# Introduction to Nuclear Magnetic Resonance Spectroscopy

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- Magnetic resonance (MR) is a phenomenon of resonant energy absorption by a system of nuclei (and electrons).
- Nuclear magnetic resonance (NMR) results from the intrinsic magnetic moment of the nuclei of some atoms. Magnetic moments of electrons are exploited in electron spin resonance.
- Magnetic resonance (MR) generally involves placing a sample in a strong magnetic field (to generate polarisation at a fixed resonant frequency) and detecting signals produced following application of pulsed radio-frequency electromagnetic fields (RF pulses).
- MR is a very powerful method for studying the structure of materials: used in physics, chemistry, biology, medicine etc.

- NMR spectroscopy is used for chemical analysis and for molecular structure determination

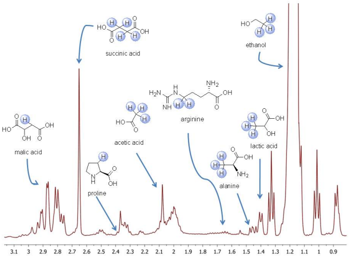


Fig.1: $^{1}$H NMR spectrum of a sample of Spanish wine (`http://www.unirioja.es/gsoe/NMR.htm`)

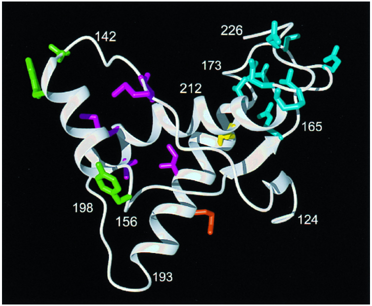


Fig.2: NMR-derived structure of a prion `http://www.pnas.org/content/94/14/7281.full`

- NMR relaxometry can be used to monitor molecular environment

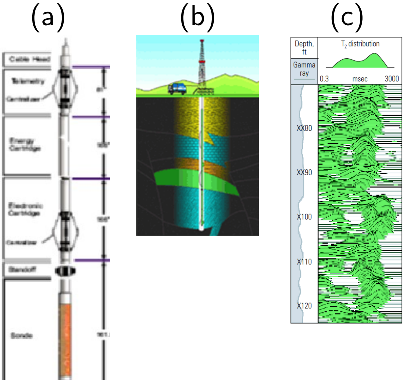


Fig.3: (a) NMR-logging probe, (b) Schematic positioning of the probe in a well, (c) $T_2$-relaxation profile along the bore. Sources: 1) Allenet al. Oilfield review, Autumn 2000; 2) Coates, Xiao NMR Logging Principles and Applications, Hulliburton

- NMR forms the basis for magnetic resonance imaging (MRI)

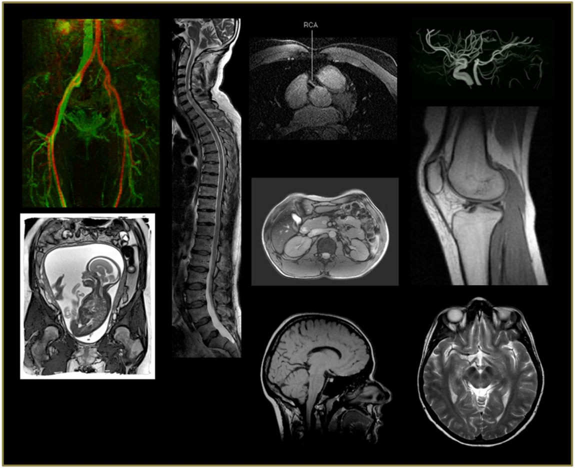


Fig.4: Example magnetic resonance images of blood vessel (in legs), fetus in utero, spine, heart, abdomen, head, blood vessels (in brain), knee, brain (courtesy of Prof. Richard Bowtell)

# 1.3. Magnetic moments in magnetic field.

- Consider charges moving in a limited volume. The position of a charge $\mathbf{e_n}$ will be given by a vector $\mathbf{r_n}$ and its velocity by $\mathbf{v_n}$. The overall magnetic moment of such a system is defined as:

$$\mathbf{M} = \frac{1}{2} \sum_n e_n \mathbf{r_n} \times \mathbf{v_n} \tag{1}$$

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- If all the charges and masses are the same, then $\mathbf{M}$ can be rewritten as:

$$\mathbf{M} = \frac{e}{2m}\sum_n m\mathbf{r_n} \times \mathbf{v_n} = \gamma \mathbf{L}, \tag{2}$$

where

$$\mathbf{L} = \sum_n \mathbf{p_n} \times \mathbf{r_n} \tag{3}$$

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- Gyromagnetic ratio(or magnetogyric):

$$\gamma = \frac{e}{2m} \tag{4}$$

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- Now using equation 2 we can obtain the equation describing the motion of vector $\mathbf{M}$:

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \tag{7}$$

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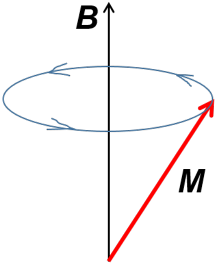
- In a uniform magnetic field directed along $z$-axis $\mathbf{B} = (0, 0, B_0)$, the equation for individual components of $\mathbf{M}$ follow the equations:




$$\frac{dM_x}{dt} = \omega_L M_y$$
$$\frac{dM_y}{dt} = -\omega_L M_x \qquad (8)$$
$$\frac{dM_z}{dt} = 0,$$

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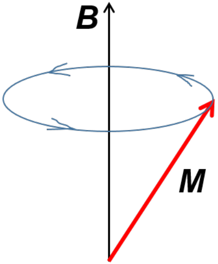


$$\begin{aligned} \frac{dM_x}{dt} &= \omega_L M_y \\ \frac{dM_y}{dt} &= -\omega_L M_x \qquad (8) \\ \frac{dM_z}{dt} &= 0, \end{aligned}$$

where $\omega_L = \gamma B_0$ - Larmor frequency.

- A solution to this system of differential equations with initial values of $M_x(0), M_y(0), M_z(0)$ has the following form:

$$\begin{aligned} M_x(t) &= M_x(0)\cos(\omega_L t) + M_y(0)\sin(\omega_L t) \\ M_y(t) &= -M_y(0)\sin(\omega_L t) + M_y(0)\cos(\omega_L t) \qquad (9) \\ M_z(t) &= M_z(0) \end{aligned}$$

# 1.4. Angular momentum operator

- In quantum mechanics physical quantities $A$ are represented by their operators $\hat{A}$. The mechanical angular momentum is replaced by its corresponding operator:

$$\mathbf{L} = \sum_n \mathbf{p_n} \times \mathbf{r_n} \longleftrightarrow \hat{\mathbf{L}} = \frac{1}{\hbar} \sum_n \hat{\mathbf{r}}_\mathbf{n} \times \hat{\mathbf{p}}_\mathbf{n} = -i \sum_n \hat{\mathbf{r}}_\mathbf{n} \times \boldsymbol{\nabla}_\mathbf{n} \quad (10)$$

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- Angular momentum operator properties. Commutation:

$$[\hat{L}_y, \hat{L}_z] = i\hat{L}_x, [\hat{L}_z, \hat{L}_x] = i\hat{L}_y, [\hat{L}_x, \hat{L}_y] = i\hat{L}_z \quad (11)$$

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- Angular momentum squared, and its commutation properties:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (12)$$

$$[\hat{L}^2, \hat{L}_x^2] = [\hat{L}^2, \hat{L}_y^2] = [\hat{L}^2, \hat{L}_z^2] = 0 \quad (13)$$

- Eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$ operators can be characterized by integer quantum numbers $l$ and $m$ respectively. These eigen functions will be denoted as $|lm\rangle$. Their eigenvalues are:

$$\hat{L}_z|lm\rangle = m|lm\rangle \tag{14}$$

$$\hat{L}^2|lm\rangle = l(l+1)|lm\rangle \tag{15}$$

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- Another useful operator are raising and lowering operators:

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y, \hat{L}_- = \hat{L}_x - i\hat{L}_y \tag{16}$$

$$\langle lm|\hat{L}_+|l(m-1)\rangle = \langle l(m-1)|\hat{L}_-|lm\rangle = \sqrt{(l+m)(l-m+1)} \tag{17}$$

- Classical magnetic moment will have its own quantum analogue, the operator of angular momentum:

$$\mathbf{M} = \gamma \mathbf{L} \longleftrightarrow \hat{\boldsymbol{\mu}} = \gamma \hbar \hat{\mathbf{L}} \tag{18}$$

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- Bohr magneton:

$$\beta = \frac{e\hbar}{2m} \approx 9.27 \cdot 10^{-24} \, \mathrm{J\,T}^{-1} \tag{19}$$

Free electron and many nuclei have spin.

These equations describe a precession of a vector **M** around the direction of the external magnetic field **B** with the frequency $\omega_0$ as shown schematically in Fig.**??**A. Such motion is called "Larmor precession" and $\omega_0 = \gamma B_0$ is called "Larmor frequency".
Of course, this primitive classical picture serves only as an illustration to the actual behaviour of magnetic moments placed into a magnetic field. However, a more rigorous description using quantum mechanics for an ensemble of magnetic moments provides a similar answer. Larmor precession of an overall magnetic moment is a real effect, and as we will see later, it is essential for acquiring of magnetic resonance spectra.
Now we'll briefly sketch the basic quantum mechanical description of a magnetic moment in a magnetic field. The angular momentum operator $\hat{\mathbf{L}}$ (which could be an orbital or spin angular momentum) is proportional to the magnetic moment operator as:

$$\hat{\boldsymbol{\mu}} = \gamma \hbar \hat{\mathbf{L}}, \tag{20}$$

The Hamiltonian of a system can be written by analogy with expression 5 as:

$$\hat{H} = -\hat{\boldsymbol{\mu}}\mathbf{B} = -\gamma \hbar \hat{I}_z B_0 = -\omega_0 \hat{I}_z, \tag{21}$$