

## 12.10: Electron Spin and the Pauli Principle

Electron Spin or Spin Quantum Number is the fourth quantum number for electrons in atoms and molecules. Denoted as  $m_s$ , the electron spin is constituted by either upward ( $m_s = +1/2$ ) or downward ( $m_s = -1/2$ ) arrows.

### Introduction

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by  $m_s$ . In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might be explained by assuming electrons act as if it has a spin. This spin can be denoted by an arrow pointing up, which is  $+1/2$ , or an arrow pointing down, which is  $-1/2$ .

The experiment mentioned above by Otto Stern and Walter Gerlach was done with silver which was put in an oven and vaporized. The result was that silver atoms formed a beam that passed through a magnetic field in which it split in two.

An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the one unpaired electron in the atom will determine the spin. There is a high likelihood for either spin due to the large number of electrons, so when it went through the magnetic field it split into two beams.

### Brief Explanation of Quantum Numbers

**Note: In this module, capital "L" will be used instead of small case "l" for angular momentum quantum number.**

A total of four quantum numbers were developed to better understand the movement and pathway of electrons in its designated orbital within an atom.

1. Principal quantum number ( $n$ ): energy level  $n = 1, 2, 3, 4, \dots$
2. Orbital Angular Momentum Quantum Number ( $L$ ): shape (of orbital)  $L = 0, 1, 2, 3, \dots n-1$
3. Magnetic Quantum Number ( $m_L$ ): orientation  $m_L =$  interval of  $(-L, +L)$
4. **Electron Spin Quantum Number** ( $m_s$ ): independent of other three quantum numbers because  $m_s$  is always  $= -1/2$  or  $+1/2$

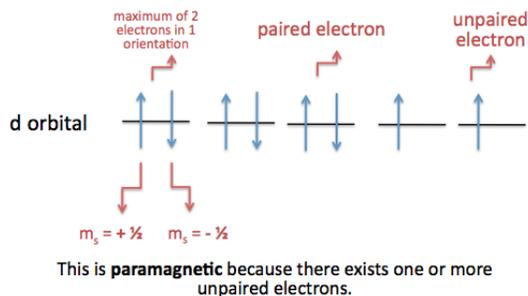
(For more information about the three quantum numbers above, see [Quantum Number](#).)

<p>s orbital </p> <p>p orbital _____</p> <p>d orbital _____</p> <p>f orbital _____</p>	<p>The lines represent how many orientations each orbital has, (e.g. the s-orbital has one orientation, a p-orbital has three orientations, etc.) and each line can hold up to two electrons, represented by up and down arrows. An electron with an up arrow means it has an electron spin of <math>+1/2</math>, and an electron with a down arrow means it has an electron spin of <math>-1/2</math>.</p> <p style="text-align: center;"><a href="#">Electron Spin</a></p>
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Significance: determines if an atom will or will not generate a magnetic field (For more information, scroll down to *Magnetic Spin, Magnetism, and Magnetic Field Lines*). Although the electron spin is limited to  $+1/2$  or  $-1/2$ , certain rules apply when assigning electrons of different spins to fill a subshell (orientations of an orbital). For more information, scroll down to *Assigning Spin Direction*.

### Magnetic Spin, Magnetism, and Magnetic Field Lines

Example :



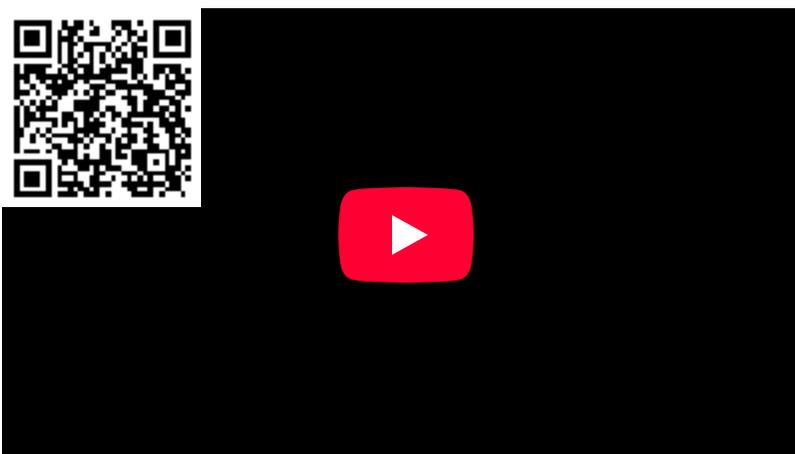
An atom with **unpaired** electrons are termed as **paramagnetic**

- results in a **net** magnetic field because electrons within the orbital are not stabilized or balanced enough
- atoms are attracted to magnets

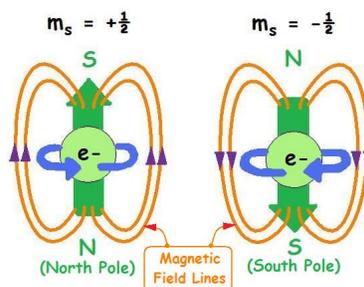
An atom with **paired** electrons are termed as **diamagnetic**

- results in **no** magnetic field because electrons are uniform and stabilized within the orbital
- atoms are not attracted to magnets

Applying concepts of magnetism with liquid nitrogen and liquid oxygen:



The magnetic spin of an electron follows in the direction of the magnetic field lines as shown below.



{{media("www.youtube.com/watch?v=uj0DFDfQajw")}}

### Assigning Spin Direction

An effective visual on how to assign spin directions can be represented by the orbital diagram (shown previously and below.) Restrictions apply when assigning spin directions to electrons, so the following Pauli Exclusion Principle and Hund's Rule help explain this. The direction of the electron spin **magnetic quantum number,  $m_s$** , can only be determined its interaction with a

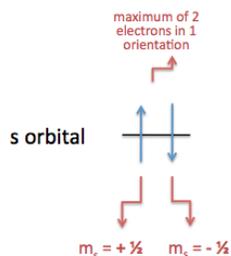
magnetic field. Electrons whose spin is parallel to an external magnetic field (spin up with  $+\frac{1}{2}$  spin) have a lower energy than those whose magnetic spin is anti-parallel (spin down with  $-\frac{1}{2}$  spin) to the external magnetic and fill first.

When one is filling an orbital, such as the p orbital, you must fill all orbitals possible with spin up electrons before assigning the opposite spin. For example, when filling the fluorine, which will have a total of two electrons in the s orbital and a total of five electrons in the p orbital, one will start with the s orbital which will contain two electrons. So, the first electron one assigns will be spin up and the next spin down. Moving on to the three p orbitals that one will start by assigning a spin up electron in each of the three orbitals. That takes up three of the five electrons, so with the remaining two electrons, one returns to the first and second p orbital and assigns the spin down electron. This means there will be one unpaired electron in fluorine so it will be paramagnetic.

## Pauli Exclusion Principle

The **Pauli exclusion principle** declares that there can only be a maximum of two electrons for every one orientation, and the two electrons must be opposite in spin direction; meaning one electron has  $m_s = +\frac{1}{2}$  and the other electron has  $m_s = -\frac{1}{2}$ .

Example:

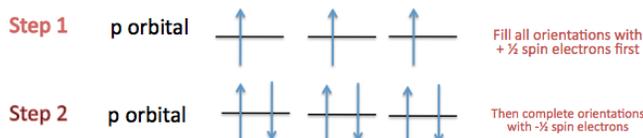


## Hund's Rule

**Hund's Rule** declares that the electrons in the orbital are filled up first by electrons whose spins are parallel to each other. Once all the orbitals are filled with unpaired  $+\frac{1}{2}$  spins, the orbitals are then filled with  $-\frac{1}{2}$  spin. (See examples below, labeled **electronic configuration**.)

Example of **Hund's Rule**:

p orbital with 6 electrons



(For more information on Pauli Exclusion Principle and Hund's Rules, see [Electronic Configuration](#).)

## Identifying Spin Direction

1. Determine the number of electrons the atom has.
2. Draw the electron configuration for the atom. See [Electronic Configurations](#) for more information.
3. Distribute the electrons, using up and down arrows to represent the electron spin direction.

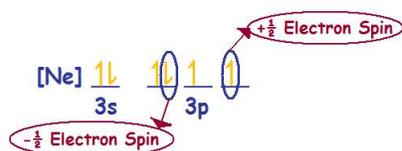
### ✓ Example 1: Sulfur

Sulfur - S (16 electrons)

Electronic Configuration:



As shown in the following image, this is a demonstration of a  $-\frac{1}{2}$  and a  $+\frac{1}{2}$  Electron Spin.



## Principal Quantum Number & (s, p, d, f) Orbitals

When given a principal quantum number,  $n$ , with either the s, p, d or f-orbital, identify all the possibilities of  $L$ ,  $m_L$  and  $m_s$ .

### ✓ Example 2

Given 5f, identify all the possibilities of the four quantum numbers.

#### Solution

In this problem, the principal quantum number is  $n = 5$  (the subshell number placed in front of the orbital, the f-orbital in this case). Since we are looking at the f-orbital, therefore  $L = 3$ . (Look under "Subshells" in the module [Quantum Numbers](#) for more information) Knowing  $L = 3$ , we can interpret that  $m_L = 0, \pm 1, \pm 2, \pm 3$  since  $m_L = -L, \dots, -1, 0, 1, \dots, +L$ . As for  $m_s$ , since it isn't specified in the problem as to whether it is  $-\frac{1}{2}$  or  $+\frac{1}{2}$ , therefore for this problem, it could be both; meaning that the electron spin quantum number is  $\pm \frac{1}{2}$ .

### ✓ Example 3

Given 6s and  $m_L = +1$ , identify all the possibilities of the four quantum numbers.

#### Solution

The principal quantum number is  $n = 6$ . Looking at the s-orbital, we know that  $L = 0$ . Knowing that  $m_L = -L, \dots, -1, 0, 1, \dots, +L$ , therefore  $m_L = +1$  is **not possible** since in this problem, the interval of  $m_L$  can only equal to 0 according to the angular momentum quantum number,  $L$ .

### ✓ Example 4

Given 4d and  $m_s = +\frac{1}{2}$ , identify all the possibilities of the four quantum numbers.

#### Solution

The principal quantum number is  $n = 4$ . Given that it is a d-orbital, we know that  $L = 2$ . Therefore,  $m_L = 0, \pm 1, \pm 2$  since  $m_L = -L, \dots, -1, 0, 1, \dots, +L$ . For  $m_s$ , this problem specifically said  $m_s = +\frac{1}{2}$ ; meaning that the electron spin quantum number is  $+\frac{1}{2}$ .

### Electron Spin: Where to begin?

First, draw a table labeled  $n$ ,  $L$ ,  $m_L$  and  $m_s$ , as shown below:

$n$	$L$	$m_L$	$m_s$

Then, depending on what the question is asking for, fill in the boxes accordingly. Finally, determine the number of electrons for the given quantum number,  $n$ , with regards to  $L$ ,  $m_L$  and  $m_s$ .

### ✓ Example 5

How many electrons can have  $n = 5$  and  $L = 1$ ? **6**

$n$	$L$	$m_L$	$m_s$
5	1	-1	$-\frac{1}{2}, +\frac{1}{2}$
		0	$-\frac{1}{2}, +\frac{1}{2}$

+1

$-\frac{1}{2}, +\frac{1}{2}$

This problem includes both  $-\frac{1}{2}, +\frac{1}{2}$ , therefore the answer is **6** electrons based on the three possible values of  $m_L$ .

### ✓ Example 6

How many electrons can have  $n = 5$  and  $m_s = -\frac{1}{2}$ ? **9**

n	L	$m_L$	$m_s$
5	4	$\pm 4$	$-\frac{1}{2}$
	3	$\pm 3$	$-\frac{1}{2}$
	2	$\pm 2$	$-\frac{1}{2}$
	1	$\pm 1$	$-\frac{1}{2}$
	0	0	$-\frac{1}{2}$

This problem only wants the Spin Quantum Number to be  $-\frac{1}{2}$ , the answer is **9** electrons based on the 9 different values of  $m_L$ .

### ✓ Example 7

How many electrons can have  $n = 3, L = 2$  and  $m_L = 3$ ? **zero**

#### Solution

n	L	$m_L$	$m_s$
3	2	NOT POSSIBLE	

Since  $m_L = -L \dots -1, 0, +1 \dots +L$  (See [Electronic Orbitals](#) for more information),  $m_L$  is not possible because  $L = 2$ , so it is impossible for  $m_L$  to be equal to 3. So, there is **zero** electrons.

### ✓ Example 8

How many electrons can have  $n = 3, m_L = +2$  and  $m_s = +\frac{1}{2}$ ? **1**

#### Solution

n	L	$m_L$	$m_s$
3	2	+2	$+\frac{1}{2}$

This problem only wants the Spin Quantum Number to be  $+\frac{1}{2}$ , the answer is **1** electron based on the value of  $m_L$  and  $m_s$ .

## References

- Petrucci, Ralph. Harwood, William. Herring, Geoffrey. Madura, Jeffery. *General Chemistry: Principles and Modern Applications, 9th Edition*. Pearson Education, Inc. New Jersey, 2007.
- Li, Gengyun. *What is the Electron Spin?* Spin Publishing, 2003.
- Motz, Lloyd and Weaver, Jefferson H. *The Unfolding Universe: A Stellar Journey*. Perseus, 1989.

## Practice Problems

- Identify the spin direction (e.g.  $m_s = -\frac{1}{2}$  or  $+\frac{1}{2}$  or  $\pm\frac{1}{2}$ ) of the outermost electron in a Sodium (Na) atom.
- Identify the spin direction of the outermost electron in a Chlorine (Cl) atom.
- Identify the spin direction of the outermost electron in a Calcium (Ca) atom.
- Given 5p and  $m_s = +\frac{1}{2}$ , identify all the possibilities of the four quantum numbers.

- Given 6f, identify all the possibilities of the four quantum numbers.
- How many electrons can have  $n = 4$  and  $L = 1$ ?
- How many electrons can have  $n = 4$ ,  $L = 1$ ,  $m_L = -2$  and  $m_s = +\frac{1}{2}$ ?
- How many electrons can have  $n = 5$ ,  $L = 3$ ,  $m_L = \pm 2$  and  $m_s = +\frac{1}{2}$ ?
- How many electrons can have  $n = 5$ ,  $L = 4$ ,  $m_L = +3$  and  $m_s = -\frac{1}{2}$ ?
- How many electrons can have  $n = 4$ ,  $L = 2$ ,  $m_L = \pm 1$  and  $m_s = -\frac{1}{2}$ ?
- How many electrons can have  $n = 3$ ,  $L = 3$ ,  $m_L = +2$ ?

**Solutions: Check your work!**

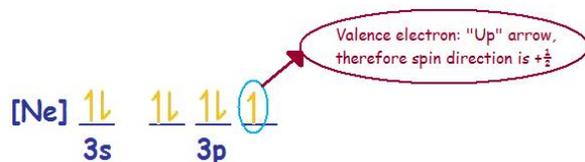
**Problem (1):** Sodium (Na) --> Electronic Configuration [Ne] 3s<sup>1</sup>



Spin direction for the valence electron or  $m_s = +\frac{1}{2}$

Sodium (Na) with a neutral charge of zero is paramagnetic, meaning that the electronic configuration for Na consists of one or more unpaired electrons.

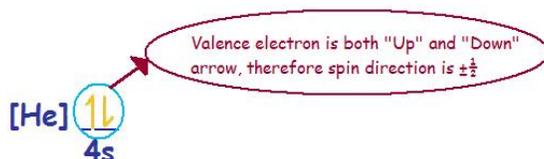
**Problem (2):** Chlorine (Cl) --> Electronic Configuration [Ne] 3s<sup>2</sup> 3p<sup>5</sup>



Spin direction for the valence electron or  $m_s = +\frac{1}{2}$

Chlorine (Cl) with a neutral charge of zero is paramagnetic.

**Problem (3):** Calcium (Ca) --> Electronic Configuration [He] 4s<sup>2</sup>



Spin direction for the valence electron or  $m_s = \pm\frac{1}{2}$

Whereas for Calcium (Ca) with a neutral charge of zero, it is diamagnetic; meaning that ALL the electrons are paired as shown in the image above.

**Problem (4):** Given 5p and  $m_s = -\frac{1}{2}$ , identify all the possibilities of the four quantum numbers.

The principal quantum number is  $n = 5$ . Given that it is a p-orbital, we know that  $L = 1$ . And based on  $L$ ,  $m_L = 0, \pm 1$  since  $m_L = -L, \dots, -1, 0, 1, \dots, +L$ . As for  $m_s$ , this problem specifically says  $m_s = -\frac{1}{2}$ , meaning that the spin direction is  $-\frac{1}{2}$ , pointing downwards ("down" spin).

**Problem (5):** Given 6f, identify all the possibilities of the four quantum numbers.

The principal quantum number is  $n = 6$ . Given that it is a f-orbital, we know that  $L = 3$ . Based on  $L$ ,  $m_L = 0, \pm 1, \pm 2, \pm 3$  since  $m_L = -L, \dots, -1, 0, 1, \dots, +L$ . As for  $m_s$ , since it isn't specified in the problem as to whether it is  $-\frac{1}{2}$  or  $+\frac{1}{2}$ , therefore for this problem, it could be both; meaning that the electron spin quantum number is  $\pm\frac{1}{2}$ .

**Problem (6):** How many electrons can have  $n = 4$  and  $L = 1$ ? 6

n	L	$m_L$	$m_s$
4	1	$\pm 1$	$-\frac{1}{2}, +\frac{1}{2}$
		0	

This problem includes both  $-\frac{1}{2}, +\frac{1}{2}$ , therefore the answer is **6** electrons based on the  $m_L$ .

**Problem (7):** How many electrons can have  $n = 4, L = 1, m_L = -2$  and  $m_s = +\frac{1}{2}$ ? zero

n	L	$m_L$	$m_s$
4	1	NOT POSSIBLE	$+\frac{1}{2}$

Since  $m_L = -L \dots -1, 0, +1 \dots +L$ ,  $m_L$  is not possible because  $L = 1$ , so it is impossible for  $m_L$  to be equal to 2 when  $m_L$  MUST be with the interval of  $-L$  and  $+L$ . So, there is zero electron.

**Problem (8):** How many electrons can have  $n = 5, L = 3, m_L = \pm 2$  and  $m_s = +\frac{1}{2}$ ? 2

n	L	$m_L$	$m_s$
5	3	$\pm 2$	$+\frac{1}{2}$
		$\pm 1$	
		0	

This problem only wants the Spin Quantum Number to be  $+\frac{1}{2}$  and  $m_L = \pm 2$ , therefore 2 electrons can have  $n = 5, L = 3, m_L = \pm 2$  and  $m_s = +\frac{1}{2}$ .

**Problem (9):** How many electrons can have  $n = 5, L = 4$  and  $m_L = +3$ ? 2

n	L	$m_L$	$m_s$
5	4	$-3, +3$	$-\frac{1}{2}, +\frac{1}{2}$
		$\pm 2$	
		$\pm 1$	
		0	

This problem includes both  $-\frac{1}{2}$  and  $+\frac{1}{2}$  and given that  $m_L = +3$ , therefore the answer is 2 electrons.

**Problem (10):** How many electrons can have  $n = 4, L = 2$  and  $m_L = \pm 1$ ? 4

n	L	$m_L$	$m_s$
4	2	$\pm 1$	$-\frac{1}{2}, +\frac{1}{2}$
		0	

This problem includes both  $-\frac{1}{2}$  and  $+\frac{1}{2}$  and given that  $m_L = \pm 1$ , therefore the answer is 4 electrons.

**Problem (11):** How many electrons can have  $n = 3, L = 3, m_L = +2$  and  $m_s = -\frac{1}{2}$ ? zero

n	L	$m_L$	$m_s$
3	3 (NOT POSSIBLE)	$\pm 2$	$-\frac{1}{2}$
		$\pm 1$	
		0	

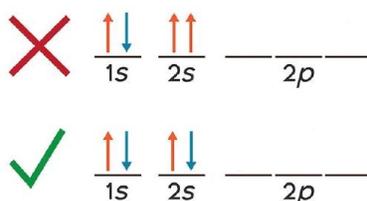
Since  $L = n - 1$ , there is **zero** electron, not possible because in this problem,  $n = L = 3$ .

## Contributors and Attributions

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The **Pauli Exclusion Principle** states that, in an atom or molecule, no two electrons can have the **same** four electronic quantum numbers. As an orbital can contain a maximum of only two electrons, the two electrons must have opposing spins. This means if one electron is assigned as a spin up (+1/2) electron, the other electron must be spin-down (-1/2) electron.

Electrons in the same orbital have the same first three quantum numbers, e.g.,  $n = 1, l = 0, m_l = 0$  for the 1s subshell. Only two electrons can have these numbers, so that their spin moments must be either  $m_s = -1/2$  or  $m_s = +1/2$ . If the 1s orbital contains only one electron, we have one  $m_s$  value and the electron configuration is written as  $1s^1$  (corresponding to hydrogen). If it is fully occupied, we have two  $m_s$  values, and the electron configuration is  $1s^2$  (corresponding to helium). Visually these two cases can be represented as



As you can see, the 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, the electrons must have opposite spins. Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Aufbau section discussed how electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there is a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of  $n$ , and thus a lower energy. What about filling the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule.

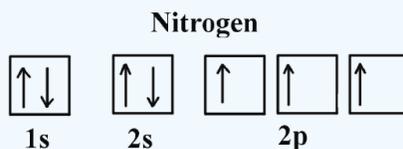
Hund's rule states that:

1. Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.
2. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin).

When assigning electrons to orbitals, an electron first seeks to fill all the orbitals with similar energy (also referred to as degenerate orbitals) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. In visualizing this process, consider how electrons exhibit the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals, they first try to get as far as possible from each other before having to pair up.

### ✓ Example 12.10.1: Nitrogen Atoms

Consider the correct electron configuration of the nitrogen ( $Z = 7$ ) atom:  $1s^2 2s^2 2p^3$

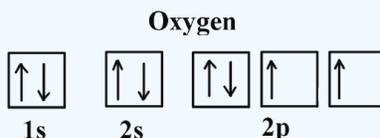


The p orbitals are half-filled; there are three electrons and three p orbitals. This is because the three electrons in the 2p subshell will fill all the empty orbitals first before pairing with electrons in them.

Keep in mind that elemental nitrogen is found in nature typically as molecular nitrogen,  $N_2$ , which requires molecular orbitals instead of atomic orbitals as demonstrated above.

### ✓ Example 12.10.2: Oxygen Atoms

Next, consider oxygen ( $Z = 8$ ) atom, the element after nitrogen in the same period; its electron configuration is:  $1s^2 2s^2 2p^4$



Oxygen has one more electron than nitrogen; as the orbitals are all half-filled, the new electron must pair up. Keep in mind that elemental oxygen is found in nature typically as molecular oxygen,  $O_2$ , which has molecular orbitals instead of atomic orbitals as demonstrated above.

### Hund's Rule Explained

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus. Electron shielding is further discussed in the next section.

For the second rule, unpaired electrons in singly occupied orbitals have the same spins. Technically speaking, the first electron in a sublevel could be either "spin-up" or "spin-down." Once the spin of the first electron in a sublevel is chosen, however, the spins of all of the other electrons in that sublevel depend on that first spin. To avoid confusion, scientists typically draw the first electron, and any other unpaired electron, in an orbital as "spin-up."

### ✓ Example 12.10.3: Carbon and Oxygen

Consider the electron configuration for carbon atoms:  $1s^2 2s^2 2p^2$ : The two 2s electrons will occupy the same orbital, whereas the two 2p electrons will be in different orbital (and aligned the same direction) in accordance with Hund's rule.

Consider also the electron configuration of oxygen. Oxygen has 8 electrons. The electron configuration can be written as  $1s^2 2s^2 2p^4$ . To draw the orbital diagram, begin with the following observations: the first two electrons will pair up in the 1s orbital; the next two electrons will pair up in the 2s orbital. That leaves 4 electrons, which must be placed in the 2p orbitals. According to Hund's rule, all orbitals will be singly occupied before any is doubly occupied. Therefore, two p orbital get one electron and one will have two electrons. Hund's rule also stipulates that all of the unpaired electrons must have the same spin. In keeping with convention, the unpaired electrons are drawn as "spin-up", which gives (Figure 1).

### Purpose of Electron Configurations

When atoms come into contact with one another, it is the outermost electrons of these atoms, or valence shell, that will interact first. An atom is least stable (and therefore most reactive) when its valence shell is not full. The valence electrons are largely responsible for an element's chemical behavior. Elements that have the same number of valence electrons often have similar chemical properties.

Electron configurations can also predict stability. An atom is most stable (and therefore unreactive) when all its orbitals are full. The most stable configurations are the ones that have full energy levels. These configurations occur in the noble gases. The noble gases are very stable elements that do not react easily with any other elements. Electron configurations can assist in making predictions about the ways in which certain elements will react, and the chemical compounds or molecules that different elements will form.

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