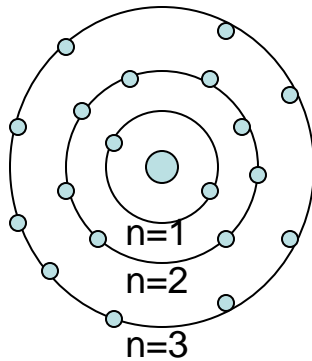


Period #2 Notes: Electronic Structure of Atoms

The logical place (for civil engineers) to begin in describing materials is at the atomic scale.

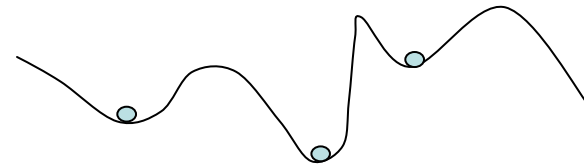
The basic elements of the atom are the proton, the neutron, and the electron:

particle	mass (grams)	electrical charge (Coulombs)
proton	1.673×10^{-24}	$+1.602 \times 10^{-19}$
neutron	1.675×10^{-24}	0
electron	9.109×10^{-29}	-1.602×10^{-19}



- The protons and neutrons of atoms occupy the nucleus which is the tight inner core region having a diameter of order 10^{-14}m (or 10^{-5}nm).
- Electrons swirl around the nucleus in orbits having radii ranging from about $.05\text{nm}$ to a few nm .
- The atomic radius is a typical measure of the size of an atom, and usually corresponds to the radius of the outermost orbital that is at least partially full.
- The field of particle physics and quantum mechanics is devoted to understanding electron orbitals, spins, and energy levels.

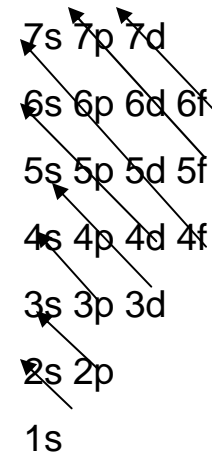
- In very general terms, the electrons of atoms tend to fill the lowest (innermost) quantum shells first, and the higher shells are occupied as the inner shells fill up.
- The energy levels of electrons in the lowest quantum shells are lower than those in higher shells.
- In this way, materials are like most other physical systems in that they tend to reside at states of minimum potential energy. For a given material system, there usually exists more than one state of minimum potential energy.



Electron quantum states: (through n=4)

Primary Quantum # (n)	Subshell or orbitals	# electrons per subshell	# electrons per shell ($2n^2$)
1	s	2	2
2	s	2	8
	p	6	
3	s	2	18
	p	6	
	d	10	
4	s	2	32
	p	6	
	d	10	
	f	14	

General order in which electrons fill orbitals

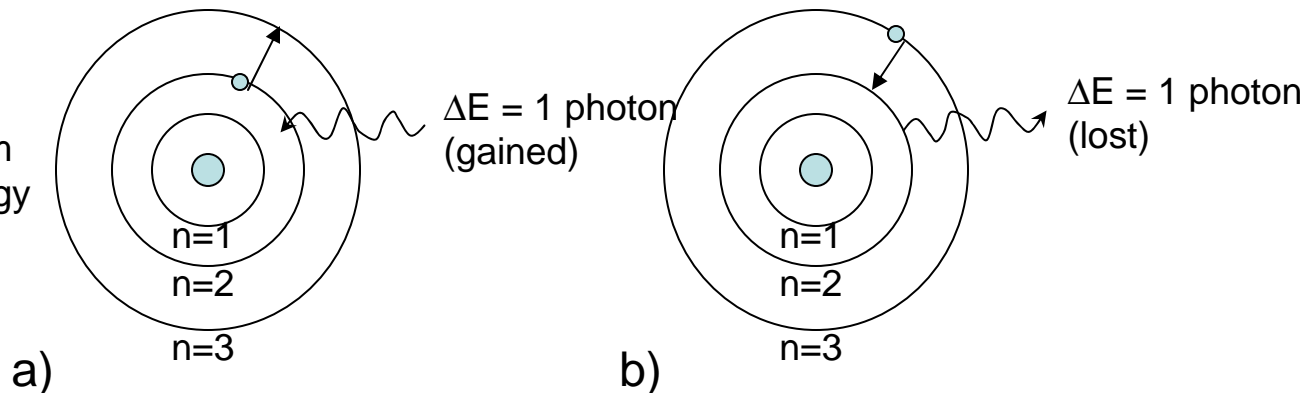


- The energy difference for an electron moving from an inner quantum shell to an adjacent outer quantum shell can be quantified. For example, energy equation of Niels Bohr for the electrons of the hydrogen atom is given below in Eq. (1) where E is the energy level in electron-volts (eV) and n is an integer called the primary quantum number.

$$E = -\frac{13.6}{n^2} eV \quad (1)$$

- The energy level for an electron in quantum shell 1 ($n=1$) is: $E_1 = -13.6 eV$;
- The energy level for an electron in quantum shell 2 ($n=2$) is: $E_2 = -3.4 eV$;
- The energy level for an electron in quantum shell 3 ($n=3$) is: $E_3 = -1.5 eV$;

Hydrogen atom: a) energy gained as electron moves from $n=2$ to $n=3$; b) energy lost as electron moves from $n=3$ to $n=2$.



- Looking at materials from a quantum mechanics point of view, the atomic energy tends to be minimized when the outermost quantum shells are either completely full or completely empty.
- The facts that (1) materials tend to reside at states of minimum potential energy and (2) atomic energy is minimized with outermost quantum shells either completely empty or full helps to explain why some commonly found chemical compounds occur.

Electro-positivity and Electro-negativity

Electro-positive elements: metallic in nature; tend to give up electrons to form positively charged ions (cations); typically have 3 or fewer electrons in outermost shells.

Electro-negative elements: non-metallic in nature; tend to accept electrons to form negatively charged ions (anions); typically have 4 or more electrons in outermost shells.

Electronegativity: measures degree to which an atom attracts electrons to itself. Values range from 0 to 4.1

•The most electropositive elements (least electronegative) are the alkali metals which come from the left side of the periodic table:

•A few common examples:

Potassium (0.9);	Sodium (1.0);
Lithium (1.0);	Calcium (1.1)

•Among the most electronegative elements, which generally come from the right side of the periodic table are:

Fluorine (4.1);	Oxygen (3.5);
Nitrogen (3.1);	Chlorine (2.9)

Types of Atomic and Molecular Bonding:

1. Primary bonding types:
 - a. Ionic (electron transfer from electro-positive elements to electro-negative elements; coulombic forces of attraction between ions; bonds formed are non-directional & strong;
 - b. Covalent (electron sharing); bonds formed can be strong; often directional;
 - c. Metallic bonding; electron sharing by generalized donation; bonds formed are strong non-directional.

2. Secondary bonding types:
 - a. Permanent dipole bonds;
 - b. Fluctuating dipole bones;

3. General comment:
 - Many of the physical, electrical, and thermal properties of civil engineering materials are dependent upon the type of bonding that occurs between atoms of compounds.
 - A general measure of the strength of the bonds forming a chemical compound is the melting temperature. Essentially this corresponds to the energy level required to break the primary bonds of the material.

1. Ionic Bonding:

- Tends to occur among elements with large differences in electronegativities (i.e. those coming from the left and right sides of the periodic table);

- Common example: Sodium chloride:

Na: 2-8-1 ($1s^2 2s^2 2p^6 3s^1$) --» Na^+ 2-8

Cl: 2-8-7 ($1s^2 2s^2 2p^6 3s^2 3p^5$) --» Cl^- 2-8-8

Melting temperature of NaCl: $T_m = 801^\circ\text{C}$

- Another example: Magnesium oxide:

Mg: 2-8-2 ($1s^2 2s^2 2p^6 3s^2$) --» Mg^{++} 2-8

O: 2-6 ($1s^2 2s^2 2p^4$) --» O^{--} 2-8

Melting temperature of MgO: $T_m = 2640^\circ\text{C}$

- Yet another example: Zirconium carbide:

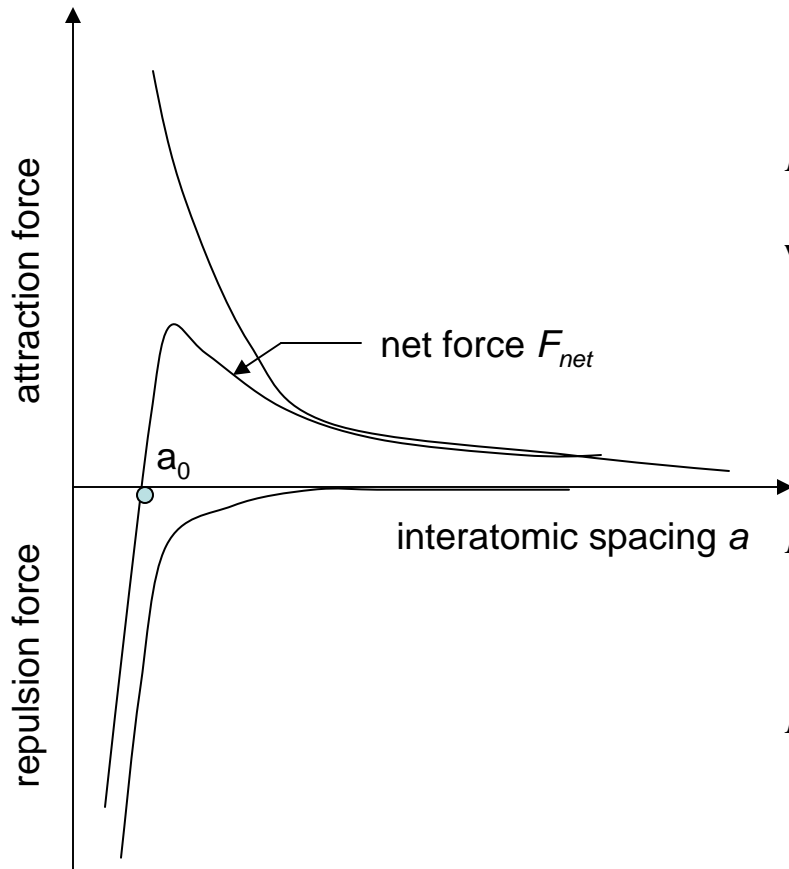
Zr: 2-8-8-2 ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$) --» Zr^{++} 2-8-8

C: 2-4 ($1s^2 2s^2 2p^2$) --» C^{--} 2-8

Melting temperature of Zr^2C : $T_m = 3500^\circ\text{C}$

- Observe: the higher the degree of ionization in the compounds, the stronger the compound.
- Also, when an atom gives up its outermost electrons to become a cation, its radius decreases.
- Similarly, when an atom attracts electrons to become an anion, its radius increases.
- The structure of most compounds with ionic bonding is crystalline (3-dimension).

a) Attraction/Repulsion Relations in Ions (Condon-Morse)



$$F_{\text{attractive}} = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 a^2}$$

where: Z_1, Z_2 is # of electrons involved in ion formation;

e = electron charge;

a = interionic spacing;

$$\epsilon_0 = 8.85 \cdot 10^{-12} \text{ C}^2 / (\text{N} \cdot \text{m}^2)$$

$$F_{\text{repulsion}} = -\frac{nb}{a^{n+1}} \text{ where: } n \text{ and } b \text{ are constants with } 7 < n < 9;$$

a = is interatomic spacing.

$$F_{\text{net}} = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 a^2} - \frac{nb}{a^{n+1}}$$

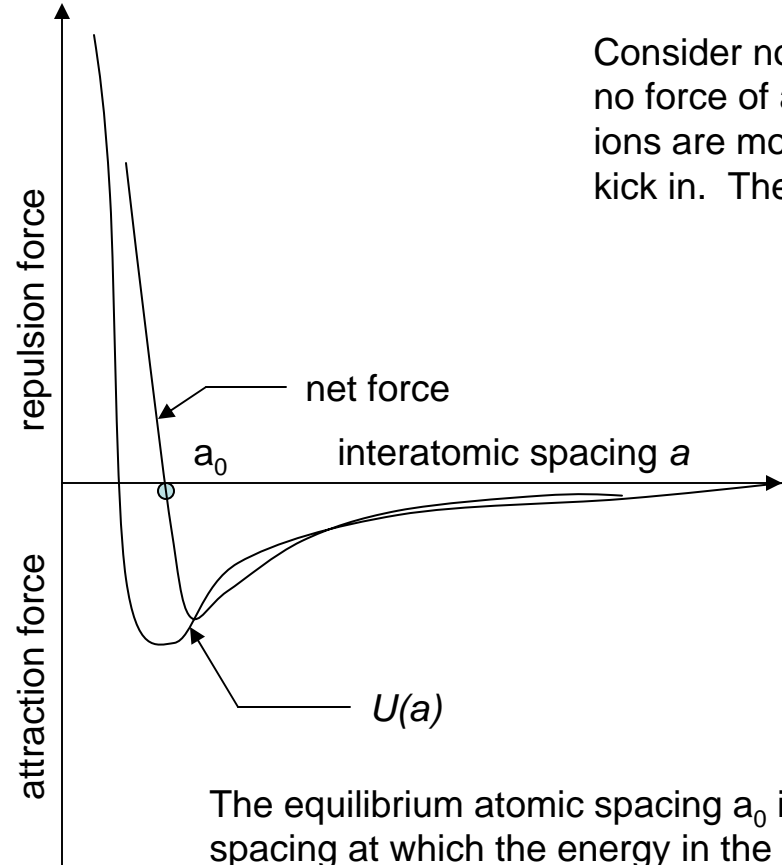
The equilibrium atomic spacing at which

$$F_{\text{net}} = 0 \text{ is } a_0.$$

Notes:

- (1) As the spacing gets smaller, the repulsion force dominates;
- (2) The bonds between two ions are broken only in tension, not compression.
- (3) This helps to explain why materials generally fail in tension rather than compression.

b) Energy Considerations:



Consider now two ions widely separated so that there is no force of attraction or repulsion between them. As the ions are moved closer, the forces of attraction/repulsion kick in. The energy associated with the ionic forces is:

$$U(a) = U_{\infty} - \int_a^{\infty} F_{net}(a') da'$$

$$= \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 a} + \frac{b}{a^n}$$

$U_{\infty} - U(a_0)$ is often referred to as the “surface energy” of a compound. This represents the energy difference between an atom at equilibrium within the lattice of the compound, and an atom at the free surface of the material infinitely separated from its nearest neighbor.

The equilibrium atomic spacing a_0 is also the spacing at which the energy in the attraction/repulsion forces is minimal.

c) Elastic Behavior of Materials:

The energy in the bonds between atoms can be expressed as a function of spacing a as follows:

$$\begin{aligned}U(a) &= \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 a} + \frac{b}{a^n} \\&= U(a_0) + \left[\frac{\partial U}{\partial a} \right]_{a_0} (a - a_0) + \frac{1}{2} \left[\frac{\partial^2 U}{\partial a^2} \right]_{a_0} (a - a_0)^2 + \dots \\&= U(a_0) + \frac{1}{2} \left[\frac{\partial^2 U}{\partial a^2} \right]_{a_0} (a - a_0)^2 + \dots\end{aligned}$$

Since the energy in the bonds is minimum at the equilibrium spacing a_0 , the first order term in the Taylor series expansion vanishes.

So, in effect the energy in the bonds is a quadratic function of a for small perturbations in atomic spacing. This is analogous to the behavior of a linear spring for which:

$$U = U_0 + \frac{1}{2} K * x^2 \quad \text{where } K \text{ is the spring stiffness, and } x \text{ is its deviation from an equilibrium position.}$$

The force in the spring is of course: $F = \frac{\partial U}{\partial x} = K * x$

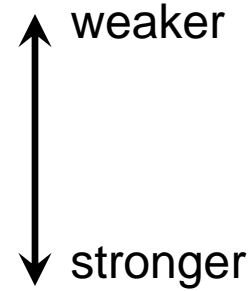
In the lattice of a material, the force on an atom due to a small change in spacing can be expressed:

$$F(a) = \frac{\partial U}{\partial a} = \left[\frac{\partial^2 U}{\partial a^2} \right]_{a_0} * (a - a_0) \quad \text{In this expression } (a - a_0) \text{ is essentially the strain in the lattice, and the second derivative taken at } a = a_0 \text{ is an elastic modulus.}$$

2. Covalent Bonding: (sharing of electrons between two atoms of similar electro-negativities)

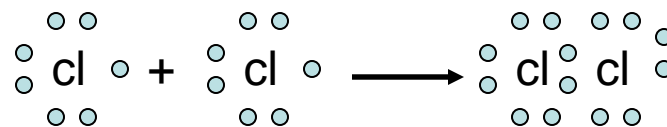
a) Molecules obtained from covalent bonding can be:

- Diatomic (each atom has just one neighbor)
- String-like (each atom has two neighbors)
- Plate-like (each atom has 3 neighbors)
- 3-dimensional and crystalline (each atom has 4 neighbors)
- The type of compound that will be formed can sometimes be predicted with the 8-N rule of covalent bonding: an atom can have at most 8-N nearest neighbors in the molecule, where N is the number of valence electrons in the atom.



b) Examples of covalently bonded diatomic molecules:

- The chlorine atom (N=7) has the following electron structure:
- Cl 2-8-7 [1s²2s²2p⁶3s²3p⁵]. In the third quantum shell, there are seven electrons. The shell would be full if there were just one more electron.
- This can be achieved by electron-sharing as follows:



- Oxygen (N=6) also forms a diatomic molecule;
- O 2-6 [$1s^2 2s^2 2p^4$].
- In the second quantum shell, there are six electrons. The shell would be full if there were just two more electrons. This is achieved by sharing of two electrons amongst two oxygen atoms.

c) String-like molecules:

- Sulfur 2-8-6 with N=6 forms string-like molecules with each atom having two nearest neighbors.
- String-like molecules are common in polymers, which generally speaking are not high-stiffness, high-strength materials.

d) 3-d covalent molecules:

- Carbon [C 2-4] with N=4 forms 3-d molecules having four nearest neighbors.
- Covalently bonded carbon molecules comprise diamonds which are among the stiffest, strongest materials in existence.

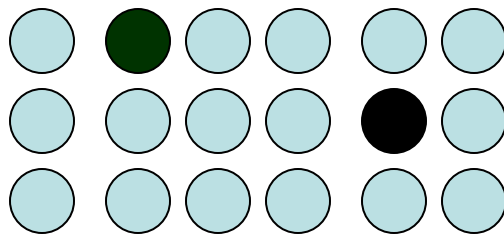
3. Metallic bonding:

- a) Elements that feature metallic bonding typically have 1-3 valence electrons in their outermost quantum shells.

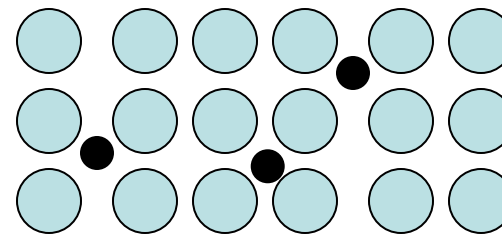
- b) The valence electrons separate from the atom (cation) and form an *electron cloud* that swirls within the lattice formed by the cations.
- c) The valence electrons are not closely associated with any one specific cation.
- d) In this sense, the sharing of electrons amongst the cations is be “generalized donation”.
- e) The electron cloud in metals helps to explain these materials typically have high thermal and electrical conductivities.
- f) The lattice structure of cations in metals is very three-dimensional. Hence metals are not comprised of string-like or plate-like molecules. For this reason, they tend to be relatively strong.
- g) Alloying in metals:

When the cations of metals form themselves in highly structured lattices, it is possible for cations of different metals to take the place of the predominant metal cations. This is generally called *substitutional alloying* and it occurs when the foreign cation has an atomic radius similar in size to that of the predominant metal and similar electronegativity.

When the foreign metal cation has an atomic radius much smaller than that of the predominant cations, then *interstitial alloying* may occur.



substitutional alloying



interstitial alloying

4. Van der Waals bonds

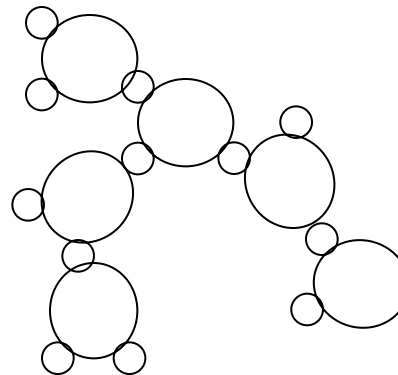
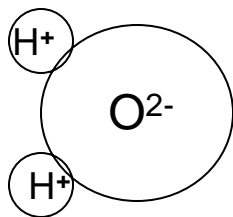
The three prior types of bonding (ionic, covalent, metallic) are the primary ones in that they form “stable” compounds in which the net charge balances are satisfied.

Often, the molecules of the stable compounds formed by primary bonding mechanisms, while having no net charge, will have some polarity. That is, a molecule might have a positive side with relatively few electrons, and a negative side with relatively many electrons.

The inter-attraction between the opposite poles of different molecules is called van der Waals bonding. Usually, the strength of such bonds is very small relative to the strengths of the primary bonds.

A special case of van der Waals bonding occurs with water molecules (H_2O). In the water molecule, the two hydrogen atoms tend to congregate on one end (positive end) and the oxygen molecule is on the other (forming the negative pole).

In liquid water, the strength of the secondary attraction/repulsion forces between polar water molecules can be as high as $1/20^{\text{th}}$ to $1/10^{\text{th}}$ as the primary bond forces.



- Hydrogen bonding associated with polar water molecules plays a vitally important role in the chemical reaction that occurs when water reacts with portland cement. Polar water molecules bond together different silicates and aluminates in portland cement to form the product “hydrated cement paste.”