

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

-
-
-

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

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

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

b) Show that at the equilibrium separation

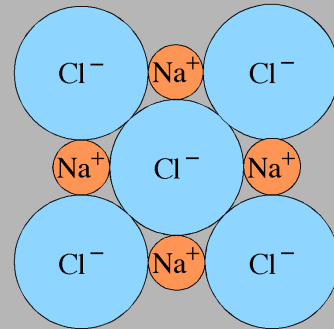
$$U(R_0) = -\frac{2Nq^2 \ln 2}{4\pi\epsilon_0 R_0} \cdot \left(1 - \frac{1}{n} \right).$$

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

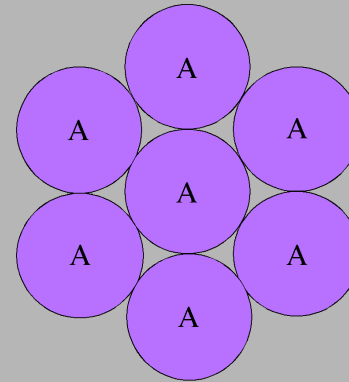
$$C = \frac{(n-1)q^2 \ln 2}{4\pi\epsilon_0 R_0}.$$

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

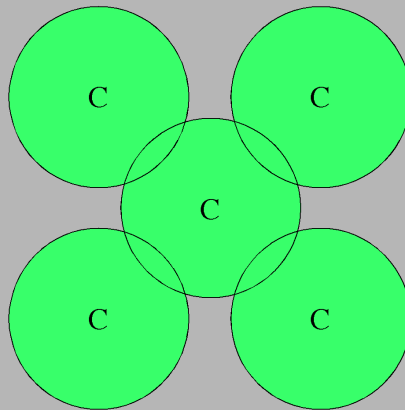
Today's lecture



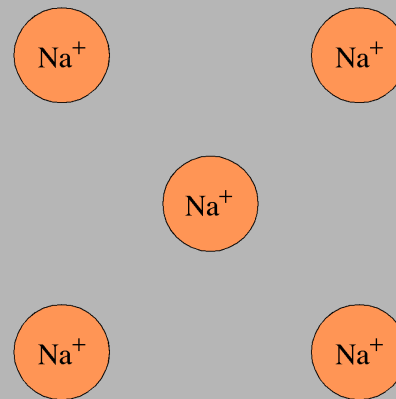
Natriumchlorid
(ionisch)



Kristallines Argon
(van der Waals)



Diamant
(kovalent)



Natrium
(metallisch)

Periodic Table

Periodic Table of the Elements

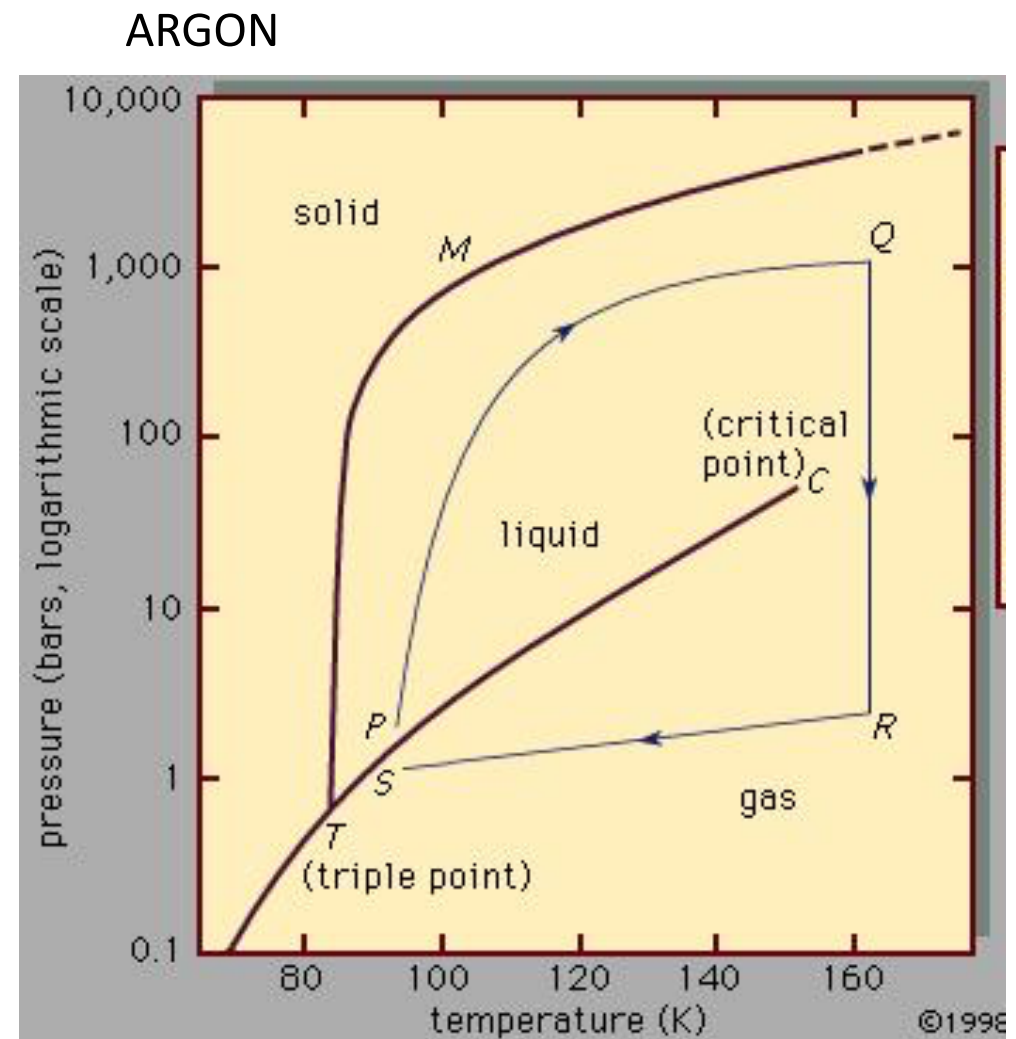
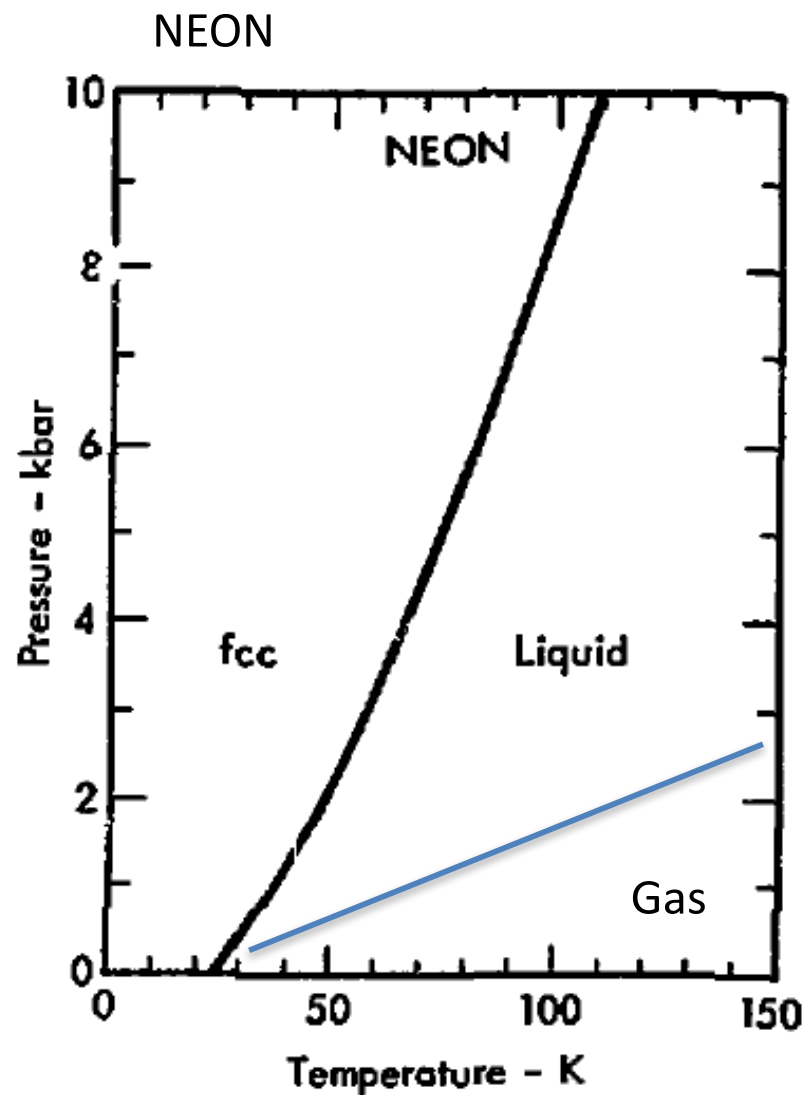
s
p
d
f

												13	14	15	16	17	18																		
												IIIA	IVA	VA	VIA	VIIA	VIIIA																		
												3A	4A	5A	6A	7A	8A																		
1	IA											5	6	7	8	9	10																		
1	IA											B	C	N	O	F	Ne																		
3	Li	4	Be											13	14	15	16	17	18																
11	Na	12	Mg	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	57-71	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn	
87	Fr	88	Ra	89-103	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Cn	113	Uut	114	Fl	115	Uup	116	Lv	117	Uus	118	Uuo	
Lanthanide Series		57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu				
Actinide Series		89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr				

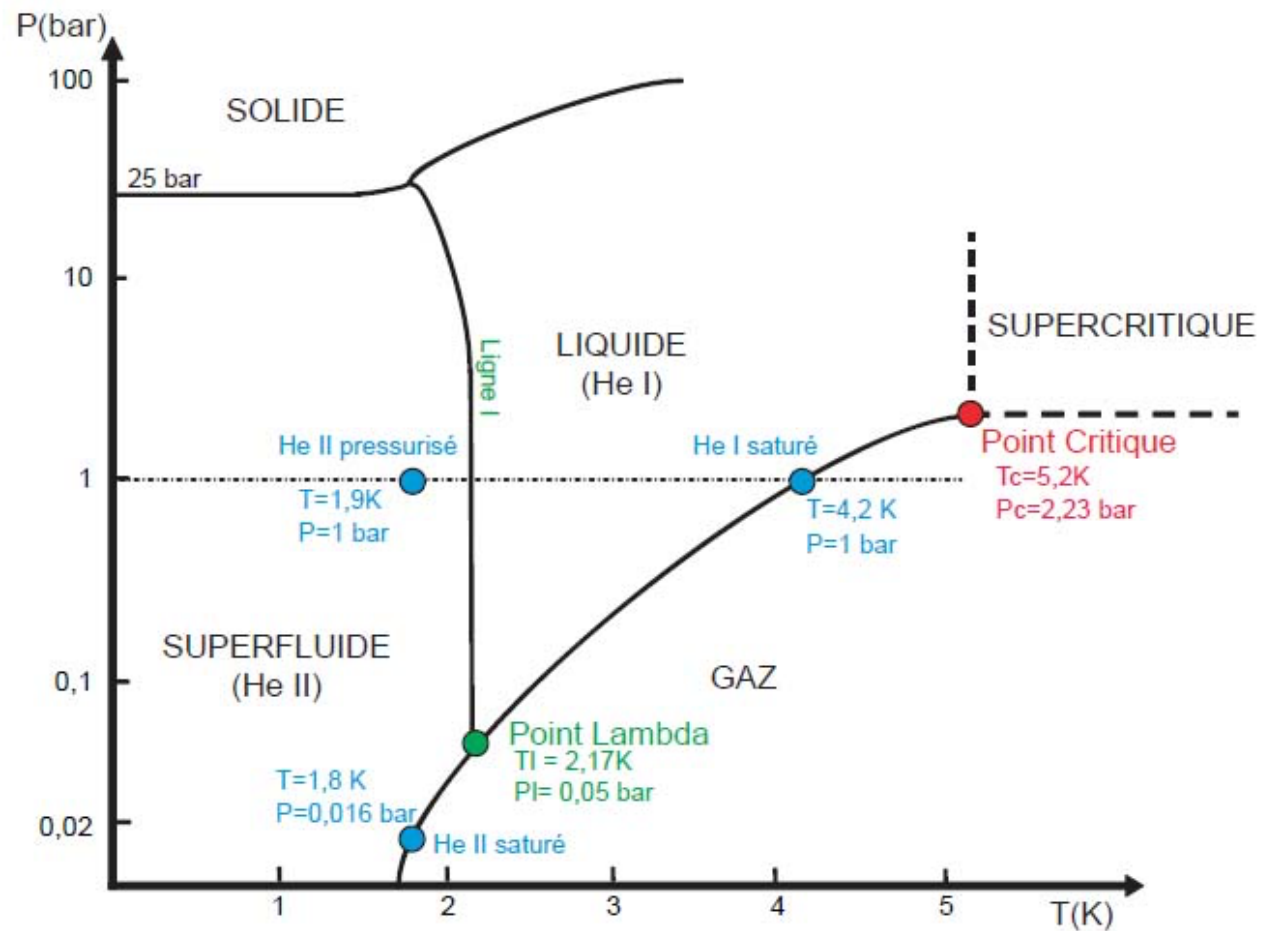
© 2015 Todd Helmenstine sciencenotes.org

<http://sciencenotes.org/periodic-table-showing-shells/>
 See also table 3 in Kittel.

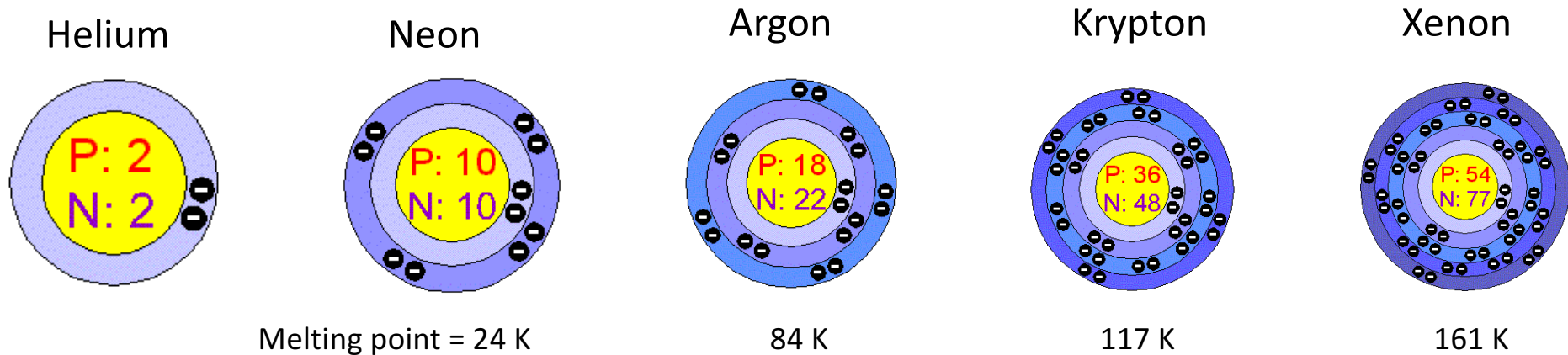
Phase diagrams:



Phase diagram of Helium



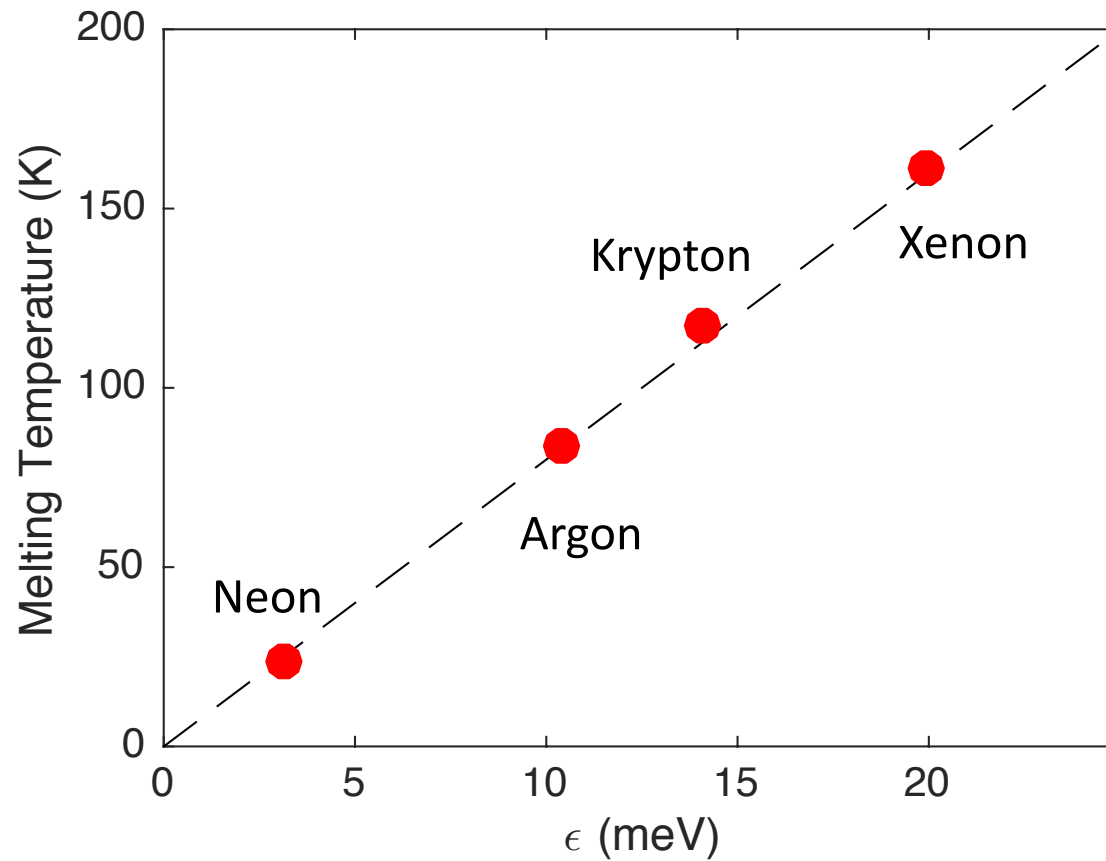
Inert gasses



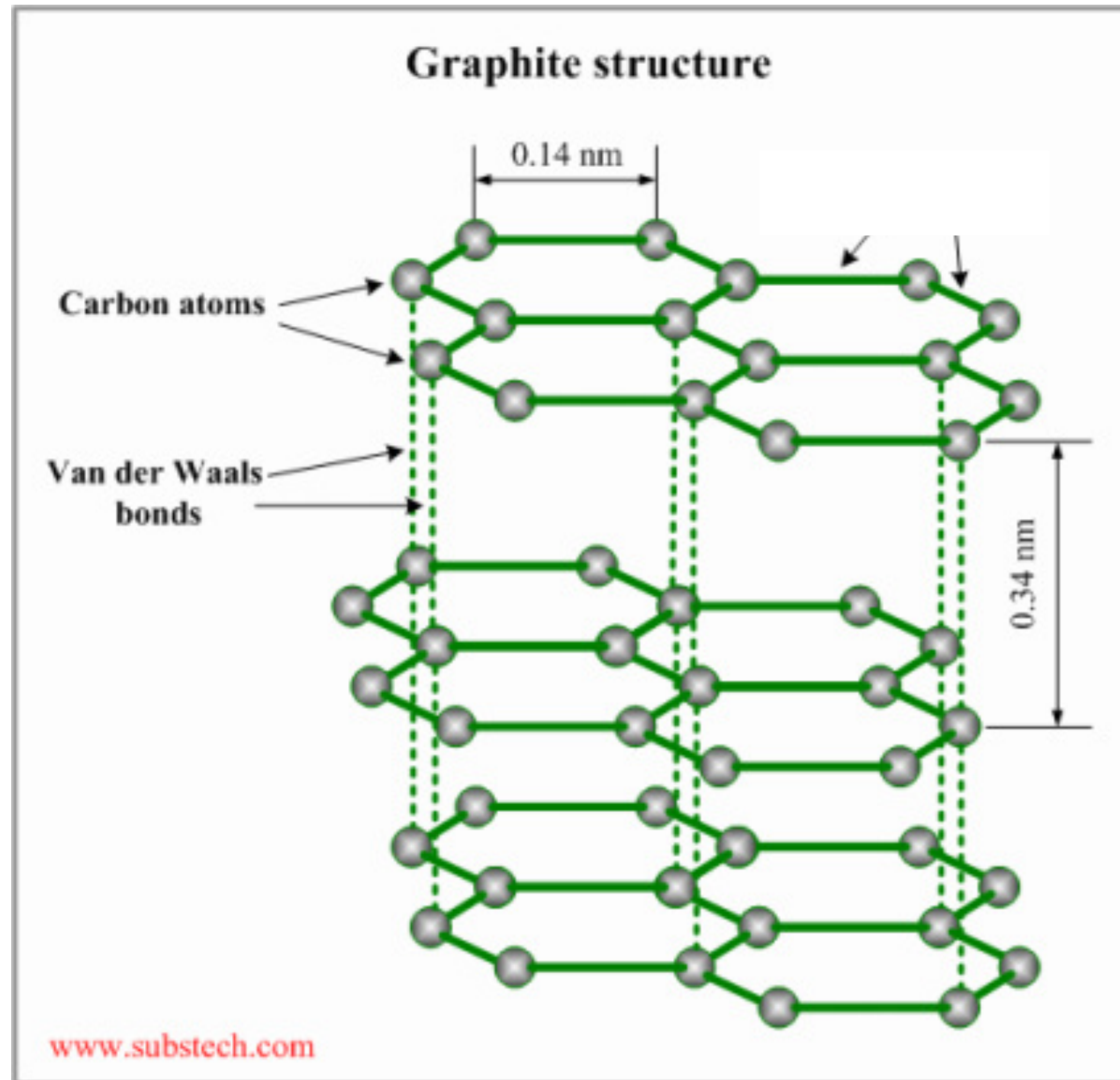
Questions:

- (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?

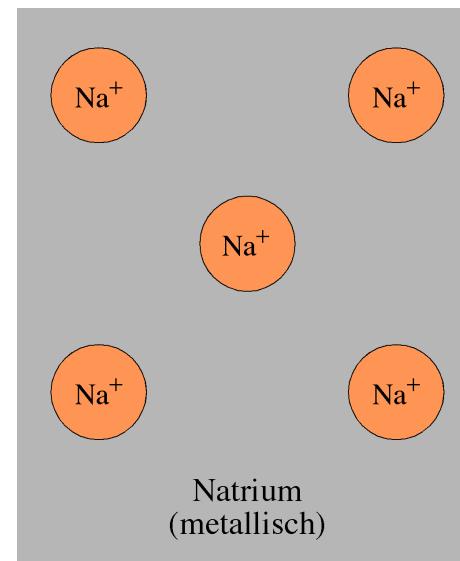
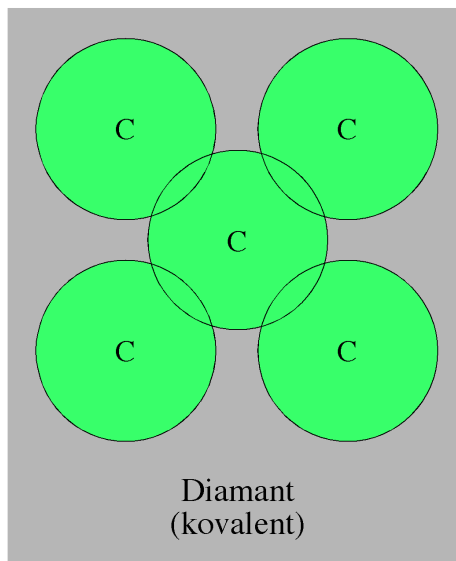
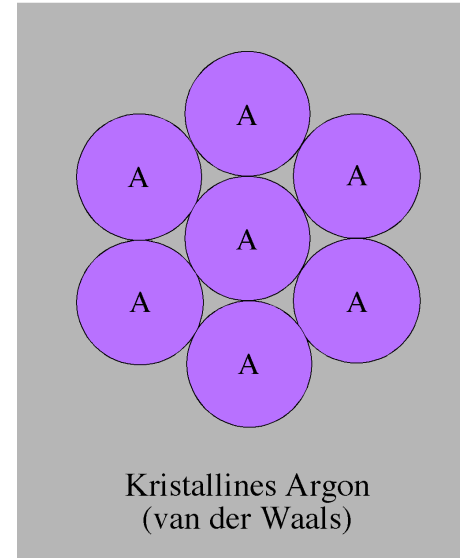
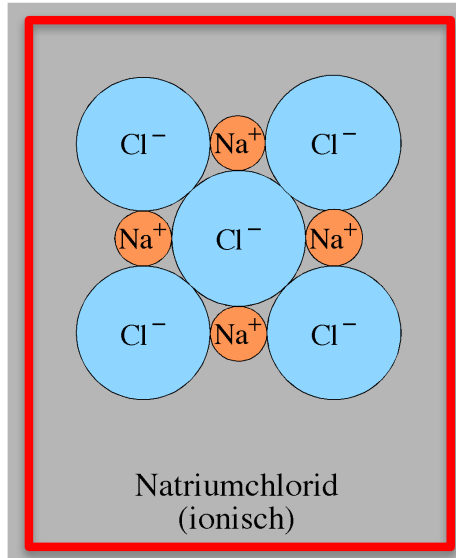
Why the melting temperature varies?



Van der Waals bonds



Today's lecture



Periodic Table

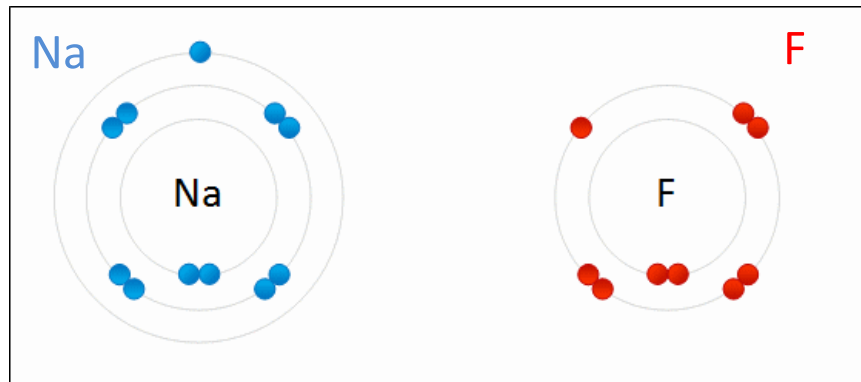
Periodic Table of the Elements

s p d f

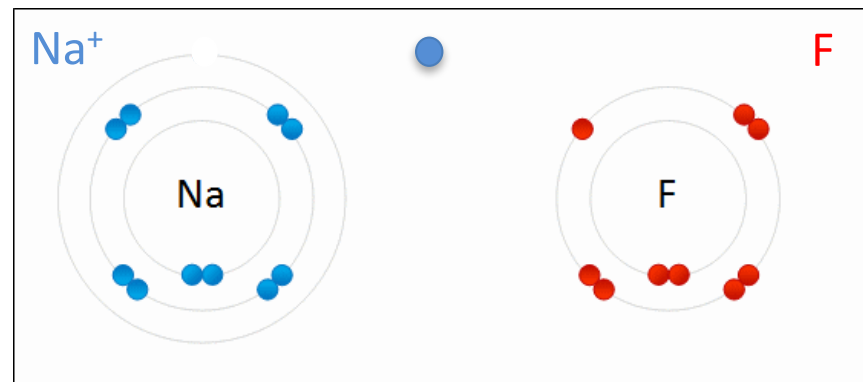
Atomic Number Atomic Mass
 Symbol
 Name
 Electron Configuration

1 IA 1A	1 H Hydrogen 1s ¹	2 IIA 2A															18 VIIIA 8A		
	3 Li Lithium [He]2s ¹	4 Be Beryllium [He]2s ²												5 B Boron [He]2s ² 2p ¹	6 C Carbon [He]2s ² 2p ²	7 N Nitrogen [He]2s ² 2p ³	8 O Oxygen [He]2s ² 2p ⁴	9 F Fluorine [He]2s ² 2p ⁵	10 Ne Neon [He]2s ² 2p ⁶
	11 Na Sodium [Ne]3s ¹	12 Mg Magnesium [Ne]3s ²	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B		13 Al Aluminum [Ne]3s ² 3p ¹	14 Si Silicon [Ne]3s ² 3p ²	15 P Phosphorus [Ne]3s ² 3p ³	16 S Sulfur [Ne]3s ² 3p ⁴	17 Cl Chlorine [Ne]3s ² 3p ⁵	18 Ar Argon [Ne]3s ² 3p ⁶
	19 K Potassium [Ar]4s ¹	20 Ca Calcium [Ar]4s ²	21 Sc Scandium [Ar]3d ¹ 4s ²	22 Ti Titanium [Ar]3d ² 4s ²	23 V Vanadium [Ar]3d ³ 4s ²	24 Cr Chromium [Ar]3d ⁵ 4s ¹	25 Mn Manganese [Ar]3d ⁵ 4s ²	26 Fe Iron [Ar]3d ⁶ 4s ²	27 Co Cobalt [Ar]3d ⁷ 4s ²	28 Ni Nickel [Ar]3d ⁸ 4s ²	29 Cu Copper [Ar]3d ¹⁰ 4s ¹	30 Zn Zinc [Ar]3d ¹⁰ 4s ²	31 Ga Gallium [Ar]3d ¹⁰ 4s ² 4p ¹	32 Ge Germanium [Ar]3d ¹⁰ 4s ² 4p ²	33 As Arsenic [Ar]3d ¹⁰ 4s ² 4p ³	34 Se Selenium [Ar]3d ¹⁰ 4s ² 4p ⁴	35 Br Bromine [Ar]3d ¹⁰ 4s ² 4p ⁵	36 Kr Krypton [Ar]3d ¹⁰ 4s ² 4p ⁶	
	37 Rb Rubidium [Kr]5s ¹	38 Sr Strontium [Kr]5s ²	39 Y Yttrium [Kr]4d ¹ 5s ²	40 Zr Zirconium [Kr]4d ² 5s ²	41 Nb Niobium [Kr]4d ⁴ 5s ¹	42 Mo Molybdenum [Kr]4d ⁵ 5s ¹	43 Tc Technetium [Kr]4d ⁵ 5s ²	44 Ru Ruthenium [Kr]4d ⁷ 5s ¹	45 Rh Rhodium [Kr]4d ⁸ 5s ¹	46 Pd Palladium [Kr]4d ¹⁰	47 Ag Silver [Kr]4d ¹⁰ 5s ¹	48 Cd Cadmium [Kr]4d ¹⁰ 5s ²	49 In Indium [Kr]4d ¹⁰ 5s ² 5p ¹	50 Sn Tin [Kr]4d ¹⁰ 5s ² 5p ²	51 Sb Antimony [Kr]4d ¹⁰ 5s ² 5p ³	52 Te Tellurium [Kr]4d ¹⁰ 5s ² 5p ⁴	53 I Iodine [Kr]4d ¹⁰ 5s ² 5p ⁵	54 Xe Xenon [Kr]4d ¹⁰ 5s ² 5p ⁶	
	55 Cs Cesium [Xe]6s ¹	56 Ba Barium [Xe]6s ²	57-71	72 Hf Hafnium [Xe]4f ¹⁴ 5d ² 6s ²	73 Ta Tantalum [Xe]4f ¹⁴ 5d ³ 6s ²	74 W Tungsten [Xe]4f ¹⁴ 5d ⁴ 6s ²	75 Re Rhenium [Xe]4f ¹⁴ 5d ⁵ 6s ²	76 Os Osmium [Xe]4f ¹⁴ 5d ⁶ 6s ²	77 Ir Iridium [Xe]4f ¹⁴ 5d ⁷ 6s ²	78 Pt Platinum [Xe]4f ¹⁴ 5d ⁹ 6s ¹	79 Au Gold [Xe]4f ¹⁴ 5d ¹⁰ 6s ¹	80 Hg Mercury [Xe]4f ¹⁴ 5d ¹⁰ 6s ²	81 Tl Thallium [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	82 Pb Lead [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	83 Bi Bismuth [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	84 Po Polonium [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	85 At Astatine [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	86 Rn Radon [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶	
	87 Fr Francium [Rn]7s ¹	88 Ra Radium [Rn]7s ²	89-103	104 Rf Rutherfordium [Rn]5f ¹⁴ 6d ⁴ 7s ²	105 Db Dubnium [Rn]5f ¹⁴ 6d ³ 7s ²	106 Sg Seaborgium [Rn]5f ¹⁴ 6d ⁴ 7s ²	107 Bh Bohrium [Rn]5f ¹⁴ 6d ⁵ 7s ²	108 Hs Hassium [Rn]5f ¹⁴ 6d ⁶ 7s ²	109 Mt Meitnerium [Rn]5f ¹⁴ 6d ⁷ 7s ²	110 Ds Darmstadtium [Rn]5f ¹⁴ 6d ⁸ 7s ²	111 Rg Roentgenium [Rn]5f ¹⁴ 6d ⁹ 7s ²	112 Cn Copernicium [Rn]5f ¹⁴ 6d ¹⁰ 7s ²	113 Uut Ununtrium [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	114 Fl Flerovium [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	115 Uup Ununpentium [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	116 Lv Livermorium [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	117 Uus Ununseptium [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	118 Uuo Ununoctium [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶	
Lanthanide Series	57 La Lanthanum [Xe]5d ¹ 6s ²	58 Ce Cerium [Xe]4f ¹ 5d ¹ 6s ²	59 Pr Praseodymium [Xe]4f ³ 6s ²	60 Nd Neodymium [Xe]4f ⁴ 6s ²	61 Pm Promethium [Xe]4f ⁵ 6s ²	62 Sm Samarium [Xe]4f ⁶ 6s ²	63 Eu Europium [Xe]4f ⁷ 6s ²	64 Gd Gadolinium [Xe]4f ⁷ 5d ¹ 6s ²	65 Tb Terbium [Xe]4f ⁹ 6s ²	66 Dy Dysprosium [Xe]4f ¹⁰ 6s ²	67 Ho Holmium [Xe]4f ¹¹ 6s ²	68 Er Erbium [Xe]4f ¹² 6s ²	69 Tm Thulium [Xe]4f ¹³ 6s ²	70 Yb Ytterbium [Xe]4f ¹⁴ 6s ²	71 Lu Lutetium [Xe]4f ¹⁴ 5d ¹ 6s ²				
Actinide Series	89 Ac Actinium [Rn]6d ¹ 7s ²	90 Th Thorium [Rn]6d ² 7s ²	91 Pa Protactinium [Rn]5f ² 6d ¹ 7s ²	92 U Uranium [Rn]5f ³ 6d ¹ 7s ²	93 Np Neptunium [Rn]5f ⁴ 6d ¹ 7s ²	94 Pu Plutonium [Rn]5f ⁶ 7s ²	95 Am Americium [Rn]5f ⁷ 7s ²	96 Cm Curium [Rn]5f ⁷ 6d ¹ 7s ²	97 Bk Berkelium [Rn]5f ⁹ 7s ²	98 Cf Californium [Rn]5f ¹⁰ 7s ²	99 Es Einsteinium [Rn]5f ¹¹ 7s ²	100 Fm Fermium [Rn]5f ¹² 7s ²	101 Md Mendelevium [Rn]5f ¹³ 7s ²	102 No Nobelium [Rn]5f ¹⁴ 7s ²	103 Lr Lawrencium [Rn]5f ¹⁴ 6d ¹ 7s ²				

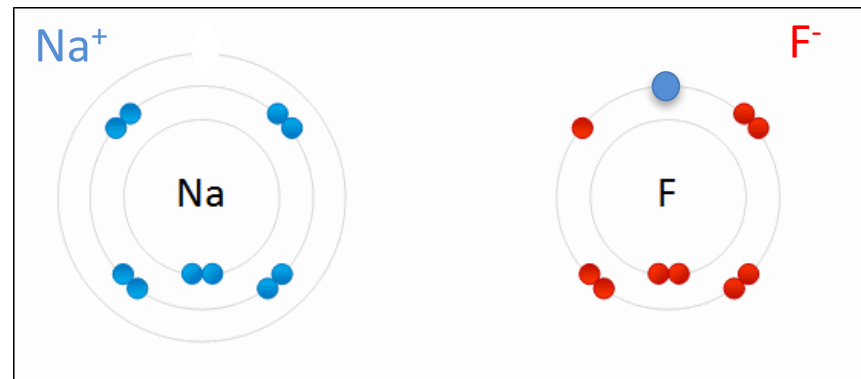
Ionic crystals



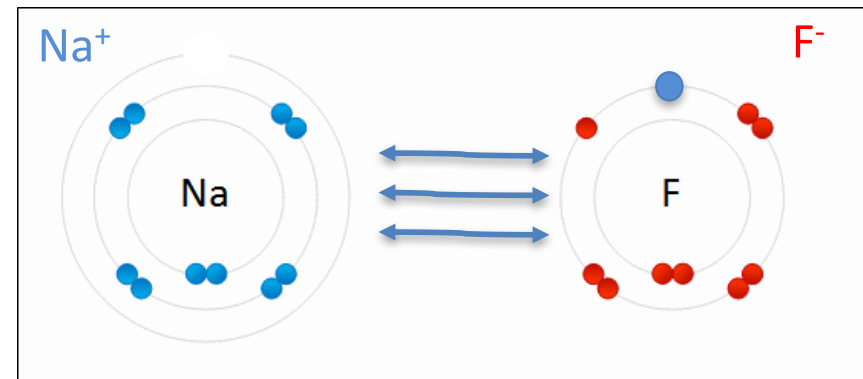
Ionization Energy = - 5.14 eV



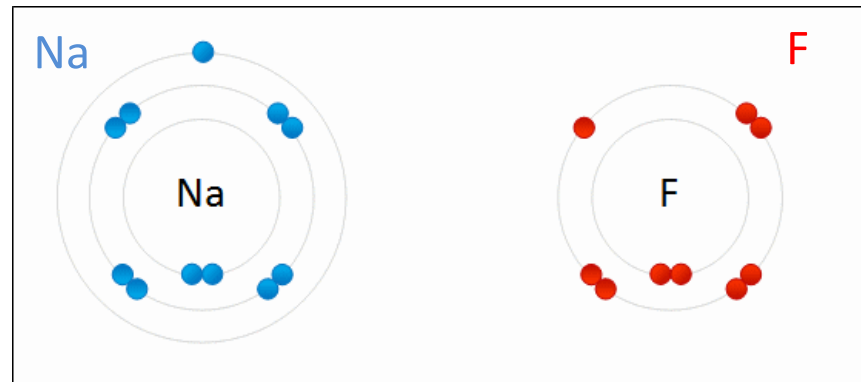
Electron affinity Energy = 3.4 eV



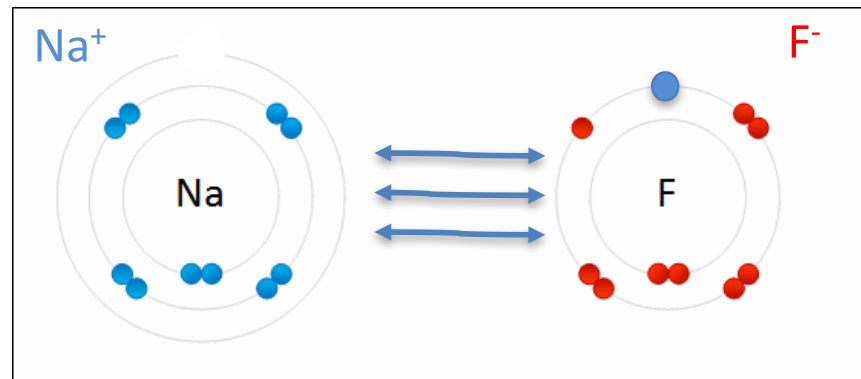
Cohesive Energy = 7.9 eV



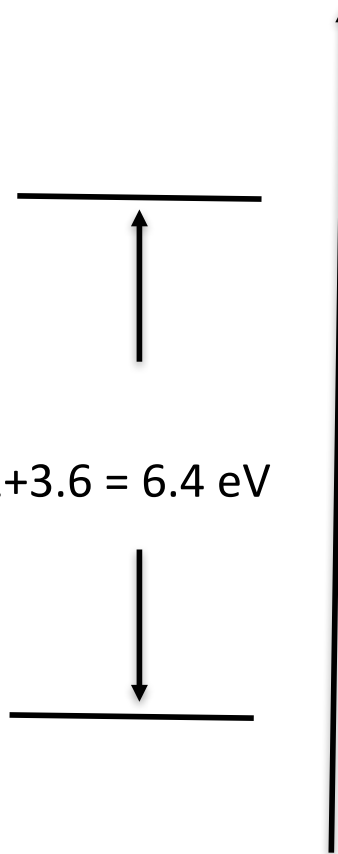
Ionic crystals



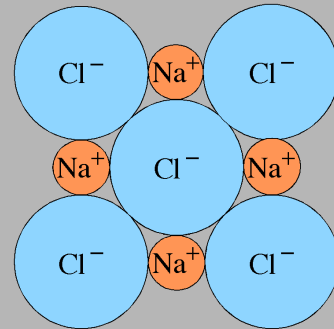
$$7.9 - 5.1 + 3.6 = 6.4 \text{ eV}$$



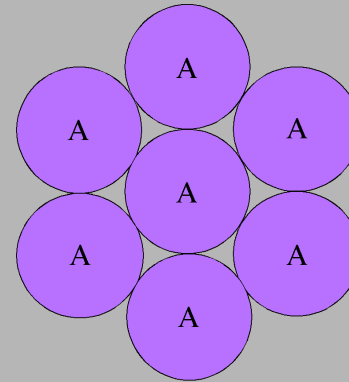
ENERGY



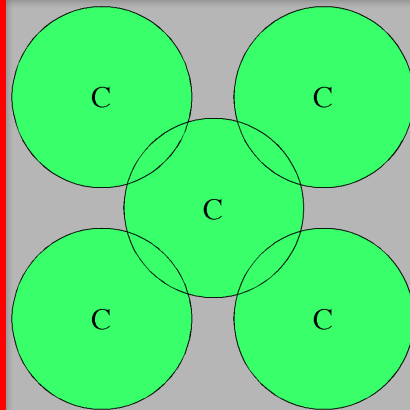
Today's lecture



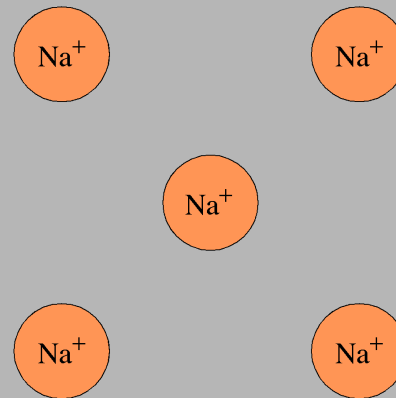
Natriumchlorid
(ionisch)



Kristallines Argon
(van der Waals)

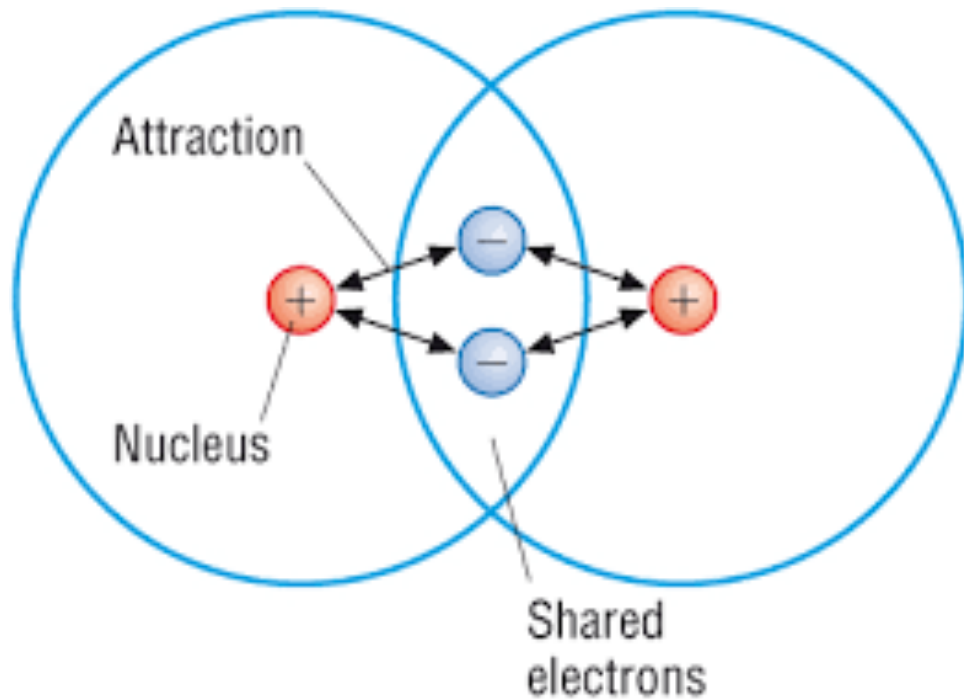


Diamant
(kovalent)

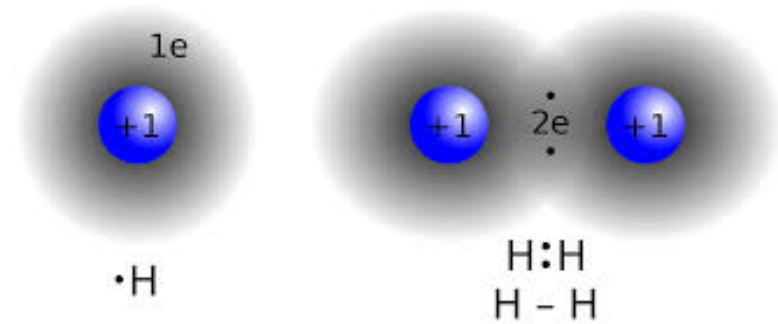


Natrium
(metallisch)

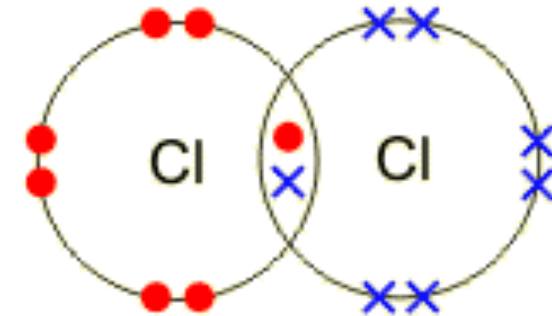
Covalent bonds



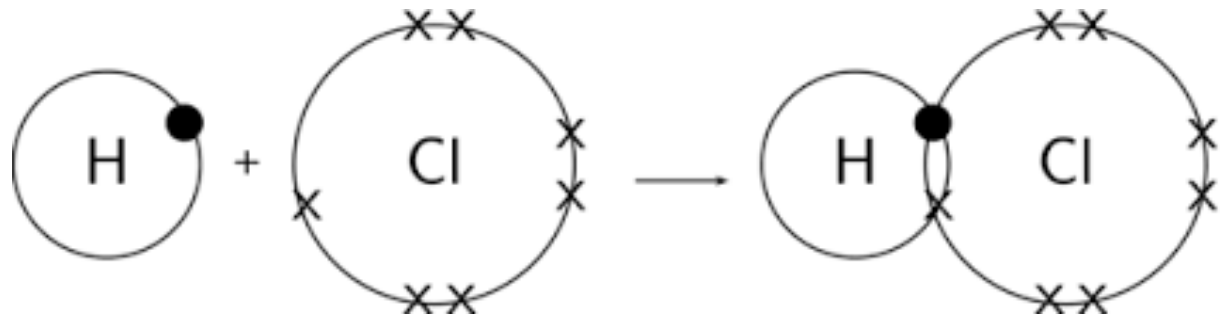
Example 1



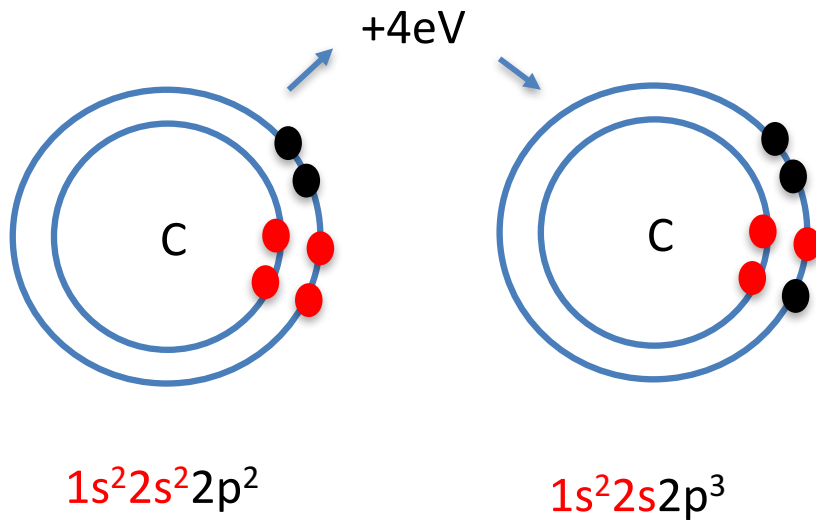
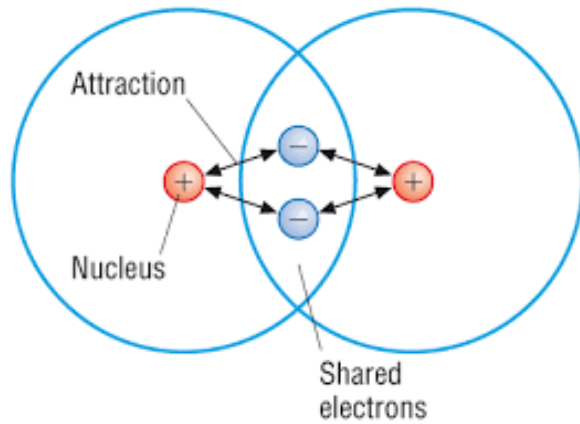
Example 2



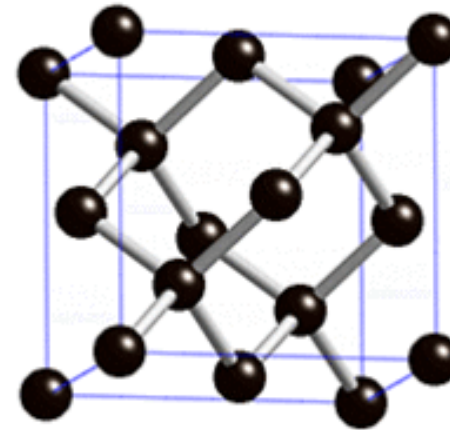
Example 3



Covalent crystals



Diamond structure

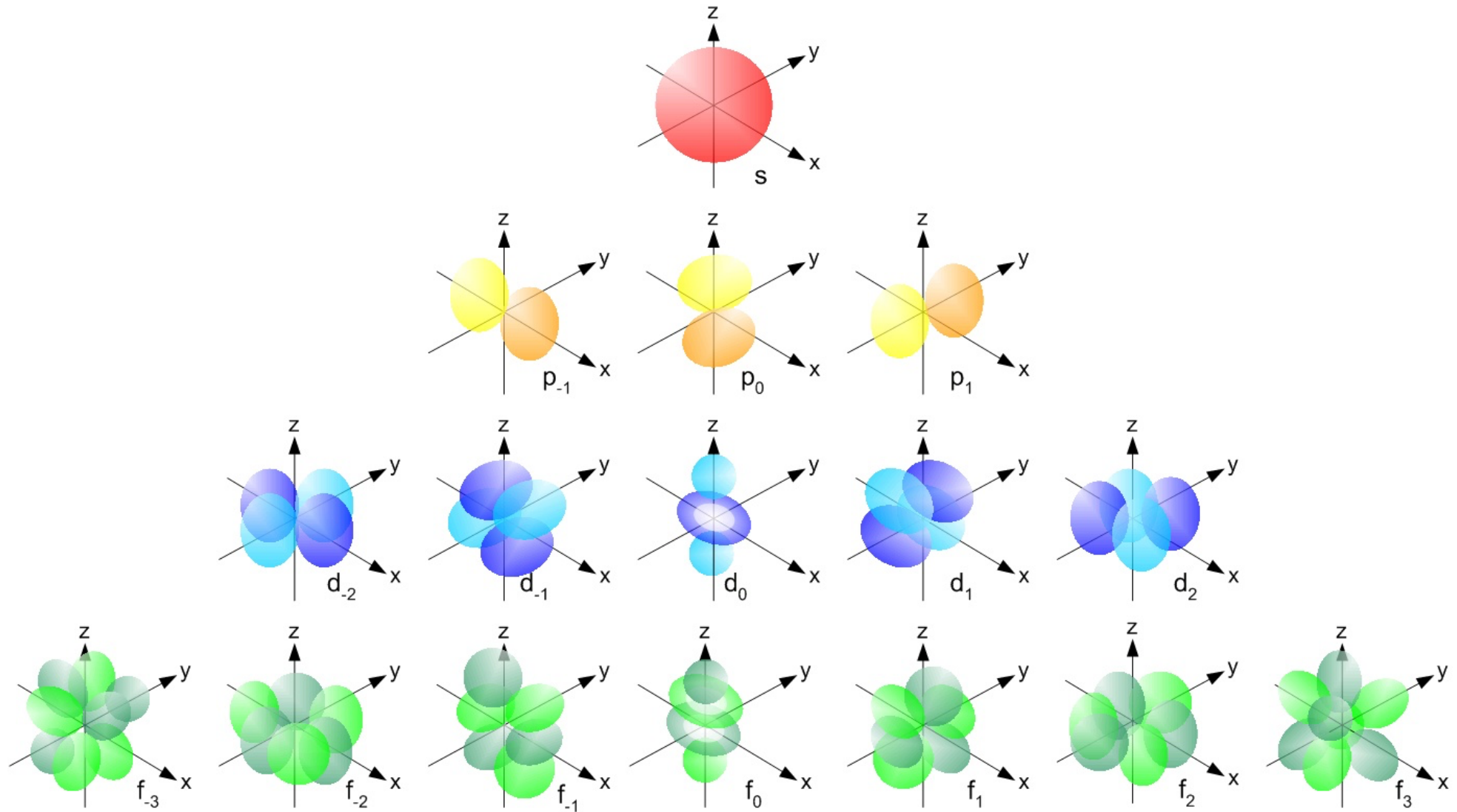


4 covalent bonds

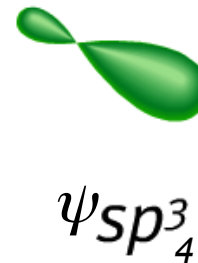
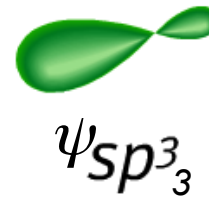
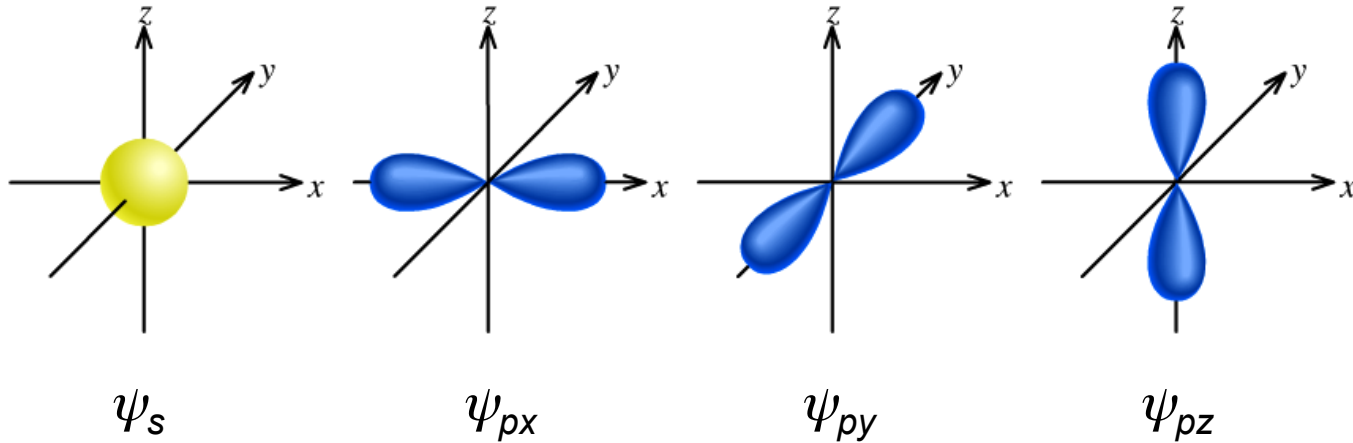
Summary

Bindungstyp	Beispiel	Bindungsenergie (eV)
Ionisch	NaCl	8.23
	LiF	10.92
Van-der-Waals	Ar	0.080
	Kr	0.116
Kovalent	Diamant	7.36
	Si	4.64
Metallisch	Na	1.13
	Fe	4.29
	W	8.66
Wasserstoff-Brücken	H ₂ O	0.52
	HF	0.30

Electronic orbitals



Orbital hybridization



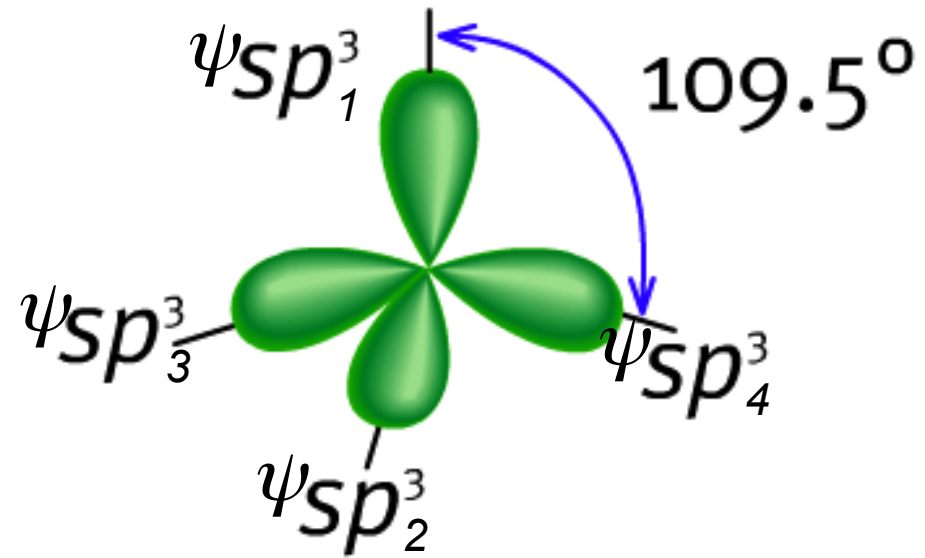
$$\frac{1}{2}(\psi_s + \psi_{px} + \psi_{py} + \psi_{pz})$$

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

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

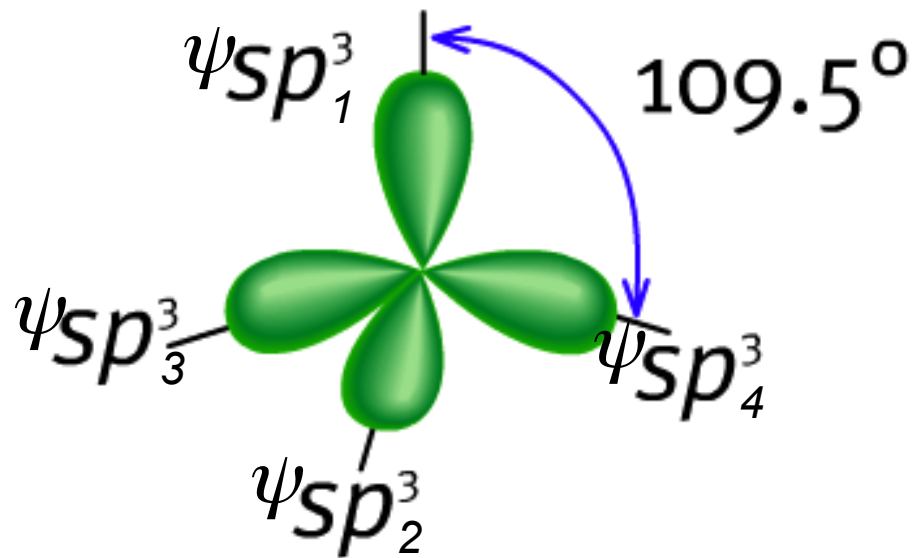
$$\frac{1}{2}(\psi_s - \psi_{px} - \psi_{py} + \psi_{pz})$$

Orbital hybridization

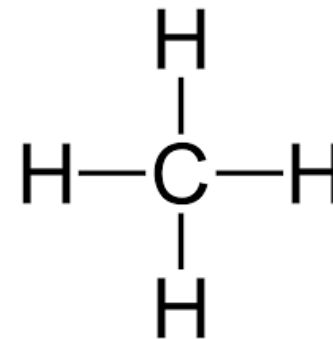
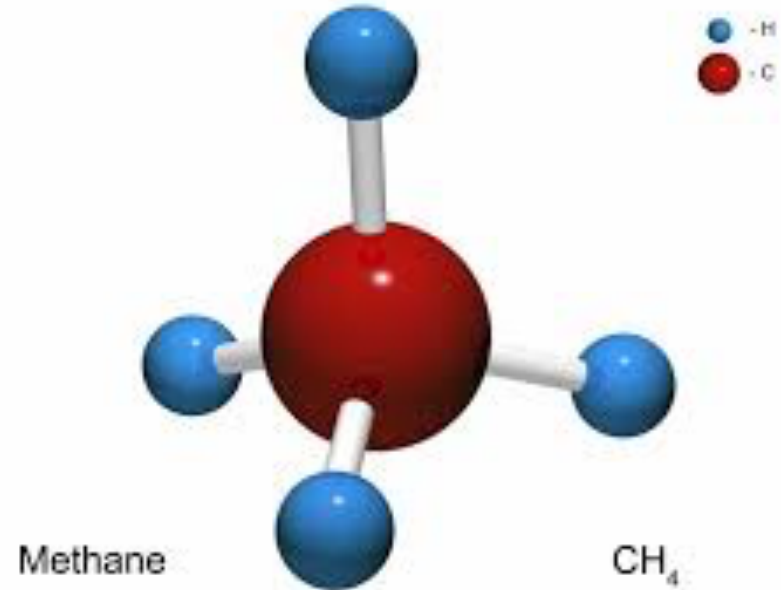


Tetraeder

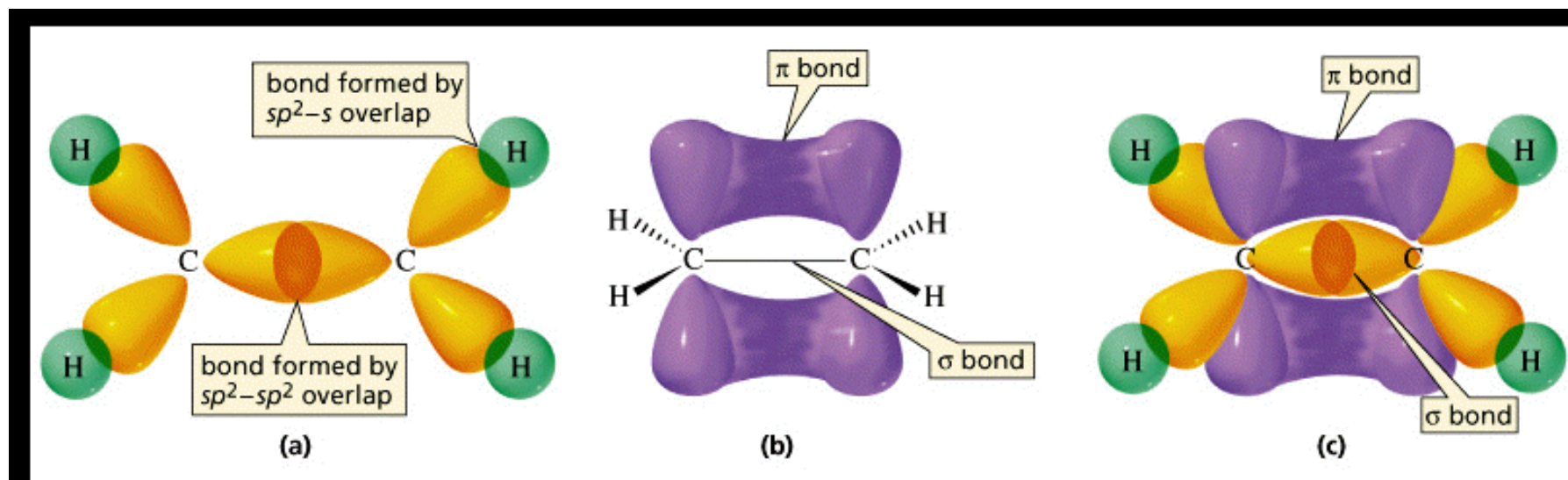
Orbital molecular theory: Example CH₄ (Methane)



Tetraeder



Orbital molecular theory: σ and π bonding



Graphene: σ and π bonding

Graphene

