CH-314 Structural Analysis
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Jigsaw 5E

The NMR Hamiltonian

[Week 1 Slides 18−29] The complete NMR Hamiltonian for a molecule in a diamagnetic condensed sample is:

$$\mathcal{H}_{NMR} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_{CS} + \mathcal{H}_J$$

1. Name all the terms. For each term, determine if it will be observable in solid state NMR, in liquid state NMR, or in both. Justify your answers. Also state which units the corresponding values are usually reported in (e.g., Hz, MHz, ppm, etc.).

H_Z represents the Zeeman interaction, usually reported in MHz → observed in both liquid and solid state NMR

H_Q represents the Quadrupolar interaction, usually reported in MHz → observed in solid state NMR but not in liquid state NMR.

in anisotropic liquids those two also could be observed

H_D represents the Dipolar interaction, usually in kHz. → observed in solid state NMR but not in liquid state NMR.

H_{CS} represents the Chemical Shift, usually in ppm → observed in both liquid and solid state NMR

H_J represents the Scalar coupling, usually in Hz → observed in both liquid and solid state NMR

2. How is each term of the Hamiltonian influenced by the magnetic field strength?

terms that depend on the magnetic field strength : H_{CS}, H_Z are directly proportional to the magnetic field strength.

terms that do not depend on the magnetic field strength : H_Q, H_D, H_J

The second order quadrupolar term is inversely proportional to B

3. Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does not?

Dipolar coupling depends on the relative orientations between the molecules, and scalar coupling does not. So in the liquid, due to the different orientations the dipolar coupling cancel out in the liquid state.

4. [Week 4 Slides 40−43] What is the main difference, in terms of molecular dynamics, between a liquid and a solid sample?

Due to the molecular tumbling, the anisotropic interactions average out, so we can only observe them in solid state NMR

or anisotropic liquids..

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Ex 1

H_Z states for the Zeeman interaction. It is observable in solid and liquid state because it only depends on the external field and not on the geometry

↳ Reported in MHz

H_Q states for the quadrupolar interaction only in solid state because in liquid, the spin overlap and averages-out

in anisotropic liquids such as liquids crystals could be observed.

↳ Reported in MHz

H_D states for the dipolar interaction. It is only observable in solid state because in liquid, the anisotropy averaged-out.

in the case of isotropic liquids it is true. If we have an anisotropic liquid we could observe it.

↳ Reported in kHz

H_{CS} states for the chemical shift. It is observable in both liquid and solid state. because shielding effect do not depend on the state.

↳ Reported in ppm

H_J states for scalar couplings. It is observable in both states because both have chemical bond.

↳ Reported in Hz

Ex 2

H_Z : proportional to the magnetic field strength $\left(\Delta E = \gamma \hbar B_0 \right)$

H_Q : independant until the second-order $\left(\hat{H}_Q \propto \frac{C_Q^2}{B_0} \right)$

H_D : independant

H_{CS} : proportional $\left(\omega = -\gamma (1-\sigma) B_0 \right)$

H_J : independant

Ex 3

Scalar Coupling	Dipolar Coupling
Indireet interaction	Direct interaction
Long range	Short range $(1/r^3)$
in Hz	in kHz

Since the dipolar interaction depend on the spatial orientation, the rapid motion of the molecules in liquid averages-out the splittings. On the other hand, since scalar coupling does not depend on orientation, it produces splitting in NMR spectra.

Ex 4

The only difference between solids and liquids is the presence or absence of rapid molecular motion.

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1. Name all the terms. For each term, determine if it will be observable in solid state NMR, in liquid state NMR, or in both. Justify your answers. Also state which units the corresponding values are usually reported in (e.g., Hz, MHz, ppm, etc.).

H_Z – zeeman interaction – both, because nothing cancels out the zeeman term, whether solid or liquid
unit: MHz or rad.s^{-1}

H_Q – quadrupolar interaction – not observable in liquid NMR because liquid NMR removes anisotropic interactions due due to fast tumbling, so the quadrupolar coupling averages out. observable in solid → no motional averaging
unit: Hz → MHz

in anisotropic liquids quadrupolar and dipolar interactions could be observed.

H_D – diapolar interaction → not observable in liquid, diapolar interactions are averaged our due to rapid tumbling observable in solid → no motional averaging
unit: Hz → kHz

H_{CS} – chemical shift → observable in liquid → tumbling averages chemical shift to a single average value → isotropic chemical shift. observable in solid, shows chemical shift anisotropy
unit: ppm

H_J – J-coupling observable in solid because Jcoupling is a scalar so it doesnt depend on molecular orientations observable in solid sometimes because it can be buried under broad lines from diapolar and quadrupolar interactions
unit: Hz

2. How is each term of the Hamiltonian influenced by the magnetic field strength?

- $H_Z = -\gamma \hbar B_0 I_Z$ → linearly dependent on B_0 (magnetic field)
- H_Q : first order : set by C_Q (quadrupolar coupling constant) $= e^2qQ/\hbar$ → independent of B_0
  second order $\propto C_Q^2/\nu_0$ → dependent on $1/B_0$
- $H_D \propto \frac{\gamma_1 \gamma_2 \hbar^2}{r^3}(3I_{1z}I_{2z} - I_1 \cdot I_2)$ 1st order : independent of B_0 (only on internuclear distance)
  2nd order : scales as D^2/ω_0 → dependent on $1/B_0$.
- $H_{CS} \sim -\gamma \hbar B_0 I \cdot \sigma \cdot \hat{B}_0$ → linear in B_0 (in Hz)
- $H_J = 2\pi \hbar I_1 . J . I_2$ → Independent of B_0 (in Hz)

Good!

3. Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does not?

Scalar : Isotropic interaction between nuclei transmitted through chemical bonds

Dipolar : Direct magnetic interactions between two magnetic dipoles, depends on orientation of magnetic field and is anisotropic $(3\cos\theta^2 - 1)$

Scalar couplings are visible in liquids producing splitting and survive molecular motion. The fast reorientation of molecules averages out the dipolar interaction to 0. (in the case of isotropic liquids, which are most of them)

4. [Week 4 Slides 40–43] What is the main difference, in terms of molecular dynamics, between a liquid and a solid sample?

The molecular motion of the molecules in a liquid sample are fast and isotropic. motion of a solid sample are anisotropic, resulting in a broader spectrum unless magic angle spinning is used.

The molecular motion in a liquid sample averages out ⇒ sharper peaks

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$$\mathcal{H}_{NMR}=\mathcal{H}_Z+\mathcal{H}_Q+\mathcal{H}_D+\mathcal{H}_{CS}+\mathcal{H}_J$$

1. Name all the terms. For each term, determine if it will be observable in solid state NMR, in liquid state NMR, or in both. Justify your answers. Also state which units the corresponding values are usually reported in (e.g., Hz, MHz, ppm, etc.).

- $\mathcal{H}_Z$:
    - Hamiltonian of the Zeeman interactions. It represents the interaction of the nuclear magnetic moments with the external field B_0.
    - It's usually expressed in MHz (order of magnitude of 100 MHZ)
    - Observable in solids and liquids, since it depends on the Larmour frequency rather than the motion of the molecules.

- $\mathcal{H}_Q$:
    - Quadrupolar interaction. Interaction of a nuclear quadrupolar moment with the electric field gradient at the nucleus,
    - Expressed in MHZ (0-100 MHZ)
    - Observed mainly in solids since the quadrupolar interaction is anisotropic and is rapidly averaged to zero in **isotropic** liquids. In solids it produces strong broadening, multiple transitions and quadrupolar lineshapes
    - **In anisotropic liquids could be observed too.**

- $\mathcal{H}_D$:
    - Dipolar interaction. Magnetic interaction between two nuclear magnetic dipoles
    - Expressed in kHz (0-20Hz)
    - Observed mainly in solids. since dipolar coupling is anisotropic (depends on orientation relative to B_0) and is averaged by rapid isotropic molecular rotation in **isotropic** liquids
    - **In anisotropic liquids could be observed too.**

- $\mathcal{H}_{CS}$:
    - Chemical Shift. Interaction of nuclear spins with the local electronic shielding. It includes an isotropic chemical shift and an anisotropic chemical shift tensor.
    - Expressed in ppm (0-2000ppm)

  - Visible in both solids and liquids. In liquids only the isotropic chemical shift is visible, whereas in solids the anisotropic chemical shift tensor gives broad, orientation-dependent lineshapes. Rapid isotropic tumbling in liquids averages out anisotropic parts of the shielding tensor, leaving a single isotropic shift; in solids the tensor components are not averaged and lead to characteristic powder lineshapes unless MAS is used.
- $\mathcal{H}_J$:
  - J-Coupling through-bond indirect coupling mediated by electrons (Fermi contact, etc.). Gives multiplet structure in spectra.
  - in Hz (0-200 Hz).
  - In theory both, but most prominent and easiest to observe in liquid-state NMR. In solids we could observe scalar couplings, but they would likely be masked by much larger dipolar broadening unless special solid-state experiments (like high rate MAS) are used.

2. How is each term of the Hamiltonian influenced by the magnetic field strength?

- $\mathcal{H}_Z = -\gamma\hbar B_0\ Iz_z$
  - Increasing B_0 increases the energy splitting proportionally and shifts resonance frequencies linearly upward.
- $\mathcal{H}_Q$
  - Only second-order quadrupolar interactions are inversely proportional
- $\mathcal{H}_D \propto (\mathbf{1}/r^{3)}\gamma_i\gamma_j\ (1-3\cos 2\theta)$
  - No dependence on B_0
- $\mathcal{H}_{CS}$:
  - Reported in ppm so field independent
  - **NOTE. We usually repor them in ppm but if we looked at them in frewuency it is field dependent as the shielding of the nucleus by the electron cloud and it is B-dependent.**
- $\mathcal{H}_J$:
  - Independent of field strength $\mathcal{H}_J = 2\pi \cdot J \cdot I_i \cdot I_j$.
  - However, at high B_0, chemical-shift differences in Hz get larger and multiplets become easier to resolve. Visibility of J-splittings improves with field, though the coupling constants themselves do not change.

not?

- Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does

Scalar J-couplings are through-bond, isotropic interactions, so rapid molecular tumbling in liquids does not average them out: they remain finite and produce the familiar multiplet splittings. Dipolar couplings are through-space, anisotropic interactions containing the angular factor $1-3\cos^2\theta$. In isotropic liquids, fast isotropic tumbling makes the time-average of this angular term equal to zero, so dipolar couplings disappear from the spectrum. Thus, J-couplings give splittings in liquids, while dipolar couplings do not.

4. [Week 4 Slides 40–43] What is the main difference, in terms of molecular dynamics, between a liquid and a solid sample?

Liquids undergo rapid molecular motion while solids do not.
In liquids, molecules undergo a very fast rotation. This rapid, random tumbling averages anisotropic interactions to their isotropic values. This phenomena results in sharp, high-resolution peaks.
In solids, molecules are fixed in orientation. Anisotropic interactions do not average out, so the full orientation-dependent chemical shift occurs. This phenomena results in Broad powder patterns unless MAS is used. **Nice!**

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1. Name all the terms. For each term, determine if it will be observable in solid state NMR, in liquid state NMR, or in both. Justify your answers. Also state which units the corresponding values are usually reported in (e.g., Hz, MHz, ppm, etc.).

	solid state NMR?	liquid state NMR?	unit
H_Z : Zeeman interaction	yes (not anisotropic)	yes 〃	MHz
H_Q : quadropolar interaction	yes	no (anisotropic → averaged)	MHz
H_D : dipolar interaction	yes	no (anisotropic → averaged)	kHz
H_{CS} : chemical shift	yes (full CSA powder pattern)	yes (but only isotropic averages (δ_{iso}))	ppm
H_J : scalar coupling	no (too low resolution due to dipolar + CSA interactions)	yes (isotropic → not averaged)	Hz

Good, but they do exist!
Here an example where it has been observed https://doi.org/10.1038/s41467-024-55126-9

in the case of anisotropic liquids (i.e. liquid crystals, both could be observed

2. How is each term of the Hamiltonian influenced by the magnetic field strength?

H_Z: $H_Z \propto \omega_0 = \gamma B_0 \rightarrow H_Z \uparrow$ as $B_0 \uparrow$

H_{CS}: the absolute CSA gets larger as $\omega_0 \uparrow$ $\rightarrow H_{CS} \uparrow$ as $B_0 \uparrow$

H_Q: if we only take 1st order term, $\underline{H_Q \text{ indep. of } B_0}$

H_D: independant of B_0 since dipolar coupling is an ...?

H_J: independant of B_0

3. Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does not?

J coupling is isotropic thus remains visible in multiplet splittings (both liquid and solid)

Dipolar coupling is anisotropic. In liquid, it is averaged thus not visible.
in isotropic liquids (which are the most common ones)

4. [Week 4 Slides 40−43] What is the main difference, in terms of molecular dynamics, between a liquid and a solid sample?

In a liquid, molecules undergo rapid + random isotropic rotational motion.
→ averaged single narrow peaks.

In a solid, molecules are fixed in orientation, only slow + restricted motion.
→ powder pattern, broad lines with all possible orientations.

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1. H_Z : [MHz]
Zeeman Interaction in both states because it exists whenever a nucleus has spin and a magnetic field.

H_Q : [MHz]
Quadripole Interation in solid state because it averages to zero due to fast isotropic tumbling for liquids. True for isotropic liquids. For anisotropic liquids could be observed

H_D : [kHz]
Dipolar Interation in solid state because it averages to zero due to fast isotropic tumbling for liquids. Same argument as above

H_{CS} : [ppm]
Chemical Shift Interaction in both states because for liquids we observe a short peak and for liquids we observe a large peak because there is no tumbling. Narrow and broad* would be more accurate

H_J : [Hz]
Scalar Coupling Interaction in both states but broadened in solids which hides the J-splitting

2. H_Z : linear dependance of B_0 because of the Larmor frequency $\omega_0 = \gamma B_0$.

H_Q : the first order term does not depend on B_0, while the second-order quadripolar shift decreases as $\frac{1}{B_0}$ making high fields reduce quadrupolar broadening

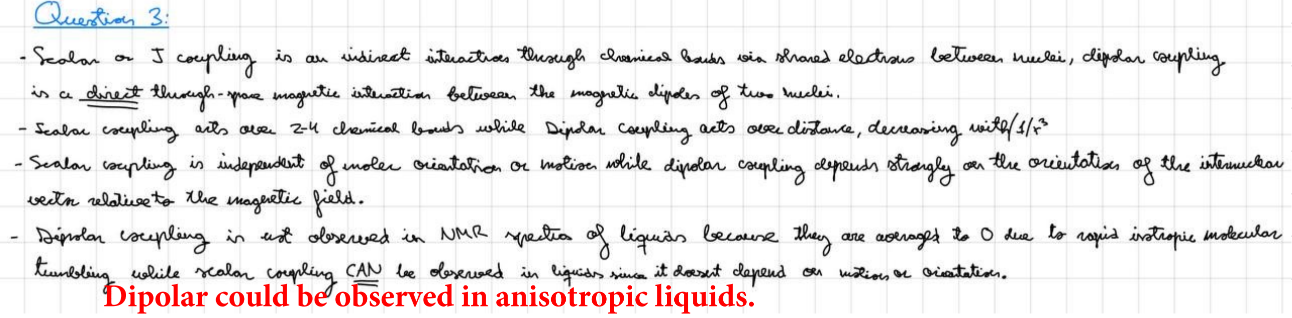
H_D : independent of B_0 because it depends only on internuclear distances and geometry, not the external field.

H_{CS} : the frequency separation increases linearly with B_0 but the ppm values stays constant. The shielding of the nucleus by the electron cloud and it is B-dependent.

H_J : Independent of B_0 since J-coupling is transmitted through electrons and does not involve the external magnetic field.

3.

Good!

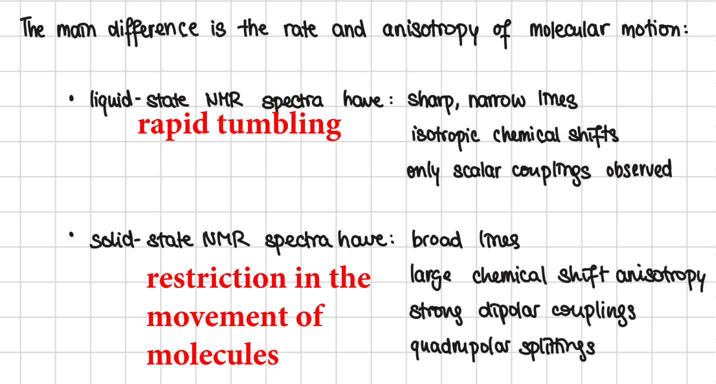


Question 3:

- Scalar or J coupling is an indirect interaction through chemical bonds via shared electrons between nuclei, dipolar coupling is a <u>direct</u> through-space magnetic interaction between the magnetic dipoles of two nuclei.
- Scalar coupling acts over 2-4 chemical bonds while Dipolar coupling acts over distance, decreasing with $1/r^3$
- Scalar coupling is independent of molec orientation or motion while dipolar coupling depends strongly on the orientation of the internuclear vector relative to the magnetic field.
- Dipolar coupling is not observed in NMR spectra of liquids because they are averaged to 0 due to rapid isotropic molecular tumbling while scalar coupling <u>CAN</u> be observed in liquids since it doesn't depend on motion or orientation.

Dipolar could be observed in anisotropic liquids.

4.



The main difference is the rate and anisotropy of molecular motion:

- liquid-state NMR spectra have: sharp, narrow lines
  isotropic chemical shifts
  only scalar couplings observed

rapid tumbling

- solid-state NMR spectra have: broad lines
  large chemical shift anisotropy
  strong dipolar couplings
  quadrupolar splittings

restriction in the movement of molecules

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$\mathcal{H}_Z$. zeeman interaction (~100 MHz) → both NMRs

$\mathcal{H}_Q$: quadrupolar interaction (0-100 MHz) → solid-state NMR

$\mathcal{H}_D$: dipolar interaction (0-20 kHz) → solid state NMR

} in liquid state, these interactions are averaged out by the isotropic nature of the phase

in anisotropic liquids (e.g. liquid crystals) both could be observed in solution-state NMR

$\mathcal{H}_{CS}$: chemical shift (0-2000 ppm) → both NMRs

$\mathcal{H}_J$: scalar coupling (0-200 Hz) → both NMRs

2. How is each term of the Hamiltonian influenced by the magnetic field strength?

zeeman interaction: $w_0 = -\gamma B_0$, B_0 dependance ⇒ magnetic field dependant

Quadrupolar interation: inversly proportional to Larmor frequency, which depends on the magnetic field

Inversiely proportional to the magneic field of the second order interaction of quadrupolar interactions

Dipolar interaction: $b_{jk} = -\frac{\mu_0}{4\pi}\frac{\gamma_j \gamma_k \hbar}{r_{jk}^3}$, no B_0 dependance ⇒ magnetic field independant

chemical shift : $w_0 = -\gamma(1-\sigma) B_0$, B_0 dependance ⇒ magnetic field dependant

scalar coupling : coupling constant explain the difference in frequency between the peaks in the spectrum of a coupled nucleus which is influenced by the magnetic field of adjacent nuclei.

3. Explain the main differences between scalar couplings and dipolar couplings. Why does one produce splittings in NMR spectra of liquids and the other one does not?

- Scalar coupling is indirect, through bond interactions btw nuclear spin that causes signal splitting and is indepedent of molecular orientation.
  ↳ doesn't move so doesn't average out.
- Dipolar is direct through space interaction that depends on the orientation of molecules in magnetic field.
  ↳ they move so they average out

4. [Week 4 Slides 40–43] What is the main difference, in terms of molecular dynamics, between a liquid and a solid sample?

- Liquid → molecules move around
- Solid → molecules are fixed. **Restricted movement, but still some vibrations**