

3.2: Electron Zeeman Hamiltonian

We consider a single electron spin S and thus drop the sum and index k in $\hat{\mathcal{H}}_{\text{EZ}}$ in Eq. (2.4). In the principal axes system (PAS) of the g tensor, we can then express the electron Zeeman Hamiltonian as

$$\begin{aligned}\hat{\mathcal{H}}_{\text{EZ}} &= \frac{\mu_B}{\hbar} B_0 (\cos \phi \sin \theta \quad \sin \phi \sin \theta \quad \cos \theta) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} \\ &= \frac{\mu_B}{\hbar} B_0 (g_x \cos \phi \sin \theta \hat{S}_x + g_y \sin \phi \sin \theta \hat{S}_y + g_z \cos \theta \hat{S}_z)\end{aligned}$$

where B_0 is the magnetic field, g_x , g_y , and g_z are the principal values of the g tensor and the polar angles ϕ and θ determine the orientation of the magnetic field in the PAS.

This Hamiltonian is diagonalized by the Bleaney transformation, providing

$$\hat{\mathcal{H}}_{\text{EZ}}^{BT} = \frac{\mu_B}{\hbar} g_{\text{eff}} B_0 \hat{S}_z \quad (3.2.1)$$

with the effective g value at orientation (ϕ, θ)

$$g_{\text{eff}}(\phi, \theta) = \sqrt{g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta} \quad (3.2.2)$$

If anisotropy of the g tensor is significant, the z axis in Eq. (3.5) is tilted from the direction of the magnetic field. This effect is negligible for most organic radicals, but not for transition metal ions or rare earth ions. Eq. (3.6) for the effective g values describes an ellipsoid (Figure 3.2).

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Figure 3.2: Ellipsoid describing the orientation dependence of the effective g value in the PAS of the g tensor. At a given direction of the magnetic field vector \vec{B}_0 (red), g_{eff} corresponds to distance between the origin and the point where \vec{B}_0 intersects the ellipsoid surface.

Concept 3.2.1 - Energy levels in the high-field approximation.

In the high-field approximation the energy contribution of a Hamiltonian term to the level with magnetic quantum numbers $m_{S,k}$ and $m_{I,i}$ can be computed by replacing the $\hat{J}_{z,j}$ operators ($J = S, I, j = k, i$) by the corresponding magnetic quantum numbers. This is because the magnetic quantum numbers are the eigenvalues of the $\hat{J}_{z,j}$ operators, all $\hat{J}_{z,j}$ operators commute with each other, and contributions with all other Cartesian spin operators are negligible in this approximation. For the electron Zeeman energy contribution is $m_S g_{\text{eff}} \mu_B B_0 / \hbar$. If the high-field approximation is slightly violated, this expression corresponds to a first-order perturbation treatment.

The selection rule for transitions in EPR spectroscopy is $|\Delta m_S| = 1, |\Delta m_I| = 0$ and it applies strictly as long as the high-field approximation applies strictly to all spins. This selection rule results from conservation of angular momentum on absorption of a microwave photon and from the fact that the microwave photon interacts with electron spin transitions. It follows that the first-order contribution of the electron Zeeman interaction to the frequencies of all electron spin transitions is the same, namely $g_{\text{eff}} \mu_B B_0 / \hbar$. As we shall see in Chapter 7, EPR spectra are usually measured at constant microwave frequency ν_{mw} by sweeping the magnetic field B_0 . The resonance field is then given by

$$B_{0,\text{res}} = \frac{h\nu_{\text{mw}}}{g_{\text{eff}} \mu_B} \quad (3.2.3)$$

For nuclear spin transitions, $|\Delta m_S| = 0, |\Delta m_I| = 1$, the electron Zeeman interaction does not contribute to the transition frequency

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