Atoms

1. Early atomic physics
2. The Schrödinger equation as a wave equation
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Hund’s rules

Atoms with many electrons

- Periodic table of elements
- Coupling schemes
- Entanglement
- Exchange interaction
- Hund’s rules
- Crystal-field, Ligand-field and the quench of the orbital angular momentum
- X-Ray Spectroscopy

Hund’s rules 1

if the valence electrons occupy a single orbital, the angular momenta of the ground state can be predicted using Hund’s rules

1st Hund’s rule

the quantum number *L* is given by the maximum of

$$\boxed{L = \max \left| \sum_{\mathrm{i}}^{\mathrm{N}} m_{\mathrm{i}} \right|}$$

the Pauli principle must be observed for the sum

Hund’s rules 1 Comment

If electrons occupy an orbital, the quantum numbers *L*, *S* and *J* of the ground state can be predicted with the help of Hund’s rules.

Even when spin-orbit coupling becomes important, the leading LS contribution to the ground state can be reliably predicted.

Hund’s rules are a consequence of the exchange interaction.

The first rule says that the total orbital angular momentum *L* is given by the maximum absolute value of the sum over the *m* quantum numbers of the occupied *m* states.

The *m* states are occupied according to the Pauli exclusion principle, whereby it is taken into account that the exchange interaction favors the parallel spin orientation.

Hund's rules 2

2nd Hund's rule

the spin quantum number *S* takes the maximal possible value in accordance with the Pauli principle.

3rd Hund's rule

spin orbit coupling

$$\hat{H}_{SL} = \xi \frac{\hat{\vec{S}}\hat{\vec{L}}}{\hbar^2}$$

$$N < (2\ell + 1) \quad \rightarrow \quad \xi > 0 \quad \rightarrow \quad J = |L - S|$$
$$N > (2\ell + 1) \quad \rightarrow \quad \xi < 0 \quad \rightarrow \quad J = L + S$$

Hund's rules 2

Comment 1

The second rule says that the total spin takes on the maximum possible value.

The third rule takes advantage of the spin-orbit coupling.

The spin orbit coupling constant ξ is positive if the orbital is less than half filled.

If the orbital is more than half filled, the spin orbit constant is negative.

In the case of a configuration that is more than half occupied by electrons, the properties can be calculated if the unoccupied orbitals are used instead of the electrons.

One speaks of electron holes that carry a positive elementary charge.

Hund’s rules 2 Comment 2

This is called an electron hole configuration.

Since the magnetic moment is aligned parallel to the angular momentum in the case of a positive elementary charge, the sign of the spin-orbit interaction must be reversed in the case of an electron-hole configuration.

The smallest possible *J* value results for an orbital that is less than half filled with electrons.

For a hole configuration, spin and orbital angular momentum add to the maximum *J* value.

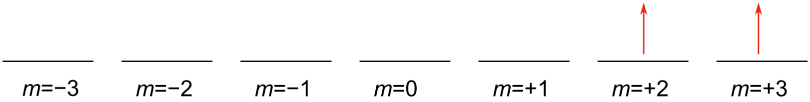
The following examples show that Hund’s rule is easy to apply.

As examples I will use ions of the rare earth elements whose valence electrons occupy the 4f orbital.

Hund’s rules 3

Example:

Pr^{3+} (atomic number $Z = 59$, electron configuration $[\mathrm{Xe}]4f^{2}$)



$$L = \max \left| \sum_{i=1}^{N=2} m_i \right| = 5, \quad S = 1 \quad \text{and} \quad J = L - S = 4$$

ground state : $\boxed{{}^{3}H_{4}}$

Hund's rules 3 Comment 1

The first example is the trivalent ion of Praseodymium.

The atomic number is 59 and there are two valence electrons that occupy the 4f orbital.

The fully occupied orbitals realize the electron configuration of xenon.

The figure shows the quantum states of the orbital angular momentum $\ell = 3$ which are labeled with the corresponding m quantum numbers.

The exchange interaction causes the electron spins to align in parallel in the ground state.

Hund's first rule requires that the absolute values of the sum of the m quantum numbers must be maximal.

Hund’s rules 3 Comment 2

Therefore the electrons are placed in the quantum states $m = +3$ and $m = +2$.

Consequently the orbital angular momentum of the ground state equals $L = 5$ and the total spin $S = 1$.

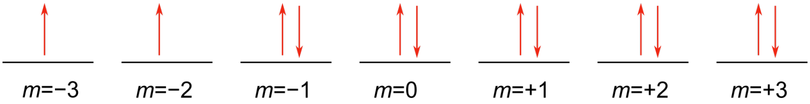
The orbital angular momentum $L = 5$ is denoted by the capital letter H according to the convention (S,P,D,F,G,H, etc.)

With an electron configuration (less than half-filled orbital) the orbital angular momentum and the spin align antiparallel and the total angular momentum is $J = 4$.

The formula outlined in red gives the notation of the ground state of Pr^{3+}.

Hund’s rules 4

Tm^{3+} (atomic number $Z = 69$, electron configuration $[\mathrm{Xe}]4\mathrm{f}^{12}$)



$$L = \max \left| \sum_{i=1}^{N=12} m_i \right| = 5, \quad S = 1 \quad \text{and} \quad J = L + S = 6$$

ground state : $\boxed{{}^3\mathrm{H}_6}$

Hund’s rules 4 Comment

In this example the ground state of trivalent thulium is discussed.

The 4f orbital is occupied by 12 electrons, so that two electrons are missing to fully occupy the orbital.

Instead of the electron configuration, the electron holes of the two missing electrons can be considered.

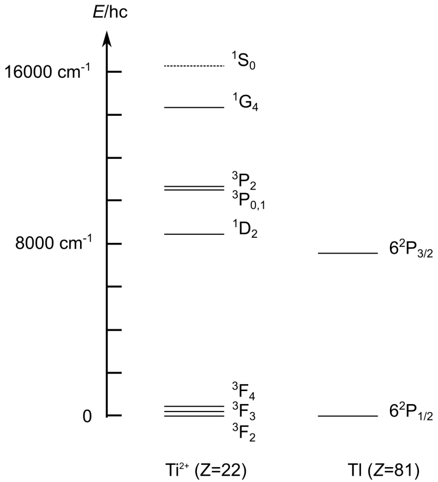
Hund’s first rule gives the value $L = 5$ for the total orbital angular momentum.

The spin of the electron holes adds up to $S = 1$ and orbital angular momentum and spin align parallel due to the positive charge of the electron holes.

The total angular momentum of the ground state is $J = 6$.

The formula outlined in red gives the notation of the ground state of Tm^{3+}.

Hund's rules 5



Hund’s rules 5

Comment 1

In the figure, the energy level scheme of the $3d^2$ configuration of Ti^{2+} ([Ar] $3d^2 4s^2$) and the energy level scheme of the $6p^1$ configuration of Tl ([Xe] $4f^{14} 5d^{10} 6s^2 6p^1$) are compared.

The energy splitting of the $3d^2$ configuration of Ti^{2+} is mainly caused by the Coulomb repulsion of the two electrons.

The energy splitting due to the spin-orbit coupling is small compared to the energy splitting caused by the repulsive force of the electrons.

The $^3F_2$ ground state of Ti^{2+} agrees with Hund’s rules.

As an extreme example, the energy level scheme of Ti^{2+} is compared with the energy level scheme of thallium.

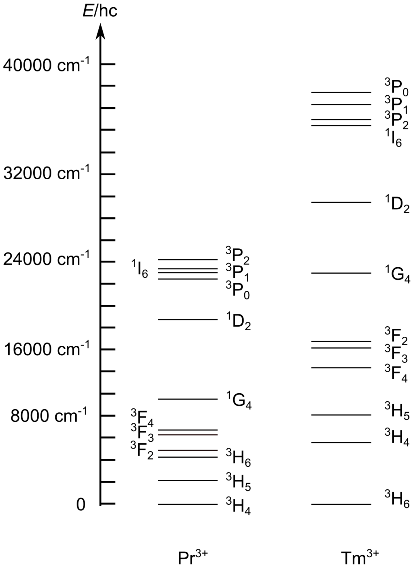
Hund's rules 5

Comment 2

The atomic number of thallium is $Z = 81$ and much larger than that of Ti^{2+} ($Z = 22$). The figure shows that the energy splitting due to the spin-orbit coupling of thallium is as great as the energy splitting due to the Coulomb repulsion in the case of Ti^{2+}.

($\lambda^{-1} = 8000\,\mathrm{cm}^{-1} = \frac{E}{hc}$, i.e. $\lambda = 1250\,\mathrm{nm}$ and
$E = 4.14 \cdot 10^{-15}\,\mathrm{eVs}\,3 \cdot 10^{10}\,\mathrm{cms}^{-1} \cdot 8000\,\mathrm{cm}^{-1} \approx 1\,\mathrm{eV}$)

Hund's rules 6



Comparison of the energy level scheme of the $4f^2$ configuration of Pr^{3+} and the energy level scheme of the $4f^{12}$ configuration of Tm^{3+}

Hund’s rules 6 Comment 1

The figure compares the energy levels schemes of Pr^{3+} and Tm^{3+}.

In the case of Ti^{2+}, the spin-orbit coupling is a small additional interaction that changes the energy level scheme only slightly.

In contrast, the energy level diagrams of praseodymium and thulium show that the influence of the spin-orbit coupling is as great as the influence of the Coulomb repulsion.

The atomic numbers of praseodymium ($Z = 59$) and thulium ($Z = 69$) are so large that the spin-orbit coupling can no longer be treated as a minor perturbation.

The energy difference between the energy levels of the spin-orbit multiplets no longer agree with the simple formula that resulted for the spin-orbit Hamilton operator, i.e. $\Delta E = E_J - E_{J-1} \propto J$ (Landé-rule).

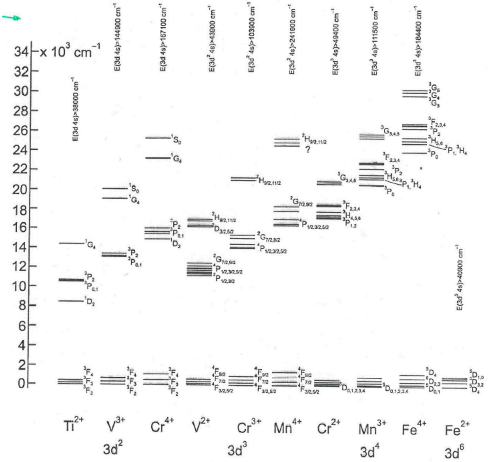
Hund’s rules 6 Comment 2

In thulium, even the order of the *J* states no longer corresponds to the spin-orbit coupling ($^3H_6$, $^3H_4$, $^3H_5$).

Nevertheless, the ground state always agrees with the prediction of Hund’s rules.

This can be confirmed both by the Zeeman splittings and by the direct measurement of the magnetic moment in the ground state.

Hund's rules 7



Hund’s rules 7

Comment

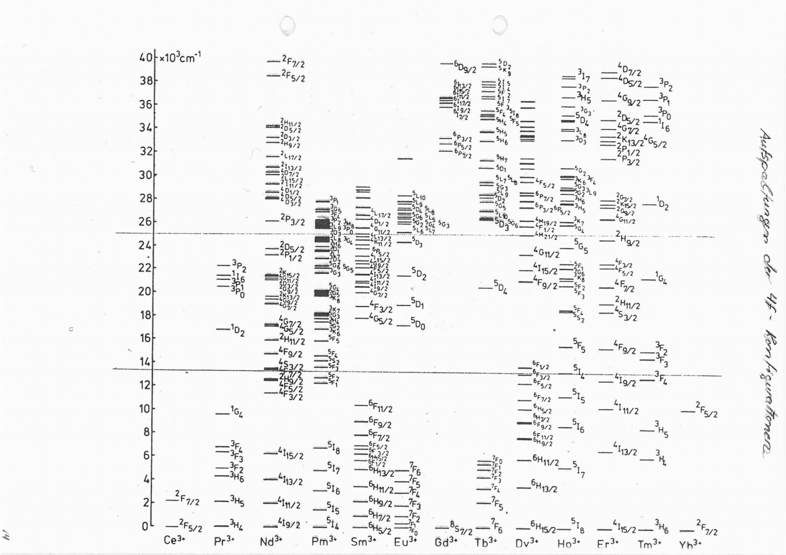
This figure shows the energy level scheme of various 3d configurations.

The spin-orbit splittings in these configurations are small compared to the splittings caused by the Coulomb repulsion.

The comparison of the energy level schemes also shows how the strength of the spin-orbit coupling increases with increasing atomic number.

In all configurations, the ground state agrees with the prediction of Hund’s rule.

Hund's rules 8



Hund’s rules 8 Comment 1

The figure compares the energy level schemes of the 4f configuration.

It starts on the left with the $4f^1$ configuration of Ce^{3+} and ends on the right with the $4f^{13}$ of Yb^{3+}.

In the case of rare earths, the spin-orbit coupling is comparable to the Coulomb repulsion of the electrons.

Therefore there are no isolated spin-orbit multiplets.

Similar to the transition metals, the comparison of Ce^{3+} and Yb^{3+} in particular shows how the spin-orbit coupling becomes stronger with increasing atomic number.

Hund's rules 8 Comment 2

The energy level diagrams also show the difference between electron configurations on the left and the electron-hole configurations on the right.

While the coupling constant of the spin-orbit interaction is positive for an electron configuration, the coupling constant for an electron-hole configuration is negative.

E.g. the total angular momentum in the ground state of Ce^{3+} $J = 5/2$, while that of Yb^{3+} $J = 7/2$.

The inversion of the spin-orbit multiplets can also be observed for the other elements.

In Gd^{3+}, half of the 4f configuration is occupied by electrons.

Hund’s rules 8 Comment 3

The energy level diagram shows that a half-filled configuration is particularly stable, similar to a completely filled configuration.

The energy splitting between the $^8S_{7/2}$ ground state of Gd^{3+} and the first excited energy levels of this configuration is particularly large.

The prediction of Hund’s rule agrees with the observation for all rare earth elements.

Ligand-field

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Ligand-field 1

Landé g-factor

$$\boxed{g_{J,L,S} = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)}}$$

effective magnetic moment

$$\boxed{\mu_{\text{eff}} = \mu_{\text{B}}\, g_{J,L,S} \sqrt{J(J+1)}}$$

Curie′s law

$$\boxed{\chi = \mu_0 N_{\text{A}} \frac{{\mu_{\text{eff}}}^2}{3k_{\text{B}} T}}$$

Ligand-field 1 Comment

The ground state of an atom can be tested by measuring the magnetic susceptibility.

The angular momenta of the ground state are determined by Hund’s rule.

The Landé g-factor of the ground state can be calculated with the quantum numbers of J, L and S.

The effective magnetic moment of the atom can be calculated using the Landé g-factor and the total angular momentum.

The magnetic susceptibility of a paramagnetic substance is given by Curie’s law.

The paramagnetic susceptibility is proportional to the square of the effective magnetic moment.

Ligand-field 2

	d^n		$g_{J,L,S}$	μ_{eff}/μ_B
Ti^{3+}	d^1	$^2D_{3/2}$	$4/5$	1.55
V^{3+}	d^2	$^3F_2$	$2/3$	1.63
Cr^{3+}	d^3	$^4F_{3/2}$	$2/5$	0.77
Mn^{3+}	d^4	$^5D_0$	0	0
Fe^{3+}	d^5	$^6S_{5/2}$	2	5.92

	d^n		$g_{J,L,S}$	μ_{eff}/μ_B
Fe^{2+}	d^6	$^5D_4$	$3/2$	6.71
Co^{2+}	d^7	$^4F_{9/2}$	$4/3$	6.63
Ni^{2+}	d^8	$^3F_4$	$5/4$	5.59
Cu^{2+}	d^9	$^2D_{5/2}$	$6/5$	3.55

Ligand-field 2 Comment

For the d^n configuration, the table shows the ground state according to Hund’s rules, the Landé g-factor and the effective moment.

The left column shows examples of ions that realize the electron configuration.

Ligand-field 3

	f^n		$g_{J,L,S}$	μ_{eff}/μ_B
Ce^{3+}	f^1	$^2F_{5/2}$	$6/7$	2.54
Pr^{3+}	f^2	$^3H_4$	$4/5$	3.58
Ne^{3+}	f^3	$^4I_{9/2}$	$8/11$	3.62
Pm^{3+}	f^4	$^5I_4$	$3/5$	2.68
Sm^{3+}	f^5	$^6H_{5/2}$	$2/7$	0.85
Eu^{3+}	f^6	$^7F_0$	0	0
Gd^{3+}	f^7	$^8S_{7/2}$	2	7.94

	f^n		$g_{J,L,S}$	μ_{eff}/μ_B
Tb^{3+}	f^8	$^7F_6$	$3/2$	9.72
Dy^{3+}	f^9	$^6H_{15/2}$	$4/3$	10.65
Ho^{3+}	f^{10}	$^5I_8$	$5/4$	10.61
Er^{3+}	f^{11}	$^4I_{15/2}$	$6/5$	9.58
Tm^{3+}	f^{12}	$^3H_6$	$7/6$	7.56
Yb^{3+}	f^{13}	$^2F_{7/2}$	$8/7$	4.54

Ligand-field 3 Comment

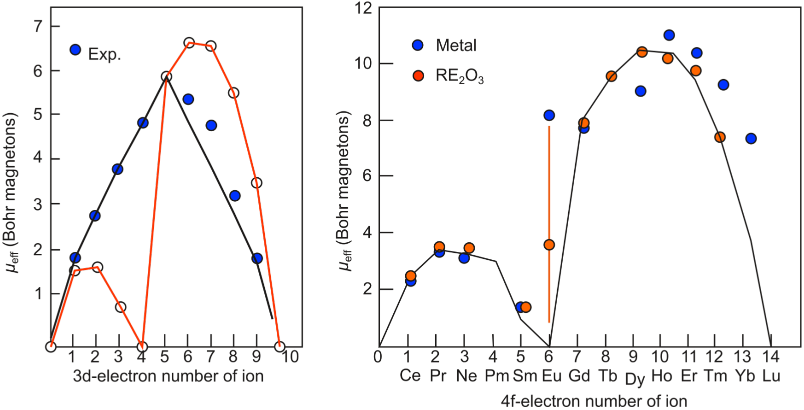
For the f^n configuration, the table shows the ground state according to Hund’s rules, the Landé g-factor and the effective moment.

The left column shows examples of ions that realize the electron configuration.

Ligand-field 4

effective magnetic moment

$$\boxed{\mu_{\text{eff}} = \mu_{\text{B}}\, g_{J,L,S}\sqrt{J(J+1)}}$$



Ligand-field 4 Comment 1

The figures compare the theoretical predictions with experimental results.

The left figure shows the comparison for the transition metal ions (3d ions).

The red line and open circles show the theoretical results and the blue dots the experimental results which can be obtained for molecules and solids containing transition metal ions.

The experimental results do not agree with theory, with the exception of the $3d^5$ configuration of Fe^{3+} or Mn^{2+}.

The black solid line shows the effective magnetic moment when only the spin of the electron configuration is taken into account.

Ligand-field 4 Comment 2

If only the g-factor $g = 2$ is used for a pure electron spin configuration, then the prediction of the theory agrees better with the experimental results.

The experimental results indicate that for the 3d configurations, the orbital angular momentum does not contribute to the magnetic moment.

This phenomenon is known as the quench of the orbital angular momentum.

The figure on the right shows the comparison for the trivalent rare earth ions.

The effective magnetic moment, which can be calculated using the Landé g factor and Hund's rules, agrees well with the experimental results.

The only exception is Eu^{3+}.

Ligand-field 4

Comment 3

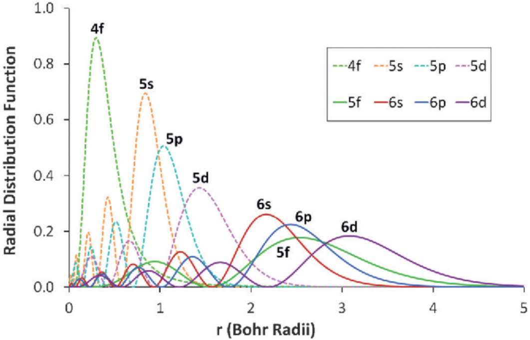
The total angular momentum of Eu^{3+} is zero, so that there should actually be no magnetic moment at all.

In the ground state of Eu^{3+}, the magnetic moment is induced by the magnetic field not as usual by splitting of the Zeeman levels but by a mixing of magnetic excited states into to ground state.

The phenomenon is named after John Hasbrouck Van Vleck, who described this type of paramagnetism in 1928.

Ligand-field 5

4f electrons are effectively screened from the influence of the surrounding atoms



the electron configuration of the RE atoms is $[Xe]4f^{n}5d^{1}6s^{2}$

The electron configuration of Xenon is $[Kr]5s^{2}4d^{10}5p^{6}$

Ligand-field 5 Comment

The effective magnetic moment of the rare earth ions follows the prediction of Hund’s rules, since the 4f electrons are effectively shielded from the environment.

The figure shows the radial probability distribution $r^2 R_{n,\ell}{}^2(r)$ for the outer orbitals of the 4f and 5f elements.

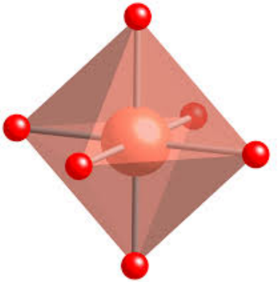
The 5d and 6s orbitals of the trivalent rare earth ions are not occupied.

But even if these electrons are missing, the 4f electrons are shielded by the fully occupied 5s and 5p orbitals of the xenon configuration ([Kr] $4d^{10}5s^{2}5p^{6}$).

Ligand-field 6

3d orbitals are not shielded from the environment by other orbitals.

- very often transition metal ions are octahedrally coordinated by N^-, O^-, Cl^- or CN^--ligands



- the 3d orbitals react strongly to the charge on the ligands

Ligand-field 6

Comment 1

In contrast to the electrons in the 4f orbitals, the electrons in the 3d orbitals are not shielded from the environment by outer orbitals.

Very often the ions of the transition metals are coordinated by ligands.

The ligands are negatively charged atoms or molecules that attach to the transition metal ion due to electrostatic attraction.

This very often creates a near octahedral environment around the transition metal ion, as shown in the figure.

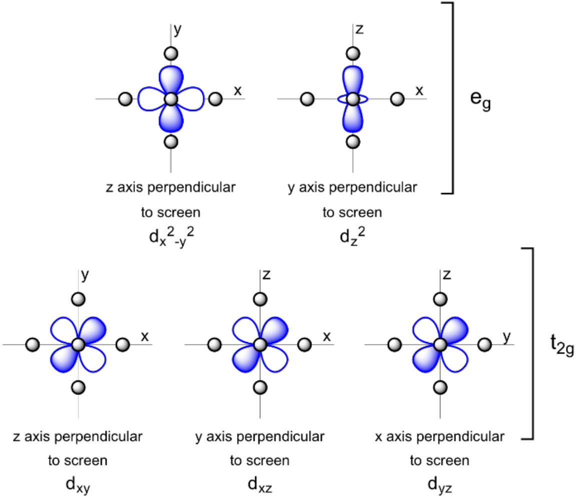
In the figure the ligands are shown as red spheres.

Ligand-field 6 Comment 2

The ligands are usually negatively charged nitrogen, oxygen, chlorine ions or cyano molecules.

The influence of the ligands on the electrons in the 3d orbital of the transition metal ion increases from nitrogen to oxygen and chlorine to cyan.

Ligand-field 7



z axis perpendicular to screen $d_{x^2-y^2}$

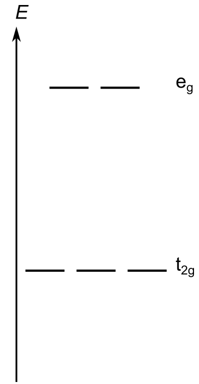
y axis perpendicular to screen d_{z^2}

z axis perpendicular to screen d_{xy}

y axis perpendicular to screen d_{xz}

x axis perpendicular to screen d_{yz}

○=Ligand point



Ligand-field 7 Comment 1

The figure shows the d orbitals, i.e. the real and imaginary parts of the spherical harmonics $Y_{\ell=2,m}$.

The $d_{x^2-y^2}$ and the d_{z^2} orbitals point directly towards the ligands.

The lobes of the d_{xy}, d_{xz}, and d_{yz} orbitals avoid the ligands.

The figure on the right shows the energy level scheme of the d orbitals.

If the electrons occupy the d_{xy}, d_{xz} or d_{yz} orbital, the potential energy is smaller than if they occupy the $d_{x^2-y^2}$ or d_{z^2} orbital.

The $d_{x^2-y^2}$, d_{z^2} orbitals are called the e_g orbitals.

The d_{xy}, d_{xz}, and d_{yz} orbitals orbitals are called the t_{2g} orbitals.

Ligand-field 7 Comment 2

The energy splitting between the t_{2g} and e_g orbitals increases with the strength of the ligands, i.e. the energy splitting is greater with cyan than with chlorine etc.

The orbital angular momentum is quenched because the angular dependence of the wave function is no longer described by the full spherical harmonics $Y_{\ell=2,m}$, but by its real and imaginary parts when ligands attach to the transition metal ion.

If the d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2} orbitals are used to calculate the expectation value of the orbital angular momentum, the result is zero or a very small number.

The movement of the electrons is influenced by the ligands and the rotation is suppressed by the ligands.

For this reason the expectation value for the orbital angular momentum disappears.

Ligand-field 7

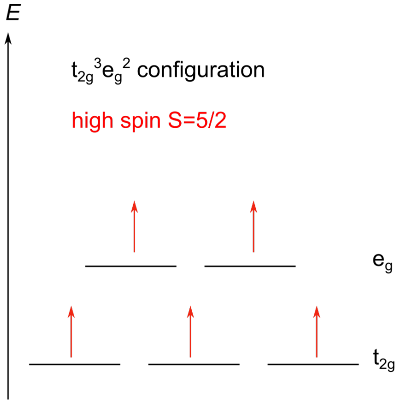
Comment 3

The spin of the electrons is not influenced by the negative charge of the ligands.

Since the orbital angular momentum is suppressed by the ligands, the magnetic moment of the 3d ions is mainly determined by the spin of the electrons.

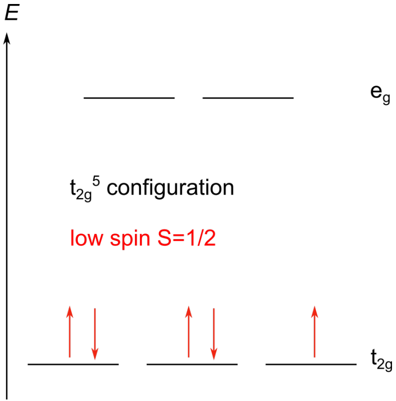
Ligand-field 8

e.g. Fe^{III}



$t_{2g}^3 e_g^2$ configuration

high spin $S=5/2$



t_{2g}^5 configuration

low spin $S=1/2$

Ligand-field 8

Comment 1

The two energy level schemes show the influence of the exchange interaction using the example of the $3d^5$ configuration of Fe^{3+} or Mn^{2+}.

The exchange interaction is based on the fact that electrons, due to the Coulomb repulsion, avoid occupying a common orbital as much as possible.

For this purpose, the spins of the electrons adjust themselves in parallel, so that a double occupation of an orbital is prevented by the Pauli principle.

In the energy level diagram on the left, the difference in potential energy due to ligands is small, so that the spins align themselves in parallel and all orbitals are occupied by electrons.

Ligand-field 8 Comment 2

The reduction in the binding energy by electron-electron repulsion due to the exchange interaction is greater than the additional potential energy that has to be expended in order to occupy the excited e_g orbitals.

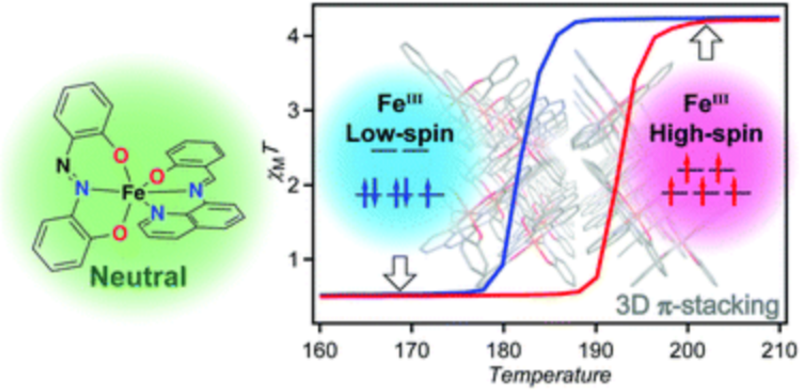
In the energy level diagram on the right, the difference in potential energy is large, so that the electrons prefer to occupy the lower t_{2g} orbitals twice.

The reduction in the binding energy by electron-electron repulsion due to the exchange interaction is smaller than the additional potential energy that has to be expended in order to occupy the e_g orbitals.

In the left energy level scheme the spins add up to $S = 5/2$, while in the right energy level scheme only the value $S = 1/2$ results.

Ligand-field 9

High spin- low-spin transition of a Fe^{III}-complex (electron configuration 3d^5)



Ligand-field 9 Comment 1

How strongly the ligands influence the 3d electrons of a transition metal can sometimes be influenced by external parameters such as pressure or temperature.

As an example, the figure shows a substance in which the influence of the ligands increases with decreasing temperature.

At high temperatures, the electrons occupy all orbitals and the spins are aligned in parallel.

Below a certain critical temperature it becomes more favorable to occupy only the lower energy levels and the spins are partially antiparallel.

At the critical temperature, the spin changes from $S = 5/2$ at high temperatures to $S = 1/2$ at low temperatures.

Ligand-field 9 Comment 2

This transition is clearly noticeable in the magnetic moment of the sample.

The diagram shows the product of susceptibility and temperature, which is proportional to the square of the effective magnetic moment.

X-Ray Spectroscopy

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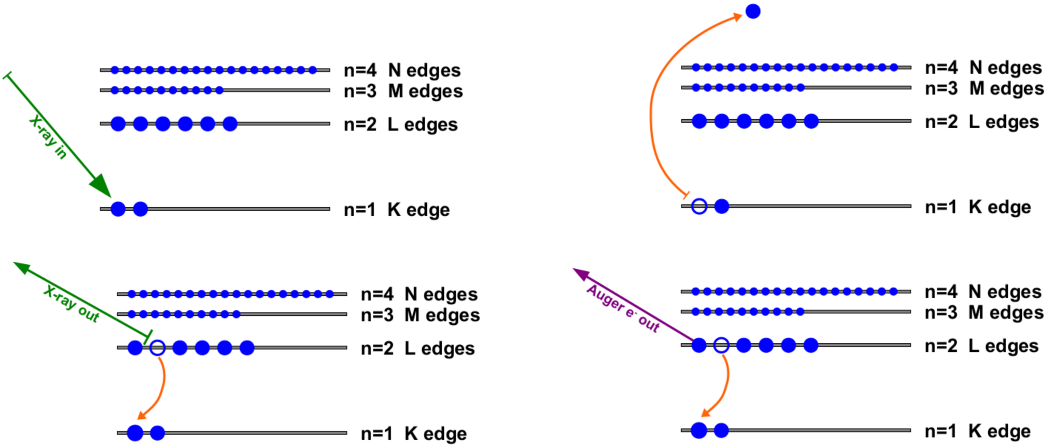
X-Ray Spectroscopy 1



X-Ray Spectroscopy 1 Comment 1

The figures outline the principle of X-ray absorption and fluorescence spectroscopy.

The atomic energy levels with the principal quantum number n are called edges, since an electron can only be knocked out of the atom if the energy of the incident X-ray beam is greater than the corresponding edge.

The blue dots show the occupation of the energy levels, although the number of dots does not correspond to the maximum possible number of electrons.

In the first figure, an X-ray photon hits an electron, which in the second figure is knocked out, leaving a occupation hole in the corresponding energy level.

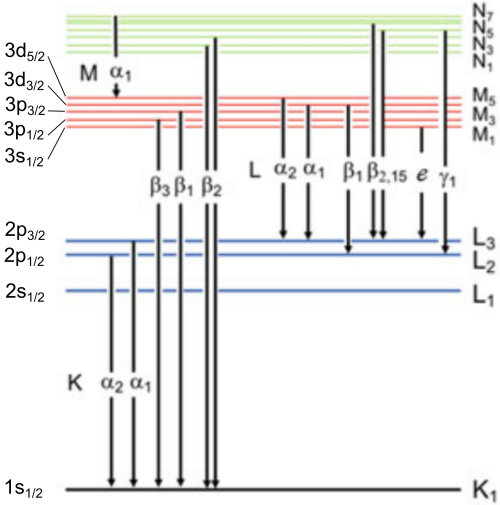
X-Ray Spectroscopy 1 Comment 2

In the third and fourth figures, this hole is filled with a higher energy electron.

In the figure on the left, an X-ray photon is emitted during the relaxation process.

Alternatively, an electron called an Auger electron can be emitted. Figure on the right.

X-Ray Spectroscopy 2: Siegbahn vs. IUPAC notation



X-Ray Spectroscopy 2 Comment 1

In the first years of the 20th century it was noticed that the spectra of the characteristic radiation are particularly clear and can be described by small modifications of the energy formula of Bohr’s atomic model.

The reason for this observation is that the energy of X-rays is large compared to the interaction energies among the electrons of an atom (e-e repulsion, spin-orbit coupling etc.).

The notation of the characteristic lines goes back to Manne Siegbahn, who was honored with the Nobel Prize in 1924 ”for his discoveries and research in the field of X-ray spectroscopy”.

The figure shows the transitions, which correspond to the characteristic lines, with the corresponding notation according to Manne Siegbahn.

Although the Siegbahn notation is somewhat confusing, it is still widely used.

X-Ray Spectroscopy 2 Comment 2

The International Union of Pure and Applied Chemistry (IUPAC) therefore proposes a systematic notation based on a compromise between the Siegbahn notation and the notation of atomic orbitals according to the Schrödinger equation.

The notation of atomic orbitals is shown on the left side of the energy level scheme, while the IUPAC notation is shown on the right.

E.g. $K_{\alpha 1}$ corresponds to the transition $K_1 \leftrightarrow L_3$, etc.

X-Ray Spectroscopy 3

Iron: Z=26

Edge	Energy (eV)
K	7112
L3	706.8
L2	719.9
L1	844.6

Line	Transition	Energy (eV)	Strength
$K\alpha_1$	K-L3	6405.2	0.580
$K\alpha_2$	K-L2	6392.1	0.294
$K\beta_1$	K-M3	7059.3	0.082
$K\beta_3$	K-M2	7059.3	0.043
$K\beta_5$	K-M4,5	7110.0	0.001

Uranium: Z=92

Edge	Energy
K	115606
L3	17166
L2	20948
L1	21757

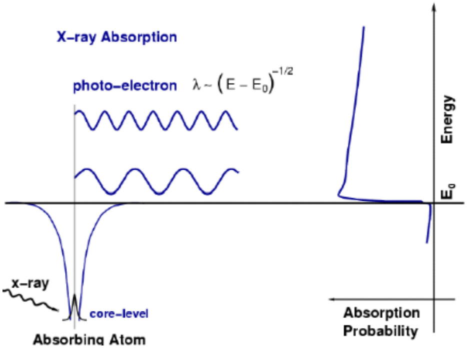
Line	Transition	Energy	Strength
$L\alpha_1$	L3-M5	13614.0	0.686
$L\alpha_2$	L3-M4	13438.0	0.077
$L\beta_2$	L3-N4,5	16387.7	0.181
$L\beta_5$	L3-O4,5	17063.2	0.038
$L\beta_6$	L3-N1	15727.0	0.013
L_ℓ	L3-M1	11618.0	0.005

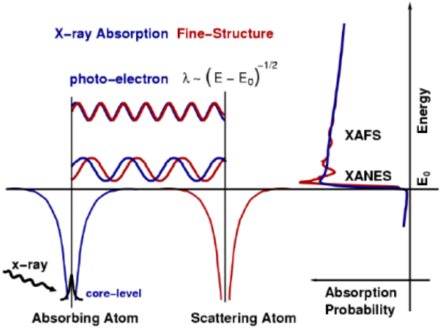
X-Ray Spectroscopy 3 Comment

The energy of the edges and characteristic lines depend on the atomic number *Z* and are tabulated (see e.g. https://www.ruppweb.org/Xray/elements.html and https://www.chess.cornell.edu/users/calculators/characteristic-emission-lines-elements)

The figure shows some examples for iron and uranium.

X-Ray Spectroscopy 4





X-Ray Spectroscopy 4 Comment 1

The figures show the principle of X-ray absorption spectroscopy.

In the lower half of the picture on the left, the wave function of a core electron is shown in its atomic potential.

The electron is knocked out of the atom by a photon of energy E.

If the energy E exceeds the binding energy E_0, the electron can propagate freely according to a de Broglie wave.

With increasing energy E the de Broglie wavelength of the free electron decreases. The figure shows two examples.

The right side of the figure shows that the absorption probability of a photon increases sharply as the energy of the photon approaches the binding energy E_0 of the electron.

X-Ray Spectroscopy 4 Comment 2

The figure neglects the fact that there are also many bound electron states just below E_0.

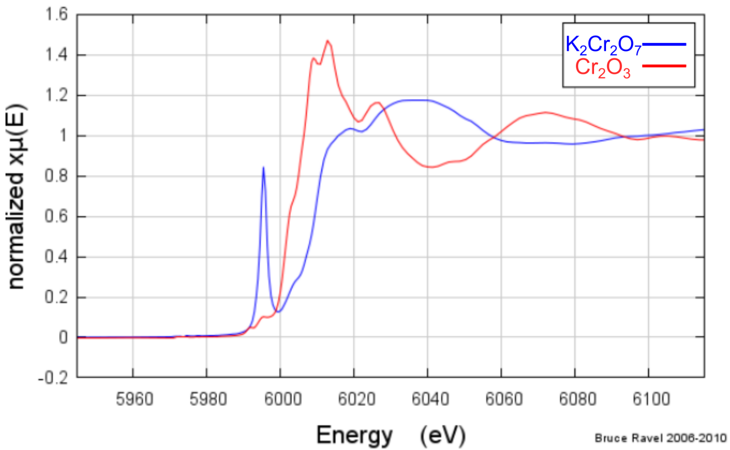
Excitations to these energy levels can also be observed just before the X-ray absorption edge.

Usually the atom is surrounded by other atoms.

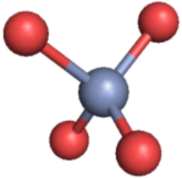
The wave of the quasi-free electron is scattered by these atoms and, depending on the energy of the electron, interference can be observed that changes the absorption probability of the incident photon.

The effect is called X-ray absorption fine structure (XAFS) and the study of these features is called X-ray absorption near-edge structure spectroscopy (XANES).

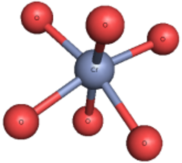
X-Ray Spectroscopy 5



$K_2Cr_2O_7$



Cr_2O_3



X-Ray Spectroscopy 5

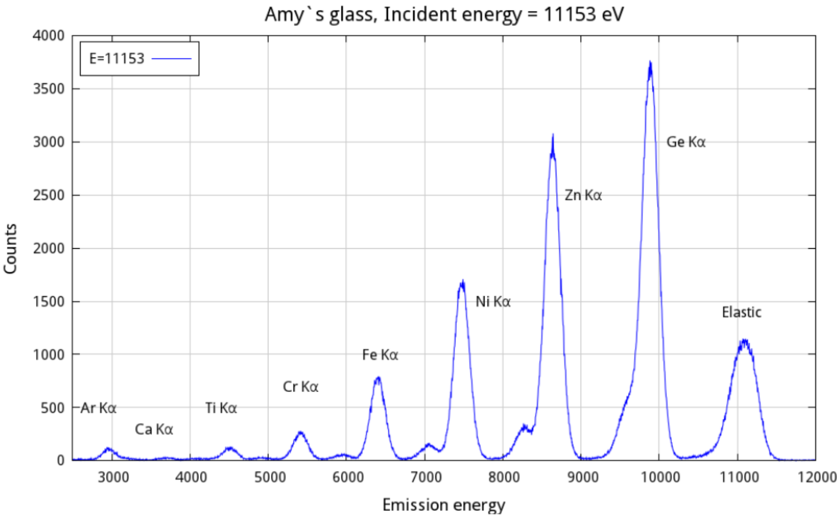
Comment

The figure shows measurements of the K-edge of Cr for two different compounds.

$K_2Cr_2O_7$ is a highly toxic compound while Cr_2O_3 is harmless.

By measuring the K-edge, both substances can be clearly distinguished from each other.

X-Ray Spectroscopy 6



X-Ray Spectroscopy 6 Comment 1

The figure shows the fluorescence spectrum of glass doped with Ge and various transition metals from Ti to Zn.

The K-edge of Si and O are 1838.9 eV and 532.0 eV, respectively. The fluorescence of these elements is therefore well below 3 keV.

The excitation energy of 11153 eV is just above the K-edge of Ge.

Therefore, the fluorescence of the 3d elements doped into the glass can be observed.

Consider the characteristic line of iron as the energy is shown on slide 3.

The strong line corresponds to K_α or more precisely to the transitions $K_1 \leftrightarrow L_3$, i.e. K_{α_1} and $K_1 \leftrightarrow L_2$, i.e. K_{α_2}.

X-Ray Spectroscopy 6 Comment 2

The weak line on the right side at about 7100 eV corresponds to K_β or more precisely to the transitions $K_1 \leftrightarrow M_{2,3}$, i.e. $K_{\beta_{1,3}}$.

Note: The transition $K_1 \leftrightarrow M_{4,5}$ shown on slide 3, i.e. K_{β_5} is obviously a forbidden transition ($\Delta\ell = \pm 2$) and its strength is correspondingly small. The figure on slide 2 only shows allowed transitions.

Revision

Summary in Questions

1. For a few examples, test Hund’s rules with the data in the tables on slide Ligand-field 2 and 3.
2. How big is the spin of Fe^{2+} in the high-spin / low-spin configuration?
3. Assign the small lines between the main peaks in the spectrum of the glass on page X-Ray Spectroscopy 6.