

4. Nuclear Magnetic Resonance

A Success Story

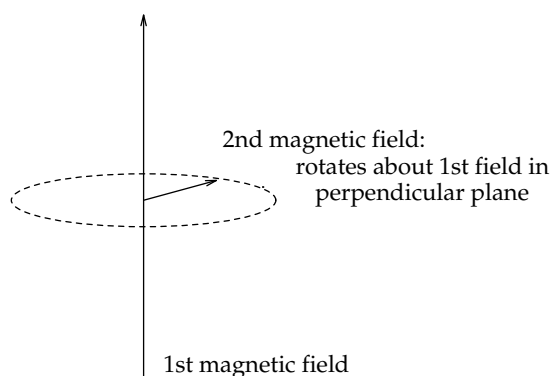
The history of nuclear magnetic resonance, NMR for short, is the first of several examples we'll encounter this semester in which discoveries in basic science have led to completely unforeseen technological developments. In the mid-1930's, a team led by I.I. Rabi of Columbia University, began performing experiments on beams of atoms, studying the current-loop-like behavior of atoms. A breakthrough occurred in the mid 1940's, when two physicists, Bloch and Purcell, independently extended these experiments to study the current-loop-like behavior of atoms in liquids. Little did they know that these experiments would later revolutionize the field of chemistry (see for example http://www.wooster.edu/chemistry/is/brubaker/nmr/nmr_landmark.html), and decades later, result in the new technologies for medical imaging.

What is NMR?

All atoms consist of a nucleus and electrons. A hydrogen atom, for example, contains one proton, which forms the nucleus, and one electron. We have seen in class that atoms behave like current loops. In fact, the nucleus itself also acts like a current loop, so there is a magnetic needle associated with the nucleus too. This magnetic needle is sometimes called the 'spin' of the nucleus.

Like all current loops, when nuclei of atoms are placed in a magnetic field, they precess about the direction of the field. The rate of precession (how fast the magnetic needle rotates about the axis of the field) is proportional to the size of the magnetic field.

The experiments of Bloch and Purcell demonstrated that the spin of a nucleus can be flipped (i.e., the sign of the projection of the needle on the field axis can be reversed) by applying a second magnetic field. The second field must be perpendicular to the original field, and the direction of the second field must rotate about the axis of the first field. *When the rate of rotation of the second field is equal to the rate of precession of the nuclear spin, the spin flips.* This matching of rotational rates is called *resonance*.

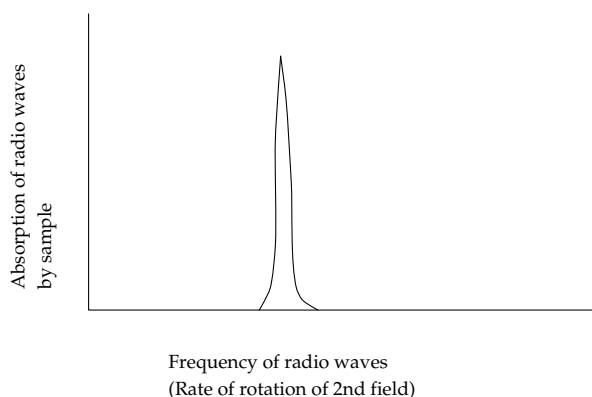


How is such an experiment performed in the laboratory?

- Put the sample (which could be a chunk of some solid, a container of liquid, or even your body) in a uniform magnetic field.

- Apply a second rotating magnetic field perpendicular to the uniform field by shining radio waves on the sample. The frequency of the radio waves is equal to the rate of rotation of the magnetic field.
- Step through many different frequencies of radio waves, and measure the absorption of radio waves by the sample.
- When the frequency of the radio waves is equal to the rate of precession of a particular nucleus in the sample, the spin of that nucleus flips over, and absorbs the energy of the radio waves.

Example of an NMR Spectrum



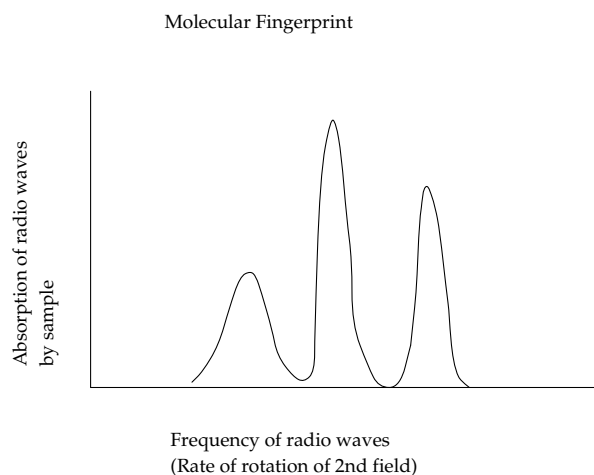
Note that only when the frequency of the radio wave is tuned just right do the spins absorb the energy of the radio waves and flip. A plot of this type is called an NMR spectrum. It is possible to measure the spectra of nuclei of various types of atoms. The hydrogen nucleus is the most common type of nucleus tracked in NMR experiments.

NMR spectroscopy (the measurement of NMR spectra) can be thought of as a sensitive way of measuring the magnetic field that atoms in the sample experience. By determining the frequency of radio waves needed to flip the nuclear spins, we are in fact measuring the rate at which the nuclei are precessing. This rate, in turn, is proportional to the magnetic field seen by the atom.

What information does an NMR spectrum tell us?

In addition to being a useful tool for nuclear physicists who are interested in exploring properties of atomic nuclei, NMR has also become an important tool for chemists who want to get information about the structure of molecules. In a solid or liquid containing many, many atoms, each nucleus feels the total magnetic field acting on it. This includes the large uniform field the sample is placed in during the experiment, as well as the small magnetic fields due to all the magnetic needles of nearby atoms. Thus even though all the atoms in the sample are in the same external magnetic field, the total magnetic field experienced by each atom differs, depending on where it is located in relation to other atoms in the sample. Since the rate of precession depends on the total magnetic field that the atom feels, different nuclei will precess at different rates. Thus the spectrum of a molecule will likely consist of many peaks, slightly shifted from each other:

Measuring the radio-wave frequency at which each peak occurs helps determine which atoms are near which other atoms (in other words, the local chemical environment around each atom).



The relative heights of the peaks gives us information about the number of atoms in each type of environment. This information allows chemists to figure out the positions of different atoms within a molecule. Note also that each molecule has its own unique NMR spectrum, which acts as a fingerprint. This fingerprint can be used to identify the presence or absence of a certain molecule in a sample. Here at Georgetown, Professor de Dios of the chemistry department uses NMR as a tool for determining the structure of large biological molecules such as proteins (see <http://bouman.chem.georgetown.edu/research.html>).

How does this make an MRI image?

An MRI machine actually measures the density of hydrogen in your body, which, in turn, is a measure of the concentration of water in your tissues. This concentration varies from one tissue type to another (muscle, fat, bone, tumors, etc.) so that the NMR signal can be used to reconstruct a three-dimensional image of the organs, muscles, tendons, and bones in your body. It took almost thirty years of concerted engineering effort to transform these results from basic physics research into the medical diagnostic tool that is currently in use. This is not atypical. *Many benefits of basic scientific research have their full effects felt decades later, when those concepts can be applied to products for sale to the public!*