Magnetism-Background

- Magnetism is a property of matter in which there is a force of repulsion or attraction between like or unlike poles. *Only a few solid materials are naturally magnetic.*
- *Because we can't see magnetism,* a model or mental picture can help us visualize the atoms that make up the solid.
- Electrons in most atoms exist in pairs, with each electron spinning in an opposite direction.
Magnetism - Background

- Each spinning electron causes a magnetic field to form around it. In most materials, the magnetic field of one electron is cancelled by an opposite magnetic field produced by the other electron in the pair.

- The atoms in materials such as iron, cobalt and nickel have unpaired electrons, so they don't cancel the electrons' magnetic fields.

- As a result, each atom of these elements acts like a very small magnet.
Introduction to Magnetochemistry

• The processes which create magnetic fields in an atom are
  – Nuclear spin. Some nuclei, such as a hydrogen atom, have a net spin, which creates a magnetic field.
  – Electron spin. An electron has two intrinsic spin states (similar to a top spinning) which we call up and down or alpha and beta.
  – Electron orbital motion. There is a magnetic field due to the electron moving around the nucleus.

• Each of these magnetic fields interact with one another and with external magnetic fields. However, some of these interactions are strong and others are negligible.
Magnetism

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law (~1834), states that:

When a substance is placed within a magnetic field, $H$, the field within the substance, $B$, differs from $H$ by the induced field, $4\pi I$, which is proportional to the intensity of magnetization, $I$.

That is; $B = H + 4\pi I$

$B$ = the magnetic field within the substance  
$H$ = the applied magnetic field  
$I$ = the intensity of magnetisation

$\frac{B}{H} = 1 + 4\pi \frac{I}{H}$ or $\frac{B}{H} = 1 + 4\pi \kappa$

where $B/H$ is called the magnetic permeability of the material and $\kappa$ is the magnetic susceptibility per unit volume, $(I/H)$

By definition, $\kappa$ in a vacuum is zero,

so, $B = H$. 
Molar susceptibility

It is usually more convenient to measure mass (gram) susceptibility, $\chi_g$, which is related to the volume susceptibility through the density.

$$\chi_g = \kappa / \rho$$

where $\rho$ is the density.

Finally to get our measured quantity on a basis that can be related to atomic properties, we convert to molar susceptibility

$$\chi_m = \chi_g \times \text{MW}$$

($\text{MW} = \text{molecular weight of the sample}$)
Calculation of $\mu$ from $\chi$

\[ \chi_m = N\mu^2 / 3kT \]

where $N$ is Avogadro's No.; $k$ is the Boltzmann and $T$ the absolute temp

Rewriting this gives the magnetic moment as

\[ \mu = 2.828 \sqrt[1/2]{\chi_m T} = 2.828(\chi_m T)^{1/2} \]
Many transition metal salts and complexes are paramagnetic due to partially filled d-orbitals.

The experimentally measured magnetic moment ($\mu$) (and from the equation in the previous page) can provide some important information about the compounds themselves:

- No of unpaired electrons present
- Distinction between HS and LS octahedral complexes
- Spectral behavior, and
- Structure of the complexes
Sources of Paramagnetism

Orbital motion of the electron generates ORBITAL MAG. MOMENT ($\mu_l$)

Spin motion of the electron generates SPIN MAG. MOMENT ($\mu_s$)

$l = \text{orbital angular momentum}; s = \text{spin angular momentum}$

For multi-electron systems

\[ L = l_1 + l_2 + l_3 + \ldots \]
\[ S = s_1 + s_2 + s_3 + \ldots \]

\[ \mu_{l+s} = [4S(S+1)+ L(L+1)]^{1/2} \quad \text{B.M.} \]
For TM-complexes, the magnetic properties arise mainly from the exposed $d$-orbitals. The $d$-orbitals are perturbed by ligands. 

\[ \boxed{\mu_{I+s} = \left[4S(S+1) + L(L+1)\right]^{1/2} \text{B.M.}} \]

\[ \mu_s = \left[4S(S+1)\right]^{1/2} \text{B.M.} \]

\[ S = n \left(\frac{1}{2}\right) = n/2; \text{ n = no of unpaired electrons} \]

Hence

\[ \mu_s = \left[4\left(n/2\right)\left(n/2+1\right)\right]^{1/2} \text{B.M.} \]

\[ = \left[n(n+2)\right]^{1/2} \text{B.M.} \]

This is called Spin-Only Formula

\[ \mu_s = 1.73, 2.83, 3.88, 4.90, 5.92 \text{ BM for n = 1 to 5, respectively} \]
There must be an unfilled / half-filled orbital similar in energy to that of the orbital occupied by the unpaired electrons. If this is so, the electrons can make use of the available orbitals to circulate or move around the center of the complexes and hence generate $L$ and $\mu_L$.

Essential Conditions:

• The orbitals should be degenerate ($t_{2g}$ or $e_g$)
• The orbitals should be similar in shape and size, so that they are transferable into one another by rotation about the same axis (e.g. $d_{xy}$ is related to $d_{x^2-y^2}$ by a rotation of $45^\circ$ about the z-axis).
• Orbitals must not contain electrons of identical spin.
When does orbital angular momentum contribute?

For an octahedral complex

<table>
<thead>
<tr>
<th>Condition</th>
<th>$t_{2g}$ set</th>
<th>$e_g$ set</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Obeyed</td>
<td>Obeyed</td>
</tr>
<tr>
<td>2</td>
<td>Obeyed</td>
<td>Not obeyed</td>
</tr>
<tr>
<td>3</td>
<td>Since 1 and 2 are satisfied</td>
<td>Does not matter</td>
</tr>
<tr>
<td></td>
<td>condition 3 dictates whether</td>
<td>since condition 2</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}$ will generate $\mu_1$ or not</td>
<td>is already not obeyed</td>
</tr>
</tbody>
</table>

These conditions are fulfilled whenever one or two of the three $t_{2g}$ orbitals contain an odd no. of electrons.

Exercise: Work-out all possible cases of $d^n$ LS and HS cases with orbital contribution.

HS:  
LS:
## Orbital contribution in Octahedral Complexes

<table>
<thead>
<tr>
<th>Ion</th>
<th>Config</th>
<th>OAM?</th>
<th>μ&lt;sub&gt;so&lt;/sub&gt;</th>
<th>μ&lt;sub&gt;obs&lt;/sub&gt;</th>
<th>μ&lt;sub&gt;S+L&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>Ti(III)</td>
<td>d1</td>
<td>yes</td>
<td>1.73</td>
<td>1.6-1.7</td>
<td>3.00</td>
</tr>
<tr>
<td>V(IV)</td>
<td>d1</td>
<td>yes</td>
<td>1.73</td>
<td>1.7-1.8</td>
<td></td>
</tr>
<tr>
<td>V(III)</td>
<td>d2</td>
<td>yes</td>
<td>2.83</td>
<td>2.7-2.9</td>
<td>4.47</td>
</tr>
<tr>
<td>Cr(IV)</td>
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<td>yes</td>
<td>2.83</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>V(II)</td>
<td>d3</td>
<td>no</td>
<td>3.88</td>
<td>3.8-3.9</td>
<td>5.20</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>d3</td>
<td>no</td>
<td>3.88</td>
<td>3.7-3.9</td>
<td></td>
</tr>
<tr>
<td>Mn(IV)</td>
<td>d3</td>
<td>no</td>
<td>3.88</td>
<td>3.8-4.0</td>
<td></td>
</tr>
<tr>
<td>Cr(II)</td>
<td>d4 h.s.</td>
<td>no</td>
<td>4.90</td>
<td>4.7-4.9</td>
<td>5.48</td>
</tr>
<tr>
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<td>2.83</td>
<td>3.2-3.3</td>
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<tr>
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<td>4.9-5.0</td>
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</tr>
<tr>
<td>Mn(III)</td>
<td>d4 l.s.</td>
<td>yes</td>
<td>2.83</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>d5 h.s.</td>
<td>no</td>
<td>5.92</td>
<td>5.6-6.1</td>
<td>5.92</td>
</tr>
<tr>
<td>Mn(II)</td>
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<tr>
<td>Fe(III)</td>
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<td>Fe(III)</td>
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<td>1.73</td>
<td>2.0-2.5</td>
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</tr>
<tr>
<td>Fe(II)</td>
<td>d6 h.s.</td>
<td>yes</td>
<td>4.90</td>
<td>5.1-5.7</td>
<td>5.48</td>
</tr>
<tr>
<td>Co(II)</td>
<td>d7 h.s.</td>
<td>yes</td>
<td>3.88</td>
<td>4.3-5.2</td>
<td>5.20</td>
</tr>
<tr>
<td>Co(II)</td>
<td>d7 l.s.</td>
<td>no</td>
<td>1.73</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
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<tr>
<td>Cu(II)</td>
<td>d9</td>
<td>no</td>
<td>1.73</td>
<td>1.7-2.2</td>
<td>3.00</td>
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### Orbital contribution in Tetrahedral Complexes

<table>
<thead>
<tr>
<th>Ion</th>
<th>Config</th>
<th>OAM?</th>
<th>$\mu_{so}$</th>
<th>$\mu_{obs}$</th>
<th>$\mu_{S+L}$</th>
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<tbody>
<tr>
<td>Cr(V)</td>
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<td>Cr(IV)</td>
<td>d2</td>
<td>no</td>
<td>2.83</td>
<td>2.8</td>
<td>4.47</td>
</tr>
<tr>
<td>Mn(V)</td>
<td>d2</td>
<td>no</td>
<td>2.83</td>
<td>2.6-2.8</td>
<td></td>
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<tr>
<td>Fe(V)</td>
<td>d3</td>
<td>yes</td>
<td>3.88</td>
<td>3.6-3.7</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td>d4</td>
<td>yes</td>
<td>4.90</td>
<td>-</td>
<td>5.48</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>d5</td>
<td>no</td>
<td>5.92</td>
<td>5.9-6.2</td>
<td>5.92</td>
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<td>Fe(II)</td>
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<td>no</td>
<td>4.90</td>
<td>5.3-5.5</td>
<td>5.48</td>
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<td>Co(II)</td>
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<td>3.88</td>
<td>4.2-4.8</td>
<td>5.20</td>
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<tr>
<td>Ni(II)</td>
<td>d8</td>
<td>yes</td>
<td>2.83</td>
<td>3.7-4.0</td>
<td>4.47</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>d9</td>
<td>yes</td>
<td>1.73</td>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>
Although $\mu$ normally develops from GS, sometimes ES also may contribute, especially the GS-ES energy difference is very small.

Example:
Take Ni$^{2+}$ octahedral; $d^8$; GS: $t_{2g}^6e_g^2$ no $\mu_l$

ES: $t_{2g}^5e_g^3$ $\mu_l$ contributes

Similarly,
Take Co$^{2+}$ tetrahedral; $d^7$ GS: $e^4t_{2g}^3$ no $\mu_l$

ES: $e^3t_{2g}^4$ $\mu_l$ contributes

Therefore; $\mu_{obs} > \mu_s$ for both $O_h$ Ni$^{2+}$ and $T_d$ Co$^{2+}$
Magnetic Properties of lanthanides

- 4f electrons are too far inside $4f^{n}5s^{2}5p^{6}$ (compared to the d electrons in transition metals)
- Therefore, 4f normally unaffected by surrounding ligands
- Hence, the magnetic moments of Ln$^{3+}$ ions are generally well-described from the coupling of spin and orbital angular momenta ~ Russell-Saunders Coupling to give J vector

- Spin orbit coupling constants are large (ca. 1000 cm$^{-1}$)
- Ligand field effects are very small (ca. 100 cm$^{-1}$)
  - Only ground J-state is populated
  - Spin-orbit coupling $>>$ ligand field splittings

- Magnetism is essentially independent of environment
• Magnetic moment of a J-state is expressed by:

\[ \mu = g_J \sqrt{J(J+1)} \mu_B \]
\[ g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \]

\[ J = L+S, \; L+S-1, \ldots \ldots \; L-S \]

• For the calculation of g value, we use
  minimum value of J for the configurations up to half-filled;
  i.e. J = L−S for f^0-f^7 configurations
  maximum value of J for config. more than half-filled;
  i.e. J = L+S for f^8-f^{14} configurations

• For f^0, f^7, and f^{14}, L = 0, hence \( \mu_J \) becomes \( \mu_S \)
<table>
<thead>
<tr>
<th>config</th>
<th>g.s.</th>
<th>No. e-</th>
<th>color</th>
<th>calc'd</th>
<th>obsd</th>
</tr>
</thead>
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<tr>
<td>La</td>
<td>$4f^0$</td>
<td>$^1S_0$</td>
<td>0</td>
<td>Colorless</td>
<td>0</td>
</tr>
<tr>
<td>Ce</td>
<td>$4f^1$</td>
<td>$^2F_{5/2}$</td>
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<td>Colorless</td>
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<td>Pr</td>
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<td>$^3H_4$</td>
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<td>Nd</td>
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<td>$^4I_{9/2}$</td>
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<td>Lilac</td>
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<td>Pm</td>
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<tr>
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<td>$^7F_0$</td>
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<td>0</td>
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<tr>
<td>Gd</td>
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<td>$^8S_{7/2}$</td>
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<td>Colorless</td>
<td>7.94</td>
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<tr>
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<td>$^7F_6$</td>
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<td>9.72</td>
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<td>Dy</td>
<td>$4f^9$</td>
<td>$^6H_{15/2}$</td>
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<td>Yellow</td>
<td>10.65</td>
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<tr>
<td>Ho</td>
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<td>$^5I_8$</td>
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<td>Yellow</td>
<td>10.6</td>
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<tr>
<td>Er</td>
<td>$4f^{11}$</td>
<td>$^4I_{15/2}$</td>
<td>3</td>
<td>Rose-pink</td>
<td>9.58</td>
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<tr>
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<td>$^3H_6$</td>
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<td>$^2F_{7/2}$</td>
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<td>Colorless</td>
<td>4.54</td>
</tr>
<tr>
<td>Lu</td>
<td>$4f^{14}$</td>
<td>$^1S_0$</td>
<td>0</td>
<td>Colorless</td>
<td>0</td>
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</tbody>
</table>
Sample Landè Calculation for a Ln$^{3+}$ ion

e.g Pr$^{3+}$ [Xe]4f$^2$; find Ground State from Hund's Rules

- $S = 1/2 + 1/2 = 1$
- $L = 3 + 2 = 5$
- $J = 6, 5, 4$; $J = 4$ is chosen for f$^2$
- $g = (3/2) + [1(1+1) - 5(5+1)]/2(4)(4+1) = 0.8$

$\mu_J = 3.577$ B.M. Experiment = 3.4 - 3.6 B.M

- Landé formula fits well with observed magnetic moments for all but Sm$^{III}$ and Eu$^{III}$ ions.

- Moments of these ions are altered from the Landé expression by temperature-dependent population of low-lying excited J-state(s)
Use of Ln\(^{3+}\) Magnetic Moments?

NMR Shift Reagents - paramagnetism of lanthanide ions is utilized to spread resonances in 1H NMR of organic molecules that coordinate to lanthanides.
Magnetic States of Matter

- **Diamagnet** - A diamagnetic compound has all of its electron spins paired giving a net spin of zero. Diamagnetic compounds are weakly repelled by a magnet.

- **Paramagnet** - A paramagnetic compound will have some electrons with unpaired spins. Paramagnetic compounds are attracted by a magnet. Paramagnetism derives from the spin and orbital angular momenta of electrons. This type of magnetism occurs only in compounds containing unpaired electrons, as the spin and orbital angular momenta is cancelled out when the electrons exist in pairs.

- Compounds in which the paramagnetic centres are separated by diamagnetic atoms within the sample are said to be magnetically dilute.
Magnetic States of Matter

- If the diamagnetic atoms are removed from the system then the paramagnetic centers interact with each other. This interaction leads to **ferromagnetism** (in the case where the neighboring magnetic dipoles are aligned in the same direction) and **antiferromagnetism** (where the neighboring magnetic dipoles are aligned in alternate directions).
Magnetic States of Matter

Curie-Weiss Law for anti-ferromagnetic substance

Curie Law for paramagnetic substance

Curie-Weiss Law for ferromagnetic substance

\[\frac{1}{\chi} \quad \text{vs} \quad T (K)\]
Figure B23-3
Shriver & Atkins Inorganic Chemistry, Fourth Edition
Paired spins

Polarization (favourable alignment)
Figure B23-6
Shriver & Atkins Inorganic Chemistry, Fourth Edition
Magnetic States of Matter

• These two forms of paramagnetism show characteristic variations of the magnetic susceptibility with temperature.

• In the case of ferromagnetism, above the Curie point the material displays "normal" paramagnetic behavior. Below the Curie point the material displays strong magnetic properties. Ferromagnetism is commonly found in compounds containing iron and in alloys.

• For antiferromagnetism, above the Neel point the material displays "normal" paramagnetic behavior. Below the Neel point the material displays weak magnetic properties which at lower and lower temperatures can become essentially diamagnetic. Antiferromagnetism is more common and is found to occur in transition metal halides and oxides, such as TiCl$_3$ and VCl$_2$. 
Problem:

- Account for the magnetic moments of $(\text{Et}_4\text{N})_2\text{[NiCl}_4\text{]}$ recorded at 80 and 300 K.
- 80K  300K
- 3.25  3.89 B.M.
- Ni$^{2+}$ is a d$^8$ metal ion.
- The formula suggests a 4 coordinate complex and we can assume that the complex is tetrahedral with a d electron configuration of e$^4$ t$_2^4$ therefore the spin-only magnetic moment can be calculated as 2.83 BM.
- Why did we ignore the possibility of it being square-planar?
- The free ion Russell-Saunders ground term is $^3F$ (L=3 and S=1) which will give rise to a lowest energy T term in a tetrahedral field and hence the resultant magnetic moment is expected to be temperature dependent and have a direct orbital contribution.
• The observed values may be quite different then to the calculated spin only magnetic moment.
• The value of $\mu_{S+L}$ can be calculated as: $\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$
  
  $= \sqrt{8+12} = \sqrt{20} = 4.47$ B.M.
• If you use the spin-only formula $\mu_s = \sqrt{n(n+2)} = \sqrt{8} = 2.8$ BM
• Now go back and check above the observed magnetic moments at the given temperatures. What do you conclude?
• From the observed values it can be seen that the magnetic moment of the $d^8$ Ni$^{2+}$ complex is intermediate between the $\mu_s$ and $\mu_{S+L}$ values (probably due to partial quenching of the orbital angular momentum contribution) and is dependent on temperature.