The Simulation and Optimization of NMR Experiments Using a Liouville Space Method

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Maple Conference 2006

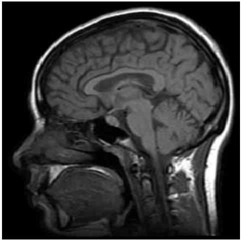
Outline

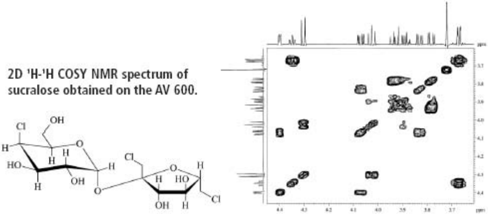
1. Introduction
   - Applications of NMR
   - Pulse NMR with MAPLE
   - Liouville Space Method
2. The simulation of pulse NMR
   - The spin echo of a 2-spin ($\frac{1}{2}$) system
   - Optimization problem

Outline

Applications of NMR

- MRI
- Chemistry



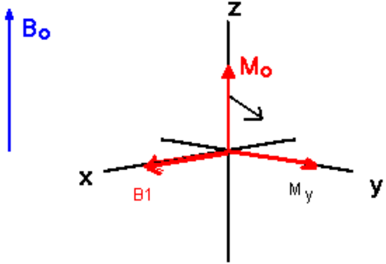


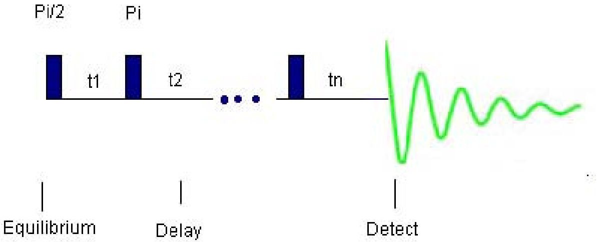
source: http://www.chemistry.mcmaster.ca/facilities/nmr/CHEMbrochure.pdf

Outline

Pulse NMR Experiments

- A Spin System
- Pulse Sequences





Pulse NMR with MAPLE

- A spin system is finite and described by a series of matrix manipulation.
- Maple is ideally suited to analyze and predict the behavior of a spin system.
- Our Goal:
  - To simulate the strong-coupled spin system
  - To optimize the NMR experiments

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Liouville Space Method

- Vector of observables (ρ)
- Evolution of the spin system
  Equation:

$$i\frac{\partial}{\partial t}\rho = L\rho \tag{1}$$

  Solution:

$$\rho(t) = e^{iLt}\rho(0) \tag{2}$$

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Computing the exponential

- To run ⟨ `MatrixExponential(L,I*t)` ⟩ or ⟨ `MatrixExponential(I*L*t)` ⟩
- To diagonalize the Liouvillian matrix

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Examples

- Four observables for a single spin ($\frac{1}{2}$) system: $|1_0)$, $|1_{+1})$, $|1_{-1})$ and $|0)$
- Equilibrium state of a 2-spin ($\frac{1}{2}$) system: <0,0,1,0,0,0,0,0,1,0,0,0,0,0,0,0>
- The single quantum positive block of the Liouvillian matrix for a 2-spin ($\frac{1}{2}$) system:

$$\begin{bmatrix} \omega_B & 1/2\,J_{AB} & 0 & -1/2\,J_{AB} \\ 1/2\,J_{AB} & \omega_B & -1/2\,J_{AB} & 0 \\ 0 & -1/2\,J_{AB} & \omega_A & 1/2\,J_{AB} \\ -1/2\,J_{AB} & 0 & 1/2\,J_{AB} & \omega_A \end{bmatrix}$$

Examples

The single quantum positive block of the Liouvillian matrix for a 3-spin $(\frac{1}{2})$ system:

$$
\left[\begin{array}{ccccccccccccccc}
\omega_C & 0 & -1/2\,J_{BC} & 1/2\,J_{BC} & 0 & -1/2\,J_{AC} & 0 & 0 & 0 & 0 & 1/2\,J_{AC} & 0 & 0 & 0 & 0 \\
0 & \omega_B & 1/2\,J_{BC} & -1/2\,J_{BC} & 0 & 0 & 0 & -1/2\,J_{AB} & 0 & 0 & 0 & 1/2\,J_{AB} & 0 & 0 & 0 \\
-1/2\,J_{BC} & 1/2\,J_{BC} & \omega_B & 0 & 0 & 0 & -1/2\,J_{AC} & 0 & -1/2\,J_{AB} & 0 & 0 & 0 & 1/2\,J_{AB} & 0 & 1/2\,J_{AC} \\
1/2\,J_{BC} & -1/2\,J_{BC} & 0 & \omega_C & 0 & 0 & 0 & 0 & -1/2\,J_{AC} & -1/2\,J_{AB} & 0 & 0 & 0 & 1/2\,J_{AC} & 1/2\,J_{AB} \\
0 & 0 & 0 & 0 & \omega_A & 1/2\,J_{AC} & 0 & 1/2\,J_{AB} & 0 & 0 & -1/2\,J_{AC} & -1/2\,J_{AB} & 0 & 0 & 0 \\
-1/2\,J_{AC} & 0 & 0 & 0 & 1/2\,J_{AC} & \omega_A & -1/2\,J_{BC} & 0 & 1/2\,J_{AB} & 1/2\,J_{BC} & 0 & 0 & -1/2\,J_{AB} & 0 & 0 \\
0 & 0 & -1/2\,J_{AC} & 0 & 0 & -1/2\,J_{BC} & \omega_B-\omega_C+\omega_A & 1/2\,J_{BC} & 0 & 0 & 0 & 1/2\,J_{AC} & 0 & 0 & 0 \\
0 & -1/2\,J_{AB} & 0 & 0 & 1/2\,J_{AB} & 0 & 1/2\,J_{BC} & \omega_A & 1/2\,J_{AC} & -1/2\,J_{BC} & 0 & 0 & 0 & -1/2\,J_{AC} & 0 \\
0 & 0 & -1/2\,J_{AB} & -1/2\,J_{AC} & 0 & 1/2\,J_{AB} & 0 & 1/2\,J_{AC} & \omega_A & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1/2\,J_{AB} & 0 & 1/2\,J_{BC} & 0 & -1/2\,J_{BC} & 0 & -\omega_B+\omega_C+\omega_A & 1/2\,J_{AB} & 0 & 0 & 0 & 0 \\
1/2\,J_{AC} & 0 & 0 & 0 & -1/2\,J_{AC} & 0 & 0 & 0 & 0 & 1/2\,J_{AB} & \omega_C & 0 & -1/2\,J_{BC} & 1/2\,J_{BC} & -1/2\,J_{AB} \\
0 & 1/2\,J_{AB} & 0 & 0 & -1/2\,J_{AB} & 0 & 1/2\,J_{AC} & 0 & 0 & 0 & 0 & \omega_B & 1/2\,J_{BC} & -1/2\,J_{BC} & -1/2\,J_{AC} \\
0 & 0 & 1/2\,J_{AB} & 0 & 0 & -1/2\,J_{AB} & 0 & 0 & 0 & 0 & -1/2\,J_{BC} & 1/2\,J_{BC} & \omega_B & 0 & 0 \\
0 & 0 & 0 & 1/2\,J_{AC} & 0 & 0 & 0 & -1/2\,J_{AC} & 0 & 0 & 1/2\,J_{BC} & -1/2\,J_{BC} & 0 & \omega_C & 0 \\
0 & 0 & 1/2\,J_{AC} & 1/2\,J_{AB} & 0 & 0 & 0 & 0 & 0 & 0 & -1/2\,J_{AB} & -1/2\,J_{AC} & 0 & 0 & \omega_B+\omega_C-\omega_A
\end{array}\right]
$$

Computational Complexity of n-spin ($\frac{1}{2}$) systems

Number of Spins	2	3	4	5
Number of Observables	16	64	256	1024
Liouvillian Matrix	16×16	64×64	256×256	1024×1024
5-Quantum				1
4-Quantum			1	10
Triple Quantum		1	8	45
Double Quantum	1	6	28	120
Single Quantum	4	15	56	210
Zero Quantum	6	20	70	252

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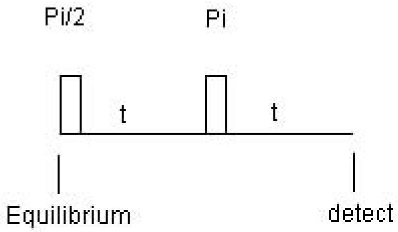
Code: The spin echo of a 2-spin ($\frac{1}{2}$) system




```
> EquVector := <0,0,1,0,0,0,0,0,1,0,0,0,0,0,0,0>:
> RotateEqu1 :=
MatrixVectorMultiply(eval(WignerAlpha,[alpha=Pi/2]),EquVector):
> Evaluation1 :=MatrixVectorMultiply(ExpL,RotateEqu1):
> WignerAlpha2 := eval(WignerAlpha,[alpha=Pi]):
> RotateEqu2 := MatrixVectorMultiply(WignerAlpha2,Evaluation1):
> Evaluation2 := MatrixVectorMultiply(ExpL,RotateEqu2):
> Evaluation := eval(Evaluation2,[t=tau]):
> scalar1 := [seq(Multiply(Transpose(Evaluation),
  SQEigenvectorsNorm[i]),
  i=1..ColumnDimension(SQEigenvectors))]:
> scalar2 := [seq(Multiply(Transpose(SQEigenvectorsNorm[i]),
  TotalXYVector),  i=1..ColumnDimension(SQEigenvectors))]:
> IntensityOriginal := <seq(simplify(scalar1[i]*scalar2[i]),
```

Results: The spin echo of a 2-spin ($\frac{1}{2}$) system

One of the intensities:

$$1/4\left(-e^{i\tau\left(J+\sqrt{J^2+4\,\delta^2}\right)}\left(1-(\sin(2\,\theta))^2\right)+e^{i\tau\,J}\left(1-(\sin(2\,\theta))^2\right)\right.$$
$$\left.-e^{i\tau\left(J+\sqrt{J^2+4\,\delta^2}\right)}\sin(2\,\theta)+e^{i\tau\left(J+\sqrt{J^2+4\,\delta^2}\right)}\right)\sqrt{2}$$

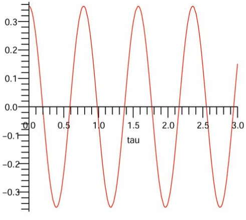
Results: the spin echo of a 2-spin ($\frac{1}{2}$) system

One of intensities of a weakly-coupled system:

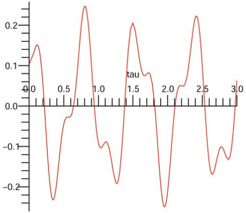
$$1/4\, e^{i\tau\, J} \sqrt{2}$$

One of intensities of a strong-coupled system:

$$-1/8 \left(-e^{i\tau\left(J+\sqrt{J^2+4\,\delta^2}\right)} - e^{i\tau\, J} + e^{i\tau\left(J+\sqrt{J^2+4\,\delta^2}\right)} \sqrt{2} \right) \sqrt{2}$$



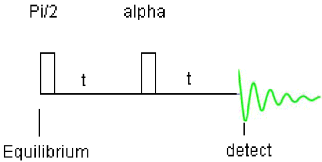
A Weakly-coupled system

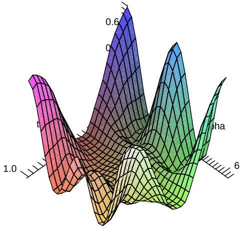


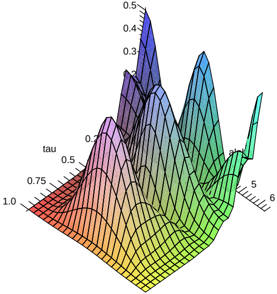
A Strong-coupled system

Outline

Optimization problem: a simple case







Summary

- We have developed tools for pulse, delay, and detection.
- Maple provides a good way to simulate NMR of strongly coupled nuclear spins, both symbolically and numerically.
- The computational complexity grows quickly in Liouville space.

Current & Future Tasks

- Recently, we developed other tools of pulse NMR experiments such as phase cycling, a n-spin system, relaxation.
- Challenges & Outlook
    - To get the accurate formula ($exp^{(i*L-R)*t}$) symbolically
        - To run $\langle$ `MatrixExponential(L,I*t)` $\rangle$ or $\langle$ `MatrixExponential(I*L-R,t)` $\rangle$
        - To solve the eigenvectors and form the diagonalization of (I*L-R)
    - To solve the optimization problems

Thanks!

Questions?