

3.1: Physical origin of the g shift

Bound electrons are found to have g values that differ from the value g_e for the free electron. They depend on the orientation of the paramagnetic center with respect to the magnetic field vector \vec{B}_0 . The main reason for this g value shift is coupling of spin to orbital angular momentum of the electron. Spin-orbit coupling (SOC) is a purely relativistic effect and is thus larger if orbitals of heavy atoms contribute to the SOMO. In most molecules, orbital angular momentum is quenched in the ground state. For this reason, SOC leads only to small or moderate g shifts and can be treated as a perturbation. Such a perturbation treatment is not valid if the ground state is degenerate or near degenerate.

The perturbation treatment considers excited states where the unpaired electron is not in the SOMO of the ground state. Such excited states are slightly admixed to the ground state and the mixing arises from the orbital angular momentum operator. For simplicity, we consider a case where the main contribution to the g shift arises from orbitals localized at a single, dominating atom and by single-electron SOC. To second order in perturbation theory, the matrix elements of the g tensor can then be expressed as

$$g_{ij} = g_e \delta_{ij} + 2\lambda \Lambda_{ij} \quad (3.1.1)$$

where δ_{ij} is a Kronecker delta, the factor λ in the shift term is the spin-orbit coupling constant for the dominating atom, and the matrix elements Λ_{ij} are computed as

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0 | \hat{l}_i | n \rangle \langle n | \hat{l}_j | 0 \rangle}{\epsilon_0 - \epsilon_n} \quad (3.1.2)$$

where indices i and j run over the Cartesian directions x , y , and z . The operators \hat{l}_x , \hat{l}_y , and \hat{l}_z are Cartesian components of the angular momentum operator, $|n\rangle$ designates the orbital where the unpaired electron resides in an excited-state electron configuration, counted from $n = 0$ for the SOMO of the ground state configuration. The energy of that orbital is ϵ_n .

Since the product of the overlap integrals in the numerator on the right-hand side of Eq. (3.2) is usually positive, the sign of the g shift is determined by the denominator. The denominator is positive if a paired electron from a fully occupied orbital is promoted to the ground-state SOMO and negative if the unpaired electron is promoted to a previously unoccupied orbital (Figure 3.1). Because the energy gap between the SOMO and the lowest unoccupied orbital (LUMO) is usually larger than the one between occupied orbitals, terms with positive numerator dominate in the sum on the right-hand side of Eq. (3.2). Therefore, positive g shifts are more frequently encountered than negative ones.

Copy and Paste
Image here.
Delete this
placeholder image

Figure 3.1: Admixture of excited states by orbital angular momentum operators leads to a g shift by spin-orbit coupling. The energy difference in the perturbation expression is positive for excitation of a paired electron to the ground-state SOMO and negative for excitation of the paired electron to a higher energy orbital.

The relevant spin-orbit coupling constant λ depends on the element and type of orbital. It scales roughly with Z^4 , where Z is the nuclear charge. Unless there is a very low lying excited state (near degeneracy of the ground state), contributions from heavy nuclei dominate. If there are none, as in organic radicals consisting of only hydrogen and second-row elements, g shifts of only $\Delta g < 10^{-2}$ are observed, typical shifts are $1 \dots 3 \times 10^{-3}$. Note that this still exceeds typical chemical shifts in NMR by one to two orders magnitude. For first-row transition metals, g shifts are of the order of 10^{-1} .

For rare-earth ions, the perturbation treatment breaks down. The Landé factor g_J can then be computed from the term symbol for a doublet of levels

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (3.1.3)$$

where J is the quantum number for total angular momentum and L the quantum number for orbital angular momentum. The principal values of the g tensor are $\epsilon_x g_J$, $\epsilon_y g_J$, and $\epsilon_z g_J$, where the ϵ_i with $i = x, y, z$ are differences between the eigenvalues of

\hat{L}_i for the two levels.

If the structure of a paramagnetic center is known, the g tensor can be computed by quantum chemistry. This works quite well for organic radicals and reasonably well for most first-row transition metal ions. Details are explained in [KBE04].

The g tensor is a global property of the SOMO and is easily interpretable only if it is dominated by the contribution at a single atom, which is often, but not always, the case for transition metal and rare earth ion complexes. If the paramagnetic center has a C_n symmetry axis with $n \geq 3$, the g tensor has axial symmetry with principal values $g_x = g_y = g_{\perp}$, $g_z = g_{\parallel}$. For cubic or tetrahedral symmetry the g value is isotropic, but not necessarily equal to g_e . Isotropic g values are also encountered to a very good approximation for transition metal and rare earth metal ions with half-filled shells, such as in Mn(II) complexes ($3d^5$ electron configuration) and Gd(III) complexes ($4f^7$).

This page titled [3.1: Physical origin of the \$g\$ shift](#) is shared under a [CC BY-NC 4.0](#) license and was authored, remixed, and/or curated by [Gunnar Jeschke](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.