Solid-State NMR Spectroscopy
Principles and Applications

EDITED BY

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Department of Chemistry
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Contents

Preface

In the 50 or so years since NMR was first invented, solid-state NMR has seen a steady increase in popularity, until the 1980s when its expansion was rapid. Its initial lack of use relative to solution-state NMR was because of the inherent lack of resolution in solid-state NMR spectra (if nothing is done to deliberately improve it). The sudden increase in its popularity went hand-in-hand with the invention of new techniques that enabled high resolution to be achieved even in the solid state.

This latter development was to a large extent driven by increasing numbers of chemical problems for which solid-state NMR promised great utility if higher resolution could be obtained, and which could not be solved by other techniques. The chemical problems to which solid-state NMR has been applied since then are very diverse indeed. The vast majority can be divided into one of two areas: molecular structure determination, studies of which are now virtually routine for determining molecular structures and intermolecular packing. For those solids which do not form suitable single crystals, powder XRD can give useful information, but refinement of the structures relies on very high-resolution XRD patterns; currently structures for molecules with up to 20 or so atoms can be refined, but no bigger. Solid-state NMR can provide useful information on the number of molecules in the asymmetric unit and on the site symmetry of the molecule in the lattice to assist in the refinement of powder XRD data. Alternatively, it can be used to measure internuclear distances directly, and often with great accuracy. For amorphous and disordered solids, such as inorganic glasses and organic polymers, solid-state NMR has provided, and continues to provide, invaluable structural information which, as yet, *cannot be obtained by any other technique*. For instance, ranges of Si–O–Si bond angles in silicate glasses have been obtained by correlating chemical shifts with these angles.

While diffraction techniques are very good at determining static molecular structure on suitable samples, they often give a poor overall picture of a material, because they indicate little about the dynamics in the system. Even relatively simple organic molecules undergo continuous conformational exchange in the solid state at ambient temperature. To ignore this feature of a material is to ignore a major determinant of its properties. The motional degrees of freedom in solids determine, for instance, their brittleness and flexiblity. They also determine the entropy of the phase and, through this, contribute to the phase diagram for the material. There have been many studies of molecular dynamics in polymers using solid-state NMR, and these are discussed in Chapter 10. These are not the only areas for molecular dynamics studies however, and solid-state NMR has played a major role in studies on glasses, which is discussed in Chapter 8. As more sophisticated techniques become available to study more complex motions and sequences of motions, this area can be expected to find yet further applications. Biopolymers and oriented proteins, such as membrane proteins, are one new area currently being explored (Chapter 7).

Solution and solid-state NMR are both excellent methods of determining chemical composition. The chemical shift allows different chemical sites to be distinguished and intensities of NMR lines are (at least in principle) directly proportional to the number of each site in the sample. A further feature of solid-state NMR is its ability to distinguish different polymorphs. This is especially valuable to the pharmaceutical industry, for instance, as frequently it is only one particular polymorph of a compound that is the active drug they require; furthermore, other polymorphs may actually be harmful. In order to license the drug, pharmaceutical companies must demonstrate that they are manufacturing the right polymorph and no other, and solid-state NMR is one of the few techniques that allow unequivocal identification of polymorphs.

All of these applications of solid-state NMR require that (as in solution-state NMR) the signals from different chemical sites can be resolved from each other in some way. As intimated above, solid-state NMR spectra are characteristically composed of broad lines. The linebroadening arises from the various interactions which act on the nuclear spins: anisotropic chemical shielding, dipole–dipole coupling between magnetic nuclear dipoles and, for nuclei with spin I greater than $\frac{1}{2}$, quadrupole coupling. All of these are discussed in subsequent chapters. In solution, rapid random tumbling of the molecules averages each of these interactions to zero, so that their direct effects are rarely seen in the NMR spectrum.[1] Removing the effects of these interactions from solid-state NMR spectra has received, and indeed continues to receive, much attention and is discussed extensively in Chapter 2. However, we should not be too quick to remove the effects of these interactions without trace. They all depend on details of molecular and/or electronic structure, and so, by inference, we can in principle gain information on these factors from studying these interactions through solid-state NMR spectra. In practice, dipole–dipole coupling is being used very successfully to measure internuclear distances. The chemical shielding interaction is relatively easily used to the extent of observing empirical correlations between shielding values and geometric factors such as bond angles in molecules. Only recently, however, have *ab initio* calculations of shielding and quadrupole-coupling interactions become good enough to extract information from experimentally observed values by comparing them with calculated ones for different molecular geometries. As *ab initio* calculations improve still further and become more routine for the chemist, this application is expected to increase.

The first part of this book deals with what I call the basics of solid-state NMR; what the spectra look like under the influence of the various nuclear spin interactions, how to record spectra and how to interpret them. These chapters, while reviewing current work in the respective areas of each chapter are not intended to be exhaustive reviews. Rather, they concentrate on what are currently considered to be the most useful or widely applicable experiments, and therefore on those which someone new to solid-state NMR might venture into. The references cited also reflect this approach. Obviously I have referenced work where I have used it, but, in addition, I have added those references that I think will be the most useful starting points for new solid-state NMR spectroscopists.

The second part of the book deals with specific areas of science where solid-state NMR has played a major part in recent years, and these chapters provide extensive reviews of the chosen areas. That is not to say that solid-state NMR has not made big impacts elsewhere, or will not in the future, but we had to stop somewhere! In essence, NMR provides an excellent *local* probe of solids. It is invaluable in cases where other structural techniques are found wanting.

Note

1. They do however continue to affect relaxation times. In addition, larger molecules may not tumble at rates high enough to average the interaction on the NMR timescale; this leads to linebroadening in ^{13}C and ^{1}H spectra of large proteins in solution. The NMR timescale in this instance refers to the linewidth caused by the interaction in the absence of molecular motion; rates of motion which are large compared to the linewidth cause effective averaging. Molecules in liquid-crystalline solvents do not tumble isotropically, so some residual vestige of the nuclear interactions remains and influences the NMR spectrum.

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I am very grateful to all the authors who have contributed to this book for writing chapters which demonstrate the huge scope of solid-state NMR and point forward to many more applications in the future. There are, however, many more people who have contributed to this book and one of those, who deserves special thanks, is friend and colleague, Dr James Keeler, who in the last ten years has done his best to teach me something about NMR. He has also been invaluable in the production of this book by his insightful comments and awkward questions. Professor Cynthia Jameson and Dr Oleg Antzutkin have both contributed hugely by their respective comments on various parts of the book

Nicky McDougal, Niko Loening and Matthew Jones have done painstaking work in proof-reading and gently pointing out the more incomprehensible sentences. My husband, Dr Neil Piercy, has kept my computer working, dealt with awkward graphics, and many times has stepped in to rescue the printer, when for the umpteenth time, it decided to give up the ghost part way through printing out a chapter. More importantly, he has kept me supplied with chocolate and tea during the more hectic parts of the writing.

A large part of this book was written while on sabbatical leave from Cambridge University and I am very grateful to Professor Brian Johnson for allowing me to have this valuable period of leave. However, I still could not have produced this book without the peace and quiet afforded by an old farmhouse on Garrow Tor in the middle of Bodmin Moor, Cornwall, England. This was made possible by Julie Mansfield and Rio, the horse who provided transport while I was there.

Finally, there are a number of other people who each played a valuable part: John and Rose Duer, Annie Burton and Jane Moore.

Melinda Duer

Part I

The Theory of Solid-State NMR and its Experiments

Chapter 1
The Basics of Solid-State NMR

Melinda J. Duer

This chapter is concerned with the basics of how to describe nuclear spin systems in NMR experiments. To this end, we first consider the classical vector model, which in many cases, provides a sufficient description of an uncoupled spin system. As soon as there are interactions between the spins, such as dipolar or quadrupolar coupling, we must use a quantum mechanical model to describe the dynamics of the spin system. We will use the *density operator* approach, which combines a quantum mechanical modelling of individual spins or sets of coupled spins with an ensemble averaging over all the spins (or sets of spins) in the sample.

The latter sections of the chapter deal with the various internal nuclear spin interactions, (chemical shielding, dipole–dipole coupling and quadrupole coupling), their quantum mechanical description and their effect on an NMR spectrum.

1.1 The vector model of pulsed NMR

In the semi-classical model of NMR, only the net magnetization arising from the nuclei in the sample and its behaviour in magnetic fields is considered. It is a suitable model with which to consider the NMR properties of isolated spin-$\frac{1}{2}$ nuclei, i.e. those which are not coupled to other nuclei. This model also provides a convenient picture of the effects of radiofrequency pulses on such a system. Only a brief description is given here in order to define the terms and concepts that will be used throughout this book.

1.1.1 Nuclei in a static, uniform magnetic field

The net magnetization (which is equivalent to a bulk magnetic moment) arising from the nuclei in a sample is **M** and is the vectorial sum of all the individual magnetic moments associated with all the nuclei (Fig. 1.1):

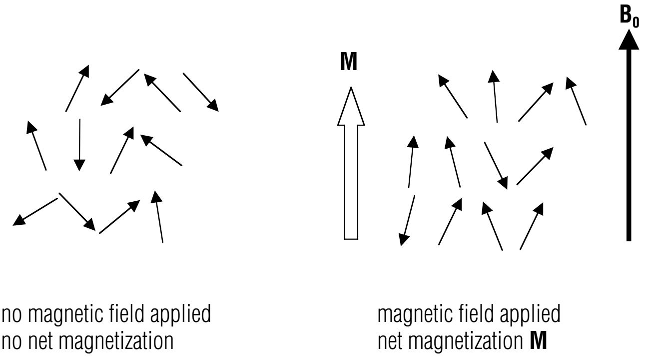

Fig. 1.1 The classical model of the formation of net nuclear magnetization in a sample. In the absence of a magnetic field, the individual nuclear magnetic moments (represented by vector arrows here) have random orientation so that there is no net magnetization. In the presence of an applied magnetic field, however, the nuclear magnetic moments are aligned preferentially with the applied field, except that thermal effects cause a distribution of orientations rather than perfect alignment. Nevertheless, there is in this case, a net nuclear magnetization.

$$\mathbf{M} = \sum_i \mu_i \tag{1.1}$$

where μ_i is the magnetic moment associated with the ith nucleus. In turn, each nuclear magnetic moment is related to the *nuclear spin* $\mathbf{I}_i$ of the nucleus by

$$\mu_i = \gamma \mathbf{I}_i \tag{1.2}$$

γ is the magnetogyric ratio, a constant for a given type of nucleus. Thus we can write the net magnetization of the sample as

$$\mathbf{M} = \gamma \mathbf{J} \tag{1.3}$$

where **J** is the net spin angular momentum of the sample giving rise to the magnetization **M**. If the nuclei are placed in a uniform magnetic field **B** as in the NMR experiment, a torque **T** is exerted on the magnetization vector:

$$\mathbf{T} = \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{J} \tag{1.4}$$

In turn, the torque in this situation is given by

$$\mathbf{T} = \mathbf{M} \times \mathbf{B} \tag{1.5}$$

Combining Equations (1.3) to (1.5), we can write,

$$\frac{\mathrm{d}\mathbf{M}}{\mathrm{d}t} = \gamma \mathbf{M} \times \mathbf{B} \tag{1.6}$$

which describes the motion of the magnetization vector **M** in the field **B**. It can be shown that Equation (1.6) predicts that **M** precesses about a fixed **B** at a constant rate $\omega = \gamma B$.

In NMR, the applied magnetic field is generally labelled $\mathbf{B}_0$ and is taken to be along z, i.e. $\mathbf{B} = (0, 0, B_0)$ in the above equations. The frequency with which the magnetization precesses about this field is defined as ω_0, the *Larmor frequency*:

$$\omega_0 = \gamma B_0 \tag{1.7}$$

1.1.2 The effect of rf pulses

An electromagnetic wave, such as a radiofrequency (rf) wave, has associated with it an oscillating magnetic field, and it is this field which interacts with the nuclei in addition to the static field in the NMR experiment. The rf wave is arranged in the NMR experiment so that its magnetic field oscillates along a direction perpendicular to z and the $\mathbf{B}_0$ field. Such an oscillating field can be thought of as a vector which can be written as the sum of two components rotating about $\mathbf{B}_0$ in opposite directions. The frequencies of these two components can be written as $\pm\omega_{\mathrm{rf}}$, where ω_{rf} is the frequency of the rf pulse. Furthermore, it can be shown that only the component which rotates in the same sense as the precession of the magnetization vector $\mathbf{M}$ about $\mathbf{B}_0$ has any significant effect on $\mathbf{M}$; we will henceforth label this component $\mathbf{B}_1(t)$. The effect of this field is most easily seen by transforming the whole problem into a rotating frame of reference which rotates at frequency ω_{rf} around $\mathbf{B}_0$; in this frame $\mathbf{B}_1$ appears static, i.e. its time dependence is removed. We can see what happens to the $\mathbf{B}_0$ field in this frame by examining the effect of a similar rotating frame in the absence of an rf pulse, i.e. in the case of the static, uniform magnetic field considered previously. We concluded that in the presence of a field $\mathbf{B}_0$ only that the magnetization vector $\mathbf{M}$, would precess around $\mathbf{B}_0$ at frequency ω_0. If the pulse is *on resonance*, i.e. $\omega_0 = \omega_{\mathrm{rf}}$, then the magnetization vector appears stationary in the rotating frame. In effect, the $\mathbf{B}_0$ field is removed in this frame; the effective static field parallel to z is zero. So, in the presence of a pulse, the only field remaining in the rotating frame is the $\mathbf{B}_1$ field. As in the case of the magnetization experiencing the static field $\mathbf{B}_0$ in the laboratory frame, the result of this interaction is that the magnetization vector $\mathbf{M}$ precesses about the resultant field, which is now $\mathbf{B}_1$, at frequency γB_1. We define this *nutation frequency* γB_1 as ω_1.

The direction of the magnetic field due to the rf pulse can be anywhere in the xy plane. The *phase* of a pulse, ϕ_{rf}, is defined as the angle $\mathbf{B}_1$ makes to the x axis in the rotating frame. The pulse does not have to be applied on resonance; indeed there will be many, many cases in solid-state NMR experiments when the pulse will be off resonance at least for part of the total spectrum available. In a frame rotating at ω_{rf} about $\mathbf{B}_0$, in the absence of a pulse, the Larmor precession frequency is reduced from ω_0 to $\omega_0 - \omega_{\mathrm{rf}}$ about $\mathbf{B}_0$. We can infer from this that there is an effective static field along z in this frame of $(\omega_0 - \omega_{\mathrm{rf}})/\gamma$, rather

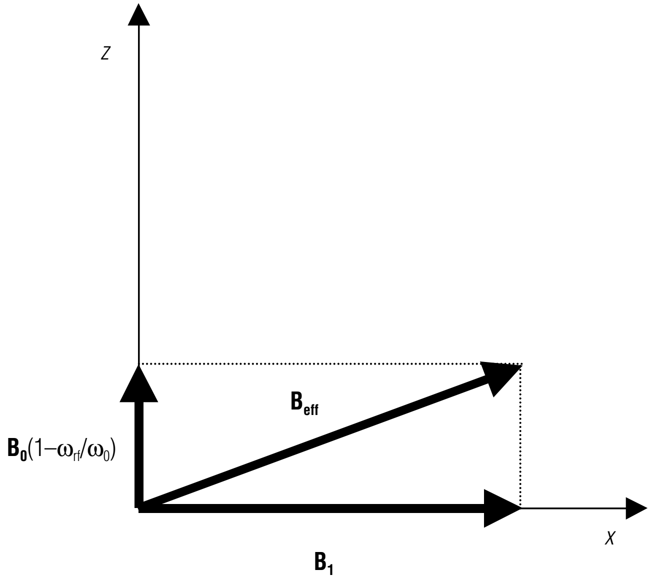

Fig. 1.2 The magnetic fields present in the rotating frame of reference. The rotating frame rotates about *z* at the frequency of the rf pulse, ω_{rf}. The pulse is applied along *x*. The field due to the pulse appears static in the rotating frame, and the static field $\mathbf{B}_0$ appears to be reduced by a factor of $\omega_{\mathrm{rf}}/\omega_0$, where ω_0 is the Larmor frequency, $\omega_0 = \gamma B_0$. The net effective field in the rotating frame is the vectorial sum of the components along *x* and *z*, $\mathbf{B}_{\mathrm{eff}}$. It is this field that the nuclear spin magnetization precesses around.

than zero, as in the on-resonance case. The magnetic fields present in the rotating frame are then those shown in Fig. 1.2; there is a field of magnitude $(\omega_0 - \omega_{\mathrm{rf}})/\gamma$ along z and B_1 along x (for a pulse with phase 0°). The magnetization precesses around the resultant field $\mathbf{B}_{\mathrm{eff}}$ shown in Fig. 1.2.

NMR spectroscopists talk generally of an rf pulse ‘flipping’ the magnetization. The flip angle, θ_{rf}, of an on-resonance pulse is the angle that the pulse field $\mathbf{B}_1$ turns the magnetization during time τ_{rf}:

$$\theta_{\mathrm{rf}} = \omega_1 \tau_{\mathrm{rf}} = \gamma B_1 \tau_{\mathrm{rf}} \tag{1.8}$$

Thus, a 90° pulse is simply one which has a flip angle of $\theta_{\mathrm{rf}} = \pi/2$ radians or 90°. The corresponding pulse length is referred to as the 90° pulse length. RF pulses along *x* in the rotating frame are referred to as ‘*x* pulses’, those along *y* as ‘*y* pulses’, and so on.

By definition, positive rotations are anticlockwise about the given axis. So, after a 90° *x* pulse (for shorthand labelled $90°_x$), nuclear magnetization $\mathbf{M}$ which started along z, is left lying along $-y$ (Fig. 1.3). From the point at which the rf pulse is turned off, the magnetization acts under the only magnetic field remaining, which is the effective field along z, of magnitude $(\omega_0 - \omega_{\mathrm{rf}})/\gamma$, i.e. zero if the rotating frame frequency ω_{rf} is the same as the Larmor frequency, ω_0. If the effective field along z is zero, then the magnetization is stationary in the rotating frame after the pulse is switched off; if non-zero, the magnetization precesses around z from the position it was in at the end of the pulse at frequency $\omega_0 - \omega_{\mathrm{rf}}$.

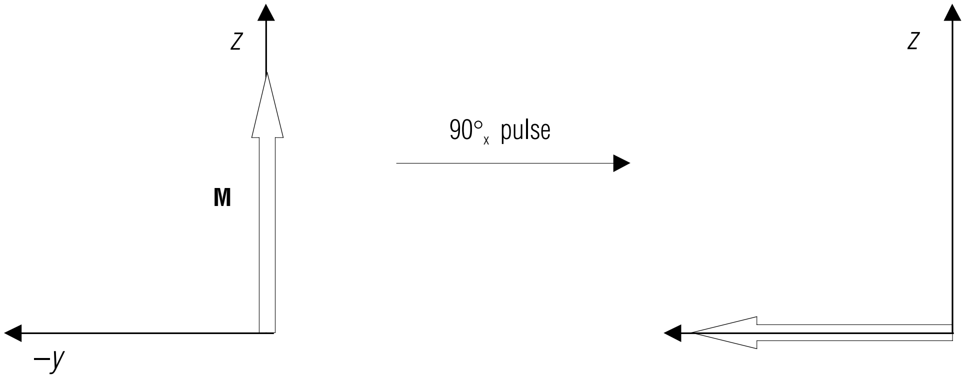

Fig. 1.3 The effect of a 90°$_x$ on-resonance pulse on equilibrium magnetization in the rotating frame. The equilibrium magnetization rotates by 90° about x and ends up along $-y$.

1.2 The quantum mechanical picture: hamiltonians and the Schrödinger equation

In the quantum mechanical picture, we start from a consideration of individual nuclei and from this generate a picture for the whole collection of nuclei in a sample. This is called the *ensemble average*. We will often refer to the *spin system* by which we mean a nuclear spin or collection of interacting nuclear spins, in a specified environment, such as a static magnetic field along z, for instance. We will find that the state of a spin system at equilibrium is in one of a number of possible states or *eigenstates*, whose specific form depends on the nature of the spin system. In an NMR experiment, we have a sample which is composed of many identical spin systems. For instance, if each spin in the sample is isolated from other nuclei (so that there are no interactions between nuclei) and in the same chemical environment, then the spin system is a single nuclear spin subjected to whatever magnetic fields are present in the NMR experiment. The sample contains many such (identical) spin systems, the state of each being one of the possible eigenstates of the spin system. The proportion of the spin systems in the sample in any one eigenstate is given by a Boltzmann distribution for a sample which is at thermal equilibrium. In an NMR experiment, we measure the behaviour of the whole sample, not of individual spin systems. From the preceding discussion, it is clear that the behaviour of the sample depends not only on the nature of the possible eigenstates of the spin systems in the sample, but also on the population of each eigenstate over the sample as a whole. This will lead us to describe the state of each spin system in the sample as a superposition of the possible eigenstates for the spin system. The superposition state is the same for all identical spin systems and takes into account the probability of occurrence of each eigenstate, so leading to a proper description of the behaviour of the whole sample of spin systems.

Box 1.1 Quantum mechanics and NMR

In this box, we describe the key concepts in quantum mechanics which are used when discussing NMR and define the terms which will be used throughout this book.

Wavefunctions

In quantum mechanics, the state of a system, such as a nuclear spin or collection of spins in some specified environment, is described by a wavefunction, a mathematical function which depends on the spatial and spin coordinates of the nuclei in the system. We shall denote wavefunctions by the symbol ψ or Ψ. The wavefunctions themselves can often be specified by a set of *quantum numbers*, which in turn determine the values of the physical observables for the system.

Operators, physical observables and expectation values

We actually determine the value of any physical observable for the system by using the appropriate *operator* corresponding to the observable. An operator is simply something which acts on a function to produce another function, e.g. multiply by y, $\mathrm{d}/\mathrm{d}x$ and so on. Throughout this work, we shall denote operators by '$\wedge$', to distinguish them from functions, etc.

The value of a physical observable in a state described by ψ is equal to the *expectation value* of the corresponding operator. For an operator $\hat{A}$, the expectation value $\langle A \rangle$ is

$$\langle A \rangle = \frac{\int \psi * \hat{A} \psi \ \mathrm{d}\tau}{\int \psi * \psi \ \mathrm{d}\tau} \tag{i}$$

where the integrals are over all the spatial and spin coordinates of the wavefunction ψ.

Schrödinger's equation, eigenfunctions and eigenvalues

The wavefunction for a nuclear spin system in which all interactions are time invariant is the solution of the time-independent Schrödinger equation:

$$\hat{H} \psi = E \psi \tag{ii}$$

$\hat{H}$ is the energy operator for the system, called the *hamiltonian*. The form of the hamiltonian varies from system to system and depends on the interactions in the spin system. The quantity E is the energy of the system. Equation (ii) is that of an *eigenvalue* equation; the general form of such an equation for an operator $\hat{A}$ is

$$\hat{A}f = af \tag{iii}$$

where f is an eigenfunction of the operator $\hat{A}$ and a is the eigenvalue of $\hat{A}$ corresponding to the eigenfunction f. Thus the problem of finding the wavefunction for a system is one of finding the eigenfunctions of the relevant hamiltonian operator. In general, there are a set of eigenfunctions which solve (iii) for any given operator. The set of all the functions which solve (iii) is called a *complete set*. That is, any other function can be written as some linear combination of this complete set.

If the spin system is subject to a time-dependent interaction (as will often be the case in NMR experiments), then the wavefunction describing the state of the system is necessarily time dependent. We must then solve the time-dependent Schrödinger equation:

$$\hat{H}(t)\psi(t) = i\hbar\frac{\partial\psi(t)}{\partial t} \tag{iv}$$

where the time-dependent interaction is represented by a time-dependent hamiltonian.

Spin operators and spin states

The total nuclear wavefunction Ψ, can be approximately factorized into a spatial and a spin part:

$$\Psi = \psi_{\text{spin}}\psi_{\text{space}} \tag{v}$$

where ψ_{spin} is a function, the *nuclear spin wavefunction* describing the spin state of the nucleus, which depends only on the nuclear spin coordinates and ψ_{space} is a function depending only on the spatial coordinates of the nucleus. We shall be dealing almost exclusively with the wavefunctions describing the *spin states* of nuclei. Fortunately, the spin and spatial parts of a nuclear wavefunction are largely uncoupled; that is, the spatial position of a nucleus is largely unaffected by its spin coordinates and *vice versa*.[1]*

Continued on p. 10

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* Notes are given on p. 71.

Box 1.1 *Cont.*

To determine the spin properties of a nucleus, we operate on the nuclear spin wavefunction with *spin operators*, i.e. operators which act only on the spin coordinates of the nuclear wavefunction.

For a single spin, a consistent set of spin operators which allow all possible spin properties of a nucleus to be determined are: $\hat{I}^2$, the operator for the magnitude of the nuclear spin squared, $\hat{I}_x$, $\hat{I}_y$ and $\hat{I}_z$, which are the operators for the x, y and z components of nuclear spin respectively. These are *single spin operators*, i.e. they act only on wavefunctions describing one spin. These are related via

$$\hat{I}^2 = \hat{I}_x^2 + \hat{I}_y^2 + \hat{I}_z^2 \tag{vi}$$

If two operators commute, it can be shown that they have identical eigenfunctions. The *commutator* of two operators $\hat{A}$ and $\hat{B}$, $\lfloor \hat{A}, \hat{B} \rfloor$ is defined as

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{vii}$$

Now $\hat{I}^2$ commutes with $\hat{I}_z$. Hence, $\hat{I}^2$ and $\hat{I}_z$ have identical eigenfunctions; they are specified by the quantum numbers I and m and are denoted ψ_{Im}. The eigenfunctions of $\hat{I}_z$ for $I = \frac{1}{2}$ are often denoted α ($m = \frac{1}{2}$) and β ($m = -\frac{1}{2}$). The quantum number I can take the values $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$, etc. and m, the values $I, I-1, \ldots, -I$. Hence, we talk of ^{1}H being a 'spin-$\frac{1}{2}$' nucleus, i.e. $I = \frac{1}{2}$, ^{23}Na, a spin-$\frac{3}{2}$ nucleus ($I = \frac{3}{2}$) and so on.

The eigenvalues corresponding to the ψ_{Im} are defined by the eigenvalue equations:

$$\begin{aligned} \hat{I}^2\psi_{Im} &= I(I+1)\hbar\psi_{Im} \\ \hat{I}_z\psi_{Im} &= m\hbar\psi_{Im} \end{aligned} \tag{viii}$$

However, in NMR, the factor of $\hbar$ in these eigenvalues is commonly ignored, and included instead as part of the operator, i.e.

$$\begin{aligned} \hat{I}^2\psi_{Im} &= I(I+1)\psi_{Im} \\ \hat{I}_z\psi_{Im} &= m\psi_{Im} \end{aligned} \tag{ix}$$

or

$$\begin{aligned} \hbar\hat{I}^2\psi_{Im} &= I(I+1)\hbar\psi_{Im} \\ \hbar\hat{I}_z\psi_{Im} &= m\hbar\psi_{Im} \end{aligned} \tag{x}$$

We shall adopt this latter convention also. The expectation values of $\hat{I}^2$ and $\hat{I}_z$ (see Equation (i)), i.e. the magnitude of the nuclear spin angular momentum squared and the z component of the nuclear spin angular momentum respectively, when the wavefunction describing the system is an eigenfunction of $\hat{I}^2$ and $\hat{I}_z$ are given by: