

# Magnetic Resonance Spectroscopy

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In our discussion of spectroscopy, we have shown that absorption of E.M. radiation occurs on resonance: When the frequency of applied E.M. field matches the energy splitting between two quantum states.

Magnetic resonance differs from these other methods in the sense that we need to immerse the same in a magnetic field in order to see the levels that we probe with an external (rf or  $\mu$ wave) field. (Two fields: Static magnetic and E.M.)

We will be probing the energy levels associated with the spin angular momentum of nuclei and electrons: NMR--nuclear magnetic resonance and ESR/EPR--electron spin resonance.

## **Angular momentum:**

In our treatment of rotational energy levels, we said that the energy levels depended on the rotational angular momentum,  $L$ , which was quantized:

$$\bar{L}^2 = \hbar^2 J(J+1) \quad J = 0, 1, 2, \dots \text{ rot. quant. number}$$

- Degeneracy of  $J$  was  $(m_j = 0, \dots, \pm J) \rightarrow (2J+1)$
- We related  $\bar{L}^2$  to the energy levels

$$E_{\text{rot}} = \frac{\bar{L}^2}{2I} \propto \bar{B}J(J+1)$$

Actually, **all angular momentum is quantized.**

If a particle can spin, it has A.M. and quantized  $E$  levels.

In particular, we also have to be concerned with the **spin of individual nuclei and electrons.**

You already know that electrons have...

**ORBITAL angular momentum**

$$\bar{M}^2 = \hbar^2 \ell(\ell + 1)$$

$\ell = 0, 1, 2, \dots$  orbital angular momentum quantum number

degeneracy of orbitals:  $2\ell + 1$  from...

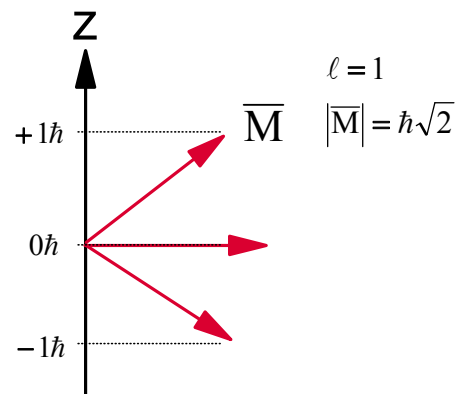
$m_\ell = -\ell, \dots, +\ell$  magnetic quantum number

$m_\ell$  represents the quantization of the components of  $M$ :

Projection of  $M$  onto  $\hat{z}$  axis:

$$M_z = m_\ell \hbar$$

(How we choose  $\hat{z}$  doesn't matter until we apply a magnetic field.)



Now, the angular momentum that we are concerned with is:

**Electron Spin Angular Momentum**

$$\bar{S}^2 = \hbar^2 s(s + 1)$$

$s$ : electron spin quantum number =  $\frac{1}{2}$

$\frac{1}{2}$  for each unpaired  $e^-$

$$S_z = m_s \hbar$$

$m_s : \pm \frac{1}{2}$  ( $-S, -S + 1, \dots, +S$ )

one unpaired  $e^-$

Two paired electrons:  $s = 0$ .

Two unpaired electrons (triplet):  $s = 1$ .

## **Nuclear spin angular momentum**

$$\vec{I}^2 = \hbar^2 I(I+1) \quad I: \text{ nuclear spin quantum number}$$

$$I_z = m_I \hbar \quad m_I: -I, -I+1, \dots, I$$

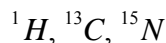
### **What is I ?**

- Each proton/neutron has a spin quantum number of 1/2.
- Spin of many nucleons add to give  $I$ .
- Pairing dictated by a shell model of nucleus.  
(analogous -not identical- to electron spin pairing)
- Protons and neutrons add separately.
- Spins pair up. Paired spins  $\rightarrow I = 0$ .

### **Some basic rules:**

1. For even number of protons plus even number of neutrons:  $I = 0$ .  $^{12}\text{C}$ ,  $^{16}\text{O}$
2. For mixed even/odd number of nucleons, spin is half-integer. ( $1/2 > I > 9/2$ )

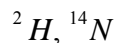
For one unpaired nucleon  $\rightarrow I = 1/2 \quad m_I = \pm 1/2 \quad \text{degeneracy } 2I + 1 = 2$



So the proton and electron are similar—both spin  $1/2$  particles. We'll talk about these two particles more specifically...

3. For odd/odd number of nucleons,  $I$  is integer  $> 0$ .

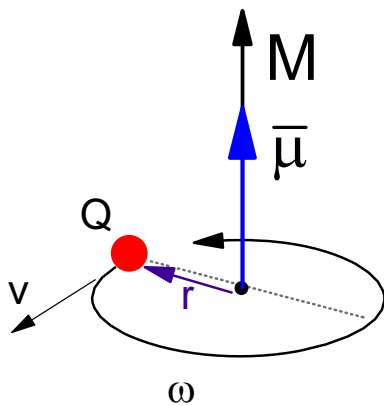
Two unpaired nucleons  $\rightarrow I = 1 \quad m_I = 0, \pm 1$



- For spin  $\frac{1}{2}$  particles ( $I$  or  $s = \frac{1}{2}$ ) there are two degenerate energy states.
- When you put these in a magnetic field you get a splitting.
  - A low energy state aligned with the field, and
  - A high energy state aligned against the field

### Classical picture:

- Think of our electron or nucleus as a charged particle with angular momentum,  $\bar{M}$ .
- A circulating charge produces a magnetic field.
- This charge possesses a magnetic dipole moment  $\bar{\mu}$  that can be affected by an applied magnetic field.



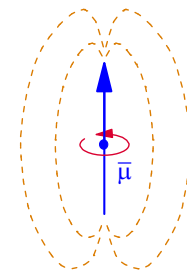
$$\bar{M} = m(\bar{v} \times \bar{r})$$

$$\bar{\mu} = Q(\bar{v} \times \bar{r}) / 2c$$

The dipole lies along  $\bar{M}$  and the strength of  $\bar{\mu}$  is proportional to  $\bar{M}$ :

$$\bar{\mu} = \frac{Q}{2mc} \bar{M} \equiv \gamma \cdot \bar{M}$$

$\gamma$  is the gyromagnetic ratio



### Quantum:

For electrons:

$$\bar{\mu}_e = \frac{-e}{2m_e c} g_e \bar{S}$$

g factor (2.0023)

$$= -\gamma_e \bar{S}$$

For nuclei:

$$\bar{\mu}_N = \frac{+e}{2m_N c} g_N \bar{I}$$

$g_N = 5.6$  for  $^1\text{H}$

$$= \gamma_N \bar{I}$$

$g$  is a relativistic quantum mechanical correction.

If we immerse this system in a magnetic field,  $\vec{B}$ , which is oriented along the  $z$  axis

The interaction potential is

$$E_{\text{int}} = -\vec{\mu} \cdot \vec{B}$$

The spins align along the magnetic field:

$$E_{\text{int}} = -\mu_z B$$

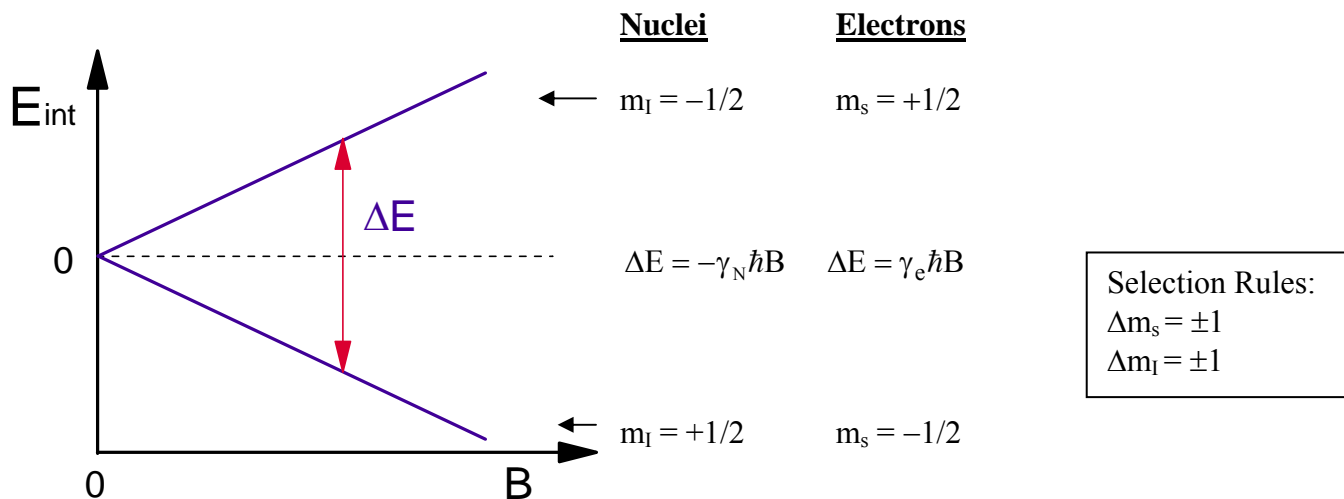
Since  $\mu_z = -\gamma_e S_z$  and  $\mu_z = \gamma_N I_z$ ,

using  $S_z = \hbar m_s$  and  $I_z = \hbar m_I$  we have

For electrons:  $E_{\text{int}} = \gamma_e \hbar m_s B$   $m_s = \pm \frac{1}{2}$

For nuclei:  $E_{\text{int}} = -\gamma_N \hbar m_I B$   $m_I = \pm \frac{1}{2}$

So, as we increase the magnetic field strength, the two energy levels – originally degenerate – split, one increasing in energy and one decreasing in energy. This is known as the **Zeeman effect**.



- Now we have a system that can absorb E.M. radiation on resonance:  $\Delta E = h\nu$
- $\nu$  is the applied frequency (in the radio frequency range)
- Frequency domain spectrometer: Typically sweep  $\mathbf{B}$  and hold  $\nu$  constant.

$$\nu = \frac{\gamma B}{2\pi} \quad (\text{Larmor frequency})$$

**Typical numbers:**

Nuclear Magnetic Resonance

Electron Spin Resonance

$$|\mu_H| = 2.8 \times 10^{-23} \cdot (\pm 1/2) \text{ erg/gauss}$$

$$|\mu_e| = -1.8 \times 10^{-20} \cdot (\pm 1/2) \text{ erg/gauss}$$

for B = 10 kG:

$$\nu = 42.6 \text{ MHz}$$

$$\nu = 28 \text{ GHz}$$

Typical:

$$300 \text{ MHz}/70 \text{ kG}$$

$$9.5 \text{ GHz}/3.4 \text{ kG}$$

Typical population difference  $\Delta N = (N_- - N_+)/ (N_- + N_+) \approx 0.005\%$  at 300 K for 300 MHz NMR. Cooling to 4 K gives you a factor of 75 in signal!

## The Chemical Shift

Thus far you would think that all  $^1\text{H}$  absorb at same frequency. Fortunately, in practice different nuclei absorb at frequencies that differ with chemically different species.

The resonance frequency depends on the “effective” magnetic field that a proton feels.

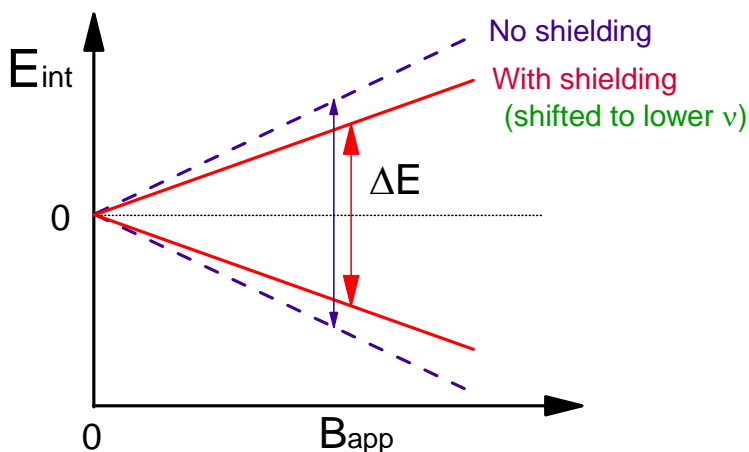
This can differ for different types of  $^1\text{H}$  due to local electron currents that counteract the applied field. → **Shielding**

$$B_{\text{eff}} = B_{\text{app}} (1 - \sigma)$$

$\sigma$ : screening constant  
typically  $10^{-6}$

$$\begin{aligned} E_{\text{int}} &= -\mu_{\text{N}} \cdot B_{\text{eff}} \\ &= -\gamma_{\text{N}} \hbar m_I B_{\text{app}} (1 - \sigma) \end{aligned}$$

$$\nu = \frac{\gamma B_{\text{app}}}{2\pi} (1 - \sigma)$$



Shift of frequency due to screening: Chemical Shift

Typically you measure the chemical shift due to screening relative to a standard (TMS).

$$\nu_i - \nu_{\text{ref}} = \frac{\gamma B_{\text{app}}}{2\pi} (\sigma_{\text{ref}} - \sigma_i)$$

Measure positions in  $\delta$ : ppm.  $10^{-6} \delta_i = \frac{\nu_i - \nu_{\text{ref}}}{\nu_{\text{ref}}} \approx (\sigma_{\text{ref}} - \sigma_i)$

The magnitude of the shielding depends on how the motion of electrons modifies the local field. (Interaction between field and electron angular momentum)

Qualitatively, proton NMR spectra can be interpreted by considering electronegativity of bound functional groups. Greater E.N. draws electrons away from  $^1\text{H}$ , lowering the resonance field and giving a larger  $\delta$ . Similar arguments can be used to describe trends with type of carbon bonding (HC-C, HC=C, or HC $\equiv$ C) or hydrogen bonding strength.

For protons shielding constants are approximately  $\sigma < 10^{-5}$  ( $\delta < 10$  ppm). Other nuclei have larger chemical shifts ( $\sigma < 10^{-3}$ ) because they have more electrons to screen the nucleus.

## Couplings between spins

Based on the effects of screening (chemical shift), we would expect one line for each nucleus in an NMR spectrum.

Actually there is usually additional structure, with each line split into several others. (Both in NMR and ESR)

- Splittings arise when different magnetic spins on nuclei and/or electrons interact with each other.
- The interactions change the spin energies to give new lines.
- Understanding the interaction allows you to reveal structural information such as connectivity.

The couplings between two magnetic dipoles can be written as  $E_{\text{coupling}} \propto \bar{\mu}_1 \cdot \bar{\mu}_2$ . For instance, the electrostatic interaction between two dipoles is proportional to factors that describe the dipoles' strength, orientation, and separation:  $\frac{\mu_1 \mu_2}{R_{12}^3} \langle 3 \cos^2 \theta - 1 \rangle$ .

There are a number of possible couplings between unpaired electrons ( $a, b, c, \dots$ ) and/or nuclear spins ( $i, j, k, \dots$ ):

	Spin Coupling		Coupling term
1.	Nuclear-nuclear (“J”) coupling	NMR	$\bar{\mu}_N(i) \cdot \bar{\mu}_N(j) = \gamma_N(i) \gamma_N(j) \bar{I}_i \cdot \bar{I}_j$
2.	Electron-electron (“fine”) coupling		$\bar{\mu}_e(a) \cdot \bar{\mu}_e(b) = \gamma_e \gamma_e \bar{S}_a \cdot \bar{S}_b$
3.	Electron-nuclear (“hyperfine”) coupling	ESR	$\bar{\mu}_e(a) \cdot \bar{\mu}_N(i) = \gamma_e \gamma_N(i) \bar{S}_a \cdot \bar{I}_i$

In general, the magnitude of these effects vary by orders of magnitude, since the magnitude of electron spin and nuclear spin dipoles ( $\gamma$ ) are so different.

$$E_{\text{fine}} \gg E_{\text{hfc}} \gg E_J$$

Let's examine the most important effects for NMR and ESR:



## NMR (#1)

### J-coupling: Interaction between protons:

$$E_{Jc} = h J_{ij} m_I(i) m_I(j) \quad m_I = \pm \frac{1}{2}$$

$J$ : nuclear spin coupling constant; typically 1-10 Hz.

**Note:** J-coupling is a nuclear-nuclear magnetic dipole coupling, but it does not refer to the direct through-space electrostatic interaction described on the previous page. Instead it is an indirect through-bond spin-spin interaction. For NMR in solutions, the direct interaction vanishes when you consider the fast rotation of molecules with respect to the magnetic field.

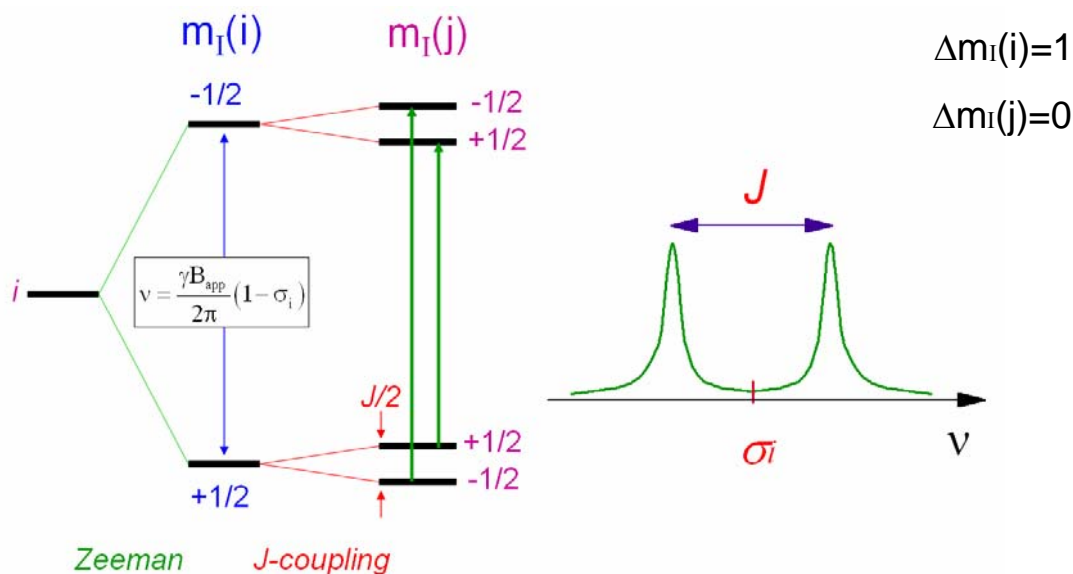
### Total nuclear interaction energy with spins

Sum of nuclear Zeeman interaction and J coupling:

$$E_{int} = E_{nZ} + E_{Jc}$$

$$v_i = -B_{app} \gamma_N(i) m_I(i) (1 - \sigma_i) + \sum_{i \neq j} J_{ij} m_I(i) m_I(j) \quad \begin{array}{l} m_I(i) = \pm \frac{1}{2} \\ m_I(j) = \pm \frac{1}{2} \end{array}$$

Coupling of a spin  $\frac{1}{2}$  nucleus to another spin  $\frac{1}{2}$  nucleus:



### ESR (#3)

**Dominant effect: hyperfine coupling**

$$E_{\text{hfc}} = h a_{\text{bi}} m_s(b) m_I(i)$$

$a$ : hyperfine coupling constant; typically 1-100 MHz

**Total interaction energy of electron and nuclear spins:**

$$E_{\text{int}} = E_{\text{eZ}} + E_{\text{hfc}} + \cancel{E_{\text{nZ}}} + \cancel{E_{\text{Jc}}}$$

$$v_b = -B_{\text{app}} \gamma_e m_s(b) (1 - \sigma_b) + \sum_{i,j,\dots} a_{\text{bi}} m_s(b) m_I(i) + \dots$$

Remember:

$$E_{\text{eZ}} \gg E_{\text{hfc}} \gg E_{\text{nZ}} \gg E_{\text{Jc}}$$

eZ = electron Zeeman  
hfc = hyperfine coupling  
nZ = nuclear Zeeman  
Jc = J coupling

Sum of electron Zeeman effect and hyperfine interaction. Nuclear Zeeman energy and J-coupling is relatively small in comparison.

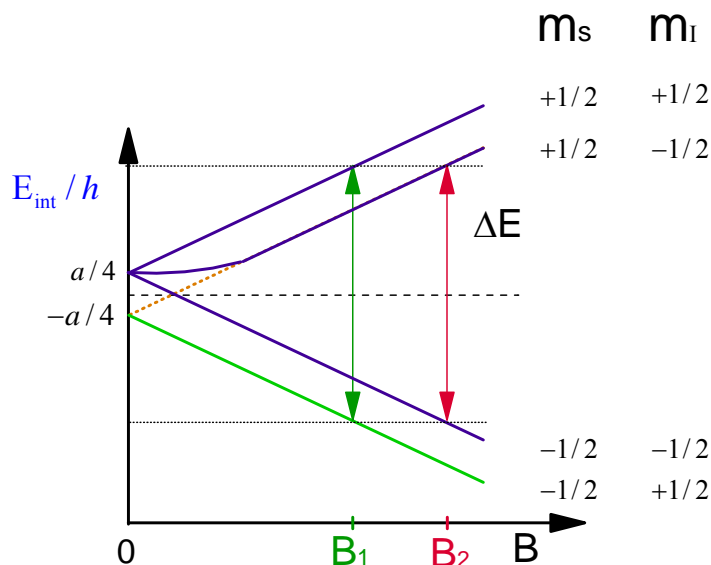
### ESR Example: H atom – 1 proton and 1 electron

$$\begin{aligned} E_{\text{int}} &= E_{\text{eZ}} + E_{\text{hfc}} \\ &= -\hbar B \gamma_e m_s + h a m_s m_I \end{aligned}$$

With no coupling: two states, with splitting as before.

With coupling:

$$m_s = \pm \frac{1}{2}; m_I = \pm \frac{1}{2} \quad \text{and} \quad m_s m_I = \pm \frac{1}{4}$$



$$\Delta m_s = 1$$

$$\Delta m_I = 0$$

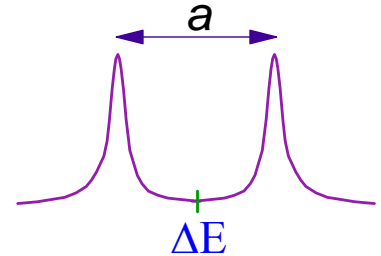
This is similar to the previous example:

At zero field: two states with energies  $E = +\frac{1}{4}\hbar a$  and  $E = -\frac{1}{4}\hbar a$

These correspond to  $\bar{F} = 0$  and  $\bar{F} = 1$ , where  $\bar{F} = \bar{S} + \bar{I}$  is the total spin angular momentum.  
( $M_F = -F \dots +F$ )

With increasing field, degenerate states split. By sweeping field with constant resonance frequency  $\Delta E = \hbar\nu$ , we see resonances at two fields,  $B_1$  and  $B_2$ .

$$B_1 = \frac{\Delta E - a/2}{\hbar\gamma_e} \quad \text{and} \quad B_2 = \frac{\Delta E + a/2}{\hbar\gamma_e}$$



so that the field splitting gives the hyperfine coupling:  $a = \hbar\gamma_e(B_2 - B_1)$

Alternatively, you could stay in a fixed field  $B$  and sweep the rf frequency  $\Delta E$ , and you would observe two resonances:

$$\Delta E / \hbar = \gamma_e B \pm a/2$$

Again the frequency splitting gives the hyperfine coupling.

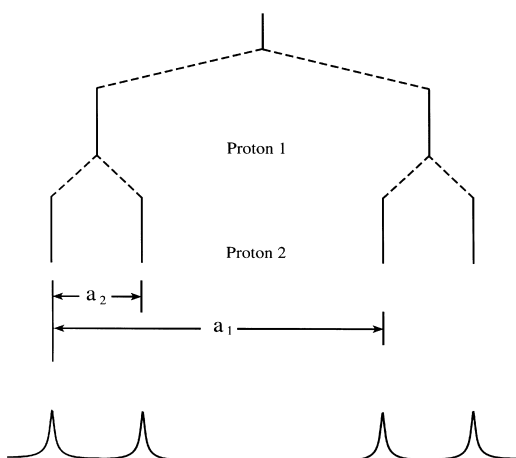
## Splitting Patterns

For multiple nuclei coupled to an unpaired electron

$$E_{\text{hfc}} = h \sum_{i,j,\dots} a_{bi} m_s(b) m_l(i)$$

We can expect each hyperfine interaction to split the remaining transition into a pair of peaks split by  $a$ . The overall spectrum can be predicted diagrammatically by a pattern of splittings in which one electron resonance is sequentially split in frequency by each hyperfine coupling interaction:

Two inequivalent couplings  $a_1$  and  $a_2$ :



Two equivalent couplings ( $a_1 = a_2$ ):

