

Condensed Matter Physics

- Solid State Physics: An Introduction, by [Philip Hofmann](#) (2nd edition 2015, **ISBN-10:** 3527412824, **ISBN-13:** 978-3527412822, [Wiley-VCH Berlin](#)).
- (Advanced Texts in Physics) Harald Ibach, Hans Lüth (auth.) - Solid-State Physics_ An Introduction to Principles of Materials Science-Springer-Verlag Berlin Heidelberg (2009)-2

Bonds between atoms: contents

- bonding in general, attractive and repulsive forces, cohesive energy
- ionic bonding
- covalent bonding
- metallic bonding
- hydrogen bonding and van der Waals bonding
- relationship between bonding type and some physical properties of a solid (in particular melting point)

Bonding in solids: the general idea

- valence electrons (of the outer shell) achieve bonding (like in chemistry)
- decrease in total energy stabilises the solid (the solid's energy is lower than that of sum of atoms it is made of)
- so the energy gain by the bonding must be higher than the energy it costs to promote electrons from the atomic orbitals to the electronic states of the solid.
- this energy difference is a measure for the strength of the bond. It is called the **cohesive energy**.

$$\text{cohesive energy} = \text{energy of atoms} - \text{energy of solid}$$

Repulsive force

- Fig 1.1 Solid State Physics: An Introduction, by Philip Hofmann Wiley-VCH Berlin

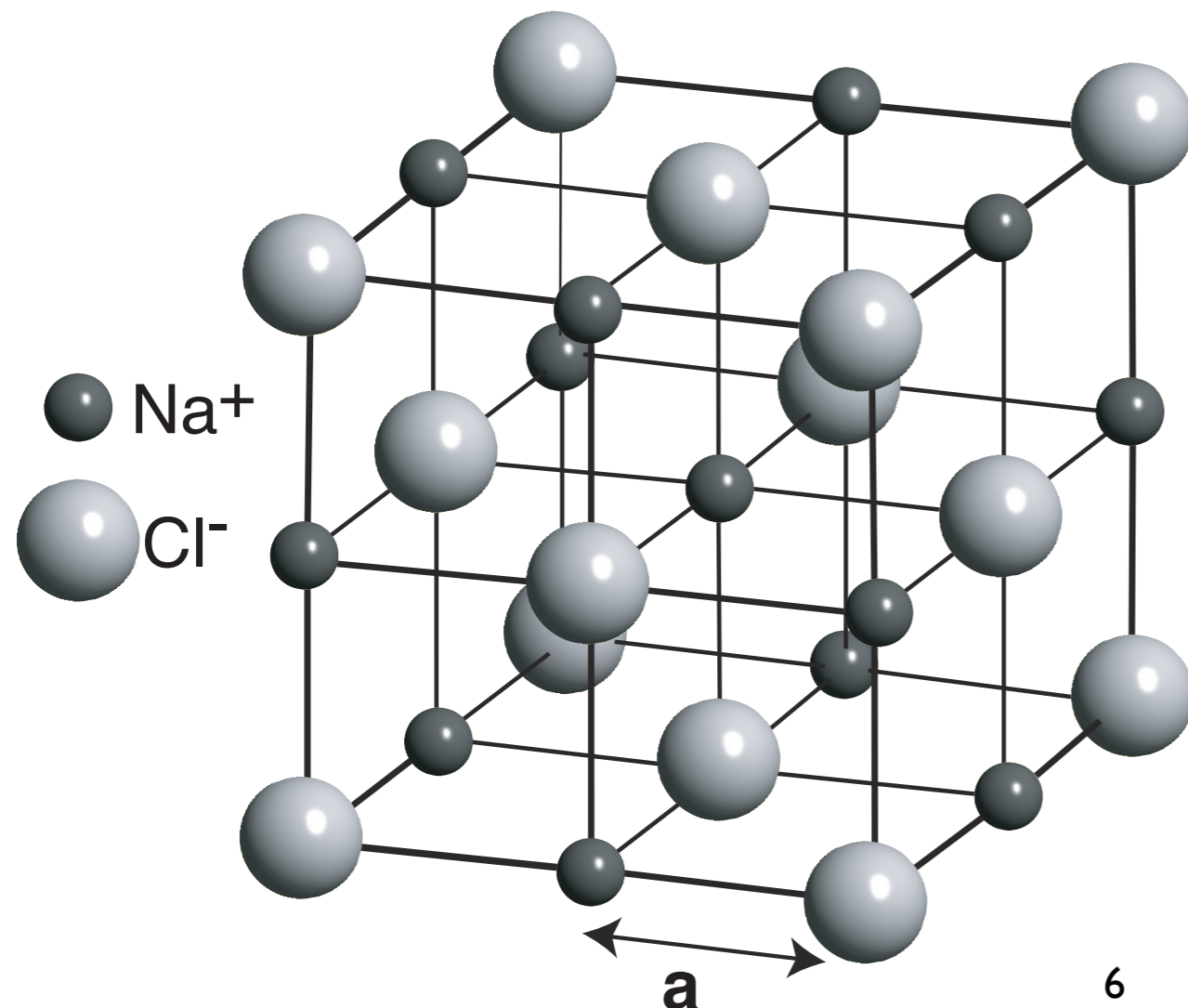
$$\phi(r) = -\frac{B}{r^m}$$

$$n > m$$

Ionic bonding

- form positive and negative ions (here Na^+ and Cl^-)
- bonding is achieved by electrostatic force and a classical treatment is (partially) meaningful.

example NaCl (rock salt): cubic structure



Turning Atoms in Ions

example: NaCl

how much energy does it cost?

ionization energy Na: 5.1 eV

electron affinity Cl: 3.6 eV

net energy cost: $(5.1 \text{ eV} - 3.6 \text{ eV}) = 1.5 \text{ eV}$ per pair

Ionic bonding

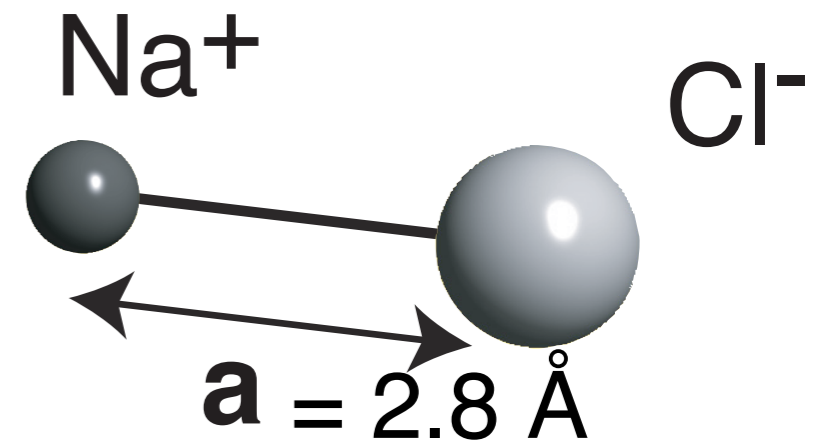
example: NaCl

what is the energy gain?

potential energy:

$$E_{Coulomb} = -\frac{e^2}{4\pi\epsilon_0 a}$$

this amounts to 5.1 eV per pair



so the total gain is
 $5.1 \text{ eV} - 1.5 \text{ eV} = 3.6 \text{ eV}$

Ionic bonding

example: NaCl

but this was just a molecule: what about the electrostatic energy gain in the solid?

consider the centre Na ion

energy gain from next 6 Cl:

$$E = -6 \frac{e^2}{4\pi\epsilon_0 a}$$

energy loss from next 12 Na:

$$E = +12 \frac{e^2}{4\pi\epsilon_0 a \sqrt{2}}$$

next we get 8 more Cl ions and the total becomes

$$E = -\frac{e^2}{4\pi\epsilon_0 a} \times \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \right)$$

Ionic bonding

example: NaCl

eventually the series converges
and we get (for one ion)

$$E = -1.748 \frac{e^2}{4\pi\epsilon_0 a} = -M_d \frac{e^2}{4\pi\epsilon_0 a}$$

M_d is called the Madelung constant.

It is specific for a given structure.

Ionic bonding

$$E = -1.748 \frac{e^2}{4\pi\epsilon_0 a} = -M_d \frac{e^2}{4\pi\epsilon_0 a}$$

so the total lattice energy for one mole of NaCl

because there are Na and Cl ions

$$E_{tot} = \frac{2E_{Na} \times N_a}{2}$$

to count every pair only once

This gives 861 kJmol^{-1} . The experiment gives 776 kJmol^{-1}

Note: this is the **lattice energy**, not the **cohesive energy** (the lattice energy minus the energy to turn atoms into ions).

Covalent bonding

- A simple view on other covalent bonds.

The covalent bond: simple picture

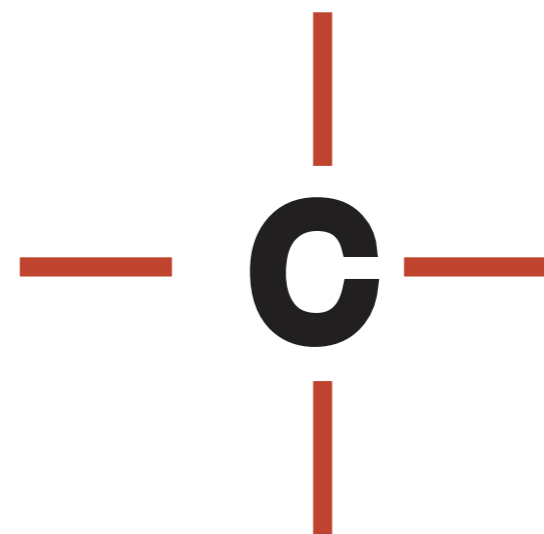


The covalent bond: less simple picture (hydrogen molecule)

$$H = -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{\hbar^2 \nabla_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|} + \frac{1}{R} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|} \right\}$$

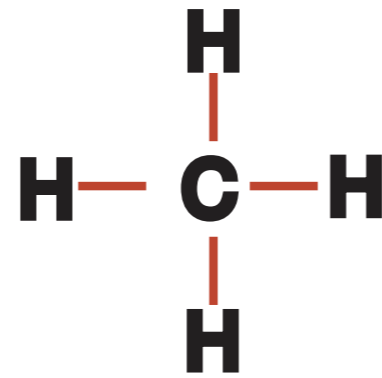
$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \pm \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1))$$

The covalent bond: simple picture

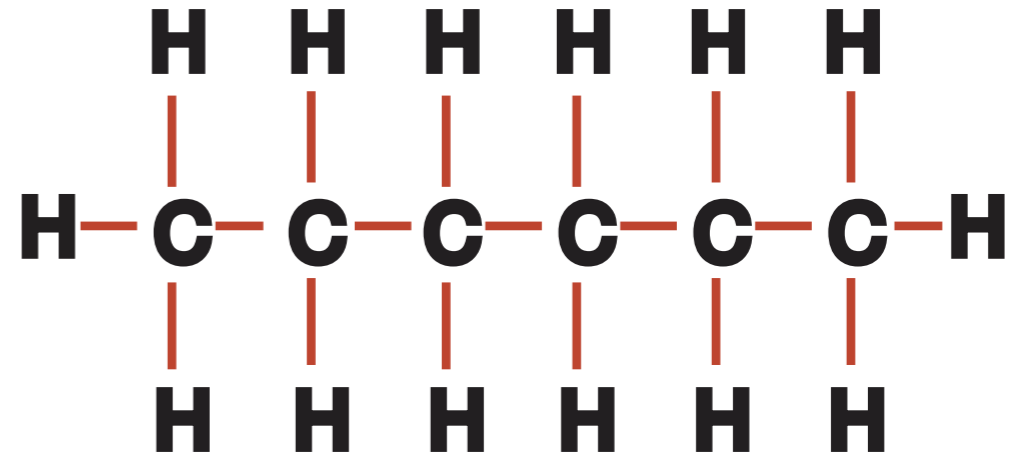
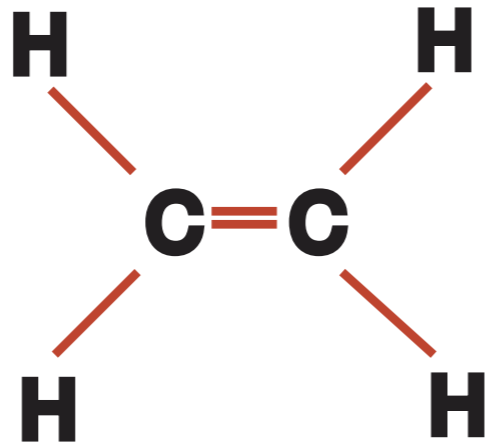


The covalent bond: simple picture

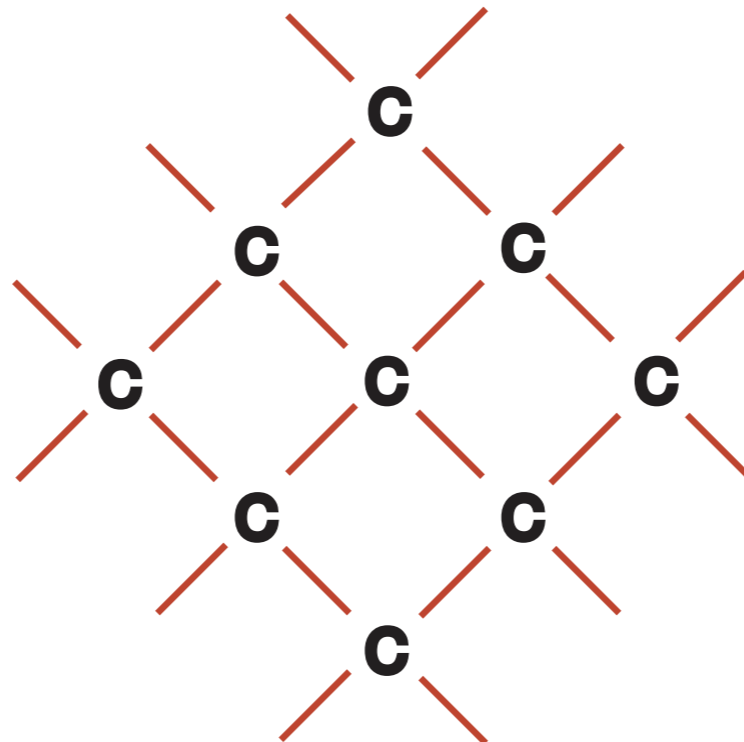
methane



hydrocarbons



C-based solid

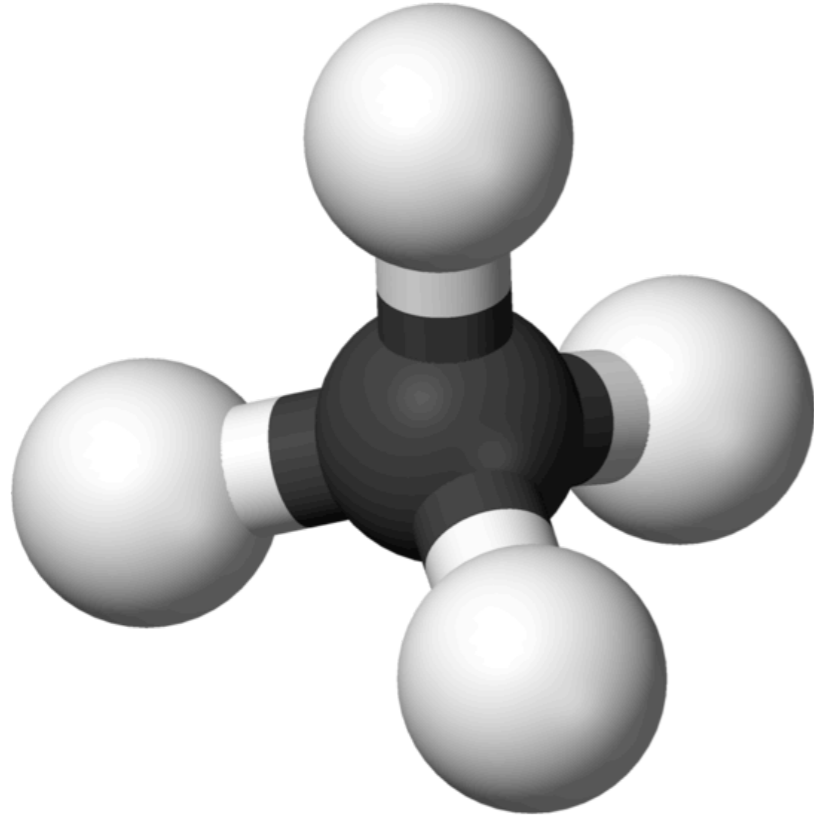


The covalent bond: a closer look at C

- electron configuration: 2 s and 2 p electrons
- formation of four sp^3 hybrid orbitals as linear combination between the s and three p orbitals
- directional character of p orbitals is also found in sp^3 orbitals.

The covalent bond: sp^3 bonding

methane



diamond

Bonding in most semiconductors

- Tetrahedral (sp^3) configuration almost ubiquitous: diamond, Si, Ge, III-V (GaAs, AlAs, InP), II-VI (CdS, CdTe)

Bonding in most semiconductors

- Tetrahedral (sp^3) configuration almost ubiquitous: diamond, Si, Ge, III-V (GaAs, AlAs, InP), II-VI (CdS, CdTe)

The covalent bond: sp^2 bonding

- formation of three sp^2 hybrid orbitals as linear combination between the s and two p orbitals. One p-orbital remains

Covalent bonding

- Cohesive energies similar to ionic bonding, in the eV range.
- Very directional bonding.