Introduction to the Electronic Spectra of TM complexes

CFT is ideal for d\(^1\) (d\(^9\)) systems but tends to fail for the more common multi-electron systems.

This is because of d (electron-electron) repulsions in addition to the crystal field effects of the repulsion of the metal electrons by the ligand electrons.

To deal with this we introduce the concept of an electronic state.

The Electronic state refers to energy levels available to a group of electrons, just as electronic configurations refer to the way in which the electrons occupy the d orbitals.

When describing electronic configurations, lower case letters are used, eg t\(_{2g}\)\(^1\) etc. For electronic states, upper case (CAPITAL) letters are used and by analogy, a T state is triply degenerate and an E state is doubly degenerate.
Revision on Quantum Numbers (QN)

\( n \) = Principal QN \( \Rightarrow \) size of orbital and its energy  
\( l \) = Azimuthal/Orbital QN \( \Rightarrow \) shape of orbital \( \Rightarrow \) 0, 1, 2, 3…..n-1  
\( m_l \) = Magnetic QN  
\( m_s \) = Spin QN \( \Rightarrow \pm \frac{1}{2} \) for a single electron

<table>
<thead>
<tr>
<th></th>
<th>L</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>orbital</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>( m_l )</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

\( m_l \) is a subset of \( l \), where \( m_l \) take values from \( l \)…. 0….\(-l\).

There are thus \((2l + 1)\) values of \( m_l \) for each \( l \) value,

i.e. for the 1 s orbital \((l = 0)\), 3 p orbitals \((l = 1)\), 5 d orbitals \((l = 2)\), etc.
Russell-Saunders (R-S) coupling

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied.

In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterise the electronic states of atoms.

The interactions that can occur are of three types:
- spin-spin coupling $\Rightarrow S$
- orbit-orbit coupling $\Rightarrow L$
- spin-orbit coupling $\Rightarrow J$

There are two principal coupling schemes used:
- Russell-Saunders (or L - S) coupling
- $j$ - $j$ coupling.
Russell-Saunders (R-S) coupling

In the Russell Saunders scheme (named after Henry Norris Russell, 1877-1957 a Princeton Astronomer and Frederick Albert Saunders, 1875-1963 a Harvard Physicist and published in Astrophysics Journal, 61, 38, 1925) it is assumed that:


This is found to give a good approximation for first row transition series where J coupling can generally be ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.
Russell-Saunders (R-S) coupling

Spin-Spin coupling
S - the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual ms together and is as a result of coupling of spin quantum numbers for the separate electrons.

The total spin is normally reported as the value of $2S + 1$, which is called the multiplicity of the term:

<table>
<thead>
<tr>
<th>S</th>
<th>0</th>
<th>$\frac{1}{2}$</th>
<th>1</th>
<th>$\frac{3}{2}$</th>
<th>2</th>
<th>$\frac{5}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2S + 1$</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>singlet</td>
<td>doublet</td>
<td>triplet</td>
<td>quartet</td>
<td>quintet</td>
<td>sextet</td>
</tr>
</tbody>
</table>
Russell-Saunders (R-S) coupling

**Orbit-Orbit coupling**
L - the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows:

By analogy with the notation s, p, d, … for orbitals with \( l = 0, 1, 2, \ldots \), the total orbital angular momentum of an atomic term is denoted by the equivalent upper case letter:

**Total Orbital Momentum**

\[
L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \ldots
\]

S P D F G\ldots(omitting J)
Russell-Saunders (R-S) coupling

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Russell-Saunders (R-S) coupling

Spin-Orbit coupling

Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number.

Multiplicity occurs when several levels are close together and is given by the formula \((2S+1)\).

The multiplicity is written as a left superscript representing the value of L and the entire label of a term is called a term symbol.

The Russell Saunders term symbol is then written as: \((2S+1)L\)
Russell Saunders term symbol

Examples:
For a d¹ configuration:
\[ S = \frac{1}{2}, \text{ hence } (2S+1) = 2; \quad L=2 \]
and the ground term is written as \( ^2\!D \) \( \rightarrow \) doublet dee

For an s¹p¹ configuration:
\[ S = \text{ both } \frac{1}{2}, \text{ hence } (2S+1) = 3; \quad \text{or paired hence } (2S+1) = 1; \quad L=0+1=1 \]
and the terms arising from this are \( ^3\!P \) (triplet pee) or \( ^1\!P \) (singlet pee)
Which is the ground term?

For a p¹d¹ configuration: terms arising are \( ^3\!F \) (triplet eff) or \( ^1\!F \) (singlet eff)
TRY THIS AT HOME
The Ground Terms are deduced by using Hund's Rules:

1) The Ground Term will have the maximum multiplicity.
2) If there is more than 1 Term with maximum multiplicity, then the Ground Term will have the largest value of L.
Thus for a $d^2$ the rules predict $^3F < ^3P < ^1G < ^1D < ^1S$

A simple graphical method for determining just the ground term alone for the free-ions uses a "fill in the boxes" arrangement.

Note the idea of the "hole" approach:

A $d^1$ configuration is treated as similar to a $d^9$ configuration.

$d^1$ has 1 electron more than $d^0$ and
$d^9$ has 1 electron less than $d^{10}$ i.e. a hole.
## Calculating d-ion Ground Terms

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>2↑</th>
<th>1↑</th>
<th>0↑</th>
<th>-1↑</th>
<th>-2↑</th>
<th>L</th>
<th>S</th>
<th>Ground Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$</td>
<td>2↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>1/2</td>
<td>$^2\text{D}$</td>
</tr>
<tr>
<td>$d^2$</td>
<td>3↑</td>
<td>1↑</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>1</td>
<td>$^3\text{F}$</td>
</tr>
<tr>
<td>$d^3$</td>
<td>3↑</td>
<td>3/2↑</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>3/2</td>
<td>$^4\text{F}$</td>
</tr>
<tr>
<td>$d^4$</td>
<td>2↑</td>
<td>2↑</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>2</td>
<td>$^5\text{D}$</td>
</tr>
<tr>
<td>$d^5$</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>0</td>
<td>5/2</td>
<td>$^6\text{S}$</td>
</tr>
<tr>
<td>$d^6$</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2</td>
<td>2</td>
<td>$^5\text{D}$</td>
</tr>
<tr>
<td>$d^7$</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>3</td>
<td>3/2</td>
<td>$^4\text{F}$</td>
</tr>
<tr>
<td>$d^8$</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>3</td>
<td>1</td>
<td>$^3\text{F}$</td>
</tr>
<tr>
<td>$d^9$</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2↑</td>
<td>2</td>
<td>1/2</td>
<td>$^2\text{D}$</td>
</tr>
</tbody>
</table>

The overall result shown in the Table is that:
- 4 configurations ($d^1$, $d^4$, $d^6$, $d^9$) give rise to D ground terms,
- 4 configurations ($d^2$, $d^3$, $d^7$, $d^8$) give rise to F ground terms
- $d^5$ configuration gives an S ground term.
Calculating d-ion Ground Terms

To calculate $L$, use the labels for each column to determine the value of $L$ for that box, then add all the individual box values together.

E.g. for a $d^7$ configuration:
in the +2 box are 2 electrons, so $L$ for that box is $2 \times 2 = 4$
in the +1 box are 2 electrons, so $L$ for that box is $1 \times 2 = 2$
in the 0 box is 1 electron, $L$ is 0
in the -1 box is 1 electron, $L$ is $-1 \times 1 = -1$
in the -2 box is 1 electron, $L$ is $-2 \times 1 = -2$
Total value of $L$ is $+4 +2 +0 -1 -2 = 3 \rightarrow F$ term.

To calculate $S$, simply sum the unpaired electrons using a value of $\frac{1}{2}$ for each. For maximum multiplicity $S = 2s+1 = 2(3/2) + 1 = 4$.
Combining the two yields the ground term for a $d^7$ ion as $^4F$.

Note that for 5 electrons with 1 electron in each box then the total value of $L$ is 0. Also $L$ for a $d^1$ configuration = $L$ for a $d^9$. 
## Terms for $3d^n$ free ion configurations

The Russell Saunders term symbols for all the free ion configurations are given in the Table below.

<table>
<thead>
<tr>
<th>Configuration</th>
<th># of energy levels</th>
<th>Ground Term</th>
<th>Excited Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1, d^9$</td>
<td>1</td>
<td>$^2D$</td>
<td>-</td>
</tr>
<tr>
<td>$d^2, d^8$</td>
<td>5</td>
<td>$^3F$</td>
<td>$^3P, ^1G, ^1D, ^1S$</td>
</tr>
<tr>
<td>$d^3, d^7$</td>
<td>8</td>
<td>$^4F$</td>
<td>$^4P, ^2H, ^2G, ^2F, 2 \times ^2D, ^2P$</td>
</tr>
<tr>
<td>$d^4, d^6$</td>
<td>16</td>
<td>$^5D$</td>
<td>$^3H, ^3G, 2 \times ^3F, ^3D, 2 \times ^3P, ^1I, 2 \times ^1G, ^1F, 2 \times ^1D, 2 \times ^1S$</td>
</tr>
<tr>
<td>$d^5$</td>
<td>16</td>
<td>$^6S$</td>
<td>$^4G, ^4F, ^4D, ^4P, ^2I, ^2H, 2 \times ^2G, 2 \times ^2F, 3 \times ^2D, ^2P, ^2S$</td>
</tr>
</tbody>
</table>

Note that $d^n$ gives the same terms as $d^{10-n}$
The ligand field splitting of TM complex ground terms

Thus far our discussion refer only to free atoms, we will now take it a step further to the domain of TM complex ions.

The treatment will be restricted to complex ions in an $O_h$ crystal field.

The ground term energies for TM complexes are affected by the influence of a ligand field. The effect of a ligand field is that:

d orbitals split into $t_{2g}$ and $e_g$ subsets.
By analogy the D ground term states split into $T_{2g}$ and $E_g$.

f orbitals are split to give subsets known as $t_{1g}$, $t_{2g}$ and $a_{2g}$.
By analogy, the F ground term when split by a crystal field will give states known as $T_{1g}$, $T_{2g}$, and $A_{2g}$.

S orbitals are never split, hence S ground terms are also not split.
Correlating the splitting of spectroscopic terms in $O_h$ ligand field

<table>
<thead>
<tr>
<th>R-S term</th>
<th>Number of states</th>
<th>Terms in $O_h$ symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>$E_g, T_{2g}$</td>
</tr>
<tr>
<td>F</td>
<td>7</td>
<td>$A_{2g}, T_{1g}, T_{2g}$</td>
</tr>
</tbody>
</table>

For simplicity, spin multiplicities are not included in the table since they remain the same for each term.

Note: The ground term for first-row transition metal ions is either:

$\rightarrow$ D, F or S which in high spin $O_h$ are split into A, E or T states. These are called molecular term symbols $\rightarrow$ serves a function similar to atomic term symbols discussed earlier on.

Note that it is important to recognise that the F ground term here refers to states arising from d orbitals and not f orbitals and depending on whether it is in an octahedral or tetrahedral environment the lowest term can be either $A_{2g}$ or $T_{1g}$. 
Q.
What is the ground term of the configurations:
(a) $3d^5$ of Mn$^{2+}$ and
(b) $3d^3$ of Cr$^{3+}$?

Answer:
If done correctly you should come up with $(a) = ^6S$ (a sextet ess term) and $(b) = ^4F$ (a quartet eff term).

Remember the first rule for a ground term ➔ maximum multiplicity

- $S = 2\frac{1}{2} ➔ 2S + 1 ➔ 2 \times 2\frac{1}{2} + 1 = 6 ➔$ A sextet
  $L = 2 + 1 + 0 -1 -2 = 0 ➔ ^6S$ term

(b) $S = 1\frac{1}{2} ➔ 2S + 1 ➔ 2 \times 1\frac{1}{2} + 1 = 4 ➔$ A quartet
  $L = 2 + 1 + 0 = 3 ➔ ^4F$ term
Correlation of spectroscopic terms- D Term

One approach taken when we consider the Russell-Saunders scheme with the various electronic states makes use of what are called Orgel diagrams. The relevant Orgel diagram for the D ground state is given below:

$d^4$, $d^9$ tetrahedral $T_{2g}$

$d^1$, $d^6$ tetrahedral

$d^4$, $d^9$ octahedral

$E_g$

Increasing ligand field 0 Increasing ligand field

$\Delta$

Orgel diagram for a D term
For Fe(II) high spin oct complex the free ion electronic configuration is \( d^6 \) and in the oct CF it is \( t_{2g}^4 e_g^2 \).

The R-S scheme that takes into account the e-e interactions is a free ion ground state of \( ^5D \).
In oct & tet crystal fields, this D state is split into \( E(g) \) and \( T_2(g) \) terms.

To decide which side of the D Orgel diagram should be applied to the interpretation can be quickly determined by looking at the electronic configuration and noting that the ground state is triply degenerate and the excited state is doubly degenerate (i.e. we must use the right-hand-side).

It is expected then that there should be 1 absorption band found in the electronic spectrum and that the energy of the transition corresponds directly to \( \Delta_o \).
The transition is written in a notation that is read from right to left, which in this case is \( ^5E_g \leftarrow ^5T_{2g} \).
Electronic spectra

Energy level diagram for D term in octahedral ligand field

Ligand field strength

Energy

Ligand field strength

Energy

UV spectrum of \([\text{Ti(H}_2\text{O)}_6]^{3+}\)
Correlation of spectroscopic terms- F Term
For ALL octahedral complexes, except high spin d\textsuperscript{5}, simple CFT would predict that only 1 band should appear in the electronic spectrum and that the energy of this band should correspond to the absorption of energy equivalent to $\Delta$.

In practice however, ignoring spin-forbidden lines, this is only observed for those ions with D free ion ground terms i.e., d\textsuperscript{1}, d\textsuperscript{9} as well as d\textsuperscript{4}, d\textsuperscript{6}.

The observation of 2 or 3 peaks in the electronic spectra of d\textsuperscript{2}, d\textsuperscript{3}, d\textsuperscript{7} and d\textsuperscript{8} high spin octahedral complexes requires further treatment involving electron-electron interactions.

Using the Russell-Saunders (LS) coupling scheme, these free ion configurations give rise to F free ion ground states which in octahedral and tetrahedral fields are split into terms designated by the symbols $A_{2g}$, $T_{2g}$ and $T_{1g}$.
Correlation of spectroscopic terms- F Term

The ground term of the $d^3 V^{3+}$ is $^3F$ which gives rise to $^3A_{2g}$, $^3T_{1g}$, $^3T_{2g}$ in the oct crystal field.

The two $e_g \leftarrow t_{2g}$ transitions of the excited state are thus labeled: $^3T_{2g} \leftarrow ^3T_{1g}$ and $^3A_{2g} \leftarrow ^3T_{1g}$.

Note that whenever the ground state is an F term there will be a P term found at higher energy with the same spin multiplicity.
Types of transition

1. Charge transfer, either ligand to metal or metal to ligand.
   - these are often extremely intense
   - are generally found in the UV region but they may have a tail into the visible spectrum.

2. d-d or ligand field transitions are transitions between orbitals that are predominantly metal d orbitals
   - the separation is characterised by the strength of $\Delta_o$.
   - can occur in both the UV and visible region.
   - transitions usually have small to medium intensities.
Selection rules for electronic spectra of TM complexes.

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

1. **The Spin Rule** $\Delta S = 0$

2. **The Orbital Rule (Laporte)** $\Delta l = +/- 1$

The first rule states that allowed transitions must involve the promotion of electrons without a change in their spin. Eg antiparallel pair of electrons cannot be converted to a parallel pair, so a singlet ($S=0$) cannot under a transition to a triplet state ($S=1$).

The second rule states that if the molecule has a centre of symmetry, transitions within a given set of $s$, $p$ or $d$ orbitals are forbidden. That is $s-s$, $p-p$, $d-d$ and $f-f$ transitions are forbidden, but $s-p$, $p-d$, and $d-f$ transitions are allowed. This rule applies to $O_h$ complexes but not $T_d$. 
Selection rules for electronic spectra of TM complexes.

Relaxation of the Rules can occur through:

a) Spin-Orbit coupling $\Rightarrow$ gives rise to weak spin forbidden bands

b) Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric $\Rightarrow$ Absorption of light at that moment is then possible.

c) $\pi$-acceptor and $\pi$-donor ligands can mix with the d-orbitals $\Rightarrow$ transitions are no longer purely d-d.