2
NMR Interactions

Lecture notes by Assaf Tal

In the previous lecture we learned that the dynamics of a quantum system is governed by the Liouville equation:

$$\frac{d\rho}{dt} = \frac{1}{i\hbar}\left[\hat{H}, \rho\right].$$

What determines the time evolution of the system is its Hamiltonian. We've already encountered the simple Hamiltonian of a magnetic moment in an external field:

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B}(t).$$

In this chapter we will introduce the different interactions – Hamiltonians – in NMR, and try to give you a feel for their relative importance and when they can be neglected.

A Classification of Interactions

Before "rushing in" it would make sense to classify interactions somehow into subgroups. We will follow several dichotomies:

1. **Electric vs. magnetic:** Some interactions are magnetic in nature. Some derive from the electric charge distribution in the nucleus.
2. **Internal vs. external:** External interactions occur between the nuclear magnetic moments and fields created by the scientist. They are "external" in the sense that they do not originate in the microscopic environment of the spin but imposed from the "outside".
3. **Inter- vs. Intra-molecular:** some of the internal interactions occur within a molecule, while others occur between different molecules. This distinction is important in liquid state NMR, where inter-molecular interactions tend to average out to 0 while intra-molecular ones tend to remain (although this sweeping statement must be regarded with caution, as we shall see).

Interaction Magnitudes

When does an interaction become important? It is important to get a good understanding of the "magnitude" of different interactions. This makes it easier for us to neglect some interactions. Even when we want to take small interactions into account we can use an approximation called the **secular approximation**, which makes dealing with them easier.

Although the dimensions of $\hat{H}$ are those of energy – that is, Joules – we will find it much easier to think in terms of frequencies in NMR. We do this by dividing the Hamiltonian by $\hbar$:

$$\hat{H} \qquad \text{Joules}$$
$$\hat{H}/\hbar \qquad \text{Hz}$$

Let's do a simple exercise to illustrate this. In a static magnetic field $\mathbf{B} = B_0\hat{\mathbf{z}}$, for a hydrogen (spin-1/2) nucleus,

$$\hat{H} = -\hat{M}_z B_0 = -\gamma \hat{S}_z B_0 = -\frac{\gamma B_0 \hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The magnitude of the elements of $\hat{H}$ in a 3 Tesla field is:

$$\left|\frac{\gamma B_0 \hbar}{2}\right| \approx \left|\frac{2\pi \cdot 42.57 \cdot 10^6 \frac{\text{rad·Hz}}{\text{T}} \cdot (3\text{ T}) \cdot \left(10^{-34} \frac{\text{J·sec}}{\text{rad}}\right)}{2}\right|$$
$$\approx 4 \cdot 10^{-25} \text{ J}$$

These represent the energy levels of the system in question. A more physically meaningful quantity would actually be the distance between energy levels, not their absolute energy:

$$\left|\frac{\gamma B_0 \hbar}{2} - \left(-\frac{\gamma B_0 \hbar}{2}\right)\right| = \left|\gamma B_0 \hbar\right| \approx 8 \cdot 10^{-25} \text{ J}.$$

Dividing by $\hbar$, we have

$$\tfrac{1}{\hbar}\hat{H} = -\frac{\gamma B_0}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \equiv -\omega_0 I_z, \quad I_z \equiv \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The "magnitude of $\hat{H}$" now becomes

$$\left|\omega_0\right| \approx 2\pi \cdot 42.57 \cdot 10^6 \, \tfrac{\text{rad}\cdot\text{Hz}}{\text{T}} \cdot \left(3\ \text{T}\right) \approx 8 \cdot 10^8 \ \text{rad}\cdot\text{Hz} .$$

Since this is in angular frequency, we can divide by 2π radians and obtain

$$\nu_0 = \frac{\omega_0}{2\pi \cdot \text{rad}} \approx 127 \ \text{MHz} .$$

So, one might say that the magnitude of the interaction with the external static field is 127 MHz (for a proton at 3T).

Dimensionless Spin Operators

Another thing we'll do is "factor" the dimensions out of the spin operators, by defining

$$\hat{\mathbf{I}} = \tfrac{1}{\hbar} \mathbf{S} .$$

Now we have a dimensionless quantity $\hat{\mathbf{I}}$ and this means we can lump all of the parts and bits that have to do with dimensions outside the main Hamiltonian.

General Form For The Hamiltonians

Let's look at the simple and only Hamiltonian we've seen so far: the magnetic field interaction:

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B} .$$

What this means is that we've defined a "vector of matrices",

$$\hat{\mathbf{M}} = \begin{pmatrix} \hat{M}_x \\ \hat{M}_y \\ \hat{M}_z \end{pmatrix}$$

so that

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B} = -\begin{pmatrix} \hat{M}_x & \hat{M}_y & \hat{M}_z \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix} .$$

We can stick an identity matrix in the middle as well:

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B} = -\begin{pmatrix} \hat{M}_x & \hat{M}_y & \hat{M}_z \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

Many NMR interaction Hamiltonians can be put in the form:

$$\hat{H} = -\begin{pmatrix} \text{spin operators} \\ \text{vector} \end{pmatrix} \begin{pmatrix} \text{matrix containing} \\ \text{spatial variables} \end{pmatrix} \begin{pmatrix} \text{field} \\ \text{vector} \end{pmatrix}$$

Another common form is

$$\hat{H} = -\begin{pmatrix} \text{spin operators} \\ \text{vector} \end{pmatrix} \begin{pmatrix} \text{matrix containing} \\ \text{spatial variables} \end{pmatrix}$$
$$\cdot \begin{pmatrix} \text{spin operators} \\ \text{vector} \end{pmatrix}$$

Dipoles and Quadrupoles

The electric field from a static charge consists of radial field lines "emanating" from or into the charge, depending on whether it is positive or negative:
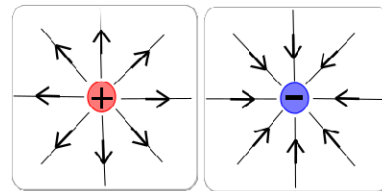

If you take two charges, positive and negative, and put them right on top of each other, they will cancel out perfectly. However, if you just put them "slightly" off one another they will create field lines that look like this:
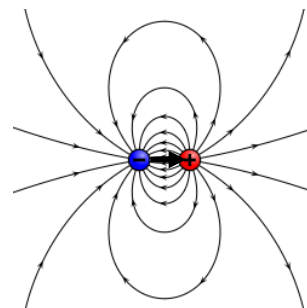
This is what's known as a dipolar field. What does "slightly" mean? It means that the separation should be much smaller than the point of observation, i.e., the field is dipolar only when we look far enough from the dipole.

Now, can we continue this reasoning and use two dipoles to "cancel out" each other? Naively we'd think that put one dipole on top of the other would do the trick. However, two dipoles means you have four charges, so they create four dipoles and they all need to cancel out. This is done by placing them like this:
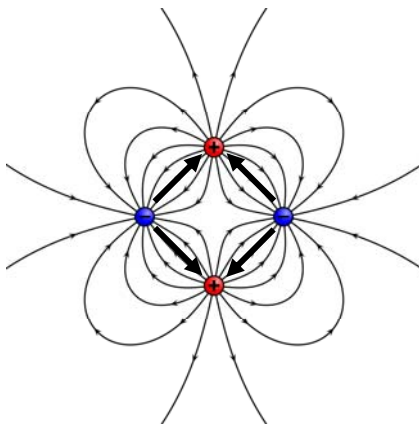
This distribution is known as a quadrupolar field. We can keep on going and create octapole moments, etc (I actually don't know what a 16-charge distribution is called).

What's the point of this discussion? After all, we're not dealing with electric fields. In fact, there aren't even any magnetic monopoles (charges). However, it turns out that the shapes of the fields appear when dealing with magnetic fields. For example, the magnetic moment of the nucleus creates a dipolar field. We will also encounter a quadrupole (electric) field. Then we will have dipolar interactions between two dipoles, etc, so it's a good idea to just keep in mind where these terms come from and what is meant by a dipolar or quadrupole field.

The Secular Approximation

All of NMR happens in an external magnetic static large field, B_0, taken to point along the z-axis. We need this field to polarize our sample, since at room temperature the nuclear spins are all randomly oriented in a macroscopic sample and

we can't detect them (the interaction with this external field is called the Zeeman interaction).

The presence of such a large B_0 field means that we can often **neglect** those parts of other interactions that aren't pointing along the direction of the main field:
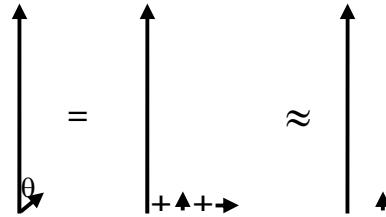
It makes sense that we can neglect a small component in the presence of a large one, but why only the perpendicular one? Here is a simple argument which, while not rigorous, will help you see where this neglect comes from. Let's write out the two vectors, assuming without loss of generality **A**, the large vector, points along z and **B**, the small vector, is in the xz plane:

$$\mathbf{A} = (0, 0, A)$$
$$\mathbf{B} = (B \sin \theta, 0, B \cos \theta)$$

Adding them,

$$\mathbf{A} + \mathbf{B} = (B \sin \theta, 0, A + B \cos \theta).$$

The size of this vector is

$$
\begin{aligned}
|\mathbf{A} + \mathbf{B}| &= \sqrt{B^2 \sin^2 \theta + (A + B \cos \theta)^2} \\
&= \sqrt{B^2 \sin^2 \theta + A^2 + 2AB \cos \theta + B^2 \cos^2 \theta} \\
&= \sqrt{A^2 + B^2 + 2AB \cos \theta} \\
&= A \sqrt{1 + 2 \left(\frac{B}{A} \right) \cos \theta + \left(\frac{B}{A} \right)^2}
\end{aligned}
$$

Now we can do a Taylor expansion:

$$\sqrt{1 + ax + bx^2} \approx 1 + \frac{ax}{2}$$

with x=B/A, a=2cos(θ) and b=1, getting

$$\left|\mathbf{A}+\mathbf{B}\right| \approx A + B\cos\theta \ .$$

We see that the magnitude of the joint vector doesn't "see" the perpendicular component. It's as if we approximated $\mathbf{B} \approx (0, 0, B\cos\theta)$ and added **A+B**. The same thing happens in the secular approximation: an expansion is made in a case where there is a large (Zeeman) interaction and a small interaction, and the end result is as if we had included only the parallel component of the interaction.

Motional Averaging

Most interactions we'll see will have some dependence on the orientation of the molecules. In isotropic liquids, the fast molecular rotational and translational diffusion tend to average out those quantities. However, some interactions will have *isotropic* parts: parts that do not depend on orientation and do not get averaged out. It's important to keep track of what "goes away" and what stays, and we shall do so.

Even when an interaction gets averaged out, it doesn't become meaningless. Averaged interactions appear as random fluctuating fields to the nuclear spin. Such stochastic external fields lead to **relaxation**: they cause the nuclear spin to return to thermal equilibrium once perturbed. They increase the entropy of the system and provide coupling to its other degrees of freedom, i.e., to a "thermal bath" An example of this is the quadrupole interaction. In liquids it gets averaged to zero. However, nuclei with non-zero quadrupole moments have very short relaxation times due to the fluctuating fields due to fast molecular motion.

External Fields

External fields refers to fields created by us, as scientists, in the lab. The general form of an interaction of a magnetic moment with an external magnetic field is

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B}_{ext} \ .$$

Zeeman (B₀) Interaction

Here $\mathbf{B}_{ext} = \mathbf{B}_0$ is a constant, static, homogeneous magnetic field created by a powerful NMR magnet:

> The sole purpose of the spectrometer is to generate a large and very stable and homogeneous magnetic field, denoted $\mathbf{B}_0$. The purpose of this field is to polarize the nuclear magnetic moments, creating a macroscopic magnetic moment which can then be detected using methods we'll discuss below.

The larger B_0, the greater the polarization and the greater the resulting signal, which is why high fields are desirable in NMR.

What makes a magnet "good"?

1. *High field.* Today's MRI magnets are about 1.5-3 Teslas, going to about 10T, while NMR magnets are about 10 T, going up to about 20 T (large bore magnets are more difficult to design, hence the difference between MRIs, with ~60 cm bore size, and NMRs, with ~cm bore size).

2. *Spatial homogeneity.* The spatial homogeneity of the magnet is probably as important as its field strength. A good magnet will have a homogeneity of about 10 ppm over the sample; that is, there will not be any spatial variations of more than 10 times a millionth of the main field. This is then brought down even further another order or two of magnitude using special additional superconducting coils during installation, as well as pieces of ferromagnetic iron placed around the main magnet, called *passive shims.*

3. *Temporal stability.* The magnetic field must remain very stable over time. A good magnet will "drift" by no more than about 10^{-7} of its

nominal value in an hour. So a 10 Tesla magnet should not change by more than a µT in an hour – again, a highly demanding spec.

4. *Weight & space*. NMR magnets tend to be large. This is unavoidable but at some point they become ridiculously so. The 10.5 T human MRI in U. Minnesota weighs 110 tons and is 4 meters in length. The 1 GHz (23.5T) Bruker Avance 1000 magnet weighs 11 tons and occupies an entire 2-floor room.

5. *Price*. We're talking science so we won't talk about the economics of MR, but this is a major factor influencing magnet economy. A great magnet will just not get manufactured if it can't make a profit.

There are three major magnet technologies:

1. *Permanent magnets* are limited at ~0.2 T. For this field, about 10 tons of ferromagnetic materials are required, making higher fields very impractical.

2. *Resistive magnets*: These magnets are based on a very simple principle: a ring of current I and radius R will generate a magnetic field perpendicular to the ring's plane at its center.

$$\mathbf{B} = \frac{\mu_0 I}{2R}\hat{\mathbf{z}} \quad \text{(at center)}$$
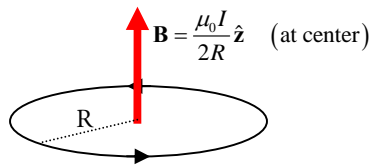
We can take a wire and make multiple turns, building up a cylindrical structure of stacked rings:
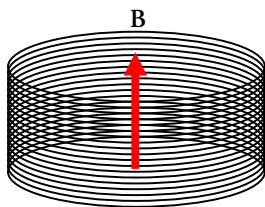
One can approximate the field along the center of such a solenoid as:

$$\mathbf{B} = \mu n I \hat{\mathbf{z}}$$

where n is the number of turns per unit length, I the current and µ is the magnetic permeability of the medium inside the coil. For empty space, $\mu = \mu_0 = 4\pi \cdot 10^{-7}$ N·A^{-2}.

Let's do a quick calculation. If we apply 1 turn per mm (1000 turns per meter) and use the maximum current one can draw from a home outlet (say, 16 A), the field created will be

B=0.02 Tesla = 200 Gauss

To contrast, the earth's average magnetic field is about 0.5 Gauss. Can we go higher? At some point the amount of current through the wires will become so high so as to melt down the wires, even with cooling.

3. *Superconducting magnets*: Today's NMR magnets can reach fields of up to ~20 Tesla. They do this by using superconducting wires, made usually out of niobium-titanium (NbTi) which can carry enormous amounts of current, around 100 A, without generating any heat. The NbTi wires are enclosed in a copper sheath to stabilize them mechanically and thermally. This enables NMR engineers to pump a great deal of current through each superconductive wire. The superconducting wires need to be kept at very low temperatures of a few Kelvins, which is achieved by submerging them in liquid helium at 4K. The modern NMR magnet is actually a very sophisticated thermos, designed to keep the Helium isolated and cool the wires to below 4K. Further layers of either vacuum or liquid nitrogen keep the temperature down and the wires protected from room temperature.

Superconducting magnets constitute the bulk of our modern MR technology. There are two design problems with superconductive magnets:

1. Whenever some small defect is introduced into the system – say, a small amount of friction – loss of superconductivity is generated and propagates throughout the magnet. This is a very violent process called **quenching**, in which the magnet suddenly heats up, dissipating the liquid helium and nitrogen it is enclosed in. These rapidly expand and can cause the magnet to explode if measures are not provided for releasing

pressure (such measures are in place in modern MR magnets, do not fear). Another problem with quenching is that it quickly eats up the oxygen in the room and can lead to suffocation if proper ventilation isn't provided. In other words, if a magnet quenches, keep your distance and call a specialized engineer.

2. A more fundamental issue is that superconducting wires can only carry a limited amount of current at a given field strength and temperature. If one desires stronger magnets, either more wire or lower temperatures are needed. Moreover, the higher the current the lower this **critical field** B_c becomes:
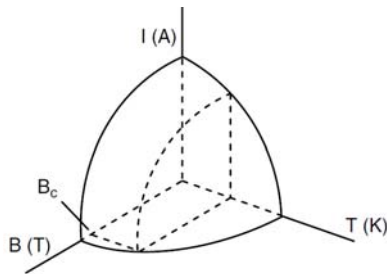
A matter of notation: magnet strengths are often not stated in Tesla but in MHz. As we've seen in chapter 1, a magnetic moment placed in a magnetic field will precess with a frequency $\omega = \gamma B_0$. What one often quotes is $\omega / 2\pi$ for protons, for which $\gamma = 2\pi \cdot 42.57$ kHz/mT. For example, when one speaks of a "500 MHz" NMR spectrometer, they mean

$$B_0 = \frac{\omega}{\gamma} = \frac{\nu}{\not\gamma} = \frac{500 \text{ MHz}}{42.57 \cdot \frac{\text{kHz}}{\text{mT}}} = 11.75 \text{ Tesla}$$

where I have defined

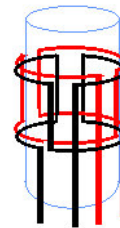$$\not\gamma \equiv \frac{\gamma}{2\pi}.$$

Radiofrequency (RF) Fields

If you look inside an NMR spectrometer you will find that through its center sits a probe. A typical one looks like this:

The sample sit on top of the probe enclosed in a coil called the RF coil. A typical RF coil might look like this (this is what's called a saddle coil):

The radiofrequency fields are created by coil wrapped around the sample. In their most simple form, they look like this:

$$\mathbf{B}_{RF}(t) = \begin{pmatrix} B_1 \cos(\omega t + \varphi) \\ 0 \\ 0 \end{pmatrix}.$$

Modern RF coils are connected to a waveform generator which actually allows almost arbitrary shaping of the envelope and phase of the RF field:

$$\mathbf{B}_{RF}(t) = \begin{pmatrix} B_1(t) \cos(\omega t + \varphi_{RF}(t)) \\ 0 \\ 0 \end{pmatrix}.$$

The typical amplitude of B_1 is limited at about 1 mT for NMR spectrometers and about 20 μT for MRI scanners. Why the difference? It has to do with the radius of the coil. We've seen that for a single loop,

$$\mathbf{B} = \frac{\mu_0 I}{2R}\hat{\mathbf{z}} \quad (\text{at center})$$

The larger R is, the smaller the field (for the same current I).

The RF coil is used to excite the magnetic moments from thermal equilibrium to facilitate their detection, and also to pick up their signal.
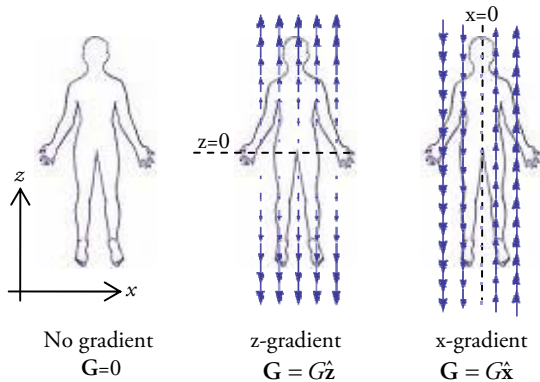
Gradient Fields

Gradient coils are wrapped around the sample to create a spatially linearly-varying magnetic field in the z-direction. So far, the RF and main fields have been spatially homogeneous. The general shape of the gradient field is:

$$\mathbf{B}_{grad}\left(\mathbf{r},t\right)=\begin{pmatrix}0\\0\\\mathbf{G}(t)\cdot\mathbf{r}\end{pmatrix}.$$

We can "shape" the gradient field by shaping $\mathbf{G}(t)$, by shaping the current passing through the gradient coils. However, they are built to always be linear in position, $\mathbf{r}$.

It is important to understand visually what sort of fields the different gradient coils generate. The following illustration focuses on the case of a human subject placed in constant gradient in an MRI scanner:

No gradient $\mathbf{G}=0$	z-gradient $\mathbf{G}=G\hat{\mathbf{z}}$	x-gradient $\mathbf{G}=G\hat{\mathbf{x}}$
$\mathbf{B}_{eff}=\begin{pmatrix}0\\0\\0\end{pmatrix}$	$\mathbf{B}_{eff}=\begin{pmatrix}0\\0\\Gz\end{pmatrix}$	$\mathbf{B}_{eff}=\begin{pmatrix}0\\0\\Gx\end{pmatrix}$

Effective field in the rotating frame for the cases of no gradient (left), z-gradient (middle) and x-gradient (right).

In all cases the gradient field superimposes a field pointing along the z-axis! This means the Larmor frequency of the spins will become position dependent. This is used extensively to perform magnetic resonance imaging (MRI), and has some further uses such as coherence pathway selection which we will only briefly touch on this course.

Typical maximal magnitudes for G are about 40 mT/m on clinical MRI scanners and up to even T/m on NMR spectrometers. This creates a linear dispersion of frequencies across the object being studied: γGL where L is the object's size. For a human body L~1 m and $\gamma GL \sim 1.7$ MHz , while for a sample, L~2 cm and $\gamma GL \sim 0.9$ MHz . In both cases maximal field dispersions are about a MHz.

Nuclear Dipolar Interactions

The Dipolar Hamiltonian

$$\frac{\hat{H}}{\hbar}=b_D\hat{\mathbf{I}}_1^{\ T}\cdot D\cdot\hat{\mathbf{I}}_2$$

where the dimensionless quantities are

$$\hat{\mathbf{I}}_1=\begin{pmatrix}\hat{I}_{1x}\\\hat{I}_{1y}\\\hat{I}_{1z}\end{pmatrix}$$

$$D=\begin{pmatrix}1-3\sin^2\theta\cos^2\varphi & 3\sin^2\theta\sin\varphi\cos\varphi & 3\sin\theta\cos\theta\cos\varphi\\3\sin^2\theta\sin\varphi\cos\varphi & 1-3\sin^2\theta\sin^2\varphi & 3\sin\theta\cos\theta\sin\varphi\\3\sin\theta\cos\theta\cos\varphi & 3\sin\theta\cos\theta\sin\varphi & 1-3\cos^2\theta\end{pmatrix}$$

$$\hat{\mathbf{I}}_2=\begin{pmatrix}\hat{I}_{2x}\\\hat{I}_{2y}\\\hat{I}_{2z}\end{pmatrix}$$

and

$$b_D\equiv\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r_{21}^3}.$$

The constant b_D really tells us how large the interaction is. For two protons about 0.2 nm apart,

$$\left|\frac{b_D}{2\pi}\right|\approx 15\text{ kHz}.$$

This is much smaller than the Zeeman interaction, which is on the order of ~0.1-1.0 GHz.

Derivation

Let's put a dipole moment $\mathbf{m}_1$ at the center of our coordinate system and orient it along the z-axis. The energy of its interaction with an external field

B is $-\mathbf{m}_1 \cdot \mathbf{B}$. Now imagine this field $\mathbf{B}_{21}$ is created by a second dipole $\mathbf{m}_2$ at the position of the first dipole:

$$\mathbf{B}_{21}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{3(\mathbf{m}_2 \cdot \hat{\mathbf{r}}_{21})\hat{\mathbf{r}}_{21} - \mathbf{m}_2}{r_{21}^3}$$

where $\mathbf{r}_{21}$ is a distance vector pointing from dipole 2 to 1, and $\hat{\mathbf{r}}_{21}$ is a unit vector in the same direction. Thus:

$$\begin{aligned} E &= -\mathbf{m}_1 \cdot \mathbf{B}_{21} \\ &= \frac{\mu_0}{4\pi} \frac{\mathbf{m}_2 \cdot \mathbf{m}_1 - 3(\mathbf{m}_2 \cdot \hat{\mathbf{r}}_{21})(\mathbf{m}_1 \cdot \hat{\mathbf{r}}_{21})}{r_{21}^3} \\ &= \frac{\mu_0}{4\pi} \frac{\mathbf{m}_2 \cdot \mathbf{m}_1 - 3(\mathbf{m}_2 \cdot \hat{\mathbf{r}}_{12})(\mathbf{m}_1 \cdot \hat{\mathbf{r}}_{12})}{r_{21}^3} \end{aligned}$$

where we've used $\mathbf{r}_{21} = -\mathbf{r}_{12}$. Now, we replace the classical moments with magnetic moment operators, and use $\hat{\mathbf{M}} = \gamma \hbar \hat{\mathbf{I}}$, to obtain

$$\begin{aligned} \frac{\hat{H}}{\hbar} &= \frac{\mu_0 \gamma_1 \gamma_2 \hbar}{4\pi r_{21}^3} \left[\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 - 3(\hat{\mathbf{I}}_2 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{r}}_{12}) \right] \\ &\equiv b_D \left[\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 - 3(\hat{\mathbf{I}}_2 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{r}}_{12}) \right] \end{aligned}$$

Now, we use spherical coordinates to represent the direction vector:

$$\hat{\mathbf{r}}_{12} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta).$$

Plugging this in, we obtain

$$\frac{\hat{H}}{\hbar} = b_D \begin{bmatrix} \hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z} \\ -3(\hat{I}_{2x}\sin\theta\cos\varphi + \hat{I}_{2y}\sin\theta\sin\varphi + \hat{I}_{2z}\cos\theta) \\ \cdot(\hat{I}_{1x}\sin\theta\cos\varphi + \hat{I}_{1y}\sin\theta\sin\varphi + \hat{I}_{1z}\cos\theta) \end{bmatrix}$$

After opening this up and collecting terms we get the form presented at the beginning of this section. Note that θ is the angle between the vector connecting the two spins and the external magnetic field, taken to be along the z-axis.

Secular Approximation

As noted before, the secular approximation means dropping out all terms not "along B_0". This means

retaining only the components containing only I_z, which considerably simplifies H:

$$\frac{\hat{H}}{\hbar} \approx b_D \left(\tfrac{3\cos^2\theta - 1}{2}\right)\left[3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \right].$$

This form works for both *homonuclear* and *heteronuclear* spins. Further simplification occurs for *heteronuclear spins*, i.e. spins belonging to different nuclei, in which case one can further approximate $\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \approx \hat{I}_{1z}\hat{I}_{2z}$ and obtain

$$\frac{\hat{H}}{\hbar} \approx b_D \left(3\cos^2\theta - 1\right)\hat{I}_{1z}\hat{I}_{2z}.$$

Motional Averaging

In isotropic liquids, molecules tumble randomly in all orientations and our intuition tells us that, at least to an extent, an orientation-dependent interaction such as dipolar coupling should average to zero. Let's take a closer look at this.

We separate dipolar interactions to three groups: intramolecular, occurring between spins in the same molecules; short range intermolecular, occurring between "close" molecules; and long-range, occurring between "far" molecules.

Looking first at intra-molecular couplings, image a diatomic molecule tumbling quickly. As the molecule tumbles, θ changes randomly:
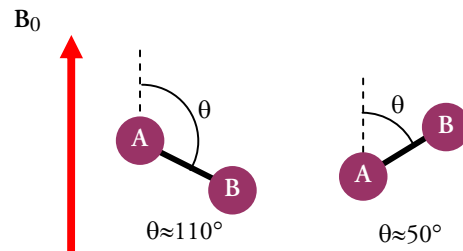
So, θ (and φ) vary randomly. However, what happens to the coefficient $3\cos^2(\theta) - 1$? Well, this coefficient does not vary symmetrically about 0:
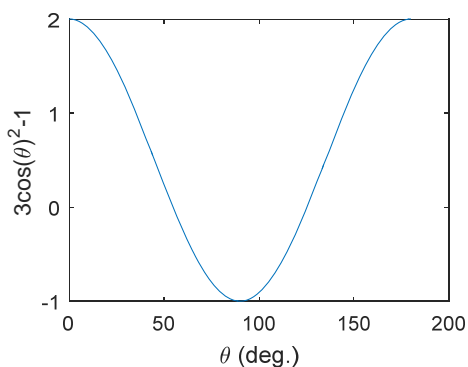
Does this pose a problem? We can only know by calculating the angular average:

$$\int \left(3\cos^2\theta - 1\right) d\Omega$$
$$= \int_0^{2\pi} \int_0^{\pi} \left(3\cos^2\theta - 1\right)\sin\theta\, d\theta\, d\varphi$$
$$= \int_0^{2\pi} \int_1^{-1} \left(3x^2 - 1\right) dx\, d\varphi$$
$$= 0$$

where we performed the substitution x=cosθ on the third line. So, the intramolecular dipolar interaction does indeed average out to 0.

Long range dipolar interactions are separated into two: short and long range. Image a "sphere" around each molecule representing the distance it diffuses during the NMR experiment:
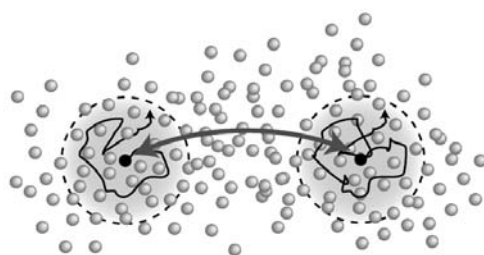
Long-range intermolecular interaction
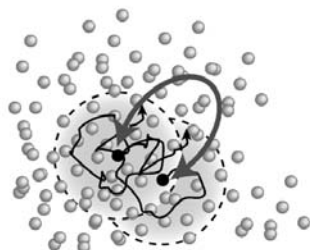
Short-range intermolecular interaction

Short range molecules basically diffuse around each other, causing θ to vary randomly in the full range [0,π], while for long range interactions θ does not vary randomly because of spatial constraints of the molecules. Thus, short range interactions get averaged out while long range ones do not. However, because $b_D \sim 1/r^3$, these interactions are very small and usually negligible in most NMR experiments.

The Chemical Shift

Origins

If you place an atom in an external constant field B_0, the electrons orbiting the nucleus will **shield** the nucleus from B_0. The field at the nucleus will therefore be $B_0 - \Delta B$. Furthermore, this shielding will be proportional to the main field: double B_0 and you also double the amount of shielding, so $\Delta B = \eta B_0$, meaning the field observed at the nucleus will be $B = (1-\eta)\cdot B_0$. This is called the **chemical shift**. Why chemical? Well, the amount of shielding, η, will depend on the electronic configuration around the nucleus; that is, on the *chemistry* of the atom or molecule. Typical magnitudes for η in proton liquid state NMR are about 10^{-5}-10^{-8}, or 0.01-10 ppm. Thus, the chemical shift is much smaller than the Zeeman interaction and, unlike many other interactions, it scales with B_0.

The physical origin of the chemical shift has to do with Faraday's. In short, Faraday's law tells us that when we place a current loop in an external magnetic field B_0, an opposing current will be generated, given by the time derivative of the magnetic flux:

$$\varepsilon_{\text{Faraday}} = -\frac{d\left(\text{magnetic flux}\right)}{dt} = -\frac{d}{dt}\int_{\text{loop}} \mathbf{B}\cdot d\mathbf{S}\,.$$

In the chemical shift effect the electrons orbiting the nucleus play the role of the current loops, which are then placed in the strong B_0 (Zeeman) field.

The chemical shift is closely related to diamagnetism, in which a material placed in an external constant field B_0 will generate a field ΔB that opposes and diminishes B_0. For example, if we place a uniform diamagnetic sphere in an external

field, the field will induce many atomic magnetic moments on the sphere's rim which will create the opposing ΔB field:
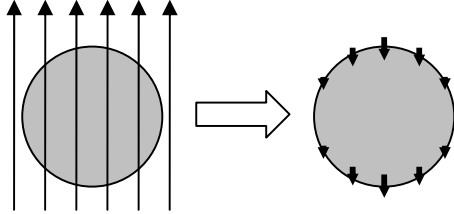
Usually $\Delta B \ll B_0$, but in extreme cases it can even match is, as is the case in super conductors, in which the magnetic field of the induced moments completely cancels out B_0 inside, known as the Meissner effect. In general we refer to the creation of a diamagnetic field opposing the main field as diamagnetic screening.

The chemical shift is non-isotropic and depends on the orientation of the molecule with respect to B_0. The simplest example is that of a benzene ring. When it is perpendicular to B_0, the aromatic electrons go around in a circle and create a magnetic field, while when it is parallel to B_0 no such current exists:
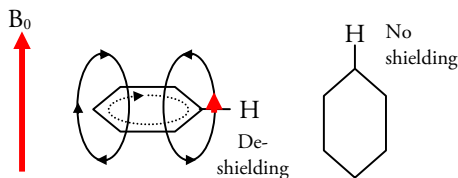
Hamiltonian

A linear, non-isotropic shift proportional to the main field can be represented by a Hamiltonian of the form

$$
\begin{aligned}
H_{cs} &= -\hat{\mathbf{M}} \cdot \mathbf{B}_{induced} \\
&= -\gamma\hbar\hat{\mathbf{I}} \cdot \boldsymbol{\sigma} \cdot \mathbf{B}_0 \\
&= -\gamma\hbar \begin{pmatrix} \hat{I}_x & \hat{I}_y & \hat{I}_z \end{pmatrix} \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}
\end{aligned}
$$

where we've assumed our external field lies along the z-axis. The matrix $\boldsymbol{\sigma}$ is called the chemical shift tensor. It depends on two things:

1. The overall shape of the electrons orbiting the nucleus.
2. The orientation of the molecule with respect to the external field $\mathbf{B}_0$.

It is a dimensionless quantity on the order of 0.01-10 ppm for protons, as noted above. It has a very simple physical interpretation:

> σ_{ij} is the field creating in the ith direction when applying an external field $\mathbf{B}$ in the jth direction (i,j=x,y,z)

For example, consider the Benzene ring shown above in its planar orientation, and the induced field felt by the proton in-plane with the ring. If we apply an external field about the z-axis, we induce a positive (de-shielding) field at the position of the proton, and hence we deduce the form of the last column is:

$$
\mathbf{B}_{ind} = \begin{pmatrix} ? & ? & 0 \\ ? & ? & 0 \\ ? & ? & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_{ext} \end{pmatrix}
$$

$$
= \begin{pmatrix} 0 \\ 0 \\ \sigma_{zz} B_{ext} \end{pmatrix}
$$

If we apply the external field about x, we generate no induced field because there is no flux through the ring, indicating the first row should be 0:


$$
\mathbf{B}_{ind} = \begin{pmatrix} 0 & ? & 0 \\ 0 & ? & 0 \\ 0 & ? & \sigma_{zz} \end{pmatrix} \begin{pmatrix} B_{ext} \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}
$$

The same goes for a magnetic field along the y-axis:

$$
\mathbf{B}_{ind} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ B_{ext} \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}
$$

So here we have our chemical shift tensor. The exact value of σ_{zz} will depend on the shape of the ring, distance of the proton from it, etc ...

It is obvious from the above discussion that the chemical shift tensor depends on the orientation of the molecule with respect to the external field B_0. For example, if we have repeated the same exercise for a benzene ring parallel to the field, we would have gotten a somewhat different answer:

$$\mathbf{B}_{ind} = \begin{pmatrix} ? & ? & 0 \\ ? & ? & 0 \\ ? & ? & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ B_{ext} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\mathbf{B}_{ind} = \begin{pmatrix} \sigma_{xx} & ? & 0 \\ 0 & ? & 0 \\ 0 & ? & 0 \end{pmatrix}\begin{pmatrix} B_{ext} \\ 0 \\ 0 \end{pmatrix}$$
$$= \begin{pmatrix} \sigma_{xx}B_{ext} \\ 0 \\ 0 \end{pmatrix}$$

$$\mathbf{B}_{ind} = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ B_{ext} \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$
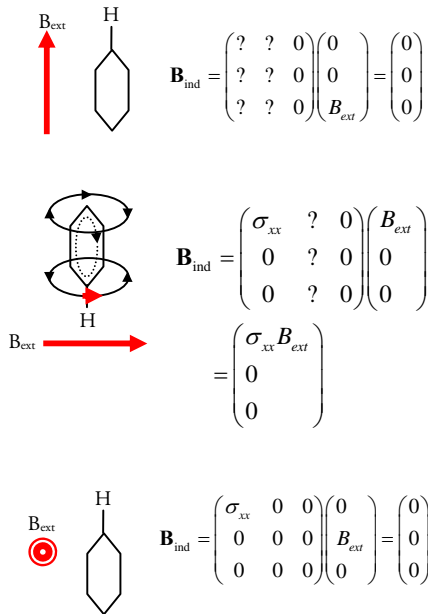
It should be clear that $\sigma_{xx} = \sigma_{zz}$ in these two cases since all we did was rotate the problem. In general, $\boldsymbol{\sigma}$ will be a function of the orientation of the molecule with respect to the main field.

Secular Approximation

The chemical shift is much smaller than the Zeeman interaction and we can apply the secular approximation to it. This means we will only retain the component of the induced field which is parallel to B_0:

$$\mathbf{B}_{ind} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} = \begin{pmatrix} \sigma_{xz}B_0 \\ \sigma_{yz}B_0 \\ \sigma_{zz}B_0 \end{pmatrix} \approx \begin{pmatrix} 0 \\ 0 \\ \sigma_{zz}B_0 \end{pmatrix}$$

Thus, the Hamiltonian becomes:

$$H_{cs} = -\hat{\mathbf{M}} \cdot \mathbf{B}_{induced} \approx -\gamma\hbar\sigma_{zz}(\Theta)B_0$$

where the notation $\sigma_{zz}(\Theta)$ reminds us that the coefficients of the chemical shift tensor depend on the orientation of the molecule with respect to the main field.

Motional Averaging

What happens to the chemical shift as we average over all orientations? Does it disappear like the dipolar interaction? Well, no.

The energy of a system cannot depend on the orientation of the system it is described in. Therefore,

$$H_{cs} = -\mathbf{m} \cdot \mathbf{B}_{ind} = \mathbf{m}^T \mathbf{B}_{ind}$$

is coordinate-independent. Using $\mathbf{B}_{ind} = \boldsymbol{\sigma}\mathbf{B}_{ind}$,

$$H_{cs} = \mathbf{m}^T \boldsymbol{\sigma}\mathbf{B}_{ind} .$$

This should have the **same** numerical value in another coordinate system:

$$H_{cs} = \mathbf{m}^{T}\,'\boldsymbol{\sigma}'\mathbf{B}_{ind}\,' = \mathbf{m}^T \boldsymbol{\sigma}\mathbf{B}_{ind} .$$

Now, we know how vectors transform

$$\mathbf{m} \to R\mathbf{m}, \qquad \mathbf{m}^T \to (R\mathbf{m})^T = \mathbf{m}^T R^T$$
$$\mathbf{B} \to R\mathbf{B}$$

so

$$H_{cs} = \mathbf{m}^T R^T \boldsymbol{\sigma}'R\mathbf{B}_{ind} = \mathbf{m}^T \boldsymbol{\sigma}\mathbf{B}_{ind} .$$

Comparing these two expressions, which must be true for any combination of vectors and matrices, we deduce that

$$R^T \boldsymbol{\sigma}'R = \boldsymbol{\sigma}$$

or (multiplying by R from the left and R^T from the right):

$$\boldsymbol{\sigma}' = R\boldsymbol{\sigma}R^T ,$$

which gives us the transformation rule for any 3×3 tensor. This means that as the molecule reorients, the chemical shift tensor changes as $R\boldsymbol{\sigma}R^T$. Now, note that

$$\mathrm{tr}\left(R\boldsymbol{\sigma}R^{T}\right)=\mathrm{tr}\left(R^{T}R\boldsymbol{\sigma}\right)=\mathrm{tr}\left(\boldsymbol{\sigma}\right)$$

The trace of the chemical shift tensor does not change as a function of time, even though we reorient our system. I will not prove it explicitly here, but this **invariant** quantity of the tensor is the only one that survives under motional averaging:

$$\sigma\xrightarrow[\text{averaging}]{\text{motional}}\sigma_{iso}=\begin{pmatrix}\frac{\mathrm{tr}(\boldsymbol{\sigma})}{3}&0&0\\0&\frac{\mathrm{tr}(\boldsymbol{\sigma})}{3}&0\\0&0&\frac{\mathrm{tr}(\boldsymbol{\sigma})}{3}\end{pmatrix}.$$

So, under motional averaging and the secular approximation,

$$H_{cs}\approx-\gamma\hbar\tfrac{1}{3}\mathrm{tr}\left(\boldsymbol{\sigma}\right)B_{0}.$$

Atomic Mass Increases the Range of Chemical Shifts

Heavier atoms have a wider range of chemical shifts (in ppm) because of the existence and contribution of lower lying electronic states. The range of chemical shifts is about 10 ppm for protons (^{1}H), about 200 ppm for carbon (^{13}C), and many thousands for lead (^{209}Pb).
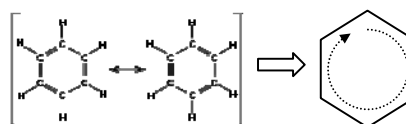
Local vs Non-Local Shielding

Local shielding is the "simplest" kind of shielding that results from electron currents surrounding the nucleus. Here the main factor influencing the amount of shift for different groups is the electron density around the nucleus. Nearby groups will withdraw electrons from a nucleus, an effect known as **electronegativity**. Some groups/atoms do so more than others. For example, consider what happens to the chemical shift of the protons of a CH_3 group as we attach different atoms to the remaining C bond:

X atom (CH_3X)	Predicted ppm	Electronegativity
H	0.23	2.3
I	2.16	2.4
Br	2.68	2.7
Cl	3.05	2.7
OH	3.4	O=3.6
F	4.26	4.2

The higher the electronegativity the more it "draws" electrons, the less shielded the methyl H nuclei become, the higher their resonance frequency (and ppm).

high ppm ←$\overset{\text{more electronegative neighbors}}{\underset{\text{less shielding}}{}}$— low ppm
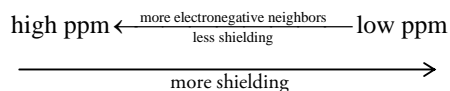
more shielding →

Another form of local shielding comes from **resonance** (aka mesomerism). Here, electrons are delocalized and withdrawn from an atom. This is a non-local effect (although the shielding is local, because the effect is directly applied to the electrons orbiting the nucleus in question). An example of this is a benzene ring in which there are two resonant structures which alternate between them and cause an electron current in the ring:

A third effect is **hybridization**, in which orbitals change their shape upon being combined in molecules, making electrons move closer or farther away from the nucleus and changing their effective shielding.

Non-local shielding, on the other hand, refers to non isotropic electron distributions that can also affect the chemical shift of far-away nuclei. Let's first think about an isotropic electron distribution. The diamagnetic shielding currents induced by the external magnetic field to not change as we rotate the molecule because, well, it's isotropic! However, if we think about what happens to an attached nucleus – say, a proton – then this proton is occasionally shielded and occasionally deshielded:

H shielded   H de-shielded
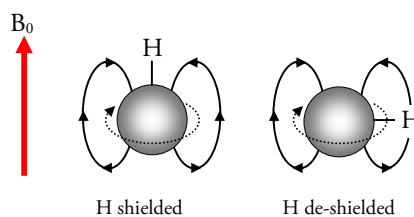
Scalar (Spin-Spin, J) Coupling

Origins (Direct Coupling)

The scalar coupling, also called J-coupling, is independent of the field B_0. It is an interaction between two nuclear moments mediated by their joint electronic structure (chemical bond). Consider for example a ^{1}H-^{13}C bond:
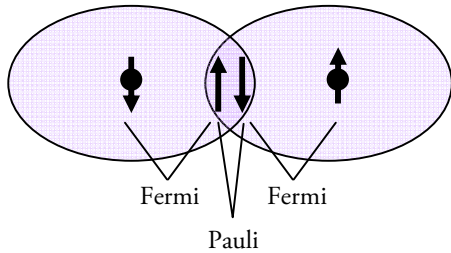
It thus stems from two types of interactions acting in unison:

1. Electron A's magnetic dipole moment creates a non-zero magnetic field at the position of nucleus A. This is called the **Fermi contact interaction**, because it is proportional to the probability of finding the electron at the nucleus, which is non-zero for *s*-states.
2. Electron A and B have opposite magnetic moments because of **Pauli's exclusion principle**.
3. Finally, electron B creates a non-zero magnetic field at the position of nucleus B.

Both the chemical shift and J-coupling tie in NMR closely with chemistry: the first via the electron cloud, and the second via electronic (chemical) bonds. Both are **intramolecular** interactions.

J-coupling is also dependent on the molecule's orientation, much like the dipolar interaction. As the molecule physically rotates the nuclear spin remains unchanged, which means that, like the dipolar interaction, J-coupling is described by a tensor.

Origins (Geminal & Vicinal Coupling)

J-couplings extend over more than one bond. For example, in a ^{1}H-^{12}C-^{1}H covalent bond the outer electrons of the carbon "merge" with the electron cloud of the hydrogen. Due to Hund's rule, the electronic spins of the carbon's electrons (which are closer to the carbon nucleus due to its charge)

tend to remain parallel to minimize the system's energy:
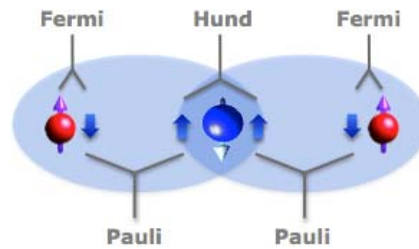
This has an interesting consequence: J-coupling coefficients

Hamiltonian

The J-coupling hamiltonian is

$$\frac{H_J}{\hbar} = 2\pi \hat{\mathbf{I}}_1 \cdot \mathbf{J} \cdot \hat{\mathbf{I}}_2$$

where $\mathbf{J}$ is the J-coupling tensor

$$\mathbf{J} = \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix}.$$

The elements of the tensor $\mathbf{J}$ have dimensions of frequency (Hz).

Motional Averaging

After averaging only the trace survives, much like with the chemical shielding tensor:

$$\mathbf{J} \xrightarrow{\text{motional averaging}} \mathbf{J}_{iso} = \begin{pmatrix} \frac{\text{tr}(\mathbf{J})}{3} & 0 & 0 \\ 0 & \frac{\text{tr}(\mathbf{J})}{3} & 0 \\ 0 & 0 & \frac{\text{tr}(\mathbf{J})}{3} \end{pmatrix}$$

Substituting this back into the Hamiltonian:

$$\begin{aligned} \tfrac{1}{\hbar} \hat{H}_J &= 2\pi \tfrac{\text{tr}(\mathbf{J})}{3} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \equiv 2\pi J \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \\ &= 2\pi J \left(\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z} \right). \end{aligned}$$

The full matrix form of this Hamiltonian for two spin-1/2s is

$$\frac{1}{\hbar}\hat{H}_J = \begin{pmatrix} \frac{\pi J}{2} & 0 & 0 & 0 \\ 0 & -\frac{\pi J}{2} & \pi J & 0 \\ 0 & \pi J & -\frac{\pi J}{2} & 0 \\ 0 & 0 & 0 & \frac{\pi J}{2} \end{pmatrix}$$

Typical values for hydrogen couplings are:

Bond	Name	Magnitude
H-H	direct	$^1J \approx 275$ Hz
H-C-H	geminal	$^2J \approx 5\text{-}10$ Hz
H-C-C-H	vicinal	$^3J \approx 5\text{-}20$ Hz
H-C-C-C-H	N/A	$^4J \approx$ Usually too small
H-C-C-C-C-H	N/A	$^5J \approx$ Usually too small

The Sign of J

Note also that an **odd** number of bonds leads to positive J-coupling coefficients, while an even number leads to a negative value (i.e. for an even number of bonds the minimum energy configuration is obtained when both nuclear spins are parallel, meaning that for H to be minimal J must be negative).

Secular Approximation

J-coupling exists between two spins, each with its own resonant frequency:

$$\frac{1}{\hbar}\hat{H} = \omega_1 \hat{I}_{1z} + \omega_2 \hat{I}_{2z} + 2\pi J \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 .$$

The secular approximation for the J-coupling Hamiltonian is such that when the difference in chemical shifts is much larger than J:

$$|\omega_2 - \omega_1| \gg J .$$

In this case

$$\frac{1}{\hbar}\hat{H}_J \approx 2\pi J \hat{I}_{1z}\hat{I}_{2z} .$$

For two spin-halves,

$$\frac{1}{\hbar}\hat{H}_J = \begin{pmatrix} \frac{\pi J}{2} & 0 & 0 & 0 \\ 0 & -\frac{\pi J}{2} & 0 & 0 \\ 0 & 0 & -\frac{\pi J}{2} & 0 \\ 0 & 0 & 0 & \frac{\pi J}{2} \end{pmatrix}$$

secular + motional averaging

The Karplus Equation

J is not just an annoying constant that splits lines, but can actually convey useful information and assist in analysis and peak assignment. For lactate, J-coupling assisted us in assigning peaks to chemical groups, since we knew the CH should yield four lines (split three times by CH_3) while CH_3 should yield two lines (split once by CH). This helped us assign the resonances in the spectrum without even knowing anything about their chemical shift a-priori.

The value of the J-coupling constant can yield structural information about a molecule. A scientist by the name of Martin Karplus found an empirical relation between the magnitude of vicinal (3-bond) $^3J_{HH}$ couplings and the dihedral angle ϕ of the bonds:
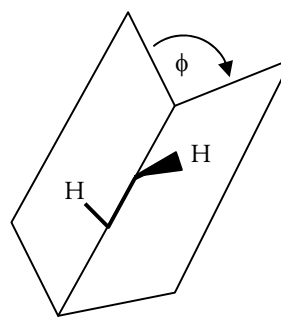

$$^3J(\phi) = A\cos^2(\phi) + B\cos(\phi) + C$$

Basically, each plane is defined by the C-C bond and the corresponding C-H bond, and ϕ is the angle between the two planes. The Karplus curve usually looks something like:
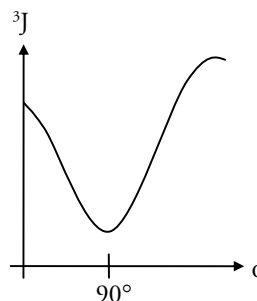

The idea is that the overlap between molecular orbitals – and hence the strength of the exchange interaction – varies when the angle ϕ changes. The

overlap is minimal when the wavefunctions are orthogonal, so ^3J tends to be smallest when $\phi=90°$.

The **Karplus equation** (above) is a major tool in structural chemistry. For example, the vicinal coupling changes between cis and trans configurations of double-bond alkenes:

<div align="center">cis   trans</div>
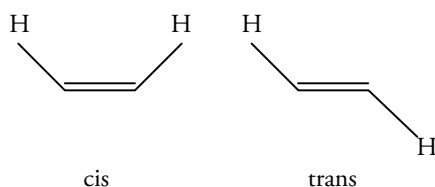
This difference is seen for example in 1,1-difluoroethylene:
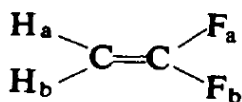
The ^3J coupling constant of H_a to F_b (trans) is different from the coupling of H_b to F_b (cis).

Incidentally, Karplus's original JACS paper from 1963 remains one of the journal's most cited papers of all time, and Karplus himself is a notable theoretical chemist who won the 2013 nobel prize (although not for his NMR work, but for his theoretical chemical modeling work).

Electron-Nuclear Interactions

Orbital Angular Momentum

The classical picture of the electron is one in which it orbits the nucleus in a circle or ellipse. This is similar to a loop of current which, as we've remarked, creates a magnetic moment associated with the electrons' orbital motion. However, we do not actually see this in molecules or solids due to a phenomenon known as **quenching of the orbital angular momentum**, in which the atoms in most molecules do not have orbital angular momentum. This surprising fact shows up also when trying to understand e.g. transition metal solids. We will not discuss its origins here and simply state it as a fact and assume it to be so (which is true for the vast majorities of systems you will encounter in NMR, and more so in liquid state NMR).

Paramagnetic Interactions

Most materials studied in NMR are diamagnetic. Their total electronic spin is zero due to the Pauli exclusion principle: electron spins line up in anti-parallel pairs and cancel each other out. When this doesn't happen – i.e., in paramagnetic materials – one must taken into account the paramagnetic interactions between a nuclear and an electron (intrinsic) spin. Typical Hamiltonian magnitudes are in the ~100 kHz range. Examples of paramagnetic materials include liquid oxygen (O_2), or proteins with metal coordination complexes such as myoglobin.

We will not deal with paramagnetic NMR in this course.

Chemical Shift

We've already treated the chemical shift interaction. To be consistent, it should also be classified as an electron-nucleus interaction.

Spin-Rotation Interactions

As a molecule rotates its electrons rotate as well, creating effective currents which will also interact with the nucleus. Except in gases, this is in general a negligibly small interaction which we will not describe in this course.

Quadrupolar Interaction

Spins > ½ have a non-spherically symmetric charge distribution in the nucleus. This distribution interacts with the electrical field gradients created by the electrons. This is called the quadrupolar interaction. But where does the magnetic moment come in? For reasons we will not go into here, this interaction *appears* magnetic, as if having to do with coupling of the nuclear magnetic moment to itself. As far as I know there is no semi-classical derivation of this, and this is a completely QM phenomenon[1].

The quadrupolar Hamiltonian is:

$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{\mathbf{I}} \cdot \mathbf{V}(\Theta) \cdot \hat{\mathbf{I}}$$

---

[1] If you, the knowledgeable and/or resourceful reader, can semi-classically derive the quadrupolar Hamiltonian without invoking the Wigner-Eckart theorem, you're getting a straight A in this course.

e is the electron's charge, and Q is the quadrupole moment of the nucleus in question:

Nuclide	Spin I	Quadrupole moment $Q/10^{-28}\,\mathrm{m}^2$
^{2}H	1	$2{\cdot}8 \times 10^{-3}$
^{6}Li	1	-8×10^{-4}
^{7}Li	$\frac{3}{2}$	-4×10^{-2}
^{10}B	3	8.5×10^{-2}
^{11}B	$\frac{3}{2}$	$4{\cdot}1 \times 10^{-2}$
^{14}N	1	1×10^{-2}
^{17}O	$\frac{5}{2}$	$-2{\cdot}6 \times 10^{-2}$
^{35}Cl	$\frac{3}{2}$	$-0{\cdot}10$
^{37}Cl	$\frac{3}{2}$	$-7{\cdot}9 \times 10^{-2}$
^{59}Co	$\frac{7}{2}$	$0{\cdot}38$
^{75}As	$\frac{3}{2}$	$0{\cdot}29$
^{127}I	$\frac{5}{2}$	$-0{\cdot}79$
^{133}Cs	$\frac{7}{2}$	-3×10^{-3}
^{181}Ta	$\frac{7}{2}$	3

The matrix V is the electric field gradient matrix (EFG), having units of volt per meter^2. It basically is comprised of the second order derivatives of the field potential:

$$\mathbf{V} = \begin{pmatrix} \partial_{xx}V & \partial_{xy}V & \partial_{xz}V \\ \partial_{yx}V & \partial_{yy}V & \partial_{yz}V \\ \partial_{zx}V & \partial_{zy}V & \partial_{zz}V \end{pmatrix}$$

where

$$\partial_{ij}V \equiv \frac{\partial^2 V}{\partial x_i \partial x_j}, \qquad i,j = x,y,z\,.$$

Secular Approximation

For most nuclei (but not all!) the secular approximation is justified. Under this approximation, the Hamiltonian has the general form:

$$H_Q^{(1)} = \omega_Q \tfrac{1}{2}\left(3\cos^2\theta - 1\right)\left(3\hat{I}_z^2 - I(I+1)\hat{I}\right)$$

Motional Averaging

The secular approximation exhibits the same sort of angular dependence as the dipolar approximation, and hence gets averaged to zero under motional averaging. Even without motional averaging, the trace of the electric field gradient tensor is zero and as such it gets averaged to zero in liquids.

Interaction	Hamiltonian $\left(\hat{H}/\hbar\right)$	Typical Magnitudes (Maximum)
Zeeman	$\frac{1}{\hbar}\hat{\mathbf{M}}\cdot\mathbf{B}_0 = -\omega_0\hat{I}_z$	$\omega_0=2\pi\cdot 127$ MHz (^{1}H at 3 T) $\omega_0=2\pi\cdot 30$ MHz (^{13}C @ ~3 T) $\omega_0=2\pi\cdot 500$ MHz (^{1}H @ ~11 T)
RF field	$-\frac{1}{\hbar}\hat{\mathbf{M}}\cdot\mathbf{B}_{RF}(t)$ $= -\gamma B_1\begin{bmatrix}\cos\left(\phi_{RF}(t)\right)\hat{S}_x \\ -\sin\left(\phi_{RF}(t)\right)\hat{S}_y\end{bmatrix}$	$\omega_1=2\pi\cdot 1$ kHz (Proton at peak B_1 in clinical MRI scanner)
Gradient field	$-\frac{1}{\hbar}\hat{\mathbf{M}}\cdot\mathbf{B}_{grad}(\mathbf{r},t) = -\left(\gamma\mathbf{G}(t)\cdot\mathbf{r}\right)\hat{I}_z$	$\Delta\omega_g = \gamma G\Delta z \sim 100$ kHz (over head in clinical MRI) $\Delta\omega_g = \gamma G\Delta z \approx 1$ MHz (over NMR sample tube)
Chemical Shift	General form: $\hat{H} = -\frac{1}{\hbar}\hat{\mathbf{M}}\cdot\mathbf{B}_{induced}$ where $\mathbf{B}_{induced} = \boldsymbol{\delta}(\Theta)\mathbf{B}_0 = \begin{pmatrix}\delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz}\end{pmatrix}\mathbf{B}_0$ In isotropic liquids: $\hat{H}_{cs} = -\delta_{iso}\omega_0\hat{I}_z$	$\delta\sim 10^{-6}$ (ppm) Protons at 3 T: 1 kHz
Electric Quadrupole	$\omega_Q\hat{\mathbf{I}}\cdot\mathbf{V}(\Theta)\cdot\hat{\mathbf{I}}$ Secular approximation: $H_Q^{(1)} = \omega_Q^{(1)}\left(3\hat{I}_z^2 - I(I+1)\hat{I}\right)$	
Dipolar	$b_{jk}\left(3\left(\hat{\mathbf{I}}_j\cdot\hat{\mathbf{r}}_{jk}\right)\left(\hat{\mathbf{I}}_k\cdot\hat{\mathbf{r}}_{jk}\right) - \hat{\mathbf{I}}_j\cdot\hat{\mathbf{I}}_k\right)$ Secular approximation, homonuclear spins: $d_{jk}\left(3\hat{I}_{jz}\hat{I}_{kz} - \hat{\mathbf{I}}_j\cdot\hat{\mathbf{I}}_k\right)$ Secular approximation, heteronuclear spins: $d_{jk}2\hat{I}_{jz}\hat{I}_{kz}$ where $d_{jk} = b_{jk}\dfrac{3\cos^2\Theta_{jk}-1}{2}$, and Θ_{jk} is the angle between the vector joining the two spins and the external magnetic field.	Two protons 0.2 nm apart: $\left\vert\dfrac{b_{jk}}{2\pi}\right\vert \approx 15$ kHz
Spin rotation	Unimportant in liquids and solids.	
J-Coupling	$2\pi\hat{\mathbf{I}}_j\cdot\mathbf{J}_{jk}\cdot\hat{\mathbf{I}}_k$ Isotropic liquids: $2\pi J\hat{I}_{jz}\hat{I}_{kz}$	$J\sim 1$-100 Hz for protons coupled to other nuclei
Paramagnetic Shift	Interaction with unpaired electronic magnetic moments.	~50-100 kHz