

# Lecture #8

## Nuclear Spin Hamiltonian\*

- Topics
  - Introduction
  - External Interactions
  - Internal Interactions
- Handouts and Reading assignments
  - van de Ven: Chapters 2.1-2.2
  - Biographies: Ramsey, Zeeman
  - Levitt, Chapters 7 (optional)

\* many figures in this lecture from Levitt.

# The Spin Density Operator

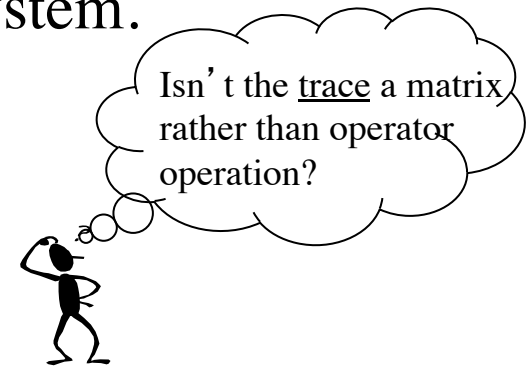
- Spin density operator:  $\hat{\sigma}(t)$ 
  - Completely describes the state of a spin system.

- The expectation of any observable  $\hat{A}$ :

$$\text{pure state: } \langle \hat{A} \rangle = \text{Tr}\{\hat{\sigma}_\psi \hat{A}\}$$

“inner product” in Liouville space

$$\text{statistical mixture of states: } \overline{\langle \hat{A} \rangle} = \text{Tr}\{\hat{\sigma} \hat{A}\}$$



- Example:  $x$ ,  $y$ , and  $z$  magnetization:

$$M_x = \gamma \hbar \overline{\langle \hat{I}_x \rangle} = \gamma \hbar \text{Tr}\{\hat{\sigma} \hat{I}_x\} \quad \text{similarly} \quad \begin{aligned} M_y &= \gamma \hbar \text{Tr}\{\hat{\sigma} \hat{I}_y\} \\ M_z &= \gamma \hbar \text{Tr}\{\hat{\sigma} \hat{I}_z\} \end{aligned}$$

# Liouville-von Neuman Equation

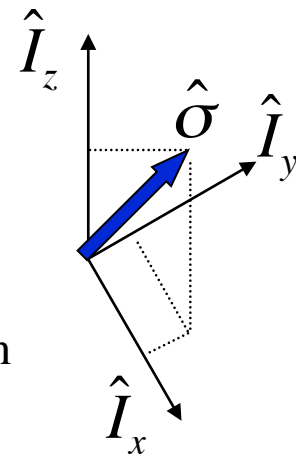
- Time evolution of  $\hat{\sigma}(t)$ :

$$\frac{\partial}{\partial t} \hat{\sigma} = -i[\hat{H}, \hat{\sigma}] = -i\hat{H}\hat{\sigma}$$

- Hamiltonian  $\hat{H}$  - operator corresponding to energy of the system

- If  $\hat{H}$  time independent:  $\hat{H}(t) = \hat{H}$

$$\hat{\sigma}(t) = \underbrace{e^{-i\hat{H}t} \hat{\sigma}(0) e^{i\hat{H}t}}_{\text{textbook notation}} = \underbrace{e^{-i\hat{H}t}}_{\text{Superoperator notation}} \hat{\sigma}(0)$$



$\hat{\sigma}$  rotates around  
in operator space

- Key: find the Hamiltonian!

# The Spin Hamiltonian Revisited

- In general,  $\hat{H}$  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) interaction with dipole field of other nuclei
  - 3) spin-spin coupling

- Life is easier if:
  - $\hat{H}_i$  are time independent.

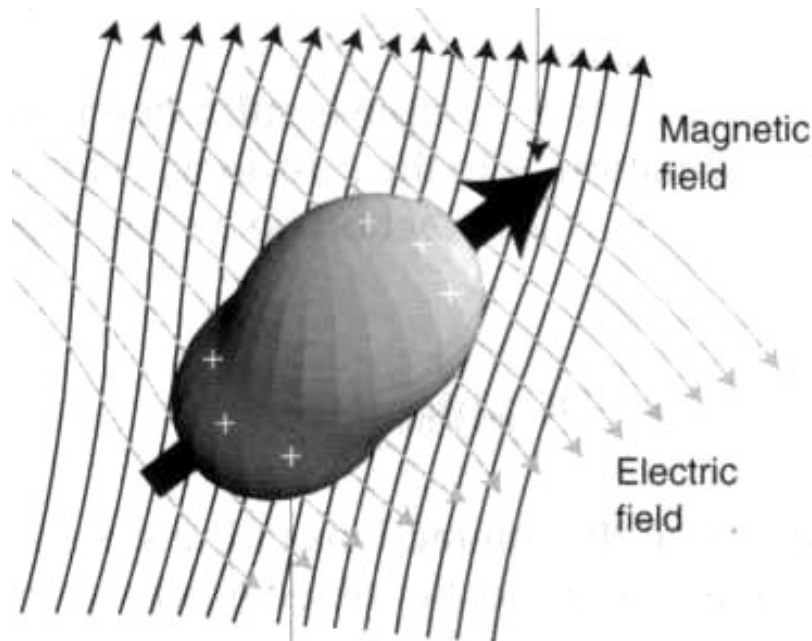
Terms that depend on spatial orientation may average to zero with rapid molecular tumbling (as if often seen in vivo).

- $\hat{H}_i, \hat{H}_j$  terms commute,  
then rotations  $e^{-i\hat{H}t} \hat{\sigma}$  can be computed in any order.

$$[\hat{H}_i, \hat{H}_j] = 0 \quad \Rightarrow \quad e^{-i(\hat{H}_1 + \hat{H}_2)t} = e^{-i\hat{H}_1t} e^{-i\hat{H}_2t} = e^{-i\hat{H}_2t} e^{-i\hat{H}_1t}$$

# Electromagnetic Interactions

- Think of an atomic nucleus as a lumpy magnet with non-uniform positive electric charge
- Nuclear spin Hamiltonian contains terms which describe the orientation dependence of the nuclear energy



Nuclear magnetic moment  
interacts with magnetic fields

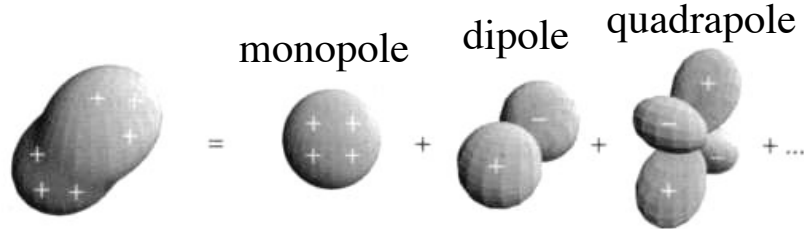
Nuclear electric charge interacts  
with electric fields

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

# Electromagnetic Interactions

- Electric Interactions

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



The diagram illustrates the expansion of a nuclear electric charge distribution. On the left, a grey, irregularly shaped volume represents the actual charge distribution. This is equated to a sum of three components: a single sphere with a '+' sign labeled 'monopole', two spheres with '+' and '-' signs labeled 'dipole', and four spheres with '+' and '-' signs labeled '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 (not obvious)

→  $\hat{H}^{elec} = 0$  (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, i.e. Spin-1/2 nuclei behaves exactly like point charges!

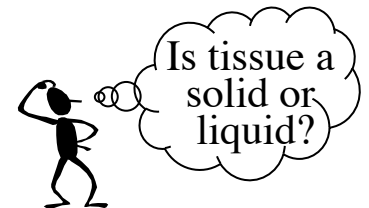
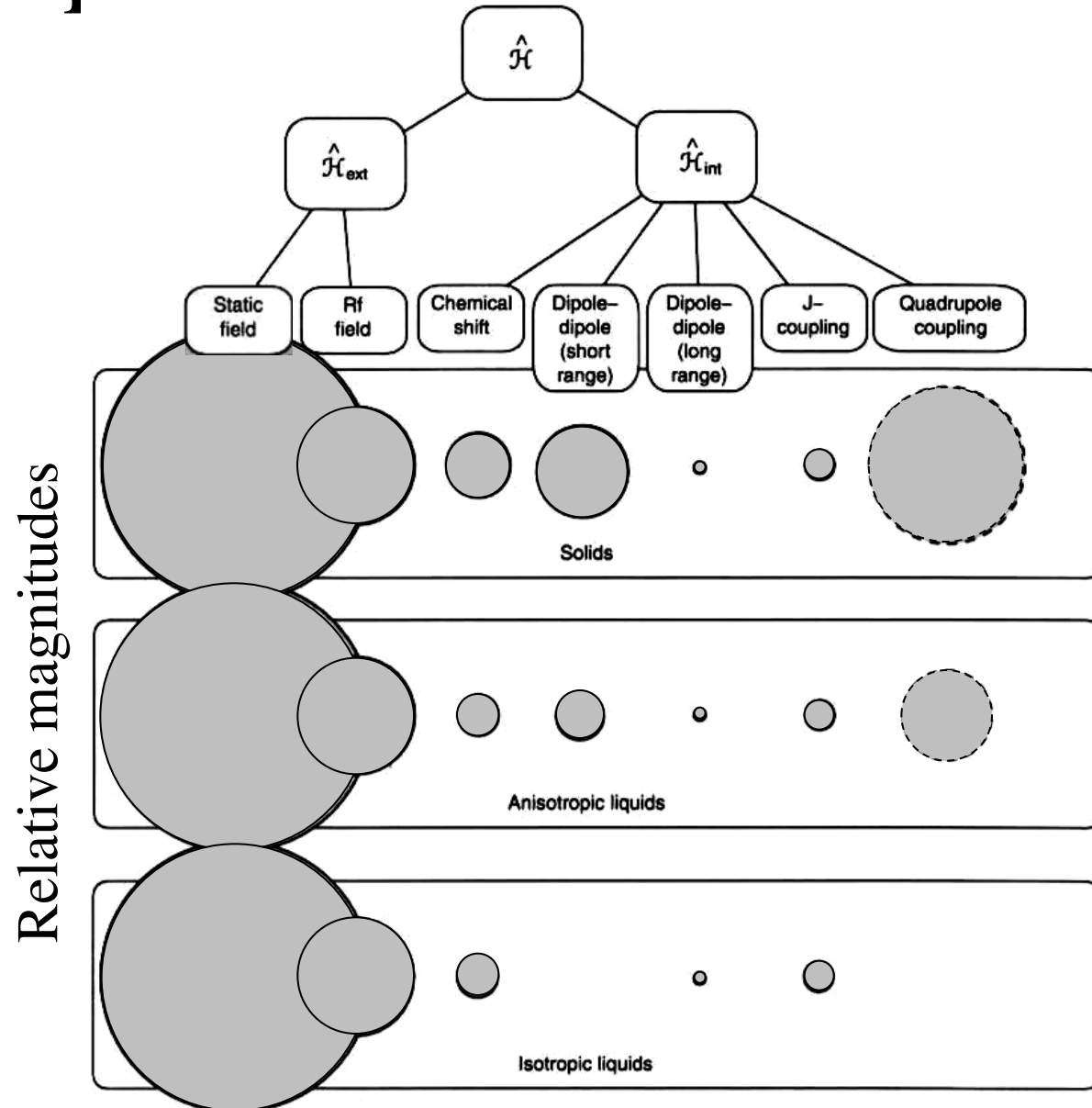
- Magnetic Interactions (we've seen this before)

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

magnetic moment

local magnetic field

# Spin Hamiltonian: Overview



# External Magnetic Fields

- Static Field  $B_0$

$$\vec{B} = B_0 \vec{e}_z \rightarrow \hat{H}^{static} = -\gamma B_0 \hat{I}_z = -\omega_0 \hat{I}_z$$

↙  
unit vector in z direction

- With RF excitation (assuming  $B_1$  along the x axis)

$$\vec{B}_{RF} = B_1 (\cos \omega t \vec{e}_x - \sin \omega t \vec{e}_y)$$

$$\rightarrow \hat{H}^{ext} = \hat{H}^{static} + \hat{H}^{RF} = -\gamma B_0 \hat{I}_z - \gamma B_1 (\hat{I}_x \cos \omega t - \hat{I}_y \sin \omega t)$$

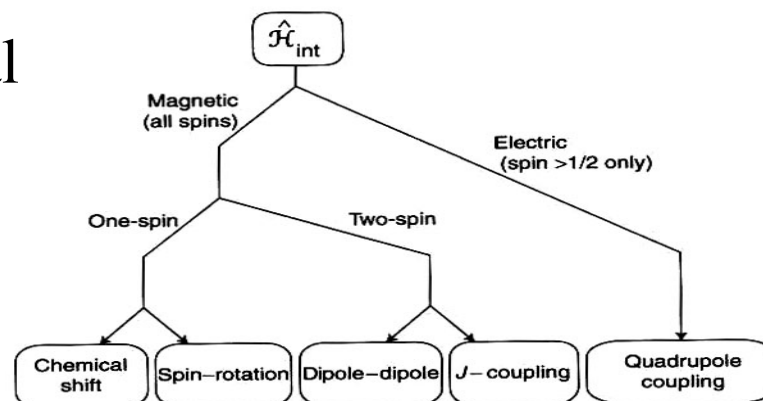
In the rotating frame, near resonance ( $\omega \approx \omega_0$ )

$$\hat{H}^{ext} \approx -\omega_1 \hat{I}_x$$



# Internal Interactions

- In general, the form of the internal nuclear spin Hamiltonian is quite complicated.



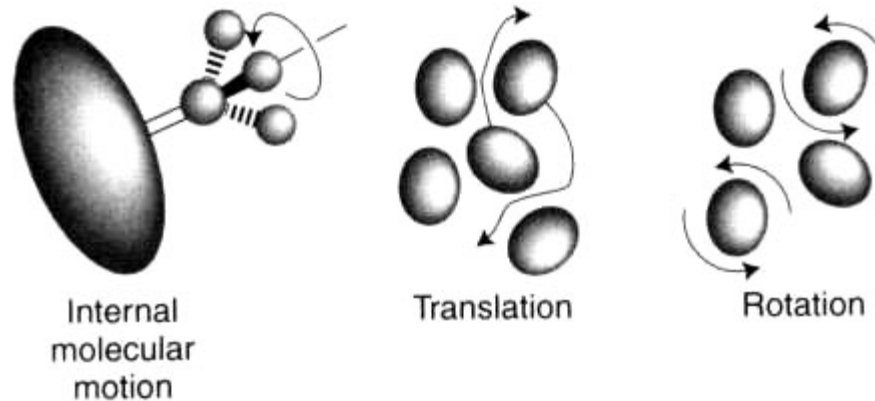
- We'll make two simplifying approximations.

$$\boxed{\hat{H}_{\text{int}}} \xrightarrow{\text{Secular approx.}} \boxed{\hat{H}_{\text{int}}^0} \xrightarrow{\text{Molecular motion}} \boxed{\overline{\hat{H}_{\text{int}}^0}}$$

1. Secular approximation: large  $B_0$  field dominate some of the internal spin interactions.
  2. Motional averaging: with rapid molecular tumbling, some interaction terms fluctuate with time and can be replaced by their motionally averaged values. Terms with zero time-average are dropped.
- Discarded internal spin Hamiltonian terms are responsible for spin relaxation.

# Motional Averaging

- Molecular motion



- Rotation

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

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

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

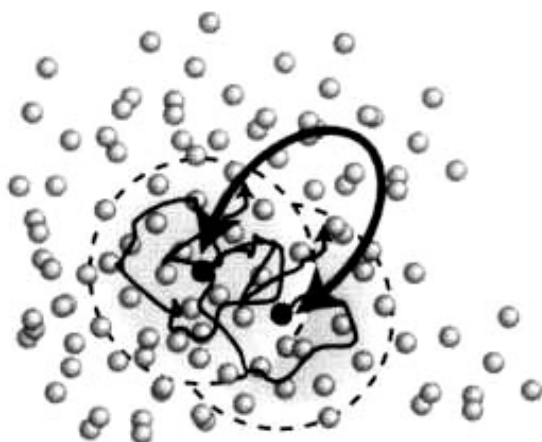
Isotropic materials:  $\overline{\hat{H}_{\text{int}}^0}^{\text{isotropic}} = \frac{1}{N} \int \hat{H}_{\text{int}}^0(\Theta) d\Theta$

normalization

# Motional Averaging

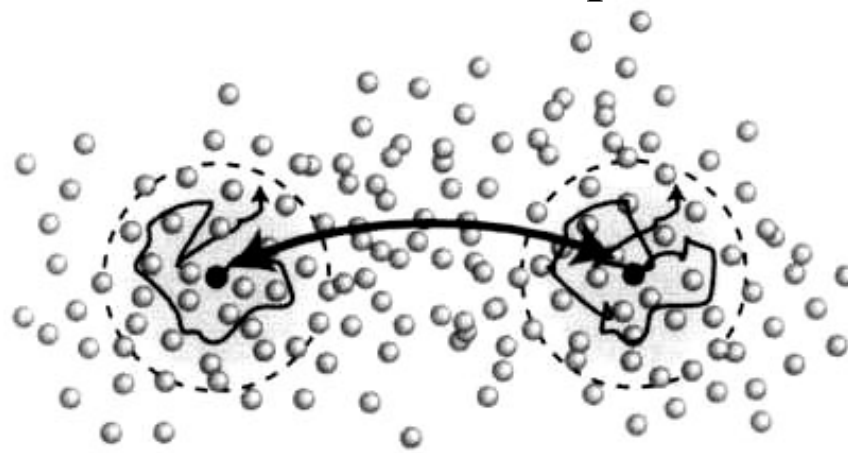
- Diffusion

On the timescale of an NMR experiment, molecules in a liquid largely diffuse within a small spherical volume a few tens of microns in diameter (known as a diffusion sphere).



Short-range intermolecular interaction

Intermolecular interactions within the diffusion sphere average out to zero.



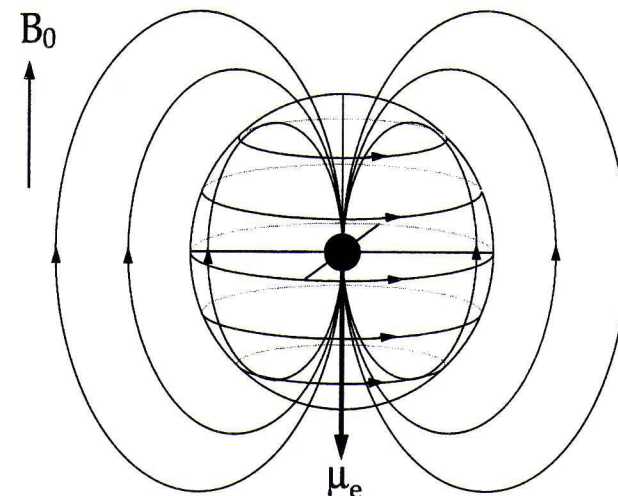
Long-range intermolecular interaction

Long-range interactions don't average to zero, but are very small.

# $B_0$ -Electron Interactions

When a material is placed in a magnetic field it is magnetized to some degree and 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 (to be revisited when we talk about field inhomogeneities and shimming).

- 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.

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

Who's this Zeeman guy?



- 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.

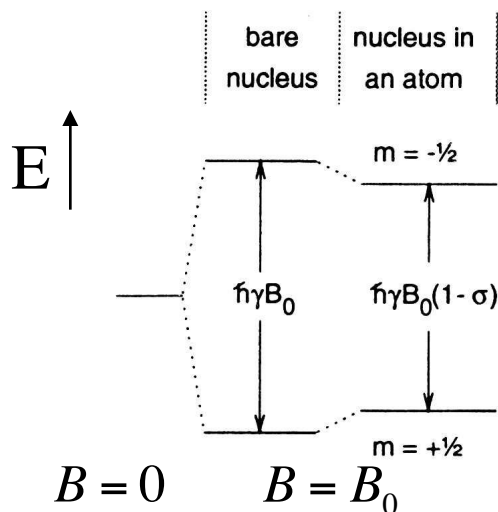
$$\sigma = \sigma_{iso} = \text{Tr}(\underline{\sigma}/3) \quad (\text{anisotropic components do contribute to spin relaxation})$$

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

$$\begin{aligned} \hat{H}_{Zeeman} &= -\gamma(1 - \sigma)B_0\hat{I}_z \\ &= -\omega\hat{I}_z \end{aligned}$$

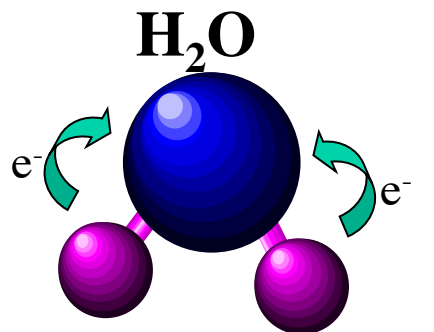
# Chemical Shift

- Energy diagram:



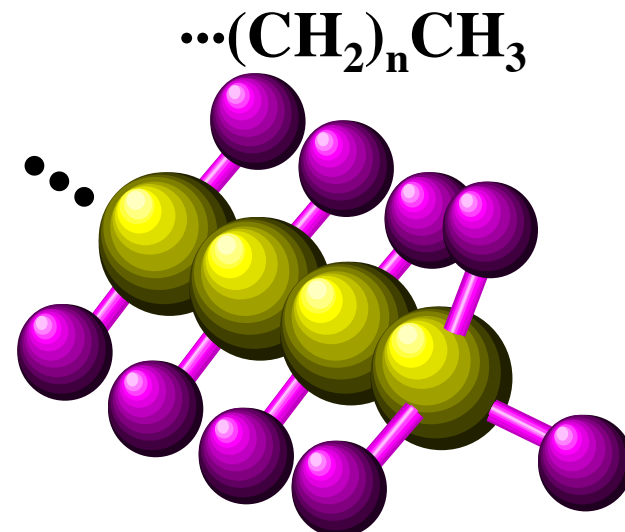
Frequency (Hz)  
 $\nu = \gamma B_0(1 - \sigma) / 2\pi$

**water**

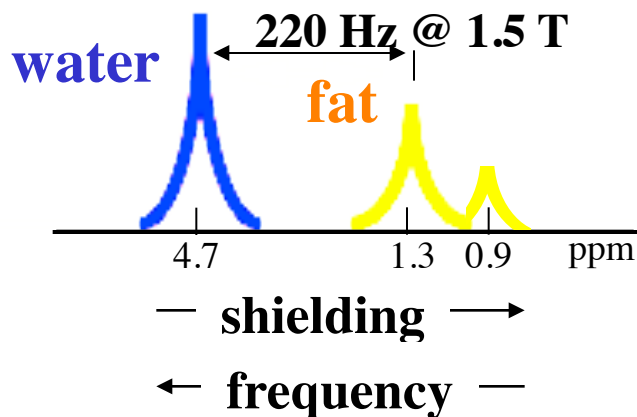


oxygen is electrophilic

**fat**



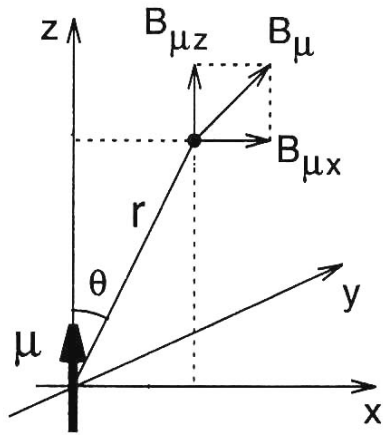
First complete theory of chemical shift was developed by Norman Ramsey in 1950.



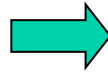
Usually plotted as relative frequency  
 $\delta = 10^6(\nu - \nu_{ref}) / \nu_{ref}$

# Magnetic Dipoles

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



Dipole at origin



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

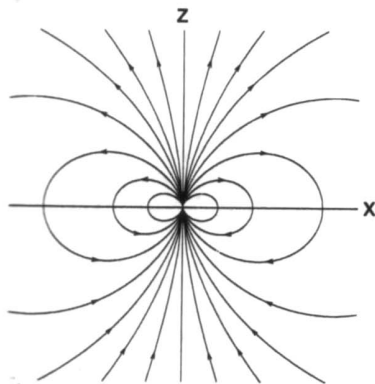
$$B_{\mu y} = 0$$

permeability of free space

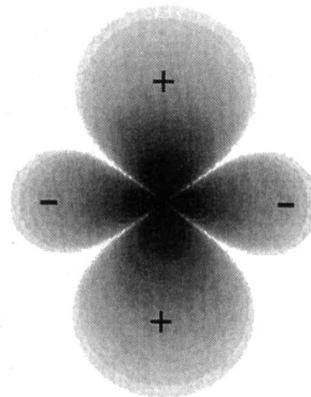
$$B_{\mu z} = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{\mu}{r^3} \right) (3 \cos^2 \theta - 1)$$

falls off as  $r^3$

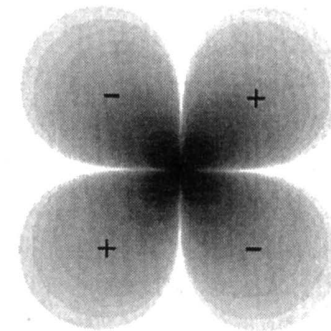
Magnetic Field in  $y=0$  plane



Lines of Force



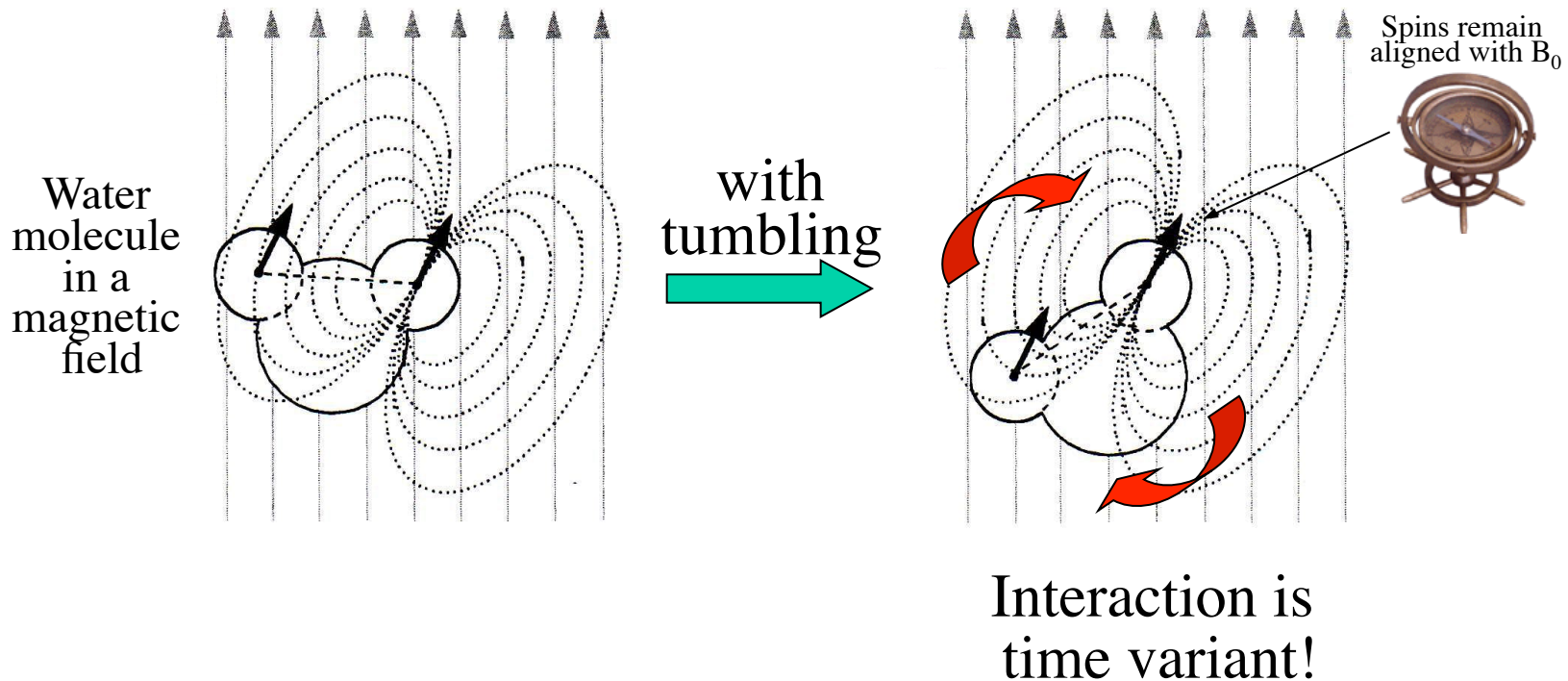
$B_{\mu z}$



$B_{\mu x}$

# 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 Dipole Hamiltonian

- Mathematically speaking, the general expression is:

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

- Secular approximation:

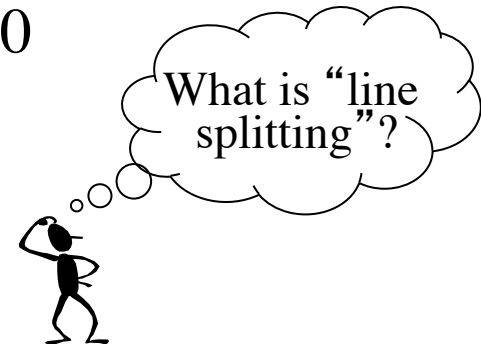
$$\hat{H}_{dipole} = d \left( 3\hat{I}_z \hat{S}_z - \hat{I} \cdot \hat{S} \right) \quad \text{where } d = -\frac{\mu_0 \gamma_I \gamma_S}{4\pi r^3} \hbar (3 \cos^2 \Theta_{IS} - 1)$$

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

- with isotropic tumbling (*e.g.* liquid):  $\overline{\hat{H}_{dipole}} = 0$

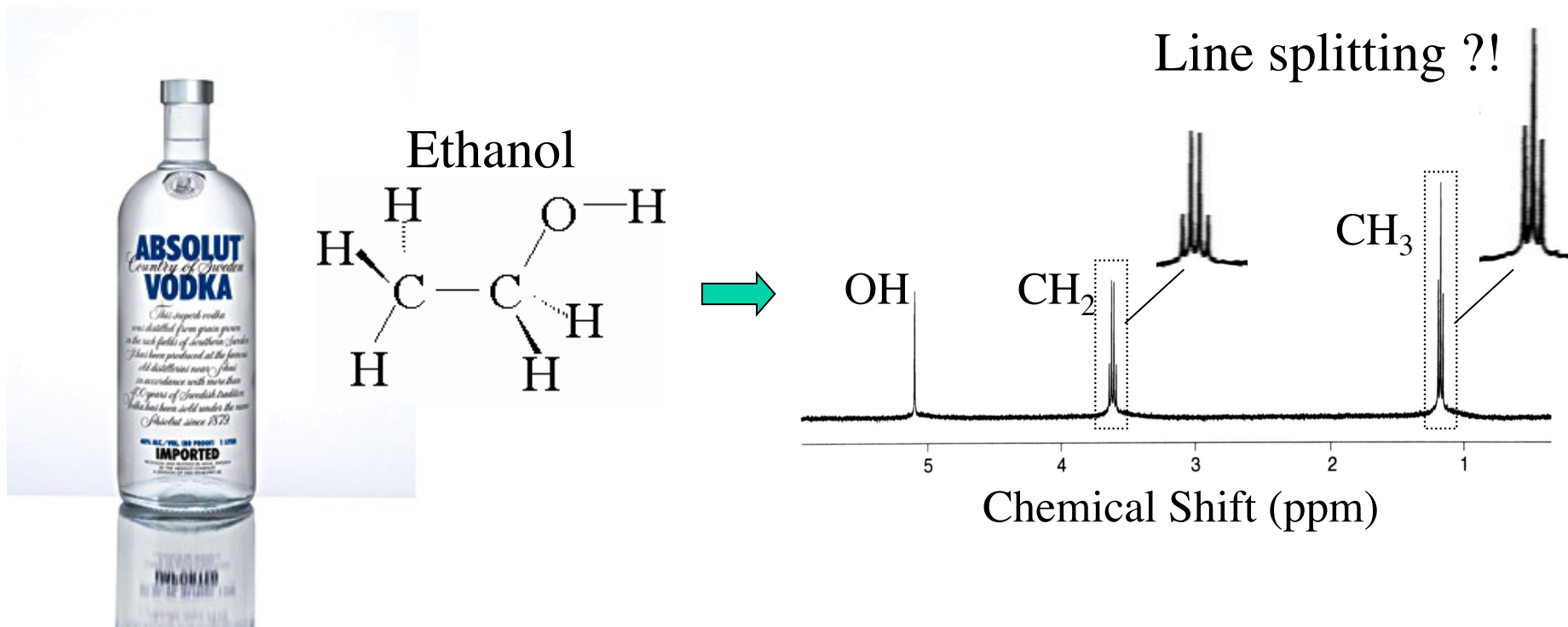
- without tumbling (*e.g.* solid): line splitting

Note: big effects on relaxation for both cases.



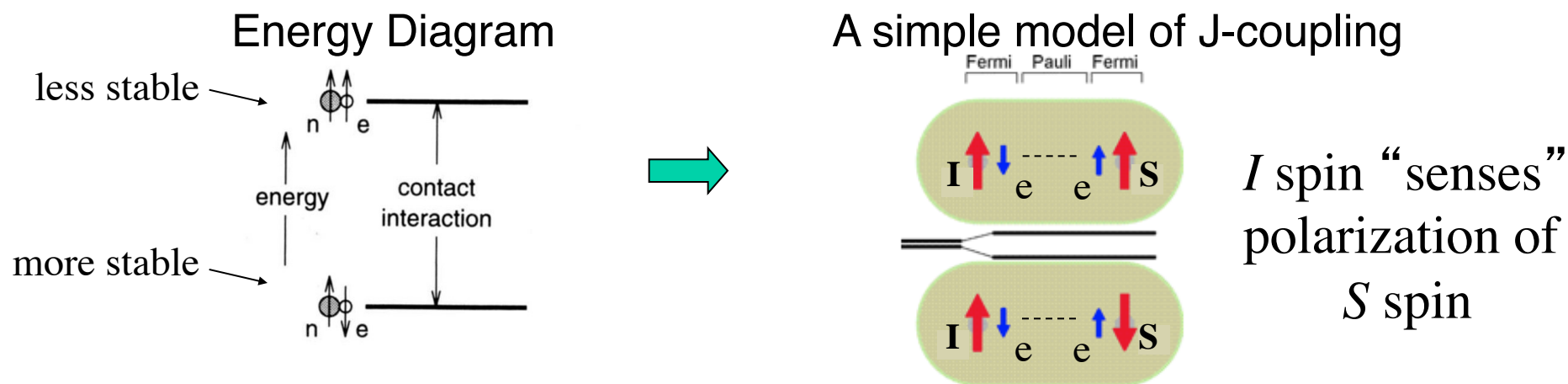
# J-Coupling

- The most obvious interactions between neighboring nuclei is their mutual dipole coupling.
- However this anisotropic interaction averages out to zero for freely tumbling molecules.
- Consider the following NMR spectrum:



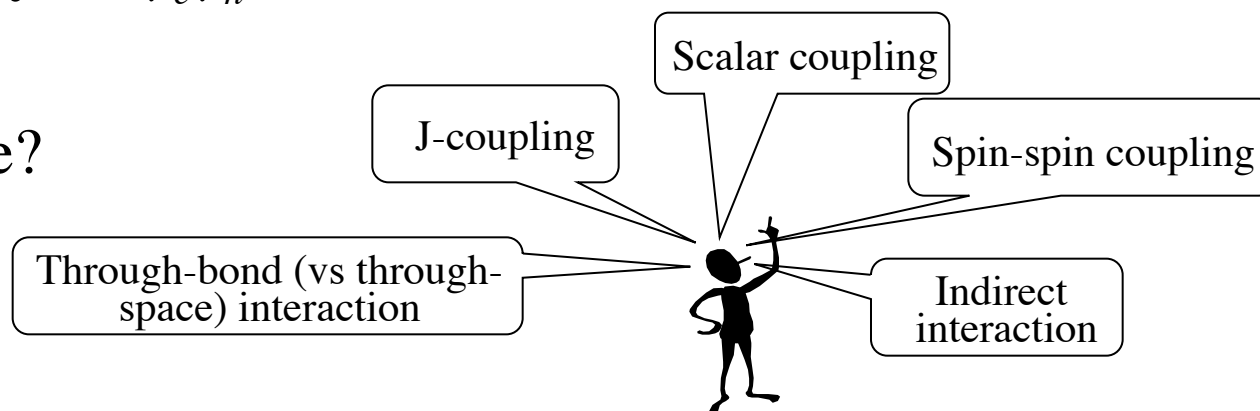
# J-Coupling: Mechanism

- 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”.

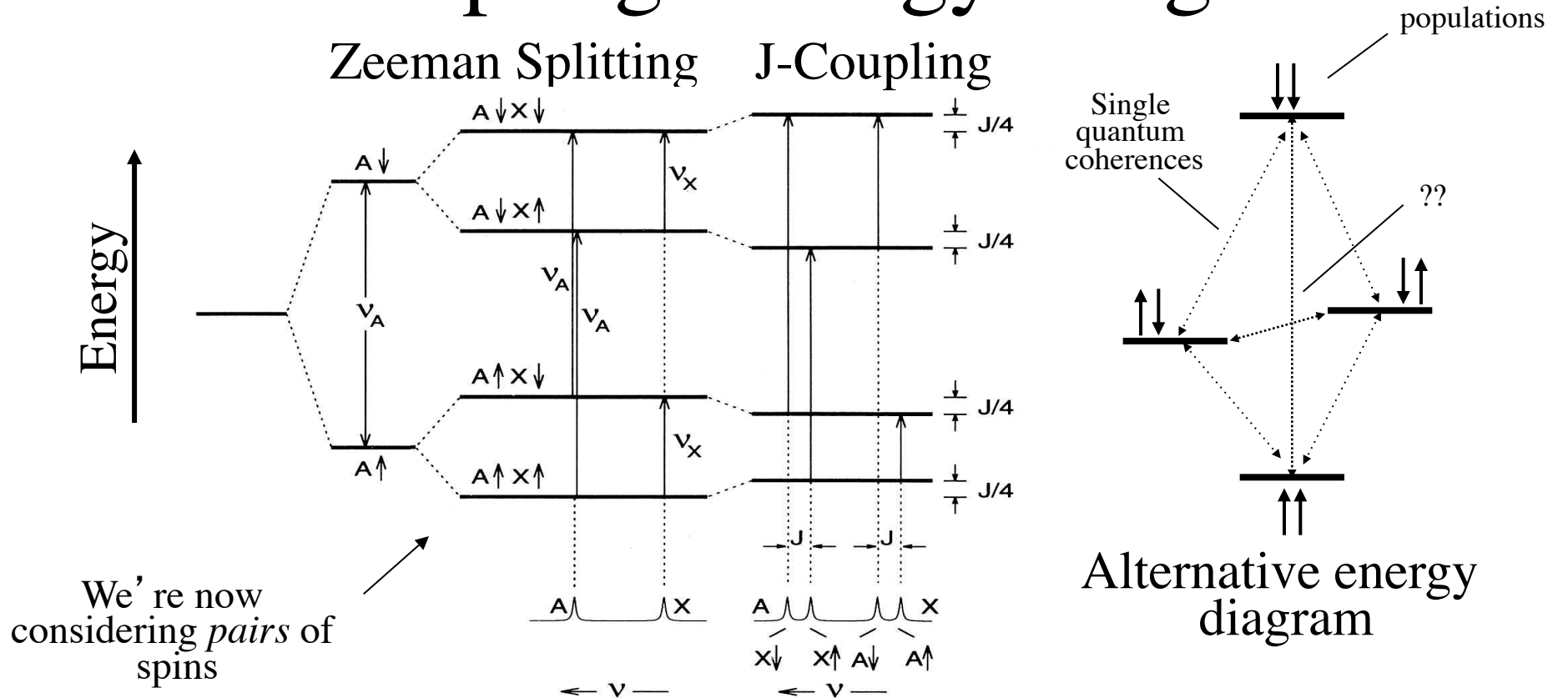


- Interaction energy  $\propto -\gamma_e \gamma_n \hat{I} \cdot \hat{S}$  ← independent of molecular orientation

- What’s in a name?



# J-Coupling: Energy Diagram



- The J-Coupling Hamiltonian

$$\hat{H}_J = \hat{I} \underline{J} \hat{S} = 2\pi \hat{I} \cdot \hat{S} = 2\pi J (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z)$$

J-coupling constant (Hz)

“product operators” 20

# Summary: Nuclear Spin Hamiltonian

- Free Precession ignore for now: effect small or time average=0

$$\hat{H} = \hat{H}_{Zeeman} + \hat{H}_{dipole} + \hat{H}_J + \hat{H}_{quadrupole}$$

vanishes for spin=1/2

$$\hat{H} = -\Omega_I \hat{I}_z + -\Omega_S \hat{S}_z + 2\pi J(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z)$$

$\Omega_I$  and  $\Omega_S$  are resonant frequencies in rotating frame:

$$\Omega_I = \gamma(1 - \sigma_I)B_0 - \omega_{rf} = \omega_I - \omega$$

$$\Omega_S = \gamma(1 - \sigma_S)B_0 - \omega_{rf} = \omega_S - \omega$$

- With RF excitation (assuming  $B_1$  along the x axis)

$$\hat{H} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z) - \omega_1^I \hat{I}_x - \omega_1^S \hat{S}_x$$

$$\hat{H} \approx -\omega_1^I \hat{I}_x - \omega_1^S \hat{S}_x \quad \text{for } \begin{cases} \omega_1^I \gg \Omega_I \text{ and } \omega_1^S \gg \Omega_S \\ \omega_1^I, \omega_1^S \gg 2\pi J \end{cases} \quad (\text{secular approx.})$$

Above equations hold for both homonuclear and heteronuclear cases.

Next lecture:  
Density Matrix, Populations, and  
Coherences

# Biography: Norman Ramsey

Norman F. Ramsey was born in Washington, D.C. and 'was educated in the United States and England; he earned five degrees in physics including the Ph.D. (Columbia 1940) and the D.Sc. (Cambridge, 1964).

Ramsey's scientific research focused on the properties of molecules, atoms, nuclei and elementary particles and includes key contributions to the knowledge of magnetic moments, the structural shape of nuclear particles, the nature of nuclear forces, the thermodynamics of energized populations of atoms and molecules (e.g. those in masers and lasers) and spectroscopy.

Ramsey not only contributed basic advances in the theoretical understanding of the physics involved in his research, he also made pioneering advances in the methods of investigation; in particular, he contributed many refinements of the molecular beam method for the study of atomic and molecular properties, he invented the separated oscillatory field method of exciting resonances and, with the collaboration of his students, he was the principal inventor of the atomic hydrogen maser. The separated oscillatory field method provides extremely high resolution in atomic and molecular spectroscopy and it is the practical basis for the most precise atomic clocks; likewise the atomic hydrogen maser made even higher levels of spectroscopic resolution possible and it also functions as the basis for atomic clocks having the highest levels of stability for periods extending to several hours.'

'During World War II his involvement with MIT's Radiation Laboratory led to the development of 3 cm radar and later he was leader of the Delivery Group of the Manhattan Project in Los Alamos. In 1947 he moved to Harvard University where he continues research and writing as the Higgins Professor of Physics, Emeritus. His research has ranged from atomic beams to particle physics.

Ramsey participated in the founding of Brookhaven National Laboratory and served as the first Chairman of its Physics Department. He was Chairman of the Atomic Energy Commission's High Energy Physics Advisory Panel in 1963 when the recommendation was made to build a 200 GeV accelerator. Ramsey was then instrumental in the creation of Fermilab as Founding President of the Universities Research Association (URA), the Laboratory's management organization, from 1966 until 1981. He smoothly oversaw the operation of the Laboratory from his URA offices in Washington when he was not personally visiting the site to be involved with Fermilab's successful development. ...

Ramsey has also served as Chairman of the General Advisory Committee of the Atomic Energy Commission ... . He has won many awards, including the Rabi Prize, the Rumford Premium of the American Academy of Arts and Sciences, and the 1988 National Medal of Science. In 1989 he received the Nobel Prize for Physics for his research leading to the development of the hydrogen maser and the cesium atomic clock.'



# Biography: Pieter Zeeman



Born at Zonnemair in the Netherlands, Zeeman studied at Leiden University and received a doctorate in 1893. This was for his work on the Kerr effect, which concerns the effect of a magnetic field on light. In 1896 he discovered another magneto-optical effect, which now bears his name – he observed that the spectral lines of certain elements are split into three lines when the sample is in a strong magnetic field perpendicular to the light path; if the field is parallel to the light path the lines split into two. This work was done before the development of quantum mechanics, and the effect was explained at the time using classical theory by Hendrik Antoon Lorentz, who assumed that the light was emitted by oscillating electrons.

This effect (splitting into three or two lines) is called the normal Zeeman effect and it can be explained using Niels Bohr's theory of the atom. In general, most substances show an anomalous Zeeman effect, in which the splitting is into several closely spaced lines – a phenomenon that can be explained using quantum mechanics and the concept of electron spin.

Zeeman was a meticulous experimenter and he applied his precision in measurement to the determination of the speed of light in dense media, confirming Lorentz's prediction that this was related to wavelength. Also, in 1918, he established the equality of gravitational and inertial mass thus reconfirming Einstein's equivalence principle, which lies at the core of general relativity theory.

Zeeman and Lorentz shared the 1902 Nobel Prize for physics for their work on magneto-optical effects.