

## 4.1: Physical origin of the hyperfine interaction

The magnetic moments of an electron and a nuclear spin couple by the magnetic dipole-dipole interaction; similar to the dipole-dipole interaction between nuclear spins discussed in the NMR part of the lecture course. The main difference to the NMR case is that, in many cases, a point-dipole description is not a good approximation for the electron spin, as the electron is distributed over the SOMO. The nucleus under consideration can be considered as well localized in space. We now picture the SOMO as a linear combination of atomic orbitals. Contributions from spin density in an atomic orbital of another nucleus (population of the unpaired electron in such an atomic orbital) can be approximated by assuming that the unpaired electron is a point-dipole localized at this other nucleus.

For spin density in atomic orbitals on the same nucleus, we have to distinguish between types of atomic orbitals. In  $s$  orbitals, the unpaired electron has finite probability density for residing at the nucleus, at zero distance  $r_{SI}$  to the nuclear spin. This leads to a singularity of the dipole-dipole interaction, since this interaction scales with  $r_{SI}^{-3}$ . The singularity has been treated by Fermi. The contribution to the hyperfine coupling from spin density in  $s$  orbitals on the nucleus under consideration is therefore called Fermi contact interaction. Because of the spherical symmetry of  $s$  orbitals, the Fermi contact interaction is purely isotropic.

For spin density in other orbitals ( $p, d, f$  orbitals) on the nucleus under consideration, the dipole-dipole interaction must be averaged over the spatial distribution of the electron spin in these orbitals. This average has no isotropic contribution. Therefore, spin density in  $p, d, f$  orbitals does not influence spectra of fast tumbling radicals or metal complexes in liquid solution and neither does spin density in  $s$  orbitals of other nuclei. The isotropic couplings detected in solution result only from the Fermi contact interaction.

Since the isotropic and purely anisotropic contributions to the hyperfine coupling have different physical origin, we separate these contributions in the hyperfine tensor  $\mathbf{A}_{ki}$  that describes the interaction between electron spin  $S_k$  and nuclear spin  $I_i$ :

$$\mathbf{A}_{ki} = A_{\text{iso},ki} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \mathbf{T}_{ki} \quad (4.1.1)$$

where  $A_{\text{iso},ki}$  is the isotropic hyperfine coupling and  $\mathbf{T}_{ki}$  the purely anisotropic coupling. In the following, we drop the electron and nuclear spin indices  $k$  and  $i$ .

### Dipole-dipole hyperfine interaction

The anisotropic hyperfine coupling tensor  $\mathbf{T}$  of a given nucleus can be computed from the ground state wavefunction  $\psi_0$  by applying the correspondence principle to the classical interaction between two point dipoles

$$T_{ij} = \frac{\mu_0}{4\pi\hbar} g_e \mu_B g_n \mu_n \left\langle \psi_0 \left| \frac{3r_i r_j - \delta_{ij} r^2}{r^5} \right| \psi_0 \right\rangle \quad (4.1.2)$$

Such computations are implemented in quantum chemistry programs such as ORCA, ADF, or Gaussian. If the SOMO is considered as a linear combination of atomic orbitals, the contributions from an individual orbital can be expressed as the product of spin density in this orbital with a spatial factor that can be computed once for all. The spatial factors have been tabulated [KM85]. In general, nuclei of elements with larger electronegativity have larger spatial factors. At the same spatial factor, such as for isotopes of the same element, the hyperfine coupling is proportional to the nuclear  $g$  value  $g_n$  and thus proportional to the gyromagnetic ratio of the nucleus. Hence, a deuterium coupling can be computed from a known proton coupling or vice versa.

A special situation applies to protons, alkali metals and earth alkaline metals, which have no significant spin densities in  $p$ -,  $d$ -, or  $f$ -orbitals. In this case, the anisotropic contribution can only arise from through-space dipole-dipole coupling to centers of spin density at other nuclei. In a point-dipole approximation the hyperfine tensor is then given by

$$\mathbf{T} = \frac{\mu_0}{4\pi\hbar} g_e \mu_B g_n \mu_n \sum_{j \neq i} \rho_j \frac{3\vec{n}_{ij} \vec{n}_{ij}^T - \mathbf{1}}{R_{ij}^3} \quad (4.1.3)$$

where the sum runs over all nuclei  $j$  with significant spin density  $\rho_j$  (summed over all orbitals at this nucleus) other than nucleus  $i$  under consideration. The  $R_{ij}$  are distances between the nucleus under consideration and the centers of spin density, and the  $\vec{n}_{ij}$  are unit vectors along the direction from the considered nucleus to the center of spin density. For protons in transition metal complexes

it is often a good approximation to consider spin density only at the central metal ion. The distance  $R$  from the proton to the central ion can then be directly inferred from the anisotropic part of the hyperfine coupling.

Hyperfine tensor contributions  $\mathbf{T}$  computed by any of these ways must be corrected for the influence of SOC if the  $g$  tensor is strongly anisotropic. If the dominant contribution to SOC arises at a single nucleus, the hyperfine tensor at this nucleus <sup>1</sup> can be corrected by

$$\mathbf{T}^{(g)} = \frac{\mathbf{g}\mathbf{T}}{g_e} \quad (4.1.4)$$

The product  $\mathbf{g}\mathbf{T}$  may have an isotropic part, although  $\mathbf{T}$  is purely anisotropic. This isotropic pseudocontact contribution depends on the relative orientation of the  $g$  tensor and the spin-only dipole-dipole hyperfine tensor  $\mathbf{T}$ . The correction is negligible for most organic radicals, but not for paramagnetic metal ions. If contributions to SOC arise from several centers, the necessary correction cannot be written as a function of the  $g$  tensor.

## Fermi contact interaction

The Fermi contact contribution takes the form

$$A_{\text{iso}} = \rho_s \cdot \frac{2}{3} \frac{\mu_0}{\hbar} g_e \mu_B g_n \mu_n |\psi_0(0)|^2 \quad (4.1.5)$$

<sup>1</sup> Most literature holds that the correction should be done for all nuclei. As pointed out by Frank Neese, this is not true. An earlier discussion of this point is found in [Lef67] where  $\rho_s$  is the spin density in the  $s$  orbital under consideration,  $g_n$  the nuclear  $g$  value and  $\mu_n = \beta_n = 5.05078317(20) \cdot 10^{-27} \text{ J T}^{-1}$  the nuclear magneton ( $g_n \mu_n = \gamma_n \hbar$ ). The factor  $|\psi_0(0)|^2$  denotes the probability to find the electron at this nucleus in the ground state with wave function  $\psi_0$  and has been tabulated [KM85].

Copy and Paste  
Image here.  
Delete this  
placeholder image

Figure 4.1: Transfer of spin density by the spin polarization mechanism. According to the Pauli principle, the two electrons in the C-H bond orbital must have opposite spin state. If the unpaired electron resides in a  $p_z$  orbital on the C atom, for other electrons on the same C atom the same spin state is slightly favored, as this minimizes electrostatic repulsion. Hence, for the electron at the H atom, the opposite spin state (left panel) is slightly favored over the same spin state (right panel). Positive spin density in the  $p_z$  orbital on the C atom induces some negative spin density in the  $s$  orbital on the H atom.

## Spin polarization

The contributions to the hyperfine coupling discussed up to this point can be understood and computed in a single-electron picture. Further contributions arise from correlation of electrons in a molecule. Assume that the  $p_z$  orbital on a carbon atom contributes to the SOMO, so that the  $\alpha$  spin state of the electron is preferred in that orbital (Fig. 4.1). Electrons in other orbitals on the same atom will then also have a slight preference for the  $\alpha$  state (left panel), as electrons with the same spin tend to avoid each other and thus have less electrostatic repulsion. <sup>2</sup> In particular, this means that the spin configuration in the left panel of Fig. 4.1 is slightly more preferable than the one in the right panel. According to the Pauli principle, the two electrons that share the  $s$  bond orbital of the C – H bond must have antiparallel spin. Thus, the electron in the  $s$  orbital of the hydrogen atom that is bound to the spin-carrying carbon atom has a slight preference for the  $\beta$  state. This corresponds to a negative isotropic hyperfine coupling of the directly bound  $\alpha$  proton, which is induced by the positive hyperfine coupling of the adjacent carbon atom. The effect is termed "spin polarization", although it has no physical relation to the polarization of electron spin transitions in an external magnetic field.

Spin polarization is important, as it transfers spin density from  $p$  orbitals, where it is invisible in liquid solution and from carbon atoms with low natural abundance of the magnetic isotope  $^{13}\text{C}$  to  $s$  orbitals on protons, where it can be easily observed in liquid solution. This transfer occurs, both, in  $\sigma$  radicals, where the unpaired electron is localized on a single atom, and in  $\pi$  radicals, where it is distributed over the  $\pi$  system. The latter case is of larger interest, as the distribution of the  $\pi$  orbital over the nuclei can be mapped by measuring and assigning the isotropic proton hyperfine couplings. This coupling can be predicted by the McConnell equation

$$A_{\text{iso,H}} = Q_{\text{H}} \rho_{\pi} \quad (4.1.6)$$

where  $\rho_\pi$  is the spin density at the adjacent carbon atom and  $Q_H$  is a parameter of the order of  $-2.5\text{mT}$ , which slightly depends on structure of the  $\pi$  system.

<sup>2</sup> This preference for electrons on the same atom to have parallel spin is also the basis of Hund's rule.

Copy and Paste  
Image here.  
Delete this  
placeholder image

Figure 4.2: Mapping of the LUMO and HOMO of an aromatic molecule via measurements of hyperfine couplings after one-electron reduction or oxidation. Reduction leads to an anion radical, whose SOMO is a good approximation to the lowest unoccupied molecular orbital (LUMO) of the neutral parent molecule. Oxidation leads to a cation radical, whose SOMO is a good approximation to the highest occupied molecular orbital (HOMO) of the neutral parent molecule.

The McConnell equation is mainly applied for mapping the LUMO and HOMO of aromatic molecules (Figure 4.2). An unpaired electron can be put into these orbitals by one-electron reduction or oxidation, respectively, without perturbing the orbitals too strongly. The isotropic hyperfine couplings of the hydrogen atom directly bound to a carbon atom report on the contribution of the  $p_z$  orbital of this carbon atom to the  $\pi$  orbital. The challenges in this mapping are twofold. First, it is hard to assign the observed couplings to the hydrogen atoms unless a model for the distribution of the  $\pi$  orbital is already available. Second, the method is blind to carbon atoms without a directly bonded hydrogen atom.

---

This page titled [4.1: Physical origin of the hyperfine interaction](#) is shared under a [CC BY-NC 4.0](#) license and was authored, remixed, and/or curated by [Gunnar Jeschke](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.