

Chapter 2: Atomic Structure & Interatomic Bonding

Some of the important properties of solid materials depend on geometrical atomic arrangements, and also the interactions that exist among constituent atoms or molecules.

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

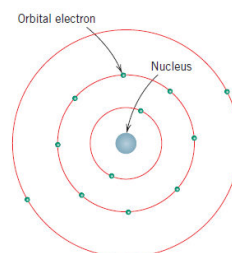


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Atomic Structure

- Each atom consists of a very small nucleus composed of **protons** and **neutrons**, which is encircled by moving electrons.
- Both electrons and protons are electrically charged
 - the charge magnitude being 1.60×10^{-19} which is
 - negative in sign for electrons
 - positive for protons;
 - electrically neutral for neutrons.
- Masses for these subatomic particles are infinitesimally small; protons and neutrons have approximately the same mass, which is significantly larger than that of an electron,

- atom – **electrons** – 9.11×10^{-31} kg
 protons
 neutrons } 1.67×10^{-27} kg



Defination: **ATOMIC NUMBER**

- Each chemical element is characterized by the number of protons in the nucleus, or the **atomic number**.
- For an electrically "**neutral**" or "**complete**" atom, the atomic number also equals the number of electrons:
 - 1 for "Hydrogen" to 92 for "Uranium".
- **atomic number** = # of protons in nucleus of atom
= # of electrons of neutral species

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Defination: **ATOMIC MASS / ATOMIC MASS UNIT**

- The **atomic mass** of a specific atom = The sum of the masses of protons and neutrons within the nucleus.
- The **atomic mass unit** (amu) : Used for computations of atomic weight.
- The **atomic weight** of an element or the **molecular weight** of a compound may be specified on the basis of "**amu per atom (molecule)**" or "**mass per mole**" of material.

$$A [=] \text{ atomic mass unit} = \text{amu} = 1/12 \text{ mass of } {}^{12}\text{C}$$

- Although the number of protons is the same for all atoms of a given element, the number of neutrons may be variable.
- Thus atoms of some elements have two or more different atomic masses, which are called **isotopes**.
- The **atomic weight of an element corresponds to the weighted average of the atomic masses of the atom's naturally occurring isotopes**.

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- In **one mole** of a substance there are **6.023×10^{23}** (**Avogadro's number**) atoms or molecules.

Atomic wt = wt of 6.023×10^{23} molecules or atoms

$$1 \text{ amu/atom} = 1 \text{ g/mol}$$

C 12.011
H 1.008 etc.

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Electronic Structure

- Electrons have wavelike and particulate properties.
 - This means that electrons are in **orbitals** defined by a probability.
 - Each orbital at discrete energy level is determined by **quantum numbers**.

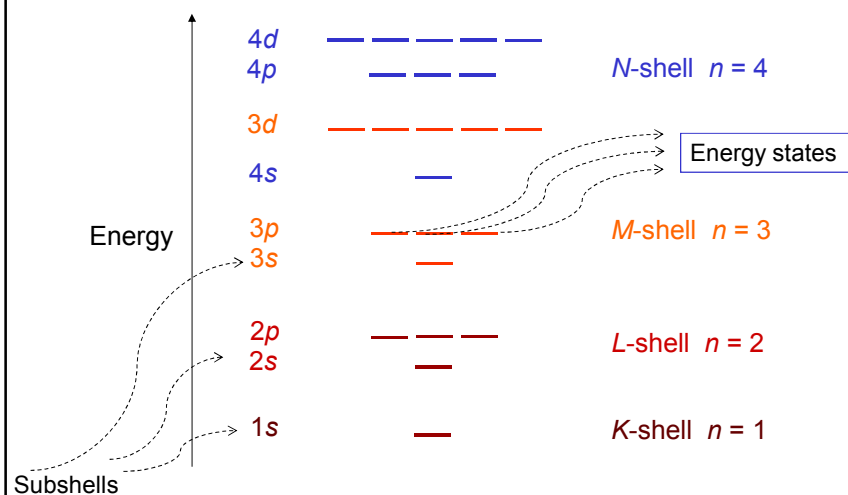
<u>Quantum #</u>	<u>Designation</u>
n = principal (energy level-shell)	K, L, M, N, O (1, 2, 3, etc.)
l = subsidiary (orbitals)	s, p, d, f (0, 1, 2, 3, ..., $n-1$)

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Electron Energy States

Electrons...

- have discrete **energy states**
- tend to occupy lowest available energy state.



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

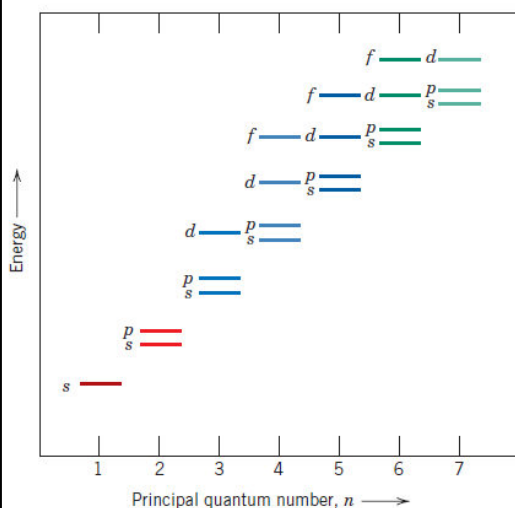
Principal Quantum Number <i>n</i>	Shell Designation	Subshells	Number of States	Number of Electrons	
				Per Subshell	Per Shell
1	K	s	1	2	2
2	L	s	1	2	8
		p	3	6	
3	M	s	1	2	18
		p	3	6	
		d	5	10	
4	N	s	1	2	32
		p	3	6	
		d	5	10	
		f	7	14	



According to “**Pauli exclusion principle**”, each electron state can hold no more than two electrons, which must have opposite spins.

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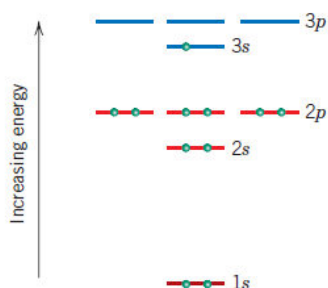
Schematic representation of the relative energies of the electrons for the various shells and subshells:



- The smaller the principal quantum number, the lower the energy level; *(the energy of a 1s state is less than that of a 2s state).*
- Within each shell, the energy of a subshell level increases with the value of the quantum number *(the energy of a 3d state is greater than a 3p, which is larger than 3s).*
- There may be overlap in energy of a state in one shell with states in an adjacent shell *(the energy of a 3d state is greater than that for a 4s).*

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When all the electrons occupy the lowest possible energies in accordance with the rules, an atom is said to be in its **“Ground State”**. However, electron transitions to higher energy states are possible.



Schematic representation of the filled and lowest unfilled energy states for a sodium (Na) atom.

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SURVEY OF ELEMENTS

- Most elements: Electron configuration **not stable**.

Element	Atomic #	Electron configuration
Hydrogen	1	$1s^1$
Helium	2	$1s^2$ (stable)
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
...
Neon	10	$1s^2 2s^2 2p^6$ (stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
...
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$ (stable)
...
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ (stable)

Nobel Gases

- Why? **Valence** (outer) shell usually not filled completely.

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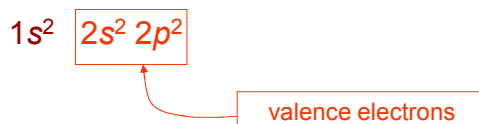
Atomic Structure

- Valence electrons determine all of the following properties
 - 1) Chemical
 - 2) Electrical
 - 3) Thermal
 - 4) Optical

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Electron Configurations

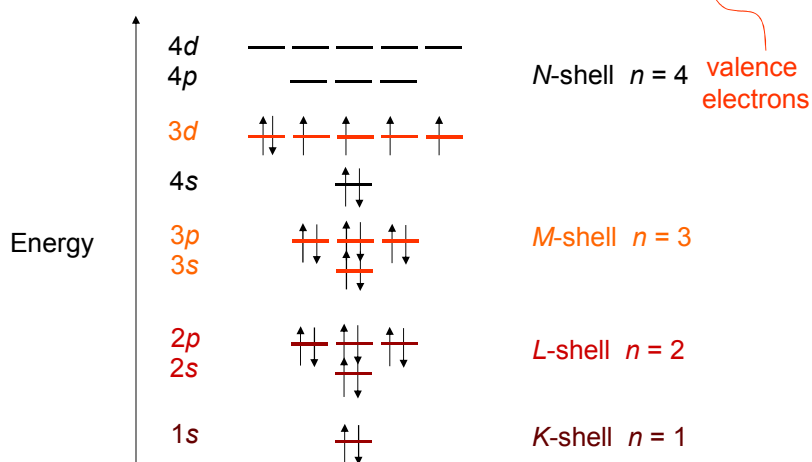
- **Valence electrons** – are those that occupy the outermost shell:
 - They participate in the bonding between atoms to form atomic and molecular structure
 - Furthermore, many of the physical and chemical properties of solids are based on these valence electrons
- example: C (atomic number = 6)



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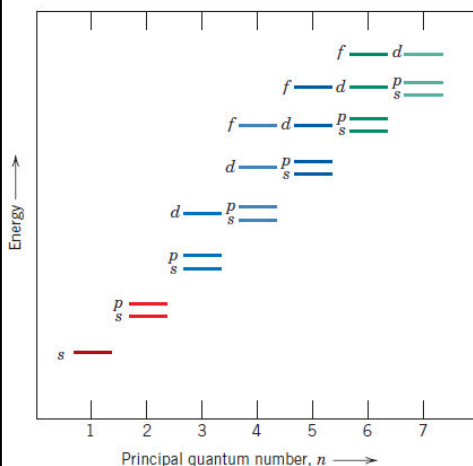
Electronic Configurations

ex: Fe - atomic # = 26 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$



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ex: **Fe** $1s^2 2s^2 2p^6 3s^2 3p^6$ **$4s^2 3d^6$**



- The number of valence electrons in the transition metals is somewhat different than main group elements.

- As you go from left to right across the periodic table, the electrons added to the transition metals go into the d-orbitals.

- However, because the energy of the 4s orbital is lower than the 3d orbital (and the 5s is lower than the 4d, etc.), the 4s orbital fills first.

- Therefore the electron configuration of iron for instance is : $4s^2 3d^6$.

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- Because the valence electrons are defined as the electrons in the *outermost* or highest energy shell, for iron, that would be the 4th shell.

- So the 6 electrons in the 3d orbital don't count.

- Only the 2 electrons in the 4s orbital count since they are in the 4th shell.

- Most transition metals thus have 2 valence electrons (although some, such as chromium, only have one because of exceptions to the filling rules -- the configuration of chromium is $[\text{Ar}]4s^1 3d^5$).

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The Periodic Table

- Columns: Similar **Valence** Structure

Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions

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Electronegativity values of the Elements

- Ranges from **0.7** to **4.0**,
- Large values: tendency to acquire electrons.

IA																	0				
H 2.1																	He -				
Li 1.0	Be 1.5															B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne -
Na 0.9	Mg 1.2															Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar -
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr -				
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe -				
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn -				
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7																			

Smaller electronegativity

Larger electronegativity

As a general rule, electronegativity increases in moving from "left to right" and from "bottom to top".

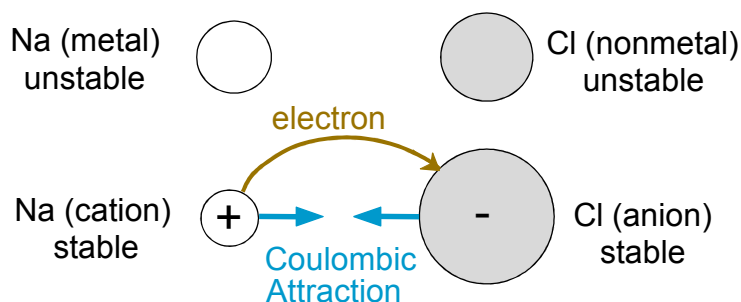
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- The bonding necessarily involves the valence electrons.
- The nature of the bond depends on the electron structures of the constituent atoms.
- Bonding arises from the tendency of the atoms to assume stable electron structures by completely filling the outermost electron shell (*like those of the inert gases*).

Ionic Bonding

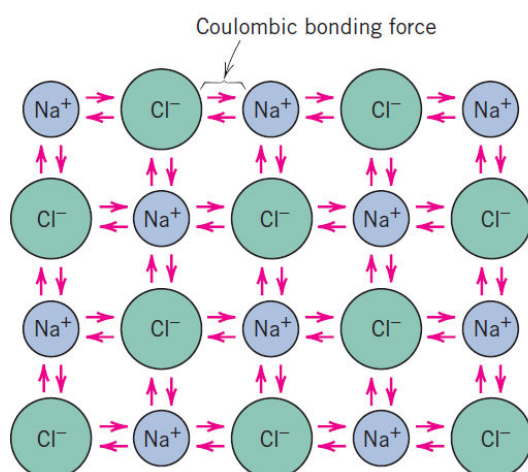
- Occurs between + and - ions.
- Requires **electron transfer**.
- Large difference in electronegativity required.
- Example: NaCl

Atoms of a **metallic element** easily give up their valence electrons to the **nonmetallic atoms**.



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Ionic Bonding



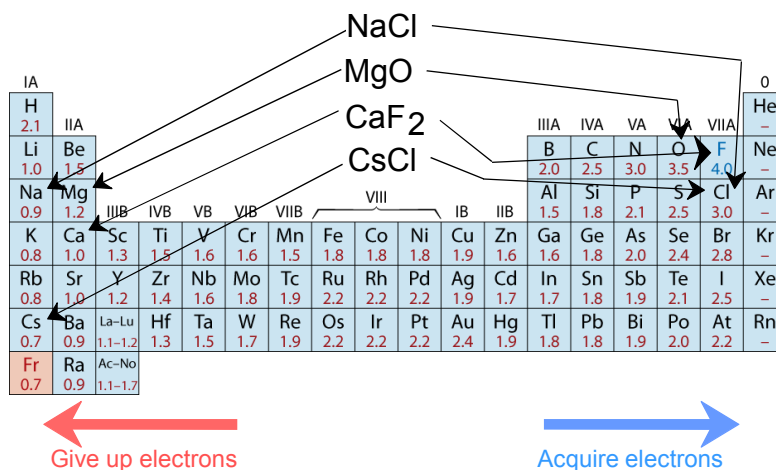
Ionic bonding is termed "**nondirectional**"; that is, the magnitude of the bond is equal in all directions around an ion.

Ionic materials are characteristically **hard** and **brittle** and, furthermore, **electrically** and **thermally insulative**.

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Examples: Ionic Bonding

- Predominant bonding in **Ceramics**



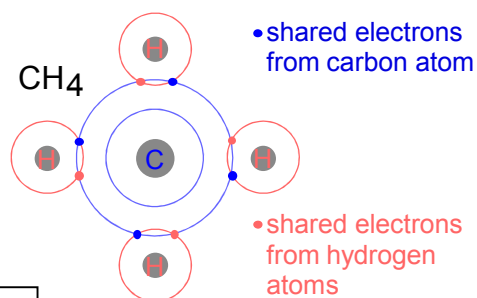
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Covalent Bonding

- similar **electronegativity** \therefore share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: CH₄

C: has 4 valence e^- ,
needs 4 more
H: has 1 valence e^- ,
needs 1 more

Tends to have stable
electron structures by
completely filling the
outermost electron shell



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Metallic Bonding

- **Metallic Bond** -- delocalized as electron cloud

Found in metals and their alloys.

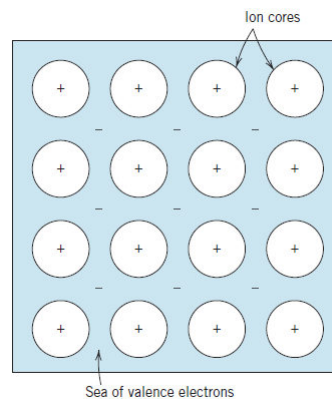
• Metallic materials have one, two, or at most, three valence electrons. These valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal.

• These electrons may be thought of “**sea of valence electrons**” or an “**electron cloud**”.

• The remaining atomic nuclei is called as **ion cores**.

• The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces. T

• These free electrons act as a “**glue**” to hold the ion cores together.



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Some general behaviors of the various material types (i.e., metals, ceramics, polymers) may be explained by bonding type.

- **Metals** are good conductors of both electricity and heat, as a consequence of their free electrons. They are free to drift throughout the entire metal.
- **Ionically and covalently bonded materials** are typically electrical and thermal insulators, due to the absence of large numbers of free electrons.

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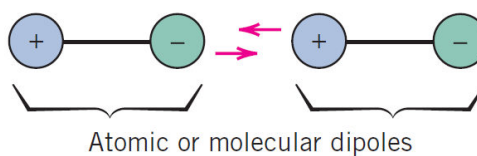
SECONDARY BONDING

Weak in comparison to the primary or chemical ones.

Secondary bonding forces arise from atomic or molecular **dipoles**.

An electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule.

The bonding results from the coulombic attraction between the **positive end** of one dipole and the **negative region** of an adjacent one.



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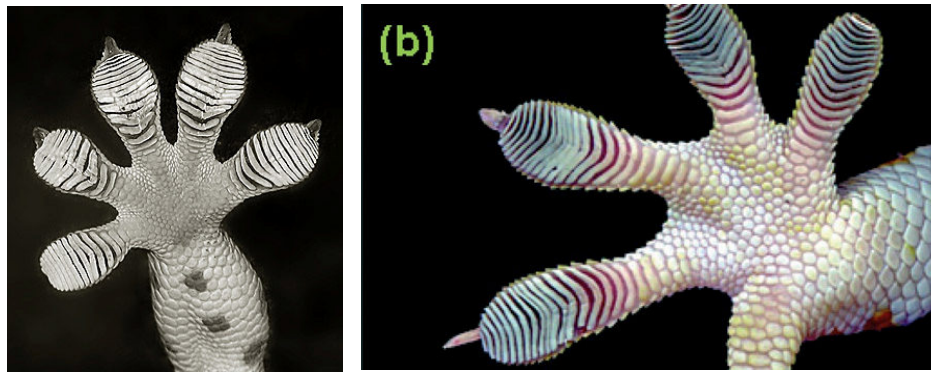


GECKO



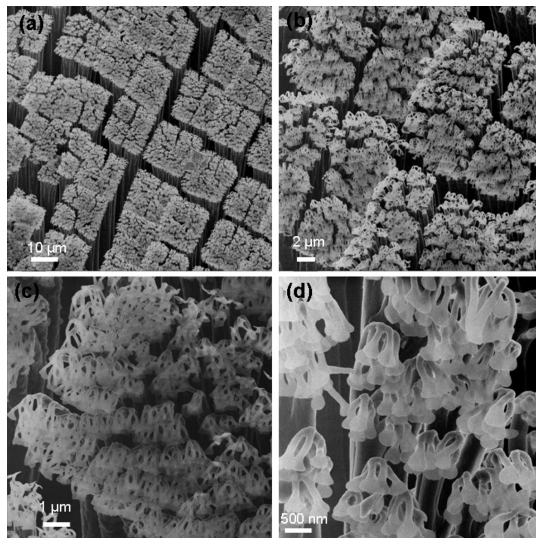
Geckos, harmless tropical lizards, are extremely fascinating and extraordinary animals. They have very sticky feet that cling to virtually any surface. This characteristic makes it possible for them to rapidly run up vertical walls and along the undersides of horizontal surfaces. In fact, a gecko can support its body mass with a single toe!

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The secret to this remarkable ability is the presence of an extremely large number of microscopically small hairs on each of their toe pads. When these hairs come in contact with a surface, weak forces of attraction (i.e., **van der Waals** forces) are established between hair molecules and molecules on the surface.

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- The fact that these hairs are so small and so numerous explains why the gecko grips surfaces so tightly.

- To release its grip, the gecko simply curls up its toes, and peels the hairs away from the surface.

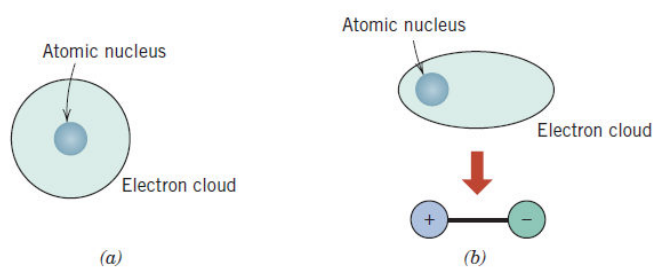
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SECONDARY BONDING

- Fluctuating dipoles

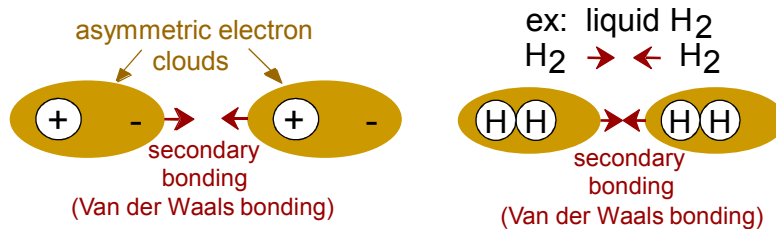
- A dipole may be created or induced in an atom or molecule that is normally **electrically symmetric**. (*The overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus*)

- All atoms are experiencing constant vibrational motion that can cause **instantaneous and short-lived distortions** of this electrical symmetry for some of the atoms or molecules: **Creation of small electric dipoles**.



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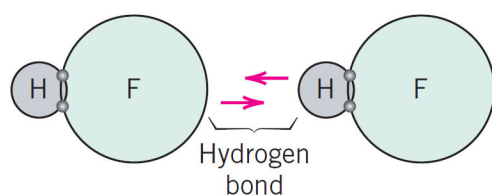
- Fluctuating dipoles



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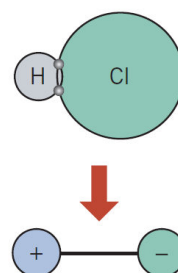
- Permanent **dipoles** - molecule induced

Polar Molecules: Permanent dipole moments exist in some molecules by virtue of an asymmetrical arrangement of positively and negatively charged regions.

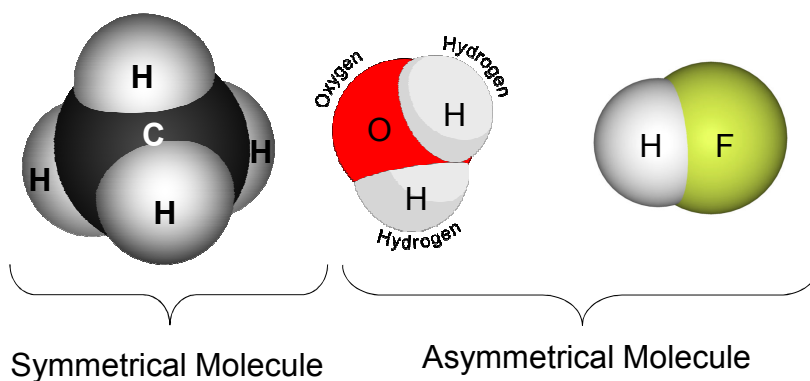


Van der Waals forces will also exist between adjacent polar molecules.

Polar Molecule

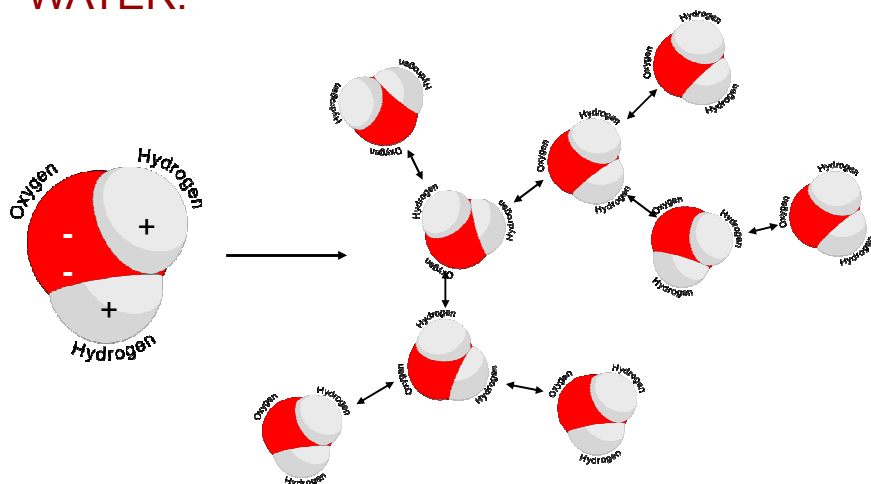


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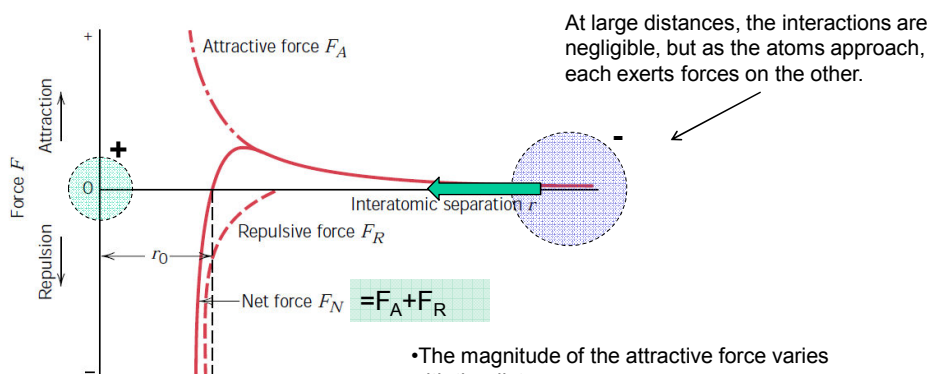
WATER:



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Bonding Forces and Energies

The principles of atomic bonding are best illustrated by considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.



- The magnitude of the attractive force varies with the distance.
- Ultimately, the outer electron shells of the two atoms begin to overlap, a strong repulsive force F_R comes into play.

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Bonding Forces and Energies

When F_A and F_R become equal, there is **no** net force:

$$F_A + F_R = 0$$

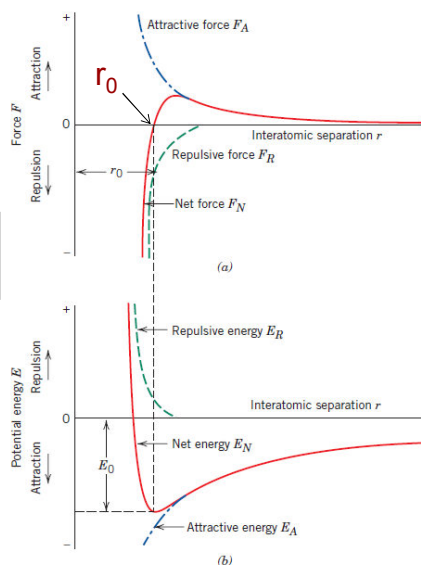
(State of equilibrium exists at $r=r_0$)



The centers of the two atoms will remain separated by the **equilibrium spacing** r_0
(Approximately 0.3 nm)

$$E = \int F dr$$

$$\begin{aligned} E_N &= \int_{\infty}^r F_N dr \\ &= \int_{\infty}^r F_A dr + \int_{\infty}^r F_R dr \\ &= E_A + E_R \end{aligned}$$

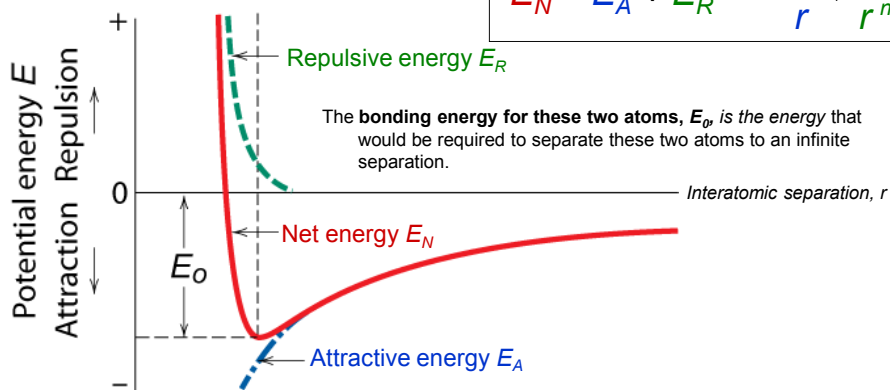


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Bonding Forces and Energies

- Energy – minimum energy most stable
 - Energy balance of **attractive** and **repulsive** terms

$$E_N = E_A + E_R = -\frac{A}{r} + \frac{B}{r^n}$$

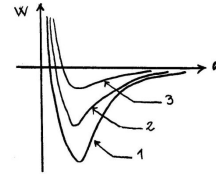


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•The magnitude of bonding energy and the shape of the energy-versus interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding.

•A number of material properties depend on

- E_0 ,
- Curve shape, and
- Bonding type.



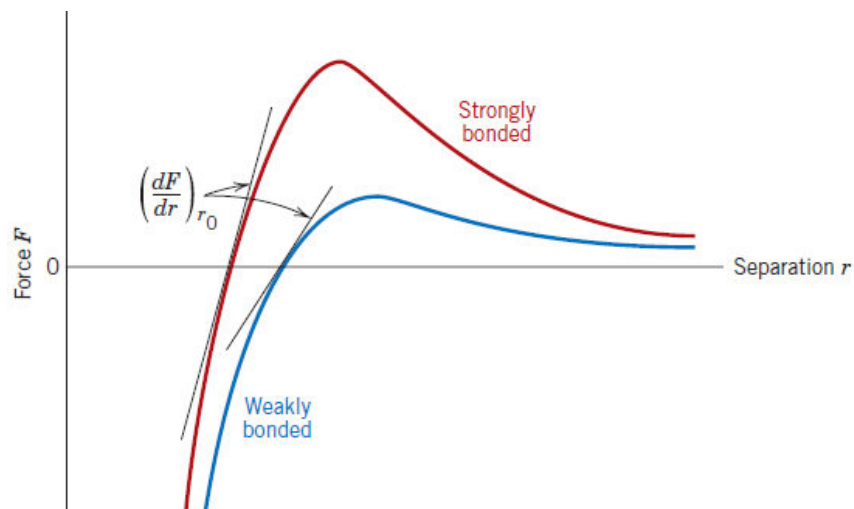
•Materials having large bonding energies typically also have **high melting temperatures**;

•At room temperature, solid substances are formed for large bonding energies, whereas for small energies the gaseous state is favored;

•Liquids prevail when the energies are of intermediate magnitude.

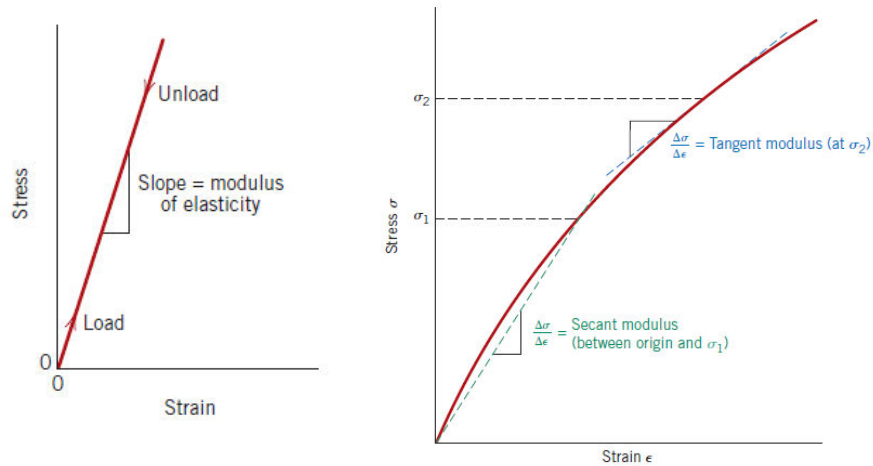
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•The mechanical stiffness (**Modulus of elasticity**) of a material is dependent on the shape of its force-versus interatomic separation curve. The slope for a relatively stiff material at the $r=r_0$ position on the curve will be quite steep; slopes are shallower for more flexible materials.



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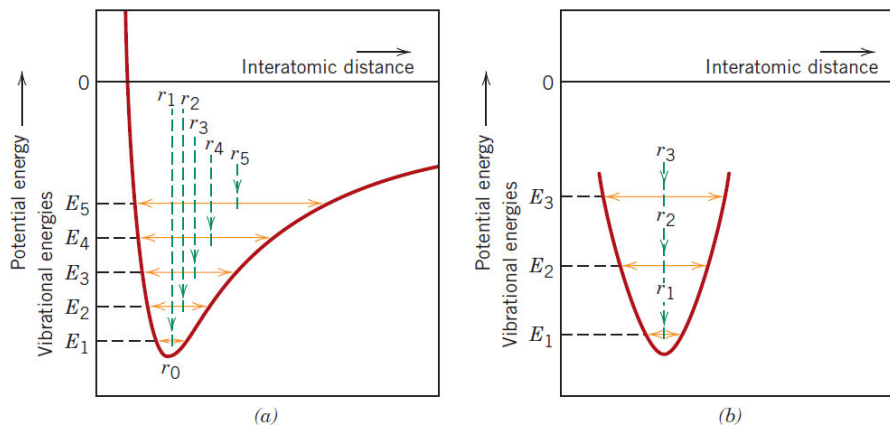
Mechanical stiffness (**Modulus of elasticity**)



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•Furthermore, how much a material expands upon heating or contracts upon cooling (that is, its linear coefficient of thermal expansion) is related to the shape of its E_0 -versus- r_0 curve.

•A deep and narrow “**trough or well**” which typically occurs for materials having large bonding energies, normally correlates with a low coefficient of thermal expansion and relatively small dimensional alterations for changes in temperature.



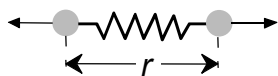
Summary: Bonding

Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors , ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

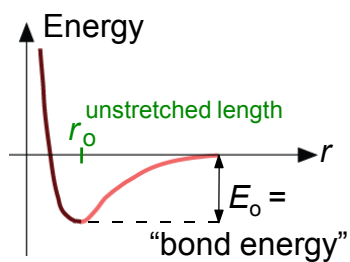
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Properties From Bonding: T_m

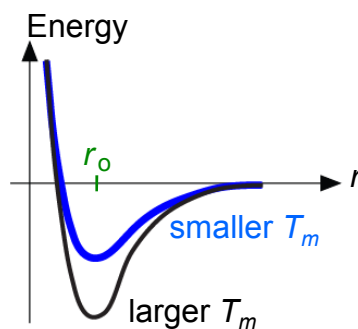
- Bond length, r



- Bond energy, E_0



- Melting Temperature, T_m

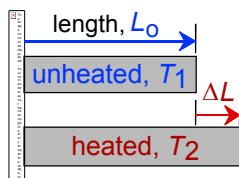


T_m is larger if E_0 is larger.

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Properties From Bonding : α

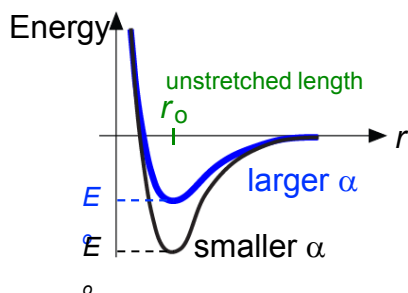
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_0} = \alpha (T_2 - T_1)$$

- $\alpha \sim$ symmetric at r_0



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Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m
large E
small α

Metals

(Metallic bonding):

Variable bond energy

moderate T_m
moderate E
moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m
small E
large α

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