Effects of the Dipole-Dipole Interaction in Media

Alan Dotts
The dipole-dipole Hamiltonian can be split into terms for each coupled spin.

- $\hat{H}_{DD, full} = \sum_{j < k} \hat{H}_{jk, full}$

### Homonuclear Case

- $\hat{H}_{jk, DD} (\Theta_{jk}) = d_{jk} (3 \hat{I}_{jz} \hat{I}_{kz} - \hat{I}_j \cdot \hat{I}_k)$

### Heteronuclear Case

- $\hat{H}_{jk, DD} (\Theta_{jk}) = 2d_{jk} \hat{I}_j \hat{I}_k$

Useful if $d_{jk}$ term cancels

- $d_{jk} = 1/2 b_{jk} (3 \cos^2 \Theta_{jk} - 1)$
Secular vs. Nonsecular

- $\hat{H} = \hat{A} + \hat{B}$ \( a_n \) are the eigenvalues of $\hat{A}$

- The eigenvalues correspond to different energy states.

- In general the two terms do not commute.
The secular approximation of B takes only the block diagonal terms of the matrix.

\[
\hat{B}^0 = \begin{bmatrix}
x & 0 & 0 & 0 & 0 & 0 & \ldots \\
0 & x & x & 0 & 0 & 0 & \ldots \\
0 & x & x & 0 & 0 & 0 & \ldots \\
0 & 0 & 0 & x & 0 & 0 & \ldots \\
0 & 0 & 0 & 0 & x & 0 & \ldots \\
0 & 0 & 0 & 0 & 0 & x & \ldots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots 
\end{bmatrix}
\]

- Good for \(|b_{mn}| \ll |a_m - a_n|\)
- Blocks are the degenerate or near degenerate eigenvalues of A.
Effects on NMR Spectra

- Spreading out of Absorption Spectra.
  - The off-diagonal terms that survive the secular approximation are degenerate or near degenerate.
  - Allows absorption of photons with close but slightly different energies.
  - Peaks in spectra are not well resolved.
Effects on NMR Spectra
Relaxation

- Sensitive to non-secular dipole-dipole components.
- T1
  - Spin-Lattice relaxation
  - Movement of spin distributions back to Boltzman.
- T2
  - Spin-spin relaxation
  - Decay of coherence of oscillating spins.
Relaxation for spin 1/2

- Direct dipole-dipole coupling between two spins.
  - Changes the local magnetic field as molecules rotate.
  - Generally the largest effect.
- Chemical shift anisotropy
  - Changes as molecule tumbles through liquid.
  - Next most important.
  - More important for higher field strengths.
- Spin-rotation
  - Wobbling of spin relative to magnetic field.
  - Generally small in liquids, dominates in gasses.
**Autocorrelation Function**

- Assume fluctuating transverse field with zero average.
  - $\langle B_x(t) \rangle = 0$

- Mean square fluctuations are not zero
  - $\langle B_x^2(t) \rangle \neq 0$

- Autocorrelation function
  - $G(\tau) = \langle B_x(t) B_x(t+\tau) \rangle \neq 0$

- Fast Fluctuations
- Slow Fluctuations
Spectral Density

- The spectral density is the Fourier transform of the autocorrelation function.
  
  \[ J(\omega) = 2 \int_0^\infty G(\tau) \exp(-i \omega \tau) \]

- Slow fluctuations give narrow spectral density
- Fast fluctuations give broad spectral density
$T_c$ and Relaxation

- $T_c$ is the decay constant for the autocorrelation function.
  - $G(\tau) = \langle B_x^2 \rangle \exp(-|\tau|/\tau_c)$

- In general the relaxations follow a trend depending on $T_c$. 

![Graph showing the trend of $T_1$ and $T_2$ with respect to $T_c$.]
In Solid

- All intermolecular and intramolecular couplings are important.

- Lattice means no averaging due to translation.

- Fixed orientation means no averaging due to rotational motion.
Magic Angle Spinning

- $\hat{H}^{DD}_{jk}(\Theta_{jk}) = d_{jk} (3 \hat{I}_{jz} \hat{I}_{kz} - \hat{I}_j \cdot \hat{I}_k)$
- $d_{jk} = 1/2 b_{jk} (3 \cos^2 \Theta_{jk} - 1)$
- Contains terms with $3 \cos^2 \Theta_{jk} - 1$
  - Dipole Dipole interaction cancels when $3 \cos^2 \Theta_{jk} - 1 = 0$
  - $\Theta_{magic} = \arctan \sqrt{2} \approx 54.74^\circ$
- Geometric canceling of the Hamiltonian.
In Isotropic Liquid

- The secular terms “average out” in a liquid.
- Uniform in all orientations
  - \[ \int_0^{\pi} (3 \cos^2 \Theta_{jk} - 1) \sin \Theta_{jk} \, d \Theta_{jk} = 0 \]
  - Sin term is due to the probability of being in a perpendicular vs. a parallel orientation.
  - Area element proportional to \( \sin \Theta_{kj} \)
Isotropic Liquid

- The short range intermolecular terms average to zero due to translational motion.
- Long range term is very small and can be ignored.
In Liquid Crystal

- There is a preferred orientation.
  - The integral over orientations does not give zero.
  - There is no “averaging out”.

- Short range intermolecular
  - Still averages due to translation

- Long range intermolecular
  - Still small and can be ignored
In Solution

- Molecules spinning randomly in solution.
  - Uniform in all orientations.
  - Similar to isotropic liquid.
  - Integrating over all orientations gives zero.
- Intermolecular component averages.
  - Translational motion fast enough
In Solution

• When does the intramolecular term survive?
• Molecules have a preferred orientation.
  • Same as the anisotropic liquid or liquid crystal.
  • Preferred orientation means no averaging out.
• Molecules are spinning slowly
  • True for large molecules.
  • Not all orientations are sampled within time.
  • Part of the integral survives.