6.2 Isotropic Interactions in Dinuclear Compounds

The most important developments in molecular magnetism in the last three decades have concerned compounds wherein several magnetic centers interact. These magnetic moment carriers may be transition metal ions, rare earth ions, or organic radicals.

The simplest case: isotropic interaction between two identical magnetic centers

In other words, we are looking at a single molecule with two magnetic moment carriers, for example Cu$_2$(OAc)$_3$(OH)$_2$ (J. Chem. Soc. 1956, 3837; structure shown below). There are two copper(II) ions (d$^9$), each with one unpaired electron apiece. The question is, do these two magnetic moments interact, and if so, how?

Many Cu(II) salts display Curie-Weiss paramagnetic behavior.

Cu(OAc)$_2$·H$_2$O does not!

It turns out that it forms a dimeric complex (above).

Q. What does C-W behavior look like?

Q. What type of behavior is this?
• Let us call the two copper(II) ions A and B.

• If the two ions do not interact with one another, then the local spins \( S_A = S_B = \frac{1}{2} \) are appropriate quantum numbers to use.

• However, if the two ions do interact with one another, either through the bridging acetate ligands or through space, then the local spins \( S_A = S_B = \frac{1}{2} \) are not good quantum numbers. We must use either \( S = 0 \) or \( S = 1 \) to describe the entire system.

• Now the question is, which is the lower in energy (and by how much); \( S = 0 \) or \( S = 1 \)?

• Another way of putting this is, if the two spins do not interact, then there will be no energy difference between an \( S = 0 \) state and an \( S = 1 \) state. However, if they do interact, then one of these will be lower in energy than the other. The stronger the interaction, the larger the difference in energy between these states!

• Let \( E(S = 0) \) and \( E(S = 1) \) be the energies of the two pair states.

• Let \( J \) be the energy gap separating \( E(S = 0) \) and \( E(S = 1) \), defined as

\[
 J = E(S = 0) - E(S = 1)
\]

• \( J \) is often referred to as the isotropic interaction parameter or spin coupling constant.

• When \( S = 0 \) is the ground state, the interaction is antiferromagnetic coupling, and \( J \) is negative.

• When \( S = 1 \) is the ground state, the interaction is ferromagnetic coupling, and \( J \) is positive.

• The latter situation is much less frequent than the former. About 95% of copper(II) dinuclear compounds present an antiferromagnetic interaction.

\[
\begin{array}{c|c|c}
 n & E_n^{(0)} & E_n^{(1)} \\
\hline
 1 & 0 & -\beta J \\
 2 & 0 & 0 \\
 3 & 0 & \beta J \\
 4 & 1 & 0 \\
\end{array}
\]

If the energy of the triplet state is taken as the origin, the \( E_n^{(0)} \) and \( E_n^{(1)} \) coefficients are
The isotropic interaction is formally described by a coupling between the local spin operators $\hat{S}_A$ and $\hat{S}_B$.

The phenomenological Hamiltonian accounting for this was first introduced by Heisenberg, then later discussed by Dirac and Van Vleck. It is now known at the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian. It may be written as follows:

$$\hat{H} = -J \hat{S}_A \cdot \hat{S}_B$$

or more generally as $\hat{H}_{ij} = -J_{ij} \sum \hat{S}_i \cdot \hat{S}_j$

It is worth noting here that throughout the literature, one finds that there are actually four common ways of writing this so-called “spin Hamiltonian”. The above definition is the one that matches our drawing in which we consider the energy difference between the spin triplet and the spin singlet to be $J$ such that $J$ is negative if the spin singlet is the ground state (i.e. AFM coupling).

In the HDVV Hamiltonian, we must calculate the product of spin angular momentum operators $\hat{S}_A$ and $\hat{S}_B$. A product of spin operators my be expressed in terms of component and total spin angular momentum operators:

Since $\hat{S}_{\text{total}}^2 = (\hat{S}_A + \hat{S}_B)^2$

$$= \hat{S}_A^2 + \hat{S}_B^2 + 2\hat{S}_A \cdot \hat{S}_B$$

then $\hat{S}_A \cdot \hat{S}_B = \frac{1}{2}(\hat{S}_{\text{total}}^2 - \hat{S}_A^2 - \hat{S}_B^2)$

Since $S^2 = S(S+1)$,

the energy of the $S_{\text{total}}$ state resulting from the interaction of species with $S_A$ and $S_B$ states is give by:

$$E_{\text{Total}} = -\frac{1}{2}J_{AB}S_{\text{Total}}(S_{\text{Total}} + 1) - S_A(S_A + 1) - S_B(S_B + 1)$$

Note that in order for our initial definition $J = E(S = 0) - E(S = 1)$ to be obeyed, we can simply choose an appropriate origin (in this case $E(S = 0; M_S = 0) = 0$) and this gives us:

$$E(S) = -\frac{J}{2}S(S + 1)$$

such that $E(S = 0; M_S = 0) = 0$ and $E(S = 1; M_S = 0) = -J$

Notice that the HDVV Hamiltonian accounts for an energy splitting arising due to intramolecular interactions in the absence of an applied magnetic field (i.e., $E_n^{(0)}$).
If a magnetic field $\mathbf{H}$ is applied, then the microstates of the $S = 1$ state ($M_S = -1, 0, 1$) will no longer have the same energy. As we have already seen, the energies of each spin microstate depend on the Zeeman splitting:

$$E_n = 0 + E_n^{(1)}H + 0 + ... = M_S g \beta H$$

therefore $E_n^{(1)} = M_S g \beta$

and the Hamiltonian that describes this is

$$\hat{H} = g \beta \hat{S} \cdot H$$

So, if we restrict ourselves to the simple case wherein the local states have no first-order angular momentum and we consider that our two magnetic centers are identical, with $S_A = S_B$, and symmetry related within the dinuclear unit, then the total spin Hamiltonian taking into account magnetic coupling and Zeeman perturbation is

$$\hat{H} = -J(\hat{S}_A \cdot \hat{S}_B) + \beta(\hat{S}_A g_A + \hat{S}_B g_B) \cdot H$$

The values $g_A$ and $g_B$ are the local $g$-tensors, which, in our hypothesis, are equal. Moreover, we are assuming that they are isotropic with the $g$ principal value.

So, using both the zero order energy (from magnetic coupling) and the first order energy (from Zeeman splitting), our Van Vleck energy power series becomes

$$E_n = E_n^{(0)} + E_n^{(1)}H$$

where

$$E_n^{(0)} = E(S)$$

$$= -\frac{J}{2} [S(S + 1) - S_A(S_A + 1) - S_B(S_B + 1)]$$

and

$$E_n^{(1)} = M_S g \beta$$

If we plug these into our Van Vleck formula, we get:

$$\chi = \frac{N_A}{kT} \sum_{n=0}^{M_A=+S} \frac{E_n^{(1)}^2 \exp(-E_n^{(0)}/kT)}{\sum_{n=0}^{M_n=+S} \exp(-E_n^{(0)}/kT)}$$

RECALL: $\sum_{S} M_S^2 = \frac{1}{2} S(S+1)(2S+1)$

$$= \frac{N_A}{kT} \sum_{S} \sum_{M_S=+S} (M_S g \beta)^2 \exp(-E(S)/kT)$$

$$= \frac{N_A g^2 \beta^2}{kT} \sum_{S} (2S + 1) \exp(-E(S)/kT)$$

$$= \frac{N_A g^2 \beta^2}{3kT} \sum_{S} (S+1)(2S + 1) \exp(-E(S)/kT)$$

SIMPLIFIED V.V.!!
• If we plug in the approximate numerical value for the constants:

\[
\chi = \frac{0.125 \cdot g^2 \text{ emu K mol}^{-1}}{T} \sum_S S(S+1)(2S+1) \exp \left( \frac{-E(S)}{kT} \right) \sum_S (2S+1) \exp \left( \frac{-E(S)}{kT} \right)
\]

• We can also modify the denominator to incorporate the Weiss constant:

\[
\chi = \frac{0.125 \cdot g^2 \text{ emu K mol}^{-1}}{(T - \Theta)} \sum_S S(S+1)(2S+1) \exp \left( \frac{-E(S)}{kT} \right) \sum_S (2S+1) \exp \left( \frac{-E(S)}{kT} \right)
\]

This is an easy-to-use V.V. equation specifically for two equivalent spin centers with no zero-field splitting or second order Zeeman effects.

***HOMEWORK: Prove to yourself that, for the Cu(II)-Cu(II) system above, this V.V. equation simplifies to the so-called Bleany-Bowers equation:

\[
\chi = \frac{2N_A g^2 \beta^2}{kT \left[ 3 + \exp(-J/kT) \right]}
\]

• The V.V. equation and the resulting Bleany-Bowers equation relate magnetic susceptibility (\(\chi\)) to temperature (T). They can be used to fit experimental data in order to determine the values of J and g.

If we look back at our Cu$_2$(OAc)$_4$(OH)$_2$ model complex, we find that the authors have fit the \(\chi\) vs. T data using the Bleany-Bowers equation.

The best fit gives:

\[J = -296 \text{ cm}^{-1}\]
\[g = 2.09\]

Q. What kind of exchange coupling is this?
Let’s look at what the above Bleaney-Bowers equation predicts for different values of $J$ (assuming $g = 2$):

Notice that the $\chi$ vs. $T$ plot is very useful for looking at an AFM coupled system, but it is would be quite difficult to detect an FM coupled system simply by visual inspection. It is equally difficult to achieve a good fit for an FM coupled system using a $\chi$ vs. $T$ plot.

For this reason, it is common to plot $\chi T$ vs. $T$ instead.

Using a $\chi T$ vs. $T$ plot, it is much easier to see the effect of coupling and to model this effect with a V.V. equation. Note that the above graph actually uses $kT/|J|$ as the x-axis, but since $k$ and $J$ are constants, the graph has the same appearance as if $T$ were the x-axis.
• Why does the $\chi T$ vs. $T$ plot have this $J$-dependent appearance?

For $J = 0$, we have non-interacting spin centers, so this is Curie behavior.

For $J > 0$, the spin centers are interacting such that the highest multiplicity state (largest $S$) is the ground state. At high temperature (i.e. room temperature) there will be occupation of excited states (those with smaller values of $S$) according to the Boltzmann distribution. As the temperature is decreased, the excited states are thermally depopulated (the smallest $S$ first, then the next smallest, etc.) until, at low enough $T$, only the ground state (largest $S$) is populated. This results in an increase in the value of $\chi T$ upon decreasing $T$. At temperatures lower than that required to depopulate all excited state, the value of $\chi T$ remains constant...it is the value that we can look up in our tables (see previous notes).

For $J < 0$, the same type of phenomenon occurs, only the ground state is the smallest $S$ state and the excited states that are thermally populated at room temperature are all large values of $S$. Thus a decrease in the value of $\chi T$ occurs as the temperature is lowered. Note that in the above plot, $S = 0$ is the ground state because we are assuming an interaction between two equivalent spin centers.

• Let’s look at the same case, only using two equivalent spin centers of higher multiplicity: local spins $S_A = S_B = 5/2$ (high spin Fe$^{3+}$ or Mn$^{2+}$)

To the left are the energy levels $E(S)$ from coupling between the two local spins and to the right are the Zeeman splitting of the $M_S$ states upon application of a magnetic field $H$.

In this diagram, the energy of the $S = 0$ state is arbitrarily set to zero.

If the coupling is AFM, then the values of $J$ are negative and the $S = 0$ state is lower in energy than the $S > 0$ states.

If the coupling is FM, then the values of $J$ are positive and the $S = 0$ state is higher in energy than the $S > 0$ states.

So, how did we come up with the energy differences between $S$ states in units of $J$ and how did we come up with the energies of the Zeeman splittings?
To arrive at the above energy level “tree”, we simply used our Hamiltonian:

\[
\hat{H} = -J(\hat{S}_A \cdot \hat{S}_B) + \beta(\hat{S}_A g_A + \hat{S}_B g_B) \cdot H
\]

In other words,

1. We solved for the values of \( E_n^{(0)} = E(S) \)

\[
E^{(0)} = -\frac{J}{2}[S(S + 1) - S_A(S_A + 1) - S_B(S_B + 1)]
\]

For two interacting local spins \( S_A = S_B = 5/2 \), the lowest value \( S = 0 \),
the highest value \( S = 5 \),
and the other integer values \( (S = 1, 2, 3, 4) \) are in between.

For \( S = 0 \),
\[
E(0) = -\frac{J}{2}[0(0 + 1) - \frac{5}{2}(\frac{5}{2} + 1) - \frac{5}{2}(\frac{5}{2} + 1)] = -\frac{J}{2}[\frac{35}{4} - \frac{35}{4}] = \frac{35J}{4} = 8.75J
\]

For \( S = 1 \),
\[
E(1) = -\frac{J}{2}[1(1 + 1) - \frac{5}{2}(\frac{5}{2} + 1) - \frac{5}{2}(\frac{5}{2} + 1)] = -\frac{J}{2}[\frac{2}{4} - \frac{35}{4}] = \frac{31J}{4} = 7.75J
\]

For \( S = 2 \),
\[
E(0) = -\frac{J}{2}[2(2 + 1) - \frac{5}{2}(\frac{5}{2} + 1) - \frac{5}{2}(\frac{5}{2} + 1)] = -\frac{J}{2}[6 - \frac{35}{4} - \frac{35}{4}] = \frac{23J}{4} = 5.75J
\]

...etc...

<table>
<thead>
<tr>
<th>( S )</th>
<th>Calc’d ( E(S) )</th>
<th>Adjusted ( E(S) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.75J</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>7.75J</td>
<td>-J</td>
</tr>
<tr>
<td>2</td>
<td>5.75J</td>
<td>-3J</td>
</tr>
<tr>
<td>3</td>
<td>2.75J</td>
<td>-6J</td>
</tr>
<tr>
<td>4</td>
<td>-1.25J</td>
<td>-10J</td>
</tr>
<tr>
<td>5</td>
<td>-6.25J</td>
<td>-15J</td>
</tr>
</tbody>
</table>

***HOMEWORK: Prove the last three entries in the above table to yourself.
Create a similar table for two non-equivalent local spins \( S_A = \frac{1}{2} \) and \( S_B = 2 \).
2. Next we solved for the splitting of the $M_5$ microstates for each value of $S$ upon application of a magnetic field using

$$E_n^{(1)} = M_5 g \beta$$

For example, the $S = 3$ state has microstates $M_5 = \pm 3, \pm 2, \pm 1, 0$

So the energies of the microstates split as

- $3g\beta$, $2g\beta$, $g\beta$, $0$, $g\beta$, $2g\beta$, $3g\beta$

***HOMEWORK: Prove to yourself that all the Zeeman splittings shown in the energy “tree” can be derived this way.

- Now, if we use our simplified V.V. equation

$$\chi = \frac{N_\beta g^2 \beta^2}{3kT} \sum_{S} S(S+1)(2S+1) \exp\left(-\frac{E(S)}{kT}\right)$$

and plug in all the possible values of $S$ and their resulting energy values $E(S)$, we can come up with an expression for $\chi$ that is specific to this case:

$$\chi = \frac{2N_\beta g^2 \beta^2}{kT} \sum_{S} S(S+1)(2S+1) \exp\left(-\frac{E(S)}{kT}\right)$$

with $x = J/kT$

***HOMEWORK: Go home and prove this to yourself!!

**Derivation of a similar expression is a nice exam question!***

The variables in the above equation are the values of $J$, $g$ and $T$.

Obviously, we can choose values of $T$.

The values of $J$ and $g$ are dependent on the specific molecule.

Set $g = 2$, and plot $\chi$ as a function of $T$ for several values of $J$... (see left)

Note that the difference in appearance of the plots is a function of the strength of AFM coupling of the local spins.