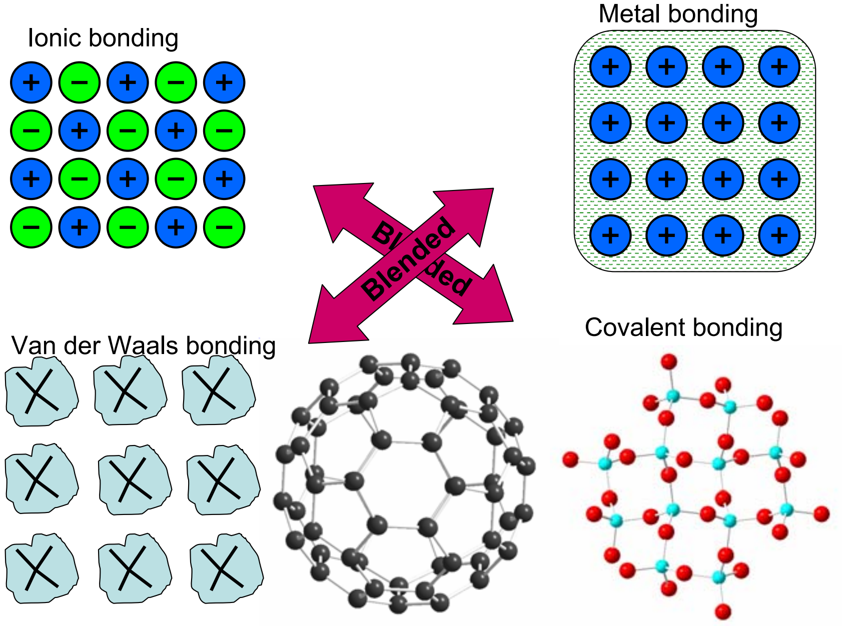
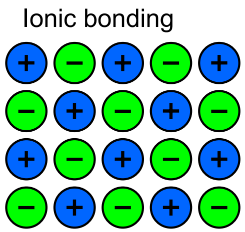
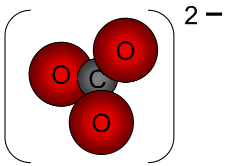
Kap. 2
Chemical bonding

Crystalline materials show a range of different bond types:

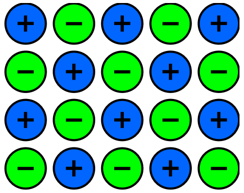




Ions are charged species



Ionic bonding



Non-directional
High coordination number as possible
Charged, non-compressible, non-polarizable spheres

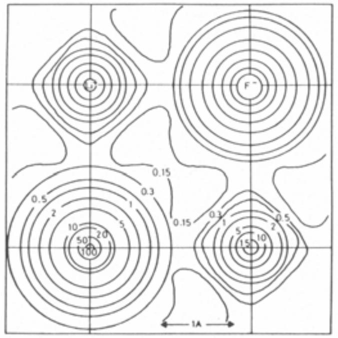
Purely ionic binding rarely occurs,
a net charge of more than +1 are unlikely

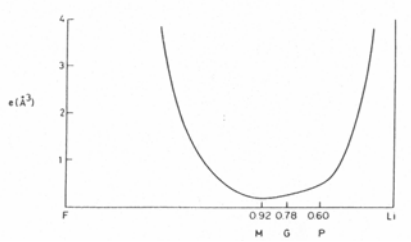
Useful as starting point to visualize structures

For visualization, one needs a set of ionical radiis

Ionic radiis

The ionical radiis from Pauling and Goldschmidt have been revised due to information from present high-quality X-ray diffraction work.

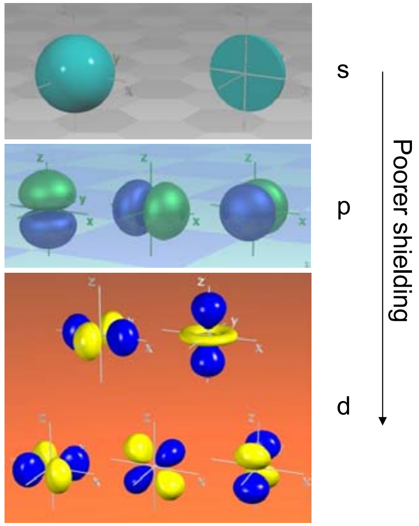




a) Ions are essentially spherical
b) Ions are composed of a central core with most of the electrons and an outer sphere with very little electron density.
c) Assignment of radii is difficult

Ionic radiis

The size of an ion is depenant on how the outer orbitals shield the charge from the nucleus.



s- and p-block, radi increase with atomic number for any vertical group.

For isoelectronic series of cations, radii decrease with increaseing charge, Na^+, Mg^{2+}, Al^{3+} and Si^{4+}

Cation radius decrease with increaseing oxidation state, V^{2+}, V^{3+}, V^{4+}, V^{5+}

Cation radius increase with coordination number, CN = 4 vs. CN = 6

Lanthanide contraction and transition contraction due to poor shielding

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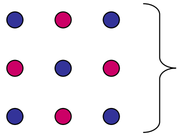
Ionic radiis

Based on empirical values



$a = 2(r_M+r_X)$

Consistent sett of values

The values are dependent on:

Coordination number
Type of coordination polyhedra
Oxidation number

Metallic oxides
Sett of radiis dependent on type of orbitals used??

Ionic structures – bond strength

Force between two ions:

$$F = \frac{(Z_+e)(Z_-e)}{r^2}$$

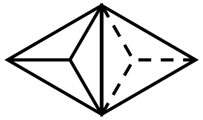
Electrostatic bond strength:

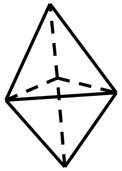
$$ebs = \frac{m}{n}$$

The charge is divided among the number of bonds.

The sum of ebs on an ion must ballance the charge

$$\sum \frac{m}{n} = x$$

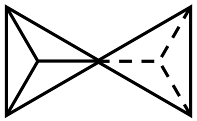


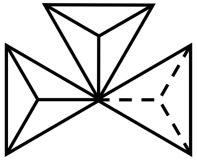


Spinel: $MgAl_2O_4$
Octahedral Al^{3+} → ebs = 3/6 = ½
Tetrahedral Mg^{2+} → ebs = 2/4 = ½

→ Oxygen tetrahedraly surrounded by 3 Al and 1 Mg:
$\Sigma ebs(3Al3+ + 1Mg2+) = 2$

SiO_2 ?





$$M_mX_x$$

$$\frac{CN(M)}{CN(X)} = \frac{x}{m}$$

Ionic structures – bond strength

Example:

NaCl type structure, Na^+ in octahedra holes → $CN(Na^+) = 6$

$CN\ (Cl^-)$?

$CN\ (Cl^-) = 1/1*6 = 6$

CaF_2 type structure, F^- in tetrahedra holes → $CN(F^-) = 4$

$CN\ (Ca^{2+})$?

$CN\ (Ca^{2+}) = 2/1*4 = 8$

Rutil type structure (TiO_2); $CN(Ti^{4+}) = 6$

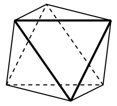
$CN\ (O^{2-})$?

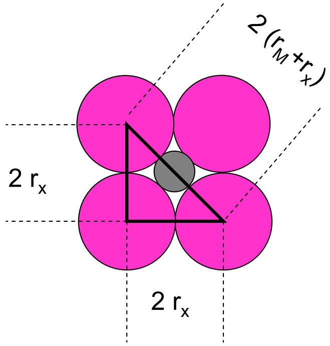
$CN\ (O^{2-}) = 1/2*6 = 3$

Ionic structures – Radius ratio

Ideally ions surround themselves with as many ions op the oposite charge as possible. The ions must be in contact → CN depends on the radius ratios.

Consider an octahedra:



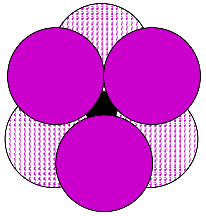


$$(2r_x)^2 + (2r_x)^2 = [2(r_M + r_x)]^2$$

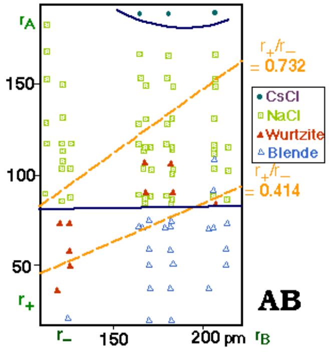
$$2r_x\sqrt{2} = 2(r_M + r_x)$$

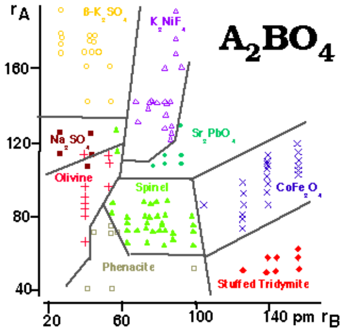
$$r_M / r_x = \sqrt{2} - 1 = 0.414$$

Octaeder hole



Ionic structures – Radius ratio





Ionic structures – general principles

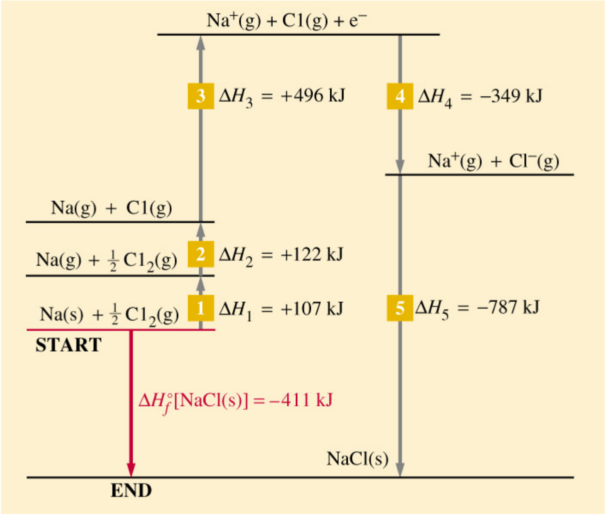
1. Ions are in fact charged, elastic and polarizable spheres
2. Geometrical annrangement

contraction:	anion – cation
repulsion:	anion – anion cation – cation

3. As high coordination number as possible to maximize net electrostatic attraction. Depends on the ratio of ion radii.
4. Next neighbour ions are as far as possible. → Maximization of volume!
5. Local electroneutrality. Valence = Σ electrostatic bond strength

Born Haber cycle

The lattice energy can be calculated by using Hess law and the following scheme:



Ionic structures – Lattice energy

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$, $\Delta H = U$ Sublimation energy

$$F = \frac{(Z_+)(Z_-)e^2}{r^2}$$

Force between two ions

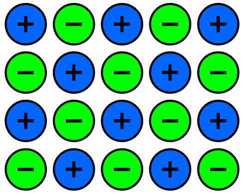
$$V = \int_\infty^r F\,dr = -\frac{(Z_+)(Z_-)e^2}{r}$$

Columbic potential energy

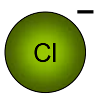
$$V = \frac{B}{r^n} \qquad n = 5\ldots12$$

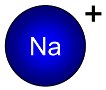
Short-range repulsive forces

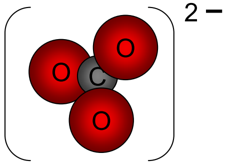
Ionic bonding

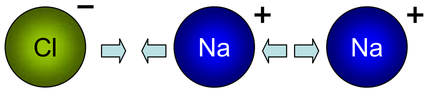


Ions are charged species



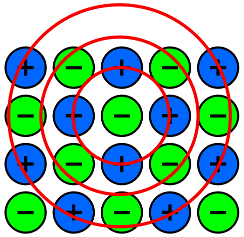


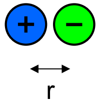




$E_{bond} = E_{electro} - E_{rep}$

Madelung energy





$$E_e = \frac{(+e)(-e)}{4\pi\varepsilon_0 r} = \frac{-e^2}{4\pi\varepsilon_0 r}$$

Like charges repell each other

$$E_e = \left(\frac{-e^2}{4\pi\varepsilon_0 r}\right)\times(Geometry)\times(ioniccharge)$$

$$E_e = N_A\left(\frac{-e^2}{4\pi\varepsilon_0 r}\right)\alpha Z^2$$

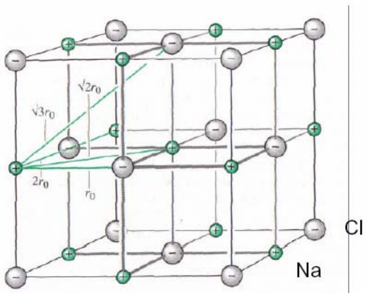
Ionic structures – Lattice energy - NaCl

Na$^+$ is surrounded by 6 Cl$^-$

$$V = -\frac{6(Z_+)(Z_-)e^2}{r}$$

Na$^+$ is surrounded by 12 next neighbour Na$^+$ at √2r

$$V = +\frac{12(Z_+)(Z_-)e^2}{\sqrt{2}r}$$



Na$^+$ is surrounded again by 8 Cl$^-$ at √3r

$$V = -\frac{8(Z_+)(Z_-)e^2}{\sqrt{3}r}$$

$$V = -\frac{(Z_+)(Z_-)e^2}{r}\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+....\right)$$

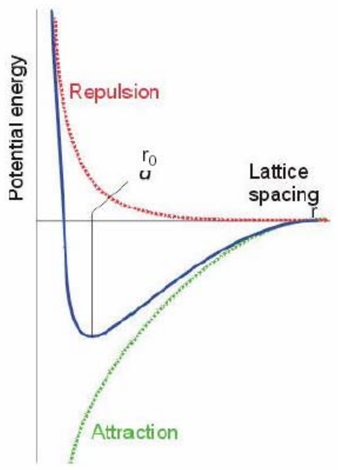
Ionic structures – Lattice energy

$$V = -\frac{(Z_+)(Z_-)e^2}{r}\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+....\right) \Rightarrow V = -\frac{(Z_+)(Z_-)e^2}{r}NA$$

N = mole of ions

Madelung constants

Structure type	α
Rock salt	**1.748**
CsCl	**1.763**
Wurtzie	**1.641**
Sphalerite	**1.638**
Fluorite	**2.520**
Rutile	**2.408**



Ionic structures – Lattice energy – Reduced constant

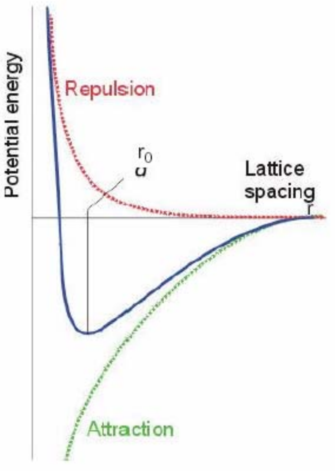
$$V = -\frac{(Z_+)(Z_-)e^2}{r}\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+....\right) \Rightarrow V = -\frac{(Z_+)(Z_-)e^2}{r}NA$$

N = mole of ions

Madelung constants

Structure type		α	α
Rock salt	**M^+X^-**	**1.748**	**1.748**
CsCl	**M^+X^-**	**1.763**	**1.763**
Wurtzie	**$M^{2+}X^{2-}$**	**1.641**	**1.641**
Sphalerite	**$M^{2+}X^{2-}$**	**1.638**	**1.638**
Fluorite	**$M^{2+}X_2^-$**	**2.520**	**1.68**
Rutile	**$M^{4+}X_2^{2-}$**	**2.408**	**1.60**

$$E_e = N_A\left(\frac{e^2}{4\pi\varepsilon_0 r}\right)\alpha(Z_M Z_X)^2\frac{m+n}{2}$$



The Kapustinskii equation

Kapustinskii found that if the Madelung constant for a given structure is divided by the number of ions in one formula unit (n) the resulting values are almost constant:

Structure	Madelung const.(A)	A/v	Coordination
CsCl	1.763	0.88	8:8
NaCl	1.748	0.87	6:6
CaF_2	2.519	0.84	8:4
α-Al_2O_3	4.172	0.83	6:4

general lattice energy equation that can be applied to any crystal regardless of the crystal structure

$$U = -\frac{1200.5VZ_+Z_-}{r_c+r_a}\left(1-\frac{0.345}{r_c+r_a}\right)\ \text{kJ mol}^{-1}$$

The Kapustinskii equation

Most important advantage of the Kapustinski equation:

It is possible to apply the equation for lattice calculations of crystals with polyatomic ions (e.g. KNO_3, $(NH_4)_2SO_4$ ...).

A set of „thermochemical radii“ was derived for further calculations of lattice enthalpies

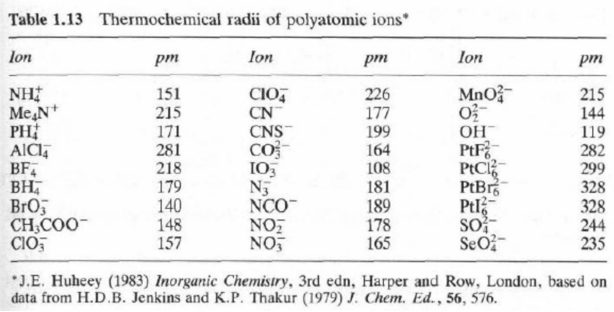


Table 1.13 Thermochemical radii of polyatomic ions*

Ion	*pm*	*Ion*	*pm*	*Ion*	*pm*
NH_4^+	151	ClO_4^-	226	MnO_4^{2-}	215
Me_4N^+	215	CN^-	177	O_2^{2-}	144
PH_4^+	171	CNS^-	199	OH^-	119
$AlCl_4^-$	281	CO_3^{2-}	164	PtF_6^{2-}	282
BF_4^-	218	IO_3^-	108	$PtCl_6^{2-}$	299
BH_4^-	179	N_3^-	181	$PtBr_6^{2-}$	328
BrO_3^-	140	NCO^-	189	PtI_6^{2-}	328
CH_3COO^-	148	NO_2^-	178	SO_4^{2-}	244
ClO_3^-	157	NO_3^-	165	SeO_4^{2-}	235

*J.E. Huheey (1983) *Inorganic Chemistry*, 3rd edn, Harper and Row, London, based on data from H.D.B. Jenkins and K.P. Thakur (1979) *J. Chem. Ed.*, **56**, 576.

Ionic structures – Lattice energy

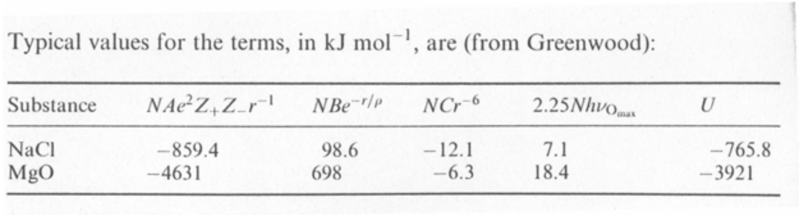
Attractive electrostatic forces

Van der Waals attractive forces

$$U = -\frac{Ae^2 Z_+ Z_- N}{r} + BNe^{-r/\rho} - CNr^{-6} + 2.25Nh\nu_{O\,max}$$

Born repulsive term

Zero point energy

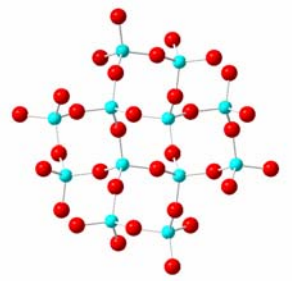


Typical values for the terms, in kJ mol^{-1}, are (from Greenwood):

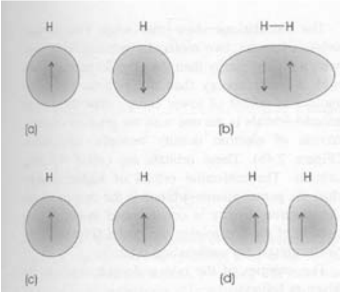
Substance	$NAe^2Z_+Z_-r^{-1}$	$NBe^{-r/\rho}$	NCr^{-6}	$2.25Nh\nu_{O_{max}}$	U
NaCl	−859.4	98.6	−12.1	7.1	−765.8
MgO	−4631	698	−6.3	18.4	−3921

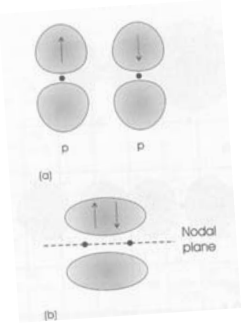
Crystalline materials show a range of different bond types:

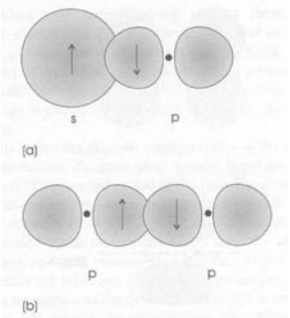
Covalent bonding



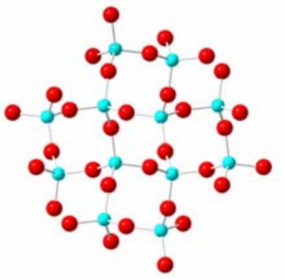
Covalent bonding is a result of orbital overlaps
Spins in overlapping orbitals must be antiparallel

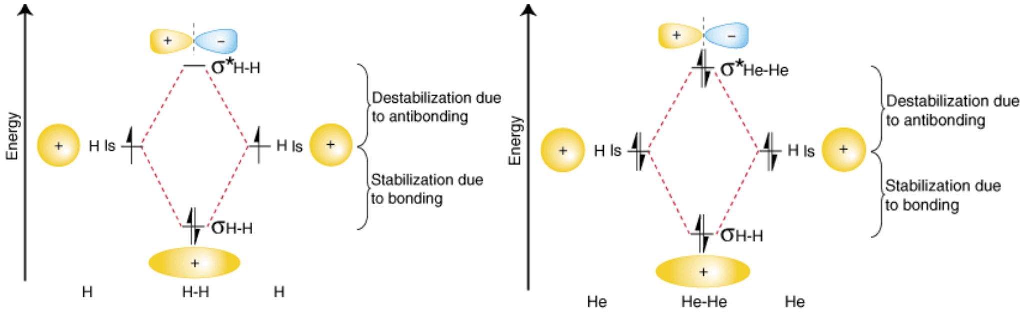


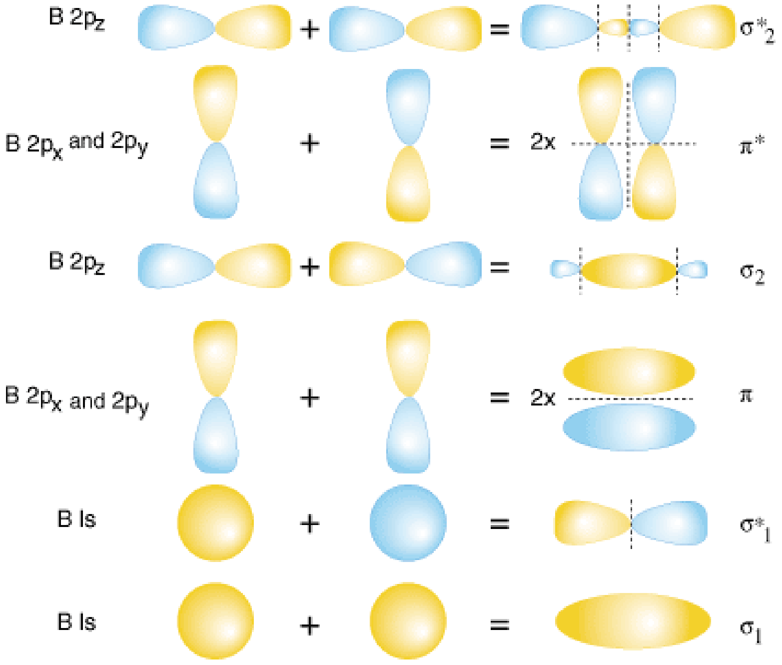




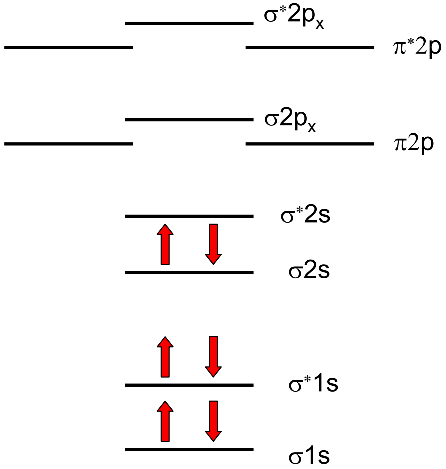
Covalent bonding







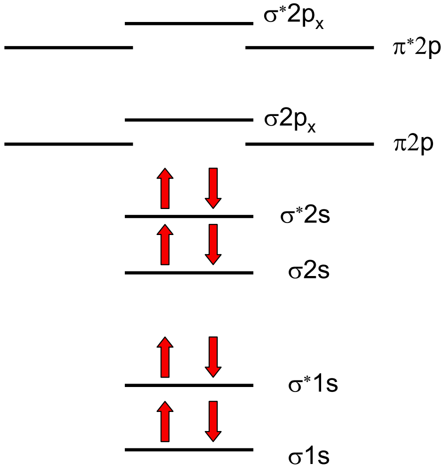
Li_2



$[He_2](\sigma 2s)^2$

Bond length = 0.267 nm
Bond energy = 101 kJ/mol

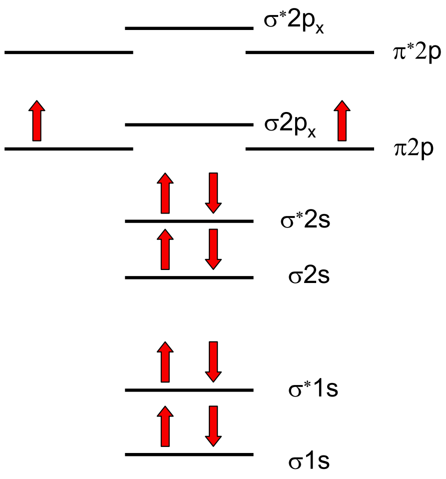
Be_2



$[He_2](\sigma 2s)^2(\sigma^*2s)^2$

Bond length = - nm
Bond energy = - kJ/mol

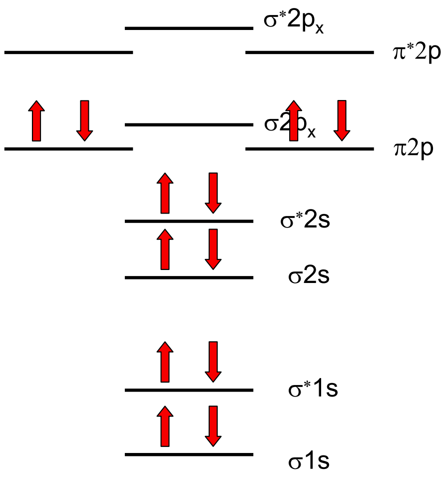
B_2



$[Be_2](\pi 2p)^2$

Bond length = 0.159 nm
Bond energy = 289 kJ/mol

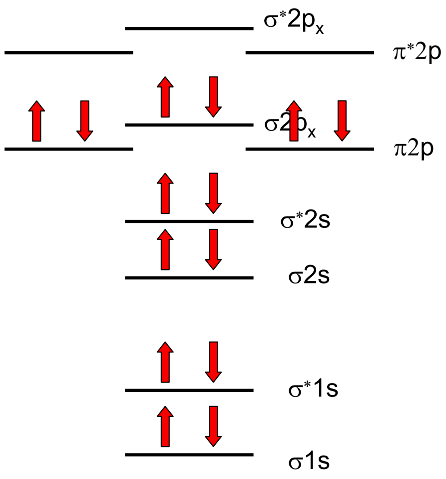
C_2



$[Be_2](\pi 2p)^4$

Bond length = 0.124 nm
Bond energy = 599 kJ/mol

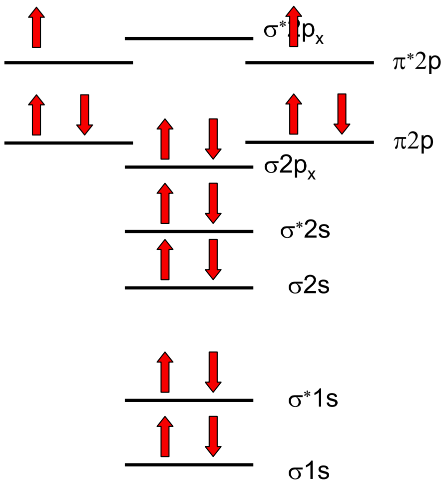
N_2



$[Be_2](\pi 2p)^4(\sigma 2p_x)^2$

Bond length = 0.110 nm
Bond energy = 941 kJ/mol

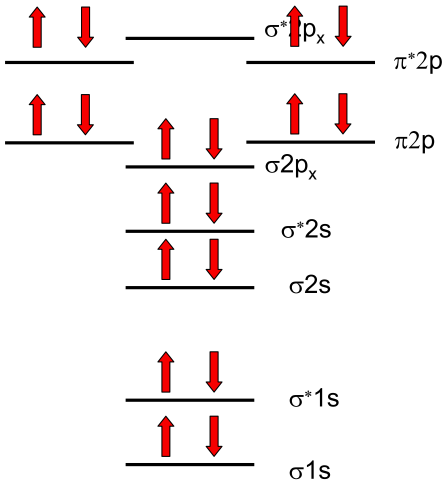
O_2



$[Be_2](\pi 2p)^4(\sigma 2p_x)^2(\pi^*2p)^2$

Bond length = 0.121 nm
Bond energy = 494 kJ/mol

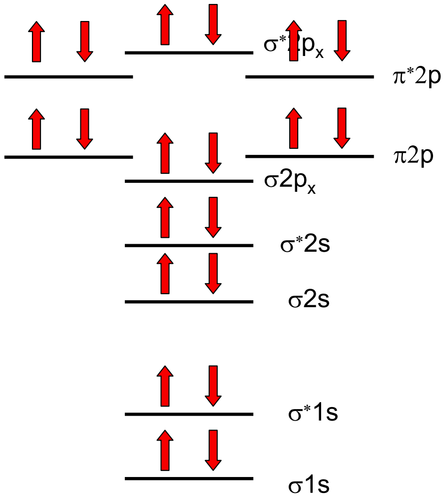
F_2



$[Be_2](\pi 2p)^4(\sigma 2p_x)^2(\pi^* 2p)^4$

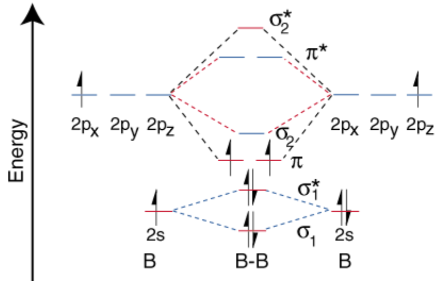
Bond length = 0.142 nm
Bond energy = 254 kJ/mol

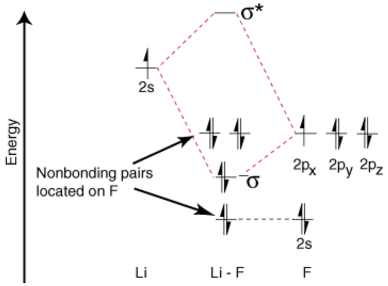
Ne_2



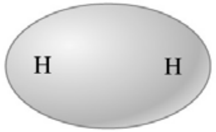
$[Be_2](\pi 2p)^4(\sigma 2p_x)^2(\pi^* 2p)^4(\sigma 2p_x)^2$

Bond length = 0.142 nm
Bond energy = 254 kJ/mol

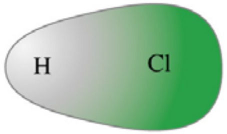




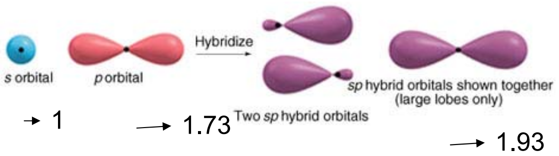
Nonpolar covalent bond

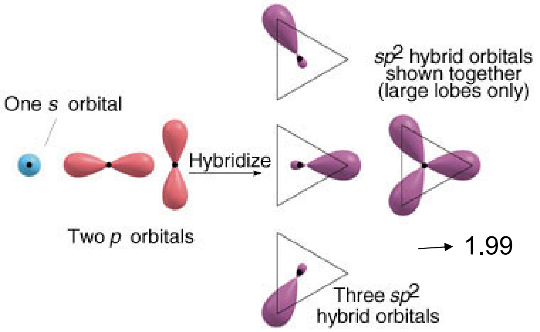


Polar covalent bond

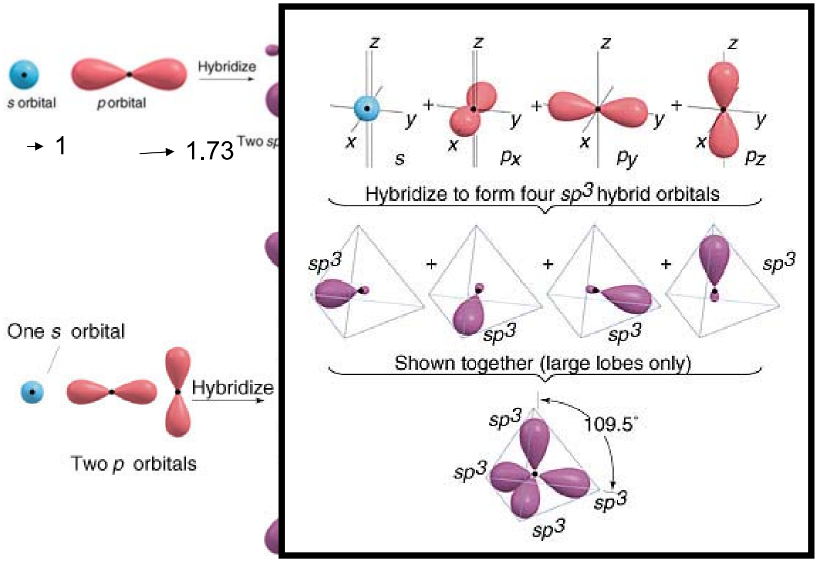


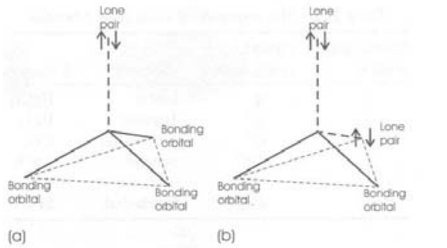
Orbital hybridisation





Orbital hybridisation





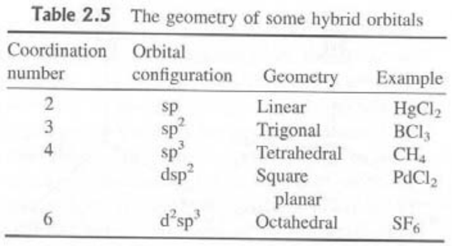
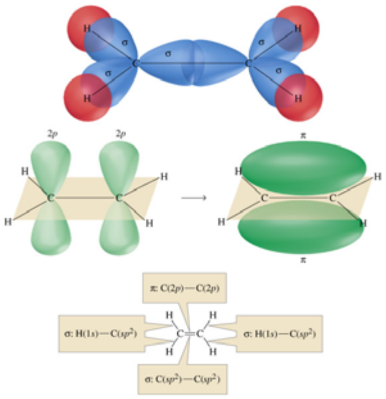


Table 2.5 The geometry of some hybrid orbitals

Coordination number	Orbital configuration	Geometry	Example
2	sp	Linear	$HgCl_2$
3	sp^2	Trigonal	BCl_3
4	sp^3	Tetrahedral	CH_4
	dsp^2	Square planar	$PdCl_2$
6	d^2sp^3	Octahedral	SF_6

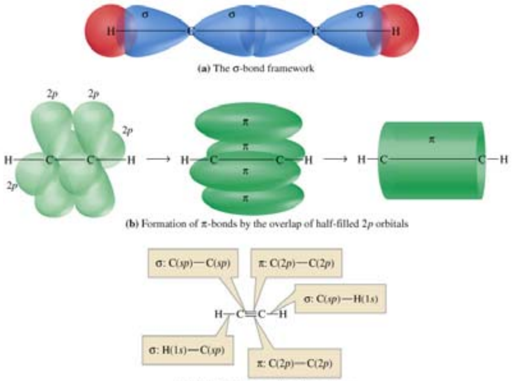
Multiple bonds



(a) The σ-bond framework

(b) The formation of a π-bond by the overlap of the half-filled 2p orbitals

(c) Hybridization and bonding scheme

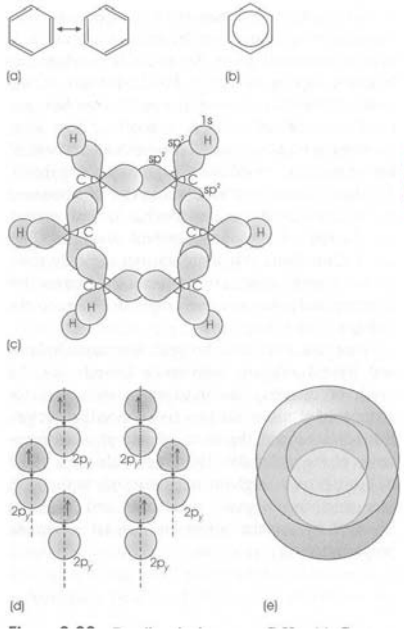


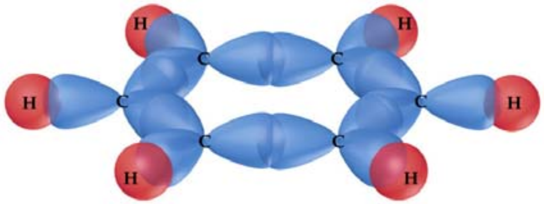
(a) The σ-bond framework

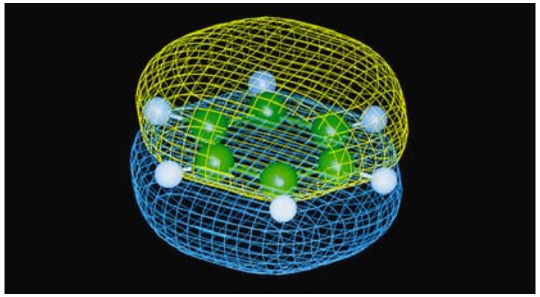
(b) Formation of π-bonds by the overlap of half-filled 2p orbitals

(c) Hybridization and bonding scheme

Resonance



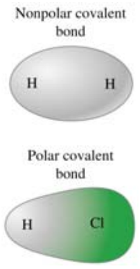




Partial covalent bonding

Covalent bonding occurs when the outer electronic charge density on an anion is polarized towards and by a neighbouring cation.

The net effect is electron density between the atoms.



SrO	NaCl-type
BaO	NaCl-type
HgO	linear O-Hg-O segments

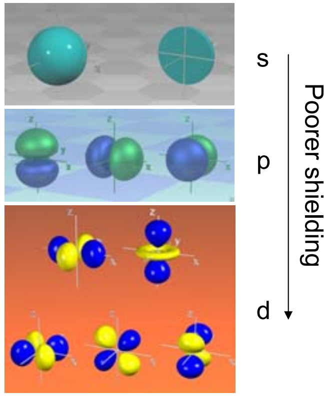
AlF_3	ReO_3 related ionic solid
$AlCl_3$	Layered polymeric structure
$AlBr_3$	Molecular Al_2Br_6 dimer
AlI_3	Molecular Al_2I_6 dimer

↑ Increasing differense in electronegativity

Sandersons model

The properties of solids is much dependent on how valence electrons 'feel the situation'.

Effective nuclear charge



Correlations between effective nuclear charge and:

-Ionization potential
-Electron affinity
-Electronegativity χ
-Atomic radius

Sandersons model – Atomic radii

Atomic radii vary considerably depending on CN and polarity of bond.

Non-polar covalent radii (r_c) can be measured accurately (C-C)

Non-polar covalent radii

Partial charge

$$r = r_c - B\delta$$

Sandersons atomic radii

Atom specific constant

The partial charges can not be measured directly but estimated from Sandersons electronegativity scale.

Sandersons model – Electronegativity

Sanderson developed a new elevtronegativity table (S) where:

$$S = \frac{D}{D_a}$$

Electron density of the atom

Electron density derived from linear interpolation of inert gas elements.

Principle of electronegativity equalization

$$S_b = \sqrt{S_{Na} S_F} = 2.006$$

The electronegativity is divided between both atoms in the bond

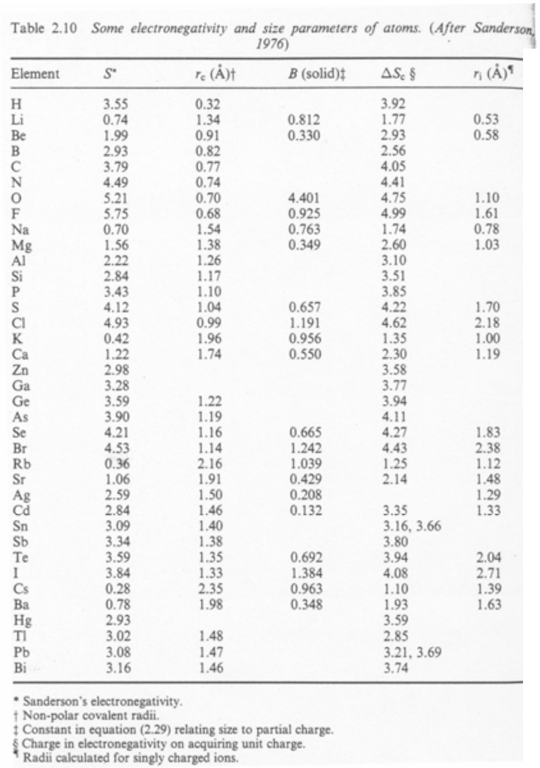


Table 2.10 *Some electronegativity and size parameters of atoms. (After Sanderson, 1976)*

Element	S^*	r_c (Å)†	B (solid)‡	ΔS_c §	r_i (Å)¶
H	3.55	0.32		3.92	
Li	0.74	1.34	0.812	1.77	0.53
Be	1.99	0.91	0.330	2.93	0.58
B	2.93	0.82		2.56	
C	3.79	0.77		4.05	
N	4.49	0.74		4.41	
O	5.21	0.70	4.401	4.75	1.10
F	5.75	0.68	0.925	4.99	1.61
Na	0.70	1.54	0.763	1.74	0.78
Mg	1.56	1.38	0.349	2.60	1.03
Al	2.22	1.26		3.10	
Si	2.84	1.17		3.51	
P	3.43	1.10		3.85	
S	4.12	1.04	0.657	4.22	1.70
Cl	4.93	0.99	1.191	4.62	2.18
K	0.42	1.96	0.956	1.35	1.00
Ca	1.22	1.74	0.550	2.30	1.19
Zn	2.98			3.58	
Ga	3.28			3.77	
Ge	3.59	1.22		3.94	
As	3.90	1.19		4.11	
Se	4.21	1.16	0.665	4.27	1.83
Br	4.53	1.14	1.242	4.43	2.38
Rb	0.36	2.16	1.039	1.25	1.12
Sr	1.06	1.91	0.429	2.14	1.48
Ag	2.59	1.50	0.208		1.29
Cd	2.84	1.46	0.132	3.35	1.33
Sn	3.09	1.40		3.16, 3.66	
Sb	3.34	1.38		3.80	
Te	3.59	1.35	0.692	3.94	2.04
I	3.84	1.33	1.384	4.08	2.71
Cs	0.28	2.35	0.963	1.10	1.39
Ba	0.78	1.98	0.348	1.93	1.63
Hg	2.93			3.59	
Tl	3.02	1.48		2.85	
Pb	3.08	1.47		3.21, 3.69	
Bi	3.16	1.46		3.74	

* Sanderson's electronegativity.

† Non-polar covalent radii.

‡ Constant in equation (2.29) relating size to partial charge.

§ Charge in electronegativity on acquiring unit charge.

¶ Radii calculated for singly charged ions.

Sandersons model – Partial charge

Partial charge is the ratio of change in electronegativity undergone by an atom on bond formation to the change it would have undergone on becoming completely ionic with charge + or -1

A point of reference is necessary.
The bonds in NaF is 75% ionic.

The change in electronegativity on acquiring a + or -1 charge is ΔS_c:

$$\Delta S_c = 2.08\sqrt{S}$$

Partial charge can then be defined as:

$$\delta = \frac{\Delta S}{\Delta S_c} \qquad \Delta S = S - S_b$$

Example: BaI$_2$

$S_{Ba} = 0.78$ $\qquad \Delta S_c^{Ba} = 1.93$

$S_I = 3.84$ $\qquad \Delta S_c^{I} = 4.08$

$Sb = \sqrt[3]{(0.78*3.84*3.84)} = 2.26$

$\Delta S_{Ba} = 2.26 – 0.78 = 1.48$

$\Delta S_I = -3.84 + 2.26 = -1.58$

$$\delta = \frac{\Delta S_{Ba}}{\Delta S_c^{Ba}} = \frac{1.48}{1.93} = 0.78 \qquad Ba^{+0.78}$$

$$\delta = \frac{\Delta S_I}{\Delta S_c^{I}} = -\frac{1.58}{4.08} = -0.39 \qquad I^{-0.39}$$

Atomic radius can be calculated from: $r = r_c - B\delta$

	Ba	I
r_c	1.98 Å	1.33 Å
B	0.348	1.384

r_{Ba} = 1.98 Å – 0.348*0.78 Å = 1.71 Å

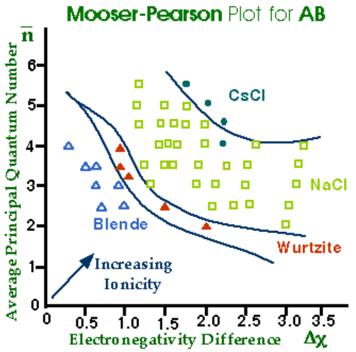
r_I = 1.33 Å + 1.384*0.39 Å = 1.87 Å

Ba-I = 3.58 Å, Observed: 3.59 Å!

Mooser – Pearson plots and ionicities

The radius ratio is unsatisfactory in prediction of structure type.

Alternative: Plot the -
Average principal quantum number vs. **Difference in electronevativity**



Huger ions with large Dx gives ionic structures.

Smaller atoms tend to have directional bonding.

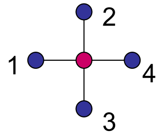
Bond valence and bond length

Valence bond theory is easily adaptable to *molecules*.

An approach for crystalline solids is to introduce *bond valence (bv)*.

The sum of *bv* for all bonds to an atom must equal the *valence* of that atom. -> *the valence sum rule.*

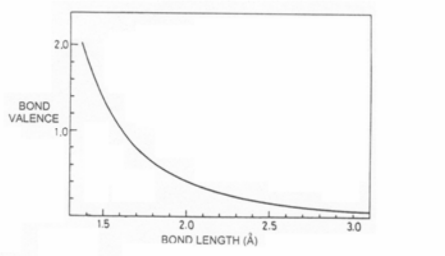
$$V_i = \sum_j bv_{ij}$$



The *bv* is found empirically from other structures and vary with bond length

Each bond is treated as an individual

$$b_{ij} = \left(\frac{R_0}{R}\right)^N$$

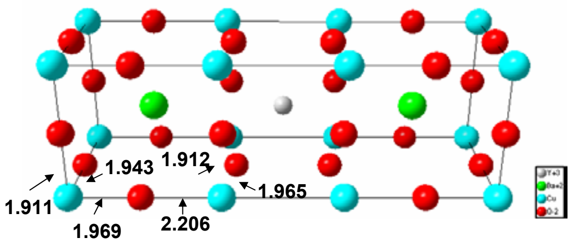


Bond valence and bond length

The bond valence scheme van be used to:

- **a) Check the correctness of a proposed structure.**
- **b) Locate hydrogen atoms for structures determined by X-ray diffraction**
- **c) Distinguish between Al^{3+} and Si^{4+} in aluminosoilicates.**

Bond valence and bond length, example YBCO



What is the oxidation state for Cu?

$$V_{Cu} = \sum_{j=1}^{6} b_{Cu,j} = \sum_{J=1}^{6} c\left(\frac{R_0}{R_{Cu,j}}\right)^N$$

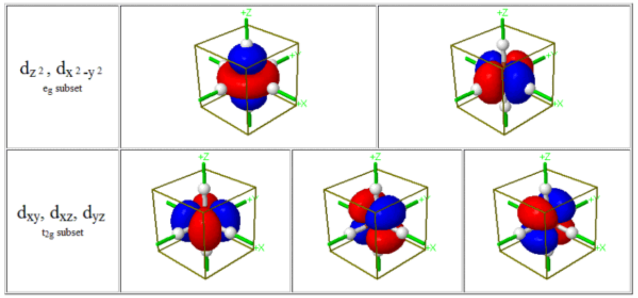
For Cu:
c = 0.333; R_0=206.8 pm ; N=5.4

$V_{Cu(1)}$ = 2*0.510+2*0.466+2*0.434 = 2.82

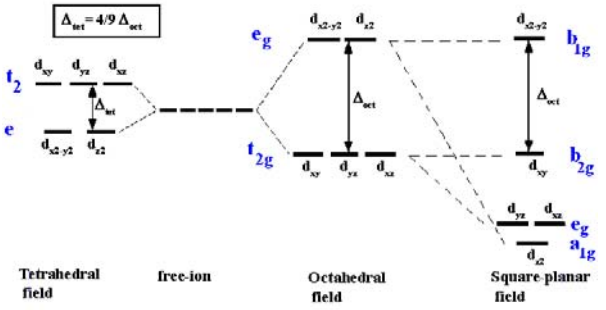
$V_{Cu(2)}$ = 2*0.509+2*0.439+1*0.235 = 2.13

$Y^{3+}Ba^{2+}{}_2Cu^{?}{}_3O_7$ leads to a Cu average of 2.33

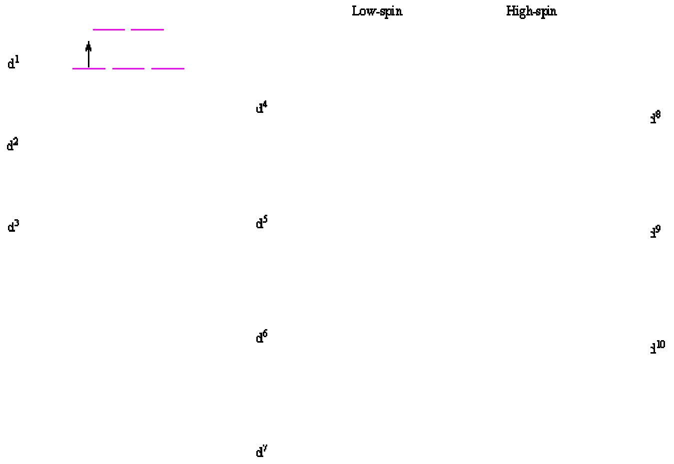
Non-bonding electron effects, Crystal field theory



Crystal field d orbital splitting diagrams for common stereochemistries.

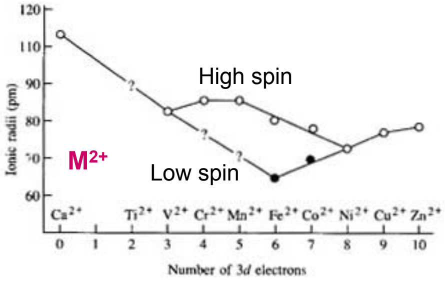


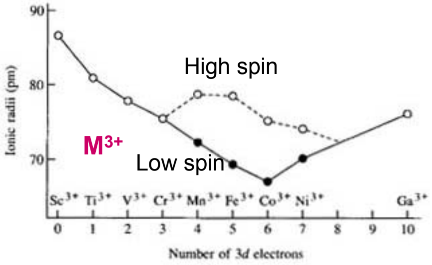
Non-bonding electron effects, Crystal field theory



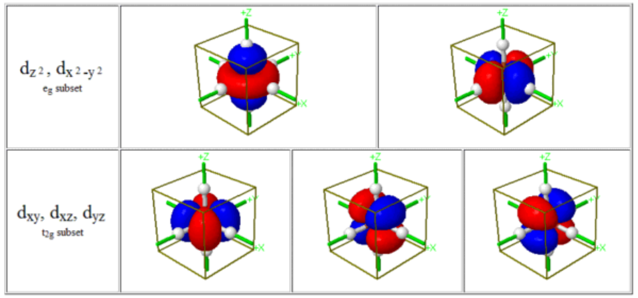
Non-bonding electron effects, Crystal field theory

Ionic Radii. For a given oxidation state, the ionic radius decreases steadily on going from left to right in a transition series.
Populating antiboding orbitals (i.e. filling the e_g levels in an octahedron) leads to an increase in ionic radius and to weaker bonds. Therefore, the ionic radius depends on the spin state of the metal (i.e. high spin or low spin).



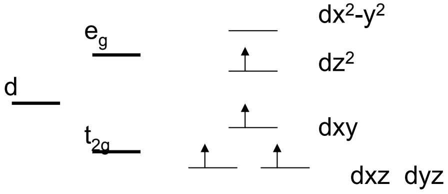


Non-bonding electron effects, Jahn-Teller

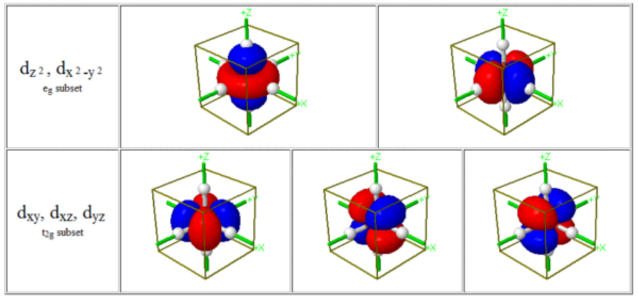


d^4 (HS)

Mn3+ (HS)

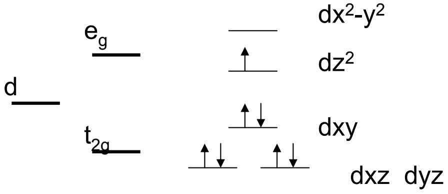


Non-bonding electron effects, Jahn-Teller

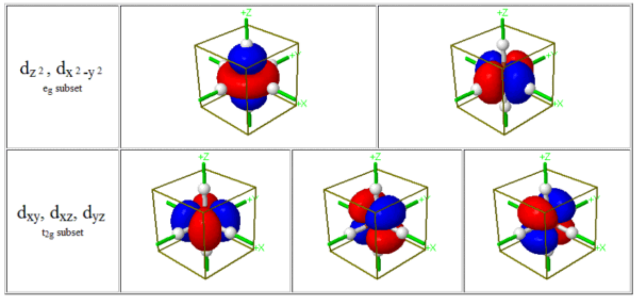


d^7 (LS)

Ni3+ (LS)

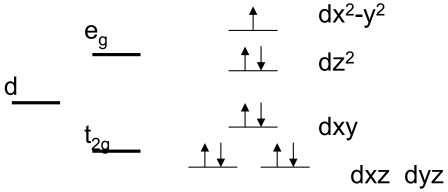


Non-bonding electron effects, Jahn-Teller

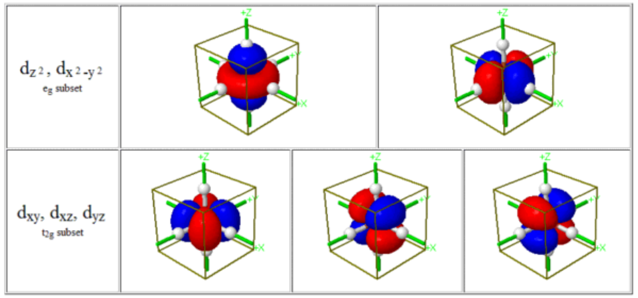


d^9

CuCl2

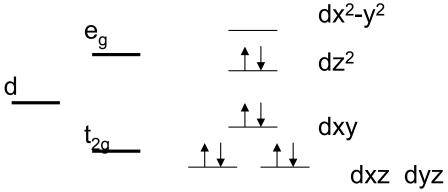


Non-bonding electron effects, d^8



d^8

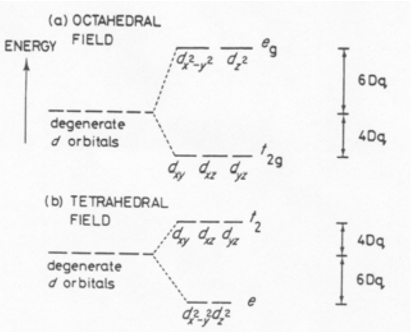
PdO, PtO



Crystal field stabilization

Low – spin $\Delta_{cryst.field} > P$
High – spin $\Delta_{cryst.field} < P$

Δ(5d) > Δ(4d) > Δ(3d)
low spin **high spin**



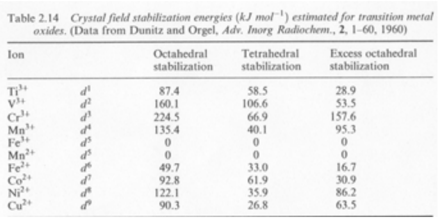


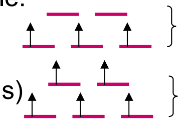
Table 2.14 *Crystal field stabilization energies (kJ mol⁻¹) estimated for transition metal oxides.* (Data from Dunitz and Orgel, *Adv. Inorg Radiochem.*, **2**, 1–60, 1960)

Ion		Octahedral stabilization	Tetrahedral stabilization	Excess octahedral stabilization
Ti^{3+}	d^1	87.4	58.5	28.9
V^{3+}	d^2	160.1	106.6	53.5
Cr^{3+}	d^3	224.5	66.9	157.6
Mn^{3+}	d^4	135.4	40.1	95.3
Fe^{3+}	d^5	0	0	0
Mn^{2+}	d^5	0	0	0
Fe^{2+}	d^6	49.7	33.0	16.7
Co^{2+}	d^7	92.8	61.9	30.9
Ni^{2+}	d^8	122.1	35.9	86.2
Cu^{2+}	d^9	90.3	26.8	63.5

Octahedric field: Crystal field stabilization

$$= \frac{\Delta}{10}\left[4n_{t2g} - 6n_{eg}\right]$$

Example:

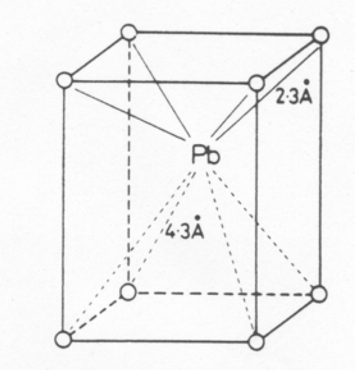


V^{2+} Δ CFSE = Δ/10[4*3-0] = 1.2Δ

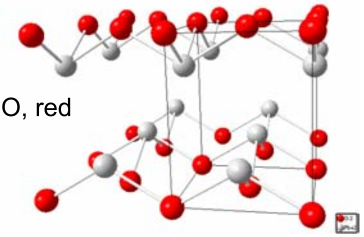
Mn^{2+} (hs) Δ CFSE = Δ/10[4*3-6*2] = 0

Non-bonding electron effects, Inert pair effect

Heavy p-group elements **(Tl, Sn, Pb, Sb)** commonly show valence two less than group valence.



PbO, red



Factors determining the structure

Size

r_M/r_X CN = 2,4,6,8…

Bonding type

Ionic	CN	**Covalent**	**Metallic**
MX	1	Directional dependant	dense packed
MX2	2	bonds, hybridization	structures
MX3	3		
..	..	sp^3 tetrahedra	tetr. holes
..	..	d^2sp^3 octahedra	oct. holes
MXn	n		trig. holes
			trig. bipyr.

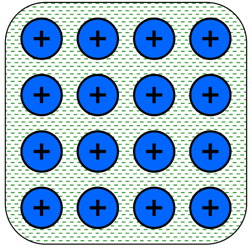
polyhedra

energetical ordering

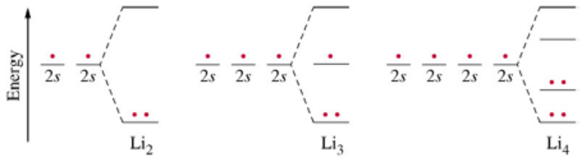
Electronical effects such as 'lone pairs', ligand field stabilizations

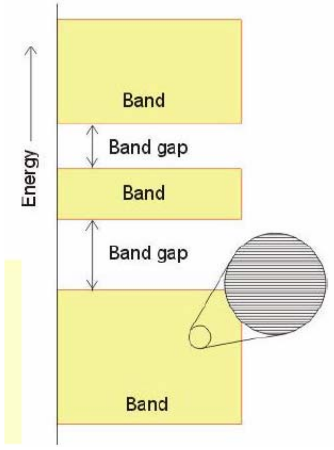
Crystalline materials show a range of different bond types:

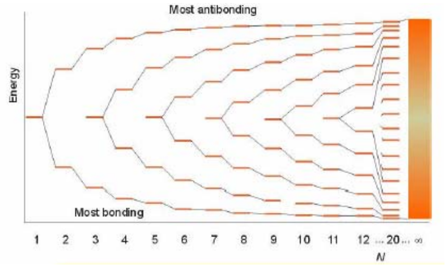
Metal bonding

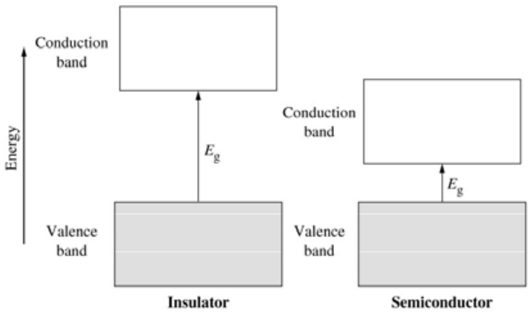


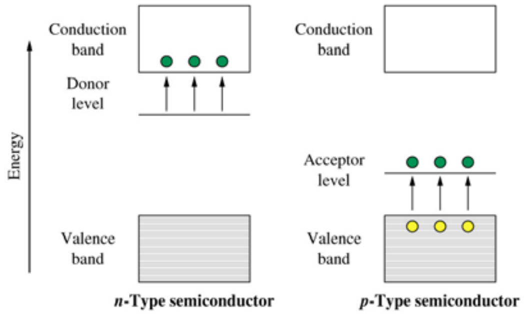
Metallic bonding











Broadening of atomic orbital into energy bands

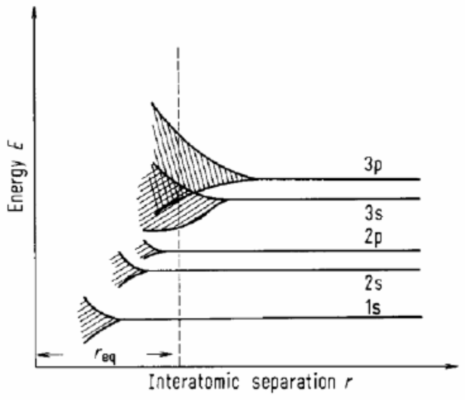
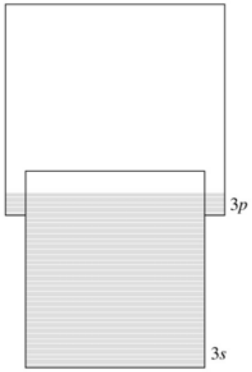


Figure 1.7(b)
ELECTRONIC ENERGY STATES FOR Mg

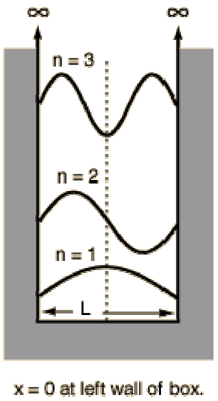
The broadening is dependent on the orbital overlap

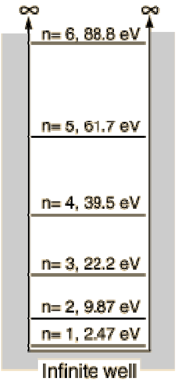
Will Mg ([Ne]$3s^2$) be a metal?

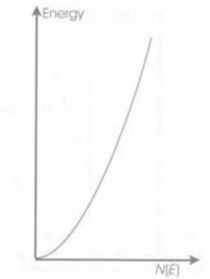


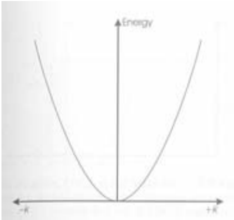
Free electron gas

The electrons are free to move through the solid as if it were an electron gas in a container determined by the outer perimeter of the solid.

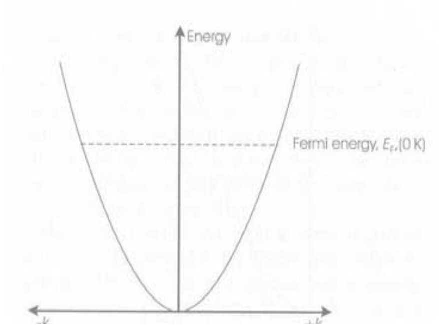


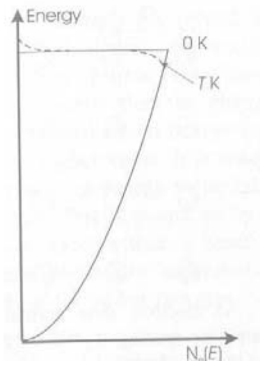


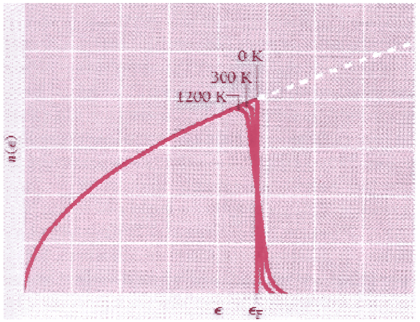




The Fermi energy

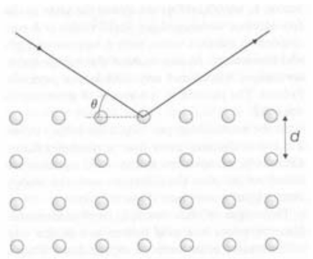






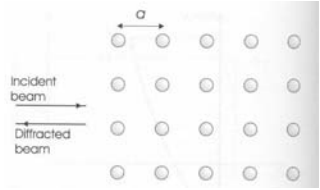
Brillouin zones

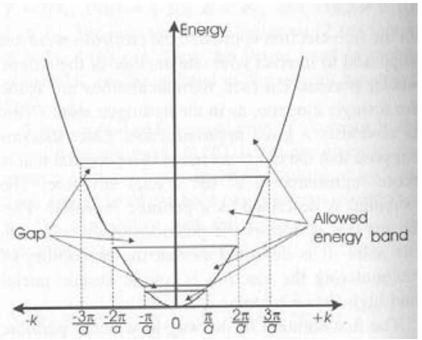
Moving electrons do interact with the atomic nucleus!



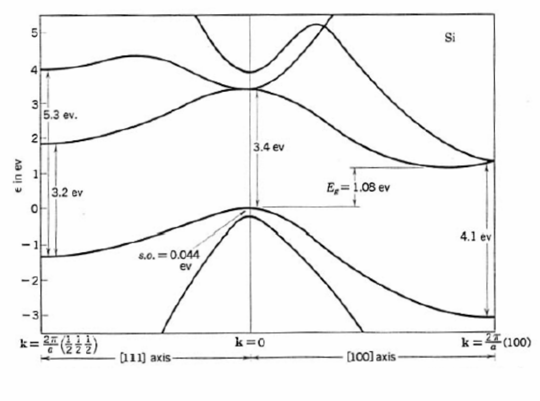
$$n\lambda = 2d\sin\theta = \frac{\pi n}{2\boldsymbol{k}}$$

$$\boldsymbol{k} = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}, \pm\frac{4\pi}{a}, \ldots$$





Brillouin zones



BAND STRUCTURE OF SILICON

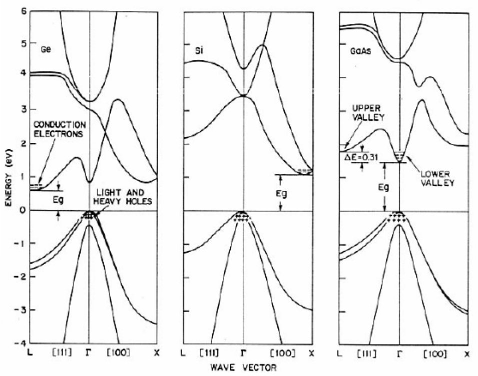
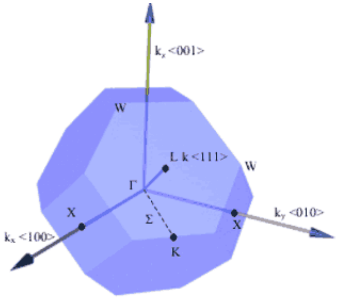


Figure 1.12
ENERGY-BAND STRUCTURES OF Ge, Si, and GaAs



Bands in ionic and covalent solids