# Basic Theory of Solid-State NMR

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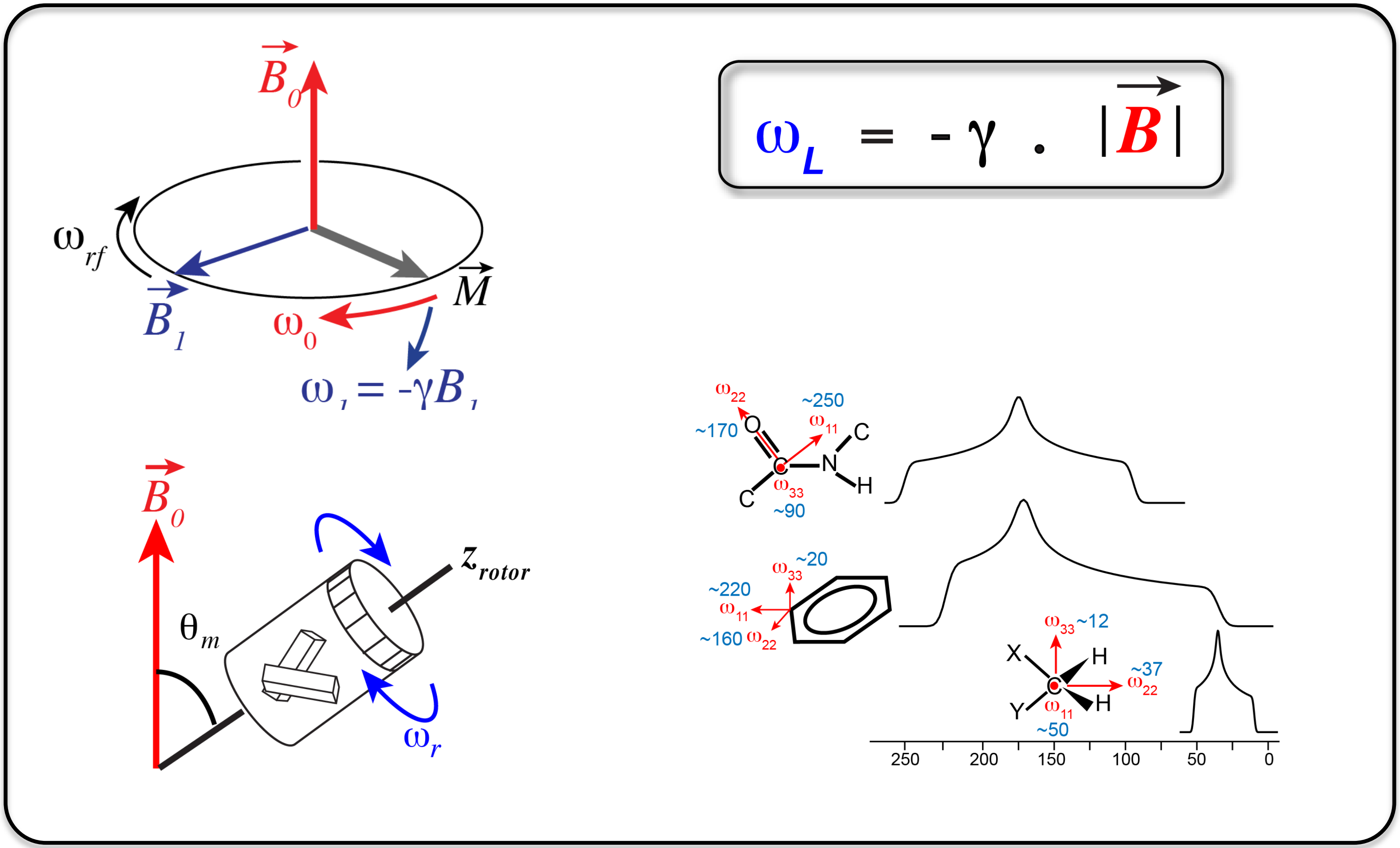
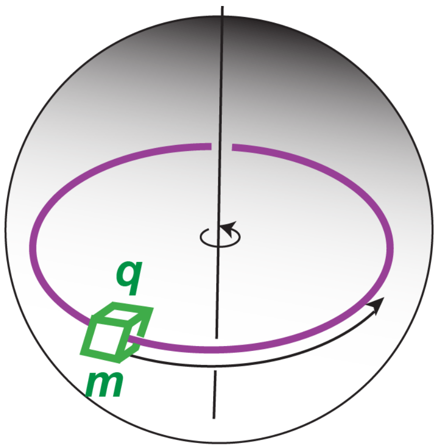


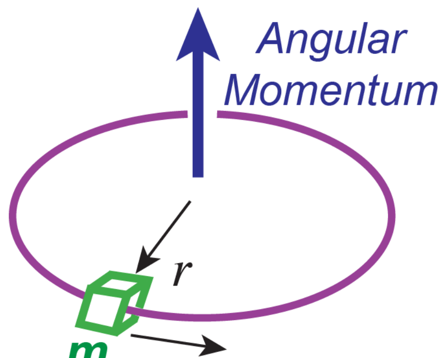

**Pre-ISMAR NMR Workshop, Moreton Bay Research Station, North Stradbroke Island, Univ. Queensland, Brisbane, Australia, August 18-20, 2023**

# Magnetic Dipole Moment From Nuclear Spins




Volume element of mass m and charge q

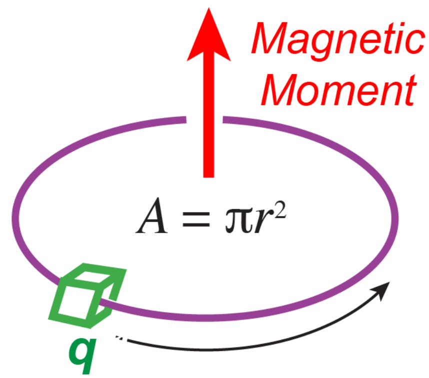
$$\vec{S} = \vec{r} \times \vec{p}$$

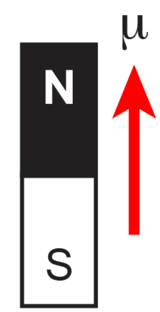



$$\vec{p} = m\vec{v}$$

$$S = rp = rmv$$

$$\vec{\mu} = \vec{e}_A\, A\, I$$



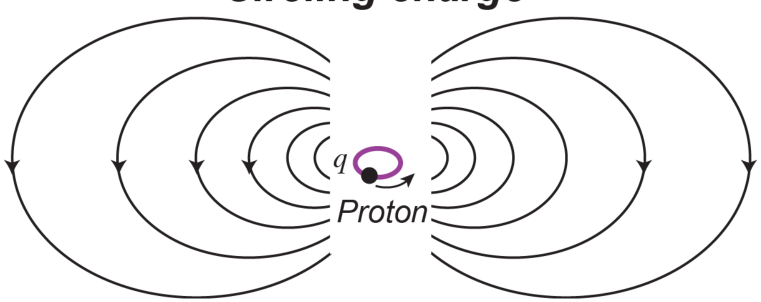




$$\mu = \pi r^2 \frac{q}{T} = rv\frac{q}{2} = S \cdot \frac{q}{2m}$$

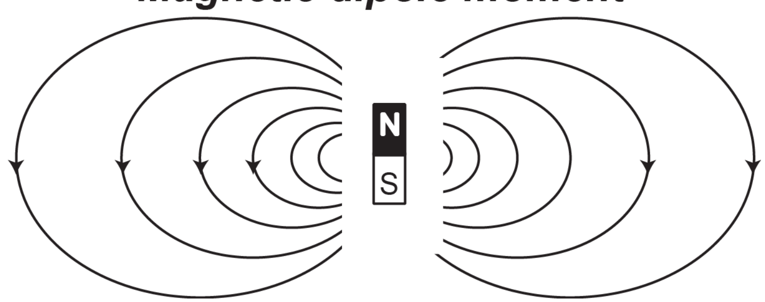
$$\boxed{\vec{\mu} = \gamma \vec{S}}$$

$$\gamma_N = g_N \frac{e}{2m_p}$$

**Circling charge**



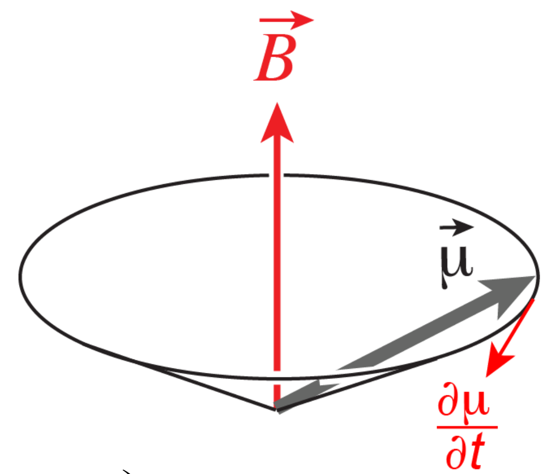

**Magnetic dipole moment**




- ***Energy*** of a magnetic dipole in a B field: $E = -\vec{\mu} \bullet \vec{B}$
- ***Torque*** on a magnetic dipole in a B field: $\vec{\tau} = \vec{\mu} \times \vec{B}$

# Precession of the Magnetic Moment Around B

$$\left.\begin{aligned} \vec{\tau} &= \vec{\mu}\times\vec{B} \\ \vec{\tau} &= \frac{d\vec{S}}{dt} = \frac{1}{\gamma}\frac{d\vec{\mu}}{dt} \end{aligned}\right\} \Rightarrow \boxed{\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu}\times\vec{B}}$$




(*Recall linear motion:* $\vec{F} = d\vec{p}/dt$)

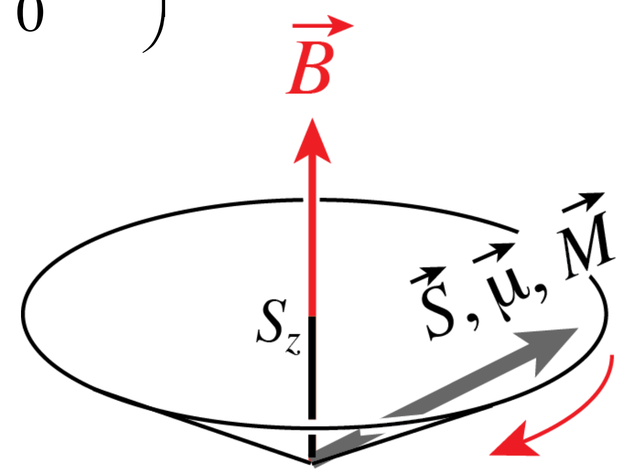
Bloch eqn

$$\vec{\mu}\times\vec{B} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \mu_x & \mu_y & \mu_z \\ 0 & 0 & B_0 \end{vmatrix} \Rightarrow \begin{pmatrix} d\mu_x/dt \\ d\mu_y/dt \\ d\mu_z/dt \end{pmatrix} = \gamma \begin{pmatrix} \mu_y B_0 \\ -\mu_x B_0 \\ 0 \end{pmatrix}$$

$$= \vec{i}\,\mu_y B_0 - \vec{j}\,\mu_x B_0 + \vec{k}\cdot 0$$

Solution of the Bloch eqn, for $\mu(0)$ in the $x$-$z$ plane:

$$\begin{cases} \mu_x(t) = \mu_x(0)\cos\omega t \\ \mu_y(t) = \mu_x(0)\sin\omega t \\ \mu_z(t) = \mu_z(0) \end{cases}$$




Larmor frequency $\omega = -\gamma B$

*The precessing M generates a voltage in the sample coil, which is detected.*

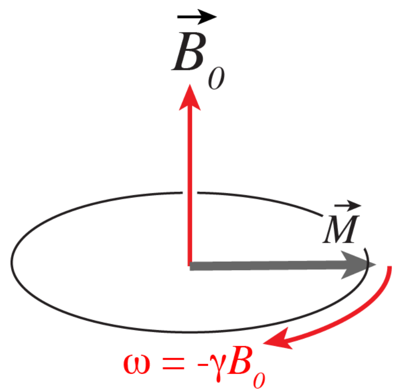
# Fields, Frequencies, Energies & RF Irradiation

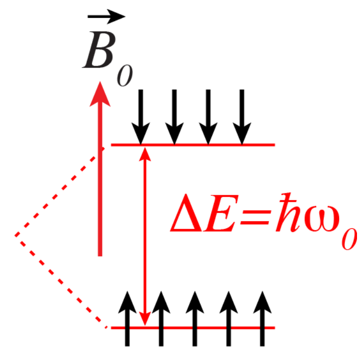
$\vec{B}_0$  $\omega_0 = -\gamma\left|\vec{B}_0\right| = 2\pi\nu_0$  $E = -\vec{\mu}\cdot\vec{B}_0$

$B_0 = 18.8$ Tesla

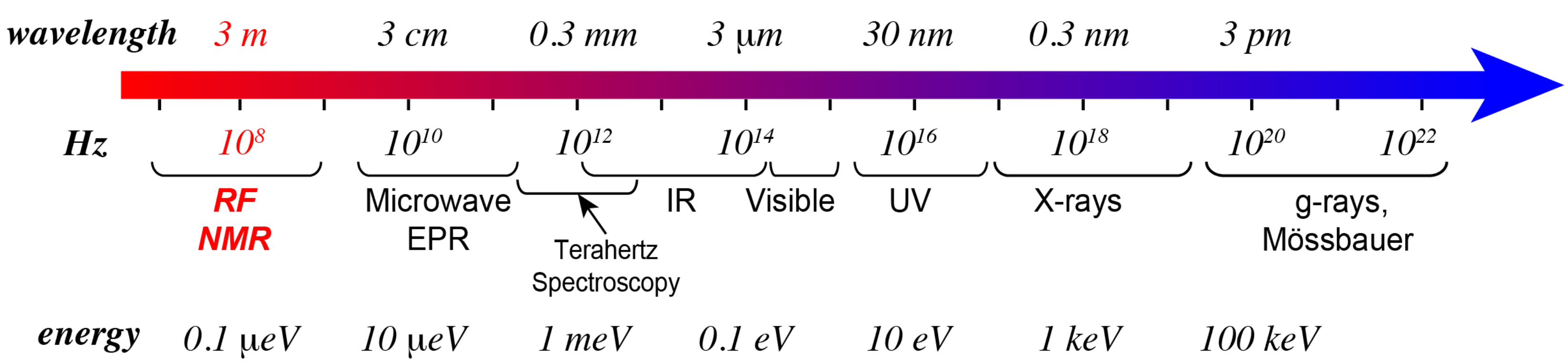
$^1$H Larmor frequency:
$\omega_0 = -2\pi$ 800 MHz

$\Delta E = \hbar\omega_0$
Energy splitting




Precession frequency = transition frequency



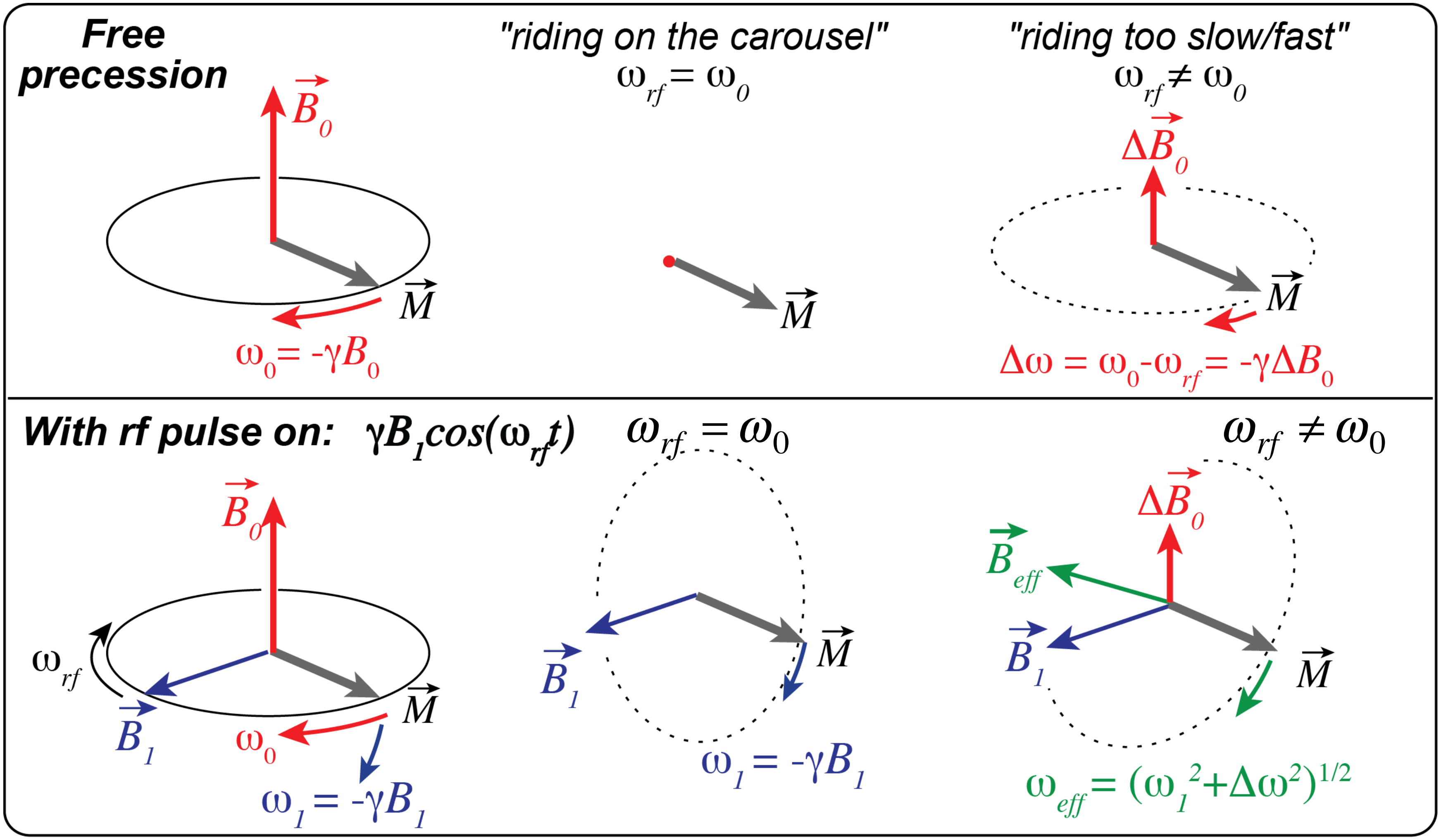

***Apply weak EM irradiation @ Larmor frequency: Radiofrequency pulses***

# Resonance, the Rotating Frame, and RF Pulses

Lab frame

Rotating frame, On resonance

Rotating frame, Off resonance



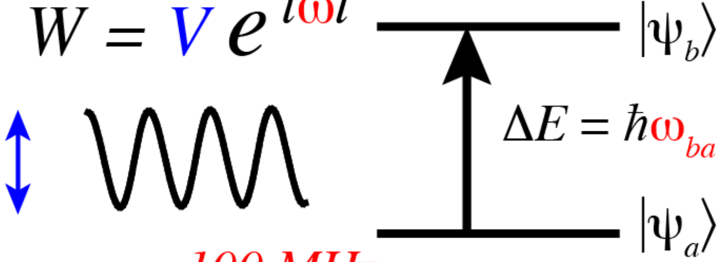

$$\frac{\omega_{rf}}{2\pi} \sim 50 - 1000\ MHz, \quad \frac{\omega_1}{2\pi} \sim 50 - 100\ kHz$$

# Resonance: Maximizing Transition Probability

Apply EM irradiation $\mathrm{V}\left(=\hbar\gamma B_1\right) << \Delta E\left(=\hbar\gamma B_0\right)$

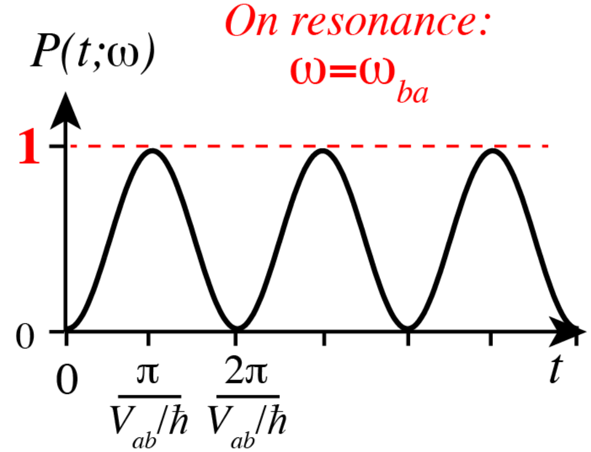
$$W = V\,e^{i\omega t}$$

$V/\hbar = \gamma B_1$
~100 kHz




$\omega_{ab},\ \omega$ ~100 MHz

*On resonance:* $\omega=\omega_{ba}$




Complete transition ($P_{ab}$=1) can be achieved even when the applied field strength $V_{ba}=\hbar\omega_1 << \hbar\omega_0$.

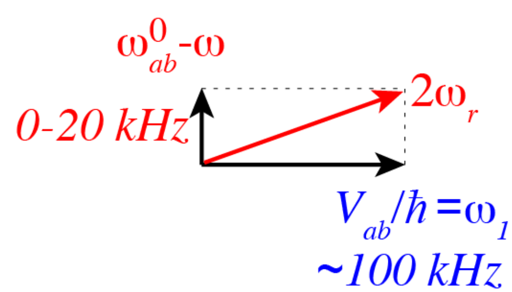
$$P_{ab}(t) = \frac{\left|V_{ba}\right|^2}{4\hbar^2}\frac{\sin^2\omega_r t}{\omega_r^2}$$

$\omega=\omega_{ab}$

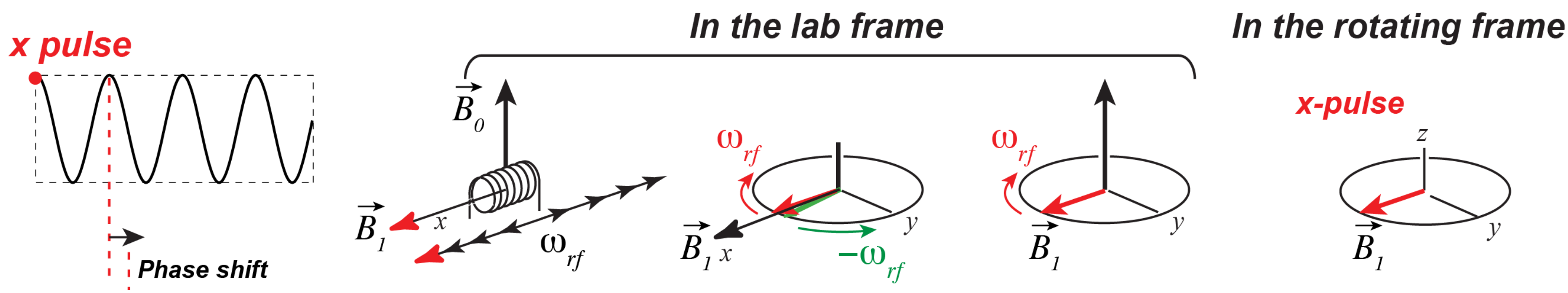
$$= \sin^2\omega_r t$$

*Rabi frequency:*

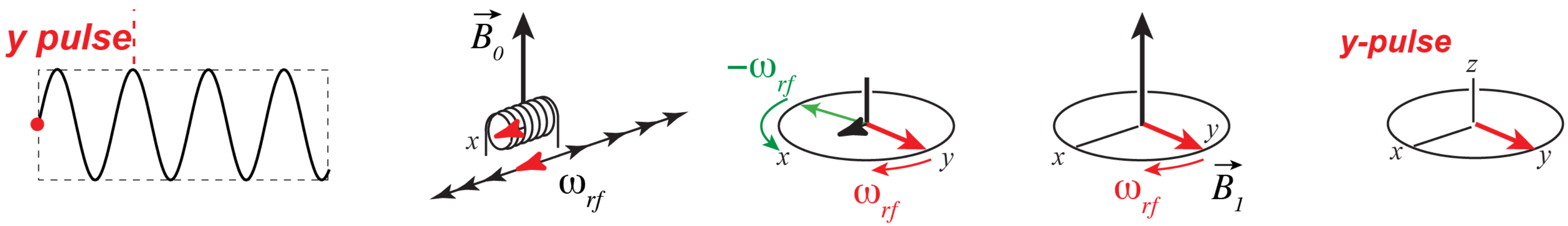
$$\omega_r = \frac{1}{2}\sqrt{\left(\omega_{ba}^0-\omega\right)^2+\left|V_{ab}\right|^2/\hbar^2}$$



# The Phase of RF Pulses



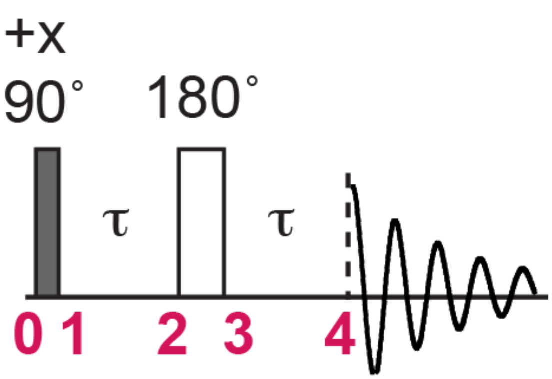

$$\vec{B}_1^{Lab}(t) = B_1\begin{pmatrix}\cos\omega_{rf}t\\0\\0\end{pmatrix} = \frac{B_1}{2}\begin{pmatrix}\cos\omega_{rf}t\\ \sin\omega_{rf}t\\0\end{pmatrix} + \frac{B_1}{2}\begin{pmatrix}\cos\omega_{rf}t\\-\sin\omega_{rf}t\\0\end{pmatrix} \Rightarrow \vec{B}_1^{Lab}(t) = \frac{B_1}{2}\begin{pmatrix}\cos\omega_{rf}t\\-\sin\omega_{rf}t\\0\end{pmatrix} \Rightarrow \vec{B}_1^{rot}(t) = \frac{B_1}{2}\begin{pmatrix}1\\0\\0\end{pmatrix}$$



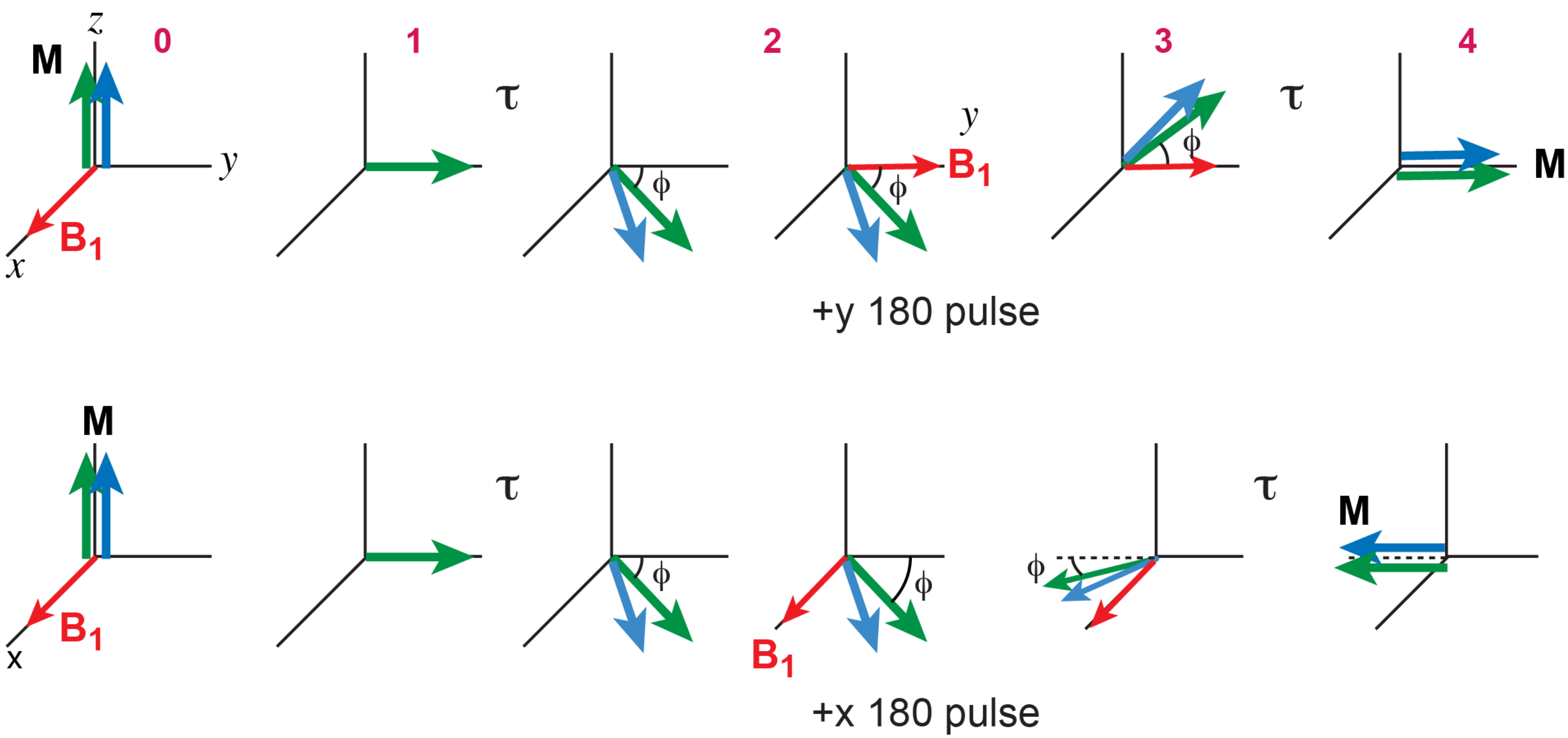

$$\vec{B}_1^{Lab}(t) = B_1\begin{pmatrix}\sin\omega_{rf}t\\0\\0\end{pmatrix} = \frac{B_1}{2}\begin{pmatrix}\sin\omega_{rf}t\\ -\cos\omega_{rf}t\\0\end{pmatrix} + \frac{B_1}{2}\begin{pmatrix}\sin\omega_{rf}t\\ \cos\omega_{rf}t\\0\end{pmatrix} \Rightarrow \vec{B}_1^{Lab}(t) = \frac{B_1}{2}\begin{pmatrix}\sin\omega_{rf}t\\ \cos\omega_{rf}t\\0\end{pmatrix} \Rightarrow \vec{B}_1^{rot}(t) = \frac{B_1}{2}\begin{pmatrix}0\\1\\0\end{pmatrix}$$

- Change in *phase* of $B_1(t)$ by 90° in the *lab frame* corresponds to a change in *direction* of $B_1$ in the *rotating frame* (e.g. from *x* to *y*)
- Pulse *phase* can also change due to *frequency* change: PMLG = FSLG.

# Effects of RF Pulses: Spin Echo & Vector Model




- Precession at different frequencies in the rotating frame.
- Effect of rf pulses: left-hand rule.



# A Central Equation: Local Fields & Frequencies

$$\boxed{\omega_L = -\gamma \cdot \left| \vec{B} \right|}$$

Resonance frequency

Magnetic field at the nucleus

*Probe local magnetic fields at the nucleus*

$$\vec{B} = \vec{B}_0 + \vec{B}_{electrons} + \vec{B}_{X,dipole}$$

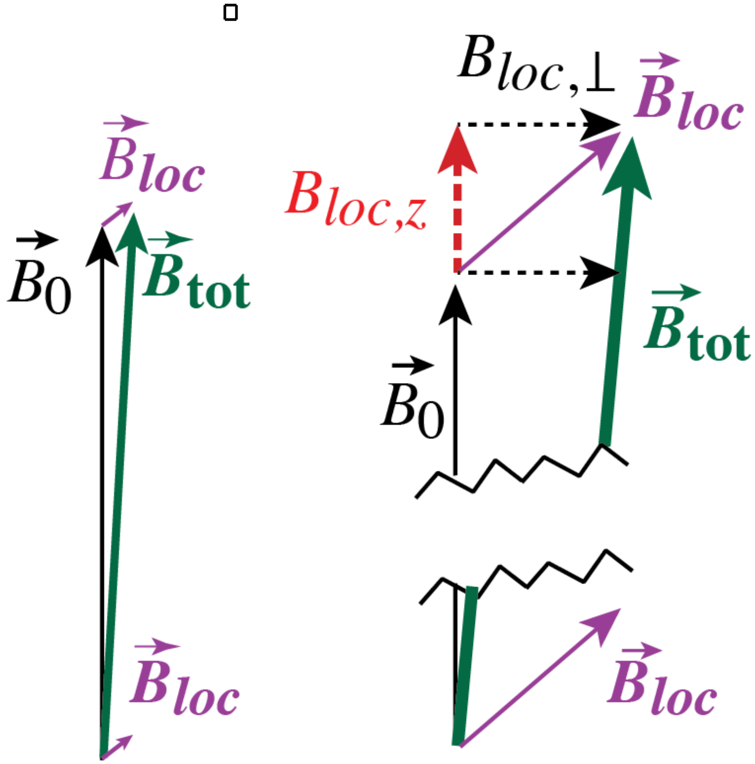
*superconducting magnet*

*chemical shift (bonding)*

*fields of other magnetic dipoles, ~ $1/r^3$*

- Local fields from electrons & other nuclei are much weaker than the Zeeman field …

# Truncation of Weak Interactions by Zeeman Interaction




$$\left|\vec{B}_{tot}\right| = \left|\vec{B}_0 + \vec{B}_{loc}\right| = \sqrt{\left(B_0 + B_{loc,//}\right)^2 + B_{loc,\perp}^2}$$

$$= \left(B_0 + B_{loc,//}\right)\sqrt{1 + \frac{B_{loc,\perp}^2}{\left(B_0 + B_{loc,//}\right)^2}}$$

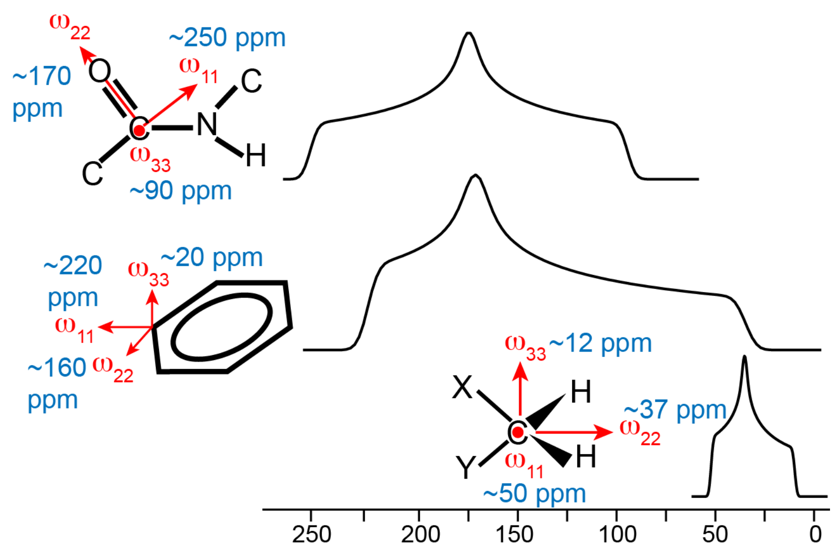
$$\underset{\text{Taylor expansion}}{=} \left(B_0 + B_{loc,//}\right)\left[1 + \underbrace{\frac{B_{loc,\perp}^2}{2\left(B_0 + B_{loc,//}\right)^2} + \ldots}_{<<\ 1}\right]$$

$$\approx B_0 + B_{loc,//}$$

$$\boxed{\omega_L \approx -\gamma\left(B_0 + B_{loc,//}\right) = \omega_0 + \omega_{loc,//}}$$

# Nuclear Spin Interactions: Hamiltonians

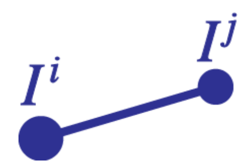
$$\hat{H}_{Zeeman} = -\gamma \hat{I}_z B_0$$




*chemical shielding tensor*

$$\hat{H}_{CS} = \gamma \vec{\hat{I}} \cdot \boldsymbol{\sigma} \cdot \vec{B}_0$$

$$\hat{H}_D = -\frac{\mu_0}{4\pi} \sum_j \sum_k \gamma_j \gamma_k \frac{3\left(\vec{\hat{I}}^{\,j} \cdot \vec{r}_{jk} / r_{jk}\right)\left(\vec{\hat{I}}^{\,k} \cdot \vec{r}_{jk} / r_{jk}\right) - \vec{\hat{I}}^{\,j} \cdot \vec{\hat{I}}^{\,k}}{r_{jk}^3}$$




*electric quadrupole moment*

$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \vec{\hat{I}} \cdot \mathbf{V} \cdot \vec{\hat{I}}$$

*electric field gradient tensor*

*Hamiltonians expressed in frequency units.*

# Truncated Hamiltonians: Keep the Operators that Commute with the Zeeman Interaction

$$\hat{H}_{Zeeman} = \omega_0 \cdot \hat{I}_z \gg H_{CS,D,Q}$$

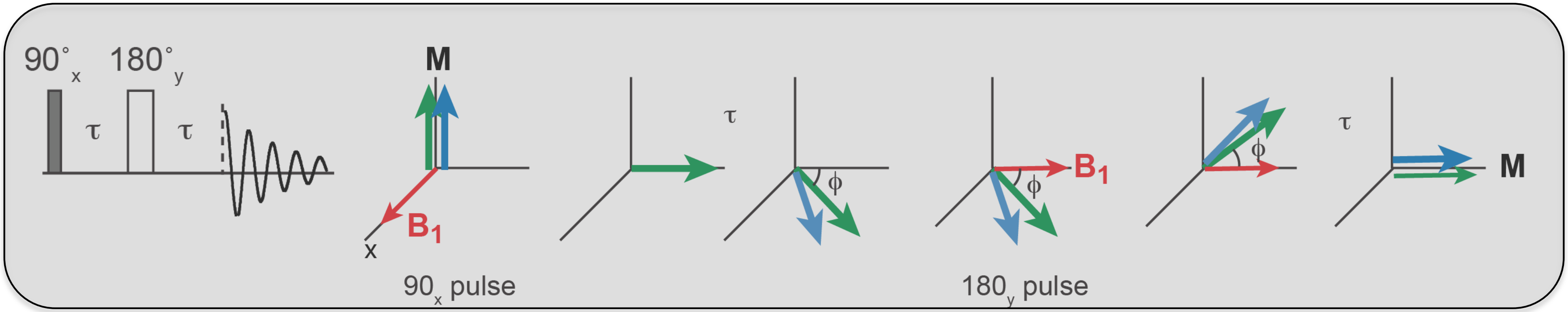
$$\begin{cases} \hat{H}_{CS} = \gamma \sigma_{zz}^{Lab} B_0 \cdot \hat{\boldsymbol{I}}_z = \left[ \sigma_{iso}\omega_0 + \frac{1}{2}\delta\left(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi\right)\right] \cdot \hat{\boldsymbol{I}}_z \\ \hat{H}_{D,IS} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma_I\gamma_S}{r^3}\frac{1}{2}\left(3\cos^2\theta - 1\right) \cdot \mathbf{2}\hat{\boldsymbol{I}}_z\hat{\boldsymbol{S}}_z \\ \hat{H}_{D,II} = -\frac{\mu_0}{4\pi}\hbar\sum_j\sum_k\frac{\gamma^2}{r_{jk}^3}\frac{1}{2}\left(3\cos^2\theta_{jk} - 1\right) \cdot \left(\mathbf{3}\hat{\boldsymbol{I}}_z^j\hat{\boldsymbol{I}}_z^k - \hat{\vec{\boldsymbol{I}}}^j \cdot \hat{\vec{\boldsymbol{I}}}^k\right) \\ \hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar}V_{zz}^{Lab}\left(\mathbf{3}\hat{\boldsymbol{I}}_z\hat{\boldsymbol{I}}_z - \hat{\vec{\boldsymbol{I}}} \cdot \hat{\vec{\boldsymbol{I}}}\right), \text{ where } V_{zz}^{Lab} = \frac{1}{2}eq\left(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi\right) \end{cases}$$

$$\hat{H}_{Local} = \underbrace{\left[\omega_{iso} + \omega_{aniso}(\theta,\phi)\right]}_{\downarrow} \cdot \underbrace{\left(Spin\ Part\right)}_{\downarrow}$$

*spatial part, affected by MAS & sample alignment*

*Affected by rf pulses*

# Describing Pulse Sequences For Coupled Spin Systems




The vector model cannot conveniently describe

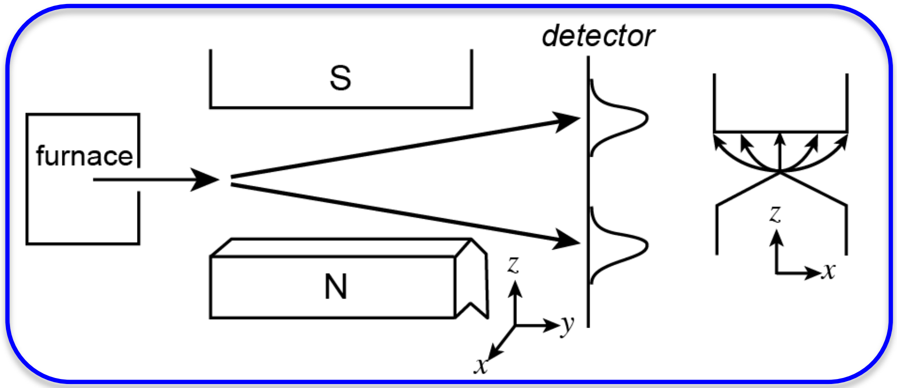
- how dipolar & J interactions change the magnetization;
- complex multiple-pulse sequences.

*Need to use density operators.*

# Pure Spin States and Spin Operators

***Spin states***

- Spin AM is quantized (proved by the *Stern-Gerlach expt*). Spin-1/2 nuclei have 2 basis states: $|\uparrow\rangle$ and $|\downarrow\rangle$.




- In a suitably chosen basis, the above *states* are represented by vectors:

$$|\uparrow\rangle \hat{=} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \ |\downarrow\rangle \hat{=} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- A *pure* spin state is a linear superposition of the basis states:

$$|\psi\rangle = C_+|\uparrow\rangle + C_-|\downarrow\rangle \hat{=} \begin{pmatrix} C_+ \\ C_- \end{pmatrix}$$

***Spin operators***

- are QM observables with eigenvalue eqns: $\hat{I}_z|\pm z\rangle = \pm\frac{1}{2}|\pm z\rangle, \ \hat{I}_x|\pm x\rangle = \pm\frac{1}{2}|\pm x\rangle, \ etc.$

- ***follow commutation rules***:

$$\boxed{\left[\hat{I}_x, \hat{I}_y\right] = i\hat{I}_z, \quad \left[\hat{I}_y, \hat{I}_z\right] = i\hat{I}_x, \quad \left[\hat{I}_z, \hat{I}_x\right] = i\hat{I}_y}$$

*Commutator:* $\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$

- are rep'ed by 2 x 2 matrices (Pauli matrices) for spin-1/2 nuclei:

$$\hat{I}_x \hat{=} \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \hat{I}_y \hat{=} \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \hat{I}_z \hat{=} \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{I}_x^2 = \hat{I}_y^2 = \hat{I}_z^2 = \frac{1}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{4}\hat{1}$$

# A Mixture of Spins: Density Operator

- A *statistical ensemble* of spins can only be described by a density operator:

$$\hat{\rho} = \sum_k p_k |\psi_k\rangle\langle\psi_k| = \sum_k p_k \begin{pmatrix} c_+ \\ c_- \end{pmatrix} \begin{pmatrix} c_+^* & c_-^* \end{pmatrix} = \sum_k p_k \begin{pmatrix} c_+ c_+^* & c_+ c_-^* \\ c_- c_+^* & c_- c_-^* \end{pmatrix}$$

- At thermal equilibrium:

$$\hat{\rho}_{eq} = \frac{e^{-\hat{H}/kT}}{Tr\left(e^{-\hat{H}/kT}\right)} \approx \frac{1}{2I+1}\left(\hat{1} - \frac{\hat{H}}{kT}\right) \Rightarrow \hat{\rho}_{eq}' \approx \frac{1}{2I+1}\left(\frac{\hbar\gamma B_0}{kT}\hat{I}_z\right) \propto \hat{I}_z$$

***Trace, sum of diagonal***

$\hbar\omega_0 << kT$

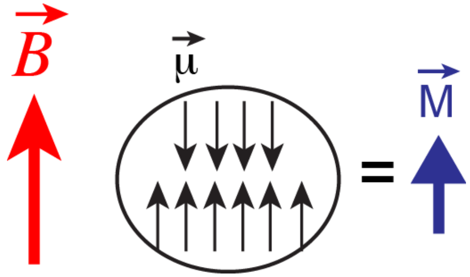
***Dropped: commutes with all operators***

- Average value of an observable *A*:

$$\langle A \rangle \equiv \overline{\langle \psi | \hat{A} | \psi \rangle} = Tr\left(\hat{\rho}\hat{A}\right)$$

- The observable in NMR is the magnetization...

- ***Magnetization****:* the sum of all magnetic dipole moments:




$$\vec{M} = \gamma\left\langle \hat{\vec{I}} \right\rangle = \begin{pmatrix} \left\langle \hat{I}_x \right\rangle \\ \left\langle \hat{I}_y \right\rangle \\ \left\langle \hat{I}_z \right\rangle \end{pmatrix} = \gamma \begin{pmatrix} Tr\left(\hat{\rho}\hat{I}_x\right) \\ Tr\left(\hat{\rho}\hat{I}_y\right) \\ Tr\left(\hat{\rho}\hat{I}_z\right) \end{pmatrix}$$

- The only non-zero traces are: $Tr\left(\hat{I}_x^2\right),\ Tr\left(\hat{I}_y^2\right),\ Tr\left(\hat{I}_z^2\right)$

- So the *x*, *y* magnetization are ***non-0 only when $\rho$ contains $I_x$ and $I_y$ terms***:

*e.g. for* $\hat{\rho} = \cos\omega t \cdot \hat{I}_x + \sin\omega t \cdot \hat{I}_y,$

$$\left\langle \hat{I}_x \pm i\hat{I}_y \right\rangle = Tr\left(\left(\cos\omega t \cdot \hat{I}_x + \sin\omega t \cdot \hat{I}_y\right)\left(\hat{I}_x \pm i\hat{I}_y\right)\right) = \cos\omega t \pm i\sin\omega t$$

$$= e^{\pm i\omega t} = f\left(t\right)$$

When the density operator contains $I_x$, $I_y$ terms, then *x* and *y* magnetization can be observed.

# Time Evolution of the Density Operator

$$|\psi(0)\rangle \overset{\hat{H}}{\Rightarrow} |\psi(t)\rangle \qquad \rho(0) \underset{\textit{dipolar couplings, etc}}{\overset{\textit{rf pulses, chem shifts}}{\Rightarrow}} \rho(t)$$

*Schrödinger* eqn → *von Neumann* eqn

$$i\hbar \frac{d|\psi\rangle}{dt} = \hat{H}|\psi\rangle \qquad \frac{d\hat{\rho}}{dt} = -i\left[\hat{H},\hat{\rho}\right]$$

- If H and ρ commute, then ρ does not change with time (e.g. $S_z$ magnetization is not affected by $I_z S_z$ dipolar coupling).
- If H is time-independent, then the formal solution to the von Neumann eqn is:

$$\hat{\rho}(t) = e^{-i\hat{H}t}\hat{\rho}(0)e^{i\hat{H}t} = \hat{U}(t)\hat{\rho}(0)\hat{U}^{-1}(t), \textit{ where } U(t) = e^{-i\hat{H}t} \textit{ is the propagator.}$$

- More useful solution: *(obtained by Taylor-expanding the above exponential operators)*

$$\boxed{\hat{\rho}(t) = \hat{\rho}(0)\cos\omega t + \frac{\left[\hat{H},\hat{\rho}(0)\right]}{i\omega}\sin\omega t,} \qquad \textit{provided } \left[\hat{H},\left[\hat{H},\hat{\rho}(0)\right]\right] = \omega^2\hat{\rho}(0)$$

# Evolution of ρ Under Two-Spin Dipolar Coupling

Let $\hat{\rho}(0) = \hat{I}_x$, $\quad \hat{H}_{IS} = \omega_{IS} 2\hat{I}_z\hat{S}_z$

$$\hat{\rho}(0) \overset{H_{IS}}{\Rightarrow} \hat{\rho}(t)?$$

$$\hat{\rho}(t) = \hat{\rho}(0)\cos\omega t + \frac{\left[\hat{H},\hat{\rho}(0)\right]}{i\omega}\sin\omega t, \quad \textit{provided} \ \left[\hat{H},\left[\hat{H},\hat{\rho}(0)\right]\right] = \omega^2\hat{\rho}(0)$$

$$\left[\hat{H},\hat{\rho}(0)\right] = \left[\omega_{IS} 2\hat{I}_z\hat{S}_z,\hat{I}_x\right] = \omega_{IS} 2\left[\hat{I}_z,\hat{I}_x\right]\hat{S}_z = \omega_{IS}\cdot 2i\hat{I}_y\hat{S}_z$$

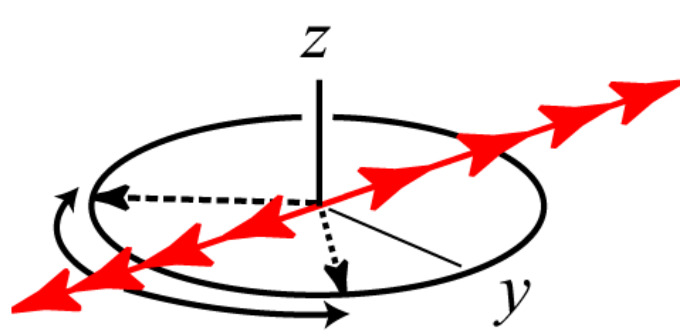
$$\left[\hat{H},\left[\hat{H},\hat{\rho}(0)\right]\right] = \left[\omega_{IS} 2\hat{I}_z\hat{S}_z,\omega_{IS}\cdot 2i\hat{I}_y\hat{S}_z\right] = \omega_{IS}^2 4i\left[\hat{I}_z\hat{S}_z,\hat{I}_y\hat{S}_z\right] = \omega_{IS}^2 4i\left[\hat{I}_z,\hat{I}_y\right]\hat{S}_z^2$$

$$= \omega_{IS}^2 i\left(-i\hat{I}_x\right) = \omega_{IS}^2\hat{I}_x$$

*Thus,* $\left[\hat{H},\left[\hat{H},\hat{\rho}(0)\right]\right] = \omega^2\hat{\rho}(0)$ *is satisfied, with* $\omega = \omega_{IS}$

$$\hat{\rho}(t) = \hat{I}_x\cos\omega t + 2\hat{I}_y\hat{S}_z\sin\omega t$$

*Detected as x-magn.* *unobservable.*



# Spatial Part of Spin Hamiltonians: Orientation Dependence

*The nuclear spin Hamiltonians are truncated to:*

$$\hat{H}_{CS} = \left[ \omega_{iso} + \frac{1}{2}\delta\left(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi\right) \right] \cdot \hat{I}_z$$

$$\hat{H}_{D,IS} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma_I\gamma_S}{r^3}\frac{1}{2}\left(3\cos^2\theta - 1\right) \cdot 2\hat{I}_z\hat{S}_z$$

$$\hat{H}_{D,II} = -\frac{\mu_0}{4\pi}\hbar\sum_j\sum_k\frac{\gamma^2}{r_{jk}^3}\frac{1}{2}\left(3\cos^2\theta_{jk} - 1\right) \cdot \left(3\hat{I}_z^j\hat{S}_z^k - \hat{\vec{I}}^j \cdot \hat{\vec{I}}^k\right)$$

$$\hat{H}_Q = \frac{eQeq}{2I(2I-1)\hbar}\frac{1}{2}\left(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi\right)\left(3\hat{I}_z\hat{I}_z - \hat{\vec{I}} \cdot \hat{\vec{I}}\right)$$

$$\hat{H}_{Local} = \underbrace{\left[\omega_{iso} + \omega_{aniso}(\theta,\phi)\right]}_{\downarrow} \cdot \underbrace{(Spin\ Part)}_{\downarrow}$$

*spatial part, affected by MAS & sample alignment*

*Affected by rf pulses*

# Orientation Dependence of NMR Frequencies

$$\hat{H}_{CS} = \gamma \hat{\vec{I}} \cdot \overleftrightarrow{\sigma} \cdot \vec{B}_0 \;\Rightarrow\Rightarrow\; \left[\omega_{iso} + \frac{1}{2}\delta\left(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi\right)\right]\cdot \hat{I}_z$$

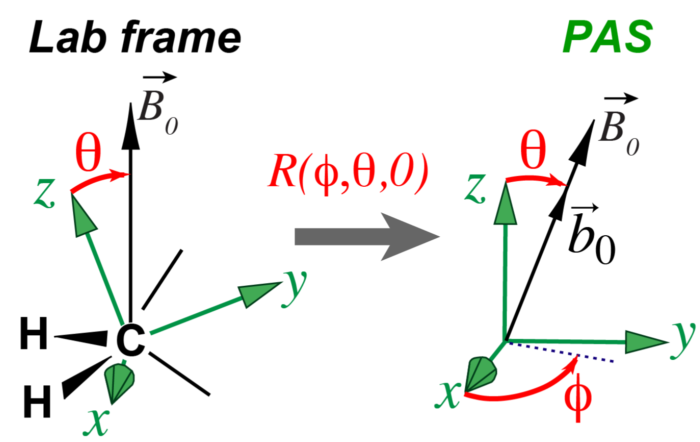
$$\hat{H}_{CS} = \gamma \hat{\vec{I}} \cdot \overleftrightarrow{\sigma} \cdot \vec{B}_0 = \gamma \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \begin{pmatrix} \sigma_{xx}^{Lab} & \sigma_{xy}^{Lab} & \sigma_{xz}^{Lab} \\ \sigma_{yx}^{Lab} & \sigma_{yy}^{Lab} & \sigma_{yz}^{Lab} \\ \sigma_{zx}^{Lab} & \sigma_{yz}^{Lab} & \sigma_{zz}^{Lab} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \underset{truncation}{=} \gamma I_z \sigma_{zz}^{Lab} B_0$$

$$= \gamma I_z B_0 \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \sigma_{zz}^{Lab} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad \boxed{= \gamma I_z B_0 \cdot \left(\vec{b}_0^T \;\; \overleftrightarrow{\sigma} \;\; \vec{b}_0\right)^{any\ frame}}$$

***bilinear, invariant with coordinate change***

Choose the **principal axis system** (PAS) where the CS tensor is diagonal

$$\overleftrightarrow{\sigma}^{PAS} \equiv \begin{pmatrix} \sigma_{xx}^{PAS} & 0 & 0 \\ 0 & \sigma_{yy}^{PAS} & 0 \\ 0 & 0 & \sigma_{zz}^{PAS} \end{pmatrix}$$




$$\vec{b}_0 = (\sin\theta\cos\phi \quad \sin\theta\sin\phi \quad \cos\theta)$$

# Chemical Shift Anisotropy

$$\hat{H}_{CS} = \gamma I_z B_0 \cdot \left( \vec{b}_0^T \ \overleftrightarrow{\sigma} \ \vec{b}_0 \right)^{PAS}$$

$$= \left( \cos\phi \sin\theta, \ \sin\phi \sin\theta, \ \cos\theta \right) \begin{pmatrix} \omega_{xx}^{PAS} & 0 & 0 \\ 0 & \omega_{yy}^{PAS} & 0 \\ 0 & 0 & \omega_{zz}^{PAS} \end{pmatrix} \overbrace{\begin{pmatrix} \cos\phi \sin\theta \\ \sin\phi \sin\theta \\ \cos\theta \end{pmatrix}}^{\vec{b}_0^{PAS}} I_z$$

Principal values: $\boldsymbol{\omega_{ii}^{PAS} = \omega_0 \sigma_{ii}^{PAS}}$

$$= \left( \omega_{xx}^{PAS} \cos^2\phi \sin^2\theta + \omega_{yy}^{PAS} \sin^2\phi \sin^2\theta + \omega_{zz}^{PAS} \cos^2\theta \right) \cdot I_z$$

*Isotropic shift :* $\omega_{iso} \equiv \frac{1}{3}\left( \omega_{xx} + \omega_{yy} + \omega_{zz} \right)$

*Anisotropy parameter :* $\delta \equiv \omega_{zz}^{PAS} - \omega_{iso}$

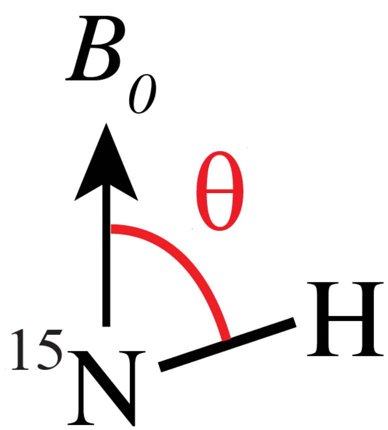
*Asymmetry parameter :* $\eta \equiv \dfrac{\omega_{yy} - \omega_{xx}}{\omega_{zz} - \omega_{iso}}$

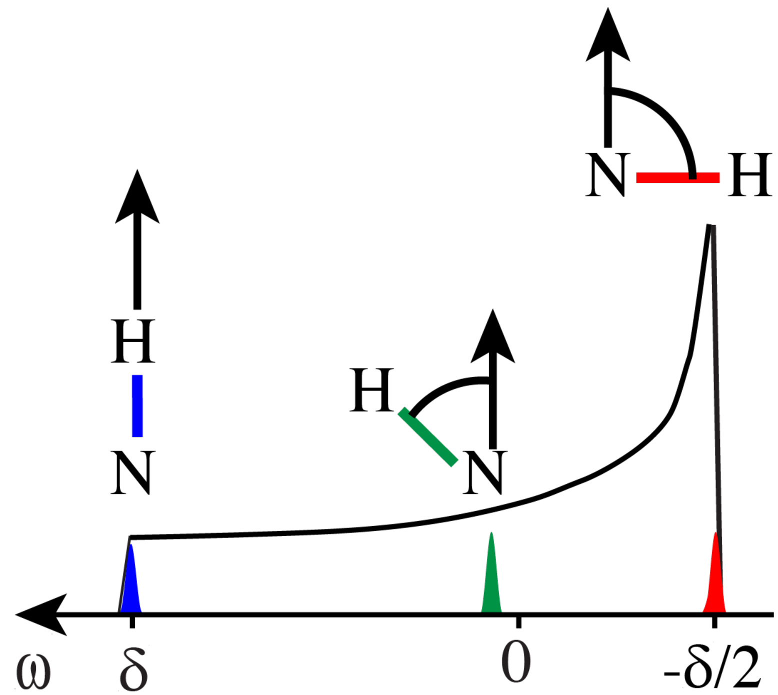
- (θ, ϕ): orientations of the molecules in the sample: powder, oriented, single crystal...
- (δ, η): electronic environment at the nuclear spin –> structure info.

$$\omega(\theta,\phi;\delta,\eta) = \frac{\delta}{2}\left( 3\cos^2\theta - 1 - \eta \sin^2\theta \cos 2\phi \right) + \omega_{iso}$$

# NMR Frequencies are Orientation-Dependent

$$\omega(\theta,\phi;\delta,\eta)=\frac{\delta}{2}\left(3\cos^2\theta-1-\eta\sin^2\theta\cos 2\phi\right)+\omega_{iso}$$




Orientation dependence allows the measurement of:

- Helix orientation in lipid bilayers;
- Changes in bond orientation due to motion;
- Torsion angles, i.e. relative orientation of molecular segments.

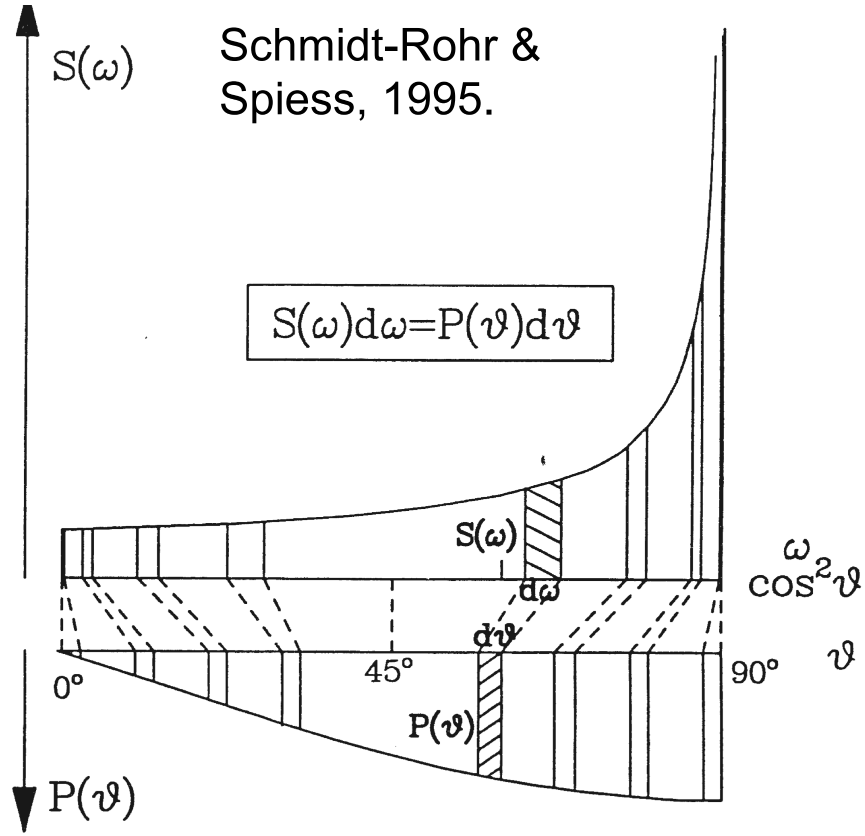
# Static Powder Patterns

Static NMR spectra reflect the orientation distribution of the molecules.

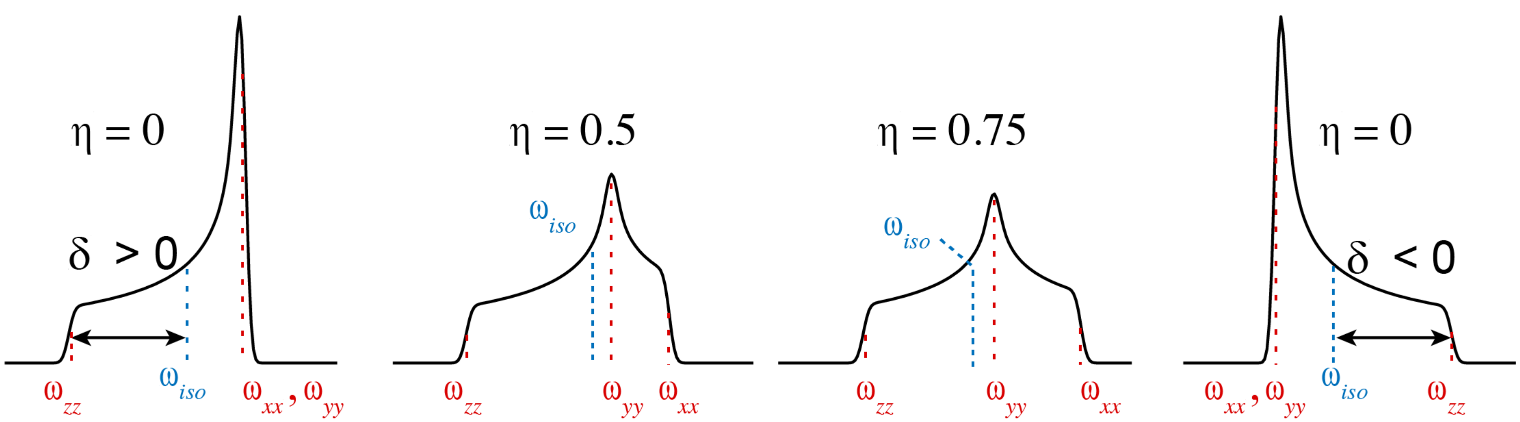
For η=0, $\omega(\theta) = \frac{1}{2}\delta\left(3\cos^2\theta - 1\right) + \omega_{iso}$

$$P(\theta)|d\theta| = S(\omega)|d\omega|, \quad \textit{and } P(\theta) = \sin\theta$$

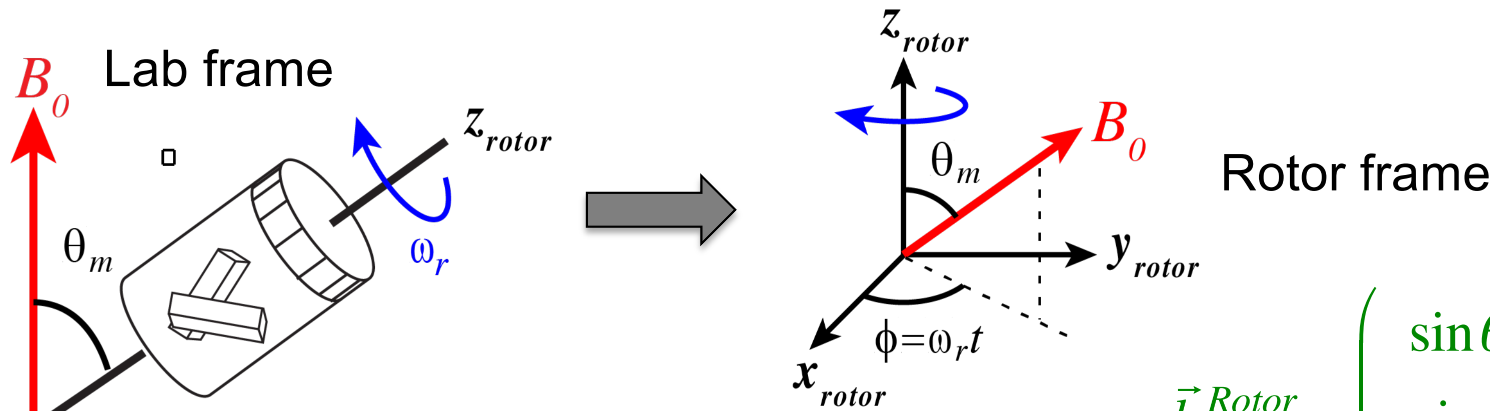
$$\Rightarrow \ S(\omega) = P(\theta)\left|\frac{d\theta}{d\omega}\right| = \frac{1}{\left(6\delta\left(\omega + \delta/2\right)\right)^{1/2}}$$




3 principal values: directly read off from maximum and step positions.



# Spinning the Sample: $\hat{H}_{Local}(t) = \omega(t)\cdot(Spin\ \ Part)$




$$\vec{b}_0^{Rotor} = \begin{pmatrix} \sin\theta_m \cos\omega_r t \\ \sin\theta_m \sin\omega_r t \\ \cos\theta_m \end{pmatrix}$$

$$\omega_{CS}(\theta,\phi(t)) = \omega_0 \cdot \left(\vec{b}_0^T \ \ \vec{\boldsymbol{\sigma}} \ \ \vec{b}_0\right)^{Rotor}$$

$$= \left(\sin\theta_m \cos\omega_r t,\ \sin\theta_m \sin\omega_r t,\ \cos\theta_m\right) \begin{pmatrix} \omega_{xx}^{rotor} & \omega_{xy}^{rotor} & \omega_{xz}^{rotor} \\ \omega_{yx}^{rotor} & \omega_{yy}^{rotor} & \omega_{yz}^{rotor} \\ \omega_{zx}^{rotor} & \omega_{zy}^{rotor} & \omega_{zz}^{rotor} \end{pmatrix} \begin{pmatrix} \sin\theta_m \cos\omega_r t \\ \sin\theta_m \sin\omega_r t \\ \cos\theta_m \end{pmatrix}$$

$$= \omega_{iso} + \cancel{\frac{1}{2}\left(3\cos^2\theta_m - 1\right)}\left(\omega_{zz}^{rotor} - \omega_{iso}\right) - \left(\omega_{yy}^{rotor} - \omega_{xx}^{rotor}\right)\sin^2\theta_m \cos 2\omega_r t$$
$$+ \omega_{xy}^{rotor} \sin^2\theta_m \sin 2\omega_r t + \omega_{xz}^{rotor} \sin 2\theta_m \cos\omega_r t + \omega_{yz}^{rotor} \sin 2\theta_m \cos\omega_r t$$

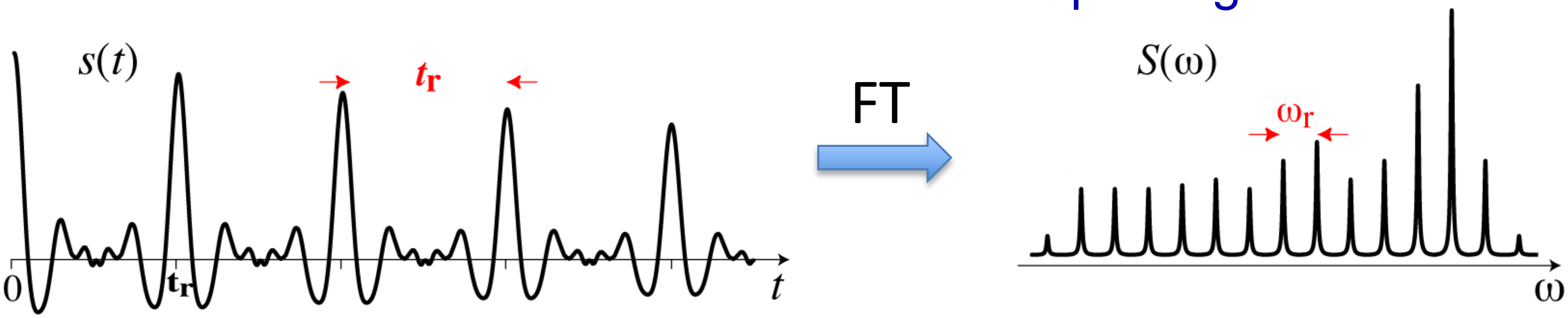
$\boldsymbol{\theta_m} = 54.7°$: $\frac{1}{2}\left(3\cos^2\boldsymbol{\theta_m} - 1\right) = 0$ $\quad$ $\boldsymbol{\theta_m} \neq 54.7°$: *OMAS, SAS, DAS...*

# Periodic Time Signal Under Magic-Angle Spinning

$$\omega_{CS}(\theta_m, \omega_r t) = \omega_{iso} + \cancel{0} - \left(\omega_{yy}^{rotor} - \omega_{xx}^{rotor}\right)\sin^2\theta_m \cos 2\omega_r t + \omega_{xy}^{rotor}\sin^2\theta_m \sin 2\omega_r t + \ldots$$

At $t = nt_r,\ \omega_{CS}(\theta_m, \omega_r t) = \omega_{iso} \;\Rightarrow\; f(t_r) = e^{i\omega_{iso}t}$

Rotation echoes　　　　　　Spinning sidebands

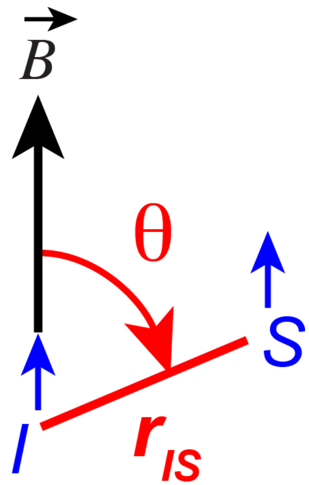



- At all times: $f(t) = e^{i\int_0^t \omega_{CS}(t')dt'} = e^{i\omega_{iso}t} e^{i\int_0^t \omega_{CSA}(t')dt'}$

- At 60 – 100 kHz MAS: $\omega_r >> \omega_{ij}^{rotor}$

$$\int_0^t \omega_{CS}(t')dt' = \omega_{iso}t + \sum_{i,j} c_{ij} \cancel{\frac{\omega_{ij}^{rotor}}{\omega_r}} \cos n_{ij}\omega_r t \;\rightarrow\; \boxed{f(t) \approx e^{i\omega_{iso}t}}$$

# Dipolar Coupling




$$\overleftrightarrow{D}^{PAS} = \begin{pmatrix} D_{xx}^{PAS} & 0 & 0 \\ 0 & D_{yy}^{PAS} & 0 \\ 0 & 0 & D_{zz}^{PAS} \end{pmatrix} = \begin{pmatrix} -\delta/2 & 0 & 0 \\ 0 & -\delta/2 & 0 \\ 0 & 0 & \delta \end{pmatrix}$$

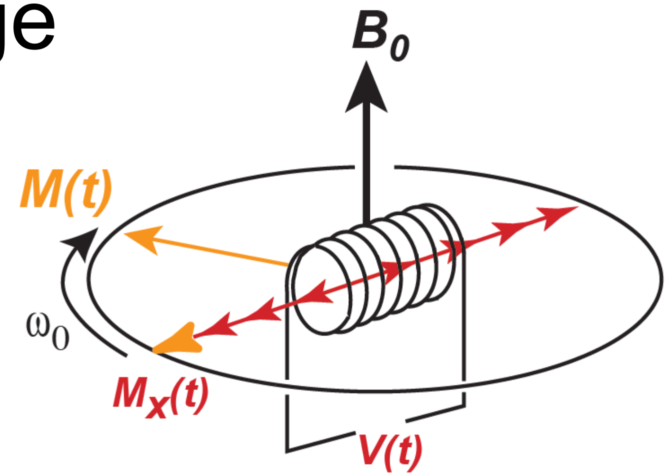
- Tensor is along the internuclear vector, $\eta = 0$.
- Isotropic component = 0.

$$\omega_{IS}(\theta;\delta) = \frac{1}{2}\delta\left(3\cos^2\theta - 1\right), \quad \textit{where } \delta = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma_I\gamma_S}{r^3}$$

**Common dipolar coupling constants (δ):**

- $^{1}H$-$^{1}H$ in $CH_2$ groups: ~1.8 Å, ~32 kHz (includes 1.5 x for homonuclear)
- $^{13}C$-$^{1}H$ single bond: 1.1 Å, ~23 kHz
- $^{15}N$-$^{1}H$ single bond: 1.05 Å, ~10 kHz
- $^{13}C$-$^{13}C$ single bond: 1.54 Å (aliphatic), ~3.1 kHz; 1.4 Å (aromatic), ~4.2 kHz
- $^{13}C$-$^{15}N$ bonds in protein backbones: ~1.5 Å, 0.9 – 1.0 kHz

# Detecting the NMR Signal - Voltage




The precessing M induces a voltage in the rf coil, which is detected.

$$\begin{cases} B_x(t) = \mu_0 M_x(t) = \mu_0 M_0 \sin\omega_L t \\ \textit{Magnetic flux: } \phi(t) = \int B(t)\, dA \end{cases}$$

*Voltage:* $U \equiv -\dfrac{d\phi}{dt} = -\mu_0 \int \dfrac{dM_x(t)}{dt} dA = -\mu_0 \omega_L M_0 \cos\omega_L t \int dA$

*NMR signal* $\propto \omega_L M_0 \cos\omega_L t \Rightarrow \dfrac{S}{N} \propto \dfrac{\omega_L M_0 \cos\omega_L t}{\sqrt{\omega_L}}$

$M_0 = \mu(n_+ - n_-) \propto \mu \bullet \dfrac{\Delta E}{T} \Rightarrow M_0 = N(\gamma\hbar)^2 B_0 \dfrac{1}{4kT}$

$\Delta E \propto \gamma\hbar B_0$

$\Rightarrow \boxed{\dfrac{S}{N} \propto \dfrac{\gamma^{5/2} B_0^{3/2}}{T}}$

- NMR time signal if every spin experiences the same B field (a single site):

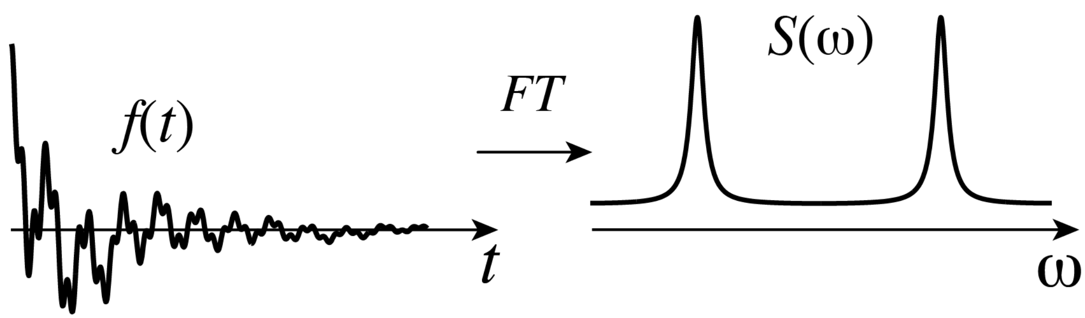
$$f(t) = U(t) \propto \omega_L M_0 \cos\omega_L t$$

# Time Signal & Frequency Spectra of Many Sites: Fourier Transform

- The time signal of many sites is a superposition of many frequency components with weighting factors S(ω):

$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S(\omega)\cos(\omega t)\,d\omega$$

- Fourier transform of the time signal gives the spectrum S(ω) :




$$\boxed{S(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(t)\, e^{-i\omega t}\, dt}$$

Many useful Fourier theorems relate $f(t)$ and S(ω):

- Inverse width: dwell time = 1/spectral width, $\Delta\nu_{1/2} = 1/\pi T_2$
- Convolution theorem
- Integral theorem
- Symmetry theorem …

## *Online resources for basic & advanced ssNMR:*

http://winterschool.mit.edu/

https://spindynamics.org/group/?page_id=18

## *Textbooks for ssNMR:*

Schmidt-Rohr and Spiess: Multidimensional Solid-state NMR and Polymers, 1994

Haeberlen: High Resolution NMR in Solids: Selective Averaging, 1976, Adv. Magn. Reson.