

NMR Shifts. II – magnetic and quadrupole shift conventions.

Overview: As noted in part I, both the magnetic and quadrupole shifts rely upon second-order tensors. Generally, it suffices to report the full tensors and their orientations. However especially for chemical shifts there are several choices and in some cases competing labels and notations.

Magnetic shifts: The magnetic shifts are the Knight shifts and chemical shifts; as noted in part I, the definitions overlap but essentially the Knight shift is the part due to unpaired spins in metals and semiconductors, and the chemical shift (appearing in all materials) is the orbital contribution. Where spins and orbital shifts are coupled there is no strict dividing line. Notation: “*uniaxial*” or simply “*axial*” symmetry refers to rotational symmetry about a particular axis, as for example a spinning top, and “anisotropy” often refers to departures from axial symmetry, however (see below) “axiality”, “anisotropy”, and “asymmetry” are used in sometimes conflicting ways. A method which avoids all this is to report the 3 principal values (plus orientation if available), e.g. reporting K_{11} , K_{22} , and K_{33} , plus normally the isotropic value, $K_{iso} = \frac{1}{3}(K_{11} + K_{22} + K_{33})$. This is the most straightforward and it is specifically recommended for chemical shifts by IUPAC.² For high-symmetry sites where $K_{11} = K_{22} = K_{33}$, K_{iso} will be the only nonzero term and eqn. [1] in part I applies. Even where symmetry is lacking, rapid tumbling in liquids (or fast magic-angle spinning) can average the axial and anisotropy terms to zero, and K_{iso} (or δ_{iso}) will be the observed quantity.

Rather than the principal values, traditionally for *Knight shifts* one often sees:

$$\begin{aligned} K_{iso} &= \frac{1}{3}(K_{11} + K_{22} + K_{33}) \\ K_{ax} &= \frac{1}{6}(2K_{33} - K_{11} - K_{22}) = \frac{1}{2}(K_{33} - K_{iso}) \\ K_{aniso} &= \frac{1}{2}(K_{22} - K_{11}), \end{aligned} \quad [2]$$

These are defined such that for axial-symmetry Knight shifts, $K_{ax} = \frac{1}{3}(K_{||} - K_{\perp})$, where $K_{||}$ is the shift measured parallel to the axis of symmetry, always defined as $K_{||} = K_{33}$. However in many publications these differ by factors of 2 or 3, beware! K_{ax} in [2] is also $-\frac{1}{2}$ the Haeberlen reduced anisotropy (ζ) defined below. In [2] as well as for the Haeberlen case, by convention $|K_{33} - K_{iso}|$ has the largest magnitude of the three principal values (so K_{33} is furthest removed from K_{iso}), and K_{11} is the 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 ($K_{ax} < 0$). Finally note that for the ordering of principal values given by this convention to be maintained, one needs to have $|K_{aniso}| < |K_{ax}|$, and both of these parameters should have the same sign.

Similar to [2], the Haeberlen convention has *reduced anisotropy* (ζ) and *asymmetry* (η):

$$\begin{aligned} \zeta &= (\delta_{iso} - \delta_{33}) \quad \leftarrow \text{reduced anisotropy: can have either sign} \\ \eta &= (\delta_{22} - \delta_{11}) / \delta \quad \leftarrow \text{asymmetry: between 0 and 1} \\ \Delta\delta &= \delta_{33} - (\delta_{11} + \delta_{22})/2 = \frac{3}{2}\zeta \quad \leftarrow \text{alternative, “anisotropy”} \end{aligned} \quad [3]$$

This is typically applied for chemical shifts, not K . The reduced anisotropy ζ is sometimes written Δ or δ , and the anisotropy $\Delta\delta$ is an alternative form which differs by a factor 3/2, a bit confusing. Just as for the Knight shift definitions, δ_{33} is defined as furthest from δ_{iso} , so ζ can have either sign, however with proper ordering of the principal values η will always be between 0 and 1. (Other values of η mean principal values out of conventional order, in which case the parameters can be rearranged.) η is thus similar to the η defined for the EFG tensors. Also note,

IUPAC recommends that Haeberlen principal values be reported as zz, yy, xx rather than $33, 22, 11$; see reference 2 for more details.

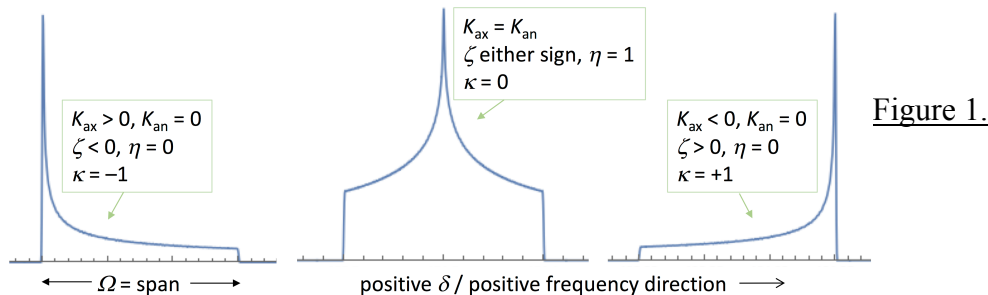


Figure 1 shows some examples, displayed as we often do in our lab for Knight shifts, paramagnetic shift increasing to the right. The two extreme cases (on the right and left) are axial symmetry cases, with opposite signs of K_{ax} (or ζ).

The Haeberlen convention parameters are the ones often given in publications when reporting chemical shifts, although with sometimes confusing naming conventions. The NMR computation program Simpson uses this convention; Dmfit also uses this convention, but with ζ referred to as the axiality, and η referred to as 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 referred to in general as the set of magnitudes of these terms.

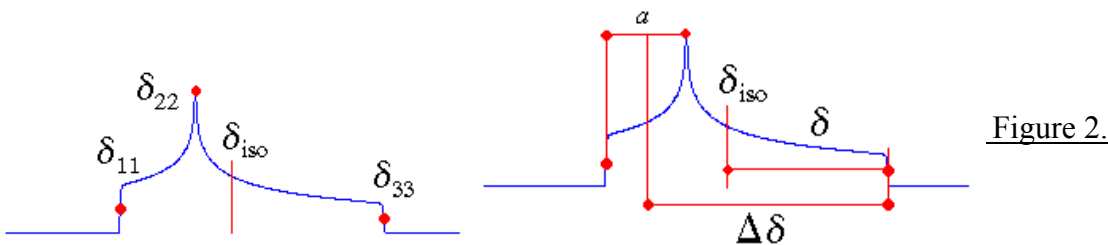
One more set of conventions^{2,3} is the Herzfeld-Berger, or “Maryland notation”, used by the quadfit program:

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

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

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. (Skew outside of ± 1 means the principal values are out of order.) As seen in Fig. 1, Ω is the entire width of the line, whereas the skew measures the relative position of the singularity.

Figure 2 shows 2 plots from <http://anorganik.uni-tuebingen.de/klaus/nmr/index.php> (website of Klaus Eichele³) with a powder pattern on the left in terms of principal values, and on the right, the reduced anisotropy (δ in that plot means ζ) and reduced anisotropy $\Delta\delta$. 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.)



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

Returning to Knight shift conventions, in our lab we often refer to Carter *et al.*,¹ in which another combination of parameters is defined, with K_{iso} the same, but K_1 and K_2 twice as large as K_{ax} and K_{aniso} (eqn. [2]). In terms of [2] the Carter *et al.* parameters are:

$$K_1 = 2K_{ax}; \quad K_2 = 2K_{aniso} = (K_{22} - K_{11});$$

$$\varepsilon \equiv K_2/K_1 = (K_{22} - K_{11})/(K_{33} - K_{iso}). \quad [5]$$

In this notation ε is identical to 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,

$$K_{11} = K_{iso} - \frac{1}{2}(K_1 + K_2) = K_{iso} - \frac{1}{2}K_1(1 + \varepsilon);$$

$$K_{22} = K_{iso} - \frac{1}{2}(K_1 - K_2) = K_{iso} - \frac{1}{2}K_1(1 - \varepsilon)$$

$$K_{33} = K_{iso} + K_1. \quad [6]$$

Similar to K_{ax} , K_{aniso} , the standard parameter range is $|K_1| > |K_2|$ and with both of these parameters having the same sign. Note that $K_1 = -\zeta$ and $\eta = \varepsilon = K_2/K_1$, further connecting these to the Haerberlen parameters, or for the span and skew $\Omega = |(3K_1 + |K_2|)/2|$, and $\kappa = -\frac{3}{2}(K_1 - |K_2|)/\Omega$ (the latter two assuming K_1, K_2 are in the standard range). The reverse of this is $K_1 = \pm(\frac{3+|\kappa|}{6})\Omega$ and $K_2 = \pm(\frac{1-|\kappa|}{2})\Omega$, with the (+) signs for negative κ , and vice-versa.

Finally, consider axial-symmetry: two principal values are equal, and the shift measured with field along the symmetry axis is twice as far from δ_{iso} as the perpendicular shift. Figure 1 has two examples of axial powder patterns, shown on the right & left side of the figure. In this case:

- (i) Knight shift convention [2]: $K_{aniso} = 0$, and K_{ax} reduces to $(K_{33} - K_{11})/3$ [this is $(1/3)$ *(width of line); K_{ax} still can have either sign].
- (ii) Haerberlen convention [3]: asymmetry $\eta = 0$; reduced anisotropy $\zeta = (\delta_{iso} - \delta_{33})$ is equal to $(2/3)$ of the line-width, still with either sign.
- (iii) Herzfeld-Berger [4] Skew has values $\kappa = \pm 1$, however no values between. Span remains positive and equal to the overall width of the powder pattern.
- (iv) Carter *et al.*, $K_2 = 0$ and $K_1 = (K_{33} - K_{iso})$.

Quadrupole shifts: For quadrupole shifts¹, 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. For example the 2 parameters may be reported as ν_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 orientation is normally relevant only for single crystal studies, although in low symmetry cases the relative orientation of the magnetic and EFG tensors becomes important in determining the powder pattern. In higher symmetry cases where the point group determines the principal axis orientations, these will be the same for the EFG and magnetic tensors.

Since the overall sign of the V_{ij} tensor cannot be determined from NMR shifts, only the relative signs are important, and typically V_{zz} is defined as a positive number, with axes defined so that $|V_{zz}|$ has the largest magnitude among the 3 principal values, 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 $\nu_Q = (1/2, 3/20, 1/14, \text{ and } 1/24, \text{ respectively})$ times C_Q .

Finally, for axial symmetry 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 Klaus Eichele website, <http://anorganik.uni-tuebingen.de/klaus/nmr> >> Tensor Conventions >> Chemical Shift Tensors