

## Module I, Lecture 06: Spin Interaction Hamiltonians, part I

Spins interact with their environment and with each other through their associated magnetic moments. Within non-relativistic quantum theory the corresponding interaction Hamiltonians are obtained by replacing magnetic moment vectors with spin operators in the classical electromagnetic theory equations. That is a fairly simple procedure on its own, but the unfortunate reality is that a large number of historical conventions exist on how exactly to describe the amplitudes and directions of those interactions.

### Parameterization of spin interactions

Due to the nature of the spin Hamiltonian approximation (see Lecture 1) the tensors describing all types of spin interactions are diagonalizable 3x3 matrices. The purpose of diagonalization in this context:

$$\boldsymbol{\sigma} = \mathbf{VDV}^{-1} = \begin{pmatrix} & & \\ & \mathbf{V} & \\ & & \end{pmatrix} \begin{pmatrix} \sigma_{XX} & 0 & 0 \\ 0 & \sigma_{YY} & 0 \\ 0 & 0 & \sigma_{ZZ} \end{pmatrix} \begin{pmatrix} & & \\ & & \\ & & \mathbf{V}^{-1} \end{pmatrix} \quad (1)$$

is to separate the amplitude and the orientation part of the interaction. The amplitudes in the three primary directions are contained in the eigenvalues and the orientation information in the eigenvectors, which are the columns of  $\mathbf{V}$  matrix, which is usually unitary, and so the  $\mathbf{VDV}^{-1}$  transformation corresponds to a rotation. A given interaction tensor  $\boldsymbol{\sigma}$  is called

- *isotropic* if  $\sigma_{XX} = \sigma_{YY} = \sigma_{ZZ}$
- *axial* if  $\sigma_{XX} = \sigma_{YY} \neq \sigma_{ZZ}$
- *rhombic* if  $\sigma_{XX} \neq \sigma_{YY} \neq \sigma_{ZZ}$
- *traceless* if  $\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ} = 0$

Anisotropy parameters reported in magnetic resonance literature are usually linear combinations and other functions of eigenvalues intended to describe the deviation of the interaction from perfect spherical symmetry. There is unfortunately a large amount of variation in the reporting styles – the current IUPAC recommendation is to always explicitly list the three eigenvalues in Hz. Historical conventions, some of them rather dangerous from the algebraic point of view, are listed below. With the exception of the spherical tensor notation (which is algebraically sound and will be useful later), they should be avoided if at all possible:

1. *Isotropic + anisotropy + asymmetry (Haeberlen notation)*

$$\begin{aligned} \sigma_{\text{Iso}} &= \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) \\ \Delta\sigma &= \sigma_{ZZ} - \frac{1}{2}(\sigma_{XX} + \sigma_{YY}) \quad \text{or} \quad \zeta = \sigma_{ZZ} - \sigma_{\text{Iso}} \\ \eta &= \frac{3}{2} \frac{\sigma_{YY} - \sigma_{XX}}{\Delta\sigma} = \frac{\sigma_{YY} - \sigma_{XX}}{\zeta} \end{aligned} \quad (2)$$

The eigenvalues are assumed to be ordered as

$$|\sigma_{ZZ} - \sigma_{\text{Iso}}| \geq |\sigma_{XX} - \sigma_{\text{Iso}}| \geq |\sigma_{YY} - \sigma_{\text{Iso}}| \quad (3)$$

This convention is ill-defined around the points where  $\Delta\sigma = 0$  and suffers from the label switching problem for nearly isotropic and nearly axial tensors, because eigenvalues are ordered explicitly. An alternative ordering of eigenvalues, known as *Mehring notation*, is

$$\sigma_{XX} \leq \sigma_{YY} \leq \sigma_{ZZ} \quad (4)$$

The label switching problem complicates spectral fitting procedures – fitting error functionals are not in general differentiable at axis switching points.

2. *Isotropic + span + skew (Maryland notation)*

$$\begin{aligned} \sigma_{\text{Iso}} &= \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) \\ \Omega &= \sigma_{ZZ} - \sigma_{XX} \quad \kappa = \frac{3}{2} \frac{\sigma_{\text{Iso}} - \sigma_{YY}}{\Omega} \end{aligned} \quad (5)$$

with eigenvalues in Mehring order. These parameters give a physically intuitive picture of shielding powder patterns. There is a singularity around  $\Omega = 0$  and a label switching problem for nearly axial and nearly isotropic tensors.

3. *Isotropic + axiality + rhombicity*

$$\text{Iso} = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) \quad \text{Ax} = 2\sigma_{ZZ} - (\sigma_{XX} + \sigma_{YY}) \quad \text{Rh} = \sigma_{XX} - \sigma_{YY} \quad (6)$$

with eigenvalues in Mehring order. There are no denominators (and therefore singularities), but there is an axis switching problem because eigenvalues are ordered explicitly.

4. *Spherical tensor notation*

STN does not require diagonalization, the parameters are expressed directly *via* the elements of the 3×3 interaction tensor matrix. There are no axis labels and therefore no label switching problem. There are also no system-dependent denominators:

$$\begin{aligned} \sigma^{(2,2)} &= +(\sigma_{11} - \sigma_{22} - i\sigma_{12} - i\sigma_{21})/2 & \sigma^{(1,1)} &= -(\sigma_{31} - \sigma_{13} - i\sigma_{32} + i\sigma_{23})/2 \\ \sigma^{(2,1)} &= -(\sigma_{13} + \sigma_{31} - i\sigma_{23} - i\sigma_{32})/2 & \sigma^{(1,0)} &= -i(\sigma_{12} - \sigma_{21})/\sqrt{2} \\ \sigma^{(2,0)} &= +(2\sigma_{33} - \sigma_{11} - \sigma_{22})/\sqrt{6} & \sigma^{(1,-1)} &= -(\sigma_{31} - \sigma_{13} + i\sigma_{32} - i\sigma_{23})/2 \\ \sigma^{(2,-1)} &= +(\sigma_{13} + \sigma_{31} + i\sigma_{23} + i\sigma_{32})/2 & \sigma^{(0,0)} &= -\text{Tr}(\boldsymbol{\sigma})/\sqrt{3} \\ \sigma^{(2,-2)} &= +(\sigma_{11} - \sigma_{22} + i\sigma_{12} + i\sigma_{21})/2 & & \end{aligned} \quad (7)$$

These coefficients are defined in relation to the irreducible spherical tensor expansion (more on this later) of interaction Hamiltonians:

$$\hat{L} \cdot \boldsymbol{\sigma} \cdot \hat{S} = \sum_{\substack{k,n= \\ \{X,Y,Z\}}} \sigma_{kn} \hat{L}_k \hat{S}_n = \sigma^{(0,0)} \hat{T}_{0,0} + \sum_{m=-1}^1 \sigma^{(1,m)} \hat{T}_{1,m} + \sum_{m=-2}^2 \sigma^{(2,m)} \hat{T}_{2,m} \quad (8)$$

From the group-theoretical and relaxation-theoretical perspective, this is the most consistent and appropriate way of specifying interaction tensor anisotropy and orientation parameters.

5. *Quadrupolar interaction parameters*

For historical reasons, nuclear quadrupolar interaction has its own specification convention:

$$\chi = \frac{e^2 q_{ZZ} Q}{\hbar} \quad \eta = \frac{q_{XX} - q_{YY}}{q_{ZZ}} \quad (9)$$

where  $\{q_{XX}, q_{YY}, q_{ZZ}\}$  are the eigenvalues of the electric field gradient tensor,  $e$  is the electron charge,  $eQ$  is the quadrupole moment of the nucleus,  $S$  is the spin of the nucleus and eigenvalues are in Haeberlen order. Quadrupolar interaction is “traceless by convention”: the sum  $q_{XX} + q_{YY} + q_{ZZ}$  is not zero (see Poisson’s equation), but the isotropic term does not affect spin dynamics and is for that reason usually dropped from consideration.

## 6. Zero field splitting parameters

For different historical reasons, electron zero-field splitting also has its own parameterization:

$$D = \frac{3}{2} \sigma_{ZZ} \quad E = \frac{\sigma_{XX} - \sigma_{YY}}{2} \quad (10)$$

with eigenvalues in Mehring order. This interaction is traceless.

From a more general algebraic perspective, every  $3 \times 3$  interaction tensor has three rotation invariants:

$$I_{\sigma} = \text{Tr}(\sigma), \quad II_{\sigma} = \frac{1}{2} (\text{Tr}(\sigma)^2 - \text{Tr}(\sigma^2)), \quad III_{\sigma} = \det(\sigma) \quad (11)$$

$I_{\sigma}$  determines the isotropic part and survives the rotational averaging,  $II_{\sigma}$  determines relaxation properties in liquids and powder patterns in solids,  $III_{\sigma}$  is not presently used in Magnetic Resonance. The following relation links the three invariants:

$$\sigma^3 - I_{\sigma} \sigma^2 + II_{\sigma} \sigma - III_{\sigma} \mathbf{1} = 0 \quad (12)$$

## Survey of interactions: chemical shielding

This is the coupling of the nuclear spin, via its associated magnetic dipole moment, to the external magnetic field. The magnetic field at the nucleus contains the contribution from the external field *per se* and from the electronic structure perturbation produced by that field:

$$\vec{B} = \vec{B}_0 + \vec{B}_{\text{ind}} \quad (13)$$

To a good approximation (because magnetic interactions are very weak), the induced field  $\vec{B}_{\text{ind}}$  is a linear function of the applied field  $\vec{B}_0$ :

$$\vec{B} = \vec{B}_0 + \delta \vec{B}_0 \quad (14)$$

where  $\delta$  is a  $3 \times 3$  matrix that is a function of the electronic structure of the system. The energy of a point magnetic dipole  $\vec{\mu}$  placed into this environment is:

$$E = -\vec{\mu} \cdot \vec{B} = -\vec{\mu} \cdot (\mathbf{1} + \delta) \cdot \vec{B}_0 \quad (15)$$

and therefore the expression for the components of  $\delta$  can be obtained as a derivative of energy:

$$\delta_{ij} = -\frac{\partial^2 E}{\partial \mu_i \partial B_j} \quad (16)$$

The problem of computing  $\delta$  is therefore equivalent to the problem of computing, with sufficient accuracy, the total energy of the system in the presence of a magnetic field. Because magnetic interactions are weak, this is usually done with perturbation theory.

For a charged particle (such as the electron) in the presence of a magnetic field, the momentum operator is modified due to presence of the Lorentz force:

$$\hat{\vec{p}} \rightarrow \hat{\vec{p}} + q\vec{A} \quad (17)$$

where  $\vec{A}$  is the vector potential. In the presence of an external field and a point magnetic dipole at the origin it acquires the following form (see your electromagnetism course):

$$\vec{A}(\vec{r}) = \frac{1}{2}\vec{B} \times \vec{r} + \frac{\mu_0}{4\pi} \cdot \frac{\vec{\mu} \times \vec{r}}{r^3} \quad (18)$$

With this in place, the full Hamiltonian becomes:

$$\hat{H} = \sum_k \frac{(\hat{\vec{p}}_k + q_k \vec{A}(\vec{r}_k))^2}{2m_k} + \hat{U} \quad (19)$$

where  $\hat{U}$  contains all the usual electrostatic interaction terms. After defining the perturbation operator  $\hat{H}_1$  as the difference between Equation (19) and the unperturbed Hamiltonian:

$$E^{(2)} = E^{(0)} + \langle 0 | \hat{H}_1 | 0 \rangle + \sum_{n=1}^{\infty} \frac{\langle 0 | \hat{H}_1 | n \rangle \langle n | \hat{H}_1 | 0 \rangle}{E_0 - E_n} \quad (20)$$

$$\hat{H}_1 = \sum_k \frac{q_k (\hat{\vec{p}}_k \cdot \vec{A}(\vec{r}_k)) + q_k^2 (\vec{A}(\vec{r}_k) \cdot \vec{A}(\vec{r}_k))}{2m_k} \quad (21)$$

In practice, the energy and its derivatives are computed using *ab initio* methods or DFT. The first term in Equation (20) does not depend on the magnetic field and vanishes on differentiation. The second term only includes the contributions from the ground state, for historical reasons it is called *diamagnetic*. The third term contains a sum over all excitations and is known as the *paramagnetic* term. It becomes particularly important in systems with low-lying excitations, because the denominators are small. Equation (20) is not applicable to systems with a degenerate or near-degenerate ground state.

The effective form of the spin interaction that Equation (15) generates is a bilinear coupling between the spin and the applied magnetic field:

$$\hat{H}_{CS} = \hat{\vec{L}} \cdot \mathbf{A} \cdot \vec{B} \quad (22)$$

in which the matrix  $\mathbf{A}$  is known as the chemical shielding tensor, in most cases it is rhombic. The shielding tensor may also contain small anti-symmetric components, which are experimentally very difficult to detect and do not at present play any practical role in magnetic resonance spectroscopy.

### Survey of interactions: inter-nuclear dipolar interaction

To very high accuracy, nuclear spins may be treated as point dipoles. In classical physics, the vector potential and the magnetic induction of a point magnetic dipole  $\vec{\mu}$  are:

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\vec{\mu} \times \vec{r}}{r^3} \quad \Rightarrow \quad \vec{B} = \vec{\nabla} \times \vec{A} = \dots = \frac{\mu_0}{4\pi} \frac{3(\vec{\mu} \cdot \vec{r})\vec{r} - r^2\vec{\mu}}{r^5} \quad (23)$$

The interaction energy of two point magnetic dipoles therefore is:

$$E = -\vec{\mu} \cdot \vec{B} = -\frac{\mu_0}{4\pi} \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{r} \cdot \vec{\mu}_2) - r^2(\vec{\mu}_1 \cdot \vec{\mu}_2)}{r^5} \quad (24)$$

where  $\vec{r}$  is now the vector connecting the two dipoles. The corresponding quantum mechanical Hamiltonian is then obtained by replacing the magnetic dipole vectors with the corresponding spin operators:

$$\hat{H}_{\text{DD}} = -\frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar}{r^5} \left( 3(\hat{S}_1 \cdot \vec{r})(\vec{r} \cdot \hat{S}_2) - r^2 (\hat{S}_1 \cdot \hat{S}_2) \right) = -\frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar}{r^5} \times$$

$$\begin{pmatrix} \hat{S}_X^{(1)} \\ \hat{S}_Y^{(1)} \\ \hat{S}_Z^{(1)} \end{pmatrix}^T \begin{pmatrix} 3(x_1 - x_2)^2 - r^2 & 3(x_1 - x_2)(y_1 - y_2) & 3(x_1 - x_2)(z_1 - z_2) \\ 3(y_1 - y_2)(x_1 - x_2) & 3(y_1 - y_2)^2 - r^2 & 3(y_1 - y_2)(z_1 - z_2) \\ 3(z_1 - z_2)(x_1 - x_2) & 3(z_1 - z_2)(y_1 - y_2) & 3(z_1 - z_2)^2 - r^2 \end{pmatrix} \begin{pmatrix} \hat{S}_X^{(2)} \\ \hat{S}_Y^{(2)} \\ \hat{S}_Z^{(2)} \end{pmatrix} \quad (25)$$

where  $\gamma_1$  and  $\gamma_2$  are the magnetogyric ratios of the two spins. It is easy to see that the trace of the matrix in Equation (25) is zero. A brute-force diagonalization can demonstrate that the rhombicity is also zero. Point dipole interaction is therefore traceless and axial.

### Survey of interactions: nuclear spin-rotation coupling

A collection of charges  $\{q_n\}$  moving at radius-vectors  $\{\vec{r}_n\}$  with velocities  $\{\vec{v}_n\}$  generates the following magnetic induction at the origin:

$$\vec{B} = \frac{\mu_0}{4\pi} \sum_n q_n \frac{\vec{v}_n \times \vec{r}_n}{r_n^3} \quad (26)$$

This expression can be rewritten in terms of linear momenta  $\vec{p}_n = m_n \vec{v}_n$ . The expression for angular momenta  $\vec{J}_n = \vec{r}_n \times \vec{p}_n$  then becomes apparent and we get:

$$\vec{B} = -\frac{\mu_0}{4\pi} \sum_n \frac{q_n}{m_n r_n^3} \vec{J}_n \quad (27)$$

where  $m_n$  is the mass of  $n$ -th charge and  $\vec{J}_n$  is its angular momentum around the origin. After replacing the angular momentum with the corresponding quantum mechanical operator and plugging Equation (27) into the nuclear Zeeman interaction Hamiltonian, we get:

$$\hat{H}_{\text{SR}} = \sum_k \gamma_k \vec{B} \cdot \hat{S}_k = -\frac{\mu_0}{4\pi} \sum_{nk} \frac{\gamma_k q_n}{m_n r_n^3} (\hat{J}_n \cdot \hat{S}_k) \quad (28)$$

where  $\gamma_k$  is the magnetogyric ratio of the  $k$ -th nucleus and  $\hat{S}_k$  are the corresponding nuclear spin operators. Note the presence of mass in the denominator. After the sum is taken over the moving charges, the spin-rotation Hamiltonian acquires the following generic form:

$$\hat{H}_{\text{SR}} = -\sum_k \hat{J} \cdot \mathbf{A}_k \cdot \hat{S}_k \quad (29)$$

where minus is there for historical reasons, the molecule is now assumed to be rigid with the molecular angular momentum operator  $\hat{J}$ ,  $\hat{S}_k$  are nuclear spin operators and  $\mathbf{A}_k$  are experimentally determined *spin-rotation coupling tensors*, which are in general different for each nucleus.

Nuclear spin-rotation tensors have two distinct contributions. One comes from the relative motion of the other nuclei – it presents a simple geometric problem in the rigid molecule approximation and an easy MD simulation in the general case. The other comes from the electrons and is the second derivative of the electronic energy with respect to the molecular angular momentum and nuclear spin:

$$\mathbf{A}_k^{(\text{el})} = -\frac{\partial^2 E^{(\text{el})}}{\partial \vec{J} \partial \vec{S}} \quad (30)$$

It may be shown that this derivative is proportional to the paramagnetic part of the chemical shielding tensor. The following equation relates the two:

$$\mathbf{A}_k^{(el)} = 2\gamma_k \boldsymbol{\sigma}_k^{(para)} \mathbf{I}^{-1} \quad (31)$$

where  $\mathbf{I}$  is the inertia tensor. For further details see recent papers by Jürgen Gauss and co-authors.

### Survey of interactions: quadrupolar coupling

Nuclei with spin greater than  $\frac{1}{2}$  have non-spherical charge distribution, and the resulting electric quadrupole moment can interact with the electric field gradient. Because the direction of nuclear quadrupole moment is rigidly connected to the direction of the spin, this electrostatic interaction also manifests itself as a spin interaction, which is effectively quadratic – the spin “interacts with itself”:

$$\hat{H}_Q = -\frac{eQ}{2I(2I-1)} \hat{L} \cdot \mathbf{V} \cdot \hat{L} \quad V_{ij} = \frac{\partial E_i}{\partial x_j} = \frac{\partial^2 \varphi}{\partial x_i \partial x_j} \quad (32)$$

where  $eQ$  is the quadrupole moment of the nucleus (a fundamental constant),  $I$  is the spin of the nucleus,  $\vec{E}$  is the electric field vector and  $\varphi$  is the electrostatic potential. The isotropic component of the quadrupolar interaction is related via Poisson’s equation to the electron charge density at the nucleus, which may be considerable:

$$\sum_k V_{kk} = \frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = \Delta \varphi = 4\pi \left[ q_N - e |\psi(\vec{r}_N)|^2 \right] \quad (33)$$

but the corresponding contribution to the nuclear spin Hamiltonian is static:

$$\hat{L}_X^2 + \hat{L}_Y^2 + \hat{L}_Z^2 = \hat{L}^2 = I(I+1) \hat{E} \quad (34)$$

and for that reason is commonly dropped from consideration, because it amounts to the overall energy shift of the entire system. Therefore, it is only the traceless part of  $\hat{H}_Q$  that does in practice influence spin dynamics. In the principal axis frame and using the quadrupolar parameters introduced above the Hamiltonian becomes:

$$\hat{H}_Q = -\frac{\chi}{4I(2I-1)} \left[ 3\hat{I}_Z^2 - \hat{I}^2 + \frac{\eta}{2} (\hat{I}_X^2 - \hat{I}_Y^2) \right] \quad (35)$$

Note that with spin- $\frac{1}{2}$  Pauli matrices the Hamiltonian above is proportional to the unit matrix and does not affect system dynamics – quadrupolar coupling only exists for spin-1 nuclei and higher.

### Survey of interactions: J-coupling

J-coupling is a bilinear coupling between two nuclear spins. Its anisotropy is commonly ignored, and the corresponding orientational average is known in NMR as simply the *scalar coupling*. In that case the Hamiltonian acquires a particularly simple *isotropic* form:

$$\hat{H}_J = \begin{pmatrix} \hat{L}_X & \hat{L}_Y & \hat{L}_Z \end{pmatrix} \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \begin{pmatrix} \hat{S}_X \\ \hat{S}_Y \\ \hat{S}_Z \end{pmatrix} = a (\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y + \hat{L}_Z \hat{S}_Z) = a (\hat{L} \cdot \hat{S}) \quad (36)$$

The dominant contribution to  $\hat{H}_J$  comes from the electronic structure perturbations caused by Fermi contact interaction with the electrons, which is isotropic:

$$\hat{H}_{\text{FC}} = \frac{8\pi\hbar}{3} \sum_{kn} \gamma_k \gamma_n \delta(\vec{r}_{kn}) \hat{L}_k \cdot \hat{S}_n \quad (37)$$

where  $\hat{S}_n$  are nuclear spin operators and  $\hat{L}_k$  are electron spin operators. Long-range  $J$ -couplings often have contributions from the electronic structure perturbations caused by point dipole interactions of nuclei with the electrons:

$$\hat{H}_{\text{DD}} = -\frac{\mu_0}{4\pi} \hbar \sum_{kn} \gamma_k \gamma_n \left( \frac{3(\hat{L}_k \cdot \vec{r}_{kn})(\vec{r}_{kn} \cdot \hat{S}_n)}{r_{kn}^5} - \frac{(\hat{L}_k \cdot \hat{S}_n)}{r_{kn}^3} \right) \quad (38)$$

The total energy of the system to second order in these perturbations is:

$$E^{(2)} = E^{(0)} + \langle 0 | \hat{H}_{\text{FC}} + \hat{H}_{\text{DD}} | 0 \rangle + \sum_{n=1}^{\infty} \frac{\langle 0 | \hat{H}_{\text{FC}} + \hat{H}_{\text{DD}} | n \rangle \langle n | \hat{H}_{\text{FC}} + \hat{H}_{\text{DD}} | 0 \rangle}{E_0 - E_n} \quad (39)$$

The  $J$ -coupling between spins  $a$  and  $b$  is obtained as a second derivative of this energy with respect to nuclear magnetic moments:

$$J_{ij}^{(a,b)} = \frac{\partial^2 E^{(2)}}{\partial \mu_i^{(a)} \partial \mu_j^{(b)}} \quad (40)$$

where  $i$  and  $j$  indices run over  $\{x, y, z\}$ . The terms involving only the ground state  $|0\rangle$  in equation (39) are called *diamagnetic* and are relatively easy to compute (only the ground state is required). The terms involving excitations are called *paramagnetic* and are considerably more expensive.