Lecture General Chemistry
Winter Term 2022/23

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

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Metals vs. Salts

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

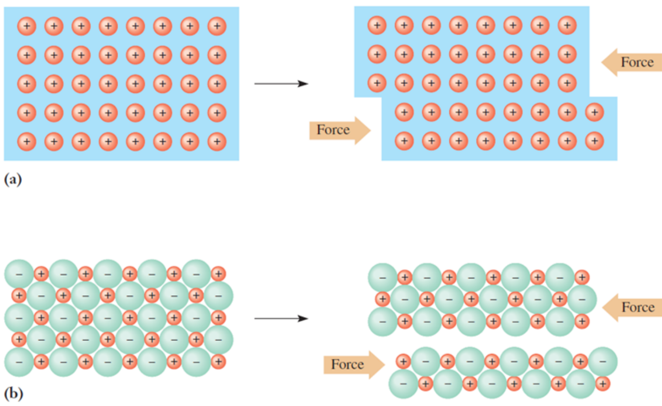
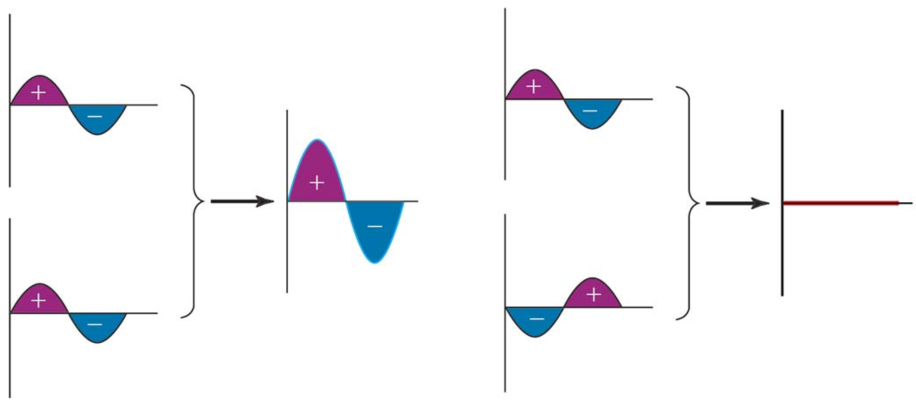


Figure 13-36 (a) In a metal, the positively charged metal ions are immersed in a delocalized "cloud of electrons." When the metal is distorted (e.g., rolled into sheets or drawn into wires), the environment around the metal atoms is essentially unchanged, and no new repulsive forces occur. This explains 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.

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

The covalent bond

Superposition of wave functions



(a) In-phase (constructive) overlap

(b) Out-of-phase (destructive) overlap

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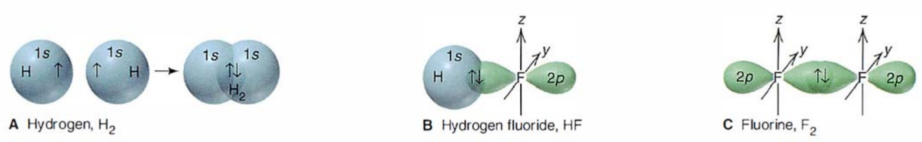
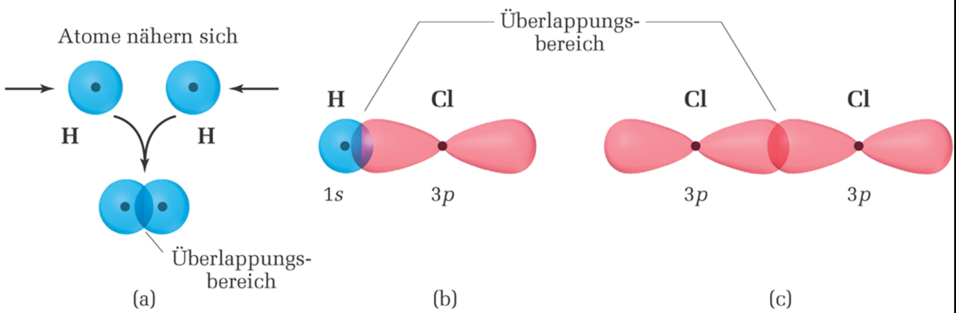
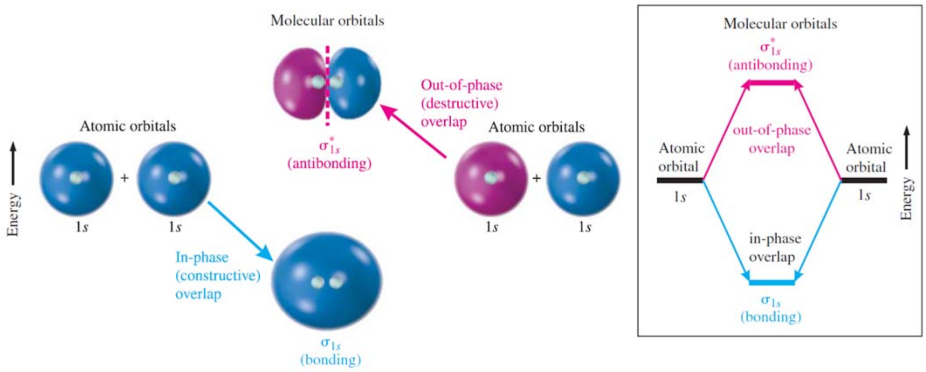
Covalent bond





σ-1s-Molecular orbitals



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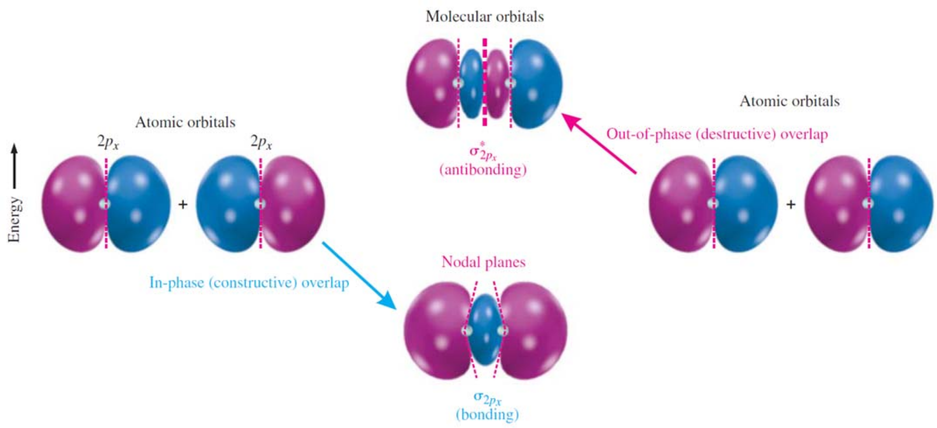
σ-2p-Molecular orbitals



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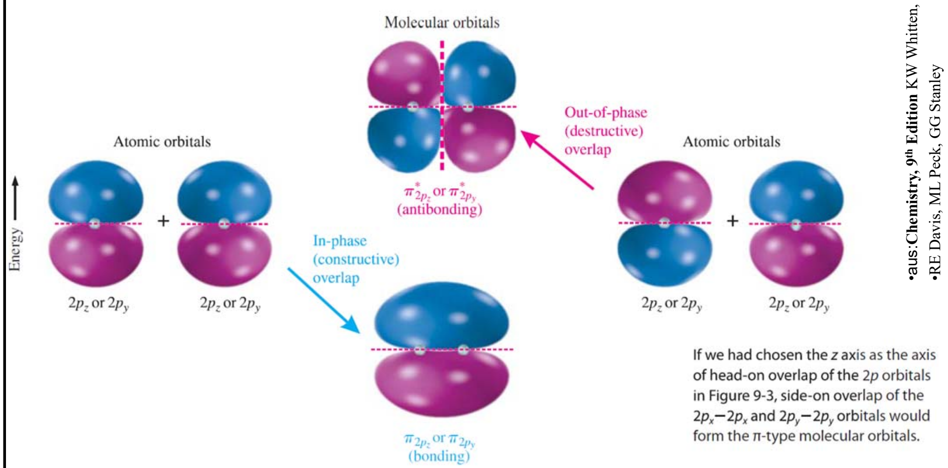
•RE Davis, ML Peck, GG Stanley

Π-2p-Molekular orbitals



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.

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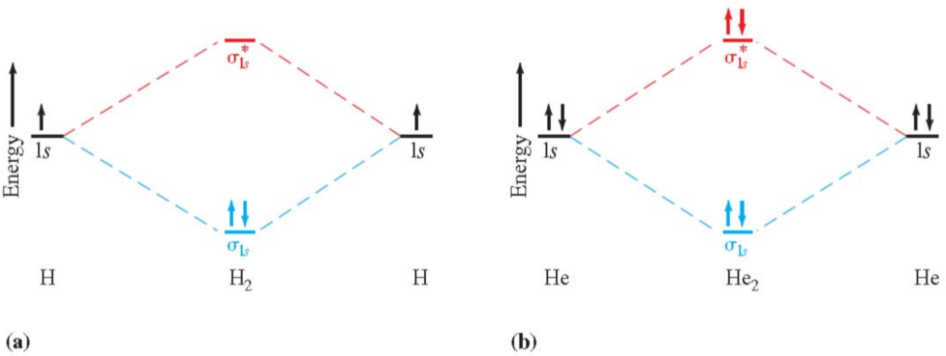
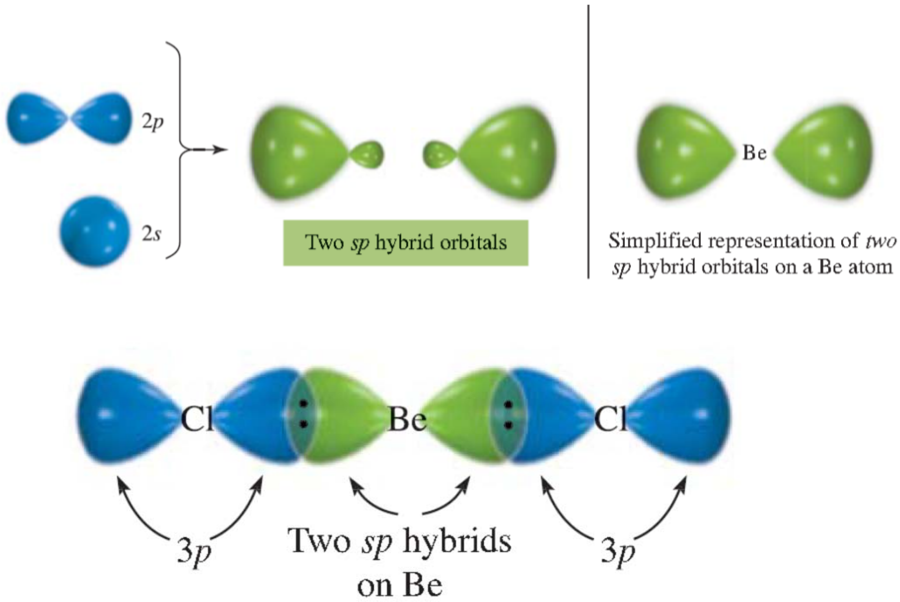


Figure 9-6 Molecular orbital diagrams for (a) H_2 and (b) He_2.

Increasing energy (not to scale)	H_2	He_2[c]	Li_2[b]	Be_2[c]	B_2[b]	C_2[b]	N_2
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]
	—	—	↑↓
	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
π_{2p_y}, π_{2p_z}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	↑↓	↑↓	↑↓
	↑↓	↑↓	↑↓
	↑↓	↑↓	↑↓
	↑↓	↑↓	↑↓
	↑↓	↑↓	↑↓
	yes	no	no
	2	1	0
	1.21	1.43	—
	498	155	—

Increasing energy (not to scale)	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]
σ^*_{2p}	—	—	—	—	—	—	—		—	—	↑↓
$\pi^*_{2p_y}, \pi^*_{2p_z}$	— —	— —	— —	— —	— —	— —	— —		↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	—	—	—	—	—	—	↑↓	π_{2p_y}, π_{2p_z}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p_y}, π_{2p_z}	— —	— —	— —	— —	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
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

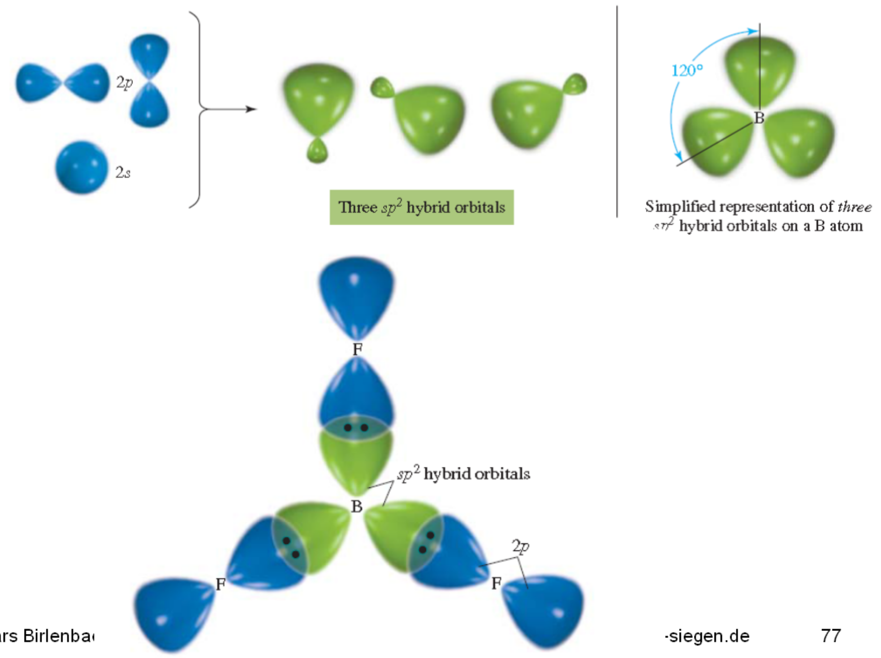
$$\psi_1 = \frac{1}{\sqrt{3}} 2s + \sqrt{\frac{2}{3}} 2p_z$$

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

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

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

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



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

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

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

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

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

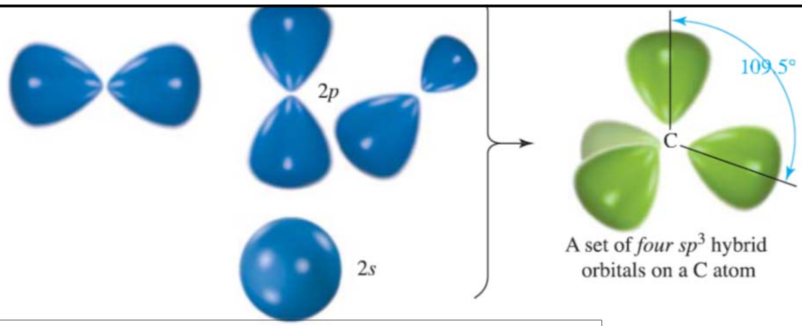
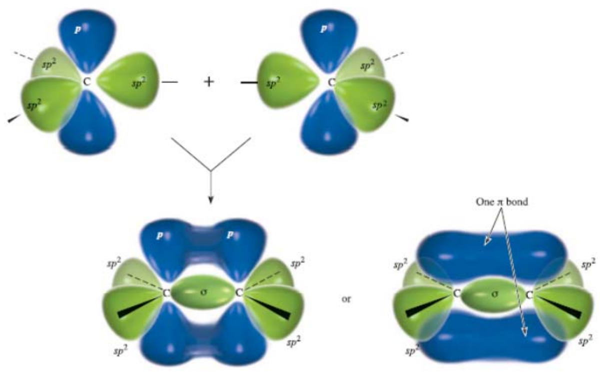


TABLE 6.5
The complete hydrogenlike atomic wave functions for $n = 1$, 2, and 3. The quantity Z is the atomic number of the nucleus, and $\sigma = Zr/a_0$, where a_0 is the Bohr radius.

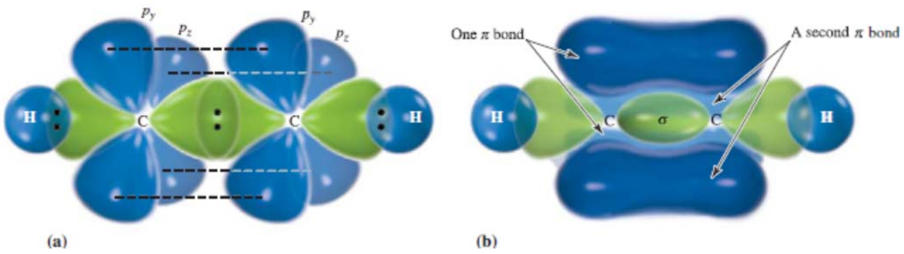
$n = 1$,	$l = 0$,	$m = 0$	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2$,	$l = 0$,	$m = 0$	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
	$l = 1$,	$m = 0$	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}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

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

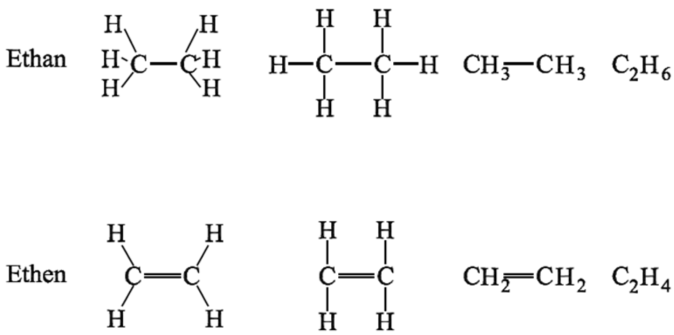
Double bonds



Triple bonds

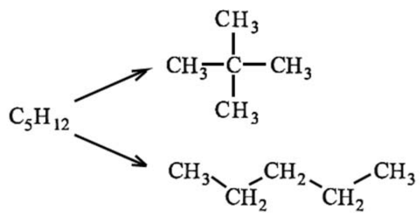


Structural and total formulas



structural formula total formula

Structural and total formulas

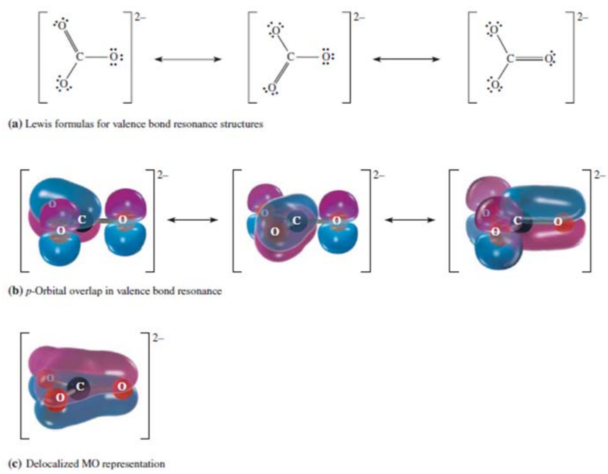


2.2-Dimethyl-propan
(Tetramethyl-methan, Neopentan)

n-Pentan

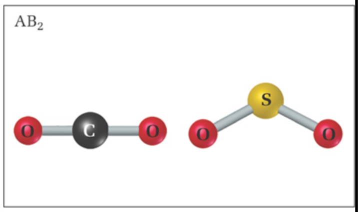
total formula structural formula

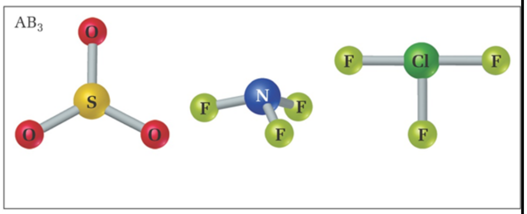
Delocalized bonds: mesomerism



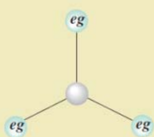
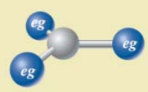
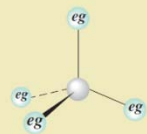
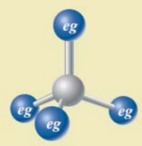
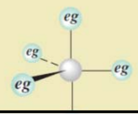
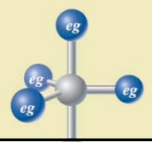
Bonding form and molecular geometry

- Diatomic molecules: always linear
- Three-atom molecules: linear or angled
- More atoms: more complicated shapes





VSEPR-Model

Electron Groups on Central Atom	Electronic Geometry* Orientation of Electron Groups	Description; Angles†	Line Drawing‡	Ball and Stick Model
2		linear; 180°		
3		trigonal planar; 120°		
4		tetrahedral; 109.5°		
5		trigonal bipyramidal; 90°, 120°, 180°		

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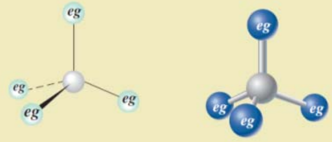
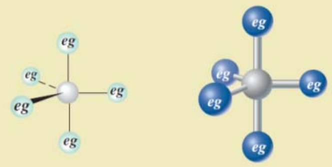
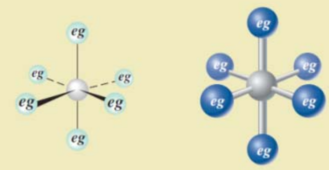
3		120°		
4		tetrahedral; 109.5°		
5		trigonal bipyramidal; 90°, 120°, 180°		
6		octahedral; 90°, 180°		

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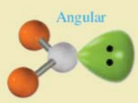
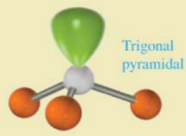
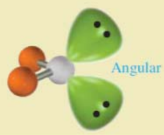
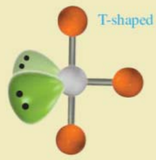
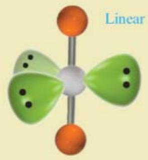
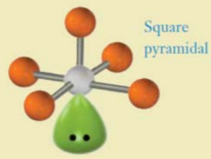
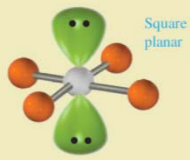
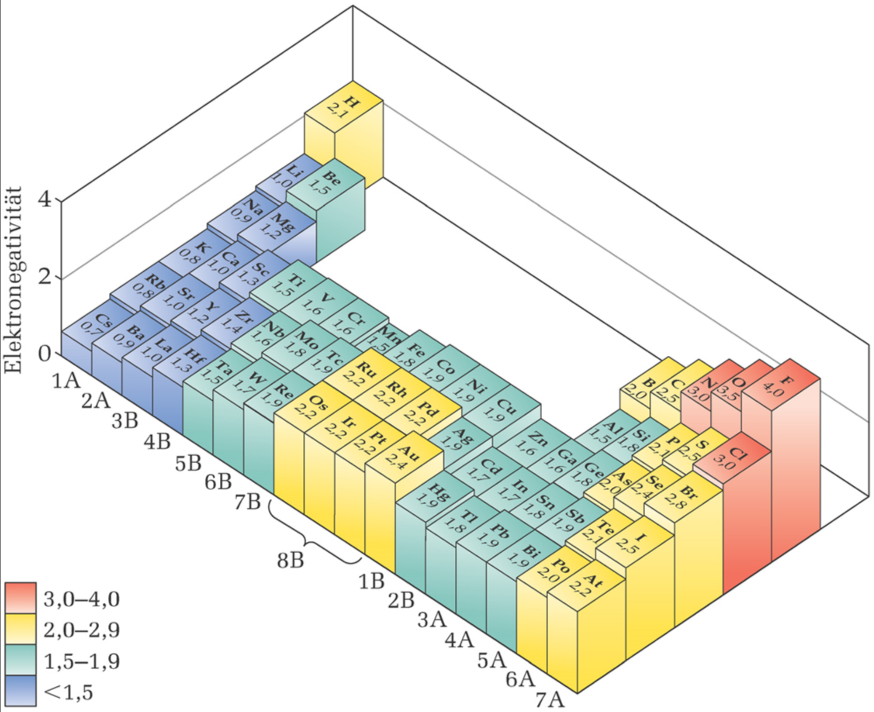
•RE Davis, ML Peck, GG Stanley

General Formula	Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_2U	3	trigonal planar	sp^2	1		O_3, NO_2^-, SO_2
AB_3U	4	tetrahedral	sp^3	1		NH_3, SO_3^{2-}
AB_2U_2	4	tetrahedral	sp^3	2		H_2O, NH_2^-

General Formula	Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_4U	5	trigonal bipyramidal	sp^3d	1		SF_4
AB_3U_2	5	trigonal bipyramidal	sp^3d	2		ICl_3, ClF_3
AB_2U_3	5	trigonal bipyramidal	sp^3d	3		XeF_2, I_3^-

General Formula	Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_5U	6	octahedral	sp^3d^2	1		IF_5, BrF_5
AB_4U_2	6	octahedral	sp^3d^2	2		XeF_4, IF_4^-

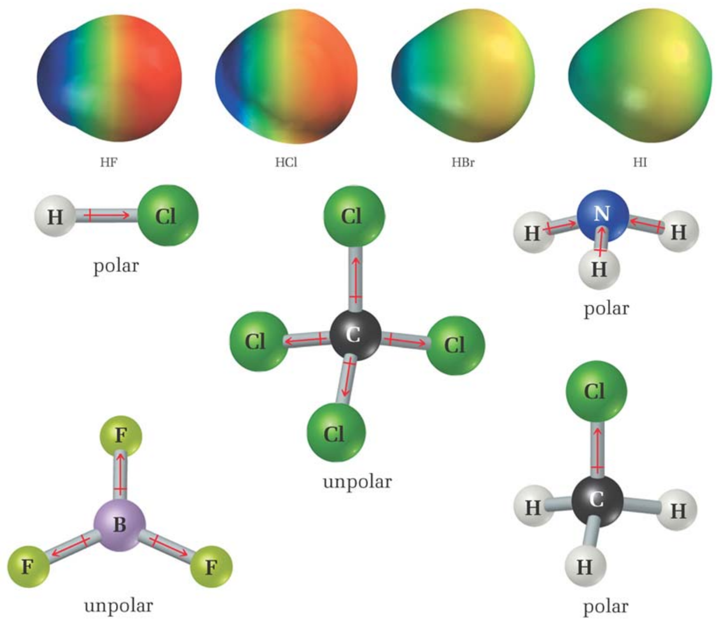


Abbildungen aus: Brown-LeMay, Chemie
siehe www.pearson-studium.de

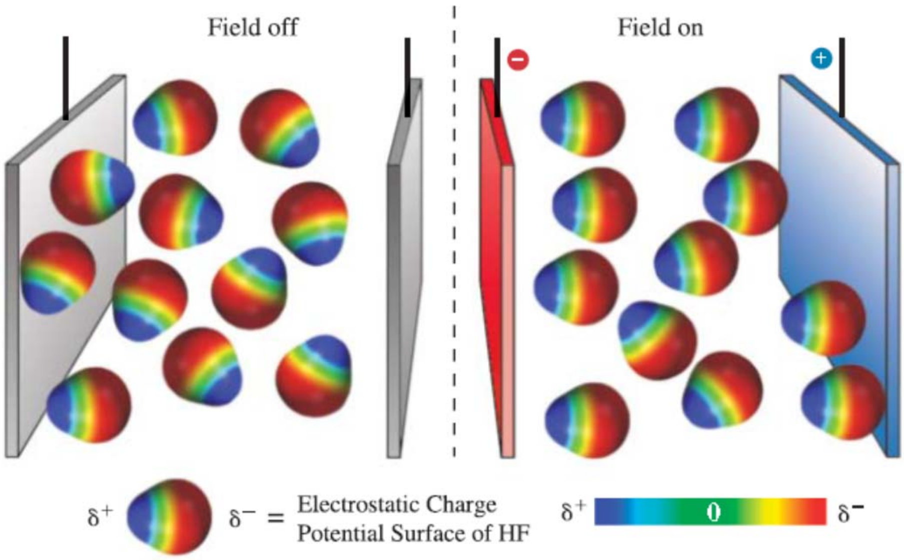
Distribution of electronic density:
Dipol moments

- Low electronic density: blue
- high electronic density: red
- average electronic density: green

Lars Birlenbach
birlenbach@chemie.uni-siegen.de



Orientation of dipoles in electrical fields



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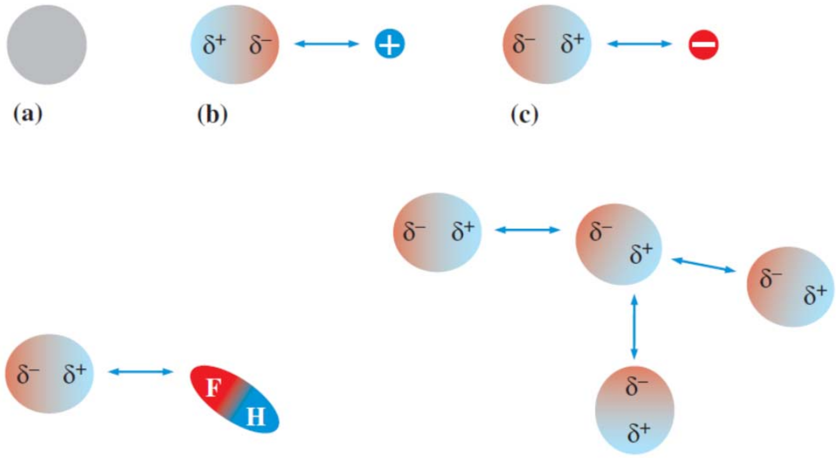
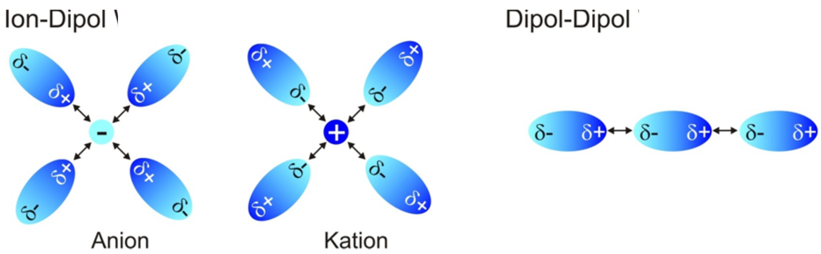
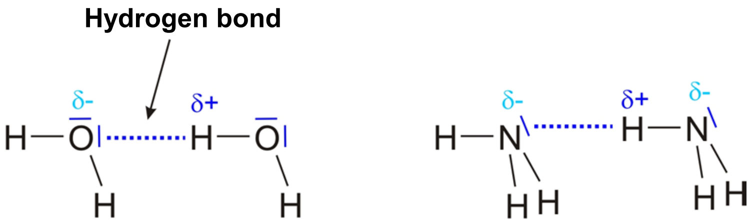
Induced dipol moments



Intermolecular forces



Hydrogen bonds



Possible partners: N,O,F,Cl