

2.2: Interactions in electron-nuclear spin systems

General consideration on spin interactions

Spins interact with magnetic fields. The interaction with a static external magnetic field B_0 is the Zeeman interaction, which is usually the largest spin interaction. At sufficiently large fields, where the high-field approximation holds, the Zeeman interaction determines the quantization direction of the spin. In this situation, m_S is a good quantum number and, if the high-field approximation also holds for a nuclear spin I_i , the magnetic quantum number $m_{I,i}$ is also a good quantum number. The energies of all spin levels can then be expressed by parameters that quantify spin interactions and by the magnetic quantum numbers. The vector of all magnetic quantum numbers defines the state of the spin system.

Spins also interact with the local magnetic fields induced by other spins. Usually, unpaired electrons are rare, so that each electron spin interacts with several nuclear spins in its vicinity, whereas each nuclear spin interacts with only one electron spin (Fig. 2.1). The hyperfine interaction between the electron and nuclear spin is usually much smaller than the electron Zeeman interaction, with exceptions for transition metal ions. In contrast, for nuclei in the close vicinity of the electron spin, the hyperfine interaction may be larger than the nuclear Zeeman interaction at the fields where EPR spectra are usually measured. In this case, which is discussed in Chapter 6, the high-field approximation breaks down and $m_{I,i}$ is not a good quantum number. Hyperfine couplings to nuclei are relevant as long as they are at least as large as the transverse relaxation rate $1/T_{2n}$ of the coupled nuclear spin. Smaller couplings are unresolved.

In some systems, two or more unpaired electrons are so close to each other that their coupling exceeds their transverse relaxation rates $1/T_{2e}$. In fact, the isotropic part of this coupling can by far exceed the electron Zeeman interaction and often even thermal energy $k_B T$ if two unpaired electrons reside in different molecular orbitals of the same organic molecule (triplet state molecule) or if several unpaired electrons belong to a high-spin state of a transition metal or rare earth metal ion. In this situation, the system is best described in a coupled representation with an

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Figure 2.1: Scheme of interactions in electron-nuclear spin systems. All spins have a Zeeman interaction with the external magnetic field B_0 . Electron spins (red) interact with each other by the dipole-dipole interaction through space and by exchange due to overlap of the singly occupied molecular orbitals (green). Each electron spin interacts with nuclear spins (blue) in its vicinity by hyperfine couplings (purple). Couplings between nuclear spins are usually negligible in paramagnetic systems, as are chemical shifts. These two interactions are too small compared to the relaxation rate in the vicinity of an electron spin.

electron group spin $S > 1/2$. The isotropic coupling between the individual electron spins does not influence the sublevel splitting for a given group spin quantum number S . The anisotropic coupling, which does lead to sublevel splitting, is called the zero-field or fine interaction. If the electron Zeeman interaction by far exceeds the spin-spin coupling, it is more convenient to describe the system in terms of the individual electron spins $S_i = 1/2$. The isotropic exchange coupling J , which stems from overlap of two singly occupied molecular orbitals (SOMOs), then does contribute to level splitting. In addition, the dipole-dipole coupling through space between two electron spins also contributes.

Concept 2.2.1 - Singly occupied molecular orbital (SOMO).

Each molecular orbital can be occupied by two electrons with opposite magnetic spin quantum number m_S . If a molecular orbital is singly occupied, the electron is unpaired and its magnetic spin quantum number can be changed by absorption or emission of photons. The orbital occupied by the unpaired electron is called a singly occupied molecular orbital (SOMO). Several unpaired electrons can exist in the same molecule or metal complex, i.e., there may be several SOMOs.

Nuclear spins in the vicinity of an electron spin relax much faster than nuclear spins in diamagnetic substances.¹ Their transverse relaxation rates $1/T_{2n,i}$ thus exceed couplings between nuclear spins and chemical shifts. These interactions, which are very important in NMR spectroscopy, are negligible in EPR spectroscopy. For nuclear spins $1/2$ no information on the chemical identity of a nucleus can be obtained, unless its hyperfine coupling is understood. The element can be identified via the nuclear Zeeman

interaction. For nuclear spins $I_i > 1/2$, information on the chemical identity is encoded in the nuclear quadrupole interaction, whose magnitude usually exceeds $1/T_{2n,i}$.

An overview of all interactions and their typical magnitude in frequency units is given in Figure 2.2. This Figure also illustrates another difference between EPR and NMR spectroscopy. Several interactions, such as the zero-field interaction, the hyperfine interaction, larger dipole-dipole and exchange couplings between electron spins and also the anisotropy of the electron Zeeman interaction usually exceed the excitation bandwidth of the strongest and shortest microwave pulses

¹ There is an exception. If the electron spin longitudinal relaxation rate exceeds the nuclear Zeeman interaction by far, nuclear spin relaxation is hardly affected by the presence of the electron spin. In this situation, EPR spectroscopy is impossible, however, that are available. NMR pulses sequences that rely on the ability to excite the full spectrum of a certain type of spins thus cannot easily be adapted to EPR spectroscopy.

The electron-nuclear spin Hamiltonian

Considering all interactions discussed in Section 2.2.1, the static spin Hamiltonian of an electron-nuclear spin system in angular frequency units can be written as

$$\begin{aligned}\hat{\mathcal{H}}_0 &= \hat{\mathcal{H}}_{EZ} + \hat{\mathcal{H}}_{NZ} + \hat{\mathcal{H}}_{\text{HFI}} + \hat{\mathcal{H}}_{\text{ZFI}} + \hat{\mathcal{H}}_{\text{EX}} + \hat{\mathcal{H}}_{\text{DD}} + \hat{\mathcal{H}}_{\text{NQI}} \\ &= \frac{\mu_B}{\hbar} \sum_k \vec{B}_0^T \mathbf{g}_k \vec{S}_k + \sum_i \omega_{I,i} \hat{I}_{z,i} + \sum_k \sum_i \vec{S}_k^T \mathbf{A}_{ki} \vec{I}_i + \sum_{S_k > 1/2} \vec{S}_k^T \mathbf{D}_k \vec{S}_k \\ &\quad + \sum_k \sum_{l \neq k} J_{kl} \hat{S}_{z,k} \hat{S}_{z,l} + \sum_k \sum_{l \neq k} \vec{S}_k^T \mathbf{D}_{kl} \vec{S}_l + \sum_{I_i > 1/2} \vec{I}_i^T \mathbf{P}_i \vec{I}_i\end{aligned}$$

where index i runs over all nuclear spins, indices k and l run over electron spins and the symbol T denotes the transpose of a vector or vector operator. Often, only one electron spin and one nuclear spin have to be considered at once, so that the spin Hamiltonian simplifies drastically. For electron group spins $S > 1$, terms with higher powers of spin operators can be significant. We do not consider this complication here.

The electron Zeeman interaction $\hat{\mathcal{H}}_{EZ}$ is, in general, anisotropic and therefore parametrized by g tensors \mathbf{g}_k . It is discussed in detail in Chapter 3. In the nuclear Zeeman interaction $\hat{\mathcal{H}}_{NZ}$, the nuclear Zeeman frequencies $\omega_{I,i}$ depend only on the element and isotope and thus can be specified without knowing electronic and spatial structure of the molecule. The hyperfine interaction is again anisotropic and thus characterized by tensors \mathbf{A}_{ki} . It is discussed in detail in Chapter 4. All electron-electron interactions are explained in Chapter 5. The zero-field interaction $\hat{\mathcal{H}}_{\text{ZFI}}$ is purely anisotropic and thus characterized by traceless tensors \mathbf{D}_k . The exchange interaction is often purely isotropic $\hat{\mathcal{H}}_{\text{EX}}$ and any anisotropic contribution cannot be experimentally distinguished from the purely anisotropic dipole-dipole interaction $\hat{\mathcal{H}}_{\text{DD}}$. Hence, the former interaction is characterized by scalars J_{kl} and the latter interaction by tensors \mathbf{D}_{kl} . Finally, the nuclear quadrupole interaction $\hat{\mathcal{H}}_{\text{NQI}}$ is characterized by traceless tensors \mathbf{P}_i .

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Figure 2.2: Relative magnitude of interactions that contribute to the Hamiltonian of electron-nuclear spin systems.

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