

ATOMIC MULTIPLY THEORY

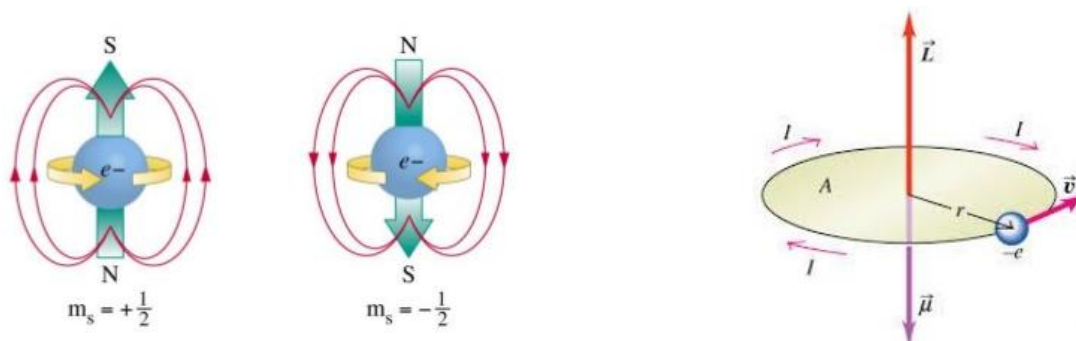
Atomic multiplet theory is the description of the atomic structure with quantum mechanics. The main concepts have been discussed in the lectures on optical spectroscopy. Here we repeat the basic aspects, which are needed for a general understanding of the concepts. We add spin-orbit coupling that is important for x-ray absorption. The starting point is the relativistic Schrödinger (or Dirac) equation of a single electron in an atom, $H\Psi = E\Psi$. In atoms where more than one electron is present there are four terms in the atomic Hamiltonian: The kinetic energy (H_K), the interaction between the nucleus and the electrons (H_N), the electron-electron repulsion (H_{ee}) and the spin-orbit coupling of each electron (H_{ls}). The total Hamiltonian is then given by:

$$H_{ATOM} = H_K + H_N + H_{ee} + H_{ls} = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i) l_i \cdot s_i$$

The kinetic energy and the interaction with the nucleus are the same for all electrons in a given atomic configuration. They define the average energy of the configuration (H_{av}). The electron-electron repulsion and the spin-orbit coupling define the relative energy of the different terms within this configuration. We only use these two interactions to determine the relative energies of the possible configurations of the multi/electron states.

THE GROUND STATE OF HYDROGEN AND HELIUM

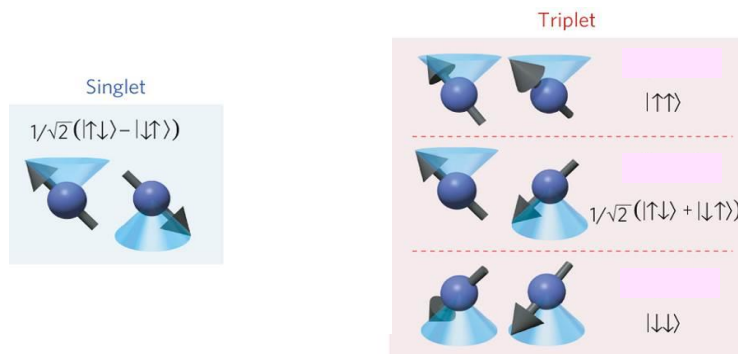
We start with the hydrogen atom. A convenient way to describe the electronic nature of a state is to give its main quantum numbers. The ground state of the hydrogen atom has one electron in the 1s shell, i.e. $1s^1$.



Graphical representation of the spin (left) and orbital moment (right).

This state has a spin S of $\frac{1}{2}$ that can be oriented south ($m_s = +\frac{1}{2}$) or north ($m_s = -\frac{1}{2}$) and an angular momentum L of 0. The term symbol is a shorthand way to describe the quantum numbers of a state, where they are given as ^{2S+1}L . The term symbol of the ground state of a hydrogen atom is 2S .

The ground state of the helium atom has two electrons in the 1s shell, i.e. $1s^2$. This state has a spin moment S of 0 as the two spins cancel each other. The angular momentum L is also 0. The term symbol of the ground state of a hydrogen atom is 1S . The first excited state of helium contains an electron in the 1s orbital and a second electron in the 2s orbitals. This presents a classic case of a 2-electron state. Each orbital contains an electron that can be either spin up or spin down, creating four different combinations of the two spins, respectively $|\frac{1}{2}\rangle|\frac{1}{2}\rangle$, $|\frac{1}{2}\rangle|-\frac{1}{2}\rangle$, $|-\frac{1}{2}\rangle|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle|-\frac{1}{2}\rangle$. The addition of the two electrons yields three two-electron states with total spin momentum $S=1$, respectively $|1,1\rangle = |\frac{1}{2}\rangle|\frac{1}{2}\rangle$, $|1,0\rangle = \frac{1}{\sqrt{2}}(|\frac{1}{2}\rangle|-\frac{1}{2}\rangle + |-\frac{1}{2}\rangle|\frac{1}{2}\rangle)$ and $|1,-1\rangle = |-\frac{1}{2}\rangle|-\frac{1}{2}\rangle$. In addition there is one state with total spin momentum $S=0$, i.e. $|0,0\rangle = \frac{1}{\sqrt{2}}(|\frac{1}{2}\rangle|-\frac{1}{2}\rangle - |-\frac{1}{2}\rangle|\frac{1}{2}\rangle)$. The two-electron states are indicated as $|1,1\rangle$, which means that its S quantum number is 1 and its M_s quantum number is also 1, etc.



Singlet and triplet states of the $1s2s$ configuration of the excited state of helium.

QUANTUM NUMBERS AND TERM SYMBOLS

The overview of quantum numbers of a single electron and two electrons in an atom, as well as their nomenclature, is given in the table. The principal quantum number **N** is not important for the angular symmetry of a state. For a single electron, the quantum numbers are indicated with the orbital angular momentum **L**, the spin angular momentum **S** of $\frac{1}{2}$, total angular momentum **J**, with two values $L+1/2$ and $L-1/2$, the magnetic quantum number M_L , spin magnetic quantum number M_S , and the total magnetic quantum number M_J .

name	symbol	Values (single electron)	Values (two electrons)
Azimuthal Quantum Number Orbital Angular Momentum	L	$L_{(min)}= 0$ $L_{(max)}=N-1$	$L_{(min)}= L_1-L_2 $ $L_{(max)}=L_1+L_2$
Magnetic Quantum Number	M_L	$M_{L(min)}=-L$ $M_{L(max)}=L$	$M_{L(min)}=-L$ $M_{L(max)}=L$
Spin Quantum Number	S	$S=1/2$	$S_{(min)}= 0$ $S_{(max)}=1$
Spin Magnetic Quantum Number	M_S	$M_{S(min)}=-S$ $M_{S(max)}=S$	$M_{S(min)}=-S$ $M_{S(max)}=S$
Total Angular Momentum Quantum Number	J	$J_{(min)}=L-S$ $J_{(max)}=L+S$	$J_{(min)}=L-S$ $J_{(max)}=L+S$
Total Magnetic Quantum Number	M_J	$M_{J(min)}=-J$ $M_{J(max)}=J$	$M_{J(min)}=-J$ $M_{J(max)}=J$

Overview of the quantum numbers and their nomenclature. The steps in between the minimum and maximum values is 1.0 in all cases.

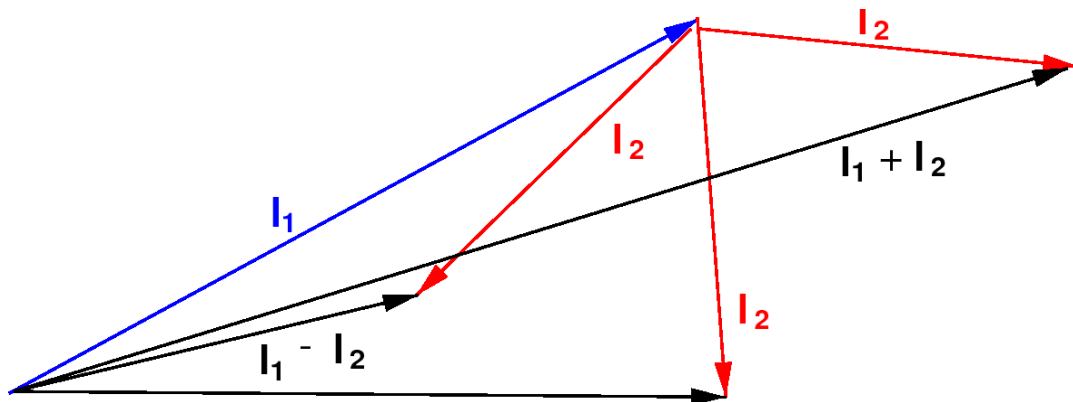
For a 2-electron configuration the maximum orbital angular momentum **L** is equal to the addition of the two individual orbital angular momenta, L_1 and L_2 . The same rule applies to the spin angular momentum, implying that the spin angular momentum of two electrons can be either 1 or 0, and the total angular momentum **J** takes the values from $|L-S|$ to $L+S$ by the step 1. For multi-electron configurations with quantum numbers **L**, **S**, and **J**, in general, a term symbol is written as $^{2S+1}L_J$, where the orbital angular momentum **L** is indicated with their familiar notation: **S** for $L=0$, **P** for $L=1$, etc. In the absence of spin-orbit coupling, all terms with the same **L** and **S** have the same energy, giving an energy level that is $(2L+1)(2S+1)$ -fold degenerate. When spin-orbit coupling is important, the terms are split in energy according to their **J**-value with a degeneracy of $2J+1$. The quantity $2S+1$ is called the spin multiplicity of the term, and the terms are called singlet, doublet, triplet, quartet, etc. according to $S = 0, 1/2, 1, 3/2$, etc. A single s electron has an orbital angular momentum $l=0$, a spin angular momentum $S=1/2$ and a total angular momentum $j=1/2$. There is only one term symbol $^2S_{1/2}$. For one p electron, $L=1$, $S=1/2$, and **J** can be $1/2$ or $3/2$, corresponding to term symbols $^2P_{1/2}$ and $^2P_{3/2}$. Similarly a single d electron has term symbols $^2D_{3/2}$ and $^2D_{5/2}$ and a single f-electron $^2F_{5/2}$ and $^2F_{7/2}$. The degeneracy of these states is given by $2J+1$. The general rules for adding two electrons are given by the addition of momenta.

ADDITION OF MOMENTA

It is often required to add the momenta from two sources together to get states of definite total momentum. As an example, assume we are adding the orbital angular momentum from two electrons, L_1 and L_2 to get a total angular momentum J . We will show that the total angular momentum quantum number takes on every value in the range

$$|\ell_1 - \ell_2| \leq j \leq \ell_1 + \ell_2.$$

We can understand this qualitatively in the **vector model** pictured below. We are adding two quantum vectors.



Graphical representation of vector addition: $l_1 + l_2$

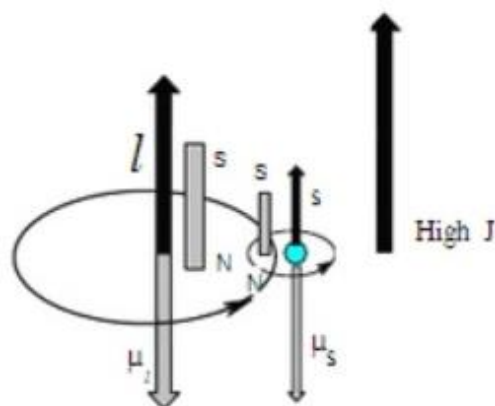
This addition is exactly the same for all momenta S , L and J , for example:

- Add the orbital angular momentum to the spin angular momentum for an electron in an atom as $J=L+S$;
- Add the orbital angular momenta together for two electrons in an atom $L=L_1+L_2$;
- Add the spins of two particles together $S=S_1+S_2$;
- Add the total angular momenta of two electrons together $J=J_1+J_2$

Essentially this rule governs all addition of momenta: Adding $L_1=3$ with $L_2=2$ yields as maximum $L_{\max}=L_1+L_2=5$ and as minimum $L_{\min}=|L_1-L_2|=1$, with all possible values of L differing by an integer in-between. L can be 1, 2, 3, 4 or 5. It can always be checked if all values of L are found by adding the degeneracies of each state. The degeneracy of each moment is given as $2L+1$. The degeneracy of $L_1=3$ is 7 and the degeneracy of $L_2=2$ is equal to 5. In total there are 7 times 5 is 35 possibilities. Adding the degeneracies of the final moments L yields $\sum(2L+1) = 3+5+7+9+11 = 35$. It is always useful to check the completeness of the result by calculating the total degeneracies. Exactly the same rules apply for adding $S_1 + S_2$, or $L_1 + S_1$ to yield the total moment J .

SPIN-ORBIT COUPLING

The consequences of spin-orbit coupling have been described above, but the physical origin of spin-orbit coupling has not been treated yet. Spin-orbit coupling is a consequence of the inclusion of relativistic effects and it follows directly from the Dirac equation that can be considered as the relativistic Schrödinger equation. Classically one can make the following reasoning (that is not exactly correct, but it gives a good idea). Consider a hydrogen atom with the electron that orbits around the nucleus. Then one can also look at it as a proton orbiting the electron, i.e. the electron feels the electrostatic field of the proton but it also feels an effective current. This current produces a magnetic field that interacts with the magnetic moment of the electron. The spin-orbit coupling is graphically indicated in the figure below. The orbital moment of the electron (l) can be parallel or anti-parallel to the spin moment of the electron (s), yielding $l+s$ respectively $l-s$.



Graphical representation of spin-orbit coupling

COUPLING SCHEMES WITH ONE ELECTRON PER SHELL

Coupling schemes of states that have only one electron or one hole per shell can be calculated by applying the vector addition rules as described above. For example in case of a $1s2s$ configuration there will be 2×2 or 4 combinations. The term symbols can be determined directly from multiplying the individual term symbols. Multiplication of terms A and B is written as $A \otimes B$. For $^2S \otimes ^2S$, this gives $L = 0$ and $S = 0$ or 1 . This gives the term symbols 1S and 3S . The respective degeneracies are 1 and 3, adding up to 4. Because there is no orbital moment ($L=0$) one does not have to consider spin-orbit coupling.

The term symbols of a $2p3p$ configuration will have 6×6 or 36 combinations. $^2P \otimes ^2P$ gives $L = 0, 1, 2$ and $S = 0$ or 1 . This gives the term symbols $^1S, ^1P, ^1D$ and $^3S, ^3P$ and 3D . The respective degeneracies are 1, 3, 5 and 3, 9, 15 adding up to 36. Adding the J-values, one finds for the singlet states just a single J, i.e. $^1S_0, ^1P_1, ^1D_2$. The triplet states each form three J-term symbols 3P_2 plus 3P_1 plus 3P_0 and 3D_3 plus 3D_2 plus 3D_1 . The 3S state has $L=0$, hence also only one J state as 3S_1 . We find two term symbols with $J=0$ (1S_0 and 3P_0), four with $J=1$, three with $J=2$ and one with $J=3$.

COUPLING SCHEMES WITH MORE THAN ONE ELECTRON PER SHELL

In case of a $2p^2$ configuration, the first electron has six quantum states available, the second electron only five. This is due to the **Pauli Exclusion Principle** that forbids two electrons to have the same quantum numbers n_p , m_l and m_s . Because the sequence of the two electrons is not important, one divides the number of combinations by two and obtains fifteen possible combinations. A $2p$ electron has quantum numbers $L=1$ and $S=1/2$. This gives the six individual combinations with $M_L=+1, 0$ or -1 and $M_S=+1/2$ or $-1/2$. We will use a shorthand notation and write $|1,+>$ to indicate the quantum numbers. One can create a 2-electron state by adding two of these $|M_{La}, M_{Sa}>$ combinations, for example $|1,+> + |1,->$. This yields a two-electron state with $|M_L, M_S>$ quantum numbers equal to $|2,0>$. The fifteen combinations of adding two $2p$ electrons are indicated.

$ m_{la}, m_{sa}>$	$ m_{lb}, m_{sb}>$	$ M_L, M_S>$	#	$ m_{la}, m_{sa}>$	$ m_{lb}, m_{sb}>$	$ M_L, M_S>$	#
$ 1,+>$	$ 1,->$	$ 2, 0>$	1	$ 1, ->$	$ -1, ->$	$ 0, -1>$	1
$ 1,+>$	$ 0,+>$	$ 1, 1>$	1	$ 0, +>$	$ 0, ->$	$ 0, 0>$	3
$ 1,+>$	$ 0,->$	$ 1, 0>$	1	$ 0, +>$	$ -1, +>$	$ -1, 1>$	1
$ 1,+>$	$ -1,+>$	$ 0, 1>$	1	$ 0, +>$	$ -1, ->$	$ -1, 0>$	1
$ 1,+>$	$ -1,->$	$ 0, 0>$	1	$ 0, ->$	$ -1, +>$	$ -1, 0>$	2
$ 1,->$	$ 0,+>$	$ 1, 0>$	2	$ 0, ->$	$ -1, ->$	$ -1, -1>$	1
$ 1,->$	$ 0,->$	$ 1, -1>$	1	$ -1, +>$	$ -1, ->$	$ -2, 0>$	1
$ 1,->$	$ -1,+>$	$ 0, 0>$	2				

The 15 combinations of one-electron states $|m_{la}, m_{sa}>$ and $|m_{lb}, m_{sb}>$ of a $2p^2$ configuration. The fourth column counts the degeneracy of the total symmetry $|M_L, M_S>$ states

These fifteen $|M_L, M_S\rangle$ states can be put into a table collecting their overall M_L and M_S quantum numbers. This yields the following result:

$2p^2$	$M_S = 1$	$M_S = 0$	$M_S = -1$		$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$	0	1	0			1D	
$M_L = 1$	1	2	1		3P	1D 3P	3P
$M_L = 0$	1	3	1		3P	1D 3P	3P
$M_L = -1$	1	2	1		3P	1D 3P	3P
$M_L = -2$	0	1	0			1D	

(Left) The number of states with a $|M_L, M_S\rangle$ combination; (Right) All the possible term symbols of a $3p^2$ configuration.

It can be seen that there are three states with $|M_L, M_S\rangle = |0,0\rangle$, two states $|M_L, M_S\rangle = |1,0\rangle$ and $|-1,0\rangle$ and a number of other states. If one works out the symmetry properties of these states, one will find a number of so-called irreducible representations, or irrep. An irrep defines a single configuration with a defined L and S value. The energies of all the $|M_L, M_S\rangle$ states within an $|L, S\rangle$ irrep is the same. The rules on quantum numbers as outlined above apply also for irreps. This gives a lead to derive the irreps directly from the number of $|M_L, M_S\rangle$ states as given in the table. The presence of a $|2,0\rangle$ implies that this state is part of an irrep with L equal to, at least, 2. An irrep with $L=2$ has five states with M_L values between -2 and $+2$. The only associated M_S value is $M_S=0$, which implies that there is an irrep with $|L, S\rangle = |2,0\rangle$, which is a 1D term symbol.

One can remove these five states from the table and then one is left with ten states, containing $M_L = \pm 1$ and $M_S = \pm 1$. The next term symbol one finds has $|L, S\rangle = |1,1\rangle$, which is a 3P term symbol. A 3P term symbol has nine states and one is left with one additional state with $M_S = M_L = 0$. This state belongs to an $|L, S\rangle = |0,0\rangle$ term symbol, or 1S . We have found that the $2p^2$ configuration contains the terms 3P , 1D and 1S , with respective degeneracies of $3 \times 3 = 9$, $1 \times 5 = 5$ and $1 \times 1 = 1$. It can be checked that total degeneracy adds up to fifteen. Including J in the discussion we have the values 1D_2 , 1S_0 and 3P_2 plus 3P_1 plus 3P_0 . Focusing on the J -values, we have two $J=0$, one $J=1$ and two $J=2$ values. Because X-ray absorption calculations are carried out in intermediate coupling, the J -value is important; the total calculation is split into its various J -values.

Conf.	J	Term Symbols	Deg.	$\Sigma(2J+1)$
$1s^0$	0	1S_0	1	1
$1s^1$	1/2	$^2S_{1/2}$	1	2
$1s^1 2s^1$	0	1S_0	1	4
	1	3S_1	1	
$2p^1$ $=2p^5$	1/2	$^2P_{1/2}$	1	6
	3/2	$^2P_{3/2}$	1	
$2p^2$ $=2p^4$	0	1S_0 3P_0	2	15
	1	3P_1	1	
	2	1D_2 3P_2	2	
$2p^3$	1/2	$^2P_{1/2}$	1	20
	3/2	$^4S_{3/2}$ $^2P_{3/2}$ $^2D_{3/2}$	3	
	5/2	$^2D_{5/2}$	1	
$2p^1 3p^1$	0	1S_0 3P_0	2	36
	1	1P_1 3S_1 3P_1 3D_1	4	
	2	1D_2 3P_2 3D_2	3	
	3	3D_3	1	

Configurations of s and p electrons. The term symbols are sorted for their J value. The third column gives the number of term symbols per J-value. The last column gives the overall degeneracy of the configuration.

TERM SYMBOLS OF D-ELECTRONS

The LS term symbols for a $3d^14d^1$ configuration can be found similarly by multiplying the term symbols for the configurations $3d^1$ and $4d^1$. For ${}^2D \otimes {}^2D$, this gives $L = 0, 1, 2, 3$ or 4 and $S = 0$ or 1 . The ten LS term symbols of the $3d^14d^1$ configuration are ${}^1S, {}^1P, {}^1D, {}^1F, {}^1G$ plus ${}^3S, {}^3P, {}^3D, {}^3F, {}^3G$. The total degeneracy of the $3d^14d^1$ configuration is 100. In the presence of spin-orbit coupling, a total of eighteen term symbols is found. Due to the Pauli exclusion principle, a $3d^2$ configuration does not have the same degeneracy as the $3d^14d^1$ configuration. In total there are $10 \times 9 / 2 = 45$ possible states. Following the same procedure as for the $2p^2$ configuration, one can write out all 45 combinations of a $3d^2$ configuration and sort them by their M_L and M_S quantum numbers. Analysis of the combinations of the allowed M_L and M_S quantum numbers yields the term symbols ${}^1G, {}^3F, {}^1D, {}^3P$ and 1S . This is a sub-set of the term symbols of a $3d^14d^1$ configuration. The term symbols can be divided into their J-quantum numbers as ${}^3F_2, {}^3F_3, {}^3F_4, {}^3P_0, {}^3P_1, {}^3P_2, {}^1G_4, {}^1D_2$ and 1S_0 . In case of a $3d^3$ configuration a similar approach shows that the possible spin-states are doublet and quartet. By adding the degeneracies, it can be checked that a $3d^3$ configuration has 120 different states, i.e. $10 \times 9 / 2 \times 8 / 3$. The general formula to determine the degeneracy of a $3d^n$ configuration is:

$$\binom{10}{n} = \frac{10!}{(10-n)!n!}$$

	M _S =1	M _S =0	M _S =-1	1	M _S =0	-1
M _L =4	0	1	0		¹ G	
M _L =3	1	2	1	³ F	¹ G ³ F	³ F
M _L =2	1	3	1	³ F	¹ G ³ F ¹ D	³ F
M _L =1	2	4	2	³ F ³ P	¹ G ³ F ¹ D ³ P	³ F ³ P
M _L =0	2	5	2	³ F ³ P	¹ G ³ F ¹ D ³ P ¹	³ F ³ P
M _L =-1	2	4	2	³ F ³ P	¹ G ³ F ¹ D ³ P	³ F ³ P
M _L =-2	1	3	1	³ F	¹ G ³ F ¹ D	³ F
M _L =-3	1	2	1	³ F	¹ G ³ F	³ F
M _L =-4	0	1	0		¹ G	

(Left) The number of states with a $|M_L, M_S\rangle$ combination; (Right) All the possible term symbols of a $3d^2$ configuration.

Important for the 2p X-ray absorption edge are the configurations of the $2p^5 3d^n$ final states. The term symbols of the $2p^5 3d^n$ states are found by multiplying the configurations of $3d^n$ with a 2P term symbol. For example 2P times 3P yields $^2S + ^2P + ^2D + ^4S + ^4P + ^4D$. The tables with J-value degeneracies are also important for crystal field effects. The total degeneracy of a $2p^5 3d^n$ state is given as:

$$6 \times \binom{10}{n} = 6 \times \frac{10!}{(10-n)!n!}$$

For example, a $2p^5 3d^5$ configuration has 1512 possible states. Analysis shows that these 1512 states are divided into 205 term symbols, implying in principle 205 possible final states. If all these final states have finite intensity then depends on the selection rules.

THE MATRIX ELEMENTS

Above we have found the number and symmetry of the states of a certain $3d^n$ configuration. The next task is to calculate the matrix elements of these states with the Hamiltonian H_{ATOM} . As discussed above, H_{ATOM} includes the electron-electron interaction H_{ee} and the spin-orbit coupling H_{LS} :

$$H_{ee} + H_{LS} = \sum_{\text{pairs}} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i) L_i \cdot S_i$$

We first discuss the matrix elements of the electron-electron interaction. Because this Hamiltonian commutes with L^2 , S^2 , L_z and S_z , the off-diagonal elements all are zero. A simple example is a $1s2s$ configuration consisting of 1S and 3S terms. The respective energies can be shown to be:

$$\begin{aligned} \left\langle ^1S \left| \frac{e^2}{r_{12}} \right| ^1S \right\rangle &= F^0(1s2s) + G^0(1s2s) \\ \left\langle ^3S \left| \frac{e^2}{r_{12}} \right| ^3S \right\rangle &= F^0(1s2s) - G^0(1s2s) \end{aligned}$$

Note that the triplet state is threefold degenerate and the average energy of the $1s2s$ configuration equals $F^0(1s2s) - 1/2 G^0(1s2s)$. F^0 and G^0 are the Slater-Condon parameters (or Slater parameters) for respectively the direct Coulomb repulsion and the Coulomb exchange interaction. The main result can be stated as 'the singlet and the triplet state are split by the exchange interaction'. This energy difference is $2G^0(1s2s)$. An analogous result is found for a $1s2p$ state for which the singlet and triplet states are split by $2/3G^0(1s2p)$. The pre-factor is determined by the degeneracy of the $2p$ -state. The general formulation of the matrix elements of two-electron wave functions can be written as:

$$\left\langle ^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| ^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

To obtain this result the radial parts F^k and G^k have been separated using the Wigner-Eckhart theorem and Hamiltonian $1/r_{12}$ has been expanded. For equivalent electrons g_k is not present and the maximum value of k equals l_1+l_2 .

THE ENERGY LEVELS OF TWO D ELECTRONS

The energies of the representations of the $3d^2$ configuration are found from the calculation of f_2 and f_4 for the five term symbols 1S , 3P , 1D , 3F and 1G . To a very good degree of approximation, the Slater-Condon parameters F^2 and F^4 have a constant ratio: $F^4 = 0.62 F^2$. The approximate energies of the five term symbols are listed below. In case of the $3d$ transition metal ions, F^2 is approximately equal to 10 eV. This gives for the five term symbols the energies respectively as: 3F at -1.8 eV, 1D at -0.1 eV, 3P at +0.2 eV, 1G at +0.8 eV and 1S at +4.6 eV. The 3F -term symbol has lowest energy and is the ground state of a $3d^2$ system. This is in agreement with the Hund's rules, which will be discussed in the next section. The three states 1D , 3P and 1G are close in energy some 1.7 to 2.5 eV above the ground state. The 1S state has a very high energy of 6.3 eV above the ground state, the reason being that two electrons in the same orbit strongly repel each other.

	f_2	f_4	Energy
1S	$2/7$	$2/7$	$0.46F^2$
3P	$3/21$	$-4/21$	$0.02F^2$
1D	$-3/49$	$4/49$	$-0.01F^2$
3F	$-8/49$	$-1/49$	$-0.18F^2$
1G	$4/49$	$1/441$	$0.08F^2$

The energies of the five term symbols of a $3d^2$ configuration. The energy in the last column is calculated using the fact that the radial integrals F^2 and F^4 are a constant ratio of 0.62.

MORE THAN TWO ELECTRONS

For three or more electrons the situation is considerably more complex. It is not straightforward to write down an anti-symmetrized three-electron wave function. It can be shown that the three-electron wave function can be built from two-electron wave functions with the use of the so-called coefficients of fractional parentage. More details can be found in books on atomic physics.

HUND'S RULES

We now discuss the ground state symmetries of the transition metal compounds, which are characterized with a partly filled 3d band. The term symbols with the lowest energy are found after calculating the matrix elements, following the rules as described above. The finding of the 3F state as the ground state of a $3d^2$ configuration is an example of the so-called Hund's rules. On the basis of experimental information Hund did formulate three rules to determine the ground state of a $3d^n$ configuration. For $3d^n$ configurations though, the rules are correct, as is also confirmed by the atomic multiplet calculations. The three Hund rules are:

1. Term symbol with maximum S
2. Term symbol with maximum L
3. Term symbol with maximum J (if the shell is more than half full)

The energy of a configuration is lowest if the electrons are as far apart as possible. The first Hund's rule 'maximum spin' can be understood from the Pauli principle: Electrons with parallel spins must be in different orbitals, which on overall imply larger separations, hence lower energies. This is for example evident for a $3d^5$ configuration, where the 6S state has its five electrons divided over the five spin-up orbitals, which minimizes their repulsion. In case of $3d^2$, the first Hund's rule implies that either the 3P or the 3F -term symbol must have lowest energy. The second Hund's rule states that the 3F term symbol is lower than the 3P term symbol. Again the reason is that the 3F wave function tends to minimize electron repulsion. In a 3F configuration, the electrons are orbiting in the same direction. That implies that they can stay a larger distance apart on the average since they could always be on the opposite side of the nucleus. For a 3P configuration, some electrons must orbit in the opposite direction and therefore pass close to each other once per orbit, leading to a smaller average separation of electrons and therefore a higher energy. The third rule implies that the ground state of a $3d^8$ configuration is 3F_4 , while it is 3F_2 in case of a $3d^2$ configuration.

HUNDS RULE GROUND STATES OF TRANSITION METAL & RARE EARTH IONS

There is a simple procedure to determine the Hund's rule ground state of every atom by making a table that includes the M_L and M_S values for a 3d or 4f electron. Assume that we would like to determine the ground state of a $3d^2$ system. Then we can fill the two $|M_L, M_S\rangle$ states from the top left, in this case $|2, \uparrow\rangle$ and $|1, \uparrow\rangle$, where \uparrow indicates a M_S value of $+1/2$. Adding the values together yields the total L and S value of the $3d^2$ system, i.e. $L = 3$ and $S=1$ or a $3F$ ground state. Adding the third Hund's rule gives the J-value of the ground state. Because the shell is less than half-full, the minimum J-value is the ground state, i.e. 3F_2 . Similarly a $3d^3$ system has a ${}^4F_{3/2}$ ground state, etc.

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

Determination of the Hund's rule ground state for a $3d^2$ configuration. Add the first electron (blue) into the microstate with spin-up state with the highest m_l value, i.e. $m_l=2$ and $m_s= \frac{1}{2}$. Add the second electron into the microstate with $m_l=1$ and $m_s= \frac{1}{2}$. Adding the m_l values yields the L value of the Hund's rule ground state. Adding the m_s values yields the S value of the Hund's rule ground state. This gives $L=3$ and $S=1$, i.e. the 3F ground state.

The same procedure can be used for 4f and 5f systems. A $3f^4$ system has $S=2$ from the four spin-up electrons and $L = 3+2+1+0=6$. This yields a 5I_4 ground state, etc. Note that atomic term symbols count up to 6, including G-states for $J=4$, H-states for $J=5$ and I-states for $J=6$.

EXERCISES (SELF TEST)

Question 1

The K edge of oxygen atoms can be described with atomic multiplets.

- What is the term symbol of the ground state?
- Determine all term symbols, including their J values, for a $1s^1 2p^5$ configuration
- How many peaks are visible in the $2p^4 \rightarrow 1s^1 2p^5$ transition from the ground state?

Assume that the experiments are performed at a temperature where all spin-orbit split states of the lowest LS term symbol are partly occupied.

- How many peaks are now visible in the spectrum? Explain.

Question 2

A Ni^{2+} ion has a $3d^8$ ground state. Its LS-term symbols are respectively 1S , 3P , 1D , 3F and 1G .

- What is the total degeneracy for a $3d^8$ configuration?
- What is the ground state, including its J quantum number?
- In 3p x-ray absorption, a 3p electron is excited to the 3d band. Determine the LSJ term symbols of the $3p^5 3d^9$ configuration.
- What is the total degeneracy for a $3p^5 3d^9$ configuration?
- How many peaks are visible in the 3p XAS spectral shape? Explain.
- How many peaks are visible if the calculation is repeated with the 3d spin-orbit coupling set to zero.

Question 3

- What is the ground state of a dysprosium atom, which contain nine occupied 4f electrons? Explain.
- What is the atomic ground state of Thulium ($4f^{12}$)? Explain.