

## NMR Shifts. I – Introduction and tensor/crystal symmetry.

These notes were developed for my group as introduction to NMR shifts and notation.

**1) Basic shift definitions and notation:** For nonmagnetic materials, normally the magnetic field induces a perturbative response small enough that the effect of the applied field ( $H_o$ ) can be considered to be linear. The resulting magnetic response is a local field ( $H_{loc}$ ) proportional to  $H_o$  felt by the nucleus. In the linear-response limit, the contributions add, so we can write,

$\langle \vec{H}_{loc} \rangle = (\vec{K} + \vec{\delta}) \cdot \vec{H}_o$ , in terms of the Knight shift ( $K$ ) and chemical shift ( $\delta$ ). The angle bracket denotes a time average, which is what is measured by the static NMR spectrum. The electric quadrupole shifts are often too large to be treated by first-order perturbation. The relevant terms in the Hamiltonian are,  $H = H_{Z_o} + \Delta H_{magn} + \Delta H_Q$ , where the first term is the Zeeman interaction of the nucleus with the applied field  $H_o$ , the second term is the Zeeman contribution due to  $H_{loc}$ , and the last term is the quadrupole interaction with electric field gradients. For more detail on these see for example Ref. 1. Some important considerations are as follows:

(i) **Electric quadrupole shifts:** The associated shifts normally add to the magnetic shifts; Slichter's book or the review by Carter, Bennett, and Kahan provide a good summary.<sup>1</sup> Quadrupole shifts and splittings are often treated in first- plus second-order perturbation, although situations where such a perturbation expansion is invalid are not uncommon. To first-order, the shifts are independent of the applied field, while to second order the expressions are proportional to  $\nu_Q^2 / \nu_L$ . In general the Larmor frequency in the denominator ( $\nu_L$ ) should be considered to include both  $H_o$  plus the local field  $H_{loc}$  (thus including  $K$  and  $\delta$ ). If the quadrupole terms are too large to be treated as a perturbation, everything must be diagonalized together, a rather more complicated situation.

(ii)  **$K$  vs.  $\delta$ :** The Knight shift and chemical shift are divided (somewhat artificially) such that  $K$  refers to the effect of metallic unpaired spins and  $\delta$  is the effect of closed orbitals. This is discussed later; for now we consider them as interchangeable magnetic shift contributions, either individually or as a sum. Note that by convention  $K$  is sometimes given in % and  $\delta$  in ppm—the scale must of course always be specified when reporting the data.

(iii) **Effective fields:**  $K$  includes the Fermi-contact term, which is of relativistic origin and not really a magnetic field; however its effect is the same as if an effective magnetic field were being applied. (Also in ferromagnets or antiferromagnets, the exchange field acting on the nucleus may be of similar origin, and not an actual magnetic field.) The term  $H_{loc}$  should thus not necessarily be taken literally as if an actual field at the nucleus.

(iv) **Standard notation:** More on shift notation is given in part II, however note that IUPAC is the standards organization in chemistry, thus for chemical shifts the IUPAC notation is preferred: “delta”, or  $\delta$ , is the chemical shift, defined as  $\delta = (\nu - \nu_{ref}) / \nu_{ref}$  (note paramagnetic sign), where  $\nu_{ref}$  is the NMR frequency of the reference compound (see next section). The shielding,  $\sigma$ , is also used, given approximately as  $\sigma = -\delta$  (or by reversing the entire shift tensor). The chemical shift was historically referred to as  $\sigma$ , leading to lingering sign confusion, so usually it is best to state which sign convention is being used when reporting results, and to watch for sign reversal when reading papers. [For IUPAC notation, see Harris, et al.<sup>2</sup>, which also lists preferred reference standards, has notes on solvent effects and other issues.]

There is no set of standards governing the Knight shift; however the general definition is  $K = (\nu - \nu_{ref}) / \nu_{ref}$  (always defined with  $K > 0$  for positive-frequency, paramagnetic shifts).

Small differences arise depending upon whether  $\nu_{ref}$  is the reference compound frequency, the frequency including the chemical shift, or even the estimated frequency of the bare nucleus. For this reason it is best to make as clear as possible how the shift was calculated, and what was the standard reference material.

(v) **Shift references:** Though shifts may be thought of as a change in frequency relative to the “unshifted nucleus”, one can almost never measure the bare nucleus, at least to the accuracy required for NMR. Normally shifts are reported relative to an agreed-upon standard, listed for example in Ref. 2. Measurements thus only provide a relative measure of local fields, so for example when comparing the Korringa law,  $K^2 T_1 T = const.$  it is important to realize that  $K$  contains an arbitrary offset, even if the chemical shift is believed to be small. A secondary standard is one with a narrow line whose shift is well known relative to the primary standard.

Absolute NMR shifts for standard ions, relative to their bare nuclei, are known for some cases reasonably well [see Ref. 3.]. This can be done for example by measuring the proton NMR shift in water, which can be calculated very precisely, and that of a dissolved ion, combined with the calculation and measurement of the isolated atom of a given species (which can sometimes be calculated reasonably well). This can be of increasing importance since when calculating *ab initio* shifts the results are obtained relative to the bare nucleus while measurements are always obtained relative to a reference standard such as a dissolved ion.

**2) Tensor shifts and Notation in crystals:** In the simplest cases  $K$  and  $\delta$  are dimensionless numbers giving the ratio of local field to applied field (eqn. [1]). For more general symmetries the local and applied field directions may differ, and the shifts are *tensors*. The external field is by convention always defined in the  $z$  direction. For magnetic shifts we consider only large- $H_0$  cases for which linear-response applies, and secular ( $zz$ ) terms are the only relevant ones. (Other considerations may apply for example in permanent magnets.) The shift is thus given by the  $K_{zz}$  and  $\sigma_{zz}$  tensor elements, whose values change as the sample is rotated so that the direction of  $z$  changes with respect to the local crystal environment.  $K$  and  $\delta$  are symmetric tensors, thus there is a principal axis system (PAS) fixed in the crystal frame that will diagonalize each tensor (with the same PAS for both only in high symmetry cases). The crystal’s principal axes will be referred to here as 1, 2, 3 (as opposed to the lab-frame axes  $x, y, z$ ). To determine the  $zz$  tensor elements for a given orientation requires knowing the three principal values,  $K_{11}$ ,  $K_{22}$ , and  $K_{33}$  (and the same for the  $\delta$  tensor), plus two angles locating  $z$  relative to each PAS.

Quadrupole shifts: These are by construction tensor-oriented, with shifts and splittings controlled by a second-rank tensor,  $V_{ij}$ . More on the notation is given in part II, however the symmetry considerations controlling  $V_{ij}$  are the same as for the second-order tensors for  $K$  and  $\delta$ .

**Symmetry** can constrain the  $K_{ij}$ ,  $\delta_{ij}$ , and  $V_{ij}$  principal values and axis orientations for a given site: for example if the nucleus sits on a reflection plane, one principal axis will be perpendicular to the plane, determining the orientation of at least one PAS vector. The same holds with a 2-fold axis: one PAS vector must be parallel to such an axis. With a 3-, 4-, or 6- fold axis (or even an *improper* 4-fold axis, denoted  $-4$  or  $\bar{4}$ ) one PAS vector is parallel to the symmetry axis, and the two principal *values* perpendicular to this axis must be identical, so the system has at least *axial symmetry*. The rotoinversion 3-fold axis ( $-3$  or  $\bar{3}$ ) includes a proper 3-

fold symmetry so it is also axial. Note that these refer to the site symmetry, not the overall crystal symmetry.

For sufficiently high symmetry (for example a tetrahedral site as in silicon or GaAs) all principal values are identical, and the tensor is isotropic, with shift independent of orientation:

$$\Delta f = \gamma H_{loc} / 2\pi = \gamma H_o (K + \delta) / 2\pi = f_o (K + \delta). \quad [1]$$

In the opposite extreme, in absence of any symmetry, all principal values are distinct, and quadrupole and magnetic PAS orientations will in general be different.

The site symmetry can be determined if the Wyckoff symbol and space group is known. A good source is [www.cryst.ehu.es/cryst/get\\_wp.html](http://www.cryst.ehu.es/cryst/get_wp.html) (Bilbao server WYCKPOS tool): keying in the space group brings up a table of Wyckoff positions (e.g. 2a, 8c, etc.), where the third column is the site symmetry. Among these, for example 2mm has a 2-fold axis with two mirror planes along this axis (the mirror planes thus determine all three PAS orientations following the description above), while -4 is the *improper* (rotoinversion) 4-fold rotation axis (axial symmetry), etc. A convenient table of 3D point groups is on Wikipedia on the “crystallographic point groups” page; I captured the table here in the Appendix (2<sup>nd</sup> table), along with an example of the Wyckoff positions shown by the Bilbao server. The Bilbao-server Wyckoff Positions include point groups in Hermann-Mauguin notation, which is also the format in the first two columns of the Wikipedia table in the Appendix.

In the Wikipedia table in the appendix, the symmetries are organized by “crystal system” going from triclinic at the top to cubic at the bottom: this does not mean the crystal system of the crystal itself, for example a site with tetragonal-type symmetry could be found in a cubic lattice. An example of this situation: space group #217, site 12d has symmetry “-4..” which is a tetragonal point group (4-fold axis), even though space group 217 is for cubic crystals. Based on the considerations stated above for *n*-fold axes, from the table we see the triclinic point-group symmetries have no 2- or higher-fold axes and do not constrain the shift tensor at all; in monoclinic the 2-fold axis determines only one principal axis orientation, but all 3 principal values may be different; in orthorhombic all 3 orientations are determined, but also in general 3 different principal values; tetragonal, trigonal, and hexagonal site symmetries are *axial* along the axis of the 3, 4, or 6-fold rotation; cubic cases (T for tetrahedral, O for octahedral) are *isotropic* with all principal values equal. Thus for the space group 217, 12d site example noted above, this site’s -4 symmetry falls in the tetragonal category, and the improper 4-fold rotation implies axial symmetry. For a given site, any symmetry-based orientation constraints apply to *K*,  $\delta$ , as well as the EFG’s for a given site, since all of these cases rely upon the transformation properties of a 2<sup>nd</sup> rank tensor.

Following the above procedure and knowing the Wyckoff position, you can determine whether there are symmetry constraints on the principal values. To find the PAS *orientations relative to the crystal* for a given site you need to determine the orientations of the point group symmetry axes for the site. The Bilbao server gives orientation information for the point-group symmetries, (the International Tables for Crystallography can help in deciphering these). For example, the space group 217 example given above (& see table in Appendix) the 12d site is point-group -4.. where the dots are place-holders to show that the -4 axis is in the first position: this means the 100 axis for the cubic crystal; thus the symmetry axis of the axial tensors is along 100. A second example: the 12e site in this case is “2.mm” symmetry, same as mm2 in our point-group table, with one 2-fold axis and two mirrors. By agreement for the Bilbao site, the two m’s are in the second and third position, corresponding to (111) and (110) orientations respectively for a cubic crystal. Thus the 3 principal axes would be in (111), (1,-1,0) and (1,1,-2) directions,

or permutations of these for the 12 different 12e sites. For the axis orientation conventions in other symmetries, details are given in the International Tables for Crystallography, but also see this site (which may or may not be permanent), describing the orientation conventions for different crystal systems along with other useful information:  
<http://xrayweb.chem.ou.edu/notes/symmetry.html>.

### 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 C. Jameson, "Chemical Shift Scales on an Absolute Basis", eMagRes 2011; and Jameson & Mason, in *Multinuclear NMR*, ed. Mason (Plenum 1987) ch. 3.

**Appendix:** First table, Wyckoff positions (from Bilbao server) for the specific case of space group #217. Second table, Point Group table copied from Wikipedia "Crystallographic point group" page.

### Wyckoff Positions of Group 217 (*I-43m*)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
			(0,0,0) + (1/2,1/2,1/2) +
48	h	1	(x,y,z) (-x,-y,z) (-x,y,-z) (x,-y,-z) (z,x,y) (z,-x,-y) (-z,-x,y) (-z,x,-y) (y,z,x) (-y,z,-x) (y,-z,-x) (-y,-z,x) (y,x,z) (-y,-x,z) (y,-x,-z) (-y,x,-z) (x,z,y) (-x,z,-y) (-x,-z,y) (x,-z,-y) (z,y,x) (z,-y,-x) (-z,y,-x) (-z,-y,x)
24	g	..m	(x,x,z) (-x,-x,z) (-x,x,-z) (x,-x,-z) (z,x,x) (z,-x,-x) (-z,-x,x) (-z,x,-x) (x,z,x) (-x,z,-x) (x,-z,-x) (-x,-z,x)
24	f	2..	(x,1/2,0) (-x,1/2,0) (0,x,1/2) (0,-x,1/2) (1/2,0,x) (1/2,0,-x) (1/2,x,0) (1/2,-x,0) (x,0,1/2) (-x,0,1/2) (0,1/2,x) (0,1/2,-x)
12	e	2.m m	(x,0,0) (-x,0,0) (0,x,0) (0,-x,0) (0,0,x) (0,0,-x)
12	d	-4..	(1/4,1/2,0) (3/4,1/2,0) (0,1/4,1/2) (0,3/4,1/2) (1/2,0,1/4) (1/2,0,3/4)
8	c	.3m	(x,x,x) (-x,-x,x) (-x,x,-x) (x,-x,-x)
6	b	-42. m	(0,1/2,1/2) (1/2,0,1/2) (1/2,1/2,0)
2	a	-43m	(0,0,0)

Crystal system	Hermann-Mauguin		Shubnikov <sup>[1]</sup>	Schoenflies	Orbifold	Coxeter	Order
	(full)	(short)					
Triclinic	1	1	<b>1</b>	$C_1$	11	[ ] <sup>+</sup>	1
	$\bar{1}$	$\bar{1}$	$\bar{\mathbf{2}}$	$C_i = S_2$	×	[2 <sup>+</sup> ,2 <sup>+</sup> ]	2
Monoclinic	2	2	<b>2</b>	$C_2$	22	[2] <sup>+</sup>	2
	m	m	<b>m</b>	$C_s = C_{1h}$	*	[ ]	2
	$\frac{2}{m}$	2/m	<b>2 : m</b>	$C_{2h}$	2*	[2,2 <sup>+</sup> ]	4
Orthorhombic	222	222	<b>2 : 2</b>	$D_2 = V$	222	[2,2] <sup>+</sup>	4
	mm2	mm2	<b>2 · m</b>	$C_{2v}$	*22	[2]	4
	$\frac{2}{m} \frac{2}{m} \frac{2}{m}$	mmm	<b>m · 2 : m</b>	$D_{2h} = V_h$	*222	[2,2]	8
Tetragonal	4	4	<b>4</b>	$C_4$	44	[4] <sup>+</sup>	4
	$\bar{4}$	$\bar{4}$	$\bar{\mathbf{4}}$	$S_4$	2×	[2 <sup>+</sup> ,4 <sup>+</sup> ]	4
	$\frac{4}{m}$	4/m	<b>4 : m</b>	$C_{4h}$	4*	[2,4 <sup>+</sup> ]	8
	422	422	<b>4 : 2</b>	$D_4$	422	[4,2] <sup>+</sup>	8
	4mm	4mm	<b>4 · m</b>	$C_{4v}$	*44	[4]	8
	$\bar{4}2m$	$\bar{4}2m$	$\bar{\mathbf{4}} · m$	$D_{2d} = V_d$	2*2	[2 <sup>+</sup> ,4]	8
	$\frac{4}{m} \frac{2}{m} \frac{2}{m}$	4/mmm	<b>m · 4 : m</b>	$D_{4h}$	*422	[4,2]	16
Trigonal	3	3	<b>3</b>	$C_3$	33	[3] <sup>+</sup>	3
	$\bar{3}$	$\bar{3}$	$\bar{\mathbf{6}}$	$S_6 = C_{3i}$	3×	[2 <sup>+</sup> ,6 <sup>+</sup> ]	6
	32	32	<b>3 : 2</b>	$D_3$	322	[3,2] <sup>+</sup>	6
	3m	3m	<b>3 · m</b>	$C_{3v}$	*33	[3]	6
	$\bar{3} \frac{2}{m}$	$\bar{3}m$	$\bar{\mathbf{6}} · m$	$D_{3d}$	2*3	[2 <sup>+</sup> ,6]	12
Hexagonal	6	6	<b>6</b>	$C_6$	66	[6] <sup>+</sup>	6
	$\bar{6}$	$\bar{6}$	<b>3 : m</b>	$C_{3h}$	3*	[2,3 <sup>+</sup> ]	6
	$\frac{6}{m}$	6/m	<b>6 : m</b>	$C_{6h}$	6*	[2,6 <sup>+</sup> ]	12
	622	622	<b>6 : 2</b>	$D_6$	622	[6,2] <sup>+</sup>	12
	6mm	6mm	<b>6 · m</b>	$C_{6v}$	*66	[6]	12
	$\bar{6}m2$	$\bar{6}m2$	<b>m · 3 : m</b>	$D_{3h}$	*322	[3,2]	12
	$\frac{6}{m} \frac{2}{m} \frac{2}{m}$	6/mmm	<b>m · 6 : m</b>	$D_{6h}$	*622	[6,2]	24
Cubic	23	23	<b>3/2</b>	$T$	332	[3,3] <sup>+</sup>	12
	$\frac{2}{m} \bar{3}$	$m\bar{3}$	$\bar{\mathbf{6}}/2$	$T_h$	3*2	[3 <sup>+</sup> ,4]	24
	432	432	<b>3/4</b>	$O$	432	[4,3] <sup>+</sup>	24
	$\bar{4}3m$	$\bar{4}3m$	<b>3/<math>\bar{4}</math></b>	$T_d$	*332	[3,3]	24
	$\frac{4}{m} \bar{3} \frac{2}{m}$	$m\bar{3}m$	$\bar{\mathbf{6}}/4$	$O_h$	*432	[4,3]	48