2 Theory

2.1 A Classical Description of the EPR Experiment

2.1.1 The Bulk Magnetization

To describe the EPR experiment in a classical way, the interaction of the macroscopic bulk magnetization with the applied microwave frequency has to be regarded. If one considers a large ensemble of non-interacting classical magnetic moments in a high magnetic field ($\sim$ 1 T) at low temperatures ($\sim$ 1 K), the resulting macroscopic magnetization $\mathbf{M}$ would be approximately equal to $N_v\mu$. N_v is the number of dipoles per unit volume. [2, 12]
If the classical equation of motion is applied for a magnetic moment with an angular momentum in a magnetic field to the bulk magnetization, one gets

$$\frac{\mathrm{d}\mathbf{M}}{\mathrm{d}t} = \mathbf{M} \times \frac{-g\beta_\mathrm{e}}{\hbar}\mathbf{B}(t). \tag{2.1}$$

Equation 2.1 describes a precession of the magnetization vector about the axis of the static external magnetic field vector (in the following set as the z-axis of the coordinate system). The precessional frequency is called the *Lamor frequency*, ω_0. [12]

$$\omega_0 = \frac{g_\mathrm{e}\beta_\mathrm{e}\mathbf{B}_0}{\hbar} \tag{2.2}$$

2.1.2 The Rotating Frame

At equilibrium the magnetization vector is aligned parallel to the axis of the static external magnetic field vector. To move it away from its equilibrium position one can apply an alternating magnetic field, $\mathbf{B}_1$, oscillating with the Larmor frequency of the observed spins perpendicular to the external magnetic field vector. Usually linearly polarized fields are used for this purpose. For convenience, the direction of $\mathbf{B}_1$ is defined as the x-axis of the laboratory coordinate system. In this case the linear polarized alternating

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magnetic field can be described as a superposition of two circularly polarized alternating magnetic fields: A right-handed polarized fields,

$$B_{1x}^{(r)}(t) = B_1 \cos(\omega_{\mathrm{mw}} t), \quad B_{1y}^{(r)}(t) = B_1 \sin(\omega_{\mathrm{mw}} t), \quad B_{1z}^{(r)}(t) = 0, \tag{2.3}$$

and a left-handed polarized field,

$$B_{1x}^{(l)}(t) = B_1 \cos(\omega_{\mathrm{mw}} t), \quad B_{1y}^{(l)}(t) = -B_1 \sin(\omega_{\mathrm{mw}} t), \quad B_{1z}^{(l)}(t) = 0, \tag{2.4}$$

whereat ω_{mw} is the frequency of the microwave radiation. The right-handed polarized fields follows the precession of the magnetization vector, whereas the left-handed polarized field precesses in the opposite direction. Therefore, only the right-handed polarized field influences the magnetization vector distinctly. [12]
However, with a time-dependent field like this, equation 2.1 cannot be solved analytically. The solution to this problem is to define our coordinate system such that it rotates with ω_{mw} anti-clockwise about the z-axes. Then the time dependency of $B_1^{(r)}$ is removed. Such a coordinate system is called a *rotating frame*. [12]

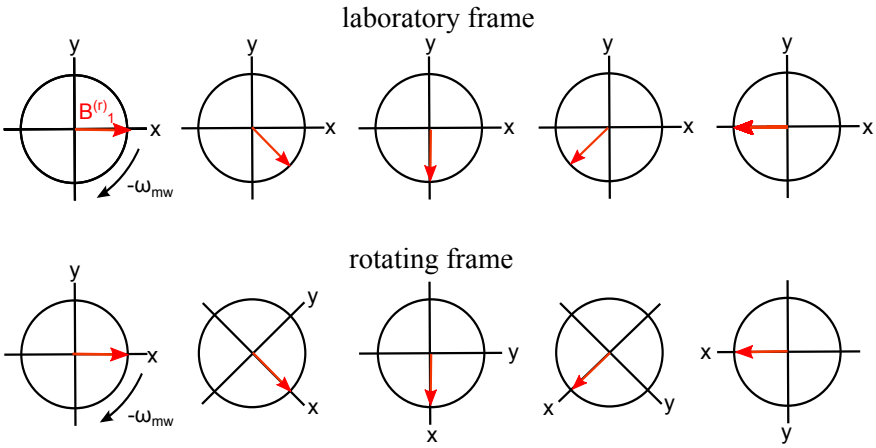

Figure 2.1: Sketch of the movement of a right-handed polarized magnetic field, $B_1^{(r)}$, in a laboratory and a rotating frame. [13]

In the rotating frame the magnetization vector precesses with the difference between its Larmor frequency, ω_0, and the frequency of the applied microwave

radiation, ω_{mw}. The frequency difference is called the *resonance offset*, Ω_S. [12]

$$\Omega_S = \omega_0 - \omega_{\mathrm{mw}} \tag{2.5}$$

2.1.3 The Bloch Equations

In a rotating frame equation 2.1 can be written as a set of linear equations:

$$\begin{aligned} \frac{\mathrm{d}M_x}{\mathrm{d}t} &= -\Omega_S M_y, \\ \frac{\mathrm{d}M_y}{\mathrm{d}t} &= \Omega_S M_x - \omega_1 M_z, \\ \frac{\mathrm{d}M_z}{\mathrm{d}t} &= -\omega_1 M_y \end{aligned} \tag{2.6}$$

$$\text{with } \omega_1 = \frac{g_x \beta_{\mathrm{e}} B_1}{\hbar} \tag{2.7}$$

However, those equations cannot be a complete description of the motion of the magnetization vector in a magnetic field, as they do not predict that after some time the magnetization vector will reach its equilibrium position and align with the external magnetic field. To explain this observation relaxation processes have to be taken into account. The z-component of the magnetization vector relaxes with the so-called longitudinal relaxation time, T_1, while the x- and y-component relax with the so-called transversal relaxation time, T_2. [12]
These considerations lead us to the *Bloch equations*:

$$\begin{aligned} \frac{\mathrm{d}M_x}{\mathrm{d}t} &= -\Omega_S M_y - \frac{M_x}{T_2}, \\ \frac{\mathrm{d}M_y}{\mathrm{d}t} &= \Omega_S M_x - \omega_1 M_z - \frac{M_y}{T_2}, \\ \frac{\mathrm{d}M_z}{\mathrm{d}t} &= -\omega_1 M_y - \frac{M_z - M_0}{T_1} \end{aligned} \tag{2.8}$$

2.1.4 Pulses

As mentioned above in the rotating frame the magnetization vector precesses about the z-axis with the resonance offset frequency, Ω_S. If one applies microwave (m.w.) irradiation, there is an additional precession about the m.w. field direction with the frequency ω_1. Both fields (the m.w. and static one) add up to an effective field $\mathbf{B_{eff}}$. The precession of the magnetization vector about the effective field is called *nutation*. Its frequency given by

$$\omega_{\text{eff}} = \sqrt{\Omega_S^2 + \omega_1^2}. \tag{2.9}$$

The angle between the effective field and the z-axis is

$$\theta = arctan(\frac{\omega_1}{\Omega_S}). \tag{2.10}$$

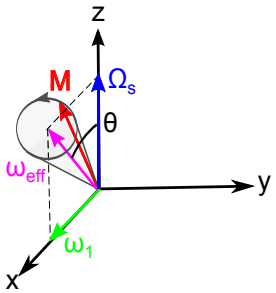

Figure 2.2: Nutation of the magnetization vector **M** during microwave irradiation with amplitude ω_1, shown in the laboratory frame. The vector moves with the frequency ω_{eff} on a cone inclined by the angle θ. [3]

If the frequency of the microwave radiation, ω_{mw}, equals the Larmor frequency, ω_0, of the observed spin, the resonance offset, Ω_S, will become zero. Thus, θ will be 90° and the nutation frequency ω_{eff} will be equal to ω_1. Such a pulse is called an *on-resonance pulse*. For an on-resonance pulse the motion of the equilibrium magnetization is very simple. It is just rotated from the z-axis towards the -y-axis. The angle through which the magnetization is rotated is given by:

$$\beta = w_1 * t_{\text{p}}, \tag{2.11}$$

where t_{p} is the time for which the m.w. pulse is applied. However, if the difference between the applied m.w. radiation and the Larmor frequency is too big, then $\Omega_S \gg \omega_1$ and therefore $\theta \approx 0$ (*off-resonance pulse*) . [3, 12, 13]

Consequently, the difference between the radiation frequency and the Larmor frequency may not be too big to accomplish a good population inversion. Therefore, the inversion bandwidth of a single m.w. pulse is quite limited and we have to think of another way of inverting spins to be able to do broadband EPR. A technique for gaining high inversion efficiency over a broad bandwidth is the *fast adiabatic passage*. [14]

2.1.5 Fast Adiabatic Passage

In the fast adiabatic passage the frequency of the applied m.w. radiation varies with time. It is swept at a rate that is small compared to the m.w. amplitude (adiabatic condition). Moreover, adiabatic rotations must be much shorter than the relaxation times T_1 and T_2. If those conditions are fulfilled the magnetization vector $\mathbf{M}$ will remain parallel to the effective field $\mathbf{B_{eff}}$ during the sweep. With such an experiment, one can achieve a high excitation bandwidth with a constant flip angle even if B_1 is very inhomogeneous. [14–16]

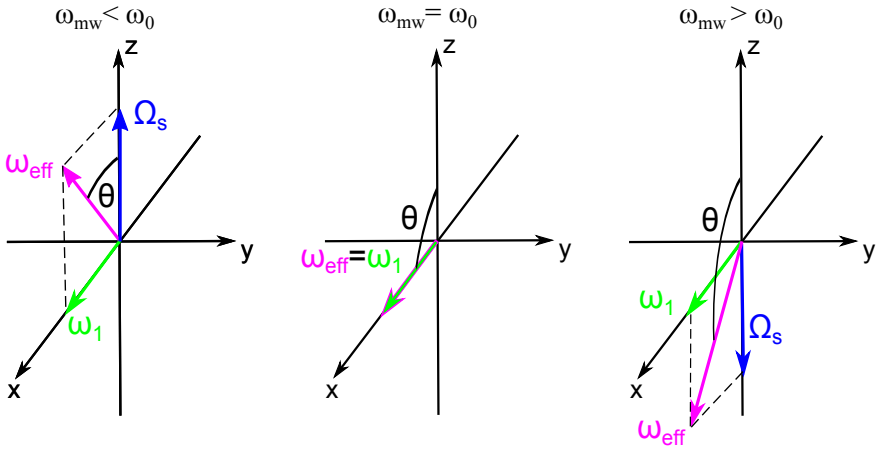

Figure 2.3: Illustration of the effective field vector, ω_{eff}, and its components, ω_1 and Ω_S during the fast adiabatic passage in a FM frame. If the adiabatic condition is fulfilled, the magnetization vector $\mathbf{M}$ will remain parallel to the effective field during the sweep. [15]

To visualize the motion of the magnetic field vector, a frequency-modulated (FM) frame is used. The FM frame rotates with the variable frequency of the applied m.w. radiation. Thus, the orientation of ω_1 remains time

independent during an adiabatic passage. Figure 2.3 shows the motion of the effective field during an adiabatic pulse. When the pulse starts, $\omega_{\mathrm{mw}} < \omega_0$ therefore the effective field ω_{eff} is tilted only a bit away from the z-axis. Then the frequency increases until it is at resonance ($\omega_{\mathrm{mw}} = \omega_0$) so that ω_{eff} lies on the x-axes. After that ω_{mw} is further increased so that it becomes off resonant again ($\omega_{\mathrm{mw}} > \omega_0$). [15]

2.2 A Quantum-Mechanical Description of EPR

2.2.1 Spin-Hamiltonians

2.2.1.1 The Static Spin Hamiltonian

The static spin Hamiltonian $\mathcal{H}_0$ describes the energies of states within the ground state of a paramagnetic species. It doesn't contain space coordinates but only spin coordinates. [3]

$$\mathcal{H}_0 = \mathcal{H}_{\mathrm{EZ}} + \mathcal{H}_{\mathrm{ZFS}} + \mathcal{H}_{\mathrm{HF}} + \mathcal{H}_{\mathrm{NZ}} + \mathcal{H}_{\mathrm{NQ}} + \mathcal{H}_{\mathrm{NN}} \tag{2.12}$$

The operator $\mathcal{H}_{\mathrm{EZ}}$ represents the Hamiltonian of the electron Zeeman interaction (see chapter 1.1.2), whereas $\mathcal{H}_{\mathrm{NZ}}$ specifies the *nuclear Zeeman interaction*. The hyperfine coupling (see chapter 1.1.3.2) is delineated by $\mathcal{H}_{\mathrm{HF}}$. The mathematical expression of the *nuclear quadrupole interaction* is $\mathcal{H}_{\mathrm{NQ}}$. This interaction is characteristic for nuclei with spin $I \geq 1$, as those have a non-spherical charge distribution. The *zero-field splitting* is described by $\mathcal{H}_{\mathrm{ZFS}}$. This field-independent splitting of the ground states is either caused by the dipole-dipole coupling of the electrons in a spin system with $S > 1/2$ or by spin-orbit coupling. The *dipole-dipole interaction between two nuclei* is covered with $\mathcal{H}_{\mathrm{NN}}$. [3] For the investigated systems only the electron and nuclear Zeeman effect as well as the hyperfine coupling and the zero-field splitting have to be considered. Therefore, only those Hamiltonians will be explained in detail in the following.

Electron Zeeman Interaction As mentioned above an electron has an intrinsic angular momentum that is quantized in two states ($m_{\mathrm{s}} = \pm\frac{1}{2}$). The splitting of these energy levels in a magnetic field is called the Zeeman interaction. It can be described with the electron Zeeman Hamiltonian:

$$\mathcal{H}_{\mathrm{EZ}} = \frac{\beta_{\mathrm{e}}}{h}\mathbf{B}_0^T\mathbf{g}\mathbf{S}, \tag{2.13}$$

where $\mathbf{B}_0^T$ is the transpose of the static magnetic field vector and $\mathbf{g}$ is the g-tensor. [3, 17]
In anisotropic systems the Zeeman interaction can depend on the orientation of the system with respect to the external magnetic field (see chapter 1.1.3.1). Therefore, the g-factor has to be a tensor:

$$\mathbf{g} = \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \tag{2.14}$$

If $\mathbf{B}_0$ is parallel to the x(y,z)-axis of the molecule internal coordinate system, the Zeeman splitting is $\frac{\beta_e}{h} B_0 g_x$ ($\frac{\beta_e}{h} B_0 g_y$, $\frac{\beta_e}{h} B_0 g_z$). If the external field isn't aligned with any primary axis of the molecule internal coordinate system, then all three diagonal elements contribute to the effective g-value: [3]

$$g_{\text{eff}} = \sqrt{g_x^2 \sin^2\theta \cos^2\varphi + g_y^2 \sin^2\theta \sin^2\varphi + g_z^2 \cos^2\varphi} \tag{2.15}$$

θ and φ are the polar angles that define the orientation of the external magnetic field vector $\mathbf{B}_0$ with respect to the molecule internal coordinate system (see figure 2.4). [3]

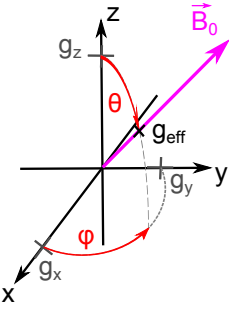

Figure 2.4: Orthorhombic model of the g-tensor shown in the laboratory frame. The coordinate systems represent the orientation of the spin with respect to the external field $\vec{B}_0$. [17]

This leads to the fact that at a constant frequency for different field strengths, molecules with different orientations are excited. Figure 2.5 shows the simulated EPR spectrum of an anisotropic system with $S = \frac{1}{2}$ and the probability that the spin with a specific orientation with respect to $\mathbf{B}_0$

is excited at a given value of B_0. The figure makes clear, that different orientations are excited at different m.w. energies or field strengths.

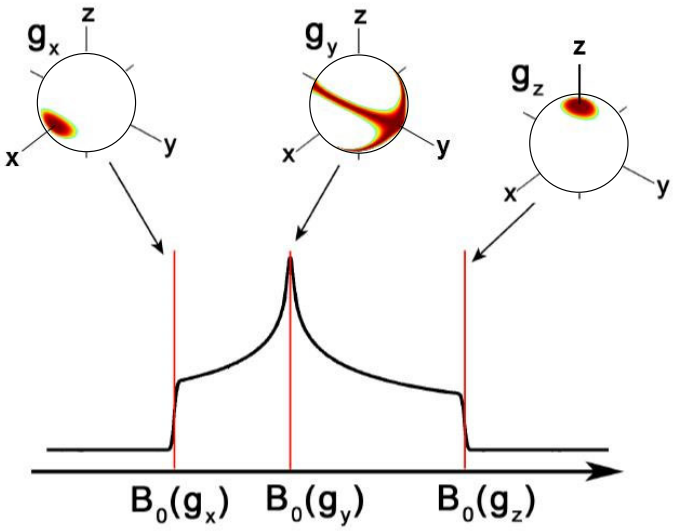

Figure 2.5: Simulation of the EPR spectrum of an anisotropic system with $S = \frac{1}{2}$. The coordinate systems represents the orientation of the spin. The x-axis of the graph shows the norm of the $\mathbf{B}_0$ vector. The spheres show the probability that the spin is excited, if the B-vector points from the point of origin to a point on the sphere. The brighter the color, the lower is the possibility that the spin is excited for this norm and orientation of $\mathbf{B}_0$. This simulation was done by Dr. Udo Kielmann, ETH Zurich, Switzerland [17].

Nuclear Zeeman Interaction The nuclear Zeeman interaction can be expressed analogously to the electron Zeeman interaction:

$$\mathcal{H}_{\mathrm{NZ}} = \frac{\beta_{\mathrm{n}} g_{\mathrm{n}}}{h} \mathbf{B}_0^T \mathbf{I}. \tag{2.16}$$

Instead of the Bohr magneton, β_{e}, the nuclear magneton β_{n}, instead of the electron Zeeman tensor $\mathbf{g}$, the nuclear Zeeman factor g_{n} and instead of the electron spin angular momentum operator $\mathbf{S}$, the nuclear spin vector operator $\mathbf{I}$ are used. In most EPR-experiments the nuclear Zeeman interaction can be considered to be isotropic. [3]

Hyperfine Coupling The Hamiltonian of the hyperfine coupling, $\mathcal{H}_{\mathrm{HF}}$, consists of the *Fermi contact interaction*, $\mathcal{H}_{\mathrm{F}}$, and the *electron-nuclear dipole-dipole coupling*, $\mathcal{H}_{\mathrm{DD}}$. It can be expressed as:

$$\mathcal{H}_{\mathrm{HF}} = \mathbf{S}^T\mathbf{A}\mathbf{I}, \tag{2.17}$$

where $\mathbf{A}$ is the hyperfine tensor and $\mathbf{I}$ the nuclear spin vector operator. [3] The Fermi contact interaction accounts for the possibility that the positions of the electron and nuclear spin overlap. It is given by:

$$\mathcal{H}_{\mathrm{F}} = a_{\mathrm{iso}}\mathbf{S}^T\mathbf{I}, \tag{2.18}$$

whereat a_{iso} is the isotropic hyperfine coupling constant. While the Fermi contact interaction is isotropic, the electron-nuclear dipole-dipole coupling depends on the relative orientation of the nuclear and the electron spin. [3] It is described by

$$\mathcal{H}_{\mathrm{DD}} = \mathbf{S}^T\mathbf{T}\mathbf{I}, \tag{2.19}$$

with $\mathbf{T}$ being the anisotropic dipolar coupling tensor. For an anisotropic g factor the hyperfine tensor $\mathbf{A}$ can now be written as: [3]

$$\mathbf{A} = a_{\mathrm{iso}}1 + \frac{\mathbf{g}\mathbf{T}}{g_{\mathrm{e}}}. \tag{2.20}$$

Zero-Field Splitting Strongly interacting electrons (group spin $S > \frac{1}{2}$), like for example in transition metal or lanthanide ions, are described by $\mathcal{H}_{\mathrm{ZFS}}$:

$$\mathcal{H}_{\mathrm{ZFS}} = \mathbf{S}^T\mathbf{D}\mathbf{S} \tag{2.21}$$

whereat $\mathbf{D}$ is the symmetric and traceless zero-field interaction tensor. In the principal axes system of $\mathbf{D}$, $\mathcal{H}_{\mathrm{ZFS}}$ becomes:

$$\begin{aligned}\mathcal{H}_{\mathrm{ZFS}} =& D_xS_x^2 + D_yS_y^2 + D_zS_z^2 \\ =& D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2). \\ \text{with } D = \frac{3}{2}D_z \text{ and } E =& \frac{1}{2}(D_x - D_y)\end{aligned} \tag{2.22}$$

For cubic symmetry, $D = E = 0$; for axial symmetry, $D \neq 0, E = 0$; and for even lower symmetries, $D \neq 0, E \neq 0$. For spins with $S > 2$ even further distortions have to be considered.[3]

2.2.1.2 Weak Coupling between Electron Spins

While strongly interacting electrons are only of minor importances for this thesis, the interaction between weakly coupled electron spins is the fundamental effect on which this work is based. The complete Hamiltonian for a system consisting of two weakly coupled electron spins is given by the Hamiltonians for each individual spin system $\mathcal{H}_0(S_1)$ and $\mathcal{H}_0(S_2)$ (see equation 2.12) and two coupling terms, $\mathcal{H}_{\text{exch}}$ and $\mathcal{H}_{\text{dd}}$. [3]

$$\mathcal{H}_0(S_1, S_2) = \mathcal{H}_0(S_1) + \mathcal{H}_0(S_2) + \mathcal{H}_{\text{exch}} + \mathcal{H}_{\text{dd}} \tag{2.23}$$

$\mathcal{H}_{\text{exch}}$ - **The Exchange Coupling** The exchange coupling is caused by significant overlapping between the orbitals of the two spins. In this case the unpaired electrons can be exchanged. The Hamiltonian of the exchange coupling is given by

$$\mathcal{H}_{\text{exch}} = \mathbf{S}_1^T \mathbf{J} \mathbf{S}_2, \tag{2.24}$$

where $\mathbf{J}$ is the exchange coupling tensor. [3]

$\mathcal{H}_{\text{dd}}$ - **The Dipole-Dipole Coupling** The operator of the dipole-dipole coupling is constructed in an analogous manner to the exchange coupling term. Instead of $\mathbf{J}$, the dipole-dipole coupling tensor $\mathbf{D}$ is used.

$$\mathcal{H}_{\text{dd}} = \mathbf{S}_1^T \mathbf{D} \mathbf{S}_2, \tag{2.25}$$

If the anisotropy of the $\mathbf{g}$-tensor can be neglected and the two electrons can be described as point dipoles, the $\mathbf{D}$ is given by:

$$\mathbf{D} = \frac{\mu_0}{4\pi\hbar} \frac{g_1 g_2 \beta_e^2}{r_{12}^3} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} = \begin{pmatrix} -\omega_{\text{dd}} & 0 & 0 \\ 0 & -\omega_{\text{dd}} & 0 \\ 0 & 0 & 2\omega_{\text{dd}} \end{pmatrix}, \tag{2.26}$$

where r_{12} is the distance between the two electron spins, μ_0 is the vacuum permeability and ω_{dd} is the dipole-dipole coupling. [3]

2.2.1.3 The Oscillatory Hamiltonian

Transitions between different electron spin states can be induced by an electromagnetic field with a frequency close to the corresponding Larmor

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