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# Spectroscopy 3: magnetic resonance

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One of the most widely used spectroscopic procedures in chemistry makes use of the classical concept of resonance. The chapter begins with an account of conventional nuclear magnetic resonance, which shows how the resonance frequency of a magnetic nucleus is affected by its electronic environment and the presence of magnetic nuclei in its vicinity. Then we turn to the modern versions of NMR, which are based on the use of pulses of electromagnetic radiation and the processing of the resulting signal by Fourier transform techniques. The experimental techniques for electron spin resonance resemble those used in the early days of NMR. The information obtained, however, is very useful for the determination of the properties of species with unpaired electrons.

When two pendulums share a slightly flexible support and one is set in motion, the other is forced into oscillation by the motion of the common axle. As a result, energy flows between the two pendulums. The energy transfer occurs most efficiently when the frequencies of the two pendulums are identical. The condition of strong effective coupling when the frequencies of two oscillators are identical is called resonance.

Resonance is the basis of a number of everyday phenomena, including the response of radios to the weak oscillations of the electromagnetic field generated by a distant transmitter. In this chapter we explore some spectroscopic applications that, as originally developed (and in some cases still), depend on matching a set of energy levels to a source of monochromatic radiation and observing the strong absorption that occurs at resonance.

## The effect of magnetic fields on electrons and nuclei

The Stern-Gerlach experiment (Section 12.8) provided evidence for electron spin. It turns out that many nuclei also possess spin angular momentum. Orbital and spin angular momenta give rise to magnetic moments, and to say that electrons and nuclei have magnetic moments means that, to some extent, they behave like small bar magnets. Therefore, we can expect that the application of a magnetic field should affect atoms and molecules. We first establish how the energies of an atom

depend on the strength of an external field and then see how we can use magnetic field effects as the bases of spectroscopic techniques for the study of structure and dynamics of complex molecules.

### 18.1 The energies of electrons in magnetic fields

Electrons possess magnetic moments as a result of their orbital and spin angular momenta and these moments interact with an external magnetic field. Classically, the energy of a magnetic moment  $\mu$  in a magnetic field  $B$  is equal to the scalar product

$$E = -\mu \cdot B \quad (18.1)$$

Quantum mechanically, we write the hamiltonian as

$$H = -\hat{\mu} \cdot B \quad (18.2)$$

To write an expression for  $\hat{\mu}$ , we recall from Section 13.8 that the magnetic moment is proportional to the angular momentum. Therefore, the magnetic moment operator is expected to be proportional to the angular momentum operator. For an electron possessing orbital angular momentum we write

$$\hat{\mu} = \gamma_e \hat{I} \quad \text{and} \quad H = -\gamma_e B \cdot \hat{I} \quad (18.3)$$

where  $\hat{I}$  is the orbital angular momentum operator and  $\gamma_e$  is a constant called the magnetogyric ratio of the electron. If the magnetic moment is treated as arising from the circulation of an electron of charge  $-e$ , standard electromagnetic theory gives

$$\gamma_e = -\frac{e}{2m_e} \quad (18.4)$$

The negative sign (arising from the sign of the electron's charge) shows that the orbital moment is antiparallel to its orbital angular momentum (as was depicted in Fig. 13.28).

Consider the interaction of the  $z$ -component of the orbital magnetic moment,  $\mu_z$ , with a steady magnetic field  $B_0$  along the  $z$ -direction.<sup>1</sup> It follows from eqn 3 that

$$\hat{\mu}_z = \gamma_e \hat{I}_z \quad \text{and} \quad H = -\hat{\mu}_z B_0 = -\gamma_e B_0 \hat{I}_z \quad (18.5)$$

where  $\hat{\mu}_z$  is the component of the orbital magnetic moment operator along the  $z$ -direction and the operator  $\hat{I}_z$  has eigenfunctions  $\psi_{m_l}$  with eigenvalues  $m_l \hbar$ . It follows that the  $z$ -component of the orbital magnetic moment and the energy of interaction are, respectively,

$$\mu_z = \gamma_e m_l \hbar \quad \text{and} \quad E = -\gamma_e m_l \hbar B_0 \quad (18.6)$$

From eqn 4, the possible values of  $\mu_z$  are

$$\mu_z = -\frac{e}{2m_e} \times m_l \hbar = -\mu_B m_l \quad (18.7)$$

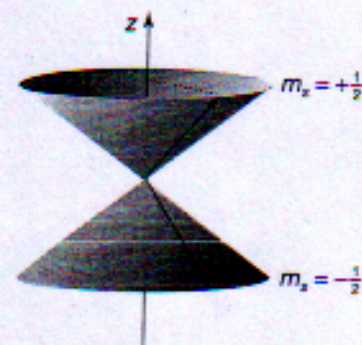
where the Bohr magneton,  $\mu_B$ , is

$$\mu_B = \frac{e\hbar}{2m_e} \quad (18.8)$$

Its numerical value is  $9.724 \times 10^{-24} \text{ J T}^{-1}$ . The Bohr magneton is often regarded as the fundamental quantum of magnetic moment. Therefore, in the presence of a

1.  $B$  is actually the magnetic induction, and is measured in tesla, T;  $1 \text{ T} = 1 \text{ kg s}^{-2} \text{ A}^{-1}$ . The unit gauss, G, is also occasionally used:  $1 \text{ T} = 10^4 \text{ G}$ .

The scalar product (or 'dot product') of two vectors  $a$  and  $b$  is given by  $a \cdot b = ab \cos \theta$ , where  $a$  and  $b$  are the magnitudes of  $a$  and  $b$ , respectively, and  $\theta$  is the angle between  $a$  and  $b$ .



The interactions between the  $m_s$  states of electron and an external magnetic field may be visualized as the precession of the vectors representing the angular momentum on the cones drawn here.

magnetic field, an electron in a state with quantum number  $m_s$  has an additional contribution to its energy given by

$$E_{m_s} = \mu_B m_s B_0 \quad (18.9)$$

The spin magnetic moment of an electron, which has a spin quantum number  $s = \frac{1}{2}$  (Section 12.8), is also proportional to its spin angular momentum. However, the spin magnetic moment and hamiltonian operators are, respectively,

$$\hat{\mu}_s = g_e \gamma_e \hat{s} \quad \text{and} \quad H = -g_e \gamma_e B_0 \hat{s}_z \quad g_e = 2.002\,319 \dots \quad (18.10)$$

where  $\hat{s}$  is the spin angular momentum operator and the extra factor  $g_e$  is called the ***g-value*** of the electron. The *g-value* arises from relativistic effects and from interactions of the electron with the electromagnetic fluctuations in the vacuum that surround the electron.

Again we consider the interaction between the *z*-component of the spin magnetic moment with a magnetic field of magnitude  $B_0$  in the *z*-direction. We write

$$\hat{\mu}_z = g_e \gamma_e \hat{s}_z \quad \text{and} \quad H = -g_e \gamma_e B_0 \hat{s}_z \quad (18.11)$$

where the operator  $\hat{s}_z$  has eigenfunctions  $\alpha$  (also denoted as  $\uparrow$ ) and  $\beta$  (also denoted as  $\downarrow$ ) corresponding to the quantum numbers  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ , respectively. It follows that, for an electron in a state  $m_s$ ,

$$\mu_z = g_e \gamma_e m_s \hbar \quad \text{and} \quad E_{m_s} = -g_e \gamma_e m_s \hbar B_0 = g_e \mu_B m_s B_0 \quad m_s = \pm \frac{1}{2} \quad (18.12)$$

In the absence of a magnetic field, the states with different values of  $m_l$  and  $m_s$  are degenerate. When a field is present, the degeneracy is removed: the state with  $m_s = +\frac{1}{2}$  moves up in energy by  $\frac{1}{2} g_e \mu_B B_0$  and the state with  $m_s = -\frac{1}{2}$  moves down by  $\frac{1}{2} g_e \mu_B B_0$ . The different energies arising from an interaction with an external field are sometimes represented on the vector model by picturing the vectors as **precessing**, or sweeping round their cones, with the rate of precession proportional to the energy of the state (Fig. 18.1).

## 18.2 The energies of nuclei in magnetic fields

The spin quantum number,  $I$ , of a nucleus is a fixed characteristic property of a nucleus and may be an integer or a half-integer but is never negative (Table 18.1). A nucleus with spin quantum number  $I$  has the following properties:

- 1 An angular momentum of magnitude  $(I(I+1))^{1/2} \hbar$ .
- 2 A component of angular momentum  $m_I \hbar$  on an arbitrary axis, where  $m_I = I, I-1, \dots, -I$ .
- 3 If  $I > 0$ , a magnetic moment with a constant magnitude and an orientation that is determined by the value of  $m_I$ .

**Table 18.1** Nuclear constitution and the nuclear spin quantum number

Number of protons	Number of neutrons	$I$
even	even	0
odd	odd	integer (1, 2, 3, ...)
even	odd	half-integer ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ )
odd	even	half-integer ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ )

**Table 18.2\*** Nuclear spin properties

Nuclide	Natural abundance/%	Spin $I$	$g$ -factor, $g_I$	$\gamma/(10^7 \text{ T}^{-1} \text{ s}^{-1})$
$^1\text{n}$		$\frac{1}{2}$	-3.826	-18.32
$^1\text{H}$	99.98	$\frac{1}{2}$	5.586	26.75
$^2\text{H}$	0.02	1	0.857	4.10
$^{13}\text{C}$	1.11	$\frac{1}{2}$	1.405	6.73
$^{14}\text{N}$	99.64	1	0.404	1.93

\* More values are given in the Data section. Note that  $\gamma = g_I \mu_N / \hbar$ .

According to the second property, the spin, and hence the magnetic moment, of the nucleus may lie in  $2I + 1$  different orientations relative to an axis. A proton has  $I = \frac{1}{2}$  and its spin may adopt either of two orientations; a  $^{14}\text{N}$  nucleus has  $I = 1$  and its spin may adopt any of three orientations; both  $^{12}\text{C}$  and  $^{16}\text{O}$  have  $I = 0$  and hence zero magnetic moment.

The energy of interaction between a nucleus with a magnetic moment  $\mu$  and an external magnetic field  $B$  may be calculated by using operators analogous to those of eqn 3:

$$\hat{\mu} = \gamma \hat{I} \quad \text{and} \quad \hat{H} = -\gamma B \hat{I} \quad (18.13)$$

where  $\gamma$  is the characteristic value of the magnetogyric ratio for the nucleus under study (Table 18.2). The magnetic moment is sometimes expressed in terms of the nuclear  $g$ -factor,  $g_I$ , and the nuclear magneton,  $\mu_N$ , by using

$$\gamma \hbar = g_I \mu_N \quad \mu_N = \frac{e \hbar}{2m_p} = 5.051 \times 10^{-27} \text{ J T}^{-1} \quad (18.14)$$

where  $m_p$  is the mass of the proton. Nuclear  $g$ -factors vary between  $-6$  and  $+6$  (see Table 18.2): positive values of  $g_I$  and  $\gamma$  denote a magnetic moment that is parallel to the spin; negative values indicate that the magnetic moment and spin are antiparallel. The nuclear magneton is about 2000 times smaller than the Bohr magneton, so nuclear magnetic moments are about 2000 times weaker than the electron spin magnetic moment. The components of spin angular momentum relative to the  $z$ -axis are  $m_I \hbar$ , where  $m_I = I, I - 1, \dots, -I$ , and the corresponding components of the spin magnetic moment are

$$\mu_z = \gamma m_I \hbar \quad (18.15)$$

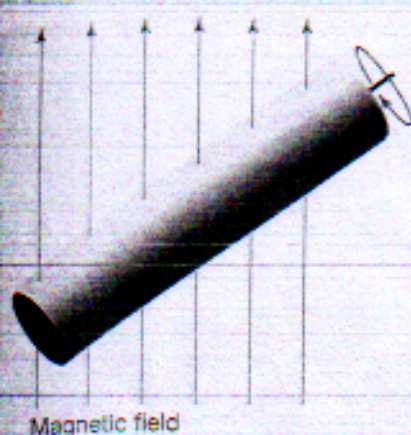
In a magnetic field  $B_0$  in the  $z$ -direction, the  $2I + 1$  orientations of the nucleus have different energies, which are given by

$$E_{m_I} = -\mu_z B_0 = -\gamma \hbar B_0 m_I \quad (18.16)$$

These energies are often expressed in terms of the Larmor frequency,  $\nu_L$ :

$$E_{m_I} = -m_I h \nu_L \quad \nu_L = \frac{\gamma B_0}{2\pi} \quad (18.17)$$

For the remainder of this chapter we will assume that  $\gamma$  is positive, as is the case for the majority of nuclei. In such cases, the states with negative values of  $m_I$  lie above states with positive values of  $m_I$ . Equation 17 also shows that, the stronger the



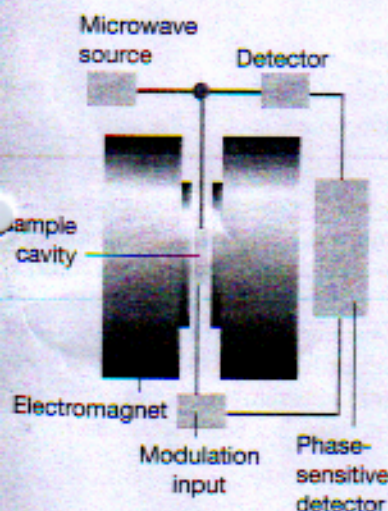
**18.47** In magic angle spinning, the sample spins at  $54.74^\circ$  (that is,  $\arccos(1/3)^{1/2}$ ) to the applied magnetic field. Rapid motion at this angle averages dipole-dipole interactions and chemical shift anisotropies to zero.

We have seen that chemical shifts arise from the ability of the applied field to generate electron currents in molecules. In general, this ability depends on the orientation of the molecule relative to the applied field. In solution, when the molecule is tumbling rapidly, only the average value of the chemical shift is relevant. However, the anisotropy is not averaged to zero for stationary molecules in a solid, and molecules in different orientations have resonances at different frequencies. The chemical shift anisotropy also varies with the angle between the applied field and the principal axis of the molecule as  $1 - 3 \cos^2\theta$ .

### (b) The reduction of linewidths

Fortunately, there are techniques available for reducing the linewidths of solid samples. One technique, **magic-angle spinning (MAS)**, takes note of the  $1 - 3 \cos^2\theta$  dependence of both the dipole-dipole interaction and the chemical shift anisotropy. The 'magic angle' is the angle at which  $1 - 3 \cos^2\theta = 0$ , and corresponds to  $54.74^\circ$ . In the technique, the sample is spun at high speed at the magic angle to the applied field (Fig. 18.47). All the dipolar interactions and the anisotropies average to the value they would have at the magic angle; but at that angle they are zero. The difficulty with MAS is that the spinning frequency must not be less than the width of the spectrum, which is of the order of kilohertz. However, gas-driven sample spinners that can be rotated at up to 25 kHz are now routinely available, and a considerable body of work has been done.

Pulsed techniques similar to those described in the previous section may also be used to reduce linewidths. The dipolar field of protons, for instance, may be reduced by a decoupling procedure. However, because the range of coupling strengths is so large, radiofrequency power of the order of 1 kW is required. Elaborate pulse sequences have also been devised that reduce linewidths by averaging procedures that make use of twisting the magnetization vector through an elaborate series of angles.



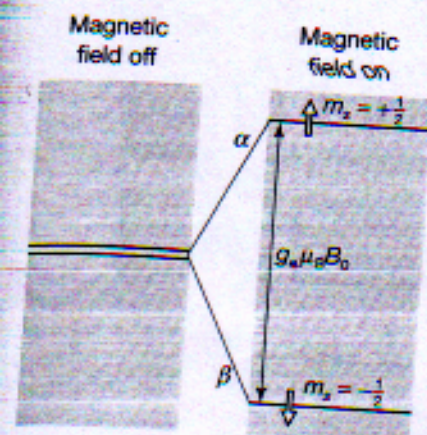
**18.48** The layout of a continuous-wave ESR spectrometer. A typical magnetic field is 0.3 T, which requires 9 GHz (3 cm) microwaves for resonance.

## Electron spin resonance

Electron spin resonance (ESR) is less widely applicable than NMR because it cannot be detected in normal, spin-paired molecules and the sample must possess unpaired electron spins. It is used to study radicals formed during chemical reactions or by radiation, radicals that act as probes of biological structure (Box 18.2), many *d*-metal complexes, and molecules in triplet states (such as those involved in phosphorescence, Section 17.3b). The sample may be a gas, a liquid, or a solid, but the free rotation of molecules in the gas phase gives rise to complications.

### 18.13 The ESR spectrometer

Both Fourier-transform (FT) and continuous-wave (CW) ESR spectrometers are available. The FT-ESR instrument is based on the concepts developed in Section 18.7, except that pulses of microwaves are used to excite electron spins in the sample. The layout of the more common CW-ESR spectrometer is shown in Fig. 18.48. It consists of a microwave source (a klystron or a Gunn oscillator), a cavity in which the sample is inserted in a glass or quartz container, a microwave detector, and an electromagnet with a field that can be varied in the region of 0.3 T. The ESR spectrum is obtained by monitoring the microwave absorption as the field is changed, and a



**18.2** Electron spin levels in a magnetic field. Note that the  $\beta$  state is lower in energy than the  $\alpha$  state (because the magnetogyric ratio of an electron is negative). Resonance is achieved when the frequency of the incident radiation matches the frequency corresponding to the energy separation.

magnetic field, the higher the Larmor frequency. For protons, a field of 12 T corresponds to a Larmor frequency of about 500 MHz.

### 18.3 Magnetic resonance spectroscopy

The magnetic resonance experiment is the resonant absorption of radiation by nuclei or unpaired electrons exposed to a magnetic field. From eqn 12, the separation between the  $m_l = -\frac{1}{2}$  and  $m_l = +\frac{1}{2}$  levels of an electron spin in a magnetic field  $B_0$  is

$$\Delta E = E_\alpha - E_\beta = g_e \mu_B B_0 \quad (18.18)$$

If the sample is exposed to radiation of frequency  $\nu$ , the energy separations come into resonance with the radiation when the frequency satisfies the **resonance condition** (Fig. 18.2):

$$h\nu = g_e \mu_B B_0 \quad (18.19)$$

At resonance there is strong coupling between the electron spins and the radiation, and strong absorption occurs as the spins make the transition  $\beta \rightarrow \alpha$ . **Electron spin resonance (ESR)**, or **electron paramagnetic resonance (EPR)**, is the study of molecules and ions containing unpaired electrons by observing the magnetic fields at which they come into resonance with monochromatic radiation. Magnetic fields of about 0.3 T (the value used in most commercial ESR spectrometers) correspond to resonance with an electromagnetic field of frequency 10 GHz ( $10^{10}$  Hz) and wavelength 3 cm. Because 3 cm radiation falls in the microwave region of the electromagnetic spectrum, ESR is a microwave technique.

The energy separation between the  $m_l = +\frac{1}{2}$  ( $\uparrow$  or  $\alpha$ ) and the  $m_l = -\frac{1}{2}$  ( $\downarrow$  or  $\beta$ ) states of **spin- $\frac{1}{2}$  nuclei**, which are nuclei with  $I = \frac{1}{2}$ , is

$$\Delta E = E_\beta - E_\alpha = \frac{1}{2} \gamma \hbar B_0 - (-\frac{1}{2} \gamma \hbar B_0) = \gamma \hbar B_0 = h\nu_l \quad (18.20)$$

and resonant absorption occurs when the resonance condition (Fig. 18.3)

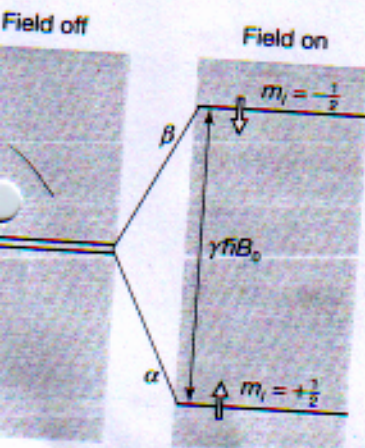
$$h\nu = \gamma \hbar B_0 = h\nu_l \quad (18.21)$$

is fulfilled. That is, an  $\alpha \rightarrow \beta$  transition occurs at  $\nu = \nu_l$ . In its simplest form, **nuclear magnetic resonance (NMR)** is the study of the properties of molecules containing magnetic nuclei by applying a magnetic field and observing the frequency of the resonant electromagnetic field. Larmor frequencies of nuclei at the fields normally employed typically lie in the radiofrequency region of the electromagnetic spectrum, so NMR is a radiofrequency technique. For example, at 12 T, protons come into resonance at about 500 MHz (the Larmor frequency at that magnetic field).

For much of this chapter we consider spin- $\frac{1}{2}$  nuclei, but NMR is applicable to nuclei with any nonzero spin. As well as protons, which are the most common nuclei studied by NMR, spin- $\frac{1}{2}$  nuclei include  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  nuclei.

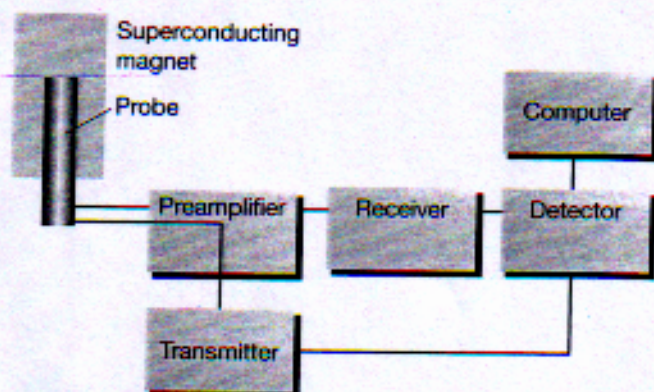
## Nuclear magnetic resonance

Although the NMR technique is simple in concept, NMR spectra can be highly complex. However, they have proved invaluable in chemistry, for they reveal so much structural information. A magnetic nucleus is a very sensitive, noninvasive probe of the surrounding electronic structure.



nuclear spin energy levels of a nucleus with positive magnetogyric ratio (example,  $^1\text{H}$  or  $^{13}\text{C}$ ) in a magnetic field. Resonance occurs when the energy separation of the levels matches the energy of the incident radiation in the electromagnetic field.

**18.4** The layout of a typical NMR spectrometer. The link from the transmitter to the detector indicates that the high frequency of the transmitter is subtracted from the high frequency received signal to give a low frequency signal for processing.



radio

550  
KHz

### 18.4 The NMR spectrometer

An NMR spectrometer consists of the appropriate sources of radiofrequency electromagnetic radiation and a magnet that can produce a uniform, intense field. In simple instruments, the magnetic field is provided by a permanent magnet. For serious work, a **superconducting magnet** capable of producing fields of the order of 2 T and more is used (Fig. 18.4). The sample is placed in the cylindrically wound magnet. In some cases the sample is rotated rapidly to average out magnetic inhomogeneities. However, sample spinning can lead to irreproducible results, and is often avoided. Although a superconducting magnet operates at the temperature of liquid helium (4 K), the sample itself is normally at room temperature.

The use of high magnetic fields has several advantages, the most important being that they simplify the appearance of spectra and so allow them to be interpreted more readily. A further advantage is that the rate of energy uptake by the sample is greater in a high field. There are two contributions to this increase. One comes from the greater population difference between the upper and lower spin states at high fields, for the population difference is approximately proportional to  $B$ . The second contribution stems from the greater energy of each absorbed photon, which is also proportional to  $B$ . It follows that overall the signal is proportional to  $B^2$ .

#### Justification 18.1

According to the Boltzmann distribution, the ratio of populations is

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/kT} \approx 1 - \frac{\Delta E}{kT}$$

where expansion of the exponential term is appropriate for  $\Delta E \ll kT$ , a condition usually met for electron and nuclear spins. It follows that

$$\frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{\Delta E}{2kT} = \frac{\gamma \hbar B}{2kT}$$

and the population difference is proportional to  $B$ . The energy of the photon absorbed when a nucleus makes a transition from its lower state to its higher state is  $h\nu$ ; at resonance  $\nu$  is equal to  $\nu_L$ , and  $\nu_L$  is proportional to  $B$ . Hence, at resonance, each photon has an energy that is proportional to  $B$ . The net rate of energy absorption is proportional to the population difference multiplied by the energy of each absorption event (the photon energy), so overall the net rate is proportional to  $B^2$ .

## 18.5 The chemical shift

Nuclear magnetic moments interact with the local magnetic field. The local field may differ from the applied field because the latter induces electronic orbital angular momentum (that is, the circulation of electronic currents) which gives rise to a small additional magnetic field  $\delta B$  at the nuclei. This additional field is proportional to the applied field, and it is conventional to write

$$\delta B = -\sigma B_0 \quad [18.22]$$

where the dimensionless quantity  $\sigma$  is called the **shielding constant** of the nucleus ( $\sigma$  is usually positive but may be negative). The ability of the applied field to induce an electronic current in the molecule, and hence the strength of the resulting local magnetic field experienced by the nucleus, depends on the details of the electronic structure near the magnetic nucleus of interest, so nuclei in different chemical groups have different shielding constants. The calculation of reliable values of the shielding constant is very difficult, but trends in it are quite well understood and we concentrate on them.

### (a) The $\delta$ -scale of chemical shifts

Because the total local field is

$$B_{\text{loc}} = B_0 + \delta B = (1 - \sigma)B_0 \quad [18.23]$$

the Larmor frequency is

$$\nu_L = \frac{\gamma B_{\text{loc}}}{2\pi} = (1 - \sigma) \frac{\gamma B_0}{2\pi} \quad [18.24]$$

This frequency is different for nuclei in different environments. Hence, different nuclei, even of the same element, come into resonance at different frequencies.

It is conventional to express the resonance frequencies in terms of an empirical quantity called the **chemical shift**, which is related to the difference between the resonance frequency,  $\nu$ , of the nucleus in question and that of a reference standard,  $\nu^\circ$ :

$$\delta = \frac{\nu - \nu^\circ}{\nu^\circ} \times 10^6 \quad [18.25]$$

The standard for protons is the proton resonance in tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$ , commonly referred to as TMS), which bristles with protons and dissolves without reaction in many liquids. Other references are used for other nuclei. For  $^{13}\text{C}$ , the reference frequency is the  $^{13}\text{C}$  resonance in TMS; for  $^{31}\text{P}$  it is the  $^{31}\text{P}$  resonance in 85 per cent  $\text{H}_3\text{PO}_4(\text{aq})$ . The advantage of the  $\delta$ -scale is that shifts reported on it are independent of the applied field (because both numerator and denominator are proportional to the applied field).

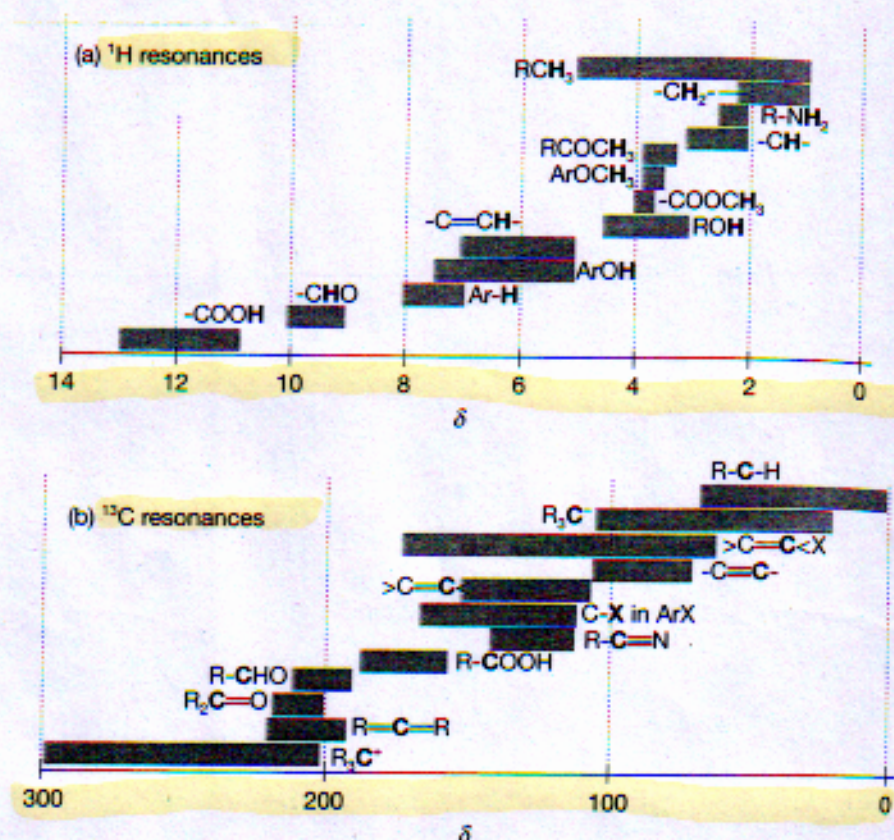
#### Illustration 18.1

A nucleus with  $\delta = 1.00$  (which is often, but unnecessarily, expressed as 1.00 ppm on account of the  $10^6$  in the definition of  $\delta$ ) in a spectrometer operating at 500 MHz will have a shift relative to the reference equal to

$$\nu - \nu^\circ = (500 \text{ MHz}) \times (1.00) \times 10^6 = 500 \text{ Hz}$$

In a spectrometer operating at 100 MHz, the shift relative to the reference would be only 100 Hz.





18.5 The range of typical chemical shifts for (a)  $^1\text{H}$  resonances and (b)  $^{13}\text{C}$  resonances.

The relation between  $\delta$  and  $\sigma$  is obtained by substituting eqn 24 into eqn 25:

$$\delta = \frac{(1 - \sigma)B_0 - (1 - \sigma^\circ)B_0}{(1 - \sigma^\circ)B_0} \times 10^6 = \frac{\sigma^\circ - \sigma}{1 - \sigma^\circ} \times 10^6 = (\sigma^\circ - \sigma) \times 10^6 \quad (18.26)$$

As the shielding,  $\sigma$ , gets smaller,  $\delta$  increases. Therefore, we speak of nuclei with large chemical shifts as being strongly **deshielded**. Some typical chemical shifts are given in Fig. 18.5. As can be seen from the illustration, the nuclei of different elements have very different ranges of chemical shifts. The ranges exhibit the variety of electronic environments of the nuclei in molecules.

By convention, NMR spectra are plotted with  $\delta$  increasing from right to left. Consequently, in a given applied magnetic field the Larmor frequency also increases from right to left. In a continuous wave (CW) spectrometer, in which the radiofrequency is held constant and the magnetic field is varied (a 'field sweep experiment'), the spectrum is displayed with the applied magnetic field increasing from left to right: a nucleus with a small chemical shift experiences a relatively low local magnetic field, so it needs a higher applied magnetic field to bring it into resonance with the radiofrequency field. Consequently, the right-hand (low chemical shift) end of the spectrum was previously known as the 'high field end' of the spectrum.

### (b) Resonance of different groups of nuclei

The existence of a chemical shift explains the general features of the spectrum of ethanol shown in Fig. 18.6. The  $\text{CH}_3$  protons form one group of nuclei with  $\delta = 1$ . The two  $\text{CH}_2$  protons are in a different part of the molecule, experience a different local magnetic field, and resonate at  $\delta = 3$ . Finally, the OH proton is in another environment, and has a chemical shift of  $\delta = 4$ . The increasing value of  $\delta$  (that is, the decrease