

5.2: Dipole-dipole interaction

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

$$E = -\frac{\mu_0}{4\pi} \cdot \mu_1 \mu_2 \cdot \frac{1}{r^3} \cdot (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi) \quad (5.2.1)$$

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

$$E = -\frac{\mu_0}{4\pi} \cdot \mu_1 \mu_2 \cdot \frac{1}{r^3} \cdot (3 \cos^2 \theta - 1) \quad (5.2.2)$$

which is the form known from NMR spectroscopy.

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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.

Dipole-dipole Hamiltonian

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

$$\hat{H}_{\text{dd}} = \hat{S}_1^T \underline{D} \hat{S}_2 = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \mu_B^2 \left[\hat{S}_1 \hat{S}_2 - \frac{3}{r^2} \left(\hat{S}_1 \vec{r} \right) \left(\hat{S}_2 \vec{r} \right) \right] \quad (5.2.3)$$

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

$$\hat{H}_{\text{dd}} = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \mu_B^2 [\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F}] \quad (5.2.4)$$

with the terms of the dipolar alphabet

$$\begin{aligned}\hat{A} &= \hat{S}_z \hat{I}_z (1 - 3 \cos^2 \theta) \\ \hat{B} &= -\frac{1}{4} [\hat{S}^+ \hat{I}^- + \hat{S}^- \hat{I}^+] (1 - 3 \cos^2 \theta) \\ \hat{C} &= -\frac{3}{2} [\hat{S}^+ \hat{I}_z + \hat{S}_z \hat{I}^+] \sin \theta \cos \theta e^{-i\phi} \\ \hat{D} &= -\frac{3}{2} [\hat{S}^- \hat{I}_z + \hat{S}_z \hat{I}^-] \sin \theta \cos \theta e^{i\phi} \\ \hat{E} &= -\frac{3}{4} \hat{S}^+ \hat{I}^+ \sin^2 \theta e^{-2i\phi} \\ \hat{F} &= -\frac{3}{4} \hat{S}^- \hat{I}^- \sin^2 \theta e^{2i\phi}\end{aligned}$$

Usually, EPR spectroscopy is performed at fields where the electron Zeeman interaction is much larger than the dipole-dipole coupling, which has a magnitude of about 50MHz at a distance of 1 nm and of 50kHz 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

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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 thus leads to a splitting of the observer spin transition, which is twice the product of the local field with the gyromagnetic ratio of the observer spin.

the difference between the electron Zeeman frequencies 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. It is thus possible to excite spin pairs for which only the secular part of the spin Hamiltonian needs to be considered,

$$\hat{H}_{\text{dd}} = \omega_{\perp} (1 - 3 \cos^2 \theta) \hat{S}_z \hat{I}_z \quad (5.2.5)$$

with

$$\omega_{\perp} = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \mu_B^2 \quad (5.2.6)$$

The dipole-dipole coupling then has a simple dependence on the angle θ between the external magnetic field \vec{B}_0 and the spin-spin vector \vec{r} and the coupling 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). Since the average of the second Legendre polynomial $(1 - 3 \cos^2 \theta) / 2$ over all angles θ vanishes, the dipole-dipole interaction vanishes under fast isotropic motion. 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

$$d = \omega_{\perp} (1 - 3 \cos^2 \theta) \quad (5.2.7)$$

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 couplings 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

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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 $d > 1/T_2$.

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 by the local magnetic field 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.

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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.

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 weakcoupling 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).

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

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