Week 5

Magnetic Resonance Spectroscopy

5.1   Lecture 8: Magnetic Resonance Spectroscopy

1/31:

- Refer to Chapter 14 of McQuarrie and Simon [1].

- There is both NMR (nuclear magnetic resonance) and ESR (electron spin resonance) or EPR (electron paramagnetic resonance).

    - The last two are the same thing.

- Two fields: The static magnetic field, and the probing *electro*magnetic field.

- Derivation of quantized angular momentum.

    - In molecules, there is a multiplicity/degeneracy of states that grows as $2J+1$. They have quantized angular momentum.
    - So is the orbital angular momentum of electrons!
    - Putting atoms into a magnetic field *creates* the anisotropy necessary for discussing the z-component (or any coordinate component) of angular momentum.
    - Spin angular momentum: Just means that the objects (e.g., electrons and nuclei) have a property that looks a lot like spin and/or angular momentum.
    - We say that each nucleon has a spin of 1/2. Protons and neutrons add separately.
        - ■ Even number of protons and neutrons? Spin 0.
        - ■ Mixed even/odd? We have actual nuclear spin.
            - ➢ We need a nucleus like this to detect!
        - ■ Odd/odd? We have 0 spin again.
    - We focus on spin 1/2 particles. These have two degenerate energy states that split in a magnetic field.

- Classical picture of spin angular momentum.

    - Picture a charged particle with angular momentum. The circulating charge produced a magnetic field which aligns along the direction of the angular momentum.
    - Indeed, a spinning charged particle behaves like a dipole.
    - $\gamma = 2mc$ is the **gyromagnetic ratio**.

- Quantum spin angular momentum.

    - Basically the same thing; we just rephrase everything from before in the language of operators.

- **Zeeman effect**: Two energy levels split with increasing B.

- **Larmor frequency**: The frequency $\nu = \gamma B/2\pi$ in the radio frequency range that induces a shift.

- Typical operating conditions.

    - NMR vs. ESR: NMR has a stronger magnetic field, longer EM excitation radio waves, and significantly lower gyromagnetic ratios.

    - There is only a tiny difference between nuclear state occupation at room temperature; hence supercooling to get something detectable.

- What is the magnetic dipole doing in the magnetic field?

    - No constraints on the x and y components of I.

    - A dipole in a field experiences a torque.

        ■ Dipole precesses around B at the Larmor frequency ν.

    - FT-NMR spectrometers use pulsed rf fields to synchronize and detect the procession of spins.

- Lots of good extension material on NMR; also worth rewatching at some point!

5.2   Lecture 9: Magnetic Resonance Spectroscopy 2

2/2:   • Summary of last time.

    - The quantity that we're measuring is spin angular momentum $\bar{I}$, which is a vector quantity.

    $$|\bar{I}| = \hbar\sqrt{I(I+1)}$$

    where $I = 1/2$ is the nuclear spin quantum number.

    - The other quantity of concern is the projection $I_z = m_I \hbar$ where $m_i = \pm 1/2$.

    - In a magnetic field, we break degeneracy, getting $E(m_I) = -\gamma_N \hbar m_I B$ and $\Delta E = -\gamma_N \hbar B$.

    - Electromagnetic resonance is achieved when the frequency ν of incident radiation satisfies $h\nu = \Delta E$.

- The interest in chemistry: Chemical shift.

    - There are small variations in the frequency for different types of protons depending on the surrounding electron density.

    - Measured frequency depends on effective magnetic field.

        ■ Shielding: The influence of electrons around the nucleus on the effective magnetic field.

        ■ The effective field is smaller than the applied field.

    - Shielding *decreases* the splitting (this is why nearby highly polar groups lead to large shifts, while alkanes have small shifts).

- Measuring the chemical shift.

    - We measure the difference in the Larmor frequency relative to a standard (TMS).

    - Shielding is a small effect (on the order of 10^{-6}, so we use ppm δ).

    - Example: 1 ppm at $500\,\text{MHz}$ is $\nu = 500\,\text{Hz}$, which is tiny (on the order of microjoules).

- Chemical shift charts (from OChem) are included in the slides.

- FT-NMR spectrometers.

    - How do we make these measurements?

    - NMR spectrometers are almost all working in FT mode these days.

– They use pulsed radiofrequency (r.f.) fields and detect the precession of spins.

– Precession of one spin in a magnetic field occurs at the Larmor frequency.

– Applying an excitation field creates a superposition of $m_s = \pm 1/2$ states. The net dipole is now perpendicular, and precesses that way (i.e., in the xy plane) in a mathematically describable fashion.

– Putting your superconducting coil along the x- or y-axis allows you to detect changes.

• **Magnetization**: The macroscopic alignment of magnetic dipoles $\bar{M} = \sum \bar{\mu}$.

– At equilibrium, $\bar{M}$ aligns along $\bar{B}$.

– An rf field rotates magnetization to x: This is a **π/2-pulse** or a **90°-pulse**.

– We detect precessing magnetization and return to equilibrium during the **free-induction decay**. An FT of the decay then generates our spectrum.

• Relaxation mechanism.

– Spin state lifetime (T_1).

  ■ "Spin-lattice" or "longitudinal" relaxation.
  ■ Recovery of the magnetization along z.
  ■ A molecular property.
  ■ Transfer of energy to the environment.
  ■ The return of magnetization to equilibrium has a characteristic time constant T_1 which appears in the time vs. relaxation plot $1 - \mathrm{e}^{-t/T_1}$.

– Dephasing (T_2).

  ■ "Transverse" relaxation.
  ■ Loss of magnetization in the xy-plane of many different sources.
  ■ We have the loss described by e^{-t/T_2}.

– These two processes are not independent.

• There are numerous types of NMR experiments.

– In our lab, we just scratch the surface.

– We use a population inversion to measure T_1.

  ■ **π-pulse** to invert magnetization.
  ■ Wait for relaxation.
  ■ Read out following another **π/2-pulse**.

– Two-dimensional spectroscopy.

  ■ Heteronuclear single quantum coherence spectroscopy (HSQC).
  ■ Excite ^{1}H; transfer its magnetization to ^{13}C, which is nice because ^{13}C is hard to excite on its own.
  ■ Transfer back to ^{1}H and detect.
  ■ Tells us which protons transfer magnetization.