

## 5.4 Applying Quantum Mechanics to Electrons in Atoms

### Warm Up

1. What part of Bohr's theory remains as part of the quantum mechanical view of the atom?  
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2. Quantum mechanics replaces the concept of an electron orbit with an orbital. What is an electron orbital?  
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3. The laws of probability are a necessary part of describing electron behaviour. Why?  
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### Starting with Hydrogen — One on One

In this section, we will apply the quantum mechanical model of the atom to describing electrons in the atoms of the elements. We will begin with hydrogen and then use that information to expand our discussion to include multi-electron atoms.

In section 5.3, the analogy of a guitar string helped to explain the requirement of standing waves for the allowed energy states of electrons in atoms. If we solve Schrödinger's wave equation for the allowed energy states for hydrogen, we see that each energy state results in different numbers and types of orbitals. The equation shows us that the higher the energy, the greater the number and types of orbitals present.

### Quantum Numbers

In an atom, these three-dimensional electron waves or orbitals are more complicated than a standing wave on a guitar string. To describe them, quantum mechanics employs the use of special numbers called **quantum numbers**. Each quantum number specifies something different about the orbitals and electrons. We will discuss these numbers as we investigate the orbitals associated with each of allowed energy states for hydrogen.

#### The Principal Quantum Number ( $n$ )

The first quantum number is called the **principal quantum number** ( $n$ ). It indicates the relative size of the atomic orbital.

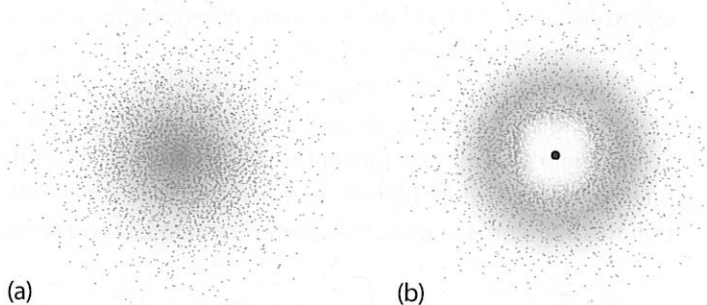
We have already been introduced to this number because it also represents the allowed energy states for the electron. We know that the value of  $n$  can be a positive integer (1, 2, 3, and so on).

When hydrogen's electron is in the lowest allowed energy state or ground state, then  $n = 1$ . Schrödinger's equation shows us where an electron possessing that amount of energy will most likely be found. When we represent this pictorially, we see an electron "probability density diagram" resembling a spherical cloud. The cloud is what you might see if you could take many snapshots of the hydrogen electron around the nucleus and then superimpose all of them onto one picture. At the centre of this cloud is the hydrogen nucleus. The cloud's density is not uniform throughout, but is greater near the nucleus.

and decreases as we move away. This tells us that the probability of locating the electron is higher closer to the nucleus and lower further away from the nucleus.

As we move out from the nucleus, we find that hydrogen's electron in its ground state is likely to spend most of its time a slight distance from the nucleus, rather than at the nucleus itself. This is called the "radial probability." It's interesting to note that the electron's distance from the nucleus to the region of highest probability corresponds exactly to the orbit for this electron that Bohr calculated. Remember, however, that Bohr assumed the electron followed a circular path and would always be found at that distance from the nucleus. Quantum mechanics describes this as the most probable distance from the nucleus for the electron.

When we enclose the cloud in a volume representing about a 90% probability of finding the electron, we call this the 1s orbital. The number "1" represents the principal quantum number, telling us the size of the orbital, and the letter "s" refers to the type or "shape" of the orbital. Figure 5.4.1(a) shows an artistic representation of what a spherical 1s orbital might look like if viewed from the outside. Figure 5.4.1(b) is a cross-sectional view showing radial probability (indicated by greater dot density a slight distance from nucleus).



**Figure 5.4.1** (a) A view of a spherical 1s orbital from the outside; (b) A cross-sectional view of a spherical 1s orbital

## The Second Quantum Number ( $\ell$ )

The second quantum number is called the **angular momentum quantum number** ( $\ell$ ). It is related to the shape of an atomic orbital.

The different values of  $\ell$  at each energy level represent the number of orbital shapes or sublevels that exist in that energy level. That number equals the energy level itself. So for  $n = 1$ , there is only one orbital type or shape, namely the s orbital.

Each new energy level has one new orbital shape in addition to those existing in the previous level. So if hydrogen's electron is "excited" and absorbs enough energy to reach the second allowed energy state, then  $n = 2$  and two orbital shapes or sublevels exist. There is an s orbital with a shape identical to the 1s, except larger, called the 2s orbital. This means that the electron with this greater amount of energy will spend more of its time farther from the nucleus. There is also a new shape: a p orbital. As  $n = 2$ , we call it a 2p orbital and it resembles a dumbbell or long balloon pinched in the middle (where the nucleus is located).

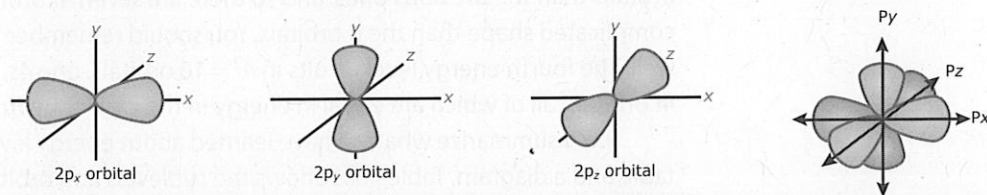
## The Third Quantum Number ( $m_\ell$ )

The third quantum number, called the **magnetic quantum number** ( $m_\ell$ ) tells us the orientation in space of a given atomic orbital.

The number of possible different orientations in space for any orbital shape also represents the number of individual orbitals of that particular shape or sublevel.

Only a single  $s$  orbital exists in any given energy level because a spherical cloud can only have one orientation in 3D space. However, this new  $p$  sublevel includes three separate orbitals, each with a different spatial orientation. If we consider a 3D set of Cartesian coordinates, one is oriented along an imaginary  $x$ -axis (with the nucleus at the origin) called a  $2p_x$  orbital. The other two are oriented along the  $y$ - and  $z$ -axes and are called the  $2p_y$  and  $2p_z$  orbitals respectively. Each of these  $2p$  orbitals is identical in energy to the others. For hydrogen, they are also identical in energy to the  $2s$  orbital. Chemists call orbitals of equal energy "degenerate" orbitals.

In Figure 5.4.2, note that the lobes of each  $p$  orbital in the first three diagrams disappear at the origin where the nucleus is located. This means that the amplitude of the electron wave at the nucleus is zero. A wave amplitude of zero is called a node, and it tells us that there is a zero probability of locating the electron here. In the far left diagram in Figure 5.4.2, all three  $2p$  orbitals are shown together. Once again, the nucleus is at the centre or origin.



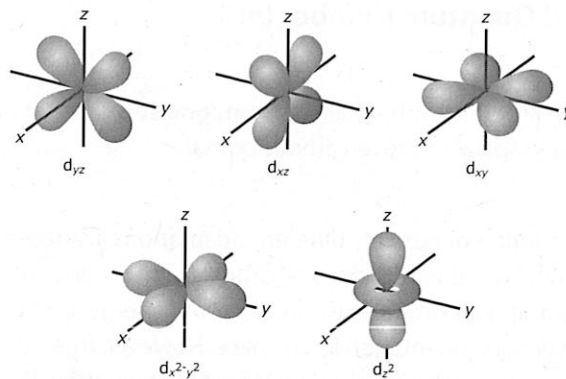
**Figure 5.4.2** The  $p$  orbitals are each shown individually in the first three diagrams. The last diagram shows them all together.

We noted earlier that the number of different sublevels in any energy level equals the value of  $n$ . We also see here that a total of four orbitals exists in the second energy level. So the value  $n^2$  tells us the number of orbitals existing in the  $n^{\text{th}}$  energy level. In this case, there are  $2^2 = 4$  orbitals: one  $2s$  and three  $2p$  orbitals.

The three quantum numbers, taken together, will always specify a particular atomic orbital because they tell us all we need to know about that orbital: its size, shape, and orientation in space.

If hydrogen's electron absorbs enough energy to reach the third allowed energy state, then  $n = 3$  and three different orbital shapes or sublevels exist. As expected, we see one spherical  $3s$  orbital and three dumbbell-shaped  $3p$  orbitals. But we also discover a third sublevel whose orbitals have a more complicated shape. This is called the  $3d$  sublevel and it contains five different orbitals, each with a different spatial orientation. Orbitals in a given sublevel are equal in energy to each other, and in hydrogen's case, are also equal in energy to all of the other orbitals in the energy level. This means that in a given energy level, hydrogen's electron has an equal likelihood of occupying any of them.

Although the  $d$  orbitals are shown in Figure 5.4.3, you may not be required to remember either their shapes or their names. You should, however, know that there are five of them.



**Figure 5.4.3** The d orbitals

Notice that as  $n = 3$ , there are three sublevels: 3s, 3p, and 3d. Also, there are a total of nine orbitals: one 3s orbital, three 3p orbitals, and five 3d orbitals corresponding to  $3^2$ .

Finally, let's elevate hydrogen's electron to the fourth energy level, where  $n = 4$ . A higher energy level means that the electron will spend more of its time farther from the nucleus than when it possesses energy equal to  $n = 1, 2$ , or 3. Therefore, the orbitals or "charge clouds" are larger.

In the fourth energy level, we see the expected 4s, three 4p, and five 4d orbitals. As well, because  $n = 4$ , we also see a fourth shape called the 4f sublevel. Each higher energy level introduces another sublevel with a greater number (by two) of more complicated orbitals than the previous ones, and so there are seven 4f orbitals, each with a more complicated shape than the d orbitals. You should remember the number of f orbitals as well. The fourth energy level results in  $4^2 = 16$  orbitals: one 4s, three 4p, five 4d, and seven 4f orbitals, all of which are equal in energy in the case of hydrogen.

Let's summarize what we have learned about energy levels and orbitals using a table and a diagram. Table 5.4.1 shows the sublevels and orbitals for the first four energy levels. Figure 5.4.4 is the energy diagram for hydrogen showing the sublevels and orbitals present from  $n = 1$  through  $n = 4$ . Each circle represents an orbital. Note that all the sublevels are of equal energy in each allowed energy state.

**Table 5.4.1** Sublevels and orbitals for the first four energy levels

Principal Quantum Number or Energy Level ( $n$ )	Number of Orbital Shapes or Sublevels per Energy Level ( $n$ )	Total Number of Orbitals per Energy Level ( $n^2$ )
1	1 – 1s sublevel	1 – the 1s orbital
2	2 – 2s sublevel 2p sublevel	4 – one 2s orbital three 2p orbitals
3	3 – 3s sublevel 3p sublevel 3d sublevel	9 – one 3s orbital three 3p orbitals five 3d orbitals
4	4 – 4s sublevel 4p sublevel 4d sublevel 4f sublevel	16 – one 4s orbital three 4p orbitals five 4d orbitals seven 4f orbitals

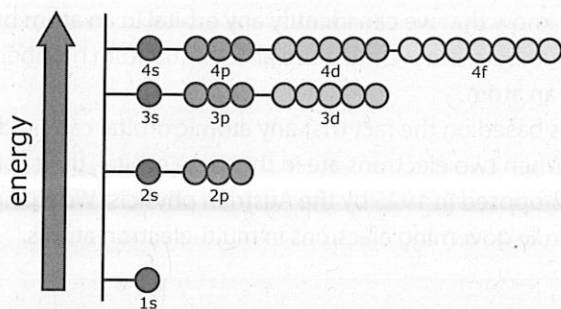


Figure 5.4.4 Energy diagram for hydrogen. Each circle represents an orbital

### Quick Check

- State what each of the three quantum numbers described above tells us about atomic orbitals.  
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- (a) What is the difference between a 1s and a 2s orbital?  
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 (b) What is the difference between a  $2p_x$  orbital and a  $2p_y$  orbital?  
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- How many different orbitals are available to an excited hydrogen electron in the fourth energy level?  
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### The Orbitals of Multi-Electron Atoms

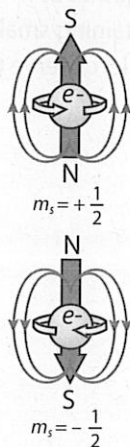


Figure 5.4.5 The spin quantum number ( $m_s$ ) identifies which possible spin an electron has.

Hydrogen is the simplest atom with one proton in the nucleus surrounded by one electron in a 1s orbital in its ground state. There are no electron-electron interactions, and in any excited state, all of the atomic orbitals available to that single electron are of equal energy.

We might expect a different situation, however, for multi-electron atoms. Electrons are charged particle-waves. It seems reasonable to conclude that they will affect each other when two or more of them occupy the same region of space around an atom's nucleus — and they do.

To describe those electrons in multi-electron atoms, we must introduce several additional considerations.

Experiments have shown that the single electron in hydrogen generates a tiny magnetic field as if the electron were a spinning charge. Also, in any sample of hydrogen, analyzing the many atoms present shows two opposing magnetic fields. This tells us that in half of the atoms, the electrons seem to spin in one direction and, in the remainder of the atoms, in the other direction. An electron's spin is as fundamental a part of its nature as its charge.

The fourth quantum number is called the **spin quantum number** ( $m_s$ ). It tells us the two possible electron spins, either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

## The Pauli Exclusion Principle

We already know that we can identify any orbital in an atom by the use of the first three quantum numbers, but we must use all four quantum numbers mentioned to specify any electron in an atom.

This is based on the fact that any atomic orbital can hold a maximum of two electrons. When two electrons are in the same orbital, their spins must be opposite. Originally proposed in 1925 by the Austrian physicist Wolfgang Pauli, this can be viewed as the first rule governing electrons in multi-electron atoms.

1. The **Pauli exclusion principle**: No two electrons in the same atom can be described by the same set of four quantum numbers.

If two electrons are in the same atomic orbital, they therefore have the same first three quantum numbers. Because they then must have opposite spins, their fourth quantum numbers are different.

We noted earlier that the total number of orbitals existing in any level  $n$  equals  $n^2$ .

If two electrons can occupy each orbital, the maximum number of electrons that can exist in any energy level  $n$  is given by  $2n^2$ .

A further consideration for multi-electron atoms is the effect of electron-electron repulsions on the relative energies of the sublevels in a given energy level. For hydrogen, where no repulsive forces exist, all of the sublevels in any energy level have identical energies. This is not the case for atoms of other elements. Although the same types of orbitals exist in multi-electron atoms, their relative energies are different. Repulsive forces cause a sublevel with a greater number of orbitals to have a greater energy. Therefore the order of sublevel energies is:

$$s < p < d < f.$$

Consider Figure 5.4.6. Compare this energy diagram for a multi-electron atom with Figure 5.4.4 for hydrogen. Note that in several cases energies get closer together as  $n$  increases. In these cases, repulsive forces are such that some sublevels containing smaller orbitals actually have higher energies than some larger orbitals. For example, observe the relative energy of the 3d compared to the 4s sublevel.

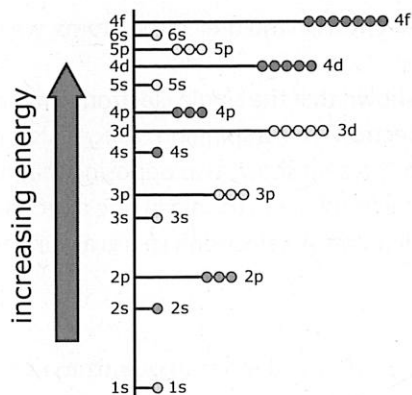


Figure 5.4.6 Energy diagram for multi-electron atoms

## Quick Check

1. What does the fourth quantum number tell us about electrons?

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2. Why can't two electrons in the same atom have the same four quantum numbers?

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3. What is the maximum number of electrons that can exist in the energy levels  $n = 1$  through  $n = 4$ ?

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## Electron Configurations and Orbital Diagrams

We are now in a position to organize electrons into orbitals for the atoms of the elements. Understanding this organization will prove to be a powerful tool as we discuss the periodic table and bonding in the next chapter. In beginning this process, we introduce the second rule associated with describing electrons in multi-electron atoms.

2. The **Aufbau principle**: When filling orbitals, the lowest energy orbitals available are always filled first. ("Aufbau" means a building or a construction in German.)

The order for filling orbitals is given above in Table 5.4.1, showing sublevel energies. We start at the lowest energy orbitals and move up.

Let's begin with hydrogen. In its lowest energy or ground state, hydrogen's electron exists in the 1s orbital. We can represent this in two ways:

1. We can use a shorthand notation called an **electron configuration**, which is written in the format  $n\ell^{\#}$  showing the energy level, sublevel, and number of electrons respectively. Hydrogen's electron configuration is therefore written as:  $1s^1$ . Read as "one s one," this tells us that hydrogen's one electron resides in the 1s orbital in its ground state.
2. We can construct an **orbital diagram**, which depicts electrons and their spin using arrows facing up and down. The arrows are placed inside boxes or over lines representing individual orbitals in sublevels. Hydrogen's orbital diagram is shown as:



The configuration for the next element, helium, is  $1s^2$ . This is read "one s two" rather than "one s squared." Following the Pauli exclusion principle, the orbital diagram shows the two electrons with opposite spins in the now full 1s orbital:



To indicate increasing sublevel energy, the boxes can be written vertically or also left to right to save space on a page. Let's continue below by moving past helium to the elements in period 2 of the periodic table using horizontally written orbital diagrams.

Note that period 2 corresponds to the second energy level,  $n = 2$ . Following the Aufbau principle:

	Electron Configuration	Orbital Diagram INCREASING ENERGY →		
		1s	2s	2p
lithium	$1s^2 2s^1$	$\uparrow\downarrow$	$\uparrow$	$\square \square \square$
beryllium	$1s^2 2s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\square \square \square$
For the 2p sublevel:				
boron	$1s^2 2s^2 2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \square \square$

Note that the sum of the superscript numbers equals the total number of electrons present.

We must now use the third rule governing orbitals in multi-electron atoms:

3. **Hund's rule:** When orbitals of equal energy are being filled, the most stable configuration is the one with the maximum number of unpaired electrons with the same spin.

So carbon and nitrogen's orbital diagrams are:

carbon	$1s^2 2s^2 2p^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \uparrow \square$
nitrogen	$1s^2 2s^2 2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \uparrow \uparrow$

After nitrogen, we must again begin to pair electrons:

oxygen	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$
fluorine	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow$
neon	$1s^2 2s^2 2p^6$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$

After a noble gas, a new period begins in the periodic table and so too, a new energy level. As we begin period 3, let's represent the elements up to scandium in Table 5.4.2 using electron configurations only. We can condense electron configurations using **core notation**, in which the configuration of the previous noble gas is represented by that noble gas symbol in square brackets as shown in the table. Outer electrons are indicated in **bold** type.

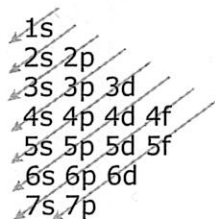


**Table 5.4.2** Electron Configurations of Period 3 Elements up to Scandium

Element	Full Electron Configuration	Core Notation
sodium	$1s^2 2s^2 2p^6 3s^1$	[Ne] $3s^1$
magnesium	$1s^2 2s^2 2p^6 3s^2$	[Ne] $3s^2$
aluminum	$1s^2 2s^2 2p^6 3s^2 3p^1$	[Ne] $3s^2 3p^1$
silicon	$1s^2 2s^2 2p^6 3s^2 3p^2$	[Ne] $3s^2 3p^2$
phosphorus	$1s^2 2s^2 2p^6 3s^2 3p^3$	[Ne] $3s^2 3p^3$
sulphur	$1s^2 2s^2 2p^6 3s^2 3p^4$	[Ne] $3s^2 3p^4$
chlorine	$1s^2 2s^2 2p^6 3s^2 3p^5$	[Ne] $3s^2 3p^5$
argon	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ne] $3s^2 3p^6$
potassium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	[Ar] $4s^1$
calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	[Ar] $4s^2$
scandium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	[Ar] $4s^2 3d^1$

Notice in the table that, as we move from argon to potassium, the 4s sublevel starts to fill before the 3d sublevel. After the 4s sublevel, the 3d sublevel starts to fill, reaching the first transition metal, scandium. Although the 3d sublevel fills after the 4s sublevel, the 3d sublevel still contains electrons that spend most of their time nearer the nucleus and so is inside the 4s sublevel. Some periodic tables indicate the electron configurations in order of sublevel size and so will show scandium's configuration as [Ar]  $3d^1 4s^2$ .

Figure 5.4.7 is a simple way of remembering the order for filling sublevels. We begin at the top with the 1s and fill that sublevel. After reaching the end of each arrow, we then start at the top of the next arrow below it. When using this diagram, you must remember how many electrons each sublevel can hold.



**Figure 5.4.7** This diagram indicates the order for filling sublevels.

## Ions and Other Charged Topics

Recall that a cation has fewer electrons than the original neutral atom and an anion has more. This means that the electron configurations for ions will be different than those for neutral atoms.

The process is easily shown using examples. To write the electron configuration for the  $S^{2-}$  anion, we simply need to add two more electrons to the last unfilled sublevel. Thus the configuration:  $1s^2 2s^2 2p^6 3s^2 3p^4$  for the S atom becomes:  $1s^2 2s^2 2p^6 3s^2 3p^6$  for the  $S^{2-}$  anion. Notice that the sulphide anion now has the same electron configuration as the nearest noble gas argon. The sulphide ion is therefore considered to be **isoelectronic** with argon because the two species have the same number and configuration of electrons.

To write cation configurations, electrons are always removed *from the outermost orbitals with the highest energy first*. Therefore, it is sometimes worthwhile to first write the neutral atom's configuration in core notation with the final orbitals listed from smallest to largest, rather than in the order the orbitals fill. Then remove the appropriate electrons from the outer orbitals first.

For example, if asked to write the configuration for the  $Sn^{4+}$  ion, first write the configuration for a neutral Sn atom as  $[Kr] 4d^{10} 5s^2 5p^2$  rather than writing  $[Kr] 5s^2 4d^{10} 5p^2$ .

Now remove the four *outermost* electrons to give the configuration for  $Sn^{4+}$ :  $[Kr] 4d^{10}$ . This avoids the error of removing two 4d electrons to give  $[Kr] 5s^2 4d^8$ . Note that an  $Sn^{2+}$  ion would form by losing the two 5p electrons, as they are at higher energy than the 5s.

As a final note, there are several exceptions to the orbital filling order discussed here. The elements Cr, Cu, Mo, Ag, and Au are examples of such exceptions. Your teacher may choose to discuss these and others and the possible reasons.

We shouldn't be surprised that irregularities exist. We have already seen ample evidence that the quantum world is full of surprises!