NMR Shifts. II – magnetic and quadrupole shift conventions.

As noted in part I, both the magnetic and quadrupole shifts rely upon second-rank tensors. Outside of reporting the full tensor elements and the corresponding orientations, there are several other standard notations encountered, which are summarized here.

Magnetic shifts: These include the Knight shift (K) and chemical shift (δ). These have equivalent (and additive) effects on NMR spectra and are used here more or less interchangeably, although K is normally considered to be the contribution due to unpaired spins in metals and semiconductors, while δ is the orbital contribution appearing in insulators as well as conductors. If spin-orbit coupling is considered, there can be no strict dividing line.

Orientations of the tensors are determined by crystal-determined symmetry. In these notes both X,Y,Z and 1,2,3 are used to refer to the tensor axes, according to differing conventions.

For high-symmetry sites the shift tensor has identical diagonal values ($K_{11} = K_{22} = K_{33}$), and $K_{iso} = \frac{1}{3}(K_{11} + K_{22} + K_{33})$ will be the orientation-independent shift. Rapid tumbling in liquids or fast magic-angle spinning in some cases can also average orientation-dependent terms to zero, and K_{iso} (or δ_{iso}) is the only observed quantity. *Uniaxial* or simply "*axial*" symmetry cases have rotational symmetry about a particular axis, making the two perpendicular principal values equal to each other. In more general cases all three values are distinct. However as noted below the terms "axiality", "anisotropy", and "asymmetry" are used in various and sometimes conflicting ways. A method which avoids conflicting terminology is to report the 3 principal values (plus orientation if available), e.g. reporting K_{11}, K_{22}, and K_{33}, plus normally K_{iso} -- this is the most straightforward and it is specifically recommended for chemical shifts by IUPAC.[2]

Traditionally for *Knight shifts* one often sees:

$$K_{iso} = \tfrac{1}{3}(K_{11} + K_{22} + K_{33})$$
$$K_{ax} = \tfrac{1}{6}(2K_{33} - K_{11} - K_{22}) = \tfrac{1}{2}(K_{33} - K_{iso})$$
$$K_{aniso} = \tfrac{1}{2}(K_{22} - K_{11}), \qquad [2]$$

These are defined such that for axial-symmetry cases, $K_{ax} = \frac{1}{3}(K_{||} - K_{\perp})$, where $K_{||}$ is the shift measured parallel to the axis of symmetry, always defined as $K_{||} = K_{33}$. However in many older publications referring to Knight shifts these differ by factors of 2 or 3, this can cause confusion! K_{ax} is also equivalent to 1/2 the Haeberlen reduced anisotropy (ζ) defined below. For [2] as well as for the Haeberlen case, by convention $|K_{33} - K_{iso}|$ has the largest magnitude vs. the other two principal values (and K_{33} is thus furthest removed from K_{iso}), and K_{11} is furthest from K_{33}. The result is an increasing or decreasing arrangement, $K_{33} > K_{22} > K_{11}$ or $K_{33} < K_{22} < K_{11}$, where the sign of K_{ax} determines whether K_{33} is largest ($K_{ax} > 0$) or smallest ($K_{ax} < 0$). For this convention to be maintained, one must have $|K_{aniso}| \leq |K_{ax}|$, and both of these parameters should have the same sign. In the limiting case when $K_{aniso} = K_{ax}$, the principal values are equally spaced, with $K_{22} = K_{iso}$, and the overall sign of K_{aniso} and K_{ax} determines whether K_{33} or K_{11} is largest.

For chemical shifts[2-4], the Haeberlen convention is similar to the above definitions. The *anisotropy* and *asymmetry* are defined according to:

$$\zeta = (\delta_{ZZ} - \delta_{iso}) \qquad \leftarrow \text{reduced anisotropy: can have either sign}$$
$$\eta = {(\delta_{YY} - \delta_{XX})}/{\zeta} \qquad \leftarrow \text{asymmetry: between 0 and 1} \qquad [3]$$
$$\Delta\delta = \delta_{ZZ} - (\delta_{XX} + \delta_{YY})/2 = \tfrac{3}{2}\zeta \qquad \leftarrow \text{"anisotropy"}$$

Following convention the principal axes are defined here according to *X, Y, Z* rather than 1, 2, 3. Note that the reduced anisotropy ζ is sometimes written Δ or δ. Just as in [2], δ_{ZZ} is defined as the term furthest from δ_{iso}, so ζ can have either sign, and principal values are ordered so that $0 \leq \eta \leq 1$. η is thus similar to the parameter η defined for EFG tensors.

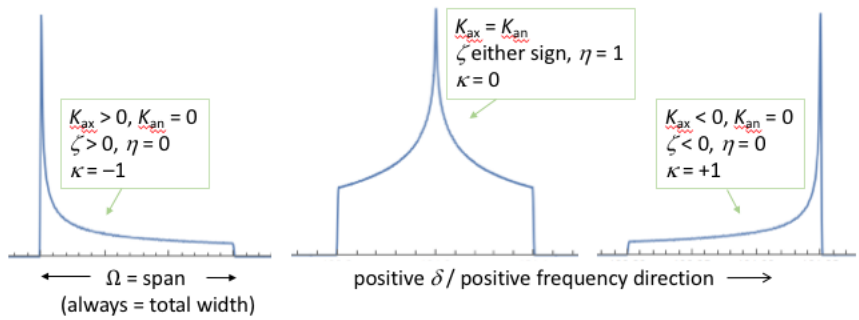

Figure 1.

Figure 1 shows three cases, displayed as often done for Knight shifts, paramagnetic shift increasing to the right, the reverse of the more common convention in chemistry. The two extreme cases on the right and left are axial symmetry cases, with opposite signs of K_{ax} (and ζ).

The Haeberlen convention parameters are often used to report chemical shifts. The NMR computation program Simpson uses this convention; Dmfit also uses this convention, with ζ referred to as the axiality and η the anisotropy. In Wien2k (as of version 16) ab-initio-computed chemical shifts are given in terms of $\Delta\delta$, η, as well as the individual principal values in Haeberlen convention. Sometimes the chemical shift anisotropy or simply "CSA" is also referred to in general as the set of magnitudes of these terms.

Another convention[2-4] is the Herzfeld-Berger, or "Maryland notation", used by the quadfit program:

$$\Omega = \delta_{11} - \delta_{33} \quad \leftarrow\text{(Span measures entire width of line, always positive)},$$

$$\kappa = 3(\delta_{22} - \delta_{iso})/\Omega \quad \leftarrow\text{(Skew is between } -1 \text{ and } 1). \qquad [4]$$

In this case δ_{33} is defined to have the smallest value rather than the largest distance from δ_{iso}, so Ω is always positive, and the arrangement is $\delta_{33} < \delta_{22} < \delta_{11}$. Unlike the cases above where $\eta = 0$ (or $K_{aniso} = 0$) corresponds to axial-symmetry, κ is either +1 or –1 in axial symmetry. (Skews outside the range between ±1 mean the principal values are in a different order from the standard ordering given here.) As seen in Fig. 1, Ω is the entire width of the line, and the skew (κ) measures the relative position of the singularity.

Figure 2 shows two plots from Ref. 4: a powder pattern on the left with features identified in terms of principal values, and on the right, the reduced anisotropy (δ in that plot is our ζ) and reduced anisotropy $\Delta\delta$ are indicated. With the usual plotting convention of chem shift increasing to the left, the left panel agrees with the IUPAC preference for principal values: δ_{11} is the largest. (As noted above we often plot things reversed, *K* increasing to the right, typical for Knight shifts.)

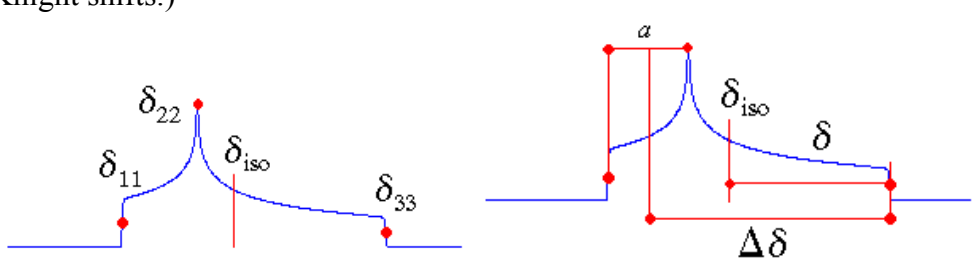

Figure 2.

As shown in the left part of Fig. 2, the three principal values of K or δ can be completely determined by observing the singularity and step-edge positions. (There is no such simple method if the chemical shift becomes mixed with a quadrupole shift.)

Another Knight shift convention is from Carter *et al.*,[1] defined with K_1 and K_2 each twice as large as K_{ax} and K_{aniso} from eqn. [2]. As always, $K_{iso} = \frac{1}{3}(K_{11} + K_{22} + K_{33})$. The Carter *et al.* parameters are:

$$K_1 = (K_{33} - K_{iso}) = 2K_{ax};\ K_2 = (K_{22} - K_{11}) = 2K_{aniso};$$
$$\varepsilon \equiv K_2/K_1 = (K_{22} - K_{11})/(K_{33} - K_{iso}). \qquad [5]$$

Here ε is just the same as η, and either ε or K_2 can be used to represent departures from axial symmetry. The principal values in Carter *et al.* notation are,

$$K_{11} = K_{iso} - \tfrac{1}{2}(K_1 + K_2) = K_{iso} - \tfrac{1}{2}K_1(1 + \varepsilon);$$
$$K_{22} = K_{iso} - \tfrac{1}{2}(K_1 - K_2) = K_{iso} - \tfrac{1}{2}K_1(1 - \varepsilon)$$
$$K_{33} = K_{iso} + K_1. \qquad [6]$$

The same as for the set [2] the standard parameter space is $|K_1| > |K_2|$ with both of these parameters having the same sign, thus $0 \le \varepsilon \le 1$.

Conversions: $K_1 = \zeta = \frac{2}{3}\Delta\delta = 2K_{ax}$ and $\eta = \varepsilon = K_2/K_1$; $K_2 = 2K_{aniso}$ connects [2], [5] and [6] to the Haeberlen parameters. To convert to span and skew $\Omega = |(3K_1 + |K_2|)/2|$ and $\kappa = -\frac{3}{2}(K_1 - |K_2|)/\Omega$ (assuming K_1, K_2 are in the standard range as defined above), or $\kappa = \pm\frac{1-\varepsilon}{1+\varepsilon/3}$, with + for negative K_1. The reverse of this is $K_1 = \pm(\frac{3+|\kappa|}{6})\Omega$ and $K_2 = \pm(\frac{1-|\kappa|}{2})\Omega$, with (+) signs for negative κ, or vice-versa, or $\varepsilon = 3(\frac{1-|\kappa|}{3+|\kappa|})$. For $\kappa = 0$ ($K_1 = K_2$ or $\varepsilon = 1$) cases, positive signs make K_{11} smallest and K_{33} largest, while negative signs reverse this. Finally, $\Delta\delta = \pm(\frac{3+|\kappa|}{4})\Omega$, with signs as noted above, and $\eta = 3(\frac{1-|\kappa|}{3+|\kappa|})$.

For the specific case of axial-symmetry, two principal values will be equal, and the shift measured along the symmetry axis ($\delta_{||}$) is twice as far from δ_{iso} as the perpendicular shift ($\delta_\perp$). In figure 1 the axial cases are the two extreme cases shown on the right & left side of the figure. For these situations:

(i) Knight shift convention [2]: $K_{aniso} = 0$. $K_{ax} = (K_{33} - K_{11})/3$ [magnitude equal to (powder pattern width)/3, but with either sign]. $K_{ax} = (K_{||} - K_\perp)/3$.

(ii) Haeberlen convention [3]: $\eta = 0$; reduced anisotropy $\zeta = \frac{2}{3}(\delta_{ZZ} - \delta_{XX})$ equals (2/3) of the powder line-width, with either sign. $\Delta\delta$ magnitude equal to full powder-pattern width (same magnitude as span in axial cases.) $\Delta\delta = (\delta_{||} - \delta_\perp)$ or $\zeta = \frac{2}{3}(\delta_{||} - \delta_\perp)$.

(iii) Herzfeld-Berger [4] Skew=$\kappa = \pm 1$, however no values between. Span remains positive and equal to the overall width of the powder pattern. $\Omega = |\delta_{||} - \delta_\perp|$; sign($\kappa$) same as sign($\delta_{||} - \delta_\perp$).

(iv) Carter et al., $K_2 = \varepsilon = 0$ and $K_1 = (2/3)(K_{33} - K_{11})$, having either sign. $K_1 = (2/3)(K_{||} - K_\perp)$.

Quadrupole shifts: For quadrupole shifts[1], the relevant tensor, $V_{ij} = {\partial^2 V}/{\partial i \partial j}$ (representing the electric field gradients, or EFG's), is traceless as well as being symmetric, so there is no

"isotropic EFG" and only 2 parameters are needed to determine the principal values rather than the 3 parameters needed for magnetic shifts. These 2 parameters will typically be given as ν_Q and η as defined below, or possibly in terms of C_Q and η. In addition, similar to the magnetic shift tensor, a set of two angles is needed to determine the EFG tensor principal axis orientation relative to the applied magnetic field.

The <u>orientation</u> of the quadrupole and magnetic shift tensors may be relevant only for single crystal studies, although in low symmetry cases the relative orientations of the magnetic and EFG tensors also become important in determining the powder pattern. In cases of sites having axial symmetry, the *z* axes of the EFG and magnetic tensors must align. In more general cases where the point group determines the axis orientations but not their values (orthorhombic point group cases as defined in part I of these notes), the EFG and magnetic tensor axes will align but the axis labels may need to be interchanged, e.g. $z \leftrightarrow x$ or $x \leftrightarrow y$ etc. In lower symmetries the relative orientations of the two tensors would have to be determined and specified, e.g. with up to three Euler angles required to specify the relative alignment.

Since the overall sign of the V_{ij} tensor cannot be determined from NMR shifts, only the relative signs are important, so often V_{zz} is defined as a positive number, with $|V_{zz}|$ associated with the largest magnitude principal value, and with the ordering $V_{zz} > V_{yy} > V_{xx}$. The 2 parameters then become $\nu_Q = \frac{3eQV_{zz}}{2I(2I-1)h}$ (or $\frac{3e^2qQ}{2I(2I-1)h}$ using by convention eq to represent V_{zz}), and $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$, with Q the nuclear quadrupole moment. The parameter ν_Q is, for example, equal to the separation in the powder pattern between the two satellite singularities closest to the central transition [sharp peaks due to the (1/2-3/2) and (–1/2 to –3/2) resonances] to first-order for systems with axial symmetry where the first-order quadrupole contribution is much larger than the anisotropic magnetic shifts.

In an alternative notation (such as used by Quadfit software), $C_Q = eQV_{zz}/h$ is given instead of the parameter ν_Q. For the half-integer nuclei I = (3/2, 5/2, 7/2, 9/2), these are related by $\nu_Q =$ ($1/2$, 3/20, 1/14, and 1/24, respectively) times C_q.

Finally, for <u>axial symmetry</u> cases, $\eta = 0$, so the single parameter ν_Q determines the magnitudes of the EFG tensor elements, and the corresponding shifts.

References:

1 C. P. Slichter *Principles of Magnetic Resonance*, (Springer, 1996); G. C. Carter, L. H. Bennett, and D. J. Kahan, *Metallic Shifts in NMR* (Pergamon, New York, 1977).
2 R. K. Harris et al., "Further conventions for NMR shielding and chemical shifts", Pure Appl. Chem. 80, 59-84 (2008).
3 H. Saito, I Ando, A Ramamoorthy, Prog Nucl Magn Reson Spectrosc. 57, 181 (2010).
4 Klaus Eichele website, http://anorganik.uni-tuebingen.de/klaus/nmr >> Tensor Conversions >> Chemical Shift Tensors