IntroductiontoEngineeringMaterials

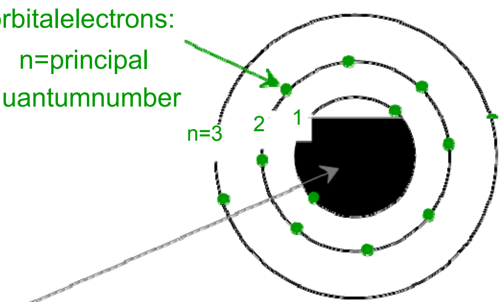
AtomicstructureandBonding

Overview

- Electrons,protonsandneutronsinatoms(BohrandQMmodels).
- IP,EA,χ,andperiodictrends.
- Bondingbetweenatoms.
- Intermolecularforces.
- Relationtomacroscopicproperties.

1

Electronsin atoms



AdaptedfromFig. 2.1, *Callister6e.*

AtomicmassA≈ Z+N

Electronsindiscreteorbitals.

Bohratom:

1) electronsareparticlesthatrevolve aroundthenucleus.

2) quantizedangularmomentum.

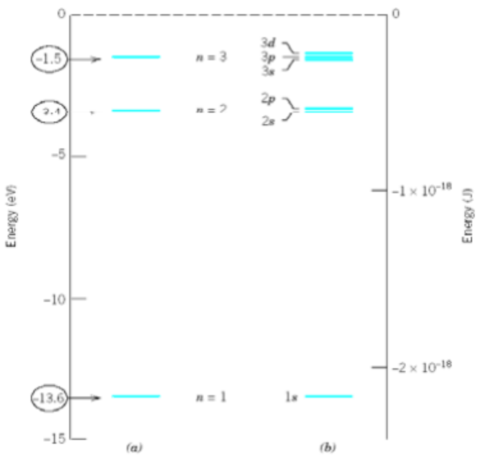
QuantumMechanics:

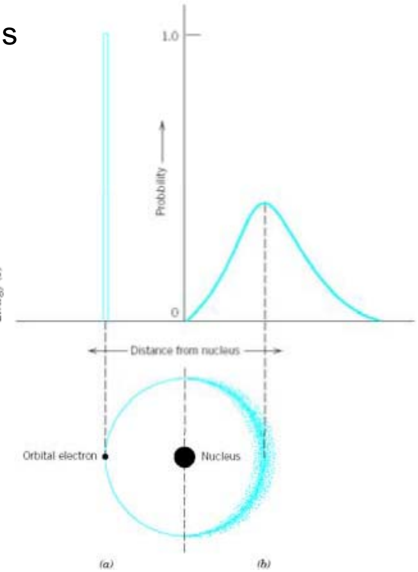
Waveormatrixmechanics

→Probability.

2

Comparison of Bohr and QM models





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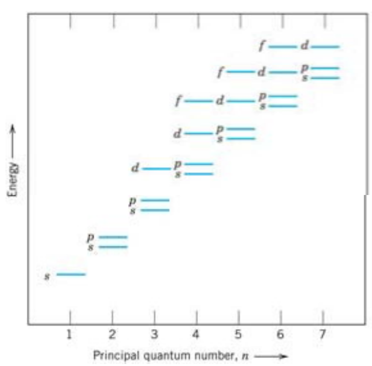
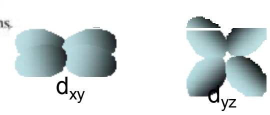
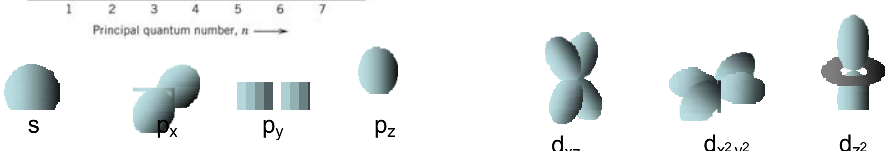


FIGURE 2.4 Schematic representation of the relative energies of the electrons for the various shells and subshells. (From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Atomic orbitals





Electrons...

- have discrete energy states (Quantized).
- tend to occupy lowest available energy state.

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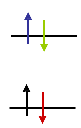
Quantumnumbers

- **Principal**:n=1,2,3,4…
- **Angularmomentum**:l=0,1,2,3…,n–
  1=s,p,d,f…s=sharp,p=principal,
  d=diffuse,f=fundamental
- **Magnetic**:m_l=0,±1,±2,±3…,±l
  Determines the number of statesinagivenl subshell (2l +1 total)
- **Spin**:m_s=±1/2

e.g.

2s

1s



n= 2,l =0, m_l= 0,m_s=1/2	n=2,l=0, m_l=0,m_s=-1/2
n= 1,l =0, m_l= 0,m_s=1/2	n=1,l=0, m_l=0,m_s=-1/2

Whichatom is this? **Be**

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ElectronConfiguration

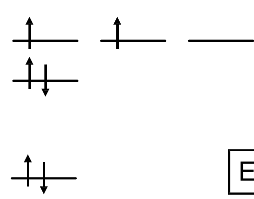
-Shorthandnotationtorepresentwhichstateselectrons occupyinanatom(withoutspecifyingelectronspin).

e.g.Carbon

2p

2s

1s



Electronconfiguration:$1s^22s^22p^2$

Note
- eachenergylevelcanonlyholdtwoelectronsofoppositespin **(Pauliexclusionprinciple).**
- fordegeneratelevels(e.g.2p-orbitals),eachorbitalisfilled with oneelectronbeforeelectronsarepairedup.

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Electronconfiguration

1 electroninthes-orbital:**Alkalimetals**
Li,Na,K,Rb…

2 electronsinthes-orbital:**Alkalineearths**
Be,Mg,Ca…

Filleds-orbitaland4electronsinp-orbital:**Chalcogens**
O,S, Se…

Filleds-orbitaland5electronsinp-orbital:**Halogens**
F,Cl, Br…

Partially filled d-orbital:**Transitionmetals**
e.g.Mn,Fe,Co…

→ **Valenceelectrons**determinewhichgroupatomsbelongto.

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Stableconfiguration

Stable electron configurations...

- havecompletesandpsubshells
- tendtobeinert.

Z	Element	Configuration
2	He	$1s^2$
10	Ne	$1s^2 2s^2 2p^6$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Noblegases

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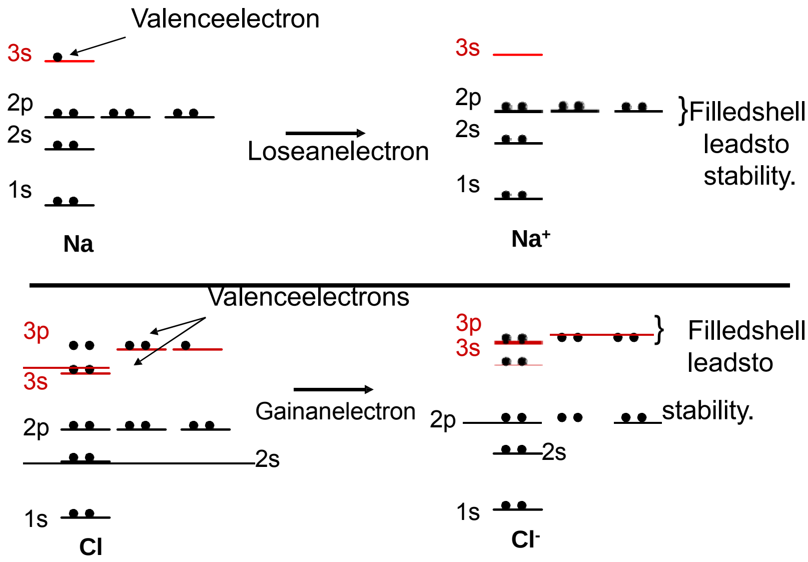
Valenceelectrons



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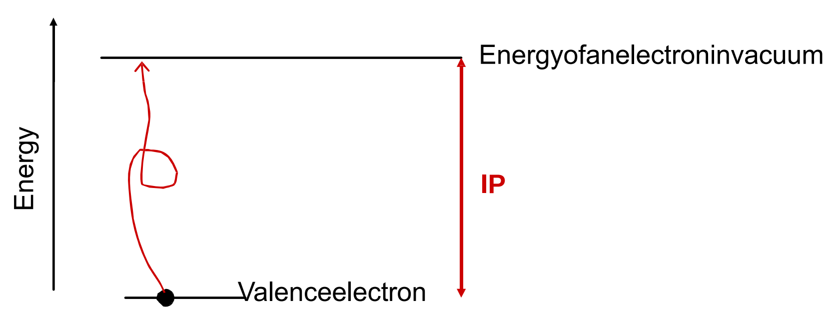
How much energy does it require to take an electronout ofan atom?



- **Ionizationpotential(IP):**Energyrequiredtopulloutavalence electron(invacuum).

By convention,IPispositive (i.e.needto putin energytopull out theelectron).

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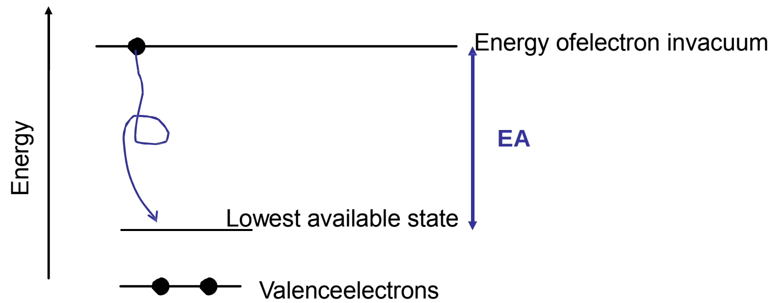
How much energy does it require to placeanelectronin an atom?



• **ElectronAffinity(EA):**Energygainedbyputtinganelectronin(from vacuum).

By convention,EAis negative(i.e.electrongoesfromhigherenergy stateinvacuumtolowerenergystateinatom).

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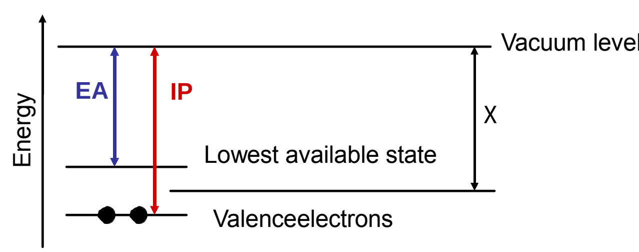
How do we determine whenan atom willaccept an electron or giveoneup?



• **Electronegativity(χ):**a measureofhowlikelyanatomwilltakeup or giveupanelectron

Asimple(andintuitive) definition: $\chi \sim \frac{IP+EA}{2}$

-Whentwoatomsarebroughttogether,theatomwith largerχwillhave higherelectrondensityarounditsnucleus.

-LargerΔχ ⟶ moreionicbond.

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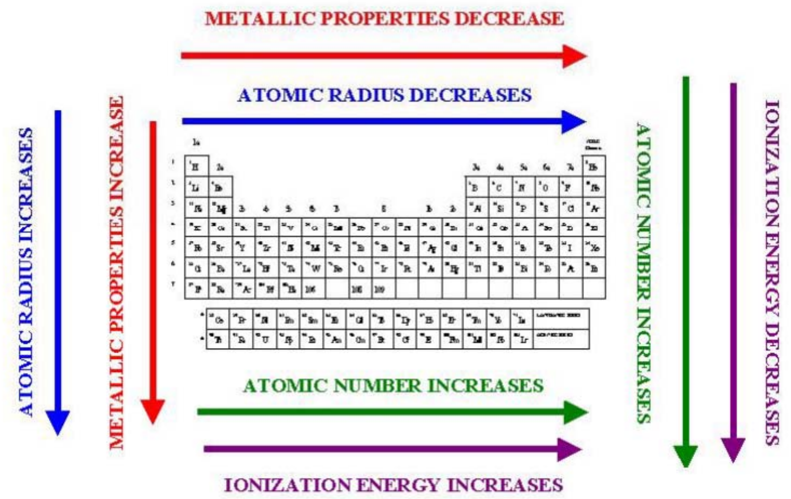

SUMMARY OF TRENDS IN THE PERIODIC TABLE

Robertson

MatSE 101

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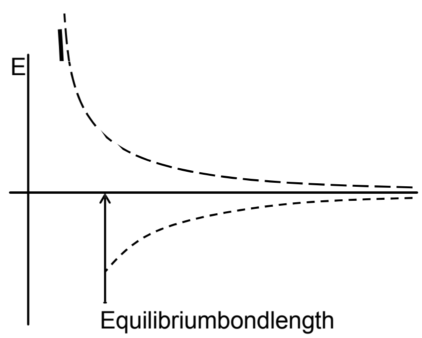
Bonding

Primary

Ionic
Covalent
Metallic

SecondaryDi
pole-dipole
H-bonds
Dipole-induced-dipole
Fluctuating dipoles



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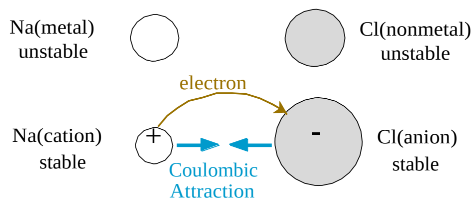
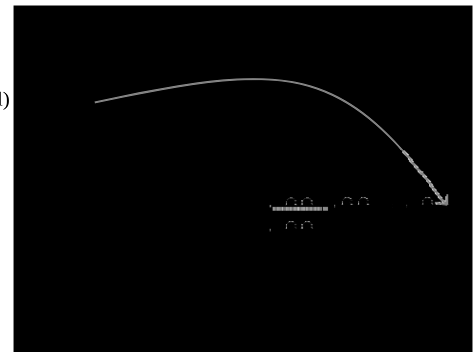
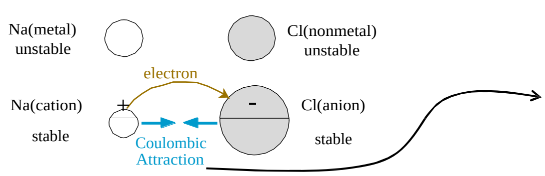
IonicBonding

- Occursbetween+and-ions.
- Requires electron transfer.
- Large difference in electronegativityrequired.
- Example: NaCl





IonicBonding



$$E_A = \frac{z_1 z_2 e^2}{4\pi\varepsilon_o r}$$

Sincez_1=+1forNa$^+$andz_2=-1forCl$^-$

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

Negativeenergymeansattractiononly.
Willtheatomscollapseonthemselves?

No,thereisalsorepulsiveenergy(e.g.e-erepulsion)

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

*B*and*n*dependonatomsinvolved.
Inmanycases*n~8.*

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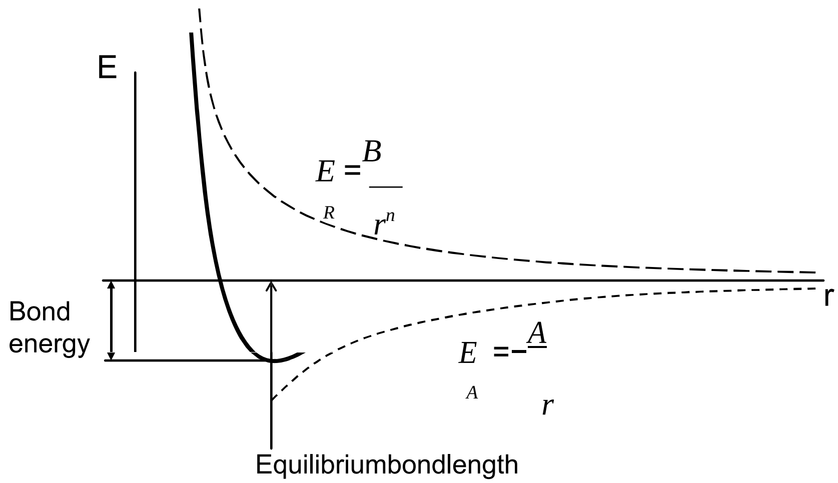
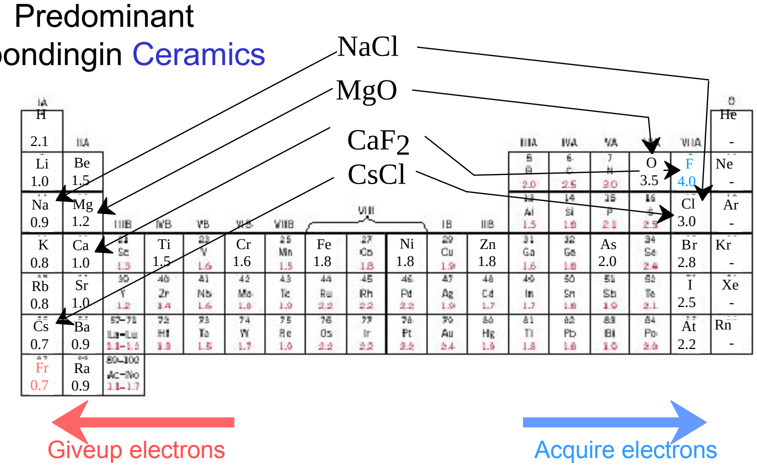
IonicBonding



Note: Other typesof bonds can alsobe described ina similar manner 17

IonicBonding:examples

- Predominant bondingin Ceramics



AdaptedfromFig.2.7,*Callister6e.*(Fig.2.7 isadaptedfromLinusPauling,*The NatureoftheChemical Bond*,3rdedition,Copyright 1939and1940,3rdedition.Copyright1960by Cornell University.

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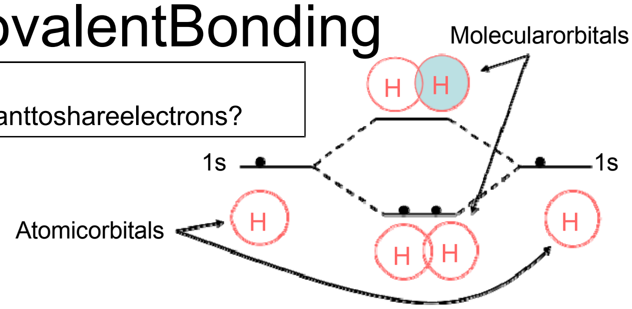
CovalentBonding

- “Sharing”ofelectrons
- Whydosomeatomswanttoshareelectrons?

- Example1: H_2

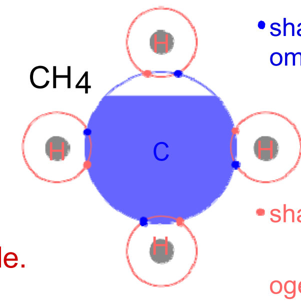


- Example2: CH_4

C:has4valencee,needs4more

H:has1valencee,needs1more

Electronegativities aresameorcomparable.



• sharedelectronsfromcarbonatom

• sharedelectrons fromhydrogenatoms

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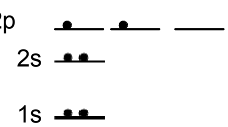
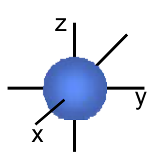
atomicorbitalsforcarbon:



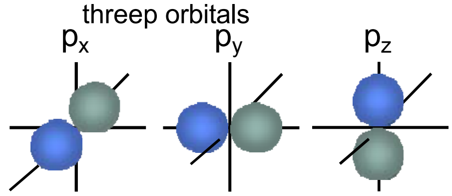
4valenceelectronsbut twodifferenttypes orbitals. H’sonCH_4shouldbe equivalent.

AtomicOrbitals

ans-orbital

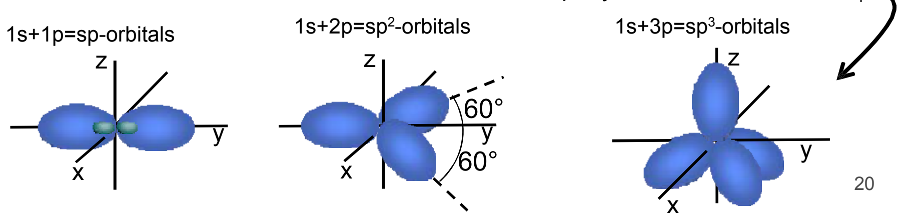


threep orbitals



Hybridization

sp3hybridizationforC in CH_4



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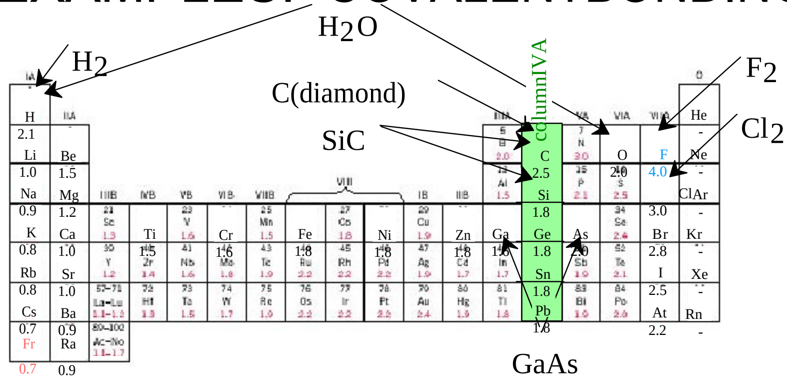
EXAMPLES: COVALENT BONDING



- Molecules with nonmetals
- Molecules with metals and nonmetals
- Elemental solids (RHS of Periodic Table)
- Compound solids (about column IVA)

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% ionic character

Most bonds between two different types of atoms are somewhere in between ionic and covalent.

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

χ_j = electronegativity of atom j

KEY POINT: Larger electronegativity difference → more ionic

Exampleproblem

- Orderthe following semiconductorsfrom mostcovalentto mostionic.
  1) ZnS,GaP,CuCl
  2) ZnS,ZnSe,ZnO

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What'ssoimportantaboutionicityof bonds?

- Chemicalproperties
  - NaCl(highlyionicsolid)dissolvesreadilyin waterbut Si(covalent solid) does not.
- Electronicproperties
  - Ionicityof the bonds willhaveastrong influenceon thebandgapandother electronicproperties.
- Allpropertiesofmaterialsarelargelydeterminedbyt hetypesandstrengthofbondsbetweentheconstitue ntatoms.

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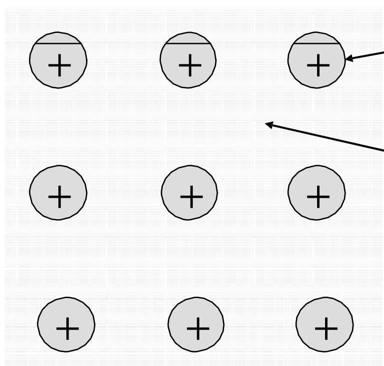
MetallicBonding

• Arisesfrom a sea ofdonatedvalenceelectrons



• Primarybondformetalsandtheiralloys.
• LargeatomicradiusandsmallIPwill morelikely leadtometallicbonding.

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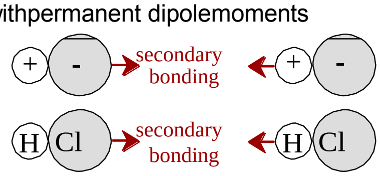
SecondaryBonds:IntermolecularForces

VanderWaals

• **Dipole-dipoleinteraction**:secondarybond betweenmoleculeswithpermanent dipolemoments

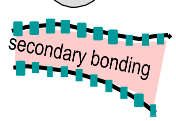
-generalcase:
-ex:liquidHCl



AdaptedfromFig.2.14, *Callister6e.*

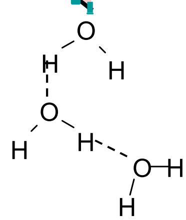
AdaptedfromFig.2.14, *Callister6e.*

-ex:polymer



FromCallister6eresourceCD.

• **Hydrogenbonding**



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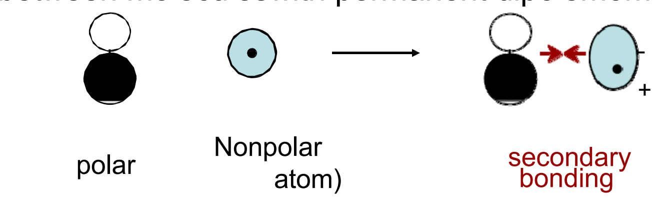
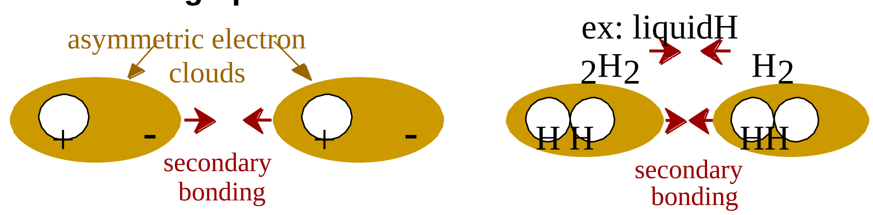
- **Dipole-induced-dipoleinteraction**:secondarybond between moleculeswith permanent dipolemoments



- **Fluctuatingdipoles**



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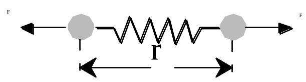
SUMMARY: BONDING

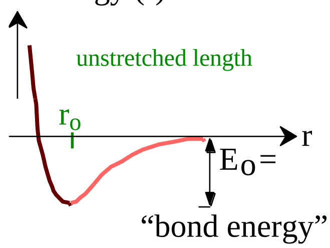
Type	BondEnergy	Comments
Ionic	Large!	Nondirectional(ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors,ceramics polymerchains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional(metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

PROPERTIES FROM BONDING: T_M

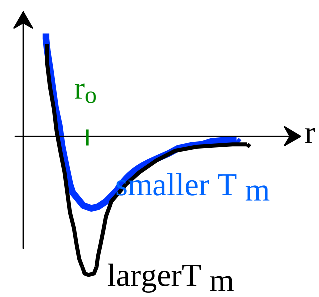
- Bond length, r



- Bond energy, E_o



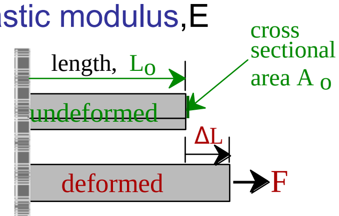
- Melting Temperature, T_m



T_m is larger if E_o is larger.

PROPERTIES FROM BONDING: E

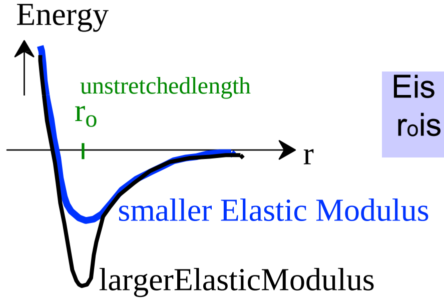
- Elastic modulus, E



Elastic modulus

$$\frac{F}{A_o} = E\frac{\Delta L}{L_o}$$

- E ~ curvature at r_o



E is larger if curvature at r_o is larger.

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SUMMARY:BONDINGandMaterials’properties

Ceramics

(Ionic&covalentbonding):

Large bond energy

largeT_ml

argeE

smallα

Metals

(Metallicbonding):

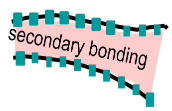
Variable bondenergy

moderate$T_m$moder

ateE moderateα

Polymers

(Covalent& Secondary):



DirectionalProperties

Secondarybondingdominates

smallT

smallE

largeα

3
1