

7.2: Theoretical description of CW EPR

This section overlaps with Section 2.7 of the NMR lecture notes.

Spin packet lineshape

All spins in a sample that have the same resonance frequency form a **spin packet**. In the following we also assume that all spins of a spin packet have the same longitudinal and transverse relaxation times T_1 and T_2 , respectively. If the number of spins in the spin packet is sufficiently large, we can assign a magnetization vector to the spin packet. Dynamics of this magnetization vector with equilibrium magnetization M_0 during microwave irradiation is described by the Bloch equations in the rotating frame. In EPR spectroscopy, it is unusual to use the gyromagnetic ratio. Hence, we shall denote the resonance offset by

$$\Omega_S = \frac{g\mu_B}{\hbar} B_0 - 2\pi\nu_{\text{mw}}$$

where ν_{mw} is the microwave frequency in frequency units. The rotating-frame Bloch equations for the three components of the magnetization vector can then be written as

$$\begin{aligned}\frac{dM_x}{dt} &= -\Omega_S M_y - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \Omega_S M_x - \omega_1 M_z - \frac{M_y}{T_2} \\ \frac{dM_z}{dt} &= \omega_1 M_y - \frac{M_z - M_0}{T_1}\end{aligned}$$

where $\omega_1 = g_{\perp} \mu_B B_1 / \hbar$ is the microwave field amplitude in angular frequency units and g_{\perp} is the mean g value in the plane perpendicular to the static magnetic field. The apparent sign difference for the Ω_S and ω_1 terms arises from the different sense of spin precession for electron spins compared to nuclear spins with a positive gyromagnetic ratio.

If the spin packet is irradiated at constant microwave frequency, constant microwave power, and constant static magnetic field B_0 for a sufficiently long time (roughly $5T_1$), the magnetization vector attains a steady state. Although the static field is swept in a CW EPR experiment, assuming a steady state is a good approximation, since the field sweep is usually slow compared to T_2 and T_1 . Faster sweeps correspond to the rapid scan regime that is not treated in this lecture course. In the steady state, the left-hand sides of the differential equations (7.2) for the magnetization vector components must all be zero,

$$\begin{aligned}0 &= -\Omega_S M_y - \frac{M_x}{T_2} \\ 0 &= \Omega_S M_x - \omega_1 M_z - \frac{M_y}{T_2} \\ 0 &= \omega_1 M_y - \frac{M_z - M_0}{T_1} \quad \cdot \{ \text{stationary state} \}\end{aligned}$$

This linear system of equations has the solution

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$$M_x = M_0 \omega_1 \frac{\Omega T_2^2}{1 + \Omega^2 T_2^2 + \omega_1^2 T_1 T_2}$$

$$M_y = -M_0 \omega_1 \frac{T_2}{1 + \Omega^2 T_2^2 + \omega_1^2 T_1 T_2}$$

$$M_z = M_0 \frac{1 + \Omega^2 T_2^2}{1 + \Omega^2 T_2^2 + \omega_1^2 T_1 T_2}, \text{ (stationary state)}$$

where M_z is not usually detected, M_x is in phase with the exciting microwave irradiation and corresponds to the dispersion signal, and M_y is out of phase with the exciting irradiation and corresponds to the absorption line. Unperturbed lineshapes are obtained in the linear regime, where the saturation parameter

$$S = \omega_1^2 T_1 T_2$$

fulfills $S \ll 1$. One can easily ascertain from Eq. (7.4) that in the linear regime M_y increases linearly with increasing ω_1 , which corresponds to proportionality of the signal to the square root of microwave power. M_z is very close to the equilibrium magnetization. Within this regime, a decrease of 6 dB in microwave attenuation, i.e., a power increase by 6 dB, increases signal amplitude by a factor of 2. Lineshape does not depend on ω_1 in the linear regime. Therefore, it is good practice to measure at the highest microwave power that is still well within the linear regime, as this corresponds to maximum signal-to-noise ratio. For higher power the line is broadened.

Within the linear regime, M_y takes the form of a Lorentzian absorption line

$$M_y(\Omega) = M_0 \omega_1 T_2 \frac{1}{1 + \Omega^2 T_2^2}, \text{ (linear regime)}$$

with linewidth $1/T_2$ in angular frequency units. The peak-to-peak linewidth of the first derivative of the absorption line is $\Gamma_{pp} = 2/\sqrt{3}T_2$. Since CW EPR spectra are measured by sweeping magnetic field, we need to convert to magnetic field units,

$$\Gamma_{pp, \text{field sweep}} = \frac{2}{\sqrt{3}T_2} \cdot \frac{\hbar}{g\mu_B}$$

The linewidth of a spin packet is called homogeneous linewidth. If T_2 is the same for all spin packets, this homogeneous linewidth is proportional to $1/g$, a fact that needs to be taken into account in lineshape simulations for systems with large g anisotropy. For most samples, additional line broadening arises from unresolved hyperfine couplings and, in the solid state, g anisotropy. Therefore, T_2 cannot usually be obtained by applying Eq. (7.7) to the experimentally observed peak-to-peak linewidth.

Saturation

For microwave power larger than in the linear regime, the peak-to-peak linewidth increases by a factor $1 + S$. If a weak signal needs to be detected with maximum signal-to-noise ratio it is advantageous to increase power beyond the linear regime, but not necessarily to the maximum available level. For very strong irradiation, $S \gg 1$, the term 1 can be neglected in the denominator of Eqs. (7.4) for the magnetization vector components. The on-resonance amplitude of the absorption line is then given by

$$M_y(\Omega = 0) = M_0 / \omega_1 T_1, \left(\omega_1^2 T_1 T_2 \gg 1 \right)$$

i.e., it is inversely proportional to ω_1 . In this regime, the amplitude decreases with increasing power of the microwave irradiation.

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Figure 7.5: Progressive saturation measurement on the membrane protein LHCII solubilized in detergent micelles in nitrogen atmosphere. Residue V229 was mutated to cysteine and spin-labelled by iodoacetamidoPROXYL. Experimental data points (red) were obtained at microwave attenuations of

23, 20, 17, 11
, and
8 dB
with a full power
(0 dB)
of
200 mW
. The fit by Eq. (7.9) (black line) provides
 $P_{1/2} = 3 \text{ mW}$
and
 $\epsilon = 1.24$
.

Semi-quantitative information on spin relaxation can be obtained by the progressive power saturation experiment, where the EPR spectrum is measured as a function of microwave power P_{mw} . Usually, the peak-to-peak amplitude of the largest signal in the spectrum is plotted as a function of $\sqrt{P_{\text{mw}}}$. Such saturation curves can be fitted by the equation

$$A(P_{\text{mw}}) = \frac{I\sqrt{P_{\text{mw}}}}{\left[1 + \left(2^{1/\epsilon} - 1\right)P_{\text{mw}}/P_{1/2}\right]^\epsilon}$$

where the inhomogeneity parameter ϵ takes the value 1.5 in the homogeneous limit and 0.5 in the inhomogeneous limit. Usually, ϵ is not known beforehand and is treated as a fit parameter. The other fit parameters are I , which is the slope of the amplitude increase with the square root of microwave power in the linear regime, and $P_{1/2}$, which is the half-saturation power. More precisely, $P_{1/2}$ is the incident mw power where A is reduced to half of its unsaturated value. Figure 7.5 shows experimental data from a progressive saturation measurement on spin-labelled mutant V229C of major plant light harvesting complex LHCII solubilized in detergent micelles in a nitrogen atmosphere and a fit of this data by Eq. (7.9).

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