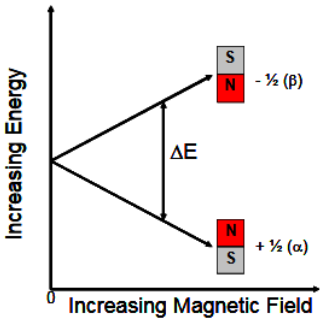
1.2: How does absorption of energy generate an NMR spectrum?

In the absence of an external magnetic field the two spins in the previous figure would be randomly oriented and their energies degenerate, in other words they would have identical energies. However in the presence of an applied magnetic field, the energies of the two spin states diverge and the spins orient themselves with respect to the applied field. The larger the magnetic field, the greater the difference in energy between the spin states. For most spin ½ nuclei, the + ½ (α) spin state is of lower energy and corresponds to having the spin aligned with the applied field while the - ½ (β) spin state can be thought of as having the spin opposed to the applied field.



The difference in energy between the states, ΔE, depends on the strength of the applied magnetic field, B_o, according to Eq. 1.2.1. In this equation γ is the gyromagnetic ratio, a fundamental property of each type of nucleus and h is Plank's constant. Table 1 shows values of the gyromagnetic ratio for several common NMR nuclei.

$$\Delta E = \frac{\gamma h B_o}{2\pi} \tag{1.2.1}$$

Table 1. Properties of Nuclei Commonly Studied by NMR[1]

Element	Atomic Number	Mass Number	Spin	Natural Abundance	Gyromagnetic Ratio γ (10^7 rad·s^{-1}·T^{-1})	Reference Compound
Hydrogen	1	1	½	99.985%	26.7522128	Me_4Si
Deuterium	1	2	1	0.0115	4.10662791	$(CD_3)_4Si$
Carbon	6	13	½	1.07	6.728284	Me_4Si
Nitrogen	7	15	½	0.368	-2.71261804	$MeNO_2$
Fluorine	9	19	½	100	25.18148	CCl_3F
Silicon	14	29	½	4.6832	-5.3190	Me_4Si
Phosphorus	15	31	½	100	10.8394	H_3PO_4
Selenium	34	77	½	7.63	5.1253857	Me_2Se
Cadmium	48	113	½	12.22	-5.9609155	Me_2Cd

1. R.K. Harris, E. D. Becker, S. M. C. De Menezes, R. Goodfellow, P. Granger, Pure. Appl. Chem. 73:1795-1818 (2001). http://www.iupac.org/publications/pa.../7311x1795.pdf

The signal in NMR is produced by absorption of electromagnetic radiation of the appropriate frequency. Energy absorption causes the nuclei to undergo transitions from the lower energy (α) to the higher energy (β) spin states. If we think about the spins as bar magnets, absorption of energy at the right frequency causes the spins to flip with respect to the applied field. As is the case with other spectroscopic methods, the difference in population of these two quantized states can be expressed by the Boltzmann equation, Eq. 1.2.2 where k is Boltzmann's constant, 1.38066 x 10^{-23} J·K^{-1}, and T is the temperature in degrees Kelvin.

$$\frac{N_{upper}}{N_{lower}} = e^{-\frac{\Delta E}{kT}} \tag{1.2.2}$$

Equation 1.2.2 relates the ratio of the number of nuclei in the upper (higher energy) spin state and the lower energy spin state to the energy difference between the spin states, ΔE, and therefore, the magnitude of the applied magnetic field, B_o (Eq. 1.2.1). In NMR the difference in energy in the two spin states is very small therefore the population difference is also small (about 1 in 10,000 for ^{1}H in an 11.74 T magnetic field). Because this population difference is the source of our signal, NMR is inherently a less sensitive technique than many other spectroscopic methods.

? Exercise 1.2.2

Given the same magnetic field and temperature, how would the difference in population for ^{1}H and ^{31}P compare?
