6.2. van der Waals interactions
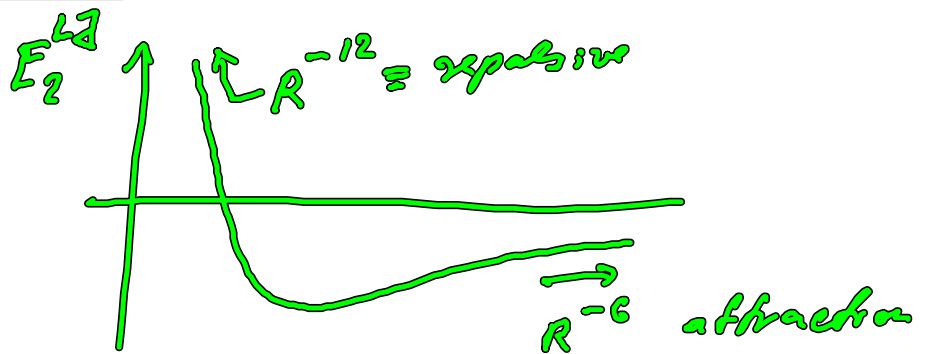
interaction between
2 atoms is described
by a very simple
potential
(pair potential)

E_2^{LJ}

$\hookleftarrow R^{-12} \equiv$ repulsive

$\overrightarrow{R^{-6}}$ attraction

<u>Solid</u> assume that pair potentials are good enough

$$\frac{E}{M} = \frac{1}{M} \cdot \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^{M,M} E_2^{LJ}\left(|\vec{R}_I - \vec{R}_J|\right)$$

$$= \frac{1}{2} \sum_{I=2}^{M} E_2^{LJ}\left(|\vec{R}_I|\right)$$

$$= 2\varepsilon \sum_{I=2}^{M} \left\{ \left(\frac{\sigma}{|\vec{R}_I|}\right)^{12} - \left(\frac{\sigma}{|\vec{R}_I|}\right)^{6} \right\}$$

ε, σ are obtained from gas phase experiments
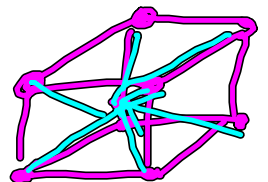(or 2 atom interaction theory)

introduce dimensionless parameter

$$|\vec{R}_I| = \alpha_I \cdot d \qquad\qquad d = \begin{array}{l}\text{distance}\\ \text{between nearest}\\ \text{neighbors}\end{array}$$

$$\frac{E}{M} = 2\varepsilon \left\{ \left(\frac{\sigma}{d}\right)^{12} A_{12}^{crystal} - \left(\frac{\sigma}{d}\right)^{6} A_{6}^{crystal} \right\}$$

$$A_n^{crystal} \uparrow = \sum_{I=2}^{M} \alpha_I^{-n} = \text{structure parameter}$$

stands for fcc, bcc, sc, ... etc.

structure parameters

crystal	sc	bcc	fcc
#nn	4	8	12
$A_{12}^{crystal}$	8.4	12.25	14.45
$A_{6}^{crystal}$	5.69	8.24	8.61

equilibrium lattice constant:

$$\frac{dE}{dc} = 0; \quad 2\varepsilon \, 3^{12} (-12) \, C_0 \, A_{12}^{\text{crystal}} = 2\varepsilon \, A_6^{\text{crystal}} \, 3^6 \, C_0^{-7} \, (6)$$

$$\left| \frac{1}{2} \right.$$

$$\boxed{C_0 = 2 \left(\frac{A_6^{\text{crystal}}}{2 A_{12}^{\text{crystal}}} \right)^6}$$

$$\boxed{E^{\text{coh., crystal}} = -\frac{E^{\text{crystal}}(C_0)}{n} = \varepsilon \left(\frac{A_6^{\text{crystal}}}{2 A_{12}^{\text{cryst}}} \right)^2}$$

<u>lattice constant</u> only given by ε and the structure parameters

<u>cohesive energy</u> only given by ε and the structure parameters.

The lattice structure of LJ − crystals is that of maximum $\left(\frac{A_6^{\text{crystal}}}{2 A_{12}^{\text{crystal}}} \right)^2$

$\left(\frac{A_6^{\text{crystal}}}{2 A_{12}^{\text{crystal}}} \right)^2$	sc	bcc	fcc
	5,69	8,24	8,61

$\Longrightarrow$ LJ − crystals assume the fcc structure

		Ne	Ar	Kr	Xe
C_0 (Å)	theory	3.13	3.75	3.99	4.33
	exp.	2.99	3.71	3.98	4.34
E_{coh} (meV)	theory	27	89	120	172
	exp.	20	80	110	170

impressive agreement with a most simple theory.

relatively large interatomic distances

Reason: repulsion sets in only because the whole atom is closed shell

$\Rightarrow$ overlap between wavefunctions of different atoms is small.

energy levels ε

$3s^0$

gap

$2p^6$

$2s^2$

nearest neighbor distance: C

C_0 equilibrium

bandwidth ≈ 0.5 eV

for example

Ne
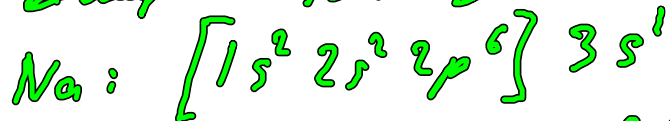
noble gas solids are insulators

6.3 Ionic bonding

Atoms and ions with a closed shells are particularly stable

For example Na & Cl

Na : $[1s^2 2s^2 2p^6] 3s^1$

Cl : $[1s^2 2s^2 2p^6] 3s^2 3p^5$

$\Rightarrow$ Na$^+$ & Cl$^-$ $\equiv$ closed shells ions

general true for group I and group VII

elements

(also to some extent for
group II & group VI atoms)

Once we revealed the energy Na, Cl $\rightarrow$ Na$^+$, Cl$^-$
for free atoms (ions), we may evaluate
how the ions bond and what type of solid
they may form.

<u>Figure</u>   ionisation / affinity
$\Rightarrow$ group I & group II elements
have low ionisation energy
(H is a clear exception; it actuates
a special type of bond $\rightarrow$ Friday)
electron affinities are high for group VI & VII

Na, Cl $\longrightarrow$ Na$^+$, Cl$^-$ cost
free atoms   free ions $\approx 1.5\, eV$

Interaction between atoms (ions!)

$$\hookrightarrow \sim \frac{1}{|\vec{R}|}$$

Naive — but not completely wrong — perception: ionic crystal = collection of hard, charged spheres

$$E_2^{\text{Ionic}} \equiv \text{pair potential}$$

$$= \frac{C}{|\vec{R}|^{12}} - \boxed{\frac{e^2}{4\pi \varepsilon_0} \frac{1}{|\vec{R}|}}$$

↑ attractive for Na^+ & Cl^-

(+: Na^+ and Na^+ or Cl^- and Cl^-)

evaluate this attractive part for 2.5 – 3 Å distances

$$\Rightarrow = -5\,eV \text{ gain}$$

a rough, convenient choice; analogous to Lennard-Jones

based the solid

again assume pair potentials are good enough.

i.e. ions remain <u>spherical</u>; no charge transfer
when ions get close.

<u>no quantum mechanics necessary to</u> } <u>not justified</u>
<u>describe ionic bonding</u> (but it works)

$$\frac{E}{M} \approx \sum_{I=2}^{M} \left(\frac{C}{|\vec{R}_I|^{12}} - \frac{\pm e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{R}_I|} \right)$$

± 1 means: $+1$ when I refers to a
cation (Na^+) and -1 when I refers
to an anion (Cl^-).

$$\vec{R}_I = \alpha_I \, c \qquad \equiv \text{ same as before (LJ part)}$$

$$\frac{E^{crystal}(c)}{M} = \left\{ \frac{C}{c^{12}} \underbrace{A_{12}^{crystal}}_{\text{as before}} - \frac{e^2}{4\pi\varepsilon_0} \underbrace{A_{Madelung}^{crystal}}_{\text{different to LJ}} \right.$$
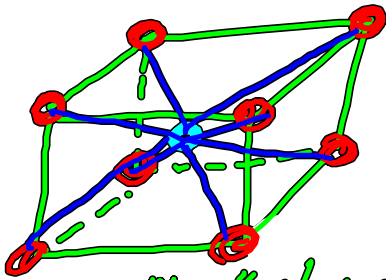
$$\underline{A_{Madelung}^{crystal}} = \sum_{I=2}^{M} \frac{\pm 1}{\alpha_I} \qquad \text{This sum converges "conditionally"}$$
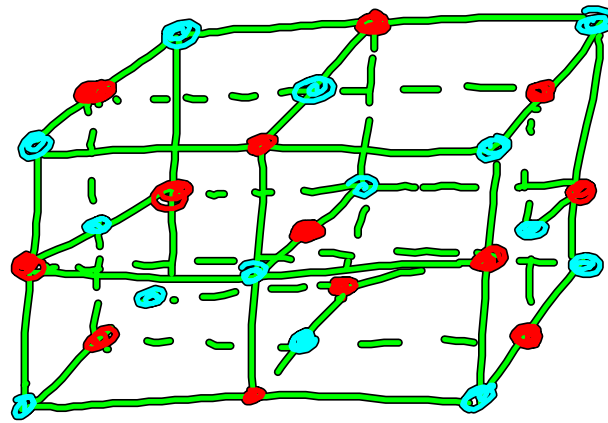
<u>Ewald summation</u> ⟹ one and <u>only result</u>

<u>Some important structure for ionic crystals</u>
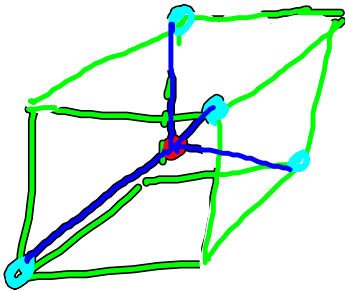   Na Cl

Cs Cl — structure

Like a "bcc" structure
but center atom is different

ead
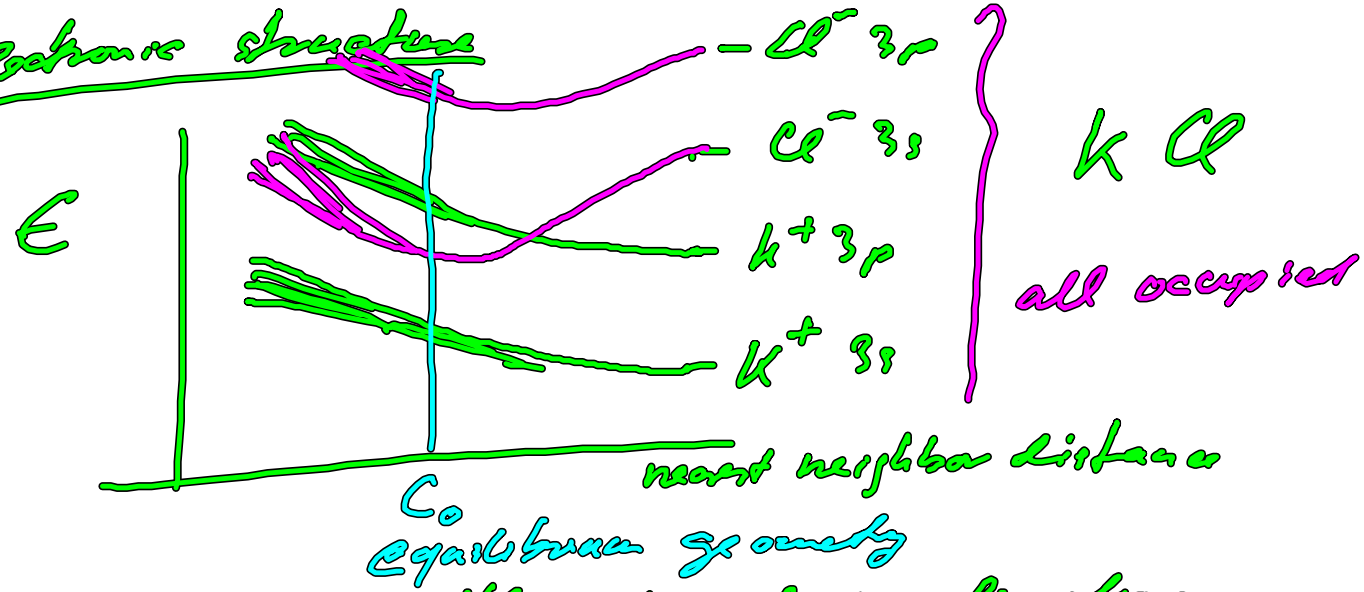atom
has
6
neighbors

Zn S   zincblende

4 fold
coordinated
atom

crystal structure	A madel crystal	# nn
	1.76	8
Cs Cl		6
NaCl	1.75	4
Zincblende	16.4	4
Wurzite	1.64	

↓
evaluate cohesion energy
compare to experiment
(or to good calculation)

⟹ 90% - 95% come indeed from
this simple theory.

electronic structure

E

$-Cl^- 3p$
$-Cl^- 3s$
$K^+ 3p$
$K^+ 3s$

} KCl

all occupied

nearest neighbor distance

c_0
equilibrium geometry

some — but little — overlap of wavefunctions of different atoms is present

Pauling's radius rule

if ionic radii of anion (-1) and cation $(+1)$ are similar $\Rightarrow$ CsCl structure.

ionic radii R^+, R^-

$1 > \dfrac{R^+}{R^-} > 0.73$: CsCl structure

$0.73 > \dfrac{R^+}{R^-} > 0.41$: NaCl structure

$0.41 > \dfrac{R^+}{R^-} > 0.23$: ZnS structure

follows from simple algebra and hard spheres. — Just try !

6.4 Covalent Bonding

In general atoms or ions are __not__ hard spheres
(just sometimes it works
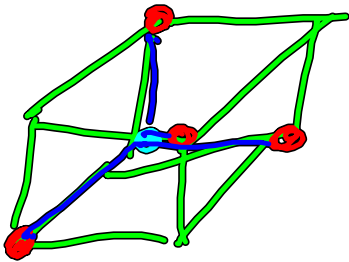   ⟶ ([L] & simple ionic crystal)

Typically atoms or ions change when
brought together.
Electrons are shared — not evenly.
— When directionality matters (when atoms are
not hard spheres) we get different (new)
structures
The best example for covalent bonding is
Carbon : C (also Si, Ge, GaAs, ...—
are good candidates).

⟹ zincblende or diamond.

diamond structure all atoms are
the same

zincblende structure : two
different atoms (blue & red)

— directional bonding implies that shear (or bending) of a crystal is difficult. Covalent crystals are quite brittle.

— description in terms of pair potentials is not possible. Quantum mechanics, i.e. the <u>shell structure</u> of atoms & atomic & molecular <u>orbitals</u> are key to understanding. These are related to D^2 term (kinetic energy of electrons).

$\Rightarrow$ we need **full** DFT calculations. For these systems DFT full (LDA or GGA) work well.

6.4.1 Hybridization and covalent bond formation

Carbon free atom : $2s^2 2p^2$
<u>in the atom</u> form sp^3 hybrids based linear combinations

$$\phi^1 = \tfrac{1}{2} \left(s + p_x + p_y + p_z \right)$$
$$\phi^2 = \tfrac{1}{2} \left(s + p_x - p_y - p_z \right)$$
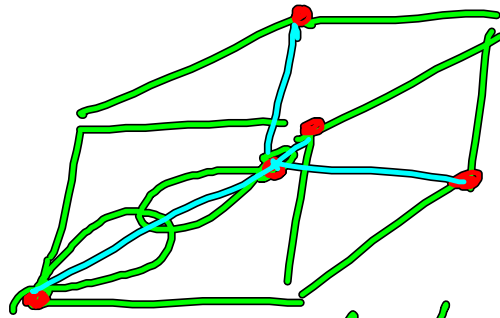$$\phi^3 = \tfrac{1}{2} \left(s - p_x + p_y - p_z \right)$$
$$\phi^4 = \tfrac{1}{2} \left(s - p_x - p_y + p_z \right)$$
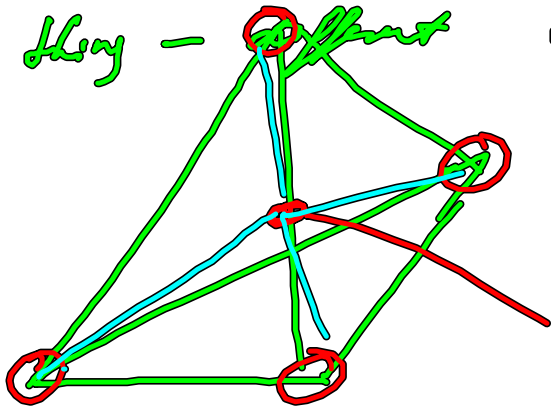
each of them look

this "excitation": $s^2 p^2 \longrightarrow s^1 p^3$

The four sp^3 orbitals point into 4 directions

Same thing — different tetrahedral

atom at center of tetrahedron