Zero-Field Splitting

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We derived the Zeeman and hyperfine Hamiltonians. This post derives the next term: zero-field splitting (ZFS). The next post derives the exchange interaction and then combines everything into a full spin Hamiltonian.

I use $\mathscr{H}$ for the full spin Hamiltonian. Sub-Hamiltonians are written as hatted H's (for example, $\hat{H}_Z$).

Zero-field splitting (ZFS) comes from one electron's spin generating a magnetic field that acts on another electron's magnetic moment. Even with no external magnetic field, this dipole–dipole interaction shifts spin energy levels. ZFS is an electron–electron analog of the hyperfine interaction.

We start from the magnetic field of a point dipole derived in the previous note:

$$\vec{B}(\vec{r}) = \underbrace{\left(\frac{\mu_0}{4\pi r^3}\right)[3(\vec{\mu}_n \cdot \hat{r})\hat{r} - \vec{\mu}_n]}_{\text{dipolar term}} + \underbrace{\left(2\frac{\mu_0}{3}\right)\vec{\mu}_n \delta^3(\vec{r})}_{\text{contact (isotropic) term}}.$$

The contact term arises from a point-like nucleus. For electron–electron interactions, electrons do not coincide exactly, so there is no delta-contact term. Only the $\frac{1}{r^3}$ dipolar field remains.

The magnetic field generated by electron 1 is

$$\vec{B}_1(\vec{r}) = \left(\frac{\mu_0}{4\pi r^3}\right)[3(\vec{\mu}_1 \cdot \hat{r})\hat{r} - \vec{\mu}_1], \quad \hat{r} = \frac{\vec{r}}{r}.$$

A second electron at $\vec{r}$ has magnetic moment $\vec{\mu}_2$. Its energy in this field is

$$U = -\vec{\mu}_2 \cdot \vec{B}_1(\vec{r}) = \left(\frac{\mu_0}{4\pi r^3}\right)[-\vec{\mu}_1 \cdot \vec{\mu}_2 + 3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r})].$$

Now promote $U \to \hat{H}_{\text{ZFS}}$. Use

$$\hat{\vec{\mu}}_i = -g_e \mu_B \frac{\hat{\vec{S}}_i}{\hbar}, \quad \mu_B = \frac{e\hbar}{2m_e}.$$

Replacing $\vec{\mu}_{1,2}$ with $\hat{\vec{\mu}}_{1,2}$ gives

$$\hat{H}_{\text{ZFS}} = -\left(\frac{\mu_0}{4\pi}\right)\left(\frac{(g_e\mu_B)^2}{\hbar^2}\right)\left(\frac{1}{r^3}\right)\left[-\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 + 3\left(\hat{\vec{S}}_1 \cdot \hat{r}\right)\left(\hat{\vec{S}}_2 \cdot \hat{r}\right)\right].$$

Equivalently,

$$\hat{H}_{\text{ZFS}} = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{(g_e\mu_B)^2}{\hbar^2}\right)\left(\frac{1}{r^3}\right)\left[\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 - 3\left(\hat{\vec{S}}_1 \cdot \hat{r}\right)\left(\hat{\vec{S}}_2 \cdot \hat{r}\right)\right].$$

To put this into a tensor form, expand the dot products. For $i, j \in (x, y, z)$,

$$\vec{S}_1 \cdot \vec{S}_2 = \sum_{i \in (x,y,z)} S_{1i} S_{2i},$$

$$\left(\vec{S}_1 \cdot \hat{r}\right)\left(\vec{S}_2 \cdot \hat{r}\right) = \left(\sum_i S_{1i}\hat{r}_i\right)\left(\sum_j S_{2j}\hat{r}_j\right) = \sum_{i,j} S_{1i}(\hat{r}_i\hat{r}_j)S_{2j} = \sum_{i,j} S_{1i}\left(\frac{r_i r_j}{r^2}\right)S_{2j}.$$

Substitute into the Hamiltonian:

$$\hat{H}_{\text{ZFS}} = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{(g_e\mu_B)^2}{\hbar^2}\right)\left(\frac{1}{r^3}\right)\left(\sum_i S_{1i}S_{2i} - 3\sum_{i,j} S_{1i}\left(\frac{r_i r_j}{r^2}\right)S_{2j}\right).$$

Rewrite the first sum using δ_{ij}:

$$\hat{H}_{\text{ZFS}} = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{(g_e\mu_B)^2}{\hbar^2}\right)\left(\sum_{i,j}\left(\frac{\delta_{ij}}{r^3}\right)S_{1i}S_{2j} - 3\sum_{i,j}\left(\frac{r_i r_j}{r^5}\right)S_{1i}S_{2j}\right).$$

So

$$\hat{H}_{\text{ZFS}} = \sum_{i,j} S_{1i}\left[\left(\frac{\mu_0}{4\pi}\right)\left(\frac{(g_e\mu_B)^2}{\hbar^2}\right)\left(\frac{\delta_{ij}}{r^3} - \frac{3r_i r_j}{r^5}\right)\right]S_{2j}.$$

Define the tensor D_{ij}:

$$D_{ij}(\vec{r}) = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{(g_e\mu_B)^2}{\hbar^2}\right)\left(\frac{\delta_{ij}}{r^3} - \frac{3r_i r_j}{r^5}\right).$$

Then the ZFS Hamiltonian is

$$\hat{H}_{\text{ZFS}} = \sum_{i,j \in (x,y,z)} S_{1i}, D_{ij}(\vec{r}), S_{2j} = \hat{\vec{S}}_1 \cdot D \cdot \hat{\vec{S}}_2.$$

D and E

The tensor in parentheses is traceless. Taking the trace,

$$\sum_i\left(\frac{\delta_{ii}}{r^3} - \frac{3r_i r_i}{r^5}\right) = \sum_i\left(\frac{1}{r^3}\right) - 3\sum_i\left(\frac{r_i^2}{r^5}\right) = \frac{3}{r^3} - \frac{3}{r^5}\left(r_x^2 + r_y^2 + r_z^2\right) = 0.$$

So if we diagonalize D in the defect's principal axes, we can write

$$D_{ij} = \begin{pmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{pmatrix}, \quad D_x + D_y + D_z = 0.$$

For the silicon vacancy $V_{\text{Si}}^- \in C_{3V}$, symmetry gives $D_x = D_y$. Together with tracelessness, $2D_x + D_z = 0$, so

$$D_x = D_y = -\frac{1}{2}D_z.$$

Define scalars D, E by

$$D = \frac{3}{2}D_z, \quad E = \frac{1}{2}(D_x - D_y).$$

D measures axial splitting. E measures deviation from perfect axial symmetry. In practice, $E \approx 0$.

Then

$$D_{\text{diag}} = \begin{pmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{pmatrix} = \begin{pmatrix} -\frac{D}{3} + E & 0 & 0 \\ 0 & -\frac{D}{3} - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{pmatrix}.$$

Raising and Lowering

From $\hat{H}_{\text{ZFS}} = \hat{\vec{S}} \cdot D \cdot \hat{\vec{S}}$, expanding in the principal axes gives

$$\begin{aligned}\hat{H}_{\text{ZFS}} &= \left(-\frac{D}{3} + E\right)\hat{S}_x^2 + \left(-\frac{D}{3} - E\right)\hat{S}_y^2 + \frac{2}{3}D\hat{S}_z^2 \\ &= D\left(\hat{S}_z^2 - \frac{1}{3}\left(\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2\right)\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right).\end{aligned}$$

The Cartesian operators relate to raising and lowering via

$$\hat{S}_+ |s, m\rangle = \left(\hat{S}_x + i\hat{S}_y\right)|s, m\rangle = \sqrt{s(s+1) - m(m+1)}\, |s, m+1\rangle,$$

$$\hat{S}_- |s, m\rangle = \left(\hat{S}_x - i\hat{S}_y\right)|s, m\rangle = \sqrt{s(s+1) - m(m-1)}\, |s, m-1\rangle.$$

Putting this together yields a compact action of $\hat{H}_{\text{ZFS}}$ on $|s, m\rangle$:

$$\begin{aligned}\hat{H}_{\text{ZFS}} |s, m\rangle &= Dm^2 |s, m\rangle - \frac{D}{3}(s(s+1))\, |s, m\rangle \\ &+ \frac{E}{2}(s(s+1) - m(m+1))\, |s, m+2\rangle \\ &+ \frac{E}{2}(s(s+1) - m(m-1))\, |s, m-2\rangle.\end{aligned}$$

ZFS splits levels even when no external B field is applied. It also introduces $m \to m \pm 2$ mixing, which leads to weak "forbidden" transitions and a faint half-field response in EDMR spectra. A simulation that resolves half-field features needs to include ZFS accurately.