

Introduction to Solids: Structure and bonding in solids: Overview of crystal lattices and their role in defining material properties. Classification of solids into metals, semiconductors, and insulators based on bonding and electron behavior.

Electronic Properties of Materials: Band theory explaining conduction, valence bands, and energy gaps in different material types. Detailed examination of Fermi level, density of states, and their implications for electronic behavior.

Phonons and Thermal Properties: The role of lattice vibrations (phonons) in thermal and electronic properties. Concepts like specific heat and thermal conductivity in relation to material structure and temperature.

Books:

- Foundations of Materials Science and Engineering – Smith and Hashemi, Ch2: 2.4, 2.5
- Principles of Electronic Materials and Devices – S. O. Kasap, Ch 1, 1.1-1.3

Quantum materials:

- Materials having properties that cannot be easily described by classical physics.
- Include topological materials, low-dimensional materials, etc.

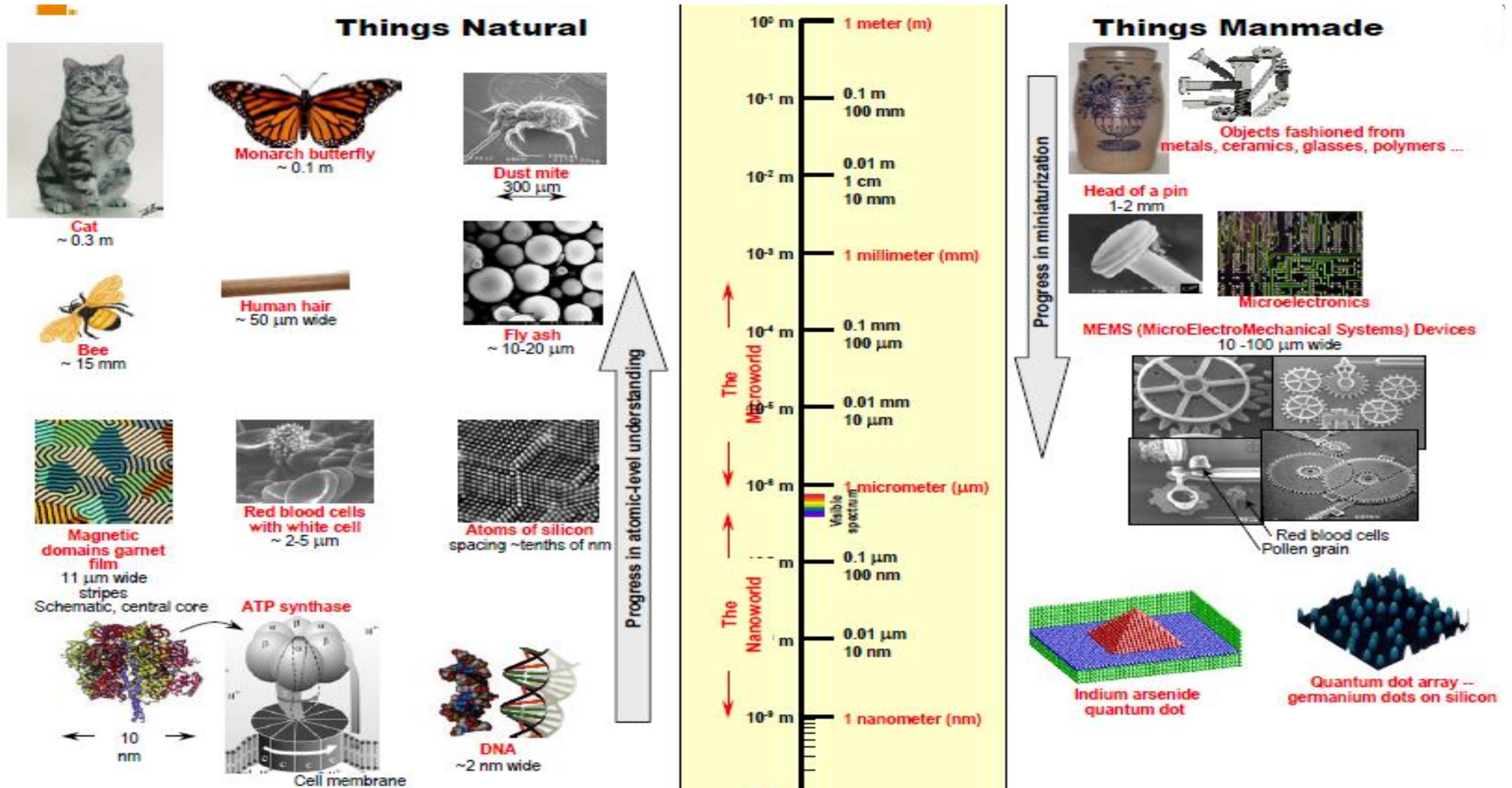
The ability to manipulate these materials at the nanoscale opens up possibilities for creating innovative quantum devices.



Different states of matter!

We will talk about solids only.

Materials at different length scales



Why a solid is solid?

A solid is a state of matter with a definite shape and volume.

The constituents (atoms/ions/molecules) are held together closely as well as strongly

- BONDS

Bond length:

Atoms approach each other only to a certain distance and on bond formation they will maintain *that* distance (equilibrium distance).

Bond strength:

Energy required to separate two atoms from their equilibrium spacing to an infinite distance apart.

- **Attractive energy** that brings them together
- **Repulsive energy** that keeps the atoms a certain distance apart

The total potential energy of the system is then the sum of the attractive and repulsive components:

Why a solid is solid?

Since the atoms are held at a particular distance (equilibrium distance, r_o), the **resultant force must be zero at that point!**

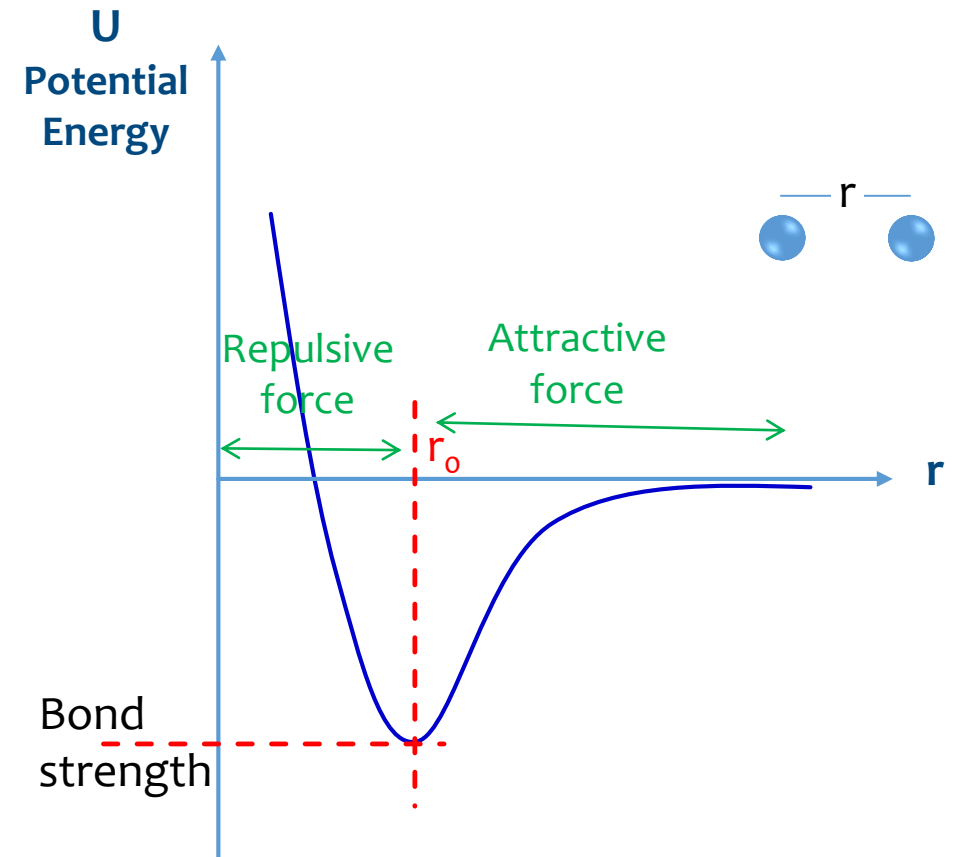
At $r = r_o$, the attractive force and the repulsive force will balance out.

- potential energy will be minimum

- $F = -\frac{dU}{dr}$

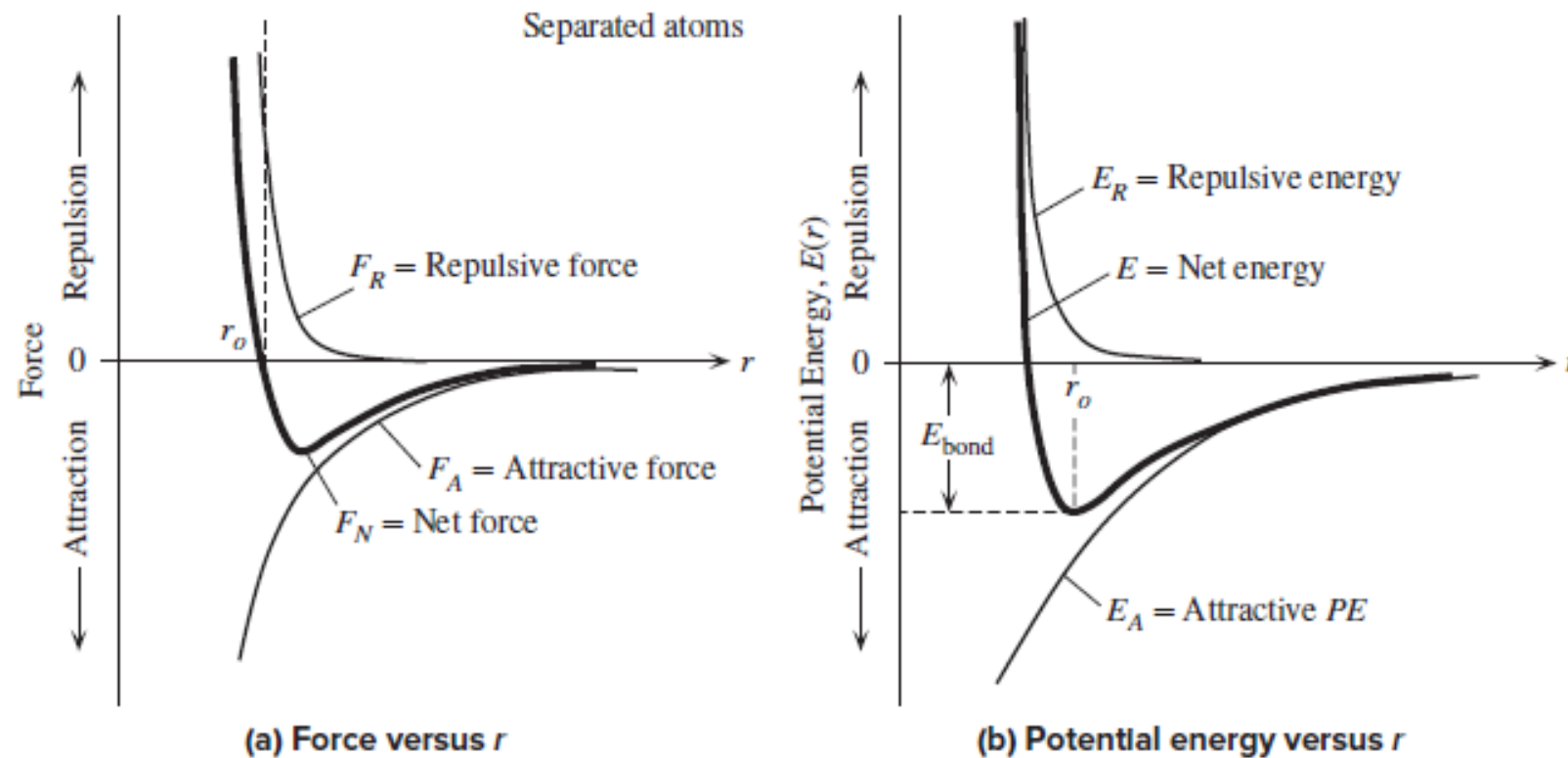
Attractive part of PE comes from the chemical affinity/attractive force which is lowering the energy as atoms/molecules come together. The interaction (and hence the exponent m) depends on the involved atoms/molecules.

Repulsive part comes from Pauli principle: when the electronic clouds start to overlap, the energy of the system increases abruptly. The value of n is determined by the outer electron configuration.



$$U = U_{\text{attractive}} + U_{\text{repulsive}} = -\frac{a}{r^m} + \frac{b}{r^n}$$

Why a solid is solid?

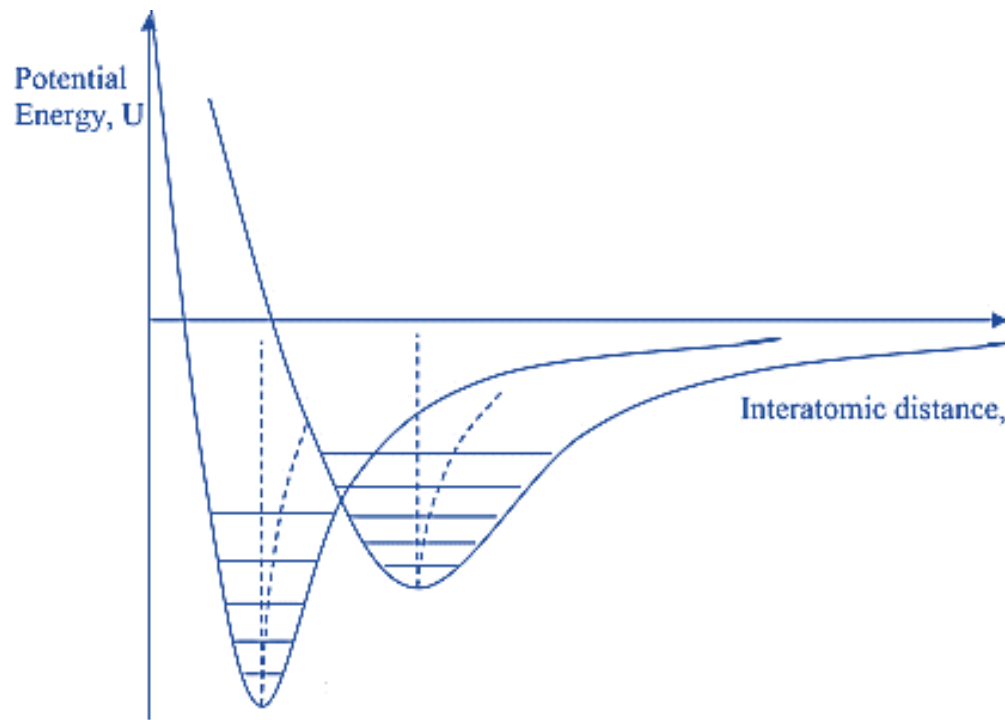


$$F = - \left. \frac{dU}{dr} \right|_{r=r_0} = 0,$$
$$U = -\frac{a}{r^m} + \frac{b}{r^n}, \quad r_0 = \left(\frac{nb}{ma} \right)^{\frac{1}{n-m}}$$

Information from PE vs r curve

Materials with a deep well have:

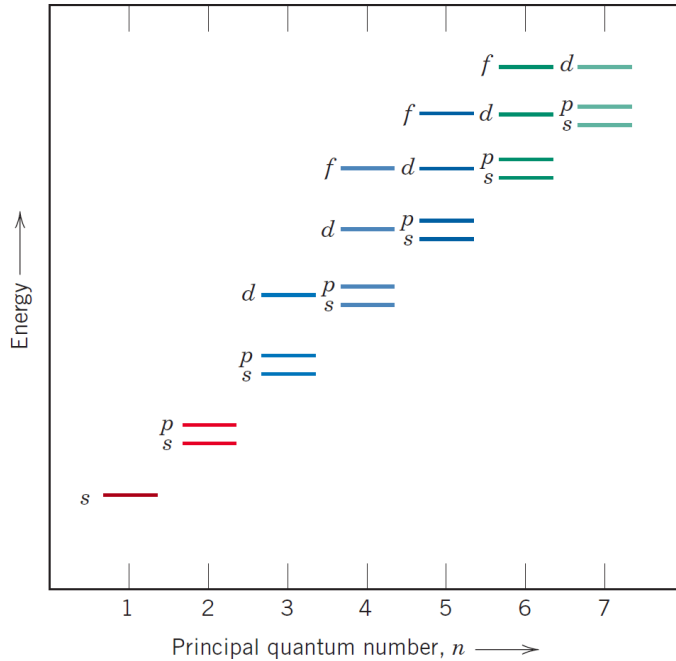
- a high melting point (More Binding energy)
- high elastic modulus (related to stretching of bonds at equilibrium, more curvature at $r = r_o$)
- low thermal expansion coefficient (Less shallow)



Stability of atoms and chemical bonds

Electrons in atoms have discrete energy states and tend to occupy lowest available energy levels.

The electronic structure of atoms governs their interaction with other atoms.



		<div><div><div>Alkali metals</div><div>Alkaline-earth metals</div><div>Transition metals</div><div>Other metals</div><div>Other nonmetals</div></div><div><div>Halogens</div><div>Noble gases</div><div>Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)</div><div>Actinoid elements</div></div></div>																		
period	group	1*											13	14	15	16	17	18		
	1	1	2											5	6	7	8	9	10	
		H	Li	Be											B	C	N	O	F	Ne
	2																			
	3	Na	Mg											Al	Si	P	S	Cl	Ar	
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og		
lanthanoid series		6	58	59	60	61	62	63	64	65	66	67	68	69	70	71				
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
actinoid series		7	90	91	92	93	94	95	96	97	98	99	100	101	102	103				
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Filled outer shells result in a stable configuration as in noble gases (s^2p^6 configuration).

*Atoms with incomplete outer shells strive to reach stable configuration by **sharing or transferring** electrons among each other for maximal stability.*

Electronegativity (X) of an atom is the tendency of the atom to attract electrons towards itself during the formation of bonds with other atoms.

Pauling's Electronegativities of Elements

H																
2.1																
Li	Be											B	C	N	O	F
1.0	1.5											2.0	2.5	3.0	3.5	4.0
Na	Mg											Al	Si	P	S	Cl
0.9	1.2											1.5	1.8	2.1	2.5	3.0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2

Primary Bonds

- Ionic bond
- Covalent bond
- Metallic bond

Secondary Bonds

- Hydrogen bond/ Coordinate bond
- van der Waals bond

Electronegativity difference, ΔX decides the type of bonds!

ΔX is very large

Atoms with Low X can easily give up their valence electrons to the atoms with larger X value becoming ions in the process and forming **IONIC bond**.

ΔX is very small with large X values

Sharing of valence electrons to complete the subshells of each atom – **COVALENT bond**.
Shared electrons are confined to the bonding atoms.

ΔX is very small with small X values

When many metal atoms are brought together valence electrons are lost from individual atoms and become collectively shared by all the ions – **METALLIC bonds**.

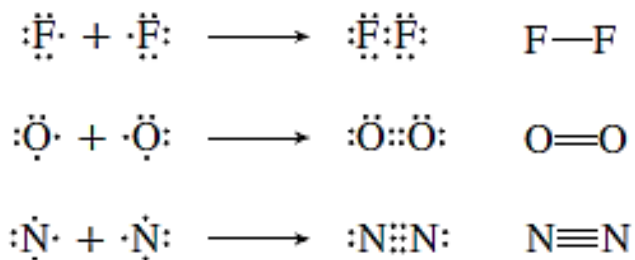
The valence electrons become delocalized and form an electron gas or electron cloud, permeating the space between the ions.

Types of bonds – IONIC bonds

- Due to coulomb interaction between oppositely charged ions.
- Energy required for ionization of the atoms is low as compared to lowering in the overall energy due to bond formation.
- Non-directional because coulomb interaction is non-directional. So, ions tend to form as many bonds as geometrically possible.
- The Coulomb term is dependent on the charges of the ions forming the bond. Ionic crystals with multivalent ions have generally stronger bonds and hence higher melting points than crystals with univalent ions.
- Ionic solids are strong, brittle materials with high melting temperatures compared to metals.
- Soluble in polar liquids such as water.
- All the electrons are within the rigidly positioned ions, therefore, ionic solids are typically electrical insulators.
- Compared to metals and covalently bonded solids, ionically bonded solids have lower thermal conductivity since ions cannot readily pass vibrational kinetic energy to their neighbors.
- When melted or dissolved in water, ionic materials can conduct electricity through ionic diffusion

Types of bonds – COVALENT bonds

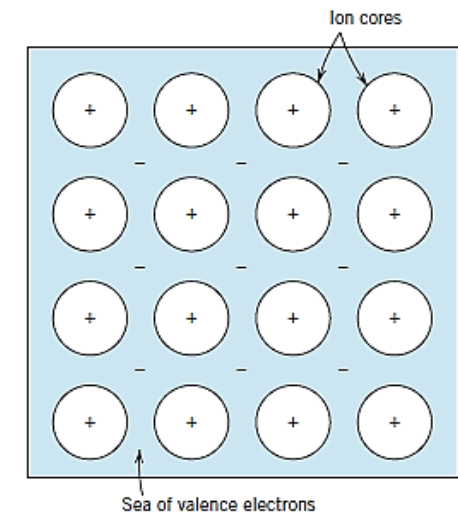
- ΔX is very small with large X values for each atoms
- The covalent bond formation results from the sharing of valence electrons to complete the subshells of each atom.
- The number of covalent bonds that is possible for a particular atom is determined by the number of valence electrons. The atoms will form as many shared pairs as needed to complete their outer electronic structure



- The covalent bond is strongly directional: It is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.
- The directional nature and strength of the covalent bond also make these materials non-ductile. Under a strong force, they exhibit brittle fracture.
- Due to the strong Coulombic attraction between the shared electrons and the positive nuclei, the covalent bond energy is very high.
- Poor electrical conductivity - All valence electrons are locked in the bonds between the atoms

Types of bonds – METALLIC bonds

- ΔX is very small with small X values for each atom.
- When many metal atoms are brought together
 - valence electrons are lost from individual atoms and become collectively shared by all the ions.
 - The bond is a collective sharing of electrons.
 - Valence electrons become delocalized and form an electron gas or electron cloud, permeating the space between the ions.
- Bonding is essentially due to the attraction between the stationary metal ions and the freely wandering electrons between the ions.
- As a consequence of being a collective phenomenon the metallic bonds are non-directional.
 - i. Close packed crystal structures with high coordination numbers.
 - ii. Under an applied force, metal ions are able to move with respect to each other – ductile and malleable.
 - iii. Lack of rigidity, hence lower strength and melting points as compared to ionic and covalent solids.
- Delocalized/free electron cloud contributes to high electrical and thermal conductivities.



- Bond will be more metallic in nature for less number of valence electrons/atoms.
- For more valence electrons the cores will have more positive charge and hence larger interaction between the cores and the cloud there by decreasing the “delocalization” of electron cloud.
- Alkaline-Earth metals have higher MPs as compared to alkaline metals.

Bonding between atoms is generally not just of one type; rather, it is a mixture of bond types.

(1) *ionic-covalent*, (2) *metallic-covalent*, (3) *metallic-ionic*, and (4) *ionic-covalent-metallic*.

Ionic-covalent:

Pauling's equation to determine the percentage ionic character of bonding in a compound AB:

$$\% \text{ of ionic character} = \left(1 - e^{-0.25(X_A - X_B)^2}\right) \times 100$$

X_A and X_B are the electro-negativities of the atoms A and B

Metallic -Covalent:

For example, transition metals have mixed metallic-covalent bonding.

Their high melting point is attributed to mixed metallic-covalent bonding.

We define Covalent-Metallivities (C-M) based on their Melting Point in °C as compared to that for carbon in diamond form (3500 °C).

Carbon → C-M = 4 (maximum, C-C bond in diamond is considered purely covalent)

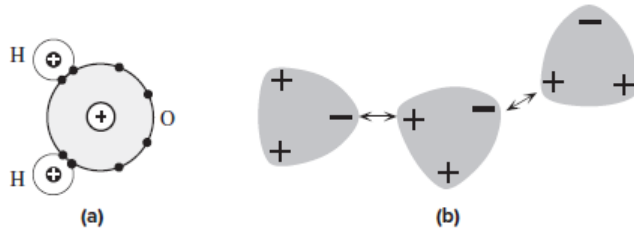
Fe → 1535 °C → C-M = $(4/3500) \times 1535 = 1.754$

% Covalent Character = $(1.75/4) \times 100 = (1535/3500) \times 100 = 43.7 \%$

% Metallic Character = $100 - 43.7 = 56.3$

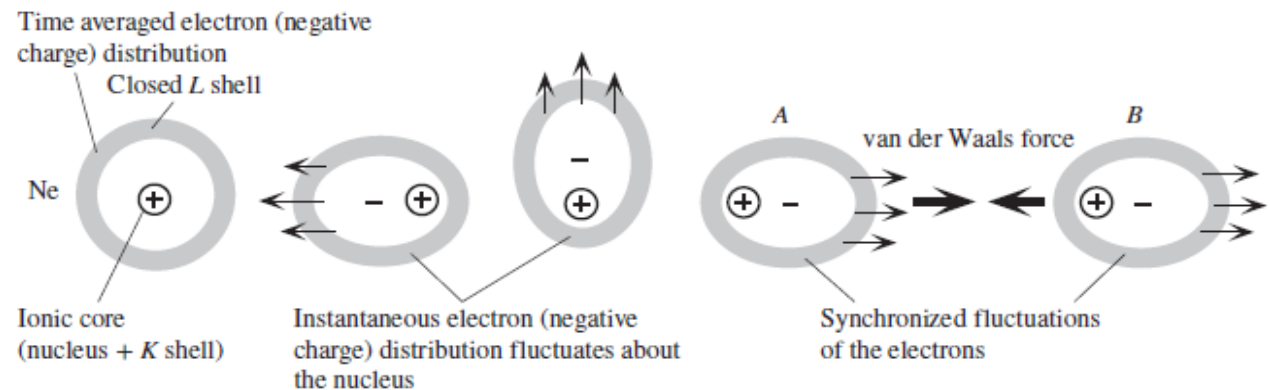
$X = 0 \rightarrow$ Secondary Bond Formation

- The driving force for primary atomic bond formation is the lowering of the energy of the bonding electrons.
- The driving force for secondary bonding is the attraction of the electric dipoles contained in atoms or molecules.
- Electric dipoles interact with each other by electrostatic (Coulombic) forces, and thus atoms or molecules containing dipoles are attracted to each other by these forces. Even though the bonding energies of secondary bonds are weak, they become important.



Hydrogen Bond/Coordinate Bond

- These are formed between polar molecules
- Directional in nature
- Solids are insulators



Van der Waals Bond

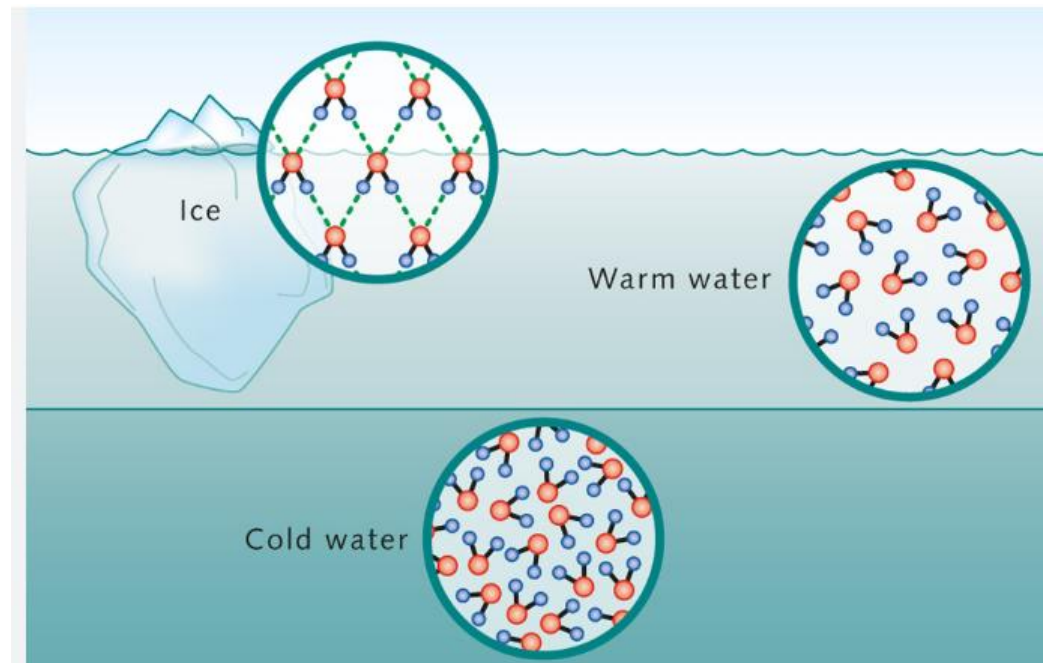
- Due to induced synchronization of the electronic motions around the nuclei, and we refer to this as *induced-dipole-induced-dipole interaction*.
- Weaker than permanent dipole interactions

Types of bonds in solids

Examples of Substances with Different Types of Interatomic Bonding

Type of Bond	Substance	Bond Energy, kJ/mol	Melting Point, (°C)	Characteristics
Ionic	CaCl	651	646	Low electrical conductivity, transparent, brittle, high melting point
	NaCl	768	801	
	LiF	1008	870	
	CuF ₂	2591	1360	
	Al ₂ O ₃	15,192	3500	
Covalent	Ge	315	958	Low electrical conductivity, very hard, very high melting point
	GaAs	~315	1238	
	Si	353	1420	
	SiC	1188	2600	
	Diamond	714	3550	
Metallic	Na	109	97.5	High electrical and thermal conductivity, easily deformable, opaque
	Al	311	660	
	Cu	340	1083	
	Fe	407	1535	
	W	844	3370	
van der Waals	Ne	2.5	−248.7	Weak binding, low melting and boiling points, very compressible
	Ar	7.6	−189.4	
	CH ₄	10	−184	
	Kr	12	−157	
	Cl ₂	31	−103	
Hydrogen bonding	HF	29	−92	Higher melting point than van der Waals bonding, tendency to form groups of many molecules
	H ₂ O	50	0	

Bonds in solids



Primary Bonds	Secondary Bonds
$X \neq 0$	$X \sim 0$
Metallic, Ionic, Covalent	Hydrogen, Van der Waals
Outermost electron interactions	Dipole-dipole interactions
Bond length: 0.1–0.2 nm	Bond length: 0.2–0.5 nm
Bond energy: 1–10 eV/bond	Bond energy: 0.01–0.5 eV/bond