Dipole-Dipole Interaction

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History

- Original Paper – Bloembergen, Purcell and Pound Harvard
- Looking at relaxation effects.
- Found the Dipole Dipole Interaction contribute to both spin lattice and spin spin relaxation.
Quantum Mechanical Spin

• Start with the magnetic moment.
  • \( \vec{\mu} = \gamma \vec{J} = \hbar \gamma \vec{I} \)
• \( I^2 \) has eigenvalues \( I(I+1) \)
  • \( I \) is either integer or half integer.
• \( I^2 \) commutes with any component of \( I \).
  • Can specify \( I^2 \) and \( I_z \) simultaneously.
  • \( I_z \) has eigenvalues of \( m = I, I-1, \ldots, -I \)
• In an external magnetic field, the Hamiltonian is then:
  • \( H = -\gamma \hbar H_0 I_z \)
The eigenvalues of the Hamiltonian give the energy states.

\[ E = -γ \hbar H_0 m \quad , \quad m = I, I - 1, \ldots, -I \]

For absorption of photons, the photon energy must equal difference between energy levels.

For alternating magnetic field, the RF, we obtain a perturbation of the Hamiltonian:

\[ H_{\text{pert}} = -γ \hbar H_0^0 I_x \cos(\omega t) \]

The operator \( I_x \) between states \( m', m \) vanishes unless \( m' = m + 1 \).

\[ \hbar \omega = \Delta E = γ \hbar H_0 \quad , \quad \text{therefore} \quad \omega = γ H_0 \]
Dipole-Dipole Interaction

- For two closely spaced Dipoles with moments $\mu_1$ and $\mu_2$, the potential energy is:

$$ E = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3 (\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5}, \quad \vec{\mu}_1 = \gamma_1 \hbar \vec{I}_1, \quad \vec{\mu}_2 = \gamma_2 \hbar \vec{I}_2 $$

- From here we can infer a general dipolar contribution to the Hamiltonian for $N$ spins:

$$ H_d = \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \frac{\vec{\mu}_j \cdot \vec{\mu}_k}{r_{jk}^3} - \frac{3 (\vec{\mu}_j \cdot \vec{r}_{jk})(\vec{\mu}_k \cdot \vec{r}_{jk})}{r_{jk}^5} $$

- In component form gives elements such as:

$$ \gamma_1 \gamma_2 \hbar^2 I_{1x} I_{2x} \frac{1}{r^3} $$
The x and y elements of I can be rewritten in terms of the raising and lowering operators:

- \( I^{\pm} = I_x \pm \ell I_y \)

We can also change from Cartesian to spherical coordinates.

Doing this we get the general Hamiltonian:

\[
H_d = \frac{\gamma_1 \gamma_2 \hbar^2}{r^3} (A + B + C + D + E + F)
\]
The Alphabet of the Dipole-Dipole

\[ H_d = \frac{\gamma_1 \gamma_2 \hbar^2}{r^3} (A + B + C + D + E + F) \]

\[ A = I_{1z} I_{2z} (1 - 3\cos^2 \theta) \]
\[ B = -\frac{1}{4} (I_1^+ I_2^- + I_1^- I_2^+) (1 - 3\cos^2 \theta) \]
\[ C = -\frac{3}{2} (I_1^+ I_{2z} + I_{1z} I_2^+) \sin \theta \cos \theta e^{-\imath \phi} \]
\[ D = -\frac{3}{2} (I_1^- I_{2z} + I_{1z} I_2^-) \sin \theta \cos \theta e^{\imath \phi} \]
\[ E = -\frac{3}{4} I_1^+ I_2^+ \sin^2 \theta e^{-2\imath \phi} \]
\[ F = -\frac{3}{4} I_1^- I_2^- \sin^2 \theta e^{2\imath \phi} \]

• Since the magnitude of the dipolar contribution is much less that the Zeeman Hamiltonian, solve it first then perturb by the dipolar contribution.
2 Spin $\frac{1}{2}$ System

- System of two identical spin $\frac{1}{2}$ moments.
  - $H_Z = -\gamma \hbar H_0 I_{1z} - \gamma \hbar H_0 I_{2z}$
  - $E_Z = -\gamma \hbar H_0 m_1 - \gamma \hbar H_0 m_2$
- States are given by $[+\text{-}), [-+\text{)}, [+\text{+})$ and $[-\text{-})$
- $A$ is proportional to $I_{1z} I_{2z}$, therefore connecting $[m_1 m_2)$ and $(m_1 m_2]$
- For the raising and lowering operators:
  - $I_z I^\pm |l, m\rangle = (m \pm \hbar) I^\pm |l, m\rangle$
- Therefore they connect $[m_1,m_2)$ with $(m_1 \pm 1, m_2]$
The other terms of the dipole-dipole Hamiltonian include the raising and lowering operators. Therefore they connect an energy state to a different higher or lower energy state.

The B term includes both a raising and lowering operator.

- It simultaneously flips both spins, raising one and lowering the other.
- This requires the two moments to be in different states.
- Therefore it only connects the zero energy state to the other degenerate zero energy state.
● The C and D terms both include a single raising or lowering operator.
  • The D term raises the energy state by flipping a single spin down.
  • The C term lowers the energy state by flipping a single spin up.

● The E and F terms both have two raising or lowering operators.
  • The F term raises the energy state from the lowest to highest by flipping both down.
  • The E term lowers the energy state from highest to lowest by flipping both spins up.
Effects

- C and D work to allow absorptions at twice the resonate frequency.
- E and F work to allow absorptions near zero frequency.
- Both terms are small compared to the absorption and the resonate frequency, since the local field produced by the dipole is much smaller than the external field.
A and B Terms

• The A and B terms connect states of the same energy. Either the same state, or states that are degenerate in energy.

• This allows for interactions between dipoles that do not emit energy.

• Contributes to line broadening in the absorption spectra.
Systems With More Spins

• In a crystalline lattice, there are more than two dipoles to consider. For an estimate, you can find the local field at a given dipole by the field produced by the neighboring dipoles.

• In a liquid, there is no lattice. The molecules are free to move in the solution and there is an averaging out.