6.3: Generation and detection of nuclear coherence by electron spin excitation

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. In principle, 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}). Such modulation arises from forbidden transitions during the refocusing pulse, which redistribute coherence among the four transitions. The coherence transfer echoes are modulated by the difference of the resonance frequencies before and after the transfer by the π pulse, in which the resonance offset Ω_S cancels, while the nuclear spin contributions do not cancel. This two-pulse ESEEM experiment is not usually applied for measuring hyperfine couplings, as the appearance of the combination frequencies ω_{hfi} and ω_{sum} complicates the spectra and linewidth is determined by electron spin transverse relaxation, which is much faster the nuclear spin transverse relaxation.

Better resolution and simpler spectra can be obtained by indirect observation of the evolution of nuclear coherence. Such coherence can be generated by first applying a $\pi/2$ pulse to the electron spins, which will generate electron spin coherence on allowed transitions with amplitude proportional to $\cos\eta$ and on forbidden transitions with amplitude proportional to $\sin\eta$. After a delay τ a second $\pi/2$ pulse is applied. Note that the block $(\pi/2) - \tau - (\pi/2)$ is part of the EXSY and NOESY experiments in NMR. The second $\pi/2$ pulse will generate an electron spin magnetization component along z for half of the existing electron spin coherence, i.e., it will "switch off" half the electron spin coherence and convert it to polarization. However, for the coherence on forbidden transitions, there is a chance $\cos\eta$ that the nuclear spin is not flipped, i.e. that the coherent superposition of the nuclear spin states survives. For electron spin coherence on allowed transitions, there is a chance $\sin\eta$ that the "switching off" of the electron coherence will lead to a "switching on" of nuclear coherences. Hence, in both these pathways there is a probability proportional to $\sin\eta\cos\eta = \sin(2\eta)/2$ that nuclear coherence is generated. 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 operator formalism as outlined in Section 6.2.2. We find

$$\begin{aligned}
\left\langle \hat{S}^\alpha \hat{I}_x \right\rangle &= -\sin(\Omega_S\tau)\sin(2\eta)\sin\left(\frac{\omega_\beta}{2}\tau\right)\cos(\omega_\alpha\tau) \\
\left\langle \hat{S}^\alpha \hat{I}_y \right\rangle &= -\sin(\Omega_S\tau)\sin(2\eta)\sin\left(\frac{\omega_\beta}{2}\tau\right)\sin(\omega_\alpha\tau) \\
\left\langle \hat{S}^\beta \hat{I}_x \right\rangle &= -\sin(\Omega_S\tau)\sin(2\eta)\sin\left(\frac{\omega_\alpha}{2}\tau\right)\cos(\omega_\beta\tau) \\
\left\langle \hat{S}^\beta \hat{I}_y \right\rangle &= -\sin(\Omega_S\tau)\sin(2\eta)\sin\left(\frac{\omega_\alpha}{2}\tau\right)\sin(\omega_\beta\tau)
\end{aligned}$$

This expression can be interpreted in the following way. Nuclear coherence is created with a phase as if it had started to evolve as $\hat{I}_x$ at time $\tau = 0$ (last cosine factors on the right-hand side of each line). It is modulated as a function of the electron spin resonance offset Ω_S and zero exactly on resonance (first factor on each line). The integral over an inhomogeneously broadened, symmetric EPR line is also zero, since $\int_{-\infty}^{\infty}\sin(\Omega_S\tau)\mathrm{D}\Omega_S = 0$. However, this can be compensated later by applying another $\pi/2$ pulse. The amplitude of the nuclear coherence generally scales with $\sin 2\eta$, since one allowed and one forbidden transfer are required to excite it and $\sin(\eta)\cos(\eta) = \sin(2\eta)/2$ (second factor). 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 ω_β. Likewise, the amplitude of the coherence with frequency ω_β is modulated as a function of τ with frequency ω_α (lines 3 and 4). At certain values of τ no coherence is created at the transition with frequency ω_α, at other times maximum coherence is generated. Such behavior is called blind-spot behavior. In order to detect all nuclear frequencies, an experiment based on the $(\pi/2) - \tau - (\pi/2)$ nuclear coherence generator has to be repeated for different values of τ. Why and how CW EPR spectroscopy is done Sensitivity advantages of CW EPR spectroscopy The CW EPR experiment

Considerations on sample preparation Theoretical description of CW EPR Spin packet lineshape Saturation