CHM2C1-B Physical Spectroscopy

Electronic spectra of atoms (~~and diatomics~~)

- Essential readings:

  - Atkins, Elements of Physical Chemistry, Chapter 13
    Exercises 13.1-11, 13.22-25, 13.28-31 (page 322-323)
  - Housecroft & Sharpe, Inorganic Chemistry, Chapters 1.4-1.9, 20.6
    Exercises (pages 9,14,21,22), Problem 20.12 (page 486)

  with particular emphasis on Atomic Term Symbols (energy levels) and
  Electronic Transitions in atoms (isolated, under ligand-fields).

- Materials that overlap with other modules will be treated only briefly.

- Electronic excitations in diatomic molecules will not be treated.

- The lecture slides can be downloaded from
  http://www.chem.bham.ac.uk/labs/ando/chm2c1Slide.pdf

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

R_{H}=Rydberg constant=109677cm^{-1}

Lyman $(n_1=1)$, Balmer $(n_1=2)$,
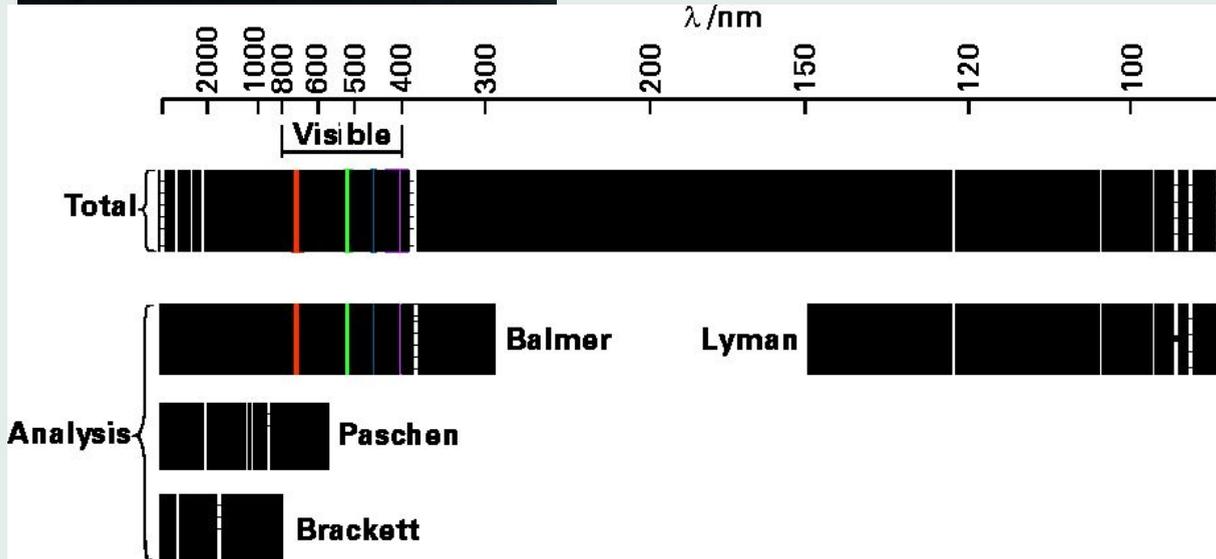Paschen $(n_1=3)$, Brackett $(n_1=4)$,

Fig 13.1/P: The Spectrum of Atomic Hydrogen
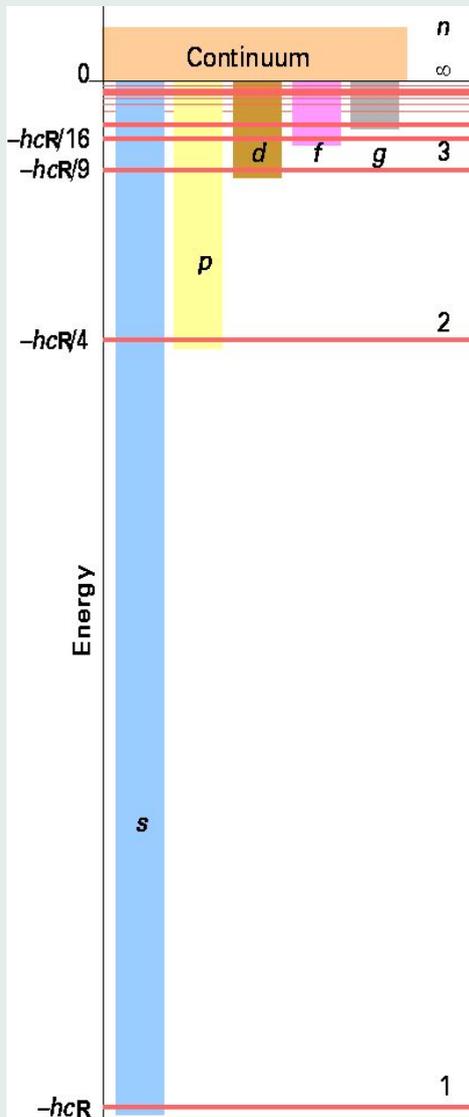Emitted light from Hydrogen discharge lamp

Fig 13.2/P:
The Energy Levels of Hydrogen Atom

For Hydrogenic Atoms H, He$^+$, Li^{2+}, $\cdots$
(i.e., one-electron atoms)

$$E_n = -hcR\frac{Z^2}{n^2} \propto -\frac{Z^2}{n^2}$$

The constant R depends on the atomic mass m_N via the reduced mass μ:
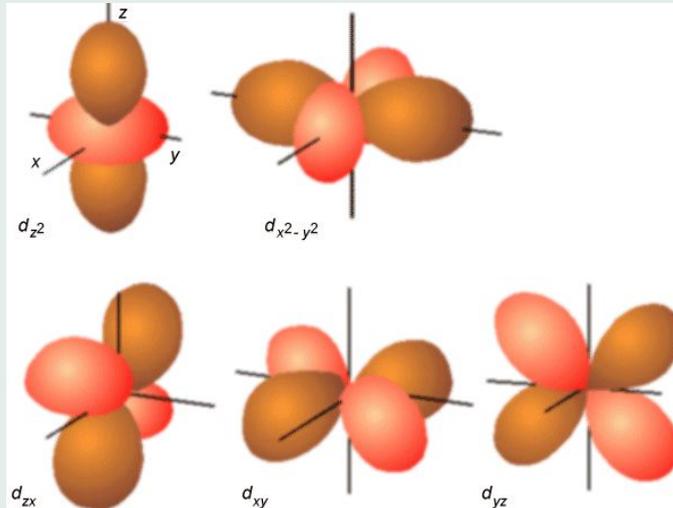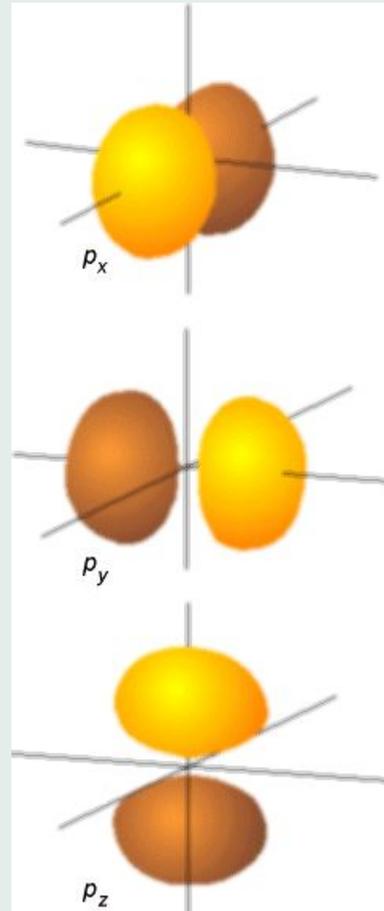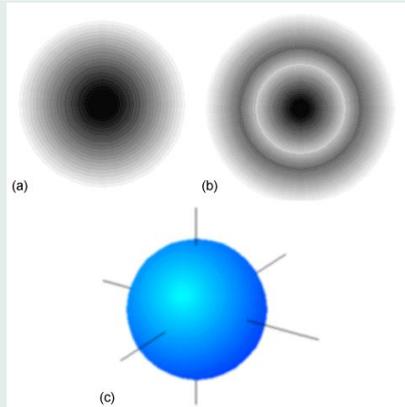
$$R \propto \mu, \qquad \mu = \frac{m_e m_N}{m_e + m_N}$$

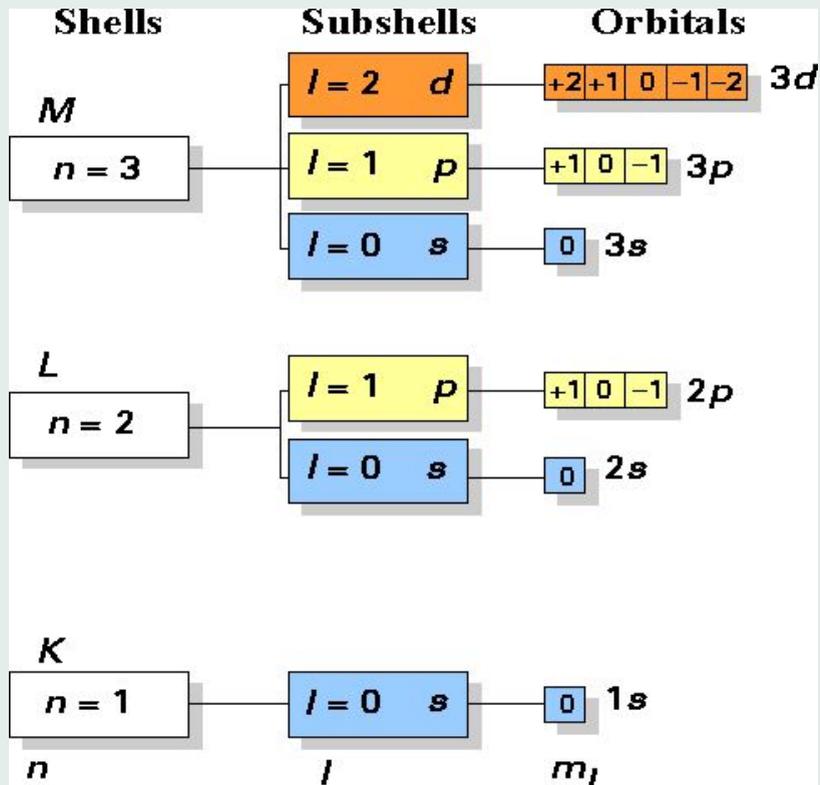However, because $m_e \ll m_N$,
$\mu \simeq m_e$ and $R \simeq R_{\mathrm{H}}$

Self-test 13.1/P: The shortest wavelength transition in the Paschen series in hydrogen occurs at 821 nm; at what wavelength does in occur in Li^{2+}?

s, p, d Atomic Orbitals (Cartesian representation)

Shells (n), Subshells (l), Orbitals (m_l)

Fig 13.3/P

Shells	Subshells	Orbitals
	$l = 2$ d	$+2$ $+1$ 0 -1 -2 $3d$
M $n = 3$	$l = 1$ p	$+1$ 0 -1 $3p$
	$l = 0$ s	0 $3s$
L $n = 2$	$l = 1$ p	$+1$ 0 -1 $2p$
	$l = 0$ s	0 $2s$
K $n = 1$	$l = 0$ s	0 $1s$
n	l	m_l

Self-test 13.3/P: How many orbitals are there in a shell with $n = 5$?
Try: Self-study exercises/Inorg Chem, p.9,14

<u>Self-study exercises/I</u>

1. If m_l has values of -1, 0, +1, write down the corresponding value of l.

2. If l has values 0, 1, 2 and 3, deduce the corresponding value of n.

3. For $n=1$, what are the allowed values of l and m_l?

1. Write down the possible types of atomic orbital for $n=4$.

2. Which atomic orbital has values of $n=4$ and $l=2$?

3. Give the three quantum numbers that describe a $2s$ atomic orbital.

1. Write down two possible sets of quantum numbers to describe an electron in a $3s$ atomic orbital.

2. If an electron has the quantum numbers $n=2$, $l=1$, $m_l=1$ and $m_s=+\frac{1}{2}$ which type of atomic orbital is it occupying?
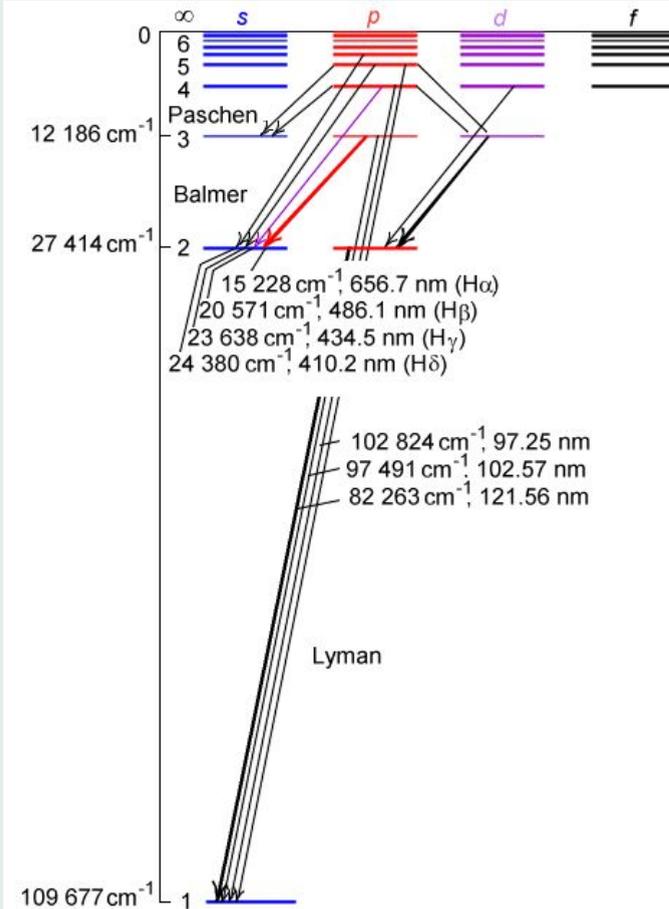
Fig 13.11/P: Appearance of the Spectrum of Atomic Hydrogen.

(Note: Hydrogenic atoms $\Rightarrow$ Orbital energies depend only on n.)

Selection Rules for Hydrogenic Atoms

$$\Delta l = \pm 1, \quad (\Delta m_l = 0, \pm 1)$$

$$s \leftrightarrow p \leftrightarrow d \leftrightarrow f \cdots$$

The principal quantum number n can change by any amount.

Example 13.1/P: To what orbitals may a 4d electron make spectroscopic transitions?

Self-test 13.5/P: To what orbitals may a 4s electron make spectroscopic transitions?

The building-up (Aufbau) principle (Sec 13.11/P)

1. The order of occupation of orbitals is
   $$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, ...$$

2. Each orbital may accommodate up to two electrons (Pauli principle)

3. Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

4. In its ground state, an atom adopts a configuration with the greatest number of unpaired electrons (Hund's rule)

Self-test 13.6/P:
Predict the ground-state electron configuration of sulfur.

Self-test 13.7/P:
Predict the electron configuration of a Cu^{2+} ion and an S^{2-} ion.

Exercise 13.25/P:
Give the electron configuration of the ground states of the first 18 elements in the periodic table.

Self-study exercises/I

1. ~~Where, in the above argument, is the Pauli exclusion principle applied?~~

2. Will the three electrons in the P $3p$ atomic orbitals possess the same or different values of the spin quantum number?

1. Values of Z for Li, Na, K and Rb are 3, 11, 19 and 37 respectively. Write down their ground state configuration and comment on the result.

2. How are the ground state electronic configurations of O, S and Se (Z=8, 16, 34 respectively) alike? Give another element related in the same way.

1. Show that the electronic configuration $1s^2 2s^2 2p^1$ for B corresponds to each electron having a unique set of four quantum numbers.

2. The ground state of N is $1s^2 2s^2 2p^3$. Show that each electron in the $2p$ level possesses a unique set of four quantum numbers.

Term symbols (Sec 13.16/P, Box 20.5/I)

$$^{(2S+1)}L_J$$

- $L = \underline{\text{total}}$ orbital angular momentum quantum number

$$
\begin{array}{ccccc}
L & 0 & 1 & 2 & 3 & \dots \\
& S & P & D & F & \dots
\end{array}
$$

  Two electrons with l_1, l_2 give
  $$L = l_1 + l_2, \ l_1 + l_2 - 1, \ \cdots, |l_1 - l_2|$$

- $S = \underline{\text{total}}$ spin angular momentum quantum number
  $$S = s_1 + s_2, \ s_1 + s_2 - 1, \ \cdots, |s_1 - s_2|$$
  (But it's easier to count the number of up and down spins)
  $$2S + 1 = \text{spin multiplicity (singlet, double, triplet, ...)}$$

- $J = \underline{\text{total}}$ angular momentum quantum number
  $$J = L + S, \ L + S - 1, \ \cdots, |L - S|$$

Self-test 13.8/P
What terms and levels can arise from the configuration $4p^1 3d^1$?
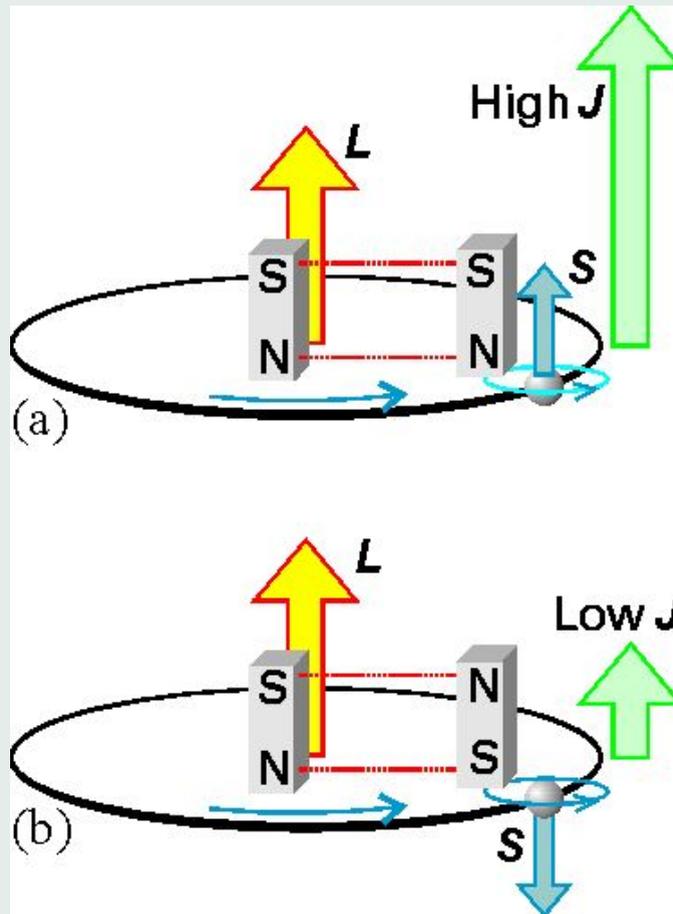
Spin-orbit Coupling

Fig 13.17/P: The magnetic interaction responsible for spin-orbit coupling.

Hund's Rule for the Lowest Energy Term of a given configuration

1. Highest Multiplicity $2S + 1$

2. Highest value of L

3. $\begin{cases} \text{Lowest value of } J \text{ when less than half-filled} \\ \text{or} \\ \text{Highest value of } J \text{ when more than half-filled} \end{cases}$

Example: $...4p^1\, 3d^1$ configuration   (Self-test 13.8/P)

$\Rightarrow {}^1F_3,\, {}^1D_2,\, {}^1P_1,\, {}^3F_{4,3,2},\, {}^3D_{3,2,1},\, {}^3P_{2,1,0}$

1. $\Rightarrow {}^3F_{4,3,2},\, {}^3D_{3,2,1},\, {}^3P_{2,1,0}$

2. $\Rightarrow {}^3F_{4,3,2}$

3. $\Rightarrow {}^3F_2$

In fact, it's much easier to find the lowest term only:

1. two unpaired electrons $\Rightarrow$ highest $S = 1 \Rightarrow 2S + 1 = 3$

2. one in p and one in $d \Rightarrow$ highest $L = 1 + 2 = 3 \Rightarrow {}^3F$

3. $L = 3,\, S = 1 \Rightarrow J = 4, 3, 2$; less than half-filled $\Rightarrow {}^3F_2$

Exercise 13.31/P

The ground configuration of a Ti^{2+} ion is $[Ar]3d^2$.

What is the term of lowest energy and which level of that term lies lowest?

1. two unpaired electrons $\Rightarrow$ highest $S = 1 \Rightarrow 2S + 1 = 3$

2. two in d in parallel spin $\Rightarrow$ highest $L = 1 + 2 = 3 \Rightarrow {}^3\text{F}$

3. $L = 3$, $S = 1 \Rightarrow J = 4, 3, 2$; less than half-filled $\Rightarrow {}^3\text{F}_2$
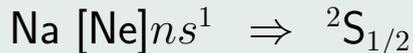
Now, try:

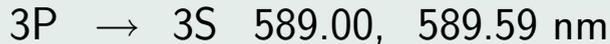|		
C	$[He]2s^2\,2p^2$	${}^3\text{P}_0$
N	$[He]2s^2\,2p^3$	${}^4\text{S}_{3/2}$
O	$[He]2s^2\,2p^4$	${}^3\text{P}_2$
Cr^{3+}	$[Ar]3d^3$	${}^4\text{F}_{3/2}$
Mn^{3+}	$[Ar]3d^4$	${}^5\text{D}_0$
Fe^{3+}	$[Ar]3d^5$	${}^6\text{S}_{5/2}$

Selection Rules for Many-electron Atoms

- $\Delta S = 0$
- $\Delta L = 0, \pm 1,$
- $\Delta l = \pm 1$ for the electron excited in the transition
- $\Delta J = 0, \pm 1$ but $J = 0 \rightarrow J = 0$ is forbidden

The rules on J are exact. Those on l, L, S presume that these quantum numbers are well-defined.

Example: Na atom

Na $[\text{Ne}]ns^1 \;\Rightarrow\; {}^2S_{1/2}$
Na $[\text{Ne}]np^1 \;\Rightarrow\; {}^2P_{3/2}, \; {}^2P_{1/2}$
Na $[\text{Ne}]nd^1 \;\Rightarrow\; {}^2D_{5/2}, \; {}^2D_{3/2}$

Observed lines include:

5S	$\rightarrow$	3P	616.07,	615.42 nm
3P	$\rightarrow$	3S	589.00,	589.59 nm
4D	$\rightarrow$	3P	568.82,	568.26 nm

Ligand-field Splitting

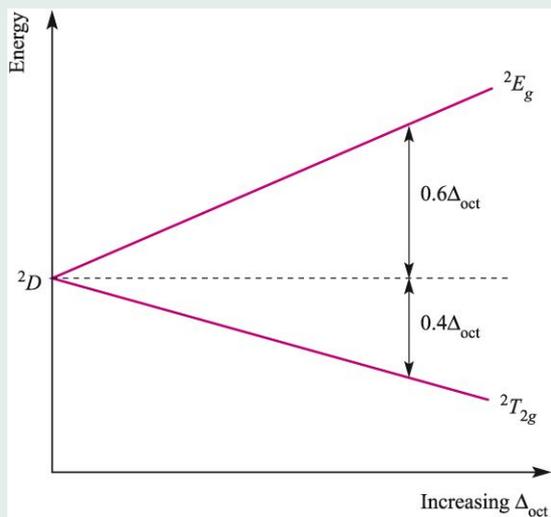| Atom	$2L+1$	$\longrightarrow$	Octahedral	degeneracies
S	1		A_{1g}	1
P	3		T_{1g}	3
D	5		$E_g + T_{2g}$	$2 + 3$
F	7		$A_{2g} + T_{2g} + T_{1g}$	$1 + 3 + 3$

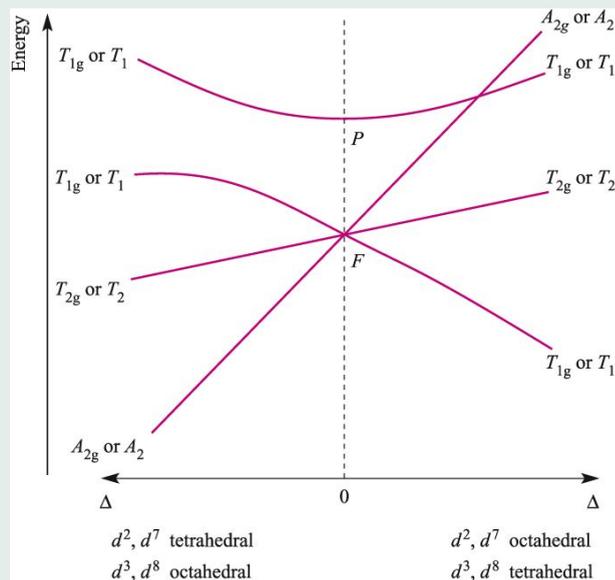Fig 20.16/I: d^1 ion in an Octahedral field
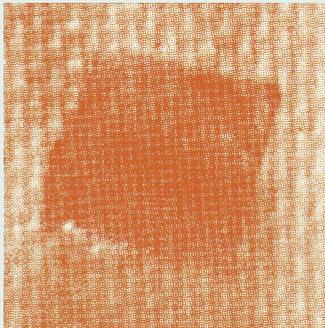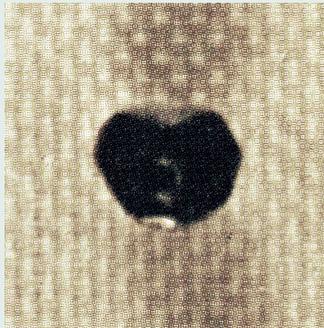
Try: Problem 20.12/I (p.486)

Fig 20.18/I: Orgel diagram for d^2, d^3, d^7, d^8 ions.
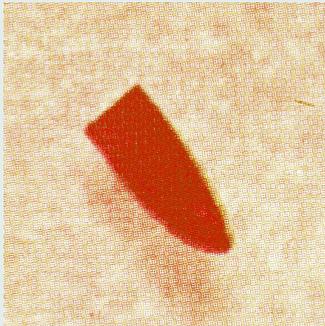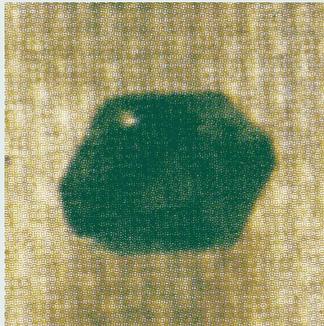
Colours from d-electrons

KMnF$_3$

Y$_3$Al$_5$O$_{12}$: Cr

Dy$_3$Al$_5$O$_{12}$

Al$_2$O$_3$: Cr

RbNiF$_3$

BaAl$_{12}$O$_{19}$: Fe