Introduction to Nuclear Magnetic Resonance Spectroscopy

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Introduction. Magnetic moment in magnetic field.

- Introduction to Magnetic Resonance
- Applications of NMR
- Magnetic moments in magnetic field.
- Orbital angular momentum operator
- Spin angular momentum operator
- Spin in a magnetic field
- Equilibrium magnetization
- Resonant energy absoption.
- Populations dynamics in two-level system.

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- 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.

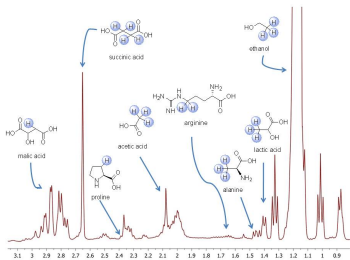- NMR spectroscopy is used for chemical analysis and for molecular structure determination
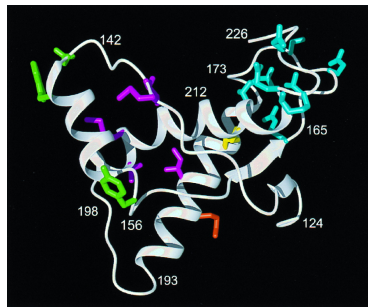

Fig.1: ^{1}H NMR spectrum of a sample of Spanish wine (http://www.unirioja.es/gsoe/NMR.htm)

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

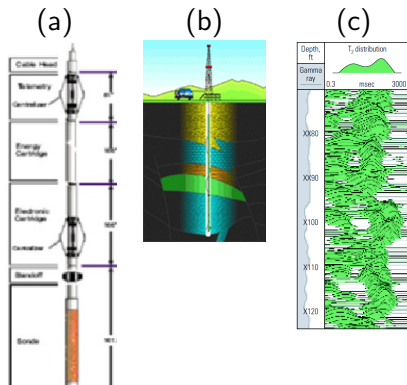- NMR relaxometry can be used to monitor molecular environment

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)
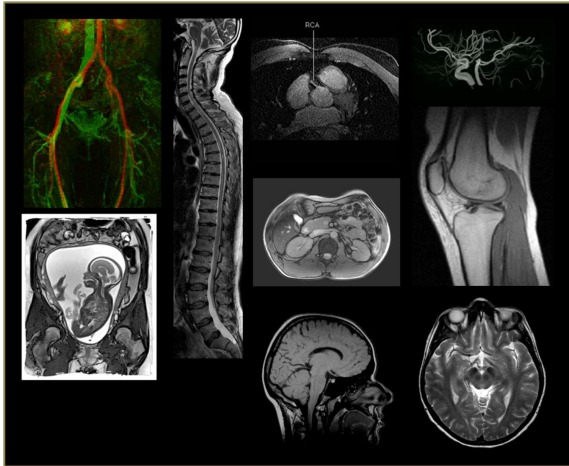

Fig.4: Example magnetic resonance images of blood vessel (in legs), fetus in utero, spine, heart, abdomen, head, blood vessels (in brain), knee, brain (courtesy of Prof. Richard Bowtell)

1.3. Magnetic moments in magnetic field.

How magnetic moments interact with magnetic field? What equations determine the motion?

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Consider charges moving in a limited volume. The position of a charge 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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$$\gamma = \frac{e}{2m} \tag{4}$$

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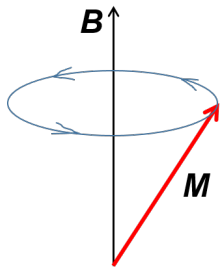The torque acting on the system:

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

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \qquad (7)$$

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.

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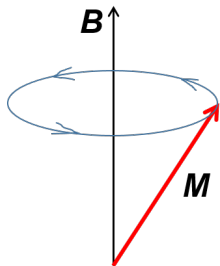

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A solution to this system of differential equations with initial values of $M_x(0), M_y(0), M_z(0)$ has the following form:

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

In quantum mechanics physical quantity A ise represented by an operator $\hat{A}$. 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:

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

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Angular momentum squared, and its commutation properties:

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

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

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:

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

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Another useful operator are raising and lowering operators:

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

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

Calculate $[\hat{L}_+, \hat{L}_x] =?$, $[\hat{L}_+, \hat{L}_-] =?$

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Problem

Calculate $[\hat{L}_+, \hat{L}_x] =?$, $[\hat{L}_+, \hat{L}_-] =?$

Solution

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

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

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

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

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

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

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.

1.5. Spin angular momentum operator

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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
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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.

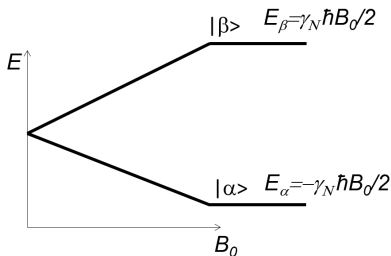**Suggested reading:**   Harris: 1.1, 1.2, 1.3, 1.4, 1.6, 2.4

Let's quantum mechanically describe the system of spins in the magnetic field. Eq. 5 can be rewritten in a form of Hamiltonian:

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

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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]:

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

ω_L and ν_L is the Larmor frequency (anglular and cyclic respectively). For simplicity the Hamiltonian $\mathcal{H}$ can be written in frequency units: $\hat{H} = \dfrac{1}{2\pi\hbar}\mathcal{H} = \nu_L \hat{I}_z$.

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Nucleus	Natural abundance %	Nuclear spin (I)	Larmor frequency at 11.744T, MHz	γ_N, Gyromagnetic ratio (10^7 rad/T*s)
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^{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_β follow Boltzmann distribution:

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

when $\gamma B_0 \ll kT$.

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

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

- What is the value of $\dfrac{\gamma_N \hbar B_0}{kT}$ for proton nuclei (^{1}H) at 9.4 T magnetic field at 300 K?

- What is the value of $\dfrac{\gamma_e \hbar B_0}{kT}$ electron (^{1}H) at 9.4 T magnetic field at 4 K?

Electron charge	$e = 1.602 \cdot 10^{-19}$ C
Electron mass	$m_e = 9.109 \cdot 10^{-31}$ kg
Proton mass	$m_p = 1.673 \cdot 10^{-27}$ kg
Plank constant	$\hbar = 1.054 \cdot 10^{-34} \dfrac{\text{J} \cdot \text{s}}{rad}$
Proton g-factor	$g_p = 5.585$
Electron g-factor	$g_e = 2.0023$
Nuclear magneton	$\beta_N = 5.05 \cdot 10^{-27}$ J $\cdot$ T^{-1}
Bohr magneton	$\beta_e = 9.27 \cdot 10^{-24}$ J $\cdot$ T^{-1}
Proton gyromagnetic ratio	$\gamma_N = 26.7519 \cdot 10^7 \dfrac{\text{rad}}{\text{T} \cdot s}$
Electron gyromagnetic ratio	$\gamma_e = 1.76 \cdot 10^{11} \dfrac{\text{rad}}{\text{T} \cdot s}$
Boltzmann constant	$k = 1.38 \cdot 10^{-23}$ J $\cdot$ K^{-1}
Avogadro's constant	$N_A = 6.023 \cdot 10^{23}$ mol^{-1}

How does a system of spins interact with electromagnetic interaction?

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

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

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Note! The matrix element $|\langle a|\hat{F}|\rangle b|$ represents the selection rules for various levels, if it equals to zero, the transition in forbidden, otherwise - allowed.

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:
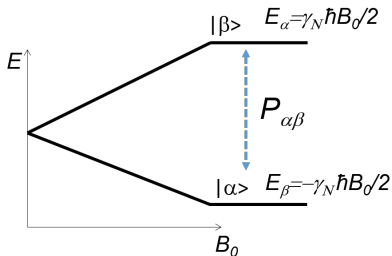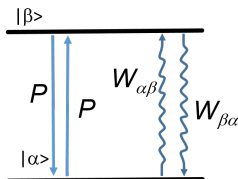
$$P_{\alpha\beta} = \frac{\pi}{2\hbar}(\gamma H_1)^2\delta(E_{\alpha\beta} - \hbar\omega), \qquad (30)$$

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:

$$P_{\alpha\beta} = \frac{\pi}{2\hbar}(\gamma H_1)^2\delta(E_{\alpha\beta} - \hbar\omega), \qquad (30)$$
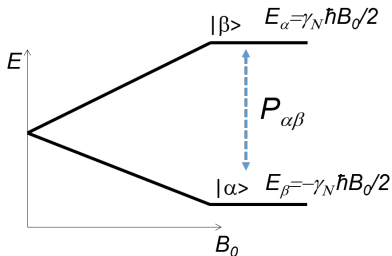
The effect of resonant absorption (and emission) of electromagnetic irradiation at the frequency matching the energy difference in a nuclear system is called Nuclear Magnetic Resonance (NMR).

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.

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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:

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

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:

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

or

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

where $T_1 = \dfrac{1}{2W}$ is called spin-lattice relaxation time determines how quickly a spin system reaches a thermal equilibrium with environment.

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where $T_1 = \dfrac{1}{2W}$ 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.

Suggested reading: Harris 1.5, 1.7, Slichter 1.3
Harris 1.20 - CW NMR spectrometer

Chemical shifts and J-couplings. NMR spectra in liquids.

- Chemical shifts.
- J-couplings.
- J-couplings in AX system.
- Interpreting simple NMR spectra
- Range of J-couplings. Are they useful for structure determination?
- Heteronuclear J-couplings.
- J-coupling in equivalent system.
- J-coupling in AB system.

Electrons in atoms in molecules interact with external magnetic field and in turn produce their own magnetic field B_0. The Larmor frequency get shifted in a chemical specific manner - this is known as the chemical shift. The spin Hamiltonian for a nucleus is:

$$\hat{H} = -\gamma_N \hbar (1 - \sigma) B_0 \hat{I}_z, \tag{38}$$

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Classical illustration of diamagnetic chemical shift:

$$\boldsymbol{\omega} = \frac{e}{2m_e} \mathbf{B_0}$$

$$\mathbf{j} = -e[\boldsymbol{\omega} \times \mathbf{r}]\rho_e = -\frac{e^2}{2m_e}[B_0 \times \mathbf{r}]\rho_e$$

$$d\mathbf{B_i} = \frac{\mu_0}{4\pi r^3}[\mathbf{j} \times \mathbf{r}]dV$$

$$d\mathbf{B_i} = -\frac{\mu_0 e^2}{8\pi m_e r^3}[[\mathbf{B_0} \times \mathbf{r}] \times \mathbf{r}]\rho_e dV$$

$$B_{iz} = -B_0 \frac{\mu_0 e^2}{8\pi m_e} \int \rho_e \frac{x^2 + y^2}{r^3} dV$$

Quantum mechanical result:

$$\sigma = -\frac{\mu_0 e^2}{8\pi m_e} \langle \Psi | \frac{x^2 + y^2}{r^3} | \Psi \rangle$$
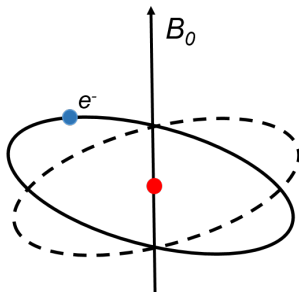
Let's calculate the effect of ring current in cyclic aromatic molecules. Consider benzene molecule:
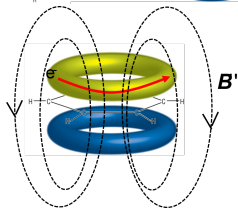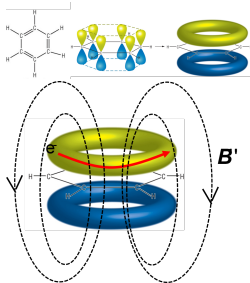

Fig.5: (top) Schematic repsresentation of electron orbitals in a benzene molecule, (bottom) local fields in a benzene molecule produced by electron currents induced by a magnetic field.

2.1. Chemical shifts.

Let's calculate the effect of ring current in cyclic aromatic molecules. Consider benzene molecule:

Larmor precession frequency of electrons $\omega_L = \frac{eB_0}{2m_e}$. Current can be calculated as charge 6e, divided by precession period $\frac{2\pi}{\omega_L}$:
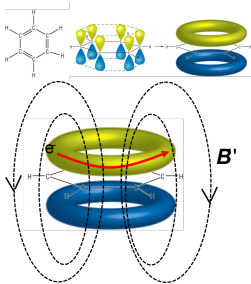
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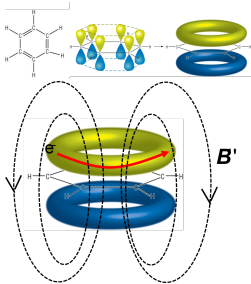

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$$B_i = -\frac{\mu_0}{4\pi}\frac{m}{r^3} = \frac{3\mu_0 e^2}{8\pi}\frac{r^2}{(r+d)^3}B_0 \tag{41}$$

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Fig.5: (top) Schematic repsresentation of electron orbitals in a benzene molecule, (bottom) local fields in a benzene molecule produced by electron currents induced by a magnetic field.

Given benzene molecule radius $r = 1.4$ Å, CH-bond length $d = 1.1$ Åwe obtain:

$$\sigma \approx -5.3 \cdot 10^{-6}, \sigma_{iso} \approx -1.8 \cdot 10^{-6} \qquad (43)$$

2.1. Chemical shifts.
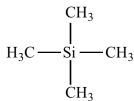
Chemical shifts are usually measured in ppm's and are referenced with respect to the signals of tetramethylsilane (TMS).
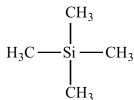
$$\delta = \frac{\nu_{sample} - \nu_{TMS}}{\nu_{TMS}} \times 10^6 \, \text{ppm} \qquad (44)$$

$$\delta = (\sigma_{TMS} - \sigma_{sample}) \times 10^6 \, \text{ppm} \qquad (45)$$

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{H}_3\text{C} - \text{Si} - \text{CH}_3 \\
| \\
\text{CH}_3
\end{array}
$$

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H_3C—$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}$—$CH_3$

$$\delta = \frac{\nu_{sample} - \nu_{TMS}}{\nu_{TMS}} \times 10^6 \text{ppm} \quad (44)$$

$$\delta = (\sigma_{TMS} - \sigma_{sample}) \times 10^6 \text{ppm} \quad (45)$$

In general the ^{1}H chemical shift is greater for nuclei to atoms/bonds that reduce the electron density at the atom.
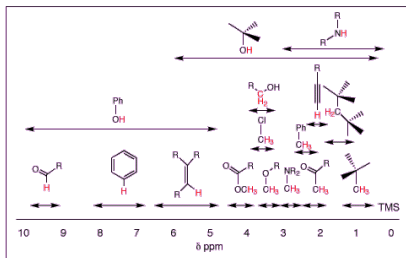
Fig.6: Chemical shifts in various organic molecules Source: `http://orgchem.colorado.edu/Spectroscopy/nmrtheory/protonchemshift.html`

2.1. Chemical shifts.

Consider the ^{1}H-spectrum of methyl acetate.
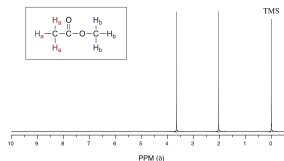- the TMS appears at 0 ppm

Fig.7: ^{1}H spectrum of methyl acetate. Source: http://chemwiki.ucdavies.edu/Organic_Chemistry

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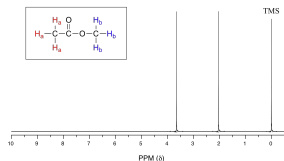
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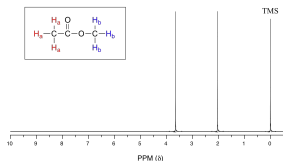- two resonances correpond to protons of the two methyl groups

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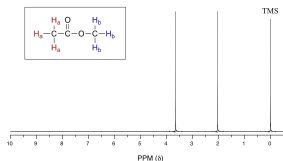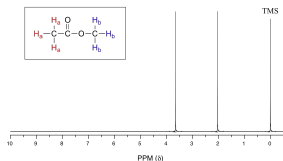Consider the ^{1}H-spectrum of methyl acetate.

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- the TMS appears at 0 ppm
- chemical shift increases from right to left
- two resonances correpond to protons of the two methyl groups
- the presence of electronegative oxygen atom in methoxy group produces weaker shielding (σ) thus makes bigger chemical shift δ
- three nuclei of methyl groups resonate at the same frequency. Peak heights are the same.

For other nuclei, paramagnetic shifts which arise from mixing of excited state with the ground state dues to the effect of the applicaed field, B_0 on the Hamiltonian can be important, and the range of chemical shifts is usully larger than for ^1H nuclei.
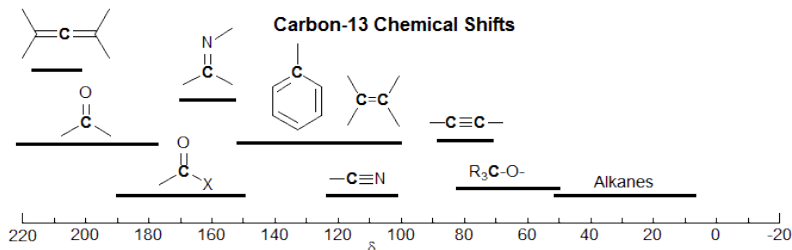

Fig.8: ^{13}C chemical shifts, https://www.chem.wisc.edu/areas/reich/nmr/

2.2. J-couplings.

Nuclear spins interact with one another. In solution, one prominent spin-spin interaction is called J-coupling.

This intra-molecular scalar coupling is caused by the combination of two effects: the Pauli principle means that the electons in the bond have opposite spin-state(spin-up and spin-down), while hyperfine couplings (specifically Fermi contact interaction) means that it is energetically favourable for each nuclear spin to be anti-parallel to the electron spin.
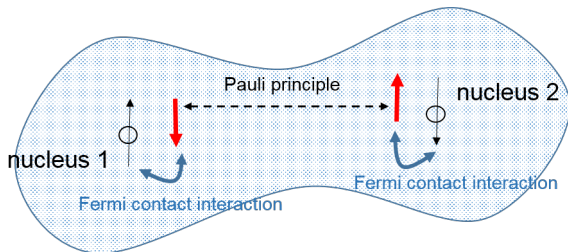

Fig.9: Origin of J-couplings. Low energy configuration in which nuclear spins are antiparallel

Let's find the eigenstates of a Hamiltonian with J-coupling

Hamiltonian of J-coupling in solution (all anisotropy is averaged):

$$
\begin{aligned}
\hat{H} &= J\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 = J(\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z}) = \\
&= J\hat{I}_{1z}\hat{I}_{2z} + \frac{J}{2}(\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+})
\end{aligned}
\tag{46}
$$

J is usually measured in units of frequency, i.e. Hz.

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\end{aligned}
\tag{46}
$$

J is usually measured in units of frequency, i.e. Hz.

In frequency units the full spin Hamiltonian for a system of two nuclei A and B of the same kind would be:

$$
\hat{H} = -\nu_0(1-\sigma_A)\hat{I}_{Az} - \nu_0(1-\sigma_B)\hat{I}_{Bz} + J\hat{I}_{Az}\hat{I}_{Bz} + \frac{J}{2}(\hat{I}_{A+}\hat{I}_{B-} + \hat{I}_{A-}\hat{I}_{B+})
\tag{47}
$$

Let's find the eigenstates of a Hamiltonian with J-coupling

For two coupled spins $\frac{1}{2}$ the Hamiltonian matrix in the basis of functions $|1\rangle = |\alpha_1\alpha_2\rangle, |2\rangle = |\alpha_1\beta_2\rangle, |3\rangle = |\beta_1\alpha_2\rangle, |4\rangle = |\beta_1\beta_2\rangle$

The Hamiltonian matrix of such a system are:

$$H_{ik} = \langle i|\hat{H}|k\rangle = \begin{bmatrix} -\frac{\nu_A + \nu_B}{2} + \frac{J}{4} & 0 & 0 & 0 \\ 0 & -\frac{\nu_A - \nu_B}{2} - \frac{J}{4} & \frac{J}{2} & 0 \\ 0 & \frac{J}{2} & \frac{\nu_A - \nu_B}{2} - \frac{J}{4} & 0 \\ 0 & 0 & 0 & -\frac{\nu_A + \nu_B}{2} + \frac{J}{4} \end{bmatrix} \quad (48)$$

when $|\nu_A - \nu_B| \gg J$ the off-diagonal terms due to $\hat{I}_{A\pm}\hat{I}_{B\mp}$ can be neglected. That is a called AX system. When off-diagonal terms cannot be neglected, we deal with a so called AB system.

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Let's consider nuclei of the same type (i.e. both ^{1}H or both ^{13}C).
When $\gamma_N \hbar \, | \, \omega_1 - \omega_2 \, | \ll J$,

Eq.29 is non-zero when corresponding matrix element is not zero. The selection rules for two nuclei then : $\langle i | \hat{I}_{1x} + \hat{I}_{2x} | k \rangle \neq 0$.
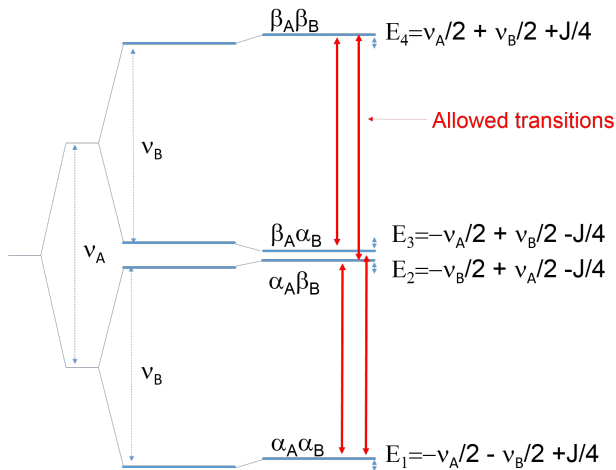

Fig.10: Level diagram for two J-coupled spins in AX system

In a more general case, when $I_A, I_B \neq \frac{1}{2}$, the energy levels follow the following equation:

$$E = -\nu_A m_1 - \nu_0 (1 - \sigma_B) m_2 + J m_1 m_2 \qquad (50)$$

The allowed transitions for spin A have the following frequencies:

$$\nu = \nu_A + m_B J, \qquad (51)$$

where $m_B = -I_B, -(I_B - 1)...(I_B - 1), I_B$ is the projection of nuclear spin B. The resonance line is therefore being split into several components. Similarly, for spin B:

$$\nu = \nu_B + m_A J, \qquad (52)$$

For one coupled nucleus:

$$\nu = \nu_A + m_B J, \qquad (53)$$

For two coupled nuclei:

$$\nu = \nu_A + m_B J + m_C J, \qquad (54)$$

For three:
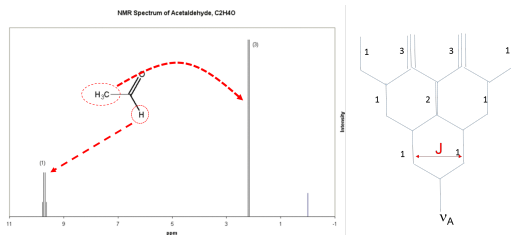
$$\nu = \nu_A + m_B J + m_C J + m_D J, \qquad (55)$$

Fig.11: Spectrum of acetaldehyde. Source: https://chem242.wikispaces.com

Problem

Draw schematically ^{1}H spectrum of ethyl alcohol? Proton Larmor frequency is 90 MHz (i.e. treat as AX system).

```
    H  H
    |  |
H - C - C - O - H
    |  |
    H  H
```
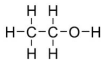
$\delta_{CH3} = 1.22$ ppm, $\delta_{CH2} = 3.68$ ppm, $\delta_{OH} = 2.61$ ppm, consider only $J_{CH2-CH3} = 7.29$ Hz.

Problem

Draw schematically ^{1}H spectrum of ethyl alcohol? Proton Larmor frequency is 90 MHz (i.e. treat as AX system).

```
    H  H
    |  |
H - C - C - O - H
    |  |
    H  H
```
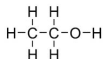
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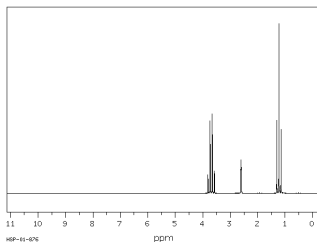

Fig.12: Ethanol spectrum at 90 MHz in CDCl$_3$

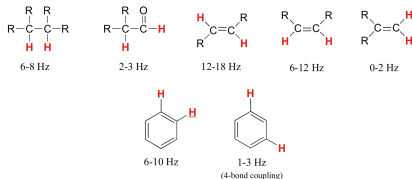# 2.5. Range of J-couplings. Are they useful for structure determination?

Fig.13: Typical J-couplings `https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/`

Is there any simple meaning to J-couplings? Karplus equation is an empiric formula for J coupling as a function of a dihedral angle ϕ.
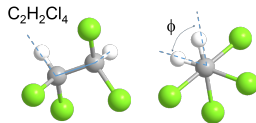
$$J = A\cos\phi + B\cos 2\phi + C \tag{56}$$
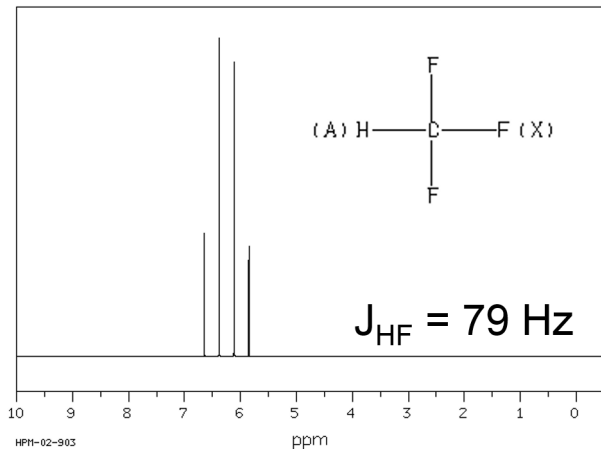

Fig.14: Dihedral angle in 1,1,2,2-tetrachlorethane

2.6. Heteronuclear J-couplings.

Heteronuclear systems are automatically AX systems, i.e.
$| \nu_A - \nu_B | \gg J$.

Example: trifluromethane (fluoroform)

^{1}H NMR spectrum

J_{HF} = 79 Hz

HPM-02-903

ppm

- J-couplings and chemical shift to an extent are unique in different molecules, and NMR spectra help in identifying chemical compounds by their spectra.
- Chemical shifts originate from magnetic field shielding by electrons.
- CS report on the chemical environment of a nucleus
- J-couplings cause spectral splittings.
  Suggested reading: Harris 1.8, 1.9, 1.11, 1.12, 1.13, 8.2, 8.9., 8.23
  For more detailed quantum mechanical theory of chemical shifts: Slichter 4.1-4.5, for detailed theory of J-couplings: Slichter 4.9

Are protons in CH3 or CH2 groups coupled to one another?
Yes. But they are equivalent and therefore not observed.

$$\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z} + \hat{I}_{3z}) + J(\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3) \qquad (57)$$

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Let's rewrite the last term as:

$$\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3 = \frac{1}{2}(\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3)^2 - \frac{1}{2}(\mathbf{I}_1^2 + \mathbf{I}_2^2 + \mathbf{I}_3^2) \qquad (58)$$

2.7. J-coupling in equivalent system.

Are protons in CH3 or CH2 groups coupled to one another?
Yes. But they are equivalent and therefore not observed.

$$\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z} + \hat{I}_{3z}) + J(\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3) \qquad (57)$$

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We can introduce new operator: $\mathbf{F} = \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3$. Given that
$I_1 = I_2 = I_3 = \frac{1}{2}$ the Hamiltonian can be rewritten using this new operator:

$$\hat{H} = -\nu_0\hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \qquad (59)$$

2.7. J-coupling in equivalent system.

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$$\hat{H} = -\nu_0\hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \qquad (59)$$

Eigenfunctions of this Hamiltonian are functions $|FM_F\rangle$, where $F = \frac{1}{2}$ or $\frac{3}{2}$.

$$\hat{H} = -\nu_0 \hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \qquad (60)$$

Selection rules for transitions: $\langle i|\hat{F}_x|k\rangle \neq 0$, since $\hat{F}_x = \dfrac{\hat{F}_+ + \hat{F}_-}{2}$,

the selection rules then are: $\langle i|\hat{F}_\pm|k\rangle \neq 0$ Since
$\hat{F}_\pm = const|FM_F \pm 1\rangle$, the allowed transition does not change the
second term in Eq.60.

$$\hat{H} = -\nu_0 \hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \qquad (60)$$

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the selection rules then are: $\langle i|\hat{F}_\pm|k\rangle \neq 0$ Since
$\hat{F}_\pm = const|FM_F \pm 1\rangle$, the allowed transition does not change the
second term in Eq.60.

Strictly speaking if a molecule contains only nuclei of one type,
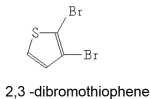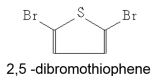and no other J-splitting will not be observed. Examples:
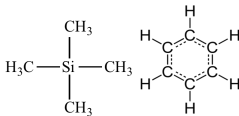
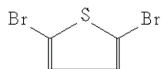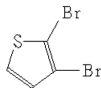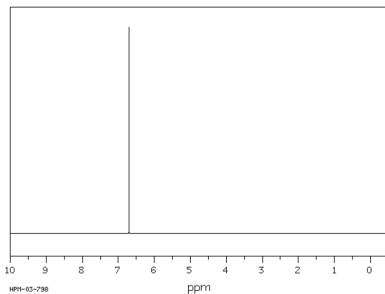tetramethylsilane (TMS), benzene

Problem

Sketch the ^{1}H NMR spectra of 2,3-dibromothiophene and 2,5-dibromothiophene? ^{79}Br and ^{81}Br are quadrupolar nuclei, and their J-couplings can be ignored.

2,5 -dibromothiophene

2,3 -dibromothiophene

2,5 -dibromothiophene

2,3 -dibromothiophene
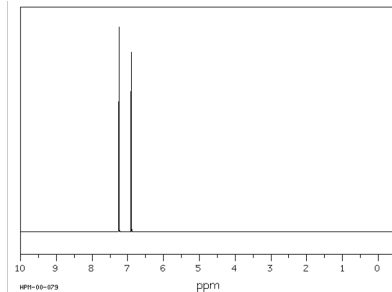
2.8. J-coupling in AB system.

What happens if $\nu_A - \nu_B \gg J$ is no longer true?

- The matrix of spin Hamiltonian is:

$$\begin{bmatrix} -\dfrac{\nu_A + \nu_B}{2} + \dfrac{J}{4} & 0 & 0 & 0 \\ 0 & -\dfrac{\nu_A - \nu_B}{2} - \dfrac{J}{4} & \dfrac{J}{2} & 0 \\ 0 & \dfrac{J}{2} & \dfrac{\nu_A - \nu_B}{2} - \dfrac{J}{4} & 0 \\ 0 & 0 & 0 & -\dfrac{\nu_A + \nu_B}{2} + \dfrac{J}{4} \end{bmatrix} \tag{61}$$

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0 & -\dfrac{\nu_A - \nu_B}{2} - \dfrac{J}{4} & \dfrac{J}{2} & 0 \\
0 & \dfrac{J}{2} & \dfrac{\nu_A - \nu_B}{2} - \dfrac{J}{4} & 0 \\
0 & 0 & 0 & -\dfrac{\nu_A + \nu_B}{2} + \dfrac{J}{4}
\end{bmatrix}
\tag{61}
$$

- The general way of solving is finding the eigenvalues and eigenvalues and eigenfunctions of this Hamiltonian.

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0 & \dfrac{J}{2} & \dfrac{\nu_A - \nu_B}{2} - \dfrac{J}{4} & 0 \\
0 & 0 & 0 & -\dfrac{\nu_A + \nu_B}{2} + \dfrac{J}{4}
\end{bmatrix}
\tag{61}
$$

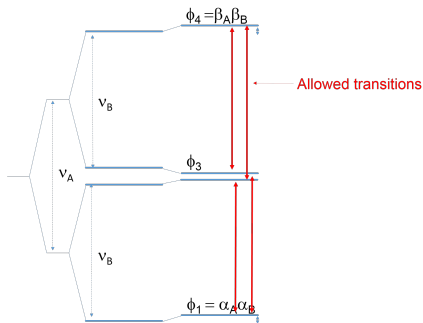- The general way of solving is finding the eigenvalues and eigenvalues and eigenfunctions of this Hamiltonian.
- the solution can be represented by following replacements:

$$
\begin{aligned}
\frac{\nu_A - \nu_B}{2} &= \frac{\delta}{2} = C \cos 2\theta \\
\frac{J}{2} &= C \sin 2\theta \\
C &= \frac{1}{2}\sqrt{\delta^2 + J^2}, \tan 2\theta = \frac{J}{\delta}, \bar{\nu} = \frac{\nu_A + \nu_B}{2}
\end{aligned}
\tag{62}
$$

In this notation the eigenvalues and eigenfunctions are:

$$E_1 = -\bar{\nu} + \frac{J}{4} \quad \phi_1 = |\alpha_A \alpha_B\rangle$$
$$E_2 = -\frac{J}{4} - C \quad \phi_2 = \sin\theta |\alpha_A \beta_B\rangle - \cos\theta |\beta_1 \alpha_2\rangle$$
$$E_3 = -\frac{J}{4} + C \quad \phi_2 = \cos\theta |\alpha_A \beta_B\rangle + \sin\theta |\beta_1 \alpha_2\rangle$$
$$E_4 = \bar{\nu} + \frac{J}{4} \quad \phi_4 = |\beta_A \beta_B\rangle$$

$$(63)$$

Fig.15: Level diagram for AB system of J-coupled nuclei.

Problem

Calculate the transition probability between levels 1 and 2?(Hint: use Eq.29)

Problem

Calculate the transition probability between levels 1 and 2?(Hint: use Eq.29)

For transition $1 \leftrightarrow 2$ we have:

$$
\begin{aligned}
I_{1\leftrightarrow2} \sim &\mid \langle 1|\hat{I}_{Ax} + \hat{I}_{Bx}|2\rangle \mid^2 = \\
= &\langle 1|\frac{\hat{I}_{A+} + \hat{I}_{A-}}{2} + \frac{\hat{I}_{B+} + \hat{I}_{B-}}{2}|2\rangle^2 = \\
= &\left(\langle \alpha_A \alpha_B|\frac{\hat{I}_{A+} + \hat{I}_{A-}}{2} + \frac{\hat{I}_{B+} + \hat{I}_{B-}}{2}|\sin\theta|\alpha_A\beta_B\rangle + \cos\theta|\beta_A\alpha_B\rangle\right)^2 = \\
= &\left(\frac{\cos\theta + \sin\theta}{2}\right)^2 = \frac{1 + \sin 2\theta}{4}
\end{aligned}
$$

$$(64)$$

2.8. J-coupling in AB system.

For all the transitions we obtain:

Transition	Frequency	Intensity:
$4 \leftrightarrow 2$	$\bar{\nu} + C + \dfrac{J}{2}$	$\dfrac{1 - \sin 2\theta}{4}$
$3 \leftrightarrow 1$	$\bar{\nu} + C - \dfrac{J}{2}$	$\dfrac{1 + \sin 2\theta}{4}$
$4 \leftrightarrow 3$	$\bar{\nu} - C + \dfrac{J}{2}$	$\dfrac{1 + \sin 2\theta}{4}$
$2 \leftrightarrow 1$	$\bar{\nu} - C - \dfrac{J}{2}$	$\dfrac{1 - \sin 2\theta}{4}$
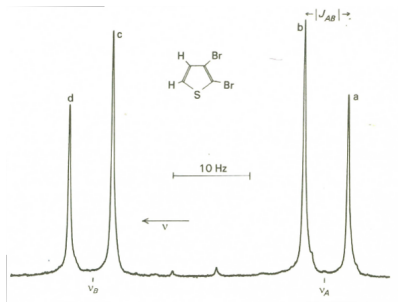
Fig.16: 100 MHz ^{1}H NMR spectrum of 2,3-dibromothiophene, $\mid \nu_A - \nu_B \mid = 30.5$ Hz, $J = 5.7$ Hz

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$4 \leftrightarrow 3$	$\bar{\nu} - C + \dfrac{J}{2}$	$\dfrac{1 + \sin 2\theta}{4}$
$2 \leftrightarrow 1$	$\bar{\nu} - C - \dfrac{J}{2}$	$\dfrac{1 - \sin 2\theta}{4}$

Consider following scenarios:

1. $J \ll \delta$ means that $\sin 2\theta \ll 1$ and $C \approx \dfrac{\delta}{2}$. The leads to AX system shown Fig.52B

2. $\delta \ll J$ means that $\sin 2\theta \approx 1$. A strong double and two weak sattelite lines in Fig.52C.
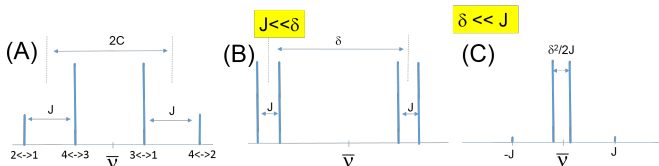

Fig.17: Schematic spectra in several cases (A) $\mid \nu_A - \nu_B \mid \sim J$,(B) weakly coupled nuclei $\mid \nu_A - \nu_B \mid \gg J$, (C) very weak J-coupling $\mid \nu_A - \nu_B \mid \ll J$

2.8. J-coupling in AB system.
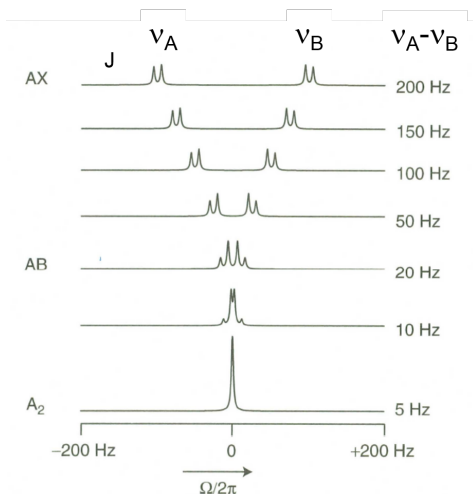
Fig.18: Spectra of spin $\frac{1}{2}$ pairs for $J = 10$ Hz as a function of Larmor frequency difference.

- Splittings in equivalent systems are not observed.
- The case of strong J-couplings can be treated exactly.

Suggested reading: Harris 1.14, 2.17, 2.10

NMR spectra of solids.

- Dipolar coupling Hamiltonian.
- Powder spectra of dipolar coupled nuclei.
- Chemical shift anisotropy.
- Magic angle spinning.
- Quadrupolar interaction.

3.1. Dipolar coupling Hamiltonian.

- Nuclear magnetic moments of nuclei interact via dipolar interaction. (It is averaged to zero in liquids). Classical expression for such interaction is:
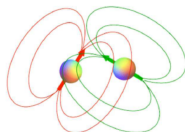
$$E = -(\mathbf{m_1 B_{dip}}) =$$
$$= \frac{\mu_0}{4\pi}\left(\frac{3(\mathbf{m_1 r})(\mathbf{m_2 r})}{r^5} - \frac{\mathbf{m_1 m_2}}{r^3}\right),$$

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- The field induced by another one proton at the location of other proton spaced apart by 1.6 Å is $B_{dip} \sim \dfrac{m}{r^3} \approx 0.7$mT or $\dfrac{g_N \beta_N B_{dip}}{2\pi\hbar} \approx 30$ kHz.

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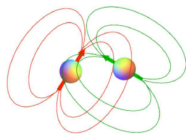
$$E = -(\mathbf{m_1 B_{dip}}) =$$
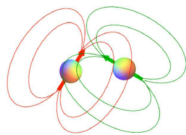$$= \frac{\mu_0}{4\pi}\Big(\frac{3(\mathbf{m_1 r})(\mathbf{m_2 r})}{r^5} - \frac{\mathbf{m_1 m_2}}{r^3}\Big),$$

- The field induced by another one proton at the location of other proton spaced apart by 1.6 Åis $B_{dip} \sim \dfrac{m}{r^3} \approx 0.7$mT or $\dfrac{g_N \beta_N B_{dip}}{2\pi\hbar} \approx 30$ kHz.

- In quantum mechanics the magnetic moments $\mathbf{m_1}$,$\mathbf{m_2}$ are replaced with operators $g_{1,2}\beta_{1,2}\hat{I}_{1,2} = \gamma_{1,2}\hbar\hat{I}_{1,2}$, giving rise to a spin Hamiltonian of dipolar interaction:

$$\mathcal{H}_{dip} = \frac{\mu_0}{4\pi}\frac{\gamma_1\gamma_2\hbar^2}{r^3}\sum_{i,j=x,y,z}(3\hat{I}_{1i}\hat{I}_{2j} - \mathbf{\hat{I}_1\hat{I}_2}) \qquad (65)$$

3.1. Dipolar coupling Hamiltonian.

Expanding the spin operator products and using spherical polar coordinates (r, θ, ϕ):

$$\hat{H}_{dip} = \frac{\mu_0}{8\pi^2}\frac{\gamma_1\gamma_2\hbar}{r^3}(A + B + C + D + E + F), \text{ where} \quad (66)$$

$$
\begin{aligned}
A &= -\hat{I}_{1z}\hat{I}_{2z}(3\cos^2\theta - 1) \\
B &= \frac{1}{4}(\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+})(3\cos^2\theta - 1) \\
C &= -\frac{3}{2}(\hat{I}_{1z}\hat{I}_{2+} + \hat{I}_{1+}\hat{I}_{2z})\sin\theta\cos\theta e^{-i\phi} \\
D &= -\frac{3}{2}(\hat{I}_{1z}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2z})\sin\theta\cos\theta e^{i\phi} \\
E &= -\frac{3}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\theta e^{-i2\phi} \\
F &= -\frac{3}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\theta e^{i2\phi}
\end{aligned}
\quad (67)
$$

Each of these terms is a product of a combination of spin operator products with geometrical factor, that depends on θ and ϕ. Only A commutes with the two-spin Zeeman Hamiltonian.

In liquids the dipolar interaction rapidly fluctuates dues to molecular reorientation

Problem

Show that dipolar interaction terms averaged over many orientations are zero.

3.1. Dipolar coupling Hamiltonian.

The spin Hamiltonian of two dipolar coupled nuclei including the nuclear Zeeman interactions has the following form:

$$\hat{H} = -\nu_1 \hat{I}_{1z} - \nu_2 \hat{I}_{1z} + H_{dip}, \tag{68}$$

where $\nu 1, \nu_2$ are the nuclear Larmor frequencies. If $|\nu_1 - \nu_2| \gg \dfrac{\mu_0}{4\pi} \dfrac{\gamma_1 \gamma_2 \hbar}{r^3}$ then all non-diagonal terms in the Hamiltonian can be neglected:

$$\hat{H} = -\gamma_1 B_0 \hat{I}_{1z} - \gamma_2 B_0 \hat{I}_{1z} + \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar}{r^3} (3\cos^2\theta - 1) \hat{I}_{1z} \hat{I}_{2z} = \tag{69}$$

$$= -\nu_1 m_1 - \nu_2 m_2 + \Delta m_1 m_2, \tag{70}$$

where $\Delta = \dfrac{\mu_0}{8\pi^2} \dfrac{\gamma_1 \gamma_2 \hbar}{r^3} (3\cos^2\theta - 1)$. The spectrum then would consist of two doublets centered around ν_1 and ν_2 and split by Δ.

3.1. Dipolar coupling Hamiltonian.

If $| \nu_1 - \nu_2 | \sim \dfrac{\mu_0}{4\pi} \dfrac{\gamma_1 \gamma_2 \hbar}{r^3}$ then we need to include A and B terms, yeilding a Hamiltonian:

$$\hat{H} = -\gamma_1 B_0 \hat{I}_{1z} - \gamma_2 B_0 \hat{I}_{1z} + \Delta(\hat{I}_{1z}\hat{I}_{1z} - \frac{1}{4}(\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+})) \quad (71)$$

If $\nu_1 = \nu_2$ this Hamiltonian can be diagonalized in the siglet and triplet functions with their respective energies:

$$\begin{aligned}
|s\rangle &= \frac{|\alpha\beta\rangle - |\beta\alpha\rangle}{\sqrt{2}} & E_s &= 0 \\
|t_1\rangle &= |\alpha\alpha\rangle & E_{t1} &= -\gamma B_0 - \frac{\Delta}{4} \\
|t_0\rangle &= \frac{|\alpha\beta\rangle + |\beta\alpha\rangle}{\sqrt{2}} & E_{t0} &= \frac{\Delta}{2} \\
|t_{-1}\rangle &= |\beta\beta\rangle & E_{t1} &= \gamma B_0 + \frac{\Delta}{4}
\end{aligned} \quad (72)$$

Problem

Which transitions are allowed? (Hint: use Eq.29)

Problem

Which transitions are allowed? (Hint: use Eq.29)

Singlet and triplet functions have a total spin of 0 and 1 respectively. Introduce an operator of total spin $\hat{\mathbf{F}} = \hat{\mathbf{I}}_1 + \hat{\mathbf{I}}_2$. Its eigenfunctions $|FM_F\rangle$ coincide with singlet ($F = 0$) and triplet ($F=1$) functions.

$F_+|FM_F\rangle = \sqrt{F(F+1) - M_F(M_F+1)}|FM_F+1\rangle$ operator can only change functions within one manifold, i.e a transition between singlet and triplet is forbidden. The only allowed transitions are in triplet manifold, changing $\delta M_F = \pm 1$. These are $|t_0\rangle \leftrightarrow |t_1\rangle$ and $|t_0\rangle \leftrightarrow |t_{-1}\rangle$.

The transition frequencies are:

$$\begin{aligned}
\nu_{0,1} &= \gamma B_0 - \frac{3}{4}\Delta \\
\nu_{0,-1} &= \gamma B_0 + \frac{3}{4}\Delta
\end{aligned} \tag{73}$$

The two limiting cases were treated analytically and correponding schematic spectra are shown in Fig.63.
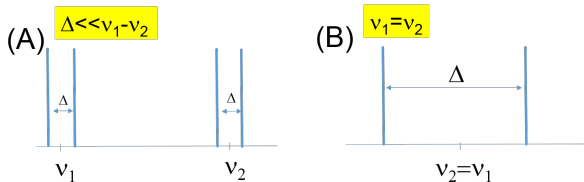

Fig.19: Schematic representation of single orientation spectra for (A) $\mid \nu_1 - \nu_2 \mid \gg \Delta$ and (B) $\nu_1 = \nu_2$.

3.2. Powder spectra of dipolar coupled nuclei.

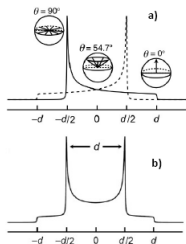
Fig.20: Powder patter dues to a pair of dipolar coupled spins (a) Dotted and continuous lines correspond to different transition. Angles shows related to continous line. (b) Sum of contributions.
$d = \dfrac{3\Delta}{2}$

In most solids multiple spins interact via dipolar couplings, but in crystals of $CaSO_4 \cdot 2H_2O$ the water molecules are rather isolated from one another approximating an isolated pair. Studying the spectra as a function of crystal orientation help obtain orientational information.

In polycrystalline samples (powders) all values of θ will be simultaneously present and the spectrum is formed from a weighted superposition of the lines generated by the two transitions for all θ-values. The weighting related to the number of spin-pairs whose inter-nuclear vector takes a particular values of θ. This varies as $\sin\theta$ so that a "powder pattern" in the spectrum takes the form shown in Fig.64 .

3.2. Powder spectra of dipolar coupled nuclei.

The characteristic spectra shape is called "powder pattern". The two sharp features are called Pake doublet.
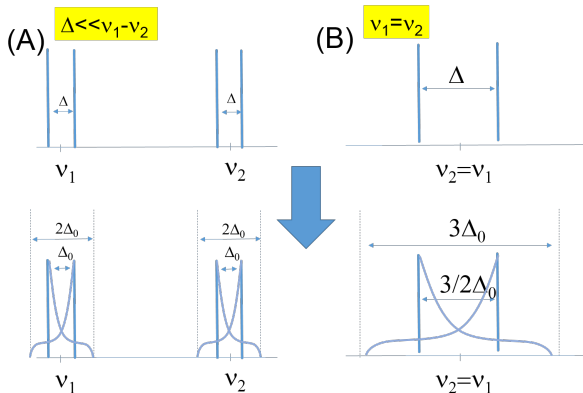
Fig.21: Schematic representation of polycrystalline spectra for (A) $\mid \nu_1 - \nu_2 \mid \gg \Delta_0$, and (B) $\nu_1 = \nu_2$, where $\Delta_0 = \dfrac{\mu_0}{8\pi^2} \dfrac{\gamma_1 \gamma_2 \hbar}{r^3}$

3.3. Chemical shift anisotropy.

Raw NMR spectra from solids often form single broad peaks due to dipolar effects, along with the effects of chemical shift anisotropy, which often makes interpretation of spectra more complicated.

Fig.22: ^{13}C NMR spectrum of 13C-labelled glycine: (a) 125 MHz solid state; (b) 75 MHz liquid state. From D.D. Laws, H.-M. Bitter, A.Jerschow., Angew. Chem. Int. Ed. 41, 3096 (2002)

Chemical shift anisotropy results from the dependence of the level of shielding of a nucleus on the orientation of nearby bonds with respect to the magnetic field.
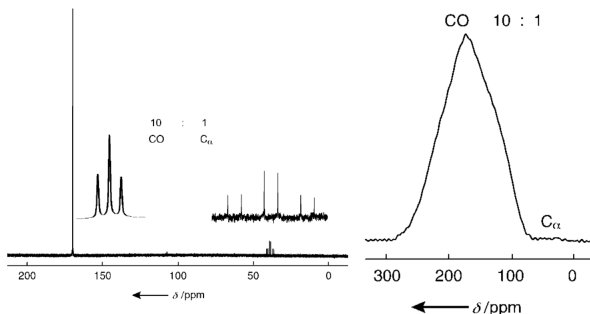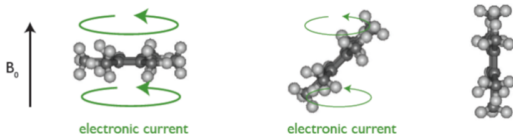

Fig.23: Dependence of shielding on the molecular orientation with respect to external magnetic field. (www.solidstatenmr.org.uk)

The effect is characterized by a shielding tensor which relates the induced shielding $\delta\mathbf{B}$ to the applied field B_0 taking into account the orientational dependence.

$$\begin{bmatrix} \delta B_x \\ \delta B_y \\ \delta B_z \end{bmatrix} = - \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ B_0 \end{bmatrix} \tag{74}$$

This introduces a term in the Hamiltonian of the form,
$\hat{H}_{CSA} = -\gamma(\delta\mathbf{B} \cdot \hat{\mathbf{I}})$.

In secular approximation, when the nuclear Zeeman interaction $\gamma B_0 \gg \gamma \sigma_{i,j} B_0$, which is why the secular spin Hamiltonian is truncated to:

$$\hat{H}_{CSA} = \gamma \sigma_{zz} B_0 \tag{75}$$

In the laboratory frame in order σ_{zz} component can be found from a full tensor using a product with a unit vector along the direction of B_0:

$$\sigma_{zz}^{lab} = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \mathbf{b_0}^{\mathrm{T}} \boldsymbol{\sigma} \mathbf{b_0} \tag{76}$$

3.3. Chemical shift anisotropy.

In the principle axis system the tensor has the following form:

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{bmatrix} \qquad (77)$$

The expression in Eq.76 is a true scalar, i.e. it does not depend in which reference frame it is written. We can write it in the principle axis system of the tensor, where the direction of magnetic field is $\mathbf{b_{PAS}} = \begin{bmatrix} \sin\theta\cos\phi, & \sin\theta\sin\phi, & \cos\theta \end{bmatrix}$.

$$\sigma_z z^{lab} = \mathbf{b_0}^{\mathrm{T}} \boldsymbol{\sigma}^{\mathbf{lab}} \mathbf{b_0} = \mathbf{b_{PAS}}^{\mathrm{T}} \boldsymbol{\sigma}^{\mathbf{PAS}} \mathbf{b_{PAS}} = \qquad (78)$$

$$= \sigma_1 \sin^2\theta \cos^2\phi + \sigma_2 \sin^2\theta \sin^2\phi + \sigma_3 \cos^2\theta \qquad (79)$$

3.3. Chemical shift anisotropy.

PAS axis are usually chosen such that σ_3 component is the largest. We can use a more convenient notation, by replacing:

$$\sigma_{iso} = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} \text{- isotropic chemical shift} \qquad (80)$$

$$\Delta = \sigma_3 - \sigma_{iso} \text{- anisotropy} \qquad (81)$$

$$\eta = \frac{\sigma_1 - \sigma_2}{\sigma_3} \text{- asymmetry} \qquad (82)$$

Using this notation the σ_{zz}^{lab} can be found using a compact equation:

$$\sigma_{zz}^{lab} = \sigma_{iso} + \frac{\Delta}{2}(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi) \qquad (83)$$

3.4. Magic angle spinning.

Magic angle spinning is a technique where the sample is rapidly spun around the axis tilted with respect to $54.5\,\deg$ with respect to magnetic field. It allows to removing (almost) all anisotropy arising from the dipolar and CSA interactions. For instance, for dipolar interaction consider two nuclei A and B. Place the beginning of coordinates at A, Z-axis is pointed along the rotation axis and choose X, Y-axis such that magnetic field $\mathbf{B}$ is in xz-plane $\mathbf{B} = B_0 \begin{bmatrix} \sin\alpha, & 0, & \cos\alpha \end{bmatrix}$.

The radius-vector connecting the two nuclei:

$$\mathbf{r_{AB}} = r_{AB} \begin{bmatrix} \sin\gamma_{AB}\cos\phi_{AB}, & \sin\gamma_{AB}\phi_{AB}, & \cos\gamma_{AB} \end{bmatrix} \qquad (84)$$

Since the sample is spinning, then:

$$\phi_{AB} = \phi_{AB}^0 + \Omega t, \qquad (85)$$

where ϕ_{AB}^0 is some initial phase.

3.4. Magic angle spinning.

We are interested averaging of $(1 - 3\cos^2 \theta_{AB})$. Since:

$$\cos \theta_{AB} = \frac{(\mathbf{r_{AB}B})}{r_{AB}B_0} = \sin \gamma_{AB} \cos \phi_{AB} \sin \alpha + \cos \gamma_{AB} \cos \alpha \quad (86)$$

then:

$$1 - 3\cos^2 \theta = 1 - 3\sin^2 \gamma_{AB} \cos^2 \phi_{AB} \sin^2 \alpha - 3\cos^2 \gamma_{AB} \cos^2 \alpha - \tag{87}$$

$$- 6\sin \gamma_{AB} \cos_{AB} \sin \alpha \cos \gamma_{AB} \cos \alpha \tag{88}$$

For phases linearly varying with time $\overline{\cos \phi_{AB}} = 0$, $\overline{\cos^2 \phi_{AB}} = \dfrac{1}{2}$, therefore:

$$\overline{1 - 3\cos^2 \theta_{AB}} = -\frac{1}{2}(1 - 3\cos^2 \alpha)(1 - 3\cos^2 \gamma_{AB}) \tag{89}$$

When α is to the "magic angle" of $\theta_m = 54.7$ deg, $\cos^2 \theta_m = \dfrac{1}{3}$ and the expression in Eq.89 is zero and independet on γ_{AB}. It means the dipolar interaction is averaged to zero and it does not show up in the spectrum. So if the spinning is fast enough (i.e. $\Omega \gg \dfrac{\gamma_1 \gamma 2 \hbar}{r^3}$ or $\gamma \sigma_{max} B_0$)instead of wide lines due to CSA or dipolar only sharp lines (liquid-state like) spectrum arises.

All nuclei with a spin greated that $\frac{1}{2}$ have an electric quadrupole moment in a ddition to the magnetic dipole moment, possessed by spin-$\frac{1}{2}$ nuclei. Electric quadrupoles interact with electric field gradients. In atoms and molecules the electrons and nuclei create electric fields (and electric field gradients) at the location of a nucleus. Effectively, one can say that electric fields of a molecule tend to reorient a nucleus in a certain way. Quadrupolar moment is a tensor and is proportional to a tensor combined of spin components (Wigner-Eckart theorem). We will not derive the equation for such coupling, but go straight to the result. The quadrupolar coupling Hamiltonian is:

$$\hat{H}_Q = \frac{eQ}{6I(2I-1)\hbar} \sum_{i,j=x,y,z} \hat{I}_i eq_{ij} \hat{I}_j, \tag{90}$$

where eQ is a quadrupole moment, a constant depends only on a nuclear species, eq_{ij} are the components of electric field gradient tensor.

The quadrupolar interaction tensor is traceless, i.e. has only two independent components. If its principal components are defined as $q_{xx}^{PAS}, q_{yy}^{PAS}, q_{zz}^{PAS}$, then two parameters describing the tensor can be introduced:

$$\chi = \frac{e^2 q_{zz}^{PAS} Q}{\hbar} \text{ -quadrupole coupling constant} \qquad (91)$$

$$\eta_Q = \frac{q_{xx}^{PAS} - q_{yy}^{PAS}}{q_{zz}^{PAS}} \text{ -asymmetry parameter} \qquad (92)$$

In the PAS the hamiltonian has a form:

$$\hat{H}_Q = \frac{\chi}{4I(2I-1)} \Big(3\hat{I}_z^2 - I(I+1)) + \eta_Q(\hat{I}_x^2 - \hat{I}_x^2) \Big) \qquad (93)$$

In case of axial symmetry, $\eta_Q = 0$, the Hamiltonian of a quadrupolar nucleus in the magnetic field:

$$\hat{H} = -\nu_0 \hat{I}_z + \frac{\chi}{8}(3\cos^2\theta - 1)\frac{3\hat{I}_z^2 - I(I+1)}{I(2I-1)}, \qquad (94)$$

where θ is the direction of the magnetic field in the PAS of quadrupolar tensor. Since the selection rule is $\Delta m_I = \pm 1$ the transition frequencies are:

$$\nu = \nu_0 - \frac{3}{8}\chi\frac{2m_I - 1}{I(2I-1)}(3\cos^2\theta - 1) \qquad (95)$$