When an atomic nucleus is placed in a magnetic field, the ground state will split into different energy levels proportional to the strength of the magnetic field. This effect is known as Zeeman splitting. While the Zeeman interaction is useful for identifying different types of nuclei placed in magnetic fields, structural and dynamic information may be obtained by considering other magnetic and electronic interactions coupling with the nucleus. These interactions are perturbations to the Zeeman interaction. The full NMR Hamiltonian may therefore be expressed as

$$\hat{H} = \hat{H}_{\text{Zeeman}} + \hat{H}_J + \hat{H}_{\text{CS}} + \hat{H}_{\text{DD}} + \hat{H}_Q$$

where $\hat{H}_{\text{Zeeman}}$ is the Zeeman interaction, $\hat{H}_J$ is the $J$ coupling, $\hat{H}_{\text{CS}}$ is the chemical shift coupling, $\hat{H}_{\text{DD}}$ is the dipolar coupling, and $\hat{H}_Q$ is the quadrupolar coupling. The relative magnitude of these interactions is shown in the table below. The Zeeman interaction is the largest, followed by the quadrupolar interactions which are on the order of MHz. The chemical shift and the dipolar coupling are on the order of kHz while the scalar coupling is the smallest which is only tens of Hz. Clearly, some of these interactions are more pronounced than others.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Magnitude (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeeman</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Quadrupolar</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Chemical Shift</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Dipole</td>
<td>$10^3$</td>
</tr>
<tr>
<td>$J$</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1. Magnitude of different NMR interactions

In the liquid state, the dipolar and anisotropic contribution to the chemical shift are averaged due to the molecular reorientation occurring in liquids. The averaging of these interactions gives the characteristically narrow isotropic peaks. Additionally, liquid state NMR primarily looks at spin $\frac{1}{2}$ nuclei ($^{13}\text{C}$, $^1\text{H}$) which eliminates any quadrupole interactions. Only the $J$ coupling and isotropic part of the chemical shift remains. In the solid state, molecular reorientation does not occur and the solids may have a variety of bond lengths and angles of a given chemical site. These factors broaden in the NMR spectrum with the broadest peaks over 1MHz wide!

Chemical Shift

The most commonly investigated interaction in both liquid and SSNMR is chemical shift. The chemical shift is used to differentiate between chemically inequivalent sites. Chemical inequivalence is due to a variety of phenomena, such as differences in bond lengths and angles, bonding to different atoms, bond types and coordination environments. Chemical inequivalence is caused by changes to the local electronic environment surrounding the nucleus.
Figure 1. $^{13}$C spectrum of ethanol. The carbon peaks are at 18 and 58 ppm, while the reference compound is assigned a chemical shift of zero. The two peaks are due to the chemical inequivalence of the local electronic structure surrounding the nucleus.

In the solid state, any asymmetry of the chemical shift will give broad lineshapes. As electronic and magnetic effects are coupled, it is not surprising that the electronic interactions affect the NMR signal. Passing a current through a loop of wire generates a magnetic field perpendicular to the direction of the applied current. Similarly, electrons, which have charge (current) and orbit (loop) the nucleus, create a magnetic field. This magnetic field can either enhance or diminish the externally applied magnetic field, $B_0$, the nucleus experiences. Consequently, the energy needed to promote a nuclear transition will change. This is the basis of chemical shift. Often scientists use different terms to describe relative peak positions. The figure below illustrates these relative terms and some common axes with the arrows denoting the direction a given parameter increases.

Figure 2. Graphic representation of different terms and units commonly used to describe relative chemical shifts. The arrows denote the direction in which the quantity increases.

J Coupling

This is also known as scalar coupling or spin spin coupling. By analyzing the chemical shift in NMR spectra, we can know some information of the molecular fine structure. To know more information about fine structure of molecule, spin-spin coupling can be introduced as a useful source. Since each nucleus can be thought of as a small magnet, the orientation of that magnet has an effect on the local magnetic field experienced by other nuclei. The J coupling is mediated through bonds. An NMR peak will split into $N+1$ peaks, where $N$ is the number of NMR active nuclei within 3 chemical bonds. A peak is not split by chemically equivalent nuclei! An example of this is shown below for ethyl acetate. The blue methyl hydrogens exhibit a peak at 1.3ppm. These 3 hydrogens are J-coupled to the 2 red hydrogens resulting in 3 peaks for the blue hydrogens.
Dipolar Coupling

Dipolar coupling is a through-space coupling of two NMR active nuclei. Simply put, the dipolar coupling is the magnetic effect on nucleus 1 due to the magnetic field generated by nucleus 2. This is different from J couplings, which are through-bond couplings. The dipolar coupling of spins is either between two of the same nuclei (homonuclear dipolar coupling) or between two different nuclei (heteronuclear dipole coupling). The natural abundance of the NMR active nuclei and the space between the nuclei directly influence the size of the dipolar coupling in solid systems. For magnetically dilute systems, such as $^{13}\text{C}$, the chance that 2 NMR active nuclei are close to one another is small and the dipolar coupling can be neglected. The distance between the two nuclei also affects the magnitude of the interaction. As the distance between two magnets is increased, the interaction between them diminishes.

Quadrupolar Coupling

A majority of NMR active nuclei are not spin $^{1/2}$. In these cases the quadrupolar coupling must be considered. Just as
the nucleus contains a magnetic dipole moment, it also contains an electric quadrupolar moment. This quadrupolar moment interacts with electric field gradients (EFG) generated by uneven charge distribution within the nucleus. The coupling of the quadrupolar moment and the EFG are known as the quadrupolar coupling. For a spin $^{1/2}$ system, the charge is spherically distributed about the nucleus and consequently no quadrupolar coupling is observed. As shown in the figure, when the spin $>^{1/2}$, the charge distribution in the nucleus is no longer spherical and quadrupolar coupling occurs.

![Figure 5. Graphical depiction of the charge distribution between a spin 1/2 (red) nucleus and a quadrupolar nucleus (green).](image)

This distribution of charge gives rise to the quadrupolar coupling. Shown below is a $^{87}$Rb ($I=3/2$) spectrum which has been broadened by quadrupolar broadening. The magnitude of the broadening masks any information about chemical shift, j-coupling, or dipolar coupling.

![Figure 6: A $^{87}$Rb spectrum broadened due to quadrupolar interactions.](image)

References

Outside Links

2. http://www2.mpip-mainz.mpg.de/docume...teractions.pdf

Contributors

• Derrick Kaseman (UC Davis)