



# ***1. Symmetry, Group Theory, and Electronic Structure***

## ***2. Ground State Spectroscopic Methods***

### **2.1 Nuclear Magnetic Resonance**

### 2.2 Electron Paramagnetic Resonance

### 2.3 Mössbauer Spectroscopy

## ***3. Excited State Spectroscopic Methods***

## ***4. Other Physical Methods***

### The Zeeman effect... the foundation of magnetic resonance

- effect of magnetic field ( $B$ ) on isolated nucleus with  $I > 0$ ?
  - nuclear spin (angular momentum) states will split (e.g.  $I = 3/2$ )
  - energy splitting of the nuclear wavefunction is determined by *nuclear Zeeman Hamiltonian*

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

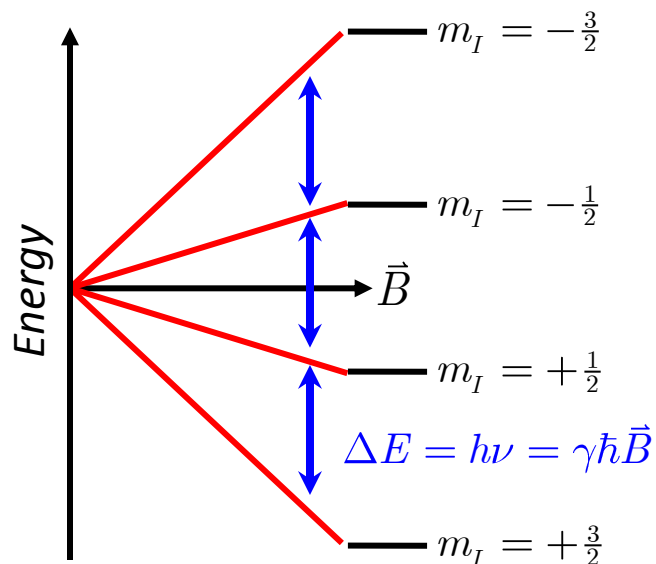
$\vec{\mu}$  = nuclear magnetic moment     $\vec{B}$  = magnetic field vector  
 $\gamma$  = gyromagnetic ratio             $\vec{I}$  = nuclear spin vector

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

$$= -\gamma\hbar B_0 m_I$$

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

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



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

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

### Classical Model for Nuclear Zeeman Effect

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

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

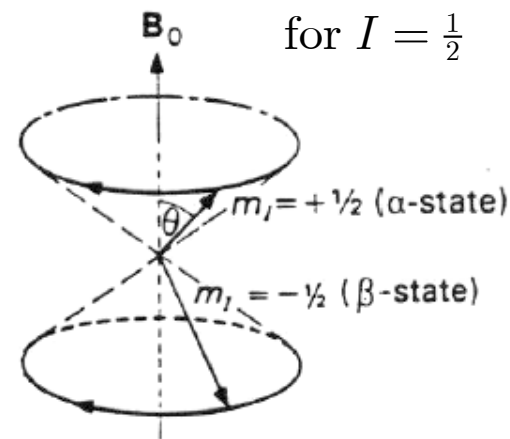
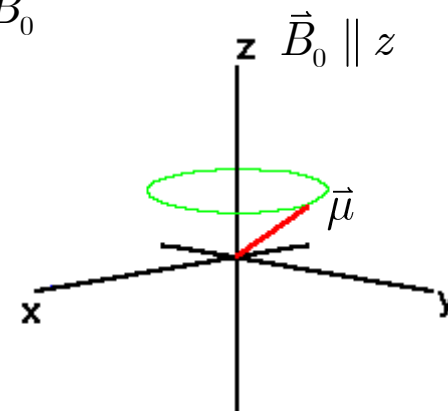
- cone angle depends on  $\mu$ , which depends on  $m_I$

- $2I+1$  different values
- also depends on  $\gamma$

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

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

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



## 2.1 Nuclear Magnetic Resonance

- define *classical* gyromagnetic ratio for any magnetic particle

- for  $e^- \rightarrow$  Bohr magneton 
$$\gamma_e = \mu_B = \frac{e\hbar}{2m_e} = 9.2741 \times 10^{-24} \text{ JT}^{-1}$$

- for  $p^+ \rightarrow$  nuclear magneton 
$$\gamma_H = \mu_N = \frac{e\hbar}{2m_p} = 5.05095 \times 10^{-27} \text{ JT}^{-1}$$

- but  $\gamma$  is more complicated since these are *relativistic quantum particles*

- Need fudge factor – the Lande  $g$ -factor – such that

- In NMR, we normally use  $\gamma_N \rightarrow$  in EPR everything is discussed in terms of  $g$ -values

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

- Important properties when considering nuclear spin:

- Nuclear spin ( $I$ ), magnetic moment ( $\mu$ ), magnetogyric ratio ( $\gamma$ )

- Natural abundance ( $C$ )

- Relative Receptivity ( $D^P$ )

- relative to  $^{13}\text{C}$

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

### ***Important factors relating to nuclear spin***

- Nuclear spin ( $I$ )
- magnetic moment ( $\mu$ )
- magnetogyric ratio ( $\gamma$ )
- natural abundance ( $C$ )
- relative receptivity ( $D^P$ )
  - relative to  $^{13}\text{C}$

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

## 2.1 Nuclear Magnetic Resonance

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

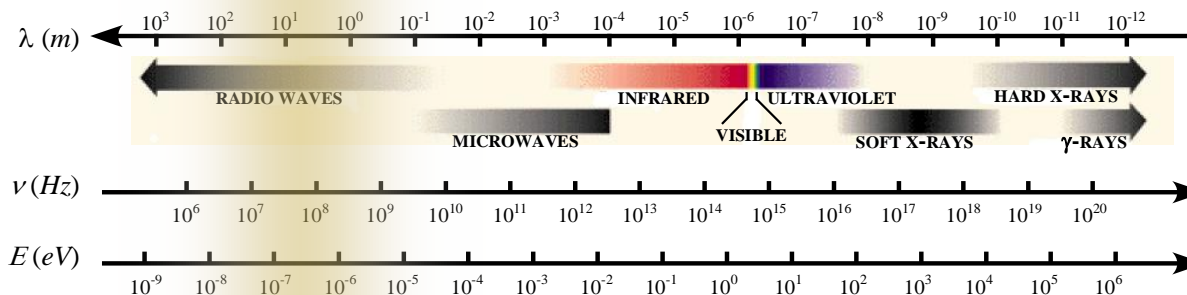
## 2.1 Nuclear Magnetic Resonance

### Periodic Table of the Elements

<b>H</b>																	<b>He</b>
<b>Li</b>	<b>Be</b>											<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
<b>Na</b>	<b>Mg</b>											<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>
<b>Rb</b>	<b>Sr</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	<b>Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>
<b>Cs</b>	<b>Ba</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>		<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	<b>Hg</b>	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	<b>Po</b>	<b>At</b>	<b>Rn</b>

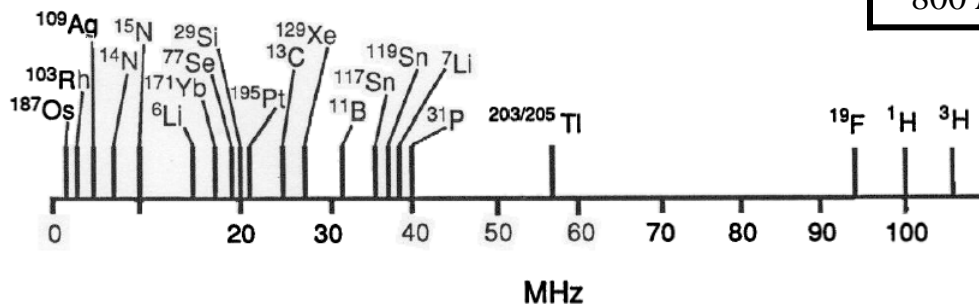
NMR active nuclei  
 Frequently measured nuclei  
 Not active nuclei

## Energy required to induce nuclear transitions



- Depends on applied magnetic field ( $B_0$ )  $\rightarrow \Delta E = h\nu = \gamma\hbar\vec{B}_0$ 
  - In a 2.35T magnetic field,  $^1\text{H}$  resonates at 100 MHz  $\rightarrow \sim 10^{-7}$  eV
  - Spectrometers are discussed based on frequency required to induce  $^1\text{H}$  nuclear transition
- Depends on nucleus

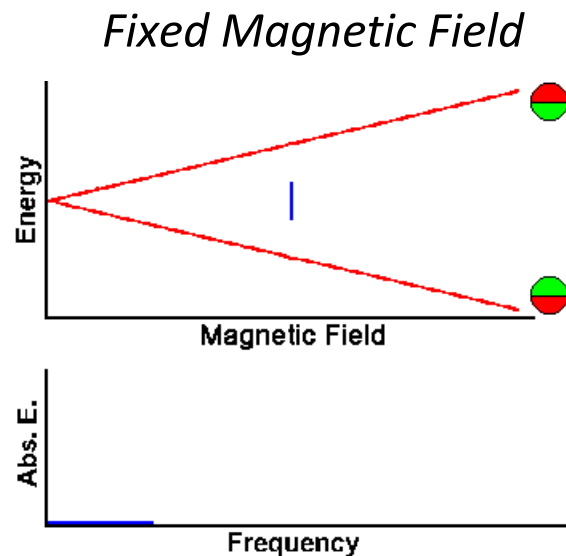
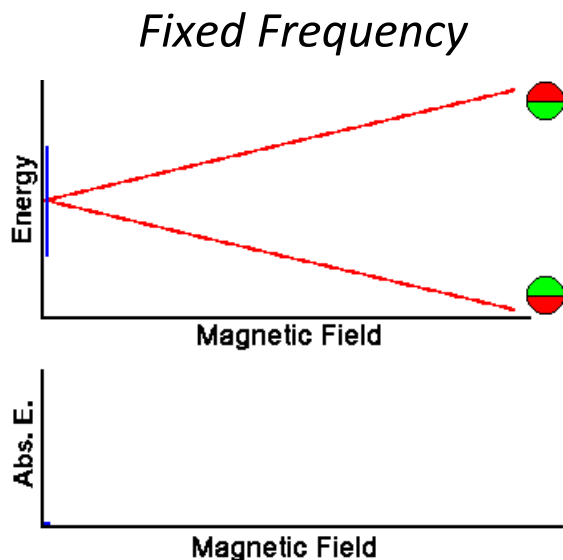
300 MHz	7.05 T
400 MHz	9.40 T
500 MHz	11.75 T
800 MHz	18.80 T





### Approaches to Performing NMR Experiments

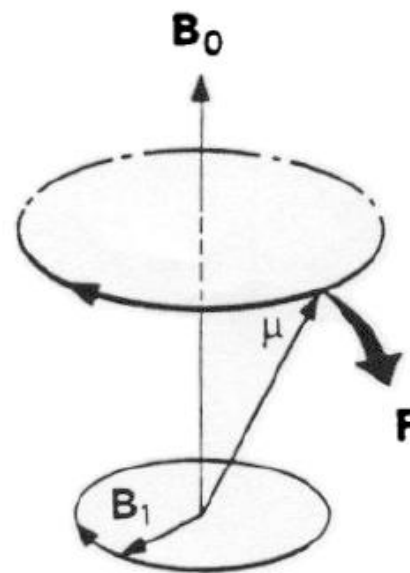
- Continuous Wave (CW) Experiments → traditional approaches



- Pulsed Experiments → modern approach
  - use *pulsed* magnetic fields to cause perturbation → watch effect over time
  - relies on Fourier methods to transform from time domain to frequency domain
  - use effect of *oscillating magnetic field* to induce transitions  $t \text{ s} \rightarrow \nu \text{ s}^{-1}$

### ***Classical Effect of Rotating Field on Larmor Precession***

- apply rotating  $B_1$  field  $\perp$  to homogeneous  $B_0$  field – what happens?
- under most circumstances – nothing
  - rotating field does not interact with  $\vec{\mu}$
  - unless @ same frequency
- if  $B_1$  rotates at *Larmor frequency* ( $\nu$ )
  - rotating field can couple with magnetic moment  $\vec{\mu} \cdot \vec{B}_1$
  - results in force ( $F$ ) acting to increase  $\theta$ 
    - *remember*: difference between  $m_l$  states in magnetic field is the angle  $\theta$  with respect to  $B_0$
  - applied to QM: can produce  $\Delta m_l \rightarrow$  induces NMR transitions!
- Basic approach used in pulsed techniques (*vide infra*)



### NMR Chemical Shifts

- If  $\nu_0 = \frac{\gamma}{2\pi} B_0$  was the whole story, NMR would be pretty much useless
  - could be used for elemental analysis (maybe) but
  - every  $^1\text{H}$  nucleus would have same Larmor Frequency  $\rightarrow$  at the same energy!

- Fortunately, electronic environment affects response to  $B_0$

- This effect could be described in two possible ways:

*usual way of thinking in NMR*

- different nuclei see different magnetic fields

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

- different nuclei have different gyromagnetic ratios

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

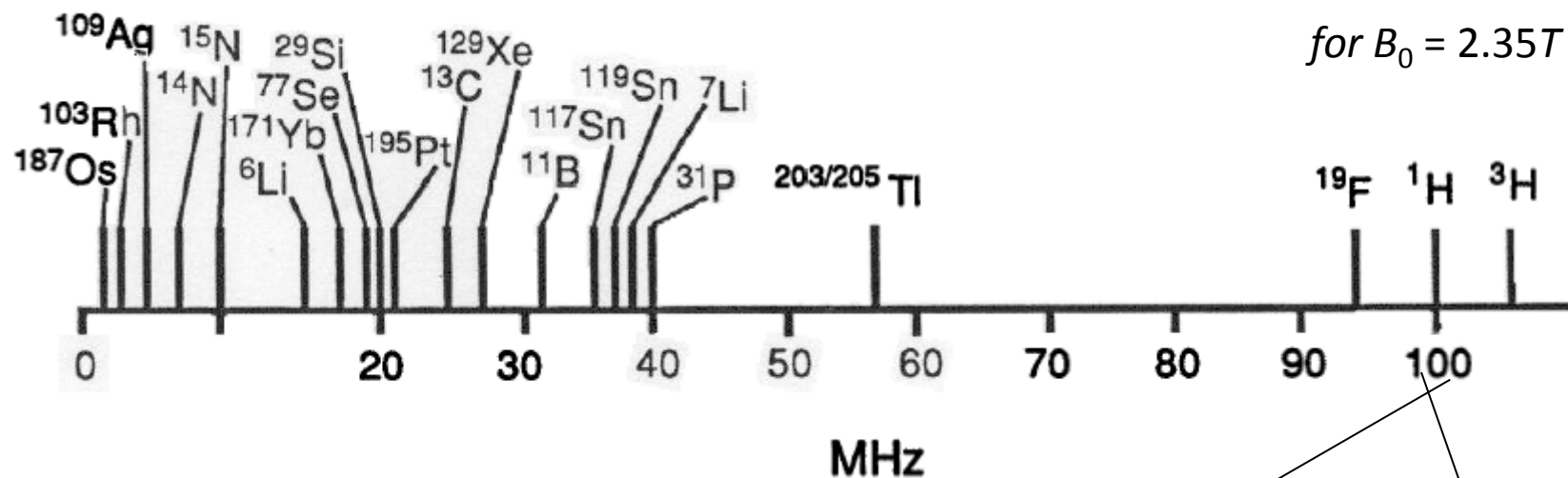
- Either way - Larmor frequency depends on chemical environment

- $\sigma_i$  is “shielding constant”

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

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

## 2.1 Nuclear Magnetic Resonance

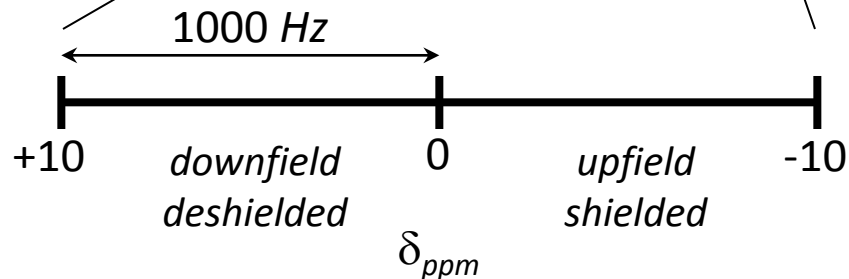


$$\delta_{ppm} = \frac{\nu - \nu_0}{\nu_0} \times 10^6$$

Chemical shifts are empirical parameters that are determined relative to “standards”

e.g. for  $^1\text{H} \rightarrow \text{Si}(\text{CH}_3)_4$  (TMS)

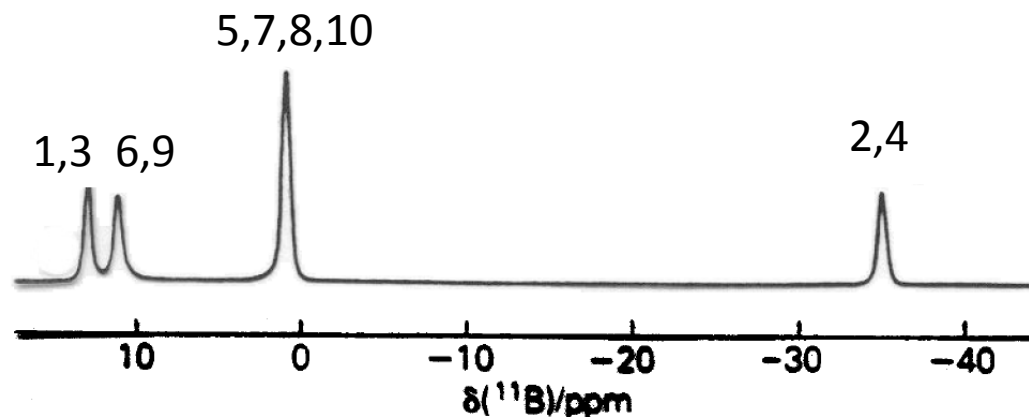
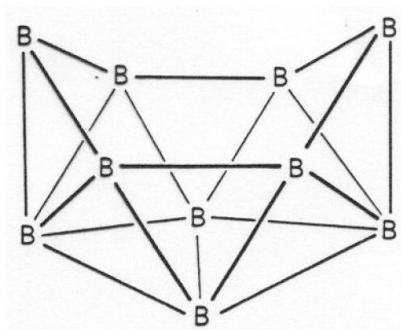
[in practice, modern spectrometers perform internal calibration, which obviates need for external standards – but better safe than sorry]



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

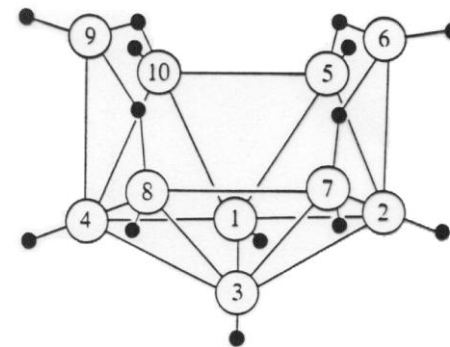
## 2.1 Nuclear Magnetic Resonance

- e.g. 115 MHz (8.2T)  $^{11}\text{B}$  NMR of  $\text{B}_{10}\text{H}_{14}$  ( $^1\text{H}$  decoupled)



- Intensity mechanism exactly the same for all nuclei of same type:
  - sample concentration
  - # of nuclei of a particular type
  - isotopic distribution
- Chemically identical nuclei are at same position
- But what about interactions with other nuclei?
  - Angular momenta should be able to couple...

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



### Coupling of Angular Momenta → Scalar Coupling

- connected angular momenta can couple with each other
  - electron spin with orbital angular momentum (spin-orbit coupling)
  - electron spin with electron spin (magnetic coupling of metal ions)
  - nuclear spin with nuclear spin (scalar coupling)
- coupling is *independent* of magnetic field
  - strength of coupling is a scalar ( $\alpha$ ) that connects each of the angular momenta...
 
$$\vec{J}_{12} = \alpha \vec{J}_1 \cdot \vec{J}_2 = \alpha \vec{J}_2 \cdot \vec{J}_1 = \vec{J}_{21}$$

- Consider two nuclei with  $I_1$  and  $I_2$ , respectively...

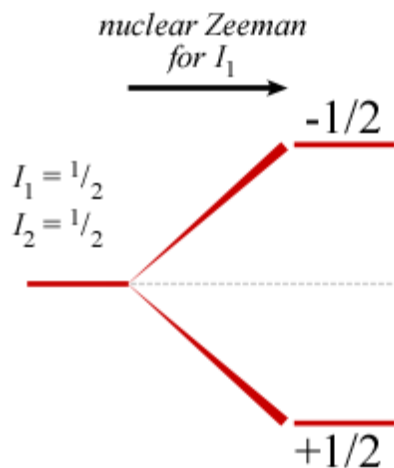
$$H_{sc} = +J_{12} \vec{I}_1 \cdot \vec{I}_2$$

scalar coupling term  
or J-coupling term

$$\begin{aligned} H'_{\vec{I}_1, \vec{I}_2} &= H_{\text{nuclear Zeeman on } \vec{I}_1} + H_{\text{nuclear Zeeman on } \vec{I}_2} + H_{\text{scalar coupling of } (\vec{I}_1, \vec{I}_2)} \\ &= -\hbar\gamma \vec{B}_{eff} \cdot \vec{I}_1 + -\hbar\gamma \vec{B}_{eff} \cdot \vec{I}_2 + J_{12} \vec{I}_1 \cdot \vec{I}_2 \\ &= \underbrace{-\hbar\gamma B_0 (1 - \sigma_1) m_{I_1} - \hbar\gamma B_0 (1 - \sigma_2) m_{I_2}}_{\text{Zeeman terms (field dependent)}} + \underbrace{J_{12} m_{I_1} m_{I_2}}_{\text{scalar coupling (field independent)}} \end{aligned}$$

## 2.1 Nuclear Magnetic Resonance

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



← but this is not what we  
see experimentally!

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

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

Chem 529 (2009-W2)

## 2.1 Nuclear Magnetic Resonance

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

- in our current case

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

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

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

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

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

$$\begin{aligned} \alpha &= +\frac{1}{2} \\ \beta &= -\frac{1}{2} \end{aligned} \quad \text{such that} \quad \alpha_1\beta_2 \equiv +\frac{1}{2}, -\frac{1}{2}$$

- the two degenerate configurations must be *symmetrized*  $\rightarrow$  create another set of basis functions...

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

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

$$\begin{aligned} \left\langle \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \middle| \frac{1}{\sqrt{2}}(\beta_1\alpha_2 + \alpha_1\beta_2) \right\rangle &= \frac{1}{2} \langle \alpha_1\beta_2 | \beta_1\alpha_2 \rangle + \langle \alpha_1\beta_2 | \alpha_1\beta_2 \rangle + \langle \beta_1\alpha_2 | \beta_1\alpha_2 \rangle + \langle \beta_1\alpha_2 | \alpha_1\beta_2 \rangle \\ &= \frac{1}{2} (0 + 1 + 1 + 0) \\ &= 1 \mapsto \text{symmetric} \end{aligned}$$

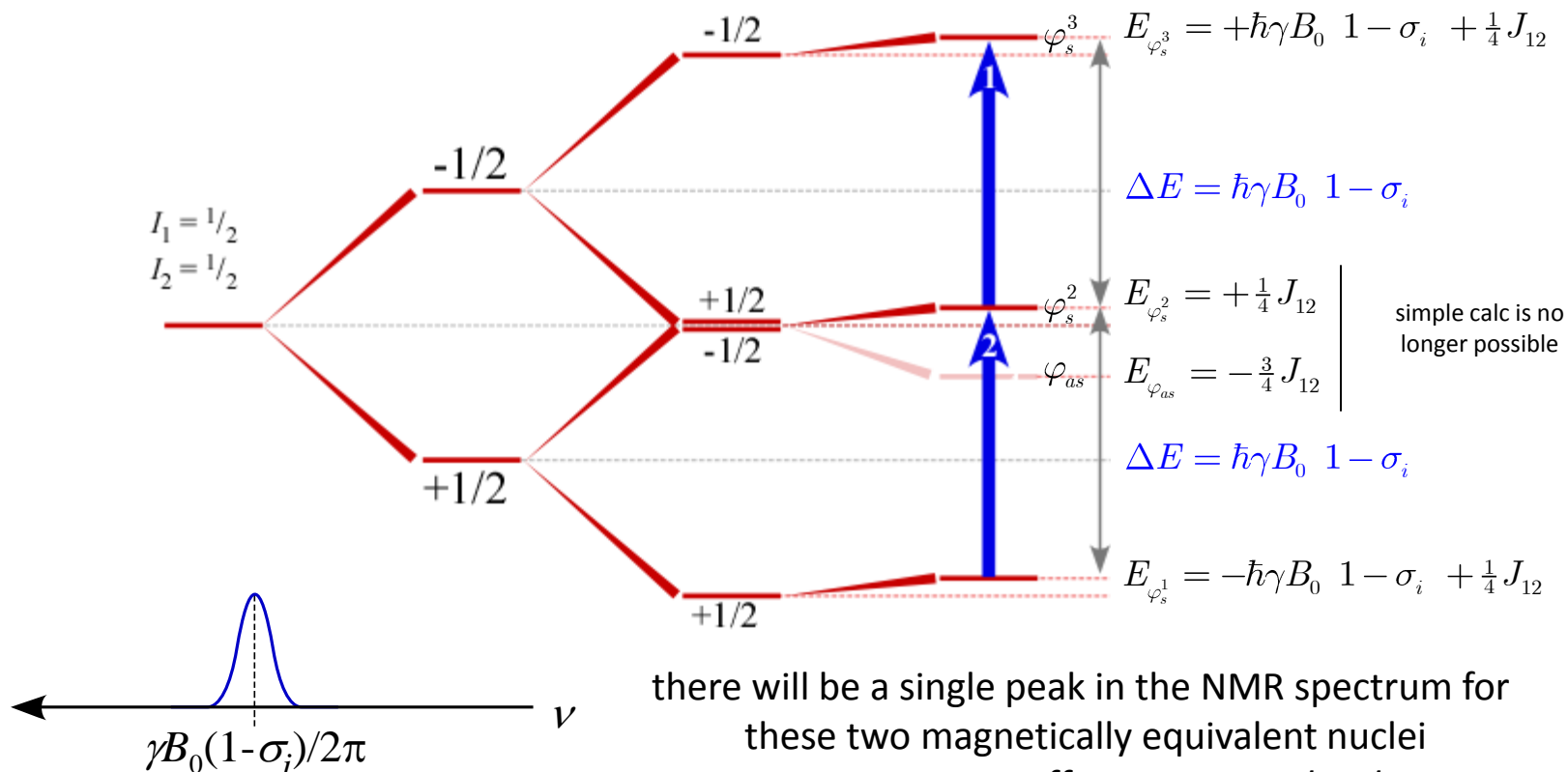
$$\begin{aligned} \left\langle \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \middle| \frac{1}{\sqrt{2}}(\beta_1\alpha_2 - \alpha_1\beta_2) \right\rangle &= \frac{1}{2} \langle \alpha_1\beta_2 | \beta_1\alpha_2 \rangle - \langle \alpha_1\beta_2 | \alpha_1\beta_2 \rangle - \langle \beta_1\alpha_2 | \beta_1\alpha_2 \rangle + \langle \beta_1\alpha_2 | \alpha_1\beta_2 \rangle \\ &= \frac{1}{2} (0 - 1 - 1 + 0) \\ &= -1 \mapsto \text{antisymmetric} \end{aligned}$$



## 2.1 Nuclear Magnetic Resonance

- this causes a few issues...
  - hidden selection rule → can't change symmetry
  - the energies we've calculated are wrong
- we get a new (correct) energy level diagram for this special case

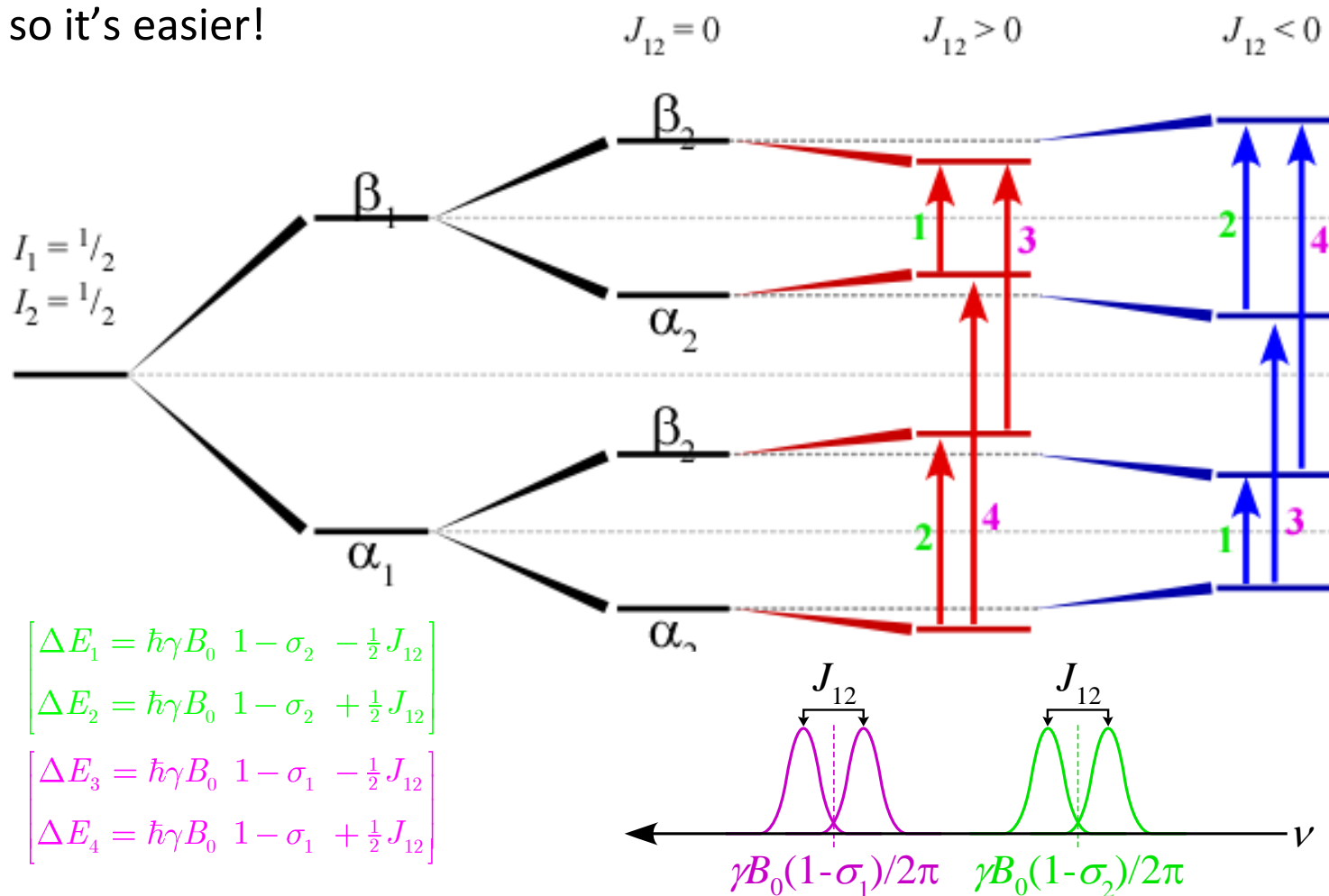
$$\begin{aligned} \varphi_s^1 &= \alpha_1\alpha_2 \mapsto \text{symmetric} \\ \varphi_{as} &= \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \mapsto \text{antisymmetric} \\ \varphi_s^2 &= \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \mapsto \text{symmetric} \\ \varphi_s^3 &= \beta_1\beta_2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



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

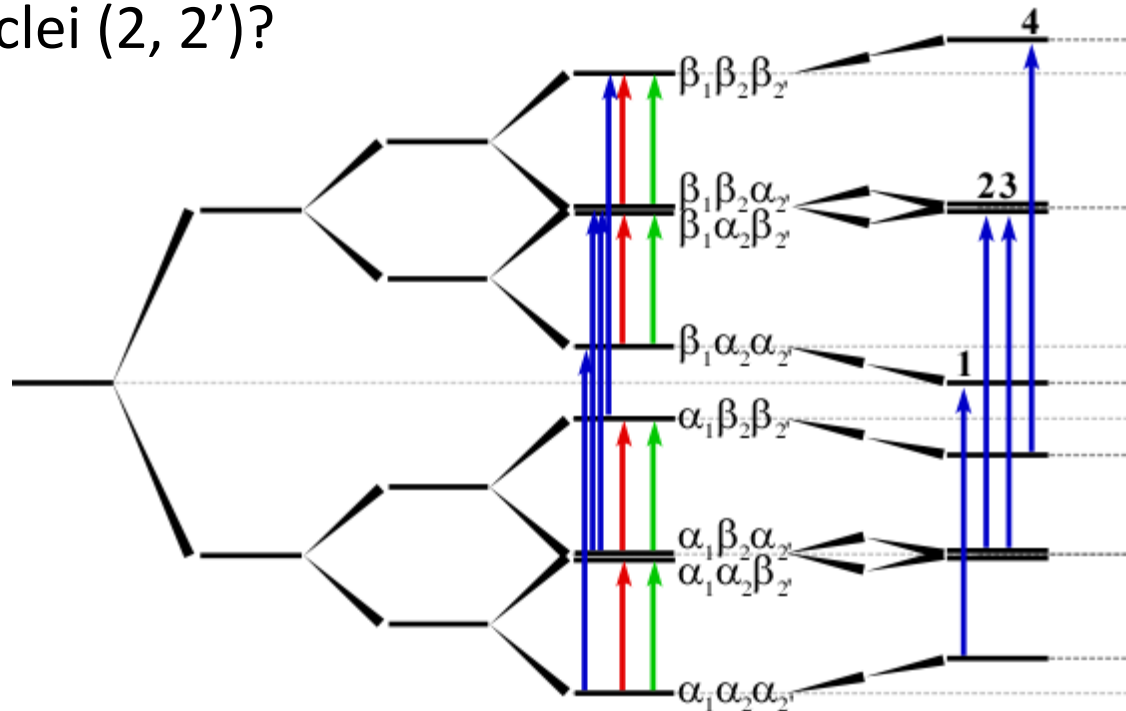
## 2.1 Nuclear Magnetic Resonance

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

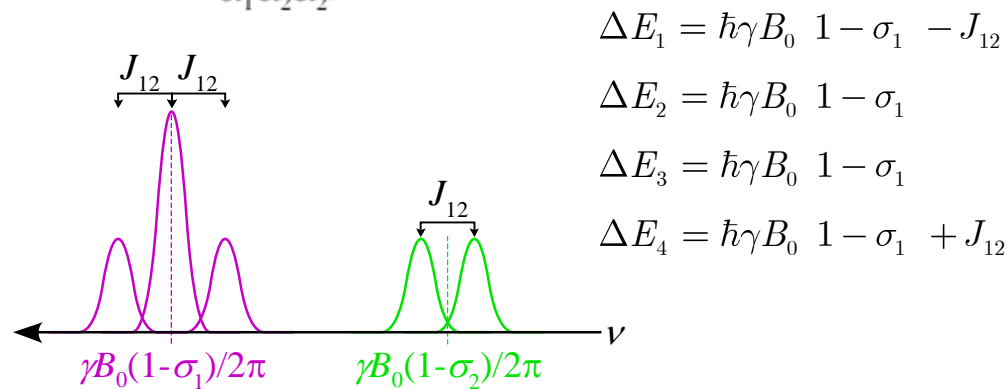


## 2.1 Nuclear Magnetic Resonance

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



$$\begin{aligned}
 E_{\varphi_{\beta_1\beta_2\beta_2'}} &= -\frac{\hbar\gamma}{2}[-B_0(1-\sigma_1) - 2B_0(1-\sigma_2)] + \frac{1}{2}J_{12} \\
 E_{\varphi_{\beta_1\beta_2\alpha_2'}} &= -\frac{\hbar\gamma}{2}[-B_0(1-\sigma_1)] \\
 E_{\varphi_{\beta_1\alpha_2\beta_2'}} &= -\frac{\hbar\gamma}{2}[-B_0(1-\sigma_1)] \\
 E_{\varphi_{\beta_1\alpha_2\alpha_2'}} &= -\frac{\hbar\gamma}{2}[-B_0(1-\sigma_1) + 2B_0(1-\sigma_2)] - \frac{1}{2}J_{12} \\
 E_{\varphi_{\alpha_1\beta_2\beta_2'}} &= -\frac{\hbar\gamma}{2}[+B_0(1-\sigma_1) - 2B_0(1-\sigma_2)] - \frac{1}{2}J_{12} \\
 E_{\varphi_{\alpha_1\beta_2\alpha_2'}} &= -\frac{\hbar\gamma}{2}[+B_0(1-\sigma_1)] \\
 E_{\varphi_{\alpha_1\alpha_2\beta_2'}} &= -\frac{\hbar\gamma}{2}[+B_0(-\sigma_1)] \\
 E_{\varphi_{\alpha_1\alpha_2\alpha_2'}} &= -\frac{\hbar\gamma}{2}[+B_0(-\sigma_1) + 2B_0(-\sigma_2)] + \frac{1}{2}J_{12}
 \end{aligned}$$



$$\begin{aligned}
 \Delta E_1 &= \hbar\gamma B_0(1-\sigma_1) - J_{12} \\
 \Delta E_2 &= \hbar\gamma B_0(1-\sigma_1) \\
 \Delta E_3 &= \hbar\gamma B_0(1-\sigma_1) \\
 \Delta E_4 &= \hbar\gamma B_0(1-\sigma_1) + J_{12}
 \end{aligned}$$