Lecture 19: The Aufbau Principle

• Reading: Zumdahl 12.11-12.13

• Outline:
  – Spin
  – The Aufbau Principle
  – Filling up orbitals and the Periodic Table
Spin

• Further experiments demonstrated the need for one more quantum number.

• Specifically, some particles (electrons in particular) demonstrated inherent angular momentum.
Spin (cont.)

• The new quantum number is $m_s$ (analagous to $m_l$).

• For the electron, $m_s$ has two values: $+1/2$ and $-1/2$
The Aufbau Principal

- For polyelectronic atoms, a direct solution of the Schrodinger Eq. is not possible.

- When we construct polyelectronic atoms, we use the hydrogen-atom orbital nomenclature to discuss in which orbitals the electrons reside.

- This is an approximation (and it is surprising how well it actually works).
The Aufbau Principal (cont.)

- When placing electrons into orbitals in the construction of polyelectronic atoms, we use the Aufbau Principle.

- This principle states that in addition to adding protons and neutrons to the nucleus, one simply adds electrons to the hydrogen-like atomic orbitals.

- Pauli exclusion principle: No two electrons may have the same quantum numbers. Therefore, only two electrons can reside in an orbital (differentiated by $m_s$).
The Aufbau Principal (cont.)

• Finally, orbitals are filled starting from the lowest energy.

• Example: Hydrogen

\[
\begin{array}{c}
\uparrow \\
1s
\end{array}
\begin{array}{c}
\square \\
2s
\end{array}
\begin{array}{c}
\square \square \square \\
2p
\end{array}
1s^1
\]

• Example: Helium (Z = 2)

\[
\begin{array}{c}
\uparrow \downarrow \\
1s
\end{array}
\begin{array}{c}
\square \\
2s
\end{array}
\begin{array}{c}
\square \square \square \\
2p
\end{array}
1s^2
\]
The Aufbau Principal (cont.)

- Lithium (Z = 3)
  \[ 1s^2 2s^1 \]

- Berillium (Z = 4)
  \[ 1s^2 2s^2 \]

- Boron (Z = 5)
  \[ 1s^2 2s^2 2p^1 \]
The Aufbau Principal (cont.)

• Carbon ($Z = 6$)

\[ \begin{array}{ccc}
1s & 2s & 2p \\
\downarrow\downarrow & \uparrow\downarrow & \uparrow\uparrow
\end{array} \quad 1s^22s^22p^2 \]

_Hund’s Rule:_ Lowest energy configuration is the one in which the maximum number of unpaired electrons are distributed amongst a set of degenerate orbitals.

• Nitrogen ($Z = 7$)

\[ \begin{array}{ccc}
1s & 2s & 2p \\
\downarrow\downarrow & \uparrow\downarrow & \uparrow\uparrow\uparrow\uparrow
\end{array} \quad 1s^22s^22p^3 \]
The Aufbau Principal (cont.)

• Oxygen (Z = 8)

\[ 1s^2 2s^2 2p^4 \]

• Fluorine (Z = 9)

\[ 1s^2 2s^2 2p^5 \]

• Neon (Z = 10)

\[ 1s^2 2s^2 2p^6 \text{ full} \]
The Aufbau Principal (cont.)

- Sodium ($Z = 11$)
  
  \[ \begin{array}{c}
  \text{Ne} \\
  3s \\
  \end{array} \quad \uparrow \quad 1s^2 2s^2 2p^6 3s^1 \quad \Rightarrow \quad [\text{Ne}] 3s^1 \]

- Argon ($Z = 18$)
  
  \[ \begin{array}{c}
  \text{Ne} \\
  3s \\
  \end{array} \quad \uparrow \downarrow \quad \uparrow \downarrow \quad \uparrow \downarrow \quad \uparrow \downarrow \quad \text{[Ne] } 3s^2 3p^6 \]
The Aufbau Principal (cont.)

- We now have the orbital configurations for the first 18 elements.

- Elements in same column have the same # of valence electrons!
The Aufbau Principal (cont.)

- Similar to Sodium, we begin the next row of the periodic table by adding electrons to the 4s orbital.

- Why not 3d before 4s?
  - 3d is closer to the nucleus
  - 4s allows for closer approach; therefore, is energetically preferred.
The Aufbau Principal (cont.)

• Elements Z=19 and Z= 20:

  Z= 19, Potassium: 1s^22s^22p^63s^23p^64s^1 = [Ar]4s^1
  Z= 20, Calcuim: 1s^22s^22p^63s^23p^64s^2 = [Ar]4s^2

• Elements Z=21 to Z=30 have occupied d orbitals:

  Z= 21, Scandium: 1s^22s^22p^63s^23p^64s^23d^1 = [Ar] 4s^23d^1
  Z = 24, Chromium: [Ar] 4s^13d^5 exception
  Z= 30, Zinc: 1s^22s^22p^63s^23p^64s^23d^{10} = [Ar] 4s^23d^{10}
- This orbital filling scheme gives rise to the modern periodic table.
After Lanthanum ([Xe]6s^25d^1), we start filling 4f.
• After Actinium ([Rn]7s\(^2\)6d\(^1\)), we start filling 5f.
The Aufbau Principal (cont.)

- Heading on column given total number of valence electrons.
The Aufbau Principal (cont.)

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*Lanthanide series:

58 59 60 61 62 63 64 65 66 67 68 69 70 71

**Actinide series:

90 91 92 93 94 95 96 97 98 99 100 101 102 103
Summary

• Electrons go into hydrogen-like orbitals to construct polyelectronic atoms.

• Remember the adjacent “trick” for remembering how to fill orbitals.