Ground State Electron Configurations

• The actual wavefunction of a multi-electron atom is very complicated.

• In the orbital approximation, we suppose that a reasonable first approximation to this exact wavefunction is obtained by thinking of each electron as occupying its “own” orbital.

• The orbital approximation allows us to express the electronic structure of an atom by reporting its configuration, the list of occupied orbitals.

GROUND STATE CONFIGURATION for first 6 elements.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>1s(^1)</td>
<td>1s(^2)</td>
<td>1s(^2)2s(^1)</td>
<td>1s(^2)2s(^2)</td>
<td>1s(^2)2s(^2)2p(^1)</td>
<td>1s(^2)2s(^2)2p(^2)</td>
</tr>
</tbody>
</table>

We have a problem…
…there are three 2p orbitals…where do we put the electrons?
How can we fill 2 electrons into the three p orbitals, obeying the **Pauli principle**?

There are several possible ways of filling 2 electrons into three degenerate p orbitals.

The resulting microstates are NOT necessarily degenerate!

Identify the **ground state** using **Hund’s rule** (*maximum multiplicity*)…

…*maximum* # of parallel spins results in lowest e⁻ - e⁻ repulsion.

The above diagram roughly depicts the relative energy difference between these three ways of filling 2 electrons into the three p orbitals.

*Ground State:* \( 1s^22s^22p_x^12p_y^1 \) (or \( 1s^22s^22p_x^12p_z^1 \) or \( 1s^22s^22p_y^12p_z^1 \))

[CAUTION: these don’t explicitly state the electron’s spin!]
The 4\textsuperscript{th} Quantum Number

In order to discuss atomic orbital energies, we use 3 quantum numbers:

- **Principal** \( n \) (majority contribution to energy)
- **Angular momentum** \( l \) (orbital shape)
- **Magnetic** \( m_l \) (orbital orientation)

These 3 quantum numbers are the \textbf{spatial} quantum numbers.

⇒ together, they describe the 3D appearance of the orbital in space
⇒ the spatial probability distribution of an e\textsuperscript{-} described by that orbital

The 4\textsuperscript{th} quantum number is necessary to fully describe an e\textsuperscript{-} in an orbital.

\[ \text{Spin} \quad m_s \quad \text{(orientation of electron “spin”) MEANING?} \]

\[ m_s = + \frac{1}{2}, - \frac{1}{2} \]

An electron is either “spin up” or “spin down”.

The explanation of \textbf{Hund’s rule} is complicated, but it reflects the quantum mechanical property of \textbf{spin correlation}, that electrons with parallel spins have a tendency to stay well apart and hence repel each other less.
electron-electron repulsions and the Aufbau principle

We have already seen that e-e repulsions affect:

1) Ionization Potentials (See Li)
2) Electron Affinities (See Cl & F)
3) Ground State Configurations (e.g., C)

Let’s look again at the ordering of atomic orbitals, paying particular attention to the 3d and 4s in transition metals.
The Electronic Configurations of the Elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Total Electrons</th>
<th>Orbital Diagram</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>$1s^1$</td>
<td>$1s^1$</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>$1s^2$</td>
<td>$1s^2$</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>$1s^2 2s^1$</td>
<td>$1s^2 2s^1$</td>
</tr>
<tr>
<td>Be</td>
<td>4</td>
<td>$1s^2 2s^2$</td>
<td>$1s^2 2s^2$</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>$1s^2 2s^2 2p^1$</td>
<td>$1s^2 2s^2 2p^1$</td>
</tr>
</tbody>
</table>

**HOMEWORK FOR TUTORIAL**: Fill in electrons for C, N, O, F, Ne, Na & Mg
## Electronic Configuration

<table>
<thead>
<tr>
<th>Z</th>
<th>neutral</th>
<th>+ve ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1s^1</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>1s^2</td>
</tr>
<tr>
<td>3</td>
<td>Li ([He] 2s^1)</td>
<td>1s^2</td>
</tr>
<tr>
<td>4</td>
<td>Be ([He] 2s^2)</td>
<td>[He] 2s^1</td>
</tr>
<tr>
<td>5</td>
<td>B ([He] 2s^2 2p^1)</td>
<td>[He] 2s^2</td>
</tr>
<tr>
<td>6</td>
<td>C ([He] 2s^2 2p^2)</td>
<td>[He] 2s^2 2p^1</td>
</tr>
<tr>
<td>7</td>
<td>N ([He] 2s^2 2p^3)</td>
<td>[He] 2s^2 2p^2</td>
</tr>
<tr>
<td>8</td>
<td>O ([He] 2s^2 2p^4)</td>
<td>[He] 2s^2 2p^3</td>
</tr>
<tr>
<td>9</td>
<td>F ([He] 2s^2 2p^5)</td>
<td>[He] 2s^2 2p^4</td>
</tr>
<tr>
<td>10</td>
<td>Ne ([He] 2s^2 2p^6)</td>
<td>[He] 2s^2 2p^5</td>
</tr>
<tr>
<td>11</td>
<td>Na ([Ne] 3s^1)</td>
<td>[Ne]</td>
</tr>
<tr>
<td>12</td>
<td>Mg ([Ne] 3s^2)</td>
<td>[Ne] 3s^1</td>
</tr>
<tr>
<td>13</td>
<td>Al ([Ne] 3s^2 3p^1)</td>
<td>[Ne] 3s^2</td>
</tr>
<tr>
<td>14</td>
<td>Si ([Ne] 3s^2 3p^2)</td>
<td>[Ne] 3s^2 3p^1</td>
</tr>
<tr>
<td>15</td>
<td>P ([Ne] 3s^2 3p^3)</td>
<td>[Ne] 3s^2 3p^2</td>
</tr>
<tr>
<td>16</td>
<td>S ([Ne] 3s^2 3p^4)</td>
<td>[Ne] 3s^2 3p^3</td>
</tr>
<tr>
<td>17</td>
<td>Cl ([Ne] 3s^2 3p^5)</td>
<td>[Ne] 3s^2 3p^4</td>
</tr>
<tr>
<td>18</td>
<td>Ar ([Ne] 3s^2 3p^6)</td>
<td>[Ne] 3s^2 3p^5</td>
</tr>
<tr>
<td>19</td>
<td>K ([Ar] 4s^1)</td>
<td>[Ar]</td>
</tr>
<tr>
<td>20</td>
<td>Ca ([Ar] 4s^2)</td>
<td>[Ar] 4s^1</td>
</tr>
<tr>
<td>21</td>
<td>Sc ([Ar] 3d^1 4s^2)</td>
<td>[Ar] 3d^1 4s^1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>partial filling of both 3d and 4s in Sc^+</td>
</tr>
<tr>
<td>22</td>
<td>Ti ([Ar] 3d^2 4s^2)</td>
<td>[Ar] 3d^2 4s^1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>partial filling of both 3d and 4s in Ti^+</td>
</tr>
<tr>
<td>23</td>
<td>V ([Ar] 3d^3 4s^2)</td>
<td>[Ar] 3d^4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4s is empty for V^+</td>
</tr>
</tbody>
</table>
24  Cr  [Ar] 3d$^5$ 4s$^1$
25  Mn  [Ar] 3d$^5$ 4s$^2$
26  Fe  [Ar] 3d$^6$ 4s$^2$
27  Co  [Ar] 3d$^7$ 4s$^2$
28  Ni  [Ar] 3d$^8$ 4s$^2$
29  Cu  [Ar] 3d$^{10}$ 4s$^1$
30  Zn  [Ar] 3d$^{10}$ 4s$^2$
31  Ga  [Ar] 3d$^{10}$ 4s$^2$ 4p$^1$
32  Ge  [Ar] 3d$^{10}$ 4s$^2$ 4p$^2$
33  As  [Ar] 3d$^{10}$ 4s$^2$ 4p$^3$
34  Se  [Ar] 3d$^{10}$ 4s$^2$ 4p$^4$
35  Br  [Ar] 3d$^{10}$ 4s$^2$ 4p$^5$
36  Kr  [Ar] 3d$^{10}$ 4s$^2$ 4p$^6$
37  Rb  [Kr] 5s$^1$
38  Sr  [Kr] 5s$^2$
39  Y  [Kr] 4d$^1$ 5s$^2$
40  Zr  [Kr] 4d$^2$ 5s$^2$
41  Nb  [Kr] 4d$^4$ 5s$^1$
42  Mo  [Kr] 4d$^5$ 5s$^1$
43  Tc  [Kr] 4d$^5$ 5s$^2$
44  Ru  [Kr] 4d$^7$ 5s$^1$
45  Rh  [Kr] 4d$^8$ 5s$^1$
46  Pd  [Kr] 4d$^{10}$
47  Ag  [Kr] 4d$^{10}$ 5s$^1$
48  Cd  [Kr] 4d$^{10}$ 5s$^2$

**CHEM 2060 Lecture 9: Electronic Configurations**

24  Cr  [Ar] 3d$^5$ 4s$^1$  only 1e$^-$ in 4s for Cr…4s empty for Cr$^+$
25  Mn  [Ar] 3d$^5$ 4s$^1$  partial filling of both 3d and 4s in Mn$^+$
26  Fe  [Ar] 3d$^6$ 4s$^1$  partial filling of both 3d and 4s in Fe$^+$
27  Co  [Ar] 3d$^8$ 4s$^1$  4s is empty for Co$^+$
28  Ni  [Ar] 3d$^9$ 4s$^1$  4s is empty for Ni$^+$
29  Cu  [Ar] 3d$^{10}$ 4s$^1$  1e$^-$ in 4s for Cu…4s empty for Cu$^+$
30  Zn  [Ar] 3d$^{10}$ 4s$^2$  partial filling of both 3d and 4s in Zn$^+$
31  Ga  [Ar] 3d$^{10}$ 4s$^2$ 4p$^1$  4d is empty for Y$^+$…different from Sc$^+$
32  Ge  [Ar] 3d$^{10}$ 4s$^2$ 4p$^2$  partial filling of both 4d and 5s in Zr$^+$
33  As  [Ar] 3d$^{10}$ 4s$^2$ 4p$^3$  only 1e$^-$ in 5s for Nb.. 5s empty in Nb$^+$
34  Se  [Ar] 3d$^{10}$ 4s$^2$ 4p$^4$  only 1e$^-$ in 5s for Mo.. 5s empty Mo$^+$
35  Br  [Ar] 3d$^{10}$ 4s$^2$ 4p$^5$  partial filling of both 4d and 5s in Tc$^+$
36  Kr  [Ar] 3d$^{10}$ 4s$^2$ 4p$^6$  5s empty in both Pd and Pd$^+$
37  Rb  [Kr] 5s$^1$  1e$^-$ in 5s for Ag…5s empty for Ag$^+$
38  Sr  [Kr] 5s$^2$
There are several exceptions (of different types) to the Aufbau principle.

The oversimplified filling rules that we learned in first year chemistry work up to $Z = 20$ (calcium), but are no longer accurate for heavier elements where the energy difference between $n$ and $n+1$ is smaller.

**3d and 4s orbitals** (K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn)

In atoms (charge = 0), **4s fills first**...we say that “4s is lower than 3d”

**EXCEPTIONS** occur for Cr and Cu.

- Chromium $[\text{Ar}]3d^5\ 4s^1$ half-filled 3d orbital shell
- Copper $[\text{Ar}]3d^{10}\ 4s^1$ filled 3d orbital shell

**WHY?**

Because we are being “naïve” by simply referring to the energy of orbitals! By saying “4s is lower than 3d”, we are neglecting the impact of e-e repulsion!
The ground state electronic configurations of the 0, +1, and +2 oxidation states of the element scandium (Sc) provide a really good example for this argument.

\[
\begin{align*}
\text{Sc} & \rightarrow \text{[Ar] 3d}^1 \text{4s}^2 \\
\text{Sc}^+ & \rightarrow \text{[Ar] 3d}^1 \text{4s}^1 \\
\text{Sc}^{2+} & \rightarrow \text{[Ar] 3d}^1
\end{align*}
\]

⇒ The 3d and 4s orbitals are close in energy...
   ...the energy difference is small enough that the effect of \(e^-e^-\) repulsion dictates the ground state configurations.

There are a number of experimental values that can help probe this issue:

Experimental energy required to **excite one electron** from 4s to 3d in Sc:

\[
\text{Sc ([Ar]3d}^1\text{4s}^2) \rightarrow \text{Sc ([Ar]3d}^2\text{4s}^1) \quad \Delta E = 2.03 \text{ eV}
\]

Experimental **ionization potentials** from 3d versus from 4s in Sc:

\[
\begin{align*}
\text{Sc ([Ar]3d}^1\text{4s}^2) & \rightarrow \text{Sc}^+ ([\text{Ar}3d]4s^1) + e^- \quad IP_{4s} = 6.62 \text{ eV} \\
\text{Sc ([Ar]3d}^1\text{4s}^2) & \rightarrow \text{Sc}^+ ([\text{Ar}4s]^2) + e^- \quad IP_{3d} = 7.98 \text{ eV}
\end{align*}
\]
We are now left with a dilemma…

If it is easier to remove an electron from the 4s orbital than from the 3d orbital, shouldn’t that mean that the 3d orbital is lower in energy than the 4s?

Why, then, is the 4s orbital filled before the 3d orbital?

**ANSWER:** It is more accurate to consider the relative energies of electronic configurations than of atomic orbitals.

In other words, the energies of the electronic configurations ultimately dictate the *apparent* ordering of the atomic orbital energies.

The 4s orbital is more diffuse than the 3d orbital.

But the 4s orbital also penetrates to the nucleus better than the 3d orbital.
For most of the 1\textsuperscript{st} row transition metal elements, the ground state is:
\[
[\text{Ar}]3d^x4s^2 \quad (4s \text{ fills first})
\]
…because e-e repulsion is decreased by filling the diffuse 4s orbital first.

Note exceptions often occur with:
Exactly ½-filled and full shells
- Chromium $3d^54s^1$
- Copper $3d^{10}4s^1$

These exceptions reflect a quantum mechanical stabilization of exactly ½-filled or full (sub)shells.
For ALL of the 1st row transition metal dications (or higher oxidation states), the ground state is:

\[ \text{[Ar]}3d^x \text{ (4s is empty)} \]

When we start removing electrons from the system, we increase the overall nuclear charge “felt” by all the remaining electrons…

…we’ve decreased the shielding!

As a result, the atomic orbitals contract (become less diffuse).

The reduction in the “diffuse-ness” of the 4s orbital results in an increase in e-e repulsion between electrons occupying this orbital.

For \( M^+ \), this reduction in the “diffuse-ness” of the 4s orbital does not always outweigh the “natural” orbital energy ordering (3d lower than 4s).

For \( M^{2+} \), \( M^{3+} \), \( M^{4+} \), etc., the result is that occupation of only the 3d orbitals results in a lower energy electronic configuration…we say “3d is lower than 4s”.
ORBITAL ENERGIES OF THE NON-HYDROGEN ATOMS

\[ n = \infty \]

\[ n = 4 \]
\[ n = 3 \]
\[ n = 2 \]
\[ n = 1 \]

Energy

Hydrogen

\[ n = 1 \quad l = 0 \]
1s

Non-hydrogen

4s 3p 3d 3s 2p 2s