II. Nuclear Spin Hamiltonian

The nuclear spin Hamiltonian consists of a number of terms that describe physically different interactions of the nuclear spins. Some of these terms are related to the apparatus, and some to the physical properties of the sample. Some cause shifts, while others cause broadening of the NMR lines. As we have outlined in the introduction, it is the behavior of these Hamiltonian terms under motions (mostly, but not exclusively, rotations) in both spatial and spin coordinate spaces that enters basically all considerations about obtaining high resolution in spectra of both solid and liquid samples. In this chapter we study this behavior for the nuclear spin Hamiltonian terms relevant to diamagnetic, nonconducting substances. It is to this class of substances that, by and large, high-resolution NMR has been limited to date, although the so-called magic-angle sample-spinning high-resolution techniques have also been applied to metals.

A. Interactions of Nuclear Spins in Diamagnetic Nonconducting Substances

The nuclear spin Hamiltonian in diamagnetic nonconducting substances can be expressed in the following tabular form:

<table>
<thead>
<tr>
<th>Term</th>
<th>Coupling of nuclear spins with</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hbar \mathcal{H} = \hbar \mathcal{H}_2$</td>
<td>external static magnetic fields</td>
</tr>
<tr>
<td>+ $\hbar \mathcal{H}_{rt}$</td>
<td>external rf magnetic fields</td>
</tr>
<tr>
<td>+ $\hbar \mathcal{H}_{CS}$</td>
<td>induced magnetic fields originating from orbital motions of electrons</td>
</tr>
<tr>
<td>+ $\hbar \mathcal{H}_Q$</td>
<td>electric field gradients</td>
</tr>
<tr>
<td>+ $\hbar \mathcal{H}_{SR}$</td>
<td>magnetic moment associated with the molecular angular momentum</td>
</tr>
<tr>
<td>+ $\hbar \mathcal{H}_D$</td>
<td>each other, directly through their magnetic dipole moments</td>
</tr>
<tr>
<td>+ $\hbar \mathcal{H}_I$</td>
<td>each other, indirectly via electron spins</td>
</tr>
</tbody>
</table>

We shall now give a few comments on each of these terms.
II. NUCLEAR SPIN HAMILTONIAN

1. ZEEMAN HAMILTONIAN $\mathcal{H}_Z$

The static applied magnetic field $B_{st}$ is usually chosen as $(0, 0, B_z)$, where we assume tacitly that it is constant in space. We shall have to drop this assumption occasionally. This choice of $B_{st}$ leads to

$$\mathcal{H}_Z = -\sum_i \mu_i B_z = -h B_z \sum_i \gamma_i I_z I^i,$$

(2-1)

where $\mu_i$ and $\gamma_i$ are, respectively, the magnetic moment and the magnetogyric ratio of the $i$th nucleus; $i$ runs over all nuclei of the sample; $\omega_0^i = \gamma_i B_z$.

2. RADIO FREQUENCY HAMILTONIAN $\mathcal{H}_{rf}$

The rf field is usually applied perpendicular to the static field. We choose it parallel to the $x$ axis:

$$B_{rf} = (B_1(t) \cos[\omega t + \phi(t)], 0, 0).$$

(2-2)

This form of $B_{rf}$ implies an rf irradiation that may be modulated in both its amplitude and phase, but that has a constant carrier frequency $\omega/2\pi$. Consequently, we have

$$\mathcal{H}_{rf} = -h B_1(t) \cos[\omega t + \phi(t)] \sum_i \gamma_i I_z I^i.$$  

(2-3)

In multiple-resonance experiments $B_{rf}$ consists of a sum of fields that differ, in particular, but not only, in their carrier frequencies $\omega^i$.

3. CHEMICAL SHIFT OR NUCLEAR MAGNETIC SHielding HAMILTONIAN $\mathcal{H}_{CS}$

This Hamiltonian can be written in the form

$$\mathcal{H}_{CS} = \hbar \sum_i \gamma_i I^i \cdot \sigma^i \cdot B,$$

(2-4)

where $\sigma^i$ is a tensor of rank two, characteristic for each nuclear site; $-\sigma^i \cdot B$ is the magnetic field induced by the electrons at the site of the $i$th nucleus. Usually one restricts $B$ to $B_{st}$. We shall be concerned particularly with $\sigma$ tensors in this volume.

4. THE QUADRUPOlar HAMILTONIAN $\mathcal{H}_Q$

This Hamiltonian can be written in the form

$$\mathcal{H}_Q = \sum_i \frac{eQ^i}{6I^i(2I^i - 1)} \sum_{\alpha, \beta = 1}^3 V_{\alpha\beta}^i \left[ \frac{3}{2} (I^i_\alpha I^i_\beta + I^i_\beta I^i_\alpha) - \delta_{\alpha\beta}(I^i)^2 \right]$$

(2-5a)

$$= \sum_i \frac{eQ^i}{6I^i(2I^i - 1)} I^i \cdot V^i \cdot I^i,$$

(2-5b)
A. INTERACTIONS OF NUCLEAR SPINS

where \( eQ \) and \( I \) are, respectively, the nuclear quadrupole moment and the nuclear spin quantum number of the \( i \)th nucleus; \( V_{i\beta} \) is the second \((x, \beta)\) derivative of the electric potential at the site of the \( i \)th nucleus.

5. THE SPIN–ROTATION INTERACTION HAMILTONIAN

The relation
\[
\hat{\mathcal{H}}_{SR} = \hbar \sum_m \sum_i \mathbf{I}_i \cdot \mathbf{C}^{i,m} \cdot \mathbf{J}^m
\]
(2-6)
describes the coupling of the nuclear spins \( i \) of a molecule \( m \) with the magnetic moment associated with the angular momentum \( \mathbf{J}^m \) of that molecule. Here \( i \) runs over all nuclei in the molecule \( m \), and \( m \) runs over all molecules of the sample. Henceforth we shall drop the index \( m \). The spin–rotation interaction tensor \( \mathbf{C}^i \) depends, in principle, on the molecular rotational quantum number \( J \): \( \mathbf{C}^i = \mathbf{C}^i(J) \). This dependence, however, is weak and may often be neglected. \( \mathbf{C}^i \) would be independent of \( J \) altogether if the nuclear geometrical configuration were independent of \( J \).

\( \mathcal{H}_z, \mathcal{H}_{rf}, \mathcal{H}_{CS}, \mathcal{H}_Q, \) and \( \mathcal{H}_{SR} \) are sums of single-spin Hamiltonians. The next two terms are many-spin Hamiltonians. They couple, in principle, every spin of the sample with all others.

6. THE DIPOLAR HAMILTONIAN \( \mathcal{H}_D \)

This Hamiltonian is given by
\[
\hat{\mathcal{H}}_D = \sum_{i<k} \left( -\frac{\gamma_i}{r_{ik}^3} \mathbf{I}_i \cdot \mathbf{J}_k \right) \left[ \mathbf{r}_{ik} \cdot \mathbf{J}_k \right] (2-7a)
\]
\[
= \sum_{i<k} \left( -2\gamma_i r_{ik}^3 \right) \sum_{\alpha, \beta=1}^{3} \left[ I_{\alpha i} \cdot D_{k\beta}^{ik} \cdot I_{\beta k} \right],
\]
(2-7b)
where \( \mathbf{r}_{ik} \) is the vector from nucleus \( i \) to nucleus \( k \), and \( |r_{ik}| = r_{ik} \). The components \( D_{k\beta}^{ik} \) of the tensor \( \mathbf{D}^{ik} \) are just the coefficients going with \( I_{\alpha i} I_{\beta k} \).

7. THE INDIRECT SPIN–SPIN COUPLING TERM

This term may be written
\[
\hat{\mathcal{H}}_{ij} = \hbar \sum_{i<k} \mathbf{I}_i \cdot \mathbf{J}_{ik} \cdot \mathbf{I}_k,
\]
(2-8)
where \( \mathbf{J}_{ik} \) again is a tensor of rank two.

Let us call \( \mathcal{H}_z \) and \( \mathcal{H}_{rf} \) external Hamiltonians because they depend, apart from nuclear properties \((\gamma_i)\) only on external parameters \((B_z, B_i(t), \varphi(t), \ldots)\), which are under control of the experimenter. Consequently we call \( \mathcal{H}_{CS}, \mathcal{H}_Q, \)
II. NUCLEAR SPIN HAMILTONIAN

\( H_{\lambda} = C^\lambda \sum_{\alpha, \beta = 1}^{3} I_\alpha R_{\alpha \beta}^\lambda A_{\beta}^\lambda = C^\lambda \sum_{\alpha, \beta = 1}^{3} R_{\alpha \beta}^\lambda T_{\beta \alpha}^\lambda. \) (2-9)

The \( C^\lambda \) depend only on fundamental constants \( (\hbar, e) \) and properties of a definite nuclear state \( s (I_s^i, \gamma_{in}^i, Q_s^i) \), which mostly but not always is the nuclear ground state. In this case we shall drop—as we did before—the index \( s \). In particular, the \( C^\lambda \) are constants with respect to rotations:

\[
C^\lambda = \begin{cases} 
1, & \text{for } \lambda = \text{SR, J}, \\
\gamma_{i}^a, & \text{for } \lambda = \text{CS}, \\
\frac{eQ_i}{6I(I - 1)\hbar}, & \text{for } \lambda = Q, \\
-2\gamma_{i}^a\gamma_{i}^b\hbar, & \text{for } \lambda = D.
\end{cases}
\]

(2-10a) (2-10b) (2-10c) (2-10d)

The differences between \( C^{CS} \) and \( C^{SR} \), and between \( C^D \) and \( C^J \) have their origin in conventions of defining the \( H^\lambda \), and not in physics!

The \( T_{\beta \alpha}^\lambda \) are dyadic products constructed from two vectors, one of which is always a nuclear spin vector, whereas the other one \( (\mathbf{A}^\lambda) \) can be the same nuclear spin vector \( (\lambda = Q) \), another nuclear spin vector \( (\lambda = D, J) \), the external magnetic field \( (\lambda = CS) \), or the molecular angular momentum vector \( J (\lambda = SR) \).

The \( R^\lambda (C^i, V^i, \sigma^i, D^{ik}, J^{ik}) \) depend on a definite electronic state—mostly but not exclusively—the electronic ground state of the molecule or crystal, and parametrically on nuclear geometrical configurations, and vibrational and rotational states of the molecules.

All \( R^\lambda \) are tensors of rank two. Hence they can be decomposed into their irreducible constituents with respect to the full 3d rotation group, \( 03: R = R^{(0)} + R^{(1)} + R^{(2)}. \)

\( R^{(0)} = \frac{1}{2} \text{Tr } \mathbf{1} = \mathbf{1} \) is the isotropic constituent. \( \mathbf{1} \) is the unit dyadic. The components of the traceless antisymmetric \( (R^{(1)}) \) and traceless symmetric \( (R^{(2)}) \) constituents are given, respectively, by

\[
R_{\alpha \beta}^{(1)} = \frac{1}{2}(R_{\alpha \beta} - R_{\beta \alpha}) \quad \text{and} \quad R_{\alpha \beta}^{(2)} = \frac{1}{2}(R_{\alpha \beta} + R_{\beta \alpha}) - R \delta_{\alpha \beta}.
\]

C, \( \sigma \), and \( J \) can contain, in principle, all three constituents. However, only the isotropic and traceless symmetric parts are measurable by spectroscopic techniques (see Chapter III, Section D). \( D \) and \( V \) are traceless symmetric by their very nature. In what follows we shall therefore ignore eventual antisymmetric constituents and shall treat all \( R^\lambda \) as symmetric.

There exist principal axes systems (PAS)—different from each other in
A. INTERACTIONS OF NUCLEAR SPINS

general—for all $R^\lambda$. These PAS's are fixed in some molecular or crystal frame and eventually they move together with the molecule or crystal. The $R^\lambda$-tensors assume very simple forms in their respective PAS's: They become diagonal. The diagonal elements in the PAS are called principal components, $R_{xx}$, $R_{yy}$, $R_{zz}$.

The following convention is chosen to label the axes:

$$|R_{zz} - R| \geq |R_{xx} - R| \geq |R_{yy} - R|.$$  \hspace{1cm} (2-11)

The quantities between the absolute signs, $R_{xx} - R$, are the principal components of $R^{(2)}$.

It is often convenient to introduce instead of the three parameters $R_{xx}$ three new parameters, one of which is

$$R = \frac{1}{3} \text{Tr } R,$$  \hspace{1cm} (2-12)

and the other two, $\delta$ and $\eta$, are defined by

$$\delta = R_{zz} - \frac{1}{3} \text{Tr } R = R_{zz} - R,$$  \hspace{1cm} (2-13)

$$\eta = \frac{R_{yy} - R_{xx}}{R_{zz} - \frac{1}{3} \text{Tr } R} = \frac{R_{yy} - R_{xx}}{\delta}.$$  \hspace{1cm} (2-14)

In terms of the $R_{xx}$ and of the new parameters $R$, $\delta$, $\eta$ we have in the PAS

$$R(\text{PAS}) = \begin{bmatrix} R_{xx} & & \\
& R_{yy} & \\
& & R_{zz} \end{bmatrix} = R^{1} + \delta \begin{bmatrix} -\frac{1}{2}(1+\eta) & & \\
& -\frac{1}{2}(1-\eta) & \\
& & 1 \end{bmatrix}.$$  \hspace{1cm} (2-15)

$R^{D} = R^{Q} = 0$. In high-resolution NMR in fluids $R^{CS} = \frac{1}{3} \text{Tr } \sigma = \sigma$, and $R^{i,ik} = \frac{1}{3} \text{Tr } J^{ik} = J^{ik}$ are called, respectively, “chemical shifts” and (scalar) “coupling constants.” $C = \frac{1}{3} \text{Tr } C \neq 0$, in general; however, it causes at most line broadening but never line shifts or line splittings in NMR spectra of condensed matter.

$\delta^{i,ik} = r^{i,ik}$. The quadrupole resonance community calls $\delta^{Q,i}$ “field gradient” (at the site of nucleus $i$) and denotes it by eq. $\frac{1}{2} \delta^{CS,i} = \sigma_{zz}^{i} - \frac{1}{2}(\sigma_{xx}^{i} + \sigma_{yy}^{i})$ may be called chemical shift or nuclear magnetic shielding anisotropy of the $i$th nucleus. For axially symmetric shielding tensors with $\sigma_{xx} = \sigma_{yy} = \sigma_{z}$ and $\sigma_{zz} = \sigma_{z}$ the total anisotropy range is $\Delta \sigma = \sigma_{z} - \sigma_{z} = \frac{1}{2} \delta^{CS}$. $\delta^{i,ik}$ and $\delta^{SR,i}$ have not yet been given special names.

$\eta^{\lambda}$ ($\lambda = D, Q, CS, J, SR$) is called the asymmetry parameter of the corresponding tensor. $\eta^{0} = 0$ means, obviously, that $R^\lambda$ is axially symmetric. The dipolar interaction between two magnetic moments is axially symmetric about the line interconnecting the moments, hence $\eta^{D} = 0$. 

II. NUCLEAR SPIN HAMILTONIAN

B. Behavior of Internal Hamiltonians under Rotations

All techniques used for selective averaging in NMR rely on rotations of one kind or another of our internal Hamiltonians. The behavior under rotations of any physical property can be studied most easily when this property is expressed in terms of components of irreducible spherical tensor operators, denoted by $T_{lm}$ or $R_{lm}$. The behavior of irreducible spherical tensor operators under rotations is well known. The books by Edmonds, 1 Rose, 2 and Brink and Satchler 3 are recommended for an introduction to spherical tensor operators.

The equivalent of Eq. (2-9) in irreducible spherical tensor operator calculus is

$$\mathcal{H}_\lambda = C^i \sum_l \sum_{m=-l}^{l} (-1)^m R_{lm}^i T_{lm}^\lambda,$$

where the $R_{lm}^i$ derive from the $R_{a\beta}^i$ and the $T_{lm}^\lambda$ from the $T_{a\beta}^\lambda$. If we start with symmetric 2nd-rank cartesian tensors $R_{a\beta}^i$, only $R_{lm}^i$'s with $l = 0, 2$ will be nonzero. If we consider the $R^\lambda$ tensors in their principal axes systems, only components with $m = 0, \pm 2$ are nonzero.

We shall denote the components of irreducible spherical tensor operators $R_{lm}$ in their respective PAS’s by $\rho_{lm}$. The relations between the nonzero $\rho_{lm}$’s and the $R_{aa}$ (or $R$, $\delta$, and $\eta$) are

$$\rho_{00} = \frac{1}{2} \operatorname{Tr} R = R,$$  \hspace{1cm} (2-17)

$$\rho_{20} = \sqrt{\frac{3}{2}} (R_{zz} - \frac{1}{2} \operatorname{Tr} R) = \sqrt{\frac{3}{2}} \delta,$$  \hspace{1cm} (2-18)

$$\rho_{2\pm 2} = \frac{1}{4} (R_{yy} - R_{xx}) = \frac{1}{2} \eta \delta.$$  \hspace{1cm} (2-19)

We shall express the $T_{lm}^\lambda$ (derived from the $T_{a\beta}^\lambda = I_\alpha A_{\beta}^\lambda$) in the laboratory frame of reference because the $I_\alpha, A_{\beta}^\lambda$ are basically linked to that frame 4; therefore, we must express the $R_{lm}^i$ also in the laboratory frame.


4 This is obvious for the components of the magnetic fields, both static and oscillatory, but it is also true for the spin components. The spin components are the dynamic variables in NMR experiments. It is their time evolution that we observe using laboratory equipment and hence naturally in a laboratory frame of reference. The role of the $D$, $V$, $J$, $\sigma$, and $C$ tensors is quite different: they are parameters that govern the time evolution of the dynamic variables, i.e., of the spin system. The time evolution of the spin system carries information about the parameters in which we are ultimately interested.
B. ROTATIONS OF INTERNAL HAMILTONIANS

Being irreducible spherical tensor operators, they may be expressed in the laboratory frame in terms of the $\rho_{lm}$, and of the Wigner rotation matrices $\mathcal{D}_{m'm}^l(\alpha^l, \beta^l, \gamma^l)$ (see, e.g., Edmonds):

$$R_{lm}^l = \sum_{m'} \mathcal{D}_{m'm}^l(\alpha^l, \beta^l, \gamma^l) \rho_{lm'}^l,$$

(2-20)

where $\alpha^l, \beta^l, \gamma^l$ (the triple of which we shall denote by $\Omega^l$) are the Euler angles by which the laboratory frame can be brought into coincidence with the $\lambda$th principal axes system. $\mathcal{D}_{m'm}^l = \delta_{m'm}$ for $\Omega = 0$, i.e., when the laboratory frame and the principal axes system coincide. In such a situation $R_{lm}^l = \rho_{lm}$, as it should.

$\mathcal{D}_{00}^l$ is a constant (unity). The only Wigner matrix actually needed in our context is the $\mathcal{D}_{m'm}^l$ matrix given in Table 2-1.

We can now turn to the last factors in Eq. (2-9) or (2-16). The elements of the dyadic product $T_{\mu\nu}^l = I_\lambda A_{\mu\nu}^l$ form a basis for a nine-dimensional, reducible representation of the rotation group. Its reduction leads to the desired irreducible bases sets $T_{lm}^l$. The reduction can be carried out once and for all for dyadic products. The results are listed in Table 2-2. We omit the 3d bases, because their counterparts in Eq. (2-16), the $R_{1m}^l$'s vanish (or are ignored). The following definitions have been used in Table 2-2:

$$I_\pm = I_x \pm iI_y,$$

(2-21)

$$I_{+1} = -\frac{1}{\sqrt{2}} I_+; \quad I_0 = I_z; \quad I_{-1} = +\frac{1}{\sqrt{2}} I_-.$$

(2-22)

Similar definitions have been used for the components of $B_{st}$. The idea of these definitions is to express also vector components in terms of irreducible spherical tensor components, thus, e.g., $I_{\pm 1} = T_{1 \pm 1}, I_0 = T_1, I_{-1} = T_{-1}$.

Equations (2-16)-(2-20) and Tables 2-1 and 2-2 enable us now to express all internal Hamiltonians in terms of rotational invariants ($\mathcal{C}^l$), irreducible spherical tensor operators ($\rho_{lm}^l, T_{lm}^l$), and elements of the Wigner matrix $\mathcal{D}_{m'm}^2$. We shall discuss explicitly two examples ($\mathcal{H}_D$ and $\mathcal{H}_{CS}$), which are of the greatest importance in the field of high-resolution NMR in solids.

1. Dipolar Hamiltonian $\mathcal{H}_D$

We recall

$$C_{D,ik}^{\alpha\beta} = -2\gamma^I_i \gamma^k_h, \quad \rho_{20}^{D,ik} = \sqrt{2} \delta^{D,ik} = \sqrt{\frac{2}{3}} r_{ik}^{-3}, \quad \rho_{2m'}^{D} = 0, \text{ for } m' \neq 0.$$

Equation (2-20) yields

$$R_{2m}^{D,ik} = \mathcal{D}_{2m}^2(\Omega^{D,ik}) \sqrt{\frac{2}{3}} r_{ik}^{-3}.$$
### TABLE 2-1
Wigner Rotation Matrix $\mathcal{R}_{m,m}'(\alpha, \beta, \gamma)$

<table>
<thead>
<tr>
<th>$m'$</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>−1</th>
<th>−2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\frac{(1 + \cos \beta)^2}{4} e^{2i(\alpha + \gamma)}$</td>
<td>$\frac{1 + \cos \beta}{2} \sin \beta e^{i(2\gamma + \alpha)}$</td>
<td>$\frac{1 - \cos \beta}{2} \sin \beta e^{i(2\gamma - \alpha)}$</td>
<td>$\frac{1}{4} (1 - \cos \beta)^2 e^{2i(\gamma - \alpha)}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$-\frac{1 + \cos \beta}{2} \sin \beta e^{i(2\alpha + \gamma)}$</td>
<td>$\left[ \cos^2 \beta - \frac{1 - \cos \beta}{2} \right] e^{i(\alpha + \gamma)}$</td>
<td>$\frac{1 + \cos \beta}{2} - \cos^2 \beta \right] e^{i(\gamma - \alpha)}$</td>
<td>$\frac{1 - \cos \beta}{2} \sin \beta e^{i(\gamma - 2\alpha)}$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>$\frac{\sqrt{3}}{2} \sin^2 \beta e^{2i\beta}$</td>
<td>$-\frac{3}{2} \sin 2\beta e^{i\alpha}$</td>
<td>$\frac{\sqrt{3}}{2} \sin 2\beta e^{-i\alpha}$</td>
<td>$\sqrt{3} \sin^2 \beta e^{-2i\alpha}$</td>
<td></td>
</tr>
<tr>
<td>−1</td>
<td>$-\frac{1 - \cos \beta}{2} \sin \beta e^{i(2\alpha - \gamma - \gamma)}$</td>
<td>$\left[ \frac{1 + \cos \beta}{2} - \cos^2 \beta \right] e^{i(\alpha - \gamma)}$</td>
<td>$\frac{1 + \cos \beta}{2} - \cos^2 \beta \right] e^{-i(\alpha + \gamma)}$</td>
<td>$\frac{1}{4} (1 + \cos \beta)^2 e^{i(2\alpha + \gamma)}$</td>
<td></td>
</tr>
<tr>
<td>−2</td>
<td>$\frac{(1 - \cos \beta)^2}{4} e^{2i(\alpha - \gamma)}$</td>
<td>$\frac{1 - \cos \beta}{2} \sin \beta e^{i(2\alpha - \gamma)}$</td>
<td>$\frac{1 + \cos \beta}{2} \sin \beta e^{-i(\alpha + \gamma)}$</td>
<td>$\frac{1 + \cos \beta}{2} \sin \beta e^{-i(2\alpha + \gamma)}$</td>
<td>$\frac{1}{4} (1 + \cos \beta)^2 e^{-2i(\alpha + \gamma)}$</td>
</tr>
</tbody>
</table>
**TABLE 2-2**

**One- and Five-Dimensional Irreducible Standardized Bases Sets** $T_{lm}$ of O3 Contained in $I_s A_s$

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\lambda$</th>
<th>$I_s A_s$</th>
<th>$T_{00}$</th>
<th>$T_{20}$</th>
<th>$T_{2\pm 1}$</th>
<th>$T_{2\pm 2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shielding.</td>
<td>CS</td>
<td>$I_s^2 B_s$</td>
<td>$I_0^2 B_0$</td>
<td>$\frac{\sqrt{2}}{3} I_0^2 B_0$</td>
<td>$\frac{1}{\sqrt{2}} I_{\pm 1}^2 B_0$</td>
<td>0</td>
</tr>
<tr>
<td>Spin rotation</td>
<td>SR</td>
<td>$I_s^2 J_s$</td>
<td>$I^1 \cdot J$</td>
<td>$\frac{1}{\sqrt{6}} [3I_0^2 J_0 - I^1 \cdot J]$</td>
<td>$\frac{1}{\sqrt{2}} [I_{\pm 1}^1 J_0 + I_0^1 J_{\pm 1}]$</td>
<td>$I_{\pm 1}^1 J_{\pm 1}$</td>
</tr>
<tr>
<td>Quadrupole</td>
<td>Q</td>
<td>$I_s^2 I_s^1$</td>
<td>$(I^1)^2$</td>
<td>$\frac{1}{\sqrt{6}} [3(I_0^1)^2 - (I^1)^2]$</td>
<td>$\frac{1}{\sqrt{2}} [I_{\pm 1}^1 I_0^1 + I_0^1 I_{\pm 1}]$</td>
<td>$(I_{\pm 1}^1)^2$</td>
</tr>
<tr>
<td>Dipole</td>
<td>D</td>
<td>$I_s^1 I_s^1$</td>
<td>$I^1 \cdot I^1$</td>
<td>$\frac{1}{\sqrt{6}} [3I_0^1 I_0^1 - I^1 \cdot I^1]$</td>
<td>$\frac{1}{\sqrt{2}} [I_{\pm 1}^1 I_0^1 + I_0^1 I_{\pm 1}]$</td>
<td>$I_{\pm 1}^1 I_{\pm 1}$</td>
</tr>
<tr>
<td>Indirect spin–spin</td>
<td>J</td>
<td>$I_s^1 I_s^k$</td>
<td>$I^1 \cdot I^k$</td>
<td>$\frac{1}{\sqrt{6}} [3I_0^1 I_0^k - I^1 \cdot I^k]$</td>
<td>$\frac{1}{\sqrt{2}} [I_{\pm 1}^1 I_0^k + I_0^k I_{\pm 1}]$</td>
<td>$I_{\pm 1}^1 I_{\pm 1}$</td>
</tr>
</tbody>
</table>
Inserting $R_{2m}^{D,ik}$ and $C_{0m}^{D,ik}$ into Eq. (2-16) leads to
\[
\mathcal{H}_{D,ik} = -\sqrt{6} \gamma_n i_n^k h r_{ik}^{-3} \sum_m (-1)^m \mathcal{D}_{0m,-m}^{2m} T_{2m}^{D,ik}.
\] (2-23)

Now the $\mathcal{D}_{0m}^2$ are—apart from a constant factor—identical with the spherical harmonics $Y_{2m}$, which behave under rotations exactly as the $R_{lm}$:
\[
\mathcal{D}_{0m}^2(\alpha, \beta, \gamma) = (4\pi/5)^{1/2} Y_{2m}(\beta \alpha).
\] (2-24a)

Similarly,
\[
\mathcal{D}_{m}^2(\alpha, \beta, \gamma) = (-1)^m (4\pi/5)^{1/2} Y_{2m}(\beta \gamma).
\] (2-24b)

The $Y_{lm}$ are normalized such that
\[
\int_{\text{sphere}} Y_{lm} Y_{l'm'}^* \, ds = \delta_{ll'} \delta_{mm'},
\] (2-25)

where $ds$ is the surface element on the sphere.

Note that the $\mathcal{D}_{0m}^2$'s actually do not depend on $\gamma$; note also that $\beta_{D,ik}$ and $\alpha_{D,ik}$ are identical, respectively, with the polar angles $\phi_{ik}$ and $\varphi_{ik}$ of the internuclear vector $\mathbf{r}_{ik}$ in the laboratory frame.

Inserting Eq. (2-24) into Eq. (2-23) and reintroducing the indices $k$ and $i$, we have finally\(^5\)
\[
\mathcal{H}_D = -2(6\pi/5)^{1/2} h \sum_{i < k} \gamma_n i_n^k r_{ik}^{-3} \sum_m (-1)^m Y_{2m,-m}(\beta_{ik}, \varphi_{ik}) T_{2m}^{D,ik}.
\] (2-26)

The $T_{2m}^{D,ik}$ are given explicitly in the last row of Table 2-2. This form of $\mathcal{H}_D$ is the most useful one not only for discussing high-resolution NMR in solids but also for, e.g., discussing nuclear magnetic relaxation phenomena.\(^6\)

2. SHIELDING HAMILTONIAN $\mathcal{H}_{CS}$

In irreducible spherical tensor notation the shielding Hamiltonian of a given nucleus assumes the form
\[
\mathcal{H}_{CS} = \gamma_n \sum_{l=0,2} \sum_{m=-l}^{+l} (-1)^m R_{l,-m}^{CS} T_{lm}^{CS}.
\] (2-27)

On the right-hand side of the following equations we shall drop the index CS.

\(^5\) Equation (2-26) differs from Eq. (2) of Haeberlen and Waugh\(^6\) by a factor of 2. This is due to a different definition of the $T_{lm}^D$. In Haeberlen and Waugh\(^6\) the definition of Slichter\(^7\) has been used.


B. ROTATIONS OF INTERNAL HAMILTONIANS

Introducing the principal axes shielding components $\rho_{lm}$ into Eq. (2-27) gives

$$\mathcal{H}_{CS} = \sum_{l=0,2} \sum_{m=-l}^{+l} (-1)^m T_{lm} \gamma_n \sum_{m'} D_{m',-m}^l \rho_{lm'}$$

$$= \gamma_n T_{00} \rho_{00}$$

$$+ \gamma_n \sum_{m=-2}^{+2} (-1)^m T_{2m} \sum_{m'} D_{m',-m}^2 \rho_{2m'}$$

$$= \omega_0 \sigma I_0$$

$$+ \omega_0 \left\{ \sqrt{2} I_0 \left[ \frac{\sqrt{2}}{2} D_{00}^2 + \frac{\eta}{2} (D_{02}^2 + D_{0-2}^2) \right] \right\}$$

$$- \frac{1}{\sqrt{2}} I_{-1} \left[ \frac{\sqrt{2}}{2} D_{01}^2 + \frac{\eta}{2} (D_{02}^2 + D_{0-2}^2) \right]$$

$$- \frac{1}{\sqrt{2}} I_{+1} \left[ \frac{\sqrt{2}}{2} D_{0,-1}^2 + \frac{\eta}{2} (D_{02}^2 + D_{0-2}^2) \right].$$

There are no terms $l = 2$, $m = \pm 2$, because the $T_{2m}$ involved are zero. The $m = 0$ terms, i.e., the secular terms, are of the greatest importance. We give three more formulations for them [Eqs. (2-29)–(2-31)].

Inserting Eq. (2-24b) into Eq. (2-28c) gives

$$\mathcal{H}_{CS,\text{secular}} = \omega_0 I_0 \left\{ \sigma + (8\pi/15)^{1/2} \left[ \frac{3}{2} Y_{20}^2 + \frac{\eta}{2} (Y_{22} + Y_{2,-2}) \right] \right\}. \tag{2-29}$$

The arguments of the spherical harmonics are $\beta, \gamma = \beta^{CS}, \gamma^{CS}$.

By inserting the appropriate trigonometric expressions for the $Y_{2m}$'s we get

$$\mathcal{H}_{CS,\text{secular}} = \omega_0 I_0 \left\{ \sigma + \delta \left[ \frac{3 \cos^2 \beta - 1}{2} + \frac{1}{2} \eta \sin^2 \beta \cos 2\gamma \right] \right\}. \tag{2-30}$$

By direct evaluation one may convince oneself that

$$\mathcal{H}_{CS,\text{secular}} = \omega_0 I_0 \sigma_{zz} \tag{2-31}$$

where $\sigma_{zz}$ is the zz-shielding component in the laboratory frame.

While admittedly Eq. (2-31) looks much simpler than Eqs. (2-29) and (2-30), the latter have the definite advantage that they display much clearer (i) the rotational behavior of $\mathcal{H}_{CS,\text{secular}}$ and (ii) the parameters on which it depends. Note that $\mathcal{H}_{CS,\text{secular}}$ does not depend on the Euler angle $\alpha$. This reflects the fact that the NMR experiment is invariant under rotations about the applied field. Still another expression for $\mathcal{H}_{CS,\text{secular}}$ will be needed and given in Chapter III, (Eq. 3-6).