6.3 Asymmetric Dinuclear Compounds and Trinuclear Compounds

Let us now suppose that the A and B magnetic centers are not symmetry related.

- This occurs in heterodinuclear compounds with different $S_A$ and $S_B$ local spins.
- This occurs in bimetallic compounds containing metal ions of the same nature but in different chemical environments.
- This occurs in species containing both a metal ion and an organic radical.

For now, we will neglect local anisotropy and anisotropic interactions.

- The spin Hamiltonian we developed in the symmetric case is still valid:
  \[
  \hat{H} = -J(\hat{S}_A \cdot \hat{S}_B) + \beta(\hat{S}_A g_A + \hat{S}_B g_B) \cdot H
  \]
- And the pair states are defined by the integer values $S = |S_A - S_B| \ldots S_A + S_B$ with relative energies given by
  \[
  E(S) = -\frac{J}{2} S(S + 1)
  \]
- The system still has a regular spin state structure, so we can still build an energy level “tree” as before.
- This regularity leads to a simple correspondence between the nature of the interaction and the shape of the $\chi T$ versus $T$ plot.

The high-temperature limit of $\chi T$ (for $kT >> |J|$) is the sum of what is expected for each of the magnetic centers, i.e.

\[
(\chi T)_HT = \frac{N_A \beta^2}{3k} \left[ g_A^z \cdot S_A (S_A + 1) + g_B^z \cdot S_B (S_B + 1) \right]
\]

where $g_A$ and $g_B$ denote the principal values of the local $g$-tensors assumed to be isotropic.

In the absence of coupling interactions ($J = 0$), the value of $\chi T$ remains constant over the whole temperature range (i.e. Curie behavior).

e.g. for a complex with one Cu$^{2+}$ and one Ni$^{2+}$ ion in octahedral symmetries

\[
\begin{align*}
  S_{Cu} &= \frac{1}{2} \quad S_{Ni} = 1 \\
  \text{(assume } g_{Cu} = g_{Ni} = 2) \\
  (\chi T)_{HT} &= 0.375 + 1.000 = 1.3755 \text{ cm}^3 \text{ K mol}^{-1} \\
  \end{align*}
\]

(look up table values!)
If the coupling interaction is AFM ($J < 0$), then the ground state is the smallest value $S = |S_A - S_B|$ and the highest excited state is $S = S_A + S_B$.

In the case of AFM coupling, then, $\chi T$ continuously decreases on cooling and tends toward the low-temperature limit:

$$ (\chi T)_{LT} = \frac{N_A g_S^2 \beta^2}{3k} [ (S_A - S_B)^2 + |S_A - S_B| ] $$

where $g_S(S = |S_A - S_B|)$ is related to the local $g$-factors (see notes ahead).

In the case of FM coupling, $\chi T$ continuously increases on cooling and tends toward the low-temperature limit:

$$ (\chi T)_{LT} = \frac{N_A g_S^2 \beta^2}{3k} [ (S_A + S_B)(S_A + S_B + 1) ] $$

where $g_S(S = S_A + S_B)$ is again related to the local $g$-factors (see notes ahead).

For a complex with one Cu$^{2+}$ and one Ni$^{2+}$ ion in octahedral symmetries $d^9$ $d^8$, $S_{Cu} = \frac{1}{2}$ and $S_{Ni} = 1$ (assume $g_S = 2$)

If the coupling is AFM, $S = \frac{1}{2}$

$$(\chi T)_{LT} = 0.375 \text{ cm}^3 \text{ K mol}^{-1} \quad \text{(look up table values!)}$$

If the coupling is FM, $S = 3/2$

$$(\chi T)_{LT} = 1.876 \text{ cm}^3 \text{ K mol}^{-1} \quad \text{(look up table values!)}$$

- For an asymmetrical dinuclear complex, there is no reason for the $g_A$ and $g_B$ tensors to be equal.

- Each $g_S$ tensor associated with the pair state of spin $S$ has to be calculated as a function of $g_A$ and $g_B$ by:

$$ g_S = M_S \langle S, M_S | g_A \hat{S}_A + g_B \hat{S}_B | S, M_S \rangle $$

E.g. using our Cu$^{2+}$ and Ni$^{2+}$ ion example, $S_{Cu} = \frac{1}{2}$ and $S_{Ni} = 1$ so the two possible pair states $S = \frac{1}{2}$ and $S = 3/2$ are separated by $3J/2$.

The local spin functions $|M_S>$ for Cu(II) are $|\pm 1/2>$

and for Ni(II) are $|\pm 1>$ and $|0>$
The spin functions $|S,M_S>$ for the doublet and quartet pair states may be written as linear combinations of the $|M_S(Cu), M_S(Ni)>$ product functions:

\[
|\frac{1}{2}, \pm \frac{1}{2} \rangle = \left( \sqrt{3}/3 \right) \left( |\frac{1}{2}, \pm 1 \rangle - |\frac{1}{2}, 0 \rangle \right) \\
|\frac{3}{2}, \pm \frac{1}{2} \rangle = \left( \sqrt{3}/3 \right) \left( |\frac{1}{2}, 1 \rangle + \sqrt{2} |\frac{1}{2}, 0 \rangle \right) \\
\]

and

\[
|\frac{1}{2}, + \frac{1}{2} \rangle = |\frac{1}{2}, 1 \rangle \\
|\frac{3}{2}, + \frac{1}{2} \rangle = \left( \sqrt{3}/3 \right) \left( |\frac{1}{2}, 1 \rangle + |\frac{1}{2}, -1 \rangle \right) \\
|\frac{3}{2}, - \frac{1}{2} \rangle = |\frac{1}{2}, -1 \rangle \\
\]

Plugging this into our equation gives us:

\[
g_{1/2} = \frac{4g_{Ni} - g_{Cu}}{3} \\
g_{3/2} = \frac{2g_{Ni} + g_{Cu}}{3}
\]

This is a tedious calculation, and it is easier to simply read the values from the table to the right.

### Table 6.2. Relationships between $g_s$, $g_A$, and $g_B$ Tensors in Asymmetrical Dinuclear Compounds with A and B Magnetic Centers

<table>
<thead>
<tr>
<th>$S_A$</th>
<th>$S_B$</th>
<th>$S$</th>
<th>$g_A$</th>
<th>$g_B$</th>
</tr>
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<tbody>
<tr>
<td>1/2</td>
<td>1</td>
<td>1/2</td>
<td>-1/3</td>
<td>4/3</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/3</td>
<td>2/3</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>3/2</td>
<td>1</td>
<td>-1/4</td>
<td>5/4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>1/4</td>
<td>3/4</td>
</tr>
<tr>
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<td>2</td>
<td>3/2</td>
<td>-1/5</td>
<td>6/5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/2</td>
<td>1/5</td>
<td>4/5</td>
</tr>
<tr>
<td>1/2</td>
<td>5/2</td>
<td>2</td>
<td>-1/6</td>
<td>7/6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1/6</td>
<td>5/6</td>
</tr>
<tr>
<td>1</td>
<td>3/2</td>
<td>1/2</td>
<td>-2/3</td>
<td>5/3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3/2</td>
<td>4/15</td>
<td>11/15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/2</td>
<td>2/5</td>
<td>3/5</td>
</tr>
<tr>
<td>1</td>
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<td>1/3</td>
<td>2/3</td>
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<td>-2/5</td>
<td>5/7</td>
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<td>5/2</td>
<td>2/5</td>
<td>3/35</td>
</tr>
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<td>2</td>
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<td>1/5</td>
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<td>1/2</td>
<td>-4/3</td>
<td>7/3</td>
</tr>
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<td>12/35</td>
<td>23/35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2</td>
<td>26/63</td>
<td>37/63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2</td>
<td>4/9</td>
<td>5/9</td>
</tr>
</tbody>
</table>

a This table must be read as follows (see the first line): for the $S = 1/2$ pair state arising from the interaction between $S_A = 1/2$ and $S_B = 1$ local states, we have $g_i = -g_3/3 + 4g_0/3$. 

Section 6.3 - 3
• In fact, the $M_S = \pm 1/2$ components arising from the doublet and quartet pair states couple through the Zeeman perturbation. This gives rise to off-diagonal components in the second-order Zeeman coefficients. The $E_n^{(0)}$, $E_n^{(1)}$, and $E_n^{(2)}$ coefficients are shown in the table below, where $\delta = (g_{\text{Cu}} - g_{\text{Ni}})/3$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$E_n^{(0)}$</th>
<th>$E_n^{(1)}$</th>
<th>$E_n^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$-g_{1/2}^2/2$</td>
<td>$4\delta^2\beta^2/3$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$g_{1/2}^2/2$</td>
<td>$4\delta^2\beta^2/3$</td>
</tr>
<tr>
<td>3</td>
<td>$-3J/2$</td>
<td>$-3g_{3/2}^2/2$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>$-3J/2$</td>
<td>$-3g_{3/2}^2/2$</td>
<td>$-4\delta^2\beta^2/3$</td>
</tr>
<tr>
<td>5</td>
<td>$-3J/2$</td>
<td>$3g_{3/2}^2/2$</td>
<td>$-4\delta^2\beta^2/3$</td>
</tr>
<tr>
<td>6</td>
<td>$-3J/2$</td>
<td>$3g_{3/2}^2/2$</td>
<td>0</td>
</tr>
</tbody>
</table>

Using these values, the V.V. equation gives $\chi$ as a function of $g_{1/2}$, $g_{3/2}$, $J$, and applied $T$.

$$\chi = \frac{N_A\beta^2 g_{1/2}^2}{4kT} \cdot \frac{10g_{3/2}^2 \exp(3J/2kT)}{1 + 2 \exp(3J/2kT)} - \frac{8\delta^2\beta^2}{3J} \cdot \frac{1 - \exp(3J/2kT)}{1 + 2 \exp(3J/2kT)}$$

The value of $\delta$ is on the order of $10^{-1}$ and the latter term is extremely small and actually may be reasonably neglected, except when the doublet and quartet pair states are very close to each other.

• **THERE IS AN EASIER WAY OF ESTIMATING $g_S$ !**

The Wigner-Eckart theorem can be used to generalize the relations between local and pair tensors and generates the following equation:

$$g_S = \frac{(1+c)g_A + (1-c)g_B}{2} \quad \text{with} \quad c = \frac{S_A(S_A+1) - S_B(S_B+1)}{S(S+1)}$$

This is how the values in Table 6.2 were generated.
Trinuclear Compounds and Compounds of Higher Nuclearity

- Here we consider discrete molecular species containing more than two magnetic centers. In such cases, the microscopic nature of the interaction between adjacent centers is rigorously the same as in dinuclear compounds, but the presence of more than two spin carriers may lead to new magnetic behaviour.

- Simple case: symmetrical triangular or linear ABA trinuclear compounds

The basic spin structure of such compounds has two equal A-B interaction pathways and an A-A pathway.

The local spins are $S_{A1} = S_{A2} = S_A$ and $S_B$.

The interactions are denoted $J$ and $J'$.

In the absence of an applied magnetic field (zero field; $H = 0$), and neglecting local anisotropies and anisotropic interactions, the spin Hamiltonian describing the low lying states may be written as

$$\hat{H} = -J \left( \hat{S}_{A1} \cdot \hat{S}_B + \hat{S}_{A2} \cdot \hat{S}_B \right) - J' \left( \hat{S}_{A1} \cdot \hat{S}_{A2} \right)$$

If we define two new spin operators:

$$\hat{S}' = \hat{S}_{A1} + \hat{S}_{A2} \quad \text{and} \quad \hat{S} = \hat{S}' + \hat{S}_B$$

We can rearrange the above spin Hamitonian equation to get:

$$\hat{H} = -J \left( \hat{S}'^2 - \hat{S}_{A1}^2 - \hat{S}_{A2}^2 - \hat{S}_B^2 \right) - J' \left( \hat{S}'^2 - \hat{S}_{A2}^2 - \hat{S}_{A1}^2 \right)$$

The relative energies in zero field are then expressed as

$$E(S, S') = -\frac{J}{2} S(S+1) - \frac{J'}{2} S'(S'+1)$$
Clearly, from the above definitions, \( S' \) varies by an integer value from 0 to \( 2S_A \), and for each value of \( S' \), \( S \) varies by an integer value from \( |S' - S_B| \) to \( S' + S_B \).

- To determine the magnetic susceptibility, we must add the Zeeman perturbation \( \hat{H}_{ZE} \) to the zero field spin Hamiltonian. \( \hat{H}_{ZE} \) is

\[
\hat{H}_{ZE} = \beta \left[ g_A \left( \hat{S}_{A1} + \hat{S}_{A2} \right) + g_B \hat{S}_B \right] \cdot H
\]

- The local \( g \)-tensors are assumed to be isotropic with the \( g_A \) and \( g_B \) principal values. A \( g_{S,S'} \) factor corresponds to each of the spin states with the energy \( E(S,S') \), which is related to \( g_A \) and \( g_B \) through

\[
g_{S,S'} = g_A \left[ S(S+1) + S'(S'+1) - S_B(S_B+1) \right] + g_B \left[ S(S+1) - S'(S'+1) + S_B(S_B+1) \right] / 2S(S+1)
\]

- Using this information and the V.V. equation, we can derive the following expression for the magnetic susceptibility (ignoring all the second order Zeeman coefficients):

\[
\chi = \frac{N_A \beta^2}{3kT} \sum_{S=0}^{2S_A} \sum_{S=-S_A}^{S_A} \sum_{S=0}^{2S_B} \sum_{S=-S_B}^{S_B} \frac{g_{S,S'}^2 S(S+1)(2S+1) \exp \left[ -E(S,S') / kT \right]}{(2S+1) \exp \left[ -E(S',S') / kT \right]}
\]

A simple case in which all three spin centers are identical \( S_A = S_B = \frac{1}{2} \)

 e.g., a trinuclear copper(II) species

---

**Figure 10.1.** Molecular structure of the triangular copper(II) cation \([\text{Cu}_3(\text{pao})_3\text{OH}]^{2+}\) with \( \text{H}_{\text{pao}} = \text{pyridine-2-aldehyde-oxime} \). The structure is projected down the threefold axis. The \( \mu_3 \text{-OH group} \) is pulled out from the \( \text{Cu}_3 \) plane toward the sulfato counterion (from ref. [10.2]).
• For this case, we can use our energy expression to derive the three possible energy levels:

\[ E(S, S') = -\frac{J}{2} S(S + 1) - \frac{J' - J}{2} S'(S' + 1) \]

were \( S' \) is given by \( \hat{S}' = \hat{S}_A + \hat{S}_A \)

since \( S_A = \frac{1}{2} \), then \( M_{S_A} = \pm \frac{1}{2} \)
and all possible combination give values \( M_{S'} = \pm 1, 0, 0 \)
therefore \( S' \) has two possible values, 0 and 1

and \( S \) is given by \( \hat{S} = \hat{S}' + \hat{S}_B \)

since \( S_B = \frac{1}{2} \), then \( M_{S_B} = \pm \frac{1}{2} \)
for \( S' = 0 \), \( M_{S'} = 0 \)
therefore there are only two possible values of \( M_S = \pm \frac{1}{2} \)
and therefore only one possible value of \( S = 1/2 \)

for \( S' = 1 \), \( M_{S'} = \pm 1, 0, -1 \)
and there are six values of \( M_S = \pm 3/2, \pm 1/2, \pm 1/2, \pm 1/2, \pm 1/2, \pm 3/2 \)
therefore two possible values of \( S = 3/2, 1/2 \)

so

for \( S' = 0, S = 1/2 \)
\( E(1/2,0) = -\frac{J}{2} \frac{1}{2} (\frac{1}{2} + 1) - \frac{J' - J}{2} 0(0 + 1) = -\frac{3J}{8} \)

for \( S' = 1, S = 3/2 \)
\( E(3/2,1) = -\frac{J}{2} \frac{3}{2} (\frac{3}{2} + 1) - \frac{J' - J}{2} 1(1 + 1) = -\frac{7J}{8} - \frac{8J'}{8} \)

for \( S' = 1, S = \frac{1}{2} \)
\( E(1/2,1) = -\frac{J}{2} \frac{1}{2} (\frac{1}{2} + 1) - \frac{J' - J}{2} 1(1 + 1) = +\frac{5J}{8} - \frac{8J'}{8} \)

<table>
<thead>
<tr>
<th>Energy</th>
<th>Calc'd</th>
<th>Origin adjusted</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(1/2, 0)</td>
<td>-3J/8</td>
<td>-J + J'</td>
</tr>
<tr>
<td>E(3/2, 1)</td>
<td>-7J/8 - 8J'/8</td>
<td>-3J/2</td>
</tr>
<tr>
<td>E(1/2, 1)</td>
<td>+5J/8 - 8J'/8</td>
<td>0</td>
</tr>
</tbody>
</table>

***HOMEWORK: Do the same for \( S_A = \frac{1}{2} \) and \( S_B = 5/2 \).***
• Notice that when the structure is that of a perfect triangle, such that $J = J'$, the two singlet states are degenerate!

If $J < 0$ (AFM coupling), this gives rise to what is known as spin frustration.

![Diagram of AFM and FM coupling](image)

• Consequence of spin frustration: highly degenerate ground state
  MANY equally probable and acceptable combinations of spin.

  Therefore, even at $T = 0$ K, many states are populated $\rightarrow$ novel thermodynamics!
  $\rightarrow$ novel magnetics

• So-called spin glasses show spin frustration effects and are arguably a new state of matter (?) This is outside the course parameters of molecule-based materials, however.

***HOMEWORK: Can you come up with other geometric models that ought to show spin frustration?***
Okay, let’s get back to our triangle of Cu(II) model...

- If \( J >> J' \), then we essentially have a linear system.

  In this case, if \( J < 0 \) (AFM), then the ground state is \( E(1/2, 1) \), which corresponds to the spin structure:

\[
\begin{array}{c}
\uparrow \\
| \\
\downarrow
\end{array}
\]

If \( J > 0 \) (FM), then the ground state is \( E(3/2, 1) \), which corresponds to the spin structure:

\[
\begin{array}{c}
\uparrow \\
| \\
\downarrow \\
\downarrow \\
\uparrow
\end{array}
\]

- In order to derive an equation for the magnetic susceptibility from the V.V. formula, we first need to figure out all the appropriate \( g \) values using

\[
g_{s,s'} = \frac{g_A [S(S+1) + S'(S'+1) - S_B (S + 1)] + g_B [S(S+1) - S'(S'+1) + S_B (S + 1)]}{2S(S+1)}
\]

We get:

\[
g_{\pm,1} = \frac{(4g_A - g_B)}{3} \\
g_{\pm,0} = \frac{(2g_A + g_B)}{3} \\
g_{\pm,0} = g_B
\]

- Putting all our information into the V.V. equation, we get

\[
\chi = \frac{N A^2}{4kT} \frac{g_{\pm,1}^2 + g_{\pm,0}^2 \exp \left( \frac{(J - J')}{kT} \right) + 10g_{\pm,1}^2 \exp \left( \frac{3J}{2kT} \right)}{1 + \exp \left( \frac{(J - J')}{kT} \right) + 2 \exp \left( \frac{3J}{2kT} \right)}
\]

***HOMEWORK: Prove the above equation to yourself. Derive the equation for magnetic susceptibility for the \( S_A = 1/2 \) and \( S_B = 5/2 \) case. ***
**One more example: Linear Mn(II)Cu(II)Mn(II) Species: \( S_A = \frac{5}{2}, S_B = \frac{1}{2} \)**

- The relative energies of the low-lying states can be easily calculated using the same method as above and the energy spectrum can be represented as below:

\[
\begin{align*}
E(9/2, 5) &= 0 \\
E(11/2, 5) &= -11J/2 \\
E(7/2, 4) &= -J/2 \\
E(9/2, 4) &= -5J \\
E(5/2, 3) &= -J \\
E(7/2, 3) &= -9J/2 \\
E(3/2, 2) &= -3J/2 \\
E(5/2, 2) &= -4J \\
E(1/2, 1) &= -2J \\
E(3/2, 1) &= -7J/2 \\
E(1/2, 0) &= -3J
\end{align*}
\]

![Energy spectrum of the low-lying states in a linear Mn(II)Cu(II)Mn(II) trinuclear species. Each state is represented by an arrow whose length is equal to the spin \( S \) associated with this state. The Cu(II)–Mn(II) interaction parameter is noted \( J \), and the interaction between terminal Mn(II) ions is assumed to be negligible.](image)

***HOMEWORK: Verify that the above is correct.***

- This is an interesting case in which the spin structure is irregular.

- If the coupling constant \( J < 0 \) (AFM) then the ground state energy is \( E(9/2, 5) \). If the coupling constant \( J > 0 \) (FM) then the ground state energy is \( E(11/2, 5) \).

- As you can see from the energy spectrum above, this will give an odd shape to the \( \chi T \) versus \( T \) curve since neither of these is the lowest possible spin state.

- The high temperature limit \((\chi T)_{HT}\) of \( \chi T \) is equal to the sum of the contributions of the isolated ions:

\[
(\chi T)_{HT} = \frac{N_A B^2}{12k} \left( 70g_{Mn}^2 + 3g_{Cu}^2 \right) = 9.1 \text{ cm}^3 \text{ K mol}^{-1} \quad \text{for } g_{Mn} = g_{Cu} = 2
\]
• If the coupling is AFM \((J < 0)\), then upon cooling the first state to be thermally depopulated is \(E(11/2, 5)\), which has the highest spin. This decreases \(\chi T\) as would be expected for an AFM coupled system.

• However, upon further cooling, excited states with lower spins than the ground state \(E(9/2, 5)\) are depopulated leading to an increase in \(\chi T\)!

• The low temperature limit \((\chi T)_{LT}\) for the AFM coupled system is

\[
(\chi T)_{LT} = \frac{33N_A \beta^2}{4k} \approx 12.4 \text{ cm}^3 \text{ K mol}^{-1} \text{ for } g_{Mn} = g_{Cu} \approx 2
\]

where \(g_{\frac{5}{2}} = (12g_{Mn} - g_{Cu})/11\)

Notice that this is higher than the high temperature limit!

• Here is a real example of such a molecule and the measured magnetic susceptibility data:

![Chemical structure](image)

**Figure 10.7.** Skeleton of the trinuclear cation \([\text{Mn(Me}_6\text{-14ane-N}_4)\text{]}_2\text{Cu(pba)}\text{]}^{2+}\) with \(\text{Me}_6\text{-14ane-N}_4 = \pm 5,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradecane, and pba = 1,3-propylenebis(oxamato)}\) (from ref. [10.12]).

![Magnetic susceptibility plot](image)

**Figure 10.8.** \(\chi T\) versus \(T\) plot for \([\text{Mn(Me}_6\text{-14ane-N}_4)\text{]}_2\text{Cu(pba)}\text{]}(\text{CF}_3\text{SO}_3\text{)}_2\text{2H}_2\text{O}\) (from ref. [10.12]).