General Rules of Electron Configuration

There are a set of general rules that are used to figure out the electron configuration of an atomic species: Aufbau's Principle, Hund's Rule and the Pauli-Exclusion Principle. Before continuing, it's important to understand that each orbital can be occupied by two electrons of opposite spin (which will be further discussed later). The following table shows the possible number of electrons that can occupy each orbital in a given subshell.

<table>
<thead>
<tr>
<th>subshell</th>
<th>number of orbitals</th>
<th>total number of possible electrons in each orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>p</td>
<td>3 (px, py, pz)</td>
<td>6</td>
</tr>
<tr>
<td>d</td>
<td>5 (d_x^2-y^2, d_z^2, d_xy, d_xz, d_yz)</td>
<td>10</td>
</tr>
<tr>
<td>f</td>
<td>7 (f_z^3, f_xz^2, f_xyz, f_x(x^2-3y^2), f_yz^2, f_z(x^2-y^2), f_y(3x^2-y^2))</td>
<td>14</td>
</tr>
</tbody>
</table>

Using our example, iodine, again, we see on the periodic table that its atomic number is 53 (meaning it contains 53 electrons in its neutral state). Its complete electron configuration is 1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^5. If you count up all of these electrons, you will see that it adds up to 53 electrons. Notice that each subshell can only contain the max amount of electrons as indicated in the table above.
Aufbau Principle

The word ‘Aufbau’ is German for ‘building up’. The Aufbau principle, also called the building-up principle, states that electrons occupy orbitals in order of increasing energy. The order of occupation is as follows:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 5d < 6p < 7s < 5f < 6d < 7p

Another way to view this order of increasing energy is by using Madelung’s Rule:

\[
\begin{array}{c|c|c|c|c}
\ell = 0 & \ell = 1 & \ell = 2 & \ell = 3 \\
n=1 & 1s^2 & & \\
n=2 & 2s^2 2p^6 & & \\
n=3 & 3s^2 3p^6 3d^{10} & & \\
n=4 & 4s^2 4p^6 4d^{10} 4f^{14} & & \\
n=5 & 5s^2 5p^6 5d^{10} 5f^{14} & & \\
n=6 & 6s^2 6p^6 6d^{10} 6f^{14} & & \\
n=7 & 7s^2 7p^6 7d^{10} 7f^{14} & & \\
\end{array}
\]

Figure 1. Madelung’s Rule is a simple generalization which dictates in what order electrons should be filled in the orbitals, however there are exceptions such as copper and chromium.

This order of occupation roughly represents the increasing energy level of the orbitals. Hence, electrons occupy the orbitals in such a way that the energy is kept at a minimum. That is, the 7s, 5f, 6d, 7p subshells will not be filled with electrons unless the lower energy orbitals, 1s to 6p, are already fully occupied. Also, it is important to note that although the energy of the 3d orbital has been mathematically shown to be lower than that of the 4s orbital, electrons occupy the
4s orbital first before the 3d orbital. This observation can be ascribed to the fact that 3d electrons are more likely to be found closer to the nucleus; hence, they repel each other more strongly. Nonetheless, remembering the order of orbital energies, and hence assigning electrons to orbitals, can become rather easy when related to the periodic table.

To understand this principle, let's consider the bromine atom. Bromine (Z=35), which has 35 electrons, can be found in Period 4, Group VII of the periodic table. Since bromine has 7 valence electrons, the 4s orbital will be completely filled with 2 electrons, and the remaining five electrons will occupy the 4p orbital. Hence the full or expanded electronic configuration for bromine in accord with the Aufbau principle is 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^10 4p^5. If we add the exponents, we get a total of 35 electrons, confirming that our notation is correct.

**Hund's Rule**

Hund's Rule states that when electrons occupy degenerate orbitals (i.e. same n and l quantum numbers), they must first occupy the empty orbitals before double occupying them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all alpha electrons or all beta electrons). Nitrogen, for example, has 3 electrons occupying the 2p orbital. According to Hund's Rule, they must first occupy each of the three degenerate p orbitals, namely the 2px orbital, 2py orbital, and the 2pz orbital, and with parallel spins (Figure 2). The configuration below is incorrect because the third electron occupies does not occupy the empty 2pz orbital. Instead, it occupies the half-filled 2px orbital. This, therefore, is a violation of Hund's Rule (Figure 2).

![Figure 2](image)

**Pauli-Exclusion Principle**

Wolfgang Pauli postulated that each electron can be described with a unique set of four quantum numbers. Therefore, if two electrons occupy the same orbital, such as the 3s orbital, their spins must be paired. Although they have the same...
principal quantum number \((n=3)\), the same orbital angular momentum quantum number \((l=0)\), and the same magnetic quantum number \((m_l=0)\), they have different spin magnetic quantum numbers \((m_s=+1/2\) and \(m_s=-1/2)\).

**Electronic Configurations of Cations and Anions**

The way we designate electronic configurations for cations and anions is essentially similar to that for neutral atoms in their ground state. That is, we follow the three important rules: Aufbau's Principle, Pauli-exclusion principle, and Hund's Rule. The electronic configuration of cations is assigned by removing electrons first in the outermost p orbital, followed by the s orbital and finally the d orbitals (if any more electrons need to be removed). For instance, the ground state electronic configuration of calcium \((Z=20)\) is \(1s^22s^22p^63s^23p^6\). The calcium ion \((Ca^{2+})\), however, has two electrons less. Hence, the electron configuration for \(Ca^{2+}\) is \(1s^22s^22p^6\). Since we need to take away two electrons, we first remove electrons from the outermost shell \((n=4)\). In this case, all the 4p subshells are empty; hence, we start by removing from the s orbital, which is the 4s orbital. The electron configuration for \(Ca^{2+}\) is the same as that for Argon, which has 18 electrons. Hence, we can say that both are isoelectronic.

The electronic configuration of anions is assigned by adding electrons according to Aufbau's building up principle. We add electrons to fill the outermost orbital that is occupied, and then add more electrons to the next higher orbital. The neutral atom chlorine \((Z=17)\), for instance has 17 electrons. Therefore, its ground state electronic configuration can be written as \(1s^22s^22p^63s^23p^5\). The chloride ion \((Cl^-)\), on the other hand, has an additional electron for a total of 18 electrons. Following Aufbau's principle, the electron occupies the partially filled 3p subshell first, making the 3p orbital completely filled. The electronic configuration for \(Cl^-\) can, therefore, be designated as \(1s^22s^22p^63s^23p^6\). Again, the electron configuration for the chloride ion is the same as that for \(Ca^{2+}\) and Argon. Hence, they are all isoelectronic to each other.

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only paramagnetism, and diamagnetism are discussed here.

**Paramagnetism**

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. **Hund's Rule** states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, \(\text{O}_2\) is a good example of paramagnetism (that is best understood with molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:
As shown in Video 9.6.1, since molecular oxygen ($O_2$) is paramagnetic, it is attracted to the magnet. In contrast, molecular nitrogen, ($N_2$), has no unpaired electrons and it is diamagnetic (discussed below); it is therefore unaffected by the magnet.

**Note**

Paramagnetism is a form of magnetism whereby materials are attracted by an externally applied magnetic field.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include ($Sc^{3+}$), ($Ti^{4+}$), ($Zn^{2+}$), and ($Cu^{+}$). These metals are not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

**Diamagnetism**

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly repelled by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 9.6.1.
Diamagnetic materials are repelled by the applied magnetic field.

Diamagnetism, to a greater or lesser degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show some other form of magnetism (such paramagnetism), the diamagnetic contribution becomes negligible.

**How to tell if a substance is paramagnetic or diamagnetic**

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more electrons unpaired) or diamagnetic (all electrons paired)