

An Exploration of Nuclear Magnetic Resonance (NMR) Spectroscopy

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1 Introduction

Nuclear Magnetic resonance is a phenomenon that occurs when an atom's nuclei are immersed in a static magnetic field while exposed to a second oscillating magnetic field. Whether or not this is experienced is dependent on if the atomic nuclei possess a characteristic called spin. Nuclear magnetic resonance (NMR) spectroscopy uses the interaction of electromagnetic radiation with matter to acquire information about molecules and is often used by chemists to elucidate chemical structure. Many nuclei may be studied, however hydrogen (1H) and carbon (^{13}C) are the most common due to their abundance within chemical structures. Notice, the most abundant isotopes, 2H and ^{12}C respectively, do not possess spin property. NMR can be used in both solution and solid-state structural determination, proving it to be a versatile instrument in chemical studies.

Atoms routinely used for NMR:

Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin
1H	1	0	1/2
^{13}C	0	1	1/2
^{14}N	1	1	0
^{19}F	1	0	1/2
^{23}Na	1	2	3/2
^{31}P	1	0	1/2

1.1 Nuclear Spin

The majority of atomic nuclei possess a property referred to as **spin**. Spin refers to the concept that nuclei behave as if they are "spinning". Spin states are not of equivalent energy in an applied magnetic field as the nucleus is a charged particle, creating a field of its own. The nucleus is said to have a magnetic moment (μ) of its own. This moment is generated by its charge and spin. Spin comes in multiples of 1/2 and can be either positive (clockwise) or negative (counterclockwise). The nuclear magnetic moments (μ) in each of the two cases are pointed in opposite directions. Within an applied magnetic field, all protons

have their magnetic moments either aligned with the field (+ spin) or opposed to it (- spin).

Protons, electrons, and neutrons all possess spin – however NMR spectroscopy focuses solely on unpaired nuclear spins. Two or more particles with spins having opposite signs can pair up and eliminate the observable manifestation of spin.

Atoms that possess an odd mass, an odd atomic number, or both are said to have a quantized **spin angular momentum** and a magnetic moment. Magnitude of spin angular moment is defined using the equation:

$$[(I + 1)]^{1/2}\hbar \tag{1.1}$$

For each nucleus with spin, the number of allowed spin state it may adopt is quantized, and denoted by I , the nuclear spin quantum number. Where I is a physical constant, and there are $2I+1$ allowed spin states within the integral difference between $+I$ to $-I$.

$$+I, (I-1), \dots, (-I + 1), -I$$

For example, the hydrogen nucleus contains two spin states, $[2(1/2) + 1=2]$, $+1/2$, $-1/2$, with the spin quantum number $I=1/2$. The most common nuclei that possess spin include:

Element	1_1H	2_1H	${}^{12}_6C$	${}^{13}_6C$	${}^{14}_7N$	${}^{16}_8O$	${}^{17}_8O$	${}^{19}_9F$	${}^{31}_{15}P$
Nuclear spin quantum number	1/2	1	0	1/2	1	0	5/2	1/2	1/2
Number of spin states	2	3	0	2	3	0	6	2	2

The nuclear magnetic resonance phenomenon occurs when nuclei aligned within the applied field are induced to absorb energy and change their spin orientation with respect to the applied field. The stronger the magnetic field, the greater the energy difference between the possible spin states. The magnitude of the energy-level separation also is dependent on the nucleus involved. Each nucleus has a different ratio of magnetic moment to angular momentum that is charge and mass dependent.

1.2 Peak Integration

NMR spectrum not only distinguishes how many different types of protons are within a molecule, but also how many of each type is present. In 1H NMR, the area under a peak is proportional to the number of hydrogens generating that peak. The area of these peaks is integrated, which rises in height by an amount proportional to the area under the peak. The height of the integral line does not give the absolute number of hydrogens but does give the relative number of each *type* of hydrogen. For an integral to be used, there must be a second to which it may be referred to.

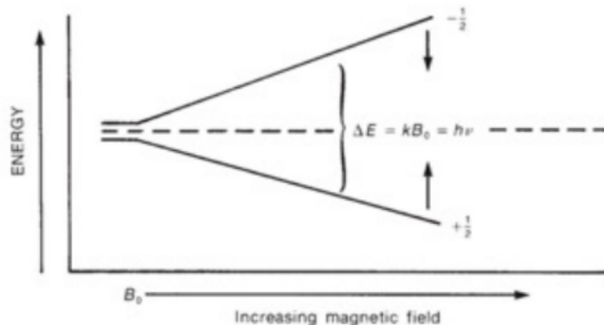


Figure 1: Spin-state energy separation as the applied magnetic field increases

2 Chemical Shifts

The NMR frequency of a molecule's nucleus is determined by its gyromagnetic ratio (γ) and the strength of the magnetic field (B), using the equation:

$$V = \frac{\gamma B}{2\pi} \quad (2.1)$$

Not all nuclei have identical resonance frequencies: V depends on the local electron distribution. This effect is called **chemical shift**, allowing one to distinguish between different atoms within a molecule as their effective fields vary.

2.1 Shielding

Similar to how a current flowing through a wire induces a magnetic field, when an atom is placed within a magnetic field, its electrons travel in the direction of the applied field. This causes a small magnetic field localized at the nucleus that opposes the applied field. This is called **diamagnetic anisotropy**.

Each proton in a molecule is shielded from the applied magnetic field and its magnitude is dependent on the surrounding electron density. The greater the electron density surrounding the nucleus, the greater the induced counter field opposing the applied field. As a result, the nucleus absorbs radiofrequency radiation at a lower frequency. The field of the nucleus can be written as:

$$B = B_0 - B' = B_0(1 - \sigma) \quad (2.2)$$

Where B' is the magnetic field in the opposing direction and is proportional to B_0 and B' . Sigma, the constant of proportionality between B' and B_0 is called the **shielding constant**.

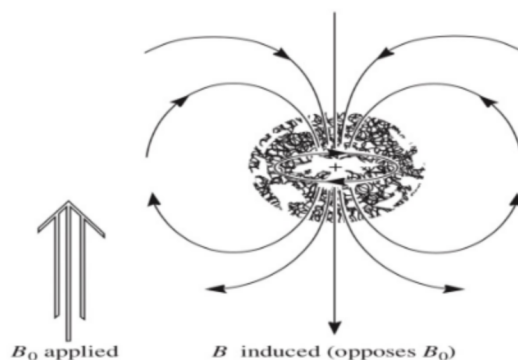


Figure 2: The applied field induces circulation of valence electrons, generating a magnetic field that opposes the applied field.

The standard reference used to demonstrate chemical shielding is tetramethylsilane (TMS) with the molecular formula: $\text{Si}(\text{CH}_3)_4$, as the protons of its methyl groups are more shielded than most other compounds. The shift for a given proton on TMS depends on the strength of an applied magnetic field, which is spectrometer dependent. To overcome this, we can use what is called the **chemical shift** (δ):

$$\delta = \frac{\text{shift in Hz}}{\text{spectrometer frequency in MHz}} \quad (2.3)$$

Delta is a molecular property, independent of the magnetic field used to measure it, by which a proton resonance is shifted from the spectrometer's basic operating frequency. δ values are quoted ppm values and are reported as such.

Signals within the spectra are plotted with δ and V increasing from right to left. The more heavily shielded the nuclei (larger σ , smaller ν , smaller δ) appear on the right-hand side of the spectrum.

2.2 Contributions to nuclear shielding

The nuclear shielding constant (σ) can be broken down into four parts:

1. σ = local diamagnetic shielding
2. + local paramagnetic shielding
3. + shielding due to remote currents
4. + other sources of shielding

Local diamagnetic and paramagnetic shielding come from the electrons within the immediate vicinity. The third refers to the diamagnetic and paramagnetic effects of electrons circling nearby nuclei. The final piece, other sources of shielding, include electric field shifts, intermolecular forces, solvent shifts, unpaired electrons, etc.

2.2.1 local diamagnetic shifts

Local diamagnetic currents are dependent on the electron density around the nucleus. The larger the electron density, the greater the shielding and the smaller the chemical shift (δ). In 1H NMR this can be applied to halide complexes (X-R), where X is I, Cl, Br, or F and R denotes a string of hydrocarbons, C_xH_x respectively. As the electronegativity of the halogens increase, electron density is withdrawn from the hydrocarbon chain, deshielding the protons. However, the further away from the electronegative halide, the deshielding effects dissipate. Similar behavior is experienced in monosubstituted benzenes, electron withdrawing groups attached to the ring deshield the ring protons; and electron donating groups tend to shield protons.

2.2.2 Hybridization

The second important set of trends is due to the hybridization of an atom in which a hydrogen is attached to. sp^3 carbon atoms have resonance in the limited range from 0-2 ppm. In an sp^2 C-H bond, the carbon has more s character which results in similar behavior to electronegativity. Thus, the chemical shifts are greater in the 5-6 ppm range. Aromatic hydrogens appear even further downfield, (7-8 ppm) as resonance effects are greater than hybridization.

Sp hydrogen read at a lower ppm value than one might expect, 2-3ppm. This is attributed to anisotropy, as one would expect sp hybridization to be more electronegative than sp^2 . The opposite is observed. **Anisotropy** refers to a chemical shift that is not easily explained. The anomalous shift is due to the presence of an unsaturated π system in the vicinity of the atom in question.

3 Spin-spin coupling

The magnetic interactions between nuclei, known as spin-spin coupling (or spin-spin splitting), refers to the resonances a specific molecule contains. Spin-spin coupling can be explained using the **n + 1 rule**. Each type of proton “senses” the number of equivalent protons (n) on the carbon atom(s) next to the one in which it is bonded, and its resonance peaks is split into (n+1) components. The splitting causes for NMR lines to split into a number of components with characteristic relative intensities and spacing.

Spin-spin coupling arises because hydrogens on adjacent atoms can “sense” one another. The hydrogen on Carbon A can sense the spin direction of the hydrogen on carbon B, where the hydrogens on carbon B have either spin + 1/2 or -1/2. This results in the chemical shift of proton A to be influenced by

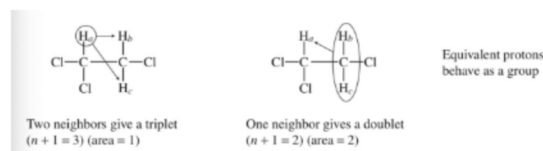


Figure 3: demonstration of the $(n+1)$ rule

the direction of the spin in proton B, this is called **coupling**. The magnetic environment is affected by whether proton B has a $+1/2$ (spin up) or $-1/2$ (spin down) spin. Carbons with spin up undergo 1H NMR transitions ($H \uparrow C \downarrow$ to $H \downarrow C \uparrow$) at frequency *lower* than the chemical shift, due to the transition from an energetically unfavorable state (parallel spin) to a favorable one (antiparallel spin) and vice versa. Note: only transitions in which one spin flips is allowed, ($H \uparrow C \uparrow$ to $H \downarrow C \downarrow$) is forbidden.

A physical model of spin-spin coupling is not easy to develop, however there are theoretical models available. According to the Dirac model, electrons in the intervening bonds between two nuclei transfer spin information from one nucleus to another by interaction between the nuclear and electronic spins. Electrons near the nucleus are assumed to have the lowest energy interaction with the nucleus when the electron (small arrow) spin has a direction of spin opposite of the nucleus (bold arrow). The size of the coupling constant diminishes as the number of intervening bonds increase.

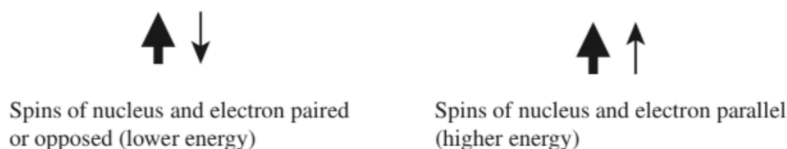


Figure 4: Unpaired and paired nuclear and electron spin

3.0.1 The coupling constant

The distance between the peaks is referred to as the coupling constant (J). This constant measure how strongly a nucleus is affected by the spin states of its neighbors.

$$E = hJ_{AX}m_Am_X \quad (3.1)$$

Where m_A and m_X refer to the magnetic quantum numbers of the two nuclei and J_{AX} is the spin-spin coupling constant. J_{AX} is measured in Hz and can either be a positive or negative value.

- Antiparallel arrangements: favorable interactions $J_{AX} > 0$
- Parallel arrangements: unfavorable interactions $J_{AX} < 0$

3.1 Multiplet patterns

At this point we assumed that all pairs of spins are weakly coupled, and all nuclei spin are $-1/2$ unless otherwise stated. However, this is not always the case. The term equivalent nuclei is used to describe spins in identical environments with identical chemical shifts. Nuclei containing similar shifts are likely to be strongly coupled and when labeling molecules, are assigned adjacent letters in the alphabet (A,B,C, etc). Whereas, spins with difference chemical shifts are labelled by letters far apart in the alphabet (A,M,X,etc.).

3.1.1 Coupling of two inequivalent spin-1/2 nuclei (AMX)

When protons attached to a single carbon are chemically equivalent the $n + 1$ rule successfully predicts the splitting pattern. When protons attached to a single carbon are chemically nonequivalent (different chemical shifts), the $n + 1$ rule no longer applies. In the AMX spin system, J_{AM} , J_{AX} , J_{MX} are used to describe the three nuclei with different chemical shifts and three distinct coupling constants. Four peaks of identical area are expected because there are four non-degenerate arrangements of the M and X spins ($M \uparrow X \uparrow$; $M \uparrow X \downarrow$; $M \downarrow X \uparrow$; $M \downarrow X \downarrow$). These peaks are displaced from the chemical shifts of A by simple combinations of the coupling to spin A. Resulting in the signal being doubled a first time for the first coupling (resulting doublet) and then doubled again for the second coupled, causing the peak to be doubled once again. This type of splitting is called a doublet of doublets or an "assumed triplet".

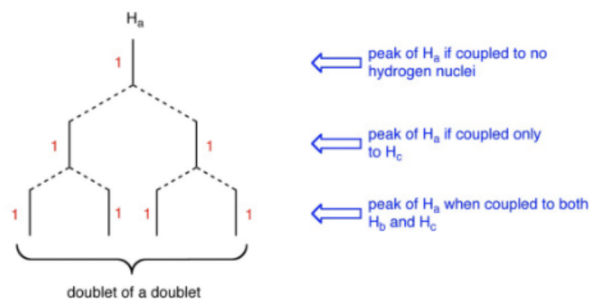


Figure 5: doublet of doublet coupling

3.1.2 Coupling to two equivalent spin-1/2 nuclei (AX_2)

If a nucleus of interest has a spin quantum number $> 1/2$, its multiplet structure can be predicted the same way of as for a nucleus with spin $1/2$. However, nuclei with $I > 1/2$ possess, in addition to a magnetic dipole moment, an electric quadrupole moment that can interact with local electric field gradients. For molecules in solution, these interactions can lead to efficient relaxation of

the quadrupolar nucleus and NMR signals that are so broad that the expected multiplet patterns are obscured.

For A ($I=1/2$) coupled to X ($I>1/2$), the principles for spin-1/2 nuclei can easily be extended. The magnetic moment of a spin- I particle has $2I+1$ orientations with respect to the magnetic field B_0 . Therefore, a nucleus coupled to a single X spin with quantum number I should show a multiplet comprising $2I + 1$ lines with equal spacing and amplitudes. Note however, quadrupolar relaxation may obscure these results.

3.2 Equivalent nuclei

Up until now the word “equivalent” has been termed loosely, however there are two types of equivalences: chemical and magnetic.

Consider the two compounds CH_2F_2 and $CH_2=CF_2$ and their coupling to two fluorine’s F_a and F_b . In CH_2F_2 the two protons feature the same chemical shifts, and each have identical couplings to F_a and F_b ; therefore, are magnetically equivalent. More generally, a set of nuclei with identical chemical shifts are **magnetically equivalent** if their spin coupling constants satisfy the relationship:

1. Magnetically equivalent nuclei must have identical chemical shifts (**isochronous**)
2. Magnetically equivalent nuclei must have equal coupling (J values) to all other nuclei in the molecule ($J_{ax} = J_{bx} = J_{cx} = \dots$)

Magnetically equivalent nuclei, even if they are close enough to be coupled do not split one another and read only as one signal. This does not imply that coupling does not occur between magnetically equivalent nuclei; it means only that no observable spin-spin splitting results from the coupling.

The same cannot be said for $CH_2=CF_2$ as the molecule can feature both different conformations. If a plane of symmetry or an axis of symmetry renders two or more nuclei equivalent by symmetry they are deemed as **chemically equivalent**. This pertains to all molecules in chemically identical environments and often exhibit the same chemical shift.

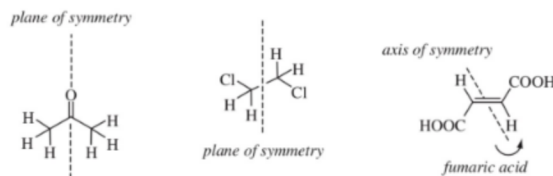


Figure 6: chemically equivalent nuclei due to axis of symmetry

The NMR spectra of molecules containing chemically equivalent spins are much more complex than for similar compounds with magnetically equivalent nuclei. Spin-spin interactions within a group of magnetically equivalent nuclei

do not produce multiplet splitting. This is due to the four allowed transitions, in which one of the spins flips independently of the other. When both δv and J are both zero, the four transitions are degenerate, and the spectra reads as a single line at the chemical shift ppm value. When chemically equivalent nuclei have the same chemical shift and do not split each other, the nuclei are said to be magnetically equivalent as well as chemically equivalent.

The state described by the wave function $2^{-1/2} (\alpha_A \beta_B - \beta_A \alpha_B)$ appears as a singlet and has no net magnetism as the magnetic moments of the two spins cancel. To conclude, scalar couplings between magnetically equivalent nuclei do not produce multiplet splitting's because of the changes in transition probabilities and NMR frequencies arising from the mixing of spin state and the spin-spin interaction.

3.2.1 Strong coupling

Thus far we have looked at weak coupling $|\delta v| \gg |J|$, and $\delta v = 0$ for equivalent nuclei. For strong coupling the difference in frequencies is reduced, keeping J fixed. The inner component of each signal increases in amplitude, while the outer components become weaker. The two signals move together as their chemical shifts difference decreases, until at $\delta v = 0$, the inner lines coincide, and the outer lines vanish.

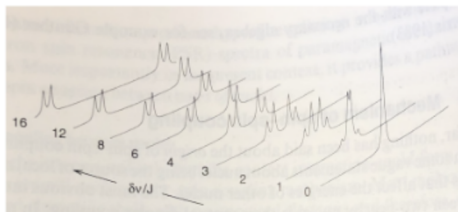


Figure 7: Strong coupling peaks

The effect of scalar coupling is to modify energies and wavefunctions by mixing the $\alpha_A \beta_B$ and $\beta_A \alpha_B$ states. This results in a change in the transition probabilities of the NMR signal lines, the inner lines becoming stronger (more present) and outer lines weaker (less present). Resulting in a small gap δv between $\alpha_A \beta_B$ and $\beta_A \alpha_B$ relative to J . According to this convention, in the above spectra AX is referred to as weak coupling and AB as strong coupling. The intensity distortions resulting from strong coupling is often referred to as the roof effect. In the presence of strong coupling so that doublets are no longer centered at their chemical shift:

$$C = [(\delta v)^2 + J^2]^{1/2} \quad (3.2)$$

This becomes more complex when more than two spins are involved. Multiplet patterns become difficult to recognize. Changes in transition probabilities

cause otherwise forbidden transitions to be observed, and chemical shifts and coupling constants can no longer be predicted via computation. A strongly coupled spin state can be made weakly coupled by using a higher field spectrometer as coupling constants are independent of the static magnetic field.

3.3 Mechanisms of spin-spin coupling

The most obvious interaction between two nearby nuclei is their mutual dipolar coupling. Similarly, to how magnets interact neighboring nuclei sense one another's orientation by virtue of their dipolar magnetic field. The principal source of scalar coupling in molecules is an indirect interaction mediated by the electrons involved in chemical bonding.

3.3.1 Contact interaction

The electron is a spin-1/2 particle with a gyromagnetic ratio more than 660 times that for a proton. Electrons feature strong dipolar magnetic interactions with nearby nuclei. The dipolar interactions of an electron and a nucleus is replaced by an isotropic interaction known as Fermi contact interaction whose strength is proportional to the scalar product of the two magnetic moments.

$$\text{contact interaction} \propto -\gamma_e \gamma_n \mathbf{I} \cdot \mathbf{S} \quad (3.3)$$

Where \mathbf{I} and \mathbf{S} are respectively the nuclear and electron spin angular momentum vectors. The electron has a negative gyromagnetic ratio ($e < 0$), therefore, the nucleus $n > 0$ is stabilized if the nuclear spins are antiparallel ($\mathbf{I} \cdot \mathbf{S} < 0$) and destabilized if parallel ($\mathbf{I} \cdot \mathbf{S} > 0$). The isotropic interaction allows an electron to sense the orientation of a nearby nuclear spin, in a way that survives the orientational averaging effect of rapid molecular tumbling. The contact interaction provides splitting in both electronic and electron spin resonance (ESR) spectra of paramagnetic molecules.

3.3.2 Indirect coupling between nuclei

At a glance it seems unlikely that contact interaction could form the basis of nuclear spin-spin coupling mechanism, as the majority of molecules have closed electron shells with no unpaired electrons. For a basic understanding of spin-spin coupling within diamagnetic molecules consider the ground state wavefunction of H_2 :

$$\Psi_0 = \phi_0(\alpha_a \beta_b - \beta_a \alpha_b) \quad (3.4)$$

Where ϕ_0 is the molecular orbital and the rest is the electron spin wavefunction. The two electrons are partaking in constructive overlap, in a bonding, $1s$ atomic orbital. From the form of Ψ_0 it can be determined that the spatial distribution of the (α) and (β) ground state of both electrons is identical.

The nucleus-electron coupling can flip the spin of one of the electrons, converting antiparallel spins to parallel spins while simultaneously flipping the nuclear spin in the opposite sense to conserve angular momentum. The electron spin flip must be accompanied by spin excitation as it is forbidden for two electrons with parallel spins to be accompanying the same orbital as per the Pauli principal. The excited state wavefunction is:

$$\Psi_1 = \phi_1(\alpha_a\beta_b + \beta_a\alpha_b) \quad (3.5)$$

With a symmetrical spin part and a spatial part ϕ_1 which differs from ϕ_0 due to the antibonding orbital contribution. As a result, the mixing of singlet and triplet states becomes a linear combination of Ψ_0 and Ψ_1 . Since ϕ_0 and ϕ_1 are different shapes, the probability of finding an electron in state α no longer have the same probability for the same electron with opposite spin, as the electron wave function has become spin polarized.

If proton A has $m = -1/2(\beta_A)$, the contact interaction and wavefunction mixing results in an excess of α electron spins and the depletion of β electron spins. The spin of one nucleus senses the spin of another.

This model can be extended to larger molecules as well. The protons will be coupled providing there exist delocalized molecular orbitals. For the molecule CH_2 , we can picture the CH bonds as an interacting two-center two-electron bond. The spins of the electron in one of the CH bonds are polarized via their contact interaction with the exchange interaction with the H nucleus. This polarization is transferred to the other CH bond by the exchange interaction between electrons in the two bonds. The spin polarization of the second bond is felt by the second proton via its contact interaction.

The signs of coupling constants in this model cannot easily be predicted without detailed knowledge of the low-lying excited state wave function. However, NMR is typically independent of these signs so it does not pose a huge problem. For even larger molecules, the strength of coupling is likely to fall off quite quickly as the number of bonds increase.

3.4 Properties of Scalar Coupling

Scalar coupling is the isotropic part (independent on the molecular orientation) of the J coupling, therefore not affected by molecular tumbling. The J coupling arises due to indirect interaction between the two nuclear spins, where the interaction is mediated by the electrons participating in the bond(s) connecting the nuclei. The strength of coupling interactions is highly dependent on the *s*-electron character of the ground state. The coupling is not affected by the strength nor the direction of the external magnetic field, in contrast to the difference in resonance frequencies that arise from nuclear shielding. Calculations of spin-spin coupling require accurate wavefunctions for a large number of excited states. However, it is easier to make an estimate of J_{HH} : the proton-proton coupling constant in H_2 . The paramagnetic excited state in H_2 should

be roughly equal to the contact interaction of atomic hydrogen (A_H). To find the J_{HH} of the ground state (ψ_0), we have to mix a small fraction of (ψ_1) into the contact interaction. Perturbation theory shows that γ is the order of $A_H/\Delta E$, where ΔE is the electronic excitation energy. Most coupling constants are smaller than 280 Hz as the interaction occurs through more than one chemical bond or the two molecules participating in bonding have a smaller gyromagnetic ratio than 1H .

3.4.1 Three-bond couplings

The most useful spin-spin couplings are those involving nuclei separated by three bonds ($^3J_{HH}$). Three-bond coupling lies primarily within the conformation of the molecule and can be used to elucidate structural information. For example, in a H-C-C-H fragment, the coupling constants are found to vary with the dihedral angle between the two H-C-C planes. We can apply the 'Karplus relation:'

$$^3J = A + B\cos\theta + C\cos^2\theta \quad (3.6)$$

Although it is possible to calculate approximations for the above variables (A,B,C) it is easier to treat them as coefficients and determined empirically using known conformationally rigid model compounds, as the utility of 3 bond coupling lies principally in conformation analysis.

The interpretation of couplings in molecules whose conformations change rapidly are somewhat more difficult, their two observed $^3J_{\alpha\beta}$ is averaged and weighted according to the three energy minima. Thus as follows:

$$\begin{aligned} J_{\alpha\beta 1} &= P_1J_g + P_2J_g + P_3J_t \\ J_{\alpha\beta 2} &= P_1J_g + P_2J_t + P_3J_g \end{aligned} \quad (3.7)$$

Where J_t and J_g are the trans and gauche constants, $\theta = 180^\circ$ and $\theta = \pm 60^\circ$ respectively, and $P_1 + P_2 + P_3 = 1$. The relative populations of the three rotamers (conformations) can be then determined if J_t and J_g can be obtained from rigid molecules.

3.4.2 Long-range couplings

Protons coupling within three bonds are typically very small values (<1 Hz), with the exception of molecules featuring conjugated π systems. Larger J_{HH} values occur.

3.4.3 Dipolar coupling

Dipolar interactions are not responsible for NMR splitting of liquids but are an important for understanding solid state NMR and relaxation. Not to be

confused with J coupling which is mediated through bonded electrons. The dipolar coupling between two nuclei depends on the distance between them, and the angle of bond relative to the external magnetic field.

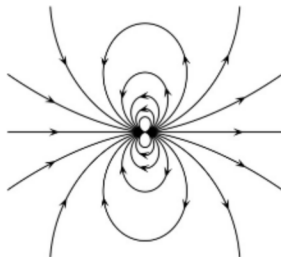


Figure 8: Example of the dipolar magnetic field

3.4.4 Magnetic field of a point dipole

Every nucleus with a non-zero spin quantum number has a **magnetic dipole**. The magnetic moment μ , sitting at the center of a coordinate system and pointing along the positive z axis produces a magnetic field \mathbf{B}_μ . The components of \mathbf{B}_μ along the x, y and z axis are as follows:

$$\begin{aligned} B_{\mu x} &= \left(\frac{\mu_0}{4\pi}\right)\left(\frac{\mu}{r^3}\right)(3\sin\theta\cos\theta) \\ B_{\mu y} &= 0 \\ B_{\mu z} &= \left(\frac{\mu_0}{4\pi}\right)\left(\frac{\mu}{r^3}\right)(3\cos^2\theta-1) \end{aligned} \quad (3.8)$$

Where μ_0 is the permeability of a vacuum: $4\pi \times 10^{-7} \text{ Hm}^{-1}$ and μ is the magnitude of the magnetic moment μ .

3.4.5 Dipolar interaction between nuclei in solids

In dipolar coupling, the effect one nucleus has on another may now be investigated. Looking at the X spectrum of an AX spin system ($\mathbf{x} = (r, \theta)$, A is at the origin). A and X both have spin-1/2 nuclei but contain different gyromagnetic ratios. Both nuclear spins are quantized along the field direction (z axis) so that the vertical axis coincides with B_0 . The resonance frequency of X is determined by the net field in this direction $B_0 \pm B_{\mu z}^A$ where $B_{\mu z}^A$ is the dipolar field generated by A.

$$\begin{aligned} \text{Heteronuclear dipolar splitting/Hz} &= k_{AX}(3\cos^2\theta - 1) \\ 2\pi K_{AX} &= \left(\frac{\mu_0}{4\pi}\right)\frac{\hbar\gamma_A\gamma_X}{r_{AX}^3} \end{aligned} \quad (3.9)$$

These are the NMR spectra one would observe for an isolated AX pairs in a single crystal as it is rotated around a magnetic field. As θ changes from 0 to 90, the doublet splitting decreases, goes through zero at 54.7 (the magic angle) and then increases as θ goes to 90.

For a powder sample, each AX pair has a unique θ . Powder spectrum is the sum of the single crystal spectra for θ between 0 and 90, each weighted by $\sin \theta$ to take into account the probability of finding an AX pair with orientation θ . Adding these spectra together provide a unique shaped referred to as "horns". This corresponds to $\theta \approx 90^\circ$ while the wings come from the $\theta \approx 0^\circ$ orientations (Fig.7).

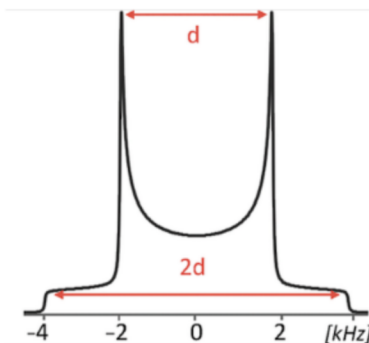


Figure 9: Heteronuclear dipolar-coupled peak

Homonuclear dipolar coupling produce single crystal and powder spectra that are mostly identical to those from heteronuclear interaction. The only difference is the observed splitting containing an extra factor of 3/2.

$$\begin{aligned} \text{Homonuclear dipolar splitting}/Hz &= \frac{3}{2} K_{AX} (3\cos^2\theta - 1) \\ 2\pi K_{AX} &= \left(\frac{\mu_0}{4\pi}\right) \frac{\hbar\gamma^2}{r_{AX}^3} \end{aligned} \quad (3.10)$$

The 3/2 arises because the homonuclear dipolar interaction mixes the spin state $\alpha_\alpha \beta_x$ and $\beta_\alpha \alpha_x$. This does not occur in heteronuclear coupling as the gap between the two spin states is greater than the strength of interaction.

References

- Hore, P. J. *Nuclear Magnetic Resonance*. Oxford University Press, 1989.
- Hornak, Joseph P. *The Basics of NMR.*, www.cis.rit.edu/htbooks/nmr/inside.htm.
- Pavia, Donald L., et al. *Introduction to Spectroscopy*. Cengage Learning, 2015.