

4.3: Spectral manifestation of the hyperfine interaction

Liquid-solution EPR spectra

Since each nucleus splits each electron spin transition into $2I + 1$ transitions with different frequencies, the number of EPR transitions is $\prod_i (2I_i + 1)$. Some of these transitions may coincide if hyperfine couplings are the same or integer multiples of each other. An important case, where hyperfine couplings are exactly the same are chemically equivalent nuclei. For instance, two nuclei $I_1 = I_2 = 1/2$ can have spin state combinations $\alpha_1\alpha_2$, $\alpha_1\beta_2$, $\beta_1\alpha_2$, and $\beta_1\beta_2$. The contributions to the transition frequencies are $(A_1 + A_2)/2$, $(A_1 - A_2)/2$, $(-A_1 + A_2)/2$, and $(-A_1 - A_2)/2$. For equivalent nuclei with $A_1 = A_2 = A$ only three lines are observed with hyperfine shifts of A , 0 , and $-A$ with respect to the electron Zeeman frequency. The unshifted center line has twice the amplitude than the shifted lines, leading to a $1 : 2 : 1$ pattern with splitting A . For k equivalent nuclei with $I_i = 1/2$ the number of lines is $k + 1$ and the relative intensities can be inferred from Pascal's triangle. For a group of k_i equivalent nuclei with arbitrary spin quantum number I_i the number of lines is $2k_i I_i + 1$. The multiplicities of groups of equivalent nuclei multiply. Hence, the total number of EPR lines is

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Figure 4.3: Hyperfine splitting in the EPR spectrum of the phenyl radical. The largest hyperfine coupling for the two equivalent ortho protons generates a triplet of lines with relative intensities $1 : 2 : 1$. The medium coupling to the two equivalent meta proton splits each line again into a $1 : 2 : 1$ pattern, leading to 9 lines with an intensity ratio of $1 : 2 : 1 : 2 : 4 : 2 : 1 : 2 : 1$. Finally, each line is split into a doublet by the small hyperfine coupling of the para proton, leading to 18 lines with intensity ratio $1 : 1 : 2 : 2 : 1 : 1 : 2 : 2 : 4 : 4 : 2 : 2 : 1 : 1 : 2 : 2 : 1$.

where index i runs over the groups of equivalent nuclei.

$$n_{\text{EPR}} = \prod_i (2k_i I_i + 1) \quad (4.3.1)$$

Figure 4.3 illustrates on the example of the phenyl radical how the multiplet pattern arises. For radicals with more extended π systems, the number of lines can be very large and it may become impossible to fully resolve the spectrum. Even if the spectrum is fully resolved, analysis of the multiplet pattern may be a formidable task. An algorithm that works well for analysis of patterns with a moderate number of lines is given in [CCM16].

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Liquid-solution nuclear frequency spectra

As mentioned in Section 4.2 the secular hyperfine coupling A can be inferred from nuclear frequency spectra as well as from EPR spectra. Line widths are smaller in the nuclear frequency spectra, since nuclear spins have longer transverse relaxation times $T_{2,i}$. Another advantage of nuclear frequency spectra arises from the fact that the electron spin interacts with all nuclear spins whereas each nuclear spin interacts with only one electron spin (Figure 4.4). The number of lines in nuclear frequency spectra thus grows only linearly with the number of nuclei, whereas

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Figure 4.4: Topologies of an electron-nuclear spin system for EPR spectroscopy (a) and of a nuclear spin system typical for NMR spectroscopy (b). Because of the much larger magnetic moment of the electron spin, the electron spin "sees" all nuclei, while each nuclear spin in the EPR case sees only the electron spin. In the NMR case, each nuclear spin sees each other nuclear spin, giving rise to very rich, but harder to analyze information.

it grows exponentially in EPR spectra. In liquid solution, each group of equivalent nuclear spins adds $2S + 1$ lines, so that the number of lines for N_{eq} such groups is

$$n_{\text{NMR}} = (2S + 1)N_{\text{eq}} \quad (4.3.2)$$

The nuclear frequency spectra in liquid solution can be measured by CW ENDOR, a technique that is briefly discussed in Section 8.1.2.

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Figure 4.5: Energy level schemes (a,c) and nuclear frequency spectra (b,d) in the weak hyperfine coupling (a,b) and strong hyperfine coupling (c,d) cases for an electron-nuclear spin system $S = 1/2$, $I = 1/2$. Here, ω_I is assumed to be negative and A is assumed to be positive. (a) In the weak-coupling case, $|A|/2 < |\omega_I|$, the two nuclear spin transitions (green) have frequencies $|\omega_I| \pm |A|/2$. (b) In the weak-coupling case, the doublet is centered at frequency $|\omega_I|$ and split by $|A|$. (c) In the strong-coupling case, $|A|/2 > |\omega_I|$, levels cross for one of the electron spin states. The two nuclear spin transitions (green) have frequencies $|A|/2 \pm |\omega_I|$. (d) In the strong-coupling case, the doublet is centered at frequency $|A|/2$ and split by $2|\omega_I|$.

A complication in interpretation of nuclear frequency spectra can arise from the fact that the hyperfine interaction may be larger than the nuclear Zeeman interaction. This is illustrated in Figure 4.5. Only in the weak-coupling case with $|A|/2 < |\omega_I|$ the hyperfine doublet in nuclear frequency spectra is centered at $|\omega_I|$ and split by $|A|$. In the strong-coupling case, hyperfine sublevels cross for one of the electron spin states and the nuclear frequency $|\omega_I| - |A|/2$ becomes negative. As the sign of the frequency is not detected, the line is found at frequency $|A|/2 - |\omega_I|$ instead, i.e., it is "mirrored" at the zero frequency. This results in a doublet centered at frequency $|A|/2$ and split by $2|\omega_I|$. Recognition of such cases in well resolved liquid-state spectra is simplified by the fact that the nuclear Zeeman frequency $|\omega_I|$ can only assume a few values that are known if the nuclear isotopes in the molecule and the magnetic field are known. Figure 4.6 illustrates how the nuclear frequency spectrum of the phenyl radical is constructed based on such considerations. The spectrum has only 6 lines, compared to the 18 lines that arise in the EPR spectrum in Figure 4.3.

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Figure 4.6: Schematic ENDOR (nuclear frequency) spectrum of the phenyl radical at an X-band frequency where $\omega_I/(2\pi) \approx 14\text{MHz}$ (a) Subspectrum of the two equivalent ortho protons. The strong-coupling case applies. (b) Subspectrum of the two equivalent meta protons. The weak-coupling case applies. (c) Subspectrum of the para proton. The weak-coupling case applies. (d) Complete spectrum.

Solid-state EPR spectra

In the solid state, construction of the EPR spectra is complicated by the fact that the electron Zeeman interaction is anisotropic. At each individual orientation of the molecule, the spectrum looks like the pattern in liquid state, but both the central frequency of the multiplet and the hyperfine splittings depend on orientation. As these frequency distributions are continuous, resolved splittings are usually observed only at the singularities of the line shape pattern of the interaction with the largest anisotropy. For organic radicals at X-band frequencies, often hyperfine anisotropy dominates. At high frequencies or for transition metal ions, often electron Zeeman anisotropy dominates. The exact line shape depends not only on the principal values of the g tensor and the hyperfine tensors, but also on relative orientation of their PASs. The general case is complicated and requires numerical simulations, for instance, by EasySpin.

However, simple cases, where the hyperfine interaction of only one nucleus dominates and the PASs of the g and hyperfine tensor coincide, are quite often encountered. For instance, Cu(II) complexes are often square planar and, if all four ligands are the same, have a C_4 symmetry axis. The g tensor then has axial symmetry with the C_4 axis being the unique axis. The hyperfine tensors of ^{63}Cu and ^{65}Cu have the same symmetry and the same unique axis. The two isotopes both have spin $I = 3/2$ and very similar gyromagnetic ratios. The spectra can thus be understood by considering one electron spin $S = 1/2$ and one nuclear spin $I = 3/2$ with axial g and hyperfine tensors with a coinciding unique axis.

In this situation, the subspectra for each of the nuclear spin states $m_I = -3/2, -1/2, +1/2$ and $+3/2$ take on a similar form as shown in Figure 3.3. The resonance field can be computed by solving

$$\hbar\omega_{mw} = \frac{\mu_B}{B_{0,res}} \left(2g_{\perp}^2 \sin^2 \theta + g_{\parallel}^2 \cos^2 \theta \right) + m_I [A_{iso} + T (3 \cos^2 \theta - 1)] \quad (4.3.3)$$

where θ is the angle between the C_4 symmetry axis and the magnetic field vector \vec{B}_0 . The singularities are encountered at $\theta = 0^\circ$ and $\theta = 90^\circ$ and correspond to angular frequencies $\mu_B B_0 g_{\parallel} + m_I A_{\parallel}$ and $\mu_B B_0 g_{\perp} + m_I A_{\perp}$.

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Figure 4.7: Construction of a solid-state EPR spectrum for a copper(II) complex with four equivalent ligands and square planar coordination. The g_{\parallel} and A_{\parallel} principal axes directions coincide with the C_4 symmetry axis of the complex (inset). (a) Subspectra for the four nuclear spin states with different magnetic spin quantum number m_I . (b) Absorption spectrum. (c) Derivative of the absorption spectrum.

The construction of a Cu(II) EPR spectrum according to these considerations is shown in Figure 4.7. The values of g_{\parallel} and A_{\parallel} can be inferred by analyzing the singularities near the low-field edge of the spectrum. Near the high-field edge, the hyperfine splitting A_{\perp} is usually not resolved. Here, g_{\perp} corresponds to the maximum of the absorption spectrum and to the zero crossing of its derivative.

Solid-state nuclear frequency spectra

Again, a simpler situation is encountered in nuclear frequency spectra, as the nuclear Zeeman frequency is isotropic and chemical shift anisotropy is negligibly small compared to hyperfine anisotropy. Furthermore, resolution is much better for the reasons discussed above, so that smaller hyperfine couplings and anisotropies can be detected. If anisotropy of the hyperfine coupling is dominated by through-space dipole-dipole coupling to a single center of spin density, as is often the case for protons, or by contribution from spin density in a single p or d orbital, as is often the case for other nuclei, the hyperfine tensor has nearly axial symmetry. In this case, one can infer from the line shapes whether the weak-or strong-coupling case applies and whether the isotropic hyperfine coupling is positive or negative (Figure 4.8). The case with $A_{iso} = 0$ corresponds to the Pake pattern discussed in the NMR part of the lecture course.

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Figure 4.8: Solid-state nuclear frequency spectra for cases with negative nuclear Zeeman frequency ω_I . (a) Weak-coupling case with $A_{iso} > 0$ and $|A_{iso}| > T$. (b) Weak-coupling case with $A_{iso} < 0$ and $|A_{iso}| > T$. (c) Strong-coupling case with $A_{iso} > 0$ and $|A_{iso}| > T$. (d) Strong-coupling case with $A_{iso} < 0$ and $|A_{iso}| > T$.

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