

Week 9

???

9.1 NMR Spectroscopy

- 2/28:
- Announcements.
 - Second HW is due Friday at noon.
 - We should have everything we need for it after today.
 - The final will be from 8:00-9:20am on Tuesday.
 - It is solely on Anderson's lectures (it's just a second midterm).
 - Not open note. Shouldn't be too many things to memorize: $g\beta H$, magnetic moment formulas, gnarly stuff like the EXAFS formula we don't need to have memorized.
 - We now start the lecture.
 - Relation between EPR and NMR.
 - There are many parallels.
 - NMR is more common than EPR, and much more complicated.
 - We will start with some simpler NMR examples to build a foundation.
 - NMR background/underlying principles.
 - Like an electron has $S = \pm 1/2$, nuclei also have a given spin I .
 - While a single electron can only be $S = 1/2$, a single nucleus can be $I = 0, 1/2, 1, 3/2, \dots$
 - A few rules about I .
 1. A nucleus with an odd mass number has a half-integer spin.
 2. A nucleus with an even mass number and an odd atomic number has an integer spin.
 - Examples: Deuterium, ^{14}N , etc.
 3. A nucleus with an even mass number and an even atomic number has zero spin.
 - We now investigate the **Zeeman splitting** of an $I = 1/2$ nucleus.
 - Like electron spins in EPR, nuclear spins align with or against applied magnetic fields.
 - The splitting is as in Figure 6.2a.
 - We know that $\Delta E = \gamma \hbar B_0$, where γ is the gyromagnetic ratio and B_0 is the applied field.
 - The notes also consider the $I = 1$ case.

- **Zeeman splitting:** The energy difference between a spin aligned with and against a magnetic field.
- **Larmor frequency:** The frequency of electromagnetic radiation that induces a spin flip. *Also known as resonant frequency. Denoted by ν_0 . Given by*

$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

- Takeaway: A nucleus's resonant frequency is determined by γ and B_0 .
- Typical values for B_0 , γ , and ν_0 .
 - B_0 : 1.4-14 T.
 - ν_0 : 60-600 MHz, though we can go higher.
- Example: The Larmor frequency of some common NMR nuclei under a 9.4 T magnet.
 - ^1H : We have that

$$\nu_0 = \frac{\gamma B_0}{2\pi} = \frac{(26.8 \times 10^7 \text{ T}^{-1} \text{ s}^{-1})(9.4 \text{ T})}{2\pi} = 4.0 \times 10^8 \text{ s}^{-1} = 400 \text{ MHz}$$
 - ^{13}C : 100 MHz.
 - ^{31}P : 162 MHz.
 - ^2H : 61 MHz.
- The key limitation of NMR is *sensitivity*.
 - The sensitivity for NMR is pretty atrocious. This is because all relevant energies are pretty small (radiofrequency region) and thus hard to detect.
 - Quantitatively, sensitivity is proportional to the magnetogyric ratio cubed times the number of nuclei (equivalently, the concentration).
 - This is why MRI is really tough.
 - Also why you need really big magnets for NMR.
 - Additional limitation: The signal increases by the square of the applied field strength.
 - How is this limiting??
- Aside: Hyperpolarization for NMR.
 - Goal: Enhance signal intensity by further polarizing nuclear spins.
 - Essentially, if you have four particles in the spin ground state and three in the spin excited state, exciting one of the ground state spins won't cause a significantly measurable change. However, if you *hyperpolarize* the system so that there are, for example, six particles in the ground state and only one in the excited state, then inducing an excitation causes a far greater change.
 - You can do this with **dynamic nuclear polarization**, particularly **triplet DNP**.
 - Also something akin to ENDOR with Zeeman splitting and microwaves to get a huge polarization buildup. Nobody has pulled this off *in situ* yet, but that's a goal.
 - There's a scientist in Texas (possibly Christian Hilty??) looking into **parahydrogen**.
- **Dynamic nuclear polarization:** A technique for hyperpolarization involving the transfer of spin polarization from electrons to nuclei. *Also known as DNP.*
- **Triplet DNP:** Photoexciting a singlet to a triplet and then harnessing intersystem crossing to selectively populate the $M_s = 0$ state before transferring this polarization to the nuclei.
- **Parahydrogen:** The spin isomer of hydrogen with the two proton spins aligned antiparallel.

- The key advantage of NMR is *resolution*.
 - The specific frequency of a given nuclei is often exquisitely sensitive to its chemical environment.
 - NMR is a Qbit technique: We're using the nuclear spin as a quantum sensor for the system.
 - This really comes down to shielding.
- Shielding.
 - A useful (but technically inaccurate) classical analogy.
 - If we have an electron and we apply a magnetic field H_0 to it in the z -direction, our electron will begin to circulate around it and induce a magnetic field in the opposite ($-z$) direction.
 - The angular frequency ω_1 equals $eH_0/2m_e$.
 - Takeaway: Applied magnetic fields result in slight changes depending on the nuclear environment.
 - Because nuclei have very small energy splittings, we can resolve very small energy changes in our NMR spectra; this is the origin of the ppm splitting we're familiar with.
- Shielding originates primarily from three places.
 1. Nucleus: Specifically how electron-rich or -poor it is.
 2. Solvent: The electrons therein will strongly influence the magnetic field felt by the nuclei.
 3. Chemical environment: Bonds, functional groups, other nuclei, electrons, etc.
- Parts 1 and 3 (electron richness and nuclear factors) are related to each other and are important.
 - We usually correct for part 2 using a known solvent shift and an internal standard.
- Measuring and describing the **chemical shift**.
 - 1 ppm is a shift in the resonant frequency of a given nucleus. Specifically,

$$1 \text{ ppm} = \frac{\nu_1 - \nu_{\text{ref}}}{\nu_0 \cdot 10^6}$$
 - ν_1 is the measured Larmor frequency for a given nucleus.
 - ν_{ref} refers to a single compound that we reference against, e.g., TMS.
 - ν_0 is the predicted Larmor frequency for said nucleus based on its γ .
 - Thus, at 60 MHz (for example), 1 ppm = 60 Hz.
 - Chemical shift lingo.
 - More *shielded* nuclei require *higher fields*, have a *lower chemical shift*, and are positioned relatively *upfield*.
 - More *deshielded* nuclei resonate at *lower fields*, have a *higher chemical shift*, and are positioned relatively *downfield*.
- Line widths.
 - Recall from EPR: τ denotes **lifetime**.
 - We're limited by the Heisenberg uncertainty principle

$$\Delta E \Delta t = \hbar \quad \Longleftrightarrow \quad \Delta E = \frac{\hbar}{\tau}$$
 - It follows that a long lifetime τ gives you a small ΔE and a sharp line.
 - Typical lifetimes: $\tau_{\text{NMR}} = 1 - 100 \text{ s}$, $\tau_{\text{rot}} = 10^{-9} \text{ s}$, $\tau_{\text{vib}} = 10^{-6} \text{ s}$.
- **Lifetime**: The time that a signal will remain polarized. *Denoted by τ , Δt .*

- **Chemical shift.** Denoted by σ . Given by

$$\sigma = \sigma_d + \sigma_p + \sigma_R + \sigma_e + \sigma_{\text{int}}$$

- Each of the five variables represents a contribution to the nucleus from some magnetic component.
- σ_d is our diamagnetic term.
 - Usually positive, so it causes signals to shift downfield.
 - Most important for ^1H NMR.
 - Correlates with the s -electron density at the nucleus; thus can give us a direct readout of the electron density of the nucleus. Also, more electron rich means more shielded.
- σ_p is our paramagnetic term.
 - Usually negative, so it causes signals to shift upfield.
 - Most important for heavier elements (e.g., ^{31}P , ^{119}Sn , etc.).
 - A large term in general (larger than σ_d ??).
 - Distinct usage from paramagnetic *samples* (diamagnetic nuclei can have paramagnetic terms).
- σ_R is for ring currents.
 - Consider a benzene ring for instance. The large induced ring current creates two cones of positive shift and negative regions outside.
 - Other multiple bonds also contribute in various ways.
 - For more details, see the discussion associated with Figure 9.1 below.
- σ_e is for electric fields.
- σ_{int} is for intermolecular effects.
- The latter three are often combined into σ_N .
- Recall...
 - $\sigma > 0$ means an upfield shift (lower ppm)
 - $\sigma < 0$ means a downfield shift (higher ppm).
- Benzene ring current effects.

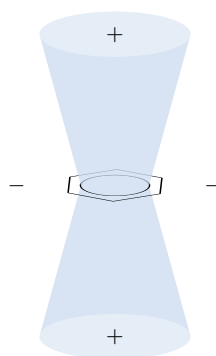


Figure 9.1: The effect of the ring current in benzene.

- It's a fake ring current.
- It's a quantum mechanical effect from the interaction of the magnetic field with the degenerate π system.
- But still, it's a useful classical picture.
- Something with Zwitterionic character may be able to give you a "real" ring current.

- Most of us have probably seen some of this before. But now we'll move onto something we haven't seen: Heavier nuclei.
- With heavier nuclei, σ_p dominates.
 - The spread is much bigger than with ^1H NMR.
 - σ_d is still there but is typically small and much more constant.
- Contributions to σ_p .
 - The orbital angular momentum, largely from the p, d, f orbitals.
 - We do *not* consider electron spin here, just orbital spin.
 - The magnitude of σ_p is controlled by mixing.
 - Mixing in other states mixes in their angular momentum.
 - Most common when there is lowered symmetry, low-lying excited states, and lots of EWGs.
 - Mathematically, we describe σ_p with the **Ramsey equation**.
- **Ramsey equation:** The equation giving the relative magnitude of σ_p . *Given by*

$$\sigma_p \propto - \left[\frac{1}{E_{\text{es}}} - E_{\text{gs}} \right] \left\langle \frac{1}{r^3} \right\rangle [\pi\text{-bonding term}]$$

- es denotes the excited state.
- gs denotes the ground state.
- Rationalizing the energy separation (first) term.
 - Alkanes have strong bonds and no low-lying excited states, while alkenes will have lower excited states.
 - Thus, σ_p is greater for alkenes than alkanes, for example.
 - Takeaway: Unsaturation typically leads to larger paramagnetic terms.
- Rationalizing the $1/r^3$ term.
 - It is related to how close electrons are to the nucleus.
 - EWGs decrease electron-electron repulsions, moving electrons closer to the nucleus, thus increasing σ_p and shift heavier nuclei more downfield.
- The π -bonding term is complicated; we will not discuss it further.
 - It is summed over all relevant interactions.
 - Depends on the system at hand.
- Thus, the chemical shift can provide important chemical information.
- However, it can also provide other useful information, such as on **coupling**.
- **First order system:** A system in which the spread of the nuclei is much higher in ppm than the coupling constant, i.e., in which the following equation is satisfied.

$$\Delta\nu = |\nu_A - \nu_X| \gg J_{AX}$$

- ν_A is the frequency/ppm shift of nucleus A.
- ν_X is the frequency/ppm shift of nucleus X.
- J_{AX} is the coupling constant between A and X.
- Coupling is relatively simple in first order systems.
- We will not get into second order splitting, which occurs when the above inequality is not satisfied and is very complicated.

- Example: Consider the following molecule, which has two nuclei of interest (each with $I = 1/2$).

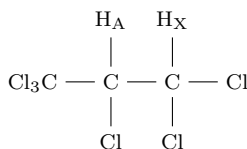


Figure 9.2: NMR coupling of two neighboring nuclei.

- Comments on the molecule.
 - A nasty molecule chemically; would probably destroy the ozone layer and such.
 - Only two spin-active proton nuclei.
 - We stick on the CCl_3 group to put the two protons in different chemical environments (gets rid of the reflection plane that would be there if CCl_3 were just Cl).
- Let's look at the peak structure of A first.
 - X can have one of two values: $M_I = \pm 1/2$.
 - Thus, A can be in two marginally different chemical environments, and hence should appear as a doublet.
- The same is true of X.
- Thus, the full ^1H NMR spectrum should consist of a pair of doublets.
- There are two types of coupling.
 1. **Dipolar coupling.** Occurs “through space.”

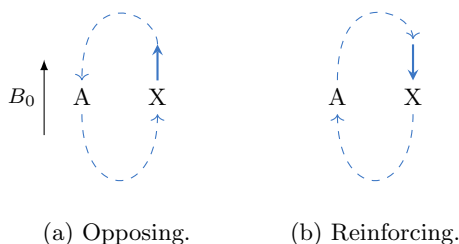


Figure 9.3: Dipolar coupling.

- Having a nearby element X that is magnetized is like bringing an additional magnet close to A, affecting its chemical environment.
- X can oppose or reinforce the applied magnetic field B_0 at A (see Figure 9.3).
- The field is given by

$$B_{AX} = \gamma_A \gamma_X \cdot \frac{3 \cos^2 \theta - 1}{r_{AX}^2}$$

- γ 's are gyromagnetic ratios.
- r_{AX} is assumed to be big; thus distance is important.
 - Is the exponent a 2 or a 3??
- θ is the angle between the two nuclear spin axes (of A and X).
- What exactly is this field??
- Dipolar coupling averages to zero in solution but still affects relaxation.
- When ^{31}P NMR is run, it is done proton decoupled to get bigger shifts.
 - How is this relevant??

2. Scalar coupling. Occurs “through bond.”

- Dominates in solution.
- We have that

$$E_{\text{scalar}} = hJM_{I,A}M_{I,X}$$

- J is our coupling constant in Hertz.
- Notes on J .

- Can be positive or negative, but in most cases, we don’t care what its sign is. We can determine this experimentally if we need it, though.
- Proportional to the s -character of the bond.
- Independent of H , so the same on all instruments.

- Dipolar coupling example: The $\text{C}_3\text{Cl}_6\text{H}_2$ doublets.

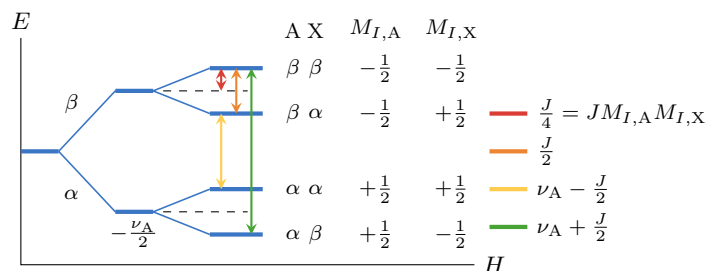


Figure 9.4: Formation of a pair of NMR doublets.

- Analysis of the first splitting (originates from the applied magnetic field).
 - Of the left two connecting lines, the lower one is referred to as the **α -manifold** and the upper one is referred to as the **β -manifold**.
 - What exactly are these?? Relation to α, β designation of spin from Labalme [1].
 - The energy of the upper state at the end of the β -manifold is given by

$$E = -\frac{\gamma}{2\pi}B_0(1 - \sigma_A)M_{I,A} = -\nu_A M_{I,A} = \frac{\nu_A}{2}$$

- There is a sign flip in the last equality because $M_{I,A}$ is negative.

- Per the definitions of the green and yellow gaps in Figure 9.4, the energy difference between the two states at the end of the α - and β -manifolds will just be ν_A .
 - Takeaway: In the absence of coupling, one peak corresponds to A at the frequency ν_A .
- We now factor in the second splitting (originates from coupling).
 - We label the resultant states with a second set of β 's and α 's.
 - The signs are related to the signs of the fields from the other nucleus.
 - Selection rule: $\Delta M_I = \pm 1$.
 - Thus, only $\alpha\alpha \rightarrow \beta\alpha$ (yellow) and $\alpha\beta \rightarrow \beta\beta$ (green) are allowed.
 - From the frequencies of these two transitions, the splitting in the doublet is

$$J = \left(\nu_A + \frac{J}{2} \right) - \left(\nu_A - \frac{J}{2} \right)$$

- J is typically small compared to ν_A .
 - Takeaway: Factoring in coupling, we will observe a *doublet* centered around ν_A . However, ν_A is no longer an allowable transition; only the yellow and green ones are (note that these are centered around ν_A). The peaks corresponding to the yellow and green transitions will be separated by J , as described above.

- Scalar coupling example: A diatomic molecule.



Figure 9.5: Scalar coupling in a diatomic molecule.

- How scalar coupling works in more detail (very complicated, but a nice simplistic picture).
 - Empirical observation: Electrons and nuclei prefer to align antiparallel.
 - Notice how each nucleus in Figure 9.5 is aligned antiparallel to the nearest electron.
 - Naturally, the electrons are also aligned antiparallel since they are in the same bonding orbital.
 - Thus, the neighboring nuclei prefer to be anti-parallel because of the indirect interaction chain of nucleus-electron, electron-electron, electron-nucleus.
- At this point, some of our previous observations should make more sense.
 - Example: Scalar coupling scales with s -character because greater s -character maximizes electron-nucleus interactions.
- We have no way of measuring the sign of J in an NMR experiment. In order to do the transition, we can see why s -character matters: The more the electrons interact with the nucleus (higher s -character means closer to nuclei), the stronger the effect will be.
 - What is the effect?? What is scalar coupling? How does it show up? How do all of the equations fit together?
- On the sign of J for neighboring nuclei.
 - If we have a single bond, then $J > 0$ and antiparallel spins are more stable.
 - If we have a double bond, then $J < 0$ and parallel spins are more stable.
 - In general, an odd number of bonds means $J > 0$ and an even number of bonds means $J < 0$.
 - > There are many exceptions, though.
- On the magnitude of J .
 - 2-bond: $^2J_{\text{HH}} = 10 - 25$ Hz. Are these values negative?? sp^2 can be +41 Hz.
 - 3-bond: $^3J_{\text{HH}} = 0 - 25$ Hz.
- Coupling constants and electronic proximity to the nucleus.

Compound	Hybridization	J_{CH} (Hz)	EWG	χ	J_{CH} (Hz)
Ethane	sp^3	125	$\text{CH}_3\text{-F}$	4.0	150
Ethene	sp^2	156	$\text{CH}_3\text{-Cl}$	3.2	150
Benzene	sp^2	159	$\text{CH}_3\text{-OH}$	3.4	141
Cubane		160	CH_4	2.2	125
Acetylene	sp	248	$\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{I})$	1.3	120
H-H	s	284	$\text{CH}_3\text{-Li}$	0.98	98

Table 9.1: Coupling constants and molecular electronics.

- The last coupling constant on the left is technically a J_{HH} , not a J_{CH} .
- The left exhibits the expected trend based on s -character: Compounds that maximize s -character and place electrons closer to the nucleus have higher coupling constants.
- The right exhibits the expected trend based on **Bent's rule**: Compounds with less electronegative EWGs must give more s -character to bonding; thus, there is less s -character to promote (scalar) coupling and the coupling constant diminishes.

- You can quantitatively derive this stuff with MO theory.
- Observing these coupling constants: They show up under ^{13}C NMR that isn't proton decoupled.
- **Bent's rule:** More electronegative elements prefer p -character.
 - See Labalme [2] for more.
- Aside: Diamond vacancy centers in quantum computing.
 - One of the first things used for a quantum computer was an NMR.
 - The first quantum computation was performed via NMR spectroscopy.
 - It was a funky molecule, just enough stuff to do quantum computation, but it worked.
- A couple more notes about coupling constants.

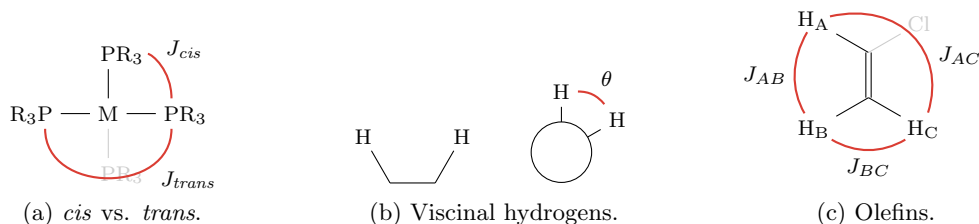


Figure 9.6: Special cases in coupling.

1. *cis* vs. *trans* metal complexes.
 - $J_{trans} > J_{cis}$.
 - Example: If we have a square planar coordination compound with four phosphenes, the two pairs of *trans* ligands will (independently) couple more than any of the four pairs of *cis* ligands.
 - Why: Same argument as *trans* effect; make an MO argument that *trans* will overlap better.
 2. Vicinal coupling: Coupling of atoms separated by two other atoms.
 - Example: Two hydrogens on different carbons of ethane.
 - Coupling magnitude: Depends on the dihedral angle θ from the Newman projection.
 - For syn and anti conformers, J will be larger.
 - For gauche conformers, J will be smaller.
 3. Olefins.
 - Example: Vinyl chloride.
 - $J_{AC} = 12 - 18$ Hz. Sometimes referred to as *trans*.
 - $J_{BC} = 0 - 3$ Hz. Sometimes referred to as *gem*.
 - $J_{AB} = 6 - 12$ Hz. Sometimes referred to as *cis*.
- A more realistic view of spins under a magnetic field.
 - We may treat the collection of polarized molecules as an ensemble of spins in space.
 - However, just because a magnetic field has been applied doesn't mean that each nuclear spin is perfectly poised along the z -axis.
 - Rather, there are still residual x - and y -components that will precess around the z -axis.
 - We have, in fact, a whole distribution of spins which are arranged in some cone around the z -axis. We do indeed have a random and equally dispersed x, y -spins.
 - The precession is called a **Larmor precession** and occurs at the **Larmor frequency**.

- The NMR experiment.
 - What we do is take the ensemble of spins and apply a 90° radiofrequency pulse to project the net magnetization onto the x -axis. Then, we monitor the precession rate about the xy -plane.
 - This is called a **Hahn Echo experiment**.
 - We also use this technique in pulsed EPR experiments.
 - We then Fourier transform the wave to get it back to normal.
 - Misc. notes.
 - The x - and y -components vary in time.
 - Both α and β (up and down) spins precess at the same frequency.
 - Chemically equivalent nuclei precess at the same frequency, but are not necessarily in phase.
 - While the x - and y -components are scattered, there is still net polarization along z and hence a net magnetization in this direction.
- Next time.
 - Wikipedia description of the Hahn Echo experiment (really good).
 - A bit more on NMR, too, to be wrapped up at the beginning of the lecture.