

3. Crystal Binding

What keeps crystals together ?

What causes bonding?

Goal of this chapter:

What keeps crystals together ?

- Types of attractive and repulsive forces
- Behavior as a function of distance
- Preferred direction, impact on geometry
- Impact on properties

Crystals are classified with respect to their bonding type

- Ionic crystals
- Covalent crystals
- Metals
- Hydrogen bonds
- Van der Waals crystals

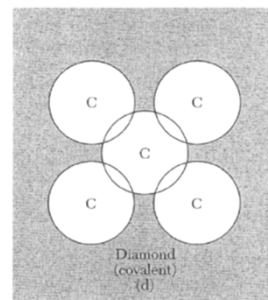
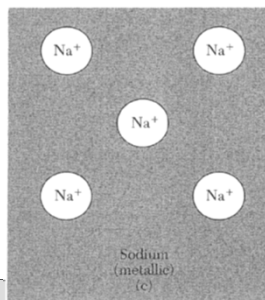
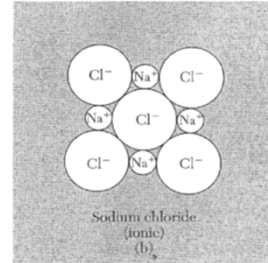
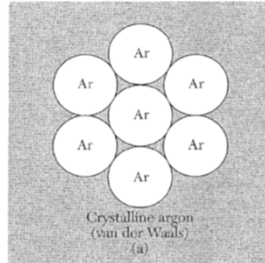
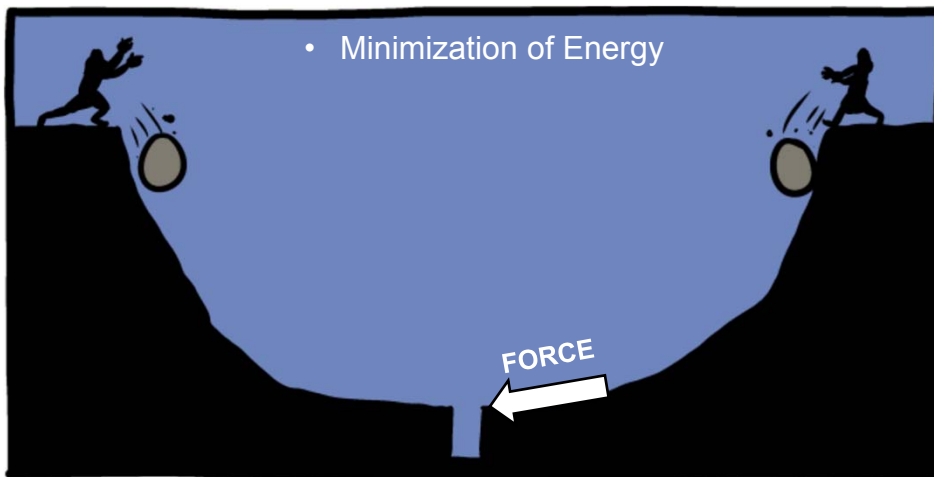


Figure from KI

What causes bonding?



Adapted from: <http://www.smbc-comics.com/?id=3554>

What keeps crystals together ?

- **Electrostatic interaction** between negative charges of the electrons and positive charges of the nuclei !
- Induced dipoles
- Magnetic and gravitational forces negligible
- Different types of bonding because of **different distributions of valence electrons**

For stability: relative energies are important

Cohesive energy:

- Energy needed to separate a crystal into neutral free atoms at rest

$$E(\text{crystal}) - E(\text{atoms})$$

Lattice energy (ionic crystals):

- Energy needed to separate an ionic crystal into free ions (at infinite distance) at rest

$$E(\text{crystal}) - E(\text{ions})$$

stable if energy of the combined system is lower than the separated fragments by more than $\sim k_B T$ (ca. 25meV at 300K)

- immediate consequences for melting temperatures and bulk moduli

Cohesive energies:

- Inert gas (and organic) crystals weakly bound
- Alkali metals have intermediate values
- Covalent crystals characterized by stronger bonding
- Transition metals quite strongly bound

Table from KI

Table I Cohesive energies

Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer.

Li 158. 1.63 37.7	Be 320. 3.32 76.5											B 561 5.81 134	C 711 7.37 170	N 474 4.92 113.4	O 251. 2.60 60.03	F 81.0 0.84 19.37	Ne 1.92 0.020 0.46									
Na 107. 1.113 25.67	Mg 145. 1.51 34.7											Al 327. 3.39 78.1	Si 446. 4.63 106.7	P 331. 3.43 79.16	S 275. 2.85 65.75	Cl 135. 1.40 32.2	Ar 7.74 0.080 1.85									
												← kJ/mol →					← eV/atom →					← kcal/mol →				
K 90.1 0.934 21.54	Ca 178. 1.84 42.5	Sc 376 3.90 89.9	Ti 468. 4.85 111.8	V 512. 5.31 122.4	Cr 395. 4.10 94.5	Mn 282. 2.92 67.4	Fe 413. 4.28 98.7	Co 424. 4.39 101.3	Ni 428. 4.44 102.4	Cu 336. 3.49 80.4	Zn 130 1.35 31.04	Ga 271. 2.81 64.8	Ge 372. 3.85 88.8	As 285.3 2.96 68.2	Se 237 2.46 56.7	Br 118. 1.22 28.18	Kr 11.2 0.116 2.68									
Rb 82.2 0.852 19.64	Sr 166. 1.72 39.7	Y 422. 4.37 100.8	Zr 603. 6.25 144.2	Nb 730. 7.57 174.5	Mo 658 6.82 157.2	Tc 661. 6.85 158.	Ru 650. 6.74 155.4	Rh 554. 5.75 132.5	Pd 376. 3.89 89.8	Ag 284. 2.95 68.0	Cd 112. 1.16 26.73	In 243 2.52 58.1	Sn 303. 3.14 72.4	Sb 265. 2.75 63.4	Te 211 2.19 50.34	I 107. 1.11 25.62	Xe 15.9 0.16 3.80									
Cs 77.6 0.804 18.54	Ba 183. 1.90 43.7	La 431. 4.47 103.1	Hf 621. 6.44 148.4	Ta 782. 8.10 186.9	W 859. 8.90 205.2	Re 775. 8.03 185.2	Os 788. 8.17 188.4	Ir 670. 6.94 160.1	Pt 564. 5.84 134.7	Au 368. 3.81 87.96	Hg 65. 0.67 15.5	Tl 182. 1.88 43.4	Pb 196. 2.03 46.78	Bi 210. 2.18 50.2	Po 144. 1.50 34.5	At 19.5 0.202 4.66	Rn									
Fr 160 1.66 38.2	Ra 410. 4.25 98.	Ac	Ce 417. 4.32 99.7	Pr 357. 3.70 85.3	Nd 328. 3.40 78.5	Pm	Sm 206. 2.14 49.3	Eu 179. 1.86 42.8	Gd 400. 4.14 95.5	Tb 391. 4.05 93.4	Dy 294. 3.04 70.2	Ho 302. 3.14 72.3	Er 317. 3.29 75.8	Tm 233. 2.42 55.8	Yb 154. 1.60 37.1	Lu 428. 4.43 102.2										

3.1 Van der Waals crystals

typically noble gas crystals or molecular crystals

Crystals of noble (inert) gases:

Electron distribution in the crystalline state similar to that of the free atoms !

All electron shells completely filled (stable !!!)

→ spherically symmetric charge distributions

→ close packed structures (fcc) except He: zero point motion !

Table 4 Properties of inert gas crystals
(Extrapolated to 0 K and zero pressure)

Nearest-neighbor distance, in Å	Experimental cohesive energy		Melting point, K	Ionization potential of free atom, eV	Parameters in Lennard-Jones potential, Eq. 10	
	kJ/mol	eV/atom			ϵ , in 10^{-16} erg	σ , in Å
He (liquid at zero pressure)				24.58	14	2.56
Ne 3.13	1.88	0.02	24.56	21.56	50	2.74
Ar 3.76	7.74	0.080	83.81	15.76	167	3.40
Kr 4.01	11.2	0.116	115.8	14.00	225	3.65
Xe 4.35	16.0	0.17	161.4	12.13	320	3.98

- Transparent insulators
- Weakly bound
- Low melting temperatures

Table from KI

Spherical charge distributions → **no external field !**

What keeps those crystals together ?

3.1.1 Van der Waals-London interactions (dispersion forces)

- Manifestation of **electron correlation** (correlated motion of electrons)
- “time averaged charge distribution“ insufficient description of actual situation !

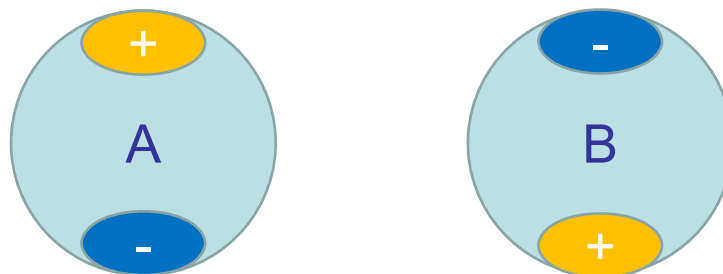
dipole-dipole interaction

(as a 1st approximation)

a.) origin of the dipole moments

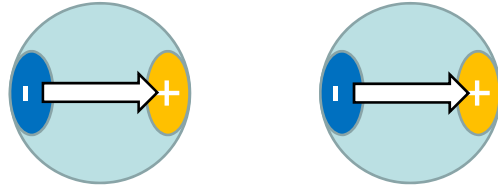
- What about **non-polar noble gas atoms** (or non-polar molecules) molecules without a permanent dipole moment ?

Consider spherically symmetrical fragments



Electron fluctuations result in *non-permanent* dipole
Dipole in A *induces* dipole in B

a.) origin of the dipole moments



- attractive interaction like with induction forces
- dispersion forces

Manifestation of **correlated movement of the electrons**

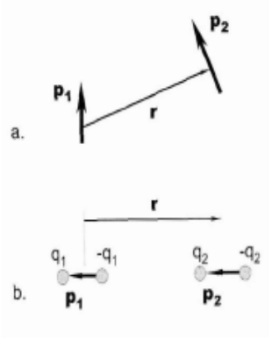
(*electron correlation effects !*)

- Molecular crystals: e.g., molecule with dipole moment interacts with molecule without dipole moment → **induction forces**

following: Schwoerer and Wolf, „Organische Molekulare Festkörper“ (Wiley-VCH)

b.) interaction between two dipoles

Interaction potentials and forces



general case:

$$V = \frac{1}{4\pi\epsilon_0} \frac{\vec{p}_1 \vec{p}_2 - 3(\vec{p}_1 \vec{e}_r)(\vec{p}_2 \vec{e}_r)}{r^3}$$

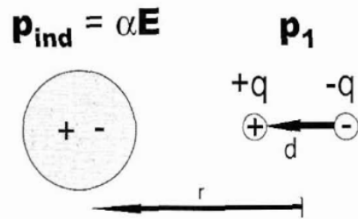
Parallel dipoles:

$$V = -\frac{1}{4\pi\epsilon_0} \frac{2p_1 p_2}{r^3} \quad F = -\frac{dV}{dr} = -\frac{1}{4\pi\epsilon_0} \frac{6p_1 p_2}{r^4}$$

Figure from Schwoerer and Wolf

c.) induced dipoles

Figure from Schwoerer and Wolf



induced dipole moment p_{ind}

$$\vec{p}_{ind} = \alpha \vec{E}$$

With field generated by p_1

$$E = \frac{1}{4\pi\epsilon_0} \left[\frac{+q}{(r-d/2)^2} + \frac{-q}{(r+d/2)^2} \right] e_r$$

And for $r \gg d$:

$$\vec{E} = \frac{1}{4\pi\epsilon_0} \frac{2\vec{p}_1}{r^3}$$

$$F = -\frac{1}{4\pi\epsilon_0} \frac{6p_1 p_{ind}}{r^4} = -\frac{1}{(4\pi\epsilon_0)^2} \frac{12p_1^2 \alpha}{r^7}$$

$$V = -\int_{\infty}^r F \cdot dr = -\frac{1}{(4\pi\epsilon_0)^2} \frac{2p_1^2 \alpha}{r^6}$$

Side remark- molecular crystals:

$$V_{disp} = -\int_{\infty}^r F dr = -\frac{1}{(4\pi\epsilon_0)^2} \frac{A'' \alpha^2}{r^6}$$

A' (and $A''=A'/6$) molecule specific factors

melting points ($^{\circ}C$) of various organic crystals

Consider:

deviations from spherical symmetry

F anisotropic; in fact higher moments than dipole moments need to be considered

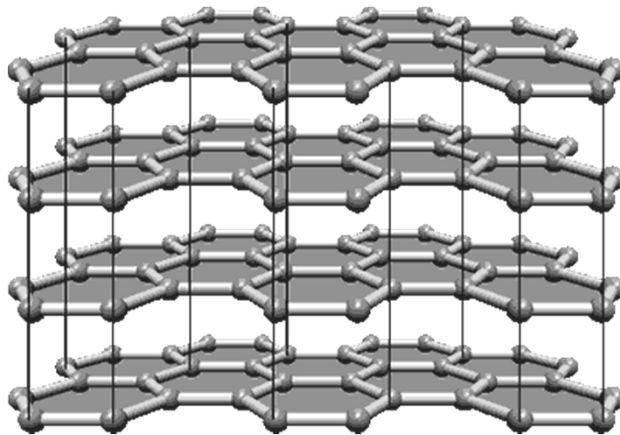
$F \sim 1/r^7 \rightarrow$ short range !

$F \sim \alpha^2 \rightarrow$ large for highly polarizable systems with large number of π -electrons

o-Xylol	-25
Cyclooctatetraen	-4
n-Hexan	-95
Benzol	5.5
Naphthalin	80
Anthracen	216
Tetracen	357
Hexacen	380

Schwoerer and Wolf

- van-der-Waals bonding is weak, *but*
- *every atom counts* ($\sim 0.1\text{eV/atom}$)



sites.google.com

3.1.2 Repulsive interaction

Why don't atoms crash into each other ?

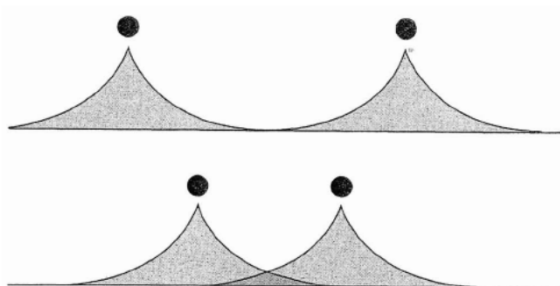


Figure from KI

Figure 4 Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.

Approaching atoms:

Overlapping charge distributions \rightarrow changes electrostatic energy of the system

Bonding ? – e.g., in the case of covalent bonds (depends on „shape“ of overlap distribution and occupation of hybrid states)

Repulsion ? Certainly at very short distances – Why ?

To a large part because of the **Pauli exclusion principle**

- **Two electrons cannot have their quantum numbers equal !**
- **I.e., each state - specified by its quantum numbers – can be occupied only by a single electron**

Qualitative picture:

- Electron distributions overlap → electrons from atom A tend in part to “occupy states“ of atom B, which are already occupied by electrons from B.
- → atoms with closed shells can overlap only if this is accompanied by the “promotion“ of electrons to some sort of unoccupied high energy states of the atoms
- QM more appropriate: Occupation of “antibonding“ states; consequence of requirement of **orthogonality of wavefunctions**

- Shape of the potential hard to determine from first principles
- Empirical determination by fitting to experimental data on noble gases

$$\text{either: } V(r) = \frac{B}{r^{12}} \quad \text{or: } V(r) = \lambda \exp\left(-\frac{r}{\rho}\right)$$

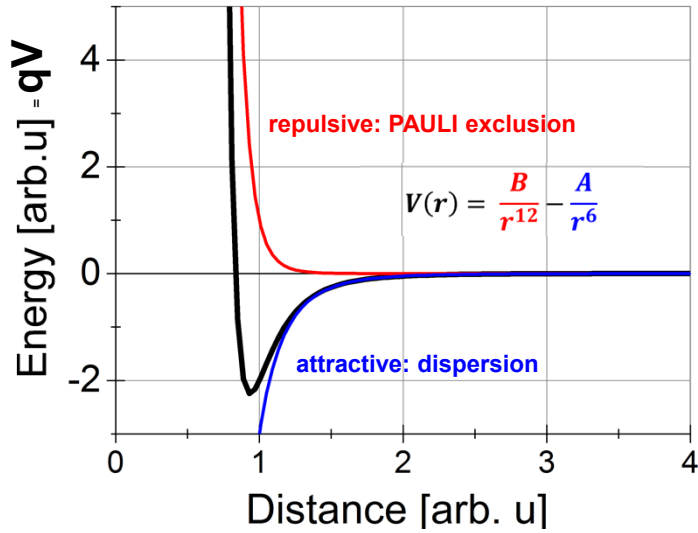
B, λ, ρ ... empirical parameters

- Parameters can be determined from independent measurements in the gas phase

Together with the van der Waals term:

$$V = -\frac{A}{r^6}$$

Lennard-Jones Potential



Lennard- Jones potential

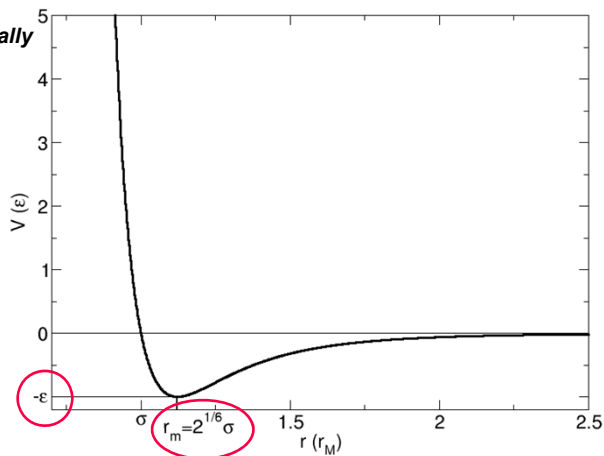
$$V(r) = \frac{B}{r^{12}} - \frac{A}{r^6} = 4\varepsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} = \varepsilon \left\{ \left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right\}$$

A, B, or ε, σ, or ε, r_m are empirically determined parameters

inter-atomic force determined by:

$$F(r) = -\frac{dV(r)}{dr}$$

Plot taken from: <http://de.wikipedia.org/wiki/Lennard-Jones-Potential>



3.1.3 From the interatomic potential (pair of atoms) to the cohesive energy (the crystal)

Cohesive energy (neglecting kinetic energy of the noble gas atoms):

$$U_{tot} = \frac{1}{2} N 4 \epsilon \left\{ \sum_j' \left(\frac{\sigma}{p_{ij} R} \right)^{12} - \sum_j' \left(\frac{\sigma}{p_{ij} R} \right)^6 \right\}$$

Independent of the chosen "i"!
with:
 $r_{ij} = p_{ij} R$

add energetic contributions of all atoms, but avoid double counting
summation over all "other" atoms
distance between reference atom i and all other atoms (R ... nearest-neighbor distance)

Evaluate for fcc structure: $\sum_j' \frac{1}{p_{ij}^{12}} = 12.1318$ $\sum_j' \frac{1}{p_{ij}^6} = 14.4539$

Close to number of nearest neighbors in fcc structure (i.e., 12)

→ the nearest neighbours count primarily !

Equilibrium distance: $\frac{dU_{tot}}{dR} \equiv 0 \implies \frac{R_0}{\sigma} = 1.09$

Experimentally determined values:

$$\frac{R_0}{\sigma}(He) = 1.14; \frac{R_0}{\sigma}(Ar) = 1.11; \frac{R_0}{\sigma}(Kr) = 1.10; \frac{R_0}{\sigma}(Ne) = 1.09$$

Light atoms: deviation due to zero point energy !

Directional	Weak
Bond Energies	5 – 50 meV / atom
Occurs when	Always
Examples:	Rare gas clusters, organic crystals
Model Potential:	Lennard-Jones
Packing density	Dense
Decays	r^{-6}

3.2 Ionic crystals

- Consist of positively and negatively charged ions
- Primarily consequence of **electrostatic interaction between oppositely charged ions**
- Typical structures: **NaCl** and **CsCl**

Figure from KI

Ions of a simple ionic crystal:

- Closed shell structure
- Low ionisation energies
- Thus, spherical charge distribution

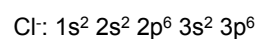
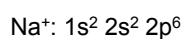
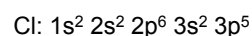
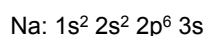
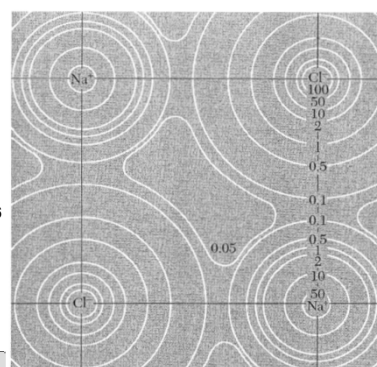
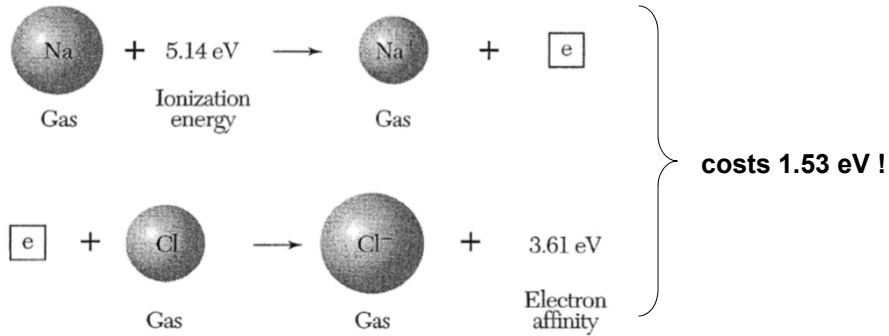


Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.



Why does a Na⁺Cl⁻ crystal form ?



Attractive Coulomb term: (Na⁺Cl⁻ pair: 5.1 eV)

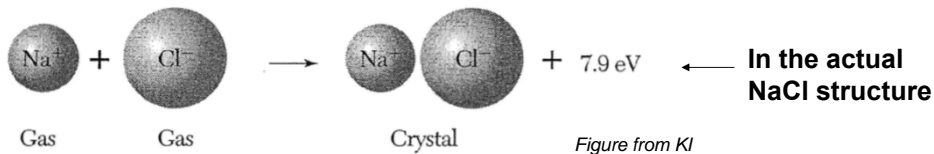


Figure from KI

Fundamentals of Solid State Physics

Bonding in an ionic crystal

Lowest total energy structure considering:

- Repulsive interactions (comparable to noble gases)
- Electrostatic interaction (Madelung energy)
- Van der Waals interaction *supposedly* only 1 to 2% of total cohesive energy (i.e., neglected)

Madelung energy:

Sum of all interaction energies for one particular atom i: $U_i = \sum_j U_{ij}$

with:

$$U_{ij} = \lambda \exp\left(-\frac{r_{ij}}{\rho}\right) \pm \frac{1}{4\pi\epsilon_0} \frac{q^2}{r_{ij}}$$

(empirical) repulsive term + for the same, - for opposite charges Coulomb interaction (in SI units)

Fundamentals of Solid State Physics

with $r_{ij} = p_{ij}R$

and considering the repulsive interaction only for nearest neighbors

$$U_{ij} \begin{cases} \lambda \exp\left(-\frac{R}{\rho}\right) - \frac{1}{4\pi\epsilon_0} \frac{q^2}{R} & (\text{nearest neighbors}) \\ \pm \frac{1}{4\pi\epsilon_0} \frac{q^2}{p_{ij}R} & (\text{other atoms}) \end{cases}$$

one obtains

$$U_{tot} = NU_i = N \left(z\lambda \exp\left(-\frac{R}{\rho}\right) - \frac{1}{4\pi\epsilon_0} \frac{\alpha q^2}{R} \right)$$

With N being the number of K^+A^- pairs, z being the number of nearest neighbors and α , the Madelung constant given by

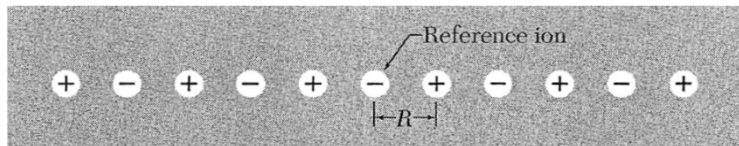
$$\alpha := \sum_j' \frac{(\pm)}{p_{ij}}$$

Calculating the equilibrium distance from $dU_{tot}/dR=0$, and inserting the obtained expression into the equation for U_{tot} , one obtains:

$$U_{tot} = \frac{N\alpha q^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{\rho}{R_0} \right)$$

α typically calculated numerically using a computer

Example: Madelung constant of a linear chain:



$$\alpha := \sum_j' \frac{(\pm)}{p_{ij}}$$

$$\alpha = 2 \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right) = 2 \ln 2$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

Structure	α
Sodium chloride, NaCl	1.747565
Cesium chloride, CsCl	1.762675
Zinc blende, cubic ZnS	1.6381

Figure and table from KI

Bonding in KCl:

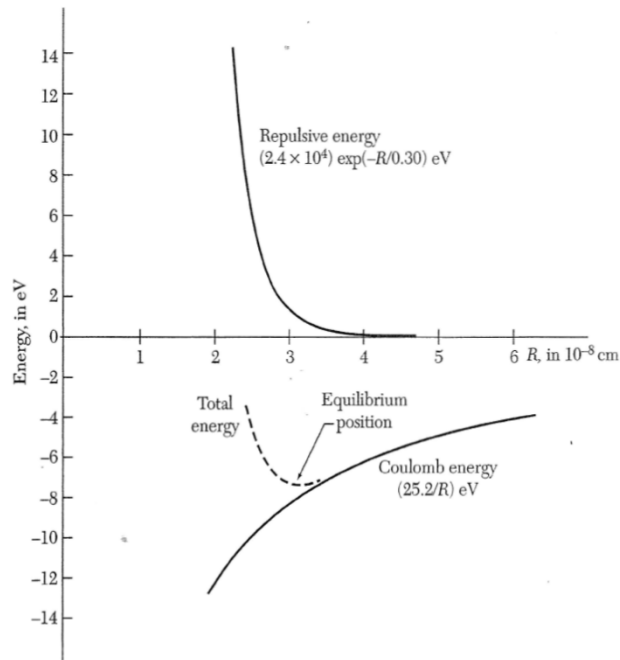


Figure from KI

Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

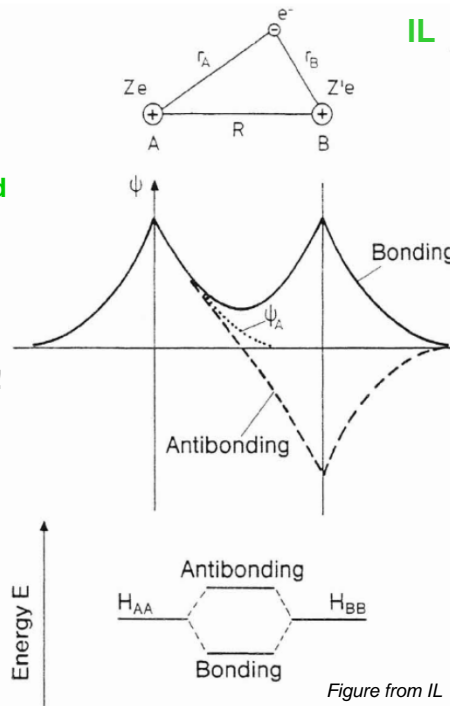
Directional	None
Bond Energies	1 – 9 eV / 100 – 900 kJ/mol
Occurs when	- Atoms have strongly different ionization energies, electron affinities, electronegativities
Examples:	NaCl, CaF ₂ , CsCl, ...
Potential:	Coulomb + Pauli repulsion
Packing density	Dense
Decays	r^{-1}

3.3 Covalently bonded crystals

- classical **electron pair** or **homopolar bond**
- bonding involves “**pairing of electrons**“ between atoms
- typically two electrons involved
- preferentially located between bonded atoms
- antiparallel spin
- **covalent bond highly directional**

Covalent bonding of a H₂ molecule

- Molecular orbitals as **symmetric and antisymmetric linear combinations** of the H1s orbitals
- **Bonding orbital** below, **antibonding** above atomic energy levels
- Piling up of charge between atoms !
- Bonding strength maximum, if **bonding orbital doubly occupied** (2 electrons with antiparallel spin) and **antibonding orbital empty**
- → only partially occupied single-atomic orbitals efficiently participate in bonding



Some orientations favor the overlap others are unfavorable

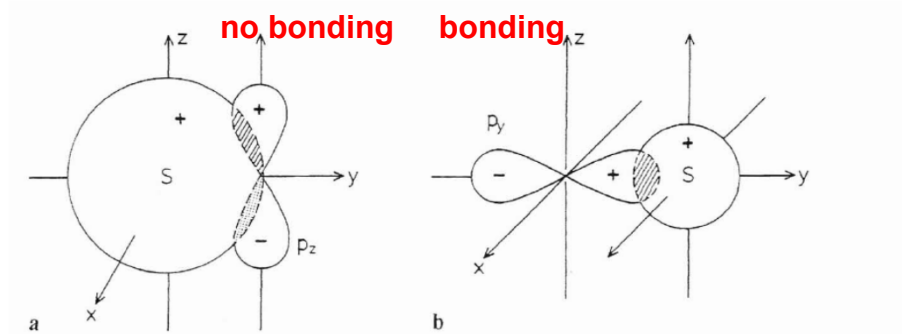


Fig. 1.3 a, b. Pictorial representation of the spatial overlap between an s - and a p -wavefunction of hydrogen. The "size" of the wavefunction is illustrated by a surface of constant wavefunction amplitude. (a) A situation in which the overlap cancels due to sign reversal of the p_z -wavefunction. (b) Nonvanishing overlap between s - and p_x -wavefunctions

Figure from IL

Covalent bond highly directional !

What about C, Si, Ge ?

Lack 4 electrons for a closed shell (noble gas) configuration

C-atom: $1s^2 2s^2 2p^2$

- To be able to make 4 bonds needs to have 4 singly occupied orbitals

$1s^2 2s^2 2p^3$ (costs a significant amount of energy)

→ formation of hybrid orbitals

For example, four sp_3 hybrids:

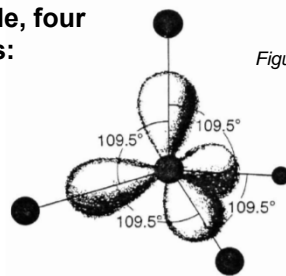
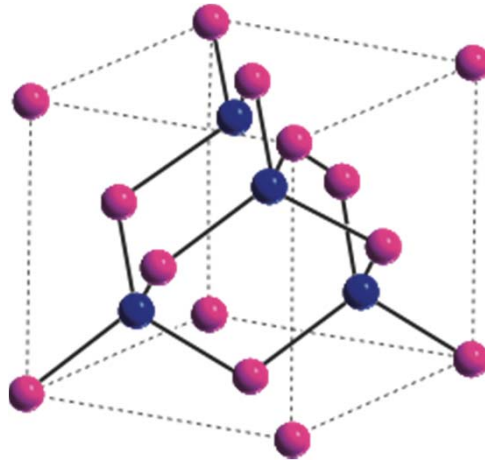


Figure from IL

→ four singly occupied orbitals in a tetrahedral conformation that can result in 4 single bonds !

Fig. 1.4. The tetrahedral configuration of nearest neighbors in the lattice of C, Si, Ge and α -Sn. This structure is favored because its periodic repetition fills three-dimensional space, and because it enables the formation of sp^3 hybrid orbitals from the s , p_x , p_y , and p_z states. The figure displays the orbitals of diamond (C). The orbitals of Si, Ge, and α -Sn possess additional nodes



Connected tetrahedrons

And what about a crystalline solid ?

Qualitatively the same situation !

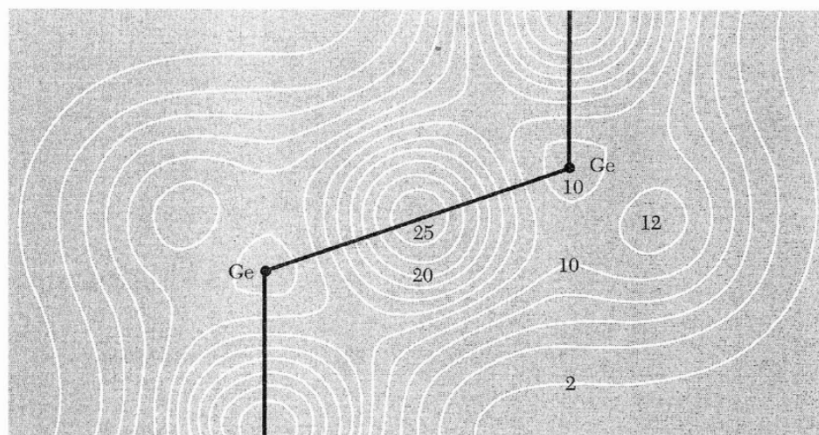


Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)

Directional	Strong
Bond Energies	1.4 – 9 eV / 140 – 900 kJ/mol
Occurs when	- Unpaired electrons
Examples:	Si, Ge, organic molecules
Potential:	wave-function overlap
Packing density	Not necessarily dense
Decays	e^{-r}

Covalent and ionic bonding only **two limiting cases**

Continuous transition between these “extremes“

Table from KI

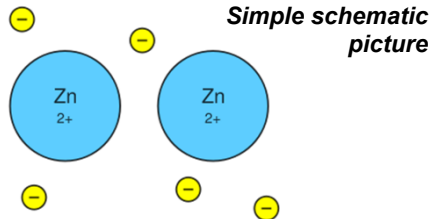
Table 8 Fractional ionic character of bonds in binary crystals

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00		
SiC	0.18	GaAs	0.31
Ge	0.00	GaSb	0.26
ZnO	0.62	AgCl	0.86
ZnS	0.62	AgBr	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61	MgO	0.84
CdO	0.79	MgS	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
		NaCl	0.94
InP	0.42	RbF	0.96
InAs	0.36		
InSb	-0.32		

After J. C. Phillips, *Bonds and bands in semiconductors*.

3.4 Bonding in metals

- Valence electrons (1 or 2) in metals become conducting electrons
- highly mobile (“smeared out“, “delocalized“)
- “collective“ effect



Cohesive energy:

Picture from: http://en.wikipedia.org/wiki/Metallic_bond

- Energy of valence electrons reduced compared to atoms
- Interaction of nuclei with conducting electrons

Periodic Table of Elements

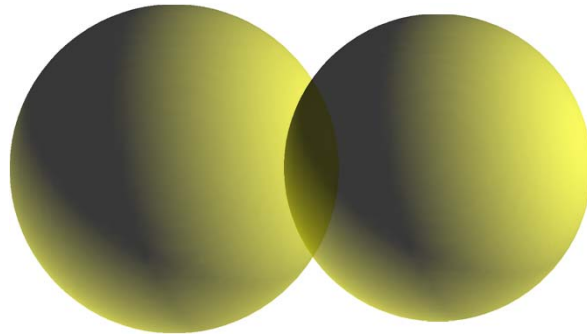
The periodic table is color-coded to show different classes of elements: Metals (blue), Metalloids (red), and Non-Metals (green). The transition metals are highlighted in a darker blue. Below the table, brackets indicate the s, d, and s blocks.

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110	111	112	113	114				

Labels below the table: s, d, s

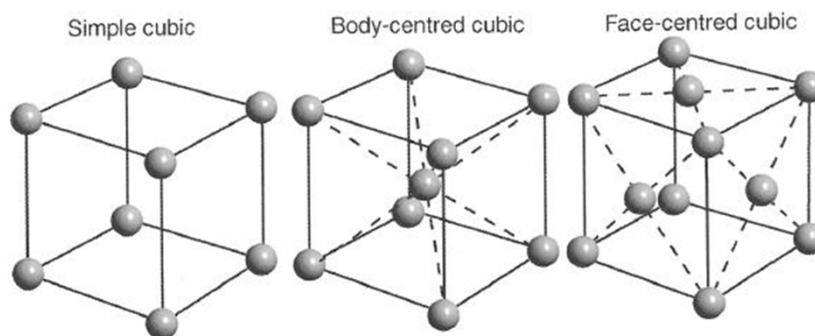
http://www.thegeoexchange.org/chemistry/naming/resources/metals_nonmetals.php

Directionality: s-states



$S \sim \text{const.}$

Directionality



packing fraction $p = \text{volume occupied by spheres} / \text{total volume}$

$p_{sc} = 0,52$, $p_{bcc} = 0.68$, $p_{fcc} = 0.74$

coordination number = number of next neighbours \rightarrow sc: 6, bcc: 8, fcc: 12

Large atoms

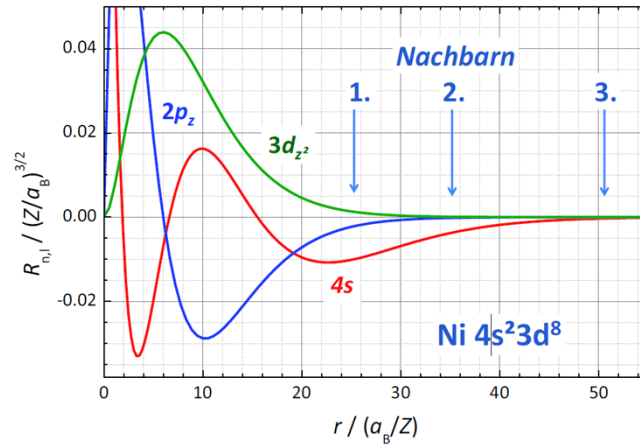


Abb. 3.21: Die Amplitude der $2p_z$ -, $3d_{z^2}$ - und der $4s$ -Wellenfunktion von Ni.

• Gross, Marx, "Festkörperphysik", Oldenbourg Verlag

Transition metals:

Higher cohesive energies because of additional bonding !

d-electrons:

- more localized with weaker overlap
- produce kind of covalent framework
- main contribution to the binding energy

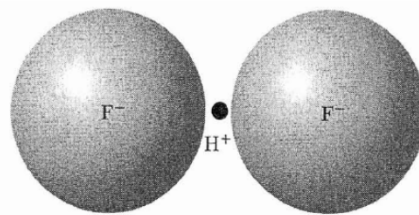
3.5 Hydrogen bonds

Partly following:
http://en.wikipedia.org/wiki/Hydrogen_bond

H attached to highly electronegative atom like N, O, or F
 + another electronegative atom is in its vicinity

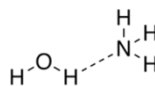
- H to a large extent “looses“ electron and becomes positively charged
- attracted by two atoms with strong forces
- strongly ionic character

Figure 13 The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.



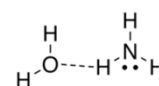
Hydrogen bonds can vary in strength from $(1\text{-}2 \text{ kJ mol}^{-1})$ to extremely strong $>155 \text{ kJ mol}^{-1}$:

- $\text{F}-\text{H}\cdots\text{F}$ (155 kJ/mol or 40 kcal/mol)
- $\text{O}-\text{H}\cdots\text{N}$ (29 kJ/mol or 6.9 kcal/mol)
- $\text{O}-\text{H}\cdots\text{O}$ (21 kJ/mol or 5.0 kcal/mol)
- $\text{N}-\text{H}\cdots\text{N}$ (13 kJ/mol or 3.1 kcal/mol)
- $\text{N}-\text{H}\cdots\text{O}$ (8 kJ/mol or 1.9 kcal/mol)



hydrogen bond donor

hydrogen bond acceptor



hydrogen bond acceptor

hydrogen bond donor

Up to “weak“ covalent bonds

BUT: recently in many systems role of vdW interactions thought to be more important than assumed previously – just due to sheer number of interacting atoms !

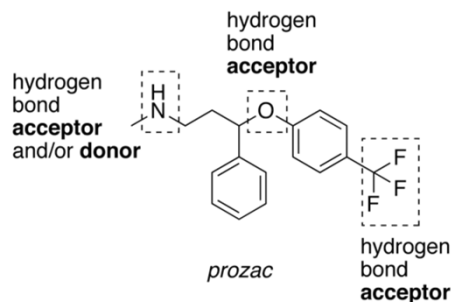
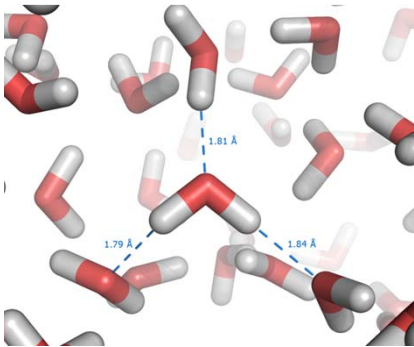
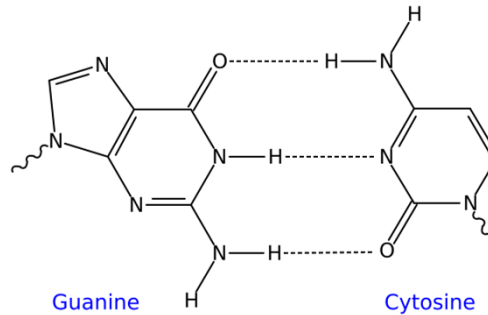


Figure from:
http://en.wikipedia.org/wiki/Hydrogen_bond

Bonding in DNA

Figures from:
http://en.wikipedia.org/wiki/Hydrogen_bond



Bonding in water and ice with their peculiar properties (together with interaction of dipoles)

a summary about forces

interaction type	range	directional	energy [kJ / mol]	energy [k _B T]
charge – charge	$\sim r^{-1}$	no	100 - 900	40 - 360
metal bond		no	100 - 900	40 - 360
covalent	very short	yes	100 - 900	40 - 360
hydrogen bond	very short	yes	10 - 155	4 - 62
dipole – dipole	$\sim r^{-3}$	yes	20	8
van der Waals	$\sim r^{-6}$	weakly	0,5 - 5	0,2 - 2

but: in organic systems are many van der Waals bonds parallel to each other and the bond energies sum up, for large organic objects the van der Waals forces can even become long range forces !!