III. Manifestations of Nuclear Magnetic Shielding in NMR Spectra of Solids

A. General Remarks

We have already stated that measuring the NMR parameters $\sigma^i$, $D^ik$, $V^i$, etc., is one of the principal goals of experimental NMR. There are three main factors governing the experimenter's access to these parameters:

1. the relative size of the internal Hamiltonians,
2. the averaging processes operative—intentionally or unintentionally—in both ordinary $r$ and spin spaces,
3. the manner in which the internal Hamiltonians manifest themselves in NMR spectra, particularly in NMR spectra of solids.

In many cases $\mathcal{H}_D$ greatly exceeds other internal Hamiltonians, in particular $\mathcal{H}_{CS}$. It then renders $\sigma$ inaccessible to measurement. In isotropic liquids, fast random molecular motions average out $\mathcal{H}_D$, but likewise they average out all anisotropic constituents of $\mathcal{H}_{CS}$. Only the isotropic constituent of $\sigma$ becomes measurable. The major achievement of selective averaging by multiple-pulse sequences is that it provided a technique by which it is possible to suppress $\mathcal{H}_D$ in solids by an averaging process in spin space that leaves alive all constituents of $\mathcal{H}_{CS}$. By this technique the full $\sigma$ tensors become accessible to measurement.

In this chapter we discuss the types of spectra encountered when $\mathcal{H}_{CS}$ either is the dominant part of the total spin Hamiltonian or when it is made the dominant part by selectively suppressing the homo- and heteronuclear dipolar spin–spin coupling terms.

Let us consider a perfect single crystal and let us recall two definitions:

Two nuclei are called crystallographically equivalent if they are related by any one of the symmetry elements of the space group of the crystal.
Two nuclei are called magnetically equivalent if they are related by one of
the translation and/or inversion elements of the space group.8 These latter
symmetry elements constitute an invariant subgroup of the space group.

Using these definitions, we may state:

(1) The tensorial parameters $\sigma$ and $V$ are identical for magnetically
equivalent nuclei, i.e., $\sigma^I \equiv \sigma^k$, $V^I \equiv V^k$ for magnetically equivalent nuclei $I$ and $k$.

(2) $\sigma$ and $V$ of crystallographically equivalent nuclei $I$ and $k$ are related
by the rotation-reflection parts of the symmetry operations by which the
nuclei $I$ and $k$ are related. The invariance of $\sigma$ and $V$ against inversions is a
consequence of the symmetry of these tensors ($\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$; $V_{\alpha\beta} = V_{\beta\alpha}$, or
alternatively, $\rho_{\alpha\pm\beta} = 0$). Effects of hypothetical nonvanishing constituents
of $\sigma$ are discussed below.

(3) The NMR spectra of idealized samples, in which only single-particle
Hamiltonians such as $H_{CS}$ and $H_Q$ are operative, are independent super-
positions of the spectra from magnetically nonequivalent nuclei.

Each partial spectrum consists of $N_I$ sharp lines, where $N_I$ depends on the spin
quantum number $I$ and the ratio $\hbar \omega_0 / e^2 q^I Q^I$. For $\hbar \omega_0 / e^2 q^I Q^I \gg 1$, $N_I = 2I$.
For $I = 1/2$, $N_I$ is just 1. Line splitting, and eventually line broadening, is caused
by the many-particle interactions $H_D$ and $H_I$. We disregard them in this
chapter.

If there are $N_m$ magnetically nonequivalent sites for a given isotope in a
single crystal, its (idealized) NMR spectrum consists of $N_I \times N_m$ sharp lines.
In special orientations of the crystal with respect to $B$, some of the lines will
coalesce. In any case the number of lines is limited, although often it is not
very small.

Let us consider a crystal with $N_c$ crystallographically equivalent but
magnetically nonequivalent sites for an isotope with, say, spin $I = 1/2$. These
sites contribute $N_c$ lines to the spectrum. Of course, we would like to know
which of these lines arises from which site. Now it is very important to realize
that it is impossible in principle to decide—on the basis of complete structural
and NMR information—which of these lines must be assigned to which site.
In other words, there is no symmetry argument on which an assignment could
be based. With the procedures to be described in the following section we

8 Note that neither crystallographically nor magnetically equivalent nuclei are automatically
equivalent nuclei according to the definition used in high-resolution NMR in fluids,
where equivalence is defined with respect to molecular symmetry, and scalar couplings
$J^{1k}$ are taken into account.9

can, in principle, determine a $\sigma$ tensor for each of the $N_c$ lines. These tensors transform among themselves under the symmetry operations by which the crystallographically equivalent sites are related.

Crystallographically nonequivalent sites can, in general, be distinguished: The corresponding $\sigma$ tensors cannot be brought into exact coincidence by any one of the symmetry operations of the space group. There is, however, still the question of which set of lines (or $\sigma$ tensors) belongs to which set of crystallographically equivalent sites. Again there is no symmetry argument that allows an assignment of the different sets of related lines to the corresponding sets of crystallographically equivalent sites if these sites are general sites. Special sites, however, can be distinguished from general sites. Sites on $n$-fold axes, as well as on screw axes, mirror and glide planes, and inversion centers are called special sites.

The lines from two sites related by, e.g., a mirror plane coincide when $B_{st}$ falls into that mirror plane. This line then has double intensity in comparison to a line from a site on the mirror plane. More important, however, the former line splits when $B_{st}$ moves out of the mirror plane, whereas the latter does not.

For magnetic resonance experiments planes perpendicular to $n$-fold axes (screw axes) are equivalent to mirror planes. Lines from sites on inversion centers can be distinguished from other lines again by their smaller intensity.

In summary, symmetry arguments are very valuable for handling the assignment problem, but often they do not lead to its complete solution. Assignments must then be based on additional information, for instance, NMR data from related compounds, or on theoretical grounds. Such assignments are usually highly reliable but inevitably they incorporate some kind of assumption.

**B. Single Crystals Available**

We start with a case in which all sites are magnetically equivalent for the isotope in which we are interested. For simplicity we suppose $I = \frac{1}{2}$. There is only one line in the spectrum. We ask ourselves how we can determine the desired shielding parameters from the spectral position of this line. Obviously we must render the line position dependent on an external parameter. The orientation of the crystal with respect to the external magnetic field plays the role of this external parameter.

In the approximation—usually an excellent one—in which we restrict ourselves to secular terms of the internal Hamiltonian [terms with $m = 0$ in Eq. (2-16)] the position of the one line in the spectrum is governed by

$$H^i_{\text{CS, secular}} = \gamma_n I_0 B_0 \{\sigma^I + \sqrt{\frac{2}{3}} R^{\text{CS}, i}_{20}\} = \omega_0 I_0 \{\sigma^I + \sqrt{\frac{2}{3}} \sigma^I_{20}\}$$
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[cf. Eq. (2-27)]. To save indices we set $R_{2m}^{\text{CS},i} = \sigma_{2m}^i$. The upper Zeeman level ($m_j = -\frac{1}{2}$) is shifted by an amount $-\frac{1}{2}\hbar\omega_0\{\sigma^i + \sqrt{3}\sigma_{20}^i\}$, and the lower ($m_j = +\frac{1}{2}$) by the same amount in the opposite direction. Hence the position $\omega^i$ of the line relative to the position $\omega^b$ of the line of the bare nucleus ($\sigma^b = 0$) is given in units of $2\pi$ Hz by

$$\omega^i - \omega^b = -\omega_0\{\sigma^i + \sqrt{3}\sigma_{20}^i\} = -\omega_0\sigma_{zz}^i. \quad (3-1)$$

The position of the line of the bare nucleus is not known. Therefore, in practice, we do not reference $\omega^i$ against $\omega^b$, but against $\omega^\text{ref}$, which is the line position of a reference sample for which $\sigma_{20}^i$ vanishes for one reason or another (e.g., motional averaging or cubic crystal symmetry).

$$\omega^i - \omega^\text{ref} = -\omega_0\{\sigma^i - \sigma^\text{ref} + \sqrt{3}\sigma_{20}^i\} \quad (3-2)$$

is all that we can measure in an NMR experiment. The scalar shielding parameter that we can measure—in principle, not only in practice—is not $\sigma^i$, but $\sigma^i - \sigma^\text{ref}$.

In Eq. (2-30) we have expressed $\sigma_{20}^i$ in terms of $\delta^i, \eta^i$ and $\beta^i, \gamma^i$. Recall that $\beta^i$ and $\gamma^i$ are the Euler angles by which the laboratory system of coordinates (henceforth denoted by LABS) can be brought into coincidence with the PAS of $\sigma^i$. Although $\beta^i$ and $\gamma^i$ are parameters on which $\omega^i - \omega^\text{ref}$ directly depends, they are not the parameters in which we are ultimately interested.

The parameters in which we are ultimately interested are $\sigma^i - \delta^\text{ref}, \delta^i, \eta^i$, and the Euler angles $\alpha^', \beta^', \gamma^' (\equiv \Omega^')$, which relate some arbitrarily chosen, crystal fixed orthogonal axes system (CRS) with the shielding principal axes system.

What is needed, therefore, is an expression for $\sigma_{20}^i$ in terms of $\delta^i, \eta^i, \Omega^i$, and the Euler angles $\alpha^{''}, \beta^{''}, \gamma^{''} (\equiv \Omega^{''})$, which relate the laboratory and the crystal fixed frames. Such an expression is obtained easily by applying Eq. (2-20) twice:

$$\sigma_{20}^i(\text{LABS}) = \sum_{m'} D_{m^*0}^{2}\left(\Omega^{''}\right)\sigma_{2m'}(\text{CRS}) = \sum_{m'} D_{m^*0}^{2}\left(\Omega^{''}\right)\sum_{m'} D_{m^*m'}^{2}\left(\Omega^i\right)\rho_{2m^*i}^{\text{CS},i}$$

$$= \sum_{m'} D_{m^*0}^{2}\left(\Omega^{''}\right)\delta^i \left[\sqrt{3} D_{0m'}^{2}\left(\Omega^i\right) + \frac{1}{3}\eta^i\left[D_{2m'}^{2}\left(\Omega^i\right) + D_{-2m'}^{2}\left(\Omega^i\right)\right]\right]. \quad (3-3)$$

Recall that the $D_{2m^*0}^{2}$ actually do not depend on $\alpha^{''}$. In fact, $\omega^i$ must not depend on $\alpha^{''}$ since the line position must be invariant under rotations of the crystal about the external magnetic field.

Often it is very useful to express the relation between the LABS and the CRS not by the Euler angles $\alpha^{''}, \beta^{''}, \gamma^{''}$—which are always hard to visualize, and one of which does not enter the result in any case—but by the polar angles $\delta, \varphi$, which specify the direction of the external magnetic field in the
crystal fixed frame. $\beta''$, $\gamma''$ and $\vartheta$, $\varphi$ are related by

\begin{align}
\beta'' &= \vartheta, \quad (3-4a) \\
\gamma'' &= \pi - \varphi \quad (3-4b)
\end{align}

(see, e.g., Fig. 1.1 of Edmonds').

Using Eqs. (2-24b), (3-4a), and (3-4b), and well-known symmetry relations among the spherical harmonics, we get

$$
\mathcal{D}_{m',0}^2(\Omega'') = (-1)^m (4\pi/5)^{1/2} Y_{2m'}(\beta'', \gamma'') = (-1)^m (4\pi/5)^{1/2} Y_{2m'}(\vartheta, \pi - \varphi) = (4\pi/5)^{1/2} Y_{2,-m'}(\vartheta, \varphi). \quad (3-5)
$$

Inserting Eqs. (3-5) and (3-3) into Eq. (3-2) gives the line position in terms of the desired parameters:

$$
\omega^i - \omega^{\text{ref}} = -\omega_0 \left\{ \sigma^i - \sigma^{\text{ref}} + (8\pi/15)^{1/2} \sum_{m'} Y_{2,-m'}(\vartheta, \varphi) \right\}
$$

$$
\times \left[ (3/2)^{1/2} \mathcal{D}_{0m'}^2(\Omega_i') + \frac{1}{2} \eta^i (\mathcal{D}_{2m'}^2(\Omega_i') + \mathcal{D}_{-2m'}^2(\Omega_i')) \right].
$$

(3-6)

$\vartheta$ and $\varphi$ are external parameters. Six different, nondegenerate choices of $\vartheta$, $\varphi$ lead to six different line positions from which we may calculate, in principle, the desired parameters. This is, however, not the typical procedure.

Usually one rotates the crystal about an axis perpendicular to the external field and records what is called a rotation pattern. Stated differently, one records $\omega^i - \omega^{\text{ref}}$ when the external field moves in a plane of the crystal. Three rotation patterns with three different choices of the rotation axes are usually needed. The rotation patterns are always of the form

$$
- [\omega^i(\Phi) - \omega^{\text{ref}}]/\omega_0 = C^i + A^i \cos 2(\Phi - \Phi_{\text{max}}^i), \quad (3-7)
$$

where $\Phi$ is the rotation angle (counted from an arbitrary zero); $C^i$, $A^i$, and $\Phi_{\text{max}}^i$ are constants that are (complicated) functions of $\alpha_i'$, $\beta_i'$, $\gamma_i'$, $\sigma^i - \sigma^{\text{ref}}$, $\delta^i$, $\eta^i$, and of the choice of the rotation axis. These functions become reasonably simple only if $\eta^i = 0$ (axially symmetric shielding tensor) and if we choose the axes $x_{\text{CR}}$, $y_{\text{CR}}$, $z_{\text{CR}}$ of the CRS as rotation axes. Figure 3-1 and Table 3-1 show how we get the desired internal parameters directly from the rotation patterns in such a simple case.

In the general case ($\eta \neq 0$) one usually determines these parameters by a least-squares computer fit analysis of the data of the rotation patterns. Equation (3-6) is a good starting point for the required program.
Fig. 3-1. (a) Example of rotation patterns when $\sigma$ is axially symmetric; $\delta > 0$, $\alpha = 30^\circ$, $\beta = 60^\circ$ have been chosen. The lowest points in each pattern are the same. For $\delta < 0$ the highest points would be the same. Note what is plotted on the ordinate axis! $\omega$ is the resonance position of the line for $B_0 = \text{const}$; $\omega_0 = \gamma n B_0$.

(b) Stereographic projection of (1) the crystal fixed frame $x_{CR}$, $y_{CR}$, $z_{CR}$; (2) the unique shielding axis ($Z$) and the $XY$ plane of the shielding principal axes system; (3) the paths of $\mathbf{B}_s$ when the crystal is rotated about the $z_{CR}$, $y_{CR}$, and $x_{CR}$ axes; the rotation axis is always perpendicular to $\mathbf{B}_s$ (4) $\Phi_{max,x}$, $\Phi_{max,y}$, $\Phi_{max,z}$; $\Phi_{min,x}$, $\Phi_{min,y}$, $\Phi_{min,z}$.

When taking rotation patterns it is always wise to draw a figure like (b).
TABLE 3-1

<table>
<thead>
<tr>
<th>Rotation axis $a$</th>
<th>$C_a$</th>
<th>$\Phi_a$</th>
<th>$A_a$</th>
<th>$\Phi_{\text{max},a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{CR}}$</td>
<td>$\sigma - \sigma_{\text{ref}} + \frac{\delta}{4}(1 - 3 \sin^2 \beta \cos^2 \alpha)$</td>
<td>$\varphi$</td>
<td>$\frac{3}{4}\delta(1 - \sin^2 \beta \cos^2 \alpha)$</td>
<td>$\frac{1}{2}\arcsin\left[\frac{\sin 2\beta \sin \alpha}{1 - \sin^2 \beta \cos^2 \alpha}\right]$</td>
</tr>
<tr>
<td>$y_{\text{CR}}$</td>
<td>$\sigma - \sigma_{\text{ref}} + \frac{\delta}{4}(1 - 3 \sin^2 \beta \sin^2 \alpha)$</td>
<td>$\varphi$</td>
<td>$\frac{3}{4}\delta(1 - \sin^2 \beta \sin^2 \alpha)$</td>
<td>$\frac{1}{2}\arcsin\left[\frac{\sin 2\beta \cos \alpha}{1 - \sin^2 \beta \sin^2 \alpha}\right]$</td>
</tr>
<tr>
<td>$z_{\text{CR}}$</td>
<td>$\sigma - \sigma_{\text{ref}} + \frac{\delta}{4}(1 - 3 \cos^2 \beta)$</td>
<td>$\varphi$</td>
<td>$\frac{3}{4}\delta \sin^2 \beta$</td>
<td>$\alpha$</td>
</tr>
</tbody>
</table>

(a) $\frac{1}{3}(C_x + C_y + C_z) = \sigma - \sigma_{\text{ref}}$

(b) $A = A_x + A_y + A_z = \Delta \sigma$

(c) $\sin^2 \beta = 2 \frac{A_z}{A} \; \sin 2\beta = \frac{2A_z \sin^2 \Phi_{\text{max},z} - A}{A \cos \Phi_{\text{max},z}} \sin 2\Phi_{\text{max},y}$

(d) $\alpha = \Phi_{\text{max},z}$

* Equation (a) holds also in the general case ($\eta \neq 0$), as does Eq. (b) if at least one of the axes of the PAS coincides with one of the axes of the CRS, and provided $\Delta \sigma$ is interpreted as $\frac{1}{3}\delta(3 + \eta) = \sigma_{zz} - \sigma_{xx}$. The sign of $\delta$ can be determined from whether the lowest or highest points in all patterns are the same or nearly the same for $1 \gg \eta \neq 0$. For $\delta < 0$ "max" must be replaced by "min."
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C. Only Powders Available\(^1^0\)

1. POWDER PATTERN LINESHAPES

A powder consists of a multitude of randomly oriented single crystals. Consider a group of crystallographically equivalent nuclei and suppose that their shielding tensors are axially symmetric. If we plot the orientations of the unique axes of all these tensors in the powder sample on a sphere we get a distribution that is constant over the sphere. Alternatively, we may plot on a sphere the direction of \( \mathbf{B}_{st} \) (specified by \( \theta, \varphi \)) as seen in the PAS of each nucleus. This alternative makes it easy to drop the restricting assumption of axially symmetric shielding tensors.

The distribution we get is again constant over the sphere. Each point on the sphere corresponds to a definite orientation of \( \mathbf{B}_{st} \) with respect to a shielding principal axes system and hence to a definite NMR spectral line position. It is obtained from Eq. (3-6) by setting \( \Omega' = (0,0,0) \), which means making the CRS and the PAS coincide. Since \( \mathbb{D}_{m_m}(0) = \delta_{m_m} \) we obtain

\[
\omega^i - \omega^{\text{ref}} = -\omega_0 \{ \sigma^i - \sigma^{\text{ref}} + (8\pi/15)^{1/2} \\
\times \delta^i [(3/2)^{1/2}Y_{20}(\theta, \varphi) + \frac{1}{2}\eta^i(Y_{2,2}(\theta, \varphi) + Y_{2,-2}(\theta, \varphi))] \}
= -\omega_0 \{ \sigma^i - \sigma^{\text{ref}} + \delta^i \left[ \frac{1}{2} (3 \cos^2 \theta - 1) + \frac{1}{2} \eta^i \sin^2 \theta \cos 2\varphi \right] \}.
\]

(3-8)

The orientational dependence of the line position is contained in

\[
\omega = \omega_0 \delta \left[ \frac{1}{2} (3 \cos^2 \theta - 1) + \frac{1}{2} \eta \sin^2 \theta \cos 2\varphi \right],
\]

(3-9)

where, for simplicity, we have dropped the indices \( i \) from the parameters \( \eta \) and \( \delta \). Using Eq. (3-9) we now can draw curves \( \omega = \text{const} \) on our sphere. Two examples are given in Figs. 3-2 and 3-4.

The NMR spectrum of a powder sample is a superposition of the NMR lines from all the nuclei of all the grains of the sample. The intensity \( I(\omega) \) of the spectrum, when integrated over an interval \( \omega_a \cdots \omega_b \) is proportional to the number of nuclei whose NMR lines fall into that interval. This means it is proportional to the area between the curves \( \omega = \omega_a \) and \( \omega = \omega_b \) on our sphere (it is clear that we need consider only one hemisphere, in fact, only one octant of the sphere):

\(^{10}\) The subject matter of this section is treated, e.g., by Bloembergen and Rowland.\(^{11,12}\) However, it is our experience that students often have a very hard time following their articles. Therefore, we discuss here the underlying ideas in a rather detailed manner and hope that this is warranted from a didactic point of view.


Fig. 3-2. Stereographic projection of curves $\omega = \text{const}$ (actually curves $\vartheta = \text{const}$) when $\sigma$ is axially symmetric, $\eta = 0$. Units are $\omega_0\delta$. Notice the large distance of the curves for $\vartheta \to 0$ and $\vartheta \to \pi/2$.

$$\int_{\omega_a}^{\omega_b} I(\omega) \, d\omega = N \int \int \sin \vartheta \, d\vartheta \, d\varphi. \quad (3-10)$$

$N$ is a normalization factor which we are free to choose in such a way that $\int_{-\infty}^{+\infty} I(\omega) \, d\omega = 1$. $N = 2/\pi$ if eventually we integrate over one octant of the sphere.

First let us consider the special case $\eta = 0$.

Figure 3-2 shows the curves $\omega = \omega_n = \text{const}$. Equal increments of $\omega_n$ have been chosen. $\omega$ depends only on $\vartheta$. The curves $\omega = \text{const}$ are actually curves $\vartheta = \text{const}$. We integrate Eq. (3-10) over $\varphi$ (from $\varphi = 0$ to $\varphi = \pi/2$). In the remaining integral over $\vartheta$ we introduce

$$\omega = \omega_0 \delta \cos^2 \vartheta - 1$$

as a new integration variable. This gives

$$\int_{\omega_a}^{\omega_b} I(\omega) \, d\omega = \frac{1}{\sqrt{3} \omega_0 \delta} \int_{\omega_a}^{\omega_b} \frac{d\omega}{[1 + (2\omega/\omega_0 \delta)]^{1/2}}. \quad (3-11)$$
Equation (3-11) holds for arbitrary integration limits $\omega_a$, $\omega_b$; hence we can equate the integrands and obtain

$$I(\omega) = \frac{1}{\sqrt{3} \omega_0 \delta} \left[ 1 + (2\omega/\omega_0 \delta) \right]^{1/2}, \quad -\omega_0 \delta/2 \leq \omega \leq \omega_0 \delta.$$  

(3-12)

Figure 3-3 shows $I(\omega)$, which is the idealized powder pattern when $\sigma$ is axially symmetric. It diverges for $\omega \to -\frac{1}{2} \omega_0 \delta$. We hope that Figure 3-2 provides a “look and see” understanding for this divergence. Note, in particular, the spacing of the curves $\omega = \omega_n$! Figure 3-3 also makes clear how the desired internal parameters $\sigma - \sigma_{\text{ref}}$ and $\Delta \sigma = \frac{3}{2} \delta$ can be determined from a powder pattern. Naturally no information about the direction of the unique axis relative to a crystal fixed frame can be derived from powder patterns.$^{13}$  

To treat the general case, $\eta \neq 0$, let us first introduce $x = -\cos \theta$ and then $\omega = \frac{1}{2} \omega_0 \delta [3x^2 - 1 + \eta (1 - x^2) \cos 2\varphi]$ as new integration variables in the right-hand integral of Eq. (3-10). The first step leads to

$$\frac{2}{\pi} \int \int dx \, d\varphi,$$

where the dots indicate integration limits. The second step leads to

$$\int_{\omega_a}^{\omega_b} I(\omega) \, d\omega = \frac{2}{\pi} \int_{\omega_a}^{\omega_b} d\omega \int_{\varphi_1}^{\varphi_0} \Delta(\varphi, \omega) \, d\varphi. \quad (3-13)$$

Fig. 3-3. Powder pattern when $\sigma$ is axially symmetric. The divisions on the axis correspond to the lines $\omega = \text{const}$ in Fig. 3-2. Similarly, the shaded areas in Figs. 3-2 and 3-3 correspond to each other.

$^{13}$ By comparing $^{19}$F multiple-pulse powder patterns of $C_6F_6$ at different temperatures and exploiting the knowledge that $C_6F_6$ molecule rotates rapidly about their 6-fold axes in the solid state at higher temperatures Mehring et al.$^{14}$ were able to determine the unique axis of the $^{19}$F shielding tensor. $C_6F_6$, however, is an exceptional case.

φ₁ and φ₂ are the lower and upper integration limits of the φ-integral, respectively. We shall specify them shortly. Δ(φ, ω) is the Jacobian $\frac{\partial x}{\partial \omega} = \frac{1}{\omega_3} \left[ (3 - \eta \cos 2\phi) \left( \frac{2\omega}{\omega_3} + 1 - \eta \cos 2\phi \right) \right]^{-1/2}.$ (3-14)

We have introduced the abbreviation $\omega_3 = \omega_0 \delta$ and similarly we shall define $\omega_2 = -\frac{1}{2} \omega_0 \delta (1 - \eta) = \omega_0 \sigma_{yy}^{(2)}$ and $\omega_1 = -\frac{1}{2} \omega_0 \delta (1 + \eta) = \omega_0 \sigma_{xx}^{(2)}.$ By the same argument used in the paragraph following Eq. (3-11) we can now equate the integrands of the ω integrals in Eq. (3-13):

$$I(\omega) = \frac{2}{\pi \omega_3} \int_{\phi_1}^{\phi_2} \left( 3 - \eta \cos 2\phi \right)^{-1/2} \left( \frac{2\omega}{\omega_3} + 1 - \eta \cos 2\phi \right)^{-1/2} d\phi.$$ (3-15)

Let us now turn to φ₁ and φ₂. We integrate only over one octant of the sphere; we choose the upper left one in Fig. 3-4. It is clear from Fig. 3-4 that we must distinguish two cases:

![Fig. 3-4. Stereographic projection of curves ω = const when σ is nonaxially symmetric. η = $\frac{1}{3}$ has been chosen in this example. Units are $\omega_0 \delta = \omega_3.$ For $\omega/\omega_3 < \omega_2/\omega_3 = -\frac{1}{2} (1 - \eta)$ the curves cross the equator. The crossing meridian φ₁ is determined by $\omega/\omega_3 = -\frac{1}{2} [1 - \eta \cos 2\phi].$](image-url)
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(i) \(\omega_2 \leq \omega \leq \omega_3 \rightarrow \varphi_i = 0, \varphi_u = \frac{\pi}{2}\),

(ii) \(\omega_1 \leq \omega \leq \omega_2 \rightarrow \varphi_i = \frac{1}{2} \arccos \left[ \frac{1}{\eta} \left(1 + \frac{2\omega}{\omega_3}\right) \right], \varphi_u = \frac{\pi}{2}\).

To proceed, we introduce the new integration variable \(z = \cos 2\varphi\). We get

\[
I(\omega) = \frac{1}{\pi \omega_3 \eta} \int_{z_l}^{z_u} \frac{dz}{[(1-z^2)(3/\eta-z)((1/\eta)[(2\omega/\omega_3)+1]-z)]^{1/2}},
\]

\(z_u = 1\) (case i), \(z_u = \frac{1}{\eta} \left(\frac{2\omega}{\omega_3} + 1\right)\) (case ii), \(z_l = -1\) (cases i, ii).

This integral is tabulated, e.g., in the “Table of Integrals, Sums, Series and Products” by Gradshteyn and Ryzhik.\(^{15}\) Note that the zeros \(z_n\) of the polynomial under the root are known; note also that the sequence of the \(z_n\)'s (which is crucial) is different in cases i and ii.

Calculating the required parameters from \(z_l, z_u, \) and the \(z_n\)'s we finally get

\[
I(\omega) = \pi^{-1} \left[ (\omega_3 - \omega_2)(\omega - \omega_1) \right]^{-1/2} \left\{ \left( \frac{(\omega_3 - \omega)(\omega_2 - \omega_1)}{(\omega_3 - \omega_2)(\omega - \omega_1)} \right)^{1/2} \right\}^{1/2} F\left\{ \left( \frac{(\omega_3 - \omega)(\omega_2 - \omega_1)}{(\omega_3 - \omega_2)(\omega - \omega_1)} \right)^{1/2}, \frac{\pi}{2} \right\},
\]

for \(\omega_2 \leq \omega \leq \omega_3\), and

\[
I(\omega) = \pi^{-1} \left[ (\omega_3 - \omega)(\omega_2 - \omega_1) \right]^{-1/2} \left\{ \left( \frac{(\omega_3 - \omega)(\omega_2 - \omega_1)}{(\omega_3 - \omega)(\omega_2 - \omega_1)} \right)^{1/2} \right\}^{1/2} F\left\{ \left( \frac{(\omega_3 - \omega)(\omega_2 - \omega_1)}{(\omega_3 - \omega)(\omega_2 - \omega_1)} \right)^{1/2}, \frac{\pi}{2} \right\},
\]

for \(\omega_1 \leq \omega \leq \omega_2\).

\(F(k, \varphi)\) is the (incomplete) elliptic integral of the first kind, and,

\[
K(\arcsin k) = F(k, \pi/2)
\]

is the complete elliptic integral of the first kind. We have normalized \(I(\omega)\) such that the area under \(I(\omega)\) is unity. Figure 3-5 shows an example. The discontinuities \(\omega_3, \omega_2, \omega_1\) immediately yield \(\sigma_{zz}, \sigma_{yy}, \sigma_{xx}\) or, alternatively, \(\delta, \eta, \) and \(\sigma\).

Before leaving the subject of nuclear-shielding powder lineshapes a final

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remark should be made. We have already emphasized that by investigating powders one does not get information about principal shielding directions. Hence single-crystal studies are always potentially superior to powder studies. In practice, however, there may be exceptions to this rule. Remember that all crystallographically equivalent nuclei contribute to one and the same powder pattern. Now, in molecular solids the nuclear shielding is often dominated so much by molecular properties that not only all crystallographically, but all chemically equivalent nuclei (nuclei related by molecular symmetry operations) contribute to one and the same pattern. This may result for highly symmetric molecules (C₆F₆, P₄, C₆H₆, etc.) in powder patterns simple enough to be analyzed, whereas the corresponding single-crystal spectra may resist an analysis due to too large a number of often unresolved lines.

2. Moments of Shielding Powder Patterns

The $n$th moment of a (normalized) lineshape function $I(\omega)$ or, in other terms, the mean value $\langle \omega^n \rangle$ of $\omega^n$ is defined as

$$\langle \omega^n \rangle = \int_{-\infty}^{+\infty} I(\omega) \omega^n d\omega. \quad (3-17)$$

This definition requires a specification of the point about which the moments are to be taken. We choose it such that $\langle \omega \rangle = 0$. This choice is consistent with Eq. (3-9). We call that point in the spectrum $\bar{\omega}$. $\bar{\omega}$ and $\langle \omega^2 \rangle$ of pure shielding powder patterns can be determined experimentally even when the experimental patterns are strongly affected by internal Hamiltonians other than $\mathcal{H}_{CS}$, e.g., by $\mathcal{H}_D$. The precise conditions under which this holds true are discussed by Van der Hart and Gutowsky.\(^\text{16}\)

A third quantity that is accessible experimentally is $\omega_{1/2}$ defined by

$$\int_{-\infty}^{\infty} I(\omega) \, d\omega = \frac{1}{2}. \quad (3-18)$$

$\omega_{1/2}$ divides the area under $I(\omega)$ in two equal halves. For symmetric patterns $\omega_{1/2} = \bar{\omega}$.

By inserting the squares of both sides of Eq. (3-9) in both sides of Eq. (3-10) and extending the integration limits appropriately, we obtain in a straightforward manner

$$\langle \omega^2 \rangle = (\omega_0 \delta)^2 \frac{1}{15} (3 + \eta^2). \quad (3-19)$$

We were unsuccessful in finding an explicit formula for $\bar{\omega} = \omega_{1/2}$; therefore, we give in Fig. 3-6 a graphic plot of $f(\eta) = (\omega_0 \delta)^{-1} |(\bar{\omega} - \omega_{1/2})|$ versus $\eta$. To determine $\delta$ and $\eta$ ($\sigma$ is fixed by $\bar{\omega}$ itself) from measured values of $\bar{\omega}$, $\omega_{1/2}$, and $\langle \omega^2 \rangle$ a plot of

$$g(\eta) = \langle \omega^2 \rangle^{-1/2} |\bar{\omega} - \omega_{1/2}| = f(\eta) \left[ \frac{15}{3 + \eta^2} \right]^{1/2}$$

is helpful and is given in Fig. 3-6. $g$ is a measurable quantity. Knowing $g$ we can immediately get $\eta$ from Fig. 3-6. Knowing $\eta$ and $\langle \omega^2 \rangle$ one can find $\delta$ from Eq. (3-19). The sign of $\delta$ is the same as the sign of $\bar{\omega} - \omega_{1/2}$.

This is a simple procedure to determine $\delta$ and $\eta$ (and $\sigma$). However, we are afraid that it will rarely produce accurate results, at least as far as $\eta$ is concerned. Its drawback is that $|\bar{\omega} - \omega_{1/2}|$ never exceeds $\frac{1}{12}$ of the total width of the spectrum. Therefore, nowadays most workers prefer to analyze their powder patterns by least-squares computer fit programs, as we do ourselves. Nevertheless, the procedure described above may help sometimes to get quickly results, if only preliminary ones.
D. Antisymmetric Constituents of $\sigma$

In the past few years there has been considerable discussion about a non-vanishing antisymmetric constituent of $\sigma$. The discussion runs, in fact, on two levels:

(i) Do antisymmetric constituents exist at all?
(ii) Given they exist, how do they manifest themselves in NMR spectra?

The first of these questions has been answered in the affirmative, at least to the extent that there are no symmetry arguments forbidding an antisymmetric constituent of $\sigma$. Buckingham and Malm\textsuperscript{17} have provided a valuable table that tells which of the elements of both the symmetric ($\sigma^{(s)}$) and antisymmetric ($\sigma^{(a)}$) constituents of $\sigma$ can be nonzero for a given nuclear site symmetry. We shall draw upon that table later in this section. These authors have also described a model system with nonvanishing elements of $\sigma^{(a)}$. Schneider\textsuperscript{18} and Griffin \textit{et al.}\textsuperscript{19} have dealt with the second of the above questions. They showed that $\sigma^{(a)}$ affects NMR line positions only in second order. We shall rederive their results here by a different, completely straightforward, and simple approach, and shall indicate how an experiment could be devised to demonstrate the existence of $\sigma^{(a)}$ in real physical systems.

In cartesian coordinates the Hamiltonian in question has the form

$$ h_\mathcal{H}^{(a)} = \gamma_n \hbar \mathbf{I} \cdot \sigma^{(a)} \cdot \mathbf{B}_{st}. $$

Again we drop indices designating nuclei. In the principal axes system of the symmetric constituent of $\sigma$ we have

$$ \sigma^{(a)} = \begin{bmatrix} 0 & \sigma^{(a)}_{XY} & \sigma^{(a)}_{XZ} \\ -\sigma^{(a)}_{XY} & 0 & \sigma^{(a)}_{YZ} \\ -\sigma^{(a)}_{XZ} & -\sigma^{(a)}_{YZ} & 0 \end{bmatrix}. $$

We recall that in the axes system chosen the elements of $\sigma^{(a)}$ are identical with the off-diagonal elements of $\sigma$ itself.

In irreducible spherical tensor notation $\mathcal{H}^{(a)}$ reads as follows:

$$ \mathcal{H}^{(a)} = \gamma_n \sum_m (-1)^m R_{1,-m}^{CS} T_{1m}^{CS}. $$

\textsuperscript{19} R. G. Griffin, J. D. Ellett, M. Mehring, J. G. Bulitt, and J. S. Waugh, \textit{J. Chem. Phys.} \textbf{57}, 2147 (1972); also see Kneubühl.\textsuperscript{20}
where

\[
T_{1,1}^{cs} = \left(1/\sqrt{2}\right)(I_1 B_0 - I_0 B_1) \rightarrow (1/\sqrt{2})I_1 B_0, \\
T_{1,0}^{cs} = \left(1/\sqrt{2}\right)(I_1 B_{-1} - I_{-1} B_1) \rightarrow 0, \\
T_{1,-1}^{cs} = \left(1/\sqrt{2}\right)(I_0 B_{-1} - I_{-1} B_0) \rightarrow -\left(1/\sqrt{2}\right)I_{-1} B_0.
\]

(3-23)

The expressions following the arrows in Eqs. 3-23 give the \(T_{1m}^{cs}\)'s for our usual choice of \(B_0\). Again, we denote the \(R_{1m}^{cs}\)'s in the principal axes system of \(\sigma^{(a)}\) by \(\rho_{1m}^{cs}\). The \(\rho_{1m}^{cs}\) are given in terms of the cartesian components of \(\sigma^{(a)}\) by

\[
\rho_{11}^{cs} = (\sigma_{X1}^{(a)} + i\sigma_{Y1}^{(a)}), \\
\rho_{10}^{cs} = -i\sqrt{2}\sigma_{Y1}^{(a)}, \\
\rho_{1,-1}^{cs} = (\sigma_{X2}^{(a)} - i\sigma_{Y2}^{(a)}).
\]

(3-24a,b,c)

Equation (2-20), with \(l = 1\) expresses the \(R_{1m}^{cs}\)'s needed in Eq. (3-22) by the \(\rho_{1m}^{cs}\)'s and by the elements of the Wigner rotation matrix \(\mathcal{D}^{1}_{mm'}\):

\[
R_{1m}^{cs} = \sum_{m'}\mathcal{D}^{1}_{mm'}(\Omega)\rho_{1m'}^{cs}.
\]

(3-25)

The Euler angles \((\alpha, \beta, \gamma) = \Omega\) are the same as, e.g., in Eq. (2-28). This is assured by our choice of the frame of reference in which we specified the \(\rho_{1m}^{cs}\)'s.

By inserting Eq. (3-25) and Eqs. (3-23a)-(3-23c) into Eq. (3-22) we get \(\mathcal{H}^{(a)}_{cs}\) in a form that is convenient for our discussion:

\[
\mathcal{H}^{(a)}_{cs} = \hbar \gamma_0 \sum_{m_1,m_2} (-1)^m\mathcal{D}^{1}_{m_1,-m} \rho_{1m'}^{cs} T_{1m}^{cs}
\]

\[
= \hbar \omega_0 \frac{1}{\sqrt{2}} \sum_{m_1} \left(\mathcal{D}^{1}_{1,-1} I_{-1} - \mathcal{D}^{1}_{-1,1} I_1\right) \rho_{1m'}^{cs}.
\]

(3-26)

We approach the manifestation of \(\mathcal{H}^{(a)}_{cs}\) in NMR spectra of solids by perturbation theory. The total Hamiltonian that we consider is

\[
\mathcal{H} = \mathcal{H}_z + \mathcal{H}^{(a)}_{cs} + \mathcal{H}^{(a)}_{cs},
\]

(3-27)

where \(\mathcal{H}_z\) is the unperturbed Hamiltonian. The perturbation approach will work well so long as all \(\sigma_{ab} \ll 1\).

For \(I = \frac{1}{2}\), \(\mathcal{H}_z\) defines two eigenstates, \(|-\rangle\) and \(|+_\rangle\), with energies \(\frac{1}{2}\hbar \gamma_0 B_0 = \frac{1}{2}\hbar \omega_0\), and \(-\frac{1}{2}\hbar \omega_0\). In first order only the so-called secular terms \(\mathcal{H}^{(a)}_{cs,\text{secular}}\) of \(\mathcal{H}^{(a)}_{cs}\) [see Eq. (2-29)] cause energy level shifts. The corresponding resonance shifts in the NMR spectrum have been discussed in detail in Section B. \(\mathcal{H}^{(a)}_{cs}\), in particular, has no diagonal elements between the eigenstates of \(\mathcal{H}_z\). This is immediately clear from Eq. (3-26). Both \(\mathcal{H}^{(a)}_{cs}\) and the nonsecular terms of \(\mathcal{H}^{(a)}_{cs}\) do cause second-order energy shifts. For the upper
D. ANTISYMMETRIC CONSTITUENTS OF $\sigma$

level ($| - \rangle$) the shift is

$$\epsilon_u = \frac{|\langle - \mid \hat{H}^{(a)}_{CS} + \hat{H}^{(e)}_{CS, \text{nonsecular}} \mid + \rangle|^2}{\hbar \omega_0};$$

for the lower level ($| + \rangle$) it is $\epsilon_i = -\epsilon_u$. Hence, the second-order angular frequency shift is

$$\Delta \omega_2 = \frac{2\epsilon_u}{\hbar}$$

$$= \omega_0 \left| \langle - \mid \left\{ \sum_m D_{m1}^+ \rho_{1m}^{CS} - \delta \left[ \sqrt{\frac{1}{2}} D_{01}^2 + \frac{1}{2} \eta (D_{21}^2 + D_{-2,1}^2) \right] \right\} I_{-1} \mid + \rangle \right|^2$$

$$= \frac{1}{2} \omega_0 |\cdots|^2.$$  
(3-28)

Note that the index $m$ is one in all the $D_{m,m}^+$ that enter Eq. (3-28). This means that every term has a factor $e^{iz}$ (see Table 2-1), which drops out on performing the $|\cdots|^2$ operation: rotations of the crystal about the magnetic field are unobservable by NMR.

Equation (3-28) tells us that the resonance position of our spectral line is affected by the antisymmetric constituent of $\sigma$ only in second order. However, the second-order shift $\Delta \omega_2$ is not entirely due to $\sigma^{(a)}$; a considerable part of it arises from $\sigma^{(e)}$. We now discuss a specific example.

We shall not consider a completely general antisymmetric tensor but one whose $XY$ (and $YX$) components only are nonzero. From the spherical components of $\sigma^{(a)}$ only $\rho_{10}^{CS}$ will be nonzero as a consequence. According to Buckingham and Malm’s table they chose a (a) applies for $C_2$, $C_s$, and $C_{2h}$ nuclear site symmetries. Equation (3-28) simplifies in this special case:

$$\Delta \omega_2 = \frac{1}{2} \omega_0 \sum_{m=1}^{2} \left( D_{m1}^+ \rho_{1m}^{CS} - \delta \left[ \sqrt{\frac{1}{2}} D_{01}^2 + \frac{1}{2} \eta (D_{21}^2 + D_{-2,1}^2) \right] \right) I_{-1} | + \rangle$$

$$= \omega_0 \left| \left( \sum_{m=1}^{2} D_{m1}^+ \rho_{1m}^{CS} - \delta \left[ \sqrt{\frac{1}{2}} D_{01}^2 + \frac{1}{2} \eta (D_{21}^2 + D_{-2,1}^2) \right] \right) I_{-1} | + \rangle \right|^2$$

$$= \omega_0 \left( \sin^2 \beta \sigma^{(a)}_{XY} - \delta \left[ \frac{3}{2} \sin 2\beta \right] + \frac{1}{2} \eta \sin \beta \left[ (1 + \cos \beta) e^{2i\gamma} - (1 - \cos \beta) e^{-2i\gamma} \right] \right)^2$$

$$\approx \omega_0 \left( \sin^2 \beta \sigma^{(a)}_{XY} - \delta \eta \sigma^{(e)}_{XY} \sin \beta \sin 2\gamma + \frac{1}{2} \delta^2 \eta^2 \sin^2 \beta \sin^2 2\beta \right)$$

$$+ \frac{1}{2} \delta^2 \sin^2 2\beta \left( 3 - 6\eta \cos 2\gamma + \eta^2 \cos^2 2\gamma \right).$$

We now ask ourselves how does the second-order shift manifest itself in rotation patterns. In the spirit of our previous discussion of rotation patterns we rotate the magnetic field $B_{st}$ about three orthogonal crystal fixed axes. For simplicity we choose the principal axes system of $\sigma^{(a)}$ of the nucleus considered as crystal fixed axes system. Thus we rotate $B_{st}$ successively in the $XY$, $XZ$, and $YZ$ planes. For ease of comparison we also indicate the first-order shifts $\Delta \omega_1$. These are obtained in a straightforward way from Eq. (2-30).

(i) $B_{st}$ rotates in the $XY$ plane ($\gamma$ is running, $\beta = \frac{1}{2}\pi$):
\[ \Delta \omega_2(\gamma; \beta = \frac{1}{2} \pi) = \frac{1}{2} \omega_0 \left( (\sigma_X^{(a)})^2 - \delta \eta \sigma_Y^{(a)} \sin 2\gamma + \frac{1}{6} \delta^2 \eta^2 \sin^2 2\gamma \right) \]
\[ = \frac{1}{2} \omega_0 \left( (\sigma_X^{(a)})^2 + \frac{1}{6} \delta^2 \eta^2 \right) - \delta \eta \sigma_Y^{(a)} \sin 2\gamma - \frac{1}{6} \delta^2 \eta^2 \cos 4\gamma \}, \]  
(3-30a)

\[ \Delta \omega_1(\gamma; \beta = \frac{1}{2} \pi) = -\omega_0 \{[\sigma - \sigma^{\text{ref}} - \frac{1}{2} \delta] + \frac{1}{2} \delta \eta \cos 2\gamma \}. \]  
(3-30b)

(ii) \( \mathbf{B}_{st} \) rotates in the \( XZ \) plane (\( \beta \) is running, \( \gamma = 0 \)):

\[ \Delta \omega_2(\beta; \gamma = 0) = \frac{1}{2} \omega_0 \left\{ \sin^2 \beta (\sigma_X^{(a)})^2 + \frac{1}{6} (3 - \eta)^2 \sin^2 2\beta \right\} \]
\[ = \frac{1}{2} \omega_0 \left\{ \left( \frac{1}{2} (\sigma_X^{(a)})^2 + \frac{1}{2} \delta^2 (3 - \eta)^2 \right) \right. \]
\[ - \frac{1}{2} (\sigma_X^{(a)})^2 \cos 2\beta - \frac{1}{3} \delta^2 (3 - \eta)^2 \cos 4\beta \}, \]  
(3-31a)

\[ \Delta \omega_1(\beta; \gamma = 0) = -\omega_0 \left\{ \left[ \sigma - \sigma^{\text{ref}} + \frac{1}{2} \delta (1 + \eta) \right] + \frac{1}{2} \delta (3 - \eta) \cos 2\beta \right\}. \]  
(3-31b)

(iii) \( \mathbf{B}_{st} \) rotates in the \( YZ \) plane (\( \beta \) is running, \( \gamma = \frac{1}{2} \pi \))

\[ \Delta \omega_2(\beta; \gamma = \frac{1}{2} \pi) = \frac{1}{2} \omega_0 \left\{ \sin^2 \beta (\sigma_X^{(a)})^2 + \frac{1}{6} \delta^2 (3 + \eta)^2 \sin^2 2\beta \right\} \]
\[ = \frac{1}{2} \omega_0 \left\{ \left[ \frac{1}{2} (\sigma_X^{(a)})^2 + \frac{1}{2} \delta^2 (3 + \eta)^2 \right] \right. \]
\[ - \frac{1}{2} (\sigma_X^{(a)})^2 \cos 2\beta - \frac{1}{3} \delta^2 (3 + \eta)^2 \cos 4\beta \}, \]  
(3-32a)

\[ \Delta \omega_1(\beta; \gamma = \frac{1}{2} \pi) = -\omega_0 \left\{ \left[ \sigma - \sigma^{\text{ref}} + \frac{1}{2} \delta (1 - \eta) \right] + \frac{1}{2} \delta (3 + \eta) \cos 2\beta \right\}. \]  
(3-32b)

Equations (3-30)–(3-32) show that the inclusion of second-order terms—quadratic in the shielding components—results in a number of new features of the rotation patterns:

(a) The rotation patterns are no longer purely \( \pi \) periodic. They do have terms that are \( \frac{1}{2} \pi \) periodic (\( \cos 4\gamma; \cos 4\beta \)). This has been emphasized by Schneider.\textsuperscript{18} However, the \( \frac{1}{2} \pi \)-periodic terms are not related to antisymmetric shielding components. Hence \( \frac{1}{2} \pi \)-periodic terms in rotation patterns are not manifestations of \( \sigma^{(a)} \). They should alert the experimenter to look for manifestations of \( \sigma^{(a)} \) in the \( \pi \)-periodic terms but more so to check his experimental setup, because most probably they are an indication that something went wrong in the experiment.

(b) The average shift is no longer \( \sigma - \sigma^{\text{ref}} \). However, by considering the average shift at just one field strength \( B_0 \) there is no way to detect the difference.

(c) For our special choice of \( \sigma^{(a)} \) the most conspicuous manifestation of antisymmetric shielding occurs in the \( XY \)-rotation pattern where \( \sigma_Y^{(a)} \) enters linearly. In the \( XZ \) and \( YZ \) patterns \( \sigma^{(a)} \) enters squared and its effect is only
to simulate slightly modified values of the anisotropy and asymmetry parameters.

Let us focus our attention on two nuclei, 1 and 2, related by a center of symmetry. The space group \( \text{Pcmn} \), e.g., is consistent with the symmetry requirements for Eqs. (3-30a)–(3-32b) and the presence of a center of symmetry. For \( \sigma^{(a)} = 0 \) the NMR lines from nuclei 1 and 2 coincide. For \( \sigma^{(a)} \neq 0 \) they are split in the \( XY \)-rotation pattern. By definition the sign of \( \sigma^{(a)}_{XY} \) is opposite for two nuclei related by a center of symmetry.

Equation (3-30a) tells us how large, or rather how small, the splitting \( \delta \omega \) will be:

\[
|\delta \omega/\omega_0| = |\delta \eta \sigma^{(a)}_{XY} \sin 2\gamma|. \tag{3-33a}
\]

The maximum splitting will be reached for \( \sin 2\gamma = 1 \):

\[
|\delta \omega_{\text{max}}/\omega_0| = |\delta \eta \sigma^{(a)}_{XY}|. \tag{3-33b}
\]

Naturally the splitting is quadratically small in shielding parameters \( (\delta, \sigma^{(a)}_{XY}) \). Unfortunately, \( \eta < 1 \) enters as an additional factor.

For light nuclei such as \(^1\text{H}\) and \(^{13}\text{C}\), where \( \delta \) and—hopefully—\( \sigma^{(a)}_{XY} \) may be of the order of \( 2 \times 10^{-5} \) and \( 2 \times 10^{-4} \), respectively, there is nowadays hardly a chance to observe such a line splitting due to \( \sigma^{(a)} \). We repeat: This line splitting is the most conspicuous manifestation of \( \sigma^{(a)} \). On the other hand, for heavy nuclei such as \(^{207}\text{Pb}\), where \( \delta \) and \( \sigma^{(a)}_{XY} \) may range up to \( 10^{-2} \) or even higher, an experimental demonstration of the line splitting described above and hence a detection of \( \sigma^{(a)} \) seems feasible under favorable circumstances.

We warned above against experimental pitfalls. One that an experimenter must be prepared to encounter and that is liable to produce "false" line splitting is small-angle twinning of the sample crystal. Equal intensities of the two components of the split line, or even better unsplit resonance lines from a pair of quadrupolar nuclei related by a center of symmetry, are valuable and convincing checks for the absence of crystal twinning.