} + a_{-1/2}^* \begin{bmatrix} 0 & 1 \end{bmatrix} \right) \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \left(a_{1/2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + a_{-1/2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \right)} \\ &= \frac{1}{2} \left(\overline{|a_{1/2}|^2} - \overline{|a_{-1/2}|^2} \right) \end{aligned} \quad (3.39)$$

The respective classical and quantum statistical averages are both playing a role, the $\overline{|a_{1/2}|^2}$ and $\overline{|a_{-1/2}|^2}$ representing the respective probabilities, for each sub-ensemble, that the act of measurement forces the particles into either the spin-up or spin-down quantum states, while the bar averages these quantum probabilities between each sub-ensemble.

Equation 3.39 may be interpreted by saying that the ensemble averaged expectation value of I_z is determined by the difference in population between the upper and lower energy levels. This difference is said to describe the polarisation of the ensemble. A population difference will arise in thermal equilibrium according to the Boltzmann probability factor. In thermal equilibrium the two levels, separated by $\hbar\gamma B_0$, will have populations

$$\overline{|a_{\pm 1/2}|^2} = \frac{\exp(\pm \hbar\gamma B_0 / 2k_B T)}{\exp(-\hbar\gamma B_0 / 2k_B T) + \exp(\hbar\gamma B_0 / 2k_B T)} \quad (3.40)$$

At room temperature, in a typical laboratory magnet, the energy difference $\hbar\gamma B_0$ is over five orders of magnitude smaller than the Boltzmann energy $k_B T$. In consequence the expression for the populations may be written, with a high degree of accuracy, as

$$\overline{|a_{\pm 1/2}|^2} = \frac{1}{2} \left(1 \pm \frac{1}{2} \hbar\gamma B_0 / k_B T \right) \quad (3.41)$$

and in general, for any I , may be written

$$\overline{|a_m|^2} = \frac{1}{2I+1} \left(1 + m \hbar\gamma B_0 / k_B T \right) \quad (3.42)$$

Measurement of the x - or y -components of angular momentum provide interesting examples by way of contrast. This particular observable provides the signal in the NMR experiment. For $I = \frac{1}{2}$, I_x is the off-diagonal operator

$$I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (3.43)$$

so that

$$\overline{\langle \Psi | I_x | \Psi \rangle} = \frac{1}{2} \left[\overline{a_{1/2}^* a_{-1/2}} + \overline{a_{1/2} a_{-1/2}^*} \right] \quad (3.44)$$

while

$$I_y = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad (3.45)$$

and

$$\overline{\langle \Psi | I_y | \Psi \rangle} = \frac{-i}{2} \left[\overline{a_{1/2}^* a_{-1/2}} - \overline{a_{1/2} a_{-1/2}^*} \right] \quad (3.46)$$

The terms in the brackets are said to describe the degree of ‘single-quantum coherence’ of the ensemble. This average is quite different from that represented by eqn 3.39 and reflects the degree of phase coherence between the $|\frac{1}{2}\rangle$ and $|\frac{-1}{2}\rangle$ states. This coherence is apparent when we write the amplitude terms in Argand form (see eqn 3.2)

$$\begin{aligned} \overline{\langle \Psi | I_x | \Psi \rangle} &= \frac{1}{2} \overline{|a_{1/2}| |a_{-1/2}| (\exp(-i(\delta_{1/2} - \delta_{-1/2})) + \exp(i(\delta_{1/2} - \delta_{-1/2})))} \\ &= \frac{1}{2} \overline{|a_{1/2}| |a_{-1/2}| \cos(\delta_{1/2} - \delta_{-1/2})} \end{aligned} \quad (3.47)$$

and

$$\begin{aligned} \overline{\langle \Psi | I_y | \Psi \rangle} &= -\frac{i}{2} \overline{|a_{1/2}| |a_{-1/2}| (\exp(-i(\delta_{1/2} - \delta_{-1/2})) - \exp(i(\delta_{1/2} - \delta_{-1/2})))} \\ &= -\frac{1}{2} \overline{|a_{1/2}| |a_{-1/2}| \sin(\delta_{1/2} - \delta_{-1/2})} \end{aligned} \quad (3.48)$$

$|a_{1/2}| |a_{-1/2}|$ is always positive. It is the non-random nature of $\overline{\exp(i(\delta_{1/2} - \delta_{-1/2}))}$, the ensemble average of phase differences between the quantum states, which renders the quantum coherence non-zero.

In the case of spins in thermal equilibrium in a magnetic field directed along z , the phenomena represented by eqns 3.39, 3.44, and 3.46 have a simple interpretation that is illustrated in Fig. 3.8. First, the thermal equilibrium state is such that when the spins are expressed in terms of energy eigenstates, the phase differences between the quantum states are random, leading to the terms $\overline{a_{1/2}^* a_{-1/2}}$ being zero and no transverse magnetisation existing. Second, the thermal equilibrium ensemble has a slightly higher population, $|a_{1/2}|^2$, in the lower energy state so that a net positive angular momentum z -component (i.e. longitudinal magnetisation) exists. Indeed, as we will see in the next chapter, when the spin- $\frac{1}{2}$ ensemble is disturbed from its thermal equilibrium state, it is still only the ‘spin excess’ $|a_{1/2}|^2 - |a_{-1/2}|^2$ that is visible in any experiment.

Of course, once such a disturbance occurs, and we create coherent superposition states with $\overline{a_{1/2}^* a_{-1/2}}$ non zero, then the simple picture given by Fig. 3.8 is of no help. For properly handling the effects of both polarisation and coherence in spin ensembles, we will need a new type of picture and a new type of quantum mechanical operator, one that enables the calculation of statistical averages of quantum mechanical operators with extraordinary ease. This operator we call the density matrix.

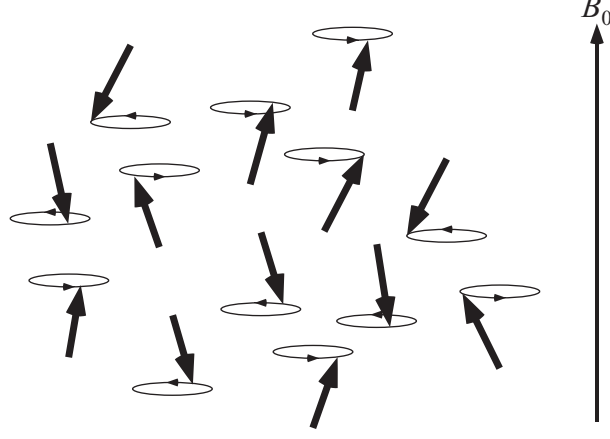


Fig. 3.8 Schematic for an ensemble of spin- $\frac{1}{2}$ particles immersed in a magnetic field B_0 in which the precessing phases are represented by angular positions in an Argand plane. There is a spin excess of lower energy ‘up’ states meaning $|a_{1/2}|^2 - |a_{-1/2}|^2$ is non-zero, while phase incoherence leads to $\overline{a_{1/2}^* a_{-1/2}} = 0$.

3.2.2 Density matrix properties

The density matrix ρ , is defined by

$$\rho = \overline{|\Psi\rangle\langle\Psi|} = \sum_{\Psi} p_{\Psi} |\Psi\rangle\langle\Psi| \quad (3.49)$$

Suppose ρ is written as a matrix in the chosen $\{|m\rangle\}$ angular momentum representation. Then the matrix elements of ρ are

$$\begin{aligned} \langle m|\rho|m'\rangle &= \sum_{\Psi} p_{\Psi} \langle m|\Psi\rangle\langle\Psi|m'\rangle \\ &= \overline{a_m a_{m'}^*} \end{aligned} \quad (3.50)$$

where, to remind the reader, the bar above a quantity is a shorthand notation for the ensemble average sum $\sum_{\Psi} p_{\Psi}$. The usefulness of ρ resides in the fact that the ensemble averaged expectation value for a measurement with operator A is given by

$$\overline{\langle\Psi|A|\Psi\rangle} = \text{Tr}(A\rho) \quad (3.51)$$

where the right-hand side represents the trace or diagonal sum over the matrix product $A\rho$. It can easily be seen that eqn 3.51 gives results identical to eqns 3.39, 3.44, and 3.46 for the previously chosen examples. However, let us demonstrate the relation $\overline{\langle A \rangle} = \text{Tr}(A\rho)$ by working in a general representation of eigenstates $\{|\alpha\rangle\}$.

$$\begin{aligned}
\text{Tr}(A\rho) &= \sum_{\alpha} \left\langle \alpha \left| A \sum_{\Psi} p_{\Psi} |\Psi\rangle \langle \Psi| \right| \alpha \right\rangle \\
&= \sum_{\Psi} p_{\Psi} \sum_{\alpha} \langle \Psi | \alpha \rangle \langle \alpha | A | \Psi \rangle \\
&= \sum_{\Psi} p_{\Psi} \langle \Psi | A | \Psi \rangle
\end{aligned} \tag{3.52}$$

where the completeness relation has been used in the final step. This is precisely the result, eqn 3.37, that we required from a simple consideration of statistics.

3.2.3 Evolution and the quantum Liouville equation

Some properties of ρ should be noted. First it contains all the information we need to calculate the value of any observable quantity of interest. Second, the evolution of ρ with time may be simply deduced from the Schrödinger equation and may be written

$$i \frac{\partial}{\partial t} \rho = [\mathcal{H}, \rho] \tag{3.53}$$

This relation is known as the Liouville equation [13] and yields for the case of constant Hamiltonian \mathcal{H} ,

$$\rho(t) = U(t) \rho(0) U^{-1}(t) \tag{3.54}$$

and where the Hamiltonian is time-varying, the overall evolution may be broken down into a succession of sequential incremental evolution steps involving time intervals sufficiently short that $\mathcal{H}(t)$ is taken as constant for that increment.

3.2.4 Pure states, mixed states and quantum coherence

Finally, there are some rules about the elements of ρ . The diagonal elements are probabilities and so must be real numbers between 0 and 1, while the sum of the diagonal elements, $\text{Tr}(\rho)$, is just the sum of state probabilities and therefore equals unity. The density matrix is Hermitian, that is to say $\rho^{\dagger} = \rho$, an obvious consequence of the fact that $\langle \alpha | \rho | \alpha' \rangle = \overline{a_{\alpha} a_{\alpha'}^*}$. A special case arises when the respective quantum states of all the sub-ensembles are identical, in other words when $p_{\Psi} = 1$ for some particular common Ψ . In that case the ensemble state is deemed ‘pure’ so that both $\text{Tr}(\rho) = 1$ and $\text{Tr}(\rho^2) = 1$. This second equality is a consequence of the density matrix for the pure state ensemble being simply $|\Psi\rangle \langle \Psi|$.

Two instructive examples, in the case of spin- $\frac{1}{2}$ are

$$\rho = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix} \tag{3.55}$$

and

$$\rho = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix} \tag{3.56}$$

Both are Hermitian and satisfy the requirements for the diagonal elements of density matrices. Both return a zero value for $\langle I_z \rangle$. But the first is a mixed state corresponding

to equal numbers of spins in up and down states. The second is a pure state consisting of a single sub-ensemble in which the quantum particles are in the same superposition $|\Psi\rangle = \frac{1}{\sqrt{2}}|\frac{1}{2}\rangle + \frac{1}{\sqrt{2}}|-\frac{1}{2}\rangle$. Multiplying this state by a common phase factor $\exp(i\delta)$ would yield the same density matrix, and hence the same result for any measurements. In this sense the absolute phase of a quantum state is irrelevant. It is the relative phase between basis states that determines the off-diagonal elements, $\overline{a_m a_{m'}^*}$ of the density matrix, and this is measurable as the degree of quantum coherence.

We are now in a position to see how the polarisations, $\overline{|a_\alpha|^2}$, and coherences, $\overline{a_\alpha a_{\alpha'}^*}$ of the superposition states determine the density matrix elements. For spin- $\frac{1}{2}$

$$\rho = \begin{bmatrix} \overline{|a_{1/2}|^2} & \overline{a_{1/2} a_{-1/2}^*} \\ \overline{a_{1/2}^* a_{-1/2}} & \overline{|a_{-1/2}|^2} \end{bmatrix} \quad (3.57)$$

Non-zero off-diagonal elements of the density matrix inform us about the degree of quantum coherence in the ensemble. To have such a coherence, superposition states must be present. To be non-zero, there must exist phase coherence between the amplitudes of those superposition states. We can easily see that the existence of quantum coherence in the case of spin- $\frac{1}{2}$ corresponds to non-zero expectation values for I_x and I_y .

Using eqns 3.49 and 3.51 and the matrices for the operators I_x , I_y , and I_z , it is straightforward to show that for $I = 1/2$

$$\rho = \begin{bmatrix} \frac{1}{2} + \overline{\langle I_z \rangle} & \overline{\langle I_x \rangle} - i \overline{\langle I_y \rangle} \\ \overline{\langle I_x \rangle} + i \overline{\langle I_y \rangle} & \frac{1}{2} - \overline{\langle I_z \rangle} \end{bmatrix} \quad (3.58)$$

The requirements $\text{Tr}(\rho) = 1$ and $\rho^\dagger = \rho$ mean that for spin- $\frac{1}{2}$ only three real numbers are needed to specify all the four matrix elements of ρ and therefore the results of any measurement. In other words, all states of the ensemble for independent spin- $\frac{1}{2}$ nuclei may be described by specifying the components of the vector $(\overline{\langle I_x \rangle} \mathbf{i} + \overline{\langle I_y \rangle} \mathbf{j} + \overline{\langle I_z \rangle} \mathbf{k})$. In macroscopic terms this is equivalent to specifying the magnetisation vector, $N\gamma\hbar(\overline{\langle I_x \rangle} \mathbf{i} + \overline{\langle I_y \rangle} \mathbf{j} + \overline{\langle I_z \rangle} \mathbf{k})$, where N is the number of spins per unit volume.

3.3 Tensor bases for the density matrix

3.3.1 Liouville space for spin- $\frac{1}{2}$

The set of spin- $\frac{1}{2}$ operators $\{I_{\alpha=x,y,z}\}$, taken together with $I_{\alpha=0} = \frac{1}{2}\mathbf{1}$, satisfy all the requirements of a vector space in which the inner product is defined by $\text{Tr}(I_\alpha I_\beta)$. Indeed that space provides a density matrix basis in which the basis vectors are orthogonal as $\text{Tr}(I_\alpha I_\beta) = \frac{1}{2}\delta_{\alpha\beta}$. In this manner any density matrix may be written as the linear superposition

$$\rho = \rho_0 \frac{1}{2}\mathbf{1} + \rho_x I_x + \rho_y I_y + \rho_z I_z \quad (3.59)$$

where $\rho_0 = 1$ and the ρ_α are real. Table 3.1 shows this Cartesian spin operator density matrix basis. Note that the I_z operator is diagonal and therefore gives information about the population terms $|a_{1/2}|^2$, and $|a_{-1/2}|^2$, whereas I_x and I_y are off-diagonal operators and tell us about the coherences, $\overline{a_{1/2}a_{-1/2}^*}$. The I_0 operator gives no information, as we shall see.

Since the set $\{I_{\alpha=0,x,y,z}\}$ span all possible Hermitian operators for spin- $\frac{1}{2}$ we can in fact write any quantum mechanical operator in this basis

$$A = A_0 \frac{1}{2} \mathbb{1} + A_x I_x + A_y I_y + A_z I_z \quad (3.60)$$

and the ensemble averaged expectation value by

$$\overline{\langle A \rangle} = \text{Tr}(\rho A) = \frac{1}{2} \sum_{\alpha=0,x,y,z} A_\alpha \rho_\alpha \quad (3.61)$$

Note how this simple vector basis allows for a very simple description of the Liouville equation. Equation 3.53 may be written

$$i \sum_{\alpha} \dot{\rho}_\alpha = \sum_{\alpha,\beta} \rho_\alpha \mathcal{H}_\beta [I_\beta, I_\alpha] \quad (3.62)$$

We can take advantage of the fact the the identity matrix commutes with all spin operators, and that $\dot{\rho}_0 = 0$, and restrict eqn 3.62 to the terms $\alpha = x, y, z$. This constancy of the identity term in the density matrix and its lack of influence in dynamics is such that it can generally be ignored. Its only role is to ensure $\text{Tr}(\rho) = 1$.

Of course, the commutation relationships for angular momentum operators mean that the right-hand side of eqn 3.62 is a simple linear superposition of the I_α . Using the orthogonality of the I_α under the trace operation, we find a simple set of coupled first-order differential equations for the density matrix coefficients, ρ_α . This enables us to solve for the dynamics in terms of a simple precessional motion. For example, if the Hamiltonian is the Zeeman operator, $-\omega_0 I_z$, then the solution is

$$\begin{aligned} \rho_0(t) &= 1 \\ \rho_x(t) &= \rho_x(0) \cos(\omega_0 t) + \rho_y(0) \sin(\omega_0 t) \\ \rho_y(t) &= \rho_y(0) \cos(\omega_0 t) - \rho_x(0) \sin(\omega_0 t) \\ \rho_z(t) &= \rho_z(0) \end{aligned}$$

This picture of evolution in terms of a simple precession between two components of the density matrix make for powerful insight when considering the behaviour of nuclear spins in magnetic resonance experiments.

The choice of a Cartesian basis for the spin operators is arbitrary and is analogous to the description of light in terms of linear polarisation. The equivalent of a circular polarisation standpoint would be to use the basis set $\{I_z, I_+, I_-\}$, as shown in Table 3.2. As we will see in the next sections, this basis has the advantage of special transformation properties under rotation.

Table 3.1 Cartesian operator density matrix basis for $I=1/2$

Angular momentum operator basis	$ m\rangle\langle m' $ Ket–bra basis	Name
$\frac{1}{2}\underline{1}$	$\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	Identity
I_x	$\frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	1-quantum coherence
I_y	$\frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$	1-quantum coherence
I_z	$\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	z -polarisation

Table 3.2 Spherical tensor operator basis for $I=1/2$

Tensor component	Angular momentum operator basis	$ m\rangle\langle m' $ Ket–bra basis	Name
T_{00}	$\underline{1}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	Identity
T_{10}	I_z	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	z -polarisation
T_{11}	$-\frac{1}{\sqrt{2}}I_+$	$\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & -1 \\ 0 & 0 \end{bmatrix}$	1-quantum coherence
T_{1-1}	$\frac{1}{\sqrt{2}}I_-$	$\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$	1-quantum coherence

3.3.2 Liouville space for $I > \frac{1}{2}$

These ideas can be extended to higher dimensional systems such as higher angular momenta ($I > 1/2$) or multiple spin problems, where couplings between the spins necessitate a description in terms of multiple spin operators. The Cartesian basis has a natural extension to the case of multiple spin systems. Take, for example, the case of two spins, i and j , which may be coupled via an interaction involving both spin operators (examples are the dipolar and spin–spin scalar interactions covered in Section 3.4). A basis for the density matrix exists, involving products of angular momentum operators, I_{ix} , I_{iy} , I_{iz} and I_{jx} , I_{jy} , I_{jz} . Such a product operator basis is immensely powerful in describing the evolution of spin systems in nuclear magnetic resonance [14, 15].

For the moment we focus on single-spin operators, but for $I > \frac{1}{2}$, for which there exist more than two basis states. A nuclear spin system with three or more basis states and energy levels can no longer be described by a density matrix expressed in

Table 3.3 Cartesian operator density matrix basis for $I=1$

Angular momentum operator basis	$ m\rangle\langle m' $ Ket-bra basis	Name
$\underline{1}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	Identity
I_x	$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$	1-quantum coherence
I_y	$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix}$	1-quantum coherence
I_z	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	z -polarisation
$\frac{1}{\sqrt{6}} (3I_z^2 - 2\underline{1})$	$\frac{1}{\sqrt{6}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	Quadrupolar order
$\frac{1}{\sqrt{2}} (I_z I_y + I_y I_z)$	$\frac{1}{2} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & i \\ 0 & -i & 0 \end{bmatrix}$	Antiphase 1-quantum coherence
$\frac{1}{\sqrt{2}} (I_z I_x + I_x I_z)$	$\frac{1}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}$	Antiphase 1-quantum coherence
$\frac{1}{\sqrt{2}} (I_x^2 - I_y^2)$	$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$	2-quantum coherence
$\frac{1}{\sqrt{2}} (I_x I_y + I_y I_x)$	$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{bmatrix}$	2-quantum coherence

a basis of the four operators comprising I_x , I_y , I_z and the identity matrix. What is required is a basis of the appropriate tensor rank. To illustrate, consider the case of $I = 1$ where the kets have a three-dimensional basis $\{|m\rangle\} = \{|1\rangle, |0\rangle, |-1\rangle\}$. Here eight matrices, in addition to the identity operator, are required.³ We can generate the required Liouville basis by taking products of the spin operators, labelling these products T_α . Again, we will require the T_α , and T_β to be orthogonal under the trace operation. Table 3.3 shows this Cartesian Liouville basis for the case $I = 1$.

³In general for an n - dimensional representation, the number of independent operators and independent coefficients is $n^2 - 1$, meaning eight for spin-1, 15 for spin- $\frac{3}{2}$ and so on.

Table 3.4 Cartesian product operator basis for coupled $I=1/2$ nuclei (first part)

Angular momentum operator basis	$ m\rangle\langle m' $ Ket-bra basis	Name
$\frac{1}{2}\mathbb{1}$	$\frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	identity
I_{ix}, I_{jx}	$\frac{1}{2} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	1-quantum coherence
I_{iy}, I_{jy}	$\frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}, \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ -i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \end{bmatrix}$	1-quantum coherence
I_{iz}, I_{jz}	$\frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}, \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$	z -polarisation

3.3.3 Product operator Liouville space for two coupled spin- $\frac{1}{2}$ nuclei

Suppose we have two spins, i and j , coupled by some interaction that requires the system to be treated as a combined quantum system. The product operator basis of Section 3.1.2 is particularly effective when the spins' interactions are described by Hamiltonian terms diagonal in this basis.

Note that the 4×4 matrix required for the two-spin system implies 16 independent basis vectors in Liouville space, so that 16 product operators are needed, including terms such as zero-quantum coherence states, for which no counterpart exists in a single-spin $I > 1/2$ system. Now the density matrix is

$$\begin{aligned}
\rho = & \rho_0 \frac{1}{2}\mathbb{1} + \rho_{ix}I_{ix} + \rho_{jx}I_{jx} + \rho_{iy}I_{iy} + \rho_{jy}I_{jy} + \rho_{iz}I_{iz} + \rho_{jz}I_{jz} \\
& + \rho_{aix}2I_{ix}I_{jz} + \rho_{ajx}2I_{iz}I_{jx} + \rho_{aiy}2I_{iy}I_{jz} + \rho_{ajy}2I_{iz}I_{jy} \\
& + \rho_{izjz}2I_{iz}I_{jz} + \rho_{ZQCx}(2I_{ix}I_{jx} + 2I_{iy}I_{jy}) + \rho_{ZQCy}(2I_{iy}I_{jx} - 2I_{ix}I_{jy}) \\
& + \rho_{2QCx}(2I_{ix}I_{jx} - 2I_{iy}I_{jy}) + \rho_{2QCy}(2I_{ix}I_{jx} - 2I_{iy}I_{jy})
\end{aligned} \tag{3.63}$$

Table 3.5 Cartesian product operator basis for coupled $I=1/2$ nuclei (continued)

Angular momentum operator basis	$ m\rangle\langle m' $ Ket-bra basis	Name
$2I_{iz}I_{jz}$	$\frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	Longitudinal 2-spin order
$2I_{ix}I_{jz}, 2I_{iz}I_{jx}$	$\frac{1}{2} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}, \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix}$	Antiphase 1-quantum coherence
$2I_{iy}I_{jz}, 2I_{iz}I_{jy}$	$\frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix}, \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{bmatrix}$	Antiphase 1-quantum coherence
$2I_{ix}I_{jx} + 2I_{iy}I_{jy},$ $2I_{iy}I_{jx} - 2I_{ix}I_{jy}$	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$	0-quantum coherence ZQC_x, ZQC_y
$2I_{ix}I_{jx} - 2I_{iy}I_{jy},$ $2I_{ix}I_{jx} - 2I_{iy}I_{jy}$	$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$	2-quantum coherence $2QC_x, 2QC_y$

Tables 3.4 and 3.5 list these product operators along with their matrix representation in the product representation of I_{1z} and I_{2z} eigenstates. These operators are very convenient to work with when the Hamiltonian involves terms that act as simple rotations in Cartesian space (for example, the effect of resonant radiofrequency pulses in NMR) or terms that are diagonal in the I_{1z} and I_{2z} operators, for example the Zeeman interaction and the scalar coupling⁴ $2\pi JI_{iz}I_{jz}$.

In Chapter 4 we will meet specific examples of such terms, and we will also introduce a pictorial representation of these operators due to Sørensen *et al.* [15], which is both extensively used and which provides a helpful visualisation tool.

⁴See later in Section 3.4.

3.3.4 Spherical tensors

The Cartesian basis has some merit in the description of magnetic resonance, where the Hamiltonian is generally expressed in terms of Cartesian spin operators. Hence the evolution of the density matrix under the Liouville equation (eqn 3.53) is simply determined by the operator algebra, eqn 3.13, especially for the case of rotations induced by radiofrequency pulses in the Cartesian axis frame. And, as we shall see, the observable quantities in magnetic resonance are the transverse magnetisations, I_x and I_y . For these reasons product combinations of Cartesian angular momentum operators are very convenient for the description of magnetic resonance phenomena. However, for higher-order spin systems, their transformation properties under rotation are somewhat complicated, though straightforward to calculate. Indeed, when considering rotations, a natural basis to use are spherical tensors, for which a rotation characterised by the Euler angles (α, β, γ) is given by the Wigner rotation matrix $D^{(k)}(\alpha, \beta, \gamma)$, the same transformation property as for the $(2k+1)$ spherical harmonics of rank k . That has particular relevance when dealing with spin states, since the rank L $Y_{LM}(\theta, \phi)$ are the eigenfunctions of the orbital angular momentum operators \mathbf{L}^2 and L_z as [9–11]

$$\begin{aligned}\mathbf{L}^2 Y_{LM}(\theta, \phi) &= L(L+1) Y_{LM}(\theta, \phi) \\ L_z Y_{LM}(\theta, \phi) &= M Y_{LM}(\theta, \phi)\end{aligned}\tag{3.64}$$

where L and M are the angular momentum quantum number and azimuthal quantum number, respectively.

Specifically, the rotation properties of the spherical tensor, T_{kq} , under the Euler rotation is

$$D^{(k)} T_{kq} D^{(k)-1} = \sum_{q'} D_{q'q}^{(k)} T_{kq'}\tag{3.65}$$

where the $D_{q'q}^{(k)}$ are the matrix elements of $D^{(k)}$. In group theoretical terms, eqn 3.65 describes the general transformation properties of an irreducible tensor, T_{kq} , of rank k and order q . Note in particular that a rotation may alter the order but not the rank of the tensor. Consider the example of orbital angular momentum $L = 1$. The three spatial eigenfunctions $Y_{LM}(\theta, \phi)$ are given by $Y_{10}(\theta, \phi)$, $Y_{11}(\theta, \phi)$, and $Y_{1-1}(\theta, \phi)$. The Wigner rotation matrix $D^{(1)}(\alpha, \beta, \gamma)$, which describes the transformation between these states under the Euler rotation, is the same matrix used to describe the rotation of $I = 1$ kets for which $m = 1, 0, -1$. In general, for spin quantum number I for which the $(2I+1)$ basis kets are $|Im\rangle$, the rotation is given by eqn 3.27.

When we are dealing with transformations of operators in spin space, as opposed to transforming the kets themselves, it is important to distinguish the rank of the operator from the rank of the ket space. For example, the angular momentum operators I_x , I_y , and I_z transform as rank-1 tensors, whether they belong to $I = 1/2$, $I = 1$, or $I > 1$. However, whereas for spin- $\frac{1}{2}$ these rank-1 tensor operators (along with the identity) are all that are needed to form a basis for any density matrix, or indeed any observable operator such as the Hamiltonian, for higher spin ensembles, higher rank operators will be needed. Note also that half-integer rank is possible in ket space, in which case the matrix is double valued under rotation, a rotation by 2π being the negative identity

Table 3.6 Spherical tensor operator basis for $I = 1$

Tensor component	Angular momentum operator basis	$ m\rangle\langle m' $ Ket–bra basis	Name
T_{00}	$\underline{\underline{1}}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	Identity
T_{10}	I_z	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	z-polarisation
T_{11}	$-\frac{1}{\sqrt{2}}I_+$	$\begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{bmatrix}$	1-quantum coherence
T_{1-1}	$\frac{1}{\sqrt{2}}I_-$	$\begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$	1-quantum coherence
T_{20}	$\frac{1}{\sqrt{6}}(3I_z^2 - 2\underline{\underline{1}})$	$\frac{1}{\sqrt{6}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	Quadrupolar order
T_{21}	$-\frac{1}{2}(I_z I_+ + I_+ I_z)$	$-\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{bmatrix}$	Antiphase 1-quantum coherence
T_{2-1}	$\frac{1}{2}(I_z I_- + I_- I_z)$	$\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{bmatrix}$	Antiphase 1-quantum coherence
T_{22}	$\frac{1}{2}I_+^2$	$\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	2-quantum coherence
T_{2-2}	$\frac{1}{2}I_-^2$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$	2-quantum coherence

and a rotation by 4π the positive identity matrix. By contrast, in the transformation of operators, only integer rank is permitted.

The lowest rank for operators in spin space is the identity operator, T_{00} . Those for $k = 1$ are I_z , and the operators formed by linear combinations of I_x and I_y , namely, $-I_+/\sqrt{2}$ and $I_-/\sqrt{2}$. All higher rank tensors can be formed from appropriate products of these. The rule for forming a spherical tensor $T_{KQ}(\mathbf{A}_1)$, by making products of lower rank tensors, follows that for combining angular momenta, namely

$$T_{KQ}(\mathbf{A}_1, \mathbf{A}_2) = \sum_{q_1} \langle k_1 q_1 k_2 q_2 | KQ \rangle T_{k_1 q_1}(\mathbf{A}_1) T_{k_2 q_2}(\mathbf{A}_2) \quad (3.66)$$

where $q_2 = Q - q_1$, the $\langle k_1 q_1 k_2 q_2 | K Q \rangle$ are Clebsch–Gordon coefficients, and \mathbf{A}_1 and \mathbf{A}_2 are all the other variables upon which the tensors depend. For single-spin operators, \mathbf{A}_1 and \mathbf{A}_2 are identical. The same Clebsch–Gordon rules for angular momentum addition apply in determining the rank of the tensors. In other words $k = k_1 + k_2, k_1 + k_2 - 1, \dots, |k_1 - k_2|$ and, as stated above, $q_2 = Q - q_1$. Suppose $k_1 = k_2 = 1$. Then Clebsch–Gordon superpositions of products generate the nine tensors $T_{2\pm 2}, T_{2\pm 1}, T_{20}, T_{1\pm 1}, T_{10}$, and T_{00} .⁵

Table 3.6 shows the standard spherical tensor basis set for spin-1 [16]. In this form they are orthogonal but not normalised. Unit spherical tensors may be defined by [17]

$$\hat{T}_{KQ} = \frac{1}{K!} \left[\frac{(2K+1)(2I-K)!2K(2K)!}{(2K+I+1)!} \right]^{1/2} T_{KQ} \quad (3.67)$$

with the orthonormal relationship

$$\text{Tr} \left(\hat{T}_{KQ} \hat{T}_{K'Q'}^\dagger \right) = \delta_{KK'} \delta_{QQ'} \quad (3.68)$$

the \dagger symbol representing the Hermitian conjugate operation.

Any density matrix may then be written

$$\rho = \sum_{K,Q} \rho_Q^K \hat{T}_{KQ} \quad (3.69)$$

where the coefficients, ρ_Q^K are referred to as Fano statistical tensors [9, 10] and are given by

$$\rho_Q^K = \text{Tr} \left(\hat{T}_{KQ}^\dagger \rho \right) \quad (3.70)$$

Most importantly when considering the evolution of the density matrix under the effect of a Hamiltonian operator expressed in the spherical tensor basis, we have the following commutation relations, true for all spin quantum number I ,

$$[T_{10}, T_{KQ}] = Q T_{KQ} \quad (3.71)$$

and

$$[T_{1\pm 1}, T_{KQ}] = \mp \frac{1}{\sqrt{2}} [(K \mp Q)(K \pm Q + 1)]^{1/2} T_{KQ\pm 1} \quad (3.72)$$

These relations are useful in determining how our spin system will evolve in the presence of the Zeeman Hamiltonian ($\sim T_{10}$) or, as we shall soon see, radiofrequency pulses ($\sim T_{1\pm 1}$). For spin-1, a Hamiltonian of higher rank is possible, namely the electric quadrupole interaction ($\sim T_{20}$). Table 3.7 shows the relevant commutators for spin-1 [18].

Suppose we consider some Hamiltonian \mathcal{H} that may be written in terms of our T_{KQ} basis. Now consider some initial state of the time-dependent density matrix $\rho(t)$, which comprises a single Fano component so that $\rho(0) = \rho_{Q_0}^{K_0} T_{K_0 Q_0}$. Then evolution under \mathcal{H} will be determined by the commutator $[\mathcal{H}, T_{K_0 Q_0}]$. Suppose that commutator

⁵For example, $T_{11} = T_{10}T_{11} - T_{11}T_{10}$.

Table 3.7 Commutation relations for $I = 1$ spherical tensor operators.

	T_{10}	T_{11}	T_{1-1}	T_{20}	T_{21}	T_{2-1}	T_{22}	T_{2-2}
T_{10}	0	T_{11}	$-T_{1-1}$	0	T_{21}	$-T_{2-1}$	$2T_{22}$	$-2T_{2-2}$
T_{11}	$-T_{11}$	0	$-T_{10}$	$-\sqrt{3}T_{21}$	$-\sqrt{2}T_{22}$	$-\sqrt{3}T_{20}$	0	$-\sqrt{2}T_{2-1}$
T_{1-1}	T_{1-1}	T_{11}	0	$\sqrt{3}T_{2-1}$	$\sqrt{3}T_{20}$	$\sqrt{3}T_{22}$	$\sqrt{2}T_{21}$	0
T_{20}	0	$\sqrt{3}T_{21}$	$-\sqrt{3}T_{2-1}$	0	$\frac{\sqrt{3}}{2}T_{11}$	$-\frac{\sqrt{3}}{2}T_{1-1}$	0	0
T_{21}	$-T_{21}$	$\sqrt{2}T_{22}$	$-\sqrt{3}T_{20}$	$-\frac{\sqrt{3}}{2}T_{11}$	0	$\frac{1}{2}T_{10}$	0	$\frac{1}{\sqrt{2}}T_{1-1}$
T_{2-1}	T_{2-1}	$\sqrt{3}T_{20}$	$-\sqrt{3}T_{22}$	$\frac{\sqrt{3}}{2}T_{1-1}$	$-\frac{1}{2}T_{10}$	0	$-\frac{1}{\sqrt{2}}T_{11}$	0
T_{22}	$-2T_{22}$	0	$-\sqrt{2}T_{21}$	0	0	$\frac{1}{\sqrt{2}}T_{11}$	0	T_{10}
T_{2-2}	$2T_{2-2}$	$\sqrt{2}T_{2-1}$	0	0	$-\frac{1}{\sqrt{2}}T_{1-1}$	0	$-T_{10}$	0

results in a unique spherical tensor component $T_{K_1Q_1}$. Table 3.7 suggests that this is most likely if our Hamiltonian is also a pure spherical tensor. Now suppose that the commutator $[\mathcal{H}, T_{K_1Q_1}]$ returns $T_{K_0Q_0}$, again a common occurrence in Table 3.7. In that case our evolution problem reduces to a pair of coupled equations and the effect of \mathcal{H} is simply a precession of our density matrix between the states $T_{K_0Q_0}$ and $T_{K_1Q_1}$. It turns out that a wide class of physical phenomena in NMR is so describable.

Spherical tensors for coupled spins

In eqn 3.66 we saw how to construct spherical tensors of two spins, $T_{KQ}(\mathbf{A}_1, \mathbf{A}_2)$ from appropriate tensor products, at that point applying this general relation to single-spin operators where $\mathbf{A}_1 = \mathbf{A}_2$. Here we apply the same relation to spherical tensors for coupled spin systems, where we deal with products of operators, $T_{k_1q_1}(i)$ and $T_{k_2q_2}(j)$, corresponding to different spin spaces, i and j .

$$T_{KQ}(i, j) = \sum_{q_1} \langle k_1q_1 k_2q_2 | KQ \rangle T_{k_1q_1}(i) T_{k_2q_2}(j) \quad (3.73)$$

where again, $q_2 = Q - q_1$ and the $T_{KQ}(i, j)$ transform under rotations according to the Wigner matrices $D^{(K)}(\alpha, \beta, \gamma)$.

For two spin- $\frac{1}{2}$ nuclei, the operators $T_{k_1q_1}(i)$ are of rank-1 or, in the case of a single-spin operator where either the i or j spin is represented by the identity, of rank-0. Using the Clebsch–Gordon coefficients for combining spin-1, and spin-0, we obtain the $T_{KQ}(i, j)$ tensors shown in Table 3.8, using the notation $T_{KQ}(R_i R_j)$ to indicate whether we are dealing with two-spin or one-spin operators, R being the rank.⁶ Clearly the distinction of two sets of single-spin operators for i and j will make for a larger set than Table 3.6, where there were nine spin tensors. Furthermore, because the products involve operators in different spaces, the commutation relationships for angular momenta no longer apply, as in the case of single-spin operators and this leads to cross product terms with no counterpart in single-spin systems. Finally there exists a scalar product which, unlike the case of single-spin operators, is quite distinct

⁶Here we use the abbreviation 0-QC, 1-QC and 2-QC to refer to zero-, single- and double-quantum coherence respectively.

Table 3.8 Spherical tensors for two coupled spin- $\frac{1}{2}$ nuclei

Type	$T_{KQ}(R_i R_j)$	Operator product	Name
Identity	$T_{00}(00)$	$\frac{1}{2}\mathbb{1} \otimes \mathbb{1}$	
Scalar product	$T_{00}(11)$	$-\frac{2}{\sqrt{3}}\mathbf{I}_i \cdot \mathbf{I}_j$	Spin-spin coupling
Spin I_i	$T_{10}(10)$	$I_{iz} \otimes \mathbb{1}$	z-polzn
	$T_{1\pm 1}(10)$	$\mp \frac{1}{\sqrt{2}}I_{i\pm} \otimes \mathbb{1}$	1-QC
Spin I_j	$T_{10}(01)$	$\mathbb{1} \otimes I_{jz}$	z-polzn
	$T_{1\pm 1}(01)$	$\mp \frac{1}{\sqrt{2}}\mathbb{1} \otimes I_{j\pm}$	1-QC
Cross product	$T_{10}(11)$	$\frac{1}{\sqrt{2}}[I_{i-}I_{j+} - I_{i+}I_{j-}]$	0-QC
	$T_{1\pm 1}(11)$	$[I_{iz}I_{j\pm} - I_{i\pm}I_{jz}]$	
Second rank	$T_{20}(11)$	$(\frac{2}{3})^{1/2}[3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j]$	Longit 2 spin order
	$T_{2\pm 1}(11)$	$\mp [I_{iz}I_{j\pm} + I_{i\pm}I_{jz}]$	Antiphase 1-QC
	$T_{2\pm 2}(11)$	$I_{i\pm}I_{j\pm}$	2-QC

from the identity. These factors lead to 16 linearly independent two-spin tensors in Table 3.8 [19–21].

Definition of multiple-quantum coherence

The idea of quantum coherence derives from the non-zero ensemble average of the product of eigenstate amplitudes $\overline{a_m^* a_{m'}}$ that appears off the density matrix diagonal. The ensemble phase coherence between these state amplitudes is brought about by the quanta of radiofrequency energy that couple these states in a transition. Such a non-zero density matrix element corresponds to a coherent superposition of the two eigenstates $|m\rangle$ and $|m'\rangle$ [22].

$$|\psi_{mm'}\rangle = a_m|m\rangle + a_{m'}|m'\rangle \quad (3.74)$$

This non-equilibrium state contributes non-zero matrix density matrix elements $\rho_{mm'} = |m\rangle\langle m'|$ and $\rho_{m'm} = |m'\rangle\langle m|$. Just as each eigenstate is characterised by magnetic quantum number m , so each coherence $\rho_{mm'}$ is characterised by a magnetic quantum number difference $p = m - m'$. p is known as the coherence order [22].

Subsequently, under the free precession of a Zeeman Hamiltonian, the coupled states precess synchronously. For example, in a single quantum transition, where m and m' differ by one, $\overline{a_m^* a_{m\pm 1}}$ oscillates at the Larmor frequency and represents a precessing magnetic dipole detectable using the receiver coil tuned to that Larmor frequency. Where $\Delta m \neq \pm 1$, the quantum coherence is not directly detectable in this manner.

In practice, the creation of various orders of multiple-quantum coherence is not performed by direct absorption of multiple radiofrequency (RF) field quanta, but by using a combination of RF pulses and the various interaction terms in the spin

Hamiltonian. These terms allow specific evolutionary migrations of the density matrix elements depending on the spin character of each term. In particular, spin-spin scalar coupling, dipolar interactions, and quadrupole interactions allow the generation of various higher-order coherences beyond $\Delta m = \pm 1$. In turn, the various pathways of evolution provide information to the spectroscopist, pathways which act as a signature for these interactions. Hence, pathway selectivity can provide a filtering process that can be used to identify spins of interest.

The definition of multiple-quantum coherence depends on the chosen basis. Suppose we consider product operators in a basis of I_z , I_+ , and I_- operators. Clearly the degree or ‘order’ p of quantum coherence is also given by the number of raising operators minus the number of lowering operators. In that case we say that a p -quantum coherence corresponds to a density matrix with non-vanishing elements only in the p th off-diagonal, and we could write our density matrix in such a basis as $\rho = \sum_p \rho_p$. These are apparent in Table 3.3. Under the influence of a Zeeman Hamiltonian ωI_z , the p -quantum coherence oscillates at frequency $p\omega$. In general we may write the effect of a rotation about the z -axis by

$$\exp(-i\phi I_z) \rho_p \exp(i\phi I_z) = \rho_p \exp(-ip\phi) \quad (3.75)$$

When spherical tensors, T_{kq} , are used to represent the density matrix, the degree of multiple-quantum coherence is determined by the order q , as apparent in Table 3.6. A p -quantum coherence corresponds to a $T_{k\pm p}$ spherical tensor operator, the maximum order being limited by the tensor rank k . For example, a double-quantum coherence could be represented by $T_{22} + T_{2-2}$ and a single-quantum coherence by $I_x = -\frac{1}{\sqrt{2}}(T_{11} - T_{1-1})$ or by the antiphase single-quantum coherence represented by $T_{21} - T_{2-1}$. For pure orders of defined sign, T_{22} and T_{2-2} represent $p = 2$ and $p = -2$, respectively.

For a system of K coupled spins- $1/2$, p may take values from $-K$ to K . In this case we replace the single-spin operator I_z of eqn 3.75 by $\sum_{i=1}^K I_{iz}$. Note that in the case of coupled spins additional orders of coherence are possible. In particular, in Table 3.8 note the cross product terms $T_{10}(11)$ and $T_{11}(1 \pm 1)$, which have no equivalent in single-spin systems. In particular, the term $T_{10}(11)$ reduces to I_z for a single spin while $T_{11}(11)$ is identical to I_+ . But in the case of a two-spin system, $T_{10}(11)$ is a unique state of the density matrix known as a zero-quantum coherence. We return to this peculiar state of coupled spin systems in Chapter 4.

3.4 The spin Hamiltonian

Atomic nuclei interact with their atomic and molecular environment through various multipole orders of electromagnetic interaction: electric monopole (charge), magnetic dipole, and electric quadrupole. All nuclei possess charge, the source of Coulombic binding of electrons in the atom. Most possess spin and hence a magnetic dipole, and thereby are sensitive to magnetic fields, whether externally applied, or from surrounding atomic electrons or neighbouring nuclear dipoles. Those nuclei with spin greater than $\frac{1}{2}$ will possess an electric quadrupole moment and so will be sensitive to gradients in electric fields arising from surrounding molecular orbitals. Only the dipole and quadrupole operators involve the nuclear spin and hence only these interactions are apparent in the nuclear spin precession observed in NMR.

Of course the spin electrons that surround atomic nuclei in condensed matter or in gases possess far greater magnetic character than any nearby nuclei. But in diamagnetic materials, the subject of most of our interest, those electrons are spin-paired in accordance with the Pauli principle, and so their magnetic dipole fields vanish. For molecules with unpaired electrons, the electron–nuclear hyperfine interaction plays an important role in the nuclear spin Hamiltonian, contributing a term $A \mathbf{I} \cdot \mathbf{S}$, where S is the electron spin operator. Hyperfine interactions are typically measured in megahertz and may be comparable with the nuclear Zeeman interaction with a large laboratory magnetic field.

3.4.1 The i -spin Hamiltonian

Here we will focus on diamagnetic materials, for which the hyperfine interaction is absent. We can therefore write the spin Hamiltonian for a single nucleus labelled i as

$$\begin{aligned} \mathcal{H}_i &= \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{CS}} + \mathcal{H}_{\text{scalar}} + \mathcal{H}_{\text{Q}} + \mathcal{H}_{\text{D}} \\ &= -\gamma B_0 I_{iz} - \gamma \mathbf{I}_i \cdot \underline{\underline{\delta}} \cdot \mathbf{B}_0 + \sum_j 2\pi J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j + \mathbf{I}_i \cdot \underline{\underline{\mathbf{Q}}} \cdot \mathbf{I}_i + \sum_j \mathbf{I}_i \cdot \underline{\underline{\mathbf{D}}}_{ij} \cdot \mathbf{I}_j \end{aligned} \quad (3.76)$$

The Zeeman interaction is already familiar to us. The remaining terms are, respectively, the chemical shift, the internuclear spin–spin scalar coupling, the electric quadrupole interaction, and the internuclear dipolar interaction. The chemical shift and the spin–spin coupling give spectral information containing a chemical fingerprint for the molecule hosting the nuclear spin of interest. The nuclear quadrupole and internuclear dipolar terms provide a signature for molecular orientation or structural ordering. Each term involves a tensor product of spin and field operators, and in a different context each would be worthy of a complete discussion. But what makes them of interest to us here is the possibility of using these effects to obtain molecular specificity in translational motion measurements. For that reason our discussion is limited. In the next chapter we return to the spin Hamiltonian and consider its effect in NMR experiments, where the additional effect of RF pulses makes for a rich diversity of evolution schemes. In the present chapter we provide a brief outline of these interactions. Further description can be found elsewhere in a number of excellent texts [23–26].

Equation 3.76 is written, for convenience, in terms of products of vector spin operators and Cartesian tensor spatial operators $\underline{\underline{\delta}}$, $\underline{\underline{\mathbf{Q}}}$, and $\underline{\underline{\mathbf{D}}}$. In practice we seldom need to use these full expressions. In laboratory superconducting magnets the Zeeman interaction strength is on the order of thousands of megahertz, much greater than the remaining terms. As a consequence, the Zeeman term defines the zeroth order quantum mechanical basis set in terms of I_z operators. All the remaining terms are at least three orders of magnitude smaller, and so act as perturbations in the zeroth order frame. For the purpose of this book, we need mostly consider only first-order perturbations, corresponding to diagonal (secular) terms of the respective Hamiltonians in the I_z frame, which we write with subscript zero. However, the off-diagonal terms will be of importance in their ability to cause transitions between quantum states, thus contributing to T_1 and T_2 relaxation.

Note that where the full spin Hamiltonian expressions are needed, for example where the Zeeman field is weak or in the case of strong J-couplings where the difference

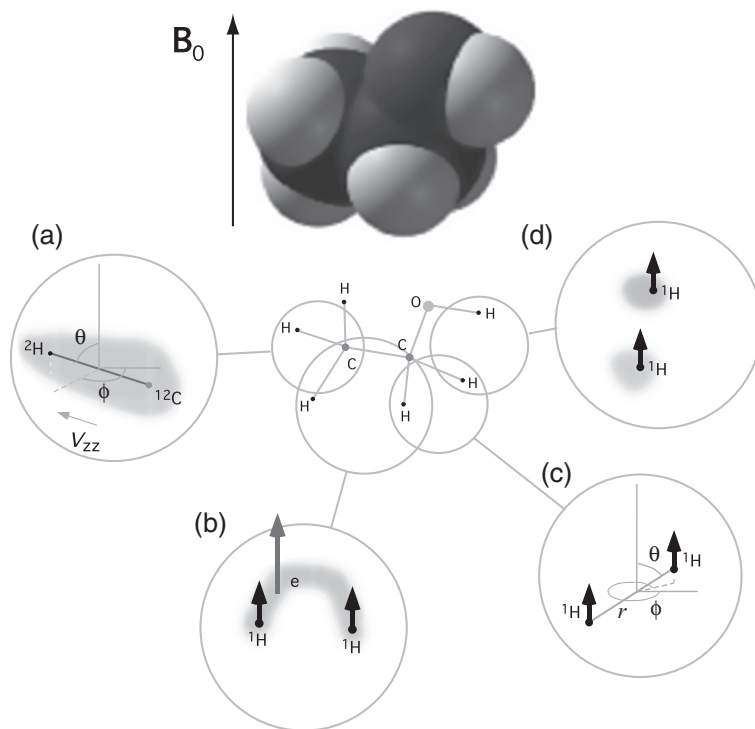


Fig. 3.9 Schematic representation of various interactions in the spin Hamiltonian for an ethanol molecule immersed in a magnetic field, \mathbf{B}_0 . (a) The electric quadrupole interaction resulting from the electric field gradient, V_{zz} associated with the molecular orbital around a $C-^2H$ bond. (b) The scalar spin–spin interaction mediated by the molecular orbital electrons. (c) The inter-nuclear through-space dipolar interaction. (d) The chemical shift associated with differing diamagnetic shielding of the nuclei by electrons in parts of the molecular orbital that differ chemically.

between the chemical shifts is small, it can be convenient to use a spherical tensor representation of the Hamiltonian. This approach is discussed in Section 3.3.4.

3.4.2 The Hamiltonian in terms of tensor products

The Hamiltonian for a spin system is a scalar and, as such, must transform under rotations as a rank-0 tensor. That means that the product of the spin tensor and the spatial tensor that comprise the Hamiltonian operator must be proportional to T_{00} [11]. A special case of eqn 3.66 arises when the two tensors of the same rank ($k = k_1 = k_2$) are combined to produce a tensor of zero rank and order T_{00} . In this case the Clebsch–Gordon coefficient is just $(-1)^{(k-q)}(2k+1)^{-1/2}$ and

$$T_{00} = (-1)^k (2k+1)^{-1/2} \sum_k (-1)^q T_{kq} T_{k-q} \quad (3.77)$$

Table 3.9 Spherical harmonics to second rank

Y_{KQ}	
Y_{00}	$\sqrt{\frac{1}{4\pi}}$
Y_{10}	$\sqrt{\frac{3}{4\pi}} \cos \theta$
$Y_{1\pm 1}$	$\mp \sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i\phi)$
Y_{20}	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
$Y_{2\pm 1}$	$\mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta \exp(\pm i\phi)$
$Y_{2\pm 2}$	$\mp \sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(\pm i2\phi)$

Table 3.10 Spin Hamiltonian terms in spherical tensor form, along with secular parts. The quadrupole interaction is taken to be symmetric ($\eta = 0$).

name	spherical tensor form
Zeeman (secular)	$-\gamma B_0 T_{10}$
Scalar coupling (full)	$-2\pi J (3\pi)^{1/2} T_{00}(11) Y_{00}$
Scalar coupling (secular)	$2\pi J \frac{1}{3} \left[T_{20}(11) - \frac{1}{\sqrt{2}} T_{00}(11) \right]$
Quadrupole (full)	$\frac{3eV_{zz}Q}{4I(2I-1)\hbar} (24\pi/5)^{1/2} \sum_q (-1)^q T_{2q} Y_{2-q}(\theta, \phi)$
Quadrupole (secular)	$\frac{3eV_{zz}Q}{4I(2I-1)\hbar} (24\pi/5)^{1/2} T_{20} Y_{20}(\theta, \phi)$
Dipolar (full)	$\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} (24\pi/5)^{1/2} \sum_q (-1)^q T_{2q}(11) Y_{2-q}(\theta, \phi)$
Dipolar (secular)	$\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} (24\pi/5)^{1/2} T_{20}(11) Y_{20}(\theta, \phi)$

Since $(-1)^k (2k+1)^{-1/2}$ is a constant for a given spin or spatial tensor, we may write

$$\mathcal{H} = \text{const} \sum_q (-1)^q T_{kq}(\mathbf{I}) Y_{k-q}(\theta, \phi) \quad (3.78)$$

where the spatial tensor is represented by a spherical harmonic and $T_{kq}(\mathbf{I})$ is a spin tensor for single (T_{kq}) or coupled ($T_{kq}(11)$) spins, as given respectively in Tables 3.6 and 3.8. All the terms in eqn 3.76 are scalars of this form. For example, the Zeeman Hamiltonian is proportional to $\sum_q (-1)^q T_{1q} Y_{1-q}(\theta, \phi)$, where the angles refer to the orientation of the magnetic field with respect to the representation z -axis.

Because the Zeeman Hamiltonian generally dominates in magnetic resonance, we define, by convention, the representation z -axis as the field direction, making $\theta = 0$ and hence retaining only the $T_{10}Y_{10}(0, \phi) = T_{10}$. As explained in Section 3.4, in calculating the evolution of the spin system we retain only the secular parts of the remaining spin Hamiltonian terms.

3.4.3 Precession diagrams for $I = 1/2$ and $I = 1$

What is the starting point for the density matrix of nuclear spins? Most often we will find that it is the state of thermal equilibrium in a magnetic field. In the next section we look at the thermal equilibrium state in some detail. Having considered that, we will then be in a position to describe the magnetic resonance phenomenon using the following scheme. First we must define the spin Hamiltonian that represents all possible energies of interaction, the dominant term in most cases being the Zeeman interaction due to the laboratory magnetic field used to polarise the spin system, a polarisation direction we label as the z -axis. We then represent the state of the spin system by the density matrix, generally taking as our starting point the thermal equilibrium condition. We will find that equilibrium is often describable by $\rho(0) \sim I_z = T_{10}$. Next we allow the spin system to evolve in the presence of the spin Hamiltonian, using the Liouville equation to predict the outcome. We will see that the starting point for that evolution will be the generation of a non-equilibrium state of the spin system by means of a resonant radiofrequency pulse. Then, at the detection stage of the experiment, we directly measure the precession of macroscopic spin magnetisation. We will see that this corresponds to a measurement of I_x and I_y or $T_{1\pm 1}$ components of the density matrix.

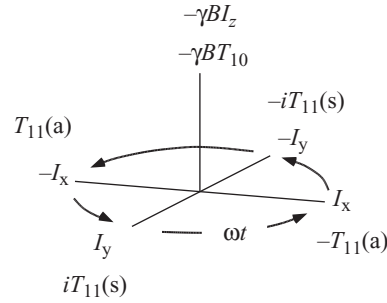


Fig. 3.10 Rotating frame precession diagrams for states of the density matrix in the presence of a Zeeman interaction. The density matrix states and the Hamiltonian are labelled in both Cartesian and spherical tensor form. The precession frequency is $\omega = \gamma B$.

To follow the behaviour of the spin system from thermal equilibrium to ultimate detection, we need only monitor the progress of the density matrix under successive evolution. Understanding this process is often aided by simple precession diagrams, as shown in Fig. 3.10 in which the evolution of I_x and I_y under an I_z Zeeman Hamiltonians is shown. Note that we may cyclically commute this diagram to obtain the evolution of I_y , and I_z under an I_x Hamiltonian and so on. Of course a purely Zeeman-like

evolution is all that is possible for $I = 1/2$, but Fig. 3.10 applies equally to higher spins where the Hamiltonian is pure Zeeman. Note that we may also represent the terms in Fig. 3.10 using spherical tensor operators, where $I_z = T_{10}$, $I_x = -T_{11}(a)$, and $I_y = iT_{11}(s)$, the symmetric and antisymmetric combinations being defined by

$$\begin{aligned} T_{11}(s) &= 2^{-1/2} (T_{11} + T_{1-1}) \\ T_{11}(a) &= 2^{-1/2} (T_{11} - T_{1-1}) \end{aligned} \quad (3.79)$$

For higher spin systems, $I \geq 1$, rank 2, and higher tensors may play a role in addition to the rank 1 tensors of Fig. 3.10. In Fig. 3.10 some relevant precessions for $I = 1$ are shown [17]. In each case the vertical axis represents the tensorial nature of the Hamiltonian term, while the two transverse axes represent two density matrix tensor states that interchange in a precessional motion as a result of the commutator relationships returning a simple pair of coupled equations. Note that these refer to the behaviour of independent nuclei experiencing magnetic or quadrupole interactions. Later we will look at the appropriate description of the density matrix for spin systems where special Hamiltonian terms result in a coupling of spins.

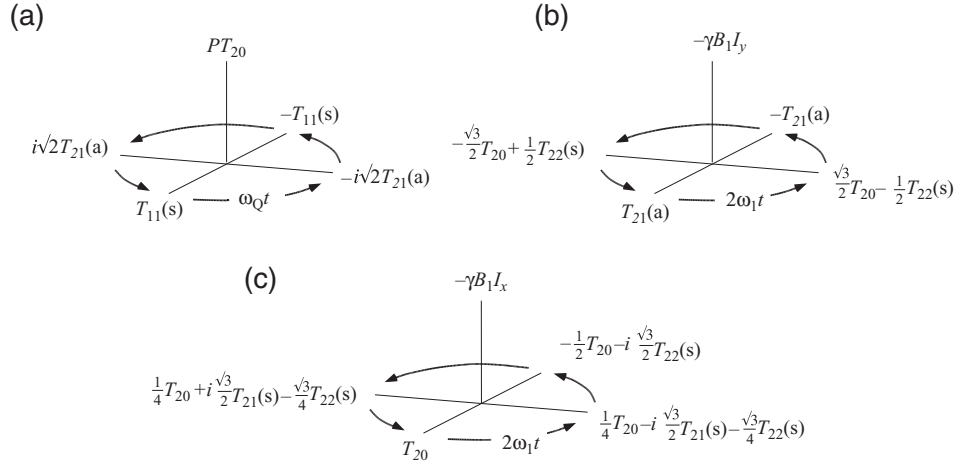


Fig. 3.11 Precession of density matrix states in the spherical tensor formalism applicable for $I = 1$. (s) and (a) refer to symmetric and antisymmetric combinations of tensor components. (a) shows the evolution of I_y ($T_{11}(s)$) under the quadrupole interaction, PT_{20} . The precession frequency is $\sqrt{3}/2P$. (b) shows the evolution of $T_{21}(a)$ into the quadrupole polarisation state, T_{20} under I_y . Note that the Larmor precession frequency is doubled for this second rank tensor. (c) shows the evolution of T_{20} under I_x . Note that this is no longer a simple precession between two states with components given by $\cos(2\omega_1 t)$ and $\sin(2\omega_1 t)$, respectively, but a transformation between T_{20} , T_{21} , and T_{22} states according to the irreducible representation of the rotation group $D^{(2)}$.

The question arises as to whether in practice spherical tensors or Cartesian tensors made of products of Cartesian spin operators, I_α , are easiest to manage in the descrip-

tion of spin evolution. Of course, the spherical tensors do provide a clean definition of higher-order coherences. For example, note the identity of T_{22} with double-quantum coherence in Table 3.6 by comparison with Table 3.3, where superpositions of product operators are needed. But in considering density matrix evolution, the advantage is not so obvious. When considering the effect of higher order spin tensor terms in the Hamiltonian, the scalar coupling, the quadrupole interaction, and the dipolar interaction, the spherical tensor formalism allows us to use the power of irreducible tensor representations to calculate relevant commutators and precessions. But the evolutions of higher-order spherical tensors under both RF pulses and other spin Hamiltonian terms are often complex, as seen in Fig. 3.11. And in considering the effect of the RF field, predicting the behaviour of tensors made from products of Cartesian spin operators is undoubtedly much easier, since the RF field ideally engenders a simple rotation of the I_α .

3.4.4 Spherical tensor precession for coupled spin- $\frac{1}{2}$

To write the two-spin magnetisation in spherical tensor form we note

$$\begin{aligned} I_{ix} + I_{jx} &= -2^{-1/2} [T_{11}(10) - T_{1-1}(10)] - 2^{-1/2} [T_{11}(01) - T_{1-1}(01)] \\ &= -T_{11}(10, a) - T_{11}(01, a) \end{aligned} \quad (3.80)$$

and

$$\begin{aligned} I_{iy} + I_{jy} &= -2^{-1/2} i [T_{11}(10) + T_{1-1}(10)] - 2^{-1/2} [T_{11}(01) + T_{1-1}(01)] \\ &= iT_{11}(10, s) + iT_{11}(01, s) \end{aligned} \quad (3.81)$$

where the $T_{11}(01, a)$ and $T_{11}(01, s)$ are antisymmetric and symmetric combinations as defined in eqn 3.79. Suppose the spin Hamiltonian is that of an AB spin system, namely

$$\begin{aligned} H &= -\Delta\omega [I_{iz} + I_{jz}] - \frac{1}{2}\delta [I_{iz} - I_{jz}] + 2\pi J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \\ &= -\Delta\omega [T_{10}(10) + T_{10}(01)] - \frac{1}{2}\delta [(T_{10}(10) - T_{10}(01))] - 2\pi J_{ij} \frac{2}{\sqrt{3}} T_{00}(11) \end{aligned} \quad (3.82)$$

where $\Delta\omega$ is the average chemical shift in the rotating frame and δ is the chemical shift difference between the i and j spin.

Figure 3.12 shows a rare example of a particularly simple precession of a two-spin tensor term, the double-quantum coherence $T_{22}(11)$ in the presence of the scalar spin-spin interaction and with a chemical shift frequency difference between the i and j spins [19]. Only the mean Larmor frequency plays a role and we find that the precession rate is twice the Larmor frequency. This same frequency doubling behaviour is found for single-spin double-quantum coherence formed as a result of the quadrupole interaction.

3.5 The thermal equilibrium density matrix

3.5.1 The Boltzmann form of the density matrix

What is the meaning of thermal equilibrium? Consider two systems each containing an ensemble of quantum particles, each being in thermal equilibrium with the same ‘heat

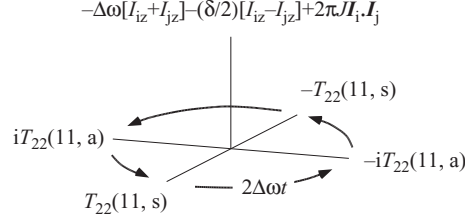


Fig. 3.12 Precession of double-quantum coherence represented by symmetric and antisymmetric combinations of $T_{22}(11)$ under the influence of the general two spin scalar coupling and chemical shift Hamiltonian of eqn 3.82. Only the average frequency appears and the double-quantum coherence precesses at twice the Larmor frequency.

bath' or 'thermal reservoir' at temperature T . If one of the systems is removed from thermal contact with the reservoir, but kept in thermal isolation, then its physical properties will remain unaltered with time. That means that its density matrix does not change, and given our rule for density matrix evolution, the Liouville eqn 3.53, we have [27]

$$[\mathcal{H}, \rho] = 0 \quad (3.83)$$

where \mathcal{H} is the Hamiltonian for this particular system. Hence the thermal equilibrium density matrix must be a simple function of the Hamiltonian, for example a power series.

Now suppose we were to decouple both the two original systems from the reservoir such that they remain coupled together but otherwise isolated. Then, since each was in thermal equilibrium at the same temperature T , each will remain with its physical properties unaltered with time, and the combined system density matrix will also commute with the combined system Hamiltonian. Of course, that Hamiltonian is the sum of each, while the combined system density matrix is an outer product of each individual ρ . Hence we may deduce that the density matrix must be of the form

$$\rho_{eq} = \alpha \exp(-\beta \mathcal{H}) \quad (3.84)$$

where α is a normalisation constant and β measures the property that each system shares with the reservoir, namely, the temperature T . Following the same arguments outlined in Chapter 1, we may show that β is the familiar Boltzmann factor $1/k_B T$. In thermal equilibrium, the density matrix ρ for an ensemble of nuclear spins obeying Boltzmann statistics may be written

$$\rho_{eq} = \frac{\exp(-\mathcal{H}/k_B T)}{\text{Tr}(\exp(-\mathcal{H}/k_B T))} \quad (3.85)$$

3.5.2 Nuclear spins in thermal equilibrium—the high temperature approximation

Without writing down a complete Hamiltonian at this point, we will list some of the terms and their relative strengths expressed in frequency units. First and foremost is the Zeeman interaction of the nuclear spins with the laboratory polarizing magnetic

field, typically hundreds of megahertz for protons in superconducting magnets. Next is the interaction with laboratory radiofrequency field, at around 100 kHz. Smaller still are the internuclear dipole interactions and electric quadrupole interactions, of a few tens of kilohertz, the chemical shifts caused by electron shielding at parts per million of the magnetic field, and finally the electron mediated spin–spin couplings, typically a few tens of hertz. For other stable nuclei, all with smaller gyromagnetic ratios than the proton, the Zeeman term is weaker but equally so are the remaining interactions.⁷ Even for the dominant Zeeman interaction, the ratio $\mathcal{H}/k_B T$ in eqn 3.85 is around 10^{-5} for protons at room temperature. Sub-milliKelvin temperatures are required to Zeeman-polarise nuclear spins in laboratory magnetic field. To a very good approximation therefore, and excepting some very rare cases,⁸ eqn 3.85 may be expanded in a power series in which only the leading terms, linear in $\mathcal{H}/k_B T$, are retained, so that

$$\rho_{eq} \approx \frac{\underline{\underline{1}} - \mathcal{H}/k_B T}{\text{Tr}(\underline{\underline{1}} - \mathcal{H}/k_B T)} \quad (3.86)$$

Allowing that the Zeeman Hamiltonian, $\mathcal{H}_{\text{Zeeman}} = -\gamma B_0 I_z$, dominates and noting $\text{Tr}(I_z) = 0$, the high temperature approximation (HTA) results,

$$\rho_{eq} \approx \frac{1}{2I+1} \left(\underline{\underline{1}} + \frac{\gamma \hbar B_0 I_z}{k_B T} \right) \quad (3.87)$$

the factor $2I+1$ being the trace of $\underline{\underline{1}}$.

Three immediate consequences arise from eqn 3.87. First, we can now calculate the thermal equilibrium angular momentum and the thermal equilibrium magnetisation for N spins per unit volume immersed in a magnetic field, B_0 , as

$$\begin{aligned} \langle I_z \rangle_{eq} &= \text{Tr}(I_z \rho_0) \\ &= \frac{1}{2I+1} \frac{\text{Tr}(\gamma B_0 \hbar I_z^2)}{k_B T} \\ &= \frac{\gamma B_0 \hbar I(I+1)}{3k_B T} \end{aligned} \quad (3.88)$$

and

$$\begin{aligned} M_{eq} &= N \gamma \hbar \text{Tr}(I_z \rho_{eq}) \\ &= \frac{N \gamma^2 B_0 \hbar^2 I(I+1)}{3k_B T} \end{aligned} \quad (3.89)$$

where we have used the identity

$$\text{Tr}(I_x^2) = \text{Tr}(I_y^2) = \text{Tr}(I_z^2) = \frac{1}{3} (2I+1)I(I+1) \quad (3.90)$$

Second, we can see that evolution under the dominant Zeeman Hamiltonian leaves ρ_{eq} unchanged, since the evolution operator arising from a static magnetic field,

⁷There are exceptions but these will not concern us here. For example, $I > 1/2$ nuclei in the solid state may have electric quadrupole interactions of tens of megahertz.

⁸An example being the case of long-range intermolecular dipolar interactions for which higher-order terms in the density matrix play a role, as discussed in Chapter 11.

$U(t) = \exp(i\gamma B_0 I_z t)$ clearly commutes with ρ_0 . This means that we will need to disturb the spins from equilibrium if we are to observe their precession. Finally, we note that since $\underline{1}$ commutes with any spin Hamiltonian whatever, the only part of the thermal equilibrium state of the density matrix in the HTA that is subject to experimental manipulation is the part proportional to I_z . For that reason, and to within an arbitrary constant, we may generally write our starting condition as

$$\rho_{eq} \sim I_z \quad (3.91)$$

or more precisely

$$\rho_{eq} \approx \frac{1}{2I+1} \frac{\gamma B_0 \hbar}{k_B T} I_z \quad (3.92)$$

3.5.3 Higher terms in the expansion—breakdown of the high temperature approximation

Note that we have used a single-spin picture when calculating the equilibrium magnetisation. In other words, we have described ρ in terms of single-spin operators. A naive extension in the case of many spins would be to write,

$$\rho_{eq} \sim \sum_i I_{iz} \quad (3.93)$$

In most NMR experiments such a starting density matrix serves us well. However, on closer inspection a more precise way of writing an N-spin density matrix is

$$\begin{aligned} \rho_{eq} &= \rho_{1eq} \otimes \rho_{2eq} \otimes \rho_{3eq} \cdots \otimes \rho_{Neq} \\ &= (2I+1)^{-N} \Pi_i (\underline{1} + \beta\gamma B_0 \hbar I_{iz}) \end{aligned} \quad (3.94)$$

Equation 3.94 involves N one-spin operators of the form $\beta\gamma B_0 \hbar I_{iz}$, $N^2/2$ two-spin operators $(\beta\gamma B_0 \hbar)^2 I_{iz} I_{jz}$, and higher-order spin operators in succession. W.S. Warren [28, 29] has pointed out that despite $\beta\gamma B_0 \hbar$ being typically small ($\sim 10^{-5}$ for protons), the large value of N ensures that the higher-order terms in ρ_{eq} do not vanish whether they become observable or not.

The magnetic resonance experiment starts by rotating all I_{iz} operators in the density matrix to I_{ix} or I_{iy} , so that $(\beta\gamma B_0 \hbar)^2 I_{iz} I_{jz}$ converts to $(\beta\gamma B_0 \hbar)^2 I_{ix} I_{jx}$, for example. As we shall see in the next chapter, such bilinear spin operator terms in the density matrix are not directly observable in NMR experiments, the observable in NMR being $\sum_i (I_{ix} + iI_{iy})$. For these higher-order terms to become observable, there needs to exist in the spin Hamiltonian, terms that can subsequently convert the bilinear $(\beta\gamma B_0 \hbar)^2 I_{ix} I_{jx}$ density matrix term back to simple magnetisation. Such terms must themselves be bilinear in the spin operators and these need to exist for all $N^2/2$ pairs. One candidate is the sum of long range dipolar couplings between distant spins. We will examine the effect of these intermolecular dipolar interactions in more detail in Chapter 11.

3.5.4 A closer look at thermal equilibrium

Our requirements for the density matrix in thermal equilibrium were simply that it be diagonal in the energy representation, and that its diagonal elements represent

the thermal equilibrium Boltzmann populations. For thermal equilibrium in a static magnetic field, the energy eigenstates are labelled by the azimuthal quantum number m , basis state amplitudes by $a_m = |a_m| \exp(i\delta_m)$, diagonal density matrix elements by $|a_m|^2$, and off-diagonal by $a_m^* a_{m'}$. Thermal equilibrium therefore requires a random phase distribution over the δ_m [25, 30].

Of course, any measurement of energy while in thermal equilibrium will, via the state reduction process, force all spins into their energy eigenstates, such that, for each spin, $|a_m|$ is non-zero for only one value of m . Our density matrix is unchanged, but the ensemble now occupies a specific subset of equilibrium possibilities. This new state has more than a lack of phase coherence between a_m and $a_{m'}$. Quite simply, no superposition states exist once the Zeeman thermal equilibrium energy is measured.

Is there any way we could distinguish between these two versions of thermal equilibrium? Certainly there is no ensemble measurement which could separate them, since both have identical density matrices. Only by selecting individual spins from the ensemble and independently measuring their properties could we make such a distinction. So what is the correct description of thermal equilibrium? To understand this we need to appreciate the role of the additional fluctuating interactions that permit the thermal equilibrium state to be obtained by exchange of energy between the spins and the environment. These interactions provide the spin-lattice relaxation process and to be effective they must induce transitions between the energy eigenstates $|m\rangle$ of the Zeeman spin system. That requires both that the interactions have non-zero matrix elements between the energy eigenstates and that they contain fluctuation frequencies matching the energy differences. But if they perform this task, then they can also generate superposition states from eigenstates. The point is that they do so with random phase, keeping any off-diagonal elements of the density matrix zero. Hence, even if we were to start with an ensemble in which every spin was in an energy eigenstate such that the requirement for the thermal equilibrium density matrix was fulfilled, the fluctuating interactions would very soon induce transitions in which randomly phased superposition states existed, but in which the diagonal elements of the density matrix were preserved. The true thermal equilibrium state is this most general manifestation.

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