The Pauli Exclusion Principle

The Pauli Exclusion Principle states that electrons in a single atom or molecule must have unique quantum numbers. This arises because they are fermions. Recall possible values for quantum numbers:

- Principal quantum number: $\{n = 1, 2, 3, \ldots\}$
- Angular quantum number: $\{l = 0, 1, 2, \ldots n-1\}$
- Magnetic quantum number: $\{m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l\}$

Q1

Write the electron configuration for the helium atom in its ground electronic state. In what orbital(s) will the electrons be found?

What is the value of the principal quantum number, $n$, for these two electrons?

What is the value of the angular quantum number, $l$, for these two electrons?

What is the value of the magnetic quantum number, $m_l$, for these two electrons?

What is the value of the spin quantum number, $m_s$, for these two electrons?
Adding Angular Momenta

One might naively think that you could get the total orbital angular momentum of a multi-electron atom by simply adding up the $l$ values of the individual electrons. The problem with this idea is that the momenta of the various electrons are not necessarily pointing in the same direction. If two electrons are revolving in the same direction as each other, you would add their $l$ values.

$$L = \sum_i^n l_i$$ \label{8.8.4A}

If they were revolving opposite to each other, you would subtract them. If they are revolving at some off-axis angle relative to each other, you would partially subtract them.

$$\vec{L} = \sum_i^{N} \vec{l}_i$$ \label{eq1}

$$\vec{S} = \sum_i^{N} \vec{s}_i$$ \label{eq2}

To figure out all of the possible combinations of $l$ for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases:

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, ... , |l_1 - l_2|$$ \label{8.8.5A}

$$S = |s_1 + s_2|, |s_1 + s_2 - 1|, ... , |s_1 - s_2|$$ \label{eq9}

Because $L$ and $S$ measures the magnitude of a vector, it cannot ever be negative. The sums in Equations \ref{eq1} and \ref{eq2} are vector sums, but the z-component of those total angular momenta are scalar sums:

$$M_L = \sum_i^{N} m_l$$ \label{eq3}

$$M_S = \sum_i^{N} m_s$$ \label{eq4}

Q2

For the helium atom in the ground state, fill out the table below to identify possible $L$, $M_L$ and $M_S$ values for the electronic configuration you identified previously.

Table \(\PageIndex{1}\): The collective angular momenta of the electrons in a multi-electron atom comes from addition of the angular momentum for individual electrons.

<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Electron 1</th>
<th>Electron 2</th>
<th>Total Angular momenta</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>$l$</td>
<td>$l$</td>
<td>$L=\frac{3}{2}$</td>
</tr>
<tr>
<td>Quantum Number</td>
<td>Electron 1</td>
<td>Electron 2</td>
<td>Total Angular momenta</td>
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</tr>
<tr>
<td>( l )</td>
<td></td>
<td></td>
<td>( S = l )</td>
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<tr>
<td>( m_\ell )</td>
<td></td>
<td></td>
<td>( M_\ell = l )</td>
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<tr>
<td>( m_s )</td>
<td></td>
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<td>( M_S = l )</td>
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</tbody>
</table>
Term Symbols are Used to Describe Total Angular Momenta in an Atom

In electronic spectroscopy, an atomic term symbol specifies a certain electronic state of an atom (usually a multi-electron one), by briefing the quantum numbers for the angular momenta of that atom. The form of an atomic term symbol implies Russell-Saunders coupling. Transitions between two different atomic states may be represented using their term symbols, to which certain rules apply. The electronic configuration identified in Q1 is not as complete a description of the electronic structure as possible. Term symbols usually represent electronic states in the Russell-Saunders coupling scheme, where a typical atomic term symbol consists of the spin multiplicity, the symmetry label and the total angular momentum of the atom.

\[
^{2S+1}L_J \label{term}\]

We generate \(L\) and \(S\) values from the values of \((M_L)\) and \((M_S)\).

**The Base Reflects the Total Orbital Angular Momentum**

We use the same symbolism for an electron in a single-electron wavefunction (i.e., \(\psi\)) to describe the total angular momentum of the (typically multi-electron) atom: \(\langle L\rangle\) (Table \(\PageIndex{2}\)). There is no great reason for doing this other than to correlate the terms for the two systems (i.e., the \(\langle L\rangle\) number should be just as fine, but we do not do that). Table \(\PageIndex{2}\): Designation of total orbital angular momentum in an atom via a letter.

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

**The Superscript Reflects the Total Spin Angular Momentum**

To denote the total spin angular momentum of the atom, the spin-degeneracy is added to the superscript of the term symbol as \((2S+1)\). There is no great reason for doing this other than to express the number of spin states (degeneracy) possible (i.e., the \((S)\) number should be just as fine, but we do not do that).

**The Subscript Reflects the Total Angular Momentum**

We can introduce a total angular momentum value that addressed both total spin (\(\langle \vec{S} \rangle\)) and total orbital angular momenta (\(\langle \vec{L} \rangle\)) as a vector sum (e.g., just two terms like in Equation \ref{eq1}). The value of \(\langle J \rangle\) comes from adding orbital, \(\langle L \rangle\), and spin, \(\langle S \rangle\), angular momentum as a vector sum (e.g., Equation \ref{eq5}):

\[
\underbrace{\vec{J} = \vec{L} + \vec{S}}_{\text{total angular momentum amplitude}} \label{eq5}\]

Possible values of \(\langle J \rangle\) that range from

\[|J| = |L-S|, |L-S+1|,...,L+S-1, L-S \label{eq6}\]

Fortunately, we do use the \(\langle J \rangle\) number direction in the term symbol, instead of degeneracy for spin angular momentum or an arbitrary letter designation for orbital angular momentum.
Q3

How many possible spin states (i.e., spin degeneracy) for the helium atom in the ground state configuration.

How many possible total angular moment states (i.e., J values from Equation \ref{eq6}) for the helium atom in the ground state configuration.

What is the term symbol for the helium atom in the ground state configuration.
Excited-State Helium Configurations

There is not anything special about identifying the states in an excited-state v.s ground-state electron configuration and the associated terms symbols. However, excited state are often open-shell systems (i.e., partially filled orbitals) which gives rise to many microstates each with a unique term symbol.

Q4

When an atom has a filled valence shell, we refer to it as a closed shell. For this situation, the term symbol is always the same. What is the atomic state arising from a closed shell configuration (you need to address all three aspects individually in term $\ref{term}$) ?

Q5

All electrons in complete, filled shells do not contribute to the atomic state and can be ignored. We only consider the valence shell and any unfilled shells. If we promote one electron in helium to an excited state, what will be the values of the four quantum numbers for the two electrons?

<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Electron 1</th>
<th>Electron 2</th>
<th>Total Angular momenta</th>
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<tbody>
<tr>
<td>(n)</td>
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<tr>
<td>(l)</td>
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<td>(S=1)</td>
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<tr>
<td>(m_l)</td>
<td></td>
<td>(M_L =1)</td>
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<tr>
<td>(m_s)</td>
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<td>(M_S=1)</td>
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What are the term symbols for the atomic states that arise from this electron configuration?

Q6

What is the electron configuration of boron in its ground state?
Which electrons contribute to the boron atomic microstates?
What are the atomic states arising from the boron ground state?
When an atom has a shell that is more than half filled, we consider the missing electrons when adding angular momentum rather than adding the angular momentum from the electrons present in the shell.

What is the electron configuration of fluorine in its ground state?

Which electrons contribute to the fluorine atomic states?

What are the atomic states arising from the fluorine ground state?

What is the electron configuration of carbon in its ground state? Which electrons contribute to the atomic states?

What is the principal quantum number, n, for the electrons in the valence shell?

What are the possible values of the angular quantum number, \( l \), for the electrons in the valence shell?

What are the possible values of the magnetic quantum number, \( m_l \), for the electrons in the valence shell?

What are the possible values of the spin quantum number, \( m_s \), for the electrons in the valence shell?
Remembering that electrons in the atom must have unique quantum numbers, what are the possible combinations of $m_l$ and $m_s$?

<table>
<thead>
<tr>
<th>Total of $M_L$</th>
<th>$m_l$ of Electron 1</th>
<th>$m_l$ of Electron 2</th>
<th>$m_s$ of Electron 1</th>
<th>$m_s$ of Electron 1</th>
<th>Total of $M_s$</th>
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To figure out the atomic states, we need to sum the $m_l$ and sum the $m_s$ quantum numbers to get $M_L$ and $M_S$, respectively.

\[
M_L = \sum_{i=1}^N m_l(i) \\
M_S = \sum_{i=1}^N m_s(i)
\]

If $l = 1$, what values are possible for $m_l$? 

If $L = 1$, what values are possible for $M_L$? 

If $S = 1$, what values are possible for $m_s$? 

If $S = 1$, what values are possible for $M_S$?
To have an atomic state with $L=1$, we must have the appropriate $M_L$ states to comprise the total $L$ state, that is, when \(L=1\), \(M_L= -1, 0, 1\).

What is the largest value of \(M_L\) in your table for carbon? What value of \(L\) can lead to that value of \(M_L\)?

What is the value of \(M_S\) for this value of \(M_L\)? What value of \(S\) can lead to that value of \(M_S\)?

For this largest value of ML and thus L, what other values of ML must contribute to the state with this value of L?

What atomic states will arise from this combination of L and S?

What \(M_L\) and \(M_S\) values are left?