Movement of an electrical charge (which is the basis of electric currents) generates a magnetic field in a material. Magnetism is therefore a characteristic property of all materials that contain electrically charged particles and for most purposes can be considered to be entirely of electronic origin.

![Diagram of current direction and magnetic field](image)

**The Right Hand Rule for an induced magnetic field**

In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes whereas the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties.

Historically, magnetism has been recognized for thousands of years. An account, that is probably apochryphal, tells of a shepherd called Magnes in Crete who around 900 B.C discovered the naturally occurring magnet lodestone (a form of the the spinel magnetite, Fe$_3$O$_4$) in a region later named Magnesia. Supposedly while he was walking over a deposit, the lodestone pulled the nails out of his sandals and the metal tip from his staff.

**The Classical Theory of Magnetism**

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law states that when a substance is placed within a magnetic field, $\langle H \rangle$, the field within the substance, $\langle B \rangle$, differs from $\langle H \rangle$ by the induced field, $\langle 4\pi I \rangle$, which is proportional to the intensity of magnetization, $\langle I \rangle$. That is;

$$\langle B \rangle = \langle H \rangle + 4\pi\langle I \rangle$$

where $\langle B \rangle$ is the magnetic field within the substance and $\langle H \rangle$ is the applied magnetic field and $\langle I \rangle$ is the intensity of magnetization.

Lenz's Law (1834)

Lenz's Law can also be written as

$$\langle B \rangle = \langle H \rangle + 4\pi\langle I \rangle$$
\[
\frac{B}{H} = 1 + \frac{4\pi I}{H}
\]

or

\[
\frac{B}{H} = 1 + 4\pi \kappa
\]

where

- \(\frac{B}{H}\) 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 under those conditions the equation would reduce to \(\frac{B}{H}\). It is usually more convenient to measure mass than volume and the mass susceptibility, \(\chi_g\), is related to the volume susceptibility, \(\kappa\), through the density.

\[
\chi_g = \frac{\kappa}{\rho}
\]

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

\[
\chi_m = \chi_g \times RMM
\]

Since this value includes the underlying diamagnetism of paired electrons, it is necessary to correct for the diamagnetic portion of \(\chi_m\) to get a corrected paramagnetic susceptibility.

\[
\chi'_m = \chi_m + \chi_{dia}
\]

Examples of these corrections are tabulated below.

*Table of Diamagnetic Corrections (Pascal's constants, \(10^{-6}\) c.g.s. units)*

<table>
<thead>
<tr>
<th>Ion</th>
<th>DC</th>
<th>Ion</th>
<th>DC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>6.8</td>
<td>Co²⁺</td>
<td>12.8</td>
</tr>
<tr>
<td>K⁺</td>
<td>14.9</td>
<td>Co³⁺</td>
<td>12.8</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>13.3</td>
<td>Ni²⁺</td>
<td>12.8</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>40</td>
<td>VO²⁺</td>
<td>12.5</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>12.8</td>
<td>Mn³⁺</td>
<td>12.5</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>12.8</td>
<td>Cr³⁺</td>
<td>12.5</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>12.8</td>
<td>Cl⁻</td>
<td>23.4</td>
</tr>
<tr>
<td>Ion</td>
<td>DC</td>
<td>Ion</td>
<td>DC</td>
</tr>
<tr>
<td>-------</td>
<td>-----</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>Br⁻</td>
<td>34.6</td>
<td>SO₄²⁻</td>
<td>40.1</td>
</tr>
<tr>
<td>I⁻</td>
<td>50.6</td>
<td>OH⁻</td>
<td>12</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>18.9</td>
<td>C₂O₄²⁻</td>
<td>34</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>32</td>
<td>OAc⁻</td>
<td>31.5</td>
</tr>
<tr>
<td>IO₄⁻</td>
<td>51.9</td>
<td>pyr</td>
<td>49.2</td>
</tr>
<tr>
<td>CN⁻</td>
<td>13</td>
<td>Me-pyr</td>
<td>60</td>
</tr>
<tr>
<td>NCS⁻</td>
<td>26.2</td>
<td>Acac⁻</td>
<td>62.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>13</td>
<td>en</td>
<td>46.3</td>
</tr>
<tr>
<td>EDTA⁴⁻</td>
<td>~150</td>
<td>urea</td>
<td>33.4</td>
</tr>
</tbody>
</table>

These can be converted to S.I units of m³ mol⁻¹ by multiplying by 4 π x 10⁻⁷.

There are numerous methods for measuring magnetic susceptibilities, including, the **Gouy, Evans and Faraday methods**. These all depend on measuring the force exerted upon a sample when it is placed in a magnetic field. The more paramagnetic the sample, the more strongly it will be drawn toward the more intense part of the field.

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**Determination of Magnetic Susceptibility**

- **The Gouy Method:** The underlying theory of the Gouy method is described here and a form for calculating the magnetic moment from the collected data is available as well.
- **The Evans method:** The Evans balance measures the change in current required to keep a pair of suspended magnets in place or balanced after the interaction of the magnetic field with the sample. The Evans balance differs from that of the Gouy in that, in the former the permanent magnets are suspended and the position of the sample is kept constant while in the latter the position of the magnet is constant and the sample is suspended between the magnets.

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**Orbital contribution to magnetic moments**

From a quantum mechanics viewpoint, the magnetic moment is dependent on both spin and orbital angular momentum contributions. The spin-only formula used last year was given as:

\[ \mu_{s.o.} = \sqrt{4S(S+1)} \]
and this can be modified to include the orbital angular momentum

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

An orbital angular momentum contribution is expected when the ground term is triply degenerate (i.e. a triplet state). These show temperature dependence as well.

In order for an electron to contribute to the orbital angular momentum the orbital in which it resides must be able to transform into an exactly identical and degenerate orbital by a simple rotation (it is the rotation of the electrons that induces the orbital contribution). For example, in an octahedral complex the degenerate $t_{2g}$ set of orbitals ($d_{xz}, d_{yx}, d_{yz}$) can be interconverted by a $90^\circ$ rotation. However the orbitals in the $e_g$ subset ($d_{z^2}, d_{x^2-y^2}$) cannot be interconverted by rotation about any axis as the orbital shapes are different; therefore an electron in the $e_g$ set does not contribute to the orbital angular momentum and is said to be quenched. In the free ion case the electrons can be transformed between any of the orbitals as they are all degenerate, but there will still be partial orbital quenching as the orbitals are not identical.

Electrons in the $t_{2g}$ set do not always contribute to the orbital angular moment. For example in the $d^3$, $t_{2g}^3$ case, an electron in the $d_{xz}$ orbital cannot by rotation be placed in the $d_{yz}$ orbital as the orbital already has an electron of the same spin. This process is also called quenching.

Tetrahedral complexes can be treated in a similar way with the exception that we fill the $e$ orbitals first, and the electrons in these do not contribute to the orbital angular momentum. The tables in the links below give a list of all $d^1$ to $d^9$ configurations including high and low spin complexes and a statement of whether or not a direct orbital contribution is expected.

- Octahedral complexes
- Tetrahedral complexes

A and E ground terms

The configurations corresponding to the $A_1$ (free ion S term), E (free ion D term), or $A_2$ (from F term) do not have a direct contribute to the orbital angular momentum. For the $A_2$ and E terms there is always a higher T term of the same multiplicity as the ground term which can affect the magnetic moment (usually by a only small amount).

$$\mu_{\text{eff}} = \mu_{\text{(s.o.)}} (1-\alpha \lambda /\Delta) \label{eq10}$$

where $\alpha$ is a constant (2 for an E term, 4 for an $A_2$ term) and $\lambda$ is the spin-orbit coupling constant which is generally only available for the free ion but this does give important information since the sign of the value varies depending on the orbital occupancy.

Some spin-orbit coupling constants for 1st row TM ions

<table>
<thead>
<tr>
<th>metal ion</th>
<th>Ti(III)</th>
<th>V(III)</th>
<th>Cr(III)</th>
<th>Mn(III)</th>
<th>Fe(II)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
</tbody>
</table>
For \((d^1)\) to \((d^4)\) the value is positive hence \(μ_{(eff)}\) is less than \(μ_{(so)}\) and for \((d^6)\) to \((d^9)\) the value is negative hence \(μ_{(eff)}\) is greater than \(μ_{(so)}\). \(Δ\) is the crystal field splitting factor which again is often not available for complexes.

For the tetrahedral Co(II) ion, \(\text{CoCl}_4^{2-}\), the observed experimental magnetic moment, \(μ_{obs} = 4.59\) Bohr Magneton (B.M.) The spin-only magnetic moment, \(μ_{s.o.} = 3.88\) B.M. which is not in good agreement. How can we improve the analysis?

Since the ground term in the tetrahedral field is split from a \(^4F\) to a \(^4A_2\) term then we can apply the Equation \ref{eq10}. For an \(\langle A\rangle\) term the constant \(α = 4\). The spin-orbit coupling constant, \(λ\) for the free ion is \(-172\) cm\(^{-1}\) which we can use as an approximation and \(Δ = 3100\) cm\(^{-1}\). Hence

\[
μ_{(eff)} = 3.88 \times (1 - (4 \times 172) / 3100)
\]

which comes out at \(μ_{eff} = 4.73\) B.M.

This gives a much better fit than the spin-only formula. In the case of the series:

\(\text{CoI}_4^{2-}, \text{CoBr}_4^{2-}, \text{CoCl}_4^{2-}, \text{Co(NCS)}_4^{2-}\)

the magnetic moments have been recorded as 4.77, 4.65, 4.59, 4.40 BM assuming that \(λ\) is roughly a constant, then this variation shows the inverse effect of the spectrochemical series on the magnetic moment, since \(Δ\) is expected to increase from I- to NCS-.

---

**T ground terms**

The configurations corresponding to the \(T_2\) term (from D) or a \(T_1\) term (from an F term) are those where there is a direct contribution to orbital angular momentum expected. The magnetic moments of complexes with T terms are often found to show considerable temperature dependence. This is as a result of spin-orbit coupling that produces levels whose energy differences are frequently of the order \(kT\), so as a result, temperature will have a direct effect on the population of the levels arising in the magnetic field.

In a Kotani plot \(μ_{eff}\) is plotted against \(kT/λ\) and when this corresponds to a value of 1 then \(μ\) equals the "spin-only" value. If this is extrapolated to infinity then the value corresponds to \(μ_{S+L}\).
Measuring the magnetic moment at 80 K and 300 K often shows up this variation with temperature.

Example \(\PageIndex{1}\):

Account for the magnetic moments of the complex, \((\text{Et}_4\text{N})_2\text{[NiCl}_4\text{]}\) recorded at 80, 99 and 300 K.

<table>
<thead>
<tr>
<th>80K</th>
<th>99K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>3.43</td>
<td>3.89 B.M.</td>
</tr>
</tbody>
</table>

\(\text{Ni}^{2+}\) 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 \(^3\text{F}\) (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:

\[
\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}
\]

or

\[
\mu_{S+L} = \sqrt{8 + 12}
\]

or

\[
\mu_{S+L} = \sqrt{20} = 4.472\;\text{B.M.}
\]
From the observed values it can be seen that the magnetic moment of the $d^8 \text{Ni}^{2+}$ complex is intermediate between the $\mu_{so}$ and $\mu_{S+L}$ values (probably due to partial quenching of the orbital angular momentum contribution) and is dependent on temperature. Further worked examples and some selected magnetic data are available.

Contributors

- {{template.ContribLancashire()}}