For closed shell systems, a new orbital, for example by variational principle, consists of spherical functions for appropriate quantum numbers and orbital approximation is valid. For heavier atoms with atomic number Z:

\[ a_0 = \frac{4\pi \varepsilon_0}{\mu_e e^2} \]

The last term seems to be the least important because correlation between \( \mathbf{I} \) and \( \mathbf{S} \) is much smaller (if ever exists) as compared to \( \mathbf{I} \cdot \mathbf{S} \). Thus we need to compare \( \frac{\zeta \mathbf{I} \cdot \mathbf{S}}{E_k} \) with \( \zeta \mathbf{I} \cdot \mathbf{S} \). We saw for hydrogen that the latter is of the order of \( a^4 \sim 10^{-4} \). For heavier atoms with atomic number Z:

\[ < \zeta \mathbf{I} \cdot \mathbf{S} > \approx Z^2 a^4 n^4 \]

and is still much smaller than \( 1/n^2 \) if \( Z \) is not very high. Coulombic repulsion between the electrons is on the order of \( 1/n^2 \), allowing us to conclude that, at least for light atoms (\( Z < 40 \)), it is safe to assume that perturbation due to electron-electron repulsion is of greater importance. As a result, for light atoms, the total L and S are 'good' quantum numbers and orbital approximation is valid.

We start with an arbitrary Slater determinant:

\[ \Psi = \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \cdots & \phi_N(2) \\ \vdots & \cdots & \vdots \\ \phi_1(N) & \cdots & \phi_N(N) \end{vmatrix} = \frac{1}{J^{2N}} \]

\[ \psi \]

with electrons placed into spin-orbitals (one electron functions) \( \phi_i = R(r_i)Y_{lm}(\theta_i, \phi_i) \), where \( Y_{lm}(\theta, \phi) \) - are spherical functions for appropriate \( l \) and \( m \), and \( R(r_i) \) represents a radial function which would need to be found for a new orbital, for example by variational principle.

For closed shell systems:

\[ \Psi = \frac{1}{J^{2N}} \begin{vmatrix} \phi_1(1) & \bar{\phi}_1(1) & \phi_2(1) & \bar{\phi}_2(1) & \cdots & \phi_N(1) & \bar{\phi}_N(1) \\ \phi_1(2) & \bar{\phi}_1(2) & \phi_2(2) & \bar{\phi}_2(2) & \cdots & \phi_N(2) & \bar{\phi}_N(2) \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots \\ \phi_1(N) & \bar{\phi}_1(N) & \phi_2(N) & \bar{\phi}_2(N) & \cdots & \phi_N(N) & \bar{\phi}_N(N) \end{vmatrix} \]
Atomic Energy Levels

Configurations

For many practical purposes, when exact energies are not of primary concern, one can use only one configuration. The ground state configurations are fairly well described by the Aufbau principle which tells that the order of placing electrons on the orbitals should follow the scheme below:

The order reflects a combination of increasing energy of atomic orbitals with principal quantum number and increasing effect of shielding for more remote electrons with high azimuthal quantum number.

Exceptions:

- half filled and completely filled orbitals are more stable causing, for example, for Cr the ground state configuration to be 4s\(^1\)3d\(^3\), rather than 4s\(^2\)3d\(^4\).
- For positive ions, the order of orbitals is more hydrogen like (shielding is less important), thus Cu\(^{2+}\)[Ar] 3d\(^9\), since E_{d}^{+} < E_{s}^{+}.

Each configuration is usually degenerate, i.e., it has more than one state.

Terms

In multielectron atom, all the angular and spin momenta of electrons must add vectorially to make corresponding total angular momentum \(\mathbf{J}\). In light atoms, where spin-orbit coupling is small, the total orbital angular momentum: \(L = \sum L_{i}\) and total spin \(S = \sum S_{i}\) are relatively good quantum numbers by themselves, and the total angular momentum can be calculated as a vector sum:

\[
\mathbf{J} = L + S
\]

That scheme is also called the Russel-Sanders coupling scheme.

Without spin-orbit coupling, the operators \(H, L^{2}, J_{z}\) and \(S\) commute, and thus, a simultaneous eigenfunction of all five operators could be labelled by the corresponding eigenvalues:

\[
\psi = |n,L,M_{L},S,M_{S}\rangle
\]

Without external fields and spin orbit coupling, levels associated with (19) are \((2S + 1)\) times degenerate due to the spin (different \(M_{S}\)) and \(2L + 1\) times degenerate due to different \(M_{L}\), i.e., total degeneracy is:

\[
g = (2S + 1)(2L + 1)
\]

These \((2S + 1)(2L + 1)\) states of \(|n,L,M_{L},S,M_{S}\rangle\) with different projections \(M_{S}\) and \(M_{L}\) are labelled with the term symbol \(^{2S+1}L_{L}\). In the same way as one electron orbitals, the values of \(L\) are labelled as:

<table>
<thead>
<tr>
<th>(L)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>label</td>
<td>S</td>
<td>P</td>
<td>D</td>
<td>F</td>
<td>G</td>
</tr>
</tbody>
</table>

What terms arise from a particular configuration? Symmetry restrictions impose limitations on how these terms are constructed. For example, configuration 1s\(^2\)2s\(^1\) (as we saw with He), with electrons on different orbitals, produces two terms, a singlet \(^1S\) and a triplet, \(^3S\), four states altogether.

Configurations with a completely filled subshell correspond to one state, \(^1S\). For the same reason, when reducing a configuration into terms, only electrons from incomplete subshell(s) have to be considered.

Let’s take the carbon atom in 1s\(^2\)2s\(^2\)2p\(^2\) configuration. As we concluded above, only 2p\(^2\) have to be considered. We have to consider possible distributions of two p electrons among six spin orbitals in a manner consistent with the Pauli exclusion principle. The possible states are often referred to as microstates and, in fact, correspond to individual Slater determinants. For example, a microstate \(|1,0\rangle\) means \(m_{11} = 1, m_{12} = 1/2, m_{21} = 0, m_{12} = -1/2\). The number of microstates in a configuration can be calculated based on degeneracy of each orbital.

In general, total degeneracy of a configuration is \(2^{(2L + 1)}\) per electron and total degeneracy is calculated by multiplying all individual ones. If electrons belong to the same orbital then Pauli exclusion principle prevents them from having the same set of quantum numbers. Then second electron has only \(2^{(2L + 1) - 1}\) + 1 options for placing. Besides, we have to recognize that in multiplying \(2^{(2L + 1)}\) \(\times\) \(2^{(4L + 1)}\) we count twice the same states.

Total degeneracy for \(k\) electrons on an \(l\) orbital equals:

\[
g = \frac{(2L+1)^{2k}}{(2L_{1}+1)^{2k_{1}}(2L_{2}+1)^{2k_{2}}\ldots (2L_{n}+1)^{2k_{n}}}\]

In case of np\(^2\), there are 15 corresponding microstates:

SLATER DETERMINANTS FOR CONFIGURATION np\(^2\).

2
\[
|L\rangle = 0, 1, 2
\]

Often one needs to know only the lowest energy term. Hund proposed a set of empirical rules helping to identify it. 

\[
\begin{array}{|c|c|c|}
\hline
M_L & M_S = 1 & M_S = 0 \\
\hline
2 & 1,1 & \\
1 & 1,0,1,0 & 1,0 \\
0 & 1,1,1,0,0,1,1 & 1,1 \\
-1 & 0,1,1,0 & 0,1 \\
-2 & -1,1 & \\
\hline
\end{array}
\]

Note that some microstates, such as \(1,1\), are impossible, due to Pauli principle, and thus simultaneous \(M_L = 2\) and \(M_S = 1\) is impossible as well. The microstate \(1,1\) clearly belongs to \(^1D\) (\(|1,1\rangle = |^1D, M_L = 2\rangle\), while \(|1,0\rangle\) belongs to \(^3P\), but neither \(|1,0\rangle\), nor \(|1,0\rangle\) are eigenfunctions of the \(L^2\) and \(L_z\). The correct combinations can be deduced by application of the lowering operator \(L\) to \(|^1D, M_L = 2\rangle\):

\[
L|\langle 1,1| + \langle 1,0| \rangle = \frac{1}{\sqrt{2}} \left( |1,0\rangle + |1,1\rangle \right)
\]

Similarly, the state:

\[
|\langle 1,0| + |1,1| \rangle
\]

is orthogonal to \(|^1D, M_L = 1, M_S = 0\rangle\). Finishing symmetrization for all the microstates, we find that there are:

\[
\begin{align*}
^1D \cdot g &= (2S + 1)(2L + 1) = 5 \\
^3P \cdot g &= (2S + 1)(2L + 1) = 9 \\
^1S \cdot g &= (2S + 1)(2L + 1) = 1
\end{align*}
\]

Altogether 15 - in agreement with the number of microstates.

Analogous procedure can be used for other configurations. The procedure could be somewhat tedeous, so here is a table to help in that journey:

**Atomic Terms Arising from \(p^n\) and \(d^n\) Configurations.**

\[
\begin{array}{|c|c|c|}
\hline
p^1 & \equiv \text{P} & d^1, d^3 \equiv \text{D} \\
\hline
p^2 & \equiv \text{S}, \ 1D, 1P & d^2, d^6 \equiv \text{S}, 1D, 1G, 1P, 1F \\
\hline
p^3 & \equiv \text{P}, 1D, 3S & d^3, d^9, d^3 \equiv \text{P}, 2D, 2F, 2G, 2H, 2P, 2F \\
\hline
p^4 & \equiv \text{S}, 1D, 3P & d^4, d^6 \equiv \text{S} (twice), 1D (twice), 1F, 1G (twice), 1I, 1P (twice), 1F (twice), 1G, 1H, 1D \\
\hline
p^5 & \equiv \text{P} & d^5 \equiv \text{S}, 3P, 2D (three), 2F (twice), 2G (twice), 2H, 2I, 2P, 2F, 2G, 3S \\
\hline
\end{array}
\]

Often one needs to know only the lowest energy term. Hund proposed a set of empirical rules helping to identify it. 

**Hund’s rules:**

1) the term with highest spin multiplicity \(2S + 1\) lies lowest in energy (i.e. for \(P\) it is \(^3P\))
2) if this rule does not select a unique term, then the term with the highest \(L\) value lies lowest in energy
3) (in advance) the lowest energy state has
- **lowest J**, if the subshell is **less than half-filled**
- **highest J**, if the subshell is **more than half-filled**

The order of the higher energy terms and states often reflects the Hund’s rules but it is not strict there.

**Pictorial representation method** allows a simple visual way to apply the Hund’s rules.

For that purpose,
- 2\(l+1\) boxes are drawn for different orbitals
- each box is labeled with an \(m_l\) and electrons are placed into boxes to maximize \(M_L = \sum m_l\) and \(M_S = \sum m_s\).

Start with the highest \(m_l\) and proceed placing electrons in boxes with spin up. When all boxes are filled, continue with spins down.

Examples:

C 2p\(^2\):

\[
\begin{array}{ccc}
  m_l = 1 & 0 & -1 \\
  \uparrow & \uparrow & \downarrow \\
  M_L = 1 \\
  M_S = 1
\end{array}
\]

i.e. the lowest energy term is \(^3\)P

Co 3d\(^7\):

\[
\begin{array}{cccc}
  m_l = 2 & 1 & 0 & -1 -2 \\
  \uparrow \uparrow \uparrow \uparrow \downarrow \\
  M_L = 3 \\
  M_S = \frac{3}{2}
\end{array}
\]

i.e. the lowest energy term is \(^4\)F

That pictorial approach is also useful in finding all possible terms. Identification of unique terms could be simpler if we recognize that each term is \((2S+1)(2L+1)\) times degenerate and we need to identify only one microstate in the corner, say with highest \(M_S\) and highest \(M_L\) belonging to that term. We will place arrows representing electrons with appropriate spins into boxes following Pauli exclusion principle and identify "cornered microstates", i.e. avoid placing electrons with empty orbitals between them.

Examples:

np\(^3\) configuration

First we start with maximized \(S\) and vary \(L\):

\[
\begin{array}{ccc}
  m_l = 1 & 0 & -1 \\
  \uparrow & \uparrow & \downarrow \\
  M_L = 0 \\
  M_S = 3/2
\end{array}
\]

i.e. \(^4\)S-term, the lowest energy one, \((2S+1)(2L+1) = 4\) times degenerate

This is the only option with electrons having highest total spin.

Now we have to consider options with pairing them:

\[
\begin{array}{ccc}
  m_l = 1 & 0 & -1 \\
  \uparrow \uparrow \uparrow \downarrow \\
  M_L = 2 \\
  M_S = 1/2
\end{array}
\]

i.e. \(^2\)D-term, \((2S+1)(2L+1) = 10\) times degenerate

\[
\begin{array}{ccc}
  m_l = 1 & 0 & -1 \\
  \uparrow \uparrow \uparrow \downarrow \\
  M_L = 1 \\
  M_S = 1/2
\end{array}
\]

i.e. \(^2\)P-term, \((2S+1)(2L+1) = 6\) times degenerate

nd\(^2\) configuration

First we start with maximized \(S\) and vary \(L\):

\[
\begin{array}{ccc}
  m_l = 2 & 1 & 0 \\
  \uparrow \uparrow \\
  M_L = 3 \\
  M_S = 1
\end{array}
\]

i.e. \(^3\)F-term, the lowest energy one, \((2S+1)(2L+1) = 21\) times degenerate.
What about microstate

<table>
<thead>
<tr>
<th>$m_i$</th>
<th>2 1 0</th>
<th>1 -2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_L$</td>
<td>2</td>
<td>$M_S = 1$</td>
</tr>
<tr>
<td>$M_S$</td>
<td>1</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$m_i$</td>
<td>2 1 0</td>
<td>1 -2</td>
</tr>
<tr>
<td>$M_L$</td>
<td>4</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$M_S$</td>
<td>0</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$m_i$</td>
<td>2 1 0</td>
<td>1 -2</td>
</tr>
<tr>
<td>$M_L$</td>
<td>2</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$M_S$</td>
<td>0</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$m_i$</td>
<td>2 1 0</td>
<td>1 -2</td>
</tr>
<tr>
<td>$M_L$</td>
<td>1</td>
<td>$M_S = 1$</td>
</tr>
<tr>
<td>$M_S$</td>
<td>1</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$m_i$</td>
<td>2 1 0</td>
<td>1 -2</td>
</tr>
<tr>
<td>$M_L$</td>
<td>0</td>
<td>$M_S = 0$</td>
</tr>
<tr>
<td>$M_S$</td>
<td>0</td>
<td>$M_S = 0$</td>
</tr>
</tbody>
</table>

First impression is to assign it to $^3D$-term, but it is not. I

- $^3G$-term, the lowest energy one, $(2S + 1)(2L + 1) = 9$ times degenerate
- $^1D$-term, the lowest energy one, $(2S + 1)(2L + 1) = 5$ times degenerate
- $^3P$-term, the lowest energy one, $(2S + 1)(2L + 1) = 9$ times degenerate
- $^1S$-term, the lowest energy one, $(2S + 1)(2L + 1) = 1$ times degenerate

A simple way to recognize what terms are possible, is based on symmetry considerations.

**Spin-orbit coupling and the lowest energy state.**

The effects of spin-orbit coupling can be included into Hamiltonian in a general form:

$$H_{SO} = \sum \langle L_i \rangle \cdot \vec{s}^*$$

but it is not very convenient because of the presence of the individual $\vec{l}$ and $\vec{s}$ angular momenta. For a given term, however, an equivalent can be derived (Wigner-Eckart theorem):

$$H'_{SO} = \zeta \langle L, S \rangle \vec{L} \cdot \vec{S}$$

where numerical constant $\zeta(L, S)$ is often referred to as the spin-orbit coupling. This form is only applicable within a single isolated $2S + 1$ L and assumes no interactions with other terms. Now the $L_{\zeta}$ and $S_{\zeta}$ no longer commute with $H$. The set of commuting observables now is $\{H, \vec{J}, \vec{L}, S^z, J_z\}$ rather than $\{H, \vec{L}, \vec{S}, S^z, J_z\}$ where $\vec{J} = \vec{L} + \vec{S}$

is total angular momentum. When $\zeta$ increases, the various terms begin to interact and spin orbital coupling in the form (28) is no longer accurate. THe individual terms can no longer be considered independently. This means that the true wavefunctions are no longer eigenfunctions of $L^2$ and $S^2$. Nevertheless, will take them as approximately correct for light atoms. That scheme is called the **Russel-Sanders** coupling scheme.

A "good" set of quantum numbers now is $|n, L, S, J, M_J\rangle$ and the energy of each state now will depend on all of them but $M_J$. From (28) and (29):

$$\vec{L} \cdot \vec{S} = \frac{1}{2} \left( J^2 - L^2 - S^2 \right)$$

the first energy correction in this new basis set is:

$$<H'_{SO}> = \zeta <\vec{L} \cdot \vec{S}> = \frac{1}{2} \zeta (J(J + 1) - L(L + 1) - S(S + 1))$$

So, each term is now split into states $\frac{2S + 1}{2} L_J$. Depending on the sign of $\zeta$, the lowest energy will be either with highest or lowest $J$. The **third Hund's rule** state that $\zeta$ is positive when the subshell is less than half-filled and negative, when the subshell is more than half-filled. Usually, $\zeta$ is negative for the half-filled subshell. An easy way to explain that sign change is to think of going from a completely filled subshell; then lack of electrons can be viewed as holes, i.e. positive signs with corresponding change of sign for $\zeta$.

Thus, for C ($2s^22p^1$) we have the lowest energy term $^3P$ split into three states: $^1P_0, ^3P_1, ^1P_2$ with $^3P_0$ being the ground state. For O ($2s^22p^5$), which has the same lowest energy term, $^1P$, the ground state is $^3P_2$ instead.

Note that:
- $J$ can go only from $J_{	ext{min}} = |L - S|$ to $J_{	ext{max}} = L + S$
- Each state $\frac{2S + 1}{2} L_J$ is $2J + 1$ times degenerate due to different projections of $M_J$.
- Complete state specification lists the configuration, the term symbol, and the J value.

For example, the ground state of C: $2s^22p^1\text{^1P}_0$
The latter degeneracy by $M_J$ can be broken by external (electric and magnetic) fields.