

NMR Shifts. III – computing Knight shifts and chemical shifts:

1) Shift mechanisms, hyperfine fields, Susceptibility: While K and δ are formally identical, typically K refers to shifts in metals or due to conduction electrons (normally electron spin-related), while δ refers to effects in insulators and due to non-conduction electrons (orbital-related). Here I discuss mostly the 3 main terms:

- the contact interaction, which causes Knight shifts in simple metals (giving K_p or the Pauli Knight shift);
- the diamagnetic shielding, a chemical shift term important for insulators, notation δ_{dia} (often negligible, in metals), and
- the orbital shift (K_{orb}) or paramagnetic chemical shift (δ_{para}). Sometimes this term can be defined as a Knight shift *or* chemical shift, depending on whether we have an insulator or metal; they are really one and the same.

Shift mechanisms omitted from this list include: notably for transition metals the core polarization—for this see for example the Carter *et al.* review¹—and also the small spin-dipolar shift (K_{dip}) and the nuclear-nuclear shift (δ_n); these are mentioned briefly below. Furthermore note that spin orbit interactions are neglected here, allowing us to make the approximation that the spin and orbital susceptibilities are completely separate. Characterizing the shifts in solids where spin-orbit coupling is significant (as might be the case with heavy atoms present) can be difficult, and this is a topic of current research. Understanding of spin-orbit effects is somewhat more developed for molecular systems, as for example discussed by Pyykkö, *Theor. Chem. Acc.* 103, 214-216 (2000).

Generically, the magnetic shifts can be expressed in the general form,

$$K_i = H_{HF} \chi_i \quad \text{or} \quad \delta_i = H_{HF} \chi_i, \quad [6]$$

where χ is the electron susceptibility (per atom), for spins or orbital moments of a particular localized orbital, and H_{HF} represents a hyperfine field for the specific interaction. H_{HF} is the effective magnetic field at the nucleus per electron moment. Note that we are in CGS units; χ per atom has units cm^3 , and H_{HF} measures the field per moment (G/μ has units cm^{-3}). Hence K and δ obtained from [6] are dimensionless as would be expected. For anisotropic interactions, the spin portion of H_{HF} is typically replaced by the spin hyperfine tensor, represented by \vec{A} . \vec{A} appears in the section below—and note that it has units of energy (hyperfine field multiplied by $\gamma\hbar$).

2) Hyperfine fields; Fermi contact and other spin shifts: Consider first the Hamiltonian representing low-order interactions of the nucleus (I) with electron spin (S) and orbital (L) moments:

$$\mathcal{H} = \sum \vec{I}_i \cdot \vec{J} \cdot \vec{I}_j + \sum \vec{I}_i \cdot \vec{A} \cdot \vec{S}_j + \frac{\gamma e^2}{mMc^2 r^3} \sum \vec{I}_i \cdot \vec{L}_j + [A^2 \text{ term}]. \quad [7]$$

The last term is not always included, but as we see below it contributes to diamagnetism and the diamagnetic shift. The first term includes direct dipole-dipole interactions between nuclei as well as indirect (electron-mediated) parts, but it does not normally lead to net shifts so it will be disregarded below. [To the extent that neighboring nuclei have nonzero polarization this term may give an additional shift (δ_n), however its contribution is almost always overwhelmed by larger shifts.] \vec{A} is the hyperfine spin tensor described above, not the same as the vector potential A appearing in the last term. \vec{A} generally consists of the usual dipole field plus the delta-function Fermi contact term:

$$\mathcal{H}_{IS} = \gamma \hbar g \mu_B \sum \left\{ \frac{3(I_i \cdot \hat{r})(S_j \cdot \hat{r}) - I_i \cdot S_j}{r^3} - \frac{8\pi\delta(r)}{3} I_i \cdot S_j \right\}. \quad [8]$$

The sum extends over the N nuclear sites i as well as all of the electrons j ; for energy per site we should divide by N . However since the nuclei act independently I dispensed with the i summation below. [8] looks like a Zeeman interaction and can be expressed formally via an effective local field:

$$\mathcal{H} \equiv -\gamma \hbar I \cdot H_{loc}. \quad [9]$$

The first term in [8] is normally small but it can be important for transition metals with partially filled d bands, where it results in the dipolar Knight shift (K_{dip}).

The contact term in [8] connects the nucleus to the wavefunction at $r = 0$ (or within the volume of the nucleus). For practical purposes this is relevant for s -electrons only. Since electron spin dynamics are much faster than NMR time scales, the shift corresponding to an energy difference between I_z m -states is proportional to the average s -orbital spin $\langle S_z \rangle$:

$\langle E \rangle_m = \langle \psi | \mathcal{H} | \psi \rangle_m = -\gamma \hbar g \mu_B \frac{8\pi |\varphi_s(o)|_{FS}^2}{3} m \langle S_z \rangle$. The FS subscript designates an average over participating states on the Fermi surface. In terms of the s -partial Pauli susceptibility (given as susceptibility per atom), $\langle S_z \rangle = (\chi_p)_s H_o / (g\mu_B)$, and the energy average becomes

$\langle E \rangle_m = -\gamma \hbar m \frac{8\pi |\varphi_s(o)|_{FS}^2}{3} (\chi_p)_s H_o$. Finally, one can see that the definition [1] corresponds to $H_{loc} \equiv H_o K$, and combining with [9] for $\Delta m = 1$ we can obtain the positive shift,

$$K_p = \left\{ \frac{8\pi |\varphi_s(o)|_{FS}^2}{3} \right\} (\chi_p)_s. \quad [10]$$

Positive means that Δf is greater than zero (“downfield shift”). The curly-bracket term in [10] is the same as H_{HF} . For a given species, atomic-based values of the Fermi-contact H_{HF} often may suffice as a reasonable approximation, and a table of such fields are listed for example in Carter *et al.*¹ (e.g. $H_{HF} = 10$ MG is found for valence s electrons in indium, which is the effective field at the nucleus if a single unpaired electron populated this orbital). K_p is isotropic since the spin susceptibility is direction-independent. Dipolar spin contributions to K are in general anisotropic due to the directional dependence of the dipole interaction, however normally the presence of shift anisotropy indicates the contribution of a paramagnetic orbital shift, discussed later.

Reconstructing the logic from the last paragraph, we see that K (or δ) can be obtained by computing $-\langle \Delta E_{nucl} \rangle / (\gamma \hbar H_o)$ provided ΔE corresponds to a term linear in $\gamma \hbar$ and in H_o ; such linearity was assumed above. More generally, this can be expressed at least for isotropic cases,

$$K = -\frac{\partial^2 \langle E \rangle}{\partial \mu \partial H_o} \quad \text{or} \quad \delta = -\frac{\partial^2 \langle E \rangle}{\partial \mu \partial H_o}, \quad [11]$$

where $\mu = \gamma \hbar$ is the nuclear moment. The average energy refers to that of a particular nuclear state. To compare, it is useful to recall that the susceptibility is also be obtained by a similar derivative,

$$\chi = \frac{\partial M}{\partial H} \equiv -\frac{1}{V} \frac{\partial^2 \langle E \rangle}{\partial H_o^2}, \quad [12]$$

where the thermodynamic relation in [12] gives the volume susceptibility (unitless in cgs). The magnetization is formally related to the derivative of the free energy, but in this case it suffices to use the average energy.

Other spin-shift terms aside from Fermi contact may appear when, for example, unpaired spins lead to a Curie-type paramagnetic susceptibility. In such cases [10] may be replaced by, $K_{para} = H_{HF} \chi_{Curie}$, where H_{HF} here refers to the relevant local interaction between the nucleus and paramagnetic spin. This leads to an obvious Curie-like dependence of the shift and linewidths. In cases with no direct overlap, the dipole interaction may provide the spin-nuclear coupling to the paramagnetic spins, although in such cases because of the symmetry of the dipolar field, in isotropic systems the net shift will be zero.

Returning to the Knight shift [10], note that χ_p represents the Pauli susceptibility, $\chi_p \Rightarrow \mu_B^2 g(\epsilon_F)$ in the limit of weak interactions in simple metals, however the derivation is more general and χ_p in [10] can be replaced by the exact solution as long as it is limited to the on-site s -partial term for the site of interest. For example with e-e interactions the Stoner-enhanced susceptibility may apply, $\chi_o \Rightarrow \chi_o / (1 - Ug(\epsilon_F))$. Korringa relaxation theory applies in these cases, giving $1/T_1 \propto T$, and this can be used as a means to separate the spin parts of K , since the orbital shift mechanisms defined below do not lead to relaxation processes in solids. However, note that the simple Korringa-product $K^2 T_1 T = \hbar \gamma_e^2 / (4\pi k_B \gamma_n^2)$ is numerically exact only in the limit of weak interactions.² See also the review of van der Klink and Brom, Prog. Nucl. Magn. Reson. Spectrosc. 36 (2000) 89–201 for more information.

3) Orbital shifts and perturbation theory:³

Hamiltonian: Consider the magnetic field \vec{H}_{el} felt by the electron (at r) due to the nuclear dipole μ plus external field H_o : its the vector potential is,

$$\vec{A} = (\vec{H}_o \times \vec{r}) / 2 + (\vec{\mu} \times \vec{r}) / r^3. \quad [13]$$

[This is in the symmetric gauge centered at the nucleus.] The vector potential augments the electron momentum operator: $\vec{p} = (-i\hbar \vec{\nabla} + e\vec{A}/c)$. Squaring to obtain the Hamiltonian,

$\mathcal{H} = p^2 / 2m$, yields terms linear and bi-linear in A :

$$\mathcal{H} = \mathcal{H}_0 - \frac{ie\hbar}{mc} \vec{A} \cdot \vec{\nabla} + \frac{e^2}{2mc^2} A^2 \equiv \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2. \quad [14]$$

We will see that \mathcal{H}_2 yields diamagnetic shifts, and \mathcal{H}_1 yields paramagnetic shifts.

(a) Electron susceptibilities: It is instructive to derive these terms first. Note that in this case we consider only the H_o term in A , disregarding the nucleus. From [12] we see that terms in the energy bilinear in H_o are needed. The diamagnetic term comes from

$$\mathcal{H}_2 = \frac{e^2}{2mc^2} A^2 = \frac{e^2}{8mc^2} (H_o r \sin \theta)^2, \text{ and the corresponding average energy is}$$

$E = \langle \psi_o | \mathcal{H}_2 | \psi_o \rangle$. The derivative [12] yields the expression,

$$\chi_{dia} = -\frac{e^2}{4mc^2} \langle \psi_o | x^2 + y^2 | \psi_o \rangle, \quad [15]$$

where $|\psi_o\rangle$ represents the ground state wavefunction (all-electron, includes core as well as valence states). The result is the per-atom susceptibility.

For the paramagnetic shift the relevant term is,

$$\mathcal{H}_1 = \frac{-ie\hbar}{mc} \vec{A} \cdot \vec{\nabla} = \frac{ie\hbar}{2mc} (\vec{r} \times \vec{H}_o) \cdot \vec{\nabla} = \frac{ie\hbar}{2mc} (\vec{\nabla} \times \vec{r}) \cdot \vec{H}_o = \mu_B \vec{L} \cdot \vec{H}_o. \quad [16]$$

Because of quenching of angular momentum, the ground state for non-magnetic materials normally has zero expectation value for L_z . So, the first-order perturbation term $\Delta E = \langle 0 | \mathcal{H}_1 | 0 \rangle$ vanishes, and we need second-order perturbation theory, where the cross term bilinear in H_o is:

$$\Delta E = (\mu_B H_o)^2 \sum_i \frac{|\langle \psi_i | L_z | \psi_o \rangle|^2}{E_o - E_i}. \quad [17]$$

The sum is over all excited states $|\psi_i\rangle$. From the derivative [12] we obtain the Van Vleck susceptibility:

$$\chi_{VV} = 2\mu_B^2 \sum_i \frac{|\langle \psi_i | L_z | \psi_o \rangle|^2}{E_i - E_o}. \quad [18]$$

The term is always positive (notice that I reversed the denominator, and that $E_i > E_o$). It is sometimes called temperature independent paramagnetism, or ‘‘TIP’’. It is important if the filled and unfilled valence states come from the same $L \neq 0$ shell, so that the matrix element is non-zero, and largest when there is a small gap between these states.

(b) Diamagnetic chemical shift (‘‘Shielding’’):

Comparing to the derivation of χ_{dia} above, the relevant cross term in \mathcal{H}_2 linear in both μ and

H_o (& see [13]) is $\Delta \mathcal{H}_2 = \frac{e^2}{8mc^2} \frac{H_o \mu}{r^3} (r \sin \theta)^2$. As before $\Delta E = \langle \psi_o | \mathcal{H}_2 | \psi_o \rangle$ is the first-order energy difference, and the derivative [11] yields

$$\delta_{dia} = -\frac{e^2}{2mc} \langle \psi_o | \frac{x^2 + y^2}{r^3} | \psi_o \rangle. \quad [19]$$

The diamagnetic nuclear shielding depends only on the shape and density of the electron cloud, and all electrons contribute, including core states, s states, etc. For filled shells, or a powder

average, we obtain the isotropic shift, $\delta_{dia} = \frac{e^2}{3mc} \langle \psi_o | \frac{1}{r} | \psi_o \rangle$. The contribution of a single orbital

with known $\langle \frac{1}{r} \rangle$ would be $\delta_{dia} = \frac{e^2}{3mc} \langle \frac{1}{r} \rangle$. Comparing [6], notice that this can be put in the

standard form $\delta_i = H_{HF} \chi_i$, with $H_{HF} = 2 \langle \frac{1}{r} \rangle / \langle r^2 \rangle$. Note also that deep core states would likely

require a Dirac-equation treatment, hence some numerical corrections, although in NMR we measure shifts relative to a reference compound, for which the core contribution is presumably nearly unchanged.

(c) Paramagnetic term:

Compare [16], but with the nuclear dipole term also included in \vec{A} ([13]), we can see that the relevant term is $\Delta\mathcal{H}_1 = \frac{e\hbar}{mc} \vec{L} \cdot \left(\frac{\vec{H}}{2} + \frac{\vec{\mu}}{r^3} \right)$, and the energy linear in both μ and H_o is:

$$\Delta E = \mu_B^2 \frac{H_o \mu}{2} \sum_i \frac{\{ \langle \psi_0 | L_z | \psi_i \rangle \langle \psi_i | L_z / r^3 | \psi_0 \rangle + c.c. \}}{E_o - E_i} \quad [20]$$

The derivative [11] yields:

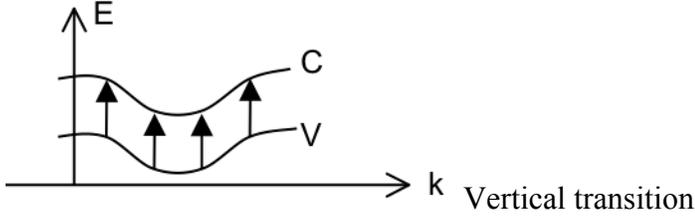
$$\delta_{para} = \frac{\mu_B^2}{2} \sum_i \frac{\{ \langle \psi_0 | L_z | \psi_i \rangle \langle \psi_i | L_z / r^3 | \psi_0 \rangle + c.c. \}}{E_i - E_o}. \quad [21]$$

This term is positive definite, hence paramagnetic. Sum is over all excited states $|\psi_i\rangle$, which makes the matrix elements challenging to calculate. Only p or d (or f) states contribute because of the angular momentum matrix elements. δ_{para} may be large in transition metals where filled and empty d states are close in energy. It is also in general anisotropic, since the superposition of angular momentum sub-states contained in the local orbitals in $|\psi_i\rangle$ will change upon change of crystal orientation. Notice also that as long as a single orbital dominates the matrix elements we can write $\delta_{para} = H_{HF} \chi_{VV}$, and for this case $H_{HF} = \frac{1}{2} \left\langle \frac{1}{r^3} \right\rangle$. Estimates of the $1/r^3$ average can be found in tables of atomic functions (example: Fraga *et al.*, Handbook of Atomic Data is in the TAMU library) and used for estimating the shift vs. susceptibility.

(d) Gauge problem and extended crystal systems:

The derivations above for orbital susceptibilities and chemical shifts may have additional challenges when extended to solid-state systems, when the vector potential [13] is defined in a gauge centered around a particular nucleus. In neighboring cells the basic relationships are in principle still valid, but the contributions pick up large additional terms that cancel but make calculations somewhat impractical. A number of improved methods have been introduced in recent years to address these and related issues^{4,5,6}. The method introduced for FLAPW computations, and implemented in the WIEN2k code⁵ uses the alternative current density formulation of the shifts, as described below.

Conceptually, it may be helpful to examine the matrix elements involved in paramagnetic shielding for solids from [21] by considering that the wave functions $|\psi_o\rangle$ and $|\psi_i\rangle$ are constructed of localized orbitals with relatively small overlap $|\psi_i\rangle = \sum |\varphi(R_j)\rangle e^{i\vec{k}\cdot\vec{R}_j} / \sqrt{N}$ (tight binding limit). One method to address the gauge problem is to re-define the center of the gauge in each unit cell,⁵ in which case the Hamiltonian appears unchanged compared to that of the isolated atom. Since the operator L_z acts only upon the local orbitals, the integral $\langle \psi_0 | L_z | \psi_i \rangle$ will be nonzero only for a vertical (virtual) transition in k -space across the band-gap. This is similar to the (real) interband transitions familiar in optics (see figure) and such states are also the ones coupled by the paramagnetic shift matrix elements in weakly interacting systems.



(e) **Current density:** In QM the current density is derived by expanding the time derivative:

$$\frac{\partial}{\partial t} |\psi|^2 = \psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \psi. \quad [22]$$

Since $|\psi|^2 \equiv \rho$ is the probability density, we can formulate a continuity equation, $\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot \vec{j}$, where j is a probability current. Derivatives on the right of [22] are obtained from the Schrödinger equation and from [14],

$$\frac{\partial}{\partial t} \psi = -\frac{i}{\hbar} \mathcal{H} \psi = +\frac{i\hbar}{2m} \left(\nabla + \frac{ie}{\hbar c} A \right)^2 \psi - \frac{i}{\hbar} (U_o + \mu_B \vec{H} \cdot \vec{S}) \psi. \quad [23]$$

With a little algebra we obtain,

$$\vec{j} = -\frac{i\hbar}{2m} \left[\psi^* \vec{\nabla} \psi - (\vec{\nabla} \psi^*) \psi \right] + \frac{e}{mc} \vec{A} \psi^* \psi. \quad [24]$$

Defining the vector potential as in [13], it turns out that the first term results in the paramagnetic susceptibility, and the second the diamagnetic part.

Diamagnetic susceptibility: Consider for simplicity a spherically symmetric atom. With H_o along $+z$, the vector potential [13] circulates in the $+\phi$ direction. The electric current density is $-e$ times [24], giving current loops that contribute to an induced moment opposing the applied field. A loop at (r, θ) with cross-section $r dr d\theta$ (see sketch below) has radius $r \sin \theta$, and magnetic moment (cgs units):

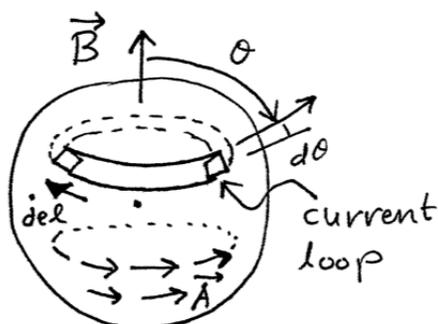
$$d\vec{\mu} = \frac{I \cdot \text{area}}{c} (-\hat{z}) = \frac{e^2}{mc^2} A \psi_o^* \psi_o (r dr d\theta) \pi r^2 \sin^2 \theta (-\hat{z}), \quad [25]$$

taking the last term from [24]. Using $A = H_o r \sin \theta / 2$, and integrating,

$$\begin{aligned} \vec{\mu} &= (-\hat{z}) \frac{e^2 H_o}{4mc^2} \int 2\pi r^2 dr d\theta \sin \theta (r^2 \sin^2 \theta \psi_o^* \psi_o) \\ &= (-\hat{z}) \frac{e^2}{4mc^2} H_o \langle r^2 \sin^2 \theta \rangle \end{aligned} \quad [26]$$

which is equivalent to [15] multiplied by H_o . Thus χ_{dia} per atom is the same as derived before.

The first term in [24] similarly leads to the paramagnetic term, although note that the ground state ψ_o has no net circulation, so the first-order perturbed wavefunction must be used in this case.



Current density and vector potential for χ_{dia} calculation.

The chemical shifts can be obtained by using the current [24] plus the Biot-Savart law to obtain the magnetic field acting on the nucleus. This is the basis for the method used in refs. 6. Note that the above-mentioned gauge problems must still be addressed for extended solids; Laskowski and Blaha address this⁶ using a method of Pickard and Mauri⁴ to reformulate the two contributions to the induced current into a single expression that is gauge invariant. The resulting DFT-based current density depends entirely upon obtaining an accurate ground-state electron density and its response to a magnetic field. The second paper⁶ addresses the results obtained from different DFT functional choices in the FLAPW method, and it appears from these reports that the PBE functional yields results within about 80% of the correct results, with hybrid functionals surprisingly giving results that are not particularly improved. The tentative conclusion is that these discrepancies can be attributed in most part to difficulty in correctly estimating energies of excited states (which affects the results even though the specific method used involves directly calculating the field-dependence of the ground-state wavefunctions, rather than calculating unoccupied states as in intermediate step for perturbation theory, as in the method leading up to eqn. [21]).

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