

6.1: Physical picture

The $S = 1/2, I = 1/2$ spin system

The basic phenomena can be well understood in the simplest possible electron-nuclear spin system consisting of a single electron spin $S = 1/2$ with isotropic g value that is hyperfine coupled to a nuclear spin $I = 1/2$ with a magnitude of the hyperfine coupling that is much smaller than the electron Zeeman interaction. In this situation the high-field approximation is valid for the electron spin, so that the hyperfine Hamiltonian can be truncated to the form given by Eq. (4.9). Because of the occurrence of an $\hat{S}_z \hat{I}_x$ operator in this Hamiltonian, we cannot simply transform the Hamiltonian to the rotating frame for the nuclear spin I . However, we don't need to, as we shall consider only microwave irradiation. For the electron spin S , we transform to the rotating frame where this spin has a resonance offset Ω_S . Hence, the total Hamiltonian takes the form

$$\hat{H}_0 = \Omega_S \hat{S}_z + \omega_I \hat{I}_z + A \hat{S}_z \hat{I}_z + B \hat{S}_z \hat{I}_x \quad (6.1.1)$$

in the rotating frame for the electron spin and the laboratory frame for the nuclear spin. Such a Hamiltonian is a good approximation, for instance, for protons in organic radicals.

The Hamiltonian deviates from the Hamiltonian that would apply if the high-field approximation were also fulfilled for the nuclear spin. The difference is the pseudo-secular hyperfine coupling term $B \hat{S}_z \hat{I}_x$. As can be seen from Eq. (4.10), this term vanishes if the hyperfine interaction is purely isotropic, i.e. for sufficiently fast tumbling in liquid solution,¹ and along the principal axes of the hyperfine tensor. Otherwise, the B term can only be neglected if $\omega_I \gg A, B$, corresponding to the high-field approximation of the nuclear spin. Within the approximate range $2|\omega_I|/5 < |A| < 10|\omega_I|$ the pseudo-secular interaction may affect transition frequencies and makes formally forbidden transitions with $\Delta m_S = 1, \Delta m_I = 1$ partially allowed, as m_I is no longer a good quantum number.

Local fields at the nuclear spin

The occurrence of forbidden transitions can be understood in a semi-classical magnetization vector picture by considering local fields at the nuclear spin for the two possible states α_S and

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Figure 6.1: Local fields (multiplied by the gyromagnetic ratio γ_I of the nuclear spin) at the nuclear spin in the two states α_S and β_S of an electron spin $S = 1/2$. The quantization axes are along the effective fields $\tilde{\omega}_\alpha/\gamma_I$ and $\tilde{\omega}_\beta/\gamma_I$ and are, thus, not parallel.

β_S of the electron spin. These local fields are obtained from the parameters ω_I, A , and B of the Hamilton operator terms that act on the nuclear spin. When divided by the gyromagnetic ratio of the nuclear spin these terms have the dimension of a local magnetic field. The local field corresponding to the nuclear Zeeman interaction equals the static magnetic field B_0 and is the same for both electron spin states, since the expectation value of \hat{I}_z does not depend on the electron spin state. It is aligned with the z direction of the laboratory frame (blue arrow in Figure 6.1). Both hyperfine fields arise from Hamiltonian terms that contain an \hat{S}_z factor, which has the expectation value $m_S = +1/2$ for the α_S state and $m_S = -1/2$ for the β_S state. The A term is aligned with the z axis and directed towards $+z$ in the α_S state and towards $-z$ in the β_S state, assuming $A > 0$ (violet arrows). The B term is aligned with the x axis and directed towards $+x$ in the α_S state and towards $-x$ in the β_S state, assuming $B > 0$ (green arrows).

The effective fields at the nuclear spin in the two electron spins states are vector sums of the three local fields. Because of the B component along x , they are tilted from the z direction by angle η_α in the α_S state and by angle η_β in the β_S state. The length of the sum vectors are the nuclear transition frequencies in these two states and are given by

$$\omega_\alpha = \sqrt{(\omega_I + A/2)^2 + B^2/4}$$

$$\omega_\beta = \sqrt{(\omega_I - A/2)^2 + B^2/4}$$

For $|\omega_I| > 2|A|$, the hyperfine splitting is given by

$$\omega_{\text{hfs}} = |\omega_{\alpha} - \omega_{\beta}| \quad (6.1.2)$$

and the sum frequency is given by

$$\omega_{\text{sum}} = \omega_{\alpha} + \omega_{\beta} \quad (6.1.3)$$

For $|\omega_I| > 2|A|$, the nuclear frequency doublet is centered at $\omega_{\text{sum}}/2$ (Fig. 6.2(c)). The sum frequency is always larger than twice the nuclear Zeeman frequency. None of the nuclear frequencies can become zero, the minimum possible value $B/2$ is attained in one of the electron spin states for matching of the nuclear Zeeman and hyperfine interaction at $2|\omega_I| = |A|$. For $|\omega_I| < 2|A|$ the nuclear frequency doublet is split by ω_{sum} and centered at $\omega_{\text{hfs}}/2$ (Fig. 6.2(d)). The tilt angles η_{α} and η_{β} (Figure 6.1) can be inferred from trigonometric relations and are given by

$$\eta_{\alpha} = \arctan\left(\frac{-B}{2\omega_I + A}\right)$$

$$\eta_{\beta} = \arctan\left(\frac{-B}{2\omega_I - A}\right)$$

Consider now a situation where the electron spin is in its α_S state. The nuclear magnetization from all radicals in this state at thermal equilibrium is aligned with $\vec{\omega}_{\alpha}$. Microwave excitation causes transitions to the β_S state. In this state, the local field at the nuclear spin is directed along $\vec{\omega}_{\beta}$. Hence, the nuclear magnetization vector from the radicals under consideration is tilted by angle 2η (Figure 6.1) with respect to the current local field. It will start to precess around this local field vector. This corresponds to excitation of the nuclear spin by flipping the electron spin, which is a formally forbidden transition. Obviously, such excitation will occur only if angle 2η differs from 0° and from 180° . The case of 0° corresponds to the absence of pseudo-secular hyperfine coupling ($B=0$) and is also attained in the limit $|A| \ll |\omega_I|$. The situation $2\eta \rightarrow 180^\circ$ is attained in the limit of very strong secular hyperfine coupling, $|A| \gg |\omega_I|$. Forbidden transitions are observed for intermediate hyperfine coupling. Maximum excitation of nuclear spins is expected when the two quantization axes are orthogonal with respect to each other, $2\eta = 90^\circ$.

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Figure 6.2: Electron-nuclear spin system $S=1/2, I=1/2$ in the presence of pseudo-secular hyperfine coupling. (a) Level scheme. In EPR, $\Delta m_S = 1, \Delta m_I = 0$ transitions are allowed (red), in NMR $\Delta m_S = 0, \Delta m_I = 1$ transitions are allowed (blue), and the zero- and double-quantum transitions with $\Delta m_S = 1, \Delta m_I = 1$ are formally forbidden. (b) EPR stick spectrum. Allowed transitions have transition probability $\cos^2 \eta$ and forbidden transitions probability $\sin^2 \eta$. The spectrum is shown for $|\omega_I| > 2|A|$. For $|\omega_I| < 2|A|$, the forbidden transitions lie inside the allowed transition doublet. (c) NMR spectrum for $|\omega_I| > 2|A|$. (d) NMR spectrum for $|\omega_I| < 2|A|$.

¹ The product of rotational correlation time τ_r and hyperfine anisotropy must be much smaller than unity