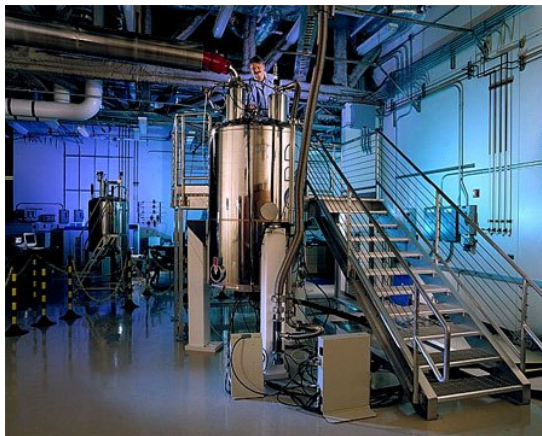


12.1: THEORY OF NUCLEAR MAGNETIC RESONANCE (NMR)

NUCLEAR PRECESSION, SPIN STATES, AND THE RESONANCE CONDITION

Some types of atomic nuclei act as though they spin on their axis similar to the Earth. Since they are positively charged they generate an electromagnetic field just as the Earth does. So, in effect, they will act as tiny bar magnets. Not all nuclei act this way, but fortunately both ^1H and ^{13}C do have nuclear spins and will respond to this technique.



NMR SPECTROMETER

In the absence of an external magnetic field the direction of the spin of the nuclei will be randomly oriented (see figure below left). However, when a sample of these nuclei is placed in an external magnetic field, the nuclear spins will adopt specific orientations much as a compass needle responds to the Earth's magnetic field and aligns with it. Two possible orientations are possible, with the external field (*i.e.* parallel to and in the same direction as the external field) or against the field (*i.e.* antiparallel to the external field). See figure below right.

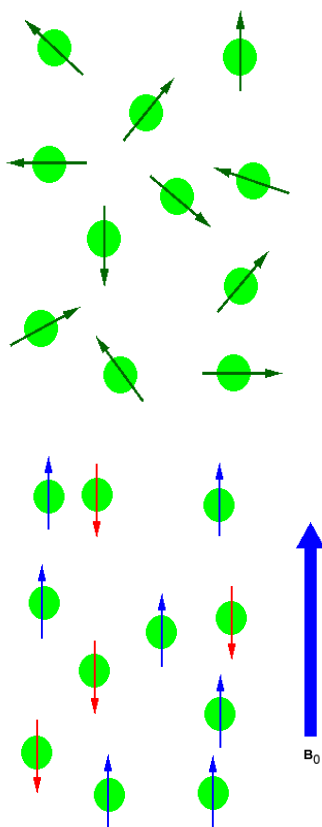
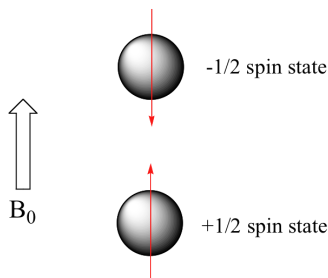


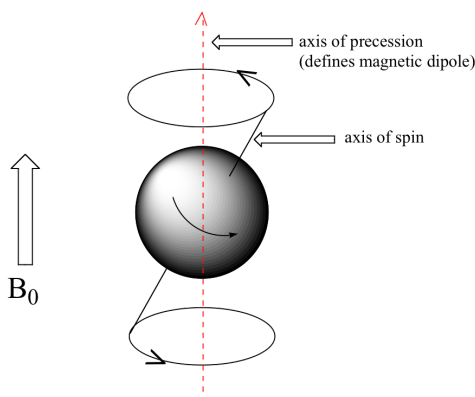
Figure 1: (Left) Random nuclear spin without an external magnetic field. (Right) Ordered nuclear spin in an external magnetic field

When the same sample is placed within the field of a very strong magnet in an NMR instrument (this field is referred to by NMR spectroscopists as the **applied field**, abbreviated B_0) each hydrogen will assume one of two possible **spin states**. In what is referred to as the $+\frac{1}{2}$ spin state, the hydrogen's magnetic moment is aligned *with* the direction of B_0 , while in the $-\frac{1}{2}$ spin state it is aligned *opposed* to the direction of B_0 .



Because the $+\frac{1}{2}$ spin state is slightly lower in energy, in a large population of organic molecules slightly more than half of the hydrogen atoms will occupy this state, while slightly less than half will occupy the $-\frac{1}{2}$ state. *The difference in energy between the two spin states increases with increasing strength of B_0 .* This last statement is in italics because it is one of the key ideas in NMR spectroscopy, as we shall soon see.

At this point, we need to look a little more closely at how a proton spins in an applied magnetic field. You may recall playing with spinning tops as a child. When a top slows down a little and the spin axis is no longer completely vertical, it begins to exhibit **precessional motion**, as the spin axis rotates slowly around the vertical. In the same way, hydrogen atoms spinning in an applied magnetic field also exhibit precessional motion about a vertical axis. It is this axis (which is either parallel or antiparallel to B_0) that defines the proton's magnetic moment. In the figure below, the proton is in the $+\frac{1}{2}$ spin state.

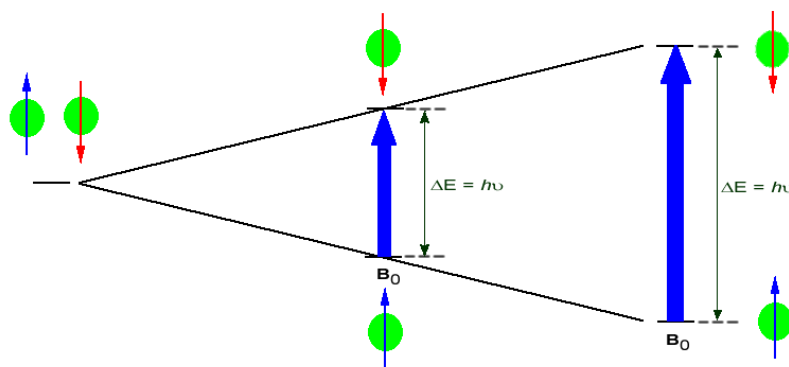


The **frequency of precession** (also called the **Larmour frequency**, abbreviated ω_L) is simply the number of times per second that the proton precesses in a complete circle. A proton's precessional frequency increases with the strength of B_0 .

If a proton that is precessing in an applied magnetic field is exposed to electromagnetic radiation of a frequency ν that matches its precessional frequency ω_L , we have a condition called **resonance**. *In the resonance condition, a proton in the lower-energy $+\frac{1}{2}$ spin state (aligned with B_0) will transition (flip) to the higher energy $-\frac{1}{2}$ spin state (opposed to B_0). In doing so, it will absorb radiation at this resonance frequency $\nu = \omega_L$.* This frequency, as you might have already guessed, corresponds to the energy difference between the proton's two spin states. With the strong magnetic fields generated by the superconducting magnets used in modern NMR instruments, the resonance frequency for protons falls within the radio-wave range, anywhere from 100 MHz to 800 MHz depending on the strength of the magnet.

If the ordered nuclei are now subjected to EM radiation of the proper frequency the nuclei aligned with the field will absorb energy and "spin-flip" to align themselves against the field, a higher energy state. When this spin-flip occurs the nuclei are said to be in "resonance" with the field, hence the name for the technique, **Nuclear Magnetic Resonance** or NMR.

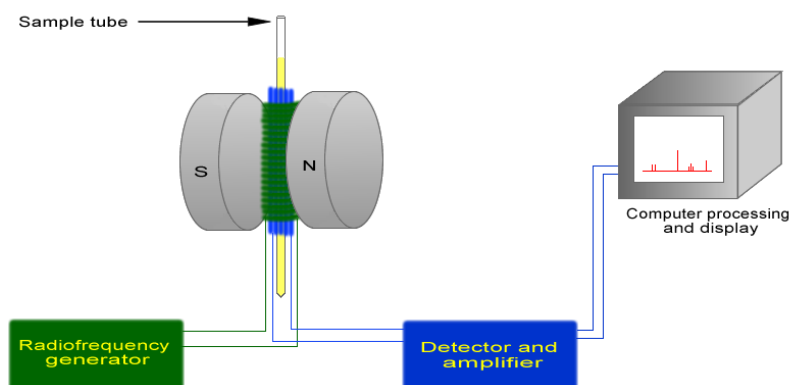
The amount of energy, and hence the exact frequency of EM radiation required for resonance to occur is dependent on both the strength of the magnetic field applied and the type of the nuclei being studied. As the strength of the magnetic field increases the energy difference between the two spin states increases and a higher frequency (more energy) EM radiation needs to be applied to achieve a spin-flip (see image below).



Superconducting magnets can be used to produce very strong magnetic field, on the order of 21 tesla (T). Lower field strengths can also be used, in the range of 4 - 7 T. At these levels the energy required to bring the nuclei into resonance is in the MHz range and corresponds to radio wavelength energies, *i.e.* at a field strength of 4.7 T 200 MHz bring ^1H nuclei into resonance and 50 MHz bring ^{13}C into resonance. This is considerably less energy than is required for IR spectroscopy, $\sim 10^{-4}$ kJ/mol versus $\sim 5 - 50$ kJ/mol.

^1H and ^{13}C are not unique in their ability to undergo NMR. All nuclei with an odd number of protons (^1H , ^2H , ^{14}N , ^{19}F , ^{31}P ...) or nuclei with an odd number of neutrons (*i.e.* ^{13}C) show the magnetic properties required for NMR. Only nuclei with even number of both protons and neutrons (^{12}C and ^{16}O) do not have the required magnetic properties.

The basic arrangement of an NMR spectrometer is displayed below. A sample (in a small glass tube) is placed between the poles of a strong magnetic. A radio frequency generator pulses the sample and excites the nuclei causing a spin-flip. The spin flip is detected by the detector and the signal sent to a computer where it is processed.



Exercise

1. If in a field strength of 4.7 T, H^1 requires 200 MHz of energy to maintain resonance. If atom X requires 150 MHz, calculate the amount of energy required to spin flip atom X's nucleus. Is this amount greater than the energy required for hydrogen?
2. Calculate the energy required to spin flip at 400 MHz. Does changing the frequency to 500 MHz decrease or increase the energy required? What about 300 MHz.

Answer

1.

$$E = h\nu$$

$$E = (6.62 \times 10^{-34})(150 \text{ MHz})$$

$$E = 9.93 \times 10^{-26} \text{ J}$$

The energy is equal to 9.93×10^{-26} J. This value is smaller than the energy required for hydrogen (1.324×10^{-25} J).

2.

$$E = h\nu$$

$$E = (6.62 \times 10^{-34})(400 \text{ MHz})$$

$$E = 2.648 \times 10^{-25} \text{ J}$$

The energy would increase if the frequency would increase to 500 MHz, and decrease if the frequency would decrease to 300 MHz.

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