Achievements

Lecture 1: VESTA plotting of crystal structures

Lecture 2: How to describe a crystal structure

-- Crystal lattice

-- Basis

Lecture 3 +4: How to resolve crystal structures

-- Reciprocal space

-- Scattering theory (Form and Structure Factor)

-- Resolving the crystal structure of a superconductor

Lecture 5: How to crystals bind together

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Tasks

(1) Read chapter 4: (12 pages)

Crystal vibrations

(2) Who is summarizing next week?

(3) Install Mathematica (as many of you).

(4) Solve exercise sheet 4

Exercise 1 *Binding energy*

a) Show that for a potential of the form $U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$ an equilibrium can only be reached if $n > m$.

b) For a pure van der Waals attraction the potential is often written as

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

Calculate the binding energy (cohesive energy) E_B and the equilibrium distance R_0.

c) Calculate the effect of thermal expansion, $\Delta R_0(T)/R_0$, on a linear chain of atoms with the potential of part b. Assume that the thermal energy $k_B T \ll E_B$ allows motion of the atoms around the equilibrium position. Think about in what boundaries the atoms can move. From this deduce the average position and compare the result with R_0.

Hint: Use the expansion $1/(1 \pm \epsilon) \approx 1 \mp \epsilon + \epsilon^2 + \ldots$ up to the second order and $\sqrt[n]{1+\epsilon} = 1 + \epsilon/n + \ldots$ for $\epsilon \to 0$.

Exercise 2 *Madelung constant*

Calculate the Madelung constant for an infinitely long, evenly spaced, linear chain of ions with alternating anions and cations of charge $\pm e$.

Exercise 3 *Linear ionic crystal*

Consider a line of $2N$ ions of alternating charge $\pm q$ with a repulsive potential energy A/R^n between nearest neighbours.

a) Show that the expression for the potential energy can be approximated by

$$U(R) = N\left[\frac{2A}{R^n} - \frac{2\ln 2q^2}{4\pi\epsilon_0 R}\right].$$

b) Show that at the equilibrium separation

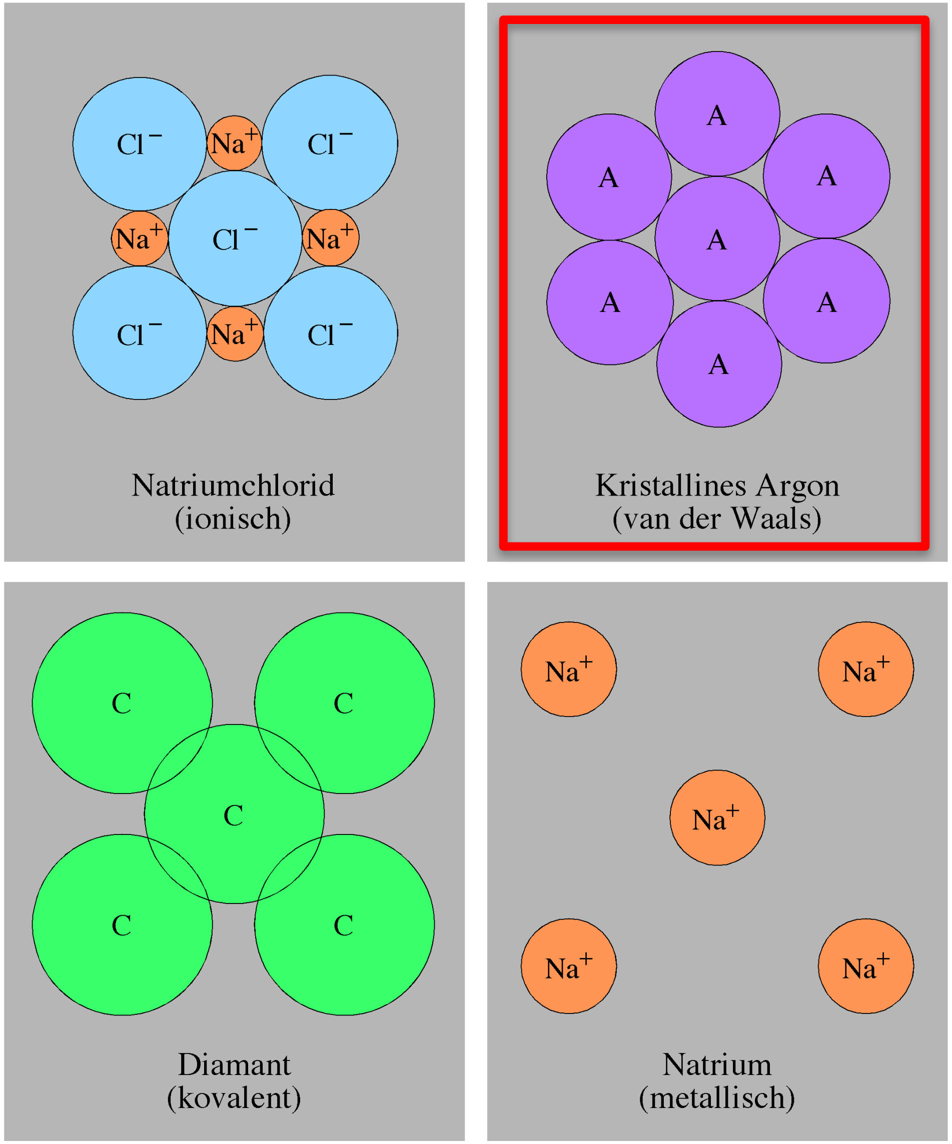
$$U(R_0) = -\frac{2Nq^2\ln 2}{4\pi\epsilon_0 R_0}\cdot\left(1-\frac{1}{n}\right).$$

c) Let the crystal be compressed so that $R_0 \to R_0(1-\delta)$. Show that the work done in compressing a unit length of the crystal has the leading term $\frac{1}{2}C\delta^2$, where

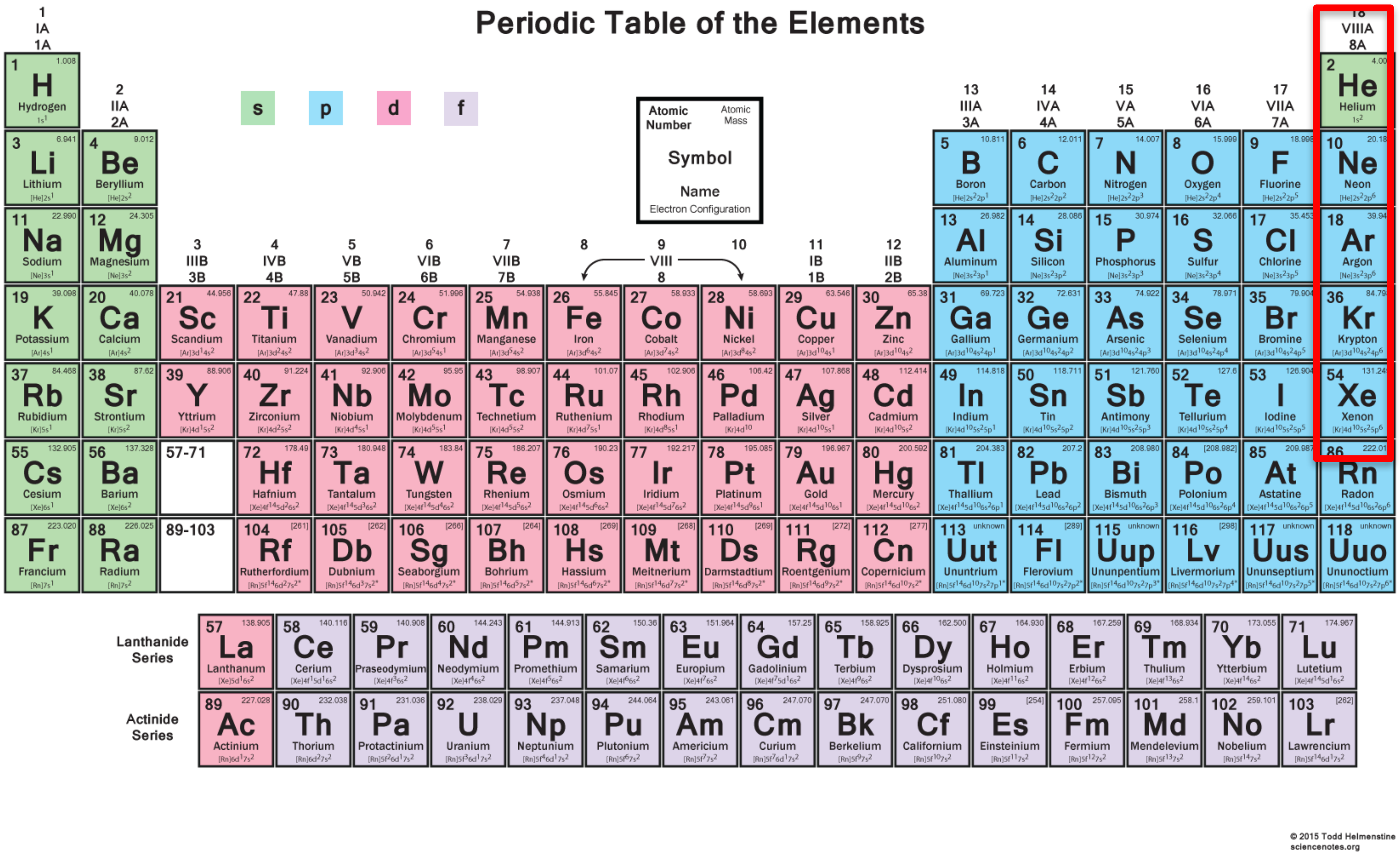
$$C = \frac{(n-1)q^2\ln 2}{4\pi\epsilon_0 R_0}.$$

Note: Use the complete expression for $U(R)$ instead of $U(R_0)$.

Today's lecture



Periodic Table

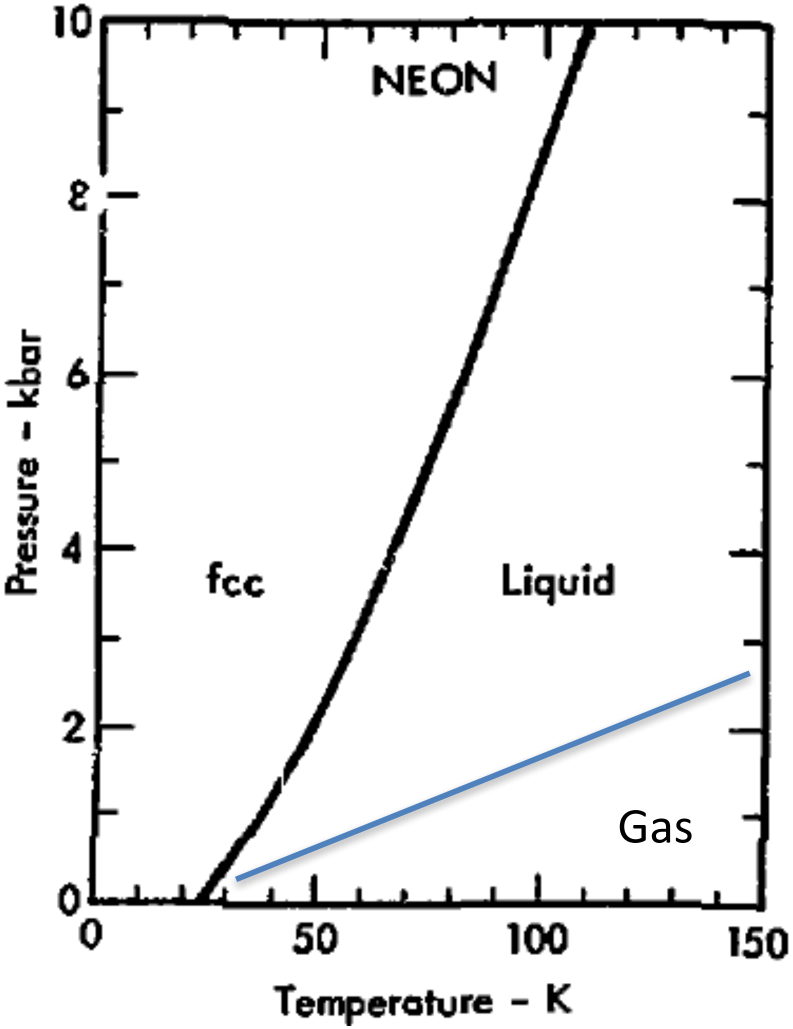


http://sciencenotes.org/periodic-table-showing-shells/

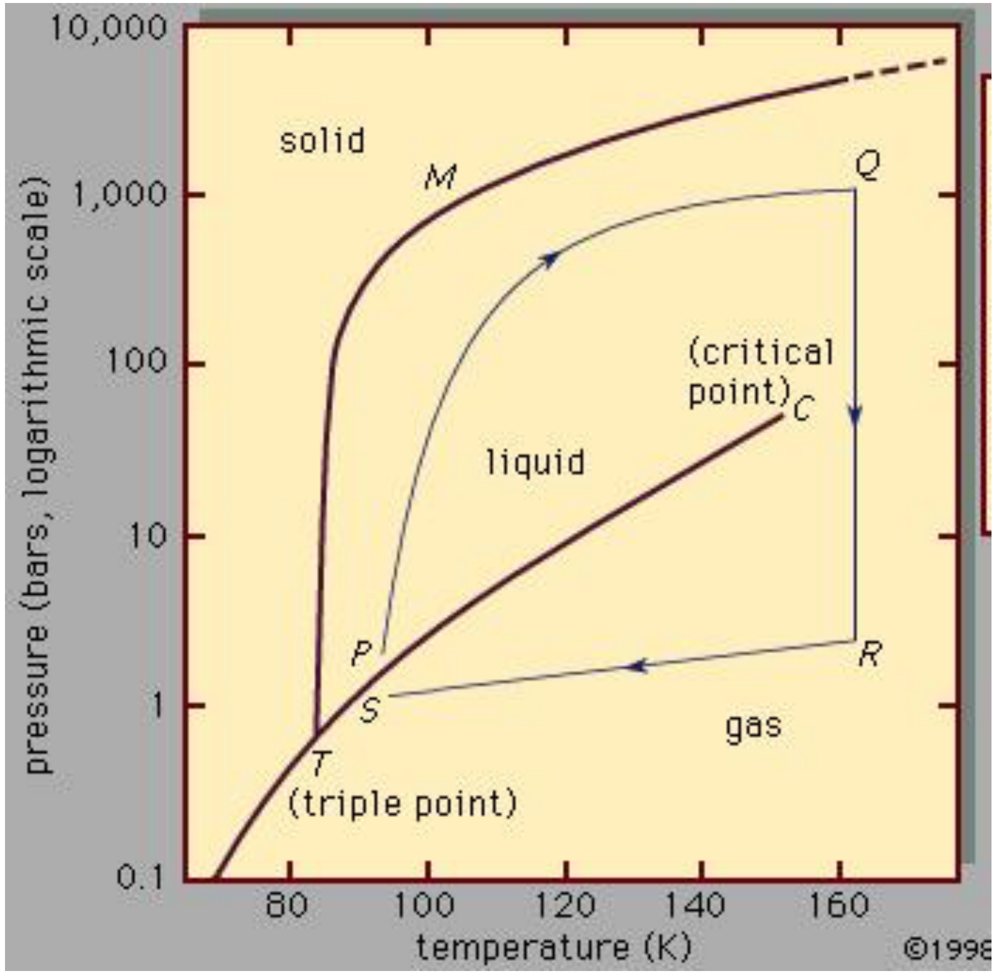
See also table 3 in Kittel.

Phase diagrams:

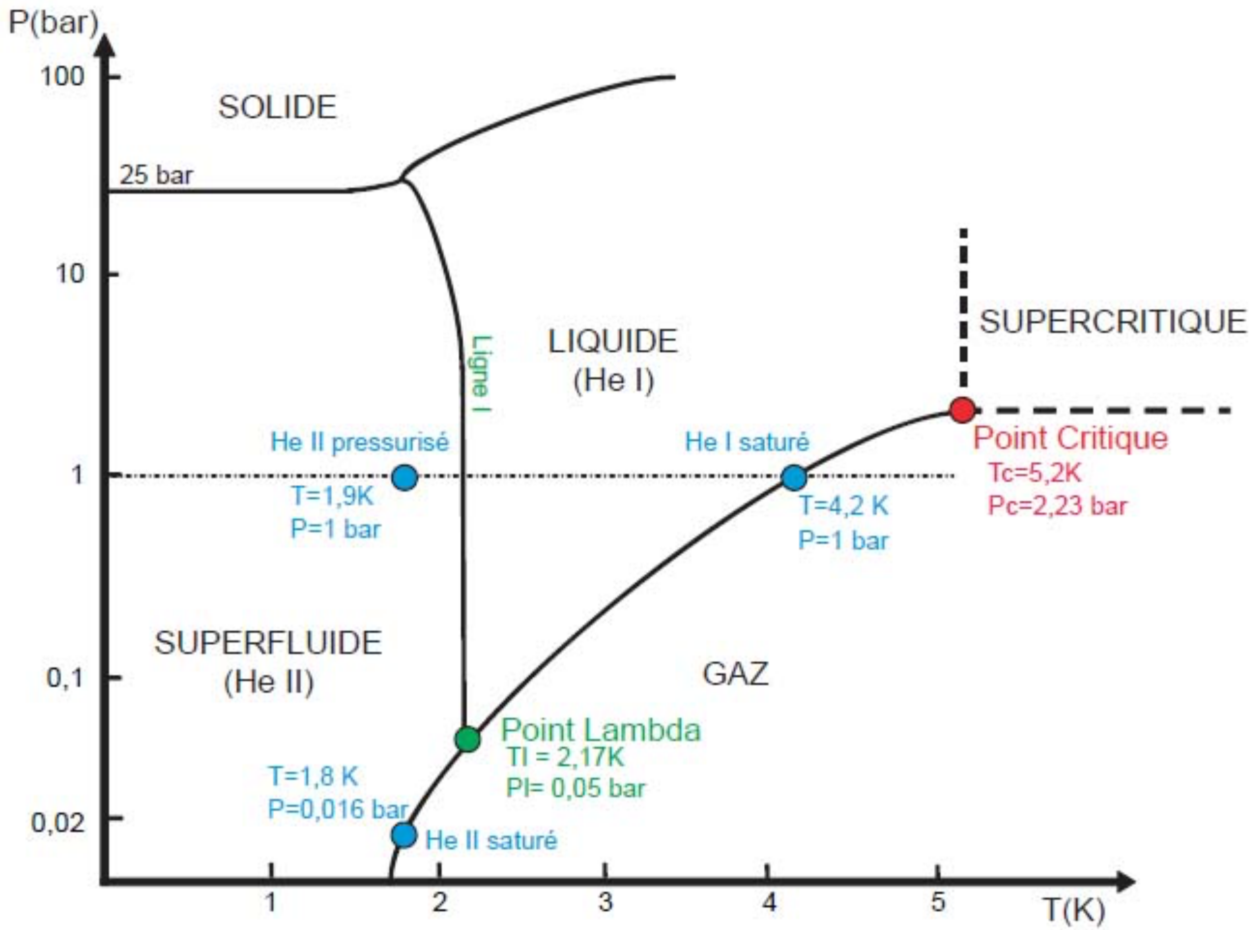
NEON



ARGON

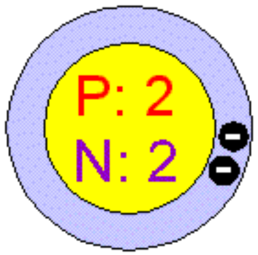


Phase diagram of Helium

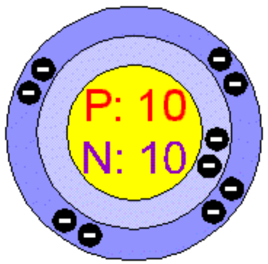


Inert gasses

Helium

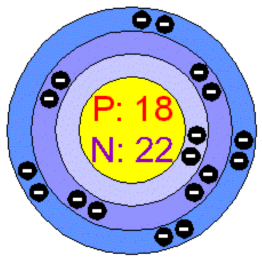


Neon



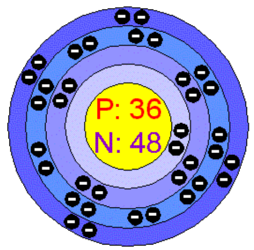
Melting point = 24 K

Argon



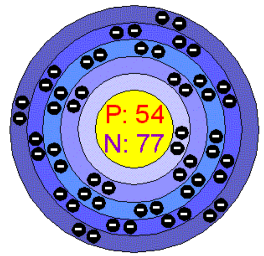
84 K

Krypton



117 K

Xenon

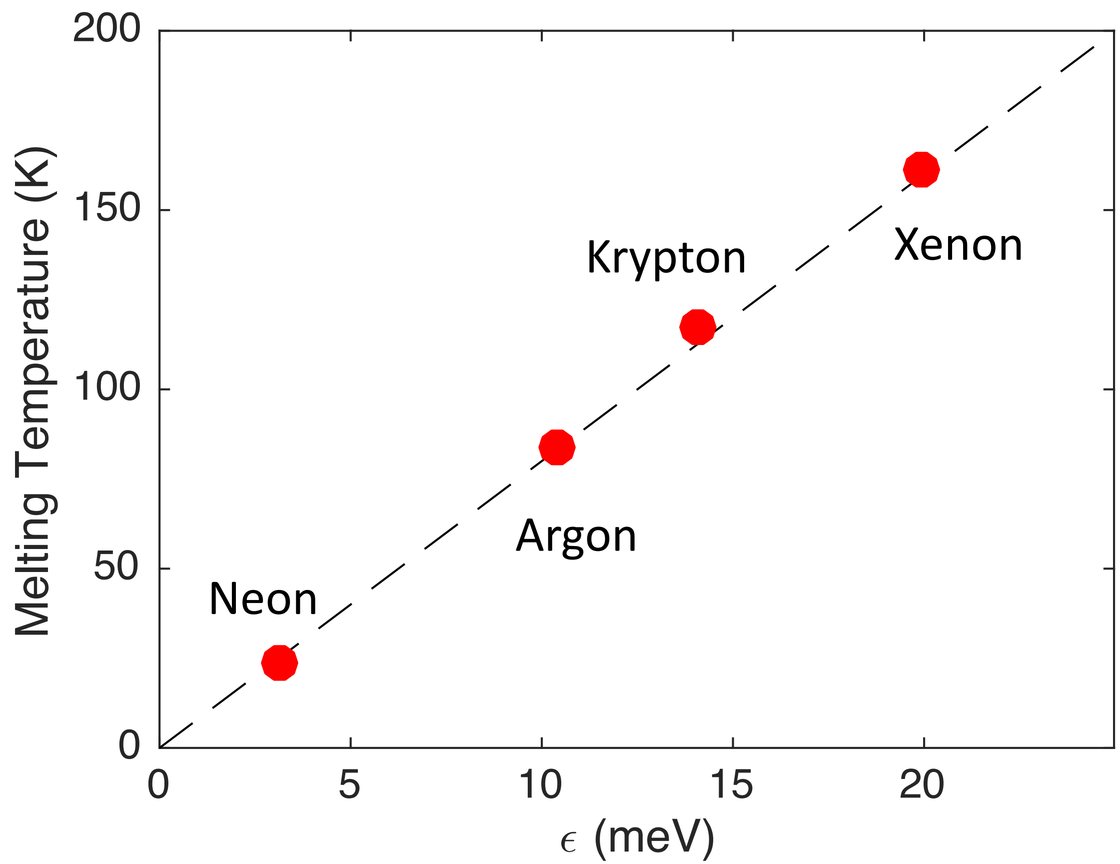


161 K

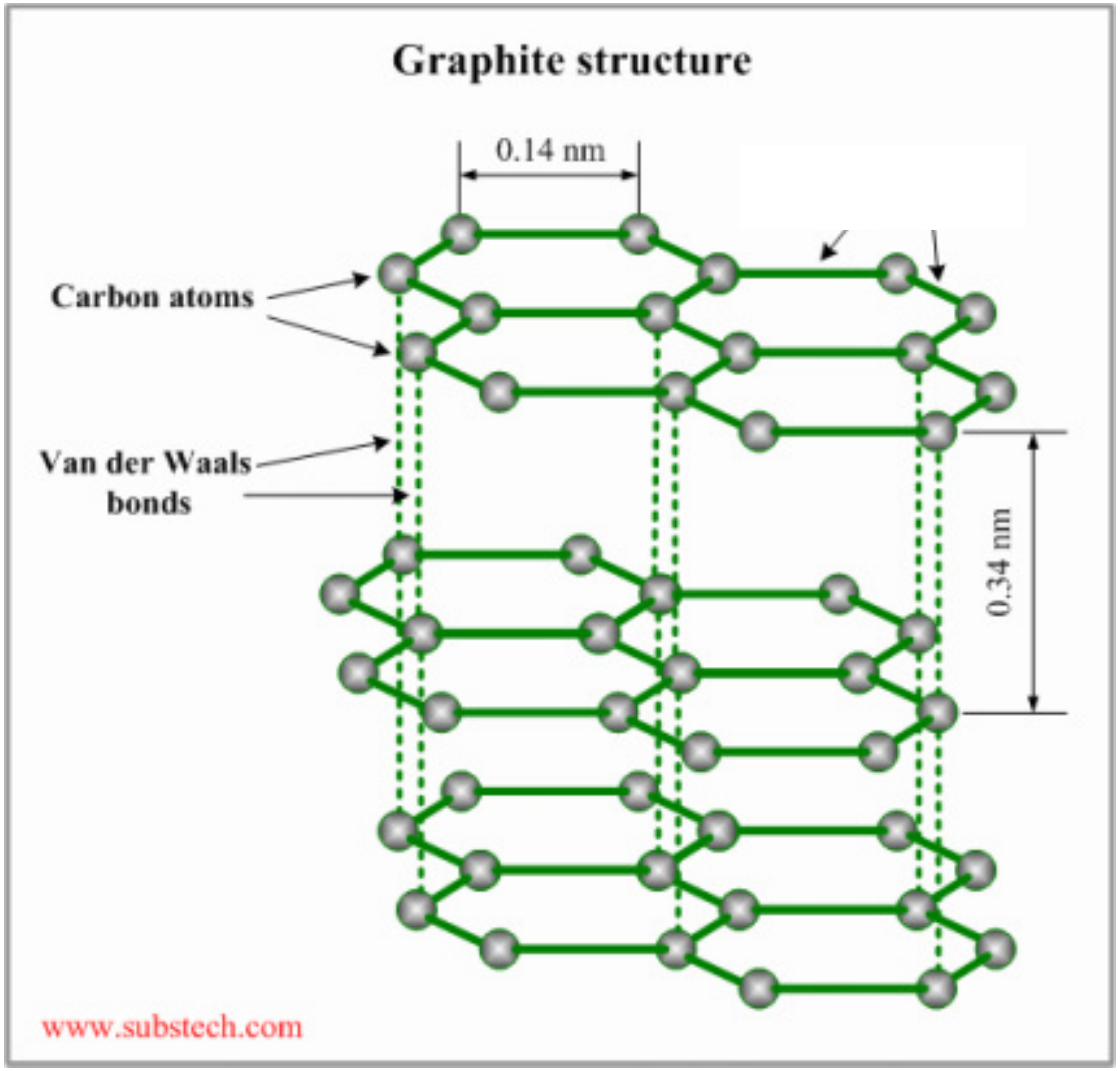
Questions:

(1) Why are these gasses solidifying in FCC rather than BCC?
(2) What are the “glue” that binds these atoms together in the solid form?
(3) Why are the melting point rather low?
(4) Why are the inert gasses having different melting points?

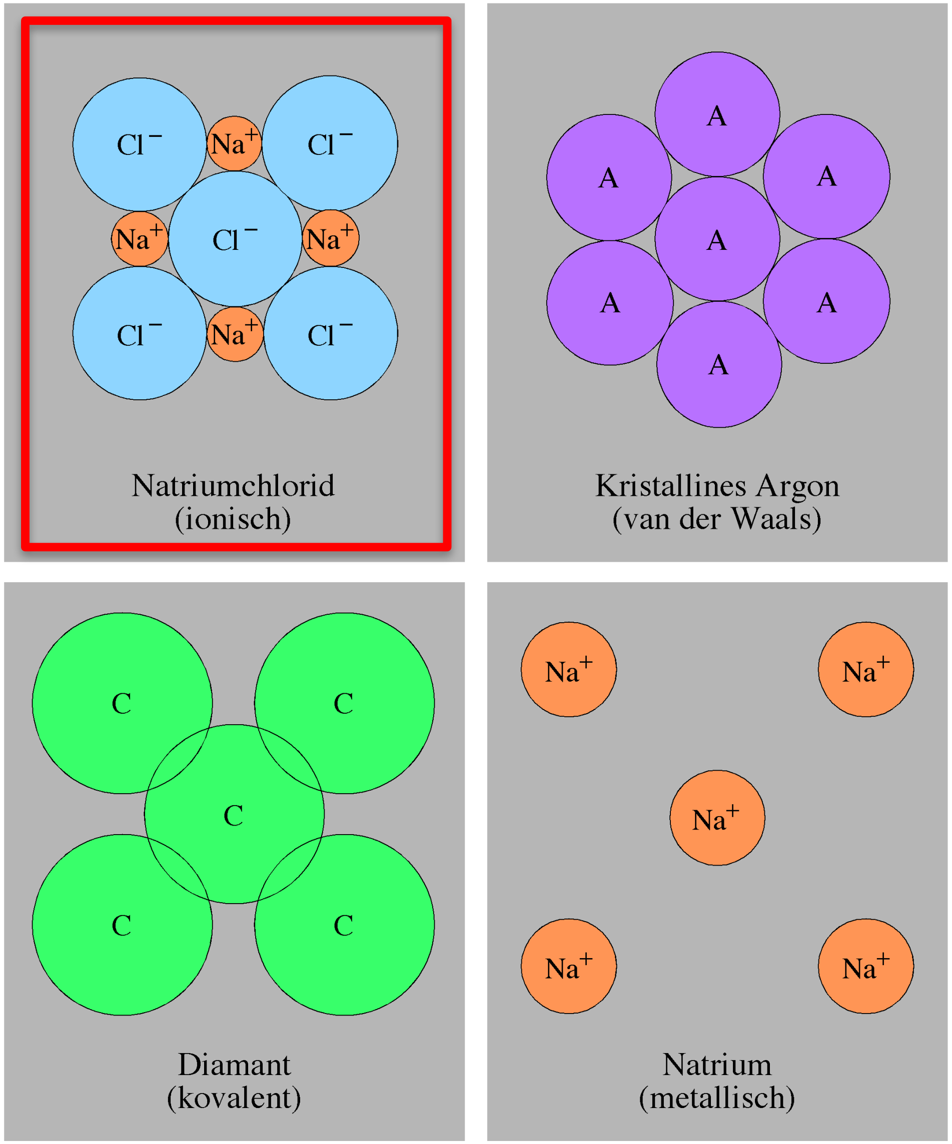
Why the melting temperature varies?



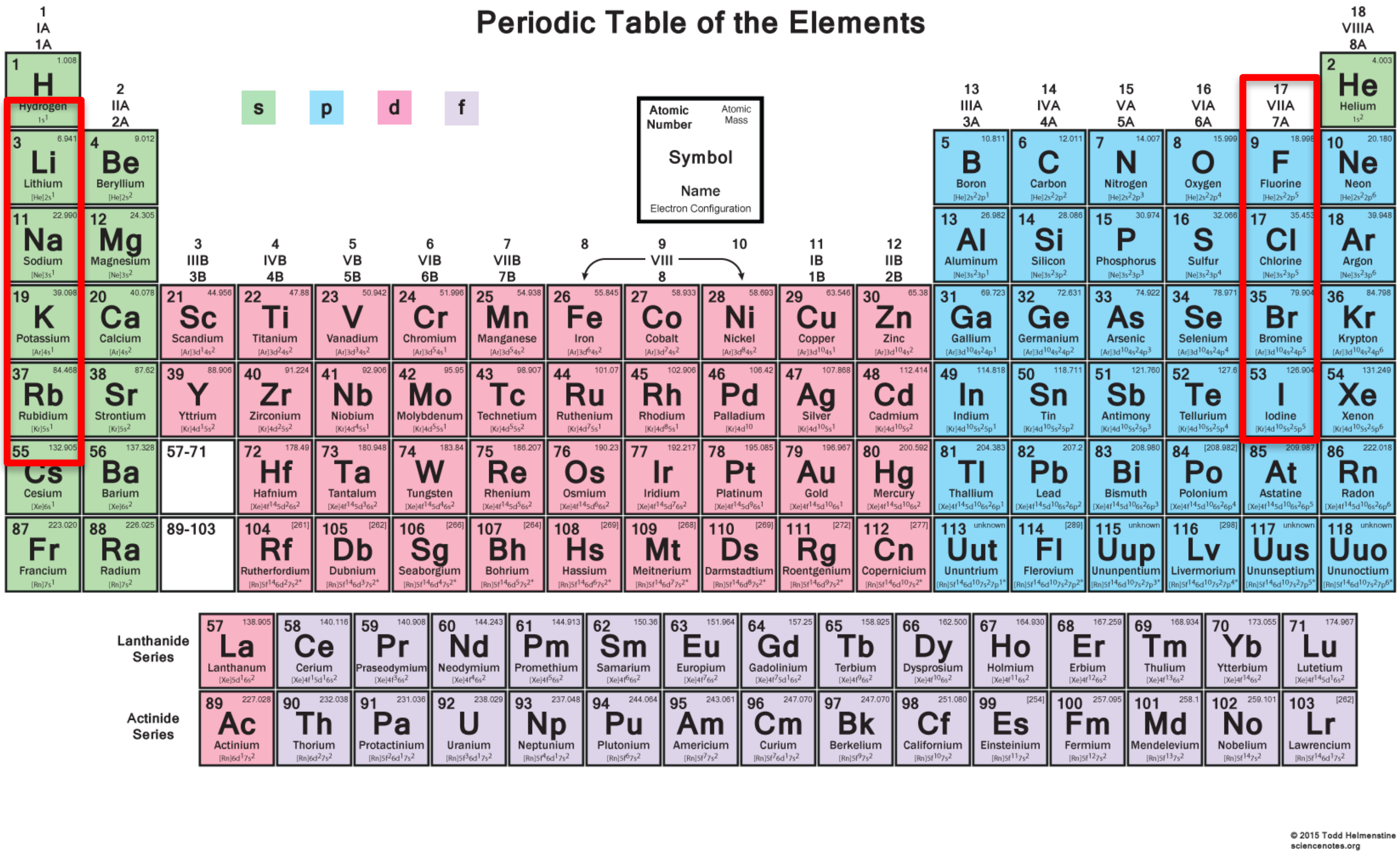
Van der Waals bonds



Today's lecture

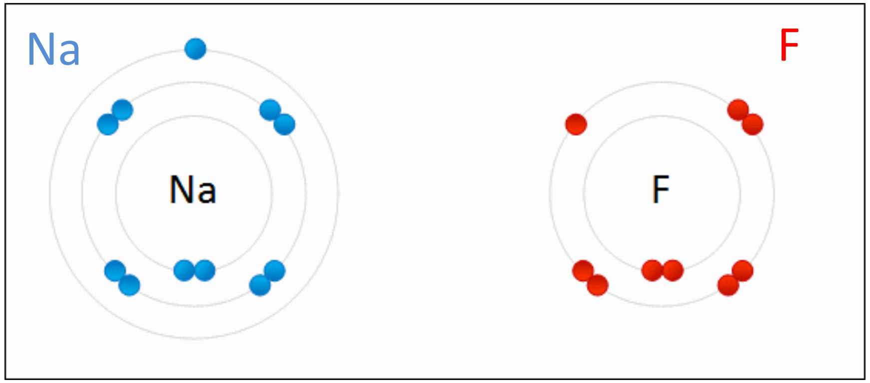


Periodic Table

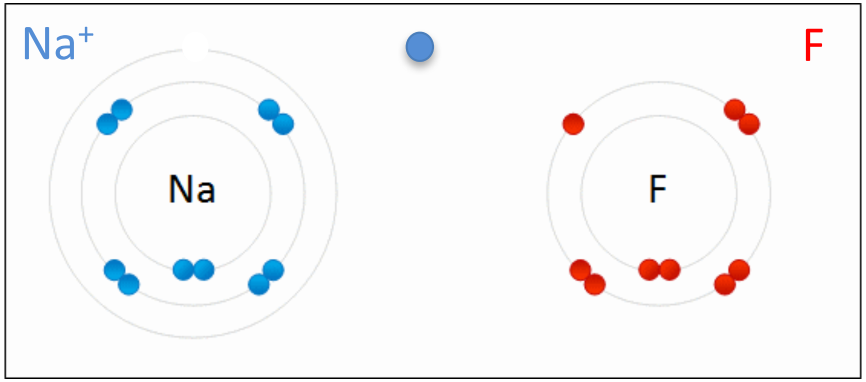


http://sciencenotes.org/periodic-table-showing-shells/

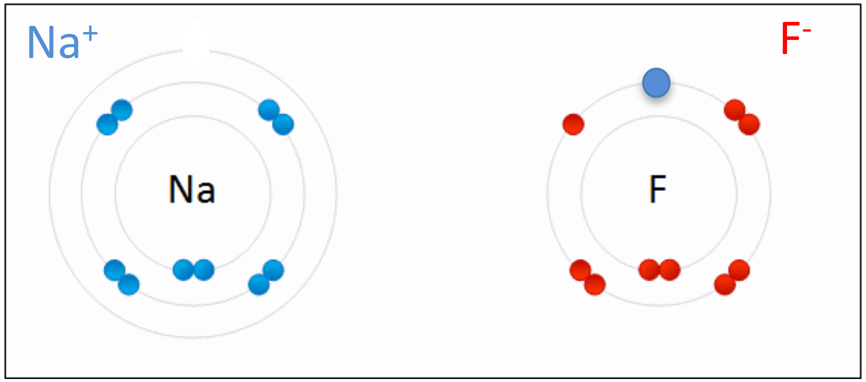
Ionic crystals



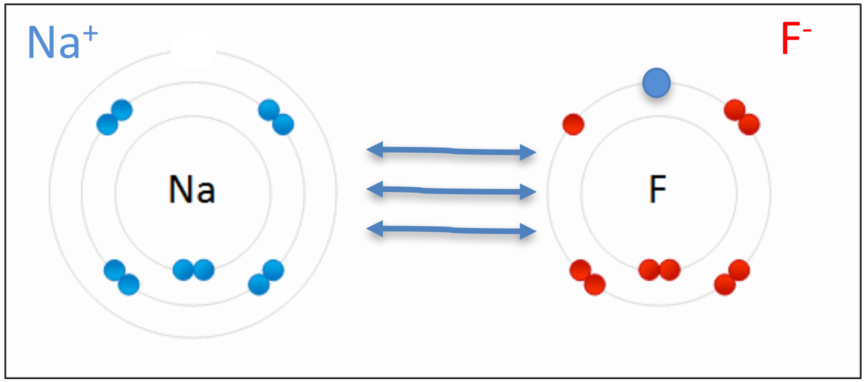
Ionization Energy = - 5.14 eV



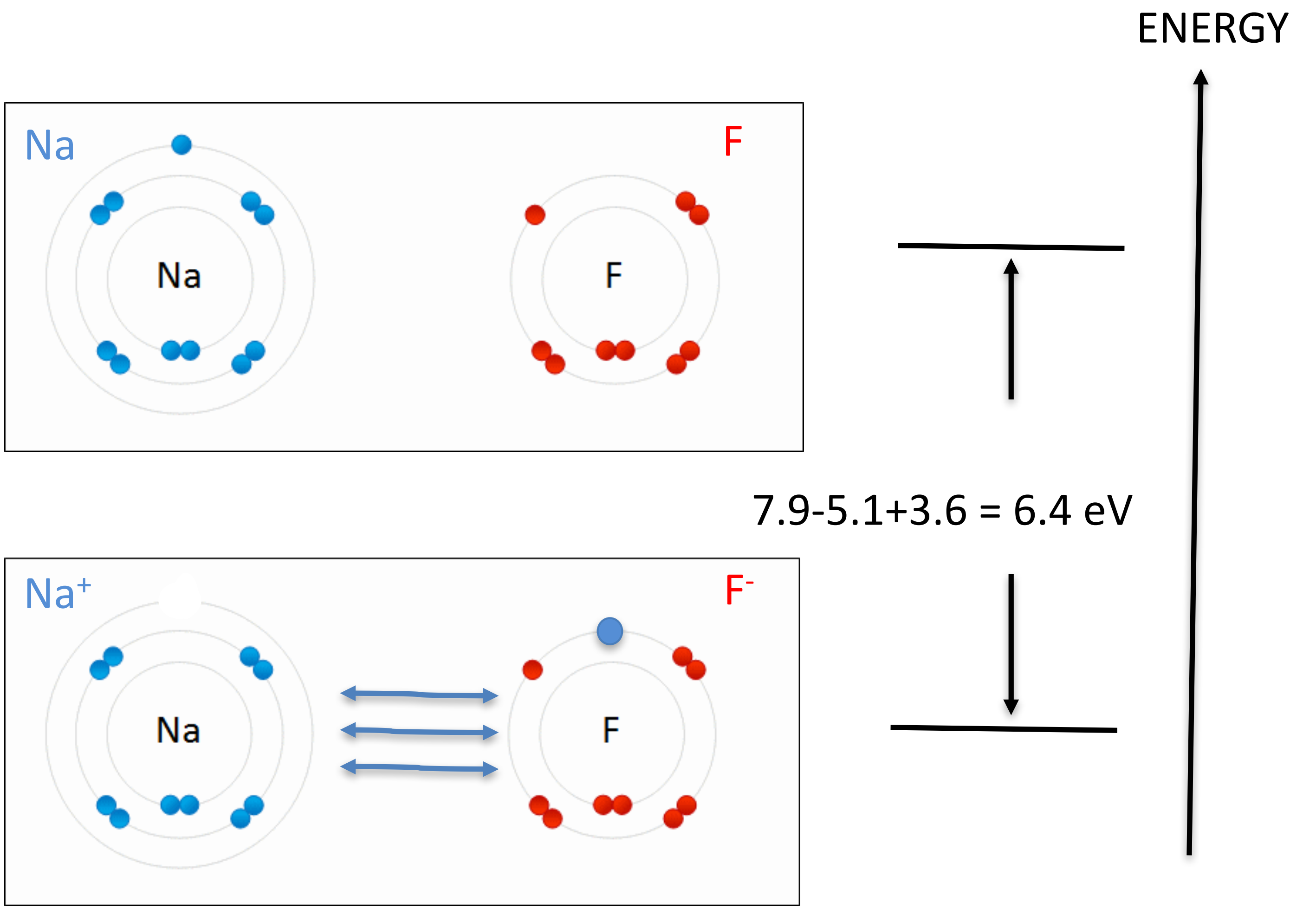
Electron affinity Energy = 3.4 eV



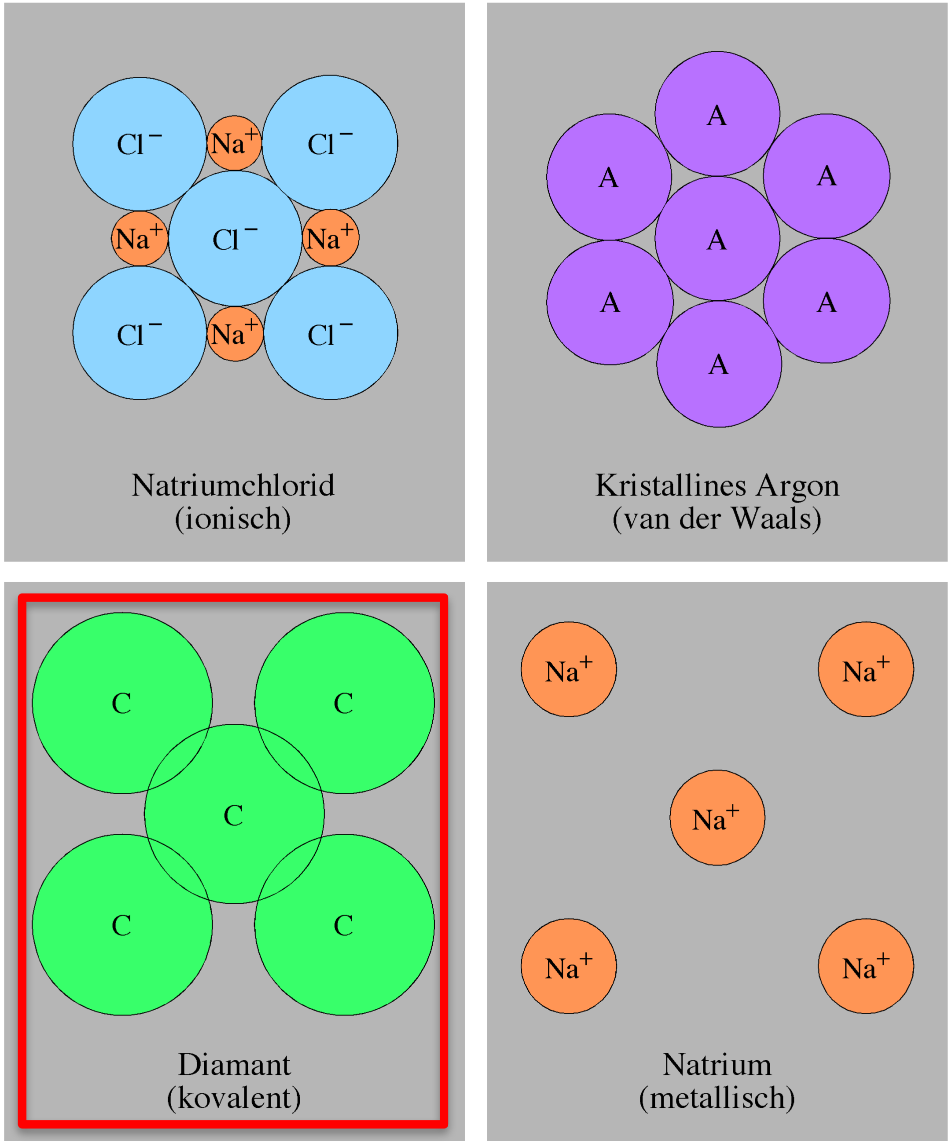
Cohesive Energy = 7.9 eV



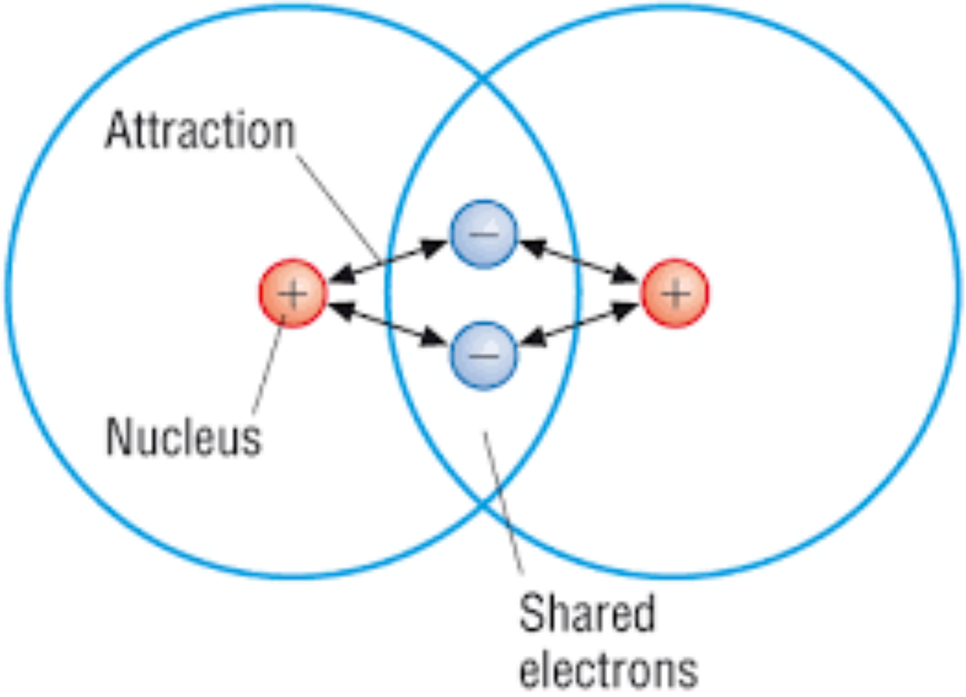
Ionic crystals



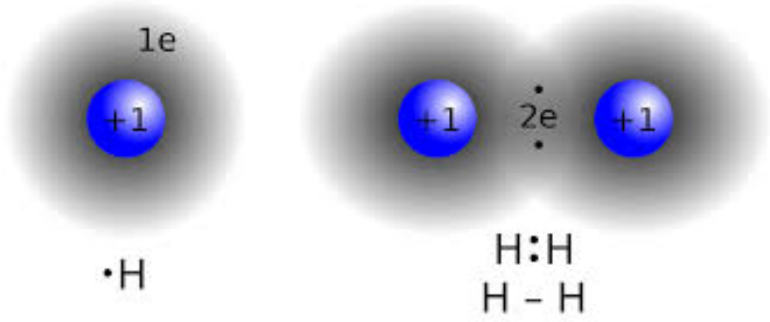
Today's lecture



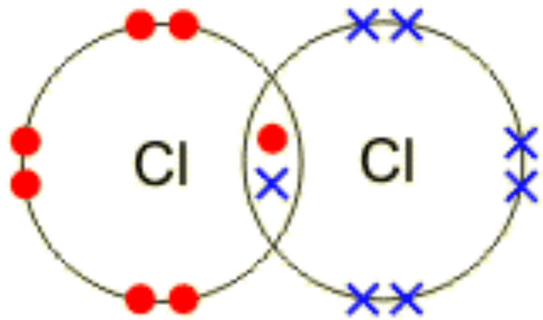
Covalent bonds



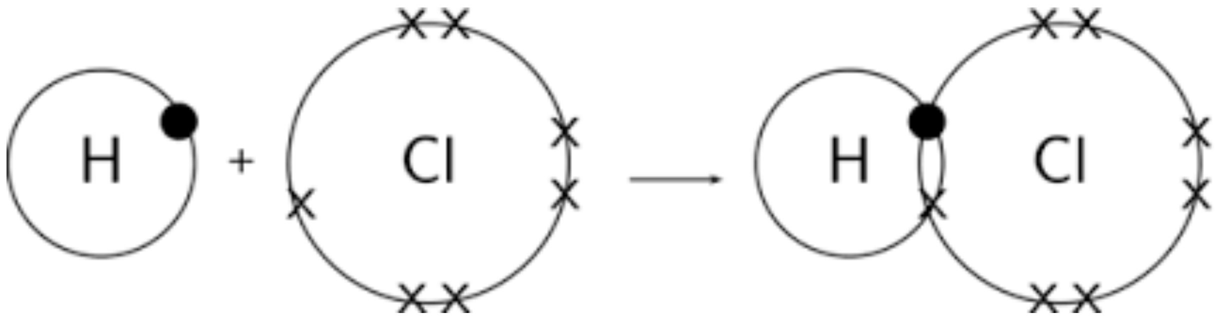
Example 1



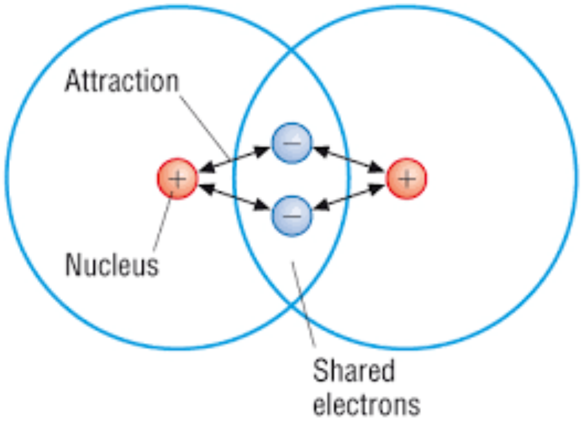
Example 2

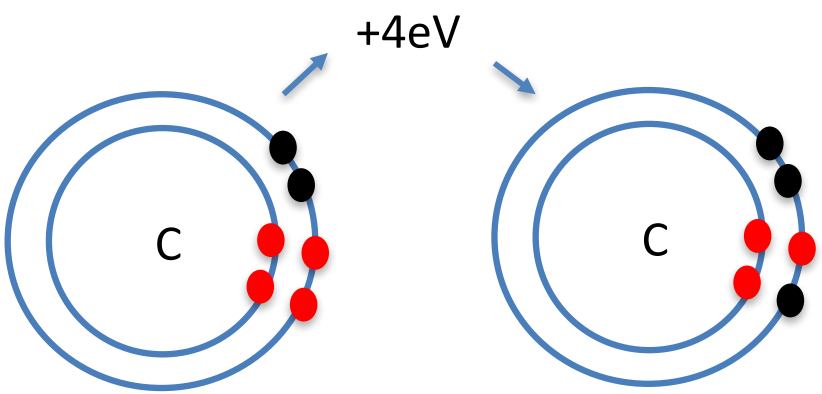


Example 3



Covalent crystals

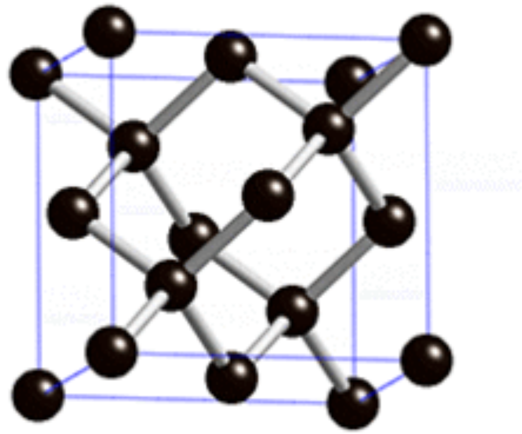




$1s^2 2s^2 2p^2$

$1s^2 2s 2p^3$

Diamond structure

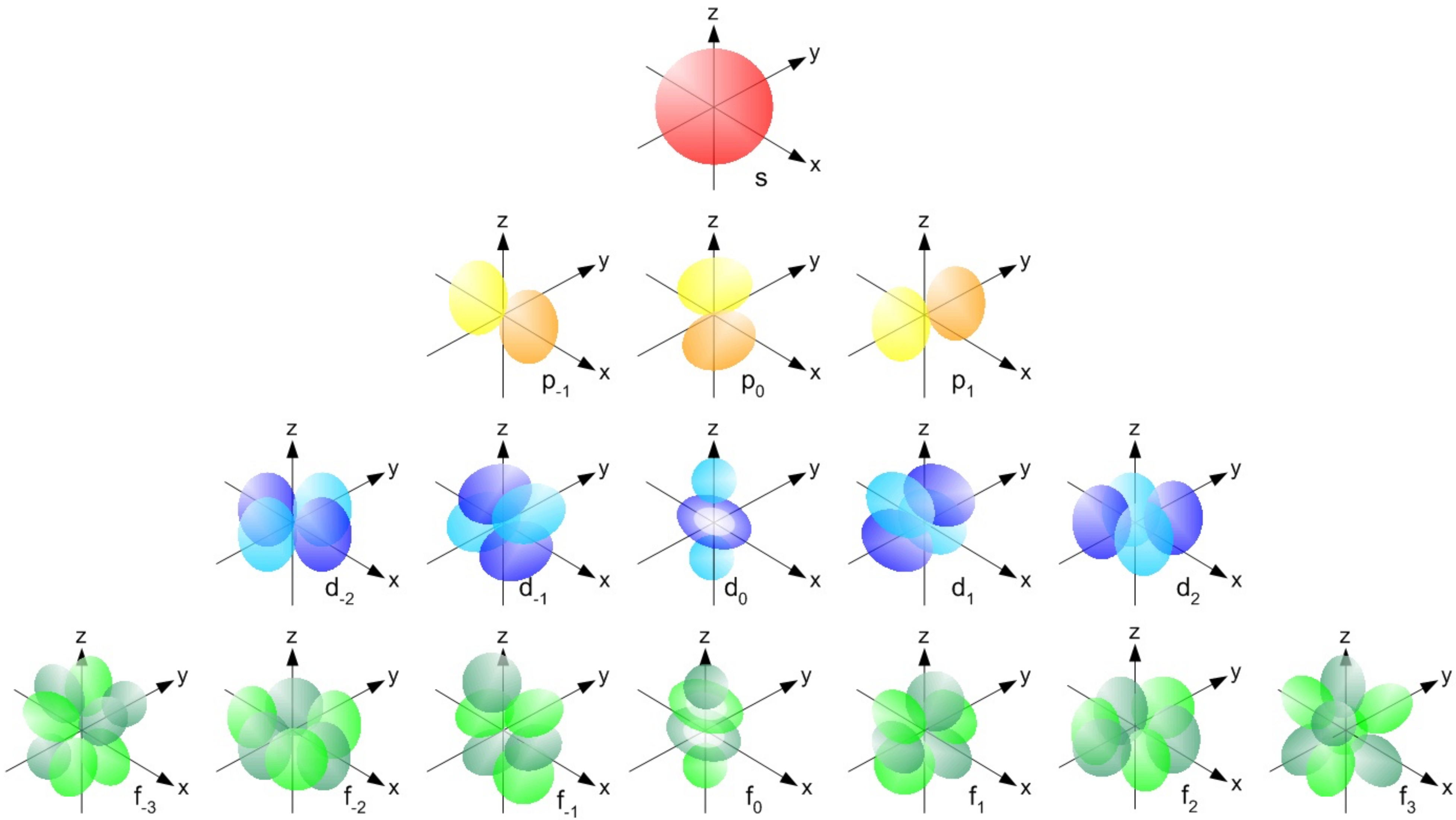


4 covalent bonds

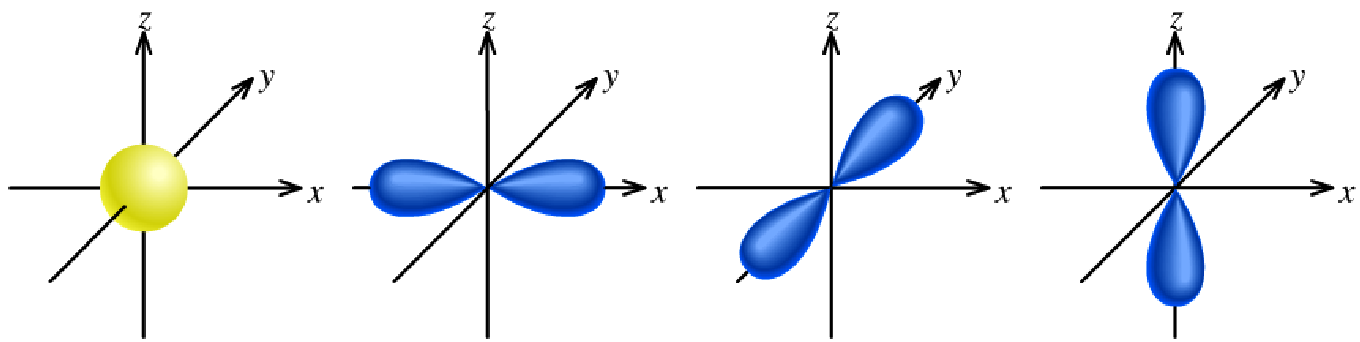
Summary

Bindungstyp	Beispiel	Bindungsenergie (eV)
Ionisch	NaCl LiF	8.23 10.92
Van-der-Waals	Ar Kr	0.080 0.116
Kovalent	Diamant Si	7.36 4.64
Metallisch	Na Fe W	1.13 4.29 8.66
Wasserstoff-Brücken	H_2O HF	0.52 0.30

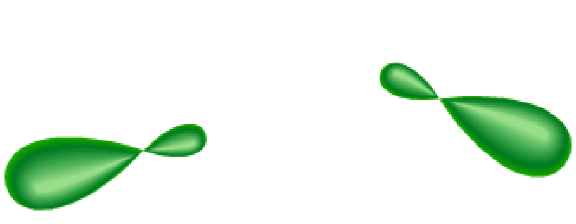
Electronic orbitals



Orbital hybridization



ψ_s ψ_{px} ψ_{py} ψ_{pz}



$\psi_{sp^3_1}$ $\psi_{sp^3_2}$ $\psi_{sp^3_3}$ $\psi_{sp^3_4}$

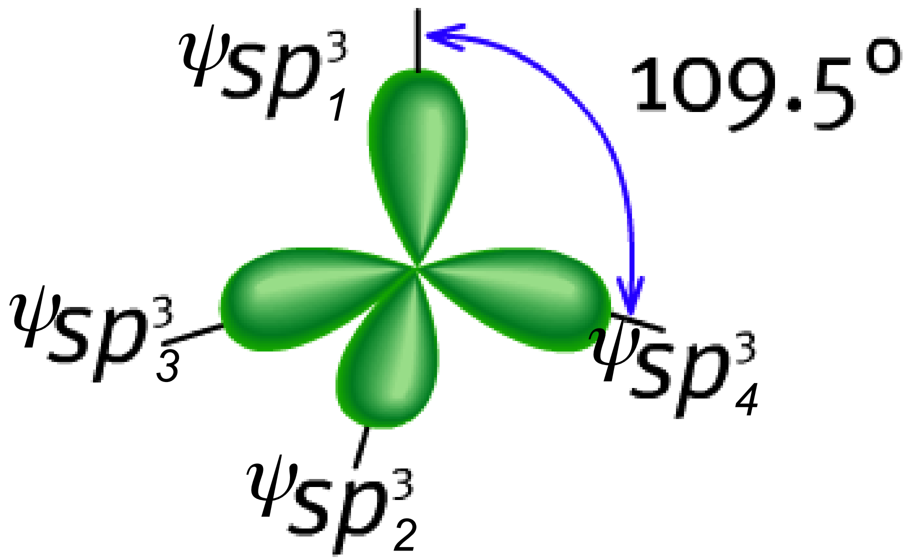
$1/2(\psi_s + \psi_{px} + \psi_{py} + \psi_{pz})$

$1/2(\psi_s + \psi_{px} - \psi_{py} - \psi_{pz})$

$1/2(\psi_s - \psi_{px} + \psi_{py} - \psi_{pz})$

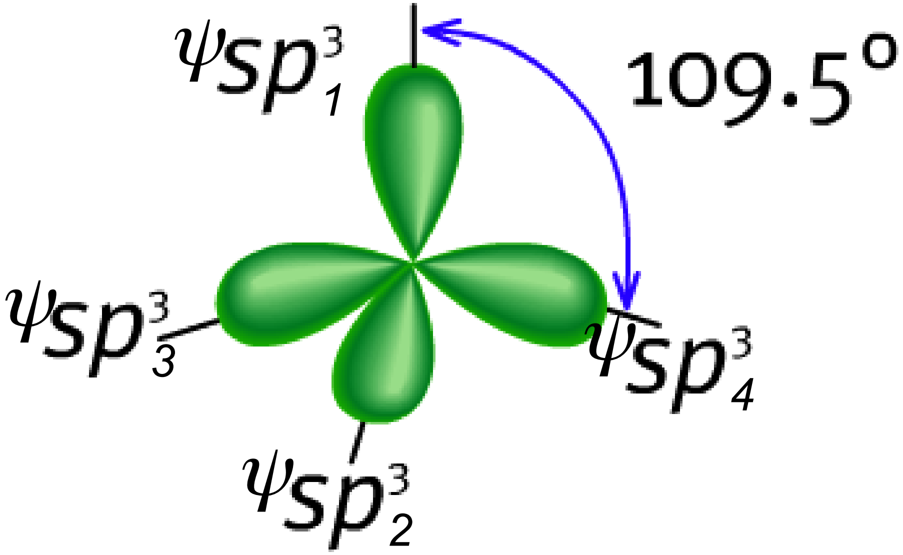
$1/2(\psi_s - \psi_{px} - \psi_{py} + \psi_{pz})$

Orbital hybridization

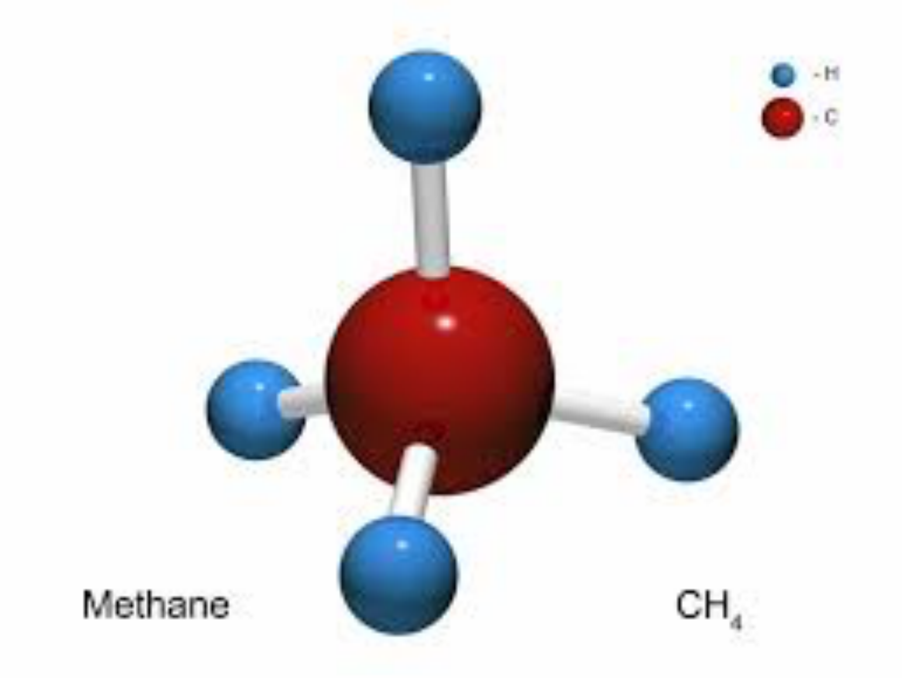


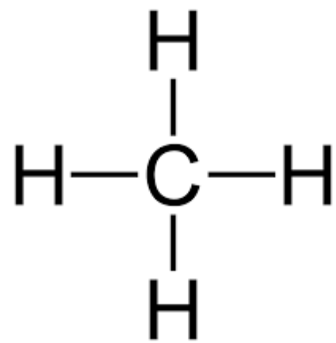
Tetraeder

Orbital molecular theory: Example CH_4 (Methane)

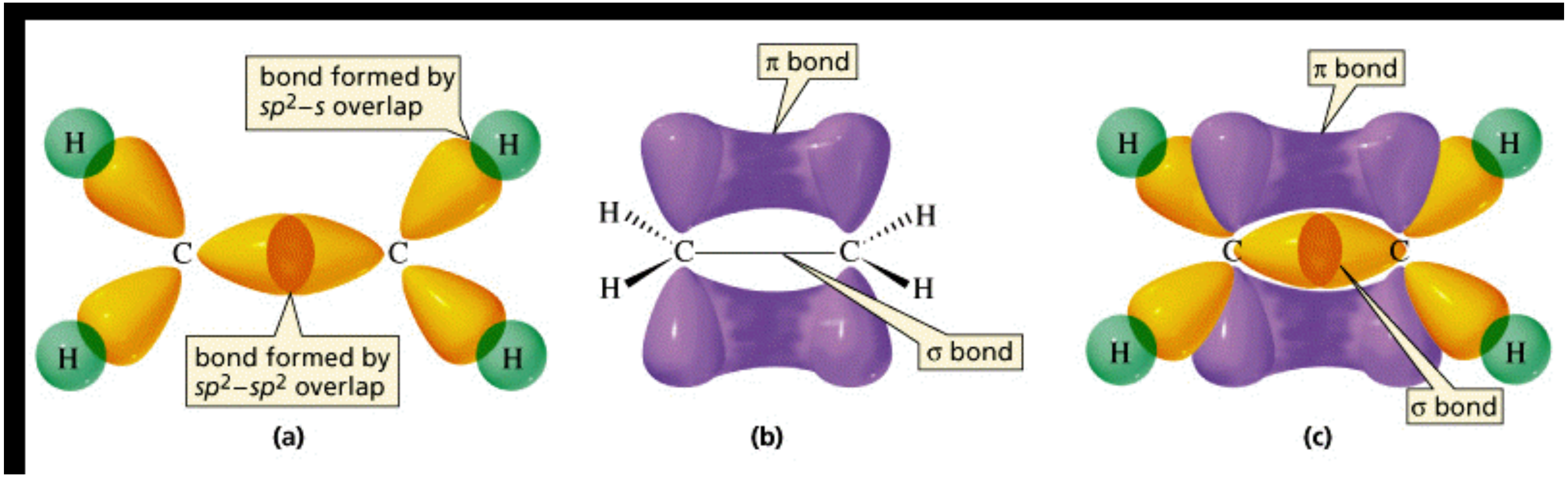


Tetraeder





Orbital molecular theory: σ and π bonding



Graphene: σ and π bonding

Graphene