General Chemistry
Winter Term 2023/24

Dr. Lars Birlenbach
Physikalische Chemie 1 (PC1)
AR-F0102
Tel.: 0271 740 2817
eMail: birlenbach@chemie.uni-siegen.de

- Website (Slides, Excercises):
- http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/

Login Data for slides:
User: Ludwig
Password: Boltzmann

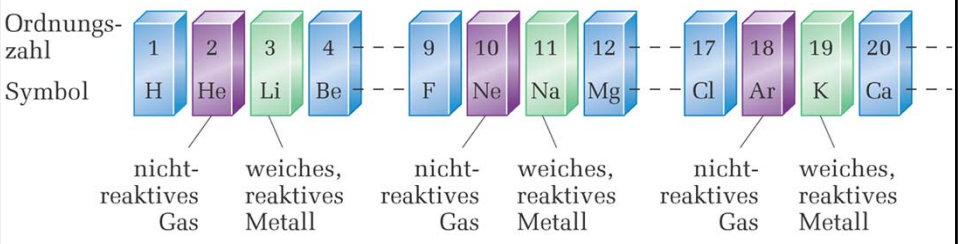
Electronic configuration for Chlorine

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration
1, 2	1	0	0	$\pm\frac{1}{2}$	$1s^2$
3, 4	2	0	0	$\pm\frac{1}{2}$	$2s^2$
5–10	2	1	−1	$\pm\frac{1}{2}$	$2p^6$
	2	1	0	$\pm\frac{1}{2}$	
	2	1	+1	$\pm\frac{1}{2}$	
11, 12	3	0	0	$\pm\frac{1}{2}$	$3s^2$
13–17	3	1	−1	$\pm\frac{1}{2}$	$3p^5$
	3	1	0	$\pm\frac{1}{2}$	
	3	1	+1	$+\frac{1}{2}$ or $-\frac{1}{2}$*	

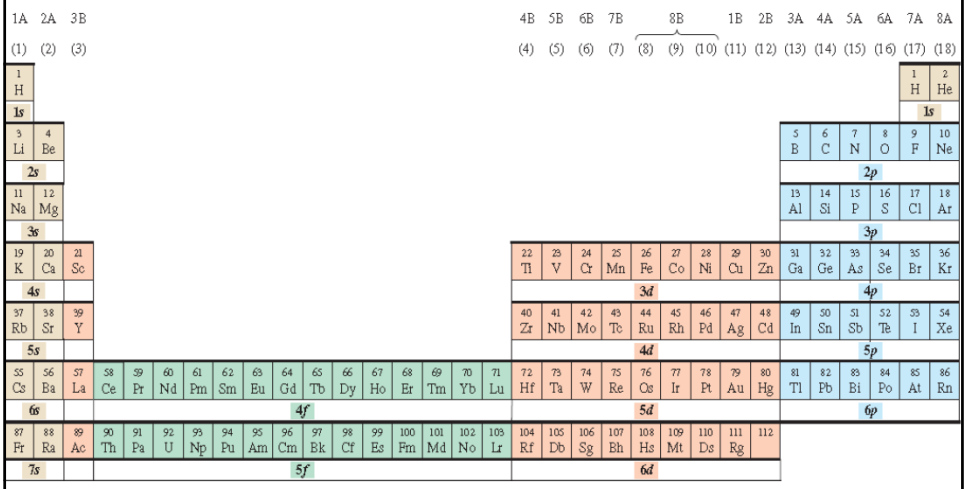
Electronic configurations

n	ℓ	m_ℓ	m_s	Electron Capacity of Subshell = $4\ell + 2$	Electron Capacity of Shell = $2n^2$
1	0(1*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0(2*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
	1(2*p*)	$-1, 0, +1$	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
3	0(3*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
	1(3*p*)	$-1, 0, +1$	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2(3*d*)	$-2, -1, 0, +1, +2$	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
4	0(4*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
	1(4*p*)	$-1, 0, +1$	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2(4*d*)	$-2, -1, 0, +1, +2$	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
	3(4*f*)	$-3, -2, -1, 0, +1, +2, +3$	$\pm\frac{1}{2}$ for each value of m_ℓ	14	

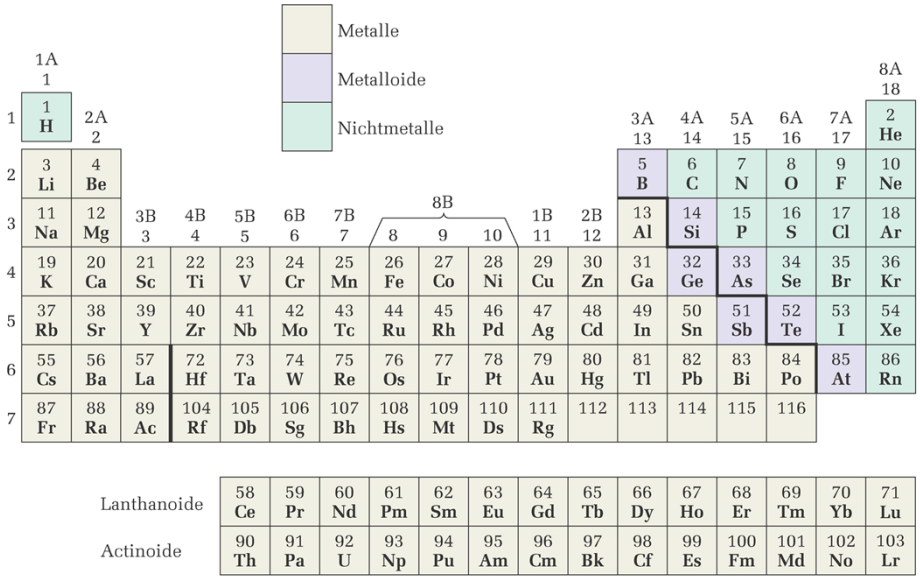
Discovery of the periodic system: patterns

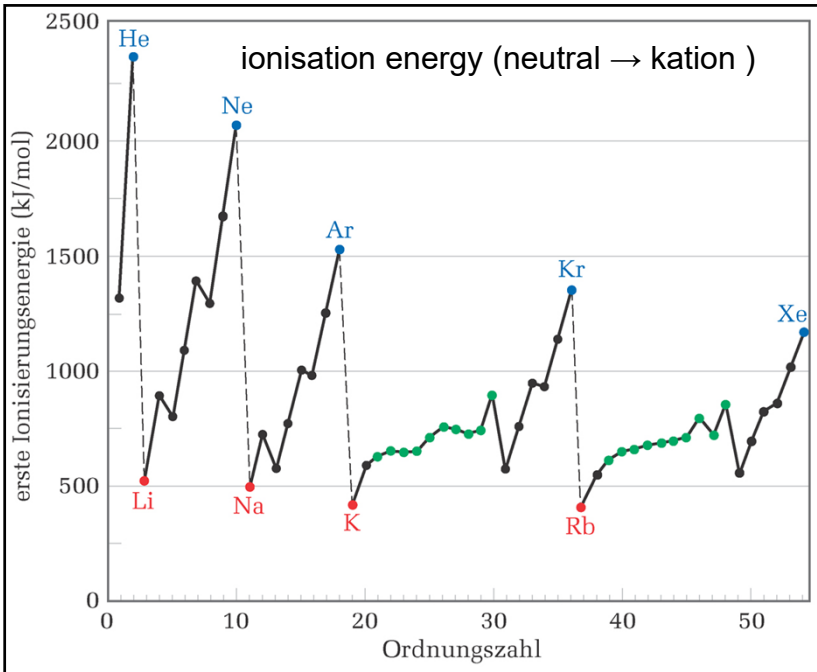


PSE and Orbitals



PSE and chemical properties





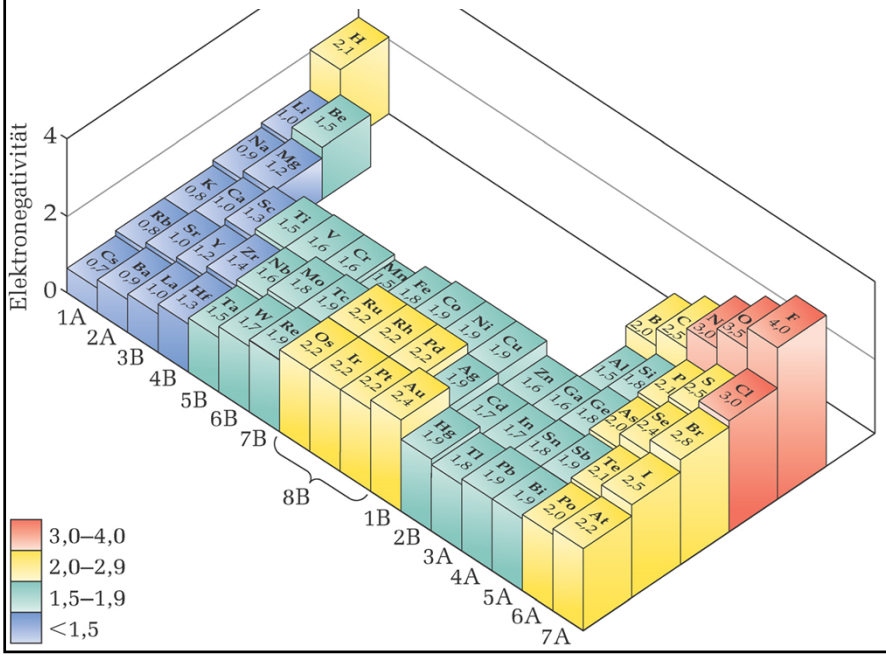
Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

Elektron affinities (neutral → Anion)

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0

Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

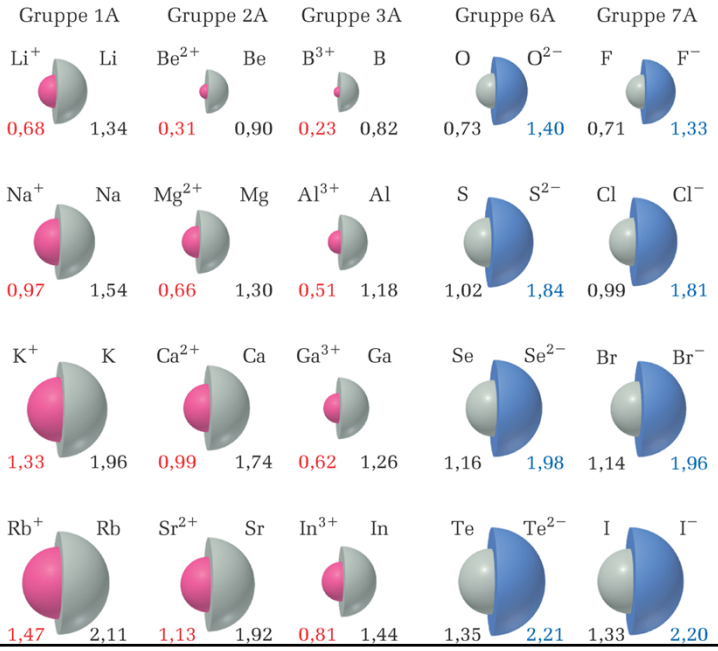
Electronegativity



Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

46

Size of Atoms and Ions in Å

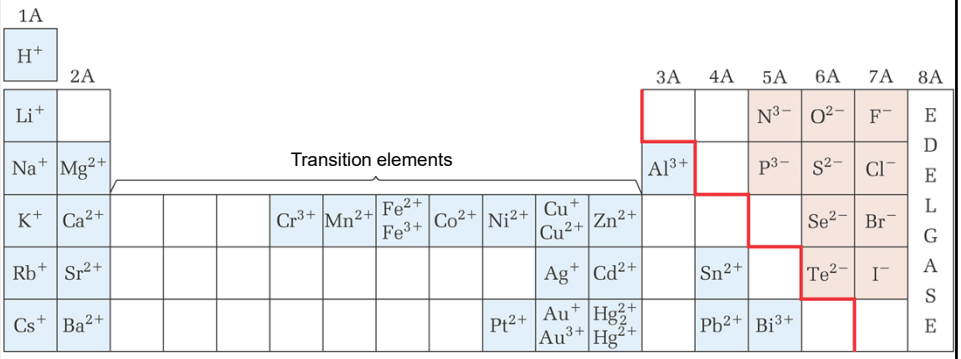


Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

Lars Birlenb

47

Common ions



Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

Valence electrons

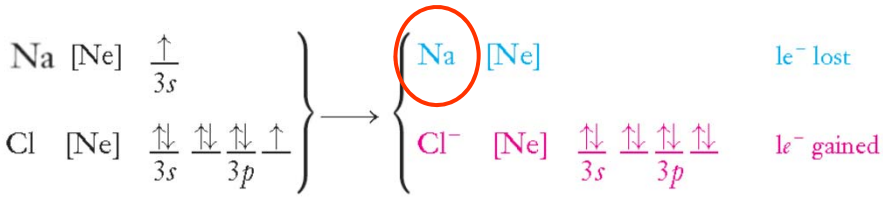
Group	1A	2A	3A	4A	5A	6A	7A	8A
Number of electrons in valence shell	1	2	3	4	5	6	7	8 *(except He)*
Period 1	H·							He:
Period 2	Li·	Be:	·B·	·C·	·N·	·O:	·F:	:Ne:
Period 3	Na·	Mg:	·Al·	·Si·	·P·	·S:	·Cl:	:Ar:
Period 4	K·	Ca:	·Ga·	·Ge·	·As·	·Se:	·Br:	:Kr:
Period 5	Rb·	Sr:	·In·	·Sn·	·Sb·	·Te:	·I:	:Xe:
Period 6	Cs·	Ba:	·Tl·	·Pb·	·Bi·	·Po:	·At:	:Rn:
Period 7	Fr·	Ra:						

•aus: **Chemistry, 9th Edition** KW Whitten,
•RE Davis, ML Peck, GG Stanley

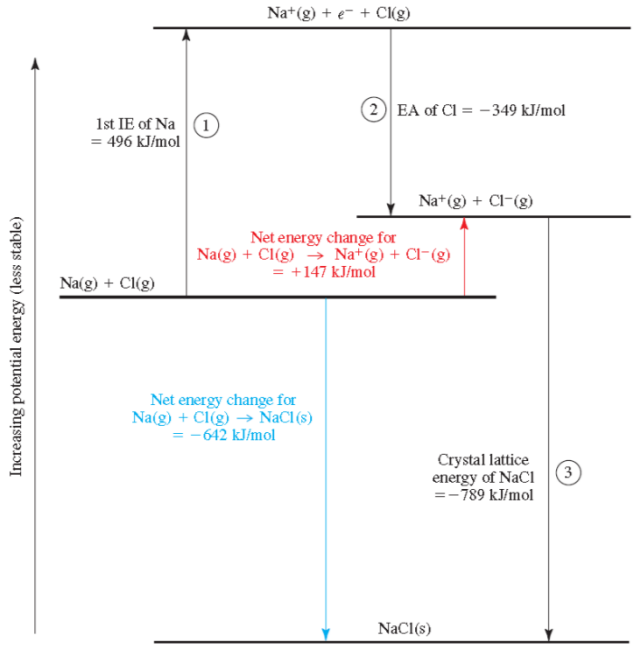
The chemical bond

- ionic bond
- metallic bond
- covalent bond (molecules)

Na + Cl → NaCl

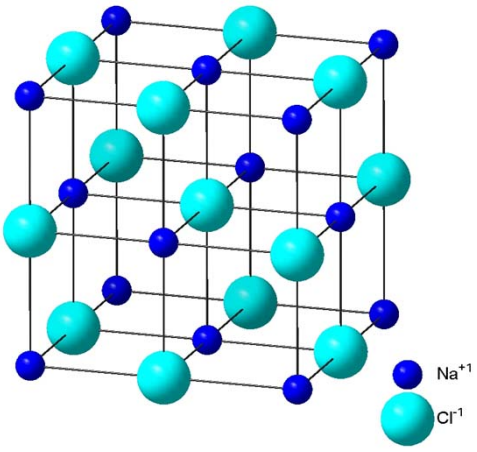


•aus: **Chemistry, 9th Edition** KW Whitten,
•RE Davis, ML Peck, GG Stanley



•aus:**Chemistry, 9th Edition** KW Whitten,
•RE Davis, ML Peck, GG Stanley

Ionic Bond



Elementary cells in cubic crystal lattice

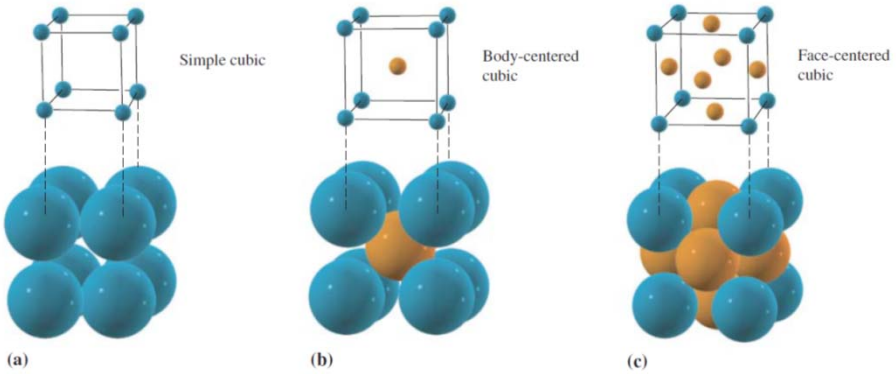
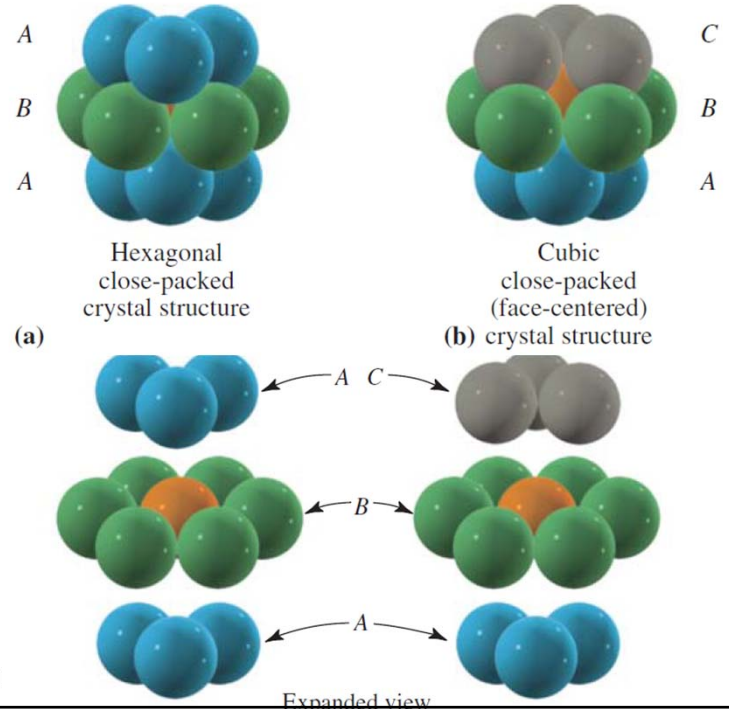
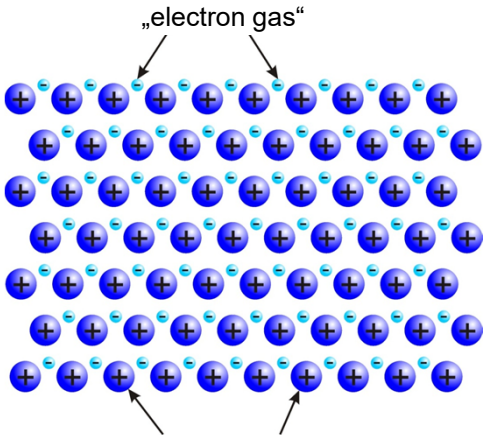


Figure 13-25 Unit cells for (a) simple cubic, (b) body-centered cubic, and (c) face-centered cubic. The spheres in each figure represent *identical* atoms or ions; different colors are shown *only* to help you visualize the spheres in the center of the cube in body-centered cubic (b) and in face-centered cubic (c) forms.



Chemical bonds: metallic



Band model

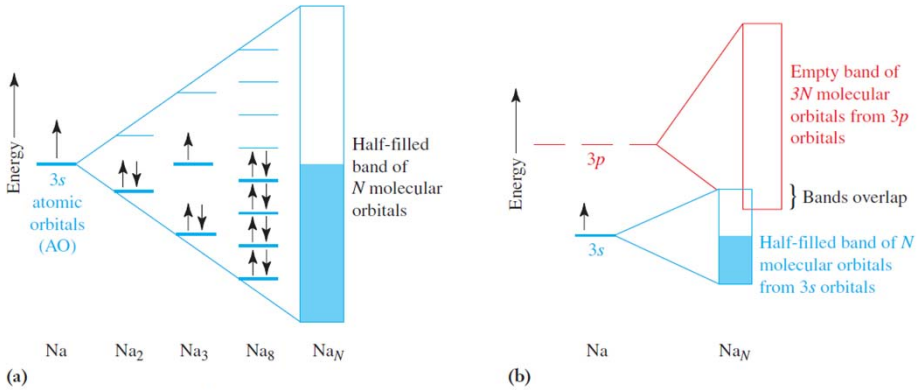


Figure 13-33 (a) The band of orbitals resulting from interaction of the 3*s* orbitals in a crystal of sodium. (b) Overlapping of a half-filled "3*s*" band (*blue*) with an empty "3*p*" band (*red*) of Na_N crystal.

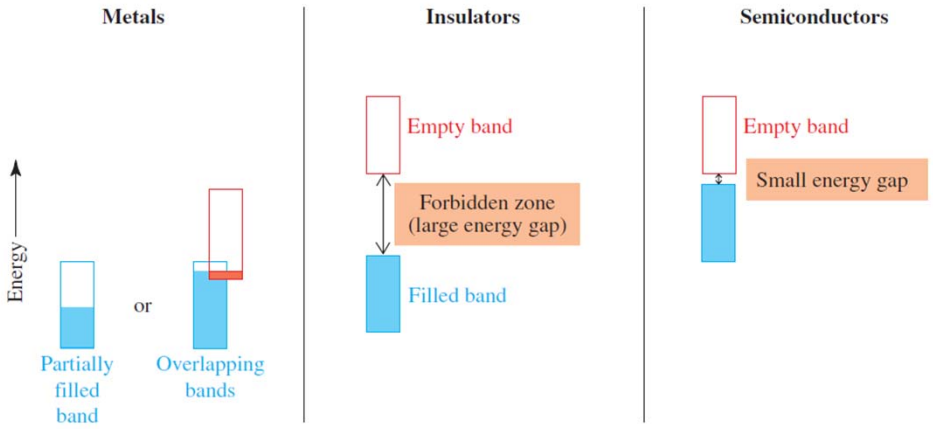


Figure 13-35 Distinction among metals, insulators, and semiconductors. In each case an unshaded area represents a conduction band.

Metals vs. Salts

A crystal can be cleaved into smaller crystals that have the same appearance as the larger crystal.

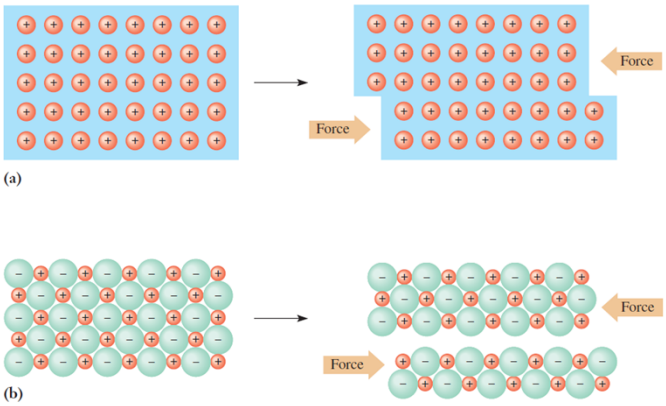
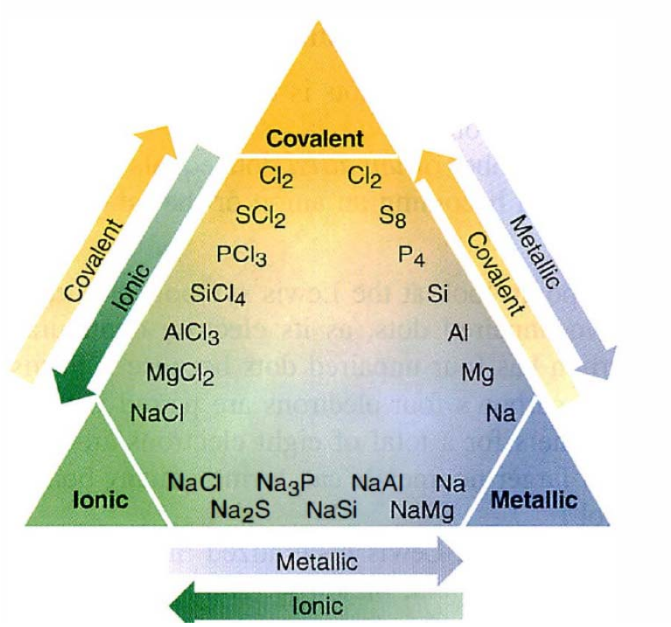
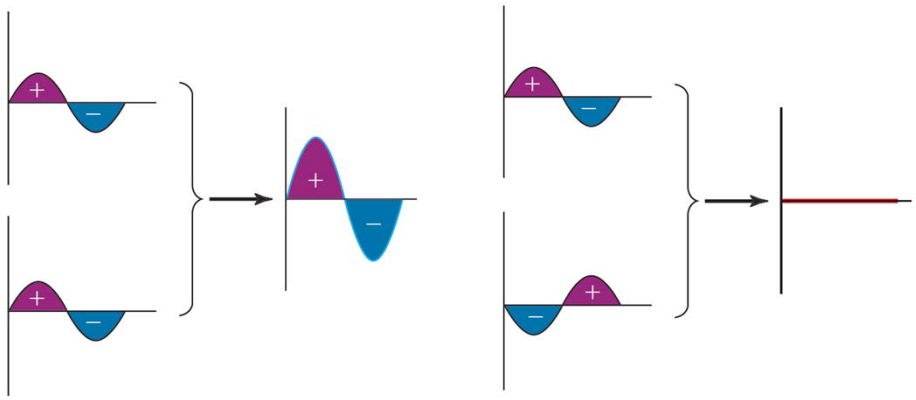


Figure 13-36 (a) In a metal, the positively charged metal ions are immersed in a delocalized "cloud of electrons." When the metal is distorted (e.g., rolled into sheets or drawn into wires), the environment around the metal atoms is essentially unchanged, and no new repulsive forces occur. This explains why metal sheets and wires remain intact. (b) By contrast, when an ionic crystal is subjected to a force that causes it to slip along a plane, the increased repulsive forces between like-charged ions cause the crystal to break or cleave along a crystal plane.



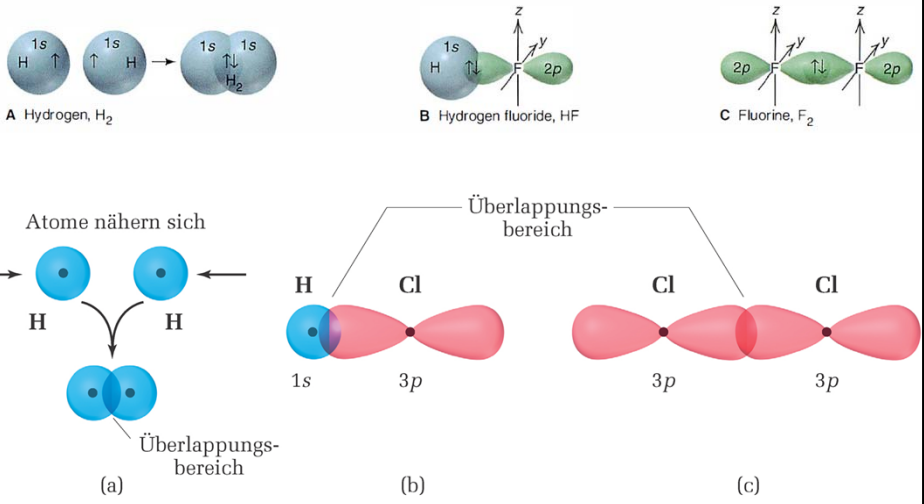
The covalent bond

Superposition of wave functions

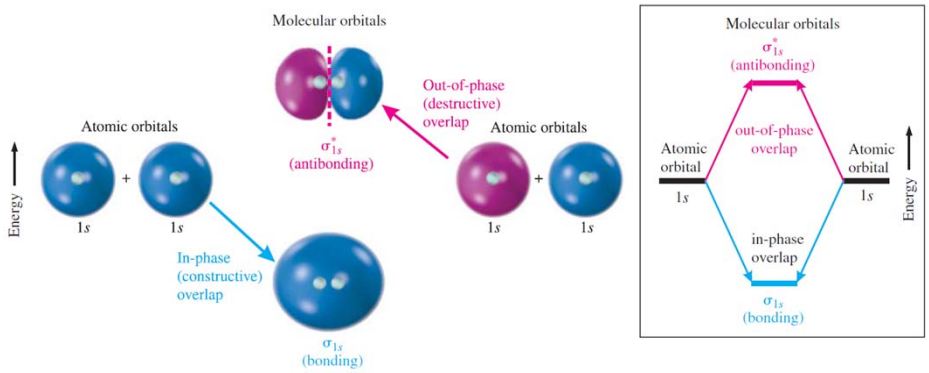


(a) In-phase (constructive) overlap (b) Out-of-phase (destructive) overlap

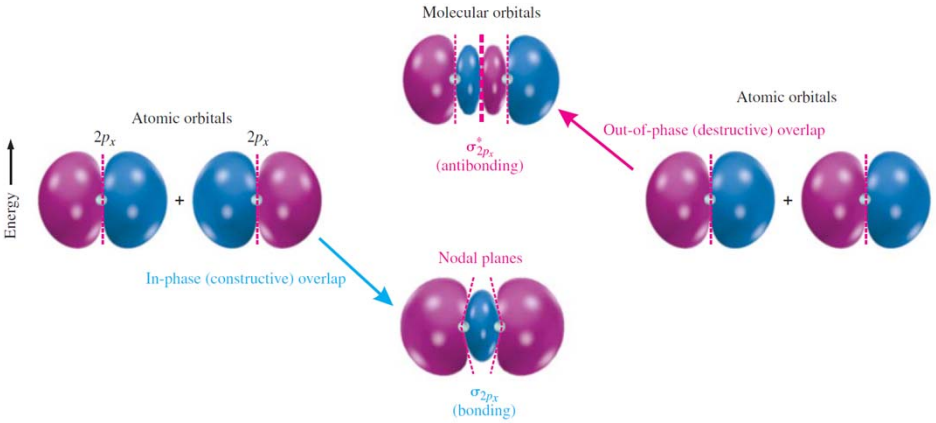
Covalent bond



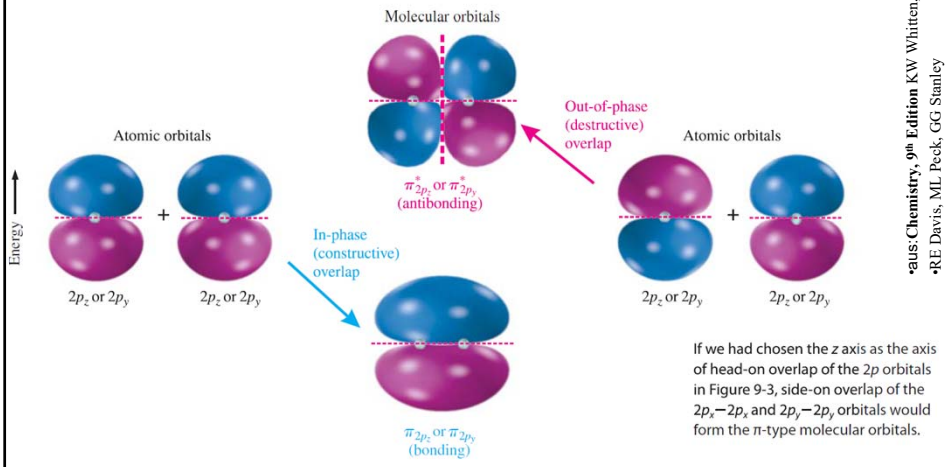
σ-1s-Molecular orbitals



σ-2p-Molecular orbitals



Π-2p-Molekular orbitals



•aus: **Chemistry, 9th Edition** KW Whitten, •RE Davis, ML Peck, GG Stanley

If we had chosen the *z* axis as the axis of head-on overlap of the 2*p* orbitals in Figure 9-3, side-on overlap of the $2p_x$–$2p_x$ and $2p_y$–$2p_y$ orbitals would form the π-type molecular orbitals.

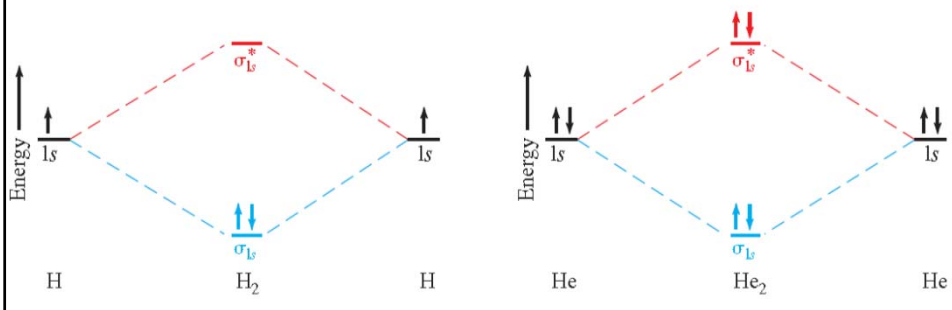
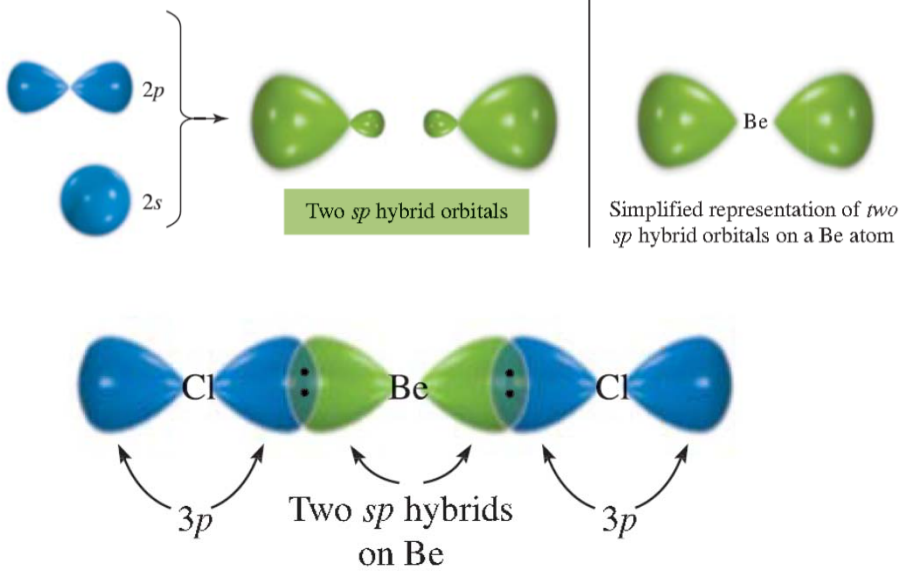


Figure 9-6 Molecular orbital diagrams for (a) H_2 and (b) He_2.

	H_2	He_2[c]	Li_2[b]	Be_2[c]	B_2[b]	C_2[b]	N_2
Increasing energy (not to scale) ↑							
σ^*_{2p}	—	—	—	—	—	—	—
$\pi^*_{2p_y}$, $\pi^*_{2p_z}$	— —	— —	— —	— —	— —	— —	— —
σ_{2p}	—	—	—	—	—	—	↑↓
π_{2p_y}, π_{2p_z}	— —	— —	— —	— —	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ^*_{2s}	—	—	—	↑↓	↑↓	↑↓	↑↓
σ_{2s}	—	—	↑↓	↑↓	↑↓	↑↓	↑↓
σ^*_{1s}	—	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{1s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Paramagnetic?	no	no	no	no	yes	no	no
Bond order	1	0	1	0	1	2	3
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09
Observed bond energy (kJ/mol)	436	—	110	9	≈ 270	602	945

	O_2	F_2	Ne_2[c]
σ^*_{2p}	—	—	↑↓
$\pi^*_{2p_y}$, $\pi^*_{2p_z}$	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
π_{2p_y}, π_{2p_z}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓
σ^*_{1s}	↑↓	↑↓	↑↓
σ_{1s}	↑↓	↑↓	↑↓
Paramagnetic?	yes	no	no
Bond order	2	1	0
Observed bond length (Å)	1.21	1.43	—
Observed bond energy (kJ/mol)	498	155	—

	H_2	He_2^c	Li_2^b	Be_2^c	B_2^b	C_2^b	N_2	O_2	F_2	Ne_2^c
Increasing energy (not to scale) ↑										
σ^*_{2p}	—	—	—	—	—	—	—	—	—	⇅
$\pi^*_{2p_y}, \pi^*_{2p_z}$	— —	— —	— —	— —	— —	— —	— —	↑ ↑	⇅ ⇅	⇅ ⇅
σ_{2p}	—	—	—	—	—	—	⇅	⇅ ⇅	⇅ ⇅	⇅ ⇅
π_{2p_y}, π_{2p_z}	— —	— —	— —	— —	↑ ↑	⇅ ⇅	⇅ ⇅	⇅	⇅	⇅
σ^*_{2s}	—	—	—	⇅	⇅	⇅	⇅	⇅	⇅	⇅
σ_{2s}	—	—	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅
σ^*_{1s}	—	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅
σ_{1s}	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅
Paramagnetic?	no	no	no	no	yes	no	no	yes	no	no
Bond order	1	0	1	0	1	2	3	2	1	0
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09	1.21	1.43	—
Observed bond energy (kJ/mol)	436	—	110	9	≈ 270	602	945	498	155	—

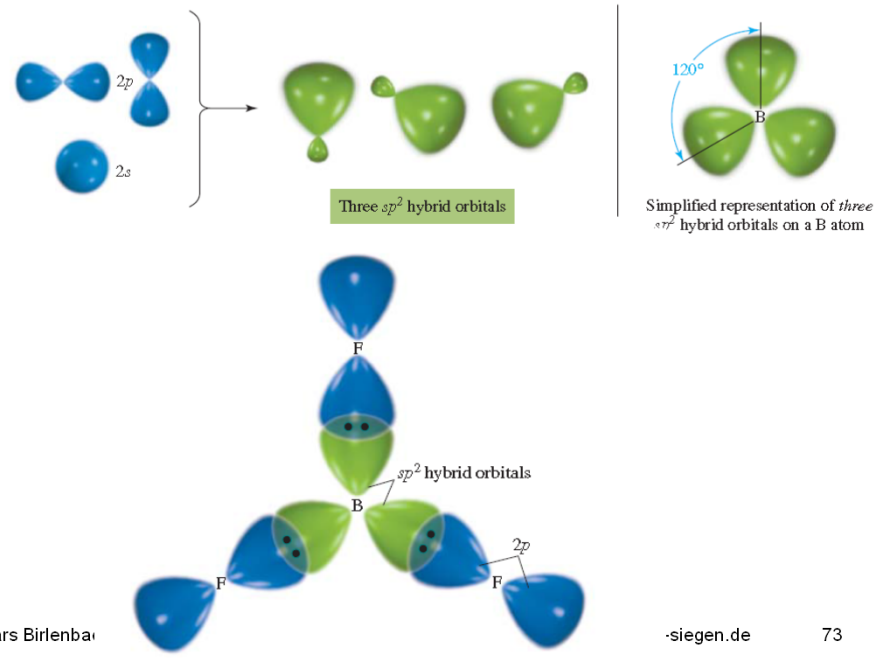


Mathematical modeling of hybrid orbitals

$$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$

aus: McQuarrie, Simon: Physical Chemistry. University Science Books

Three sp^2 hybrid orbitals point toward the corners of an equilateral triangle:

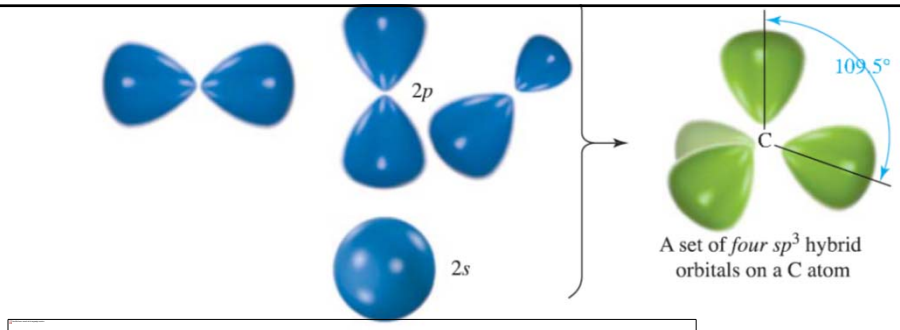


$$\psi_1 = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z$$

$$\psi_2 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x$$

$$\psi_3 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x$$

aus: McQuarrie, Simon: Physical Chemistry. University Science Books



$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$$

$$\psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$$

$$\psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

aus: McQuarrie, Simon: Physical Chemistry. University Science Books

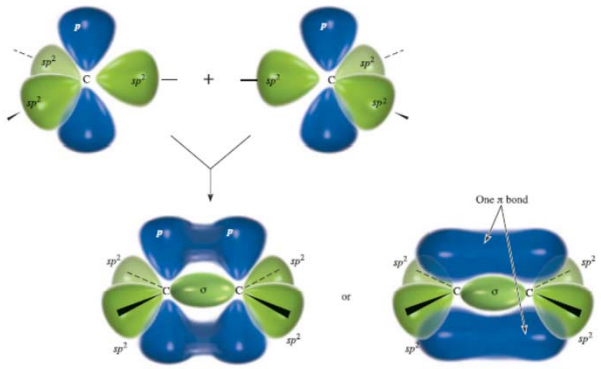
TABLE 6.5

The complete hydrogenlike atomic wave functions for $n = 1$, 2, and 3. The quantity Z is the atomic number of the nucleus, and $\sigma = Zr/a_0$, where a_0 is the Bohr radius.

$n = 1$,	$l = 0$,	$m = 0$	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2$,	$l = 0$,	$m = 0$	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$
	$l = 1$,	$m = 0$	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta$
	$l = 1$,	$m = \pm 1$	$\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta e^{\pm i\phi}$
$n = 3$,	$l = 0$,	$m = 0$	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
	$l = 1$,	$m = 0$	$\psi_{310} = \frac{1}{81}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3} \cos\theta$
	$l = 1$,	$m = \pm 1$	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3} \sin\theta e^{\pm i\phi}$
	$l = 2$,	$m = 0$	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
	$l = 2$,	$m = \pm 1$	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin\theta \cos\theta e^{\pm i\phi}$
	$l = 2$,	$m = \pm 2$	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2\theta e^{\pm 2i\phi}$

aus: McQuarrie, Simon: Physical Chemistry. University Science Books

Double bonds



Triple bonds