

Lecture #2: Review of Spin Physics

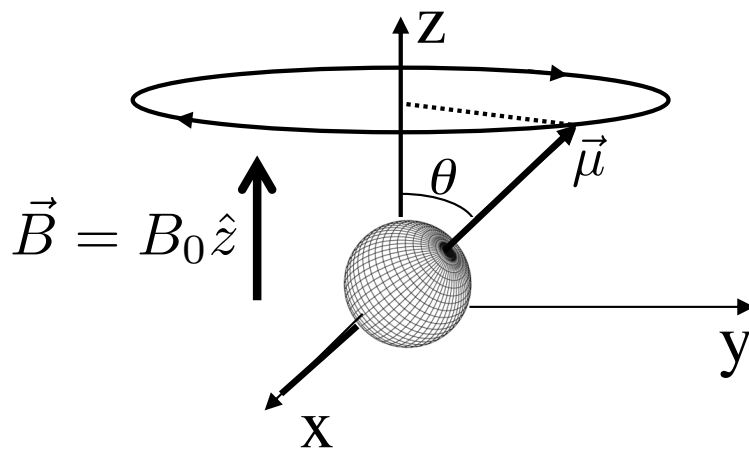
- Topics
 - Spin
 - The Nuclear Spin Hamiltonian
 - Coherences
- References
 - Levitt, Spin Dynamics

Nuclear Spins

- Protons (as well as electrons and neutrons) possess intrinsic angular momentum called “spin”, which gives rise to a magnetic dipole moment.

$$|\mu| = \underbrace{\gamma}_{\text{gyromagnetic ratio}} \underbrace{\hbar}_{\text{Plank's constant}} \underbrace{\frac{1}{2}}_{\text{spin}}$$

- In a magnetic field, the spin precesses around the applied field.



Precession frequency
 $\omega_0 \equiv \gamma B_0$

Note: Some texts use $\omega_0 = -\gamma B_0$.

Energy = $-\vec{\mu} \cdot \vec{B} = -|\mu| B \cos \theta$
 How does the concept of energy differ between classical and quantum physics



- Question: What magnetic (and electric?) fields influence nuclear spins?

The Nuclear Spin Hamiltonian

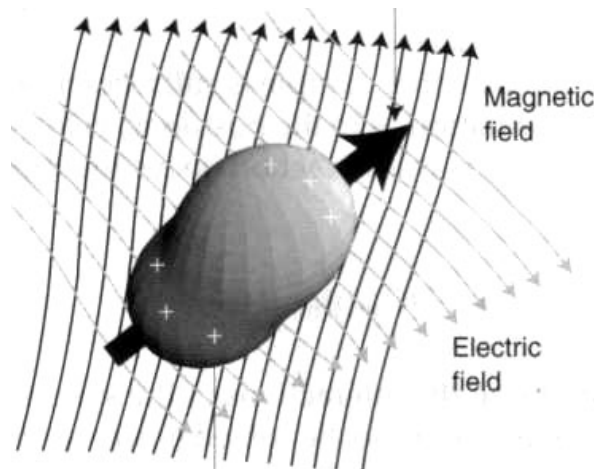
- \hat{H} is the sum of different terms representing different physical interactions.

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \dots$$

- Examples:
- 1) interaction of spin with B_0
 - 2) interactions with dipole fields of other nuclei
 - 3) nuclear-electron couplings

- In general, we can think of an atomic nucleus as a lumpy magnet with a (possibly non-uniform) positive electric charge
- The spin Hamiltonian contains terms which describe the orientation dependence of the nuclear energy

$$\hat{H} = \hat{H}^{elec} + \hat{H}^{mag}$$



The nuclear magnetic moment interacts with magnetic fields

The nuclear electric charge interacts with electric fields

Electromagnetic Interactions

- Magnetic interactions

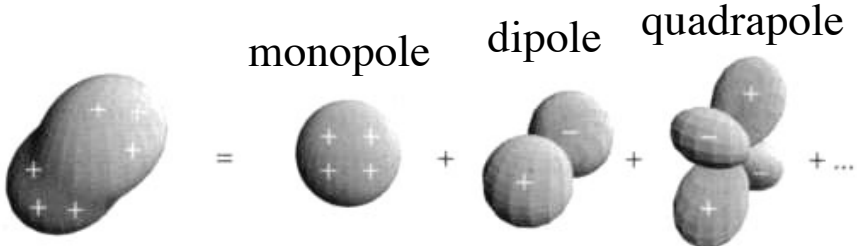
$$\hat{H}^{mag} = -\vec{\mu} \cdot \vec{B} = -\gamma \hbar \hat{I} \cdot \vec{B}$$

magnetic moment

local magnetic field

- Electric interactions

Nuclear electric charge distributions can be expressed as a sum of multipole components.



The diagram illustrates the decomposition of a nuclear charge distribution into multipole components. On the left, a single irregularly shaped grey blob with several '+' signs represents the total charge distribution. This is shown to be equivalent to the sum of three components: a single sphere with '+' signs (monopole), two spheres with '+' and '-' signs (dipole), and four spheres with '+' signs arranged in a quadrupole pattern (quadrupole). Below the diagram is the equation: $C(\vec{r}) = C^{(0)}(\vec{r}) + C^{(1)}(\vec{r}) + C^{(2)}(\vec{r}) + \dots$

Symmetry properties: $C^{(n)}=0$ for $n>2I$ and odd interaction terms disappear

$$\hat{H}^{elec} = 0 \text{ (for spin } I = 1/2)$$

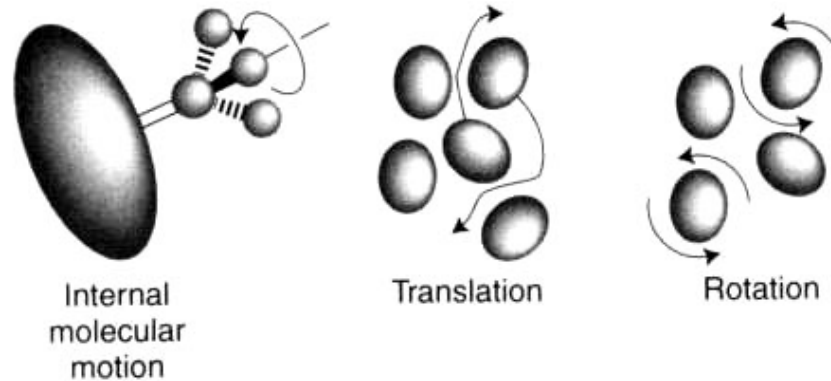
$$\hat{H}^{elec} \neq 0 \text{ (for spin } I > 1/2)$$

Hence, for spin- $1/2$ nuclei there are no electrical energy terms that depend on orientation or internal nuclear structure, and they behave exactly like point charges! Nuclei with spin $> 1/2$ have electrical quadrupolar moments.



Motional Averaging

- Molecular motion



- Previously, we used averaging to simplify the Hamiltonian

Molecular orientation depends on time and Hamiltonian terms can be written as $\hat{H}_{\text{int}}^0(\Theta(t))$. These terms were replaced by their time averages:

$$\underbrace{\overline{\hat{H}}_{\text{int}}^0}_{\text{Secular Hamiltonian}} = \frac{1}{\tau} \int_0^{\tau} \hat{H}_{\text{int}}^0(\Theta(t)) dt \xrightarrow{\text{ergodicity}} \overline{\hat{H}}_{\text{int}}^0 = \int \hat{H}_{\text{int}}^0 p(\Theta) d\Theta$$

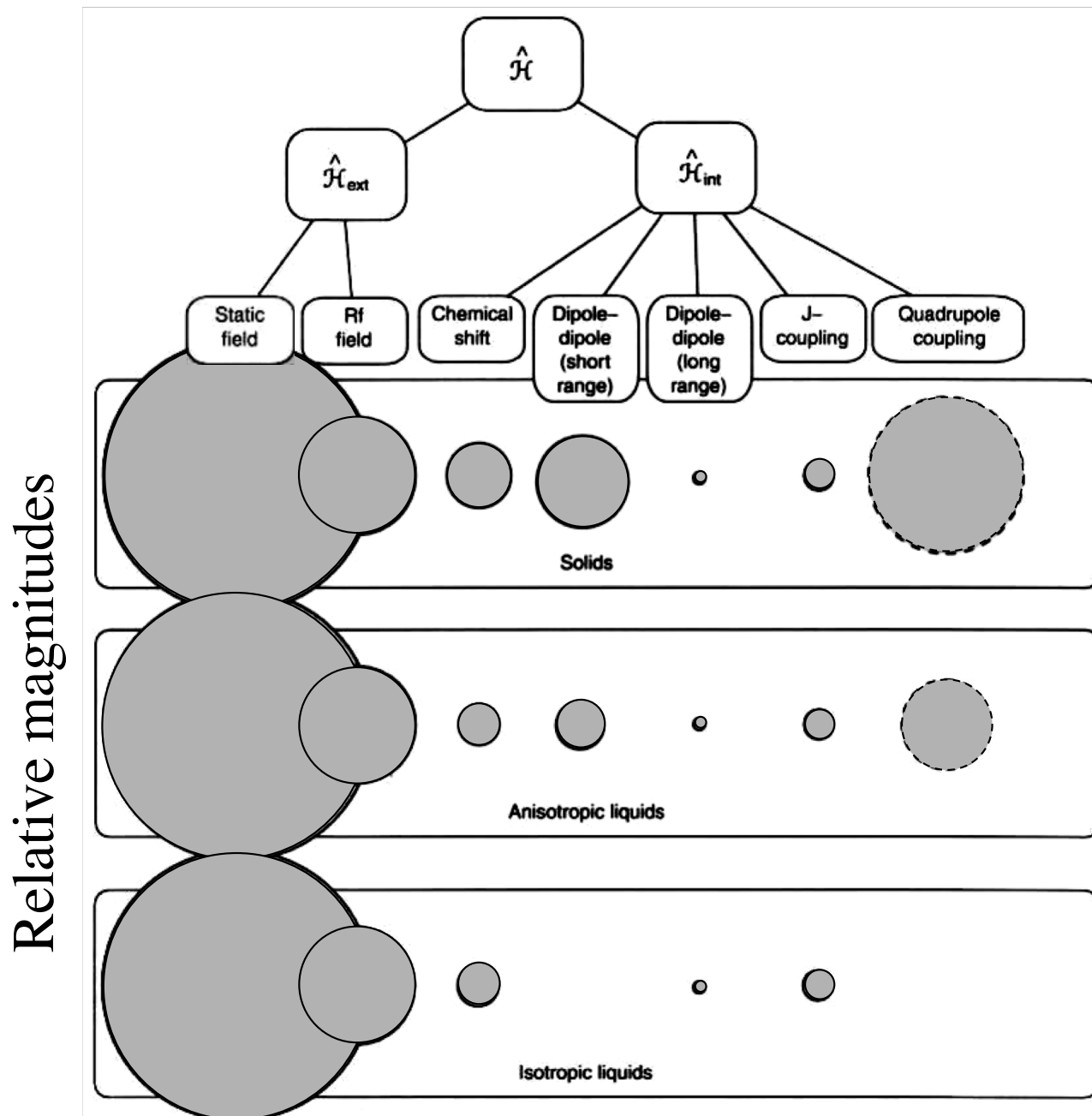
Isotropic materials: $\overline{\hat{H}}_{\text{int}}^{\text{isotropic}} = \frac{1}{N} \int \hat{H}_{\text{int}}^0(\Theta) d\Theta$

$p(\Theta)$ = probability density for molecule having orientation Θ

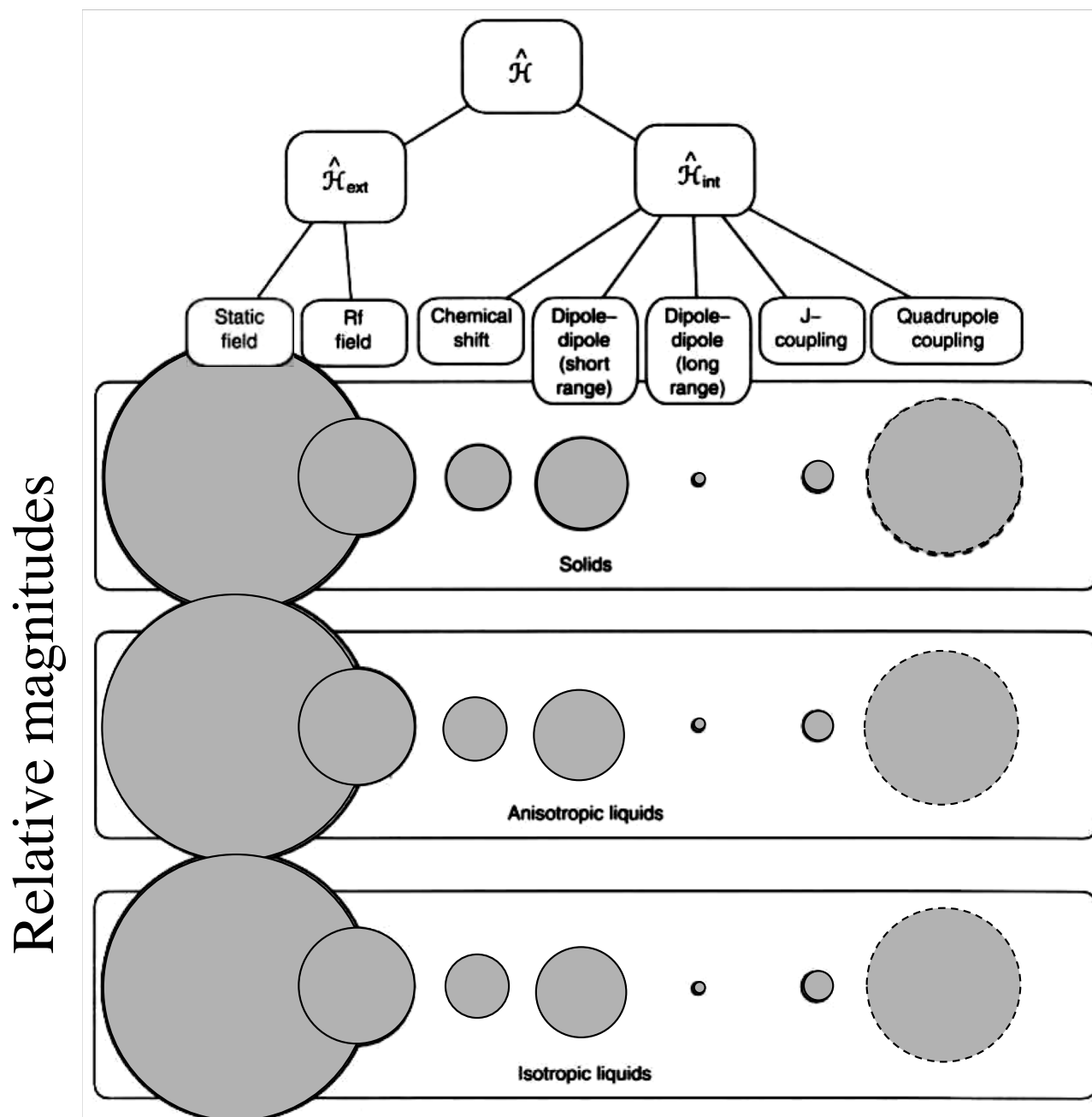
normalization

- We no longer want to make this approximation. Instead, the time variations will be analyzed as perturbations.

Time-averaged Spin Hamiltonian



Instantaneous Spin Hamiltonian



Simplifications

- In general, the nuclear spin Hamiltonian is quite complicated.
- We'll regularly make use of two simplifications.
 1. For terms in the Hamiltonian that are periodic, we change to a rotating frame of reference.


$$\underbrace{\hat{H}'}_{\text{rotating frame}} = e^{-i\omega t \hat{I}_z} \underbrace{\hat{H}}_{\text{laboratory frame}} = e^{-i\omega t \hat{I}_z} \hat{H} e^{i\omega t \hat{I}_z}$$

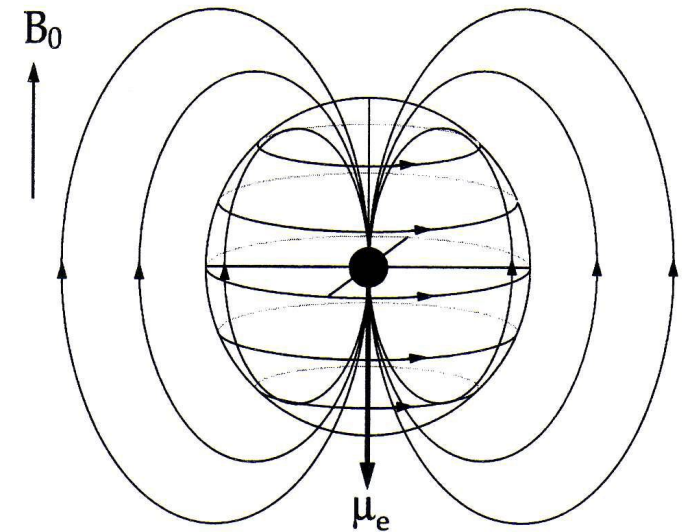
$$\hat{H}(t) = -\omega_0 \hat{I}_z - \omega_1 (\hat{I}_x \cos \omega t - \hat{I}_y \sin \omega t) \quad \longrightarrow \quad \hat{H}_{eff} = -(\omega_0 - \omega) \hat{I}_z - \omega_1 \hat{I}_x$$

2. The secular approximation

B_0 -Electron Interactions

When a material is placed in a magnetic field it is magnetized to some degree and this modifies the field...

Shielding: Electrons in an atom circulate about B_0 , generating a magnetic moment opposing the applied magnetic field. 



- Global effects: magnetic susceptibility

$$B_0^s = (1 - \chi)B_0$$

field inside sample
bulk magnetic susceptibility
applied field

Hereafter we'll use " B_0 " to refer to the internal field.

- Local effect: Chemical Shift

Different atoms experience different electron cloud densities.



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

shielding constant
 (Don't confuse with the spin density operator!)

The Zeeman Hamiltonian

- The interaction energy between the magnetic field, \vec{B} , and the magnetic moment, $\vec{\mu} = \gamma\vec{I}$, is given by the Zeeman Hamiltonian.

$$\text{Classical: } E = -\gamma\vec{B} \cdot \vec{I} \quad \rightarrow \quad \text{QM: } \hat{H}_{zeeman} = -\gamma\vec{B} \cdot \hat{I}$$

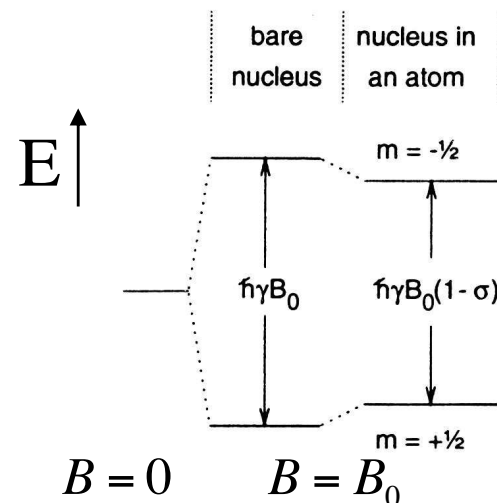
- The formal correction for chemical shielding is:

$$\hat{H}_{zeeman} = -\gamma\hat{I}(1 - \underline{\sigma})\vec{B} \quad \text{where} \quad \underline{\sigma} = 3 \times 3 \text{ shielding tensor}$$

- In vivo*, rapid molecular tumbling averages out the non-isotropic components. $\sigma = \sigma_{iso} = \text{Tr}(\underline{\sigma}/3)$

- Hence for $\vec{B} = [0, 0, B_0]$:

$$\hat{H}_{Zeeman} = -\gamma(1 - \sigma)B_0\hat{I}_z$$



Chemical Shielding Tensor

- Electron shielding is in general anisotropic, i.e. the degree of shielding depends on the molecular orientation.
- The shielding tensor can be written as the sum of three terms:

$$\underline{\underline{\sigma}} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} = \sigma_{iso} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \underline{\underline{\sigma}}^{(1)} + \underline{\underline{\sigma}}^{(2)}$$

See Kowalewski, pp 105-6 for details.

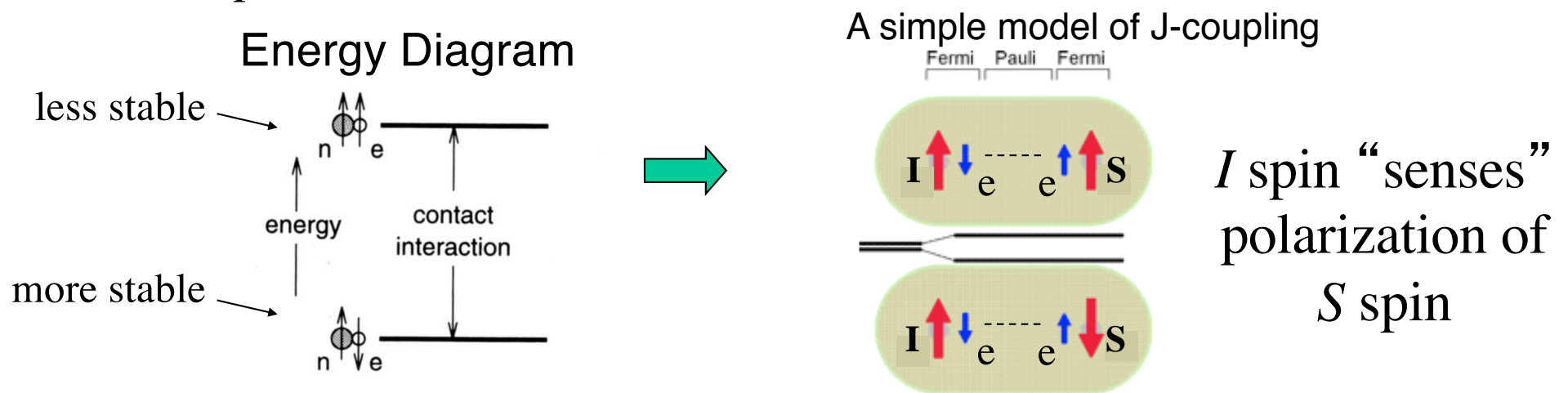
$\sigma_{iso} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$

antisymmetric symmetric and traceless

- Both $\underline{\underline{\sigma}}^{(1)}$ and $\underline{\underline{\sigma}}^{(2)}$ are time-varying due to molecular tumbling.
- $\underline{\underline{\sigma}}^{(2)}$ gives rise to a relaxation mechanism called chemical shift anisotropy (CSA). (to be discussed later in the course)
- $\underline{\underline{\sigma}}^{(1)}$ causes only 2nd order effects and is typically ignored.

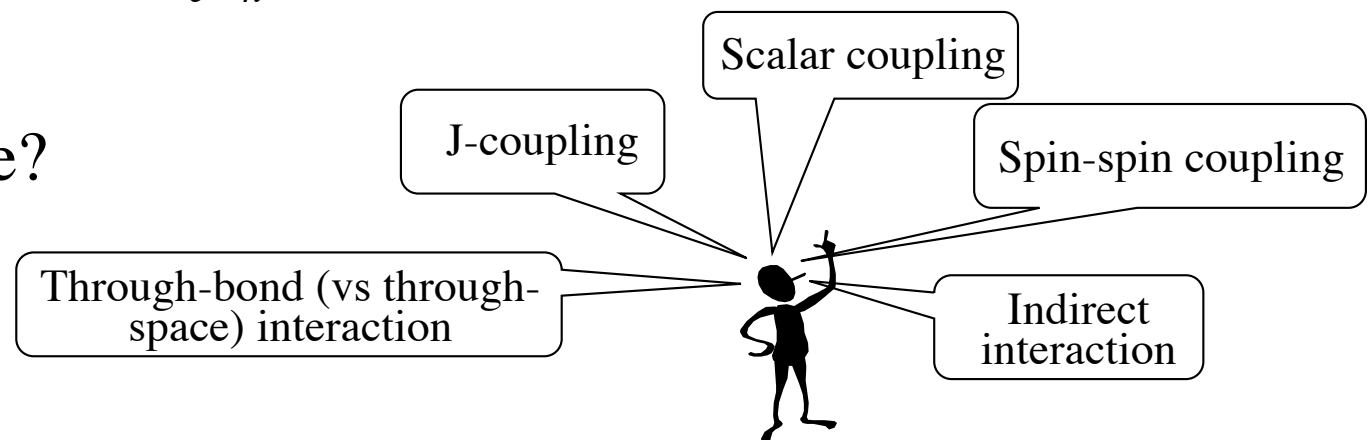
J-Coupling: Mechanism

- At *very* small distances (comparable to the nuclear radius), the dipolar interaction between an electron and proton is replaced by an *isotropic* interaction called “Fermi contact interaction”.



- Interaction energy $\propto -\gamma_e \gamma_n \hat{I} \cdot \hat{S}$ ← independent of molecular orientation

- What’s in a name?



A little foreshadowing...

J-Coupling and Relaxation

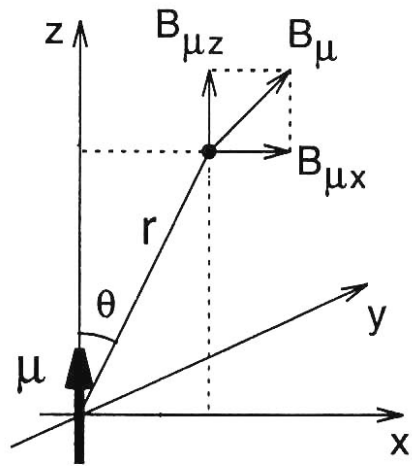
- Because J is unchanged with molecular tumbling, J-coupling typically does not contribute to relaxation.

$$\hat{H}_J = 2\pi J \hat{I} \cdot \hat{S} \quad \text{where} \quad J(\Theta(t)) = J$$

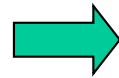
- However, there are a few cases where J can become “effectively” time-varying.
 - Case 1: the S spin is engaged in chemical exchange
 - Case 2: the T_1 of the S spin itself is $\ll 1/J$.
- These cases are called scalar relaxation of the first and second kind respectively, and both are important for the study of MRI contrast agents.

Magnetic Dipoles

- Nuclei with spin $\neq 0$ act like tiny magnetic dipoles.



Dipole at origin



$$B_{\mu x} = \left(\frac{\mu_0}{4\pi} \right) \left(\frac{\mu}{r^3} \right) (3 \sin \theta \cos \theta)$$

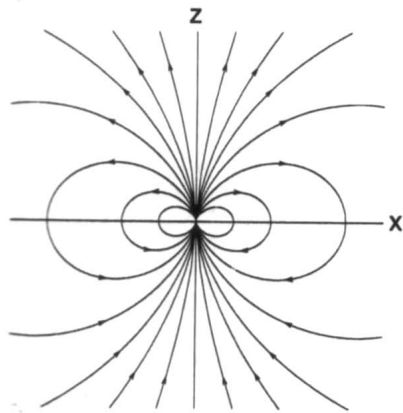
$$B_{\mu y} = 0$$

permeability of free space

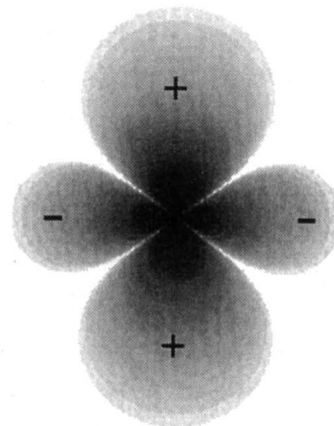
$$B_{\mu z} = \left(\frac{\mu_0}{4\pi} \right) \left(\frac{\mu}{r^3} \right) (3 \cos^2 \theta - 1)$$

falls off as r^3

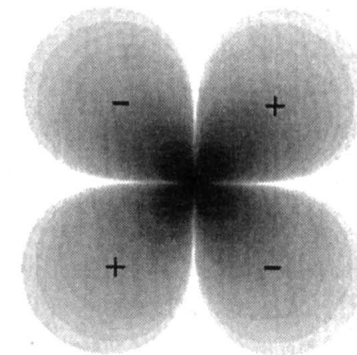
Magnetic Field in $y=0$ plane



Lines of Force



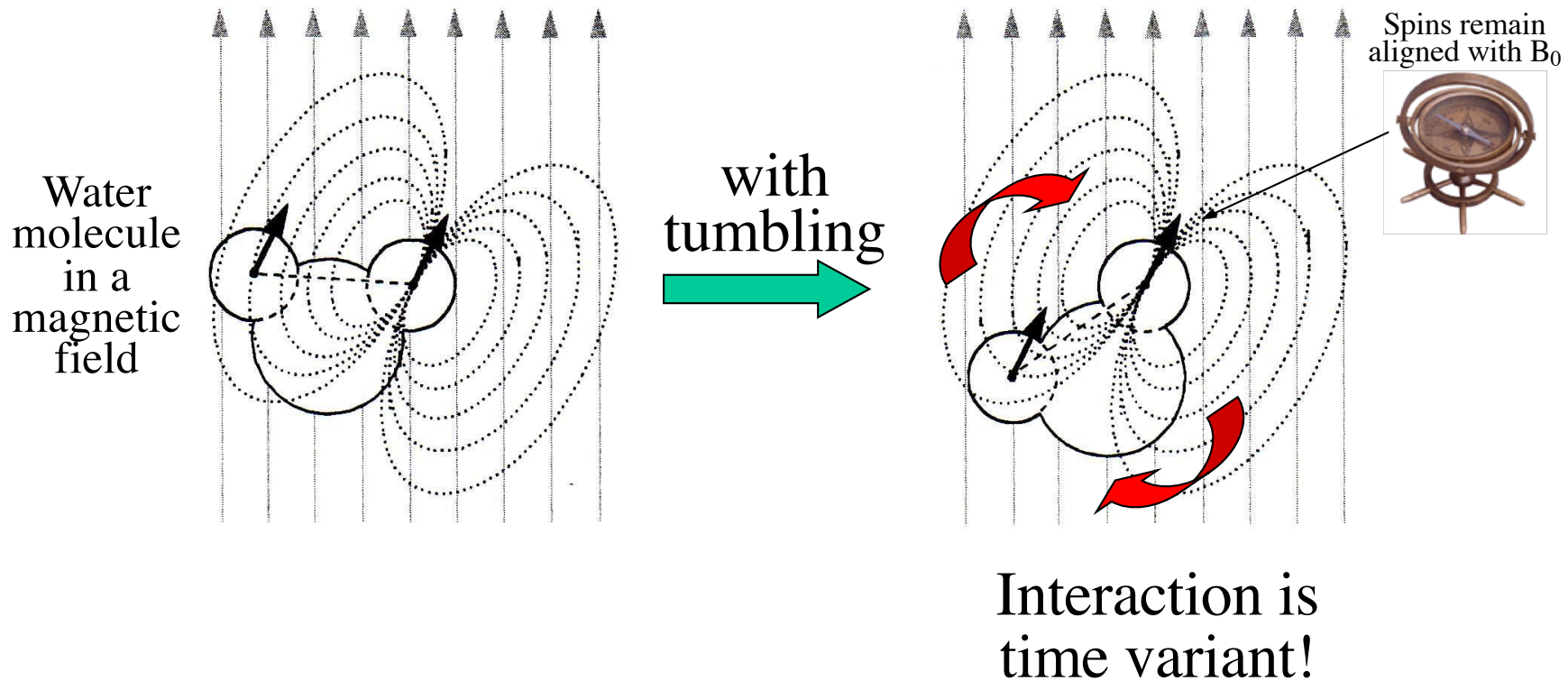
$B_{\mu z}$



$B_{\mu x}$

Dipolar Coupling

- Dipole fields from nearby spins interact (i.e. are coupled).
- Rapid fall off with distance causes this to be primarily a intramolecular effect.



The Nuclear Dipolar Coupling Hamiltonian

- Mathematically speaking, the general expression is:

$$\hat{H}_{dipole} = -\frac{\mu_0 \gamma_I \gamma_S}{4\pi r^3} \hbar \left(\hat{I} \cdot \hat{S} - \frac{3}{r^2} (\hat{I} \cdot \vec{r})(\hat{S} \cdot \vec{r}) \right) \quad \text{where } \vec{r} \text{ vector from spin } I \text{ to spin } S$$

- Secular approximation:

$$\hat{H}_{dipole} = d \left(3\hat{I}_z \hat{S}_z - \hat{I} \cdot \hat{S} \right) \quad \text{where } d = -\frac{\mu_0 \gamma_I \gamma_S}{4\pi r^3} \hbar \left(3\cos^2 \Theta_{IS} - 1 \right)$$

dipole coupling constant
angle between B_0 and vector from spins I and S

- With isotropic tumbling, the time average of $\hat{H}_{dipole} = 0$
- However, the temporal variations of $\hat{H}_{dipole}(t)$ are typically the dominant source of T_1 and T_2 relaxation in vivo.

Quadrupolar Interactions

- Nuclei with spin $I > \frac{1}{2}$ have a electrical quadrupolar moment due to their non-uniform charge distribution.
- This electrical quadrupole moment interacts with local electric field gradients
 - Static E-field gradients results in shifts of the resonance frequencies of the observed peaks.
 - Dynamic (time-varying) E-field gradients result in relaxation.
- Quadrupolar coupling Hamiltonian (secular approximation):

$$\hat{H}_Q = \frac{3eQ}{4I(2I-1)\hbar} \overset{\text{Coupling constant}}{V_0} \left(3\hat{I}_z^2 - \hat{I} \cdot \hat{I} \right)$$

Looks like an interaction of a spin with itself.

Electric field gradient – dependent on molecular orientation

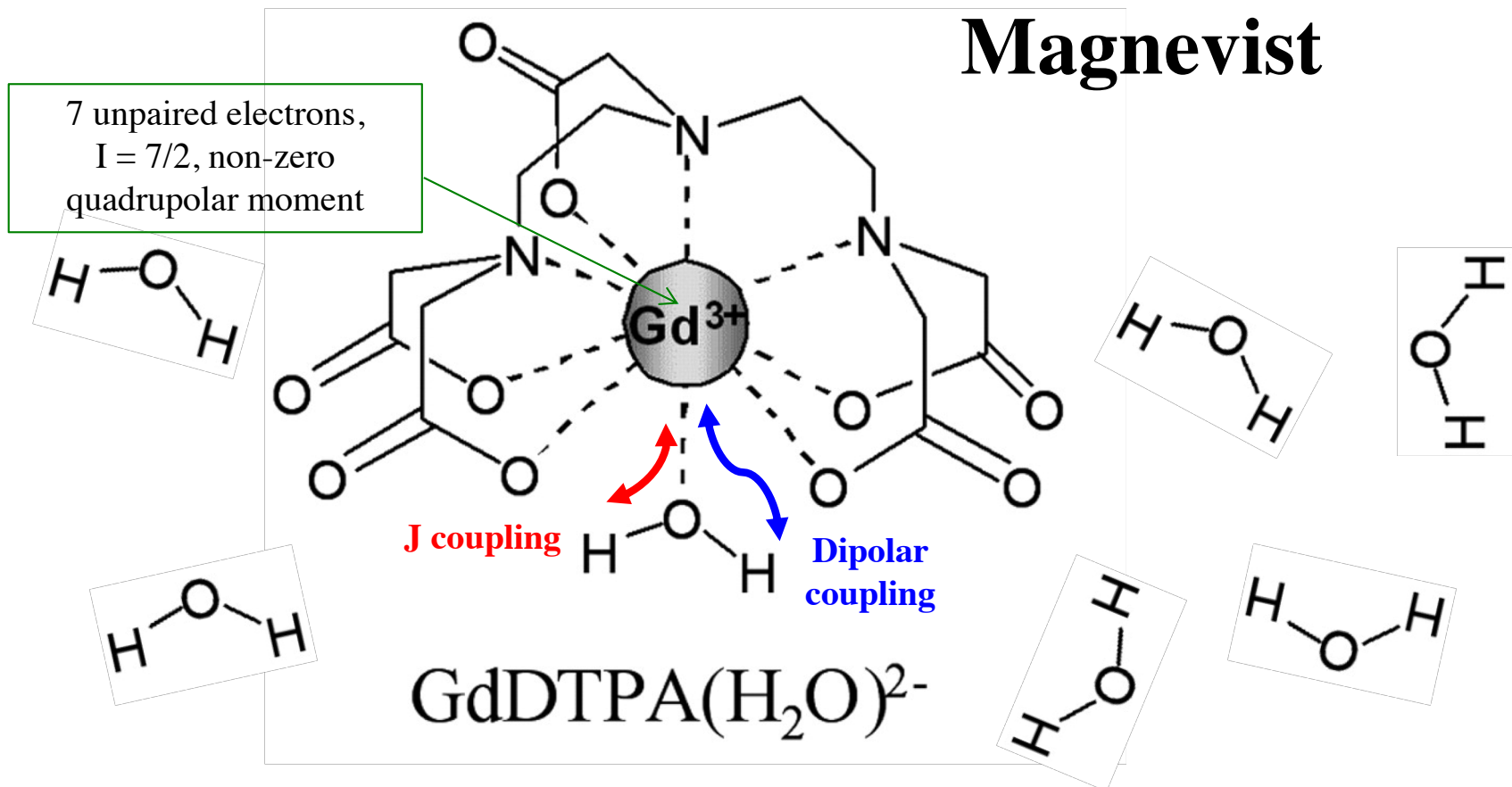


What's the spin of Gd^{3+} with its 7 unpaired electrons?

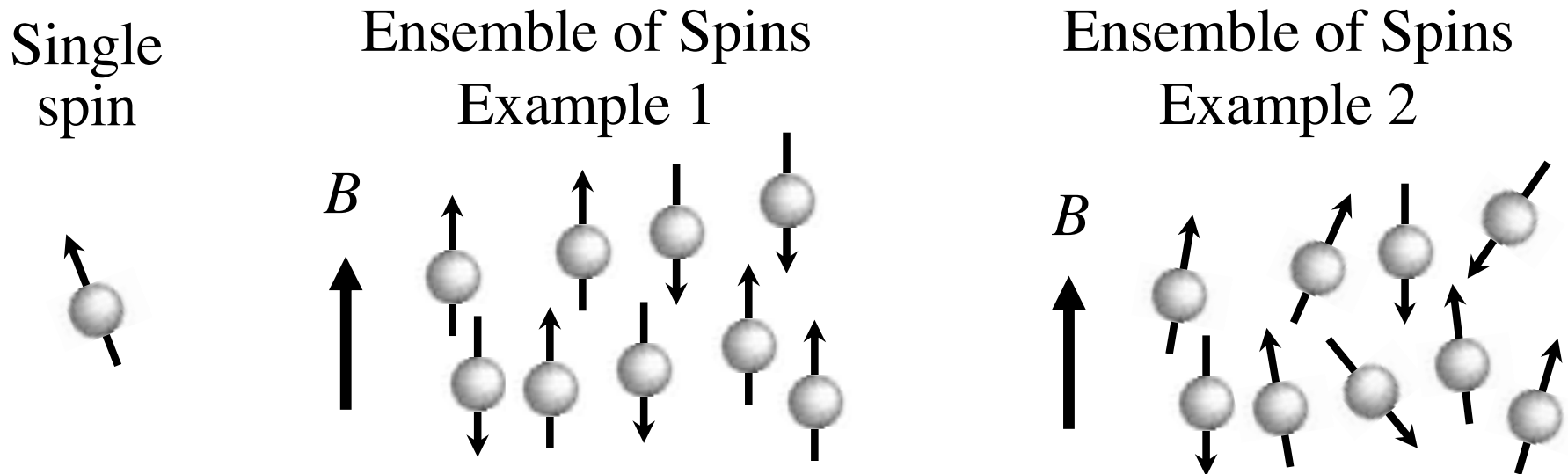
A little foreshadowing...

Nucleus-unpaired electron couplings

- Both nuclear-electron J and dipolar coupling occur.
- Important for understanding MR contrast agents.



Polarization

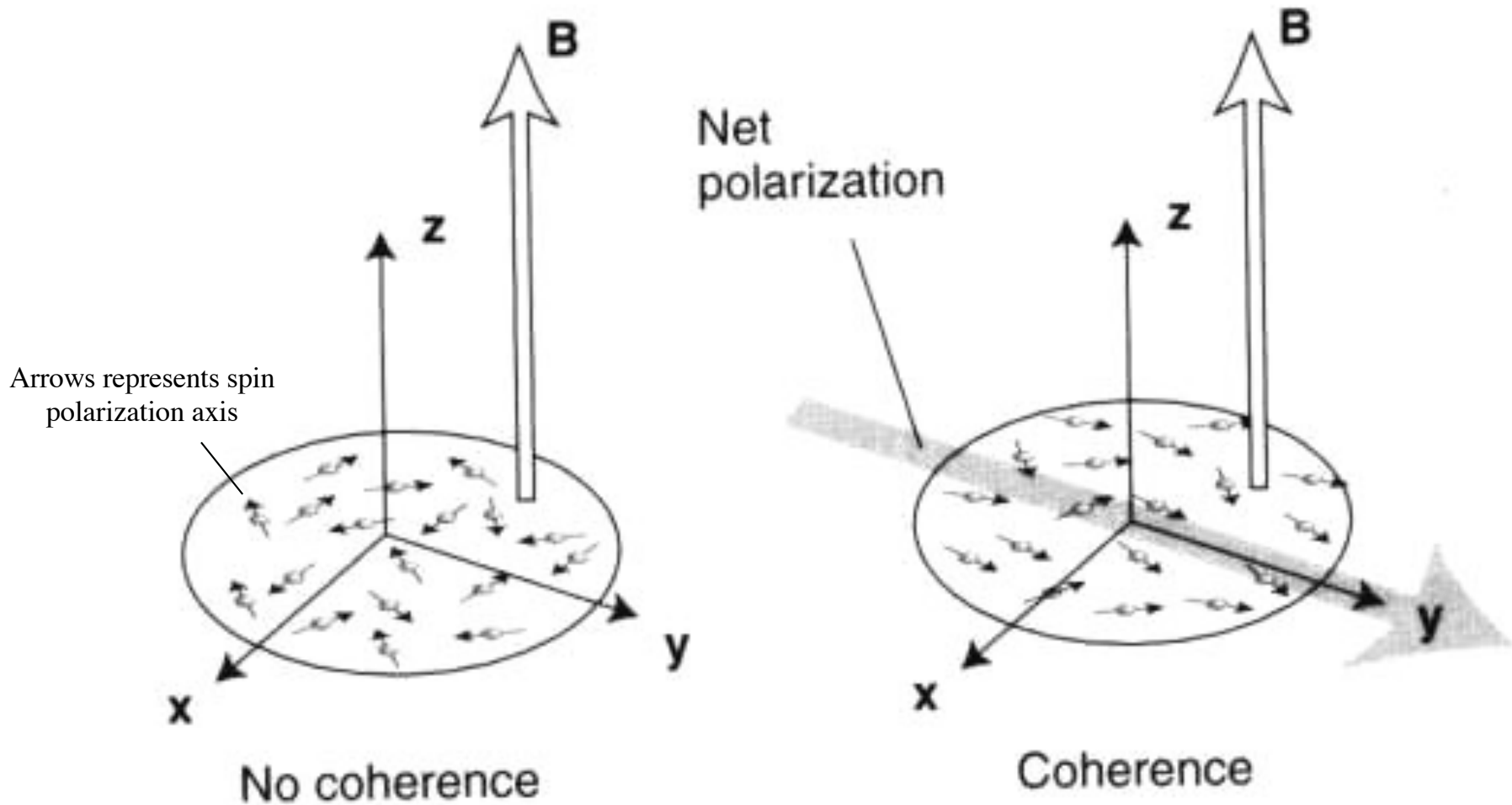


“Professor Bloch has told you how one can detect the precession of the magnetic nuclei in a drop of water. Commonplace as such experiments have become in our laboratories, I have not yet lost a feeling of wonder, and of delight, that this delicate motion should reside in all the ordinary things around us, revealing itself only to him who looks for it. I remember, in the winter of our first experiments, just seven years ago, looking on snow with new eyes. There the snow lay around my doorstep - great heaps of protons quietly precessing in the earth’s magnetic field.”

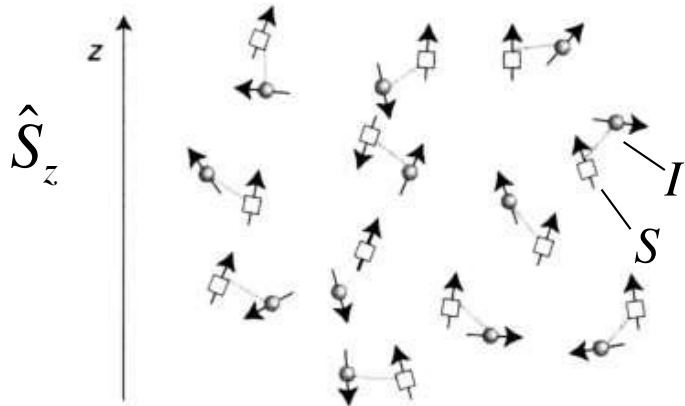
- Edward Purcell, Nobel Lecture 1952

- In tissue, we are always dealing with a large number of nuclei, and the net magnetization is given by: $\vec{M} = \sum_{\text{volume}} \vec{\mu}$

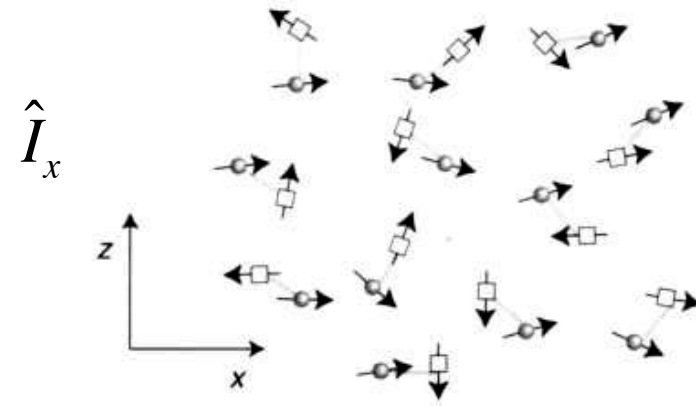
Phase Coherence



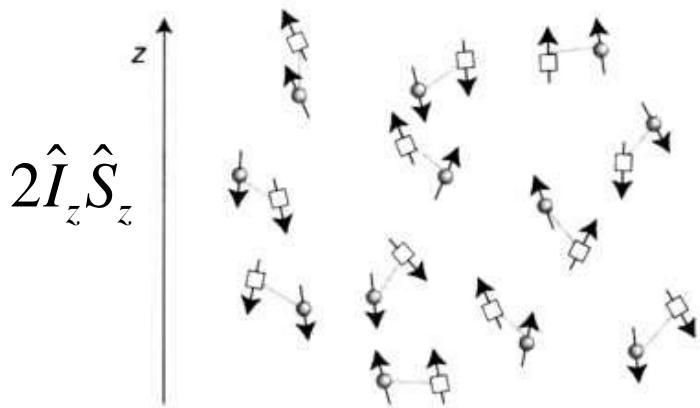
Two-spin Phase Coherences



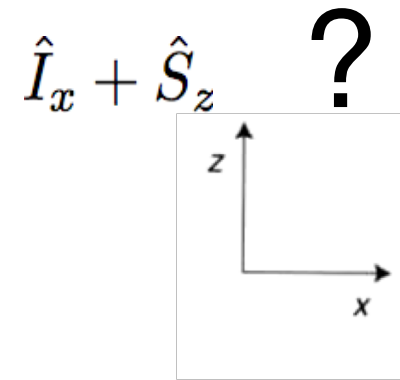
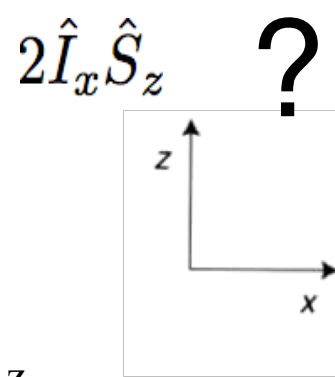
Net tendency for S spins to be +z
 No net tendency for I spins in any direction



No net tendency for S spins in any direction
 Net tendency for I spins to be +x



No net tendency for I or S spins to be $\pm z$
 If I or S is $\pm z$, increased probability paired spin is $\pm z$



Magnetization = Phase Coherences

- Some coherences are observable with Rf coils,

$$M_x = \gamma \hbar \overline{\langle \hat{I}_x \rangle}, \quad M_y = \gamma \hbar \overline{\langle \hat{I}_y \rangle}$$

“x magnetization”

“y magnetization”

...while others are not.

$$M_z = \gamma \hbar \overline{\langle \hat{I}_z \rangle} \quad \text{“z magnetization”}$$

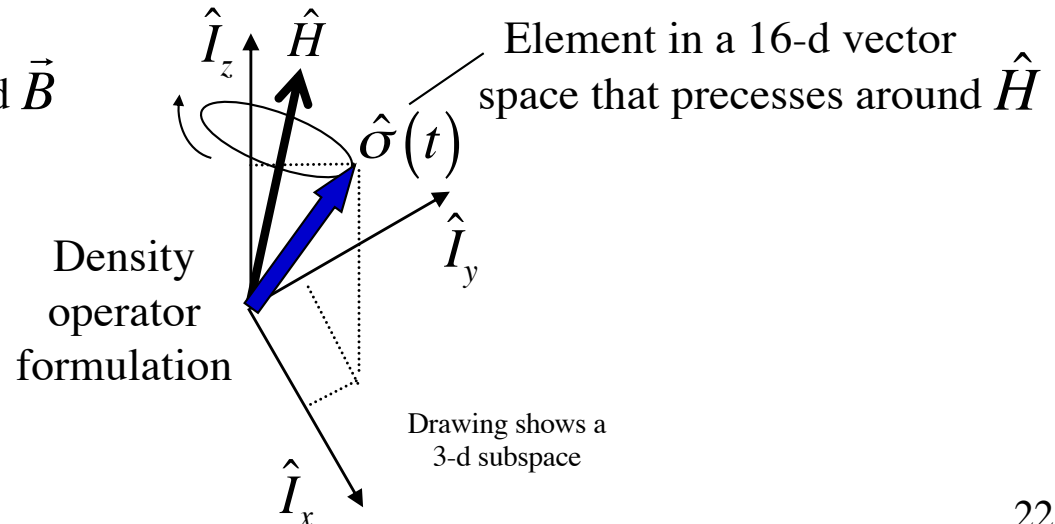
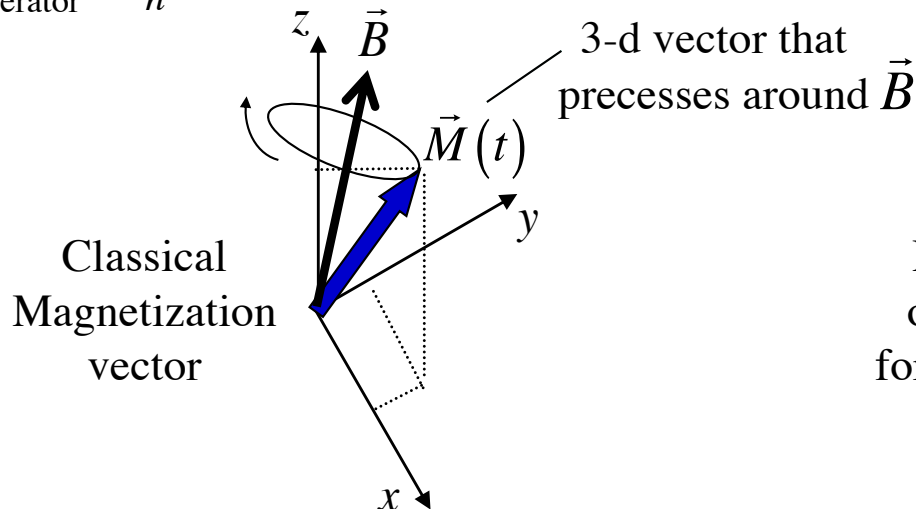
$$C_{xz} = \gamma \hbar \overline{\langle 2\hat{I}_x \hat{S}_z \rangle}, \quad C_{zz} = \gamma \hbar \overline{\langle 2\hat{I}_z \hat{S}_z \rangle}$$

“antiphase x” “longitudinal two-spin order”

- The total coherence for an ensemble of paired spins can be described by a linear combination of 16 terms, and there is a very elegant mathematical formalism to keep track of these coherences:

$$\hat{\sigma} = \sum_n b_n \hat{O}_n \quad \text{where} \quad \hat{O}_n \in \left\{ \frac{1}{2} \hat{E}, \hat{I}_x, \hat{S}_x, \hat{I}_y, \hat{S}_y, \hat{I}_z, \hat{S}_z, 2\hat{I}_x \hat{S}_z, 2\hat{I}_y \hat{S}_z, \dots, 2\hat{I}_z \hat{S}_z \right\}$$

density operator



Key Concept: temporal and spatial magnetic field variations* cause loss/gain of phase coherence (= “relaxation”)!

* also electric field variations for spins $> \frac{1}{2}$

- Our ultimate strategy will be to write the Hamiltonian as the sum of a large static component plus a small time-varying perturbation.

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t)$$

Rad226a/BioE326a

Rad226b/BioE326b

- Then look for an equation of the form:

$$\frac{\partial}{\partial t} \hat{\sigma} = -i\hat{H}_0 \hat{\sigma} - \hat{\Gamma} (\hat{\sigma} - \hat{\sigma}_B)$$

Relaxation superoperator

Rotations Relaxation

This equation is known as the Master Equation of NMR.

Note the similarity to Bloch's equations:

$$\frac{d\vec{M}}{dt} = \underbrace{\gamma \vec{M} \times B_0 \hat{z}}_{\text{Rotations}} - \underbrace{\frac{M_x \hat{x} + M_y \hat{y}}{T_2}}_{\text{Relaxation terms}} - \underbrace{\frac{(M_z - M_0) \hat{z}}{T_1}}_{\text{Relaxation terms}}$$

Next lecture:
Basics of Relaxation