

Lecture notes

Nuclear magnetic resonance

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These notes are based on a series of introductory lectures on nmr given to graduate physics students at ycm, University of Mysore, as part of the PHYS204 course on spectroscopy and Fourier optics.

Please e-mail hello@vhbelvadi.com with your thoughts or suggestions, or if you spot any errors. These notes are – and will probably always remain – a work in progress. They may be updated and, if they are, the latest version of this document will always be available for download at <http://vhbelvadi.com/notes/> for anybody interested in it.

A note on references: Footnotes are marked by superscript numbers ^x, equations by parentheses (x) and references to the appendix by square brackets [x].

Contents

1	Spin-field interactions	1
1.1	Magnetons	1
1.2	Energy levels	2
1.3	Larmor precession	3
1.4	Population, or why absorption is favoured over emission	4
2	Perturbations	5
2.1	Time evolution of spin	5
3	Relaxation	7
3.1	Rate of magnetisation	7
3.2	Spin-Lattice relaxation	8
3.3	Chemical shift	9
3.4	Spin-spin interaction	10
4	NMR of an ethanol molecule	10
5	Fourier Transforms in NMR	12
5.1	Pulses	12
5.2	A note on Fourier Transform spectroscopy	12
A	Some useful results	a
B	Bibliography	a

Changelog:

v.1.0 Initial.

P.S. \LaTeX needs much better line breaking capabilities for equations. If packages better than breqn and the split and multiline environments built into amsmath exist, or if you have written one yourself, please send me an e-mail. Thank you.

Over the course of these notes our focus will remain on understanding how atoms and molecules respond when various electromagnetic waves are incident on them. Specifically, we want to understand how any electromagnetic radiation *interacts* with some particle and we want to see what comes out of such an interaction. Often this involves energy spectra, which means we end up using spectroscopy to study these phenomena.

All our discussions, then, will cover five areas of interest: the basics of spin-field interactions; nuclear magnetic resonance and electron spin resonance; and microwave, infrared and Raman spectroscopies.

1 Spin-field interactions

Most of us are familiar with mechanical resonance, which, to put it briefly, is when a system absorbs an increased amount of energy due to its natural frequency of vibration matching its frequency of oscillation. As we will see later, this match of frequencies is what lends the name *resonance* to certain phenomena at atomic and molecular scales.

If we imagine some charged particle to be precessing about some axis, we realise there exists a circular current along the locus of precession. In turn this means there exists a magnetic field and, by extension, a magnetic dipole. A spinning, charged particle, therefore, is not unlike a bar magnet placed along the precession axis.

1.1 Magnetons

The spin of a nucleus is given by the spin quantum number, s , which is related to the angular momentum \mathbf{I} as $\mathbf{I} = \hbar\sqrt{s(s+1)}$ with s taking values $0, \frac{1}{2}, 1, \frac{3}{2}$ etc., a total of $2s + 1$ possible components¹. Ideally, the magnetic moment is given by

$$\boldsymbol{\mu} = \frac{q}{2m}\mathbf{I} = \frac{q\hbar}{2m}\sqrt{s(s+1)}$$

I say ‘ideally’, because this expression treats particles (like electrons and neutrons) as point particles, which they are not. Correcting for this requires that we introduce a multiplicative numerical factor that is often represented by G and takes various values depending on the particle in question, e.g. it is often written as $g \approx 2$ for electrons.

$$\boldsymbol{\mu} = G \left(\frac{q\hbar}{2m} \right) \sqrt{s(s+1)}$$

measured in joule per tesla. The factor in parentheses is often collected together as

$$\beta = \frac{q\hbar}{2m} \tag{1}$$

¹For example, in the z-direction, $I_z \equiv I, I-1, I-2, \dots, 0, \dots, -(I-2), -(I-1), -I$, which is a total of $2I + 1$ components.

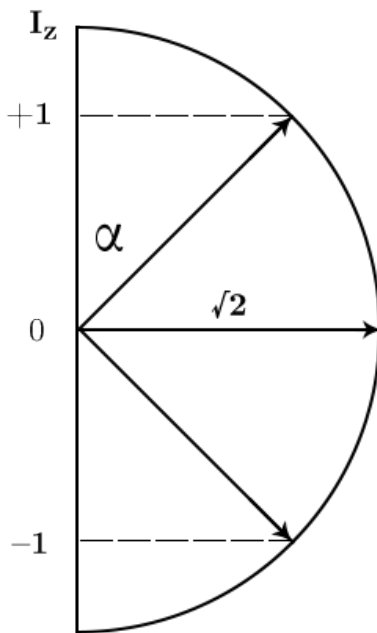
and retains the units of joule per tesla since both G and s are dimensionless. This is known as the *Bohr magneton*. For protons specifically, this quantity is called the *nuclear magneton* and is represented by β_N . Generally

$$\mu = g\beta\sqrt{s(s+1)} \quad (2)$$

describes the dipole of any spinning, charged particle, with the direction of s determining the direction of μ .

1.2 Energy levels

Consider, for example, the $s = 1$ case and, for simplicity, only the z -direction. As we saw in §1.1, $\mathbf{I} = \sqrt{2}$ and $I_z = +1, 0, -1$. We can diagrammatically justify these values (see fig. 1) using the *vector model of spin*.



In case of electrons we have $I_z = 0, +\frac{1}{2}, -\frac{1}{2}$ and, although we have omitted it here, it is important to remember that these stated values of I_z are, in fact, multiples of \hbar , the Dirac constant or the reduced Planck constant.

The energy of such a system is given in terms of the magnetic momentum and the applied field, \mathbf{B} , as $E = \mu \cdot \mathbf{B}$, but we will restrict ourselves, for simplicity again, to the z -direction. The energy may then be written as $E = \mu_z B_z$ and the energy gap between, say, I_z and $I_z + 1$, is given by

$$\begin{aligned} \Delta E &= |E_{I_z+1} - E_{I_z}| \\ &= |g\beta(I_z + 1)B_z - g\beta I_z B_z| \\ &= g\beta B_z \end{aligned} \quad (3)$$

Figure 1: Spin orientations of a nucleus for the $s = 1$ case leaves us with $\mathbf{I} = \sqrt{2}$ (omitting the \hbar factor for simpler representation). This can be drawn as a semi-circle with a radius of $\sqrt{2}$, whose vector arrows can give us $+1, 0$ and -1 as a possible set of components for \mathbf{I} (along the I_z direction in this case). The loci of the two radii vectors corresponding to ± 1 trace out the path of precession of our spinning charge.

in joule, or,

$$\frac{\Delta E}{h} = \frac{g\beta B_z}{h} \quad (3)$$

in hertz. This energy gap, or energy difference, plays a key role in spectroscopy. Whenever a particle's spin transitions from one energy level to another, whether upwards or downwards, it either absorbs or emits energy equal to this energy gap resulting in a corresponding energy spectrum.

The Hamiltonian given by (3) ignores any possible translation under the influence of B_z . We also assume, throughout, that the magnetic field applied is uniform.

The energy gap in hertz is of particular significance since it tells us the frequency of this absorbed or emitted radiation. As you probably realise, we are inching towards categorising this as microwave, infrared etc., but we are yet to get there.

One last point worth noting here is that, quantum mechanically, $s = n$ or $n/2$ for $n \in \mathbb{Z}$. As a result, \mathbf{I} can never be n or $n/2$ and the vector arrows will never point along I_z , to wit, the particle will never spin about the axis but will instead precess about it. The study of this precession leads us to our next discussion.

1.3 Larmor precession

Let us now focus our attention on a precessing nucleus. Its dipole moment is given by (2) under the condition that $\beta = \beta_N$. The frequency related to the ratio of the magnetic moment to the angular momentum is known as the *Larmor frequency*. More accurately,

$$\omega = \frac{\text{Magnetic moment}}{\text{Angular momentum}} B_z = \frac{\mu}{2\pi\mathbf{I}} B_z$$

which, from (2) and the definition of \mathbf{I} , can be written as

$$\begin{aligned} \omega &= \frac{g\beta_N \sqrt{s(s+1)}}{2\pi\hbar \sqrt{s(s+1)}} B_z \\ \Rightarrow \omega &= \frac{g\beta_N B_z}{h} \end{aligned} \quad (4)$$

Comparing with (3) we realise that (4) is really just the separation frequency existing between energy levels². In other words, interactions (exchange of energy) can occur only when the frequency of the incident electromagnetic radiation matches that of the precessing particle. This is where the resonance comes in. At any other (non-resonant) frequency, no energy exchange (read, interaction) occurs.

There are specific terms given to this: if the particle under consideration is a nucleus, we talk about *nuclear magnetic resonance*, often shortened to nmr; and if the particle is an electron, we talk about *electron spin resonance*, or esr.

It is worth mentioning, briefly, how the resonant frequency can be determined experimentally, since we will talk about this idea a lot going forwards. There are two ways of doing this, both of which probably look simpler on paper than they are in practice: we could apply a certain magnetic field to an ensemble of

²The change from β to β_N is simply because we chose to look at nuclei in particular now.

identical nuclei and vary the energy of the radiation incident on them until absorption/emission occurs, or we could fix the energy of the incident radiation and vary the strength of the magnetic field applied over a suitable range until we notice absorption/emission.

In either case, the point of absorption/emission will mark the *resonant frequency* of the chosen nuclei. The ensemble is itself a practical consideration: the absorption/emission will be more pronounced than if we had a single nucleus.

Here is a helpful summary of what we discussed so far: we start off with an ensemble of atoms or molecules with nuclear/electronic spins aligned in arbitrary directions, then we apply an external magnetic field that results in the spins all precessing about an axis either parallel or antiparallel to the field direction (but the spins themselves are never aligned along the field). They precess with the Larmor frequency (4) and they take a small amount of time between when the field is applied and when their precession axes are aligned with the field (we will discuss this in the coming sections).

1.4 Population, or why absorption is favoured over emission

The presence of some ΔE means we can almost always identify a lower and an upper energy level. ΔE will be the difference between them. For a given ΔE then, we can write the ratio of the number of particles at these levels, called their population, N , is given by

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp\left(-\frac{\Delta E}{kT}\right)$$

and, on plugging in the appropriate values, the ratio turns out to be roughly one³. The actual value, in an ensemble of nuclei, is about 128 in two-million [B2], which is an order of $\approx 10^{-5}$ or 10^{-6} . This is problematic since it means only about 0.06% of all nuclei in a sample can be detected through NMR. The vast numbers of nuclei mean, on the other hand, that this is much less restrictive for practical purposes than it appears to be.

However, under the experimental conditions (described in §1.3) that we used to determine Larmor frequency, a characteristic property, one that might even be commonsensical, is that the probability of energy transition between spin states is proportional to the population of the initial state. The greater the population of the initial state the more likely it is that a transition will occur from that state.

If the ratio of populations in two energy levels is one, i.e. the upper and lower energy level populations are alike, then the occurrence of transitions upwards and downwards must both be equally likely. If we start from equilibrium, however, such as from a normal room temperature state or the stp state, the system is going to be in the lowest energy state and will therefore see a greater population in the

³The energy width, ΔE , for electrons and the nuclei is 7×10^{-26} J and 6×10^{-24} J respectively.

lower energy states by and large, resulting in the predominance of upwards spin transitions, meaning a slightly greater favour exists towards absorption.

As this goes on, though, the ratio tends to one and no more absorption occurs since both absorption and emission take place at the same rate. Such a system is said to be *saturated*.

2 Perturbations

That absorption results in excitation should be clear from our previous discussion. With the right interaction, i.e. in the right radiation environment or magnetic field, the excited atoms and molecules start to lose energy that they emit. This can be captured as an *emission spectrum* and is called a *nuclear induction spectrum* since the emission does occur without external (induced) interaction.

2.1 Time evolution of spin

The ideas discussed up to (and in) §1.3 were somewhat elementary⁴ and we will have to go into them in greater detail to better understand the processes occurring, specifically with respect to the x and y axes. We used β to reduce μ in §1.1 but we can also reduce it using the gyromagnetic ratio, γ , as our constant of proportionality:

$$\mu = \frac{Gq}{2m} \hbar s \sqrt{s(s+1)} = \gamma \mathbf{I}$$

If the energy, as we saw in §1.2, is given by the Hamiltonian, $H = \mu \cdot \mathbf{B}$, we can incorporate spins (whose information is contained in \mathbf{I}) and write this as

$$H \text{ (or } E) = \gamma \mathbf{I} \cdot \mathbf{B} \quad (5)$$

The wave function (of the nucleus, since we have decided to focus on it for now) can be written as a linear combination of the spin up and down states:

$$\phi = a \uparrow + b \downarrow \quad (\text{or we can use spinors}) \quad \phi = \begin{pmatrix} a \\ b \end{pmatrix}$$

with \uparrow referring to a spin of $\hbar/2$ in the z direction (given that we apply B_z) and \downarrow referring to a spin of $-\hbar/2$ opposite to B_z .

The three components of spin, I_x , I_y and I_z , are now $\hbar/2$ times the three Pauli spin matrices, σ_x , σ_y and σ_z respectively. If we split the applied magnetic field into two components,

$$\mathbf{B} = B_0 \hat{z} + B_1 (\hat{i} \cos \omega t - \hat{j} \sin \omega t)$$

where B_1 is called the perturbing field and tells us how the applied \mathbf{B} , being in the z direction, weakly affects the x and y components of spin. Applying the Pauli

⁴The whole idea of having a bar magnet analogy for a precessing spin vector was to ease ourselves out of our classical physics comfort zone.

spin matrices, $I_j = (\hbar/2) \sigma_j$, and the above equation into (5) we end up with the Hamiltonian

$$H = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 e^{i\omega t} \\ \omega_1 e^{-i\omega t} & -\omega_0 \end{pmatrix} \quad (6)$$

where $\omega_0 = \gamma B_0$ and $\omega_1 = \gamma B_1$. And, from what we saw in (4) earlier, ω_0 is nothing but the Larmor frequency.

In the unperturbed case we may write this using the unsteady Schrödinger equation, $i\hbar \dot{\phi} = iH\phi$, and ignoring the ω_1 components, as

$$i\hbar \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

with $\phi = a \uparrow + b \downarrow$ where $a = a_0 e^{i\omega t/2}$ and $b = b_0 e^{-i\omega t/2}$ for a_0 and b_0 being the values at $t = 0$. The fact that the probability, $|\phi|^2$, has $|a|^2 = |a_0|^2$ and $|b|^2 = |b_0|^2$ means the probability of measuring \uparrow and \downarrow remains constant with time. The spin up and down along S_z for an applied B_z are the energy (eigen)states for the steady system.

What about the x and y axes then? This is where our perturbation comes in. Whereas in the steady state we ignored the ω_1 components (or the B_1 term into which \mathbf{B} splits) we need to include them when we account for perturbation:

$$i\hbar \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 e^{i\omega t} \\ -\omega_1 e^{-i\omega t} & -\omega_0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

The equation becomes complex and we will not go over the exact solution since it is outside the scope of these notes⁵, but we will focus on its important results. The eigenvalue contains the term

$$f = \sqrt{\frac{\omega_1^2}{(\omega - \omega_0)^2 + \omega_1^2}} \quad (7)$$

known as the *resonance factor*. This is maximum when $\omega = \omega_0$.

It also gives the values for a and b as

$$a = \left\{ a_0 \left[\cos \left(\frac{\omega_1 t}{2f} \right) - if \frac{\omega - \omega_0}{\omega_1} \sin \left(\frac{\omega_1 t}{2f} \right) \right] + b_0 if \sin \left(\frac{\omega_1 t}{2f} \right) \right\} e^{i\omega t/2}$$

and

$$b = \left\{ b_0 \left[\cos \left(\frac{\omega_1 t}{2f} \right) - if \frac{\omega - \omega_0}{\omega_1} \sin \left(\frac{\omega_1 t}{2f} \right) \right] + a_0 if \sin \left(\frac{\omega_1 t}{2f} \right) \right\} e^{i\omega t/2}$$

for a_0 and b_0 , the coefficients of the \uparrow and \downarrow states at $t = 0$.

⁵To solve this equation, substitute $a = \alpha e^{i\omega t/2}$ and $b = \beta e^{i\omega t/2}$ and find the eigenvalues.

Now think of nuclei starting in the \downarrow state. That is, $|b_0| = 1$ and $a_0 = 0$. The probability that such a nucleus may be found in a higher energy level is non-zero, i.e. it is no longer a steady state:

$$|a|^2 = f^2 \sin^2 \left(\frac{\omega_1 t}{2f} \right)$$

and likewise for $|b|^2$. The graph of such a function looks like a positive sine wave (lying only in the first quadrant), implying that the nucleus flip-flops constantly over time between a certain ground state and a probable higher energy state. The frequency of this flip-flopping is known as the *Rabi flopping frequency*.

3 Relaxation

When an external magnetic field, B_z (say), is applied to a nuclear or electronic system, the spins to orient themselves (as shown in fig. 1) along the field direction. In this process some of their energy is lost either to the surroundings, such as to the lattice, or to other nuclei/electrons. The time it takes for $(1/e)^{\text{th}}$ of the excess (excited state) energy ($\approx 37\%$ of it) to be dissipated in this way through energy-sharing is called the *relaxation time*. The process of sharing energy with other nuclei or the lattice is known as the *relaxation process*. During relaxation, the spin returns to equilibrium.

When this sharing of excess energy occurs between nuclei or electrons, the process is termed *spin-spin relaxation*, and when it occurs between an atom and the lattice that it is a part of, the process is termed *spin-lattice relaxation*.

3.1 Rate of magnetisation

Time for another summary: atoms with arbitrarily aligned spin vectors in the absence of any external fields line up parallel to the direction of an applied magnetic field. This is known as *bulk longitudinal magnetisation*. The population of nuclei in the lower energy level (N_l) is ever so slightly greater than the population in the higher/upper energy level (N_u). Going further, we realise that the magnetisation (M_z) must naturally be proportional to this population difference:

$$M_z \propto N_l - N_u$$

If a transition has to occur from u to l , as discussed in §1.4, the transitions from each energy level must be proportional to the initial population of that energy level. If we define some rate constant, H , then the transitions from u result in a rate of population loss given by HN_u . This constant is the same for l , i.e. the population loss occurs at a rate of HN_l , since we assume that whatever is lost from u is gained by l and vice versa, depending on whether there is relaxation or excitation. Let us say l loses to u . The rate of loss of population is then given by

$$\frac{dN_l}{dt} = -HN_l + HN_u$$

Likewise we have an equation for loss from u as well.

The problem with this approach is, this suggests that at equilibrium, both rates of population loss are zero and $N_l = N_u$, which we know is untrue. We can solve this by introducing a population deviation: if the equilibrium population was N_l^0 , then the current population will be $(N_l - N_l^0)$. So the correct equation is

$$\frac{dN_l}{dt} = -H(N_l - N_l^0) + H(N_u - N_u^0)$$

and similarly for \dot{N}_u too.

The rate of magnetisation is now

$$\begin{aligned} \frac{dM_z}{dt} &= \frac{d(N_l - N_u)}{dt} = [-H(N_l - N_l^0) + H(N_u - N_u^0)] - [-H(N_l - N_l^0) + H(N_u - N_u^0)] \\ &= -2H(N_l - N_l^0 + N_u - N_u^0) = -2H(M_z - M_z^0) \end{aligned}$$

(The last step comes from the proportionality $M_z \propto N_l - N_u$).

Absorbing the constants into a term called the *rate constant*, R , we have

$$\frac{dM_z}{dt} = -R(M_z - M_z^0) \quad (8)$$

with $M_z \equiv M_z(t)$. This equation tells us three important things:

1. At equilibrium there is no rate of change of magnetisation (and why should there be, since It is equilibrium after all).
2. The more the nucleus gets magnetised away from its equilibrium position, the slower it gets magnetised.
3. The negative sign means the rate of magnetisation will work against the nucleus, trying to return it to equilibrium.

In the end, these are things we expected to see and we now have mathematical proof of it.

3.2 Spin-Lattice relaxation

If we integrate (8) over time, we get

$$\begin{aligned} \int \frac{dM_z}{(M_z(t) - M_z^0)} &= - \int dt R \\ \Rightarrow \ln(M_z(t) - M_z^0) &= -Rt + \eta \end{aligned}$$

where the integration constant, η , may be determined at $t = 0$ as $\ln(M_z(0) - M_z^0)$ giving us

$$\begin{aligned}\ln(M_z(t) - M_z^0) &= -Rt + \ln(M_z(0) - M_z^0) \\ \ln\left(\frac{M_z(t) - M_z^0}{M_z(0) - M_z^0}\right) &= -Rt \\ \frac{M_z(t) - M_z^0}{M_z(0) - M_z^0} &= \exp(-Rt) \\ \therefore M_z(t) &= (M_z(0) - M_z^0) \exp(-Rt) + M_z^0\end{aligned}\quad (9)$$

What (9) tells us is that the magnetisation returns⁶ from whatever it was at some initial time $t = 0$ to its equilibrium state, M_z^0 , exponentially. The factor $t = R^{-1} = T_1$, the time constant of the exponential, is called the *spin-lattice relaxation time*.

3.3 Chemical shift

We have seen that most nuclei have a magnetic moment ($\mu = \gamma \mathbf{I}$) that is related to various energy levels (6) depending on the applied magnetic field that the nucleus is placed in. But all of this was for an isolated nuclei. We now have to discuss how these properties of a nucleus are affected by the presence of an electron and how it can help us determine molecular structures.

Often the resonant frequency, $\nu_r \propto \omega = \gamma \mathbf{B}_z$, and the applied magnetic field, B_z , at which resonance occurs, both need to be stated. To simplify this representation, we state the resonant frequency with respect to a reference compound. For nuclear resonance experiments, a commonly used chemical compound is tetramethylsilane (TMS), with (say) a resonant frequency of ν_{tms} , giving us the relationship

$$\delta = \frac{\nu - \nu_{tms}}{\nu_{tms}}$$

where δ is called the *chemical shift* of the sample with resonant frequency, ν . The chemical shift is usually an extremely small quantity, as a result of which it is multiplied by 10^6 and stated in terms of parts per million (ppm).

Given that the chemical shift of an atom or molecule is related to the same parameters as its resonant frequency, knowing the chemical shift can also help us determine various nuclear properties.

Much like nuclei, we saw earlier that electrons too have a magnetic field and the interactions between the electronic and nuclear magnetic fields can give rise to various different chemical shifts. A compound can exhibit different (and different numbers of) chemical shifts, and this is usually characteristic of the molecule

⁶Possibly even after excitation: $t = 0$ does not imply ground state; we can always choose to start our clock after exciting the nuclear spin.

since it is a direct effect of the electron distribution about its atoms, which means chemical shifts can help us model the structure of molecules.

3.4 Spin-spin interaction

An important parameter in any NMR experiment is the shielding constant, σ . The application of a magnetic field causes the electrons around a nucleus to be induced with a magnetic field, B_1 , that causes a change in the localised field, B_{local} , as

$$B_{local} = (1 - \sigma) B_1$$

and, substituting this equation into $\nu = \gamma B_{loc}/2\pi$, we end up with $\omega = \gamma B_1(1 - \sigma)$.

The energy of interaction is then $-E = h\nu_A m_A + h\nu_B m_B$ for two nuclei, A and B, with m taking values 0 and ± 1 in each case.

Besides this, interaction between nuclei is also possible, being given by

$$-E = h\nu_A m_A + h\nu_B m_B + hJ_{AB} m_A m_B$$

Generally, hydrogen atoms contribute greatly to chemical shifts. In fact,

1. The same nucleus, in the presence of different neighbours, gives rise to peaks (at some ppm) at different positions (hence *shifts*).
2. The area of a peak is directly proportional to the number of equivalent nuclei.

For an influence to be substantial, it must be $\approx 0.01 \mu\text{T}$ or greater.

4 NMR of an ethanol molecule

We saw in §3.3 etc. that two atoms or electrons close enough to each other can exert an influence on each other's magnetic fields and, in turn, on each other's spectral lines. We now examine this using ethanol as an example.

The three hydrogens in CH_3 are equivalent magnetically and chemically. We focus, normally, on the hydrogen atoms which are most responsive to induced energy fluctuations. An ethanol molecule is of the form A_3B_2 , where the subscripts refer to the number of hydrogen atoms, i.e. CH_3 and CH_2 respectively.

Consider two lines, each representing the A_3 and B_2 groups. That is, we start with an uncoupled system and proceed as follows:

1. The A and B lines each split into a doublet (two possible spins) at every step.
2. The A line splits twice (due to B_2) and the B line splits thrice (due to A_3).
3. The first doublet split is uncoupled. But the next split sees each of the first two doublet lines splitting into two and the middle two lines overlap.

4. For the third split, the three lines each split into doublets and the splits of the middle line couple with one line each of its neighbours giving rise to four peaks.
5. The process follows Pascal's triangle going 1-1 and 1-2-1 for A_3 and going 1-1, 1-2-1 and 1-3-3-1 for B_2 . B goes three splits deep for reasons explained in point 2 above.
6. This leaves us with four peaks for B, i.e. the CH_2 component, and three peaks for A, i.e. the CH_3 component.
7. In reverse, the fact that we have $n = 3$ peaks means that component must be bonded to another component with $n - 1 = 2$ H atoms. Similarly, the fact that we have $n = 2$ peaks for CH_3 means it is bonded to a component with $n - 1 = 2$ H atoms and we know this is true, i.e. it is CH_2 .
- 8.

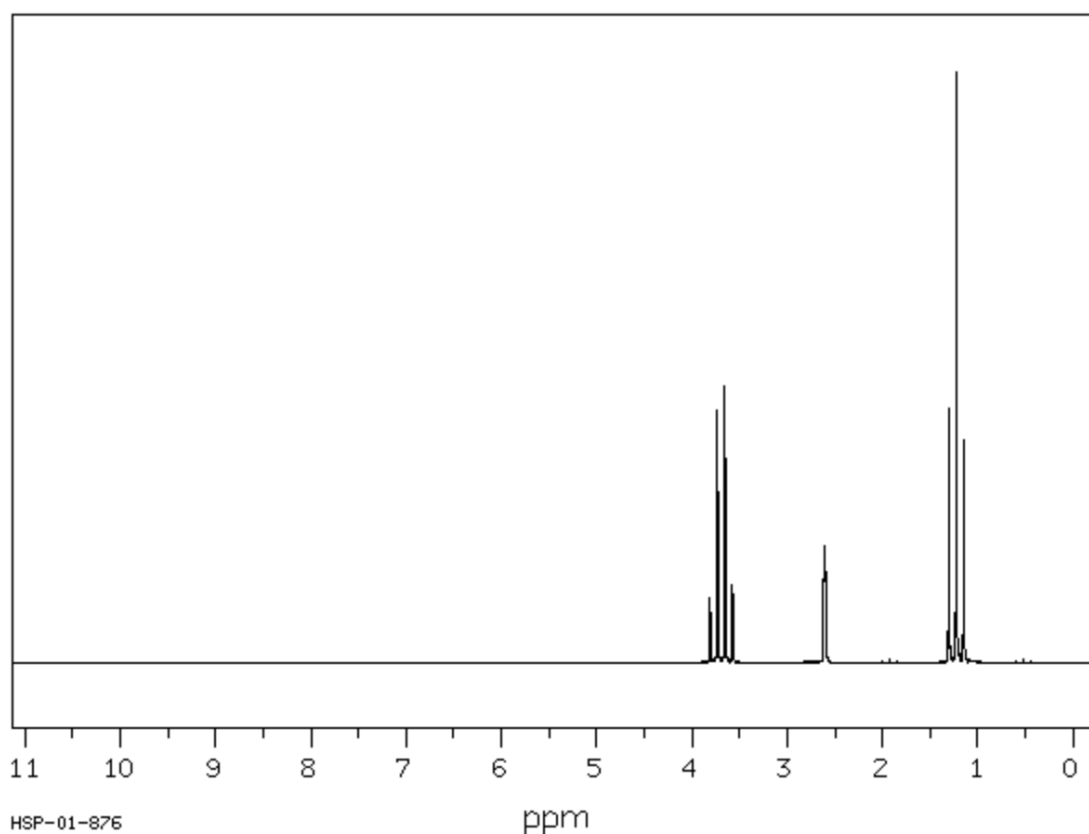


Figure 2: NMR spectrum of a $\text{CH}_3\text{CH}_2\text{OH}$ molecule. Courtesy, SDBS.

Referring to the picture of an actual HNMR spectrum for ethanol in fig. 2 we see that the CH_2 peaks have a huge chemical shift of ≈ 4 ppm. This is due to the leftover bond of the C atom being bonded to the electronegative O atom. Hence the $\text{CH}_3\text{—CH}_2\text{—OH}$ structure of ethanol (and vice versa we can form an educated guess as to what the spectrum would look like for ethanol, knowing its structure).

5 Fourier Transforms in NMR

5.1 Pulses

In three dimensions, the loci of the spin vector in fig. 1 forms a cone. The bulk magnetisation of this cone, as discussed in 3.1 and 3.2 is along the direction of the applied field. More often than not it points in the same direction as the applied field too, although sometimes it is antiparallel to it. One of these (the parallel one by convention) is an *up* spin and the other is a *down* spin.

Suppose a field B_x is now applied, \mathbf{M} , being of gyroscopic nature, starts precessing around the applied B_x field.

Say we start with an applied field of some B_z T and a precession frequency ν_i . Applying $B_x = \alpha B_z$ T, i.e., some fraction, α of B_z , will then leave us with a frequency of $\alpha\nu$ with which \mathbf{M} precesses around B_x . That is, \mathbf{M} will now take $(\alpha\nu)^{-1}$ s to precess once about the x axis.

Suppose we only apply B_x for one-half of $(\alpha\nu)^{-1}$ s, \mathbf{M} will only complete half a precession, going from its position on the $\pm z$ axis to the $\mp z$ axis. This is called a 180° pulse. Suppose we apply it for only one-quarter the time period of one full precession, \mathbf{M} will go from its position along the $\pm z$ axis to the x - y plane. This is called a 90° pulse.

Once B_x is taken away, the influence of B_z dominates (in fact the applied B_z is all there is left, ideally) and \mathbf{M} once again resorts to gyrating, but this time about the z axis, as it slowly loses energy (relaxes) and spirals back to its original position, the position where our spin vectors formed the conic loci that we started with.

The signal output during such relaxation following the application of a perpendicular pulse is what becomes the subject of Fourier Transformation spectroscopy.

5.2 A note on Fourier Transform spectroscopy

Generally, picking up emission spectra by sweeping a detector across the electromagnetic spectrum is slow. Further, this too could only be done across the visible and UV ranges since technology did not permit anything else. We turned to Fourier transforms (FT) to overcome these drawbacks.

Assuming (ideally) that the emission spectrum is a sine/cosine wave, a detector responds to this input by giving out a sine/cosine wave as well. This would be against time on the x axis. Now suppose that we have another sine/cosine wave slightly out of step with the first, the detector sees not two but one combined wave. The amplitude of the combined wave increases as the two waves constituting it become in-phase and vice versa⁷.

⁷The associated diagram has been omitted here for good reason: it looks exactly like the rather

We are now left with having to find the frequency and the amplitude of each of the two waves (or more if there were more waves initially). Generally, we need to solve for $2n$ variables when we have the combined effect of n waves.

The FT of a time-varying curve is a plot (usually of two sharp lines) on the amplitude v. frequency graph. FT takes us from the ‘time domain’ to the ‘frequency domain’. For now⁸, the general trend to keep in mind is that the greater the number of frequencies in the original wave, the faster its FT decays. We use this relationship as a start to reverse the combination process using FT to arrive at the constituent waves. In an FT, all the information contained in the original wave is still left intact, although only implicitly.

...

familiar pulsating interference pattern obtained by superimposing two waves.

⁸The details of FT are part of the 403 curriculum.

Appendices

A Some useful results

- 1.

B Bibliography

1. Colin Banwell and Elaine McCash, *Fundamentals of molecular spectroscopy*, 5th edition (McGraw Hill Education, 2014).
2. Thomas L. James, *Fundamentals of NMR*, Dept of Pharmaceutical Chemistry, UC San Francisco, 1998. Available at <https://goo.gl/MjerdC>.