

## 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.<sup>2</sup> 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  $\delta_{iso}$ ) 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 ( $\zeta$ ) 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* ( $\zeta$ ) and *asymmetry* ( $\eta$ ):

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

This is typically applied for chemical shifts, not  $K$ . The reduced anisotropy  $\zeta$  is sometimes written  $\Delta$  or  $\delta$ , 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,  $\delta_{33}$  is defined as furthest from  $\delta_{iso}$ , so  $\zeta$  can have either sign, however with proper ordering of the principal values  $\eta$  will always be between 0 and 1. (Other values of  $\eta$  mean principal values out of conventional order, in which case the parameters can be rearranged.)  $\eta$  is thus similar to the  $\eta$  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.

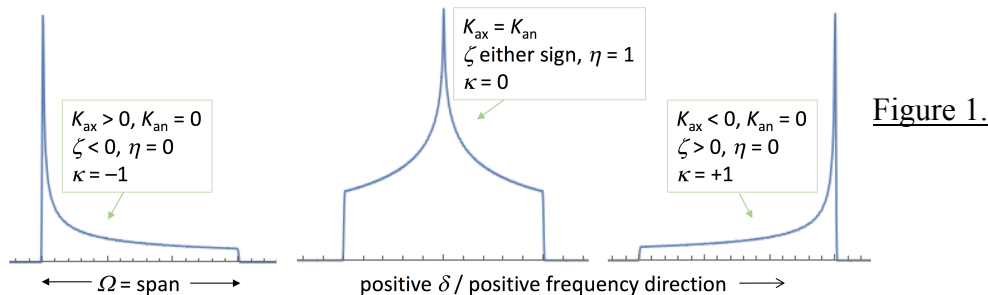


Figure 1 shows some examples, displayed as we often do in our lab for Knight shifts, paramagnetic shift increasing to the right. The two extreme cases (on the right and left) are axial symmetry cases, with opposite signs of  $K_{ax}$  (or  $\zeta$ ).

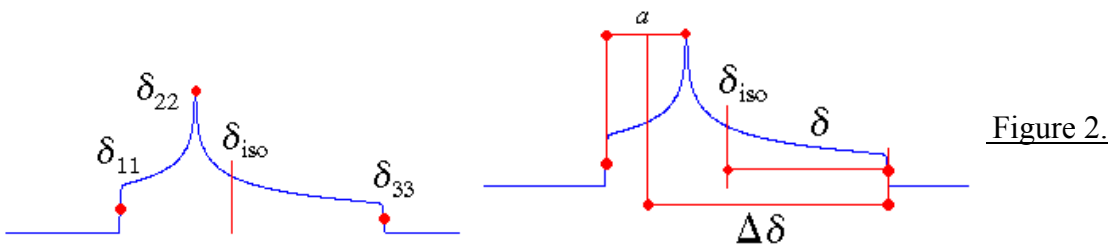
The Haeberlen convention parameters are the ones often given in publications when reporting chemical shifts, although with sometimes confusing naming conventions. The NMR computation program Simpson uses this convention; Dmfit also uses this convention, but with  $\zeta$  referred to as the axiality, and  $\eta$  referred to as the anisotropy. In Wien2k (as of version 16) ab-initio-computed chemical shifts are given in terms of  $\Delta\delta$ ,  $\eta$ , 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<sup>2,3</sup> is the Herzfeld-Berger, or “Maryland notation”, used by the quadfit program:

$$\begin{aligned} \Omega &= \delta_{11} - \delta_{33} \leftarrow (\text{Span measures entire width of line, always positive}), \\ \kappa &= 3(\delta_{22} - \delta_{iso}) / \Omega \leftarrow (\text{Skew is between } -1 \text{ and } 1). \end{aligned} \quad [4]$$

In this case  $\delta_{33}$  is defined to have the smallest value rather than the largest distance from  $\delta_{iso}$ , so  $\Omega$  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,  $\kappa$  is either +1 or -1 in axial symmetry. (Skew outside of  $\pm 1$  means the principal values are out of order.) As seen in Fig. 1,  $\Omega$  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 Eichele<sup>3</sup>) with a powder pattern on the left in terms of principal values, and on the right, the reduced anisotropy ( $\delta$  in that plot means  $\zeta$ ) 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:  $\delta_{11}$  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.*<sup>1</sup> 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  $\varepsilon$  is identical to  $\eta$ , and either  $\varepsilon$  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).

Finally, consider axial-symmetry: two principal values are equal, and the shift measured with field along the symmetry axis is twice as far from  $\delta_{iso}$  as the perpendicular shift. Figure 1 has two examples. In this case:

- (i) Knight shift convention [2]:  $K_{aniso} = 0$ , with  $K_{ax}$  reducing to  $(K_{33} - K_{11})/3$  [(width of line)/3, but still with  $\pm$ sign].
- (ii) Haerberlen convention [3]:  $\eta = 0$ ;  $\zeta = (\delta_{iso} - \delta_{33})$  is equal to  $(2/3)$  of the line-width, still with either sign.
- (iii) Herzfeld-Berger [4]  $\kappa = \pm 1$  (but no values between).
- (iv) Carter *et al.*,  $K_2 = 0$  and  $K_1 = (K_{33} - K_{iso})$ .

**Quadrupole shifts:** Finally note that for the quadrupole shifts<sup>1</sup>, the relevant tensor,  $V_{ij} = \partial^2 V / \partial i \partial j$ , is traceless as well as being symmetric, so only 2 parameters need to be defined, rather than the 3 parameters needed for the magnetic shifts. Also since the overall sign of the  $V_{ij}$  tensor does not affect NMR shifts, usually  $V_{zz}$  is given as a positive number, with the axes defined so that  $|V_{zz}|$  has the largest magnitude among the 3 principal values, with the ordering  $V_{zz} > V_{yy} > V_{xx}$ . The 2 parameters are typically  $\nu_Q = 3eQV_{zz}/[2I(2I - 1)h]$  and  $\eta = (V_{xx} - V_{yy})/V_{zz}$ , with  $Q$  = nuclear quadrupole moment. In a few alternative cases (such as used by Quadfit software),  $C_Q = eQV_{zz}/h$  is given instead of the parameter  $\nu_Q$ . Thus for the half-integer nuclei  $I = (3/2 - 9/2)$ , these are related by  $\nu_Q = (1/2, 3/20, 1/14, \text{ and } 1/24)$  times  $C_Q$ .

## 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