Spectroscopy 3: magnetic resonance
The effect of magnetic fields on electrons and nuclei

The Stern-Gerlach experiment provided evidence for electron spin. Many nuclei also possess spin angular momentum. Orbital and spin angular momenta give rise to magnetic moments – nuclei have magnetic moments means that, to some extent, the behave like small bar magnets. Therefore, 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.

The energies of electrons in magnetic field

Electrons possess magnetic moments as a results of their orbital and spin angular momenta. Classically, the energy of a magnetic moment $\mu$ in a magnetic filed $B$ is $E = -\mu \cdot B$
Quantum mechanically, we write Hamiltonian: $H = -\hat{\mu} \cdot B$

The magnetic momentum is proportional to the angular momentum and the magnetic moment operator is expected to be proportional to the angular momentum operator:

$\hat{\mu} = \gamma_e \hat{l}$

$H = -\gamma_e B \cdot \hat{l}$

$\hat{l}$ - the orbital angular momentum operator
$\gamma_e$ - 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 $-e$, according to electromagnetic theory

$\gamma_e = -\frac{e}{2m_e}$
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

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

The possible values of $\mu_z$ are

$$
\mu_z = -\frac{e}{2m_e} \times m_l \hbar = -\mu_B m_l
$$

$$
\mu_B = \frac{e\hbar}{2m_e} \quad \text{- the \textbf{B}orh \textbf{m}agneton} = 9.724 \times 10^{-24} \text{ J T}^{-1} \quad \text{– the fundamental quantum of magnetic moment.}
$$

Therefore, in the presence of a magnetic field, an electron in a state with quantum number $m_l$ has an additional contribution to its energy:

$$
E_{m_l} = \mu_B m_l B_0
$$

The spin magnetic moment of an electron (with a spin quantum number $s = 1/2$) is also proportional to its spin angular momentum. The spin magnetic moment and Hamiltonian operators are:

$$
\hat{\mu} = g_e \gamma_e \hat{\mathbf{s}} \quad H = -g_e \gamma_e \mathbf{B} \cdot \hat{\mathbf{s}} \quad g_e = 2.002319…
$$

$\hat{\mathbf{s}}$ - the spin angular momentum operator; $g_e$ is called the \textbf{g-value} of the electron. It arises from relativistic effects and from interactions of the electron with the electromagnetic fluctuations in the vacuum that surround the electron.

Now we again consider the interaction between the $z$-component of the spin magnetic moment with a magnetic field $B_0$ in the $z$-direction:

$$
\hat{\mu}_z = g_e \gamma_e \hat{s}_z \quad H = -g_e \gamma_e B_0 \cdot \hat{s}_z
$$

The operator $\hat{s}_z$ has eigenfunctions $\alpha (\uparrow)$ and $\beta (\downarrow)$ corresponding to the quantum numbers $m_s = +1/2$ and $m_s = -1/2$.

Then, $\mu_z = g_e \gamma_e m_s \hbar$ and $E_{m_s} = -g_e \gamma_e m_s \hbar B_0 = g_e \mu_B m_s B_0$ for $m_s = \pm 1/2$
In the absence of a magnetic field, the states with different $m_l$ and $m_s$ are degenerate. When a field is present, the degeneracy is removed: the state with $m_s = +1/2$ moves up in energy by $(1/2)g_e\mu_B B_0$, the state with $m_s = -1/2$ moves up in energy. Picture this as precessing vectors – the rate of precession is proportional to the energy of the state.

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. $I$ has the following properties:

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

Nuclear constitution and the nuclear spin quantum number

<table>
<thead>
<tr>
<th>Number of protons</th>
<th>Number of neutrons</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>even</td>
<td>0</td>
</tr>
<tr>
<td>odd</td>
<td>odd</td>
<td>integer (1, 2, 3, …)</td>
</tr>
<tr>
<td>even</td>
<td>odd</td>
<td>half-integer (1/2,…)</td>
</tr>
<tr>
<td>odd</td>
<td>even</td>
<td>half-integer (1/2,…)</td>
</tr>
</tbody>
</table>

Nuclear spin properties for some nuclei are given in Table 14.2.
According to the second property, the spin, and hence the magnetic moment, of the nucleus may lie in $2I + 1$ different orientations relative to the axis. A proton has $I = 1/2$ and its spin may adopt either of two orientations; a $^{14}$N nucleus has $I = 1$ and its spin may adopt any of three orientations; both $^{12}$C and $^{16}$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:

$$\hat{\mu} = \gamma \hat{l} \quad \hat{H} = -\gamma B \cdot \hat{l}$$

$\gamma$ - the characteristic value of the magnetogyric ratio for the nucleus. The magnetic moment is sometimes expressed in terms of the nuclear g-factor, $g_I$, and the nuclear magneton, $\mu_N$:

$$\gamma \hbar = g_I \mu_N \quad \mu_N = \frac{e \hbar}{2m_p} = 5.051 \times 10^{-27} \text{ JT}^{-1}$$

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

$$\mu_z = \gamma m_I \hbar$$

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

$$E_{m_I} = -\mu_z B_0 = -\gamma \hbar B_0 m_I$$
Often, these energies are expressed in terms of the Larmor frequency, $\nu_L$:

$$E_{m_I} = -m_I h \nu_L$$

$$\nu_L = \frac{\gamma B_0}{2\pi}$$

For the majority of nuclei, $\gamma$ is positive and in such cases, the states with negative values of $m_I$ lie above the states with positive values of $m_I$. The stronger the magnetic field, the higher the Larmor frequency. For protons, a field of 12 T corresponds to a Larmor frequency of $\sim 500$ MHz.

**Magnetic resonance spectroscopy**

The magnetic resonance experiment is the resonant absorption of radiation by nuclei or unpaired electrons exposed to a magnetic field. The separation between $m_s = +1/2$ and $m_s = -1/2$ levels of an electron spin in a magnetic field $B_0$ is

$$\Delta E = E_\alpha - E_\beta = g_e \mu_B B_0$$

If the sample is exposed to radiation of frequency $\nu$, the energy separation may come into resonance with radiation. This happens when the frequency satisfies the resonance condition:

$$h \nu = g_e \mu_B B_0$$

At resonance, there is a 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)** – the study of molecules and ions containing unpaired electrons by observing the magnetic field at which they come into resonance with monochromatic radiation. Magnetic fields of $\sim 0.3$ 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 – the microwave region of the electromagnetic spectrum. ESR is a microwave technique.
The energy separation between \( m_I = +\frac{1}{2} \) and \( m_I = -\frac{1}{2} \) states of spin-1/2 nuclei (with \( I = 1/2 \)) is

\[
\Delta E = E_\alpha - E_\beta = \frac{1}{2} \gamma \hbar B_0 - \left( -\frac{1}{2} \gamma \hbar B_0 \right) = \gamma \hbar B_0 = h\nu_L
\]

Resonant absorption occurs when the resonance condition is met:

\[
h\nu = \gamma \hbar B_0 = h\nu_L
\]

Therefore, an \( \alpha \to \beta \) transition occurs at \( \nu = \nu_L \). In its simplest form, nuclear magnetic resonance (NMR) is the study of 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 radio frequency region – NMR is a radio frequency technique. NMR is applicable to nuclei with any nonzero spin (\(^{13}\)C, \(^{19}\)F, \(^{31}\)P).

**Nuclear magnetic resonance**

Although the concept of NMR is simple, NMR spectra can be highly complex – they have proved invaluable in chemistry. They reveal so much structural information.

A magnetic nucleus is a very sensitive, noninvasive probe of the surrounding electronic structure.

**The NMR spectrometer**

An NMR spectrometer consists of the appropriate sources of radio-frequency electromagnetic radiation and a magnet that can produce a uniform intense field. In simple instruments, the magnetic field is provided by a permanent magnet.
In serious instruments, a superconducting magnet producing fields up to 2 T and more is used. The sample is placed in the cylindrically wound magnet. Although a superconducting magnet operates at the temperature of liquid He (4 K), the sample itself is normally at room temperature.

The use of high magnetic field has several advantages: they simplify the appearance of spectra, the rate of energy uptake by the sample is greater in a high field. There two contributions to this increase: greater population difference between the upper and lower spin states (proportional to $B$) and the greater energy of each absorbed photon (also proportional to $B$). Overall the signal is proportional to $B^2$.

**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 (the circulation of electronic currents) which gives rise to a small additional magnetic field $\delta B$ at the nuclei. The additional field is proportional to the applied field:

$$\delta B = -\sigma B_0$$

$\sigma$ - the shielding constant of the nucleus (it is dimensionless and 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 \( \delta \)-scale of chemical shifts

The total local field is

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

The Larmor frequency is

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

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

Conventionally, the resonance frequencies are expressed in terms of an empirical quantity, the chemical shift, related to the difference between the resonance frequency \( \nu \) of the nucleus in question and that of a reference standard, \( \nu^\circ \):

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

The standard for protons is the proton resonance in TMS (tetramethyl silane, Si(CH\(_3\))\(_4\)), for \(^{13}\)C – the \(^3\)C resonance in TMS, for \(^{31}\)P – the \(^{31}\)P resonance in H\(_3\)PO\(_4\).

The advantage of the \( \delta \)-scale – shifts reported on it are independent of the applied field.

The relation between \( \delta \) and \( \sigma \):

\[
\delta = \frac{(1 - \sigma)B_0 - (1 - \sigma^\circ)B_0}{(1 - \sigma^\circ)B_0} \times 10^6 = \frac{\sigma^\circ - \sigma}{1 - \sigma^\circ} \times 10^6 \approx (\sigma^\circ - \sigma) \times 10^6
\]

As the shielding, \( \sigma \), gets smaller, \( \delta \) increases. Nuclei with large chemical shifts are strongly deshielded.
The nuclei of different elements have very different ranges of $\delta$. By convention, NMR spectra are plotted with $\delta$ increasing from right to left. 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’.
Resonances of different groups of nuclei

The existence of a chemical shift explains the general features of the spectrum of ethanol. The CH$_3$ protons form one group of nuclei with $\delta \approx 1$. The two CH$_2$ protons are in a different part of the molecule, experience a different local magnetic field and have $\delta \approx 3$. The OH proton has another environment and $\delta \approx 4$. The increasing value of $\delta$ (the decrease of shielding) is consistent with the electron withdrawing power of the O atom: it reduces the electron density of the OH proton most, and that proton is strongly deshielded. It reduces the electron density of the distant methyl protons least, and those nuclei are least deshielded.

The relative intensities of the signals (the areas under the absorption lines) can be used to help distinguish which group of lines correspond to which chemical group. The determination of the area under an absorption line – the integration of the signal. Spectrometers can integrate the absorption automatically. In ethanol the group intensities are in the ratio 3:2:1 because there are three CH$_3$ protons, two CH$_2$ protons, and one OH proton in each molecule. Counting the number of magnetic nuclei as well as noting their chemical shifts helps to identify the compound.
The origin of shielding constants

The calculation of shielding constants is difficult because it requires detailed information about the distribution of electron density in the molecule. In last 15 years, a great progress was achieved in quantum chemical calculations (solving the Schrödinger equation for electronic motion in the molecule approximately to obtain molecular orbitals and energy levels) of shielding constants and NMR chemical shifts, especially for nuclei like $^{13}\text{C}$, $^{11}\text{B}$, $^{31}\text{P}$, transition metals, and other heavy nuclei. However, the accuracy of chemical shift calculations still remains in the range of 2-5 ppm, which is not sufficient for the quantitative prediction or assignment of $^1\text{H}$ chemical shifts. So, it is often easier to understand the different contributions to chemical shifts by studying empirical information.

The empirical approach: the observed shielding constant is the sum of 3 contributions:

$$\sigma = \sigma(\text{local}) + \sigma(\text{neighbor}) + \sigma(\text{solvent})$$

The local contribution – the contribution of the electrons of the atom that contains the nucleus in question. The neighboring group contribution – the contribution from the groups of atoms that form the rest of the molecule. The solvent contribution – the contribution from the solvent molecule.

The local contribution

Includes diamagnetic contribution, $\sigma_d$, and paramagnetic contribution, $\sigma_p$:

$$\sigma(\text{local}) = \sigma_d + \sigma_p$$

$\sigma_d$ – opposes the applied magnetic field and shields the nucleus.

$\sigma_p$ – reinforces the applied magnetic field and deshields the nucleus. $\sigma_d > 0$ $\sigma_p < 0$
The diamagnetic contribution arises from the ability of the applied field to generate a circulation of charge in the ground electronic state distribution of the atom. The circulation generates a magnetic field that opposes the applied field and hence shields the nucleus. \( \sigma_d \) depends on the electron density close to the nucleus and can be calculated using the **Lamb formula**: 

\[
\sigma_d = \frac{e^2 \mu_0}{12\pi m_e} \left\langle \frac{1}{r} \right\rangle
\]

\( \mu_0 \) – the vacuum permeability; \( r \) – the electron-nucleus distance.

**Example.** To calculate \( \sigma_d \) for the proton in a free H atom, we need to calculate the expectation value of \( 1/r \) for an H1s orbital.

\[
\psi = \left( \frac{1}{4\pi} \right)^{1/2} \frac{1}{2} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}
\]

\[
\left\langle \frac{1}{r} \right\rangle = \int \frac{\psi \psi^*}{r} d\tau = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\varphi \int_0^\pi d\theta \int_0^\infty r e^{-2r/a_0} dr = \frac{4}{a_0^3} \int_0^\infty r e^{-2r/a_0} dr = \frac{1}{a_0}
\]

(Because \( \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \))

\[
\sigma_d = \frac{e^2 \mu_0}{12\pi m_e a_0} = 1.78 \times 10^{-5}
\]

Diamagnetic contribution is the only contribution in the closed-shell free atom and also for distributions of charge that have spherical or cylindrical symmetry. Thus, it is the only contribution to the local shielding from inner cores of atoms – cores remain spherical even though the atom may be a component of a molecule and its valence electron distribution highly distorted. The diamagnetic contribution is broadly proportional to the electron density of the atom containing the nucleus of interest.
The shielding is decreased if the electron density on the atom is reduced by the influence of an electronegative atom nearby. That reduction in shielding results in an increase in deshielding and hence to an increase in the chemical shift $\delta$ as the electronegativity of a neighboring atom increases: as the electronegativity increases, $\delta$ increases.

The local paramagnetic contribution, $\sigma_p$, arises from the ability of the applied field to force the electrons to circulate through the molecule using orbitals unoccupied in the ground state. It is zero in free atoms and around the axis of linear molecule where the electrons can circulate freely and a field applied along the internuclear axis is unable to force them into other orbitals. Large paramagnetic contributions can be expected from small atoms in molecules with low-lying excited states – the paramagnetic contribution is the dominant contribution for atoms other than H.

**Neighboring group contributions**

The neighboring group contribution arises from the currents induced in nearby groups of atoms. Consider the influence of the neighboring group X on the proton H in a H-X molecule. The applied field generates current in the electron distribution of X and gives rise to an induced magnetic moment proportional to the applied field; the constant of proportionality is the magnetic susceptibility, $\chi$, of the group X. The proton H is affected by this induced magnetic moment in two ways:

1) the strength of the additional magnetic field acting on the proton is inversely proportional to $r^3$, $r$ – the distance between H and X;

2) the field at H depends on the anisotropy of the magnetic susceptibility of X, i.e., the variation of $\chi$ with the angle that X makes to the applied field.
Assume that the magnetic susceptibility of X has two components, $\chi_\parallel$ and $\chi_\perp$, parallel and perpendicular to the symmetry axis of X. The axis of symmetry of X makes an angle $\theta$ to the vector connecting X and H. To examine the effect of anisotropy of the magnetic susceptibility X on the shielding constant, consider $\theta = 0$.

A molecule H-X is free to tumble and some of the time the H-X axis will be perpendicular to the applied field and then only $\chi_\perp$ will contribute to the induced magnetic moment that shield X from the applied field. The result is deshielding of the proton H, $\sigma$(neighbor) $< 0$ (2). When the applied field is parallel to the H-X, only $\chi_\parallel$ contributes to the induced magnetic moment at X. The result is shielding of the proton H (3). As the molecule tumbles and the H-X axis takes all possible angles relative to the applied field, the effects of anisotropic magnetic susceptibility do not average to zero only if $\chi_\parallel \neq \chi_\perp$.

To a good approximation, the shielding constant $\sigma$(neighbor) is

$$\sigma$(neighbor) $\propto (\chi_\parallel - \chi_\perp) \left(1 - 3\cos^2\theta\right)$$

$\chi_\parallel$ and $\chi_\perp$ are both negative for a diamagnetic species.
The neighboring group contribution may be positive or negative according to the relative magnitudes of the two magnetic susceptibilities and the relative orientation of the nucleus: if $54.7^\circ < \theta < 125.3^\circ$, then $1 - 3\cos^2\theta$ is positive, but is negative otherwise.

A special case of a neighboring group – in aromatic compounds. The strong anisotropy of the magnetic susceptibility of the benzene ring – the ability of the field to induce a **ring current**, a circulation of electrons around the ring, when it is applied perpendicular to the molecular plane. Protons in the plane are deshielded, but any atom lying above or below the plane are shielded.

**The solvent contribution**

A solvent can also influence the local magnetic field experienced by a nucleus. Some effects arise from specific interactions between the solute and the solvent (hydrogen-bond formation and other forms of Lewis acid-base complex formation). The magnetic susceptibility of the solvent molecules (especially if they are aromatic) can also be the source of a local magnetic field. If there are steric interactions between a solute molecule and a solvent molecule, then protons in the solute may experience shielding or deshielding effects according to their location relative to the solvent molecule.
The NMR spectra of species that contain protons with widely different chemical shifts are easier to interpret than those in which the shifts are similar, so the appropriate choice of solvent may help to simplify the appearance and interpretation of the spectrum.

**The fine structure**

The splitting of resonances into individual lines is called the **fine structure** of the spectrum. It arises because each magnetic nucleus may contribute to the local field experienced by the other nuclei and so modify their resonance frequencies. The strength of the interaction is expressed in terms of the **scalar spin coupling constant**, \( J \), in hertz (Hz). The energy of interaction is proportional to the scalar product of the two interacting spins:

\[
E \propto I_1 \cdot I_2
\]

The constant of proportionality in this expression is \( J \). More precisely it is \( \hbar J / \hbar^2 \), because each angular momentum is proportional to \( \hbar \).

Spin coupling constants are independent of the strength of the applied field because they do not depend on the latter for their ability to generate local fields. If the resonance line of a particular nucleus is split by a certain amount by a second nucleus, then the resonance line of the second nucleus is split by the first to the same extent.

**The energy levels of coupled system**

Consider an AX system, a molecule that contains two spin-(1/2) nuclei A and X with very different chemical shifts in the sense that the difference in chemical shift corresponds to a frequency that is large compared to their spin-spin coupling.
There are four spin states for a spin-(1/2) system:

\[ \alpha_A \alpha_X \quad \alpha_A \beta_X \quad \beta_A \alpha_X \quad \beta_A \beta_X \]

The energy depends on the orientation of the spins in the external magnetic field. If spin-spin coupling is neglected, the energy is given by

\[ E = -\gamma h (1 - \sigma_A) B m_A - \gamma h (1 - \sigma_X) B m_X = -h \nu_A m_A - h \nu_X m_X \]

\[ \nu_A, \nu_X \] – the Larmor frequencies of A and X; \( m_A, m_X \) – their quantum numbers.

This expression gives four lines on the left of the figure. The spin-spin coupling depends on the relative orientations of the two spins.

It is proportional to the products \( m_A m_X \); the constant of proportionality is \( hJ \). The energy including spin-spin coupling is

\[ E = -h \nu_A m_A - h \nu_X m_X + hJ m_A m_X \]

If \( J > 0 \), a lower energy is obtained when \( m_A m_X < 0 \) (if one spin is \( \alpha \) and the other is \( \beta \). A higher energy is obtained if both spins are \( \alpha \) or both spins are \( \beta \). The opposite is true if \( J < 0 \). The resulting energy level diagram for \( J > 0 \) is shown on the right of the figure. The \( \alpha \alpha \) and \( \beta \beta \) states are both raised by \( (1/4)hJ \) and the \( \alpha \beta \) and \( \beta \alpha \) states are both lowered by \( (1/4)hJ \). When a transition of nucleus A occurs, nucleus X remains unchanged. Therefore, the A resonance is a transition with \( \Delta m_A = -1 \) and \( \Delta m_X = 0 \).
There are two such transitions: $\beta_A \leftarrow \alpha_A$ when the X nucleus is $\alpha_X$ and $\beta_A \leftarrow \alpha_A$ when the X nucleus is $\beta_X$. The energies of the transitions are

$$\Delta E = h\nu_A \pm \frac{1}{2}hJ$$

Therefore, the A resonance consists of a doublet of separation $J$ centered on the chemical shift of A.

Similar arguments are applied to the X resonance, which consists of two transitions according to whether the A nucleus is $\alpha$ or $\beta$.

The transition energies are

$$\Delta E = h\nu_X \pm \frac{1}{2}hJ$$

Therefore, the X resonance also consists of two lines of separation $J$, but they are centered on the chemical shift of X.

**Patterns of coupling**

In an AX system, spin-spin coupling will result in four lines in the NMR spectrum: instead of a single line from A, we get a doublet of lines separated by $J$ and centered on the chemical shift characteristic of A. The same splitting occurs in the X resonance: instead of a single line, the resonance is a doublet with splitting $J$ (the same value as for the splitting of A) centered on the chemical shift characteristic of X.

The X resonance in an AX$_n$ species (for example, AX$_2$ or AX$_3$) is also a doublet with splitting $J$: a group of equivalent nuclei resonates like a single nucleus.
The only difference for the X resonance of AXₙ – the intensity is \( n \) times greater as that of AX. The A resonance in AXₙ is however quite different from that in AX. For example, consider AX₂ with two equivalent X nuclei. The resonance of A is split into a doublet of separation \( J \) by one X, and each line of this doublet is split again by the same amount by the second X. This splitting results in three lines in the intensity ratio 1:2:1 (because the central frequency can be obtained in two ways). The A resonance of an AₙX₂ species would also be a 1:2:1 triplet of splitting \( J \), but the intensity of the A resonance would be \( n \) times as great as that of AX₂.

Three equivalent X nuclei (in AX₃) split the resonance of A into four lines of intensity ratio 1:3:3:1 and separation \( J \). The X resonance is still a doublet of separation \( J \). In general, \( n \) equivalent spin-(1/2) nuclei split the resonance of a nearby spin or group of equivalent spins into \( n + 1 \) lines with an intensity distribution given by Pascal’s triangle (4).
The easiest way of constructing the pattern of fine structure is to draw a diagram in which successive rows shows the splitting of a subsequent proton. It is easily extended to molecules containing nuclei with $I > 1/2$.

Example. Accounting for the fine structure in a spectrum

Account for the fine structure in the NMR spectrum of the C-H protons of ethanol. We need to consider how each group of equivalent protons (for example, three methyl protons) split the resonances of the other groups of protons. Each splitting pattern can be decided by referring to Pascal’s triangle. The three protons of the CH$_3$ group split the resonance of the CH$_2$ protons into a 1:3:3:1 quartet with a splitting $J$. The two protons of the CH$_2$ group split the resonance of the CH$_3$ protons into a 1:2:1 triplet with the same splitting $J$. All the lines mentioned so far are split into doublets by the OH protons, but the splitting cannot be detected because the OH protons migrate rapidly from molecules to molecule and their effect averages to zero.
The magnitudes of coupling constants

The scalar coupling constant of two nuclei separated by $N$ bonds is denoted $^N J$, with subscripts for the types of nuclei involved: $^1 J_{\text{CH}}$ – the coupling constant for a proton joined directly to $^{13}\text{C}$ atoms; $^2 J_{\text{CH}}$ – the coupling constant when the same two nuclei are separated by two bonds (as in $^{13}\text{C-C-H}$). A typical value of $^1 J_{\text{CH}}$ is 120-250 Hz; $^2 J_{\text{CH}}$: -10-20 Hz. $^3 J$ and $^4 J$ can give detectable effects in a spectrum, but coupling over larger number of bonds can generally be ignored. One of the longest range couplings detected so far - $^9 J_{\text{HH}} = 0.4$ Hz between the CH$_3$ and CH$_2$ protons in CH$_3$C≡CC≡CC≡CCH$_2$OH.

The sign of $J_{XY}$ indicates whether the energy of two spins is lower when they are parallel ($J < 0$) when they are antiparallel ($J > 0$). $^1 J_{\text{CH}}$ is often positive, $^2 J_{\text{HH}}$ is often negative, $^3 J_{\text{HH}}$ is often positive, etc. $J$ also varies with the angle between the bonds. A $^3 J_{\text{HH}}$ coupling constant is often found to depend on the dihedral angle $\phi$ (5) according to the Karplus equation

\[
J = A + B \cos \phi + C \cos 2\phi
\]

$A$, $B$, $C$ – empirical constants with values close to +7 Hz, -1 Hz, and +5 Hz. It follows that the measurements of $^3 J_{\text{HH}}$ in a series of related compounds can be used to determine their conformations. The coupling constant $^1 J_{\text{CH}}$ also depends on the hybridization of the C atom:

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>$^1 J_{\text{CH}}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>250</td>
</tr>
<tr>
<td>sp$^2$</td>
<td>160</td>
</tr>
<tr>
<td>sp$^3$</td>
<td>125</td>
</tr>
</tbody>
</table>
Equivalent nuclei

A group of nuclei are **chemically equivalent** if they are related by a symmetry operation of the molecule and have the same chemical shifts. Chemically equivalent nuclei are nuclei that would be regarded as ‘equivalent’ according to ordinary chemical criteria. Nuclei are **magnetically equivalent** if, as well as being chemically equivalent, they also have identical spin-spin interactions with any other magnetic nuclei in the molecule.

Consider the difference between CH$_2$F$_2$ and CH$_2$=CF$_2$. In each of these molecules the protons are chemically equivalent: they are related by symmetry and undergo the same chemical reactions. However, in CH$_2$F$_2$ the protons are magnetically equivalent but in CH$_2$=CF$_2$ they are not. One proton in the latter has spin-coupling interaction with a *cis* F nucleus, whereas the other proton has a *trans* interaction with it. In CH$_2$F$_2$ both protons are equally distant from the two F nuclei and so there is no distinction between them. Strictly speaking, the CH$_3$ protons in ethanol are magnetically inequivalent on account of their different interactions with CH$_2$ protons in the next group. However, they are in practice made magnetically equivalent by the rapid rotation of the CH$_3$ group, which averages out any differences. Magnetically inequivalent species can give very complicated spectra (24 lines in the spectrum of CH$_2$=CF$_2$).

An important feature of chemically equivalent magnetic nuclei is that, although they couple together, the coupling has no effect on the appearance of the spectrum.
Strongly coupled nuclei

We so far have described the extreme case in which the differences in chemical shifts are much greater than the spin-spin coupling constants. In such cases it is simple to identify groups of magnetically equivalent nuclei. The spectra are then called first-order spectra.

Transitions cannot be allocated to definite groups when the difference in their chemical shifts are comparable to their spin-spin coupling interactions. The complicated spectra that are then obtained are called strongly coupled spectra (or second-order spectra) and are much more difficult to analyze. Because the difference in resonance frequencies increases with the field, but spin-spin coupling constants are independent of it, a second-order spectrum may become simpler (and first-order) at high fields because individual groups of nuclei become identifiable again.

An AX system (which consists of two nuclei with a large chemical shift difference) has a first order spectrum. An AB system (with two nuclei of similar chemical shifts), gives a spectrum typical of a strongly coupled system. An AX system may have widely different Larmor frequencies because A and X are nuclei of different elements (such as $^{13}$C and $^1$H) – a heteronuclear spin system. AX may also denote a homonuclear spin system in which the nuclei are of the same element but in markedly different environments.
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, many $d$-metal complexes, and molecules in triplet states (such as those involved in phosphorescence). The sample may be a gas, a liquid, or a solid. But free rotation of molecules in the gas phase gives rise to complications.

The ESR spectrometer

A typical continuous-wave (CW) ESR spectrometer 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 (this requires 9 GHz (3cm) microwaves for resonance). The ESR spectrum is obtained by monitoring the microwave absorption as the field is changed, and a typical spectrum is shown in the Figure. The peculiar appearance of the spectrum, which is in fact the first derivative of the absorption, arises from the detection technique, which is sensitive to the slope of the absorption curve.
The equation \[ h\nu = g_e \mu_B B_0 \]
gives the resonance frequency for a transition between the \( m_s = -1/2 \) and \( +1/2 \) levels of a free electron in terms of the \( g \)-value \( g_e \approx 2.0023 \). The magnetic moment of an unpaired electron in a radical also interacts with an external field, \( g \)-value is different. \( g \)-value differs from that for the free electron because of local magnetic fields induced by the molecular framework of the radical.

\[ h\nu = g \mu_B B_0 \]

\( g \) – the \textit{g-value} of the radical. Many organic radicals have \( g \)-values close to 2.0027; inorganic radicals have \( g \)-values in the 1.9-2.1 range; paramagnetic \textit{d}-metal complexes have \( g \)-values in a wider range (0 to 6).

The deviation of \( g \) from \( g_e = 2.0023 \) depends on the ability of the applied field to induce local electron currents in the radical, and therefore its value gives some information about the electronic structure – the \( g \)-value plays a similar role in ESR as the shielding constant in NMR. However, because \( g \)-value differ very little from \( g_e \) in many radicals (2.003 for H, 1.999 for NO\(_2\), 2.01 for ClO\(_2\)), its main use in chemical applications is to aid identification of the species present in the sample.
For example, the center of the ESR spectrum of the methyl radical occurred at 329.40 mT in a spectrometer operating at 9.2330 GHz. Its $g$-value is therefore

$$ g = \frac{h \nu}{\mu_B B} = \left( \frac{6.62608 \times 10^{-34} \text{ Js}}{9.2330 \times 10^9 \text{ s}^{-1}} \right) \times \left( 9.2740 \times 10^{-24} \text{ JT}^{-1} \right) \times (0.32940 T) = 2.0027 $$

Just as in the case of the chemical shift in NMR spectroscopy, the $g$-value is anisotropic – its magnitude depends on the orientation of the radical with respect to the applied field. In solution, when the molecule is tumbling rapidly, only the average $g$-value is observed. Anisotropy of the $g$-value is observed only for radicals trapped in solids.

**Hyperfine structure**

The most important features of the ESR spectra are their **hyperfine structure**, the splitting of individual resonance into components. The term ‘hyperfine structure’ means the structure of a spectrum that can be traced to interactions of the electrons with nuclei other than a result of the latter’s point electric charge. The source of the hyperfine structure in ESR – the magnetic interaction between the electron spin and the magnetic moments of the nuclei present in the radical.

**The effects of nuclear spin**

Consider the effect on the ESR spectrum of a single H nucleus located somewhere in radical. The proton spin is a source of magnetic field and, depending on the orientation of the nuclear spin, the field it generates adds or subtracts from the applied field: 

$$ B_{loc} = B + a m_I $$

$$ m_I = \pm 1/2 $$

$a$ – the **hyperfine coupling constant**.
Half the radicals in a sample have $m_I = +1/2$, so half resonate when the applied field satisfies the condition

$$h\nu = g\mu_B \left( B + \frac{1}{2}a \right) \quad B = \frac{h\nu}{g\mu_B} - \frac{1}{2}a$$

The other half (with $m_I = -1/2$) resonate when

$$h\nu = g\mu_B \left( B - \frac{1}{2}a \right) \quad B = \frac{h\nu}{g\mu_B} + \frac{1}{2}a$$

Therefore, instead of a single line, the spectrum shows two lines of half the original intensity separated by $a$ and centered on the field determined by $g$.

If the radical contains an $^{14}$N atom ($I = 1$), its ESR spectrum consists of three lines of equal intensities, because the $^{14}$N nucleus has three possible spin orientations, and each spin orientation is possessed by one third of all the radicals in the sample. In general, a spin-$I$ nucleus splits the spectrum into $2I + 1$ hyperfine lines of equal intensity.

When there are several magnetic nuclei present in the radical, each one contributes to the hyperfine structure. In the case of equivalent protons (for example, the two CH$_2$ protons in the CH$_3$CH$_2$ radical) some of the hyperfine lines are coincident. If the radical contains $N$ equivalent protons, then there are $N + 1$ hyperfine lines with a binomial intensity distribution (the intensity distribution given by Pascal’s triangle). The spectrum of the benzene radical anion, which has seven lines with intensity ratio $1:6:15:20:15:6:1$, is consistent with a radical containing six equivalent protons.
Example. Predicting the hyperfine structure of an ESR spectrum

A radical contains one $^{14}$N nucleus ($I = 1$) with hyperfine constant 1.61 mT and two equivalent protons ($I = 1/2$) with hyperfine constant 0.35 mT. Predict the form of the ESR spectrum.

We consider the ESR structure that arises from each type of nucleus or group of equivalent nuclei in succession. So, we split a line with one nucleus, then each of those lines is split by a second nucleus (or group of nuclei), etc. It is best to start with the nucleus with largest hyperfine splitting; however, any choice could be made – the order in which nuclei are considered does not affect the consideration. The $^{14}$N nucleus gives three hyperfine lines of equal intensity separated by 1.61 mT.

Each line is split into doublets of spacing 0.35 mT by the first proton, and each line of these doublets is split into doublets with the same 0.35 mT splitting. The central lines of each split doublet coincide, so the proton splitting gives 1:2:1 triplets of internal splitting 0.35 mT. The spectrum is thus consists of three equivalent 1:2:1 triplets.

The hyperfine structure of an ESR spectrum is a kind of fingerprint that helps to identify the radicals present in a sample. Because the magnitude of the splitting depends on the distribution of the unpaired electron near the magnetic nuclei present, the spectrum can be used to map the molecular orbital occupied by the unpaired electron.
For example, because the hyperfine splitting in C₆H₆⁻ is 0.375 mT, and one proton is close to a C atom with 1/6 the unpaired electron spin density (because the electron is spread uniformly around the ring), the hyperfine splitting caused by a proton in the electron spin entirely confined to a single adjacent C atom should be $6 \times 0.375 \text{ mT} = 2.25 \text{ mT}$. If in another aromatic radical we find a hyperfine splitting constant $a$, then the spin density, $\rho$, the probability that an unpaired electron is on the atom, can be calculated using the McConnell equation:

$$ a = Q\rho $$  

$Q = 2.25 \text{ mT}$

$\rho$ - the spin density on a C atom; $a$ – the hyperfine splitting observed for the H atom to which it is attached.

Example. The hyperfine structure of the ESR spectrum of the radical anion (naphthalene)⁻ can be interpreted as arising from two groups of four equivalent protons. Those at the 1, 4, 5, and 8 positions in the ring have $a = 0.490 \text{ mT}$ and for those in the 2, 3, 6, and 7 positions have $a = 0.183 \text{ mT}$. The densities obtained by using the McConnell equation are 0.22 and 0.08, respectively.