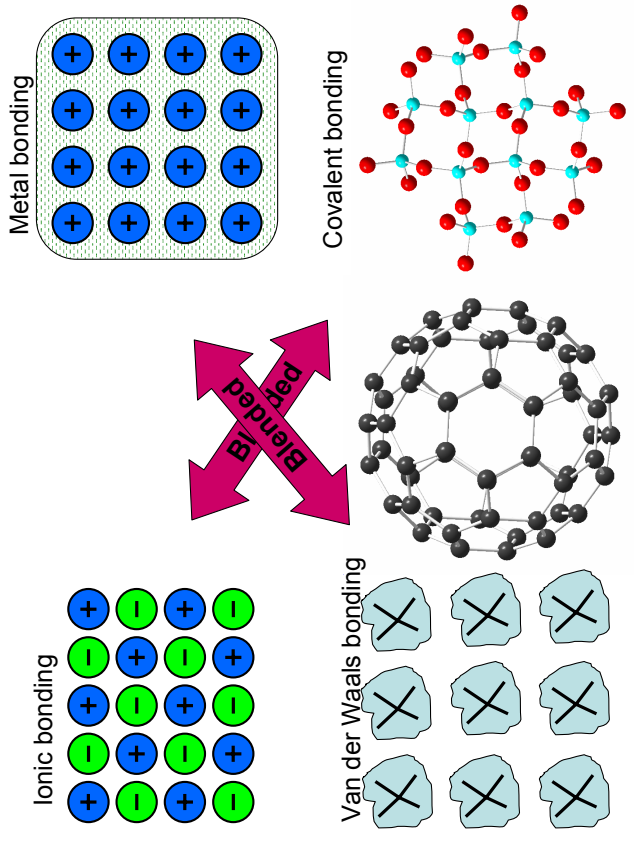
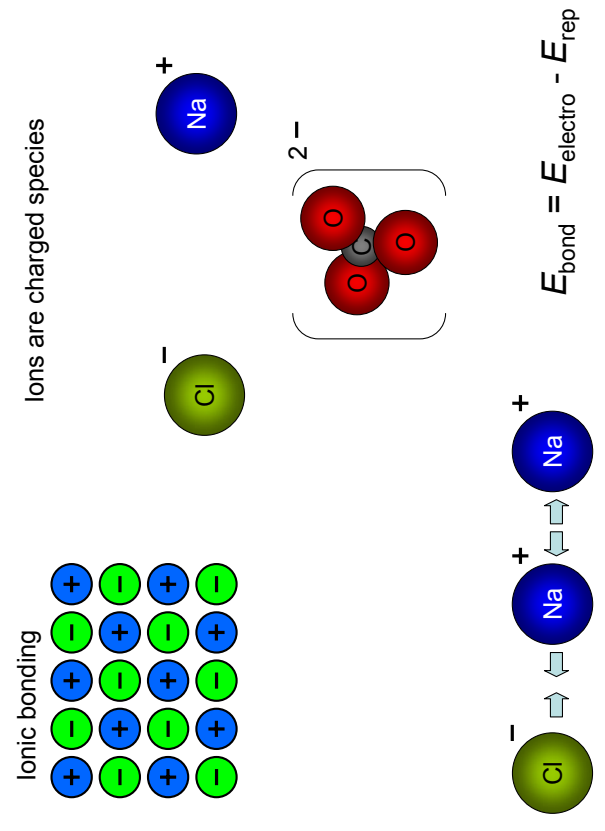


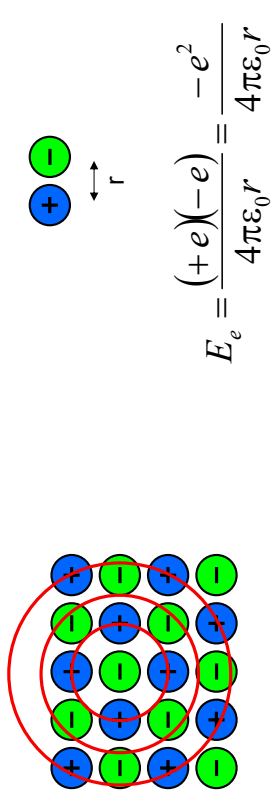
Crystalline materials show a range of different bond types:



# Kap. 2 Chemical bonding



## Madelung energy



Like charges repel each other

$$E_e = \left( \frac{-e^2}{4\pi\epsilon_0 r} \right) \times (\text{Geometry}) \times (\text{ionic charge})$$

$$E_e = N_A \left( \frac{-e^2}{4\pi\epsilon_0 r} \right) \alpha Z^2$$

## Ionic structures – Lattice energy - NaCl

Na<sup>+</sup> is surrounded by 6 Cl<sup>-</sup>

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

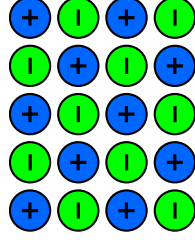
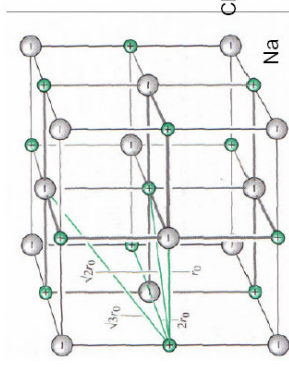
Na<sup>+</sup> is surrounded by  $\sqrt{12}$  next neighbour Na<sup>+</sup> at  $\sqrt{2}r$

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

Na<sup>+</sup> is surrounded again by 8 Cl<sup>-</sup> at  $\sqrt{3}r$

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

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



## Ionic bonding

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

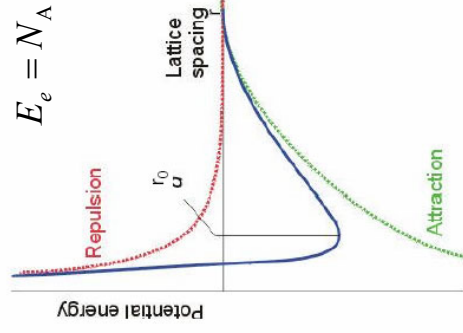
Purely ionic bonding rarely occurs,  
a net charge of more than +1 are unlikely

Useful as starting point to visualize structures

**For visualization, one needs a set of ionic radii**

## Madelung energy

$$E_e = N_A \left( \frac{e^2}{4\pi\epsilon_0 r} \right) \alpha (Z_M Z_X)^2 \frac{m+n}{2}$$



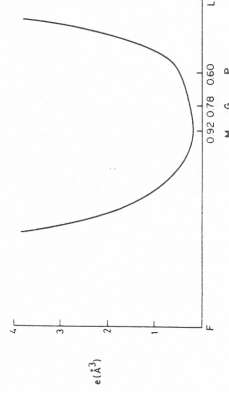
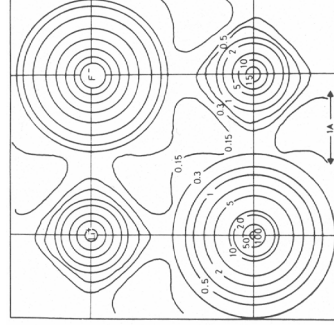
**Table 2.1** Reduced Madelung constants,  $\alpha$

Structure	Formula	Example	$\alpha$
Halite	$M^+X^-$	NaCl	1.748
Caesium chloride	$M^+X^-$	CsCl	1.763
Sphalerite	$M^{2+}X^{2-}$	ZnS	1.638
Wurtzite	$M^{2+}X^{2-}$	ZnO	1.641
Fluorite	$M^{2+}X^{2-}$	CaF <sub>2</sub>	1.68
Rutile	$M^+X_2^-$	TiO <sub>2</sub>	1.60

Ions also show repulsive forces when they are too close!

## Ionic radii

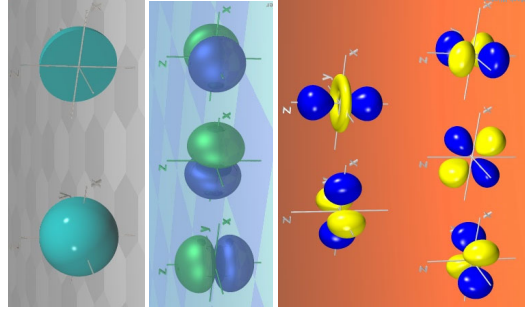
The ionic radii from Pauling and Goldschmidt have been revised due to information from present high-quality X-ray diffraction work.



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

## Ionic radii

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



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

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

Cation radius decrease with increasing oxidation state,  $\text{V}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ ,  $\text{V}^{5+}$

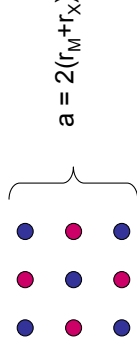
Cation radius increase with coordination number, CN = 4 vs. CN = 6

Lanthanide contraction and transition contraction due to poor shielding

s  
p  
d

Poorer shielding

## Ionic radii



Based on empirical values

Consistent set of values

The values are dependent on:

Coordination number  
Type of coordination polyhedra  
Oxidation number

### Metallic oxides

Set of radii dependent on type of orbitals used??

## Ionic structures – general principles

1. Ions are in fact charged, elastic and polarizable spheres
2. Geometrical arrangement  
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 =  $\Sigma$  electrostatic bond strength

## Ionic structures – bond strength

Force between two ions: 
$$F = \frac{(Z_+e)(Z_-e)}{r^2}$$

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

Electrostatic bond strength:

The charge is divided among the number of bonds.

$$\sum_n^m = x$$

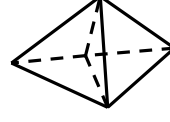
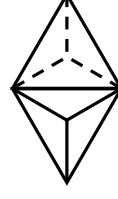
The sum of ebs on an ion must balance the charge

Spinel:  $\text{MgAl}_2\text{O}_4$

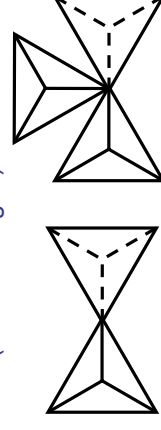
Octahedral  $\text{Al}^{3+} \rightarrow \text{ebs} = 3/6 = 1/2$

Tetrahedral  $\text{Mg}^{2+} \rightarrow \text{ebs} = 2/4 = 1/2$

→ Oxygen tetrahedrally surrounded by 3 Al and 1 Mg:  
 $\Sigma \text{ebs}(3\text{Al}^{3+} + 1\text{Mg}^{2+}) = 2$



$\text{SiO}_2$  ?



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

## Ionic structures – bond strength

Example:

NaCl type structure, Na<sup>+</sup> in octahedra holes → CN(Na<sup>+</sup>) = 6

CN (Cl<sup>-</sup>)?

CN (Cl<sup>-</sup>) = 1/1\*6 = 6

CaF<sub>2</sub> type structure, F<sup>-</sup> in tetrahedra holes → CN(F<sup>-</sup>) = 4

CN (Ca<sup>2+</sup>)?

CN (Ca<sup>2+</sup>) = 2/1\*4 = 8

Rutil type structure (TiO<sub>2</sub>); CN(Ti<sup>4+</sup>) = 6

CN (O<sup>2-</sup>)?

CN (O<sup>2-</sup>) = 1/2\*6 = 3

## Ionic structures – bond strength

Table 2.1 *Electrostatic bond strengths of some cations*

Cation	Coordination number(s)	<i>ebs</i>
Li <sup>+</sup>	4, 6	$\frac{1}{4}, \frac{1}{6}$
Na <sup>+</sup>	6, 8	$\frac{1}{6}, \frac{1}{8}$
Be <sup>2+</sup>	3, 4	$\frac{1}{3}, \frac{1}{4}$
Mg <sup>2+</sup>	4, 6	$\frac{1}{4}, \frac{1}{6}$
Ca <sup>2+</sup>	8	$\frac{1}{8}$
Zn <sup>2+</sup>	4	$\frac{1}{4}$
Al <sup>3+</sup>	4, 6	$\frac{1}{4}, \frac{1}{6}$
Cr <sup>3+</sup>	6	$\frac{1}{6}$
Si <sup>4+</sup>	4	$\frac{1}{4}$
Ge <sup>4+</sup>	4, 6	$\frac{1}{4}, \frac{1}{6}$
Ti <sup>4+</sup>	6	$\frac{1}{6}$
Th <sup>4+</sup>	8	$\frac{1}{8}$

Table 2.2 *Allowed and unallowed combinations of corner-sharing oxide polyhedra*

Allowed	Example	Unallowed
2SiO <sub>4</sub> tet.	Silica	> 2SiO <sub>4</sub> tet.
1MgO <sub>4</sub> tet. + 3AlO <sub>6</sub> oct.	Spinel	3AlO <sub>4</sub> tet.
1SiO <sub>4</sub> tet. + 3MgO <sub>6</sub> oct.	Olivine	1SiO <sub>4</sub> tet. + 2AlO <sub>4</sub> tet.
8LiO <sub>4</sub> tet.	Li <sub>2</sub> O	4TiO <sub>6</sub> oct.
2TiO <sub>6</sub> oct. + 4CaO <sub>12</sub> dod.	Perovskite	
3TiO <sub>6</sub> oct.	Rutile	

## Ionic structures – bond strength

Example:

NaCl type structure, Na<sup>+</sup> in octahedra holes → CN(Na<sup>+</sup>) = 6

CN (Cl<sup>-</sup>)?

CN (Cl<sup>-</sup>) = 1/1\*6 = 6

CaF<sub>2</sub> type structure, F<sup>-</sup> in tetrahedra holes → CN(F<sup>-</sup>) = 4

CN (Ca<sup>2+</sup>)?

CN (Ca<sup>2+</sup>) = 2/1\*4 = 8

Rutil type structure (TiO<sub>2</sub>); CN(Ti<sup>4+</sup>) = 6

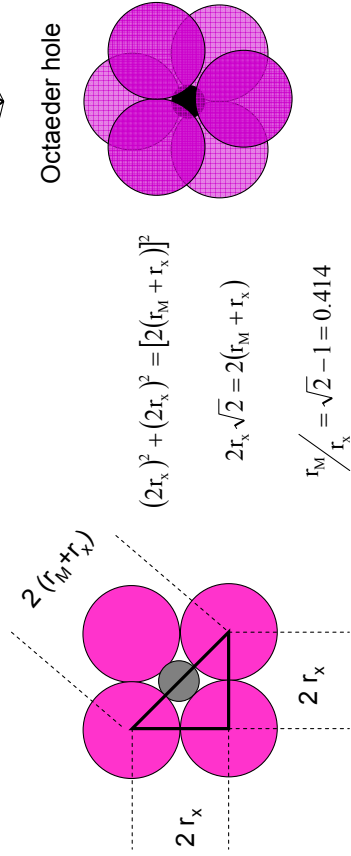
CN (O<sup>2-</sup>)?

CN (O<sup>2-</sup>) = 1/2\*6 = 3

## Ionic structures – Radius ratio

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

Consider an octahedra:



## Ionic structures – Radius ratio

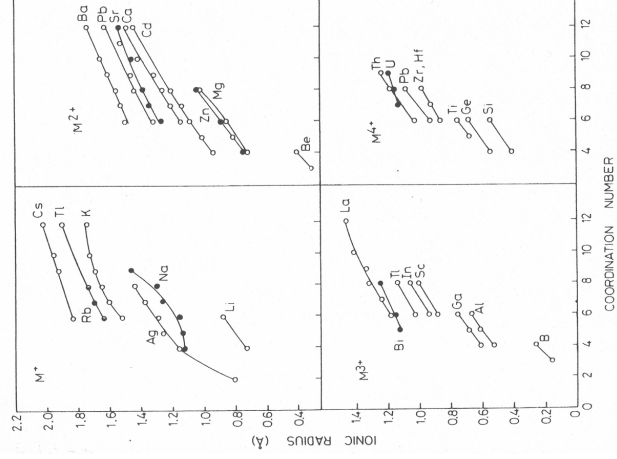


Table 2.4 *Structures and radius ratios of oxides, MO<sub>2</sub>*

Oxide	Calculated radius ratio*	Observed structure type
CO <sub>2</sub>	~0.1	Molecular (CN = 2)
SiO <sub>2</sub>	0.32	Silica (CN = 4)
GeO <sub>2</sub>	{ 0.43	{ Silica (CN = 4)
	{ 0.54	{ Rutile (CN = 6)
TiO <sub>2</sub>	0.59	Rutile (CN = 6)
SnO <sub>2</sub>	0.66	Rutile (CN = 6)
PbO <sub>2</sub>	0.73	Rutile (CN = 6)
HfO <sub>2</sub>	{ 0.68	{ Fluorite (CN = 8)
	{ 0.77	{ Fluorite (CN = 8)
CeO <sub>2</sub>	{ 0.75	{ Fluorite (CN = 8)
	{ 0.88	{ Fluorite (CN = 8)
ThO <sub>2</sub>	0.95	Fluorite (CN = 8)

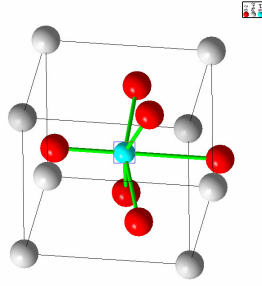
\* Since cation radii vary with CN, Fig. 2.3, radius ratios may be calculated for different CNs. The CNs used here are shown in parentheses. Calculations are based on  $r_{O^{2-}} = 1.26 \text{ \AA}$ .

## Ionic structures – Radius ratio, borderline

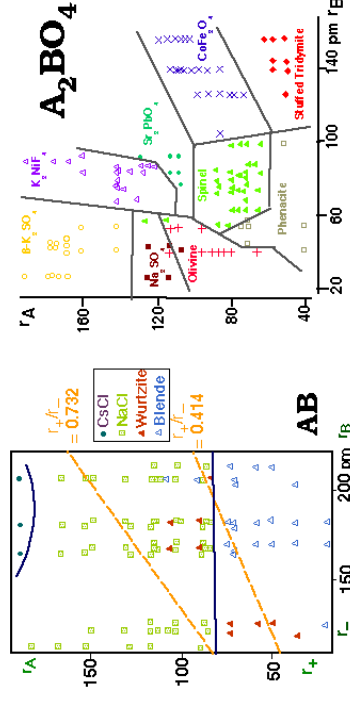
GeO<sub>2</sub> has polymorphs where Ge may have CN = 4 or 6

Al<sup>3+</sup> may be found in octahedral environments for spinel MgAl<sub>2</sub>O<sub>4</sub>, but also in tetrahedras for silicates.

Ti in PbTiO<sub>3</sub> is slightly too small and may rattle. Displaced by 0.2 Å.



## Ionic structures – Radius ratio



## Ionic structures – Lattice energy



Sublimation energy

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

Force between two ions

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

Coulombic potential energy

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

n = 5...12 Short-range repulsive forces

## Ionic structures – Lattice energy

Attractive electrostatic forces

$$U = -\frac{Ae^2Z_+Z_-}{r} + BNe^{-r/\rho} - CNr^{-6} + 2.25Nh\nu_{\text{Omax}}$$

Van der Waals attractive forces

Born repulsive term

Zero point energy

Typical values for the terms, in kJ mol<sup>-1</sup>, are (from Greenwood):

Substance	$NAe^2Z_+Z_-r^{-1}$	$BNe^{-r/\rho}$	$CNr^{-6}$	$2.25Nh\nu_{\text{Omax}}$	$U$
NaCl	-859.4	98.6	-12.1	7.1	-765.8
MgO	-4631	698	-6.3	18.4	-3921

## 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 <sub>2</sub>	2.519	0.84	8:4
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	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 Kapustinskii equation:

It is possible to apply the equation for lattice calculations of crystals with polyatomic ions (e.g. KNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ...).

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

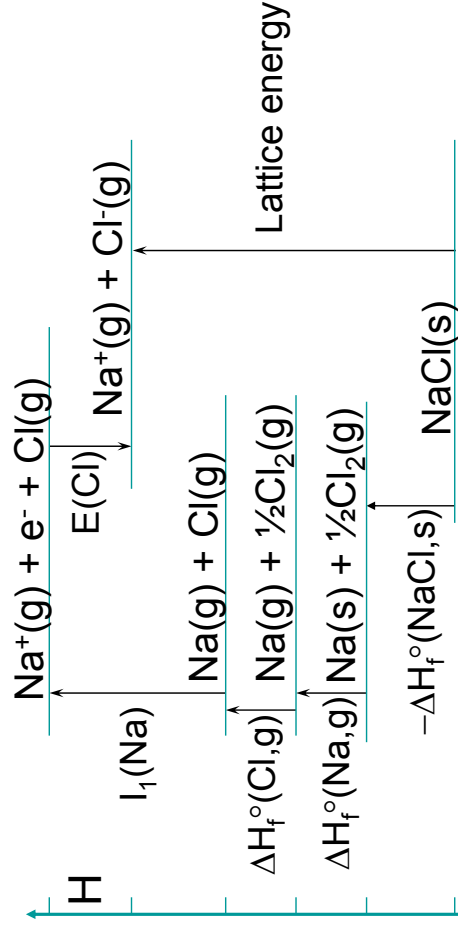
Table 1.13 Thermochemical radii of polyatomic ions\*

Ion	pm	Ion	pm	Ion	pm
NH <sub>4</sub> <sup>+</sup>	151	ClO <sub>4</sub> <sup>-</sup>	226	MnO <sub>4</sub> <sup>2-</sup>	215
Me <sub>4</sub> N <sup>+</sup>	215	CN <sup>-</sup>	177	O <sub>3</sub> <sup>2-</sup>	144
PH <sub>4</sub> <sup>+</sup>	171	CNS <sup>-</sup>	199	OH <sup>-</sup>	119
AlCl <sub>4</sub> <sup>-</sup>	281	CO <sub>3</sub> <sup>2-</sup>	164	PF <sub>6</sub> <sup>-</sup>	282
BF <sub>4</sub> <sup>-</sup>	218	IO <sub>3</sub> <sup>-</sup>	108	PtCl <sub>6</sub> <sup>2-</sup>	299
BH <sub>4</sub> <sup>-</sup>	179	N <sub>3</sub> <sup>-</sup>	181	PtBr <sub>6</sub> <sup>2-</sup>	328
BrO <sub>3</sub> <sup>-</sup>	140	NCO <sup>-</sup>	189	PU <sub>6</sub> <sup>3-</sup>	328
CH <sub>3</sub> COO <sup>-</sup>	148	NO <sub>2</sub> <sup>-</sup>	178	SO <sub>3</sub> <sup>2-</sup>	244
ClO <sub>3</sub> <sup>-</sup>	157	NO <sub>3</sub> <sup>-</sup>	165	SeO <sub>4</sub> <sup>2-</sup>	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.

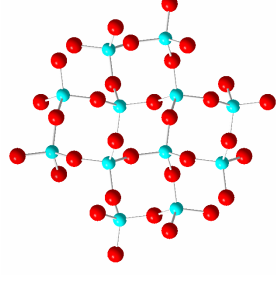
## Born Haber cycle

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



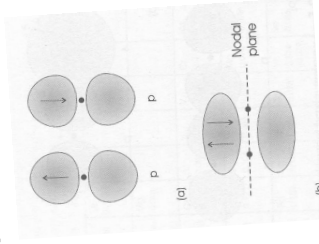
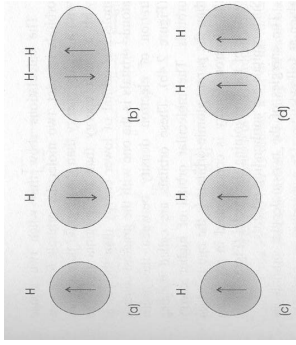
Crystalline materials show a range of different bond types:

Covalent bonding

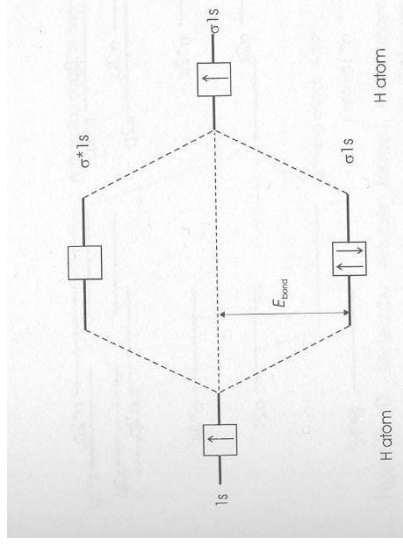
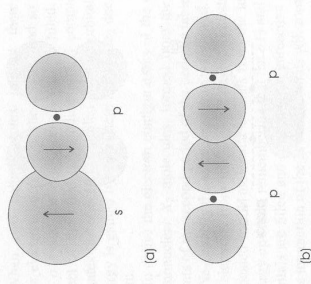
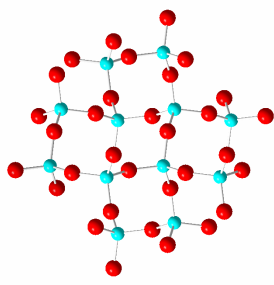




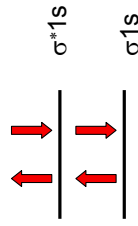
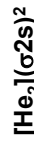
Covalent bonding is a result of orbital overlaps  
Spins in overlapping orbitals must be antiparallel!



Covalent bonding

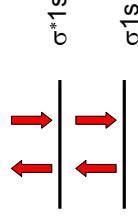
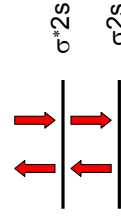


**Li<sub>2</sub>**



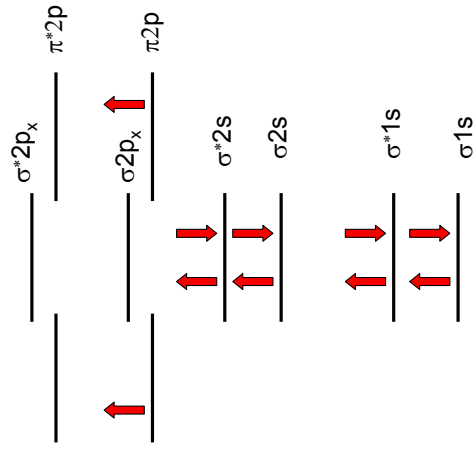
Bond length = 0.267 nm  
Bond energy = 101 kJ/mol

**Be<sub>2</sub>**



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

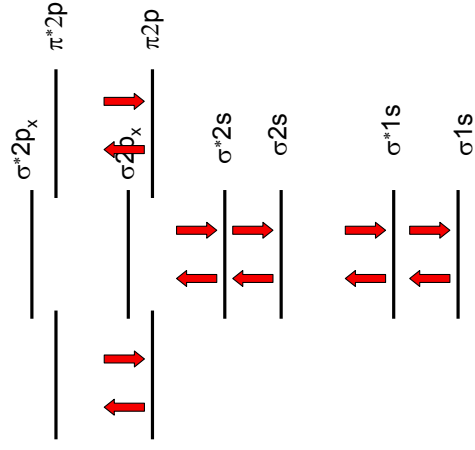
# B<sub>2</sub>



$$[\text{Be}_2](\pi 2p)^2$$

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

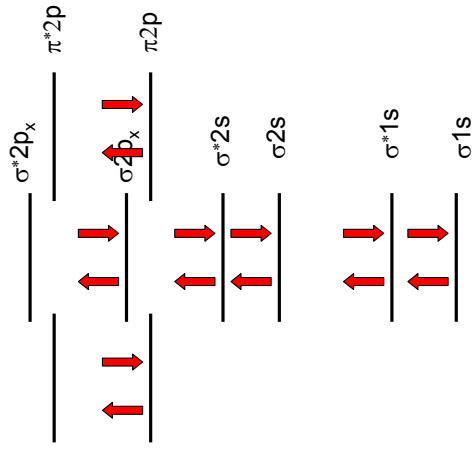
# C<sub>2</sub>



$$[\text{Be}_2](\pi 2p)^4$$

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

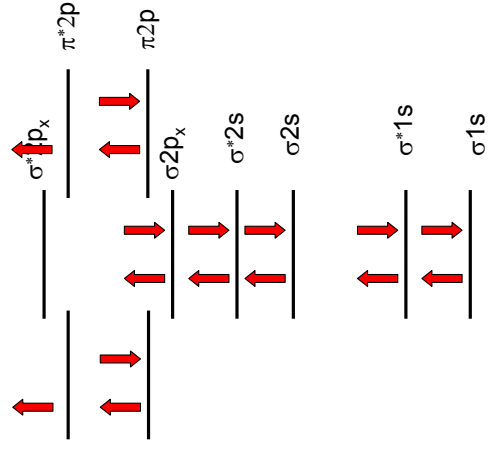
# N<sub>2</sub>



$$[\text{Be}_2](\pi 2p)^4(\sigma 2p_x)^2$$

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

# O<sub>2</sub>

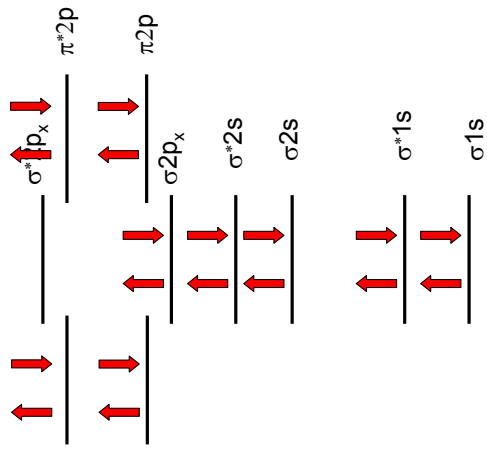


$$[\text{Be}_2](\pi 2p)^4(\sigma 2p_x)^2(\pi^* 2p)^2$$

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

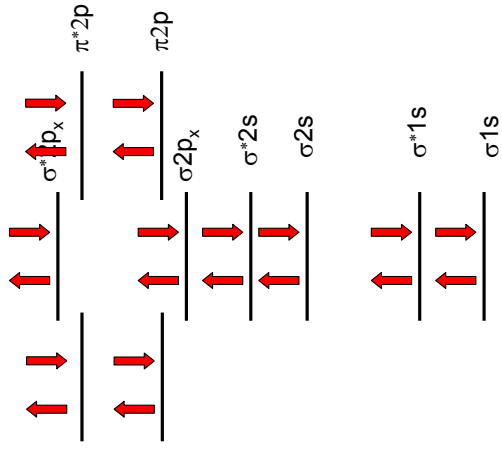


# F<sub>2</sub>



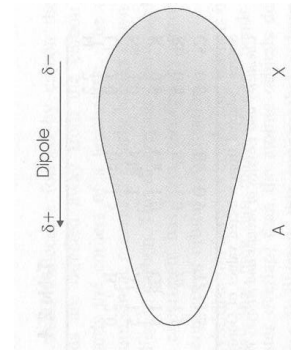
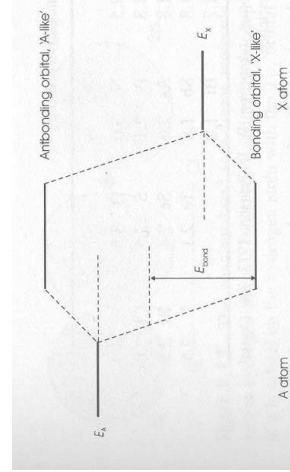
Bond length = 0.142 nm  
Bond energy = 254 kJ/mol

# Ne<sub>2</sub>

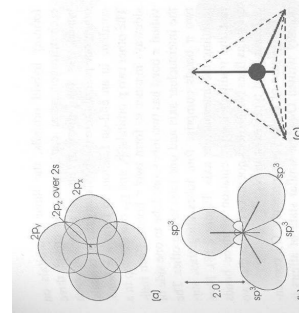
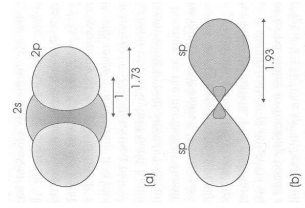
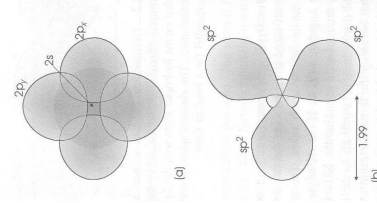
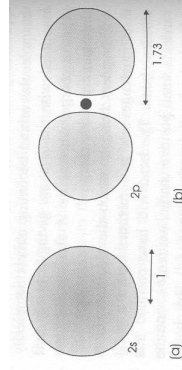


Bond length = 0.142 nm  
Bond energy = 254 kJ/mol

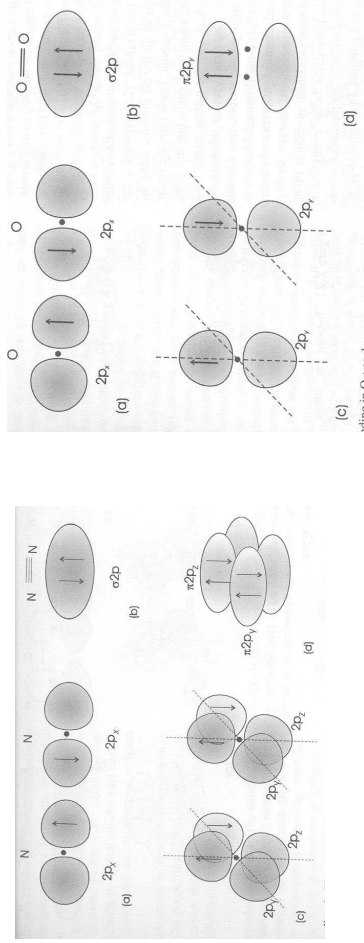
## Bonding between unlike atoms



## Orbital hybridisation

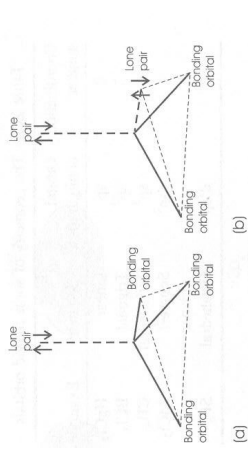


## Multiple bonds

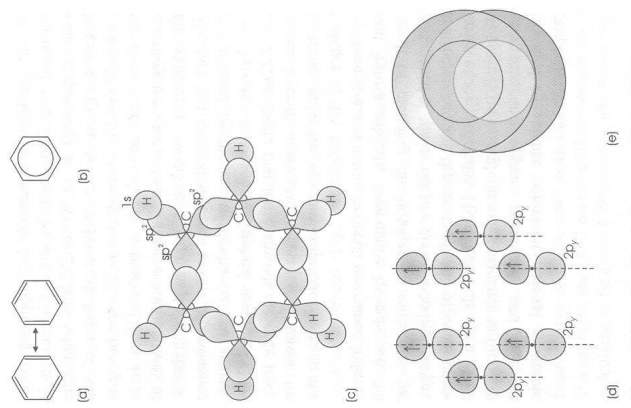


**Table 2.5** The geometry of some hybrid orbitals

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	$SF_6$



## Resonance



## Partial covalent bonding

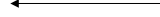
Covalent bonding occurs when the outer electronic charge density on an anion is polarized towards and by a neighbouring cation.

The net effect is electron density between the atoms.

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

**AlF<sub>3</sub>** ReO<sub>3</sub> related ionic solid  
**AlCl<sub>3</sub>** Layered polymeric structure  
**AlBr<sub>3</sub>** Molecular Al<sub>2</sub>Br<sub>6</sub> dimer  
**AlI<sub>3</sub>** Molecular Al<sub>2</sub>I<sub>6</sub> dimer

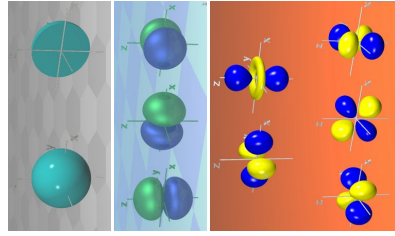
Increasing difference in electronegativity



## Sandersons model

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

### Effective nuclear charge



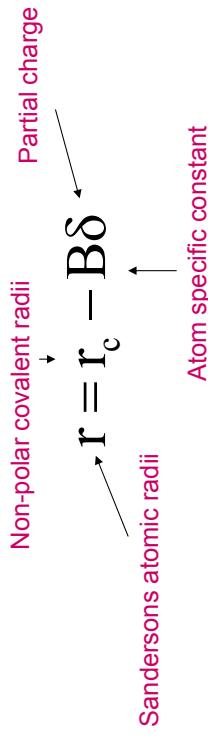
Correlations between effective nuclear charge and:

- Ionization potential
- Electron affinity
- Electronegativity  $\chi$
- 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)



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

## Sandersons model – Electronegativity

Sanderson developed a new electronegativity table (S) where:

Electron density of the atom

$$S = \frac{D}{D^a}$$

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)‡	$\Delta S_c$ §	$r_1$ (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	0.38
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	4.73	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	2.24	1.16		3.07	
Si	2.64	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	4.63	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			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	2.14	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  $\Delta S_c$ :

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

Partial charge can then be defined as:

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

## Example: $BaI_2$

$$S_{Ba} = 0.78 \quad \Delta S_{c,Ba} = 1.93$$

$$S_I = 3.84 \quad \Delta S_{c,I} = 4.08$$

$$S_b = 3 \times (0.78 \times 3.84 \times 3.84) = 2.26$$

$$\Delta S_{Ba} = 2.26 - 0.78 = 1.48$$

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

$$\delta = \frac{\Delta S_{Ba}}{\Delta S_{c,Ba}} = \frac{1.48}{1.93} = 0.78 \quad \text{Ba}^{+0.78}$$

$$\delta = \frac{\Delta S_I}{\Delta S_{c,I}} = -\frac{1.58}{4.08} = -0.39 \quad \text{I}^{-0.39}$$

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

Ba	I
1.98 Å	1.33 Å
0.348	1.384

$$r_{Ba} = 1.98 \text{ Å} - 0.348 \times 0.78 \text{ Å} = 1.71 \text{ Å}$$

$$r_I = 1.33 \text{ Å} + 1.384 \times 0.39 \text{ Å} = 1.87 \text{ Å}$$

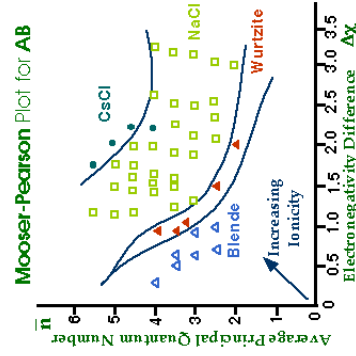
$$Ba-I = 3.58 \text{ Å}, \text{ Observed: } 3.59 \text{ Å!}$$

## Mosser – Pearson plots and ionicities

The radius ratio is unsatisfactory in prediction of structure type.

Alternative: Plot the -

**Average principal quantum number vs. Difference in electronegativity**



Huger ions with large  $\Delta\chi$  gives ionic structures.

Smaller atoms tend to have directional bonding.

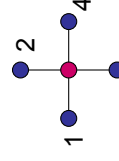
## Bond valence and bond length

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.  $\rightarrow$  *the valence sum rule*.

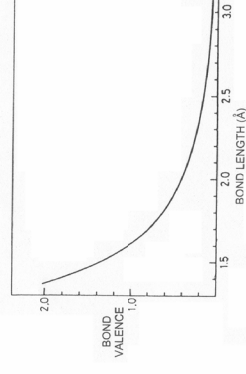
$$V_i = \sum_j bv_{ij}$$



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

Each bond is treated as an individual

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

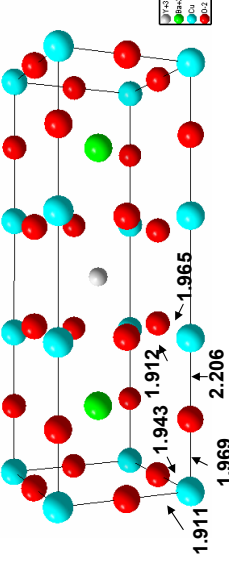


## Bond valence and bond length

The bond valence scheme can be used to:

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

## 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:

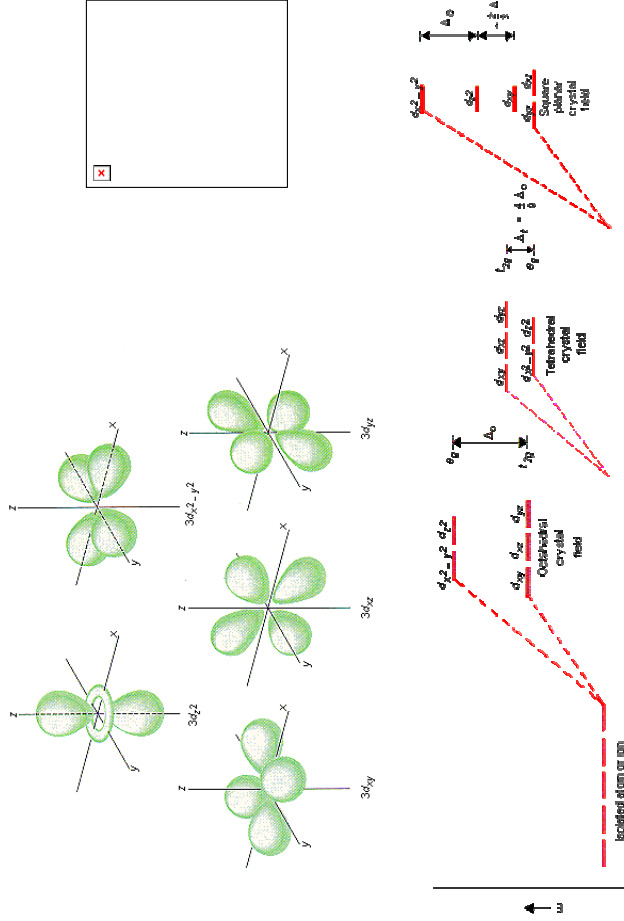
$$c = 0.333; R_0 = 206.8 \text{ pm}; N = 5.4$$

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

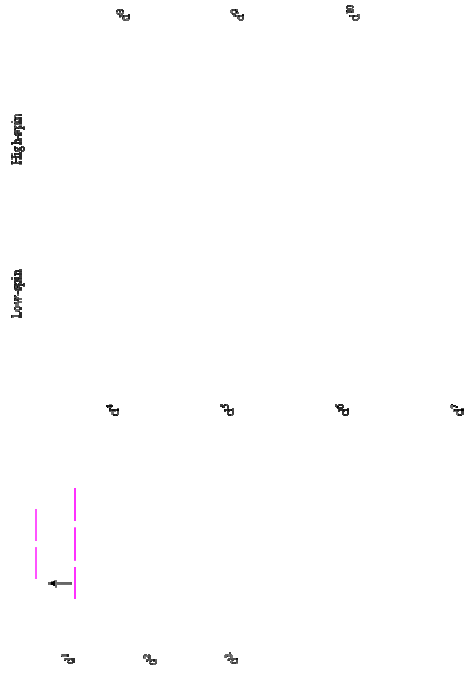
$$V_{Cu(2)} = 2 \cdot 0.509 + 2 \cdot 0.439 + 1 \cdot 0.235 = 2.13$$

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

## Non-bonding electron effects, Crystal field theory

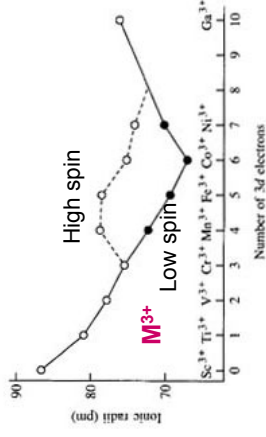
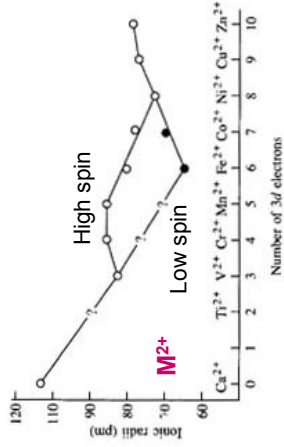


## Non-bonding electron effects, Crystal field theory

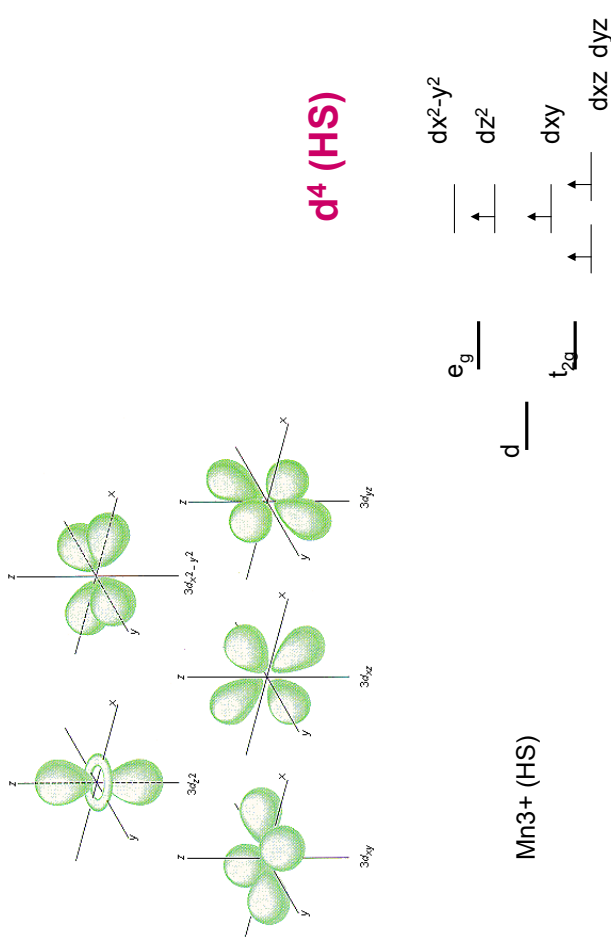


## Non-bonding electron effects, Crystal field theory

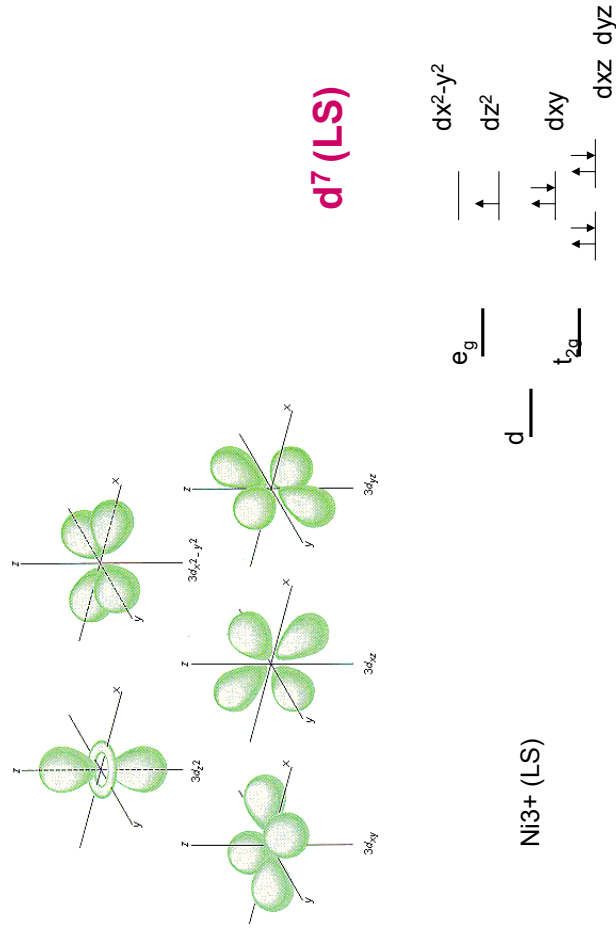
**Ionic Radii.** For a given oxidation state, the ionic radius decreases steadily on going from left to right in a transition series. Populating antibonding orbitals (i.e. filling the  $e_g$  levels in an octahedron) leads to an increase in ionic radius and to weaker bonds. Therefore, the ionic radius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



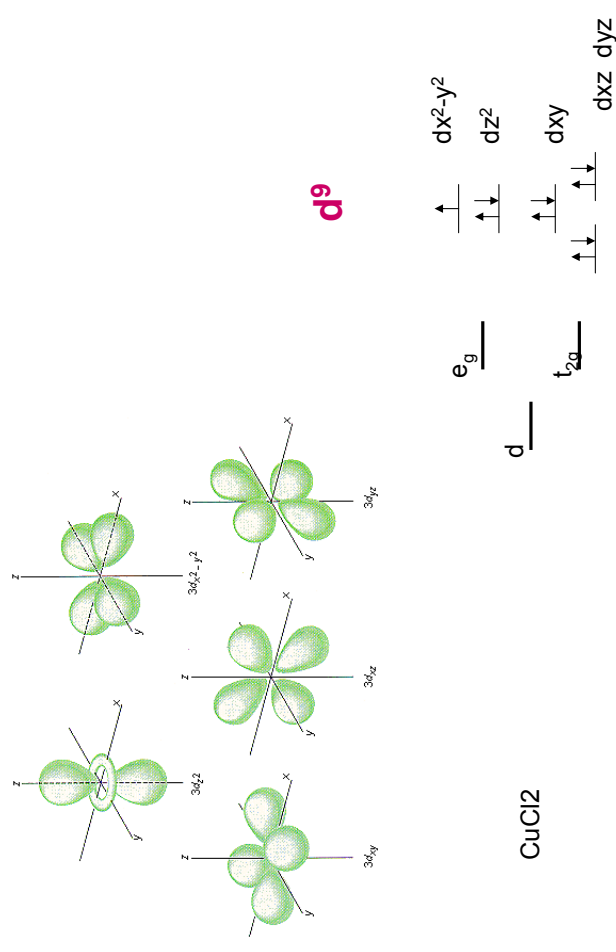
## Non-bonding electron effects, Jahn-Teller



## Non-bonding electron effects, Jahn-Teller

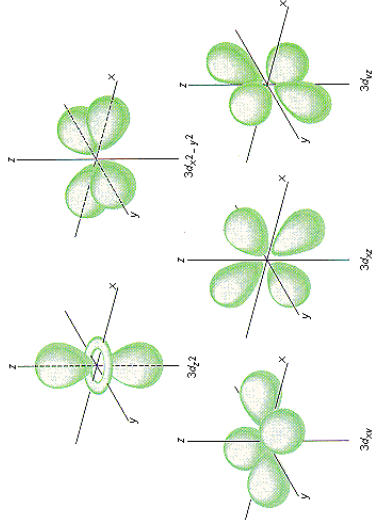


## Non-bonding electron effects, Jahn-Teller

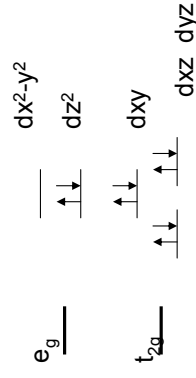




## Non-bonding electron effects, d<sup>8</sup>



PdO, PtO



## Crystal field stabilization

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

$\Delta(5d) > \Delta(4d) > \Delta(3d)$  **high spin**  
**low spin**

Octahedral field: Crystal field stabilization

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

Example:  $V^{2+}$   $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$  }  $\Delta$  CFSE =  $\Delta/10[4*3-0] = 1.2\Delta$   
 $Mn^{2+}$  (hs)  $\uparrow\uparrow \uparrow\uparrow \uparrow\uparrow \uparrow\uparrow$  }  $\Delta$  CFSE =  $\Delta/10[4*3-6*2] = 0$

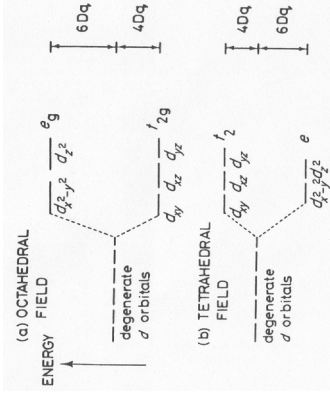
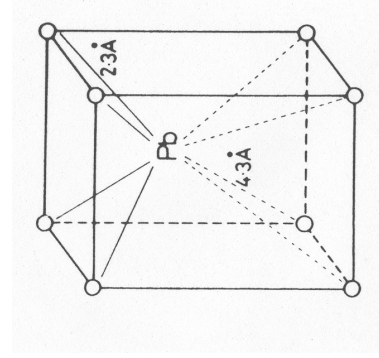


Table 2.14 Crystal field stabilization energies (kJ mol<sup>-1</sup>) estimated for transition metal oxides. (Data from Dumiz and Orgel, Adv. Inorg. Radiochem., 2, 1–60, 1960)

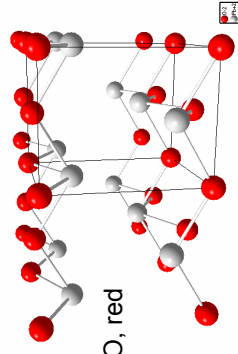
Ion	Octahedral stabilization	Tetrahedral stabilization	Excess octahedral stabilization
Ti <sup>3+</sup>	87.4	58.5	28.9
V <sup>3+</sup>	126.5	86.9	39.6
Cr <sup>3+</sup>	224.5	166.9	157.6
Mn <sup>3+</sup>	135.4	40.1	95.3
Fe <sup>3+</sup>	0	0	0
Mg <sup>2+</sup>	0	0	0
Mn <sup>2+</sup>	47	31	16.7
Co <sup>2+</sup>	92.8	61.9	30.9
Ni <sup>2+</sup>	122.1	35.9	86.2
Cu <sup>2+</sup>	90.3	26.8	63.5

## 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

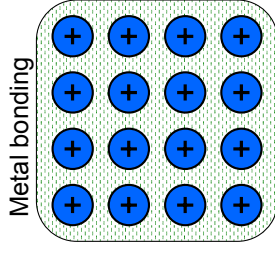
**Ionic** **Covalent** **Metallic**

CN	Directional dependant bonds, hybridization	dense packed structures
MX	sp <sup>3</sup> tetrahedra	tetr. holes
MX2	d <sup>2</sup> sp <sup>3</sup> octahedra	oct. holes
MX3		trig. holes
..		trig. bipy.
..		
MXn		
polyhedra		
energetical ordering		

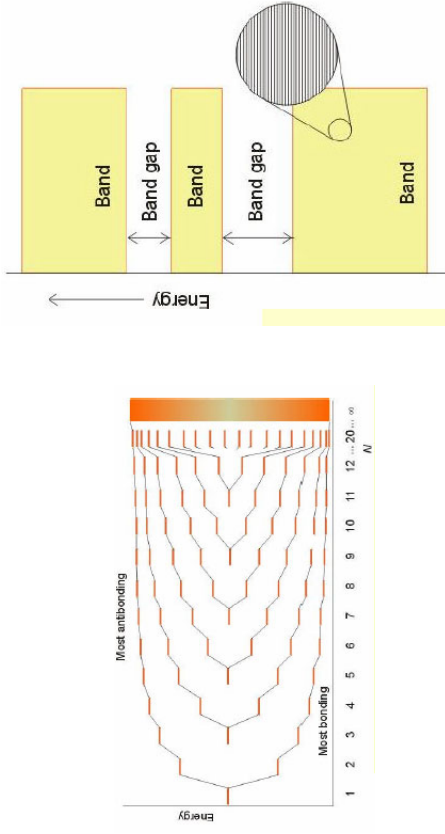
Electronical effects such as 'lone pairs', ligand field stabilizations



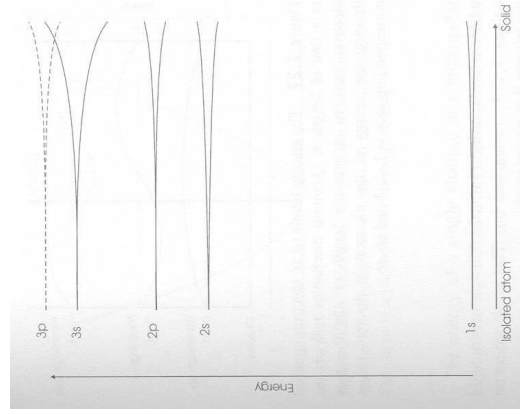
## Crystalline materials show a range of different bond types:



## Metallic bonding



## Broadening of atomic orbital into energy bands

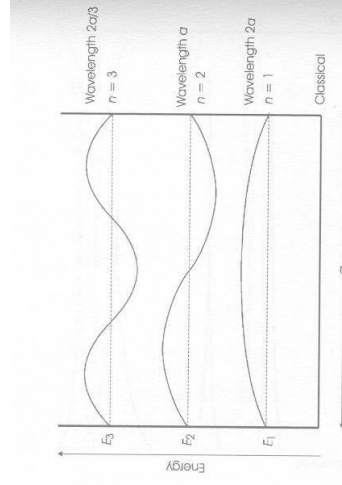
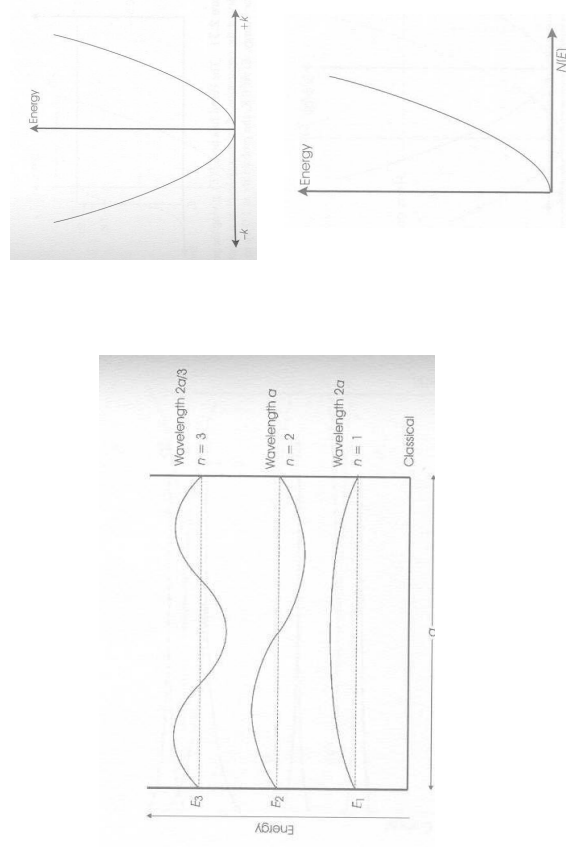


The broadening is dependent on the orbital overlap

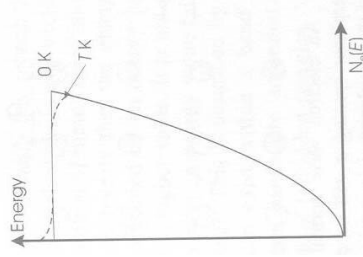
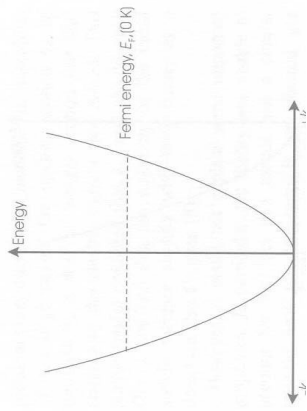
Will Mg ( $[\text{Ne}]3s^2$ ) be a metal?

## 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

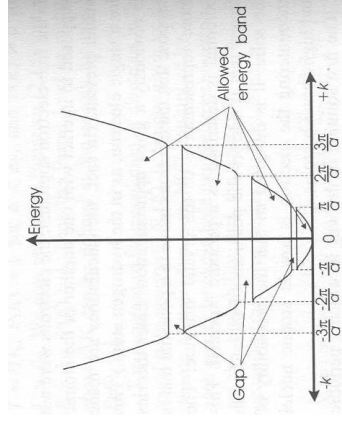
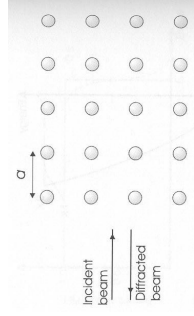
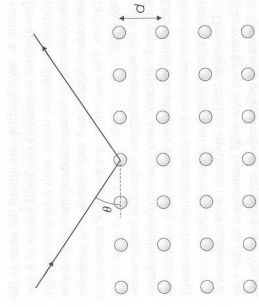


## Brillouin zones

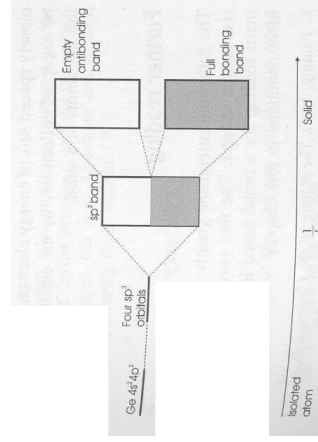
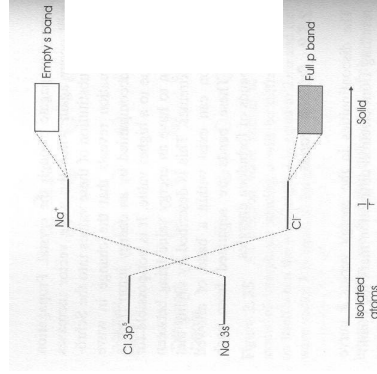
Moving electrons do interact with the atomic nucleus!

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

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



## Bands in ionic and covalent solids



## Moores-Pearson Plot for AB

