1/2/2024

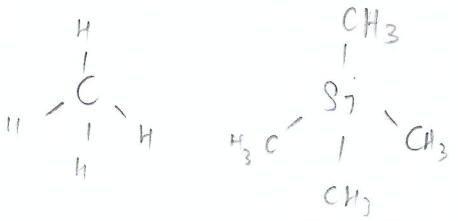
NMR Problem set / summary

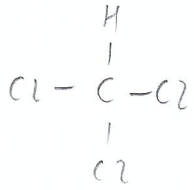
- how to self-study ? = how to discover ?

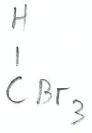
↳ create your own easier problems / examples / thought experiments
(Ms Rathi's problems are too hard)

↳ draw ! play around !

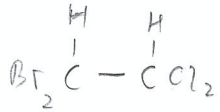
read !
use problems to summarize what you've learnt







just draw ! create !



$CH_3 - CH_2 - CH_3$

$CH_3 - CH_2 - CH_2Cl$

$CH_2Br - CH_2 - CH_2Cl$?!

FUN !

- Don't try to memorize/understand all the facts Ms. Rathi is giving us. Instead, what problems did Rabi / Bloch try to solve ? how can you rediscover the facts Ms. Rathi is saying ?

- Read more ! start from :
→ Wikipedia (recommends books !)
→ Experimental organic chemistry books
→ search up spectra of : 3-bromo-1-chloropropane, (1-)Chloropropane

if you don't understand, try making problems !

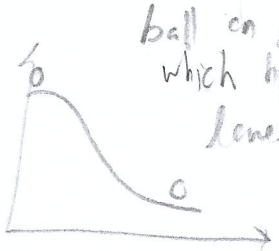
NMR homework / summary

1. how is it measured?

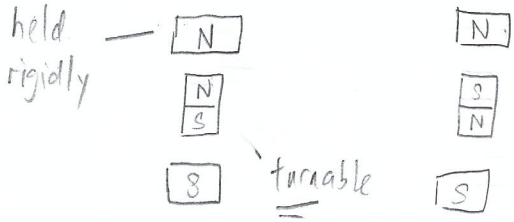
Tip: Wikipedia : history of NMR

2. which ones NMR-active / absorbs / "responds"

^{1}H, $^{2}_{1}D$, ^{12}C, $^{13}_{6}C$



3. Which one has higher energy? which one once turned, through small angle
- returns to original position?
- which one would not return to original position?

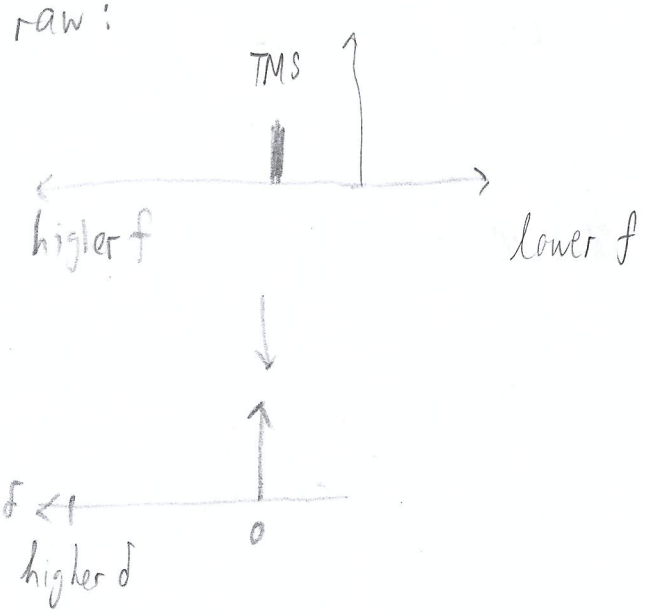


P.s. like poles repel, unlike, attract

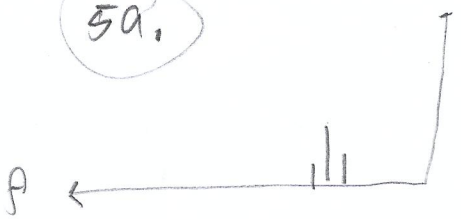
4. What do raw spectra look like?

(read up on data reduction how to...)

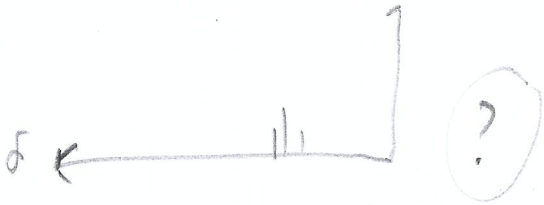
raw:



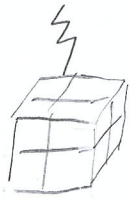
5a.



how does spectrum change when B-field ↑ ?
(shift to higher / lower f ?)



5b. Faraday cage ⟷ lightning rod.



outside: strong E-field
inside: weak E-field

what do you think of:

bare proton H

same e-

Lots of e- ?

metals have conduction e- too!
many e- !

5c. Suppose we have a mixture of:

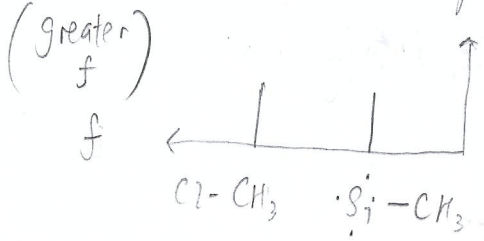
$Cl-CH_3$ $\cdot\dot{S}i-CH_3$

↑ electronegative

↑ electropositive

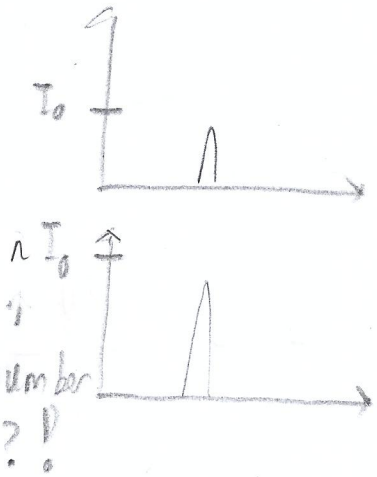
who's (H) has more / less e- density ?
who's (H) experience stronger / weaker B ?
who's (H) needs more / less energy to flip ?
who's (H) needs greater / smaller freq. (f) to flip ?

→ what's the spectra ?



6. idea of splitting: thought experiments:

- 6a): (H) single free H

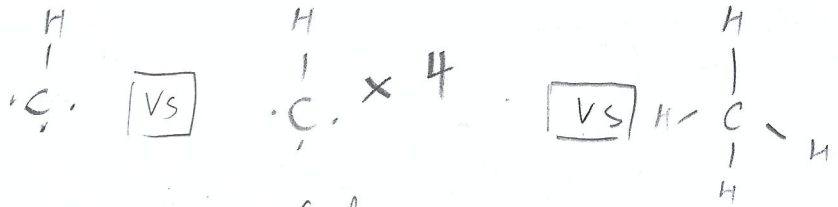


how do their intensity compare?

how many times the other?

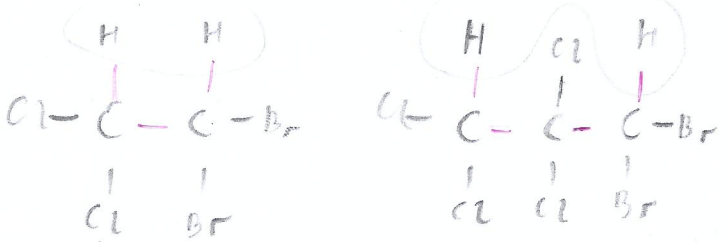
3 free H's (H) (H) (H)

6b): imagine:

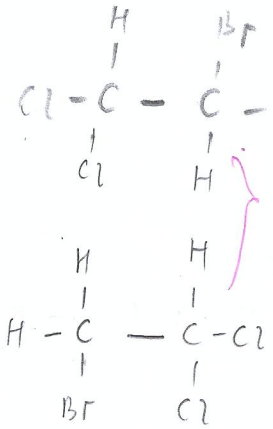


(of course, these two slightly diff. environment, but otherwise ... same?)

6c): imagine:



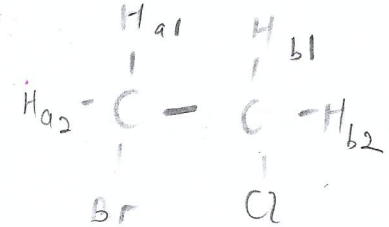
which ones interact more?



can these interact?

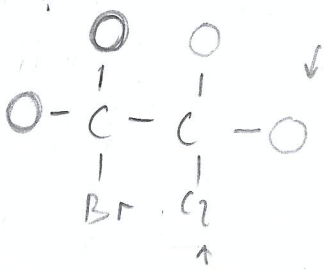
"wires"

6d): imagine:



are H_{a1} & H_{a2} "equivalent"?

H_{a1} & H_{b1} ?

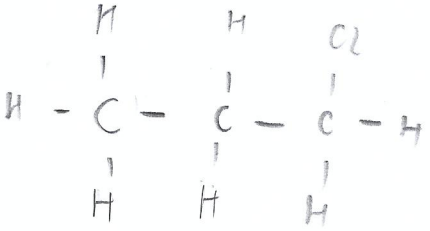


more e⁻ deficient

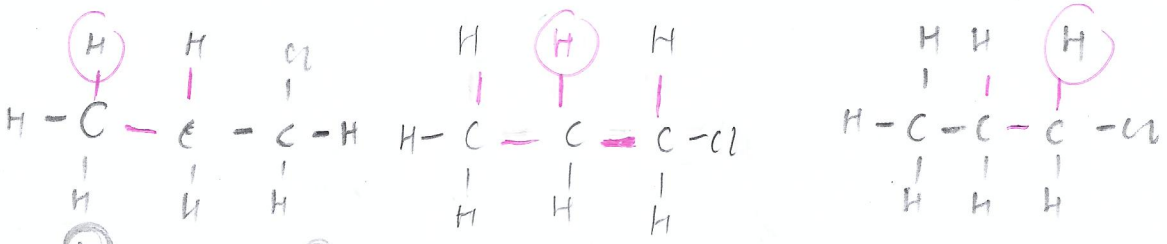
more electronog.

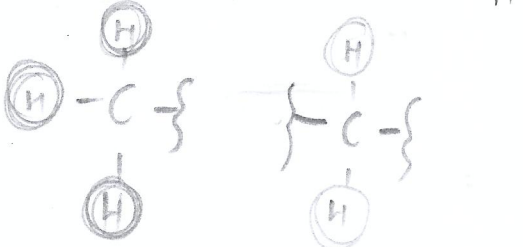
How would you define equivalence? e⁻ density?

6e):



how many "environments?"

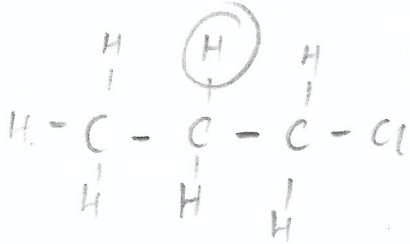


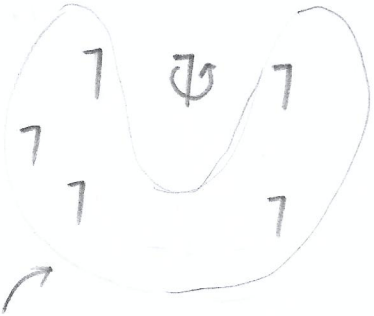


(equivalent protons)

distance to Cl ??

see 2nd one:

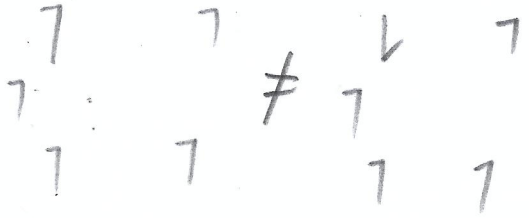


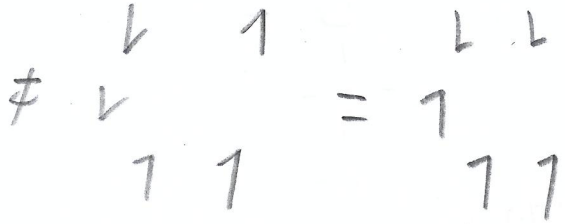


we target the circled H !:

"environment"

substructure of environment: how many such substructures?





all have 5 neighbours, but... ⟶ (no. of H's with 1... etc)

frequency sweep: as we sweep, only equivalent H will flip together at a specific freq.

idea: $n_1 + n_2$ = total no. of "neighbours"

$$(\uparrow + \downarrow)^n = \binom{n}{0}\uparrow^n + \binom{n}{1}\uparrow^{n-1}\downarrow + \binom{n}{2}\uparrow^{n-2}\downarrow^2 + \cdots + \binom{n}{n}\downarrow^n$$

like $(x+y)^n$

notice how each term is different (like xy^3 vs x^2y^2)

$\binom{n}{r}$ counts the multiplicity. (no. of equivalent)

i.e. $\downarrow\downarrow$ $\quad$ $\downarrow\uparrow$ $\quad$ $\uparrow\uparrow$

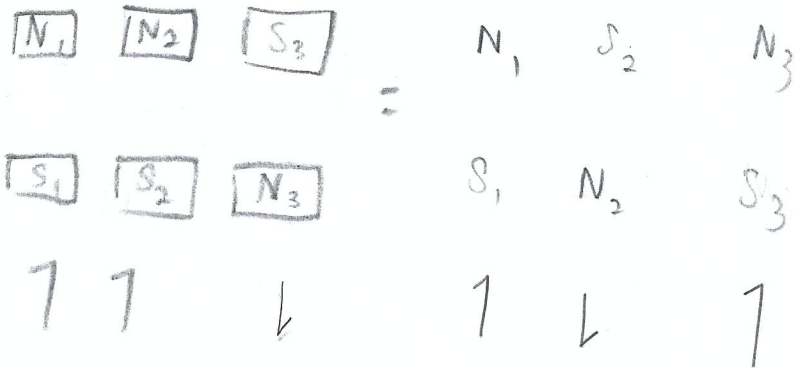
count. $\uparrow\uparrow$ $\quad$ $\downarrow\uparrow$ $\quad$ $\uparrow\downarrow$

one , two , three , ... , $\binom{5}{2}$

why are they equivalent? ... $\uparrow\uparrow$

a bad analogy:

imagine each $\uparrow\downarrow$ as magnets



$\uparrow\uparrow$ $\quad$ $\downarrow$ $\quad$ $\uparrow$ $\quad$ $\downarrow$ $\quad$ $\uparrow$

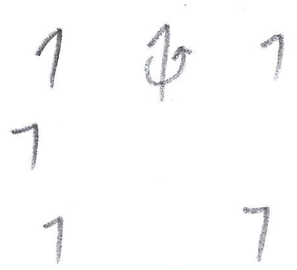
$B_{net} = B_1 + B_2 + B_3$ (magnetic fields add / superposition)

only B_{net} matters, so:

$\uparrow\uparrow\downarrow = \uparrow\downarrow\uparrow = \downarrow\uparrow\uparrow$

(B_{net} due to H's only / chemical environment; still get B_{ext} due to NMR machine!)

now put all together:



↻ = this one will be flipping around

the flipping guy

: ⇅ ↑↑↑↑↑

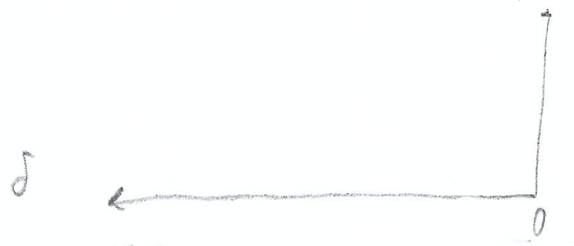
5+1 combinations: = 6

↑↑↑↑↑
↓↓↓↓↓
↑↑↑↑↓ → permutation equivalent #
↑↑↑↓↓
↑↑↓↓↓
↑↓↓↓↓

$\binom{n}{0}, \binom{n}{1}, \dots, \binom{n}{n}$

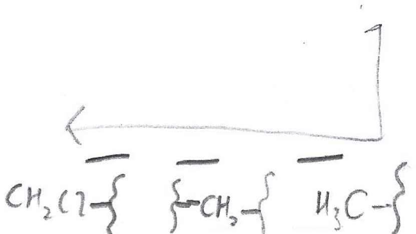
n+1 distinct terms

now, predict spectra:

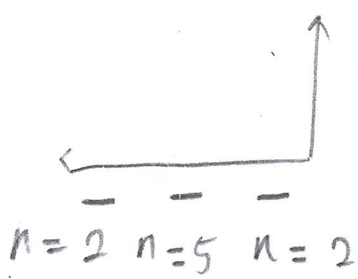


① rank according to shielding ⇔ electroneg.

e-deficient



② splitting: "n+1"



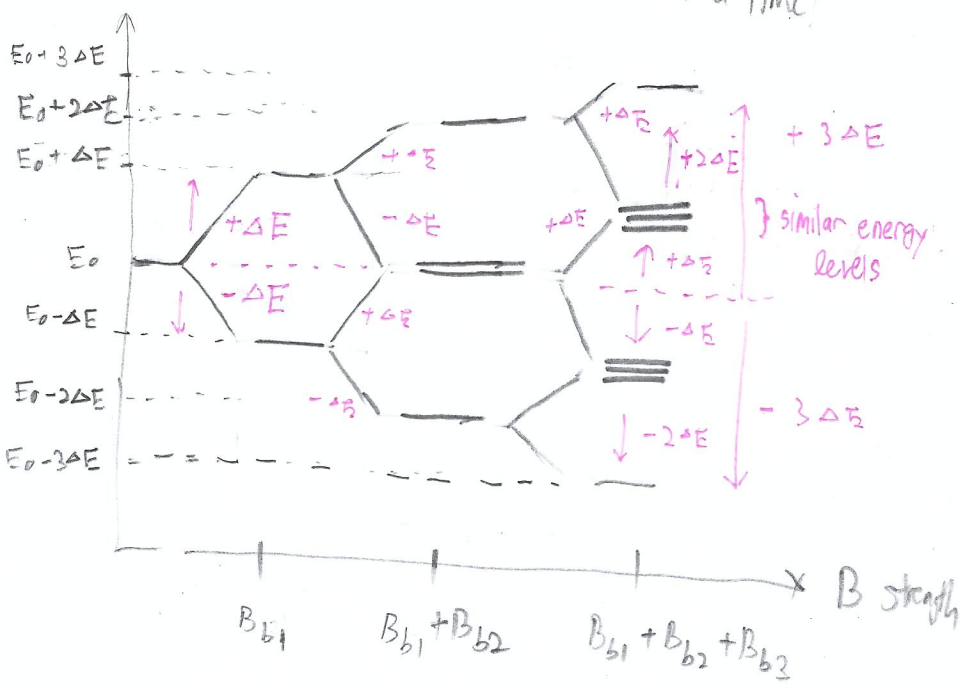
energy splitting

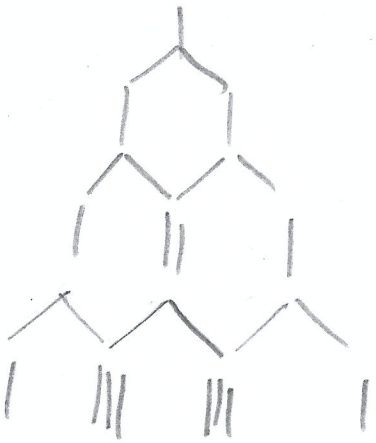
H_A H_{B1} H_{B2} H_{B3} (A is flipping)

how to count no. of lines & intensity ?

build up the $B_{net} = B_{b1} + B_{b2} + B_{b3}$

one field at a time!





1 1 1

1 2 1

1 3 3 1

(count no of vertical lines)

P.S. what if

H_A H_{B1} H_{B2} H_{C1} ??

then we need $\pm\Delta E_B$, $\pm\Delta E_C$? try !