

Part 4

Nuclear Spin Interactions

- 8 Nuclear Spin Hamiltonian**
- 9 Internal Spin Interactions**

8

Nuclear Spin Hamiltonian

It is a goal of this book to explain the *dynamics* of nuclear spins. To do this we need to solve the time-dependent Schrödinger equation for the nuclei. The first step is to write down the Hamiltonian operator.

The next two chapters give the form of the nuclear spin Hamiltonian in diamagnetic materials and attempt to explain physically why it looks as it does.

8.1 Spin Hamiltonian Hypothesis

The nuclear spins are not alone. Any real sample contains an astronomical number of electrons as well as nuclei. In principle, the Schrödinger equation involves the motions of all the nuclei and all the electrons, and the Hamiltonian operator involves the interactions between all of these particles.

In principle, the quantum state of the entire sample is fully described by a wave function $|\psi_{\text{full}}\rangle$, which contains information as to the positions, velocities, and spin states of all the electrons and nuclei. This wavefunction obeys the time-dependent Schrödinger equation:

$$\frac{d}{dt}|\psi_{\text{full}}(t)\rangle = -i\hat{\mathcal{H}}_{\text{full}}|\psi_{\text{full}}(t)\rangle$$

where the Hamiltonian $\hat{\mathcal{H}}_{\text{full}}$ contains all interactions in the system.

This equation is complete, but useless. It cannot be solved in any realistic situation. For the purposes of NMR, one works with a much simpler equation, in which only the nuclear spin states appear:

$$\frac{d}{dt}|\psi_{\text{spin}}(t)\rangle \cong -i\hat{\mathcal{H}}_{\text{spin}}|\psi_{\text{spin}}(t)\rangle \quad (8.1)$$

Here, $|\psi_{\text{spin}}\rangle$ is the spin state of the nuclei and $\hat{\mathcal{H}}_{\text{spin}}$ is the *nuclear spin Hamiltonian*. The nuclear spin Hamiltonian contains only terms that depend on the directions of the nuclear spin polarizations. This assumes the magnetic and electrical influences of the rapidly moving electrons are blurred out, so that only their average is seen. These 'blurred-out' electronic influences are contained in the spin Hamiltonian $\hat{\mathcal{H}}_{\text{spin}}$.

This massive simplification is called the *spin Hamiltonian hypothesis*. It rests on a separation of time-scales for nuclear and electronic motions. The electronic motions are so rapid that the nuclear spins only sense a time average of the fields they generate. Furthermore, the nuclear spin energies are assumed to be too small to affect the motions of the electrons within the molecules, or the motions of the molecules themselves. In practice, the nuclear spin Hamiltonian is a secure concept for almost all systems at ordinary temperatures.¹

From now on, the operator $\hat{\mathcal{H}}$ is taken to imply the nuclear spin Hamiltonian, and the quantum states $|\psi\rangle$ are taken to imply the nuclear spin states.

8.2 Electromagnetic Interactions

First consider a single atomic nucleus. The nucleus interacts with its environment because (i) it has an electric charge, which interacts with electric fields, and (ii) it may have a magnetic moment, which interacts with magnetic fields.

In order to understand many NMR phenomena, it is important to realize that many nuclei are not spherical. In general, the atomic nucleus should be visualized as a small lumpy magnet, with (i) a magnetic moment and (ii) a non-uniform distribution of positive electric charge:

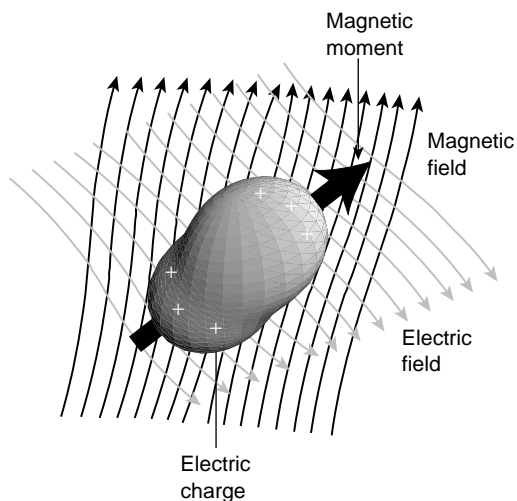


Figure 8.1

Interaction of the nucleus with electric and magnetic fields.

The nucleus interacts with the surrounding fields in two ways: it may move bodily in space, or it may rotate.

The motion of the nucleus in space, and the motion of the surrounding electrons, is the subject of molecular structure and spectroscopy. It is a very important subject, but is not of direct consequence for NMR.

NMR is concerned with the *rotational* motion of nuclei. If the nucleus rotates, then the nuclear magnetic moment and nuclear electric charges rotate with it. This changes the energy of the nucleus, because the nuclear electric charges and the nuclear magnetic moment both adopt a different orientation with respect to the surrounding fields:

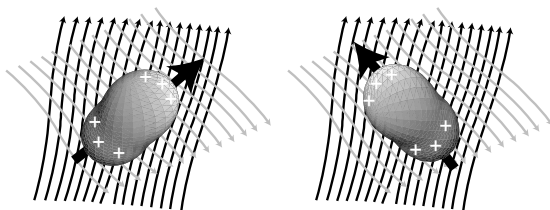


Figure 8.2

The energy of the nucleus depends on its orientation with respect to the fields.

The nuclear spin Hamiltonian contains terms that describe this *orientation dependence* of the nuclear energy. In general, there are two terms: an *electric spin Hamiltonian*, which describes the way the nuclear *electric energy* changes as the nucleus rotates, and a *magnetic spin Hamiltonian*, which describes the way the nuclear *magnetic energy* changes as the nucleus rotates. The spin Hamiltonian operator for nucleus I_j may therefore be written as

$$\hat{\mathcal{H}}_j = \hat{\mathcal{H}}_j^{\text{elec}} + \hat{\mathcal{H}}_j^{\text{mag}} \quad (8.2)$$

8.2.1 Electric spin Hamiltonian

The distribution of electric charge in the nucleus is denoted by the symbol $\mathbb{C}(\mathbf{r})$.

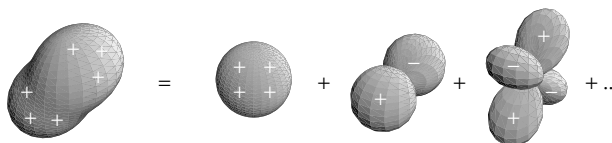
It is very convenient to represent this 'lumpy' charge distribution as a superposition of *electric multipoles*:

$$\mathbb{C}(\mathbf{r}) = \mathbb{C}^{(0)}(\mathbf{r}) + \mathbb{C}^{(1)}(\mathbf{r}) + \mathbb{C}^{(2)}(\mathbf{r}) + \dots \quad (8.3)$$

Here, $\mathbb{C}^{(0)}$ represents a *spherical* charge distribution, $\mathbb{C}^{(1)}$ represents a *dipolar* electric charge distribution, $\mathbb{C}^{(2)}$ represents a *quadrupolar* electric charge distribution, and so on. Mathematically, these functions are proportional to the spherical harmonics, and have exactly the same form as the s-, p- and d-orbitals in a hydrogen atom:

Figure 8.3

Decomposition of the electric charge distribution into multipole components.



The magnitude of the $\mathbb{C}^{(0)}$ term is the *total electric charge* of the nucleus, the magnitude of the $\mathbb{C}^{(1)}$ term is called the *electric dipole moment* of the nucleus, the magnitude of the $\mathbb{C}^{(2)}$ term is called the *electric quadrupolar moment* of the nucleus, and so on.

Now suppose that the nucleus is immersed in an electric environment, which may be represented by an *electric potential field* $V(\mathbf{r})$, which depends on position:

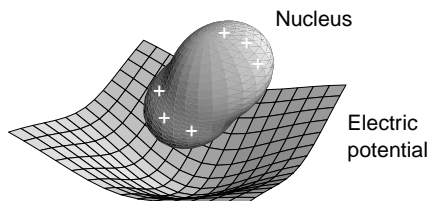


Figure 8.4

Interaction of the nucleus with an electric potential field.

In a real molecule, the centre of the nucleus adopts a stable position at a minimum of the electric potential. Note, however, that the electric potential may still vary from one side of the nucleus to the other, which influences its rotational motion.

The electric potential field may be represented as a superposition of terms:

$$V(\mathbf{r}) = V^{(0)}(\mathbf{r}) + V^{(1)}(\mathbf{r}) + V^{(2)}(\mathbf{r}) + \dots$$

Here, $V^{(0)}$ is the electric potential at the centre of the nucleus, $V^{(1)}$ is the potential *gradient* at the centre of the nucleus (proportional to the difference in the potential from one side of the nucleus to the other), $V^{(2)}$

is the *gradient of the gradient* (i.e. how much the *slope* of the potential changes from one side of the nucleus to the other), and so on. (For explicit expressions, see the text by Slichter in *Further Reading*.)

The electric interaction energy of the nucleus and the field may be written as follows:

$$E_{\text{elec}} = E_{\text{elec}}^{(0)} + E_{\text{elec}}^{(1)} + E_{\text{elec}}^{(2)} + E_{\text{elec}}^{(3)} + \dots$$

where each term comes from the interaction of a single multipole component of the charge distribution with a different aspect of the potential:

$$\begin{aligned} E_{\text{elec}}^{(0)} &= \int \mathbf{dr} \mathbb{C}^{(0)} V^{(0)}(\mathbf{r}) \\ E_{\text{elec}}^{(1)} &= \int \mathbf{dr} \mathbb{C}^{(1)} V^{(1)}(\mathbf{r}) \\ E_{\text{elec}}^{(2)} &= \int \mathbf{dr} \mathbb{C}^{(2)} V^{(2)}(\mathbf{r}) \end{aligned} \quad (8.4)$$

and so on.

The first term $E_{\text{elec}}^{(0)}$ corresponds to the point charge approximation for the atomic nucleus. This term is decisive for atomic and molecular structure, since it represents the electrostatic forces between the nuclei and the electrons. However, it is of *no direct* importance in NMR. It is only responsible for holding the nuclei in place at their appropriate molecular sites.

The term $E_{\text{elec}}^{(1)}$ represents the interaction of the nuclear electric dipole moment with the gradient of the electric potential, i.e. the electric field. Since the electric fields inside a molecule are enormous, this term might be expected to be huge. However, a very special circumstance intervenes. Nuclear physicists have shown that, within experimental error, there is *no nuclear electric dipole moment*.² The electric terms $E_{\text{elec}}^{(1)}$, $E_{\text{elec}}^{(3)}$, $E_{\text{elec}}^{(5)}$... all vanish.

In addition, there is another symmetry property, which links the *shape* of the nucleus to the *value of the nuclear spin*:³

$$\mathbb{C}^{(n)} = 0 \quad \text{for } n > 2I \quad (8.5)$$

This means that the series in Equation 8.3 does not go on for ever, but cuts off at $2I$.

This has consequences. Let us examine the situation for nuclei with $I = 1/2$, and then proceed to nuclei of higher spin.

Spin-1/2 nuclei. For spin-1/2 nuclei, all electric multipole moments vanish except $\mathbb{C}^{(0)}$ (but see Note 4). The only interaction between the nuclear spin and the electric potential is via the $E_{\text{elec}}^{(0)}$ term. This means that, for spins-1/2, *there are no electric energy terms that depend on the orientation or internal structure of the nucleus*. This is quite extraordinary. It means, for example, that the 47 protons and 62 neutrons in a nucleus of ^{109}Ag behave *exactly* like a single point charge at the nuclear centre, as far as electrical effects are concerned. The same holds for any spin-1/2 nucleus. Whatever the electrical environment, the nuclear electric energy is totally independent of the orientation of the nucleus in space. A spin-1/2 nucleus is not ‘lumpy’, but behaves as a perfectly smooth, magnetic, billiard ball:

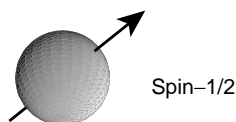


Figure 8.5

A spin-1/2 nucleus is spherical.

For spin-1/2 nuclei, the electric interactions vanish:

$$\hat{\mathcal{H}}_j^{\text{elec}} = 0 \quad (\text{for spin } I = 1/2) \quad (8.6)$$

It is quite fantastic that this result may be derived purely on the grounds of symmetry and without any detailed calculations.

For spins-1/2, the magnetic effects are left with a completely free hand. These nuclei really behave like perfect magnetic gyroscopes mounted on absolutely frictionless bearings.

Spins $I > 1/2$. For higher spin nuclei, the electric charge distribution is not spherically symmetrical. The electric energy of the nucleus depends on its orientation with respect to the rest of the molecule. The most important term is usually $E_{\text{elec}}^{(2)}$, which represents the interaction of the quadrupole charge distribution of the nucleus with the $V^{(2)}$ term, which we called above the gradient of the gradient of the electric potential. Since the gradient of the potential is the same as the electric field, the gradient of the gradient of the potential is the same as the gradient of the electric field. The main orientation-dependent electric term is therefore the interaction of the *electric quadrupole moment* of the nucleus with the *electric field gradient* in the surrounding space:⁵

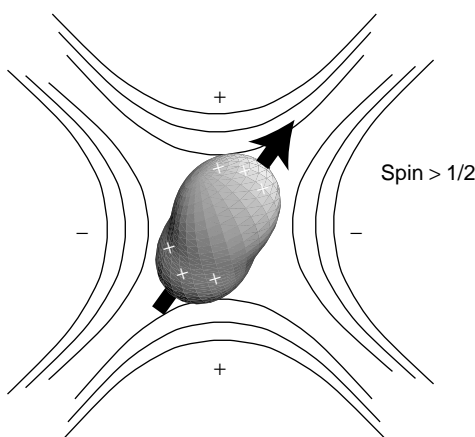


Figure 8.6

Interaction of a spin $> 1/2$ nucleus with the electric field gradient.

The electric part of the spin Hamiltonian is therefore called the electric quadrupole interaction:

$$\hat{\mathcal{H}}_j^{\text{elec}} = \hat{\mathcal{H}}_j^{\text{Q}} \quad (\text{for spin } I \geq 1) \quad (8.7)$$

The full form of the quadrupolar spin Hamiltonian is given in Appendix A.5. The quadrupole interaction depends on a property of the nucleus (the nuclear quadrupole moment) as well as a property of the molecular environment (the electric field gradient). For many nuclei of spin $I > 1/2$, the quadrupole coupling is often as large as many megahertz, and in some cases hundreds of megahertz.

The term *quadrupolar nucleus* means 'nucleus of spin $I > 1/2$ '. The NMR of quadrupolar nuclei is a more complicated and richer field than that of spins-1/2, because there are electric as well as magnetic influences on the reorientation of the nuclei. Generally speaking, the NMR of quadrupolar nuclei is technically more difficult than the NMR of spin-1/2 nuclei. There are some exceptions: for example, ^2H is a relatively 'friendly' quadrupolar nucleus, since its electric quadrupolar moment is rather small. The NMR of quadrupolar nuclei is an important and expanding field (see *Further Reading*).

8.2.2 Magnetic spin interactions

The nuclear magnetic dipole moment interacts with the surrounding magnetic field. Suppose that the magnetic field at the site of the nucleus is described by a three-dimensional vector \mathbf{B} :

$$\mathbf{B} = B_x \mathbf{e}_x + B_y \mathbf{e}_y + B_z \mathbf{e}_z \quad (8.8)$$

where \mathbf{e}_x , \mathbf{e}_y and \mathbf{e}_z are unit vectors along three orthogonal directions in space:

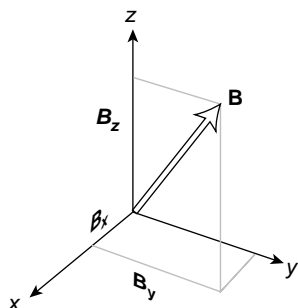


Figure 8.7
The magnetic field vector.

The nuclear magnetic moment is equal to the spin angular momentum multiplied by the gyromagnetic ratio γ_j . The relationship between the magnetic moment and angular momentum operators is

$$\hat{\boldsymbol{\mu}}_j = \gamma_j \hat{\mathbf{I}}_j \quad (8.9)$$

or, more, explicitly:

$$\hat{\boldsymbol{\mu}}_j = \gamma_j (\hat{I}_{jx} \mathbf{e}_x + \hat{I}_{jy} \mathbf{e}_y + \hat{I}_{jz} \mathbf{e}_z)$$

The nuclear magnetic energy for spin I_j depends on *minus the dot product* of the magnetic moment and the field:

$$\hat{\mathcal{H}}_j^{\text{mag}} = -\hat{\boldsymbol{\mu}}_j \cdot \mathbf{B} \quad (8.10)$$

The magnetic energy is at a minimum when the magnetic moment is parallel to the field, and is at a maximum when the magnetic moment is aligned in the opposite direction to the field (just like a compass needle, which minimizes its magnetic energy by aligning with the field):

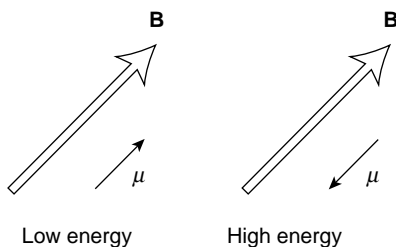


Figure 8.8
Magnetic energy.

Equations 8.8 and 8.9 may be combined to give

$$\hat{\mathcal{H}}_j^{\text{mag}} = -\gamma_j (B_x \hat{I}_{jx} + B_y \hat{I}_{jy} + B_z \hat{I}_{jz}) \quad (8.11)$$

8.3 External and Internal Spin Interactions

The electric and magnetic fields experienced by a nuclear spin may originate from the external apparatus or from the sample itself. In the first case, one speaks of *external spin interactions*. In the second case, the term *internal spin interactions* is used.

External spin interactions are purely magnetic, except in exotic circumstances.⁶ In almost all cases, one uses applied magnetic fields of various types to manipulate the nuclear spins.

Internal spin interactions are purely magnetic for spins $\leq 1/2$. In the case of spins $> 1/2$, the electric quadrupolar interaction is also involved.

It is a remarkable feature of NMR that the external interactions are usually much larger than the internal interactions. In other words, the nuclear spins are *more strongly coupled to the external apparatus than to their own molecular environment*.

It is hard to emphasize enough how unusual this situation is. In most forms of spectroscopy, the behaviour of the system is set by the molecular structure itself and information is gained by relatively weak external perturbations. The inverted situation in NMR leads to extraordinary possibilities, because it means that, in a sense, the 'system under study' includes the apparatus itself, whereas the 'weak probing' is done, in a sense, by the molecules. It is instructive to consider the extraordinary pulse sequences used in NMR as artificial 'spectroscopic systems' that are probed, non-destructively, by a weak 'molecular observer!' No other spectroscopy offers such a bizarre inversion of roles.

8.3.1 Spin interactions: summary

The following diagram summarizes the overall organization of the spin interactions:

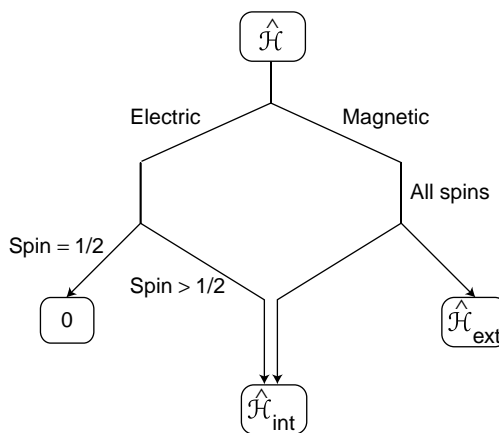


Figure 8.9
Organization of the spin interaction terms.

8.4 External Magnetic Fields

The NMR spectrometer usually supplies up to three kinds of external magnetic field.

1. The main superconducting solenoid provides a very strong, very homogeneous, static magnetic field, called here \mathbf{B}^0 (see Section 4.1).

2. The r.f. coil in the probe generates an r.f. oscillating field, denoted here $\mathbf{B}_{\text{RF}}(t)$ (see Section 4.4). In normal circumstances, this field is as spatially homogeneous as possible.
3. Suitably equipped spectrometers may also provide a magnetic field gradient field, called here $\mathbf{B}_{\text{grad}}(\mathbf{r}, t)$. This field is much weaker than \mathbf{B}^0 , is dependent on the position coordinate \mathbf{r} , and may have a controlled time dependence. This field is provided by the gradient coils (see Section 4.7).

The physical configuration of the first two applied magnetic fields is shown below:

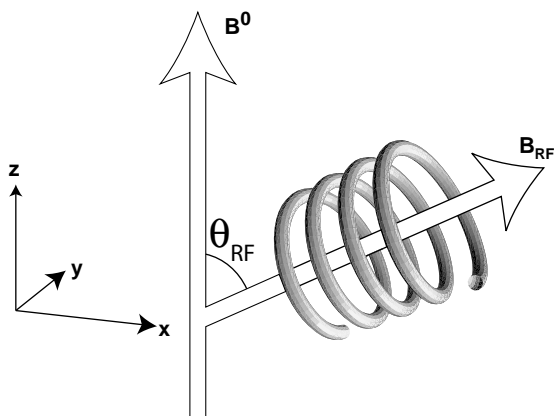


Figure 8.10

The laboratory frame, the r.f. coil, and the applied fields \mathbf{B}^0 and \mathbf{B}_{RF} . The gradient fields are parallel to \mathbf{B}^0 and are not shown.

Ideally, the r.f. field \mathbf{B}_{RF} is perpendicular to the static field \mathbf{B}^0 . However, in some cases, physical constraints make it necessary to tilt the r.f. coil away from the perpendicular (this is true, for example, in magic-angle-spinning NMR experiments; see Section 19.6). The tilt angle between the r.f. field and the static field is denoted here θ_{RF} .

The external part of the spin Hamiltonian is therefore given to a good approximation by:

$$\hat{\mathcal{H}}_{\text{ext}}(t) = \hat{\mathcal{H}}_{\text{static}} + \hat{\mathcal{H}}_{\text{grad}}(\mathbf{r}, t) + \hat{\mathcal{H}}_{\text{RF}}(t) \quad (8.12)$$

where

$$\begin{aligned} \hat{\mathcal{H}}_{\text{static}} &= \sum_j \hat{\mathcal{H}}_j^{\text{static}} \\ \hat{\mathcal{H}}_{\text{grad}}(\mathbf{r}, t) &= \sum_j \hat{\mathcal{H}}_j^{\text{grad}}(\mathbf{r}, t) \\ \hat{\mathcal{H}}_{\text{RF}}(t) &= \sum_j \hat{\mathcal{H}}_j^{\text{RF}}(t) \end{aligned} \quad (8.13)$$

and the sums are taken over all spins in the sample. Here, $\hat{\mathcal{H}}_j^{\text{static}}$ is the interaction of each spin I_j with the longitudinal static field \mathbf{B}^0 , $\hat{\mathcal{H}}_j^{\text{grad}}$ is the interaction of each spin I_j with the gradient field \mathbf{B}_{grad} , and $\hat{\mathcal{H}}_j^{\text{RF}}$ is the interaction of each spin with the r.f. field \mathbf{B}_{RF} generated by the r.f. coil.

It is usual to choose an axis system in which the static field is along the z -axis, while the oscillating field is in the xz -plane. This is called the *laboratory reference frame*.

8.4.1 Static field

The static field is written in the laboratory frame:

$$\mathbf{B}^0 = B^0 \mathbf{e}_z$$

(lightface symbols are used for the *magnitudes* of vectors).

The spin Hamiltonian for the interaction of each spin with the static longitudinal field B^0 is given by

$$\hat{\mathcal{H}}_j^{\text{static}} = -\gamma_j B^0 \hat{I}_{jz} \quad (8.14)$$

This is called the *nuclear Zeeman interaction*.

The term $-\gamma_j B^0$ may be identified as the Larmor frequency of spin I_j . This is discussed in Section 9.1, after including the chemical shift, which slightly changes the Larmor frequency.

8.4.2 Radio-frequency field

The r.f. coil generates a field \mathbf{B}_{RF} along the tilted axis shown in Figure 8.10. During an r.f. pulse on a single spectrometer channel, the magnitude of this field oscillates at the spectrometer reference frequency ω_{ref} . Between pulses, the r.f. field is equal to zero. If the pulse is perfectly rectangular, then the r.f. field has the form:

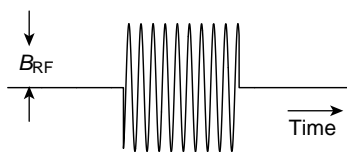


Figure 8.11

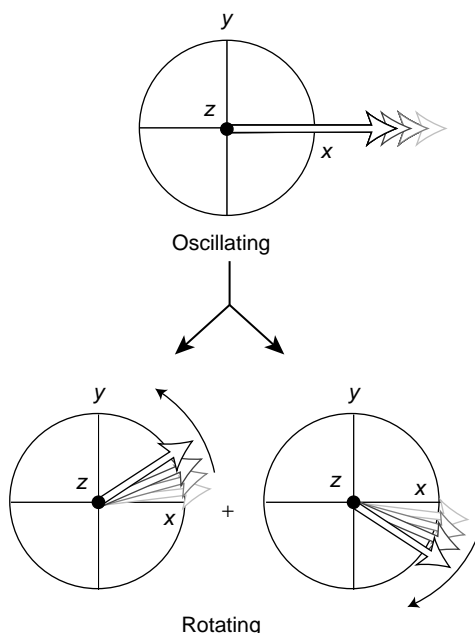
The oscillating r.f. field.

This corresponds to

$$\mathbf{B}_{\text{RF}}(t) = \begin{cases} B_{\text{RF}}(\mathbf{e}_z \cos \theta_{\text{RF}} + \mathbf{e}_x \sin \theta_{\text{RF}}) \cos(\omega_{\text{ref}} t + \phi_p) & \text{during an r.f. pulse} \\ 0 & \text{otherwise} \end{cases} \quad (8.15)$$

where the *maximum* r.f. amplitude during the pulse is denoted B_{RF} .

The r.f. field consists of a longitudinal component proportional to $\cos \theta_{\text{RF}}$ plus a transverse component proportional to $\sin \theta_{\text{RF}}$. It turns out to be useful to imagine that the transverse oscillating field is actually a sum of two *rotating* components. Both components rotate in the xy -plane, at the same frequency, but in opposite directions:

**Figure 8.12**

The oscillating r.f. field may be represented as the sum of two rotating fields.

(This shows the view from above.) The transverse component rotating in the same sense as the spin precession (negative for spins with $\gamma > 0$, positive sense for spins with $\gamma < 0$) is called the *resonant component* of the r.f. field. The transverse component rotating in the opposite sense to the Larmor frequency (positive for spins with $\gamma > 0$, and negative sense for spins with $\gamma < 0$) is called the *non-resonant* r.f. field component.

Mathematically, the oscillating r.f. field is expressed as

$$\mathbf{B}_{\text{RF}}(t) = \mathbf{B}_{\text{res}}^{\text{RF}}(t) + \mathbf{B}_{\text{non-res}}^{\text{RF}}(t) + \mathbf{B}_{\text{long}}^{\text{RF}}(t)$$

where the two transverse components are as follows:

$$\mathbf{B}_{\text{res}}^{\text{RF}}(t) = \begin{cases} \frac{1}{2} B_{\text{RF}} \sin \theta_{\text{RF}} \{ \cos(\omega_{\text{ref}} t + \phi_p) \mathbf{e}_x + \sin(\omega_{\text{ref}} t + \phi_p) \mathbf{e}_y \} & \text{during an r.f. pulse} \\ 0 & \text{otherwise} \end{cases}$$

$$\mathbf{B}_{\text{non-res}}^{\text{RF}}(t) = \begin{cases} \frac{1}{2} B_{\text{RF}} \sin \theta_{\text{RF}} \{ \cos(\omega_{\text{ref}} t + \phi_p) \mathbf{e}_x - \sin(\omega_{\text{ref}} t + \phi_p) \mathbf{e}_y \} & \text{during an r.f. pulse} \\ 0 & \text{otherwise} \end{cases}$$

and the longitudinal r.f. field is given by

$$\mathbf{B}_{\text{long}}^{\text{RF}}(t) = \begin{cases} B_{\text{RF}} \cos \theta_{\text{RF}} \cos(\omega_{\text{ref}} t + \phi_p) \mathbf{e}_z & \text{during an r.f. pulse} \\ 0 & \text{otherwise} \end{cases}$$

For spins with positive γ , the frequency ω_{ref} is negative; for spins with negative γ , the frequency ω_{ref} is positive.

It may be shown that, under ordinary circumstances, the longitudinal and non-resonant components of the r.f. field have almost no influence on the motion of the spins. They may safely be neglected.⁷ The transverse part of the spin Hamiltonian may therefore be approximated as

$$\hat{\mathcal{H}}_j^{\text{RF}}(t) \cong \begin{cases} -\omega_{\text{nut}}^j \{ \cos(\omega_{\text{ref}}t + \phi_p) \hat{I}_{jx} + \sin(\omega_{\text{ref}}t + \phi_p) \hat{I}_{jy} \} & \text{during an r.f. pulse} \\ 0 & \text{otherwise} \end{cases} \quad (8.16)$$

where the *nutaton frequency* ω_{nut}^j is defined as

$$\omega_{\text{nut}}^j = |\tfrac{1}{2}\gamma_j B_{\text{RF}} \sin \theta_{\text{RF}}| \quad (8.17)$$

When we come to the quantum theory, we will see that Equation 8.16 is much easier to handle than Equation 8.15, even though it appears to be more complicated.

The nutation frequency ω_{nut}^j is a measure of the resonant r.f. field strength, experienced by spin I_j , expressed in angular frequency units. The meaning of the term ‘nutation’ is discussed in Section 10.8. Typically, the nutation frequency $\omega_{\text{nut}}^j/2\pi$ is in the range 1 – 200 kHz. Therefore, it is three to four orders of magnitude smaller than the Larmor frequency, even under the strongest r.f. pulses.

The factor 1/2 in Equation 8.17 arises because one-half of the r.f. field amplitude is ‘wasted’ on the non-resonant rotating component.⁸ The factor $\sin \theta_{\text{RF}}$ takes into account the tilt angle of the r.f. coil. In the optimal case, the axis of the r.f. coil is perpendicular to the main field $\theta_{\text{RF}} = \pi/2$, so this factor is equal to 1. A coil that is tilted away from the perpendicular is less efficient in generating a resonant r.f. field.

The above equations apply for pulses on a single spectrometer channel. Equation 8.16 is readily generalized to the multiple-channel case by adding together several similar-looking terms, with different frequencies.

8.4.3 Gradient field

The interactions of a spin I_j , located in a molecule at a spatial position $\mathbf{r} = (x, y, z)$, with field gradients along the three laboratory frame axes, are given by

$$\begin{aligned} \hat{\mathcal{H}}_j^{\text{grad}}(\mathbf{r}, t) &= -\gamma_j G_x(t) x \hat{I}_{jz} && \text{for gradient } G_x \text{ along } x\text{-axis} \\ \hat{\mathcal{H}}_j^{\text{grad}}(\mathbf{r}, t) &= -\gamma_j G_y(t) y \hat{I}_{jz} && \text{for gradient } G_y \text{ along } y\text{-axis} \\ \hat{\mathcal{H}}_j^{\text{grad}}(\mathbf{r}, t) &= -\gamma_j G_z(t) z \hat{I}_{jz} && \text{for gradient } G_z \text{ along } z\text{-axis} \end{aligned} \quad (8.18)$$

Note that in all cases the relevant spin operator is always \hat{I}_{jz} , whatever the direction of the gradient. This is because the transverse components of the gradient fields are usually far weaker than the static field, and may be ignored (see Section 8.5.2 and Chapter 4, Note 7).

8.4.4 External spin interactions: summary

The following diagram summarizes the form of the external spin interactions:

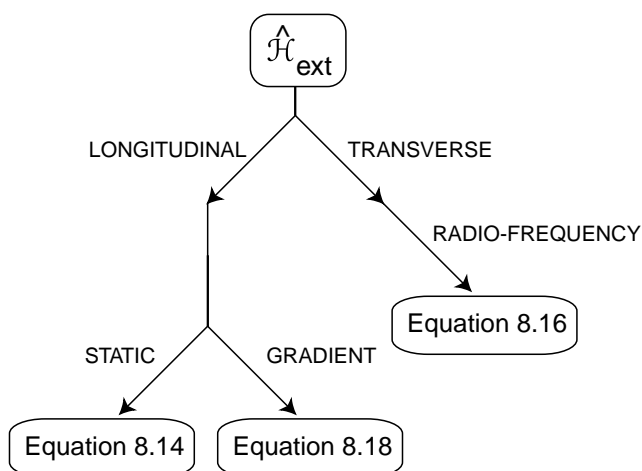


Figure 8.13
Organization of the
external spin
interactions.

8.5 Internal Spin Hamiltonian

The nuclei experience magnetic and electric fields originating from the sample itself. These interactions are included in the internal spin Hamiltonian $\hat{\mathcal{H}}_{\text{int}}$.

The following discussion concentrates on nuclear spin interactions in diamagnetic substances, which lack unpaired electron spins. See *Further Reading* for details of the nuclear spin interactions in paramagnetic materials and metals.

8.5.1 The internal spin interactions

The internal spin Hamiltonian in diamagnetic substances contains the following terms:

1. *Chemical shift terms.* These terms represent the indirect magnetic interaction of the external magnetic field and the nuclear spins, through the involvement of the electrons:

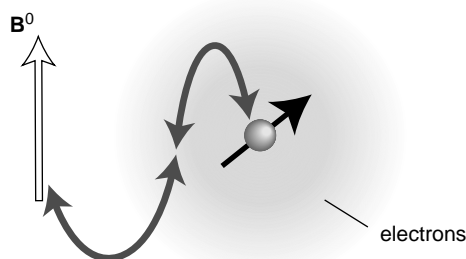


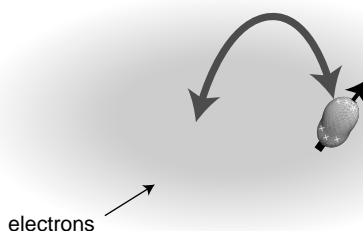
Figure 8.14
The chemical shift
interaction. The
electrons are depicted
by a grey cloud.

These terms are discussed in Section 9.1.

2. *Quadrupolar couplings.* These represent the electric interactions of spin $> 1/2$ nuclei with the surrounding electric fields:

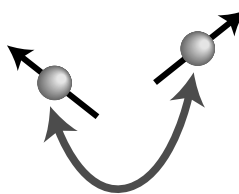
Figure 8.15

The quadrupole coupling interaction.



These terms are discussed in Section 9.2.

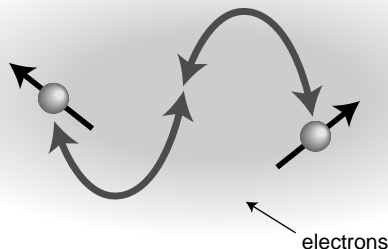
3. *Direct dipole–dipole couplings.* These represent the direct magnetic interactions of nuclear spins with each other:

**Figure 8.16**

The direct dipole–dipole coupling.

These terms are discussed in Section 9.3.

4. *J-couplings.* These represent the indirect magnetic interactions of nuclear spins with each other, through the involvement of the electrons:

**Figure 8.17**

The indirect dipole–dipole coupling (*J*-coupling).

These terms are discussed in Section 9.4.

5. *Spin–rotation interactions.* These represent the interactions of the nuclear spins with magnetic fields generated by rotational motion of the molecules:

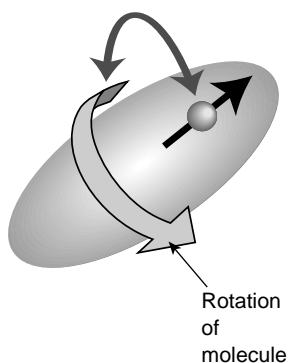


Figure 8.18
The spin-rotation interaction.

These terms are discussed in Section 9.5.

The following diagram summarizes the organization and rough magnitude of the internal spin interactions terms:

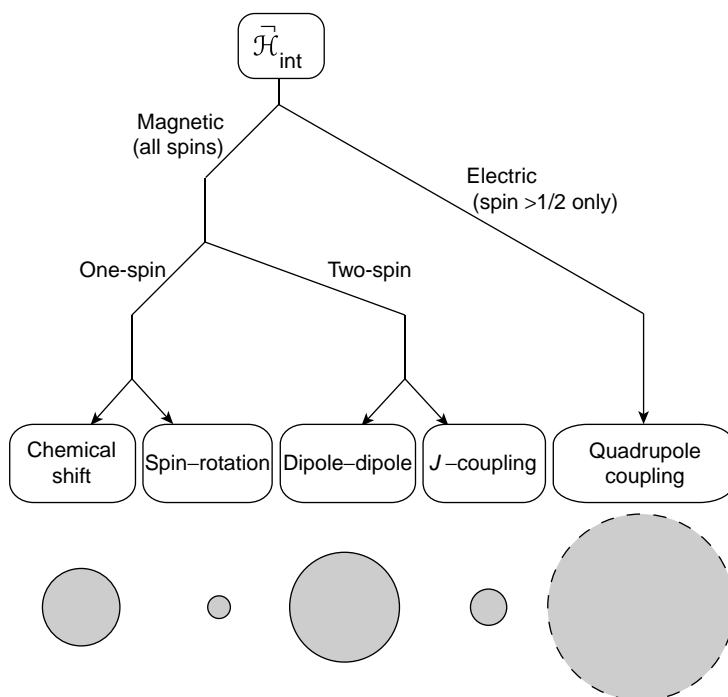


Figure 8.19
Organization of the internal spin interaction terms, and their rough relative magnitudes. The quadrupolar coupling vanishes for spins-1/2.

The circles display the typical relative size of these terms, in the absence of molecular motion. For spins $> 1/2$, the quadrupole coupling is usually the largest term. However, this term vanishes for spins-1/2.

The direct dipole–dipole couplings and chemical shift terms are usually the next largest, followed by the J -couplings and the spin–rotation interactions.

8.5.2 Simplification of the internal Hamiltonian

The mathematical forms of the nuclear spin interactions are quite complicated. Fortunately, it is usually possible to use a simplified form of the internal Hamiltonian. This is because of (i) the very strong external magnetic field and (ii) the rapid molecular motion in liquids and gases, and in some solids.

The very strong external magnetic field leads to the *secular approximation*. The rapid molecular motion leads to *motional averaging*.

As will be discussed in Section 19.3, these phenomena have a rather complicated interplay, depending on the time-scales involved. Here, I overlook these complications and summarize the situation by the following diagram:

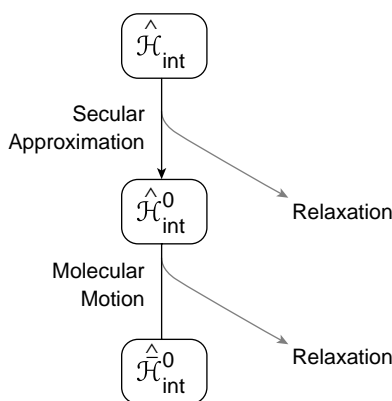


Figure 8.20
Simplification of the
internal spin
Hamiltonian.

1. The *secular approximation* of the internal spin Hamiltonian terms is discussed in Appendix A.6. It arises because the spin dynamics are dominated by the large interaction with the external magnetic field, which tends to mask some components of the internal spin interactions. The secular approximation allows each term $\hat{\mathcal{H}}_{\text{int}}$ to be replaced by a simplified form, called here $\hat{\mathcal{H}}_{\text{int}}^0$. It is usually a very good approximation, except for the case of quadrupolar spins, where a more complete treatment is often necessary.
2. *Motional averaging*. If the molecules undergo rapid molecular motion, then the interaction terms fluctuate in time. If the molecular motion is sufficiently fast, then the fluctuating interaction $\hat{\mathcal{H}}_{\text{int}}^0$ may be replaced by its *motionally averaged value*, denoted $\hat{\mathcal{H}}_{\text{int}}^0$. The parts of $\hat{\mathcal{H}}_{\text{int}}$ that have a zero time-average are discarded. Use of the motionally averaged spin Hamiltonian is usually a good approximation in gases and liquids, unless the molecular motion is slow.

The discarded parts of the internal spin Hamiltonian terms are responsible for the *relaxation* of the nuclear spin system, as sketched in Sections 2.6 and 2.7 and discussed more thoroughly in Chapter 20. For the time being we will consider the motionally averaged secular terms, which determine the form of the NMR spectrum.⁹

8.6 Motional Averaging

The form of the motionally averaged Hamiltonian depends very strongly on the type and the time-scale of molecular motion, and hence on the phase of matter.

8.6.1 Modes of molecular motion

There are three relevant modes of molecular motion, namely *internal molecular motions*, *molecular translation* and *molecular rotations*.

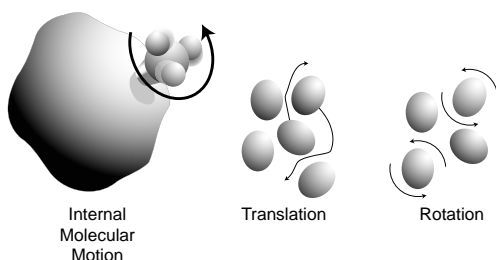


Figure 8.21
Types of molecular motion.

Internal molecular motions involve vibrations of the molecule, rotations of some internal molecular groups, and chemical isomerizations. For most of this book, I disregard the internal molecular motions and consider only the rotations or translations of the molecules as a whole. The important subject of internal molecular motion is encountered briefly in Chapter 19.

8.6.2 Molecular rotations

Molecular rotation involves a change in the *orientation* of each molecule in space.

In general, one needs *three* angles to specify the orientation of a molecule in three-dimensional space (see Appendix A.1). In this book, I will use the symbol Θ to denote the molecular orientation. Each secular Hamiltonian term depends on the molecular orientation and may be written as $\hat{\mathcal{H}}_{\text{int}}^0(\Theta)$.

In liquids and gases, and some solids, the molecular orientation depends on time. Each secular Hamiltonian term may therefore be written $\hat{\mathcal{H}}_{\text{int}}^0(\Theta(t))$. The effect of motional averaging is to replace the secular Hamiltonian by its time average, according to

$$\hat{\mathcal{H}}_{\text{int}}^0 = \tau^{-1} \int_0^\tau dt \hat{\mathcal{H}}_{\text{int}}^0(\Theta(t))$$

where τ is large. In most cases, it is possible to invoke the *ergodic hypothesis*, meaning that an average over time is equivalent to an average over molecular orientation. The basic idea is that, over a sufficiently long time, the molecules sample all possible orientations, so that a time average may be replaced by an orientational average. The motionally averaged secular Hamiltonian is given by

$$\hat{\mathcal{H}}_{\text{int}}^0 = \int d\Theta \, \mathcal{P}(\Theta) \hat{\mathcal{H}}_{\text{int}}^0(\Theta) \quad (8.19)$$

where $p(\Theta)$ is the *probability density* of the molecule having a certain orientation Θ , and the integral is taken over all orientations Θ . This probability function depends on the molecular structure, the phase of matter, and other physical variables, such as temperature and pressure.

1. In *gases* and *isotropic liquids*, all orientations are equally likely, so the probability density $p(\Theta)$ is the same for all orientations. In this case, the orientational average of a secular interaction $\hat{\mathcal{H}}_{\text{int}}^0$ is given by

$$\hat{\mathcal{H}}_{\text{int}}^{\text{iso}} = N^{-1} \int d\Theta \hat{\mathcal{H}}_{\text{int}}^0(\Theta) \quad (8.20)$$

where N is a normalization constant, chosen so that the total probability is one:

$$N = \int d\Theta$$

The expression given in Equation 8.20 is called the *isotropic average* of $\hat{\mathcal{H}}_{\text{int}}^0$.

2. In an *anisotropic liquid*, there is considerable molecular motion, but all orientations are not equally probable. In many cases, the liquid crystal is oriented along an external axis, called the *director*. Usually, molecular orientations close to the director axis are more probable than orientations far from the director:

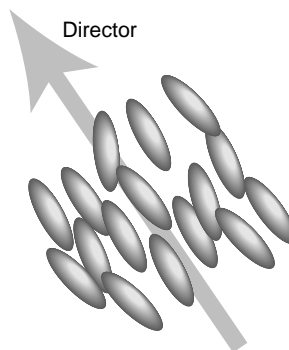


Figure 8.22

In an anisotropic liquid, the molecules orient along the director.

In many liquid crystals, the magnetic field itself acts as the director. However, more complex situations are possible, as discussed in Section 16.4.

In an anisotropic liquid, the motionally averaged spin interactions are not the same as their isotropic values: they depend on the orientation of the liquid crystal director with respect to the magnetic field.

3. In a *solid*, the atomic motion is usually heavily restricted. Each internal spin Hamiltonian term is different from its isotropic value and depends strongly on the orientation of the solid with respect to the magnetic field.

8.6.3 Molecular translations

There are two types of molecular translational motion: *diffusion*, in which the motion of neighbouring molecules is random, and *flow*, in which the molecular motion is biased in some particular direction by an external pressure gradient.

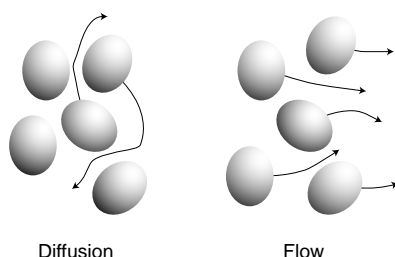


Figure 8.23
Diffusion and flow.

In most cases, significant molecular diffusion only occurs in liquids and gases. Here, it proves to be important to consider the *distance range* of molecular diffusion, on the time-scale of the NMR experiment (typically, around 0.5 s).

1. In *gases*, diffusion is extremely fast and easily extends to the physical boundaries of the sample on the time-scale of an NMR experiment. We may assume, therefore, that the positions of all molecules in a gas are exchanged during an NMR pulse sequence:

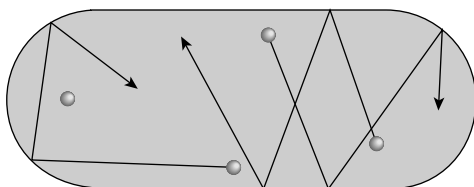


Figure 8.24
Diffusion in a gas proceeds over the entire volume of the sample.

2. In *liquids*, diffusion is much slower, depending on the molecular size and on the viscosity. It is possible to imagine a *diffusion sphere* in a liquid, within which the molecules are interchanged on the time-scale of an NMR experiment. In most liquids, such a sphere has a radius of only around 10 μm :

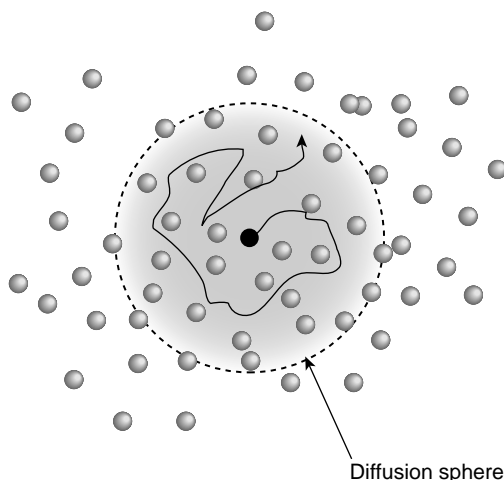


Figure 8.25
Diffusion in a liquid is restricted to a spherical volume of a few tens of micrometres in diameter, on the time-scale of an NMR experiment.

The picture above is not realistic: In practice, the diffusion sphere contains $\sim 10^{10}$ molecules, which are all in close contact.

The precise boundary of a diffusion sphere is vague, but this proves not to be too important.

3. In *solids*, the diffusional motion of the molecules is usually insignificant on the NMR time-scale.

8.6.4 Intramolecular and intermolecular spin interactions

The effect of diffusion on spin interaction terms depends on whether these interactions are *intramolecular* (involving particles on the same molecule) or *intermolecular* (involving particles on different molecules). The diagram below shows intramolecular and intermolecular couplings between nuclear spins:

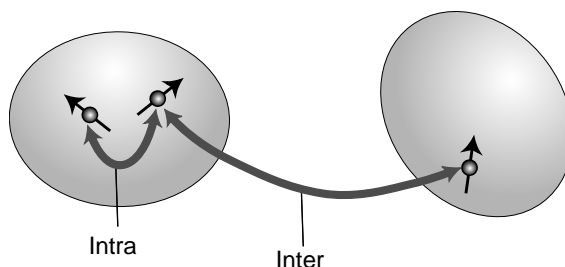


Figure 8.26
Intramolecular and intermolecular dipole-dipole couplings.

Most internal spin interactions have both intramolecular and intermolecular components. The rough relative magnitudes of these components are indicated by the following diagram:

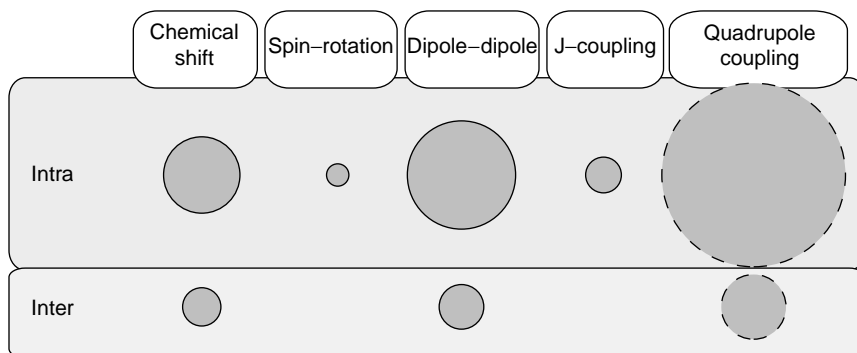


Figure 8.27
Rough relative magnitudes of the intramolecular and intermolecular components of the internal spin interactions.

To a good approximation, the J -coupling and spin-rotation interactions are purely intramolecular (see Sections 9.4 and 9.5).

In a liquid, one must also distinguish *long-range* and *short-range* intermolecular interactions. Short-range interactions involve molecules that share the same diffusion sphere. Long-range intermolecular interactions involve molecules that do not share the same diffusion sphere: The long-range interactions are far smaller than the short-range interactions, but they still lead to significant effects in some circumstances (see *Further Reading*).

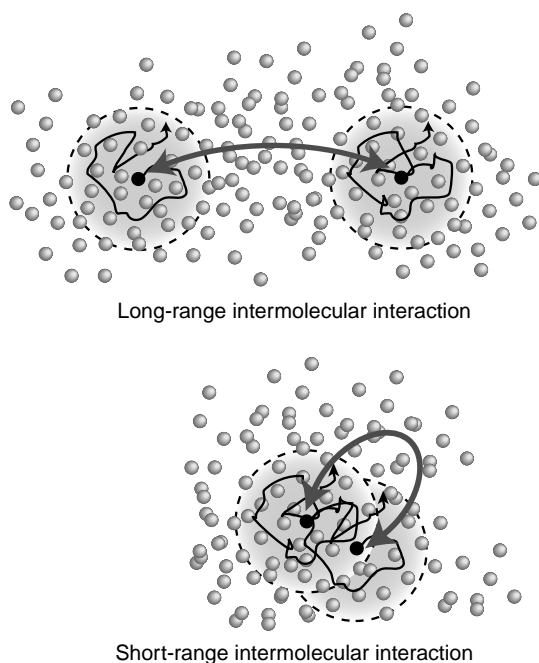


Figure 8.28
The distinction between short-range and long-range intermolecular interactions in a liquid.

8.6.5 Summary of motional averaging

The effect of motional averaging in different phases of matter may now be summarized:

1. In a *gas*, the rapid and complete rotational and translational motion averages all *intramolecular* spin interactions to their isotropic values, as given in Equation 8.20, and averages all *intermolecular* interactions to a very small value, essentially zero.¹⁰ The following flow chart summarizes the effect of motional averaging in gases:

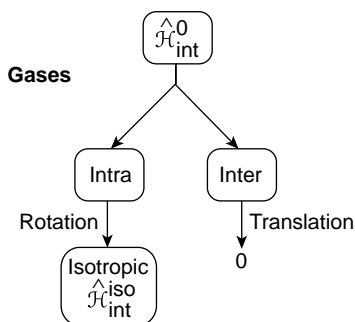


Figure 8.29
Averaging of the spin interactions in gases.

2. In an *isotropic liquid*, the rotational motion of the molecules averages all *intramolecular* spin interactions to their isotropic values, as given in Equation 8.20.

The diffusional motion of the molecules in an isotropic liquid averages the *short-range intermolecular* interactions to zero. However, the diffusional motion in a liquid is not able to average out the *long-range intermolecular interactions*.

The following flow chart summarizes the effect of motional averaging in isotropic liquids:

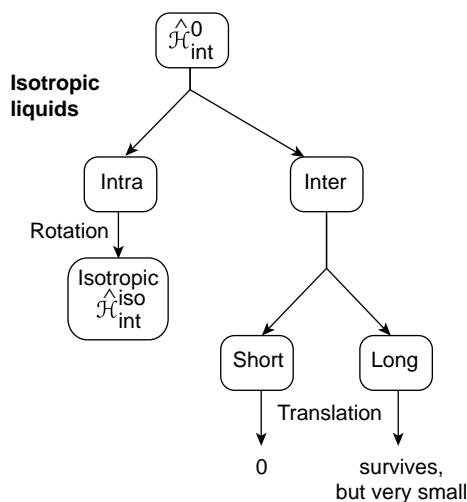


Figure 8.30

Averaging of the spin interactions in isotropic liquids.

3. In an *anisotropic liquid*, the rotational motion of the molecules averages all *intramolecular* spin interactions to values that are different from their isotropic values.

The diffusional motion of the molecules in an anisotropic liquid averages the *short-range intermolecular* interactions to zero, whereas the *long-range intermolecular interactions* survive, just as for an isotropic liquid.

The following flow chart summarizes the effect of motional averaging in anisotropic liquids:

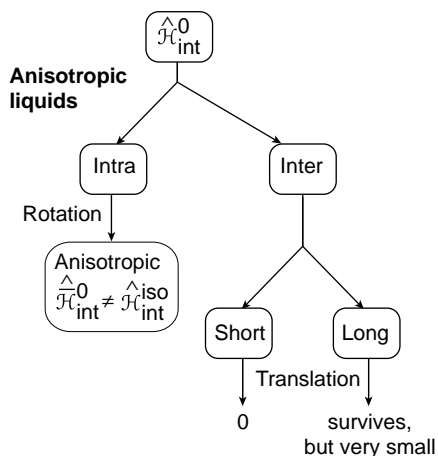


Figure 8.31

Averaging of the spin interactions in anisotropic liquids.

4. In most *solids*, the atomic motion is highly restricted and there is little averaging of the internal spin interactions, except by the restricted motions of some molecular groups. Both intramolecular and inter-

molecular spin interactions survive, and the internal spin Hamiltonian terms depend on the orientation of the sample with respect to the magnetic field:

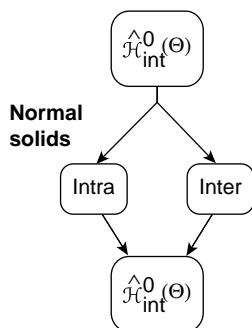


Figure 8.32

The spin interactions of a normal solid.

5. In certain molecular solids, called *plastic crystals*, an unusual situation arises. In these systems, the centres of gravity of the molecules are fixed with respect to the crystal lattice, but the molecules themselves rotate rapidly about their lattice sites, in many cases isotropically. One example is the C_{60} solid depicted in Section 1.6; another common example is provided by the hydrocarbon *adamantane*, which has the following molecular structure:

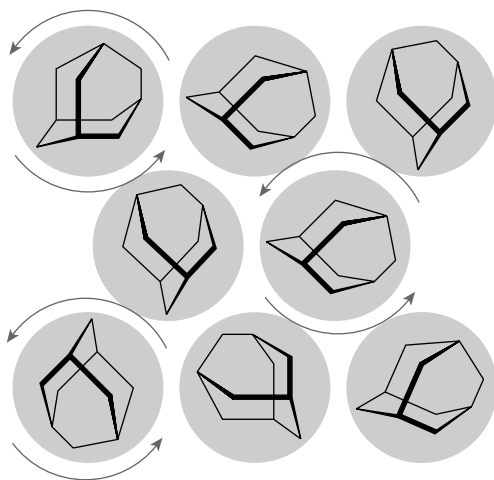
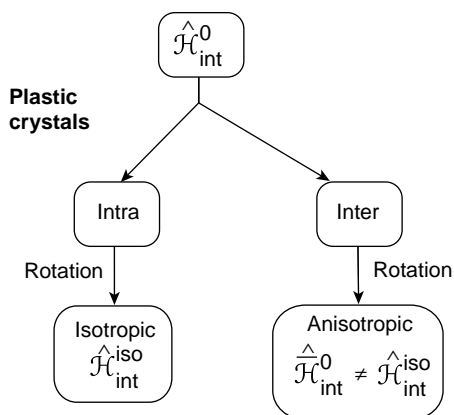


Figure 8.33

Molecular structure of adamantane.

In these special systems, the rapid molecular rotation averages out the *intramolecular* interactions to their isotropic values, whereas the averaging of the *intermolecular* interactions is incomplete, since the molecular diffusion is slow. Figure 8.34 shows a flow chart for plastic crystals.

The plastic crystal adamantane is commonly encountered as a test substance in solid-state NMR.

**Figure 8.34**

The spin interactions in a plastic crystal (assuming isotropic molecular rotation).

Notes

1. The phenomenon of *longitudinal spin relaxation* presents difficulties for the spin Hamiltonian hypothesis. As discussed in Section 2.6, the nuclear spin system relaxes towards an anisotropic equilibrium state, in which there are more spins with magnetic moments along the field than in the opposite direction to the field. This asymmetric equilibrium state would be impossible if the nuclear spin states did not have a small influence on the motion of the molecules. It follows that Equation 8.1 cannot be exactly valid and, furthermore, that NMR would be impossible if it were! See Section 20.3.6 for more on this tricky issue.
2. This property is connected with a symmetry property associated with the “standard model” of nuclear physics called *parity conservation*. Although parity conservation holds to a very good approximation, there is experimental evidence that parity-breaking leads to unconventional electric moments for heavy nuclei (see, for example C. S. Wood *et al. Science* **275**, 1759-1763 (1997)).
3. This profound and non-intuitive result may be derived from the Wigner–Eckart theorem of quantum mechanics. See the text by Slichter in *Further Reading*.
4. Nuclear physicists distinguish between the *intrinsic quadrupolar moment* of a nucleus, usually denoted Q_0 , and the *spectroscopic quadrupolar moment*, usually denoted Q . Roughly speaking, Q_0 may be regarded as the ‘true’ quadrupolar moment and Q is the result of averaging the intrinsic quadrupole moment over the angular momentum of the nucleus. Q_0 may be finite for nuclei with spin < 1 , whereas Q vanishes for such nuclei. The relevant quantity in NMR is the spectroscopic quadrupole moment Q . See e.g. P. Pyykkö, *Mol. Phys.* **99**, 1617–1629 (2001).
5. Some attempts have been made to detect the interaction of higher-order nuclear electric moments with the surrounding electric fields, e.g. see M.-Y. Liao and G. S. Harbison, *J. Chem. Phys.* **100**, 1895 (1994).
6. An exotic NMR experiment using applied electric fields to interact with the nuclear spins is described in M. Lukac and E. L. Hahn, *Adv. Magn. Reson.* **14**, 75 (1990).
7. The non-resonant and longitudinal components of the r.f. field can be important in NMR experiments in very low field, and for NMR experiments in the presence of very large internal spin interactions, such as quadrupolar couplings. For example, *overtone* NMR experiments sometimes exploit the longitudinal r.f. field. See R. Tycko and S. J. Opella, *J. Chem. Phys.* **86**, 1761 (1986).

8. It is technically possible to create an r.f. field that rotates, rather than oscillates (this is sometimes done in NMR imaging instruments). This requires that the r.f. field rotates in the correct sense with respect to the static field (see Section 2.5). In the case of a rotating r.f. field, the factor $1/2$ may be omitted in Equation 8.16.
9. The non-secular terms may cause shifts in the peak positions, called *dynamic frequency shifts*. These shifts are usually very small, except for the case of quadrupolar interactions. Dynamic frequency shifts are ignored in this book.
10. In rare cases, the chemical shift anisotropy (CSA) in gases does not average completely to zero. The residual interaction is determined by the collisions of the noble gas atoms with the walls of the container, which leads to NMR spectra that depend on the shape of the vessel. This phenomenon has been observed for gas-phase ^{129}Xe NMR; see B. M. Goodson, *J. Magn. Reson.* **155**, 157–216 (2002).

Further Reading

- For a treatment of the nuclear quadrupolar interaction, see C. P. Slichter, *Principles of Magnetic Resonance*, 3rd edition, Springer, Berlin, 1989.
- For a review of some effects involving long-range intermolecular dipolar interactions in liquids, see M. H. Levitt, *Concepts Magn. Reson.*, **8**, 77 (1996).
- For applications of long-range dipole–dipole couplings, see S. Vathyam, S. Lee and W. S. Warren, *Science*, **272**, 92 (1996) and references therein.

Exercises

- 8.1 An r.f. coil is tuned to oscillate at a frequency of $\omega_{\text{osc}}/2\pi = 50.0\text{ MHz}$. The peak value of the oscillating magnetic field in the coil is $B_{\text{RF}} = 1\text{ mT}$.
- (i) What value of the static field B^0 brings ^1H spins into resonance with the coil?
 - (ii) What is the nutation frequency ω_{nut} of ^1H spins in the coil if the static field is set to the value calculated in (i) and the coil is oriented perpendicular to the field ($\theta_{\text{RF}} = \pi/2$)?
 - (iii) What is the nutation frequency ω_{nut} of ^1H spins in the coil if the static field is set to the value calculated in (i) and the coil is at the magic angle to the field ($\theta_{\text{RF}} = \arctan \sqrt{2}$)?
 - (iv) What value of the static field B^0 brings ^{15}N spins into resonance with the coil?
 - (v) What is the nutation frequency ω_{nut} of ^{15}N spins in the coil if the static field is set to the value calculated in (iv) and the coil is oriented perpendicular to the field ($\theta_{\text{RF}} = \pi/2$)?
 - (vi) What is the nutation frequency ω_{nut} of ^{15}N spins in the coil if the static field is set to the value calculated in (iv) and the coil is at the magic angle to the field ($\theta_{\text{RF}} = \arctan \sqrt{2}$)?

9

Internal Spin Interactions

In this chapter, the internal spin interaction terms are examined in more detail.

9.1 Chemical Shift

The electrons in the molecules cause the local magnetic fields to vary on a *submolecular* distance scale. The magnetic fields experienced by nuclei at two sites in the same molecule are different if the electronic environments are different. For example, protons located in the $-\text{CH}_3$ groups of ethanol molecules experience slightly different magnetic fields than protons located in the $-\text{CH}_2$ groups. This effect is called the *chemical shift*. It is of major importance to the chemical applications of NMR.

The chemical shift is predominantly an intramolecular interaction, but it does have a significant intermolecular component as well. For example, chemical shifts are slightly different in different solvents, and are slightly different for the same molecular system in solids and in liquids. Chemical shifts may even be different for formally identical molecules in the same crystal if the asymmetric unit of the crystal structure contains more than one molecule, as is often the case.

The mechanism of the chemical shift is a two-step process. (i) The external magnetic field \mathbf{B}^0 induces currents in the electron clouds in the molecule. (ii) The circulating molecular currents in turn generate a magnetic field (called the *induced field* $\mathbf{B}_j^{\text{induced}}$):

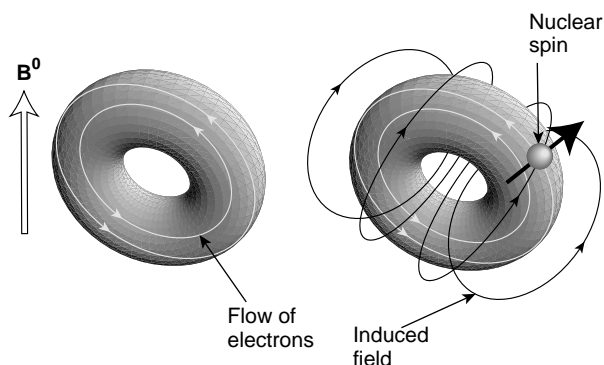


Figure 9.1
Mechanism of the
chemical shift.

The nuclear spins sense the sum of the applied external field and the induced field generated by the molecular electrons:

$$\mathbf{B}_j^{\text{loc}} = \mathbf{B}^0 + \mathbf{B}_j^{\text{induced}} \quad (9.1)$$

Typically, the induced field is only around 10^{-4} of the external field B^0 . This is small, but large enough to give rise to measurable shifts in the spin precession frequencies.

The strength of the induced currents, and hence the induced field, is directly proportional to the applied field B^0 .

The induced currents themselves may be explained by the quantum-mechanical behaviour of the electrons. Two contributions to the induced currents have been identified: (1) field-induced circulation of electrons in the ground electronic state (diamagnetic term)¹ and (2) electron circulation through participation of excited electronic states (paramagnetic term). These terms have similar magnitudes but opposite signs, which makes the calculation of accurate chemical shifts a challenging task (see *Further Reading*).

9.1.1 Chemical shift tensor

The induced field is, to a very good approximation, linearly dependent on the applied field, and may be written²

$$\mathbf{B}_j^{\text{induced}} = \boldsymbol{\delta}^j \cdot \mathbf{B}^0 \quad (9.2)$$

The symbol $\boldsymbol{\delta}^j$ represents a 3×3 matrix of real numbers, called the *chemical shift tensor* of site I_j . In matrix-vector form, the equation reads

$$\begin{pmatrix} B_{j,x}^{\text{induced}} \\ B_{j,y}^{\text{induced}} \\ B_{j,z}^{\text{induced}} \end{pmatrix} = \begin{pmatrix} \delta_{xx}^j & \delta_{xy}^j & \delta_{xz}^j \\ \delta_{yx}^j & \delta_{yy}^j & \delta_{yz}^j \\ \delta_{zx}^j & \delta_{zy}^j & \delta_{zz}^j \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B^0 \end{pmatrix} \quad (9.3)$$

which evaluates to

$$\begin{pmatrix} B_{j,x}^{\text{induced}} \\ B_{j,y}^{\text{induced}} \\ B_{j,z}^{\text{induced}} \end{pmatrix} = \begin{pmatrix} \delta_{xz}^j B^0 \\ \delta_{yz}^j B^0 \\ \delta_{zz}^j B^0 \end{pmatrix}$$

assuming that the applied static field B^0 is along the z -axis of the laboratory frame. The use of the matrix $\boldsymbol{\delta}^j$ takes into account the fact that the induced field is usually in a different direction to the applied field. For example, $\delta_{xz}^j B^0$ signifies the component of the induced field in the x -direction when the external field is applied in the z -direction. It may usually be assumed that $\boldsymbol{\delta}^j$ is symmetric, i.e. $\delta_{xy}^j = \delta_{yx}^j$, and so on.³

Why is the induced field not always parallel to the applied field? The basic idea is simple: since the induced field lines form closed loops, they must change direction as they go around the molecule. In addition, molecules have a definite three-dimensional shape, and the electrons may find it easier to circulate around certain axes. For example, electrons run readily around the doughnut-shaped orbitals in a benzene ring. If the ring is at some skewed orientation with respect to the field, one can easily imagine that the induced field runs through the hole in the doughnut and out round the sides (illustrated in Figure 9.1). The magnitude and direction of the induced field at a given nuclear site, therefore, depends on the orientation

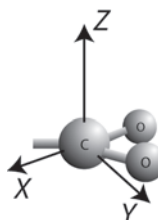
of the molecule with respect to the external field, and also on the location of the nuclear spin within the molecule.

9.1.2 Principal axes

For each nuclear site, there are three *special* directions of the external magnetic field for which the induced field *is* parallel to the external field. These special directions are always perpendicular to each other, and are called the *principal axes of the chemical shift tensor*. The principal axes are indicated by the capital letters *X*, *Y* and *Z*. Their directions often correlate with local molecular structural features. For example, consider a ^{13}C nucleus at the carbon site of a carboxylate group. In most cases, one of the principal axes of the chemical shift tensor is approximately perpendicular to the carboxylate plane. The other two principal axes are close to the CO_2 plane, with their orientation within the plane being sensitive to the local electronic environment:

Figure 9.2

The Z-principal axis of the ^{13}C chemical shift tensor of a carboxylate group is approximately perpendicular to the CO_2 plane.



The induced field is parallel to the applied field whenever the applied field is in one of these special directions:

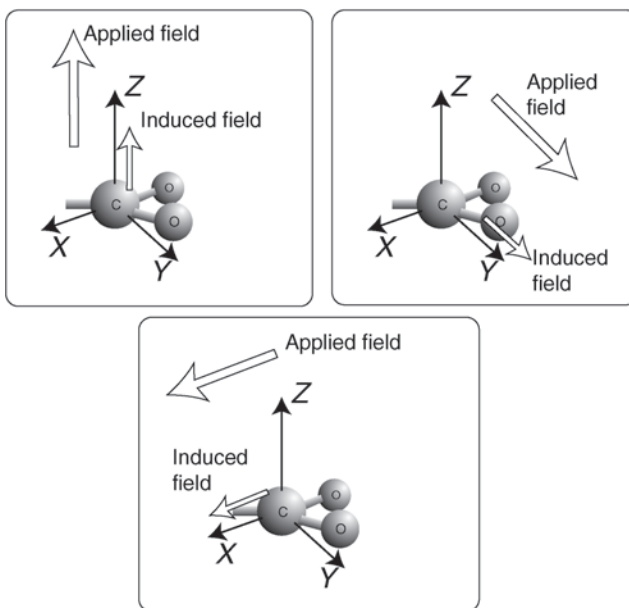


Figure 9.3

If the static magnetic field is applied along a principal axis direction, the induced field is parallel to the static field.

It is important to realize that every nuclear site in a molecule has, in general, a chemical shift tensor with a *different* principal axis system.

9.1.3 Principal values

If the external magnetic field \mathbf{B}^0 is applied along a principal axis of the chemical shift tensor of a site j , the induced field at the same site is in the same direction and is given by the following equations:

$$\mathbf{B}_j^{\text{induced}} = \delta_{XX}^j \mathbf{B}^0 \quad (\text{if } \mathbf{B}^0 \text{ is along the } X \text{ principal axis})$$

$$\mathbf{B}_j^{\text{induced}} = \delta_{YY}^j \mathbf{B}^0 \quad (\text{if } \mathbf{B}^0 \text{ is along the } Y \text{ principal axis})$$

$$\mathbf{B}_j^{\text{induced}} = \delta_{ZZ}^j \mathbf{B}^0 \quad (\text{if } \mathbf{B}^0 \text{ is along the } Z \text{ principal axis})$$

The numbers δ_{XX}^j , δ_{YY}^j and δ_{ZZ}^j are called the *principal values* of the chemical shift tensor for site j . In general, the three principal values are all different. Capital subscripts XX , YY and ZZ are used to denote the principal values.

By definition, ‘off-diagonal’ shift tensor elements, such as δ_{XZ}^j , δ_{YZ}^j , etc., are all equal to zero in the principal axis system.

9.1.4 Isotropic chemical shift

The mean of the three principal values is called the *isotropic chemical shift*:

$$\delta_j^{\text{iso}} = \frac{1}{3} (\delta_{XX}^j + \delta_{YY}^j + \delta_{ZZ}^j) \quad (9.4)$$

As discussed below, the isotropic chemical shift determines the positions of peaks in isotropic liquids. In many cases, when the term ‘chemical shift’ is used, it is the isotropic chemical shift that is meant.

9.1.5 Chemical shift anisotropy (CSA)

If all three principal values are equal, then the chemical shift tensor is said to be *isotropic*. If two or more principal values of the chemical shift tensor are different, then the chemical shift tensor is said to be *anisotropic*. The CSA quantifies the deviation from isotropy.

The most widespread convention⁴ for assigning the CSA principal values and principal axes is as follows:

1. Assign the Z principal axis to the principal value that is *furthest* from the isotropic chemical shift.
2. Assign the Y principal axis to the principal value that is *closest* to the isotropic chemical shift.
3. Assign the X principal axis to the *other* principal value. This procedure leads to the following ordering:

$$|\delta_{ZZ}^j - \delta_j^{\text{iso}}| \geq |\delta_{XX}^j - \delta_j^{\text{iso}}| \geq |\delta_{YY}^j - \delta_j^{\text{iso}}| \quad (9.5)$$

The CSA is defined as the *largest deviation in chemical shift from the isotropic value* (including the sign):

$$\delta_j^{\text{aniso}} = \delta_{ZZ}^j - \delta_j^{\text{iso}} \quad (9.6)$$

The difference between the other two principal values is quantified by a parameter which is denoted η_j , and which is known by a variety of names.⁵ In this book I use the term *biaxiality*. It is defined as follows:

$$\eta_j = \frac{\delta_{YY}^j - \delta_{XX}^j}{\delta_j^{\text{aniso}}} \quad (9.7)$$

With this set of definitions, the biaxiality η_j takes values in the range 0 to 1.

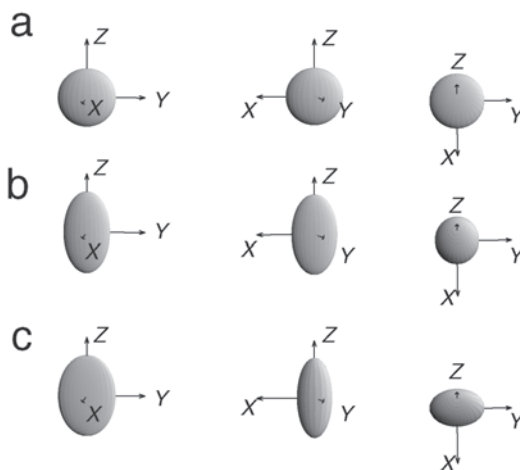
If two principal values are equal, then the biaxiality η_j is equal to zero. The chemical shift tensor is then said to be *uniaxial*.⁶

⚠ The conventional assignment of chemical shift principal values, given in Equation 9.5, does *not* generally correspond to an ascending sequence $\delta_{XX}^j \leq \delta_{YY}^j \leq \delta_{ZZ}^j$. This is commonly misunderstood.⁴

The chemical shift tensor of a particular molecular site is often represented by an ellipsoid. The principal axes of the ellipsoid coincide with the chemical shift principal values. An isotropic CSA tensor is represented by a sphere, whereas a uniaxial CSA tensor is represented by a cigar shape, and a biaxial CSA tensor is represented by a flattened ellipsoid with different dimensions in all three directions:

Figure 9.4

Ellipsoids representing CSA tensors, shown from three different viewpoints: (a) an isotropic CSA tensor ($\delta_j^{\text{aniso}} = 0$); (b) a uniaxial CSA tensor ($\delta_j^{\text{aniso}} \neq 0, \eta_j = 0$); (c) a biaxial CSA tensor ($\delta_j^{\text{aniso}} \neq 0, \eta_j \neq 0$).



In a complex molecular structure, the CSA tensors of the individual nuclear sites may be visualized by drawing a molecular structure with ellipsoids centred at the relevant molecular position. The orientation, size, and biaxiality of the ellipsoids allows one to visualize the principal values and principal axis orientations of the individual chemical shift tensors. Figure 9.5 depicts peptide planes in a protein, with typical CSA tensors attached to the ^{13}C , ^1H and ^{15}N sites.

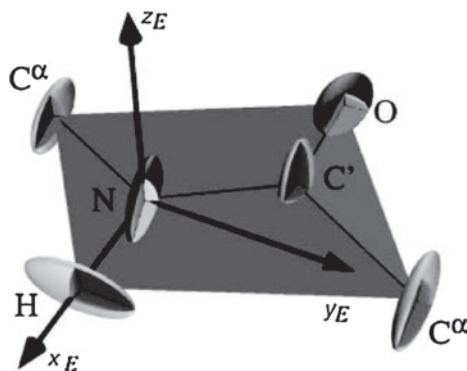


Figure 9.5 A peptide bond ($-\text{NH}-\text{CO}-$) joins adjacent amino acids in a protein. In most cases, the four atoms of the peptide bond lie close to the same plane, shown by the shaded region. The ellipsoids represent typical CSA tensors for the chemical shielding of ^{13}C , ^{15}N and ^1H nuclei at the C, N and H sites, and a typical electric field gradient tensor for the quadrupolar interaction of a ^{17}O nucleus at the carbonyl oxygen site. The arrows show an orthogonal local axis system attached to the peptide plane. Adapted from M. Bak, R. Schultz, Y. Vosegaard and N. C. Nielsen, *J. Magn. Reson.* **154**, 28–45 (2002), copyright Elsevier.

9.1.6 Chemical shift for an arbitrary molecular orientation

Suppose, now, that the direction of the magnetic field does not coincide with a principal axis direction. In this case, the observed chemical shift is not equal to one of the three principal values.

The general case may be handled by writing the CSA tensor as follows:

$$\delta^j = \mathcal{R}^j(\Theta) \cdot \begin{pmatrix} \delta_{XX}^j & 0 & 0 \\ 0 & \delta_{YY}^j & 0 \\ 0 & 0 & \delta_{ZZ}^j \end{pmatrix} \cdot \mathcal{R}^j(\Theta)^{-1} \quad (9.8)$$

where the orientation of the molecule is denoted Θ and $\mathcal{R}^j(\Theta)$ is a 3×3 *rotation matrix* that describes the relative orientation of the CSA principal axis and the external magnetic field:

$$\mathcal{R}^j(\Theta) = \begin{pmatrix} R_{xX}^j(\Theta) & R_{xY}^j(\Theta) & R_{xZ}^j(\Theta) \\ R_{yX}^j(\Theta) & R_{yY}^j(\Theta) & R_{yZ}^j(\Theta) \\ R_{zX}^j(\Theta) & R_{zY}^j(\Theta) & R_{zZ}^j(\Theta) \end{pmatrix} \quad (9.9)$$

and

$$\mathcal{R}^j(\Theta)^{-1} = \begin{pmatrix} R_{Xx}^j(\Theta) & R_{Yx}^j(\Theta) & R_{Zx}^j(\Theta) \\ R_{Xy}^j(\Theta) & R_{Yy}^j(\Theta) & R_{Zy}^j(\Theta) \\ R_{Xz}^j(\Theta) & R_{Yz}^j(\Theta) & R_{Zz}^j(\Theta) \end{pmatrix} \quad (9.10)$$

Expressions for the elements of $\mathcal{R}^j(\Theta)$ and $\mathcal{R}^j(\Theta)^{-1}$ are given in Appendix A.1.

The nuclear spin interacts with the induced field according to the recipe in Section 8.2.2. The full form of the chemical shift interaction of spin I_j is therefore

$$\begin{aligned}\hat{\mathcal{H}}_j^{\text{CS,full}} &= -\hat{\boldsymbol{\mu}}_j \cdot \mathbf{B}_j^{\text{induced}} \\ &= -\gamma_j \delta_{xz}^j(\Theta) B^0 \hat{I}_{jx} - \gamma_j \delta_{yz}^j(\Theta) B^0 \hat{I}_{jy} - \gamma_j \delta_{zz}^j(\Theta) B^0 \hat{I}_{jz}\end{aligned}\quad (9.11)$$

where

$$\delta_{zz}^j(\Theta) = R_{zX}^j(\Theta) \delta_{XX}^j R_{Xz}^j(\Theta) + R_{zY}^j(\Theta) \delta_{YY}^j R_{Yz}^j(\Theta) + R_{zZ}^j(\Theta) \delta_{ZZ}^j R_{Zz}^j(\Theta) \quad (9.12)$$

and similarly for the elements $\delta_{xx}^j(\Theta)$ and $\delta_{yy}^j(\Theta)$.

9.1.7 Chemical shift frequency

As shown in Appendix A.6, only the last term in Equation 9.11 is retained in the secular approximation. The secular chemical shift Hamiltonian, after motional averaging, is therefore

$$\hat{\mathcal{H}}_j^{\text{CS}} \cong -\gamma_j \overline{\delta_{zz}^j(\Theta)} B^0 \hat{I}_{jz} \quad (9.13)$$

where the term δ_{zz}^j depends on the molecular orientation Θ and the chemical shift principal values according to Equation 9.12.

It is convenient to combine the external interaction in Equation 8.14 and the chemical shift interaction in Equation 9.13:

$$\hat{\mathcal{H}}_j^0 = \hat{\mathcal{H}}_j^{\text{static}} + \hat{\mathcal{H}}_j^{\text{CS}} = \omega_j^0 \hat{I}_{jz} \quad (9.14)$$

where ω_j^0 is called the *chemically shifted Larmor frequency*.

In general, the chemically shifted Larmor frequency ω_j^0 depends on the motionally averaged chemical shift according to

$$\omega_j^0 = -\gamma_j B^0 \left(1 + \overline{\delta_{zz}^j(\Theta)}\right) \quad (9.15)$$

This formula neglects susceptibility effects and the chemical shift of the reference compound used to set the origin of the $\delta = 0$ scale (usually TMS).

As usual, the sign of the chemically shifted Larmor frequency ω_j^0 depends on the sign of γ_j , i.e. negative for spins with positive γ_j and positive for spins with negative γ_j .

9.1.8 Chemical shift interaction in isotropic liquids

In an isotropic liquid, the molecules tumble rapidly through every conceivable molecular orientation, with equal probability for each orientation. The observed chemical shift is therefore the *isotropic average* of the term $\delta_{zz}^j(\Theta)$:

$$\overline{\delta_{zz}^j(\Theta)} = N^{-1} \int d\Theta \delta_{zz}^j(\Theta) \quad (\text{in isotropic liquids})$$

where N is a normalization constant, chosen so that the sum probability of all orientations is unity.

The isotropic average of $\delta_{zz}^j(\Theta)$ is simply the isotropic chemical shift, as defined in Equation 9.4:

$$\overline{\delta_{zz}^j(\Theta)} = \delta_j^{\text{iso}} \quad (\text{in isotropic liquids})$$

The motionally averaged chemical shift Hamiltonian in isotropic liquids is therefore given by Equation 9.14, where the *isotropic chemical shift frequency* is defined through:

$$\omega_j^0 = -\gamma_j B^0 (1 + \delta_j^{\text{iso}}) \quad (\text{in isotropic liquids}) \quad (9.16)$$

In an isotropic liquid, the chemical shift is equal to the isotropic chemical shift and does not depend on the orientation of the sample with respect to the magnetic field.

The isotropic chemical shift is of central importance in chemistry as a diagnostic tool for molecular structure and dynamics. The literature on the subject is enormous (see *Further Reading*). Here, I simply note the following qualitative observations:

- The major contribution to the chemical shift usually comes from the influence of low-lying electronic excited states. Heavier atoms tend to have more low-lying excited states than lighter atoms, leading to a larger chemical shift range for heavy isotopes. For example, the chemical shift range for ^1H is normally only around 10 ppm, whereas for ^{13}C it is around 200 ppm. Heavy nuclei, such as ^{209}Pb , often have chemical shifts of many thousands of parts per million.
- The chemical shift δ correlates well with electronegativity: electronegative atoms, like O, Cl, F, etc, tend to withdraw electron density from neighbouring groups, increasing the local fields at the nuclei of neighbouring atoms, which leads to increased δ values.
- In rigid molecules with a well-defined three-dimensional structure, the chemical shift is influenced by neighbouring molecular units with a strong magnetic susceptibility, even if there is no direct chemical link. For example, a benzene ring readily supports induced electron currents and tends to decrease the local fields of nuclei situated close to the local symmetry axis (decreasing δ) and increase the local fields of nuclei close to the plane of the ring (increasing δ):

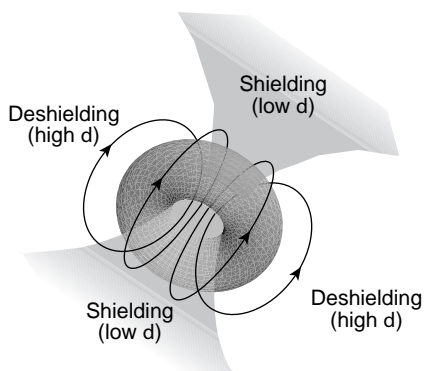


Figure 9.6
The ring current shift.

This is called the *ring-current shift*. It is sometimes used to provide clues about the secondary molecular structure.

- The isotropic chemical shift is an average over rapid molecular motions. In cases with significant dynamics, this can be quite misleading. Consider, for example, the case where a molecule may exist in two different chemical forms, each of which has a different chemical shift. The NMR spectrum normally contains two peaks for each nuclear site, corresponding to the two molecular forms. However, if a rapid chemical exchange process occurs, which causes the molecules to jump frequently from one state to the other, the NMR spectrum contains only one peak for each nuclear site, at the average chemical shift of the two species (see Section 19.5). This average chemical shift must be interpreted with care. At no time does any chemical species exist that actually has this average chemical shift.

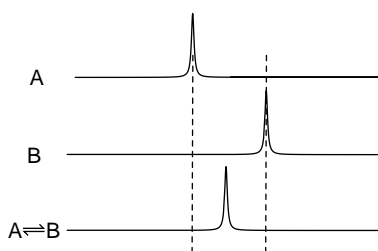


Figure 9.7

Averaging of the chemical shift over a chemical exchange process.

- The chemical shift of a spin in a particular nuclear site depends slightly on the nuclear isotopes in neighbouring nuclear sites. For example, the methyl proton chemical shifts in isotopomers of ethanol, such as $^{12}\text{CH}_3^{12}\text{CH}_2\text{OH}$, $^{13}\text{CH}_3^{12}\text{CH}_2\text{OH}$, etc., are slightly different. This small effect is called the *secondary isotope shift* (not to be confused with the *isotropic* chemical shift).⁷
- Chemical shifts are subject to fairly remote influences, such as those due to neighbouring molecules. For this reason, isotropic chemical shifts in the solid state may differ slightly from isotropic chemical shifts in solution. Similarly, chemically identical molecules in the same crystal may have slightly different chemical shifts, if they are not related by a crystal symmetry operation. This is the case when the asymmetric unit of a crystal contains more than one molecule.⁸

Typical chemical shift ranges for a number of different isotopes are given in Figure 3.31.

9.1.9 Chemical shift interaction in anisotropic liquids

In an anisotropic liquid (liquid crystal), the motional average of the chemical shift tensor element δ_{zz}^j is given by

$$\overline{\delta_{zz}^j(\Theta)} = \int d\Theta \delta_{zz}^j(\Theta) p(\Theta)$$

and $p(\Theta)d\Theta$ is the probability of the molecule having an orientation in the range Θ to $\Theta + d\Theta$. In general, this is not equal to the isotropic chemical shift δ_j^{iso} .

As a result, the NMR peak frequencies change suddenly if the system undergoes a phase transition from a liquid crystalline phase to an isotropic liquid phase:

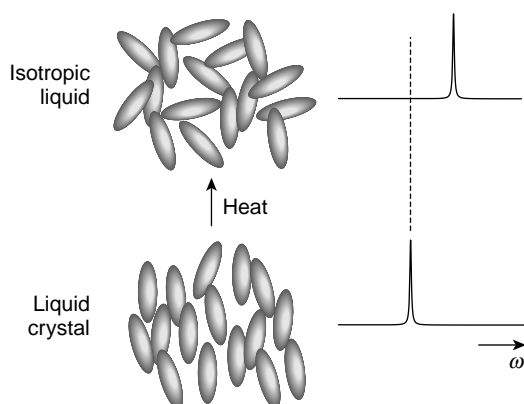


Figure 9.8
The chemical shift changes upon a phase transition.

This phenomenon makes NMR a useful spectroscopic method for studying phase transitions in liquid crystals.

9.1.10 Chemical shift interaction in solids

The chemical shift Hamiltonian in Equation 9.13 depends on the tensor component δ_{zz}^j . This chemical shift tensor element depends on the orientation Θ of the atomic framework with respect to the magnetic field. In solids, the chemical shift frequency is given by

$$\omega_j^0(\Theta) = -\gamma_j B^0 (1 + \delta_{zz}^j(\Theta)) \quad (9.17)$$

which depends on the molecular orientation, as well as the principal values and axes of the chemical shift tensor through Equation 9.12.

Consider, for example, a single crystal of a molecular solid. In this case, the molecules are lined up on a rigid lattice, and in the simplest case, all molecules have the same orientation.⁹ As a result, the chemical shift is the same for all molecules and depends on the orientation of the crystal with respect to the magnetic field. It is possible to change the chemical shift by rotating the crystal:

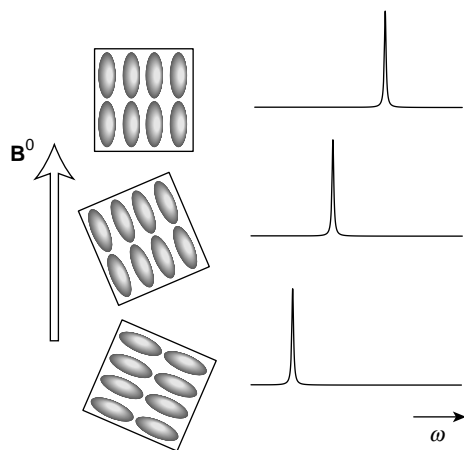


Figure 9.9
In a crystal, the chemical shift depends on the orientation of the solid with respect to the magnetic field.

A *powder*, on the other hand, the molecules have all possible orientations. The NMR spectrum of a powder is often very broad, because the chemical shift of each crystallite is different. The solid-state NMR spectrum of a powder has a typical broad shape with sharp corners, called a *powder pattern*:

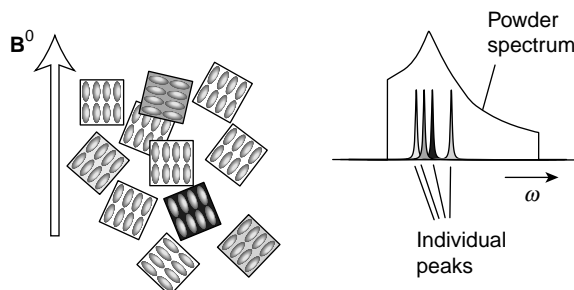
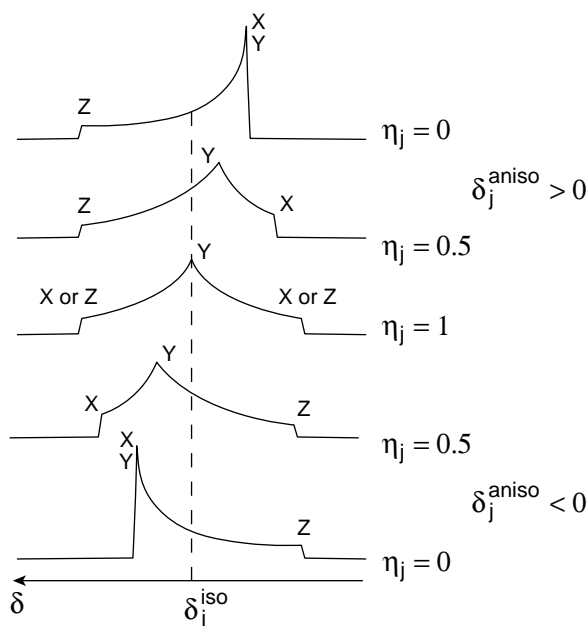


Figure 9.10
Formation of a powder pattern.

The broad pattern comes from the superposition of many sharp peaks with different frequencies, each one coming from a crystallite with a different orientation. The broadening of powder NMR spectra due to CSA is an example of *inhomogeneous broadening*.

The sharp features of a chemical shift powder pattern coincide with the principal values of the chemical shift tensor $\{\delta_{XX}^j, \delta_{YY}^j, \delta_{ZZ}^j\}$. The shape of the static powder pattern generated by nuclei in a single molecular site depends on the CSA (including the sign) and the biaxiality of the chemical shift tensor. Some typical spectral shapes for single molecular sites in a powder sample are shown in Figure 9.11. An experimental example is shown in Figure 9.12.

Figure 9.11
Powder pattern lineshapes for a single molecular site with CSA. All patterns belong to sites with the same magnitude of CSA $|\delta_j^{\text{aniso}}|$. The CSA is positive for the upper two patterns, and negative for the lower two. The sign of the CSA may be chosen arbitrarily in the case of maximum biaxiality ($\eta_j = 1$). The dashed line shows the position of the isotropic chemical shift δ_j^{iso} .



The orientation dependence of the chemical shift in a solid may be reduced greatly if there is significant molecular motion. In the extreme case of *plastic crystals* (see Section 8.6), the rapid isotropic motion of the molecules almost completely removes the CSA.

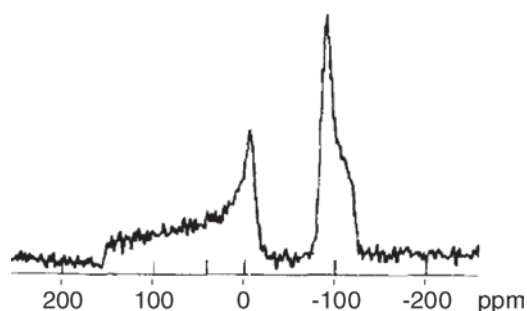


Figure 9.12 Experimental ^1H -decoupled ^{13}C spectrum for frozen acetic anhydride. The spectrum displays a powder pattern for each of the two chemically distinct ^{13}C sites. Both CSA tensors are almost uniaxial $\eta_j \cong 0$, but the sign and magnitude of the CSA are different. Reused from A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.* **59**, 569–590 (1973). Copyright 1973, American Institute of Physics.

9.1.11 Chemical shift interaction: summary

The following diagram summarizes the form of the chemical shift interaction in liquids and solids:

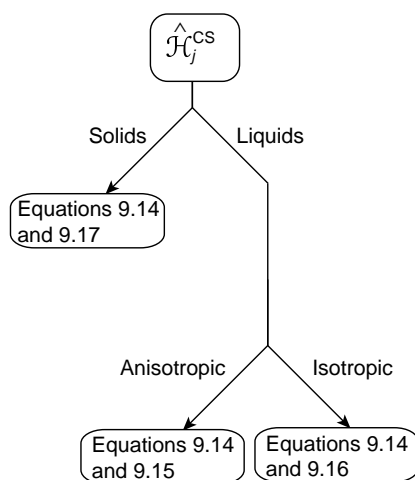


Figure 9.13
Flow diagram for the chemical shift interaction.

9.2 Electric Quadrupole Coupling

If the nuclear spin is greater than $1/2$, the electric quadrupole moment of the nucleus interacts strongly with the electric field gradients generated by the surrounding electron clouds.¹⁰ The quadrupolar coupling is predominantly, but not exclusively, an intramolecular interaction.

Table 9.1 Quadrupole moments of selected nuclear isotopes with $I > 1/2$. A complete listing of nuclear quadrupole moments may be found on the website www.webelements.com.

Isotope	Ground-state spin	Natural abundance/%	Electric quadrupole moment/ 10^{-28}m^2
^2H	1	0.012	0.2860
^6Li	1	7.59	−0.0808
^7Li	3/2	92.41	−4.01
^{11}B	3/2	80.1	4.059
^{14}N	1	99.6	2.044
^{17}O	5/2	0.038	−2.558
^{23}Na	3/2	100	10.4
^{27}Al	5/2	100	14.66
^{45}Sc	7/2	100	−22
^{51}V	7/2	99.8	−5.2
^{55}Mn	5/2	100	0.33
^{59}Co	7/2	100	0.42
^{63}Cu	3/2	69.2	−0.22
^{65}Cu	3/2	30.8	−0.204
^{87}Rb	3/2	27.8	0.132
^{93}Nb	9/2	100	−0.32

Electric quadrupole moments for several nuclear isotopes are listed in Table 9.1.

The quadrupolar coupling involves both a *nuclear* property (the quadrupole moment of the nucleus) and a *molecular* property (the electric field gradient created by the electrons at the site of the nucleus).¹¹ As a result, the nuclear quadrupole moments listed in Table 9.1 do not accurately reflect the typical magnitudes of the electric quadrupole interaction. For example, nuclei with large quadrupole moments may still have small quadrupole couplings, if the nuclear environment is so symmetric that the local electric field gradients are small. This is often the case for metal nuclei such as ^7Li ($I = 3/2$), ^{23}Na ($I = 3/2$) and ^{27}Al ($I = 5/2$), which are often found in symmetrical ionic environments. The opposite phenomenon occurs for ^{14}N ($I = 1$), which has a much smaller electric quadrupole moment than that of ^{23}Na and ^{27}Al , but which is usually found in covalently bonded sites with large local field gradients. As a result, the electric quadrupole coupling of ^{14}N is usually large, except in exceptional cases of high symmetry, such as NH_4^+ and other quaternary ions.

In order to simplify the notation, the spin index j is dropped for the rest of this section.

9.2.1 Electric field gradient tensor

The electric field gradient at the nuclear site is a tensor, similar in properties to the CSA tensor. The electric field gradient tensor at the site of a nucleus I has principal values,¹² denoted V_{XX} , V_{YY} and V_{ZZ} , that sum to zero:

$$V_{XX} + V_{YY} + V_{ZZ} = 0$$

These three principal values are associated with three principal axes, which are often close to local molecular symmetry axes. For example, Figure 9.5 shows an ellipsoid at the oxygen site, representing the local electric field gradient tensor as experienced by a ^{17}O nucleus.

The electric field gradient at the site of a nucleus I is usually specified by using two parameters, called eq and η_Q . The parameter eq is the largest principal value of the electric field gradient tensor.¹²

$$eq = V_{ZZ} \quad (9.18)$$

The parameter η_Q is the biaxiality of the electric field gradient tensor,¹² at the site of nucleus I :

$$\eta_Q = (V_{XX} - V_{YY})/V_{ZZ} \quad (9.19)$$

The biaxiality is a number between 0 and 1.

The electric field gradient tensor for an arbitrary molecular orientation Θ may be written as a 3×3 matrix as follows:

$$\mathbf{V}(\Theta) = \mathcal{R}_Q(\Theta) \cdot \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix} \cdot \mathcal{R}_Q(\Theta)^{-1}$$

where the 3×3 rotation matrix $\mathcal{R}_Q(\Theta)$ describes the relative orientation of the electric field gradient principal axis system and the static magnetic field, and Θ is the molecular orientation. Explicit expressions for $\mathcal{R}_Q(\Theta)$ are given in Appendix A.7. Note the similarity between this equation and Equation 9.8 for the CSA.

9.2.2 Nuclear quadrupole Hamiltonian

The full form of the nuclear quadrupole Hamiltonian, for an arbitrary molecular orientation, is given by the following equation:

$$\hat{\mathcal{H}}_Q^{\text{full}}(\Theta) = \frac{eQ}{2I(2I-1)\hbar} \hat{\mathbf{I}} \cdot \mathbf{V}(\Theta) \cdot \hat{\mathbf{I}} \quad (9.20)$$

where Q is the nuclear quadrupole moment, I is the nuclear spin quantum number, and the dot product has the following meaning:

$$\hat{\mathbf{I}} \cdot \mathbf{V}(\Theta) \cdot \hat{\mathbf{I}} = \hat{I}_x V_{xx}(\Theta) \hat{I}_x + \hat{I}_x V_{xy}(\Theta) \hat{I}_y + \hat{I}_x V_{xz}(\Theta) \hat{I}_z + \hat{I}_y V_{yx}(\Theta) \hat{I}_x + \dots$$

If the quadrupolar interaction is much smaller than the Zeeman interaction, then the secular approximation may be used to discard many of the terms, just as for the chemical shift. However, the large size of the quadrupolar interaction often makes it necessary to include more than one term in the series:

$$\hat{\mathcal{H}}_Q^{\text{full}} = \hat{\mathcal{H}}_Q^{(1)} + \hat{\mathcal{H}}_Q^{(2)} + \dots \quad (9.21)$$

where $\hat{\mathcal{H}}_Q^{(1)}$ is the *first-order quadrupolar Hamiltonian* and $\hat{\mathcal{H}}_Q^{(2)}$ is the *second-order quadrupolar Hamiltonian*. The inclusion of $\hat{\mathcal{H}}_Q^{(1)}$ alone is equivalent to the secular approximation, and is sufficient when the quadrupolar interaction is small. The second-order term $\hat{\mathcal{H}}_Q^{(2)}$ must be included when the quadrupolar interaction is large.¹³ Third-order terms are sometimes also necessary.

The first-order quadrupolar Hamiltonian may be written as follows:¹⁴

$$\hat{\mathcal{H}}_Q^{(1)} = \omega_Q^{(1)} \frac{1}{6} (3\hat{I}_z^2 - I(I+1)\hat{1}) \quad (9.22)$$

where $\omega_Q^{(1)}$ is the first-order quadrupolar coupling.

In general, the first-order quadrupolar coupling is given by

$$\omega_Q^{(1)} = \frac{3eQ\bar{V}_{zz}}{2I(2I-1)\hbar} \quad (9.23)$$

where \bar{V}_{zz} denotes the average of the secular electric field gradient component $V_{zz}(\Theta)$ over molecular motion. For a fixed molecular orientation Θ , this secular component is given by

$$V_{zz}(\Theta) = R_{zX}^Q(\Theta)V_{XX}R_{Xz}^Q(\Theta) + R_{zY}^Q(\Theta)V_{YY}R_{Yz}^Q(\Theta) + R_{zZ}^Q(\Theta)V_{ZZ}R_{Zz}^Q(\Theta) \quad (9.24)$$

where $R_{zX}^Q \dots$ are the elements of the rotation matrix defining the orientation of the electric field gradient principal axis system with respect to the magnetic field. This equation is similar to Equation 9.12 and leads to a complicated dependence of the quadrupolar interaction on the molecular orientation.

The second-order quadrupolar Hamiltonian is a more complex term (see *Further Reading*). The second-order quadrupole coupling is of the order of the square of the first-order quadrupole coupling divided by the Larmor frequency:

$$\omega_Q^{(2)} \sim \left| \frac{\{\omega_Q^{(1)}\}^2}{\omega^0} \right| \quad (9.25)$$

The second-order quadrupolar coupling is therefore *inversely* proportional to the external magnetic field.

9.2.3 Isotropic liquids

In an *isotropic liquid*, the first-order quadrupolar coupling $\omega_Q^{(1)}$ averages to zero. As a result, the motional average of the first-order quadrupolar Hamiltonian vanishes:

$$\hat{\mathcal{H}}_Q^{(1)} = 0 \quad (\text{in isotropic liquids}) \quad (9.26)$$

The first-order quadrupolar interaction does not influence the position of peaks in the NMR spectra of isotropic liquids, to a first approximation.¹⁵ The quadrupolar interaction does, on the other hand, strongly influence the *relaxation* of nuclear spins $> 1/2$ in isotropic liquids.

9.2.4 Anisotropic liquids

In an *anisotropic liquid* (liquid crystal), the electric field gradient term $V_{zz}(\Theta)$ does not average to zero. The first-order quadrupolar Hamiltonian in anisotropic liquids is given by Equations 9.22 and 9.23, where the electric field gradient component is averaged over molecular orientations, weighted by their probability in

the liquid crystalline phase:

$$\overline{V_{zz}(\Theta)} = \int d\Theta V_{zz}(\Theta) p(\Theta) \quad (9.27)$$

The motionally averaged quadrupolar interaction of spins $> 1/2$ jumps from zero to some finite value if the system makes a phase transition from an isotropic liquid phase to a liquid crystalline phase.

The NMR of quadrupolar nuclei such as ^2H is a very powerful method for studying the ordering and dynamics of liquid crystals.

9.2.5 Solids

In a rigid solid, the first-order quadrupolar Hamiltonian is given by Equation 9.22, where the electric field gradient element V_{zz} depends on the electric field gradient principal values and the molecular orientation in a complicated way, as described by Equation 9.24. In general, the quadrupolar Hamiltonian depends on the orientation as well as the parameters eq and η_Q defining the magnitude and biaxiality of the electric field gradient tensor.

In the NMR of solids, it is common to specify the *quadrupole coupling constant* C_Q and the biaxiality parameter η_Q (Equation 9.19). The quadrupole coupling constant of a nucleus I is defined as follows:

$$C_Q = \frac{e^2 q Q}{h} \quad (9.28)$$

The coupling constant C_Q has units of hertz. Typical values of the quadrupole coupling constant range from a few kilohertz to tens or even hundreds of megahertz.¹⁶

The first-order quadrupolar interaction in a solid is written as follows:

$$\hat{\mathcal{H}}_Q^{(1)}(\Theta) = \omega_Q^{(1)}(\Theta) \times \frac{1}{6} (3\hat{I}_z^2 - I(I+1)\hat{1}) \quad (\text{in solids}) \quad (9.29)$$

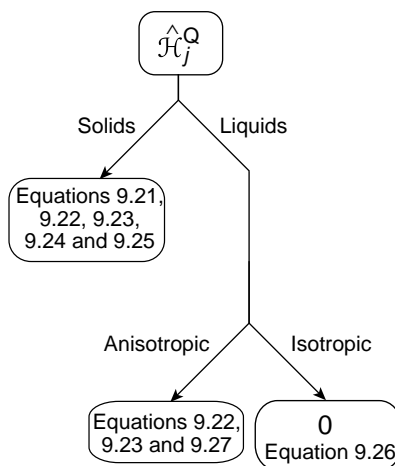
where Θ is the molecular orientation. In the case of a uniaxial electric field gradient tensor ($\eta_Q = 0$), the first-order quadrupolar coupling $\omega_Q^{(1)}$ is given in terms of C_Q by the following expression:

$$\omega_Q^{(1)}(\Theta) = \frac{3\pi C_Q}{I(2I-1)} \times \frac{1}{2} (3\cos^2\theta_Q - 1) \quad (\text{for } \eta_Q = 0) \quad (9.30)$$

where θ_Q is the angle between the principal Z-axis of the electric field gradient tensor and the static magnetic field.

9.2.6 Quadrupole interaction: summary

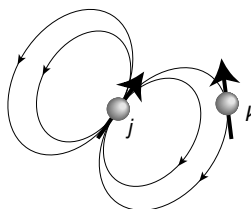
The following diagram summarizes the form of the first-order quadrupolar coupling interaction in liquids and solids:

**Figure 9.14**

Flow diagram for the first-order quadrupole interaction.

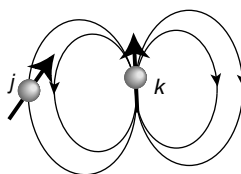
9.3 Direct Dipole–Dipole Coupling

The direct dipole–dipole coupling between spins is easy to visualize. Since each nuclear spin is magnetic, it generates a magnetic field, looping around in the surrounding space, according to the direction of the spin magnetic moment. A second nuclear spin interacts with this magnetic field:

**Figure 9.15**

Magnetic field generated by spin j at the site of spin k .

The interaction between the spins is mutual. The first nuclear spin also experiences the field generated by the second nuclear spin:

**Figure 9.16**

The dipole–dipole interaction is mutual.

This interaction is called the *through-space dipole–dipole coupling*, or *direct dipole–dipole coupling*, because the fields between the nuclear spins propagate through the intervening space, without involving the electron clouds. The more concise terms *dipole–dipole coupling* or *DD-coupling* are often used (somewhat loosely) as implying the through-space mechanism.

The dipole–dipole coupling may be either intramolecular or intermolecular.

The full form of the direct dipole–dipole interaction between spins I_j and I_k is represented in the spin Hamiltonian by the following term:

$$\hat{\mathcal{H}}_{jk}^{\text{DD,full}} = b_{jk} (3(\hat{\mathbf{I}}_j \cdot \mathbf{e}_{jk})(\hat{\mathbf{I}}_k \cdot \mathbf{e}_{jk}) - \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k) \quad (9.31)$$

where \mathbf{e}_{jk} is a unit vector parallel to the line joining the centres of the two nuclei:

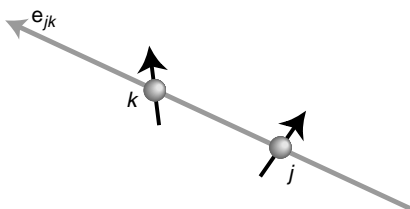


Figure 9.17

The unit vector \mathbf{e}_{jk} is parallel to the line passing through both spins.

Note that the magnitude of the vector \mathbf{e}_{jk} is defined to be $\mathbf{e}_{jk} \cdot \mathbf{e}_{jk} = 1$.

The magnitude of the through-space interaction is given by the *dipole–dipole coupling constant*, usually denoted b_{jk} , and given by

$$b_{jk} = -\frac{\mu_0 \gamma_j \gamma_k \hbar}{4\pi r_{jk}^3} \quad (9.32)$$

where γ_j and γ_k are the gyromagnetic ratios of the two spins (units of radians per second) and r_{jk} is the spin–spin distance between the two spins (units of metres). The clumsy magnetic constant $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$ is required in SI units.

Equation 9.32 provides the through-space coupling in units of radians per second. For example, two ^1H spins separated by a distance of 0.2 nm experience an interaction $b_{jk}/2\pi = -15.012 \text{ kHz}$. The interaction goes down according to the inverse cube of the internuclear distance, and scales linearly with the gyromagnetic ratio of each interacting spin. Note that the dipole–dipole coupling b_{jk} is a *constant* and does not depend on molecular orientation. The dipole–dipole spin *Hamiltonian* in Equation 9.31, on the other hand, is orientation dependent, since the vector \mathbf{e}_{jk} changes direction as the molecule rotates.

The negative sign in Equation 9.32 indicates that the coupling energy of the pair of interacting spins is minimized when both are pointing in the same direction along the internuclear vector, like two bar magnets arranged in a line, head to tail:

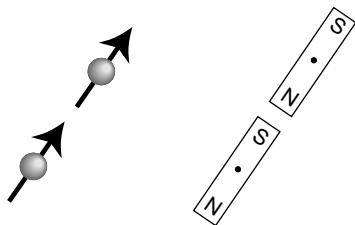
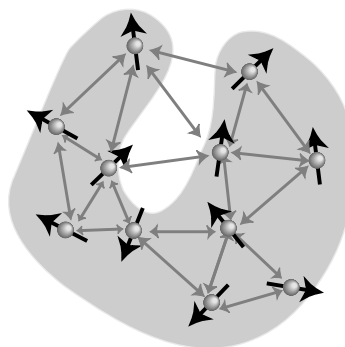


Figure 9.18

Magnetic spins are like bar magnets. Head to tail is the lowest energy configuration.

The direct dipole–dipole coupling is very useful for molecular structural studies, since it depends only on known physical constants and the inverse cube of the internuclear distance r_{jk}^{-3} . Estimation of this coupling provides a direct spectroscopic route to the distances between nuclei, and hence the geometrical form of the molecule. Measuring the through-space couplings of many spin pairs in a molecule can tie down the molecular structure and conformation unambiguously:

The NOESY and ROESY experiments (see Sections 20.6 and 20.7) make use of this principle.

**Figure 9.19**

The magnitudes of many dipole–dipole couplings may be used to determine the molecular structure.

9.3.1 Secular dipole–dipole coupling

Consider now a sample containing many spins. Each pair of spins has a direct dipole–dipole coupling, described by Equation 9.31. The dipole–dipole coupling spin Hamiltonian of the whole sample is given by

$$\hat{\mathcal{H}}^{\text{DD,full}} = \sum_k \sum_j^{k-1} \hat{\mathcal{H}}_{jk}^{\text{DD,full}}$$

The double summation takes in all *pairs* of spins in the sample. This summation over pairs may also be written:

$$\hat{\mathcal{H}}^{\text{DD,full}} = \sum_{j < k} \hat{\mathcal{H}}_{jk}^{\text{DD,full}}$$

In high magnetic field, the non-secular part of the dipole–dipole coupling terms may be discarded. The form of the secular dipole–dipole coupling depends on whether the spins I_j and I_k are of the same isotopic species or not. As described in Appendix A.6, the secular approximation is based on the energy level differences between energy eigenstates, and these energy level differences depend strongly on whether the spin system is homonuclear or heteronuclear.

If the spins are of the same isotopic species (*homonuclear case*), then the secular part of the dipole–dipole spin Hamiltonian is given by

$$\hat{\mathcal{H}}_{jk}^{\text{DD}}(\Theta_{jk}) = d_{jk} (3\hat{I}_{jz}\hat{I}_{kz} - \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k) \quad (\text{homonuclear case}) \quad (9.33)$$

where d_{jk} is the *secular dipole–dipole coupling*, given by

$$d_{jk} = b_{jk} \frac{1}{2} (3 \cos^2 \Theta_{jk} - 1) \quad (9.34)$$

and Θ_{jk} is the angle between the vector joining the spins and the external magnetic field, i.e.

$$\cos \Theta_{jk} = \mathbf{e}_{jk} \cdot \mathbf{e}_z$$

as shown below:

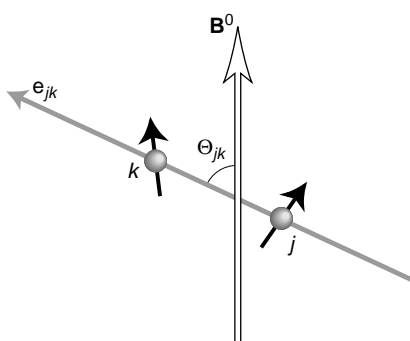


Figure 9.20

The angle Θ_{jk} is used in the calculation of the secular dipole–dipole coupling.

Note carefully the difference between the dipole–dipole coupling constant b_{jk} and the secular dipole–dipole coupling d_{jk} . The coupling constant b_{jk} depends on the distance between the spins, but does not depend on the orientation of the spin pair with respect to the magnetic field. The secular dipole–dipole coupling d_{jk} depends on the orientation and the distance.

If the spins are of different isotopic species (*heteronuclear case*), then the secular part of the direct dipole–dipole Hamiltonian is given by

$$\hat{\mathcal{H}}_{jk}^{\text{DD}}(\Theta_{jk}) = d_{jk} 2\hat{I}_{jz}\hat{I}_{kz} \quad (\text{heteronuclear case}) \quad (9.35)$$

where d_{jk} is given by Equation 9.34. In both cases, the direct dipole–dipole coupling depends on the molecular orientation, through the angle Θ_{jk} .

The secular dipole–dipole coupling has opposite sign for spin pairs aligned along the field ($\Theta_{jk} = 0$) compared with spin pairs oriented perpendicular to the field ($\Theta_{jk} = \pi/2$). The secular dipole–dipole coupling d_{jk} is equal to zero when the angle Θ_{jk} between the internuclear vector and the static field satisfies the equation

$$3 \cos^2 \Theta_{jk} - 1 = 0 \quad (9.36)$$

The solution of this equation is called the *magic angle*:

$$\Theta_{\text{magic}} = \arctan \sqrt{2} \cong 54.74^\circ \quad (9.37)$$

There is also a solution of Equation 9.36 at $\Theta_{jk} = \pi - \Theta_{\text{magic}} \cong 125.26^\circ$.

9.3.2 Dipole–dipole coupling in isotropic liquids

In an *isotropic liquid*, the secular parts of the intramolecular dipole–dipole couplings average to zero. This is easily seen by evaluating the following integral:

$$\int_0^\pi d\Theta_{jk} \sin \Theta_{jk} (3 \cos^2 \Theta_{jk} - 1) = 0 \quad (9.38)$$

The factor $\sin \Theta_{jk}$ is necessary in order to give all orientations equal probability. The area element on the surface of a sphere is proportional to $\sin \Theta_{jk}$:

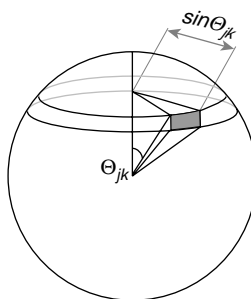


Figure 9.21

Area elements on the surface of a sphere.

The basic idea is that there are only two ways to orient a spin–spin vector along the magnetic field (up or down), whereas there are many ways of orienting a vector perpendicular to the magnetic field:

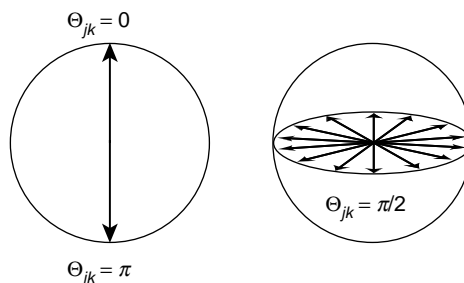


Figure 9.22

Relative probabilities for parallel and perpendicular orientations.

Similarly, the *short-range intermolecular* dipole–dipole couplings average to zero because of the translational motion of the molecules. The long-range dipole–dipole couplings do not average to zero in isotropic liquids, but these couplings are very small, and in most circumstances they may be ignored.

To a good approximation, therefore, we may write

$$\hat{\mathcal{H}}_{jk}^{\text{DD}} \cong 0 \quad (\text{in isotropic liquids}) \quad (9.39)$$

Although the secular dipole–dipole couplings essentially vanish in isotropic liquids, it is still possible to exploit the non-secular dipole–dipole couplings through their effect on the relaxation of the spin system, as discussed in Chapter 20.

9.3.3 Dipole–dipole coupling in liquid crystals

In an *anisotropic* liquid (liquid crystal), there is a preferential molecular orientation, as well as considerable translational motion of the molecules.

The *intramolecular* dipole–dipole couplings do not average out completely in an anisotropic liquid. The dipole–dipole Hamiltonian terms in an anisotropic liquid are given by Equation 9.33 in the homonuclear case and by Equation 9.35 in the heteronuclear case, where the secular dipole–dipole couplings are equal to

$$d_{jk} = b_{jk} \frac{1}{2} \overline{(3 \cos^2 \Theta_{jk} - 1)} \quad (\text{anisotropic liquids}) \quad (9.40)$$

The overbar indicates an average over all the orientations sampled by the molecules in the liquid crystalline phase, weighted by their probabilities.

The rapid diffusional motion in an anisotropic liquid averages out the *short-range intermolecular* dipole–dipole couplings, to a good approximation. The long-range intermolecular couplings survive the motional averaging, but are very small and may usually be ignored.

The form of the dipole–dipole coupling Hamiltonian in a liquid crystal is illustrated by the following diagram:

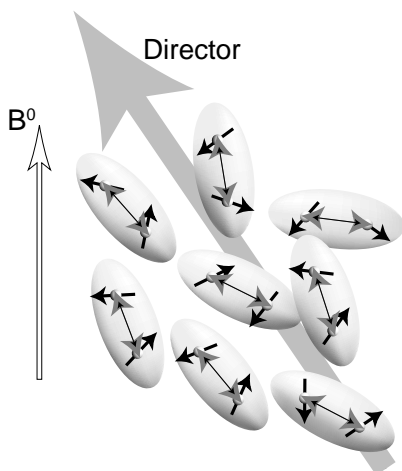


Figure 9.23
Dipole-dipole couplings
in a liquid crystal.

Note the survival of intramolecular couplings and the absence of intermolecular couplings. Intramolecular dipole–dipole couplings in an anisotropic liquid are encountered again in Section 16.4.

9.3.4 Dipole–dipole coupling in solids

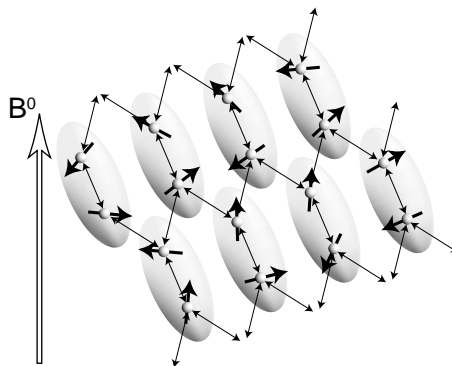
In normal solids, every spin is coupled to every other spin. The dipole–dipole part of the spin Hamiltonian in solids is given by a sum of secular terms $\hat{\mathcal{H}}_{jk}^{\text{DD}}$ for every spin pair in the sample:

$$\hat{\mathcal{H}}^{\text{DD}} = \sum_{j < k} \hat{\mathcal{H}}_{jk}^{\text{DD}} \quad (\text{in solids})$$

The terms $\hat{\mathcal{H}}_{jk}^{\text{DD}}$ are given by Equation 9.33 if the spins I_j and I_k are of the same isotopic type (homonuclear case), and by Equation 9.35 if the spins I_j and I_k are of different isotopic types (heteronuclear case).

Both inter- and intra-molecular dipole–dipole couplings are important in a normal molecular solid:

Figure 9.24
Dipole–dipole couplings in a normal molecular solid. For simplicity, only short range couplings are shown.



The situation is slightly different in plastic crystals such as adamantane (Section 8.6), since the rapid isotropic molecular rotations remove all the *intramolecular* interactions, leaving only the *intermolecular* interactions intact:

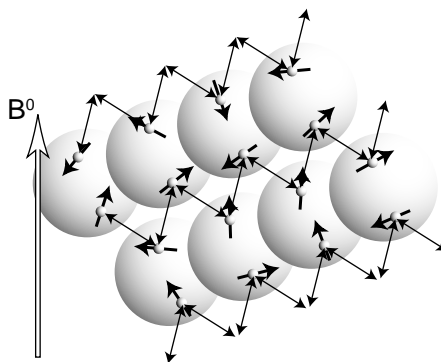


Figure 9.25
Dipole–dipole couplings in a plastic crystal.

As a result, the dipole–dipole couplings in a plastic crystal such as adamantane are much weaker than in a normal solid.

9.3.5 Dipole–dipole interaction: summary

The following diagram summarizes the form of the dipole–dipole coupling interaction in liquids and solids:

9.4 J-Coupling

Since the direct dipole–dipole coupling between nuclear spins has a zero average in isotropic liquids, it came as a great surprise to the spectroscopists of the 1950s when liquid-state NMR spectra were produced that showed clear signs of spin–spin coupling. Eventually, it was accepted that nuclear spins are coupled

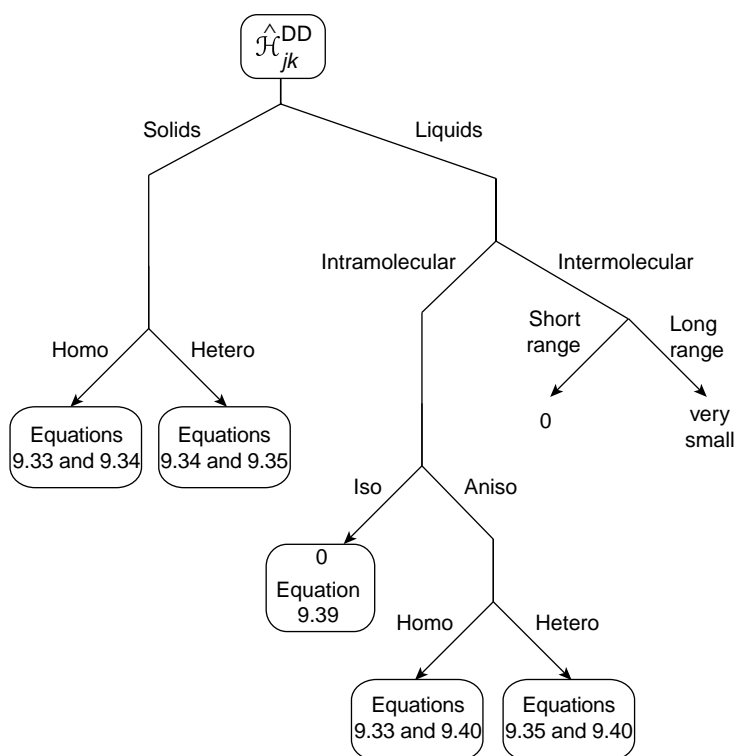


Figure 9.26
Flow diagram for the
dipole-dipole
interaction.

together even in completely isotropic liquids, because of the influence of the bonding electrons on the magnetic fields running between the nuclear spins. This type of nucleus–nucleus coupling is called *indirect*, to indicate the assistance of the bonding electrons in the coupling mechanism.

The participation of the electrons changes the orientation dependence of the interaction, thus generating an isotropic part that survives motional averaging in an isotropic liquid. The indirect coupling is usually represented by the symbol J . The terms *indirect spin–spin coupling*, *J-coupling*, and *indirect dipole–dipole coupling* are all synonyms.¹⁷

The J -coupling represents the second great link between NMR and chemistry. The chemical shift indicates the local electronic environment and the J -coupling provides a direct spectral manifestation of the *chemical bond*. Two spins have a measurable J -coupling only if they are linked together through a small number of chemical bonds, including hydrogen bonds. The J -coupling is exclusively intramolecular.

The full form of the intramolecular J -coupling interaction between spins I_j and I_k on the same molecule is

$$\hat{\mathcal{H}}_{jk}^{J,\text{full}} = 2\pi \hat{\mathbf{I}}_j \cdot \mathbf{J}_{jk} \cdot \hat{\mathbf{I}}_k \quad (9.41)$$

where \mathbf{J}_{jk} is the J -coupling tensor, a 3×3 real matrix. The factor of 2π appears because the J -coupling is invariably quoted in units of hertz, whereas all equations in this book use radians per second. In matrix-

vector form, the equation reads as follows:

$$\hat{\mathcal{H}}_{jk}^{\text{J,full}} = 2\pi (\hat{I}_{jx}, \hat{I}_{jy}, \hat{I}_{jz}) \cdot \begin{pmatrix} J_{xx}^{jk} & J_{xy}^{jk} & J_{xz}^{jk} \\ J_{yx}^{jk} & J_{yy}^{jk} & J_{yz}^{jk} \\ J_{zx}^{jk} & J_{zy}^{jk} & J_{zz}^{jk} \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_{kx} \\ \hat{I}_{ky} \\ \hat{I}_{kz} \end{pmatrix}$$

or more explicitly

$$\hat{\mathcal{H}}_{jk}^{\text{J,full}} = 2\pi J_{xx}^{jk} \hat{I}_{jx} \hat{I}_{kx} + 2\pi J_{yx}^{jk} \hat{I}_{jy} \hat{I}_{kx} + \dots$$

9.4.1 Isotropic J-coupling

The J -coupling tensor J_{jk} depends on molecular orientation. In an isotropic liquid, this tensor is averaged out by the rapid molecular tumbling. The isotropic form of the J -coupling Hamiltonian is given by

$$\hat{\mathcal{H}}_{jk}^{\text{iso}} = 2\pi J_{jk} \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k \quad (9.42)$$

or explicitly:

$$\hat{\mathcal{H}}_{jk}^{\text{iso}} = 2\pi J_{jk} (\hat{I}_{jx} \hat{I}_{kx} + \hat{I}_{jy} \hat{I}_{ky} + \hat{I}_{jz} \hat{I}_{kz})$$

The term J_{jk} is called the *isotropic J-coupling*, or the *scalar coupling*. It is equal to the average of the diagonal elements of the J -coupling tensor:

$$J_{jk} = \frac{1}{3}(J_{xx}^{jk} + J_{yy}^{jk} + J_{zz}^{jk}) \quad (9.43)$$

The term ‘scalar’ indicates that $\hat{\mathcal{H}}_{jk}^{\text{iso}}$ is independent of molecular orientation.

Equation 9.43 resembles the definition of the isotropic chemical shift (Equation 9.4). The physical arguments used to justify the form of the isotropic chemical shift may also be used to justify the step from Equation 9.41 to Equation 9.42.

The secular forms of the J -coupling Hamiltonian depend on whether the two spins are of the same isotopic type (homonuclear case) or of different isotopic type (heteronuclear case).

In the *homonuclear* case, the secular J -coupling is the same as in Equation 9.42:

$$\hat{\mathcal{H}}_{jk}^{\text{J}} = 2\pi J_{jk} \hat{\mathbf{I}}_j \cdot \hat{\mathbf{I}}_k \quad (\text{homonuclear case, isotropic liquids}) \quad (9.44)$$

In the *heteronuclear* case, the secular form of the interaction is different:

$$\hat{\mathcal{H}}_{jk}^{\text{J}} = 2\pi J_{jk} \hat{I}_{jz} \hat{I}_{kz} \quad (\text{heteronuclear case, isotropic liquids}) \quad (9.45)$$

Unlike the chemical shift, the J -coupling is independent of the applied magnetic field.

The J -coupling has a sign. A positive value of J_{jk} indicates that the spin–spin coupling makes a positive contribution to the energy when the spin polarizations are parallel and a negative contribution when the spin polarizations are opposite. In the case of negative J_{jk} , the energy changes are in the opposite direction:

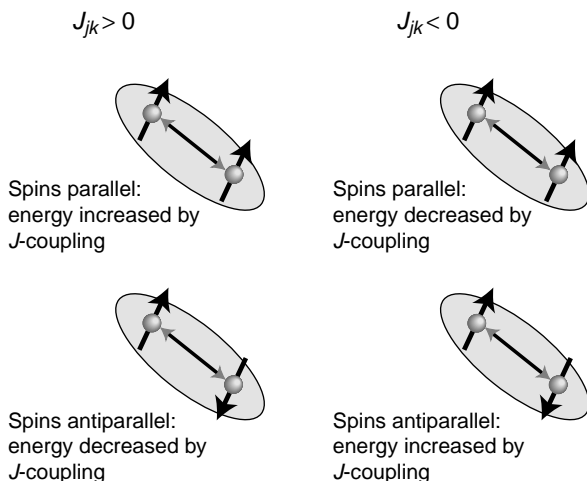


Figure 9.27
The physical meaning of the sign of J .

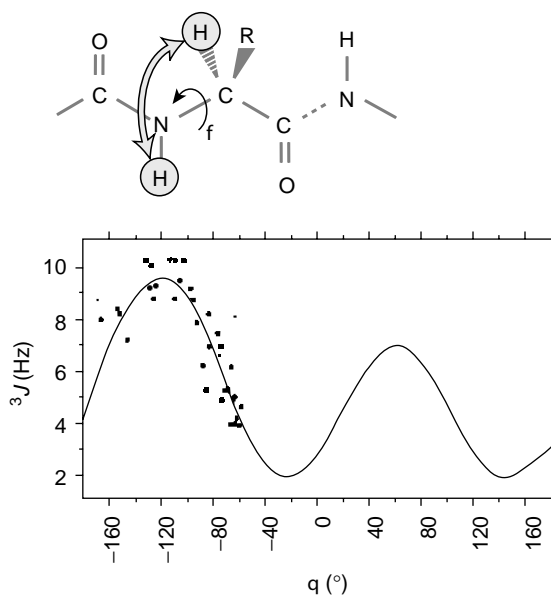


Figure 9.28 The three-bond J -couplings between H^{N} protons and H^{α} protons in a protein have a well-defined dependence on the molecular torsional angle ϕ . Each filled circle represents a single amino acid residue in a protein. The x -coordinate is the torsional angle as determined by X-ray crystallography; the y -coordinate is the J -coupling as measured by solution NMR. The solid line is a semi-empirical curve called the Karplus equation, which has the form $^3J = (6.4 \cos^2 \theta - 1.4 \cos \theta + 1.9) \text{ Hz}$, where θ is the $\text{H}-\text{N}-\text{C}-\text{H}$ torsional angle, given in terms of the backbone torsional angle ϕ by $\theta = \phi - \pi/3$. Adapted from A. Pardi, M. Billeter and K. Wüthrich, *J. Mol. Biol.*, **180**, 741–751 (1984). (Copyright Academic Press).

J_{jk} is *positive* for spins with the *same* sign of gyromagnetic ratio, connected by one chemical bond. J_{jk} is *negative* for spins with *opposite* signs of gyromagnetic ratio, connected by one chemical bond. The signs of longer-range J -couplings are variable and depend on the molecular geometry and many other factors. For protons in organic materials, three-bond J -couplings (denoted 3J) are typically around 7 Hz when averaged over all rotamers. One-bond J -couplings between ^1H and ^{13}C are typically around 135 Hz, whereas one-bond J -couplings between directly bonded ^{13}C spins are usually around 50 Hz. These figures may vary considerably, depending on the local molecular structure.

In some cases, the values of J -couplings depend in a simple way on molecular structural parameters, such as bond angles and torsional angles. For example, consider the two-bond J -coupling $^2J_{\text{XX}}$ in molecules containing the fragment X–Y–X (where X and Y are arbitrary isotopes). In general, molecules in which the X–Y–X bond angle is large have a larger value of $^2J_{\text{XX}}$ than molecules in which the X–Y–X bond angle is small. Such relationships are particularly useful for molecular structural investigations in inorganic chemistry.

Another important relationship of this kind applies to three-bond ^1H – ^1H J -couplings in rigid organic molecules. The important parameter is the *torsional angle* around the central bond transmitting the coupling. Figure 9.28 shows the measured values of 3J between amide NH protons and C^α protons in a small protein. There is a sinusoidal dependence of 3J on the torsional angle around the N– C^α bonds of the peptide links between the amino acid units. These *Karplus relationships* are used by protein NMR spectroscopists to provide information on the secondary protein structure.

9.4.2 Liquid crystals and solids

In anisotropic liquids and solids, the anisotropic part of the J -coupling survives. This J -anisotropy is usually small and is often ignored. In any case, it is very difficult to distinguish it from the direct dipole–dipole coupling, which is usually much larger and has the same form.¹⁸ I will say no more about it in this book.

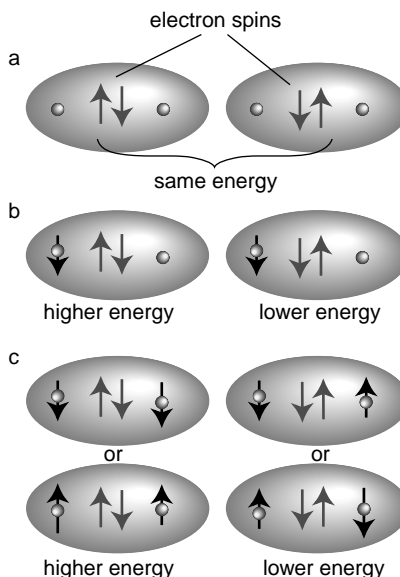


Figure 9.29
Mechanism of J -coupling through a single chemical bond. The arrows denote the direction of the spin angular momenta, and both nuclei are assumed to have positive values of γ .

9.4.3 Mechanism of the J -coupling

I now briefly outline the mechanism of the indirect spin–spin coupling.¹⁷ The reader is directed to the text by Slichter for more details (see *Further Reading*). The basic idea is illustrated in Figure 9.29, which shows a simplified situation with two nuclear spins and a bonding orbital containing two paired electron spins. Because of the Pauli principle, the electron spins are paired; and in the absence of the nuclei, the electron wavefunctions consist of an equal admixture of an ‘up–down’ state and ‘down–up’ state, these two states being exactly degenerate (Figure 9.29a). The introduction of a nuclear spin on one side changes matters, because the nuclear spin has a negative magnetic hyperfine interaction with the electron. The energy of the state shown in the right-hand side of Figure 9.29b, in which the electron spin close to the nucleus has the same direction as the nuclear spin polarization, is slightly reduced since the magnetic moments are opposite. The electron spin distribution is therefore slightly shifted by the presence of the nuclear spin: there is a slight tendency for electrons near the nucleus to be polarized in the same sense as the nucleus. When a second nucleus is introduced, the energy of the system now depends on whether the two nuclei have the same or opposite polarizations. The state in which the two nuclei have opposite polarizations is relatively low in energy, because in this state both nuclei couple to electrons with favourable spin orientations, while keeping the electron spin polarizations opposite: The state where the two nuclei have the same polarization is relatively high in energy, because it is not possible to achieve consistently favourable spin orientations (see Figure 9.29c). This mechanism, therefore, predicts a positive value of the J -coupling, as found experimentally for one-bond couplings between spins with the same sign of γ .

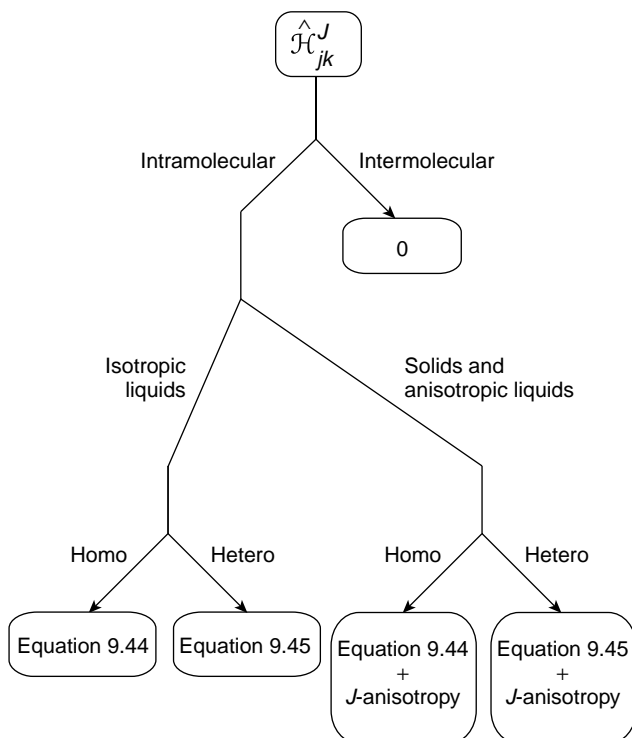


Figure 9.30
Flow diagram for the
 J -coupling interaction.

9.4.4 J -coupling: summary

Figure 9.30 summarizes the form of the J -coupling interaction in liquids and solids.

9.5 Spin–Rotation Interaction

A molecule consists of positive electric charges (nuclei) and negative electric charges (electrons). If a molecule rotates, then the charges circulate, which corresponds to an electric current. The rotation of a molecule, therefore, generates local magnetic fields, which may interact with the magnetic moments of the nuclei.

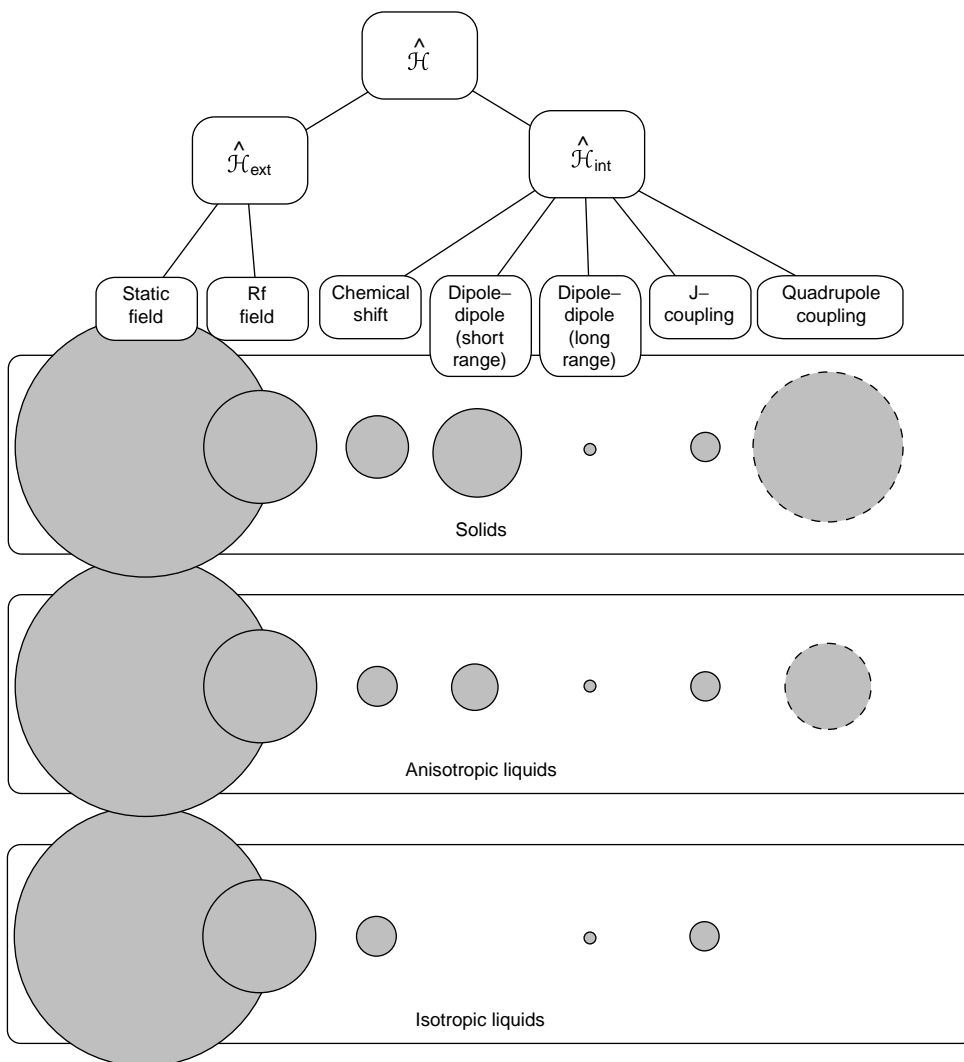


Figure 9.31 Summary of the motionally averaged spin Hamiltonian terms and their rough relative magnitudes, in different phases of matter. The quadrupolar coupling vanishes for spins-1/2.

The *spin-rotation interaction* takes into account the direct interaction between the magnetic fields generated by rapid molecular rotation and the nuclear spins.

The nuclear spin-rotation interaction is important in the microwave spectroscopy of gases, but is of only marginal importance in NMR. The secular part of the spin-rotation interaction averages to zero in isotropic liquids. However, the non-secular part of the spin-rotation interaction occasionally causes relaxation in liquids and is often a dominant relaxation mechanism in gases (see Section 20.2).

The spin-rotation interaction is also unimportant in solid-state NMR, because the molecular rotation is restricted.¹⁹

9.6 Summary of the Spin Hamiltonian Terms

Figure 9.31 gives the form and the rough relative magnitude of the motionally averaged spin Hamiltonian terms, in different phases of matter. Note that the case of isotropic liquids is very special, since all the largest internal terms average to zero. In addition, remember that the quadrupolar coupling vanishes for spins-1/2.

Notes

1. The diamagnetic contribution to the chemical shift consists of field-induced electron currents in the electronic ground states. At first sight, the existence of such currents is surprising, because in most cases the electronic ground states have an orbital angular momentum quantum number equal to $l = 0$, which sounds as if the electrons cannot circulate (circulation of the electrons implying finite orbital angular momentum). This paradox is resolved by noting that most elementary discussions of quantum mechanics are conducted in the absence of a magnetic field, and are misleading. In fact, if the Schrödinger equation is solved in the presence of a magnetic field, one finds that electrons in $l = 0$ electronic states *do* have electronic angular momentum in a magnetic field. Electron currents in $l = 0$ electronic states are responsible for a number of effects, including the bulk diamagnetism of many materials.
2. Unfortunately, the field of chemical shifts is plagued by contradictory conventions. In this book, I always use the *deshielding* convention for both isotropic and anisotropic chemical shifts, which are denoted by the symbol δ . This conforms to standard practice for isotropic shifts in solution-state NMR (δ increases from right to left in the spectrum). In solid-state NMR, on the other hand, it is quite common to use a *shielding* convention, which is usually indicated by the symbol σ . The shielding and deshielding chemical shifts have the same magnitude but opposite signs. Unfortunately, many research articles do not state which convention they use, and do not use the symbols consistently either.
3. In the most general case, the chemical shift tensor is not exactly symmetric about the diagonal (for example, $\delta_{xy}^j \neq \delta_{yx}^j$). Normally, this lack of symmetry may be ignored, since it has no direct effects on NMR lineshapes, and only a weak influence on relaxation. In this book, the *antisymmetric part of the chemical shift tensor* is ignored, and all chemical shift tensors are assumed to have symmetric matrix representations. Do not confuse the (very obscure) *antisymmetric part of the chemical shift tensor* with the common and important case of a *biaxial* chemical shift tensor ($\eta_j \neq 0$). The potential for confusion is not reduced by the common practice of calling the biaxiality η_j the 'asymmetry parameter' (see Note 5).
4. Numerical subscripts are used to indicate sequential ordering of the chemical shift principal values: $\delta_{11}^j > \delta_{22}^j > \delta_{33}^j$. When the *shielding* notation is used (see Note 2), the ordering is as follows: $\sigma_{11}^j < \sigma_{22}^j < \sigma_{33}^j$. The correspondence between $\{\delta_{xx}^j, \delta_{yy}^j, \delta_{zz}^j\}$ and $\{\delta_{11}^j, \delta_{22}^j, \delta_{33}^j\}$ depends on the sign of δ_j^{aniso} (see Figure 9.11). If δ_j^{aniso} is positive, then the correspondence is as follows: $\delta_{xx}^j = \delta_{33}^j$, $\delta_{yy}^j = \delta_{22}^j$,

and $\delta_{ZZ}^j = \delta_{11}^j$. If δ_j^{aniso} is negative, then the correspondence is instead: $\delta_{XX}^j = \delta_{11}^j$, $\delta_{YY}^j = \delta_{22}^j$, and $\delta_{ZZ}^j = \delta_{33}^j$. The convention above is due to Ulrich Haeberlen.

5. The term η_j is commonly known as the *asymmetry parameter* or the *rhombicity* of the chemical shift tensor. I find the term 'asymmetry' uninformative and confusing: the matrix representation of the *relevant* part of the CSA tensor is *always* symmetric about the diagonal, irrespective of the value of η_j (although see Note 3). I favour the term *biaxiality*, which represents analogous phenomena in liquid crystal science and in optics. The term *rhombicity* is used in similar circumstances in electron spin resonance and also has its merits.
6. The term *symmetric tensor* is sometimes used to indicate the case with $\eta_j = 0$. This is poor terminology, since the matrix representation of the relevant part of the CSA tensors is *always* symmetric about the diagonal, irrespective of the value of η_j (see Note 5). I favour the term *uniaxial* to indicate the situation with $\eta_j = 0$.
7. A *primary* isotope shift concerns, for example, the difference in chemical shifts for ^1H nuclei in CHCl_3 and for ^2H nuclei in CDCl_3 .
8. The *asymmetric unit* of a crystal is the smallest unit from which the entire crystal may be constructed by applying symmetry operations (rotations, reflections, etc.). In general, several asymmetric units combine to form a *unit cell*, from which the entire structure may be derived by translations alone.
9. Many molecular crystal structures contain more than one molecule in the *asymmetric unit*. In a single crystal at an arbitrary orientation, the number of peaks generated by one chemical site is given by the number of molecules in the asymmetric unit.
10. The conventions used for the quadrupolar interaction follow those in A. Jerschow, *Prog. NMR Spectrosc.* **46**, 63–78 (2005).
11. It is now possible to calculate chemical shift tensors and electric field gradient tensors with high accuracy and reliability in a wide variety of molecular systems, using quantum-mechanical calculations of the electronic structure. See *Further Reading*.
12. The accepted convention for assigning the principal values of the electric field gradient tensor is as follows:

$$|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$$

This is slightly different than that used for the chemical shift tensor (Equation 9.5).

13. The second-order quadrupolar term takes into account the second-order changes in the Hamiltonian *eigenvalues*, but does not take into account the perturbation of the spin *eigenstates* by the quadrupole coupling. There are some effects, such as *overtone transitions*, that require a more subtle treatment (see Chapter 13, Note 4).
14. The unity operator $\hat{1}$ is often implied, rather than being written explicitly.
15. In liquids, the motionally averaged second-order quadrupole interaction gives rise to a shift in the nuclear Larmor frequency, called the *dynamic frequency shift*.
16. The conventional definition of the quadrupole coupling constant C_Q can be misleading, since the Hamiltonian contains a factor of $2I(2I - 1)$ in the denominator (see Equation 9.30). For high spin

quantum numbers, this factor can reduce the effect of the quadrupole coupling by more than an order of magnitude. For example, the factor $2I(2I - 1)$ is equal to 72 for the spin-9/2 case.

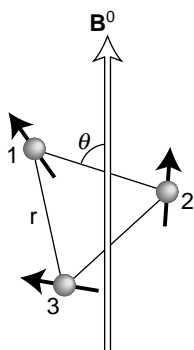
17. In certain circumstances, the J -coupling has a contribution from the *nuclear exchange interaction* as well as the indirect spin–spin coupling. The nuclear exchange coupling involves a spatial overlap of the quantum wavefunctions of the two nuclei. It is analogous to the very important *electron exchange interaction* that is of central importance in a wide range of phenomena such as chemical bonding and macroscopic magnetism. The nuclear exchange coupling is usually negligible, but it can be significant for light atoms, such as hydrogen, in compounds with a low potential barrier for nuclear exchange. For example, the nuclear exchange coupling give rises to large temperature-dependent J -couplings in certain metal hydride complexes (e.g. see K. W. Zilm and J. M. Millar, *Adv. Magn. Opt. Reson.* **15**, 163 (1990)). In special cases, the exchange coupling can be extremely large. For example, in the dihydrogen molecule (H_2), the exchange coupling between the two protons is more than 10 orders of magnitude larger than the “ordinary” J -coupling! The enormous nuclear exchange coupling between the protons in H_2 forms the basis of *parahydrogen-enhanced NMR*; e.g. see J. Natterer and J. Bargon, *Prog. NMR Spectrosc.* **31**, 293–315 (1997).
18. J -couplings involving heavy nuclei are sometimes large. In these cases, the J -anisotropy may be comparable to or even exceed the direct dipole–dipole coupling.
19. Solid samples are sometimes rapidly rotated at frequencies up to 70 kHz in order to improve the spectral resolution (see Section 19.6). It is conceivable that the rapid bulk rotation of the sample could lead to measurable spin–rotation effects at such frequencies.

Further Reading

- Other books that summarize the nuclear spin interactions are:
A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961; C. P. Slichter *Principles of Magnetic Resonance*, 3rd edition, Springer, Berlin, 1989; M. Mehring, *High Resolution NMR in Solids*, 2nd edition, Springer, Berlin, 1982. Slichter is particularly recommended for nuclear spin interactions in metallic and paramagnetic systems, and for the mechanism of the chemical shift and J -coupling.
- For a review of influences on isotropic chemical shifts, see H. Günther, “NMR Spectroscopy”, 2nd Edition, (Wiley, Chichester, 1995).
- For the calculation of spin interaction parameters using quantum chemistry techniques, see M. Kaupp, M. Bühl and V. G. Malkin, *Calculation of NMR and EPR Parameters. Theory and Applications*, Wiley–VCH, 2004.
- For a review of chemical shift anisotropies in biomolecules, including calculation techniques, see D. Sitkoff and D. A. Case, *Prog. NMR Spectrosc.* **32**, 165–190 (1998).
- For a review of spin–spin coupling tensors, including quantum calculation methods, see J. Vaara, J. Jokisaari, R. E. Wasylishen and D. L. Bryce, *Prog. NMR Spectrosc.* **41**, 187–232 (2002).

Exercises

- 9.1 (i) A molecule contains three protons I_1 , I_2 and I_3 arranged on the corners of an equilateral triangle with sides of length r . The magnetic field B^0 is in the plane of the triangle, subtending an angle θ with the line joining protons I_1 and I_2 :



- (ii) Calculate the dipole–dipole coupling constant b_{12} between spins I_1 and I_2 in the case that $r = 0.2$ nm and $\theta = \pi/2$.
- (iii) Calculate the dipole–dipole coupling constant b_{13} between spins I_1 and I_3 in the case that $r = 0.2$ nm and $\theta = \pi/2$.
- (iv) Calculate the secular dipole–dipole coupling d_{12} between spins I_1 and I_2 in the case that $r = 0.2$ nm and $\theta = \pi/2$.
- (v) Calculate the secular dipole–dipole coupling d_{13} between spins I_1 and I_3 in the case that $r = 0.2$ nm and $\theta = \pi/2$.
- (vi) Calculate all three secular dipole–dipole couplings in the case that $r = 0.2$ nm and $\theta = \pi/4$.

9.2 Suppose that the probability density of the angle Θ_{jk} between two spins I_j and I_k in an anisotropic liquid is given by

$$p(\Theta_{jk}) = \frac{3}{124}(21 + \cos 2\Theta_{jk})$$

9.3 This probability density function implies that molecular orientations with the vector \mathbf{e}_{jk} nearly parallel to the field are slightly favoured in the anisotropic liquid.

- (i) Verify that $p(\Theta_{jk})$ is normalized, i.e.

$$\int_0^\pi d\Theta_{jk} p(\Theta_{jk}) \sin \Theta_{jk} = 1$$

- (ii) Calculate the secular dipole–dipole coupling d_{jk} in the anisotropic liquid if the distance between the spins is $r = 0.3$ nm.

