Session 3: Advanced Solid State Physics

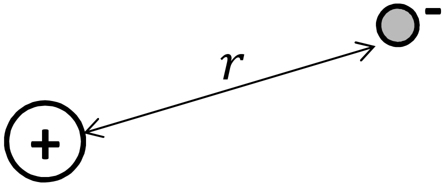
Atomic Physics
Molecules and Bonds

Outline

- Atomic Physics

Hydrogen Atom

1.
2.
3.
4.
5.



Uncertainty Principle:

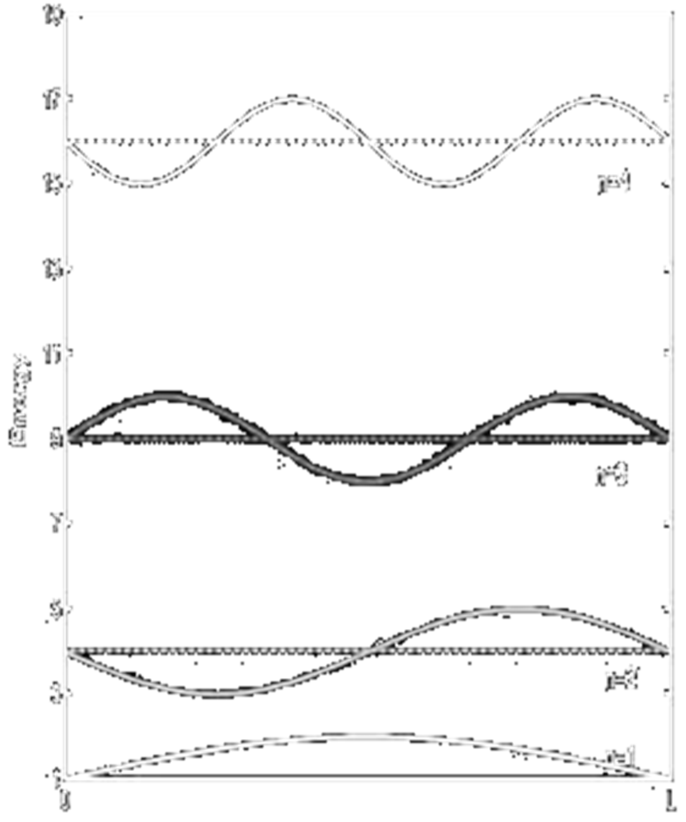
$$\Delta p \Delta x \geq h/2\pi$$

Total Energy = K.E. + P.E.

Confinement Energy of Hydrogen Atom

1.
2.
3.
4.
5.

Using the energy levels of ideal 1-D well we can estimate the confinement energy of H atom!



Wave function of Hydrogen Atom

1.
2.
3.
4.
5.

$$-\frac{\hbar^2}{2m_0}\nabla^2\Psi - \frac{e^2}{4\pi\epsilon_0 r}\Psi = E\Psi$$

B.C. : $\Psi \to 0$ as $r \to 0$

assume:

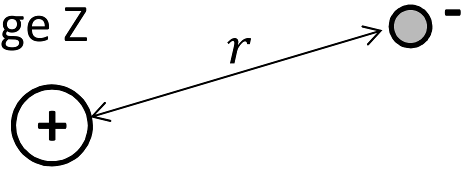
$$\Psi(r,\theta,\varphi\ ) = R(r)\Theta(\theta)\Phi(\varphi)$$

Check slides:

Hydrogenic Atom

1.
2.
3.
4.
5.

Nucleus charge Z



$$n = 1,2,3,\ldots$$

$$l = 0,1,2,3,\ldots,n-1$$
$$= s,p,d,f,g$$

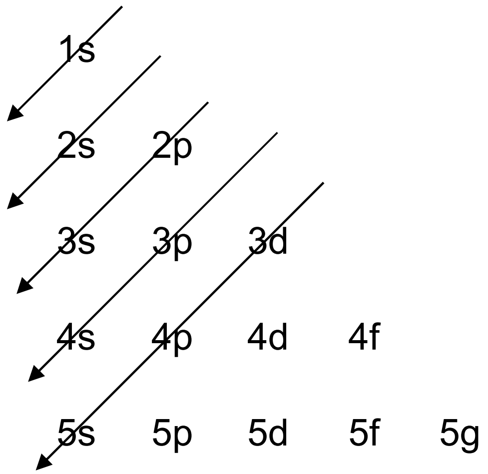
$$m = -l,\ldots,-1,0,1,\ldots,l$$

$$\sigma = \pm 1/2$$

s shell	2 eigenstate
p shell	6 eigenstate
d shell	10 eigenstate

$$E_n = -\frac{R_y}{n^2} + \text{small correction}$$

Madelung's Rule



1s

2s 2p

3s 3p 3d

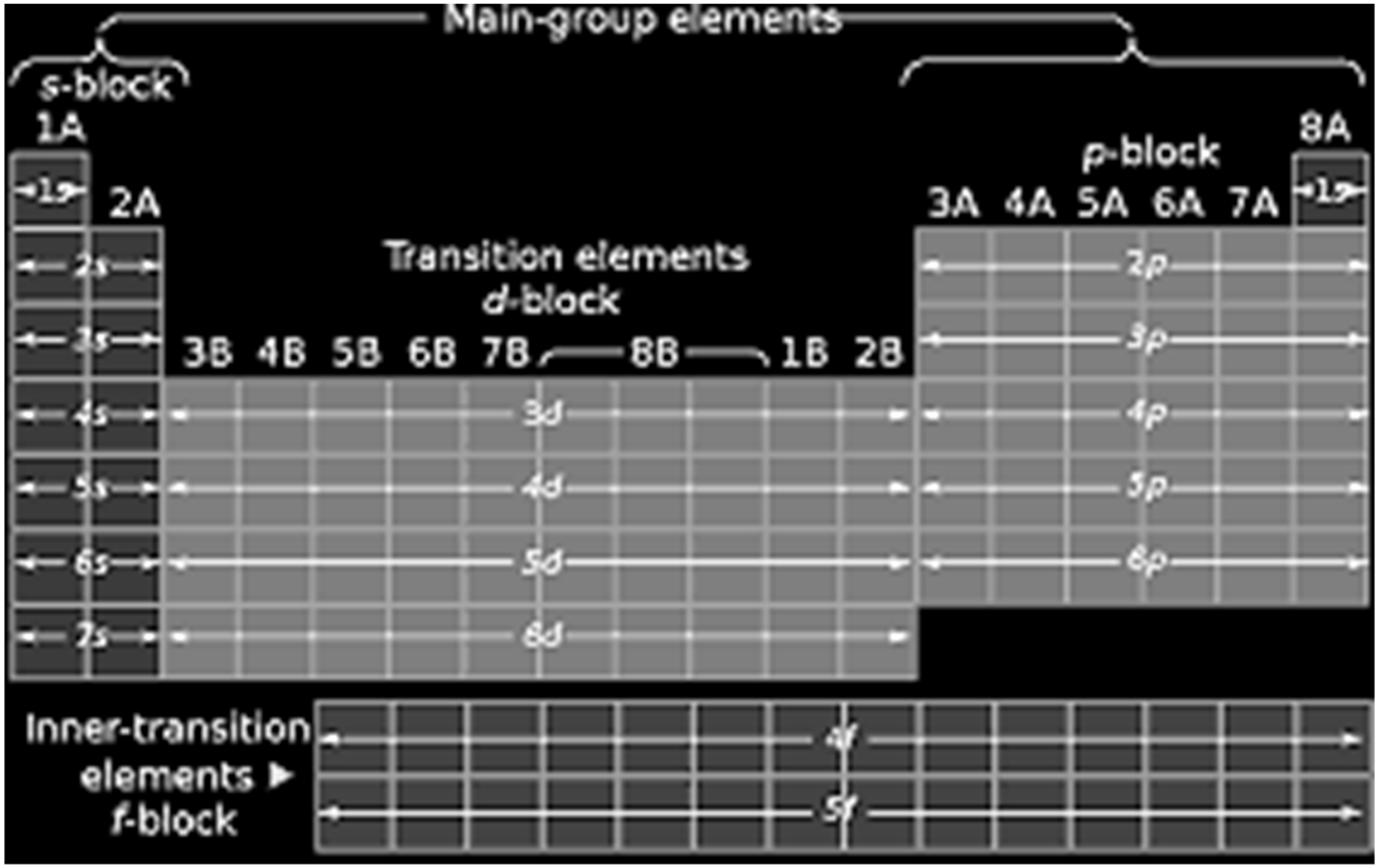
4s 4p 4d 4f

5s 5p 5d 5f 5g

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^3$$

Periodic Table

1.
2.
3.
4.
5.

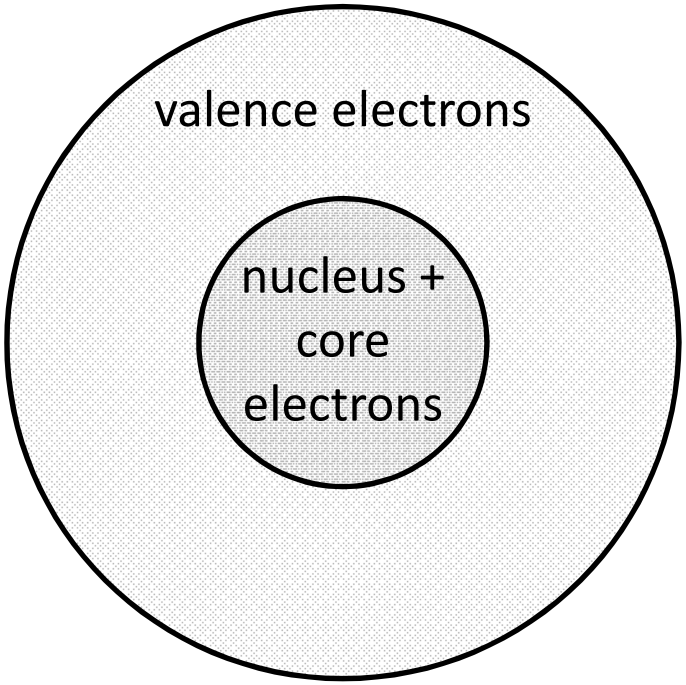


$$V(r) \neq \frac{1}{r}$$

Atomic Bonding

1.
2.
3.
4.
5.

Atoms vibrate with small amplitudes about fixed equilibrium positions. We assume that atoms are fixed, unless phonons are considered.
Atoms look like outer valence electrons orbiting around the core. Core consists of nucleus plus inner core electrons.



Ionic bond: Na^+Cl^-

Covalent bond: sharing e^- to complete an octet

H need only one atom to complete the octet and therefore we only have H_2. Silicon needs 4 e^- and so can bond to four other Si atoms, forming a crystal.

Metallic bond:

Van derWaals:

Hydrogen:

Types of bonds (Table 6.1 text)

1.
2.
3.
4.
5.

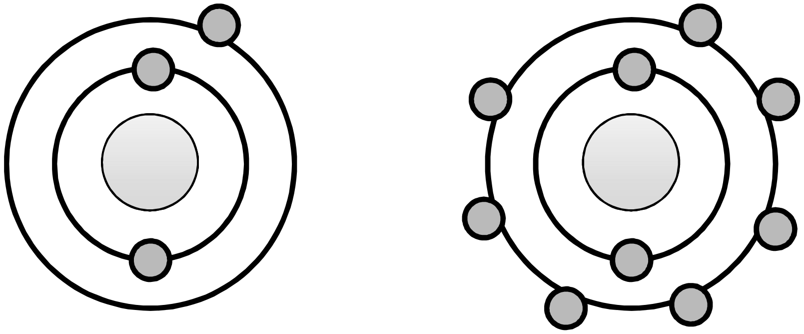
Type	Description	Typical of which compounds	Typical Properties
Ionic	Electron is transferred from one atom to another, and the resulting ions attract each other.	Binary compounds made of constituents with very different electronegativity: e.g., group I–VII compounds such as NaCl	• Hard, very brittle • High melting temperature • Electrical insulator • Water soluble
Covalent	Electron is shared between two atoms forming a bond. Energy lowered by delocalization of wavefunction	Compounds made of constituents with similar electronegativities (e.g., III–V compounds such as GaAs), or solids made of one element only such as diamond (C)	• Very hard (brittle) • High melting temperature • Electrical insulators or semiconductors
Metallic	Electrons are delocalized throughout the solid forming a glue between positive ions	Metals. Left and middle of periodic table	• Ductile, malleable (due to non-directional nature of bond). Can be hardened by adding certain impurities. • Lower melting temperature • Good electrical and thermal conductors
Molecular (van der Waals)	No transfer of electrons. Dipole moments on constituents align to cause attraction. Bonding strength increases with size of molecule or polarity of constituent	Noble gas solids, solids made of non-polar (or slightly polar) molecules binding to each other (wax).	• Soft, weak • Low melting temperature • Electrical insulator
Hydrogen	Involves hydrogen ion bound to one atom but still attracted to another. Special case because H is so small.	Important in organic and biological materials. Holds together ice	• Weak bond (stronger than vdW though) •Important for maintaining shape of DNA and proteins

Ionic Bonding

1.
2.
3.
4.
5.

Complete transfer of electrons from one atom (usually a metal) to another (non metal ion) (compounds only, not elemental solids). Bond comes from electrostatic attraction between ions.

$\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-} \rightarrow \mathrm{NaCl}$



All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond is.

- Bond is strong (high melting point, large elastic modulus)
- Not directional (high density, high coordination number)
- Compounds only
- Good insulators (except near melting point)
- Transparent up to UV (strong bonds →electrons need a lot of energy to become free)

Mathematical form: Energy ~ 1/r , Example: Sodium Chloride

Ionic Bonding

1.
2.
3.
4.
5.

$$E_{ionization} = E_{Na^{+}+e^{-}} - E_{Na}$$

$$E_{e-affinity} = E_{Cl+e^{-}} - E_{cl^{-}}$$

$$E_{cohesive} = E_{Na^{+}+Cl^{-}} - E_{NaCl}$$

$$\Delta E = E_{ion} - E_{aff} - E_{coh}$$

If $\Delta E < 0$ Then Reacts!

Ionic Bonding

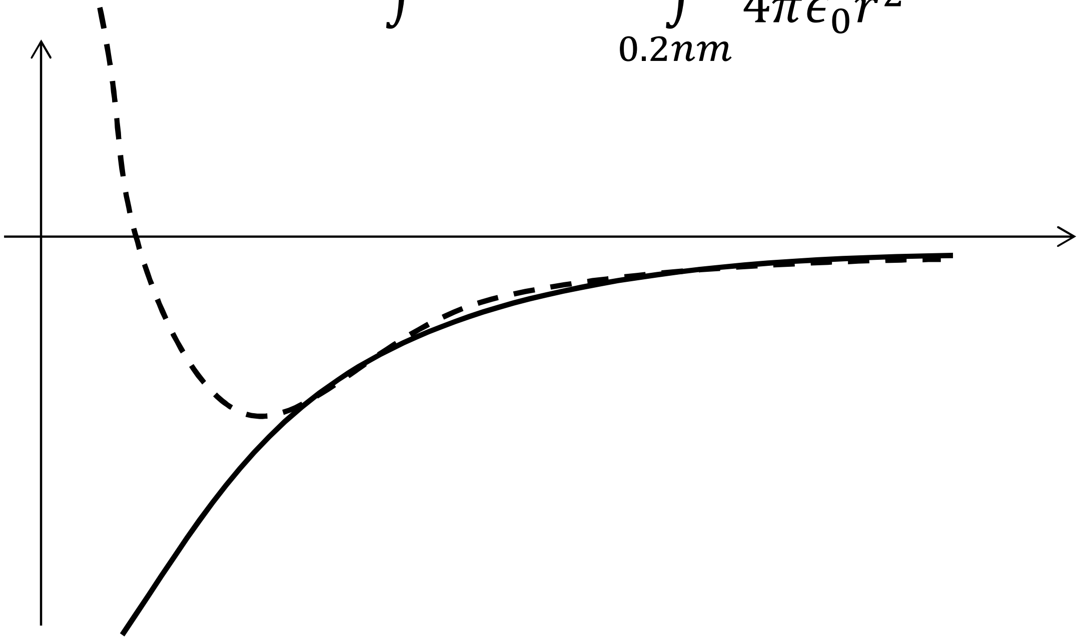
1.
2.
3.
4.
5.

Coulomb force:

$$F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

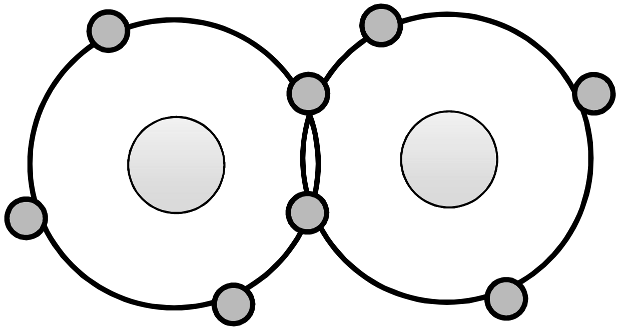
Energy needed to separate charges e and -e

$$E = \int F.dr = \int_{0.2nm}^{\infty} \frac{-e^2}{4\pi\epsilon_0 r^2} dr = 7eV$$



Covalent Bonding

1.
2.
3.
4.
5.



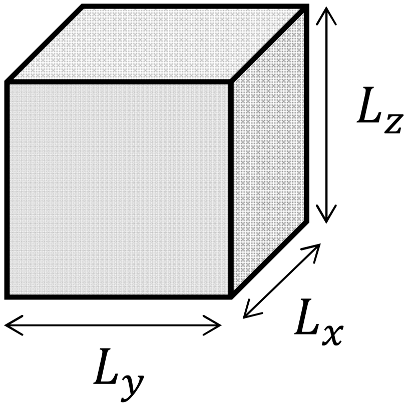
Equal sharing of electrons between atoms → both atoms have full shells (Example: Diamond, Silicon)

Note continuum of behavior, ionic → covalent (e.g. III-V compounds GaAs, InSb, are partially covalent and partially ionic.)

- Bond is strong (high melting point, large elastic modulus)
- Directional (from orientation of QM orbitals) → low density
- Saturable (limited number of bonds per atom) ↑
- Good insulators

Covalent Bonding: Square well potential

1.
2.
3.
4.
5.



$$V = \begin{cases} 0 & \text{inside cube} \\ \infty & \text{outside cube} \end{cases}$$

$$-\frac{\hbar^2}{2m_0}\nabla^2\Psi = E\Psi$$

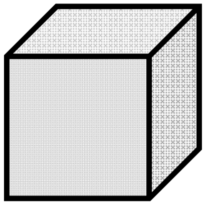
$$\Psi = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z}$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

Covalent Bonding: Square well potential

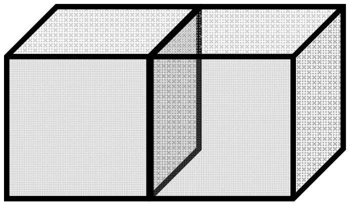
1.
2.
3.
4.
5.

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$



Energy of a particle confined to a cube L×L×L

$$E = \frac{3h^2}{8ml^2}$$



Energy of a particle confined to a cube L×L×2L

$$E = \frac{9h^2}{32ml^2}$$

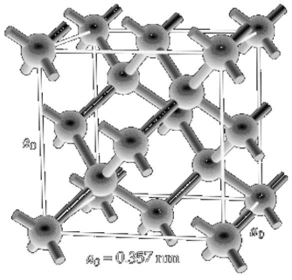
Decrease in energy:

$$E = \frac{3h^2}{16ml^2}$$

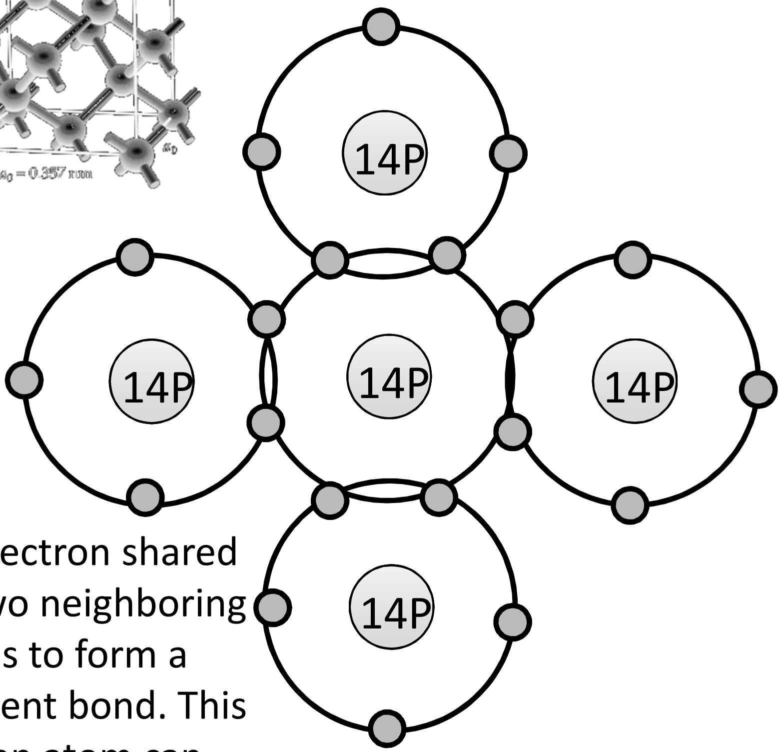
For L= 0.2 nm: ΔE =14eV

Silicon

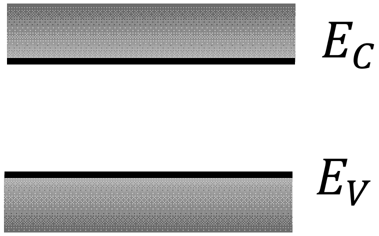
1.
2.
3.
4.
5.



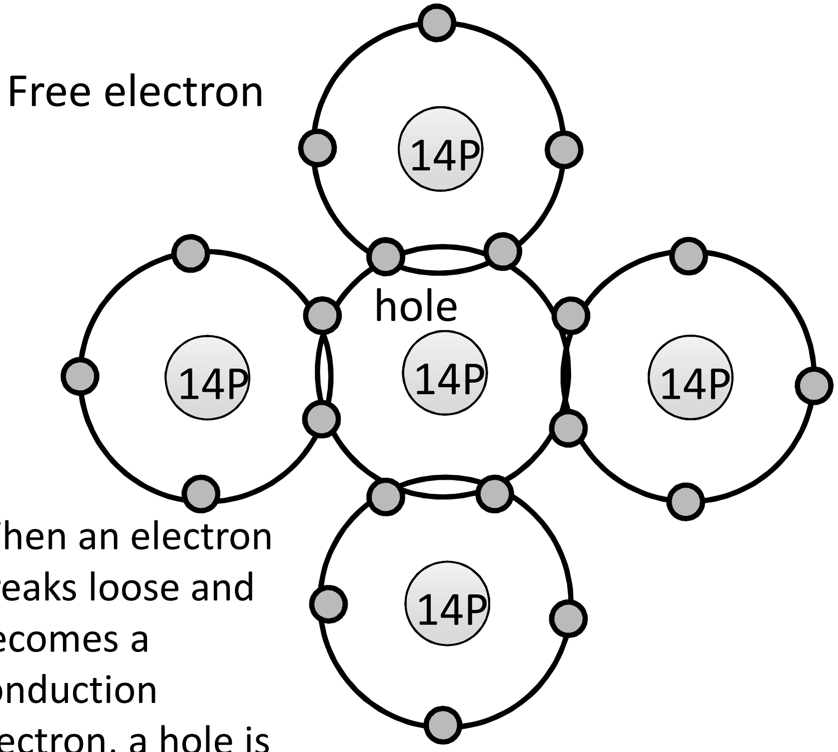
2D representation



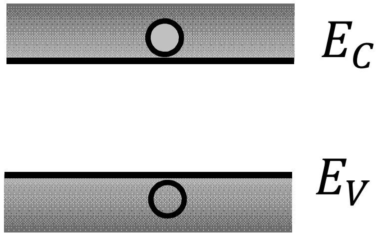
An electron shared by two neighboring atoms to form a covalent bond. This way an atom can have a stable structure with eight valence band electrons.



Generation / Recombination



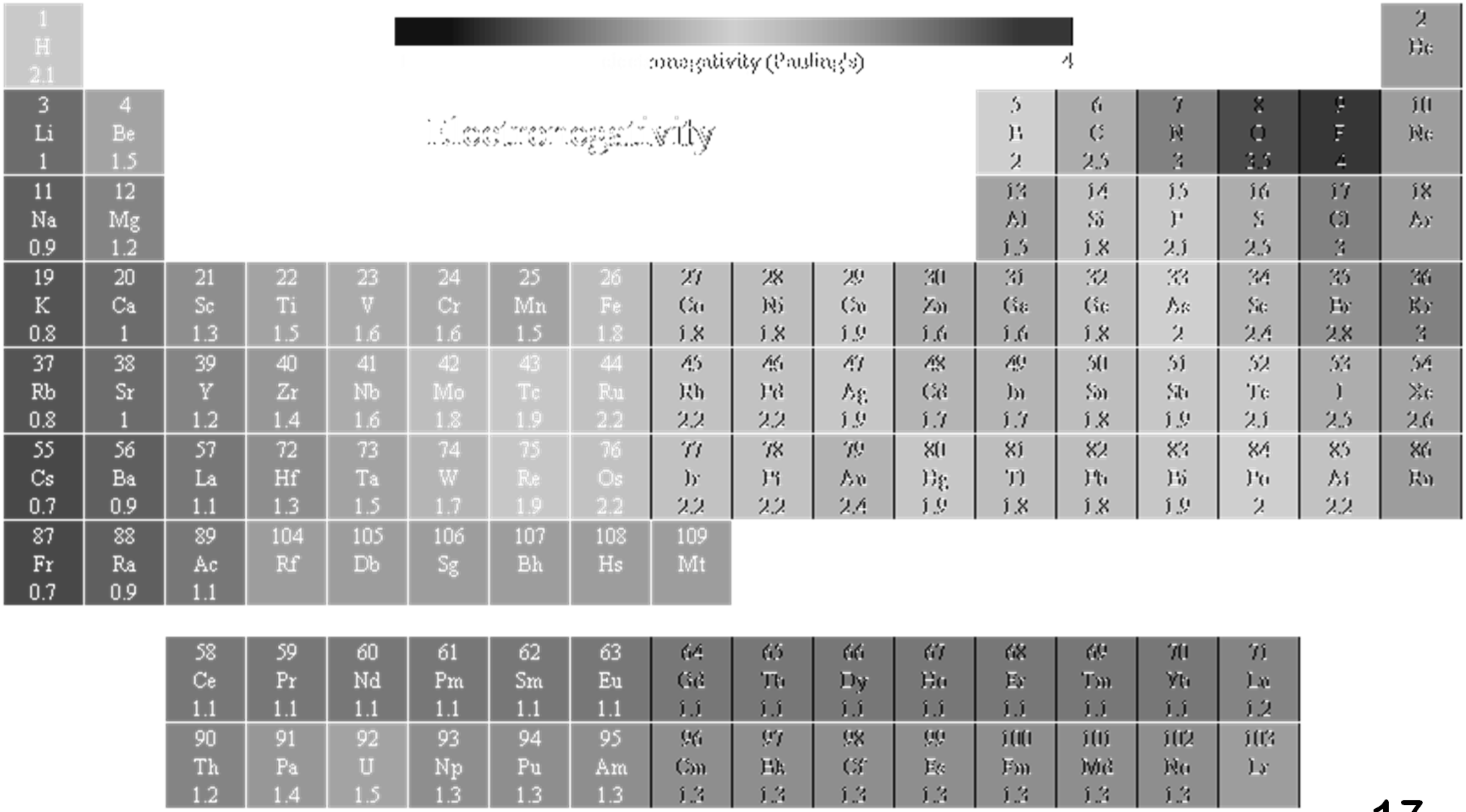
When an electron breaks loose and becomes a conduction electron, a hole is also created.



Polar Bonds

1.
2.
3.
4.
5.

Partly covalent and partly ionic. The more electronegative element will have more negative charge.



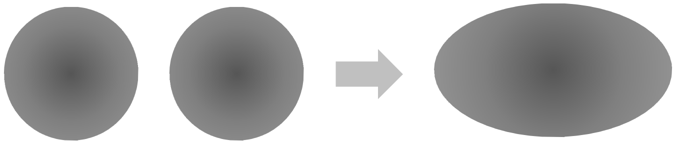
Electronegativity

Electronegativity (Pauling's) 4

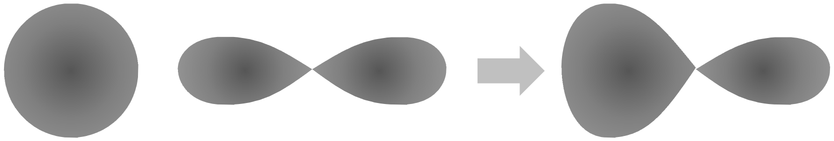
1 H 2.1																	2 He
3 Li 1	4 Be 1.5											5 B 2	6 C 2.5	7 N 3	8 O 3.5	9 F 4	10 Ne
11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3	18 Ar
19 K 0.8	20 Ca 1	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2	34 Se 2.4	35 Br 2.8	36 Kr 3
37 Rb 0.8	38 Sr 1	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe 2.6
55 Cs 0.7	56 Ba 0.9	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2	85 At 2.2	86 Rn
87 Fr 0.7	88 Ra 0.9	89 Ac 1.1	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
		58 Ce 1.1	59 Pr 1.1	60 Nd 1.1	61 Pm 1.1	62 Sm 1.1	63 Eu 1.1	64 Gd 1.1	65 Tb 1.1	66 Dy 1.1	67 Ho 1.1	68 Er 1.1	69 Tm 1.1	70 Yb 1.1	71 Lu 1.2		
		90 Th 1.2	91 Pa 1.4	92 U 1.5	93 Np 1.3	94 Pu 1.3	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.3	103 Lr		

Sigma Bonds

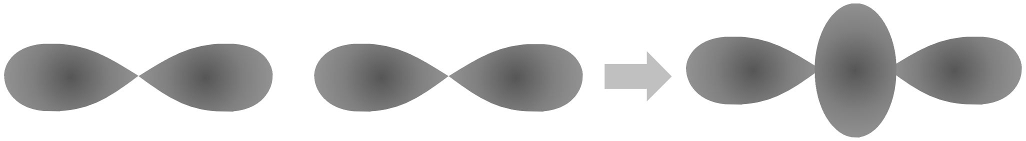
1.
2.
3.
4.
5.



Sigma bond between two s orbitals



Sigma bond between s and p orbitals

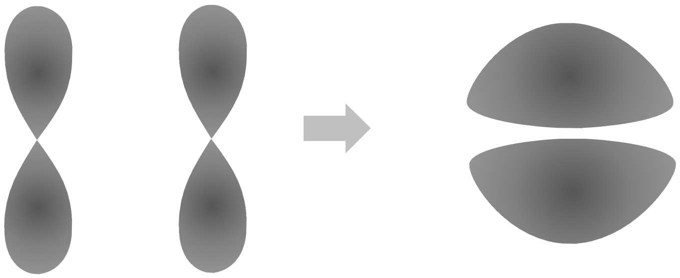


Sigma bond between two p orbitals

The angular momentum of a sigma orbital around the interatomic axis is zero. A molecule can twist around a sigma bond.

Pi Bonds

1.
2.
3.
4.
5.



Pi bond between two p orbitals

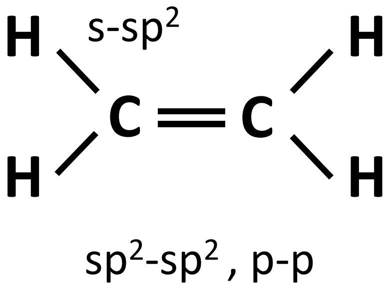
A molecule cannot twist around a Pi bond.

Single bond / double bond / triple bonds

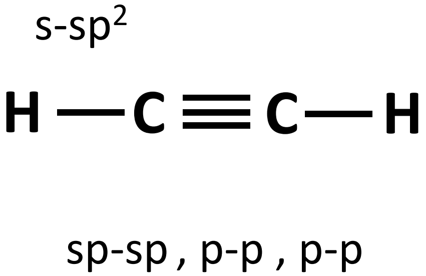
Single bond : Two electrons are shared, sigma bond

Double bond : Four electrons are shared, sigma bond + pi bond

Triple bond : Six electrons are shared, sigma bond + 2 pi bonds



ethene



acetylene

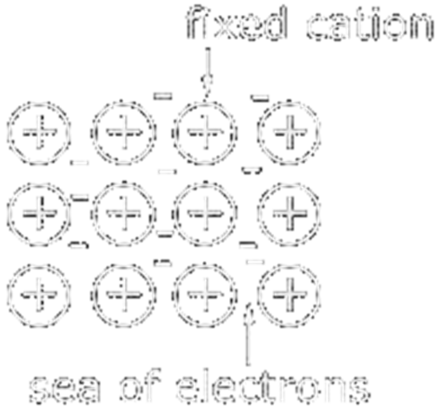
Metallic Bonding

1.
2.
3.
4.
5.

Positive ions plus gas (sea) of electrons. Think of this as the limiting case of ionic bonding in which the negative ions are electrons. (BUT electrons can't be forced to sit at lattice points from Uncertainty Principle: $\Delta p \Delta x \geq h/2$ as for electrons m is small so the zero point energy $\Delta E = \Delta p^2/2m$ is very large; the electrons would

shake themselves free and are therefore delocalized)

- Bonds are non directional (high coordination number, high density, malleable and ductile)
- Variable strength
- Free electrons → high electrical conductivity, shiny (Electric field associated with incident light makes free electrons at surface move back and forth, re-radiating the light, as a reflected beam)

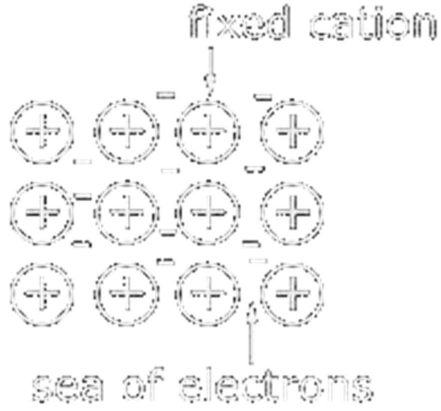


Metallic Bonding

1.
2.
3.
4.
5.

The electron wave functions spread out over the entire crystal. A three dimensional potential square well is a simple model for a metal.

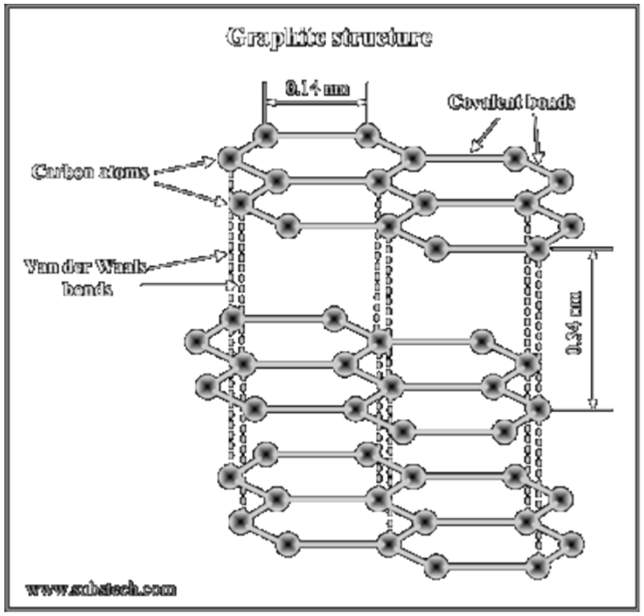
$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

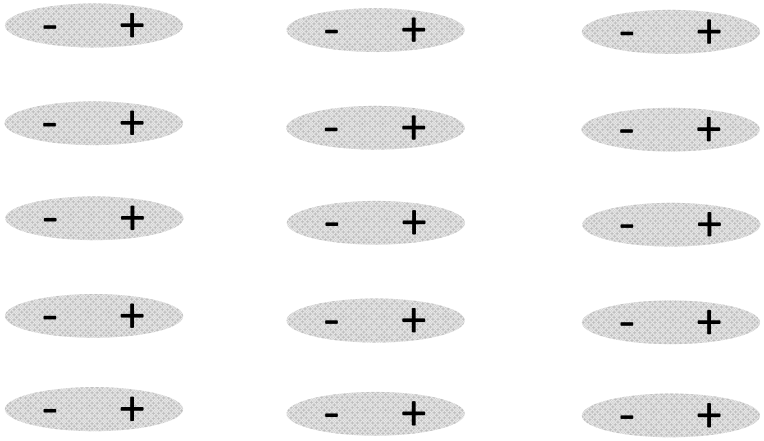


Energy mostly determines by Electrostatic force!

Van der Waals Bond

1.
2.
3.
4.
5.





Even a neutral atom with a full shell, can, at a given instant, have a dipole moment (i.e. one side of the atom more positive than the other) This instantaneous dipole will induce a dipole in a neighboring atom, and the resulting dipole-dipole interaction is the origin of the van der Waals bond. Although the original dipole time-averages to zero, the interaction does not – it is always attractive. Energy ~ $1/r^6$

- Bond is weak (→low melting point, large expansion coefficient)
- Non directional so high coordination number BUT
- Long bond lengths (→low density)

Examples: Solid inert gases (Argon, Neon), molecular solids (solid Oxygen)

Hydrogen Bonding

1.
2.
3.
4.
5.

Hydrogen loses its electron and becomes positively charged particularly easily. Therefore the region of a molecule around a hydrogen atom is often quite positive, and this allows an electrostatic bond to form between it and negative parts of neighboring molecules.
Example: ice – the strength of the hydrogen bond explains the anomalously high melting point of ice

Comparing Bonds

1.
2.
3.
4.
5.

Bond	Energy (GPa)	Example of Bond
Covalent	1,000	Diamond
Ionic	30 – 100	Salt and Ceramics
Metallic	30 – 100	Metals
Hydrogen	8	Ice
Van der Waals	2	Polythene

Valence Bond Theory

1.
2.
3.
4.
5.

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + U(r)$$

Bond potentials

Morse (covalent)

$$U(r) = U_0\left(e^{-2(r-r_0)/a} - 2e^{-(r-r_0)/a}\right)$$

Lennard-Jones (van der Waals)

$$U(r) = 4E_0\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$