Bonds between atoms: contents

at the end of this lecture you should understand....

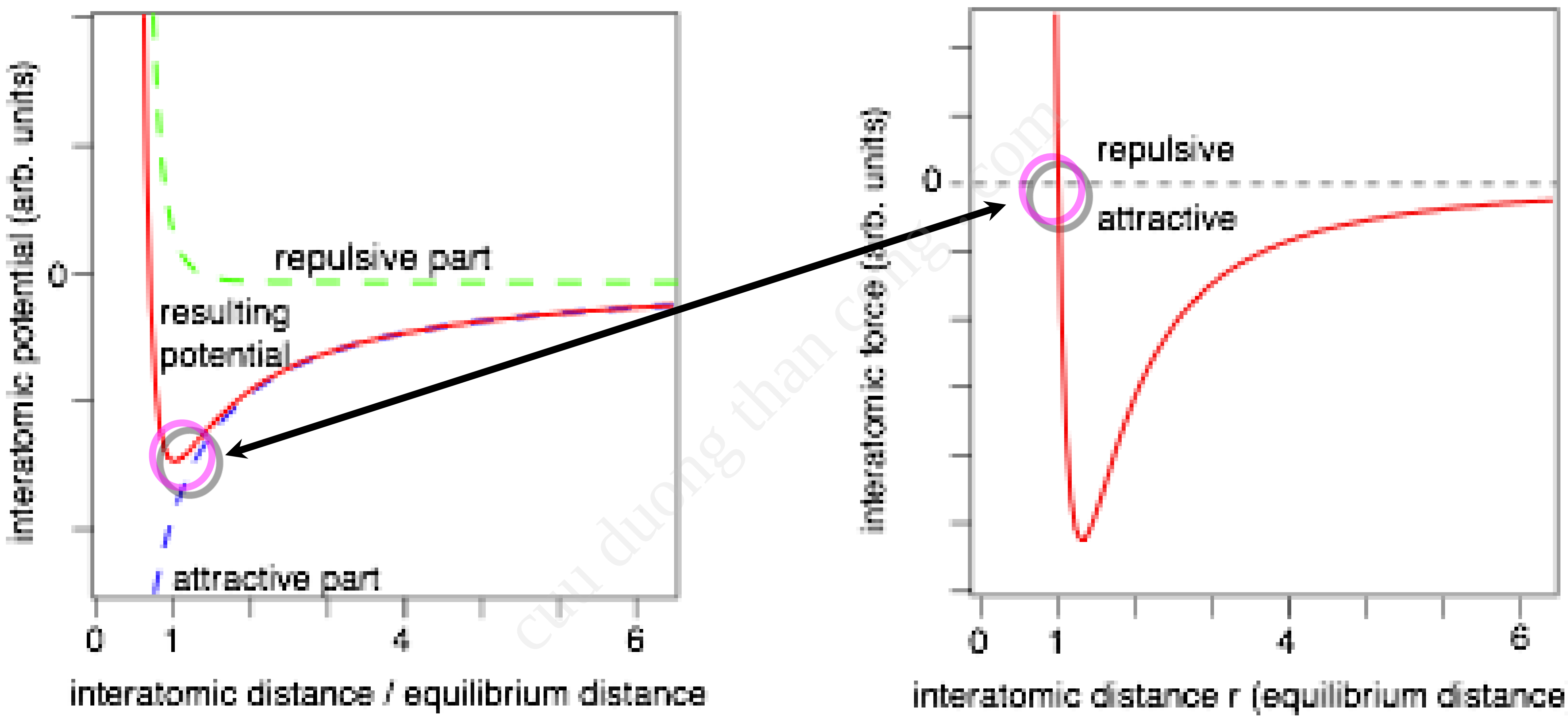
- bonding in general, attractive and repulsive forces, cohesive energy
- ionic bonding
- covalent bonding
- metallic bonding
- hydrogen bonding and van der Waals bonding
- relationship between bonding type and some physical properties of a solid (in particular melting point)

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.

cohesive energy = energy of atoms - energy of solid

Repulsive force



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

$$n > m$$

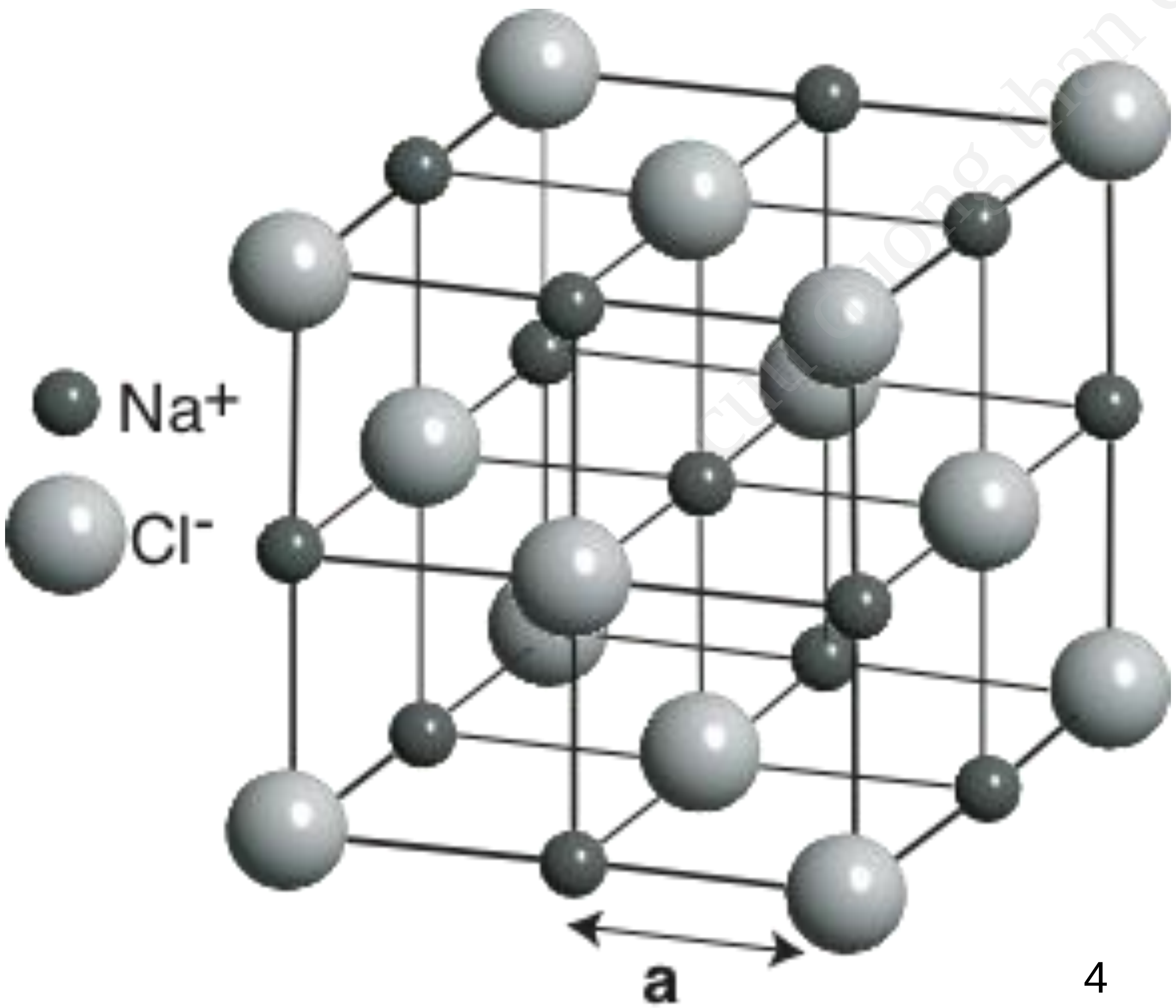
$$\mathbf{F}(\mathbf{r}) = -\mathrm{grad}\phi(\mathbf{r})$$

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

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 eV - 3.6 eV) = 1.5 eV per pair

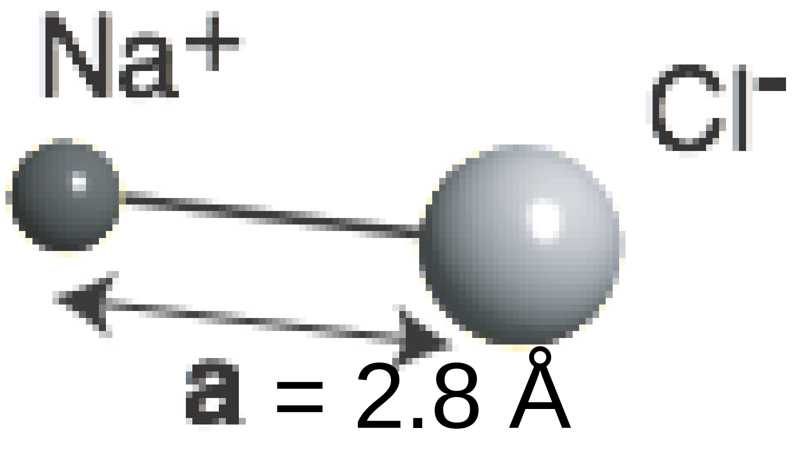
Ionic bonding

example: NaCl

what is the energy gain?

potential energy:

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



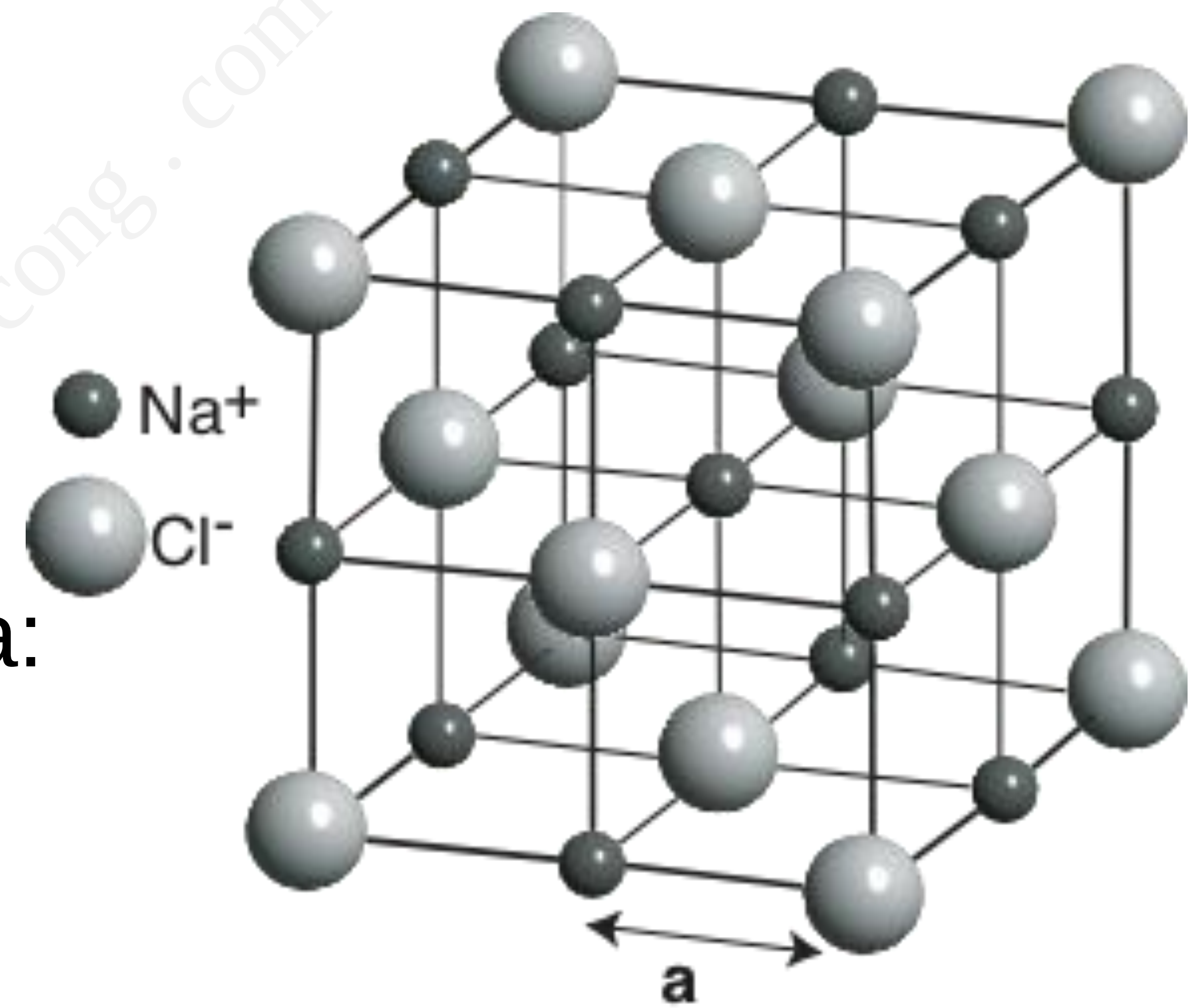
this amounts to 5.1 eV per pair

so the total gain is
5.1 eV - 1.5 eV = 3.6 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

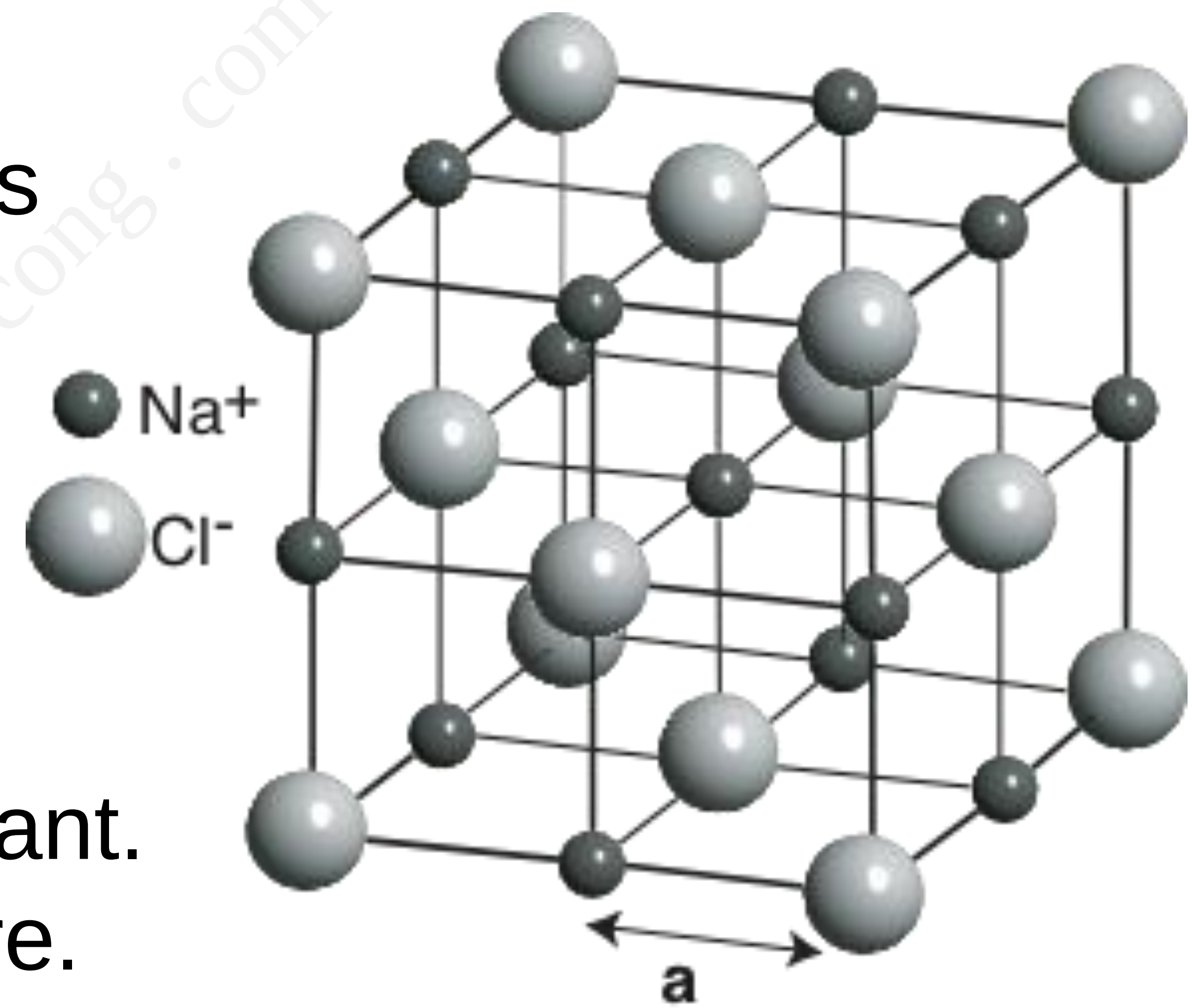
$$E = -\frac{e^2}{4\pi\epsilon_0 a} \times \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}}\right)$$

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

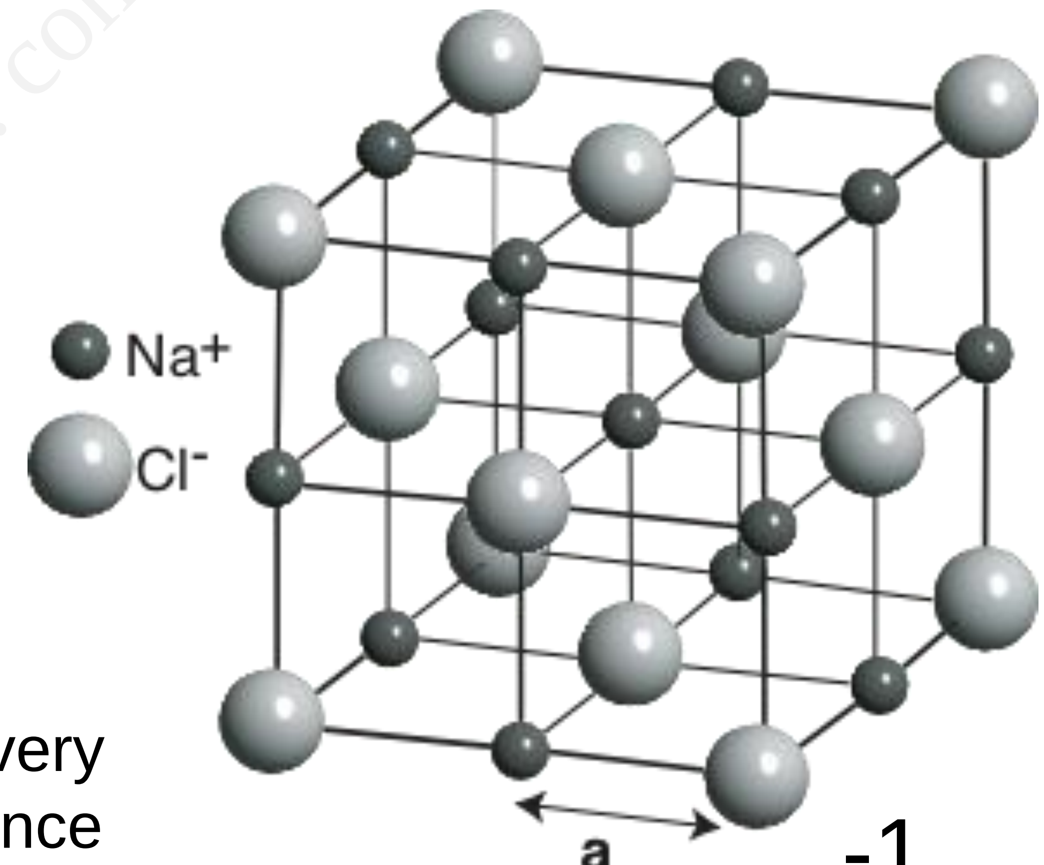
$$E = -1.748 \frac{e^2}{4\pi\epsilon_0 a} = -M_d \frac{e^2}{4\pi\epsilon_0 a}$$

so the total lattice energy for one mole of NaCl

because there are Na and Cl ions

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

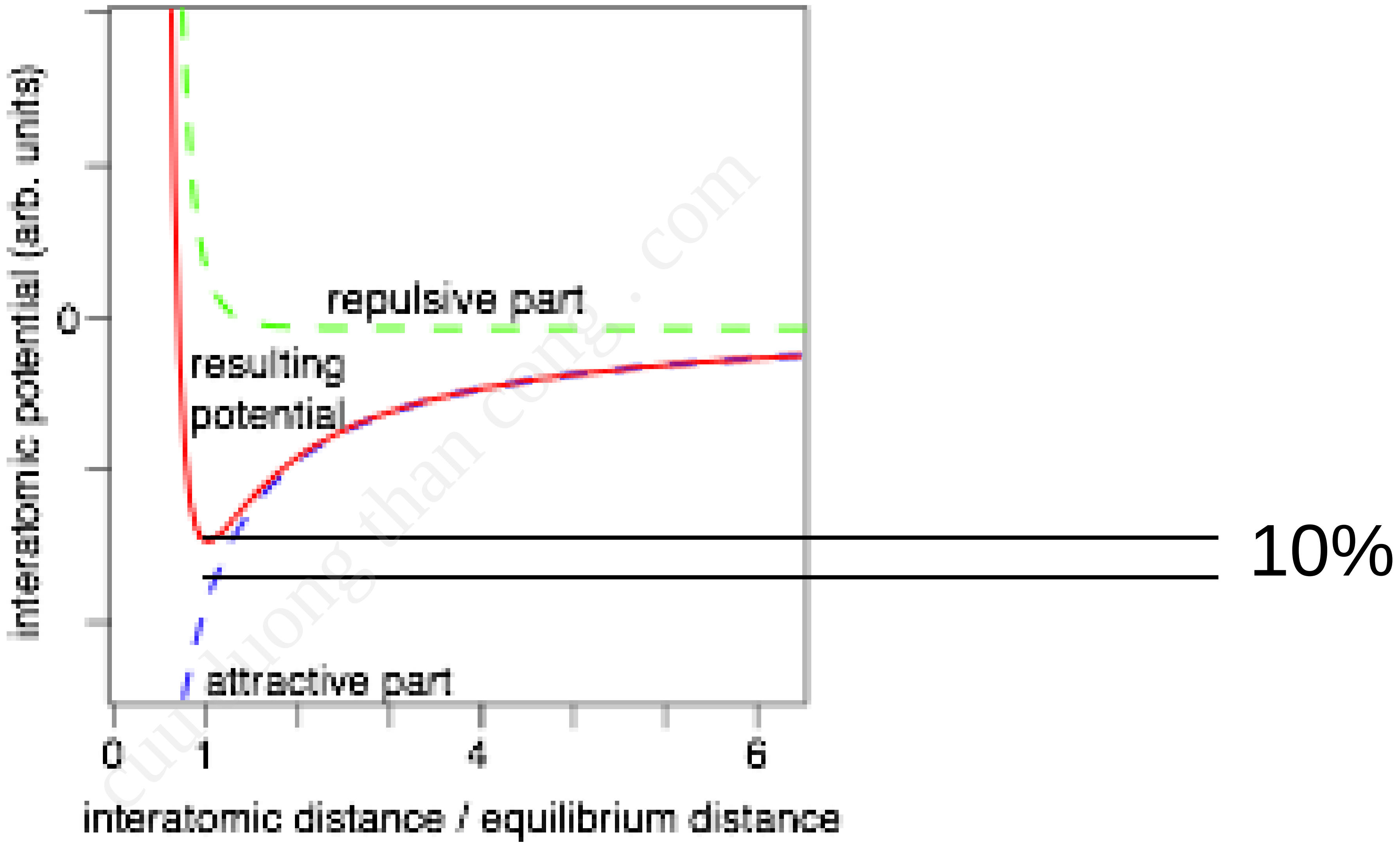
to count every pair only once



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).

Repulsive force



- The existence of a (non-classical) repulsive force causes the real cohesive energy to be slightly smaller (10%) than the value calculated by the Coulomb potential.

Covalent bonding

- A detailed view on the hydrogen molecule, identical particles (later in connection with magnetism, see online note on www.philiphofmann.net).
- A simple view on other covalent bonds.

The covalent bond: simple picture

The covalent bond: less simple picture

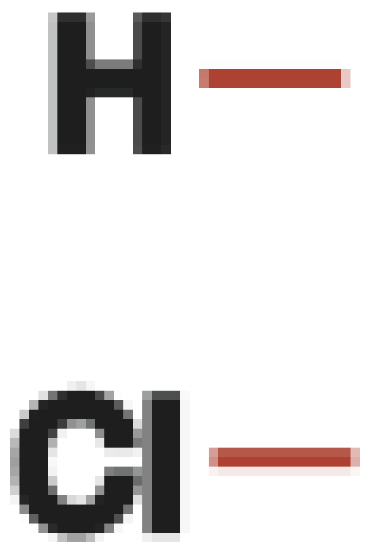
(hydrogen molecule)

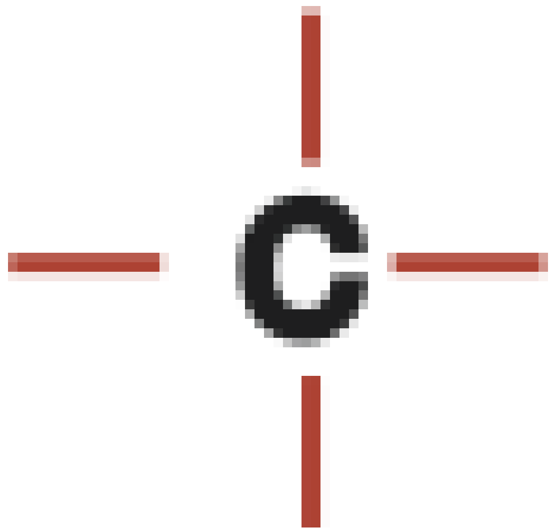
$$H = -\frac{\hbar^2\nabla_1^2}{2m} - \frac{\hbar^2\nabla_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0}\left\{-\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|} + \frac{1}{R} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B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

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

(see note on www.philiphofmann.net)

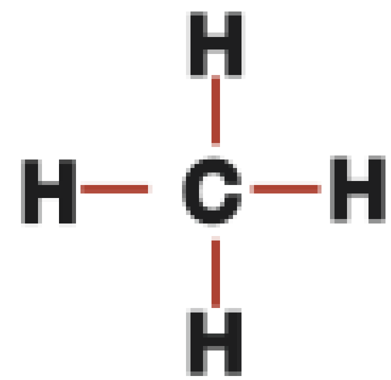
The covalent bond: simple picture



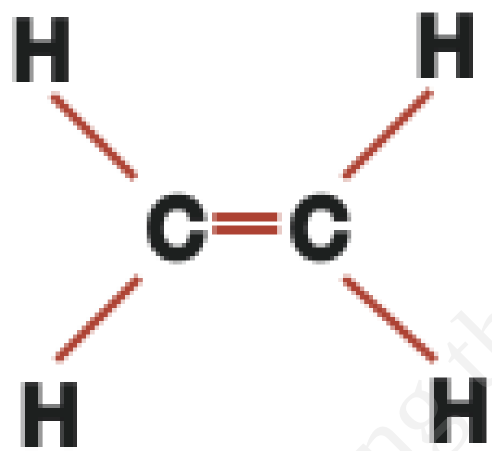


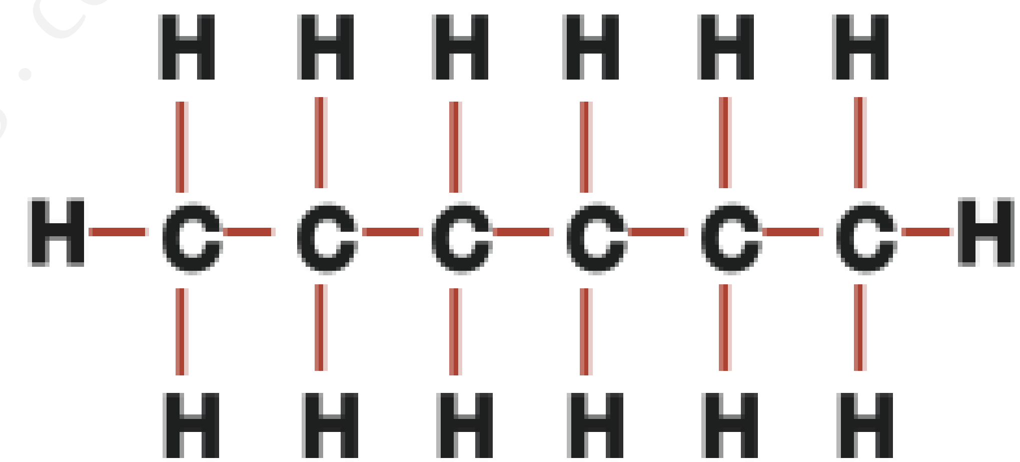
The covalent bond: simple picture

methane

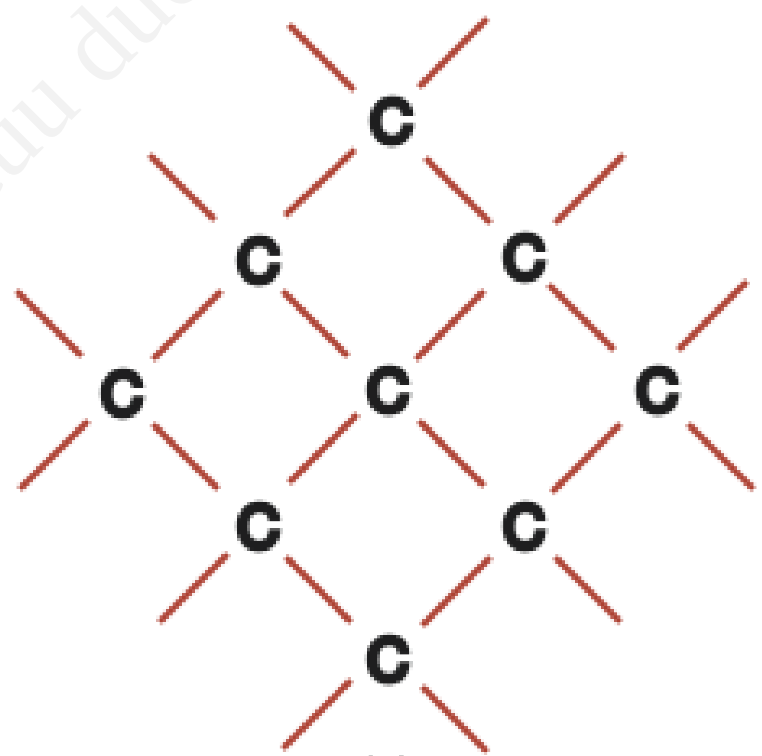


hydrocarbons



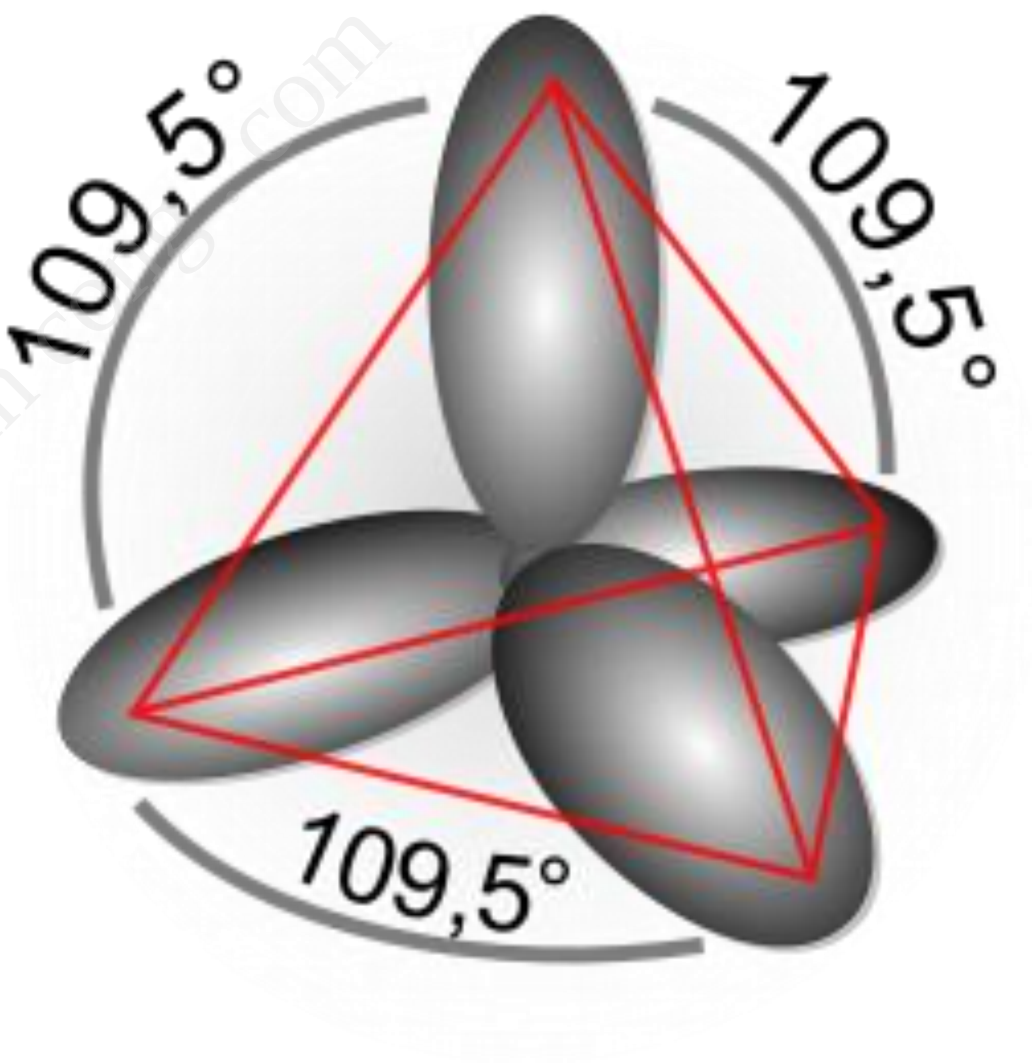


C-based solid



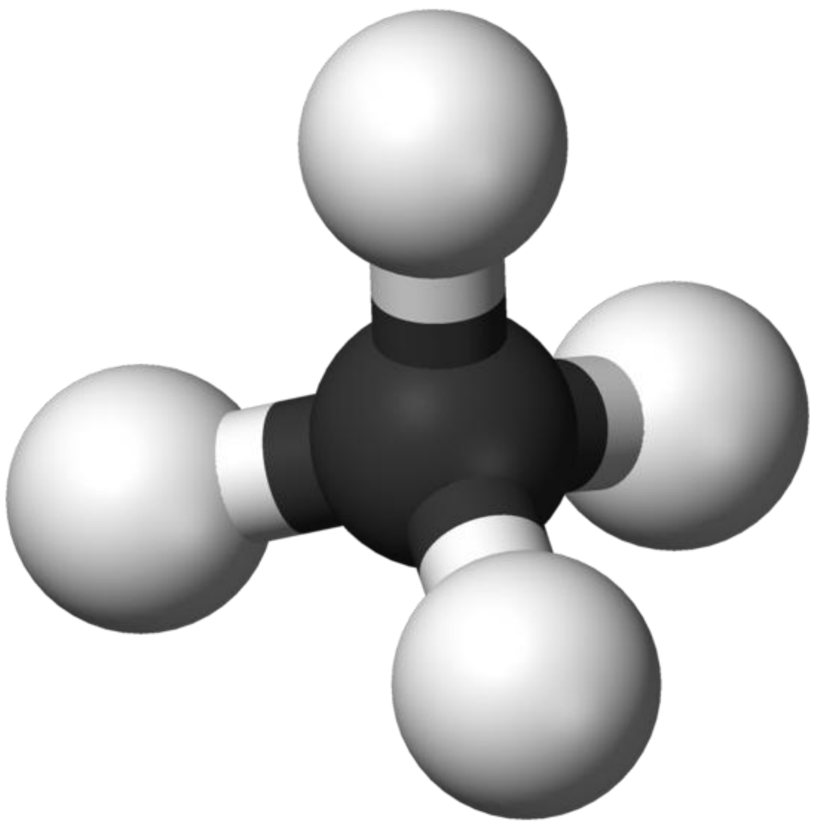
The covalent bond: a closer look at C

- 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.

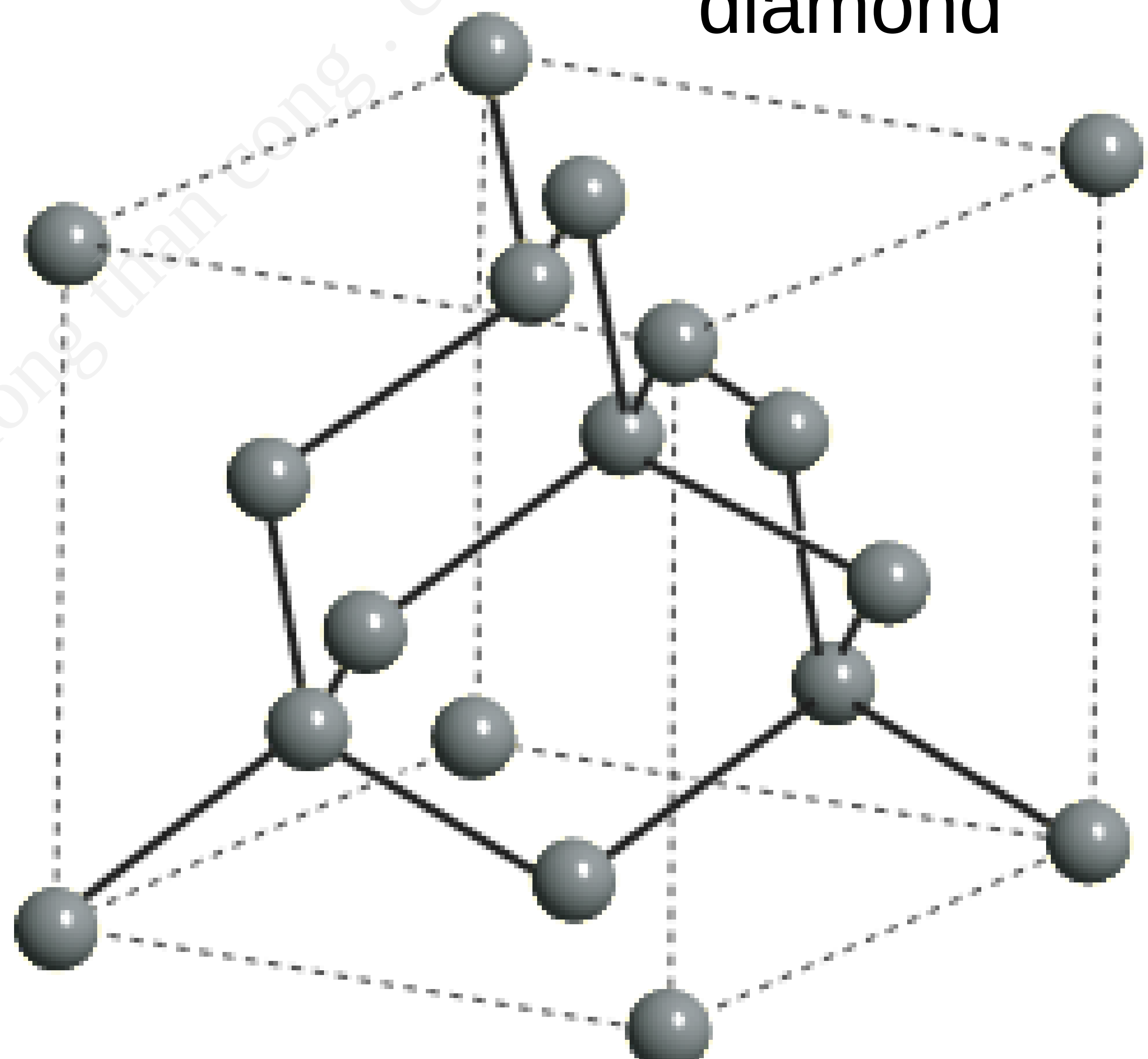


The covalent bond: sp^3 bonding

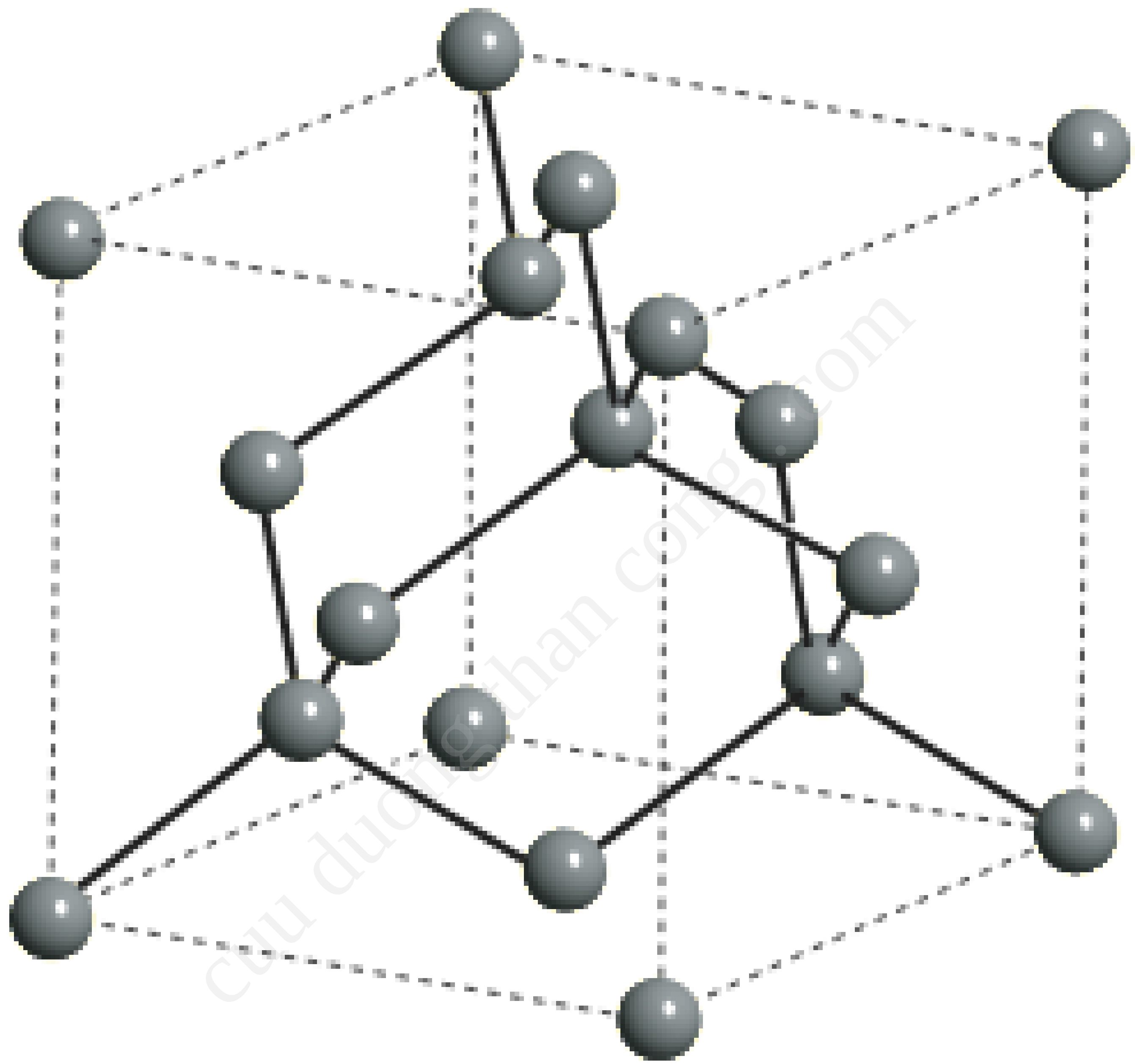
methane



diamond

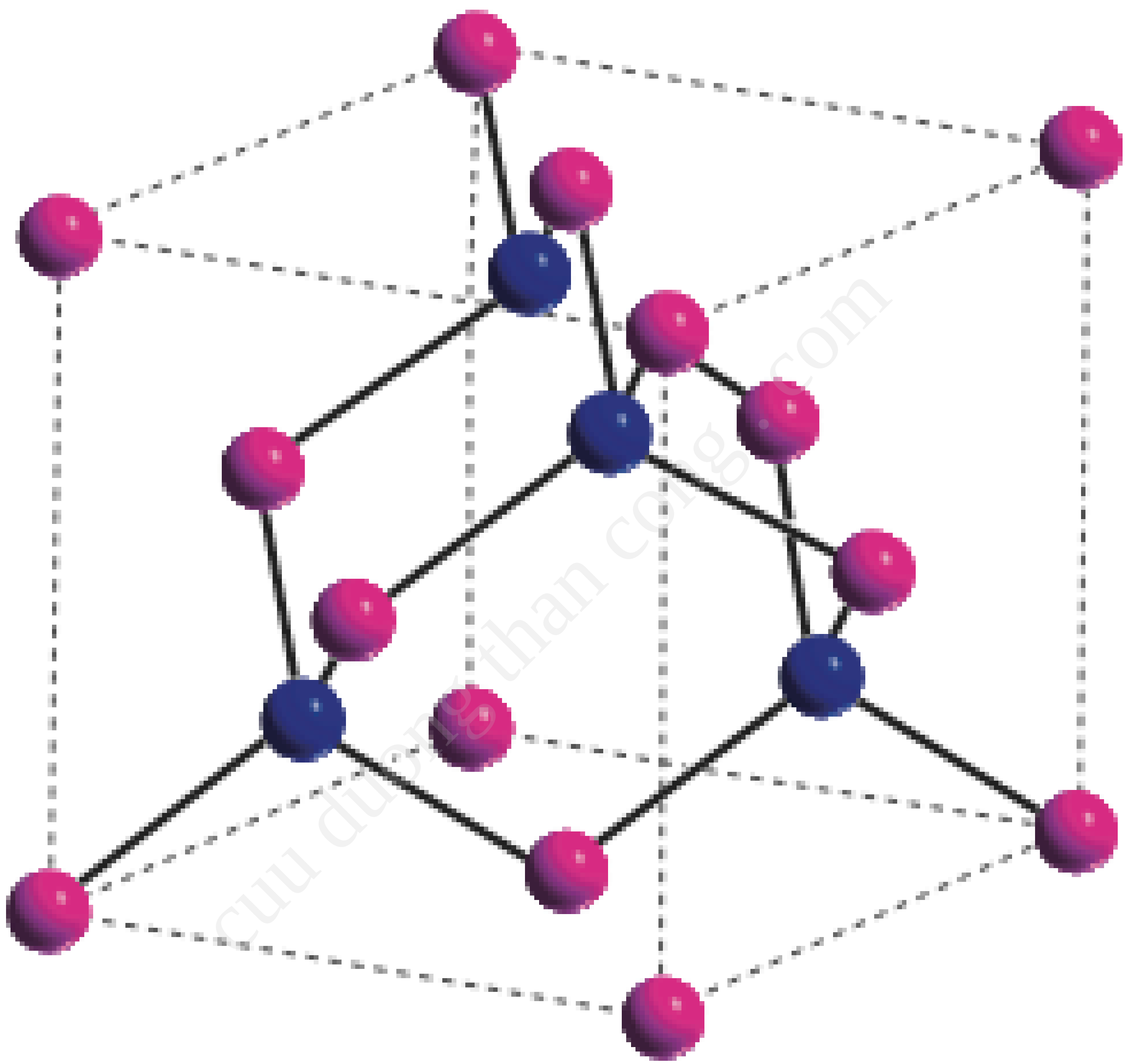


Bonding in most semiconductors



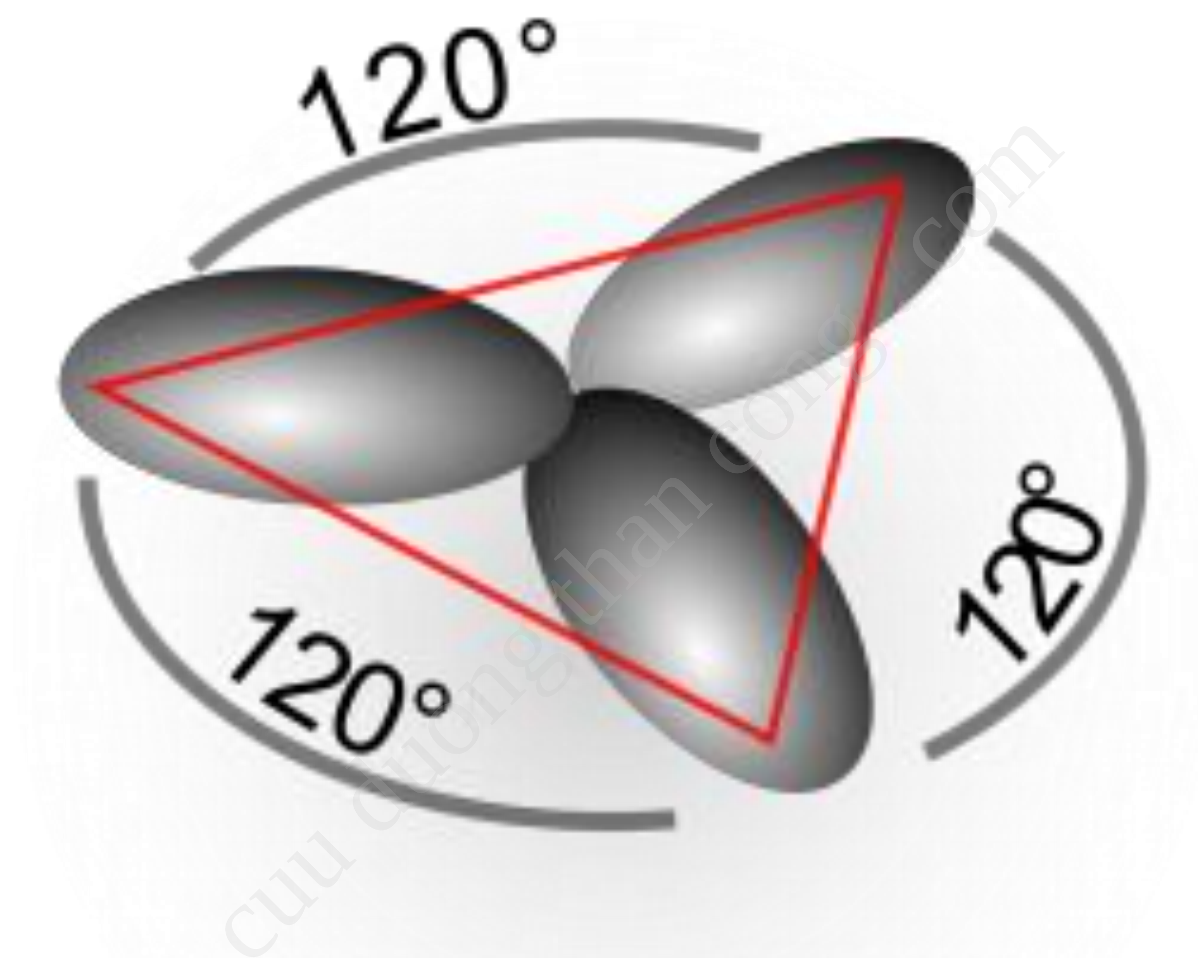
- Tetrahedral (sp^3) configuration almost ubiquitous: diamond, Si, Ge, III-V (GaAs, AlAs, InP), II-VI (CdS, CdTe)

Bonding in most semiconductors



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

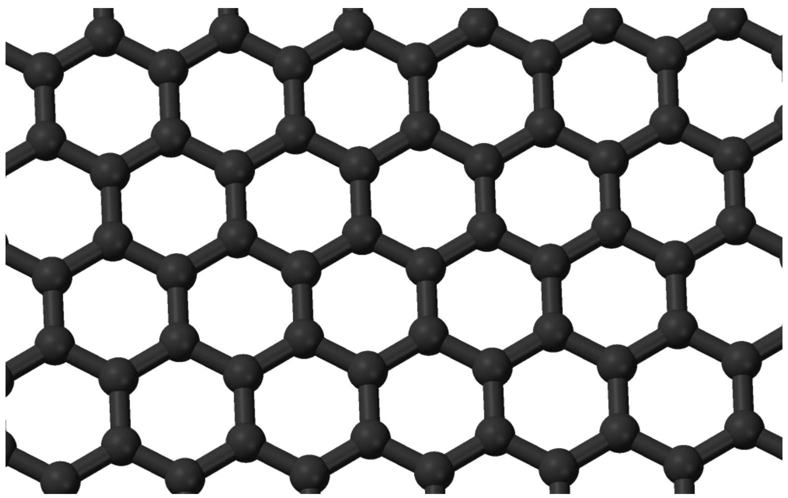
The covalent bond: sp bonding

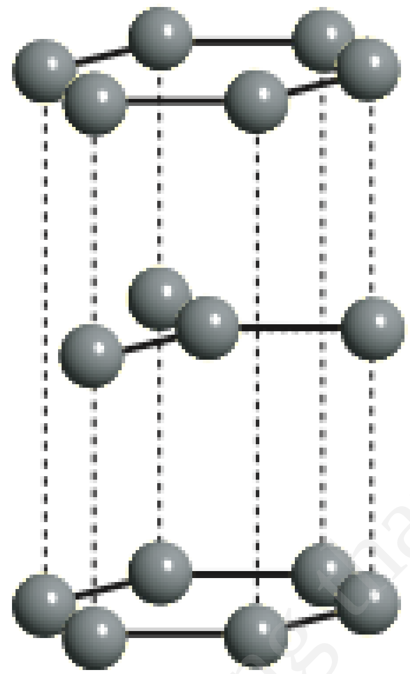


- formation of three sp^2 hybrid orbitals as linear combination between the s and two p orbitals. One p-orbital remains

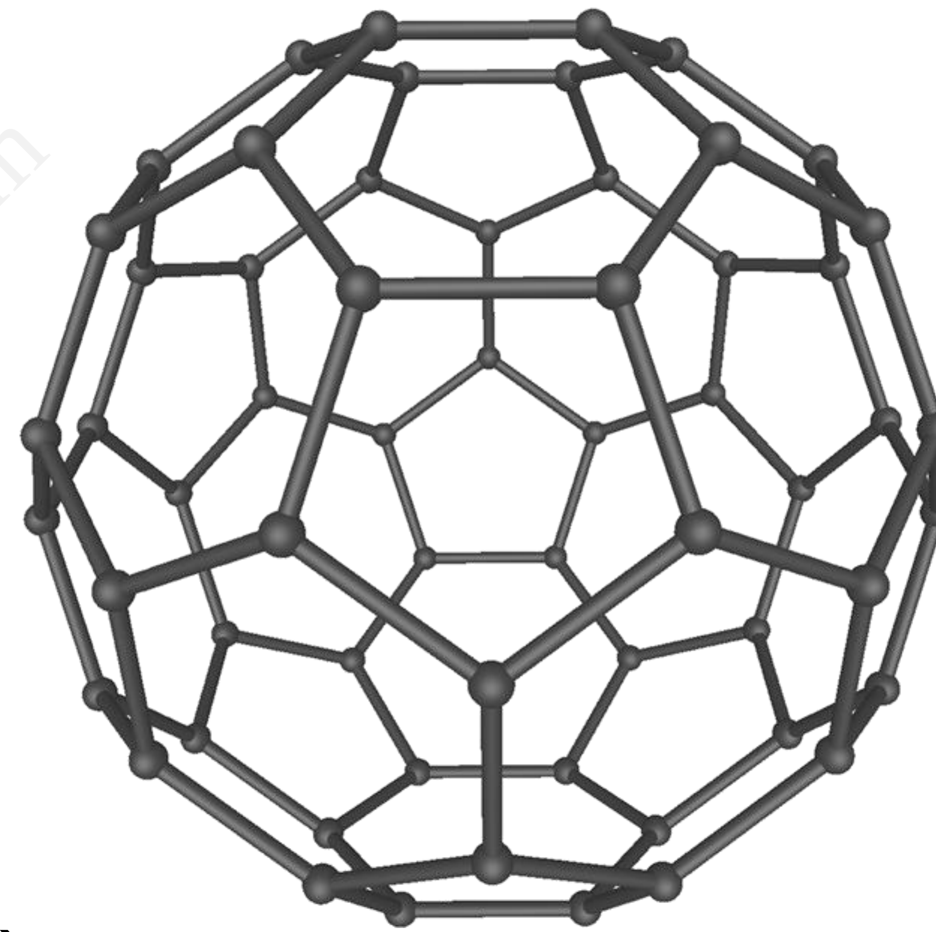
The covalent bond: sp^2 bonding

graphene / graphite

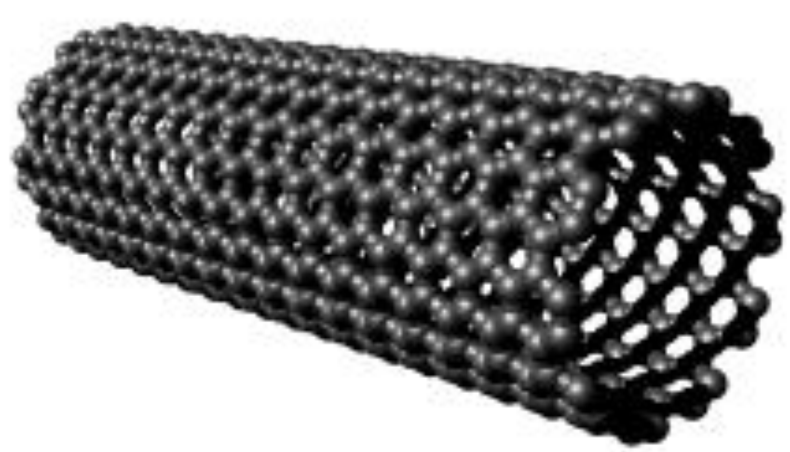




bucky-balls



carbon nanotubes
(rolled-up graphene)

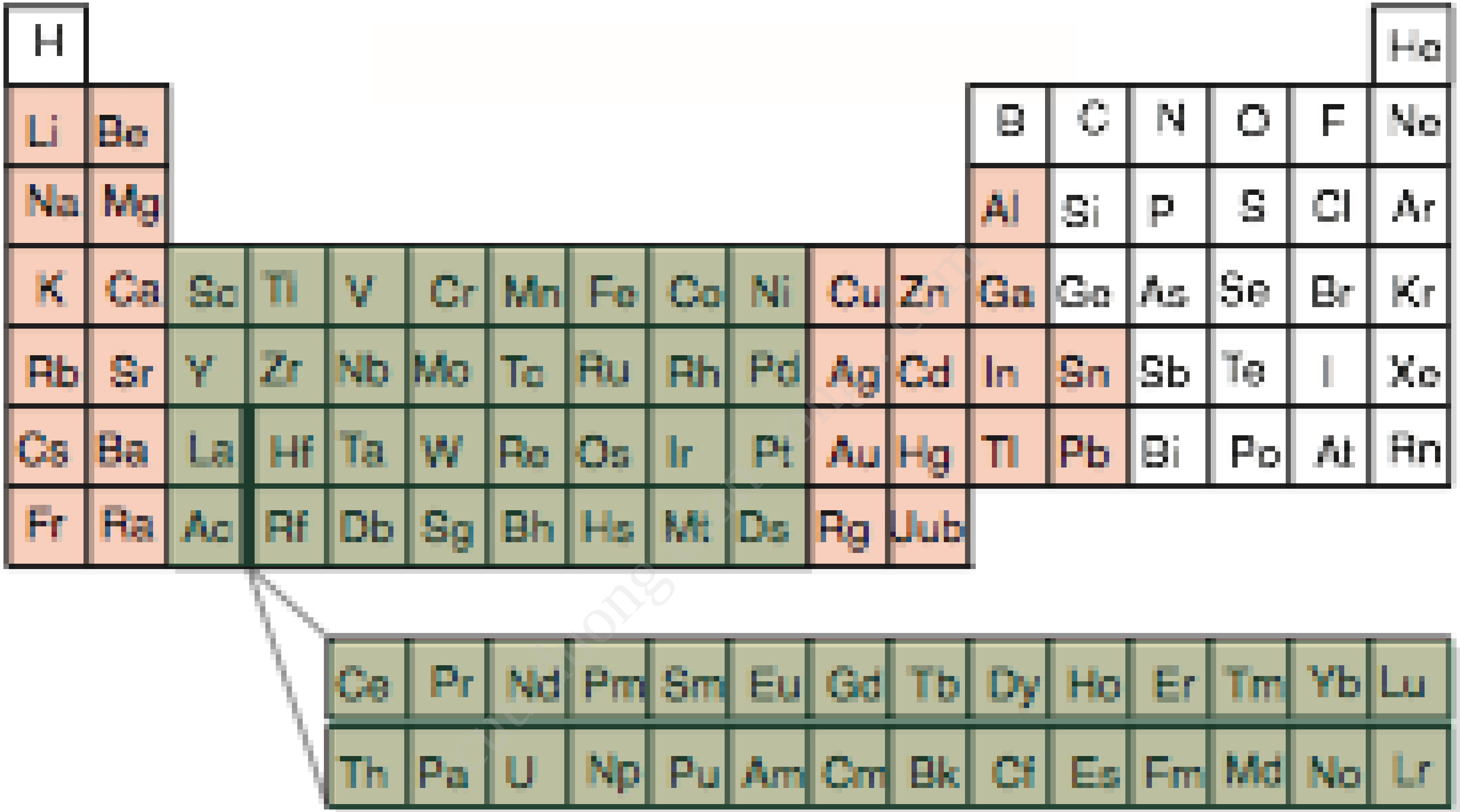


Covalent bonding

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

Metallic bonding

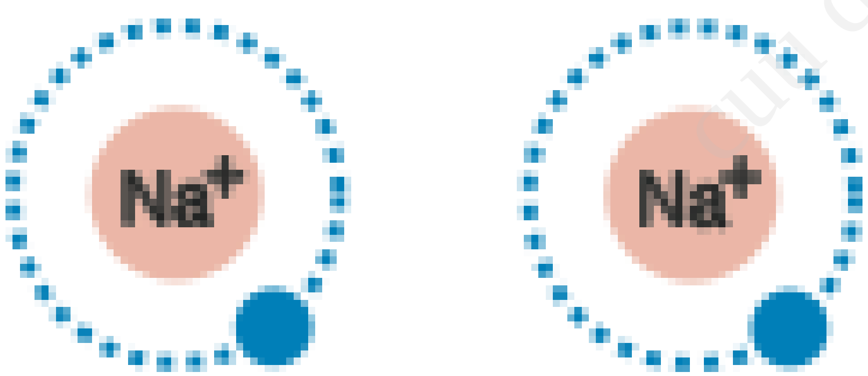
metals / non-metals

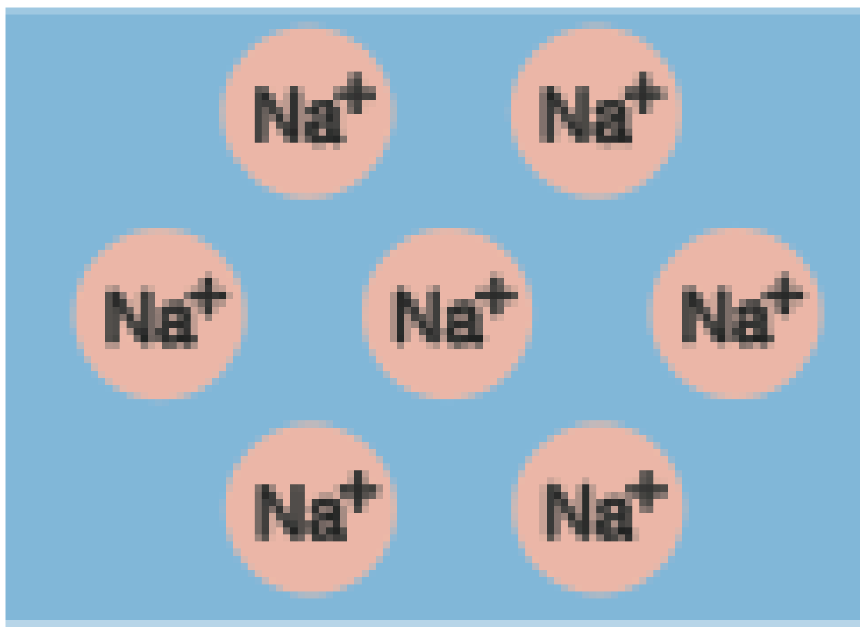


- the boundaries can be disputed
- simple metals, transition metals, noble metals

Metallic bonding (simple metals)

- outer electrons are delocalized and act as “glue” between positively charged ion cores
- generally found for elements with one, two or three valence electrons.
- cohesive energies in the eV range





Metallic bonding (simple metals): more characteristics

- smaller cohesive energies than in ionic crystals
- larger ionic radii, e.g. for Na: 3.82 Å (metal) and 1.94 Å (NaCl)
- bonding has no directional preference
- closed-packed atomic configurations are preferred: best possible overlap between the orbitals, no “holes” in the potential

Metallic bonding: why is this so favorable?

$$-\frac{\hbar^2\nabla^2}{2m}\Psi(r) + U(r)\Psi(r) = E\Psi(r)$$

kinetic energy (or Hamiltonian for a free particle)
∝ (negative) average curvature of wave function
"flatter" wave function -> lower energy

$$\Delta x \Delta p \geq \hbar/2$$

less localization -> smaller p variation

Metallic bonding: why is this so favorable?

$$-\frac{\hbar^2\nabla^2}{2m}\Psi(r) + U(r)\Psi(r) = E\Psi(r)$$

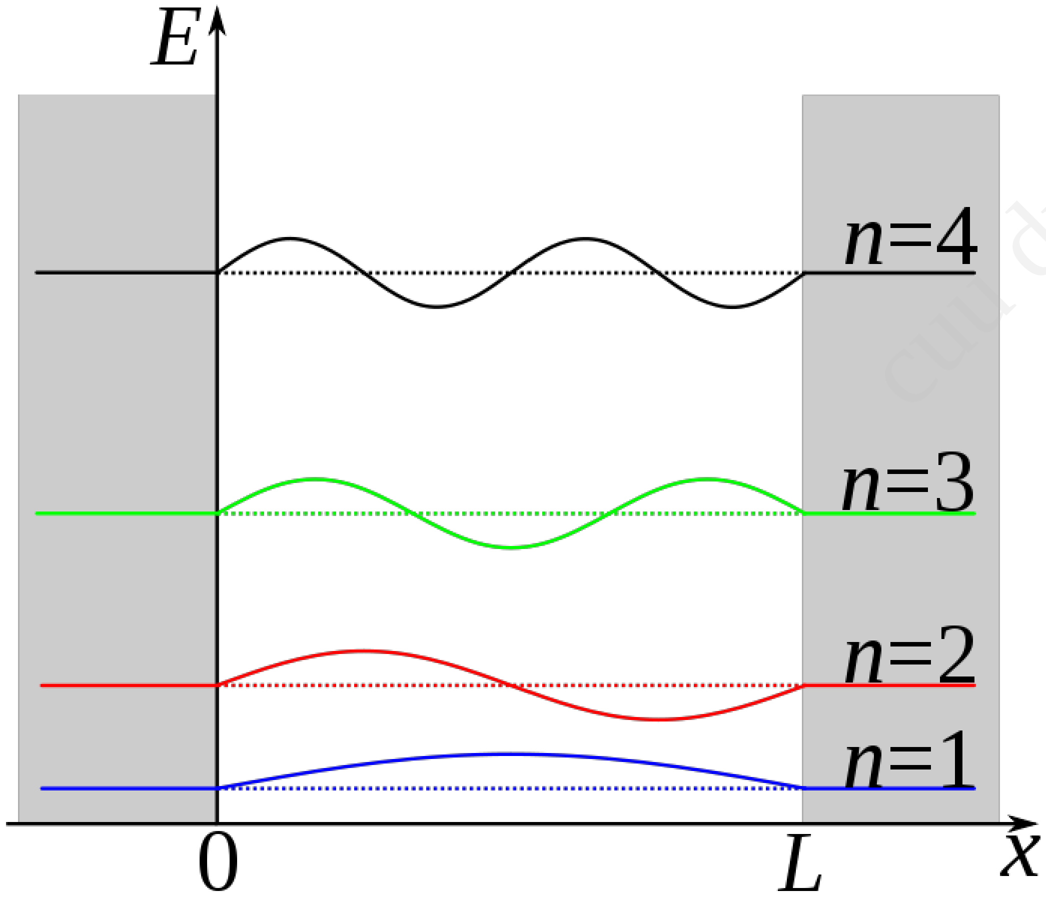
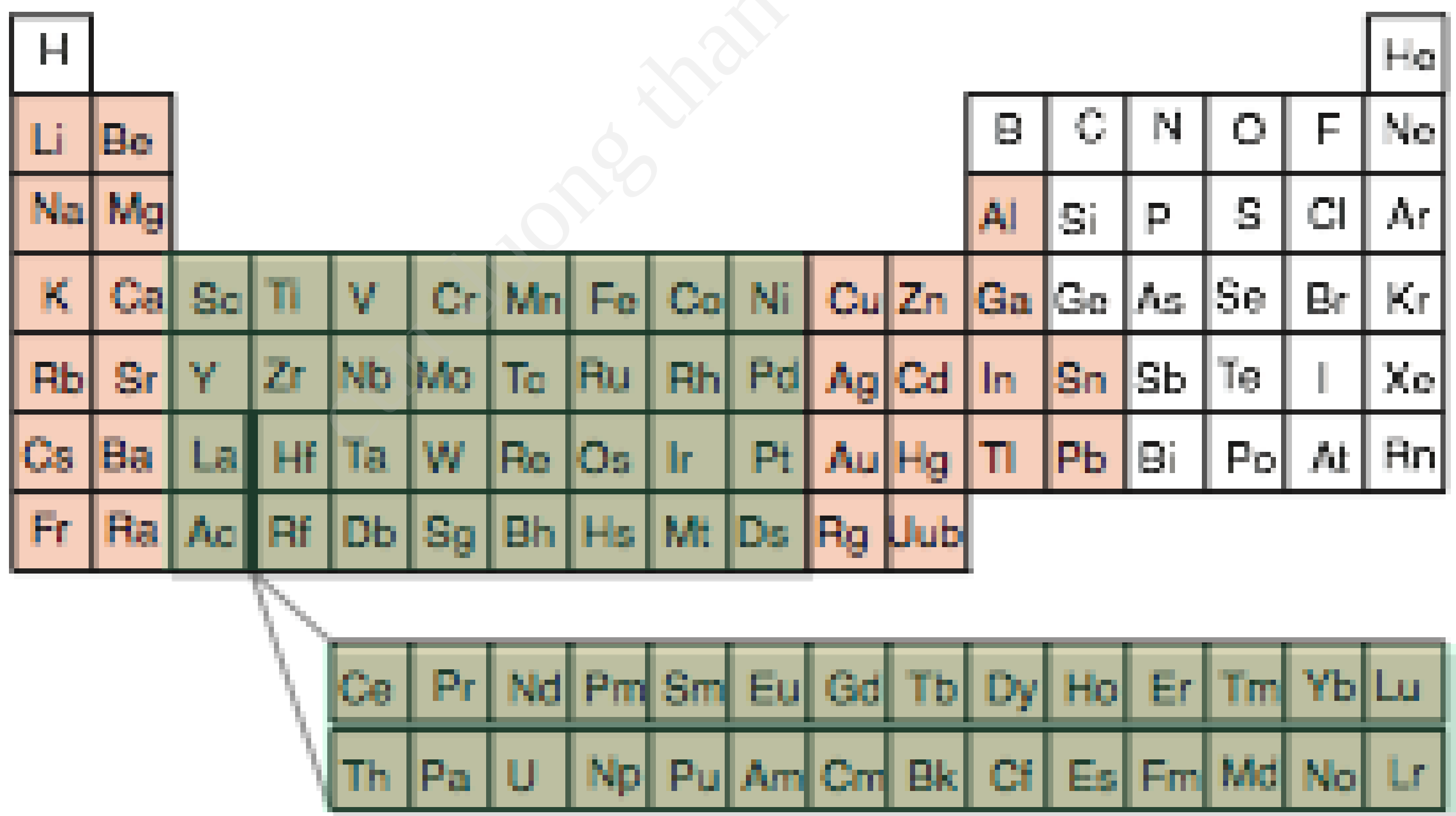


image source: wikipedia

Transition metals

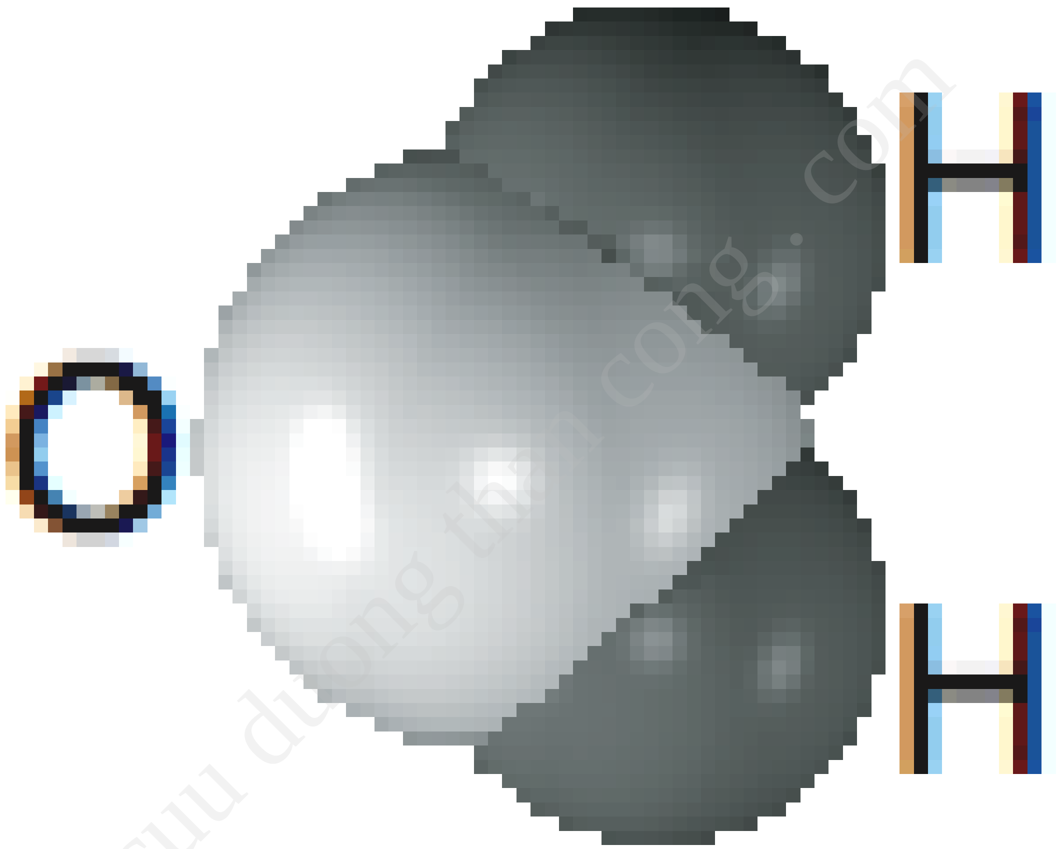
- 4s and 3d have very similar energies
- 4s electrons form delocalized metallic bonds
- 3d electrons form more local (covalent-like) bonds
- higher cohesive energies



Bonds between molecules

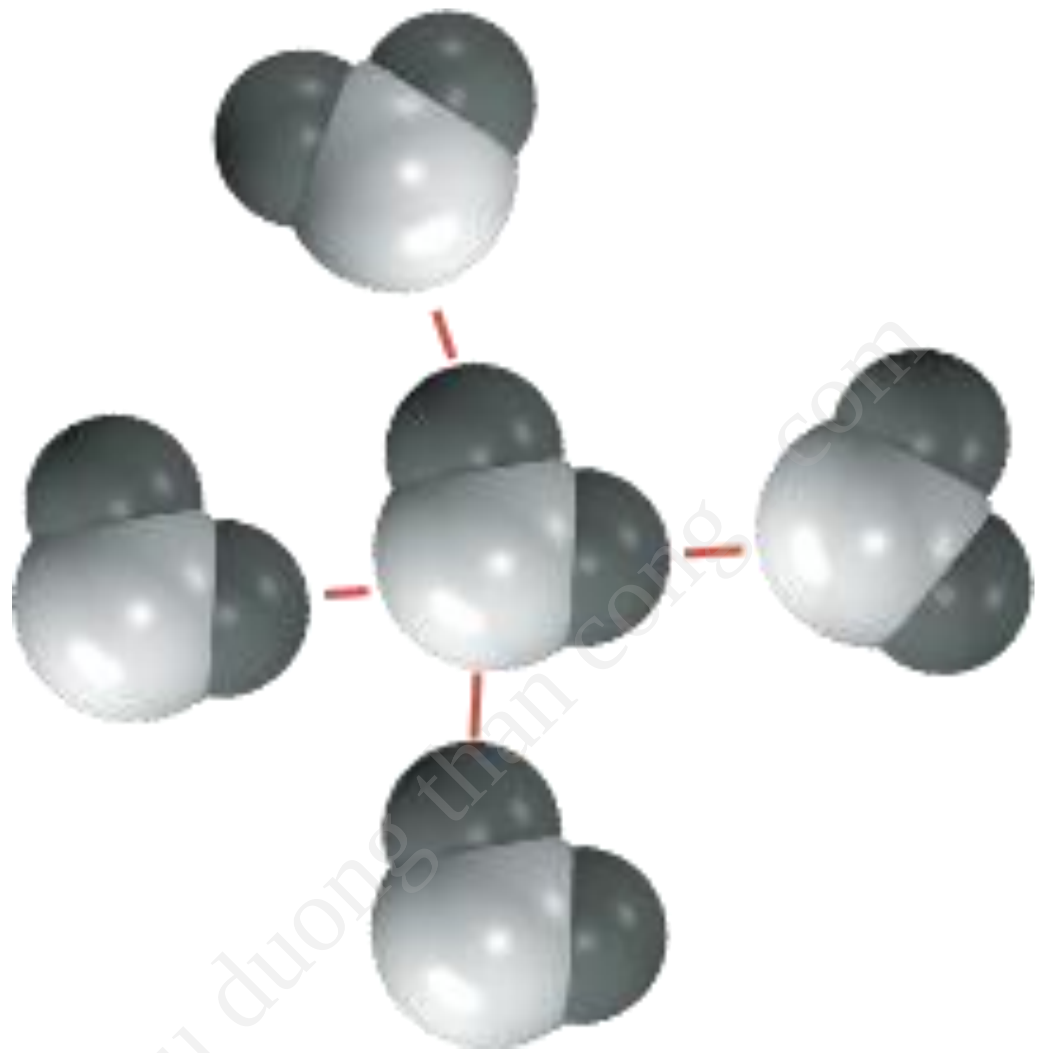
- molecular solids are very common (but not at RT)
- ice
- plastic
- DNA
- what makes molecules bond to each other?

Bonds between molecules: hydrogen bonds



permanent dipole

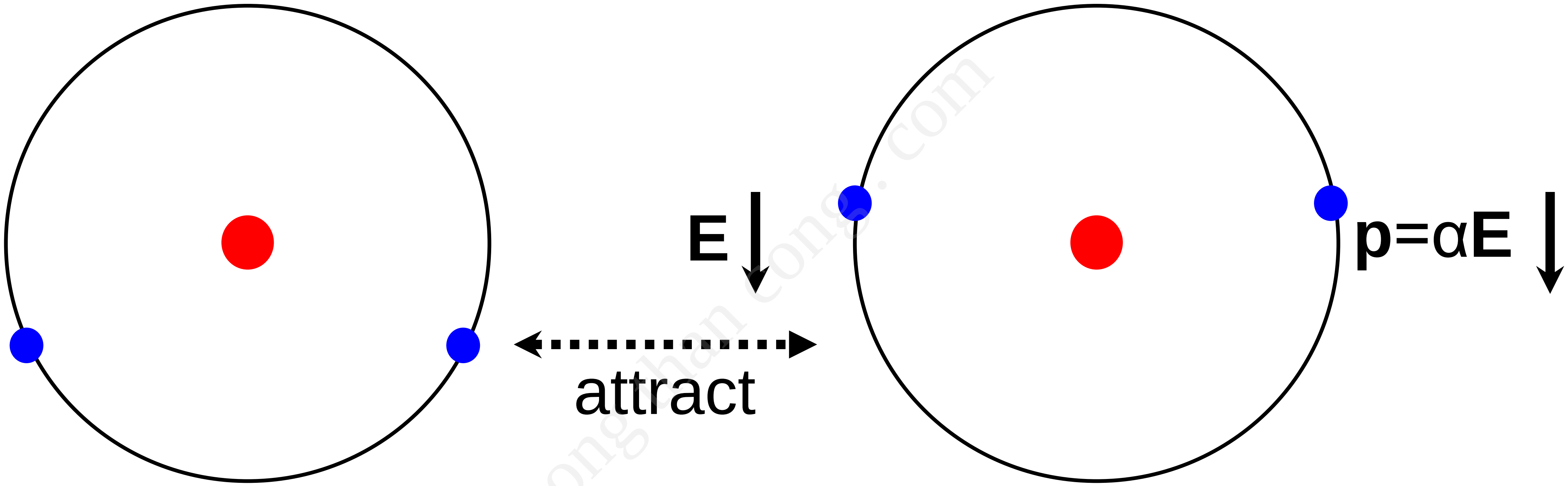
Bonds between molecules: hydrogen bonds



- H is positively charged but also very small: another “real” bond cannot be established without overlap of electron clouds (in this sense it is too big in this drawing).
- H bonding is important in ice, DNA... but not very strong

Bonds between molecules: van der Waals force

$$U = -\mathbf{E}\cdot\mathbf{p} = -\mathbf{E}\cdot\alpha\mathbf{E} \propto -\frac{1}{r^3}\alpha\frac{1}{r^3}$$

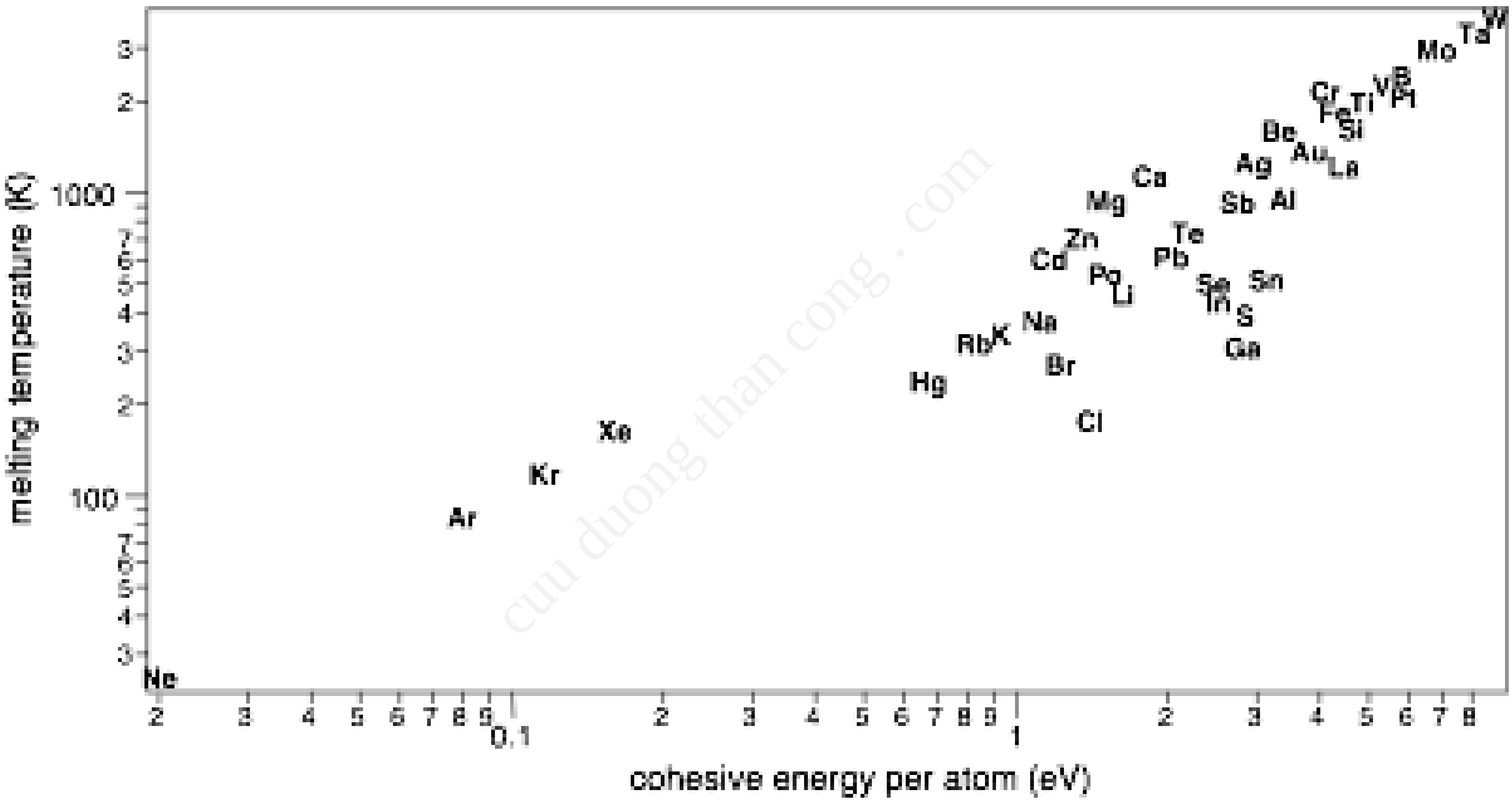


- dipole moment caused by fluctuations
- this is always present as an attractive force (even between He atoms as in this case)
- it is very weak and depends on the distance as r^{-6}

Bond type and physical properties

- How does the bond type affect the properties of a solid such as:
- mechanical strength / melting point
- electrical conductivity
- thermal conductivity
- optical properties

Bond type and physical properties



Summary

- We have looked at different types of bonding: ionic, metallic, covalent, H-bonds, van der Waals bonds.
- In reality, intermediate bonding scenarios are often found.
- We have some ideas about the relation between between the bonding type and the physical properties (at least for the melting point).