Atoms

Coupling schemes

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

Coupling schemes 1

electron-electron repulsion

$$\underline{\hat{H}_C = \sum_{i<j} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}$$

LS-scheme when spin-orbit coupling is negligible

$$\boxed{\hat{\vec{L}} = \sum_i \hat{\vec{\ell}}_i}$$

and

$$\boxed{\hat{\vec{S}} = \sum_i \hat{\vec{s}}_i}$$

Coupling schemes 1 Comment

The repulsive force between the electrons is an important interaction.

The equation underlined in red indicates the potential energy due to electron-electron repulsion.

Since the Coulomb repulsion does not affect the spin of the electrons, spins and orbital angular momenta are independent of one another as long as the spin-orbit coupling is negligibly small.

Then the orbital angular momentum of the electrons add up to a total orbital angular momentum and the spins add up to a total spin of the electron configuration.

This regime is known as the LS coupling scheme.

Coupling schemes 2

Notation of an electron configuration

$$\boxed{{}^{2S+1}L_J}$$

and

$$\underline{\hat{\vec{J}} = \hat{\vec{S}} + \hat{\vec{L}}}$$

completely occupied orbitals

$$\boxed{L = 0 \quad \text{and} \quad S = 0 \quad \text{and} \quad J = 0}$$

Coupling schemes 2

Comment

In terms of angular momentum, the notation of electron configurations is similar to the notation of a single orbital.

The symbol framed in red shows the notation.

The total orbital angular momentum is indicated by the capital letters S, P, D, F, etc.

The total angular momentum results from the sum of the total spin and the total orbital angular momentum.

When an orbital is completely occupied by electrons, the total angular momentum adds up to zero.

Therefore only the incompletely occupied orbitals contribute to the total angular momentum of the electron configuration.

Coupling schemes 3

spin orbit coupling

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

- for $Z \lesssim 50$ the LS-scheme works, i.e. $\vec{J} = \vec{L} + \vec{S}$
- for $Z \gtrsim 50$ only J and M_J are good quantum numbers

remark: nevertheless the LS notation scheme is always used to denote electron configurations

but selection rules for ΔS and ΔL break down

Coupling schemes 3

Comment 1

The spin-orbit coupling is always present.

The total orbital angular momentum and the total spin form the total angular momentum J due to the spin-orbit coupling, as long as the electron-electron repulsion dominates for atomic numbers less than $Z \approx 50$.

If the atomic number becomes large, i.e. greater than $Z \approx 50$, only the total angular momentum is strictly defined.

The selection rules $\Delta S = 0$ and $\Delta L = 0, \pm 1$ are no longer valid.

Coupling schemes 3

Comment 2

Interestingly, the LS notation is still used to describe the quantum states.

The reason for this lies in the mathematics of quantum states.

The quantum states are developed into a sum of pure LS states.

The LS quantum numbers of the largest contribution are then used to denote the overall quantum state.

Entanglement

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Entanglement 1

Elementary particles (e.g. electrons, photons etc.) are identical and cannot be identified by any type of label!

a quantum state of two elementary particles cannot be written as

$$\underline{|a\rangle_1 |b\rangle_2} \quad \text{or} \quad \underline{|a\rangle_2 |b\rangle_1}$$

If $|a\rangle_1 |b\rangle_2$ or $|a\rangle_2 |b\rangle_1$ would be quantum states of two elementary particles, one could identify the elementary particle by the quantum state it takes.

Entanglement 1 Comment

Elementary particles are identical.

It is not possible to put a label on an elementary particle.

Therefore it is by no means possible to distinguish elementary particles.

The underlined formulas $|a\rangle_1\,|b\rangle_2$ and $|a\rangle_2\,|b\rangle_1$ cannot be the quantum states of two elementary particles.

Because if one could describe a quantum state of two elementary particles in one way or another, one could identify the elementary particles based on the quantum states they occupy.

The quantum states $|a\rangle$ or $|b\rangle$ would be the label attached to the elementary particle.

Entanglement 2

Quantum state of two electrons which occupy quantum states $|a\rangle$ and $|b\rangle$

$$\boxed{|a,b\rangle_{1,2} = |a\rangle_1\,|b\rangle_2 - |a\rangle_2\,|b\rangle_1}$$

Quantum state of two photons which occupy quantum states $|a\rangle$ and $|b\rangle$

$$\boxed{|a,b\rangle_{1,2} = |a\rangle_1\,|b\rangle_2 + |a\rangle_2\,|b\rangle_1}$$

General rule for the quantum states of *N* electrons

$$\boxed{|\psi\rangle_{1,2\ldots i,\ldots j,\ldots.N} = -\,|\psi\rangle_{1,2\ldots j,\ldots i,\ldots.N}}$$

General rule for the quantum states of *N* photons

$$\boxed{|\psi\rangle_{1,2\ldots i,\ldots j,\ldots.N} = +\,|\psi\rangle_{1,2\ldots j,\ldots i,\ldots.N}}$$

Entanglement 2

Comment 1

The quantum state of the two elementary particles is a linear combination of $|a\rangle_1 \, |b\rangle_2$ and $|a\rangle_2 \, |b\rangle_1$.

The first equation outlined in red gives the linear combination for two electrons.

The quantum state is zero (i.e. $|a, b\rangle_{1,2} = |0\rangle$) when $|a\rangle = |b\rangle$.

This is the Pauli exclusion principle.

Two electrons must differ in at least one quantum number.

Entanglement 2

Comment 2

The second equation framed in red gives the linear combination for two photons.

The occupation number of a quantum state is not restricted for photons. Therefore $|a\rangle = |b\rangle$ is possible.

The third equation framed in red gives the general rule for a quantum state of N electrons.

The quantum state is antisymmetric when two electrons are exchanged, i.e. the quantum state changes sign.

The last equation framed in red gives the general rule for a quantum state of N photons.

Entanglement 2 Comment 3

The quantum state is symmetric when two photons are exchanged, i.e. the quantum state does not change the sign.

These properties of the quantum states of *N* elementary particles are called entanglement.

Entanglement is a general feature of quantum mechanics.

Particles for which $|\psi\rangle_{1,2\ldots i,\ldots j,\ldots.N} = -|\psi\rangle_{1,2\ldots j,\ldots i,\ldots.N}$ is true are called fermions.

Particles for which $|\psi\rangle_{1,2\ldots i,\ldots j,\ldots.N} = +|\psi\rangle_{1,2\ldots j,\ldots i,\ldots.N}$ is true are called bosons.

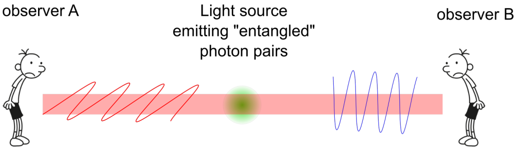
The spin of fermions is always half-integer, while the spin of bosons is always integer.

One can experiment with entangled electrons and with entangled photons.

Entanglement 3

Einstein Podolsky Rosen paradox: realization in optics

- a photon source emits entangled photons $|a,b\rangle_{1,2} = |a\rangle_1 |b\rangle_2 + |a\rangle_2 |b\rangle_1$
- the polarisation of the two quantum states $|a\rangle$ and $|b\rangle$ is perpendicular
- and the photons propagate in opposite direction towards an observer A and B



When one observer measures the polarization of his photon, the wave function collapses and the polarization of the other photon is immediately established.

Entanglement 3 Comment 1

Let us now look again at the Einstein-Podolsky-Rosen paradox.

To realize the paradox in optics, a light source is required that emits entangled photon pairs.

The formula underlined in red describes the quantum state of the two entangled photons.

The quantum states $|a\rangle$ and $|b\rangle$ differ in polarization and in the direction of propagation.

Therefore the probability that an observer will observe a certain polarization of his photon is 50 %.

Entanglement 3 Comment 2

With the measurement, the entangled quantum state collapses and the polarization of the other photon is instantly established.

This is paradoxical, but true and independent of the distance that separates the two observers (see the Nobel prizes in physics 2022 awarded to Alain Aspect, John Clauser and Anton Zeilinger: ”for experiments with entangled photons, establishing the violation of Bell inequalities and pioneering quantum information science”).

Exchange interaction

Atoms with many electrons

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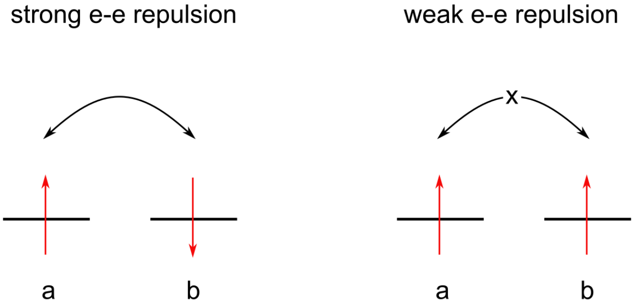
Exchange interaction 1

electron-electron repulsion

$$\boxed{\hat{H}_{12} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}$$

is sensitive to entanglement



Exchange interaction 1

Comment 1

The electron-electron repulsion reacts very sensitively to the entanglement of electron states.

The potential energy of electron-electron repulsion depends on the orientation of the electron spins due to entanglement.

The influence of the entanglement on the energy of the quantum states is called the exchange interaction.

The exchange interaction is a real quantum effect and has no analogue in classical physics.

Exchange interaction 1 Comment 2

The illustration shows what is happening.

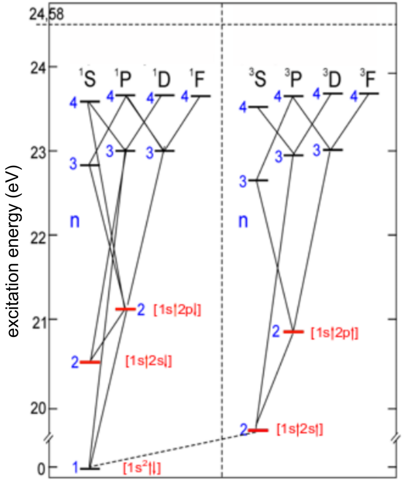
When electron spins are anti-parallel, they can jump into the same orbital and the electron repulsion energy is large, i.e. the binding energy of the electrons is greatly reduced.

When the electron spins are parallel, they cannot occupy the same orbital due to the Pauli principle and the electron repulsion is weaker since they have to stay in different orbitals.

These considerations explain many experimental observations, which can also be calculated at least numerically by solving the Schrödinger equation.

Exchange interaction 2

excited states of the helium atom



Exchange interaction 2

Comment 1

The figure shows the energy level scheme of the helium atom.

The ionisation energy is 24.58 eV above the ground state with two electrons in the 1s orbital.

The notation of the electron configuration is [$1s^2$].

The spins of the electrons are antiparallel, or more precisely the m_s quantum number has the values $\pm 1/2$.

In the figure this is indicated by two anti-parallel vectors in the notation of the electron configuration.

Four excited states are marked by red bars.

Exchange interaction 2 Comment 2

The notation of the electron configuration shows that one electron remains in the 1s orbital while the other is excited into either the 2s or 2p orbital.

The total orbital angular momentum of the electron configuration is therefore $L = 0$ or $L = 1$ and the total spin is either $S = 0$ or $S = 1$.

The notation of the energy levels is given at the top of the figure, i.e. ^{1}S,^{1}P, and ^{3}S,^{3}P.

The energy level diagram shows that the binding energy of the singlet states $E(^1\mathrm{S})$ is smaller than the binding energy of the triplet states $E(^3\mathrm{S})$.

Likewise is the binding energy $E(^1\mathrm{P})$ smaller than the binding energy $E(^3\mathrm{P})$.

That is the effect of the exchange interaction.

Exchange interaction 2 Comment 3

The level diagram also shows the electric dipole transitions.

The selection rules are $\Delta\ell = \pm 1$ and consequently $\Delta L = \pm 1$ and $\Delta S = 0$.

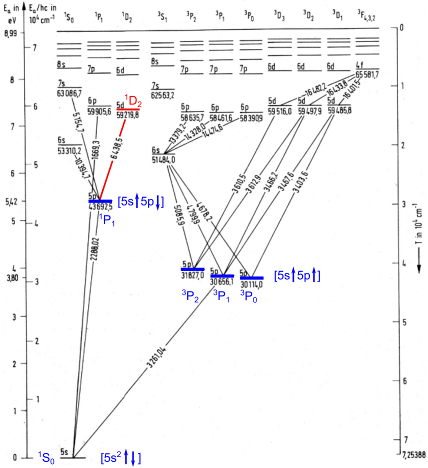
The electromagnetic spectrum of the helium atom breaks down into the transitions between the singlet states with $S = 0$ and the triplet states with $S = 1$.

The effect of the spin-orbit coupling is small and cannot be resolved in the figure.

The excited state $2^3\mathrm{S}_1$ cannot relax into the ground state $1^1\mathrm{S}_0$ through an electric dipole transition. This is indicated by the dashed line.

Exchange interaction 3

energy level scheme of cadmium (electron configuration $[\mathrm{Kr}]5s^2, 4d^{10}$)



Exchange interaction 3 Comment 1

The figure shows the excitation spectrum of the cadmium atom.

The ground state of the valence electrons is given by the 5s orbital, which is occupied by two electrons.

All other orbitals with lower energy are completely occupied with electrons.

The fully occupied orbitals realize the noble gas configuration of krypton.

The atomic number of Cadmium is $Z = 48$.

The periodic table of the elements shows that the 5s orbital is occupied by electrons before the 4d orbital.

However, if the 4d orbital is completely occupied by 10 electrons, then its binding energy is larger than that of the 5s orbital.

Exchange interaction 3

Comment 2

Consequently, in the case of the cadmium atom, the 5s electrons are the valence electrons.

Similar to helium, one electron is excited into an orbital with higher energy.

The first excited energy levels are indicated by blue bars.

One electron is excited from the 5s orbital to the 5p orbital.

These excited states are either the singlet state $^1P_1$ or the triplet states $^3P_{2,1,0}$.

The binding energy of the singlet state is reduced due to the exchange interaction compared to the binding energy of the triplet states.

For the triplet states, the splitting due to the spin-orbit coupling is visible.

Exchange interaction 3 Comment 3

The energy of the state $^3\mathrm{P}_0$ is less than the energy of the states $^3\mathrm{P}_1$ and $^3\mathrm{P}_2$.

As expected, spin and orbit are preferably aligned antiparallel.

The energy level scheme also shows the electric dipole transitions.

The selection rule is $\Delta\ell = \pm 1$ and consequently $\Delta L = \pm 1$.

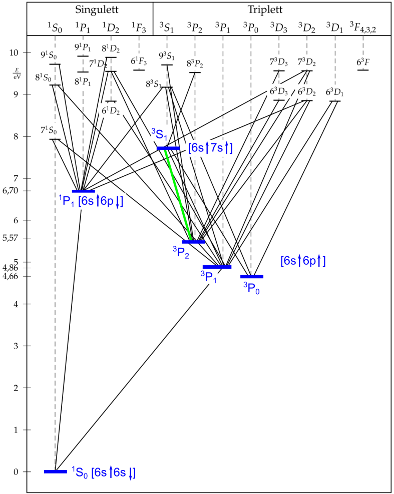
The influence of the spin-orbit coupling is small and the additional selection rule $\Delta S = 0$ is also fulfilled for cadmium .

The Zeeman effect of cadmium was discussed for the transition $^1\mathrm{P}_1 \leftrightarrow {}^1\mathrm{D}_2$.

The normal Zeeman effect can be observed since the total spin is zero.

Exchange interaction 4

energy level scheme of mercury (electron configuration $[\mathrm{Xe}]6s^2$, $4f^{14}$, $5d^{10}$)



Übergang	λ / nm
$6^1S_0 \leftrightarrow 6^1P_1$	184,95
$6^1S_0 \leftrightarrow 6^3P_1$	253,65
$6^3P_1 \leftrightarrow 7^3D_2$	265,20
$6^3P_1 \leftrightarrow 7^1D_2$	265,51
$6^3P_0 \leftrightarrow 8^3S_1$	275,28
$6^3P_1 \leftrightarrow 8^1S_0$	285,69
$6^3P_1 \leftrightarrow 8^3S_1$	289,36
$6^3P_2 \leftrightarrow 9^3S_1$	292,54
$6^3P_0 \leftrightarrow 6^3D_1$	296,72
$6^3P_2 \leftrightarrow 7^3D_3$	302,15
$6^3P_2 \leftrightarrow 7^3D_2$	302,35
$6^3P_2 \leftrightarrow 7^1D_2$	302,75
$6^3P_1 \leftrightarrow 6^3D_2$	312,57
$6^3P_1 \leftrightarrow 6^3D_1$	313,16
$6^1D_2 \leftrightarrow 6^3P_1$	313,18
$6^3P_2 \leftrightarrow 8^3S_1$	334,15
$6^3P_2 \leftrightarrow 6^3D_3$	365,02
$6^3P_2 \leftrightarrow 6^3D_2$	365,48
$6^1P_1 \leftrightarrow 8^1D_2$	390,64
$6^3P_0 \leftrightarrow 7^3S_1$	404,66
$6^3P_1 \leftrightarrow 7^1S_0$	407,78
$6^1P_1 \leftrightarrow 9^1S_0$	410,81
$6^1P_1 \leftrightarrow 7^3D_2$	433,92
$6^1P_1 \leftrightarrow 7^1D_2$	434,75
$6^3P_1 \leftrightarrow 7^3S_1$	435,83
$6^1P_1 \leftrightarrow 8^1S_0$	491,61
$6^1P_1 \leftrightarrow 8^3S_1$	502,56
$6^3P_2 \leftrightarrow 7^3S_1$	546,08
$6^1P_1 \leftrightarrow 6^3D_2$	576,96
$6^1P_1 \leftrightarrow 6^1D_1$	579,07
$8^3P_2 \leftrightarrow 7^3S_1$	690,75
$6^1P_1 \leftrightarrow 7^1S_0$	1013,98

Datenquelle:
NIST Atomic Spectra Database
v3.1.3

Exchange interaction 4 Comment 1

The figure shows the energy level scheme of mercury.

The two valence electrons occupy the 6s orbital.

As before, we can observe the effect that although the 6s, 4f and then 5d orbitals are occupied by electrons according to the periodic table of elements, it is the 6s orbital that has the smallest binding energy when all other orbitals are fully occupied.

One valence electron is excited into an orbital with higher energy.

The energy levels with the lowest excitation energy are indicated by blue bars.

One 6s electron is excited in the 6p orbital.

Exchange interaction 4 Comment 2

The singlet state $^1P_1$ results for antiparallel spin orientation and the triplet states $^3P_0$, $^3P_1$, and $^3P_2$ for parallel spin orientation.

Due to the exchange interaction, the binding energy of the singlet state is reduced compared to the binding energy of the triplet states.

The atomic number of mercury is $Z = 80$ and the spin orbit coupling is no longer negligible.

The energy level diagram shows that the level splitting due to the spin-orbit coupling is noticeable for the first excited triplet states.

The energy level scheme also shows the electric dipole transitions.

Exchange interaction 4 Comment 3

The selection rule $\Delta L = \pm 1$ still applies due to the fundamental selection rule for a single electron $\Delta \ell = \pm 1$.

Due to the strong spin-orbit coupling, the selection rule $\Delta S = 0$ is no longer valid.

The heuristic interpretation of this effect is that the motion of the electron spin is very fast due to the spin-orbit coupling, so that the orientation of the spin can change during the electric dipole transition.

The $^3\mathrm{P}_2 \leftrightarrow {}^3\mathrm{S}_1$ transition of the green mercury line is marked green in the energy level diagram.

This transition shows the anomalous Zeeman effect previously discussed.

Hund’s rules

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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

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

$$\begin{array}{ccccc} N < (2\ell + 1) & \rightarrow & \xi > 0 & \rightarrow & J = |L - S| \\ N > (2\ell + 1) & \rightarrow & \xi < 0 & \rightarrow & J = \ L + S \end{array}$$

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.

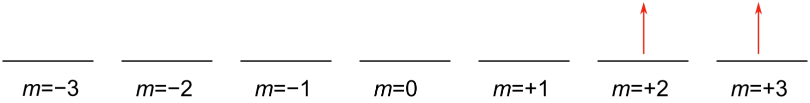
The following examples show that Hund’s rule is easy to apply.

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 : $\boxed{{}^3H_4}$

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. In trivalent praseodymium, the two 6s electrons and the single 5d electron are missing.

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 rules 3 Comment 2

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

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 $S = 1$.

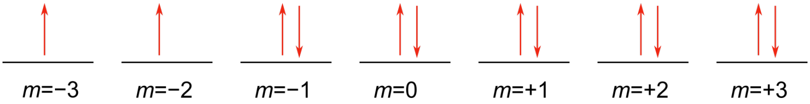
The orbital angular momentum $L = 5$ is denoted by the capital letter H according to the convention (S,P,D,F,G,H, etc.)

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 $[\mathrm{Xe}]4f^{12}$)



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

ground state : $\boxed{{}^3H_6}$

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 4f orbital.

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

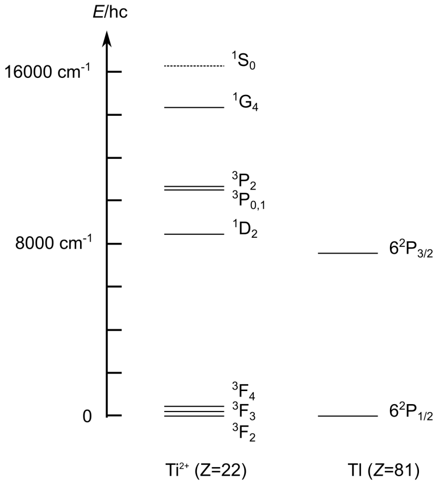
Hund's first rule gives the value $L = 5$ for the total orbital angular momentum.

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+} (atomic number $Z = 22$, [Ar] $3d^2 4s^2$) and the energy level scheme of the $6p^1$ configuration of Tl (atomic number $Z = 81$, [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.

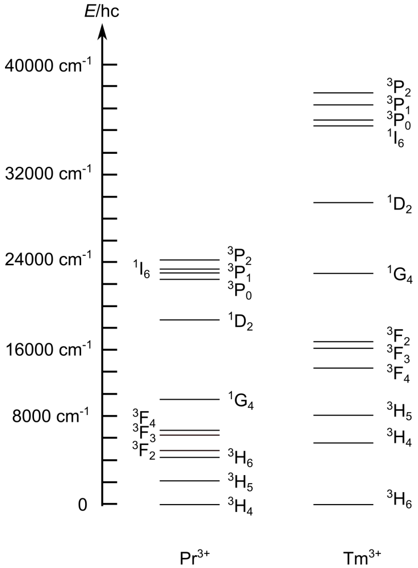
Hund's rules 5

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

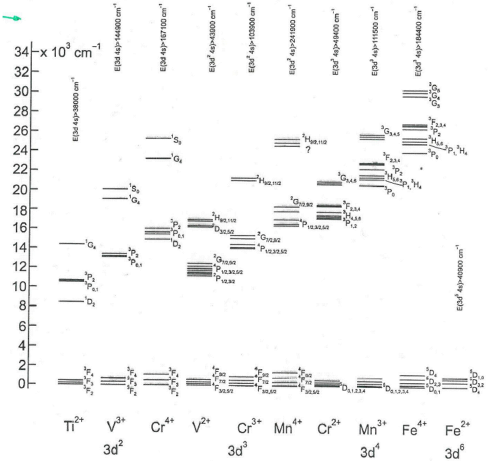
Comment 2

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

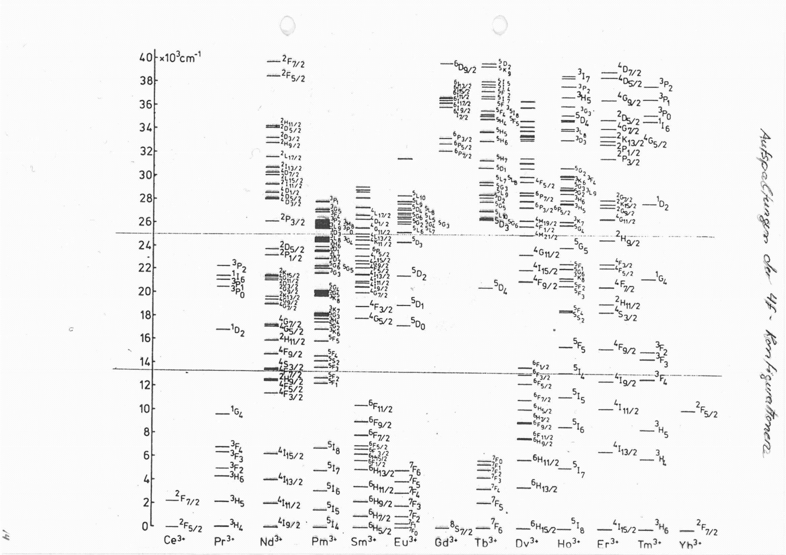
This figure shows the energy level scheme of various 3d configurations.

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

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

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

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

Curie′s law

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

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		$g_{J,L,S}$	$\mu_\mathrm{eff}/\mu_\mathrm{B}$
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		$g_{J,L,S}$	$\mu_\mathrm{eff}/\mu_\mathrm{B}$
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

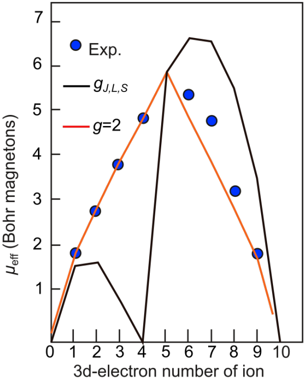
For the f^n configuration, the table shows the ground state according to Hund’s rules, the Landé g-factor and the effective moment.

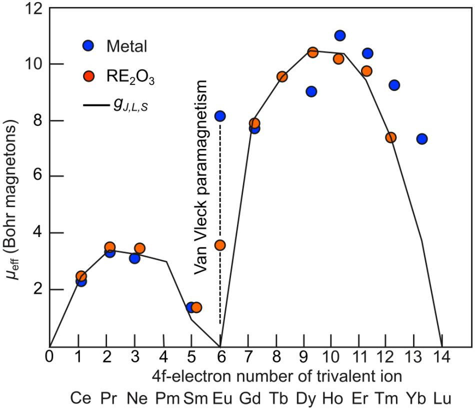
The left column shows examples of ions that realize the electron configuration.

Ligand-field 4

effective magnetic moment

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





Ligand-field 4 Comment 1

The figures compare the theoretical predictions for the 3d and 4f elements with experimental results.

The black lines connect the effective moments calculated using the Landé g-factor as given in the formula outlined in red.

The dots show the experimental results for molecules and solids containing transition metal ions (left) and the rare earth metals and trivalent rare earth ions (right).

The experimental results do not agree with theory for the transition metal ions.

There is only one exception: the $3d^5$ configuration of Fe^{3+} or Mn^{2+}, which is a pure spin configuration.

The red line in the left figure connects the effective magnetic moments when only the spin of the electron configuration is taken into account, i.e. $g = 2$.

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.

These experimental results suggest 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.

In contrast the effective magnetic moments calculated with the Landé g-factor agree well with the experimental results obtained for rare earth metals and oxides.

There is only one exception: europium metal and Eu^{3+}.

Ligand-field 4

Comment 3

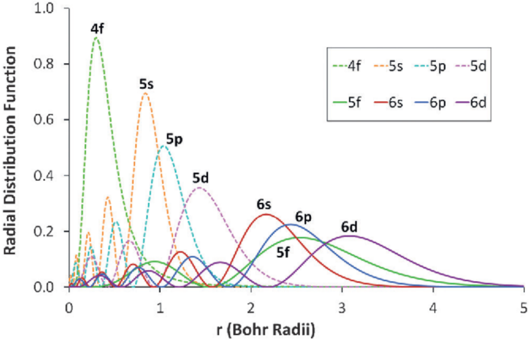
The total angular momentum of Eu^{3+} is zero, so that there should actually be no magnetic moment at all.

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

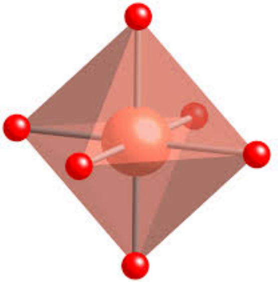
The 5d and 6s orbitals of the trivalent rare earth ions are not occupied.

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] $4d^{10}5s^25p^6$).

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.

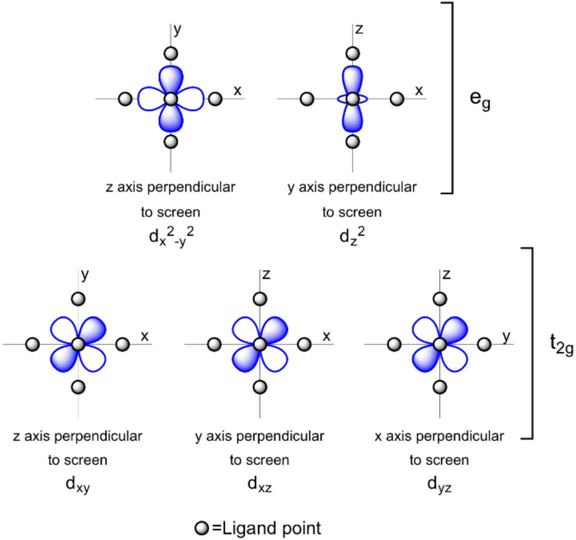
Ligand-field 6

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 $d_{x^2-y^2}$

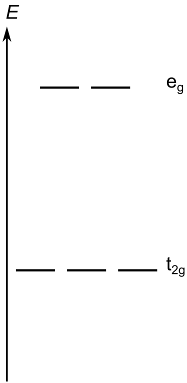
y axis perpendicular to screen d_{z^2}

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

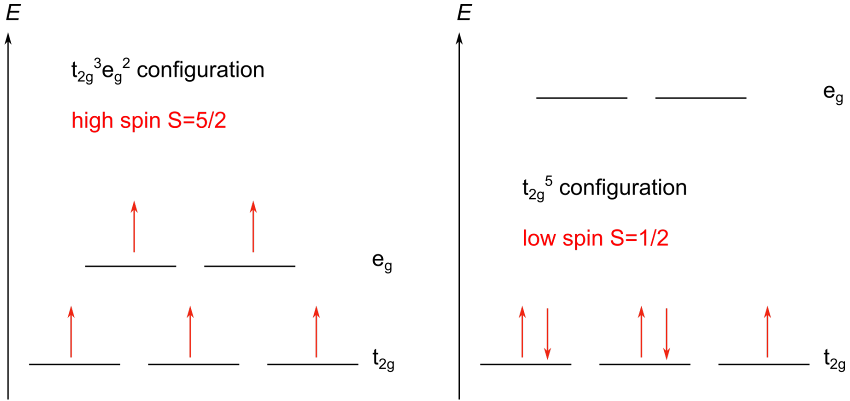
Comment 3

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}



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

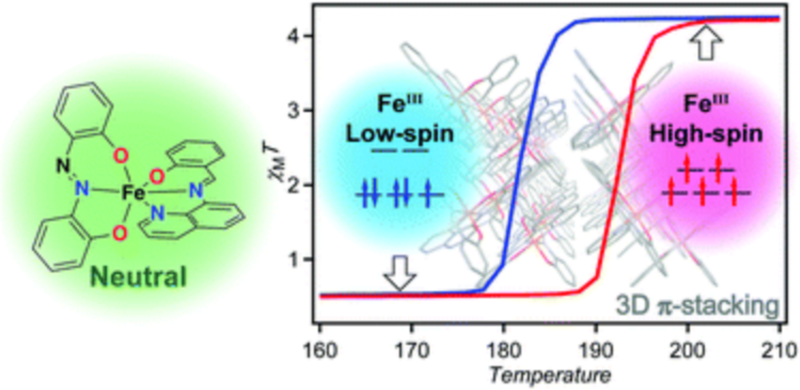
Ligand-field 8 Comment 2

In the energy level diagram on the right, the difference in potential energy is large, so that the electrons preferentially occupy the lower t_{2g} orbitals twice and align antiparallel, although this increases the effect of Coulomb repulsion.

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.

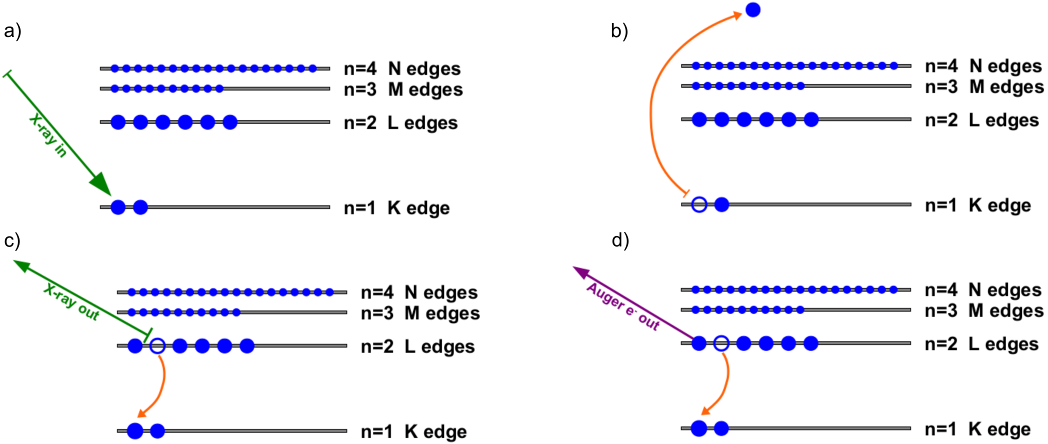
The diagram shows the product of susceptibility and temperature, which is proportional to the square of the effective magnetic moment.

X-Ray Spectroscopy

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

X-Ray Spectroscopy 1



X-Ray Spectroscopy 1

Comment

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

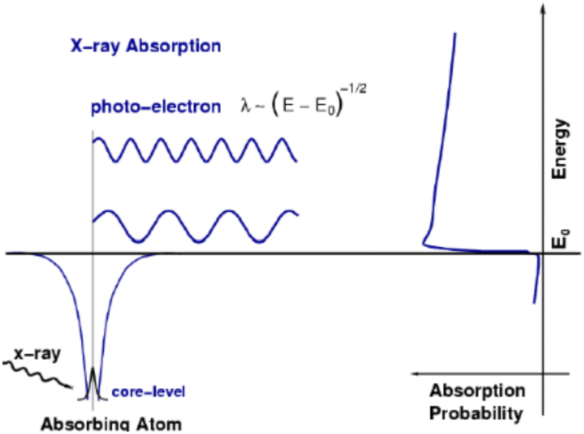
In figure a), an X-ray photon hits an electron in an atomic energy level with the main quantum number $n = 1$.

Figure b) shows that this electron can be ejected if the energy of the photon is large enough. Then an electron hole remains at the corresponding energy level.

In figures c) and d), this hole is filled with an electron that relaxes from a higher energy level.

Thereby either a photon or an electron can be emitted. This electron is called an Auger electron.

X-Ray Spectroscopy 2: The absorption edge



X-Ray Spectroscopy 2

Comment

X-ray absorption starts when the energy of the photon is high enough to emit an electron.

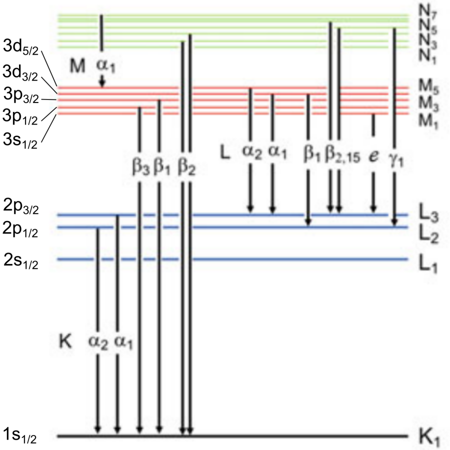
This results in a sharp edge in the X-ray absorption spectrum.

The de Broglie wavelength of the emitted electron depends on the difference between the photon energy and the binding energy of the electron.

X-Ray Spectroscopy 3: Notation of the characteristic X-ray lines

Siegbahn vs. IUPAC notation

E.g. $K_{\alpha 1}$ corresponds to the transition
$K_1 \leftrightarrow L_3$
and $K_{\alpha 2}$ to the transition
$K_1 \leftrightarrow L_2$



X-Ray Spectroscopy 3 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 3 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 4

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

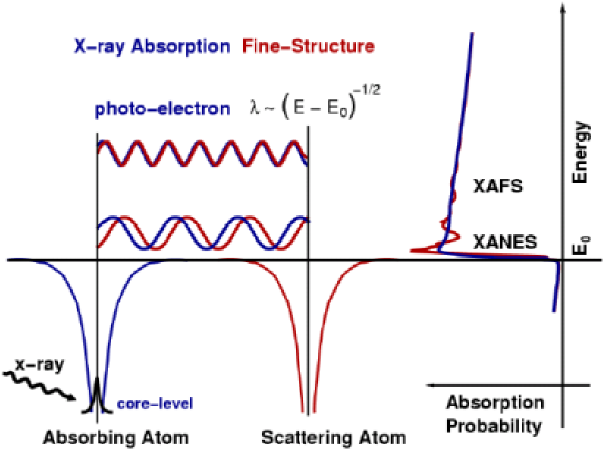
Line	Transition	Energy	Strength
$L\alpha_1$	L3-M5	13614.0	0.686
$L\alpha_2$	L3-M4	13438.0	0.077
$L\beta_2$	L3-N4,5	16387.7	0.181
$L\beta_5$	L3-O4,5	17063.2	0.038
$L\beta_6$	L3-N1	15727.0	0.013
L_ℓ	L3-M1	11618.0	0.005

X-Ray Spectroscopy 4 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 5: Fine structure of the absorption edge



X-Ray Spectroscopy 5 Comment 1

An electron is knocked out of an atom by a photon of energy E.

If the energy E exceeds the binding energy E_0, the electron can propagate freely and be described by a de Broglie wave.

With increasing energy E the de Broglie wavelength of the free electron decreases.

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.

The figure neglects the fact that there are many occupied and unoccupied energy levels below E_0.

These energy levels influence the absorption probability and lead to features in the energy range just below the X-ray absorption edge.

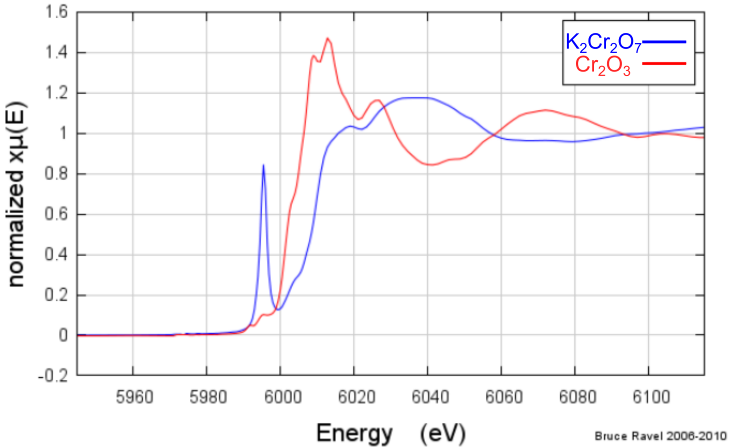
X-Ray Spectroscopy 5 Comment 2

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.

These effects are 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 6



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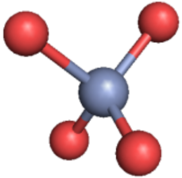
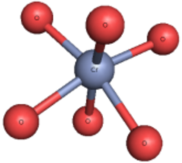
$K_2Cr_2O_7$



Cr_2O_3



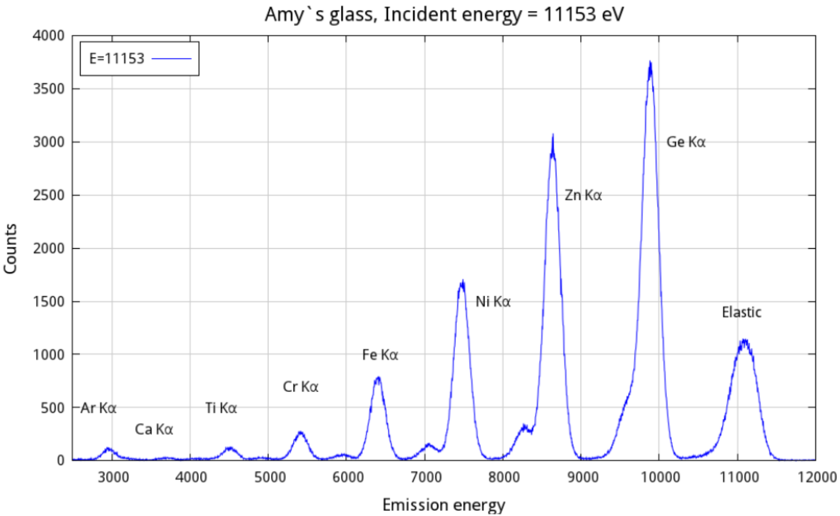
X-Ray Spectroscopy 6 Comment

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 7



X-Ray Spectroscopy 7 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 4 of this section.

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 7 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 4, i.e. K_{β_5} is obviously a forbidden electric dipole transition ($\Delta\ell = \pm 2$) and its strength is correspondingly small. The figure on slide 3 only shows allowed electric dipole transitions.

Revision

Summary in Questions

1. Describe the characteristic properties of fermions and bosons.
2. Give the entangled quantum state of two fermions.
3. Give the entangled quantum state of two bosons.
4. Entanglement affects the energy of atomic eigenstates. Why?
5. The spins of electrons prefer to align parallel in an atom due to exchange interaction. Why?