

# Atomic Structure

## Fundamentals of the Atom

An atom consists of a nucleus of protons and neutrons, surrounded by electrons. Each of the elements in the periodic table is classified according to its atomic number, which is the number of protons in that element's nucleus. Protons have a charge of +1, electrons have a charge of -1, and neutrons have no charge. Neutral atoms have the same number of electrons and protons, but they can have a varying number of neutrons. Within a given element, atoms with different numbers of neutrons are isotopes of that element. Isotopes typically exhibit similar chemical behavior to each other.

Electrons have such little mass that they exhibit properties of both particles and waves; in. We further know from Heisenberg's Uncertainty Principle that it is impossible to know the precise location of an electron. Despite this limitation, there are regions around the atom where the electron has a high probability of being found. Such regions are referred to as atomic orbitals.

## Atomic Orbitals and Quantum Numbers

The relation of a particular electron to the nucleus can be described through a series of four numbers, called the Quantum Numbers. The first three of these numbers describe the energy (Principle quantum number), shape (Angular momentum quantum number), and orientation of the orbital (magnetic quantum number). The fourth number represents the "spin" of the electron (spin quantum number). The four quantum numbers are described below.

### Principle Quantum Number ( $n$ )

The principle quantum number indicates how the distance of the orbital from the nucleus. Electrons are farther away for higher values of  $n$ . Electrons are negatively charged, so electrons that are closer to the positively charged nucleus are more powerfully attracted and tightly bound than those that are farther away. Electrons that are closer to the nucleus are thus more stable, and less likely to be lost by the atom. In other words, as  $n$  increases, so does the energy of the electron and the likelihood of that electron being lost by the atom. In a given atom, all the atomic orbitals with the same  $n$  are collectively known as a shell.  $n$  can take on integer values of 1 or higher (ex. 1, 2, 3, etc.).

### Angular Momentum Quantum Number ( $l$ )

The angular momentum quantum number describes the shape of the orbital. The angular momentum number (or subshell) can be represented either by a number (any integer from 0 up to  $n-1$ ) or by a letter ( $s, p, d, f, g$ , and then up the alphabet), with 0 corresponding to  $s$ , 1 to  $p$ , 2 to  $d$ , and so on. For example:

when  $n = 1$ ,  $l$  can only equal 0; meaning that shell  $n = 1$  has only an  $s$  orbital ( $l = 0$ ).

when  $n = 3$ ,  $l$  can equal 0, 1, or 2; meaning that shell  $n = 3$  has  $s, p$ , and  $d$  orbitals.

s orbitals are spherical, whereas p orbitals are dumbbell-shaped. d orbitals and beyond are much harder to visually represent.

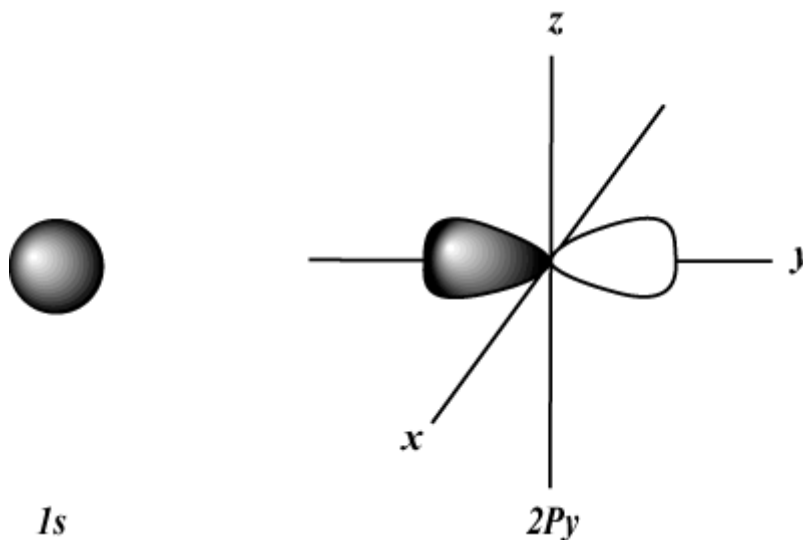


Figure 1.1: s and p atomic orbital shapes

### Magnetic Quantum Number ( $m$ )

Gives the orientation of the orbital in space; in other words, the value of  $m$  describes whether an orbital lies along the x-, y-, or z-axis on a three-dimensional graph, with the nucleus of the atom at the origin.  $m$  can take on any value from  $-l$  to  $l$ . For our purposes, it is only important that this quantum number tells us that for each value of  $n$  there may be up to one s-orbital, three p-orbitals, five d-orbitals, and so on. For example:

The s orbital ( $l = 0$ ) has one orbital, since  $m$  can only equal 0. That orbital is spherically symmetrical about the nucleus.

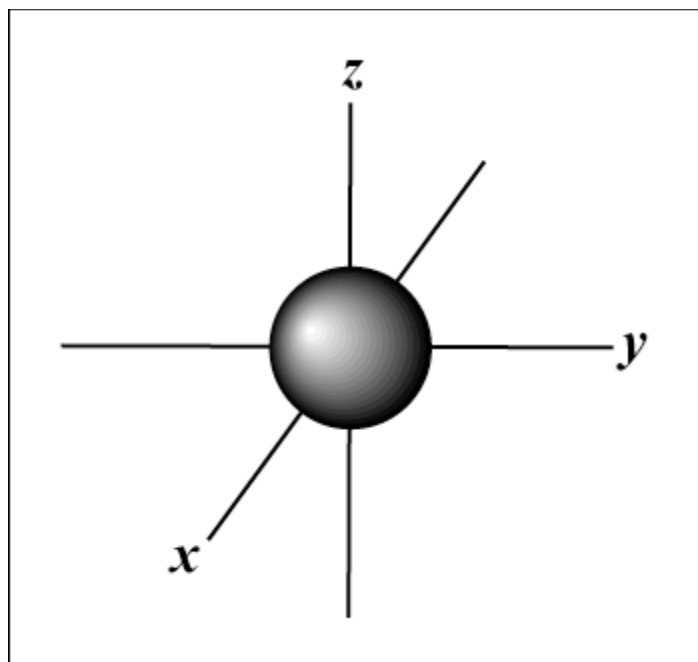


Figure 1.2: s orbital

The  $p$  orbital ( $l = 1$ ) has three orbitals, since  $m = -1, 0,$  and  $1$ . These three orbitals lie along the  $x$ -,  $y$ -, and  $z$ -axes.

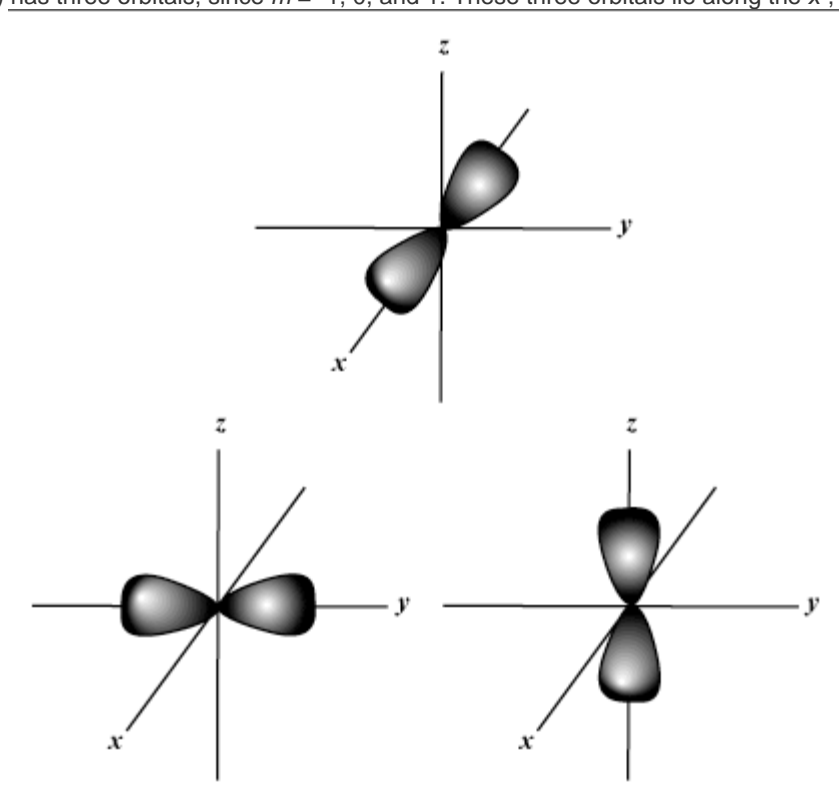


Figure 1.3: p orbitals

The  $d$  orbital ( $l = 2$ ) has five orbitals, since  $m = -2, -1, 0, 1,$  and  $2$ . It is far more difficult to describe the orientation of  $d$  orbitals, as you can see:

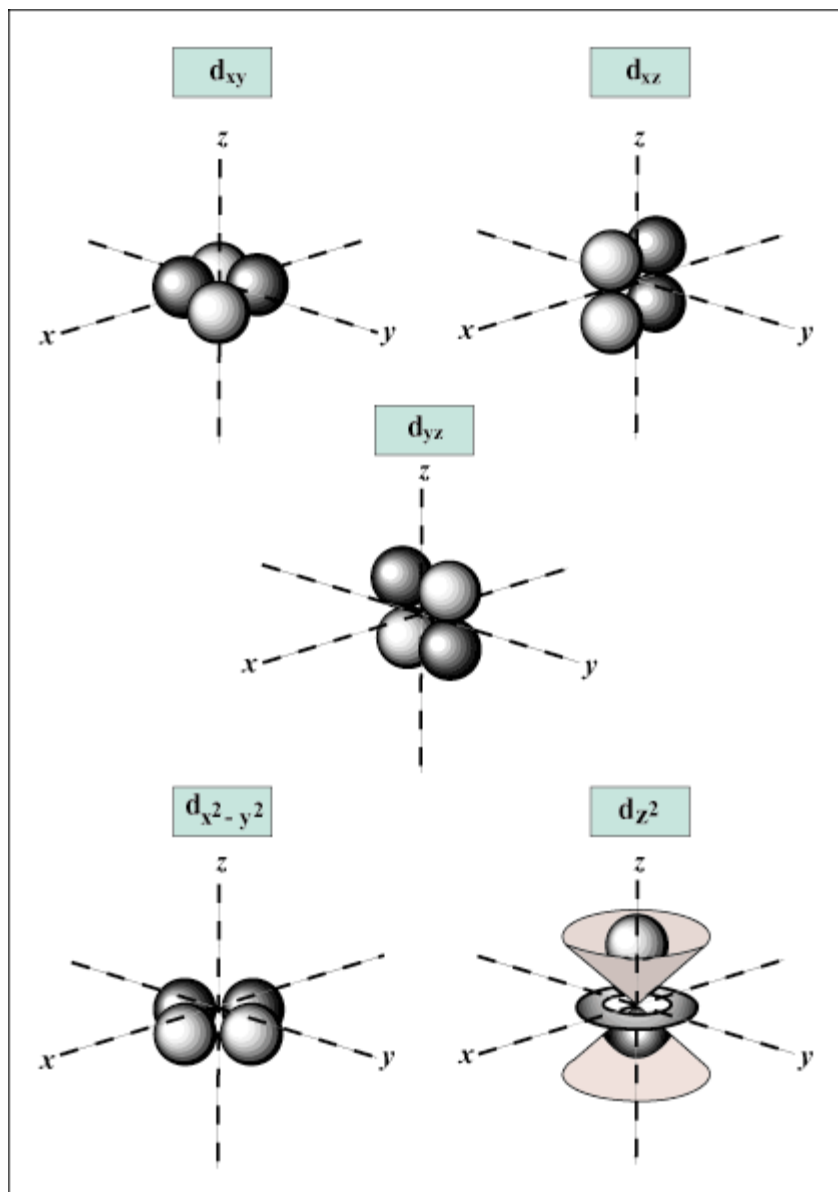


Figure 1.4: d orbitals

### Spin Quantum Number (s):

The spin quantum number tells whether a given electron is spin up (+1/2) or spin down (-1/2). An orbital contains two electrons, and each of those electrons must have different spins.

### Orbital Energy Diagrams

It is often convenient to depict orbitals in an orbital energy diagram, as seen below in . Such diagrams show the orbitals and their electron occupancies, as well as any orbital interactions that exist. In this case we have the orbitals

of the hydrogen atom with electrons omitted. The first electron shell ( $n = 1$ ) contains just the 1s orbital. The second shell ( $n = 2$ ) holds a 2s orbital and three 2p orbitals. The third shell ( $n = 3$ ) holds one 3s orbital, three 3p orbitals, and five 3d orbitals, and so forth. Note that the relative spacing between orbitals becomes smaller for larger  $n$ . In fact, as  $n$  gets large the spacing becomes infinitesimally small.

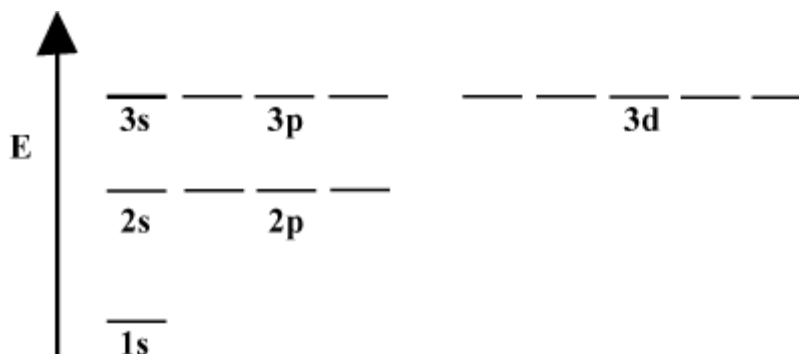


Figure 1.5: Energy diagram of the unoccupied atomic orbitals of hydrogen. Potential energy is on the y-axis.

You will see such energy diagrams quite often in your continuing study of chemistry. Notice that all orbitals with the same  $n$  have the same energy. Orbitals with identical energies are said to be degenerate (not in the moral sense!). Electrons in higher-level orbitals have more potential energy and are more reactive, i.e. more likely to undergo chemical reactions.

### Multi-electron atoms

When an atom only contains a single electron, its orbital energies depend only on the principle quantum numbers: a 2s orbital would be degenerate with a 2p orbital. However, this degeneracy is broken when an atom has more than one electron. This is due to the fact that the attractive nuclear force any electron feels is shielded by the other electrons. s-orbitals tend to be closer to the nucleus than p-orbitals and don't get as much shielding, and hence become lower in energy. This process of breaking degeneracies within a shell is known as splitting. In general s orbitals are lowest in energy, followed by p orbitals, d orbitals, and so forth.

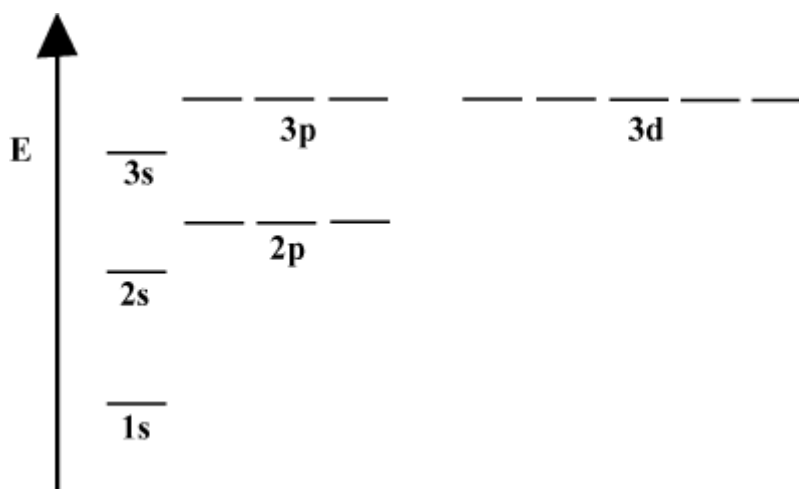


Figure 1.6: Splitting of orbital energies in multi-electron systems

### Electron Energy

The energy diagram of imply a further fact about the energy of electrons. Note that the energy levels in these diagrams do not follow a continuous line: an atom is either in one energy subshell or it is in another. There is no in between. In this way, the diagram perfectly represents the *quantized nature* of electrons, meaning that electrons can only exist at specific and defined energy levels. The energy level of an electron in a particular energy shell can be determined according to the following equation:

$$E_n = \frac{-2.178 \times 10^{-18} \text{ joules}}{n^2}$$

where  $n$  is the principal quantum number and  $E_n$  is the energy level at that quantum number. When an electron absorbs a specific quanta of energy it can jump to a higher energy level. It can also give off a specific quanta and fall back to a lower energy level. An atom whose electrons are at their lowest energy levels is said to be in the ground state. The discovery of the quantum nature of energy and electrons, first formulated by Max Planck in 1900, led to the creation of an entirely new field, quantum mechanics.