Summary of applicable formulae

1) Spin-Only magnetic moment
\[ \mu_{s.o.} = \sqrt{4S(S+1)} \text{ B.M.} \]

2) For A and E ground terms
\[ \mu_{\text{eff}} = \mu_{s.o.} \left(1 - \alpha \frac{\lambda}{\Delta} \right) \text{ B.M.} \]
Do not expect Temperature dependence.

3) For T ground terms with orbital angular momentum contribution
\[ \mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.} \]
T terms generally show marked Temperature dependence.

The examples that follow are arranged showing the experimentally observed values, the theoretical "spin-only" value and possible variations expected.

A number of the examples involve "alums" where the central Transition Metal ion can be considered to be octahedrally coordinated by water molecules.

d\(^1\)

VCl\(_4\)  
V(IV) tetrahedral

<table>
<thead>
<tr>
<th></th>
<th>80K</th>
<th>300K</th>
<th>(\mu_{s.o.} / \text{B.M.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu_{\text{eff}})</td>
<td>1.6</td>
<td>1.6</td>
<td>1.73</td>
</tr>
</tbody>
</table>

\(^{2}\)E ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell, the sign of \(\lambda\) is positive so the effect on \(\mu\) should be that \(\mu_{\text{eff}} < \mu_{s.o.}\).

VCl\(_6\)\(^{2-}\)  
V(IV) octahedral

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>(\mu_{\text{eff}})</td>
<td>1.4</td>
<td>1.8</td>
<td>1.73</td>
</tr>
</tbody>
</table>

\(^{2}\)T\(_{2g}\) ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate \(\mu_{S+L}\) from equation 3) above.  
For a full S+L contribution this would give \(\mu_{S+L} = 3 \text{ B.M.}\) which is clearly much higher than the 1.8 B.M. found at 300K.
So, $\mu_{\text{s.o.}} < \mu_{\text{obs}} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.

\[ \text{d}^2 \]

$V^{3+}$ in (NH$_4$)$_2$V(SO$_4$)$_2$.12H$_2$O (an alum)

<table>
<thead>
<tr>
<th></th>
<th>80K</th>
<th>300K</th>
<th>$\mu_{\text{s.o.}}$ / B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.7</td>
<td>2.7</td>
<td>2.83</td>
</tr>
</tbody>
</table>

$^3T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.

Since there is a direct orbital angular momentum contribution we should calculate $\mu_{S+L}$ from equation 3) above.

For a full S+L contribution this would give $\mu_{S+L} = \sqrt{20} = 4.47$ B.M. which is clearly much higher than the 2.7 B.M. found at 300K.

So, $\mu_{\text{obs}} < \mu_{\text{s.o.}} < \mu_{S+L}$
showing that the magnetic moment is significantly quenched.

In this case, there is no observed Temperature variation between 80 and 300K and it may require much lower temperatures to see the effect?

\[ \text{d}^3 \]

$Cr^{3+}$ in KCr(SO$_4$)$_2$.12H$_2$O (an alum)

<table>
<thead>
<tr>
<th></th>
<th>80K</th>
<th>300K</th>
<th>$\mu_{\text{s.o.}}$ / B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.8</td>
<td>3.8</td>
<td>3.87</td>
</tr>
</tbody>
</table>

$^4A_{2g}$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell the sign of $\lambda$ is positive so the effect on $\mu$ should be that $\mu_{\text{eff}} < \mu_{\text{s.o.}}$

\[ \text{d}^4 \]

$\text{CrSO}_4.6\text{H}_2\text{O}$

<table>
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<th>$\mu_{\text{s.o.}}$ / B.M.</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>4.8</td>
<td>4.8</td>
<td>4.9</td>
</tr>
</tbody>
</table>

$^5E_g$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be
accounted for by equation 2) above. For less than a half-filled d shell the sign of \( \lambda \) is positive so the effect on \( \mu \) should be that \( \mu_{\text{eff}} < \mu_{\text{s.o.}} \).

\[ \text{K}_3\text{Mn(CN)}_6 \]
Mn(III) low-spin octahedral

<table>
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<tr>
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<th>80K</th>
<th>300K</th>
<th>( \mu_{\text{s.o.}} ) / B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.1</td>
<td>3.2</td>
<td>2.83</td>
</tr>
</tbody>
</table>

\( ^3T_{1g} \) ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.

Since there is a direct orbital angular momentum contribution we should calculate \( \mu_{S+L} \) from equation 3) above.

For a full S+L contribution this would give \( \mu_{S+L} = \sqrt{20} = 4.47 \) B.M. which is clearly much higher than the 3.2 B.M. found at 300K.

So, \( \mu_{\text{s.o.}} < \mu_{\text{eff}} < \mu_{S+L} \)

showing that the magnetic moment is partially quenched.

In this case, there is a small Temperature variation observed between 80 and 300K.

\[ \text{K}_2\text{Mn(SO}_4\text{)}_2.6\text{H}_2\text{O (an alum)} \]
Mn(II) high-spin octahedral

<table>
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<tbody>
<tr>
<td></td>
<td>5.9</td>
<td>5.9</td>
<td>5.92</td>
</tr>
</tbody>
</table>

\( ^6A_{1g} \) ground term - hence do not expect Temperature dependence and \( L=0 \) so no orbital contribution possible.

Expect \( \mu_{\text{eff}} = \mu_{\text{s.o.}} \).

\[ \text{K}_3\text{Fe(CN)}_6 \]
Fe(III) low-spin octahedral

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<tr>
<td></td>
<td>2.2</td>
<td>2.4</td>
<td>1.73</td>
</tr>
</tbody>
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\( ^2T_{2g} \) ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.

Since there is a direct orbital angular momentum contribution we should calculate \( \mu_{S+L} \) from equation 3) above.

For a full S+L contribution this would give \( \mu_{S+L} = \sqrt{9} = 3 \) B.M. which is clearly much higher than the 2.4 B.M. found at 300K.

So, \( \mu_{\text{s.o.}} < \mu_{\text{obs}} < \mu_{S+L} \)

showing that the magnetic moment is partially quenched.
$d^6$

Fe$^{2+}$ in $(NH_4)_2Fe(SO_4)_2.6H_2O$ (an alum)
Fe(II) high-spin octahedral

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<tbody>
<tr>
<td>Temperature dependence and large variation from spin-only value may be observed at low temperatures.</td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

Since there is a direct orbital angular momentum contribution we should calculate $\mu_{S+L}$ from equation 3) above. For a full S+L contribution this would give $\mu_{S+L} = \sqrt{30} = 5.48$ B.M. which is close to the 5.5 B.M. found at 300K. So, $\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$ showing that the magnetic moment is not showing much quenching.

$T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.

$\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$ showing that the magnetic moment is not showing much quenching.

$\mu_{eff} > \mu_{s.o.}$

The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!

$Co^{2+}$ in $(NH_4)_2Co(SO_4)_2.6H_2O$ (an alum)
Co(II) high-spin octahedral

$T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.

Since there is a direct orbital angular momentum contribution we should calculate $\mu_{S+L}$ from equation 3) above. For a full S+L contribution this would give $\mu_{S+L} = \sqrt{27} = 5.2$ B.M. which is close to the 5.1 B.M. found at 300K. So, $\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$ showing that the magnetic moment is not showing much quenching.

$\mu_{eff} > \mu_{s.o.}$

The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!
$d^8$

Ni$^{2+}$ in (NH$_4$)$_2$Ni(SO$_4$)$_2$.6H$_2$O (an alum)

Ni(II) octahedral

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<tbody>
<tr>
<td>80K</td>
<td>3.3</td>
<td>3.3</td>
<td>2.83</td>
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$^3$A$_{2g}$ ground term - hence don’t expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of $\lambda$ is negative so the effect on $\mu$ should be that $\mu_{\text{eff}} > \mu_{\text{s.o.}}$.

The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!

(Et$_4$N)$_2$NiCl$_4$

Ni(II) tetrahedral

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<td>3.2</td>
<td>3.8</td>
<td>2.83</td>
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$^3$T$_2$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.

Since there is a direct orbital angular momentum contribution we should calculate $\mu_{S+L}$ from equation 3) above. For a full $S+L$ contribution this would give $\mu_{S+L} = \sqrt{20} = 4.47$ B.M. which is higher than the 3.8 B.M. found at 300K.

So, $\mu_{\text{s.o.}} < \mu_{\text{obs}} < \mu_{S+L}$ showing that the magnetic moment is partially quenched.

$d^9$

Cu$^{2+}$ in (NH$_4$)$_2$Cu(SO$_4$)$_2$.6H$_2$O (an alum)

Cu(II) octahedral

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<tbody>
<tr>
<td>80K</td>
<td>1.9</td>
<td>1.9</td>
<td>1.73</td>
</tr>
</tbody>
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$^2$E$_g$ ground term - hence don’t expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of $\lambda$ is negative so the effect on $\mu$ should be that $\mu_{\text{eff}} > \mu_{\text{s.o.}}$.

Contributors

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)