

Crystal Binding

- Kittel chapter 3
- Simon (Oxford Solid State Basics)

What holds a crystal together?

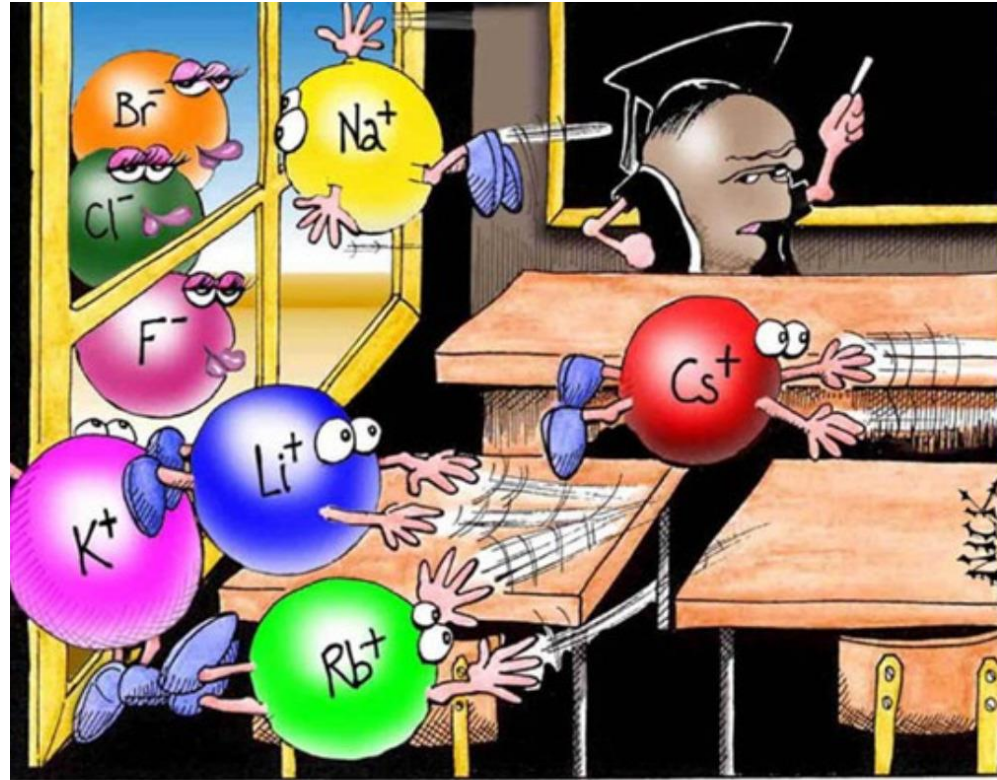
mainly,

electrostatic interaction

(also: dipole fluctuations)

(gravitational and magnetic forces: negligible)

Goal: energy minimization



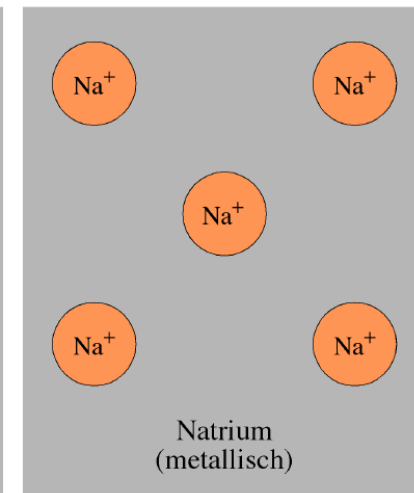
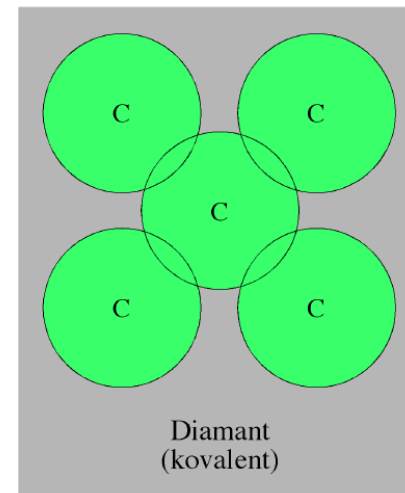
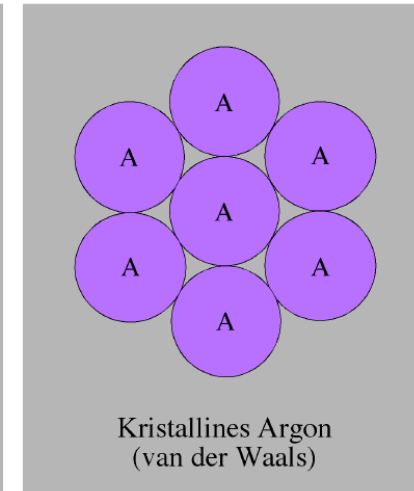
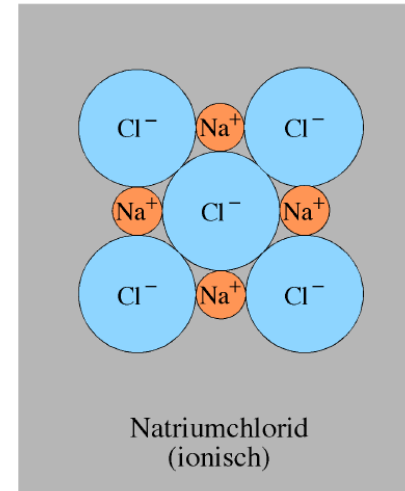
"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive..?"

Cartoon courtesy of NearingZero.net

Basic types of binding

Crystals are classified with respect to their binding type

- Van der Waals
- Ionic
- Covalent
- Metal
- Hydrogen



Van der Waals interaction

typical between inert atoms (He, Ne, Kr...) and between inert molecules (i.e. N_2)

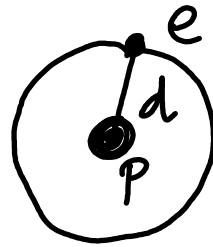
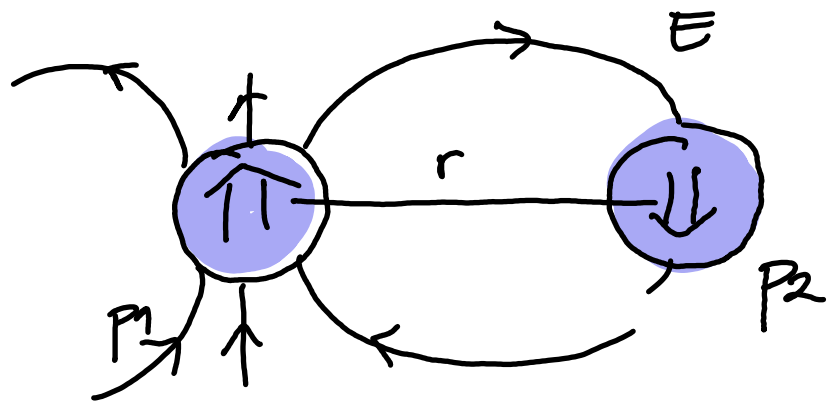
Noble (inert) gases : electron distribution in the crystalline state = free atom

- all electronic shells are completely filled
- spherically symmetric charge distributions
- closed packed structures (fcc) [except He]
- ionization energy is high
- weakly bonded : interaction between induced dipoles
→ van der Waals interaction

(recap previous class)

Van der Waals interaction

Atom 1 & 2 separated r :



- dipole moment $\vec{p} = e \cdot \vec{d}$ vector from e⁻ to the proton
- in general, e⁻ "orbits" $\rightarrow \langle p \rangle = 0$
- if \vec{E} is applied to the atom $\Rightarrow \vec{p} = \chi \vec{E}$ electric susceptibility

If we have 2 of these atoms separated r :

- if atom 1 has for a moment a dipole p_1
- then atom 2 feels $E = \frac{p_1}{4\pi\epsilon_0 r^3}$
- so, atom 2 develops $p_2 = \chi E$

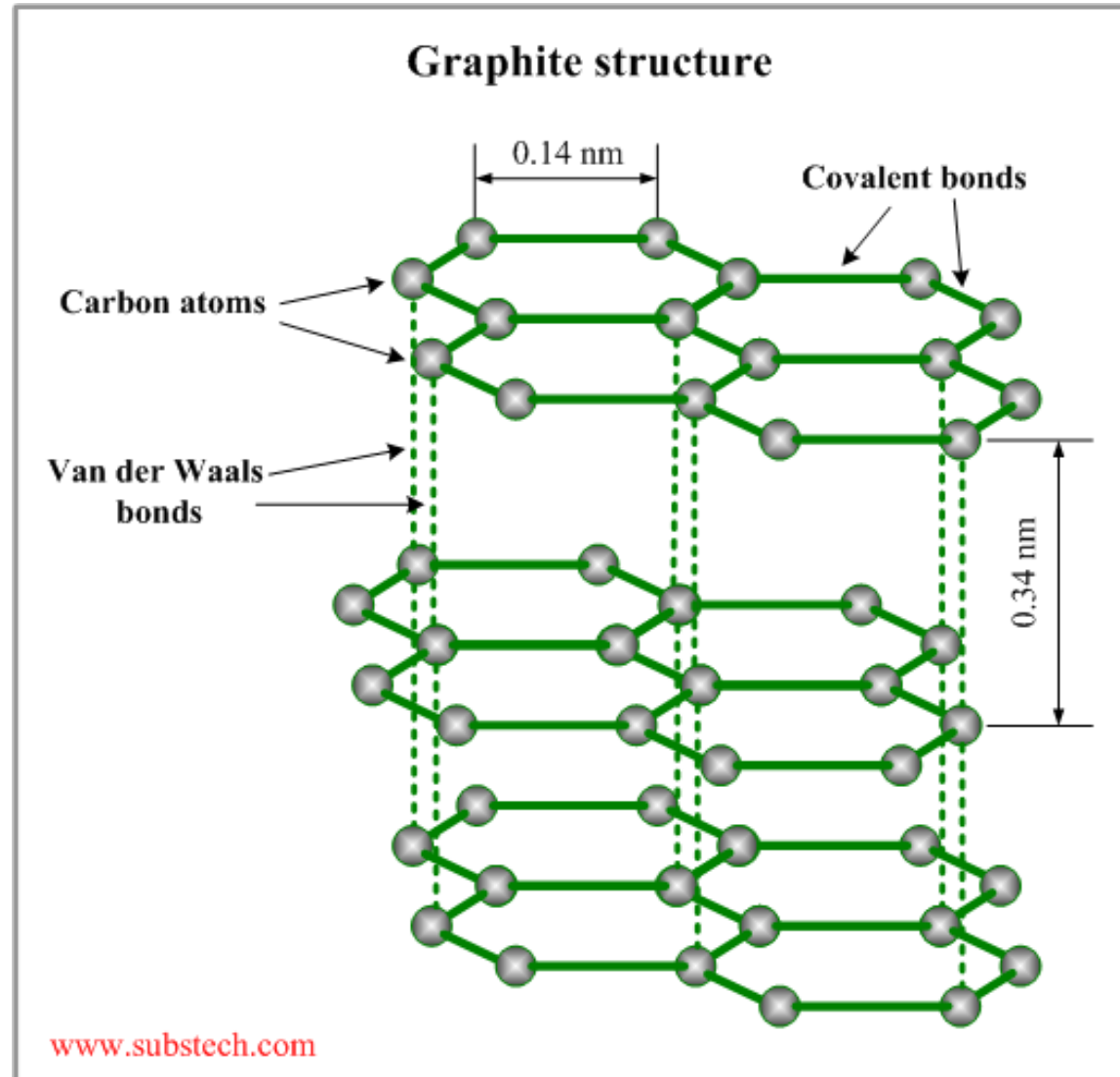
Potential energy between 2 dipoles:

$$u = \frac{-|p_1||p_2|}{4\pi\epsilon_0 r^3} = \frac{-|p_1|\chi E}{4\pi\epsilon_0 r^3} = \frac{-|p_1|^2 \chi}{(4\pi\epsilon_0 r^3)^2}$$

$$\Rightarrow \boxed{u = -\frac{A}{r^6}}$$

Always attractive!

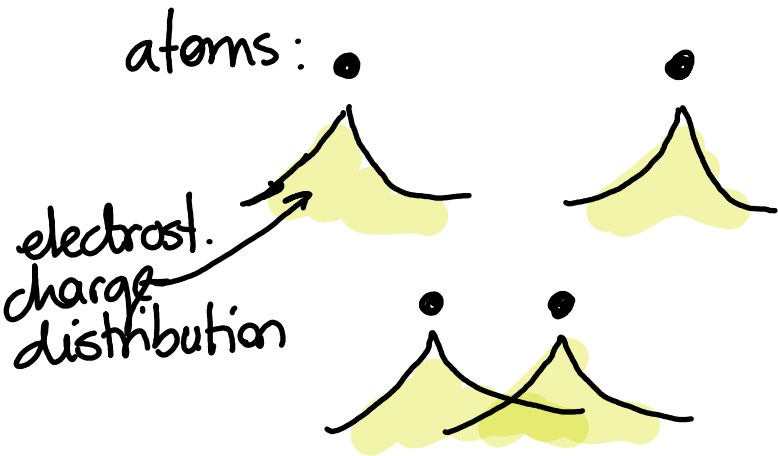
Van der Waals bonds



Van der Waals bonds used Gecko's



Repulsive interaction



as 2 atoms approach \Rightarrow potential energy \uparrow
due to Pauli exclusion princ.
 \Rightarrow repulsive interaction

Phenomenologically,

$$U_{\text{rep}}(r) \propto \frac{B}{r^{12}}$$

$B > 0$

or, equivalently,

$$U_{\text{rep}} \sim \lambda e^{-r/\rho}$$

$\lambda > 0$

λ, ρ, B are empirically determined
(from fitting data on inert gases)

Lennard-Jones potential

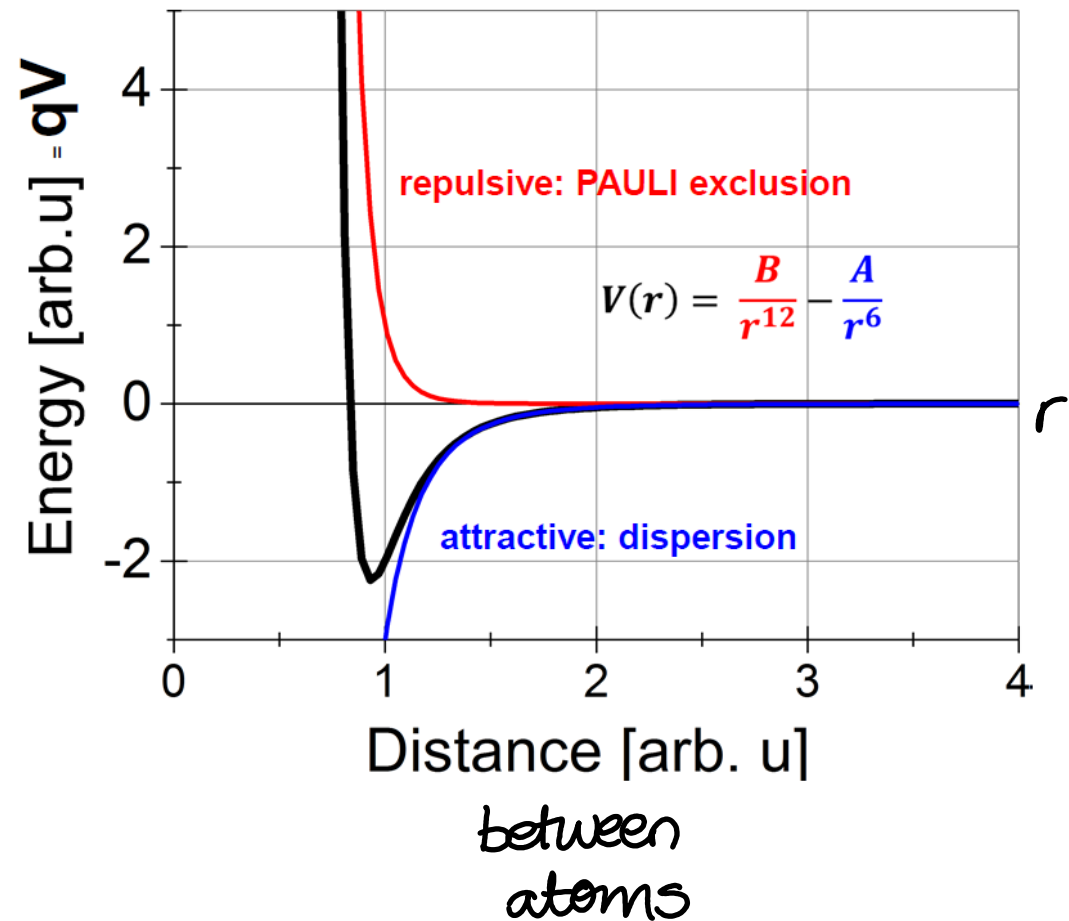
between two atoms:

$$U(R) = \frac{B}{R^{12}} - \frac{A}{R^6} \equiv 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]$$

where $A \equiv 4\pi\sigma^6$ and $B \equiv 4\pi\sigma^{12}$

Pauli
Repulsion

attractive
interact.
(van der Waals)



Equilibrium lattice constants

$$u(R) = 4\epsilon \left(\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right)$$

$$u_{TOT} = 4\epsilon \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right] \times \frac{1}{2}$$

↑
correction
factor to avoid double counting

being R_{ij} - distance between atoms

let's define $R_{ij} = p_{ij} R$ where R = distance between nearest neighbours
 $\Rightarrow p_{ij} \geq 1$

Equilibrium distance:

$$\frac{du}{dR} = 0 \Rightarrow R_0$$

Cohesive energy: $u(R_0)$

$$u_{TOT} = 4N\epsilon \left(\left(\frac{\sigma}{R} \right)^{12} \sum_{j \neq i}^N \frac{1}{p_{ij}^{12}} - \left(\frac{\sigma}{R} \right)^6 \sum_{j \neq i}^N \frac{1}{p_{ij}^6} \right)$$

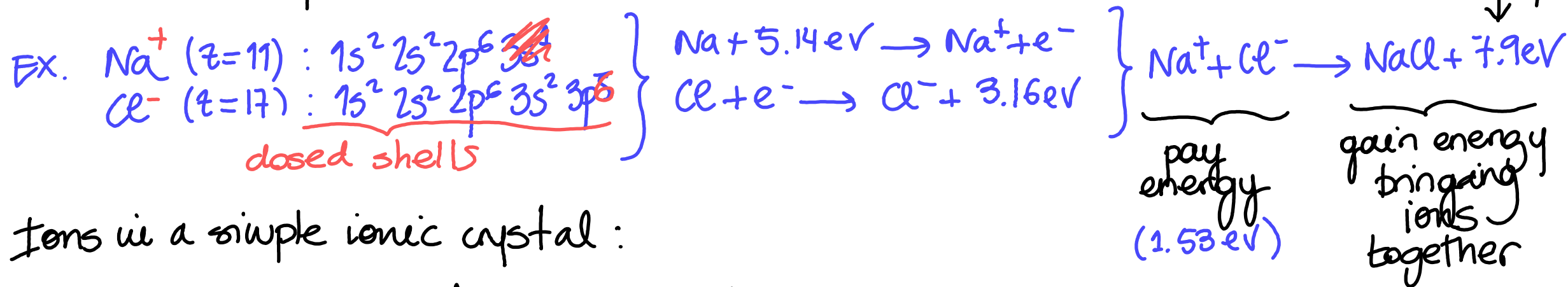
↑
fixing i and
introducing factor N

fcc: 12.1318...

fcc: 14.45392

Ionic bonding

Idea: For some compounds, it is energetically favourable to physically transfer one e^- from one atom to the other



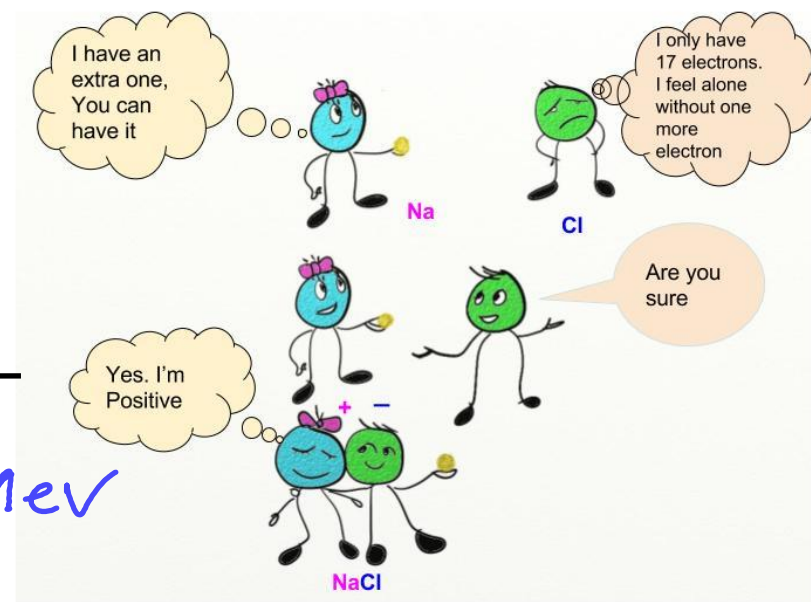
Ions in a simple ionic crystal:

- Electronic configuration: closed shells
- spherical charge distributions
- Low ionization energies

► Coulomb interaction provides most of the Lattice Energy.

NaCl (FCC, $a = 5.62 \text{ \AA}$)

$U_{\text{lattice measured}} = 7.9 \text{ eV}; \quad U_{\text{Coulomb}} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{a/2} \approx 5.1 \text{ eV}$



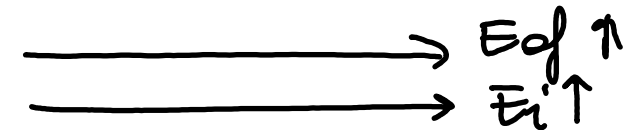
By comparing having $1e^-$ at ∞ or on the atom,

Ionization energy: Energy required to remove one electron from a neutral atom to create a positive ion

$$E_i = E(\text{Na}^+ + e^-) - E(\text{Na}) > 0$$

Electron affinity: Energy gain from creating a negative ion from a neutral atom by adding an electron

$$E_{af} = E(\text{Cl}^-) - E(\text{Cl}) < 0$$



Mulliken

$$\sqrt{\text{Electronegativity}} = \frac{\text{Electron affinity} + \text{Ionization Energy}}{2}$$

! there are many different definitions

In a bond, the e^- is always transferred from the atom with the lower to the one with the higher electronegativity

Madelung energy (Electrostatics)

$\frac{N}{2}$ "molecules" with 2 atoms of charge $\pm q$

* note: van der Waals is very small in ionic crystals!

$$U = N \sum_{i \neq j} \left(\underbrace{\lambda e^{-\frac{r_{ij}}{\rho}}}_{\text{Pauli}} \pm \underbrace{\frac{q^2}{4\pi\epsilon_0 r_{ij}}}_{\text{Coulomb}} \right) \times \underbrace{\frac{1}{2}}_{\text{correction}}$$

↑
ions
Pauli
Coulomb
correction

- define $r_{ij} = p_{ij} R$ ($R =$ nearest neighbours distance)

- consider repulsive interaction for only first neighbours: $\lambda e^{-\frac{r_{ij}}{\rho}} \approx \lambda z e^{-R/\rho}$

parameter
↓
 $\lambda z e^{-R/\rho}$
↑
number of first neigh.

then,

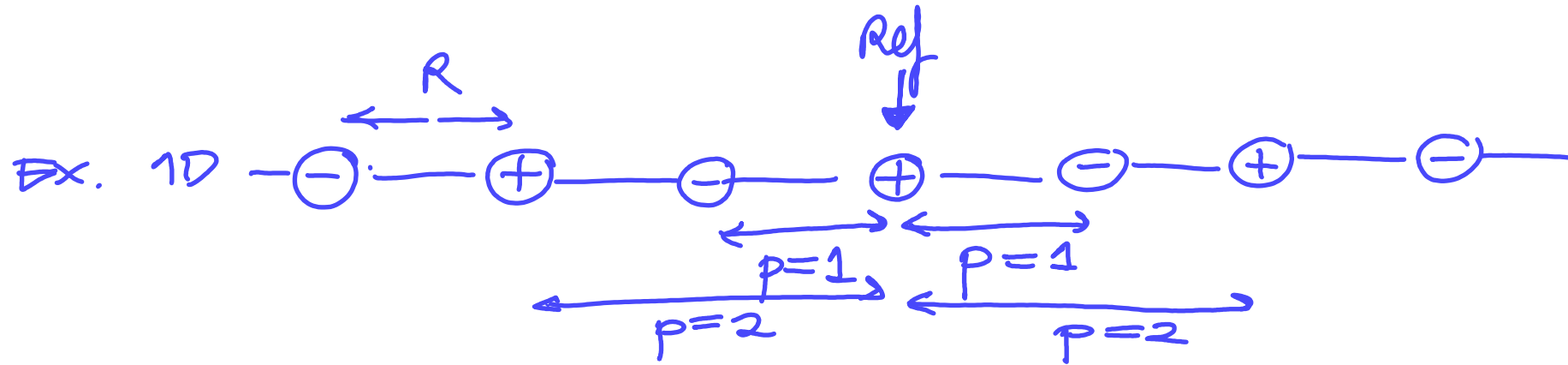
$$U_{\text{TOT}} = \frac{N}{2} \left(z \lambda e^{-R/\rho} - \frac{q^2}{4\pi\epsilon_0 R} \sum_{i \neq j} \frac{\pm 1}{p_{ij}} \right)$$

$$\alpha = \sum_{i \neq j} \frac{\pm 1}{p_{ij}} = \text{MADELUNG CONSTANT}$$

Modelung constant

$$\alpha = \sum_{i \neq j}^N \frac{\pm 1}{p_{ij}}$$

it depends on the structure
it must be positive to ensure stability



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

$$\alpha = \sum_{i \neq j}^N \frac{\pm 1}{p_{ij}} = 2 \cdot \left(1 - \frac{1}{2} + \frac{1}{3} - \dots \right) = 2 \ln 2 = 1.38629$$

Bonding in KCl

From U_{TOT} , the equilibrium distance R_0 : $\frac{dU}{dR} = 0$

Some properties of ionic solids:

- Hard materials
- High melting T (due to Coulomb int between + & - ions)
- in gl., insulators (because charges are strongly bounded to ions)

However, water (which is very polar) can dissolve them

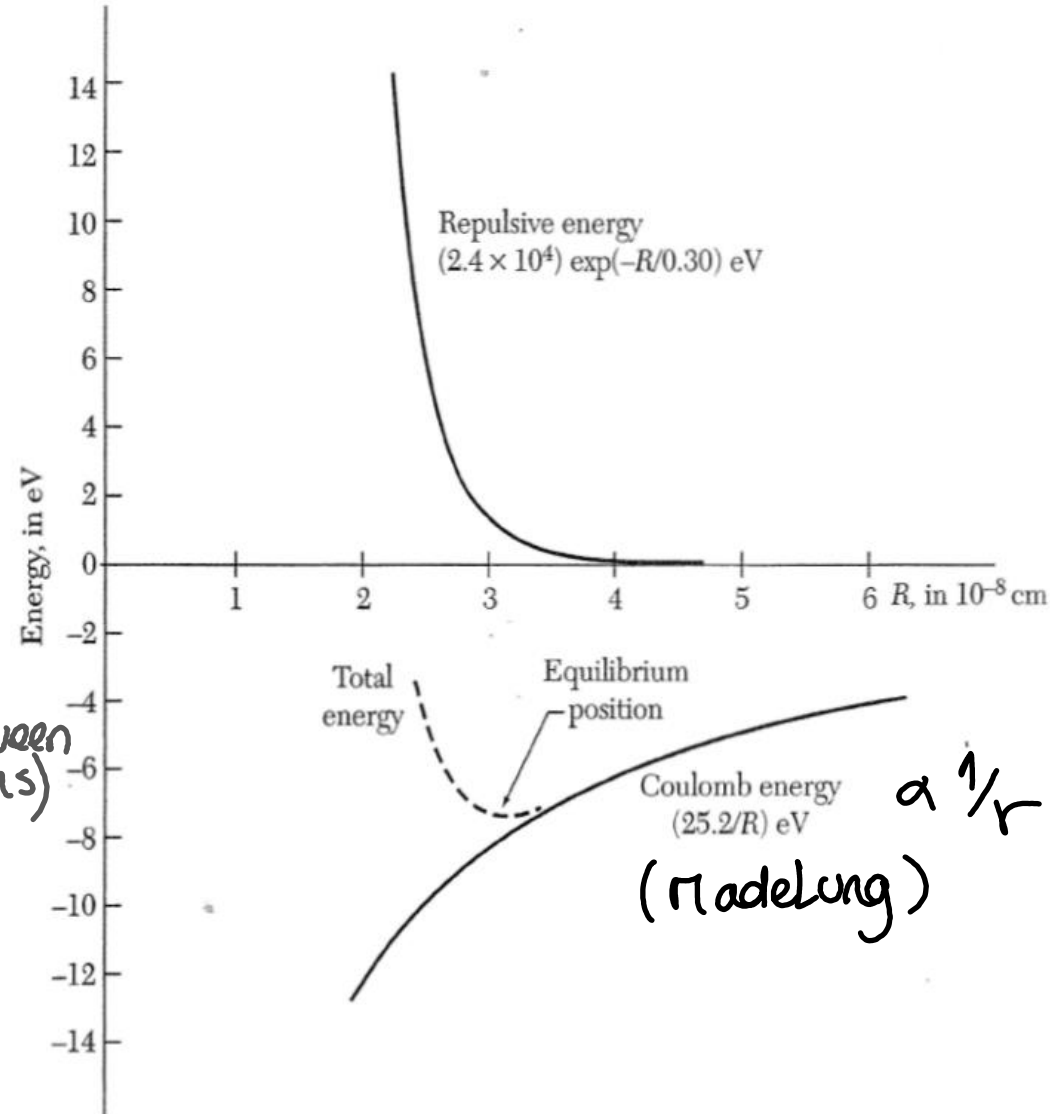
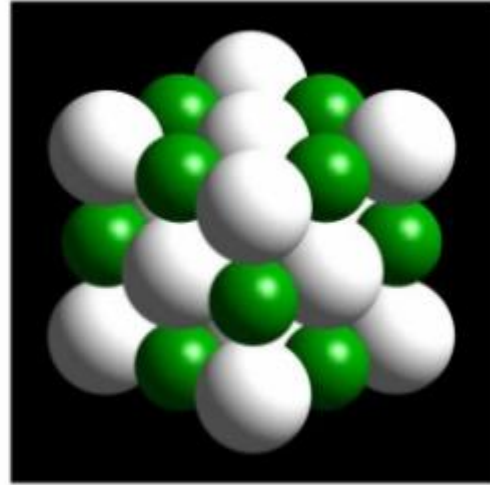
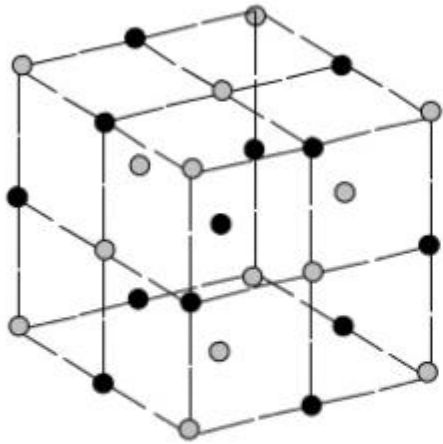


Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

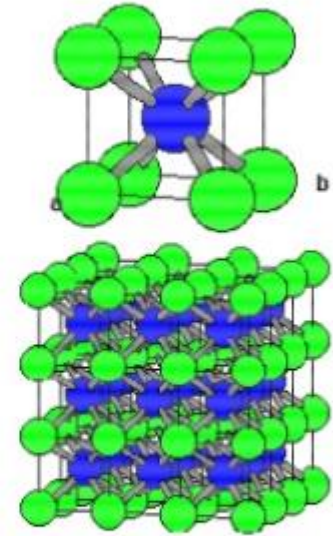
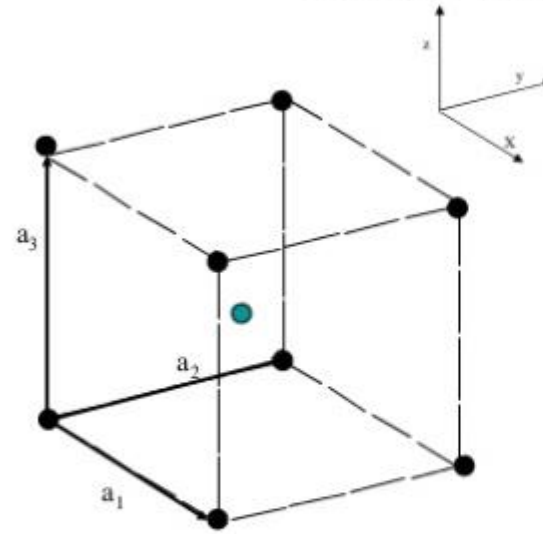
NaCl Structure



Face Centered Cubic Bravais Lattice

Favored for ionic crystals with large size difference
Close packed negative ions with small positive ions

CsCl Structure



Simple Cubic Bravais Lattice

From <http://www.ilpi.com/inorganic/structures/csl/index.html>

Favored for ionic crystals with small size difference

Covalent bonds — Si, Ge, diamond : very important bond type!

Idea: electrons are roughly shared between two atoms

- strong bonding
- directional bonding
- brittle
- electrons are preferentially located between atoms
- antiparallel alignment of spins

in gl, insulators or semiconductors

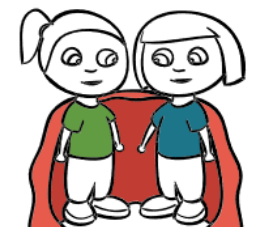
Sarah, I'm cold.

I'm cold too



Emily and Sarah
share the blanket

Wow, we both feel so
cozy and comfortable
after sharing the blanket.



Emily

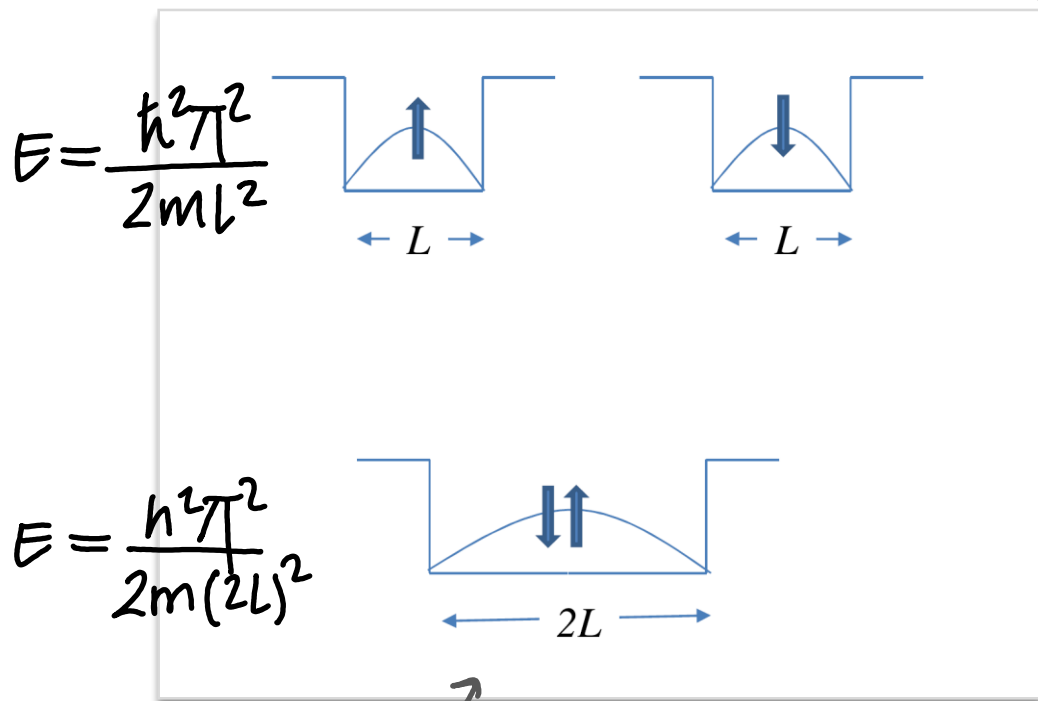
Sarah

Emily

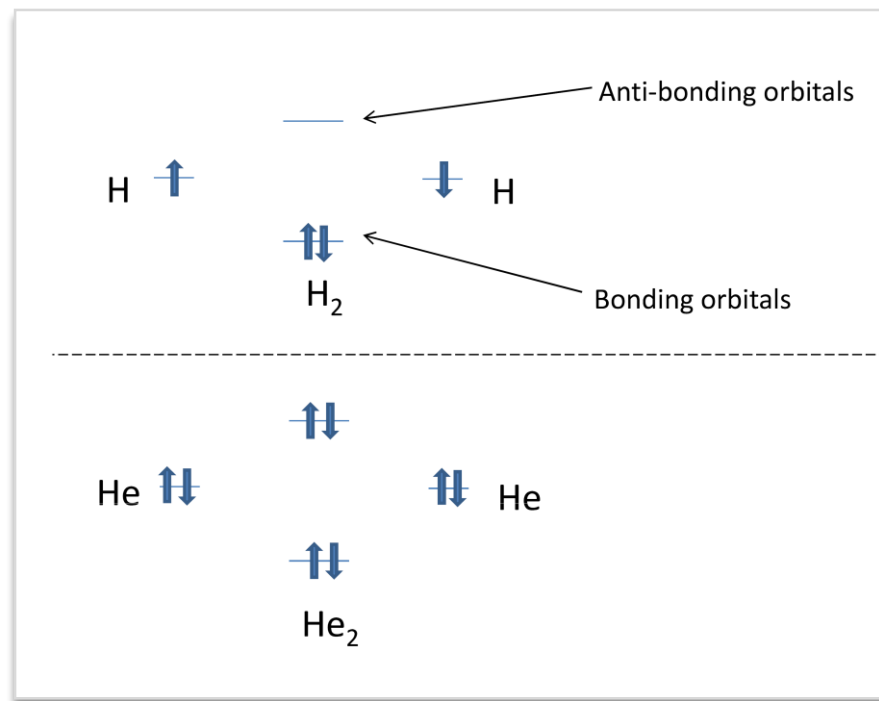
Sarah

Covalent bond

"Particle in a box picture"
 i.e. atom in a box with 1e⁻ (i.e. hydrogen atom)



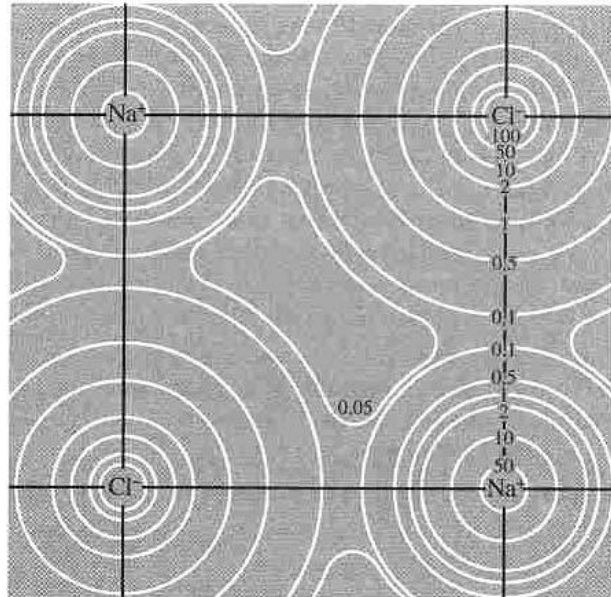
e⁻ shared between 2 atoms
 can delocalize and lower
 the energy



He: 2e⁻ per atom
 \Rightarrow bonding & antibonding filled
 \Rightarrow Total energy not reduced
 \Rightarrow He₂ does not form

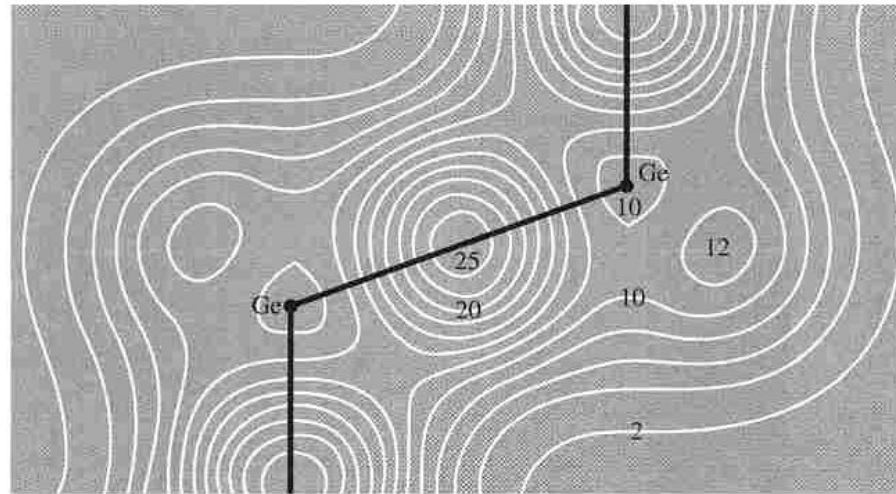
Electron density distribution

Ionic



Electron density contribution in the base plane of NaCl, after x-ray measurements

Covalent



Calculated valence electron concentration in Germanium



there is a continuous range of crystals between covalent and ionic limit.

Metallic bonding

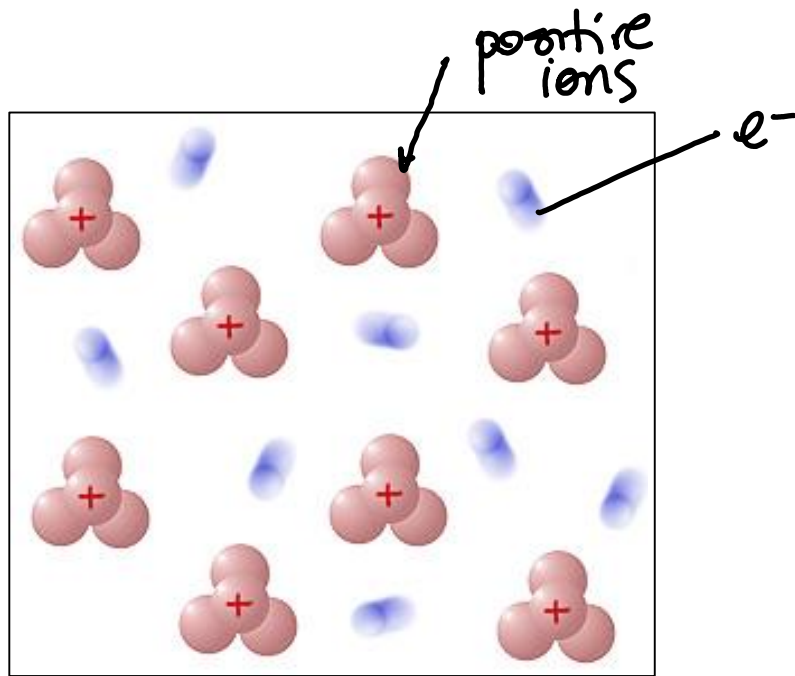
The periodic table is color-coded to show the classification of elements based on their bonding characteristics:

- Metal (Blue):** Elements on the left side of the periodic table, including groups 1, 2, and the transition metals (groups 3-10).
- Metalloid (Green):** Elements along the diagonal line separating metals from nonmetals, including Boron (B), Silicon (Si), Germanium (Ge), Arsenic (As), Antimony (Sb), and Tellurium (Te).
- Nonmetal (Yellow):** Elements on the right side of the periodic table, including groups 13-18.

1																	18
1																	2
3	4											5	6	7	8	9	10
11	12											13	14	15	16	17	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71			
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103			

Metallic bonding

Idea: "positive ions embedded in an electron sea"

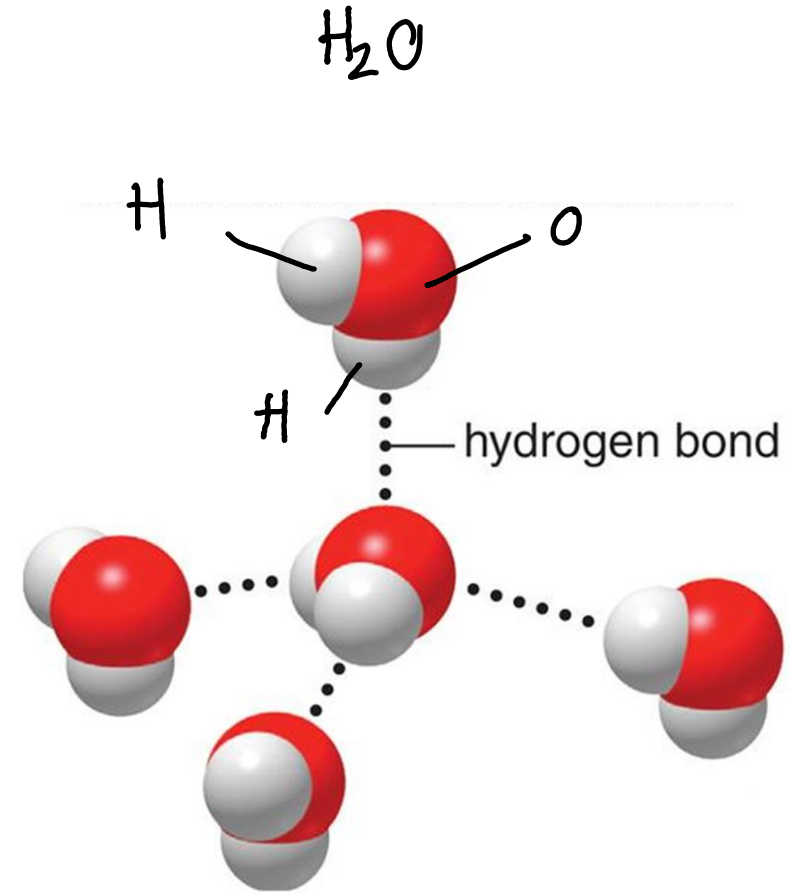
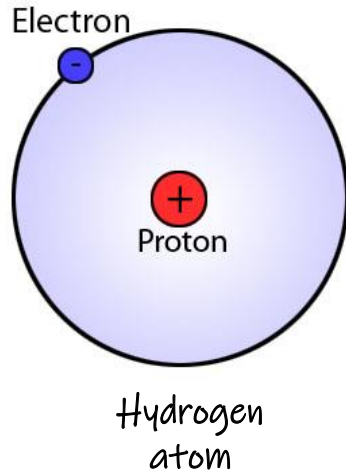


Basic properties of metals

- Excellent electric conductivities
- " thermal "
- Relatively more ductile than covalent bond

typical structures : fcc, hcp, bcc

Hydrogen bonds



Very important in biology too; i.e. they hold together strands of DNA

Types of Bonds in Solids

Type of Bonding	Description	Typical of which compounds	Typical Properties
Ionic	Electron is transferred from one atom to another, and the resulting ions attract each other	Binary compounds made of constituents with very different electronegativity: Ex, group I-VII compounds such as NaCl.	<ul style="list-style-type: none"> • Hard, Very Brittle • High Melting Temperature • Electrical Insulator • Water Soluble
Covalent	Electron is shared equally between two atoms forming a bond. Energy lowered by delocalization of wavefunction	Compounds made of constituents with similar electronegativities (ex, III-V compounds such as GaAs), or solids made of one element only such as diamond (C)	<ul style="list-style-type: none"> • Very Hard (Brittle) • High Melting Temperature • Electrical Insulators or Semiconductors
Metallic Bonds	Electrons delocalized throughout the solid forming a glue between positive ions.	Metals. Left and Middle of Periodic Table.	<ul style="list-style-type: none"> • Ductile, Maleable (due to non-directional nature of bond. Can be hardened by preventing dislocation motion with impurities) • Lower Melting Temperature • Good electrical and thermal conductors.
Molecular (van der Waals or Fluctuating Dipole)	No transfer of electrons. Dipole moments on constituents align to cause attraction. Bonding strength increases with size of molecule or polarity of constituent.	Noble Gas Solids, Solids made of Non-Polar (or slightly polar) Molecules Binding to Each Other (Wax)	<ul style="list-style-type: none"> • Soft, Weak • Low Melting Temperature • Electrical Insulators
Hydrogen	Involves Hydrogen ion bound to one atom but still attracted to another. Special case because H is so small.	Important in organic and biological materials	<ul style="list-style-type: none"> • Weak Bond (stronger than VdW though) • Important for maintaining shape of DNA and proteins

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

van der Waals bonds can sum up energies, and for large objects the van der Waals forces can even become long range forces

Learning outcomes – Crystal Binding

➤ Be familiar with the characteristics of the different type of bondings:

- van der Waals
- Ionic
- Covalent
- Metallic
- Hydrogen

