

# 3.091 - Introduction to Solid State Chemistry

## Lecture Notes No. 1

### ATOMIC AND ELECTRONIC STRUCTURE

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Sources for Further Reading:

1. Davies, D.A., Waves, Atoms and Solids, Longman, 1978.
2. DeKock, R.L., Chemical Structure and Bonding, Benjamin, 1980.
3. Brown, T.L., Chemistry, The Central Science, 5th Ed., Prentice Hall, 1991.

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#### 1. ATOMS

The familiar model of an atom is that of a small nucleus composed of protons and neutrons surrounded by rapidly moving electrons. Typically, the atomic diameter is on the order of  $10^{-10}$  m while that of the nucleus is on the order of  $10^{-15}$  m. Protons and neutrons have about the same mass (1.00728 and 1.00867 amu respectively) and each is about 1800 times as heavy as an electron. A neutron is electrically neutral, but a proton has a positive charge ( $+1.6 \times 10^{-19}$  coulomb\*) which is exactly the opposite of the negative charge of an electron. In a neutral atom, the number of electrons around the nucleus equals the number of protons in the nucleus.

The number of protons in the nucleus (the "atomic number",  $Z$ ) characterizes a chemical element. Atoms of a given *element* all have the same number of protons, yet may have different masses. The atomic mass number of an atom,  $A$ , is given by  $A = Z + N$ , where  $N$  is the number of neutrons in the nucleus. Since an element is characterized solely by  $Z$ , it follows that atoms of a given chemical element may have a varying number of neutrons. Subspecies of chemical elements with the same  $Z$  but differing  $N$  and  $A$  are called *isotopes*. The atomic weight of an element is the weighted average of the atomic masses of the various naturally occurring isotopes of the element, and the atomic weight scale is based on a value of exactly 12, after the carbon isotope that has an atomic mass number of 12.

#### 2. NUCLEI

The nucleus of an atom weighs less than the sum of the weights of its isolated component particles. The difference between the actual mass and that of the

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\*Generally adopted International Unit System.

components is called the *mass defect*. The mass defect,  $\Delta m$ , is related to the binding energy within the nucleus,  $\Delta E$  (in Joules), through Einstein's equation:

$$\Delta E = \Delta m c^2$$

where  $c$  is the velocity of light (in  $\text{m}\cdot\text{s}^{-1}$ ) and  $\Delta m$  is the mass defect (in kg). The nuclear forces which bind protons and neutrons together are strong, and the *binding energy* per nuclear particle (nucleon) amounts to about  $1.4 \times 10^{-12}$  Joules. The greatest nuclear binding energy is found in nuclei of medium atomic number (such as Fe) where  $N$  is approximately equal to  $Z$ . For nuclei of larger atomic number, such as uranium,  $N$  is about equal to  $1.5 Z$ , and the binding energy per nucleon is less. As a consequence of this decreased nuclear stability, some isotopes (of uranium, for example) are unstable. That is, if the uranium isotope,  ${}_{92}\text{U}^{235}$  ( $Z = 92$ ,  $A = 235$ ), is bombarded with neutrons, the following reaction can take place:



Here the reaction products are smaller nuclei of increased stability. (In the above convention, subscripts indicate the atomic number and the superscripts the mass number.) Notice that one incident neutron generates fission products including two neutrons - the basis for chain reactions in nuclear reactors and nuclear explosions.

Heavy nuclei (even light nuclei) which have an unfavorable ratio in the number of protons and neutrons can spontaneously *decay* by the emission of  $\alpha$  particles (helium ions) or  $\beta$  particles (electrons). These nuclei are referred to as *radioactive*. The rate at which the decay of such unstable nuclei takes place varies greatly and is indicated by the *half-life* of the material. In one half-life period, half of the unstable nuclei will have emitted radiation and thus will have changed their character (atomic number). In two half-life periods, only  $1/4$  of the nuclei will have survived. In three half-lives, only  $1/8$  of the original nuclei remain, etc. For example, the half-life of gamma-emitting "radio" cobalt,  ${}_{27}\text{Co}^{60}$  (used for X-ray therapy), is 5.3 years, whereas that of radioactive  ${}_{6}\text{C}^{14}$  is 5700 years. (Much more radiation is emitted per second by a given number of  $\text{Co}^{60}$  atoms than by the same number of  $\text{C}^{14}$  atoms.)

### 3. EXTRA-NUCLEAR ELECTRONS IN ATOMS

The first atomic theory in quantitative agreement with some experimentally determined facts was proposed in 1913 by Niels Bohr. He postulated (for atomic hydrogen) that:

- The (extra-nuclear) electron can assume only distinct (quantized) energy levels or states.
- In such energy levels, the electrons in motion will not radiate (lose) energy; on changing energy levels, radiation equivalent to the energy difference between the

levels is involved.

$$E_{\text{rad}} = E_2 - E_1 = h\nu$$

- The stable states of the atom involve motion of the electrons in circular orbits.
- The angular momentum of electrons in orbit ( $mvr$ ) is an integral number of  $h/2\pi$  units:

$$mvr = n \frac{h}{2\pi}$$

- Newtonian mechanics applies to orbiting electrons.

A pictorial view of the Bohr atomic model visualizes electrons orbiting at a velocity ( $v$ ) in well-defined spherical orbitals of radius ( $r$ ) around the nucleus. The angular momentum of the orbiting electrons can, as stated above, only assume certain values of  $n \times h/2\pi$  where  $n$  (called the principal quantum number) can assume any positive integer value, i.e. 1, 2, 3, 4, etc. to infinity (fig. 1).

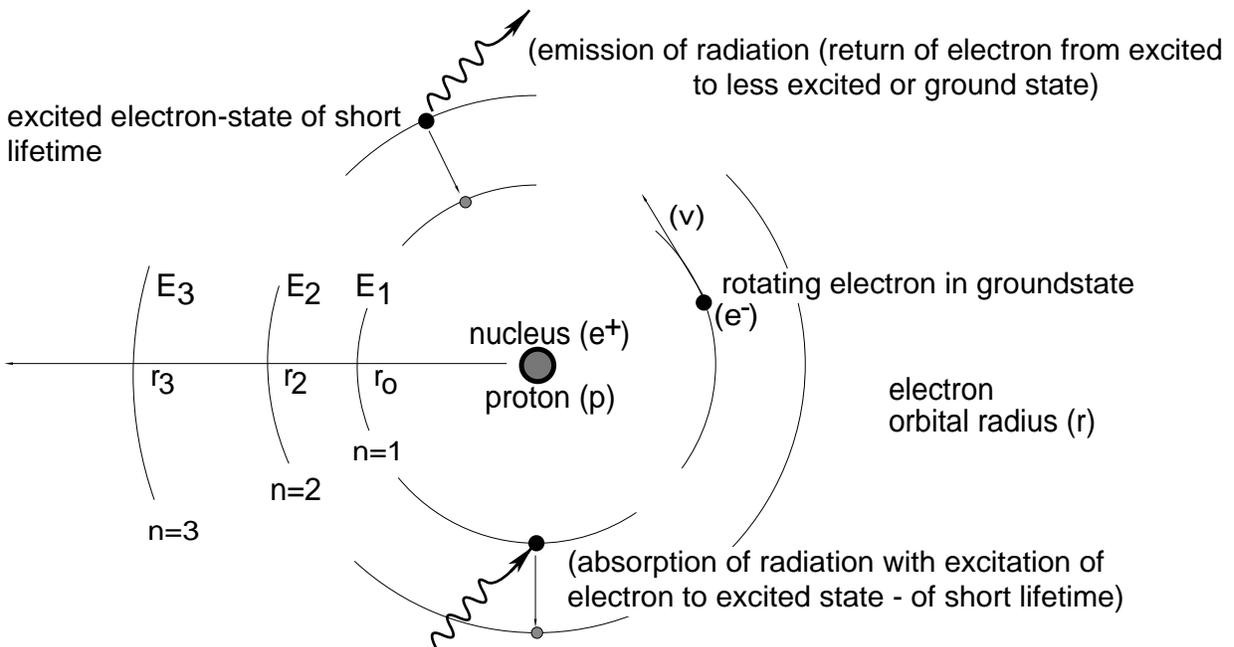


Figure 1 The Hydrogen Atom According to Bohr.

### The Hydrogen Atom

Assuming coulombic interaction and the applicability of Newtonian mechanics, the following values may be directly obtained for the hydrogen atom:

- The radius of an electron orbit (spherical) in hydrogen is given by:

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2} \quad (n = 1, 2, 3, 4, \text{ etc.})$$

$$r_n = n^2 \times \text{constant} = n^2 (0.529 \times 10^{-10}) \text{ m}$$

It can be seen that the smallest electron orbit in hydrogen - the stable orbit - is given for  $n = 1$  at  $r_0 = 0.529 \text{ \AA}$ . It is also seen that  $r$  increases with  $n^2$  ( $r = n^2 r_0$ ).

- The energy of an orbiting electron characterized by the principal quantum number ( $n$ ) is given as:

$$E_n = - \frac{1}{n^2} \times \frac{m e^4}{8 h^2 \epsilon_0^2} = - \frac{1}{n^2} \times \text{constant} \text{ [Joule]}$$

This relationship indicates that electron orbits with increasing principal quantum number ( $n$ ) assume decreasing negative values ( $1/n^2$ ) with the limiting value ( $n \rightarrow \infty$ ) being zero. For convenience, it is frequently customary to express electronic energies in terms of *wave numbers* ( $\bar{\nu}$ ) with the units of [ $\text{m}^{-1}$ ]. This conversion may readily be made since  $E = h\nu$ . Thus:

$$\bar{\nu} = \frac{1}{\lambda} = - \frac{1}{n^2} \times \frac{m e^4}{8 h^3 c \epsilon_0^2} \text{ [m}^{-1}\text{]}$$

Upon substituting numerical values for all the constants, we obtain:

$$\bar{\nu} = - \frac{10973500}{n^2} = - \frac{1}{n^2} \times 10973500 \text{ [m}^{-1}\text{]}$$

(where  $n$  is again the principal quantum number which may assume the values 1, 2, 3, 4, etc. The value of 10973500 is referred to as the *Rydberg constant* ( $R$ ; also  $R_H$  and  $R_\infty$ ) to honor the man who obtained its value from spectroscopic studies prior to the establishment of the Bohr model.)

The energy changes associated with electronic transitions and the accompanying emission of radiation (or absorption of radiation) may simply be calculated as

follows:

$$\text{Emission} = \Delta E = (E_{n_1} - E_{n_2}) = h\nu$$

Here  $n_2$  is the principal quantum number of the outer orbit and  $n_1$  is that of the inner orbit. In terms of  $\bar{\nu}$ , the wave number, we obtain for emission of radiation:

$$\bar{\nu} = \left[ \left( -\frac{10973500}{n_1^2} \right) - \left( -\frac{10973500}{n_2^2} \right) \right]$$

or

$$\Delta E = 10973500 \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \times hc$$

$$\Delta E = R \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \times hc$$

$$\Delta E = 2.1798 \times 10^{-18} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \text{ J}$$

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\text{Absorption} = \Delta E = E_{n_2} - E_{n_1}$$

$$\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Electronic transitions (fig. 2) are conveniently represented in so-called term schemes.

### Multi-Electron Systems

The limitations of the Bohr atom became apparent soon after its establishment. For example, the uranium atom would require 92 electronic orbits and it would have to assume a size which is incompatible with the experimental facts. The first modifications of the Bohr model were made by Sommerfeld, who introduced additional quantum conditions: Taking into account that individual sharp spectral lines split into several lines (of slightly differing  $\lambda$ ) if light emission takes place in a magnetic field (Zeeman effect), the following picture emerged from the Bohr atom: electronic spherical orbits (shells)

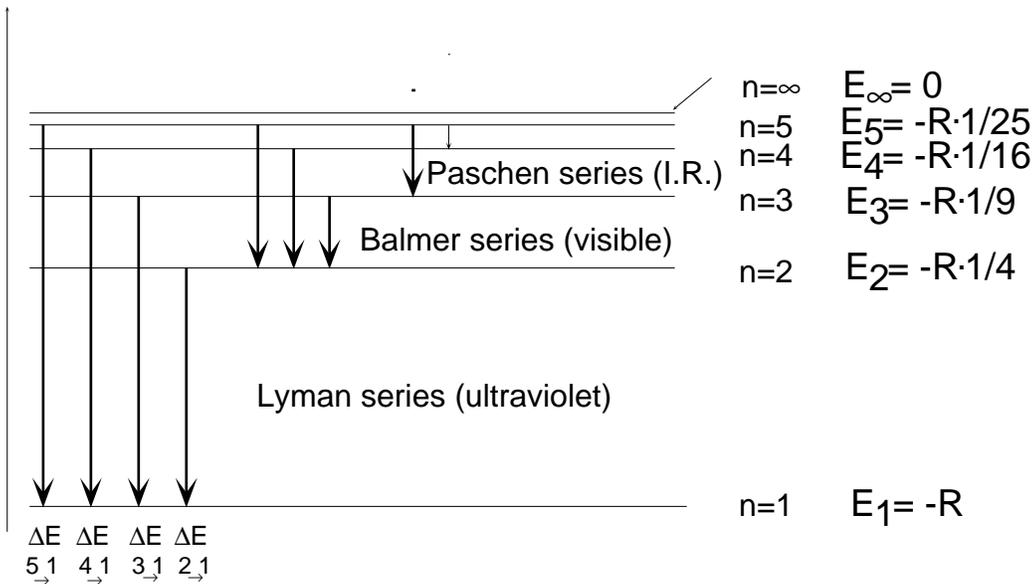
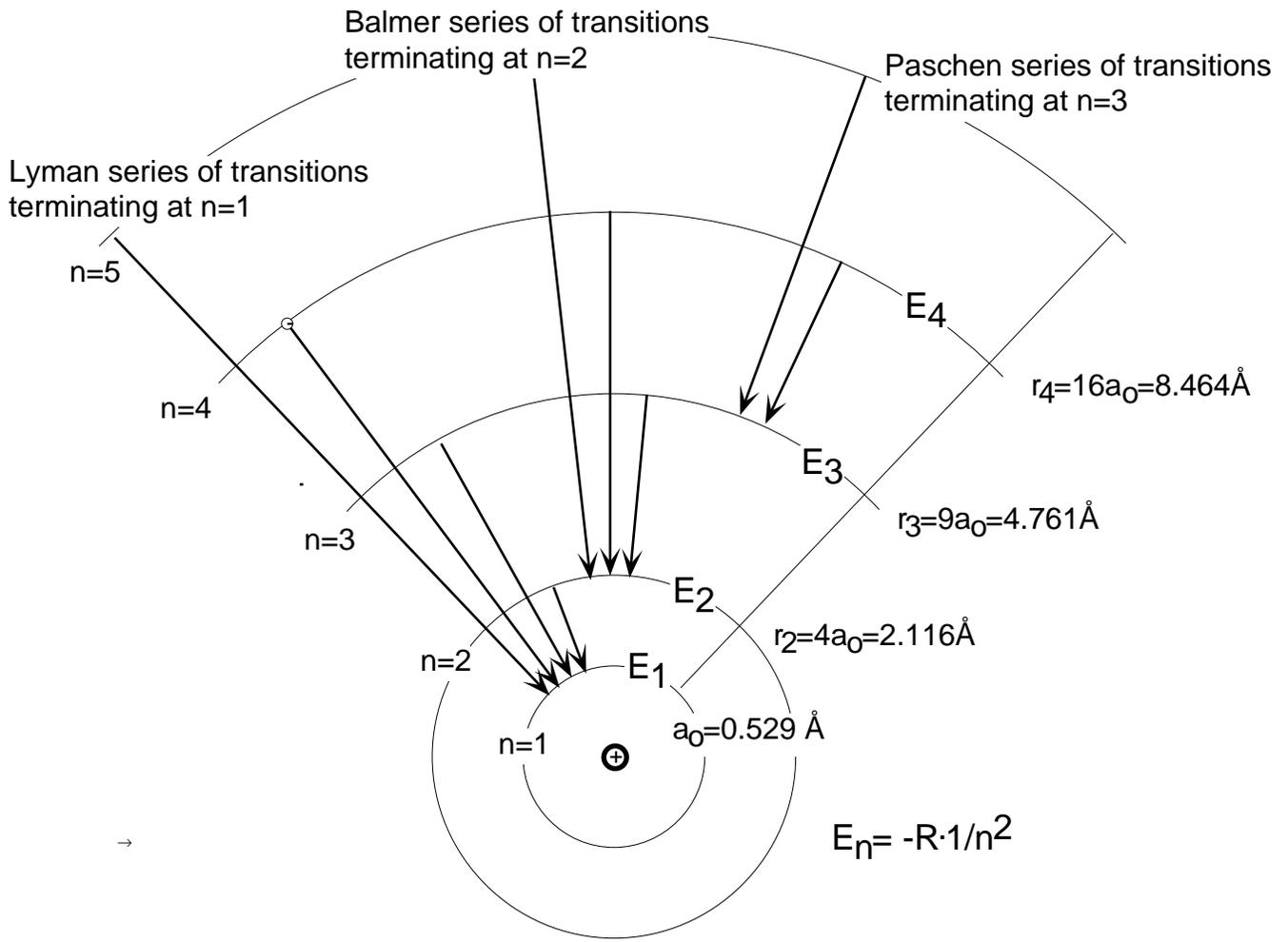


Figure 2 Electron Transitions and Related Optical Spectra in Atomic Hydrogen

may have suborbitals (orbits) which are elliptical of varying eccentricity - controlled by an additional quantum number, the orbital quantum number ( $l$ ). The eccentric orbitals may assume only particular spatial orientations controlled by the magnetic number ( $m$ ), in an external magnetic field. The observed magnetic behavior of the elements required an additional quantization (Uhlenbeck) - the introduction of the spin quantum number ( $s$ ).

According to the Bohr–Sommerfeld quantum theory, electrons move about the nucleus of an atom in well-defined orbits, each of which is characterized by four numbers, called *quantum numbers*. An electron moving in an orbit close to the nucleus has a larger (negative) energy than one in an outer orbit. Energy is therefore necessary to move an electron from an inner to an outer orbit (with smaller negative energy). Conversely, energy is released (as radiation) during the transition of an electron from an outer to an inner orbit. The (electromagnetic) radiation released consists of discrete entities or quanta, which are called *photons*. The energy of emitted photons is given by the difference in energy between the two orbits involved and is related to the frequency,  $\nu$ , or the wavelength,  $\lambda$ , of the electromagnetic radiation by:

$$E_{\text{photon}} = E_2 - E_1 = h\nu = h(c/\lambda) \quad (c = \lambda\nu)$$

where  $h$  is called the Planck's constant,  $E_2$  and  $E_1$  are the energies of the outer and inner orbits, respectively, and  $c$  is the velocity of light. Through (spectroscopic) observations of the frequencies or wavelengths of radiation emitted by an excited atom (atom with an excited electron), the differences of electron energy levels can be determined. Figure 1 shows such energy levels obtained from measurements of the wavelengths of radiation emitted by atomic hydrogen excited electrically in a gas discharge tube.

To specify the spatial location and energies of electrons in an atom requires the use of four *quantum numbers*. The "principal quantum number", ( $n$ ), determines the size of the *shell* in which a particular electron orbits around the nucleus; it also largely determines its energy. The value of  $n$  is restricted to integral values:  $n = 1, 2, 3$  and so forth. A value of  $n = 1$  signifies that the electron exists in the lowest energy state and its *orbit* is in the innermost allowed *shell*, as close to the nucleus as possible. Successively higher energy states are represented by  $n = 2, 3$ , etc. It should thus be clear that the principal quantum number of the outermost orbiting electron determines, in principle, the size of a given atom. For convenience, letters are frequently used to characterize the electronic shells of  $n = 1, 2, 3, 4$ , etc. In letter notation:

$n = 1 = \text{K shell}$   
 $n = 2 = \text{L shell}$   
 $n = 3 = \text{M shell}$   
 etc.

The second quantum number, ( $l$ ), is referred to as the “orbital” or “azimuthal quantum number”. It specifies the angular momentum of orbiting electrons and, to a minor extent, their energy. “ $l$ ” can only assume integral values ranging from  $l = 0$  to  $l = (n-1)$  (where  $n$  is the principal quantum number). Accordingly, for  $n = 1$  (the K shell),  $l$  can only assume a value of 0. For  $n = 2$ , either  $l = 0$  or  $l = 1$  is possible, etc. For convenience again, letters are used to specify the electronic state (orbit) in a given shell (characterized by  $n$ ) corresponding to the second quantum number:

$$l = 0 = s \text{ (orbit)}$$

$$l = 1 = p \text{ (orbit)}$$

$$l = 2 = d \text{ (orbit)}$$

$$l = 3 = f \text{ (orbit)}$$

An electron with  $l = 0$  is in an s-quantum state (in short, it is an s-electron), one with  $l = 1$  is in a p-state, etc. Thus, an electron with a principal quantum number  $n = 3$  and an orbital quantum number  $l = 1$  is called a 3p electron (the electron in the M shell is in a p orbital).

The third quantum number, ( $m$ ), called the “magnetic quantum number”, controls the number of allowed spatial orientations (“degeneracy”) of each orbit characterized by  $l$  in a given shell [characterized by ( $n$ )]. (Degenerate states are of identical energy. The “degeneracy” disappears in the presence of a magnetic field where different spatial orientation of orbits assume different energy values.) The total number of allowed orbital orientations for any orbital characterized by  $l$  is  $(2l + 1)$ , corresponding to  $m$  values of  $l$ ,  $(l - 1)$ ,  $(l - 2)$ , ..., 0,  $-1$ ,  $-2$ , ...,  $-l$ . An electronic state with  $l = 0$  necessarily has only  $m = 0$  and thus has no directional orientation in space; it is a spherical orbit. On the other hand, a p-state ( $l = 1$ ) allows  $m$  values of  $-1$ , 0,  $+1$ . The resulting three possible orientations are perpendicular to one another (as shown in fig. 4).

The first three quantum numbers ( $n$ ,  $l$  and  $m$ ) define atomic electron orbitals. They are related respectively to the size, shape, and spatial orientation of the orbital. The fourth quantum number,  $s$ , (called the “electron spin quantum number”), can be interpreted as determining for an orbiting electron the direction of electronic spin around its own axis. “ $s$ ” can assume values of  $+1/2$  (parallel spin) and  $-1/2$  (anti-parallel spin). For notational purposes, a positive  $s$  is conveniently represented as  $\uparrow$  and a negative  $s$  as  $\downarrow$ .

We may now summarize our findings about the electronic states in atoms. Any electron in an atom is defined by four quantum numbers, viz.:

- The principal quantum number ( $n$ ), which may have any positive integral value except zero. (In practice, because of the instability of heavy nuclei, atoms containing electrons with  $n$  values greater than 7 are unknown.)

- The orbital or azimuthal quantum number ( $l$ ), which is an integer and may have any positive value less than  $n$ , including zero.

$$0 \leq l < n$$

- The magnetic quantum number ( $m$ ), which is also an integer and may have any positive or negative value equal or less than  $l$ , including zero.

$$-l \leq m \leq +l$$

- The spin quantum number ( $s$ ) which may only assume one of two values, namely  $+1/2$  and  $-1/2$ .

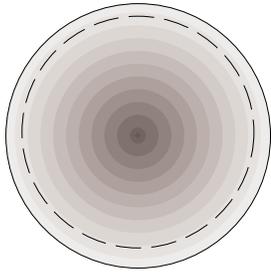
$$s = \pm 1/2$$

An important law enables us to make use of these quantum rules for the characterization of electronic states in multi-electron systems: the *Pauli Exclusion Principle*. It states that in any atom no two electrons may have the same four quantum numbers. From this principle it follows that each electronic orbital can accommodate at most two electrons differing by their spin quantum number which will be  $+1/2$  for one electron and  $-1/2$  for the other electron. (The Pauli principle is based on the fact that the separate existence of any electron depends upon its non-destruction by interference, i.e. on its wave nature.)

A further useful fact that generally simplifies understanding electronic structures is that (with exceptions stated shortly) *the quantum states for electrons follow the rule (Aufbau Principle) that the lowest  $m$ ,  $l$  and  $n$  numbers, consistent with Pauli's exclusion principle, are selected first by electrons in multi-electron atoms.* (For the spin quantum numbers, the  $+1/2$  value is given priority over the  $-1/2$  value.) Applicability of this rule is restricted to systems in which the orbitals, defined by a selected set of quantum numbers with lowest possible numerical value, correspond to orbitals of lowest energy since in all instances the lowest energy levels are filled first. The build-up of the electronic states of an atom is obtained by placement of the electrons first in the orbitals of lowest energy (the *aufbau principle* or "construction principle").

Wave mechanics (introduced by Schrödinger), unlike the quantum theory based on a planetary model, asserts that an electron in an atom cannot be considered as a particle having an orbit with a definite radius. Instead, there is a *probability* of an electron being at certain spatial positions. Hence, the location of an electron is best described in terms of its *probability density distribution*, which is sometimes called an *electron cloud*. The spatial symmetry of the probability distribution depends upon the electronic state. The electron cloud is spherically symmetric for  $s$ -electrons, but more complicated for electrons in a  $p$ -state. Examples of these distributions are shown in fig. 3 for  $1s$  and  $2p$  electrons.

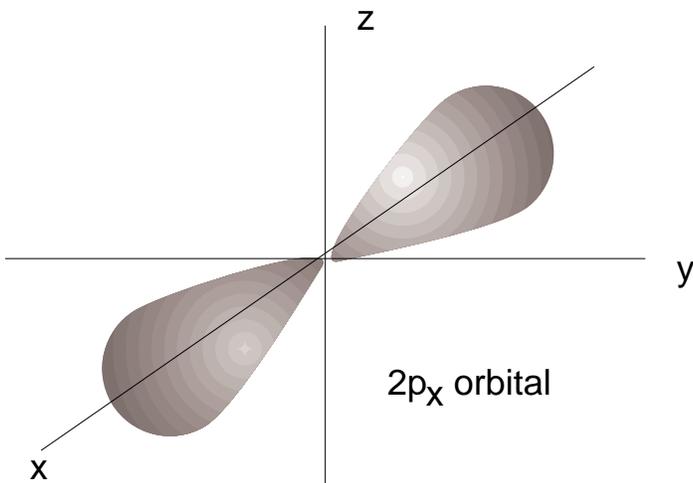
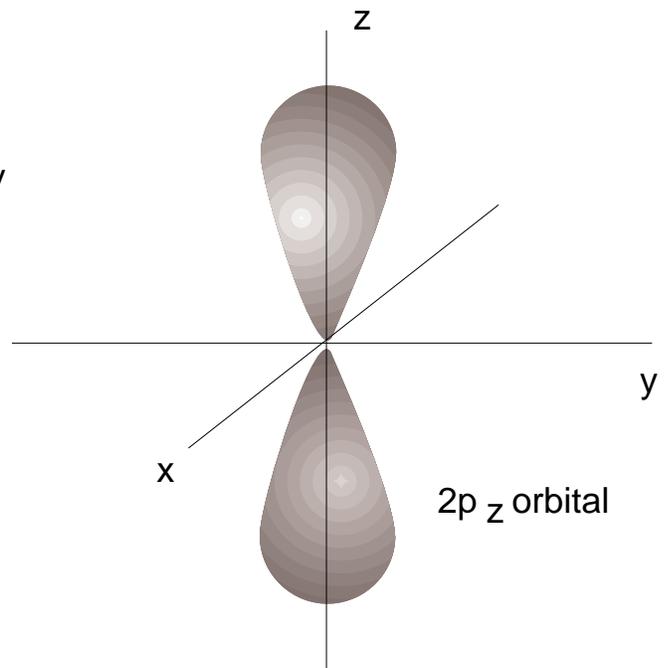
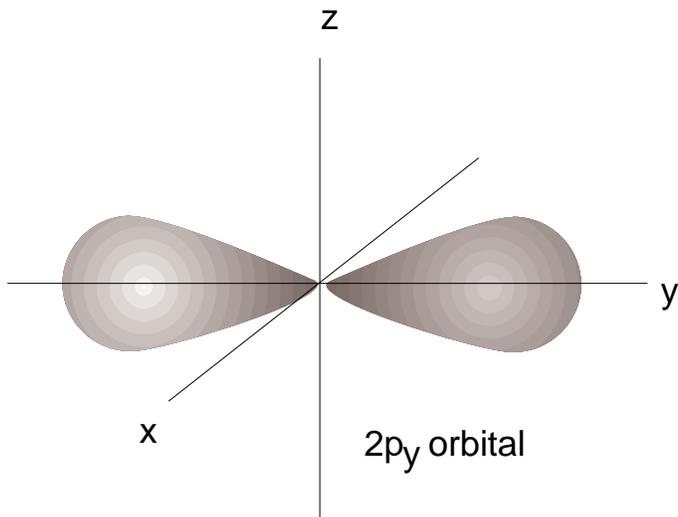
Figure 3 Conclusions on Electron Orbital Shapes based on Wave Mechanics:



99% contour of 1s electron orbital



99% contour of 2s electron orbital



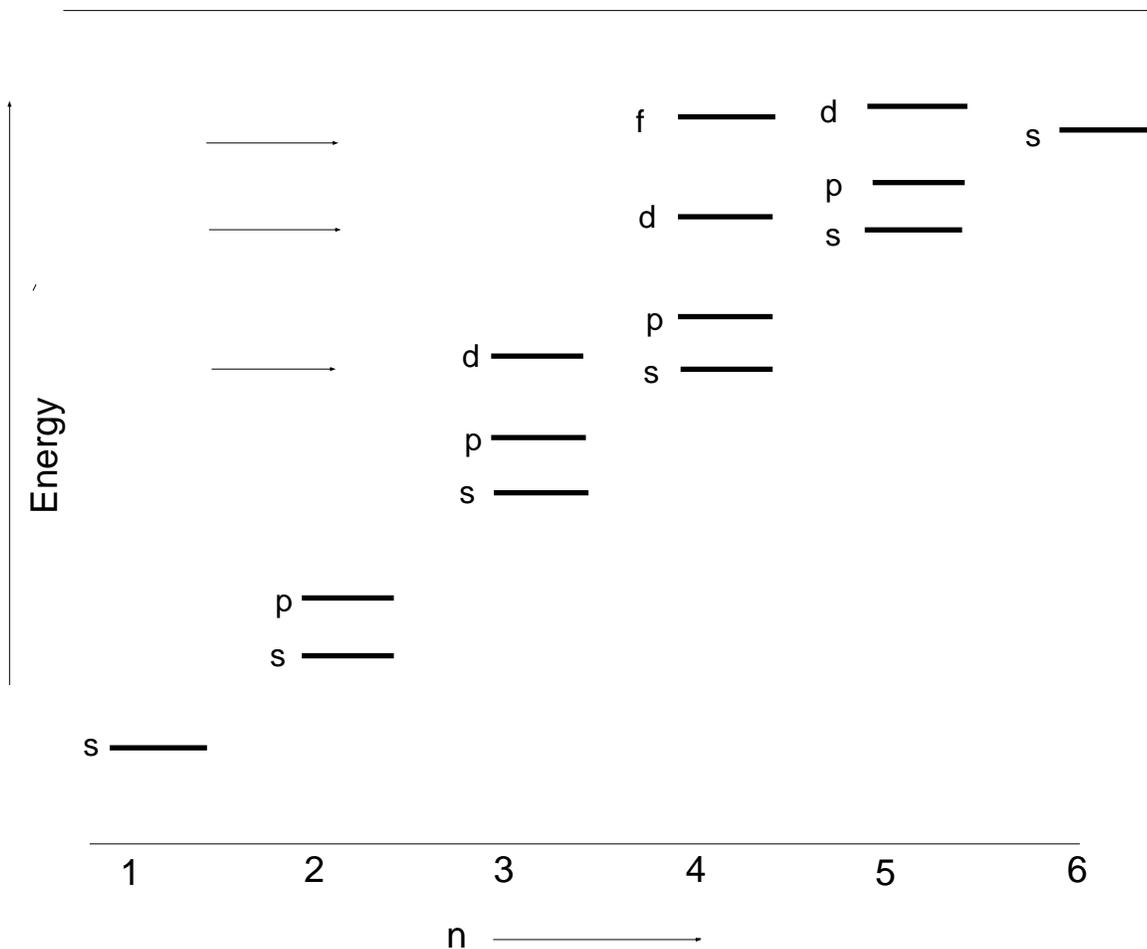
#### 4. ENERGY LEVELS AND THE AUFBAU PRINCIPLE

Consider the atom of an element containing one extra-nuclear electron: hydrogen; for electro-neutrality the charge on the nucleus must be +1. This orbiting electron (in the ground state - the lowest possible, most stable state) will have the lowest available quantum numbers in  $n$ ,  $l$  and  $m$ . That is,  $n = 1$ ; hence  $l = 0$  and  $m = 0$ ; also,  $s = +1/2$ .

In the two-electron atom helium, one electron will have the same quantum numbers as the electron in hydrogen and the other electron will have quantum numbers  $n = 1$ ,  $l = 0$ ,  $m = 0$  and  $s = -1/2$ . The element of atomic number 3 (lithium) will have two electrons with the same quantum numbers as the helium electrons, plus one electron with the quantum numbers  $n = 2$ ,  $l = 0$ ,  $m = 0$ ,  $s = +1/2$ . [Note that  $n$  must be 2 for the third electron since states such as  $(n = 1, l = 1)$  or  $(n = 1, l = 0, m = 1)$  or  $(n = 1, l = 0, m = -1)$  are not allowed. Similarly, the quantum numbers for the additional electron in beryllium (atomic number 4) are  $n = 2$ ,  $l = 0$ ,  $m = 0$ ,  $s = -1/2$ . The next electron for boron (atomic number 5) has the values  $n = 2$ ,  $l = 1$ ,  $m = -1$ ,  $s = +1/2$ , and so on.

In applying the aufbau principle to the orbital filling with increasing atomic number we have thus far inferred the tendency of the energies of electrons to follow in the same order as the principal quantum numbers; that is, successive electron shells are filled with increasing  $Z$ . This concept does not hold in all instances. For example, electrons with the quantum numbers  $n = 3$ ,  $l = 2$  (and various  $m$  values) are of higher energy than those with  $n = 4$ ,  $l = 0$ . Other *inversions* occur with  $n = 4$  and higher. These apparent irregularities in the aufbau principle, the result of an energetic overlap of orbitals in successive shells, lead to partial shell fillings and the appearance of groups of so-called transition elements. The groups are characterized (with minor exceptions) by identical outermost electron shell configurations and therefore do not exhibit, with increasing atomic number, the (expected) change in properties observed on regular shell filling for elements 2-18. (In the transition elements, with increasing atomic number the electrons are accommodated in lower lying shells which remained empty because of the above mentioned energy overlap of their orbitals.) The energy levels of the various orbitals in shells with increasing  $n$  are schematically indicated in fig. 4.

Another factor in the application of the aufbau principle is Hund's Rule which states that in atoms the electrons tend at first to fill up given orbitals ( $m$  levels) singly (with unpaired spins and spin quantum number equal to  $+1/2$ ). Only after all  $m$  levels associated with a particular  $l$  value in a given shell have been used for single-electron occupation does doubling of electrons into  $m$  levels occur. Thus the extra electron for carbon (atomic number 6) has the quantum numbers  $n = 2$ ,  $l = 1$ ,  $m = 0$ ,  $s = +1/2$  rather than  $n = 2$ ,  $l = 1$ ,  $m = -1$ ,  $s = -1/2$ . Both the effects of energy inversion and Hund's rule are very apparent when considering the electronic configuration of the elements  $Z = 18$ , 19, 20 and 21.



Relative energies of the orbitals in neutral, many-electron atoms. Electrons will always assume lowest available energy states. Accordingly, with increasing atomic numbers, the 4s states will be filled prior to the 3d states, for example.

The s, p, d, and f orbital sets:

Types of orbitals	Orbital quantum numbers	Total number of orbitals in set	Total number electrons accommodated.
s	$l=0; m=0$	1	2
p	$l=1; m=1,0,-1$	3	6
d	$l=2; m=2,1,0,-1,-2$	5	10
f	$l=3; m=3,2,1,0,-1,-2,-3$	7	14

Figure 4

The presently used notation is not the most convenient way of designating the energy levels (and wave functions) occupied by the electrons in atoms. The more informative way is a code written as follows: The principal quantum number is given first, followed by the conventional letter which designates the azimuthal (orbital) quantum number and, in a superscript, the number of electrons with that azimuthal quantum number. The code for the electronic ground state in hydrogen, therefore, is  $1s^1$ , for helium  $1s^2$ , lithium  $1s^22s^1$ , beryllium  $1s^22s^2$ , boron  $1s^22s^22p^1$ , etc. (See fig. 5 for example.) You will note that the magnetic quantum number has not been specified, but this can be done when required by writing  $p_x$  when  $m = -1$ ,  $p_y$  when  $m = +1$  and  $p_z$  when  $m = 0$ . Similar codes exist for the d and f levels. Usually such subscripts are not specified and in that case a consideration of Hund's rule will not be required.

An important fact to remember is that the number of electrons in any s, p, d or f level is limited: There are, as you know, a maximum of two electrons in any level with spin numbers  $+1/2$  and  $-1/2$ . For the p levels,  $l$  is one and, therefore, three  $m$  values ( $-1$ ,  $0$ ,  $+1$ ) are permitted, each with two electrons of spin number  $+1/2$  and  $-1/2$ , resulting in a maximum of six p electrons in any p orbital system. The reader should confirm that ten electrons are the maximum in a d system of orbitals and 14 in an f system of orbitals.

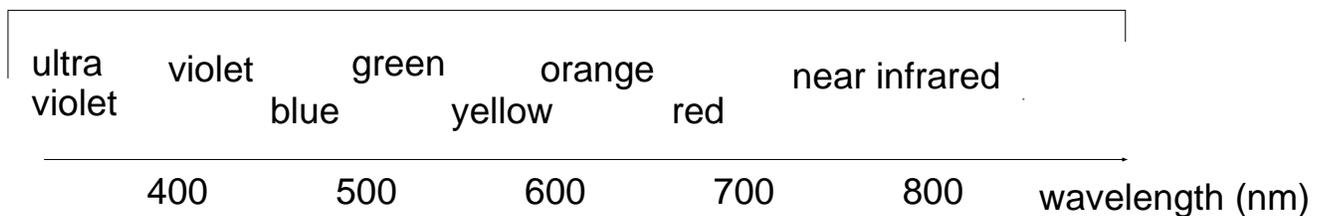
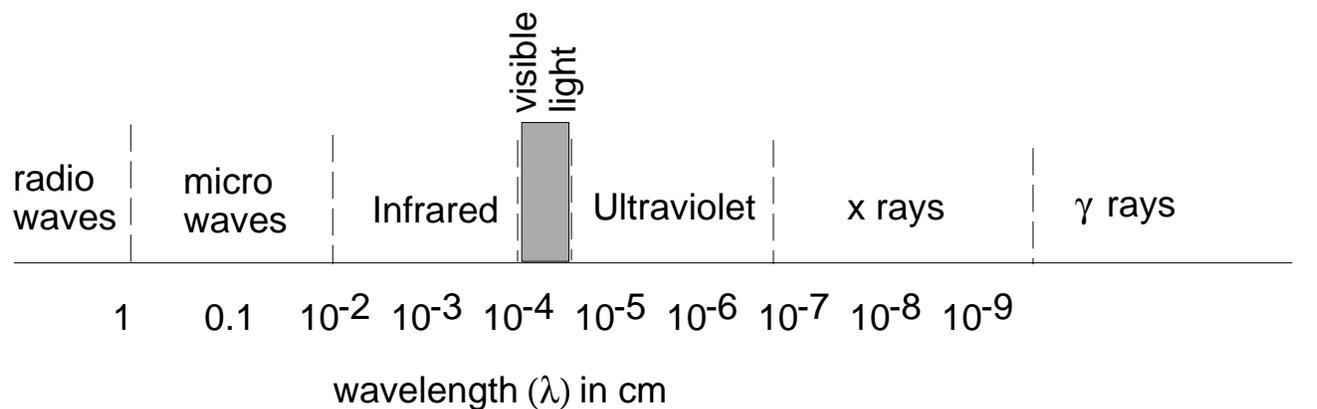
## 5. IONIZATION POTENTIAL

Electrons may be removed from isolated atoms by bombardment with other electrons and by heat, for examples. The work (energy) required to remove the most weakly bound (outermost) electron from an isolated atom is known as the "ionization energy". This energy is sometimes listed in units of Joules. More often ionization energies are given in terms of the "ionization potential". The ionization potential is the potential (V) that will accelerate an electron at rest so that it acquires a kinetic energy, sufficient to extract the outermost (most loosely bound) electron from an atom. This potential is 13.595 Volt (as listed in the PT) for the ionization of a hydrogen atom. You can also say the electron is bound to the proton by an (negative) energy equivalent to the energy of an electron accelerated by a potential of 13.595 Volt. [If you make a dimensional analysis, you will recognize that charge ( $e$ ) times potential (V) has the dimensions of energy ( $\text{kg}\cdot\text{m}^2\cdot\text{sec}^{-2}$ ) and 1 electron Volt (1eV) corresponds to  $1.6 \times 10^{-19}$  Joules.] (Note that the first ionization energies are given as first ionization potentials (V) in the Periodic Table of the Elements; see also the 3.091 courseware menu.)

It is significant that inert or noble gases have some of the highest ionization potentials. This reflects the fact that these elements have just enough electrons to completely fill a shell or a subshell which form stable configurations. On the other hand, the ionization potentials of alkali metal atoms (Li, Na, etc.) are low - the lowest, that of Cs, is only 3.89 eV. The reason for this is that alkali metal atoms have one outer s-electron beyond the stable electronic structure of an inert gas atom. Consequently this single electron in

Figure 5 Atomic Electron Affinities (EA)

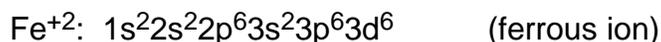
Atom	Orbital electronic configuration	EA, electron volts	Orbital electronic configuration of anion
H	1s <sup>1</sup>	0.756	(He)
F	(He) 2s <sup>2</sup> 2p <sup>5</sup>	3.45	(Ne)
Cl	(Ne) 3s <sup>2</sup> 3p <sup>5</sup>	3.61	(Ar)
Br	(Ar) 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	3.36	(Kr)
I	(Kr) 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>	3.06	(Xe)
O	(He) 2s <sup>2</sup> 2p <sup>4</sup>	1.47	(He)2s <sup>2</sup> 2p <sup>5</sup>
S	(Ne) 3s <sup>2</sup> 3p <sup>4</sup>	2.07	(Ne)3s <sup>2</sup> 3p <sup>5</sup>
Se	(Ar) 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>	(1.7)	(Ar)4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>
Te	(Kr) 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	(2.2)	(Kr)5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>
N	(He) 2s <sup>2</sup> 2p <sup>3</sup>	(-0.1)	(He)2s <sup>2</sup> 2p <sup>4</sup>
P	(Ne) 3s <sup>2</sup> 3p <sup>3</sup>	(0.78)	(Ne)3s <sup>2</sup> 3p <sup>4</sup>
As	(Ar) 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup>	(0.6)	(Ar)4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>



The visible spectrum

the outermost new shell can be removed relatively easily. (The second and successive ionization potentials of such atoms are increasingly greater.)

From a chemical and physical viewpoint, it is found that whether an atom is neutral or ionized as well as isolated or combined leads to distinctly different characteristics. It should be recognized that the notation used previously for neutral atoms can also be employed for electronic structures of ions. The electronic configurations of an iron atom and two iron ions are shown below.



## 6. ELECTRON AFFINITY

As we shall see later, the tendency of some atoms to accept, as well as to lose, electrons is important in determining how atoms combine with each other. Whereas removal of an electron always requires the expenditure of energy, acceptance of one extra electron by an atom generally is accompanied by the release of energy. The amount of energy released on acquisition of an electron is called the *electron affinity* (or “first electron affinity”). The elements on the left of the periodic table (metals) and the inert gases on the outer right have low electron affinities, whereas the non-metals have higher ones. The particularly high electron affinities of halogen atoms (F, Cl, etc.) may be attributed to the fact that these elements all lack one electron which would provide the stable electronic structure of an inert gas. By acquiring an additional electron, they increase their stability since the additional electron goes into the orbital lacking one electron and thus results in a stable,  $s^2 p^6$ , octet configuration. (See fig. 5.)

## 7. ATOMIC SIZE

The size, or volume, of an isolated atom is difficult to define explicitly since, in the electron cloud model of the atom, the probability density distribution theoretically reaches zero only at infinity. Nevertheless, the electron density falls off so rapidly at a short distance from the nucleus that some approximation of size can be made. In the hydrogen atom, for example, the electron density is very nearly zero at a distance of  $1.2 \text{ \AA}$  ( $1.2 \times 10^{-10} \text{ m}$ ) from the nucleus. The problem of defining atomic size is simplified in molecules and solids in that rather precise dimensions can be determined from interatomic distances which can be measured by diffraction techniques. Thus, in the  $\text{H}_2$  molecule the atoms are only  $0.72 \text{ \AA}$  apart, as determined from the distance between the nuclei. In this case the radius of the hydrogen atoms is taken to be  $0.37 \text{ \AA}$ , even though the size of the  $\text{H}_2$  molecule is considerably more than four times this value.

It should be apparent that the atomic radius depends upon whether an atom is isolated or combined with other atoms. The radius of an isolated atom is called the *van der Waals radius*, that of a bound atom in a molecule is the *covalent radius*, and that of a bound atom in a metal is the *metallic radius*. Van der Waals, covalent and metallic radii for some elements are listed in some periodic tables of the elements. The radii of positive ions (cations) and those of negative ions (anions) differ from the van der Waals radii. (See the 3.091 courseware menu on Athena.)

### SAMPLE PROBLEM

For hydrogen, calculate the radius ( $r$ ) and energy level ( $E_T$ ) of the electron in the lowest energy state (ground state).

\*\*\*\*\*

*Solution:*

The size of the first allowed orbit can be calculated by requiring that the centrifugal force of the orbiting electron be balanced by the coulombic attraction to the nucleus.

$$F_{\text{centr}} = \frac{mv^2}{r} \quad F_{\text{att}} = \frac{e^2}{4\pi\epsilon_0 r^2} \quad \frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

According to Bohr, the angular momentum of the electron ( $mvr$ ) is quantized in units of  $h/2\pi$ :

$$mvr = \frac{nh}{2\pi} \quad n = 1, 2, 3, \dots$$

With these quantum conditions,  $r$  for the first allowed orbit becomes:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$m^2 v^2 r^2 = \frac{me^2 r}{4\pi\epsilon_0}$$

$$\frac{n^2 h^2}{4\pi^2} = \frac{me^2 r}{4\pi\epsilon_0}$$

$$r = \frac{n^2 h^2 \epsilon_0}{\pi m e^2} = n^2 \times \text{constant}$$

For  $n = 1$ :

$$r_0 = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA}$$

The kinetic energy of the electron is  $1/2 mv^2$ . The potential energy as a function of distance from the nucleus is given by Coulomb's law as:

$$- \frac{e^2}{4\pi\epsilon_0 r}$$

The total energy is the sum of the kinetic and potential energies.

$$E_T = E_K + E_P$$

$$E_T = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

The balance of attractive and repulsive forces requires that:

$$F_{\text{centr}} = F_{\text{att}} \quad \text{Since: } \frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \quad \text{Then: } \frac{mv^2}{2} = \frac{e^2}{8\pi\epsilon_0 r}$$

Therefore:

$$E_T = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r}$$

Substitution for r now gives:

$$E_T = -\frac{1}{n^2} \times \frac{me^4}{8h^2\epsilon_0^2}$$

For n = 1:

$$E_T = -2.179 \times 10^{-18} \text{ J}$$

$$E_T = -13.6 \text{ eV}$$

**DEFINITIONS**

ATOM	The basic constituent of matter, consisting of a nucleus surrounded by electrons.
ATOMIC MASS NUMBER (A)	The combined number of protons and neutrons in a specific nucleus.
ATOMIC NUMBER (Z)	The number of protons in a specific nucleus, characteristic of a chemical element.
ATOMIC WEIGHT	<ol style="list-style-type: none"> <li>(1) The weighted mass of the naturally occurring atoms which constitute an element, relative to the value of exactly 12 for C<sup>12</sup>.</li> <li>(2) The mass, in grams, of one mole of a chemical element.</li> </ol>
ELECTRON	A negatively charged subatomic particle.
ELECTRON AFFINITY	The amount of energy released when an electron is added to the lowest possible energy level of a neutral atom.
ELECTRON DENSITY DISTRIBUTION/PROBABILITY DENSITY DISTRIBUTION	The spatial distribution of an electron in an atom, depending upon its set of quantum numbers.
ELECTRONIC CONFIGURATION	The shorthand notation used to designate the occupancy of energy levels in an individual atom.
ENERGY LEVEL	The discrete energy state of an electron in an atom, depending upon its set of quantum numbers.
FIRST IONIZATION POTENTIAL	The work which must be expended to remove an electron from a neutral atom in its ground state.
GROUND STATE	The lowest energy state of an atom. All electrons occupy energy levels sequentially from the lowest level.
HALF-LIFE	The time required for half of the atoms of an unstable, radioactive isotope to decay or for a reaction to go to 50% completion.

ION	A charged atom having either an excess or a deficiency of electrons relative to its nuclear charge.
ISOTOPE	The form of an element having the same atomic number but different atomic mass number (or atomic weight) than other forms of the element. As a rule, isotopes of an element exhibit virtually identical chemical behavior, but may exhibit quite different nuclear and physical behaviors.
NEUTRON	A neutral subatomic particle having approximately the same mass as a proton.
NUCLEUS	An extremely dense, small portion of an atom, with a radius of about $10^{-5}$ that of an atom and containing in excess of 99% of the atomic mass.
ORBITAL	A pictorial designation pertaining to the existence of an electron within a subshell, depending upon the magnetic quantum number, $m$ . Each orbital may contain a maximum of two electrons having opposite spins- i.e., electron spin quantum numbers of $+1/2$ or $-1/2$ .
PAULI EXCLUSION PRINCIPLE	The statement that each electron in an atom must have a specific set of unique quantum numbers.
PERIODIC TABLE	A chart arraying the chemical elements in order of increasing atomic number and in groups having similar chemical behavior and similar outer electronic configurations.
PHOTON	A quantum, or minimum unit, of electro magnetic energy. The energy is equal to Planck's constant, $h$ , times the frequency, $\nu$ , of the radiation.
PROTON	A positively charged subatomic particle whose charge is exactly opposite that of an electron and whose mass is about 1800 times that of an electron.
QUANTUM NUMBERS	A series of discrete numbers which catalog the state of an electron and which can be derived from wave mechanics.

SHELL	A pictorial designation pertaining to electrons having the same principal quantum number, $n$ , often indicative of the overall energy level of the electron.
SUBSHELL	A pictorial designation pertaining to the state of electrons within a shell, depending upon the second quantum number, $l$ , and indicative of the spatial distribution of the electron.

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