Lecture 31

Nuclear Magnetic Resonance

Study Goal of This Lecture

- Energy levels
- Chemical shifts
- Coupling and spectrum of two spins

31.1 About NMR

There are few points about the content we are going to introduce:

- NMR can be a stand-alone course.
- It is a very-very useful tool on chemistry, from organic/inorganic chemsitry to characterization of biological systems.
- We are not going to touch on assignments of peaks, we will focus on physical principle here.
- Brief introduction on the quantitative description using QM.

We have actually covered the basic needed for today's discussions. Recall that we said "spin looks like angular momentum" and stated that an electron spin actually interacts with magnetic field via electron spin magnetic dipole moment

$$\hat{\mu}_s = -\frac{g_e e}{2m_e}\hat{S}, \tag{31.1}$$

$$\hat{S} = \hat{S}_x \cdot \hat{x} + \hat{S}_y \cdot \hat{y} + \hat{S}_z \cdot \hat{z}, \tag{31.2}$$

when interacting with a magnetic field along the $\hat{z}$ direction, the interacting energy (Hamiltonian) is

$$\begin{aligned} \hat{H}_{int} = -\hat{\mu}_s \cdot \hat{B} = \hat{\mu}_z \cdot B \\ &= \frac{g_e e B}{2m_e}\hat{S}_z \\ &= g_e \frac{\mu_B}{\hbar} B\hat{S}_z. \end{aligned} \tag{31.3}$$

g_e is electron g factor(~ 2.002322) and μ_B is Bohr magneton, $\mu_B = \frac{e\hbar}{2m_e}$. Nuclei have spin too, although at very different energy scales. Use the same arguments, we define nuclear spin operator $\hat{I}$

$$\hat{I} = \hat{I}_x \cdot \hat{x} + \hat{I}_y \cdot \hat{y} + \hat{I}_z \cdot \hat{z}. \tag{31.4}$$

Then nuclear magnetic moment μ:

$$\mu = \frac{g_N e}{2m_p}\hat{I} = g_N \mu_N \hat{I}\frac{1}{\hbar}. \tag{31.5}$$

g_e is nuclear g factor, m_p is proton mass and μ_N is nuclear magenton. μ_N inversely depends on mass, $\mu_N/\mu_B = \frac{m_e}{m_p} \simeq \frac{1}{2000}$. Nuclear magnetic interactions is 3 orders of magnitude smaller than electron magnetic interactions. (MHz v.s. GHz)

Very often one uses the nucleus' magnetogyric ratio γ to describe μ:

$$\hat{\mu} = \gamma\hat{I} \Rightarrow \gamma = g_N \mu_N \frac{1}{\hbar}, \tag{31.6}$$

γ indicates how strongly a nuclei coupled to magnetic field $\Rightarrow$ it is a form of "coupling constants". Later, we assume $\gamma > 0$. (It can be negative, e.g. ^{15}N)

Selected nuclie that have strong magnetic properties:

Nucleus	Abundance	Spin Quantum number I	$\gamma(10^7 T^{-1} s^{-1})$	Lamor ν for $1T$ (MHz)
^{1}H	99.99	1/2	26.75	42.58
^{2}D	0.01	1	4.11	6.54
^{13}C	1.11	1/2	6.73	10.7
^{19}F	100	1/2	25.18	40.05
^{31}P	100	1/2	10.841	17.24

The interacting Hamiltonian with an external magnetic field:

$$\hat{H} = -\hat{\mu} \cdot \vec{B} = -\hat{\mu_z} B = -\gamma B \hat{I}_z, \tag{31.7}$$

therefore, for a spin $\frac{1}{2}$ nucleus with spin function $|\alpha\rangle, |\beta\rangle$

$$\hat{I}^2 |\alpha\rangle = \frac{1}{2}(\frac{1}{2}+1)\hbar^2 |\alpha\rangle = \frac{3\hbar^2}{4} |\alpha\rangle, \tag{31.8}$$

$$\hat{I}^2 |\beta\rangle = \frac{3\hbar^2}{4} |\beta\rangle, \tag{31.9}$$

$$\hat{I}_z |\alpha\rangle = \frac{\hbar}{2} |\alpha\rangle, \tag{31.10}$$

$$\hat{I}_z |\beta\rangle = \frac{-\hbar}{2} |\beta\rangle. \tag{31.11}$$

31.2 Larmor Frequency

If there is no magnetic field, the system is doubly degenerate. It splits as magnetic field is turned on:

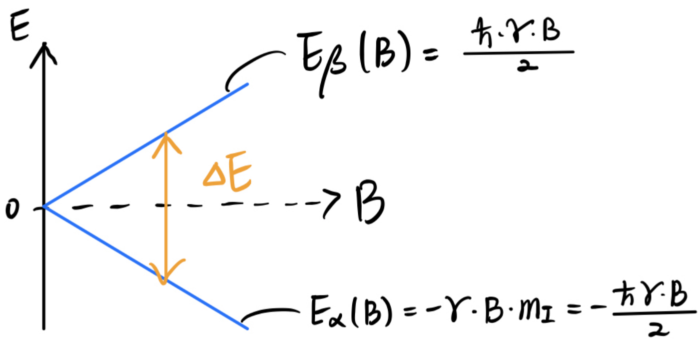

Figure 31.1: Splitting due to external magnetic field.

The transition occurs at a fixed magnetic field

$$\Rightarrow \Delta E = E_\beta(B) - E_\alpha(B) = \hbar\gamma B \equiv h\nu \tag{31.12}$$

correspond to a frequency of

$$\nu = \frac{\gamma B}{2\pi} \tag{31.13}$$

this is Larmor frequency.

The above result is for a single spin and it is looked from microscopic view. In real world, we deal with a bunch of spins → we measure macroscopic quantity, so the consideration of ensemble is required.

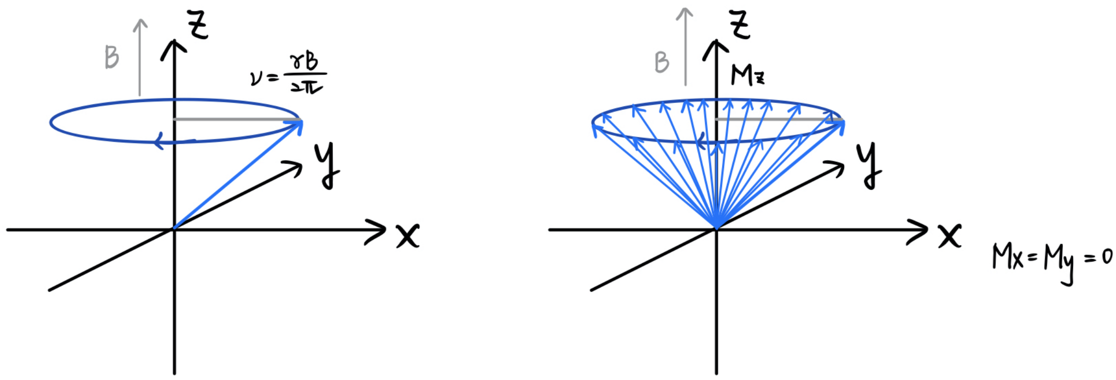

Figure 31.2: Free precessing for spin.

The measurable quantity is magnetization M, so it is important to write that "Bulk magnetization"

$$M_i = \langle \hat{\mu}_i \rangle \times d, \tag{31.14}$$

$$M_x = M_y = 0, \quad M_z \sim N_\alpha \frac{\hbar}{2} - N_\beta \frac{\hbar}{2} \sim (N_\alpha - N_\beta), \tag{31.15}$$

in general,

$$\frac{N_\alpha}{N_\beta} = exp(\frac{-\Delta E}{k_B T}) = exp(\frac{-\hbar\gamma B}{k_B T}) \simeq 1 - \frac{\hbar\gamma B}{k_B T}. \tag{31.16}$$

For example, a proton in a B field of 1 Tesla at room temperature

$$\frac{\hbar\gamma B}{k_B T} \simeq 6.86 \times 10^{-6}, \tag{31.17}$$

this is a very small amount, so the signal of NMR is very weak. Practically, it requires large magnetic field to increase the signal intensity.

31.3 Chemical Shift

NMR is useful, sensitive to chemical enviroment of a nucleus, because electrons moving around a nucleus tend to "shield" magnetic field, just like the screening of charges that we discussed before. This shielding effect can be taken into account by considering

$$B = B_0(1 - \sigma_i), \tag{31.18}$$

thus, the characteristic Larmor frequency for each nucleus becomes different

$$\nu_i = \frac{\gamma B_0}{2\pi}(1 - \sigma_i). \tag{31.19}$$

Note that the energy shift depends on magnetic field. In NMR, we use a reference compound to define the standard, for example: TMS (tetramethylsilane) is used for $^1H,^{13}C,^{29}Si$

$$\nu_{ref} = \frac{\gamma B_0}{2\pi}(1 - \sigma_{ref}), \tag{31.20}$$

therefore, the energy shift is

$$\nu_i - \nu_{ref} = \frac{\gamma B_0}{2\pi}(\sigma_{ref} - \sigma_i). \tag{31.21}$$

More often we define a field-independence spectroscopic indicator:

$$\frac{\nu_i - \nu_{ref}}{\nu_{ref}} = (\sigma_{ref} - \sigma_i) = 10^{-6} \cdot \delta_i \tag{31.22}$$

note that chemcial shift is independent of magnetic field, which makes it useful for assignment.

31.4 Splitting Pattern

In addition to chemcial shift, splitting patterns are also important for assignments:

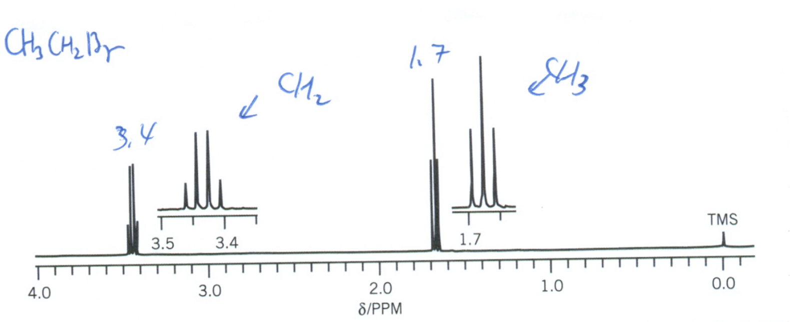

Figure 31.3: ^1H-spectrum of CH_3CH_2Br. Note the splitting pattern.

This splitting is due to coupling with neighboring spins $\Rightarrow$ spin-spin coupling(J). It will result in energy splitting of spins depending on the total spin magnetic quantum number of the neighboring spin. i.e. For n $\frac{1}{2}$-neighbor spins, the NMR line splits into $n+1$ lines. This is simply adding up $m_I = \pm\frac{1}{2}$ for each additional spin.

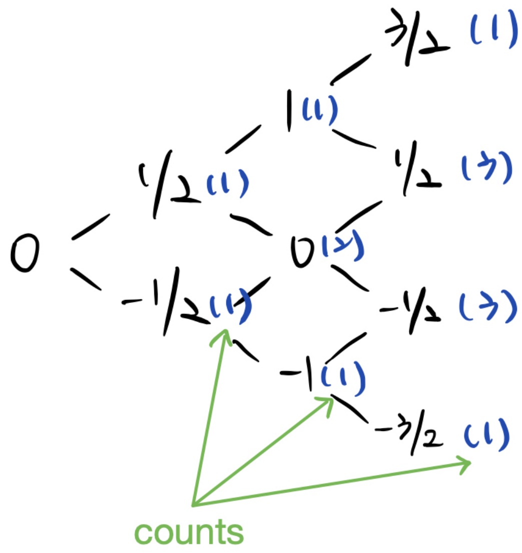

Figure 31.4: Splitting pattern.

The intensity of each split is proportional to count in above diagram. Now we ask a interesting question: Why two adjacent hydrogen do not affect each other?

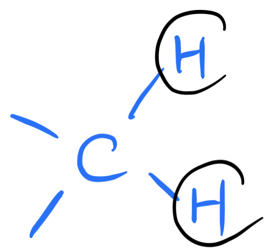

Figure 31.5: Two adjacent hydrogen.

We consider spin-spin splitting in a system of two coupled spins:

$$\begin{aligned}\hat{H} &= -\gamma B_0(1-\sigma_1)\hat{I}_{z1} - \gamma B_0(1-\sigma_2)\hat{I}_{z2} + \frac{2\pi J_{12}}{\hbar}\hat{I}_1\hat{I}_2 \\ &= E_1\hat{I}_{z1} + E_2\hat{I}_{z2} + \frac{2\pi J_{12}}{\hbar}\hat{I}_{z1}\hat{I}_{z2} + \frac{2\pi J_{12}}{\hbar}(\hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2}).\end{aligned} \tag{31.23}$$

$J_{12} > 0$, spin tends to anti-parallel to each other, anti-ferromagnetic.

$J_{12} < 0$, spin tends to parallel to each other, ferromagnetic.

For two spin$-\frac{1}{2}$ nuclei, there are totally 4 states. A basis is:

$$\begin{aligned}\psi_1 &= \alpha(1)\alpha(2), \\ \psi_2 &= \beta(1)\alpha(2), \\ \psi_3 &= \alpha(1)\beta(2), \\ \psi_4 &= \beta(1)\alpha(2).\end{aligned} \tag{31.24}$$

This basis is suitable for small J. (i.e. well seperate nucleus.) Note that $\hat{I}_{z1}$, $\hat{I}_{z2}$, $\hat{I}_{z1}\hat{I}_{z2}$ are diagonal in this basis, while the $\hat{I}_{x1}\hat{I}_{x2}, \hat{I}_{y1}\hat{I}_{y2}$ terms are off-diagonal. In this limit

$$\Delta E = |\gamma B_0(\sigma_1 - \sigma_2)| >> \frac{2\pi J_{12}}{\hbar}, \tag{31.25}$$

then we can use perturbation theory to obtain

$$\begin{aligned}E_1 &= \langle\psi_1|\hat{H}|\psi_1\rangle = -h\nu(1 - \frac{\sigma_1+\sigma_2}{2}) + \frac{hJ_{12}}{4}, \\ E_2 &= \langle\psi_2|\hat{H}|\psi_2\rangle = -\frac{h\nu_0}{2}(\sigma_1-\sigma_2) - \frac{hJ_{12}}{4}, \\ E_3 &= \langle\psi_3|\hat{H}|\psi_3\rangle = \frac{h\nu_0}{2}(\sigma_1-\sigma_2) - \frac{hJ_{12}}{4}, \\ E_4 &= \langle\psi_4|\hat{H}|\psi_4\rangle = h\nu_0(1 - \frac{\sigma_1+\sigma_2}{2}) + \frac{hJ_{12}}{4}.\end{aligned} \tag{31.26}$$

The plot of energy levels splitting:

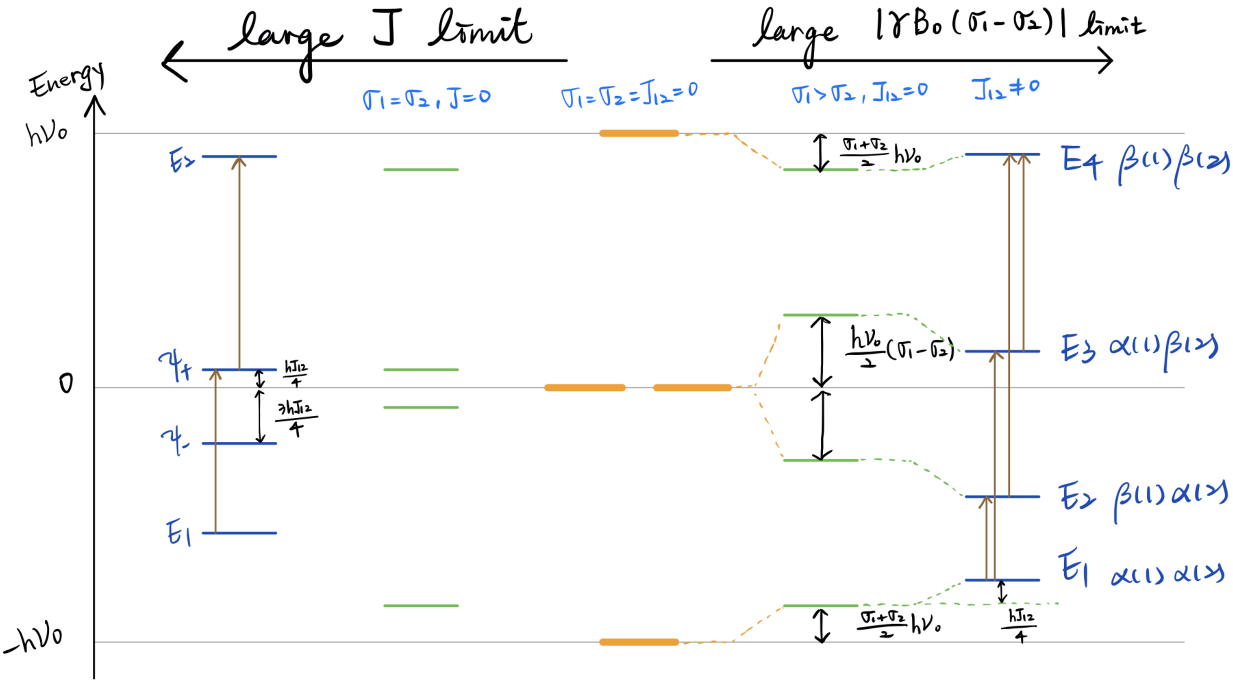

Figure 31.6: Splitting of energy levels.

Transition around the Larmor frequency ν_0 involves changing one spin, therefore the transitions:

$$
\begin{aligned}
\nu_{1\to 2} &= \nu_0(1-\sigma_1) - \frac{J_{12}}{2}, \\
\nu_{1\to 3} &= \nu_0(1-\sigma_2) - \frac{J_{12}}{2}, \\
\nu_{2\to 4} &= \nu_0(1-\sigma_2) + \frac{J_{12}}{2}, \\
\nu_{3\to 4} &= \nu_0(1-\sigma_1) + \frac{J_{12}}{2}.
\end{aligned}
\tag{31.27}
$$

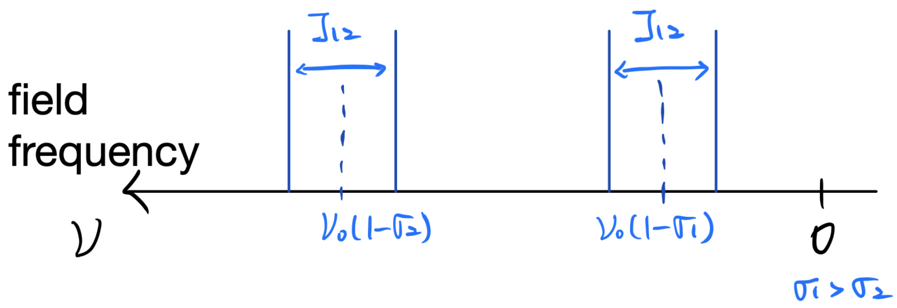

Figure 31.7: Splitting pattern on spectrum.

When in the opposite limit, $\frac{2\pi J_{12}}{\hbar} >> |\gamma B_0(\sigma_1 - \sigma_2)| \Rightarrow$ say $\sigma_1 = \sigma_2$

Large J limit, strong coupling, where first-order perturbation theory fails.

$$\hat{H} = \underbrace{-\gamma B_0(1-\sigma)(\hat{I}_{z1} + \hat{I}_{z2})}_{\substack{\text{a constant shift,} \\ \text{can be ignored.}}} + \frac{2\pi J_{12}}{\hbar}\hat{I}_1\hat{I}_2, \tag{31.28}$$

therefore, we must find eigenstates of $\hat{I}_1\hat{I}_2$.

We already know the eigenfunctions of $\hat{S}^2$

$$\begin{aligned} \phi_1 &= \alpha(1)\alpha(2), \\ \phi_- &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)], \\ \phi_+ &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)], \\ \phi_2 &= \beta(1)\beta(2). \end{aligned} \tag{31.29}$$

then, under strong coupling condition, the selection rule: (recall the transition is induced by $\hat{\mu_z}$, i.e. $\hat{I}_z$)

$$\langle\alpha(1)\alpha(2)|\hat{\mu}_z|\psi_+\rangle = \left\langle \alpha(1)\alpha(2) \middle| \hat{\mu}_z \middle| \frac{1}{\sqrt{2}}\alpha(1)\beta(2) + \frac{1}{\sqrt{2}}\beta(1)\alpha(2) \right\rangle \neq 0, \tag{31.30}$$

$$\langle\alpha(1)\alpha(2)|\hat{\mu}_z|\psi_-\rangle = \langle\alpha(1)|\hat{\mu}_z|\beta(1)\rangle - \langle\alpha(2)|\hat{\mu}_z|\beta(2)\rangle = 0, \tag{31.31}$$

and actually

$$\hat{H} = \begin{pmatrix} E_1 & 0 & 0 & 0 \\ 0 & E_2 & \frac{hJ_{12}}{2} & 0 \\ 0 & \frac{hJ_{12}}{2} & E_3 & 0 \\ 0 & 0 & 0 & E_4 \end{pmatrix}. \tag{31.32}$$

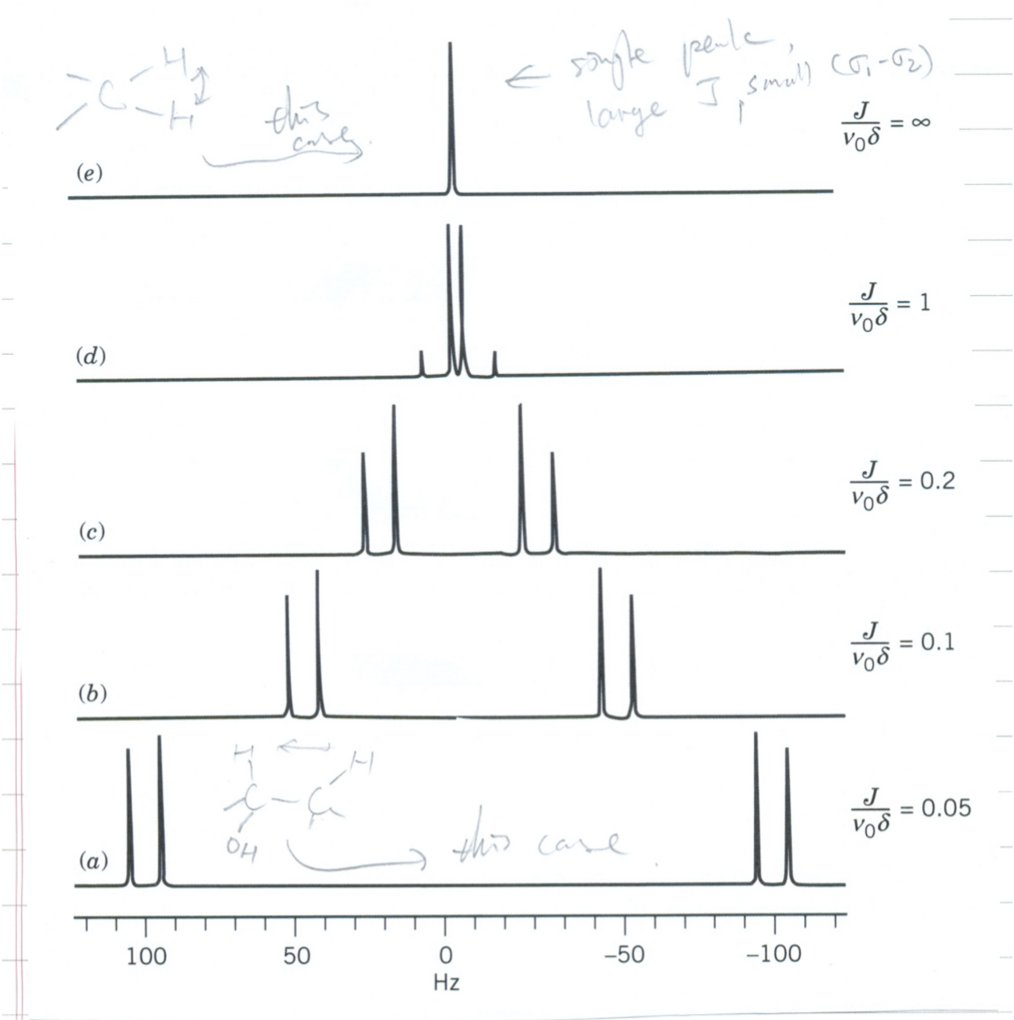

Figure 31.8: Splitting due to different coupling.