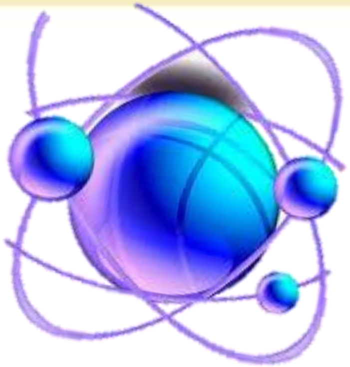
Chapter 2

Atomic Structure and Bonding



-Interatomic Bonding

–Bonding forces and energies

–Primary interatomic bonds

–Secondary bonding

–Molecules

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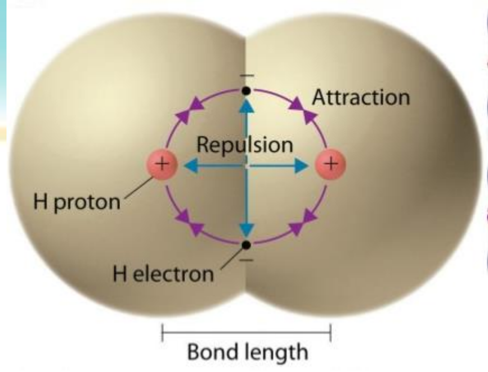
Learning Objectives

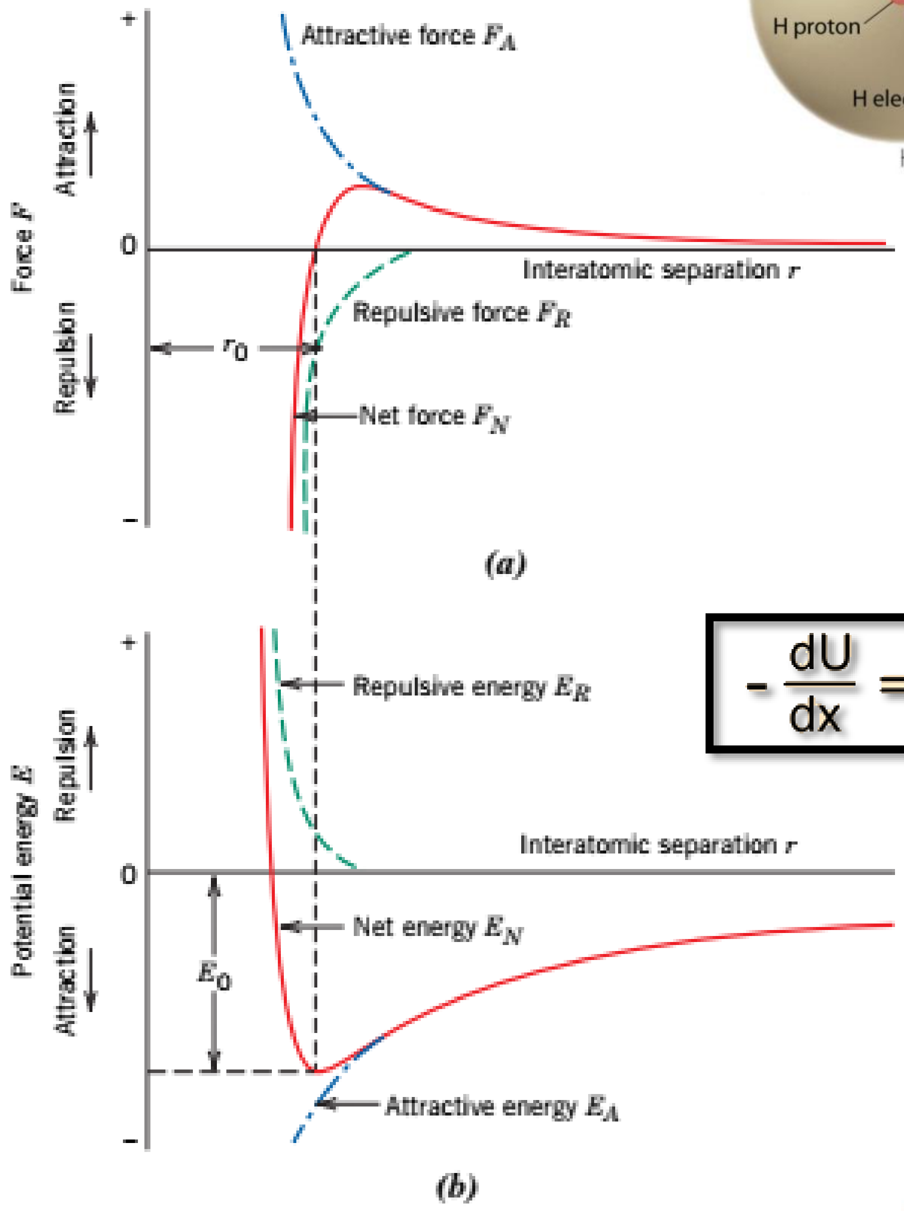
- Define four **quantum numbers** for electrons and explain the significance of each.
- Explain the arrangement of the elements in the **periodic table**.
- State the **electronic structure** of the elements.
- Explain the role of **electronegativity in bonding**.
- Define four different **mechanisms of bonding** in materials.
- Understand how **interactions between atoms or between ions** influence materials properties.
- Recognize that even though **allotropes** are composed of the same element, they can display dramatically different materials properties based on their structure (e.g., the allotropes of carbon).

Bonding Forces and Energies



- Considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.
- At larger distances, the interactions are negligible.
- As the atoms approach, each exerts forces on the other.
  – **Attractive**
  – **Repulsive**

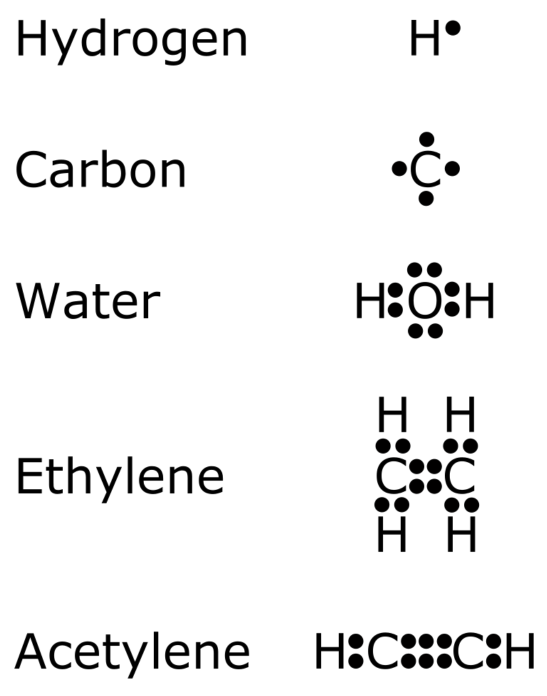
Ultimately, the outer electron shells of the two atoms begin to overlap, and a strong repulsive force comes into play

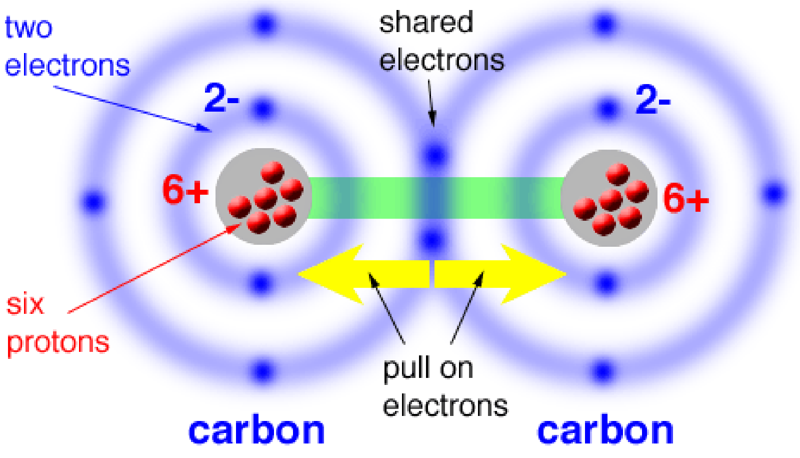


$$\boxed{-\frac{dU}{dx} = F(x)}$$

Types of Bonding

- The electronic structure of atoms defines the character of their interaction among each other.
- Filled outer shells result in a stable configuration as in noble inert gases.
- Atoms with incomplete outer shells strive to reach this noble gas configuration by sharing or transferring electrons among each other for maximal stability.
- Strong "primary" bonding results from the electron sharing or transfer.





Types of Bonding

- **Primary bonding**: **e^- 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^+ Cl^-
  - **Covalent**: electrons are shared between the molecules, to saturate the valence. Example - H_2
  - **Metallic**: the atoms are ionized, loosing some electrons from the valence band. Those electrons form a electron sea, which binds the charged nuclei in place

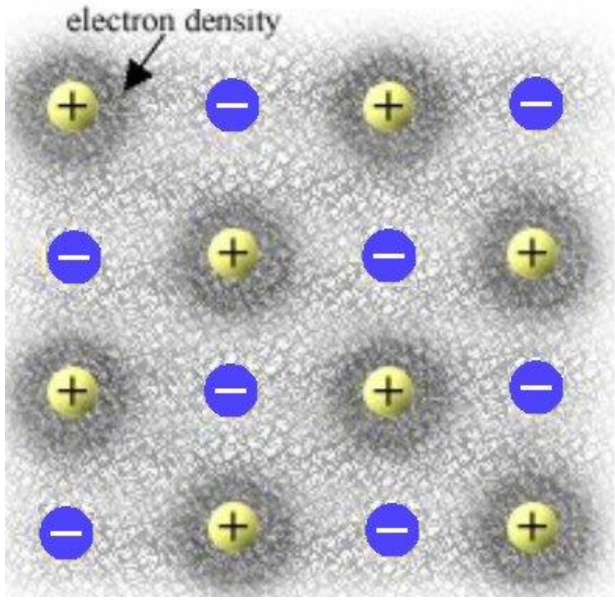
- Secondary bonds/ van der Waals bonds Mixed Bond?

e^- transferred or shared Interaction of atomic/molecular dipoles Weak (< 100 KJ/mol or < 1 eV/atom)

- **Dipole-dipole bonds** (polar molecules - H_2O, HCl...)
- **H- bonds**
- **Polar molecule-induced dipole bonds** (a polar molecule induces a dipole in a nearby nonpolar atom/molecule)
- **Fluctuating Induced Dipole** (inert gases, H_2, Cl_2…) (weakest)

(I) Ionic Bonding

Formation of ionic bond:

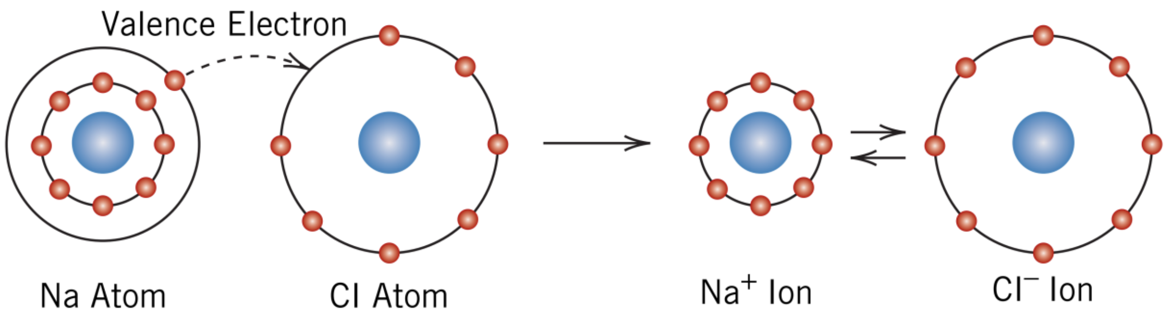


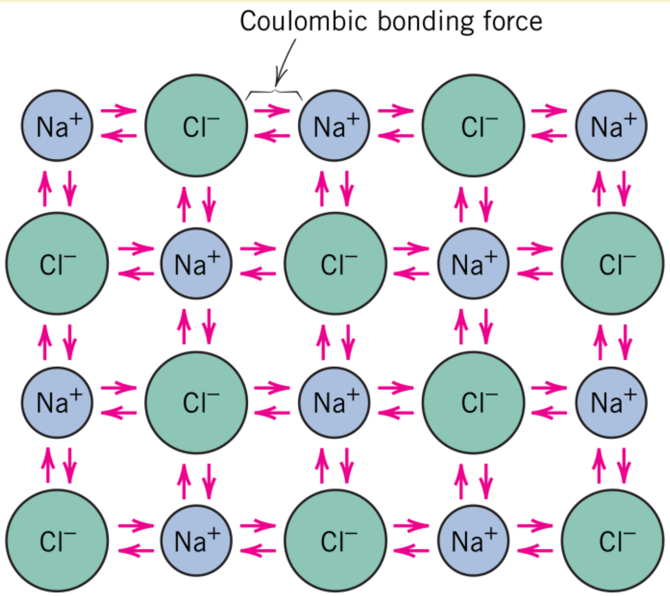
1. **Mutual ionization occurs by electron transfer**
(remember electronegativity table)
- Ion = charged atom
- Anion = negatively charged atom
- Cation = positively charged atom

2. Ions are attracted by strong coulombic interaction

- Oppositely charged atoms attract each other
- **An ionic bond is non-directional** (ions may be attracted to one another in any direction)

Ionic Bonding : Table salt (NaCl)





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

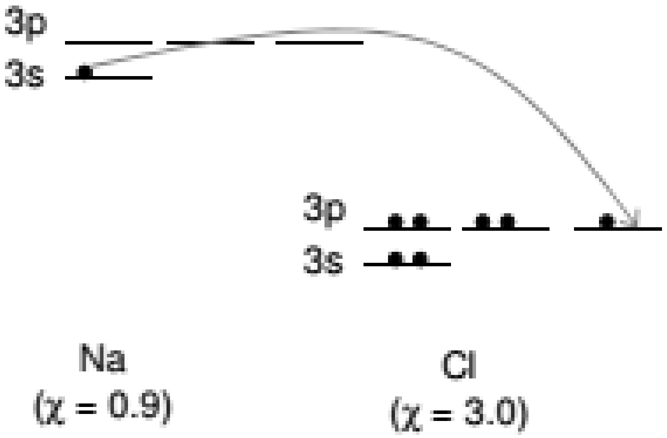
11 Protons Na $1S^2\ 2S^2\ 2P^6\ 3S^1$
11 Protons Na+ $1S^2\ 2S^2\ 2P^6$

donates e^-
10 e^- left

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

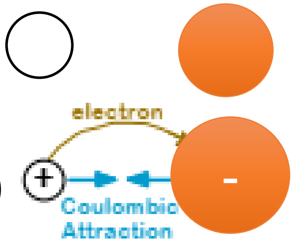
17 Protons Cl $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^5$
17 Protons Cl- $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^6$

receives e^-
18 e^-



Na (metal)
unstable

Cl (nonmetal)
unstable



Na (cation)
stable

Cl (anion)
stable

Ionic Bonding

For two isolated ions, the attractive energy E_A is a function of the interatomic distance :

$$E_A = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o r}$$

Since z_1 = +1 for Na^+ and z_2 = -1 for Cl^-

$$E_A = -\frac{e^2}{4\pi\varepsilon_o r} = -\frac{A}{r}$$

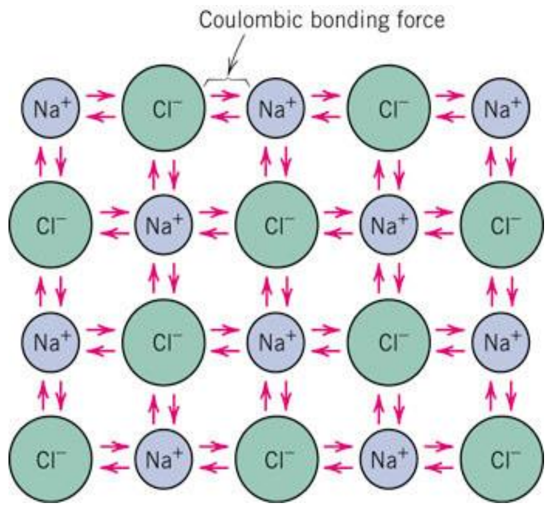
ε_0 is the permittivity of a vacuum (8.85×10^{-12} F/m), Z_1 and Z_2 are values of the valences for the two ion types, and e is the electronic charge

Negative energy means attraction only. Will the atoms collapse on themselves?

No, there is also repulsive energy (e.g. steric repulsion, e-e repulsion)

$$E_R = \frac{B}{r^n}$$

B and *n* depends on atom involved in many cases *n~8*

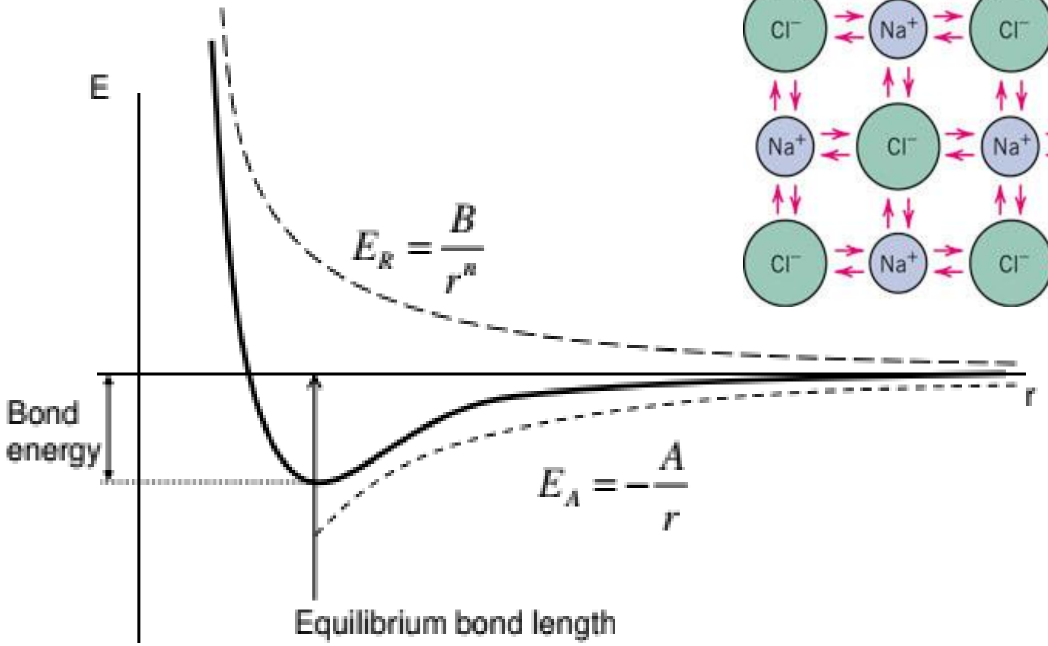


<u>Net potential energy energies</u>

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

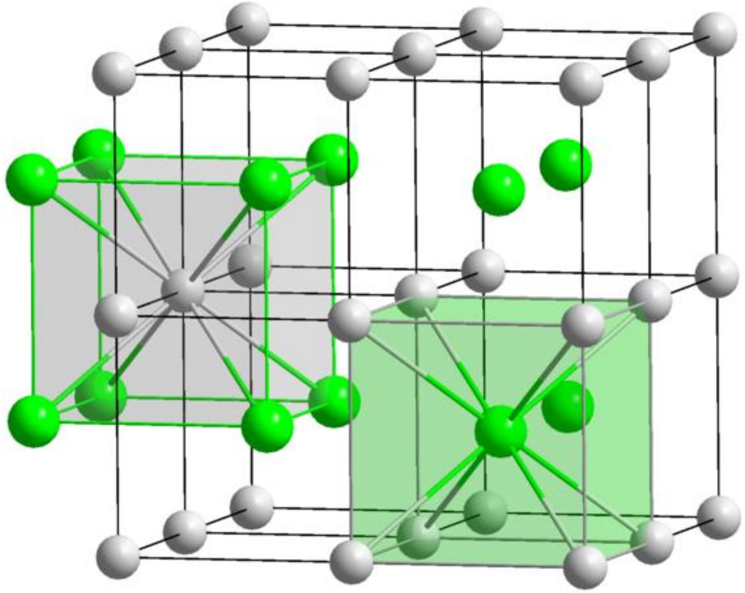
Energy released when ions comes close together

Energy absorbed when ions come close together

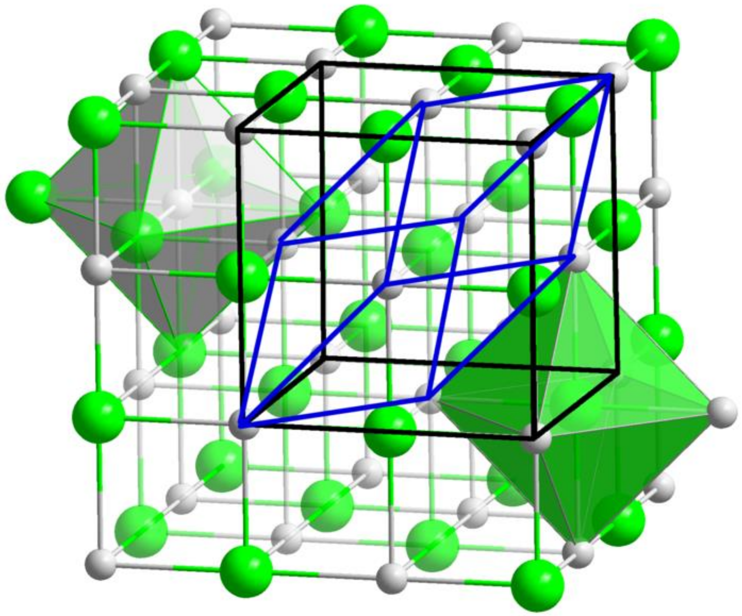


Geometric Arrangement of Ions in Ionic Solids

CsCl



NaCl



Each Cs^+ is surrounded by 8 Cl^- at the corners of its cube

?

Each Na^+ is surrounded by 6 Cl^-
FCC structure

Ionic radius

Cs^+ (0.169 nm)
Cl- (r= 0.181 nm)
Na+ (r= 0.095 nm)

The ratio of Cation/Anion radius

CsCl = 0.934 **NaCl = 0.525 nm**

As the Cation/Anion radius decreases, fewer anions can surrounds a central cation

Ionic Bonding

- Predominant bonding in Ceramics

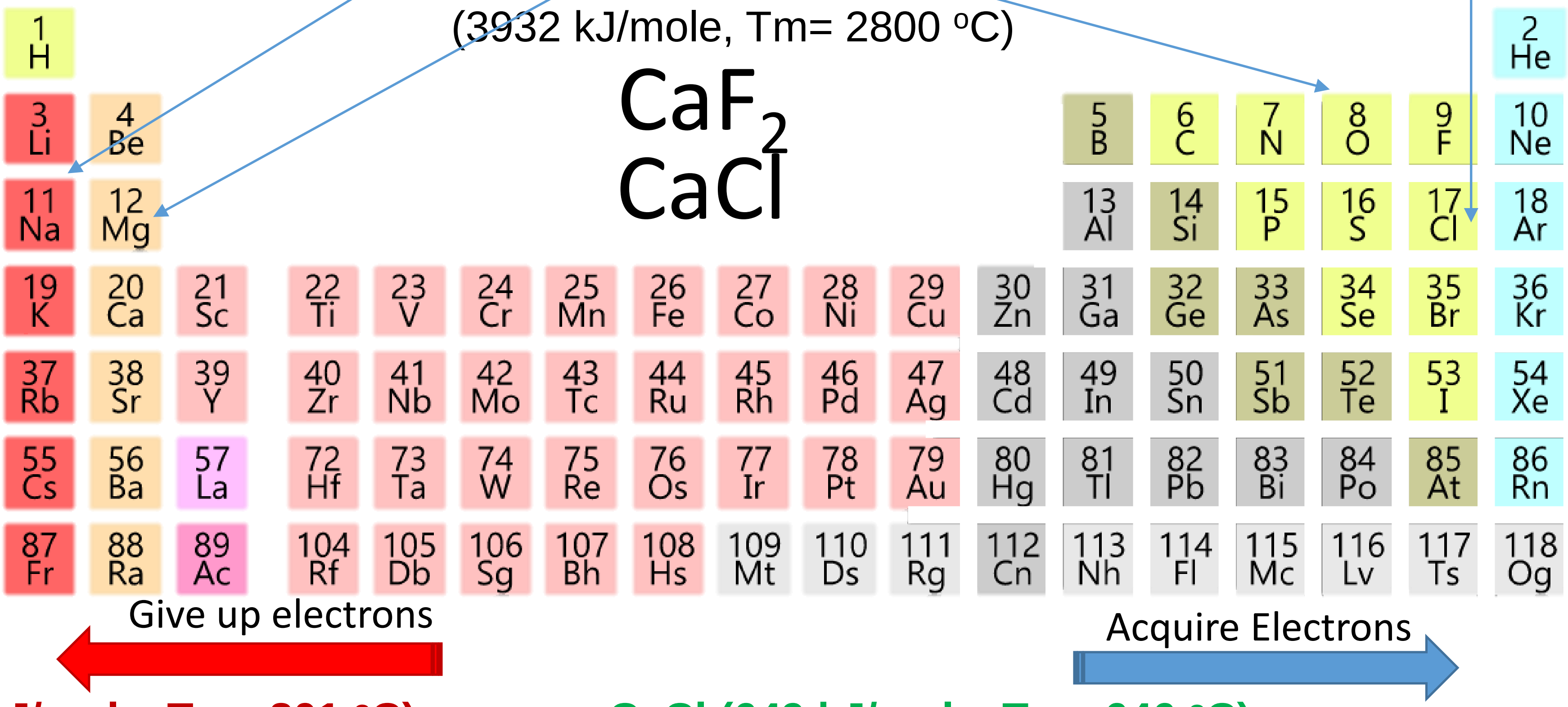
NaCl (766 kJ/mole, Tm= 801 °C)

MgO

(3932 kJ/mole, Tm= 2800 °C)

CaF_2

CaCl

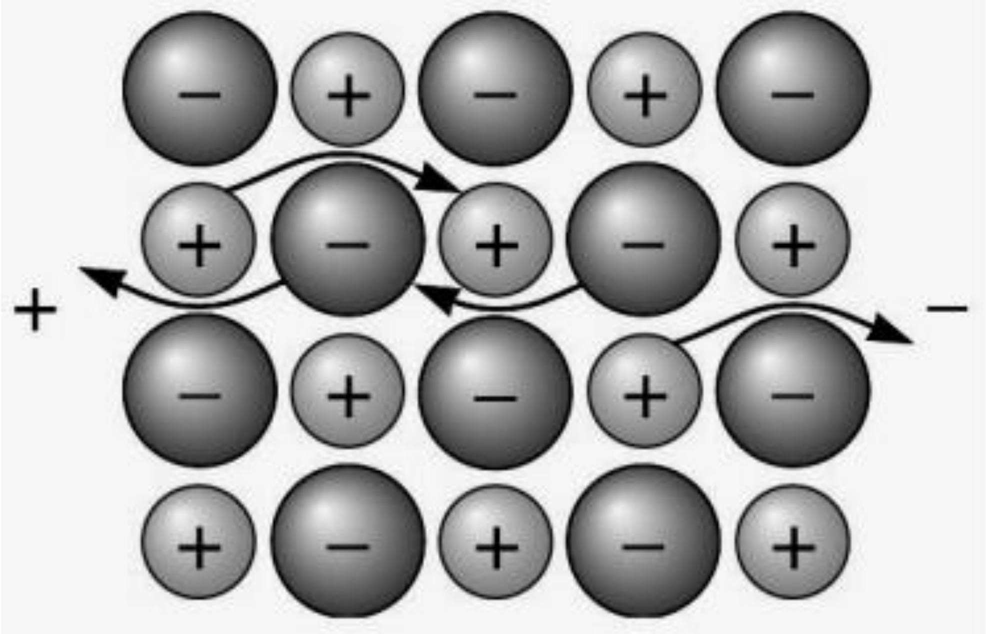


NaCl (766 kJ/mole, Tm= 801 °C) **CsCl (649 kJ/mole, Tm= 646 °C)**

- As the size of an ion increases in a group, the lattice energy decreases (bonding electron in larger ions are farther away
- Multiple bonding electron increases the lattice energy.

Ionic Bonding

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



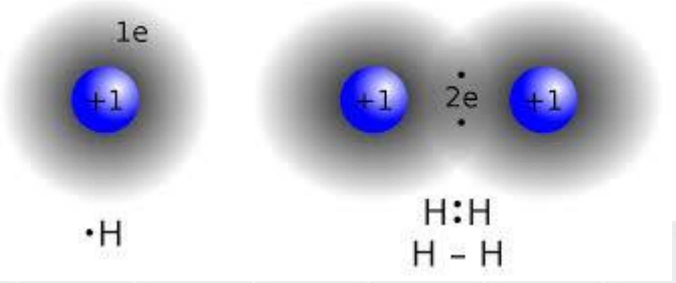
When voltage is applied to an ionic material, entire ions must move to cause a current to flow.

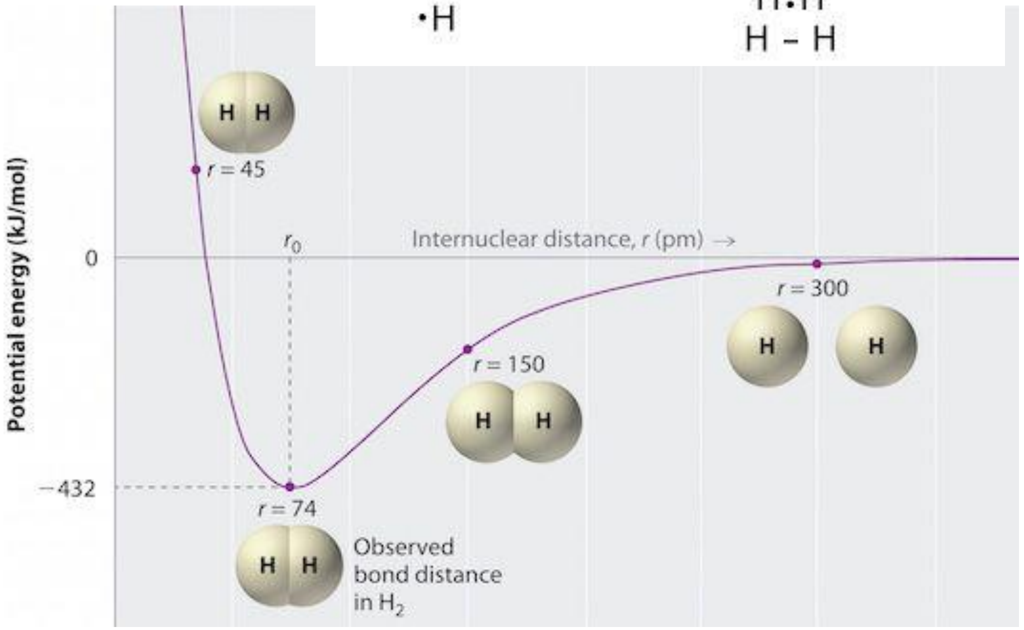
Ion movement is slow and the electrical conductivity is, therefore, poor.

Covalent Bonding

Why do some atoms want to share electrons?

Example1: H_2





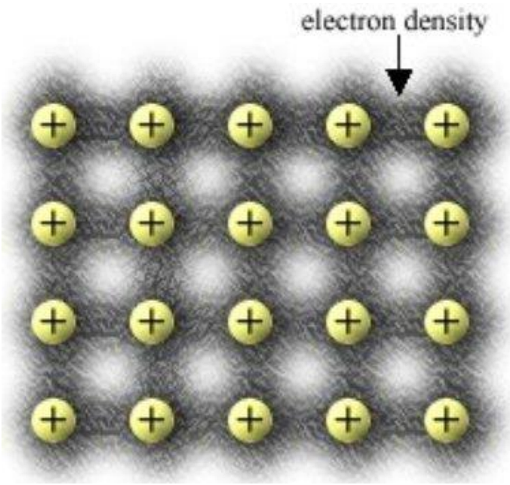
Electrons are shared between the molecules, to saturate the valence.

(Electrons are not transferred as in the ionic bonding)

- The ions repel each other, but are attracted to the electrons that spend most of the time in between ions.

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

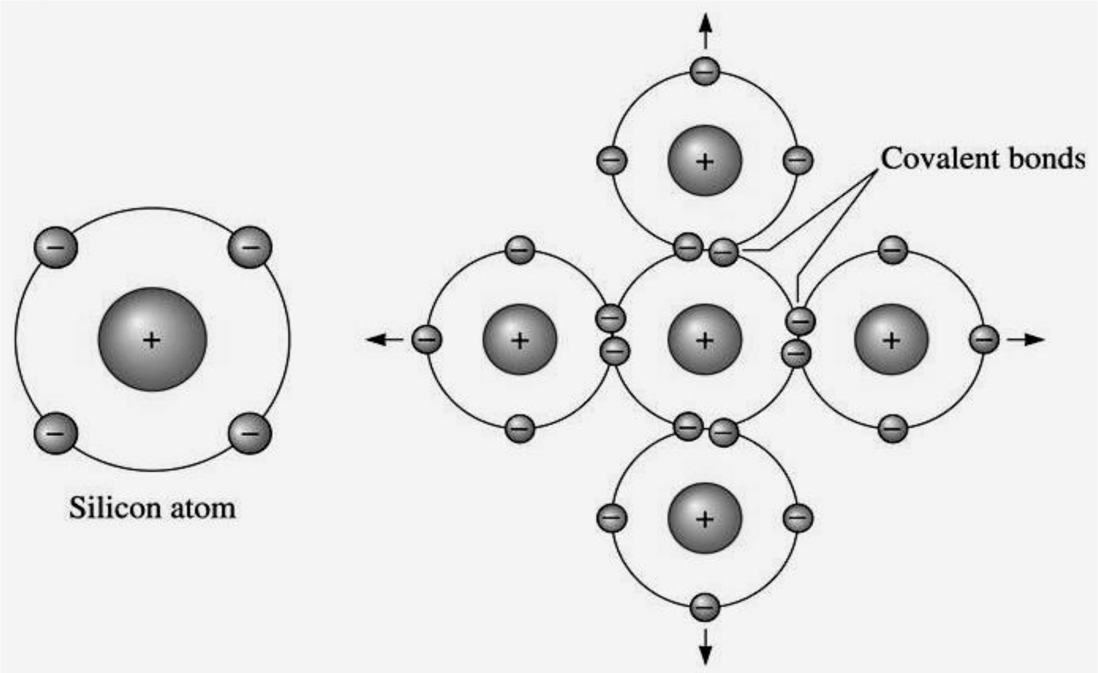


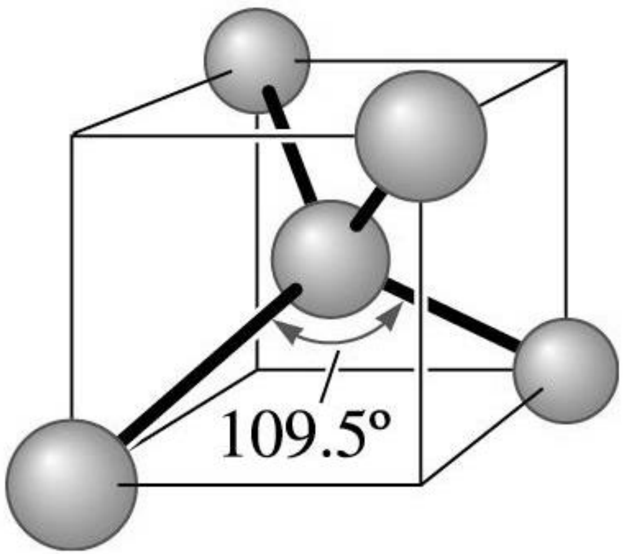
An atom can covalently bond with at most **8-N, N = number of valence electrons**

Example: Cl_2 molecule. Z_{Cl} =17 ($1S^2$ $2S^2$ $2P^6$ **$3S^2$ $3P^5$**)

N' = 7, 8 - N = 1 → can form only one covalent bond

Covalent Bonding : Silicon





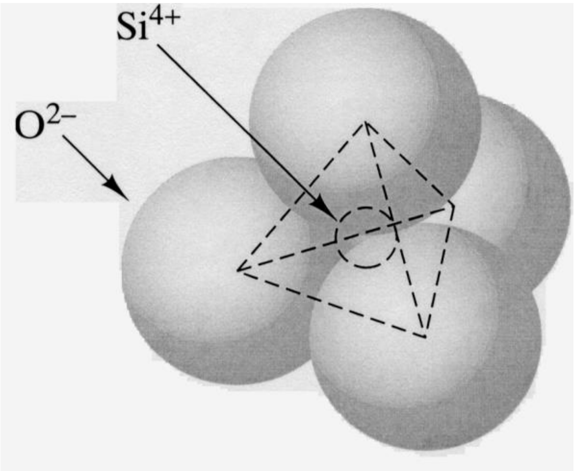


Figure 2-17 *The SiO_4^{4-} tetrahedron represented as a cluster of ions. In fact, the Si—O bond exhibits both ionic and covalent character.*

In Silicon, **with a valence of 4**,

Z_{Si}=14 ($1S^2$ $2S^2$ $2P^6$ **$3S^2$ $3P^2$**)

4 covalent bonds must be formed

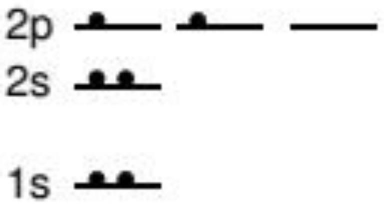
Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbital filled.

In crystalline silicon, perfect tetrahedra are formed, with angles of 109.5° between each covalent bond. If crystalline, we can only have a perfect tetrahedron for atoms with exactly the same electronegativity, i.e. Si atoms.

In SiO_2 glass, Si-O tetrahedra can be “close to perfect” as long range order is missing, in fact that bond is partly ionic /partly covalent

Covalent Bonding : Carbon Allotropes

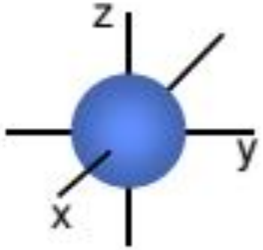
atomic orbitals for carbon:



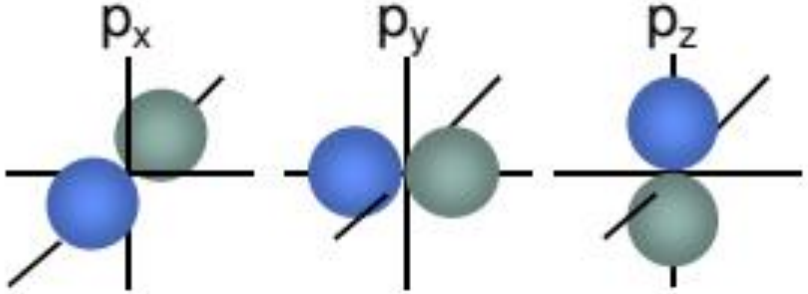
4 valence electrons but two different types orbitals. H's on CH_4 should be equivalent.

Atomic Orbitals

an s-orbital

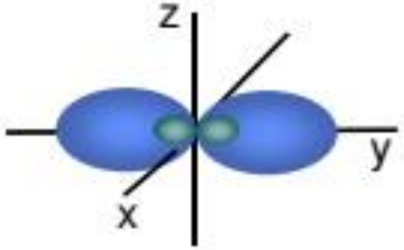


the three p orbitals

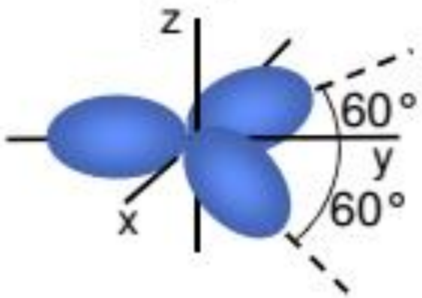


Hybridization

1s + 1p = sp-orbitals

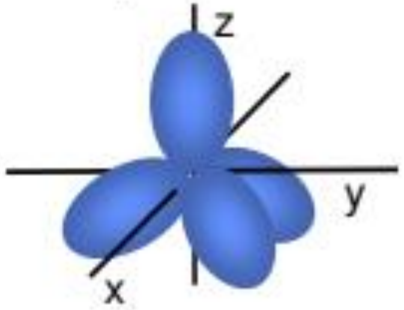


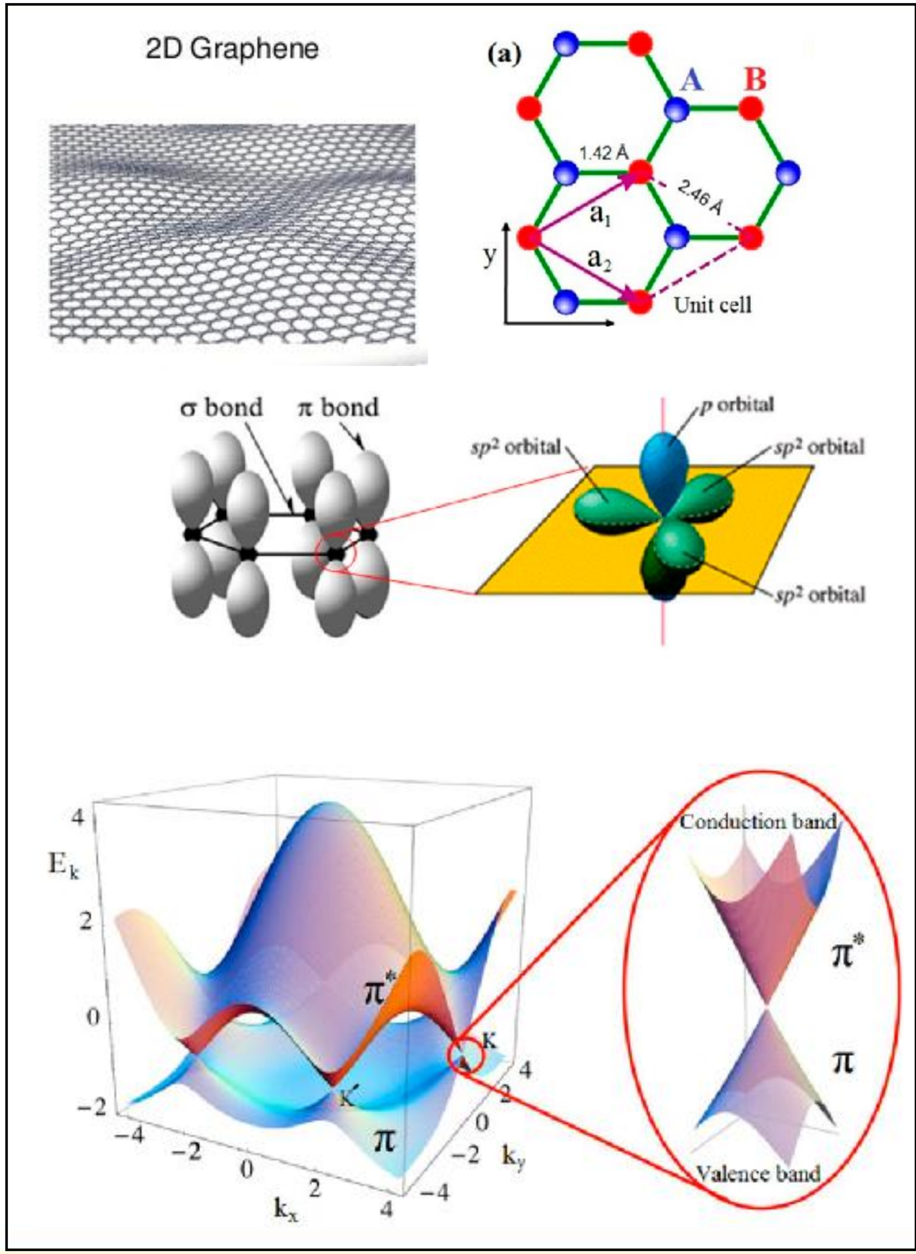
1s + 2p = sp^2-orbitals



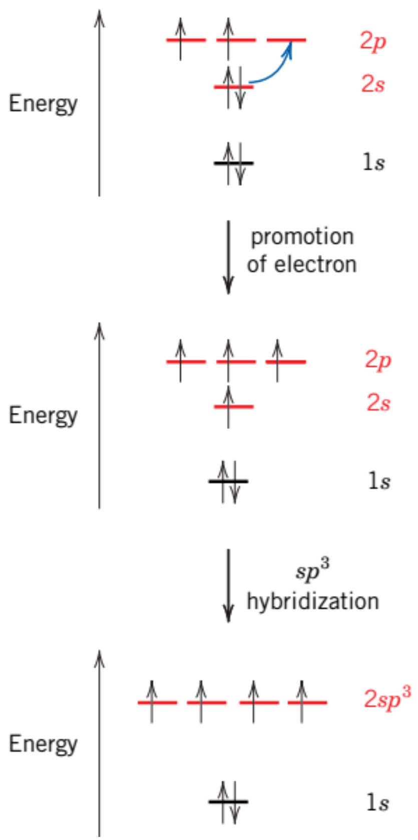
sp3 hybridization for C in CH_4

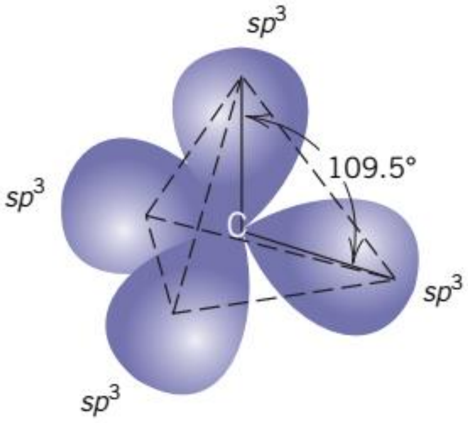
1s + 3p = sp^3-orbitals

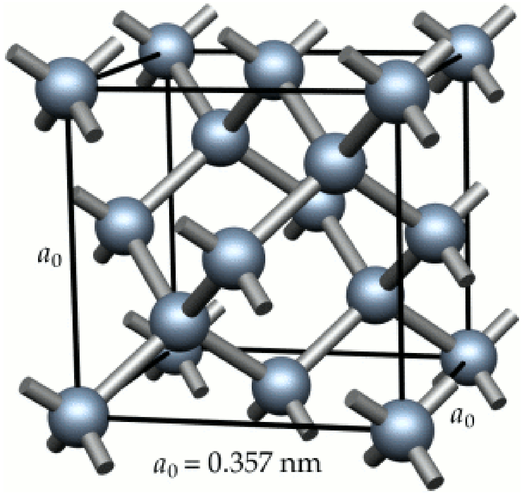




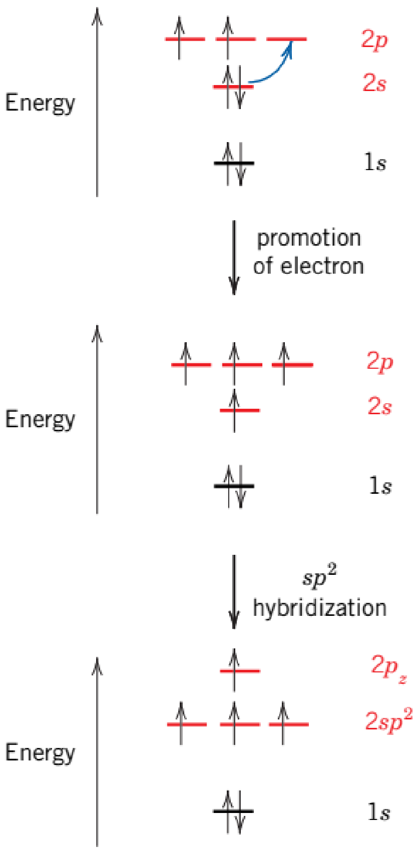
Covalent Bonding : Carbon Allotropes

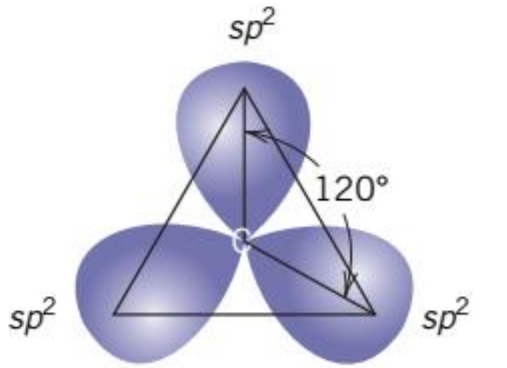


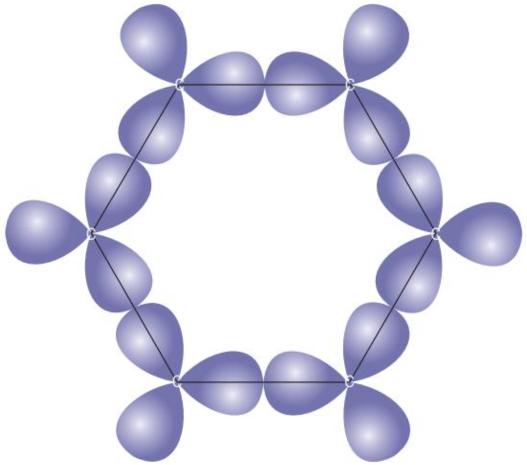




The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is bonded covalently to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.



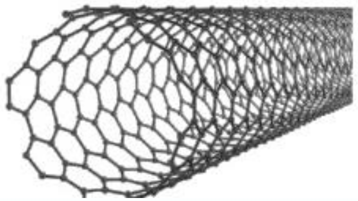


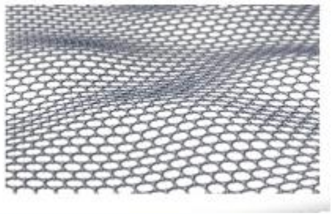


0D fullerene C60

1D CNT

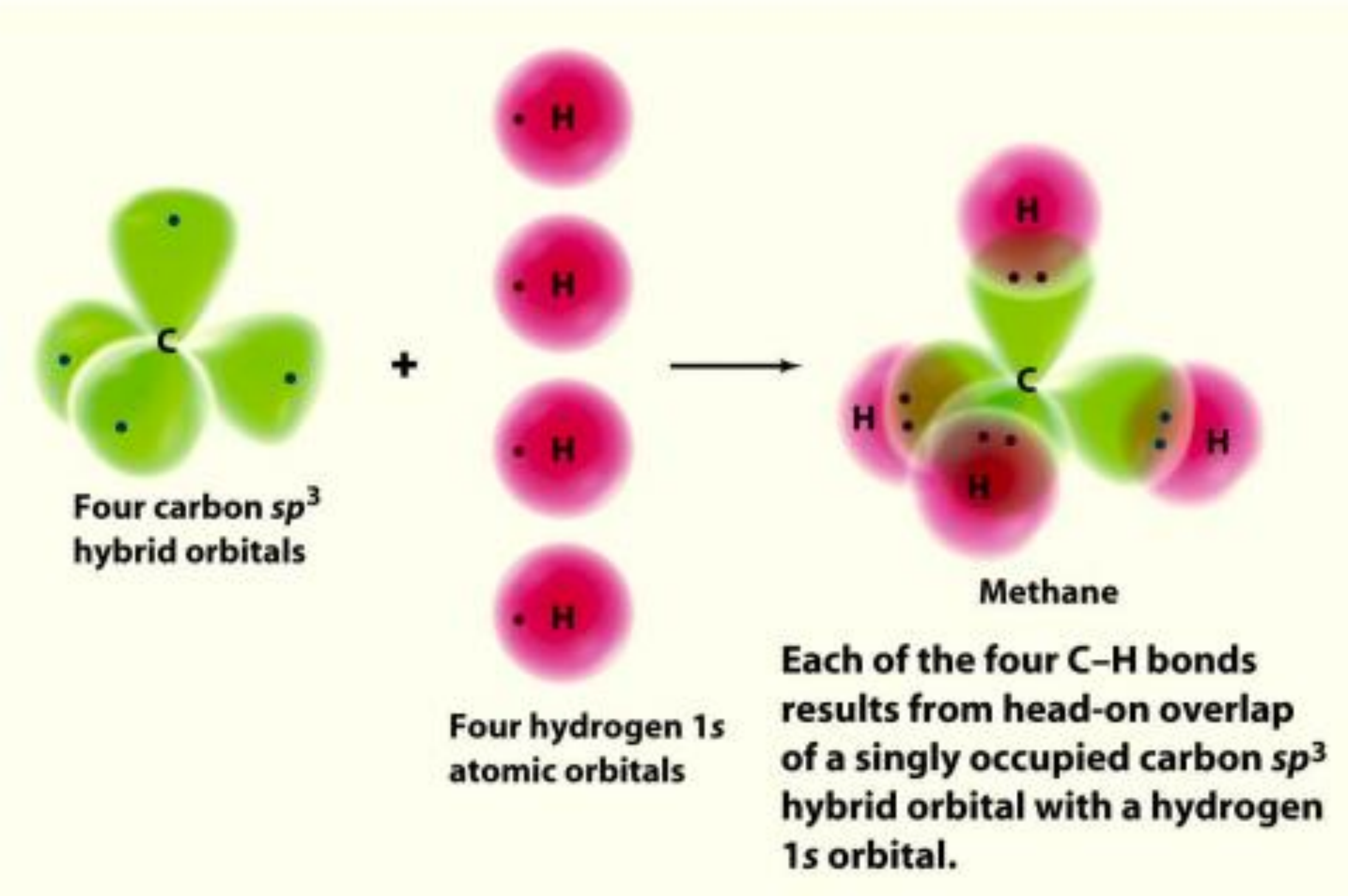
2D Graphene

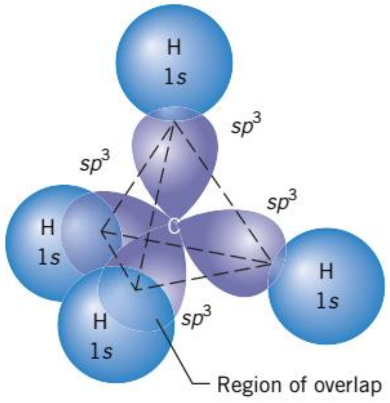




Covalent Bonding : CH4

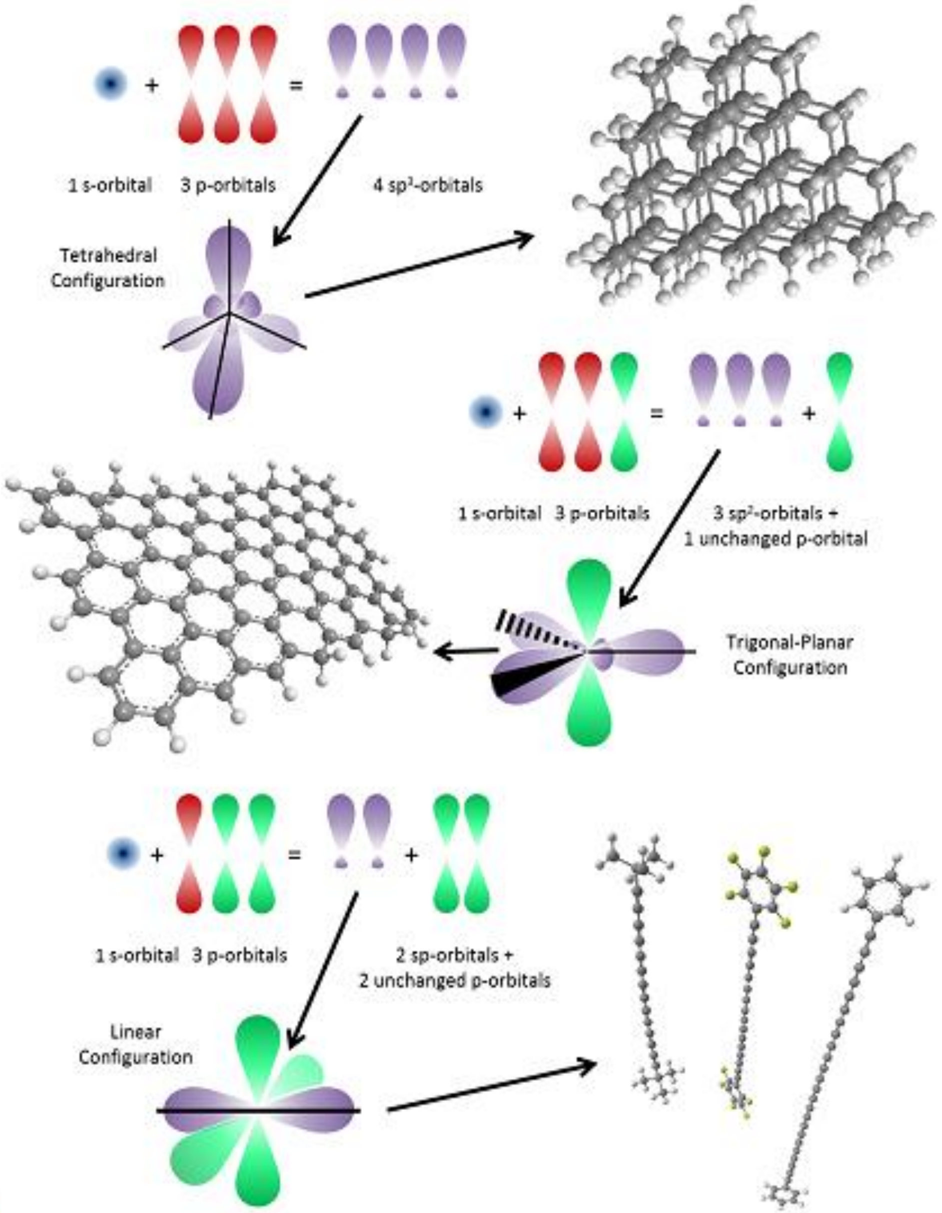
C: has 4 valence e, needs 4 more;   H: has 1 valence e, needs 1 more





Electronegativities are comparable, so electrons are shared.

Covalent Bonding : Carbon Allotropes



sp^3 Hybridisation
(Diamond, methane)

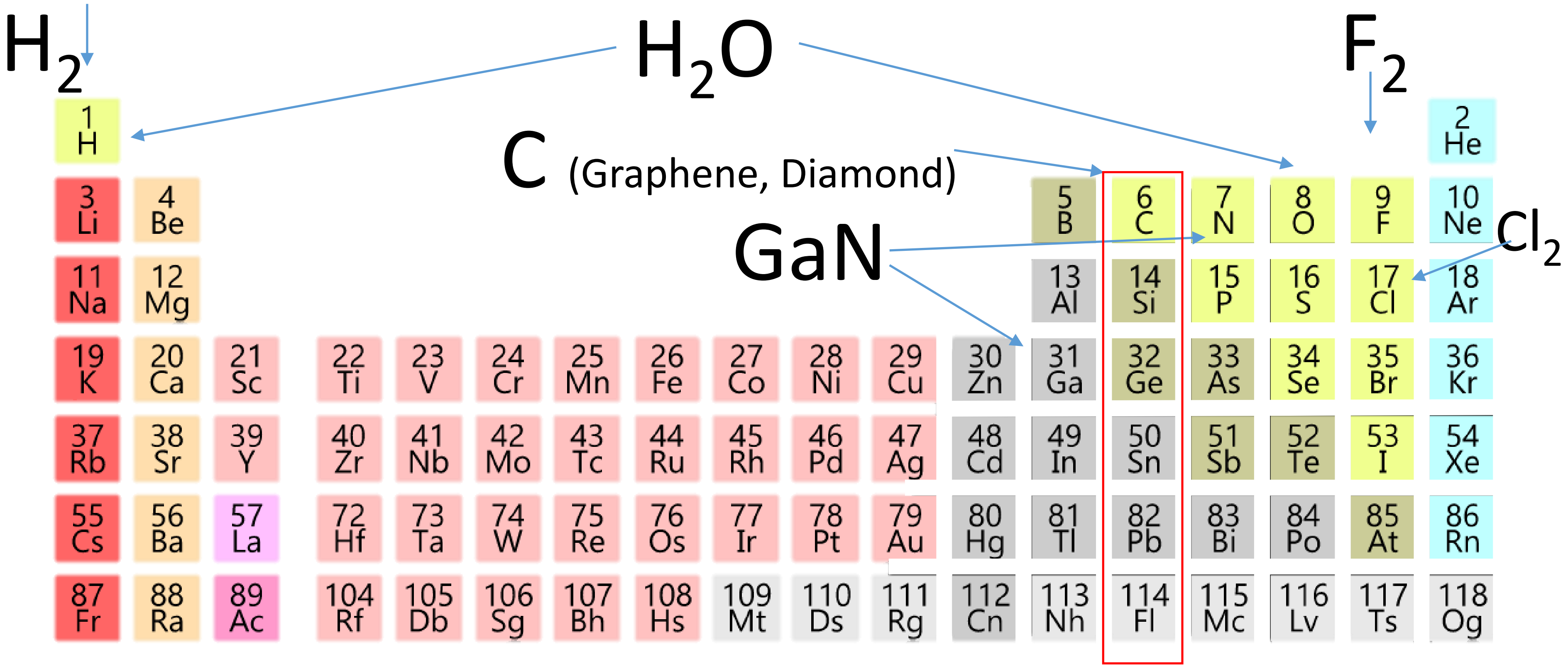
sp^2 Hybridisation
(graphene)

***sp* Hybridisation**

(heptayne, octayne and dodecayne linear acetylenic carbon, with various capping groups)

Covalent Bonding : Examples

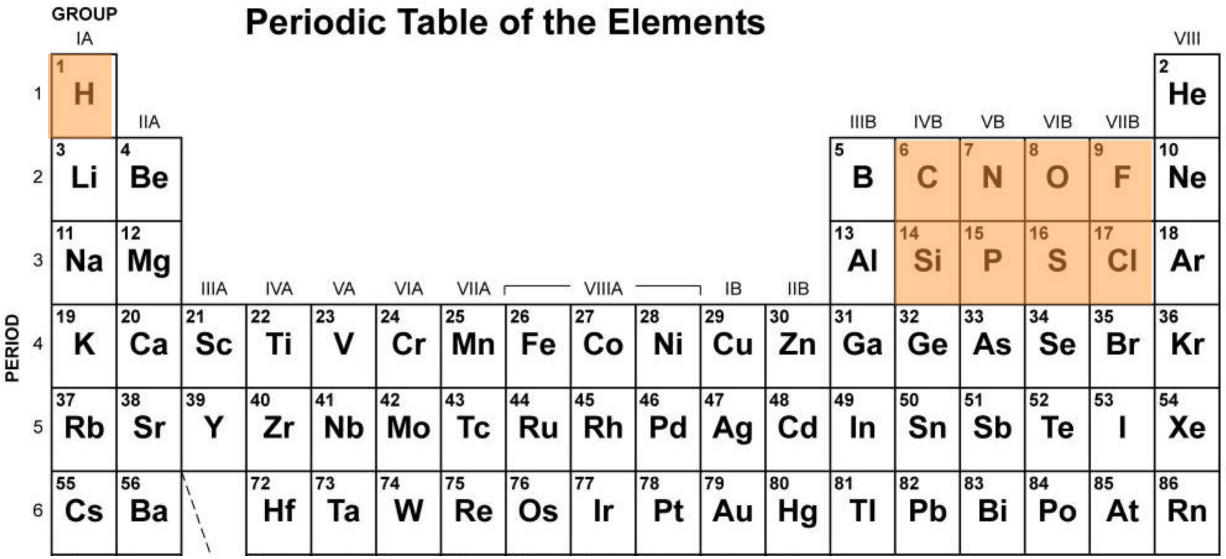
- Quantum mechanics prescribes directionality of the orbitals.
- Covalent bonds are highly directional.



- Molecules of nonmetals,
- Molecules containing metals & nonmetals,
- Elemental solids (right half side of Periodic Table)
- Compound solids (about column IV A), semiconductors, GaAs

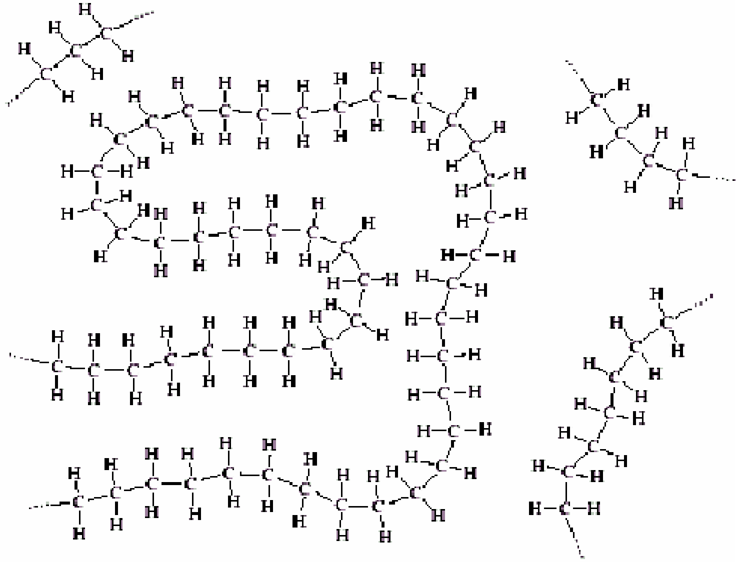
Covalent Bonding: Polymers

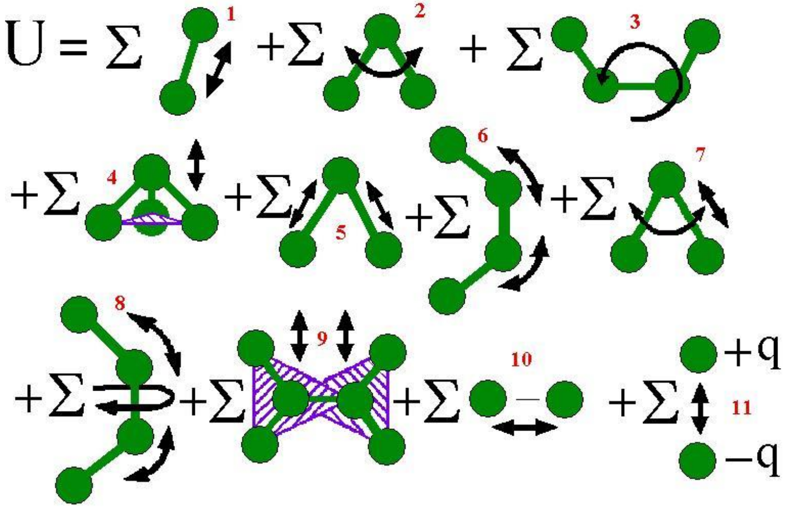
Polymers
- very large molecules
- low density, light weight materials
- maybe extremely flexible



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

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





% ionic character

The covalent bond is directional.

• The number of covalent bonds that is possible for a particular atom is determined by the number of valence electrons.
• Most bonds between two different types of atoms are somewhere in between ionic and covalent.

Very few compounds exhibit pure ionic or covalent bonding.

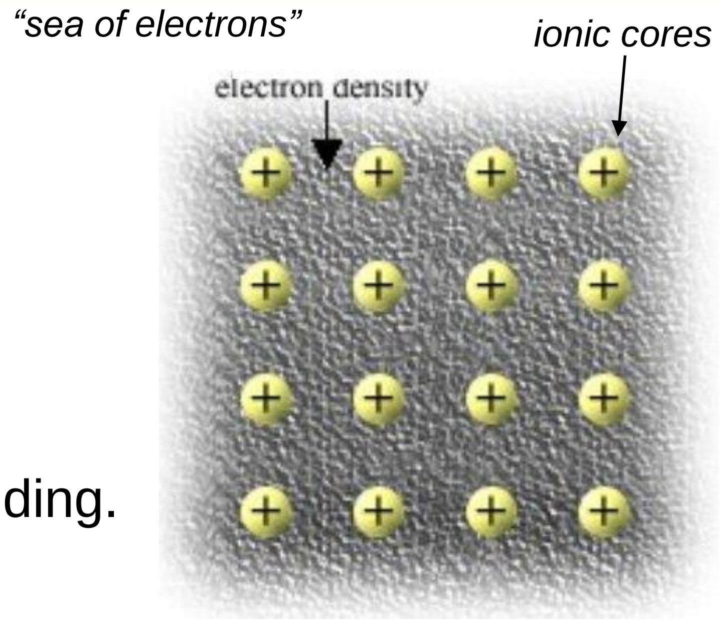
$$\% \text{ ionic character} = \{1 - \exp[-0.25(\chi_A - \chi_B)^2]\} \times 100$$

χ_j = electronegativity of atom j

Metallic Bonding

Valence electrons are detached from atoms, & spread in an **'electron sea'** that "glues" the positive ions together through the coulombic attraction.

The “bonds” do not “break” when atoms are rearranged – metals can experience a significant degree of plastic deformation.



Primary bond for metals and their alloys.

- Large atomic radius and small IP will more likely lead to metallic bonding.

Metallic bonding is found in the periodic table for Group IA and IIA elements.

Examples : Cu, Al, Au, Ag, etc.

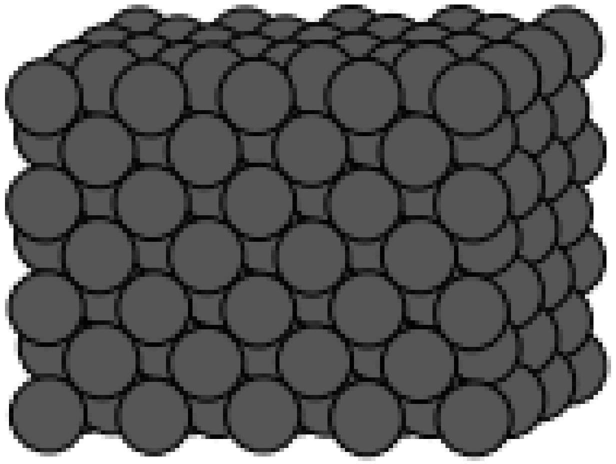
Transition metals (Fe, Ni, etc.) form mixed bonds that are comprising of metallic bonds and covalent bonds involving their **3d-electrons**. As a result the transition metals are more brittle (less ductile) than Au or Cu.

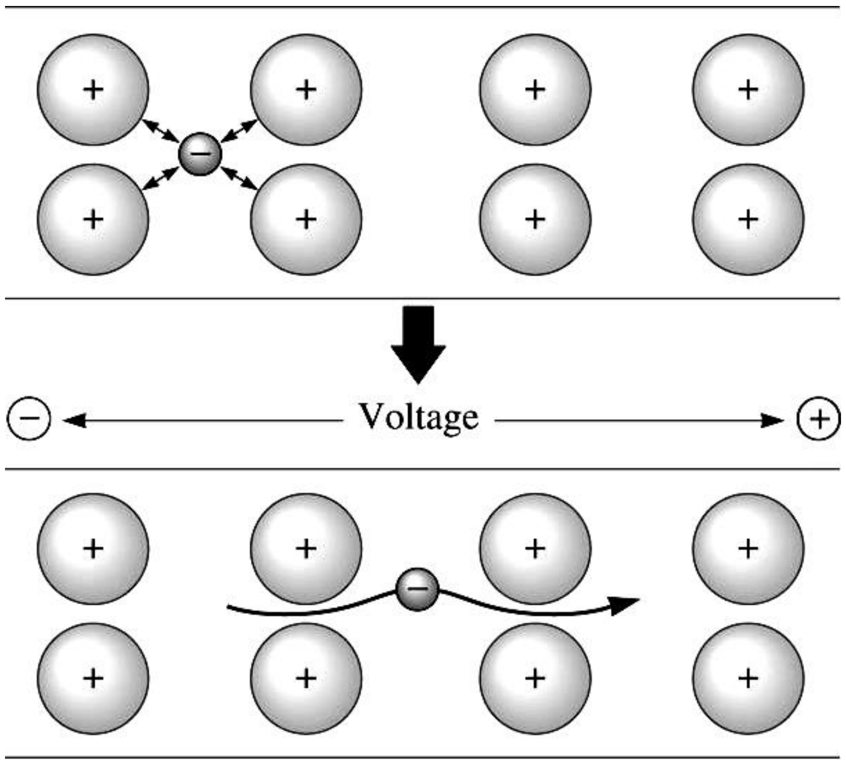
Periodic Table of the Elements

PERIOD	GROUP IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIII
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						

Metallic Bonding

As bond is nondirectional, coordination in a crystal is high





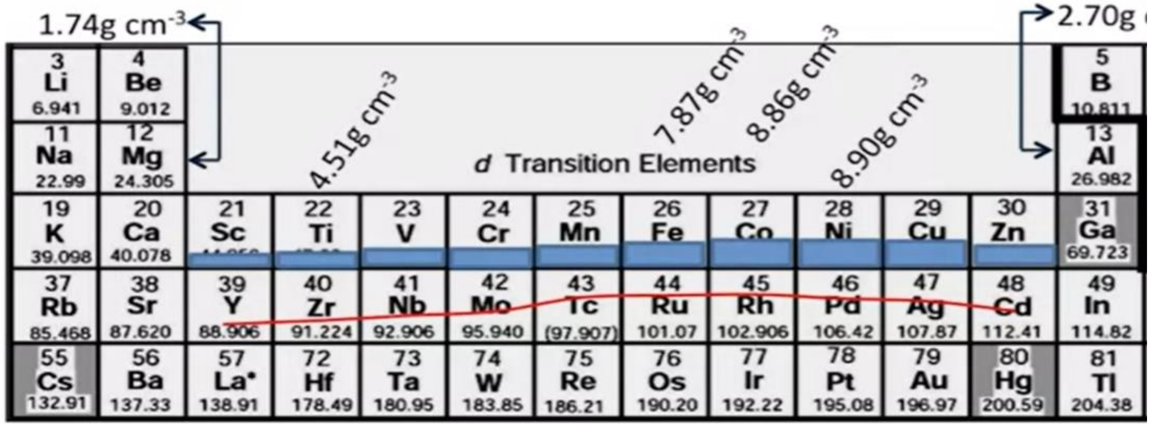
Electron delocalization is the origin of good electrical and thermal conductivities in metals.

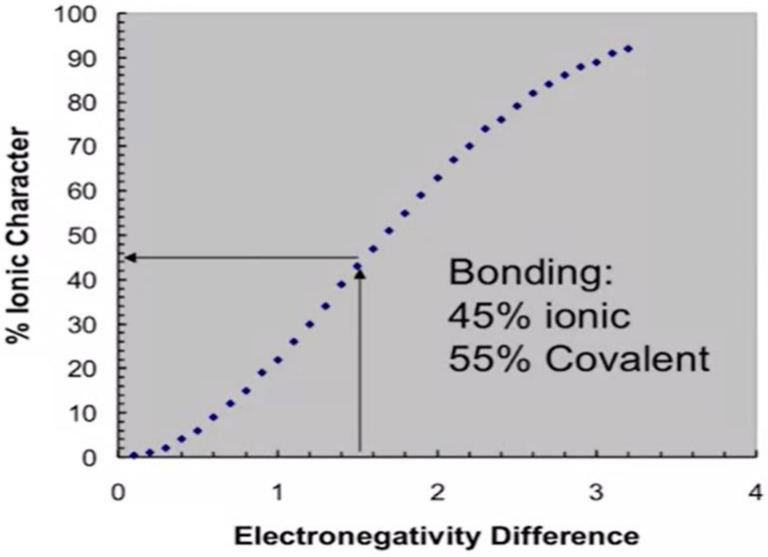
(Ionically and covalently bonded materials are typically electrical and thermal insulators, due to the absence of large numbers of free electrons)

When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current, if there are different metal atoms in between, i.e. point defects, or other crystal defects, the current is impeded, so conductivity will be high but strongly depended of perfection of crystal

Mixed Bonds

- Another important trend is an increase in the density metals toward a maximum in the middle of the row.





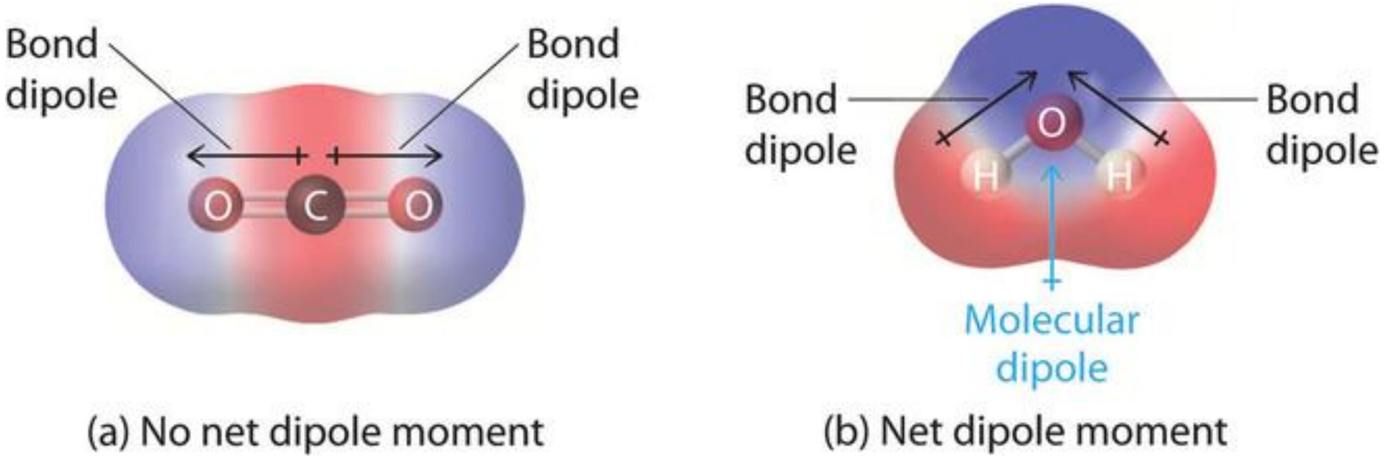
Electronegativities
Si = 1.9
O =3.44
ΔEN = 1.54

- The bonds in Group IA metals are predominately metallic, however, moving across the periodic table to the right, increases the valence and the covalent character of the bond.
- When some metals are mixed, they form intermetallic compounds with characteristic metal atom ratios, A_xB_y. Examples include: AlLi (Al_3Li), Ni_3Al, Al_3V, AlSb, CuZn, Ti_3Al and Mg_2Si. Depending upon the ΔEN, they are either a mixture of metallic/covalent or metallic/ionic. These materials are often brittle but are stable at high temperatures.

Secondary Bonding / van der Waals bonding

Secondary = van der Waals = physical bonding results from interaction of atomic or molecular dipoles and is weak, ~0.1 eV/atom or ~10 kJ/mol

(opposite to chemical bonding that involves e^- transfer)



Dipole moment (μ): Charge value x Distance between the +ve & -ve charges

$$\mu = qd$$

Classification of Secondary Bonding

- **Dipole-dipole bonds** (polar molecules - H_2O, HCl...)
- **H- bonds**
- **Polar molecule-induced dipole bonds** (a polar molecule induces a dipole in a nearby nonpolar atom/molecule)
- **Fluctuating Induced Dipole** (inert gases, H_2, Cl_2…) (weakest)

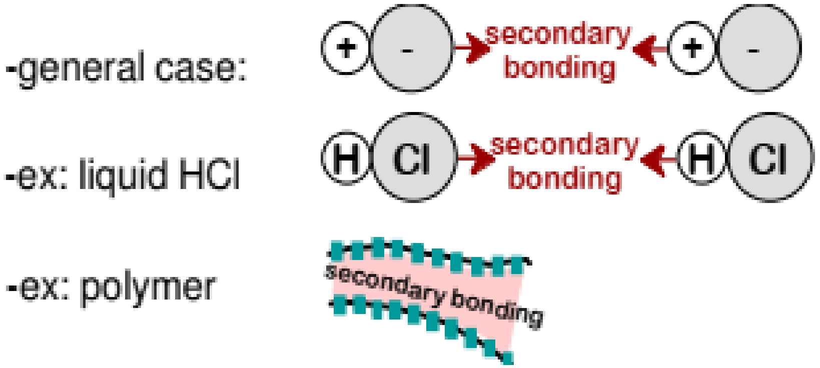
Geckos can stick to walls and ceilings because of van der Waals forces.

van der Waals Bonding

1) Dipole-dipole interaction: Secondary bond between molecules with permanent dipole moments

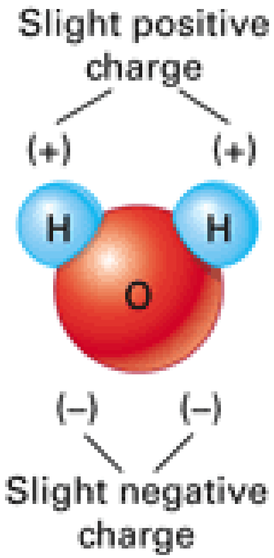
Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively charge regions (HF, HCl, H_2O).

Bonds between adjacent polar molecules – **permanent dipole bonds** – are the strongest among secondary bonds

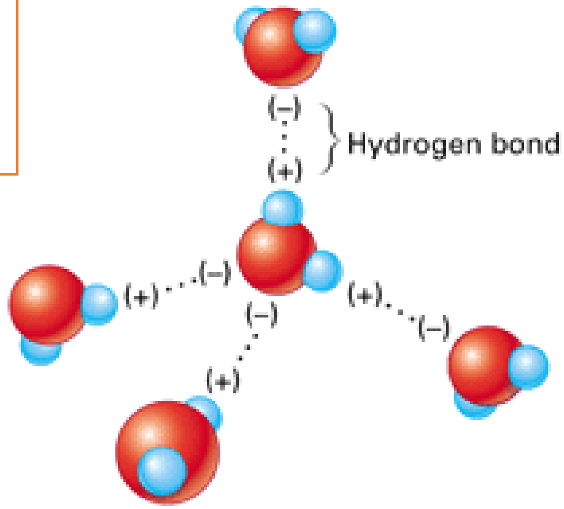


1.2) Hydrogen bonding *(special case of permanent dipole-dipole interaction between polar molecules*

Hydrogen bond among water molecule due to permanent dipole moment.
The H end of the molecule is positively charged and can bond to the negative side (O) of another H_2O molecule
(the O side of the H_2O dipole)

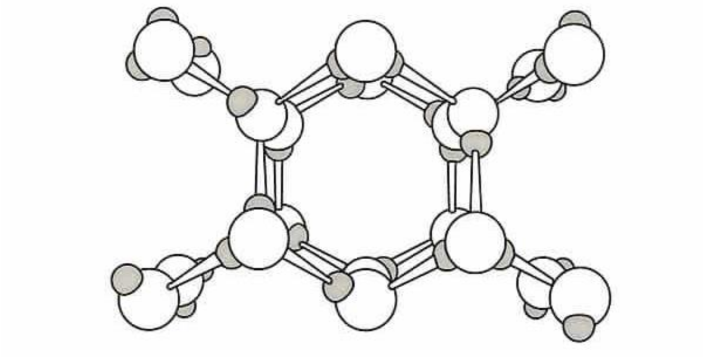


"Hydrogen bond" – secondary bond formed between two **permanent dipoles** in adjacent water molecules.

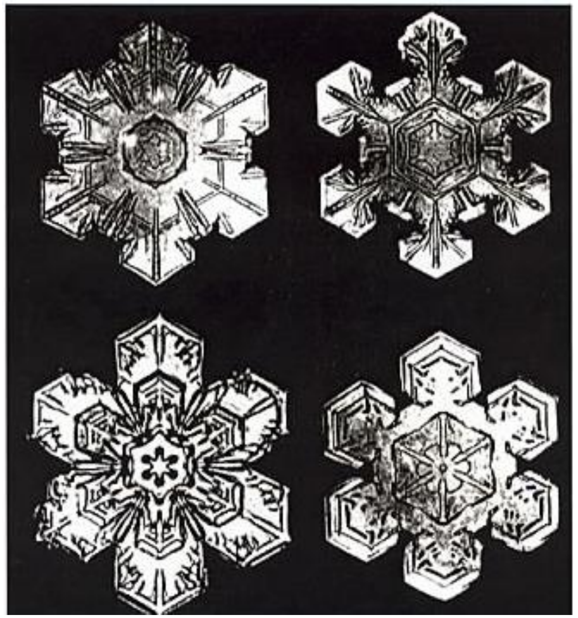


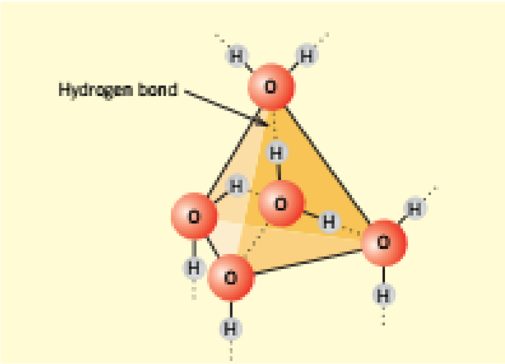
van der Waals Bonding

The Crystal Structures of Ice

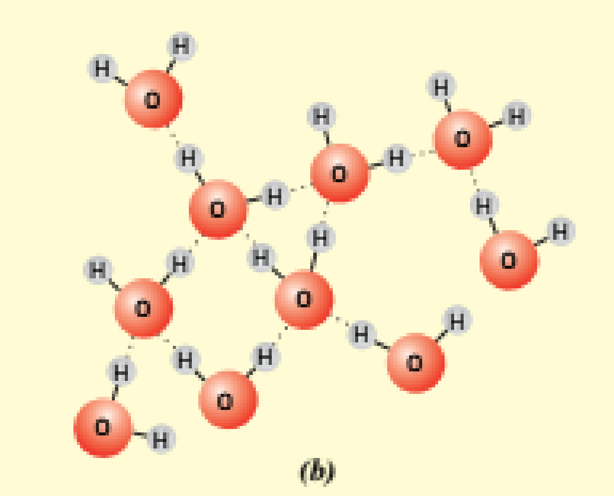


Hexagonal Symmetry of Ice Snowflakes





the molecules are not closely packed together

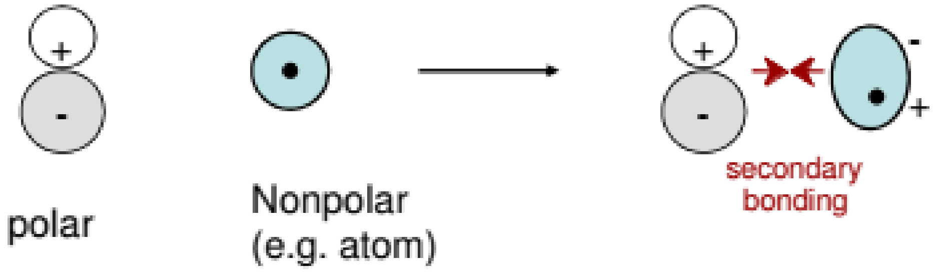


The arrangement of water (H_2O) molecules in (*a*) solid ice and (*b*) liquid water.

van der Waals Bonding

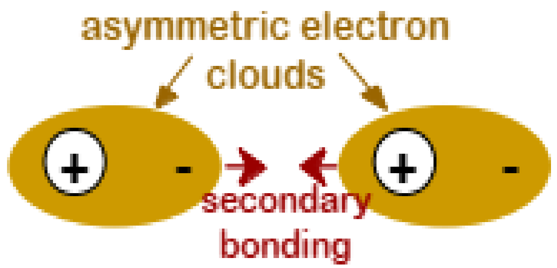
3) Polar molecule-induced dipole interaction

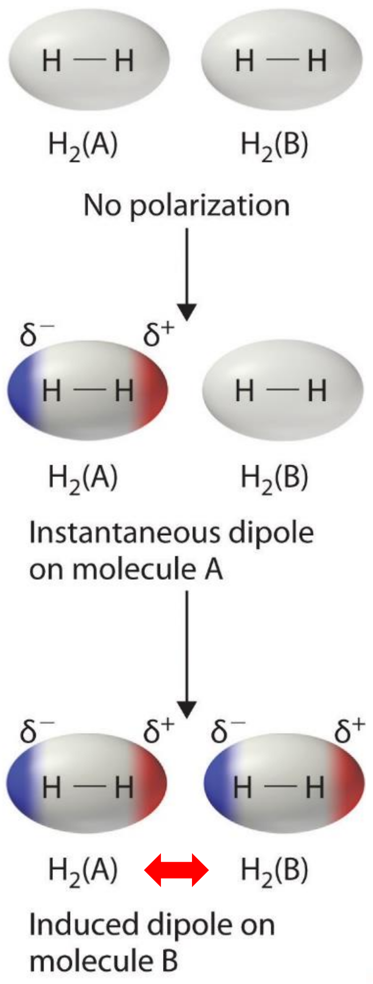
Polar molecules (with asymmetric arrangement of positively and negatively charged regions) can induce dipoles in adjacent nonpolar molecules and bond is formed due to the attraction between the permanent and induced dipoles



3) Fluctuating dipoles

Constant vibrational motion can cause distortions of electrical symmetry





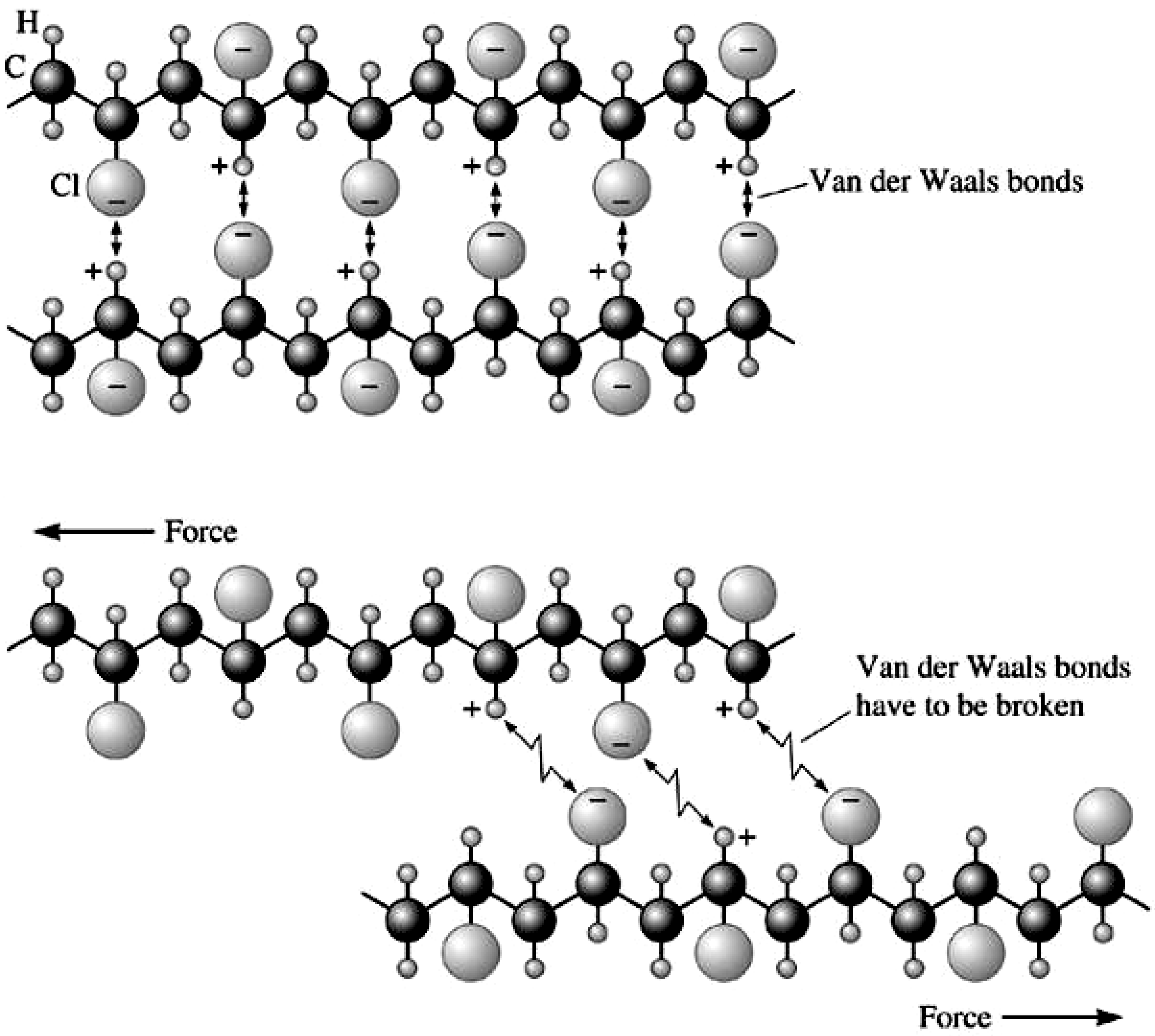
Even in electrically symmetric molecules/atoms, an electric dipole can be created by fluctuations of electron density distribution. Fluctuating electric field in one atom A is felt by the electrons of an adjacent atom, and induce a dipole momentum in this atom.

This bond due to fluctuating induced dipoles is the weakest (inert gases, H_2, Cl_2).

Ex: Liquid H_2

van der Waals Bonding

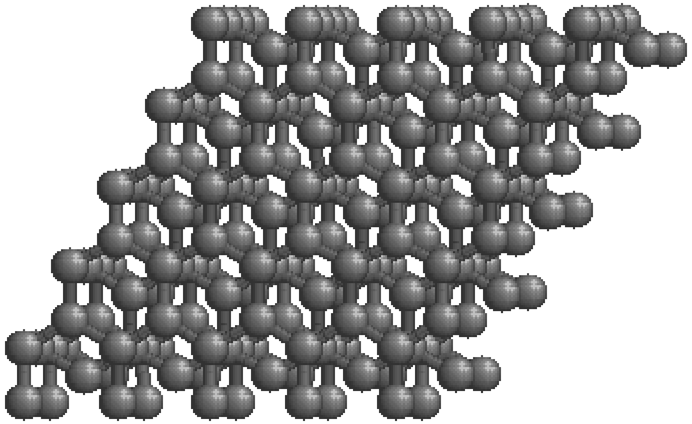
Polyvinyl chloride (PVC)

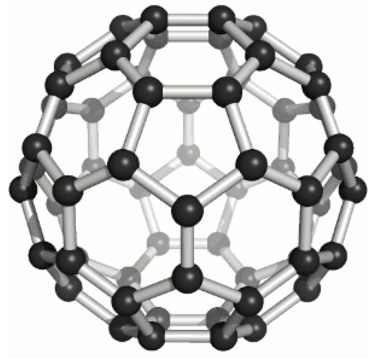


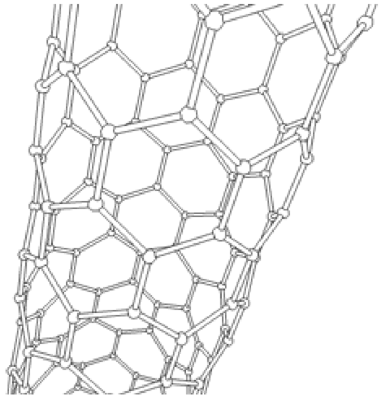
In PVC, the chlorine atoms attached to the polymer chain have a negative charge and the hydrogen atoms are positively charged. The chains are weakly bonded by van der Waals bonds.

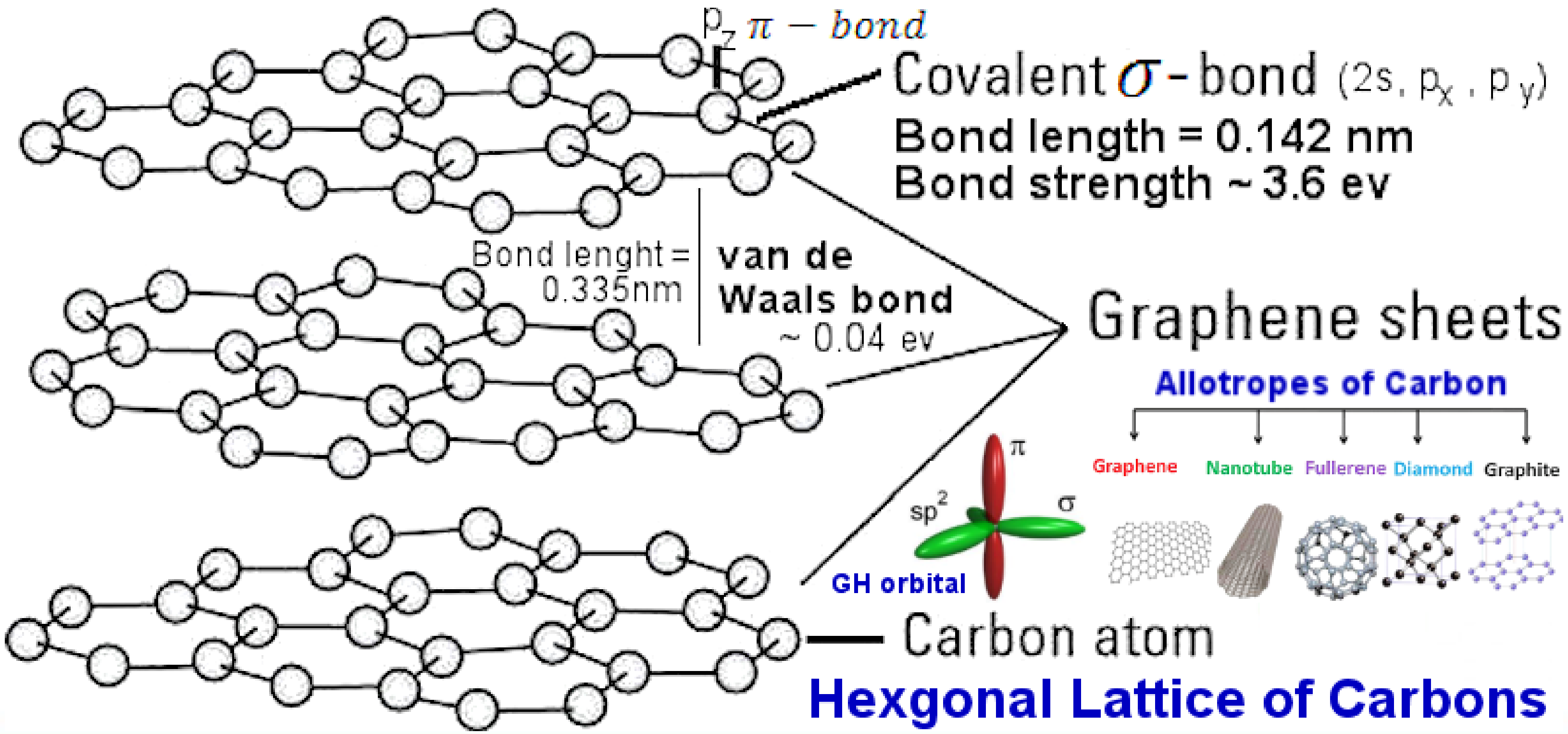
-This additional bonding makes PVC stiffer,

van der Waals Bonding



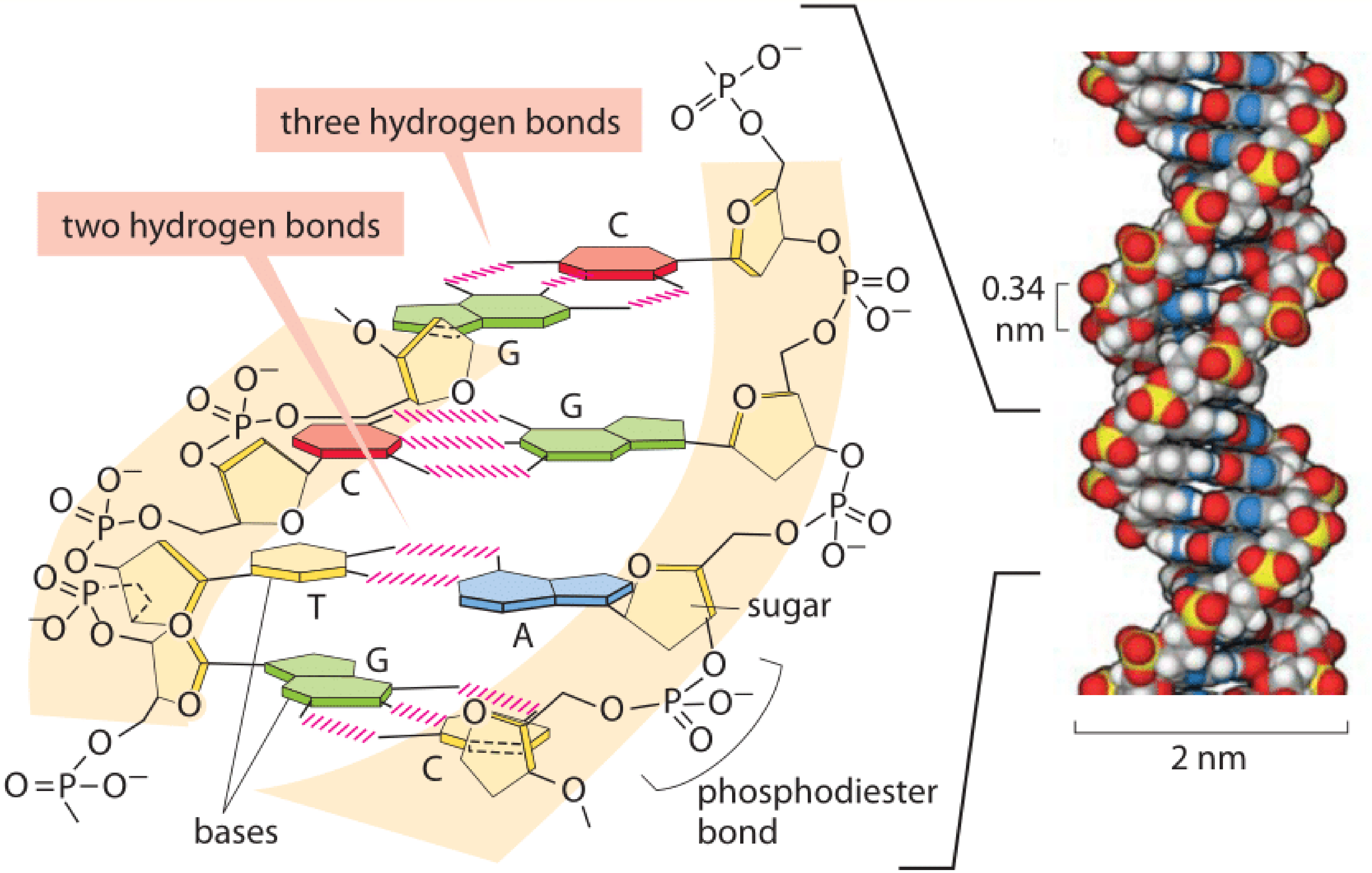




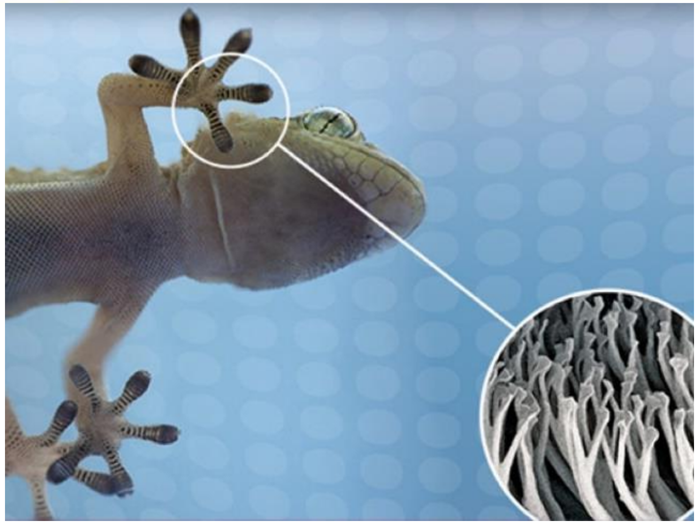


Hexgonal Lattice of Carbons

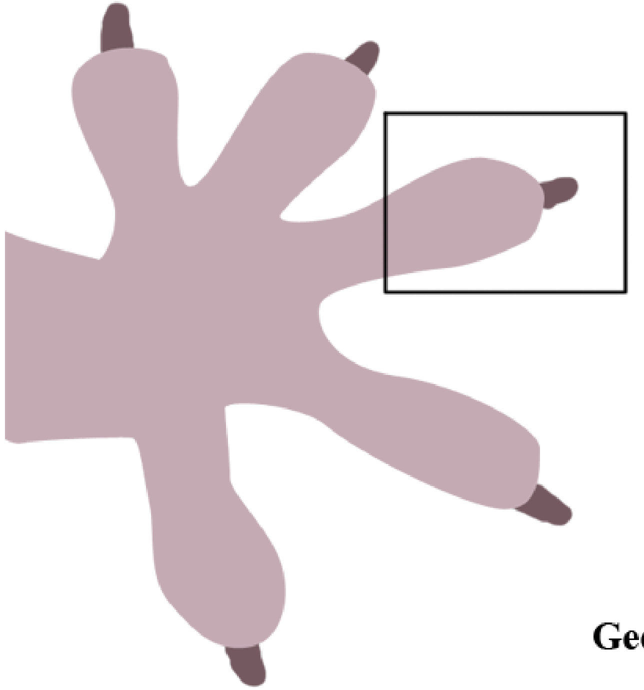
Bonding in DNA : Molecular bonding



van der Waals Bonding

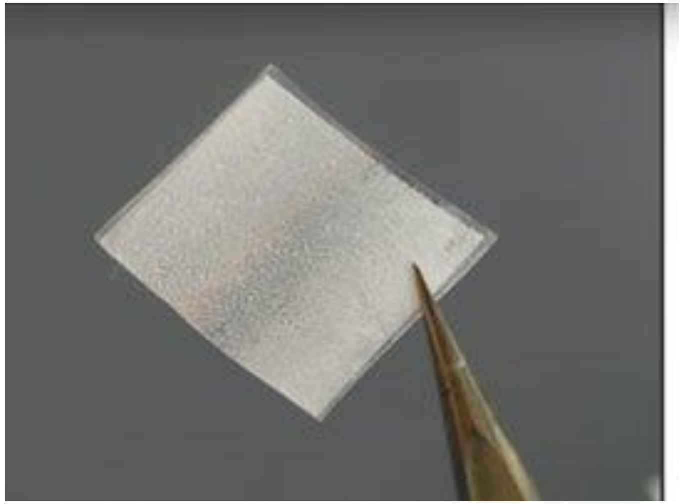


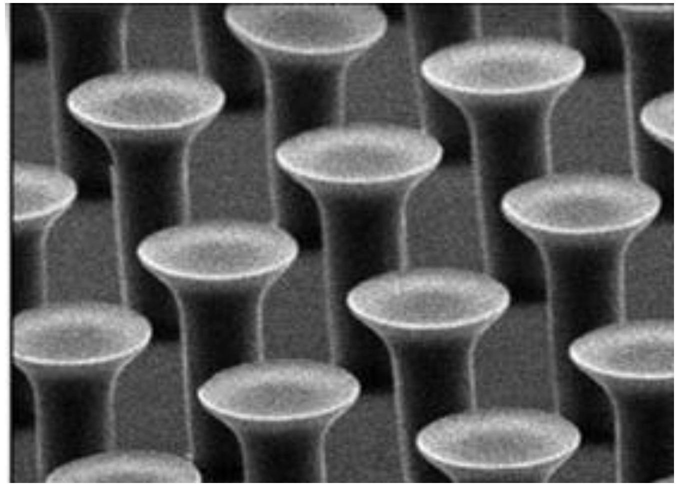
is that it is coated with millions of tiny hairs



Gecko Foot

Gecko-inspired adhesive tape finally scales to market

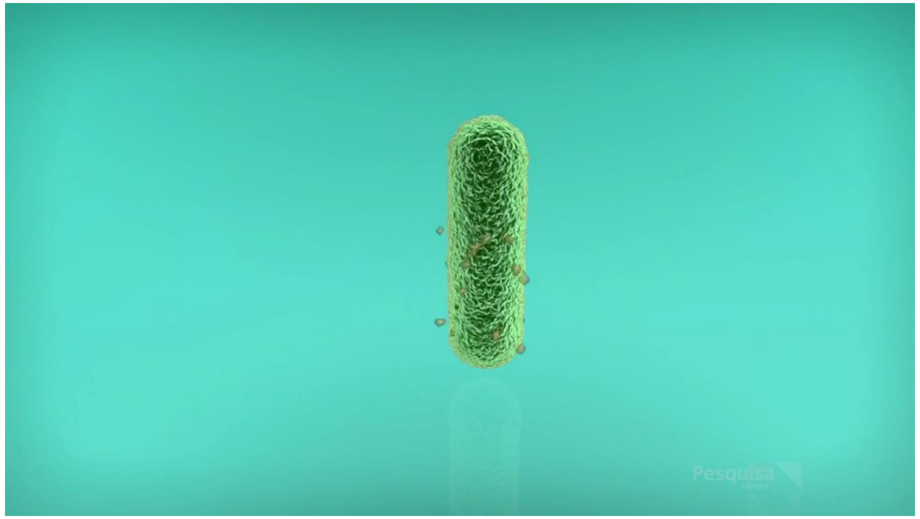


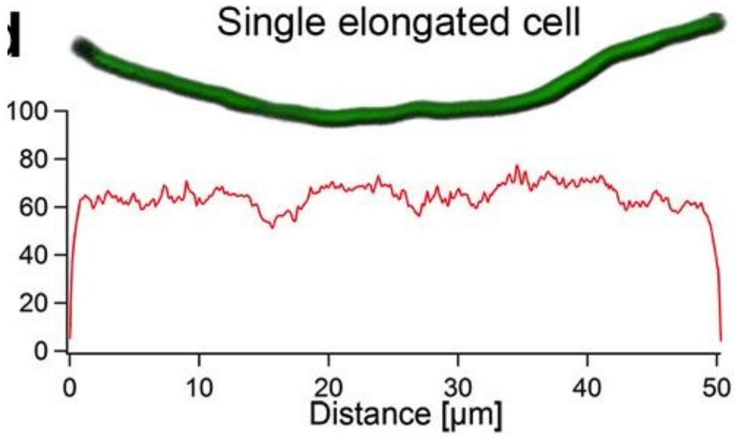


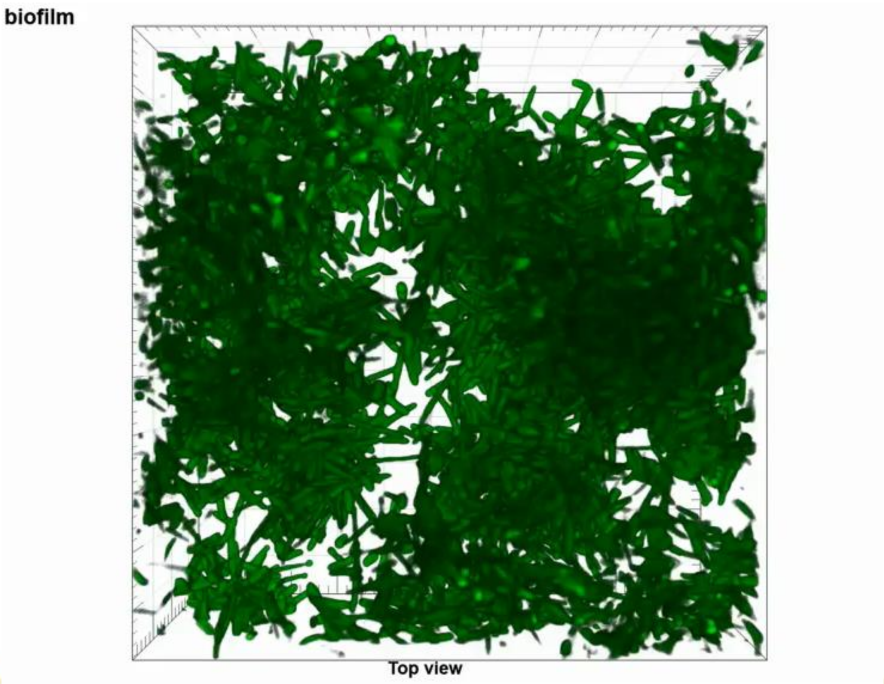
In the case of **gecko feet**, the spatulae are so small and get so close to the surface that an attractive van der Waals **force** of around 0.4 μN develops between a single spatula and a surface.

Bacterial Biofilm and Filamentation

R. Jansen, P. Sahoo et al. Scientific Reports 2015, 5, 9856

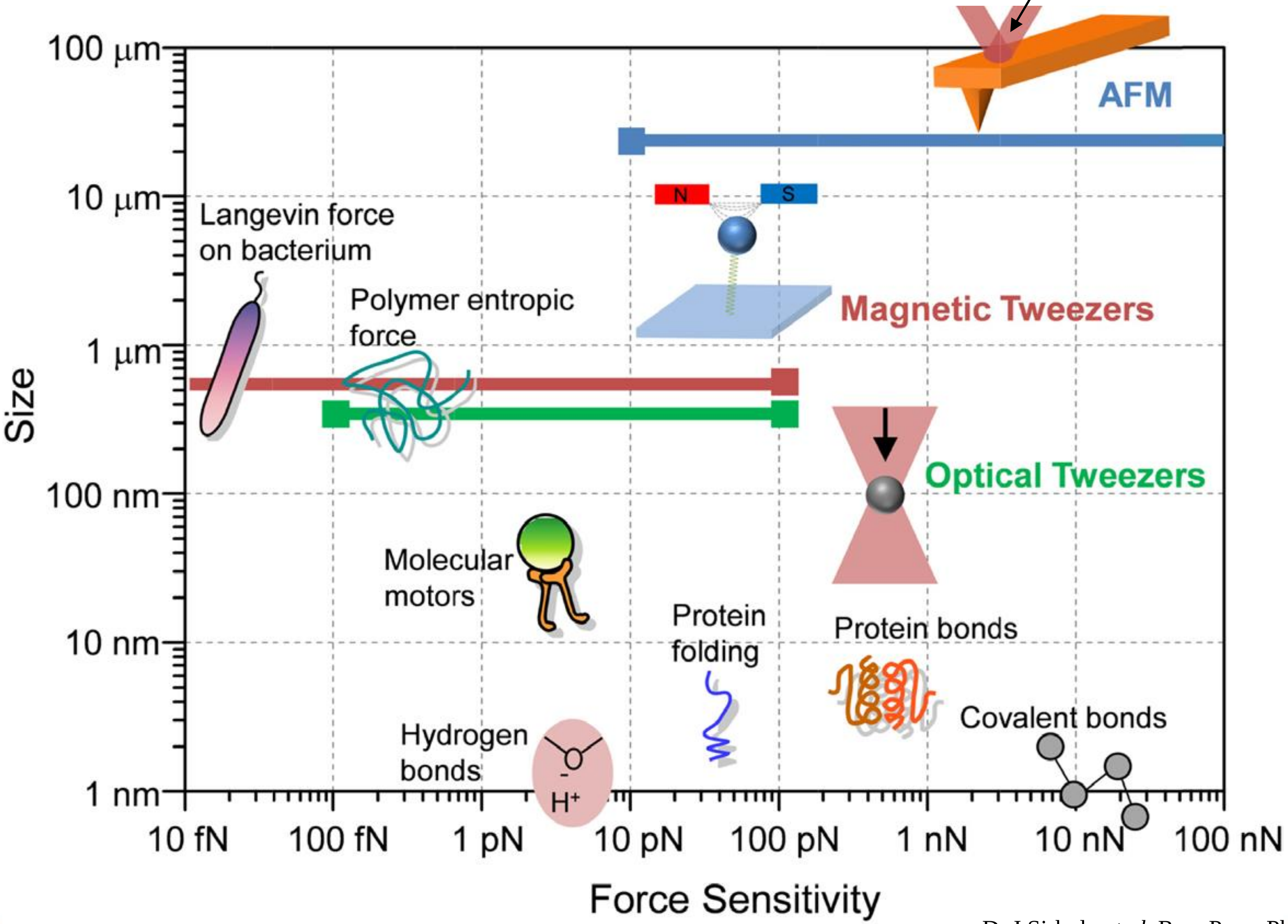






Technical Limitations: Force Sensitivity

Various molecular systems and nanomechanical transducers ~ Force sensitivity

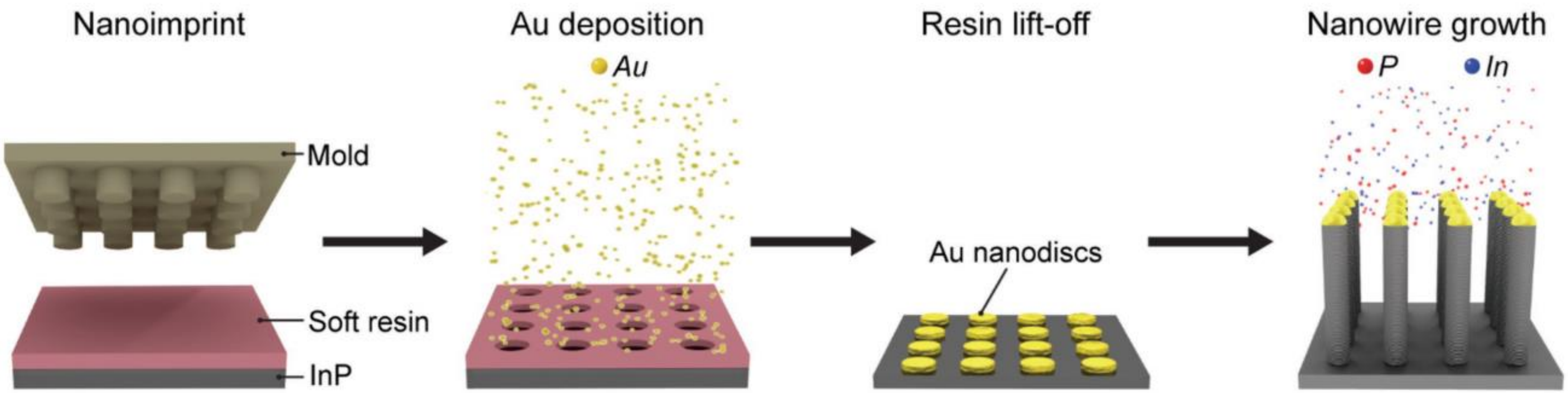


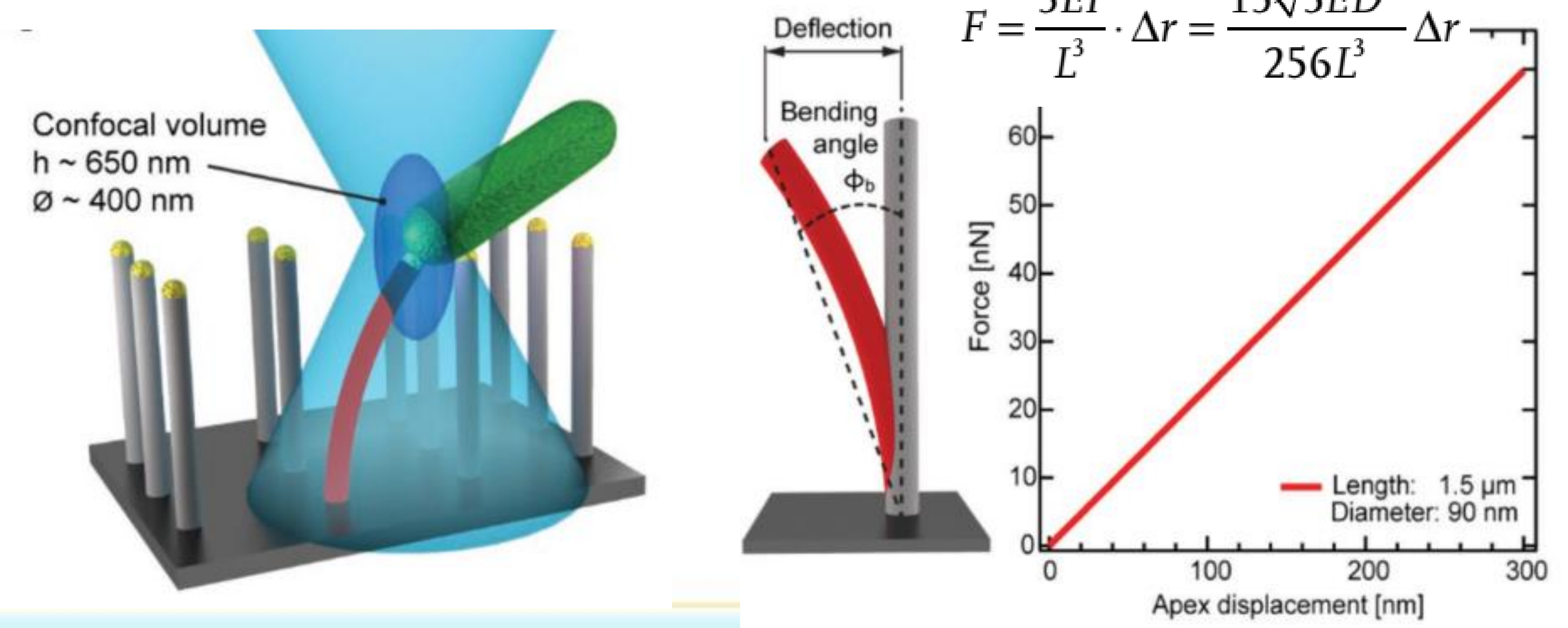
D. J Sirbuly *et al*. Rep. Prog. Phys. 2015, 78, 024101

Nanowire Arrays as Cell Force Sensor

P. Sahoo *et al.* Nano Letter **2016**, *16*, 4656

A. Silva, P. Sahoo *et al.* Small Methods **2018**, 1700411





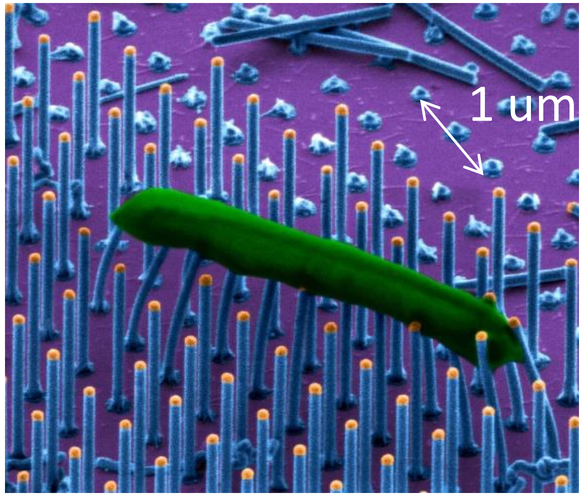
$$F = \frac{3EI}{L^3}\cdot\Delta r = \frac{15\sqrt{3}ED^4}{256L^3}\Delta r$$

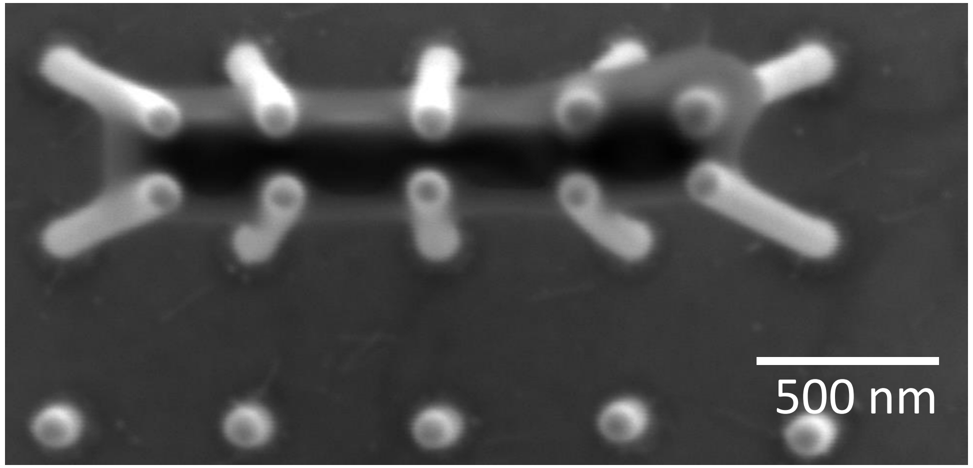
E= Young's Modulus
[~106.4 GPa for InP (111)]

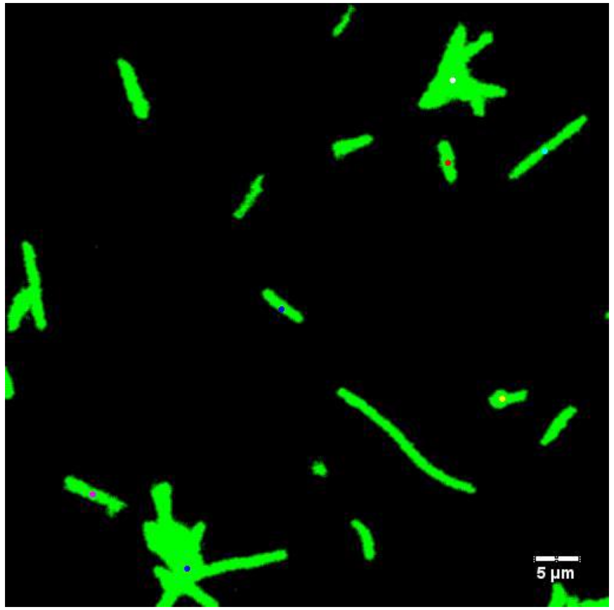
I = Second moment of inertia

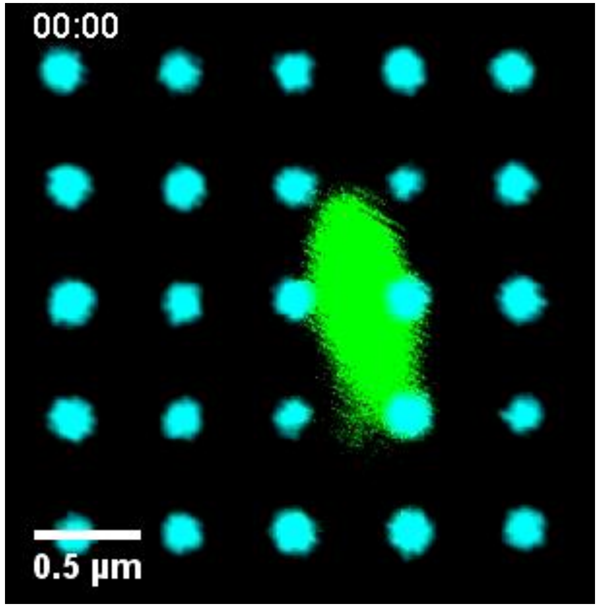
Bacterial Adhesion on Nanowire Arrays

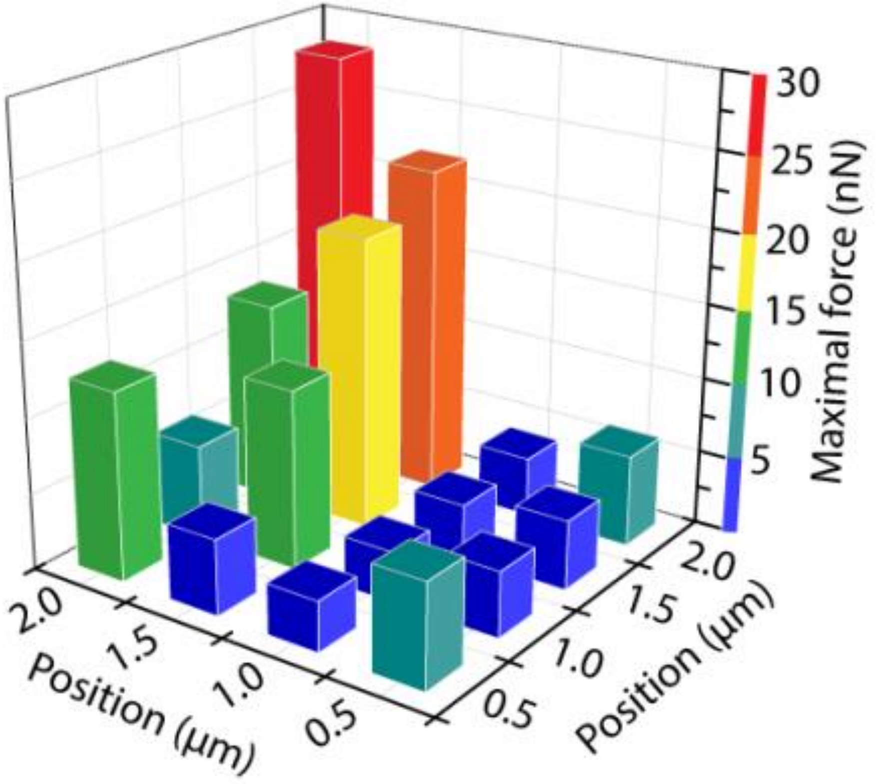
XF Bacteria on InP Nanowire Arrays





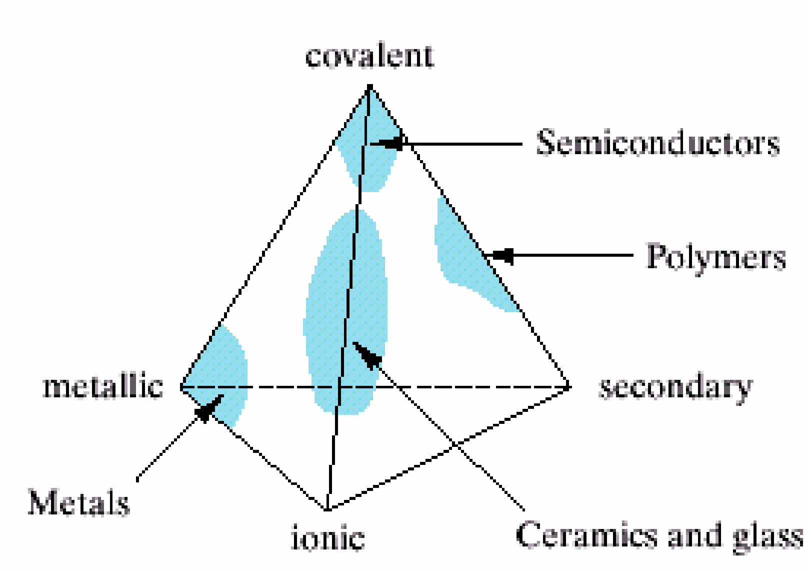


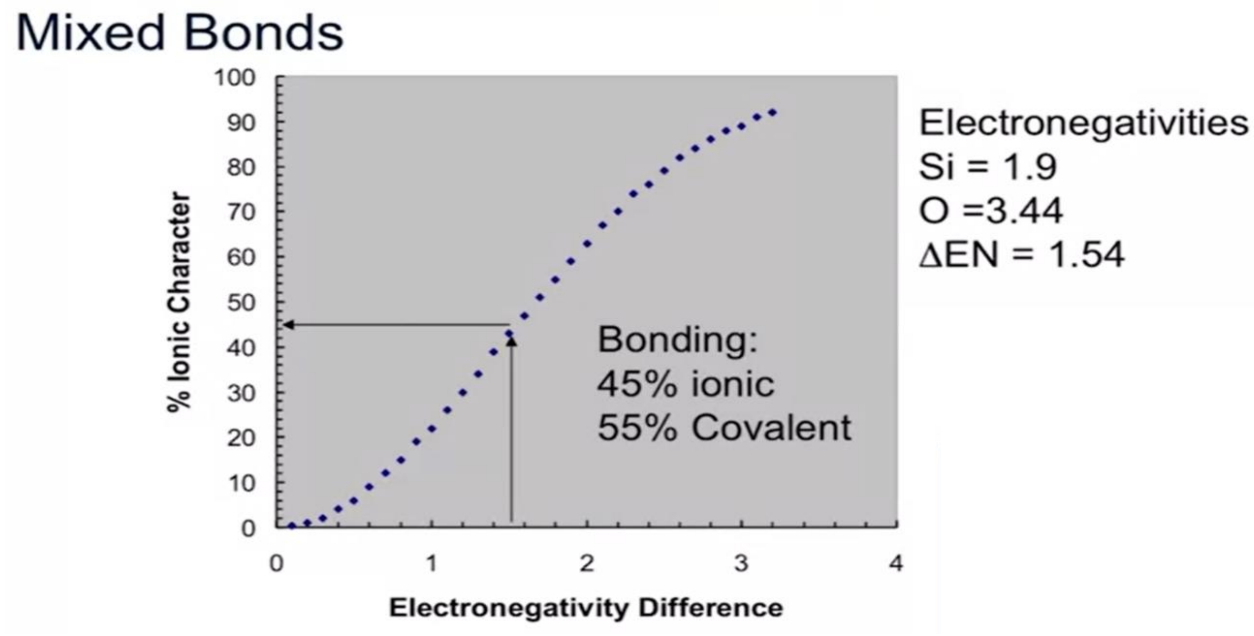




Bonding in real materials

In many materials more than one type of bonding is involved (ionic and covalent in ceramics, covalent and secondary in polymers, covalent and ionic in semiconductors.





Examples of bonding in Materials:

Metals: Metallic

Ceramics: Ionic / Covalent

Polymers: Covalent and Secondary

Semiconductors: Covalent or Covalent / Ionic

Correlation between bonding energy and melting temperature

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

Bonding Type	Substance	Bonding Energy kJ/mol (kcal/mol)	Bonding Energy eV/Atom, Ion, Molecule	Melting Temperature (°C)
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0

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

Example problem : Home work

Order the following semiconductors from most covalent to most ionic.

1) MoS_2, ZnS, GaN, CuCl
2) WSe_2, ZnS, ZnSe, ZnTe, ZnO