Introduction

This page will be devoted to understanding the finer aspects of dipolar coupling starting with expansion of the dipolar Hamiltonian. The dipolar coupling is a through space interaction, which can give insights into the proximity of two nuclei. Often dipolar coupling is confused with J-Coupling, which is mediated through bonding electrons.

Each atomic nuclei can be thought of as an individual magnet, due to the intrinsic spin of the nucleus. Therefore each nucleus generates a magnetic field, which effects the magnetic field experienced by nearby nuclei. The effect is illustrated below

![Figure 1. The magnetic field lines, and therefore the magnetic field, of the red nucleus directly effect magnetization of the blue nucleus, and vice versa.](image)

The dipolar field generated by each nucleus creates an energy shift of the nuclear spin levels apart from the Zeeman splitting. The energy of this field is given by the dipolar Hamiltonian $H_D$.

Classical Derivation of the Hamiltonian

In this section we will derive the Hamiltonian using classical physics. This is derivation is more more basic than the one outline below which uses quantum mechanics. Let's begin by considering a system which has two NMR active nuclei, I and S, shown in Figure 2. Each nucleus has a magnetic moment which may be considered a magnetic point (like point charges in the electronic equivalent).
The magnetic moment for I may be described as

$$\hat{\mu} = \gamma h \hat{I}.\]

Similar to the energy describing electric point charges, the magnetic points have an energy associated with them expressed as:

$$E_{\text{dipole}} = -\left[\frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5}\right] \frac{\mu_0}{4\pi},$$

where $r$ is the distance between the two coupled spins, and $\mu_0$ is vacuum permittivity. This gives rise to the Hamiltonian

$$\hat{H}_{DD} = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S h}{r^3} \left( A + B + C + D + E + F \right)$$

A through F is known as the dipolar alphabetical soup and is used to represent the following quantities:

$$A = \hat{I}_z \hat{S}_z (3\cos^2\theta - 1)$$

$$B = -\frac{1}{4} (\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+) (3\cos^2\theta - 1)$$

The Hamiltonian can then be expressed in term of polar coordinates given

$$|E_{\text{dipole}}| = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S h}{r^3} \left[ A + B + C + D + E + F \right].$$

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The term
\[\frac{\mu_0 h}{4\pi} \frac{1}{r^3} \gamma_I \gamma_S (Hz),\]
is known as the dipolar coupling constant which describes how large the dipolar coupling is between two nuclei at a given distance (note the \(r^3\) dependence).

Normally, only A and B need to be considered when considering dipolar coupling. As mentioned above, the dipolar coupling is on the order of kHz. The largest dipolar coupling, since it is dependent on the gyromagnetic ratios, will be \(^3\)H-\(^3\)H. The reader is encouraged to try exercises at the bottom of the page to calculate other dipolar couplings.

Obviously, the bond distance also plays a large role in the dipolar coupling, but unlike J couplings, direct bonding is not necessary for dipolar coupling to occur. Dipolar coupling becomes especially important in the elucidation of protein structure. From the dipolar coupling the distances between nuclei can be measured, which gives insight into the folding of proteins. Several pulse sequences are available to re-introduce dipolar couplings, such as REDOR and TRAPDOR. More comprehensive discussion over these sequences can be found in the 2D NMR section. Measurement of these distances occasionally becomes problematic when more than 2 sites are present. This is known as dipolar truncation, which can be avoided by selectively labeling sites.

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**Quadrupolar Treatment**

**Magnetic Field Generated from a Dipole**

Let's consider the following picture. Spin 2 is at the center of a current loop (nucleus and orbiting electrons, respectively). Then the relation of this spin to a magnetic field at point P is then the line integral from multiple expansion of

\[\vec B = \vec \nabla \times \vec A\]

\[\vec A = \frac{\mu_0 I}{4\pi} \int \frac{1}{\Omega} dl = \vec A_{mono} + \vec A_{dipole} + \vec A_{quadrupole}\]

The magnetic monopole is zero and the next largest term is the dipole contribution

\[\vec A_{\text{dipole}} = \frac{\mu \cdot \vec \mu \times r}{4\pi r^2}\]

We could also express this in the terms of operators

\[\vec A_{\text{dipole}} = I_2 \hat k = I_2 \cos \theta \hat r - I_2 \sin \theta \hat \theta\]
therefore,
\[
\vec I_2 \times \hat r = I_2 \sin \theta \hat \phi
\]
yielding
\[
\vec A_{\text{dipole}} = \frac{\mu_0 \gamma_2 \bar h I_2}{4 \pi r^2} \sin \theta \hat \phi
\]
then the dipole moment is now
\[
\vec B_{\text{dipole}} = \triangledown \times \vec A_{\text{dipole}} = \frac{\mu_0 \gamma_2 \bar h I_2}{4 \pi r^2} (2 \cos \theta \hat r + \sin \theta \hat \theta)
\]
we know that
\[
\vec I_2 = I_2 \cos \theta \hat r - I_2 \sin \theta \hat \theta
\]
and
\[
\vec I_2 \hat r = \vec I_2 \cos \theta
\]
and
\[
\vec B_{\text{Dipole}} = \frac{\mu_0 \gamma_2 \bar h I_2}{4 \pi r^3} (3 \cos \theta \hat r + \sin \theta \hat \theta - \cos \theta \hat r)
\]
\[
= \frac{\mu_0 \gamma_2 \bar h I_2}{4 \pi r^3} (3 (\vec I_2 \cdot \hat r) \hat r - \vec I_2) = \vec B_{\text{dz}}
\]
which is the coordinate free form of the dipole field from spin $I_z$ a distance $r$ away.

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Energy of The System

Now the dipolar hamiltonian corresponds to the energy of the target dipole 1 in the dipolar field $I_2$.
\[
\mu = -\gamma_1 \vec I_1 \cdot \vec B_{\text{dz}} = -\frac{\mu_0 \gamma_1 \gamma_2 \bar h}{4 \pi r^3} [3 (\vec I_1 \cdot \hat r) (\vec I_2 \cdot \hat r) - \vec I_1 \cdot \vec I_2]
\]
where
\[
\frac{\mu_0 \gamma_1 \gamma_2 \bar h}{4 \pi r^3} = \omega_D
\]
is the dipolar coupling constant. We can then re-write the dipolar Hamiltonian as
\[
[\text{H}_D = \omega_D (\vec I_1 \cdot \vec I_2 - 3 (\vec I_1 \cdot \hat r) (\vec I_2 \cdot \hat r))]
\]
where $I_1$ and $I_2$ are the operators operating on states $|m_1, m_2>$. 

Rewriting this in terms of cartesian coordinates

\[
\vec I_1 = I_{x1} \hat i + I_{y1} \hat j + I_{z1} \hat k
\]
\[
\vec I_2 = I_{x2} \hat i + I_{y2} \hat j + I_{z2} \hat k
\]
\[
\vec r = x \hat i + y \hat j + z \hat k
\]
\[
\hat r = \hat i + \hat j + \hat k
\]

and inserting these into the Hamiltonian yields:

\[
H_D = \omega_D \left[ (1 - \frac{3x^2}{r^2}) I_{x1} I_{x2} - \frac{3xy}{r^2} I_{x1} I_{y2} - \frac{3xz}{r^2} I_{x1} I_{z2} - \frac{3yz}{r^2} I_{y1} I_{z2} + (1 - \frac{3y^2}{r^2}) I_{y1} I_{y2} - \frac{3yz}{r^2} I_{y1} I_{z2} - \frac{3zx}{r^2} I_{z1} I_{x2} - \frac{3zy}{r^2} I_{z1} I_{y2} + (1 - \frac{3z^2}{r^2}) I_{z1} I_{z2} \right]
\]

which can be re-written into matrix form as

\[
H_D = \omega_D \begin{bmatrix}
    1 - \frac{3x^2}{r^2} & -\frac{xy}{r^2} & -\frac{3xz}{r^2} \\
    -\frac{3yx}{r^2} & 1 - \frac{3y^2}{r^2} & -\frac{3yz}{r^2} \\
    \frac{3zx}{r^2} & -\frac{3zy}{r^2} & 1 - \frac{3z^2}{r^2}
\end{bmatrix}
\]

\[
= \vec I_1 \cdot D \cdot \vec I_2
\]

which shows the Hamiltonian may be re-written in terms of the dot product of the two spin vectors, \(\vec I_1\) and \(\vec I_2\) via the matrix D. This matrix is a Cartesian tensor with the following properties

when x and y=0 then

\[
D = \begin{bmatrix} 1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{bmatrix}
\]

This form if D refers to all cartesian tensors and is diagonalized only in the principle axis system, which is along the internuclear vector.

The rotation into the PAS from the cartesian tensor frame is

\[
R_z(\gamma) \cdot R_y(\beta) \cdot R_z(\alpha) \cdot D \cdot R_z^{+}(\alpha) \cdot R_y^{+}(\beta) \cdot R_z^{+}(\gamma)
\]

Rotational Properties of the Hamiltonian

So far, the Hamiltonian has only been expressed in the Lab frame, which is related to the PAS through angles \(\theta\) and \(\phi\). To investigate the rotational properties of the Hamiltonian, we will convert \(\vec I_1\) and \(\vec I_2\) and \(\hat r\) in terms of spherical components.

\[
l_{\pm 1} = \mp \frac{I_{x1} \pm iI_{y1}}{\sqrt{2}}
\]
Inserting these into the derived Hamiltonian yields

\[
\hat{H}_D = \omega_D \left[ 3I_{z1}I_{z2} - \vec{I}_1 \cdot \vec{I}_2 \right] (1-3\cos^2 \theta) + X - Y - Z
\]

where

\[
X = \frac{3}{\sqrt{2}} \left[ I_{1,+1}I_{z2} + I_{z1}I_{2,+1} \right] \sin \theta \cos \theta e^{-iQ}
\]

\[
Y = \frac{3}{\sqrt{2}} \left[ I_{1,-1}I_{z2} + I_{z1}I_{2,-1} \right] \sin \theta \cos \theta e^{iQ}
\]

\[
Z = \frac{3}{2} \left[ I_{1,+1}I_{2,+1} \sin^2 \theta e^{-2iQ} - I_{1,-1}I_{2,-1} \sin^2 \theta e^{2iQ} \right]
\]

which are irreducible tensors. There for the dipolar Hamiltonian in the lab frame is just a rotation of \( T_0^{\{(2)\}} \) from the PAS! Then

\[
\hat{H}^{\text{PAS}}_D = (3I_{z1}I_{z2} - \vec{I}_1 \cdot \vec{I}_2) = \sqrt{6} \omega_D T_0^{\{(2)\}}
\]

which is related to the lab frame, which we want all interactions in the same reference frame

\[
\hat{H}^{\text{lab}}_D = D(0, \theta, \phi) \hat{H}^{\text{PAS}}_D D^+(0, \theta, \phi)
\]

Outside Links

- This is not meant for references used for constructing the module, but as secondary and unvetted information available at other site
- Link to outside sources. Wikipedia entries should probably be referenced here.

Problems

Be careful not to copy from existing textbooks. Originality is rewarded. Make up some practice problems for the future readers. Five original with varying difficulty questions (and answers) are ideal.

Contributors

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