NMR

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1 A brief history of NMR

1938, Rabi, University of Colombia, first detection of NMR in molecular beam;
1945-1946, Purcel, Harvard, detection of NMR in solid & Bloch, Stanford, detection of NMR in liquid material;
1948, Bloembergen (student of purcel), Harvard, Theory of NMR, foretell the relaxation of NMR in water;
1949, Hahn, Illinois Champaign, spin-echo NMR;
1950, Ramsey(student of (Purcel), Harvard, magnetic shielding molecular;
1965, Ernst, FT-NMR;
1973, Lauterbur, State University of New York, MRI;Nobel
1977, Mansfield, Nottingham Univ., EPI;Nobel
1991, Bellivean, Harvard, fMRI(CBV);
1992, Seiji Ogawa, Bell lab, BOLD-fMRI.

2 Basis of NMR physics

Macroscopic matter(m)→atoms(Å)→nucleus(10^{-4}Å)→quark
Nucleus is extremely small and extremely light. An important properties: spin $\boldsymbol{S}$, magnetic dipole moment $\boldsymbol{\mu}$. The relationship between $\boldsymbol{\mu}$ and $\boldsymbol{S}$ is $\boldsymbol{\mu} = \gamma \boldsymbol{S}$. Each type of nucleus has a conserved value of γ For example, $\gamma_H = 42.58 MHz/T$.

2.1 Energy and motion equations of magenetic dipole, classical model

Consider a nucleus of magnetic dipole moment $\boldsymbol{\mu}$ placed in a magnetic field $\boldsymbol{H}$, energy of the nucleus is indicated by,

$$E = -\boldsymbol{\mu} \cdot \boldsymbol{H}$$

Apparently, when direction of magnetic dipole moment is identical to direction of the magnetic field, the nucleus reaches its lowest energy. motion of the dipole

follows,

$$\frac{\mathrm{d}\boldsymbol{S}}{\mathrm{d}t} = \boldsymbol{\mu} \times \boldsymbol{H}$$

#Practice 1: prove that $\boldsymbol{S}$ rotates in space, and $\omega = \gamma|\boldsymbol{H}|$

2.2 Quantum physics of spin

Energy equation

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \boldsymbol{H} = -\mu_z H_0 = \gamma S_z H_0$$

where S is integers or half integers, and

$$S_Z = -S, -S+1, \ldots, S-1, S$$

so for each S of definite value, the number of possible values of S_z is $2S+1$.
Motion equation (isolated spin system)

$$\frac{\mathrm{d}\langle\boldsymbol{\mu}\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\langle[\mathcal{H}, \boldsymbol{mu}]\rangle = \gamma\langle\boldsymbol{\mu}\rangle \times \boldsymbol{H}$$

For multiple spins (i.e. macroscopic picture), we define Magnetization vector $\boldsymbol{M}$ as

$$\boldsymbol{M} = N\langle\boldsymbol{\mu}\rangle$$

where N is numerical density of the spins. Then it's easy to prove that

$$\frac{\mathrm{d}\boldsymbol{M}}{\mathrm{d}t} = \gamma\boldsymbol{M} \times \boldsymbol{H}$$

e.g for a hydrogen atom, $S = \frac{1}{2}\hbar$, thus $S_z = \pm\frac{1}{2}\hbar$. According to energy equation, energy of hydrogen atom is

$$E_{\frac{1}{2}} = -\frac{1}{2}\gamma\hbar H_0$$

$$E_{-\frac{1}{2}} = -\frac{1}{2}\gamma\hbar H_0$$

$$\Delta E = \gamma\hbar H_0$$

If a photon of energy ΔE is absorbed by the atom, Resonance happens:

$$\hbar\omega = \Delta E = \gamma\hbar H_0$$

$$\omega = \gamma H_0$$

According to Boltzmann distribution, the number of spins that takes value $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively follows,

$$n_+ + n_- = N$$

2

and

$$\frac{n_-}{n_+} = \exp\left(-\frac{\Delta E}{k_B T}\right)$$

which derives

$$n_+ = \frac{1}{1 + e^{-\frac{\delta E}{k_B T}}}$$

$$n_- = \frac{e^{-\frac{\delta E}{k_B T}}}{1 + e^{\frac{\delta E}{k_B T}}}$$

furthermore,

$$M_z = (n_+ - n_-)\mu = N\mu\tanh\left(\frac{\Delta E}{2k_B T}\right)$$

when condition $\Delta E << k_B T$ is satisfied,

$$M_0 = M_z = \left(\frac{N\mu^2}{k_B T}\right) H_0$$

2.3 Introducing lattice to the system, Bloch equation

If energy gap of lattice $\Delta E_{lattice} = \Delta E_{spin}$, the lattice interacts with the spin system number of spins at two levels of the lattice names n_h and n_l respectively. then,

$$\frac{dn_+}{dt} = Wn_-n_l - Wn_+n_h$$

$$\frac{dn_-}{dt} = Wn_+n_h - Wn_-n_l$$

where W denotes possibility of 'jumps'. it can be derived that

$$\frac{d\Delta N}{dt} = W\left[N\left(n_l - n_h\right) - \Delta N\left(n_l + n_h\right)\right]$$

the condition of equilibrium is

$$\frac{d\Delta N}{dt} = 0$$

indicating that

$$(\Delta N)_0 = \frac{n_l - n_h}{n_l + n_h}$$

define that

$$\frac{1}{T_1} = W(n_l + n_h)$$

, where T_1 is called Relaxation Time, then

$$\frac{d\Delta N}{dt} = \frac{(\Delta N)_0 - \Delta N}{T_1}$$

3

we time both sides of the equation by μ, thus deriving the variation of magnetization vector,

$$\frac{\mathrm{d}\boldsymbol{M}}{\mathrm{d}t} = \frac{M_0 - M_z}{T_1}\boldsymbol{k}$$

this is the second term of the Bloch equation. Introducing spin-spin interaction into the system, we derive the complete version of Bloch equation,

$$\frac{\mathrm{d}\boldsymbol{M}}{\mathrm{d}t} = \gamma\boldsymbol{M} \times \boldsymbol{H} + \frac{M_0 - M_z}{T_1}\boldsymbol{k} - \frac{M_x\boldsymbol{i} + M_y\boldsymbol{j}}{T_2}$$

where T_2 is the relaxation time of the second process. $T_1 \doteq 1\mathrm{s}$, $T_2 \doteq 100\mathrm{ms}$ in rotational coordinate,

$$\mathbf{H} \hookleftarrow \mathbf{h_{eff}} = \mathbf{H_0} + \mathbf{H_1} + \frac{\omega}{\gamma}$$

if we choose a certain coordinate in that $\omega = -\gamma\mathbf{H_0}$,then

$$\mathbf{H_{eff}} = \mathbf{H_1}$$

3   layer selection (Mansfield' work)

introduce magnetic field H_1 into the system, assume that its direction is along the x axis, then, in the rotational coordinate, the magnetic moment will rotate around the x axis, the angular velocity $\omega = \gamma H_1$.
selective excitation: we use a H_0 with gradient accumulation along the z axis,

$$H_0 = Gz\mathbf{k}$$

we choose a new H_1 which follows distribution with respect to frequency,

$$H_1(\omega) = H_1(-\gamma Gz_0 < \omega < \gamma Gz_0)$$

apply Fourier transform on the magnetic field, the magnetic field is a pulse,

$$H_1(t) = sinc(t)$$

so the magnetic momentum distribution $M_y(z)$ is the Fourier transformation of $H_1(t)$
summary: in order to realize selective excitation, we need to introduce a gradient magnetic field $\frac{\partial H_z}{\partial z} = G$,and along x axis, $H_x(t)$ is the inverse Fourier transformation of $M_y(z)$.
homework: we want to scan the region:$(-2z_0, -z_0)$and $(z_0, 2z_0)$, calculate $H_1(t)$. calculate under the two circumstances respectively:

$$1.+, +; 2.-, -$$

in reality, the pulse can only last for a few ms, so the anti-Fourier transform of $H_1(t)$ will deviate from the ideal M_y.

4 x-y plane

4.1 spatial encoding (Ernst)

$$S = \iint M_T(x,y)\mathrm{d}x\mathrm{d}y$$

how to solve $M_T(x,y)$? during the encoding process, according to Bloch equation,

$$\frac{\mathrm{d}\mathbf{M}}{\mathrm{d}t} = \gamma\mathbf{M}\times\mathbf{H}$$

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = \gamma M_y H_z$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = -\gamma M_x H_z$$

let $M_T = M_x + \mathrm{i}M_y$, then

$$\frac{\mathrm{d}M_T}{\mathrm{d}t} = \mathrm{i}\gamma M_T H_z$$

$$M_T(x,y,t) = M_T(x,y,0)\mathrm{e}^{-\mathrm{i}\gamma\int H_z\mathrm{d}t}$$

$$S = \iint M_T(x,y,0)\mathrm{e}^{-\mathrm{i}\gamma\int H_z\mathrm{d}t}\mathrm{d}x\mathrm{d}y$$

let $H_z = G_y y$, then

$$S = \iint M_T(x,y,0)\mathrm{e}^{-\mathrm{i}\gamma G_y y t}\mathrm{d}x\mathrm{d}y$$

let $H_z = G_x x + G_y y$, then

$$S = \iint M_T(x,y,0)\mathrm{e}^{-\mathrm{i}\gamma(G_x x + G_y y)t}\mathrm{d}x\mathrm{y}$$

let $\int G_x\mathrm{d}t = k_x, \int G_y\mathrm{d}t = k_y$, then

$$S(k_x,k_y) = FT\{M_T(x,y)\}$$

5 (Spoiled) Spin echo (1949,Hahn)

90° - 180° repetition
Bloch equation,

$$\frac{\mathrm{d}\boldsymbol{M}}{\mathrm{d}t} = \gamma\boldsymbol{M}\times\boldsymbol{H} + \frac{M_0 - M_z}{T_1}\boldsymbol{k} - \frac{M_x\boldsymbol{i} + M_y\boldsymbol{j}}{T_2} = \gamma\begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ M_x & M_y & M_z \\ 0 & 0 & \Delta H_0 \end{vmatrix} + \frac{M_0 - M_z}{T_1}\boldsymbol{k} - \frac{M_x\boldsymbol{i} + M_y\boldsymbol{j}}{T_2}$$

let $M_T = M_x + \mathrm{i}M_y$, then

$$\frac{\mathrm{d}M_T}{\mathrm{d}t} = -i\gamma M_T\Delta H_0 - \frac{M_T}{T_2}$$

solution to the equation is

$$M_T = M_T(0)\mathrm{e}^{-\mathrm{i}\gamma\Delta Ht-\frac{t}{T_2}}$$

phase rotates differently with different H.

we add a new signal at time τ in order that all magnetic moments turn 180 degrees.

then, after another τ, all moments converge again, creating a sharp peak, we call that spin echo.

if we don't turn moments around for 180 degrees but for 90 degrees,

$$S = S_0\mathrm{e}^{\frac{t}{T_2*}}$$

T_2* is effective relaxation time.

$$\frac{1}{T_2*} = \frac{1}{T_2} + \partial H$$

$$\begin{pmatrix} 0 \\ 0 \\ M_0 \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 \\ M_0 \\ 0 \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 \\ M_0\mathrm{e}^{-\frac{TE}{T_2}} \\ M_z \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 \\ 0 \\ M_0(1-\mathrm{e}^{-\frac{TR}{T_1}}) \end{pmatrix} \qquad (1)$$

$$\begin{pmatrix} 0 \\ 0 \\ M_0(1-\mathrm{e}^{-\frac{TR}{T_1}}) \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 \\ M_0(1-\mathrm{e}^{-\frac{TR}{T_1}}) \\ 0 \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 \\ M_0(1-\mathrm{e}^{-\frac{TR}{T_1}})\mathrm{e}^{-\frac{TE}{T_2}} \\ M_z \end{pmatrix} \Longrightarrow \begin{pmatrix} 0 \\ 0 \\ M_0(1-\mathrm{e}^{-\frac{TR}{T_1}}) \end{pmatrix}$$
$$(2)$$

5.1 homework:spoiled gradient echo

prove that for gradient echo,

$$S = S_0\frac{(1-\mathrm{e}^{-\frac{TR}{T_1}})\mathrm{sin}\theta}{1-\mathrm{cos}\theta\mathrm{e}^{-\frac{TR}{T_1}}}\mathrm{e}^{-\frac{TE}{T_2}}$$

where θ is rotation after each pulse. S reaches maximum when$\theta = \mathrm{arccos}(-\frac{TR}{T_1})$

6 Signal to Noise Ratio(SNR)

input:S_{in},N_{in}
output:S_{out},N_{out}

$$SNR = \frac{GS_{in}}{GN_{in} + N_{device}}$$

where G is Amplification Ratio of the device.

for NMR, **M** is signal, and noise is generated from device and thermal effects.

6.1 physicist's picture of SNR

Maxwell's equations,

$$\nabla \cdot \mathbf{D} = \rho_0 \tag{3}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{4}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{5}$$

$$\nabla \times \mathbf{H} = \mathbf{J_0} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \tag{6}$$

$$\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M}$$

$$Signal \propto V \propto I \propto E \propto |\frac{\partial \mathbf{B}}{\partial t}| \propto |\frac{\partial \mathbf{M}}{\partial t}| \propto H_0$$

$$SNR = \frac{S}{N} \propto H_0^\alpha$$

7 Contrast to Noise Ratio(CNR)

Suppose that half of the picture has a signal S_1 and variation σ_1, another half is S_2 and σ_2, then if $|S_1 - S - 2| > 3\sigma$, then the picture gains a high contrast.

7.1 Spin echo

$$S = M_0(1 - e^{-\frac{TR}{T_1}})e^{-\frac{TE}{T_2}}$$

$$S = S(M_0, T_1, T_2)$$

$$\Delta S = \frac{\partial S}{\partial M_0}\Delta M_0 + \frac{\partial S}{\partial T_1}\Delta T_1 + \frac{\partial S}{\partial T_2}\Delta T_2$$

$$\frac{\partial S}{\partial T_2} = M_0(1 - e^{-\frac{TR}{T_1}})\frac{TE}{T_2^2}e^{-\frac{TE}{T_2}}$$

if we want to examine variation of T1 solely, $\frac{\partial S}{\partial T_2} = 0 \Longrightarrow TE \to 0$ if we want to maximize S, $\frac{\partial S}{\partial T_2} = 0$

$$\frac{\partial^2 S}{\partial T_1 \partial TR} = S_0(\frac{1}{T_1} - \frac{TR}{T_1^2})e^{-\frac{TR}{T_1}} = 0 \Longrightarrow TR = T1$$

similarly, if we want to check the variation of T_2, there should be $T_R \longrightarrow \infty = 5T_1, TE = T_2 \ T_1 = 1s$

8   fast imaging-Echo Planar Imaging(EPI),Mansfield

40ms
sampling window $t < T_2*$
1978,Mansfield,Theory;1983,application(realization)
fMRI,brain function study

9   Blood Flow Imaging

two types of blood flow: large vessel(arteries,veins);capillaries.

9.1   new effects of moving spin

in magnetization process,blood flows continuously. during every circular, new blood flood in the district of interest, therefore, blood that has been turned around and new blood exist simultaneously.
suppose that velocity of blood flow is v, then

$$S \propto M_0 \frac{vT_R}{L} + M_0(1 - e^{-\frac{T_R}{T_1}})(1 - \frac{vT_R}{L}) = M_0 - M_0\frac{vT_R}{L}(1 - e^{-\frac{T_R}{T_1}})$$

##homework: derive the case of gradient echo, suppose that blood flow is 1. Plug flow (velocity at every spot is the same);2. lambda flow($v = v(\rho)$)

9.2   bipolar gradient

$$G_x = G_0x, 0 < t < T$$

$$G_x = -G_0x, T < t < 2T$$

according to magnetic momentum's dynamic function $(x(t) = x_0 + vt)$,

$$\omega = \gamma G_0 x(t) = \frac{\mathrm{d}\phi}{\mathrm{d}t}$$

$$\phi = \int_0^{2T} \gamma G_x x \mathrm{d}t = \gamma G v T^2$$

$$v = \frac{\Delta\phi}{\gamma G T^2}$$

if we want to measure acceleration of blood flow, we just have to add a inverse bipolar pulse subsequently.
an obstacle: measuring phase of magnetic moment.
pulse amplitude: 1m/s capillaries: 1mm/s

9.3   molecular diffusion imaging

Brown Motion 1700s
Einstein 1905
MRI is so far the one and only apparatus that is able to detect diffusion motion.
Hahn, 1950, first diffusion signal detection
Carr + Purcell, 1954, quantitative description
stejskal+Tanner(pulse bipolar gradient), 1965
LeBihan, Diffusion imaging
...
Einstein's model: drunkman problem

$$\langle x \rangle = 0$$

$$\langle x^2 \rangle = 2Dt$$

D is difussion coefficient, t is the time of measurement.
$D = 2.2 \times 10^{-5} \text{cm}^2/\text{s}$ for water in 300K

$$S = S0(without signaling)$$

$$S = S_0 \text{e}^{-bD}$$

where

$$b = \gamma^2 G^2 \delta^2 (\Delta - \frac{\delta}{3})$$

diffusion coefficient is a symmetric tensor, which consists of 9 parameters and 6
free parameters.