Outline

1 Prerequisites
2 Relaxation and spin Echo
3 Spherical Tensor Operators
4 Superoperators
5 My research work
6 References.
NMR

- NMR is a phenomenon in which the resonance frequencies of nuclear magnetic systems are investigated.
- NMR always employs some form of magnetic field (usually a strong externally applied field $B_0$ and a RF field)
- Nuclei have a magnetic moment and spin angular momentum
Random direction of spin polarization in the absence of magnetic field.
Net magnetic moment from small excess of Nuclei in +1/2 state.

$\mathbf{M}_0 \times \mathbf{y}$

$\mathbf{B}_0$ Applied magnetic field

Spin States Split in the presence of $\mathbf{B}_0$

-1/2 antiparallel

+1/2 parallel

no field

applied field $\mathbf{B}_0$
Longitudinal and Transverse Magnetizations
### Most commonly studied nuclei

<table>
<thead>
<tr>
<th>Spin-1/2 nucleus</th>
<th>NMR freq (at 10 T)</th>
<th>abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{H}$</td>
<td>426 MHz</td>
<td>99.9%</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>107</td>
<td>1.1%</td>
</tr>
<tr>
<td>$^{15}\text{N}$</td>
<td>43</td>
<td>0.4%</td>
</tr>
<tr>
<td>$^{19}\text{F}$</td>
<td>401</td>
<td>100%</td>
</tr>
<tr>
<td>$^{28}\text{Si}$</td>
<td>85</td>
<td>4.7%</td>
</tr>
<tr>
<td>$^{31}\text{P}$</td>
<td>175</td>
<td>100%</td>
</tr>
</tbody>
</table>
Applications of NMR

- Physics
  - Condensed matter physics
- Chemistry
  - Identification of material
- Biophysics
  - Analysis of Protein structure
- Medical
  - MRI (Magnetic Resonance Image)
Interactions in NMR

NRM Interactions

Internal Interactions
- 1. Chemical shift
- 2. J-Coupling
- 3. DD-Coupling

External Interactions
- 1. Applied Magnetic field
- 2. RF field
Relaxation

- T1 spin-lattice (relaxing back to precessing about the z axis)
  Recovery of Z component of magnetization.

- T2 spin-spin (fanning out)
  Decay of x, y component of magnetization.
Spin Echo

- Signal gradually decays with decay rate $T_2^*$
- After $180^\circ$ pulse, signal reforms at same rate
- Spin echo peak amplitude depends on $T_2$
Density Matrix Formalism

• A tool used to describe the state of a spin ensemble, as well as its evolution in time.

\[ \rho = |\psi> <\psi| \]

• Average of any observable

\[ \langle A \rangle = \text{Tr}(\rho A) \]

• For any state

\[ |\psi> = c_\alpha |\alpha> + c_\beta |\beta> \]

Diagonal elements = probabilities

Off-diagonal elements = "coherences" (provide info. about relative phase)
Spherical tensor operators.

• Tensors are very useful simplifying tools that encountered in spherical symmetric problems.

• Any spherical tensor operator can be found by

\[ T_{Lm} = \sqrt{\frac{4\pi}{2L+1}} Y_{Lm} \]

• Commutation relations with angular momentum operator.

\[ [J^\pm, T_{Lm}] = \sqrt{(L \mp m)(L \pm m + 1)} T_{Lm\pm1} \]

\[ [J_z, T_{Lm}] = T_{Lm} \] [2]
Transformation of Spherical tensor operators

\[ T_{L',m} = \sum_{m=-l}^{l} T_{L,m} D_{m,m}^{L}(\alpha, \beta, \gamma) \]

Wigner rotation matrices

\[ D_{m,m}^{L}(\alpha, \beta, \gamma)|L, m\rangle = \exp(-i\alpha) \exp(-i\gamma) d_{m,m}^{L}(\beta) \]

Reduced rotation matrix elements

\[ d_{m,m}^{L}(\beta) = \sum_{k} (-1)^{k+m-m} \frac{\sqrt{(L+m)!(L-m)!(L+m)!(L-m)!}}{(L-m-k)!(L+m-k)!(k+m-m)!k!} \times (\cos \frac{\beta}{2})^{2L+m-m-2k} (\sin \frac{\beta}{2})^{m-m+2k} \]
Total Hamiltonian in terms of Spherical tensor operators.

\[
H_{Total} = -\gamma B_0 T_{10} - 2\pi J \sqrt{3\pi} T_{00} Y_{00} + \frac{3eV_{zz}Q}{4I(2I - 1)} \sqrt{\frac{24\pi}{5}} \sum_m (-1)^m T_{2m} Y_{2-m} \\
+ \frac{\mu_0 \gamma^2 \hbar}{4\pi r^3} \sqrt{\frac{24\pi}{5}} (-1)^m T_{2m} Y_{2-m}
\]

\[
H_{Total} = H_z + H_{CS} + H_J + H_D
\]
Superoperators

- Liouville-von Neumann equation

\[ i\hbar \frac{d\rho}{dt} = [H, \rho] \]

- We define a superoperator

\[ \hat{L} |\rho(t)\rangle = [H, \rho(t)] \]

\[ i\hbar \frac{d |\rho(t)\rangle}{dt} = \hat{L} |\rho(t)\rangle \] [4]
Matrix representation of Superoperators

- Superoperators belong to the superoperator space.
- The difference between the Superoperator space and Hilbert space is dimensionality.
- Different physical conditions.
- Matrix representation

$$\rho = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix} \quad \quad |\rho\rangle = \begin{pmatrix} \rho_{\alpha\alpha} \\ \rho_{\beta\alpha} \\ \rho_{\alpha\beta} \\ \rho_{\beta\beta} \end{pmatrix}$$
<table>
<thead>
<tr>
<th>Name</th>
<th>Continuous representation</th>
<th>Continuous scalar product</th>
<th>Discrete representation</th>
<th>Discrete scalar product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superoperator Space</td>
<td>superoperators</td>
<td>$\sum_M \langle \hat{M}</td>
<td>\hat{P}^\dagger \hat{Q}</td>
<td>\hat{M} \rangle$</td>
</tr>
<tr>
<td>Liouville space</td>
<td>operators, Density matrices</td>
<td>$\sum_\varphi \langle \varphi</td>
<td>\hat{M}^\dagger \hat{K}</td>
<td>\varphi \rangle$</td>
</tr>
<tr>
<td>Hilbert space</td>
<td>wavefunctions</td>
<td>$\int \varphi^* (x) \psi (x) , dx$</td>
<td>$n$ -vectors</td>
<td>$\sum_n \varphi_n^* \psi_n$</td>
</tr>
</tbody>
</table>
Long lived Singlet states in solution

NMR

Singlet and Triplet states

Two coupled spins

\[ |S_0\rangle = \frac{1}{\sqrt{2}} (|\alpha \beta\rangle - |\beta \alpha\rangle), \]

\[ |T_{+1}\rangle = |\alpha \alpha\rangle, \]

\[ |T_0\rangle = \frac{1}{\sqrt{2}} (|\alpha \beta\rangle + |\beta \alpha\rangle), \]

\[ |T_{-1}\rangle = |\beta \beta\rangle. \]
Density operator for Spin pair

\[ |\psi\rangle = c_{\alpha\alpha}|\alpha\alpha\rangle + c_{\alpha\beta}|\alpha\beta\rangle + c_{\beta\alpha}|\beta\alpha\rangle + c_{\beta\beta}|\beta\beta\rangle \]

\[ \hat{\rho} = \begin{pmatrix}
  c_{\alpha\alpha} \\
  c_{\alpha\beta} \\
  c_{\beta\alpha} \\
  c_{\beta\beta}
\end{pmatrix}
\begin{pmatrix}
  c_{\alpha\alpha}^* & c_{\alpha\beta}^* & c_{\beta\alpha}^* & c_{\beta\beta}^*
\end{pmatrix} \]

\[ \hat{\rho} = \begin{pmatrix}
  \rho_{\alpha\alpha} & \rho_{\alpha+} & \rho_{+\alpha} & \rho_{++} \\
  \rho_{\alpha-} & \rho_{\alpha\beta} & \rho_{+-} & \rho_{+\beta} \\
  \rho_{-\alpha} & \rho_{-+} & \rho_{\beta\alpha} & \rho_{\beta+} \\
  \rho_{--} & \rho_{-\beta} & \rho_{\beta-} & \rho_{\beta\beta}
\end{pmatrix} \]
Equation of Motion

\[ \frac{d}{dt} \rho(t) = \hat{L}(t) \rho(t) \]

Liouvillian Space operator

\[ \hat{L}(t) = \hat{L}_{\text{coh}}(t) + \hat{\Gamma} \]

Coherent Effects

\[ \hat{L}_{\text{coh}}(t) = -i \hat{H}(t) \]

Incoherent Effects

- Dipole-dipole relaxation
- External random field relaxation
Relaxation Superoperator

For DD-relaxation

\[ \hat{\Gamma}^{jk} = -\frac{2}{5} b_j^2 \int_0^0 d\tau \sum_{m=-2}^{+2} (-1)^m G^{jk}_{2m}(\tau) \]
\[ \times \hat{R}_z(\varphi) \hat{T}^{jk}_{2m} \hat{R}_z(-\varphi) \hat{T}^{jk}_{2-m}, \]

For ERF-relaxation

\[ \hat{\Gamma}^{ERF}_{jk} = C_{jk} \gamma^2 (B_{k\text{rms}}^r)^2 \int_{-\infty}^0 d\tau \sum_{m=-1}^{+1} (-1)^m G_{1m}(\tau) \]
\[ \times \hat{R}_z(\varphi) \hat{T}^j_{1m} \hat{R}_z(-\varphi) \hat{T}^k_{1-m}, \]

\[ G^{jk}_{2m}(\tau) = \exp\{-|\tau|/\tau_{c}^{DD}\}, \]

\[ \tau_{c}^{DD} \]

Autocorrelation function

Correlation time
Relaxation of singlet-state population

\[
\hat{\mathbf{I}}_{\text{ERF}}^{ST} = \begin{pmatrix}
-V_o^S - 2V_1^S & V_1^S & V_o^S & V_1^S & 0 & 0 \\
V_1^S & -V_1^\Sigma & V_1^T & 0 & -\frac{1}{\sqrt{2}}V_1^\Delta & 0 \\
V_1^S & V_1^T & -V_o^S - 2V_1^S & V_1^T & 0 & 0 \\
V_1^S & 0 & V_1^T & -V_1^\Sigma & -\frac{1}{\sqrt{2}}V_1^\Delta & 0 \\
0 & -\frac{1}{\sqrt{2}}V_1^\Delta & 0 & V_1^\Delta & -\frac{1}{\sqrt{2}}V_1^\Sigma & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]
Final matrix of the coherent Liouvillian Superoperator.

- Shows the conversion of singlet population to singlet-triplet zero-quantum coherence then to triplet population.

\[
\hat{L}_{\text{coh}}^{ST} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & -\Delta \omega^0 \sqrt{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \Delta \omega^0 \sqrt{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\Delta \omega^0 \sqrt{2} & 0 & -\Delta \omega^0 \sqrt{2} & 0 & -2\pi J \\
-\Delta \omega^0 \sqrt{2} & 0 & -\Delta \omega^0 \sqrt{2} & 0 & 0 & 2\pi J
\end{pmatrix}
\]
Final matrix of the evolution of spin density operator.

\[
\begin{pmatrix}
-V_0^S - 2V_1^S & V_1^S & V_0^S & V_1^S & 0 & -\frac{\Delta \omega^o}{\sqrt{2}} \\
V_1^S & WV & W_1V_1 & W_2^T & -\frac{1}{\sqrt{2}} V_1^\Delta & 0 \\
V_0^S & W_1V_1 & 2WV & W_1V_1 & 0 & -\frac{1}{\sqrt{2}} V_1^\Delta \\
V_1^S & W_2^T & W_1V_1 & WV & \frac{1}{\sqrt{2}} V_1^\Delta & 0 \\
0 & -\frac{1}{\sqrt{2}} V_1^\Delta & 0 & \frac{1}{\sqrt{2}} V_1^\Delta & -R^{ST} - V_1^\Sigma & 2\pi J \\
\frac{1}{\sqrt{2}} V_1^\Delta & 0 & -\frac{1}{\sqrt{2}} V_1^\Delta & 0 & -2\pi J & -R^{ST} - V^{ST}
\end{pmatrix}
\]
Signal Obtained
Advantages and applications of long-lived states

- Store information up to 40 times longer than T1.
- Can be created in both high or low magnetic fields, the latter case very interesting for applications on humans.
- For the study of molecular transportation and storage of polarized nuclear spin coherence.
- Can be used for the investigation of slow-cross relaxation between different molecules in solutions.
# NMR for Quantum Information

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Physics of NMR is well described.</td>
<td>1. Noisy signal</td>
</tr>
<tr>
<td>2. Long decoherence times</td>
<td>2. No entanglement.</td>
</tr>
<tr>
<td>3. Small quantum computer is easy to construct.</td>
<td>3. Limited measurement.</td>
</tr>
</tbody>
</table>
Why NMR?

A major requirement of a quantum information/computer is that the coherence should last long.

- Nuclear spins in liquids retain coherence \( \sim 100 \text{’s millisecond} \) and their longitudinal state for several seconds.

- A system of N coupled spins (each spin 1/2) form an N qubit Quantum Computer.

- Unitary Transform can be applied using R.F. Pulses and various logical operations and quantum algorithms can be implemented. [7]
THANKS FOR YOUR PATIENCE