Chapter 8
Electron Configuration & Chemical Periodicity

One additional quantum number is needed to describe a property of an electron in an atomic orbital.

4. Spin Quantum Number, \( m_s \)
   
   \( m_s = +\frac{1}{2} \) or \(-\frac{1}{2}\)

An electron in an orbital is described by its set of FOUR quantum numbers.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Permitted Values</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal</td>
<td>( n )</td>
<td>Positive integers (1, 2, 3, etc.)</td>
<td>Orbital energy (size)</td>
</tr>
<tr>
<td>Angular momentum</td>
<td>( l )</td>
<td>Integers from 0 to ( n - 1 )</td>
<td>Orbital shape (The ( l ) values 0, 1, 2, and 3 correspond to s, p, d, and f orbitals, respectively.)</td>
</tr>
<tr>
<td>Magnetic</td>
<td>( m_l )</td>
<td>Integers from (-l) to 0 to (+l)</td>
<td>Orbital orientation</td>
</tr>
<tr>
<td>Spin</td>
<td>( m_s )</td>
<td>( +\frac{1}{2} ) or (-\frac{1}{2})</td>
<td>Direction of e(^{-}) spin</td>
</tr>
</tbody>
</table>

❖ “shell”: orbitals with the same \( n \) value
❖ “subshell”: orbitals with the same \( n \) & \( l \) values
   e.g., the \( n=3 \) shell contains the 3s subshell, 3p subshell, and 3d subshell.

Pauli Exclusion Principle

No two electrons in an atom can have the same set of four quantum numbers.

Therefore: a maximum of TWO electrons per orbital. (A third electron in an orbital
would have to have the same set of four quantum numbers as one of the two electrons
already there.)

Hund’s Rule

When orbitals of equal energy (“degenerate”) are available, the electron configuration of lowest
energy has the maximum number of electrons with the same spin.
**General Principles of Electron Configuration**

- Note similar electron configurations within a group, e.g., Group 5A: $ns^2np^3$
- Orbital Filling Order & Periodic Table
  
  The periodic table is our best guide to filling orbitals and writing electron configurations!
Periodic Trends

**Atomic Radius**
Usually measured using distances between nuclei of bonded atoms (e.g., “bonding atomic radius”); see Figure 8.14.

**Trends**
- **Going down a group**, atomic radius increases. This is the result of the increasing principal quantum number of the valence electrons (larger \( n \) \( \rightarrow \) larger size of orbital).
- **Going across a period (left to right)**, atomic radius decreases. This is the result of an increasing nuclear charge (Z) attracting electrons with the same principal quantum number.

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**Ionization Energy**

**Ionization energy** is defined as the minimum energy required to remove 1 mol of electrons from 1 mol of gaseous atoms/ions.

- **First ionization energy**, \( IE_1 \)
  - Defined as the amount of energy required to remove 1 mol of electrons from gaseous neutral atoms.
  - \( X(g) \rightarrow X^+(g) + e^- \)
- **Second ionization energy**, \( IE_2 \)
  - Defined as the amount of energy required to remove 1 mol of electrons from gaseous ions with a +1 charge, producing ions with a 2+ charge.
  - \( X^+(g) \rightarrow X^{2+}(g) + e^- \)

**Trends**
- **Going down a group**, first ionization energy decreases, as the result of the increasing principal quantum number of the valence electrons (larger \( n \) \( \rightarrow \) larger size of orbital).
- **Going across a period (left to right)**, first ionization energy increases. This is the result of an increasing nuclear charge (Z) attracting electrons with the same principal quantum number. The greater attraction for the electrons makes them harder to remove.

For each element, \( IE_1 < IE_2 < IE_3 \) and so forth. There is a sharp jump in \( IE \) when an inner-shell electron is removed. For example, removing the four valence electrons from C requires progressively more energy for each electron. Removing the fifth electron from C requires MUCH more energy because at that point, you are removing core electrons.

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**Table 8.5**

<table>
<thead>
<tr>
<th>( Z )</th>
<th>Element</th>
<th>Number of Valence Electrons</th>
<th>( IE_1 )</th>
<th>( IE_2 )</th>
<th>( IE_3 )</th>
<th>( IE_4 )</th>
<th>( IE_5 )</th>
<th>( IE_6 )</th>
<th>( IE_7 )</th>
<th>( IE_8 )</th>
<th>( IE_9 )</th>
<th>( IE_{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Li</td>
<td>1</td>
<td>0.52</td>
<td>2.30</td>
<td>11.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Be</td>
<td>2</td>
<td>0.90</td>
<td>1.76</td>
<td>14.85</td>
<td>21.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>3</td>
<td>0.80</td>
<td>2.43</td>
<td>3.66</td>
<td>25.02</td>
<td>32.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>4</td>
<td>1.09</td>
<td>2.35</td>
<td>4.62</td>
<td>6.22</td>
<td>37.83</td>
<td>47.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>5</td>
<td>1.40</td>
<td>2.86</td>
<td>4.58</td>
<td>7.48</td>
<td>9.44</td>
<td>53.27</td>
<td>64.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>6</td>
<td>1.31</td>
<td>3.39</td>
<td>5.30</td>
<td>7.47</td>
<td>10.98</td>
<td>13.33</td>
<td>17.33</td>
<td>21.57</td>
<td>23.07</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>7</td>
<td>1.68</td>
<td>3.37</td>
<td>6.05</td>
<td>8.41</td>
<td>11.02</td>
<td>15.16</td>
<td>19.27</td>
<td>23.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Ne</td>
<td>8</td>
<td>2.08</td>
<td>3.95</td>
<td>6.12</td>
<td>9.37</td>
<td>12.18</td>
<td>15.24</td>
<td>20.00</td>
<td>23.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>1</td>
<td>0.50</td>
<td>4.56</td>
<td>6.91</td>
<td>9.54</td>
<td>13.35</td>
<td>16.61</td>
<td>20.11</td>
<td>25.49</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Successive Ionization Energies of the Elements Lithium Through Sodium**

**Core electrons**

**Figure 8.13:** Atomic radii in picometers.

**Figure 8.16:** First ionization energies in kJ·mol\(^{-1}\).
Electron Affinity

Electron affinity is defined as the energy change with the addition of 1 mole of electrons to 1 mole of gaseous atoms/ions.

\[ X(g) + e^- \rightarrow X^-(g) \]

Gross Trends
There are many exceptions to these gross trends, which result from the arrangement of electrons in orbitals and the special stability of half-filled orbitals (Hund’s rule), among other things.

Going down a group, electron affinity generally decreases.

Going across a period (left to right), electron affinity generally increases. For the noble gases, however, the EA is negative because addition of an electron would disrupt the already-stable arrangement of electrons. The additional electron would have to reside in a higher-energy subshell.

Metallic Behavior

- Metals: typically shiny solids, moderate to high melting points, good thermal/electrical conductors, tend to lose electrons in reactions with nonmetals
- Nonmetals: everything the opposite of metals
- Metalloids: share some properties of metals and nonmetals.

Nonmetal Oxides (some solids, some liquids, some gases)
nonmetal oxide + water → ACID
e.g., SO\(_3\) + H\(_2\)O → H\(_2\)SO\(_4\)

Main Group Metal Oxides (always solids)
metal oxide + water → metal hydroxide (a BASE)
e.g., K\(_2\)O + H\(_2\)O → 2KOH

Transition metal oxides may be acidic, basic, or either! High oxidation number results in more covalent bonding.
e.g., Cr\(^{VI}\)O\(_3\) + H\(_2\)O → H\(_2\)CrO\(_4\) “chromic acid”, a strong acid—note similarity to SO\(_3\) which also has a +6 O.N.

SUMMARY of Periodic Trends

- Increases in metallic behavior
- Increases in ionization energy
- Increases in electron affinity
Development of the Periodic Table

Dmitri Mendeleev, 1870

- Table was arranged in generally increasing mass across a period, with some exceptions.
- While Meyer developed a similar table at the same time, Mendeleev gets more credit because he was able to predict the properties of as-yet undiscovered elements.

Mendeleev’s Predicted Properties of Germanium (“eka Silicon”) and Its Actual Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Predicted Properties of eka Silicon (E)</th>
<th>Actual Properties of Germanium (Ge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass</td>
<td>72 amu</td>
<td>72.61 amu</td>
</tr>
<tr>
<td>Appearance</td>
<td>Gray metal</td>
<td>Gray metal</td>
</tr>
<tr>
<td>Density</td>
<td>5.5 g/cm³</td>
<td>5.32 g/cm³</td>
</tr>
<tr>
<td>Molar volume</td>
<td>13 cm³/mol</td>
<td>13.65 cm³/mol</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>0.31 J/g·K</td>
<td>0.32 J/g·K</td>
</tr>
<tr>
<td>Oxide formula</td>
<td>EO₂</td>
<td>GeO₂</td>
</tr>
<tr>
<td>Oxide density</td>
<td>4.7 g/cm³</td>
<td>4.23 g/cm³</td>
</tr>
<tr>
<td>Sulfide formula and</td>
<td>ES₂; insoluble in H₂O;</td>
<td>GeS₂; insoluble in H₂O;</td>
</tr>
<tr>
<td>solubility</td>
<td>soluble in aqueous (NH₄)₂S</td>
<td>soluble in aqueous (NH₄)₂S</td>
</tr>
<tr>
<td>Chloride formula</td>
<td>EC₁ (≥100°C)</td>
<td>GeCl₁ (84°C)</td>
</tr>
<tr>
<td>(boiling point)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride density</td>
<td>1.9 g/cm³</td>
<td>1.844 g/cm³</td>
</tr>
<tr>
<td>Element preparation</td>
<td>Reduction of KₓE₂F₄ with sodium</td>
<td>Reduction of KₓGeF₄ with sodium</td>
</tr>
</tbody>
</table>

Properties of Monatomic Ions

- **Anion formation:** add electrons to the lowest available unfilled subshell.

- **Cation formation:** remove electrons from subshell with highest \( n \) and highest \( l \) first.
**Sizes of Ions**

*Eight minus six is two.*

**a CATION is SMALLER than its parent atom.**

**an ANION is LARGER than its parent atom.**

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**Trends in Ionic Radius**

- Down a group

- Within an isoelectronic set
  - *isoelectronic*: having the same number and configuration of electrons

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**Magnetic Properties**

- *paramagnetism*: attraction to an external magnetic field. Exhibited by species with unpaired electrons.
- *diamagnetism*: slight repulsion from external magnetic field. Exhibited by species with paired electrons.

Magnetic properties can be used to verify that in TM cation formation, the *s* electrons are removed first. Consider Ti$^{2+}$.

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**Figure 8.27: a Gouy balance**

**Figure 8.29**