

## 4.2: Hyperfine Hamiltonian

We consider the interaction of a single electron spin  $S$  with a single nuclear spin  $I$  and thus drop the sums and indices  $k$  and  $i$  in  $\hat{\mathcal{H}}_{\text{HFI}}$  in Eq. (2.4). In general, all matrix elements of the hyperfine tensor  $\mathbf{A}$  will be non-zero after the Bleaney transformation to the frame where the electron Zeeman interaction is along the  $z$  axis (see Eq. 3.5). The hyperfine Hamiltonian is then given by

$$\begin{aligned}\hat{\mathcal{H}}_{\text{HFI}} &= (\hat{S}_x \quad \hat{S}_y \quad \hat{S}_z) \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_x \\ \hat{I}_y \\ \hat{I}_z \end{pmatrix} \\ &= A_{xx} \hat{S}_x \hat{I}_x + A_{xy} \hat{S}_x \hat{I}_y + A_{xz} \hat{S}_x \hat{I}_z \\ &\quad + A_{yx} \hat{S}_y \hat{I}_x + A_{yy} \hat{S}_y \hat{I}_y + A_{yz} \hat{S}_y \hat{I}_z \\ &\quad + A_{zx} \hat{S}_z \hat{I}_x + A_{zy} \hat{S}_z \hat{I}_y + A_{zz} \hat{S}_z \hat{I}_z\end{aligned}$$

Note that the  $z$  axis of the nuclear spin coordinate system is parallel to the magnetic field vector  $\vec{B}_0$  whereas the one of the electron spin system is tilted, if  $g$  anisotropy is significant. Hence, the hyperfine tensor is not a tensor in the strict mathematical sense, but rather an interaction matrix.

In Eq. (4.7), the term  $A_{zz} \hat{S}_z \hat{I}_z$  is secular and must always be kept. Usually, the high-field approximation does hold for the electron spin, so that all terms containing  $\hat{S}_x$  or  $\hat{S}_y$  operators are non-secular and can be dropped. The truncated hyperfine Hamiltonian thus reads

$$\hat{\mathcal{H}}_{\text{HFI, trunc}} = A_{zx} \hat{S}_z \hat{I}_x + A_{zy} \hat{S}_z \hat{I}_y + A_{zz} \hat{S}_z \hat{I}_z \quad (4.2.1)$$

The first two terms on the right-hand side can be considered as defining an effective transverse coupling that is the sum of a vector with length  $A_{zx}$  along  $x$  and a vector of length  $A_{zy}$  along  $y$ . The length of the sum vector is  $B = \sqrt{A_{zx}^2 + A_{zy}^2}$ . The truncated hyperfine Hamiltonian simplifies if we take the laboratory frame  $x$  axis for the nuclear spin along the direction of this effective transverse hyperfine coupling. In this frame we have

$$\hat{\mathcal{H}}_{\text{HFI, trunc}} = A \hat{S}_z \hat{I}_z + B \hat{S}_x \hat{I}_x \quad (4.2.2)$$

where  $A = A_{zz}$  quantifies the **secular hyperfine coupling** and  $B$  the **pseudo-secular hyperfine coupling**. The latter coupling must be considered if and only if the hyperfine coupling violates the high-field approximation for the nuclear spin (see Chapter 6).

If  $g$  anisotropy is very small, as is the case for organic radicals, the  $z$  axes of the two spin coordinate systems are parallel. In this situation and for a hyperfine tensor with axial symmetry,  $A$  and  $B$  can be expressed as

$$\begin{aligned}A &= A_{\text{iso}} + T (3 \cos^2 \theta_{\text{HFI}} - 1) \\ B &= 3T \sin \theta_{\text{HFI}} \cos \theta_{\text{HFI}}\end{aligned}$$

where  $\theta_{\text{HFI}}$  is the angle between the static magnetic field  $\vec{B}_0$  and the symmetry axis of the hyperfine tensor and  $T$  is the anisotropy of the hyperfine coupling. The principal values of the hyperfine tensor are  $A_x = A_y = A_{\perp} = A_{\text{iso}} - T$  and  $A_z = A_{\parallel} = A_{\text{iso}} + 2T$ . The pseudo-secular contribution  $B$  vanishes along the principal axes of the hyperfine tensor, where  $\theta_{\text{HFI}}$  is either  $0^\circ$  or  $90^\circ$  or for a purely isotropic hyperfine coupling. Hence, the pseudo-secular contribution can also be dropped when considering fast tumbling radicals in the liquid state. We now consider the point-dipole approximation, where the electron spin is well localized on the length scale of the electron-nuclear distance  $r$  and assume that  $T$  arises solely from through-space interactions. This applies to hydrogen, alkali and earth alkali ions. We then find

$$T = \frac{1}{r^3} \frac{\mu_0}{4\pi\hbar} g_e \mu_B g_n \mu_n \quad (4.2.3)$$

For the moment we assume that the pseudo-secular contribution is either negligible or can be considered as a small perturbation. The other case is treated in Chapter 6. To first order, the contribution of the hyperfine interaction to the energy levels is then given by  $m_S m_I A$ . In the EPR spectrum, each nucleus with spin  $I$  generates  $2I + 1$  electron spin transitions with  $|\Delta m_S| = 1$  that can be labeled by the values of  $m_I = -I, -I + 1, \dots, I$ . In the nuclear frequency spectrum, each nucleus exhibits  $2S + 1$  transitions with  $|\Delta m_I| = 1$ . For nuclear spins  $I > 1/2$  in the solid state, each transition is further split into  $2I$  transitions by the nuclear

quadrupole interaction. The contribution of the secular hyperfine coupling to the electron transition frequencies is  $m_I A$ , whereas it is  $m_S A$  for nuclear transition frequencies. In both cases, the splitting between adjacent lines of a hyperfine multiplet is given by  $A$ .

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