Magnetic Resonance in Molecules

"Therefore, we can draw the conclusion that long-term exposure to high magnetic fields has no known harmful physical effect."

Nuclear Magnetic Resonance

The spin angular momentum

$$\vec{I} = \hbar\sqrt{I(I+1)}$$ I = nuclear spin (1)

Nuclei classification:

I =0 ^{12}C, ^{16}O, and ^{32}S no magnetic resonance

$I = 1/2$: ^{1}H, ^{3}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P

$I = 1$: $^{2}H(D)$, ^{14}N

$I > 1$: ^{10}B, ^{11}B, ^{17}O, ^{23}Na, ^{27}Al, ^{35}Cl, ^{59}Co

- nuclei that have a spin have a magnetic moment **μ**
- the magnetic moment is collinear with the angular momentum vector **I**

$$\hat{\mu} = \gamma \hat{I}$$ (2)

γ gyromagnetic ratio

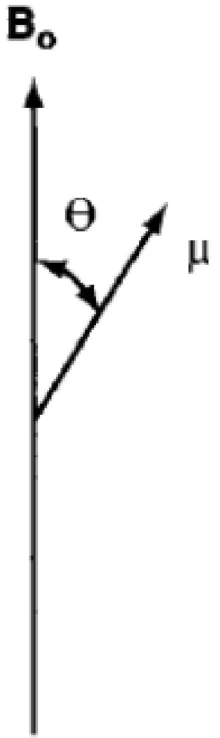
Commonly studied nuclei

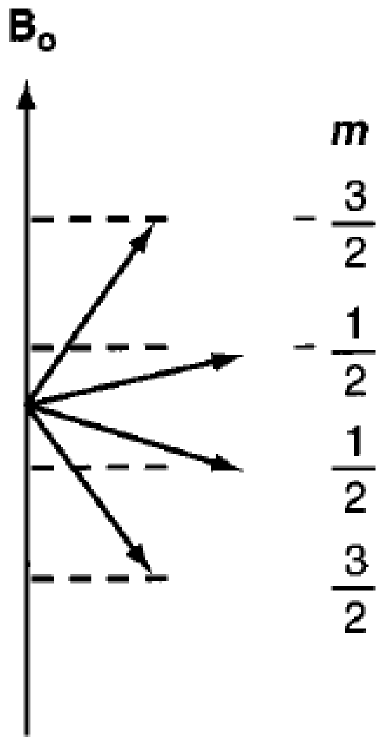
Nuclide	Spin	Natural Abundance (N_a) (%)	Natural Sensitivity (N_s) (for equal numbers of nuclei) (vs. ^1H)
Proton	$\frac{1}{2}$	99.985	1.00
Deuterium	1	0.015	0.00965
Lithium-7	$\frac{3}{2}$	92.58	0.293
Boron-10	3	19.58	0.0199
Boron-11	$\frac{3}{2}$	80.42	0.165
Carbon-13	$\frac{1}{2}$	1.108	0.0159
Nitrogen-14	1	99.63	0.00101
Nitrogen-15	$\frac{1}{2}$	0.37	0.00104
Oxygen-17	$\frac{5}{2}$	0.037	0.0291
Fluorine-19	$\frac{1}{2}$	100	0.833
Sodium-23	$\frac{3}{2}$	100	0.0925
Aluminum-27	$\frac{5}{2}$	100	0.0206
Silicon-29	$\frac{1}{2}$	4.70	0.00784
Phosphorus-31	$\frac{1}{2}$	100	0.0663
Sulfur-33	$\frac{3}{2}$	0.76	0.00226
Chlorine-35	$\frac{3}{2}$	75.53	0.0047
Chlorine-37	$\frac{3}{2}$	24.47	0.00274
Potassium-39	$\frac{3}{2}$	93.1	0.000509
Calcium-43	$\frac{7}{2}$	0.145	0.00640
Iron-57	$\frac{1}{2}$	2.19	0.0000337
Cobalt-59	$\frac{7}{2}$	100	0.277
Copper-63	$\frac{3}{2}$	69.09	0.0931
Selenium-77	$\frac{1}{2}$	7.58	0.00693
Rhodium-103	$\frac{1}{2}$	100	0.0000312
Tin-119	$\frac{1}{2}$	8.58	0.0517
Tellurium-125	$\frac{1}{2}$	7.0	0.0315
Platinum-195	$\frac{1}{2}$	33.8	0.00994
Mercury-199	$\frac{1}{2}$	16.84	0.00567
Lead-207	$\frac{1}{2}$	22.6	0.00920

Steady-state quantum mechanical description of NMR

The Hamiltonian operator $\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B}_0$

$$\mathcal{H} = -\gamma \, \mathbf{B_o} \, \mathbf{I} \quad (3)$$





The energy levels: $$E_m = -\gamma \hbar m B_0 \quad (4)$$

m take 2I+1 values: $-I, -I+1, \ldots, I-1, I$

$$\gamma\hbar = g_I \mu_N \qquad \mu_N = \frac{e\hbar}{2m_p} = 5.051 \times 10^{-27} \, \mathrm{J\,T^{-1}}$$

g_I nuclear *g-factor: -6….+6*

μ_N nuclear magneton: 2000 times weaker than Bohr magneton

Steady-state quantum mechanical description of NMR

Spin wave functions:
I = ½,

α and β α spin up (m = ½) and β spin down (m = -½)

$$I_z\alpha = \tfrac{1}{2}\alpha \qquad I_x\alpha = \tfrac{1}{2}\beta \qquad I_y\alpha = \tfrac{1}{2}i\beta$$
$$I_z\beta = -\tfrac{1}{2}\beta \qquad I_x\beta = \tfrac{1}{2}\alpha \qquad I_y\beta = -\tfrac{1}{2}i\alpha \qquad (5)$$

Raising and *lowering* operators: $I^+ = I_x + iI_y \qquad I^- = I_x - iI_y$ (6)

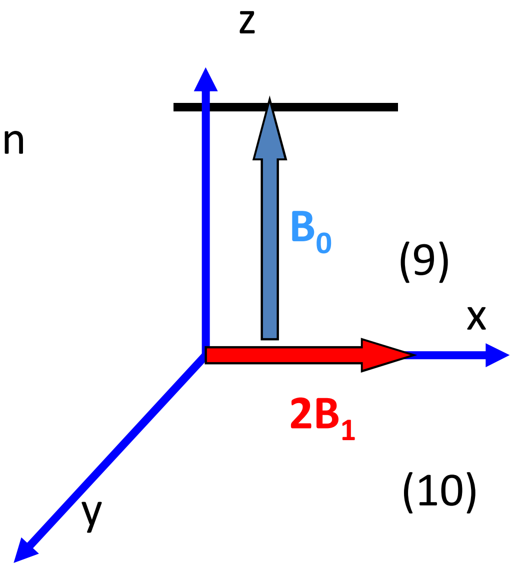
$$I^+\beta = \alpha \qquad I^-\alpha = \beta \qquad (7)$$

As matrix elements:

$\langle\alpha,\alpha\rangle = \langle\beta,\beta\rangle = 1 \qquad \langle\alpha,\beta\rangle = \langle\beta,\alpha\rangle = 0$ orthonormalization

$$\langle\alpha| I_z |\alpha\rangle = \tfrac{1}{2} \qquad \langle\alpha| I_x |\beta\rangle = \tfrac{1}{2} \qquad \langle\beta| I_x |\alpha\rangle = \tfrac{1}{2} \qquad (8)$$
$$\langle\beta| I_z |\beta\rangle = -\tfrac{1}{2} \qquad \langle\alpha| I_y |\beta\rangle = -\tfrac{1}{2}i \qquad \langle\beta| I_y |\alpha\rangle = \tfrac{1}{2}i$$

Steady-state quantum mechanical description of NMR



Spectral Transitions: $2B_1$ applied radiofrequency field in x-direction

Interaction: $\mathcal{H}' = 2\mu_x B_1 \cos 2\pi\nu t$ (9)

Probability of transition per unit time between levels m and *m′*

$$P_{mm'} = \gamma^2 B_1^{\,2} |(m|I_x|m')|^2 \,\delta(\nu_{mm'} - \nu) \quad (10)$$

non-zero $m = m' \pm 1$ non-zero $\nu_{mm'} = \nu.$

Transition frequency: $\nu_{mm'} = \dfrac{\Delta E_{mm'}}{h} = \dfrac{\gamma B_0 |m' - m|}{2\pi}$ (11)

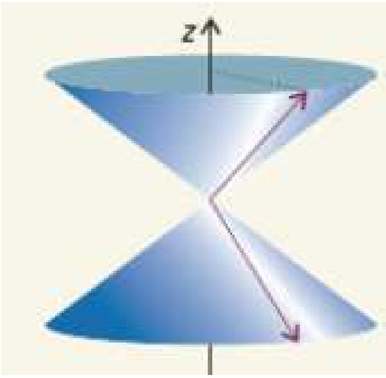
Selection rule $\Delta m = \pm 1$: $\nu = \dfrac{\gamma}{2\pi} B_0$ (12) Larmor frequency

Line shape function $\int_0^\infty g(\nu)\, d\nu = 1$ ⟶ $P_{mm'} = \tfrac{1}{4}\gamma^2 B_1^{\,2} g(\nu)$ (13)

I = 1/2

Steady-state quantum mechanical description of NMR

I =1/2



m = +1/2,
state α
lower energy

m = -1/2,
state β

The Boltzmann equation: $$\frac{n_\beta}{n_\alpha} = e^{-\Delta E/kT} \qquad (14).$$

$$\frac{n_\beta}{n_\alpha} = e^{-\gamma\hbar B_0/kT} = e^{-2\mu B_0/kT}$$

"High temperature" approximation $e^X = 1-x$:

$$\frac{n_\alpha - n_\beta}{n_\alpha} = \frac{2\mu B_0}{kT} \qquad (15)$$

^1H: $B_0 = 7T$, fractional excess is ~ 5×10^{-5} at room temperature.

The intensity of the NMR signal:

$$P_+ \propto B_+\rho(\nu)n_\alpha$$ absorption

$$P_- \propto B_-\rho(\nu)n_\beta + A_-n_\beta$$ emission

The *net* probability of absorption of rf energy:

$$P \propto B\rho(\nu)[n_\alpha - n_\beta] \qquad (16)$$

NMR : insensitive spectroscopic method

Spin-lattice relaxation

I = ½

$$n = (n_\alpha - n_\beta) \qquad n_0 = (n_\alpha + n_\beta)$$

$W_{+/-}$ = probability of up /down transition as result of the interaction with the environment

At equilibrium:
the nr. of upward and downward transitions are equal

$$W_+ n_\alpha = W_- n_\beta \tag{17}$$

$$\frac{W_+}{W_-} = \left(\frac{n_\beta}{n_\alpha}\right)_{eq} = e^{-2\mu B_0/kT} \tag{18}$$

$2\mu B_0/kT \ll 1$ W = ½ ($W^+ + W^-$) :

$$\frac{W_+}{W} = \frac{(n_\beta)_{eq}}{n_0/2} = 1 - \frac{\mu B_0}{kT}$$
$$\frac{W_-}{W} = \frac{(n_\alpha)_{eq}}{n_0/2} = 1 + \frac{\mu B_0}{kT} \tag{19}$$

Spin-lattice relaxation

total rate of change of population:

$$\frac{dn}{dt} = \frac{dn_\alpha}{dt} - \frac{dn_\beta}{dt} = 2\frac{dn_\alpha}{dt} \qquad n_0 = (n_\alpha + n_\beta) \qquad (20)$$

$$\frac{dn_\alpha}{dt} = n_\beta W_- - n_\alpha W_+ \qquad (21)$$

With eq (19) in (21):

first-order decay process

$$\frac{dn}{dt} = -2W\left(n - n_0\frac{\mu B_0}{kT}\right) \qquad (22).$$

$2W \rightarrow 1/T_1$ $\qquad$ $n_0\frac{\mu B_0}{kT} \rightarrow n_{eq}$

$$\frac{dn}{dt} = -R_1(n - n_{eq}) \qquad (23)$$

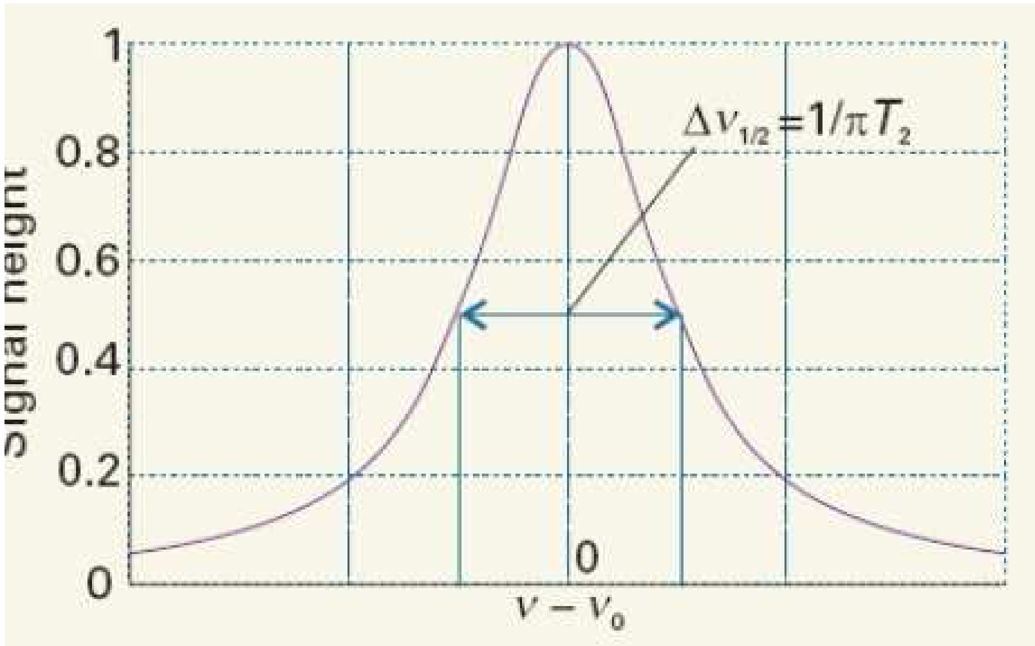
T1 depends on the type of nucleus, the physical state of the sample and the temperature .
For liquids:*T1* is usually between 10 ms and 1s.
In solids: T1 may be much longer—sometimes days.

Line widths

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2}$$

$$F(\omega) = \frac{T_2}{1 + T_2^2\omega^2}$$

1H-NMR: T_2 ~seconds



Precession of nuclear magnetic moments

A pictorial representation of the behavior of nuclear magnetic moments:

I = ½ , α, β

$$\Psi = c_\alpha \alpha e^{-iE_\alpha t/\hbar} + c_\beta \beta e^{-iE_\beta t/\hbar} \qquad (24)$$

$$= c_\alpha \alpha e^{i\gamma B_0 t/2} + c_\beta \beta e^{-i\gamma B_0 t/2}$$

The expectation value of $\mathbf{I_z}$:

$$\langle I_z \rangle = \langle \Psi^* | I_z | \Psi \rangle$$

$$= c_\alpha^2 \langle \alpha | I_z | \alpha \rangle + c_\beta^2 \langle \beta | I_z | \beta \rangle$$

$$+ c_\alpha c_\beta \langle \alpha | I_z | \beta \rangle e^{-i\gamma B_0 t} + c_\alpha c_\beta \langle \alpha | I_z | \beta \rangle e^{i\gamma B_0 t}$$

with (8)

$$= c_\alpha^2 (1/2) + c_\beta^2 (-1/2)$$

$$= 1/2 [c_\alpha^2 - c_\beta^2] \qquad (25)$$

Precession of nuclear magnetic moments

The expectation values of **Ix** and **Iy**:

$$\langle I_x \rangle = c_\alpha{}^2 \langle \alpha | I_x | \alpha \rangle + c_\beta{}^2 \langle \beta | I_x | \beta \rangle + c_\alpha c_\beta \langle \alpha | I_x | \beta \rangle e^{-i\gamma B_0 t} + c_\alpha c_\beta \langle \beta | I_x | \alpha \rangle e^{i\gamma B_0 t}$$

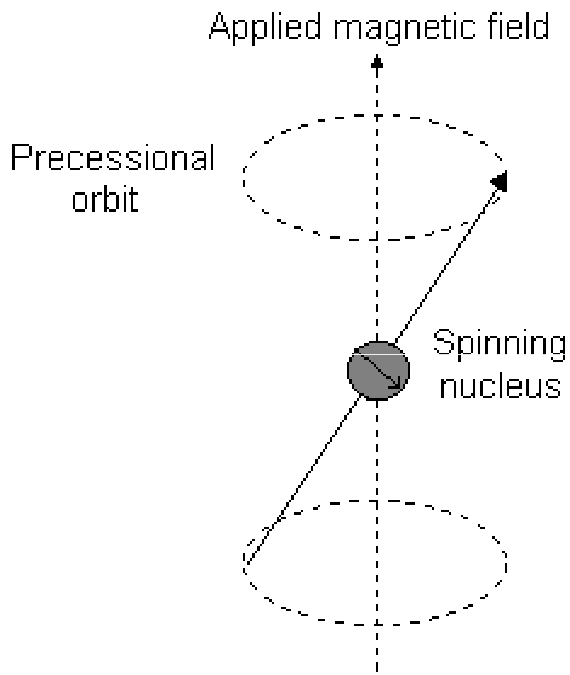
with (5)

$$= c_\alpha{}^2 \langle \alpha | \tfrac{1}{2} | \beta \rangle + c_\beta{}^2 \langle \beta | \tfrac{1}{2} | \alpha \rangle + c_\alpha c_\beta \langle \alpha | \tfrac{1}{2} | \alpha \rangle e^{-i\gamma B_0 t} + c_\alpha c_\beta \langle \beta | \tfrac{1}{2} | \beta \rangle e^{i\gamma B_0 t}$$

$$= 0 + 0 + \tfrac{1}{2} c_\alpha c_\beta [e^{i\gamma B_0 t} + e^{-i\gamma B_0 t}]$$

$$= c_\alpha c_\beta \cos \gamma B_0 t \qquad (26)$$

$$\langle I_y \rangle = c_\alpha c_\beta \sin \gamma B_0 t \qquad (27)$$

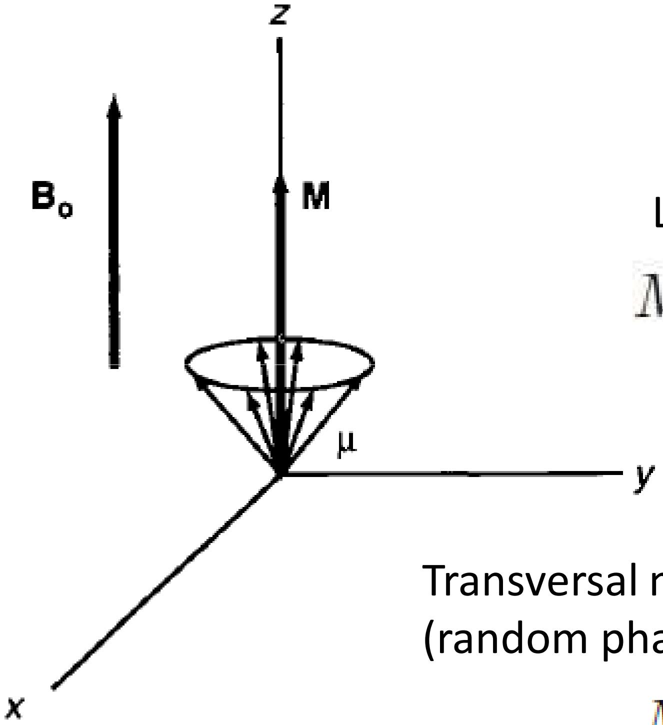


α and β mixed:
I is a vector with fixed *z* component but *x* and *y* components that execute a circular motion.

$$\omega = \gamma B_0$$

Larmor frequency

Macroscopic magnetization



$$M = \sum_{i=1}^{All\ \ spins} \mu_i \qquad (28)$$

Longitudinal magnetization:

$$M_z = M_o \sim I_z \sim c_\alpha{}^2 - c_\beta{}^2 \qquad (29)$$

Transversal magnetization at equilibrium:
(random phases in (x,y)

$$M_x = M_y = 0 \qquad (30)$$

Measure M_0 : tipping M away from the *z axis into the xy plane.*