Note : Adapted from B. Martin, J. Autschbach, J. Chem. Phys., 142(5), 054108, 2015

The expression for the total shielding for a triplet is

$$\sigma = \sigma^{orb} - \frac{\beta_e}{g_N \beta_N} \frac{1}{k_B T} \mathbf{gZA} \tag{1}$$

where σ^{orb} is the orbital shielding (defined as the only non-zero contribution to the shielding for a diagmagnetic molecule), β_e the Bohr magneton, β_N the nuclear magneton, k_B the Boltzman constant, T the temperature, $\mathbf{g}$ the g-matrix, $\mathbf{A}$ the hyperfine matrix, and $\mathbf{Z}$ the Z-matrix, the definition of which shall be discussed below.

It is assumed that $\mathbf{g}$ and $\mathbf{Z}$ have the same principle axes, however, the hyperfine tensor $\mathbf{A}$ may have different principal axes, i.e.,

$$\mathbf{gZA} = \begin{bmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & g_\parallel \end{bmatrix} \begin{bmatrix} Z_\perp & 0 & 0 \\ 0 & Z_\perp & 0 \\ 0 & 0 & Z_\parallel \end{bmatrix} \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \tag{2}$$

The expression for the isotropic contributions to the paramagnetic shielding is split up into a contact and pseudocontact part; $\sigma^P_{iso} = \sigma^c_{iso} + \sigma^{pc}_{iso}$, which may be written as

$$\sigma^c_{iso} = \frac{\beta_e A_{iso}}{3T g_n \beta_N} [g_{iso}(Z_\parallel + 2Z_\perp) + 2\Delta g(Z_\parallel - Z_\perp)] \tag{3}$$

In an axial system the energies can be shifted so that when represented in the principal axes the zero-field splitting matrix has the form

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D \end{bmatrix} \tag{4}$$

The energies of the three states in the triplet are then $\{D, 0, D\}$. The components of $\mathbf{Z}$ are then given by

$$Z_\parallel = \frac{2e^{-\beta D}}{1 + 2e^{-\beta D}} \tag{5}$$

$$Z_\perp = \frac{\frac{2}{\beta D}(1 - e^{-\beta D})}{1 + 2e^{-\beta D}} \tag{6}$$

Here, D is the energy gap between the singlet and doublet single states which comprise the triplet. The denominator is the partition function. The sign of D can in principal be positive or negative. However, in such cases it is perhaps simpler to chose an energy shift such that the energy of the states is $\{0, D, 0\}$, leading to the following expressions for components of $\mathbf{Z}$

$$Z_\parallel = \frac{2}{2 + e^{-\beta D}} \tag{7}$$

$$Z_\perp = \frac{\frac{2}{\beta D}(e^{-\beta D} - 1)}{2 + e^{-\beta D}} \tag{8}$$

With these definitions Using these expressions, expanding the exponential in powers of T, and only taking terms of $\mathcal{O}(T^3)$ and lower yields the following expressions for the contact and pseudo-contact contributions to the paramagnetic shielding:

$$\sigma^c_{iso} = C_{iso} A_{iso} \left[2g_{iso}\beta - \frac{2}{3} D \Delta g \beta^2 - \frac{1}{9} D^2 g_{iso} \beta^3 \right] \tag{9}$$

$$\sigma^{pc}_{iso} = C_{iso}\Delta A_{iso}\left[4\Delta g\beta - \frac{2}{3}D(g_{iso}+\Delta g)\beta^2 - \frac{2}{9}D^2\Delta g_{iso}\beta^3\right. (10)$$

For cases where the rhombic parameter, E, is non-zero, the orientation and energy shift may be chosen such that the zfs matrix has the form

$$\begin{bmatrix} \frac{-D}{3}+E & 0 & 0 \\ 0 & \frac{-D}{3}-E & 0 \\ 0 & 0 & \frac{2D}{3} \end{bmatrix} \tag{11}$$

Using a similar logic as to derive the expressions in the axial case, the components of $\mathbf{Z}$ for a rhombic system are given by

$$Z_{11} = \frac{\frac{2}{\beta(D+E)}\left(1-e^{\beta(D+E)}\right)}{1+e^{-\beta(D-E)}+e^{-\beta(D+E)}} \tag{12}$$

$$Z_{22} = \frac{\frac{2}{\beta(D-E)}\left(1-e^{\beta(D-E)}\right)}{1+e^{-\beta(D-E)}+e^{-\beta(D+E)}} \tag{13}$$

$$Z_{33} = \frac{\frac{1}{\beta E}\left(e^{\beta(D-E)}-e^{\beta(D+E)}\right)}{1+e^{-\beta(D-E)}+e^{-\beta(D+E)}} \tag{14}$$