
Introduction to Quantum Mechanics and Multiplet Splitting in ^1H NMR Spectrum: A Demonstration and Classroom Activity

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01/24-2014

Abstract:

Quantum mechanics is an incredibly important theory in chemistry that effectively describes the behavior of molecules, atoms, and other subatomic particles. Unfortunately, the complexity of the mathematics required to describe quantum mechanics, and the abstract nature of the particles being described, often makes it an extremely difficult topic to communicate effectively.

Nuclear magnetic resonance (NMR) spectroscopy, arguably the most important analytical technique in organic chemistry, is similarly a challenging topic to introduce to students. The abstract concepts, complex mathematics, and sometimes dizzying rotation taking place are difficult even for some faculty. As a result, many students in undergraduate chemistry courses are never exposed to these two important topics.

In this classroom demonstration we will simplify the explanation and make the abstract concepts more concrete by combining quantum mechanics and NMR spectroscopy in one demonstration. Although NMR spectra can be obtained using a number of different nuclei, we will focus on ^1H or "proton" NMR.

Introduction:

Shortly before the discovery of quantum mechanics it was discovered that the Zeeman Effect and other "fine structure" spectral lines could be explained if the electrons were spinning about their own axis. This property, known as spin angular momentum was eventually extended to protons as well. The reasoning, and mathematical explanation of this spin is beyond the scope of this demonstration, but suffice it to say that it has been well studied and now represents the fourth quantum number " m_s " (the first three are the principle, orbital, and magnetic quantum numbers).

Because protons and electrons also have a charge associated with them, this intrinsic spin causes the particle to behave as a very small magnet. (A full discussion of induction and induced magnetic fields is outside the scope of this demonstration; please consult a physics text for a detailed description of this concept.) These particle-sized "magnets" are randomly oriented in most instances, but can be forced to adopt one of only two orientations by placing the particles inside a strong magnetic field. In this situation, the particles orient themselves along the axis of

the applied magnetic field B_0 with the particle's magnetic field B_p oriented either with, or against the applied field. These two states, referred to as "spin up," and "spin down" have, as you might expect, two different energy levels as seen in Figure 1. As all matter prefers to be in the lowest energy level possible, more particles adopt the lower energy spin up orientation with the particle's magnetic field aligned with the applied magnetic field B_0 than adopt the higher energy spin down state. This population difference is what NMR spectroscopy, similar to other optical spectroscopies (UV-VIS, Infra-red, etc.) uses to generate an NMR signal.

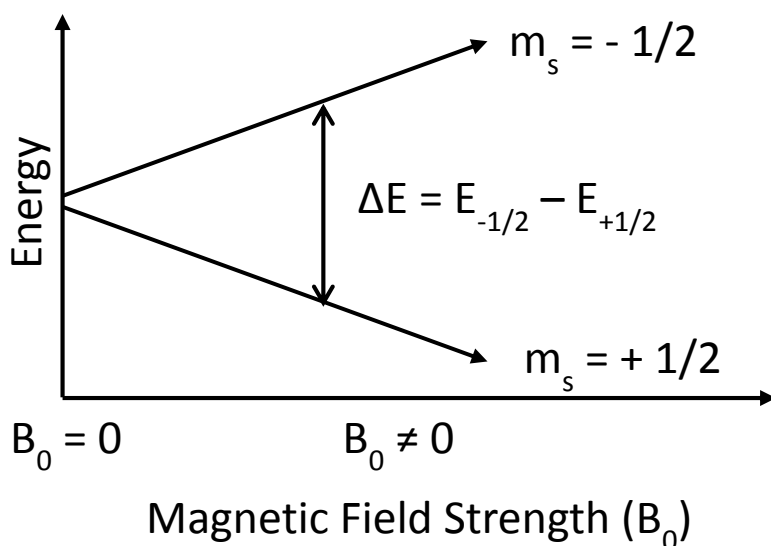


Figure 1: The effect of an external magnetic field B_0 on the spin orientation of the nucleus. The two energy levels are populated according to the Boltzmann distribution.

The fact that every chemically different proton (for $^1\text{H-NMR}$) is in a slightly different magnetic environment, means that the energy level's available to those nuclei are also slightly different. These small differences in energy from one proton to another allow the NMR signal to become (with sufficient instrumental resolution) an NMR spectrum with a different peak for each chemically unique proton.

The displacement of NMR peaks along the x-axis is known as chemical shift and reveals information about what functional groups are present near the proton responsible for a given signal. In addition, the relative integration of the signals allow NMR spectra to quantify the number of protons that are responsible for generating a given signal, and even to quantify the relative concentration of sample mixtures.

The final piece of information that an NMR spectrum tells us is the multiplicity of the signal and this is what we will focus on in today's demonstration. Multiplicity is a splitting of a given NMR spectral signal into a tightly clustered series of peaks based on the number of protons within a

given distance from the proton responsible for the signal (typically three bonds between interacting nuclei).

If we once again consider the spinning nuclei, the magnetic field produced by the spin causes small changes in the electron distribution of its bonds. These in turn effect the electron distribution of neighboring bonds, which affect the neighboring nuclei. This process is known as spin-spin coupling and is typically observable out to three bond lengths. Longer range effects are observable, but are beyond the scope of this demonstration. As both neighboring protons can be oriented either spin up or spin down, their effects on the electron cloud, and therefore on each other, will depend on all the possible spin-spin combinations. In the simplest case, when there are only two protons interacting with each other, there exist four total combinations (up-up, up-down, down-up, and down-down), but only two combinations with unique energies (up-up and down-down have identical energies, as do up-down and down-up). This causes the original NMR signal to split in two, and is known as a “doublet.” A proton with two neighboring protons would have four unique combinations but only three unique energies, up-up-up, up-up-down (up-down-up is a unique combination but has the same energy as up-up-down), and up-down-down. Because there are twice as many unique combinations for the up-up-down energy level, the height of that peak will be approximately double that of the outer peaks as shown in Figure 1.

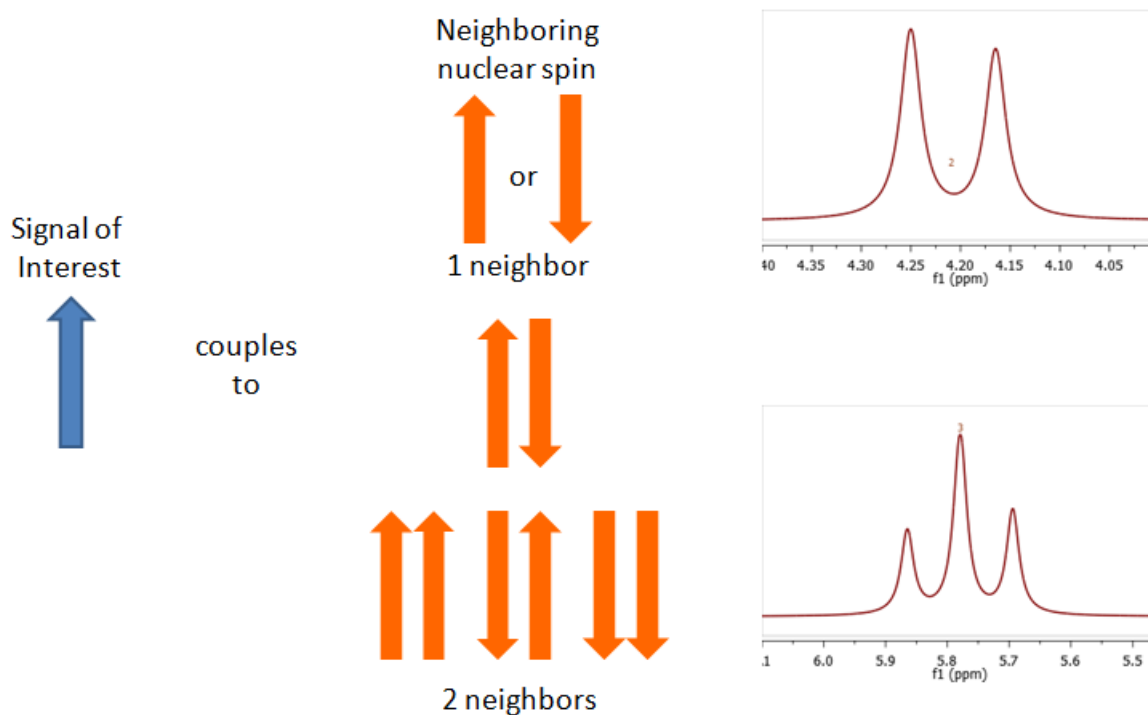


Figure 2: Spin-spin coupling to form multiplets. The formation of a doublet is created by the two unique coupling combinations between the signal nuclei (in blue) and the single neighbor (which can be up or down). The formation of a triplet results from the four unique coupling combinations between the signal nuclei and two neighboring nuclei. Although there are four unique

combinations, two of the combinations have the same energy associated with them limiting the number of peaks to three.

As mentioned above, the displacement of NMR signals along the x-axis of an NMR spectrum is dependent upon the magnetic field strength of the instrument, however, the distance between peaks making up a multiplet are not field strength dependent. This is in agreement with the multiplet being a result of the spin orientation of the nucleus on the electron cloud, an interaction that is independent of the field strength.

By measuring the spacing of the multiplet peaks we can directly observe the effect these two quantized nuclear spin states (spin up or spin down) have on their environment.

Safety:

Appropriate eye (goggles) and skin (gloves) protection should be worn at all times. Ensure proper ventilation when working with ethyl acetate.

Materials:

picoSpin45 or picoSpin80 NMR spectrometer

1 mL polypropylene syringe

22 gauge blunt tip dispensing needle

Syringe port adapter and picoSpin drain tube assembly

0.5 mL Ethyl Acetate

Procedure:

- 1) Install the NMR spectrometer in a safe location that is convenient for the demonstration. Allow the instrument to warm up and shim the instrument using water. Consult the picoSpin quickStart guide provided with your spectrometer for details. A replacement copy of the quickStart guide can be found online: <http://picospin.com/support/support-documentation/>
- 2) Attach the spectrometer drain tube assembly.
- 3) Using the syringe, draw up and then inject ethyl acetate into the spectrometer. Take care not to inject air bubbles.
- 4) Navigate to the spectrometer's Run>onePulse script.

- 5) Acquire a 16 scan averaged spectrum. This will take one minute and 45 seconds and is a good time to introduce the guided inquiry questions.
- 6) From the “Files” page of the instrument control software, download your data and open it in your institution’s preferred NMR processing software.
- 7) Process your spectra. For help with spectral processing in mNova or ACD labs software please visit the picoSpin support page <http://picospin.com/support/tutorials/>
- 8) Measure the peak spacing of the triplet.
- 9) Using the relationship $\Delta E = h\nu$ where ΔE is the energy difference observed, h is Planck’s constant, and ν is the peak separation in Hz, calculate the energy difference of the interaction between the spin up and spin down protons.
- 10) Repeat steps 7-9 for the quartet.

Guided Inquiry Pre-Questions:

Will the individual peak spacing within a given multiplet be identical? Why or why not?

Do you expect the ΔE from the triplet and the quartet to be different? Why or why not?

Guided Inquiry Post-Questions:

Assign all the peaks in your NMR spectrum and attach to your laboratory.

Was the individual peak spacing within a given multiplet identical? Why or why not?

What were the values you calculate for $\Delta E_{\text{triplet}}$ and $\Delta E_{\text{quartet}}$?

Where the values of $\Delta E_{\text{triplet}}$ and $\Delta E_{\text{quartet}}$ identical? Why or Why not?