1. Symmetry, Group Theory, and Electronic Structure

2. Ground State Spectroscopic Methods

2.1 Nuclear Magnetic Resonance

2.2 Electron Paramagnetic Resonance

2.3 Mössbauer Spectroscopy

3. Excited State Spectroscopic Methods

4. Other Physical Methods

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The Zeeman effect... the foundation of magnetic resonance

- effect of magnetic field (*B*) on isolated nucleus with *I* > 0?

  - nuclear spin (angular momentum) states will split (e.g. *I* = 3/2)

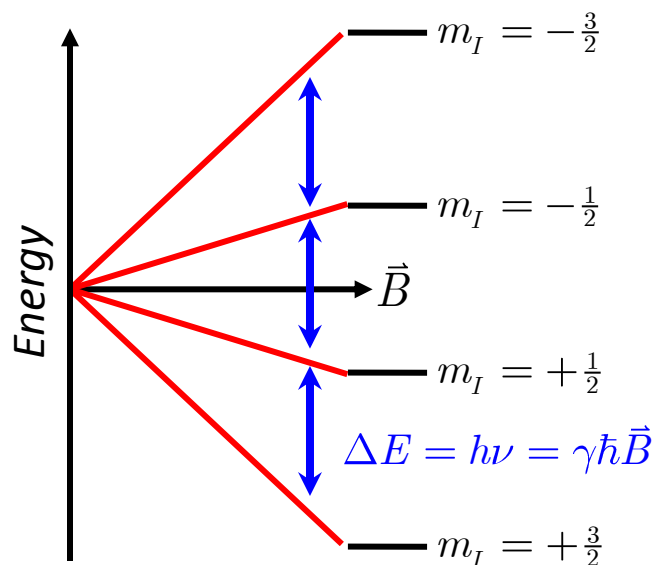 - energy splitting of the nuclear wavefunction is determined by *nuclear Zeeman Hamiltonian*

$$\boxed{H'_{nZ} = -\vec{\mu}_I \cdot \vec{B} = -\hbar\gamma\vec{I}\cdot\vec{B}}$$

$\vec{\mu}$ = nuclear magnetic moment $\vec{B}$ = magnetic field vector
γ = gyromagnetic ratio $\vec{I}$ = nuclear spin vector

$$E_{Zeeman} = -\gamma\hbar\left|\vec{B}\right|\cdot\left\langle\Psi_I\left|\vec{I}\right|\Psi_I\right\rangle$$
$$= -\gamma\hbar B_0 m_I$$

- for electric dipole allowed transition in *spherical symmetry:*

$$\text{NMR selection rule} \mapsto \boxed{\Delta m_I = \pm 1}$$

$m_I = -\frac{3}{2}$

$m_I = -\frac{1}{2}$

$\vec{B}$

$m_I = +\frac{1}{2}$

$\Delta E = h\nu = \gamma\hbar\vec{B}$

$m_I = +\frac{3}{2}$

$I = \frac{3}{2}$ gives $2(\frac{3}{2})+1 = 4$ levels

$$m_I = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

Classical Model for Nuclear Zeeman Effect

- classical magnetic moment (μ) precesses (rotates) about the axis of external magnetic field (B_0) $\rightarrow \vec{\mu}_I \cdot \vec{B}_0$

- Larmor precession with frequency:

$$\nu_0 = \frac{\gamma}{2\pi} B_0 \ or \ \omega_0 = \gamma B_0$$

$\vec{B}_0 \parallel z$

- *cone angle* depends on μ, which depends on m_I
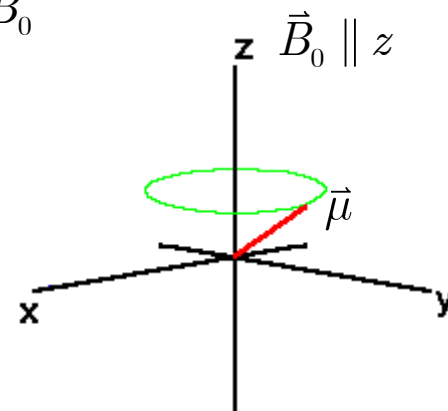 - 2I+1 different values
  - also depends on γ

$$\cos\theta = \frac{m_I}{\sqrt{I(I+1)}}$$

for $I = \frac{1}{2}$

- m_I defines magnitude of projection along direction of B_0 (z):

$$\vec{\mu} = \sqrt{I \ I+1} \, \gamma\hbar \quad \Rightarrow \quad \mu_z = m_I \gamma\hbar$$

B_0

$m_I = +\frac{1}{2}$ (α-state)

θ

$m_I = -\frac{1}{2}$ (β-state)

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- define *classical* gyromagnetic ratio for any magnetic particle

  - for $e^- \rightarrow$ *Bohr magneton*

    $$\gamma_e = \mu_B = \frac{e\hbar}{2m_e} = 9.2741 \times 10^{-24} \, JT^{-1}$$

  - for $p^+ \rightarrow$ *nuclear magneton*

    $$\gamma_H = \mu_N = \frac{e\hbar}{2m_p} = 5.05095 \times 10^{-27} \, JT^{-1}$$

- but γ is more complicated since these are *relativistic quantum particles*
  - Need fudge factor – the Lande *g*-factor – such that
  - In NMR, we normally use $\gamma_N \rightarrow$ in EPR everything is discussed in terms of *g*-values

    $$\gamma_N = \frac{g_N}{\hbar} \mu_N$$

- Important properties when considering nuclear spin:
  - Nuclear spin (*I*), magnetic moment (*µ*), magnetogyric ratio (γ)
  - Natural abundance (*C*)
  - Relative Receptivity (*D^P*)

    $$D^P = \frac{|\gamma_N|^3 C_N I_N (I_N + 1)}{|\gamma_P|^3 C_P I_P (I_P + 1)}$$

    - relative to ^{13}C

Important factors relating to nuclear spin

- Nuclear spin (*I*)

- magnetic moment (μ)

- magnetogyric ratio (γ)

- natural abundance (*C*)

- relative receptivity (D^P)

  - relative to ^{13}C

$$D^P = \frac{\left|\gamma_N\right|^3 C_N I_N (I_N + 1)}{\left|\gamma_P\right|^3 C_P I_P (I_P + 1)}$$

Isotope	Spin	% Natural Abundance	Magnetic Moment (μ/μ_N)	Magnetogyric Ratio $(\gamma/10^7)$ rad T^{-1}s^{-1}	Relative Receptivity (D^P)
e	1/2		-3.184×10^3	-1.761×10^4	2.8×10^8
^{1}H	1/2	99.985	4.83724	26.7510	5.68×10^3
^{2}H	1	0.015	1.2126	4.1064	8.21×10^{-3}
^{6}Li	1	7.42	1.1625	3.9366	3.58
^{7}Li	3/2	92.58	4.20394	10.396	1.54×10^3
^{9}Be	3/2	100.0		-3.7954	78.8
^{10}B	3	19.58	2.0792	2.8748	22.1
^{11}B	3/2	80.42	3.408	8.5827	7.54×10^2
^{13}C	1/2	1.108	1.2166	6.7263	1.000
^{14}N	1	99.63	0.57099	1.9324	5.69
^{15}N	1/2	0.37	-0.4903	-2.7107	2.19×10^{-2}
^{17}O	5/2	0.037		-3.6266	6.11×10^{-2}
^{19}F	1/2	100.0	4.5532	25.1665	4.73×10^3
^{29}Si	1/2	4.70	-0.96174	-5.3141	2.09
^{31}P	1/2	100.0	1.9602	10.829	3.77×10^2
^{33}S	3/2	0.76		2.0517	9.73×10^{-2}
^{35}Cl	3/2	75.53		2.6212	20.2
^{37}Cl	3/2	24.47		2.182	3.77

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Periodic Table of the Elements

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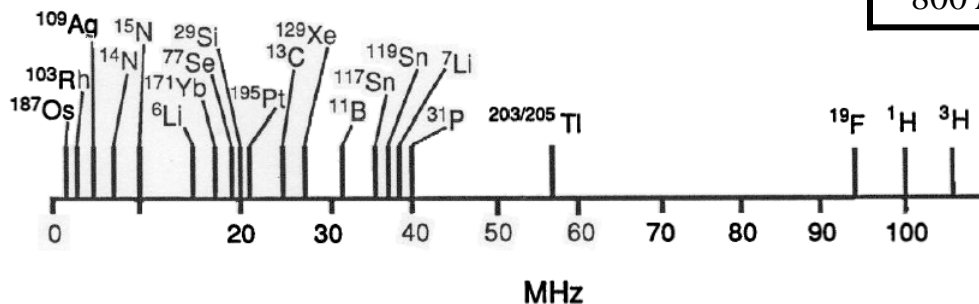Department of Chemistry

Energy required to induce nuclear transitions
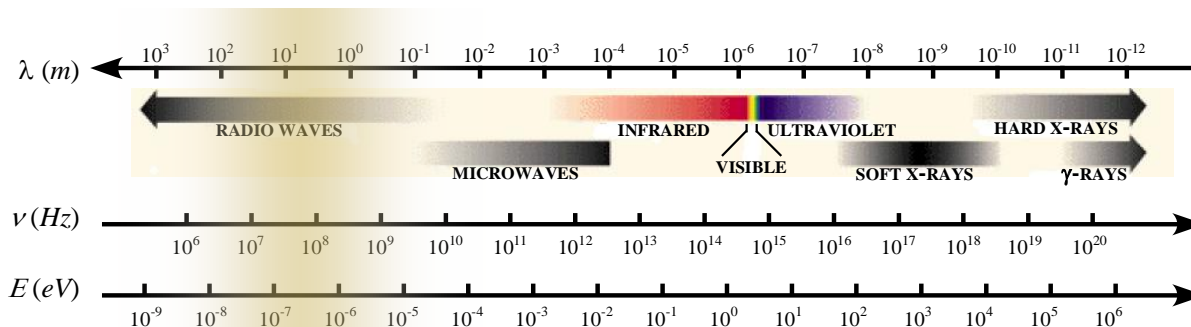
- Depends on applied magnetic field (B_0) → $\Delta E = h\nu = \gamma\hbar\vec{B}_0$

  - In a 2.35T magnetic field, ^{1}H resonates at 100 MHz → ~ 10^{-7} eV

  - Spectrometers are discussed based on frequency required to induce ^{1}H nuclear transition

300 *MHz*	7.05 *T*
400 *MHz*	9.40 *T*
500 *MHz*	11.75 *T*
800 *MHz*	18.80 *T*

- Depends on nucleus

Approaches to Performing NMR Experiments

- Continuous Wave (CW) Experiments $\rightarrow$ traditional approaches
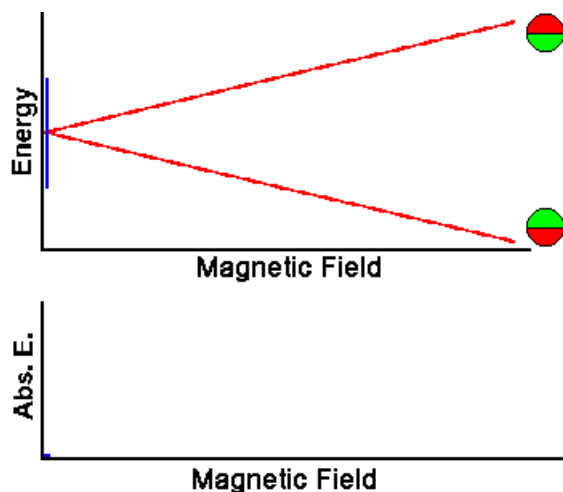
Fixed Frequency	*Fixed Magnetic Field*
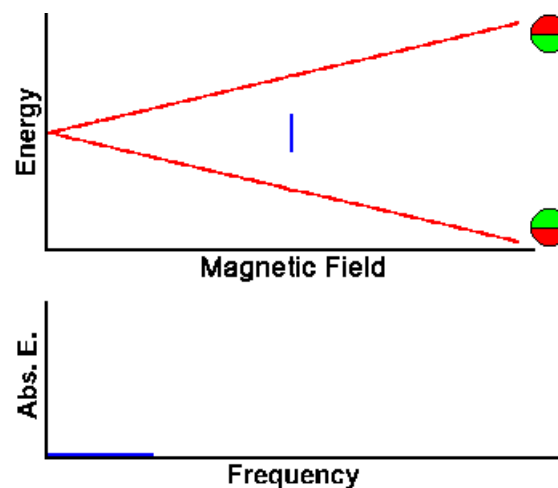
- Pulsed Experiments $\rightarrow$ modern approach
  - use *pulsed* magnetic fields to cause perturbation $\rightarrow$ watch effect over time
  - relies on Fourier methods to transform from time domain to frequency domain
  - use effect of *oscillating magnetic field* to induce transitions $\quad t\ s\ \rightarrow \nu\ s^{-1}$

Classical Effect of Rotating Field on Larmor Precession

- apply rotating B_1 field $\perp$ to homogeneous B_0 field – what happens?

- under most circumstances – nothing
  - rotating field does not interact with $\vec{\mu}$
  - unless @ same frequency

- if B_1 rotates at *Larmor frequency* (ν)
  - rotating field can couple with magnetic moment $\quad \vec{\mu} \cdot \vec{B}_1$
  - results in force (F) acting to increase θ
    - *remember*: difference between m_I states in magnetic field is the angle θ with respect to B_0
  - applied to QM: can produce $\Delta m_I \rightarrow$ induces NMR transitions!

- Basic approach used in pulsed techniques (*vide infra*)
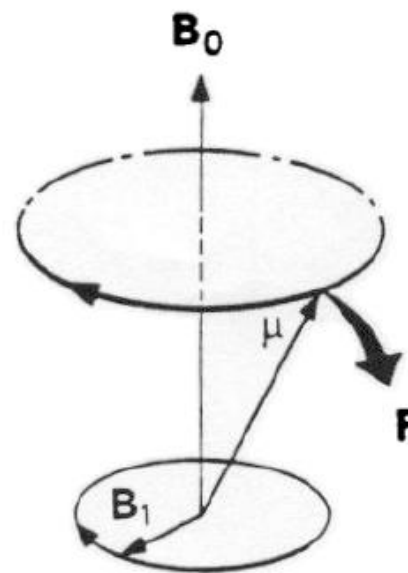
NMR Chemical Shifts

- If $\nu_0 = \dfrac{\gamma}{2\pi} B_0$ was the whole story, NMR would be pretty much useless

  - could be used for elemental analysis (maybe) but

  - every ^{1}H nucleus would have same Larmor Frequency $\rightarrow$ at the same energy!

- Fortunately, electronic environment affects response to B_0

  - This effect could be described in two possible ways:
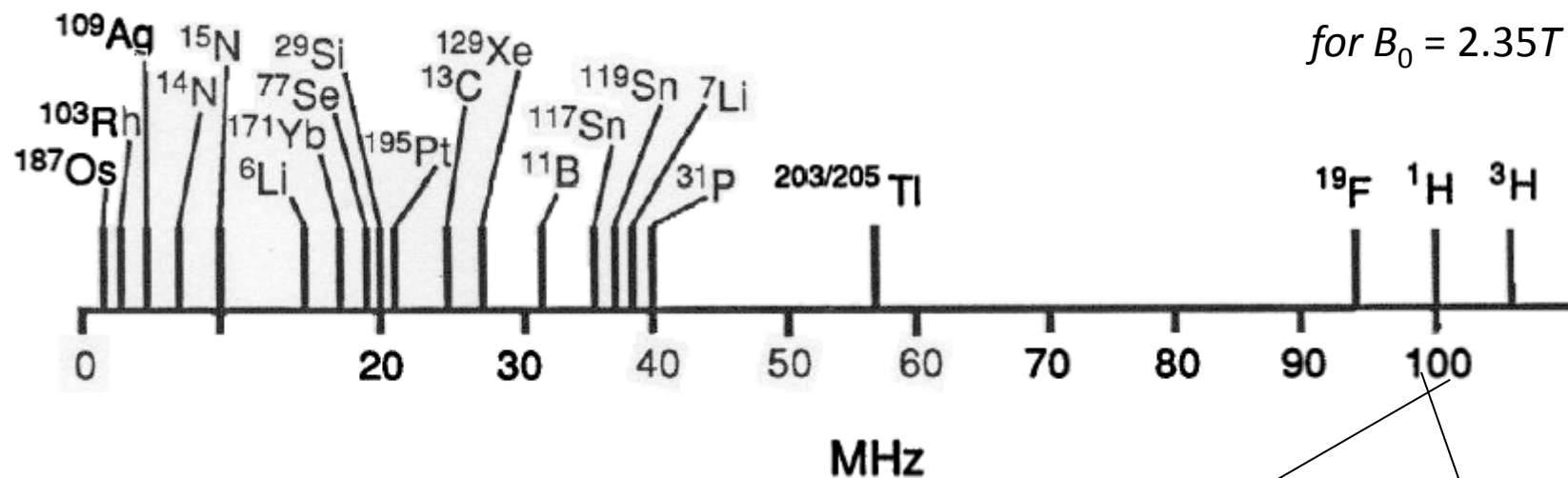
    usual way of thinking in NMR

    - different nuclei see different magnetic fields

$$\boxed{\nu_i = \frac{\gamma}{2\pi} B_{eff} = \frac{\gamma}{2\pi} B_0 (1 - \sigma_i)}$$

    - different nuclei have different gyromagnetic ratios

$$\nu_i = \frac{\gamma_{eff}}{2\pi} B_0 = \frac{\gamma_N (1 - \sigma_i)}{2\pi} B_0$$

- Either way - Larmor frequency depends on chemical environment

  - σ_i is "shielding constant"

  - usually reported as $\delta_{ppm} \rightarrow$ in *parts per million* from a reference standard

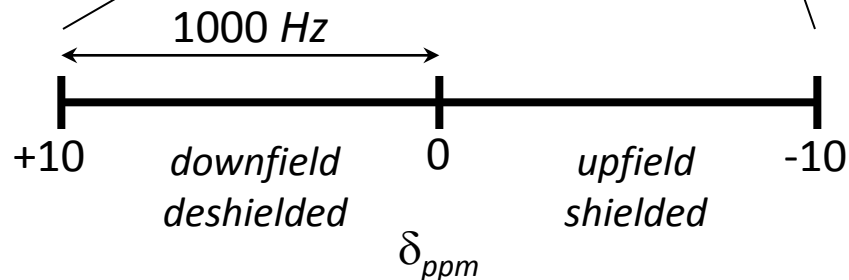$$\delta_{ppm} = \frac{\nu - \nu_0}{\nu_0} \times 10^6$$

for B_0 = 2.35T

$$\delta_{ppm} = \frac{\nu - \nu_0}{\nu_0} \times 10^6$$

Chemical shifts are empirical parameters that are determined relative to "standards"

e.g. for $^1H \rightarrow Si(CH_3)_4$ (TMS)
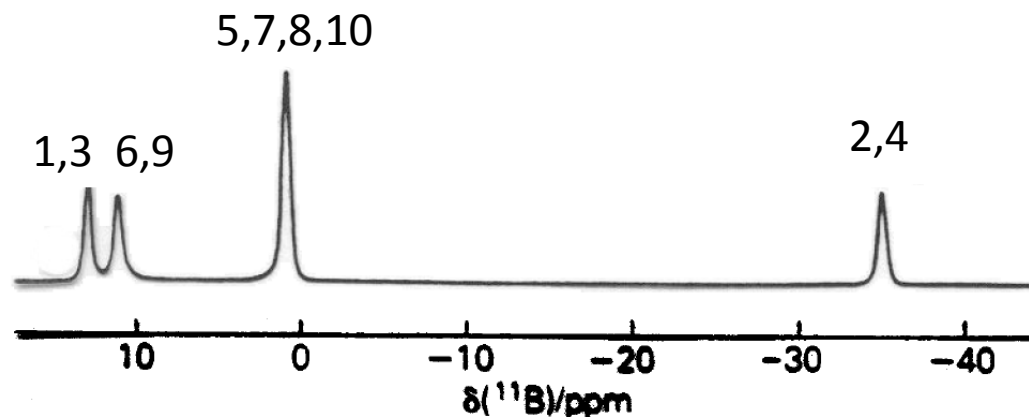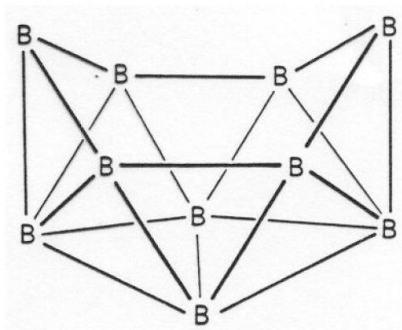
[in practice, modern spectrometers perform internal calibration, which obviates need for external standards – but better safe than sorry]

1000 *Hz*

+10   *downfield*   0   *upfield*   -10
       deshielded   *shielded*

δ_{ppm}

$$\nu_i = \frac{\gamma}{2\pi} B_{eff} = \frac{\gamma}{2\pi} B_0(1 - \sigma_i)$$

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- *e.g.* 115 MHz (8.2T) ^{11}B NMR of $B_{10}H_{14}$ (^{1}H decoupled)

5,7,8,10

1,3 6,9

2,4

$\delta(^{11}B)$/ppm

- Intensity mechanism exactly the same for all nuclei of same type:
  - sample concentration
  - # of nuclei of a particular type
  - isotopic distribution

$$I \propto \left\langle \Psi \;\; m_I^1 \; |\vec{\mu}| \; \Psi \;\; m_I^2 \right\rangle^2$$

- Chemically identical nuclei are at same position

- But what about interactions with other nuclei?
  - Angular momenta should be able to couple…

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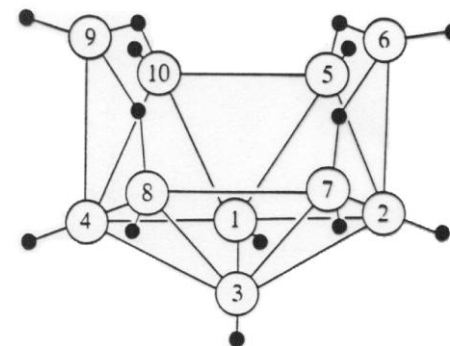
Coupling of Angular Momenta → Scalar Coupling

- connected angular momenta can couple with each other

  - electron spin with orbital angular momentum (spin-orbit coupling)

  - electron spin with electron spin (magnetic coupling of metal ions)

  - nuclear spin with nuclear spin (scalar coupling)

- coupling is *independent* of magnetic field

  - strength of coupling is a scalar (α) that connects each of the angular momenta…

$$\vec{\mathrm{J}}_{12} = \alpha \ \vec{J}_1 \cdot \vec{J}_2 \ = \alpha \ \vec{J}_2 \cdot \vec{J}_1 \ = \vec{\mathrm{J}}_{21}$$

- Consider two nuclei with I_1 and I_2, respectively…

$$H_{sc} = + J_{12} \ \vec{I}_1 \cdot \vec{I}_2$$

scalar coupling term
or J-coupling term

$$H'_{\vec{I}_1, \vec{I}_2} = H_{\text{nuclear Zeeman on } \vec{I}_1} + H_{\text{nuclear Zeeman on } \vec{I}_2} + H_{\text{scalar coupling of } (\vec{I}_1 \cdot \vec{I}_2)}$$

$$= -\hbar\gamma \ \vec{B}_{eff} \cdot \vec{I}_1 \ + -\hbar\gamma \ \vec{B}_{eff} \cdot \vec{I}_2 \ + J_{12} \ \vec{I}_1 \cdot \vec{I}_2$$

$$= \underbrace{-\hbar\gamma B_0 \ 1 - \sigma_1 \ m_{I_1} - \hbar\gamma B_0 \ 1 - \sigma_2 \ m_{I_2}}_{\substack{\text{Zeeman terms} \\ \text{(field dependent)}}} + \underbrace{J_{12} m_{I_1} m_{I_2}}_{\substack{\text{scalar coupling} \\ \text{(field independent)}}}$$

- Simplest case: 2 indistinguishable $I = {}^1/_2$ nuclei… ($J_{12} > 0$)
  - allowed transitions will be $(m_{I_1}, m_{I_2}) \rightarrow (m'_{I_1}, m'_{I_2})$ where $\Delta m_{I_1} = \pm 1$ or $\Delta m_{I_2} = \pm 1$

nuclear Zeeman for I_1

$I_1 = {}^1/_2$
$I_2 = {}^1/_2$

-1/2

+1/2
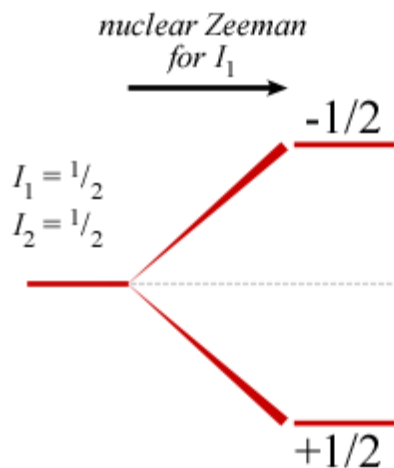
but this is not what we see experimentally!

because this solution doesn't actually satisfy the Pauli Exclusion Principle! (**???**)

$$H'_{\vec{I}_1, \vec{I}_2} = -\hbar \gamma B_0 \left(1 - \sigma_i\right) m_{I_1} - \hbar \gamma B_0 \left(1 - \sigma_i\right) m_{I_2} + J_{12} m_{I_1} m_{I_2}$$

- Pauli Exclusion Principle: valid wavefunction must be either symmetric (+1) or antisymmetric (-1) with respect to particle exchange for equivalent particles → *huh?*

$$\left(+\tfrac{1}{2}, +\tfrac{1}{2}\right) \xrightarrow{\text{exchange nuclei}} \left(+\tfrac{1}{2}, +\tfrac{1}{2}\right) \mapsto \text{symmetric}$$

  - in our current case

$$\left(-\tfrac{1}{2}, -\tfrac{1}{2}\right) \xrightarrow{\text{exchange nuclei}} \left(-\tfrac{1}{2}, -\tfrac{1}{2}\right) \mapsto \text{symmetric}$$

$$\left(+\tfrac{1}{2}, -\tfrac{1}{2}\right) \xrightarrow{\text{exchange nuclei}} \left(-\tfrac{1}{2}, +\tfrac{1}{2}\right) \mapsto PEP\ violation$$

$$\left(-\tfrac{1}{2}, +\tfrac{1}{2}\right) \xrightarrow{\text{exchange nuclei}} \left(+\tfrac{1}{2}, -\tfrac{1}{2}\right) \mapsto PEP\ violation$$

  - introduce another nomenclature to simplify our life for *S* = 1/2 systems

$$\left. \begin{array}{l} \alpha = +\tfrac{1}{2} \\ \beta = -\tfrac{1}{2} \end{array} \right| \text{such that} \quad \alpha_1 \beta_2 \equiv +\tfrac{1}{2}, -\tfrac{1}{2}$$

  - the two degenerate configurations must be *symmetrized* → create another set of basis functions…

$$\varphi_s = \tfrac{1}{\sqrt{2}} (\alpha_1 \beta_2 + \beta_1 \alpha_2) \mapsto \text{symmetric}$$

$$\varphi_{as} = \tfrac{1}{\sqrt{2}} (\alpha_1 \beta_2 - \beta_1 \alpha_2) \mapsto \text{antisymmetric}$$

$$\left\langle \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \middle| \tfrac{1}{\sqrt{2}}(\beta_1\alpha_2 + \alpha_1\beta_2) \right\rangle = \tfrac{1}{2} \left\langle \alpha_1\beta_2 \middle| \beta_1\alpha_2 \right\rangle + \left\langle \alpha_1\beta_2 \middle| \alpha_1\beta_2 \right\rangle + \left\langle \beta_1\alpha_2 \middle| \beta_1\alpha_2 \right\rangle + \left\langle \beta_1\alpha_2 \middle| \alpha_1\beta_2 \right\rangle$$

$$= \tfrac{1}{2}\ 0 + 1 + 1 + 0$$

$$= 1 \mapsto \text{symmetric}$$

$$\left\langle \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \middle| \tfrac{1}{\sqrt{2}}(\beta_1\alpha_2 - \alpha_1\beta_2) \right\rangle = \tfrac{1}{2} \left\langle \alpha_1\beta_2 \middle| \beta_1\alpha_2 \right\rangle - \left\langle \alpha_1\beta_2 \middle| \alpha_1\beta_2 \right\rangle - \left\langle \beta_1\alpha_2 \middle| \beta_1\alpha_2 \right\rangle + \left\langle \beta_1\alpha_2 \middle| \alpha_1\beta_2 \right\rangle$$
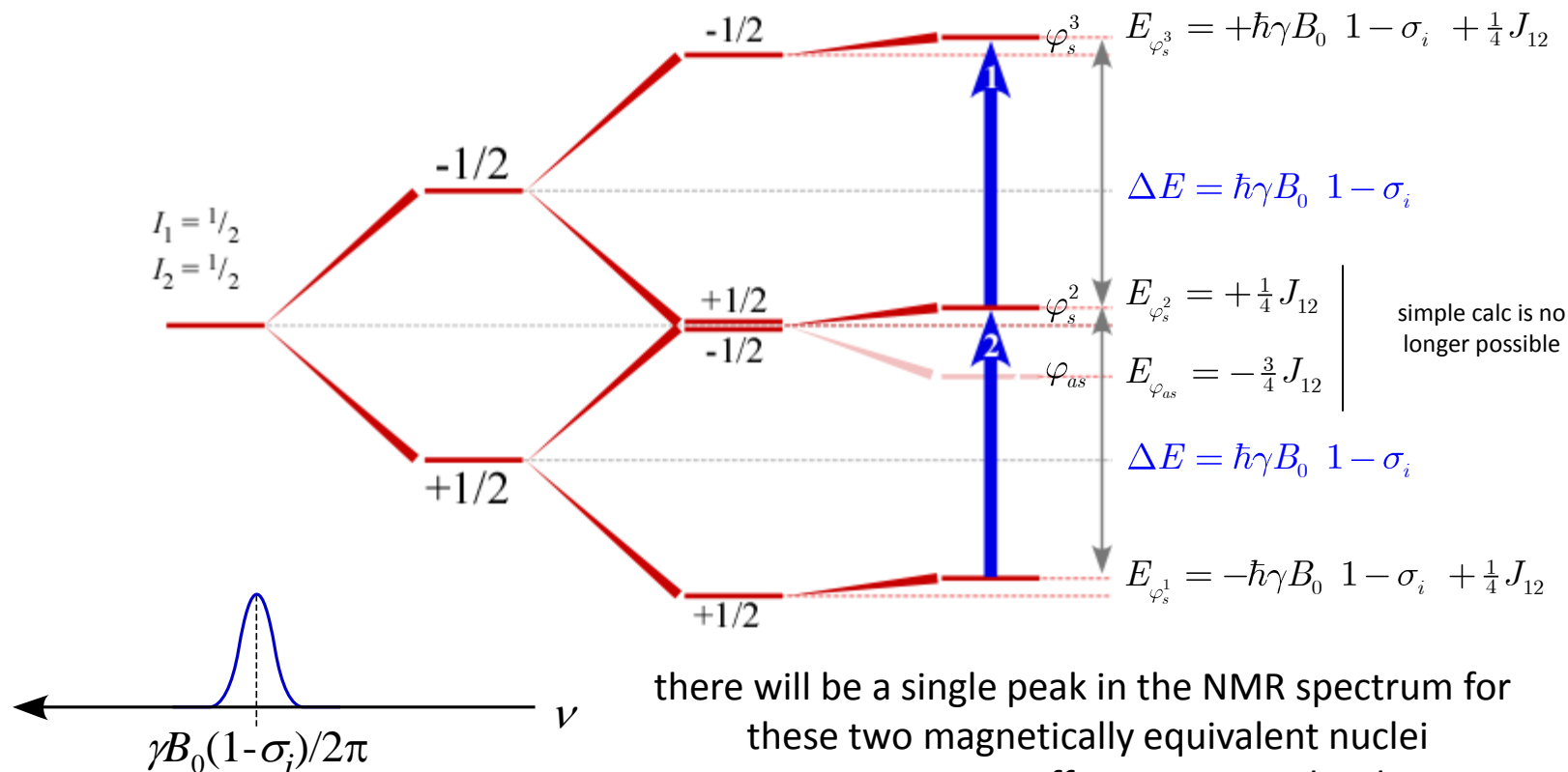
$$= \tfrac{1}{2}\ 0 - 1 - 1 + 0$$

$$= -1 \mapsto antisymmetric$$

- this causes a few issues…
  - hidden selection rule → can't change symmetry
  - the energies we've calculated are wrong

$$\varphi_s^1 = \alpha_1\alpha_2 \mapsto \text{symmetric}$$
$$\varphi_{as} = \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \mapsto \text{antisymmetric}$$
$$\varphi_s^2 = \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \mapsto \text{symmetric}$$
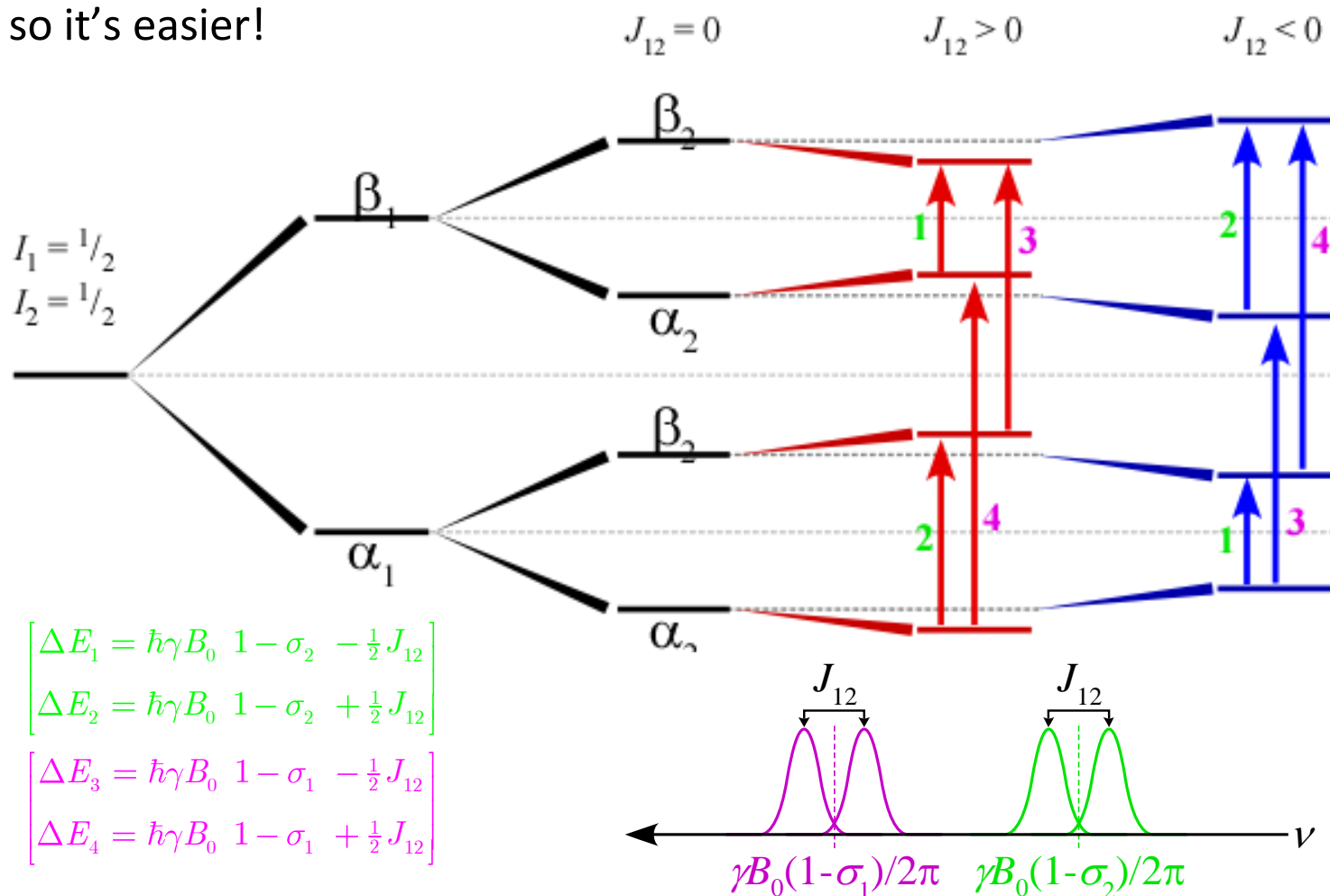$$\varphi_s^3 = \beta_1\beta_2 \mapsto \text{symmetric}$$

- we get a new (correct) energy level diagram for this special case

$$I_1 = {}^1\!/_2$$
$$I_2 = {}^1\!/_2$$

$$E_{\varphi_s^3} = +\hbar\gamma B_0\,\left(1-\sigma_i\right) + \tfrac{1}{4}J_{12}$$

$$\Delta E = \hbar\gamma B_0\,\left(1-\sigma_i\right)$$

$$E_{\varphi_s^2} = +\tfrac{1}{4}J_{12}$$
$$E_{\varphi_{as}} = -\tfrac{3}{4}J_{12}$$

simple calc is no longer possible

$$\Delta E = \hbar\gamma B_0\,\left(1-\sigma_i\right)$$

$$E_{\varphi_s^1} = -\hbar\gamma B_0\,\left(1-\sigma_i\right) + \tfrac{1}{4}J_{12}$$

$$\gamma B_0(1-\sigma_i)/2\pi \qquad \nu$$

there will be a single peak in the NMR spectrum for these two magnetically equivalent nuclei
= no **apparent** effect on energy levels

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- what if the two $I = \frac{1}{2}$ nuclei are different from each other?
  - we don't have to worry about the Pauli Exclusion Principle and all of that… so it's easier!

$$\left[\Delta E_1 = \hbar\gamma B_0 \left(1 - \sigma_2\right) - \tfrac{1}{2}J_{12}\right]$$
$$\left[\Delta E_2 = \hbar\gamma B_0 \left(1 - \sigma_2\right) + \tfrac{1}{2}J_{12}\right]$$

$$\left[\Delta E_3 = \hbar\gamma B_0 \left(1 - \sigma_1\right) - \tfrac{1}{2}J_{12}\right]$$
$$\left[\Delta E_4 = \hbar\gamma B_0 \left(1 - \sigma_1\right) + \tfrac{1}{2}J_{12}\right]$$

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- what about coupling of one $I = {}^1/_2$ nucleus (1) to two equivalent $I = {}^1/_2$ nuclei (2, 2')?

$$E\left(\varphi_{\beta_1\beta_2\beta_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[-B_0\left(1-\sigma_1\right)-2B_0\left(1-\sigma_2\right)\right]+\tfrac{1}{2}J_{12}$$

$$E\left(\varphi_{\beta_1\beta_2\alpha_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[-B_0\left(1-\sigma_1\right)\right]$$

$$E\left(\varphi_{\beta_1\alpha_2\beta_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[-B_0\left(1-\sigma_1\right)\right]$$

$$E\left(\varphi_{\beta_1\alpha_2\alpha_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[-B_0\left(1-\sigma_1\right)+2B_0\left(1-\sigma_2\right)\right]-\tfrac{1}{2}J_{12}$$

$$E\left(\varphi_{\alpha_1\beta_2\beta_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[+B_0\left(1-\sigma_1\right)-2B_0\left(1-\sigma_2\right)\right]-\tfrac{1}{2}J_{12}$$

$$E\left(\varphi_{\alpha_1\beta_2\alpha_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[+B_0\left(1-\sigma_1\right)\right]$$

$$E\left(\varphi_{\alpha_1\alpha_2\beta_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[+B_0\left(1-\sigma_1\right)\right]$$

$$E\left(\varphi_{\alpha_1\alpha_2\alpha_{2'}}\right) = -\tfrac{\hbar\gamma}{2}\left[+B_0\left(1-\sigma_1\right)+2B_0\left(1-\sigma_2\right)\right]+\tfrac{1}{2}J_{12}$$

$$\Delta E_1 = \hbar\gamma B_0\left(1-\sigma_1\right)-J_{12}$$

$$\Delta E_2 = \hbar\gamma B_0\left(1-\sigma_1\right)$$

$$\Delta E_3 = \hbar\gamma B_0\left(1-\sigma_1\right)$$

$$\Delta E_4 = \hbar\gamma B_0\left(1-\sigma_1\right)+J_{12}$$

$\gamma B_0(1-\sigma_1)/2\pi$ $\gamma B_0(1-\sigma_2)/2\pi$

General Rules about Scalar Coupling (J-Coupling)

- scalar coupling occurs only through atoms connected by chemical bonds

  - involves interactions through the electronic manifold $\rightarrow$ no covalency = no scalar coupling

  - can be considered as having three components (I_1--(e^-)--I_2)

    - efficiency of electronic bridge depends on nature and number of bonds between nuclei as well as specific angles relationship between bonds

    - nuclei are coupled to the electronic bridge through electron density at the nucleus (*s*-type contributions in the valence orbitals involved in bonding)

- magnitude of scalar coupling also depends on

  - magnitude of magnetic moments involved $\rightarrow$ $\quad J_{12} \propto \gamma_{I_1} \cdot \gamma_{I_2}$

  - nature of nuclei has dramatic impact on whether coupling is observed or not

- scalar coupling is independent of magnetic field

  - splitting will always occur at a constant ν – not constant δ_{ppm}

  - Can be used to differentiate coupling *vs.* independent signals - *e.g.* doublet signal *vs.* two singlets

- effects of scalar coupling are additive

  - the effect of J_{12} and J_{13} on I_1 is determined by applying J_{12} followed by J_{13}

  - always easier to start with largest effect and move downwards (start with J_{13} if $J_{13} > J_{12}$)

nucleus	γ (10^7 rad $T^{-1}s^{-1}$)
^{1}H	26.751
^{2}H	4.106
^{11}B	8.583
^{13}C	6.726

Chem 529 (2009-W2)
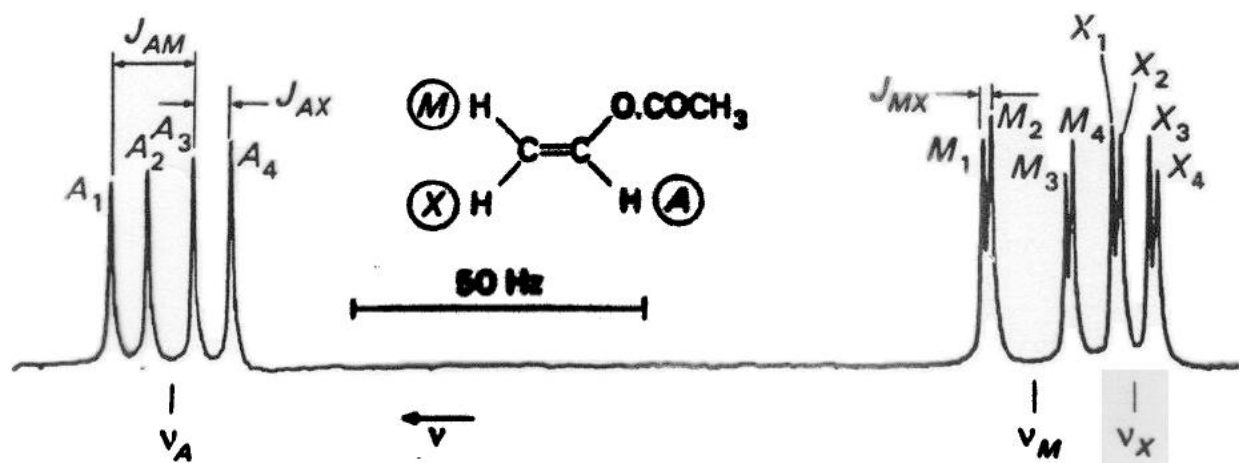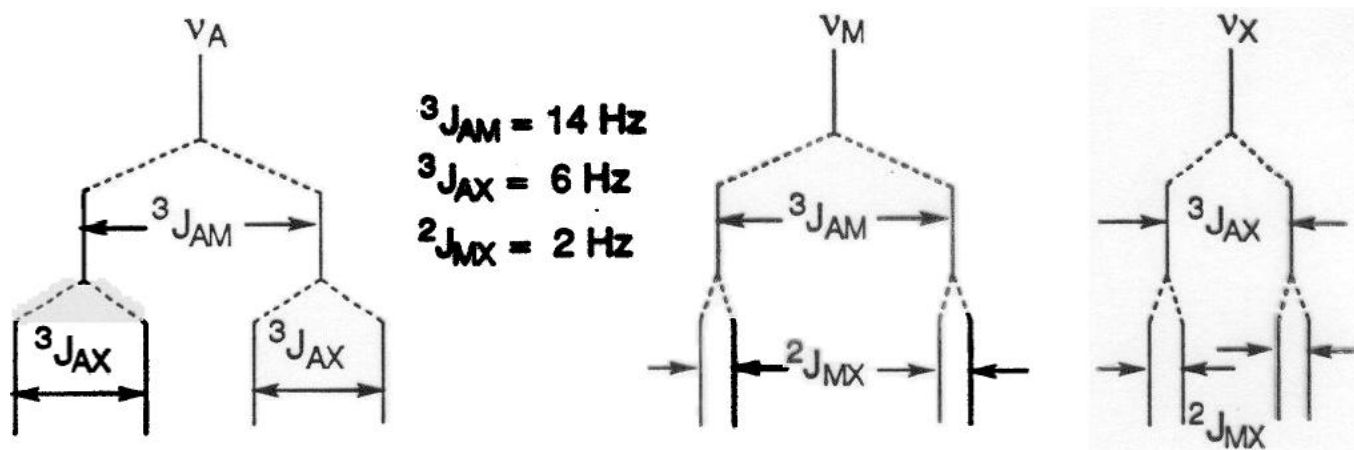
• Example: 5 coordinate phosphorus molecule…
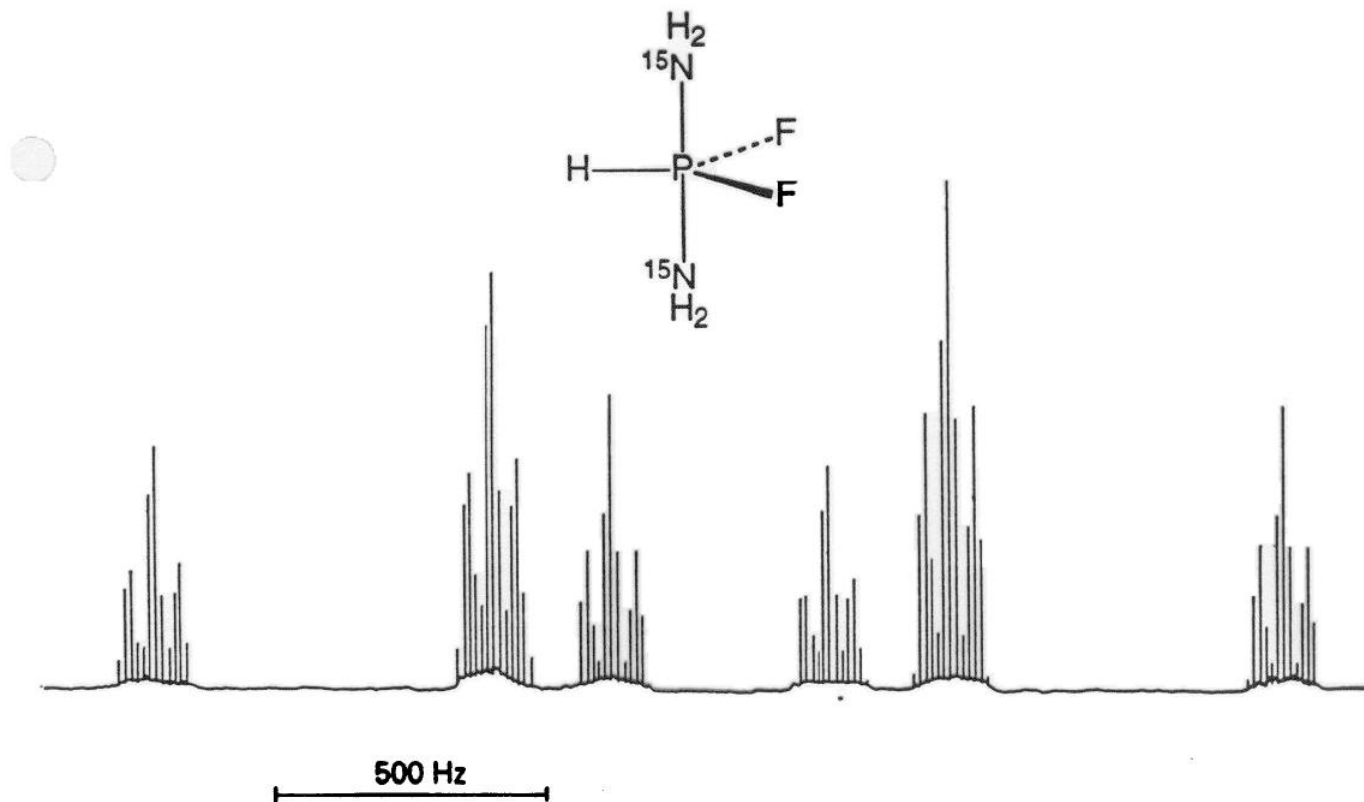
Fig. 2.9 ^{31}P NMR spectrum of $PF_2H(^{15}NH_2)_2$. It is a doublet (J_{PH}) of triplets (J_{PF}) of ~iplets (J_{PN}) of quintets (J_{PH}) – 90 lines in all.

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- Examples of multiplets in ^{1}H NMR

^{31}PMe$_3$

^2J(PH)= 3.0 Hz $n = 1$ $I_2 = 1/2$

^{14}NH$_4^+$

^1J(NH)= 52.5 Hz $n = 1$ $I_2 = 1$

^{11}BH$_4^-$

^1J(^{11}BH)= 80.5 Hz $n = 1$ $I_2 = 3/2$

^{10}BH$_4^-$

^1J(^{10}BH)= 27.2 Hz $n = 1$ $I_2 = 3$

^1J(^{11}BH)= 27.2 Hz $n = 2$ $I_2 = 3/2$
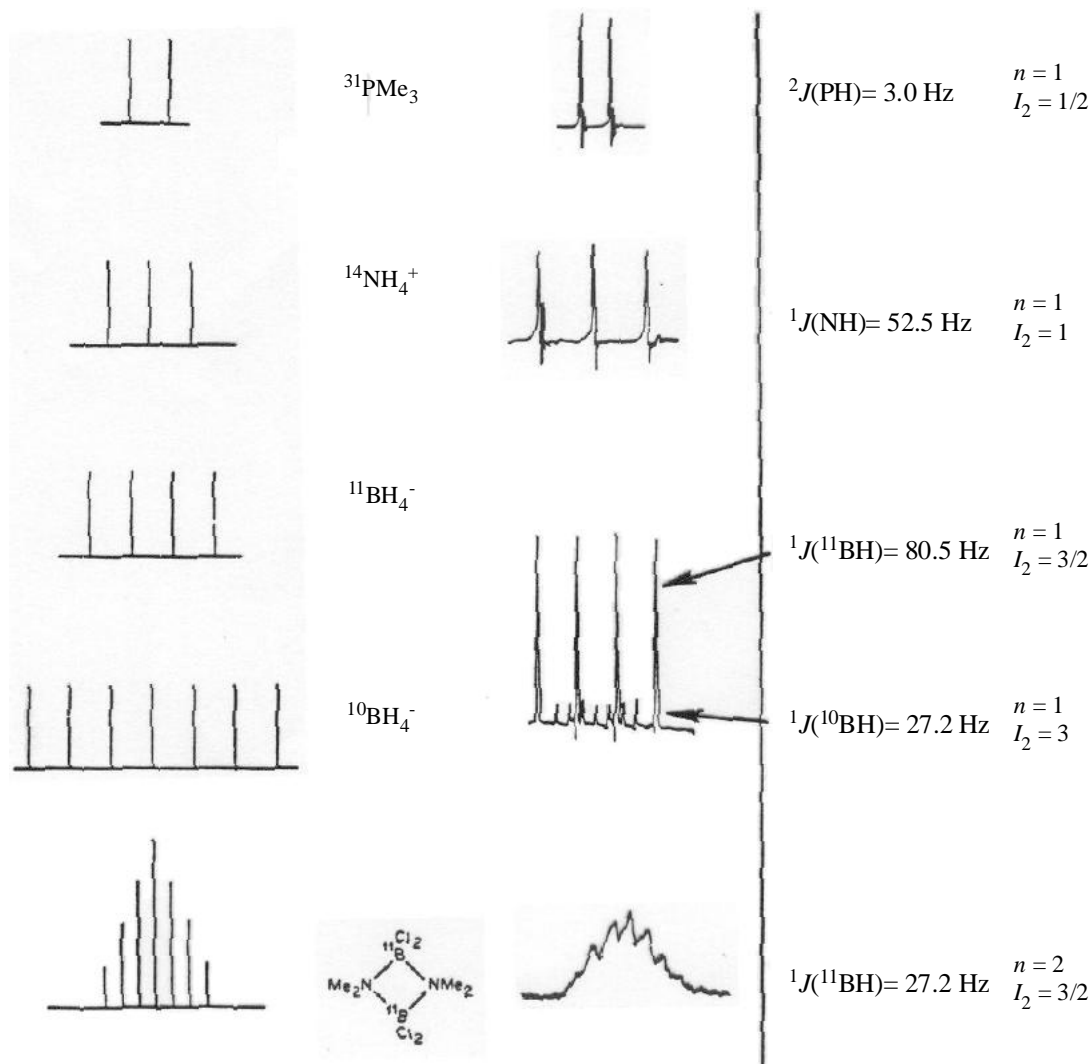
- intensity distributions due to scalar coupling – general multiplet patterns

  - depends on number of states involved

  - For coupling of $I = {}^1/_2$ nuclei – use Pascal's Tri

  - For $I > {}^1/_2$ nuclei – use energy diagrams

  - simple intensity pattern only holds in the weak coupling limit, i.e. $\Delta \nu_{12} \gg J_{12}$

- intensities in strong coupling limit causes roofing of NMR multiplets

  - roof effect $\rightarrow$ coupled multiplets point to each other

  - due to mixing of nuclear states as $\left| \Delta \nu_{12} \right| \rightarrow \left| J_{12} \right|$

    - intensity gets redistributed between transitions

    - in limit – outer peaks disappear and obtain singlet

    - this is exactly the same thing as why coupling is not observed between two magnetically equivalent nuclei
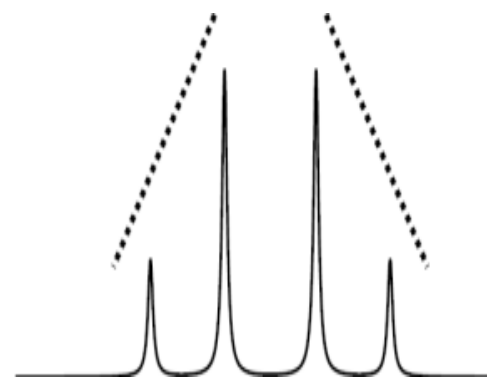
The strong coupling limit
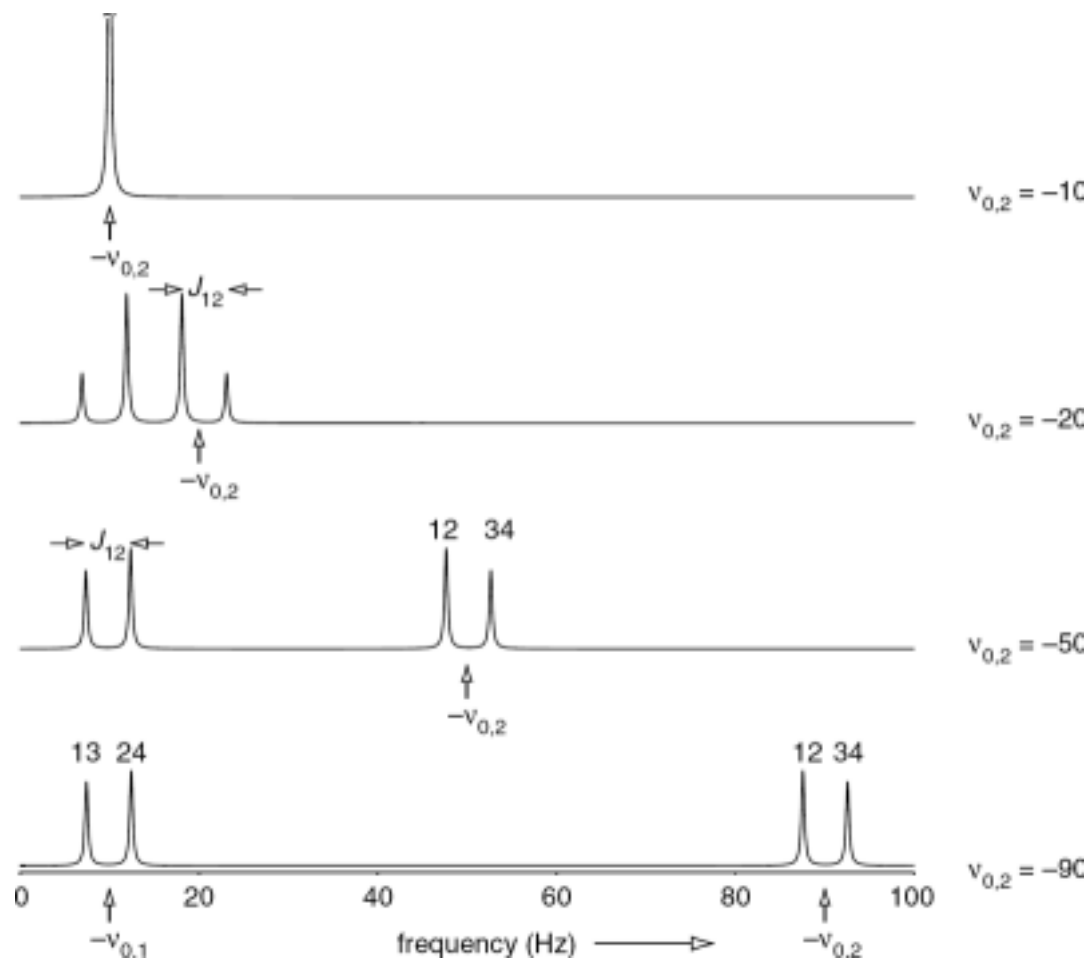
- see http://physchem.ox.ac.uk/~hmc/tlab/603/ab2.html for demonstration of effect

First Order

$$|\nu_B - \nu_A| \gg |J|$$

Second Order

$$|\nu_B - \nu_A| \sim |J|$$
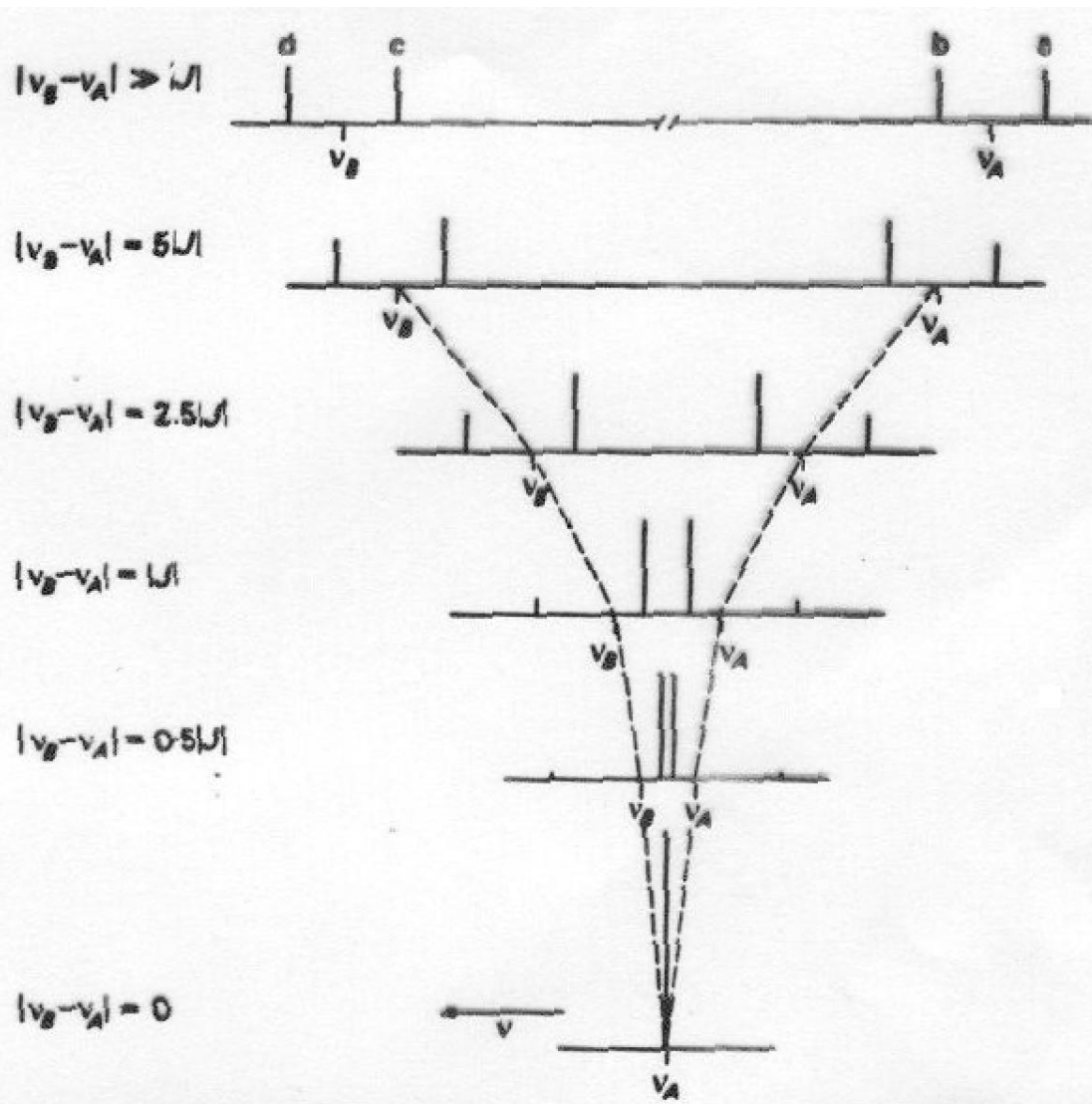
Fig. 2-3 AB spectra showing the effect of varying the ratio of the coupling constant to the difference in A and B resonance frequencies. The top spectrum is an AX type ($\theta = 0$) and the bottom is an A_2 type ($\theta = \pi/4$).

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• energy level diagram for simple strongly coupled system

these energy levels begin to mix as
they get closer and closer in energy
→ get *symmetric* & *antisymmetric* mixed states
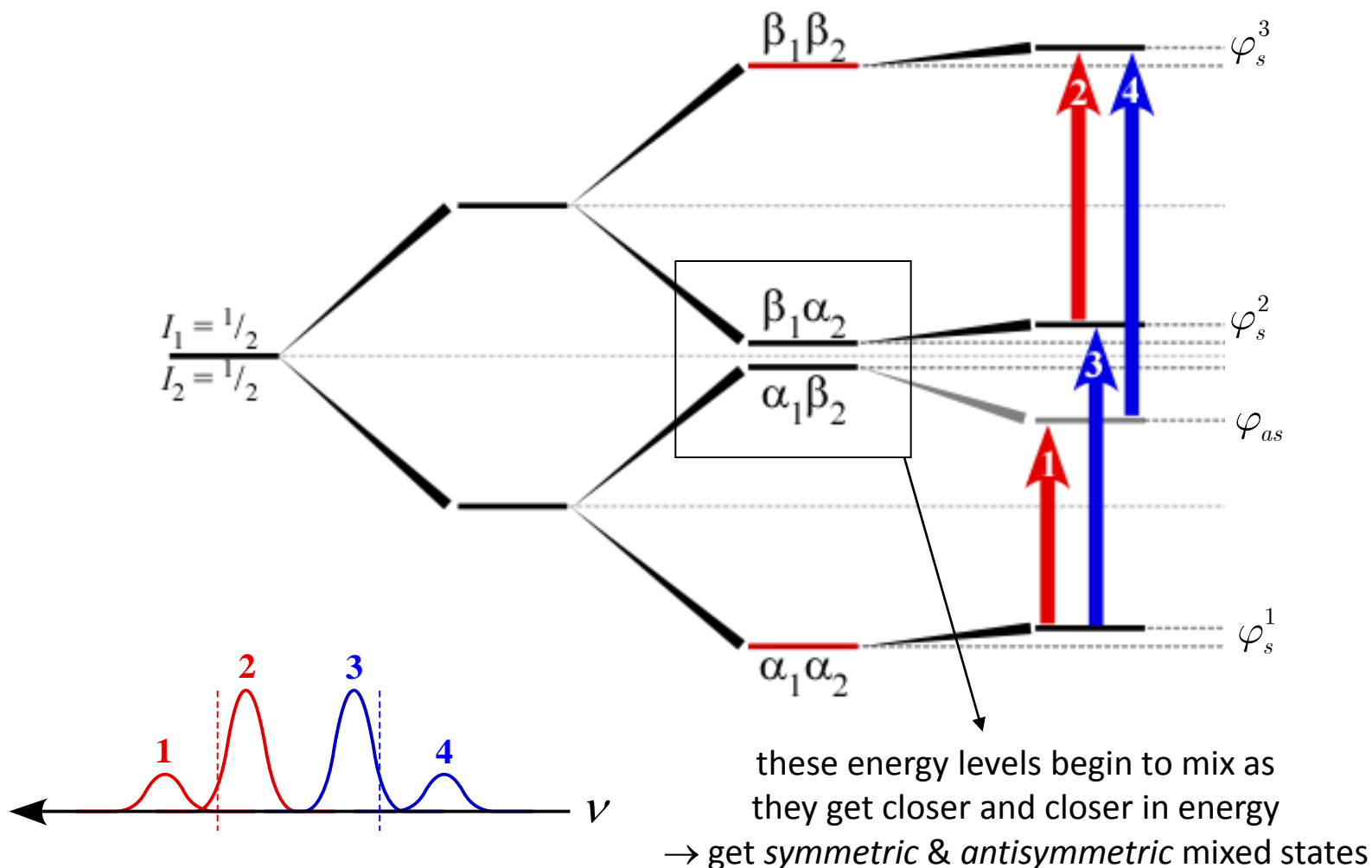
Characteristics of Second Order Spectra

- Peak intensities are not equally distributed

- Position of ν is not at centre of multiplets

- Observation of outer lines can be extremely difficult
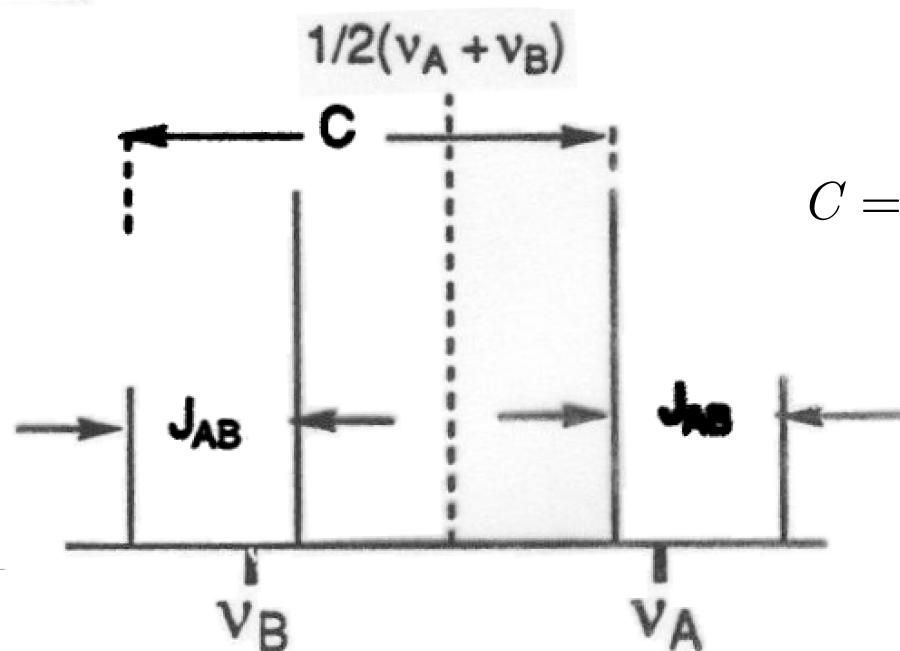
$$C = \sqrt{{\nu_B - \nu_A}^2 + J_{AB}^2}$$

- Example – using field dependence to determine

$$\Delta\nu_{AB} = 10.1ppm$$

$${}^1J_{AB} = 450Hz$$

$${}^1J_{HA} = 250Hz$$

$${}^2J_{HB} = 35Hz$$

Fig. 2-5 The 24·29 MHz ³¹P NMR spectrum of the diphosphite anion. This illustrates the *AB* part of an *ABX* spin system. The two *ab* sub-spectra are indicated.

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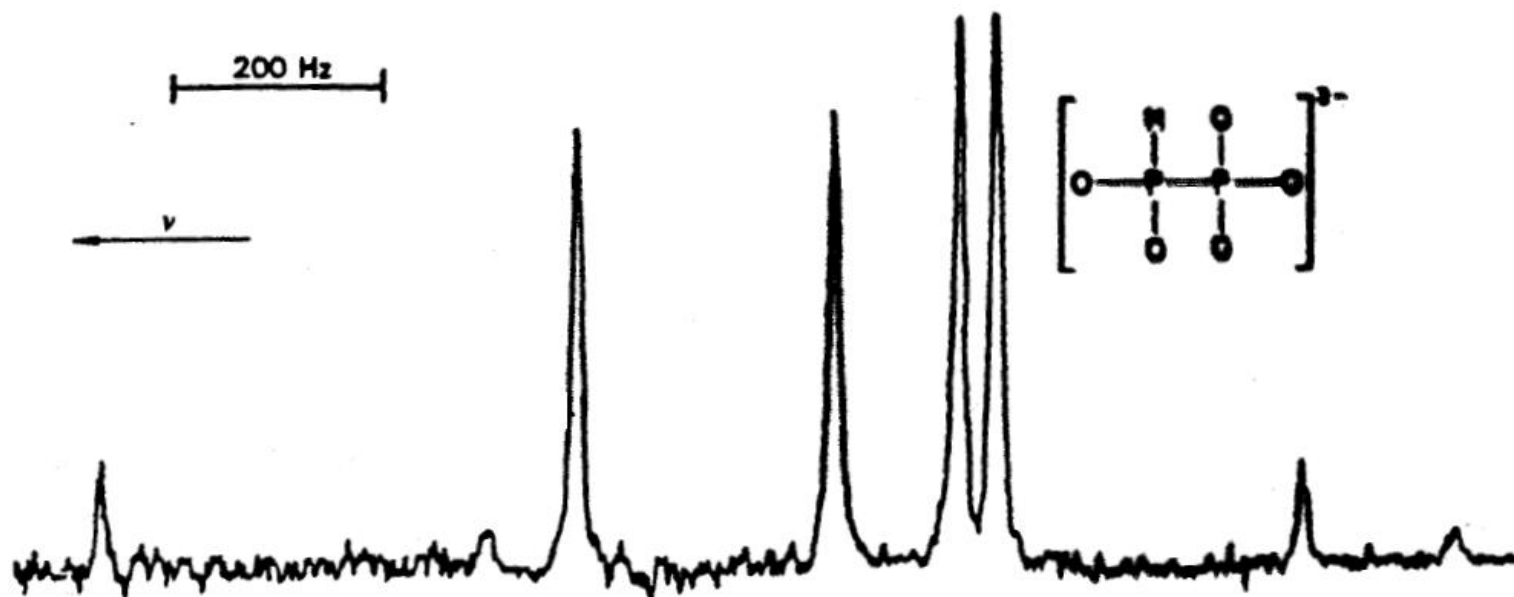
24.29 *MHz*
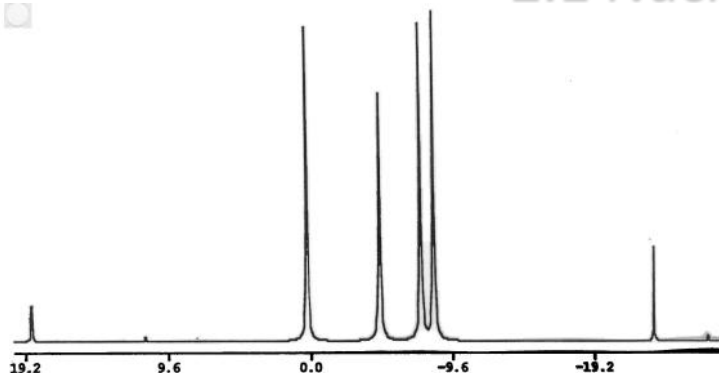
72.9 *MHz*
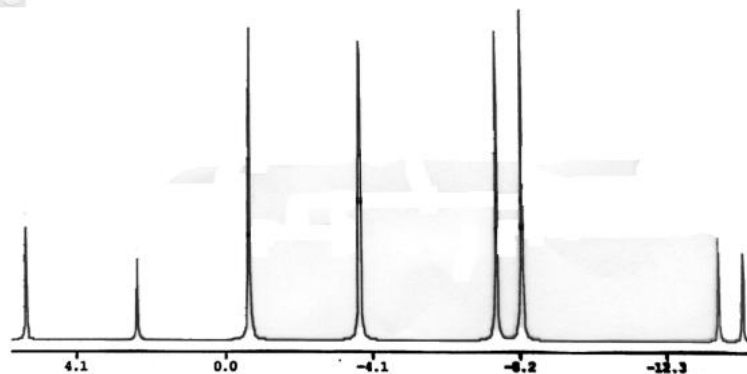
161 *MHz*

$$\Delta\nu_{AB} = 10.1 ppm$$

$$^1J_{AB} = 450 Hz$$

$$^1J_{HA} = 250 Hz$$

$$^2J_{HB} = 35 Hz$$

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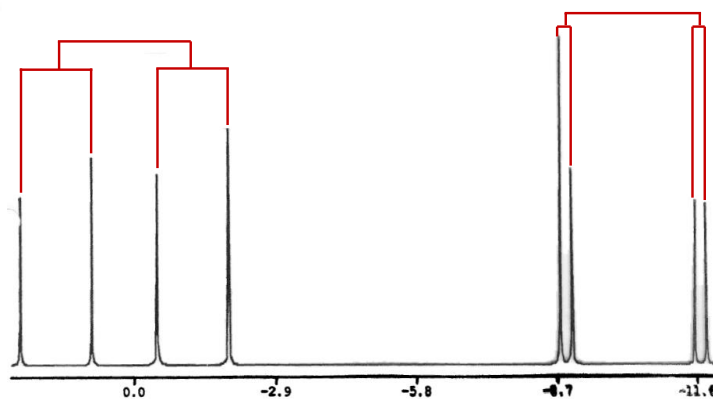
First Order and Second Order Spectra → Pople Notation

- Each independent chemical shift is designated by a capital letter
  - Choice of letter assignments depends on $\Delta\nu_{AB}$ vs. $|J_{AB}|$

- If $\Delta\nu/J$ is small → letters used to designate shifts are close: AB, ABC, …
  - This represents second order or strongly coupled systems

- If $\Delta\nu/J$ is large → letters used to designate shifts are more distant: AM, AX, …
  - This represents first order or weakly coupled systems

- *e.g.* two spins →
  - **A₂B** for strong coupling
  - **A₂X** for weak coupling

$$Y - CH_2 - HC \begin{matrix} OR \\ OR \end{matrix}$$

- *e.g.* three spins
  - **AMX** for completely weak coupling
  - **ABX** if two spins are strongly coupled
  - **ABC** if all three are strongly coupled
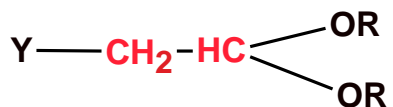
  When nuclei have identical chemical shift but different magnetic coupling, prime symbol is used:
  AA'BB' or **AA'XX'**

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A **X**

M

AA'BB'C
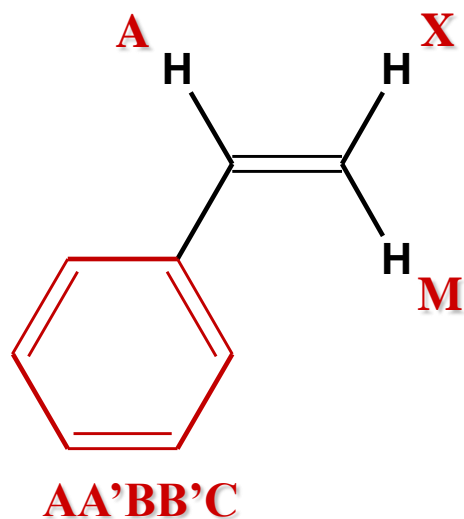
$$J_{AX} = J_{cis} = 10\ Hz$$

$$J_{AM} = J_{trans} = 17\ Hz$$

$$J_{MX} = J_{gem} = 2\ Hz$$

A : dd

M X

J_{trans} J_{cis}

HC=CH₂

1750 1740
Hz

1600 1590
Hz

7.5   7.0   6.5   6.0   5.5   5.0
ppm
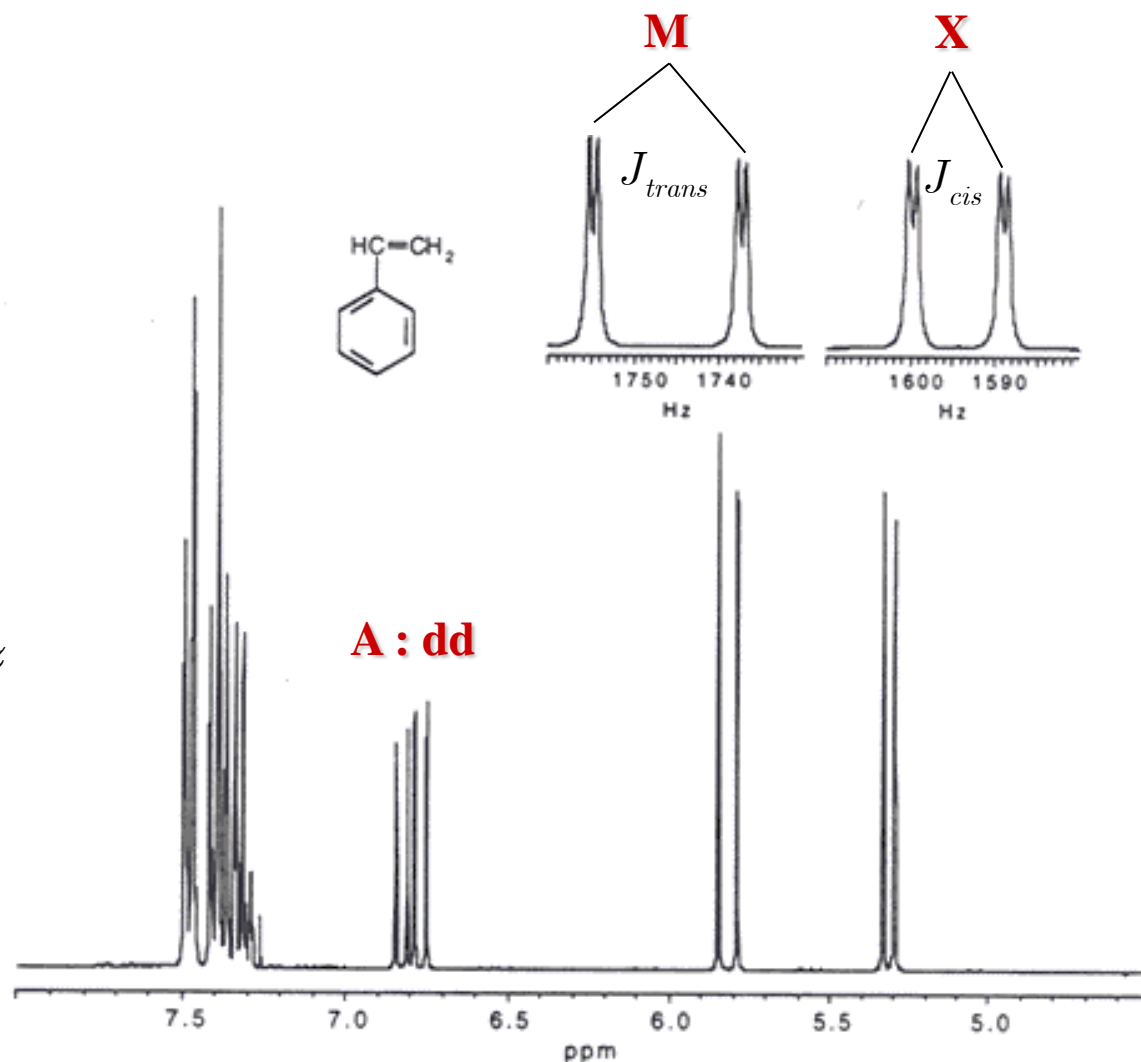
FIGURE 4.44.   Styrene in CDCl₃ at 300 MHz.

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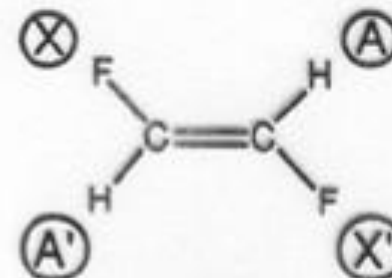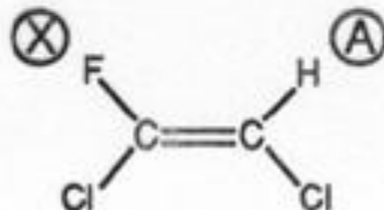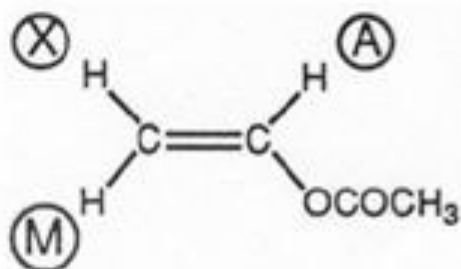
$$^3J_{A'X'} = {}^3J_{AX} \neq {}^2J_{A'X} = {}^2J_{AX'}$$

AA'XX'

[AX]$_2$
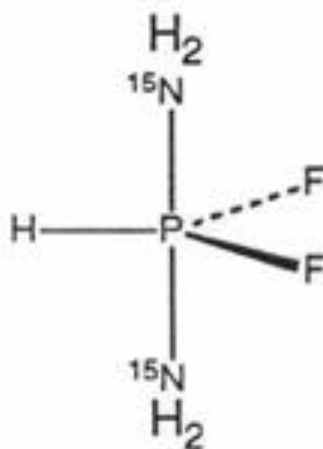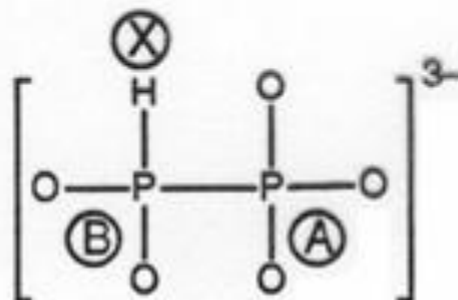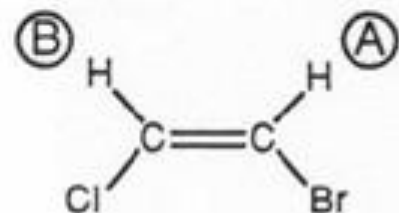
AGM$_2$Q$_2$X$_4$
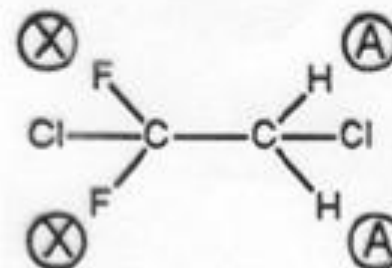
A$_2$X$_2$

Contributions to Spin-Spin Coupling

- several possible contributions to general spin-spin coupling
  - *Fermi contact (FC)* $\rightarrow$ indirect *I-I* coupling (mediated by ρ_e at nucleus)
  - diamagnetic spin-orbit (DSO) $\rightarrow$ perturbation on filled MOs caused by μ_N | scalar (*J*)
  - paramagnetic spin-orbit (PSO) $\rightarrow$ perturbation on unpaired electrons by μ_N
  - spin dipolar (SD) $\rightarrow$ direct *through-space* coupling from *dipole-dipole* interactions |
    - in solution – usually averages to zero (traceless tensor) even though it may be huge | dipolar (*D*)
    - may be observable in large systems – slow rotation, long-range packing
    - RSD (residual spin dipolar coupling) can be used to obtain structural constraints
    - magnitude of coupling can be very large – can be a significant issue in solid-state NMR
    - pronounced influence on spin relaxation $\rightarrow$ provides efficient relaxation pathways

- visualization of Fermi Contact coupling
  - through a single bond $\rightarrow$ ^1J is positive
  - through two bonds $\rightarrow$ ^2J is negative (exchange)
  - through three bonds $\rightarrow$ ^3J is positive
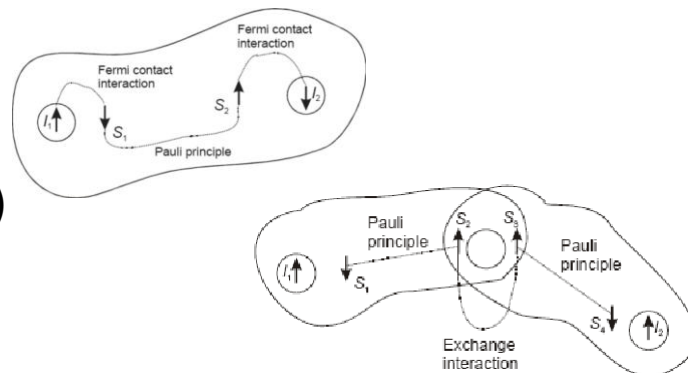
Spin-spin coupling in paramagnetic complexes

- two important contributions

  - spin-nuclear dipolar coupling $\rightarrow$ through-space coupling of nucleus with e^-

  - ***Contact shift*** $\rightarrow$ direct overlap of nuclear and electronic wavefunctions

    - In principle – coupling leads to very large J_{Ne} (in the **millions of *Hz***)

    - clearly in *strong coupling* limit such that peak intensities are not equal

    - also leads to very fast paramagnetic relaxation $\rightarrow$ very broad peaks

- Contact shift splitting collapses to intensity-weighted average ν

  - massive shift in δ_{ppm} value $\rightarrow \Delta\nu$ reflects electron spin density at nucleus
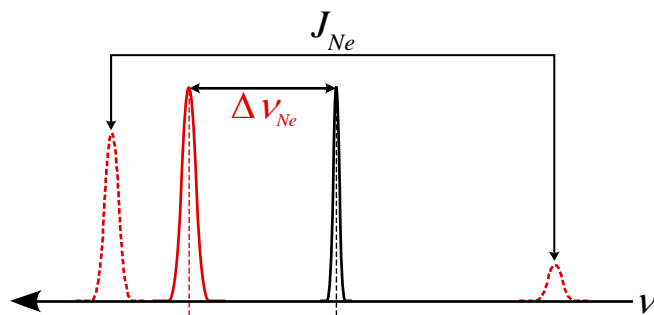
Effect of Coupling to Quadrupolar Nuclei

- Additional complication since nuclei with $I > ½$ also have an electric quadrupole moment (Q) in addition to μ.

    - induces loss of spherical symmetry at the nucleus

    - the energetic effect of Q on the nuclear wf is given by

$$E_Q = \left\langle \vec{I}_1 \middle| \hat{Q} \middle| \vec{I}_1 \right\rangle \text{ where } \hat{Q} = \frac{Q\vec{e} \cdot \vec{V}}{2I_1 \ 2I_1 + 1}$$

    - interaction depends on electric field vector (V) at the nucleus

Q > 0
Prolate

Q < 0
Oblate

- Quadrupole coupling dramatically increases relaxation rate from excited states

    - provides better relaxation pathways $\rightarrow$ broadens peaks

    - averages effect of scalar coupling $\rightarrow$ as if it doesn't exist!

- Scalar coupling is usually not observed with $I > ½$ nuclei unless...

    - very high symmetry molecule (electric field gradient = 0 at nucleus)

    - Quadrupole moment is very small $\rightarrow$ coupling to ^2H ($I = 1$) is usually observed
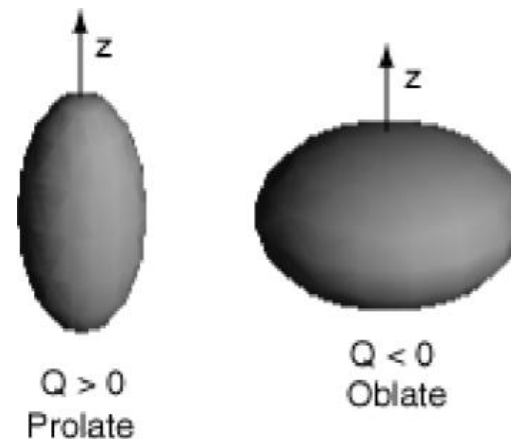
- effect of relaxation rates for quadrupolar coupling

  - if relaxation pathways are not very efficient, then scalar coupling is observed

  - however, if relaxation is fast, only average chemical shift position is observed

^{14}NH

fast

slow
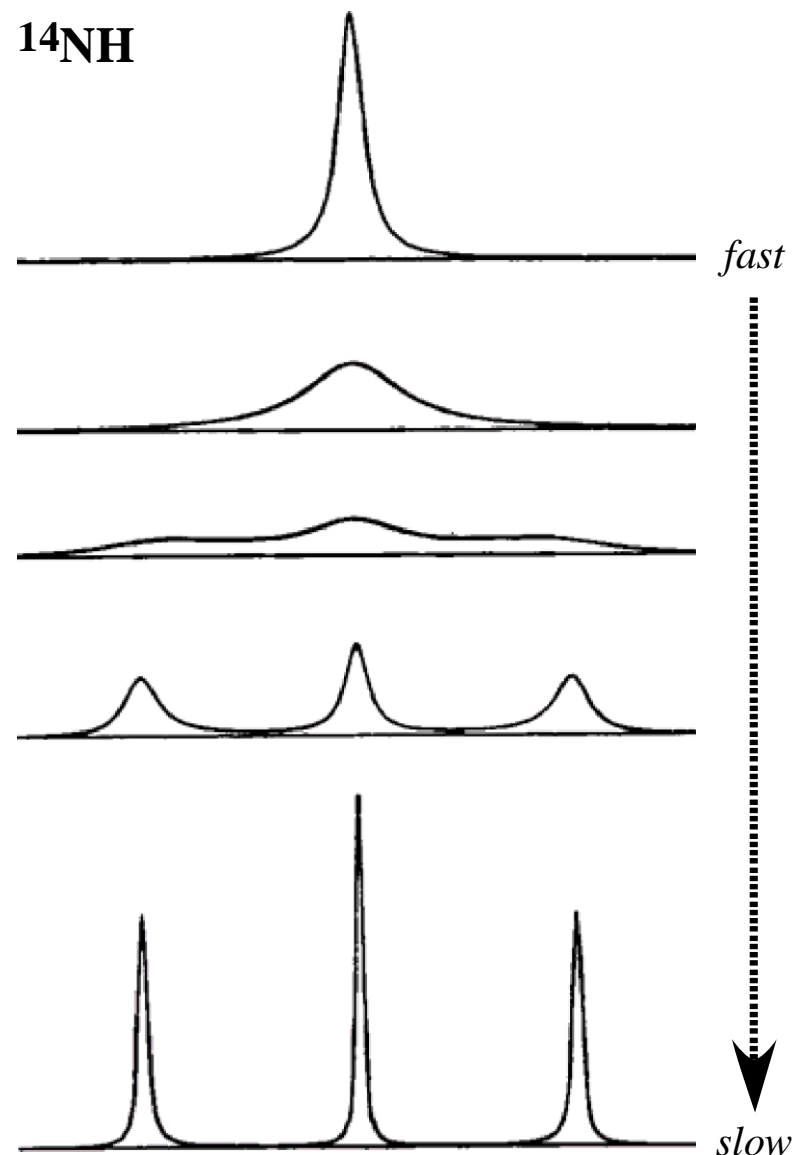
Net Magnetisation in Homogeneous Magnetic Field (B$_0$)

- Population of m_I=+1/2 is marginally greater

- All nuclei are in either of the two spin states

- Phase of spins is random…

- Overall effect is small net magnetisation (M$_0$) along z-axis of the *laboratory frame*

B_0

$m_I = +\frac{1}{2}$ $m_I = -\frac{1}{2}$

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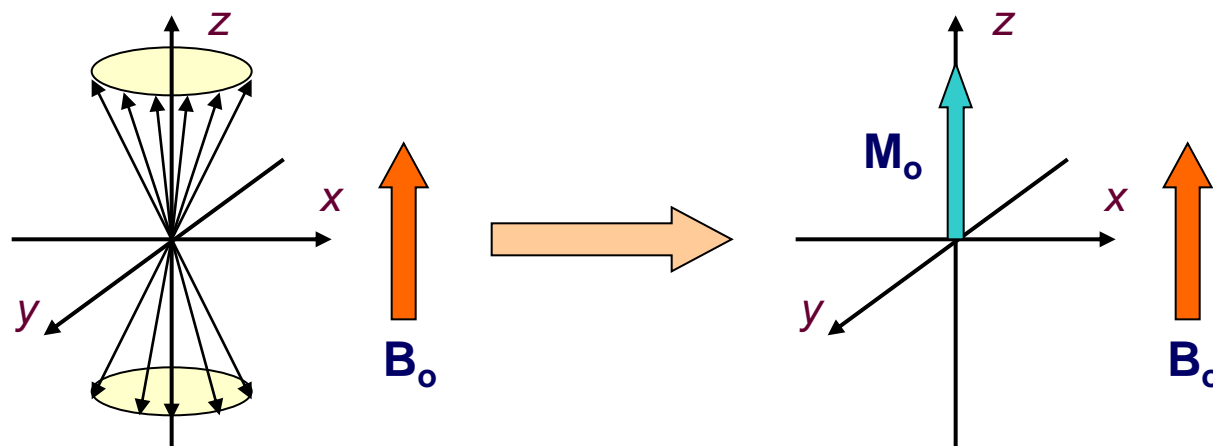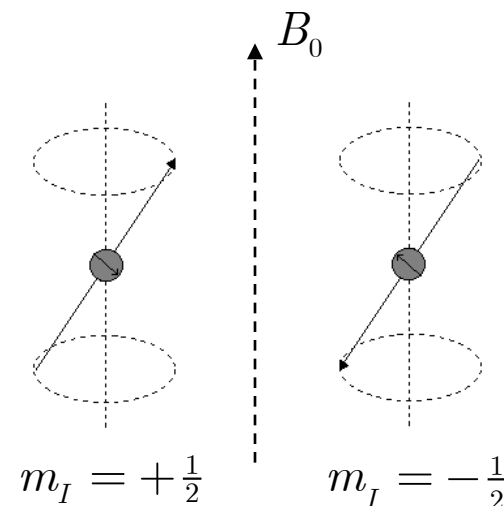
Effect of NMR Transitions on Net Magnetisation…

- Small excess of $m_I = \alpha$ nuclei are forced into $m_I = \beta$ state

- changes the net magnetisation vector…

  - *i.e.* "rotation" of M_0 by $\theta = 180º$ (π)
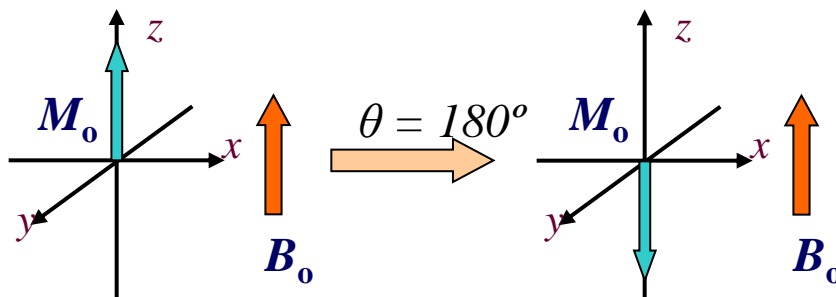
Inversion of spins

- What about 90º rotation $(\pi/2)$ of M_0?
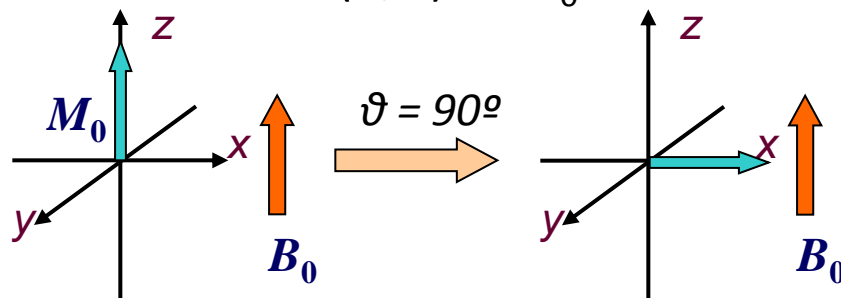
Equal population of spins

How do we perform modifications of M_0?

- apply additional magnetic field (B_1) along perpendicular axis (y)
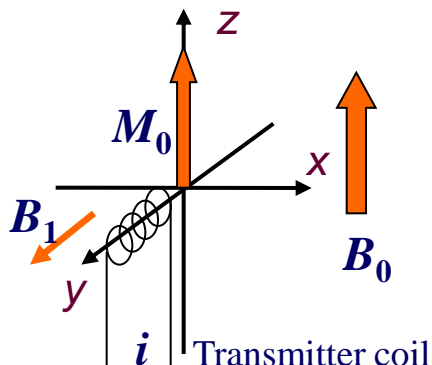
$$B_1 = C \cos \omega_0 t$$
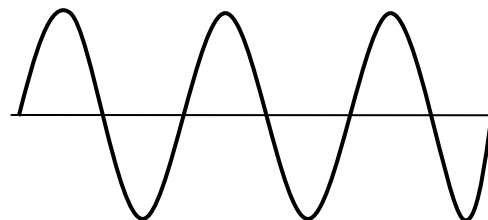
- Consider linear oscillation as sum of two circular contributions...
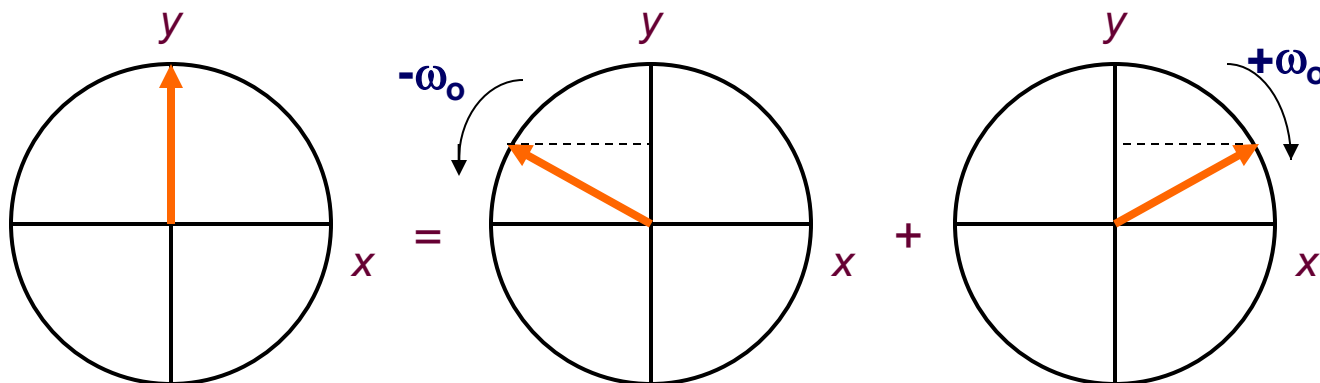
Interaction of B_1 with M_0?

- Remember that vectors composing M_0 are all precessing in the *same* direction at their *Larmor frequency* (ν_0)

$$\nu_i = \frac{\gamma}{2\pi} B_{eff}$$

- M_0 will only be affected by component of B_1 that rotates about *z*-axis in same direction as ν_0

- Resonance condition (excitation) is obtained when $\omega_0 = \nu_0$

  Important note: only those spins that are in phase with external field (B_1) will be excited…

μ

$\omega_0(B_1^+)$

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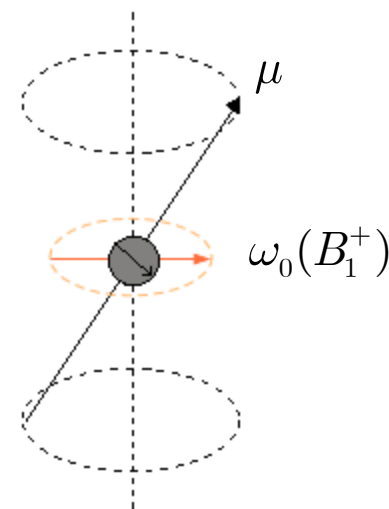
Effect of pulsed B_1 field...

- Turn on B_1 oscillating field (where $\omega_0 = \nu_0$) for period τ:
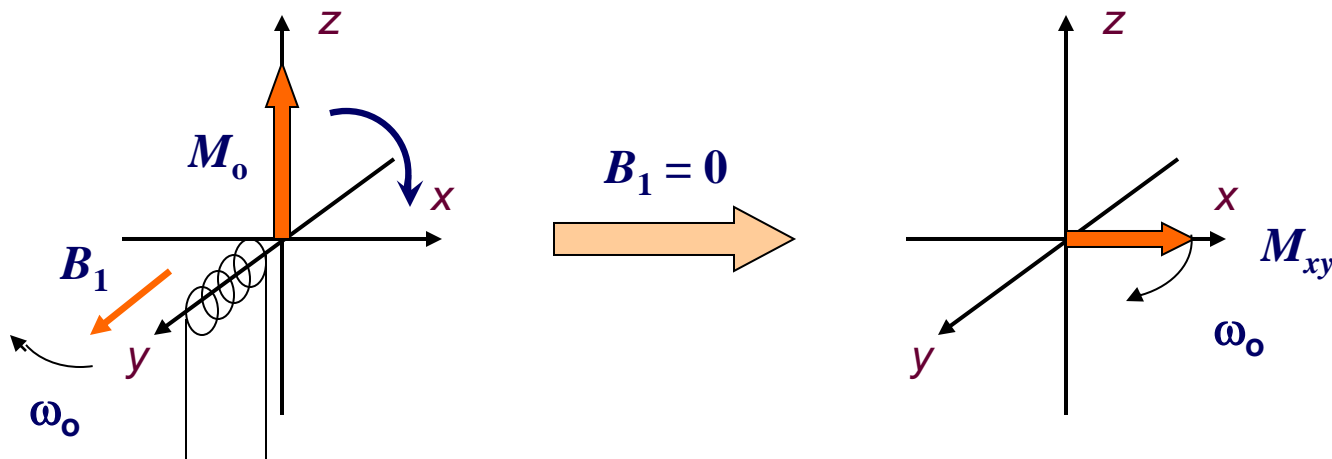
- Rotate net magnetisation into *xy* plane ($\pi/2$ pulse) due to phasing
- Change relative populations of α and β spin states
- Create excited state population – which must relax to ground state (M_0)

Remember: although individual spins are quantized, magnetisation can have many values...

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Relaxation of $M_{xy} \rightarrow M_0$

- *M_{xy}* precesses around *z*-axis

- Magnetisation returns to original orientation

- Simplify problem:

  - use **rotating frame of reference**

  - Define new coordinate system (*x'*,*y'*,*z*) that rotates around static frame of reference (laboratory frame) with angular velocity Ω

  - If $\Omega = \omega_0$ then magnetisation vector doesn't precess!

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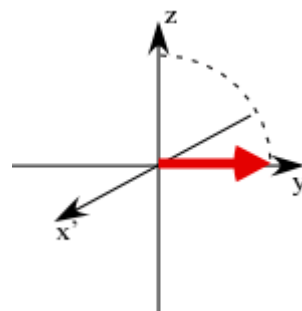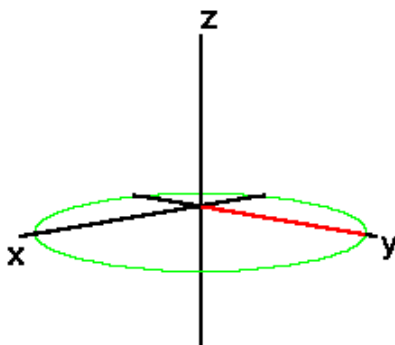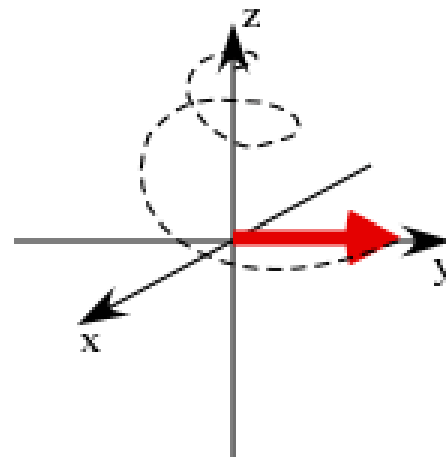
Magnetic moment as a function of time (dμ/dt)…

- In lab frame: $\dfrac{d\vec{\mu}}{dt} = \gamma\vec{\mu}\cdot\vec{B}_0$ In rotating frame: $\dfrac{d\vec{\mu}}{dt} = \gamma\vec{\mu}\cdot\vec{B}'$

$$\vec{B}' = \vec{B}_0 - \Omega/\gamma$$

  - Field looks smaller in rotating frame (precession velocity decreases)

  - Addition of B_1 field yields: $\dfrac{d\vec{\mu}}{dt} = \gamma\vec{\mu}\cdot\ \vec{B}_0 - \omega_0/\gamma + \vec{B}_1$
  - Note orientation of contributions…

$$\vec{B}' = \left.B_0 - \omega_0/\gamma\right._z + \left.B_1\right._{x'}$$

  - A strong enough RF pulse can overwhelm B_0
    - as long as it is in phase with rotating frame
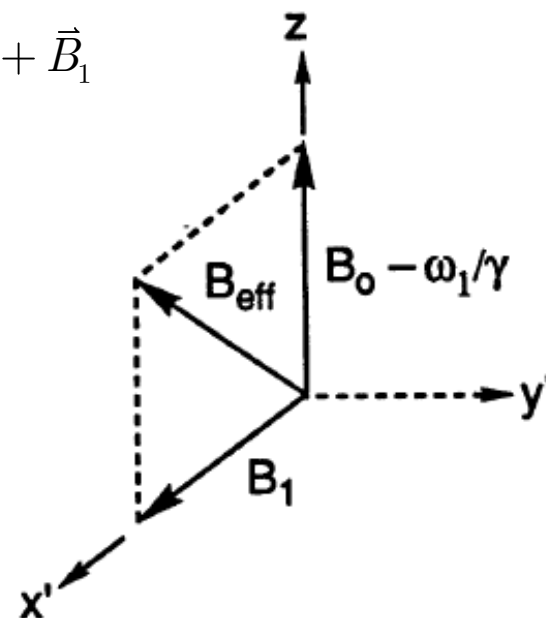
Resonance excitation using strong RF pulse: $\Omega = \omega_0 = \nu_0$

- nuclei only 'see' the applied field $B_1 \rightarrow \vec{B}' = B_0 - B_{0_z} + B_{1_{x'}} = B_{1_{x'}}$

- Pulse ($t_p \sim$ 1-50μs) rotates magnetisation vector in *y'z* plane

- Rotation angle is defined by pulse width: $\theta = \omega_0 t_p = \gamma B_1 t_p$
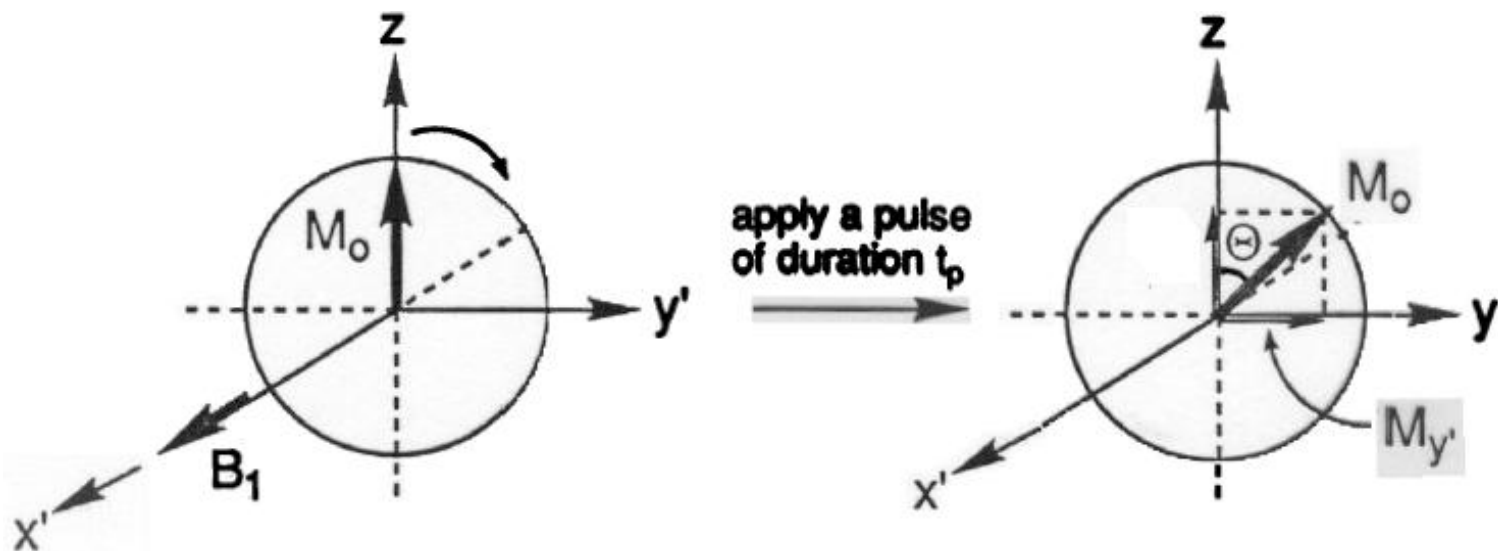
Detecting the signal…

- Put 'receiver coil' (detector) along *y'* axis

- Thus, only component of magnetisation along *y'* axis will be seen…

$$M_{y'} = M_0 \sin \; \omega_0 t_p$$

- if t_p is chosen properly, then $\theta = \pi/2$ and $M_{y'} = M_0$

- Once pulse is stopped, receiver coil is activated and the signal is seen to decay over time

$\rightarrow$ FREE INDUCTION DECAY
       (FID) of magnetic moments.

x

$\mathbf{M_{xy}}$ ω_o

y

t_p

transmitter & detector

decay in x'y' plane

detector on $\longrightarrow$

$\longrightarrow$ time
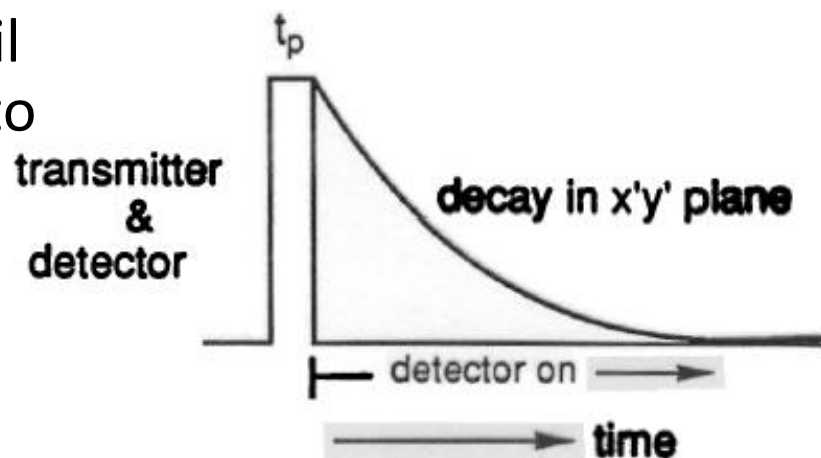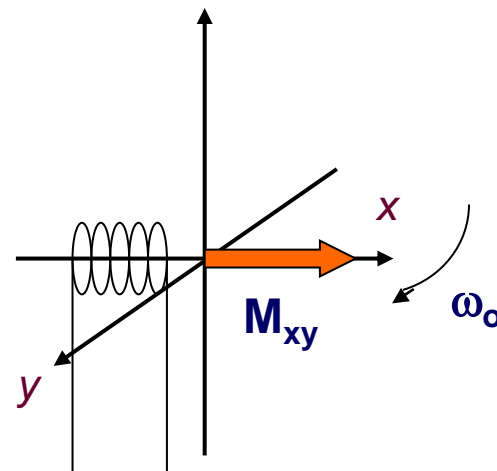
Relaxation of perturbed magnetisation vector...

- E is not easily dissipated – different from most spectroscopies

  - NMR transitions are lowest energy transitions

  - nothing else in proper energy regime

  - rotational/vibrational quenching doesn't really occur

- Relaxation times are therefore very slow ~ *seconds*
  $$\Delta E \Delta t \geq \frac{\hbar}{2}$$

  - This means that energy resolution is excellent (remember Heisenberg)
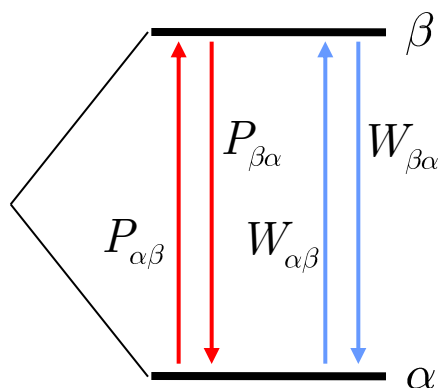
$P_{\alpha\beta}, P_{\beta\alpha}$ are induced transition probabilities

$W_{\alpha\beta}, W_{\beta\alpha}$ are relaxation probabilities

$$R_{\alpha\beta} = \left(n_\beta - n_\alpha \right) P_{\alpha\beta} \Delta E_{\alpha\beta}$$

where $R_{\alpha\beta}$ is rate of energy absorption

Transverse Relaxation → represents loss of perturbed signal

- FID of signal occurs because of _dephasing of the magnetic moments_
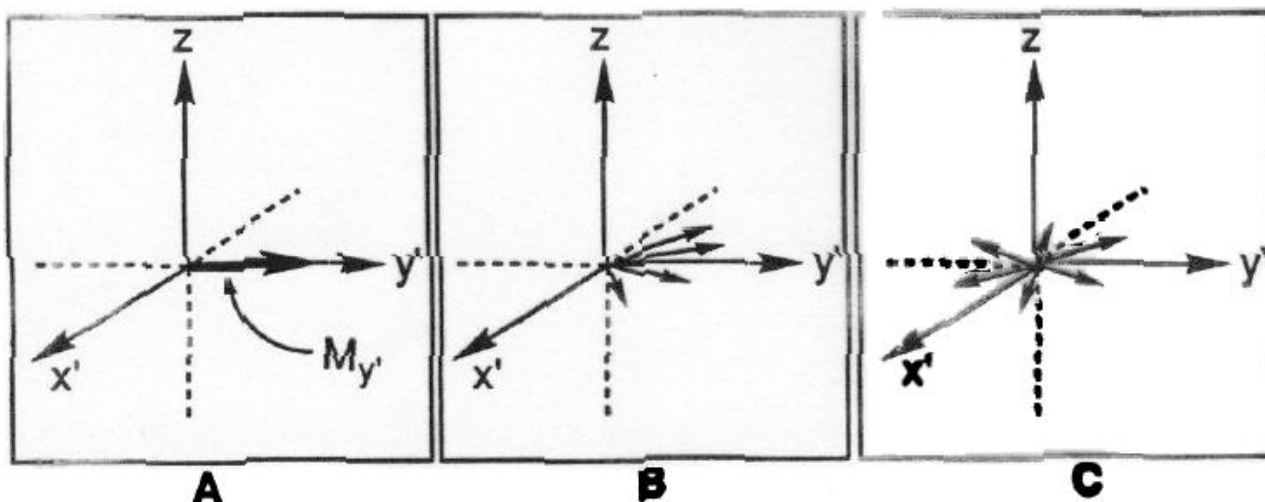
- Dephasing occurs due to
  - inhomogeneities in the magnetic field (T_{inh})
  - energy level modulations (T_2) → time-dependent changes in $\Delta E_{\alpha\beta}$ (*vide infra*)

- *transverse relaxation (continued)*

  - $\dfrac{dM_{x'}}{dt} = \dfrac{dM_{y'}}{dt} = -\dfrac{M_{y'}}{T_2^*}$ such that $M_{y'}(t) = M_{y'}(0)\exp(-t/T_2^*)$

  - Linewidths of signals depend on T_2^*: $\Delta\nu_{1/2} = \dfrac{1}{\pi T_2^*}$
    - Short lifetime = broad peak   1st order kinetic decay
    - Long lifetime = narrow peak

  - T_2^* includes *inhomogeneous field effects* and *energy level modulations*

  - $\dfrac{1}{T_2^*} = \dfrac{1}{T_2} + \dfrac{1}{T_{inh}}$

Off-resonance excitation using strong RF pulse: $\Omega = \omega_0 \neq \nu_0$

- RF pulse will still rotate magnetisation vector by angle θ

  - Changes will occur in detection… (let's assume that $\omega_0 > \nu_0$)

  - Magnetization will appear to precess about $x'y'$ plane with an angular velocity of $\Delta\nu = (\omega_0 - \nu_0)$

  - The signal will oscillate in addition to the FID behaviour: $P = \dfrac{1}{\Delta\nu} = \dfrac{1}{\omega_0 - \nu_0}$

    - Overall decay constant is still related to T_2*
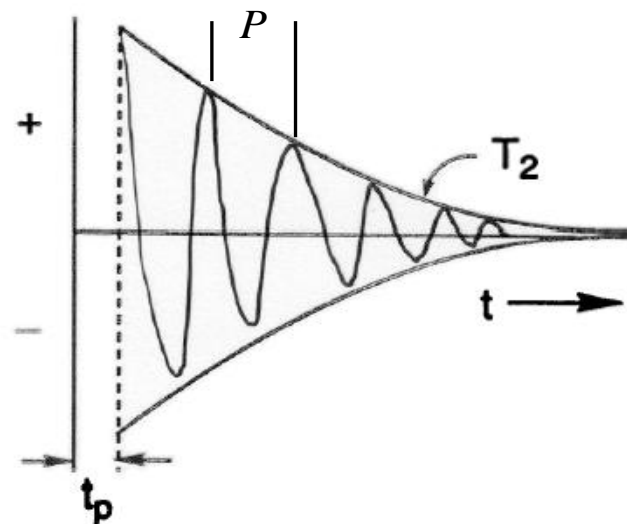
Behaviour of sinusoidal decay curve:

- $F\ t\ = M_0 \sin\theta\ \left(\cos\omega t + i\sin\omega t\right)$ **where** $\omega \propto \Delta\nu$

  $= M_0 \sin\theta\ e^{i\omega t}$

  $\theta = \omega_0 t_p = \text{tip angle}$

  $i\sin\omega t = \text{imaginary part along } x'$

- Include $T_2{}^*$ decay term: $F\ t\ = M_0 \sin\theta \int\limits_{-\infty}^{+\infty} f(\omega) e^{i\omega t} d\omega$

- Can be solved by expanding as a Fourier Series…

  - Exponential in time domain $\rightarrow$ Lorentzian in frequency domain

  - Use "fast Fourier transform" (FFT) algorithm to get real and imaginary components of spectrum

One-dimensional FT NMR Spectrum (FID Curve)

Time Domain

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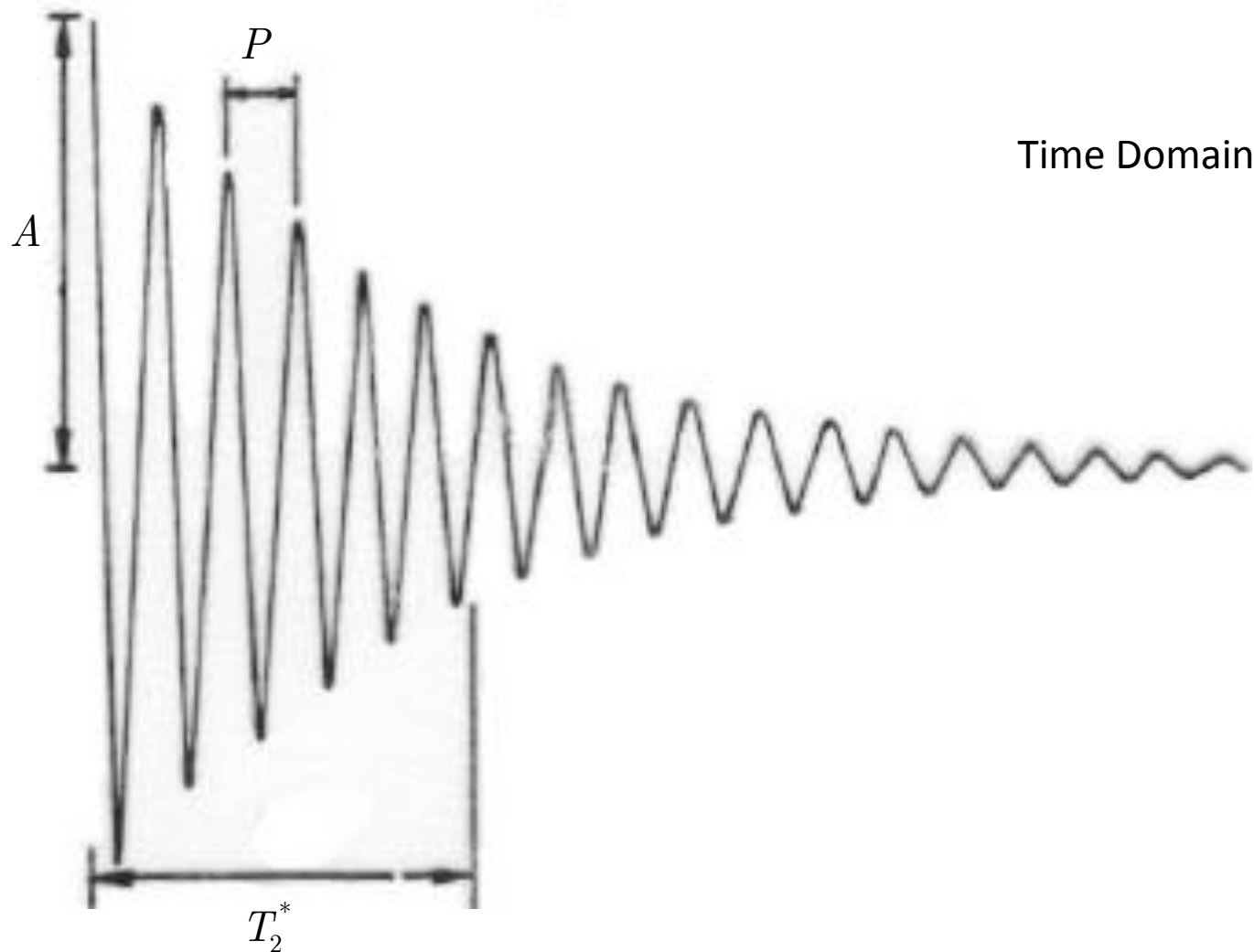
One-dimensional FT NMR Spectrum (Real Spectrum)

Frequency Domain

$\propto A\pi T_2^{*}$

$1/\pi T_2^{*}$

$1/P = \Delta\nu$

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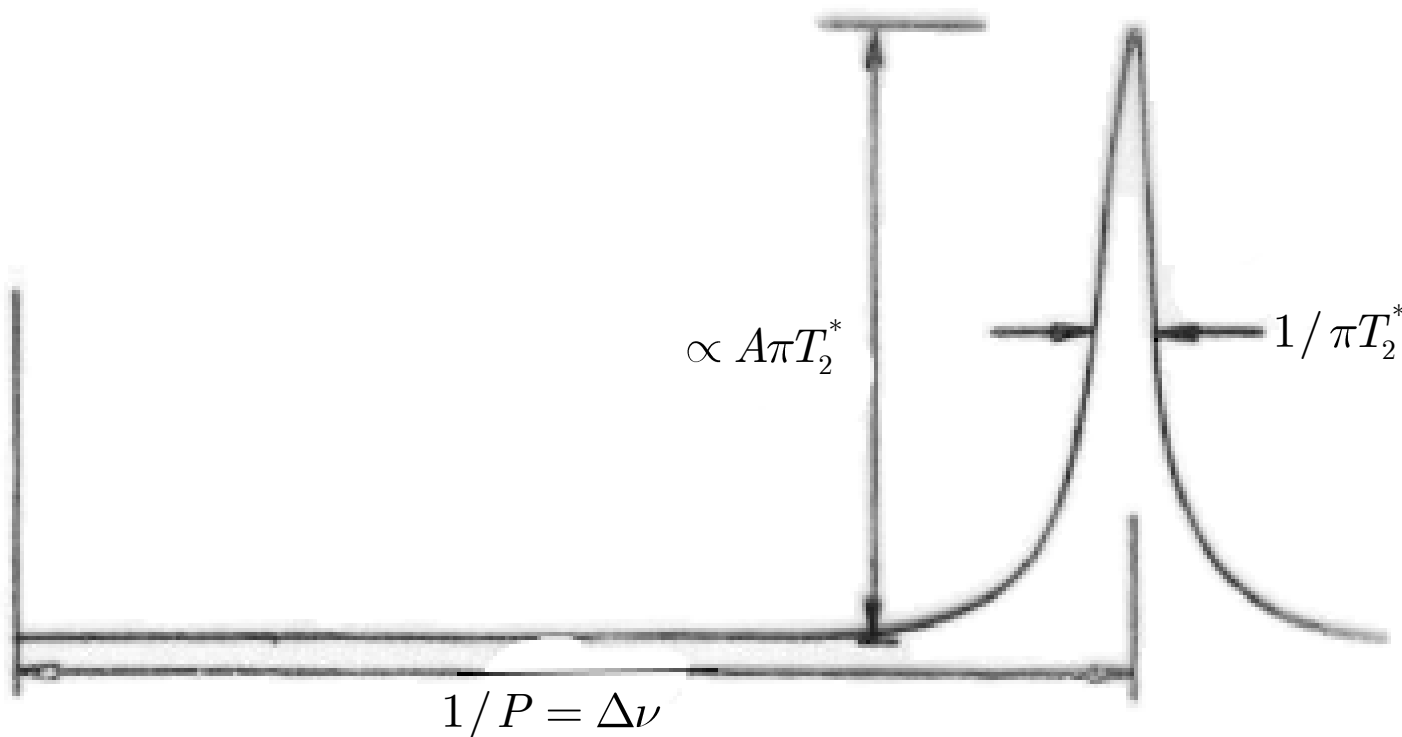
How does magnetisation relax back to ground state?

- earlier picture of relaxation assumes that all relaxation occurs at same rate:

- However, there are two types of relaxation:

  - Transverse relaxation (T_2*) $\rightarrow$ along *xy*

    - Field inhomogeneity (T_{inh})

    - Time-dependent energy level shifts (T_2)

  - Longitudinal (Spin-Lattice) relaxation (T_1) $\rightarrow$ along *z*

    - *True* relaxation through spin-flip transitions towards ground state magnetisation
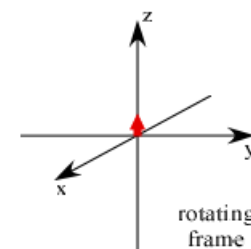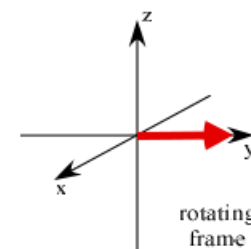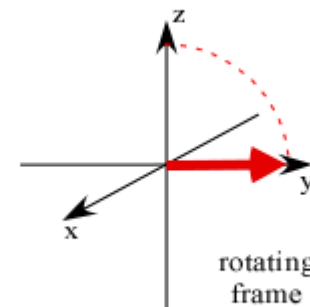
Bloch Equations – Description of Exponential decay to M_0

- Equations to describe relaxation of nuclear spins

- Two basic assumptions:
  - decay process is exponential
  - longitudinal (T_1) and transverse (T_2*) decay constants are different

- Transverse decay: $\dfrac{dM_{x'}}{dt} = -\dfrac{M_{x'}}{T_2^*}$ $\dfrac{dM_{y'}}{dt} = -\dfrac{M_{y'}}{T_2^*}$

- Longitudinal decay: $\dfrac{dM_z}{dt} = -\dfrac{M_z - M_0}{T_1}$

- Equations yield first-order differential rate equations…
  - *e.g.* $\ln\left(\dfrac{M_0 - M_z}{2M_0}\right) = -\dfrac{t}{T_1}$ for inversion-recovery: $M_z = -M_0 \ at \ t = 0$

    can get T_1 from this…

Origins of T_1 Relaxation Processes

- Dipole-dipole interactions (DD)
  - interactions with other spin active nuclei while tumbling in solution
- Shielding anisotropy (SA)
  - Molecular motion (translation) modulates local magnetic fields (in large B_0)
- Spin-Rotation interactions (SR)
  - Coupling with rotational motion (for equivalent nuclei, *e.g.* $-CF_3$)
- Scalar Coupling interactions (SC)
  - Time-dependent coupling with other nuclear spins
- Unpaired electron interactions (UE)
  - Interaction with electron spin (remember that μ_B is huge!)
- Quadrupolar interactions (Q)
  - Additional contributions to DD interactions for nuclei with $I > \frac{1}{2}$

- $$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{SA}} + \frac{1}{T_1^{SR}} + \frac{1}{T_1^{SC}} + \frac{1}{T_1^{UE}} + \frac{1}{T_1^{Q}}$$

Origins of T_2 Relaxation Processes

- List of contributors is similar to T_1 contributions…

- Magnitude of T_2 directly reflected by peak width in spectra

- not as dependent on B_0

- For more details, see:

  - Sudmeier, J.L.; Anderson, S.L.; Frye J.S.
    Concepts in Magnetic Resonance, **1990**, *2*, 197-212.

Relative values of T_1 and T_2?

- *General rule: $T_1 > T_2$*

- *why? dephasing must be complete before achieving equilibrium!*

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Standard One-Dimensional NMR Experiments

- **D1** must be long enough for system to completely relax back to ground state

  - $5T_1$ is usually reasonable

  - often times, much shorter D1 are used…

interpulse delay(D1)   pulse(P1)

acquisition time (AQ)

dead time (DE)

- duration of pulse used for RF excitation (**P1**)

- short dead time (**DE**) is needed to minimise electronic noise in the data

  - due to the RF coils – they don't turn off instantaneously

- acquisition time (**AQ**) must be long enough to obtain good statistics for FFT procedure

- *one of the biggest questions: how long should P1 be?*
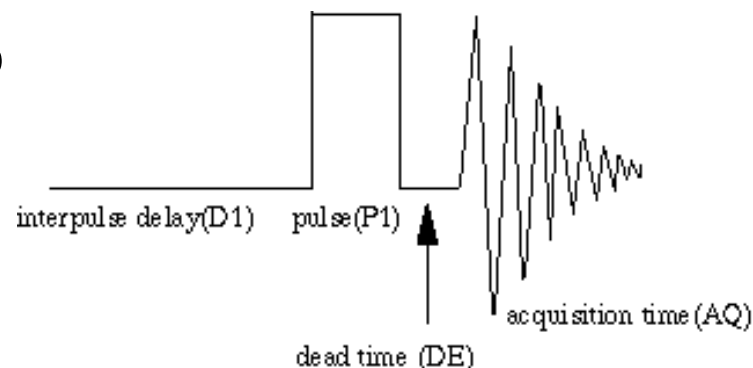
Effect of Pulse Width (t$_p$, P1) on 1D NMR Spectrum

- Spectra of ethyl benzene using single pulse experiments with differing **P1** values →

  - $\pi/2$ pulse gives best signal/noise but relaxation time is very long

  - $\pi/3$ and $\pi/6$ pulses give good data with shorter relaxation times

  - $\pi/18$ pulse gives poor signal/noise

- using a $\pi/2$ pulse gives best data per scan but at the expense of the number of scans…

  - intermediate pulse widths are often more efficient
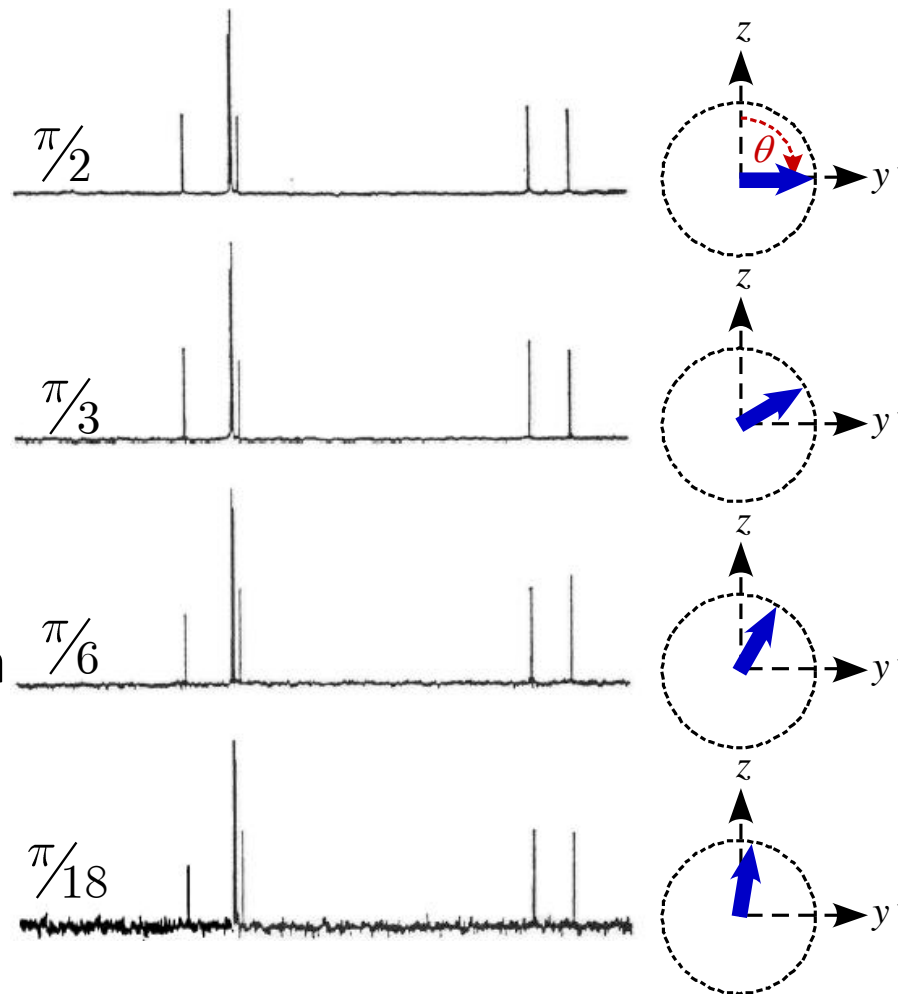
Decoupling Experiments

- In many cases, it is useful to somehow 'turn off' scalar coupling

- Two general approaches -

  - Broadband: remove all coupling to other nuclei (*e.g.* ^{1}H decoupling)

  - Selective: decouple only specific nuclei

- Basic strategy –

  - third magnetic field (B_2) causes *powerful* and *continuous* RF excitation of nuclei

  - cause rapid excitation/de-excitation of spins $\rightarrow$ rapid stimulated relaxation

  - effect on other nuclei is that the decoupled nuclei are effectively "invisible"

  - Nuclei are thus decoupled

- Additional effects –

  - in some cases (with positive NOE effect, *vide infra*), NMR signal is enhanced due to decoupling

    - e,g, ^{1}H decoupled ^{13}C NMR is significantly more sensitive

Example of ^{1}H broadband decoupling

$[P(OCH_3)_3]$
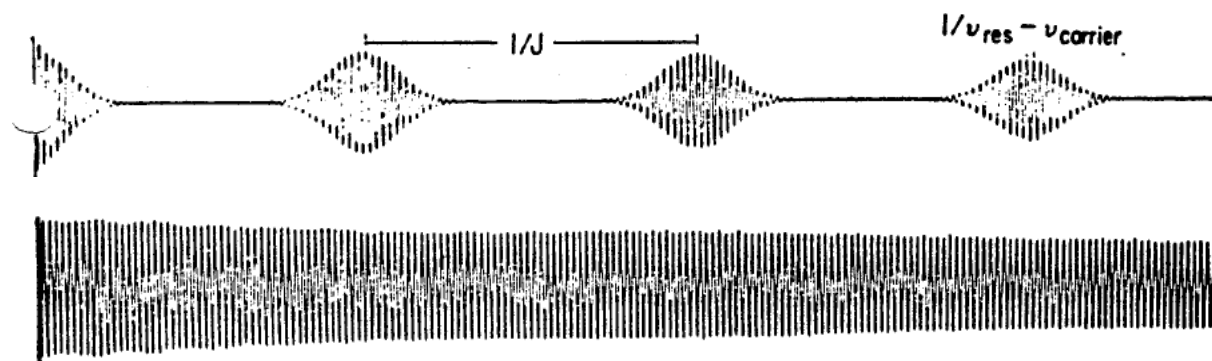
with ^{1}H coupling
(no decoupling)

without ^{1}H coupling
(with decoupling)

The Nuclear Overhauser Effect (NOE)

- from dipole-dipole relaxation between two nuclei

  - *Spin Dipolar Relaxation, D*

  - do not need scalar coupling! (J_{12} can be equal to zero)

- transition intensities depend on population differences

- Look at two $I = \frac{1}{2}$

  - Equilibration of I_2 affects populations of I_1!

  - relaxation pathways for I_2 involve I_1…

$-\frac{1}{2}, -\frac{1}{2}$

$-\frac{1}{2}, +\frac{1}{2}$

$+\frac{1}{2}, -\frac{1}{2}$

$+\frac{1}{2}, +\frac{1}{2}$

equilibrate populations

population distribution
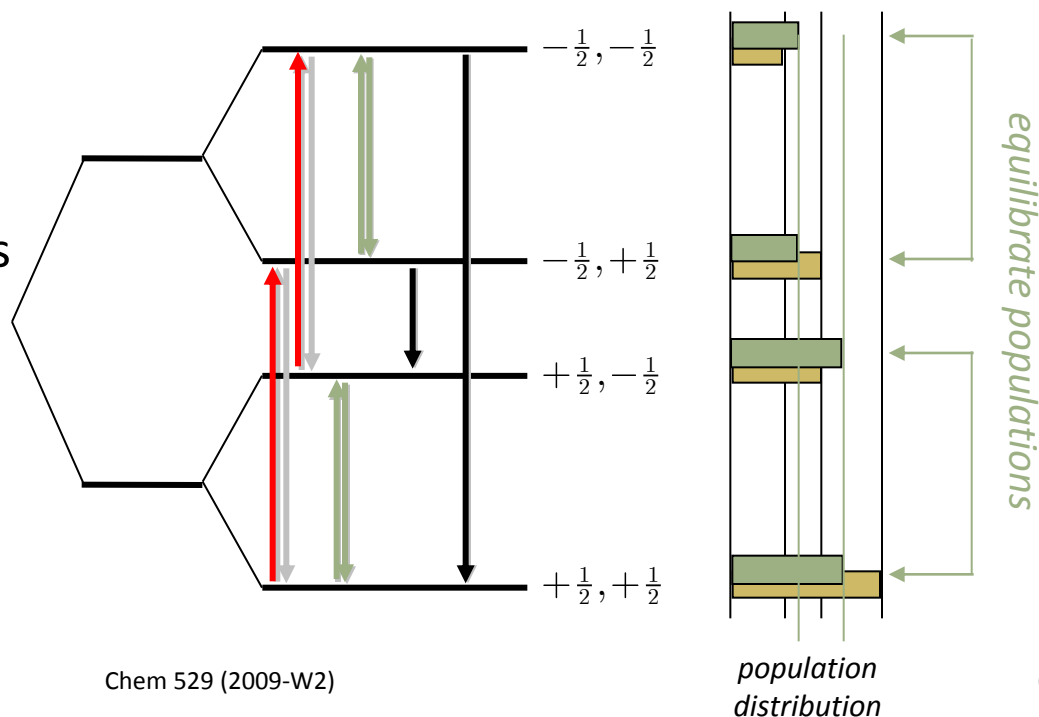
The Nuclear Overhauser Effect (NOE) – Bloch Equations

- most important thing that happens is change in relaxation rates for both of the resultant states of the I_1 nuclear transitions.

- *e.g.* consider the effect of saturating the ^1H signal (using B_2) during a ^{13}C experiment

$$\frac{dM_z(H)}{dt} = -\frac{M_z(H) - M_0(H)}{T_{1(HH)}} - \frac{M_z(C) - M_0(C)}{T_{1(CH)}} \left.\right\|$$
$$\frac{dM_z(C)}{dt} = -\frac{M_z(C) - M_0(C)}{T_{1(CC)}} - \frac{M_z(H) - M_0(H)}{T_{1(CH)}} \left.\right\|$$

under standard conditions

$$\frac{dM_z(H)}{dt} = -\frac{0 - M_0(H)}{T_{1(HH)}} - \frac{M_z(C) - M_0(C)}{T_{1(CH)}} \left.\right\|$$
$$\frac{dM_z(C)}{dt} = -\frac{M_z(C) - M_0(C)}{T_{1(CC)}} - \frac{0 - M_0(H)}{T_{1(CH)}} \left.\right\|$$

with ^1H saturation $\rightarrow M_z(H) = 0$

- let system equilibrate to $\dfrac{dM_z(C)}{dt} = 0$

$$\frac{dM_z(C)}{dt} = -\frac{M_z(C) - M_0(C)}{T_{1(CC)}} + \frac{M_0(H)}{T_{1(CH)}} = 0 \qquad \frac{M_0(H)}{T_{1(CH)}} = \frac{M_z(C) - M_0(C)}{T_{1(CC)}}$$

$$\boxed{M_z(C) = M_0(C) + \frac{M_0(H)T_{1(CC)}}{T_{1(CH)}}}$$

- ^{13}C signal depends on initial magnetization of ^{1}H vectors
- ^{13}C signal depends on ratio of CC and CH relaxation rates

- relaxation rates are dependent on $\gamma_{I_1}\gamma_{I_2}$ $\rightarrow$ NOE $\propto \dfrac{\gamma_C\gamma_C}{\gamma_C\gamma_H} = \dfrac{\gamma_C}{\gamma_H}$ or more generally $\dfrac{\gamma_{I_1}}{\gamma_{I_2}}$
- since dipolar coupling is major contributor…
    - NOE also depends on rotational correlation time (τ_c) $\rightarrow$ relative orientations vs. B_{eff}
        - For molecules rotating quickly $\rightarrow$ *positive* NOE enhancement
        - For molecules rotating slowly $\rightarrow$*negative* NOE enhancement
    - *through-space* dipole-dipole interactions drop off as $1/r^6$
        - Only close contacts (< 5Å) will be observable (useful way to get structural information)

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- Can do either 1D NOE experiments or 2D NOESY/ROESY

- 1D NOE experiments are basically decoupling experiments!!!
    - ^{1}H decoupled ^{13}C NMR is far more sensitive than normal ^{13}C due to NOE

    $$\gamma_{^1\mathrm{H}}/\gamma_{^{13}\mathrm{C}} \approx 4$$

    - Selective 1D NOE can be used to specifically evaluate dipolar coupling...
        - Defocus a particular nucleus (specific B_2 pulse)
        - Evaluate effect on intensity of all other peaks
        - Any enhancements due to NOE indicate dipolar interactions (close proximity)

Measurement of T₁ by the Inversion Recovery Method

$$\ln\left(\frac{M_0 - M_z}{2M_0}\right) = -\frac{t}{T_1} \qquad \frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

• Pulse sequence:

T_1
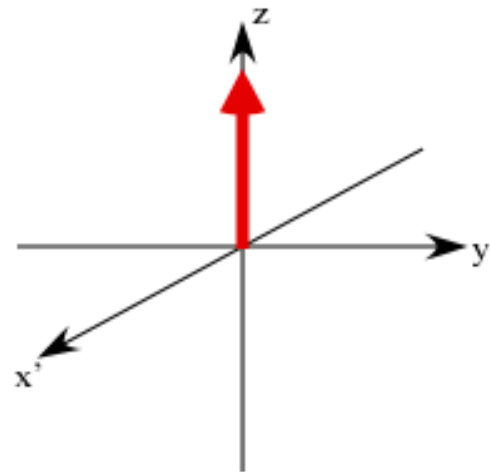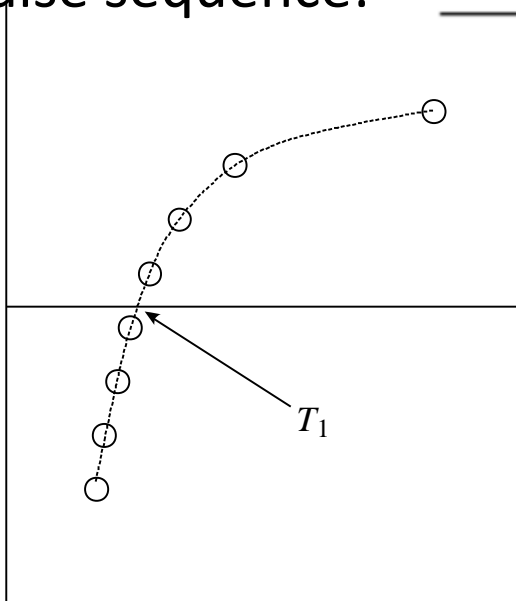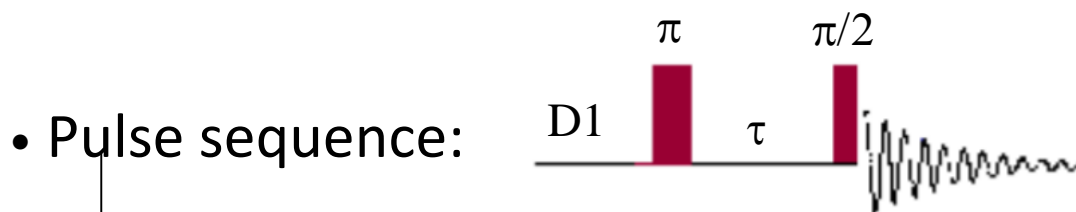
Measurement of T$_1$ by the Inversion Recovery Method
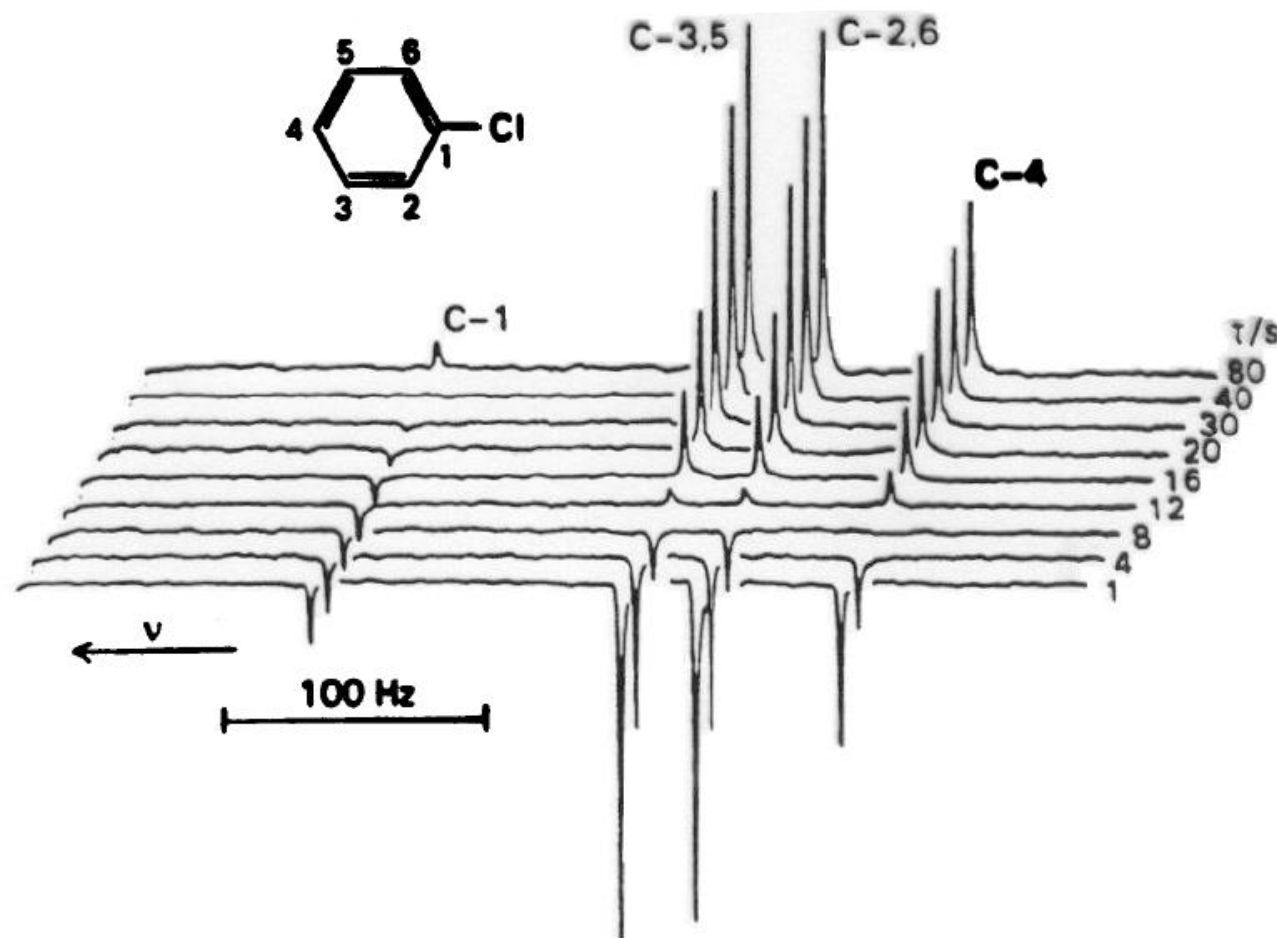
Measurement of T_2 by Spin-Echo Pulse Sequence
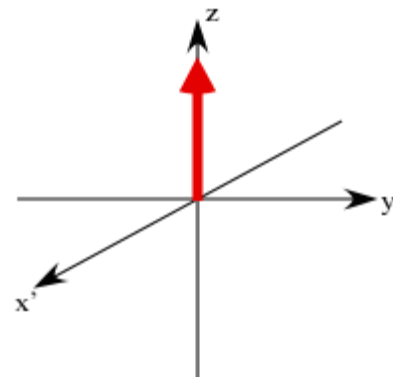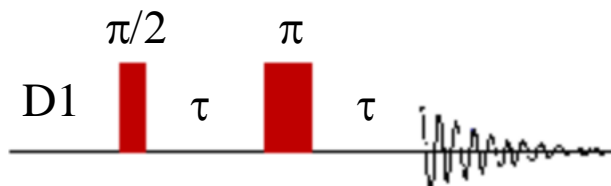
- M_y after spin echo < M_y before…

- Change delay time (τ)

- Decay of M_y signal with respect to $\tau \rightarrow T_2$

  - T_{inh} is removed due to refocusing effect of spin echo pulse
  - Direct measure of T_2 (and not T_2*)
  - Removes T_{inh} contribution to peak width as well!
  - Removes phase shift problem? (not really)

Effect of J-coupling during Spin Echo Experiment

- Remember: *chemical shift* position (ν_0) will refocus after (2τ)

  - But *J*-coupling affects precession, and therefore affects dephasing during τ time period… $\quad \theta = J_{12}\pi\tau$

  - The influence of *J* also depends on the spin state of the nucleus 2…

    - Direction of rotation depends on I_2

    - At $\tau=1/(2J)$, the terms cancel… (can be used to get *J*)

    - If we use decoupling, then *J*-coupling information is lost (converts doublet to singlet)
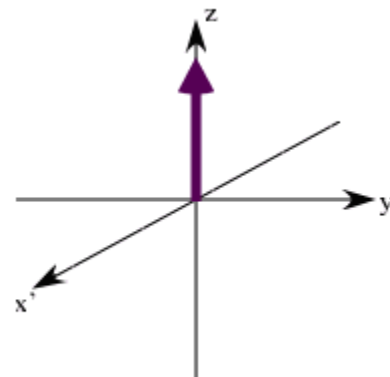
Correlation Spectroscopy (COSY)

- Use two dimensions to determine relationship between peaks…

- If homonuclear I_1 and I_2 are scalar coupled then cross-peaks will occur from the following pulse sequence… (*how*?)
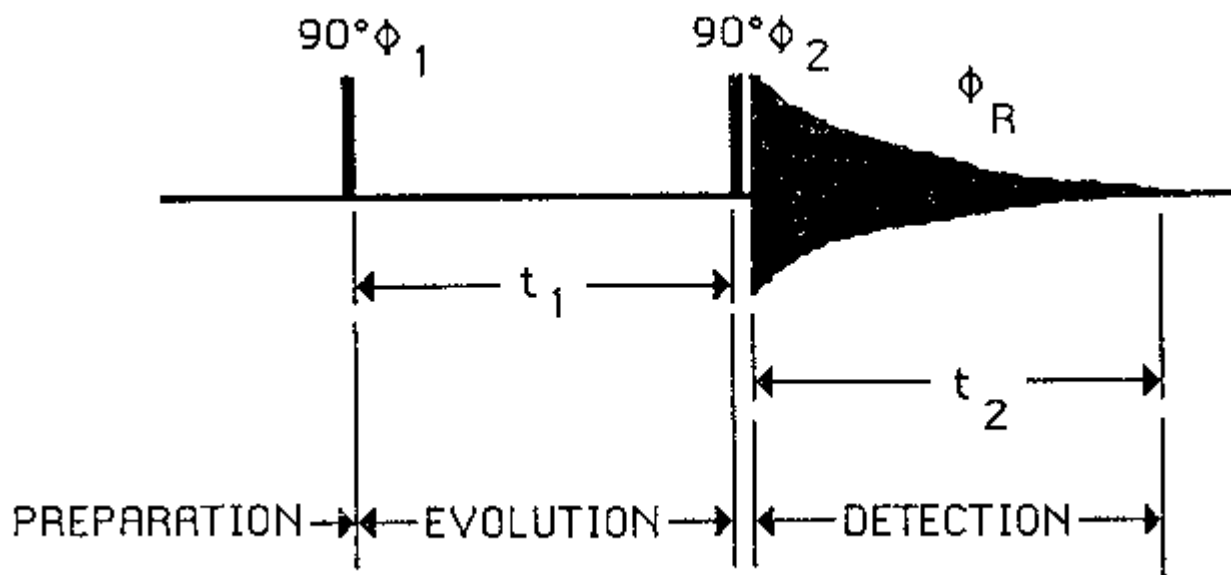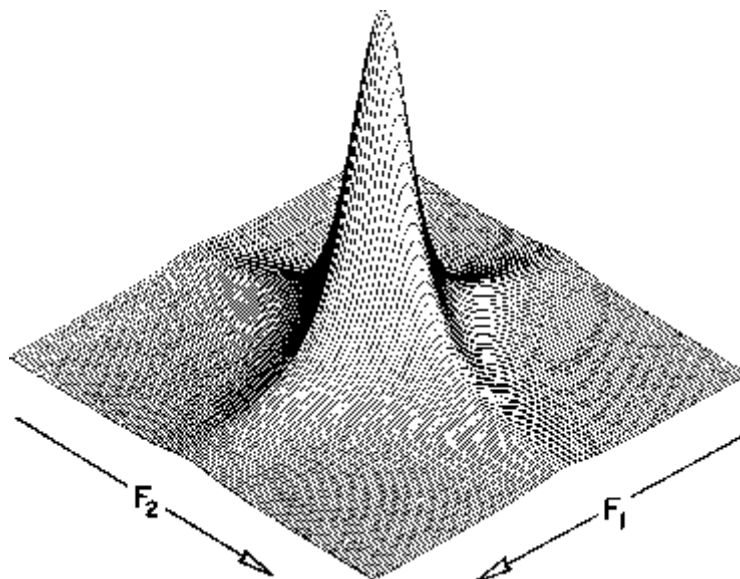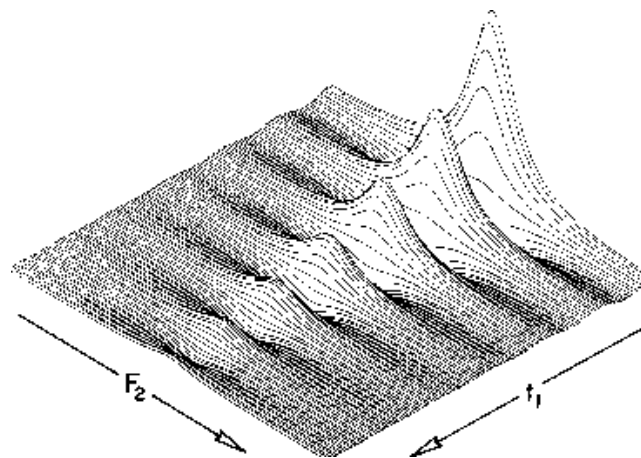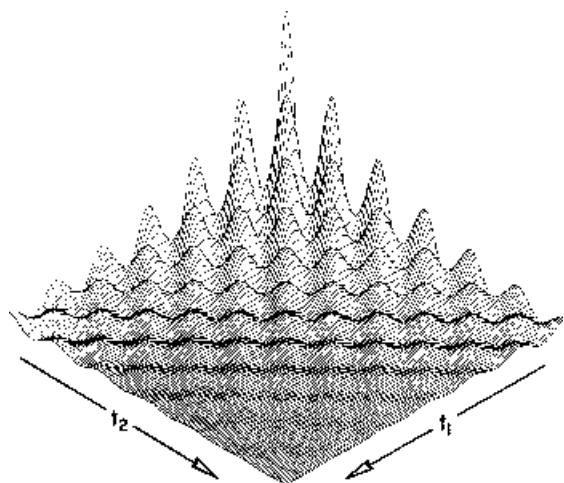
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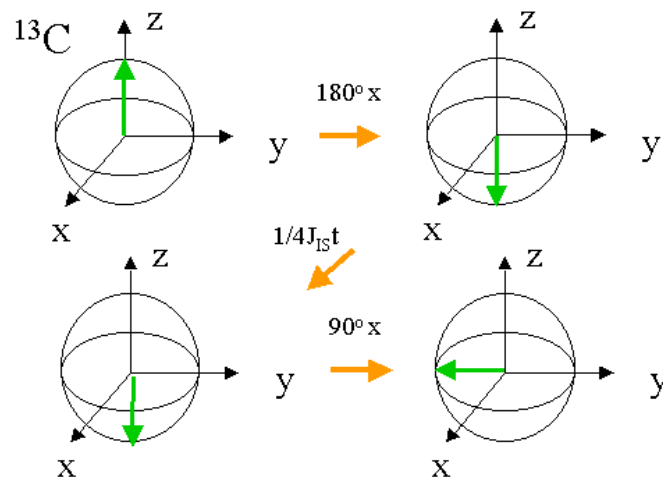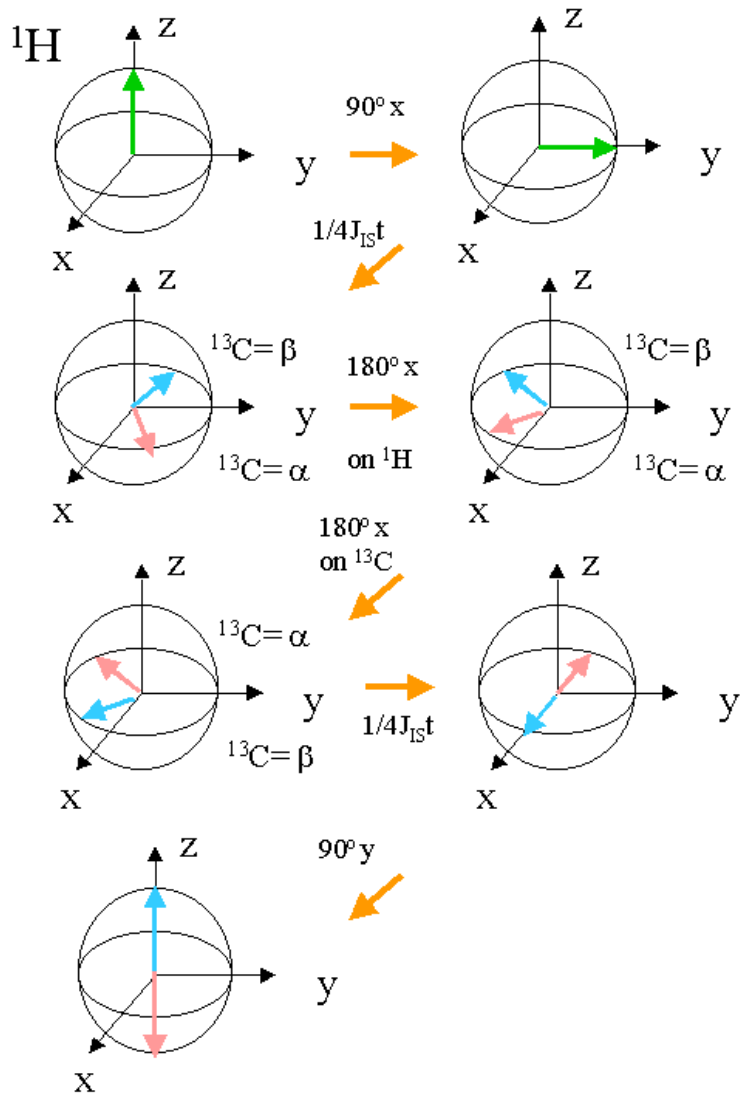Department of Chemistry

COSY of menthol

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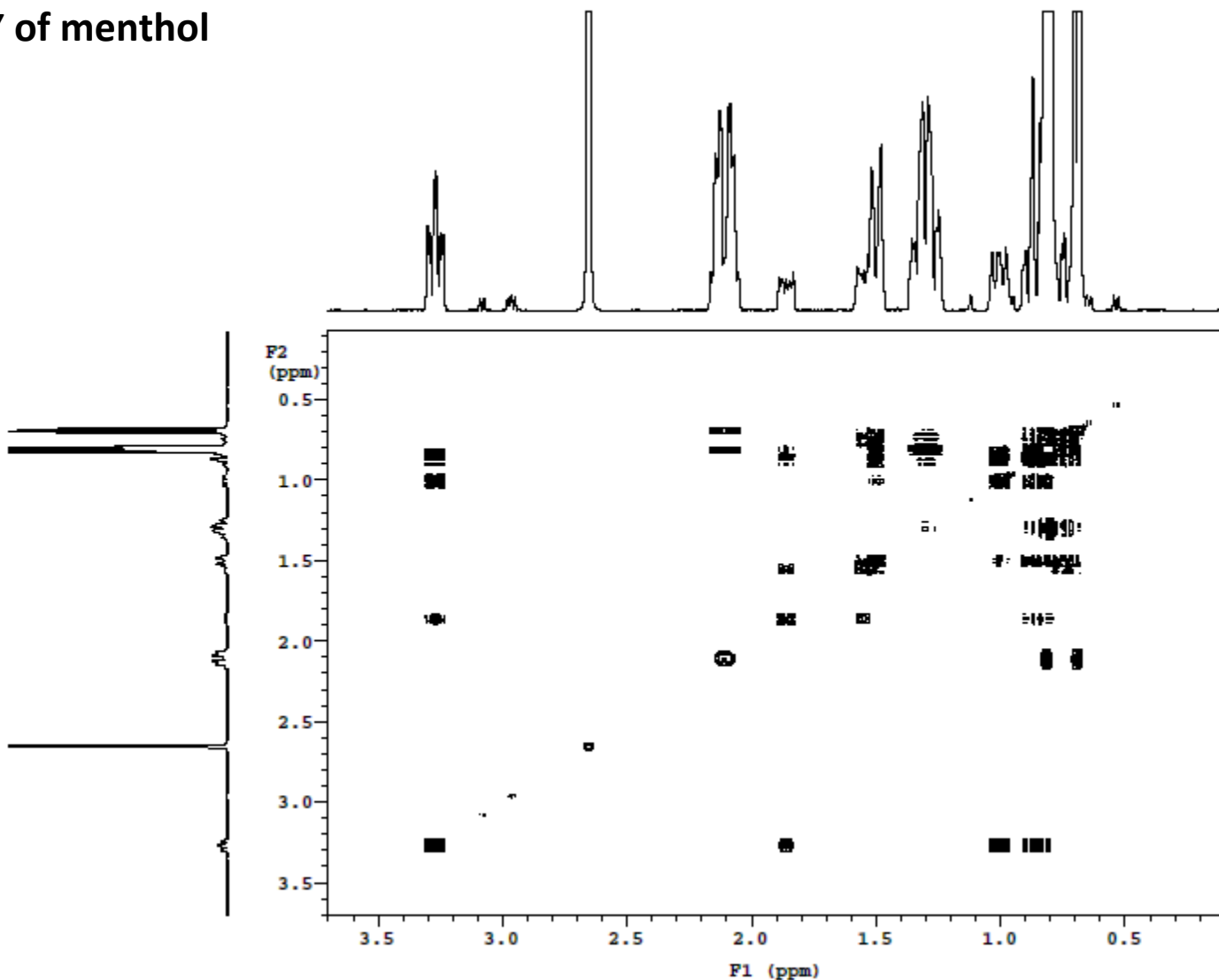
Insensitive Nuclei Enhanced by Polarization Transfer (INEPT)
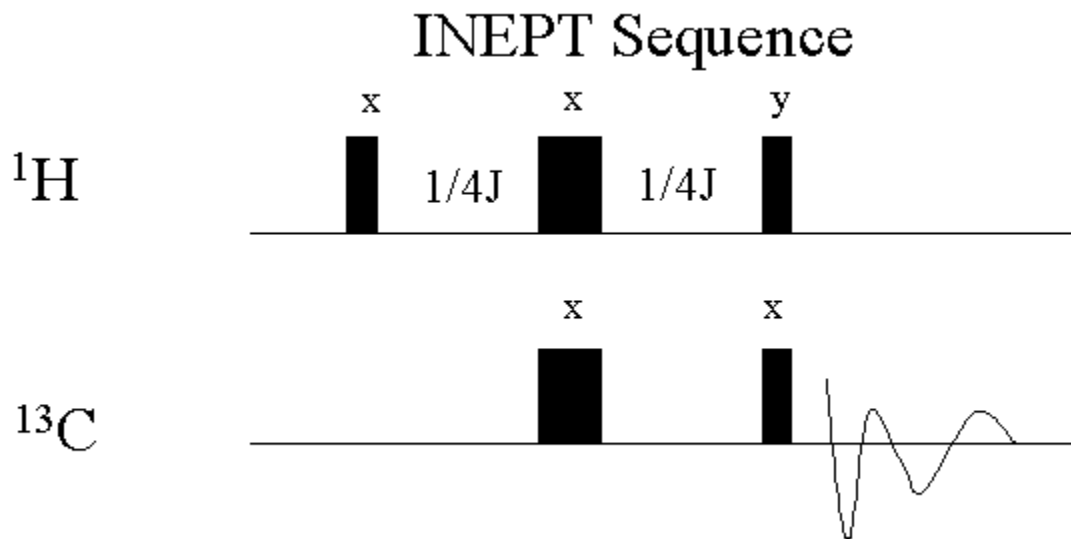
- Effect of pulse sequence is to dramatically modify spin populations such that transitions for "insensitive" nucleus (^{13}C) are dramatically enhanced

- This is done by population inversion...

^{13}C SPECTRA OF MENTHOL WITH INEPT PULSE SEQUENCE

Refocussing time, D2

Other pulse sequences...

- COSY

- NOESY

- ROESY

- TOCSY

- APT

- DEPT

- HETCOR

- HMQC
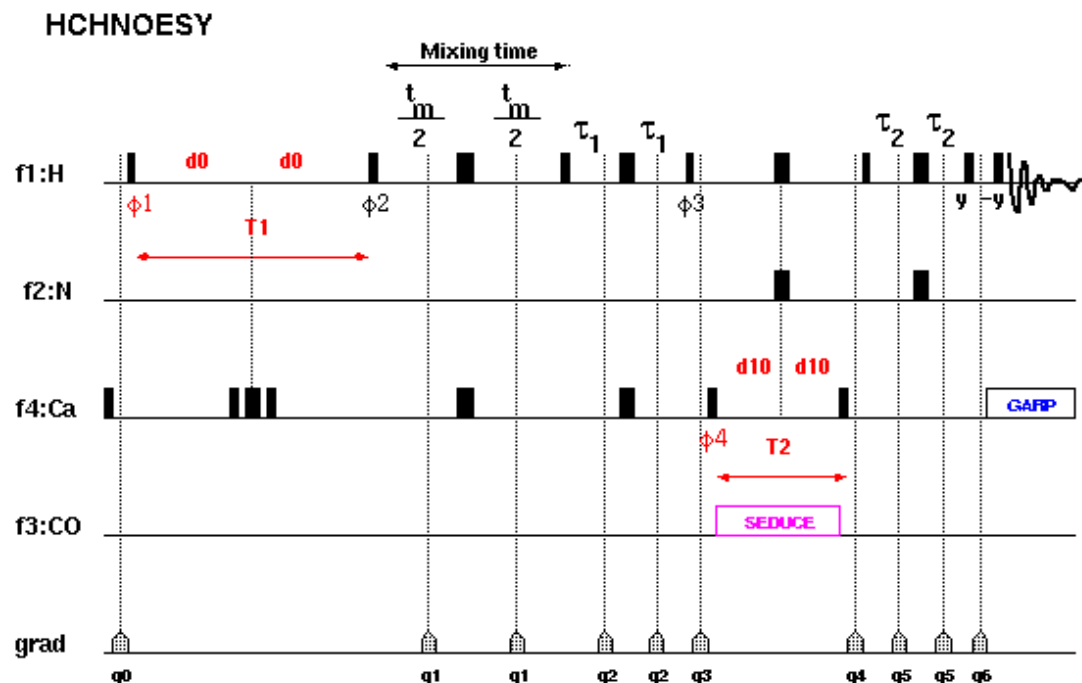
- Each uses complex pulse sequences to modify Boltzmann populations of states in order to emphasize and/or determine magnitude of coupling between different nuclei (either *J*-coupling and/or dipole coupling)
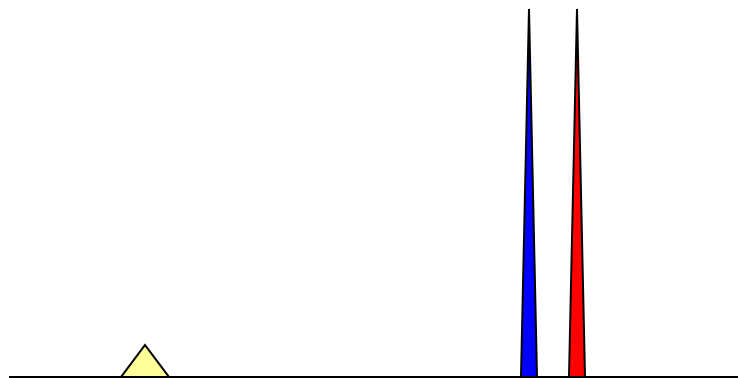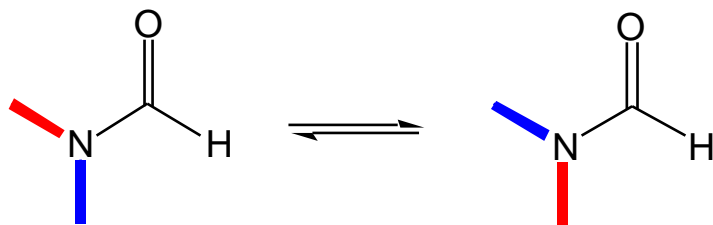
Effect of Chemical Processes on NMR parameters...

- Assumed time-independent nuclei (nothing happening to them!)

- never actually true but often a reasonable assumption

- Other situations require more detailed investigation (chemical exchange, reactivity, *etc.*)
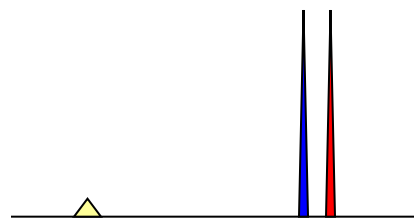
- Chemical exchange processes

K_{ex} — Conformational equilibrium

K_B — Chemical equilibrium
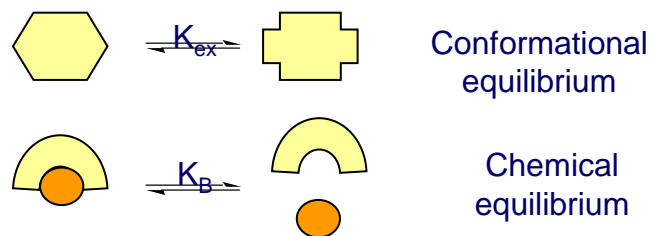
  - Example: *N,N*-dimethylformamide – rotation about C-N amide bond

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- The fact that we can see both peaks indicates that exchange process is relatively slow – but compared to what?

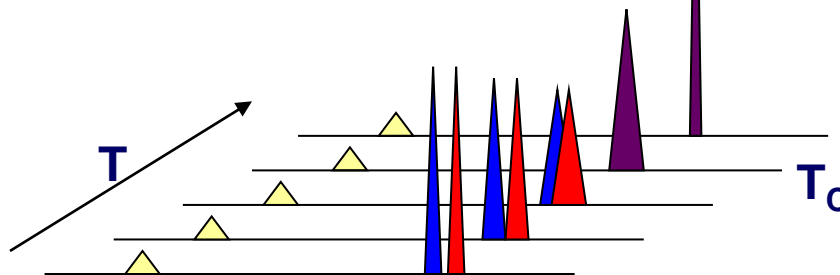$$rate \gg \frac{1}{\delta_A - \delta_B} = \frac{1}{\Delta\delta}$$

- if we increase the temperature to increase the rate of exchange...

  - we observe **coalescence** of signals
  - From such data, we can estimate the rate of exchange...

$$rate \leq \frac{1}{\Delta\delta}$$

$$k_{exchange} \approx \frac{\pi\Delta\nu}{\sqrt{2}}$$

$$\text{at} \quad T = T_{coalescence}$$

T

T$_C$

- coalescence T therefore allows calculation of exchange thermodynamics
- window for NMR evaluation of dynamic processes is 10^{-2} to 10^8 s^{-1} (huge)