Electronic Structure of Metal Atoms and Ions –
Further Splitting of Levels

electrons can have…

… orbital angular momentum \((l > 0)\) …

… and spin

magnetic moments (which can couple) are associated with these motions

this is the spin orbit interaction
To understand the electronic spectra of transition metal complexes, one needs to know the electronic states of the system.

The following **effects** lead to a **splitting of the energy levels** of transition metal atoms (and ions):

<table>
<thead>
<tr>
<th>Effect</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-electron repulsion</td>
<td>spectroscopic terms</td>
</tr>
<tr>
<td>Crystal field</td>
<td>spectroscopic terms</td>
</tr>
<tr>
<td><strong>- Spin-Orbit Interaction</strong></td>
<td><strong>multiplet</strong></td>
</tr>
<tr>
<td><strong>- Spin-Spin Interaction</strong></td>
<td><strong>magnetic states</strong></td>
</tr>
<tr>
<td><strong>- Zeeman Effect</strong></td>
<td><strong>magnetic states</strong></td>
</tr>
<tr>
<td>Hyperfine Interaction</td>
<td></td>
</tr>
</tbody>
</table>

Of these, only the first two effects are of importance in UV/Vis (electron) spectroscopy as they lead to a splitting of the energy levels which are on the same order of magnitude as the energy of the applied UV/vis light.

The other effects are of importance in **magnetism and EPR spectroscopy** (see the upcoming lectures).
Electronic Structure of Metal Atoms and Ions

Spin-Orbit Coupling

Atomic Multiplets

Magnetic Field

Zeeman States

d^n

Interelectron repulsion

weak ligand field

Electron Configuration

strong ligand field

Interelectron repulsion

CRystal-field terms

Spin-Orbit Coupling

Multiplets

Magnetic Field

Magnetic States

Zeeman States
Spin-Orbit Coupling

**Na**
- Exited state
  - $s = 1/2$, $l = 1$
  - $2S_{1/2}$
  - $2P_{1/2}$
  - $2P_{3/2}$
- Excitation wavelengths:
  - 589.16 nm (16973 cm$^{-1}$)
  - 589.76 nm (16956 cm$^{-1}$)
- Transition energy difference:
  - $\Delta E = 3\lambda / 2$
  - $\Delta E = 17$ cm$^{-1}$
  - $\lambda = 11$ cm$^{-1}$

**Na**
- Ground state
  - $s = 1/2$, $l = 0$
  - $2S_{1/2}$

**Notes**
- The diagram illustrates the spin-orbit coupling in sodium (Na) atoms, showing the energy levels and transitions between them.
Spin-Orbit coupling parameters, $\lambda$, for TM ions (ground state)

<table>
<thead>
<tr>
<th>Ion</th>
<th>d$^n$</th>
<th>Ground state</th>
<th>$\lambda$ / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>d$^1$</td>
<td>$^2$D</td>
<td>154</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>d$^2$</td>
<td>$^3$F</td>
<td>104</td>
</tr>
<tr>
<td>V$^{2+}$</td>
<td>d$^3$</td>
<td>$^4$F</td>
<td>55</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>d$^3$</td>
<td>$^4$F</td>
<td>87</td>
</tr>
<tr>
<td>Cr$^{2+}$</td>
<td>d$^4$</td>
<td>$^5$D</td>
<td>57</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>d$^4$</td>
<td>$^5$D</td>
<td>85</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>d$^6$</td>
<td>$^5$D</td>
<td>-100</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>d$^7$</td>
<td>$^4$F</td>
<td>-180</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>d$^8$</td>
<td>$^3$F</td>
<td>-335</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>d$^9$</td>
<td>$^2$D</td>
<td>-852</td>
</tr>
</tbody>
</table>

- Spin-Orbit coupling is a small perturbation, applies well for 3d elements (but not for lanthanides, actinides)
- Russel-Saunders-Coupling LS-Coupling

$H_{SO} = \zeta \mathbf{l} \cdot \mathbf{s}$

$H_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}$

$\lambda = \pm \zeta / (2S)$

Terms Symbol: $^{(2S+1)L_J}$

Energy of the term: $E(J, L, S) = 1/2\lambda [J(J+1) - L(L+1) - S(S+1)]$

Only valid for the ground term positive for $n = 1-4$

$\zeta = \text{one-electron spin-orbit coupling constant (always positive), dimension} = \text{cm}^{-1} \text{ (energy)}$

$\lambda = \text{many-electron spin-orbit coupling constant (always positive), dimension} = \text{cm}^{-1} \text{ (energy)}$
Spin-Orbit coupling parameters, $\zeta$, for some elements

Cr$^0$ $\zeta_{3d} = 227$ cm$^{-1}$
Cr$^{2+}$ $\zeta_{3d} = 230$ cm$^{-1}$
B $\zeta_{2p} = 11$ cm$^{-1}$
Mo$^{2+}$ $\zeta_{4d} = 749$ cm$^{-1}$
Mo$^{3+}$ $\zeta_{4d} = 818$ cm$^{-1}$
Tl $\zeta_{6p} = 5195$ cm$^{-1}$

Values taken from

Fig. 5.45 The variation of $\zeta_{3d}$ in the $M^{2+} (d^n)$ sequence, $\text{Sc}^{2+} (d^1) - \text{Cu}^{2+} (d^9)$. 
Spin-orbit coupling of the $d^2$ configuration

The spin orbit interaction splits the atomic terms into $j$ levels

$d^2, \lambda > 0$

Russel-Saunders Coupling (LS-coupling)
Spin-Orbit Coupling in Crystal Field Terms

Example: Terms of the $d^2$ configuration

In coordination compounds spin-orbit coupling can be of
- First order (only for orbitally degenerate states, e.g. T terms)
- Second order (for orbitally non-degenerate states, e.g. E and A terms)

Problem: Meaning of L in crystal field terms is lost
First Order Spin-Orbit Coupling, splitting of terms

In coordination compounds orbital momentum means: electron can move from one orbital to another, degenerate orbital. However, $d_{xy}$, $d_{xz}$, $d_{yz}$, and $d_{zz}$, $d_{x^2-y^2}$ are no longer degenerate in a complex.

In an octahedral complex, e-can only move within an open $t_{2g}$ shell (first order orbital momentum => of importance in magnetochemistry)

d$^1$, $d^2$, (l.s.)-$d^4$, (l.s.)-$d^5$, etc have first order orbital momentum (T ground terms), $d^3$, $d^4$ have no first order orbital momentum (A, E ground terms)

Terms with T symmetry exhibit orbital angular momentum can show spin-orbit coupling
This rule is only applicable in $O_h$ Symmetry.

$E_J = -1/2A\lambda[J(J+1)-L(L+1)-S(S+1)]$
For $(t_{2g})^n$ less than half occupied: $\lambda$ positive
more than half occupied: $\lambda$ negative

Terms with T symmetry exhibit $L = 1$,
$H_{SO} = -A\lambda LS$
Ti$^{3+}$, d$^1$, has a $^2T_{2g}$ ground term, shows first order spin-orbit coupling

$\lambda - \lambda/2$

<table>
<thead>
<tr>
<th>Energy</th>
<th>S</th>
<th>L</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>$1/2$</td>
<td>$1$</td>
<td>$1/2$</td>
</tr>
<tr>
<td>$-\lambda/2$</td>
<td>$1/2$</td>
<td>$1$</td>
<td>$3/2$</td>
</tr>
</tbody>
</table>
First Order Spin-Orbit Coupling, splitting of terms, d\(^1\) configuration

Quenching of the orbital contribution, to the magnetic moment, due to ligand field

Tetrahedral symmetry

<table>
<thead>
<tr>
<th>n</th>
<th>ground</th>
<th>(e^{n_{t_2 m}}) term</th>
<th>ligand field term</th>
<th>quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(^2D)</td>
<td>(e^1)</td>
<td>(^2E)</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>(^3F)</td>
<td>(e^2)</td>
<td>(^3A_2)</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>(^4F)</td>
<td>(e^{2t_2}^1)</td>
<td>(^4T_1)</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>(^5D)</td>
<td>(e^{2t_2}^2)</td>
<td>(^5T_2)</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>(^6S)</td>
<td>(e^{2t_2}^3)</td>
<td>(^6A_1)</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>(^5D)</td>
<td>(e^{3t_2}^3)</td>
<td>(^5E)</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>(^4F)</td>
<td>(e^{4t_2}^3)</td>
<td>(^4A_2)</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>(^3F)</td>
<td>(e^{4t_2}^4)</td>
<td>(^3T_1)</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>(^2D)</td>
<td>(e^{4t_2}^5)</td>
<td>(^2T_2)</td>
<td>No</td>
</tr>
</tbody>
</table>

These ions have \(L = 1\)
First Order Spin-Orbit Coupling, splitting of terms, d\(^1\) configuration

Quenching of the orbital contribution, to the magnetic moment, due to ligand field

**Octahedral symmetry**

<table>
<thead>
<tr>
<th>n</th>
<th>ground term</th>
<th>(t_{2g}^{n}e_{g}^{m})</th>
<th>ligand field term</th>
<th>quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>({}^{2}D)</td>
<td>(t_{2g}^{1})</td>
<td>(2^{T_{2g}})</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>({}^{3}F)</td>
<td>(t_{2g}^{2})</td>
<td>(3^{T_{2g}})</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>({}^{4}F)</td>
<td>(t_{2g}^{3})</td>
<td>(4^{A_{2g}})</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>({}^{5}D)</td>
<td>(t_{2g}^{3}e_{g}^{1})</td>
<td>(5^{E_{g}})</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>({}^{6}S)</td>
<td>(t_{2g}^{3}e_{g}^{2})</td>
<td>(6^{A_{1g}})</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>({}^{5}D)</td>
<td>(t_{2g}^{4}e_{g}^{2})</td>
<td>(2^{T_{2g}})</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>({}^{4}F)</td>
<td>(t_{2g}^{5}e_{g}^{2})</td>
<td>(4^{T_{1g}})</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>({}^{3}F)</td>
<td>(t_{2g}^{6}e_{g}^{1})</td>
<td>(2^{E_{g}})</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>({}^{2}D)</td>
<td>(t_{2g}^{6}e_{g}^{3})</td>
<td>(3^{A_{2g}})</td>
<td>Yes</td>
</tr>
</tbody>
</table>

These ions have \(L = 1\)
Second Order Spin-Orbit Coupling

TM ions with E and A ground terms show second order spin-orbit coupling

The s.o. s-o-coupling leads to a stabilization of the ground term and a destabilization of the excited state

\[
\sum \frac{\langle \Phi_e | \lambda_e LS | \Phi_g \rangle \langle \Phi_g | \lambda_g LS | \Phi_e \rangle}{E_g - E_e}
\]

A terms are stabilized by \(-8\lambda^2/\Delta_o\)
E terms are stabilized by \(-4\lambda^2/\Delta_o\)

The Zero field splitting D is also associated with the second order spin-orbit coupling (see lectures on Magnetochemistry and EPR)
Energy levels of Co$^{2+}$: e⁻/e⁻-repulsion, crystal field, 1st order spin-orbit coupling and Zeeman splitting

This will be part of the EPR lecture