

Quantum Numbers

- The Bohr model was a one-dimensional model that used one quantum number to describe the distribution of electrons in the atom. The only information that was important was the *size* of the orbit, which was described by the n quantum number. Erwin Schrödinger's model allowed the electron to occupy three-dimensional space.

Quantum Numbers

- Erwin Schrodinger (1887-1961)
- Nobel Prize, Physics 1933
- Schrodinger equation: describes how the quantum state of a physical system changes in time.



Quantum Numbers

- The three coordinates, or **quantum numbers**, that come from Schrödinger's wave equations are the principal (n), angular (l), and magnetic (m) quantum numbers. These quantum numbers describe the size, shape and orientation in space of the orbitals on an atom, respectively.

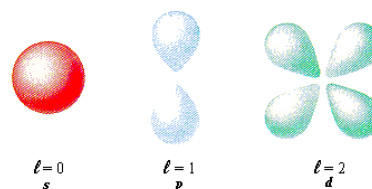
Quantum Numbers

- The **principal quantum number** (n) describes the size of the orbital. Orbitals for which $n = 2$ are larger than those for which $n = 1$, for example. Because they have opposite electrical charges, electrons are attracted to the nucleus of the atom. Energy must therefore be absorbed to excite an electron from an orbital in which the electron is close to the nucleus ($n = 1$) into an orbital in which it is further from the nucleus ($n = 2$). The principal quantum number therefore indirectly describes the energy of an orbital.

Quantum Numbers

- The **angular quantum number** (l) describes the shape of the orbital. Orbitals have shapes that are best described as spherical ($l = 0$), polar ($l = 1$), or cloverleaf ($l = 2$). They can even take on more complex shapes as the value of the angular quantum number becomes larger.

Quantum Numbers



Quantum Numbers

- There is only one way in which a sphere ($l = 0$) can be oriented in space. Orbitals that have polar ($l = 1$) or cloverleaf ($l = 2$) shapes, however, can point in different directions. We, therefore, need a third quantum number, known as the **magnetic quantum number** (m), to describe the orientation in space of a particular orbital. (It is called the *magnetic* quantum number because the effect of different orientations of orbitals was first observed in the presence of a magnetic field.)

Rules Governing the Allowed Combinations of Quantum Numbers

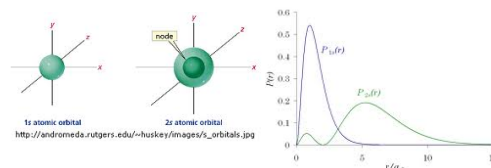
- The three quantum numbers (n , l , and m) that describe an orbital are integers: 0, 1, 2, 3, and so on.
- The principal quantum number (n) cannot be zero. The allowed values of n are therefore 1, 2, 3, 4, and so on.
- The angular quantum number (l) can be any integer between 0 and $n - 1$. If $n = 3$, for example, l can be either 0, 1, or 2.
- The magnetic quantum number (m) can be any integer between $-l$ and $+l$. If $l = 2$, m can be either -2, -1, 0, +1, or +2.

Shapes of Orbitals

- There is only one orbital in the $n = 1$ shell because there is only one way in which a sphere can be oriented in space. The only allowed combination of quantum numbers for which $n = 1$ is the following.

n	l	m	
1	0	0	1s

Shapes of Orbitals



Shapes of Orbitals

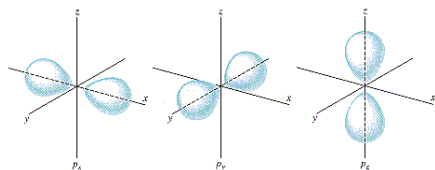
- There are four orbitals in the $n = 2$ shell.

n	l	m	
2	0	0	2s
2	1	-1	
2	1	0	2p
2	1	1	

Shapes of Orbitals

- There is only one orbital in the 2s subshell. But, there are three orbitals in the 2p subshell because there are three directions in which a p orbital can point. One of these orbitals is oriented along the X axis, another along the Y axis, and the third along the Z axis of a coordinate system, as shown in the figure below. These orbitals are therefore known as the $2p_x$, $2p_y$, and $2p_z$ orbitals.

Shapes of Orbitals



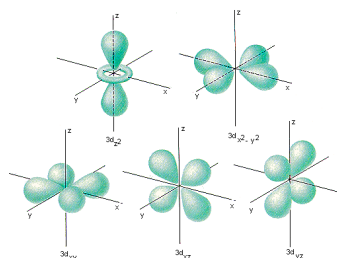
Shapes of Orbitals

- There are nine orbitals in the $n = 3$ shell.

n	l	m	
3	0	0	3s
3	1	-1	3p
3	1	0	
3	1	1	
3	2	-2	3d
3	2	-1	
3	2	0	
3	2	1	
3	2	2	

Shapes of Orbitals

- There is one orbital in the 3s subshell and three orbitals in the 3p subshell. The $n = 3$ shell, however, also includes 3d orbitals. The five different orientations of orbitals in the 3d subshell are shown in the figure below. One of these orbitals lies in the XY plane of an XYZ coordinate system and is called the $3d_{xy}$ orbital. The $3d_{xz}$ and $3d_{yz}$ orbitals have the same shape, but they lie between the axes of the coordinate system in the XZ and YZ planes. The fourth orbital in this subshell lies along the X and Y axes and is called the $3d_{x^2-y^2}$ orbital. Most of the space occupied by the fifth orbital lies along the Z axis and this orbital is called the $3d_z^2$ orbital.



Shapes of Orbitals

- The number of orbitals in a shell is the square of the principal quantum number: $1^2 = 1$, $2^2 = 4$, $3^2 = 9$. There is one orbital in an s subshell ($l = 0$), three orbitals in a p subshell ($l = 1$), and five orbitals in a d subshell ($l = 2$). The number of orbitals in a subshell is therefore $2(l) + 1$. An orbital can only hold 2 electrons.

Shapes of Orbitals

- To distinguish between the two electrons in an orbital, we need a fourth quantum number. This is called the **spin quantum number** (s) because electrons behave as if they were spinning in either a clockwise or counterclockwise fashion. One of the electrons in an orbital is arbitrarily assigned an s quantum number of $+1/2$, the other is assigned an s quantum number of $-1/2$. Thus, it takes three quantum numbers to define an orbital but four quantum numbers to identify one of the electrons that can occupy the orbital.

Electron Configurations

- The **electron configuration** of an atom describes the orbitals occupied by electrons on the atom. The basis of this prediction is a rule known as the **aufbau principle**, which assumes that electrons are added to an atom, one at a time, starting with the lowest energy orbital, until all of the electrons have been placed in an appropriate orbital.

Electron Configurations

- A hydrogen atom ($Z = 1$) has only one electron, which goes into the lowest energy orbital, the $1s$ orbital. This is indicated by writing a superscript "1" after the symbol for the orbital.
- H ($Z = 1$): $1s^1$
- The next element has two electrons and the second electron fills the $1s$ orbital because there are only two possible values for the spin quantum number used to distinguish between the electrons in an orbital.
- He ($Z = 2$): $1s^2$

Electron Configurations

- The third electron goes into the next orbital in the energy diagram, the $2s$ orbital.
- Li ($Z = 3$): $1s^2 2s^1$
- The fourth electron fills this orbital.
- Be ($Z = 4$): $1s^2 2s^2$
- After the $1s$ and $2s$ orbitals have been filled, the next lowest energy orbitals are the three $2p$ orbitals. The fifth electron therefore goes into one of these orbitals.
- B ($Z = 5$): $1s^2 2s^2 2p^1$
- When the time comes to add a sixth electron, the electron configuration is obvious.
- C ($Z = 6$): $1s^2 2s^2 2p^2$

Electron Configurations

- However, there are three orbitals in the $2p$ subshell. Does the second electron go into the same orbital as the first, or does it go into one of the other orbitals in this subshell?
- We need to understand the concept of **degenerate orbitals**. By definition, orbitals are *degenerate* when they have the same energy. The energy of an orbital depends on both its size and its shape because the electron spends more of its time further from the nucleus of the atom as the orbital becomes larger or the shape becomes more complex. In an isolated atom, however, the energy of an orbital doesn't depend on the direction in which it points in space. Orbitals that differ only in their orientation in space, such as the $2p_x$, $2p_y$, and $2p_z$ orbitals, are therefore degenerate.

Electron Configurations

- Electrons fill degenerate orbitals according to rules first stated by Friedrich Hund (**Hund's rules**):
- One electron is added to each of the degenerate orbitals in a subshell before two electrons are added to any orbital in the subshell.
- Electrons are added to a subshell with the same value of the spin quantum number until each orbital in the subshell has at least one electron.

Electron Configurations

- When the time comes to place two electrons into the $2p$ subshell we put one electron into each of two of these orbitals. (The choice between the $2p_x$, $2p_y$, and $2p_z$ orbitals is purely arbitrary.)
- C ($Z = 6$): $1s^2 2s^2 2p_x^1 2p_y^1$
- The fact that both of the electrons in the $2p$ subshell have the same spin quantum number can be shown by representing an electron for which $s = +1/2$ with an arrow pointing up and an electron for which $s = -1/2$ with an arrow pointing down. The electrons in the $2p$ orbitals on carbon can therefore be represented as follows:

Electron Configurations

- When we get to N ($Z = 7$), we have to put one electron into each of the three degenerate $2p$ orbitals. N ($Z = 7$): $1s^2 2s^2 2p^3$
- Because each orbital in this subshell now contains one electron, the next electron added to the subshell must have the opposite spin quantum number, thereby filling one of the $2p$ orbitals.
O ($Z = 8$): $1s^2 2s^2 2p^4$

Electron Configurations

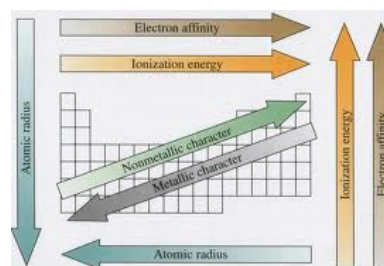
- The ninth electron fills a second orbital in this subshell. F ($Z = 9$): $1s^2 2s^2 2p^5$
- The tenth electron completes the $2p$ subshell.
Ne ($Z = 10$): $1s^2 2s^2 2p^6$

Electron Configurations

- There is something unusually stable about atoms, such as He and Ne, that have electron configurations with filled shells of orbitals. By convention, we therefore write abbreviated electron configurations in terms of the number of electrons beyond the previous element with a filled-shell electron configuration. Electron configurations of the next two elements in the periodic table, for example, could be written as follows.

Na ($Z = 11$): [Ne] $3s^1$
Mg ($Z = 12$): [Ne] $3s^2$

Periodic Trends



Atomic Radii

- As you move down a group, atomic radius increases. The number of energy levels increases as you move down a group as the number of electrons increases. Each subsequent energy level is further from the nucleus than the last. Therefore, the atomic radius increases as the group and energy levels increase.

Atomic Radii

- As you move across a period, atomic radius decreases. As you go across a period, electrons are added to the same energy level. At the same time, protons are being added to the nucleus. The concentration of more protons in the nucleus creates a "**higher effective nuclear charge**." In other words, there is a stronger force of attraction pulling the electrons closer to the nucleus resulting in a smaller atomic radius.

Atomic Radii

*Lanthanides
**Actinides

Ionic Radii

- Anions (negative ions) are larger than their respective atoms. Electron-electron repulsion forces them to spread further apart. Electrons outnumber protons; the protons cannot pull the extra electrons as tightly toward the nucleus.

Ionic Radii

- Cations (positive ions) are smaller than their respective atoms. There is less electron-electron repulsion, so they can come closer together. Protons outnumber electrons; the protons can pull the fewer electrons toward the nucleus more tightly. If the electron that is lost is the only valence electron so that the electron configuration of the cation is like that of a noble gas, then an entire energy level is lost. In this case, the radius of the cation is much smaller than its respective atom.

Ionic Radii

Atomic/Ionic Radii

5A	6A	7A
N 0.70	O ²⁻ 1.40	F ⁻ 1.36
P ³⁻ 1.71	S ²⁻ 1.84	Cl ⁻ 1.81
	Se ²⁻ 1.98	Br ⁻ 1.83
	Te ²⁻ 2.21	I ⁻ 1.97
		At ⁻ 2.16

Ionization Energy

- Definition: The energy required to remove the outermost (highest energy) electron from a neutral atom in its ground state.
- As you move down a group, first ionization energy decreases. Electrons are further from the nucleus and thus easier to remove the outermost one. **"SHIELDING"** - Inner electrons at lower energy levels essentially block the protons' force of attraction toward the nucleus. It therefore becomes easier to remove the outer electron.

Ionization Energy

- As you move across a period, first ionization energy increases. As you move across a period, the atomic radius decreases, that is, the atom is smaller. The outer electrons are closer to the nucleus and more strongly attracted to the center. Therefore, it becomes more difficult to remove the outermost electron.

