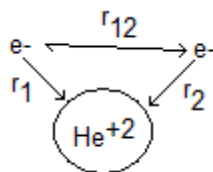


Chapter 8: Polyelectronic Atoms

One of the shortcomings of Bohr's model of the hydrogen atom was that it was not extensible to atoms that had more than one electron. The newly emerging quantum mechanics was hoped to do a better job. Unfortunately, while the hydrogen atom problem is solvable analytically, issues arise when an attempt is made to solve the problem for atoms with multiple electrons. Regardless, the first step in deriving this theory, then, is writing the Hamiltonian for the System.

Potential Energy and the Hamiltonian

The potential energy of a poly electronic atom is all electrostatic in nature. There are attractive forces between electrons and the nucleus and repulsive forces between the electrons themselves. For simplicity, we will consider the helium atom first, which has a nucleus with a charge of +2 electron charges and two electrons with -1 charges each.



The Hamiltonian for this system will have kinetic energy terms for both electrons and three terms to describe the potential energy in the system. The attractive forces will lead to negative contributions to the potential energy and the repulsive (electron-electron) force will contribute a positive value to the potential energy. In atomic units, this yields

$$\hat{H} = \hat{T}_1 + \hat{T}_2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

The $-1/r_{12}$ (electron-electron repulsion term) makes the problem unseparable into terms that relate only to a single electron. This creates a three body problem, which cannot be solved analytically.

The Orbital Approximation

The way we deal with this problem is to simply ignore the electron-electron repulsion term in the solution, and treat it phenomenologically after the fact. This is known as the **orbital approximation**, as it allows for the separation of the Hamiltonian into two terms, one of which deals in electron 1 and the other in electron 2.

$$\begin{aligned}\hat{H}_{tot} &= \hat{T}_1 - \frac{2}{r_1} + \hat{T}_2 - \frac{2}{r_2} \\ &= \hat{H}_1 + \hat{H}_2\end{aligned}$$

This is also the approximation that allows us to write electronic configurations for polyelectronic atoms. In the electronic configuration, we assume that each electron has a hydrogen-like wavefunction.

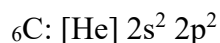
The Aufbau principle

The **aufbau principle** (German for “building up” principle), or building up principle, suggests that we can construct a description of an atom by adding subatomic particles one at a time, moving through the periodic table until we reach the element of interest.

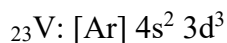
Under this description, a carbon atom (atomic number 6) is similar to a boron (atomic number 5) atom, but with one additional proton and some additional neutrons in the nucleus and one additional electron added to the electron cloud.

Electronic Configurations

Consider carbon, which is atomic number 6. Most chemists advanced to a level to which they are prepared to take a course in physical chemistry can construct an electronic configuration for ${}_6\text{C}$.



Or for ${}_{23}\text{V}$, one would write



It is a curious thing that the 4s subshell fills before the 3d subshell, since in atomic hydrogen, the 3d subshell has a lower energy. However, in polyelectronic atoms, (specifically for K and Ca) the 4s subshell is actually lower in energy than the 3d subshell. As such, according to the aufbau principle, it is the 4s subshell that fills first of the two.

However, it is important to note that the relative energies of the subshells change with changing nuclear charge and differing numbers of electrons. For example, in Sc, it is the 4s electrons that are higher in energy than the 3d electron. As such, the 4s electrons are the first to be removed when the atom is ionized.

Shells, Subshells, Orbitals and Spin

It is useful to develop some nomenclature to describe the different combinations of quantum numbers that describe the different wavefunctions for the electrons in an atom. In order to do this, we need to define a few terms that will come in handy later.

- i. **shell** – characterized by the principle quantum number n
- ii. **subshell** – characterized by n and the angular momentum quantum number l
- iii. **orbital** – characterized by n , l and the azimuthal quantum number m_l .

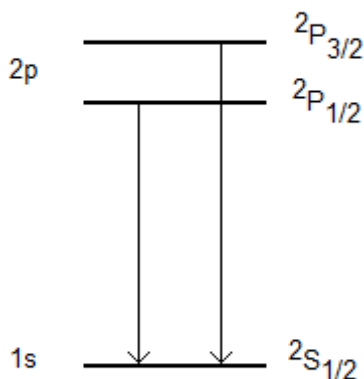
In addition to shells, subshells and orbitals, electrons have spin. The spin quantum number of an electron is $s = \frac{1}{2}$. But generally electrons are described as being “spin up” or “spin down” based on the value of the z-axis component of the spin, m_s . m_s can take values of $+\frac{1}{2}$ and $-\frac{1}{2}$. Each orbital can hold two electrons. If there are two electrons in the orbital, the spins must be pairs such that one is “spin up” and the other is “spin down.”

Orbital Diagrams

Orbital diagrams are handy to depict electronic configurations without having to resort to just quantum numbers. In an orbital diagram, each orbital is depicted using a box or a line and electrons are depicted with arrows pointing either up or down depending on the value of m_s .

Angular Momentum Coupling

Any system that has more than one source of angular momentum will be subject to coupling between those forms of angular momentum. For example, consider the emission from an excited hydrogen atom, for which the electron is in the 2p subshell the atom emits a photon as the electron relaxes to be in the ground 1s subshell. In fact, this transition is doubled as two lines can be observed if viewed at high enough resolution.



The transition is depicted in the above energy level diagram. The upper (2p) state is shown to be split into two components, one labeled $2P_{3/2}$ and one $2P_{1/2}$. The lower state has only

one component, labeled $^2S_{1/2}$. Part of the job of quantum mechanics will be to describe this splitting. The explanation comes in the form of angular momentum coupling.

There are two sources of **angular momentum** in the electronic wavefunction of the atom: the orbital angular momentum ($l = 1$) and the electron spin angular momentum ($s = 1/2$.) These angular momenta can couple to yield a total angular momentum $J = 3/2$ or $1/2$. The resultant angular momentum can be determined by the two angular momentum vectors adding in parallel or antiparallel. The result is to split the state into two components.

Term Symbols

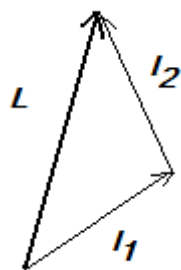
Angular momentum in atoms can be summarized using a **term symbol**. The term symbol will indicate a number of different types of angular momentum such as the total orbital angular momentum, total spin angular momentum and the total (spin + orbit) angular momentum. In the limit that **Russell-Saunders coupling** (which will be described in detail shortly) provides a good description of the atom, the term symbol used will be of the form

$$(2S+1)L_J$$

Where S is the total spin angular momentum and $(2S+1)$ is the spin degeneracy, L is the total orbital angular momentum, and J gives the total of the spin-orbit angular momentum. (The convention will be followed that lower-case letters are used to indicate one-electron properties and upper-case letters are used to describe total atom properties.)

L and S must be calculated using vectorial sums of the single-electron angular momenta (whether orbital or spin.) The vectorial sums can yield several values depending on the angle between the vectors. The possible magnitudes of the resultant vectors will be quantized, with the range of magnitudes being given by a **Clebsch series**. Consider the addition of the angular momentum vectors for two electrons in p ($l = 1$) subshells.

$$L = l_1 \oplus l_2 \\ = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \dots, |l_1 - l_2|$$



As such, the possible values of L for a p^2 configuration are

$$L = l_1 \oplus l_2 = 1 \oplus 1$$

$$= 2, 1, 0$$

As in the case of one-electron orbital angular momenta, the total orbital angular momentum is signified using a letter. The following table shows which letters are used.

One-electron		Total Atom	
l	Designation	L	Designation
0	s	0	S
1	p	1	P
2	d	2	D
3	f	3	F
4	g	4	G

The possible values of S , are given by $s_1 \oplus s_2$. (For all electrons, $s = \frac{1}{2}$.)

$$S = s_1 \oplus s_2 = \frac{1}{2} \oplus \frac{1}{2} = 1, 0$$

So the possible values of $(2S + 1)$ are 3 and 1. In other words, both triplet and singlet states arise from a p^2 configuration.

However, not all possible combinations of L and $(2S+1)$ are possible. In fact, only those values that arise from distinguishable combinations of **microstate** quantum number combinations are possible.

The Microstate Method

The number of distinguishable microstates for a given electronic configuration is given by

$$\frac{G!}{N!(G - N)!}$$

where G is the number of spin-orbit states possible for a single electron and N is the number of electrons. For a p^2 configuration, $G = 6$ and $N = 2$. So the number of microstates is given by

$$\frac{6!}{2!4!} = \frac{6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(2 \cdot 1) \cdot (4 \cdot 3 \cdot 2 \cdot 1)} = 15$$

So there are 15 possible microstates possible. Each microstate will be characterized by a value of m_l and m_s for each electron under consideration. A complete set of microstates for a p^2 configuration is shown in the table below. m_l and m_s are indicated for electrons 1 and 2 in the atom. Notice that only distinguishable combinations are shown!

	m_l		m_s		M_L	M_S	Designation
	1	2	1	2			
1	+1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+2	0	1D
2	+1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	3P
3	+1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	1D
4	+1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3P
5	+1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	1D
6	+1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	3P
7	+1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	3P
8	+1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	3P
9	+1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3P
10	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	1S
11	0	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	3P
12	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	1D
13	0	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	3P
14	0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	3P
15	-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	1D

The “Designation” column in the above table is really for bookkeeping only. For example, it should be noted that there are two microstates that yield $M_L = +1$, $M_S = 0$. One has been designated 1D and the other 3P . In fact, the wavefunctions needed to describe these term symbol components require linear combinations of both microstates.

The resulting microstates for a p^2 configuration are 1D , 3P and 1S . The methodology for determining this from the table of microstates is as follows:

1. Find the largest value of M_L and the largest value of M_S that corresponds to that value.
2. From these, find L and S for the term symbol.
3. Mark combinations of M_L and M_S that match the pattern for a given term symbol.
4. Repeat from step 1 for remaining microstates. Keep repeating until there are no microstates left.

It is very important to approach this process methodically or errors will occur in determining microstate-term symbol correlations.

Utilizing this methodology to work through the above table, we start with the largest value for M_L which is +2. The largest value of M_S that goes with it is 0. This indicates L and S values of 2 and 1 respectively. $L = 2$ indicates a D state. $S = 0$ indicates that $(2S + 1) = 1$ (or a singlet state.) So the resulting term is 1D . This will have components of $M_L = +2, +1, 0, -1, -2$. Each will have $M_S = 0$. This accounts for five of the microstates.

The largest value of M_L for the remaining microstates is $M_L = +1$. the largest value of M_S that goes with $M_L = +1$ is $M_S = +1$. This correlates to $L = 1$, $S = 1$ or a 3P state. There are nine combinations of microstates for this term symbol, one each for each combination of $M_L = +1, 0, -1$ and $M_S = +1, 0, -1$.

After these combinations are marked, the only remaining combination is $M_L = 0, M_S = 0$, which corresponds to a 1S state.

The number of microstates used for a given term symbol can be determined from $(2L+1)$ and $(2S+1)$, the orbital and spin degeneracies respectively. Consider the following table. Notice that the total of $(2L+1)(2S+1)$ is the same as the number of original microstates.

	$(2L+1)$	$(2S+1)$	$(2L+1)(2S+1)$
1D	5	1	5
3P	3	3	9
1S	1	1	1
Total			15

Spin-Orbit Coupling

The one thing that has not been determined from the microstates themselves is the total angular momentum \mathbf{J} , which is given by the vectorial sum of \mathbf{L} and \mathbf{S} . \mathbf{J} values must be determined for each term separately. This coupling of spin and orbit angular momenta will split the term states further.

$$\mathbf{J} = \mathbf{L} \oplus \mathbf{S}$$

	L	S	J	Terms
1D	2	0	2	1D_2
3P	1	1	2, 1, 0	$^3P_2, ^3P_1, ^3P_0$
1S	0	0	0	1S_0

Again, the values of the spin-orbit degeneracies, given by $(2J+1)$ can be used to determine if the coupling scheme has been done properly.

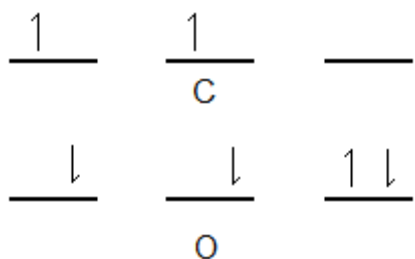
	J	$(2J+1)$
1D_2	2	5
3P_2	2	5
3P_1	1	3
3P_0	0	1
1S_0	0	1
Total		15

Again, notice that the total matches the original number of microstates.

The Hole Rule

When dealing with a subshell that is more than half filled, it is oftentimes easier (or at least less tedious) to employ the **hole rule**. The hole rule involves treating electron holes rather than the electrons themselves. Consider ${}_6\text{C}$ and ${}_8\text{O}$ as an example of complementary atoms. Carbon has a p^2 configuration and oxygen a p^4 configuration. (Added together, that makes a p^6 configuration, which closes the p-subshell and is why the two atoms are complementary.)

For each microstate in the p^2 system, there exists one in the p^4 system that when added together would complete the p-subshell. An example is shown below.



This relationship ensures that the exact same symmetry relationships hold for the p^4 system as for the p^2 system. Hence, the term symbols that arise from a p^4 system are ${}^1\text{D}$, ${}^3\text{P}$ and ${}^1\text{S}$. With spin-orbit coupling, the 3P will split into three components, ${}^3\text{P}_0$, ${}^3\text{P}_1$ and ${}^3\text{P}_2$. Of these, ${}^3\text{P}_2$ will have the lowest energy according to Hund's rule 3b, as these terms arise from a system where the subshell is more than half filled.

Hund's Rules

Hund's rules are used to determine the lowest energy state within the manifold of states generated from a given electronic configuration. The rules can be summarized as follows:

Hund's Rules

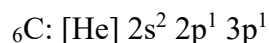
1. The lowest energy state will be the one with the largest value of **S**.
2. For multiple states with the same largest value of **S**, the lowest energy state will have the largest value of **L**.
3. For states with the same values of **L** and **S**, the lowest energy state will have
 - a. The smallest value of **J**, if the term arises from an electronic configuration in which the subshell is less than half filled
 - b. The largest value of **J**, if the term arises from an electronic configuration in which the subshell is more than half filled

For the case of a p^2 configuration, the largest value of **S** generated is $S = 1$, for the ${}^3\text{P}$ state. And within this state, the lowest energy term will be ${}^3\text{P}_0$, since p^2 corresponds to a subshell that is less than half filled.

Example: Determine the term symbols that arise from the p^3 configuration of ${}_7\text{N}$.

Nonequivalent Electrons

Consider a carbon atom in an excited state where the electronic configuration is given by



This is an example of a pp configuration (which is different than a p^2 configuration since the two electrons have different values of the principle quantum number n . In this case, a number of microstate combinations become distinguishable that would not be before. A complete set of microstates for a pp configuration is given in the table below. In this case, since the electrons are not equivalent, it is possible for both to be in orbitals where $m_l = +1$ with $m_s = +\frac{1}{2}$ since they are in different subshells.

	m_l		m_s		M_L	M_S	Designation
	2p	3p	2p	3p			
1	+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	+2	+1	3D
2	+1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+2	0	3D
3	+1	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	+2	0	1D
4	+1	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	+2	-1	3D
5	+1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	3D
6	+1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	3D
7	+1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	1D
8	+1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	3D
9	+1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3D
10	+1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	3D
11	+1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	1D
12	+1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3D
13	0	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	3P
14	0	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	3P
15	0	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	1P
16	0	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	3P
17	0	0	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3S
18	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	3S
19	0	0	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	1S
20	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3S
21	0	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	3D
22	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	3D
23	0	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	1D
24	0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	3D
25	-1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3P
26	-1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	3P
27	-1	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	1P

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28	-1	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	^3P
29	-1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	^3P
30	-1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	^3P
31	-1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	^1P
32	-1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	^3P
33	-1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-2	+1	^3D
34	-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	^3D
35	-1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-2	0	^1D
36	-1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-2	-1	^3D

In this example, there are more term symbols generated due to the fact that the electrons are not in the same subshell. The resulting term symbols are ^3D , ^3P , ^3S , ^1P , ^1P and ^1S . As such, this set of microstates includes some combinations of m_l and m_s which would not be possible if the two electrons were in the same subshell.

The Pauli Exclusion Principle

One explanation as to why the differences between the term symbols that arise from a p^2 configuration relative to a pp configuration is the **Pauli Exclusion principle**. The usual statement of the Pauli Exclusion Principle is that no two electrons in an atom can have the same set of four quantum numbers n , l , m_l and m_s . Another explanation is to simply announce that

Electrons are Fermions!

This approach is useful if you happen to know the properties of Fermions, but does not provide much insight if you do not.

A **Fermion** is a particle with half-integral spin. An obvious example (according to the statement above) is an electron which has $s = \frac{1}{2}$. Other examples include protons and neutrons and fluorine-19 nuclei (all with $\mathbf{I} = \frac{1}{2}$), aluminum-27 nuclei ($\mathbf{I} = \frac{5}{2}$) etc. Fermions have the property that the total wavefunction of a system containing two equivalent fermions must change sign if the two particles are exchanged.

The other type of particle is called a **Boson**. This is a particle with integral spin. Examples of bosons include deuterium nuclei or nitrogen-14 nuclei (both with $\mathbf{I} = 1$) or helium-4 nuclei ($\mathbf{I} = 0$.) A system containing two equivalent bosons must have a wavefunction that does not change sign for the exchange of two equivalent bosons.

$$\begin{aligned}\Psi(1,2) &= -\Psi(2,1) && \text{(for fermions)} \\ \Psi(1,2) &= \Psi(2,1) && \text{(for bosons)}\end{aligned}$$

In order to explore the properties of these types of particles, it is useful to define an operator that exchanges two equivalent particles (1 and 2).

$$\hat{O}\Psi(1,2) = \Psi(2,1)$$

$$\hat{O}\psi_m(1)\psi_n(2) = \psi_m(2)\psi_n(1)$$

In the limit that spin and orbital wavefunctions are separable (the total wavefunction can be expressed as the product of a spin function and an orbital function)

$$\Psi_{tot} = \psi_{orbital}\psi_{spin}$$

both the spin and orbital functions must be eigenfunctions of the electron exchange operator. We shall explore the properties of this operation on spin wavefunction to explore the difference between single and triplet spin wavefunctions as derived from a $pp\ p^2$ configuration.

Consider how the microstates shown in Table 1 behave under the exchange operation.

$$\begin{aligned}\hat{O}\Psi_1 &= \hat{O}\alpha(1)\alpha(2) = \alpha(2)\alpha(1) = \Psi_1 \\ \hat{O}\Psi_2 &= \hat{O}\alpha(1)\beta(2) = \alpha(2)\beta(1) = \Psi_3 \\ \hat{O}\Psi_3 &= \hat{O}\beta(1)\alpha(2) = \beta(2)\alpha(1) = \Psi_2 \\ \hat{O}\Psi_4 &= \hat{O}\beta(1)\beta(2) = \beta(2)\beta(1) = \Psi_4\end{aligned}$$

Wavefunctions Ψ_1 and Ψ_4 are eigenfunctions of \hat{O} . Wavefunctions Ψ_2 and Ψ_3 are not eigenfunctions of \hat{O} , but they are clearly related to one another through the electron exchange operation as the operation converts one into the other. The relationship suggests that linear combinations of Ψ_2 and Ψ_3 can be taken in order to construct spin wavefunctions that are eigenfunctions of \hat{O} . One linear combination is symmetric (eigenvalue = +1) and the other is antisymmetric (eigenvalue = -1). The correct, normalized linear combinations are as follows.

$$\begin{aligned}\Psi_s &= \frac{1}{\sqrt{2}}(\Psi_2 + \Psi_3) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\ \Psi_a &= \frac{1}{\sqrt{2}}(\Psi_2 - \Psi_3) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))\end{aligned}$$

Under the electron exchange operator, these linear combinations behave as follows.

$$\begin{aligned}\hat{O}\Psi_s &= \hat{O}\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))\right] = \frac{1}{\sqrt{2}}(\alpha(2)\beta(1) + \beta(2)\alpha(1)) = \Psi_s \\ \hat{O}\Psi_a &= \hat{O}\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))\right] = \frac{1}{\sqrt{2}}(\alpha(2)\beta(1) - \beta(2)\alpha(1)) = -\Psi_a\end{aligned}$$

So Ψ_s is symmetric with respect to electron interchange and Ψ_a is antisymmetric with respect to electron interchange. Noting that Ψ_1 and Ψ_4 are natural symmetric eigenfunctions of the exchange operator, it is easy to group the spin wavefunctions into triplet and singlet components according to symmetry with respect to the operator \hat{O} . The summary of these results is shown in the table below.

		Wavefunction		S	M _s
Triplet	Symmetric	Ψ_1	$\alpha(1)\alpha(2)$	1	+1
		Ψ_s	$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$		0
		Ψ_4	$\beta(1)\beta(2)$		-1
Singlet	Antisymmetric	Ψ_a	$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$	0	0

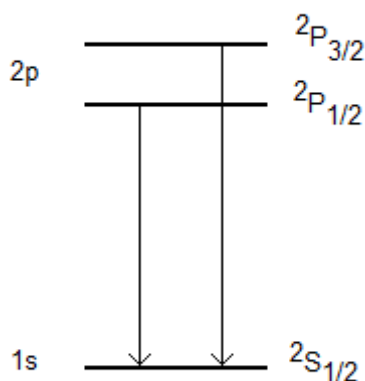
It can be seen that there are three components of the triplet spin wavefunction and only one component to the singlet function, as implied by the names “triplet” and “singlet.” More importantly, it is clear that to generate the ground state wavefunction for the atom, one *must* include contributions from paired electron spin functions (Ψ_s). So the statement of Hund’s rule that maximizing the number of electrons with the same value of m_s attains the lowest energy state is clearly incorrect, as it excludes the necessary component with $M_s = 0$.

For equivalent electrons (electrons in the same subshell, or the p^2 case) the symmetric spin wavefunction set (the triplet functions) must take antisymmetric orbital function (P). The singlet spin function, which is antisymmetric to electron exchange, must take a symmetric orbital function (D or S.) As such, the three term symbols generated are 1D , 3P and 1S . If the electrons are not equivalent, as is the case in a pp configuration, all combinations of the triplet and singlet spin functions with D, P and S orbital functions are possible and the resulting terms are 3D , 3P , 3S , 1D , 1P and 1S .

The 3D , 1P and 3S functions are not possible in the p^2 case, as these would require microstates that are either duplicates of other microstates, or microstates that involve two electrons in the same orbital with the same value of m_s . The latter is a clear violation of the Pauli Exclusion Principle since both electrons would then have the same values of n , l , m_l and m_s .

Atomic Spectroscopy

The complex spectra of atoms can be understood using term symbols, as they contain all of the symmetry and quantum number values needed. The selection rules for systems that are well described by **Russell-Saunders coupling** are



$$\Delta S = 0$$

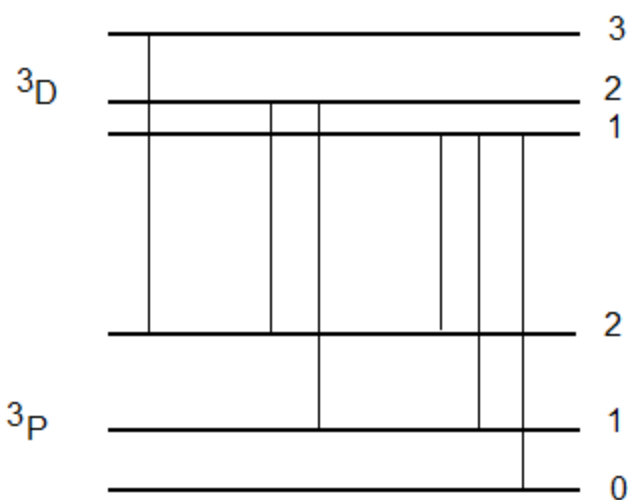
$$\Delta L = 0, \pm 1 \text{ (but not } 0 \leftrightarrow 0\text{)}$$

$$\Delta J = 0, \pm 1 \text{ (but not } 0 \leftrightarrow 0\text{)}$$

Consider a $^2P \rightarrow ^2S$ transition. An energy level diagram for such a transition is shown to the right.

The selection rules predict two lines will be observed in the spectrum. The splitting between the lines will be related to the spin-orbit coupling constant in the upper state. Note that for this transition, $\Delta S = 0$ and $\Delta L = +1$. (In spectroscopy recall that changes are always calculated as the upper state value minus the lower state value as in $\Delta L = L' - L''$.) The two lines predicted have $\Delta J = 0$ and $+1$ as depicted in the diagram.

Things get more complex for larger values of **L** and **S**. For example, consider the transition between a 3D state and a 3P state (with the 3D state as the upper state and both states increasing in energy with increasing **J**.)

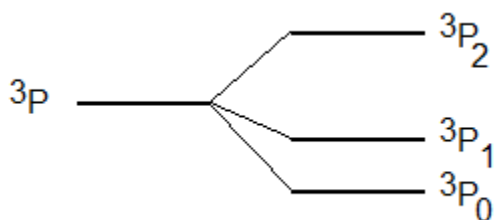


For this transition, six lines are predicted. The pattern formed by the lines can vary based on the relative values of the spin-orbit coupling constants in each level. In general, the upper state will

have the lower spin-orbit coupling constant, as electronic excitation quenches spin-orbit coupling.

Landé Interval Rule

The **Landé Interval Rule** describes the magnitude of the splittings in a term manifold. For example, it is predicted that the splitting pattern in a $3P$ state is



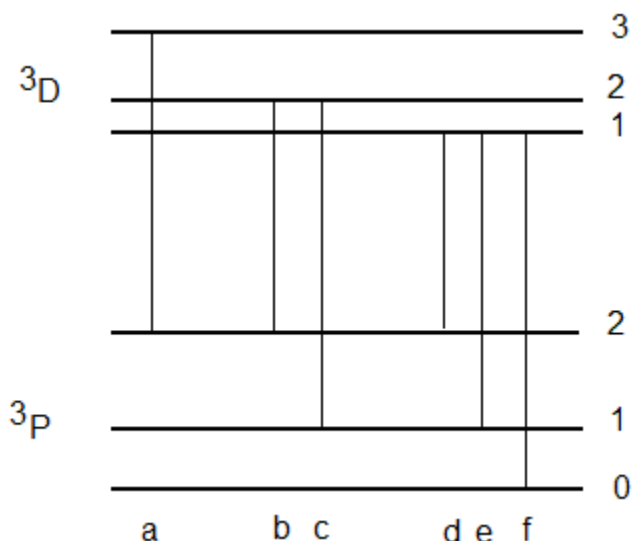
The splitting between the 3P_2 level and the 3P_1 level is twice as large as that between the 3P_1 component and the 3P_0 component. In general, the Landé Interval Rule can be stated

$$E_{J+1} - E_J = hcA(J+1)$$

where A is the **spin-orbit splitting constant** for the level. The Landé Interval Rule works well for small splittings, where the spin-orbit interaction can be treated as a perturbation to the Hamiltonian. There will generally be small deviations from the interval rule, especially when relativistic effects become important. The Landé Interval can be used to interpret the complex splitting patterns that can be seen in some atomic spectra.

The Deslandres Table.

A very useful tool that can be used in spectroscopy is the **Deslandres table**. In such a table, transitions are arranged according to upper and lower state combinations in such a way as to accentuate the differences in energy between quantum levels. For example, consider the following energy level diagram for $^3D - ^3P$ transition, where the six transitions have been labeled a-f for convenience.



Looking at the diagram, it should be clear that the difference in energy between lines b and c must be identical to that between lines d and e, since both differences give the difference in energy between the $J = 2$ and $J = 1$ components of the 3P level. Similarly, the difference in energy between lines b and d must be equal to that between lines c and e, as that is the difference in energy between the $J = 2$ and $J = 1$ levels in the 3D state.

A Deslandres table summarizes the information in the energy level diagram and also incorporates the values of the measured lines in the spectrum. Symbolically, the Deslandres table for the above transition would look as follows

		3D				
		3	$3A'$	2	$2A'$	1
3P	2	a	a-b	b	b-d	d
	$2A''$			c-b		e-d
	1	--		c	c-e	e
	A''					f-e
	0	--		--		f

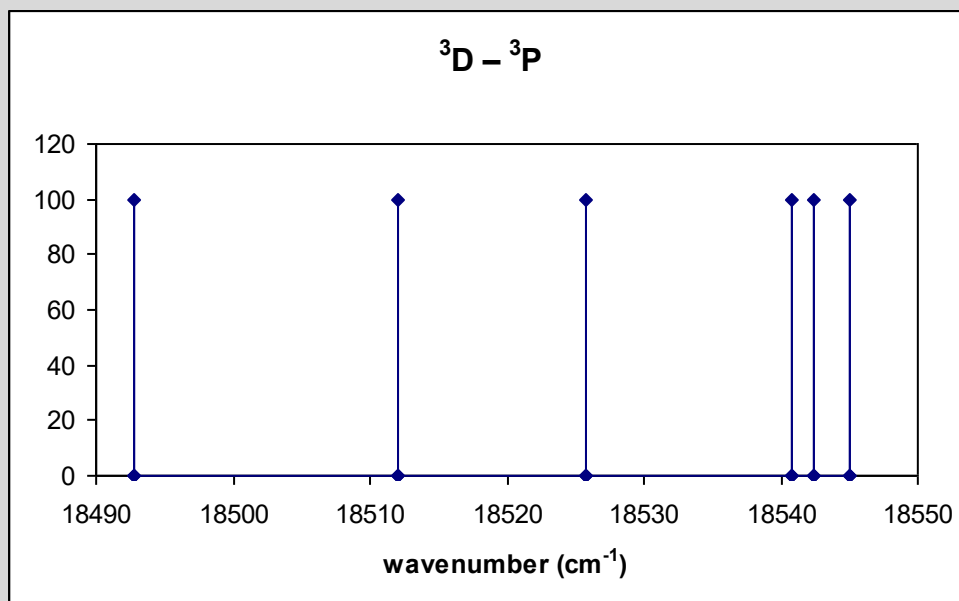
The table contains not only the line frequencies, but also the differences between them. It is the constancy of differences that confirms the assignment of the spectrum.

Example: consider the following data for a $^3D - ^3P$ transition. Assign the lines and calculate the spin-orbit coupling constants for both the upper and lower states based on your assignments.

Line	Freq (cm^{-1})
1	18492.74
2	18511.98
3	18525.82
4	18540.84

5	18542.36
6	18545.06

The stick spectrum (simulated spectrum, with transitions indicated as sticks instead of lines with a definite line shape and without intensity data indicated) looks as follows.



It would be difficult to assign the spectrum simply based on the pattern seen above. In some cases, the spectral pattern can be quite complex! A couple of things can be inferred, however, based on the energy level diagram above.

1. The smallest energy transition is for $^3D_1 - ^3P_2$ and
2. the largest energy transition is either $^3D_1 - ^3P_0$ or $^3D_2 - ^3P_1$ (depending on the relative magnitudes of the spin-orbit splittings.)

Based on these observations, we can assign the 18492.74 line.

If 18545.06 cm^{-1} is the $^3D_1 - ^3P_0$ transition, then the difference should be $3A''$. This predicts a lower level spin-orbit-coupling constant of $A'' = 17.44 \text{ cm}^{-1}$. And there must be a line at 18527.62 cm^{-1} . But there is no such line! Hence, the highest energy transition is not the $^3D_1 - ^3P_0$ transition. It must be the $^3D_2 - ^3P_1$ transition instead!

If the 18542.36 cm^{-1} line is the $^3D_1 - ^3P_0$ transition, a value of $A'' = 16.54 \text{ cm}^{-1}$ is predicted. This predicts a line at 18525.82 cm^{-1} which does exist! (This is idealized theoretical data for demonstration purposes. The Landé interval rule does not always hold as strongly as that.)

The difference between the $^3D_2 - ^3P_1$ transition and the $^3D_1 - ^3P_1$ transition is 19.24 cm^{-1} . In order to maintain a constant set of differences, there must be a line at 18511.98 cm^{-1} , which there is. This is assigned as the $^3D_2 - ^3P_2$ transition.

The only remaining line is 18540.84 cm^{-1} , which is assigned as the $^3D_3 - ^3P_2$ transition.

The final Deslandres table looks as follows.

		³ D				
		3	3A'	2	2A'	1
³ P	2	18540.84	28.86	18511.98	19.24	18492.74
	2A''			33.08		33.08
	1	--		18545.06	19.24	18525.82
	A''					16.54
	0	--		--		18542.36

In conclusion, angular momentum coupling schemes can be used to describe the states in a polyelectronic atom. These states can be used to predict the spectroscopy of these systems. In the next chapter, we will apply a number of the principles developed in this chapter in order to understand the electronic structure of diatomic molecules. This has important ramifications on both spectroscopy and bonding in these molecules, and also forms a foundation for how we think about electronic structure in larger molecules.

Vocabulary and Concepts

angular momentum	175	microstate	177
aufbau principle	174	orbital	175
Boson	182	orbital approximation.....	173
Clebsch series.....	176	Pauli Exclusion principle	182
Deslandres table	186	Russell-Saunders coupling.....	176, 184
Fermion	182	shell	175
hole rule	179	spin-orbit splitting constant.....	185
Hund's rules	180	subshell	175
Landé Interval Rule.....	185	term symbol	176

Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Describe the Orbital Approximation and explain how it leads to differences for polyelectronic atoms relative to the Hydrogen atom results.
2. Utilize the Aufbau principle to determine the ground electronic state electronic configuration for a polyelectronic atom, taking into account any important consequences of

- a. the Pauli Exclusion Principle
 - b. Hund's Rules of Maximum Multiplicity
3. Construct an orbital diagram depicting an electronic configuration, including using such a diagram to predict important properties of the ground (or any) electronic state configuration of an atom. These properties may include
 - a. Paramagnetism or diamagnetism
 - b. Total spin multiplicity or the number of total spin multiplicities associated with a given electronic configuration.
4. Use Russell-Saunders angular momentum coupling to determine the term symbols that arise for a given electronic configuration. Especially, one should be able to predict the lowest-energy term-state that arises from an electronic configuration consistent with Hund's Rules.
5. Employ electron exchange symmetry rules to construct symmetry-adapted linear combinations of spin functions that can be used to satisfy the Pauli Exclusion Principle by creating total wavefunctions that are antisymmetric with respect to the exchange of equivalent electrons.
6. Construct energy-level diagrams for term states that are consistent with Russell-Saunders coupling and the Lande Interval Rule.
 - a. Use these diagrams to predict the structure of electronic transition spectra involving these states.
 - b. Organize the data into a Deslandres Table to aid in the conformation of assignments and the calculation of spin-orbit coupling constants.

Problems

1. Write a table of microstates and predict the term simple that arise for N with an electronic configuration of $[\text{He}] 2s^2 2p^3$. Which is predicted to be the ground electronic state?
2. On the planet Zorg, electrons can exist in ζ orbitals, with $l = 3/2$ (and so $m_l = +3/2, +1/2, -1/2, -3/2$). All other rules apply (2 electrons per orbital, Hund's Rules, etc.)
 - a. How many microstates arise from a ζ^2 configuration?
 - b. Write a table of microstates for the ζ^2 configuration. What term symbols arise from this set of microstates?
3. Using the accepted conventions, draw an orbital diagram for the d electrons in V.
 - a. What is the predicted ground state term?
 - b. How many additional microstates contribute to the term?
4. Consider a $^3P - ^3P$ transition (in which both states increase in energy with increasing J.)
 - a. Draw an energy level diagram for the transition and predict the component transitions.
 - b. consider the following values: $A'' = 12.3 \text{ cm}^{-1}$, $A' = 8.4 \text{ cm}^{-1}$ and the $^3P_1 - ^3P_0$ transition occurs at 12459.3 cm^{-1} . Based on these complete a Deslandres table describing all of the component transitions and the spin-orbit spacings in the $^3P - ^3P$ transition.