A. HISTORY
Magnetite or lodestone (Fe$^{II}$OFe$^{III}$_2O$_3$) mineral in its natural state often has a strong attraction for iron and steel...mined in magnesia
but Pliny says it was named for the discoverer, a shepherd, magnes, "the nails of whose shoes and the tip of whose staff stuck fast in a magnetick field while he pastured his flocks."
Lodestone appears in Greek writings by 800 B.C.
First magnetic technological invention — compass: in China, sometime between 2637 B.C. and 1100 A.D. (!)
others say it was introduced to China in 1200s by Italians or Arabs
Early theories and experiments on magnetism were developed by the great minds of all times —
Gilbert, Descartes, Coulomb, Poisson, Green, Oertsted, Ampere, Davy, Fresnel, Faraday, Maxwell...
But: Quantum Mechanics is necessary to develop a viable model, and the model continues to evolve: MAGNETISM IS NOT A SOLVED PROBLEM

B. BASICS
All materials respond to an external magnetic field (H). The magnetization (M) of a sample is proportional to H:

\[ M = \chi H . \]

The proportionality constant, \( \chi \), is the magnetic susceptibility

C. TYPES OF MAGNETISM - see chart
The Big five
1. Diamagnetism
electrons in closed shells cause a material to be repelled by H (\( \chi < 0 \)).
Typically, \( \chi_m = -1 \times 10^{-6} \text{ emu/mol} \)
usually a very small contribution to \( \chi_{\text{exp}} \)

\[ \chi_{\text{exp}} = \chi_{\text{dia}} + \chi_{\text{para}} + \chi_{\text{Pauli}} \]
\( \chi_{\text{dia}} \) — diamagnetic term due to closed-shell (core) electrons. ALL materials have this. For our systems, which will probably have a very small \( \chi \), the diamagnetic correction is non-trivial — can be obtained from atom/group additivities or the Curie plot (see below).
\( \chi_{\text{dia}} \) is temperature and field independent.
\( \chi_{\text{para}} \) is due to unpaired electrons (= \( \chi_p \))

\( \chi_{\text{Pauli}} \) is typically seen in metals and other conductors - due to mixing excited states that are not thermally populated into the ground (singlet) state - temperature independent. Presumably not important in our systems.

ALL OTHER TYPES OF MAGNETISM REQUIRE UNPAIRED SPINS (MOMENTS) — THE INTERACTIONS AMONG SPINS DETERMINES THE TYPE OF MAGNETISM

2. Paramagnetism
randomly oriented, rapidly reorienting moments; no permanent, spontaneous magnetic moment
(M = 0 if H = 0)
spins are non-interacting (non-cooperative)
all other forms of magnetism have a critical temperature, T$_C$, below which there is some interaction of moments. Above T$_C \Rightarrow$ paramagnet

\( \chi_p \) varies with T empirically according to the Curie Law:

\[ \chi_p = \frac{C}{T} \]
C = Curie constant
or the Curie-Weiss Law:
\[ \chi_p = \frac{C}{T-\theta} \quad \theta = \text{Weiss constant} \]

\( \theta \) is indicative of *intermolecular* interactions among the moments

\( \theta > 0 \) - ferromagnetic interactions (*NOT* ferromagnetism)

\( \theta < 0 \) - antiferromagnetic interactions (*NOT* antiferromagnetism)

Using the Curie Plot:

\[ \chi_{\text{exp}} = \frac{C}{T-\theta} + \chi_T \quad (\chi_T = \chi_{\text{dia}} + \chi_{\text{Pauli}} = \text{temperature independent contribution}) \]

\[ \chi_{\text{exp}} = \frac{C}{T} + \chi_T \quad \text{(at high temperature if } \theta \text{ is small)} \]
Plot $\chi_{\text{exp}}$ vs $1/T$

slope = $C$; intercept = $\chi_0$; $\Rightarrow \chi_{\text{exp}} - \chi_T = \chi_p$

...then plot $1/\chi_p$ vs. $T$

slope = $1/C$; intercept = $\theta C$

A magnetometer measures $M$ which gives $\chi$. Do the first plot to get $\chi_T$. Then at all $T$ and $H$, $\chi_p = \chi_{\text{exp}} - \chi_T$

**The magnetization plot**

For an atom with spin $m_s$, its energy in $H$ is:

$$E(m_s) = m_s \mu_B H \quad \mu = -m_s g \mu_B$$
\( \mu_B \) is Bohr magneton (= 9.27\times 10^{-24} J/T); \( g \) is the Lande constant (= 2.0023192778)

Consider \( N \) particles, with \( n_i \) in \( i \)th level

\[
\sum_i n_i = N
\]

\[
P_i = \frac{n_i}{N} = \frac{\exp \left(-\frac{\varepsilon_i}{kT} \right)}{\sum_i \exp \left(-\frac{\varepsilon_i}{kT} \right)}
\]

\[
M = N \sum_i \mu_i P_i
\]

now, consider two spin states \( (m_s = \pm 1/2) \),

\[
M = N \sum_{m_s=-1/2}^{+1/2} \left( -m_s g \mu_B \right) \exp \left( \frac{-m_s g \mu_B H}{kT} \right)
\]

\[
= \frac{Ng \mu_B}{2} \left[ \exp \left( \frac{g \mu_B H}{2kT} \right) - \exp \left( -\frac{g \mu_B H}{2kT} \right) \right]
\]

\[
= \frac{Ng \mu_B}{2} \tanh \left( \frac{g \mu_B H}{2kT} \right)
\]

since \( \tanh(y) = \frac{e^y - e^{-y}}{e^y + e^{-y}} \)

if \( y << 1 \), \( \tanh y = y \)

therefore if \( (g \mu_B H)/2kT << 1 \) (i.e. \( H/T << 1.5 \) T/K)

\[
M = \frac{Ng^2 \mu_B^2 H}{4kT}
\]

(molar) \( \chi_{\text{exp}} = M/H = \frac{Ng^2 \mu_B^2}{4kT} = \frac{C}{T} \) = Curie – Law

Therefore Curie Law only valid if \( H/T << 1.5 \) T/K - usually true

If \( y >> 1 \), \( \tanh y \to 1 \)

\[
M_{\text{sat}} = \frac{Ng \mu_B}{2} \quad \text{(or generally, } M_{\text{sat}} = Ng \mu_B S \ldots \text{a constant - the saturation magnetization)}
\]

A more general treatment with \( \sum_{m_s=+S} \) gives \( M = Ng \mu_B S B_S(x) \), with

\[
B_S(x) \quad \text{— The Brillouin Function: } \quad B_S(x) = \frac{1}{S} \left[ \left( S + \frac{1}{2} \right) \coth \left( \left( S + \frac{1}{2} \right) x \right) - \frac{1}{2} \coth \frac{x}{2} \right]
\]

where \( x = \frac{g \mu_B H}{kT} \)

As above, there are two limiting regions of the Brillouin function:
a) For $x \gg 1$, \( B_S(x) = \frac{1}{s} \left[ (S + \frac{1}{2}) - \frac{1}{2} \right] = 1 \)

\[
 x = \frac{g \mu_B H}{kT} \gg 1 \quad \text{means} \quad \frac{H}{T} \gg \frac{k}{g \mu_B} = \frac{1.38 \times 10^{-23} \text{ J/ K}}{2 \times 9.27 \times 10^{-24} \text{ J/ T}} = 0.7 \text{ T/ K}
\]

b) For $x \ll 1$,

\[
 B_S(x) = \frac{1}{s} \left[ (S + \frac{1}{2}) \left( \frac{1}{s} + \frac{1}{2} \right) x + \frac{1}{3} \left( S + \frac{1}{2} \right) x \right] - \frac{1}{2} \left( \frac{2}{x^2} + \frac{x}{6} \right) = \frac{1}{s} \left[ \frac{1}{3} \left( S + \frac{1}{2} \right)^2 x - \frac{1}{12x} \right] = \frac{x}{3s} \left( S^2 + S + \frac{1}{4} - \frac{1}{4} \right) = \frac{(S+1)x}{3}
\]

and the initial slope of a plot of $B_S(x)$ vs $x$ will be $(S+1)/3$.

For non-interacting atoms, the mean magnetic moment, or magnetization, is

\[
 M = N<\mu_z> = Ng\mu_B SB_S(x)
\]

and so for small $x$, $N$ is proportional to $x$, that is $M \propto \frac{H}{T}$.

In fact, for $\frac{g \mu_B H}{kT} \ll 1$, $M = \chi H$, where $\chi = \frac{Ng\mu_B^2 S(S+1)}{3kT}$, which is the Curie Law.

Below are plots of molar Magnetization (in units of $\mu_B$ with $g = 2$).
The effective magnetic moment directly relates to number of spins:
\[ \mu_{\text{eff}} = g[S(S+1)]^{1/2} \mu_B \]

\[
\begin{array}{c|c}
S & \mu_{\text{eff}} / \mu_B \\
\hline
1/2 & 1.73 \\
1 & 2.83 \\
2 & 4.89 \\
\end{array}
\]

related to molar susceptibility (\( \chi_m = \text{emu/mol} \))

\[
\chi_m = \frac{N\mu_{\text{eff}}^2}{3kT} = \frac{C}{T}
\]

Therefore,

\[
\mu_{\text{eff}} = \sqrt{\frac{3kC}{N}} = 2.82 \sqrt{C}
\]

3. Ferromagnetism

moments throughout a material in 3-D tend to align parallel can lead to a spontaneous permanent M (in absence of H) but, in a macroscopic system, it is energetically favorable for spins to segregate into regions called DOMAINS - domains need not be aligned with each other.

A Domain

may or may not have spontaneous M application of H causes aligned domains to grow at the expense of misaligned domains...alignment persists when H is removed
Ferromagnetism is a critical phenomenon, involving a phase transition that occurs at a critical temperature, $T_C = $ Curie Temperature. Above $T_C \Rightarrow $ paramagnet

$T_C$ is directly proportional to $S(S+1)$

It takes energy to move domain walls - hysteresis:

$$M = \chi H_{app}$$

**Sample Magnetization**

$M = \chi H_{app}$

<table>
<thead>
<tr>
<th>$M_R$</th>
<th>Remnant Magnetization ($M$ at $H_{app} = 0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{sat}$</td>
<td>Saturation Magnetization ($M_{sat} = N\mu_B S$)</td>
</tr>
<tr>
<td>$H_C$</td>
<td>Coercive Field ($H_{app}$ required to flip $M$)</td>
</tr>
<tr>
<td>“Hard” magnetic material</td>
<td>high Coercivity</td>
</tr>
<tr>
<td>“Soft” magnetic material</td>
<td>low Coercivity</td>
</tr>
</tbody>
</table>

- Electromagnets
  - High $M_R$ and Low $H_C$
- Electromagnetic Relays
  - High $M_{sat}$, Low $M_R$, and Low $H_C$
- Magnetic Recording Materials
  - High $M_R$ and relatively High $H_C$
- Permanent Magnets
  - High $M_R$ and High $H_C$

Remanence: Magnetization of sample after $H$ is removed

Coercive field: Field required to flip $M$ (+$M$ to -$M$)

4. **Antiferromagnetism**
   - spins tend to align antiparallel in 3-D
   - no spontaneous $M$
   - no permanent $M$
   - critical temperature: $T_N$ (Neel Temperature)
   - above $T_N \Rightarrow $ paramagnet

5. **Ferrimagnetism**
   - requires two chemically distinct species with different moments
   - they couple antiferromagnetically:
   - no $M$; critical $T = T_C$ (Curie Temperature)
   - bulk behavior very similar to ferromagnetism
   - Magnetite is a ferrimagnet

6. **Other types**
DIAMAGNETISM

INCIPIENT FERROMAGNETISM
Low T; temporary alignment of moments of ions & itinerant electrons

METAMAGNETISM
Field-induced transition to magnetic state; must be below Neel temperature

ANTI-FERROMAGNETISM

FERROMAGNETISM

FERRIMAGNETISM

SPERIMAGNETISM
Two species frozen as in speromagnet; often net magnetization

SUPER-PARAMAGNETISM
Small particle size allows single domain fluctuation; destroyed by cooling below blocking temperature

PARAMAGNETISM

SPROMAGNETISM
Local moments licked into random orientation; no net magnetization

ASPEROMAGNETISM
As in speromagnetism, but some orientation; net magnetization

SPIN GLASS
Magnetic ions cooled in a nonmagnetic host; usually dilute; RKKY coupling only (?)

HELIMAGNETISM
Crystalline asperomagnet

MICTOMAGNETISM
Cluster glass; local correlations dominant

D. SPECIAL TOPICS
1. Magnetooptical Disks
   a. Reading
      Magnetic materials rotate plane polarized light
      in transmission: Faraday effect
      in reflection: Kerr effect (used in devices)
      Direction of rotation depends on polarization of M
   b. Writing
      actually a thermo-magnetic process since a high-powered laser is used to heat the sample
      1) Curie point writing-heat above T_C, then cool in applied field
      2) Threshold (or compensation point) writing - if material has a temperature dependent coercive field heat to point where H > H_c, then on cooling H < H_c
   c. Materials
      Typically rare-earth transition metal alloys (RE-TM) RE: Gd, Tb; TM: Fe, Co
Many factors to tune: $T_c$, $H_c$, Magnetic anisotropy, reflectivity, Kerr rotation, stability, etc.

2. **Spin Glasses** — one of the more intriguing new forms of magnetism may be a new state of matter, maybe not prototypical SG is an alloy, with 1-10% of a paramagnetic impurity (e.g., Fe or Mn) in a diamagnetic metal (e.g. Cu or Au) Spin coupling is mediated through the conduction electrons through the RKKY interaction (Ruderman, Kittel, Kasuya, Yosida) - oscillatory in nature

This leads to frustration:

![Diagram of spin coupling]

A critical consequence of Frustration is a highly degenerate ground state - there are MANY equally probable, equally acceptable combinations of spins Therefore, even at 0 Kelvin, many states are populated - novel thermodynamic and magnetic properties Experimentally, the hallmark of a SG is a cusp in the AC susceptibility - defines a critical temperature - $T_{SG}$ Heat capacity measurements do not reveal the some critical temperature SG do show remanence and hysteresis effects SG theory has been adopted to other problems, including: combinatorial optimization (traveling salesman) problems neural networks pre-biotic evolution

E. **MISCELLANY**

1. Units and fundamental constants
   
   - $N = 6.022 \times 10^{23}$ mol$^{-1}$
   - $g = 2.0023$
   - $k = 1.3807 \times 10^{-23}$ J/K
   - $\mu_B = 9.274 \times 10^{-24}$ J/T
   - $N\mu_B^2/k = 0.375$ emu K/mol
   - $g\mu_B/k = 1.3449$ K/T
   - $G = g^{1/2}$ cm$^{-1/2}$ s$^{-1}$
   - $T = 10^4$ G
   - $T^2 = 10$ J/emu

2. Saturation behavior of S-only paramagnets
   
   $M = M_{sat} B_S (g\mu_B H/kT)$
   
   $B_S(x) = (1/S)((S + 1/2)x \coth(S + 1/2)x - (x/2) \coth(x/2))$
10

\[ M_{\text{sat}} = N g \mu_B S = 11.18245 \text{ } \text{J/mol}\cdot\text{T} = 1.118245 \times 10^4 \text{ } \text{emu}\cdot\text{G/mol} \]

3. **Curie Law for paramagnets**

\[ M = \chi H \]

\[ \chi_T = C = \frac{N g^2 \mu_B^2 S(S+1)}{3k} = 0.125 g^2 S(S+1) \text{ } \text{emu}\cdot\text{K/mol} \]

\[ \mu_{\text{eff}} = (g^2 S(S+1))^{1/2} = (8\chi_T)^{1/2} \]

4. **Relation between saturation and Curie behaviors**

\[ \frac{C(\text{emu} \cdot \text{K})}{M_{\text{sat}}(\text{emu} \cdot \text{G})} = \frac{N g^2 \mu_B^2 S(S+1)}{3kN g \mu_B S} = \frac{g \mu_B (S+1)}{3k} = \]

\[ \frac{2.0023 \cdot 9.274 \times 10^{-28} \text{ } \text{J} / \text{G}}{3 \cdot 1.3807 \times 10^{-23} \text{ } \text{J} / \text{K}} (S+1) = 4.4831 \times 10^{-5} \frac{\text{K}}{\text{G}} (S+1) \]

**F. MAGNETIC DIMERS – THE HEISENBERG-DIRAC-VAN VLECK HAMILTONIAN**

1. **Introduction**

In section C.2 we examined primary magnetochemistry relationships for paramagnets – species with **non-interacting** spins. The magnetic properties of such materials can be described by the Curie-Weiss law (for small values of \( H/T \)), or more generally by:

\[ M = N g \mu_B S \]

However, in the next simplest case – a molecule with two **exchange-coupled** unpaired electrons – the magnetic properties cannot usually be described by this relation except at very low temperatures. This will be the case when the exchange coupling creates thermally accessible states of different spin multiplicity. Such is the case for most organic biradicals.

The Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian, eq 1, is an empirical operator that models interaction (coupling) of unpaired electrons. The form of the Hamiltonian suggests that coupling arises through interaction of spin angular momentum operators. The magnitude of the interaction depends on the interaction parameter, \( J_{ij} \) (called the exchange parameter). The \( J_{ij} \) term embodies all of the interactions that determine the ground state spin preference. The product of spin operators is a reasonable component since interaction of species containing unpaired electrons results in either a decrease (antiferromagnetic coupling) or increase (ferromagnetic coupling) in spin angular momentum. For example, two doublets can couple to yield a singlet and a triplet, the relative energies of which depend on \( J_{ij} \). By definition, for ferromagnetic (high-spin) coupling \( J_{ij} > 0 \), while for antiferromagnetic coupling, \( J_{ij} < 0 \).

\[ \hat{H}_{ij} = -2J_{ij} \hat{S}_i \hat{S}_j \]

The product of spin angular momentum operators may be expressed in terms of component and product (total) spin angular momentum operators,

\[ \hat{S}_{\text{Tot}}^2 = \left( \hat{S}_i + \hat{S}_j \right)^2 = \hat{S}_i^2 + \hat{S}_j^2 + 2\hat{S}_i \hat{S}_j \]

Therefore,

\[ \hat{S}_i \hat{S}_j = \frac{1}{2} \left( \hat{S}_{\text{Tot}}^2 - \hat{S}_i^2 - \hat{S}_j^2 \right) \]

Since the eigenvalue of \( \hat{S}^2 \) is \( S(S+1) \), the energy of the state with spin \( S_{\text{Tot}} \) resulting from interaction of species with spins \( S_i \) and \( S_j \) is given by,
Thus for two doublets (2 x multiplicity 2 = 4 states), coupling results in a triplet and a singlet (multiplicity 3 and multiplicity 1 = 4 states). In the case of ferromagnetic coupling ($J > 0$), the energy of the triplet state ($S = 1$) is,

$$E_T = -J \left[ \left( S_{\text{Tot}} \right)^{\downarrow} - S_i \left( S_i \downarrow + 1 \right) - S_j \left( S_j \downarrow + 1 \right) \right]$$

$$= -J \left[ 2 - \frac{3}{4} - \frac{3}{4} \right] = -\frac{J}{2}$$

(6)

The energy of the singlet state ($S = 0$) is,

$$E_S = -J \left[ \left( S_{\text{Tot}} \right)^{\downarrow} - S_i \left( S_i \downarrow + 1 \right) - S_j \left( S_j \downarrow + 1 \right) \right]$$

$$= -J \left[ 0 - \frac{3}{4} - \frac{3}{4} \right] = \frac{3J}{2}$$

(7)

The singlet triplet gap, $\Delta E_{ST}$, is given by,

$$\Delta E_{ST} = E_S - E_T = \frac{3J}{2} - \left( -\frac{J}{2} \right) = 2J$$

(8)

The energy level diagram for ferromagnetic coupling is shown below.

The energy level diagram for antiferromagnetic coupling is shown below.

Note that by definition of the Hamiltonian, $J < 0$ describes antiferromagnetic coupling and $J > 0$. Had we defined the Hamiltonian as $\hat{H}_{ij} = 2J_{ij} \hat{S}_i \hat{S}_j$, then $J < 0$ would be for ferromagnetically coupled spins. Therefore, when reading the literature, always note the form of the Hamiltonian to be sure of the nature of the type of exchange coupling.

2. **Measuring $J$ by Electron Paramagnetic Resonance Spectroscopy**

The intensity of the EPR signal is directly proportional to the paramagnetism which can be given by the Curie Law,

$$I_{\text{EPR}} \propto \chi = \frac{C}{T}$$

(9)
Although the paramagnetism of the triplet follows the Curie Law, the concentration of triplet is temperature dependent and is given by the Boltzmann distribution,

\[
\frac{n_T}{n_T + n_S} = [\text{TRIPLET}]_{\text{rel}} = \frac{3\exp\left(-\frac{\varepsilon_T}{RT}\right)}{3\exp\left(-\frac{\varepsilon_T}{RT}\right) + \exp\left(-\frac{\varepsilon_S}{RT}\right)}
\]

(10)

Multiplication of the numerator and denominator by \(\exp\left(\frac{\varepsilon_S}{RT}\right)\), and letting \(\varepsilon_T - \varepsilon_S = \Delta E_{ST}\) gives,

\[
[\text{TRIPLET}]_{\text{rel}} = \frac{3\exp\left(-\frac{\Delta E_{ST}}{RT}\right)}{1 + 3\exp\left(-\frac{\Delta E_{ST}}{RT}\right)}
\]

(11)

Thus, the EPR signal intensity is given by,

\[
I_{\text{EPR}} = \frac{C_T}{T}[\text{TRIPLET}]_{\text{rel}} = \frac{C_T}{T} \left[ \frac{3\exp\left(-\frac{\Delta E_{ST}}{RT}\right)}{1 + 3\exp\left(-\frac{\Delta E_{ST}}{RT}\right)} \right]
\]

(12)

A plot of EPR signal intensity versus 1/T for different singlet-triplet gaps is shown below. Note that very little change in the slope of the plot occurs as the triplet becomes more stable.

3. Measuring \(J\) by Magnetometry

Van Vleck derived a general equation for calculating paramagnetic susceptibility as a function of temperature. Use of the equation requires knowledge of the energy levels, which we calculate with the HDVV Hamiltonian (see previous section). Van Vleck began the...
derivation by letting the energy levels of the system be developed as a power series expansion in the applied field.

\[ E_n = E_n^0 + H E_n^{(1)} + H^2 E_n^{(2)} + H^3 E_n^{(3)} + \ldots \]  

(13)

The term which is independent of \( H \) is the zero-order term (and has units of J, the exchange parameter), while the term linear in \( H \) is the first-order Zeeman term, and the term that scales as \( H^2 \) is the second-order Zeeman term, and so on. Neglecting Zero-field splitting, and assuming isotropic \( g \), the total magnetic moment, \( M \), for the system is:

\[ M = N \sum_n \frac{\mu_n \exp(-E_n/k_B T)}{\sum_n \exp(-E_n/k_B T)} \]  

(14)

Where \( \mu_n \) is the magnetic moment of state \( n \) (\( \mu_n = -\partial E_n/\partial H \)). Now,

\[ \exp(-E_n/k_B T) = \exp\left[ \left( -E_n^0 - H E_n^{(1)} + H^2 E_n^{(2)} + \ldots \right)/k_B T \right] = \exp\left( -E_n^0/k_B T \right) \exp\left( -H E_n^{(1)}/k_B T \right) \exp\left( -H^2 E_n^{(2)}/k_B T \right) \ldots \]  

(15)

Ignoring \( H^2 \) and higher-order exponentials, and recalling that for small \( x \),

\[ \exp(-x) \approx 1 - x \]

Then,

\[ \exp(-E_n/k_B T) = \exp\left( -E_n^0/k_B T \right) \exp\left( -H E_n^{(1)}/k_B T \right) \ldots \approx \left( 1 - \frac{H E_n^{(1)}}{k_B T} \right) \exp\left( -E_n^0/k_B T \right) \]  

(16)

(This assumes that first-order Zeeman splitting is much smaller than exchange coupling.) and,

\[ \mu_n = -\frac{\delta E_n}{\delta H} = -E_n^{(1)} - 2H E_n^{(2)} + \ldots \]  

(17)

From the approximation and substitution we obtain,

\[ M = N \frac{\sum_n \left( -E_n^{(1)} - 2H E_n^{(2)} \right) \left( 1 - \frac{H E_n^{(1)}}{k_B T} \right) \exp\left( -E_n^0/k_B T \right)}{\sum_n \left( 1 - \frac{H E_n^{(1)}}{k_B T} \right) \exp\left( -E_n^0/k_B T \right)} \]  

(18)

If we limit the derivation to paramagnetic substances, such that \( M=0 \) at \( H=0 \), then

\[ \sum_n E_n^{(1)} \exp\left( -E_n^0/k_B T \right) = 0 \]  

(19)

Retaining only terms linear in \( H \), and ignoring second-order energy terms, we obtain,
\[ M = \frac{\sum_n \left(\frac{E_n^{(1)}}{k_BT}\right)^2 \exp\left(-\frac{E_0}{k_BT}\right)}{\sum_n \exp\left(-\frac{E_0}{k_BT}\right)} \]  

(20)

Since \( \chi = \frac{M}{H} \), then

\[ \chi = \frac{\sum_n \left(\frac{E_n^{(1)}}{k_BT}\right)^2 \exp\left(-\frac{E_0}{k_BT}\right)}{\sum_n \exp\left(-\frac{E_0}{k_BT}\right)} \]  

(21)

Recall that,

\[ E_n^{(1)} = m_s g \mu_B \text{ and } \sum_{-S}^{+S} m_s^2 = \frac{1}{3} S(S+1)(2S+1) \]  

(22)

and adding degeneracy terms gives,

\[ \chi = \frac{\sum_S S(S+1)(2S+1) \exp\left(-\frac{E_S}{k_BT}\right)}{\sum_S (2S+1) \exp\left(-\frac{E_S}{k_BT}\right)} \]  

(23)

Plugging in the constants gives,

\[ \chi = \frac{0.125 g^2 \mu_B^2 \sum_S S(S+1)(2S+1) \exp\left(-\frac{E_S}{k_BT}\right)}{T \sum_S (2S+1) \exp\left(-\frac{E_S}{k_BT}\right)} \]  

(24)

Where \( E_S \) is the energy of the exchange-coupled spin states determined using the HDVV Hamiltonian. The energies of the states (in units of \( J \)) are relative to the lowest state, which is taken as zero. The denominator can be modified according to the Curie-Weiss law to give:

\[ \chi = \frac{0.125 g^2 \mu_B^2 \sum_S S(S+1)(2S+1) \exp\left(-\frac{E_S}{k_BT}\right)}{(T - \theta) \sum_S (2S+1) \exp\left(-\frac{E_S}{k_BT}\right)} \]  

(25)

Below are plots of \( \chi T \) vs \( T \) for \( \theta = -0.01 \text{ K} \) and \(-500 \text{ cm}^{-1} \leq J \geq +500 \text{ cm}^{-1} \).
Below are plots of $\chi$ vs $T$ for $\theta = -0.01$ K and $-500$ cm$^{-1} \leq J \geq +500$ cm$^{-1}$. Note that for ferromagnetic coupling, $\chi$ increases asymptotically as the temperature is lowered, while for antiferromagnetic coupling, $\chi$ exhibits a maximum at $T_{\text{max}}$. 
The exchange coupling parameter is related to \( T_{\text{max}} \) by:

\[
|J| = 0.8 kT_{\text{max}}
\]  

(26)

Thus, a maximum in the plot of \( \chi \) vs. \( T \) is the signature of antiferromagnetic coupling.

References