

Chapter 1:

Bonding in solids

1.1 Introduction

1.2 Van der Waals bonding

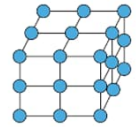
1.3 Ionic bonding

1.4 Covalent bonding

1.5 Metallic bonding

1.6 Hydrogen bonds

States of aggregation



Solid



liquid



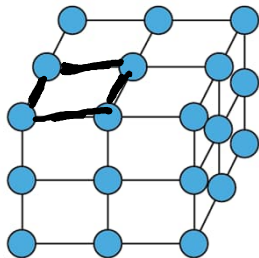
Gaseous



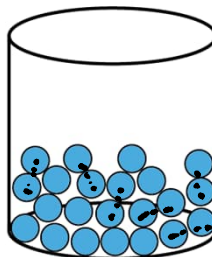
(Plasma)



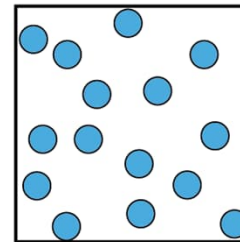
Interparticle ~~forces~~ ^{bonds} ...



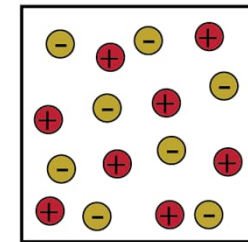
rigid
fixed



flexible
changing

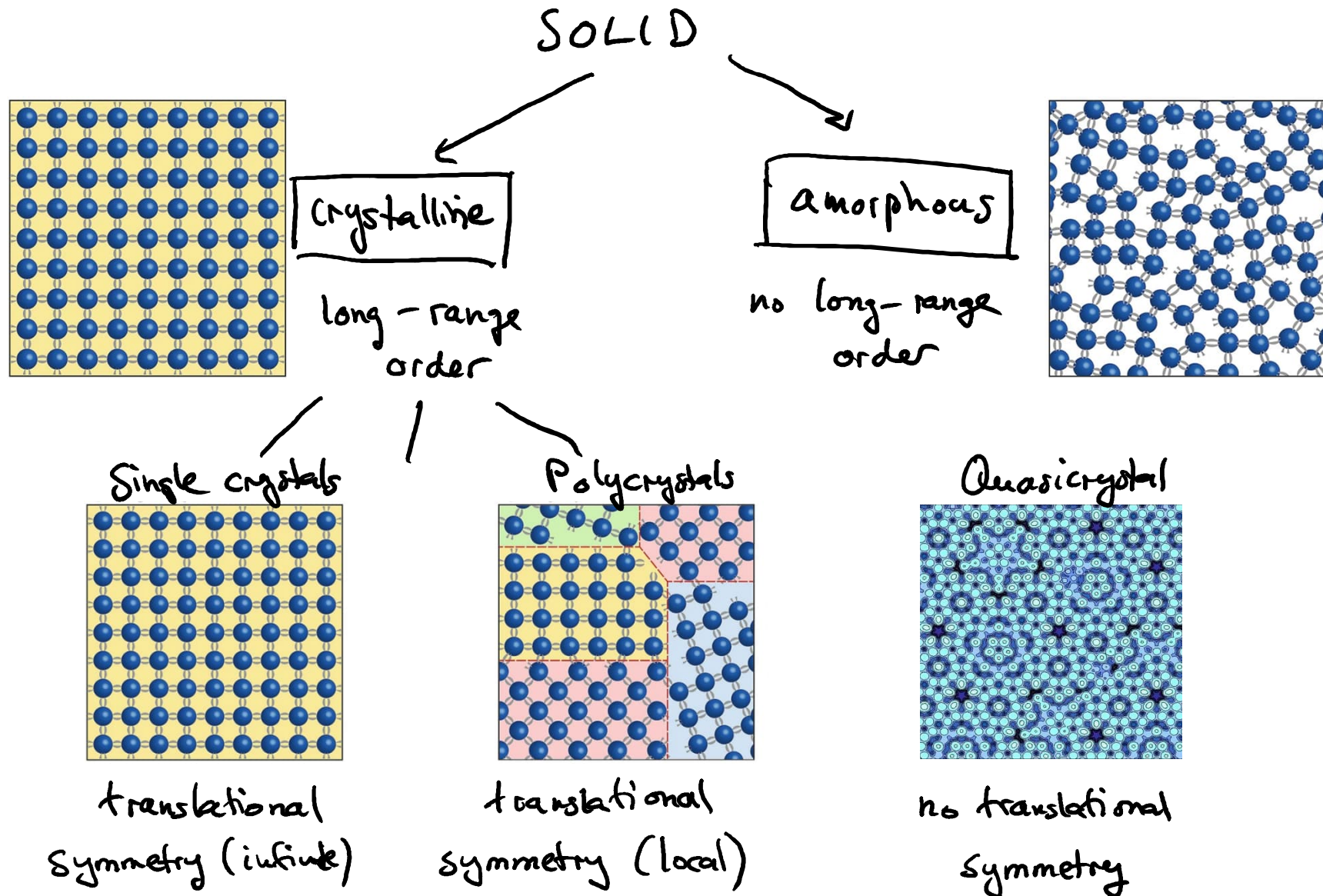
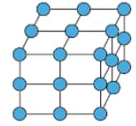


negligible

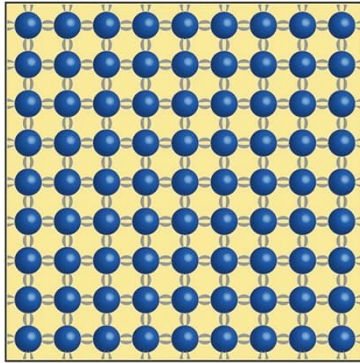
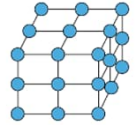


chaotic

Types of solids



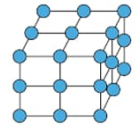
Properties of single crystal solids



Properties of single crystals:

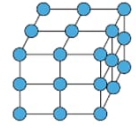
- 1) Ordered atomic arrangement
- 2) Perfect long-range order
- 3) Perfect periodicity
- 4) Structural symmetry
- 5) Infinite boundaries

Consequences of perfect crystallinity

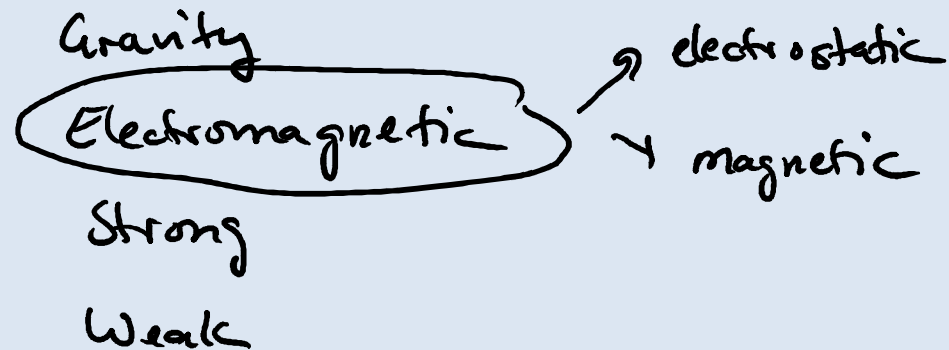


1. Ordered atomic arrangement
 - Cohesive energy
2. Perfect long-range order
 - Bragg's law (wave scattering)
 - Anisotropic macroscopic properties
3. Perfect periodicity
(static atoms)
 - Reciprocal lattice
 - Bloch's theorem
 - Electronic band structures
4. Perfect periodicity
(vibrating atoms)
 - Phonons
 - Phonon dispersion relations
5. Structural symmetries
 - Neumann's principle
 - Degeneracy of electronic states

Nature of binding forces in solids

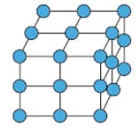


What forces hold crystals together?



- All interactions responsible for binding atoms together are ultimately electromagnetic in origin.
- Electrostatic and quantum-mechanical effects play the central role.

Principal types of binding in crystals

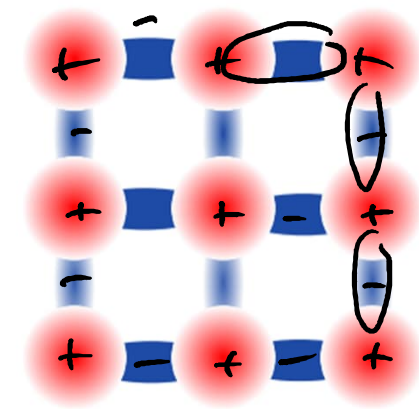
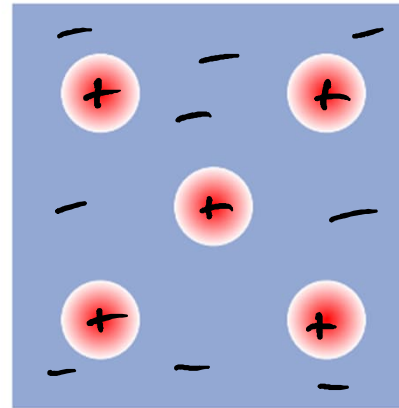
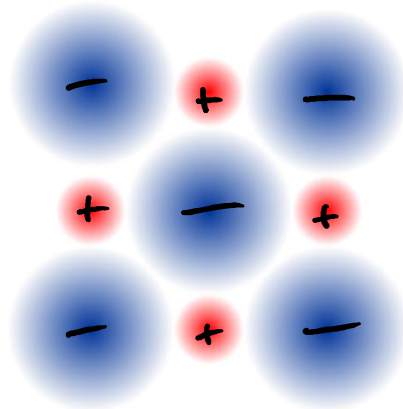


Ionic

Metallic

Covalent

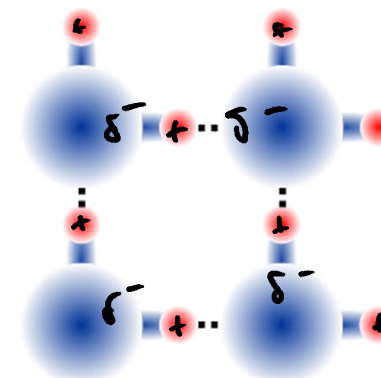
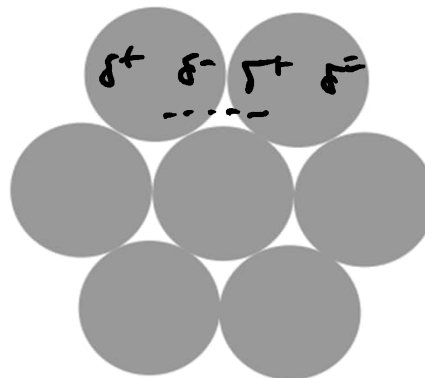
(Very)
strong
forces
(binding)



Van der Waals

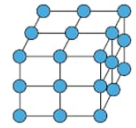
Hydrogen

Weak
binding



Types of crystals

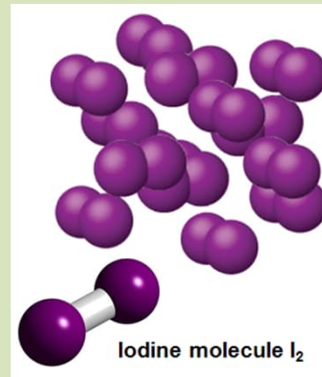
Images: Wikipedia



Molecular

Weak forces between neutral molecules

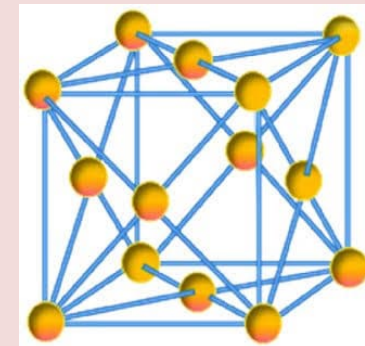
Iodine, dry ice (CO_2)



Metallic

Metal cations rest in a background „sea“ of electrons

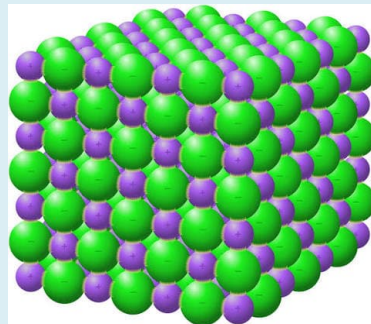
Cu, Au, Fe, Ag, ...



Ionic

Coulomb attraction between anions and cations

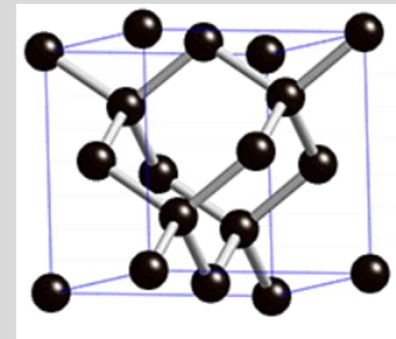
NaCl, CaF_2 , MgO



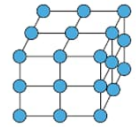
Network Covalent

Atoms share electrons via directional bonds

Diamond, SiO_2 , SiC



Cohesive energy



Energy required to disassemble a material into its constituent, isolated free atoms (or molecules/ions) at 0 Kelvin.



Gas



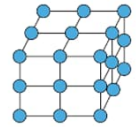
Liquid



Solid

→
Cohesive energy

Cohesive energy



Total energy of a crystal: $E_{\text{tot}} = N \cdot E_{\text{coh}}$ N : # particles in your crystal

	Li	Be	B	C	N	O	F	Ne
E_{coh} (eV/atom)	1.6	3.3	5.8	7.4	4.9	2.6	0.8	0.02

10^{23} particles / cm^3

$1\text{eV} = 1.602 \cdot 10^{-19} \text{ J}$



1cm^3 carbon

$\Rightarrow 208.000 \text{ J}$



NaCl

1cm^3 salt

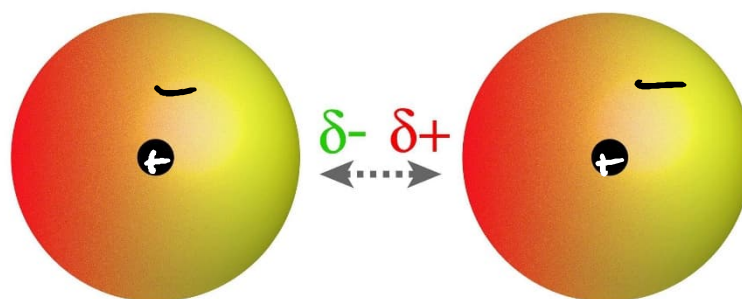
22.000 J



Smartphone battery: $20.000 - 40.000 \text{ J}$



Van der Waals bonding



neutral particles

→ electrostatic force, 22

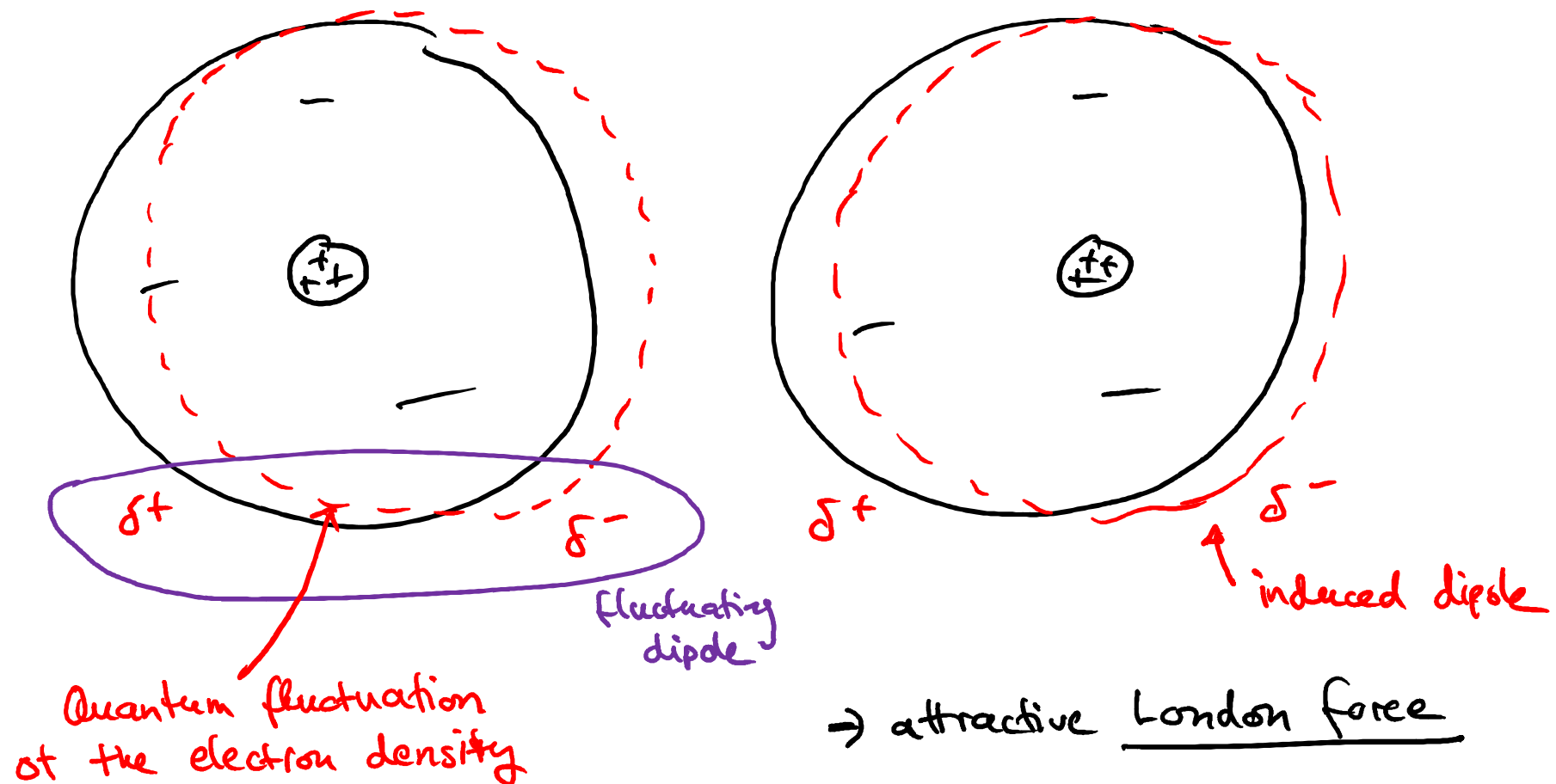
Image: Chemistry world

Van der Waals bonding



Noble gas crystals: closed shells, neutral atoms...

→ how can there be an attractive force??



Van der Waals bonding



Attractive potential:

$$\phi_{\text{att}} \propto -\frac{1}{r^6}$$

r : interparticle distance

$^6 - 4$ because we must add energy to take them apart.

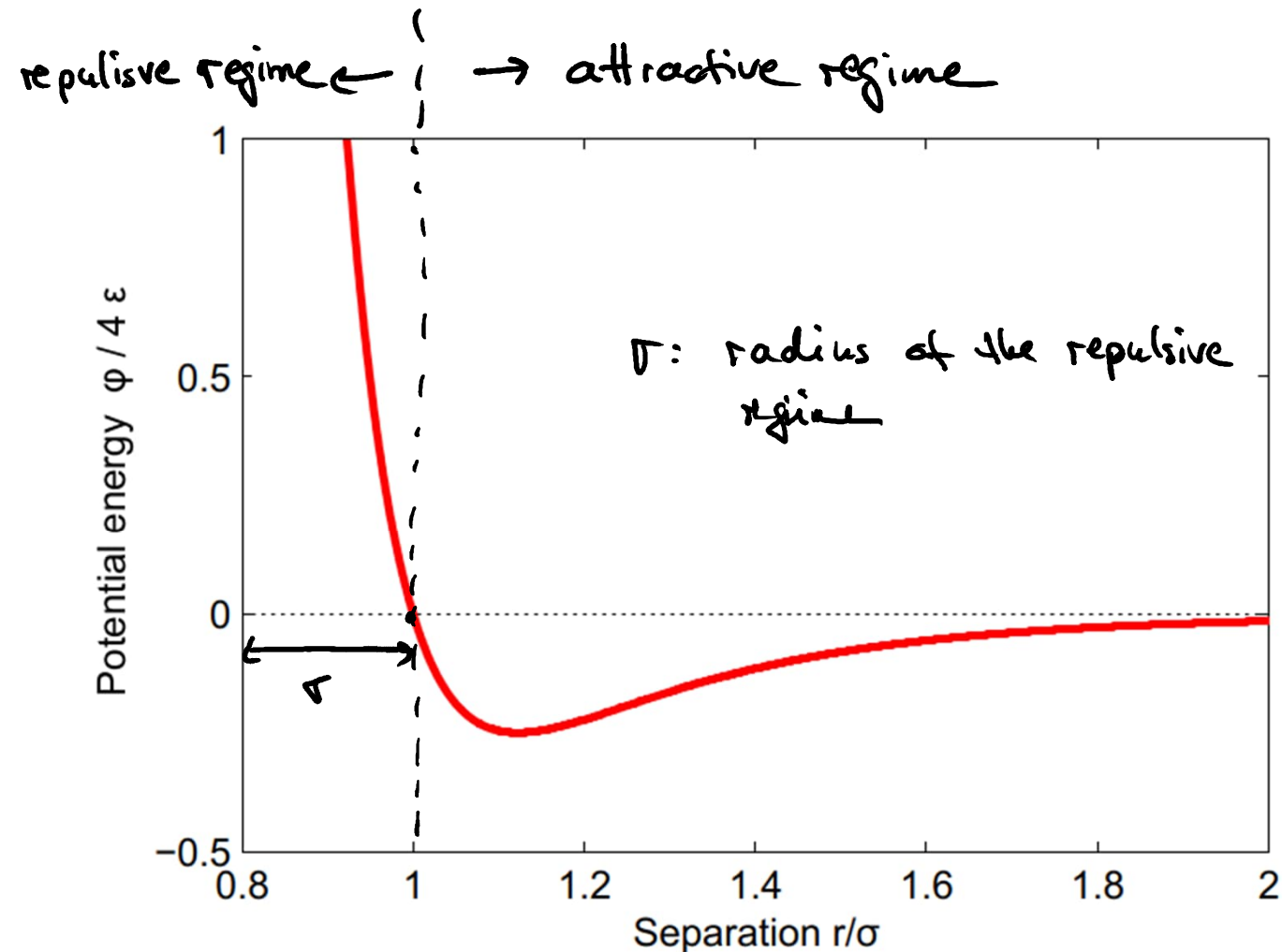
Repulsive potential : $\phi_{\text{rep}} \propto \frac{1}{r^{12}}$

Total potential:

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Lennard-Jones - potential

Lennard-Jones potential



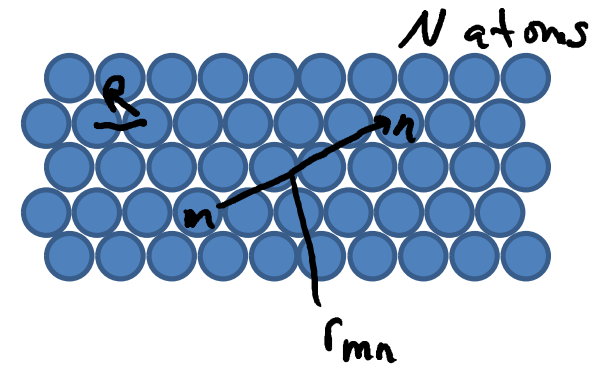
Van der Waals bonding



Energy of the entire crystal?

Potential energy of m -th atom

$$U_m^{(r_{mn})} = \sum_{n \neq m} \phi(r_{mn})$$



Total potential energy:
$$U_{\text{tot}} = \frac{1}{2} \sum_m U_m(r_{mn}) = \frac{N}{2} U_m$$

$$= \frac{1}{2} N \sum_{m \neq n} \left[\left(\frac{\sigma}{r_{mn}} \right)^{12} - \left(\frac{\sigma}{r_{mn}} \right)^6 \right]$$

r_{mn} : replace this by the nearest-neighbor distance R :

$$\boxed{r_{mn} = \kappa_{mn} \cdot R}$$

κ_{mn} : distance between m and n in units of R

Van der Waals bonding



$$U_{\text{tot}} = 2N\varepsilon \sum_{m \neq n} \left[\left(\frac{\sigma}{\alpha_{mn} R} \right)^{12} - \left(\frac{\sigma}{\alpha_{mn} R} \right)^6 \right]$$

$$= 2N\varepsilon \left[\textcircled{A_{12}} \left(\frac{\sigma}{R} \right)^{12} - \textcircled{A_6} \left(\frac{\sigma}{R} \right)^6 \right]$$

$$A_j = \sum_{m \neq n} \frac{1}{\alpha_{mn}^j} \quad j = [6, 12]$$

Find the condition for minimal energy:

$$\frac{dU_{\text{tot}}}{dR} = -2N\varepsilon \left[12 \cdot A_{12} \frac{\sigma^{12}}{R^{13}} - 6 \cdot A_6 \cdot \frac{\sigma^6}{R^7} \right] \stackrel{!}{=} 0$$

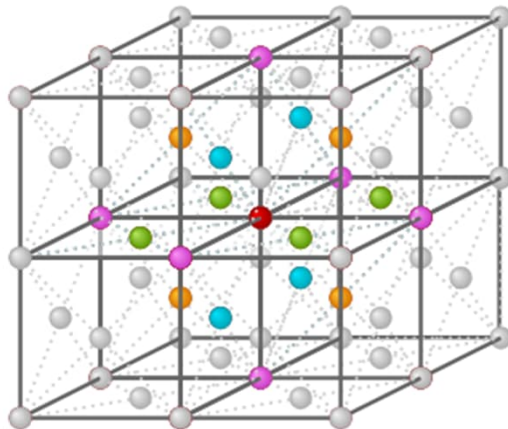
Result: $\boxed{R_0 = \left(2 \cdot \frac{A_{12}}{A_6} \right)^{1/2} \cdot \sigma}$

Van der Waals bonding



Cohesive energy: $E_{\text{coh}} = U_{\text{tot}}(R_0) = -\frac{1}{2} N \epsilon \left(\frac{A_6^2}{A_{12}} \right)$

Closed-packing structure: fcc-structure ($\rightarrow$ chapter 2.4)
 $\Rightarrow \left[R_0 = 1.09 \cdot \sigma \right]$
 $\left. \begin{array}{l} \Rightarrow A_{12} = 12 \cdot 13 \\ A_6 = 14.45 \end{array} \right\} \text{"lattice sum"}$



- reference point
- ● ● 12 nearest neighbours #12 with $\alpha=1$
- 6 next-nearest neighbours #6 with $\alpha=\sqrt{2}$
- 24 next-next-... with $\alpha=\sqrt{3}$

$$A_6 = 12 \cdot \frac{1}{(1)^6} + 6 \cdot \frac{1}{(\sqrt{2})^6} + 24 \cdot \frac{1}{(\sqrt{3})^6} + \dots$$

Van der Waals bonding



	Ne	Ar	Kr	Xe
$\mathcal{E}(\text{eV})$	0.0031	0.0104	0.014	0.02
$\sigma(\text{\AA})$	2.74	3.40	3.65	3.98
Exp. $R_0(\text{\AA})$	3.13	3.75	3.99	4.33
$R_0 = 1.09\sigma(\text{\AA})$	2.99	3.71	3.98	4.34

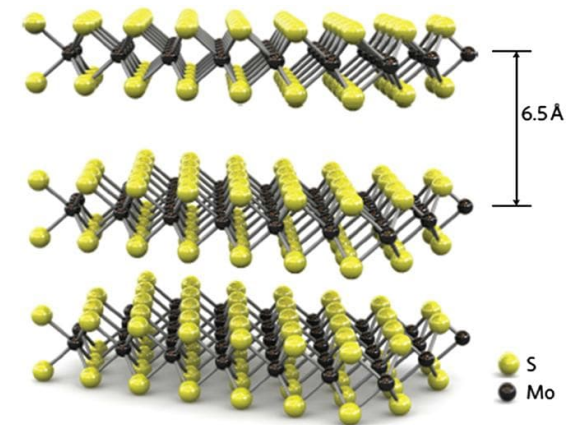
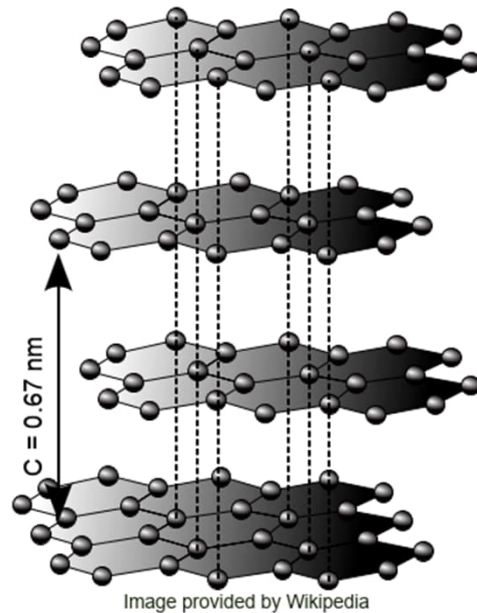
Lennard Jones parameters and nearest-neighbor distances for solid noble gases. (Ref.: Ashcroft/Mermin)

- The proportionality factor 1.09 describes well crystals from heavy noble elements (Kr, Xe).
- It deviates from experiments for lighter elements (Ne, Ar.). The reason is the zero-point energy (finite energy of a quantum mechanical system at $T = 0$ K).
- This is the reason why Helium never freezes at all!

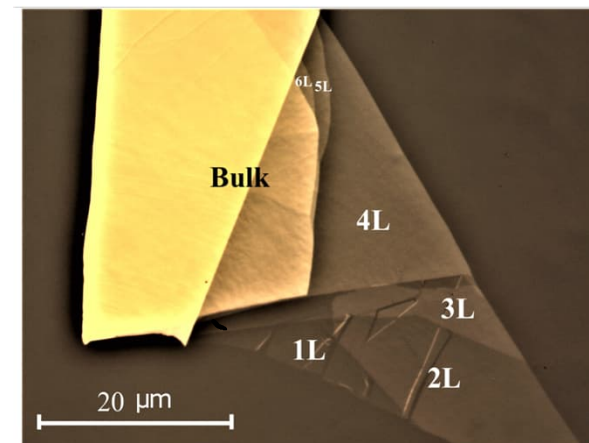
Van der Waals bonding: relevance



„Who cares about van der Waals crystals. They are not really relevant, it's just textbook stuff”



Layered materials:
Strongly bonded atomic layers
separated by van der Waals gaps.

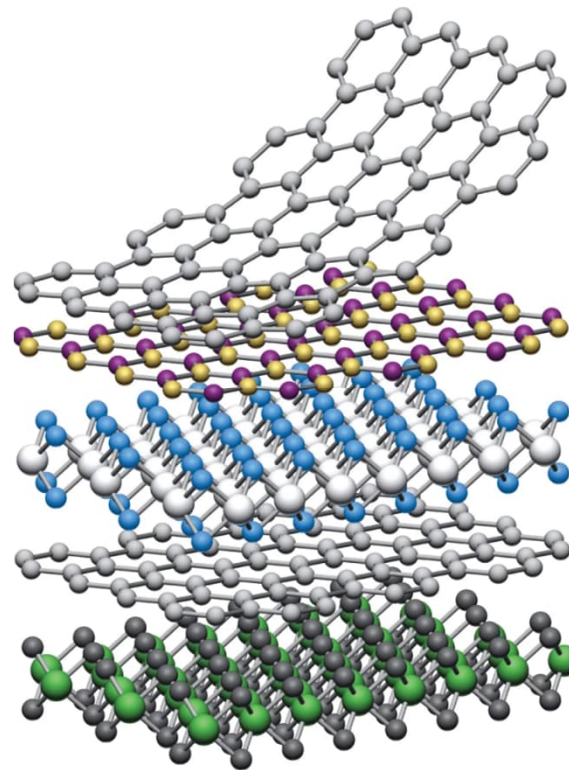
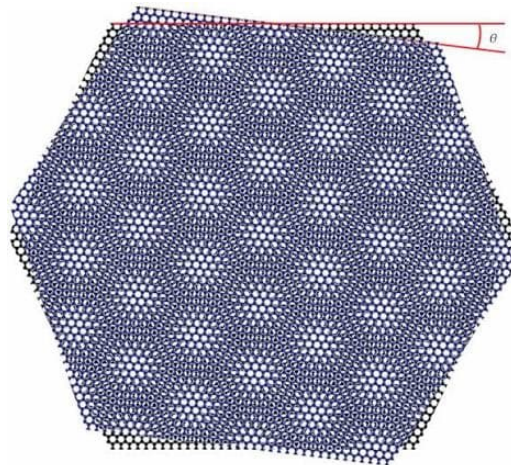


Van der Waals bonding: 2D materials

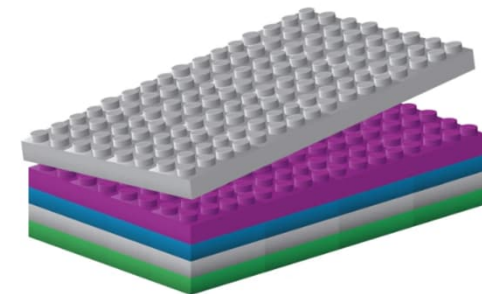


2D materials engineering: tune crystal properties by

- stacking sequence
- layer alignment
- interlayer coupling
- twist angle



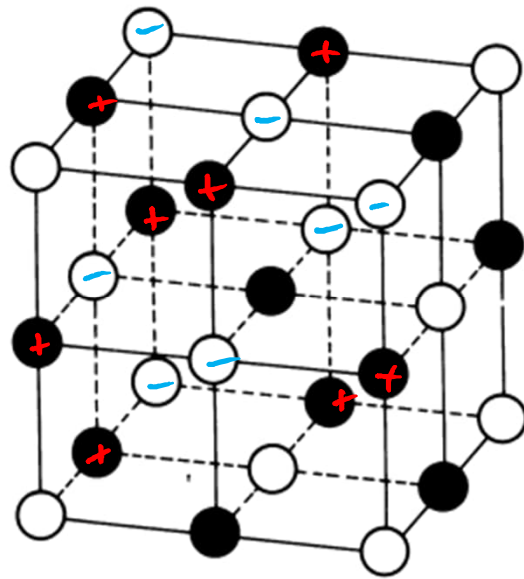
	Graphene	
	hBN	
	MoS ₂	
	WSe ₂	
	Fluorographene	



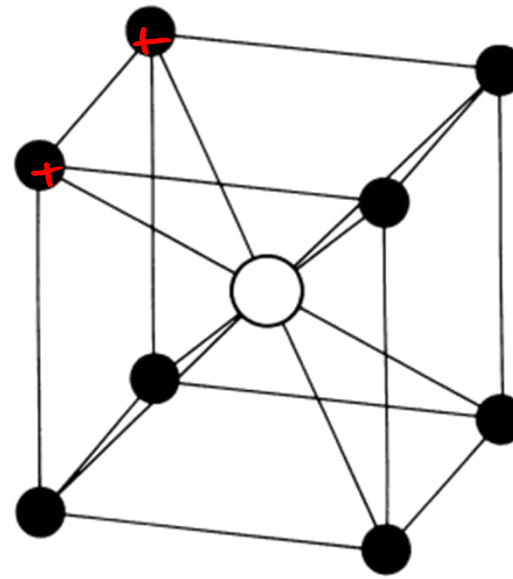
Van der Waals crystal structures are “not just textbook physics”!
They are key in determining the properties of modern layered materials!



Ionic bonding



NaCl



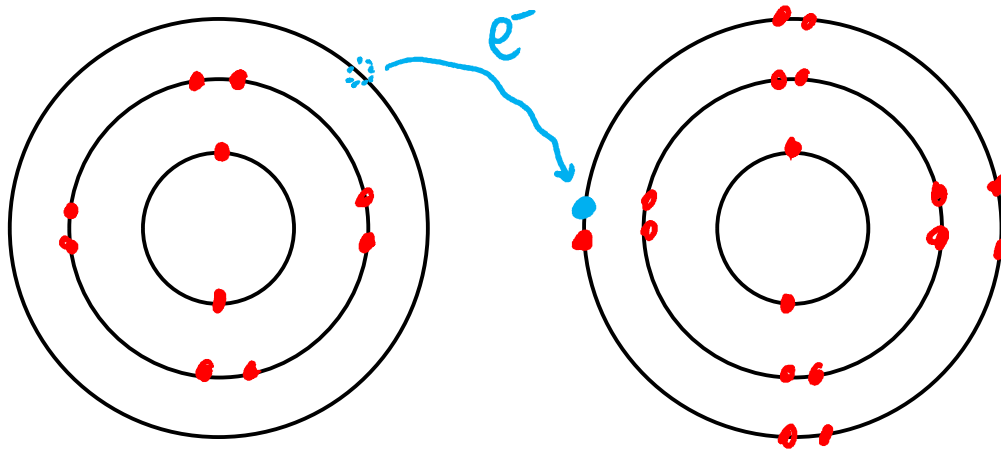
CsCl

Image modified from: Ibach, Lüth

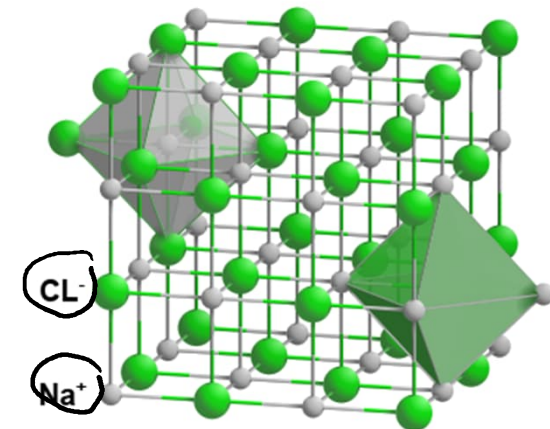
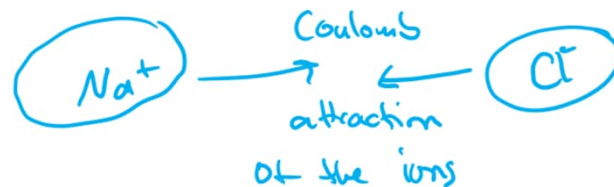
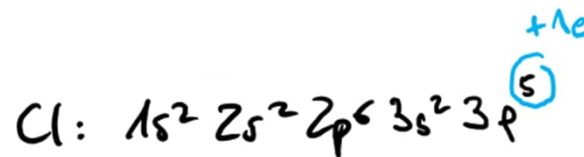
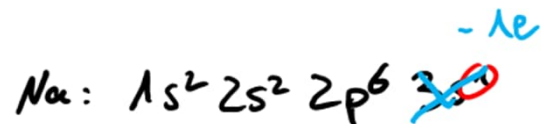
Ionic bonding



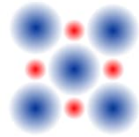
- Ionic crystals are made up of positive and negative ions.
- The atoms get ionized by gaining or losing electrons.
- They do this to obtain a closed/full outer shell.



Transferring e^- : closed shells!



Ionic bonding



Low ionization potential

High electron affinity

Atomic No. →

Symbol ←

Name →

Ionization energy ←

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.59																	2 He Helium 24.58
2 Li Lithium 5.39	Be Beryllium 9.32											5 B Boron 8.29	6 C Carbon 11.26	7 N Nitrogen 14.53	8 O Oxygen 13.61	9 F Fluorine 17.42	10 Ne Neon 21.56
3 Na Sodium 5.13	12 Mg Magnesium 7.64											13 Al Aluminium 5.98	14 Si Silicon 8.15	15 P Phosphorus 10.48	16 S Sulphur 10.36	17 Cl Chlorine 12.96	18 Ar Argon 15.75
4 K Potassium 4.34	20 Ca Calcium 6.11	21 Sc Scandium 5.56	22 Ti Titanium 6.82	23 V Vanadium 6.74	24 Cr Chromium 6.76	25 Mn Manganese 7.43	26 Fe Iron 7.90	27 Co Cobalt 7.88	28 Ni Nickel 7.63	29 Cu Copper 7.72	30 Zn Zinc 9.39	31 Ga Gallium 5.99	32 Ge Germanium 7.89	33 As Arsenic 9.78	34 Se Selenium 9.75	35 Br Bromine 11.81	36 Kr Krypton 13.99
5 Rb Rubidium 4.17	38 Sr Strontium 5.69	39 Y Yttrium 5.21	40 Zr Zirconium 6.63	41 Nb Niobium 6.75	42 Mo Molybdenum 7.09	43 Tc Technetium 7.28	44 Ru Ruthenium 7.36	45 Rh Rhodium 7.45	46 Pd Palladium 8.33	47 Ag Silver 7.57	48 Cd Cadmium 8.99	49 In Indium 5.78	50 Sn Tin 7.34	51 Sb Antimony 8.60	52 Te Tellurium 9	53 I Iodine 10.45	54 Xe Xenon 12.12
6 Cs Caesium 3.89	56 Ba Barium 5.21	57 La Lanthanum 5.57	72 Hf Hafnium 6.82	73 Ta Tantalum 7.54	74 W Tungsten 7.86	75 Re Rhenium 7.83	76 Os Osmium 8.43	77 Ir Iridium 8.96	78 Pt Platinum 8.95	79 Au Gold 9.22	80 Hg Mercury 10.43	81 Tl Thallium 6.10	82 Pb Lead 7.41	83 Bi Bismuth 7.28	84 Po Polonium 8.41	85 At Astatine 9.31	86 Rn Radon 10.74
7 Fr Francium 4.07	88 Ra Radium 5.27	89 Ac Actinium 5.17	104 Rf Rutherfordium 6	105 Db Dubnium n/a	106 Sg Seaborgium n/a	107 Bh Bohrium n/a	108 Hs Hassium n/a	109 Mt Meitnerium n/a	110 Ds Darmstadtium n/a	111 Rg Roentgenium n/a	112 Cn Copernicium n/a	113 Nh Nihonium n/a	114 Fl Flerovium n/a	115 Mc Moscovium n/a	116 Lv Livermorium n/a	117 Ts Tennessine n/a	118 Og Oganesson n/a

Lanthanides

58 Ce Cerium 5.53	59 Pr Praseodymium 5.47	60 Nd Neodymium 5.52	61 Pm Promethium 5.58	62 Sm Samarium 5.64	63 Eu Europium 5.67	64 Gd Gadolinium 6.15	65 Tb Terbium 5.86	66 Dy Dysprosium 5.93	67 Ho Holmium 6.02	68 Er Erbium 6.10	69 Tm Thulium 6.18	70 Yb Ytterbium 6.25	71 Lu Lutetium 5.42
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Actinides

90 Th Thorium 6.30	91 Pa Protactinium 5.89	92 U Uranium 6.19	93 Np Neptunium 6.26	94 Pu Plutonium 6.02	95 Am Americium 5.97	96 Cm Curium 5.99	97 Bk Berkelium 6.19	98 Cf Californium 6.28	99 Es Einsteinium 6.42	100 Fm Fermium 6.50	101 Md Mendelevium 6.58	102 No Nobelium 6.65	103 Lr Lawrencium 4.9
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Ionic bonds: Ion pair energy



$$E_{\text{coh}} = E_{\text{lat}} + (I - A)$$

Coulomb energy
of lattice

Energy cost
to form ions

Cohesive energy of ionic bonding

I : Ionization energy

A : electron affinity

NaCl: $I_{\text{Na}} = 5.1 \text{ eV}$
 $A_{\text{Cl}} = 3.6 \text{ eV}$ $\rightarrow I - A \approx 1.5 \text{ eV}$

E_{lat} : Coulomb energy of a single ion with all other ions in the crystal

Simple estimation: ion pair

$$E_{\text{lat}} = -\frac{e^2}{4\pi\epsilon_0 R_0}$$

$R_0 = 0.28 \text{ nm}$ for NaCl

negative: stable
crystal

ion pair

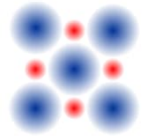
repulsion

$$\Rightarrow E_{\text{lat}} \approx -5.1 \text{ eV}$$

$$\rightarrow E_{\text{coh}} \approx -5.1 \text{ eV} + (1.5 \text{ eV}) \approx -3.5 \text{ eV}$$

Note: for two ions with the same charge, E_{lat} is positive!

Ionic bonding: Crystal energy



Entire crystal : $U_m = \sum_{n \neq m} \left[\underbrace{\frac{C}{r_{nm}^{12}}}_{\text{Pauli exclusion}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{nm}}}_{\text{Coulomb}} \right]$

(Potential energy of m-th ion)

Write again $r_{mn} = \alpha_{mn} \cdot R$

$$\Rightarrow U_m = \sum_{n \neq m} \left[\frac{C}{[\alpha_{mn} \cdot R]^{12}} + \frac{e^2}{4\pi\epsilon_0 \alpha_{mn} \cdot R} \right]$$

$$\approx z \cdot \frac{C}{R^{12}} - A \cdot \frac{e^2}{4\pi\epsilon_0 \cdot R}$$

with

z : number of nearest neighbors

A : Madelung constant

$$A = \sum_{n \neq m} \frac{\pm 1}{\alpha_{mn}} \quad (\text{often "M"})$$

Ionic bonding: Lattice energy



How to determine E_{lat} for the entire crystal and the Madelung constant?

- 6 nearest neighbors (Cl^-) at $R_0 = 0.28 \text{ nm}$ distance

$$E_{\text{lat},1} = -6 \frac{e^2}{4\pi\epsilon_0 R_0}$$

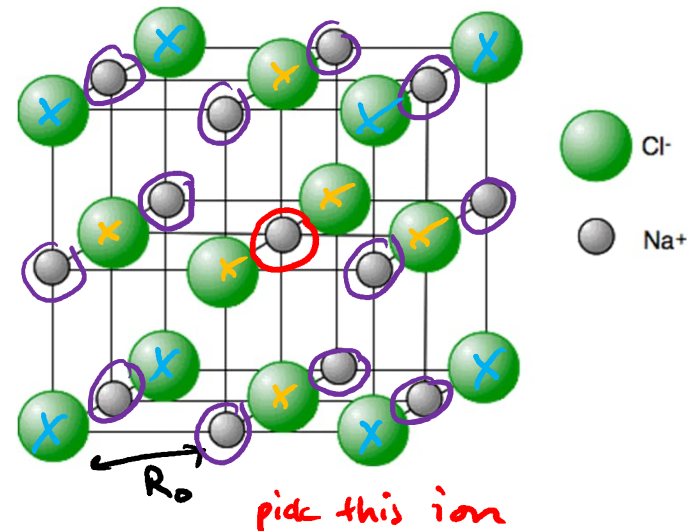
- 12 next-nearest neighbors (Na^+) at $r = \sqrt{2} R_0$

$$E_{\text{lat},2} = +12 \frac{e^2}{4\pi\epsilon_0 (\sqrt{2} R_0)}$$

- 8 Cl^- at $\sqrt{3} R_0$

$$E_{\text{lat},3} = -8 \frac{e^2}{4\pi\epsilon_0 \sqrt{3} R_0}$$

.....



$$E_{\text{lat}} = E_{\text{lat},1} + E_{\text{lat},2} + E_{\text{lat},3} + \dots$$

→ converges

Ionic bonding: Madelung constant



Convergence:
$$E_{\text{lat}} = - \underbrace{1.748}_A \cdot \frac{e^2}{4\pi\epsilon_0 R_0}$$

"Madelung constant"

Crystal structure	Madelung constant A
Cesium chloride	1.7627
Sodium chloride	1.7476
Zincblende	1.6381

Madelung constant A for selected cubic crystal structures.

Source: Ashcroft/Mermin, Solid State Physics.

Note: $A > 1$ means the energy gain for forming the entire crystal is higher than for an isolated dimer (i.e., a „NaCl“ molecule)!

Ionic bonding: Total lattice energy



Total potential of the ionic crystal

$$U_{\text{tot}} = N \cdot U_m = N \cdot \left(z \frac{C}{R^{12}} - A \cdot \frac{e^2}{4\pi\epsilon_0 R} \right)$$

Find the minimum:

$$\frac{dU_{\text{tot}}}{dR} = -N \left(12 \cdot z \frac{C}{R^{13}} - A \cdot \frac{e^2}{4\pi\epsilon_0 R^2} \right) \stackrel{!}{=} 0$$

$$\Rightarrow R_0 = \frac{48 \cdot \pi \cdot \epsilon_0 \cdot z \cdot C}{A \cdot e^2}$$

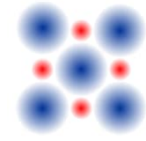
$$E_{\text{NaCl}} = 1.6 (-5.1 \text{ eV}) = -8.16 \text{ eV}$$

"Madelung boost" of lattice energy

$$E_{\text{lat}} = \frac{U_{\text{tot}}(R_0)}{N} = - \underbrace{A \cdot \frac{11}{12}}_{\approx 1.6} \cdot \frac{e^2}{4\pi\epsilon_0 \cdot R_0}$$

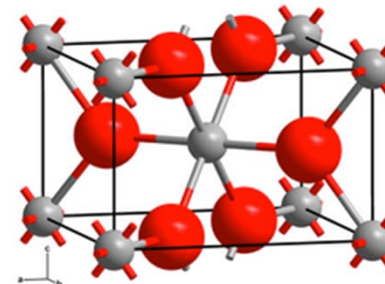
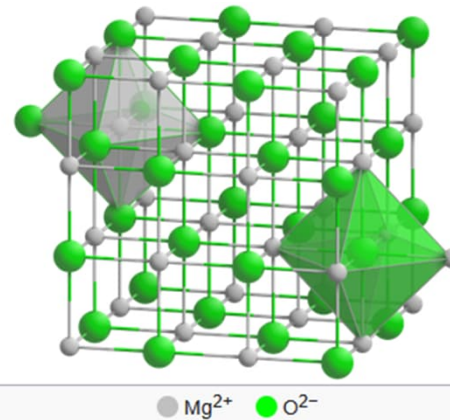
Compared to the dimer

Ionic bonding: Total lattice energy



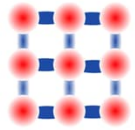
Compound	Experimental Lattice Energy ^[1]	Structure type
LiF	-1030 kJ/mol	NaCl
NaCl	-786 kJ/mol	NaCl
NaBr	-747 kJ/mol	NaCl
NaI	-704 kJ/mol	NaCl
CsCl	-657 kJ/mol	CsCl
CsBr	-632 kJ/mol	CsCl
CsI	-600 kJ/mol	CsCl
MgO	-3795 kJ/mol	NaCl
CaO	-3414 kJ/mol	NaCl
SrO	-3217 kJ/mol	NaCl
MgF ₂	-2922 kJ/mol	rutile
TiO ₂	-12150 kJ/mol	rutile

$$1 \text{ eV / ion pair} = 96.5 \text{ kJ/mol}$$



Titan(IV)-oxid in der Modifikation Rutil





Covalent bonding

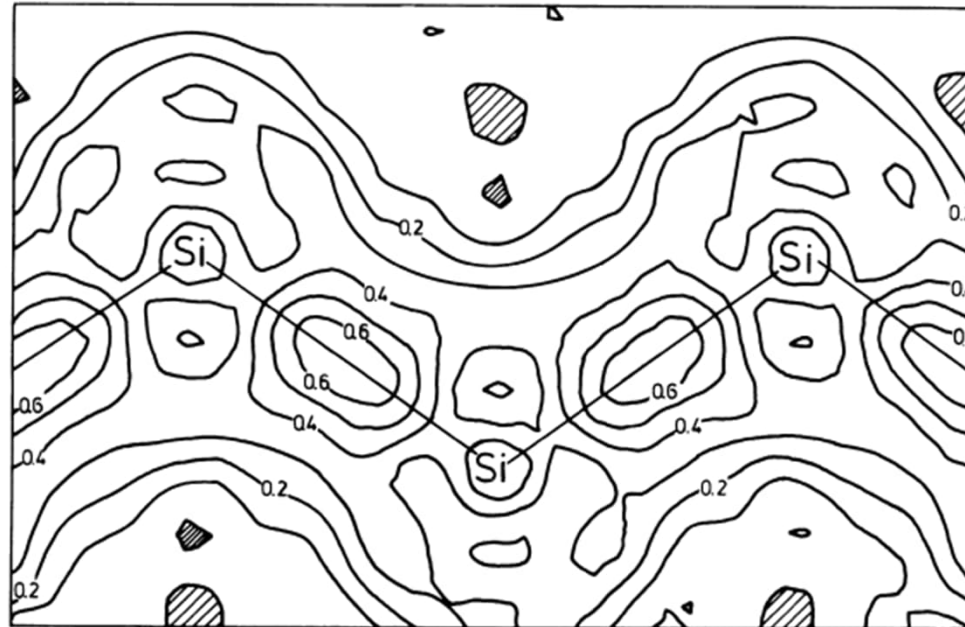
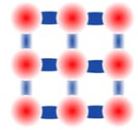
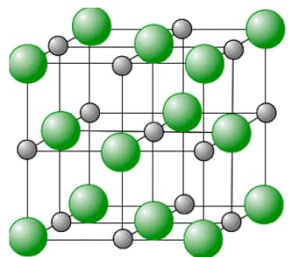
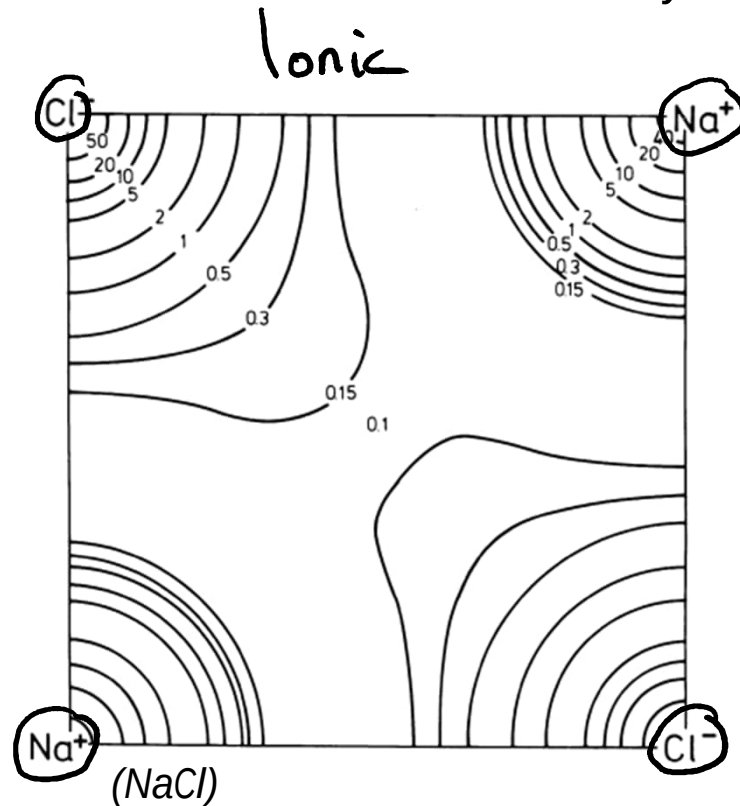


Image: Ibach, Lüth

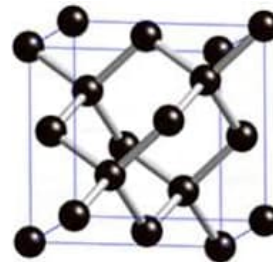
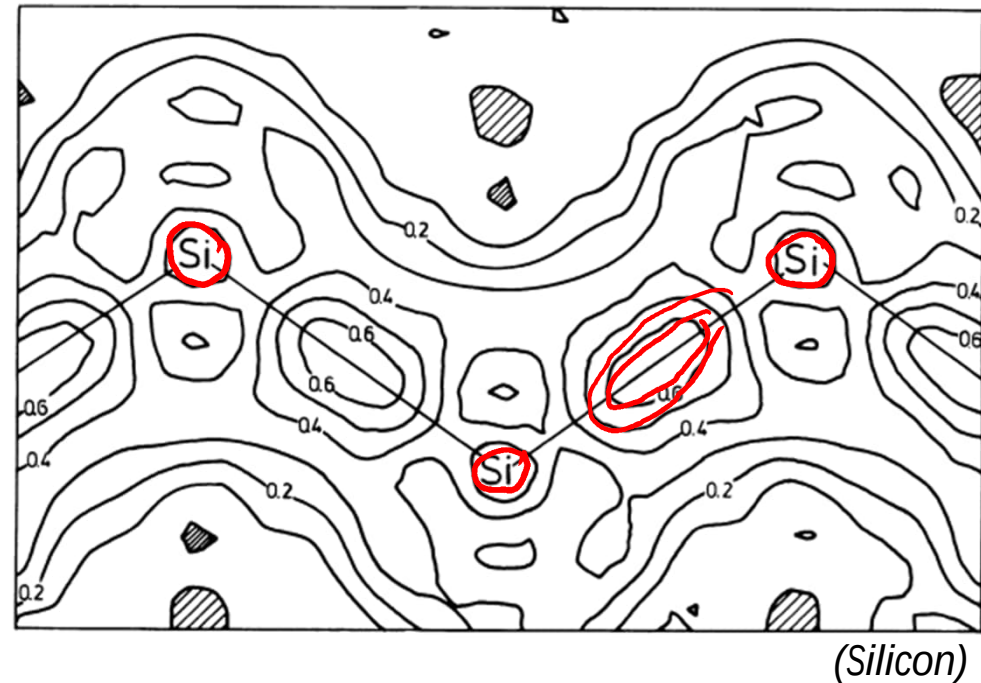
Ionic vs. covalent bonding



Density of valence electrons



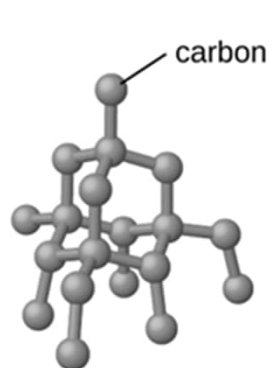
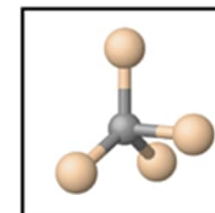
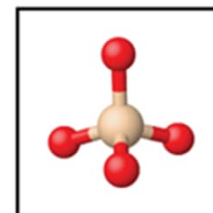
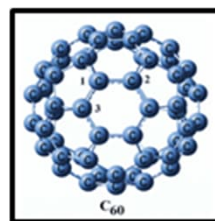
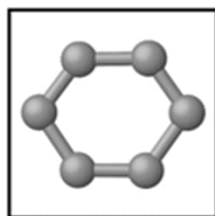
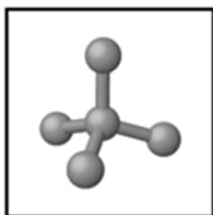
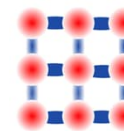
Almost no
charge between
atoms



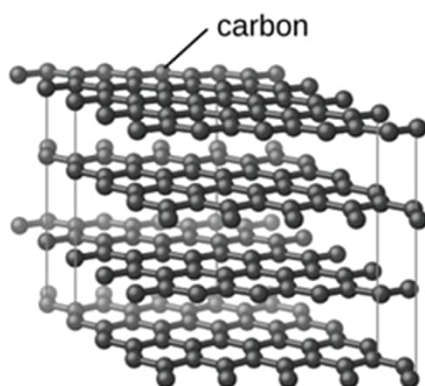
High charge concentration
between atoms
→ Sharing of electrons

Images: Ibach, Lüth

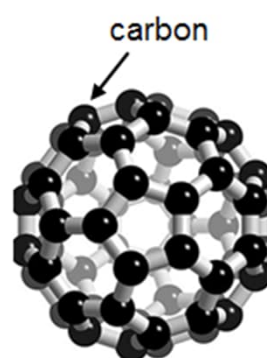
Some covalent network solids



diamond



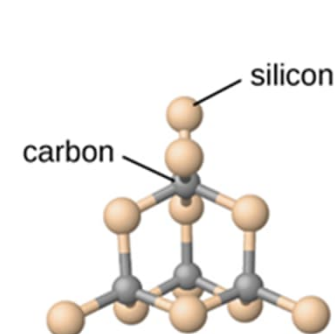
graphite



fullerene

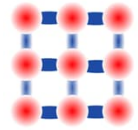


silicon dioxide

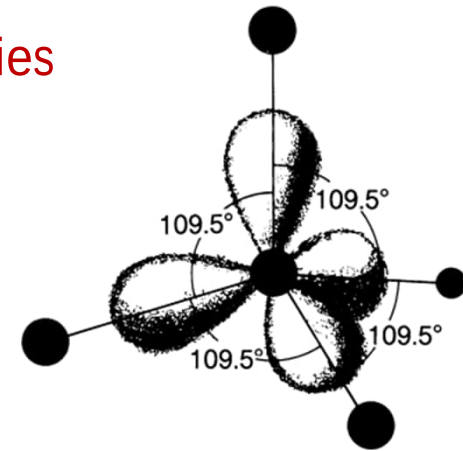


silicon carbide

Properties of covalent network solids

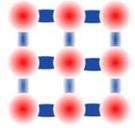


- Among the most strongest bonds, **high cohesive energies**
- Bonding arises from **sharing of electrons**
- Bonds are **highly directional** and **short-ranged**
- Simplest case: hydrogen molecule
- Examples: Diamond (C), graphite (C), Silicon (Si), Quartz (SiO₂), Germanium (Ge), Boron nitride (BN)
- Often dominant for elements with a roughly half-filled outer shell and for comparable electronegativity of the atoms (e.g. when they are the same element)
- Covalent bonds form due to constructive interference of atomic wave functions → **quantum mechanical origin**



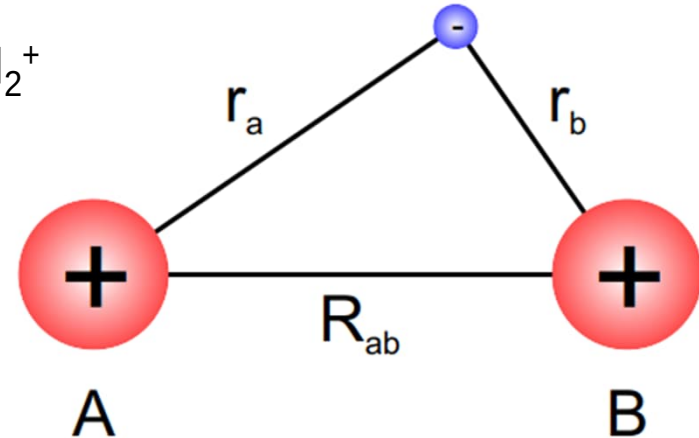
Tetrahedral nearest-neighbor configuration in the lattices of C, Si, Ge (Ibach/Lüth)

Covalent bonding: H_2^+



Start from chemistry and molecular physics: H_2^+

Hydrogen ion molecule as an easy example.

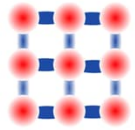


Hamiltonian:

$$H = \underbrace{-\frac{\hbar^2}{2m} \Delta - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b}}_{\text{electron}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R_{ab}}}_{\text{proton}}$$

Assume: • Protons don't move
→ neglect kinetic energy
→ constant R_{ab}

Covalent bonding: H_2^+



Ansatz : $\Psi = c_1 \varphi_a + c_2 \varphi_b$ (electronic wavefunction)

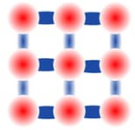
$\varphi_{a,b}$: atomic wavefunctions of individual hydrogen atoms

Task : Find energies of the electronic states

$$\begin{aligned} \text{Expectation value : } E(c_1, c_2) &= \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= \frac{\int \Psi^* H \Psi dV}{\int \Psi^* \Psi dV} \end{aligned}$$

$$\Rightarrow E = \frac{c_1^2 H_{aa} + c_2^2 H_{bb} + 2c_1c_2 H_{ab}}{c_1^2 + c_2^2 + 2c_1c_2 S}$$

Covalent bonding: H_2^+



$$\left. \begin{aligned} H_{aa} &= \int \psi_a^* H \psi_a dV \\ H_{bb} &= \int \psi_b^* H \psi_b dV \end{aligned} \right\} \text{Energy of electron when located at A or B}$$

$$H_{ab} = \int \psi_a^* H \psi_b dV = \int \psi_b^* H \psi_a dV \left. \vphantom{\int \psi_a^* H \psi_b dV} \right\} \text{"Hopping integral"}$$

$$S = \int \psi_a^* \psi_b dV \left. \vphantom{\int \psi_a^* \psi_b dV} \right\} \text{overlap integral}$$

↓
Coupling of the two wave functions

Next: minimize energy

$$\frac{\partial E}{\partial c_1} \stackrel{!}{=} 0 \quad \text{and} \quad \frac{\partial E}{\partial c_2} \stackrel{!}{=} 0$$

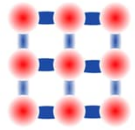
$$\begin{aligned} \Rightarrow \quad & c_1 \cdot (\overset{a}{H_{aa}} - E) + c_2 (\overset{b}{H_{ab}} - E \cdot S) \stackrel{!}{=} 0 \\ & c_1 \cdot (\overset{c}{H_{ab}} - E \cdot S) + c_2 (\overset{d}{H_{bb}} - E) \stackrel{!}{=} 0 \end{aligned}$$

Matrix A

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

$$\det(A) \stackrel{!}{=} 0$$

Covalent bonding: H_2^+



$$\det \begin{pmatrix} H_{aa} - E & H_{ab} - E \cdot S \\ H_{ab} - E \cdot S & H_{bb} - E \end{pmatrix} \stackrel{!}{=} 0$$

$$\Rightarrow (H_{aa} - E) \cdot (H_{bb} - E) - (H_{ab} - E \cdot S)^2 \stackrel{!}{=} 0$$

$$H_{aa} = H_{bb}$$

$$\Rightarrow (H_{aa} - E)^2 - (H_{ab} - E \cdot S)^2 \stackrel{!}{=} 0$$

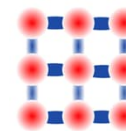
Solutions :

$$E_{\pm} = \frac{H_{aa} \pm H_{ab}}{1 \pm S}$$

energies of the
electronic orbitals
of the H_2^+ molecule

Add Proton repulsion (constant) :
$$E_{\pm} = \frac{H_{aa} \pm H_{ab}}{1 \pm S} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

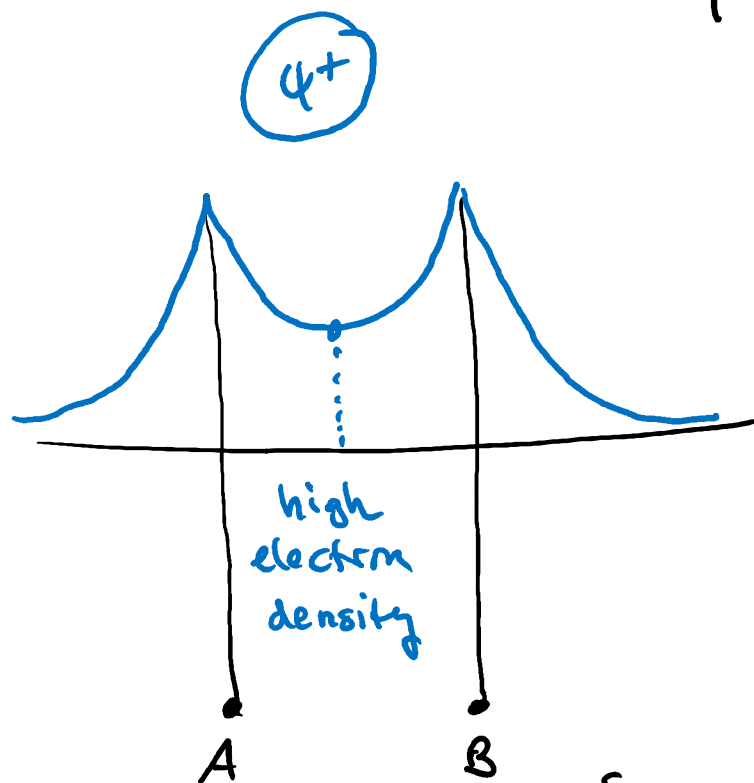
Covalent bonding: H_2^+



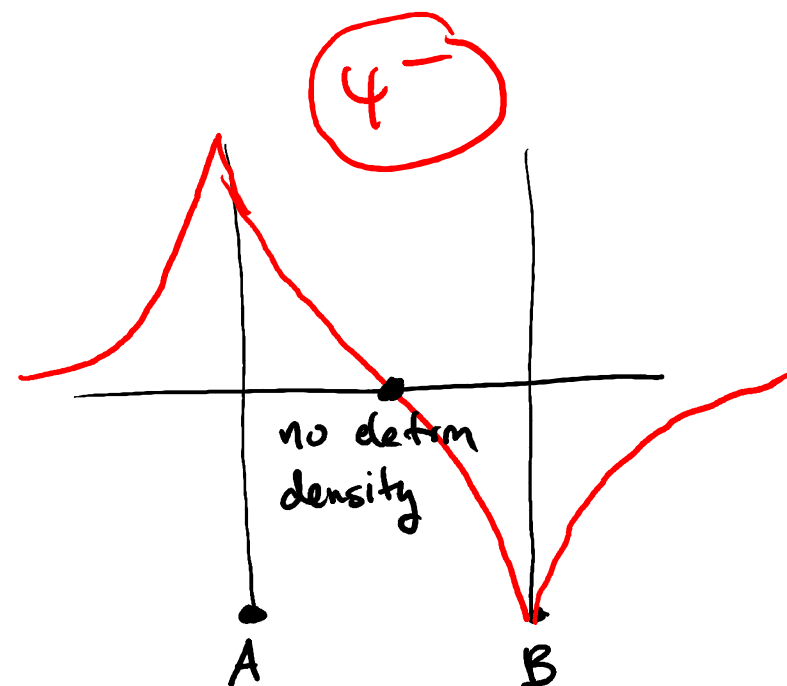
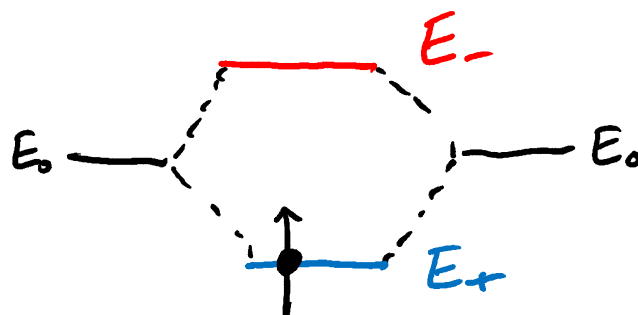
Wavefunctions: $\psi^+ = c_+ (\psi_a + \psi_b)$

$$\psi^- = c_- (\psi_a - \psi_b)$$

$$c_{\pm} = \frac{1}{\sqrt{2 \pm 2S}}$$

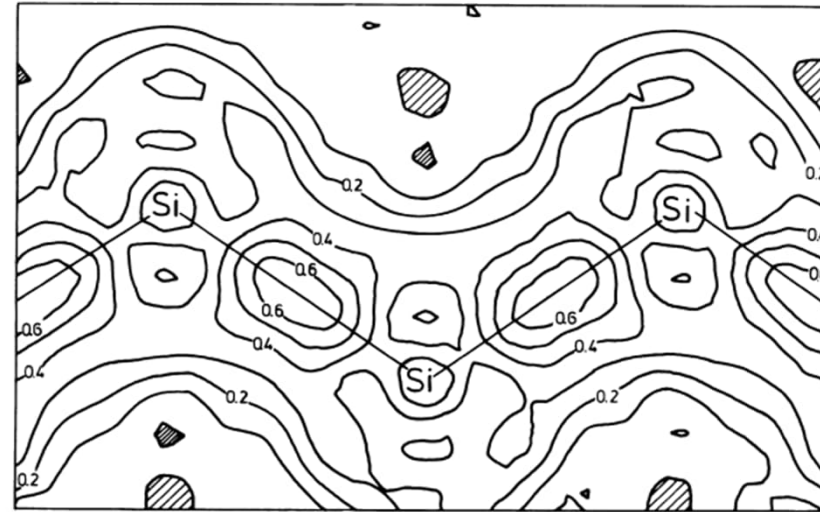
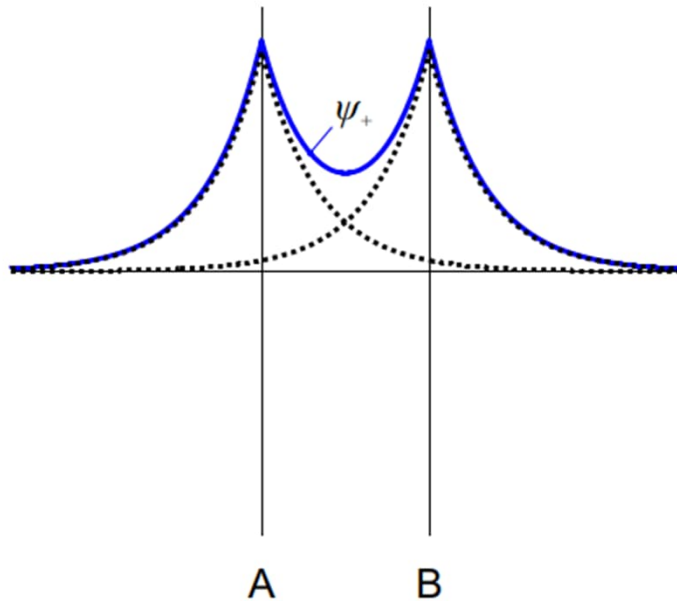
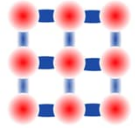


Bonding
wave function



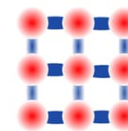
Antibonding
wave function

Covalent bonding: H_2^+

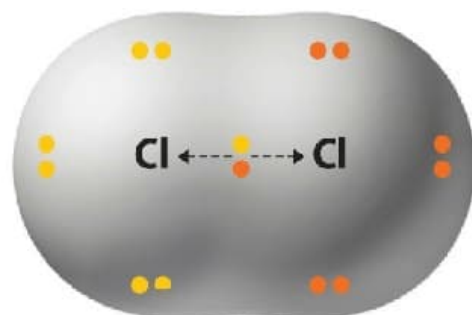


- Only partially occupied single-atomic orbitals contribute to covalent bonding (otherwise the antibonding orbitals E_- would need to become occupied)
- Covalent bonding causes a „piling up“ of charge density between the atoms
- Covalent bonds can be
 - (i) **non-polar: electron is shared equally between the atoms**
 - (ii) **polar: higher electron density towards one of the atoms**

Covalent bonding: polar vs. nonpolar

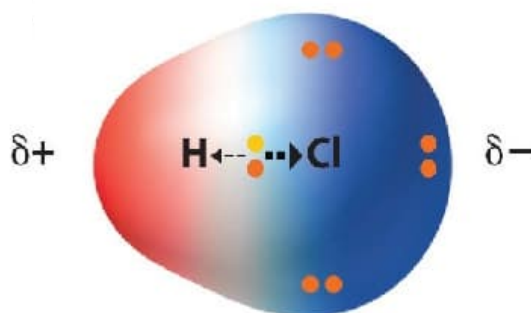


Nonpolar
covalent
bonding



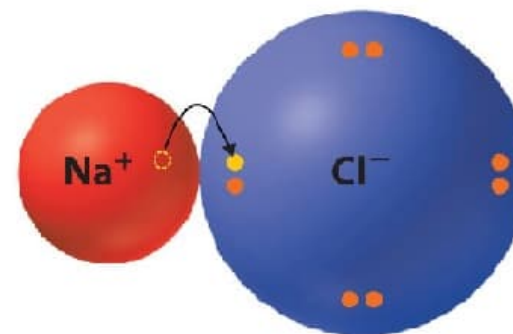
Symmetric
charge density
between atoms

Polar
covalent
bond



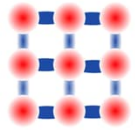
Partial
charges on the atoms,
non-symmetric
valence electron
density

Ionic



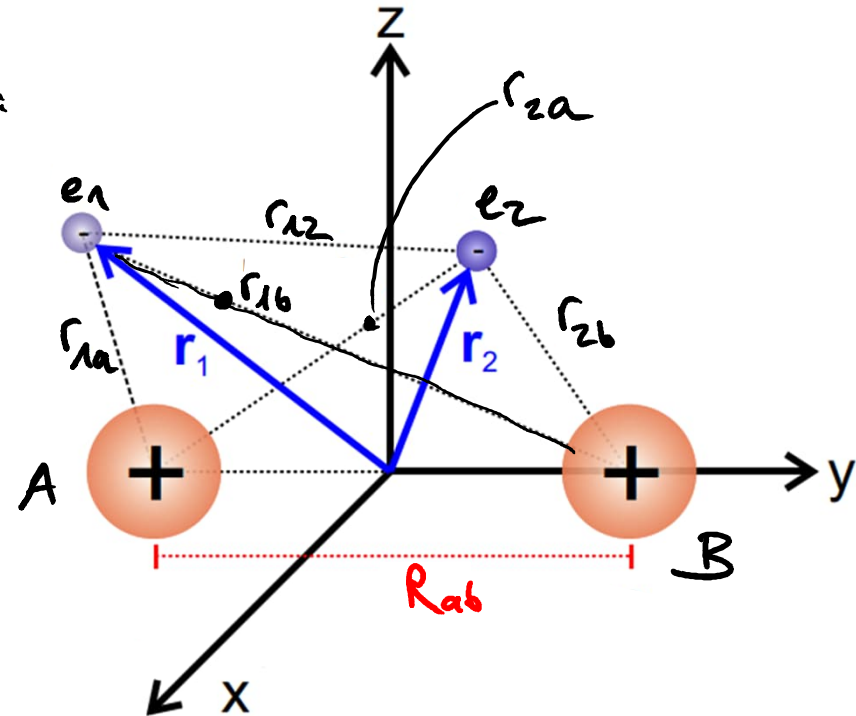
charges fully
change sites

Covalent bonding: H_2



Hamiltonian of neutral H_2 :

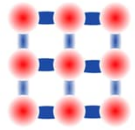
$$H = \underbrace{H_0}_{\text{individual H-atoms}} + \underbrace{H_1}_{\text{"inter-atom" interactions}}$$



$$H_0 = -\frac{\hbar^2}{2m} \nabla_{e1}^2 - \frac{\hbar^2}{2m} \nabla_{e2}^2 - \frac{e^2}{4\pi\epsilon_0 r_{1a}} - \frac{e^2}{4\pi\epsilon_0 r_{2b}}$$

$$H_1 = \underbrace{\frac{e^2}{4\pi\epsilon_0 R_{ab}}}_{(e_1, e_2)} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{(A, B)} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{1b}}}_{(e_1, B)} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{2a}}}_{(e_2, A)}$$

Covalent bonding: H_2



We need to find an Ansatz for the 2-particle wavefunction.

→ Product of both atomic wavefunction?

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2)$$

violates $\Psi(\vec{r}_1, \vec{r}_2) \neq -\Psi(\vec{r}_2, \vec{r}_1)$

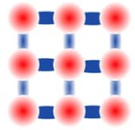
$\Psi(\vec{r}_1, \vec{r}_2)$ must be antisymmetric when exchanging the two electrons:
 $\Psi(\vec{r}_1, \vec{r}_2) = -\Psi(\vec{r}_2, \vec{r}_1)$

$$\Psi_+(\vec{r}_1, \vec{r}_2) = C_+ [\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) + \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)]$$

Ansatz

$$\Psi_-(\vec{r}_1, \vec{r}_2) = C_- [\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) - \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)]$$

Covalent bonding: H₂

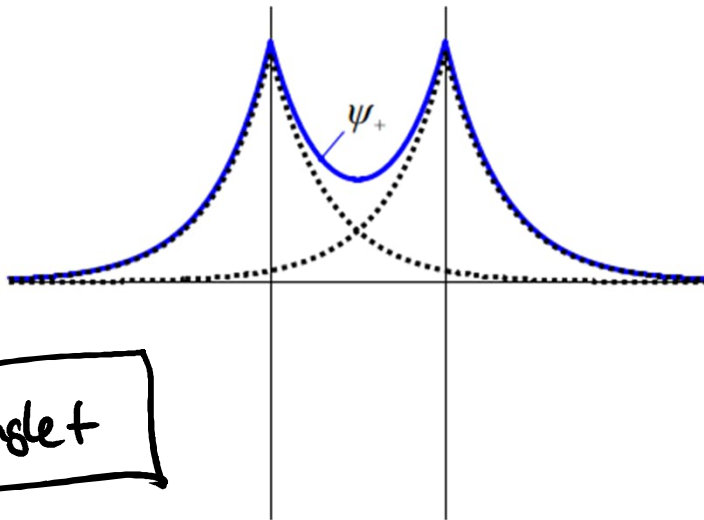


Now we have two electrons $\rightarrow$ Relative orientation of electron spin matters!

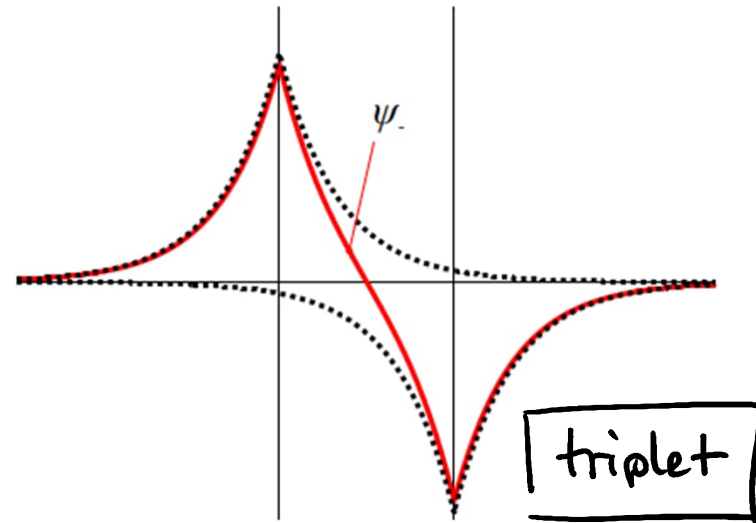
$$\psi_+ \rightarrow \psi_+^{\uparrow\downarrow}$$

antiparallel spins

$$\psi_- \rightarrow \psi_-^{\uparrow\uparrow} : \text{parallel spins}$$

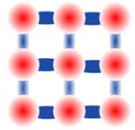


and $|\uparrow\downarrow\rangle$



and $|\uparrow\uparrow\rangle$

Covalent bonding: H_2



Goal: Get energy expectation values E_+ and E_-

Assume $\varphi_a(\vec{r})$, $\varphi_b(\vec{r})$ are normalized

$$\Rightarrow C_{\pm} = \frac{1}{\sqrt{2 \pm 2S}}$$

$$\text{with } S = \int \varphi_a^*(\vec{r}_1) \varphi_b^*(\vec{r}_2) \varphi_a(\vec{r}_2) \varphi_b(\vec{r}_1) dV_1 dV_2 \left. \vphantom{\int} \right\} \begin{array}{l} \text{overlap} \\ \text{integral} \end{array}$$
$$= \int \varphi_a^*(\vec{r}_2) \varphi_b^*(\vec{r}_1) \varphi_a(\vec{r}_1) \varphi_b(\vec{r}_2) dV_1 dV_2 \left. \vphantom{\int} \right\} \begin{array}{l} \text{overlap} \\ \text{integral} \end{array}$$

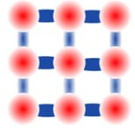
$$\text{Singlet } E_+^{\uparrow\downarrow} = 2E_0 + \frac{V+A}{1+S}$$

$$\text{Triplet } E_-^{\uparrow\uparrow} = 2E_0 + \frac{V-A}{1-S}$$

V : Coulomb integral

A : exchange integral

Covalent bonding: H_2



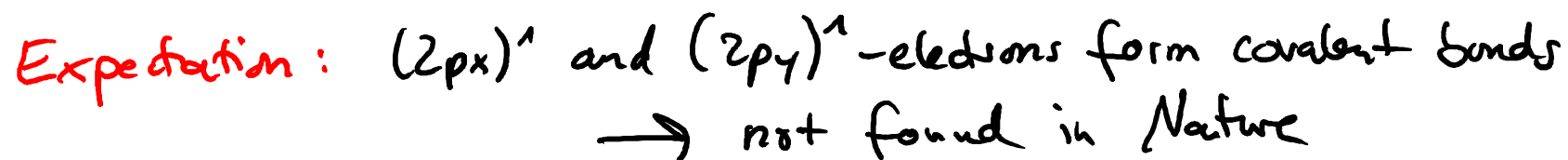
$$\begin{aligned} V &= \int \psi_a^*(\vec{r}_1) \psi_b^*(\vec{r}_2) H_1 \psi_a(\vec{r}_1) \psi_b(\vec{r}_2) dV_1 dV_2 \\ &= \int \psi_a^*(\vec{r}_1) \psi_b^*(\vec{r}_1) H_1 \psi_a(\vec{r}_2) \psi_b(\vec{r}_2) dV_1 dV_2 \end{aligned}$$

$$\begin{aligned} A &= \int \psi_a^*(\vec{r}_1) \psi_b^*(\vec{r}_2) H_1 \psi_a(\vec{r}_2) \psi_b(\vec{r}_1) dV_1 dV_2 \\ &= \int \psi_a^*(\vec{r}_2) \psi_b^*(\vec{r}_1) H_1 \psi_a(\vec{r}_1) \psi_b(\vec{r}_2) dV_1 dV_2 \end{aligned}$$

$2E_0$: Energy of the isolated atoms (H_0)

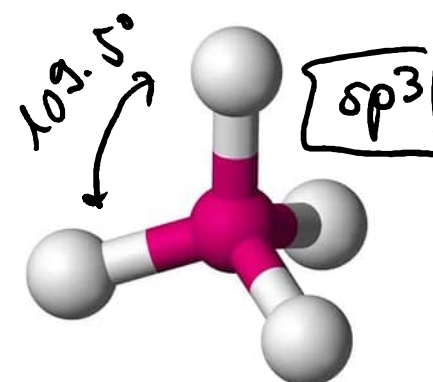
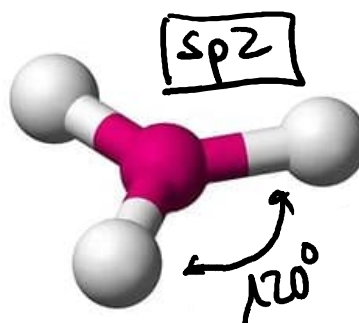
$\frac{V \pm A}{1 \pm S}$: Interaction energy (H_1)

6 12.011
C
Carbon
[He] 2s² 2p²
Nonmetal

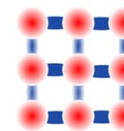


sp

A diagram showing a linear molecule with a central pink sphere and two white spheres. A curved arrow indicates a bond angle of 180° .



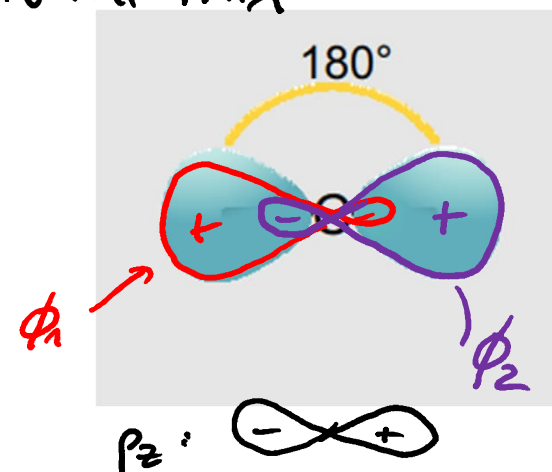
Covalent bonding: Carbon



sp-hybridization: 2s and one 2p orbital mix

$$\phi_1^{sp} = \frac{1}{\sqrt{2}} [\phi(s) + \phi(p_z)]$$

$$\phi_2^{sp} = \frac{1}{\sqrt{2}} [\phi(s) - \phi(p_z)]$$

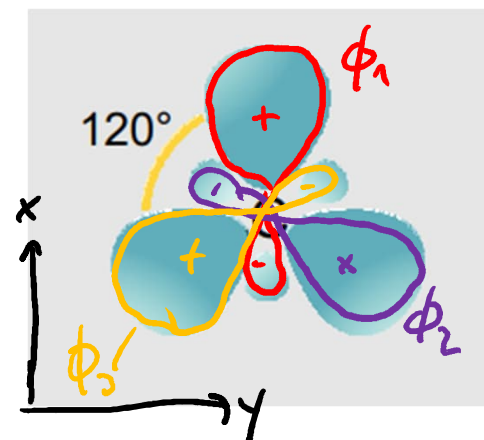


sp²-hybridization: 2s mixes with two 2p-orbitals

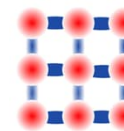
$$\phi_1^{sp^2} = \frac{1}{\sqrt{3}} [\phi(s) + \sqrt{2} \phi(p_x)]$$

$$\phi_2^{sp^2} = \frac{1}{\sqrt{3}} \left[\phi(s) - \frac{1}{\sqrt{2}} \phi(p_x) + \frac{\sqrt{3}}{\sqrt{2}} \phi(p_y) \right]$$

$$\phi_3^{sp^2} = \frac{1}{\sqrt{3}} \left[\phi(s) - \frac{1}{\sqrt{2}} \phi(p_x) - \frac{\sqrt{3}}{\sqrt{2}} \phi(p_y) \right]$$



Covalent bonding: Carbon



sp^3 - Hybridization :

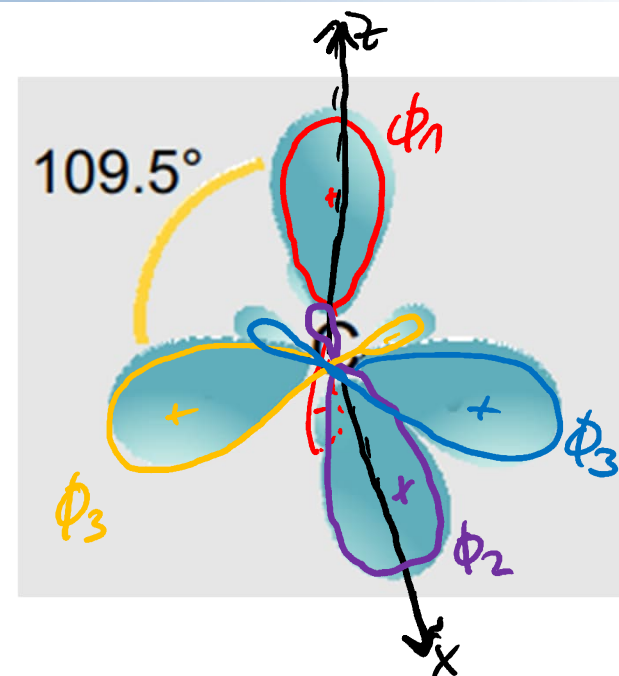
2s orbital mixes with all 2p-orbitals:

$$\phi_1^{sp^3} = \frac{1}{2} [\phi(s) + \sqrt{3} \phi(p_z)]$$

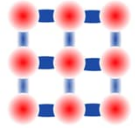
$$\phi_2^{sp^3} = \frac{1}{2} \left[\phi(s) + \sqrt{\frac{8}{3}} \phi(p_x) - \sqrt{\frac{1}{3}} \phi(p_z) \right]$$

$$\phi_3^{sp^3} = \frac{1}{2} \left[\phi(s) - \sqrt{\frac{2}{3}} \phi(p_x) + \sqrt{2} \phi(p_y) - \sqrt{\frac{1}{3}} \phi(p_z) \right]$$

$$\phi_4^{sp^3} = \frac{1}{2} \left[\phi(s) - \sqrt{\frac{2}{3}} \phi(p_x) - \sqrt{2} \phi(p_y) - \sqrt{\frac{1}{3}} \phi(p_z) \right]$$



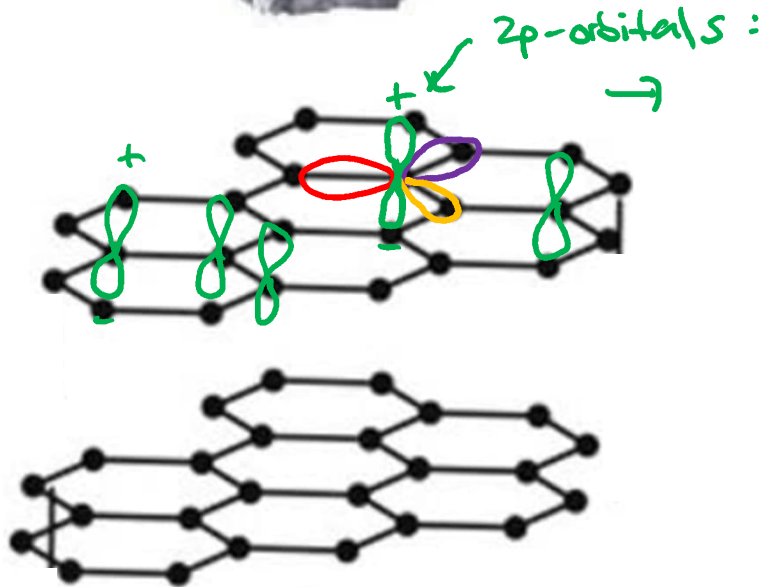
Covalent bonding: Carbon



Graphite :

sp^2 - Hybridization

Metal



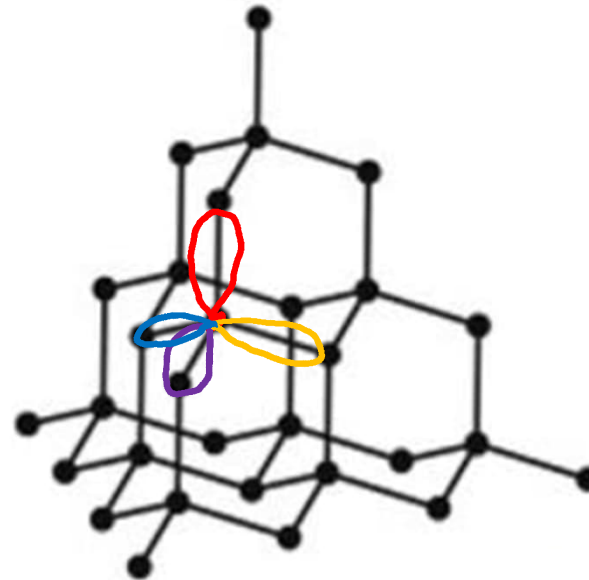
Remaining $2p$ -orbital ?
→ form delocalized π -orbitals!

Diamond :

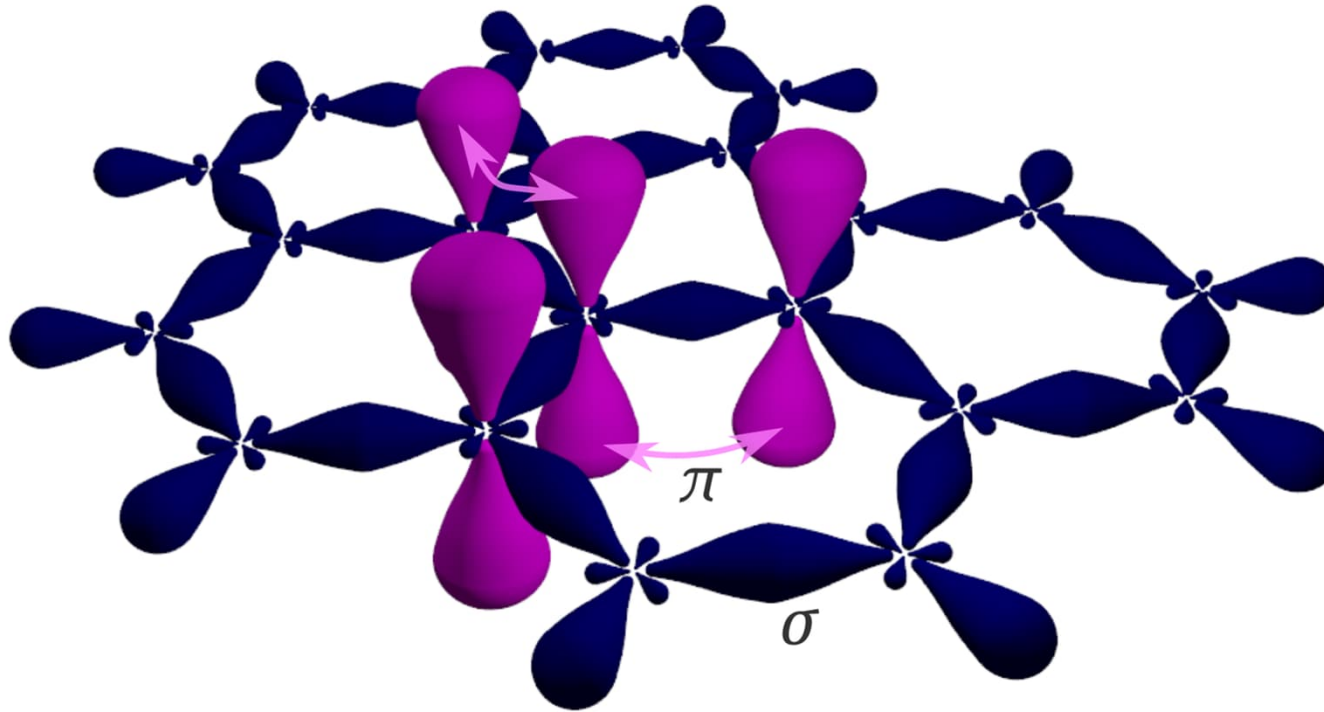
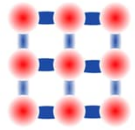
sp^3 - Hybridization



Insulator

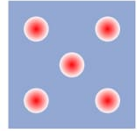


Sigma and pi-bonds in graphene

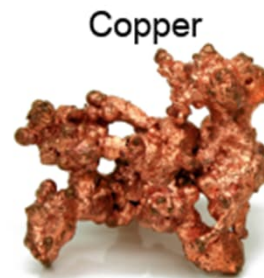
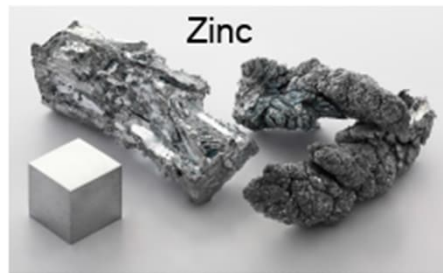


σ-bonds: covalent bonds (in-plane covalent network crystal)

π-bonds: delocalized electrons → "sea" of conduction electron
(giant π-cloud spanning the whole crystal)



Metallic bonding

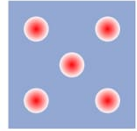


Metals are

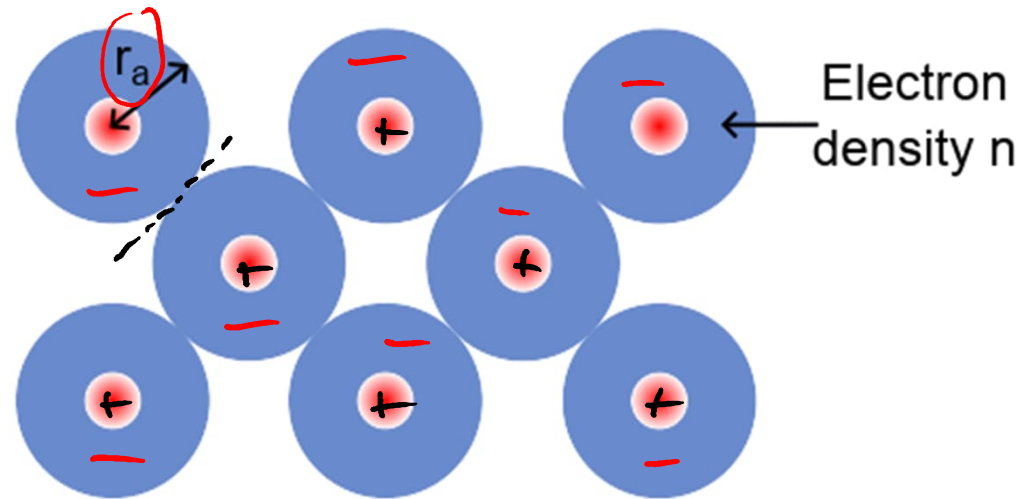
- highly reflective (shiny)
- Good electrical conductors
- Good heat conductivity
- Malleable and ductile

Reason: "sea" of electrons

Metallic bonding: “sea” of electrons



- Metallic bonding cannot be explained by
 - local charges (ionic)
 - local bond (covalent)
- Bonding is mediated by delocalized electrons



→ Define “effective” local forces

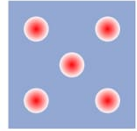
r_a : Wigner-Seitz radius

$$V_{ra} = \frac{4}{3} \pi r_a^3$$

$$n = \frac{3}{4 \pi r_a^3}$$

average electron density

Metallic bonding: repulsive energy

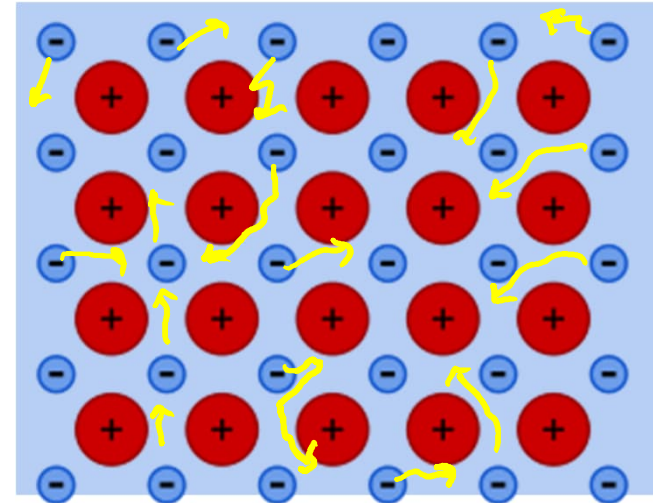


Ionic, covalent, vdw: Pauli blocking
when atomic orbitals overlap.

Metallic: Pauli exclusion principle
"within" the "sea" of electrons.

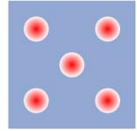
⇒ finite, average kinetic energy:

$$E_{\text{rep}} = E_{\text{av}} = \frac{3}{5} \boxed{E_F^0} = \frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} \frac{\hbar^2}{2m} \frac{1}{r_s^2} \quad E_F^0: \text{Fermi energy}$$



- Electronic states of the "sea" are electronic bands → continuum of states
- Occupation of states described by Fermi-Dirac distribution
- ~~Not~~ Not all electrons within the "Fermi sea" can occupy the same ground state! ⇒ finite kinetic energy (repulsive)

Metallic bonding: attractive energy



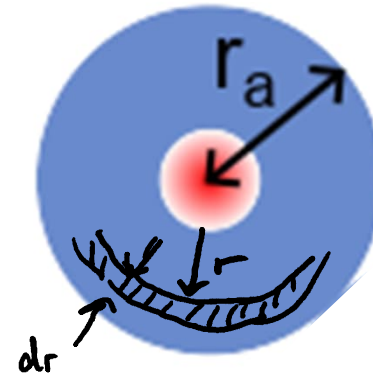
Attractive force: Screened Coulomb potential
("effective, averaged potential")

$$\phi(r) = \frac{e - \boxed{e \left(\frac{r}{r_a}\right)^3}}{4\pi\epsilon_0 r}$$

Screening term



reduces the effective charge



Within r_a : spatially homogeneous charge distribution $\rho = -e \cdot n$

$$dE_{\text{pot}} = \phi(r) \cdot \rho \cdot 4\pi r^2 dr = - \frac{3e^2}{4\pi\epsilon_0} \left(\frac{r}{r_a^3} - \frac{r^4}{r_a^6} \right) dr$$

$$\Rightarrow E_{\text{pot}} = \int_0^{r_a} dE_{\text{pot}} = - \frac{9e^2}{40\pi\epsilon_0} \cdot \frac{1}{r_a}$$

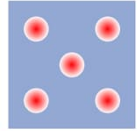
r_a : Size of e^- -cloud
 a_0 : Size of atom

$$= - \frac{9}{5} \frac{e^2}{4\pi\epsilon_0} \frac{\boxed{a_0}}{r_a}$$

Bohr radius

$$\boxed{a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}}$$

Metallic bonding: total energy



Total energy per conduction electron:

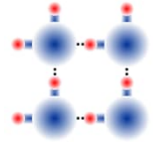
$$E_{tot} = \frac{\hbar^2}{2ma_0^2} \left[\underbrace{\frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3}}_{\text{relative sizes of atomic}} \underbrace{\left(\frac{a_0}{r_a} \right)^2}_{\text{cores vs. electron cloud}} - \frac{9}{5} \underbrace{\left(\frac{a_0}{r_a} \right)}_{\text{cores vs. electron cloud}} \right]$$

relative sizes of atomic
cores vs. electron cloud

Minimum at $\frac{r_a}{a_0} = \frac{2}{3} \left(\frac{9\pi}{4} \right)^{2/3}$

$\Rightarrow$ two atomic cores are separated by $\sim 2.6 \text{ \AA}$.

Metal	Nearest neighbor distance ($\text{\AA}$)	Binding energy (eV/atom)
Li	3.02	1.63
Na	3.66	1.11
K	4.52	0.93
Cs	5.24	0.8

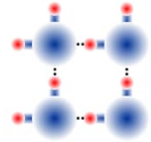


Hydrogen bonding



Most famous hydrogen-bonded crystal: Ice

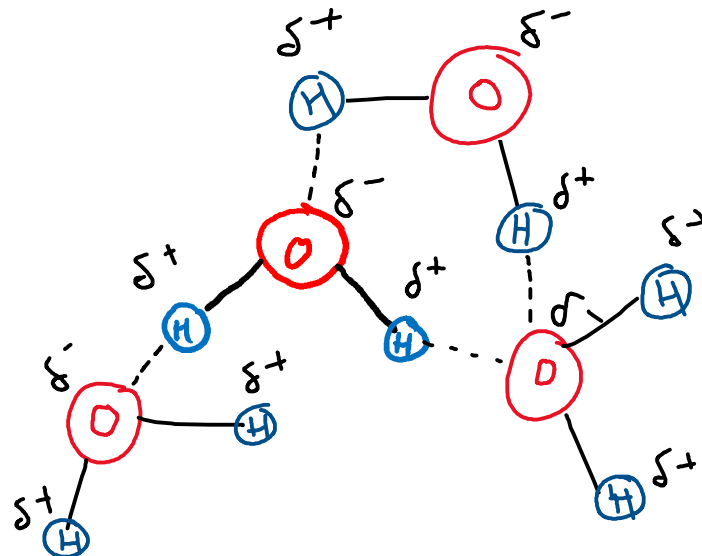
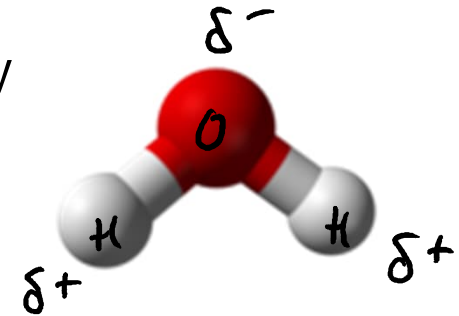
Hydrogen bonding



Occurs when a hydrogen atom is covalently bonded to a highly electronegative atom (oxygen, fluorine, nitrogen).

- strongly polar covalent bond
- H is partially negative charged
- O —||— positive —||—

→ effective "cations" and "anions"



— covalent
--- hydrogen