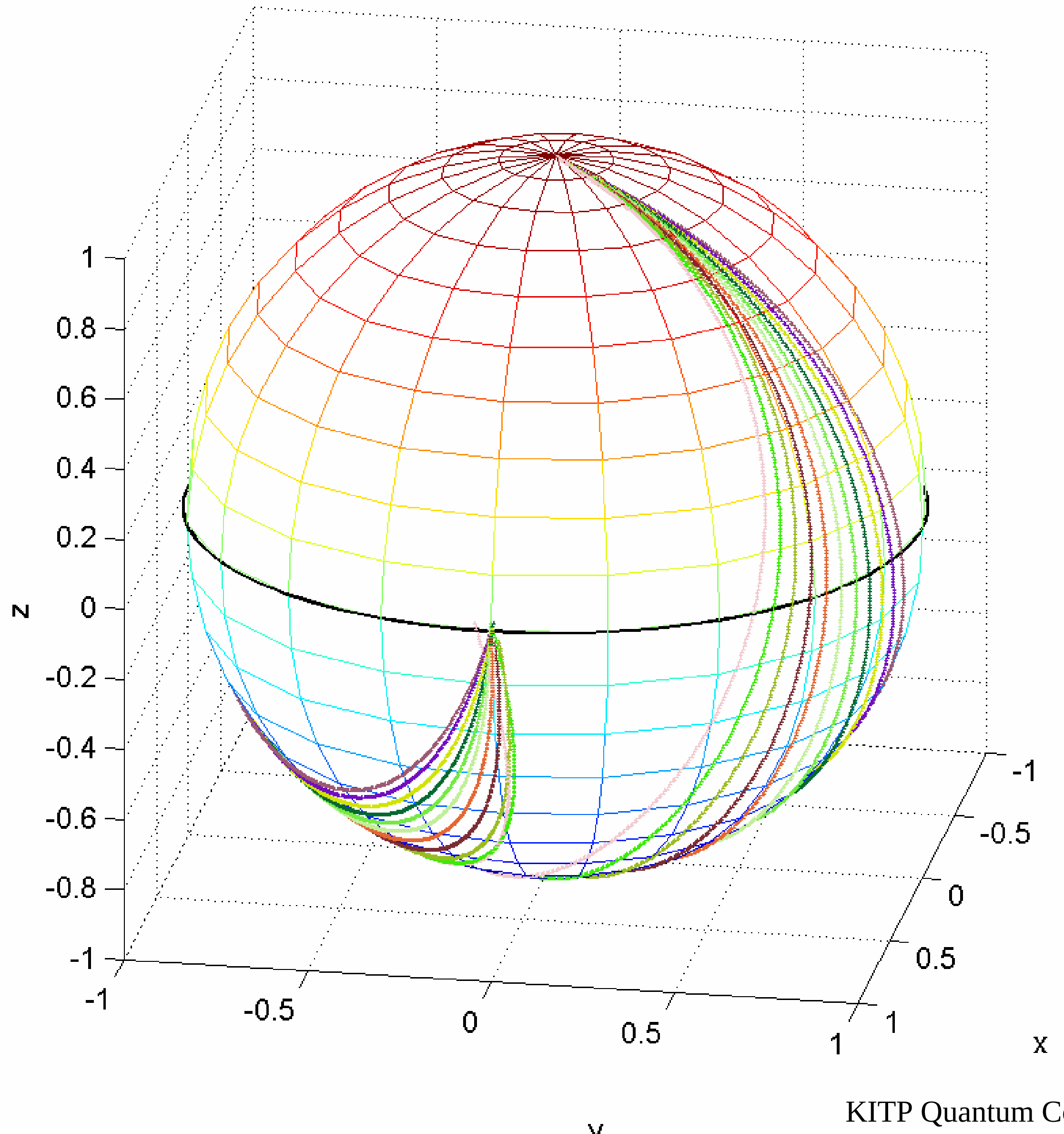
Ensemble Control

Navin Khaneja, Harvard



KITP Quantum Control, June 17, 2009

Collaborators

- Steffen Glaser
- Niels Nielsen
- Gerhard Wagner
- Robert Griffin

- James Lin
- Haidong Yuan
- Robert Zeier
- Jr Shin Li
- Jamin Sheriff
- Philip Owrutsky
- Mai Van Do

The problem of manipulating quantum systems with uncertainities or inhomogeneities in parameters govering the system dynamics is ubiquitous in coherent spectroscopy and quantum information processing.

Typical settings include
a) Resonance offsets
b) Inhomogeneities in the strength of excitation field (systematic errors)
c) Time dependent noise (nonsystematic errors)
d) Addressing errors or cross talk

Widespread use of composite pulse sequences and pulse shaping first to correct for errors or compensate for inhomogeneties

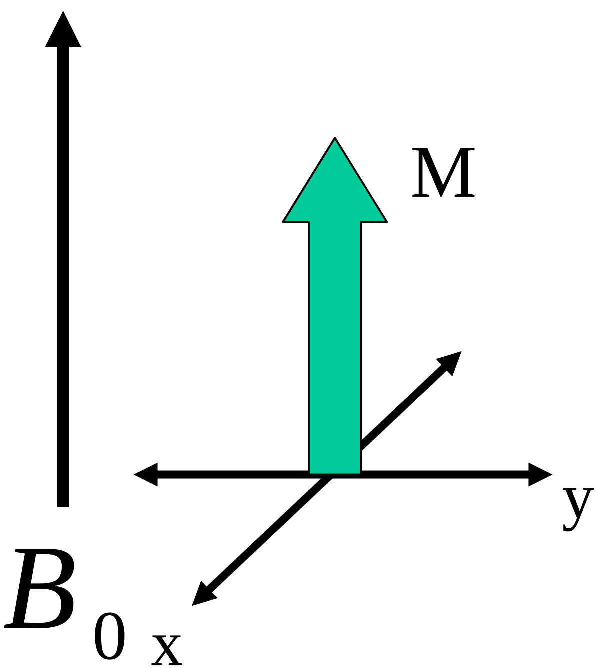
a) Understanding controllability of quantum dynamics with inhomogeneities.
b) Understanding what aspect of system dynamics makes compensation possible.
c) What kind of inhomogeneities or errors can or cannot be corrected.

Robust Control of Inhomogeneous Spin Ensembles

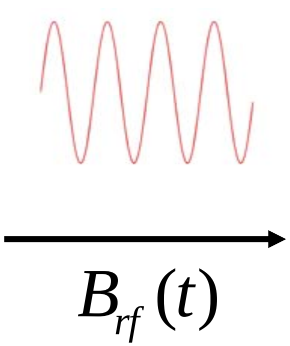
$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\omega & -\varepsilon u(t) \\ \Delta\omega & 0 & -\varepsilon v(t) \\ \varepsilon u(t) & \varepsilon v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\sqrt{u^2 + v^2} \leq A$$

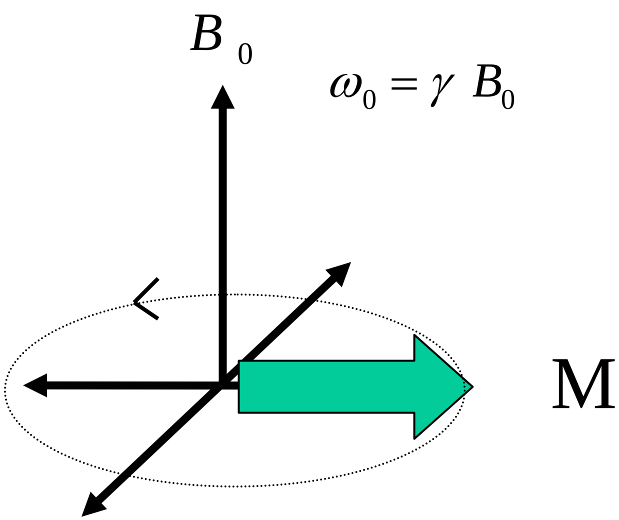
$$\varepsilon \in [1-\delta, 1+\delta]$$



$$\frac{d\vec{M}}{dt} = \gamma\,\vec{M} \times \vec{B}$$



$$\omega_0 = \gamma\,B_0$$

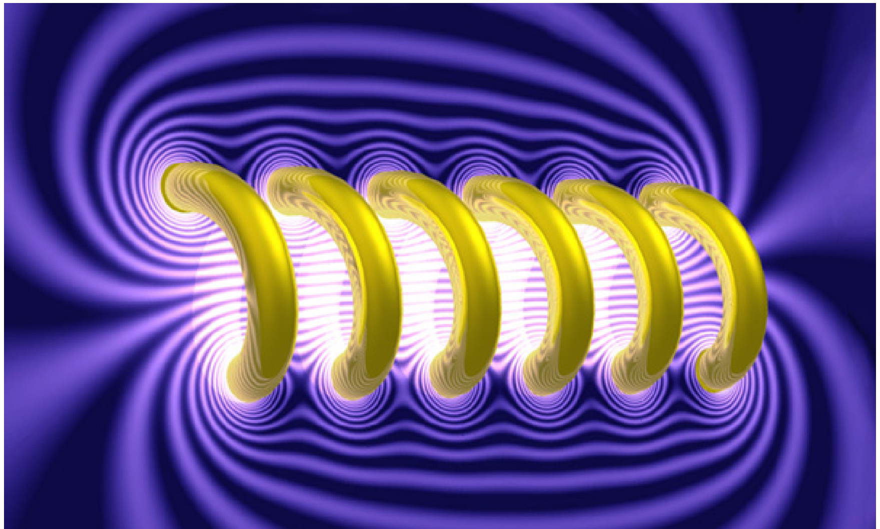


Dispersion in Control

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & 0 & -\varepsilon u(t) \\ 0 & 0 & -\varepsilon v(t) \\ \varepsilon u(t) & \varepsilon v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\varepsilon \in [1-\delta, 1+\delta]$$

$$\frac{dX}{dt} = \varepsilon\,[u(t)\Omega_x + v(t)\Omega_y]\,X$$



Lie Algebras and Polynomial Approximations

$$\frac{dX}{dt} = \varepsilon\,[u(t)\Omega_x + v(t)\Omega_y]\,X$$

$$U_\varepsilon(\Delta t) = \exp(-\varepsilon\Omega_y\Delta t)\exp(-\varepsilon\Omega_x\Delta t)\exp(\varepsilon\Omega_y\Delta t)\exp(\varepsilon\Omega_x\Delta t)$$

$$\approx I + (\Delta t)^2\underbrace{[\varepsilon\Omega_x, \varepsilon\Omega_y]}_{\varepsilon^2\Omega_z}$$

$$U_\varepsilon(-\sqrt{\Delta t})\exp(-\varepsilon\Omega_x\Delta t)U_\varepsilon(\sqrt{\Delta t})\exp(\varepsilon\Omega_x\Delta t)$$

$$\approx I + (\Delta t)^2\underbrace{[\varepsilon\Omega_x[\varepsilon\Omega_x, \varepsilon\Omega_y]]}_{-\varepsilon^3\Omega_y}$$

$$[\varepsilon\Omega_x[\varepsilon\Omega_x[\varepsilon\Omega_x[\varepsilon\Omega_x, \varepsilon\Omega_y]]] = \varepsilon^5\Omega_y$$

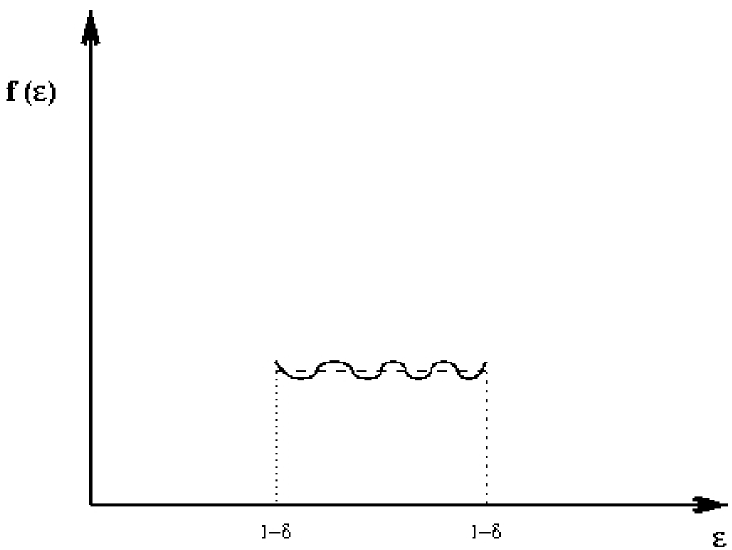
Lie Algebras and Polynomial Approximations

Using $\varepsilon\Omega_y, \varepsilon^3\Omega_y, \cdots, \varepsilon^{2k+1}\Omega_y$ as generators

$$f(\varepsilon) = \sum_k c_k \varepsilon^{2k+1}$$

Choose $f(\varepsilon)$ such that it is approx. constant for

$$\varepsilon \in [1-\delta, 1+\delta]$$



$$\exp(f(\varepsilon)\Omega_y)$$

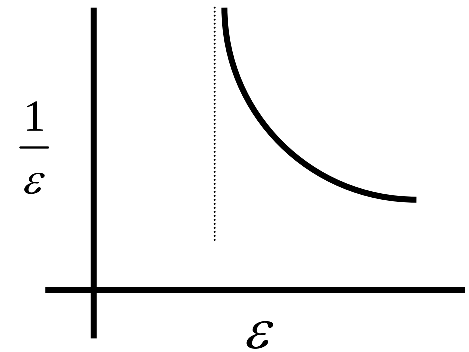
$$\Theta(\varepsilon) = \exp(f_1(\varepsilon)\Omega_x)\exp(f_2(\varepsilon)\Omega_y)\exp(f_3(\varepsilon)\Omega_x)$$

Fourier Synthesis Methods for Robust Control Design

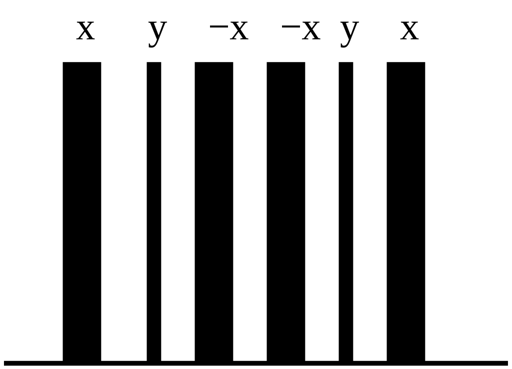
$$U_1 = \exp(k\pi\varepsilon\Omega_x)\exp(\varepsilon\frac{\beta_k}{2}\Omega_y)\exp(-k\pi\varepsilon\Omega_x)$$
$$= \exp(\varepsilon\frac{\beta_k}{2}(\cos(k\pi\varepsilon)\Omega_y + \sin(k\pi\varepsilon)\Omega_z))$$

$$U_2 = \exp(-k\pi\varepsilon\Omega_x)\exp(\varepsilon\frac{\beta_k}{2}\Omega_y)\exp(k\pi\varepsilon\Omega_x)$$
$$= \exp(\varepsilon\frac{\beta_k}{2}(\cos(k\pi\varepsilon)\Omega_y - \sin(k\pi\varepsilon)\Omega_z))$$

$$U_1U_2 \approx \exp(\varepsilon\beta_k\cos(k\pi\varepsilon)\Omega_y)$$



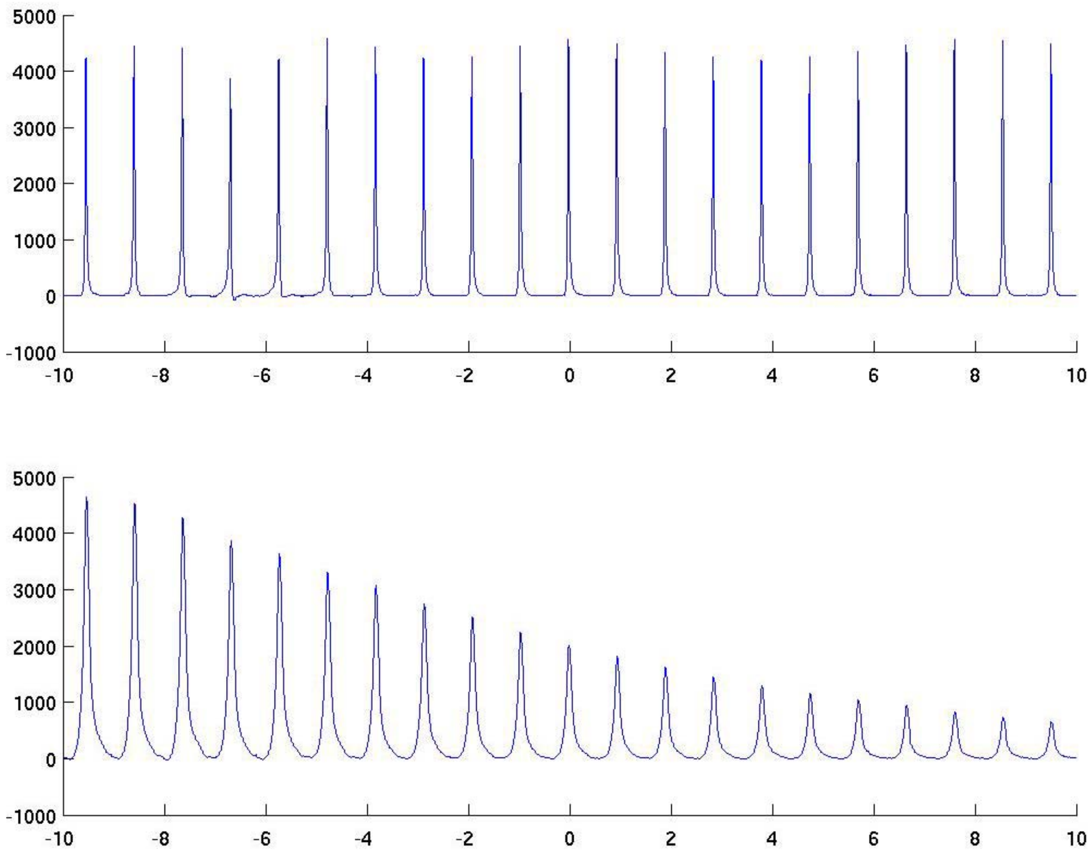
$$\sum_k \beta_k \cos(k\pi\varepsilon) = \frac{\theta}{\varepsilon}$$



B. Pryor, N. Khaneja
IEEE CDC proceedings (2007).

B. Pryor, N. Khaneja Journal of Chemical Physics (2006).

Fourier Synthesis Methods for Robust Control



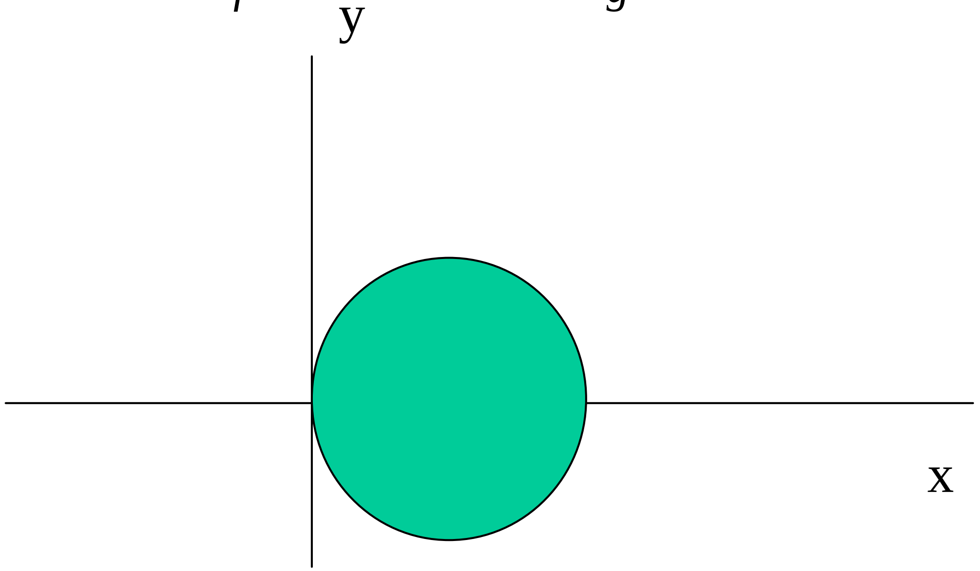
Proton NMR spectra (courtsey manoj nimbalkar)

Some Negative Results

Nil-Potent Systems Cannot be Compensated

$$\frac{d}{dt}\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \varepsilon u(t)\underbrace{\begin{bmatrix} 1 \\ 0 \\ -y \end{bmatrix}}_{f} + \varepsilon v(t)\underbrace{\begin{bmatrix} 0 \\ 1 \\ x \end{bmatrix}}_{g}$$

$$[f, g] = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$



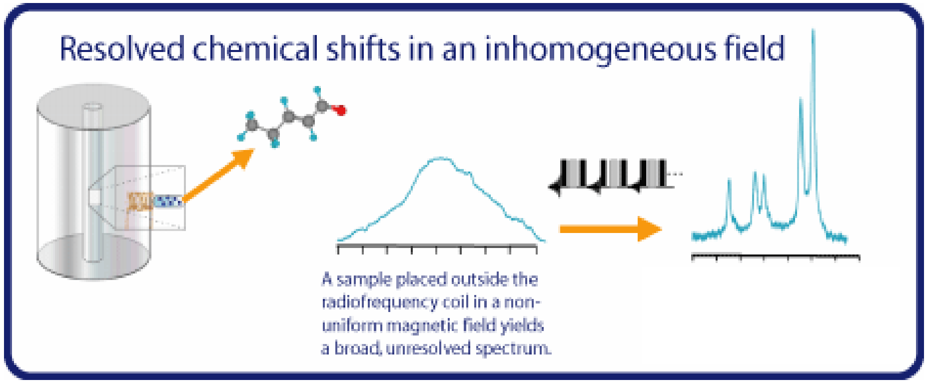
Some Negative Results

Linear systems cannot be compensated for field inhomogeneities

$$\frac{dX}{dt} = AX + \varepsilon Bu$$

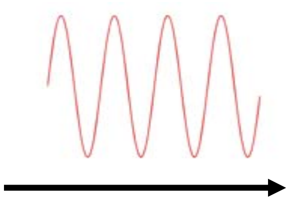
$$X(t) = e^{At} X(0) + \varepsilon \int e^{A(t-\tau)} B(\tau) u(\tau) d\tau$$

High Resolution NMR in Inhomogeneous Static Fields

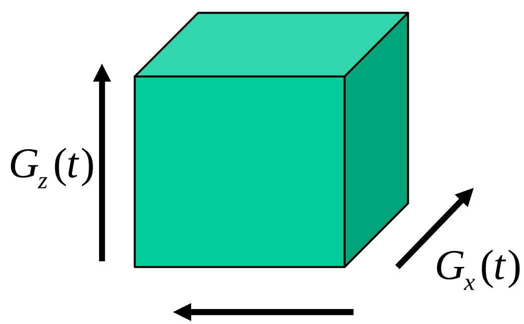


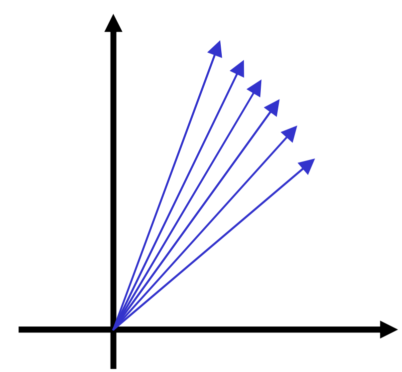
$$B(r) = B_0 + \delta B(r)$$

$$\phi(r) = \gamma(1-\sigma)B_0 T + \underbrace{\gamma \delta B(r) T}_{\delta\varphi(r)}$$



$B_{rf}(t)$



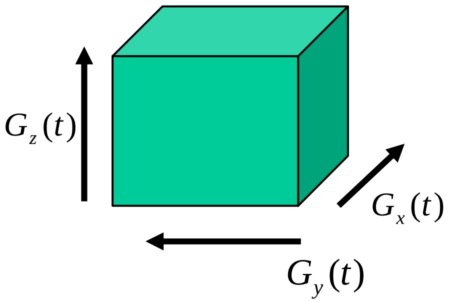


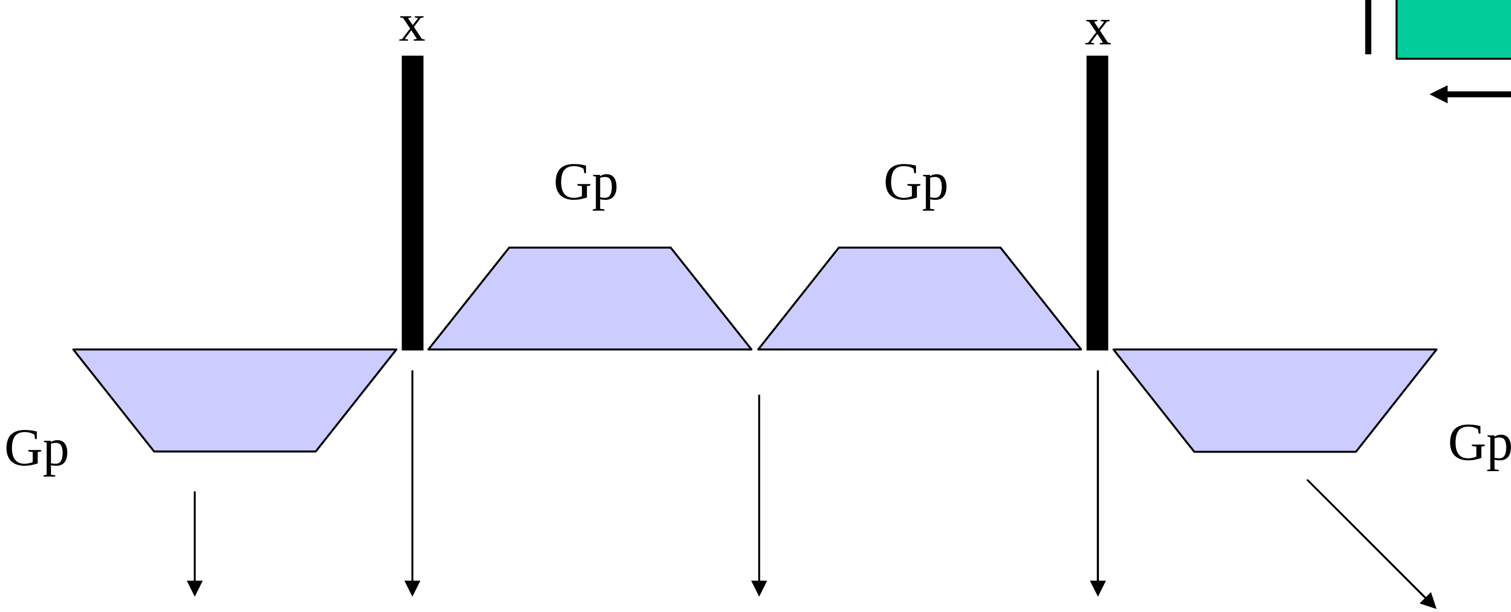
$G_y(t)$

$$\exp\left(-\delta\phi(r)\Omega_z\right)$$

Low Field, NMR magnets for process and quality control, Ex-situ NMR applications

NMR in Inhomogeneous Static Fields



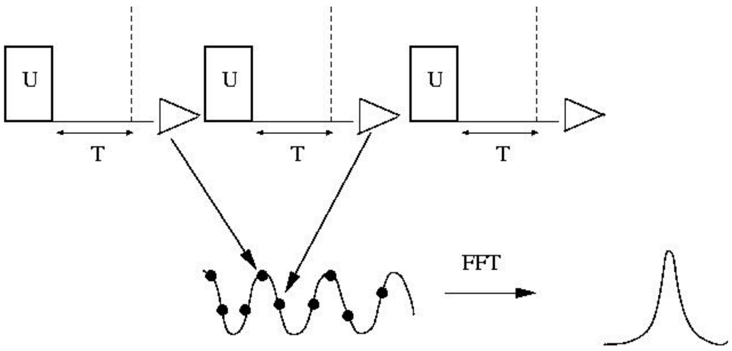


$$\exp\left(-k \bullet r\,\Omega_z\right)\exp\left(\theta_k\,\Omega_x\right)\exp\left(2k \bullet r\,\Omega_z\right)\exp\left(\theta_k\,\Omega_x\right)\exp\left(-k \bullet r\,\Omega_z\right)$$

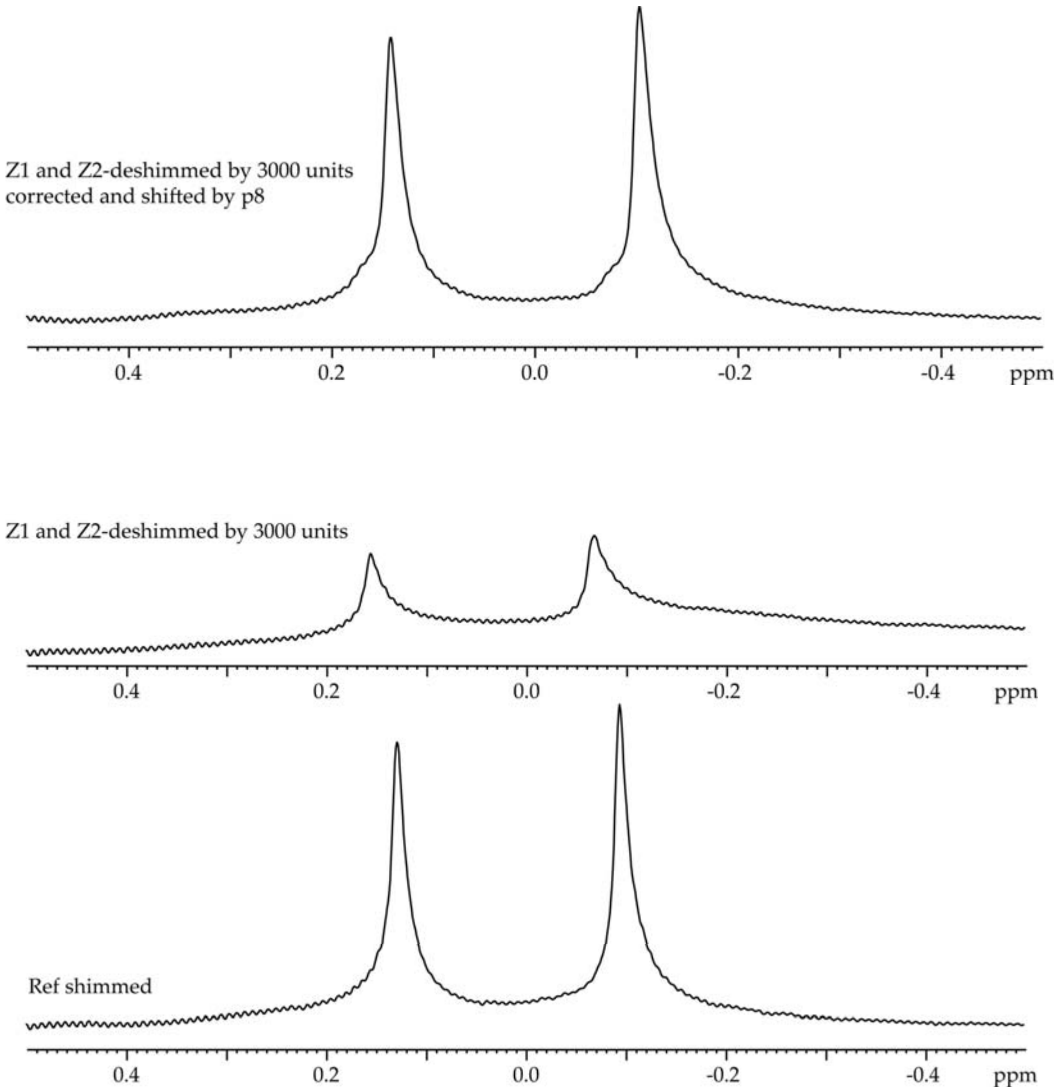
$$\approx \exp(\theta_k \cos(k \bullet r)\Omega_x)$$

$$\prod_k \exp(\theta_k \cos(k \bullet r)\Omega_z) = \exp(\sum_k \theta_k \cos(k \bullet r)\Omega_z) = \exp(-\phi(r)\Omega_z)$$

NMR in Inhomogeneous Static Fields

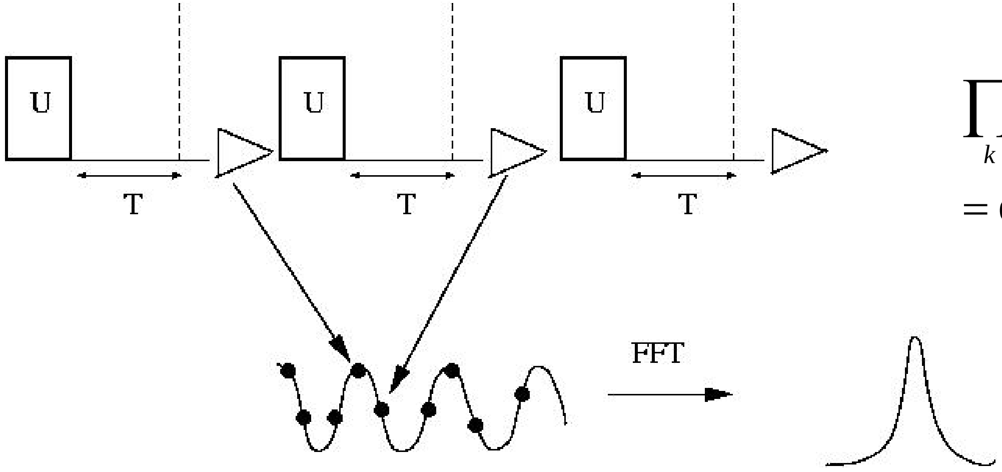


$$\delta B(z) = az + bz^2$$



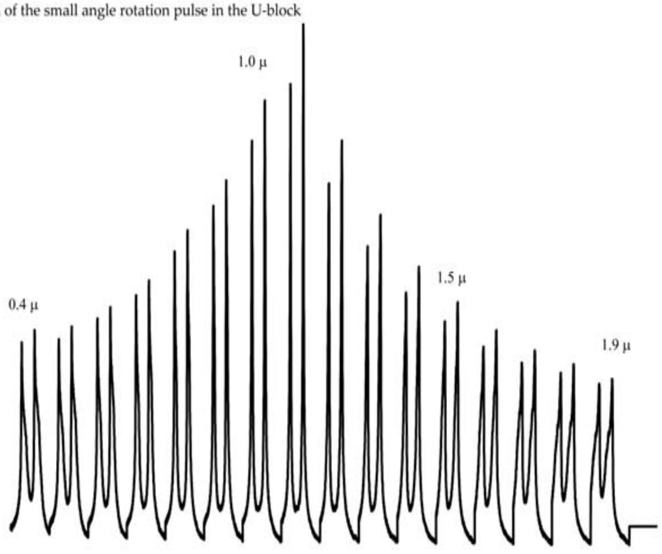
H. Arthanari et. al. JCP (2008)
B. Pryor and N. Khaneja (2007)

Imaging inhomogeneous magnetic fields with rf pulses and gradients: Line narrowing experiments



$$\prod_k \exp(\theta_k \cos(k \bullet r)\Omega_z) = \exp(\sum_k \theta_k \cos(k \bullet r)\Omega_z)$$
$$= \exp(-\phi_g(r)\Omega_z)$$

Optimization of the small angle rotation pulse in the U-block



$$\int \omega^2 S(\omega) d\omega \approx \iiint (\phi_g(r) - \delta\phi(r))^2 d^3 r$$

Ensemble Controllability of Bloch Equations

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\omega & -u(t) \\ \Delta\omega & 0 & -v(t) \\ u(t) & v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad \Delta\omega \in [-B, B]$$

$$U_\omega(\Delta t) = \exp(-\Omega_x \Delta t)\underbrace{\exp(-\omega\Omega_z \Delta t)}_{*}\exp(\Omega_x \Delta t)\exp(\omega\Omega_z \Delta t)$$

$$\approx I + (\Delta t)^2 \underbrace{[\omega\Omega_z, \Omega_x]}_{\omega\Omega_y}$$

$$[\omega\Omega_z[\omega\Omega_z, \Omega_y]] = -\omega^2\Omega_y \qquad f(\omega) = \sum c_k \omega^k$$

$$\exp(f(\omega)\Omega_y)$$

Larmor Dispersion and Strong Fields

$$\underbrace{\exp(-\omega\Omega_z\Delta t)}_{*} = \exp(-\pi\Omega_x)\underbrace{\exp(\omega\Omega_z\Delta t)}\exp(\pi\Omega_x)$$

$$U_\omega(\Delta t) = \exp(-\Omega_x\Delta t)\underbrace{\exp(-\omega\Omega_z\Delta t)}_{*}\exp(\Omega_x\Delta t)\exp(\omega\Omega_z\Delta t)$$

$$\approx I + (\Delta t)^2\underbrace{[\omega\Omega_z,\Omega_x]}_{\omega\Omega_y}$$

$$f(\omega) = \sum c_k\omega^k$$

$$\exp(f(\omega)\Omega_y)$$

Larmor Dispersion and Bounded Controls

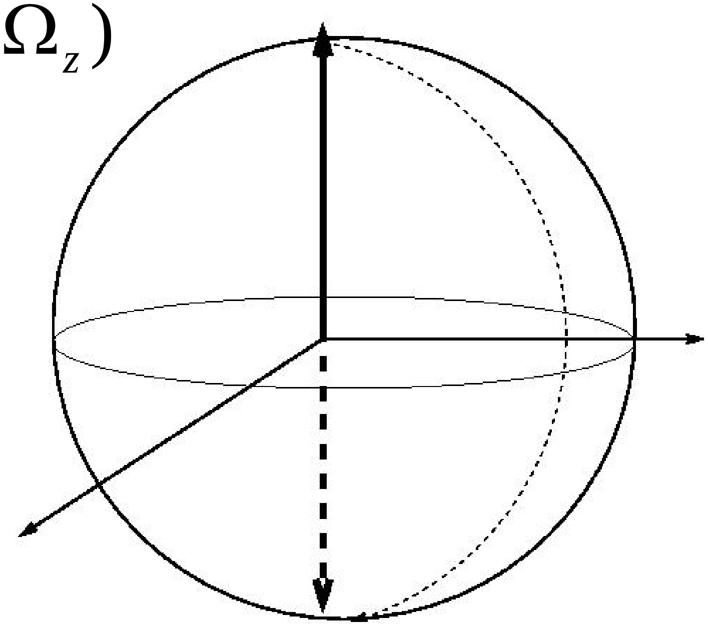
$$\underbrace{\exp(-\omega\Omega_z\Delta t)} = \exp(-\pi\Omega_x)\underbrace{\exp(\omega\Omega_z\Delta t)}\exp(\pi\Omega_x)$$

Adiabatic Passage (Hyperbolic Secant)

$$U = \exp(\beta(\omega)\Omega_z)\exp(\pi\Omega_x)\exp(\alpha(\omega)\Omega_z)$$

$$U^2 = I$$

$$\underbrace{\exp(-\omega\Omega_z\Delta t)} \approx U\underbrace{\exp(\omega\Omega_z\Delta t)}U$$



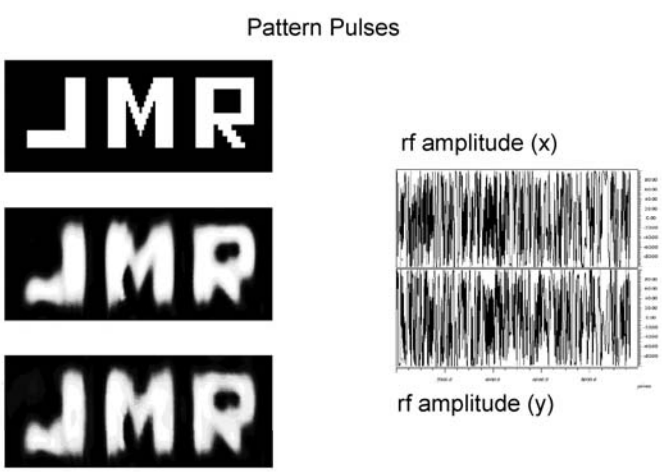
Inversion is Robust to rf-inhomogeneity

Ensemble Controllability of Bloch Equations

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\omega & -\varepsilon u(t) \\ \Delta\omega & 0 & -\varepsilon v(t) \\ \varepsilon u(t) & \varepsilon v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\exp(-\varepsilon\Omega_x\Delta t)\exp(-\omega\Omega_z\Delta t)\exp(\varepsilon\Omega_x\Delta t)\exp(\omega\Omega_z\Delta t)$$

$$\sum c_{kj}\omega^k\varepsilon^j$$



$$\Theta(\omega,\varepsilon) = \exp(f_1(\omega,\varepsilon)\Omega_y)\exp(f_2(\omega,\varepsilon)\Omega_x)\exp(f_3(\omega,\varepsilon)\Omega_y)$$

Ensemble Control in Switched Systems

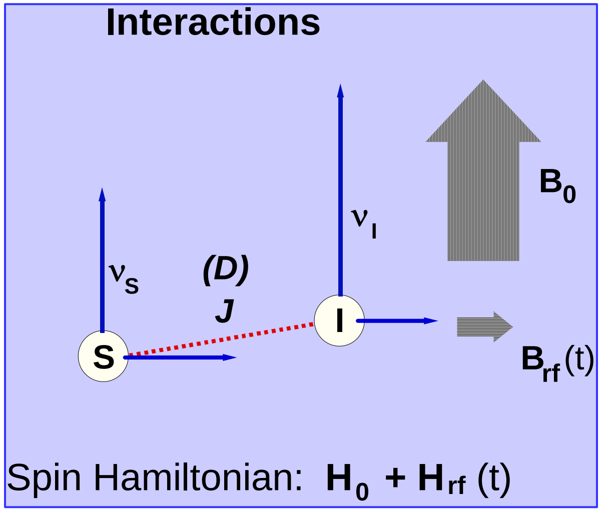
$$\frac{dX}{dt} = \varepsilon\,[u(t)\Omega_x + v(t)\Omega_y]\,X$$

$$\frac{dX}{dt} = (1+\delta)\,[A\Omega_x + \underbrace{A\Omega_y + B\cos(At + \phi(t))\Omega_y}_{+}]\,X$$

$$\frac{dX}{dt} = [\delta A\Omega_{\parallel} + \frac{\varepsilon B_{\perp}}{2}\cos(\phi(t))\Omega_{\perp} + \frac{\varepsilon B_{\perp}}{2}\sin(\phi(t))\Omega_z]\,X$$

$$\Omega_{\parallel} = \Omega_x + \Omega_y$$

Switched Control Systems

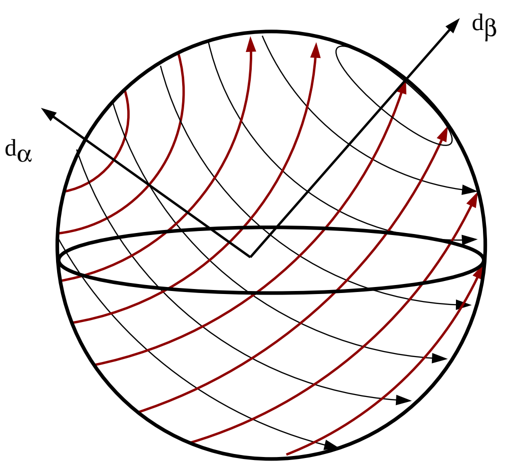


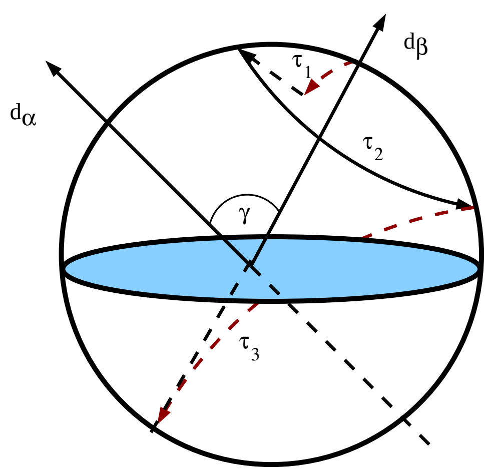
$$H_0 = \omega_s S_z + \omega_I I_z + S \cdot A \cdot I$$

$$H_0 = \omega_s S_z + \omega_I I_z + A S_z I_z + B S_z I_x$$

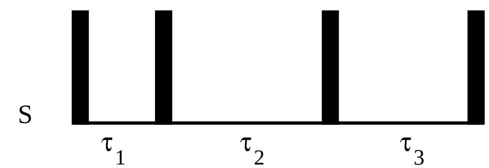
$$d_\beta = (\omega_I + A/2)\ \hat{z} + \frac{B}{2}\hat{x}$$

$$d_\alpha = (\omega_I - A/2)\ \hat{z} - \frac{B}{2}\hat{x}$$

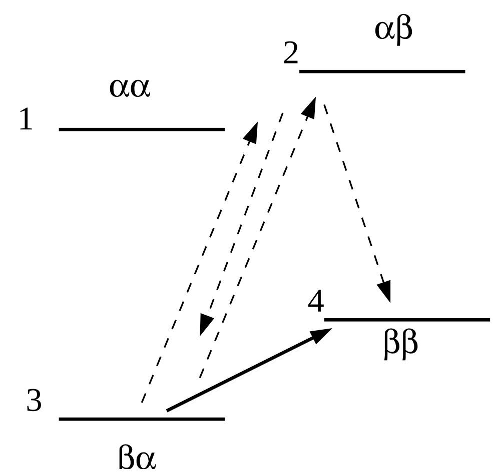




A



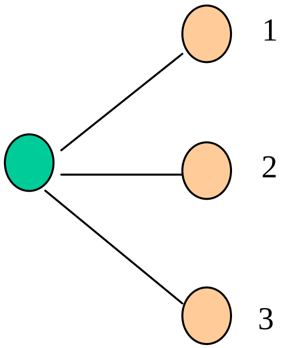
B



C

N. Khaneja PRA(2007)

Electron coupled to many nuclear spins

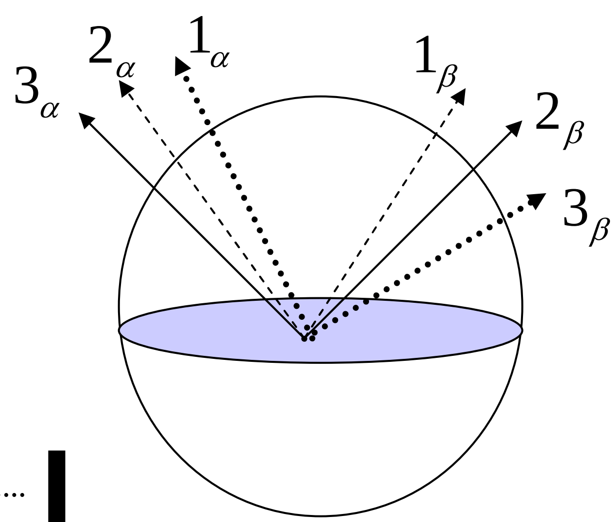


$$H_c = \sum_k A_k S_z I_z + \sum_k B_k S_z I_x$$

$$d_\alpha^k = (\omega_I - A_k/2)\ \hat{z} + \frac{B_k}{2}\ \hat{x} \qquad d_\beta^k = (\omega_I + A/2)\ \hat{z} + \frac{B}{2}\ \hat{x}$$

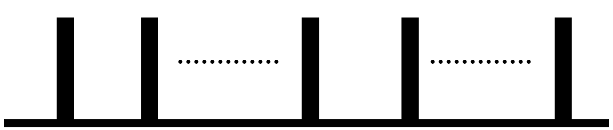
$$\omega_\alpha^k = \sqrt{(\omega_I - A_k/2)^2 + (\frac{B_k}{2})^2} \qquad \omega_\beta^k = \sqrt{(\omega_I + A_k/2)^2 + (\frac{B_k}{2})^2}$$

$$U_\alpha^k$$



$$(\omega_\alpha^k, \omega_\beta^k, \gamma^k) \neq (\omega_\alpha^j, \omega_\beta^j, \gamma^k)$$

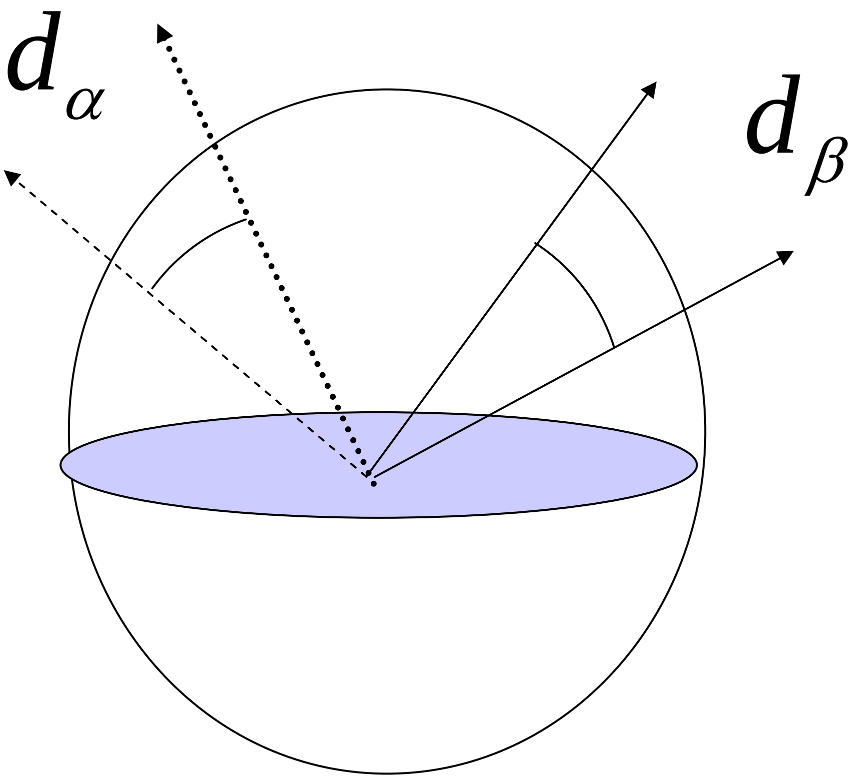
$$\omega_\alpha^j \neq \omega_\beta^j$$



$$\{I_{kp}, S_z I_{kq}\}$$

Dispersion in the Hyperfine Couplings in a Powder

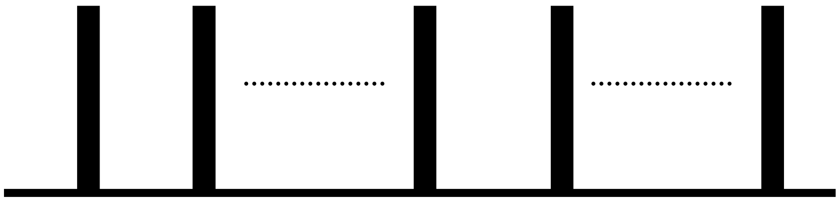
$$H_0 = \omega_s S_z + \omega_I I_z + S \cdot A(\varepsilon) \cdot I$$



$$\frac{dX}{dt} = \varepsilon \, [u(t)\Omega_x + v(t)\Omega_y] \, X$$

$$\exp(\varepsilon\Omega_x t_1)\exp(\varepsilon\Omega_y t_2)\cdots\exp(\varepsilon\Omega_x t_n)$$

Is the System Ensemble Controllable ?

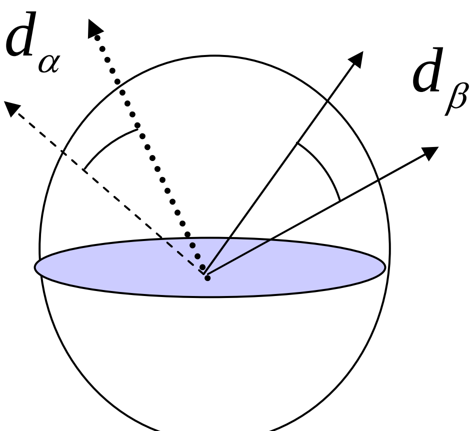


Ensemble Control in Switched Systems

$$\frac{dX}{dt} = \varepsilon \, [u(t)\Omega_a + v(t)\Omega_b] \, X$$

$$\frac{dX}{dt} = (1+\delta)\,[A\Omega_a + \underbrace{A\Omega_b + B\cos(At+\phi(t))}_{+}\Omega_b]\,X$$

$$\frac{dX}{dt} = [\delta A\Omega_{\Box} + \frac{\varepsilon B_{\perp}}{2}\cos(\phi(t))\Omega_{\perp} + \frac{\varepsilon B_{\perp}}{2}\sin(\phi(t))\Omega_z]\,X$$



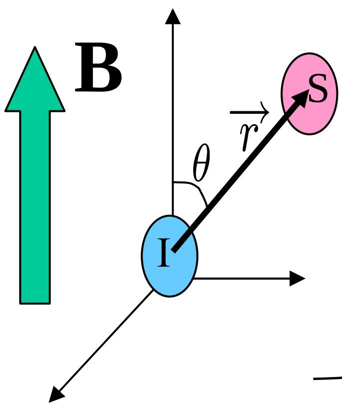
$$\Omega_{\Box} = \Omega_x + \Omega_y$$

Ensemble control in solid-state NMR

J. Am. Chem. Soc., 126 (2005)

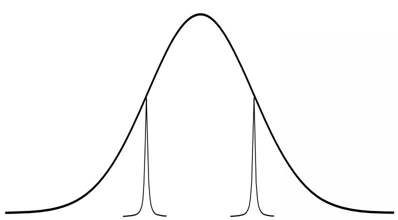
Chem. Phys. Letter (2005)

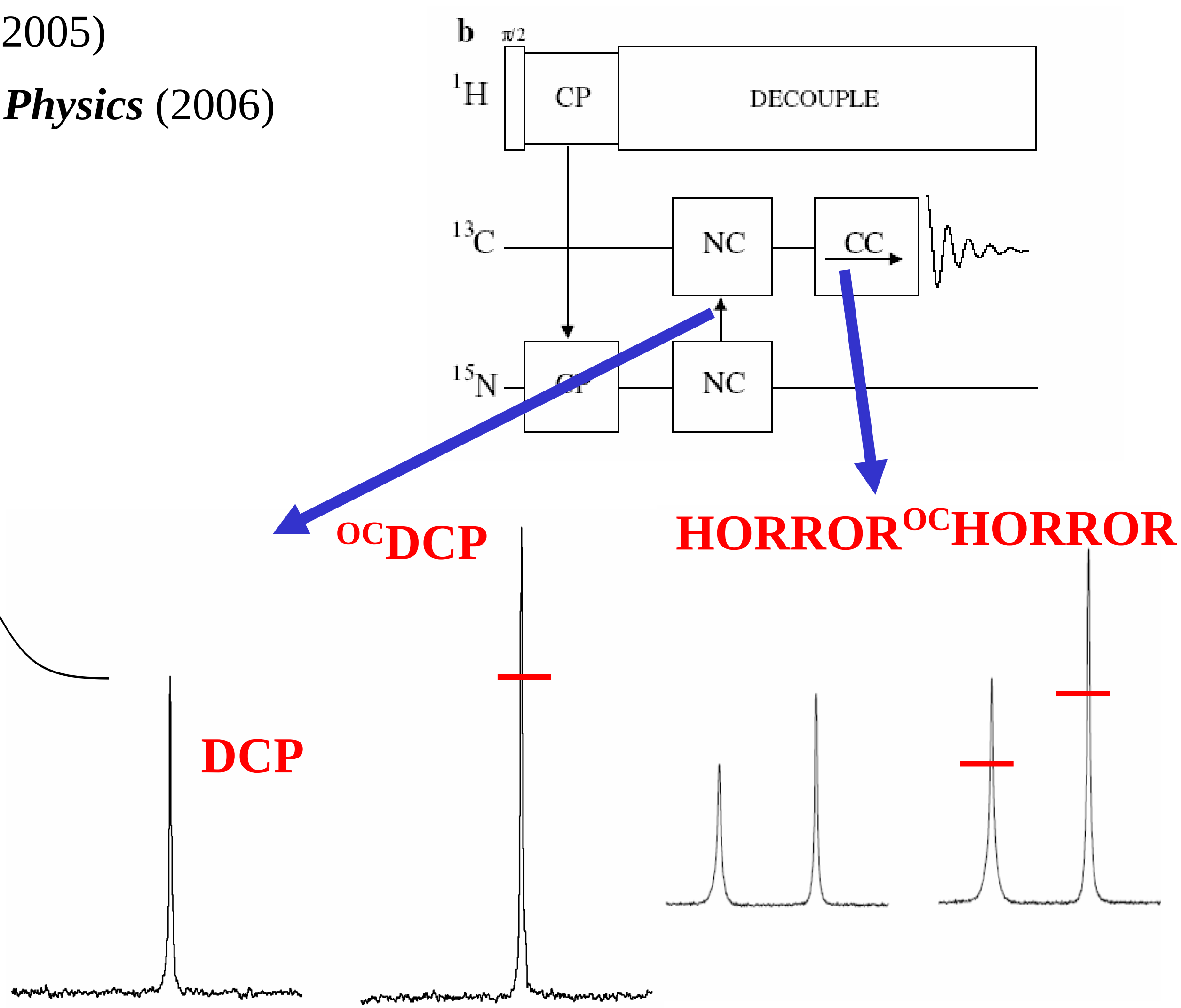
Journal of Chemical Physics (2006)



$$J = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma^I\gamma^S}{r^3}\left[3(\mathrm{I}\cdot\hat{\mathrm{r}})(\mathrm{S}\cdot\hat{\mathrm{r}}) - \mathrm{I}\cdot\mathrm{S}\right]$$

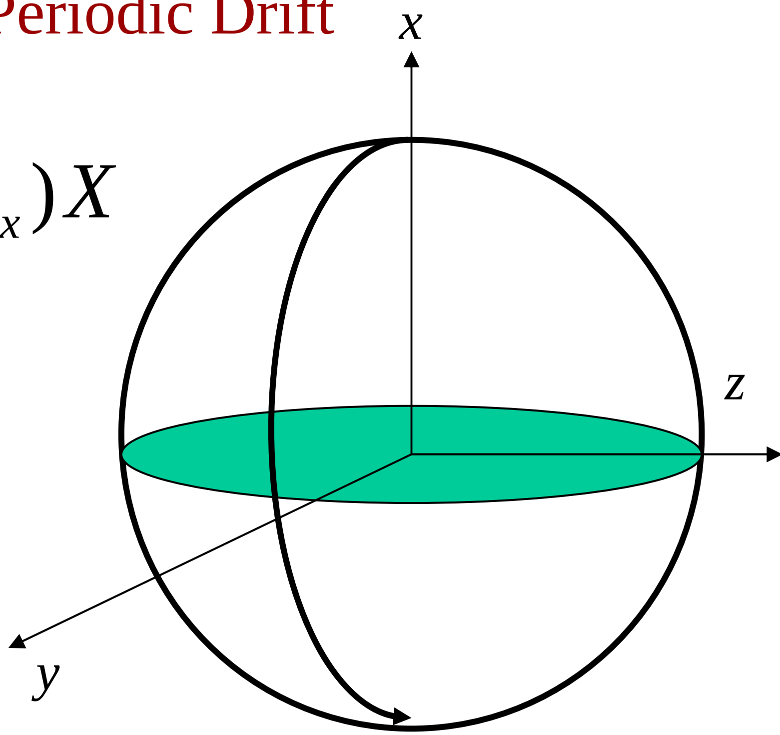
$$J \sim \frac{3\cos^2(\theta) - 1}{r^3}$$





Control of Bilinear Systems with Periodic Drift

$$\frac{dX}{dt} = (\beta \cos(\omega_r t + \gamma)\Omega_z + \varepsilon u(t)\Omega_x)X$$



$$\beta \in [\beta_1 \ \ \beta_2] \qquad \varepsilon \in [1-\delta \ \ 1+\delta]$$

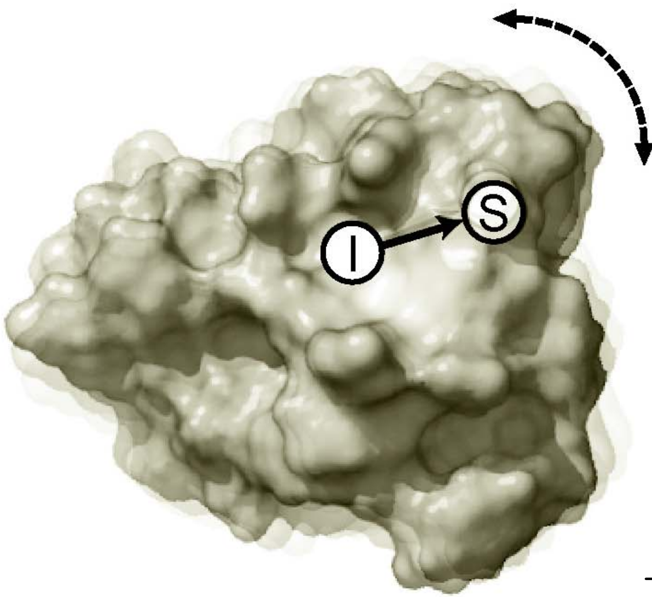
$$\gamma \in [0 \ 2\pi]$$

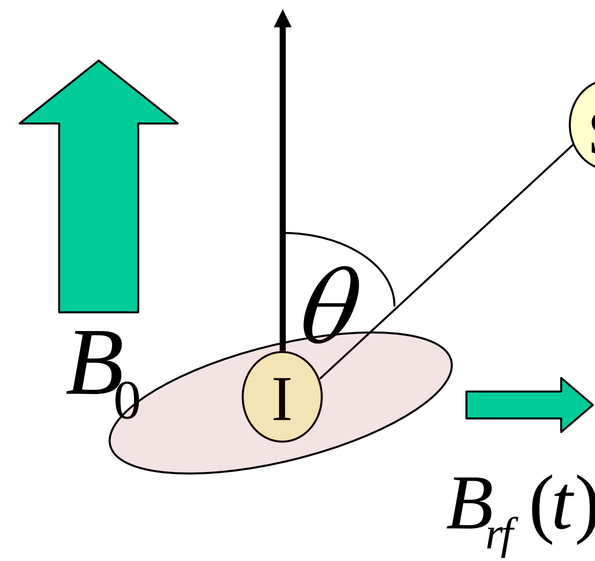
$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \rightarrow \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix}$$

$$\omega_r \ \square \ \beta$$

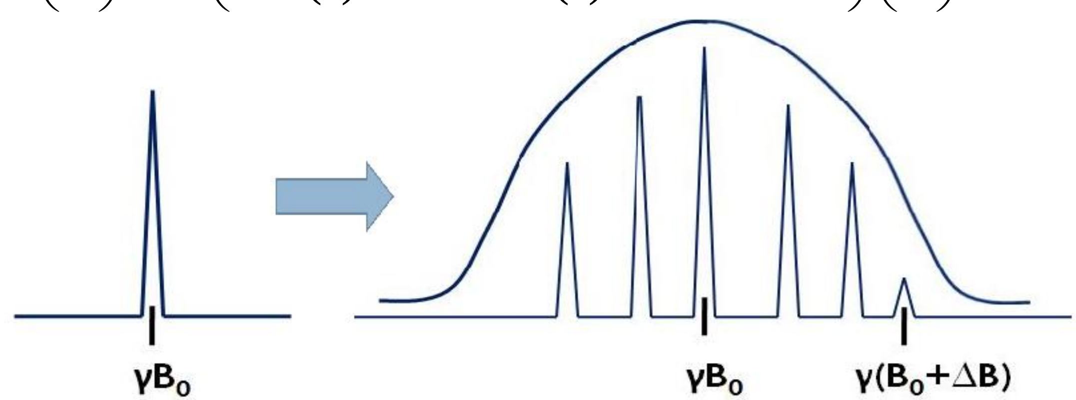
Random collisions with solvent molecules causes stochastic tumbling of the molecules averaging out non-isotropic interactions

$\tau_c \sim$ MW

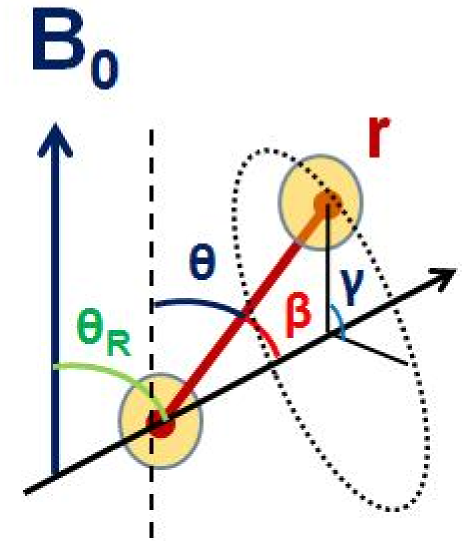




$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \gamma \begin{pmatrix} 0 & -(B_0+\Delta B) & -u(t) \\ B_0+\Delta B & 0 & -v(t) \\ u(t) & v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



MAS: Magic Angle Spinning



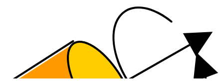
$$\frac{(3\cos^2\theta(t)-1)}{r^3} I_z S_z$$

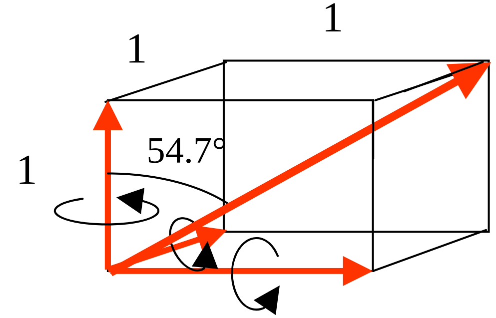
$$(3\cos^2 q_M \text{ - } 1) = 0$$

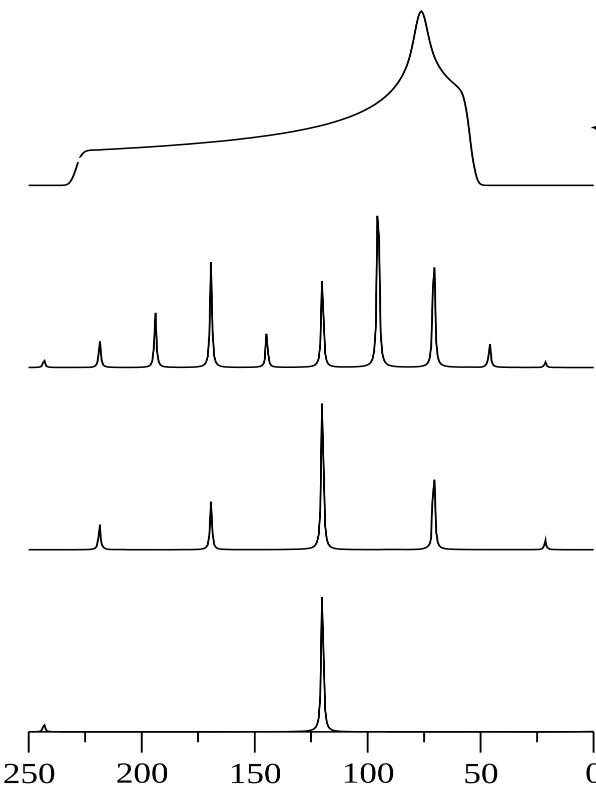
q_M = 54.7° (magic angle)

MAS (ω_r at 54.7°)

CSA = ν_{CSA}





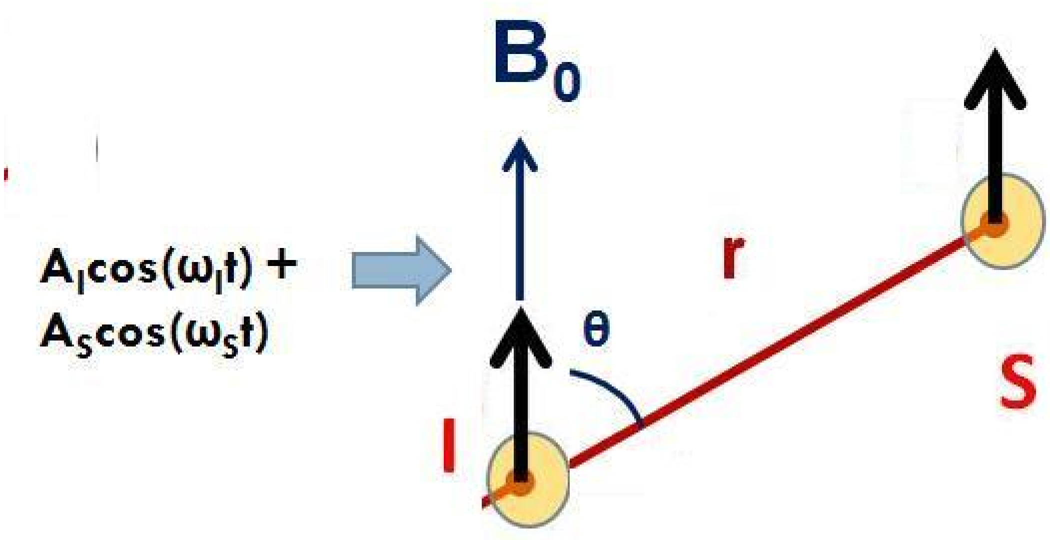


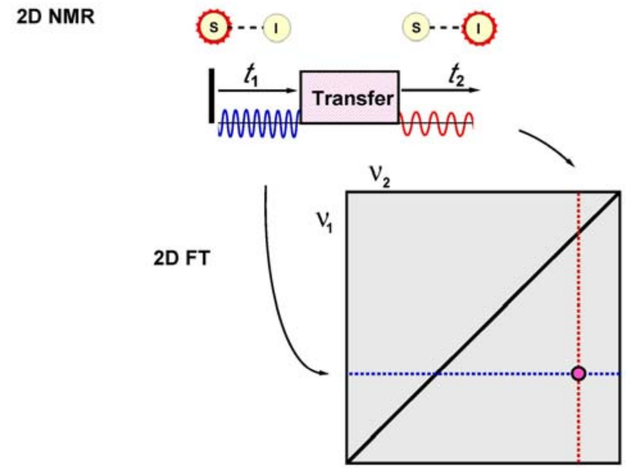
$\nu_r << \nu_{CSA}$

$\nu_r \sim \nu_{CSA}$

$\nu_r > \nu_{CSA}$

Hartmann Hahn Matching





$$I_x \rightarrow S_x$$

$$A_I - A_s = \omega_r \quad \frac{(3\cos^2\theta(t)-1)}{r^3} I_z S_z$$

$$\frac{(3\cos^2\theta(t)-1)}{r^3} \approx A\cos(\omega_r t+\gamma)+B\cos(2\omega_r t+2\gamma)$$

Hartmann Hahn Matching

$$I_z S_z + I_y S_y \qquad \Omega_z \qquad I_z S_z - I_y S_y$$

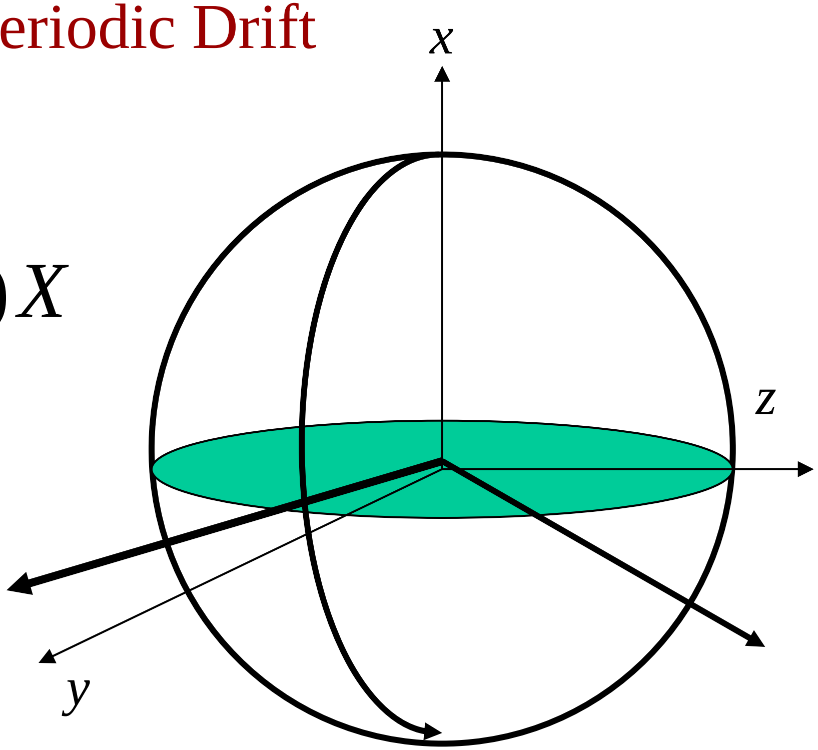
$$I_z S_y + I_y S_z \qquad \Omega_y \qquad I_z S_y + I_y S_z$$

$$\underbrace{\frac{I_x - S_x}{2}\ so(3)}_{ZQ} \qquad \Omega_x \qquad \underbrace{\frac{I_x + S_x}{2}\ so(3)}_{DQ}$$

$$\cos(\omega_r t + \gamma)\left\{(I_z S_z + I_y S_y) + (I_z S_z - I_y S_y)\right\} \xrightarrow{\omega_r (I_x - S_x)/2}$$

Control of Bilinear Systems with Periodic Drift

$$\frac{dX}{dt} = (\beta\cos(\omega_r t + \gamma)\Omega_z + \omega_r\Omega_x)X$$



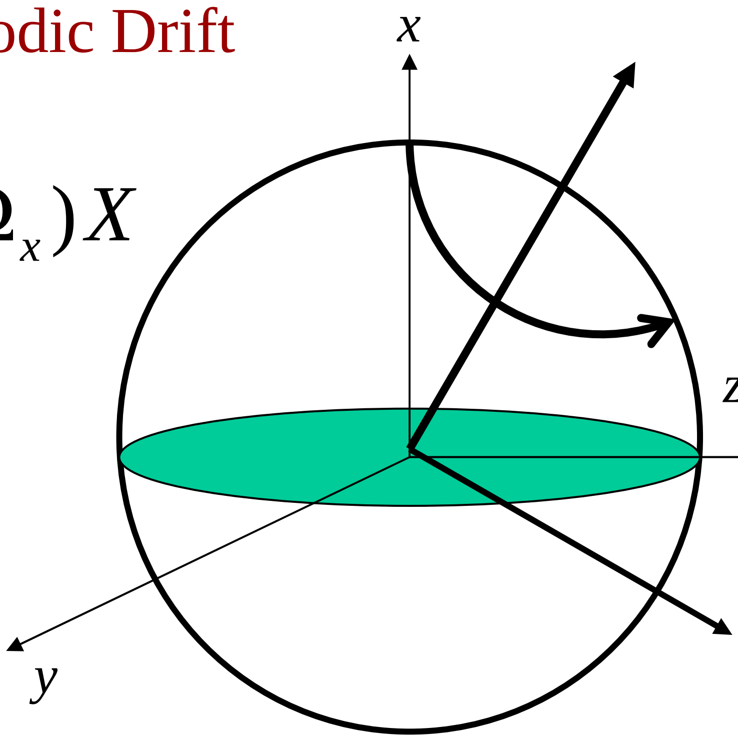
$$Y = \exp(-\omega_r\Omega_x t)X$$

$$\frac{dY}{dt} = \beta(\Omega_z\cos(\omega_r t)\cos(\omega_r t + \gamma) + \Omega_y\sin(\omega_r t)\cos(\omega_r t + \gamma))Y$$

$$\frac{dY}{dt} = \frac{\beta}{2}(\Omega_z\cos(\gamma) - \Omega_y\sin(\gamma))Y$$

Control of Bilinear Systems with Periodic Drift

$$\frac{dX}{dt} = (\beta\cos(\omega_r t + \gamma)\Omega_z + \omega_r(1+\varepsilon)\Omega_x)X$$



$$Y = \exp(-\omega_r \Omega_x t)X$$

$$\frac{dY}{dt} = \{\frac{\beta}{2}(\Omega_z\cos(\gamma) - \Omega_y\sin(\gamma)) + \varepsilon\omega_r\Omega_x\}Y$$

Phase Alternating Pulse Sequences

$$\frac{dX}{dt} = (\beta \cos(\omega_r t + \gamma)\Omega_z + \omega_r(1+\varepsilon)\Omega_x)X$$

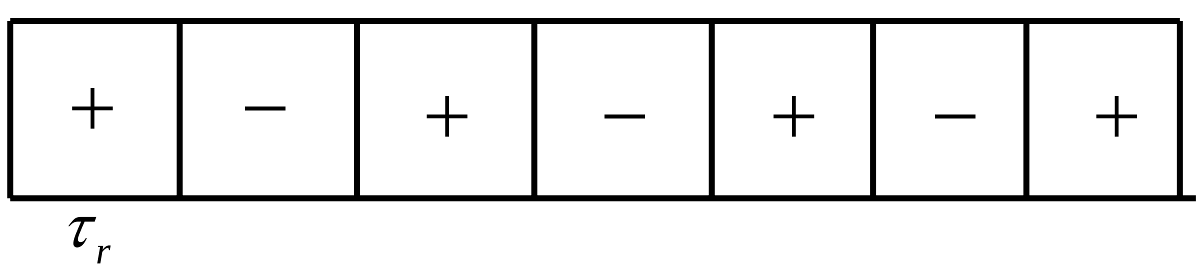
$$\frac{dX}{dt} = (\beta \cos(\omega_r t + \gamma)\Omega_z - \omega_r(1+\varepsilon)\Omega_x)X$$

$$Y_1 = \exp(-\omega_r \Omega_x t)X \qquad Y_2 = \exp(\omega_r \Omega_x t)X$$

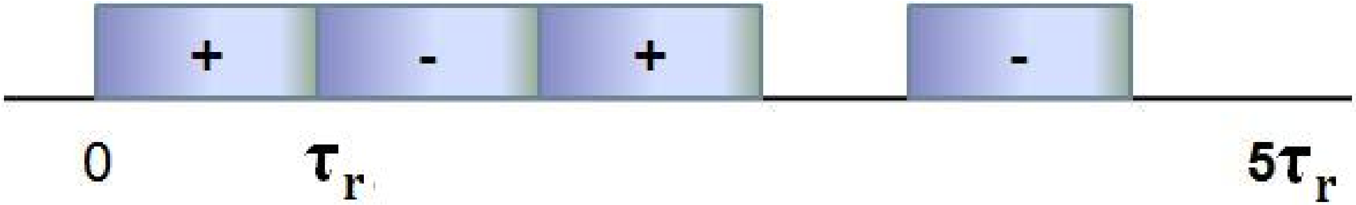
$$\frac{dY_1}{dt} = \{\frac{\beta}{2}(\Omega_z \cos(\gamma) + \Omega_y \sin(\gamma)) + \varepsilon\omega_r\Omega_x\}Y_1$$

$$\frac{dY_2}{dt} = \{\frac{\beta}{2}(\Omega_z \cos(\gamma) - \Omega_y \sin(\gamma)) - \varepsilon\omega_r\Omega_x\}Y_2$$

$$\frac{\beta}{2}\Omega_z \cos(\gamma)$$



PATCHED: Phase AlTernating Compensated by Half rotor DElays



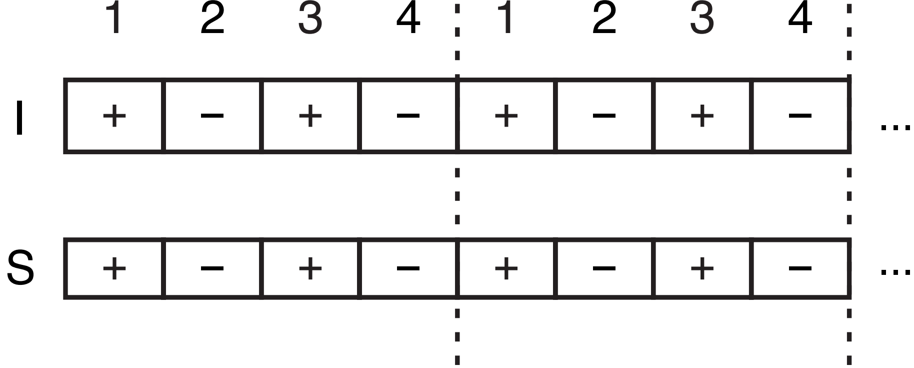
$$H_1 = \{\frac{\beta}{2}(\Omega_z \cos(\gamma) + \Omega_y \sin(\gamma)) + \delta\omega_r \Omega_x\}$$

$$H_2 = \{\frac{\beta}{2}(\Omega_z \cos(\gamma) - \Omega_y \sin(\gamma)) - \delta\omega_r \Omega_x\}$$

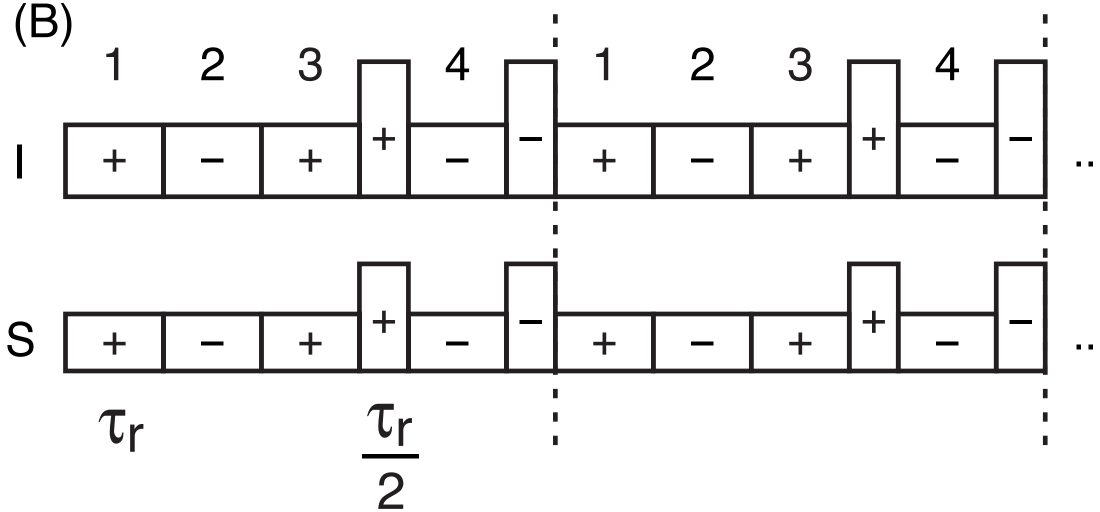
$$H_3 = \{\frac{\beta}{2}(\Omega_z \cos(\gamma) + \Omega_y \sin(\gamma)) + \delta\omega_r \Omega_x\}$$

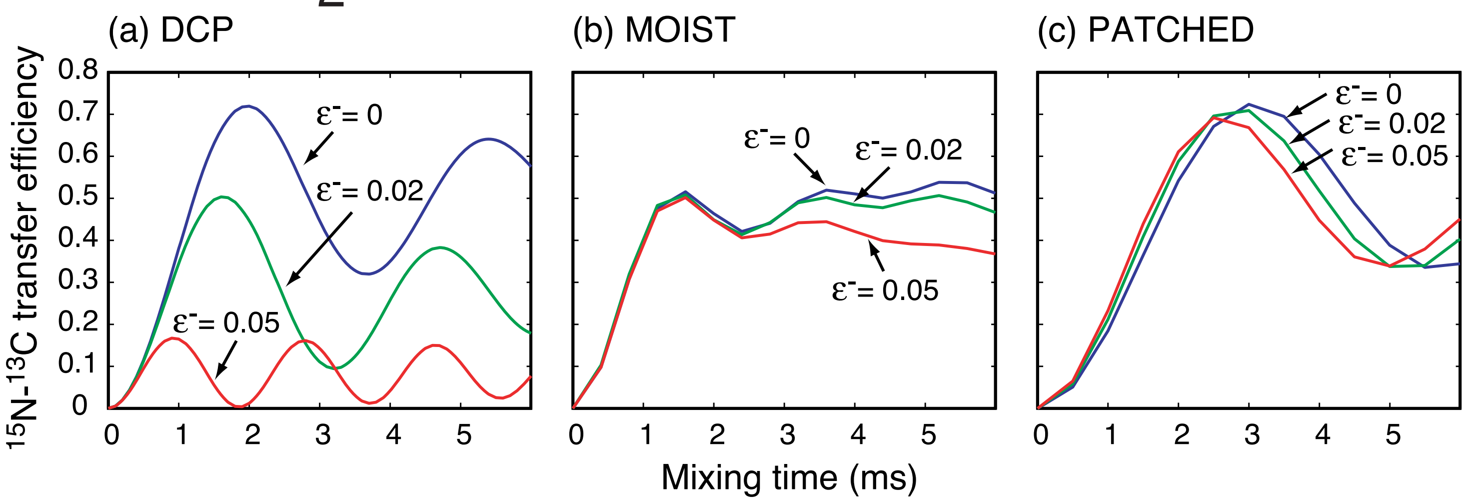
$$H_4 = \{\frac{\beta}{2}(\Omega_z \cos(\gamma + \pi) - \Omega_y \sin(\gamma + \pi)) - \delta\omega_r \Omega_x\}$$

$$H_4 = \frac{\beta}{5}(\Omega_z \cos(\gamma) + \Omega_y \sin(\gamma))$$

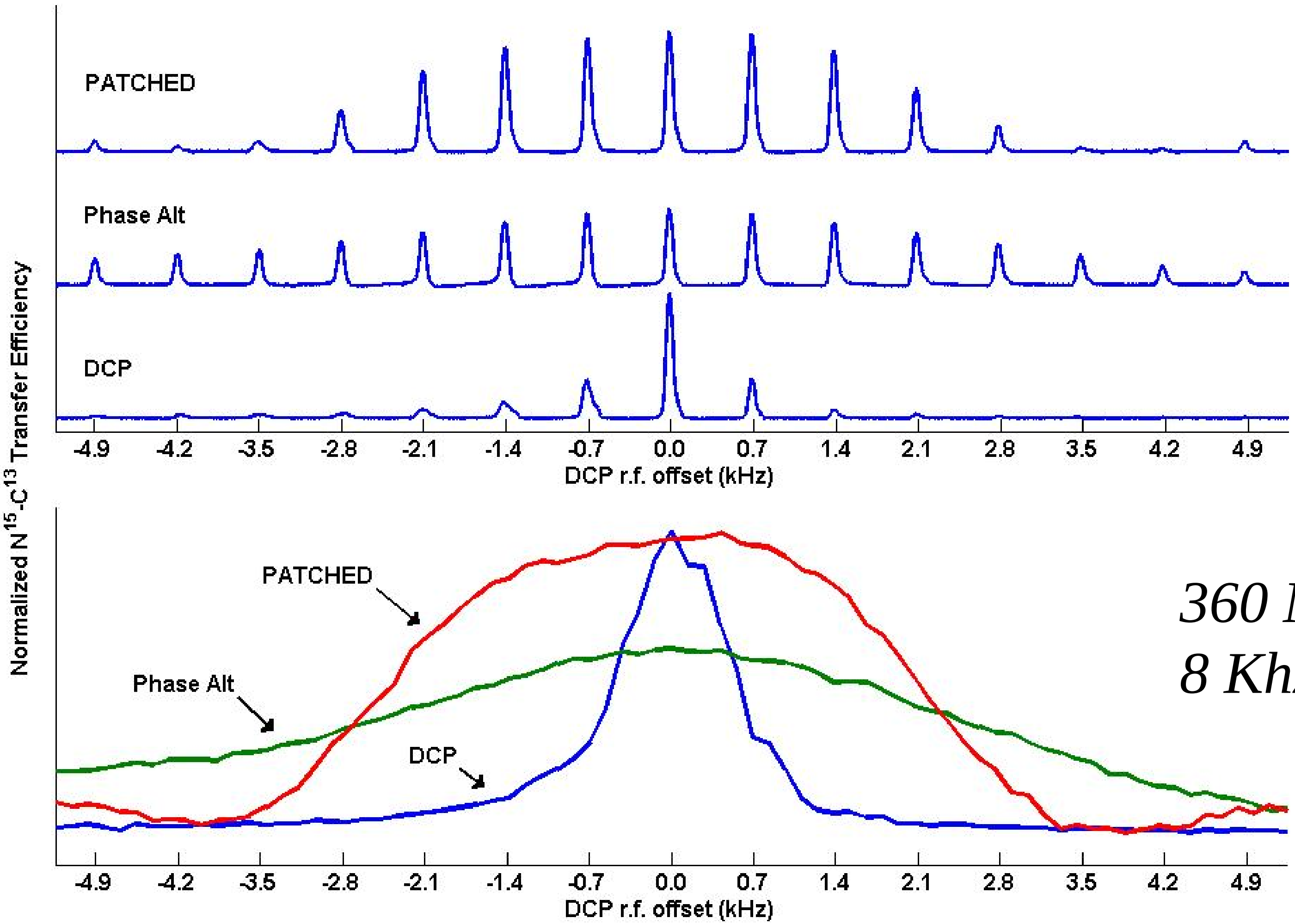

1 2 3 4 1 2 3 4
I
S
...

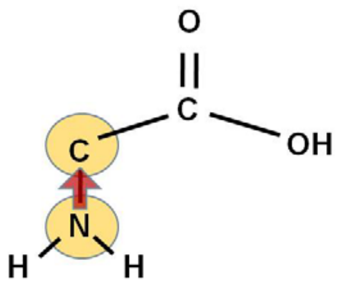
(B)


1 2 3 4 1 2 3 4
I
S
...
τr
τr/2


(a) DCP
(b) MOIST
(c) PATCHED
15N-13C transfer efficiency
Mixing time (ms)
ε⁻= 0
ε⁻= 0.02
ε⁻= 0.05

Results





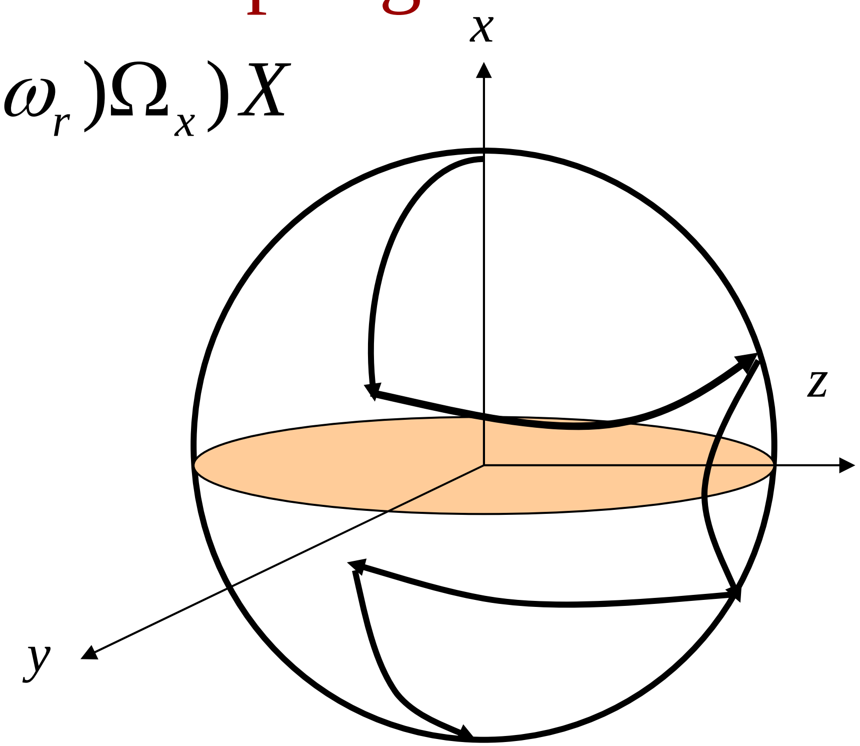
Glycine

360 Mhz 1H frequency
8 Khz spinning

J. Lin, M. Bayro, R.G. Griffin, and N. Khaneja
J.Magn.Reson. 145, 97 (2009)

Composite Dipolar Recoupling

$$\frac{dX}{dt} = (\beta\cos(\omega_r t + \gamma)\Omega_z + (u(t) + \omega_r)\Omega_x)X$$

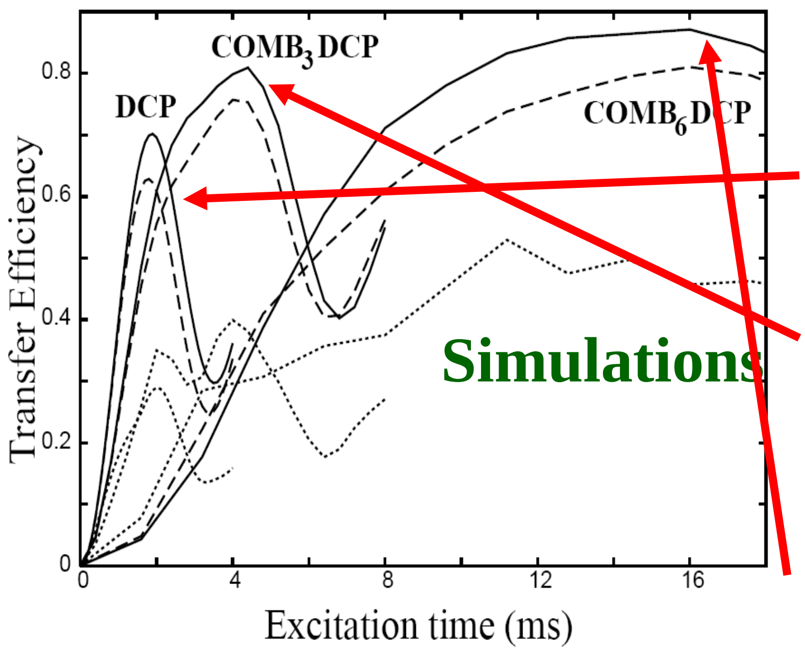


$$Y = \exp(-\omega_r \Omega_x t)X$$

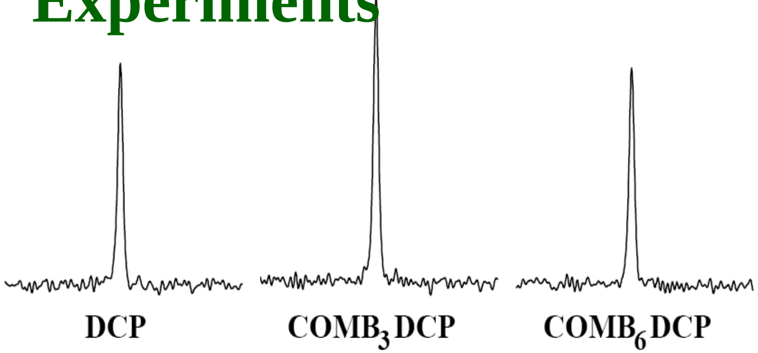
$$\frac{dY}{dt} = (\beta(\Omega_z \cos\gamma - \Omega_y \sin\gamma) + u(t)\Omega_x)Y$$

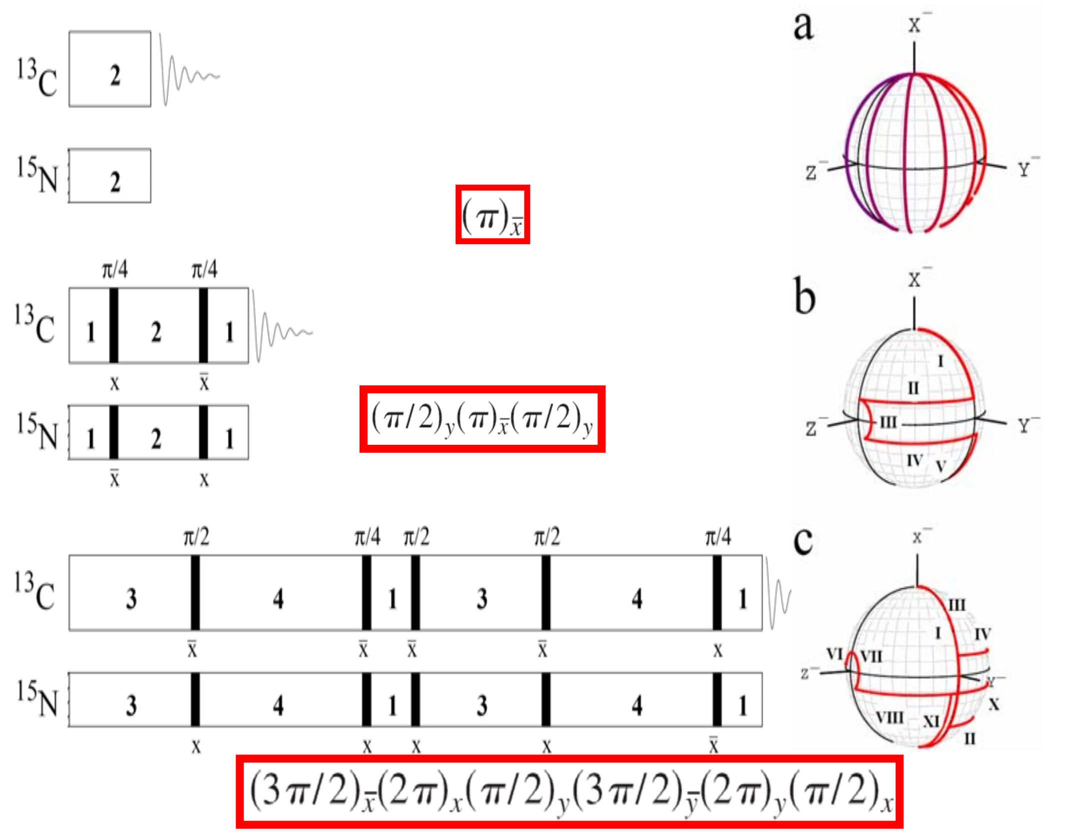
$$\frac{dX}{dt} = (\beta\cos(\omega_r t + \gamma)\Omega_z + \varepsilon(u(t) + \omega_r)\Omega_x)X$$

Composite Dipolar Recoupling



Experiments

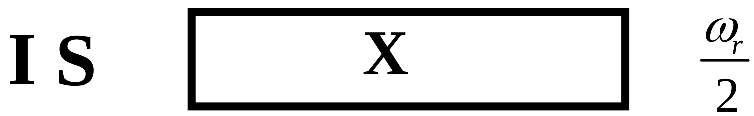




Khaneja, Kehlet, Glaser, Nielsen,
J. Chem. Phys. 124, 114503-1 – 114503-7 (2006)

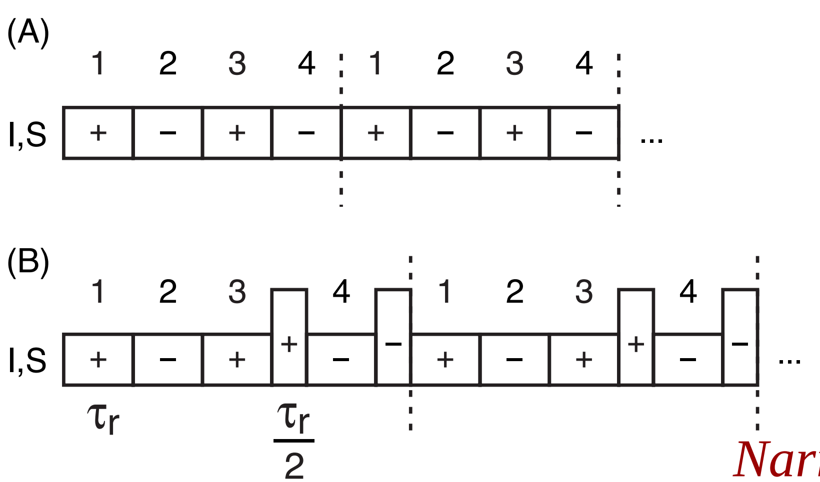
Homonuclear Recoupling

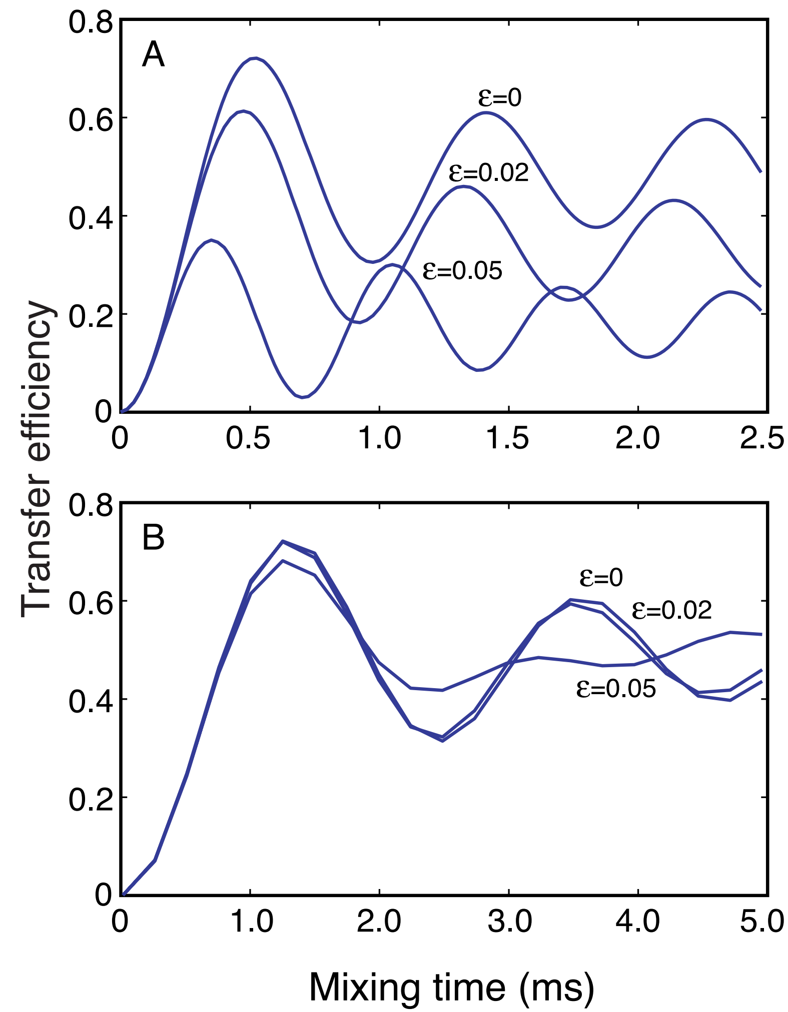
$$\cos(\omega_r t+\gamma)\left\{(I_zS_z+I_yS_y)+(I_zS_z-I_yS_y)\right\} \xrightarrow{\omega_r(I_x+S_x)/2}$$



HORROR

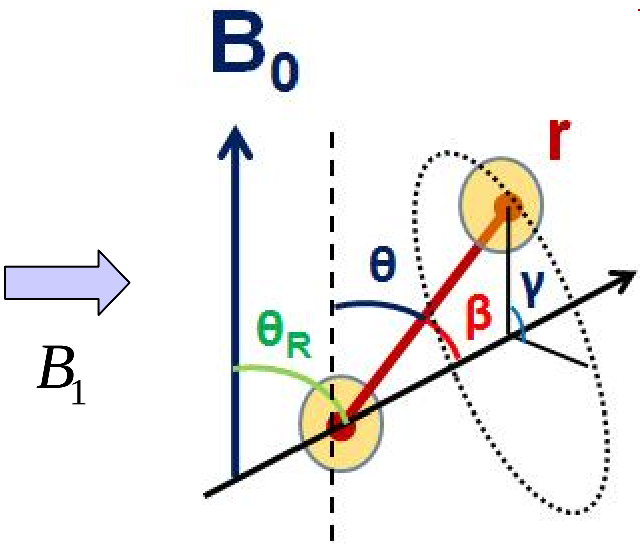
N. C. Nielsen, et al.
J.Chem.Phys. 101, 1805-1812 (1994).





Narrowband

Broadband Homonuclear Recoupling : CMRR



$$A \gg \Delta\omega_I, \Delta\omega_s, \omega_r$$

$$\phi(t) = \frac{\omega_r}{A}(1 - \cos(At))$$

$$H = \underline{\Delta\omega_I I_z} + \underline{\Delta\omega_s S_z} + AF_x - \omega_r \sin(At) F_z$$

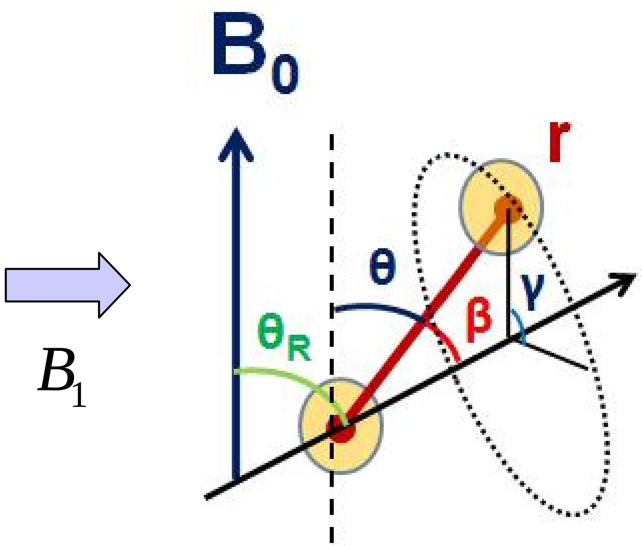
$$\kappa \cos(\omega_r t + \gamma)\left\{(I_z S_z + I_y S_y) + \underline{(I_z S_z - I_y S_y)}\right\}$$

$$\tilde{\tilde{H}} = \frac{\omega_r}{2} F_y + \kappa \cos(\omega_r t + \gamma)\left\{(I_z S_z + I_y S_y)\right\}$$

$$\kappa \cos(\omega_r t + \gamma)\left\{(I_z S_z + I_y S_y)\right\} \xrightarrow{\frac{\omega_r}{2} F_y}$$

G. De Paëpe, et al. *J.Amer.Chem.Soc.* 128, 1776-1777(2006).

High Power recoupling makes the experiment sensitive to RF-inhomogeneity



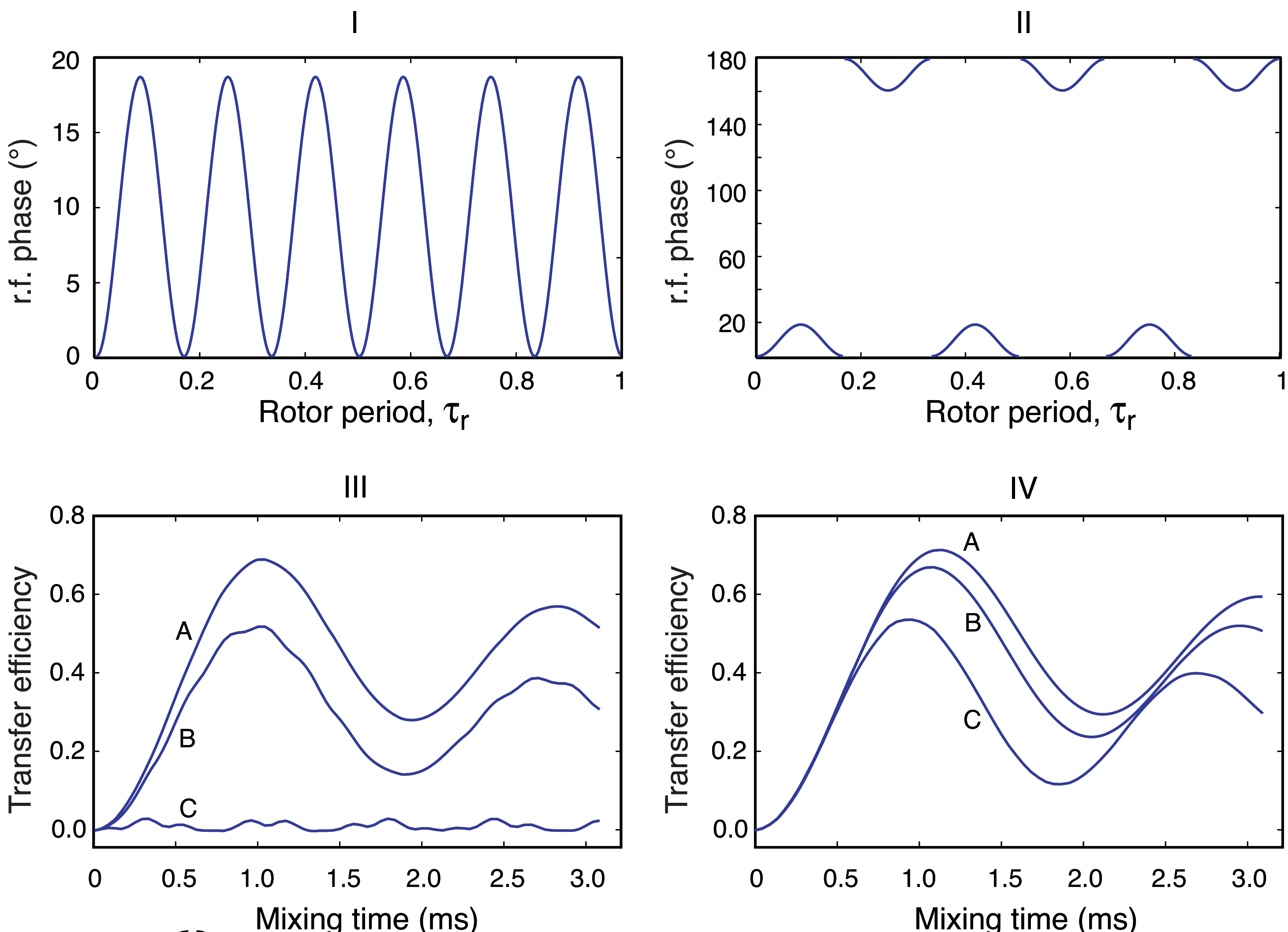
$$A \gg \Delta\omega_I, \Delta\omega_s, \omega_r$$

$$H = \Delta\omega_I I_z + \Delta\omega_s S_z + A(1+\varepsilon)F_x - \omega_r \sin(At)F_z$$

$$\kappa\cos(\omega_r t+\gamma)\left\{(I_z S_z + I_y S_y) + (I_z S_z - I_y S_y)\right\}$$

$$\tilde{\tilde{H}} = \frac{\omega_r}{2}F_y + \varepsilon A F_x + \kappa\cos(\omega_r t+\gamma)\left\{(I_z S_z + I_y S_y)\right\}$$

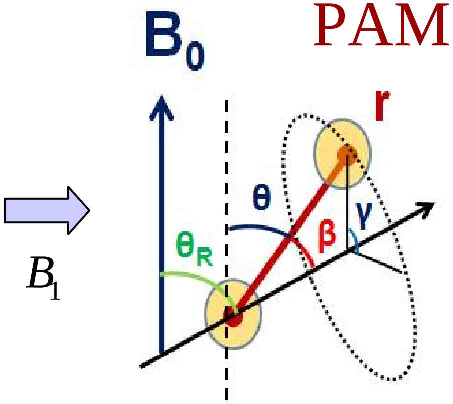
CMRR Phase Modulations



$$\phi(t) = \frac{\omega_r}{A}(1 - \cos(At))$$

$$\phi(t + \tau_c) = 180 - \phi(t)$$

PAMORE (Phase Alternating Modulated Recoupling)



$$A \gg \Delta\omega_I, \Delta\omega_s, \omega_r$$

$$\phi(t+\tau_c) = 180 - \phi(t); \quad \tau_c = \frac{2\pi}{A}$$

$$H_1 = \Delta\omega_I I_z + \Delta\omega_s S_z + A(1+\varepsilon)F_x - \omega_r \sin(At)F_z$$

$$\tilde{\tilde{H}}_1 = \frac{\omega_r}{2}F_y + \varepsilon A F_x + \kappa\cos(\omega_r t+\gamma)\left\{(I_z S_z + I_y S_y)\right\}$$

$$\kappa\cos(\omega_r t+\gamma)\left\{(I_x S_z - I_z S_y) + (I_z S_z + I_y S_y)\right\}$$

$$\tilde{\tilde{H}}_2 = \frac{\omega_r}{2}F_y - \varepsilon A F_x + \kappa\cos(\omega_r t+\gamma)\left\{(I_z S_z + I_y S_y)\right\}$$

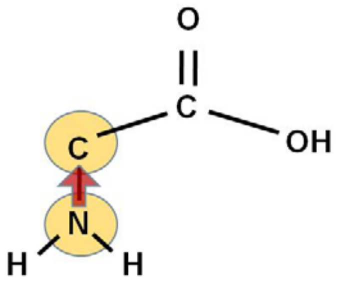
$$H_2 = \Delta\omega_I I_z + \Delta\omega_s S_z - A(1+\varepsilon)F_x + \omega_r \sin(At)F_z$$

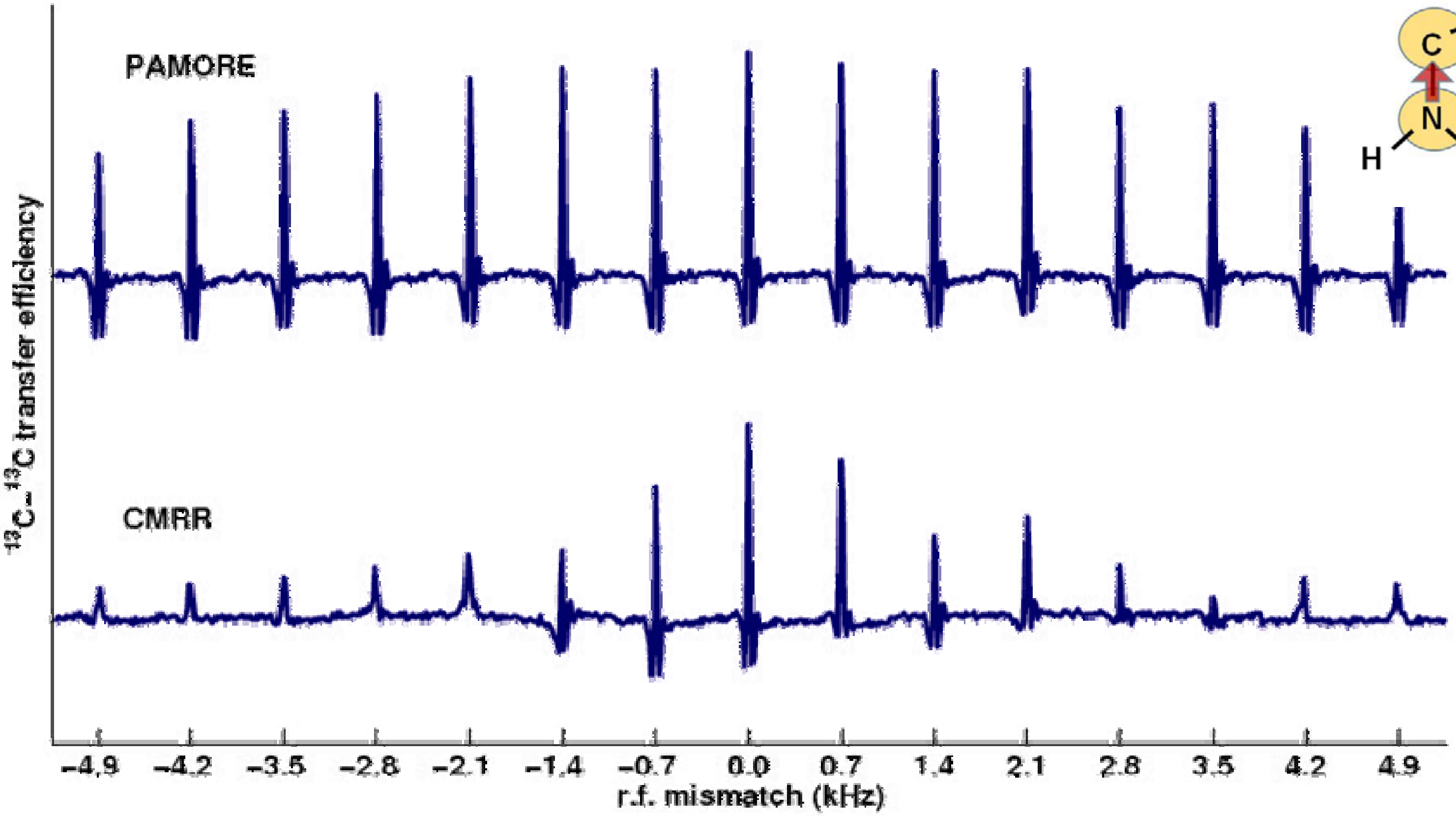
$$\kappa\cos(\omega_r t+\gamma)\left\{(I_z S_z + I_y S_y) + (I_z S_z - I_y S_y)\right\}$$

$$\tilde{\tilde{H}} = \frac{\omega_r}{2}F_y + \kappa\cos(\omega_r t+\gamma)\left\{(I_z S_z + I_y S_y)\right\}$$

Results (Homonuclear Transfer)

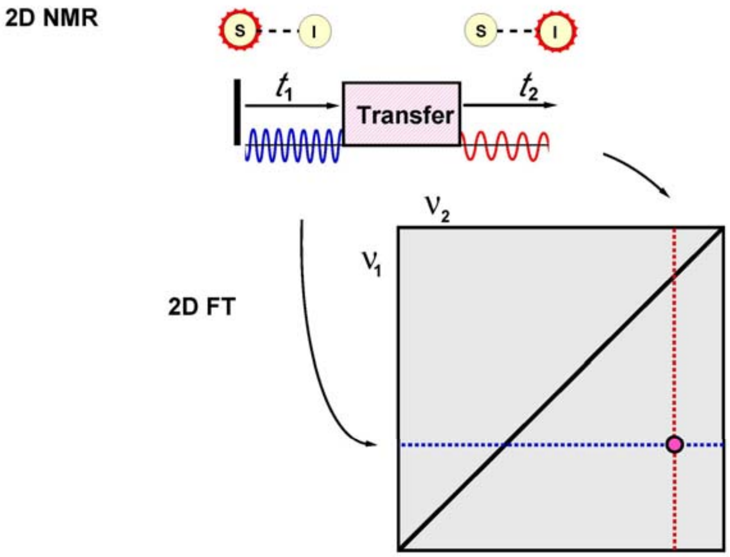
$C_\alpha \rightarrow CO$





360 Mhz
8 Khz spinning

J. Lin, M. Bayro, R.G. Griffin, and N. Khaneja
J.Magn.Reson. 145, 97 (2009)



Ensemble Control and Decoupling

$$\frac{d}{dt}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} = \begin{pmatrix} 0 & -J & 0 & 0 \\ J & 0 & -u(t) & v(t) \\ 0 & u(t) & 0 & -\omega \\ 0 & -v(t) & \omega & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix}$$

$$\max \int x_1(\tau)d\tau \qquad \omega \in [-B, B]$$

Heteronuclear Decoupling by Multiply Modulated Fields

$$H = \omega_{\mathrm{I}} \, \mathrm{I_z} + 2\,\pi\,\mathrm{J}\,\mathrm{I_z}\,\mathrm{S_z} + \omega_S \, \mathrm{S_z}$$

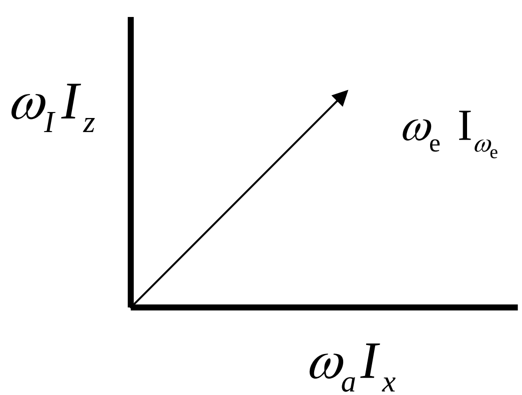
$$H = \omega_{\mathrm{I}} \, \mathrm{I_z} + 2\,\pi\,\mathrm{J}\,\mathrm{I_z}\,\mathrm{S_z} \; ; \quad \omega_{\mathrm{I}} \in [-W, W]$$

$$H_{rf} = \omega_{\mathrm{a}} \, \mathrm{I_x} + (2\omega_{\mathrm{b}} \sin \nu_b t + 4\omega_c \cos \nu_b \sin \nu_c t + \cdots) I_y$$

$$\longrightarrow \exp(-\nu_b I_{\omega_e}) \longrightarrow$$

$$H = \omega_{\mathrm{e}} \, \mathrm{I}_{\omega_{\mathrm{e}}} + 2\,\pi\,\mathrm{J}\,\mathrm{I}_{\omega_{\mathrm{e}}}\,\mathrm{S_z} + \omega_{\mathrm{b}} I_f + 2\omega_c \sin \nu_c t \; I_y$$

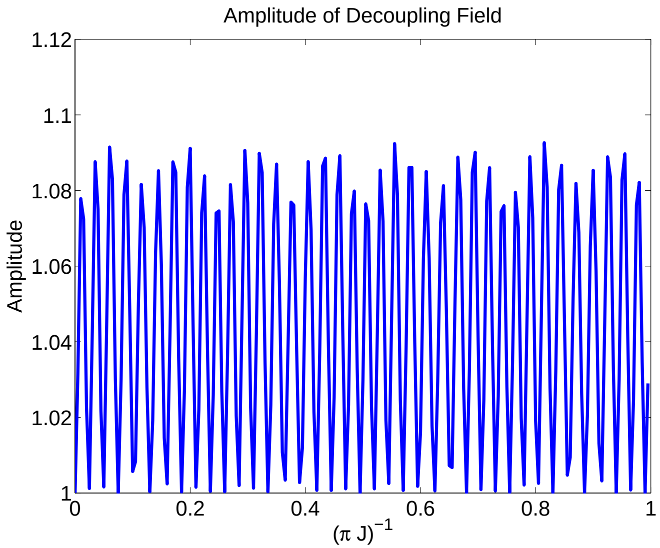
$$I_f = I_{\omega_e} \times I_y$$

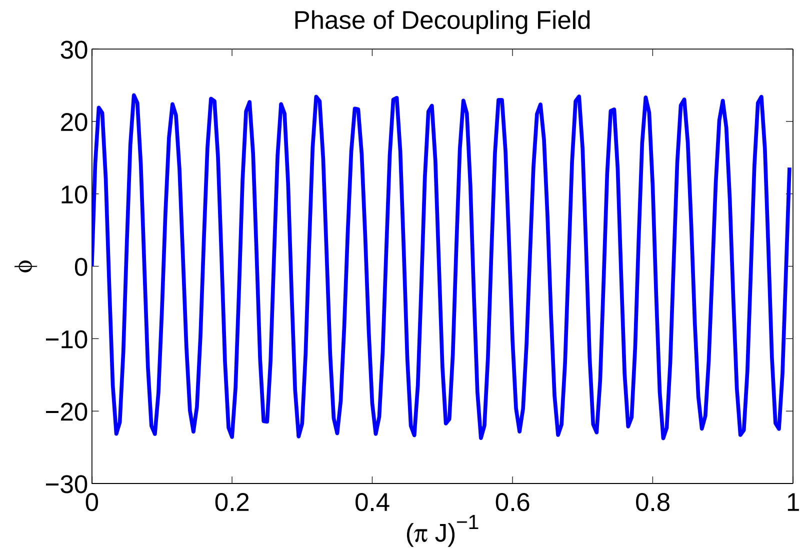


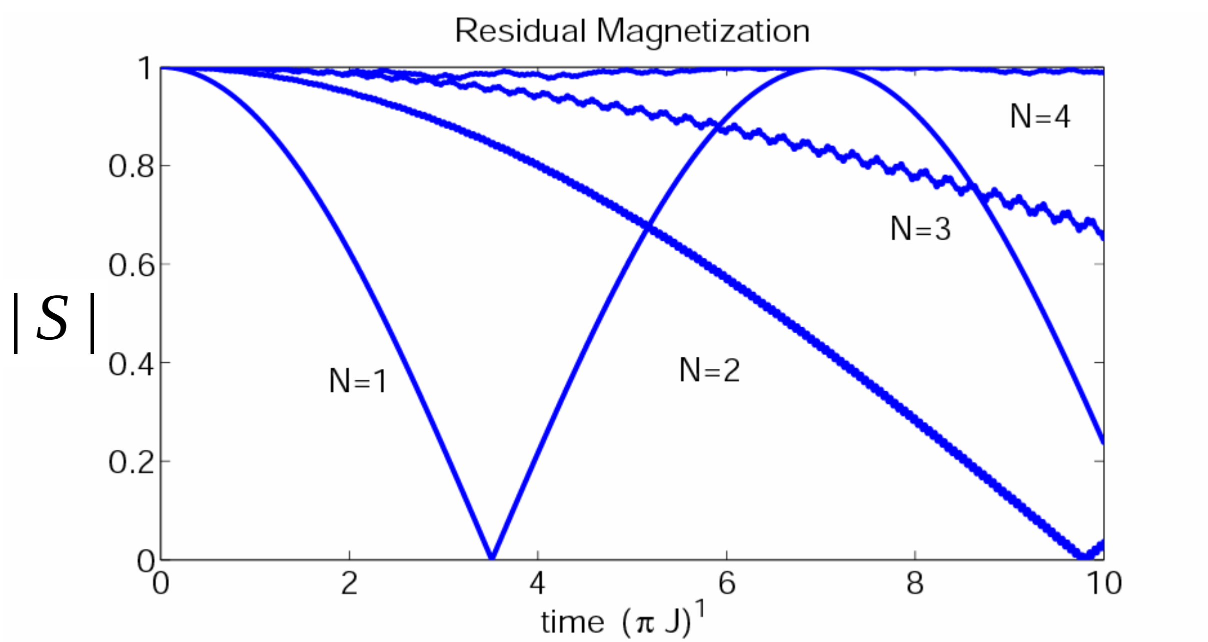
$$\omega_e \in [-C, C]$$

$$\nu_b = \frac{\sqrt{\omega_a^2 + \omega_I^2} + \omega_a}{2}$$

$$C = \frac{\sqrt{\omega_a^2 + \omega_I^2} - \omega_a}{2}$$



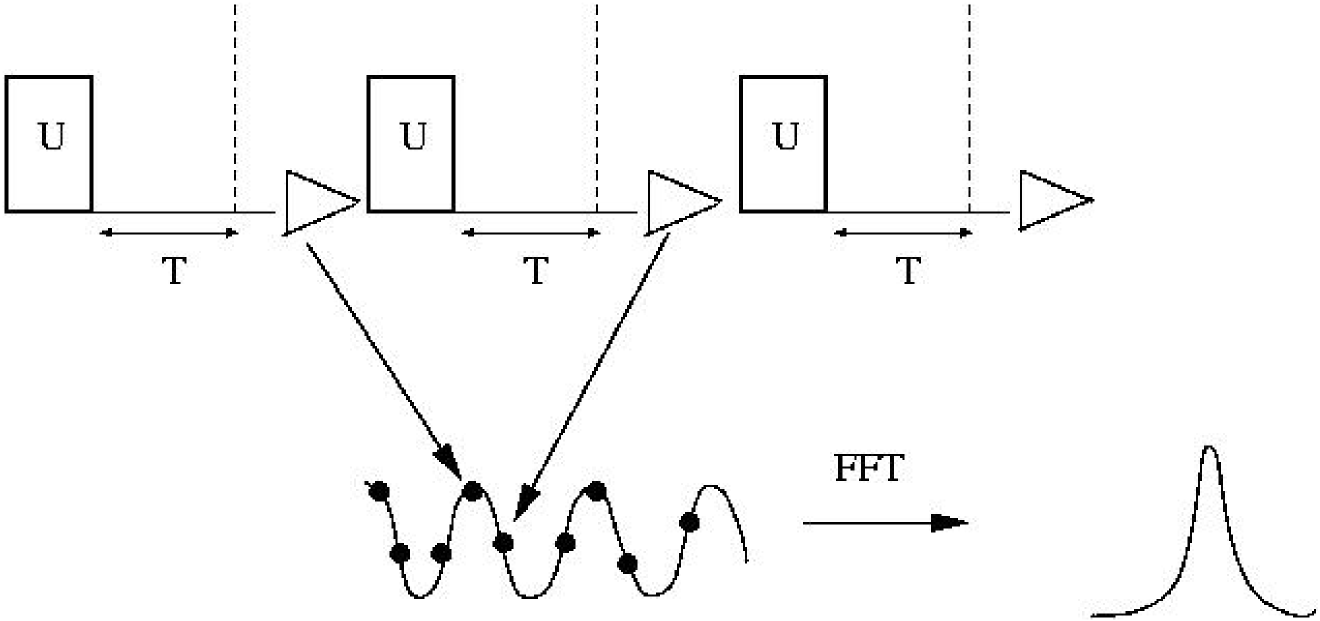




$$\frac{A_{eff}}{W} \approx 1$$

$$\frac{(\pi J)}{W} \approx .01$$

Homonuclear decoupling



$$H = \omega_I\, I_z + \omega_S\, S_z + J\, I_z\, S_z$$

Homonuclear Decoupling

$$H = \omega_I \, I_z + \omega_S \, S_z + J \, I_z \, S_z \qquad \omega_I - \omega_S \, \square \; 10J$$

$$H_T = \omega_I \, I_y + \omega_S \, S_y + J I_z S_z$$

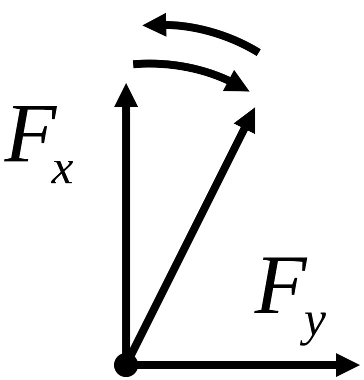
$$H_1 = \omega_I \, I_z + \omega_S \, S_z + J I_z S_z + A F_x$$

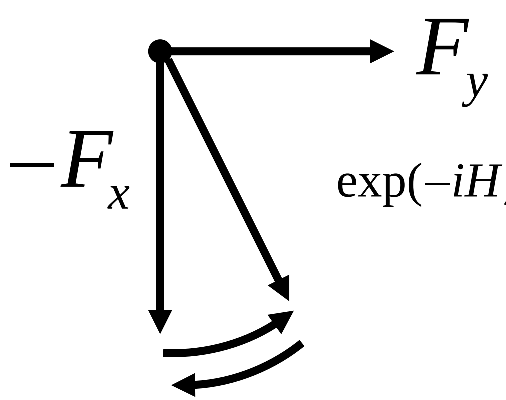
$$H_2 = -\omega_I \, I_z - \omega_S \, S_z + J I_z S_z + A F_x$$

$$H_3 = -\omega_I \, I_z - \omega_S \, S_z + J I_z S_z - A F_x$$

$$H_4 = \omega_I \, I_z + \omega_S \, S_z + J I_z S_z - A F_x$$

$$A\Delta t \, \square \, \theta \, \square \; \pi / 2$$





$$\exp(-iH_4\Delta t)\exp(-iH_3\Delta t)\exp(-iH_2\Delta t)\exp(-iH_1\Delta t)$$

Homonuclear Decoupling

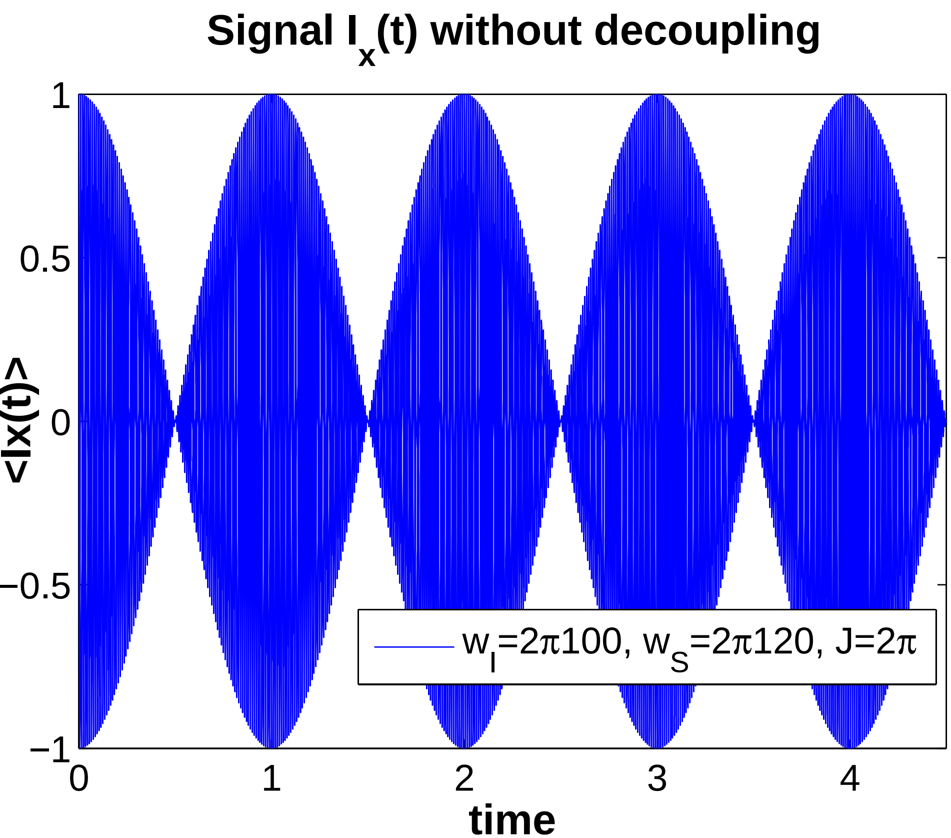
$$\omega_{\mathrm{I}} - \omega_S \;\square\; 10J$$

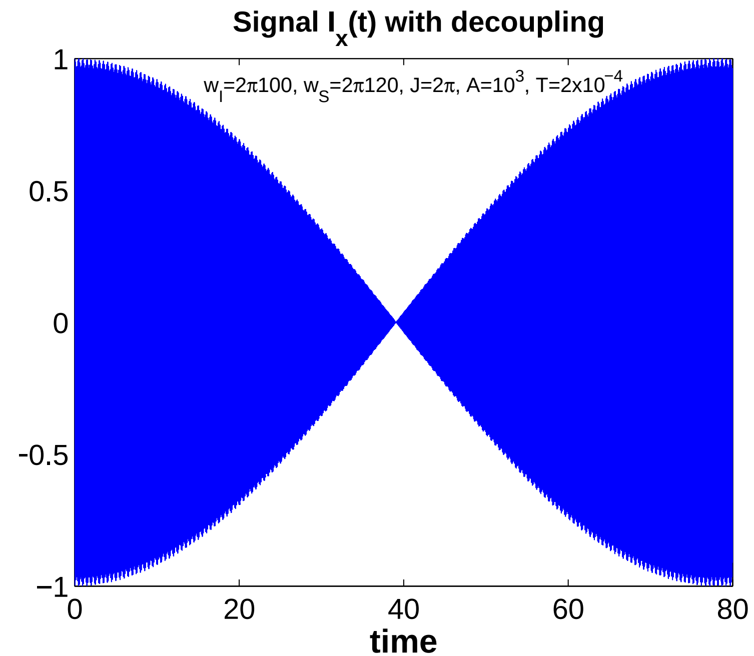
$$A\Delta t \;\square\; \theta \;\square\; 1$$

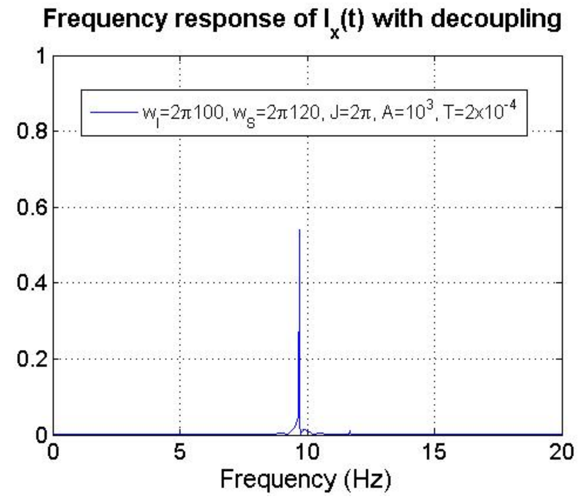
$$H = \omega_{\mathrm{I}}\, \mathrm{I_z} + \omega_S\, \mathrm{S_z} + \mathrm{J}\, \mathrm{I_z}\, \mathrm{S_z}$$

$$H_{eff} = \frac{\theta}{2}\omega_{\mathrm{I}}\, \mathrm{I_y} + \frac{\theta}{2}\omega_S\, \mathrm{S_y} + JI_zS_z + \frac{J\theta^2}{3} I_yS_y$$

Homonuclear Decoupling

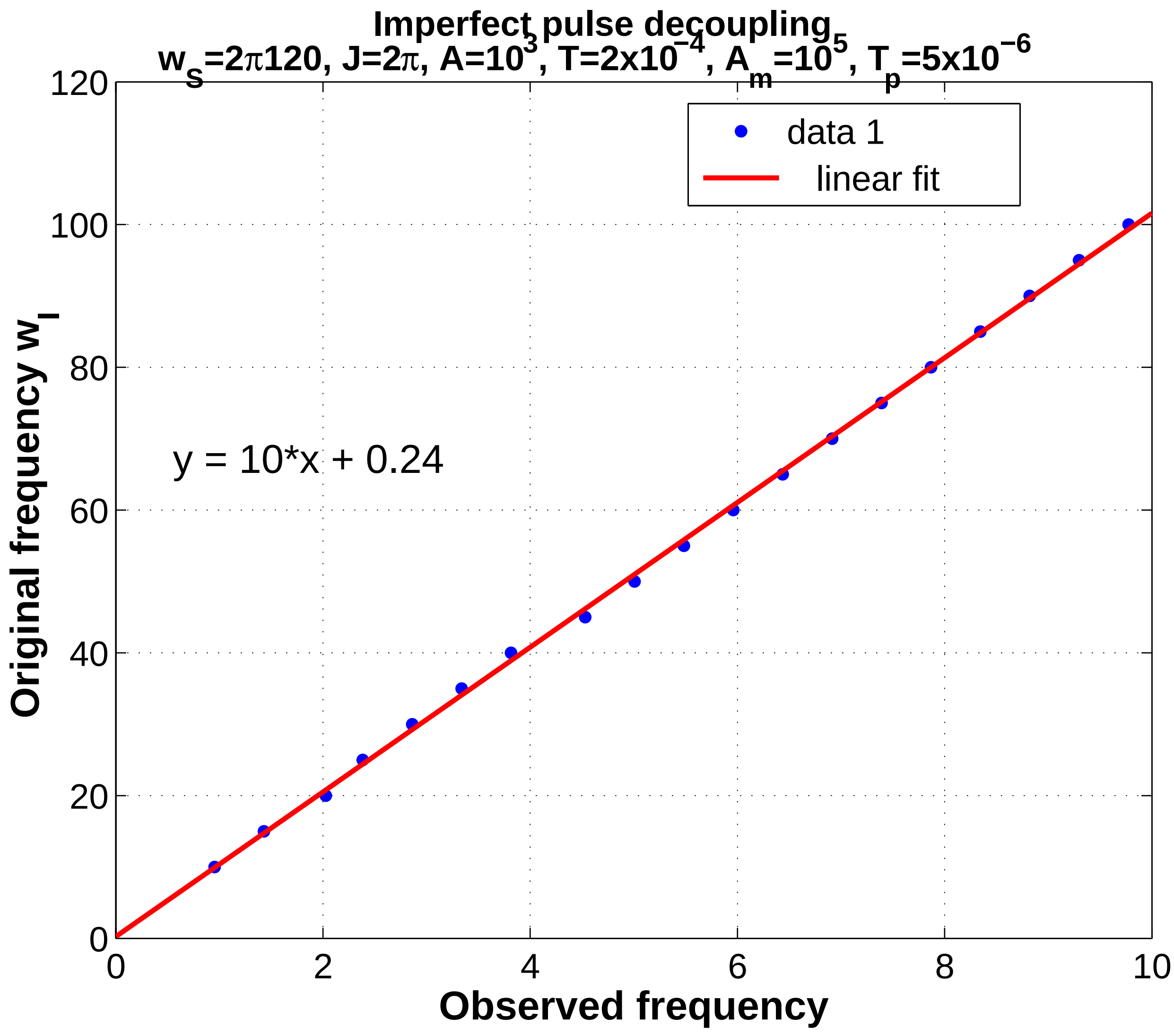






Joint work with Van Mai Do

Homonuclear Decoupling



Optimal control of inhomogeneous quantum ensembles

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\omega & -u(t) \\ \Delta\omega & 0 & -v(t) \\ u(t) & v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\min \int_0^T u^2 + v^2 dt$$

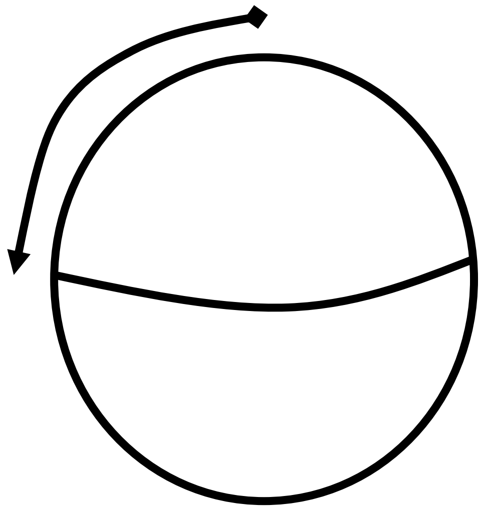
$$(0,0,1) \rightarrow (0, x(\Delta\omega), y(\Delta\omega))$$

Create desired excitation profile as a function of $\Delta\omega$

Minimum energy pulses for desired excitations (SLR Algorithm)

$$\frac{d}{dt}\psi = -\frac{i}{2}\begin{pmatrix} 0 & u - iv \\ u + iv & -2\Delta\omega \end{pmatrix}\psi$$

$$U = \prod_j \begin{pmatrix} C_j & -S_j{}^* \\ S_j & C_j \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & z^{-1} \end{pmatrix}; \quad z^{-1} = e^{-i\Delta\omega\Delta t}$$

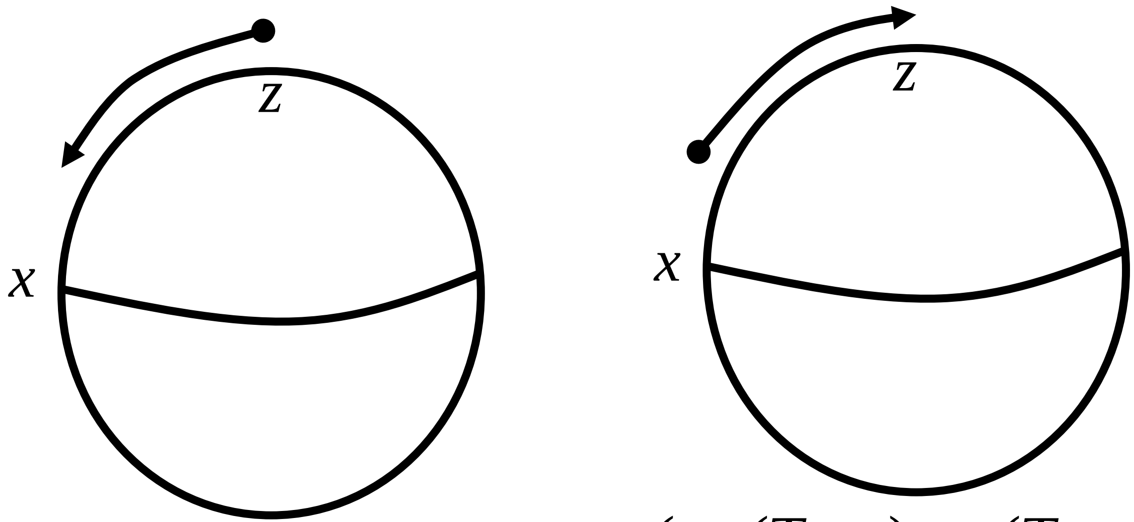


$$U = \begin{pmatrix} A_n(z) & -B_n{}^*(z) \\ B_n(z) & A_n{}^*(z) \end{pmatrix}$$

$$A_n(z) = \sum_{j=0}^{n-1} a_j z^{-j}; \quad B_n(z) = \sum_{j=0}^{n-1} b_j z^{-j}$$

$$|A_n(z)| = B_n(z) = \frac{1}{\sqrt{2}}$$

RF inhomogeneity and SLR



$(u(t), v(t))$ $\quad$ $(-u(T-t), -v(T-t))$

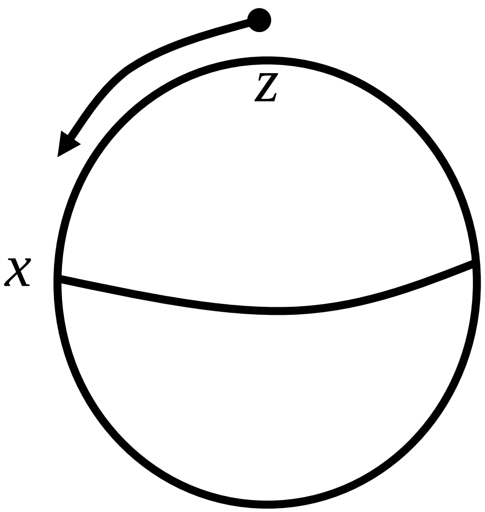
$$\frac{dX}{dt} = \varepsilon\,[A\cos\phi(t)\,\Omega_x + A\sin\phi(t)\,\Omega_y]\,X$$

$$\frac{dX}{dt} = ((1+\delta)\;A\Omega_x + \dot{\phi}\,\Omega_z)\;X$$

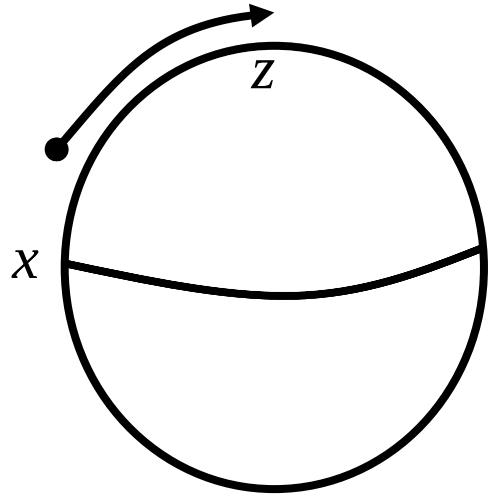
$$\frac{dX}{dt} = ((1+\delta)\;A\Omega_x + 2B\cos(At+\theta)\,\Omega_z)\;X$$

$$\frac{dY}{dt} = (\delta A\Omega_x + B\cos(\theta(t))\,\Omega_z + B\sin(\theta(t))\,\Omega_y)\,Y$$

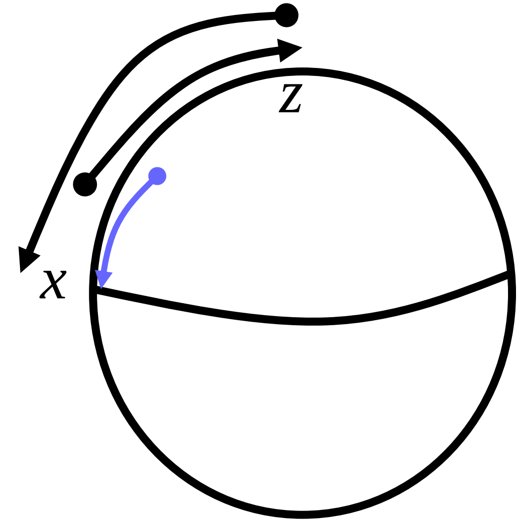
Constructing Frequency Dependent Rotation



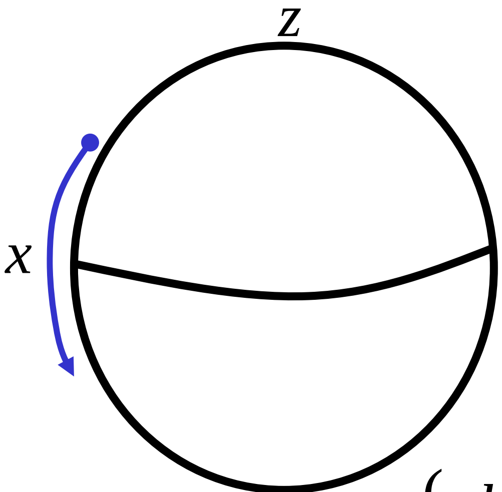
$$(u(t), v(t))$$



$$(-u(T-t), -v(T-t))$$



$$(u_c(t), v_c(t))$$



$$(-u_c(T-t), v_c(T-t))$$

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\omega & v(t) \\ \Delta\omega & 0 & -u(t) \\ -v(t) & u(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\exp(f(\Delta\omega)\Omega_y)$$

Luy and Glaser JMR, (2005)

Ensemble of Inhomogeneous Bloch Equations

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\omega & -\varepsilon u(t) \\ \Delta\omega & 0 & -\varepsilon v(t) \\ \varepsilon u(t) & \varepsilon v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\Delta\omega \in [-B, B]$$

$$\sqrt{u^2 + v^2} \leq A$$