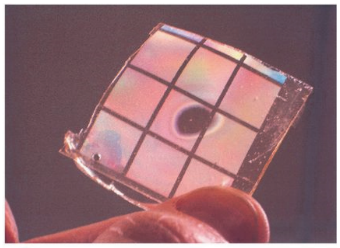
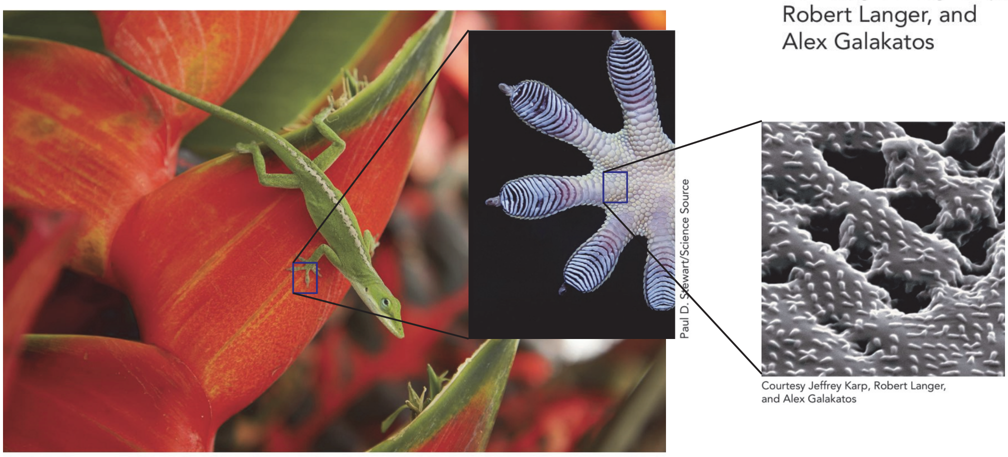
Chapter 2: Atomic Structure & Interatomic Bonding

ISSUES TO ADDRESS...

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



Courtesy Jeffrey Karp, Robert Langer, and Alex Galakatos



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Matter is made of atoms.

- **Richard P. Feynman**
  - May 11, 1918 – Feb. 15, 1988
  - American theoretical physicist
  - For his contributions to the development of quantum electrodynamics, Feynman, jointly with Julian Schwinger and Sin'ichirō Tomonaga, received the Nobel Prize in Physics in 1965.
  - The Feynman Lectures on Physics, Vol. I, II, and III. (Feynman, Leighton, Sands) (http://www.feynmanlectures.caltech.edu/)

- "If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or the atomic *fact*, or whatever you wish to call it) that *all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another*. In that one sentence, you will see, there is an *enormous* amount of information about the world, if just a little imagination and thinking are applied."

Atomic Structure (Freshman Chem.)

- **Atom –** electrons – 9.11×10^{-31} kg
  protons, neutrons } 1.67×10^{-27} kg
- **Atomic number (Z)** = the number of protons in nucleus of atom
  = the number of electrons in neutral species
- **Atomic mass (A)** = the sum of the masses of protons (Z) and neutrons (N) within the nucleus
- **Isotopes**: Atoms of some elements having two or more different atomic masses
- **Atomic weight**: the weighted average of the atomic masses of the atom's naturally occurring isotopes
- **Atomic mass unit (amu)** = 1/12 mass of ^{12}C (A= 12.00000)
- **Atomic weight** = weight of 6.022×10^{23} (Avogadro's number) molecules or atoms

1 amu/atom = 1 g/mol
C: 12.011, Fe: 55.85, H: 1.008, etc.

Electrons in Atoms

- **Some of the following properties (chemical, electrical, thermal, and optical properties) are determined by electronic structure.**
- **Quantum Mechanics**
- **Bohr Atomic Model**
  - Electrons are assumed to revolve around the atomics nucleus in discrete orbitals.
  - The energies of electrons are quantized.
- **Wave-Mechanical Model**
  - Electrons have wavelike and particulate properties.
  - Electrons are in orbitals defined by a probability.
  - Each orbital at discrete energy level is determined by quantum numbers.

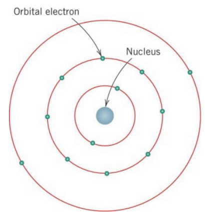
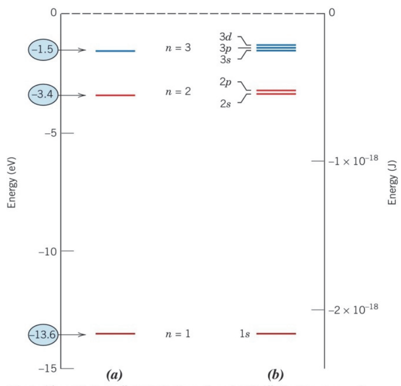


Fig. 2.1 Schematic representation of the Bohr atom.



Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, The Structure and Properties of Materials, Vol. I, Structure, p. 10. Copyright © 1964 by John Wiley & Sons, New York.

Fig. 2.2 Comparison of the Bohr hydrogen atom and the wave-mechanical hydrogen atom.

Quantum Numbers

- **Principal quantum number, *n***
  - Energy level-shell
  - Related to the size of an electron's orbital
- **Subsidiary quantum number, *l***
  - Designates the subshell
  - Related to the shape of an electron's orbital
- **Magnetic quantum number, m_l**
  - When a magnetic field is applied, these subshell states split.
- **The fourth quantum number, m_s**
  - Related to the spin moment

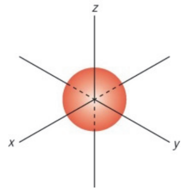


Fig. 2.4 Spherical shape of an s electron orbital.

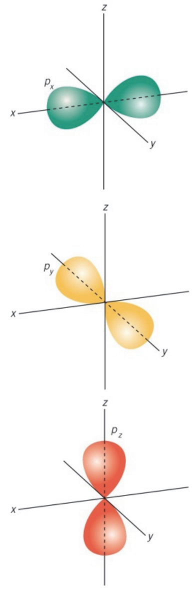
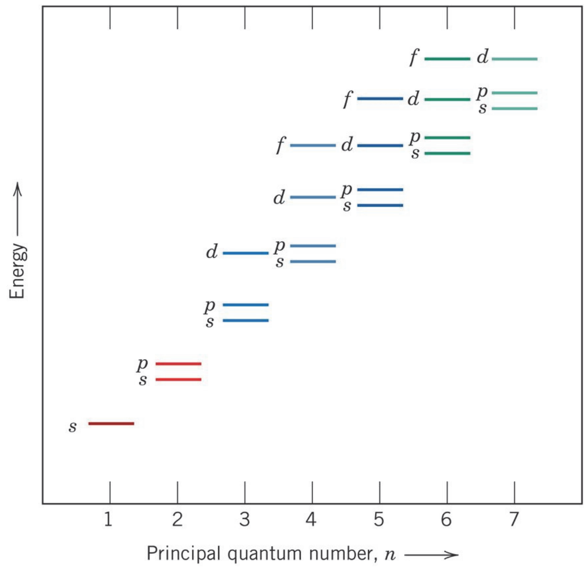


Fig. 2.5 Orientations and shapes of px, py, and pz electron orbitals.

Quantum Number	Designation
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)
m_l = magnetic	1, 3, 5, 7 ($-l$ to $+l$)
m_s = spin	½, -½

Electron Energy States



From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

Fig. 2.6 Schematic representation of the relative energies of the electrons for the various shells and subshells.

- Electrons have discrete energy states.
- Electrons tend to occupy lowest available energy state.
- The smaller the principal quantum number, the lower the energy level.
- Within each shell, the energy of a subshell level increases with the value of the l quantum number.

Electron Configurations

- **Pauli exclusion principle: each electron state can hold no more than two electrons that must have opposite spins.**

- **Ground state**

- **Electron configurations**
  - Valence electrons – those in unfilled shells
  - Filled shells more stable
  - Valence electrons are most available for bonding and tend to control the chemical properties
  - example: C (atomic number = 6)

    - $1s^2 2s^2 \boxed{2p^2}$

valence electrons

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)

Adapted from Table 2.2, *Callister & Rethwisch 9e.*

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

The Periodic Table

- Columns: Similar Valence Structure

Adapted from Fig. 2.8, *Callister & Rethwisch 9e.*

Key: 29 – Atomic number; Cu – Symbol; 63.55 – Atomic weight

Metal · Nonmetal · Intermediate

give up 1e⁻ · give up 2e⁻ · give up 3e⁻ · accept 2e⁻ · accept 1e⁻ · inert gases

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.33	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)								

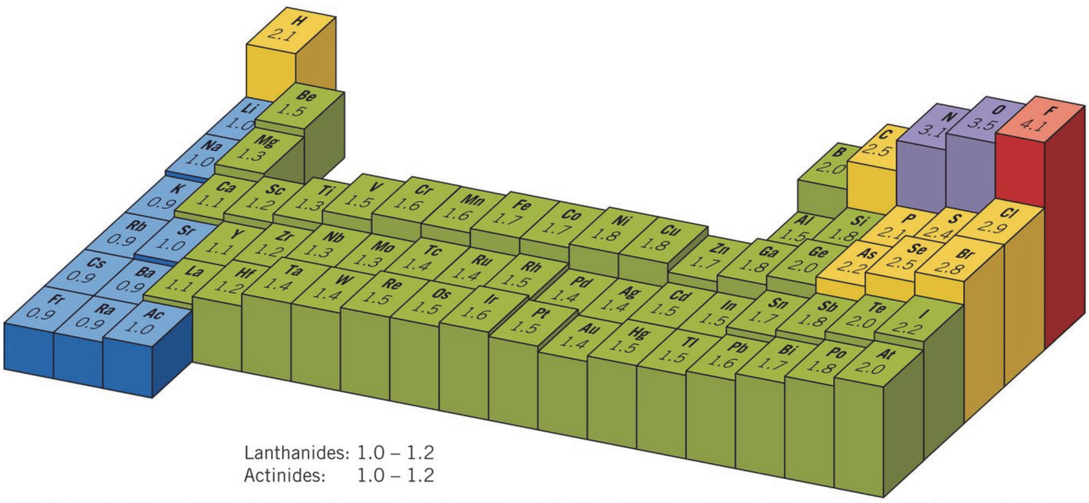
Alkali · Alkaline earth metals · Halogens · Inert gases

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

Electronegative elements: Readily acquire electrons to become - ions.

Electronegativity

- Ranges from 0.9 to 4.1,
- Large values: tendency to acquire electrons.



Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

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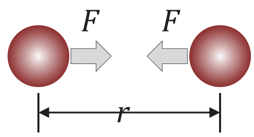
Smaller electronegativity

Larger electronegativity

2.5 Bonding Force and Energies



$$F_N(r) = F_A(r) + F_R(r)$$
$$F_N(r_0) = 0$$
$(\because r_0$ is the equilibrium position.)

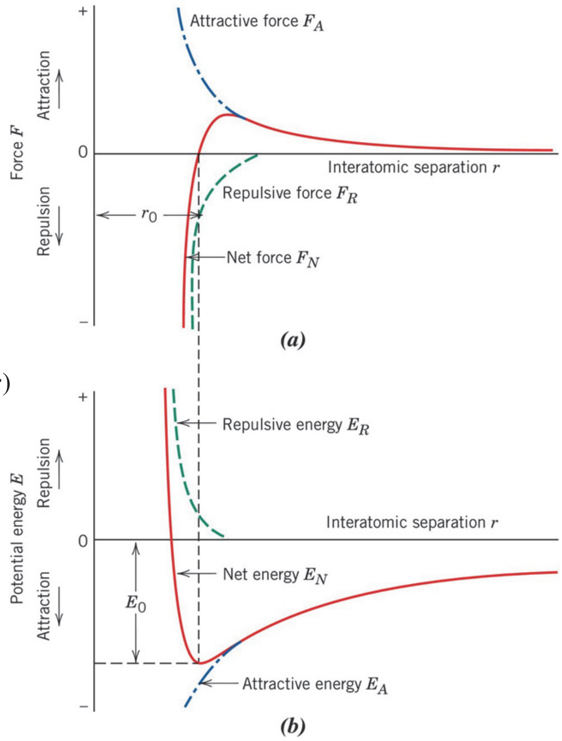
- **Force-potential energy relationship for two atoms**
  - Energy balance of attractive and repulsive terms

$$E_N(r) = \int_r^\infty F_N(\varsigma)d\varsigma = \int_r^\infty F_A(\varsigma)d\varsigma + \int_r^\infty F_R(\varsigma)d\varsigma = E_A(r) + E_R(r)$$

- **Bonding energy, E_0**
  - Minimum energy at the equilibrium position

$$E_0 = E_N(r_0)$$

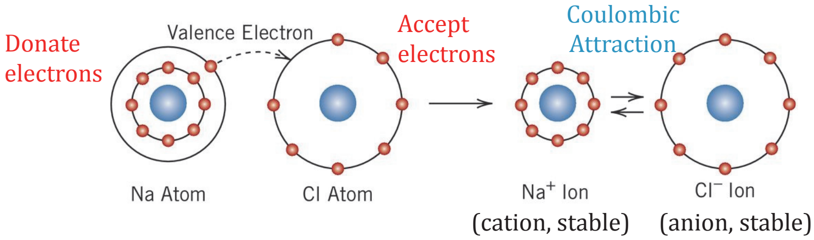
  - A number of material properties depend on the bonding energy, E0, the curve shape, and bonding type, e.g., melting temperature, mechanical stiffness (or modulus of elasticity), coefficient of thermal expansion, etc.



Adapted from Fig. 2.10(b), *Callister & Rethwisch 9e.*

2.6 Primary Interatomic Bonds: (1) Ionic Bonding

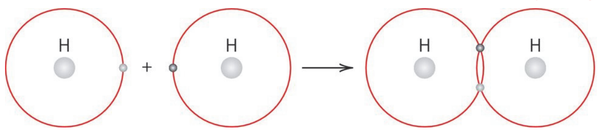
- **Ionic bonding is Always found in compounds composed of both metallic elements (+ ions) and nonmetallic elements (- ions).**
- **Ionic bonding requires electron transfer and thus large difference in electronegativity.**
- **Ex) NaCl**
  - Na (metal): Atomic Number=11, Electron Configuration=$1s^2 2s^2 2p^6 3s^1$, unstable
  - Cl (nonmetal): Atomic Number=17, Electron Configuration=$1s^2 2s^2 2p^6 3s^2 3p^5$, unstable



- **Attractive bonding force & energy: Coulombic** $E_A(r) = -\frac{A}{r},\ A = \frac{1}{4\pi\varepsilon_0}(|Z_1|e)(|Z_2|e)$
- **Repulsive energy:** $E_R(r) = \frac{B}{r^n}$
- **Ionic bonding is nondirectional (i.e., the magnitude of the bond is equal in all directions around an ion).**

(2) Covalent Bonding

- Similar electronegativity → share electrons
- Bonds determined by valence – s & p orbitals dominate bonding
- Example: H_2
  - Each H has 1 valence e-, and thus, needs 1 more.
  - Electronegativities are the same.



- Covalent bonding is directional.
- Examples: Cl_2 (Chlorine), F_2 (Fluorine), CH_4 (Methane), H_2O (Water), HNO_3 (Nitric Acid), HF (Hydrofluoric Acid), Diamond (Carbon), Si (Silicon), Ge (Germanium), GaAs (Gallium Arsenide), SiC (Silicon Carbide)
- Covalent bonds may be very strong or may be very weak.
- It is difficult to predict the mechanical properties of covalently bonded materials on the basis of their bonding characteristics.

Bond Hybridization in Carbon

- Carbon: $1s^2 2s^2 2p^2$
- Carbon can form sp^3 hybrid orbitals.
- Bonding hybrid orbitals are directional.
- For carbon, four sp^3 hybrid orbitals are directed symmetrically (tetrahedron).
- Diamond
  - Its carbon atoms are bonded to one another with sp^3 covalent hybrids.
  - Carbon-carbon bonds are very strong.
  - High melting temp. and ultrahigh hardness (the hardest of all materials).
- Polymers
  - Long chains of carbon atoms that are also bonded together using sp^3 tetrahedral bonds.
  - These chains form a zigzag structure because of this 109.5∘ interbonding angle.

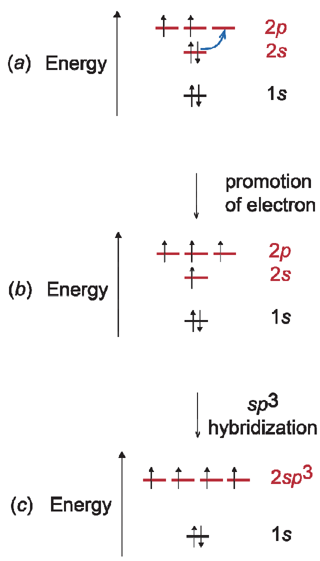
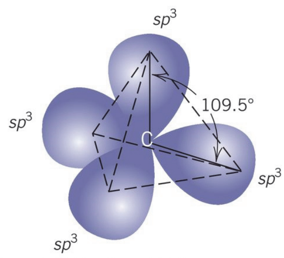


Fig. 2.13, *Callister & Rethwisch 9e.*



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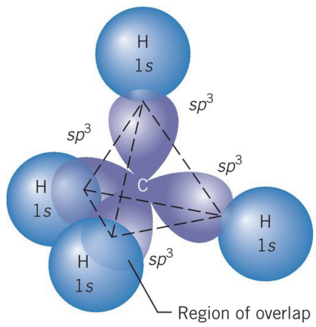

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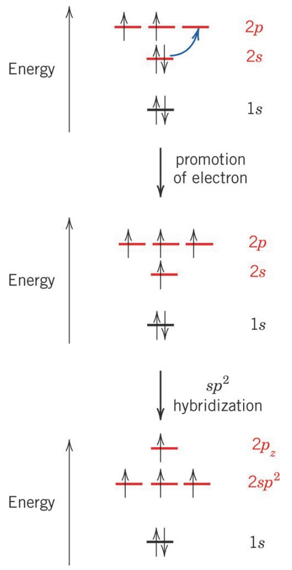
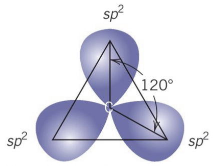
sp^2 Hybrids & (3) Metallic Bonding

- **Other types of hybrid bonds: Graphite**
  - Planar sp^2 hybrids
  - Parallel layers of interconnecting hexagons.





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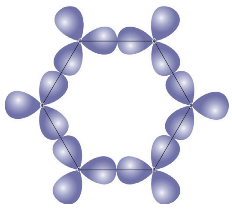
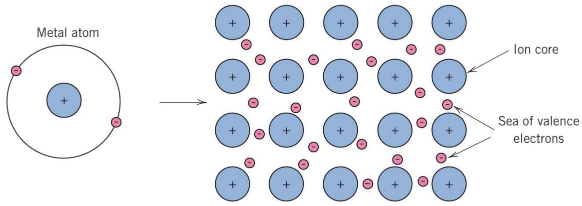
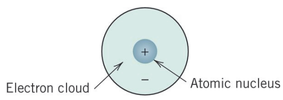


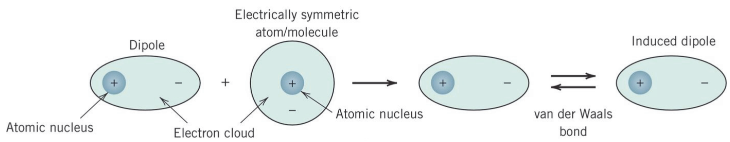
- **Metallic Bonding**
  - The valence electrons are not bounded to any particular atom in solid and are free to drift.
  - "Sea of electrons" or "electron cloud"
  - The metallic bond is nondirectional.
  - These free electrons act as a "glue" to hold the ion cores together.
  - Metals are good conductors of both electricity and heat as a consequence of their free electrons.
  - Most metals and their alloys are ductile.



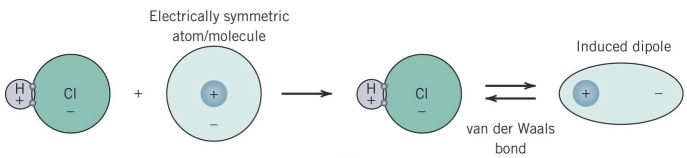
2.7 Secondary Bonding or van der Waals Bond

- **Fluctuating Induced Dipole Bonds**
  - Spontaneous dipole moments

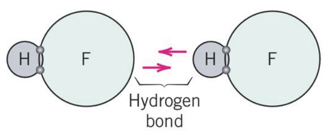




- **Polar Molecule-Induced Dipole Bonds**
  - Permanent dipole moments



- **Permanent Dipole Bonds (Hydrogen Bond)**
  - The strongest secondary bonding (the hydrogen bonding) is a special case of polar molecule bonding.
  - It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in H_2O), or nitrogen (as in NH_3).



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

Types	Primary bonds	Characteristics
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 bonding	Directional properties; secondary bonding dominates; small T_m; small E; large α