III. NUCLEAR MAGNETIC INTERACTIONS

Bibliography: - Slichter: 3.1, 3.2, 4.1 - 4.4, 4.9
- Harris: 1.8 - 1.17, 2.5 - 2.12, 8.1 - 8.4, 8.17 - 8.24

III.1 THE CHEMICAL SHIFT INTERACTION

The chemical shift interaction is, from the point of view of chemical characterization, the most important NMR interaction. It provides chemically inequivalent homonuclear spin systems with slightly different NMR resonance frequencies:

$$\mathcal{H}_{CS} = -\omega_0^1 I_{1z} - \omega_0^2 I_{2z} - \cdots$$

Fig. 1-9 Proton NMR spectrum (at 60 MHz) of a mixture of benzene and acetone with TMS (the three resonances are in that order from left to right). The resonances of benzene and acetone occur at $\delta 7\cdot 33$ and $\delta 1\cdot 97$ in this solution. The components of the solution are in the molar ratio 10:22:1, as can be verified from the integral trace superimposed on the spectrum (see Section 1-21)—the steps a, b and c are proportional to concentration in terms of numbers of protons per unit volume. The 'ringing' at the right hand side of each peak is an indication that the scan speed is too fast. The small peaks marked with arrows are spinning sidebands (see Section 1-21);
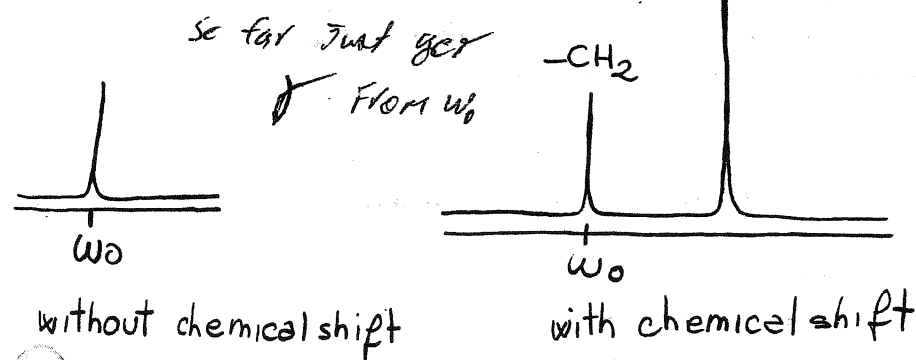
60 Hz
1 ppm

$> 60,000,000$

$60,000,050$

$$\mathcal{H}_z = -\gamma B_0 I_z = -\omega_0 I_z$$

Now
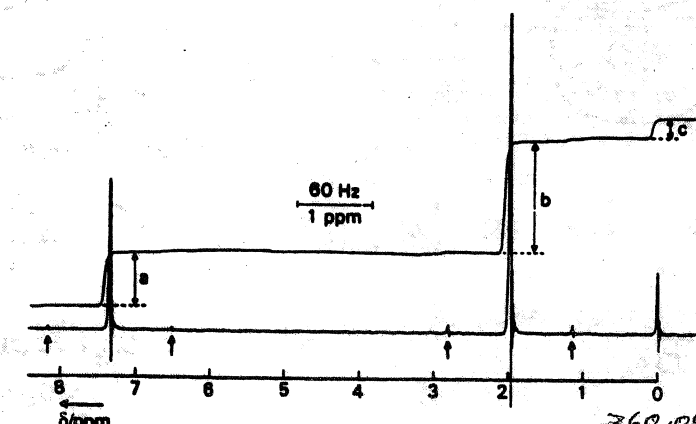
$CH_3 - CH_2 - CQ H_{z+} \mathcal{H}_{cs} = -\omega_0^1 I_{z_1} - \omega_0^2 I_z^z$

¹H NMR spectrum of ethyl chloride:

$$\boxed{\mathcal{H}_{total} = \mathcal{H}_z + \mathcal{H}_{cs}}$$

So far just get γ from ω_0

—CH₃

—CH₂

ω_0

without chemical shift

$$\left(\mathcal{H}_z = -\omega_0 (I_{1z} + I_{2z})\right)$$

ω_0

with chemical shift

$$\left(\mathcal{H}_z + \mathcal{H}_{cs}\right)$$

The integral of each peak is proportional to the number of protons in the sample which are giving origin to it.

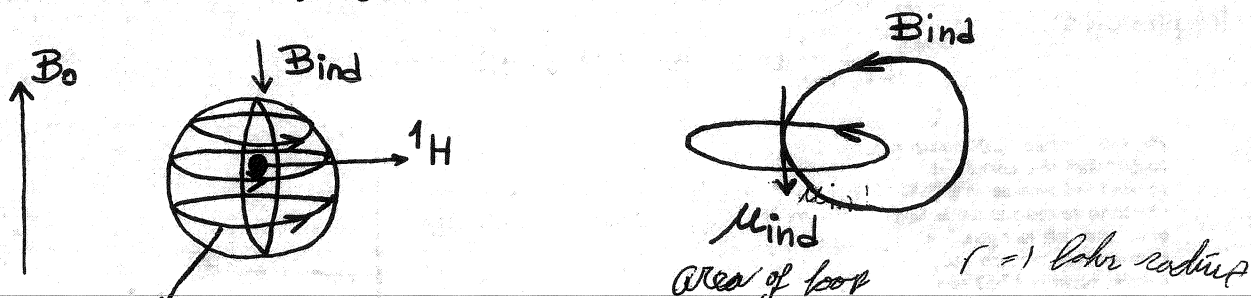# Voltage contributed # the # of protons doing the generating.

This chemical shifts arise due **to electronic currents which are induced
when placing a molecule in B_0**. The fields B_{ind} generated by these currents
add up to **the effects of B_0.**

Consider for instance a hydrogen atom:

$$\omega \simeq \frac{e}{2m_e} B_0 \Rightarrow |\mu_{ind}| = e \frac{\omega}{2\pi} \pi r^2 = \frac{e^2}{4m_e} B_0 \cdot a_0^2 \sin^2\theta$$

$$B_{ind} \propto B_0$$

a_0: Bohr radius
$\omega \simeq c B_0$

Then the actual field B determining the Larmor frequency of a spin

(−) because opposes field, shielded;
Nuc feels slightly less field.

$$B = B_0(1 - \sigma)$$

chemical shielding $\approx 10^{-6}$

NMR → one of the smallest signals of all spectroscopy

Chemically-inequivalent spins i in a molecule are shielded by different σ_i;
these are so small that they are usually expressed in ppm's = $10^6 \cdot \sigma_i$

From a practical point of view it is convenient to express the chemical shifts
with respect to a reference. In ^1H and ^{13}C NMR, this reference is usually
tetramethyl silane (TMS): $(CH_3)_4Si$.
Advantages: i) It gives only 1 signal, strong with only a 1% w/w sample.
        ii) Its resonance does not overlap with almost anything.
        iii) It is chemically inert and can be easily evaporated.

deshielded

$$\nu_x = \gamma B_0 (1-\sigma_x)$$
$$\nu_{ref} = \gamma B_0 (1-\sigma_{ref})$$

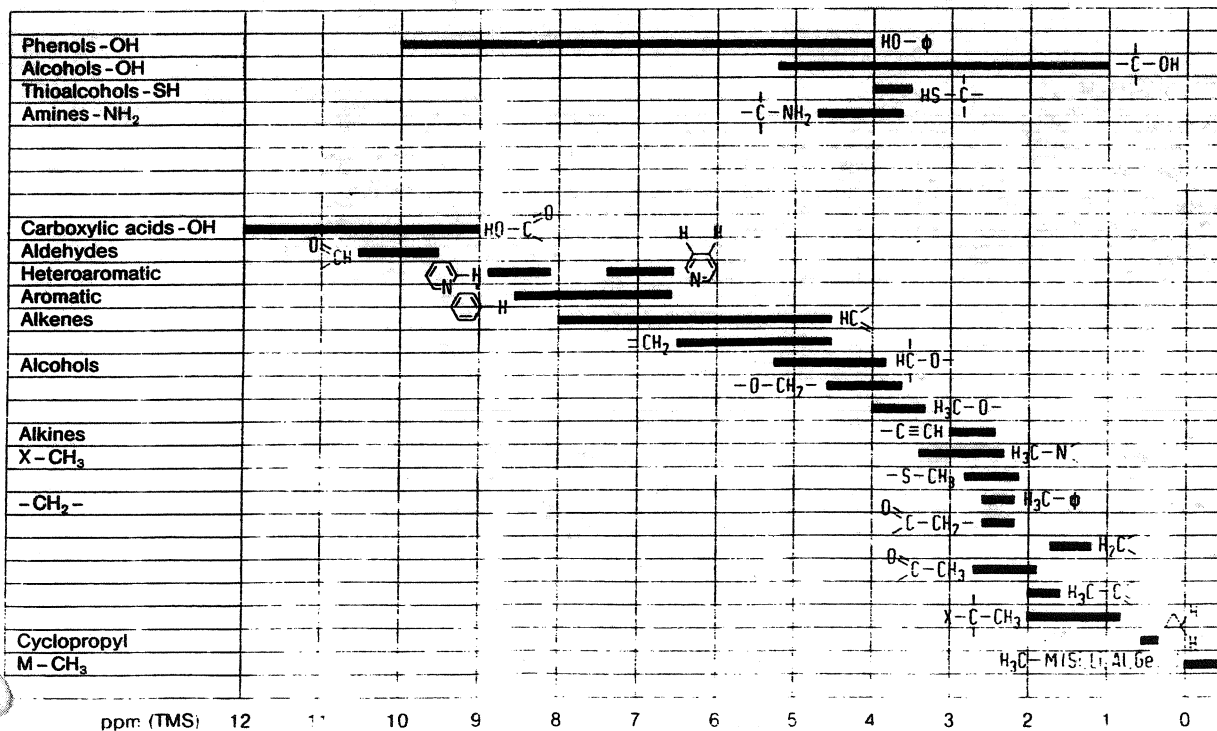$$\Delta \nu = \frac{\gamma B_0 (\sigma_{ref} - \sigma_x)}{\gamma B_0 (1 - x \cdot 10^{-6})} \times 10^6$$

By measuring the difference in frequency between a peak x and the TMS resonance, the chemical shift δ can be obtained as

$$\delta (ppm) = \frac{\nu_x - \nu_{TMS}}{\nu_{TMS}} \cdot 10^6 \qquad [\nu] = H_z$$

δ is independent of B_0.
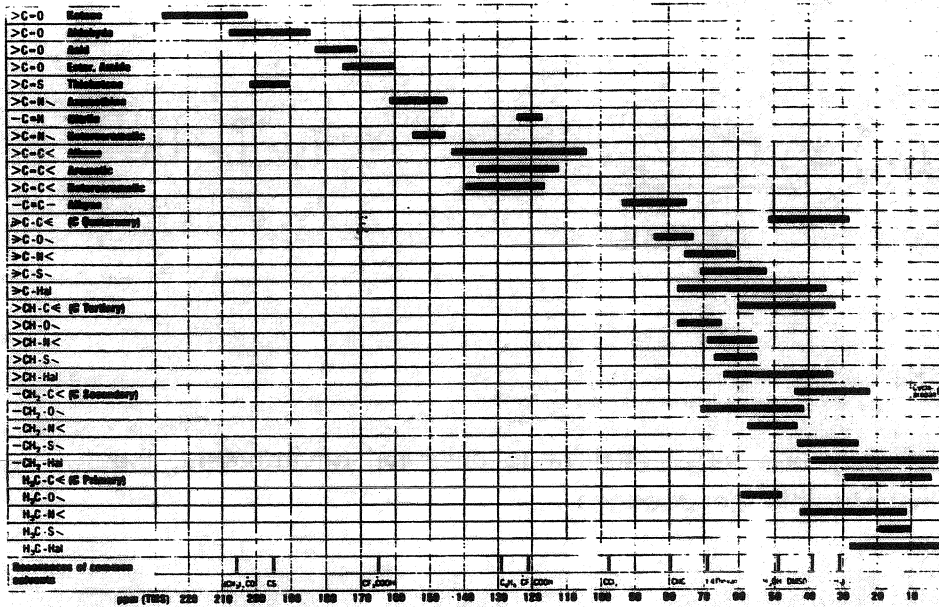
^{1}H and ^{13}C chemical shifts are very sensitive to chemical environment; the following graphs illustrate this dependence.
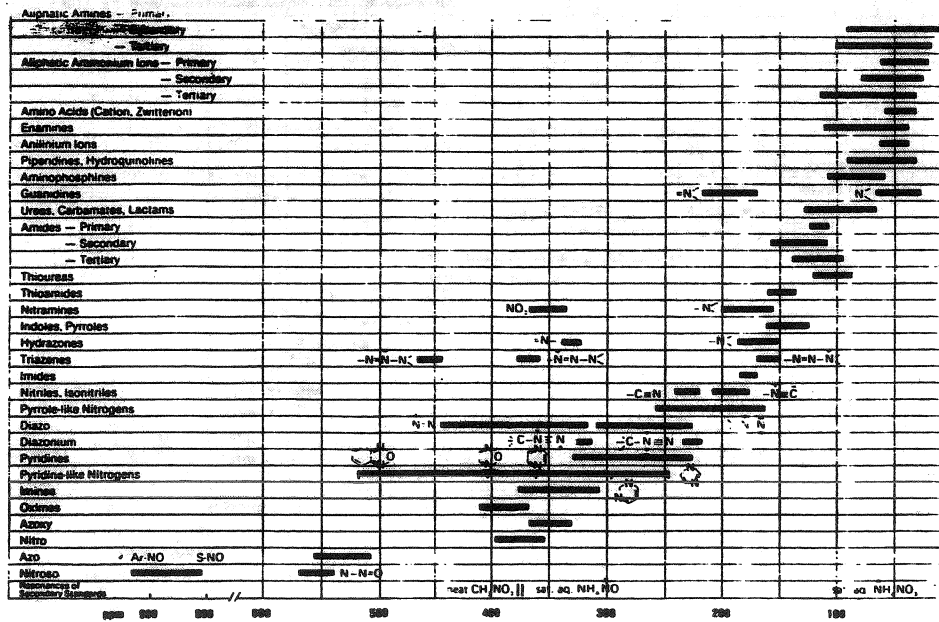
^{1}H:

13C:

Chart of 13C chemical shift ranges (ppm, TMS) for various carbon environments:

Group	
>C=O	Ketone
>C=O	Aldehyde
>C=O	Acid
>C=O	Ester, Amide
>C=S	Thioketone
>C=N~	Ammonium
—C≡N	Nitrile
>C=N~	Isonitrile/Isocyanate
>C=C<	Alkene
>C=C<	Aromatic
>C=C<	Heteroaromatic
—C≡C—	Alkyne
>C—C<	(C Quaternary)
>C—O~	
>C—N<	
>C—S~	
>C—Hal	
>CH—C<	(C Tertiary)
>CH—O~	
>CH—N<	
>CH—S~	
>CH—Hal	
—CH₂—C<	(C Secondary)
—CH₂—O~	
—CH₂—N<	
—CH₂—S~	
—CH₂—Hal	
H₃C—C<	(C Primary)
H₃C—O~	
H₃C—N<	
H₃C—S~	
H₃C—Hal	
Resonances of common solvents	

ppm (TMS) 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

15N:

Chart of 15N chemical shift ranges (ppm) for various nitrogen environments:

Group
Aliphatic Amines — Primary
— Secondary
— Tertiary
Aliphatic Ammonium Ions — Primary
— Secondary
— Tertiary
Amino Acids (Cation, Zwitterion)
Enamines
Anilinium Ions
Piperidines, Hydroquinolines
Aminophosphines
Guanidines
Ureas, Carbamates, Lactams
Amides — Primary
— Secondary
— Tertiary
Thioureas
Thioamides
Nitramines
Indoles, Pyrroles
Hydrazones
Triazenes
Imides
Nitriles, Isonitriles
Pyrrole-like Nitrogens
Diazo
Diazonium
Pyridines
Pyridine-like Nitrogens
Imines
Oximes
Azoxy
Nitro
Azo
Nitroso
Resonances of Reference Samples

ppm 900 800 700 600 500 400 300 200 100 0

III.2 THE DIPOLAR INTERACTION (NON-LOCAL INTERACTION)

(The largest of Non-local interactions)

In addition to interacting with an external magnetic field, a spin also behaves like a small magnet. Thus, the resonance frequency of a particular spin depends in principle on the location of its neighbors. nuc. has its own magnetic mom. Therefore generates mfield to other sites.

Bo

Magn Dip

B1 RECEIVING

2 (I_2)

$\vec{r}_{12}$

DONATING

1 (I_1)
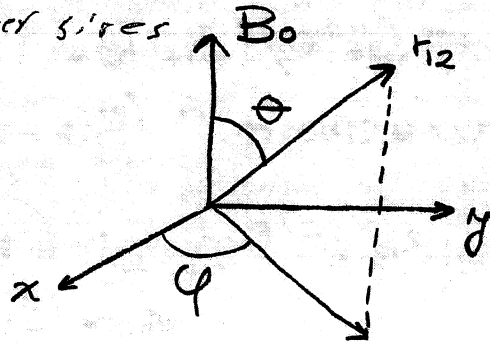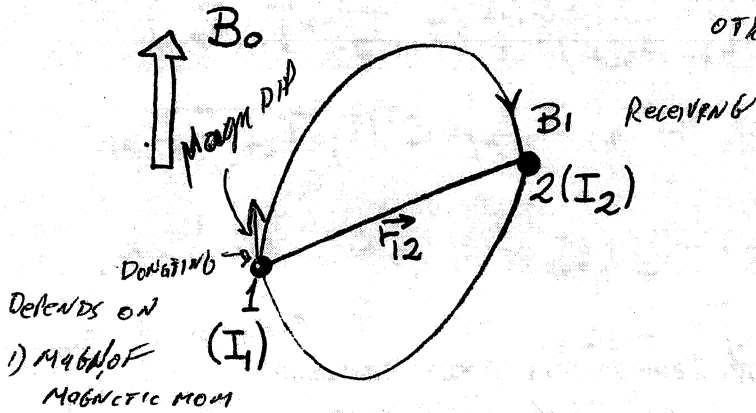
Depends on
1) Magn of magnetic mom
2) Distance
3) Orientations of magn. mom's eg) up or down spin w.r.t. Bo.

Bo

θ

r_{12}

x y φ

$$E_{dipole-dipole} = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r_{12}^3} - 3 \frac{(\vec{\mu}_1 \cdot \vec{r}_{12})(\vec{\mu}_2 \cdot \vec{r}_{12})}{r_{12}^5}$$

convenient form

To q.m. $\vec{M}_i \to \gamma_i I_i$

∮ stat. dist → scalars

$$\vec{I}_1 \cdot \vec{I}_2 = I_{1x} I_{2x} + I_{1y} I_{2y} + I_{1z} I_{2z}$$
$$= I_{1z} I_{2z} + \frac{1}{2}(I_{1+} I_{2-} + I_{1-} I_{2+})$$

This classical expression for the coupling between two magnetic dipoles gives origin to the quantum-mechanical Hamiltonian: $I_{1+} I_{2-} |\alpha_1 \alpha_2\rangle = 0$

$$\boxed{\mathscr{H}_D = \frac{\gamma_1 \gamma_2}{r_{12}^3}\left[\vec{I}_1 \cdot \vec{I}_2 - 3\frac{(\vec{I}_1 \cdot \vec{r}_{12})(\vec{I}_2 \cdot \vec{r}_{12})}{r_{12}^2}\right]}$$

Dipolar Hamilt

DIPOLAR COUPLING HAMILTONIAN $\frac{\gamma_1 \gamma_2}{r_{12}^3}: W_D$; DIPOLAR COUPLING CONSTANT

I_1 acts on spin 1 but not spin 2   know

∮ can't use 2x2 matrix as before   remember: $\alpha/\alpha\rangle$
                                              $\alpha/\beta\rangle$
Now ∮ Need larger vector space 4x4 to descr.

$\theta \equiv$ INTERNUC VECT $\cancel{b_0}$

It is convenient to expand this coupling into the "dipolar alphabet":

$W_D = $ DIP COUP CONST

$$\mathcal{H}_D = [A + B + C + D + E + F]$$ Flip-Flop Term

$$A = \frac{W_D}{2}(1 - 3\cos^2\theta) I_{1z} I_{2z} = A' I_{1z} I_{2z}$$ ← I_z opt only

$$B = \frac{W_D}{4}(1 - 3\cos^2\theta)(I_{1+} I_{2-} + I_{1-} I_{2+}) = B'(I_{1+}I_{2-} + I_{1-}I_{2+})$$ $\left. \right\} I_+$ or I_-

$$C = -\frac{3W_D}{2}\cos\theta\sin\theta\, e^{-i\phi}(I_{1z} I_{2+} + I_{1+} I_{2z}) = C'(I_{1z}I_{2+} + I_{1+}I_{2z})$$ $\left. \right\}$

$$D = C^*$$

$$E = -\frac{3W_D}{4}\sin^2\theta\, e^{-2i\phi} I_{1+} I_{2+} = E' I_{1+} I_{2+}$$ ← FLIP-FLIP raising

$$F = E^*$$ where $(I_{1+}_{2+})^* = I_{1-}_{2-}$ Flop-Flop 2 Lowering

The total Hamiltonian in the presence of both Zeeman and Dipolar interactions can then be written as

DIP COUP CONSTS ~ Few KHz

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D$$ $\mathcal{H}_Z$ or ZEEMAN $\gg$ DIP

To GET MATRIX REP, 1ST FIND BASIS SET REP

To write the matrix expression of this multispin operator, it is necessary to work on the product basis set

$$\{|\alpha_1\alpha_2\rangle, \dots\} = \{|1\rangle, |2\rangle, |3\rangle, |4\rangle\}$$

$|\alpha_1 \alpha_2\rangle$
$|\alpha_1 \beta_2\rangle$
$|\alpha_1 \beta_2\rangle$
$|\beta_1 \beta_2\rangle$

Then for instance, the 1,1-element of $\mathcal{H}$:

$$\mathcal{H}_{11} = \langle 1|\mathcal{H}|1\rangle = \langle\alpha_1\alpha_2|\mathcal{H}_Z|\alpha_1\alpha_2\rangle + \langle\alpha_1\alpha_2|\mathcal{H}_D|\alpha_1\alpha_2\rangle$$

$$= \underbrace{\langle\alpha_1|-\omega_0^1 I_{1z}|\alpha_1\rangle\langle\alpha_2|\alpha_2\rangle + \langle\alpha_1|\alpha_1\rangle\langle\alpha_2|-\omega_0^2 I_{2z}|\alpha_2\rangle}_{\mathcal{H}_Z} +$$

$I_z|\alpha_1\rangle = \frac{\alpha_1}{2} \dots$

$$+ \underbrace{\langle\alpha_1\alpha_2|(A + B + \dots + F)|\alpha_1\alpha_2\rangle}_{\mathcal{H}_D} = -\omega_0^1/2 - \omega_0^2/2 + A'/4$$

$I_+ \& I_- \rightarrow B-F = 0$

C.S. only appears along DIAG because chem shift $\propto I_z$.

95

off

A - DIAG
b - JOINS $b\alpha$ & $\alpha\beta$

Thus, the total $\mathcal{H}$ **matrix**

Sum of Larmor

Our Hamil

$$\mathcal{H} = \frac{1}{2} \cdot \begin{array}{c} \alpha\alpha \\ \beta\alpha \\ \alpha\beta \\ \beta\beta \end{array} \begin{pmatrix} A'\frac{1}{2}+\Sigma & c' & c' & 2E' \\ c'D' & A'\frac{1}{2}+\Delta & 2\cdot B' & c' \\ D' & 2\cdot B' & A'\frac{1}{2}-\Delta & c'c' \\ 2F' & D' & D' & A'\frac{1}{2}-\Sigma \end{pmatrix} \begin{array}{c} \\ \\ \\ \end{array}$$

$\quad\quad\quad\quad\quad\alpha\alpha \quad\quad\quad \beta\alpha \quad\quad \alpha\beta \quad\quad \beta\beta$

DIFF OF Larmor

$\Sigma = -\omega_o' - \omega_o^2$

$\Delta = \omega_o' - \omega_o^2$

all these coeffs (off diag) are $\propto$ to DIP coup.

$A', B', \ldots$: same as $\omega_D \cdot A, \omega_D \cdot B, \ldots$ but only the spatial part

This Hamiltonian has diagonal elements $|\Sigma| \approx$ 100's MHz, and off-diagonal elements in the order of $\omega_D \approx$ 10's kHz => the effects of $\mathcal{H}_D$ can be accurately described as a **perturbation** of $\mathcal{H}_z$. Perturbation theory indicates that the effects of $\mathcal{H}_D$ can therefore be taken into account, to first order, by calculating the eigenfuctions $\{|i\rangle\}$ of $\mathcal{H}_z$ and expressing each element of the total hamiltonian as

observable can only be the e.v.'s $\therefore$ need to DIAG. matrix: remember observed Bohr Freq

$$\mathcal{H}_{ij} = \langle i|\mathcal{H}_z|j\rangle + \langle i|\mathcal{H}_D|j\rangle = \mathcal{H}_{ij}^{\circ} + \langle i|\mathcal{H}_D|j\rangle$$

$\dfrac{E_i - E_j}{\hbar}$

$\mathcal{H}_o|j\rangle = E_j|j\rangle$

This first-order perturbation expansion is equivalent to keeping the part of $\mathcal{H}_D$ that commutes with $\mathcal{H}_z$: **truncation** by the Zeeman Hamiltonian.

Two cases have to be distinguished:

HOMONUCLEAR SYSTEM

$$|\Delta| \approx |\omega_D|$$

$$\mathcal{H} = \mathcal{H}_z + \omega_D(A+B)$$

$$= \mathcal{H}_z + \omega_D \frac{(1-3\cos^2\theta)}{2}(3I_{1z}I_{2z} - \vec{I}_1\cdot\vec{I}_2)$$

eg) A for Hetero
A+b for Homonuc

eg 5ppm apart 2 H's $\rightarrow$ 2kHz But DIP are $\approx$ 40kHz's $\therefore$ can't throw out.

$\therefore$ DIAG is >> OFF DIAG.

HETERONUCLEAR SYSTEM

$$|\Delta| \gg |\omega_D|$$

$$\mathcal{H} = \mathcal{H}_z + \omega_D A$$

$$= \mathcal{H}_z + \omega_D \frac{(1-3\cos^2\theta)}{2} I_{1z}I_{2z}$$

$\Theta) c - H$

$H_z \propto$ FIElD
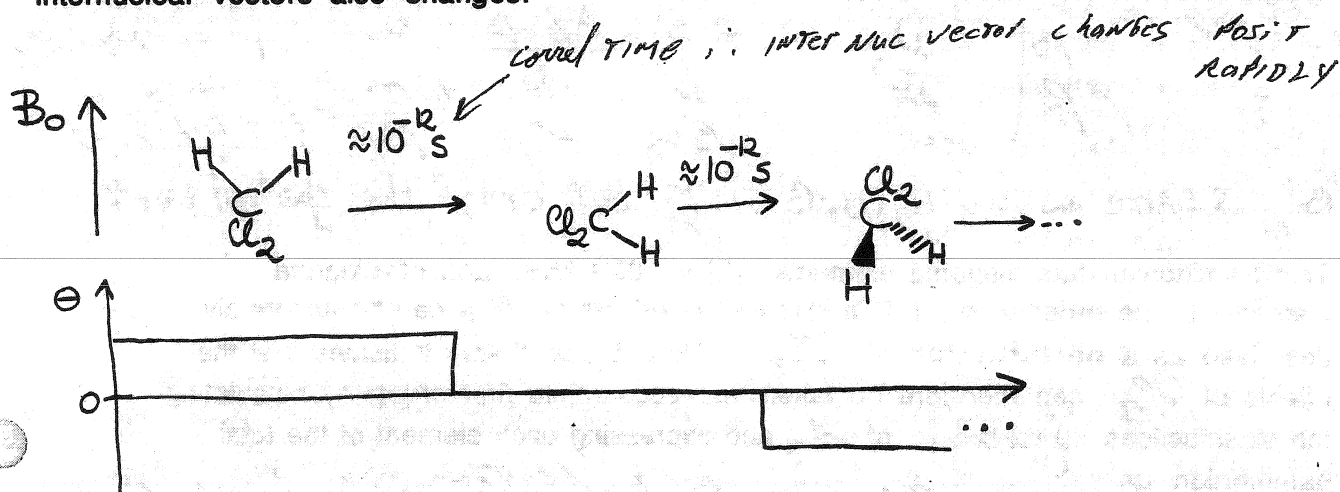
$H = 400 MHz$
$c = 100 MHz$

$\therefore \Sigma = 500 MHz$
$\Delta = 300 MHz$

III.3 ISOTROPIC TUMBLING; AVERAGING OF DIPOLAR COUPLINGS IN SOLUTION NMR

Small molecules move very fast (their orientation changes once every ca. 10^{-12} sec). Each time the orientation of the molecule changes the orientation of internuclear vectors also changes:

corel TIME ∴ INTer Nuc Vector chanGes Posit RaPIDly

This is so fast that nuclear spins detect a time average of the angular part $\langle 1-3\cos^2\theta \rangle$ of the dipolar coupling over all possible orientations θ, φ. We try to calculate the solution NMR spectrum reflecting this averaging. If it is assumed that the proportion of the time that an internuclear vector spends at a particular $\{\theta, \varphi\}$ orientation is proportional to the solid angle subtended by this orientation over the complete sphere:

∴ see Avg of 2 TERMS BOTTOM OF Prev. PaGe
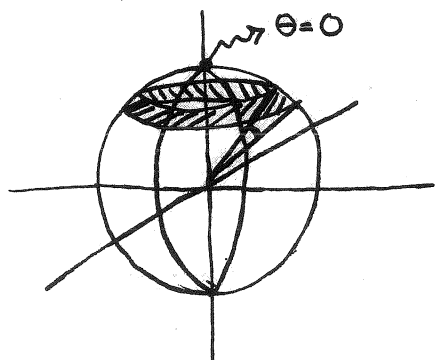
$$\frac{\text{fraction at }(\theta,\varphi)}{\text{Total reorientation time}} = \frac{\text{solid angle at }\{\theta,\varphi\}}{\text{solid angle of a sphere}} = \sin\theta\, d\theta$$

Then the *effective* Hamiltonian $\langle \mathcal{H}_D \rangle$ describing the averaged coupling is given by

$$\langle \mathcal{H}_D \rangle = \omega_D \underbrace{\langle 1-3\cos^2\theta \rangle} \cdot \text{spin part}$$

$$\alpha \int_0^{2\pi} \left[\int_0^{\pi} (1-3\cos^2\theta)\sin\theta \, d\theta \right] d\varphi \implies$$

Jacobian
method
*want to integ,
over whole
sphere*

$$\implies \boxed{\langle \mathcal{H}_D \rangle = 0}$$

There are no frequency shift due to dipole-dipole couplings in liquid-state NMR.

III.4 SPIN-SPIN (OR INDIRECT, OR SCALAR, OR J-) COUPLING

If the homogeneity of B_0 becomes high enough, the ^1H NMR spectrum of CH_3CH_2Cl goes,

from:

CH_2 CH_3

to:

quartet   triplet
= 3+1   = 2+1
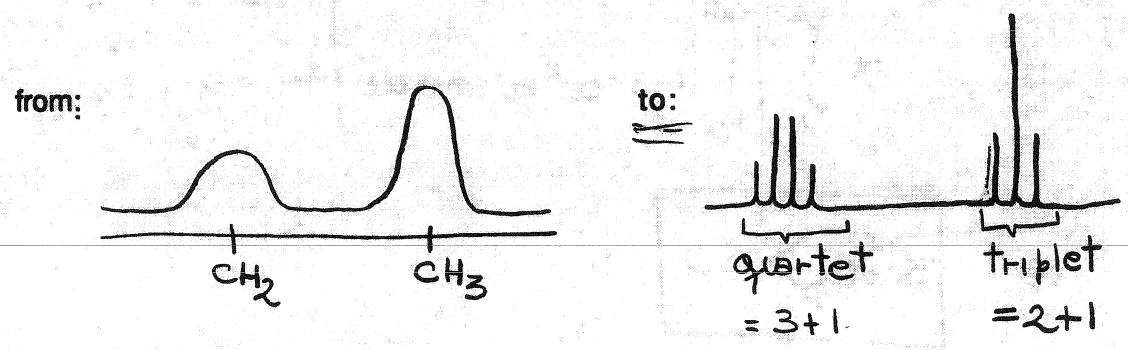
These splittings occur because **even in solution**, neighboring spins can produce on each other small magnetic fields. These fields do not travel through space but mainly through the electrons in chemical bonds (hence the name indirect):

$$H - C - C - H$$
$$A \qquad\qquad B$$

Polarized $e^{-}s$, Polarize...

spin B will experience an additional field

$+J/2$ $-J/2$
If spin A:↑   If spin A:↓
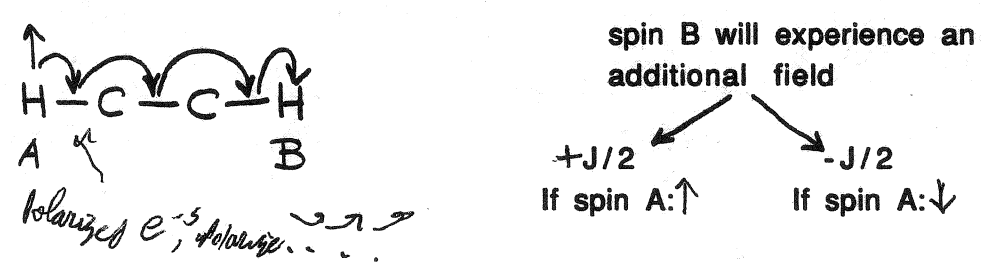
The origin of this coupling can be understood as follows: Let's assume 2 spins, whose nuclei share electrons in a molecular orbital. Since the system is diamagnetic, the spin part of this electronic wave function is formed by equal parts of

wave function

A   B   +   A   B

state 1   state 2

/// : positive spin density

\\\ : negative spin density

in bond state all $e^{-}s$ diamag

$\alpha\beta - \beta\alpha$ ∴ No net
e^{-} spin density in
α or β
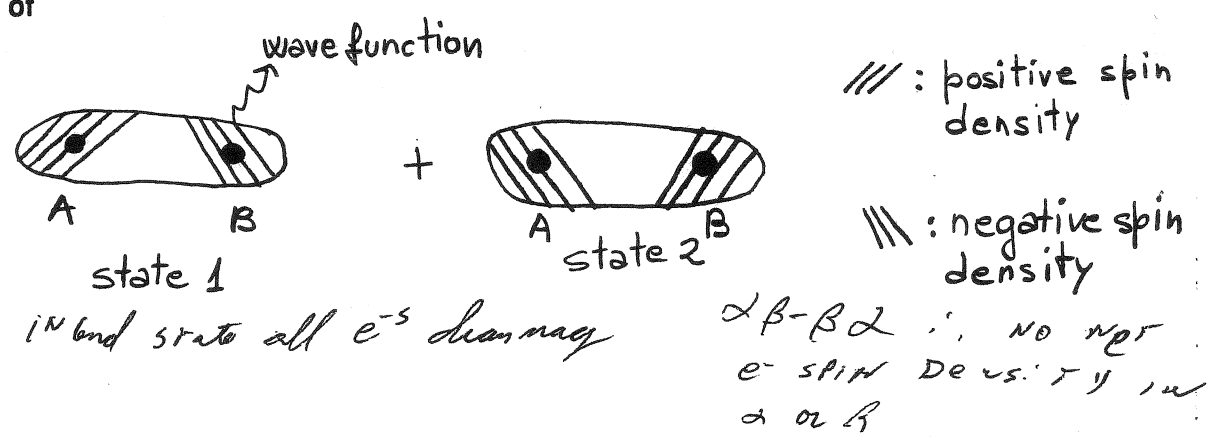
If nucleus A however has a spin ↑ , the presence of a nuclear spin-electron spin
coupling

Scalar Type
Hamil.;
Scalar coupling →

$$\mathcal{H}_{n-e} = a \cdot \vec{I}_A \cdot \vec{S}$$

← "Fermi' Contact Term"
b. e^- couples to Nucleus

Nuc ↗ e^- ↖

will favor one electron spin-density state against the other, creating a
distortion in the electronic spin density at site B.   A second electron-nuclear
coupling Hamiltonian

Hyperfine coupling =
'Fermi-contact Term

$$\mathcal{H}_{n-e} = b \cdot \vec{I}_B \cdot \vec{S}$$

will therefore create a non-zero coupling between spins A and B:

change a & b then
Northing really changes
a mutual splitting
strength is the J-Coup
J depends on amount
of Nuc.; J is bigger
for Nuclei with larger
γ_a

$$\boxed{\mathcal{H}_{spin-spin} = J \, \vec{I}_A \cdot \vec{I}_B}$$

Important consequences of this mechanism:

i) The coupling constant **J** is independent of B_0 => its value is
expressed in Hz and not in ppm.

ii) The Hamiltonian is a scalar: it only depends on the relative
orientations of spins **A** and **B**, not on the orientation of B_0.

iii) The coupling travels through electrons ⟶ **J** is sensitive to
molecular structure

J decays as the # of
bonds separating **A**
and **B** increases

iv) A spins will induce on **B** spins a shift **J** identical to the one that **B**
spins exerts on **A** spins.

$J^3 ⇒ 3$ bonds apart
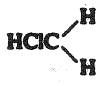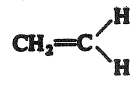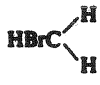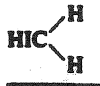away

$J^3 \to H$
$F - C - C$
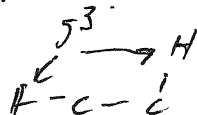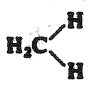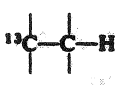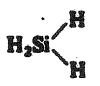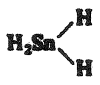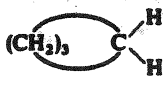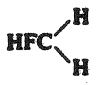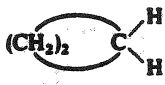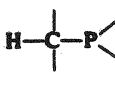
Some characteristic values for J-couplings:

TABLE 9-2 Some Representative One-Bond Coupling Constants[a]

Type	^1J (Hz)
$^1H-^1H$	280
$^{13}C-^1H$	110–260
$^{31}P-^1H$	200–700
$^{13}C-^{19}F$	−280 to −350
$^{13}C\equiv^{13}C$	170
>P—P<	100–500
F—P=O	1000

[a] As quoted in reference 1 at the end of this chapter.

TABLE 9-3 Some Representative Two-Bond Coupling Constants[a]

Homonuclear Examples				Heteronuclear Examples	
Structure	^2J (Hz)	Structure	^2J (Hz)	Structure	^2J (Hz)[b]
$H_2C\overset{H}{\underset{H}{\diagdown}}$	−12.4	$(CH_2)_5\ C\overset{H}{\underset{H}{<}}$	−13	$^{13}C-C-H$	5
$H_2Si\overset{H}{\underset{H}{\diagdown}}$	+2.8	$(CH_2)_4\ C\overset{H}{\underset{H}{<}}$	−10.5	$H-C-F$	45
$H_2Sn\overset{H}{\underset{H}{\diagdown}}$	+15.3	$(CH_2)_3\ C\overset{H}{\underset{H}{<}}$	−9	$F-C-F$	160
$HFC\overset{H}{\underset{H}{\diagdown}}$	−9.6	$(CH_2)_2\ C\overset{H}{\underset{H}{<}}$	−4.3	$H-C-P<$	7–14
$HClC\overset{H}{\underset{H}{\diagdown}}$	−10.8	$CH_2=C\overset{H}{\underset{H}{<}}$	+2.5		
$HBrC\overset{H}{\underset{H}{\diagdown}}$	−10.2				
$HIC\overset{H}{\underset{H}{\diagdown}}$	−9.2				

[a] Data from references 1 and 2 at the end of this chapter.
[b] Absolute values.

Particularly valuable information about **molecular conformation** is available from J_{HH}^3 : The J-coupling between 2 protons 3 bonds apart. The value of this J depends on the **dihedral angle** between the 2 H_A-C-C and C-C-H_B planes:

$$H_A - C - C - H_B \equiv$$
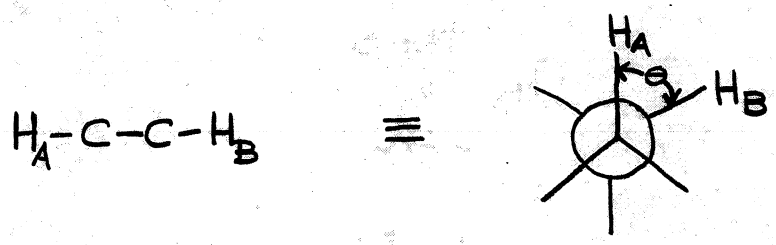
The value of J has the form

$$J_{HH}^3 = \left(7 - \cos\theta + 5\cos(2\theta)\right) \, Hz$$

Figure 9-6 is a graph of this equation. Notice how *J* reaches its maximum values at 0° (*J* = 11 Hz) and 180° (*J* = 13 Hz) and its minimum value at 90° (*J* = 2 Hz). This is because the interaction between the two vicinal orbitals (bonds) is at its maximum at 0° or 180° and decreases to nearly zero at 90°.
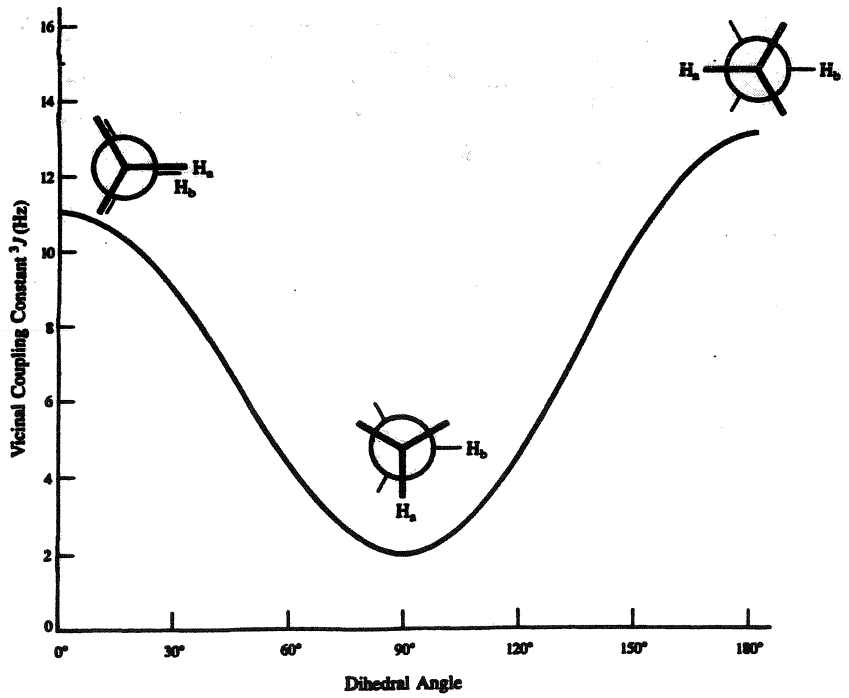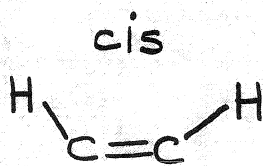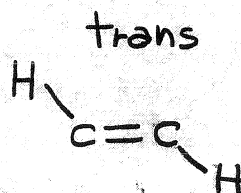

FIGURE 9-6 The Karplus relationship for vicinal coupling.

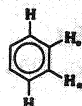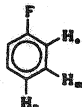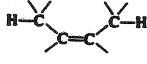**Vicinal (i.e., J³) couplings across double bonds are also dependent on structure:**

a) Free rot ~ 7 Hz
b) Dbl bonds ↑ J

cis

H—C=C—H

6–14 Hz

trans
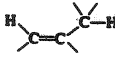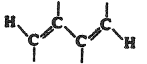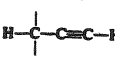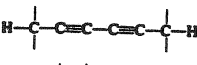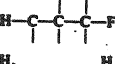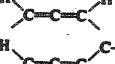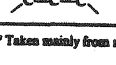
H—C=C—H

11–18 Hz

Some additional long-range J-couplings:

TABLE 9-5 Long-Range Coupling Mediated by Multiple Bonds

Interaction	Number of bonds (n)	ⁿJ (Hz)
H—H₀	3	8
H—Hₘ	4	2
H—H_p	5	0.5
F—H₀	3	8
F—Hₘ	4	7
F—H_p	5	2
H—C=C—H	5	1–2
H—C=C—H	4	–2
H—C=C—H	5	±1
H—C—C≡C—H	4	–2
H—C—C≡C—C≡C—H	7	1
H—C—C—C—F	4	5
H—C=C—H	4	6
H—C=C—C—H	5	3

ᵃ Taken mainly from reference 1 and 3 at the end of this chapter. (See Problem 7 in Self-Test II.)

TABLE 9-6 Long-Range Coupling Mediated by W-Type Overlap

Interaction	ⁿJ (Hz)	
ee'	+1.8	
ea' (ae')	–0.4	not "W"
aa'	–0.9	
H—H	1	
H—H	7	

III.5 THE NMR SIGNAL OF SEVERAL COUPLED SPINS

Recall from the previous sections that the initial state of a spin system is given by

Se Dens. Mat
(Thermal equil.)

$$\rho_{eq} = 1 + a_z I_z \quad \propto I_z$$

irrelevant

Zeeman is DOMINANT TERM
∴ leave J-coup out
& use high temp approx

After a pulse $\beta = \omega_1 \tau$ along x the density matrix becomes

Reduced dens mat.

$$\rho(\tau) = e^{i\omega_1 \tau I_x} \rho_{eq} \, e^{-i\omega_1 \tau I_x}$$ ← Dens. mat after pulse

$$= a_z \left(\cos\beta \, I_z - \sin\beta \, I_y \right) \qquad I_z \to I_y$$

not detected

Under the presence of a Hamiltonian $\mathcal{H}$, ρ starts to evolve as

$$\rho(t) = e^{-i\mathcal{H}t} \, \rho(\tau) \, e^{i\mathcal{H}t}$$

how ρ evolves under

I^+ = raising op of all the I's

and we detect a signal $S_+(t) \propto I_x + i I_y = I_+$

$$S(t) = T_r \left[\rho(t) \cdot I_+ \right]$$

$I_z = \frac{\hbar}{2} I_z$

I_y

I_x

$I_+ = I_x + I_z$

For one spin we had:

$$I_{z_1} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$

2×2 Now need a 4×4.

develop way of WRITING IN 4×4

○ eq) ove/

n = # OF COUPLED SPINS

2^n = dimensionality **(104)**

For two spins, the total angular momentum $F_z = I_{z_1} + I_{z_2}$ is calculated as

$$I_{z_1} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$\underbrace{\quad}$ I_z for Spin 1

$\underbrace{\quad}$ Identity for spin 2

↓ direct product

DOING NOTHING ON SPIN 2

(top of matrix: $\alpha\alpha$ $\beta\alpha$ | $\alpha\beta$ $\beta\beta$)

⇒ $F_z = I_{z_1} + I_{z_2} = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$

○ = TOTAL Z-ANG MOMENTUM

$\rho = 4 \times 4$

ORDER MATTERS

$$F_+ = I_{1+} + I_{2+} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & \\ 0 & 0 & 1 \\ & 0 & 0 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

○ ⟹ $T_r\left(\rho(t) F_+\right) = \rho_{21}(t) + \rho_{31}(t) + \rho_{42}(t) + \rho_{43}(t)$

ρ of states with $\Delta m = \pm 1$

In general, if one ignores relaxation effects, the signal arising from a multispin system in an NMR experiment is given by

$H = H_z + H_c + H_{DP}$ usually

$$S(t) = Tr\left(\rho(t) F_+\right)$$

$$= Tr\left(e^{-i\mathcal{H}t}\rho(\tau)e^{i\mathcal{H}t}F_+\right) \longleftarrow \text{after Pulse}$$

$$= \sum_m \langle m| e^{-i\mathcal{H}t}\rho(\tau)e^{i\mathcal{H}t}F_+|m\rangle \longleftarrow \text{For arbi. Time} \langle \text{sand} \rangle$$

$\{|m\rangle\}$: Hamiltonian eigenstate base

Remember $\mathbb{1} = \sum_{m,} |m\rangle\langle m'|$ closure

$$= \sum_m \sum_{m'} \sum_{m''} \sum_{m'''} \langle m|e^{-i/\hbar \mathcal{H}t}|m'\rangle \underbrace{}_{e^{iE_m t/\hbar}} \langle m'|\rho(\tau)|m''\rangle \langle m''|e^{i/\hbar\mathcal{H}t}|m'''\rangle \underbrace{}_{e^{-iE_{m''}t/\hbar}} \langle m'''|F_+|m\rangle$$

$$= \sum_{m,m''} \underbrace{e^{-i\omega_{mm''}t}}_{\text{Both Freq}} \underbrace{\rho_{mm''}(\tau)F_+^{m''m}}_{\text{INTENS. of Peak}} \qquad m,m'': \text{pair of transitions}$$

where

can only observe Freqs which are DIFF btgw e.v.'s of Ham.

$$\boxed{\omega_{mm''} = \frac{\langle m|\mathcal{H}|m\rangle - \langle m''|\mathcal{H}|m''\rangle}{\hbar}}$$

$\longleftarrow$ after FT.

After $\mathcal{F}T$, this signal yields peaks whose frequencies are $\omega_{mm''}$ and whose amplitudes A are

Before $S(t) = \int \mathcal{F}(w) e^{i\omega t}$

Now $S(t) = \sum e^{-W_{mm''} \nearrow} A_{m,m'} \nwarrow$
Freq Peaks Inten.

$$A_{mm''} = \rho_{mm''}(\tau) \cdot F_+^{m''m}$$

$e^{-iHt} |m'\rangle = e^{-iE_m t}|m'\rangle \cdots = |m'\rangle e^{-iE t}$

Scalar

If we start with a π/2 x pulse => $\rho_{mm''}(0) = -F_y^{mm''}$ **and** after trace

$$\boxed{A_{mm''} \propto |\langle m | F_+ | m'' \rangle|^2}$$

Amplitude = posit. #   Amp for non-zero's

* could be complex if

Quick recipe for calculating the NMR spectrum arising from an arbitrary time-independent N-nuclei Hamiltonian after a pulse:

i) Write $\mathcal{H}$ in matrix form (using any base; for instance, for spin 1/2, the 2^N Iz states $\{ |i\rangle = |\alpha\alpha \cdots \rangle, \cdots \}$)

basis set

e.g. $\langle m | F_+ = F_{1+} + F_{2+} + F_{3+} + \cdots | m' \rangle$

only works if quantum # is diff by 1

for 2 spins

ii) Diagonalize $\mathcal{H}$ Gives

eigenvalues E_j

eigenfunctions $|\psi_j\rangle = \sum_{i=1}^{2^N} c_{ij} |i\rangle$ $j = 1, \ldots, 2^N$

iii) There are $\cancel{\dfrac{(2^N)(2^N-1)}{2}}$ possible peaks $k: \dfrac{2^N(2^N-1)}{2}$?

$\nu_k = (E_j - E_{j'})/h$ — Freq of peak

$A_k = |\langle \psi_j | F_+ | \psi_{j'} \rangle|^2$ — how tall peak should be

$j', j = 1, \ldots, 2^N$ $j \neq j'$

III.6 Example #1: THE SPECTRUM OF A DIPOLE-COUPLED SPIN PAIR

Two ways to write, remember

i) Homonuclear pair:

$$\mathcal{H} = \begin{array}{c} \alpha\alpha \\ \alpha\beta \\ \beta\alpha \\ \beta\beta \end{array}\left(\begin{array}{cccc} \Sigma + \omega_D(\theta) & 0 & 0 & 0 \\ 0 & \Delta - \omega_D(\theta) & \mp\omega_D(\theta) & 0 \\ 0 & \mp\omega_D(\theta) & -\Delta - \omega_D(\theta) & 0 \\ 0 & 0 & 0 & -\Sigma + \omega_D(\theta) \end{array}\right)$$

chem shift

$$\omega_D(\theta) = \omega_D(1 - 3\cos^2\theta)/8$$

Δ = chem shift diff

$\omega_D =$ — for β Term $\beta\beta$

If the 2 spins are identical $\Rightarrow \Delta = 0$; $\Sigma = -\omega_0$

Eigenstates	Eigenvalues	Possible transitions

$|\beta\beta\rangle$ $\omega_0 + \omega_D(\theta)$

$(|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ SINGLET STATE. 0 OK

$(|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$ $-2\omega_D(\theta)$ OK

$|\alpha\alpha\rangle$ $-\omega_0 + \omega_D(\theta)$
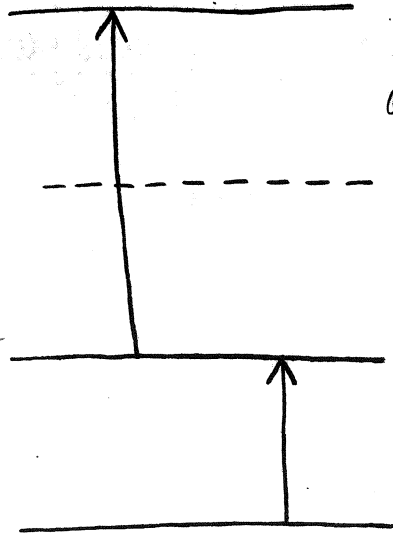
$6\omega_D$ DIFF IN chem shift

$\therefore$ see PEAKS

$$\Sigma = -\omega_{o_1} - \omega_{o_2} \quad (MHz)$$

$$\Delta = \omega_{o_1} - \omega_{o_2} \quad (kHz)$$

ii) Heteronuclear pair: $\left(|\Delta| \gg |\omega_D| \right)$ $H - C$

$$\mathcal{H} = \begin{pmatrix} \Sigma + \omega_D(\theta) & & & \bigcirc \\ & \Delta - \omega_D(\theta) & & \\ & & -\Delta - \omega_D(\theta) & \\ \bigcirc & & & -\Sigma + \omega_D(\theta) \end{pmatrix}$$

Eigenstates	Eigenvalues	Possible transitions

Transitions of F+ That F+ makes

$|\beta\beta\rangle$ $\dfrac{-\omega_o^1 - \omega_o^2}{2} + \omega_D(\theta)$

$|\alpha\beta\rangle$ $\dfrac{-\omega_o^1 + \omega_o^2}{2} - \omega_D(\theta)$ also w slow

$|\beta\alpha\rangle$ $\dfrac{\omega_o^1 - \omega_o^2}{2} - \omega_D(\theta)$

$|\alpha\alpha\rangle$ ONLY w_o^2 changes $\dfrac{\omega_o^1 + \omega_o^2}{2} + \omega_D(\theta)$

#GET 4 Peaks Now

Note that in the homonuclear case: **Whereas in the heteronuclear case:**

$$1.5\,\omega_D(1 - 3\cos^2\theta)/2$$

ω_o

$$\omega_D(1 - 3\cos^2\theta)/2$$

ω_o^1 or ω_o^2
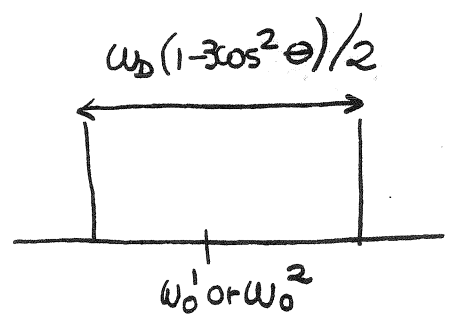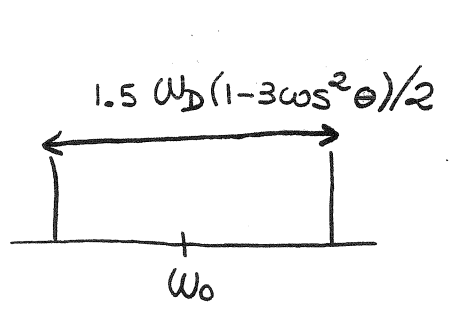
III.7 Example #2: THE SPECTRA OF J-COUPLED SPIN SYSTEMS

The rotating-frame Hamiltonian of a system of J-coupled spins is given by:

count only once so $\forall$ y

$$\mathcal{H} = -\sum_k \omega_k I_{zk} + \sum_{i<k} \sum_k J_{ik} \cdot \vec{I}_i \cdot \vec{I}_k$$

k depends on chem struct, eg) $k = 2$

As with the dipole coupling we have to distinguish 2 cases:

Hetero
Nuc

i) $|\omega_i - \omega_k| \gg J$ $\forall i,k$: Always the case in heteronuclear systems; also likely in the case of homonuclear systems at high fields

In this case the Hamiltonian of a two spin system becomes:

$$\mathcal{H} = -\omega_1 I_{1z} - \omega_2 I_{2z} + J_{12} I_{1z} I_{2z}$$

Application of the 1st order perturbative approximation is valid; I_z truncates $\vec{I}_1 \cdot \vec{I}_2$

SPIN couched @ $\omega_1 \pm J$'s

The direct product basis set $\left\{ |\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle \right\}$ are eigenstates of the Hamiltonian; and the spectrum is given by:

1 coupled to 2 = $|\alpha\rangle$ *1 coupled to 2 = $|\beta\rangle$*
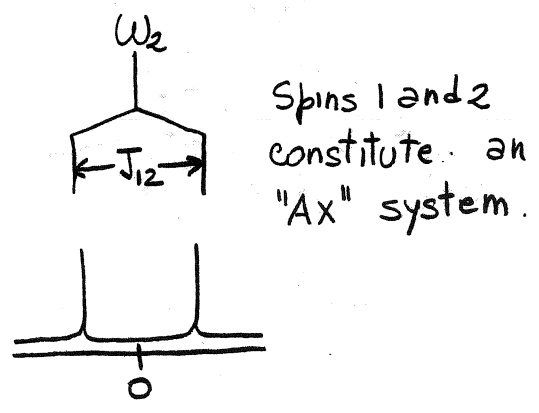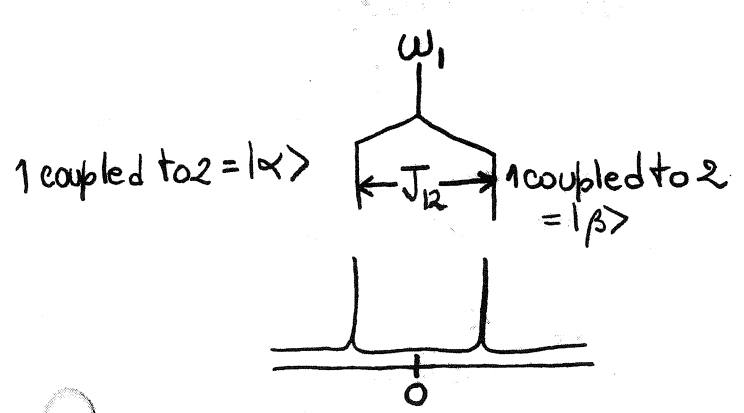
Spins 1 and 2 constitute an "AX" system.

eg) CH₂

3 peak   2 calc
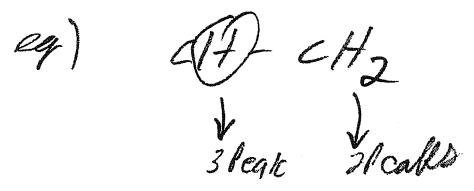
If we have spin 1 coupled to 2 identical spins 2 (AX$_2$ system)

eg) CH–CH$_2$

AX$_2$

ω_1

J

α β : split by 1st spin 2

α $2J$ β α β : split by 2nd spin 2

$\alpha\alpha$ $\alpha\beta$ $\beta\alpha$ $\beta\beta$

$\omega_1 - J$ ω_1 $\omega_1 + J$

1 : 2 : 1

ω_2

α J β

$J/2$ ω_2 $-J/2$
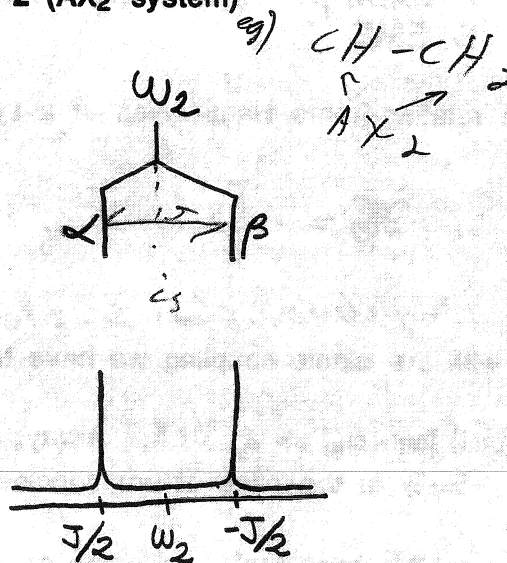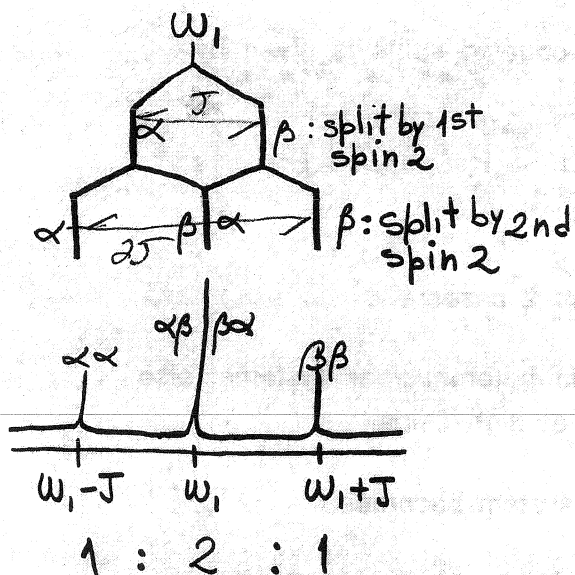
In general, 1 spin J-coupled to N identical spins will give an (N+1)-**multiplet** centered at ω_1 and with relative intensities reflecting a binomial distribution.

If we have 3 spins with first-order J-coupling among them, "AMX system"

ω_A

J_{AM}

J_{AX} J_{AX}

ω_M ω_X

AMX

J_{AM}

$Cl_2 - CH - CH - \overset{O}{\overset{\|}{C}} - OH$

Br J_{AX}

A

Now, can't assume large chem. shift J

ii) $|\omega_I - \omega_k| \approx J$: In this case, we have to solve the full Hamiltonian to get the spectrum

can't

(offsets) W = freq of irrad (for frame)

In the rotating frame

$$\mathcal{H} = -\Delta\omega_1 I_{z_1} - \Delta\omega_2 I_{z_2} + J \, \vec{I_1} \cdot \vec{I_2}$$

$$\Delta\omega_1 = \omega_1 - \omega$$
$$\Delta\omega_2 = \omega_2 - \omega$$

$$I_{1z}I_{2z} + I_{1x}I_{2x} + I_{1y}I_{2y}$$

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

Similar to DIP alphabet, but DIFF Hamil.

$\alpha\alpha$ $\beta\alpha$ DIFF btw chem shift ↑ $\alpha\beta$ $\beta\beta$

$$\mathcal{H} = \begin{array}{c} \alpha\alpha \\ \beta\alpha \\ \alpha\beta \\ \beta\beta \end{array} \left(\begin{array}{cccc} -\Sigma/2 + J/4 & 0 & 0 & 0 \\ 0 & -\Delta/2 - J/4 & J/2 & 0 \\ 0 & J/2 & \Delta/2 - J/4 & 0 \\ 0 & 0 & 0 & \Sigma/2 + J/4 \end{array} \right)$$

$$\Sigma = \Delta\omega_1 + \Delta\omega_2$$
$$\Delta = \Delta\omega_1 - \Delta\omega_2$$

$\boxed{---}$ non-diagonal matrix

OFF DIAG elements ∴ a poor basis set for Hamil ∴ Diag 2x2 subspace ∵ $\alpha\beta$ ≠ $\beta\alpha$ ∴ hard way of Diag.

The eigenvectors of $\mathcal{H}$

$$|\alpha\alpha\rangle = |1\rangle$$

$$a|\alpha\beta\rangle + b|\beta\alpha\rangle = |2\rangle$$

$$c|\alpha\beta\rangle + d|\beta\alpha\rangle = |3\rangle$$

$$|\beta\beta\rangle = |4\rangle$$

Note that the 2x2 non-diagonal part of the matrix $\begin{pmatrix} \boxed{} \end{pmatrix}$ behaves

easier like the following Hamiltonian

Diag. Method
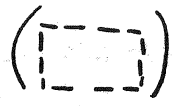
$$\mathcal{H} = -\frac{J}{4}\mathbb{1} + \Delta \cdot I_z + J I_x$$

$\underbrace{\phantom{-\frac{J}{4}\mathbb{1}}}$ energy shift (irrelevant) *shifts origin: add Back into e.v's at end only*

This looks like the Hamiltonian that we could get for a single fictitious spin 1/2 under the following offset and irradiation conditions:

$\Delta = $ *diff btw 2 chem shifts*

$$\gamma|B_{eff}| = \sqrt{\Delta^2 + J^2}$$

$$\tan\theta = J/\Delta$$

(new axis of quantization)
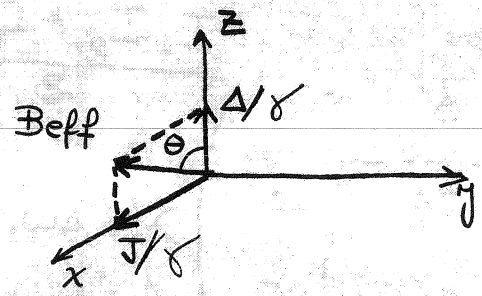
The eigenfunctions of this spin 1/2:

_When $\theta = 0$ ($J = 0$) $\longrightarrow$ $|2\rangle \longrightarrow |\alpha\beta\rangle$; $|3\rangle \longrightarrow |\beta\alpha\rangle$

_When $\theta = \pi/2$ ($\Delta = 0$) $\longrightarrow$ $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ should be indistinguishable

In addition, using the fact that

$$\langle\alpha\beta|\alpha\beta\rangle = 1$$

$$\langle\beta\alpha|\beta\alpha\rangle = 1$$

$$\langle\alpha\beta|\beta\alpha\rangle = \langle\beta\alpha|\alpha\beta\rangle = 0$$

The soln's

It is relatively easy to show that the coefficients of the eigenstates are:

$$a = \cos\frac{\theta}{2}, \quad b = \sin\frac{\theta}{2}, \quad c = -\sin\frac{\theta}{2}, \quad d = \cos\frac{\theta}{2}$$
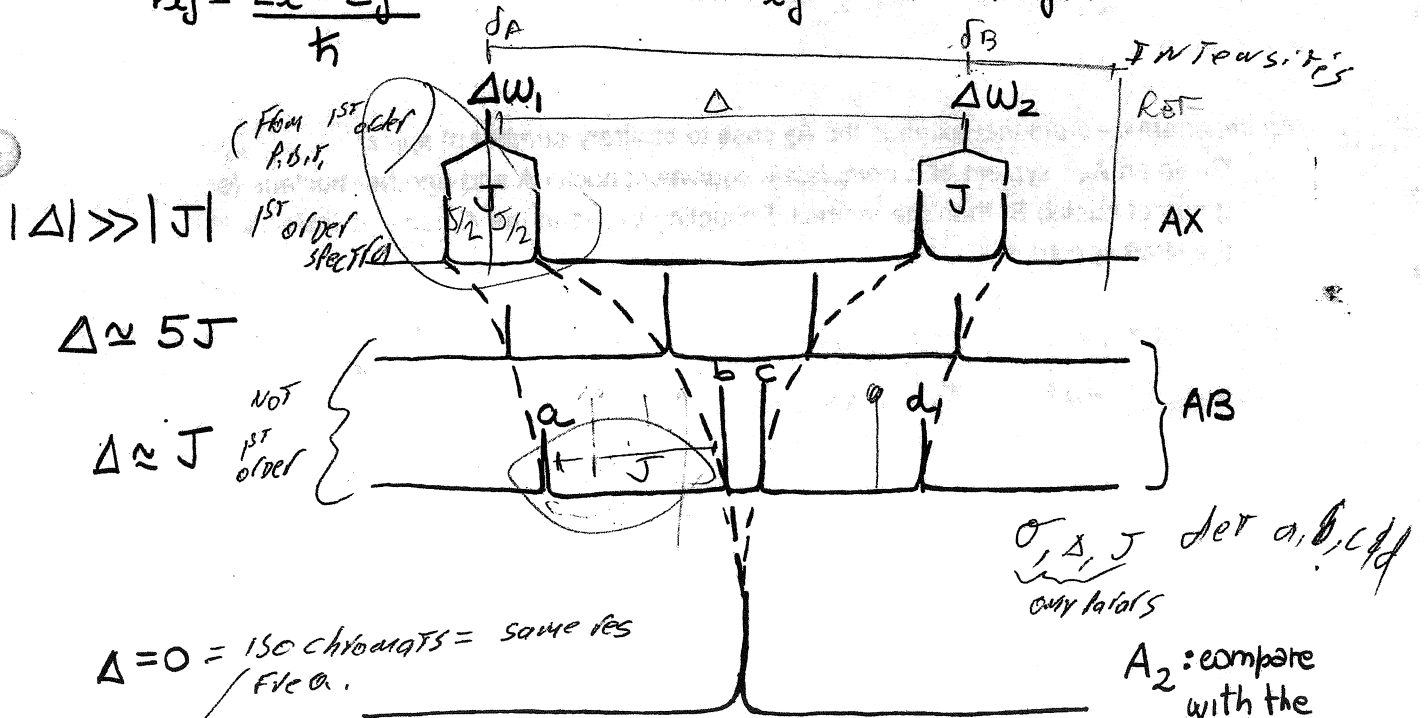
and their eigenvalues

$$E_{|2\rangle} = -\frac{J}{4} + \frac{\gamma}{2} B_{eff} \quad ; \quad E_{|3\rangle} = -\frac{J}{4} - \frac{\gamma}{2} B_{eff}$$

(add back in from before)

From here it is straightforward to calculate transition frequencies

$$\nu_{ij} = \frac{E_i - E_j}{\hbar} \qquad \text{and intensities} \quad I_{ij} \propto |\langle i | F_+ | j \rangle|^2$$

δ_A $\qquad$ δ_B $\qquad$ INTensities

(From 1st ordr P.O.T.

$|\Delta| \gg |J|$ 1st order spectra

$\Delta\omega_1$ $\qquad$ Δ $\qquad$ $\Delta\omega_2$ $\qquad$ RoT

$\frac{J}{2}$ $\frac{J}{2}$ $\qquad$ J $\qquad$ AX

$\Delta \approx 5J$

$\Delta \approx J$ NOT 1st order } AB

a b c d d

σ, Δ, J der a, b, c, d
only labels

$\Delta = 0$ = ISOchromats = same res freq.

A_2: compare with the case $\omega_b \neq 0$ $\Delta = 0$

6 TIANSiTIONS $\qquad$ $\alpha\alpha \rightarrow \beta\beta$ DOESN'T OCCUT

* DOESN'T show coupling, but J is still there
∴ same w's ⇒ ~~θ=0~~ no observable J but its still there

* inner part of doublets move faster than outer.
* INTENS of inner grows faster than outer

—— $\beta\beta$
—— $\beta\alpha$
—— $\alpha\beta$
—— $\alpha\alpha$
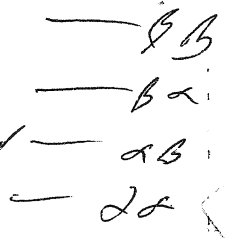
J, Σ and Δ can be extracted from the 4 frequencies a, b, c, d

$$\frac{\nu_a + \nu_d}{2} = \frac{\nu_b + \nu_c}{2} = \Sigma$$

$$\nu_b - \nu_a = \nu_d - \nu_c = J$$

$$\sqrt{(\nu_a - \nu_d)(\nu_b - \nu_c)} = |\Delta|$$

An important theorem that extends the A_2 case to arbitrary number of spins:

Given an A_nB system of n *completely equivalent* nuclei A and another nucleus (or group of nuclei) B, then the indirect J-coupling between the A nuclei is invisible in the NMR spectrum

A-B systems not seen so often
Now that B_0's are so large, $\Delta \omega$'s ↑

600 Hz vs. 600 MHz

hmWK
Show can't see J-coup here

10,00

III.8 EQUIVALENCE IN NMR

To say that N spins are **magnetically equivalent** in NMR means that:

same ⟹ i) They are chemically equivalent ⟹ *Can't Disting.*
⟹ ii) They have the same chemical shift (i.e., are isochronous)
✗ ⟹ iii) They have identical couplings to all the other nuclei in the molecule

For instance the three protons of a fast rotating CH_3 group are magnetically equivalent:

eg)

$$H_3C\text{-}CHCl_2$$
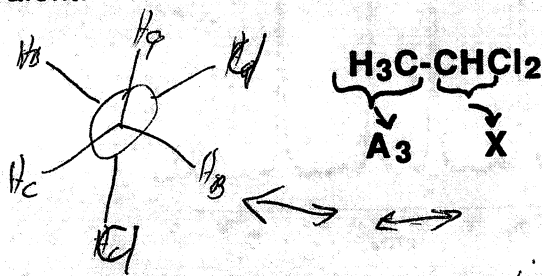
$$\underbrace{}_{A_3} \quad \underbrace{}_{X}$$: A₃X system; simple

3 Newmon strucs
∴ each are equally populated ∴ only see avg

By contrast the pair of protons ortho to the chlorine in o-dichlorobenzene are chemically equivalent but not magnetically equivalent:

same chem shifts but diff J-coup

Ha & Ha' not equally coupled to all others
∴ Ha ≠ Ha' w/ Hb Hb'
s all

$$\frac{2^4 \cdot 2^4}{2} = 128$$
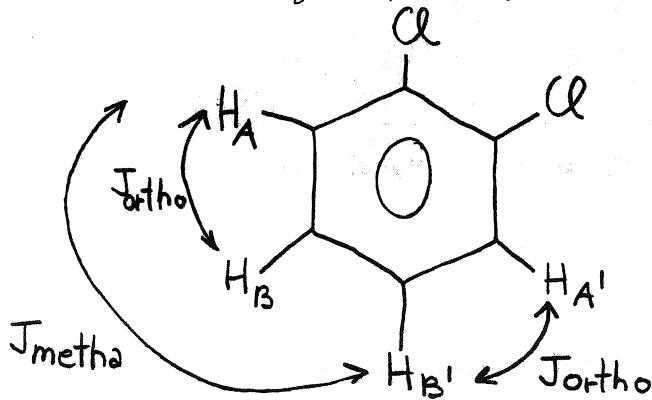
AA'BB' system very complex *AB → 4 peaks*

possible now — A & A' have same chem shifts but

usually see as @ low fields

A ⊋ b Tak J-coup Hamil commutes w/rest of hamil Thear Alopak $e^{-H} + e^{+H}$
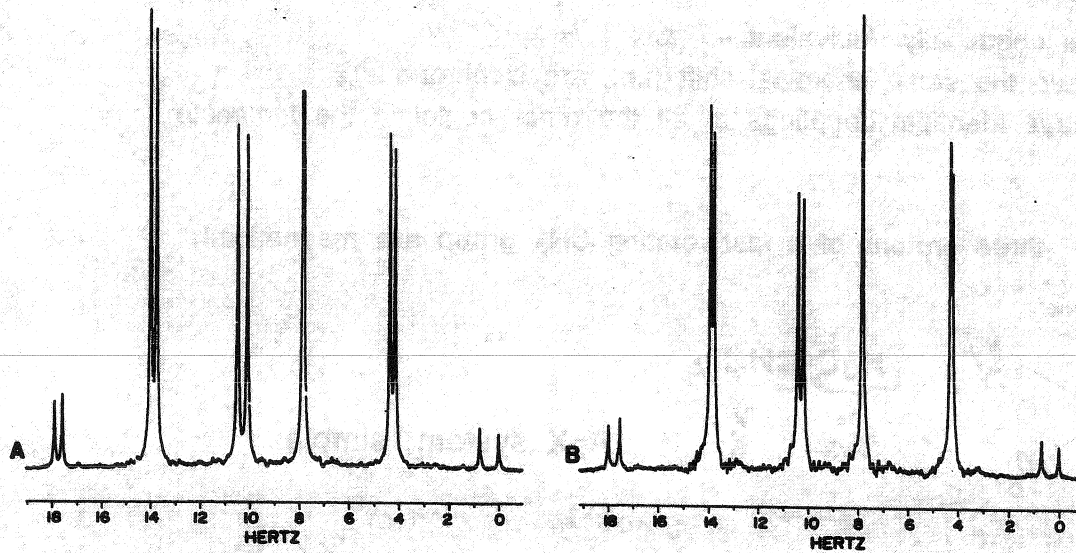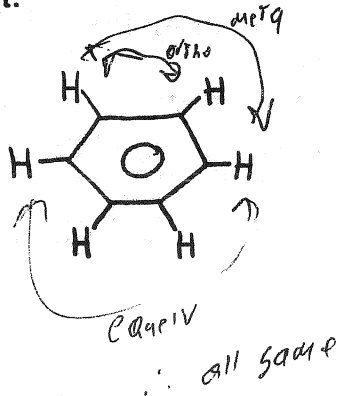
Figure 3.2 ODCB proton resolution tests at (A) 250 MHz and (B) 500 MHz; the linewidth in the latter spectrum is 0·06 Hz.

If all protons in a molecule are isochronous => they are also magnetically equivalent:

A₆ system

When we have magnetically equivalent spins things are much easier; for an **A₂B** system:

$$\mathcal{H} = -\Delta\omega_A \cdot F_{z_A} - \Delta\omega_B I_{z_B} + J_{AB} \cdot \vec{F}_A \cdot \vec{I}_B \qquad\qquad \vec{F}_A = \vec{I}_{A_1} + \vec{I}_{A_2}$$

AA'BB AA'B   DIFF coups

A special kind of inequivalence appears when groups are bonded to a **prochiral center**; e.g., a carbon that has 3 different chemical groups attached, and is directly bonded to a chiral center: *see*
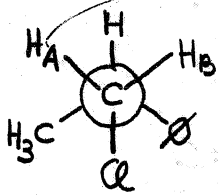
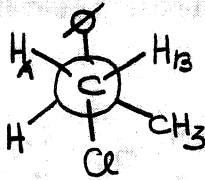$$J_{AB} \; \vec{I}_a \cdot \vec{I}_B + \vec{I}_{a'B} \; \vec{I}_{A'} \, I_B$$

can't be Diag: can't solve analytical

$$ClCH_2\overset{(*)}{-}CH(CH_3)\bigcirc$$

INEQUIV H's

Looking along the $\overset{(*)}{C}$-C bond the 3 Newman projections are:

Hₐ always has DIF env.
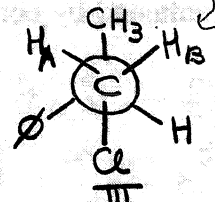
$$\overline{\delta_{\substack{A\\B}}} = P_I \cdot \delta_{\substack{A\\B}}I + P_{II}\,\delta_{\substack{A\\B}}II + P_{III}\,\delta_{\substack{A\\B}}III$$

$$\delta_{AI} = \delta_{BIII} \;;\; \delta_{AII} = \delta_{BI} \;;\; \delta_{AIII} = \delta_{BII}, \quad but\; P_{II} > P_{III} > P_I$$

$$\overline{\delta_A} \neq \overline{\delta_B}:$$ H$_A$ and H$_B$ form an AB system and therefore the J coupling among them shows in the NMR spectrum.

weighted avg → ⊘ shows J-coup

III.9 PROBLEMS

1) Demonstrate that the dipolar coupling Hamiltonian

$$\mathcal{H}_D = \frac{\gamma_1 \gamma_2}{r^3} \left[\overline{I}_1 \cdot \overline{I}_2 - 3 \left(\overline{I}_1 \cdot \overline{r} \right) \left(\overline{I}_2 \cdot \overline{r} \right) / r^2 \right]$$

gives origin to the different terms of the dipolar alphabet when rewritten in polar coordinates.

2) Calculate the matrix representing each one of the terms in the dipolar alphabet for a 2-spin system. Specify which spin states are connected by each one of the terms of the dipolar alphabet.

3) Truncation by the Zeeman Hamiltonian: Demonstrate that given two Hamiltonians, $\mathcal{H}_0$ (usually the Zeeman Hamiltonian) and $\mathcal{H}_1$ with $\|\mathcal{H}_0\| \gg \|\mathcal{H}_1\|$ the energy levels arising from a first-order perturbative treatment of $\mathcal{H}_1$ are the same as those obtained by considering a truncated Hamiltonian $\mathcal{H}_1^t$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1^t$$

where $\mathcal{H}_1 = \mathcal{H}_1^t + \mathcal{H}_1^{nc}$; $[\mathcal{H}_0, \mathcal{H}_1^t] = 0$; $[\mathcal{H}_0, \underbrace{\mathcal{H}_1^{nc}}_{non-commuting}] \neq 0$

($\mathcal{H}_1^t$ is the part of $\mathcal{H}_1$ that commutes with $\mathcal{H}_0$).

4) The direct product: Calculate the x-, y- and z-components of the total angular momentum F for a two spin 1/2 particle system. Show that these components fulfill the commutation realtionships of angular momenta.

5) Calculate the maximum number of NMR peaks that can arise from a homonuclear 4-spin system
   i) if the spins are not coupled among them.
   ii) if the spins are coupled among them.

6) Demonstrate that for a 2-spin system the signal acquired after a $(\pi/2)$ pulse is given by resonances whose intensities are

$$A_{mm''} \propto |\langle m|F_+|m''\rangle|^2$$

How will these intensities change if a (β) pulse is used?

7) **A homonuclear coupled spin pair:** Calculate the frequencies and intensities arising from a homonuclear dipole-coupled spin pair as a function of $\Sigma \approx -1/2(\omega_0^1 + \omega_0^2)$, $\Delta = \omega_0^1 - \omega_0^2$, ω_D.

8) Demonstrate that the angular part of the dipole coupling averages to zero upon fast isotropic rotation.

9) **A semi-classical model of shielding:** Consider a system composed by a single 1s electron that can move freely within a sphere of radius a_0 (the Bohr radius). Calculate the order of magnitude of the chemical shielding produced by this electron at the position of the nucleus when the system is placed inside a magnetic field B_0.

10) **The δ-scale:** Fill out the following table calculating Δv or δ for each given value of δ or Δv:

spin system	v_0(MHz)	Δv (Hz)	δ (ppm)
^{1}H at 7 T			1
^{13}C at 2.35 T		2500	
^{1}H at ?	500.4		10
^{31}P at 11.7 T			5.3
^{1}H at 11.7 T			5.3

11) Given an NMR spectrometer operating at 7 T, schematize the NMR spectra arising from the following spin systems (use the δ-scale):

    i) 4 ^1H NMR resonances appearing 300 Hz, 600 Hz, 728 Hz, and 2000 Hz above the TMS resonance.

    ii) 4 ^{13}C NMR resonances appearing -300 Hz, -600 Hz, -728 Hz, and -2000 Hz below the benzene resonance (δC_6H_6 = 128 ppm with respect to TMS).

12) Considering that the frequency dispersion of resonances in ^1H and ^{13}C NMR spectra are ca. 10 ppm and 200 ppm respectively, and that ^{13}C NMR lines have ca. 1/4 the line width of ^1H NMR peaks (in Hz):

    i) Compare the resolution power R

$$R = \frac{\text{total frequency dispersion of peaks (Hz)}}{\text{line width of one peak (Hz)}}$$

    of ^1H and ^{13}C NMR.

    ii) At what field is the resolution power of ^1H NMR comparable to that characterizing a ^{13}C NMR experiment performed at 25.1 MHz, assuming that the line widths are independent of the field.

13) A ^1H NMR experiment is performed at 300 MHz on a sample possessing 2 inequivalent sites A and B with δ_A = 4 ppm, δ_B = 6 ppm downfield (i.e., at higher frequencies) from TMS. Calculate the first 8 points of the resulting FID assuming that: the transmitter was placed at δ = 5 ppm; a spectral width of 12 ppm is used; relaxation effects can be neglected; the initial x-y magnetizations of the 2 sites after the pulse are $M_A = M_B = 1 \cdot \hat{x}$.

14) **The Karplus Equation:** $J^3_{H,H}$ coupling constants measured in cyclohexanes are usually the average of two J^3, each one arising from a different chair con formation:
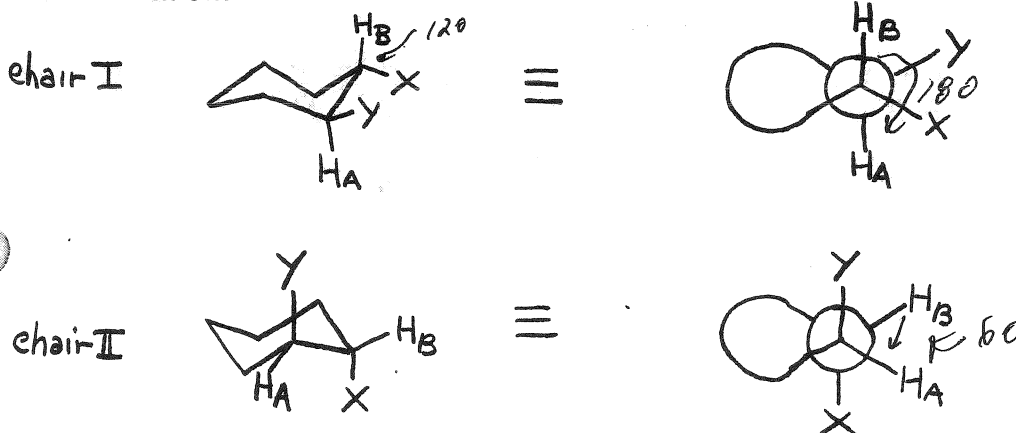
i) Estimate $J^3_{H_A, H_B}$ for each conformation.

ii) A $J^3_{H_A, H_B} = 7$ Hz is oberved for a substituted cyclohexane. Assuming that this value is the average of the two $J^3_{H_A, H_B}$ calculated in part i), estimate the relative population of each cyclohexane conformer.

15) Make a bar-graph sketch of the ^1H NMR spectrum (100 MHz) arising from the following compound; indicate the relative peak intensities and mark the peak positions in the δ-scale.

$\nu = 667$ $J = 3.6$ $\nu = 723$

$J = 1.7$ $J = 1$

$\nu = 781$ $J = 1$ $\nu = 966$
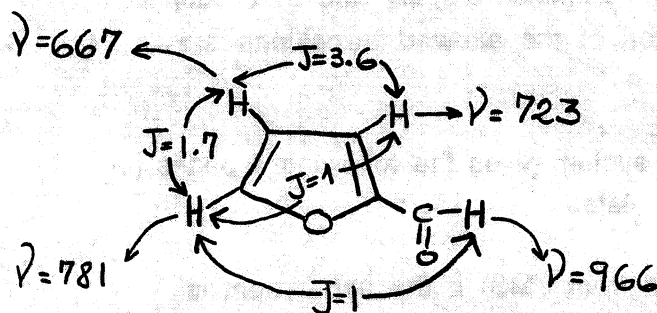
All frequencies are in Hz from TMS; all J's are in Hz; if not given, assume J = 0.

16) First-order multiplets: What are the relative peak intensities of the multiplet arising from a spin I coupled to

→ 1 spin S
→ 2 spins S
→ 3 spins S
→ 4 spins S
→ 5 spins S

In all cases, assume first-order couplings.

17) The perturbative approach to J couplings: Consider a homonuclear pair of spins A,B indirectly coupled by a coupling J and resonating Δ Hz apart. Using the expression of the spin eigenfunctions corrected by a first-order perturbative treatment of J:

$$|i\rangle^{(1)} = |i\rangle^{(0)} + J \sum_{|j\rangle^0 \neq |i\rangle^0} \frac{\langle i | \vec{I}_A \cdot \vec{I}_B | j \rangle^{(0)}}{E_i^0 - E_j^0} \qquad \{|i\rangle^0\} = \{|\alpha\alpha\rangle, \ldots, |\beta\beta\rangle\}$$

Calculate the second-order perturbative correction to the energy levels

$$E^{(2)} = {}^{(0)}\langle i | \mathcal{H}_J | i \rangle^{(1)}$$

and the expected shifts in NMR frequencies.
Assume $\Sigma = 0$

18) **Magnetic Equivalence:** Calculate the spectral frequencies arising from an A_2B system characterized by chemical shift frequencies ω_A, ω_B and by a coupling constant J. Demonstrate that the frequencies of the allowed transitions are independent of the A-A J coupling.

19) The 60 MHz ^1H NMR spectrum of an AB system gives the following 4 peaks (in Hz from TMS): 423, 418.5, 416, 411.5. Calculate:
    i) δ_A, δ_B (in ppm) and J (Hz)
    ii) the position of the four peaks (in Hz from TMS) if the experiment is recorded at 300 MHz.

20) Construct the Hamiltonian matrix for an ABX system. Can this matrix be diagonalized in an analytical way?

21) **The A_n spin theorem:** Demonstrate that given an A_nB system of n completely equivalent nuclei A and another nucleus B, the indirect J-coupling between the A nuclei is invisible in the NMR spectra of either A or B.

   Hint: Write your total Hamiltonian as

$$\mathcal{H}_{total} = \mathcal{H}_{cs}(A) + \mathcal{H}_{cs}(B) + \mathcal{H}_J(A\text{-}B) + \mathcal{H}_J(A\text{-}A)$$

   then demonstrate and exploit the fact that $\mathcal{H}_J(A\text{-}A)$ commutes with all the remaining terms.