7.2 Dipolar Interactions and Single Ion Anisotropy in Metal Ions

Up to this point, we have been making two assumptions about the spin carriers in our molecules:

1. There is no coupling between the $^{2S+1}I$ ground state and some excited state(s) arising from the same free-ion state through the spin-orbit coupling.
2. The $^{2S+1}I$ ground state has no first-order angular momentum.

Now, let’s look at how to treat molecules for which the first assumption is not true. In other words, molecules in which we can no longer neglect the coupling between the ground state and some excited state(s) arising from the same free-ion state through spin orbit coupling.

For simplicity, we will assume that there is no exchange coupling between magnetic centers, so we are dealing with an isolated molecule with, for example, one paramagnetic metal ion.

Recall:

$$L = \sum_i \hat{l}_i$$ is the total electronic orbital momentum operator

$$\hat{S} = \sum_i \hat{s}_i$$ is the total electronic spin momentum operator

where the sums run over the electrons of the open shells.

*NOTE*: The excited states are assumed to be high enough in energy to be totally depopulated in the temperature range of interest.

- This spin-orbit coupling between ground and unpopulated excited states may lead to two phenomena:
  1. anisotropy of the $g$-factor
  2. and, if the ground state has a larger spin multiplicity than a doublet (i.e., $S > \frac{1}{2}$), zero-field splitting of the ground state energy levels.

- Note that this spin-orbit coupling between the ground state and an unpopulated excited state can be described by $\lambda \hat{L} \cdot \hat{S}$. This is the same equation we will use when describing a system WITH first order angular momentum (see ahead).

The only difference is that, in the present case (NO first order angular momentum), a geometric distortion is required in order to give rise to magnetoanisotropy. Thus, the phenomenological Hamiltonian used is one related to lowering of symmetry.
Example 1. Cu(II) is $d^9$.
Ground state is a doublet state $^2T$ (i.e. $S = \frac{1}{2}$), so no ZFS is possible, but we can see
anisotropy in $g$. In an octahedral ligand field, this arises through a Jahn-Teller distortion.

- So, let’s quickly look at the case of Cu(II) in elongated tetragonal ligand field with $C_{4v}$ symmetry.

Since Cu(II) is $d^9$, the ground state is $^2B_1$. This has no first-order angular momentum.

If the Cu(II) ion is in a J.-T. distorted 6-coordinate ligand environment, ordering of
energy states is $^2B_1 < ^2A_1 < ^2B_2 < ^2E$.

If the Cu(II) ion is in a square planar 4-coordinate ligand environment, ordering of the
energy states is $^2B_1 < ^2B_2 < ^2A_1 < ^2E$.

We won’t work out the matrix elements for the coupling here, but suffice it to say that it
is possible to couple the ground state with excited states through the orbital angular
momentum operator.

For example, $^2B_1$ may couple with $^2B_2$ through the $\hat{L}_z$ component of the orbital
momentum, and with the $^2E$ excited state through the $\hat{L}_x$ and $\hat{L}_y$ components.

Ultimately, this affords:

$$g_z = g_e - 8\lambda/\Delta_1$$

where $g_e$ is the free electron $g$-factor

$$g_x = g_y = g_e - 2\lambda/\Delta_2$$

$\lambda$ is the spin-orbit coupling parameter

$\Delta_1$ is the energy difference between $^2B_1$ and $^2B_2$

$\Delta_2$ is the energy difference between $^2B_1$ and $^2E$
You see that the $g$-factor is not the same in the $z$-direction as in the $x$- and $y$-directions. This makes sense given the type of distortion we are dealing with.

For transition metal ions with more than five $d$ electrons, the spin-orbit coupling parameter $\lambda$ is negative such that $g_z > g_x = g_y > g_e$.

Typical values for Cu(II) are $g_z = 2.20$ and $g_x = g_y = 2.08$.

The molar magnetic susceptibility $\chi_u$ for a magnetic field applied along the $u$ direction (where $u = x,y,z$) is

$$\chi_u = \frac{N_A g_u^2 \beta^2}{4kT}$$

In fact, EPR spectroscopy is much more appropriate than magnetic measurements to determine accurately the anisotropy of the $g$-factor. In most cases, the magnetic data are recorded on polycrystalline samples and interpreted with an average value, $g$, of the $g$-factor defined by

$$g = \sqrt[3]{(g_x^2 + g_y^2 + g_z^2)/3}$$

Example 2. Ni(II) is $d^8$, and in $O_h$ symmetry it has a $^3T$ ground state (i.e., $S = 1$)

- There is no first-order angular momentum, but because $S > \frac{1}{2}$, ZFS of the ground state is possible through spin-orbit coupling with the excited states.
- Because it is easier to work with, we will use the $O$ point group instead of the $O_h$ point group.

$J. \text{Chem. Phys.} \ 1966, \ 44, \ 2409.$

![EPR spectrum of hydrated copper (II) nitrate](image)
NOTE: $^3T_2$ is the lower of the two excited states arising from the $t_2^5e^3$ configuration.

- A trigonal distortion lowering the symmetry from $O$ to $D_3$ splits the $^3T_2$ excited state into $^3A_1 + ^3E$, but does not affect the ground state, which remains $^3A_2$.
- Spin-orbit coupling (in this case given by $\Gamma_{S=1} = T_1$ symmetry) splits the excited state $^3T_2$ into $T_1 \times T_2 = A_2 + E + T_1 + T_2$ components, but doesn’t affect the ground state.

- Note that neither symmetry lowering nor spin-orbit coupling alone can affect the degeneracy of the ground state. However, if both perturbations are present, then splitting of the ground state occurs.

![Diagram](image)

**Figure 2.2.** Zero-field splittings of the ground state and first excited spin triplet state for a Ni(II) ion in a trigonally distorted octahedral surroundings.

- It is worth noting that the zero-field splitting does not always require the combined effect of distortion and spin-orbit coupling. In some cases it even occurs if the metal center is located in a rigidously cubic environment. This is the case for high spin $d^5$.

However, this zero-field splitting WITHOUT distortion is actually a very weak phenomenon, at most of the order of $10^{-2}$ cm$^{-1}$ for Fe(III).

Furthermore, in the case of hs-$d^5$, the effect is a deviation from Curie behaviour, but does NOT create magnetoanisotropy. This seems intuitively obvious since, in the absence of a distortion, the symmetry is not lowered.

ZFS within a $^{2S+1} \Gamma$ ground state WITHOUT first-order angular momentum is expressed by the same phenomenological Hamiltonian as the dipolar ZFS in an organic diradical:

$$\hat{H}_{p} = \hat{S} \cdot \mathbf{D} \cdot \hat{S}$$
Note that in the sense of the spin-Hamiltonian, this is an electron spin-spin interaction on a single center and is not to be confused with the spin-spin interaction between metal centers due to magnetic exchange coupling.

Again, the ZFS parameters $D$ and $E$ are used.

For a cubic symmetry, $D = E = 0$.

For an axial symmetry, $E = 0$ and if $D > 0$ the anisotropy is of the easy-plane type, while if $D < 0$ it is of the easy-axis type.

In a system where two or more ions are interacting, one must sum all the single-ion contributions:

$$\sum_i \hat{S}_i \cdot D_i \cdot \hat{S}_i$$

One must also account for the pairwise interaction between different spins for a polynuclear complex.

$$\sum_{i,j} \hat{S}_i \cdot D_{ij} \cdot \hat{S}_j$$

Now let’s look at systems WITH first order orbital moment… and therefore spin-orbit coupling of the ground state.

Consider a free metal ion in the absence of an applied magnetic field:

- If it is not an $S$ state ion, there is orbital degeneracy.
- Orbital degeneracy can be partially or fully lifted by a crystal field or ligand field environment. In which case, orbital degeneracy is present only if it is not an $A$ (or $B$) state molecule. It could be an $E$ or $T$ state molecule, for example.
- Orbital degeneracy, although a necessary condition for an orbital moment, is not the sole condition.
- The orbital moment can be likened to a current flowing around a circular ring of conducting material (classical picture).
• For **spin-orbit coupling** to occur, degeneracy must be such that there exist two or more *degenerate orbitals interconvertible by rotation about a suitable axis*.

Consider the \( d_{xz} \) and \( d_{yz} \) orbitals in an octahedral transition metal complex:

![Diagram of electron circulation](image)

- Rotation by 90° about the \( z \) axis interconverts these two orbitals.
- Electrons can circulate about the \( z \) axis by “jumping” between the \( d_{xz} \) and \( d_{yz} \) orbitals alternately.
- Electron circulation = current = orbital magnetic moment

### Four points

1. The \( d_{xy} \) and \( d_{yz} \) axes are interconvertible by the \( y \) axis, etc…

2. The idea of the electron “jumping” between orbitals is a little misleading. There is no energy barrier or energy difference between the orbitals and, although the two orbitals are orthogonal (i.e., overlap integral = 0), there is a large region in space in which they do overlap with one another…so no “empty space” or “chasm” that the electrons have to jump over. Thus the electron cloud experiences no barrier to free rotation.

3. It is usually assumed that any Jahn-Teller splitting of the \( T_{2g} \) set in octahedral symmetry is quite small, so for practical purposes, an orbital contribution to the moment arising from the \( d_{xy}, d_{xz}, d_{yz} \) degeneracy is only slightly quenched by a J.-T. distortion.

4. The \( d_{xy} \) and \( d_{z^2} \) orbitals are interconvertible by a 45° rotation about the \( z \) axis. However, in octahedral symmetry they are not degenerate and so DO NOT give rise to an orbital moment contribution.

### In Summary:

In \( O_h \) (and \( T_d \)) symmetry, only ground states of type \( T \) give rise to orbital-derived magnetic moments. The \( E \) type ground states have no such moment because \( d_{z^2} \) and \( d_{x^2-y^2} \) orbitals do not interconvert via a rotation.
In general, both orbital and spin moments will contribute to the magnetic properties exhibited by a complex. Their effects are additive (as vectors).

Furthermore, the spin and orbital moments may interact with each other, the phenomenon called spin-orbit coupling. Spin-orbit coupling splits terms that have both spin and orbital degeneracy.

There is a simple method by which one may discover whether spin-orbit coupling mixes two d orbitals:
- For each d orbital, note the number of its nodal planes which also contain the z axis (i.e., those in which the z axis lies on a nodal plane).
- If two d orbitals differ by either one or zero in these numbers, then the two orbitals may be mixed by spin-orbit coupling.

Spin-orbit coupling constants describe the magnitude of the spin-orbit coupling.

\( \zeta \) (zeta) is the one-electron spin-orbit coupling constant and is useful when comparing the relative magnitudes of spin-orbit coupling for different ions.

\( \lambda \) (lambda) is the resultant spin-orbit coupling between the resultant spin magnetic moment and the resultant orbital moment for many-electron ions. In practice, this is what is usually measured.

For ground states, the two constants are simply related by:

\[
\lambda = \pm \frac{\zeta}{2S}
\]

where \( S \) is the spin multiplicity of the ion
and the plus sign refers to \( d^1-d^4 \) ions whereas the minus sign refers to \( d^6-d^9 \) ions

- Spin-orbit coupling is basically the interaction of the magnetic moments of orbital and spin.
• It is the coupling of the spin angular momentum and orbital angular momentum vectors \( s \) and \( l \) for each electron to form a resultant \( j \).

• Strictly speaking we should then do a vector addition of all the individual values of \( j \) to form a total angular momentum \( J \) (i.e., \( j-j \) coupling).

• However, in general, the magnetic interactions that couple \( s \) to \( l \) are smaller in magnitude than the exchange interactions which couple \( s_i \) and \( s_j \), except for very heavy atoms. Therefore we can usually use the Russell-Saunders approach which simply couples \( L \) and \( S \) to form a vector \( J \).

Russell-Saunders spin orbit coupling can be described by the Hamiltonian component:

\[
\hat{H}_{LS} = \lambda \hat{L} \cdot \hat{S}
\]

where \( \lambda \) is the spin-orbit coupling constant.

**NOTE:** This Hamiltonian component is simply added into the total spin Hamiltonian.

In the case that there are no other effects to consider (i.e., no exchange coupling, no dipolar interactions, negligible coupling with excited states etc.), the Hamiltonian for a free ion with first order orbital moment is:

\[
\hat{H} = \lambda \hat{L} \cdot \hat{S} + \beta (\hat{L} + g_e \hat{S}) \cdot \hat{H}
\]

Like other ZFS effects, it contributes to \( E^0 \) in our energy power series.

Magnetic anisotropy arising from first-order orbital momentum is often very important, and the average magnetic susceptibility may not follow the Curie law, even at relatively high temperature.

Systems in which this type of ZFS effect is observed include:

- \( d^1 \) ions in \( O_h \) symmetry, e.g., Ti(III)
- \( ls-d^4 \) ions in \( O_h \) symmetry, e.g., Mn(III)
- \( hs-d^7 \) ions in \( O_h \) symmetry, e.g., Co(II)
- any \( f^{1-6} \) or \( f^{7-13} \) ions

In principle, the mathematics of the treatment of these and other ions with first-order orbital momentum has been worked out.

In practice, this ZFS effect can be on the same order of magnitude as the effect of exchange coupling, so fitting \( \chi T \) versus \( T \) data using a Hamiltonian accounting for both
effects (plus intermolecular interactions and possibly anisotropy of the g-value) can be difficult.

One of the big dangers in fitting $\chi T$ versus $T$ data is that it usually plots as a fairly featureless curve. Obviously, the more variables one uses, the more likely it is that a “good” fit is achieved. But at some point, there are so many variables that the fit becomes meaningless.

Alternatively, if two components have roughly equal contributions (as is often the case when exchange coupling occurs involving an ion with first order orbital momentum) it is often meaningless to fit the curve with “optimized” values for these two contributions.

For this reason, it is rare to find magnetic data in the literature that is fitted or modeled if the metal ion(s) are subject to ZFS from first-order orbital momentum, unless great care has been taken to remove all other zero field effects.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Orbital contribution expected?</th>
<th>Theoretical spin-only value</th>
<th>Range of experimental values found at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral complexes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>d$^5$</td>
<td>No</td>
<td>3.88</td>
<td>3.7–3.9</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>d$^6$ hs</td>
<td>Yes</td>
<td>2.83</td>
<td>ca. 2.8</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>d$^4$ ls</td>
<td>Yes</td>
<td>4.90</td>
<td>4.7–4.9</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>d$^5$ hs</td>
<td>No</td>
<td>2.83</td>
<td>3.2–3.3</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>d$^6$ hs</td>
<td>No</td>
<td>5.92</td>
<td>5.6–6.1</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>d$^5$ ls</td>
<td>Yes</td>
<td>1.73</td>
<td>1.8–2.1</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>d$^5$ ls</td>
<td>Yes</td>
<td>1.73</td>
<td>2.0–2.5</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>d$^6$ hs</td>
<td>No</td>
<td>4.90</td>
<td>5.1–5.7</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>d$^6$ hs</td>
<td>Yes</td>
<td>3.88</td>
<td>4.3–5.2</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>d$^5$ ls</td>
<td>No</td>
<td>1.73</td>
<td>1.8–2.0</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>d$^6$ ls</td>
<td>No</td>
<td>2.83</td>
<td>2.8–3.5</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>d$^6$</td>
<td>No</td>
<td>1.73</td>
<td>1.7–2.2</td>
</tr>
<tr>
<td>Tetrahedral complexes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>d$^5$</td>
<td>No</td>
<td>1.73</td>
<td>1.7–1.8</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>d$^6$</td>
<td>No</td>
<td>2.83</td>
<td>2.8–2.8</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>d$^2$</td>
<td>No</td>
<td>2.83</td>
<td>2.6–2.8</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>d$^3$ hs</td>
<td>Yes</td>
<td>3.88</td>
<td>3.6–3.7</td>
</tr>
<tr>
<td>unknown</td>
<td>d$^6$ hs</td>
<td>Yes</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>d$^6$ hs</td>
<td>No</td>
<td>5.92</td>
<td>5.9–6.2</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>d$^5$ ls</td>
<td>No</td>
<td>4.90</td>
<td>5.3–5.5</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>d$^6$</td>
<td>No</td>
<td>3.88</td>
<td>4.2–4.8</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>d$^6$</td>
<td>Yes</td>
<td>2.83</td>
<td>3.5–4.0</td>
</tr>
</tbody>
</table>

$^a$ hs = high spin, ls = low spin.

$^b$ Note that low-spin tetrahedral complexes are very rare— if any exist at all— and are not included in this table.

In the literature, many authors still treat ground-state spin-orbital coupling (s.o.c.) effects using the energy splitting parameters $D$ and $E$.

However, in this case, the ZFS parameters ($D$ and $E$) lose their traditional meaning. In other words, they are NOT associated with a reduction in symmetry due to a molecular distortion.

**Consider** a $d^2$ electron configuration in $O_h$ symmetry.

The ground state is $^{3}T_{1g}$.

The s.o.c. operator always transforms as the rotations.

In $O_h$ symmetry this is $t_{1g}$.

Thus, s.o.c. breaks the triplet microstate degeneracy ($S = 1; M_s = \pm 1, 0$) by coupling to the degenerate orbital states to give rise to $A_{1g}, E_g, T_{1g}$, and $T_{2g}$ states.

\[
\begin{array}{ccc}
& e_g & \Rightarrow \quad 3T_{1g} \\
t_{2g} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qua
Energy level diagram illustrating the various splittings determining the ground state derived from a $t_g^2$ configuration:

$$D \sim (1.25\lambda)^2/\Delta \quad \text{(for a} \quad ^3T_1 \text{ ground state)}$$

$E$ is related to rhombic distortion