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Chapter 7

Quantum Theory and the Electronic Structure of Atoms

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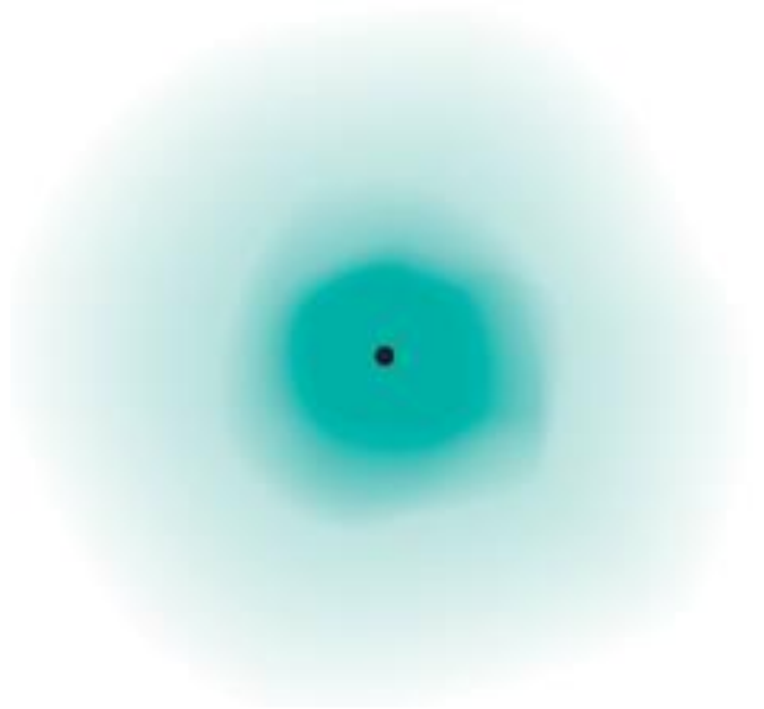
7.6
Quantum numbers

A representation of the electron density distribution surrounding the nucleus in the hydrogen atom. It shows a high probability of finding the electron closer to the nucleus.



Three **quantum numbers** are required to describe the distribution of electrons in atoms.
-The Principal Quantum Number (n)
-The Angular Momentum Quantum Number (ℓ)
-The Magnetic Quantum Number (m_ℓ)
These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them.

A fourth quantum number describes the behavior of a specific electron
-The Electron Spin Quantum Number (m_s)

The Principal Quantum Number (*n*)

n can have integral values 1, 2, 3, 4, and so forth.

n describes the “size” of the orbital.

n relates to the average distance of the electron from the nucleus in a particular orbital.

The larger *n* is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.

The Angular Momentum Quantum Number (ℓ)

The values of ℓ depend on the value of *n*.

For a given value of *n*, ℓ has possible integral values from 0 to (n – 1).

n = 1, ℓ = 0

n = 2, ℓ = 0 or 1

n = 3, ℓ = 0, 1, or 2

ℓ tells us the "shape" of the orbitals.

The value of ℓ is generally designated by the letters *s*, *p*, *d*, … as follows:

ℓ	0	1	2	3	4	5
Name of orbital	*s*	*p*	*d*	*f*	*g*	*h*

-A collection of orbitals with the same value of n is frequently called a **shell**.

-One or more orbitals with the same n and ℓ values are referred to as a **subshell**.

Example,
The shell with $n = 2$ is composed of two subshells, $\ell = 0$ and 1. These subshells are called the $2s$ and $2p$ subshells.

Where,
2 denotes the value of n, and s and p denote the values of ℓ.

The Magnetic Quantum Number (m_ℓ)

The value of $\boldsymbol{m_\ell}$ depends on the value of the $\boldsymbol{\ell}$.

For a certain value of $\boldsymbol{\ell}$, there are ($2\boldsymbol{\ell}$+ 1) integral values of $\boldsymbol{m_\ell}$ as follows:

$$-\ell,\ (-\ell + 1),\ \ldots\ 0,\ \ldots\ (+\ell - 1),\ +\ell$$

if $\boldsymbol{\ell}$= 0 (*s* orbital), $\boldsymbol{m_\ell}$ has one value (one orbital), m_ℓ= 0
if $\boldsymbol{\ell}$= 1 (*p* orbital), $\boldsymbol{m_\ell}$ has three values (three orbitals), m_ℓ= -1, 0, or 1
if $\boldsymbol{\ell}$= 2 (*d* orbital), $\boldsymbol{m_\ell}$ has five values (five orbitals), m_ℓ= -2, -1, 0, 1, or 2

The number of m_ℓ values indicates the number of **orbitals** in a **subshell** with a particular $\boldsymbol{\ell}$ value.

$\boldsymbol{m_\ell}$ describes the "orientation" of the orbital in space.
-If m_ℓ has 1 value, m_ℓ= 0, the orbital has one orientation in space.
-If m_ℓ has 3 values, m_ℓ= -1, 0, or 1, the orbitals have 3 orientations in space.
-if m_ℓ has 5 values, m_ℓ= -2, -1, 0, 1, or 2, the orbitals have 5 orientations in space.

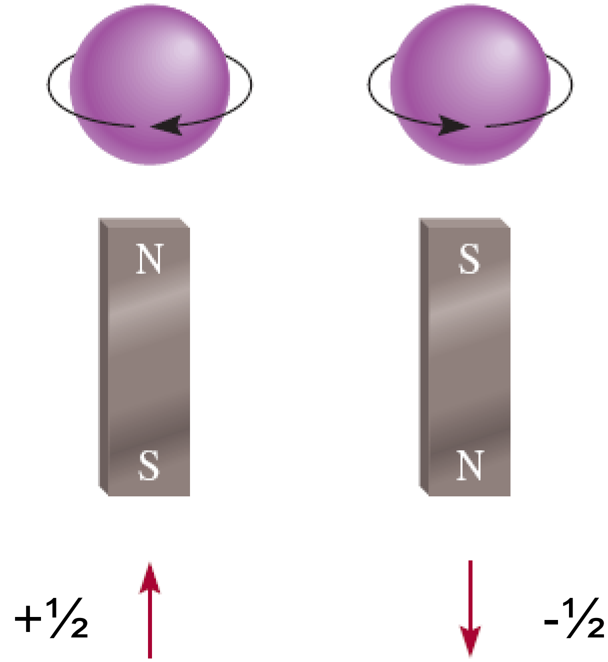
The Electron Spin Quantum Number (m_s)

Electrons act like tiny magnets.

m_s has a value of $+\frac{1}{2}$ or $-\frac{1}{2}$

m_s indicates the direction of the electron's "spin" on its own axis.

The magnetic fields generated by these two spinning motions are analogous to those from the two magnets. The upward and downward arrows are used to denote the direction of spin.



Clockwise spin of an electron

Counterclockwise spin of an electron

Relation between quantum numbers and atomic orbitals

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

- ***s*** subshell has one orbital,
- ***p*** subshell has three orbitals,
- ***d*** subshell has five orbitals.

EXAMPLE

List the values of n, ℓ, and m_ℓ for orbitals in the 4d subshell.

Solution:

n = 4.

ℓ = 2.

m_ℓ = -2, -1, 0, 1, or 2.

Practice Exercise

Give the values of the quantum numbers associated with the orbitals in the 3p subshell.

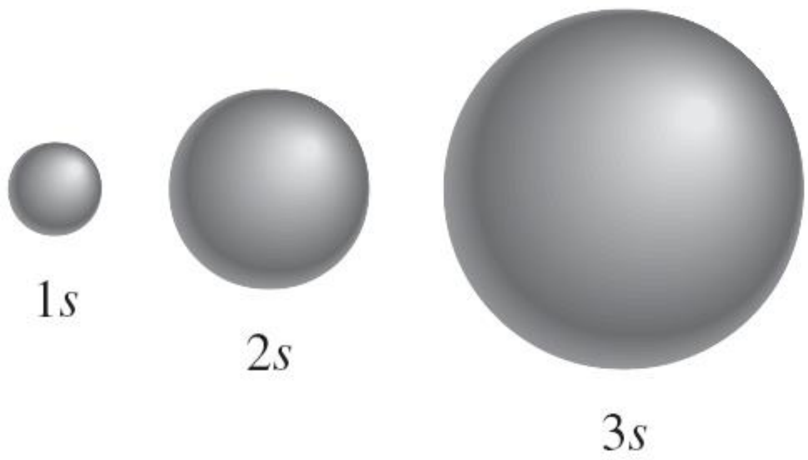
7.7
Atomic orbitals

s Orbitals

When $\ell = 0$, $(2\ell + 1) = 1$ and there is only one value of m_ℓ thus we have an *s* orbital.
$m_\ell = 0$ (one orientation in space).

s orbital represents as a **sphere**.

The figure shows boundary surface diagrams for the 1*s* , 2*s* , and 3*s* hydrogen atomic orbitals. All *s* orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases.

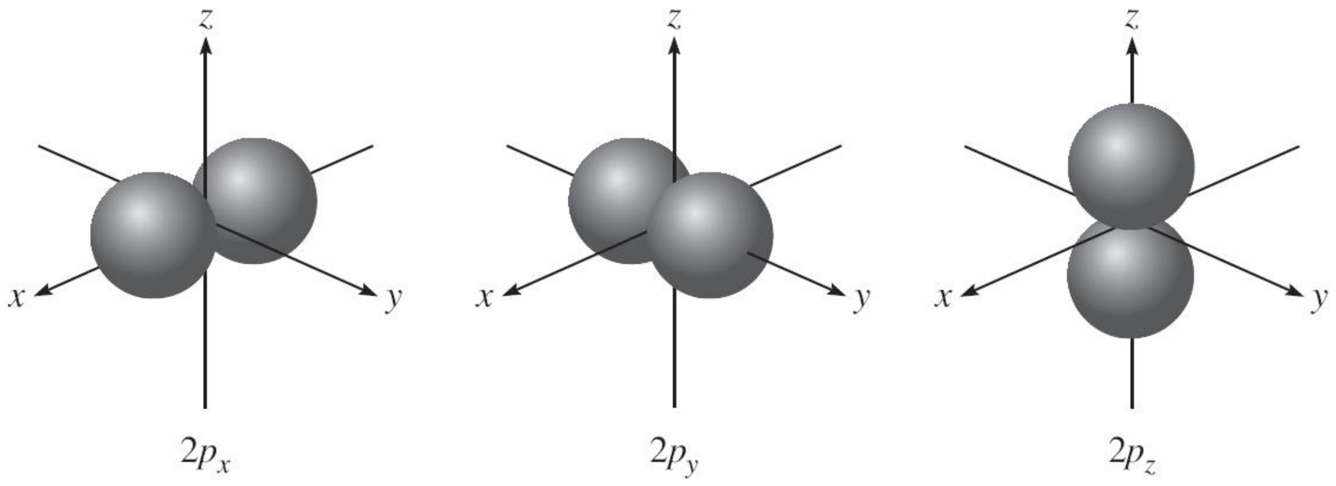


p Orbitals

When $\ell = 1$, $(2\ell + 1) = 3$ and there are three values of m_ℓ
thus we have three p orbitals; p_x, p_y, p_z
$m_\ell = -1, 0,$ or 1 (three orientations in space).

p orbitals start with the principal quantum number $n = 2$.

Starting with $n = 2$ and $\ell = 1$, we therefore have three $2p$ orbitals: $2p_x$, $2p_y$, and $2p_z$. The letter subscripts indicate the axes along which the orbitals are oriented. These three p orbitals are identical in size, shape, and energy; they differ from one another only in orientation.

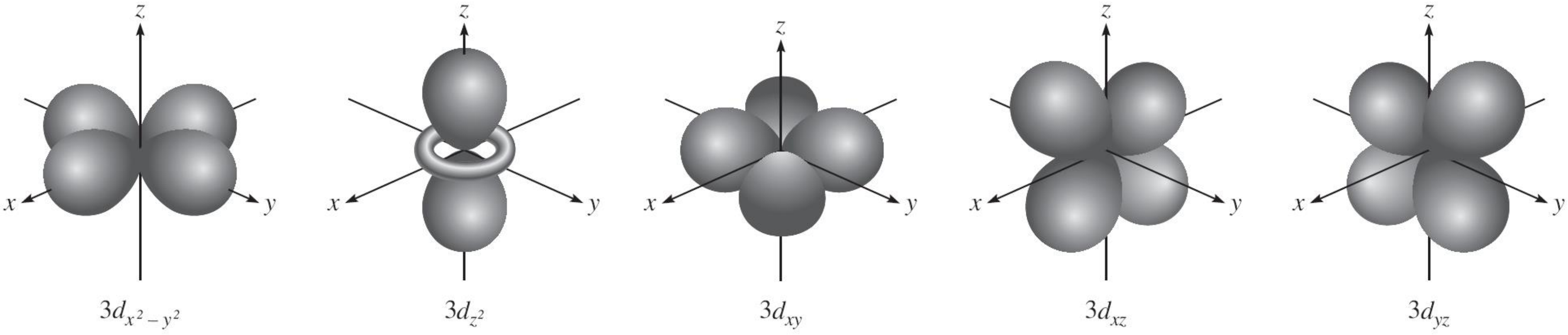


d Orbitals

When $\ell = 2$, $(2\ell + 1) = 5$ and there are five values of m_ℓ thus we have five *d* orbitals.
$m_\ell = -2, -1, 0, 1$ or 2 (five orientations in space).

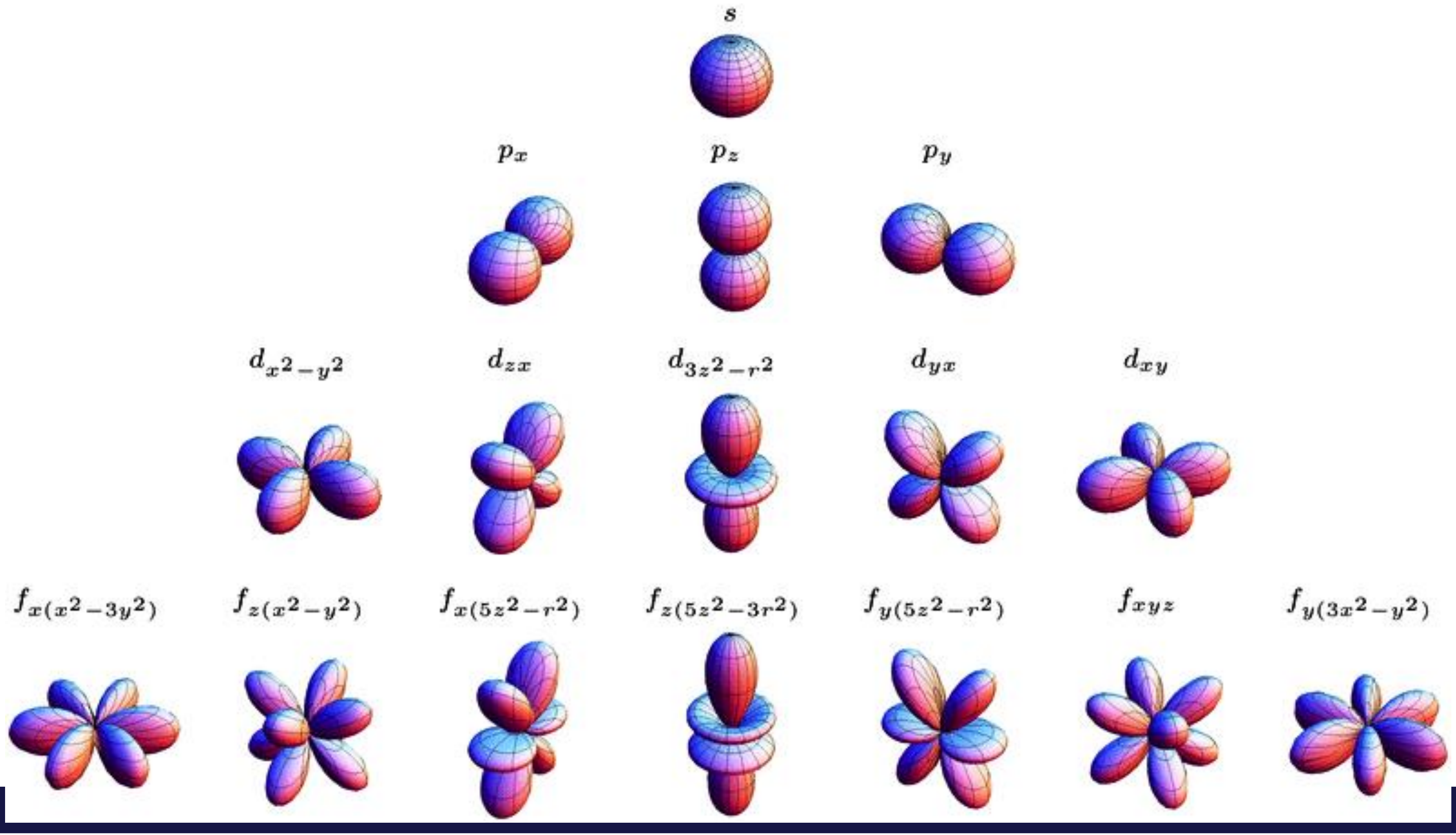
Starting with $n = 3$ and $\ell = 2$, we therefore have five 3*d* orbitals:
$3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{z^2}$, and $3d_{x^2-y^2}$

All the 3*d* orbitals in an atom are identical in energy. The *d* orbitals for which *n* is greater than 3 (4*d*, 5*d*, . . .) have similar shapes.



Other Higher-Energy Orbitals

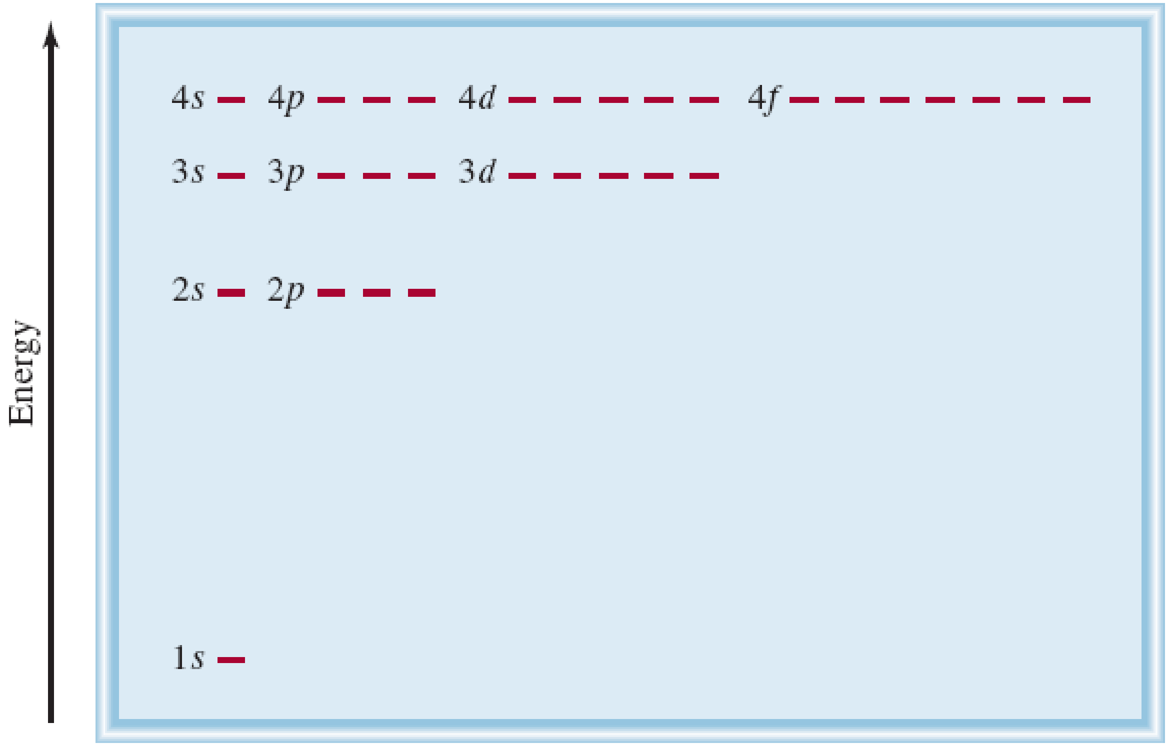
-Orbitals having higher energy than *d* orbitals are labeled *f* , *g* , *h* , . . . and so on.
-The *f* orbitals are important in accounting for the behavior of elements with atomic numbers greater than 57, but their shapes are difficult to represent.



The Energies of Orbitals

What are the relative energies of atomic orbitals?
How energy levels affect the actual arrangement of electrons in atoms.

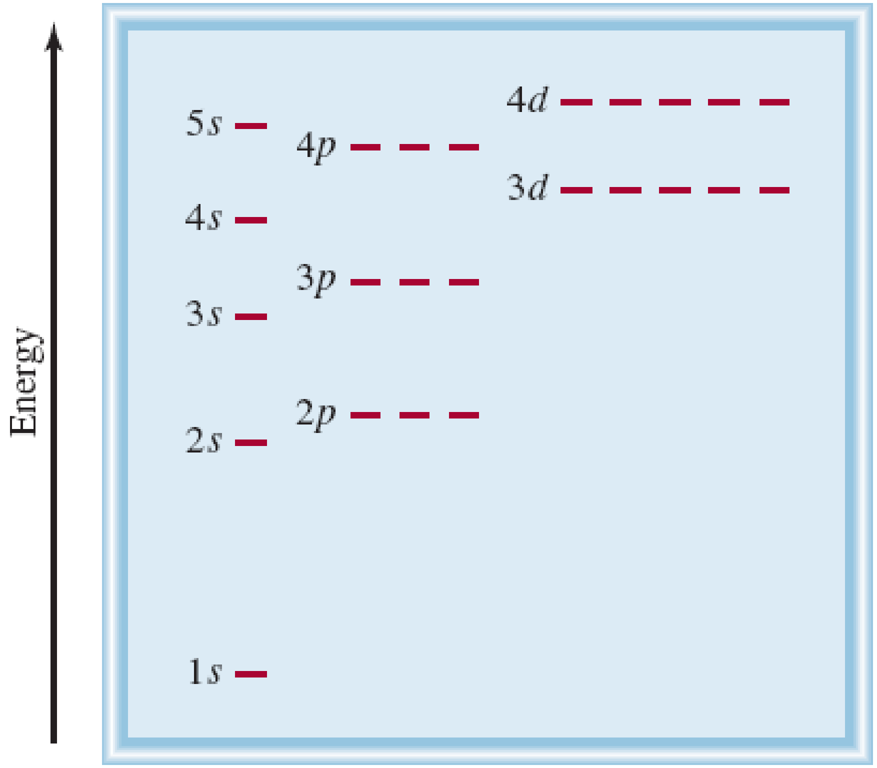
- For hydrogen atom



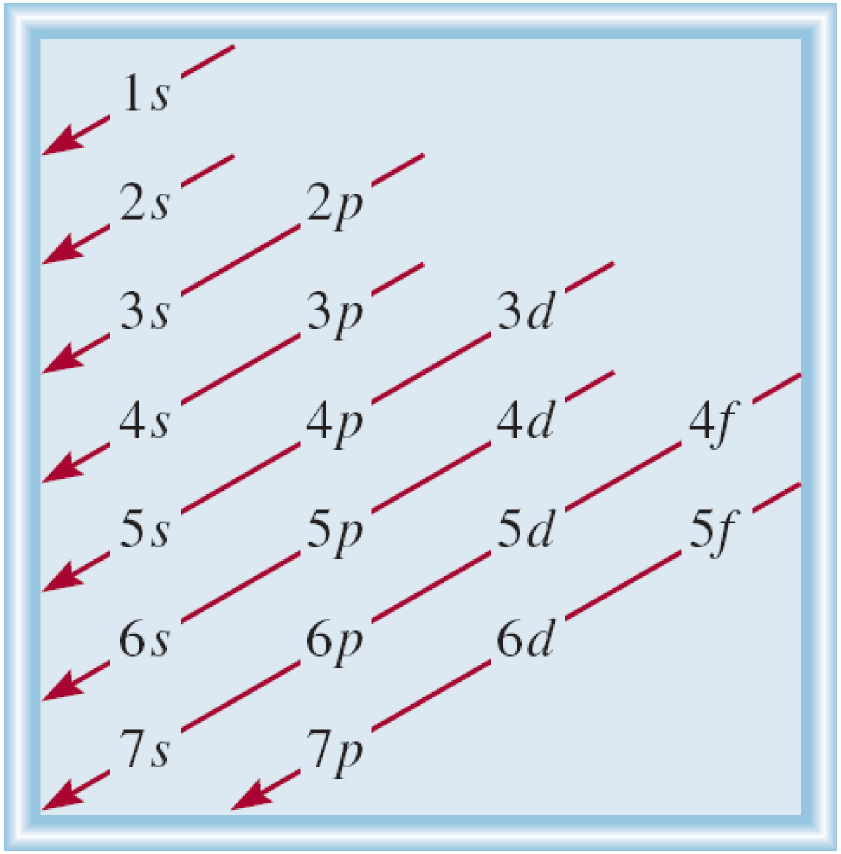
Orbital energy levels in the hydrogen atom. Each short horizontal line represents one orbital. Orbitals with the same principal quantum number *n* all have the same energy.

Thus, the energies of hydrogen orbitals increase as follows:
$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f <$ …….

- For many electron atoms



Orbital energy levels in a many-electron atom. Note that the energy level depends on both *n* and *ℓ* values.



The order in which atomic subshells are filled in a many-electron atom. Start with the 1*s* orbital and move downward, following the direction of the arrows.

Thus, the order goes as follows:

1s < 2s < 2p < 3s < 3p < 4s < 3d < . . . .

EXAMPLE

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Solution

For $n = 3$, the possible values of ℓ are 0, 1, and 2.
Thus, there is one 3*s* orbital ($n = 3$, $\ell = 0$, and $m_\ell = 0$);
there are three 3*p* orbitals ($n = 3$, $\ell = 1$, and $m_\ell = -1, 0, 1$);
there are five 3*d* orbitals ($n = 3$, $\ell = 2$, and $m_\ell = -2, -1, 0, 1, 2$).
The total number of orbitals is $1 + 3 + 5 = 9$.

The total number of orbitals for a given value of n is n^2.
So here we have $3^2 = 9$.

Practice Exercise

What is the total number of orbitals associated with the principal quantum number $n = 4$?

EXAMPLE

Give the four quantum numbers for each of the two electrons in a 6*s* orbital.

Solution

The 1st electron	The 2nd electron
$n = 6$	$n = 6$
$\ell = 0$	$\ell = 0$
$m_\ell = 0$	$m_\ell = 0$
$m_s = +½$	$m_s = -½$

EXAMPLE

Write the four quantum numbers for an electron in a 3*p* orbital.

Solution

n is 3 and ℓ must be 1

For $\ell = 1$, there are three values of m_ℓ given by -1, 0, and 1. Because the electron spin quantum number m_s can be either +1/2 or -1/2, we conclude that there are six possible ways to designate the electron using the (n, ℓ, m_ℓ, m_s) notation:

3, 1, -1, +1/2	3, 1, -1, -1/2
3, 1, 0, +1/2	3, 1, 0, -1/2
3, 1, 1, +1/2	3, 1, 1, -1/2

Practice Exercise

Write the four quantum numbers for an electron in a 4*d* orbital.

7.8
Electron configuration

Electron configuration of the atom: is how the electrons are distributed among the various atomic orbitals.

The number of electrons in a neutral atom is equal to its atomic number Z (number of proton).

denotes the number of electrons in the orbital or subshell

$$1s^1$$

denotes the principal quantum number n

denotes the angular momentum quantum number ℓ

The electron configuration can also be represented by an *orbital diagram* that shows the spin of the electron.

H $\boxed{\uparrow}$

$1s^1$

The upward arrow denotes one of the two possible spinning motions of the electron. (Alternatively, we could have represented the electron with a downward arrow.) The box represents an atomic orbital.

The Pauli Exclusion Principle: no two electrons in an atom can have the same set of four quantum numbers.

Only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins.

The Aufbau principle (the building-up principle): as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to the atomic orbitals.

In the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.

Hund's rule: the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins.

If two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs.

Element	Z	Configuration	Orbital diagram
H	1	$1s^1$	[↑]
He	2	$1s^2$	[↑↓]
Li	3	$1s^2\ 2s^1$	[↑↓] [↑]
Be	4	$1s^2\ 2s^2$	[↑↓] [↑↓]
B	5	$1s^2\ 2s^2\ 2p^1$	[↑↓] [↑↓] [↑][ ][ ]
C	6	$1s^2\ 2s^2\ 2p^2$	[↑↓] [↑↓] [↑][↑][ ]
N	7	$1s^2\ 2s^2\ 2p^3$	[↑↓] [↑↓] [↑][↑][↑]
O	8	$1s^2\ 2s^2\ 2p^4$	[↑↓] [↑↓] [↑↓][↑][↑]
F	9	$1s^2\ 2s^2\ 2p^5$	[↑↓] [↑↓] [↑↓][↑↓][↑]
Ne	10	$1s^2\ 2s^2\ 2p^6$	[↑↓] [↑↓] [↑↓][↑↓][↑↓]

EXAMPLE

What is the maximum number of electrons that can be present in the principal level for which $n = 3$?

Solution

When $n = 3$, $\ell = 0, 1,$ and 2.

The number of orbitals for each value of ℓ is given by

Value of ℓ	Number of Orbitals $(2\ell + 1)$
0	1
1	3
2	5

The total number of orbitals is nine. Because each orbital can accommodate two electrons, the maximum number of electrons that can reside in the orbitals is $2 \times 9 = 18$.

Or using the following equation

the number of electrons in a given principal energy level $n = 2n^2$.

So,,, $2(3)^2 = 18$ electrons.

Practice Exercise

Calculate the total number of electrons that can be present in the principal level for which $n = 4$.

EXAMPLE

An oxygen atom has a total of 8 electrons. Write the four quantum numbers for each of the eight electrons in the ground state.

Solution

We start with $n = 1$, so $\ell = 0$, a subshell corresponding to the 1*s* orbital. This orbital can accommodate a total of 2 electrons.

Next, $n = 2$, and ℓ may be either 0 or 1.

The $\ell = 0$ subshell contains one 2*s* orbital, which can accommodate 2 electrons.

The remaining 4 electrons are placed in the $\ell = 1$ subshell, which contains three 2*p* orbitals.

The orbital diagram is

The results are summarized in the following table:

Electron	n	ℓ	m_ℓ	m_s	Orbital
1	1	0	0	$+\frac{1}{2}$	$1s$
2	1	0	0	$-\frac{1}{2}$	
3	2	0	0	$+\frac{1}{2}$	$2s$
4	2	0	0	$-\frac{1}{2}$	
5	2	1	-1	$+\frac{1}{2}$	$2p_x, 2p_y, 2p_z$
6	2	1	0	$+\frac{1}{2}$	
7	2	1	1	$+\frac{1}{2}$	
8	2	1	1	$-\frac{1}{2}$	

Practice Exercise Write a complete set of quantum numbers for each of the electrons in boron (B).

EXAMPLE

What is the electron configuration of Mg?

Mg: 12 electrons

$1s < 2s < 2p < 3s < 3p < 4s$

$1s^2\ 2s^2\ 2p^6\ 3s^2$

2 + 2 + 6 + 2 = 12 electrons

Abbreviated as [Ne] $3s^2$

EXAMPLE

What are the possible quantum numbers for the last (outermost) electron in Cl?

Cl: 17 electrons

$1s < 2s < 2p < 3s < 3p < 4s$

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

2 + 2 + 6 + 2 + 5 = 17 electrons

Last electron added to $3p$ orbital

$n = 3$ $\quad \ell = 1$ $\quad m_\ell = -1, 0, \text{or} +1$ $\quad m_s = ½ \text{ or } -½$

General rules for assigning electrons to atomic orbitals

-Shell: electrons with the same value of n.

-Subshell: electrons with the same values of n and ℓ.

-Orbital: electrons with the same values of n, ℓ, and m_ℓ.

-Each shell or principal level of quantum number n contains n subshells.
For example, if $n = 2$, then there are two subshells (two values of ℓ) of angular momentum quantum numbers 0 and 1.

-Each subshell of quantum number ℓ contains $(2\ell + 1)$ orbitals.
For example, if $\ell = 1$, then there are three p orbitals.

-No more than two electrons can be placed in each orbital. Therefore, the maximum number of electrons is simply twice the number of orbitals that are employed.

-The maximum number of electrons that an atom can have in a principal level n is to use the formula $2n^2$.


Thank You!