Measuring NMR Relaxation Time Using an Exact Solution of the Bloch Equations

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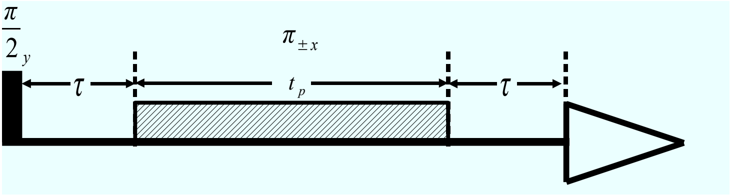
Outline

Hahn Echo

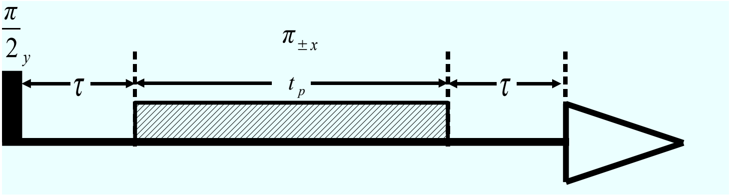


- Sample $\mathbf{S}(\omega, R_1, R_2)$
- Pulse Sequences (Operators) $\mathbf{f}$
- Collecting data $\mathbf{d}$

$$\mathbf{f}(\mathbf{S}) = \mathbf{d}$$

Objective: *Using a series of delay times τ, a series of data $\mathbf{d}$ are collected, then we analyze the data $\mathbf{d}$ to get the transverse relaxation rate $\mathbf{R}_2$ which is one of properties of sample $\mathbf{S}$.*

Hahn Echo



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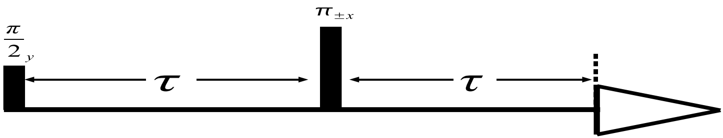

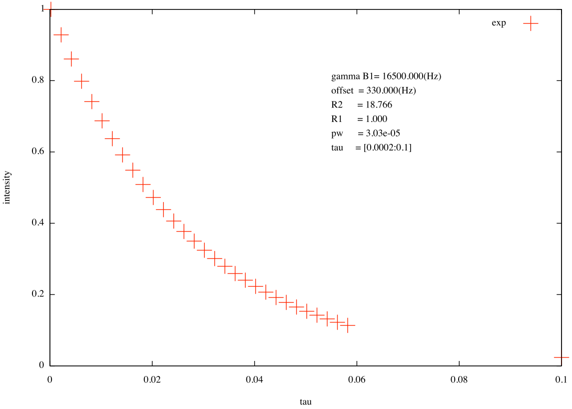

$$\gamma B_1 \times t_p \times 2\pi = \pi$$

- high power
- short duration

- $\gamma B_1 = 16500Hz$
- $\omega = 330Hz$
- $R_1 = 1s^{-1}$
- $R_2 = 18.8s^{-1}$

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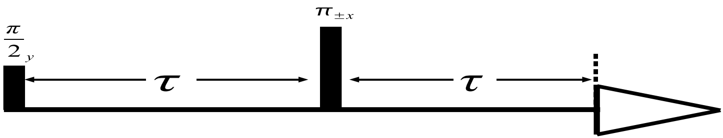

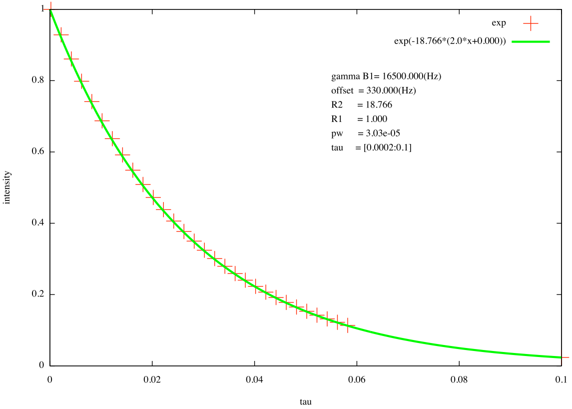

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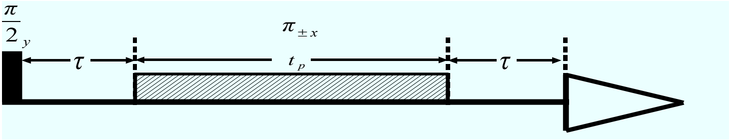
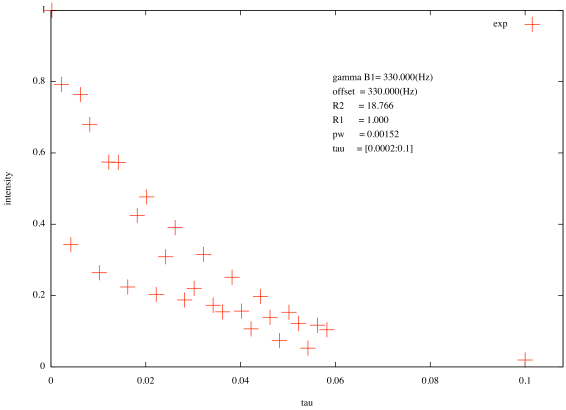
Hard Pulses are not always available

- Maximum power output by the amplifier is limited;
- Sample may boil if the power is too high;
- Some probes require low power;
- Sample may be a large molecule, which means the range of offset frequencies may be wide. For example,

$$\Delta\omega = \gamma B_1$$

Soft Pulse





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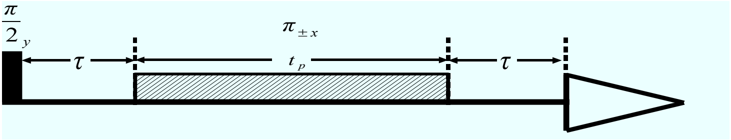

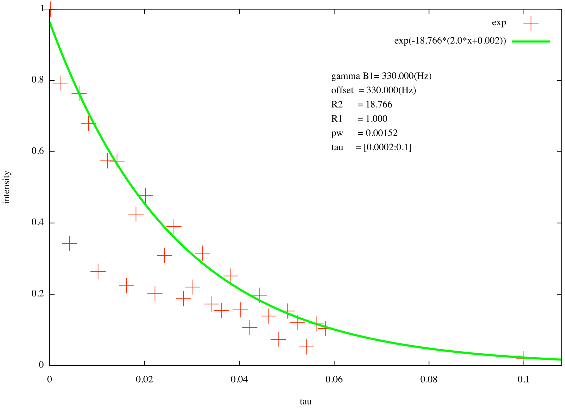

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Mathematical View of Hahn Echo

$$\frac{d\,M_x}{d\,t} = -\omega\,M_y + \gamma B_1 \sin\phi\,M_z - R_2 M_x \quad (1a)$$

$$\frac{d\,M_y}{dt} = \omega\,M_x - \gamma B_1 \cos\phi\,M_z - R_2 M_y \quad (1b)$$

$$\frac{d\,M_z}{d\,t} = -\gamma B_1 \sin\phi\,M_x + \gamma B_1 \cos\phi\,M_y - R_1\,(M_z - 1) \quad (1c)$$

$$\mathbf{M}(0) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (2)$$

$$\gamma B_1(t) = \begin{cases} 0 & 0 \le t \le \tau \\ b1 & \tau \le t \le \tau + t_p \\ 0 & \tau + t_p \le t \le 2\tau + t_p \end{cases} \quad (3)$$

signal: $\sqrt{M_x(2\tau + t_p)^2 + M_y(2\tau + t_p)^2}$

Inverse Problem: *Known* $\sqrt{M_x(2\tau_i + t_p)^2 + M_y(2\tau_i + t_p)^2}$, $(i \in [1..n])$, *find out* R_2.

Fitting Problem

$$\min \sum_{i=1}^{n} \left|\left| M_{\text{meas}}(i) - I_0 \sqrt{M_{x,i}^2 + M_{y,i}^2} \right|\right|^2$$

Subject to

$$\begin{aligned}
\frac{d\,M_x}{d\,t} &= -\omega\,M_y + \gamma B_1 \sin\phi\,M_z - R_2 M_x \\
\frac{d\,M_y}{dt} &= \omega\,M_x - \gamma B_1 \cos\phi\,M_z - R_2 M_y \\
\frac{d\,M_z}{d\,t} &= -\gamma B_1 \sin\phi\,M_x + \gamma B_1 \cos\phi\,M_y - R_1\left(M_z - 1\right)
\end{aligned}$$

with Eqs. (2), (3).

Variables: I_0 and R_2.

Bloch Equations

$$\frac{d}{dt}\begin{pmatrix} M_x \\ M_y \\ M_z \\ M_e \end{pmatrix} = \begin{pmatrix} -R_2 & -\omega & \gamma B_1 \sin\phi & 0 \\ \omega & -R_2 & -\gamma B_1 \cos\phi & 0 \\ -\gamma B_1 \sin\phi & \gamma B_1 \cos\phi & -R_1 & R_1 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} M_x \\ M_y \\ M_z \\ M_e \end{pmatrix}$$

$$\equiv \mathbf{A}\begin{pmatrix} M_x \\ M_y \\ M_z \\ M_e \end{pmatrix}$$

Then the solution of the Hahn echo can be easily expressed as

$$\mathbf{M}(2\tau + t_p) = e^{\mathbf{A}(\gamma\mathbf{B_1}=\mathbf{0})\tau}.e^{\mathbf{A}(\gamma\mathbf{B_1}=\mathbf{b1})t_p}.e^{\mathbf{A}(\gamma\mathbf{B_1}=\mathbf{0})\tau}.\mathbf{M}(0)$$

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Reformed Fitting Problem

$$\min \sum_{i=1}^{n} \left|\left| M_{\text{meas}}(i) - I_0 \sqrt{M_{x,i}^2 + M_{y,i}^2} \right|\right|^2$$

Subject to

$$\mathbf{M}(2\tau_i + t_p) = e^{\mathbf{A}(\gamma \mathbf{B_1}=\mathbf{0})\tau_i} . e^{\mathbf{A}(\gamma \mathbf{B_1}=\mathbf{b1})t_p} . e^{\mathbf{A}(\gamma \mathbf{B_1}=\mathbf{0})\tau_i} . \mathbf{M}(0) \qquad (i \in [1..n])$$

Hard Pulse:

$e^{2\tau_i R_2}$

Soft Pulse:

?

11M solved by MatrixExponential of Maple.

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Computing $Exp(\mathbf{A}t)$ via Lagrange Interpolation

Theorem

If A is an $n \times n$ matrix with n distinct eigenvalues $\lambda_1, \lambda_2, \cdots, \lambda_n$, then we have

$$e^{tA} = \sum_{k=1}^{n} e^{t\lambda_k} L_k(A),$$

where the $L_k(A)$ are Lagrange interpolation coefficients given by

$$L_k(A) = \prod_{j=1, j\neq k}^{n} \frac{A - \lambda_j I}{\lambda_k - \lambda_j}$$

for $k = 1, 2, \cdots, n$.

– T. M. Apostol, Some Explicit Formulas for the Exponential Matrix e^{tA}, The American Mathematical Monthly 76 (1969) 289 - 292.

Exact Solution of the Bloch Equations

The matrix $\mathbf{A}$ has four distinct eigenvalues: one is a real number (λ_1), two are complex conjugates ($\lambda_{2,3}$), one is zero (λ_4) .

$$\boldsymbol{\lambda} = \begin{bmatrix} \lambda_1 & \lambda_2 & \lambda_3 & \lambda_4 \end{bmatrix}^T$$

$$\begin{aligned} e^{\mathbf{A}t} &= e^{\lambda_1 t}\frac{\mathbf{A}(\mathbf{A}-\lambda_2\mathbf{I})(\mathbf{A}-\lambda_3\mathbf{I})}{\lambda_1(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)} + e^{\lambda_2 t}\frac{\mathbf{A}(\mathbf{A}-\lambda_1\mathbf{I})(\mathbf{A}-\lambda_3\mathbf{I})}{\lambda_2(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)} + \\ &\quad e^{\lambda_3 t}\frac{\mathbf{A}(\mathbf{A}-\lambda_1\mathbf{I})(\mathbf{A}-\lambda_2\mathbf{I})}{\lambda_3(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)} + \frac{(\mathbf{A}-\lambda_1\mathbf{I})(\mathbf{A}-\lambda_2\mathbf{I})(\mathbf{A}-\lambda_3\mathbf{I})}{-\lambda_1\lambda_2\lambda_3} \\ &\equiv e^{\lambda_1 t}\mathbf{L}_1(\mathbf{A}) + e^{\lambda_2 t}\mathbf{L}_2(\mathbf{A}) + e^{\lambda_3 t}\mathbf{L}_3(\mathbf{A}) + \mathbf{L}_4(\mathbf{A}) \end{aligned}$$

- process experimental data
- design new experiments

Fitting Problem with Exact Solution of the Bloch Equations

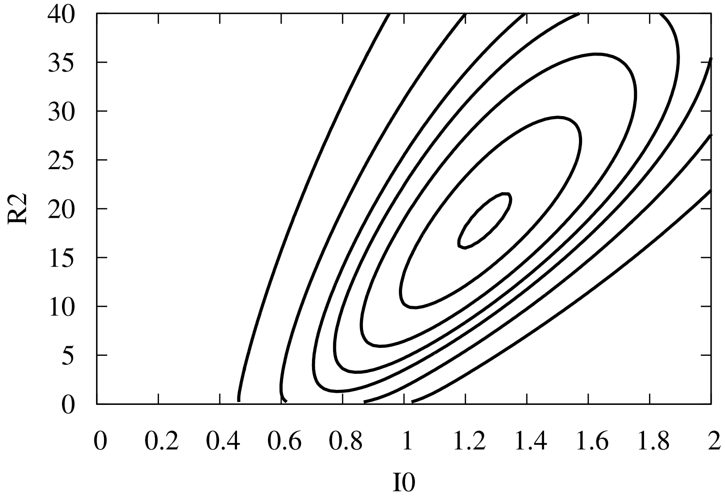
$$\min \sum_{i=1}^{n} \left|\left| M_{\text{meas}}(i) - I_0 \sqrt{M_{x,i}^2 + M_{y,i}^2} \right|\right|^2$$

Subject to

$$\begin{aligned} \lambda_j &= \cdots \qquad (j = 1, 2, 3) \\ &\vdots \\ M_{x,i} &= \cdots \\ M_{y,i} &= \cdots \end{aligned}$$

See: *Alex D. Bain, Christopher Kumar Anand, Zhenghua Nie, Exact Solution to the Bloch Equations and Application to the Hahn Echo, Journal of Magnetic Resonance, 2010. (Accepted) (doi:10.1016/j.jmr.2010.07.012)*

Fitting Problem is Solvable?



Approximate Solutions of the Bloch Equations

Approximate Eigenvalues

$$\boldsymbol{\lambda} \approx \begin{bmatrix} -R_2 \\ -R_2 + i\sqrt{b_1^2 + \omega^2} \\ -R_2 - i\sqrt{b_1^2 + \omega^2} \\ 0 \end{bmatrix}$$

Split-Operators

$$e^{(\mathbf{X}+\mathbf{Y})t} \approx e^{(t/2)\mathbf{X}} e^{(t)\mathbf{Y}} e^{(t/2)\mathbf{X}}$$

$$M_x(t) = c_1 e^{\lambda_1 t} + (c_2 \sin(Im(\lambda_2)\, t) + c_3 \cos(Im(\lambda_2)\, t)) e^{Re(\lambda_2)\, t} + c_4$$

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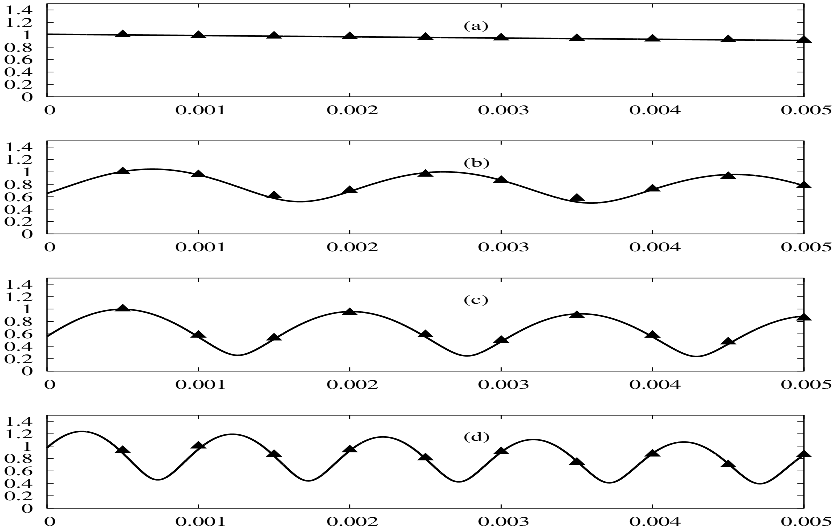
Results



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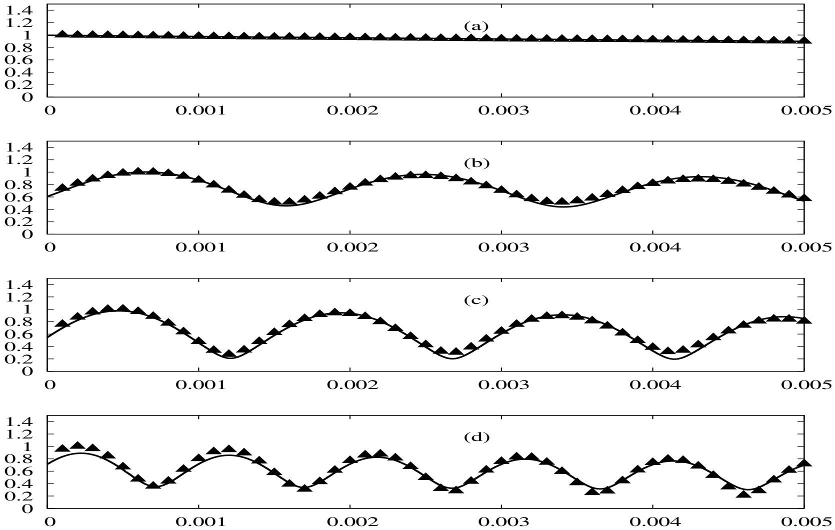
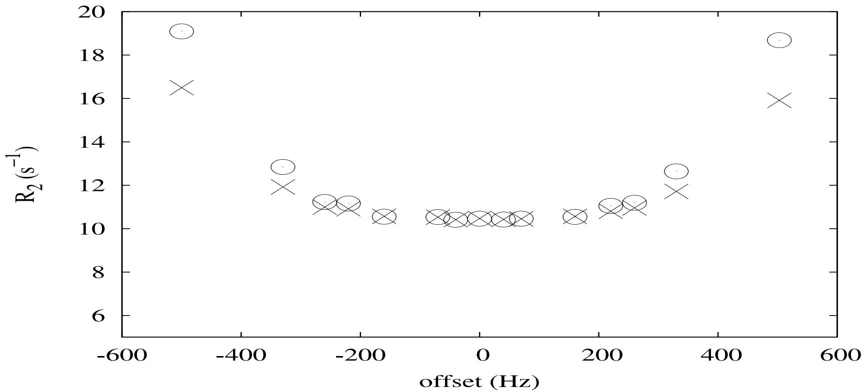


Field Inhomogeneity



$$\min \sum_{i=1}^{n} \left\| M_{\text{meas}}(i) - I_0 \sqrt{\left(\sum_k \sum_j M_{x,i,j,k}\right)^2 + \left(\sum_k \sum_j M_{y,i,j,k}\right)^2} \right\|^2$$

Conclusion

- The relaxation time is fitted by the exact solution of the Bloch equations.
- Ordinary differential constraints are pre-solved by the Lagrange interpolation method which is able to give the symbolic gradient and Hessian.
- The equivalent constrained optimization problem has been developed to dramatically reduce the size of the objective function and eliminate the computation of redundant terms.
- More complicated fitting problems can be constructed with more precise description of experiments to improve the accuracy of the measurements.
- The method can be applied to any arbitrary single spin-$\frac{1}{2}$ experiments and it is possible to extend to coupled-spin systems.

This work has been published in
Alex D. Bain, Christopher Kumar Anand, Zhenghua Nie, Exact Solution to the Bloch Equations and Application to the Hahn Echo, Journal of Magnetic Resonance, 2010. (Accepted) (doi:10.1016/j.jmr.2010.07.012)

Thanks!