

### Chapter Outline

- **Review of Atomic Structure**  
Electrons, Protons, Neutrons, Quantum mechanics of atoms, Electron states, The Periodic Table
- **Atomic Bonding in Solids**  
Bonding Energies and Forces
- **Periodic Table**
- **Primary Interatomic Bonds**  
Ionic  
Covalent  
Metallic
- **Secondary Bonding (Van der Waals)**  
Three types of Dipole Bonds
- **Molecules and Molecular Solids**

Understanding of interatomic bonding is the first step towards understanding/explaining materials properties

### Review of Atomic Structure

Atoms = nucleus (protons and neutrons) + electrons

#### Charges:

Electrons and protons have negative and positive charges of the same magnitude,  $1.6 \times 10^{-19}$  Coulombs.

Neutrons are electrically neutral.

#### Masses:

Protons and Neutrons have the same mass,  $1.67 \times 10^{-27}$  kg.

Mass of an electron is much smaller,  $9.11 \times 10^{-31}$  kg and can be neglected in calculation of atomic mass.

**The atomic mass (A)** = mass of protons + mass of neutrons

# protons gives chemical identification of the element

# **protons = atomic number (Z)**

# neutrons defines isotope number

### Atomic mass units. Atomic weight.

**The atomic mass unit (amu)** is often used to express atomic weight. 1 amu is defined as 1/12 of the atomic mass of the most common isotope of carbon atom that has 6 protons (Z=6) and six neutrons (N=6).

$$M_{\text{proton}} \approx M_{\text{neutron}} = 1.66 \times 10^{-24} \text{ g} = 1 \text{ amu.}$$

The atomic mass of the  $^{12}\text{C}$  atom is 12 amu.

**The atomic weight of an element** = weighted average of the atomic masses of the atoms naturally occurring isotopes. Atomic weight of carbon is 12.011 amu.

The atomic weight is often specified in mass per mole.

**A mole** is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms (A mole of carbon has a mass of 12 grams).

The number of atoms in a mole is called **the Avogadro number**,  $N_{\text{av}} = 6.023 \times 10^{23}$ .

$$N_{\text{av}} = 1 \text{ gram/1 amu.}$$

Example:

Atomic weight of iron = 55.85 amu/atom = 55.85 g/mol

### Some simple calculations

The number of atoms per  $\text{cm}^3$ ,  $n$ , for material of density  $d$  ( $\text{g}/\text{cm}^3$ ) and atomic mass  $M$  ( $\text{g}/\text{mol}$ ):

$$n = N_{\text{av}} \times d / M$$

Graphite (carbon):  $d = 2.3 \text{ g}/\text{cm}^3$ ,  $M = 12 \text{ g}/\text{mol}$   
 $n = 6 \times 10^{23} \text{ atoms}/\text{mol} \times 2.3 \text{ g}/\text{cm}^3 / 12 \text{ g}/\text{mol} = 11.5 \times 10^{22} \text{ atoms}/\text{cm}^3$

Diamond (carbon):  $d = 3.5 \text{ g}/\text{cm}^3$ ,  $M = 12 \text{ g}/\text{mol}$   
 $n = 6 \times 10^{23} \text{ atoms}/\text{mol} \times 3.5 \text{ g}/\text{cm}^3 / 12 \text{ g}/\text{mol} = 17.5 \times 10^{22} \text{ atoms}/\text{cm}^3$

Water ( $\text{H}_2\text{O}$ )  $d = 1 \text{ g}/\text{cm}^3$ ,  $M = 18 \text{ g}/\text{mol}$   
 $n = 6 \times 10^{23} \text{ molecules}/\text{mol} \times 1 \text{ g}/\text{cm}^3 / 18 \text{ g}/\text{mol} = 3.3 \times 10^{22} \text{ molecules}/\text{cm}^3$

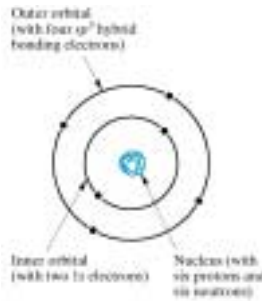
For material with  $n = 6 \times 10^{22} \text{ atoms}/\text{cm}^3$  we can calculate mean distance between atoms  $L = (1/n)^{1/3} = 0.25 \text{ nm}$ .

□ the scale of atomic structures in solids – a fraction of 1 nm or a few Å.

### Electrons in Atoms (I)

The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.

This picture looks like a mini planetary system. But quantum mechanics tells us that this analogy is not correct:



Electrons move not in circular orbits, but in 'fuzzy' orbits. Actually, we cannot tell how it moves, but only can say what is the probability of finding it at some distance from the nucleus.

Only certain "orbits" or shells of electron probability densities are allowed. The shells are identified by a **principal quantum number n**, which can be related to the size of the shell, n = 1 is the smallest; n = 2, 3 .. are larger. **The second quantum number l**, defines subshells within each shell. **Two more quantum numbers** characterize states within the subshells.

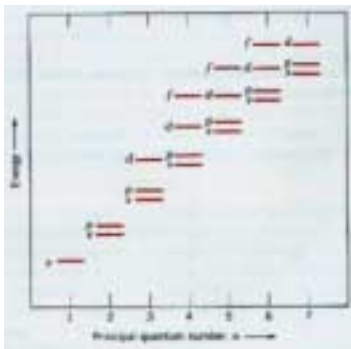
### Electrons in Atoms (II)

- The quantum numbers arise from solution of Schrodinger's equation
- Pauli Exclusion Principle: only one electron can have a given set of the four quantum numbers.

The Number of Available Electron States in Some of the Electron Shells and Subshells

| Principal O. N., n | Subshells | Number of States | Number of Electrons |           |
|--------------------|-----------|------------------|---------------------|-----------|
|                    |           |                  | Per Subshell        | Per Shell |
| 1 (l=0)            | s         | 1                | 2                   | 2         |
| 2 (l=0)            | s         | 1                | 2                   | 8         |
| 2 (l=1)            | p         | 3                | 6                   |           |
| 3 (l=0)            | s         | 1                | 2                   | 18        |
| 3 (l=1)            | p         | 3                | 6                   |           |
| 3 (l=2)            | d         | 5                | 10                  |           |
| 4 (l=0)            | s         | 1                | 2                   | 32        |
| 4 (l=1)            | p         | 3                | 6                   |           |
| 4 (l=2)            | d         | 5                | 10                  |           |
| 4 (l=3)            | f         | 7                | 14                  |           |

### Electrons in Atoms (III)

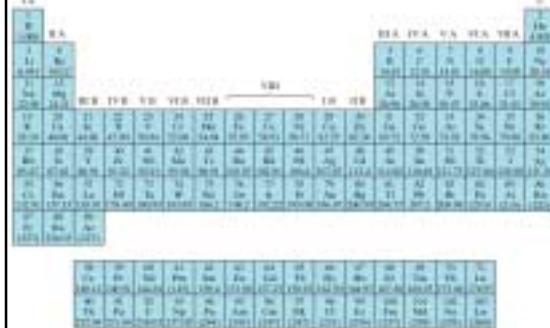


Subshells by energy: 1s,2s,2p,3s,3p,4s,3d,4s,4p,5s,4d,5p,6s,4f,...

- Electrons that occupy the outermost filled shell – **the valence electrons** – they are responsible for bonding.
- Electrons fill quantum levels in order of increasing energy (only n, l make a significant difference).

Example: Iron, Z = 26:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

### Periodic Table



Elements in the same column (Elemental Group) share similar properties. Group number indicates the number of electrons available for bonding.

- 0: Inert gases (He, Ne, Ar...) have filled subshells: chem. inactive
- IA: Alkali metals (Li, Na, K...) have one electron in outermost occupied s subshell - eager to give up electron – chem. active
- VIIA: Halogens (F, Br, Cl...) missing one electron in outermost occupied p shell - want to gain electron - chem. active

### Periodic Table - Electronegativity



Figure 2.7 from the textbook. The electronegativity values.

Electronegativity - a measure of how willing atoms are to accept electrons

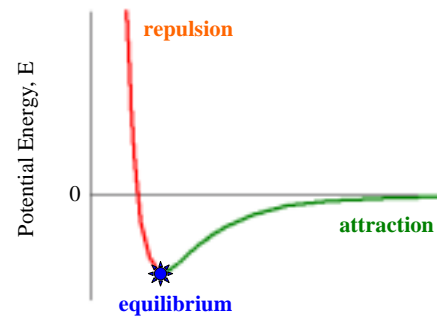
Subshells with one electron - low electronegativity

Subshells with one missing electron -high electronegativity

Electronegativity increases from left to right

Metals are electropositive – they can give up their few valence electrons to become positively charged ions

### Bonding Energies and Forces

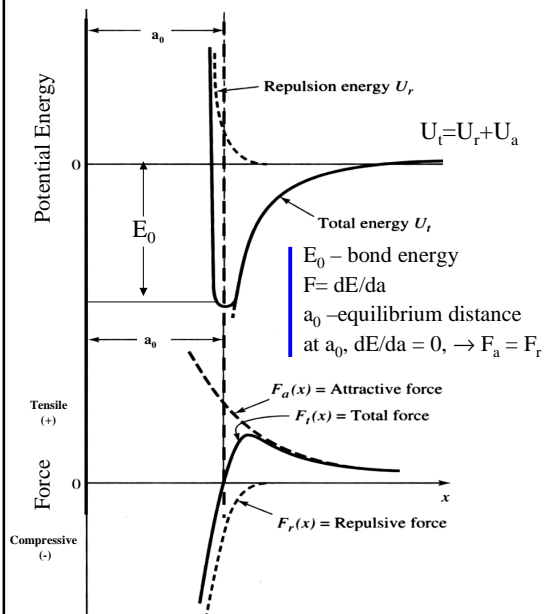


This is typical potential well for two interacting atoms

The repulsion between atoms, when they are brought close to each other, is related to the Pauli principle: when the electronic clouds surrounding the atoms starts to overlap, the energy of the system increases abruptly.

The origin of the attractive part, dominating at large distances, depends on the particular type of bonding.

### Bonding Energies and Forces



### The electron volt (eV) – energy unit convenient for description of atomic bonding

Electron volt - the energy lost / gained by an electron when it is taken through a potential difference of one volt.

$$E = q \times V$$

For  $q = 1.6 \times 10^{-19}$  Coulombs

$V = 1$  volt

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

### Types of Bonding

**Primary bonding: e<sup>-</sup> are transferred or shared**  
**Strong (100-1000 KJ/mol or 1-10 eV/atom)**

- Ionic: Strong Coulomb interaction among negative atoms (have an extra electron each) and positive atoms (lost an electron). Example - Na<sup>+</sup>Cl<sup>-</sup>
- Covalent: electrons are shared between the molecules, to saturate the valency. Example - H<sub>2</sub>
- Metallic: the atoms are ionized, losing some electrons from the valence band. Those electrons form an electron sea, which binds the charged nuclei in place

**Secondary Bonding: no e<sup>-</sup> transferred or shared**  
**Interaction of atomic/molecular dipoles**  
**Weak (< 100 KJ/mol or < 1 eV/atom)**

- Fluctuating Induced Dipole (inert gases, H<sub>2</sub>, Cl<sub>2</sub>,...)
- Permanent dipole bonds (polar molecules - H<sub>2</sub>O, HCl,...)
- Polar molecule-induced dipole bonds (a polar molecule like induce a dipole in a nearby nonpolar atom/molecule)

### Ionic Bonding (I)

Formation of ionic bond:

1. Mutual ionization occurs by electron transfer (remember electronegativity table)
  - Ion = charged atom
  - Anion = negatively charged atom
  - Cation = positively charged atom
2. Ions are attracted by strong coulombic interaction
  - Oppositely charged atoms attract
  - An ionic bond is non-directional (ions may be attracted to one another in any direction)

Example: NaCl

Na has 11 electrons, 1 more than needed for a full outer shell (Neon)

11 Protons Na 1S<sup>2</sup> 2S<sup>2</sup> 2P<sup>6</sup> 3S<sup>1</sup>

11 Protons Na<sup>+</sup> 1S<sup>2</sup> 2S<sup>2</sup> 2P<sup>6</sup>

donates e<sup>-</sup>  
10 e<sup>-</sup> left

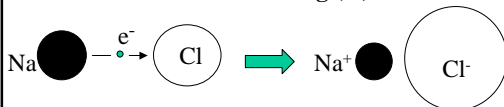
Cl has 17 electrons, 1 less than needed for a full outer shell (Argon)

17 Protons Cl 1S<sup>2</sup> 2S<sup>2</sup> 2P<sup>6</sup> 3S<sup>2</sup> 3P<sup>5</sup>

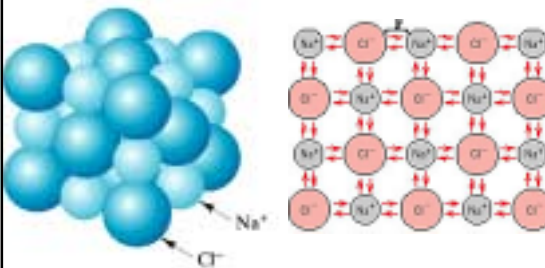
17 Protons Cl<sup>-</sup> 1S<sup>2</sup> 2S<sup>2</sup> 2P<sup>6</sup> 3S<sup>2</sup> 3P<sup>6</sup>

receives e<sup>-</sup>  
18 e<sup>-</sup>

### Ionic Bonding (II)



- Electron transfer reduces the energy of the system of atoms, that is, electron transfer is energetically favorable
- Note relative sizes of ions: Na shrinks and Cl expands



**Ionic bonds: very strong, nondirectional bonds**

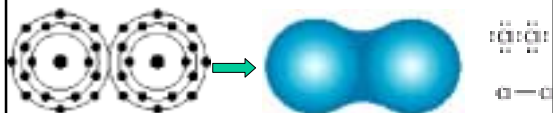
### Covalent Bonding (I)

In covalent bonding, electrons are shared between the molecules, to saturate the valency. The simplest example is the H<sub>2</sub> molecule, where the electrons spend more time in between the nuclei than outside, thus producing bonding.

**Formation of covalent bonds:**

- Cooperative sharing of valence electrons
- Can be described by orbital overlap
- Covalent bonds are HIGHLY directional
- Bonds - in the direction of the greatest orbital overlap
- Covalent bond model: an atom can covalently bond with at most 8-N', N' = number of valence electrons

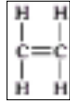
Example: Cl<sub>2</sub> molecule. Z<sub>Cl</sub> = 17 (1S<sup>2</sup> 2S<sup>2</sup> 2P<sup>6</sup> 3S<sup>2</sup> 3P<sup>5</sup>)  
 N' = 7, 8 - N' = 1 → can form only one covalent bond



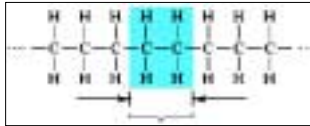
### Covalent Bonding (II)

Example: Carbon materials.  $Z_c = 6$  ( $1S^2 2S^2 2P^2$ )  
 $N^* = 4$ ,  $8 - N^* = 4 \rightarrow$  can form up to four covalent bonds

ethylene molecule:

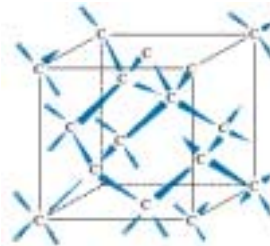


polyethylene molecule:



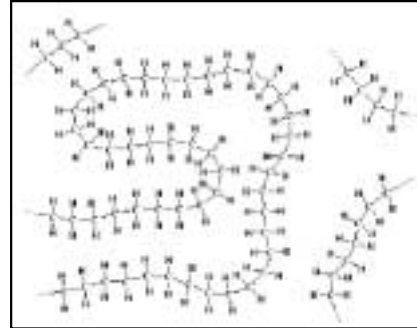
ethylene mer

diamond:  
 (each C atom has four covalent bonds with four other carbon atoms)



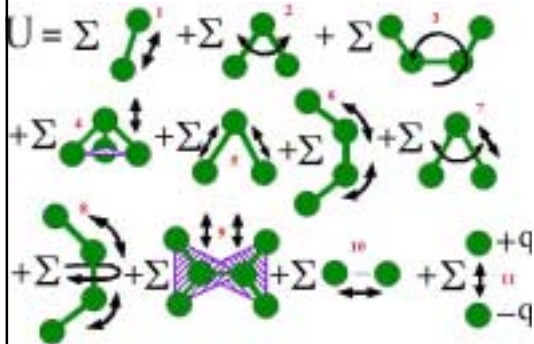
### Covalent Bonding (III)

2-D schematic of the "spaghetti-like" structure of solid polyethylene



### Covalent Bonding (IV)

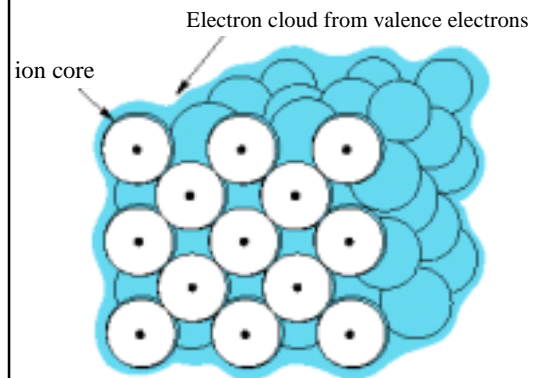
The potential energy of a system of covalently interacting atoms depend not only on the distances between atoms, but also on angles between bonds...



### Metallic Bonding

Valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the ions together.

- A metallic bond is non-directional (bonds form in any direction)  $\rightarrow$  atoms pack closely



### Secondary Bonding (I)

Secondary = van der Waals = physical (as opposite to chemical bonding that involves  $e^-$  transfer) bonding results from interaction of atomic or molecular dipoles and is weak,  $\sim 0.1$  eV/atom or  $\sim 10$  kJ/mol.



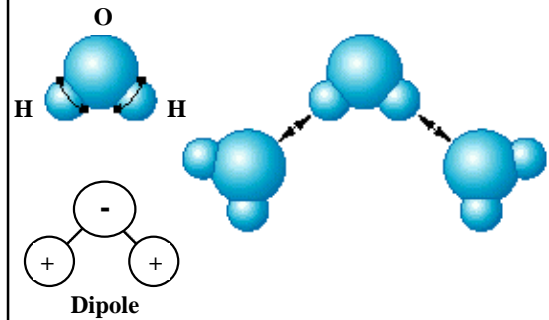
Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively regions (HCl, H<sub>2</sub>O). Bonds between adjacent polar molecules – **permanent dipole bonds** – are **strongest among secondary bonds**.

Polar molecules can **induce** dipoles in adjacent non-polar molecules and bond is formed due to the **attraction between the permanent and induced dipoles**.

Even in electrically symmetric molecules/atoms an electric dipole can be created by fluctuations of electron density distribution. Fluctuating electric field in one atom A is felt by the electrons of an adjacent atom, and induce a dipole momentum in this atom. **This bond due to fluctuating induced dipoles is the weakest (inert gases, H<sub>2</sub>, Cl<sub>2</sub>).**

### Secondary Bonding (II)

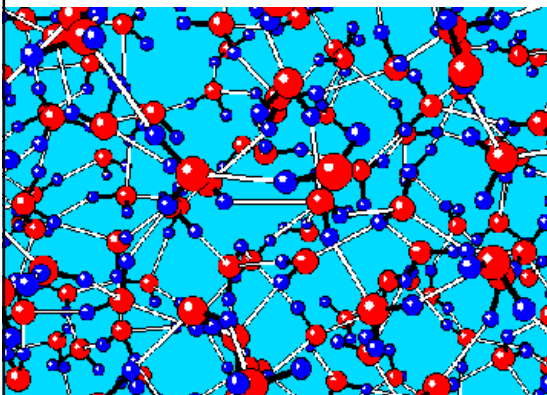
Example: hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H<sub>2</sub>O molecule (the O side of the H<sub>2</sub>O dipole)



“Hydrogen bond” – secondary bond formed between two **permanent dipoles** in adjacent water molecules.

### Secondary Bonding (III)

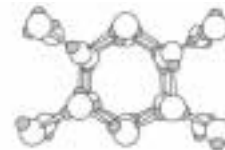
Hydrogen bonding in liquid water from a molecular-level simulation



**Molecules:** Primary bonds inside, secondary bonds among each other

### Secondary Bonding (IV)

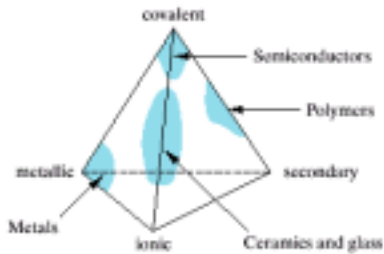
The Crystal Structures of Ice



Hexagonal Symmetry of Ice Snowflakes



Figures by Paul R. Howell

**Summary (I)****Examples of bonding in Materials:**

Metals: Metallic

Ceramics: Ionic / Covalent

Polymers: Covalent and Secondary

Semiconductors: Covalent or Covalent / Ionic

**Summary (II)****Table 2.3** Bonding Energies and Melting Temperatures for Various Substances

| Bonding Type  | Substance        | Bonding Energy       |                         | Melting Temperature [°C] |
|---------------|------------------|----------------------|-------------------------|--------------------------|
|               |                  | kJ/mol<br>(kcal/mol) | eV/Atom,<br>eV/Molecule |                          |
| Ionic         | NaCl             | 443 (105)            | 3.3                     | 801                      |
|               | MgO              | 300 (72)             | 5.2                     | 2800                     |
| Covalent      | Si               | 451 (108)            | 4.7                     | 1413                     |
|               | C (diamond)      | 713 (170)            | 7.4                     | >3550                    |
| Metallic      | Hg               | 68 (16)              | 0.7                     | -39                      |
|               | Al               | 334 (79)             | 3.4                     | 900                      |
|               | Fe               | 406 (97)             | 4.2                     | 1538                     |
|               | W                | 849 (202)            | 8.8                     | 3410                     |
| van der Waals | Ar               | 7.7 (1.8)            | 0.08                    | -189                     |
|               | Cl <sub>2</sub>  | 33 (7.8)             | 0.32                    | -102                     |
| Hydrogen      | NH <sub>3</sub>  | 55 (13.1)            | 0.36                    | -78                      |
|               | H <sub>2</sub> O | 51 (12.2)            | 0.52                    | 0                        |

**Summary (III)**

Make sure you understand language and concepts:

- Atomic mass unit (amu)
- Atomic number
- Atomic weight
- Bonding energy
- Coulombic force
- Covalent bond
- Dipole (electric)
- Electron state
- Electronegative
- Electropositive
- Hydrogen bond
- Ionic bond
- Metallic bond
- Mole
- Molecule
- Periodic table
- Polar molecule
- Primary bonding
- Secondary bonding
- Van der Waals bond
- Valence electron

**Reading for next class:****Chapter 3: The structure of crystalline solids****Unit cells****Crystal structures**

Face-centered cubic

Body-centered cubic

Hexagonal close-packed

**Density computations****Types of solids**

Single crystals

Polycrystalline

Amorphous

*Optional reading (Parts that are not covered / not tested):*

3.7–3.10 Crystallography

3.15 Diffraction

Learning objectives #5, #6