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Ch. 1. Electronic structure of atoms

MATTER is everywhere around you, from the water you drink to the air you inhale. The matter is made of elements and elements are made of atoms. In the world, we can also find light, that somehow at first sight seems different than matter. Light is warm and it has color. This chapter covers the structure of the atoms, with a focus on the structure of the many electrons that atoms are made of. It also focuses on light and the interaction of light with matter. You will be able to understand differences in electronic configuration.

“ The present is the only thing that has no end. ”
Schrödinger

1.1 The nature of light

Light—also called electromagnetic radiation—is a form of energy. When talking about light we normally refer to visible radiation. However, there are many different types of radiation. Think about the light coming from a bulb, or the radiation that warms up your food in a microwave, or even when you warm up a pizza in the oven. This section will cover the properties of light.

Light as a wave Light behaves as a wave. Waves are characterized by their frequency, wavelength and amplitude. The wavelength of a wave (λ , lambda) is the distance between identical points on successive waves (or successive peaks). The frequency of a wave (ν , nu) is the number of waves that pass through a particular point in one second. The amplitude (A) of a wave is the vertical distance from the zero to the top of the peak, or from the zero to the bottom of the peak. The amplitude of a wave is related to the intensity of the radiation. The speed of light through the vacuum is 3×10^8 m/s. However, the speed of light depends on the medium and light tends to slow down when traveling in a medium different than vacuum.

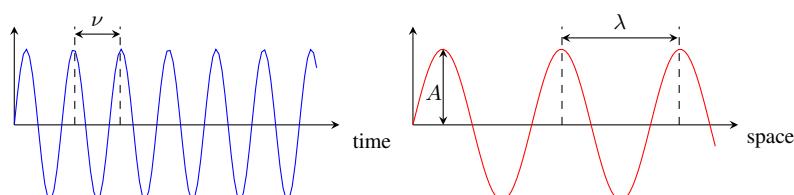


Figure 1.1 Properties of waves. Waves are characterized by its frequency, wavelength and amplitude and in the vacuum they travel at the speed of light.

Frequency and energy Light travels in time. That is the reason you can hear a whistle from afar. The *frequency* of a radiation—the frequency of a specific type of

light—characterizes how this radiation oscillates in time. The unit of frequency is the hertz and frequency is represented by the symbol ν . At the same time, frequency is connected to the energy of radiation. High frequency radiation are very energetic. Think for example of gamma rays; these type of radiation produced in nuclear plant has very high frequency and hence is very energetic. The formula that related frequency with energy is:

$$E = h\nu \quad \text{Frequency formula}$$

where:

E is the energy in joules

$h = 6.6 \times 10^{-34}$ is called Plank's constant

ν is frequency in hertz ($\text{Hz}=\text{s}^{-1}$)

As you can see in the previous formula, the frequency is directly proportional to frequency. This equation has a historical character and was established by Max Plank in 1900. When a solid is warmed up to temperatures beyond 800K—this is called a black body—it emits radiation of different color. The radiation emitted changes as the body is heated, and the light emitted goes from red to white. In the later part of the nineteenth century, experiments found that the amount of energy produced by a black body depends on the wavelength of the emitted radiation. However, none of the current theories (thermodynamics and classical physics) were able to explain that phenomena. Plank came with a solution for the dilemma. Classical physics assumes that radiant energy is a continuous and radiation can be emitted and absorbed at any amount. In order to explain the blackbody radiation, Plank suggested that there is a minimum package of energy so that radiation could only be exchanged in discrete packages. The smallest amount of energy that can be emitted in the form of electromagnetic radiation was called *quantum* and equals to $h\nu$, with h being Plank's constant. Based on his theory, the energy emitted by light can only be whole-number multiples of $h\nu$. This hypothesis was the key to solve the blackbody radiation dilemma and change physics forever, marking the beginning of a new quantum theory.

The speed of light All light travel at the same speed in the vacuum and this speed is called the speed of light, c . The numerical value of the speed of light is 299 792 458 m / s which is close to 3×10^8 m/s. When light travels in a medium, like water or glass, its velocity can be lower than the speed of light as the medium slows down the propagation of light. At the same time, the speed of light is used to relate two properties of light: the frequency and its wavelength:

$$c = \nu \cdot \lambda \quad \text{the speed of light}$$

where:

c is the speed of light in the vacuum, 3×10^8 m/s

λ is wavelength in m

ν is the frequency in Hz.

If we want λ to be in nm we can use the following formula:

$$\nu = \frac{3 \times 10^{17}}{\lambda}$$

where:

ν is frequency in Hz

λ is wavelength in nm

$3 \times 10^{17} = c \cdot 10^9$ was adjusted to be able to use λ in nm

Mind that all radiation always travels at the speed of light in a vacuum. At the same time, this speed is the maximum speed allowed for any object, based on the principles of relativity.

Wavelength and energy Light also travels in space. As it moves, it oscillates in space. Think about dropping a stone into a lake. As you drop the pebble, the energy from the pebble propagates in the surface in water. The energy of light also propagates in space and the *wavelength* of a radiation is the distance between two consecutive peaks. As such, wavelength, represented by the letter λ and oftentimes with units of nm is also related to energy by means of the formula:

$$E = \frac{1.98 \times 10^{-16}}{\lambda}$$

wavelength formula

where:

E is the energy in joules

λ is wavelength in nm

$1.98 \times 10^{-16} = h \cdot c \cdot 10^9$ was adjusted to be able to use λ in nm

Mind that wavelength is inversely related to energy. That means, the larger wavelength the smaller energy. Also mind that wavelength refers to the movement of light in space and frequency refers to the movement in time.

Sample Problem 1

Calculate: (a) the energy of a radiation with wavelength of 300nm; (b) the energy of a radiation with frequency of 10^{19} Hz; (c) the frequency of a radiation with wavelength of 300nm.

SOLUTION

(a) To answer the first question we will use the wavelength formula, as wavelength is given ($\lambda = 300\text{nm}$) and we need to calculate the energy (E), in Joules:

$$E = \frac{1.98 \times 10^{-16}}{\lambda} = \frac{1.98 \times 10^{-16}}{300} = 6.6 \times 10^{-19} \text{ J}$$

(b) To answer the second question we will use the frequency formula, as frequency is given ($\nu = 10^{19}\text{Hz}$) and we need to calculate the energy (E), in Joules:

$$E = 6.6 \times 10^{-34} \nu = 6.6 \times 10^{-34} \cdot 10^{19} = 6.6 \times 10^{-15} \text{ J}$$

(c) To answer the last question we will use the formula that related frequency with wavelength—through the speed of light—as frequency is asked and wavelength is given ($\lambda = 300\text{nm}$); mind the units of frequency are hertz:

$$\nu = \frac{3 \times 10^{17}}{\lambda} = \frac{3 \times 10^{17}}{300} = 1 \times 10^{15} \text{ Hz}$$

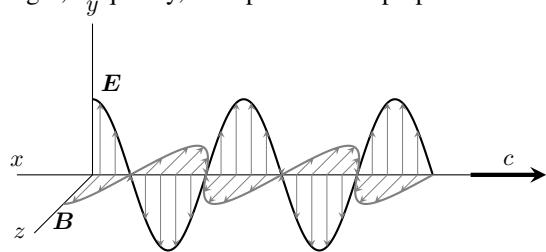
◆ STUDY CHECK

Calculate: (a) the wavelength of radiation with energy of $5.6 \times 10^{-19} \text{ J}$; (b) the

frequency of a radiation with frequency of $4.8 \times 10^{-18} \text{ J}$; (c) the wavelength of a radiation with frequency of $2 \times 10^{15} \text{ Hz}$.

The electromagnetic spectrum of light Visible light consist of electromagnetic waves, which have an electric field and magnetic field component. These two components share the same wavelength, frequency, and speed but are perpendicular to each other.

Figure 1.2 The electric (E) and magnetic (B) field components of an electromagnetic wave. Both fields are perpendicular.



The double-slit experiment: light diffraction The double-slit experiment was intended to demonstrate the wave nature of light. When a source of light passes through a narrow opening called slit a bright spot is generates on the other side of the slit. When a source of light passes through two slits surprising results arise. One would expect to see two bright spots, one per each slit. However, what you really would see would be a series of bright spots and dark spots, resulting of the interference of light. As light is a wave it can interfere and light plus light does not always gives more light, and can sometimes genera darkness. The bright spots result from the constructive interference of the light waves whereas the dark spots result from the destructive interference. Overall, waves propagate energy and the results of the propagation can be more light or less light depending on how these waves interfere.

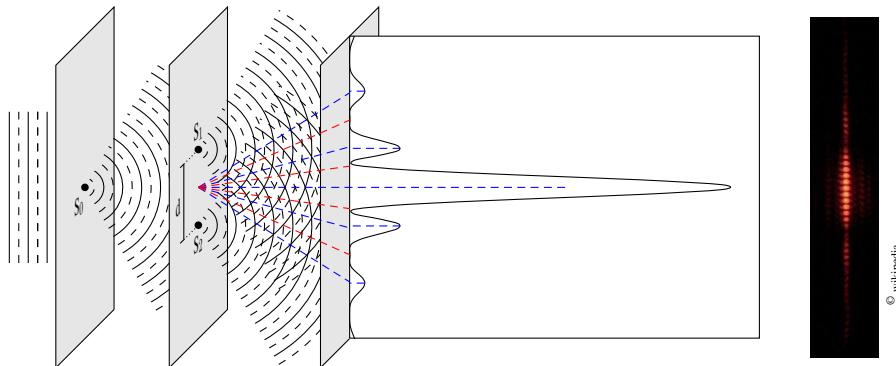


Figure 1.3 The double-slit experiment demonstrating the wave nature of light. Using one slit leads to a single bright spot. Using two slits leads to a set of patterns of light and darkness resulting from the interference of light. Red lines represent destructive interference whereas blue lines represent constructive interferences.

▼ Standing waves of a guitar



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▼ Traveling waves



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▼ Light is a wave



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Table 1.1 Types and color of radiation

Type of radiation	ν (Hz)	Color of radiation	λ (nm)
Gamma	$>3 \times 10^{19}$	Violet	380-450
X-rays	$3 \times 10^{19} - 3 \times 10^{16}$	Blue	450-485
UV	$3 \times 10^{16} - 8 \times 10^{14}$	Cyan	485-500
IR	$4 \times 10^{14} - 4 \times 10^{11}$	Green	500-565
MicroW	$3 \times 10^{11} - 3 \times 10^8$	Yellow	565-590
RadioW	$3 \times 10^8 - 3 \times 10^3$	Orange	590-625
		Red	625-740

Types and color of radiation Depending on its frequency—or on its wavelength—radiation can be classified as gamma rays, x rays, ultraviolet (UV), visible, infrared (IR), microwaves or radio waves. For example, radiation with wavelength of 10^{-2} nm belongs to gamma rays radiation, whereas radiation with wavelength of 10^4 nm belongs to the Infrared. Gamma rays are the most energetic type of radiation, whereas radio waves are the less energetic waves. At the same time, radio waves have the largest wavelength. Light not always have color. Only a small range of wavelengths belong to visible radiation and the visible spectrum correspond to the set of visible frequencies. This means you will not be able to see for example, IR radiation or gamma rays. The color of the radiation is also dependent on the wavelength—or the frequency as both are related—and for example $\lambda = 450$ nm will be blue light. Ultraviolet radiation is the most energetic visible radiation whereas infra red waves are the less energetic waves of the visible spectrum.

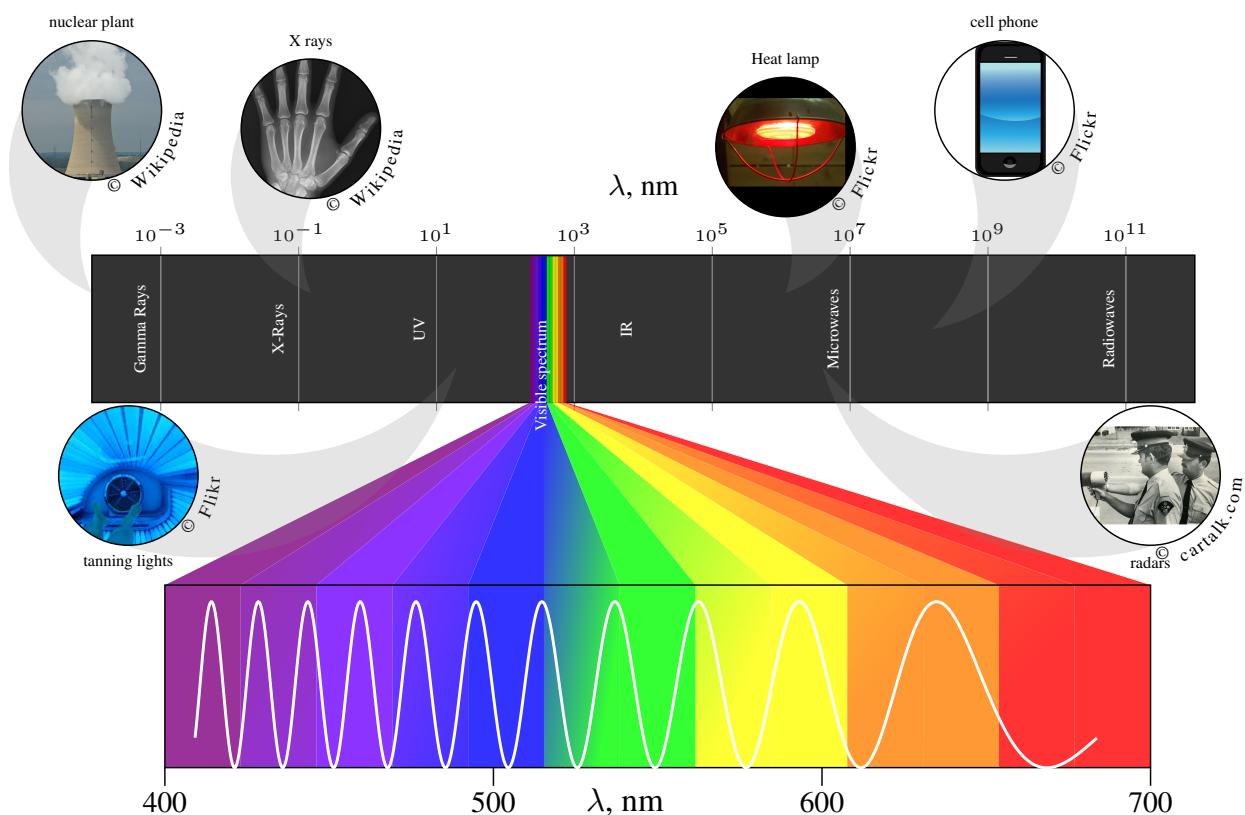


Figure 1.4 Spectrum of the electromagnetic radiation, from gamma rays (shortest wavelength) to radio waves (highest wavelength). The visible part of the spectrum ranges from 400 nm (violet) to 700 nm (red).

Sample Problem 2

Indicate: (a) the color of a radiation with $\lambda = 650\text{nm}$; (b) the type of a radiation with $\lambda = 10^5\text{ nm}$; (c) the type of a radiation with $\nu = 10^{16}\text{ Hz}$.

SOLUTION

We can answer the first questions by inspecting the figure above we can see that $\lambda = 650\text{nm}$ corresponds to red radiation. To answer the second question we will also use the figure above, where we can see that $\lambda = 10^5\text{ nm}$ belongs to the infrared. Finally, in order to answer the last question we need to convert frequency into wavelength, as the figure above only indicates wavelength. $\nu = 10^{16}\text{ Hz}$ corresponds to $\lambda = 30\text{ nm}$. Hence, this frequency corresponds to the UV.

◆ STUDY CHECK

Indicate: (a) the color of a radiation with $\nu = 7.5 \times 10^{14}\text{ Hz}$; (b) the type of a radiation with $\nu = 10^{10}\text{ Hz}$.

Electron-Volt: a new unit of energy Sometimes, it is convenient to use another energy unit, called electron-volt, that makes these values have more reasonable values.

$$1\text{eV} = 1.60218 \times 10^{-19}\text{J}$$

or

$$\frac{1\text{eV}}{1.60218 \times 10^{-19}\text{J}}$$

For example, the energy in eV of the first level is $E_1 = -13.6\text{eV}$, whereas the energy of the third level is $E_3 = -1.5\text{J}$.

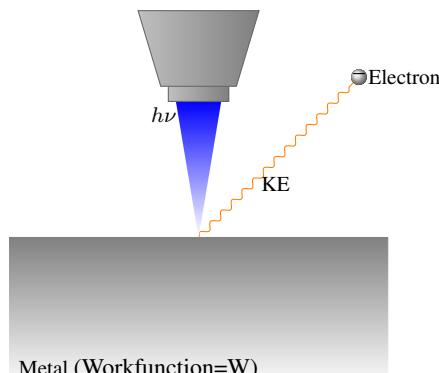


Table 1.2 Workfunctions and threshold frequencies

Element	W (eV)	ν_c, Hz
Ag	4.64	1.1×10^{15}
Ba	2.52	6.1×10^{14}
Fe	4.67	1.1×10^{15}
Al	4.20	1.0×10^{15}
Ca	2.87	6.9×10^{14}
Mn	4.1	9.9×10^{14}

Figure 1.5 The photoelectric effect: when light with frequency (ν) larger than a threshold irradiates a metal, electrons are ejected with a specific kinetic energy (KE) that depends on the work function (W) of the metal.

The photoelectric effect The photoelectric effect was a mysterious phenomena discovered early in the twentieth century. Scientist found that if you expose a metal to light, under certain conditions, it emits electrons—it produced electricity. They found that the intensity—the brightness—of the radiation was not a key component of this phenomena, and not by increasing the intensity you were able to produce electrons. The key was the frequency of the radiation. For frequencies above a specific threshold radiation was produced. If the frequency was above that threshold—called threshold radiation, ν_c —then the larger the intensity of the radiation the more electrons were produced. On that time, the current theory of light, associating intensity of light with energy, was unable to explain this phenomena. Albert Einstein used Plank's theory of the blackbody radiation to solve this mystery. He assumed that light is made of a stream

of particles called photons, each with a given energy, $h\nu$. The electrons of a metal are held by attractive forces. A property called work function W —or biding energy—tells how strongly the electrons of a metal are held together. In Table 1.2 you can find numerous workfunctions. Metals such as Fe have high workfunctions in comparison to metals such as Ca, that means it takes more energy to remove an electron from the metal. Therefore, if the energy of the radiation was enough to overcome this forces, the electron emission will happen. In other words, if $h\nu$ is larger than W the electron emission will happen and the electrons emitted will have a kinetic energy (KE) equal to:

$$KE = 4.13 \times 10^{-15} \nu - W \quad \text{Photoelectric effect}$$

where:

KE is the kinetic energy of the emitted electrons in eV

4.13×10^{-15} is called Plank's constant in eV· s, h

ν is frequency in hertz (Hz)

is the workfunction of the metal in eV

What is the threshold frequency, ν_c ? When the energy of the radiation is the same as the work-function of the metal, then electrons are ejected. This way, the threshold frequency is just the work-function of the metal converted in units of frequency:

$$\nu_c = \frac{W}{4.13 \times 10^{-15}} \quad \text{threshold frequency}$$

4.13×10^{-15} is called Plank's constant in eV· s, h , ν_c is the threshold frequency in hertz (Hz) and W is the workfunction of the metal in eV. Einsteins theory of the photoelectric effect shocked the scientific community. Before this theory, light was considered a wave. Based on Einstein's theory, wave poses properties of both a particle and a wave, and depending on the experiment one experience light as a wave or as a particle.

Sample Problem 3

A metal with workfunction of 5eV is exposed to a radiation source with frequency of 2×10^{15} Hz. Indicate whether electrons will be ejected and if so, indicate the kinetic energy of these.

SOLUTION

Using the photoelectric effect equation we have that a radiation of 10^{15} Hz frequency has an energy of

$$4.13 \times 10^{-15} \cdot 2 \times 10^{15} = 8.27 \text{eV}$$

As this values is larger than the workfunction of the metal ($W=5\text{eV}$), therefore electrons will be ejected with a kinetic energy of:

$$KE = 8.27 - 5 = 3.27 \text{eV}$$

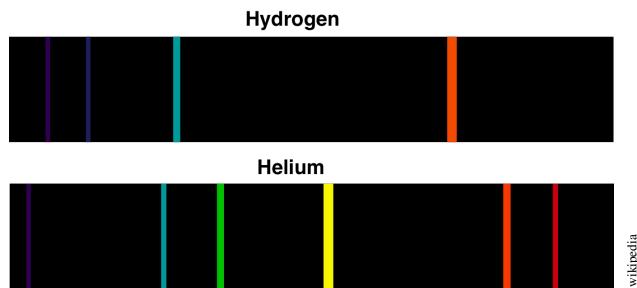
◆ STUDY CHECK

A metal with workfunction of 5eV is exposed to a radiation source with frequency of 9×10^{14} Hz. Indicate whether electrons will be ejected and if so, indicate the kinetic energy of these.

1.2 The atomic line spectra

This section will explain the atomic spectra of atoms and in particular, hydrogen. Atoms emit light, but not any type of light as they emit specific frequencies of radiation. The atomic spectrum is a representation of the different wavelengths of the radiation emitted—or absorbed—by an atom. This section will gain insight into the reasons for the emission of specific frequencies of light and will introduce the Bohr model that justifies the lines in the atomic spectrum of hydrogen.

Spectrum of atoms The absorption spectrum of an atom is a representation of the different frequencies in which an atom absorbs or emits radiation. Each atom has a distinctive emission spectrum. Some of these lines correspond to the visible spectrum, that is, they can be seen. Others correspond higher or lower parts of the spectrum. This section will cover the spectrum of hydrogen.



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Figure 1.6 Atomic spectrum of two atoms showing the lines corresponding to the visible.

Atomic line spectrum of hydrogen Newton showed that sunlight (white light) is composed of various components of different colors. Similar type of radiation called emission spectra can be produced by heating a substance. Think for example of a hot piece of metal. Both the sun and a heated piece of metal have in common the fact that their spectrum is continuous and contains all wavelengths of visible light. We can achieve a similar effect by applying a high-voltage electrical discharge to a gas. The atomic line spectrum of a gas is a set of lines on a black (or sometimes white) background. These lines correspond to radiation emitted (or absorbed) by atoms. Some of these lines correspond to the visible spectrum, that is, have color—these are called the Balmer series. Other lines correspond to other parts of the spectra of radiation. This spectrum is historically important and was used to understand the structure of the electrons in the atom. In contrast to the sunlight spectrum, the atomic spectrum of a gas is not continuous but quantized.

The Bohr model The Bohr model explains the electronic structure of hydrogen, in particular the spectrum of hydrogen and the position of the different energy levels. This model is based on the idea that the electron of hydrogen moves around the nucleus only in certain allowed circular orbits. Each orbit is called energy level, being characterized by an energy E_n and an integer number n . The following formula gives you the energy value for each level:

$$E_n = -2.178 \times 10^{-18} \frac{1}{n^2}$$

Bohr formula in J

where:

E_n is the energy of the level n in joules

n is the number of the level

$-2.178 \times 10^{-18} J = R_H$ is called the Rydberg constant ($-13.59 eV$)

For example, the energy of the first level is $E_1 = -2.178 \times 10^{-18} J$, whereas the energy of the third level is $E_3 = -5.44 \times 10^{-19} J$; the higher the n the larger—more positive—is the energy of the level.

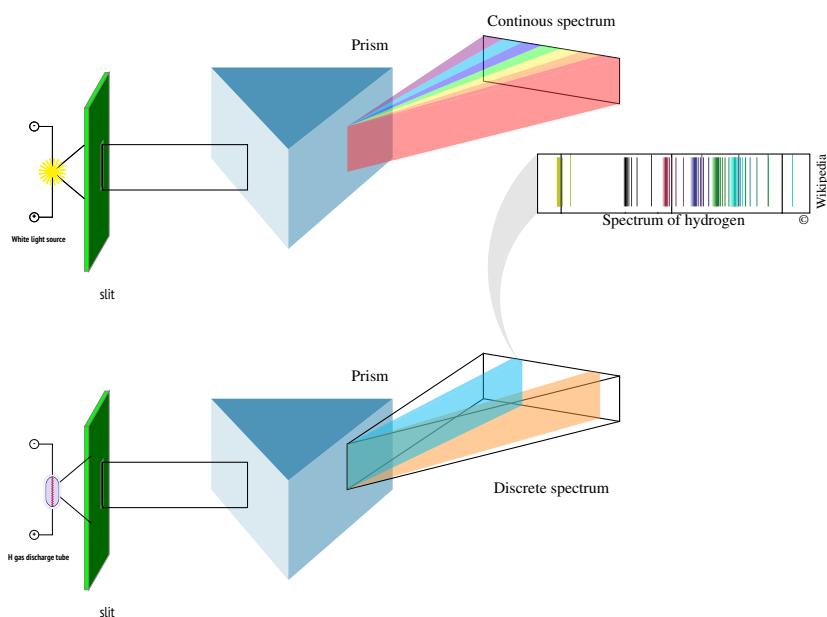


Figure 1.7 The spectrum of hydrogen: white light contains radiation of all colors of the visible spectrum whereas light coming from hydrogen contains a quantized series of lines.

Energy levels of hydrogen Let's gain deeper insight into the idea of an energy level. These are just numbers that represent the location—in energy units—of the different states that an electron can occupy in an hydrogen atom. The first level is E_1 and is the most negative energy value, being also the most stable level. In another words, the electrons in this level are tightly bonded to the nucleus. This energy levels is called the fundamental energy level. The following levels (E_2, E_3, \dots, E_n) have a more positive energy. For example, comparing E_2 and E_4 , we have that an electron on the level number four ($E_4 = -0.85 eV$) is less stable than on level two ($E_2 = -3.40 eV$). Hence it would be easier to remove an electron from level number four than from level two. For small n values the levels are spread from each other. However, when n increases, the energy levels are more and more closer to each other. Electrons occupying energy levels with n higher than one are called excited states. Finally, there are infinite number of levels and the highest energy (E_∞) level has an energy of 0J. The electron transitions between the different energy levels is what generates the emission spectrum of hydrogen.

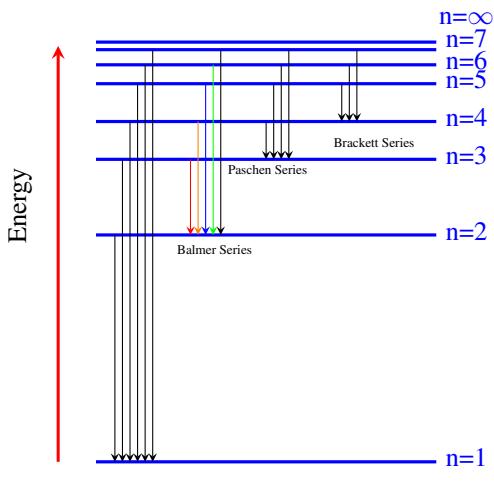


Figure 1.8 Energy levels of Hydrogen and the different emission series. Each series—called Lyman, Balmer, Paschen and Brackett—terminates at a different value of n .

Table 1.3 Emission spectrum of H

Series	n_f	n_i	Region
Lyman	1	2, 3, 4, ...	UV
Balmer	2	3, 4, 5, ...	Visible and UV
Paschen	3	4, 5, 6, ...	IR
Brackett	4	5, 6, 7, ...	IR

Transition energies Bohr's models is able to explain the atomic spectrum of hydrogen. Each line in the spectrum represents a transition between two levels of energy. For example the line at 102nm represents the transition of an electron between the level three and the level one, we call this $3 \rightarrow 1$. The atomic spectrum of hydrogen is obtained by means of exciting hydrogen atoms with energy, so that the electron jumps from a lower level into a higher level. When the atom relaxes, it emits light as the electrons move back from high every levels into lower—more stable—levels. This is called an emission. The different possible emissions have names based on the person who discovered them. For example, the set of emissions that end up in the fundamental level ($n=1$) are called the Lyman series. Similarly, the set of emissions that end up in the level ($n=2$) are called the Balmer series. For example: $3 \rightarrow 2$, $4 \rightarrow 2$ or $5 \rightarrow 2$. Only the Balmer series correspond to emissions on the visible spectra. The Lyman series belong to the ultraviolet and the Paschen and Brackett series belong to the infrared.

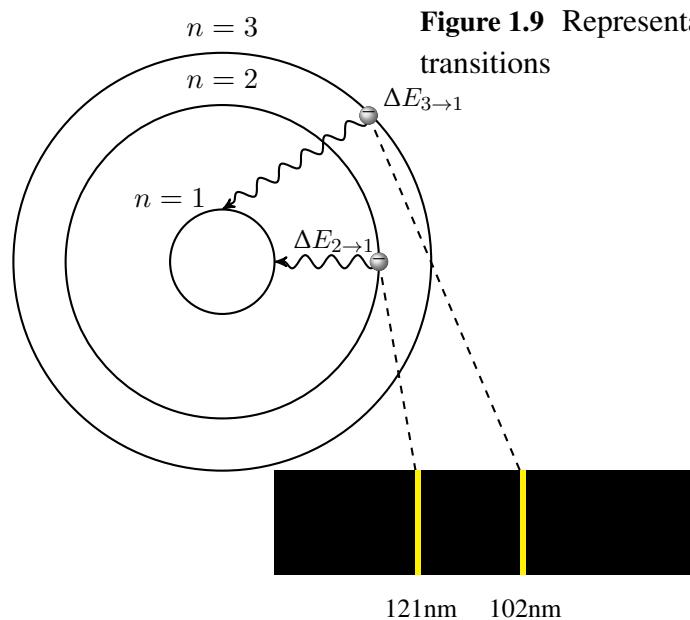


Figure 1.9 Representation of two energy transitions

Bohn's formula for energy transitions Bohr's formula gives you the values of the energy levels. If we subtract the energy values for two energy levels, we obtain the energy for a transition. The energy for an electron transition between two

energy levels, from n_1 to n_2 is given by:

$$\Delta E_{n_1 \rightarrow n_2} = -2.178 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

Energy transition formula

where:

$\Delta E_{n_2 \rightarrow n_1}$ is the energy in joules for the transition, the line in the spectra

n_2 is the number of the final level

n_1 is the number of the initial level

$-2.178 \times 10^{-18} J = R_H$ is called the Rydberg ($-13.59 eV = R_H$)

Sample Problem 4

Calculate the following transition energies:

- (a) $\Delta E_{4 \rightarrow 3}$ in J
- (b) $\Delta E_{4 \rightarrow 3}$ in eV
- (c) Calculate the final energy level for a transition with energy 1.34eV knowing the first energy level involved in the transition is $n = 3$

SOLUTION

(a) We will use the energy transition formula to calculate the energy needed to move one electron from $n_1 = 4$ to $n_2 = 3$:

$$\begin{aligned}\Delta E_{n_2 \rightarrow n_1} &= -13.59 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = -13.59 \left(\frac{1}{3^2} - \frac{1}{4^2} \right) \\ &= -13.59 \left(0.111 - 0.0625 \right) = -0.66 eV\end{aligned}$$

The transition energy is negative, this means the atom releases energy when transitioning between these two levels.

(b) We will use the energy transition formula this time in eV:

$$\begin{aligned}\Delta E_{n_2 \rightarrow n_1} &= -2.178 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = -2.178 \times 10^{-18} \left(\frac{1}{3^2} - \frac{1}{4^2} \right) \\ &= -2.178 \times 10^{-18} \left(0.111 - 0.0625 \right) = -1.058 \times 10^{-19} J\end{aligned}$$

(c) In this case, we know $\Delta E_{n_2 \rightarrow 3}$ and we know the initial level is $n_1 = 3$. We can certainly solve for n_2 :

$$1.34 = -13.59 \left(\frac{1}{n_2^2} - \frac{1}{3^2} \right) = -13.59 \left(\frac{1}{n_2^2} - \frac{1}{9} \right)$$

Solving for n_2 we have: $n_2 = 9$. Mind you need to square root n_2^2 to get the final value of n_2 .

❖ STUDY CHECK

Calculate the following transition energies: (a) $\Delta E_{9 \rightarrow 3}$ in J and (b) $\Delta E_{5 \rightarrow 4}$ in eV.

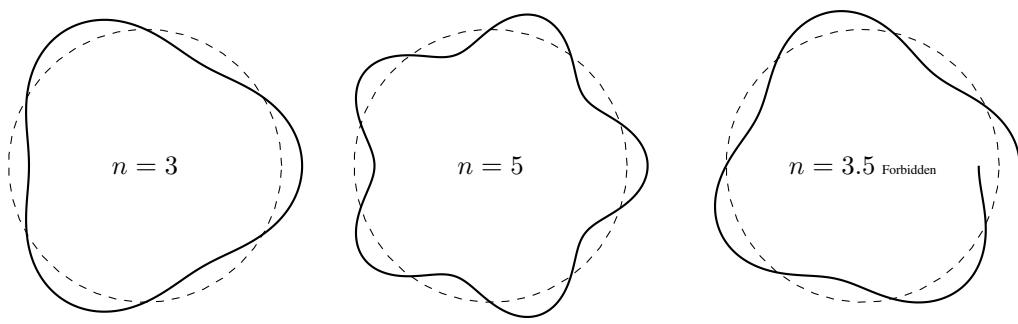


Figure 1.10 In the circular Bohr's orbits, electron could only have wavelengths that are a multiple of the orbit length, of the wave would cancel (forbidden orbits).

The wave properties of matter Bohr's models was able to explain the experimental data for the hydrogen spectrum but still scientist—not even Bohr himself—did not know why electrons were restricted to move in specific orbits. Louis de Broglie solved this questions by suggesting that if light can behave—under some conditions—as a particle, perhaps particles such as electrons, can also behave as a wave—under certain circumstances. De Broglie deduced that a particle and wave are related by the following expression:

$$\lambda = \frac{h}{m \cdot v}$$

where:

λ is De Broglie's wavelength of a particle

$6.6 \times 10^{-34} \text{ Js}$ is called Plank's constant, h

$m \cdot v$ is the momentum of a particle, p , that depends on the mass and velocity of the particle

In general the wavelength of a particle is referred as the De Broglie wavelength and the mass associated with a wavelength is called De Broglie mass. De Broglie came to this conclusion using the following reasoning: if an electron in the hydrogen atoms behaves like a wave then its wavelength (λ) must fill the length of the circular orbit ($2\pi r$) so that

$$n\lambda = 2\pi r$$

Sample Problem 5

Calculate the De Broglie wavelength of a tennis ball with mass 0.1Kg and velocity 100m/s.

SOLUTION

We will use De Broglie's relationship that associated a wavelength (λ) to a particle, in which the mass is 100g, the velocity 10m/s:

$$\lambda = \frac{6.6 \times 10^{-34} \text{ Js}}{0.1 \text{ Kg} \cdot 100 \text{ m/s}} = 6.6 \times 10^{-35} \text{ m}$$

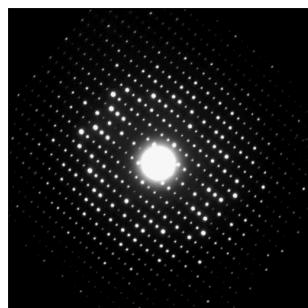
Regarding the units: remember J is Kgm^2/s^2 and therefore Js is the same as Kgm^2/s .

❖ STUDY CHECK

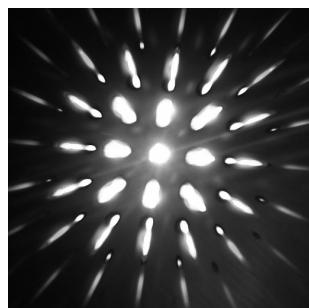
Calculate the De Broglie wavelength of an electron at a velocity of 100m/s given that an electron mass is $9 \times 10^{-31} \text{ kg}$.

Electron diffraction Following De Broglie's proposal that particles behave like waves under certain circumstances, particles, in particular, electrons were found to exhibit properties of wave. The diffraction of electrons was achieved by Davidsson and Germer by directing a beam of electrons through a thin piece of gold foil creating a pattern similar to the diffraction of x-rays.

▼Diffraction pattern of electrons ▼Diffraction pattern achieved with a laser



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Figure 1.11 Diffraction patterns produced by light and by matter

The uncertainty principle Waves result from the propagation of energy and are not localized. Electrons behave as waves under certain conditions. In order to approach the problem of trying to locate a particle that behaves as a wave, Heisenberg uncertainty principle states that it is impossible to measure simultaneously both the momentum ($m \cdot v$) and the position (x) of a particle. In other words, the uncertainty of the position (Δx) and the uncertainty on the momentum ($m \cdot \Delta v$) are linked by the relationship:

$$\Delta x \cdot m \Delta v \geq \frac{h}{4\pi} \quad (1.1)$$

This relation, involving Plank's constant h , should be interpreted as: if the uncertainty of the position is large, then the uncertainty of the velocity (or momentum) must be small. And the minimum values for the product of uncertainties if $\frac{h}{4\pi}$.

Sample Problem 6

The velocity of an electron is $2 \times 10^5 \pm 2 \times 10^3 \text{ m/s}$ given that the mass of an electron is $9 \times 10^{-31} \text{ kg}$. Calculate the minimum uncertainty in the position of the electron.

SOLUTION

We will use Heisenberg's relationship that links the uncertainty of the momentum and the position, given that the uncertainty of the velocity (Δv) is $2 \times 10^3 \text{ m/s}$ and h is $6.6 \times 10^{-34} \text{ kg m}^2/\text{s}$:

$$\Delta x \cdot 9 \times 10^{-31} \cdot 2 \times 10^3 \geq \frac{6.6 \times 10^{-34}}{4\pi}$$

We have that the uncertainty on the position Δx is larger or equal than $2.9 \times 10^{-8} \text{ m}$.

◆ STUDY CHECK

The uncertainty on the position of a particle with a mass of $1.7 \times 10^{-27} \text{ kg}$ is $\pm 10^{-11} \text{ m}$. Calculate the uncertainty on the velocity of the particle.

1.3 Quantum mechanics

Bohr's model was simplistic but still, it was able to correctly predict the fine structure of hydrogen—the atomic spectrum of hydrogen—and the energy transitions. The downside of this model resulted from considering that the electron moves in different orbits and that it did not provide a complete description of the behavior of the electrons in atoms. A correct assumption of the model was that the energy levels of the atom were quantized—electrons can only exist in specific energy levels characterized by the number n and not in a continuum of energy. This section will cover a more realistic theory that describe the structure of the atom: quantum mechanics. The outcome of this section is the existence of orbitals and quantum numbers.

Quantized energy and continuum energy Quantum mechanics is a theory shared in physics and chemistry that describe the nature of matter. It is used to do modeling in chemistry—to model molecules and atoms. Think of an engineer designing a plane. Before building and selling the plane engineers carry computer-based modeling to ensure the plane will work properly. In a similar way, chemists carry modeling to describe the properties of chemicals. The theory behind engineering modeling is classical mechanics, based in Newton's law. The theory behind chemistry modeling is quantum mechanics, based in Schrödinger equation. Classical mechanics is based on the idea that the energy of a system, a plane or a car, is continuum, that is, the car or a plane can have any possible energy, starting from zero to any number you can think of. Differently, quantum mechanics is based in the idea that the energy of a system, an atom or a molecule, is quantized, that is it can only be certain specific values.

The Schrödinger equation The Schrödinger equation is the fundamental equation in quantum mechanics. It was formulated by Erwin Schrödinger in 1926, an Austrian physicist, and it was based on complex mathematical techniques. This equation incorporates the electron behavior in terms of particle through its mass and in terms of wave through a wave-like function, Ψ .

$$\hat{H}\Psi = E\Psi$$

\hat{H} is called hamiltonian operator and contains a kinetic energy and potential energy component. Ψ , the wave function depends on the location of the space of each electron in the system. E are the energy levels. The solution of this equation required advanced calculus and will not be covered here. In contrast to simple algebraic equation in which the answer is a simple number, the result of solving the Schrödinger equation is a set of functions and a number for each of these functions. The functions are called wavefunctions ($\{\Psi_1, \Psi_2, \dots, \Psi_n\}$) and for each wavefunction there is an energy value, leading to a set of energy levels ($\{E_1, E_2, \dots, E_n\}$). The introduction of The Schrödinger's equation mark the beginning of a new field in physics and chemistry called quantum mechanics or wave mechanics. Quantum mechanics do not allow us to specify the location of an electron in an atom, however it allows to identify the area in the space where the electron is most likely to be located at a given time. Electron density refers to the probability that an electron is found in a particular region of an atom.

The wave function: orbitals In quantum mechanics the wave function Ψ of an atom or a molecule (a system) is a complex function—it has an imaginary component—that contains all information of the system. By means of this function, we can simulate

the behavior of the system and extract its properties. You want to think of Ψ as a box that contains information, in particular all information of the system you want to simulate. When expressed in spherical coordinates, Ψ depends on the position (r) and two angles (θ and φ) of each electron of the system. This function Ψ *per se* has no real meaning or interpretation. Differently, Ψ^2 its square value has a real physical interpretation, representing the probability of finding an electron near a particular point in space. An orbital is a single-electron wave function. In another words is a wave function that contains information of a single electron. The square value of an orbital represents the probability of finding an electron at a specific location. Electrons are very different than larger objects such as for example a tennis ball. Larger objects are localized, that is they are located at a specific point in space. Differently, electrons are delocalized, that means they are not located at a single point in space and time, and therefore we can only guess the probability of finding the electron an a specific point. Orbitals are mathematical functions with a radian and an angular component.

$$\Psi(r, \theta, \varphi) = \psi_n(r) \cdot Y_\ell^{m_\ell}(\theta, \varphi)$$

The radial part $\psi_n(r)$ describes how the orbital changes with the distance (r) along the space, whereas the angular part—these are called spherical harmonics, $Y_\ell^{m_\ell}$ —describes the symmetry of the orbital. As a note, the term orbital is different than the term orbit, which is used in classical physics to describe the trajectory of an object (e.g. a planet) and was used in Bohr's model to describe the different states of movement of the electrons in the hydrogen atom. When we say that an electron is at a given orbital, we mean that the electron density distribution is described by the square of the wavefunction associated with that orbital.

Orbitals are described by three quantum numbers In Bohr's model of the hydrogen atom, just a single number n was necessary to describe the electron state. Differently, in quantum mechanics, each orbital Ψ_{n,ℓ,m_ℓ} is characterized by a three quantum numbers. These numbers differentiate each orbital from the rest. They are called: the principal quantum number n , the angular quantum number ℓ and the magnetic quantum number m_ℓ . These quantum numbers are interrelated and not all combinations are allowed. We will describe this in the following, but just as an example a possible combination would be $\Psi_{1,0,0}$ and $\Psi_{1,1,0}$ would be an impossible combination. In the following, we will describe each quantum number separately.

Principal quantum number, n The principal quantum number n is related to the size of the orbital. The larger this value, the larger the orbital and hence an electron in the orbital would have a greater average distance from the nucleus. n can only be integral values such as 1, 2 or 4 and it cannot be zero.

Angular quantum number, ℓ The second quantum number ℓ is called *angular quantum number* and it describes the shape of the orbital. The values of ℓ are dictated by the value of n . In particular, ℓ goes from 0 until $n - 1$. For example if $n = 3$, therefore ℓ can be: 0, 1 or 2. As such, n and ℓ can never be the same value, that is the reason why $\Psi_{1,1,0}$ does not represent a good orbital.

Magnetic quantum number, m_ℓ The third quantum number m_ℓ is called *magnetic quantum number* and is vaguely related to the orientation of the orbital. The values of m_ℓ depend on the value of ℓ . In general m_ℓ varies in a range of numbers indulging zero, $-l, -l-1, \dots, 0, \dots, l+1, l$. For example, if $\ell = 3$, m_ℓ can be any of these values: -3, -2, -1, 0, 1, 2, or 3.

Table 1.4 Orbital Labels

ℓ value	Orbital label
0	s
1	p
2	d
3	f

Table 1.5 Values of quantum numbers

Quantum #	Values
n	1, 2, 3...
ℓ	0, 1, ..., $n-1$
m_ℓ	$-\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell$
m_s	$+1/2$ or $-1/2$

A fourth quantum number: the spin m_s Three quantum numbers are necessary to describe each orbital. Still, a fourth quantum number, the spin number m_s was necessary to understand why magnetic fields affect the emission spectra lines of hydrogen and sodium. m_s is called *spin quantum number* and can only be either $+1/2$ or $-1/2$.

Sample Problem 7

Indicate if the following combination of quantum numbers is allowed:

n	ℓ	m_ℓ	m_s	Allowed?
1	1	0	$+1/2$	
2	0	0	$+1/2$	
3	3	-1	$-1/2$	

SOLUTION

The four quantum numbers are not independent. The quantum number n is related to the quantum number ℓ and the number ℓ is related to m_ℓ . The only quantum number that is independent is the spin, m_s which can be $+1/2$ or $-1/2$. The first combination is not possible, as if $n = 1$, ℓ can only be $n - 1$, that is zero. The second combination is correct, as if $n = 2$, the number ℓ can be: 0 or 1. At the same time if $\ell = 0$, then m_ℓ can also be zero. And finally, the spin value of $+1/2$ is allowed. The last combination is not allowed, as n and ℓ cannot be the same number.

n	ℓ	m_ℓ	m_s	Allowed?
1	1	0	$+1/2$	No
2	0	0	$+1/2$	Yes
3	3	-1	$-1/2$	No

❖ STUDY CHECK

Indicate if the following combination of quantum numbers is allowed:

n	ℓ	m_ℓ	m_s	Allowed?
4	3	3	$+1/2$	
4	3	3	0	
2	1	-1	$+1/2$	

Shells and subshells (or levels and sublevels) A shell (or a level) is a collection of orbital with the same value of n . For example: $\Psi_{2,1,-1}$ and $\Psi_{2,0,1}$ belong to the same shell. A subshell (or sublevel) is a collection of orbitals with the same n and ℓ values. For example: $\Psi_{2,1,-1}$ and $\Psi_{2,1,0}$ and $\Psi_{2,1,1}$ belong to the same subshell called p . The different subshells are names with the labels: s , p , d and f .

Orbital labels: s , p , d and f There is a more convenient way to label orbitals than the Ψ_{n,ℓ,m_ℓ} notation. In this notation, s orbitals are orbitals with $\ell = 0$, whereas p orbitals have $\ell = 1$ and d orbitals have $\ell = 2$. Finally, f orbitals have $\ell = 3$. The principal quantum number should also be indicated before the label. For example, the orbitals $\Psi_{2,0,0}$ is a $2s$ (Ψ_{2s}) and the orbital $\Psi_{2,1,-1}$ is a $2p$, that is Ψ_{2p} . The magnetic quantum number is not indicated in this notation. This is the most extended notation used to represent and refer to orbitals.

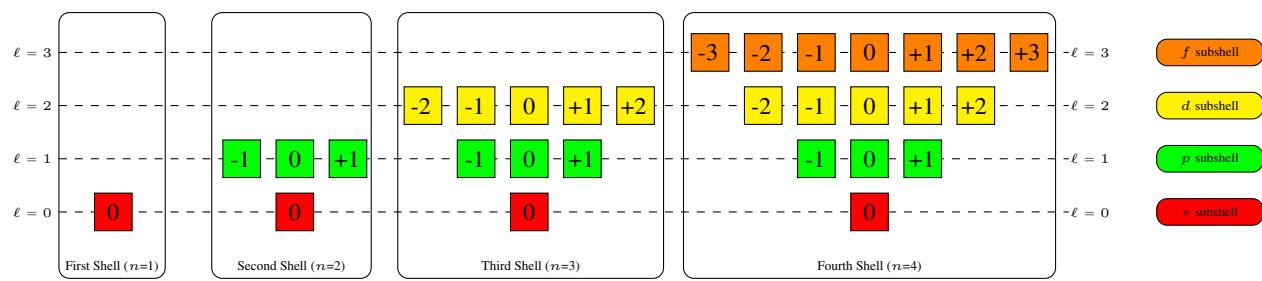


Figure 1.12 The shell and subshell distribution for different principal and angular quantum numbers. Orbitals with the same value of n belong to the same shell and orbitals with the same n and ℓ values belong to the same subshell.

1.4 Electronic structure

Different orbitals plots It is not straightforward to represent orbitals, as they extend throughout the space. However, there are three common ways to represent s orbitals, and in general any orbital: (a) by means of the surface that contains 90% of the total electron probability, (b) by means of the orbital square, and (c) by means of the radial probability distribution. Let us elaborate on the meaning of radial probability distribution. Imagine the space is made of thin shells, like in the layers of an onion. By adding all shells we have the whole space. The radial probability distribution is the total probability of finding an electron in each shell which depends on the distance from the nucleus. The radial probability distribution is useful as the maximums on this function indicate the distances from the nucleus where it is most likely to find the electrons on a particular orbital.

s orbitals s orbitals are characterized for having $n = 0$. There is a single s subshell in every shell and each s subshell contains only a single orbital. All s orbitals have an overall spherical shape with increasing size depending on the principal quantum number n . For example, the $1s$ orbital is smaller than the $2s$ and so on. The probability density plot show an interesting feature. For the $2s$ plot, the graph shown a minimum—called a node—representing the distance from the nucleus where the probability of finding an electron is zero. The number of nodes depend on the principal quantum number so that $1s$ orbitals has zero nodes, $2s$ has one node, and $3s$ has two nodes, and so on. The radian distribution plot of the $1s$ orbital also shows an interesting feature, and the distance from the nucleus where the probability of finding the electron is maximum $r = a_0$ is called Bohr's radius, 52.9pm.

p orbitals There are three different p orbitals and each subshell with n larger than 2 has a p orbital. These three p orbitals are labeled p_x, p_y and p_z , where the subindexes represent the direction of the axis along which each orbital is oriented. All three p orbitals have the same size, shape and energy. The larger the principal quantum number the larger the size of the orbital, and for example a $3p_x$ is larger than a $2p_x$. There is no relationship between the subindex labels and the values of m_ℓ . The boundary surface diagrams of p orbitals expose their shape in the form of two lobes, and with positive and one with negative sign.

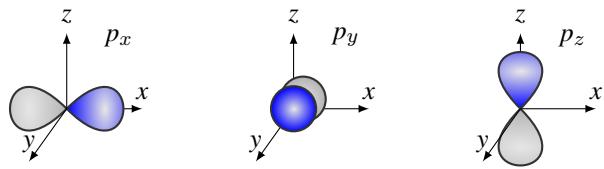


Figure 1.13 Surface plots of the three p orbitals.

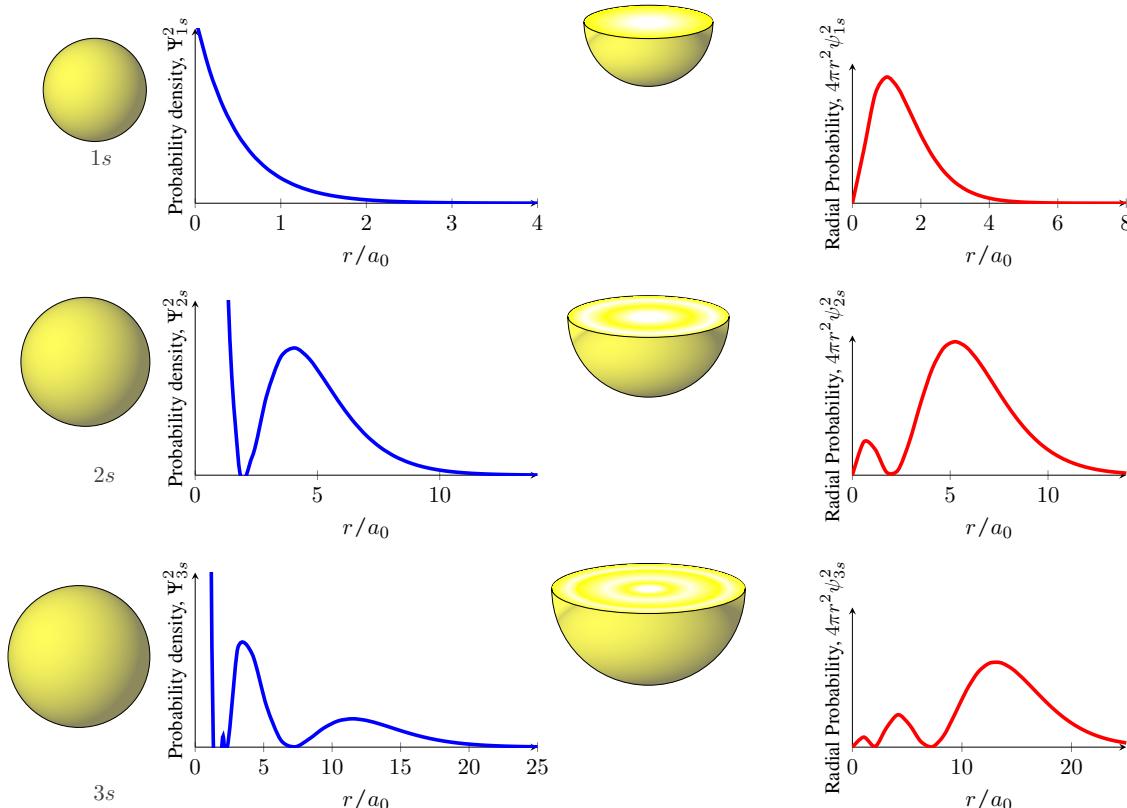


Figure 1.14 Three different representations of the s atomic orbitals of hydrogen: (left) boundary surface plots, (center) probability density plots (the orbital squared) with a sliced 3D surface plots, and (right) radial probability function. The value of a_0 , called Bohr's radius, is 52.9pm. The yellow circles inside the sliced 3D surface plots represent the orbital nodes.

d and f orbitals There are five d orbitals labeled as d_{xy} , d_{xz} , d_{yz} , d_{z^2} and $d_{x^2-y^2}$. The subindexes in the labels are not related to the quantum number m_ℓ but to the orientation of the orbital in the space. None of the d_{xy} , d_{xz} , d_{yz} orbitals cross any of the axis, but d_{z^2} and $d_{x^2-y^2}$ do. In particular, the lobes of the d_{xy} orbitals are located in the xy plane, whereas $d_{x^2-y^2}$ cross the x and y axis and the d_{z^2} crosses the z axis. All five d orbitals have the same energy. These orbitals increase in size based on the principal quantum number and the $3d$ orbitals are smaller than $4d$. There are not d orbitals in the first or second shell. Regarding the f orbitals, there are seven orbitals with very complex shapes.

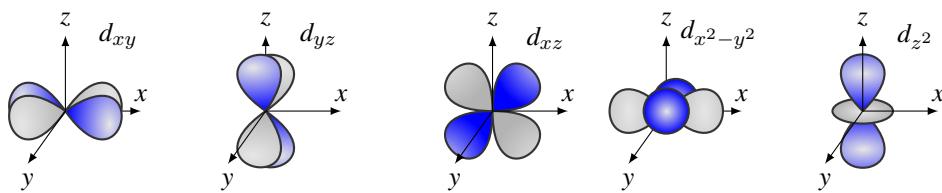


Figure 1.15 Surface plots of the three *d* orbitals.

Energies of orbitals The orbitals of hydrogen have different energy depending on the principal quantum number. The 1s orbital has the most negative—stable—energy. The 2s and 2p orbitals have both the same energy and overall have a more positive energy than the 1s. The orbitals at the third shell have a more positive energy than the orbitals in the previous shell. And the trend continues.

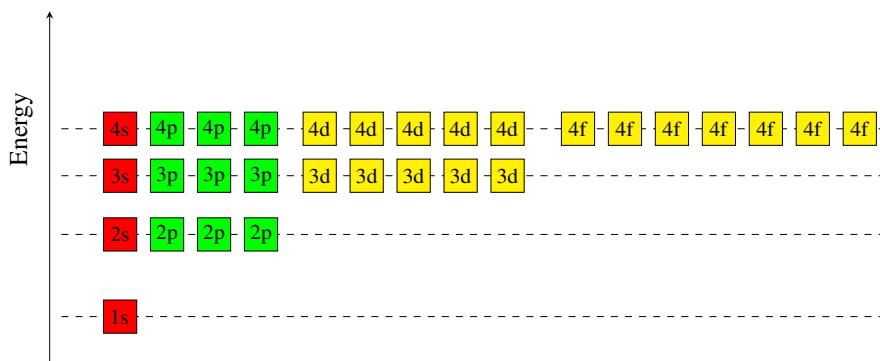


Figure 1.16 Energy of the different hydrogen orbitals. *s* orbitals have the lowest energy and hence are the most stable. Orbitals in the same shell (*2p*, *2s*) have the same energy. The larger the principal quantum number the more positive the energy, the less stable the orbital.

1.5 Electronic configuration of an atom

Atoms have in general many electrons. These electrons are arranged in the atom in a very specific way creating what we know as electronic structure. You want to think about the electronic configuration of an atom as a code that tells you the orbital location of each electron in the atom. In fact, there are two ways to present electronic configurations. One is called full electronic configuration (for example $1s^2 2s^1$) and the other one is called condensed electronic configuration (for example $[He]2s^1$). The full configuration display all orbitals in an atom, whereas the abbreviated only display the valence electrons—these electrons are less-tied to the nucleus—and the noble gas core. At the same time, every orbital is characterized by a set of numbers—these are called quantum numbers. These numbers are not independent from each other and there are constraints that relate the possible values of the quantum numbers. This section will show you how to construct electron configurations and how to extract quantum numbers from it.

Electron energy levels and sublevels The electrons in an atom are arranged in different energy levels. Some levels have lower energy and the electron in these levels are close to the nucleus being also strongly attached to it, whereas other levels have higher energy and the electrons in these levels are less attached to the nucleus. Still, each electron in an energy level have the same energy. The energy levels are labeled with a number *n* that equals to a single number such as 1, 2, 3 and so on.

The first energy level is $n = 1$ and never $n = 0$ —think of this as an apartment in a building, the first floor is flour one. For example all electrons in level one $n = 1$ have the same energy. There is a limit to the number of electrons in an energy level and we call this occupancy. Only a few electrons can occupy the lower energy levels, while more electrons can be accommodated in higher energy levels. Level one can only fit two electrons, whereas level two can fit a total number of eight electrons. The maximum number of electrons allowed in any energy level is calculated using the formula

$$2n^2 \quad (1.2)$$

in which n is the energy level. You can see by using this formula that for example, the third level can accommodate 18 electrons. Each energy level consists of one or more sublevels, which contain electrons with identical energy. The number of sublevels in each level corresponds to n . For example, in the first energy level ($n = 1$) we have only one sublevel, whereas in the third energy level ($n = 3$) we have three sublevels.

Sample Problem 8

How many electrons can you fit in the energy level $n=3$.

SOLUTION

We will use the formula $2n^2$ that gives the number of electrons that fit in a energy level n . As $n = 3$, we can fit 18 electrons in this level. Remember, the larger the energy level the more electrons we can fit.

❖ STUDY CHECK

At a given energy level you can fit 162 electrons. Identify the energy level.

The Pauli exclusion principle The Pauli exclusion principle states that no two electrons in an atom can have the same values of the four quantum numbers. It tells that each electron is unique and it has to be differentiated with a unique combination of quantum numbers. Because of this, each orbital can only accommodate two different electrons, one with $-1/2$ spin and one with $+1/2$.

Orbital Filling: the aufbau principle Atoms in general contain numerous orbitals and each orbital should be filled with electrons. In every orbital you can fill only a maximum number of electrons. For example, in a s orbital you can place a maximum of two electrons. That is why you will find s^1 orbitals and s^2 , with the latest being completely filled with electrons. In a p orbital you can place a maximum of six electrons and in a d orbital a maximum of ten. Finally, in a f orbital you can place fourteen or less electrons. For example, the orbital notation p^2 is correct as in p orbitals you can place six or less electrons. In this case, this orbital still have space to accept more electrons. Differently, the notation d^{12} is incorrect, as in d orbitals you can fit ten or less electrons and never twelve. The aufbau (build up) principle states that the electronic configuration of an atom can be obtained by adding one by one all electrons in the element. In order to fill the orbitals you should follow the Figure 1.18. You start from the top of the table and follow the arrows that indicates the orbitals ordering. For examples the first orbital to be filled will be $1s$. After that you should fill $2s$ and $2p$. After that you should fill $3s$, $3p$, $4s$, $3d$, and $4p$. There is a maximum number of electrons that can occupy each orbital. An s orbital holds a maximum of 2 electrons. A p orbital takes up to 6 electrons, a d orbital can hold up to 10 electrons, and an f orbital holds a maximum of 14 electrons. An orbital can be completely filled with electrons, partially filled or empty. For example a $3s^1$ is half-filled with one electrons and $2p^6$

is completely filled. Another example, a $3d$ orbital is empty and can accommodate a maximum of 10 electrons.

Full electron Configuration The full electron configuration of an atom is obtained by placing the total number of electrons of the atom in different orbitals with increasing energy. For example, the electron configuration for helium is written as $1s^2$ and the one for Li is $1s^22s^1$. First, how do we know the total number of electrons in an atom? That is the same as the atomic number and is indicated in the periodic table. Look for the element and the atomic number is on the top left side of the element. For example, the atomic number of hydrogen is one, and the number of electrons in He is two. Similarly, nitrogen has seven electrons. Second, how do we know which orbitals need to be filled? Figure 1.18 shows the orbital order. You need to start from the top of the image, from orbital $1s$, and proceed to the next arrow, starting from the end of the arrow. This way, after $1s$ goes $2s$ and then $2p$, $3s$, $3p$, $4s$, and $3d$. Mind that every s orbital can only fit two electrons, and p orbitals can fit six electrons, and so on. The following example will help you construct the electron configuration for a given atom.

Sample Problem 9

Obtain the full electronic configuration of C.

SOLUTION

The atomic number of C is $Z=6$ and that means C has 6 electrons. The orbital order from Figure 1.18 is: $1s, 2s, 2p, 3s, \dots$ etc. Each s orbital can fit two electrons, whereas the occupancy of the p orbitals is six electrons. Hence the electronic configuration of C is: $1s^22s^22p^2$. The s orbitals are all filled, whereas the p orbital is only occupied with two electrons.

❖ STUDY CHECK

Obtain the full electronic configuration of Ni.

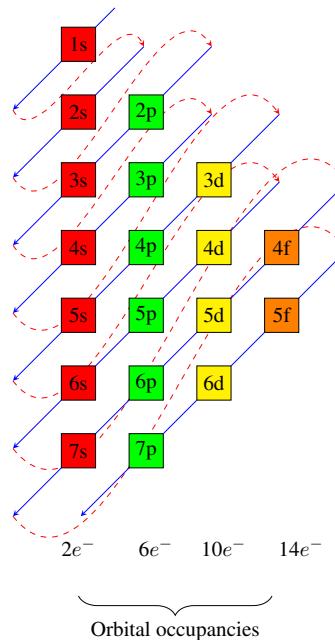
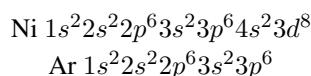
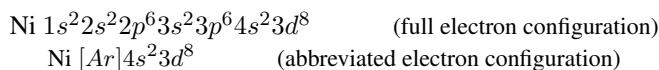


Figure 1.18 Table indicating the orbital filling order.

Abbreviated Electron Configuration and orbital diagrams Let us compare the electronic configuration of Ni and Ar. We have:



We call these configurations the *full electronic configuration*. If you look carefully, you will see that both configurations resemble and in particular the configuration of Ni is the same as the configuration of Ar with two extra orbitals added. We say Ni has the core of Ar and 10 electrons on its valence. We can represent this fact by indicating Ar with brackets:



The orbital diagrams are boxed diagrams indicating the valence electrons such as:



We call this last configuration the *abbreviated electronic configuration*. You can figure out faster the abbreviated electronic configuration by looking for the noble gas on the table on the row above the element, and the period (row on the table) of the element. Ni

is located in the period number four and the noble gas above this period is Ar. At the same time Ar has 18 electrons. That will give you the core [Ar] with 18 electrons, and the remaining 10 electrons (Ni has 28 electrons) starting by the orbital 4s, according to the period four. The electrons in the noble gas core are called *core electrons*, whereas the rest of the electrons are known as *valence electrons*. For the case of Ni, we have that it has 18 core electrons in the Ar core and 10 electrons in the valence. Let us work another example: Cd. It has 48 electrons, and is located in group 5. The noble gas on the group above is Kr with 36 electrons. The core will be Kr—the noble gas on the period above—and we start right away filling 5s electrons—Cd belongs to period five. In the valence electrons, we will place 12 electrons. Hence, the abbreviated configuration will be: [Kr]5s²4d¹⁰.

Sample Problem 10

Obtain the full and abbreviated electronic configuration of Silver (Ag, Z=47) using the fact that the 4d and 5s orbitals switch order, being the d orbital filled first.

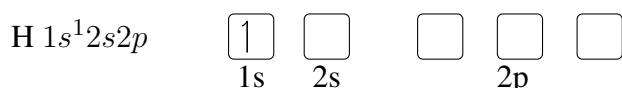
SOLUTION

The atomic number of Ag is Z=47 and that means Ag has 47 electrons. The orbital order from Figure ?? is: 1s, 2s, 2p, 3s, etc. Each s orbital can fit two electrons, whereas the occupancy of the p orbitals is six electrons, and d orbitals can fit 10 electrons. We will use the fact that the 4d orbital fills before the 5s. Hence the full electronic configuration of Ag is: 1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶4d¹⁰5s¹. As Kr is the noble gas on top with 36 electrons, the abbreviated electronic configuration of Ag is: [Kr]4d¹⁰5s¹. Ag has 36 core electrons and 11 valence electrons.

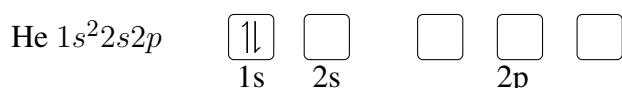
❖ STUDY CHECK

Obtain the abbreviated electronic configuration of Cobalt (Co, Z=27).

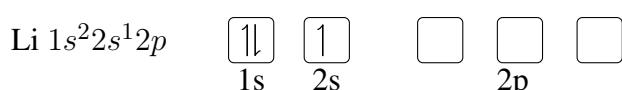
Hund's rule Let us build up the electron configuration of a series of atoms. Starting with hydrogen, with one electron, we have that only the 1s orbitals will be filled:

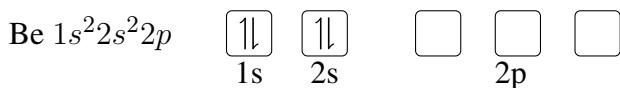


For the case of helium, with two electrons, we have that based on Pauli's principle both electrons have different quantum numbers and in order to differentiate this we will represent the pair of electron with arrows in opposite direction. We say both electrons are paired:

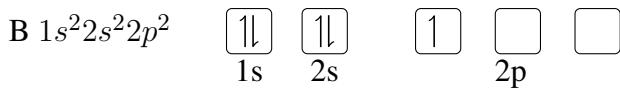


Now, for the case of Lithium and Beryllium we have a similar situation. Lithium has a single unpaired electron and Beryllium has a set of paired electrons in the 2s orbital:

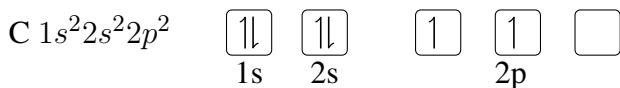




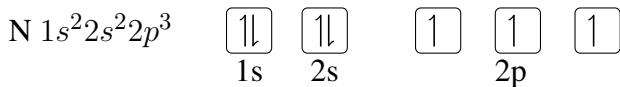
The next element, Boron, has one electron in a p orbital. As all p orbitals are degenerate—they have the same energy—we can place that single electron in any of the p orbitals. Normally, we use the one on the left:



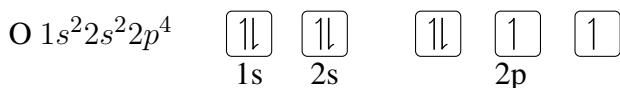
For the case of Carbon, as we need to place two electrons in the p orbitals, Hund's rule states that we need to place the electron maximizing the number of unpaired electrons. In other words, the second electron goes into a separate p orbital, just like below:



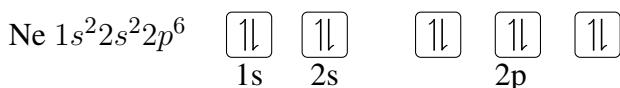
Similarly, for the case of Nitrogen we have:



Now, for the case of oxygen, as we cannot place that extra electron in a separate p orbital we have to start pairing electrons:



Finally, for the case of Neon we have the whole second shell filled with electrons:

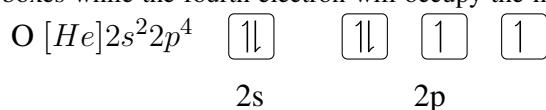


Sample Problem 11

Obtain the orbital diagram for oxygen given the electron configuration: $[He]2s^2 2p^4$

SOLUTION

The orbital diagram should include an s orbital and a p orbital. The s orbital contains a single box, whereas the p orbital contain three different boxes. The s orbital is fully occupied with two electrons, whereas the p orbital contain four electrons. The first three p electron will occupy separate boxes while the fourth electron will occupy the first box with opposite spin.



❖ STUDY CHECK

Obtain the orbital diagram for Li given the electron configuration: $[He]2s^1$.

1.6 Periodic Trends

Some atomic properties are periodic, which means that they follow a certain trends in the periodic table. These properties increases or decreases across a period and then the trend is repeated again in each successive period or group. We will consider here five atomic properties: the effective charge, atomic (or ionic) size, the ionization energy, the metallic character and the electronegativity.

Effective charge The nuclear charge (Z) of an atom is the number of protons in the nucleus. In atoms with more than one electron, each electron is exposed to a nuclear effective charge (Z_{eff}) as the electrons partially compensate the nuclear charge creating an effective nuclear charge. This way, the effective nuclear charge is the actual magnitude of positive charged experienced by an electron. In many-electron atoms, an electron is partially shielded from the positive charge of the nucleus. Among the different types of electrons in an atoms (valence and core), core electrons are more effective at shielding, and as such Z_{eff} increases from left to right across the periodic table. As the number of core electrons remains the same and the atomic number increases from left to right across the table, Z_{eff} follows this trend too. The effective nuclear charge is given by

$$Z_{eff} = Z - \sigma$$

where σ is the shielding constant.

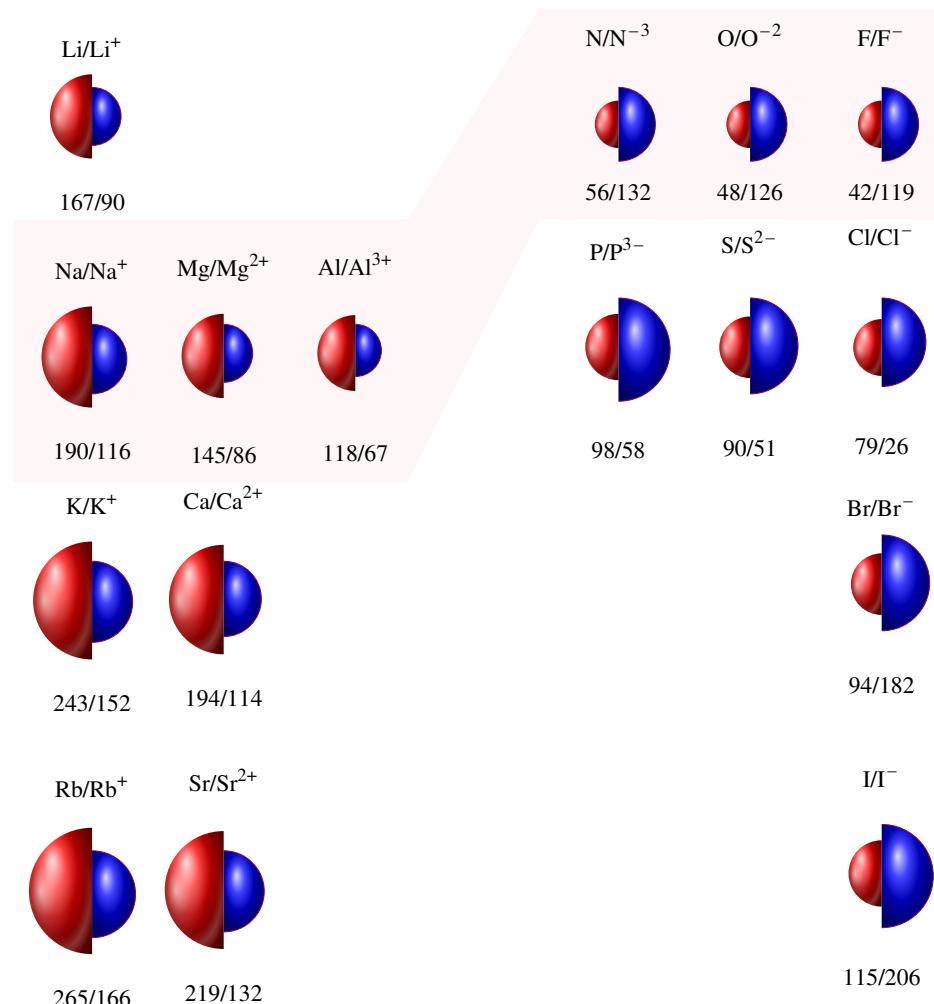


Figure 1.19 Ionic and atomic radius across the periodic table

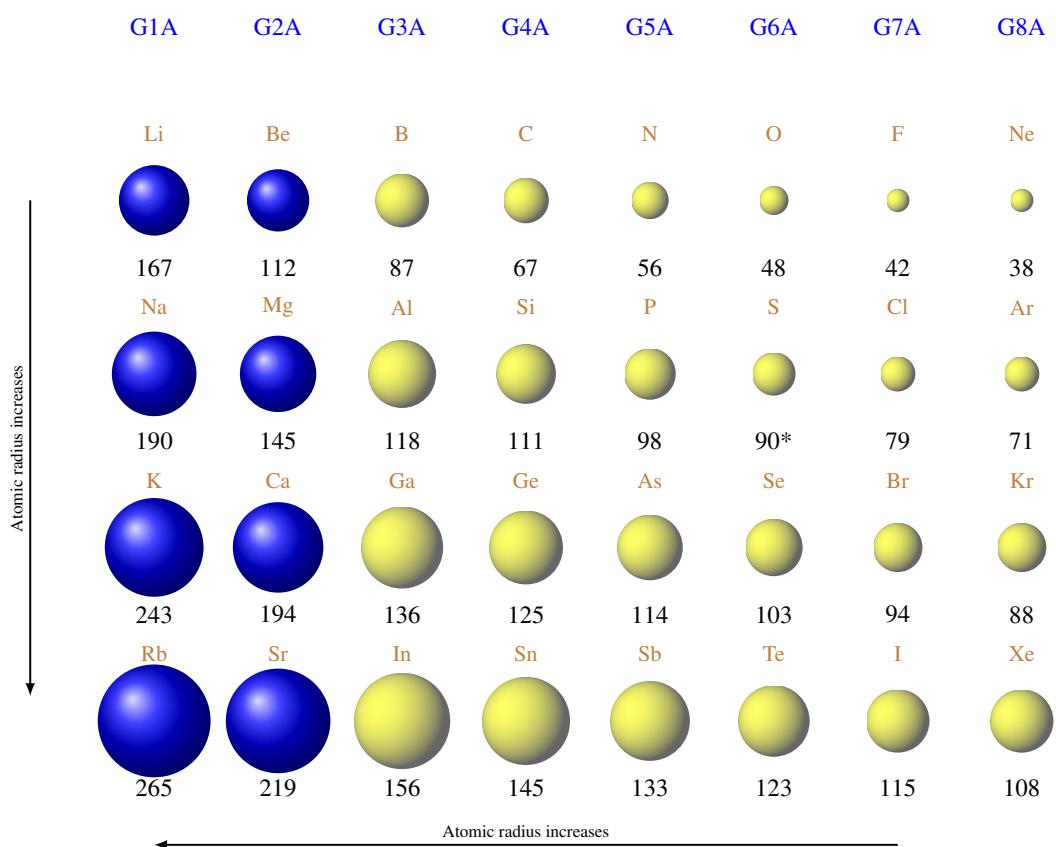


Figure 1.20 Change of atomic radius (calculated values given in pm) across the periodic table.

The value with * was estimated

Atomic radii Size of atoms can not be specified exactly as the electron density of atoms stands throughout the space. Still we can arbitrarily define the atomic radii of atoms which are obtained by measuring distances between atoms in compounds. For covalent molecules, for example O₂, we can measure the distance between the atoms in the molecule which is close to 150 pm, hence the atomic radius of oxygen—called the covalent atomic radius—should be close to 75 pm. For metallic elements we can measure the metallic radii by means of the lattice spacing between atoms. In the periodic table, the atomic radii decreases from left to right of a period and increased from top to bottom of a group.

Table 1.6 Ionization energy in the periodic table in kJ/mol

Element	Z	EI ₁	EI ₂	EI ₃	EI ₄	EI ₅	EI ₆	EI ₇	EI ₈	EI ₉	EI ₁₀
Li	3	520.2	7298.1	11815.0							*
Be	4	899.5	1757.1	14848.7	21006.6						
B	5	800.6	2427.1	3659.7	25025.8	32826.7					
C	6	1086.5	2352.6	4620.5	6222.7	37831	47277.0				
N	7	1402.3	2856	4578.1	7475.0	9444.9	53266.6	64360			
O	8	1313.9	3388.3	5300.5	7469.2	10989.5	13326.5	71330	84078.0		
F	9	1681.0	3374.2	6050.4	8407.7	11022.7	15164.1	17868	92038.1	106434.3	
Ne	10	2080.7	3952.3	6122	9371	12177	15238	19999.0	23069.5	115379.5	131432

* Shaded cells represent the removal of core electrons

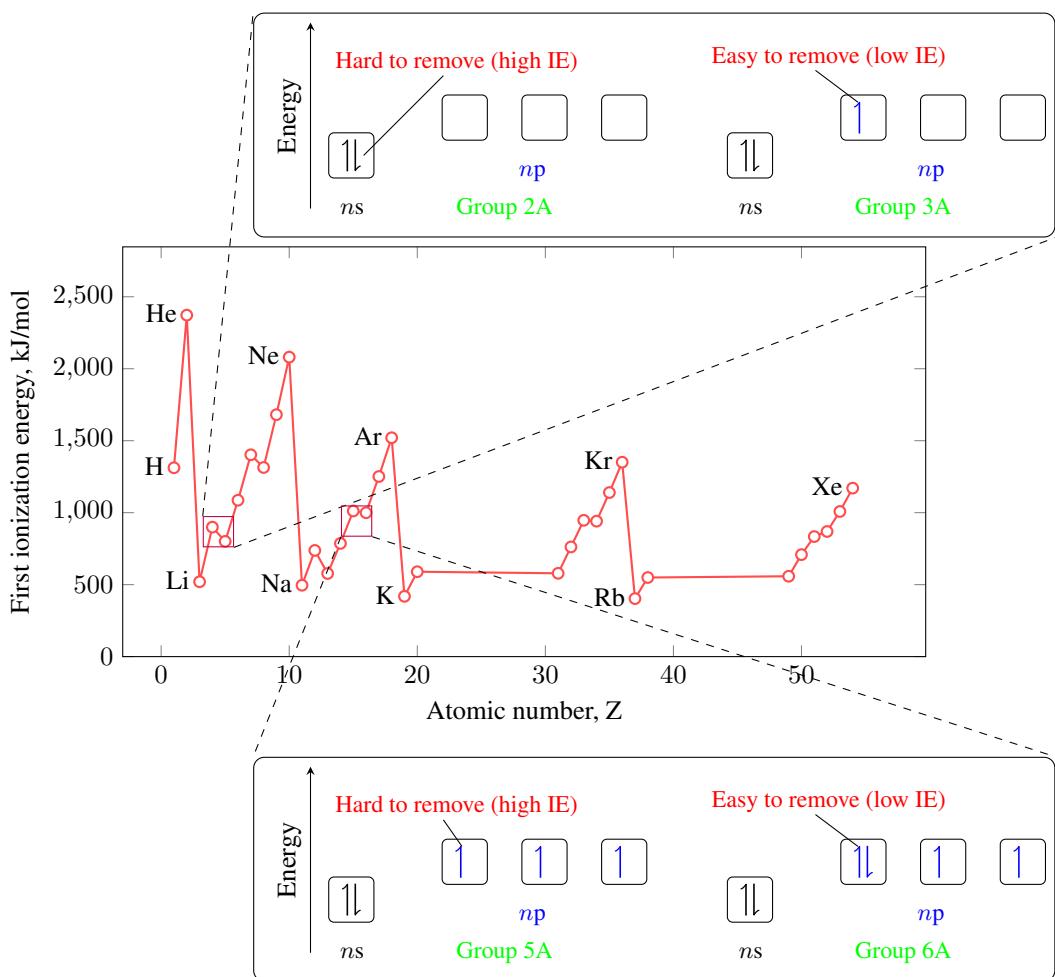
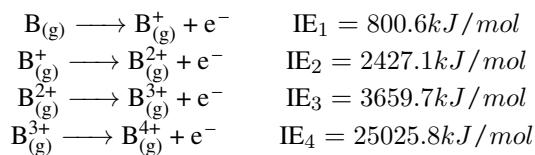


Figure 1.21 Ionization energy graphed with respect to the atomic number

Ionization Energy The *ionization energy* (IE) is the energy needed to remove an electron from an atom in gas state and its fundamental (ground) electronic state. Atoms can have numerous ionization energies. The first ionization energy (IE_1) is the energy needed to remove the highest-energy electron on an atom, whereas the second ionization energy (IE_2) is the energy needed to remove the second highest-energy electron on the atom. For the case of boron,



Given the electron configuration of Boron ($[\text{He}]2s^2 2p^1$), the first electron comes from a p orbital, whereas the second comes from a s orbital, which lays closer to the nucleus. The fourth electron comes from the core and the fourth ionization energy is considerably higher than the rest. Overall, we have that ionizing an atom from p orbitals is less costly than ionizing from s orbitals, and ionizing an atom from core orbitals is more costly than ionizing from valence orbitals. The ionization energy increases (this means more energy is needed to remove an electron) going up a group and when going across a period from left to right. In general, the ionization energy is low for the metals and high for the nonmetals. For example, if we compare the IE for H and He, as He is further right in the same period, it will have a larger IE and more energy will be needed to remove an electron ($IE_H < IE_{He}$). For the case of Li and H, the EI will be higher

for H as it is further up in the same group ($IE_H > IE_{Li}$). There are discontinuities in the IE when moving across a period. Table 1.6 gives the IE for the second period. The first discontinuity happens between groups 2A and 3A as it is easier to remove p electrons than s electrons. The second discontinuity occurs between groups 5A and 6A as it is easier to remove an electron from a double occupied p orbital than from a single occupied one.

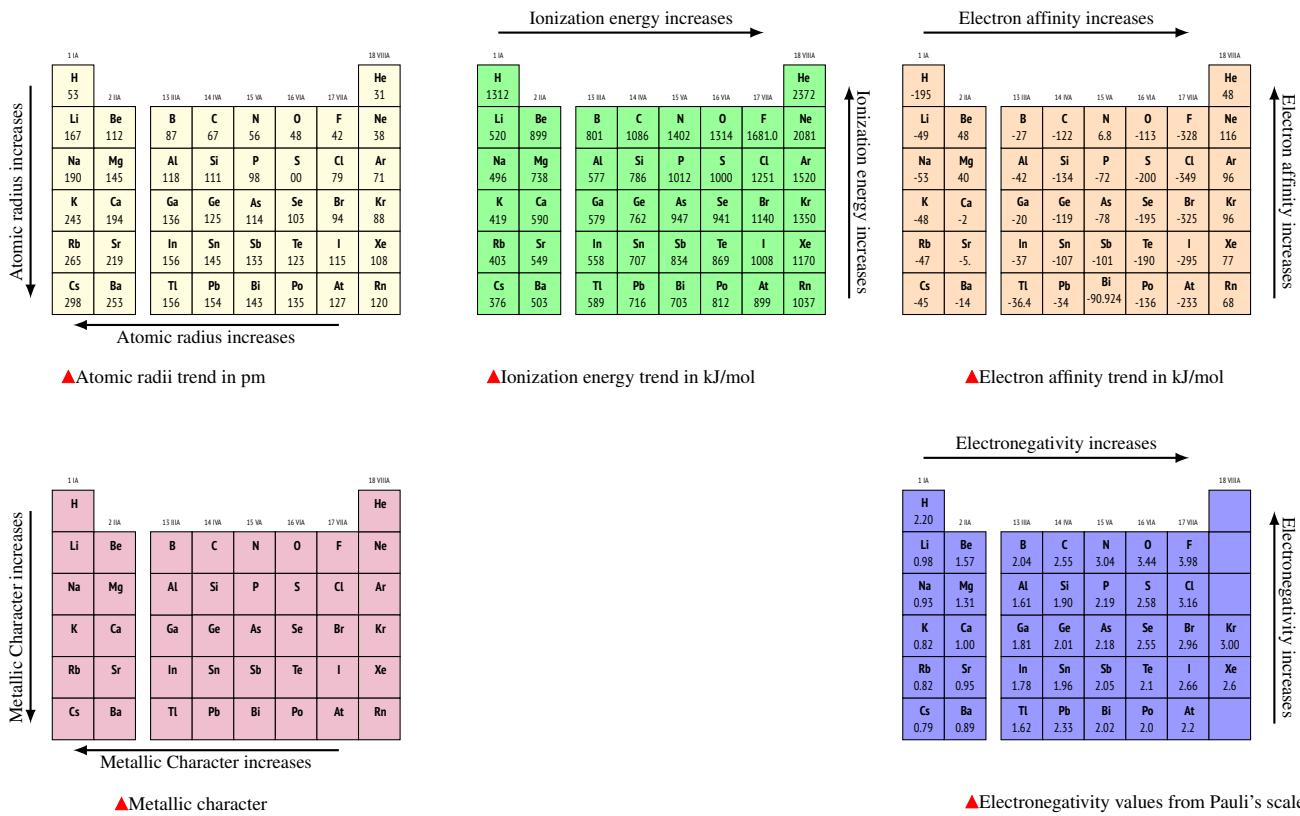


Figure 1.22 Periodic properties across the periodic table

Electron affinity The electron affinity (EA) represents the tendency of an atom to receive one or more electrons hence becoming negatively charged. Specifically, is the energy involved in the process of receiving an electron. As an example, the electron affinity of hydrogen is written as:



Here, we consider electron affinities as negative values so that the smaller (the more negative) this value the larger the tendency of the atom to accept electrons. In other words, it would be easier to add electrons to an atom with -10 kJ/mol EA, than to an atom with 10 kJ/mol EA. In the periodic table, EA decreases (becomes more negative) across a period from left to right. For example, EA for K is -48 kJ/mol and for Br is -325 kJ/mol . Hence, elements from the right of the table are more willing to gain electrons than elements from the left. On one hand, there are discontinuities in the electron affinity across a period. It is easier to add an electron to the elements in Group 1A than to elements in Group 2A, as an electron added to Group 2 elements would be placed in p orbitals and these have higher-more positive-energies. Also, it is easier to add an electron to the elements in Group 4A than to elements in Group 5A, as an electron added to Group 4 elements would be placed in p orbitals giving three unpaired

electrons, whereas electron on Group 5 are all paired and a new electron would have to add to an already occupied orbital. On the other hand, there are fewer EA variations when going across a group. Finally, when adding more than one electron, the second EA tends to be more positive-less favored-than the first electron addition.

Electronegativity, EN Atoms combine with each other by sharing or give away electron density. The *electronegativity* of an atom in a molecule is its ability to attract electron density in a bond. Imagine two people holding a pillow with their hands, with the pillow representing a pair of electrons. If one of the person is more electronegative it will pull the pillow closer to them—it will attract more the electrons. Electronegativity is loosely related to other periodic properties such as ionization energy and the electron affinity. Very electronegative atoms such as F has also a large (negative) electron affinity (easily accepts electrons) and ionization energy (do not ionize easily). There are different electronegativity scales, and the most well-known scale was developed by Linus Pauling. Electronegativity (EN) increase (the atom is more electronegative) when going up a group (column) of the table and when going across a period (row), from left to right of the table. Highly electronegative atoms are located on the top right part of the table, whereas highly electropositive atoms are located on the bottom left part of the table. EN is a relative concept, that is, the electronegativity of an atom can only be measured in relation to another atom. When comparing the EN of I and F, we found that F is more electronegative as it is further up in the same group ($EN_F > EN_I$).

Metallic character All elements in the periodic table have somehow a certain *metallic character* as they all can lose electrons as metals do—that is why metals are good conductors. The elements in the left part of the table are metals with a strong metallic character. Still, the elements in the right side of the table also have a certain metallic character (MC). The metallic character increases (the atom is more metallic) when going down a group (column) of the table and when going across a period (row) from right to left. For example, comparing K and Ca, we have that K is more metallic than Ca, as it is located further to the left in the same column ($MC_K > MC_{Ca}$). For the case of F and Cl, Cl is more metallic as it is located further down a group ($MC_{Cl} > MC_F$).

Sample Problem 12

Compare the following property for the given couple of elements:

- Atomic radius of N and F.
- Ionization energy of Na and Cs.
- Electronegativity of F and I.
- Metallic character of N and F.

SOLUTION

- You go from N to F by moving from left to right on a row of the periodic table, hence the radius of N is larger than the radius of F. This is because the atomic radius decreases from left to right on a row. (b) You go from Na to Cs by moving from up to down on a column of the periodic table, hence the ionization energy of Na is larger than for Cs. This is because the ionization energy decreases from top to bottom on a period. (c) You go from F to I by moving from down to up on a column of the periodic table, hence the electronegativity of F is larger than for I. This is because the electronegativity increased from bottom to top on a period. (d) You go from N to F by moving from left to right on a row of

the periodic table, hence the metallic character of N is larger than for F. This is because the metallic character increased from right to left on a period.

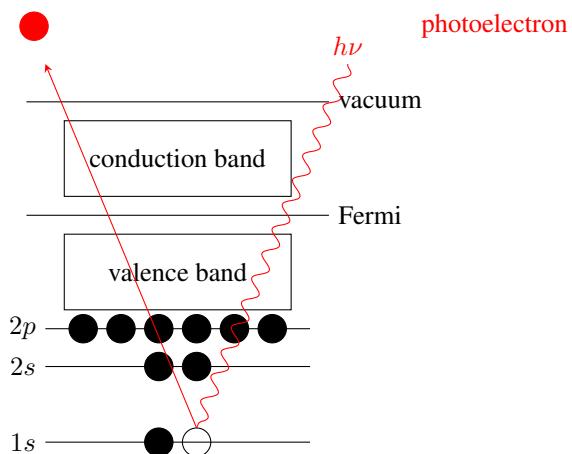
STUDY CHECK

Compare the following property for the given couple of elements: (a) Atomic radius of F and I. (b) Electronegativity of Cs and Na.

Ionic radius Atoms gaining or losing electrons become ions. When an atom loses an electron it reduces its size. In particular, when an atom loses all valence electrons its size reduces considerably. When an atom gains an electron it gains size too as this new electron needs to be placed on an occupied orbital further away from the nucleus. Some ions have common electronic configuration. For example, Na^+ and F^- both have the electron configuration: $[\text{He}]2\text{s}^22\text{p}^6$. Ions with the same electron configuration are called isoelectronic. For a series of isoelectronic ions, the larger the atomic number the smaller the ionic size due to the increase in nuclear attraction.

1.7 Photoelectron spectroscopy of atoms

Figure 1.23 A photo-electron emitted from a 1s level



Photoelectron spectroscopy is a technique used to measure the relative binding of the electrons of an atom. It is useful to experimentally obtain the energy levels of an atom and properties such as the ionization energy. The principle behind the technique is similar to the photoelectric effect. By shining light with enough energy one can remove electrons of an atom. By measuring the kinetic energy of the ejected electron and taking into account the energy of the radiation we can estimate the binding energy of the ejected electron—called photoelectron—in the atom. The name, photoelectron spectroscopy, refers to the fact that electrons are ejected with light, by using photons. This technique is used to identify the presence of specific atoms as the photoelectron peaks are element-specific, that is, each element presents a series of characteristic peaks. However, there are many factors that affect the photoelectron peaks and for example an 1s peak of H can appear at different energies depending on the nature of the atom bonded to hydrogen. In general, in the vertical axis of a PES plot you will find the relative intensity of the electrons and on the horizontal axis the energy of the photoelectron. The larger the energy the more strongly attached will be the electron in the atom and for example a 1s peak will appear at higher energy than a 2s peak. The higher the intensity of the peak the larger the number of electrons in the level resulting for the photoelectron. For example, the intensity of a 1s^2

peak should be twice the intensity of a $1s$ peak. By comparing the intensity of the peaks and the relative location one can identify the atom represented on the spectra.

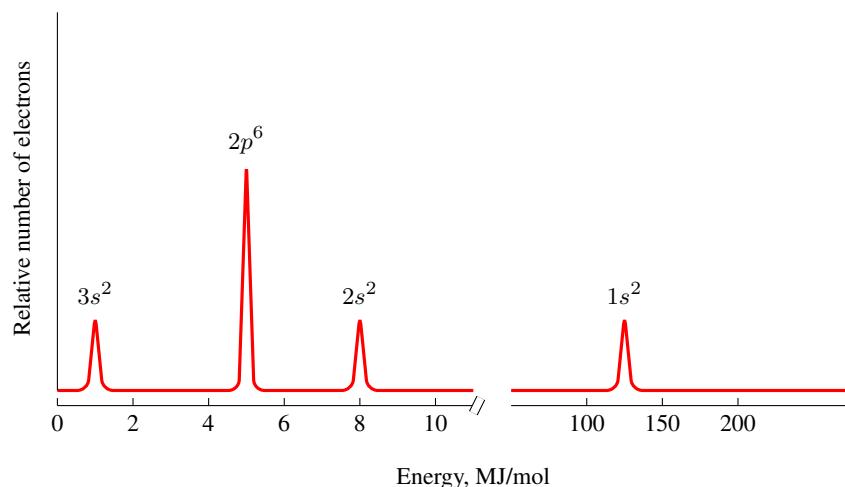


Figure 1.24 Photoelectron spectrum (PES) of Magnesium