

Review notes

CHEM 3013 HPO

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1 Liquids and solids

NMR in its most simple form concerns nuclear spins and their interactions. Evolution of a spin system $|\psi\rangle$ evolves according to the Schrödinger wave equation, where the hamiltonian \hat{H} describes the interaction.

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle \quad (1)$$

Often these interactions vary with the orientation of the molecule to the main magnetic field (they are said to be anisotropic).

Anisotropic interactions vary with orientation.

Isotropic interactions are uniform with orientation.

In solution NMR, molecules are dissolved in a solvent and undergo rotational diffusion. This means each molecule tumbles randomly, over time sampling all orientations uniformly. Molecules typically rotate on a timescale of 1 ns, which is much faster than most nuclear spin interactions take to evolve. This means that any orientation dependent interactions will only be observable as an average of all orientations.

In solid-state NMR, molecules are oriented statically with the main magnetic field. If the solid sample is a powder, it will contain all orientations uniformly within the population. Anisotropic interactions will thus be visible as a distribution within the spectrum.

In solution state, anisotropic interactions are averaged by rotation diffusion.

2 Tensors

For the purposes of this course, a tensor is just a transformation that takes a vector to some new vector.

If we apply a magnetic field vector \vec{B}_0 to a molecule, what is the resultant vector of the induced field \vec{B}_{ind} ? A tensor σ can describe this transformation.

$$\vec{B}_{\text{ind}} = \sigma \cdot \vec{B}_0 \quad (2)$$

Most spin interactions in NMR can be represented by a real symmetric 3×3 matrix. The matrix is symmetric because it equals its transpose $\sigma = \sigma^T$, i.e. elements opposite the diagonal are equal. A theorem from linear algebra tells us that all real symmetric matrices are diagonalisable by some

rotation matrix R as in equation 4. In this special orientation, the values along the diagonal are called *eigenvalues*. The columns that form the rotation matrix R are called the *principle axes* of the tensor and are orthonormal.

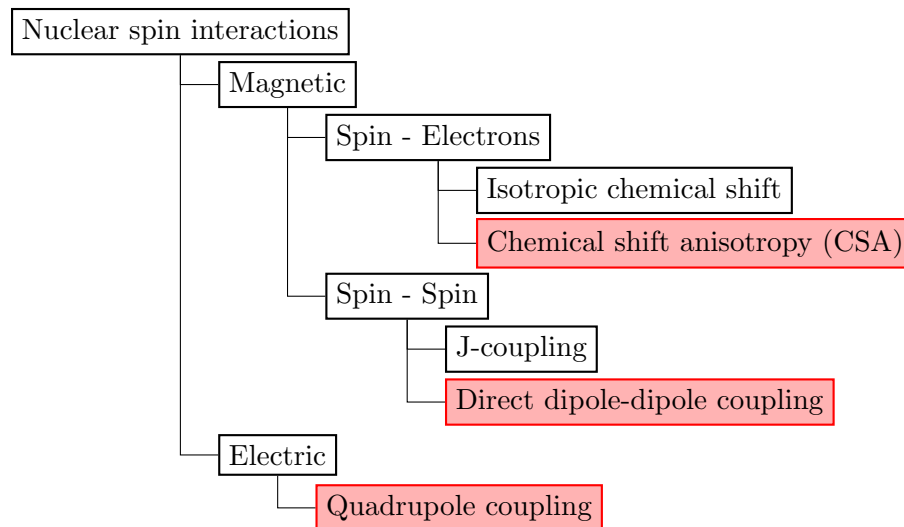
$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{bmatrix} \quad (3)$$

$$= R \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix} \cdot R^{-1} \quad (4)$$

A tensor is a vector transformation that can be represented by a matrix. This matrix has a diagonal form which is characterised by 3 eigenvalues and 3 principle axes.

3 Spin interactions overview

Interactions shown in red are anisotropic and are not usually observable in solution NMR.



In these notes, interactions between spin operators \hat{L} or \hat{S} will be considered as well as with the external magnetic field vector \vec{B}_0 . An operator is just a vector that acts on the spin system $|\psi\rangle$ to alter it in some way. In cartesian coordinates, this vector could look like this:

$$\hat{L} = \begin{bmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{bmatrix} \quad (5)$$

From these operators we can construct Hamiltonians \hat{H} to calculate an the evolution of spins for

an NMR experiment using equation 1.

4 Chemical shift

The chemical shift describes the indirect interaction of a nuclear spin with the main magnetic field \vec{B}_0 via the surrounding electrons. The Hamiltonian for the chemical shift is shown in equation 6 where \hat{L} is the spin system and σ is the chemical shift tensor.

$$\hat{H}_{CS} = \hat{L} \cdot \sigma \cdot \vec{B}_0 \quad (6)$$

Fundamentally, the spins experience an induced field \vec{B}_{ind} which depends on the orientation of the chemical shift tensor σ with respect to the magnetic field \vec{B}_0

$$\vec{B}_{ind} = \sigma \cdot \vec{B}_0 \quad (7)$$

$$\begin{bmatrix} \vec{B}_x^{ind} \\ \vec{B}_y^{ind} \\ \vec{B}_z^{ind} \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{bmatrix} \cdot \begin{bmatrix} \vec{B}_x^0 \\ \vec{B}_y^0 \\ \vec{B}_z^0 \end{bmatrix} \quad (8)$$

The chemical shift tensor can be expressed in terms of its isotropic and anisotropic part. The isotropic part is calculated from σ using the trace operation Tr which sums the diagonal elements.

$$\sigma_{iso} = \frac{1}{3} Tr[\sigma] = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (9)$$

$$\sigma = \begin{bmatrix} \sigma_{xx} - \sigma_{iso} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} - \sigma_{iso} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} - \sigma_{iso} \end{bmatrix} + \begin{bmatrix} \sigma_{iso} & 0 & 0 \\ 0 & \sigma_{iso} & 0 \\ 0 & 0 & \sigma_{iso} \end{bmatrix} \quad (10)$$

$$= CSA + \sigma_{iso} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (11)$$

In solution NMR, only the isotropic part of σ is observable. This is the commonly referred to *chemical shift* which could be 7.5 ppm for aromatic protons.

The chemical shift is anisotropic and depends on the orientation of the chemical shift tensor σ with respect to the magnetic field vector \vec{B}_0 . Only the isotropic part is observable in solution NMR.

5 Direct dipole coupling

Direct dipole coupling is the interaction of two spins via their magnetic dipoles. The magnitude of the dipole coupling depends on the orientation of the internuclear vector with respect to the external magnetic field.

$$b_{IS} = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{r^3} \quad (12)$$

$$\hat{H}_{DD} = b_{IS} \left(\frac{3}{r^2} (\hat{\vec{I}} \cdot \hat{\vec{r}})(\hat{\vec{r}} \cdot \hat{\vec{S}}) - \hat{\vec{I}} \cdot \hat{\vec{S}} \right) \quad (13)$$

$$= b_{IS} \hat{\vec{I}} \cdot \mathbf{A} \cdot \hat{\vec{S}} \quad (14)$$

$$\mathbf{A} = \begin{bmatrix} 3x^2 - r^2 & 3xy & 3xz \\ 3xy & 3y^2 - r^2 & 3yz \\ 3xz & 3xy & 3z^2 - r^2 \end{bmatrix} \quad (15)$$

$$\hat{H}_{DD} = \frac{b_{IS}}{2} (3 \cos^2 \theta_{IS} - 1) \hat{\vec{I}} \cdot \hat{\vec{S}} \quad (16)$$

The average dipole coupling over all orientations is zero. This is demonstrated equivalently for both equations below. The trace of the dipole coupling tensor \mathbf{A} is zero and the integral over the angle θ is also zero. Note that the factor $(\cos \theta)$ is required to weight a uniform distribution over a sphere.

$$Tr[\mathbf{A}] = 0 \quad (17)$$

$$\int_0^{2\pi} (3 \cos^2 \theta - 1) (\cos \theta) d\theta = 0 \quad (18)$$

6 J-coupling

J-coupling (also called indirect dipole-dipole coupling) is the interaction of two nuclear spins via electrons. This interaction is isotropic, and is sometimes called *scalar*-coupling.

$$\hat{H}_J = \hat{\vec{L}} \cdot \mathbf{J}_{LS} \cdot \hat{\vec{S}} \quad (19)$$

$$= [\hat{L}_x \quad \hat{L}_y \quad \hat{L}_z] \cdot \begin{bmatrix} J_{LS} & 0 & 0 \\ 0 & J_{LS} & 0 \\ 0 & 0 & J_{LS} \end{bmatrix} \cdot \begin{bmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{bmatrix} \quad (20)$$

$$= J_{LS} (\hat{\vec{L}} \cdot \hat{\vec{S}}) \quad (21)$$

J-coupling is an indirect and isotropic interaction between two spins, mediated by the surrounding electrons.