Introduction

We previously discussed quantum theory along with atomic orbitals and their shapes. We're still missing some pieces of the puzzle, though. How do electrons in an atom actually occupy the atomic orbitals. How does this arrangement affect the properties of an atom and the ways atoms bond with each other?

We will now discuss how an atom's electrons are arranged in atomic orbitals. Knowing a bit about this will help us figure out how atoms bond.

The Pauli Exclusion Principle

We have described (and drawn) atomic orbitals. But how many electrons can an atomic orbital hold? The answer lies in the quantum numbers, specifically the **fourth** quantum number. The first three quantum numbers (the principal quantum number, the angular momentum quantum number, and the magnetic quantum number) select the atomic orbital. For example, let's look at a set of quantum numbers of an electron:

$$n = 2 \; ; \; l = 1 \; ; \; m_l = 0$$

What do these three quantum numbers tell us about this electron? We're told that the electron is in the second **energy level** (n = 2), that the electron is in one of the "p" orbitals ($l = 1$), and we're told the orientation of the "p" orbital the electron is in. But to specify the exact electron, we need the fourth quantum number- the **spin quantum number**. Recall that this quantum number can have only two values (+½ and -½) and that no two electrons in the same atom can have the same set of four quantum numbers. So, the orbital defined above can have at most two electrons. The observation that no two electrons in an atom can have the same four quantum numbers is called the **Pauli Exclusion Principle**.

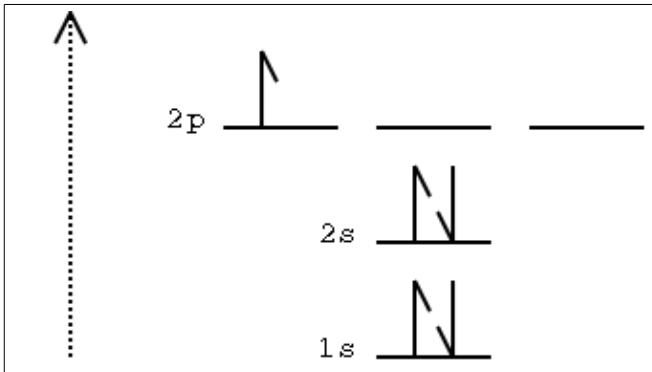
If you look at how many electrons a **subshell** can hold (subshells are represented by l values):

- For an "s" subshell, $l = 0$. This means that the only possible value for m_l is 0. m_s can have two values (as always), so the maximum number of electrons in an "s" subshell is **two**.
- For a "p" subshell, $l = 1$. This means that possible values for m_l are -1, 0, and 1. m_s can have two values, so the maximum number of electrons in a "p" subshell is **six** - two electrons for each possible value of m_l.
- For a "d" subshell, the maximum number of electrons is **ten**.
- For a "f" subshell, the maximum number of electrons is **fourteen**. See if you can verify these last two on your own.

Orbital diagrams

We represent the arrangement of electrons in an atom (the **electron configuration**) using

an **orbital diagram**, a picture that shows the arrangement by orbital. A sample orbital diagram for the boron atom is shown below. Boron has **five protons** and **five electrons**.



- Electrons are represented by arrows.
- The electron spin (the magnetic quantum number) is represented by the direction of the arrow, up or down.
- m_l is represented by the blanks (there are three blanks for the 2p subshell).
- Two electrons with the same spin can't be in the same orbital.
- The orbitals fill by energy - lower energy orbitals fill first.

Illustration 1 - Atomic orbital diagram for boron

A shorthand way to describe the arrangement of electrons (instead of drawing the diagram) is to just write the electron configuration using the subshell name with a superscript containing the number of electrons in the subshell. For example, we would write **boron**'s electron configuration as:

B: $1s^2 2s^2 2p^1$

As a further way to cut down the length of an electron configuration, we can use **noble gas core** notation. Atoms in **group VIIIA** on the periodic table are called **noble gases** (He, Ne, Ar, Kr, Xe, Rn). The electron configuration of **helium**, for example is:

He: $1s^2$

We can shorten the amount of writing we have to do by picking the noble gas with atomic number nearest **but not above** the atom we're writing about and writing it in brackets. So, we could write boron's electron configuration as

B: $[He]2s^2 2p^1$

For boron, this doesn't shorten things much, but for a large atom like cesium (with 55 electrons), this reduces the amount we have to write considerably!

<u>The valence electrons</u>

Why would we want to shorten the electron configuration using the **noble gas core** notation? Aren't those electrons we're omitting important?

To us, the most important electrons in the atom are the electrons in the **outer shell** (the highest value of n). These electrons are commonly called the **valence electrons**, and they are the electrons that usually participate in chemical reactions.

Why are these the electrons that react? The simple answer is that they're the ones on the outside of the atom. When two atoms come together, the electrons that see each other first are the valence electrons- the ones on the outside.

So, boron's valence electrons are the two electrons in its "2s" orbital and the electron in the "2p" orbitals. ($2s^2 2p^1$). The two electrons in boron's 1s orbital ($1s^2$) are buried too deep inside the atom to react.

Writing electron configurations of atoms - the periodic table

You might be wondering at this point how you write an electron configuration - how to determine the order that orbitals fill up in. We said when talking about orbital diagrams the orbitals fill up from lowest energy to highest energy. You can probably see a pattern to this already - lower "n" orbitals generally fill up before higher "n" orbitals - because they have **lower energy** than the higher orbitals. "s" orbitals generally fill up before "p" orbitals, which fill up before "d" orbitals, etc.

In fact, if you have a periodic table handy, it's very easy to write an electron configuration. Elements are arranged on the periodic table in groups which have similar electron configurations. This is illustrated on the exploded periodic table below.

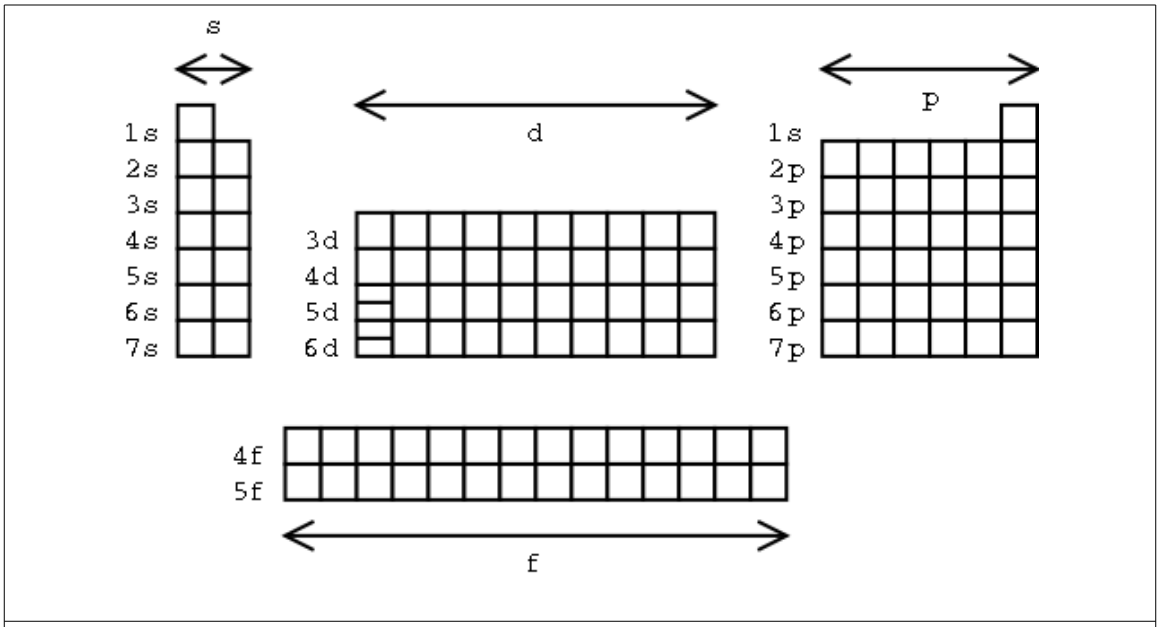


Illustration 2 - The "blocks" of the periodic table

A few notes on this diagram:

- An element's position on the table indicates the last subshell being filled with electrons.
- The "s block" is two elements wide, the "p block" is six elements wide, the "d block" is ten elements wide, and the "f block" is 14 elements wide. Where have you seen these numbers before?
- Helium. On most periodic tables, it's written at the far right of the periodic table with the other noble gases. Its electron configuration is $1s^2$, **not** $1s^1 1p^1$ (which isn't allowed by quantum mechanics).
- The **d** and **f** subshells are particularly energetic - more so than nearby **s** subshells with higher values of n! (For example, **3d** fills only after **4s** does.)
- The "f block" elements at the bottom of the table are inserted after the two elements with the extra lines in the "d block".

So, let's look at a few electron configurations:

Mg: **$1s^2 2s^2 2p^6 3s^2$** OR **[Ne]$3s^2$**

- You can trace down the periodic table with your finger to write this - start with element 1 (hydrogen) and go across each element, adding electrons to your configuration until you get to **your** element.
- The **ideal gas core** notation shows the valence electrons clearly in this example.

Fe: **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$** OR **[Ar]$4s^2 3d^6$**

- The "4s" subshell fills before the "3d". This is because "d" orbitals have a high energy and the "3d" orbitals actually have a slightly higher energy than the "4s" orbitals. The "3d" electrons are not considered valence electrons, though they do play a role in some of iron's more interesting chemical reactions.

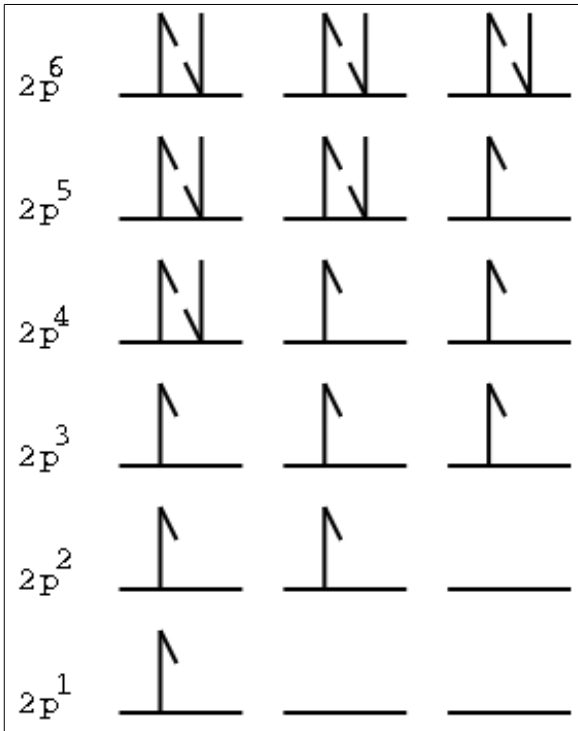
There are a few exceptions to our way to generate electron configurations from the periodic table, mainly in the transition metals, but we'll not concern ourselves much with them. They relate to the observation that filled and half-filled subshells are more stable (lower energy) than other states and are mainly found in a few of the "d block" and "f block" elements.

<u>Electron configurations, Hund's rule, and magnetism</u>

We've discussed the order in which the **subshells** fill up - but we need to talk a bit about the order in which the **orbitals** fill. There are **three** "p" orbitals within any "p" subshell, **five** "d" orbitals in any "d" subshell, etc. How do these orbitals fill up, and is there any evidence that these orbitals fill up in the way we say they do?

This question is answered by Hund's rule - which says that the lowest-energy arrangement of electrons in a subshell is obtained by filling orbitals with electrons of the same spin **before** pairing.

So, the "p" orbitals fill up like this:



- No pairing occurs until the fourth electron is put into the subshell.
- Support from Hund's rule comes from observations on the magnetic properties of the atoms.

Illustration 3 - Hund's rule

There is experimental evidence for Hund's rule. Spinning electrons are magnetic, but opposite spins cancel. So, Hund's rule predicts which elements are magnetic (those having unpaired electrons). Elements with unpaired electrons are **paramagnetic** - that is, they're attracted to a weak magnetic field. Atoms with **no** unpaired electrons are **diamagnetic** - they don't interact at all or they're repelled by the field. Elements predicted by Hund's rule to be paramagnetic have been experimentally found to be paramagnetic. *[Paramagnetism isn't the same thing as the magnetism you may have been exposed to in an introductory physics course - like from an iron magnet. Paramagnetism is a much weaker effect and is not limited to certain metals.]*

Summary

This note pack discussed electron configurations - you learned to write electron configurations for atoms using both the rule of electrons filling orbitals from lowest to highest or from using the "blocks" of the periodic table. Next, we'll talk more about the periodic table and take a brief tour of properties predicted by an element's electron configuration.