Hyperfine Couplings in “kilogauss per μ_B”

W.A. MacFarlane

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The hyperfine hamiltonian is

$$H_{hf} = A\vec{S}_1 \cdot \vec{S}_2, \tag{1}$$

where the $\vec{S}_i$ are the dimensionless spin operators, i.e. spin angular momentum operators divided by Planck's constant. Thus clearly the hyperfine coupling constant has units of **energy**, so what the heck is this unit kOe/μ_B a.k.a. kG/μ_B and why is it used?

In NMR, if you measure a shift K that is proportional to a susceptibility χ, then the proportionality constant is also known as the hyperfine coupling, A. It is related to the A above. Practically then K is a unitless quantity (e.g. ppm), and so is χ, since for example $M = \chi H$ and M and H have the same units. This is assuming we have the unitless “volume susceptibility” for χ *not* the per mole or per gram equivalent. If K and χ are unitless in

$$K = A\chi, \tag{2}$$

then so must be the coupling A. This is not helping clear things up I realize, but it is good to explore the extent of the confusion!

To get the conventional hyperfine coupling in the units kG/μ_B, we use instead

$$K = \frac{A\chi}{N_A \mu_B}, \tag{3}$$

where N_A is Avogadro's number and $\mu_B = 9.2740154 \times 10^{-21}$ erg/G is the Bohr magneton (convert to J/T if you like), i.e. about half the magnetic moment of the electron. The susceptibility is defined in the following way: The magnetic moment m of a sample (containing N moles of the compound) is measured. This moment is in units of emu in cgs. Now an emu (no relation to the large flightless bird) is a unit of magnetic moment equal to an erg per Gauss (or J/T in SI), so the “susceptibility” $\chi^{tot} = m/H$ has units of emu/G or erg/G^2 (or J/T^2 in SI). This is of course equal to units of *volume* since the square of the magnetic field is just the magnetic energy density. The molar value is gotten just by dividing χ^{tot} by N. Doing this we get the molar susceptibility in emu/mol (χ). Thus the A defined in Eq.(3) has units of (erg/Gauss per erg/Gauss^2) or just Gauss, i.e. it is a magnetic field, but confusingly one quotes this as a certain number of Gauss (kilogauss etc.) “per μ_B” because of the $1/\mu_B$ in Eq.(3). The N_A in Eq.(3), makes the resulting coupling an atomic quantity, i.e. per atom whose nucleus is coupled to the χ. If the atom in question is hyperfine coupled to Z equivalent near neighbours, it is often useful to divide A further by Z to get a hyperfine coupling per neighbouring atom.

As an example, let's calculate the hyperfine coupling for the interstitial implanted Li in Ag. Here $K = 212$ ppm (without demagnetization correction) and one can look up $\chi = 9.6 \times 10^{-6}$ emu/mol. Thus

$$A = \frac{212 \times 10^{-6} \times 9.2740154 \times 10^{-21} \times 6.0221415 \times 10^{23}}{9.6 \times 10^{-6}} \quad (4)$$

$$= \frac{212 \times 10^{-6} \times 5.5849433 \times 10^{3}}{9.6 \times 10^{-6}} \quad (5)$$

$$= 123.3 \text{ kG}/\mu_B. \quad (6)$$

Now in the octahedral site in Ag, there are 6 equivalent neighbours, so one can say the Li is coupled to each one with a coupling of $123.3/6 = 20.6$ kG$/\mu_B$. One day maybe I will try to fill in the connection with the A defined in Eq.(1) above.