In Parts I and II we only considered paramagnets with a single unpaired electron. Many important paramagnetic species have two or more unpaired electrons, e.g. transition ions and many photoexcited species. Here we consider spin triplet species (s = 1); these include, for example six-coordinate Ni(II) ions, optically excited aromatics, triplet carbenes, etc.

For an isolated s = 1 we have three sub-levels (ms = ±1,0; hence “spin triplet”). If these levels are degenerate in zero-field, then the Zeeman splitting will give rise to equidistant spacing of the levels and the two allowed EPR transitions (ms = -1→0 and 0→+1) will appear at the same field. However, in general this is not true and there is a zero-field splitting (ZFS). The origin of this is the electron-electron dipolar interaction and also spin-orbit coupling. We can introduce two ZFS parameters, D and E (axial and rhombic, respectively). The D parameter has the effect of splitting the states in zero-field according to ms2D. Hence, ms = ±1 and 0 are separated by D in zero-field. The Zeeman splitting now looks like:

and the two EPR transitions are separated by a function of D in field units. This is the “fine structure” in EPR spectra. This tends to be dominant over hyperfine structure (hence the name) because of the electron’s large magnetic moment. For axial symmetry E = 0. In
rhombic symmetry non-zero $E$ can mix states differing by $m_s = \pm 2$; for the triplet this means mixing (hence splitting) $m_s = \pm 1$ in zero-field.

The picture above is for a single orientation. ZFS is inherently anisotropic: typical powder patterns for axial and rhombic spectra are shown below together with their zero-field level spacings.

Zero-field energy levels