Lecture Notes

Physical Chemistry IV

Part 2: Electron Paramagnetic Resonance

Gunnar Jeschke





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Chapter 4 Hyperfine interaction by spin polarization (own work)
Chapter 5 Dipole-dipole interaction (own work)
Chapter 6 Deuterium ESEEM trace of a spin-labelled protein (own work)
Chapter 7 Distance distribution measurement in a spin-labelled RNA construct (collaboration with O. Duss, M. Yulikov, F. H.-T. Allain)

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1 — Introduction

1.1 General Remarks

Electron Paramagnetic Resonance (EPR) spectroscopy is less well known and less widely applied than NMR spectroscopy. The reason is that EPR spectroscopy requires unpaired electrons and, usually, electron pairing is energetically favorable. Hence, only a small fraction of pure substances exhibit EPR signals, whereas NMR spectroscopy is applicable to almost any compound one can think of. On the other hand, unpaired electrons are associated with reactivity, since electron pairing underlies the chemical bond. Accordingly, EPR spectroscopy is a very important technique for understanding radical reactions, electron transfer processes, and transition metal catalysis, which are all related to the 'reactivity of the unpaired electron'. Some species with unpaired electrons are chemically stable and can be used as spin probes to study systems where NMR spectroscopy runs into resolution limits or cannot provide sufficient information for complete characterization of structure and dynamics. This lecture course introduces the basics for applying EPR spectroscopy on reactive or catalytically active species as well as on spin probes, without going into application aspects.

Many concepts in EPR spectroscopy are related to similar concepts in NMR spectroscopy. Hence, the lectures on EPR spectroscopy build on material that has been introduced before in the lectures on NMR spectroscopy. This material is briefly repeated. It is enhanced in this script and similarities as well as differences are pointed out. Such a linked treatment of the two techniques is not found in introductory textbooks. By emphasizing this link, the course focuses on the physics that underlies NMR and EPR spectroscopy, instead of focusing on individual application fields. We aim for understanding of spectra at a fundamental level and for understanding how parameters of the spin Hamiltonian can be measured with the best possible sensitivity and resolution.

Chapter 2 of the script introduces electron spin, relates it to nuclear spin, and discusses, which interactions contribute to the spin Hamiltonian of a paramagnetic system. Chapter 3 treats the electron Zeeman interaction, the deviation of the g value of a bound electron from the g value of a free electron, and the manifestation of g anisotropy in solid-state EPR spectra. Chapter 4 introduces the hyperfine interaction between electron and nuclear spins, which provides most information on electronic and spatial structure of paramagnetic centers. Spectral manifestation in the liquid and solid state is considered for spectra of the electron spin and of the nuclear spins. Chapter 5 discusses how the coupling between electron spins is described in the spin Hamiltonian, depending on its size. Throughout Chapters 3-6, the introduced interactions of the

electron spin are related to electronic and spatial structure.

Chapter 6 discusses phenomena that occur when the hyperfine interaction is so large that the high-field approximation is violated for the nuclear spin. In this situation, formally forbidden transitions become partially allowed and mixing of energy levels leads to changes in resonance frequencies. The two most important experiments based on such forbidden transitions are explained, three-pulse electron spin echo envelope modulation (ESEEM) and the two-dimensional hyperfine sublevel correlation (HYSCORE) experiment.

Chapter 7 introduces spin-echo double resonance (SEDOR), which is applied in solid-state NMR and EPR spectroscopy in order to measure dipole-dipole couplings. Spin-spin distances can be inferred from such couplings. In EPR, this experiment is termed double electron electron resonance (DEER) and is applied to measure distance distributions.

At some points this lecture script overlaps with the NMR part of the lecture script. This is intended, in order to make the EPR script reasonably self-contained. Note also that this lecture script serves two purposes. First, it should be a help in studying the subject and preparing for the examination. Second, it is reference material when you later encounter paramagnetic species in your own research and need to obtain information on them by EPR spectroscopy.

1.2 Suggested Reading & Electronic Resources

There is no textbook on EPR spectroscopy that treats all material of this course on a basic level. However, some of the concepts are covered by a title from the Oxford Chemistry Primer series by Chechik, Carter, and Murphy [CCM16]. Physically minded students may also appreciate the older standard textbook by Weil, Bolton, and Wertz [WBW94]. On a deeper level, many concepts are treated in an Encyclopedia of Magnetic Resonance volume edited by Goldfarb and Stoll [GE18].

For some of the simulated spectra and worked examples in these lecture notes, Matlab scripts or Mathematica notebooks are provided on the lecture homepage. Part of the numerical simulations is based on EasySpin by Stefan Stoll (http://www.easyspin.org/) and another part on SPIDYAN by Stephan Pribitzer (http://www.epr.ethz.ch/software.html). Computations with product operator formalism require the Mathematica package SpinOp.m by Serge Boentges, which is available on the course homepage. An alternative larger package for such analytical computations is SpinDynamica by Malcolm Levitt (http://www.spindynamica.soton.ac. uk/). Last but not least, the most extensive package for numerical simulations of magnetic resonance experiments is SPINACH by Ilya Kuprov *et al.* (http://spindynamics.org/ Spinach.php). For quantum-chemical computations of spin Hamiltonian parameters, the probably most versatile program is the freely available package ORCA (https://orcaforum. cec.mpg.de/). Magnetic resonance of the free electron The magnetic moment of the free electron Differences between EPR and NMR spectroscopy Interactions in electron-nuclear spin systems General consideration on spin interactions The electron-nuclear spin Hamiltonian Hamiltonian of the S = 1/2, I = 1/2 spin system

2 — Electron spin

2.1 Magnetic resonance of the free electron

2.1.1 The magnetic moment of the free electron

As an elementary particle, the electron has intrinsic angular momentum called spin. The spin quantum number is S = 1/2. Hence, in an external magnetic field along z, only two possible values can be observed for the z component of angular momentum, $+\hbar/2$, corresponding to magnetic quantum number $m_S = +1/2$ (α state) and $-\hbar/2$, corresponding to magnetic quantum number $m_S = -1/2$ (β state). The energy difference between the corresponding two states of the electron results from the magnetic moment associated with spin. For a classical rotating particle with elementary charge q, angular momentum $J = \hbar S$ and mass m, this magnetic moment computes to

$$\vec{\mu}_{\text{classical}} = \frac{q}{2m} \vec{J} \,. \tag{2.1}$$

The charge-to-mass ratio for an electron spin is e/m_e , where e is the elementary charge and m_e is electron mass. This ratio is much larger for the electron than for a nucleus, where it is of the order of $-e/m_p$, with m_p being the proton mass and $m_p/m_e \approx 1836$. By introducing the Bohr magneton $\mu_{\rm B} = \hbar e/(2m_e) = 9.27400915(23) \times 10^{-24}$ J T⁻¹ and the quantum-mechanical correction factor g, we can rewrite Eq. (2.1) as

$$\vec{\mu}_{\rm e} = g\mu_{\rm B}S \ . \tag{2.2}$$

Dirac-relativistic quantum mechanics provides g = 2.1. Exact measurements have shown that the g value of a free electron deviates slightly from g = 2 The necessary correction can be derived by quantum electrodynamics, leading to $g_e = 2.00231930437378(2)$. The energy difference between the two spin states of a free electron in an external magnetic field B_0 is given by

$$\hbar\omega_S = g_e \mu_{\rm B} B_0 \,, \tag{2.3}$$

so that the gyromagnetic ratio of the free electron is $\gamma_e = -g_e \mu_B/\hbar$. This gyromagnetic ratio corresponds to a resonance frequency of 28.025 GHz at a field of 1 T, which is by a factor of about 658 larger than the nuclear Zeeman frequency of a proton.

¹This correction can also be found by a non-relativistic derivation

2.1.2 Differences between EPR and NMR spectroscopy

The main two differences between NMR and EPR spectroscopy result from this much larger magnetic moment of the electron.

- Boltzmann polarization of electron spins is larger than for nuclear spins by a factor of at least 658
- relaxation times of electron spins are shorter by roughly five to six orders of magnitude (square of γ_e/γ_n)

Faster relaxation broadens lines, which reduces sensitivity, but it also allows for faster repetition of the experiment, which, together with larger Boltzmann polarization and higher energy of microwave photons leads to higher sensitivity of EPR spectroscopy. Standard instrumentation, with an electromagnet working at a field of about 0.35 T and at microwave frequencies of about 9.5 GHz (X band) can detect about 10^{10} spins within a few seconds. This applies to samples with negligible dielectric microwave losses. In aqueous solution, organic radicals can be detected at concentrations down to 10 nM in a measurement time of a few minutes.

Due to the large magnetic moment of the electron spin the high-temperature approximation is violated already at a temperature of 4.5 K in a field of about 3.35 T corresponding to a frequency of about 94 GHz (W band). The high-field approximation may break down for a nuclear spin close to an electron spin (Chapter 6), since the hyperfine coupling between the two spins may be of the same order of magnitude as the nuclear Zeeman interaction at the magnetic fields where EPR is usually performed (0.1-10 T).



Figure 2.1: CW-EPR lineshape. We consider the situation at the instantaneous field during a field sweep (vertical dashed line). Modulation of the magnetic field with amplitude ΔB_0 (blue) causes modulation of the output signal V (red) with the same frequency and an amplitude ΔV . Phase-sensitive detection measures ΔV , which is proportional to the derivative of the absorption lineshape (grey) if ΔB_0 is much smaller than the peak-to-peak linewidth ΔB_{pp} .

The dipole-dipole interaction between two electron spins is by a factor of 658^2 larger than between two protons. Furthermore, two unpaired electrons can come closer to each other than two protons. If the two unpaired electrons both reside in a small organic molecule or are localized at the same transition or rare earth metal ion, a zero-field splitting results. This splitting can amount to a significant fraction of the electron Zeeman interaction or can even exceed it (Chapter 5). Another important difference between EPR and NMR spectroscopy is the survival of continuous-wave (CW) detection of spectra in EPR, whereas this technique has become almost extinct in NMR. The main reason for this difference is that ratio of both line width and total spectral width to the resonance frequency is much larger in EPR spectroscopy, which cancels the sensitivity advantage in detecting the free induction decay and obtaining the spectrum by Fourier transformation. Due to the larger linewidth, most or even all of the signal is lost within receiver deadtime after the excitation pulse. Due to larger total spectral width, it is usually impossible to excite the whole spectrum by a single rectangular pulse.

CW EPR spectroscopy is performed at constant microwave frequency by sweeping the external magnetic field. The detector diode collects noise over frequency band much broader than the resonance signal. Noise outside this band is suppressed by modulating the magnetic field and acquiring only the signal at the modulation frequency using a lock-in detector. This approach records the derivative of the absorption lineshape as explained in Figure 2.1.

2.2 Interactions in electron-nuclear spin systems

2.2.1 General consideration on spin interactions

Spins interact with magnetic fields. The interaction with a static external magnetic field B_0 is the Zeeman interaction, which is usually the largest spin interaction. At sufficiently large fields, where the high-field approximation holds, the Zeeman interaction determines the quantization direction of the spin. In this situation, m_S is a good quantum number. If the high-field approximation also holds for a nuclear spin I_i , the magnetic quantum number $m_{I,i}$ is also a good quantum number. The energies of spin levels can then be expressed by parameters that quantify spin interactions and by the magnetic quantum numbers. The vector of all magnetic quantum numbers defines the state of the spin system.

Spins also interact with the local magnetic fields induced by other spins. Usually, unpaired electrons are rare. Hence, each electron spin interacts with several nuclear spins in its vicinity, whereas each nuclear spin interacts with only one electron spin (Fig. 2.2). The hyperfine interaction between the electron and nuclear spin is usually much smaller than the electron Zeeman interaction, with exceptions for transition and rare earth metal ions. In contrast, for nuclei in the close vicinity of the electron spin, the hyperfine interaction may be comparable to the nuclear Zeeman interaction. This leads to breakdown of the high-field approximation and $m_{I,i}$ is then no longer a good quantum number. Hyperfine couplings to nuclei are relevant if they are at least as large as the transverse relaxation rate $1/T_{2n}$ of the coupled nuclear spin. Smaller couplings are unresolved and can be treated as a contribution to linewidths.

In some systems, two or more unpaired electrons are so close to each other that their coupling exceeds their transverse relaxation rates $1/T_{2e}$. The isotropic part of this coupling, called exchange coupling J, can exceed the electron Zeeman interaction by far. It can even exceed thermal energy $k_{\rm B}T$, if two unpaired electrons reside in different molecular orbitals of the same organic molecule (triplet state molecule) or if several unpaired electrons reside on the same transition or rare earth metal ion. In this situation, the system is best described in a coupled representation with an electron group spin S > 1/2. In the coupled representation, the isotropic coupling between the individual electron spins only contributes to the energy differences between states with different group spin S, but not to the sublevel splittings for given S. The anisotropic coupling does lead to sublevel splitting and is thus a contribution to the zero-field interaction, which is sometimes called fine interaction.

In the opposite case, where the electron Zeeman interaction by far exceeds the spin-spin coupling, it is more convenient to describe the system in terms of the individual electron spins $S_i = 1/2$. In this representation, the isotropic exchange coupling J, which stems from overlap of



Figure 2.2: Scheme of interactions in electron-nuclear spin systems. All spins have a Zeeman interaction with the external magnetic field B_0 . Electron spins (red) interact with each other by the dipole-dipole interaction through space and by exchange due to overlap of the singly occupied molecular orbitals (green). Each electron spin interacts with nuclear spins (blue) in its vicinity by hyperfine couplings (purple). Couplings between nuclear spins are usually negligible in paramagnetic systems, as are chemical shifts. These two interactions are too small compared to the relaxation rate of nuclear spins in the vicinity of an electron spin.

two singly occupied molecular orbitals (SOMOs, see below), does contribute to level splitting. In addition, the dipole-dipole coupling through space between two electron spins also contributes.

Concept 2.2.1 — **Singly occupied molecular orbital (SOMO).** Each molecular orbital (MO) can be occupied by two electrons with opposite magnetic spin quantum number $m_S = \pm 1/2$. If a molecular orbital is singly occupied, the electron is unpaired. Its magnetic spin quantum number can then be changed by absorption or emission of photons. The orbital occupied by the unpaired electron is called a singly occupied molecular orbital (SOMO). Several unpaired electrons can exist in the same molecule or metal complex, i.e., there may be several SOMOs.

Nuclear spins in the vicinity of an electron spin relax much faster than nuclear spins in diamagnetic substances.² Their transverse relaxation rates thus exceed couplings between nuclear spins and chemical shifts. These interactions, which are very important in NMR spectroscopy, are negligible in EPR spectroscopy. As a consequence, for nuclear spins 1/2 information on the chemical identity of a nucleus cannot be obtained directly without analyzing hyperfine couplings. The element can be identified by the nuclear Zeeman interaction. Note, however, that nuclear Zeeman interaction does not contribute to first order to electron spin transitions. Hence, identification of nuclear spins often requires measurement of nuclear frequencies. For nuclear spins $I_i > 1/2$, information on the chemical identity is encoded in the nuclear quadrupole interaction, whose magnitude usually exceeds the transverse relaxation rate.

An overview of all interactions and their typical magnitude in frequency units is given in Figure 2.3. This Figure also illustrates another difference between EPR and NMR spectroscopy. Several interactions, such as the zero-field interaction, the hyperfine interaction, larger dipole-dipole and exchange couplings exceed the excitation bandwidth of the strongest and shortest available microwave pulses. The same applies to the anisotropy of the electron Zeeman interaction. Thus, NMR pulses sequences, which rely on the ability to excite the full spectrum of a certain type of spins, cannot easily be adapted to EPR spectroscopy.

²There is an exception. If the electron spin longitudinal relaxation rate exceeds the nuclear Zeeman interaction by far, nuclear spin relaxation is hardly affected by the presence of the electron spin. In this situation, EPR spectroscopy is impossible, but paramagnetic NMR becomes possible. Chemical shift then acquires a large contribution from incomplete averaging of hyperfine coupling.



Figure 2.3: Relative magnitude of interactions that contribute to the Hamiltonian of electron-nuclear spin systems.

2.2.2 The electron-nuclear spin Hamiltonian

We now consider all interactions discussed above in Section 2.2.1 and formulate the static spin Hamiltonian of an electron-nuclear spin system in angular frequency units:

$$\mathcal{H}_{0} = \mathcal{H}_{\mathrm{EZ}} + \mathcal{H}_{\mathrm{NZ}} + \mathcal{H}_{\mathrm{HFI}} + \mathcal{H}_{\mathrm{ZFI}} + \mathcal{H}_{\mathrm{EX}} + \mathcal{H}_{\mathrm{DD}} + \mathcal{H}_{\mathrm{NQI}}$$

$$= \frac{\mu_{\mathrm{B}}}{\hbar} \sum_{k} \vec{B}_{0}^{\mathrm{T}} \mathbf{g}_{k} \hat{\vec{S}}_{k} + \sum_{i} \omega_{I,i} \hat{I}_{z,i} + \sum_{k} \sum_{i} \vec{S}_{k}^{\mathrm{T}} \mathbf{A}_{ki} \hat{\vec{I}}_{i} + \sum_{S_{k} > 1/2} \vec{S}_{k}^{\mathrm{T}} \mathbf{D}_{k} \hat{\vec{S}}_{k}$$

$$+ \sum_{k} \sum_{l \neq k} J_{kl} \hat{S}_{z,k} \hat{S}_{z,l} + \sum_{k} \sum_{l \neq k} \vec{S}_{k}^{\mathrm{T}} \mathbf{D}_{kl} \vec{S}_{l} + \sum_{I_{i} > 1/2} \vec{I}_{i}^{\mathrm{T}} \mathbf{P}_{i} \vec{I}_{i} . \qquad (2.4)$$

Note that index *i* runs over all nuclear spins, indices *k* and *l* run over electron spins and the symbol ^T denotes the transpose of a vector or vector operator. Often, only one electron spin and one nuclear spin have to be considered at once, so that the spin Hamiltonian simplifies drastically. For electron group spins S > 1, terms can be significant that are not linear, bilinear, or quadratic in the spin operators. Such terms feature higher powers of spin operators. We do not consider this complication here.

The electron Zeeman interaction $\hat{\mathcal{H}}_{\text{EZ}}$ is, in general, anisotropic. Therefore, it is parametrized by g tensors \mathbf{g}_k . We discuss this in detail in Chapter 3. In the nuclear Zeeman interaction terms $\hat{\mathcal{H}}_{\text{NZ}}$, the nuclear Zeeman frequencies $\omega_{I,i}$ depend only on the element and isotope. Thus, they can be specified without knowing electronic and spatial structure of the molecule. The hyperfine interaction is again anisotropic and thus characterized by tensors \mathbf{A}_{ki} . We discuss it in detail in Chapter 4.

All electron-electron interactions are explained in Chapter 5. The zero-field interaction $\hat{\mathcal{H}}_{ZFI}$ is purely anisotropic. Thus, it is characterized by traceless tensors \mathbf{D}_k . The exchange interaction is often purely isotropic $\hat{\mathcal{H}}_{EX}$. Any anisotropic contribution to it cannot be experimentally distinguished from the purely anisotropic dipole-dipole interaction $\hat{\mathcal{H}}_{DD}$. Hence, the former interaction is represented by scalars J_{kl} and the latter interaction by tensors \mathbf{D}_{kl} . Finally, the nuclear quadrupole interaction $\hat{\mathcal{H}}_{NQI}$ is characterized by traceless tensors \mathbf{P}_i .

2.2.3 Hamiltonian of the S = 1/2, I = 1/2 spin system

We now consider the Hamiltonian of the simplest non-trivial spin system in EPR, which consists of an electron spin S = 1/2 and a nuclear spin I = 1/2. In this situation, Eq. (2.4) simplifies to

$$\hat{\mathcal{H}}_{0} = \hat{\mathcal{H}}_{\mathrm{EZ}} + \hat{\mathcal{H}}_{\mathrm{NZ}} + \hat{\mathcal{H}}_{\mathrm{HFI}} = \frac{\mu_{\mathrm{B}}}{\hbar} \vec{B}_{0}^{\mathrm{T}} \mathbf{g} \hat{\vec{S}} + \omega_{I} \hat{I}_{z} + \hat{\vec{S}}^{\mathrm{T}} \mathbf{A} \hat{\vec{I}} .$$
(2.5)

We now assume that the high-field approximation applies for the electron spin and that anisotropy of the g value is negligible. The latter assumption is a good approximation for most organic radicals. We call the isotropic g value g_{iso} . With the magnetic field along z as usual, this Hamiltonian further simplifies to

$$\hat{\mathcal{H}}_0 = \frac{\mu_{\rm B}}{\hbar} g_{\rm iso} B_0 \hat{S}_z + \omega_I \hat{I}_z + \hat{S}^{\rm T} \mathbf{A} \hat{I}$$
(2.6)

$$= \frac{\mu_{\rm B}}{\hbar} B_0 g_{\rm iso} \hat{S}_z + \omega_I \hat{I}_z + A_{zx} \hat{S}_z \hat{I}_x + A_{zy} \hat{S}_z \hat{I}_y + A_{zz} \hat{S}_z \hat{I}_z .$$
(2.7)

In the last line of Eq. (2.7), we have dropped terms of the form $A_{xi}\hat{S}_x\hat{I}_i$ and $A_{yi}\hat{S}_y\hat{I}_i$ with i = x, y, z, as they are negligible if the high-field approximation applies to the electron spin.

We first consider the case, where the high-field approximation also applies for the nuclear spin, $|\omega_I| \gg |A_{zx}|$, $|A_{zy}|$, $|A_{zz}|$ and abbreviate $\omega_S = (\mu_B/\hbar)g_{iso}B_0$. We can now also drop the terms $A_{zx}\hat{S}_z\hat{I}_x$ and $A_{zy}\hat{S}_z\hat{I}_y$, which gives

$$\hat{\mathcal{H}}_0 = \omega_S \hat{S}_z + \omega_I \hat{I}_z + A_{zz} \hat{S}_z \hat{I}_z .$$
(2.8)

The spin system has four states. If the high-field approximation applies to both spins (weak-coupling case), the magnetic quantum numbers $m_S = \pm 1/2$ of the electron spin and $m_I = \pm 1/2$ of the nuclear spin are both good quantum numbers. As usual, we assign the symbol

 $|\alpha\rangle$ to m = +1/2 and $|\beta\rangle$ to m = -1/2. The four eigenstates are then $|\alpha_S \alpha_I\rangle$, $|\alpha_S \beta_I\rangle$, $|\beta_S \alpha_I\rangle$, and $|\beta_S \beta_I\rangle$.

We obtain their energies from Eq. (2.8) by replacing the spin operators \hat{S}_z and \hat{I}_z by their respective eigenvalues $m_S = \pm 1/2$ and $m_I = \pm 1/2$. Hence, the level energies are $\omega_S/2 + \omega_I/2 + A/4, \omega_S/2 - \omega_I/2 - A/4, -\omega_S/2 + \omega_I/2 - A/4$, and $-\omega_S/2 - \omega_I/2 + A/4$.

Allowed electron spin (EPR) transitions have $\Delta m_S = \pm 1$. This corresponds to $|\alpha_S \alpha_I\rangle \leftrightarrow$ $|\beta_S \alpha_I\rangle$ with angular frequency $\omega_{\text{EPR},\alpha} = |\omega_S + A_{zz}/2|$ and $|\alpha_S \beta_I\rangle \leftrightarrow |\beta_S \beta_I\rangle$ with angular frequency $\omega_{\text{EPR},\beta} = |\omega_S - A_{zz}/2|$. Likewise, allowed nuclear spin (NMR) transitions are $|\alpha_S \alpha_I\rangle \leftrightarrow |\alpha_S \beta_I\rangle$ with angular frequency $\omega_{\text{NMR},\alpha} = |\omega_I + A_{zz}/2|$ and $|\beta_S \alpha_I\rangle \leftrightarrow |\beta_S \beta_I\rangle$ with angular frequency $\omega_{\text{NMR},\beta} = |\omega_I - A_{zz}/2|$.

The NMR transitions can be indirectly detected via the electron spin by electron nuclear double resonance (ENDOR) experiments. The hyperfine splitting A_{zz} is the same in the EPR and NMR spectrum. However, it is usually much better resolved in the NMR spectrum, since transverse relaxation is much faster for electron than for nuclear spins, causing much broader lines in EPR than NMR spectra. Hence, the ENDOR experiments combine better sensitivity than in direct NMR with higher resolution than in EPR spectroscopy. The two lines are found at $|\omega_I| \pm A_{zz}/2$.

The same treatment can be applied for hyperfine couplings $\omega_S \gg |A_{zz}| \gg |\omega_I|$ (strongcoupling case), since m_I is also a good quantum number in that case. However, now the two lines are found at $|A_{zz}|/2 \pm \omega_I$. Usually, more than one nucleus contributes to ENDOR spectra. Line assignment may become complicated if different elements (isotopes) contribute, some of them in the weak-coupling and some of them in the strong-coupling regime.

We now consider the case where neither the weak-coupling nor the strong-coupling regime applies. In this situation, we cannot drop the terms the terms $A_{zx}\hat{S}_z\hat{I}_x$ and $A_{zy}\hat{S}_z\hat{I}_y$. However, if we excite and detect only the electron spin, we do not need a radiofrequency coil. Hence, the x direction in the nuclear spin laboratory frame is undefined. We can thus choose the x axis freely. If we rotate the nuclear spin Hamiltonian by an angle $\arctan(-A_{zy}/A_{zx})$, we have

$$\hat{\mathcal{H}}_0 = \omega_S \hat{S}_z + \omega_I \hat{I}_z + A \hat{S}_z \hat{I}_z + B \hat{S}_z \hat{I}_x , \qquad (2.9)$$

with $A = A_{zz}$ and $B = \sqrt{A_{zx}^2 + A_{zy}^2}$. For the electron spin, we can still go into the rotating frame,

$$\hat{H}_0 = \Omega_S \hat{S}_z + \omega_I \hat{I}_z + A \hat{S}_z \hat{I}_z + B \hat{S}_z \hat{I}_x , \qquad (2.10)$$

where $\Omega_S = \omega_S - \omega_{mw}$ and ω_{mw} is the microwave (excitation) frequency. It is inconvenient to go to the rotating frame for the nuclear spin, since the term $B\hat{S}_z\hat{I}_x$ is not negligible, but would become time-dependent in the rotating frame.

Now, m_I is no longer a good quantum number. Neither can we simply infer the level energies from Eq (2.10) by replacing spin operators by their eigenstates nor can we assume that the usual selection rules apply. In fact, they do not and transitions with $\Delta m_S = \pm 1, \Delta m_I = \pm 1$ become weakly allowed. As a disadvantage, this complicates interpretation of the spectra. However, there exist two advantages. First, the *B* term introduces additional information into the spectra. Second, it enables measurement of nuclear frequencies without direct excitation or detection of nuclear spins. This is discussed in Chapter 6. Physical origin of the *g* shift Electron Zeeman Hamiltonian Spectral manifestation of the electron Zeeman interaction Liquid solution Solid state

3— Electron Zeeman Interaction

3.1 Physical origin of the *g* shift

The g values of bound electrons generally differ from the value g_e of the free electron. Furthermore, they often depend on the orientation of the paramagnetic center with respect to the magnetic field vector \vec{B}_0 . The main reason for this orientation-dependent g value shift is coupling of spin to orbital angular momentum of the electron. This spin-orbit coupling (SOC) is a purely relativistic effect. Therefore, it is larger if orbitals on heavy atoms contribute to the SOMO. For non-linear molecules, orbital angular momentum is quenched in the ground state, i.e., the ground state has orbital angular momentum L = 0. In this situation, SOC can only occur in electronically excited states. Thus, it leads to only small or moderate g shifts, which can be computed by perturbation theory. Such a perturbation treatment is not valid if the electronic ground state is degenerate or near degenerate.

The perturbation treatment considers excited states, where the unpaired electron is not in the SOMO of the ground state (Figure 3.1). The orbital angular momentum operator slightly admixes such excited states to the ground state. For simplicity, we consider only the case where the main contribution to the g shift arises from orbitals localized at a single, dominating atom. We also assume single-electron SOC. This case provides basic understanding of the relation of g shifts to the SOC. To second order in perturbation theory, the matrix elements of the g tensor can be expressed as

$$g_{ij} = g_e \delta_{ij} + 2\lambda \Lambda_{ij} , \qquad (3.1)$$

where δ_{ij} is a Kronecker delta ($\delta_{ij} = 1$ for i = j and $\delta_{ij} = 0$ for $i \neq j$). The factor λ is the spin-orbit coupling constant for the dominating atom, and the matrix elements Λ_{ij} are computed as

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0|\hat{l}_i|n\rangle\langle n|\hat{l}_j|0\rangle}{\epsilon_0 - \epsilon_n} \,. \tag{3.2}$$

Indices *i* and *j* run over the Cartesian directions *x*, *y*, and *z*. The operators \hat{l}_x , \hat{l}_y , and \hat{l}_z are Cartesian components of the angular momentum operator, $|n\rangle$ designates the orbital where the unpaired electron resides in an excited-state electron configuration. The energy of this orbital is ϵ_n . Counting starts from n = 0 for the SOMO of the ground state configuration. Hence, *n* can be positive or negative.



Figure 3.1: Admixture of excited states by orbital angular momentum operators leads to a g shift by spin-orbit coupling. The energy difference in the perturbation expression is positive for excitation of a paired electron to the ground-state SOMO and negative for excitation of the unpaired electron to a higher energy orbital.

The product of the overlap integrals in the numerator on the right-hand side of Eq. (3.2) is usually positive. Hence, the sign of the g shift is determined by the denominator. The denominator is positive, if a paired electron from a fully occupied orbital is promoted to the ground-state SOMO ($\epsilon_n < \epsilon_0$) and negative if the unpaired electron is promoted to a previously unoccupied orbital ($\epsilon_n > \epsilon_0$, Figure 3.1). Because the energy gap between the SOMO and the lowest unoccupied orbital (LUMO) is usually larger than the one between occupied orbitals, terms with positive numerator dominate in the sum on the right-hand side of Eq. (3.2). Therefore, positive g shifts are more frequently encountered than negative ones.

The relevant spin-orbit coupling constant λ depends on the element and on the type of orbital. It scales roughly with Z^4 , where Z is the nuclear charge. Unless there is a very low lying excited state (near degeneracy of the ground state), contributions from heavy nuclei dominate. In organic radicals consisting of only hydrogen and second-row elements, there are no heavy nuclei. In this situation, g shifts of only $\Delta g < 10^{-2}$ are observed. Typical shifts are $1 \dots 3 \times 10^{-3}$. Note that this still exceeds typical chemical shifts in NMR, which are measured in ppm (10^{-6}), by one to two orders of magnitude. For first-row transition metals, g shifts are of the order of 10^{-1} .

For rare-earth ions, the perturbation treatment breaks down. The Landé factor g_J can then be computed from the term symbol for a doublet of levels

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}, \qquad (3.3)$$

where J is the quantum number for total angular momentum and L the quantum number for orbital angular momentum. The principal values of the g tensor are $\epsilon_x g_J$, $\epsilon_y g_J$, and $\epsilon_z g_J$, where the ϵ_i with i = x, y, z are differences between the eigenvalues of \hat{L}_i for the two levels.

If the structure of a paramagnetic center is known, the g tensor can be computed by quantum chemistry. This works quite well for organic radicals and reasonably well for most first-row transition metal ions. Details are explained in [KBE04].

The g tensor is a global property of the SOMO. It is easily interpretable only if it is dominated by the contribution at a single atom. This is often, but not always, the case for transition metal and rare earth ion complexes. If the paramagnetic center has a C_n symmetry axis with $n \ge 3$, the g tensor has axial symmetry with principal values $g_x = g_y = g_{\perp}$, $g_z = g_{\parallel}$. For cubic or tetrahedral symmetry, the g value is isotropic, but not necessarily equal to g_e . Isotropic g values are also encountered to a very good approximation for transition metal and rare earth metal ions with half-filled shells, such as in Mn(II) complexes ($3d^5$ electron configuration) and Gd(III) complexes ($4f^7$).

3.2 Electron Zeeman Hamiltonian

We now consider a single electron spin S and thus drop the sum and index k in $\hat{\mathcal{H}}_{\text{EZ}}$ in Eq. (2.4). In the principal axes system (PAS) of the g tensor, the electron Zeeman Hamiltonian now reads

$$\hat{\mathcal{H}}_{\text{EZ}} = \frac{\mu_{\text{B}}}{\hbar} B_0 \left(\cos \phi \sin \theta \quad \sin \phi \sin \theta \quad \cos \theta \right) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \begin{pmatrix} S_x \\ \hat{S}y \\ \hat{S}z \end{pmatrix}$$

$$= \frac{\mu_{\text{B}}}{\hbar} B_0 \left(g_x \cos \phi \sin \theta \hat{S}_x + g_y \sin \phi \sin \theta \hat{S}_y + g_z \cos \theta \hat{S}z \right).$$
(3.4)

Where B_0 is the magnetic field, g_x , g_y , and g_z are the principal values of the g tensor and the polar angles ϕ and θ determine the orientation of the magnetic field in the PAS.

This Hamiltonian is diagonalized by the Bleaney transformation, providing

$$\hat{\mathcal{H}}_{\text{EZ}}^{BT} = \frac{\mu_{\text{B}}}{\hbar} g_{\text{eff}} B_0 \hat{S}_z , \qquad (3.5)$$

with the effective g value at orientation (ϕ, θ)

$$g_{\text{eff}}(\phi,\theta) = \sqrt{g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta} .$$
(3.6)

If anisotropy of the g tensor is significant, the z axis in Eq. (3.5) is tilted from the direction of the magnetic field. This effect is negligible for most organic radicals, but not for transition metal ions or rare earth ions. Eq. (3.6) for the effective g values describes an ellipsoid (Figure 3.2).



Figure 3.2: Ellipsoid describing the orientation dependence of the effective g value in the PAS of the g tensor. At a given direction of the magnetic field vector \vec{B}_0 (red), g_{eff} corresponds to the distance between the origin and the point where \vec{B}_0 intersects the ellipsoid surface.

Concept 3.2.1 — **Energy levels in the high-field approximation.** In the high-field approximation, the energy contribution of a Hamiltonian term to the level with magnetic quantum numbers $m_{S,k}$ and $m_{I,i}$ can be computed by replacing the $\hat{J}_{z,j}$ operators (J = S, I, j = k, i) by the corresponding magnetic quantum numbers. This is because the magnetic quantum numbers are the eigenvalues of the $\hat{J}_{z,j}$ operators, all $\hat{J}_{z,j}$ operators commute with each other, and contributions with all other Cartesian spin operators are negligible. For the electron Zeeman

term, the energy contribution is $m_S g_{\text{eff}} \mu_B B_0 / \hbar$. If the high-field approximation is slightly violated, this expression corresponds to a first-order perturbation treatment.

Note that we already used this concept in Section 2.2.3. It also applies to spin quantum numbers S > 1/2, I > 1/2 and to any interaction that is linear or bilinear in the spin operators.

The selection rule for transitions in EPR spectroscopy is $|\Delta m_S| = 1$, $|\Delta m_I| = 0$. It applies strictly as long as the high-field approximation applies strictly to all spins. This selection rule results from conservation of angular momentum upon absorption of a microwave photon and from the fact that the microwave photon interacts with electron spin transitions. It follows that the first-order contribution of the electron Zeeman interaction to the frequencies of all electron spin transitions is the same, namely $g_{\text{eff}}\mu_{\text{B}}B_0/\hbar$. EPR spectra are usually measured at constant microwave frequency ν_{mw} by sweeping the magnetic field B_0 . The resonance field is then given by

$$B_{0,\rm res} = \frac{h\nu_{\rm mw}}{g_{\rm eff}\mu_{\rm B}} \,. \tag{3.7}$$

For nuclear spin transitions, $|\Delta m_S| = 0$, $|\Delta m_I| = 1$, the electron Zeeman interaction does not contribute to the transition frequency to first order.

3.3 Spectral manifestation of the electron Zeeman interaction

3.3.1 Liquid solution

In liquid solution, molecules tumble due to Brownian rotational diffusion. The time scale of this motion can be characterized by a rotational correlation time τ_{rot} that in non-viscous solvents is of the order of 10 ps for small molecules, and of the order of 1 ns to 100 ns for proteins and other macromolecules. For a globular molecule with radius r in a solvent with viscosity η , the rotational correlation time can be roughly estimated by the Stokes-Einstein law

$$\tau_{\rm r} = \frac{4\pi\eta r^3}{3k_{\rm B}T} \,. \tag{3.8}$$

The effect of such tumbling on spectral lineshapes depends on the difference $\Delta\omega$ between the transition frequencies at any two orientations of the molecule. In the fast limit, $\tau_r \max(\Delta\omega) \ll 1$, anisotropy is fully suppressed and only the isotropic average of the transition frequencies is observed. This is analogous to the fast chemical exchange limit discussed in the NMR part of the lecture course. For somewhat slower rotation, the transition frequency is modulated by molecular tumbling on the time scale of the experiment. This leads to line broadening as it shortens the transverse relaxation time T_2 . In the slow-tumbling regime, where $\tau_r \Delta \omega \approx 1$, anisotropy is incompletely averaged and line width attains a maximum. For $\tau_r \Delta \omega \gg 1$, the solid-state spectrum is observed. Lineshapes can be quantitatively simulated in a framework of multi-site exchange between the various orientations of the molecule. This is again analogous to two-site chemical exchange, but more complicated to implement. The effects depend on magnetic field, since $\Delta \omega$ depends on magnetic field if g anisotropy contributes significantly to total anisotropy of the transition frequency.

For the electron Zeeman interaction, fast tumbling leads to an average resonance field

$$B_{0,\text{res}} = \frac{h\nu_{\text{mw}}}{g_{\text{iso}}\mu_{\text{B}}}, \qquad (3.9)$$

with the isotropic g value $g_{iso} = (g_x + g_y + g_z)/3$. Line broadening from g anisotropy is almost negligible for small organic radicals in non-viscous solvents at X-band frequencies around

9.5 GHz. At W-band frequencies of 94 GHz, such broadening can be substantial for organic radicals. For transition metal complexes, this applies already at X-band frequencies. For large macromolecules or in viscous solvents, solid-state like EPR spectra can be observed in liquid solution.



Figure 3.3: Powder line shape for a g tensor with axial symmetry. (a) The probability density to find an orientation with polar angle θ is proportional to the circumference of a circle a angle θ on a unit sphere. (b) Probability density $P(\theta)$. The effective g value at angle θ is $\sqrt{g_{\perp}^2 + g_{||}^2 + \cos(2\theta)(g_{||}^2 - g_{\perp}^2)/2}$. (c) Schematic powder line shape. The pattern corresponds to $g_{\perp} > g_{||}$ for a field sweep and to $g_{\perp} < g_{||}$ for a frequency sweep. Because of the frame tilting, the isotropic value $g_{iso} = (2g_{\perp} + g_{||})/3$ is not encountered at the magic angle, although the shift is small if $\Delta g = 2(g_{||} - g_{\perp})/3 \ll g_{iso}$.

3.3.2 Solid state

For a single-crystal sample, the resonance field at any given orientation can be computed by Eq. (3.7). However, in most cases only microcrystalline powders are available or the sample is measured in glassy frozen solution. Under such conditions, all orientations contribute equally. With respect to the polar angles, this implies that ϕ is uniformly distributed, whereas the probability to encounter a certain angle θ is proportional to $\sin \theta$ (Figure 3.3). The line shape of the absorption spectrum is most easily understood for axial symmetry of the *g* tensor. Transitions are observed only in the range between the limiting resonance fields at $g_{||}$ and g_{\perp} . The spectrum has a global maximum at g_{\perp} , where $\sin(\theta)$ attains its maximum of 1, and a minimum at $g_{||}$, where $\sin(\theta) = 0$.

In CW EPR spectroscopy we do not observe the absorption line shape, but rather its first derivative.¹ This derivative line shape has sharp features at the line shape singularities of the absorption spectrum and very weak amplitude in between (Figure 3.4).

¹This results from applying field modulation and detecting the signal at the modulation frequency by a lock-in amplifier. Such a setup can provide sensitive narrow-band detection with an inherently broadband detector.



Figure 3.4: Simulated X-band EPR spectra for systems with only g anisotropy. The upper panels show absorption spectra as they can be measured by echo-detected field-swept EPR spectroscopy. The lower panels show the first derivative of the absorption spectra as they are detected by continuous-wave EPR. The unit-sphere pictures in the right upper panel visualize the orientations that are selected at the resonance fields corresponding to the principal values of the q tensor.

Concept 3.3.1 — **Orientation selection.** For a powder sample or glassy frozen solution, different resonance fields within the powder pattern correspond to different sets of orientations with respect to the magnetic field. For an axial g tensor, near the resonance field of g_{\parallel} only orientations close to the z axis of the g tensor PAS are observed. In contrast, near the resonance field for g_{\perp} , orientations within the whole xy plane of the PAS contribute. For the case of orthorhombic symmetry with three distinct principal values g_x , g_y , and g_z , narrow sets of orientations can be observed at the resonance fields corresponding to the extreme g values g_x and g_z (see right top panel in Figure 3.4). At the intermediate principal value g_y , a broad range of orientations contributes, because the same resonance field can be realized by orientations other than $\phi = 90^{\circ}$ and $\theta = 90^{\circ}$. Such orientation selection can enhance the resolution of ESEEM and HYSCORE spectra (Chapter 6) and simplify their interpretation. It can complicate interpretation of DEER data in terms of distance distributions (Chapter 7).

Physical origin of the hyperfine interaction Dipole-dipole hyperfine interaction Fermi contact interaction Spin polarization **Hyperfine Hamiltonian** Spectral hyperfine manifestation of the interaction Liquid-solution EPR spectra Liquid-solution NMR spectra of paramagnetic species Solid-state EPR spectra Solid-state NMR spectra of paramagnetic species

4 — Hyperfine Interaction

σ

4.1 Physical origin of the hyperfine interaction

The magnetic moments of an electron and a nuclear spin couple by the magnetic dipole-dipole interaction. This interaction is analogous to the dipole-dipole interaction between nuclear spins discussed in the NMR part of the lecture course. The main difference to the NMR case is that, in many cases, the point-dipole approximation for the electron spin is poor, as the electron is distributed over the SOMO. In contrast, the nucleus can be considered as well localized in space. We now picture the SOMO as a linear combination of atomic orbitals. Contributions from spin density in an atomic orbital of another nucleus can be approximated by assuming that the unpaired electron is a point-dipole localized at this other nucleus. The contributions from the individual atomic orbitals that contribute to the SOMO simply add up (Section 4.1.1, Eq. (4.3)). However, they must be added as tensors. The resulting sum tensor does not necessarily feature the axial symmetry that applies to the tensor of two interacting point dipoles.

Complications arise for spin density in atomic orbitals on the same nucleus. Here, we have to distinguish between different types of atomic orbitals. In *s* orbitals, the unpaired electron has finite probability density for residing at the nucleus, at zero distance r_{SI} to the nuclear spin. Since the dipole-dipole interaction scales with r_{SI}^{-3} , zero distance causes a singularity. This singularity occurs in only a single point and can thus be treated mathematically, as has been done by Fermi. The contribution of spin density in *s* orbitals on the nucleus under consideration is therefore called Fermi contact interaction. Because of the spherical symmetry of *s* orbitals, the Fermi contact interaction is purely isotropic.

For spin density in other orbitals (p, d, f) orbitals) of the atom, the dipole-dipole interaction with the nucleus of this atom must be averaged over the spatial distribution of the electron in these orbitals. This average has no isotropic contribution. Therefore, spin density in p, d, f orbitals does not influence resonance fields of fast tumbling paramagnetic species in liquid solution. Neither does spin density in orbitals on other nuclei. Thus, the isotropic coupling results solely from Fermi contact interaction with the nucleus under consideration. Hyperfine anisotropy can, however, contribute to linewidth unless tumbling attains the fast limit $\tau_r \Delta \omega \ll 1$.

Since the isotropic and purely anisotropic contributions have different physical origin, we separate them in the hyperfine tensor A_{ki} that describes the interaction between electron spin S_k

and nuclear spin I_i :

$$\mathbf{A}_{ki} = A_{\text{iso},ki} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix} + \mathbf{T}_{ki} , \qquad (4.1)$$

where $A_{iso,ki}$ is the isotropic hyperfine coupling and \mathbf{T}_{ki} the purely anisotropic coupling. In the following, we drop the electron and nuclear spin indices k and i.

4.1.1 Dipole-dipole hyperfine interaction

The anisotropic hyperfine coupling tensor \mathbf{T} can be computed from the ground state wavefunction ψ_0 by applying the correspondence principle to the classical interaction between two point dipoles

$$T_{ij} = \frac{\mu_0}{4\pi\hbar} g_e \mu_{\rm B} g_{\rm n} \mu_{\rm n} \left\langle \psi_0 \left| \frac{3r_i r_j - \delta_{ij} r^2}{r^5} \right| \psi_0 \right\rangle \,. \tag{4.2}$$

Such computations are implemented in quantum chemistry programs such as ORCA, ADF, or Gaussian.

If the SOMO is considered as a linear combination of atomic orbitals, the contributions from an individual orbital can be expressed as the product of spin density in this orbital with a spatial factor. This spatial factor can be computed once for all. This may be less precise than a numerical quantum-chemical computation, but provides more insight. The spatial factors have been tabulated [KM85]. In general, nuclei of elements with larger electronegativity have larger spatial factors. At the same spatial factor, as applies to isotopes of the same element, the hyperfine coupling is proportional to the nuclear g value g_n and thus proportional to the gyromagnetic ratio of the nucleus. Hence, a deuterium coupling can be computed from a known proton coupling or *vice versa*.

A special situation applies to protons, alkali metals and alkaline earth metals, which have no significant spin densities in p-, d-, or f-orbitals. In this case, the anisotropic contribution can only arise from through-space coupling to centers of spin density at other nuclei. In such a distributed point-dipole approximation, the hyperfine tensor is given by

$$\mathbf{T} = \frac{\mu_0}{4\pi\hbar} g_e \mu_{\rm B} g_{\rm n} \mu_{\rm n} \sum_{j\neq i} \rho_j \frac{3\vec{n}_{ij}\vec{n}_{ij}^{\rm T} - \vec{1}}{R_{ij}^3} , \qquad (4.3)$$

where the sum runs over all nuclei j with significant spin density ρ_j (summed over all orbitals at this nucleus) other than nucleus i under consideration. The R_{ij} are distances between the nucleus under consideration and the centers of spin density, and the \vec{n}_{ij} are unit vectors along the direction from the considered nucleus to the center of spin density. For protons in transition metal complexes, it is often a good approximation to consider spin density only at the central metal ion. To a good approximation, the distance R from the proton to the central ion can then be directly inferred from the anisotropic part of the hyperfine coupling.

Hyperfine tensor contributions T computed in any of these ways must be corrected for the influence of SOC, if the g tensor is strongly anisotropic. If the dominant contribution to SOC arises at a single nucleus, the hyperfine tensor at *this nucleus*¹ can be corrected by

$$\mathbf{T}^{(\mathbf{g})} = \frac{\mathbf{g}\mathbf{T}}{g_e} \,. \tag{4.4}$$

¹Most literature holds that the correction should be done for all nuclei. As pointed out by Frank Neese, this is not true. An earlier discussion of this point is found in [Lef67]

Usually, this is a good correction for the hyperfine coupling of the transition metal ion in a mononuclear transition metal complex. The product \mathbf{gT} may have an isotropic part, even though \mathbf{T} is purely anisotropic. This isotropic *pseudocontact* contribution depends on the relative orientation of the *g* tensor and the spin-only dipole-dipole hyperfine tensor \mathbf{T} . The correction is negligible for most organic radicals, but not for paramagnetic metal ions. If significant SOC arises at several centers, a correction is still necessary, but cannot be written as a function of the *g* tensor.

4.1.2 Fermi contact interaction

The Fermi contact contribution takes the form

$$A_{\rm iso} = \rho_s \cdot \frac{2}{3} \frac{\mu_0}{\hbar} g_e \mu_{\rm B} g_{\rm n} \mu_{\rm n} |\psi_0(0)|^2 , \qquad (4.5)$$

where ρ_s is the spin density in the *s* orbital under consideration, g_n the nuclear *g* value and $\mu_n = \beta_n = 5.05078317(20) \cdot 10^{-27}$ J T⁻¹ the nuclear magneton $(g_n\mu_n = \gamma_n\hbar)$. The factor $|\psi_0(0)|^2$ denotes the probability to find the electron at this nucleus in the ground state with wave function ψ_0 and has been tabulated [KM85].



Figure 4.1: Transfer of spin density by the spin polarization mechanism. According to the Pauli principle, the two electrons in the C-H bond orbital must have opposite spin state. If the unpaired electron resides in a p_z orbital on the C atom, the same spin state is slightly favored for other electrons on the same C atom, as this minimizes electrostatic repulsion. Hence, for the electron at the H atom, the opposite spin state (left panel) is slightly favored over the same spin state (right panel). It follows that positive spin density in the p_z orbital on the C atom induces some negative spin density in the *s* orbital on the H atom.

4.1.3 Spin polarization

Up to this point, the contributions to the hyperfine coupling could be understood in a singleelectron picture. Hartree-Fock methods in quantum chemistry would suffice to compute them. Further contributions arise from correlation of electrons in a molecule. Assume that the p_z orbital on a carbon atom contributes to the SOMO, so that the α spin state of the electron is preferred in that orbital (Fig. 4.1). Electrons in other orbitals on the same atom will then also have a slight preference for the α state (left panel). This is because electrons with the same spin tend to avoid each other, which reduces electrostatic repulsion.² In particular, the spin configuration in the left panel of Fig. 4.1 is slightly more preferable than the one in the right panel. According to the Pauli principle, the two electrons in the *s* bond orbital of the C-H bond must have opposite spin. Thus, the electron in the *s* orbital of the hydrogen atom directly bound to the spin-carrying carbon atom has a slight preference for the β state. This corresponds to a negative isotropic hyperfine coupling of the directly bound proton (α proton). This negative isotropic hyperfine coupling is

²Hund's rule is also based on this preference of electrons on the same atom to have parallel spin.

induced by and proportional to the positive hyperfine coupling of the adjacent carbon atom. The effect is termed "spin polarization", although it has no physical relation to the polarization of electron spin transitions in an external magnetic field.

Spin polarization is important, as it transfers spin density from p orbitals, where it is invisible in liquid solution, to s orbitals of protons, where it is visible. Note also that carbon atoms have low natural abundance of the magnetic isotope ¹³C, so that ¹³C hyperfine couplings lead to only weak "satellite lines". The transfer of spin density occurs, both, in σ radicals, where the unpaired electron is localized on a single atom, and in π radicals, where it is distributed over the π system. The latter case is of larger interest, as the distribution of the π orbital over the nuclei can be mapped by measuring and assigning the isotropic proton hyperfine couplings. This coupling can be predicted by the *McConnell equation*

$$A_{\rm iso,H} = Q_{\rm H} \rho_{\pi} , \qquad (4.6)$$

where ρ_{π} is the spin density at the adjacent carbon atom and $Q_{\rm H}$ is a parameter of the order of -2.5 mT, which slightly depends on structure of the π system.



Figure 4.2: Mapping of the LUMO and HOMO of an aromatic molecule via measurements of hyperfine couplings after one-electron reduction or oxidation. Reduction leads to an anion radical, whose SOMO is a good approximation to the lowest unoccupied molecular orbital (LUMO) of the neutral parent molecule. Oxidation leads to an cation radical, whose SOMO is a good approximation to the highest occupied molecular orbital (HOMO) of the neutral parent molecule.

The McConnell equation is mainly applied for mapping the LUMO and HOMO of aromatic molecules (Figure 4.2). An unpaired electron can be put into these orbitals by one-electron reduction or oxidation, respectively, without perturbing the orbitals too strongly. The isotropic hyperfine couplings of the hydrogen atom directly bound to a carbon atom report on the contribution of the p_z orbital of this carbon atom to the π orbital. The challenges in this mapping are twofold. First, it is hard to assign the observed couplings to the hydrogen atoms unless a model for the distribution of the π orbital is already available. Second, the method is blind to carbon atoms without a directly bonded hydrogen atom.

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 $\hat{\mathcal{H}}_{HFI}$ in Eq. (2.4). In general, all matrix elements of the hyperfine tensor **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

$$\hat{\mathcal{H}}_{HFI} = (\hat{S}_{x} \ \hat{S}_{y} \ \hat{S}_{z}) \begin{pmatrix} A_{xx} \ A_{xy} \ A_{xz} \\ A_{yx} \ A_{yy} \ A_{yz} \\ A_{zx} \ A_{zy} \ A_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{x} \\ \hat{I}_{y} \\ \hat{I}_{z} \end{pmatrix}$$

$$= A_{xx} \hat{S}_{x} \hat{I}_{x} + A_{xy} \hat{S}_{x} \hat{I}_{y} + A_{xy} \hat{S}_{x} \hat{I}_{z} \\
+ A_{yx} \hat{S}_{y} \hat{I}_{x} + A_{yy} \hat{S}_{y} \hat{I}_{y} + A_{yz} \hat{S}_{y} \hat{I}_{z} \\
+ A_{zx} \hat{S}_{z} \hat{I}_{x} + A_{zy} \hat{S}_{z} \hat{I}_{y} + A_{zz} \hat{S}_{z} \hat{I}_{z} .$$
(4.7)

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, as we already discussed in Section 2.2.3. The truncated hyperfine Hamiltonian thus reads

$$\hat{\mathcal{H}}_{\text{HFI,trunc}} = A_{zx}\hat{S}_{z}\hat{I}_{x} + A_{zy}\hat{S}_{z}\hat{I}_{y} + A_{zz}\hat{S}_{z}\hat{I}_{z} .$$

$$(4.8)$$

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

$$\hat{\mathcal{H}}_{\text{HFI,trunc}} = A\hat{S}_z\hat{I}_z + B\hat{S}_z\hat{I}_x , \qquad (4.9)$$

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

$$A = A_{\rm iso} + T(3\cos^2\theta_{\rm HFI} - 1)$$

$$B = 3T\sin\theta_{\rm HFI}\cos\theta_{\rm HFI}, \qquad (4.10)$$

where $\theta_{\rm HFI}$ is the angle between the static magnetic field \vec{B}_0 and the symmetry axis of the hyperfine tensor. T is the anisotropy of the hyperfine coupling. The principal values of the hyperfine tensor are $A_x = A_y = A_{\perp} = A_{\rm iso} - T$ and $A_z = A_{||} = A_{\rm iso} + 2T$. The pseudo-secular contribution B vanishes along the principal axes of the hyperfine tensor, where $\theta_{\rm HFI}$ is either 0° or 90°. It generally vanishes 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 interaction. This applies to hydrogen, alkali and earth alkali ions. We then find

$$T = \frac{1}{r^3} \frac{\mu_0}{4\pi\hbar} g_e \mu_{\rm B} g_{\rm n} \mu_{\rm n} .$$
(4.11)

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 hyperfine contribution 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 $m_I = -I, -I + 1, ... I$. 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.



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.

4.3 Spectral manifestation of the hyperfine interaction

4.3.1 Liquid-solution EPR spectra

Each nucleus splits each electron spin transition into 2I + 1 transitions with different frequencies. Hence, 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 of 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. In general, for a group of k_i equivalent nuclei with arbitrary spin quantum number I_i the number of lines (multiplicity) is $2k_iI_i + 1$. Multiplicities of groups of equivalent nuclei multiply. Hence, the total number of EPR lines is

$$n_{\rm EPR} = \prod_{i} (2k_i I_i + 1) ,$$
 (4.12)

where index *i* runs over the groups of equivalent nuclei.

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, at sufficiently large signal-to-noise ratio for seeing the outermost lines, is given in [CCM16].



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 all other nuclear spins. This gives rise to very rich, but harder to analyze spectra, especially in the solid state.

4.3.2 Liquid-solution NMR spectra of paramagnetic species

The situation that we discuss here corresponds to the regime where EPR spectra can be taken. In this regime, NMR lines are strongly broadened and are best detected indirectly via the electron spin. If electron spin longitudinal relaxation rate is much higher than hyperfine couplings, hyperfine interaction manifests as a temperature-dependent chemical shift contribution. In this regime, paramagnetic NMR can be performed with standard NMR spectrometers. This is beyond the scope of our lecture course.

As mentioned in Section 2.2.3, the secular hyperfine coupling A can be inferred from either EPR or NMR spectra, with lines being narrower in the NMR spectra. Another advantage of NMR 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 NMR spectra thus grows only linearly with the number of nuclei,³ whereas 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

$$n_{\rm NMR} = (2S+1)N_{\rm eq}$$
 (4.13)

Most paramagnetic species that can be observed in liquid solution have S = 1/2, leading to NMR spectra with one doublet per nucleus for I = 1/2. In solution, this also applies to quadrupolar nuclei with I > 1/2.

³Nuclear-nuclear couplings change that, but are unresolved for paramagnetic species



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 large case, the doublet is centered at frequency large 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 arises if the hyperfine interaction of some nuclei is larger than the nuclear Zeeman interaction. For these nuclei, the doublet is centered at A/2 and split by $2\omega_I$, as explained in Section 2.2.3. This is illustrated in Figure 4.5. In the weak-coupling case with $|A|/2 < |\omega_I|$, which applies to two of the three doublets of the phenyl radical (Figure 4.6), the doublet 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 $|\omega_I| - |A|/2$ formally becomes negative. As the sign of the frequency is not detected, this line is found at frequency $|A|/2 - |\omega_I|$ instead. In other words, the line is "mirrored" at the zero frequency. This results in the doublet centered at frequency |A|/2 and split by $2|\omega_I|$.

In well resolved liquid-state spectra, this situation can often be recognized easily, since the nuclear Zeeman frequency $|\omega_I|$ can only assume a few values. If one has a hypothesi for the structure of a radical, these values are known. Figure 4.6 illustrates how the NMR 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. This spectrum cannot be detected with a standard NMR spectrometer, as at is much broader than the bandwidth of the electronic components used in such spectrometers. Furthermore, because of the large spectral width and the large linewidth, sensitivity of direct NMR detection is very poor. Such spectra can be indirectly detected by ENDOR techniques.

4.3.3 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 singularities of the line shape pattern, which



Figure 4.6: Schematic NMR (nuclear frequency) spectrum of the phenyl radical at an X-band frequency where $\omega_I/(2\pi) \approx 14$ 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.

correspond to principal values 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.



Figure 4.7: Construction of a solid-state EPR spectrum for a copper(II) complex with four equivalent ligands and square planar coordination. The $g_{||}$ and $A_{||}$ 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.

However, simple cases are quite often encountered, where the hyperfine interaction of only one nucleus dominates and the PASs of the g and hyperfine tensor coincide. For instance, Cu(II)

complexes are often square planar. If all four ligands are the same, they have a C_4 symmetry axis. For a C_n axis with $n \ge 3$, the g tensor necessarily has axial symmetry and the C_n axis is the unique axis. For the same reason, the hyperfine tensors of ⁶³Cu and ⁶⁵Cu have axial 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 axes.

In this situation, the subspectra for each of the nuclear spin states $m_I = -3/2, -1/2, +1/2,$ and +3/2 have the same shape as shown in Figure 3.3. They do have different width and different centers. The resonance fields can be computed by solving

$$\hbar\omega_{\rm mw} = \mu_{\rm B} B_{0,\rm res} \sqrt{2g_{\perp}^2 \sin^2\theta + g_{\parallel}^2 \cos^2\theta} + m_I \left[A_{\rm iso} + T \left(3\cos^2\theta - 1\right)\right] , \qquad (4.14)$$

for $B_{0,\text{res}}$, 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 $\mu_{\text{B}}B_0g_{||} + m_IA_{||}$ and $\mu_{\text{B}}B_0g_{\perp} + m_IA_{\perp}$.

The construction of a Cu(II) EPR spectrum according to these considerations is shown in Figure 4.7. The values of $g_{||}$ and $A_{||}$ 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.



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

4.3.4 Solid-state NMR spectra of paramagnetic species

In NMR spectra, the situation is again simpler. This is because the nuclear Zeeman frequency is isotropic and chemical shift anisotropy is negligibly small compared to hyperfine anisotropy. Furthermore, resolution is much better than in EPR spectra for the reasons discussed above. As a consequence, 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, the hyperfine tensor has nearly axial symmetry. The same applies if the dominant contribution comes from spin density in a single p or d orbital. In these situations, 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.

Exchange interaction Physical origin and consequences Exchange Hamiltonian Spectral manifestation of the exchange interaction **Dipole-dipole interaction** Physical picture **Dipole-dipole Hamiltonian** Spectral manifestation of the dipole-dipole interaction Zero-field interaction Physical picture Extension to more than two electrons Kramers and non-Kramers ions Zero-field interaction Hamiltonian Spectral manifestation of zero-field splitting Effective spin 1/2 in Kramers doublets



5 — Electron-Electron Interactions

In this Chapter, we first consider the simplest case of two unpaired electrons. We then extend the treatment to more than two unpaired electrons. The latter situation is encountered for high-spin transition metal complexes and for rare-earth ion complexes.

5.1 Exchange interaction

5.1.1 Physical origin and consequences

If two unpaired electrons occupy SOMOs in the same molecule or in spatially close molecules, the wave functions ψ_1 and ψ_2 of the two SOMOs may overlap. The two unpaired electrons can couple either to a singlet state or to a triplet state. The energy difference between the singlet and triplet state is the exchange integral

$$J = -2e^2 \int \int \frac{\psi_1^*(r_1)\,\psi_2^*(r_2)\,\psi_1(r_2)\,\psi_2(r_1)}{|\vec{r_1}\vec{r_2}|} \mathrm{d}\vec{r_1}\mathrm{d}\vec{r_2}$$
(5.1)

There exist different conventions for the sign of J and the factor 2 may be missing in parts of the literature. With the sign convention used here, the singlet state is lower in energy for positive J. The singlet state S with spin wave function $(|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ is antisymmetric with respect to exchange of the two electrons. Since electrons are Fermions, this corresponds to the situation where the two electrons could also occupy the same orbital. Such bonding orbital overlap corresponds to antiferromagnetic spin ordering. For negative J, the triplet state is lower in energy, orbital overlap is anti-bonding and spin ordering ferromagnetic.

The triplet state has three substates with wave functions $|\alpha\alpha\rangle$ for the T_+ state, $(|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$ for the T_0 state, and $|\beta\beta\rangle$ for the T_- state. The T_+ and T_- state are eigenstates both in the absence and presence of the *J* coupling. The states S and T_0 are eigenstates for $J \gg \Delta\omega$, where $\Delta\omega$ is the difference between the electron Zeeman frequencies of the two spins. This is the strong-exchange case, where the coupled representation is more convenient. For the opposite case of $\Delta\omega \gg J$, the eigenstates are $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$. This case corresponds to the high-field approximation with respect to the exchange interaction. Here, the uncoupled representation is more convenient. Note that large hyperfine coupling can complicate the situation by mixing the T_+ and T_- states with the $S - T_0$ manifold.

For strong exchange, $J \gg \Delta \omega$, the energies are approximately -(3/4)J for the singlet state and $J/4 - \omega_S$, J/4 and $J/4 + \omega_S$ for the triplet substates T₋, T₀, and T₊, respectively, where ω_S is the electron Zeeman interaction for the group spin S = 1. If $J \gg 2\pi\nu_{\rm mw}$, microwave photons with energy $h\nu_{\rm mw}$ cannot excite transitions between the singlet and triplet subspace. The two subspaces can then be considered separately from each other. The singlet subspace corresponds to a diamagnetic molecule and does not contribute to EPR spectra. The spin Hamiltonian of the triplet subspace, corresponding to group spin S = 1, does not depend on J, since exchange coupling shifts all levels in this subspace by the same energy.

For J < 0, the triplet state is the ground state and thus observable by EPR spectroscopy. More often, J > 0 and the singlet state is the ground state. As long as $\hbar J$ does not exceed thermal energy $k_{\rm B}T$ by a large factor, the triplet state is thermally populated and observable. In this case, the EPR signal amplitude may increase rather than decrease with increasing temperature. For organic molecules, this situation is also rare. If $\hbar J \gg k_{\rm B}T$ and J > 0, the compound does not give an EPR signal. In order to observe the triplet state by transient EPR, the system must be photoexcited and intersystem crossing to the triplet state must occur.

Weak exchange coupling is observed in biradicals with well localized SOMOs that are separated by more than about 0.5 nm (5 Å). Such systems are more conveniently described in an uncoupled representation with two spins $S_1 = 1/2$ and $S_2 = 1/2$. In this regime, exchange coupling J decreases exponentially with the distance between the two electrons. If the two centers are not linked by a continuous chain of conjugated bonds, exchange coupling is rarely resolved at distances larger than 1.5 nm. At such distances, the exchange coupling is then by more than an order of magnitude smaller than dipole-dipole coupling between the two electrons. If the two centers are linked by a continuous chain of conjugated bonds, exchange coupling may exceed dipole-dipole coupling up to much longer distances. In such systems, |J| decreases exponentially with the number of conjugated bonds. These considerations apply if the medium is a dielectric. In conducting or semi-conducting media, exchange coupling through the medium can be relevant up to longer distances.

Exchange coupling is also significant during diffusional encounters of two paramagnetic molecules in liquid solution. Such dynamic Heisenberg spin exchange can be pictured as physical exchange of unpaired electrons between the colliding molecules. This causes a sudden change of the spin Hamiltonian, which leads to spin relaxation. A typical example is line broadening in liquid-state EPR spectra of radicals by oxygen, which has a paramagnetic triplet ground state. If radicals of the same type collide, line broadening is also observed, but the effects on the spectra can be more subtle, since the spin Hamiltonians of the colliding radicals are the same. In this case, exchange of unpaired electrons between the radicals changes only spin state, but not the spin Hamiltonian.

5.1.2 Exchange Hamiltonian

The spin Hamiltonian contribution by weak exchange coupling is

$$\hat{\mathcal{H}}_{\text{EX}} = J\left(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}\right) \,. \tag{5.2}$$

This Hamiltonian is analogous to the J coupling Hamiltonian in NMR spectroscopy. If the two spins have different g values and the field is sufficiently high $(\Delta g \mu_B B_0 / \hbar \gg J)$ ($\Delta g = |g_1 - g_2|$), the exchange Hamiltonian can be truncated in the same way as the J coupling Hamiltonian in heteronuclear NMR:

$$\hat{\mathcal{H}}_{\text{EX,trunc}} = J\hat{S}_{1z}\hat{S}_{2z} .$$
(5.3)

5.1.3 Spectral manifestation of the exchange interaction

In the absence of hyperfine coupling, the situation is the same as for J coupling in NMR spectroscopy. However, note the missing factor 2π in the EPR convention. Exchange coupling

between like spins (same electron Zeeman frequency) does not influence the spectra. For radicals in liquid solution, hyperfine coupling is usually observable. In this case, exchange coupling does influence the spectra even for like spins, as illustrated in Figure 5.1. We consider two exchange-coupled electron spins $S_1 = 1/2$ and $S_2 = 1/2$ with each of them coupled exclusively to only one nuclear spin ($I_1 = 1$ and $I_2 = 1$, respectively). For simplicity, we assume the same hyperfine coupling A_{iso} . If the exchange coupling is much smaller than the isotropic hyperfine coupling, each of the individual lines of the hyperfine triplet further splits into three lines. If the splitting is very small, it may be noticeable only as a line broadening. For $|J| \gg A_{iso}$, the electron spins are uniformly distributed over the two exchange-coupled moieties. Hence, each of them has the same hyperfine coupling to both nuclei. This coupling is half the original hyperfine coupling, since, on average, the electron spin has only half the spin density in the orbitals of a given nucleus as compared to the case without exchange coupling. For intermediate exchange couplings, complex splitting patterns arise that are characteristic for the ratio between the exchange and hyperfine coupling.



Figure 5.1: Influence of the exchange coupling J on EPR spectra with hyperfine coupling in liquid solution (simulation). Spectra are shown for two electron spins $S_1 = 1/2$ and $S_2 = 1/2$ with the same isotropic g value and the same isotropic hyperfine coupling to a nuclear spin $I_1 = 1$ or $I_2 = 1$, respectively. In the absence of exchange coupling, a triplet with amplitude ratio 1:1:1 is observed. For small exchange couplings, each line splits into a triplet. At intermediate exchange couplings, complicated patterns with many lines result. For very strong exchange coupling, each electron spin couples to both nitrogen nuclei with half the isotropic hyperfine coupling. A quintuplet with amplitude ratio 1:2:3:2:1 is observed.

5.2 Dipole-dipole interaction

5.2.1 Physical picture

The magnetic dipole-dipole interaction between two localized electron spins with magnetic moments μ_1 and μ_2 takes the same form as the classical interaction between two magnetic point dipoles. The interaction energy

$$E = -\frac{\mu_0}{4\pi} \cdot \mu_1 \mu_2 \cdot \frac{1}{r^3} \cdot \left(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi\right) \,. \tag{5.4}$$

generally depends on the two angles θ_1 and θ_2 that the point dipoles include with the vector between them and on the dihedral angle ϕ (Figure 5.2). The dipole-dipole interaction scales with the inverse cube of the distance between the two point dipoles.

In general, the two electron spins are spatially distributed in their respective SOMOs. The point-dipole approximation is still a good approximation if the distance r is much larger than the spatial distribution of each electron spin. Further simplification is possible if g anisotropy is much smaller than the isotropic g value. In that case, the two spins are aligned parallel to the magnetic field and thus also parallel to each other, so that $\theta_1 = \theta_2 = \theta$ and $\phi = 0$. Eq. (5.4) then simplifies to

$$E = -\frac{\mu_0}{4\pi} \cdot \mu_1 \mu_2 \cdot \frac{1}{r^3} \cdot \left(3\cos^2\theta - 1\right) , \qquad (5.5)$$

which is the form known from NMR spectroscopy.



Figure 5.2: Geometry of two magnetic point dipoles in general orientation. Angles θ_1 and θ_2 are included between the respective magnetic moment vectors $\vec{\mu}_1$ or $\vec{\mu}_2$ and the distance vector \vec{r} between the point dipoles. Angle ϕ is the dihedral angle.

5.2.2 Dipole-dipole Hamiltonian

We first consider the case of weak exchange coupling, where we can describe the situation in the more familiar uncoupled representation.

For two electron spins that are not necessarily aligned parallel to the external magnetic field, the dipole-dipole coupling term of the spin Hamiltonian assumes the form

$$\widehat{H}_{dd} = \widehat{S}_1^{\mathrm{T}} \underline{D} \widehat{S}_2 = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \mu_{\mathrm{B}}^2 \left[\widehat{S}_1 \widehat{S}_2 - \frac{3}{r^2} \left(\widehat{S}_1 \vec{r} \right) \left(\widehat{S}_2 \vec{r} \right) \right] \,. \tag{5.6}$$

If the electrons are distributed in space, the Hamiltonian has to be averaged (integrated) over the two spatial distributions, since electron motion proceeds on a much faster time scale than an EPR experiment.

If the two unpaired electrons are well localized on the length scale of their distances and their spins are aligned parallel to the external magnetic field, the dipole-dipole Hamiltonian takes the form

$$\hat{H}_{\rm dd} = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \mu_{\rm B}^2 \left[\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F} \right] \,. \tag{5.7}$$

with the terms of the dipolar alphabet

$$\hat{A} = \hat{S}_{z} \hat{I}_{z} \left(1 - 3\cos^{2}\theta \right) , \qquad (5.8)$$

$$\hat{B} = -\frac{1}{4} \left[\hat{S}^{+} \hat{I}^{-} + \hat{S}^{-} \hat{I}^{+} \right] \left(1 - 3\cos^{2}\theta \right) , \qquad (5.9)$$

$$\hat{C} = -\frac{3}{2} \left[\hat{S}^+ \hat{I}_z + \hat{S}_z \hat{I}^+ \right] \sin \theta \cos \theta e^{-i\phi} , \qquad (5.10)$$

$$\hat{D} = -\frac{3}{2} \left[\hat{S}^{-} \hat{I}_{z} + \hat{S}_{z} \hat{I}^{-} \right] \sin \theta \cos \theta e^{i\phi} , \qquad (5.11)$$

$$\hat{E} = -\frac{3}{4}\hat{S}^{+}\hat{I}^{+}\sin^{2}\theta e^{-2i\phi}, \qquad (5.12)$$

$$\hat{F} = -\frac{3}{4}\hat{S}^{-}\hat{I}^{-}\sin^{2}\theta e^{2i\phi}.$$
(5.13)



Figure 5.3: Explanation of dipole-dipole coupling between two spins in a local field picture. At the observer spin (blue) a local magnetic field is induced by the magnetic moment of the coupling partner spin (red). In the secular approximation, only the z component of this field is relevant, which is parallel or antiparallel to the external magnetic field \vec{B}_0 . The magnitude of this z component depends on angle θ between the external magnetic field and the spin-spin vector \vec{r} . For the α (left) and β (right) states of the partner spin, the local field at the observer spin has the same magnitude, but opposite direction. In the high-temperature approximation, both these states are equally populated. The shift of the resonance frequency of the observer spin by the presence of the coupling partner leads to a doublet splitting of the observer spin transition. The splitting is twice the product of the local field induced by the coupling partner multiplied with the gyromagnetic ratio of the observer spin.

Usually, EPR spectroscopy is performed at fields where the electron Zeeman interaction is much larger than the dipole-dipole coupling. The latter has a magnitude of about 50 MHz at a distance of 1 nm and of 50 kHz at a distance of 10 nm. In this situation, the terms \hat{C} , \hat{D} , \hat{E} , and \hat{F} are non-secular and can be dropped. The \hat{B} term is pseudo-secular and can be dropped only if the difference between the two electron Zeeman frequencies, $|\omega_{S,1} - \omega_{S,2}|$, is much larger than the dipole-dipole coupling¹. In electron electron double resonance (ELDOR) experiments, the difference of the Larmor frequencies of the two coupled spins can be selected via the difference of the two microwave frequencies used for exciting the observer spin and its coupling partner. It is thus possible to excite spin pairs for which only the secular part of the spin Hamiltonian needs to be considered,

$$\widehat{H}_{\rm dd} = \omega_{\perp} \left(1 - 3\cos^2\theta \right) \widehat{S}_z \widehat{I}_z , \qquad (5.14)$$

with

$$\omega_{\perp} = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \mu_{\rm B}^2 \,. \tag{5.15}$$

¹Hyperfine coupling of the electron spins can modify this condition.

In this situation, the dipole-dipole coupling has a simple dependence on the angle θ between the external magnetic field \vec{B}_0 and the spin-spin vector \vec{r} . It can be interpreted as the interaction of the spin with the z component of the local magnetic field that is induced by the magnetic dipole moment of the coupling partner (Figure 5.3). The dipole-dipole interaction vanishes under fast isotropic motion, since the average of the second Legendre polynomial $(1 - 3\cos^2 \theta)/2$ over all angles θ vanishes. Measurements of this interaction are therefore performed in the solid state.

The dipole-dipole tensor in the secular approximation has the eigenvalues $(\omega_{\perp}, \omega_{\perp}, -2\omega_{\perp})$. The dipole-dipole coupling d at any orientation θ is given by

$$d = \omega_{\perp} \left(1 - 3\cos^2 \theta \right) \,. \tag{5.16}$$



Figure 5.4: Energy level scheme (a) and schematic spectrum (b) for a dipole-dipole coupled spin pair at fixed orientation θ with respect to the magnetic field. The electron Zeeman frequencies of the two spins are ω_A and ω_B , respectively. Weak coupling $d \ll |\omega_A - \omega_B|$ is assumed. The dipolar splitting d is the same for both spins. Depending on homogeneous linewidth $1/T_2$, the splitting may or may not be resolved. If ω_A and ω_B are distributed, for instance by g anisotropy, resolution is lost even for $d > 1/T_2$.

5.2.3 Spectral manifestation of the dipole-dipole interaction

The energy level scheme and a schematic spectrum for a spin pair with fixed angle θ are shown in Figure 5.4a and b, respectively. The dipole-dipole coupling splits the transition of either coupled spin by d. If the sample is macroscopically isotropic, for instance a microcrystalline powder or a glassy frozen solution, all angles θ occur with probability $\sin \theta$. Each line of the dipolar doublet is then broadened to a powder pattern as illustrated in Figure 3.3. The powder pattern for the β state of the partner spin is a mirror image of the one for the α state, since the frequency shifts have opposite sign for the two states. The superposition of the two axial powder patterns is called Pake pattern (Figure 5.5). The center of the Pake pattern corresponds to the magic angle $\theta_{\text{magic}} = \arccos \sqrt{1/3} \approx 54.7^{\circ}$. The dipole-dipole coupling vanishes at this angle.

The Pake pattern is very rarely observed in an EPR spectrum, since usually other anisotropic interactions are larger than the dipole-dipole interaction between electron spins. If the weak-coupling condition $d \ll |\omega_A - \omega_B|$ is fulfilled for the vast majority of all orientations, the EPR lineshape is well approximated by a convolution of the Pake pattern with the lineshape in the absence of dipole-dipole interaction. If the latter lineshape is known, for instance from measuring analogous samples that carry only one of the two electron spins, the Pake pattern can be extracted by deconvolution and the distance between the two electron spins can be inferred from the splitting ω_{\perp} by inverting Eq. (5.15).



Figure 5.5: Pake pattern observed for a dipole-dipole coupled spin pair. (a) The splitting of the dipolar doublet varies with angle θ between the spin-spin vector and the static magnetic field. Orientations have a probability $\sin \theta$. (b) The sum of all doublets for a uniform distribution of directions of the spin-spin vector is the Pake pattern. The "horns" are split by ω_{\perp} and the "shoulders" are split by $\omega_{\parallel} = 2\omega_{\perp}$. The center of the pattern corresponds to the magic angle.

5.3 Zero-field interaction

5.3.1 Physical picture

If two unpaired electrons are strongly exchange coupled, then they are best described in the coupled representation. The singlet state with S = 0 is diamagnetic and thus not observable by EPR. In the high-field approximation, the three sublevels of the triplet state correspond to magnetic quantum numbers $m_S = -1$, 0, and +1 and are labelled T_- , T_0 , and T_+ . Splitting between these levels is dominated by the electron Zeeman interaction. The transitions $m_S = -1 \leftrightarrow 0$ and $m_S = 0 \leftrightarrow +1$ are allowed electron spin transitions, whereas the transition $m_S = -1 \leftrightarrow +1$ is a forbidden double-quantum transition.

At zero magnetic field, the electron Zeeman interaction vanishes and the magnetic quantum number m_S is not a good quantum number. Yet, the three triple sublevels are not degenerate. They exhibit zero-field splitting (ZFS). This is because the two unpaired electrons are also dipole-dipole coupled. To infer the ZFS, we need to transform the dipole-dipole part of the spin Hamiltonian from the uncoupled representation to the coupled representation, i.e., from the expression for the $S_1 = 1/2$, $S_2 = 1/2$ system given above to an expression for the triplet state with S = 1. By integration of Eq. (5.6) over the spatial distribution of the two electron spins in their respective SOMOs we obtain the a ZFS tensor D that can be cast in a form where it describes coupling of the group spin S = 1 with itself [Rie07]. Since for each configuration of the two electron spins, the dipole-dipole coupling is purely anisotropic, its integral over both SOMOs must be purely anisotropic, too. However, although for each configuration of the two electron spins, the dipole-dipole coupling has axial symmetry, the ZFS tensor does not necessarily have axial symmetry. This is because the unique axes differ between the different configurations. In general, the ZFS tensor has axial symmetry only if the system has a C_n symmetry axis with $n \geq 3$. In that case, it can be parametrized by a single value D. If the ZFS tensor is non-axial, a second parameter E is required (see Section 5.3.4). The ZFS tensor vanishes if the system has tetrahedral or cubic symmetry. The triplet sublevels at zero field are related to the principal axes directions of the zero-field interaction tensor and are therefore labeled T_x , T_y , and T_z . For transition metal and rare earth ions, spin-orbit coupling causes an additional contribution to

the ZFS tensor. Quantum-chemical prediction of the zero-field interaction is an active field of research. Quite reasonable predictions can be obtained for transition metal ions, whereas only order-of-magnitude estimates are usually possible for rare earth ions.

5.3.2 Extension to more than two electrons

The concept of the coupled representation can be extended to an arbitrary number n of strongly coupled electron spins. Cases with up to 5 strongly coupled unpaired electrons occur for transition metal ions (d shell) and cases with up to 7 strongly coupled unpaired electrons occur for rare earth ions (f shell). According to Hund's rule, in the absence of a ligand field the state with largest group spin S = n/2 is the ground state. This is because all d or f orbitals are degenerate for a bare ion and distributing the electrons as widely as possible among them minimizes Coulomb repulsion. The state with maximum group spin S is called the high-spin state. A ligand field removes degeneracy. If this leads to an energy splitting between the d (or f) levels that exceeds pairing energy, the lower orbitals are doubly occupied before higher levels are populated. Usually this leads to the low-spin state, which is the state with the smallest possible group spin S. For an even number of electrons, one unpaired electron is left and the low-spin state has S = 1/2. In a few cases, intermediate spin states are observed. Spin-crossover from a high-spin to a low -spin state may happen in some systems upon change in temperature.

5.3.3 Kramers and non-Kramers ions

We first consider a triplet species, S = 1, with zero-field states T_x , T_y , and T_z . Their energies are -2D/3, D/3 - E, and D/3 + E, so that the transition frequencies are 2|E|, |D - E|, and |D + E|. By convention, the parameters are chosen such that $|E| \le |D|/3$. Hence, none of the transition frequencies is lower than 2|E|. If the largest attainable microwave frequency is lower than 2|E|, none of the transitions can be excited at zero field. If |D| and |E| are sufficiently large, this may still apply at the largest magnetic fields B_0 that can be attained, since the levels shift by no more than $g\mu_B B_0/\hbar$. Although the system is paramagnetic, it may thus be 'EPR-silent' for practical purposes, i.e., in the whole range of accessible microwave frequencies and magnetic fields. The same phenomenon can occur for systems with an even number n > 2 of unpaired electrons that have integer spin S. Transition metal ions with this property are called non-Kramers ions. Most non-Kramers ions are hard to access by EPR spectroscopy, unless the ZFS tensor has axial symmetry (E = 0). Typical examples are Fe(II) (3d⁶, S = 2) and Ni(II) (3d⁸, S = 1).

The situation is different for an odd number n > 1 of unpaired electrons. A theorem by Kramers implies that all energy levels of such systems are at least doubly degenerate at zero field. These pairs of levels are associated with magnetic quantum numbers $\pm m_S (m_S = 1/2, 3/2, ..., S)$. At non-zero magnetic fields these pairs of levels split, to first order, by $2m_Sg\mu_BB_0/\hbar$. The 'central transition', $|-1/2\rangle \leftrightarrow |+1/2\rangle$ is allowed in the high-field approximation. The transitions between levels that are degenerate at zero field are observable even if D and E are very large. Such Kramers ions are thus accessible to EPR even in their high-spin states. Typical examples are Fe(III) (3d⁶, S = 5/2) and Co(II) (3d⁷, S = 3/2).

5.3.4 Zero-field interaction Hamiltonian

The zero-field interaction Hamiltonian is usually given as

$$\hat{\mathcal{H}}_{\rm ZFI} = \vec{\hat{S}}^{\rm T} \mathbf{D} \vec{\hat{S}} , \qquad (5.17)$$

where $^{\rm T}$ denotes the transpose of the spin vector operator. In the principal axes system of the zero-field splitting (ZFS) tensor, the Hamiltonian simplifies to

$$\hat{\mathcal{H}}_{ZFI} = D_x \hat{S}_x^2 + D_y \hat{S}_y^2 + D_z \hat{S}_z^2$$

= $D \left[S_z^2 - \frac{1}{3} S \left(S + 1 \right) \right] + E \left(S_x^2 - S_y^2 \right) .$ (5.18)

where $D = 3D_z/2$ and $E = (D_x - D_y)/2$. Note the squared spin operators. As mentioned above, the reduction to two parameters is possible, since **D** is a purely anisotropic, i.e., traceless tensor. The D, E notation presumes that D_z is the principal value with the largest absolute value (D can be negative). Together with the absence of an isotropic component, this means that D_y , which is always the intermediate value, is either closer to D_x than to D_z or exactly in the middle between these two values. Accordingly, $|E| \leq |D/3|$. At axial symmetry E = 0. At cubic symmetry, both D and E are zero. For group spin $S \geq 2$, the leading term of the ZFS is then a hexadecapolar contribution that scales with the fourth power of the spin operators $(\hat{S}_x^4, \hat{S}_y^4, \hat{S}_z^4)$.

In the high-field approximation, the ZFS contribution to the Hamiltonian is a $\omega_D S_z^2$ term. In other words, to first order in perturbation theory the contribution of the ZFS to the energy of a spin level with magnetic quantum number m_S scales with m_S^2 . For an allowed transition $m_S \leftrightarrow m_S + 1$, this contribution is $\omega_D (2m_S + 1)$. This contribution vanishes for the central transition $m_S = -1/2 \leftrightarrow 1/2$ of Kramers ions. More generally, because of the scaling of the level energies with m_S^2 , the first-order contribution of ZFS to transition frequencies vanishes for all $-m_S \leftrightarrow +m_S$ transitions.



Figure 5.6: Schematic CW EPR spectra for triplet states (S = 1) at high field. Simulations were performed at an X-band frequency of 9.6 GHz. (a) Axial symmetry (D = 1 GHz, E = 0). The spectrum is the derivative of a Pake pattern. (b) Orthorhombic symmetry (D = 1 GHz, E = 0.1 GHz).

5.3.5 Spectral manifestation of zero-field splitting

Spectra are most easily understood in the high-field approximation. Quite often, deviations from this approximation are significant for the ZFS (see Fig. 2.3), and such deviations are discussed later. The other limiting case, where the ZFS is much larger than the electron Zeeman interaction (Fe(III) and most rare earth ions), is discussed in Section 5.3.6.

For triplet states (S = 1) with axial symmetry of the ZFS tensor, the absorption spectrum is a Pake pattern (see Section 5.2.3). With continuous-wave EPR, the derivative of the absorption spectrum is detected, which has the appearance shown in Fig. 5.6(a). A deviation from axial symmetry leads to a splitting of the "horns" of the Pake pattern by 3E, whereas the "shoulders" of the pattern are not affected (Fig. 5.6(b)). Triplet states of organic molecules are often observed after optical excitation of a singlet state and intersystem crossing. Such intersystem crossing generally leads to different population of the zero-field triplet sublevels T_x , T_y , and T_z . In this situation the spin system is not at thermal equilibrium, but spin polarized. Such spin polarization affects relative intensity of the lineshape singularities in the spectra. However, the singularities are still observed at the same resonance fields, i.e., the parameters D and E can still be read off the spectra as indicated in Fig. 5.6.

Even if the populations of the triplet sublevels have relaxed to thermal equilibrium, the spectrum may still differ from the high-field approximation spectrum, as is illustrated in Fig. 5.7 for the excited naphtalene triplet (simulation performed with an example script of the software package EasySpin http://www.easyspin.org/). For D = 3 GHz at a field of about 160 mT (electron Zeeman frequency of about 4.8 GHz) the high-field approximation is violated and m_S is no longer a good quantum number. Hence, the formally forbidden double-quantum transition $m_S = -1 \leftrightarrow +1$ becomes partially allowed. To first order in perturbation theory, this transition is not broadened by the ZFS. Therefore it is very narrow compared to the allowed transitions and appears with higher amplitude. As it appears at about half of the magnetic field of single-quantum transitions, it is termed "half-field" signal.



Figure 5.7: CW EPR spectrum of the excited naphtalene triplet at thermal equilibrium (simulation at an X-band frequency of 9.6 GHz). $D \approx 3$ GHz, $E \approx 0.41$ GHz). The red arrow marks the half-field signal, which corresponds to the formally forbidden double-quantum transition $m_S = -1 \leftrightarrow +1$.

For Kramers ions, the spectra are usually dominated by the central $m_S = -1/2 \leftrightarrow 1/2$ transition, which is not ZFS-broadened to first order. To second order in perturbation theory, the ZFS-broadening of this line scales inversely with magnetic field. Hence, whereas systems with g anisotropy exhibit broadening proportional to the magnetic field B_0 , central transitions of Kramers ions exhibit narrowing with $1/B_0$. The latter systems can be detected with exceedingly high sensitivity at high fields if they do not feature significant g anisotropy. This applies to systems with half-filled shells (e.g. Mn(II), $3d^5$; Gd(III), $4f^7$). In the case of Mn(II) (Figure 5.8) the narrow central transition is split into six lines by hyperfine coupling to the nuclear spin of ⁵⁵Mn (nuclear spin I = 5/2, 100% natural abundance). Because of the $|2m_S + 1|$ scaling of anisotropic ZFS broadening of $m_S \leftrightarrow m_S + 1$ transitions, satellite transitions become the broader the larger $|m_S|$ is for the involved levels. In the high-temperature approximation, the integral intensity in the absorption spectrum is the same for all transitions. Hence, broader transitions make a smaller contribution to the amplitude in the absorption spectrum and in the first derivative that is acquired by CW EPR.



Figure 5.8: CW EPR spectrum of a Mn(II) complex (simulation at a W-band frequency of 94 GHz). D = 0.6 GHz, E = 0.05 GHz, $A(^{55}Mn) = 253$ MHz. The six intense narrow lines are the hyperfine multiplet of the central transition $m_S = -1/2 \leftrightarrow +1/2$.

5.3.6 Effective spin 1/2 in Kramers doublets

For some systems, such as Fe(III), ZFS is much larger than the electron Zeeman interaction at any experimentally attainable magnetic field. In this case, the zero-field interaction determines the quantization direction and the electron Zeeman interaction can be treated as a perturbation [Cas+60]. The treatment is simplest for axial symmetry (E = 0), where the quantization axis is the z axis of the ZFS tensor. The energies in the absence of the magnetic field are

$$\omega\left(m_S\right) = Dm_S^2 \,, \tag{5.19}$$

which for high-spin Fe(III) with S = 5/2 gives three degenerate Kramers doublets corresponding to $m_S = \pm 5/2, \pm 3/2, \text{ and } \pm 1/2$. If the magnetic field is applied along the z axis of the ZFS tensor, m_S is a good quantum number and there is simply an additional energy term $m_S g \mu_B B_0$ with g being the g value for the half-filled shell, which can be approximated as g = 2. Furthermore, in this situation only the $m_S = -1/2 \leftrightarrow 1/2$ transition is allowed. The Zeeman term leads to a splitting of the $m_S = \pm 1/2$ Kramers doublet that is proportional to B_0 and corresponds to g = 2. This Kramers doublet can thus be described as an effective spin S' = 1/2with $g_{\text{eff}} = 2$.

If the magnetic field is perpendicular to the ZFS tensor z axis, the $m_S = \pm 5/2$ and $\pm 3/2$ Kramers doublets are not split, since the S_x and S_y operator does not connect these levels. The S_x operator has an off-diagonal element connecting the $m_S = \pm 1/2$ levels that is $\sqrt{S(S+1) + 1/4}/2 = 3/2$. Since the levels are degenerate in the absence of the electron Zeeman interaction, they become quantized along the magnetic field and m_S is again a good quantum number of this Kramers doublet. The energies are $m_S 3g\mu_B B_0 + D/4$, so that the transition frequency is again proportional to B_0 , but now with an effective g value $g_{\text{eff}} = 6$. Intermediate orientations can be described by assuming an effective g tensor with axial symmetry and $g_{\perp} = 6$, $g_{||} = 2$. This situation is encountered to a good approximation for high-spin Fe(III) in hemoglobins ($g_{\perp} \approx 5.88$, $g_{||} = 2.01$).

For the non-axial case ($E \neq 0$), the magnetic field B_0 will split all three Kramers doublets. To first order in perturbation theory the splitting is proportional to B_0 , meaning that each Kramers doublet can be described by an effective spin S' = 1/2 with an effective g tensor. Another simple case is encountered for extreme rhombicity, E = D/3. By reordering principal axes (exchanging z with either x or y) one can the get rid of the S_z^2 term in Eq. (5.18), so that the ZFS Hamiltonian reduces to $E' = (S_x^2 - S_y^2)$ with E' = 2E. The level pair corresponding to the new z direction of the ZFS tensor has zero energy at zero magnetic field and it can be shown that it has an isotropic effective g value $g_{\text{eff}} = 30/7 \approx 4.286$. Indeed, signals near g = 4.3 are very often observed for high-spin Fe(III).



6.1 Physical picture

6.1.1 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 coupled to a single nuclear spin I = 1/2. This system was already introduced in Section 2.2.3, where we also assumed an isotropic g value and a hyperfine coupling that is much smaller than the electron Zeeman interaction. After truncating the Hamiltonian to the form given by Eq. (4.9) and going to the electron-spin rotating frame, we had found

$$\hat{H}_0 = \Omega_S \hat{S}_z + \omega_I \hat{I}_z + A \hat{S}_z \hat{I}_z + B \hat{S}_z \hat{I}_x .$$
(6.1)

For the nuclear spin, we are still in the laboratory frame. Such a Hamiltonian is a good approximation, for instance, for protons in organic radicals.

If the high-field approximation were also fulfilled for the nuclear spin, the pseudo-secular hyperfine coupling term $B\hat{S}_z\hat{I}_x$ would vanish. As can be seen from Eq. (4.10), this term also 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 affects transition frequencies. More important, it 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. Note that the *B* term in this Hamiltonian is not the *B* term of the dipolar alphabet. Rather, it relates to part of the *C* and *D* terms of the dipolar alphabet.

6.1.2 Local fields at the nuclear spin

That the forbidden transitions become partially allowed is most easily grasped in a semi-classical magnetization vector picture. To that end, we consider local fields at the nuclear spin for the two possible states α_S and 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

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



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 $\vec{\omega}_{\alpha}/\gamma_I$ and $\vec{\omega}_{\beta}/\gamma_I$ and are, thus, not parallel.

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 nuclear spin laboratory frame (blue arrow in Figure 6.1). The two 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

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

$$\omega_{\beta} = \sqrt{(\omega_{I} - A/2)^{2} + B^{2}/4}.$$
(6.2)

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

$$\omega_{\rm hfs} = |\omega_{\alpha} - \omega_{\beta}| \tag{6.3}$$

and the sum frequency is given by

$$\omega_{\rm sum} = \omega_{\alpha} + \omega_{\beta} \,. \tag{6.4}$$

For $|\omega_I| > 2|A|$, the nuclear frequency doublet is centered at $\omega_{sum}/2$ (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 if the nuclear Zeeman and hyperfine interaction are matched, $2|\omega_I| = |A|$. For $|\omega_I| < 2|A|$ the nuclear frequency doublet is split by ω_{sum} and centered at $\omega_{hfs}/2$ (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

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

$$\eta_{\beta} = \arctan\left(\frac{-B}{2\omega_{I} - A}\right).$$
(6.5)

We now consider a situation where the electron spin is in its α_S state. At thermal equilibrium, the nuclear magnetization from all radicals in this state is aligned with $\vec{\omega}_{\alpha}$. Microwave excitation causes transitions of the electron spin to the β_S state. In this state, the local field at the nuclear spin is directed along $\vec{\omega}_{\beta}$. Now, the nuclear magnetization vector from the radicals under consideration is tilted by angle 2η with respect to the new local field (Figure 6.1). Hence, the nuclear magnetization 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 thus observed only for intermediate hyperfine coupling. Maximum excitation of nuclear spins is expected when the two quantization axes are orthogonal with respect to each other, $2\eta = 90^\circ$.



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 $|\omega_I| > 2|A|$.

6.2 Product operator formalism with pseudo-secular interactions

6.2.1 Diagonalization of the Hamiltonian

In the NMR part of the lecture course, product operator formalism was introduced with the condition that all terms of the Hamiltonian must pairwise commute. This condition is not fulfilled

for the Hamiltonian given by Eq. (6.1), since $\hat{S}_z \hat{I}_x$ does not commute with either \hat{I}_z or $\hat{S}_z \hat{I}_z$. In order to be able to apply product operator formalism, we must first diagonalize \hat{H}_0 . A diagonal Hamiltonian features only terms with \hat{S}_z and \hat{I}_z operators. All such terms pairwise commute. Fortunately, it turns out that \hat{H}_0 can be diagonalized by the same type of rotations in spin space that are the basis of product operator formalism.

	$\langle \alpha \alpha $	$\langle \alpha \beta $	$\langle \beta \alpha $	$\langle \beta \beta $
αα⟩	Ω _s /2 +ω/2 +A/4	<i>B</i> /4		
αβ⟩	B/4	Ω _s /2 -ω/2 -A/4		
βα>			-Ω _s /2 +ω/2 -A/4	<i>-B</i> /4
ββ>			<i>-B</i> /4	-Ω _S /2 -ω/2 +A/4

Figure 6.3: Matrix representation of the S = 1/2, I = 1/2 spin Hamiltonian \hat{H}_0 given by Eq. (6.1). The Hamiltonian is block diagonal. The 2×2 blocks marked red can be diagonalized independently. The upper left red block corresponds to the α state of the electron spin and the bottom left red block to the β state of the electron spin

The 4 × 4 matrix representation of \hat{H}_0 (Figure 6.3) reveals that the Hamiltonian is blockdiagonal. The upper left 2 × 2 submatrix corresponds to the electron spin α manifold of states. In Figure 6.1 it corresponds to the right quadrant and the local field vector that is tilted by angle η_{α} with respect to the z axis. Likewise, the lower right 2 × 2 submatrix corresponds to the electron spin β manifold of states, to the left quadrant in Figure 6.1 and to the local field vector that is tilted by angle η_{β} . Hence, these submatrices can be diagonalized by rotations by angles $-\eta_{\alpha}$ and $-\eta_{\beta}$, respectively.

In order to see, how this works with product operators, we rewrite \hat{H}_0 with polarization operators \hat{S}^{α} and \hat{S}^{β} for the electron spin:

$$\hat{H}_{0} = \Omega_{S}/2\hat{S}^{\alpha} + \hat{S}^{\alpha}\omega_{I}\hat{I}_{z} + A/2\hat{S}^{\alpha}\hat{I}_{z} + B/2\hat{S}^{\alpha}\hat{I}_{x} - \Omega_{S}/2\hat{S}^{\beta} + \hat{S}^{\beta}\omega_{I}\hat{I}_{z} - A/2\hat{S}^{\beta}\hat{I}_{z} - B/2\hat{S}^{\beta}\hat{I}_{x} .$$
(6.6)

The upper line on the right-hand side of Eq. (6.6) corresponds to the upper left 2×2 submatrix in Figure 6.3. The required rotation is performed by applying the unitary transformation

$$\hat{U}^{\alpha} = \exp\left\{-i\left(\eta_{\alpha}\hat{S}^{\alpha}\hat{I}_{y}\right)\right\}$$
(6.7)

Note that $\hat{S}^{\alpha}\hat{I}_{y}$ commutes with \hat{S}^{α} and with all product operators in the second line on the right-hand side of Eq. (6.6). Analogously, the lower right 2 × 2 submatrix in Figure 6.3 is diagonalized by

$$\hat{U}^{\beta} = \exp\left\{-i\left(\eta_{\beta}\hat{S}^{\beta}\hat{I}_{y}\right)\right\}$$
(6.8)

Since $\hat{S}^{\alpha}\hat{I}_{y}$ and $\hat{S}^{\beta}\hat{I}_{y}$ also commute with each other, the two unitary transformations are independent and can be applied subsequently. This corresponds to applying the transformation into the eigenbasis of \hat{H}_{0} ,

$$\hat{U}_{\rm EB} = \exp\left\{-i\left(\eta_{\alpha}\hat{S}^{\alpha}\hat{I}_{y} - \eta_{\beta}\hat{S}^{\beta}\hat{I}_{y}\right)\right\}$$
(6.9)

which can be rewritten as

$$\hat{U}_{\rm EB} = \exp\left\{-i\left(\xi\hat{I}_y + \eta 2\,\hat{S}_z\hat{I}_y\right)\right\} \,. \tag{6.10}$$

where $\xi = (\eta_{\alpha} - \eta_{\beta})/2$ and $\eta = (\eta_{\alpha} + \eta_{\beta})/2$. The latter form is more convenient, because \hat{I}_y commutes with all operators that describe electron spin excitation and detection. Hence, for experiments without direct excitation or detection of nuclear spins, the $\xi \hat{I}_y$ term can be dropped.

6.2.2 Transformation of \hat{S}_x to the eigenbasis

Excitation and detection in EPR experiments are described by the \hat{S}_x and \hat{S}_y operators in the rotating frame. These operators act only on electron spin transitions and thus formalize the spectroscopic selection rules. In the frame of Eq. (6.1), any excitation and detection operators is a linear combination of \hat{S}_x and \hat{S}_y . However, spectroscopic transitions relate to the eigenbasis of \hat{H}_0 . In order to understand which of these transitions are excited and detected how strongly, we thus need to transform \hat{S}_x to the eigenbasis. The transformation of \hat{S}_y is analogous. We can do so by product operator formalism and can understand the result in the local field picture.

The two rotations in Eq. (6.10) about \hat{I}_y and $\hat{S}_z \hat{I}_y$ commute. As mentioned above, \hat{I}_y also commutes with \hat{S}_x . Hence, transformation of \hat{S}_x to the eigenbasis reduces to

$$\hat{S}_x \xrightarrow{\eta 2 S_z I_y} \cos \eta \ \hat{S}_x + \sin \eta \ 2 \hat{S}_y \hat{I}_y \ .$$
 (6.11)

The allowed transitions with $\Delta m_S = \pm 1$, $\Delta m_I = 0$ are driven by \hat{S}_x . Their transition moment is scaled by a factor $\cos \eta \leq 1$. Hence, it becomes smaller when $\eta \neq 0$. In order to interpret the second term, we rewrite it in terms of ladder operators $\hat{S}^+ = \hat{S}_x + i\hat{S}_y$ and $\hat{S}^- = \hat{S}_x - i\hat{S}_y$. We find

$$2\hat{S}_y\hat{I}_y = \frac{1}{2}\left(\hat{S}^+\hat{I}^- + \hat{S}^-\hat{I}^+ - \hat{S}^+\hat{I}^+ - \hat{S}^-\hat{I}^-\right).$$
(6.12)

In other words, this term drives the forbidden electron-nuclear zero- and double-quantum transitions (Fig. 6.2(a)) with a transition amplitude that is proportional to $\sin \eta$.

In recording an EPR spectrum, each transition must be both excited and detected. In other words, the amplitude is proportional to the square of the transition moment, which is the transition probability. Allowed transitions thus have an intensity proportional to $\cos^2 \eta$ and forbidden transitions a transition probability proportional to $\sin^2 \eta$ (Fig. 6.2(b)).

6.2.3 General product operator computations for the electron-nuclear spin Hamiltonian

In a product operator computation, terms of the Hamiltonian can be applied one after the other if and only if they pairwise commute. The Hamiltonian in the eigenbasis, \hat{H}_0^{EB} , fulfills this condition. We obtain it by applying \hat{U}_{EB} to \hat{H}_0 :

$$\hat{H}_0 \xrightarrow{\eta S_z I_y} \Omega_S \hat{S}_z + \omega_{\text{sum}} / 2 \, \hat{I}_z + \omega_{\text{hfi}} \, \hat{S}_z \hat{I}_z = \hat{H}_0^{\text{EB}} \,. \tag{6.13}$$

This provides a simple recipe for product operator computations in the presence of the pseudo-secular hyperfine coupling. Free evolution is computed in the eigenbasis, using \hat{H}_0^{EB} . For

application of non-selective pulses, the density operator needs to be transformed to the electron spin rotating frame/nuclear spin laboratory frame basis by applying $\hat{U}_{\text{EB}}^{\dagger}$. In product operator formalism this corresponds to a product operator transformation $\xrightarrow{-\eta \hat{S}_z \hat{I}_y}$. After application of non-selective pulses, the density operator needs to be backtransformed to the eigenbasis. Detection also needs to be performed in the electron spin rotating frame/nuclear spin laboratory frame basis.²

This concept can be extended to any non-diagonal Hamiltonian, as long as one can find a unitary transformation to the eigenbasis, which can be expressed by a single product operator term or a sum of pairwise commuting product operator terms. This is possible, for instance, for the Hamiltonian describing dipole-dipole interaction including the B term (strong-coupling situation) and for off-resonant excitation.

6.3 Generation and detection of nuclear coherence by electron spin excitation

6.3.1 Nuclear coherence generator $(\pi/2) - \tau - (\pi/2)$

We have seen that a single microwave pulse can excite coherence on forbidden electron-nuclear zero- and double-quantum transitions. This provides access to the nuclear frequencies ω_{α} and ω_{β} , which are differences of frequencies of allowed and forbidden electron spin transitions, as can be inferred from Fig. 6.2(a,b). Indeed, the decay of an electron spin Hahn echo $(\pi/2) - \tau - (\pi) - \tau - echo$ as a function of τ is modulated with frequencies ω_{α} and ω_{β} , as well as with ω_{hfi} and ω_{sum} . The modulation arises from forbidden transitions during the refocusing pulse, which redistribute coherence among the four transitions. This two-pulse ESEEM experiment is not usually applied for measuring hyperfine couplings. First, peaks at the combination frequencies ω_{hfi} and ω_{sum} complicate the spectra and, second, the two-pulse ESEEM spectrum has poor resolution compared to an NMR spectrum, since linewidth is determined by electron spin transverse relaxation.

Better resolution and simpler spectra are obtained by indirect observation of the evolution of nuclear coherence. Such coherence can be generated by applying a pulse subsequence $(\pi/2) - \tau - (\pi/2)$ to the electron spins. The first $\pi/2$ generates electron spin coherence on allowed transitions with an amplitude proportional to $\cos \eta$ and coherence on forbidden transitions with amplitude proportional to $\sin \eta$. During delay τ , these coherences acquire different phase. The second $\pi/2$ pulse converts half of the existing electron spin coherence to polarization, i.e., to magnetization along the z axis. In other words, it "switches off" half of the electron spin coherence. However, for the coherence on forbidden transitions, with probability $\cos \eta$ the nuclear spin is *not* flipped. For this fraction of the spins, coherent superposition of the nuclear spin states survives. For electron spin coherence is generated with probability $\sin \eta$ the "switching off" of the electron coherence leads to a "switching on" of nuclear coherence. Hence, in both these pathways nuclear coherence is generated with probability proportional to $\sin \eta \cos \eta = \sin(2\eta)/2$. The delay τ is required, since at $\tau = 0$ the different nuclear coherence components have opposite phase and cancel.

The nuclear coherence generated by the block $(\pi/2) - \tau - (\pi/2)$ can be computed by product

²Transition-selective pulses are best described in the eigenbasis, using operators such as $\hat{S}_x \hat{I}^{\alpha}$, $\hat{S}_x \hat{I}^{\beta}$, $\hat{S}^+ \hat{I}^-$, and $\hat{S}^+ \hat{I}^+$

operator formalism as outlined in Section 6.2.3. We find

$$\left\langle \hat{S}^{\alpha} \hat{I}_{x} \right\rangle = -\sin\left(\Omega_{S}\tau\right) \sin\left(2\eta\right) \sin\left(\frac{\omega_{\beta}}{2}\tau\right) \cos\left(\omega_{\alpha}\tau\right) \left\langle \hat{S}^{\alpha} \hat{I}_{y} \right\rangle = -\sin\left(\Omega_{S}\tau\right) \sin\left(2\eta\right) \sin\left(\frac{\omega_{\beta}}{2}\tau\right) \sin\left(\omega_{\alpha}\tau\right) \left\langle \hat{S}^{\beta} \hat{I}_{x} \right\rangle = -\sin\left(\Omega_{S}\tau\right) \sin\left(2\eta\right) \sin\left(\frac{\omega_{\alpha}}{2}\tau\right) \cos\left(\omega_{\beta}\tau\right) \left\langle \hat{S}^{\beta} \hat{I}_{y} \right\rangle = -\sin\left(\Omega_{S}\tau\right) \sin\left(2\eta\right) \sin\left(\frac{\omega_{\alpha}}{2}\tau\right) \sin\left(\omega_{\beta}\tau\right) .$$

$$(6.14)$$

This expression can be interpreted in the following way. The phase of the nuclear coherence is the same as if it had started to evolve as \hat{I}_x at time $\tau = 0$. This is seen from the last factor on the right-hand side of each line, which describes phase acquired during delay τ . The amplitude of nuclear coherence is modulated as a function of the electron spin resonance offset Ω_S (first sine factor on each line). It is zero exactly on resonance. The integral over an inhomogeneously broadened, symmetric EPR line is also zero, since $\int_{-\infty}^{\infty} \sin(\Omega_S \tau) d\Omega_S = 0$. At this point it would appear that we have not gained anything, as net nuclear coherence is zero. However, upon detection after applying a third $\pi/2$ pulse, another sine factor appears, and the integral of $\sin^2(\Omega_S \tau)$ does not vanish.

Furthermore, the amplitude of the nuclear coherence scales with $\sin 2\eta$. This can be understood by realizing that one allowed and one forbidden transfer are required to excite such coherence and that $\sin(\eta)\cos(\eta) = \sin(2\eta)/2$ (second factor). Finally, the third factor on the right-hand side of lines 1 and 2 tells that the amplitude of the coherence with frequency ω_{α} is modulated as a function of τ with frequency $\omega_{\beta}/2$. Likewise, the amplitude of the coherence with frequency ω_{β} is modulated as a function of τ with frequency $\omega_{\alpha}/2$ (lines 3 and 4). Hence, at certain values of τ , where this sine is zero, no coherence is created at the transition with frequency ω_{α} . At other times, where this sine is 1, maximum coherence is generated. This blind-spot behavior requires that the experiment is repeated for different values of τ in order to detect all nuclear frequencies.

6.4 ESEEM and HYSCORE

6.4.1 Advantages of electron-spin based detection of nuclear frequency spectra

Nuclear frequency spectra in the liquid (Section 4.3.2) and solid states (4.3.4) exhibit much better hyperfine resolution than EPR spectra, because the former spectra feature fewer and narrower lines. In fact, small hyperfine couplings to ligand nuclei in metal complexes are not usually resolved in EPR spectra and only the largest hyperfine couplings may be resolved in solid-state EPR spectra. The nuclear frequency spectra cannot be measured by a dedicated NMR spectrometer because they extend over several Megahertz to several tens of Megahertz, whereas NMR spectrometers are designed for excitation and detection bandwidths of a few tens of kilohertz. Furthermore, electron spin transitions have 660 times more polarization than proton transitions. The polarization advantage of EPR is even higher for nuclei other than protons. The larger magnetic moment of electron spins also leads to higher detection sensitivity. Therefore, it is advantageous to transfer polarization from electron spins to nuclear spins and to back transfer the response of the nuclear spins to the electron spins for detection. This can be done by electron nuclear double resonance (ENDOR) experiments, which are close in spirit to heteronuclear double resonance experiments in NMR. It can also be done by ESEEM experiments. We will first discuss one-dimensional three-pulse ESEEM and then two-dimensional HYSCORE.

6.4.2 Three-pulse ESEEM

In three-pulse ESEEM, the amplitude of a stimulated echo is observed as a function of the variable interpulse delay t at fixed interpulse delay τ (Fig. 6.4). The pulse sequence $(\pi/2) - \tau - (\pi/2) - t - (\pi/2) - \tau - echo$ consist of the nuclear coherence generator explained in Section 6.3.1, free evolution of nuclear coherence during time t, back transfer of nuclear coherence to electron coherence on allowed and forbidden transitions by the last $\pi/2$ pulse, and detection of this electron coherence at the time of echo formation after another delay of length τ .

After the nuclear coherence generator, most of the magnetization has been converted to a polarization grating that creates an unmodulated stimulated echo, while only a small fraction has been transferred to nuclear coherence. This nuclear coherence acquires phase during time t with the nuclear frequencies ω_{α} and ω_{β} . Depending on this phase, a fraction of nuclear coherence is back transferred to electron spin coherence by the last $\pi/2$ pulse. Hence, the part of the stimulated echo that arises from back transferred nuclear coherence is modulated as a function of t with frequencies ω_{α} and ω_{β} .

An expression for this echo envelope modulation can be derived by product operator formalism, using the concepts explained in Section 6.2. Disregarding relaxation, the somewhat lengthy derivation provides

$$V_{3p}(\tau,t) = \frac{1}{2} \left[V_{\alpha}(\tau,t) + V_{\beta}(\tau,t) \right] , \qquad (6.15)$$

where the terms $V_{\alpha}(\tau, t)$ and $V_{\beta}(\tau, t)$ correspond to contributions with the electron spin in its α or β state, respectively, during interpulse delay t. These terms are given by

$$V_{\alpha}(\tau, t) = 1 - \frac{k}{2} \{1 - \cos[\omega_{\beta}\tau]\} \{1 - \cos[\omega_{\alpha}(t+\tau)]\}$$

$$V_{\beta}(\tau, t) = 1 - \frac{k}{2} \{1 - \cos[\omega_{\alpha}\tau]\} \{1 - \cos[\omega_{\beta}(t+\tau)]\}.$$
(6.16)

The factors $\cos [\omega_{\beta}\tau]$ for the V_{α} term and $\cos [\omega_{\alpha}\tau]$ for the V_{β} term describe the blind spot behavior of three-pulse ESEEM. The *modulation depth* k is given by

$$k = \sin^2 2\eta = \left(\frac{B\omega_I}{\omega_\alpha \omega_\beta}\right)^2 \,. \tag{6.17}$$

We see that a second factor $\sin 2\eta$ has arisen from detection by the subsequence $\pi/2 - \tau - echo$, which is symmetric to the nuclear coherence generator $(\pi/2) - \tau - (\pi/2)$.

For small hyperfine couplings, $A, B \ll \omega_I$, we have $\omega_{\alpha} \approx \omega_{\beta} \approx \omega_I$, so that Eq. (6.17) reduces to

$$k = \frac{B^2}{\omega_I^2} , \qquad (6.18)$$

i.e., the modulation depth is inversely proportional to the square of the magnetic field. Using Eqs. (4.10) and (4.11) we find for protons that are not too close to a well localized unpaired electron

$$k = \frac{9}{4} \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{g\mu_B}{B_0}\right)^2 \frac{\sin^2(2\theta_{\rm HFI})}{r^6} , \qquad (6.19)$$

where θ_{HFI} is the angle between the electron-proton axis and the static magnetic field B_0 .



Figure 6.4: Pulse sequences for three-pulse ESEEM (a) and HYSCORE (b). In three-pulse ESEEM, time t is varied and time τ is fixed. In HYSCORE, times t_1 and t_2 are varied independently in order to obtain a two-dimensional data set.



Figure 6.5: Schematic HYSCORE spectrum for the phenyl radical (compare Fig. 4.6). Note that hyperfine couplings are given in frequency units, not angular frequency units. Signals from weakly coupled nuclei appear in the right (+, +) quadrant. To first order, these peaks are situated on a line parallel to the anti-diagonal that intersects the ν_2 axis at $2\nu_I$. The doublets are centered at ν_I and split by the respective hyperfine couplings. Signals from strongly coupled nuclei appear in the (-,+) quadrant. To first order, these peaks are situated on two lines parallel to the anti-diagonal that intersect the ν_2 axis at $-2\nu_I$ and $2\nu_I$. The doublets are centered at half the hyperfine coupling and split by $2\nu_I$.

6.4.3 HYSCORE

The HYSCORE experiment is derived from the three-pulse ESEEM experiment by inserting a microwave π pulse midway through the evolution of nuclear coherence. This splits the interpulse delay t into two interpulse delays t_1 and t_2 (Fig. 6.4(b)). These two delays are varied independently to provide a two-dimensional data set $V(t_1, t_2)$, which depends parametrically on the fixed interpulse delay τ . The inserted π pulse inverts the electron spin state. Hence, coherence that has evolved with frequency ω_{α} during interpulse delay t_1 evolves with frequency ω_{β} during interpulse delay t_2 and *vice versa*. In most cases, the weak modulation limit applies, where the HYSCORE experiment correlates only frequencies ω_{α} and ω_{β} of the same nuclear spin. The full modulation expression for the HYSCORE experiment contains a constant contribution as well as contributions that vary only with respect to either t_1 or t_2 . These contributions can be removed by background correction with low-order polynomial functions along both dimensions. The remaining modulation corresponds to only cross peaks and can be expressed as

$$V_{4p}(t_1, t_2; \tau) = \frac{k}{2} \sin\left(\frac{\omega_{\alpha}\tau}{2}\right) \sin\left(\frac{\omega_{\beta}\tau}{2}\right) \left[V^{(\alpha\beta)}(t_1, t_2; \tau) + V^{(\beta\alpha)}(t_1, t_2; \tau)\right]$$
(6.20)

with

$$V^{(\alpha\beta)}(t_1, t_2; \tau) = \cos^2 \eta \cos \left(\omega_\alpha t_1 + \omega_\beta t_2 + \omega_{\text{sum}} \frac{\tau}{2}\right) - \sin^2 \eta \cos \left(\omega_\alpha t_1 - \omega_\beta t_2 + \omega_{\text{hff}} \frac{\tau}{2}\right)$$
$$V^{(\beta\alpha)}(t_1, t_2; \tau) = \cos^2 \eta \cos \left(\omega_\beta t_1 + \omega_\alpha t_2 + \omega_{\text{sum}} \frac{\tau}{2}\right) - \sin^2 \eta \cos \left(\omega_\beta t_1 - \omega_\alpha t_2 + \omega_{\text{hff}} \frac{\tau}{2}\right)$$
(6.21)

In this representation, $\eta < 45^{\circ}$ corresponds to the weak coupling case ($|A| < 2|\omega_I|$) and $\eta > 45^{\circ}$ to the strong coupling case $(|A| > 2|\omega_I|)$, as can be inferred from Fig. 6.1. Hence, $\cos^2 \eta > \sin^2 \eta$ in the weak coupling case and $\sin^2 \eta > \cos^2 \eta$ in the strong coupling case. Therefore, in the weak coupling case, the cross peaks that correlate nuclear frequencies with the same sign ($\cos^2 \eta$ terms) are much stronger than those that correlate frequencies with opposite sign (sin² η terms). In the strong coupling case, it is the other way around. The two cases can be easily distinguished in HYSCORE spectra, as the cross peaks appear in different quadrants (Fig. (6.5). Furthermore, disregarding a small shift that arises from the pseudo-secular part B of the hyperfine coupling (see below), the cross peaks of a given isotope with spin I = 1/2 are situated on parallels to the anti-diagonal that corresponds to the nuclear Zeeman frequency ν_I . Since ν_I can be computed from the nuclear q value (or gyromagnetic ratio γ) and the static magnetic field B_0 , peak assignment for I = 1/2 nuclei is straightforward. For nuclei with I > 1/2 the peaks are further split by the nuclear quadrupole interaction. Unless this splitting is much smaller than both the hyperfine interaction and the nuclear Zeeman interaction (²H, ⁶Li), numerical simulations are required to assign the peaks and extract the hyperfine and nuclear quadrupole coupling.

The small pseudo-secular shift of the correlation peaks with respect to the anti-diagonal contains information on the anisotropy T of the hyperfine interaction (Fig. 6.6). In the solid state, the cross peaks from different orientations $\theta_{\rm HFI}$ form curved ridges. For a hyperfine tensor with axial symmetry, as it is encountered for protons not too close to a well-localized unpaired electron, the maximum shift in the diagonal direction corresponds to $\theta_{\rm HFI} = 45^{\circ}$ and is given by $9T^2/32|\omega_I|$. Since ω_I is known, T, and thus the electron-proton distance r can be computed from this maximum shift. If $A_{\rm iso} \ll \omega_I$, which is usually the case, the orientation with maximum shift is also the orientation with maximum modulation depth. This is because $\sin^2(2\eta)$ attains its maximum near the maximum of B, which is in turn attained at $\theta_{\rm HFI} = 45^{\circ}$.

The curved ridges end at their intersection with the parallel to the anti-diagonal. These points correspond to the principal values of the hyperfine tensor. Modulation depth is zero at these points. However, it is usually possible to fit the theoretical ridge to the experimentally observed ridge, as the curvature near $\theta_{\rm HFI} = 45^{\circ}$ together with the position of the $\theta_{\rm HFI} = 45^{\circ}$ point fully determines the problem.

Analysis of HYSCORE spectra requires some precaution due to the blind-spot behavior (factor $\sin\left(\frac{\omega_{\alpha}\tau}{2}\right)\sin\left(\frac{\omega_{\beta}\tau}{2}\right)$ in Eq. (6.20)) and due to orientation selection by the limited bandwidth of the microwave pulses that is much smaller than spectral width for transition metal complexes. It



Figure 6.6: Schematic HYSCORE spectrum for a proton with an axial hyperfine tensor with anisotropy T and isotropic component A_{iso} . The correlation peaks from different orientations form curved ridges (red). Curvature is the stronger the larger the anisotropy is and the ratio of squared anisotropy to the nuclear Zeeman frequency determines the maximum shift with respect to the $2\omega_I$ anti-diagonal.

is therefore prudent to measure HYSCORE spectra at several values of τ and at several observer positions within the EPR spectrum.

Separation of the dipole-dipole interaction The SEDOR experiment DEER as a constant-time SEDOR experiment Four-pulse DEER

7 — Spin-Echo Double Resonance

exp

MC/UE

distance [nm]

7.1 Separation of the dipole-dipole interaction

Precise measurement of the dipole-dipole interaction is of interest for determination of spatial structure, since this interaction scales with the inverse cube of the distance between two spins. The upper bound of the accessible length scale depends on the magnetic moments of the two coupled spins and on transverse relaxation time of the more slowly relaxing spin. For two nuclear spins, it is about 5 Å, for an electron spin and a nuclear spin, about 10 Å, and for two electron spins about 100 Å. A lower bound arises mainly for two electron spins, where exchange coupling, which cannot always be disentangled from dipole-dipole coupling, contributes significantly below 15 Å.

In most cases, dipole-dipole interaction is not the dominating interaction in an NMR or EPR spectrum. In simple cases, it can be separated by lineshape analysis. However, this approach introduces some uncertainty and limits the accessible distance range. Better accuracy of the measurement and access to smaller couplings can be achieved by experimental separation of the dipole-dipole interaction. The simplest way of doing this is the spin-echo double resonance (SEDOR) experiment, originally introduced to NMR by Kaplan and Hahn in 1958. The experiment was reinvented in a slightly different form in EPR by Salikhov, Milov, and Shirov in 1981. As an EPR experiment, it is known by the names of double electron-electron resonance (DEER) or pulsed electron electron double resonance (PELDOR).

The basic idea can be grasped from Fig. 7.1. The coupling partner (red) exerts some local field (green) on an observer spin (blue). For the orientation of spin-spin vector \vec{r} with respect to the external magnetic field \vec{B}_0 assumed in the Figure, this field counteracts the external field if the coupling partner is aligned parallel to \vec{B}_0 (situation 1) and adds to the external field if it is aligned anti-parallel (situation 2). If the spin of the coupling partner is inverted by a π pulse, the local field B_{local} changes sign. This shifts the resonance frequency of the observer spin by the dipole-dipole coupling d. When going from situation 1 to situation 2, the resonance frequency shifts by +d and when going from situation 2 to 1, it shifts by -d. In the high-field approximation, both transitions are equally likely. If this frequency change is measured in a time-domain experiment as a function of t, the two transitions generate signals proportional to $\cos(dt) + i \cdot \sin(dt)$ and $\cos(-dt) + i \cdot \sin(-dt) = \cos(dt) - i \cdot \sin(-dt)$. The total signal is thus expected to be proportional to $\cos(dt)$.



Figure 7.1: Spin inversion of the coupling partner (red) of an observer spin (blue) inverts the local magnetic field (green) that the coupling partner exerts on the observer spin. This local field change ΔB_{local} causes a change in the resonance frequency by dipole-dipole coupling d.

7.2 The SEDOR experiment

The SEDOR experiment is based on a Hahn echo experiment on the observer spins at frequency ν_1 (blue subsequence in Figure 7.2a). This subsequence refocuses the resonance offset term $\Omega_{S,1}\hat{S}_{z,1}$ of the observer spin as well as the dipole-dipole coupling $d\hat{S}_{z,1}\hat{S}_{z,2}$. The π pulse with frequency ν_2 inverts the spin state of the coupling partner (red) at the same time as the observer spin is inverted.



Figure 7.2: Pulse sequences of the SEDOR (a) and three-pulse DEER (b) experiments. (a) Delay t_1 is varied and modulation of the amplitude of the echo signal is observed. Two-dimensional Fourier transformation with respect to t_1 and t_2 correlates the dipolar spectrum (local field) to the NMR spectrum. (b) Delay t is varied at constant delay τ and the echo integral is observed.

We describe this experiment by product operator formalism for two electron spins $S_1 = 1/2$ and $S_2 = 1/2$. Magnetization on spin S_2 does not contribute to the signal. Hence, we start with the thermal equilibrium density operator of only spin S_1 , which is $\sigma_0 = -\hat{S}_{z,1}$. The $\pi/2$ pulse with phase x generates observer spin coherence $\sigma_1 = \hat{S}_{y,1}$. We find

$$\hat{S}_{y,1} \xrightarrow{dt_1 \hat{S}_{z,1} \hat{S}_{z,2}} \cos\left(\frac{dt_1}{2}\right) \hat{S}_{y,1} - \sin\left(\frac{dt_1}{2}\right) 2\hat{S}_{x,1} \hat{S}_{z,2}
\xrightarrow{\pi \hat{S}_{x,1}} - \cos\left(\frac{dt_1}{2}\right) \hat{S}_{y,1} - \sin\left(\frac{dt_1}{2}\right) 2\hat{S}_{x,1} \hat{S}_{z,2}
\xrightarrow{\pi \hat{S}_{x,2}} - \cos\left(\frac{dt_1}{2}\right) \hat{S}_{y,1} + \sin\left(\frac{dt_1}{2}\right) 2\hat{S}_{x,1} \hat{S}_{z,2}
\xrightarrow{dt_1 \hat{S}_{z,1} \hat{S}_{z,2}} \left[\sin^2\left(\frac{dt_1}{2}\right) - \cos^2\left(\frac{dt_1}{2}\right)\right] \hat{S}_{y,1} + 2\cos\left(\frac{dt_1}{2}\right) \sin\left(\frac{dt_1}{2}\right) 2\hat{S}_{x,1} \hat{S}_{z,2}
.$$
(7.1)

Using trigonometric laws, we can simplify the final expression to

$$\sigma_{\rm echo} = -\cos\left(dt_1\right)\hat{S}_{y,1} + \sin\left(dt_1\right)\,2\hat{S}_{x,1}\hat{S}_{z,2}\,. \tag{7.2}$$

The echo amplitude is proportional to $\langle \hat{S}_y \rangle$ and, hence, to $cos(dt_1)$. Fourier transformation of the echo amplitude with respect to t_1 thus provides a dipolar doublet centered at zero frequency with splitting 2d. For a powder or glass sample, we obtain a Pake pattern.

7.3 DEER as a constant-time SEDOR experiment

The SEDOR experiment works quite well in solid-state NMR, where the transverse relaxation rate is usually much smaller than the dominant dipolar couplings. Unpaired electrons are rare, so that distances between them can be long and dipolar couplings correspondingly small, while electron spin relaxation rates are comparatively high, as they roughly scale with the square of the magnetic moment. As a consequence, dipolar spectra obtained with the SEDOR sequence are strongly relaxation-broadened. Furthermore, implementation of SEDOR in EPR is expensive, since two high-power microwave amplifiers are needed for output of two overlapping pulses.

Therefore, the same separation of interactions is achieved in a slightly different way in the three-pulse DEER experiments, avoiding, both, broadening by relaxation and overlapping pulses. On the observer spin, a constant-time Hahn echo experiment with fixed delay τ is performed (blue subsequence in Figure 7.2b). As in SEDOR, this subsequence refocuses the resonance offset term $\Omega_{S,1}\hat{S}_{z,1}$ of the observer spin as well as the dipole-dipole coupling $d\hat{S}_{z,1}\hat{S}_{z,2}$. The π pulse with frequency ν_2 is now applied at a variable time after the observer $\pi/2$ pulse. Computation by product operator formalism, starting again after the $\pi/2$ pulse, provides

$$\hat{S}_{y,1} \xrightarrow{dt\hat{S}_{z,1}\hat{S}_{z,2}} \cos\left(\frac{dt}{2}\right)\hat{S}_{y,1} - \sin\left(\frac{dt}{2}\right)2\hat{S}_{x,1}\hat{S}_{z,2}
\xrightarrow{\pi\hat{S}_{x,2}} \cos\left(\frac{dt}{2}\right)\hat{S}_{y,1} + \sin\left(\frac{dt}{2}\right)2\hat{S}_{x,1}\hat{S}_{z,2}
\stackrel{d(\tau-t)\hat{S}_{z,1}\hat{S}_{z,2}}{\longrightarrow} \cos\left[d\left(t-\frac{\tau}{2}\right)\right]\hat{S}_{y,1} + \sin\left[d\left(t-\frac{\tau}{2}\right)\right]2\hat{S}_{x,1}\hat{S}_{z,2}
\xrightarrow{\pi\hat{S}_{x,1}} - \cos\left[d\left(t-\frac{\tau}{2}\right)\right]\hat{S}_{y,1} + \sin\left[d\left(t-\frac{\tau}{2}\right)\right]2\hat{S}_{x,1}\hat{S}_{z,2}
\stackrel{d\tau\hat{S}_{z,1}\hat{S}_{z,2}}{\longrightarrow} - \cos\left(dt\right)\hat{S}_{y,1} + \sin\left(dt\right)2\hat{S}_{x,1}\hat{S}_{z,2}.$$
(7.3)

Neglecting relaxation, the result is the same as for the SEDOR sequence. In this three-pulse DEER experiment, the same signal loss by transverse electron spin relaxation applies at all times

t. For exponential decay with time constant T_2 , the loss factor is $e^{-2\tau/T_2}$. In contrast, signal reduction in SEDOR, e^{-2t_1/T_2} , is on average not as strong if data are measured up to the same maximum t_1 or t, since $t < \tau$. This is a general property of constant-time experiments, which achieve better resolution at the expense of a loss in sensitivity.

7.4 Four-pulse DEER

The three-pulse DEER experiment does not solve the problem of pulse overlap completely. Time t = 0 corresponds to an overlap of the observer spin $\pi/2$ pulse with the π pulse that acts on the coupling partner. Even if two microwave amplifiers are used, data on the order of the pulse length is somewhat compromised. This introduces a dead time t_d , with data being available only at $t > t_d$. This dead time is problematic in retrieving distance distributions from the data, in particular near the lower bound of the accessible distance range. Therefore, DEER is almost invariably measured with the four-pulse sequence shown in Figure 7.3, which eliminates deadtime.

At the time of formation of the first Hahn echo (label \oplus in the ν_2 sub-sequence), the situation immediately after the observer spin $\pi/2$ pulse (label \oplus in the ν_1 sub-sequence) is restored, except for some signal loss by relaxation during time $2\tau_1$ and for a sign inversion of the magnetization if the first observer spin π pulse has the same phase as the $\pi/2$ pulse. The density operator is given by $\sigma_1 = -\hat{S}_{y,1}$. It follows that we do not need to repeat the product operator computation. Except for the inconsequential sign change, Eq. (7.3) also applies for the four-pulse DEER experiment.



Figure 7.3: Four-pulse DEER sequence, coherence transfers, and evolution of the observer spin magnetization. Pulses shown in blue are applied to the observer spin, the pump pulse shown in red is applied to its coupling partner. The echo at time $2\tau_1$ (dashed blue line) is not observed. Interpulse delays τ_1 and τ_2 are fixed, time t is varied, and the echo amplitude is observed as a function of t.

It is instructive to consider the experiment in a magnetization vector picture for an ensemble of observer spin packets with different resonance offsets $\Omega_{S,1}$ (bottom row of Figure 7.3.

Simultaneously, we follow coherence transfers in the four-level scheme in the second to bottom row in Figure 7.3. For that, we start out with coherence on only one of the observer spin transitions (wavy line in four-level scheme (1)), although in fact both transitions are excited by the $\pi/2$ pulse and refocused by the first π pulse. At the time of first echo formation, the magnetization vectors of all spin packets are aligned along the -y axis. During time t, the magnetization vectors fan out in the xy plane due to the distribution of resonance offsets of the spin packets. After that time, at point 2, the coherence is transferred to the other transition of the observer spin, which adds the dipolar coupling d to the resonance offsets of all spin packets. During the subsequent delay of duration $\tau_2 - t$, the magnetization vectors further fan out, but simultaneously, the whole fan rotates with angular frequency d in the xy plane. At point \Im , the second observer spin π pulse inverts the phase of the coherence. This corresponds to a 180° rotation of all magnetization vectors about the x axis, effectively mirroring the fan of magnetization vectors on the x axis (point 4). Spin packets with large positive resonance offset $\Omega_{S,1}$, which where leading before this pulse are now lagging, whereas spin packets with large negative resonance offset, which were lagging before the pulse are now leading. Hence, during subsequent evolution for time τ_2 , the fan closes again. The magnetization vectors of all spin packets end up at the same phase angle at point (5). However, with respect to dipolar evolution, the fan lags only by phase $d(\tau_2 - t)$ at point 4, whereas it gains phase $d\tau_2$ during time τ_2 . Hence, the magnetization vector ends up at phase angle dt at the time of second observer echo formation (point \mathfrak{S}). The magnetization amplitude along y is scaled by $\cos(dt)$.

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