Complexes that contain unpaired electrons are paramagnetic and are attracted into magnetic fields. Diamagnetic compounds are those with no unpaired electrons are repelled by a magnetic field. All compounds, including transition metal complexes, possess some diamagnetic component which results from paired electrons moving in such a way that they generate a magnetic field that opposes an applied field. The magnitude of paramagnetism is measured in terms of the magnetic moment, \(\langle \mu \rangle\), where the larger the magnitude of \(\langle \mu \rangle\), greater the paramagnetism of the compound.

**Magnetic Susceptibility**

The magnetic susceptibility measures the strength of interaction on placing the substance in a magnetic field. For chemical applications the molar magnetic susceptibility (\(\chi_{mol}\)) is the preferred quantity and is measured in \(\text{m}^3\cdot\text{mol}^{-1}\) (SI) or \(\text{cm}^3\cdot\text{mol}^{-1}\) (CGS) and is defined as

\[
\chi_{mol} = M\chi_v/\rho
\]

where \(\rho\) is the density in \(\text{kg}\cdot\text{m}^{-3}\) (SI) or \(\text{g}\cdot\text{cm}^{-3}\) (CGS) and \(M\) is molar mass in \(\text{kg}\cdot\text{mol}^{-1}\) (SI) or \(\text{g}\cdot\text{mol}^{-1}\) (CGS). There are multiple 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.

**Origin of Paramagnetism**

Electrons in most atoms exist in pairs, with each electron spinning in an opposite direction. 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 materials such as iron, cobalt and nickel have unpaired electrons, so they don't cancel the electrons' magnetic fields. As result, each atom of these elements acts like very small magnets.

There are three origins of paramagnetism in complexes:

1. **Nuclear spin** (\(\mu_n\)): Some nuclei, such as a hydrogen atom, have a net spin, which creates a magnetic field.
2. **Electron spin** (\(\mu_s\)): An electron has two intrinsic spin states (similar to a top spinning) which we call up (\(\alpha\)) and down (\(\beta\)).
3. **Electron orbital motion** (\(\mu_l\)): There is a magnetic field due to the electron moving around the nucleus.

Each of these magnetic moments interact with one another and/or with external magnetic fields to generate interesting physics. However, some of these interactions are stronger than others and can be (tentatively) ignored. For example, the nuclear spin magnetic moment (#1 above), which is central to NMR spectroscopy, is appreciably weaker than the other two moments and we can ignore it for this discussion and focus on the electronic moments.

The classical theory of magnetism was well developed before quantum mechanics with (see Lenz Law). From a quantum mechanical picture, for an individual electron in a molecule or atom, we can identify the orbital angular momentum \(\ell\) and spin angular momentum \(s\). For multi-electron systems, the total orbital angular momentum \(\langle L\rangle\) and total spin angular momentum \(\langle S\rangle\) are sum of the constituent electron spins.
\[ L = l_1 + l_2 + l_3 + \ldots \]
and
\[ S = s_1 + s_2 + s_3 + \ldots \]

The total magnetic susceptibility from both orbital and spin angular momenta is
\[
\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)} \, \mu_B
\]

where \( \mu_B \) is the Bohr Magneton (\( 9.274 \times 10^{-24} \text{ J/T} \)).

The associated nuclear magneton \( \mu_N \) attributed to nuclear spin magnetic moments is ~2000 fold smaller than the Bohr magneton. This is why we can ignore the nuclear spin components for this discussion.

That is, the rotation of electrons about the nucleus is restricted which leads to
\[ L = 0 \]
and
\[ \mu_s = \sqrt{4S(S+1)} \, \mu_B \]

Equation \ref{spin} can be simplified to
\[ S = n(1/2) = n/2 \]
where \( n \) is the number of unpaired electrons in the complex. Hence
\[
\begin{align}
\mu_s &= \sqrt{4S(S+1)} \, \mu_B \\
&= \sqrt{4(n/2)(n/2+1)} \, \mu_B \\
&= \sqrt{n(n+2)} \, \mu_B
\end{align}
\]

Equation \ref{SpinOnly} is called Spin-Only Formula. For transient metal complexes, the magnetic properties arise primarily from the exposed d-orbitals that are perturbed by ligands. Hence, experimentally measured magnetic moment can provide some important information about the compounds themselves including: (1) number of unpaired electrons present, (2) high-spin vs. low-spin states, (3) spectral behavior, and (4) even structure of the complexes (Table \ref{SpinOnlyFormula}).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Number of unpaired electrons</th>
<th>( \mu_s )</th>
<th>observed moment /( \mu_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti^{3+}</td>
<td>1</td>
<td>( \sqrt{3} \approx 1.73 , \mu_B )</td>
<td>1.73</td>
</tr>
<tr>
<td>V^{4+}</td>
<td>1</td>
<td>( \sqrt{3} \approx 1.73 , \mu_B )</td>
<td>1.68–1.78</td>
</tr>
<tr>
<td>Ion</td>
<td>Number of unpaired electrons</td>
<td>(\langle</td>
<td>\mu_s</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------</td>
<td>-----------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>1</td>
<td>(\sqrt{3} \approx 1.73 , \mu_B)</td>
<td>1.70–2.20</td>
</tr>
<tr>
<td>V(^{3+})</td>
<td>2</td>
<td>(\sqrt{8} \approx 2.83 , \mu_B)</td>
<td>2.75–2.85</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>2</td>
<td>(\sqrt{8} \approx 2.83 , \mu_B)</td>
<td>2.8–3.5</td>
</tr>
<tr>
<td>V(^{2+})</td>
<td>3</td>
<td>(\sqrt{15} \approx 3.87 , \mu_B)</td>
<td>3.80–3.90</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>3</td>
<td>(\sqrt{15} \approx 3.87 , \mu_B)</td>
<td>3.70–3.90</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>3</td>
<td>(\sqrt{15} \approx 3.87 , \mu_B)</td>
<td>4.3–5.0</td>
</tr>
<tr>
<td>Mn(^{4+})</td>
<td>3</td>
<td>(\sqrt{15} \approx 3.87 , \mu_B)</td>
<td>3.80–4.0</td>
</tr>
<tr>
<td>Cr(^{2+})</td>
<td>4</td>
<td>(\sqrt{24} \approx 4.90 , \mu_B)</td>
<td>4.75–4.90</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>4</td>
<td>(\sqrt{24} \approx 4.90 , \mu_B)</td>
<td>5.1–5.7</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>5</td>
<td>(\sqrt{35} \approx 5.92 , \mu_B)</td>
<td>5.65–6.10</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>5</td>
<td>(\sqrt{35} \approx 5.92 , \mu_B)</td>
<td>5.7–6.0</td>
</tr>
</tbody>
</table>

The small deviations from the spin-only formula for these octahedral complexes can result from the neglect of orbital angular momentum or of spin-orbit coupling. Tetrahedral \(d^3\), \(d^4\), \(d^8\) and \(d^9\) complexes tend to show larger deviations from the spin-only formula than octahedral complexes of the same ion because quenching of the orbital contribution is less effective in the tetrahedral case.