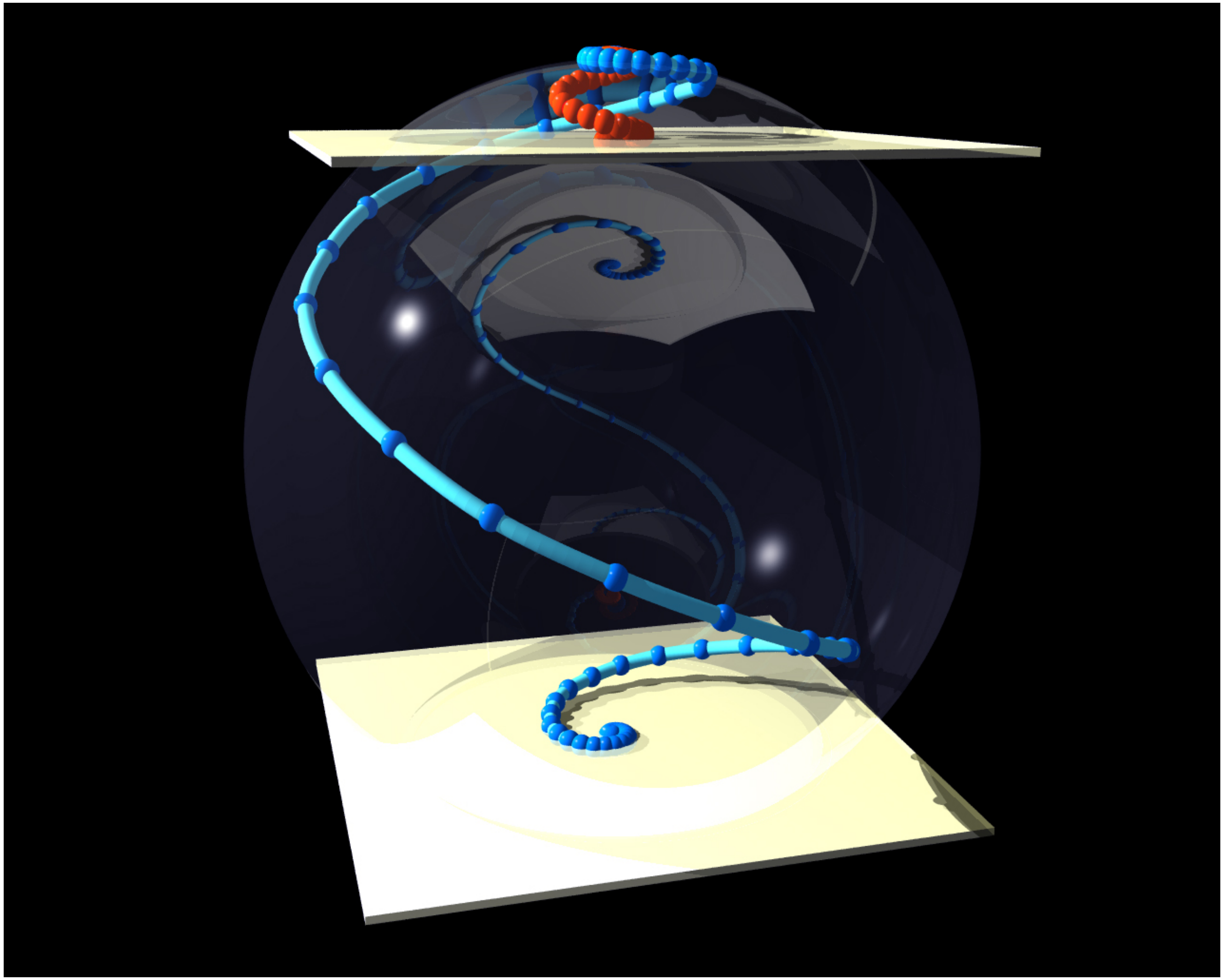
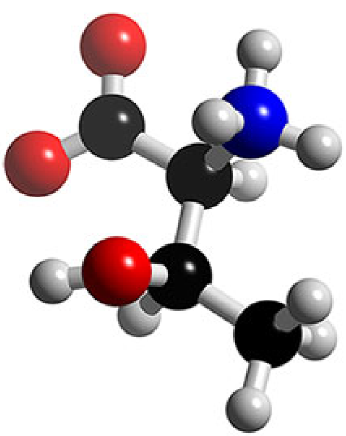
Control of Spin Systems



The Nuclear Spin Sensor

- Many Atomic Nuclei have intrinsic angular momentum called spin.
- The spin gives the nucleus a magnetic moment (like a small bar magnet).
- Magnetic moments precess in a magnetic field at a precession frequency that depends on the magnetic field strength.
- The spins are therefore beautiful, very localized (angstrom resolution) probes of local magnetic fields.
- The chemical environment of a nucleus in a molecule effects the local magnetic field on the nucleus.

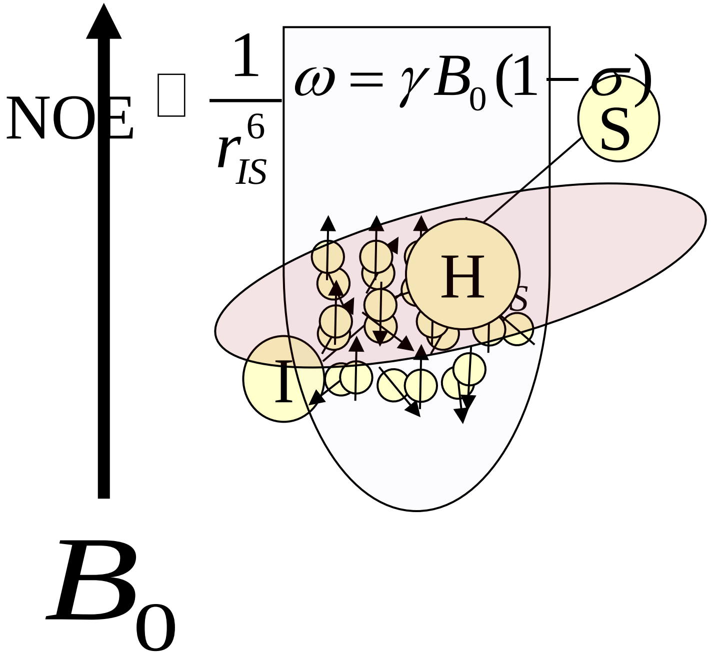


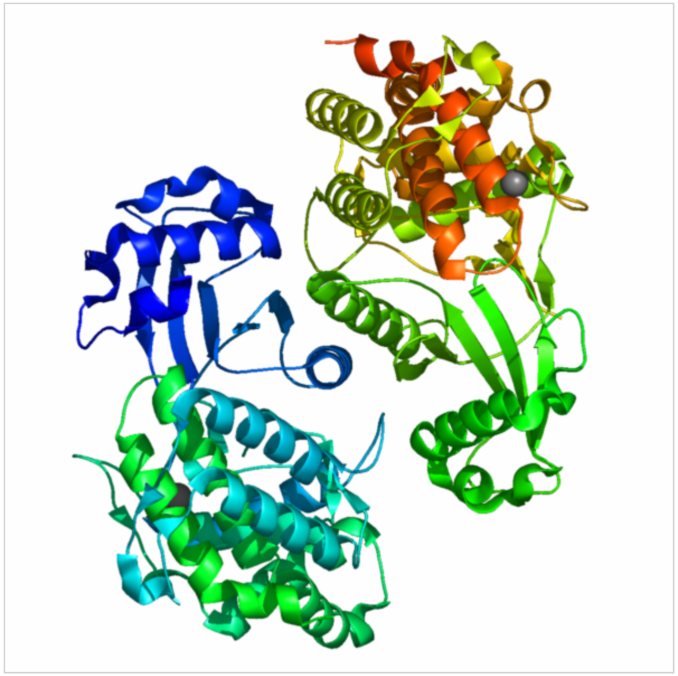
- Probing spins with radio frequency magnetic fields and observing them gives information about chemical environment of the nuclei in a non-invasive way. Therefore field of nuclear magnetic resonance is the single most important analytical tool in science.

- The magnetic moment of a single nuclear spin is too weak to detect.
- The spins are generally detected in the Bulk by making them precess coherently.
- The precession of nuclear spins is detected or observed by a Magnetic resonance technique.

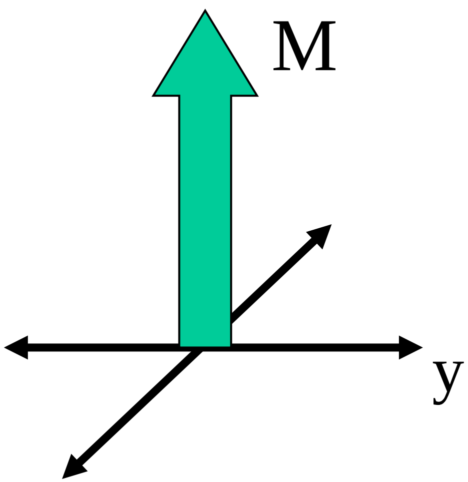
$$\mathrm{NOE} \propto \frac{1}{r_{IS}^{6}}$$

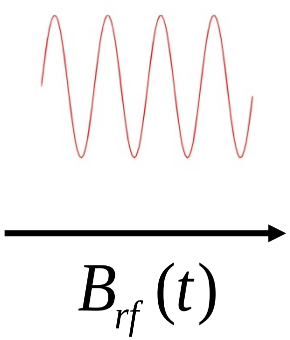
$$\omega = \gamma B_0 (1-\sigma)$$



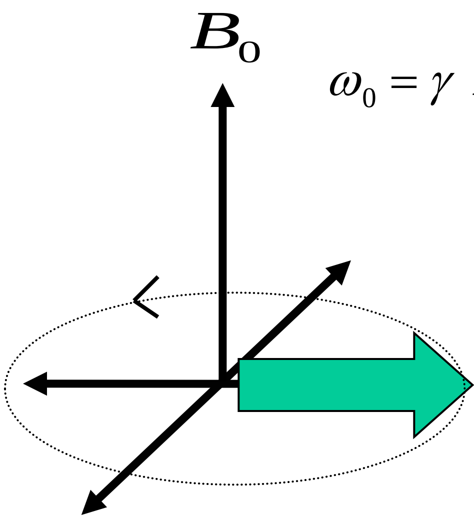


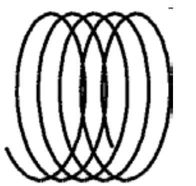
$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}$$

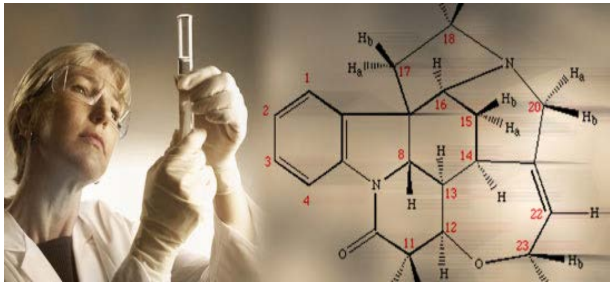




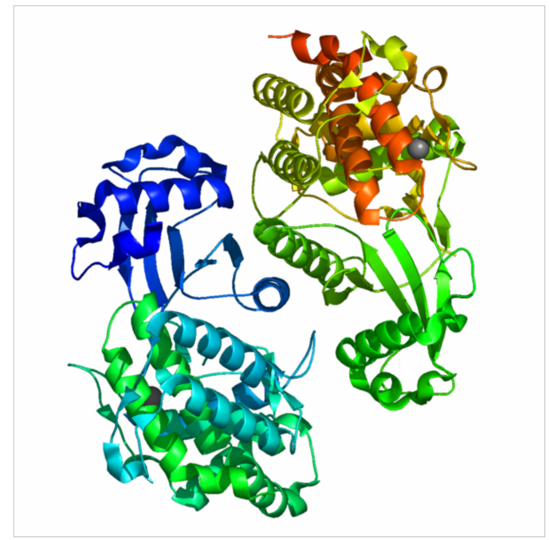
$$\omega_0 = \gamma B_0$$

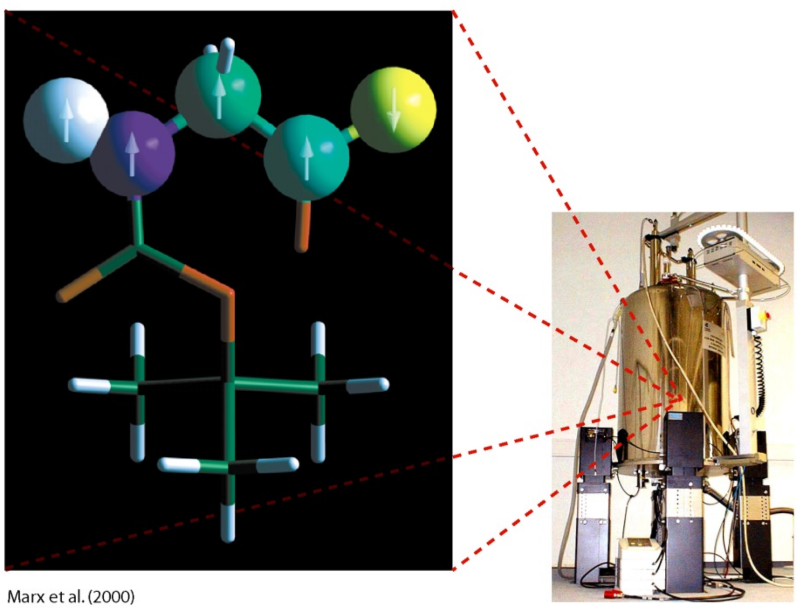






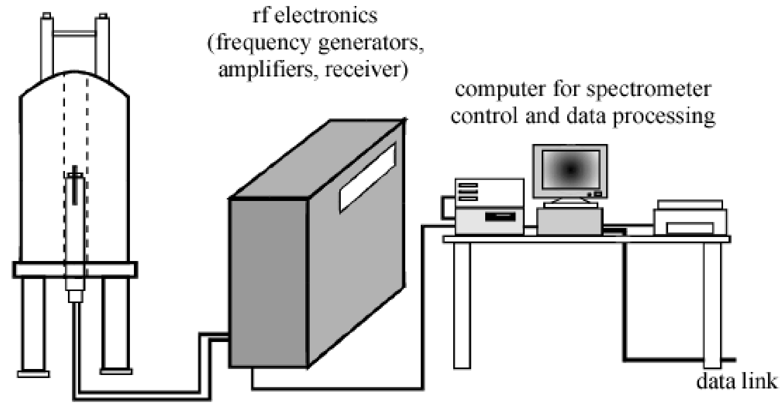
Chemistry
Pharmaceuticals
Life Science
Imaging
Food
Material Research
Process Control



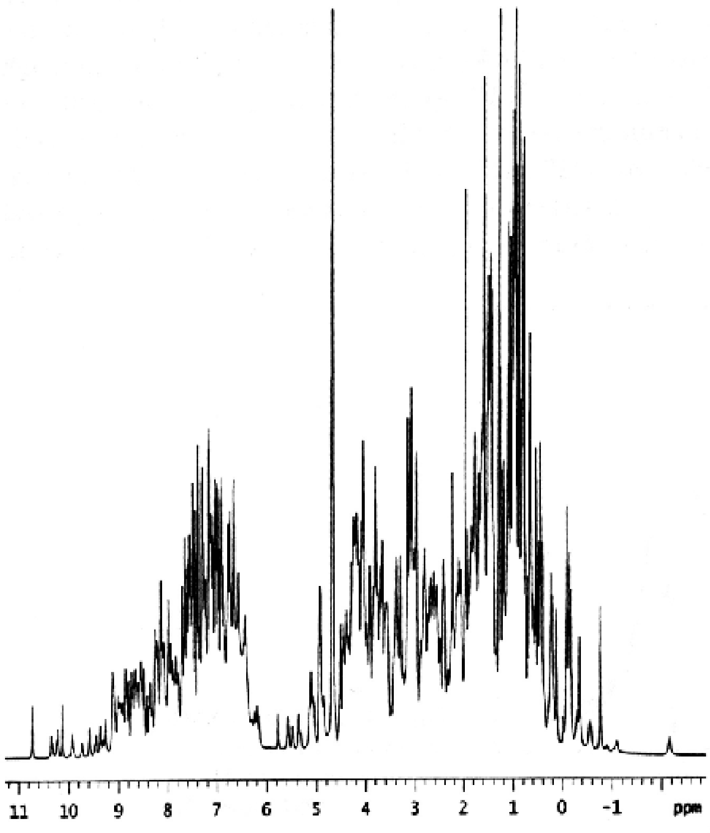


Marx et al. (2000)

NMR spectrometer

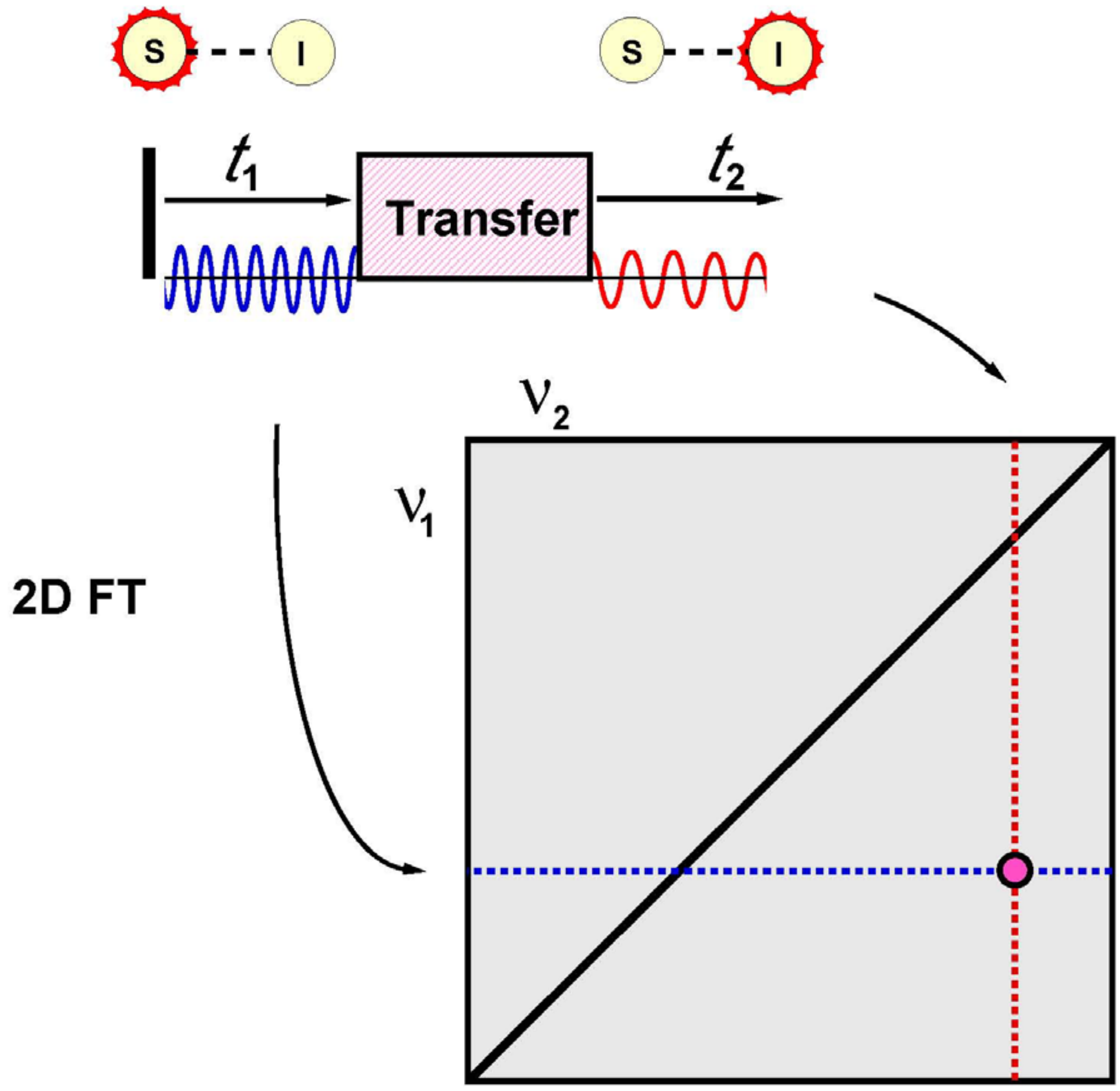


One dimensional spectrum



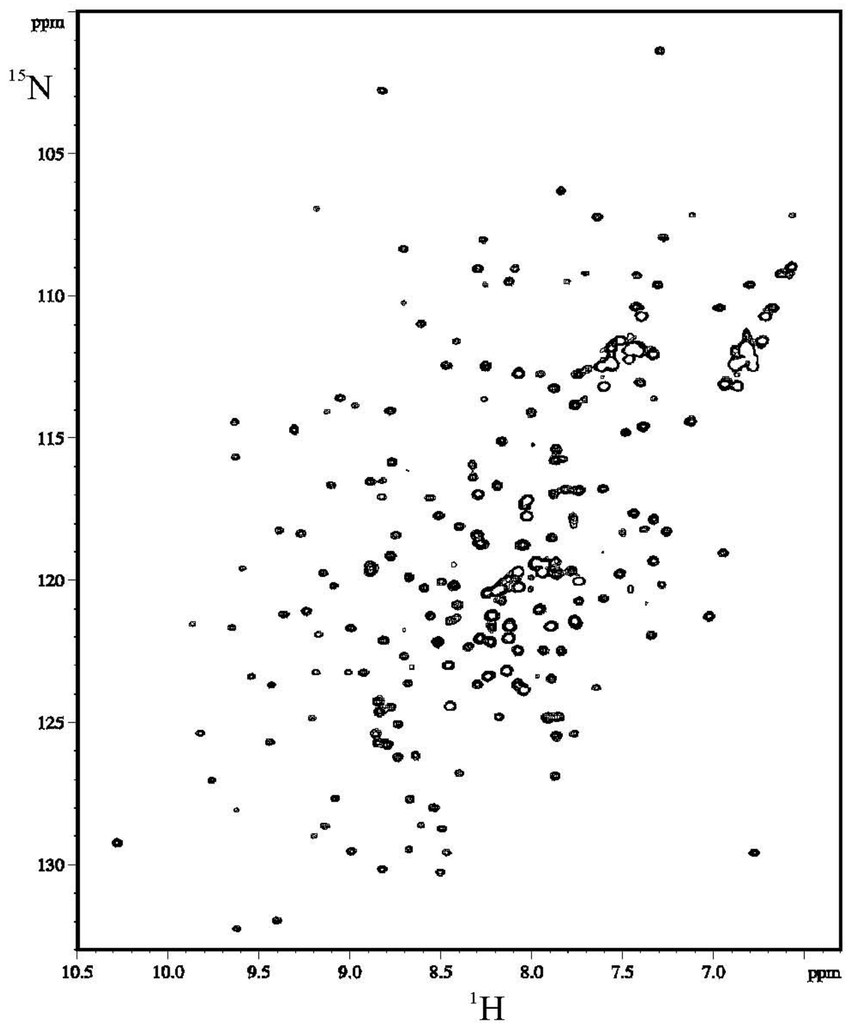
750 MHz spectrum of the protein lysozyme

2D NMR



$$s(t) = \eta \exp(-R_I t_2)\exp(-R_s t_1)\cos(2\pi\nu_S t_1)\cos(2\pi\nu_I t_2)$$

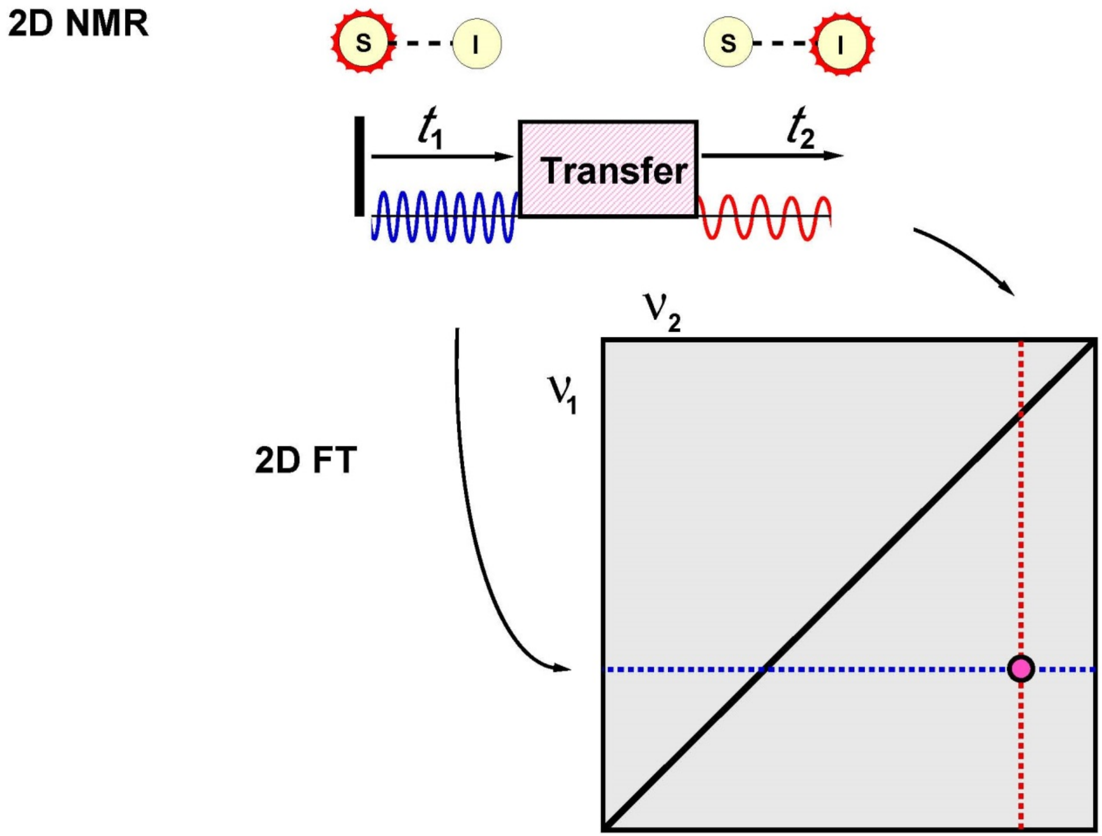
Example: ^{15}N-HSQC of p63



^{15}N labeling:

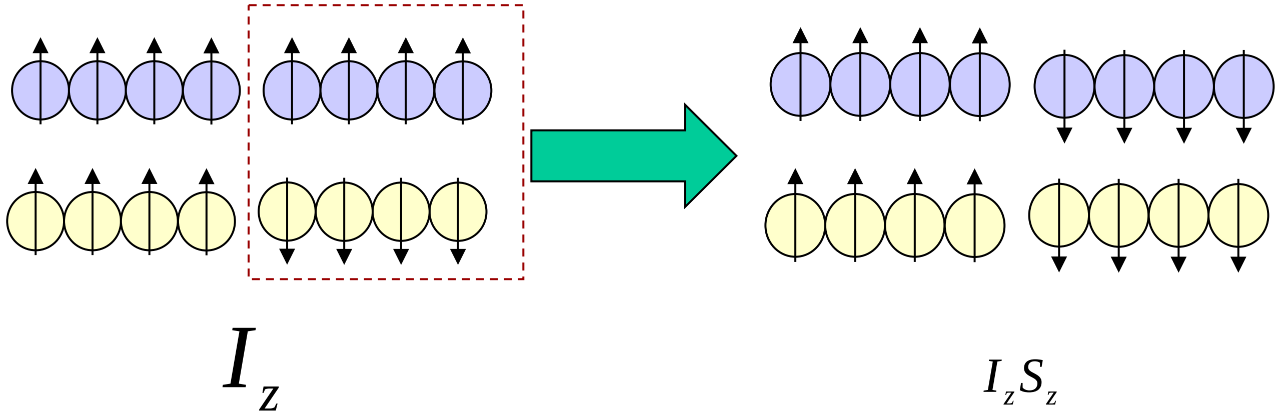
- all N atoms replaced by ^{15}N (ca. 95 % ^{15}N),
- characteristic fingerprint spectrum
- p63: 233 a.a. / 27 kDa
- measured at 750 MHz / 303 K

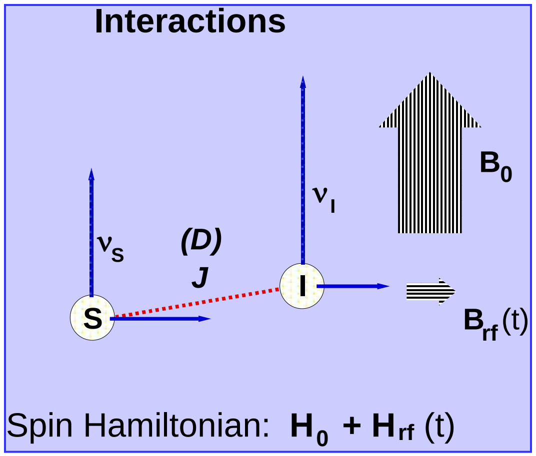
primary structure
(amino acid sequence)

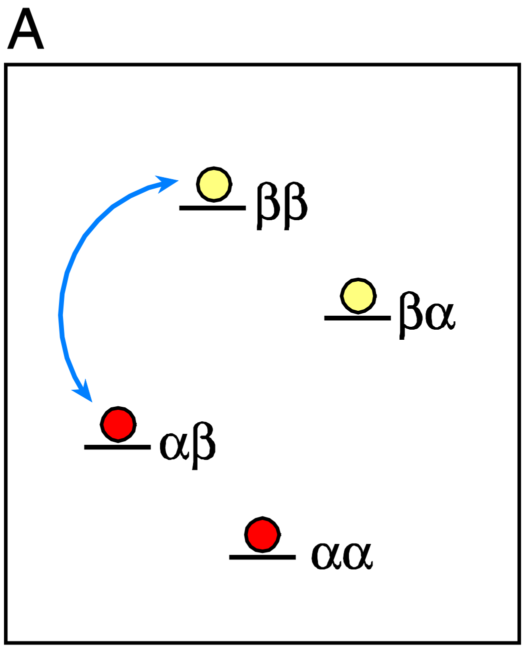


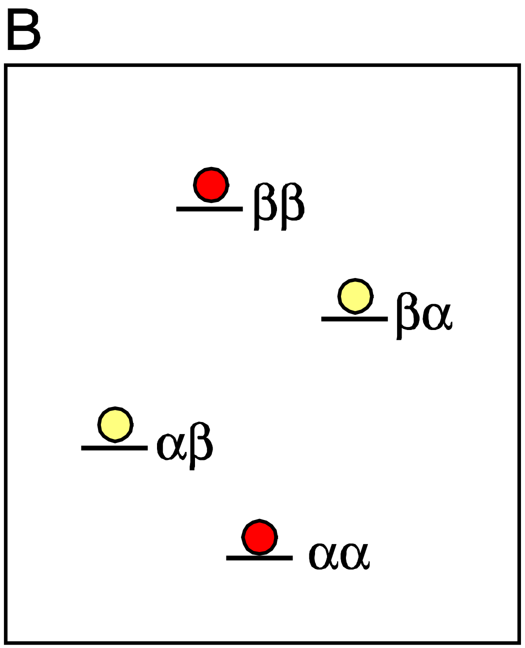
Relaxation Optimized Coherent Spectroscopy
Singular Optimal Control Problems

Transfer of Polarization



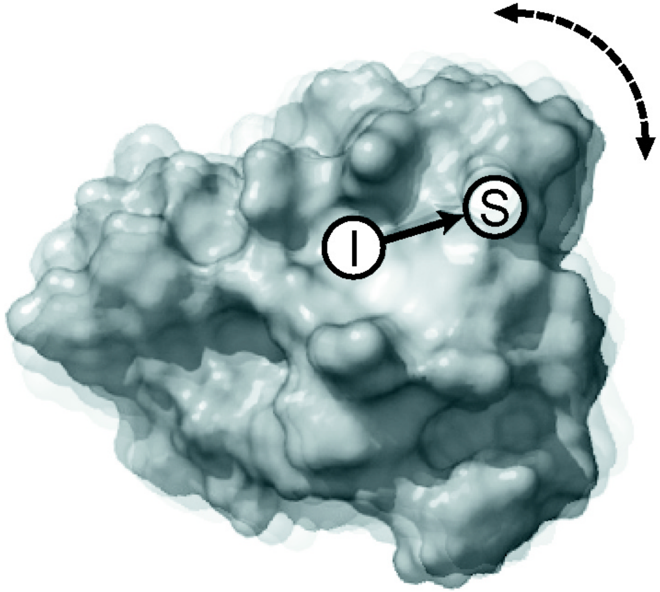


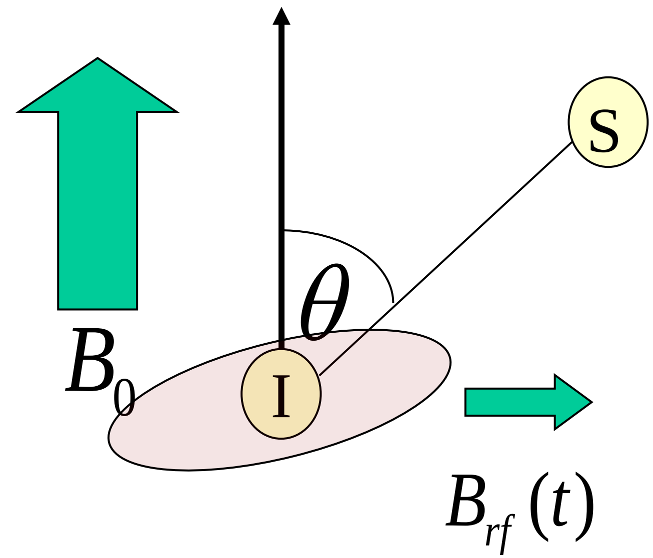




Random collisions with solvent molecules
causes stochastic tumbling of the protein molecules

$\tau_c \sim$ MW





$$C(\tau) \propto \exp(-\tau/\tau_c)$$

$$J(\omega) \approx \frac{\tau_c}{1+\omega^2\tau_c^2}$$

$$\omega\tau_c >> 1$$

$$\frac{1}{\pi T_2} = k \approx J(0)$$

$$T_1 \gg T_2$$

Spin Diffusion Limit

Optimal Control in Presence of Relaxation

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

$$\frac{d}{dt}\begin{bmatrix} \langle I_z \rangle \\ \langle I_x \rangle \\ \langle 2I_yS_z \rangle \\ \langle 2I_zS_z \rangle \end{bmatrix} = \begin{bmatrix} 0 & -u(t) & & \\ u(t) & -k & -J & \\ & J & -k & -v(t) \\ & & v(t) & 0 \end{bmatrix} \begin{bmatrix} \langle I_z \rangle \\ \langle I_x \rangle \\ \langle 2I_yS_z \rangle \\ \langle 2I_zS_z \rangle \end{bmatrix}$$

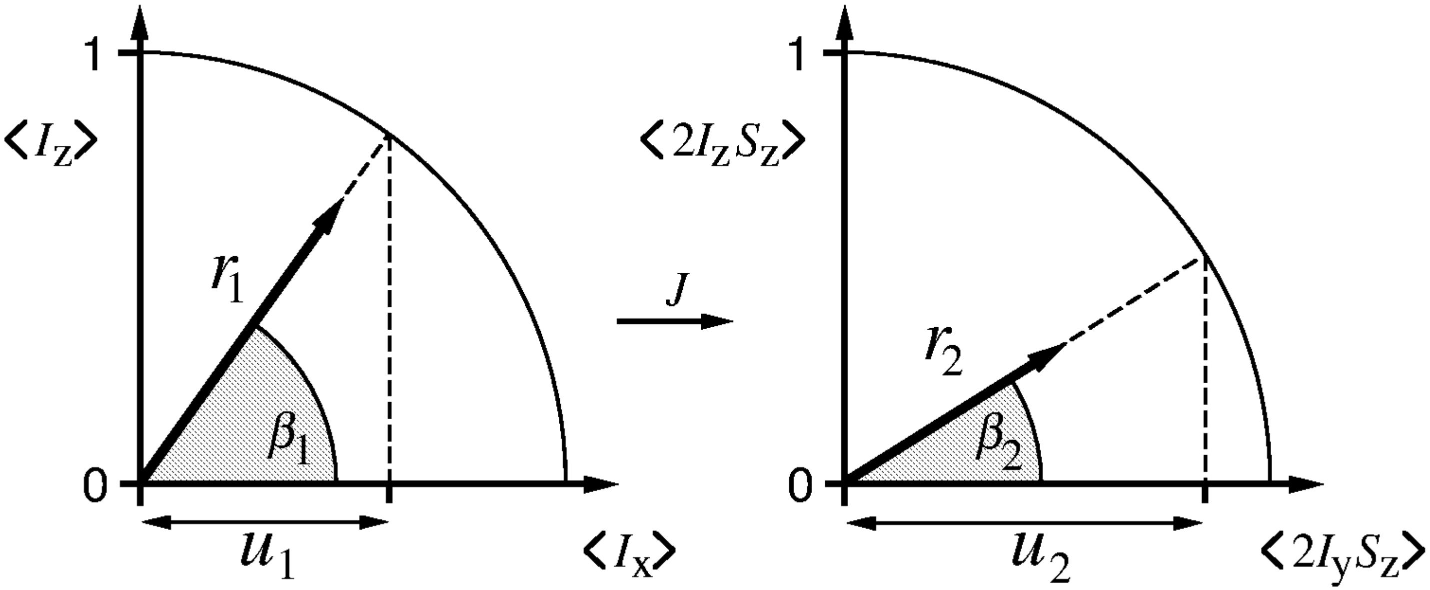
$$\xi = \frac{k}{J}$$

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

$$\eta = \sqrt{1+\xi^2} - \xi$$

$$\frac{x_3}{x_2} = \frac{\langle 2I_yS_z \rangle}{\langle I_x \rangle} = \eta$$

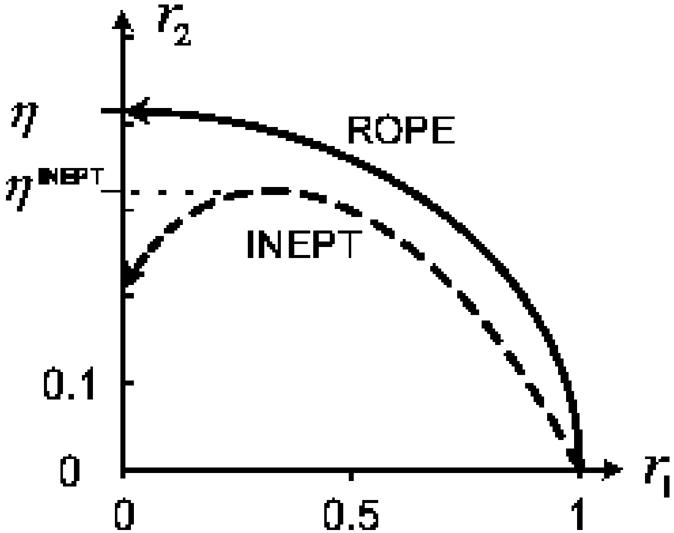
The control problem



$$\xi = \frac{k}{J}$$

$$\frac{d}{dt}\begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = \pi J \begin{bmatrix} -\xi u_1^2 & -u_1 u_2 \\ u_1 u_2 & -\xi u_2^2 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \end{bmatrix}$$

Relaxation Optimized Pulse Elements (ROPE)



$$\frac{d}{dt}\begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = \pi J \begin{bmatrix} -\xi u_1^2 & -u_1 u_2 \\ u_1 u_2 & -\xi u_2^2 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \end{bmatrix}$$

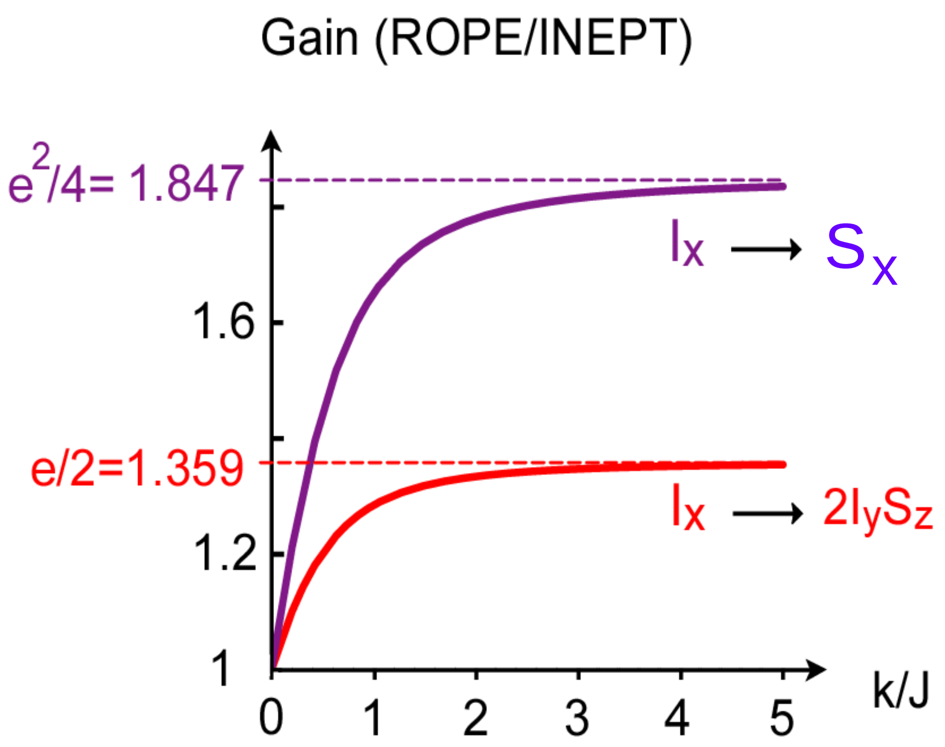
$$\max_{u_1,u_2} \begin{bmatrix} \frac{\partial V}{\partial r_1} & \frac{\partial V}{\partial r_2} \end{bmatrix} \begin{bmatrix} -\xi u_1^2 & -u_1 u_2 \\ u_1 u_2 & -\xi u_2^2 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = 0$$

$$V(r_1, r_2) = \sqrt{\eta^2 r_1^2 + r_2^2}$$

$$\eta = \sqrt{1+\xi^2} - \xi$$

$$\frac{u_2 r_2}{u_1 r_1} = \eta$$

Comparison

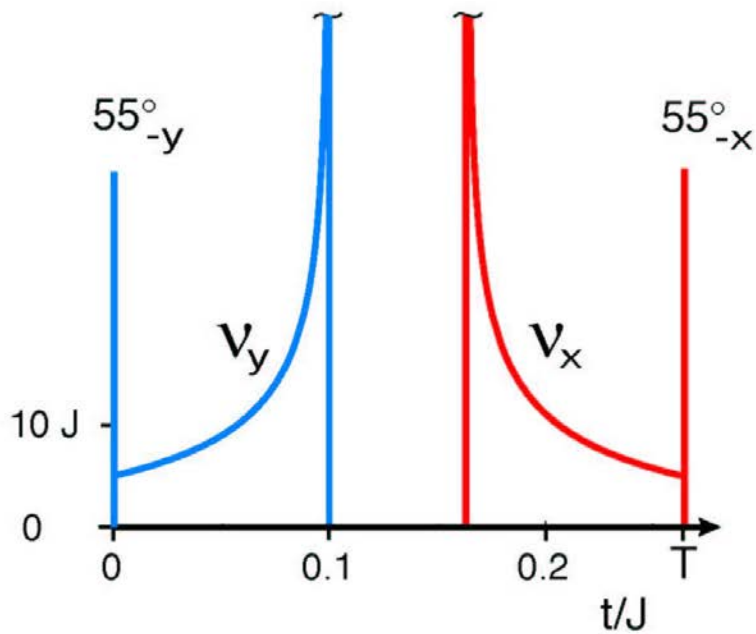


Gain (ROPE/INEPT)
e²/4= 1.847
1.6
e/2=1.359
1.2
1
0
1
2
3
4
5
k/J
Ix ⟶ Sx
Ix ⟶ 2IySz

Relaxation-
optimized
pulse
elements

Khaneja, Reiss, Luy, Glaser, J. Magn. Reson.162, 311 (2003)

ROPE Pulse Sequence

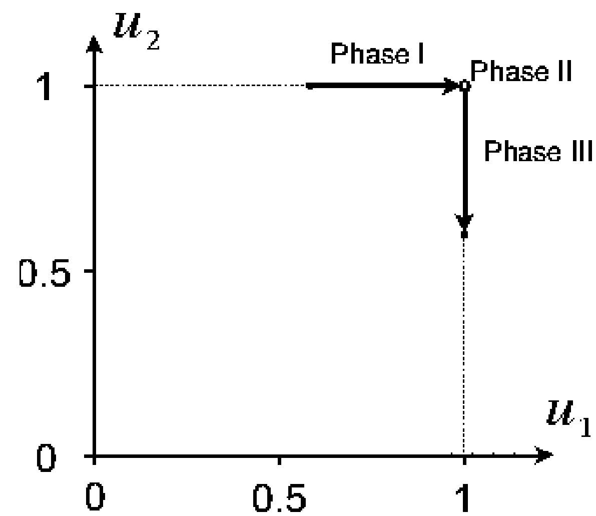


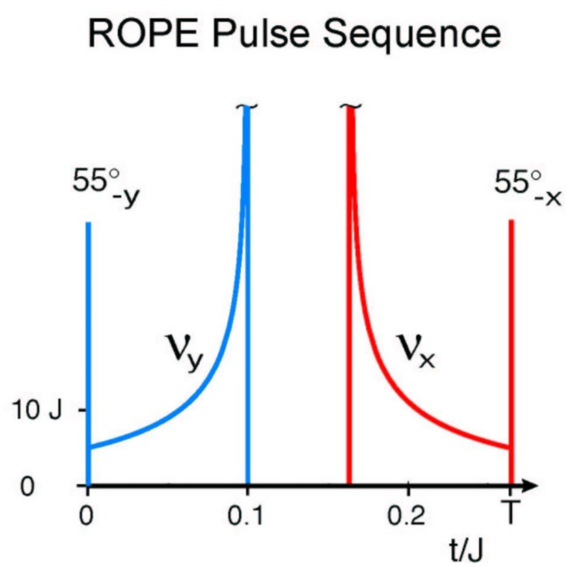
Khaneja, Reiss, Luy, Glaser JMR(2003)

$$\frac{d}{dt}\begin{bmatrix} \langle I_z \rangle \\ \langle I_x \rangle \\ \langle 2I_yS_z \rangle \\ \langle 2I_zS_z \rangle \end{bmatrix} = \begin{bmatrix} 0 & -u(t) & & \\ u(t) & -k & -J & \\ & J & -k & -v(t) \\ & & v(t) & 0 \end{bmatrix} \begin{bmatrix} \langle I_z \rangle \\ \langle I_x \rangle \\ \langle 2I_yS_z \rangle \\ \langle 2I_zS_z \rangle \end{bmatrix}$$

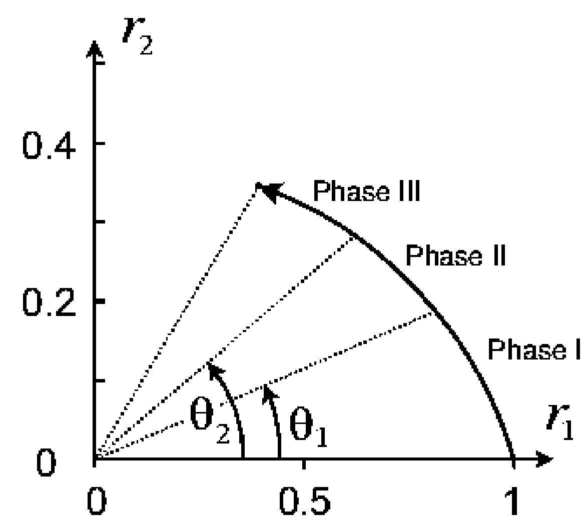
Finite Horizon Problem

$$\frac{d}{dt}\begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = \pi J \begin{bmatrix} -\xi u_1^2 & -u_1 u_2 \\ u_1 u_2 & -\xi u_2^2 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \end{bmatrix}$$





Khaneja, Reiss, Luy, Glaser JMR(2003)



Experimental Results

T = 250 K

J = 193 Hz

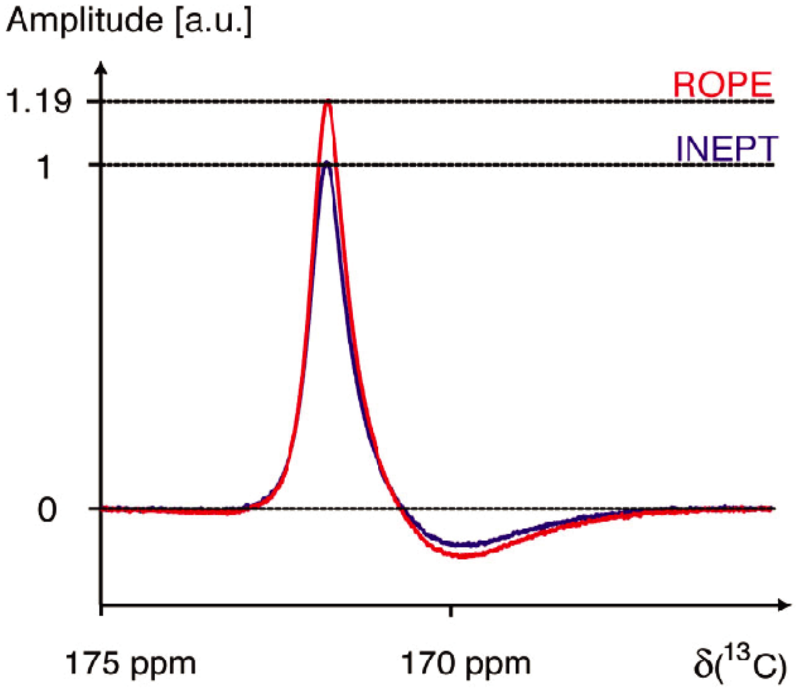
Proton frequency 500 Mhz

$T_2 = 1.4 ms$

k = 227 Hz

$\xi = 1.18$

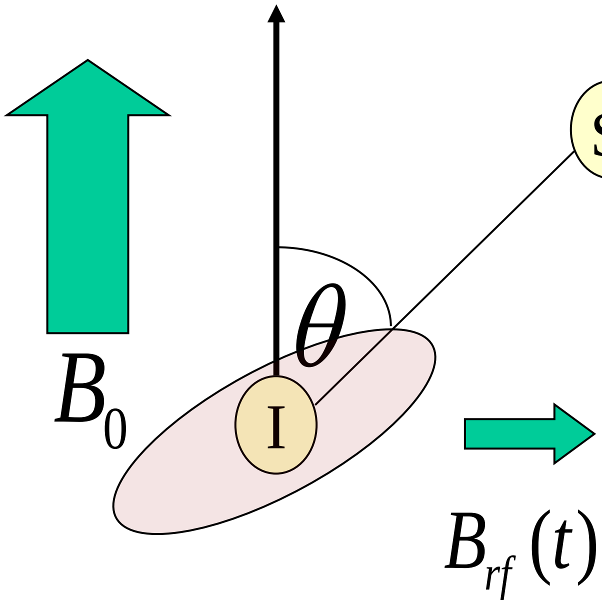
$$H_z \rightarrow H_z C_z$$

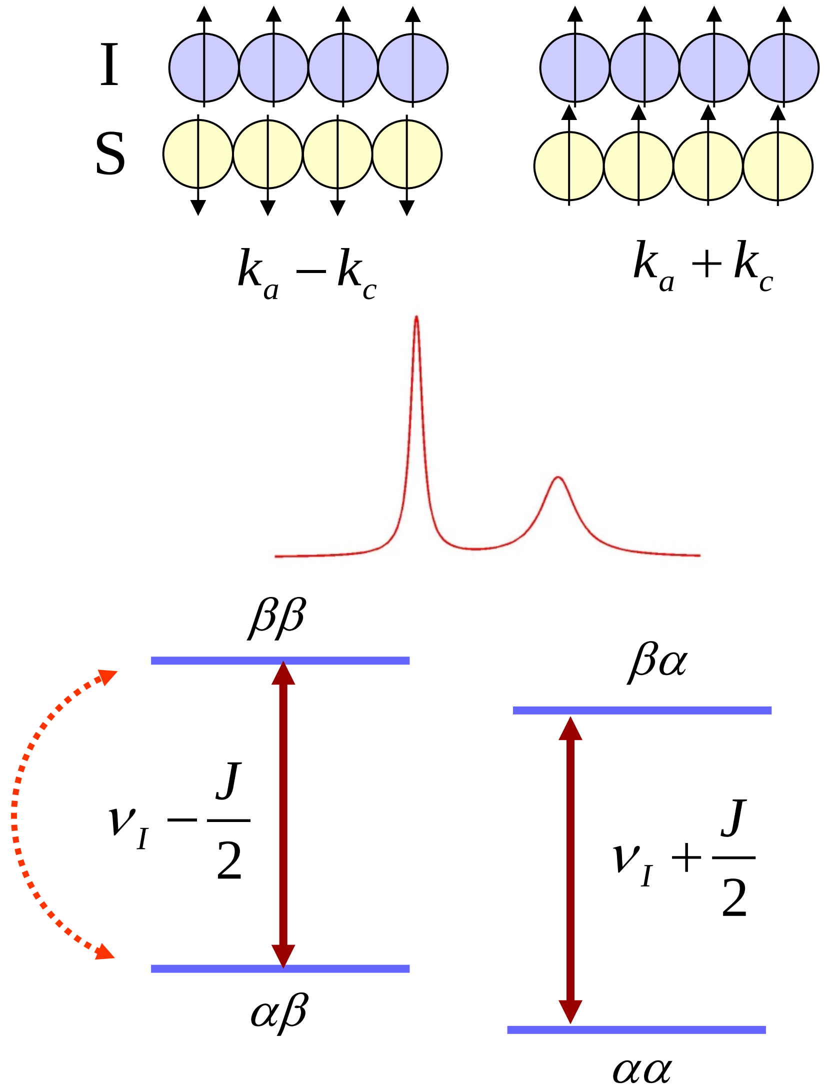


^{13}C-Formiate in 92% D_6-Glycerol and 8% D_2O (T=250 K)

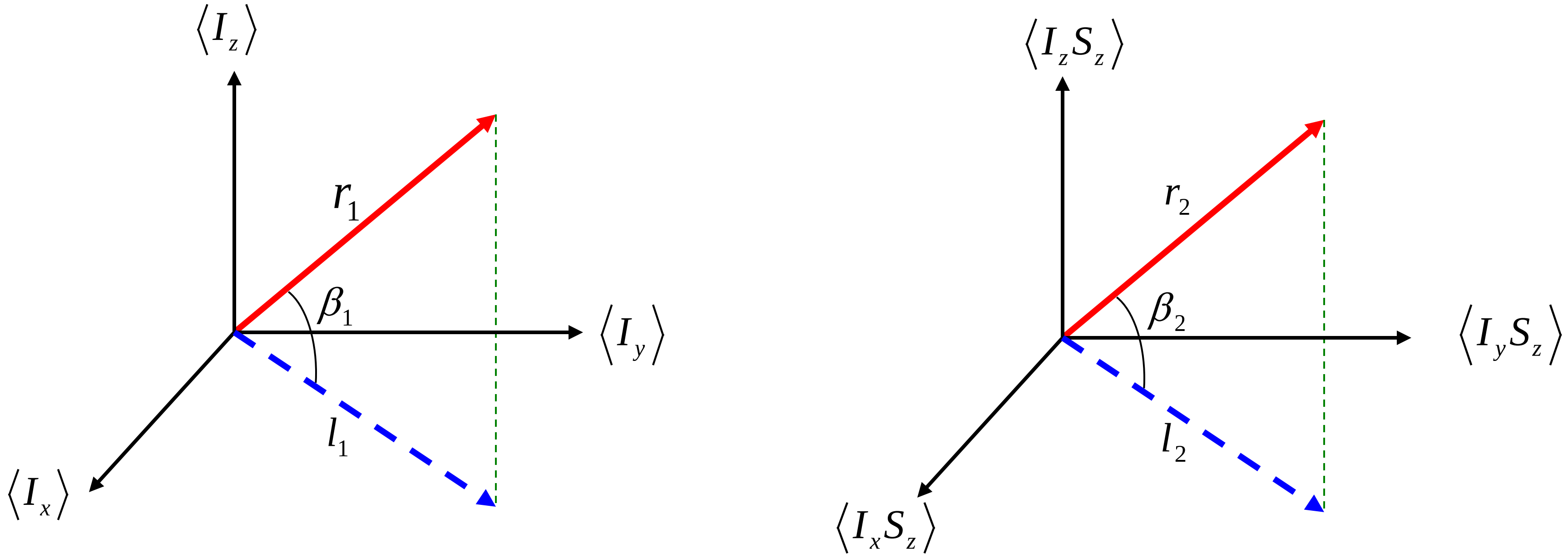
Khaneja, Reiss, Luy, Glaser JMR(2003)

Cross-Correlated Relaxation



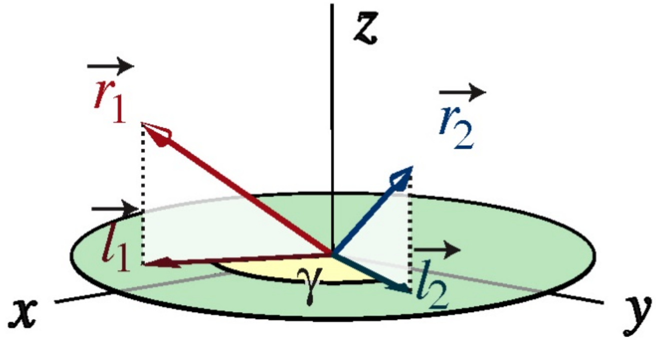


Optimal control of spin dynamics in the presence of Cross-correlated Relaxation



$$\frac{d}{dt}\begin{bmatrix} \langle I_z \rangle \\ \langle I_x \rangle \\ \langle I_y \rangle \\ \langle I_y S_z \rangle \\ \langle I_x S_z \rangle \\ \langle I_z S_z \rangle \end{bmatrix} = \begin{bmatrix} 0 & u & v & 0 & 0 & 0 \\ -u & -k_a & 0 & -J & -k_c & 0 \\ -v & 0 & -k_a & -k_c & J & 0 \\ 0 & J & -k_c & -k_a & 0 & -v \\ 0 & -k_c & -J & 0 & -k_a & -u \\ 0 & 0 & 0 & v & u & 0 \end{bmatrix} \begin{bmatrix} \langle I_z \rangle \\ \langle I_x \rangle \\ \langle I_y \rangle \\ \langle I_y S_z \rangle \\ \langle I_x S_z \rangle \\ \langle I_z S_z \rangle \end{bmatrix}$$

Optimal trajectory preserves ratio $\frac{l_2}{l_1} = \eta$ and angle γ

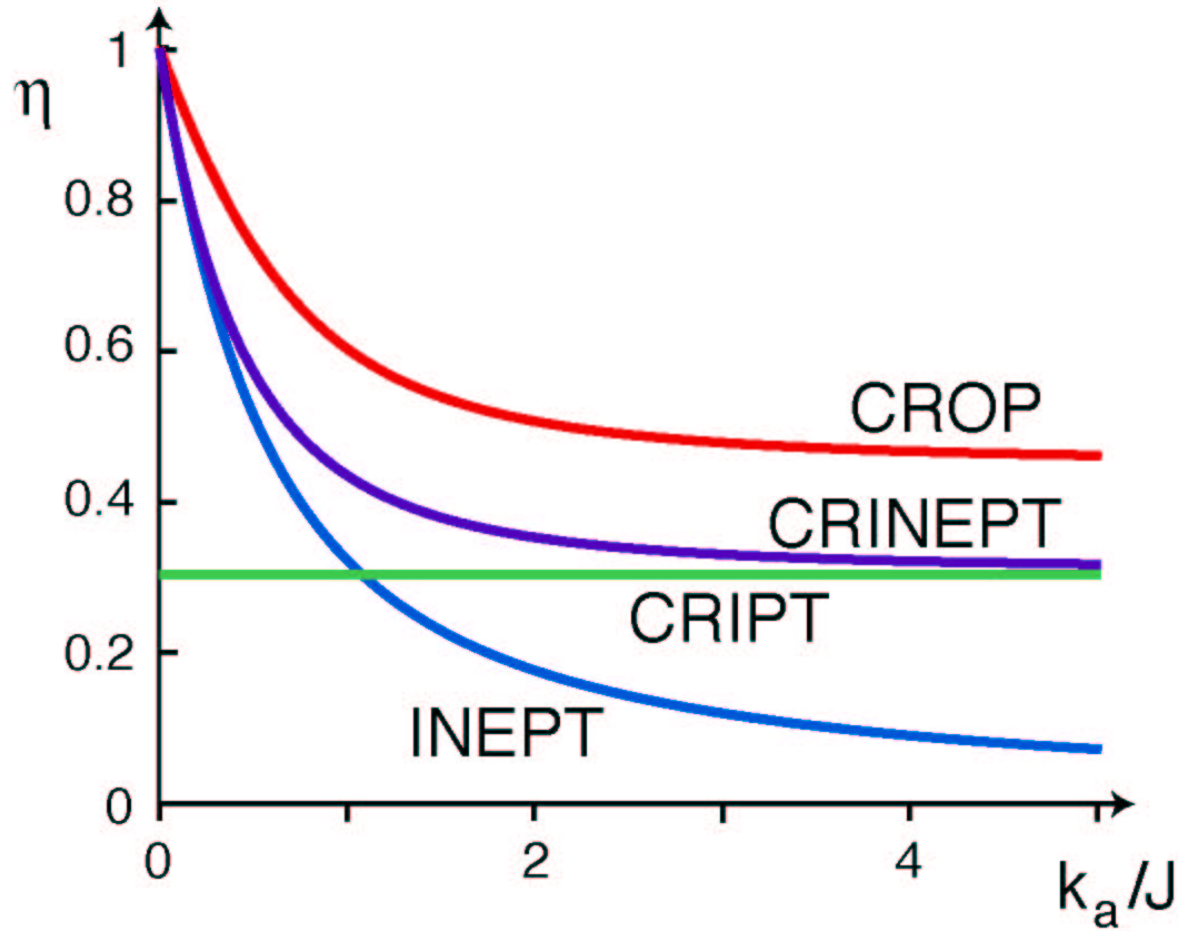


$$\frac{l_2}{l_1} = \eta = \sqrt{1+\xi^2} - \xi$$

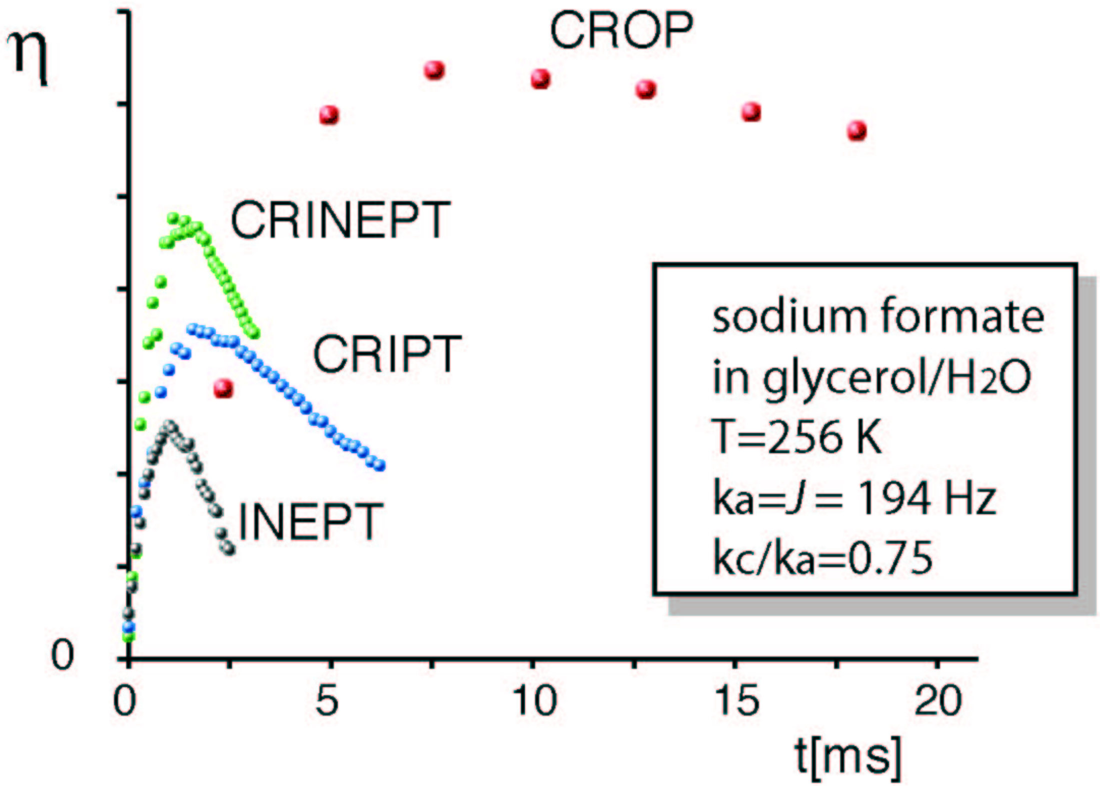
$$\xi = \sqrt{\frac{k_a^2 - k_c^2}{k_c^2 + J^2}}$$

Khaneja, Luy, Glaser PNAS(2003)

Transfer Efficiency

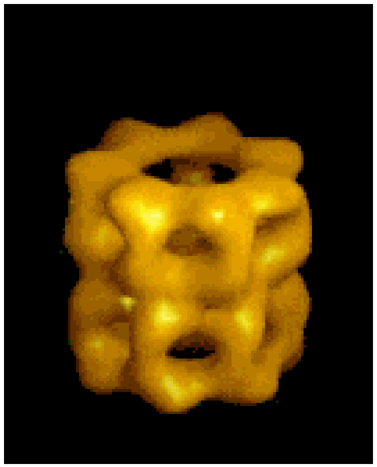


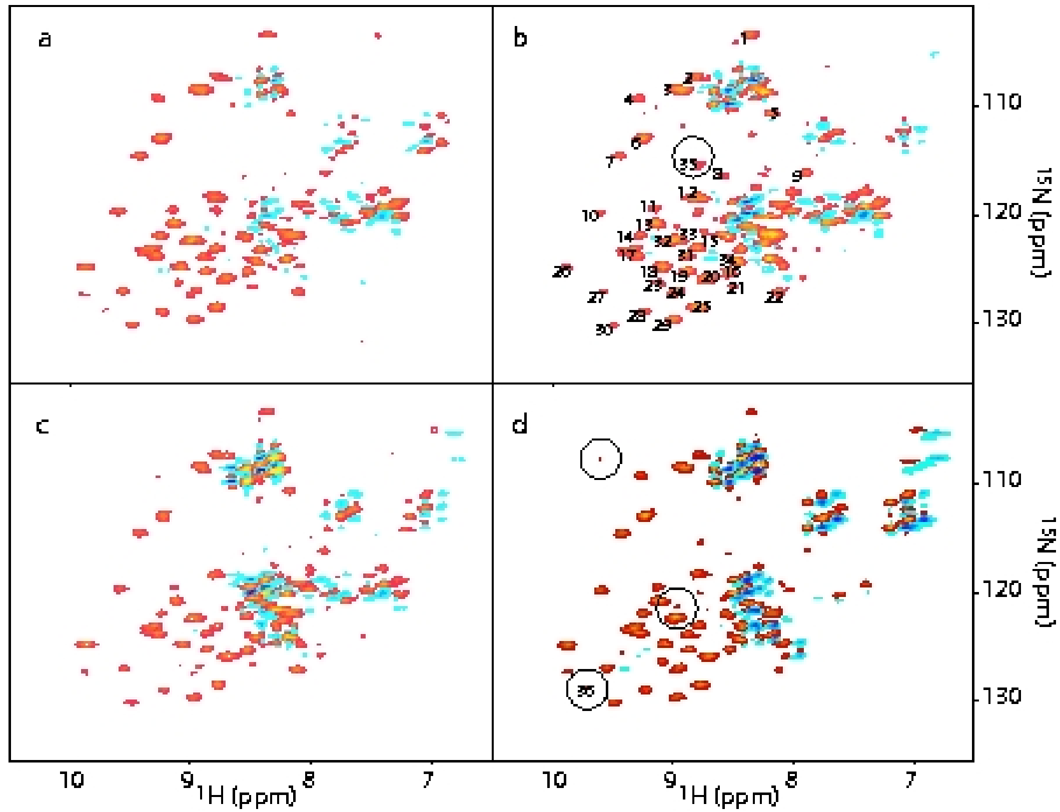
Experimental Transfer Functions



Khaneja, Luy, Glaser PNAS(2003)

TROPIC: Transverse relaxation optimized polarization transfer induced by cross-correlated relaxation.





Groel Protein: 800KDa

Room Temperature

J = 93 Hz

Proton Freq = 750Mhz

Ka = 446 Hz

Kc = 326 Hz

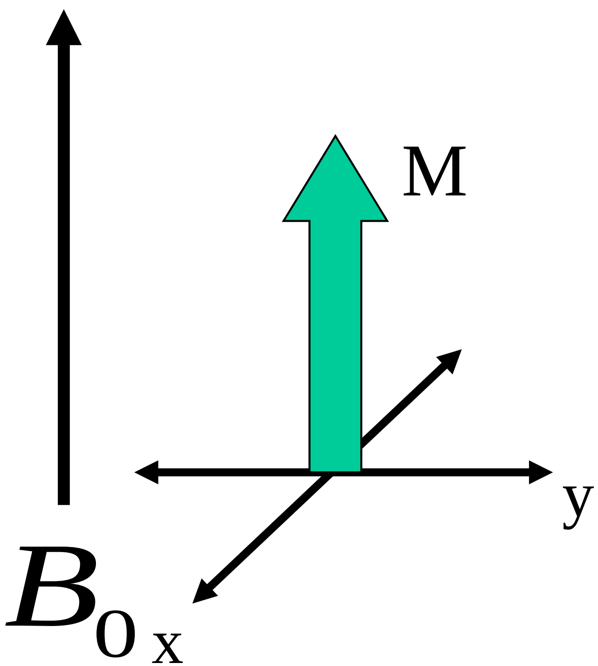
Frueh et. al ***Journal of Biomolecular NMR*** (2005)

Control of Bloch Equations

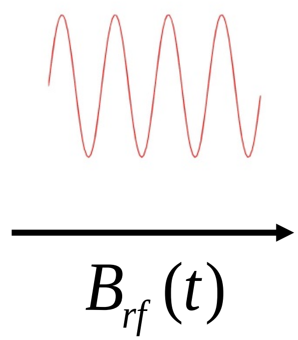
$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -\omega_0 & -u(t) \\ \omega_0 & 0 & -v(t) \\ u(t) & v(t) & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

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

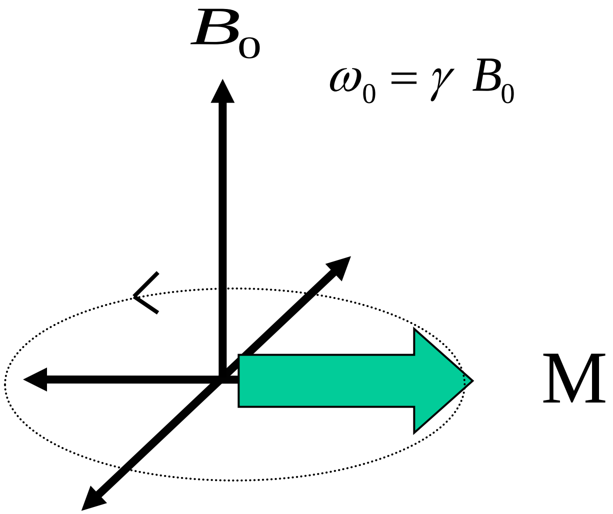
$$A \ll \omega_0$$



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



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

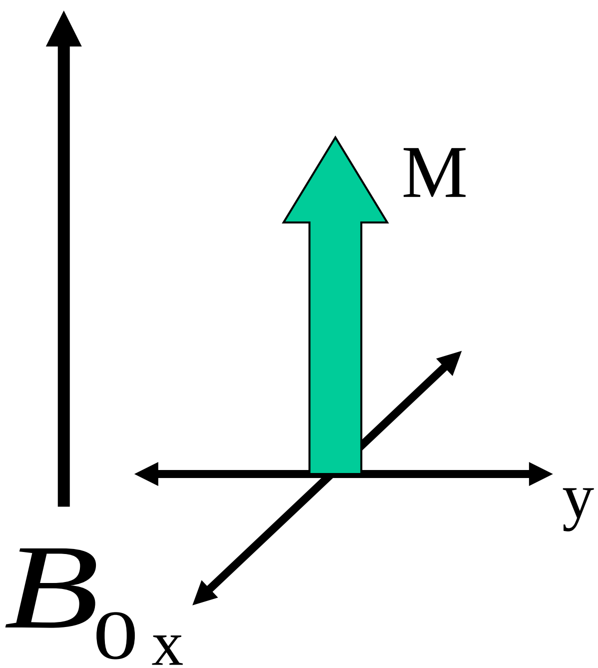


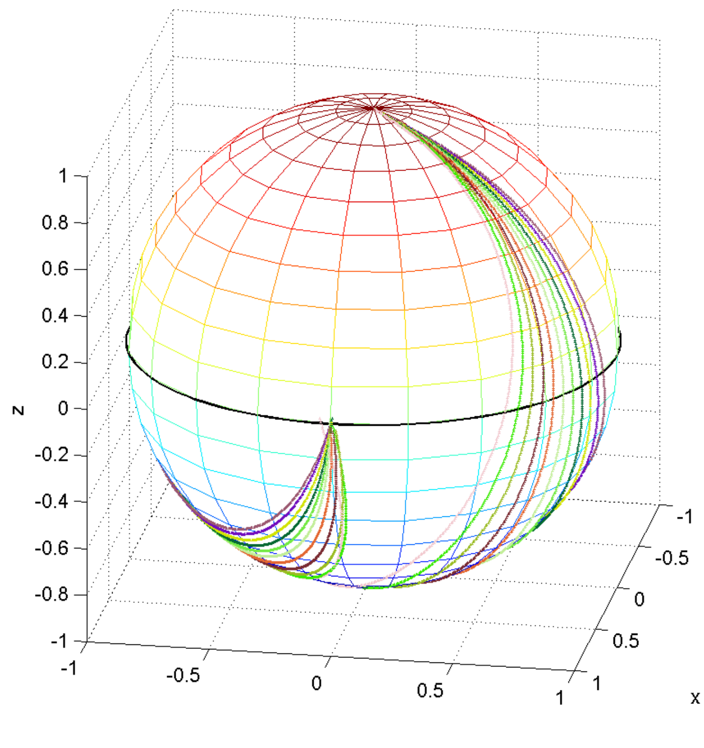
Broadband Excitation

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

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

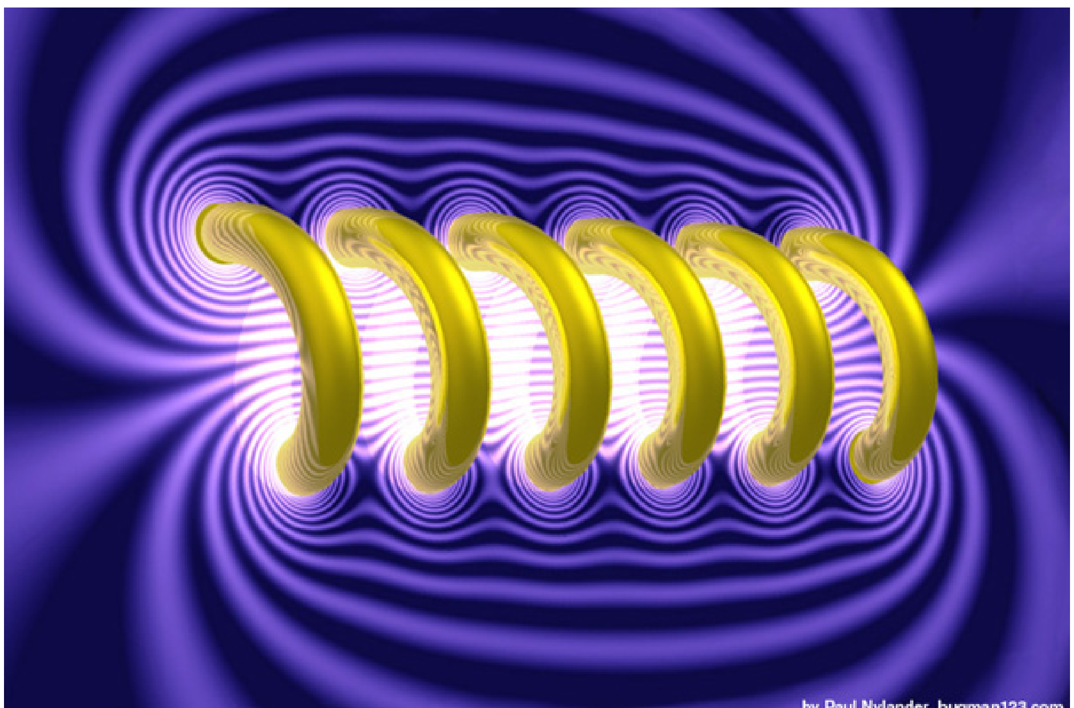
$$\varepsilon \in [1-\delta, 1+\delta]$$

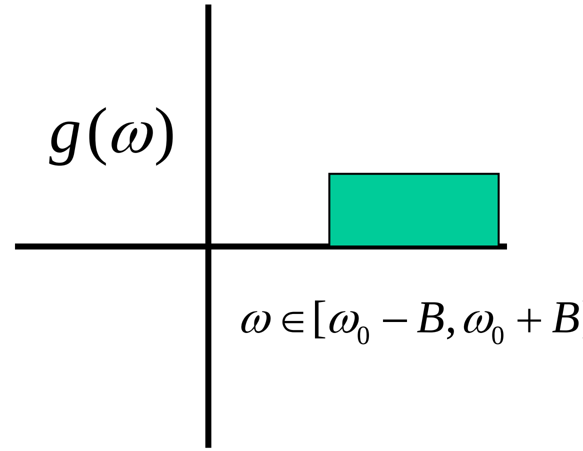


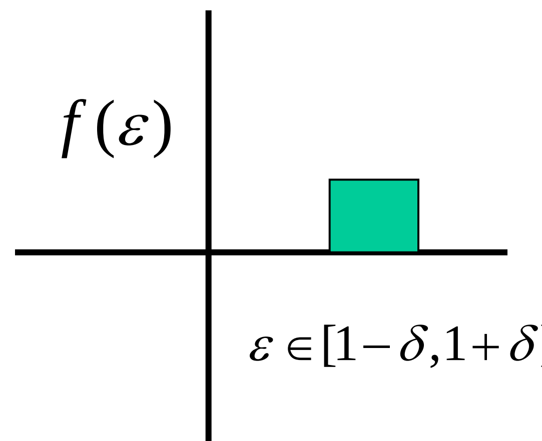


Inhomogeneous Ensemble of Bloch Equations

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

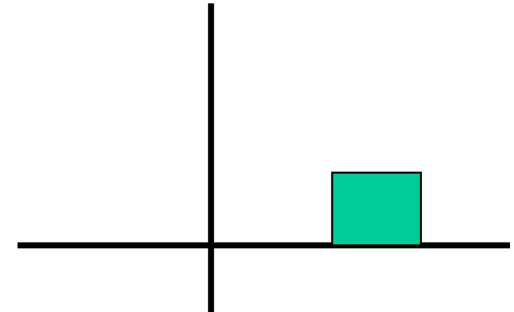






Robust Control Design

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

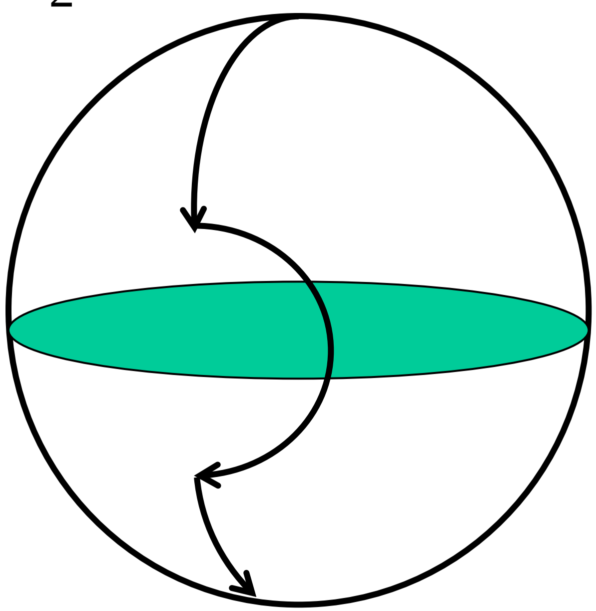


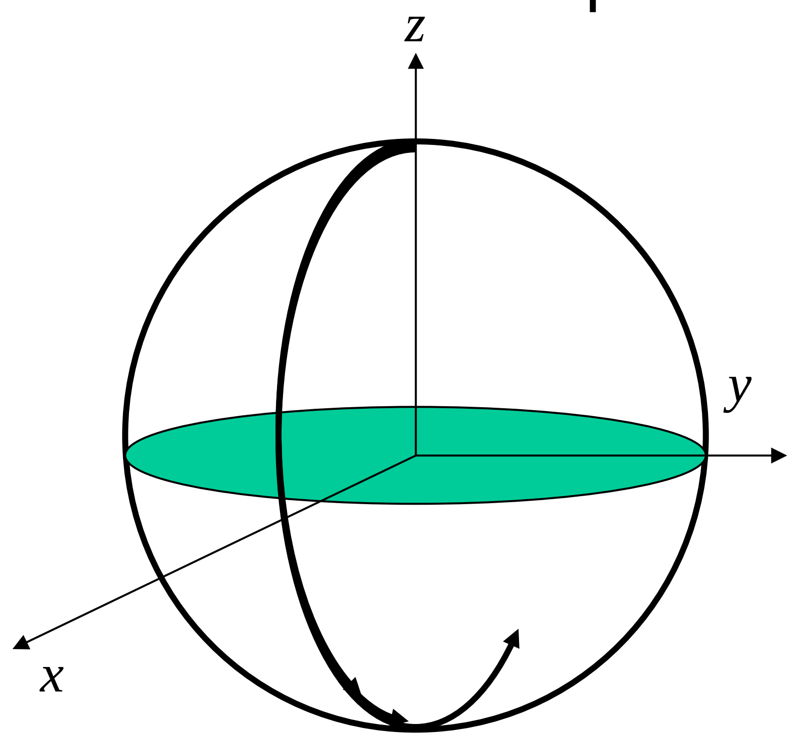
$\varepsilon \in [1-\delta, 1+\delta]$

$(\pi)_y$

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

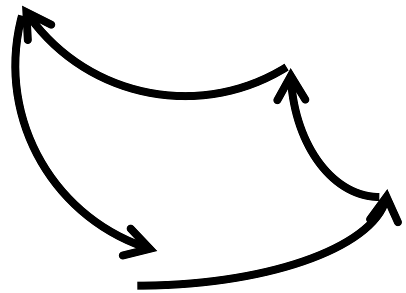
$(\frac{\pi}{2})_y - (\pi)_x - (\frac{\pi}{2})_y$





Robust Control Design by Area Generation

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



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

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

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

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

Lie Algebras, Areas and Robust Control Design

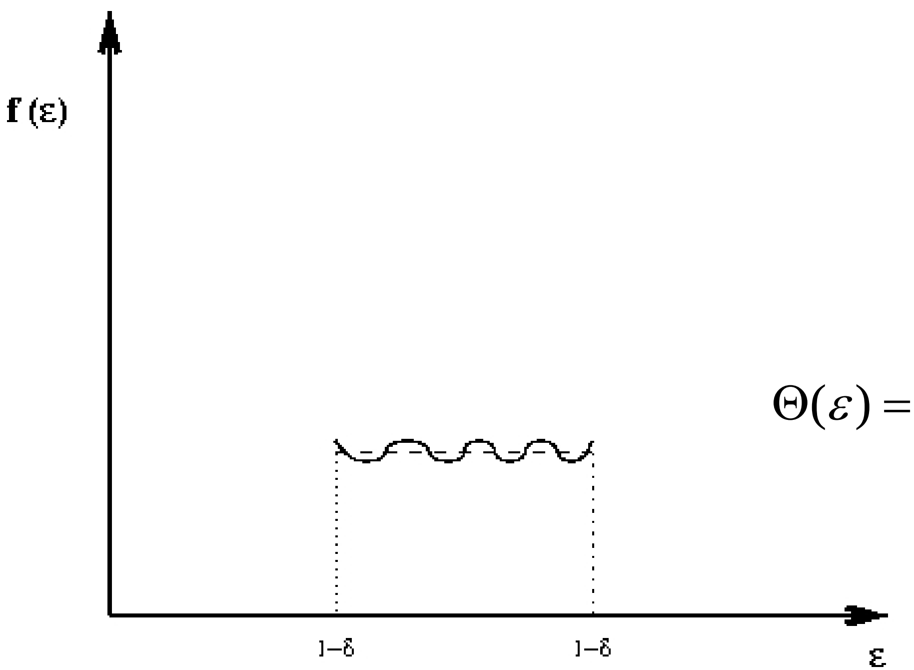
Using $\varepsilon\Omega_y, \varepsilon^3\Omega_y, \cdots, \varepsilon^{2k+1}\Omega_y$ as generators

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

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

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

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

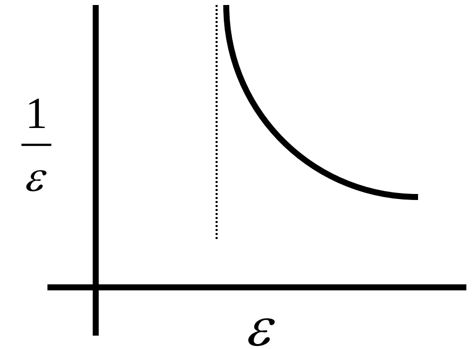


$$\Theta(\varepsilon) = \exp(f_1(\varepsilon)\Omega_x)\exp(f_2(\varepsilon)\Omega_y)\exp(f_3(\varepsilon)\Omega_x)$$

Fourier Synthesis Methods for Robust Control Design

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

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

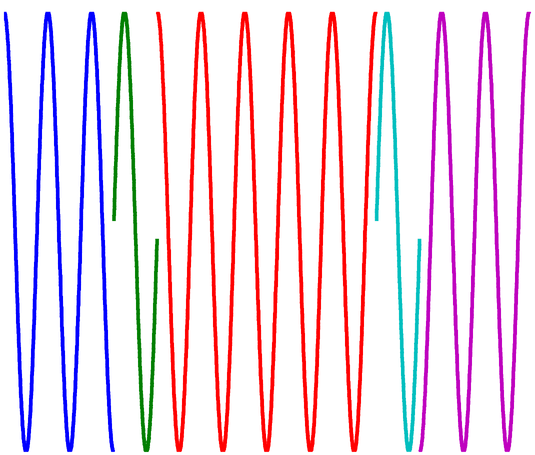


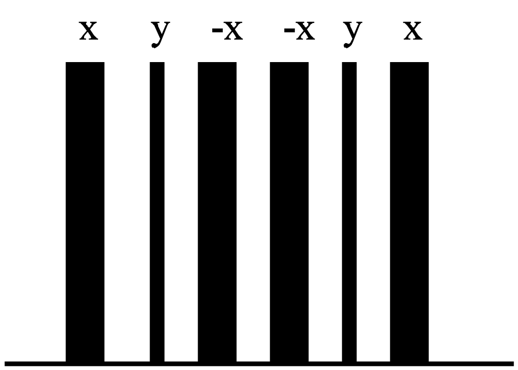
$$U_2 = \exp(-k\pi\varepsilon\Omega_x)\exp(\varepsilon\frac{\beta_k}{2}\Omega_y)\exp(k\pi\varepsilon\Omega_x)$$

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

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

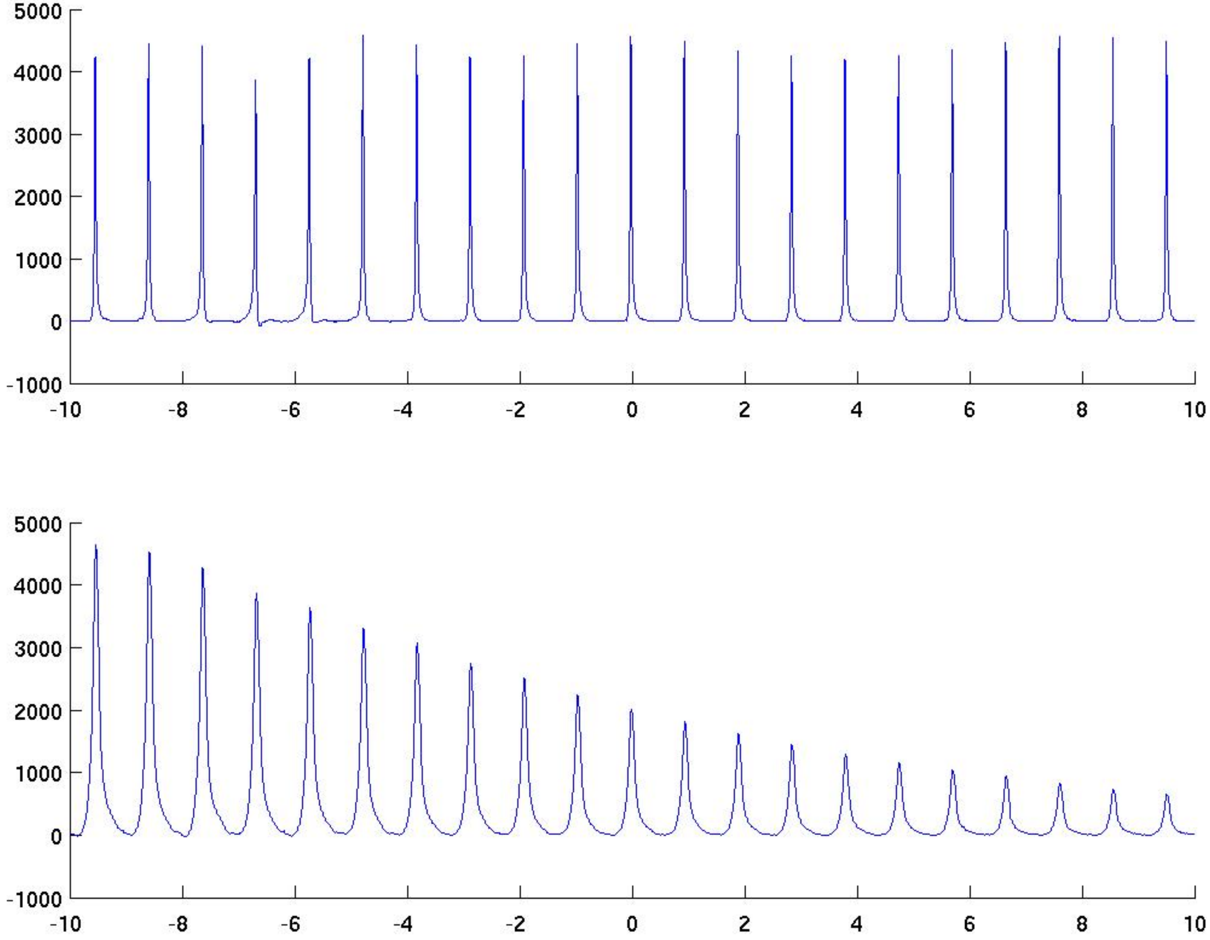
$$\sum_k \beta_k\cos(k\pi\varepsilon) = \frac{\theta}{\varepsilon}$$



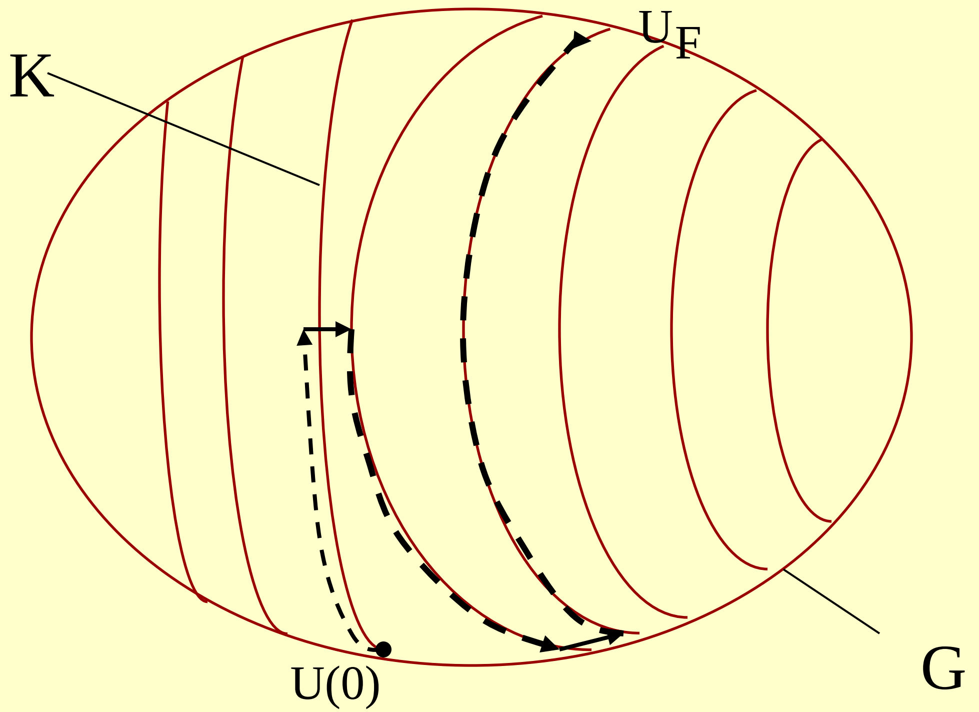


B. Pryor, N. Khaneja Journal of Chemical Physics (2006).

Fourier Synthesis Methods for Compensation



Time Optimal Control of Quantum Systems



$$\frac{dU(t)}{dt} = -i[H_d + \sum_{j=1}^{m} u_j H_j]U(t); \quad U(0) = I$$

$$k = \{-iH_j\}_{LA}$$

$$K = \exp(k)$$

Minimum time to go from U(0) to U_F is the same as minimum time to go from KU(0) to KU_F

Khaneja, Brockett, Glaser, Physical Review A , 63, 032308, 2001

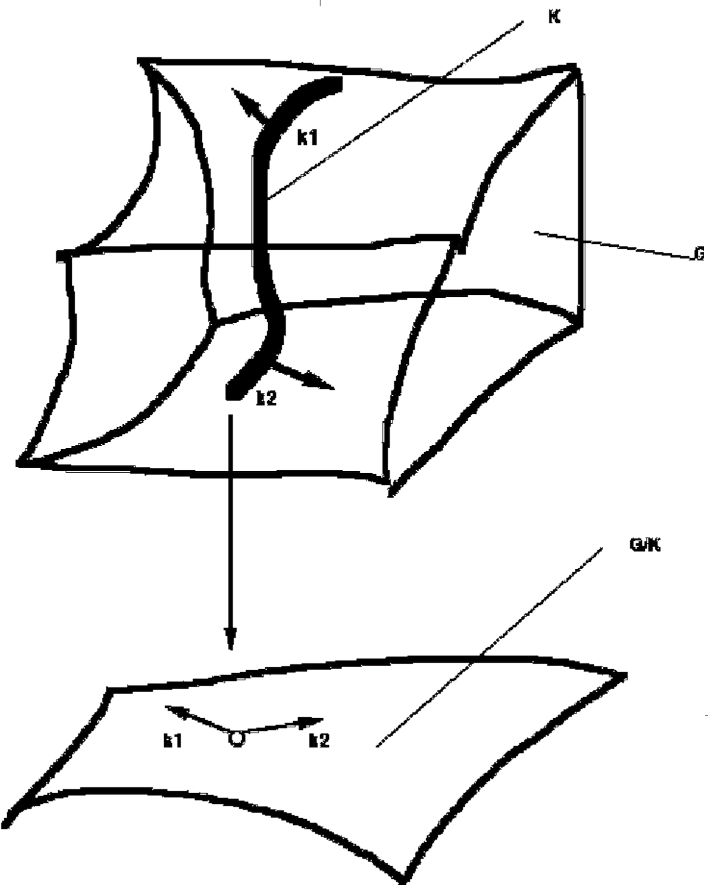
Example

$$\dot{U} = -\mathrm{i}\left(\begin{bmatrix}\lambda_1 & & \\ & \ddots & \\ & & \lambda_n\end{bmatrix} + \sum_i u_i B_i\right)\mathrm{U}$$

$$B_i \in so(n), U \in \mathrm{SU(n)}$$

Control Systems on Coset Spaces

$$\frac{dU(t)}{dt} = -i[H_d + \sum_{j=1}^{m} u_j H_j]U(t); \quad U(0) = I$$



$$K_{n+1}\exp(-iHt_n)K_n \ldots \exp(-iHt_2)K_2\exp(-iHt_1)K_1$$

$$K_{n+1}\exp(-i\,K^{\dagger}{}_n HK_n\, t_n)\ldots\exp(-i\,K^{\dagger}{}_2 HK_2\, t_2)\exp(-i\,K^{\dagger}{}_1 HK_1\, t_1)$$

G/K is a Riemannian Symmetric Space

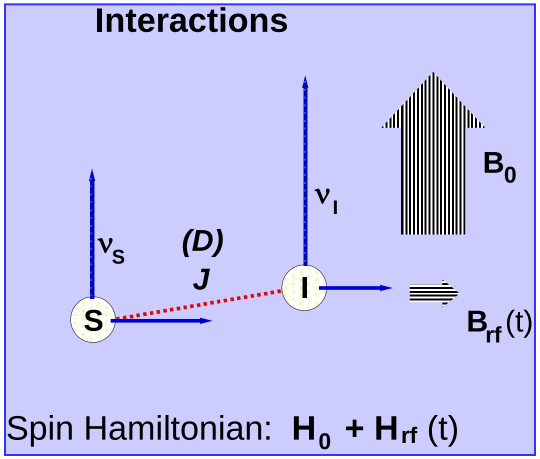
$$g = p + k; \;\; p \perp k$$

$$[p,p] \subseteq k; [k,k] \subseteq k; [p,k] \subseteq p;$$

The velocities of the shortest paths in G/K always commute!

Physical Review A, **63**, 032308 (2001)

Cartan Decompositions , Two-Spin Systems and Canonical Decomposition of SU(4)



$$\frac{dU}{dt} = -i[\sum_{\alpha,\beta} J_{\alpha\beta} I_\alpha S_\beta + u_1 I_x + u_2 I_y + u_3 S_x + u_4 S_y] U$$

$$k = \{-i\ I_\alpha, -iS_\beta\}\ ;\quad p = \{-iI_\alpha S_\beta\}$$

$$G = SU(4);\quad K = SU(2) \otimes SU(2)$$

$$I_\alpha = \sigma_\alpha \otimes I\ ;$$
$$S_\alpha = I \otimes \sigma_\alpha\ ;$$
$$I_\alpha S_\beta = \sigma_\alpha \otimes \sigma_\beta\ ;$$

$$a = \{-iI_x S_x, -iI_y S_y, -iI_z S_z\}$$

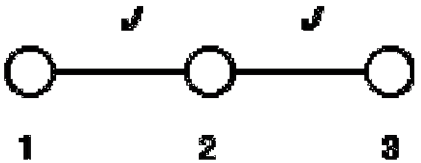
$$G = K\ \exp(-i(\alpha_x I_x S_x + \alpha_y I_y S_y + \alpha_z I_z S_z\ ))\ K$$

$$\sigma_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix};\ \sigma_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix};\ \sigma_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Physical Review A , **63**, 032308 (2001)

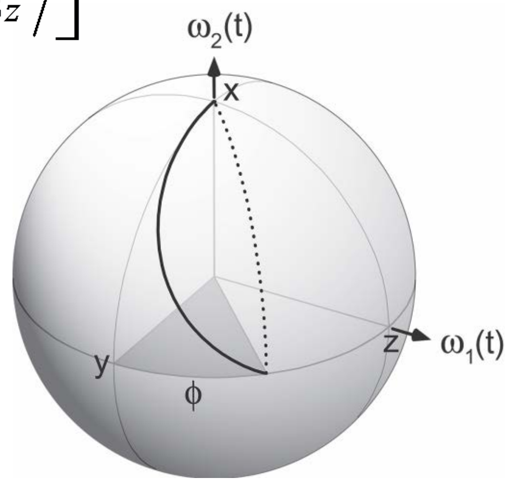
Geometry, Control and NMR

$$\frac{d}{dt}\begin{bmatrix} \langle I_{1x} \rangle \\ \langle 2I_{1y}I_{2z} \rangle \\ \langle 2I_{1y}I_{2x} \rangle \\ \langle 4I_{1y}I_{2y}I_{3z} \rangle \end{bmatrix} = \begin{bmatrix} 0 & -1 & & \\ 1 & 0 & -u & \\ & u & 0 & -1 \\ & & 1 & 0 \end{bmatrix}\begin{bmatrix} \langle I_{1x} \rangle \\ \langle 2I_{1y}I_{2z} \rangle \\ \langle 2I_{1y}I_{2x} \rangle \\ \langle 4I_{1y}I_{2y}I_{3z} \rangle \end{bmatrix}$$



$$\tan\theta = \frac{x_3}{x_2}$$

$$\frac{d}{dt}\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0 & -\cos\theta & 0 \\ \cos\theta & 0 & -\sin\theta \\ 0 & \sin\theta & 0 \end{bmatrix}\begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

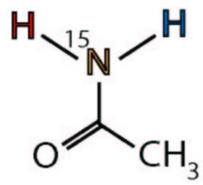


$$\theta = \omega t$$

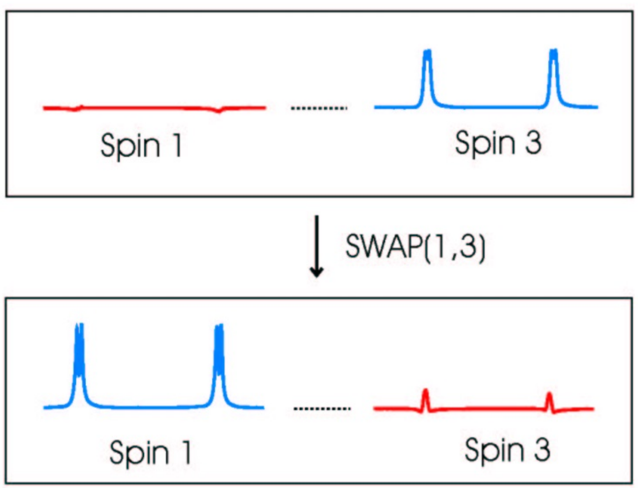
$$\exp(-i2\pi\kappa I_{1z}I_{2z}I_{3z}), \quad \frac{\sqrt{\kappa(4-\kappa)}}{2J}$$

$$\frac{(dx)^2 + (dz)^2}{y^2}$$

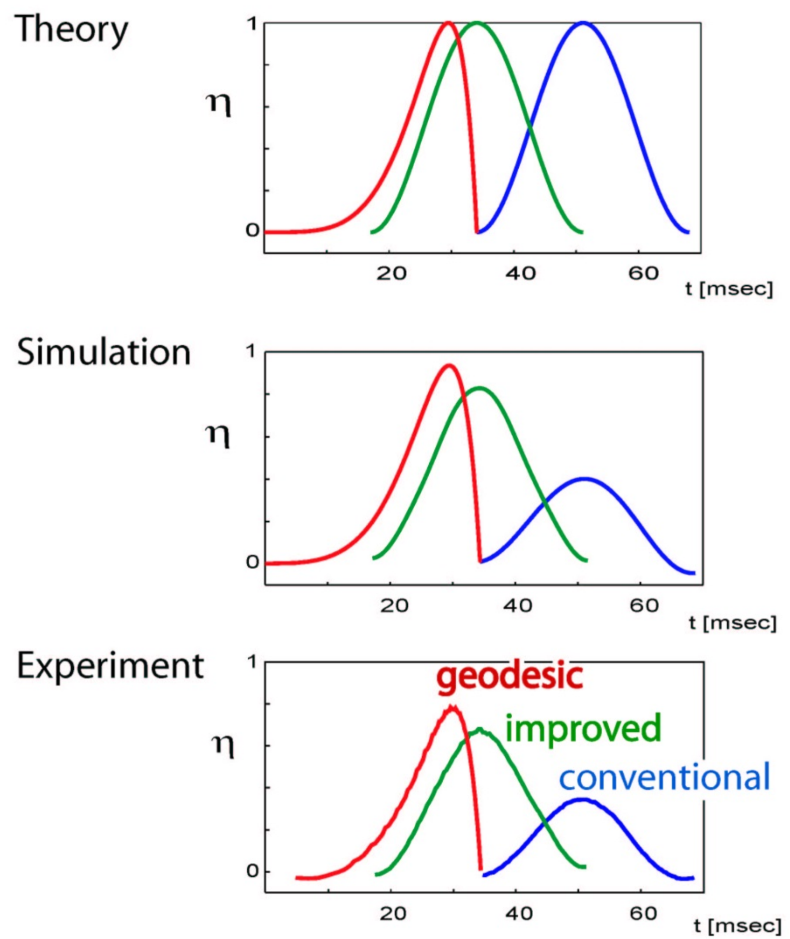
Indirect SWAP Operation



[^{15}N]-Acetamide

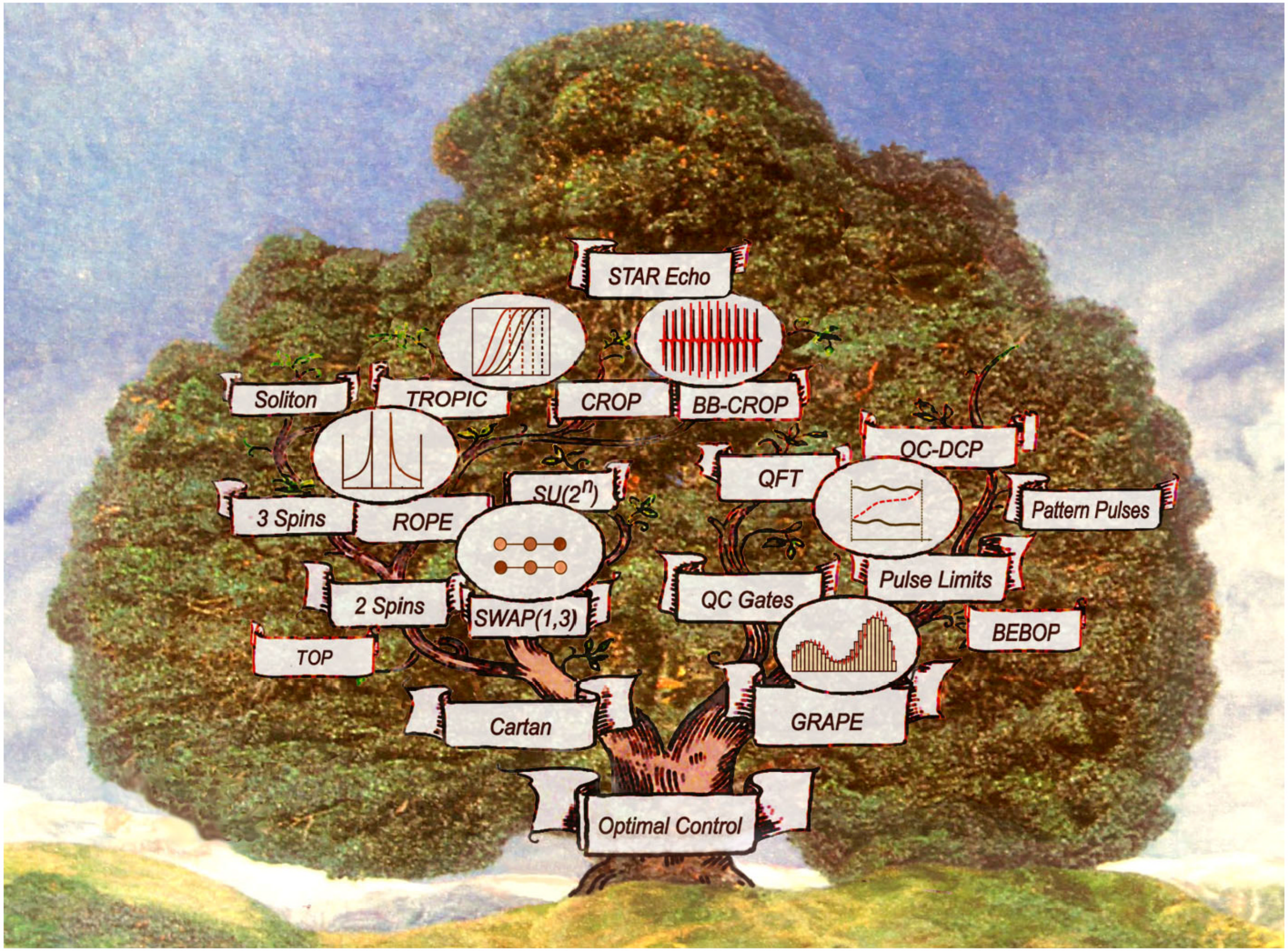


Efficiency η of indirect SWAP sequences



Reiss, Khaneja, Glaser
J. Mag. Reson. 165 (2003)

Khaneja, et. al PRA(2007)



STAR Echo
Soliton
TROPIC
CROP
BB-CROP
QC-DCP
QFT
SU(2^n)
Pattern Pulses
3 Spins
ROPE
Pulse Limits
QC Gates
2 Spins
SWAP(1,3)
BEBOP
TOP
Cartan
GRAPE
Optimal Control

Collaborators

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

- James Lin
- Jamin Sheriff
- Philip Owrutsky
- Mai Van Do
- Paul Coote
- Haidong Yuan
- Jr Shin Li
- Brent pryor

- Arthanari Haribabu