

5.3: Zero-field interaction

Physical picture

If several unpaired spins are very strongly exchange coupled, then they are best described by a group spin S . The concept is most easily grasped for the case of two electron spins that we have already discussed in Section 5.1.1. In this case, the singlet state with group spin $S = 0$ is diamagnetic and thus not observable by EPR. The three sublevels of the observable triplet state with group spin $S = 1$ correspond to magnetic quantum numbers $m_S = -1, 0$, and $+1$ at high field. These levels are split 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, yet the three triplet sublevels are not degenerate, they exhibit **zero-field splitting**. This is because the unpaired electrons are also dipole-dipole coupled. Integration of Eq. (5.6) over the spatial distribution of the two electron spins in their respective SOMOs provides a zero-field interaction tensor \mathbf{D} that can be cast in a form where it describes coupling of the group spin $S = 1$ with itself [Rie07]. At zero field, the triplet sublevels are not described by the magnetic quantum number m_S , which is a good quantum number only if the electron Zeeman interaction is much larger than the zero-field interaction. Rather, 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 , whereas the sublevels in the high-field approximation are labeled T_{-1} , T_0 , and T_{+1} .

This concept can be extended to an arbitrary number 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 is the ground state. Kramers ions with an odd number of unpaired electrons have a half-integer group spin S . They behave differently from non-Kramers ions with an even number of electrons and integer group spin S . This classification relates to **Kramers' theorem**, which states that for a time-reversal symmetric system with half-integer total spin, all eigenstates occur as pairs (Kramers pairs) that are degenerate at zero magnetic field. As a consequence, for Kramers ions the ground state at zero field will split when a magnetic field is applied. For any microwave frequency there exists a magnetic field where the transition within the ground Kramers doublet is observable in an EPR spectrum. The same does not apply for integer group spin, where the ground state may not be degenerate at zero field. If the zero-field interaction is larger than the maximum available microwave frequency, non-Kramers ions may be unobservable by EPR spectroscopy although they exist in a paramagnetic high-spin state. Typical examples of such EPR silent non-Kramers ions are high-spin Ni(II) ($3d^8, S = 1$) and high-spin Fe(II) ($3d^6, S = 2$). In rare cases, non-Kramers ions are EPR observable, since the ground state can be degenerate at zero magnetic field if the ligand field features axial symmetry. Note also that "EPR silent" non-Kramers ions can become observable at sufficiently high microwave frequency and magnetic field.

For transition metal and rare earth ions, zero-field interaction is not solely due to the dipole-dipole interaction between the electron spins. Spin-orbit coupling also contributes, in many cases even stronger than the dipole-dipole interaction. 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.

Zero-field interaction Hamiltonian

The zero-field interaction Hamiltonian is often given as

$$\hat{\mathcal{H}}_{\text{ZFI}} = \overset{\rightarrow{\mathbf{T}}}{\hat{S}} \mathbf{D} \overset{\rightarrow{\mathbf{S}}}{\hat{S}} \quad (5.3.1)$$

where 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

$$\begin{aligned} \hat{\mathcal{H}}_{\text{ZFI}} &= D_x \hat{S}_x^2 + D_y \hat{S}_y^2 + D_z \hat{S}_z^2 \\ &= D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E (S_x^2 - S_y^2) \end{aligned}$$

where $D = 3D_z/2$ and $E = (D_x - D_y)/2$. The reduction to two parameters is possible, since \mathbf{D} is a traceless tensor. In other words, the zero-field interaction is purely anisotropic. 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 $E = 0$. Axial symmetry applies if the system has a C_n symmetry axis with $n \geq 3$. 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 to first-order, the contribution of ZFS to transition frequencies vanishes for all $-m_S \leftrightarrow +m_S$ transitions.

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

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. 2.2), 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 5.3.4.

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 and even the sign of the signal may change. 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 triple 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 naphthalene triplet (simulation performed with an example script of the software package EasySpin <http://www.easyspin.org/>). For $D = 3\text{GHz}$ at a field of about 160mT (electron Zeeman frequency of about 4.8GHz) 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.

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Figure 5.7: CW EPR spectrum of the excited naphthalene triplet at thermal equilibrium (simulation at an X-band frequency of 9.6GHz). $D \approx 3\text{GHz}$, $E \approx 0.41\text{GHz}$. 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 ^{55}Mn (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 its first derivative that is acquired by CW EPR.

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

The situation can be further complicated by D and E strain, which is a distribution of the D and E parameters due to a distribution in the ligand field. Such a case is demonstrated in Fig. 5.9 for Gd(III) at a microwave frequency of 34GHz where second-order broadening of the central transition is still rather strong. In such a case, lineshape singularities are washed out and ZFS parameters cannot be directly read off the spectra. In CW EPR, the satellite transitions may remain unobserved as the derivative of the absorption lineshape is very small except for the central transition.

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

$$\omega(m_S) = Dm_S^2 \quad (5.3.2)$$

which for high-spin Fe(III) with $S = 5/2$ gives three degenerate Kramers doublets corresponding to $m_S = \pm 5/2, \pm 3/2$, 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

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Figure 5.9: Echo-detected EPR spectrum (absorption spectrum) of a Gd(III) complex with $D \approx 1.2$

GHz, a Gaussian distribution of

D

with standard deviation of

0.24GHz

and a correlated distribution of

E

(simulation at a Q-band frequency of

34GHz

courtesy of Dr. Maxim Yulikov). (a) Total spectrum (black) and contributions of the individual transitions (see legend). The signal from the central transition (blue) dominates. (b) Contributions of the satellite transitions scaled vertically for clarity.

corresponds to $g = 2$. This Kramers doublet can thus be described as an effective spin $S' = 1/2$ with $g_{\text{eff}} = 2$.

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 $g_{\perp} = 6, g_{\parallel} = 2$. This situation is encountered to a good approximation for high-spin Fe(III) in hemoglobins ($g_{\perp} \approx 5.88, g_{\parallel} = 2.01$).

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 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).

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