1. The hydrogen atom

The hydrogen atom is generally considered the most important system solved by the Schrodinger equation. The solution to this Schrodinger equation provides the basis for a discussion of multi-electron atoms, orbitals, and the Pauli exclusion principle. In addition, atoms are the starting point for the quantum mechanical description of molecules.

The hydrogen atom consists of a proton (nucleus) and an electron. Classically, the energy for the hydrogen atom is given by the expression

$$\frac{m_e v^2}{2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} = E \qquad (8.1.1)$$

where the first term on the left is the kinetic energy of the electron and the second term is the potential energy, due to the attraction of particles of opposite charge. The factor of $4\pi\varepsilon_0$ is a conversion factor so that the potential energy is expressed in units of Joules. Eq 8.1.1 also assumes that the mass of the electron is negligible compared to that of the proton (or, in general, of the nucleus). This assumption is approximately true ($m_p/m_e \cong 2000$), and can easily be corrected for when the final expression for energy is obtained.

If eq 8.1.1 is transformed into the corresponding Schrodinger equation, that equation has an exact solution. The solution is in terms of three quantum numbers

n	principal quantum number	$n = 1, 2, 3, \ldots$	(8.1.2)
ℓ	orbital angular momentum quantum number	$\ell = 0, 1, 2, \ldots, (n-1)$	(8.1.3)
m_ℓ	orbital angular momentum orientation quantum number	$m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell$	(8.1.4)

It is important to note that these three quantum numbers appear in a natural manner when the Schrodinger equation for the hydrogen atom is solved. There are two additional quantum numbers that are required to account for electron spin and which are discussed below. The quantum numbers ℓ and m_ℓ are analogous to the quantum numbers J and M_J that appear in the solution to the Schrodinger equation for rotation of a diatomic molecule. This is because both sets of quantum numbers are related to an angular momentum in the system being discussed, and all angular momenta behave in essentially the same manner. A similar pair of quantum numbers appear in other systems possessing angular momentum, such as electron spin and nuclear spin.

For hydrogen, the possible values for energy (energy levels) only depend on the value of n, the principal quantum number. The equation for the energy levels of an hydrogen atom is

$$\tilde{E}_n = - \frac{m_e e^4}{8\varepsilon_0^2 h^3 c}\frac{1}{n^2} = -\frac{R_\infty}{n^2} \quad ; \quad R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} = 109737. \text{ cm}^{-1} ; n = 1, 2, 3\ldots \qquad (8.1.5)$$

R_∞ is called the <u>Rydberg constant,</u> and is the value that would occur if the ratio of the nuclear mass (m_N) to the mass of the electron (m_e) was infinity, that is, if $m_N/m_e = \infty$. The value for R_∞ is close to the experimental value for the Rydberg constant for the most common isotope of hydrogen (^{1}H). However, if m_e in eq 8.1.5 is replaced by the <u>reduced mass</u> of the electron + proton pair

$$\mu(e,p) = \frac{m_e \, m_p}{m_e + m_p} = 0.999456 \, m_e \qquad (8.1.6)$$

the calculated value for the Rydberg constant (written as R_H) is R_H = 109678. cm^{-1}. This is the same as the experimental value to within experimental error. (Note that both R_∞ and R_H are known to several more significant figures than given above).

A diagram indicating the first few energy levels for the hydrogen atom is given in Figure 1. Note that the location and pattern for the energy levels is identical to that found experimentally (Handout 7, section 2).
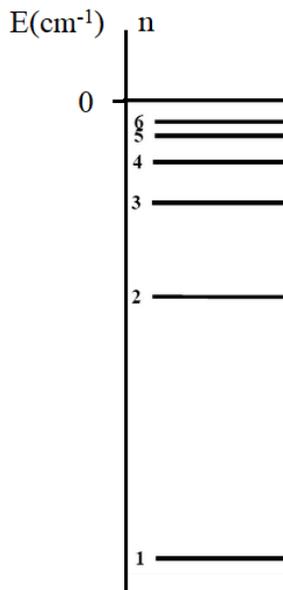

Figure 1. Energy levels for the hydrogen atom.

Based on eq 8.1.6 and the restrictions on the quantum number n, a useful expression for the energies at which a hydrogen atom absorbs or emits light can be derived. The result is

$$\tilde{E}(n_1, n_2) = R_H \left[(1/n_1)^2 - (1/n_2)^2 \right] \qquad n_2 > n_1 \qquad\qquad (8.1.7)$$

Equation 8.1.7 predicts the energies at which a hydrogen atom will absorb or emit light to move between states with quantum numbers n_1 and n_2. From the value for $\tilde{E}(n_1, n_2)$ the corresponding value for the wavelength being absorbed or emitted can be found. If we call the quantum number for the initial and final states of the hydrogen atom n_i (for the initial state) and n_f (for the final state), then

light absorption $\qquad\qquad n_i = n_1$ and $n_f = n_2$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (8.1.8)

light emission $\qquad\qquad n_i = n_2$ and $n_f = n_1$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (8.1.9)

Equation 8.1.5 can be modified to predict the energy levels for any single electron hydrogen-like cation (He$^+$, Li^{2+}, …). If this is done, the general expression for the energy levels is

$$\tilde{E}_n = -\frac{Z^2 R_\infty}{n^2} \qquad\qquad Z = \text{charge of nucleus (Z = 2 for He}^+\text{, Z = 3 for Li}^{2+}\text{…)} \qquad (8.1.10)$$

For precise work R_∞ in eq 8.1.10 should be replaced by the reduced mass of the electron + nucleus, using eq 8.1.6 and replacing m_p (mass of proton) with m_N (mass of the nucleus), but this results in only a small change in the values for energy even for the ^{4}He$^+$ ion.

2. Atomic orbitals

The solution to the Schrodinger equation gives both the allowed values for energy (energy levels) and the wavefunctions (ψ) for a system. To this point we have not been concerned about the wavefunctions that form part of the solutions to the Schrodinger equation. However, for the hydrogen atom the wavefunctions are important, as they will be the basis for descrbing without a lot of mathematics the way that atoms join together to form molecules.

The different classes of wavefunctions are described by the quantum number ℓ. The total number of wavefunctions for a particular value of ℓ is equal to the total possible values for m_ℓ.

$\ell = 0$ $m_\ell = 0$ s orbital (one total)

$\ell = 1$ $m_\ell = +1, 0, -1$ p orbitals (three total)

$\ell = 2$ $m_\ell = +2, +1, 0, -1, -2$ d orbitals (five total)

$\ell = 3$ $m_\ell = +3, +2, +1, 0, -1, -2, -3$ f orbitals (seven total)

In general, for a particular value of ℓ there will be $2\ell + 1$ <u>orbitals</u>. Note that the type of orbital is not affected by the value for the quantum number n. The quantum number n does affect the size of the orbital, and also some less important properties such as the number of radial nodes, as discussed below.

Orbitals are generally labeled by the value of the quantum number n and the symbol for the quantum number ℓ. For example, the first three families of orbitals are the 1s orbital (n = 1, $\ell = 0$), the 2s orbital (n = 2, $\ell = 0$) and the 2p orbitals (n = 2, $\ell = 1$). These three families of orbitals are shown in Figure 2. The wavefunctions in the figure correspond to the region of space where the probability of finding the electron is high (typically 90% probability), although it is the square of the wavefunction that is related to probability. Note that in general it is not possible (other than for an s-orbital) to assign a specific value for m_ℓ to a specific orbital.
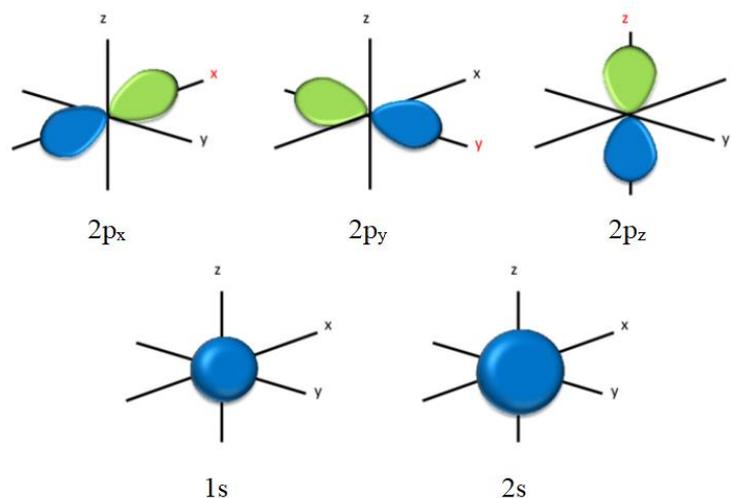
Figure 2. Size and shape of the 1s, 2s, and 2p atomic orbitals. Different colors correspond to different phases for the wavefunction.

As shown in Figure 2, the type of orbital depends only on the quantum number ℓ. The main effect of the quantum number n is on the size of an orbital. For example, both the 1s and 2s atomic orbitals are spherically symmetric, but the 2s orbital is larger than the 1s orbital. Similarly, the 3p atomic orbitals would have the same shape

as the 2p orbitals, but would be larger in size. n and ℓ also determine the number of <u>radial nodes</u> (values of r, other than r = 0 or r = ∞, where the wavefunction, and therefore the probability, is equal to zero) for an orbital. In general

$$\text{\# radial nodes} = (n - \ell) - 1 \tag{8.2.1}$$

So, for example, the 1s and 2p orbitals have no radial nodes, while the 2s orbital has one radial node.

Because the solutions to the Schrodinger equation are wavefunctions, they have some of the properties of waves. The most important of these properties is phase. As shown in Figure 3, a one dimensional wave has regions of positive and negative phase, corresponding to regions of positive or negative amplitude. The wavefunctions in Figure 2 also can have different phases in different regions, similar to the different phases of the wave in Figure 3. The 1s and 2s orbitals are all the same phase, while the two lobes of the 2p orbitals are different phases, indicated by the different colors used. In Figure 2, which color is considered positive phase and which is considered negative phase is arbitrary, since the assignment of phase does not affect the value for the square of the wavefunction.
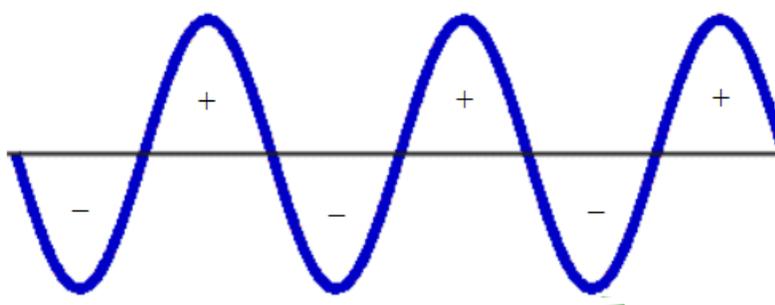

Figure 3. A one dimensional wave. Regions of positive amplitude are labeled as positive phase (+), and regions of negative amplitude are labeled as negative phase (−).

Since the probability of finding the electron in a particular location in space depends on the square of the wavefunction, there is equal probability whether the wavefunction is positive or negative phase. Phase information is, however, important when atomic orbitals are combined to form chemical bonds, as discussed in the next chapter.

3. Electron spin

The solution to the Schrodinger equation for the hydrogen atom leads to three quantum numbers, n, ℓ, and m_ℓ. However, there are two additional quantum numbers that are needed to account for the intrinsic spin of an electron. Classically, this would correspond the the angular momentum of an electron spinning around its axis (like the Earth spinning around its axis). This spin is quantized, and has two quantum numbers associated with it

$$s = \tfrac{1}{2} \qquad\qquad \text{spin angular momentum quantum number} \tag{8.3.1}$$

$$m_s = \pm\tfrac{1}{2} \qquad\quad \text{spin angular momentum orientation} \tag{8.3.2}$$
$$\text{quantum number}$$

Since electron spin is a form of angular momentum, s and m_s behave in the same way as ℓ and m_ℓ, or J and M_J. The two possible values for m_s correspond to two orientations of the spin angular momentum vector, and are often referred to as "spin up" ($m_s = +\tfrac{1}{2}$) and "spin down" ($m_s = -\tfrac{1}{2}$).

The electron in a hydrogen atom thus has five quantum numbers associated with it. These can be written as

$$n, \ell, m_\ell; s, m_s \qquad (8.3.3)$$

The quantum numbers have been placed into two groups – those found from solving the Schrodinger equation for the hydrogen atom (n, ℓ, m_ℓ) and those associated with electron spin (s, m_s). Since all electrons have the same value for the electron spin quantum number s, this quantum number is usually omitted when listing the set of quantum numbers for the electron in the hydrogen atom or the electrons in a multi-electron atom.

4. Multi-electron atoms and the Pauli principle

For a multi-electron atom there is a new type of term that appears for the potential energy, due to the repulsion that electrons exert on one another. Because of this additional term it is not possible to find an exact solution to the Schrodinger equation for any atom larger than the hydrogen atom. However, there are standard approximation methods that have been developed (some borrowed from classical mechanics) that make it possible to find solutions for the energy levels and wavefunctions that are arbitrarily close to the exact solutions. In a sense the exact solutions to a Schrodinger equation are like absolute zero in thermodynamics. Just as we can never reach absolute zero, but can get arbitrarily close to it, we can never obtain the exact solutions to a multi-electron atom, but can find solutions that are arbitrarily close to the exact solutions.

One additional requirement for a multi-electron atom (or any other multi-electron system) is that the electrons must satisfy the Pauli principle. The Pauli principle is the statement that no two electrons in the same system (an atom, molecule, or atomic or molecular ion) can have an identical set of quantum numbers. The Pauli principle is a consequence of the symmetry properties of wavefunctions, but can be applied using the statement of the principle given above. The Pauli principle applies to any collection of fermions (particles that have half-integer values for the quantum number s, such as $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$) but not to collections of bosons (particles that have integer values for the quantum number s, such as $s = 0, 1, 2, \ldots$).

The concepts of quantum numbers and orbitals, found from the solution to the Schrodinger equation for hydrogen, also apply to multi-electron atoms. One difference between a multi-electron atom and the hydrogen atom is that the energy for an electron in a multi-electron atom depends on both the quantum number n and the quantum number ℓ. This can be seen in Figure 4. The dependence of energy on ℓ in a multi-electron atom is a consequence of the additional term in the Schrodinger equation appearing in the potential energy, due to electron-electron repulsion, and so is not present in a one electron system.
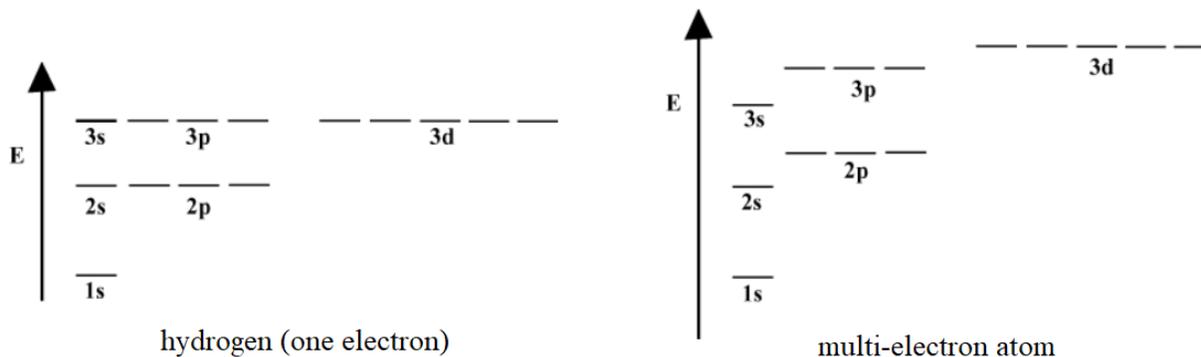

Figure 4. Energy level diagram. Left – diagram for hydrogen. Right – diagram for a multi-electron atom.

The arrangement of electrons in an atom is often given in terms of an electron configuration. In an electron configuration each orbital containing electrons is listed, along with the number of electrons in the orbital. For

example, the electron configurations for the ground (lowest energy) state of atoms of the first five elements of the periodic table are

H	$1s^1$	
He	$1s^2$	
Li	$1s^2\,2s^1$	$= [He]\,2s^1$
Be	$1s2\,2s2$	$= [He]\,2s^2$
B	$1s^2\,2s^2\,2p^1$	$= [He]\,2s^2\,2p^1$

In the above table the full electron configuration is given, along with a shorthand representation of the electron configuration, written as the configuration for a noble gas plus the additional electron containing orbitals. This shorthand notation is particularly useful for atoms with a large number of electrons.

For a particular value of n, the larger the value of ℓ the higher the energy. Unfortunately, the dependence of orbital energy on n and ℓ is complicated. Figure 5 shows a mnemonic device that can be used to find the most common ordering of energies for the orbitals in a multi-eletron atom.

Figure 5. Mnemonic device for the usual ordering of orbital energy in a multi-electron atom.

Based on this mnemonic device, the usual ordering of the energy levels of the orbitals in a multi-electron atom is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < \dots \qquad (8.4.1)$$

To find the ground state electron configuration two principles are used:

Aufbau principle – Electrons add to the lowest energy available orbital.

Pauli principle – No two electrons can have the same set of quantum numbers.

Also recall that the maximum number of electrons that can be put into a particular set of orbitals depends on the number of orbitals of a particular type (number of different values for m_ℓ) and the quantum number m_s. So

ns orbital	maximum of 2 electrons
np orbitals	maximum of 6 eletrons
nd orbitals	maximum of 10 eletrons

Use of the Aufbau and Pauli principles and the restrictions on the maximum number of electrons that can appear in a particular family of orbitals usually leads to a correct prediction of the electron configuration for the

ground state of an atom. However, because some of the orbitals are very close in energy, there are occasional small differences between the electron configuration predicted for the ground state of an atom and the actual electron configuration. The most common case of this is where moving an electron from the highest fully occupied s orbital to a d orbital results in the d orbitals being half-filled (5 electrons) or completely filled (10 electrons).

For example, the following are the predicted electron configurations for atoms of several elements:

C (6 e⁻) $1s^2\ 2s^2\ 2p^2 = [He]\ 2s^2\ 2p^2$

P (15 e⁻) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3 = [Ne]\ 3s^2\ 3p^3$

Cr (24 e⁻) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4 = [Ar]\ 4s^2\ 3d^4$ (predicted)

          $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5 = [Ar]\ 4s^1\ 3d^5$ (actual)

Rh (45 e⁻) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^7 = [Kr]\ 5s^2\ 4d^7$

Notice that for chromium (Cr) the actual electron configuration is slightly different than that predicted using the Aufbau principle, Pauli principle, and usual ordering of the energy levels. You should be aware that such exceptions occasionally happen, but you are not responsible for knowing where these exceptions occur. Also note that for atoms with a large number of electrons the shorthand notation for the electron configuration becomes more and more useful. Finally, there is a general procedure for finding the electron configuration for the ground state of an atomic ion (cation or anion) but you will not be asked to predict electron configurations for ions.

The Aufbau principle and Pauli principle are together responsible for the structure of the periodic table, as shown in Figure 6.

Figure 6. Electron configuration and organization of the periodic table.

Different regions of the periodic table corresponding to the filling of different orbitals with electrons. For example, the first row of the periodic table is formed from elements adding electrons to the 1s orbital, the second row is formed from elements adding electrons to the 2s and 2p orbitals, and so forth. Also notice that this regularity in filling of orbitals is responsible for the periodic properties observed in elements in a particular column (group) of the table. For example, the halogens (F, Cl, Br, I, At) all have an electron configuration $ns^2\ np^5$, and so have similar chemical and physical properties.

Any electron configuration that differs from that for the ground state configuration is considered an excited state configuration. For example, for phosphorus (P) we have

ground state   [Ne] $3s^2\ 3p^3$

excited state   [Ne] $3s^1\ 3p^4$

excited state   [Ne] $3s^2\ 3p^2\ 3d^1$

Any electron configuration (other than the ground state configuration) that is consistent with the Pauli principle is a possible excited electron configuration.

5. Electronic states, term symbols, spectroscopy and selection rules

Each electron in a multi-electron has its own set of quantum numbers, including values for ℓ and s (of course s = $\frac{1}{2}$ for all electrons). These quantum numbers can be used to give an overall quantum number for the combined orbital angular momentum (L) and spin angular momentum (S) for all of the electrons in the atom. While there is a relatively simple procedure that can be used to find possible values for L and S for a particular electron configuration, we are only interested in the results.

The values for L and S for a particular electronic state are indicated by use of a <u>term symbol</u>, written as follows:

$$^{2S+1}L \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (8.5.1)$$

where the left superscript is equal to 2S+1 (where S is the total spin angular momentum quantum number) and L is the symbol for the total orbital angular momentum quantum number. The letters used to represent L follow the same pattern used to represent orbitals

quantum number for a single electron   total orbital angular momentum quantum number

ℓ	symbol		L	symbol
0	s		0	S
1	p		1	P
2	d		2	D
3	f		3	F

The only difference between the symbol used for the orbital angular momentum quantum number for a single electron and the quantum number for the total orbital angular momentum is that a capital letter is used for the total orbital angular momentum.

The following are examples of writing term symbols based on the values for L and S:

L = 1, S = 1 $\quad\quad$ ^3P

L = 2, S = $^1/_2$ $\quad\quad$ ^2D

L = 0, S = 0 $\quad\quad$ ^1S

For a particular electron configuration there will be one or more term symbols, corresponding to different electronic states with different energies. For example, for the ground state electron configuration for an oxygen atom ($1s^2 \, 2s^2 \, 2p^4$) there are three different electronic states (^1S, ^1D, and ^3P).

When there is more than one electronic state for a particular electron configuration, the following two rules can be used to put the electronic states in order from lowest to highest energy:

1) The larger the value for S (and, therefore, for 2S+1) the lower the energy.

2) For two states with the same value for S, the larger the value for L the lower the energy

Using these two rules we would predict the ordering of energy for the three electronic states found for the ground electron configuration of an oxygen atom is $^3P < {}^1D < {}^1S$. It is important to note that the above two rules can only be used to compare electronic states that arise from the same electron configuration.

There is a magnetic field generated by the orbiting of electrons around a nucleus, and also by the intrinsic spin of the electrons. The interaction of these two magnetic fields has a small effect on the electronic energy, which is described by an additional quantum number J. For a particular value of L and S, the possible values of J are:

$\quad\quad$ maximum value of J = | L + S | $\quad\quad\quad\quad$ minimum value of J = | L – S |

with all values between the maximum and minumun values that differ from them by integer amounts also possible. If we use the same examples as used above for the term symbols, this gives the following possible values for J:

L = 1, S = 1 $\quad\quad$ ^3P $\quad\quad$ J = 2, 1, 0

L = 2, S = $^1/_2$ $\quad\quad$ ^2D $\quad\quad$ J = $^5/_2$, $^3/_2$

L = 0, S = 0 $\quad\quad$ ^1S $\quad\quad$ J = 0

Since the value for J has only a small effect on the energy of an electronic state, we usually do not worry about finding values of J for particular term symbols.

Atoms can absorb or emit light at energies (wavelengths) corresponding to the difference in energy between two energy levels. Just as is the case for light absorption and emission in rotational and vibrational spectroscopy, there are additional requirements besides conservation of energy, called selection rules, that must also be satisfied. For electronic states of an atom, the selection rules are:

$\quad\quad$ $\Delta S = 0$ $\quad\quad\quad\quad$ (so the total spin quantum number cannot change)

$\quad\quad$ $\Delta L = 0, \pm 1$ $\quad\quad$ (so the total orbital quantum number either does not change, or changes by ± 1)

Given a set of electronic states for an atom, use of these selection rules makes it possible to identify all of the allowed transitions that occur. If the energies of the electronic states are also known, the energies and wavelengths of the allowed transitions can be found.

As an example, consider the following electronic states for a helium atom

configuration	state(s)	$\tilde{E}$ (cm^{-1})
1s^2	^{1}S	0.
1s^1 2s^1	^{3}S	159860.
	^{1}S′	166280.
1s^1 2p^1	^{3}P	169090.
	^{1}P	171130.

Note that the lowest energy electronic state is always assigned a value of 0. cm^{-1} for its energy.

If we use the selection rules that apply for light absorption or emission by atoms, the following allowed transitions occur, listed as (lower energy state, higher energy state):

transition	Energy (cm^{-1})	Wavelength (nm)
(^{1}S,^{1}S′)	166280.	60.1
(^{1}S,^{1}P)	171130.	58.4
(^{1}S′,^{1}P)	4850.	2062.
(^{3}S,^{3}P)	9230.	1083.

The lowest few energy levels for a helium atom, and the allowed transitions between energy level, are shown in Figure 7. Helium atoms would be expected to absorb or emit light at the wavelengths appearing in the table and shown in the figure.
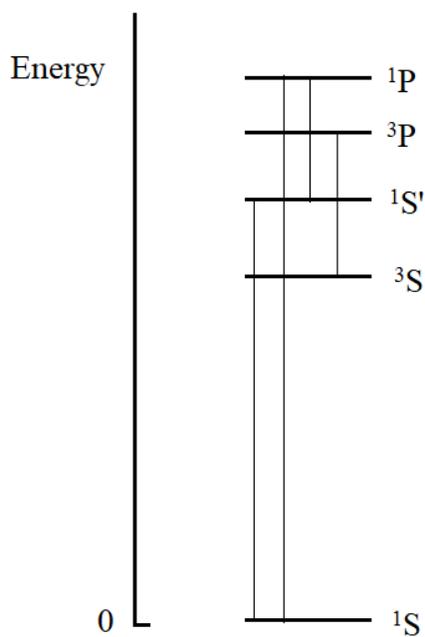

Figure 7. The lowest few energy levels for a helium atom. The allowed transitions between energy levels are as shown in the figure.

Each individual atom has its own unique wavelengths where it can absorb or emit light. These processes are the basis for two common analytical techniques – atomic absorption spectroscopy (AAS), which examines light absorption by an atomic gas, and atomic emission spectroscopy (AES), which studies light emission by an atomic gas. These techniques can not only identify the presence of a particular element in a sample of a substance, but can also make it possible to determine the concentration of each element in the sample. This has applications in analytical and forensic chemistry, metallurgy, geochemistry, and other areas of science.