5.7: Atomic Orbitals and Quantum Numbers

> **◗ Learning Objectives**
>
> - Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
> - List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the **principal quantum number**.
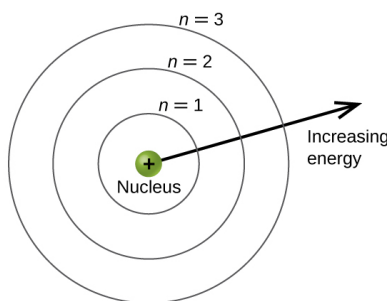

Figure 5.7.1: Different energy levels are numbered by principal quantum numbers n.

The principal quantum number is one of three quantum numbers used to characterize an orbital. Recall that an atomic orbital, which is distinct from an *orbit*, is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is l, the **angular momentum quantum number**. It is an integer that defines the shape of the orbital, and takes on the values, $l = 0, 1, 2, \ldots, n - 1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. The principal quantum number defines the general size and energy of the orbital. The l value specifies the shape of the orbital. Orbitals with the same value of l form a subshell. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with $l = 0$ are called s orbitals, which are spherically shaped probability densities. The value $l = 1$ corresponds to the p orbitals, of which there are three unique 3D orientations. The orbitals with $l = 2$ are called the d orbitals, followed by the *f-, g-, and h*-orbitals for $l = 3, 4, 5$, and there are higher values we will not consider.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a radial node. The number of radial nodes in an orbital is $n - l - 1$.
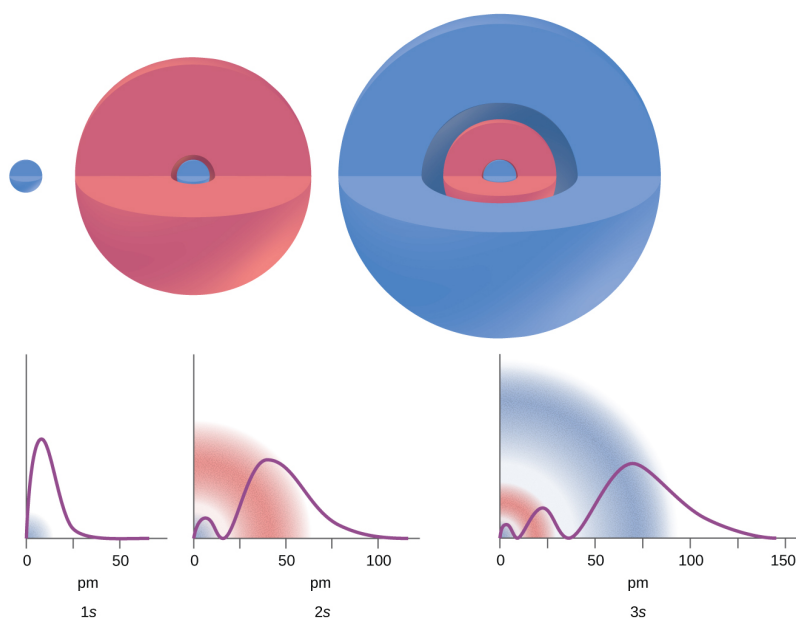
Figure 5.7.2: The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

Consider the examples in Figure 5.7.2. The orbitals depicted are of the *s* type, thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that there are $1 - 0 - 1 = 0$ places where the density is zero (nodes) for $1s$ ($n = 1$), $2 - 0 - 1 = 1$ node for $2s$, and $3 - 0 - 1 = 2$ nodes for the $3s$ orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.
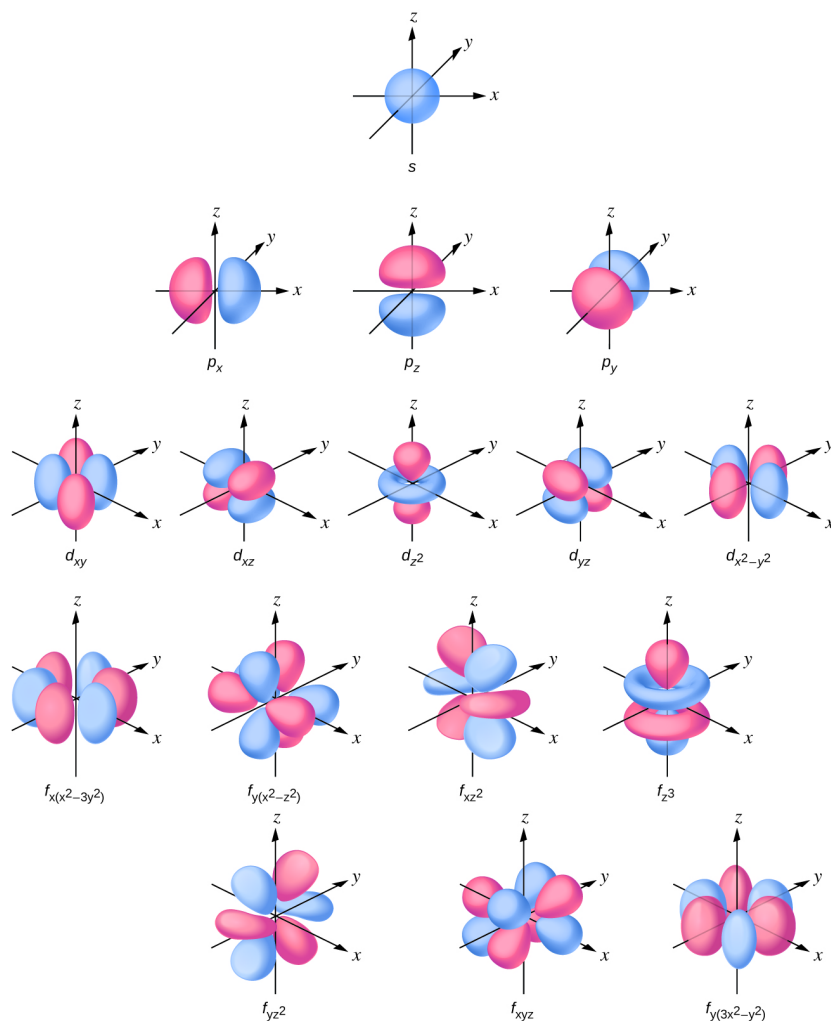
Figure 5.7.3: Shapes of s, p, d, and f orbitals.

Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell: https://youtu.be/ms7WR149fAY

If an electron has an angular momentum ($l \neq 0$), then this vector can point in different directions. In addition, the z component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the z direction, orbitals with different values of the z component of the angular momentum will have different energies resulting from interacting with the field. The magnetic quantum number, called m_l, specifies the z component of the angular momentum for a particular orbital. For example, for an s orbital, $l = 0$, and the only value of m_l is zero. For p orbitals, $l = 1$, and m_l can be equal to -1, 0, or $+1$. Generally speaking, m_l can be equal to $-l$, $-(l-1)$, …, -1, 0, $+1$, …, $(l-1)$, l. The total number of possible orbitals with the same value of l (a

subshell) is 2*l* + 1. Thus, there is one *s*-orbital for *ml = 0*, there are three *p*-orbitals for *ml = 1*, five *d*-orbitals for *ml = 2*, seven *f*-orbitals for *ml = 3*, and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure 5.7.3.
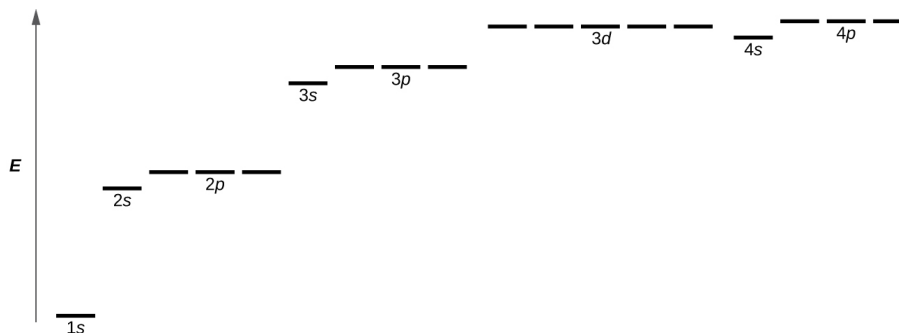

Figure 5.7.4: *The chart shows the energies of electron orbitals in a multi-electron atom.*

Figure 5.7.4 illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number *l* = 0 for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for *l* ≥ 1, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, *n*, are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies. Orbitals within the same subshell (for example *ns, np, nd, nf*, such as 2*p*, 3*s*) are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or m_s.

The other three quantum numbers, *n*, *l*, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the *z* component of the spin being in the positive direction of the *z* axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β state, with the *z* component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = -\frac{1}{2}$ and $m_s = \frac{1}{2}$ are different if an external magnetic field is applied.
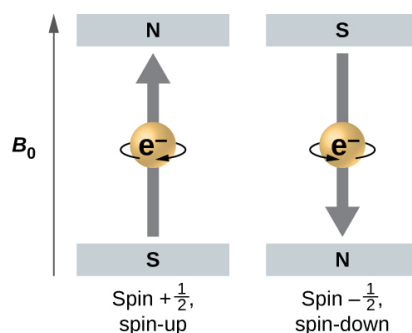
Figure 5.7.5: Electrons with spin values \(±\ce{1/2}\) *in an external magnetic field.*

Figure $5.7.5$ illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $\dfrac{1}{2}$ spin quantum number and down (in the negative *z* direction) for the spin quantum number of $-\frac{1}{2}$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = \dfrac{1}{2}$ has a slightly lower energy in an external field in the positive *z* direction, and an electron with $m_s = -\dfrac{1}{2}$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

Magnetic Quantum Number (ml) & Spin Quantum Number (ms): https://youtu.be/gbmGVUXBOBk

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: *n*, *l*, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The Pauli exclusion principle can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers *n*, *l*, and m_l), but only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values $\left(±\dfrac{1}{2} \right)$, no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table $5.7.1$.

Table 5.7.1*: Quantum Numbers, Their Properties, and Significance*

Name	Symbol	Allowed values	Physical meaning

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \leq l \leq n-1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital
spin quantum number	m_s	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

✔ Example 5.7.1: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, s, p, d, and f subshells are found in the $n = 4$ shell of an atom. For $l = 0$ (the s subshell), m_l can only be 0. Thus, there is only one 4s orbital. For $l = 1$ (p-type orbitals), m can have values of –1, 0, +1, so we find three 4p orbitals. For $l = 2$ (d-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4d orbitals. When $l = 3$ (f-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

? Exercise 5.7.1

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3$, $l = 1$;
b. $n = 5$, $l = 3$;
c. $n = 2$, $l = 0$.

Answer a

　3p

Answer b

　5f

Answer c

　2s

✔ Example 5.7.2: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$, (b) $n = 5$, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.

(b) When $n = 5$, there are five subshells of orbitals that we need to sum:

$$1 \text{ orbital labeled } 5s$$
$$3 \text{ orbitals labeled } 5p$$
$$5 \text{ orbitals labeled } 5d$$
$$7 \text{ orbitals labeled } 5f$$
$$+9 \text{ orbitals labeled } 5g$$
$$\overline{\phantom{+9 \text{ orbitals labeled } 5g}}$$
$$25 \text{ orbitals total}$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$

? Exercise 5.7.2

If a shell contains a maximum of 32 electrons, what is the principal quantum number, n?

Answer

$n = 4$

✔ Example 5.7.3: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	n	l	m_l degeneracy	Radial nodes (no.)
4f				
	4	1		
	7		7	3
5d				

Solution

The table can be completed using the following rules:

- The orbital designation is nl, where l = 0, 1, 2, 3, 4, 5, … is mapped to the letter sequence s, p, d, f, g, h, …,
- The m_l degeneracy is the number of orbitals within an l subshell, and so is $2l + 1$ (there is one s orbital, three p orbitals, five d orbitals, seven f orbitals, and so forth).
- The number of radial nodes is equal to $n - l - 1$.

Orbital	n	l	m_l degeneracy	Radial nodes (no.)
4f	4	3	7	0
4p	4	1	3	2
7f	7	3	7	3
5d	5	2	5	2

Summary of the Rules for Quantum Numbers: https://youtu.be/nRsRZUsOBzE

❓ Exercise 5.7.3

How many orbitals have $l = 2$ and $n = 3$?

Answer

The five degenerate 3d orbitals

Summary

The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The angular momentum quantum number, l, can have any integer value from 0 to $n - 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $-l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm\dfrac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

Glossary

angular momentum quantum number (l)

quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

atomic orbital

mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

d orbital

region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a d electron

electron density

a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

_f_ orbital

multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an _f_ electron

magnetic quantum number (m_l)

quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

_p_ orbital

dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a _p_ electron

Pauli exclusion principle

specifies that no two electrons in an atom can have the same value for all four quantum numbers

principal quantum number (n)

quantum number specifying the shell an electron occupies in an atom

quantum mechanics

field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

_s_ orbital

spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an _s_ electron

shell

set of orbitals with the same principal quantum number, n

spin quantum number (m_s)

number specifying the electron spin direction, either $+\dfrac{1}{2}$ or $-\dfrac{1}{2}$

subshell

set of orbitals in an atom with the same values of n and l

wavefunction (ψ)

mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

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