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

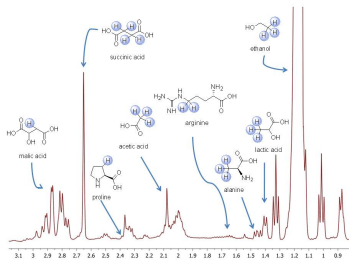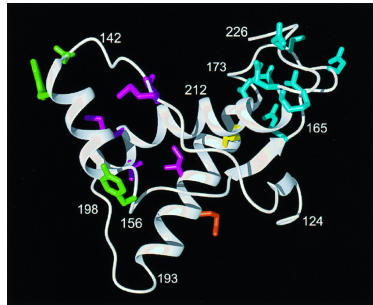Fig.1: ^{1}H NMR spectrum of a sample of Spanish wine (http://www.unirioja.es/gsoe/NMR.htm)

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
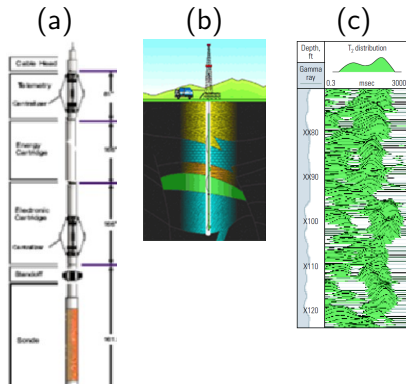

(a)　(b)　(c)

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) Allen et al. Oilfield review, Autumn 2000; 2) Coates, Xiao NMR Logging Principles and Applications, Hulliburton

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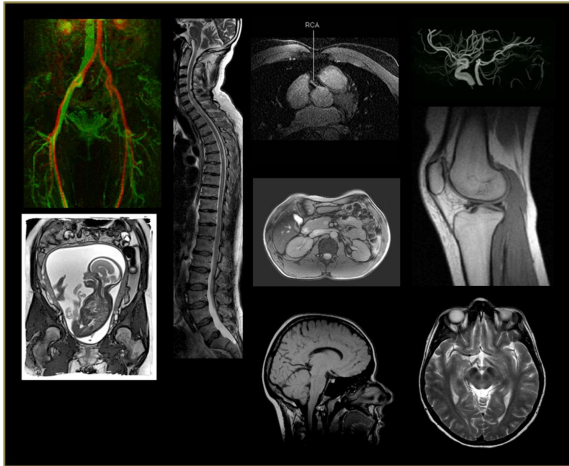

Fig.4: Example magnetic resonance images of blood vessel (in legs), fetus in utero, spine, heart, abdomen, head, blood vessels (in brain), knee, brain (courtesy of Prof. Richard Bowtell)

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

$$\mathbf{M} = \frac{1}{2} \sum_n e_n \mathbf{r_n} \times \mathbf{v_n} \qquad (1)$$

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

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

where

$$\mathbf{L} = \sum_n \mathbf{p_n} \times \mathbf{r_n} \qquad (3)$$

is the mechanical angular momentum.

- Gyromagnetic ratio(or magnetogyric):

$$\gamma = \frac{e}{2m} \qquad (4)$$

- When a magnetic moment **M** is placed into an external uniform permanent magnetic field **B**, its energy is given by:

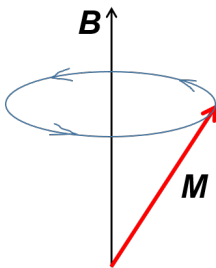$$E = -\mathbf{M} \cdot \mathbf{B} \tag{5}$$

- The torque acting on the system:

$$\frac{d\mathbf{L}}{dt} = \mathbf{M} \times \mathbf{B} \tag{6}$$

- Now using equation 2 we can obtain the equation describing the motion of vector **M**:

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

- 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:

$$\frac{dM_x}{dt} = \omega_L M_y$$

$$\frac{dM_y}{dt} = -\omega_L M_x \qquad (8)$$

$$\frac{dM_z}{dt} = 0,$$

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:

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

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

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

- Angular momentum operator properties. Commutation:

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

- 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:

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

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

- 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:

$$\mathbf{M} = \gamma \mathbf{L} \longleftrightarrow \hat{\boldsymbol{\mu}} = \gamma \hbar \hat{\mathbf{L}} \qquad (18)$$

- Given the electron charge $e = 1.6 \cdot 10^{-19}$C, and mass $m = 9.1 \cdot 10^{-31}$kg Bohr magneton:

$$\beta_e = \gamma \hbar = \frac{e\hbar}{2m} \approx 9.27 \cdot 10^{-24} \text{J·T}^{-1} \qquad (19)$$

- Similarly a nuclear magneton could be calculated for a proton (^{1}H nucleus):

$$\beta = \gamma_N \hbar = \frac{e\hbar}{2m_p} \approx 5.05 \cdot 10^{-27} \text{J·T}^{-1} \qquad (20)$$

However, real nuclei and electrons have spins (intrinsic magnetic moment). Their z-axis projection m takes integer and half-integer values: $m = \frac{1}{2}, 1, \frac{3}{2}, 2$ etc. Similar to the equation for the orbital angular momentum Eq.18. For nuclei spins we get its magnetic moment as:

$$\hat{\boldsymbol{\mu}}_{\mathbf{N}} = \gamma_N \hbar \hat{\mathbf{I}}, \qquad (21)$$

where $\hat{\mathbf{I}}$ stands for the nuclear spin operator. All the properties of angular momentum operators listed in Eqs.11-17 will be true for $\hat{\mathbf{I}}$.

- Many nuclei in the periodic table are magnetic, i.e. have spin $I \neq 0$. Their magnetic moments could be measured in units of β_N:

$$\hat{\boldsymbol{\mu}}_{\mathbf{N}} = \gamma_N \hbar \hat{\mathbf{I}} = g_N \beta_N \hat{\mathbf{I}}, \qquad (22)$$

where g_N - dimensionless g-factor.

Nucleus	Natural abundance %	Nuclear spin (I)	g_N, g-factor	γ_N, Gyromagnetic ratio (10^7 rad/T*s)
^{1}H	99.98	$\frac{1}{2}$	5.585	26.7519
^{2}H	$1.5*10^{-2}$	1	0.857	4.1066
^{13}C	1.108	$\frac{1}{2}$	1.405	6.7283
^{14}N	99.635	1	0.403	1.9338
^{15}N	0.365	$\frac{1}{2}$	-0.567	-2.712

- Electron magnetic moments can be measured in units of Bohr magnetons: $\hat{\boldsymbol{\mu}}_{\mathbf{S}} = -\gamma_e \hbar \hat{\mathbf{S}} = -g_e \beta_e \hat{\mathbf{S}}$, and for a free electron spin $g_e \approx 2.0023$.

- Applications of NMR: chemistry, biology, medicine, industry ...
- Magnetic moment in magnetic field: Classical description
- Recap of angular momentum operator properties: commutation properties.
- Nuclei have their own nuclear magnetic moment. Described using spin angular momentum operator.
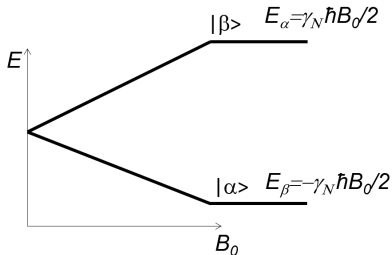
- Let's quantum mechanically describe the system of spins in the magnetic field. Eq. 5 can be rewritten in a form of Hamiltonian:

$$E = -\mathbf{M} \cdot \mathbf{B} \longleftrightarrow \mathcal{H} = -\hat{\boldsymbol{\mu}}_{\mathbf{N}} \cdot \mathbf{B} \qquad (23)$$

- when the magnetic field is directed along z-axis $\mathbf{B} = (0, 0, B_0)$:

$$\mathcal{H} = -\hat{\boldsymbol{\mu}}_{\mathbf{N}} \cdot \mathbf{B} = -\gamma_N \hbar B_0 \hat{I}_z \qquad (24)$$

- For spin $I = \dfrac{1}{2}$ such Hamiltonian produces a two-level system. Its energy levels corresponding to eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$:

- The transition between the two states requires an energy quantum[1]:

$$h\nu_L = \gamma \hbar B_0, \omega_L = \gamma B_0, \nu_L = \frac{\gamma B_0}{2\pi} \qquad (25)$$

ω_L and ν_L is the Larmor frequency (anglular and cyclic respectively)

Nucleus	Natural abundance %	Nuclear spin (I)	Larmor frequency at 11.744T, MHz	γ_N, Gyromagnetic ratio (10^7 rad/T*s)
^{1}H	99.98	$\frac{1}{2}$	500	26.7519
^{2}H	$1.5*10^{-2}$	1	76.753	4.1066
^{13}C	1.108	$\frac{1}{2}$	125.721	6.7283
^{14}N	99.635	1	36.118	1.9338
^{15}N	0.365	$\frac{1}{2}$	50.664	-2.712

NMR measurements are generally made on bulk samples which contain very large numbers of nuclear spins (e.g. 1 cm^3 contains $N \approx 6.7 \cdot 10^{22}$ ^{1}H atoms) The measured signals therefore result from the collective effect of a large number of magnetic moments that can be described using a bulk magnetization. At thermal equilibrium, the numbers of nuclei in the $|\alpha\rangle$ state N_α and $|\beta\rangle$ state N_{beta} follow Boltzmann distribution:

$$\frac{N_\alpha}{N_\beta} = e^{-\frac{\gamma B_0}{kT}} \approx (1 - \frac{\gamma B_0}{kT}), \tag{26}$$

when $\gamma B_0 \ll kT$. Overall magnetization then can be calculated as:

$$M_z = N_\alpha(-\frac{1}{2}\gamma\hbar) + N_\beta(\frac{1}{2}\gamma\hbar) = N\frac{\gamma^2\hbar^2 B_0}{4kT} \tag{27}$$

- Let's apply oscillating magnetic field to our system. A spin system Hamiltonian becomes time-dependent and for an oscillation along the x-axis we obtain:

$$
\begin{aligned}
\mathcal{H}(t) &= -\hat{\boldsymbol{\mu}}(\mathbf{B_0} + \mathbf{B(t)}) = \\
&= -\gamma\hbar\hat{I}_z(B_0 + B_1(t)) = \\
&= -\gamma\hbar\hat{I}_z B_0 - \gamma\hbar\hat{I}_x B_1\cos(\omega t),
\end{aligned}
\tag{28}
$$

where H_1 and ω are the amplitude and the frequency of the oscillating magnetic field.

- According to perturbation theory the transition probability between the initial state $|a\rangle$ and the final state $|b\rangle$ with a time dependent Hamiltonian $\hat{V}(t) = 2\hat{F}\cos(\omega t)$ is (Fermi's golden rule):
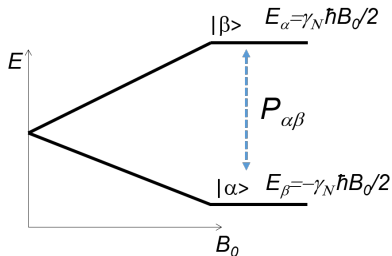
$$
P_{ab} = \frac{2\pi}{\hbar}|\langle a|\hat{F}|\rangle b|^2\delta(E_{ab} - \hbar\omega),
\tag{29}
$$

where $E_{ab} = E_a - E_b$ is an energy difference between the energies of levels a and b.

- For a two level system described before, the matrix element $\langle\alpha|\hat{I}_x|\beta\rangle = \frac{1}{2}$. The transition probability then becomes:
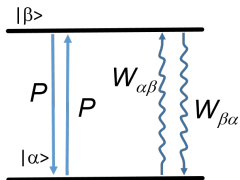
$$P_{\alpha\beta} = \frac{\pi}{2\hbar}(\gamma H_1)^2 \delta(E_{\alpha\beta} - \hbar\omega), \qquad (30)$$

- **The effect of resonant absorption (and emission) of electromagnetic irradiation at the frequency matching the energy difference in a nuclear system is called Nuclear Magnetic Resonance (NMR).**

- In a two-level system the transition will take place due to the action of external irradiation, but also due to interaction with the environment.

P - the rate of transitions driven by external field, $W_{\alpha\beta}$, $W_{\beta\alpha}$ - rates of spontaneous spin flips due to interaction with environment.

- In thermal equilibrium:

$$N_{\alpha}^0 W_{\alpha\beta} = N_{\beta}^0 W_{\beta\alpha}, \text{i.e.} \tag{31}$$

$$\frac{W_{\beta\alpha}}{W_{\alpha\beta}} = exp^{-\dfrac{\gamma\hbar B_0}{kT}} \approx 1 - \frac{\gamma\beta B_0}{kT} \tag{32}$$

- Equation for populations of levels:

$$\begin{aligned}
\frac{dN_\alpha}{dt} &= -N_\alpha(P + W_{\alpha\beta}) + N_\beta(P + W_{\beta\alpha}) \\
\frac{dN_\beta}{dt} &= N_\alpha(P + W_{\alpha\beta}) - N_\beta(P + W_{\beta\alpha})
\end{aligned} \tag{33}$$

- If we introduce the average rate of spontaneous transitions $W = \frac{1}{2}(W_{\alpha\beta} - W_{\beta\alpha})$, then $W_{\alpha\beta} = W(1 + \frac{\gamma\hbar B_0}{2kT})$ and $W_{\beta\alpha} = W(1 - \frac{\gamma\hbar B_0}{2kT})$, the equations can be rewritten:

$$\begin{aligned}
\frac{dN_\alpha}{dt} &= (N_\beta - N_\alpha)P + (N_\beta - N_\alpha)W - W\frac{\gamma\beta B_0}{2kT}N \\
\frac{dN_\beta}{dt} &= -(N_\beta - N_\alpha)P - (N_\beta - N_\alpha)W + W\frac{\gamma\beta B_0}{2kT}N
\end{aligned} \tag{34}$$

- Denote the population difference as $n = N_\beta - N_\alpha$ and thermal equilibrium population difference $n_0 = N_\beta^0 - N_\alpha^0 \approx N\dfrac{\gamma\hbar B_0}{2kT}$ the equations can be rewritten as:

$$\frac{dn}{dt} = -2nP - 2nW + 2Wn_0, \qquad (35)$$

or

$$\frac{dn}{dt} = -2nP - \frac{(n - n_0)}{T_1}, \qquad (36)$$

where $T_1 = \dfrac{1}{W}$ is called spin-lattice relaxation time determines how quickly a spin system reaches a thermal equilibrium with environment.

- In equilibrium, when $\dfrac{dn}{dt} = 0$:

$$n = \frac{n_0}{1 + 2PT_1} \qquad (37)$$

when the power is very large $PT_1 \gg 1$, $n \to 0$, i.e. the system is saturated and no signal can be observed.

- Spin $I = \dfrac{1}{2}$ in a magnetic field. Two-level system.
- System of spins in a magnetic field is capable of absorbing radiation at a resonant frequency.
- Population dynamics in a two-level system. Signal as function of radiation power and saturation.