

CHEM202

Organic Chemistry

Nick Green

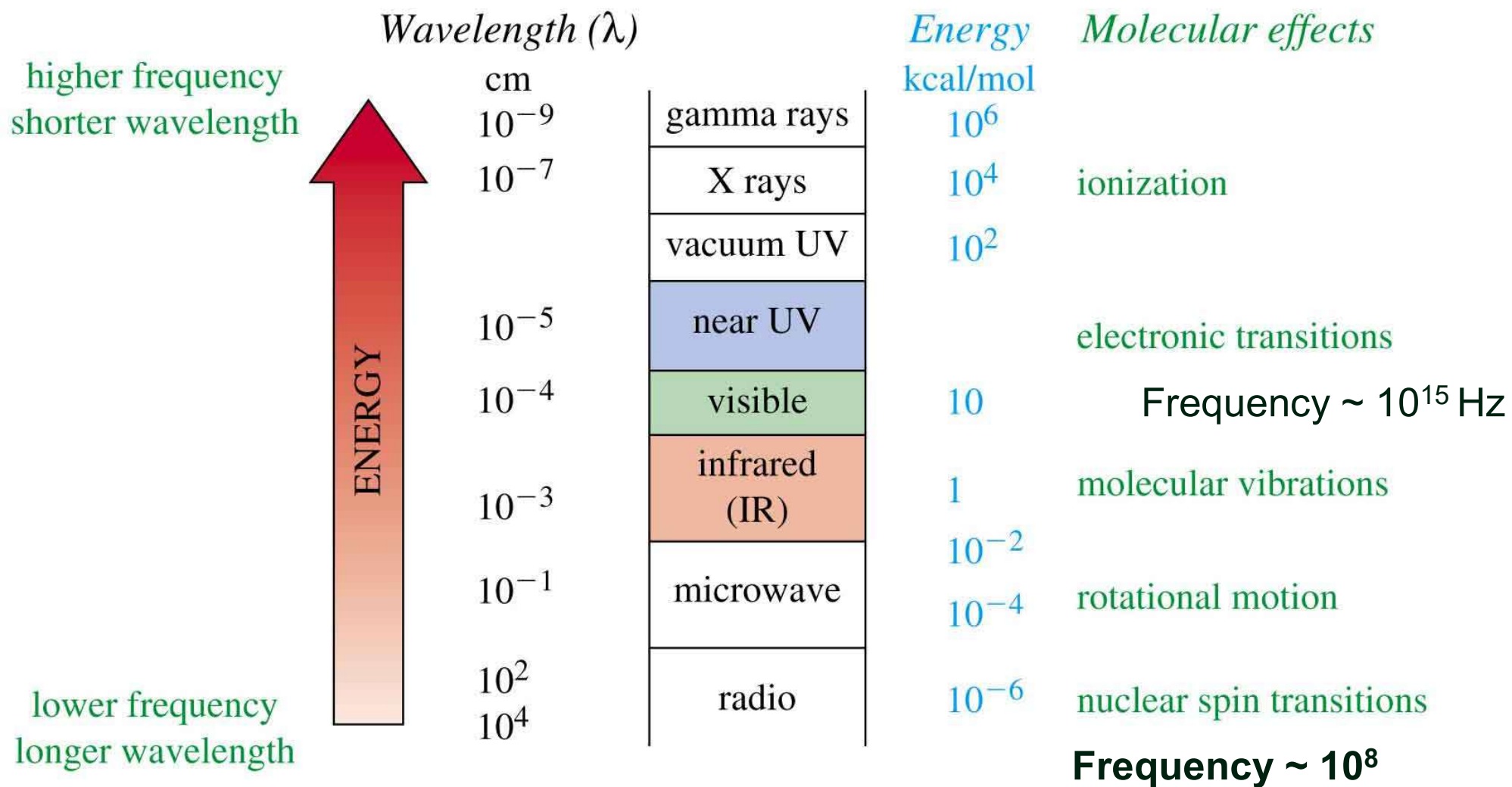
nick.green@otago.ac.nz, 3n11

Module 1: Spectroscopy and Characterisation

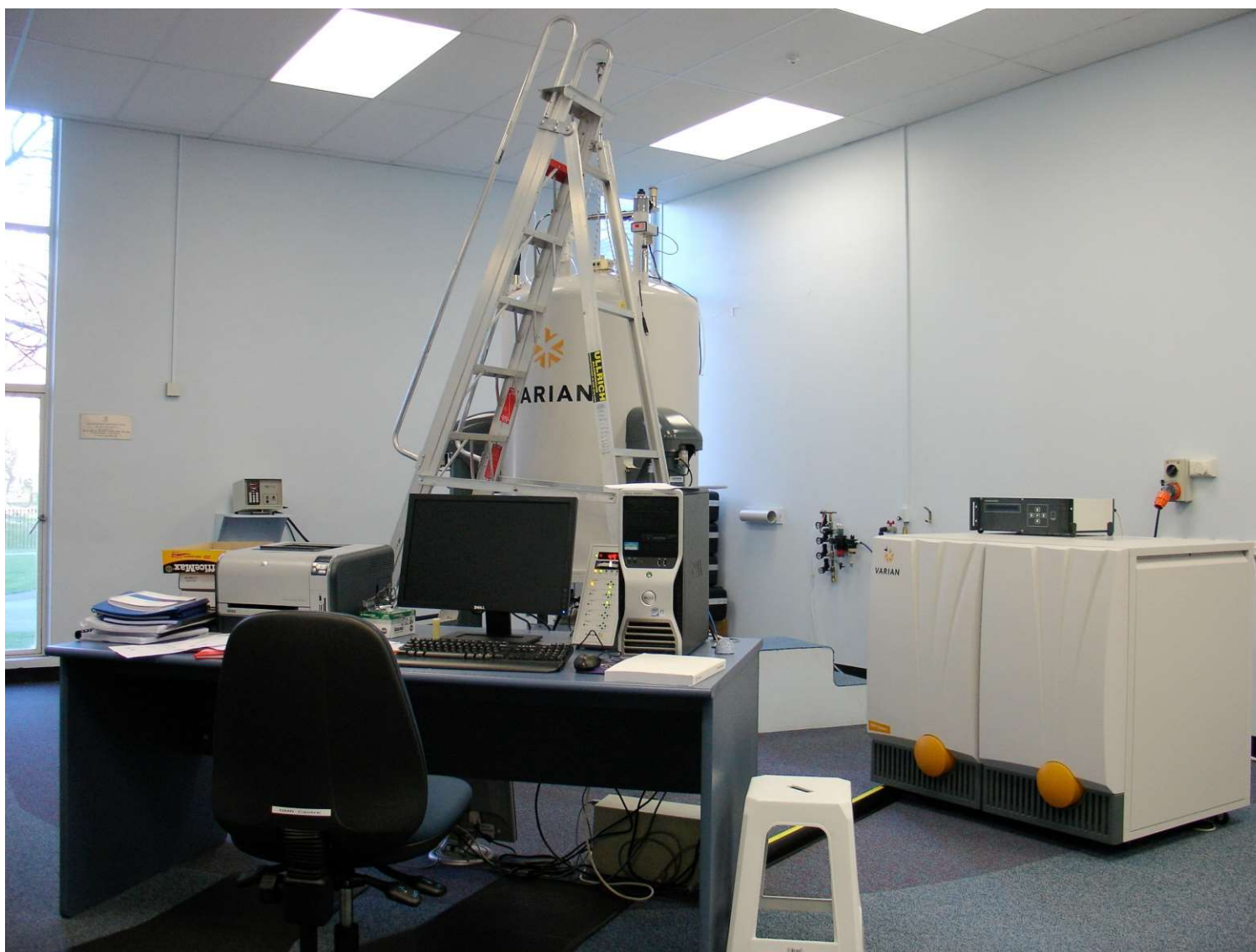
Lecture 2: NMR Spectroscopy

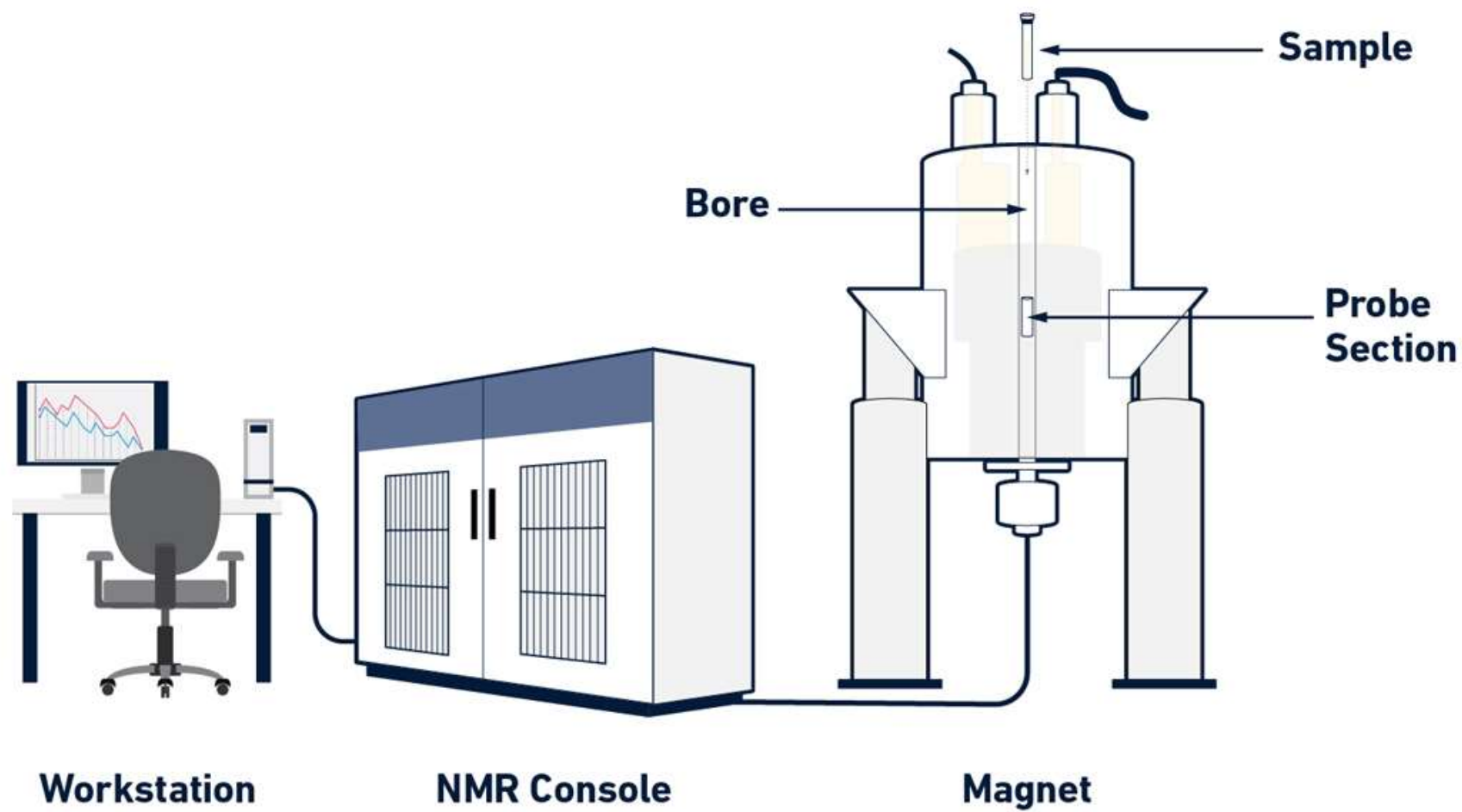
NMR is the same technique as MRI, but medical clinicians thought it best to avoid the word Nuclear in what is actually a harmless, non-invasive technique.

NMR Spectroscopy

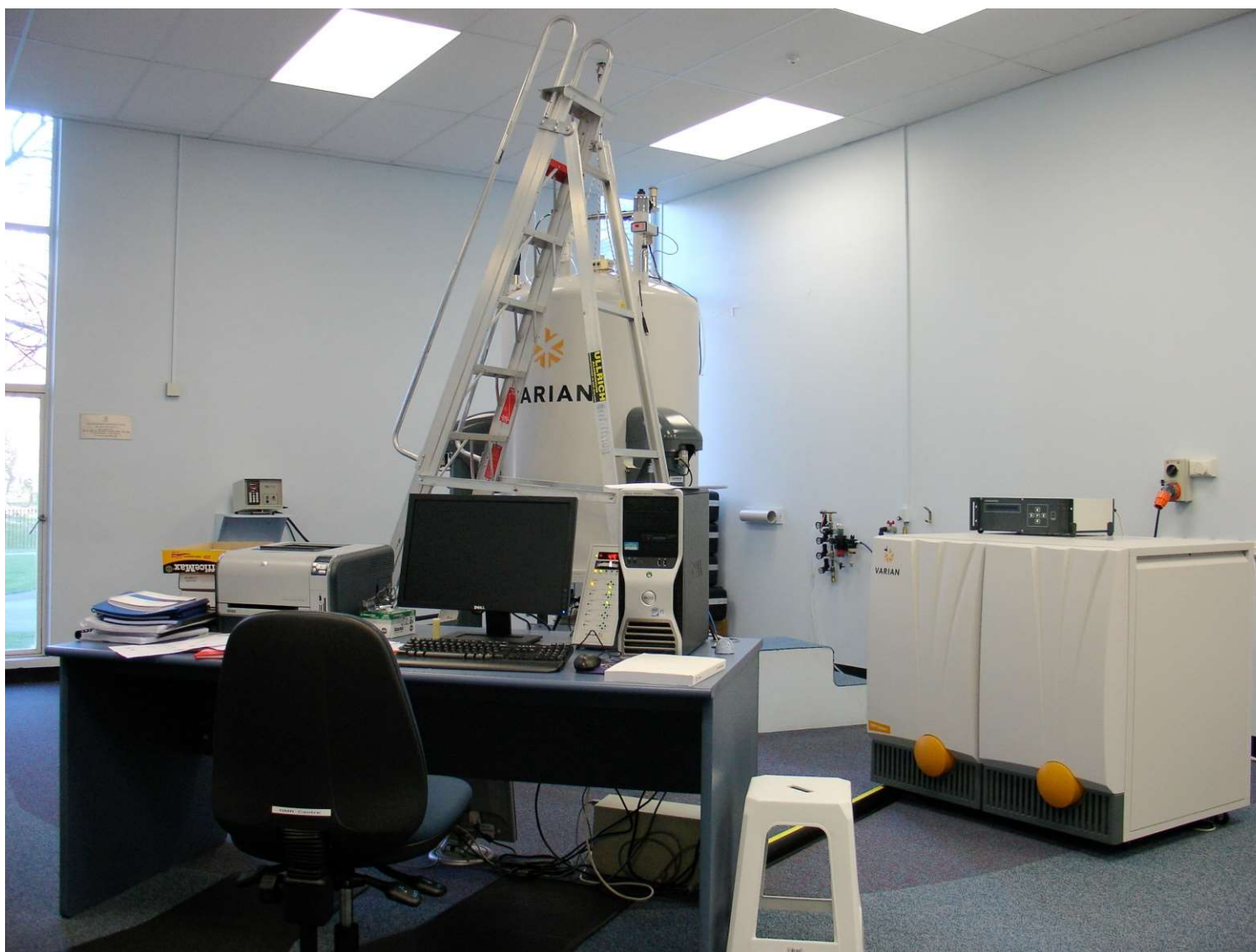


NMR Spectroscopy





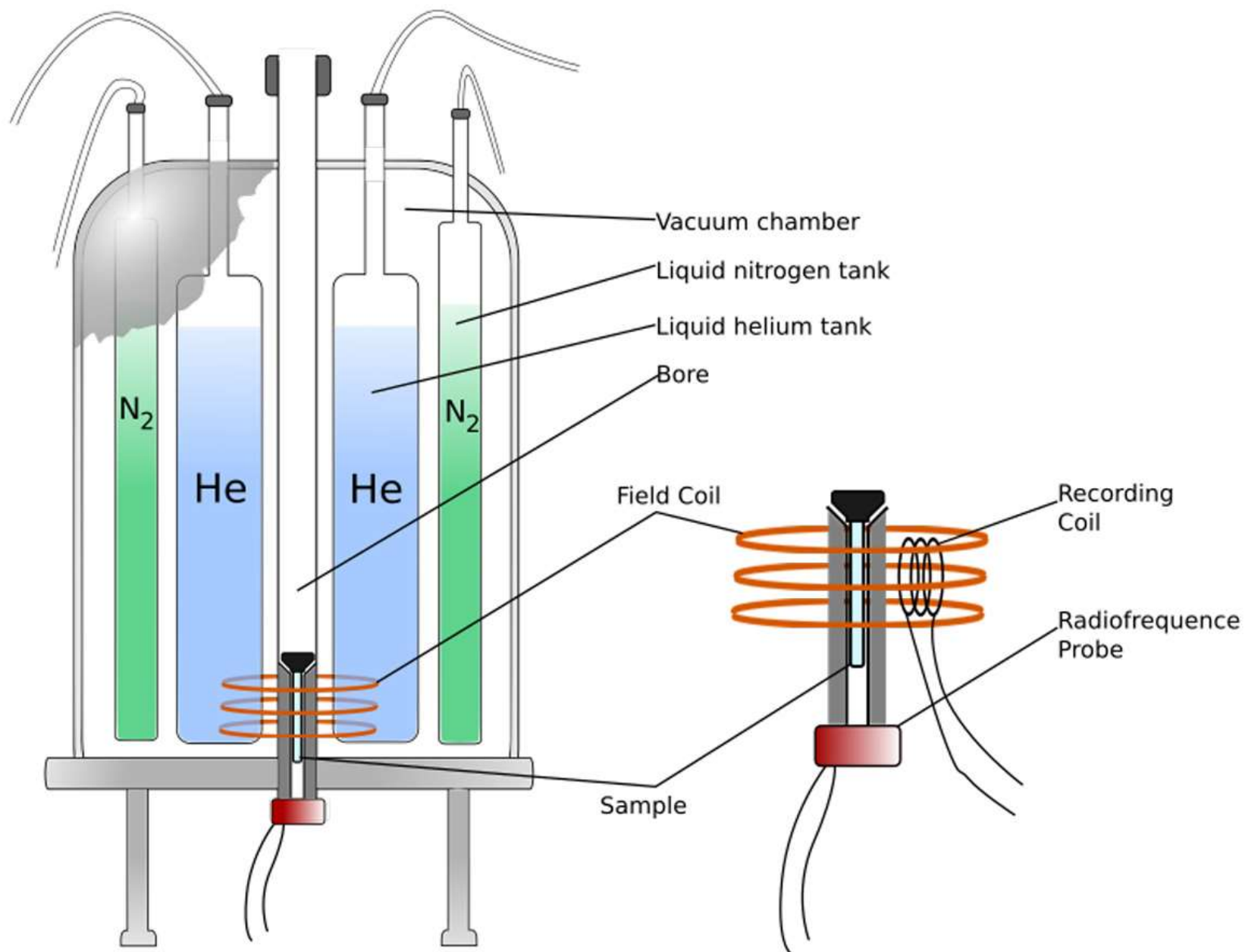
NMR Spectroscopy



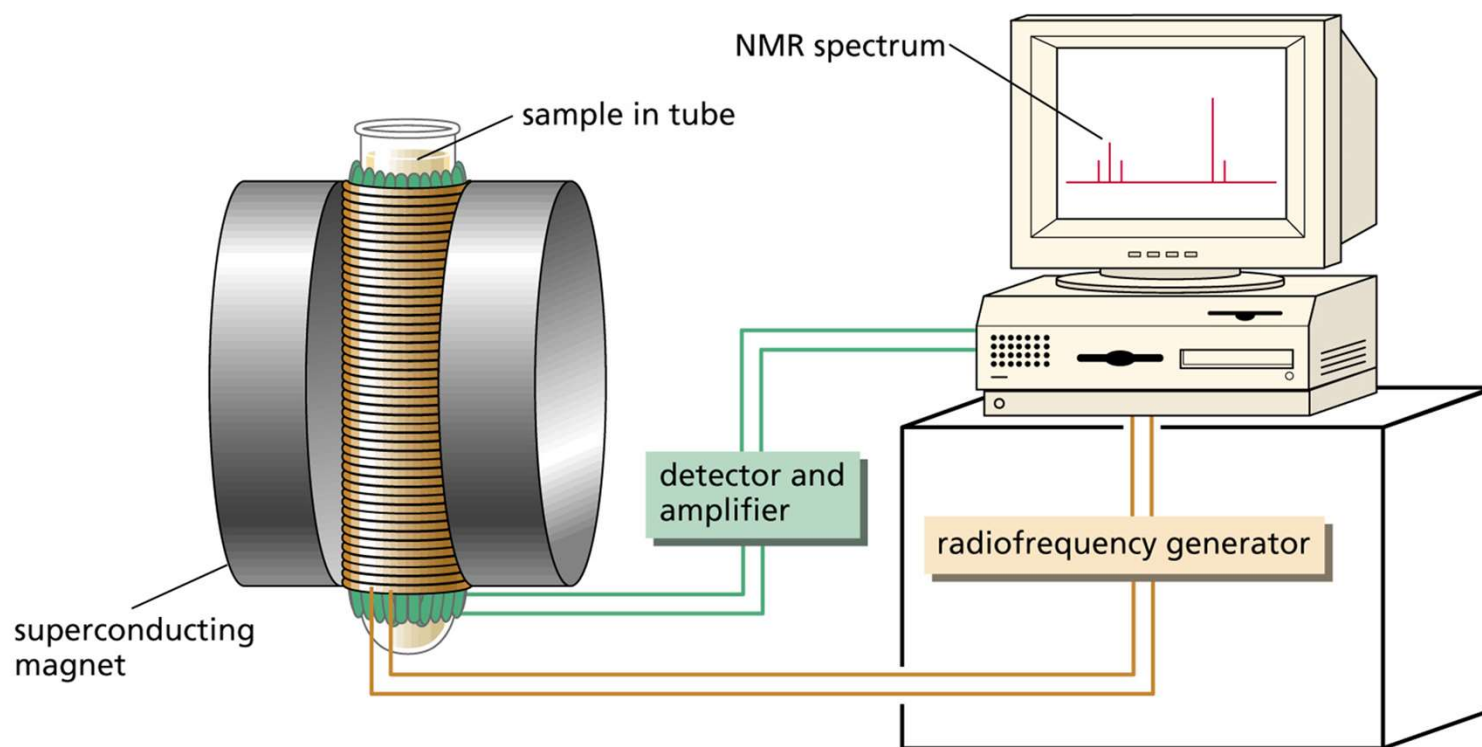
NMR Spectroscopy



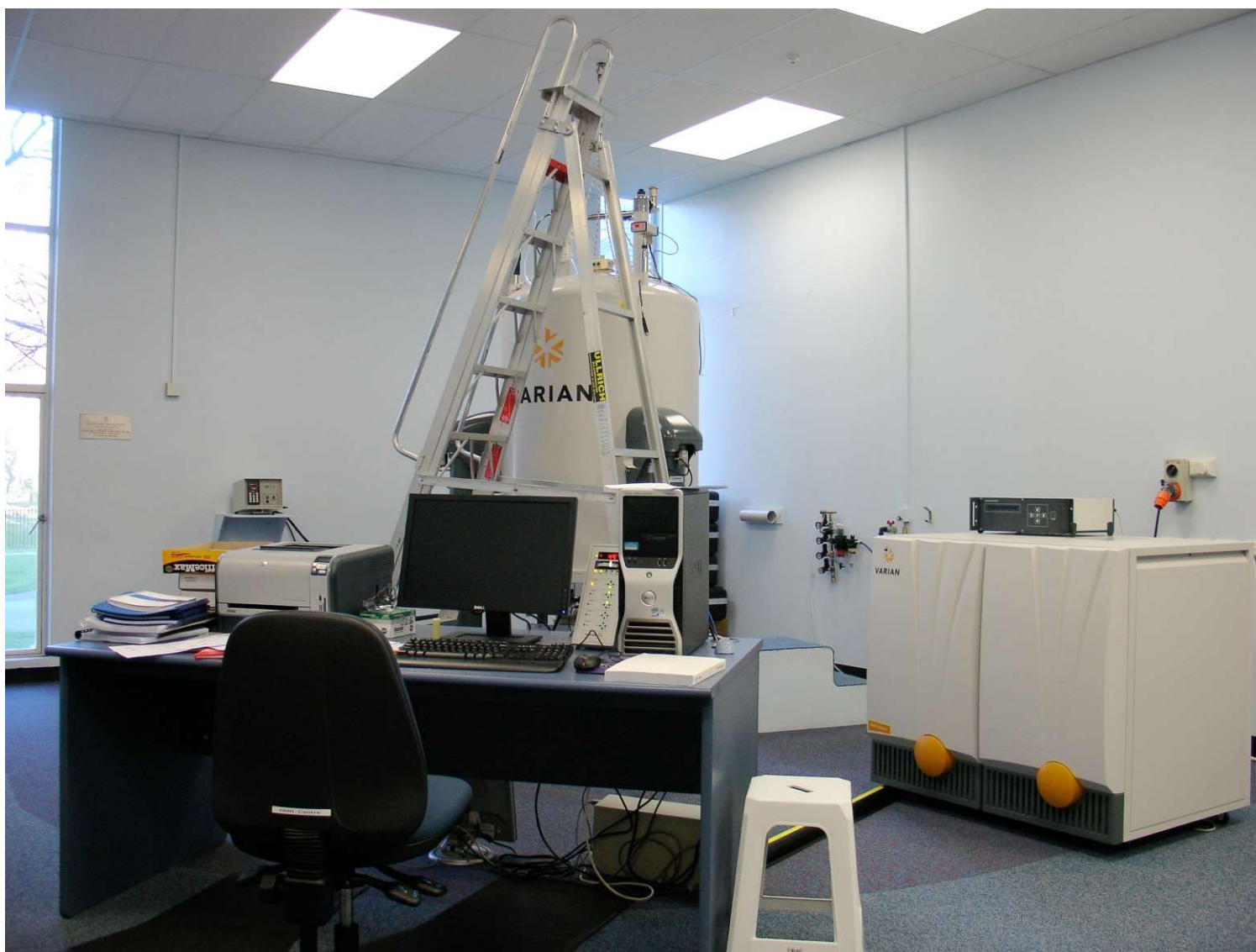
NMR Spectroscopy



NMR Spectrometer

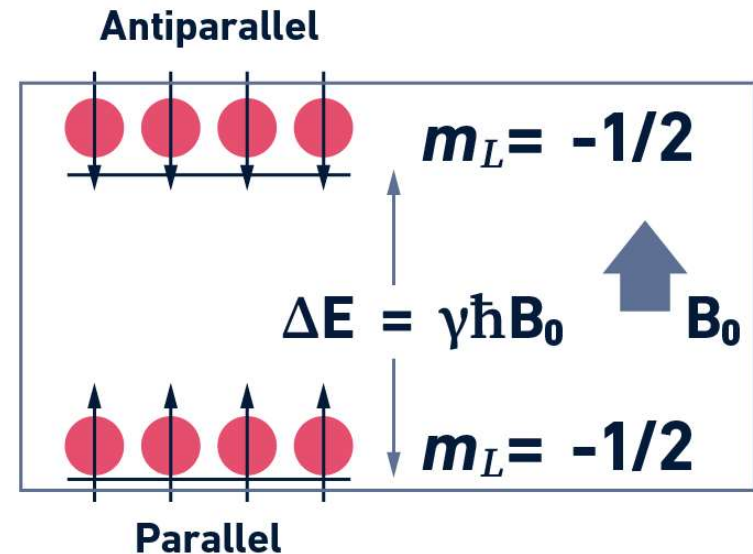
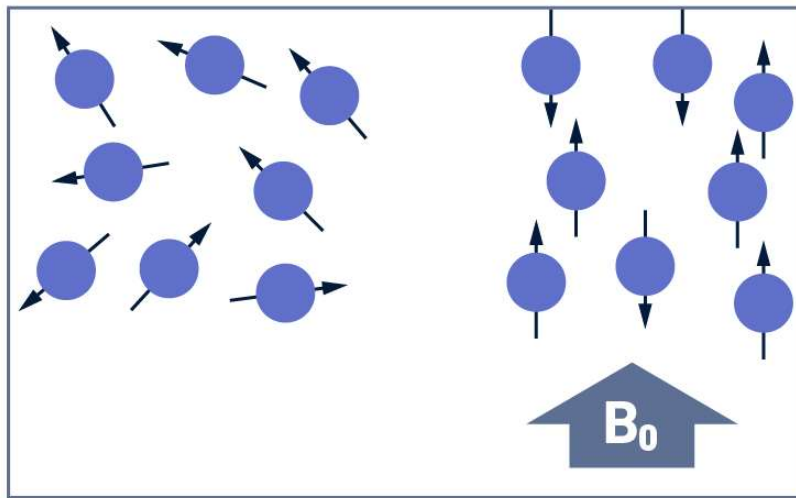


NMR Spectroscopy



Magnetisation

Certain nuclei, with an intrinsic property known as nuclear **spin**, behave as tiny magnets



In the presence of a strong magnetic field, these mini magnets will align parallel or antiparallel to the magnetic field, generating a low and high energy pair of states

The gap between states depends on the magnetic field strength
Stronger magnet, bigger energy gap, better sensitivity.

(NMR) spectroscopy

Spin, I , is a property of every isotope.

Only nuclei with non-zero spin, $I \neq 0$, can be magnetised and thus detectable by NMR

Spin is assigned by the spin quantum number (I), which may take positive integer and half-integer values (0, 1/2, 1, 3/2 etc).

Nuclei with zero spin ($I = 0$) have no magnetic field.

$I = 0$ for nuclei that have an even number of neutrons and an even number of protons
eg ^{12}C and $^{16}\text{O} \Rightarrow$ NMR invisible

Non-zero nuclear spin

$I \neq 0$, then a nucleus will be observable by NMR spectroscopy

- $I = 1/2$ for nuclei that have an odd total number of neutrons+protons (mass number) eg ^1H , ^{13}C , ^{31}P
- $I = 1$ for nuclei that have an odd number of neutrons and an odd number of protons
eg ^2H and ^{14}N

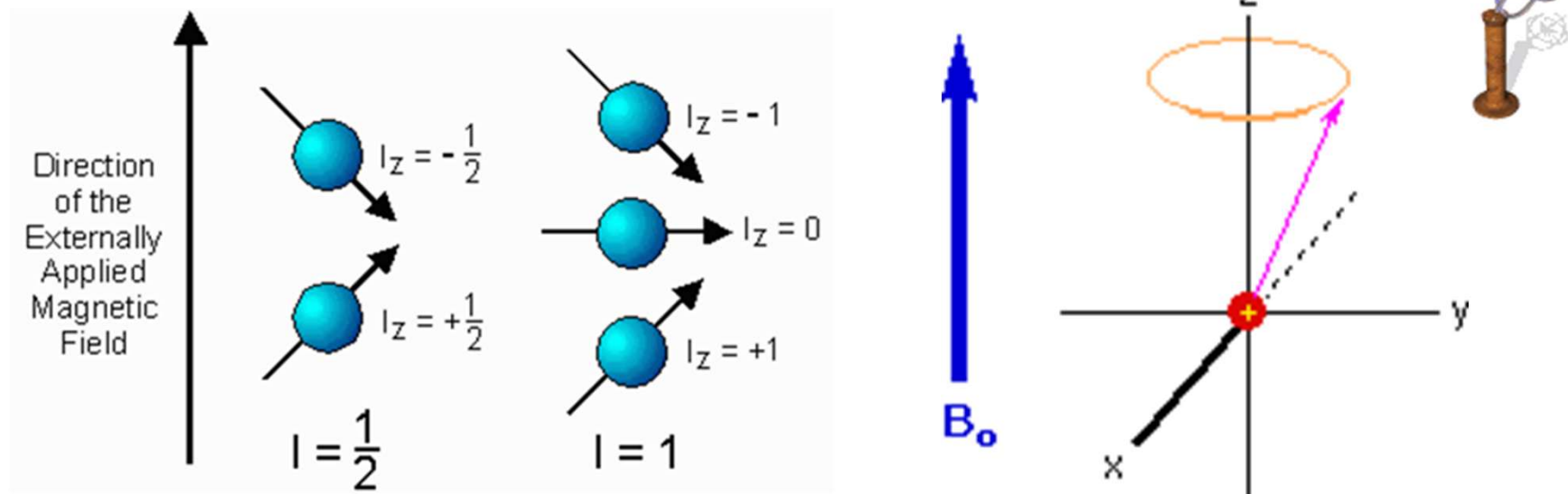
Values for spin are listed for each isotope of each element.

Magnetisation II

In reality, magnetisation is not as simple as 'parallel or antiparallel' to a magnetic field.

Nuclei possess $2I+1$ orientations (spin states) with respect to an external magnetic field (B_0). I describes the nature/shape of the that nucleus' magnetic field associated with the nuclei.

Nuclei with $I = 1/2$ have a relatively simple magnetic field and can align with ($I_z = 1/2$) or against ($I_z = -1/2$) the external magnetic field yielding two spin states.



Higher values of I imply more complex magnetic fields. 33

Gyromagnetic ratio

The strength of the magnetic field arising from a spinning nucleus is dependent on the magnetogyric ratio (gyromagnetic ratio), γ .

$$\gamma = \mu / I$$

Where, μ is the magnetic moment of the nuclei
 I is the angular momentum of the nuclei

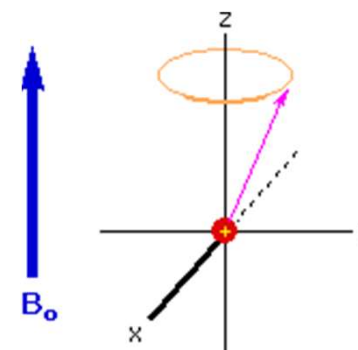
- μ and I behave as if they were parallel or anti parallel vectors.
 $\Rightarrow \gamma$ is positive for parallel and negative for antiparallel vectors.
- γ is an intrinsic nuclear property for a given nuclide

A nucleus with a large γ has a stronger magnetic field than a nucleus with a small γ . Good for NMR!

NMR active nuclei

Properties of NMR active isotopes of commonly encountered nuclides. Resonance frequencies are for a field strength of 11.74 tesla and the relative sensitivity includes a term for the intrinsic sensitivity of a nuclide and its natural abundance.

Nucleus	Natural Abundance %	Nuclear Spin (I)	Magnetogyric ratio / $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$	Resonant frequency / MHz	Relative sensitivity
^1H	99.98	$\frac{1}{2}$	26.75	500.00	1.00
^2H	0.02	1	4.11	76.75	1.45×10^{-6}
^{13}C	1.11	$\frac{1}{2}$	6.73	125.72	1.76×10^{-4}
^{14}N	99.63	1	1.93	36.12	1.01×10^{-3}
^{15}N	0.37	$\frac{1}{2}$	-2.71	50.66	3.85×10^{-6}
^{17}O	0.04	$\frac{5}{2}$	-3.63	67.78	1.08×10^{-5}
^{19}F	100.00	$\frac{1}{2}$	25.18	470.39	0.83
^{31}P	100.00	$\frac{1}{2}$	10.84	202.40	6.63×10^{-2}



Sensitivity of NMR

Signal strength depends on

- amount of sample
- natural abundance of the nuclei
- strength of the applied magnetic field
- molecular motion
- intrinsic properties of the nucleus (γ)

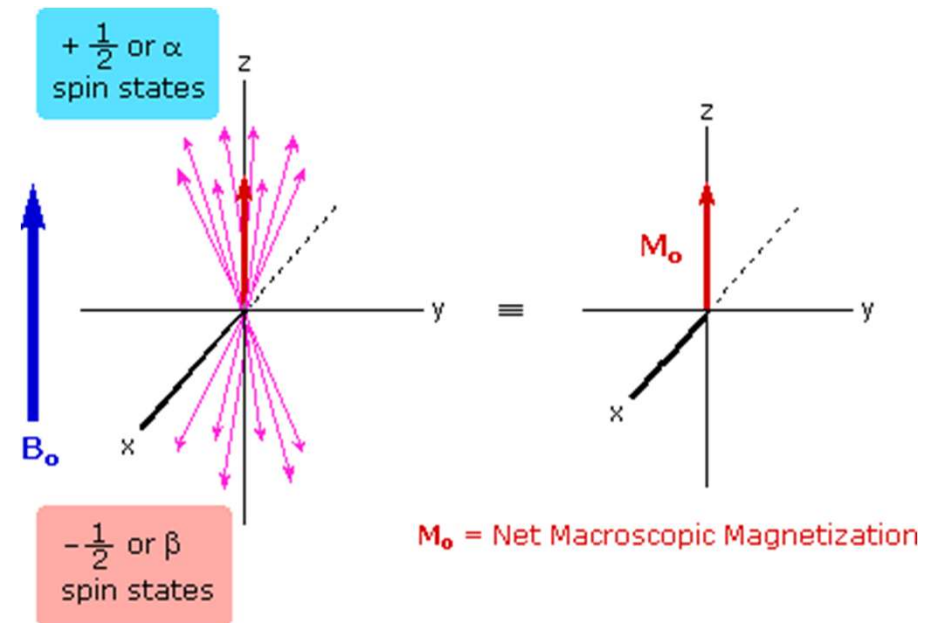
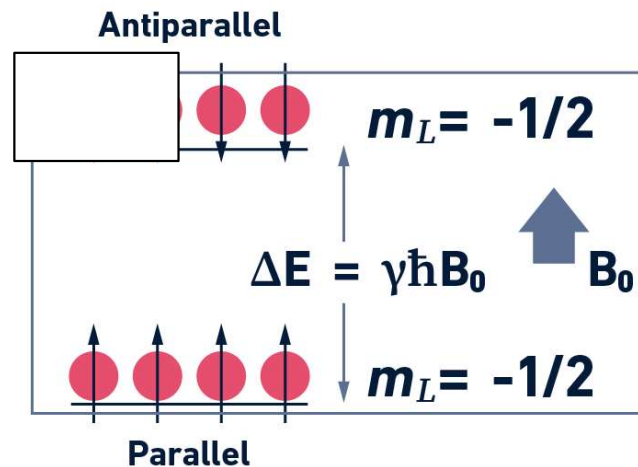
The strongest magnetic field (largest γ) is conveniently possessed by ^1H , the most common isotope of the most common element.

We shall limit our focus to spin 1/2 nuclei and in particular the ^1H and ^{13}C nuclei.

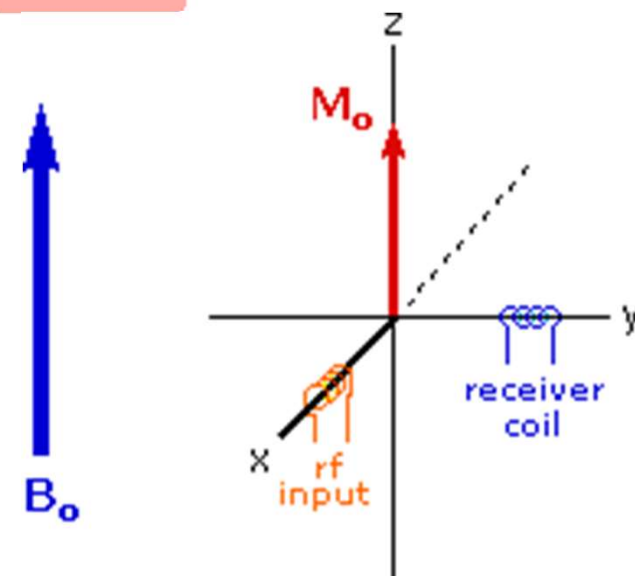
Bulk Magnetisation

Some nuclei are aligned with (low energy), some against (high energy)

The net magnetisation is aligned with the field, since more nuclei are in that state



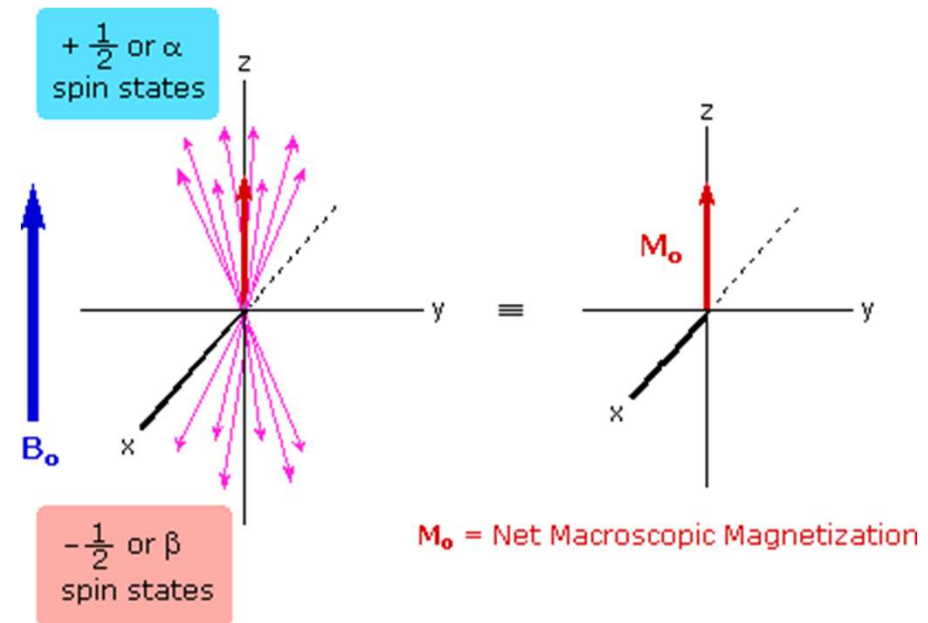
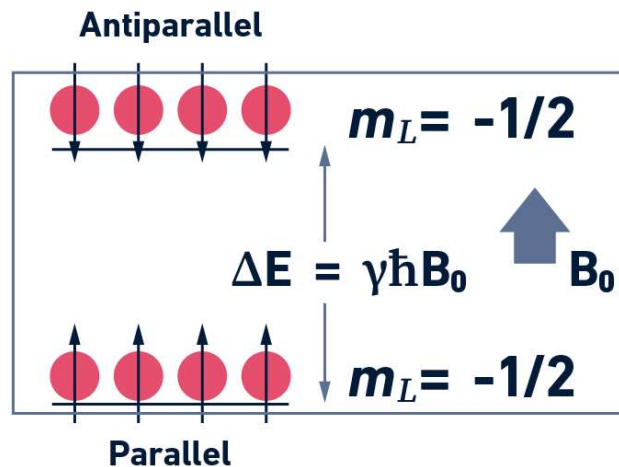
The basis of the NMR experiment is to disturb this net magnetisation via a RF pulse, promoting some nuclei into the higher energy state, decreasing the net magnetisation, and **detect the frequency of the resulting decay back to the ground state (FID)**



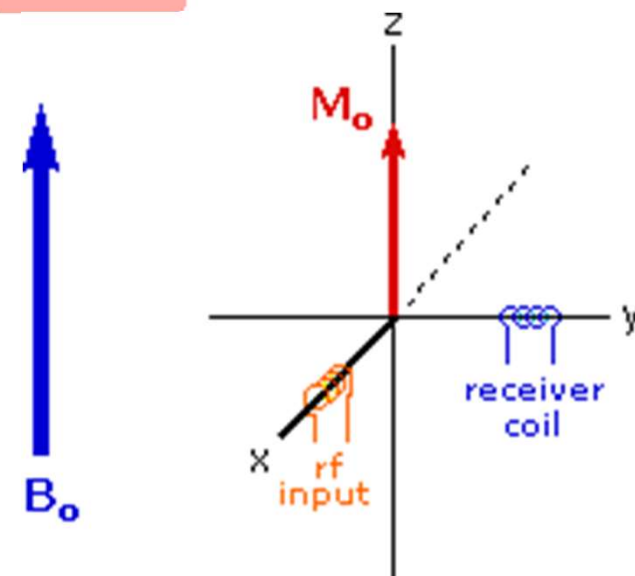
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NMR Summary

- In a magnetic field, spin active nuclei align in a finite number of directions ($2I + 1$) wrt to the magnetic field, and precess like spinning tops with a characteristic frequency
- More molecules can be found in the lowest energy states than the higher energy states, giving the bulk sample a net magnetisation
- The energy difference is small, and there are not many more molecules in the ground state compared to the higher states
- In NMR, a pulse promotes nuclei in lower energy states to higher energy states, changing the populations to be nearly equal
- Some promoted nuclei will eventually relax, returning the populations to their ground state distribution
- This disturbance of the net magnetisation is a bit like disturbing the motion of a spinning top
- The resulting change in frequency of the magnetisation as it returns to the ground distribution is measured as an FID
- The time dependent FID is deconvoluted into a frequency dependent spectrum.