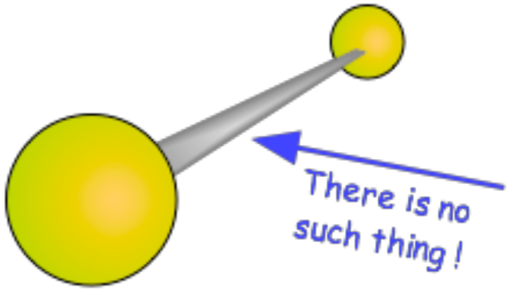
What is a chemical bond?

Claim: chemical bonds are what hold atoms together to form the more complicated aggregates that we know as molecules and extended solids



It is more useful to regard a **chemical bond** as **an effect** that causes certain atoms to join together **to form enduring structures** that have **unique physical and chemical properties**.

Most important 1: chemical bonding occurs when one or more electrons are simultaneously attracted to two nuclei.

Most important 2: A chemical bond between two atoms forms if the resulting arrangement of the two nuclei and their electrons has a lower energy than the total energy of the separate atoms.

What is a molecule?

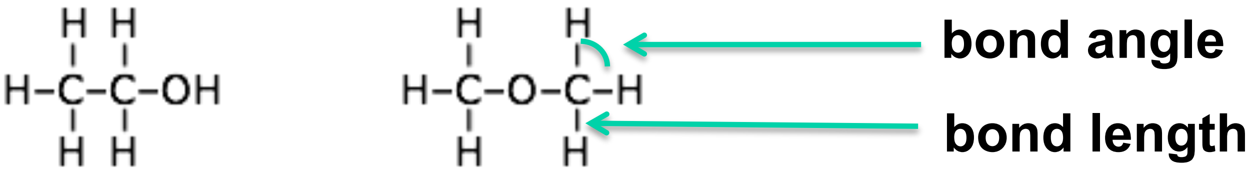
A molecule is an aggregate of atoms that possesses
distinctive observable properties

A more **restrictive definition distinguishes** between a "true" molecule that exists as an independent particle, and an **extended solid** that can only be represented by its simplest formula.

chemical species is defined by its structure.

The structure of a molecule is specified by the identity of its constituent atoms and the sequence in which they are joined together, that is, by the bonding connectivity. This, in turn, defines the bonding geometry— the spatial relationship between the bonded atoms.

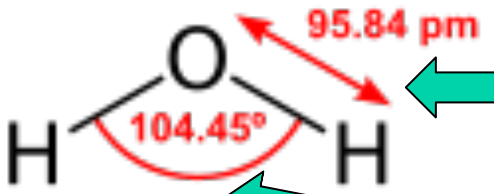
structural formulas reveal the very different connectivities



ethanol C_2H_6O

dimethyl ether C_2H_6O

Some parameters of the geometrical structure of molecules

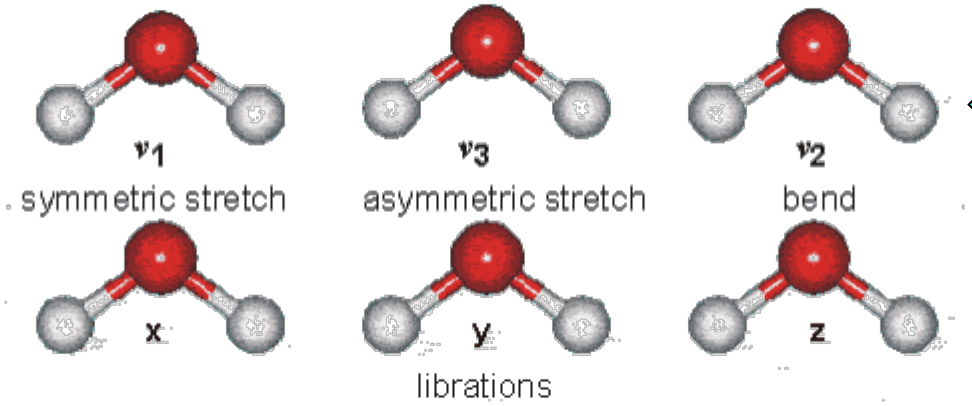


bond length

bond angle

averaged

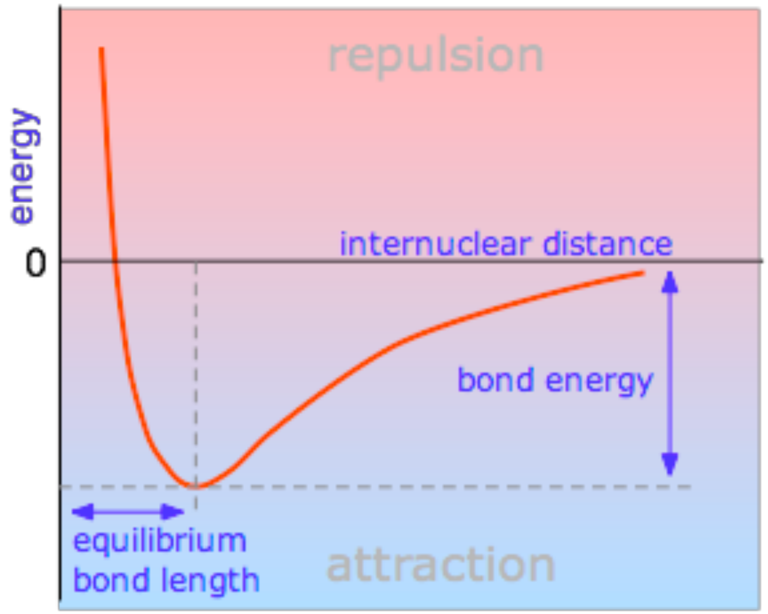
Molecules are not static!



Bond energy: the amount of **work that must be done** to pull two atoms completely apart; in other words, it is the same as the depth of the "well" in the potential energy curve. This is almost, but not quite the same as the bond dissociation energy actually required to break the chemical bond; the difference is the very small zero-point energy, related to bond vibrational frequencies.

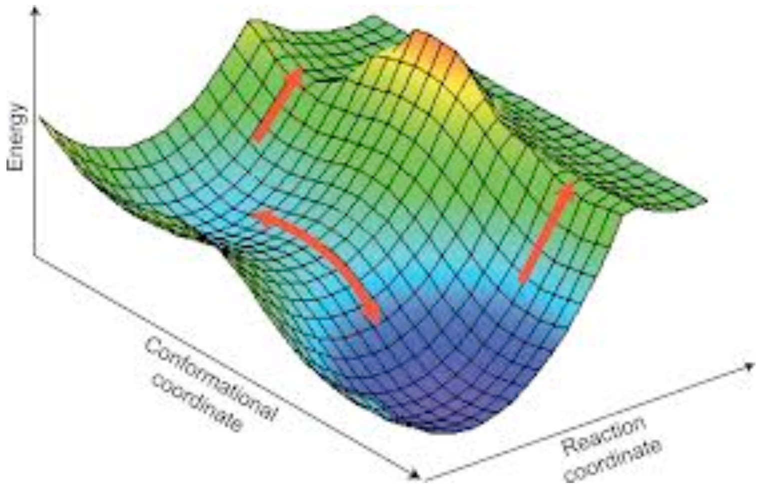
Potential energy curves

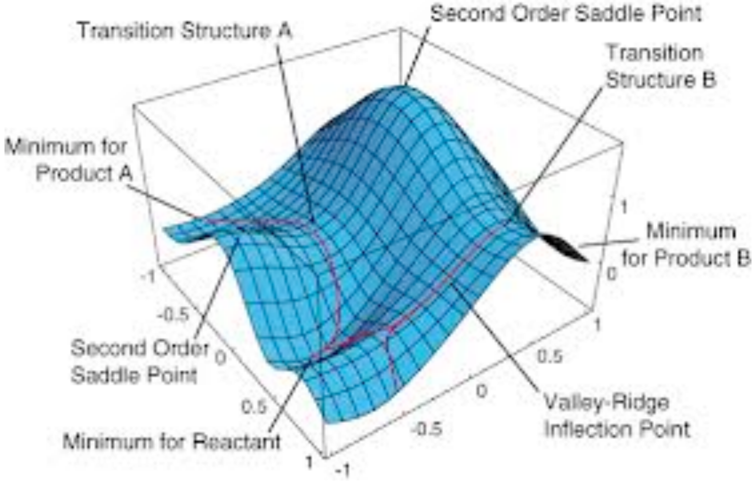
The energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning "no interaction". At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise.

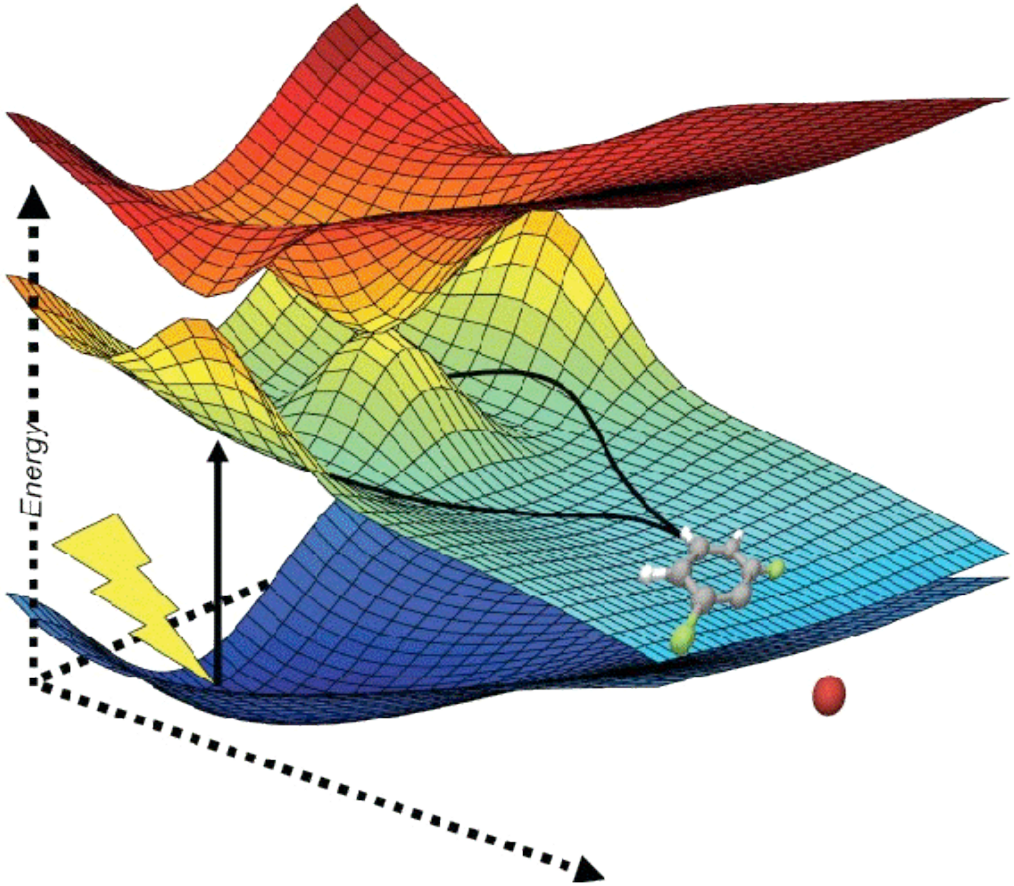


Concept of Potential Energy Surfaces

$E=E(R_1,R_2,R_3 \ldots)$ R_A – coordinates of atom A







Chemical bond

Chemical reaction: connecting, rearranging of atoms

chemical bond: an effect that causes atoms to be joined in a structure

scientific model:

a tool to explain investigated phenomena

a tool to predict properties of molecules

Models of chemical bonding

classical

quantum-mechanical

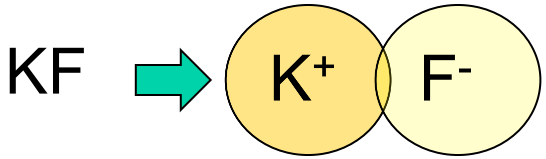
Classical models of chemical bonding

In essence - electrostatic considerations

- ionic bond +

covalent bondig

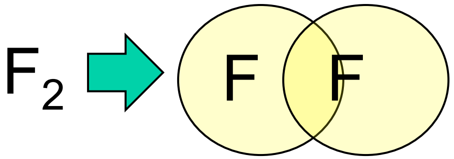
Walther Kossel, 1915, German



[Ar] [Ne]

electron configuration
of noble (rare) gases

Gilbert Newton Lewis,
1916, USA

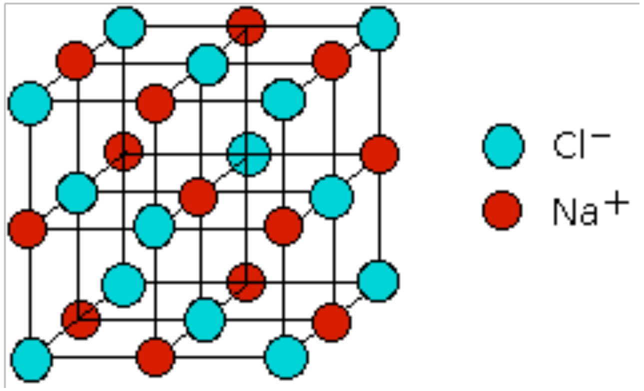


δ- polar covalent δ +

models of the chemical bond

The ionic model

Electrolytic solutions contain ions having opposite electrical charges; opposite charges attract, so perhaps the substances from which these ions come consist of positive and negatively charged atoms held together by electrostatic attraction.



this is not true generally, but a model built on this assumption does a fairly good job of explaining a rather small but important class of compounds that are called **ionic solids**.

Ionic bonds – When the complete transfer of one or more electrons from one atom to another takes place generating charged species that are held together by electrostatic interactions.

$Na(g) \rightarrow Na^+(g) + e^-$ Energy required=494kJmol-1

$Cl(g) + e^- \rightarrow Cl^-(g)$ Energy released=349kJmol-1

net change: 494 – 349 = **+145** kJ mol^{-1}.

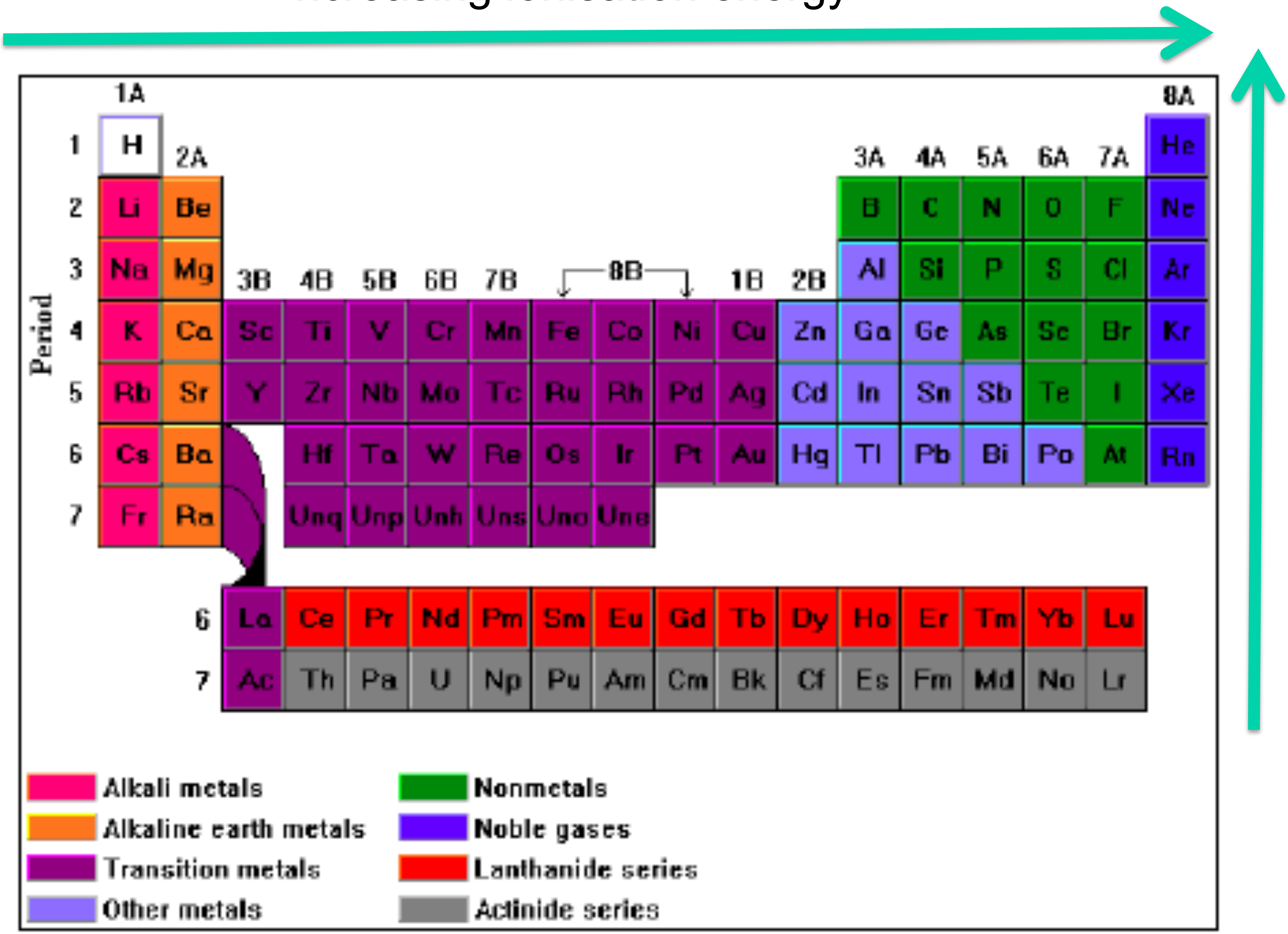
Increase in energy and hence no inducement for NaCl to form.

$Na^+(g) + Cl^-(g) \rightarrow NaCl\ (s)$ Energy released = 787 kJ mol^{-1}

net change: 145 – 787 = **-642** kJ mol^{-1}.

This is a huge decrease in energy→a solid composed of Na^+ and Cl^- ions has a lower energy than does a collection of Na and Cl atoms.

Increasing ionisation energy



Period	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Unq	Unp	Unh	Uns	Uno	Une									

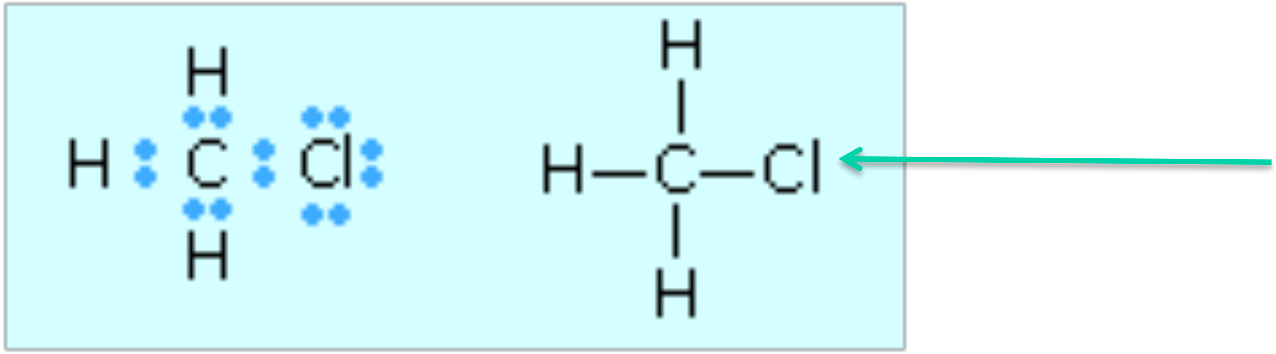
6	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
7	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- Alkali metals
- Alkaline earth metals
- Transition metals
- Other metals
- Nonmetals
- Noble gases
- Lanthanide series
- Actinide series

Shared-electron (covalent) model

This model originated with the theory developed by G.N. Lewis in 1916, and it remains the most widely-used model of chemical bonding. It is founded on the idea that a pair of electrons shared between two atoms can create a mutual attraction, and thus a chemical bond.

Usually each atom contributes one electron (one of its valence electrons) to the pair, but in some cases both electrons come from one of the atoms.



lone pair

Covalent bond - Lewis model

Shared electron pair – a unit of the covalent bond

H·   –   ·H

H:H   H–H

Number of shared electron pairs – valency

H $(1s)^1$ C $[He](2s)^2(2p)^2$ N $[He](2s)^2(2p)^3$

valency: H: 1   C: 4   N: 3

H–C≡N|

non-bonding (lone) electron pair

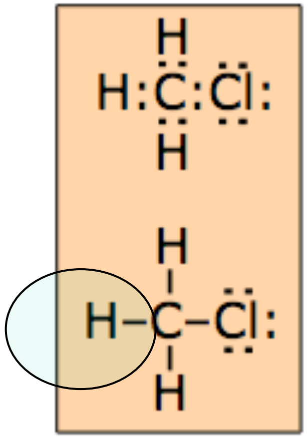
Lewis (electronic) structural formulas

(8-electron) octet rule

valence electron configuration of noble gases

– exceptions

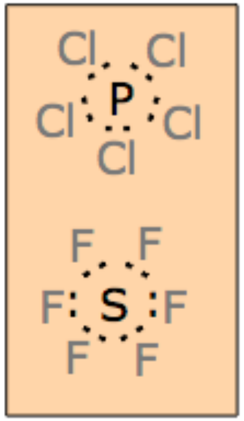
rule not always appropiate

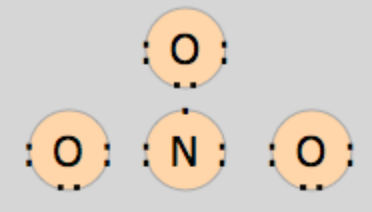


[He]

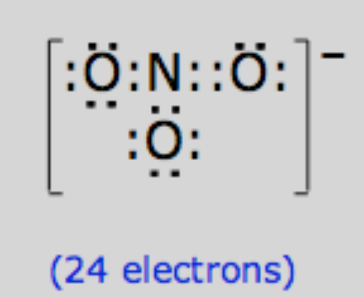
with d and f orbitals the valency is increased

- hypervalence



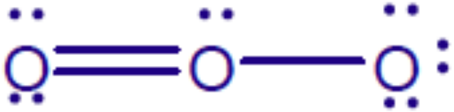


+ 1 electron



Resonance

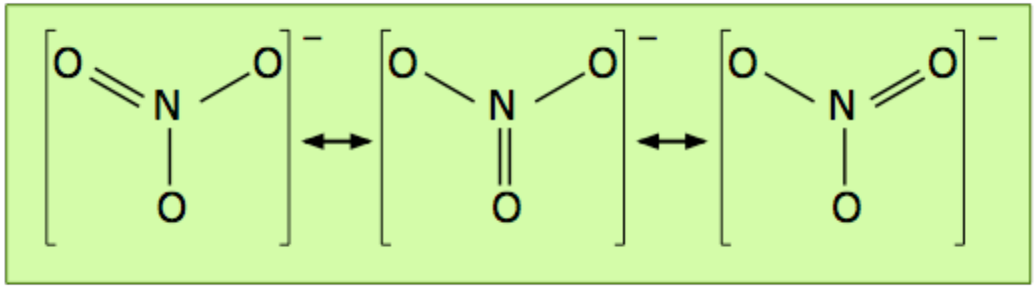
O_3



148 pm O-O and 121 pm O=O

Experiment O-O: 128 pm

resonant structures

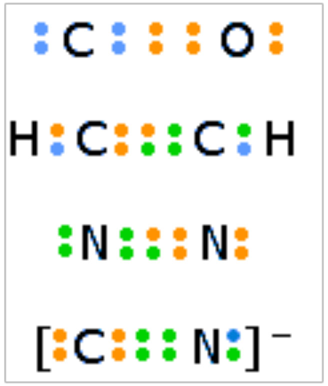


Multiple bonds

single

double

triple



quadruple	Re::::Re	$[Re_2Cl_8]^{2-}$	1964	F. A. Cotton
pentuple	Cr:::::Cr	RCrCrR (R=organic group)	2005	P. Power
sextuple	W::::::W	W_2	2006	B. Roos, et al.

Covalent bond - Lewis model

does not explain the nature of „bonding“ orbitals

„implicitly“ works with localized (unchanged) atomic orbitals

Limitation to two-center bonds

does not explain the geometric structure of molecules

Lewis model does not explain the structure!

VSEPR model – 1960 Ronald Gillespie

Valence-Shell Electron-Pair Repulsion

Regions of high electron density

bond

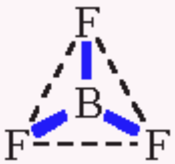
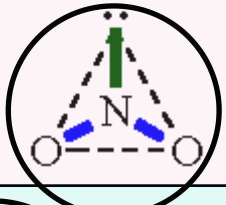
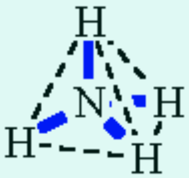
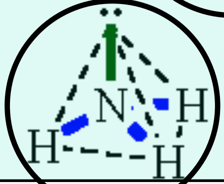
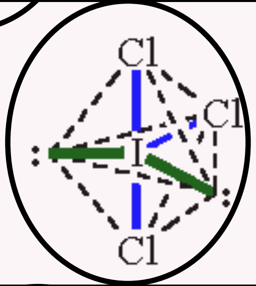
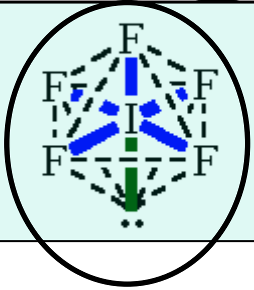
lone pair

rule: multiple bond is a single region

rule: any of the resonant structures can be used

geometric structure is determined by the repulsion of these regions!

VSEPR structures

regions with high densitties	most favorable arrangement		
2	linear	Cl—Be—Cl	
3	planar trigonal		
4	tetrahedral		
5	trigonal bypiramidal		
6	octahedral		

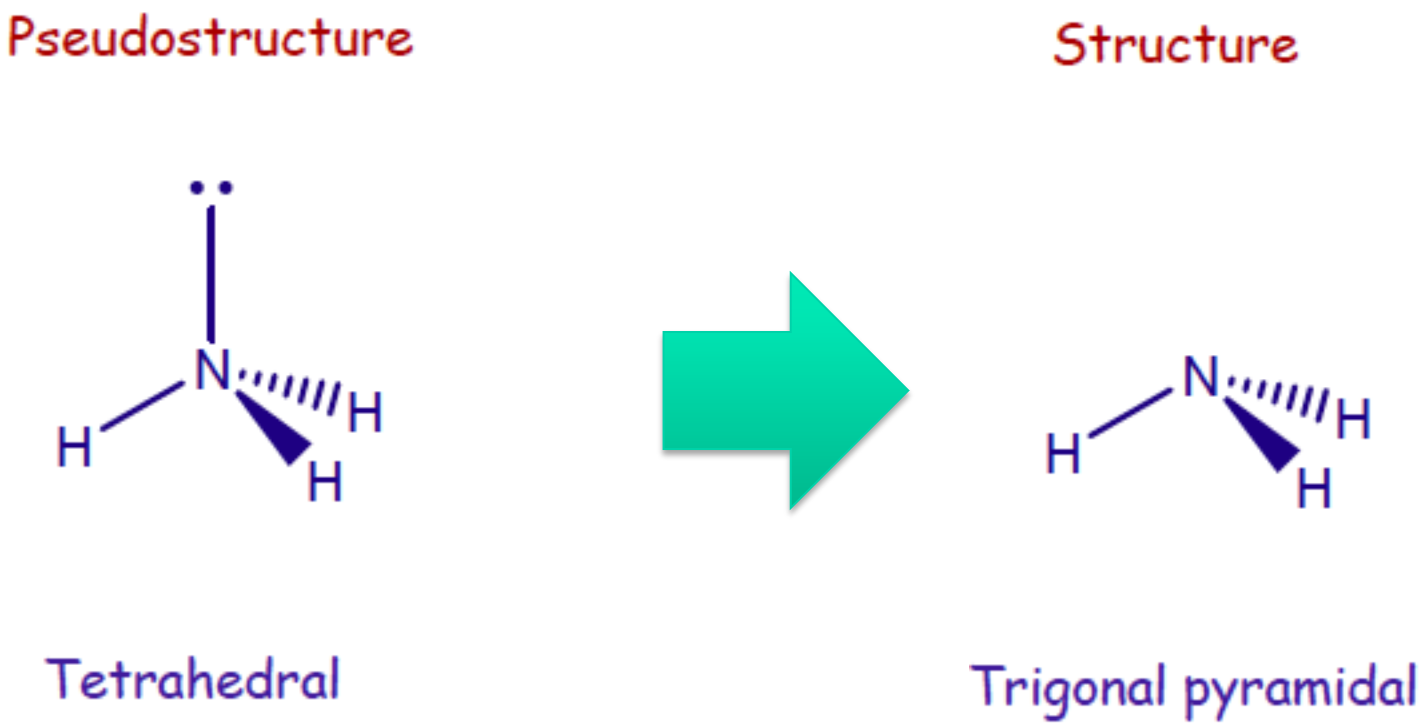
Predicting the shapes of molecules with general formula AX_nE_m

-Repulsion: LP-LP > LP-BP > BP-BP

-Lone pairs occupy the largest site (e.g. equatorial in a trigonal bipyramid)

-If all sites are equal (e.g. octahedral geometry) then lone pairs will be trans to each other (i.e. forming a 180° angle)

-Double bonds occupy more space than single bonds - Bonding pairs to electronegative substituents occupy less space than those to more electropositive substituents.



AX_3E

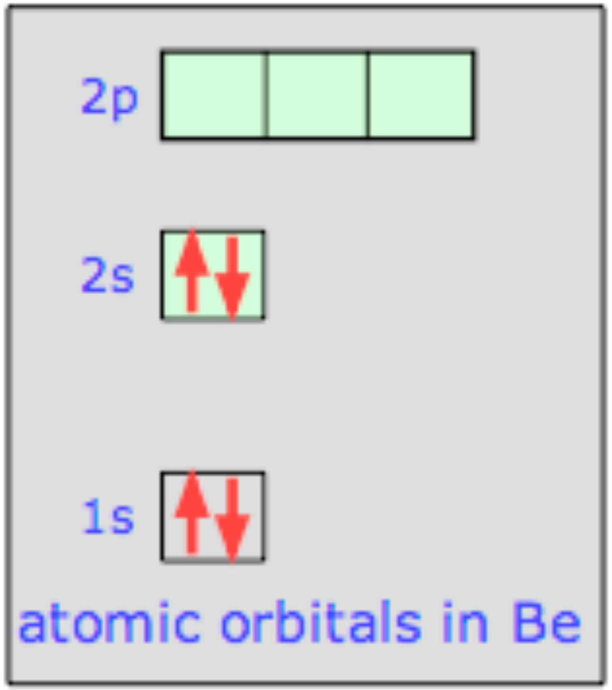
trigonal (bent)

AX_2E_2

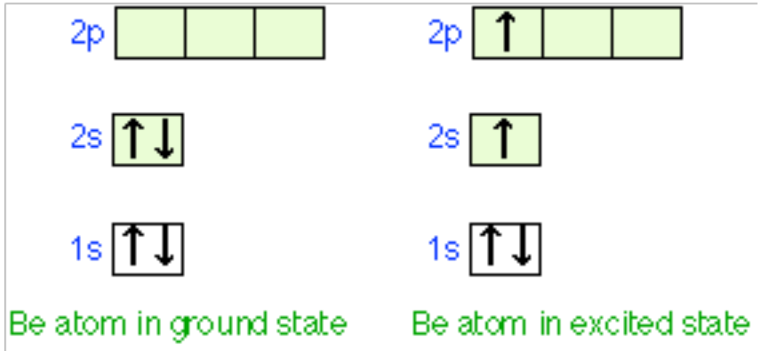
Why atomic orbitals don't work for molecules

Bonding in beryllium hydride

Consider how we might explain the bonding in a compound of divalent beryllium, such as beryllium hydride, BeH_2. The beryllium atom, with only four electrons, has a configuration of $1s^2 2s^2$. Note that the two electrons in the 2s orbital have opposite spins and constitute a stable pair that has no tendency to interact with unpaired electrons on other atoms.



The only way that we can obtain two unpaired electrons for bonding in beryllium is to promote one of the 2s electrons to the 2p level. However, the energy required to produce this excited-state atom would be sufficiently great to discourage bond formation. It is observed that Be does form reasonably stable bonds with other atoms. Moreover, the two bonds in BeH_2 and similar molecules are completely equivalent; this would not be the case if the electrons in the two bonds shared Be orbitals of different types, as in the "excited state" diagram above.



These facts suggest that it is incorrect to assume that the distribution of valence electrons that are shared with other atoms can be described by atomic-type s, p, and d orbitals at all.

Theory of hybrid orbitals (1928-)

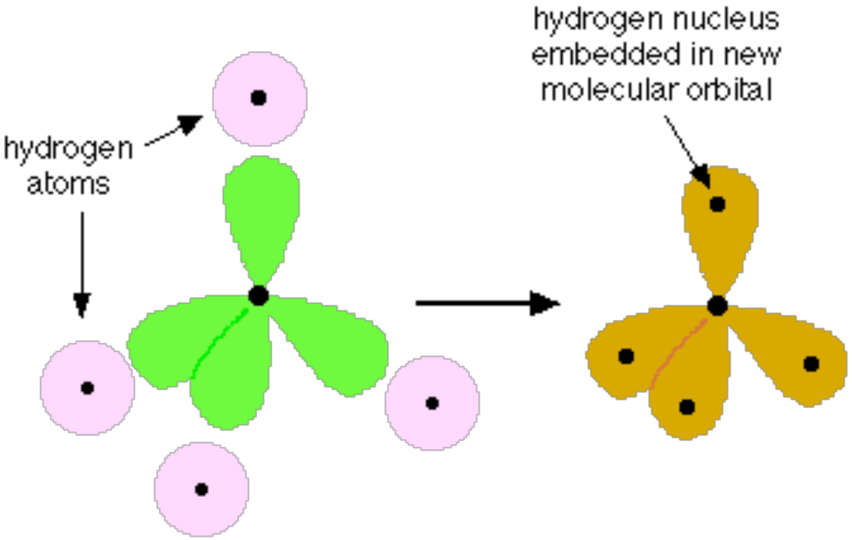
Linus Pauling (USA, 1901-1994)

Most known american chemist of 20th century,
Nobel prize: for chemistry 1954, for peace 1962

hybrid orbitals
- principle

atomic orbitals
do combine

if *s*, *p*, *d* orbitals occupied by the valence electrons of adjacent atoms are combined in a suitable way, the hybrid orbitals that result will have the character and directional properties that are consistent with the bonding pattern in the molecule.



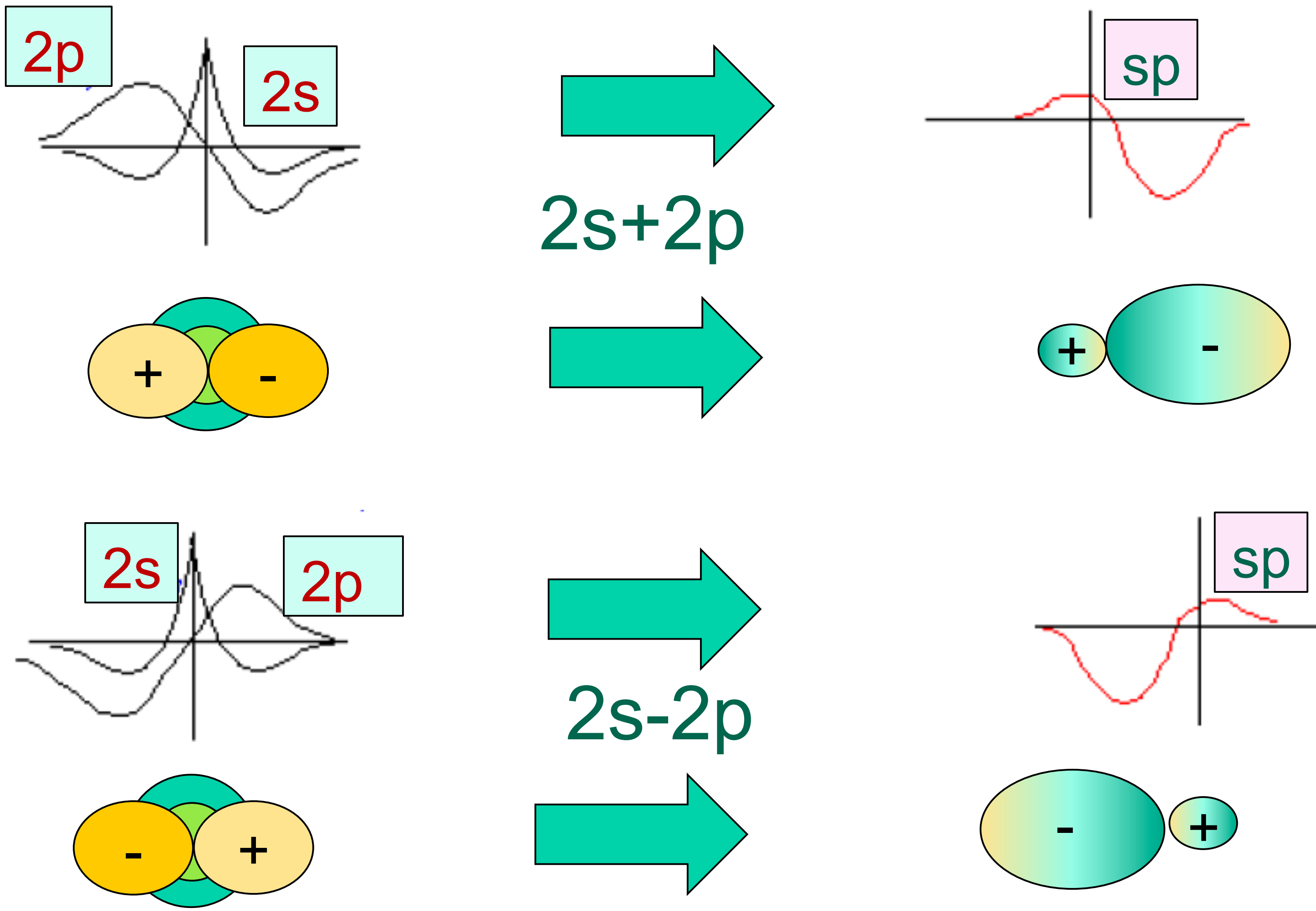
What are hybrid orbitals?

we will look at a model that starts out with the familiar valence-shell atomic orbitals, and allows them to combine to form **hybrid orbitals** whose shapes **conform** quite well to **the bonding geometry** that we observe in a wide **variety of molecules**.

orbital: region of space around the nucleus in which the probability of finding the electron exceeds some arbitrary value, such as 90% or 99%.

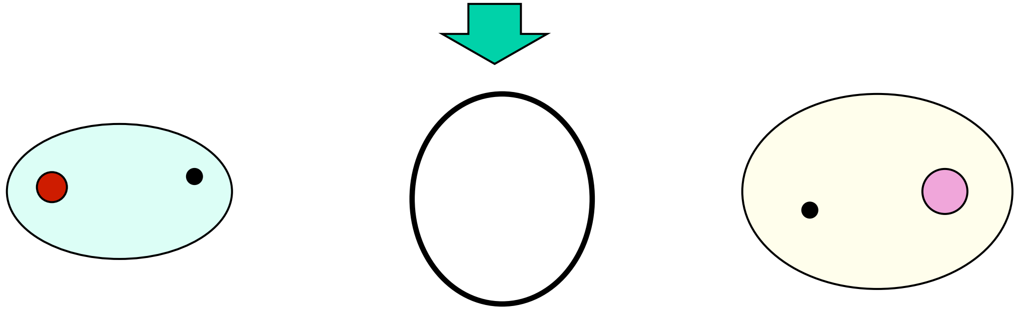
Orbitals of all types are mathematical functions that describe particular standing-wave patterns that can be plotted on a graph but have no physical reality of their own. Because of their wavelike nature, two or more orbitals (i.e., two or more functions ψ) can be combined both in-phase and out-of-phase to yield a pair of resultant orbitals which, to be useful, must have squares that describe actual electron distributions in the atom or molecule.

Constructing hybrid orbitals: Hybrid orbitals are constructed by combining the ψ functions for atomic orbitals. Because wave patterns can combine both constructively and destructively, a pair of atomic wave functions such as the s- and p-orbitals shown at the left can combine in two ways, yielding the sp hybrids shown.



Covalent bond as an overlap of atomic and/or hybrid orbitals – valence bond theory

effective overlap



atom A•

atom B•

E_A

E_{AB}

E_B

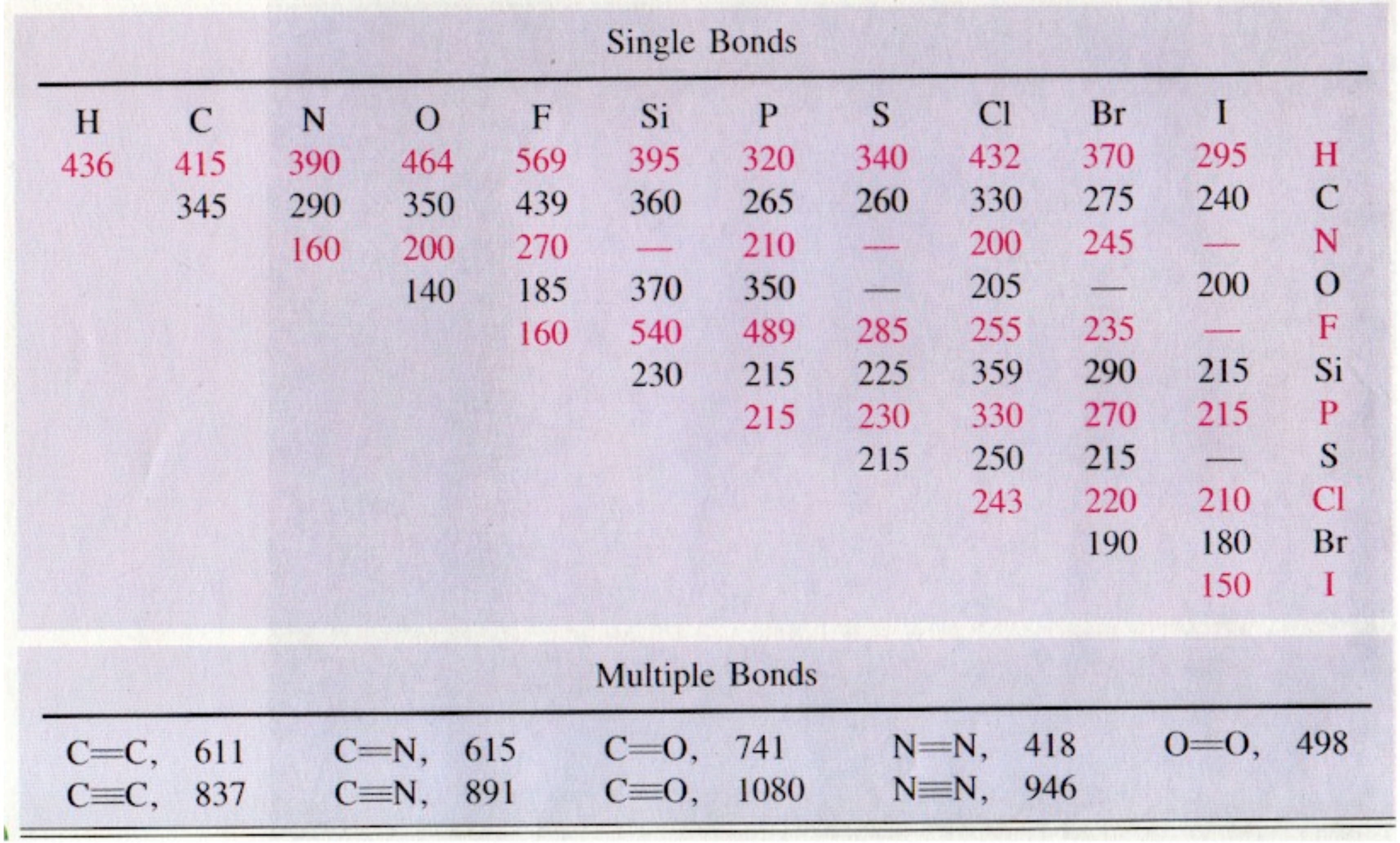
$E_v = E_{AB} - E_A - E_B$

energy of covalent bond, bonding energy

kJ/mol, eV

$\sim x\,.10^2$ kJ/mol

Bond energies in kJ/mole



Single Bonds

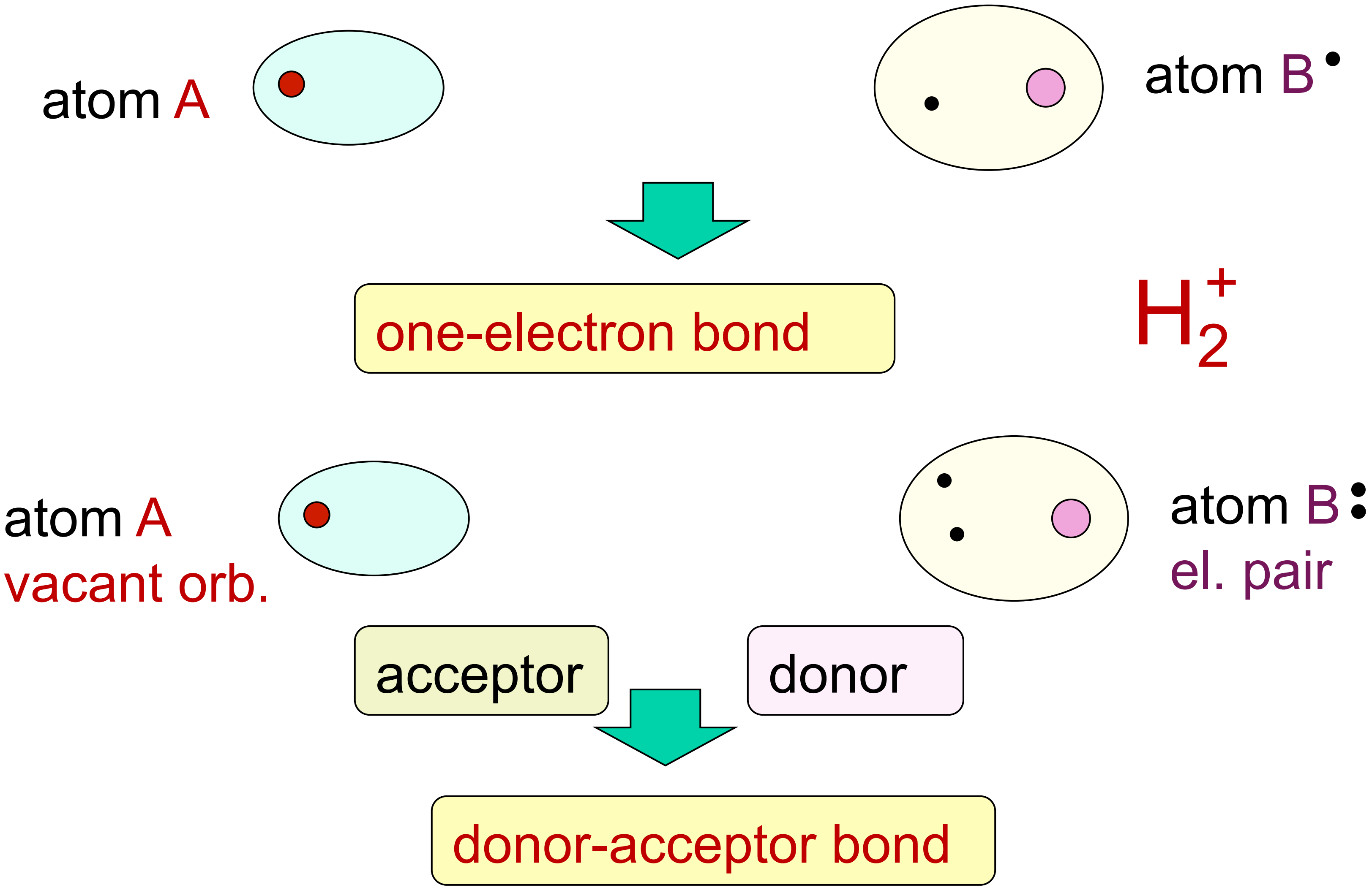
H	C	N	O	F	Si	P	S	Cl	Br	I	
436	415	390	464	569	395	320	340	432	370	295	H
	345	290	350	439	360	265	260	330	275	240	C
		160	200	270	—	210	—	200	245	—	N
			140	185	370	350	—	205	—	200	O
				160	540	489	285	255	235	—	F
					230	215	225	359	290	215	Si
						215	230	330	270	215	P
							215	250	215	—	S
								243	220	210	Cl
									190	180	Br
										150	I

Multiple Bonds

$C{=}C$, 611 $C{=}N$, 615 $C{=}O$, 741 $N{=}N$, 418 $O{=}O$, 498

$C{\equiv}C$, 837 $C{\equiv}N$, 891 $C{\equiv}O$, 1080 $N{\equiv}N$, 946

Covalent bond as an overlap of atomic and/or hybrid orbitals – valence bond theory



atom A

atom B•

one-electron bond

H_2^+

atom A
vacant orb.

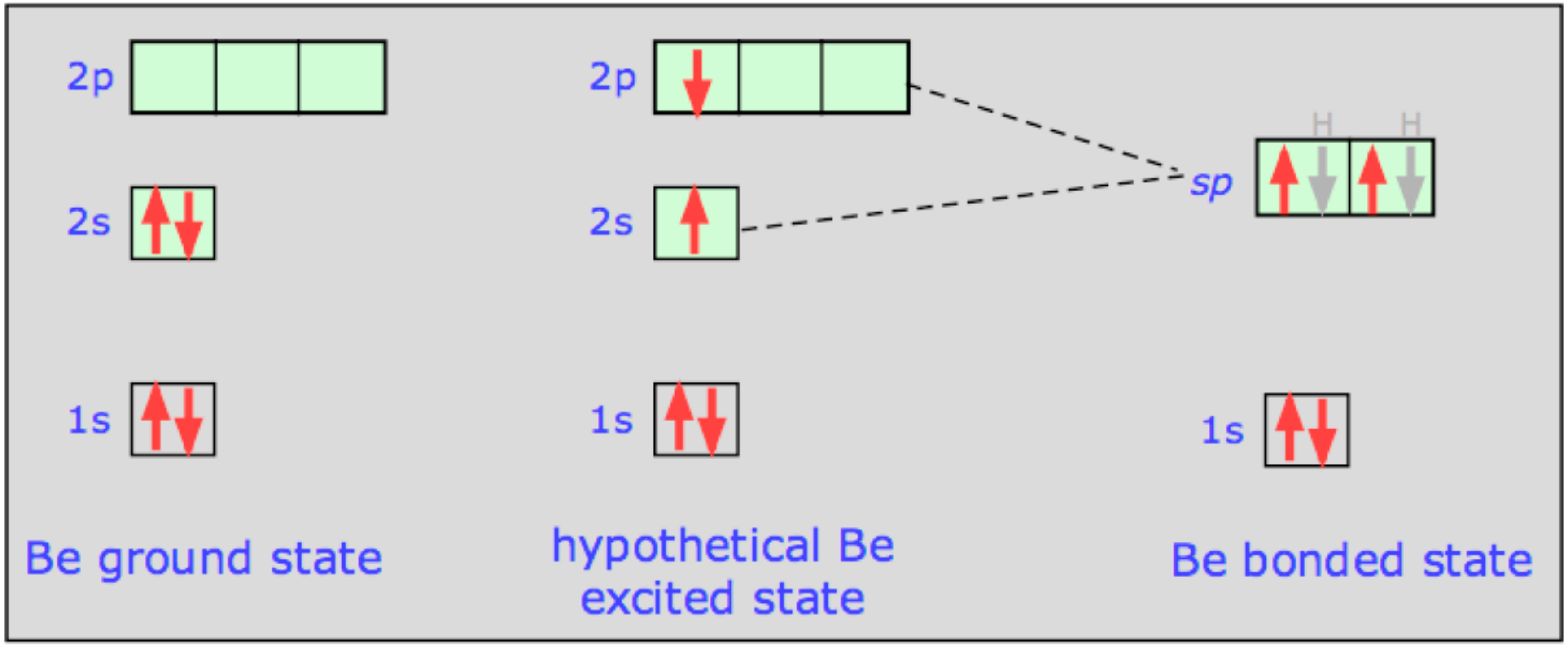
atom B:
el. pair

acceptor

donor

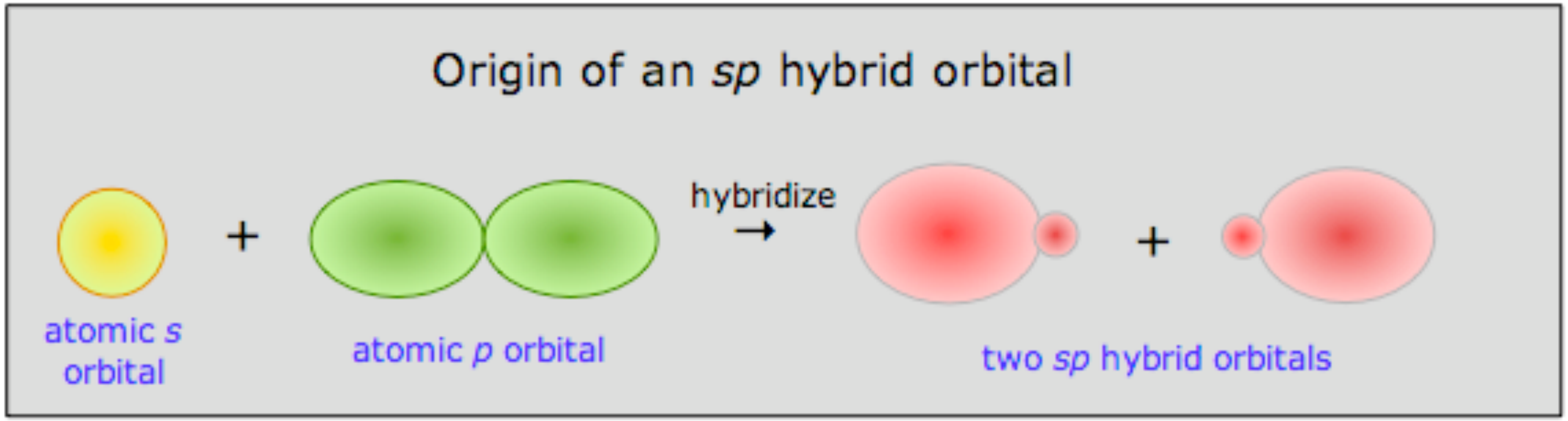
donor-acceptor bond

Energy standpoint



Notice here that 1) the total number of occupied orbitals is conserved, and 2) the two sp hybrid orbitals are intermediate in energy between their parent atomic orbitals.

In terms of plots of the actual orbital functions ψ we can represent the process as follows:

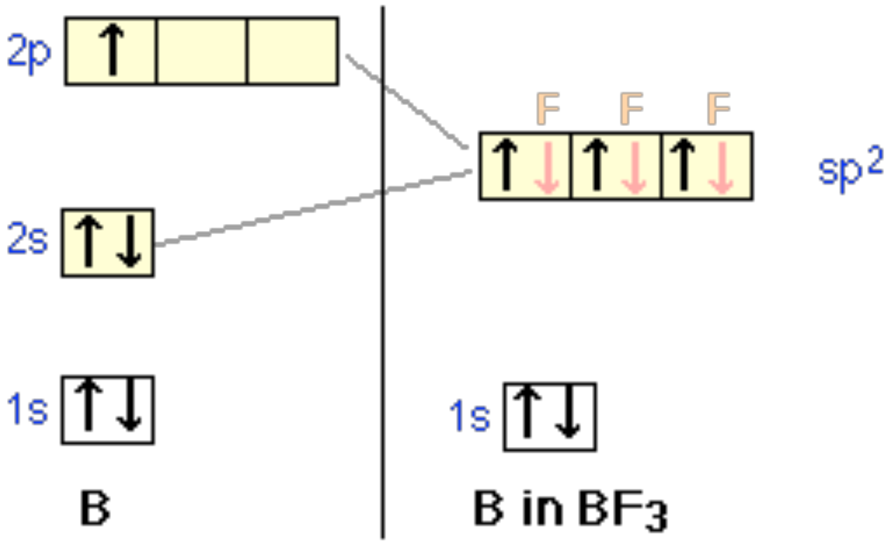


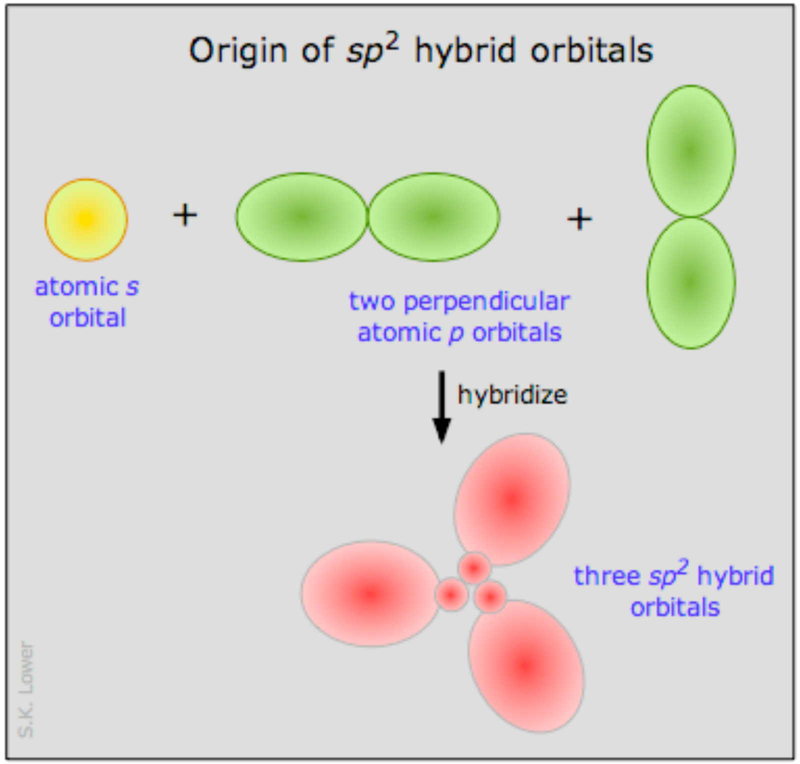
The probability of finding the electron at any location is given not by ψ, but by ψ^2, whose form is roughly conveyed by the solid figures in this illustration.

Digonal bonding: sp-hybrid orbitals

Hybrids derived from atomic s- and p orbitals

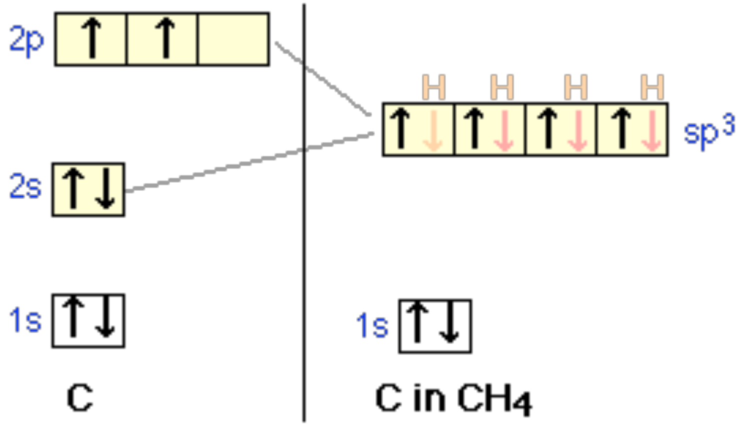
Trigonal (sp^2) hybridization





The molecule has plane trigonal geometry.

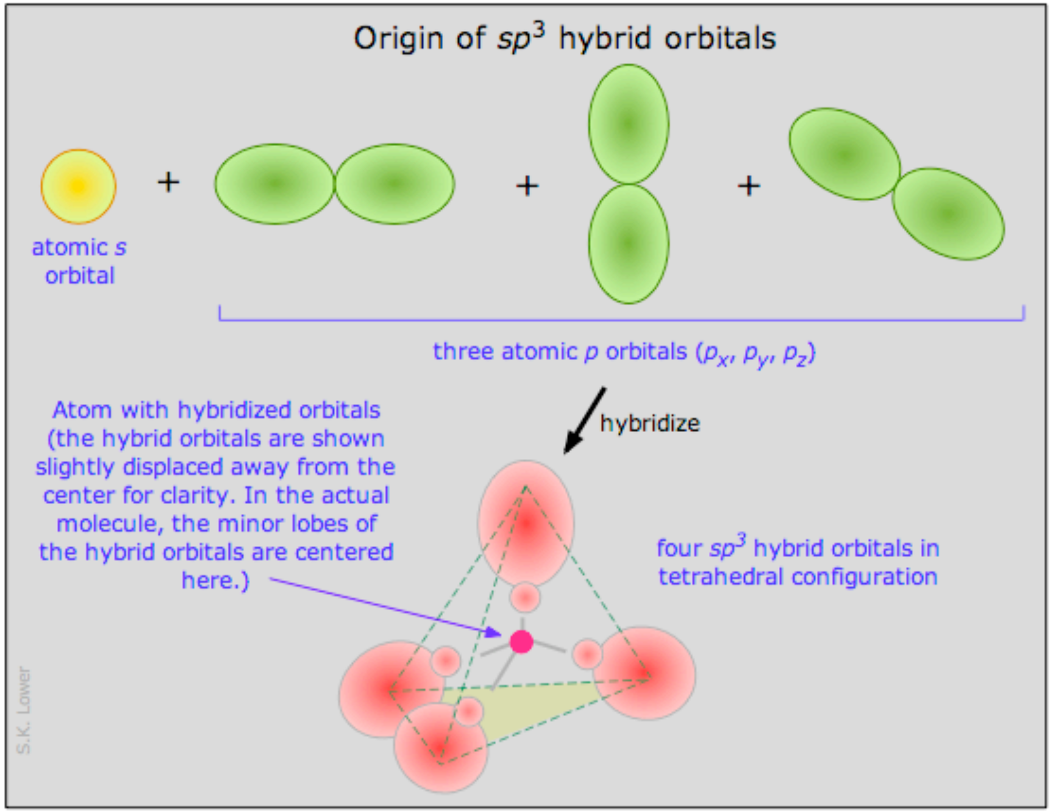
Hybrids derived from atomic s- and p orbitals



Tetrahedral (sp^3) hybridization

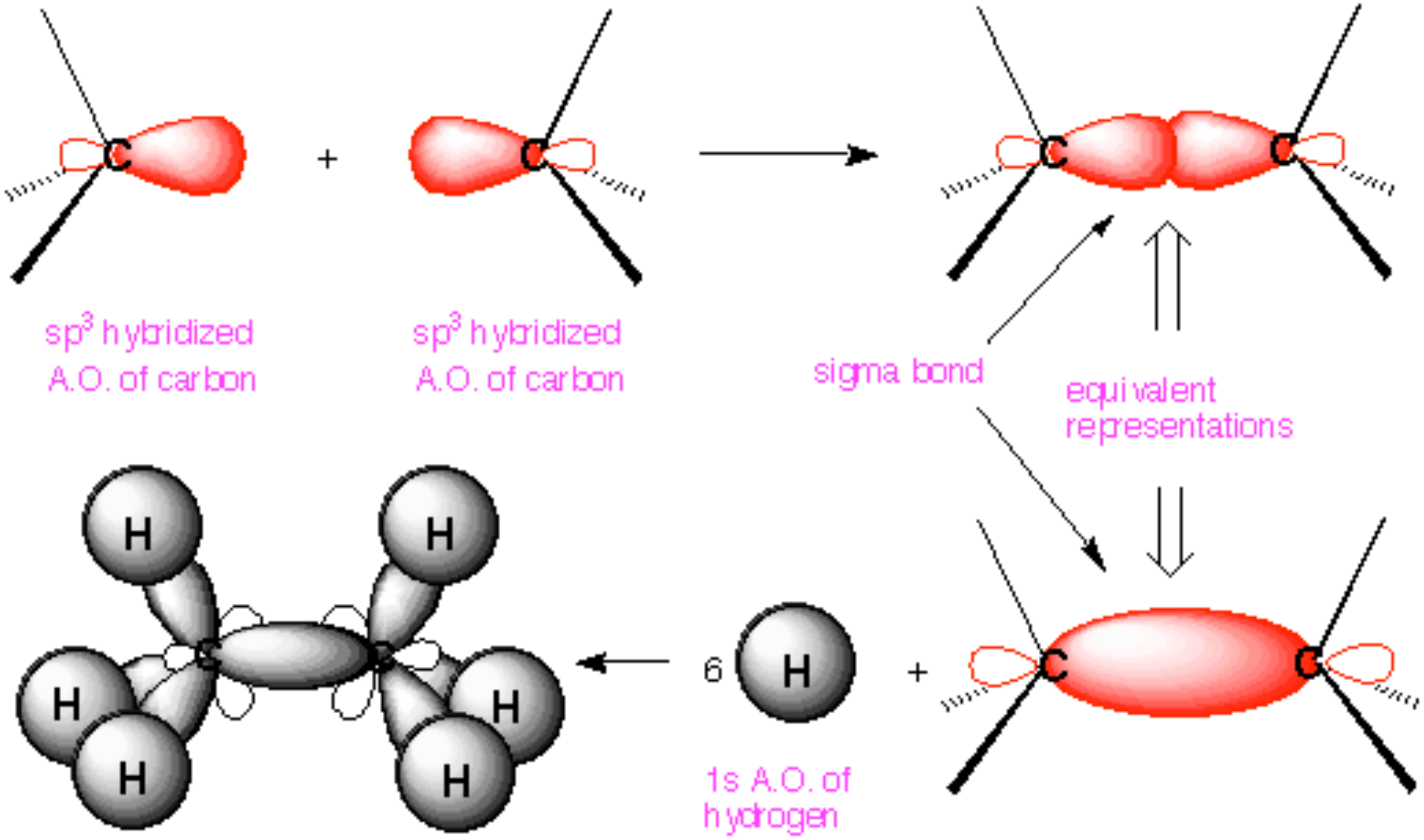
several tetravalent molecules

In the ground state of the free carbon atom, there are two unpaired electrons in separate 2p orbitals. In order to form four bonds (tetravalence), need four unpaired electrons in four separate but equivalent orbitals. We assume that the single 2s, and the three 2p orbitals of carbon mix into four sp^3 hybrid orbitals which are chemically and geometrically identical



Bonding with hybrid orbitals

The M.O.s of Ethane

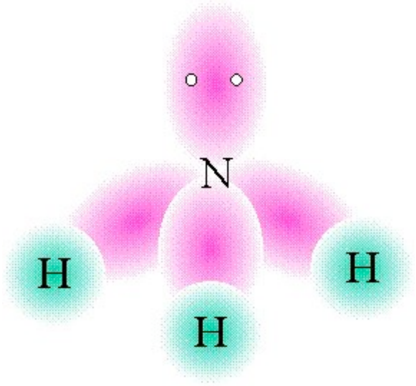


ethane
CC bond 1.54 Å, 88kcal/mol
CH bond 1.10 Å, 98 kcal/mol

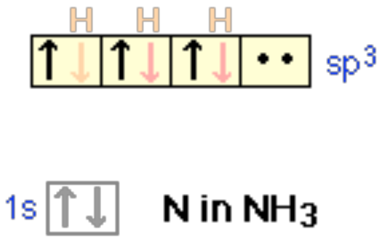
Lone pair electrons in hybrid obitals

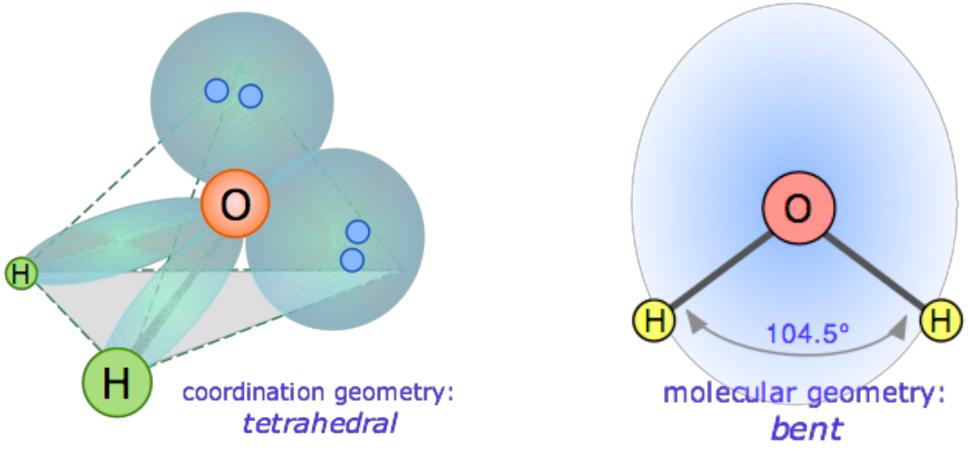
If lone pair electrons are present on the central atom, these can occupy one or more of the sp^3 orbitals. This causes the molecular geometry to be different from the coordination geometry, which remains tetrahedral.

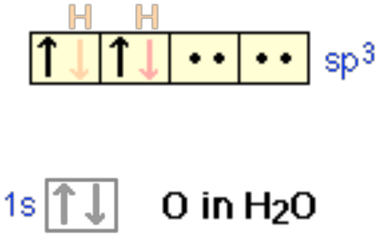
ammonia



sp^3 hybrid orbitals (tetrahedral)



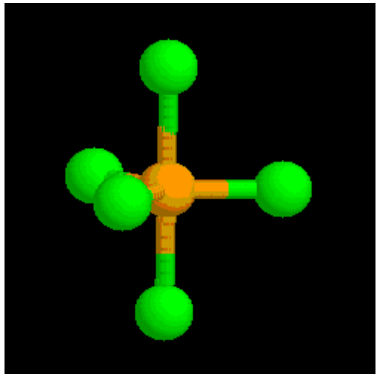


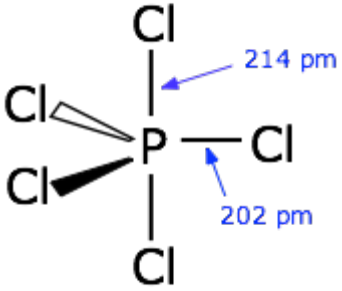


Structure: **trigonal bipyramid**
sp^3d (dsp^3) hybrid orbitals

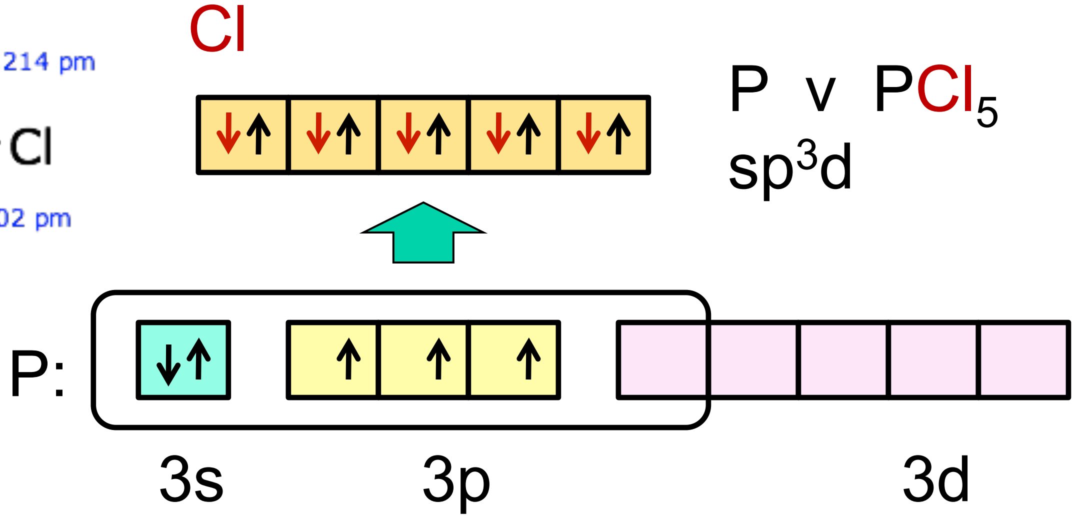
If the energies of s, p, d are close

$s+p_x+p_y+p_z+d_{z^2}$ (n) $\longrightarrow$ 5 (sp^3d)



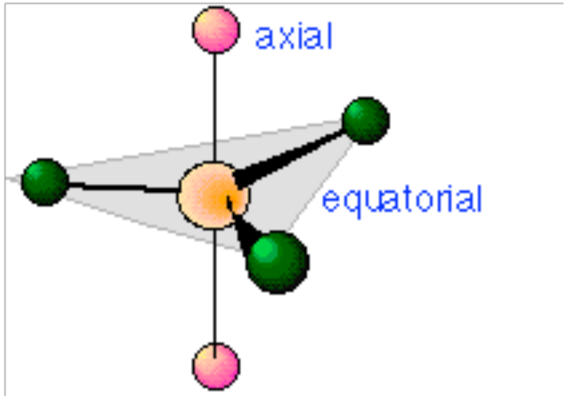


PCl_5



P v PCl_5
sp^3d

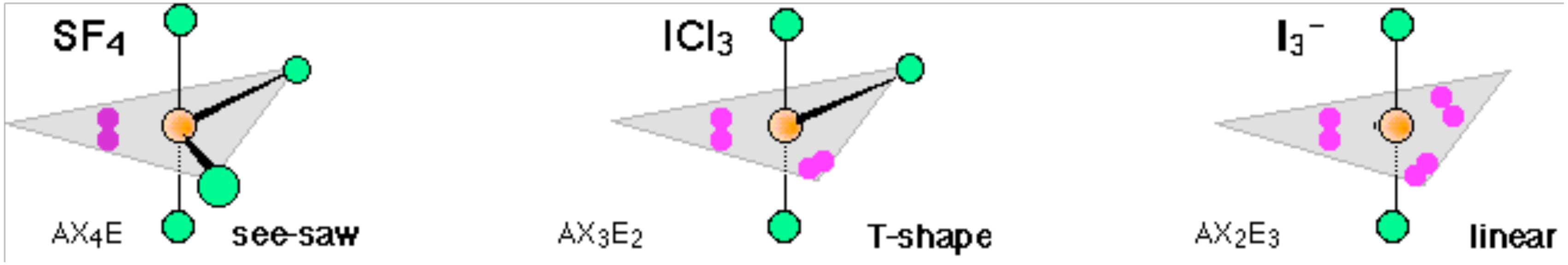
$dsp^3 \longleftarrow d_{z^2}$ (n-1) $+s+p_x+p_y+p_z$



The shape of PCl_5 and similar molecules is a **trigonal bipyramid**

$\mathbf{sp^3d}$ hybrids

With lone (non-bonding) pairs:



Structure:: **octahedron**

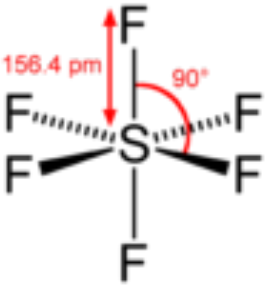
sp^3d^2 (d^2sp^3) hybrid orbitals

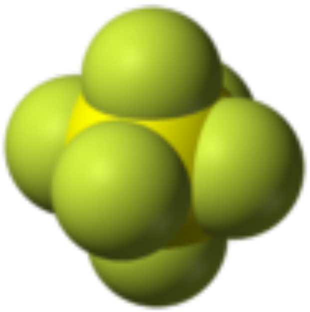
If the energies of s, p, d are close

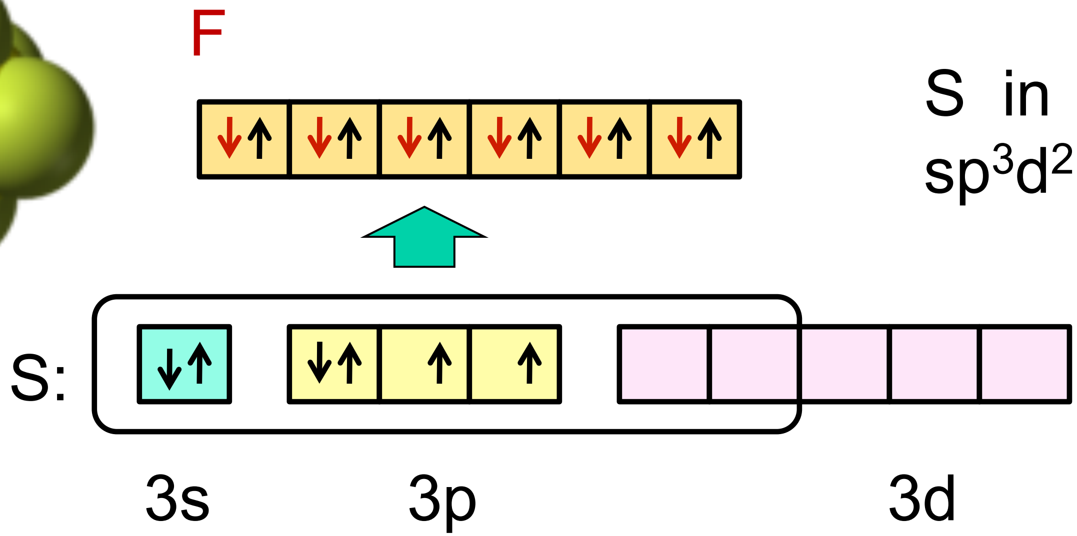
$s+p_x+p_y+p_z \longrightarrow$ 6 (sp^3d^2)

$+d_{x^2-y^2}+d_{z^2}$ (n) (n-1) 6 (d^2sp^3)

SF_6



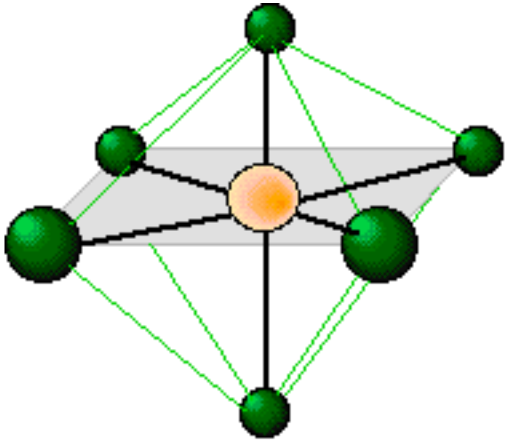




S in SF_6

sp^3d^2

Octahedral coordination



six electron pairs will try to point toward the corners of an **octahedron**

two square-based pyramids joined base to base

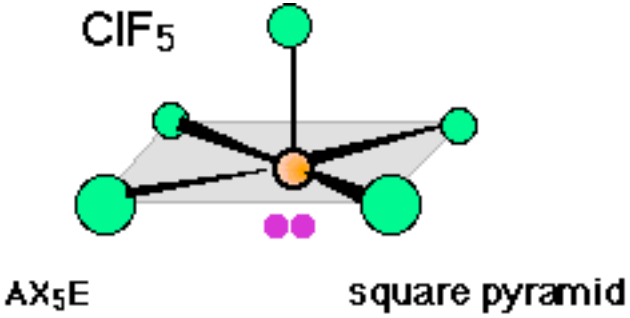
sp^3d^2 / d^2sp^3

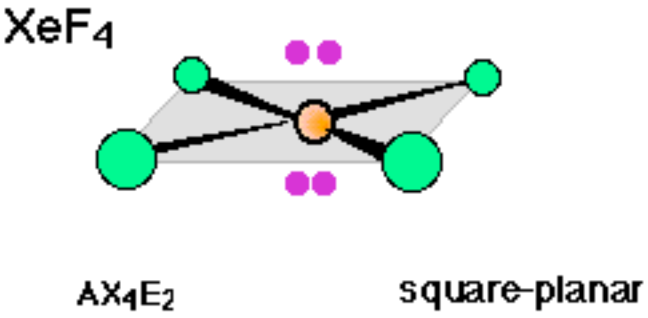
SF_6

transition metal complexes

$Fe(H_2O)_6^{3+}$

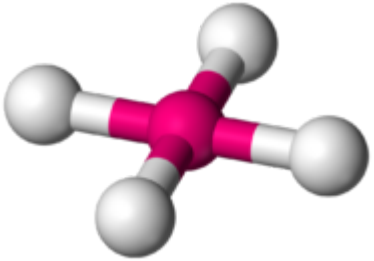
with lone pairs

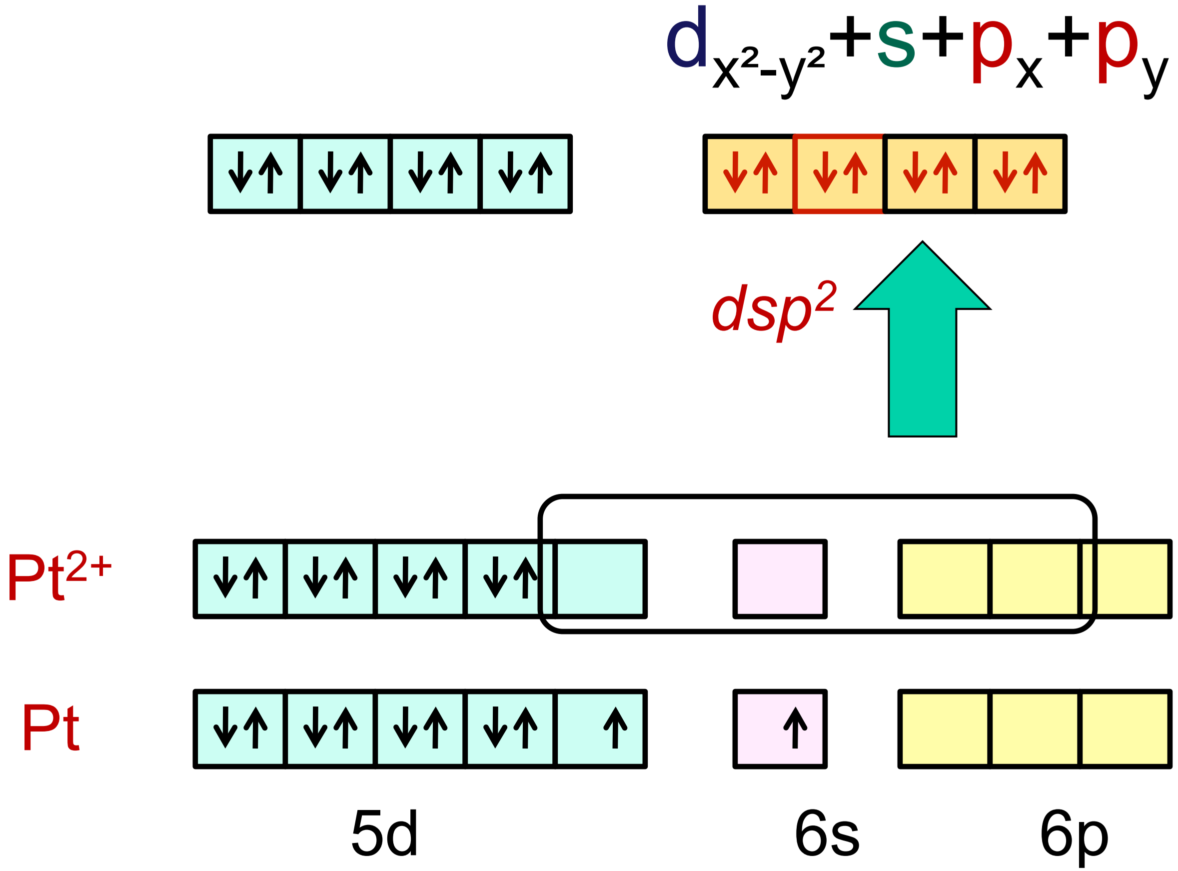




d^3s, sd^3: tetrahedron *dsp^2, sp^2d:* square

$[PtCl_4]^{2-}$





$d_{x^2-y^2}+s+p_x+p_y$

dsp^2

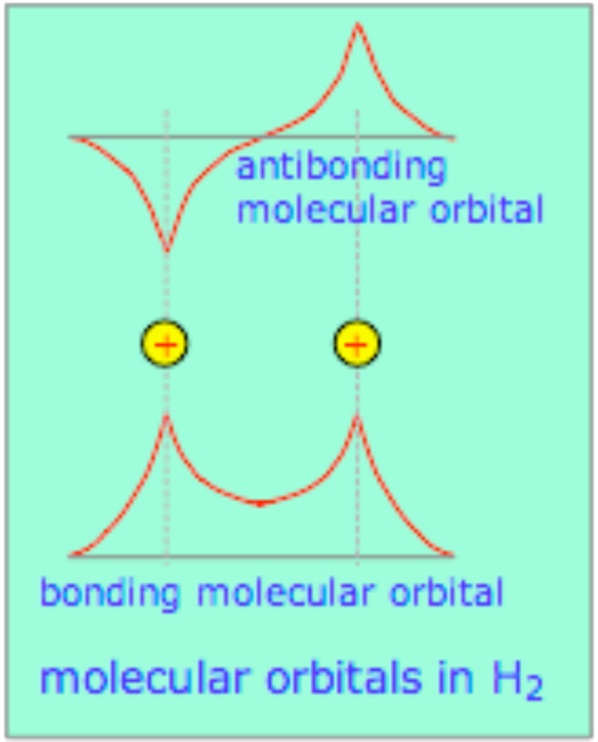
Pt^{2+}

Pt

5d 6s 6p

VSEPR fails!

The molecular orbital model



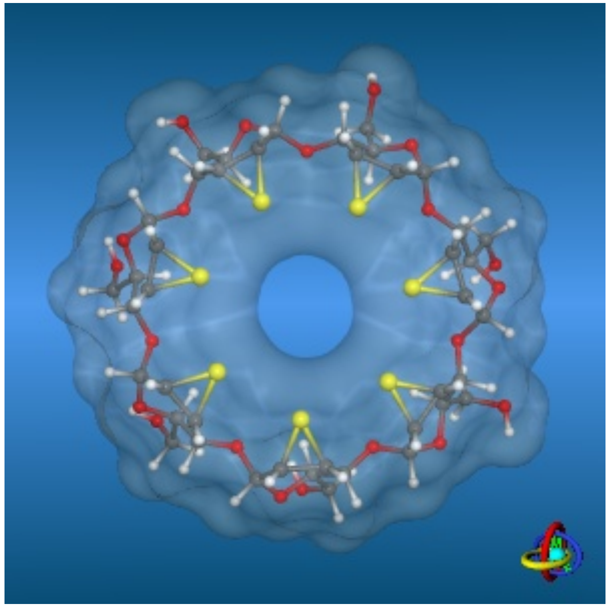
This model takes a more fundamental approach by regarding a molecule as a collection of valence electrons and positive cores. Just as the nature of atomic orbitals derives from the spherical symmetry of the atom, so will the properties of these new molecular orbitals be controlled by the interaction of the valence electrons with the multiple positive centers of these atomic cores.

These new orbitals, unlike those of the hybrid model, are delocalized; that is, they do not “belong” to any one atom but extend over the entire region of space that encompasses the bonded atoms.

Theory of molecular orbitals (MO)

local orbitals → global orbitals

MO-LCAO
Linear Combination of Atomic Orbitals



Epithio-cycloallin

$$\psi_i^{MO} = \sum_{m=1}^{N} \boxed{c_{mi}}\,\varphi_m^{AO} \qquad i=1,N$$

↑

a number – weight (importance) of m-th AO in i-th MO

electrons are not „localized“

↓

multi-center, delocalized bonds

$$\psi_i = \sum_{m=1}^{N} c_{mi}\varphi_m \qquad i=1,N$$

Maximum as many MOs as AOs!

discrete energy levels for ψ_i (MO)

equal energy for different ψ_i → degeneracy
degenerate orbitals

Aufbau principle analogic to atoms

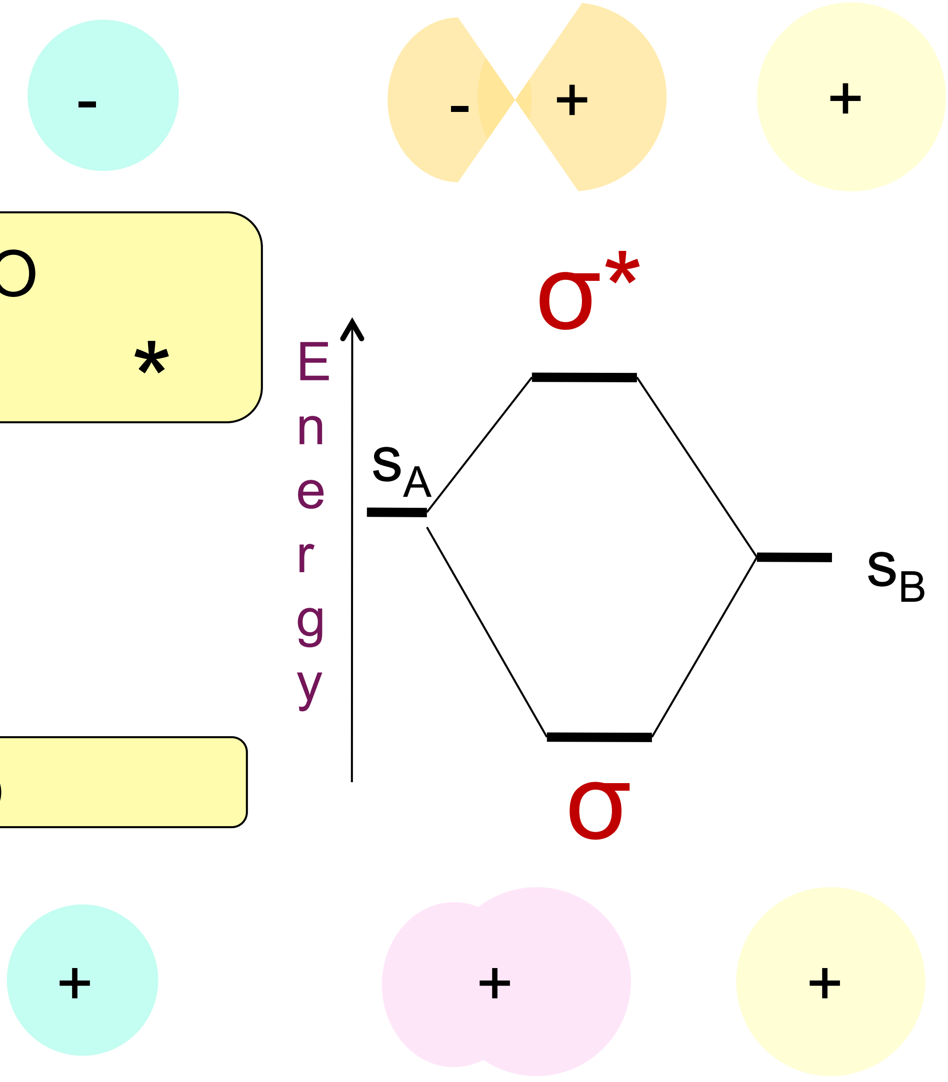
Pauli principle and Hund rule, as well

Molecular orbitals in two-atomic molecules

antibonding MO

*

s_A-s_B



MO energy diagram

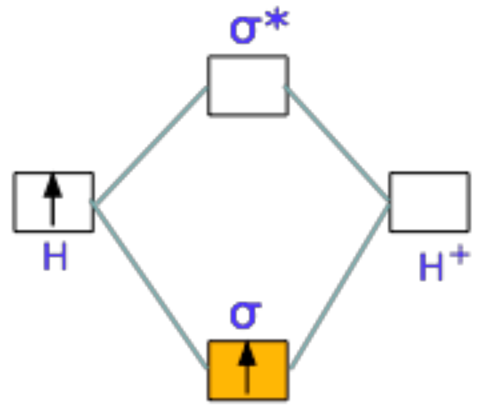
bonding MO

s_A+s_B

atom A

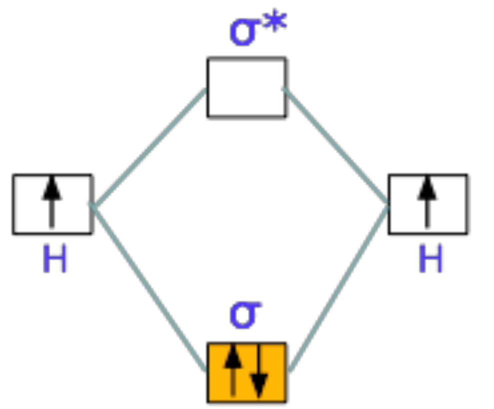
atom B

Molecular orbital diagrams



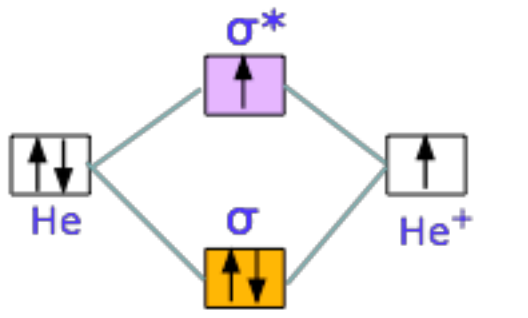
dihydrogen ion H_2^+

bond order 0.5
bond energy 270 kJ



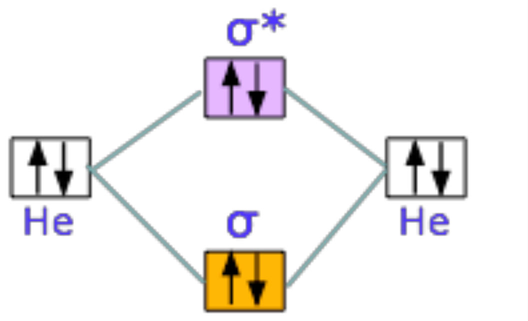
dihydrogen H_2

bond order 1
bond energy 452 kJ



dihelium ion He_2^+

bond order 0.5
bond energy 301 kJ

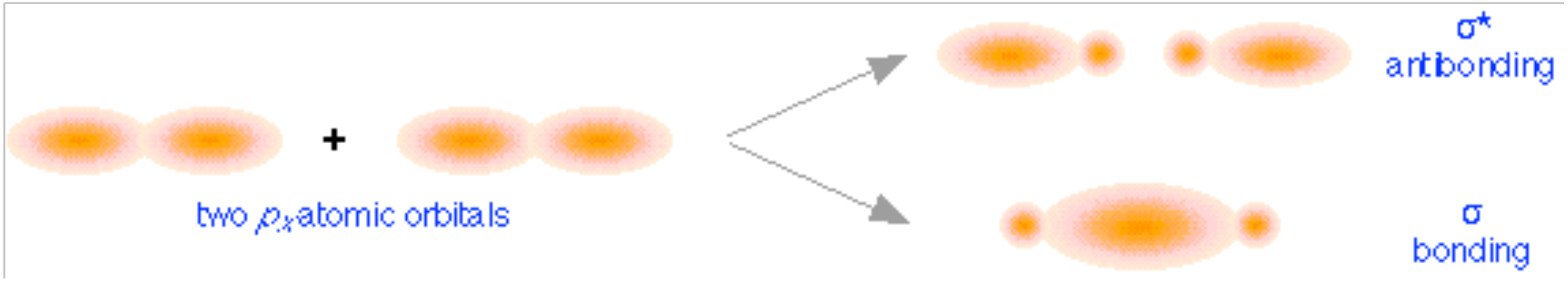


dihelium He_2

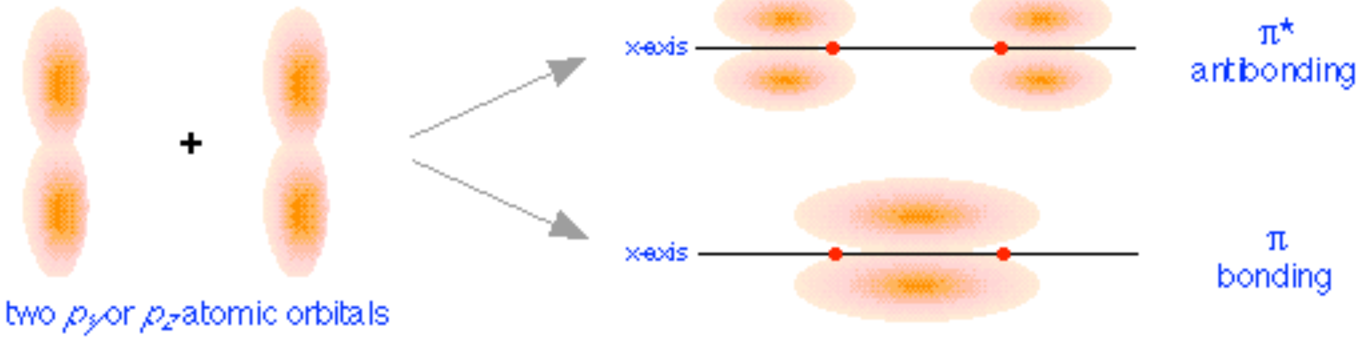
bond order 0
bond energy 0.05 kJ

Bond order is defined as the difference between the number of electron pairs occupying bonding and nonbonding orbitals in the molecule.

Sigma and pi orbitals

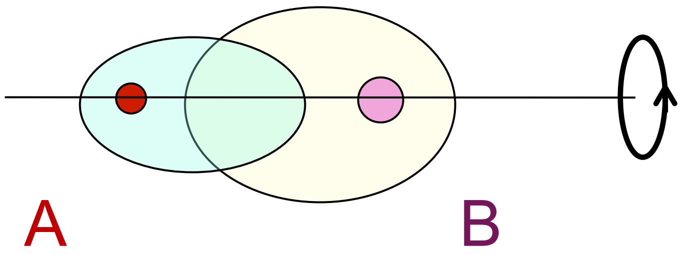


σ orbitals are **cylindrically symmetric** with respect to the line of centers of the nuclei

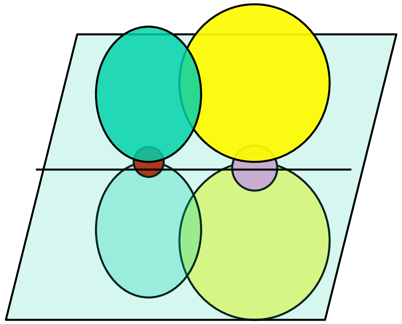


rather than being rotationally symmetric about the line of centers, these orbitals extend in both perpendicular directions from this line of centers. Orbitals having this more complicated symmetry are called π (pi) orbitals. There are two of them, π_y and π_z differing only in orientation, but otherwise completely equivalent. **Nodal plane along the bond!**

Types of covalent bonds, molecular orbitals – symmetry considerations



σ bond – circular symmetry



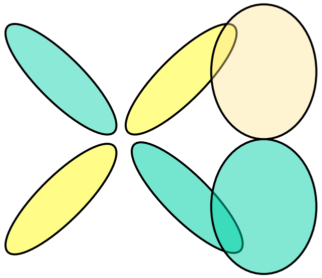
p-p

x-x

y-y

z-z

π bond – **single** nodal plane along the bond



d-p

xy-x

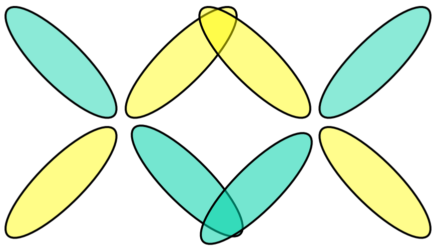
xy-y

xz-z

xz-x

yz-y

yz-z



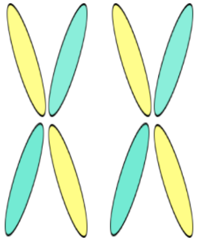
d-d

xy-x y

xz-xz

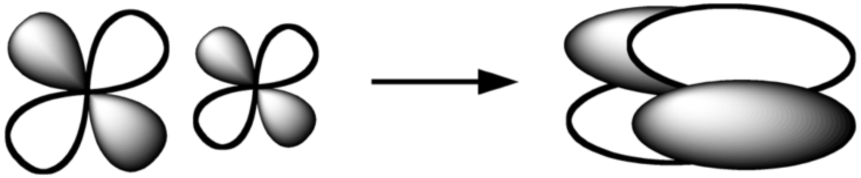
yz-yz

Types of covalent bonds, molecular orbitals – symmetry considerations

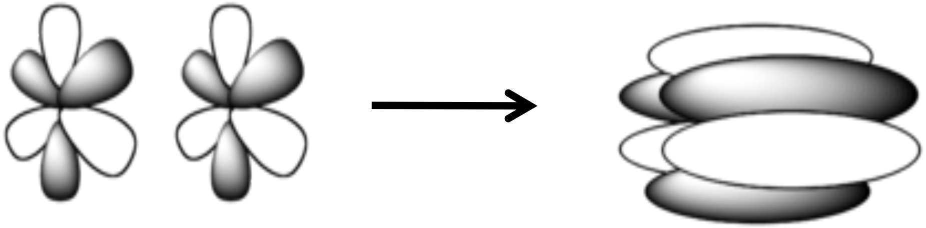


d-d

δ bond – 2 nodal plains along the bond



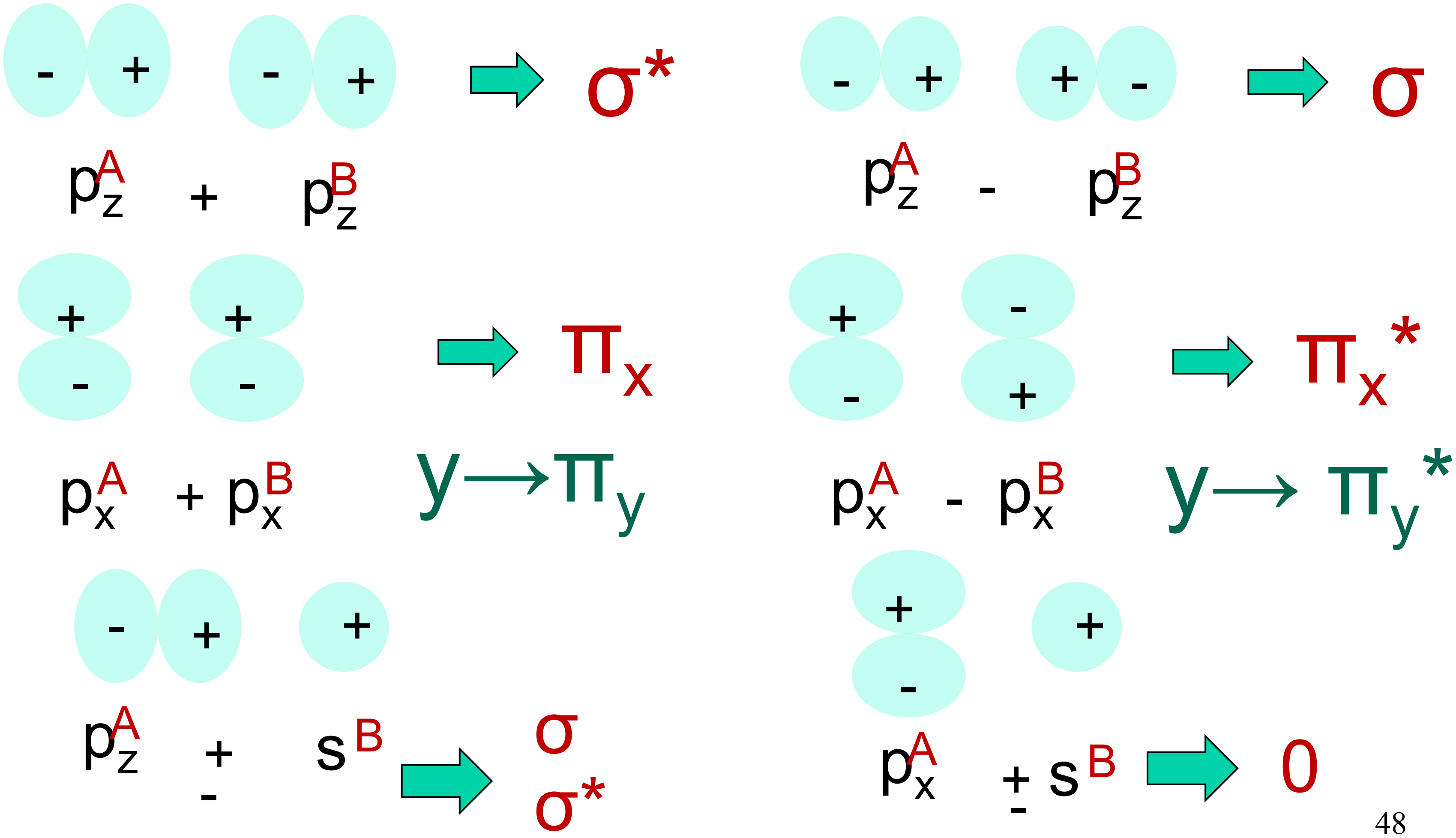
φ bond – 3 nodal plains along the bond



f-f

Molecular orbitals in two-atomic molecules

atom A $\xrightarrow[z]{}$ atom B



$p_z^A + p_z^B$ ⇨ σ^*

$p_z^A - p_z^B$ ⇨ σ

$p_x^A + p_x^B$ ⇨ π_x

y → π_y

$p_x^A - p_x^B$ ⇨ π_x^*

y → π_y^*

$p_z^A \pm s^B$ ⇨ σ, σ^*

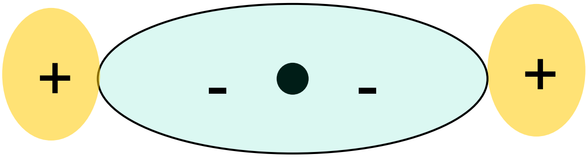
$p_x^A \pm s^B$ ⇨ 0

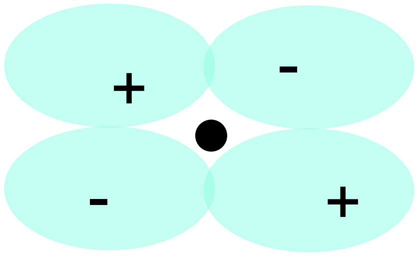
Molecular orbitals generally for molecules with a center of symmetry

ak $\sigma(x,y,z)= \sigma(-x,-y,-z)$

$\pi(x,y,z)= \pi(-x,-y,-z)$ $\Rightarrow$ σ_g π_g

„gerade“

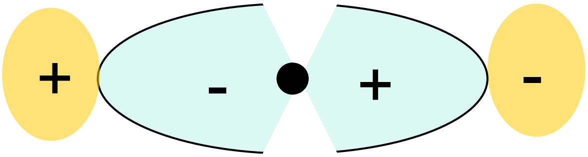


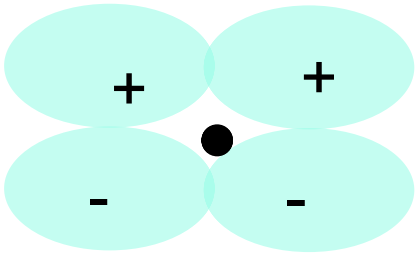


ak $\sigma(x,y,z)= -\sigma(-x,-y,-z)$

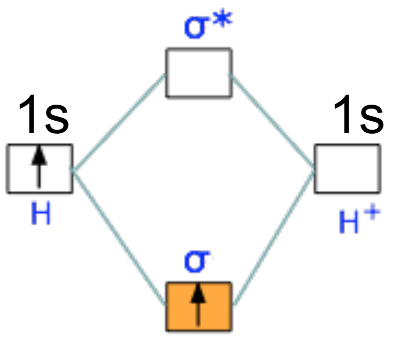
$\pi(x,y,z)= -\pi(-x,-y,-z)$ $\Rightarrow$ σ_u π_u

„ungerade“

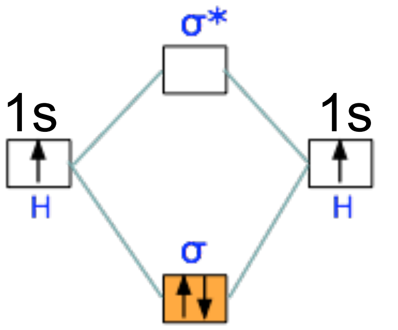




Molecular orbitals in H_2^+, H_2, He_2^+, He_2



dihydrogen ion H_2^+
bond order 0.5
bond energy 270 kJ



dihydrogen H_2
bond order 1
bond energy 452 kJ

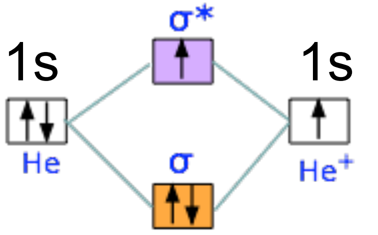
Bond energy in kJ/mol

Bond order:

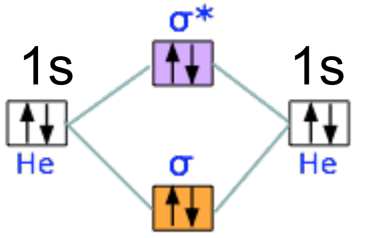
$$0.5(\Sigma e^b - \Sigma e^*)$$

e^b-> e in bonding MO

e^*-> e in antibonding MO

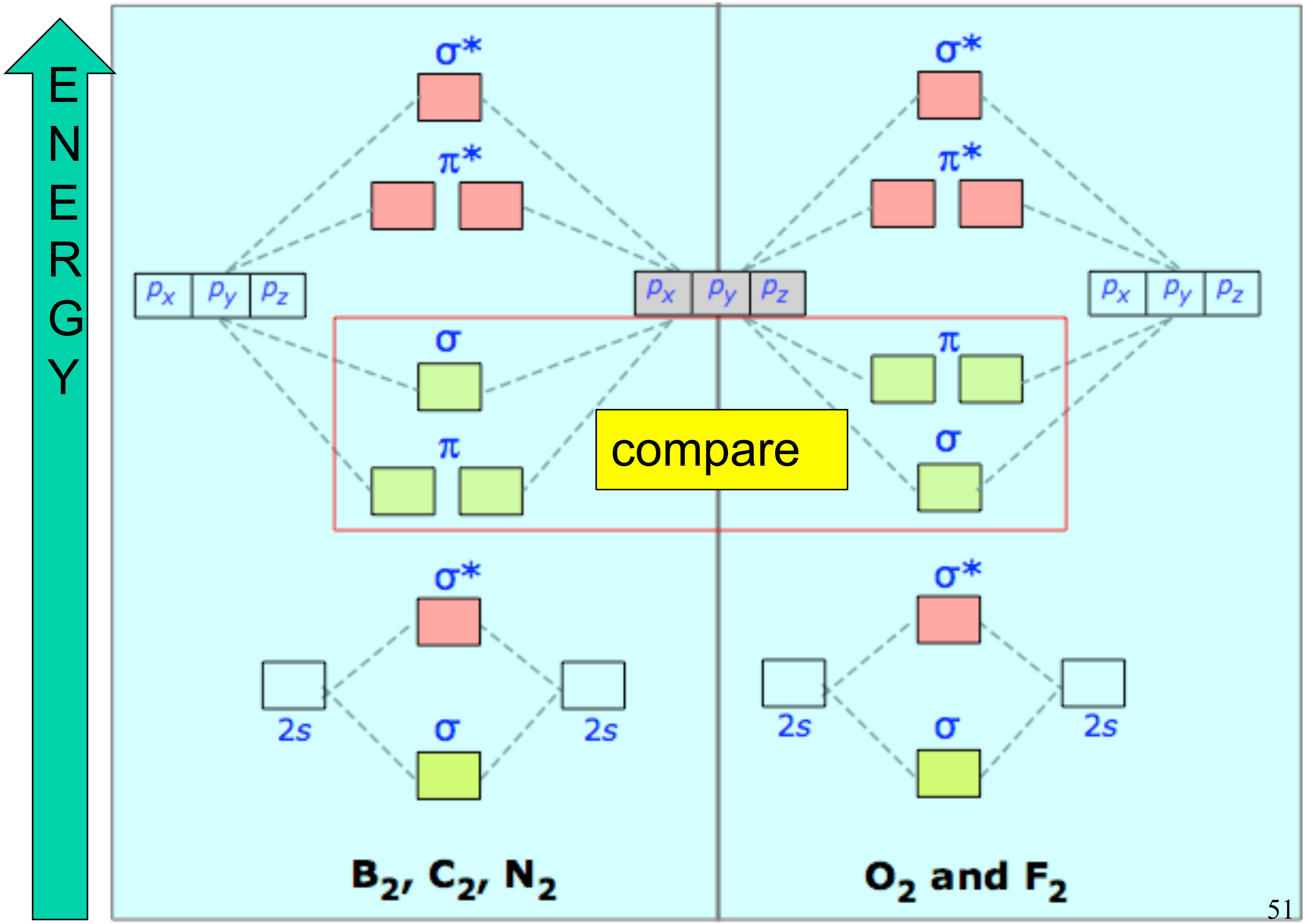


dihelium ion He_2^+
bond order 0.5
bond energy 301 kJ



dihelium He_2
bond order 0
bond energy 0.05 kJ

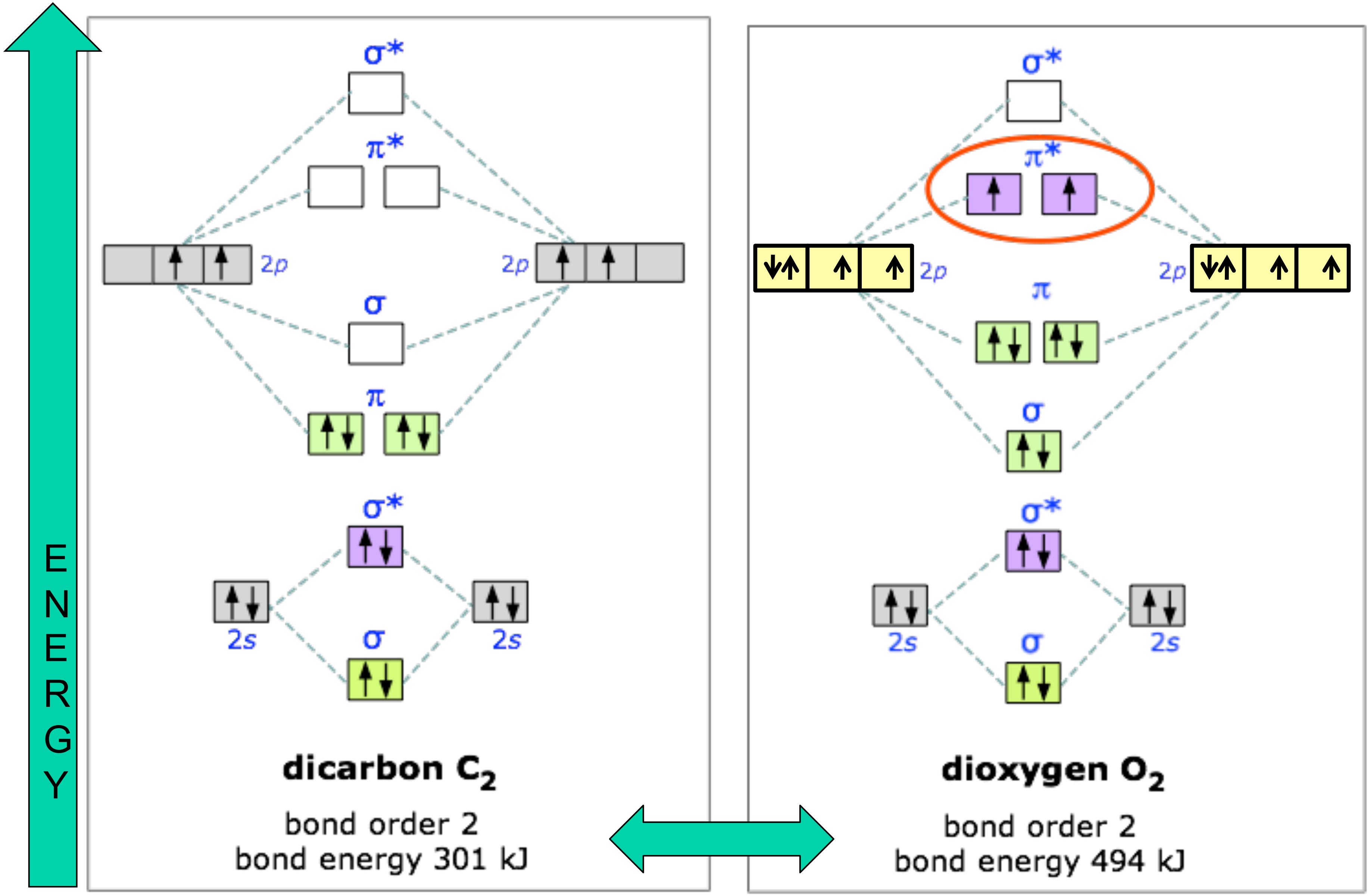
Molecular orbitals in homonuclear diatomics



compare

B_2, C_2, N_2

O_2 and F_2

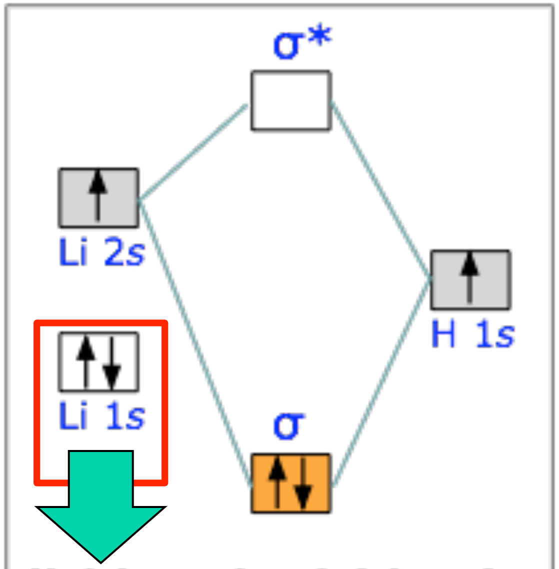


dicarbon C_2

bond order 2
bond energy 301 kJ

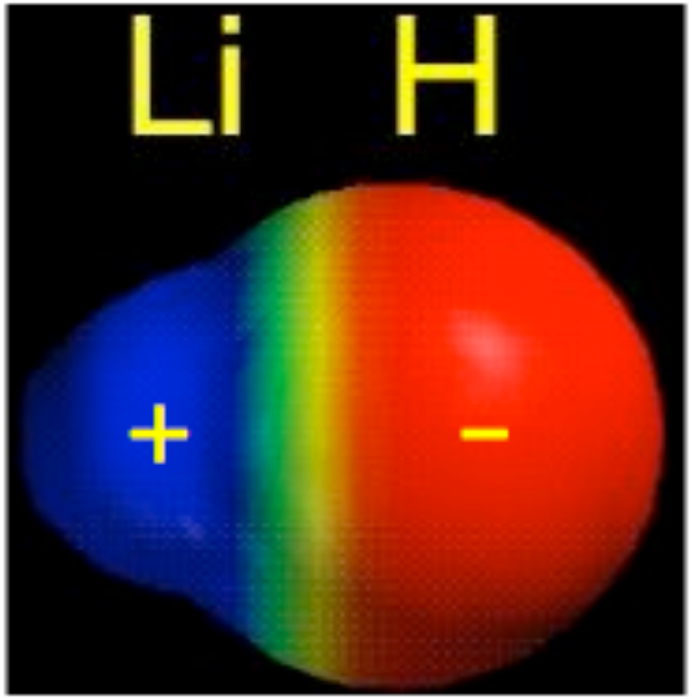
dioxygen O_2

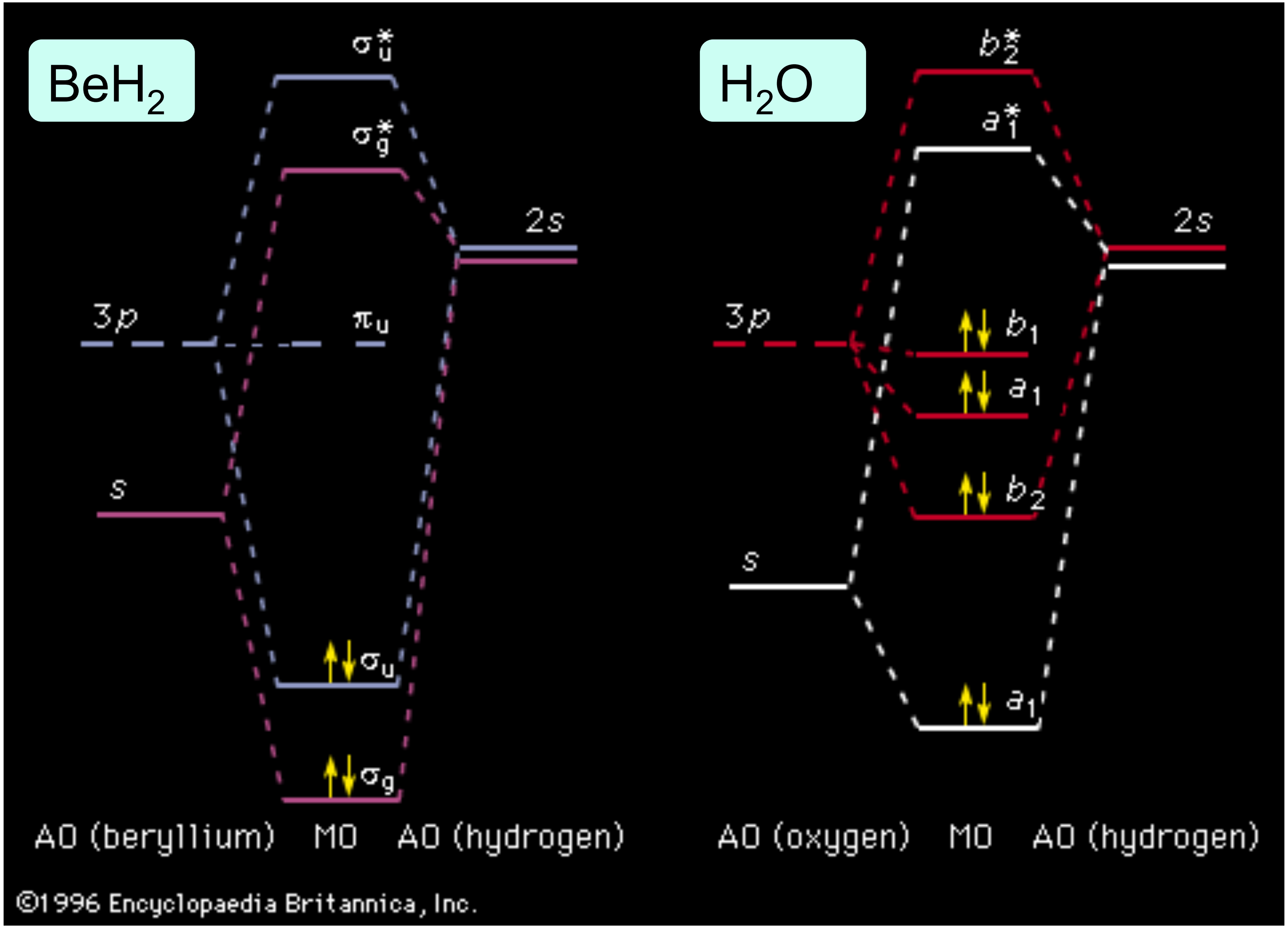
bond order 2
bond energy 494 kJ



lithium hydride LiH

bond order 1
bond energy 243 kJ




BeH$_2$
σ_u^*
σ_g^*
2s
3p
π_u
s
σ_u
σ_g
AO (beryllium)
MO
AO (hydrogen)
H$_2$O
b_2^*
a_1^*
2s
3p
b_1
a_1
b_2
s
a_1
AO (oxygen)
MO
AO (hydrogen)
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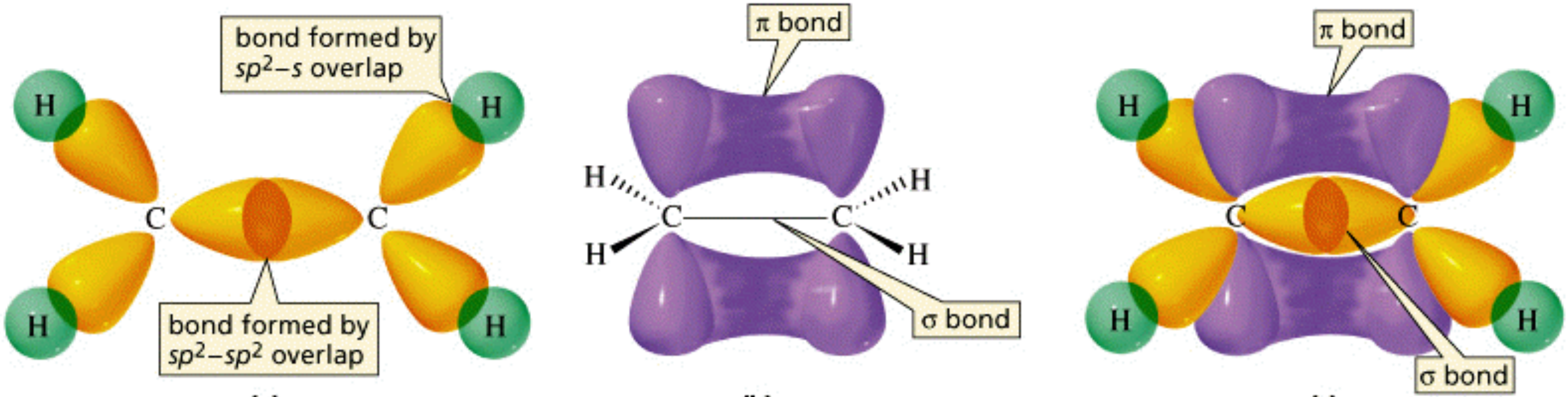
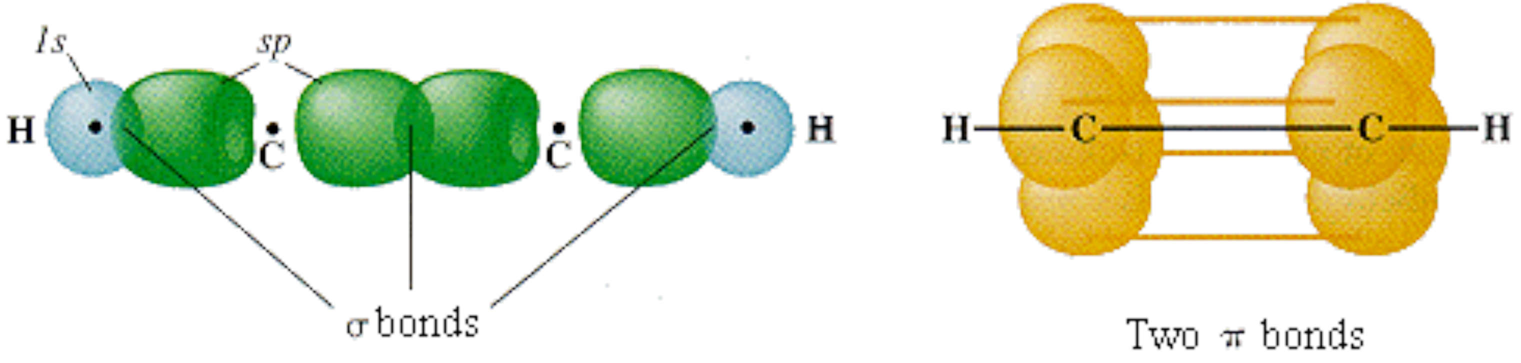
Double bond between carbon atoms *sp*^{2}



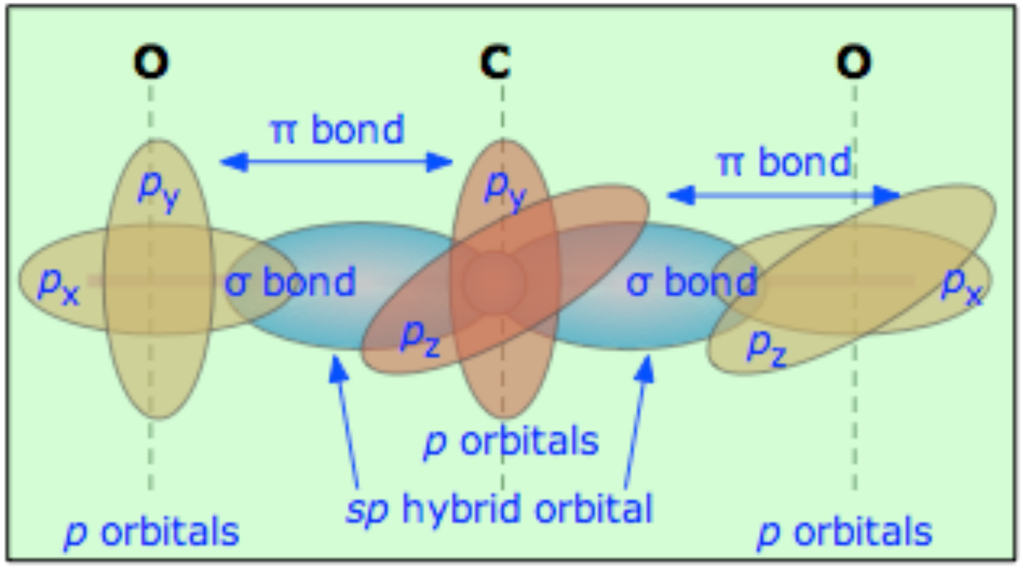
(a) (b) (c)

Triple bond between carbon atoms *sp*

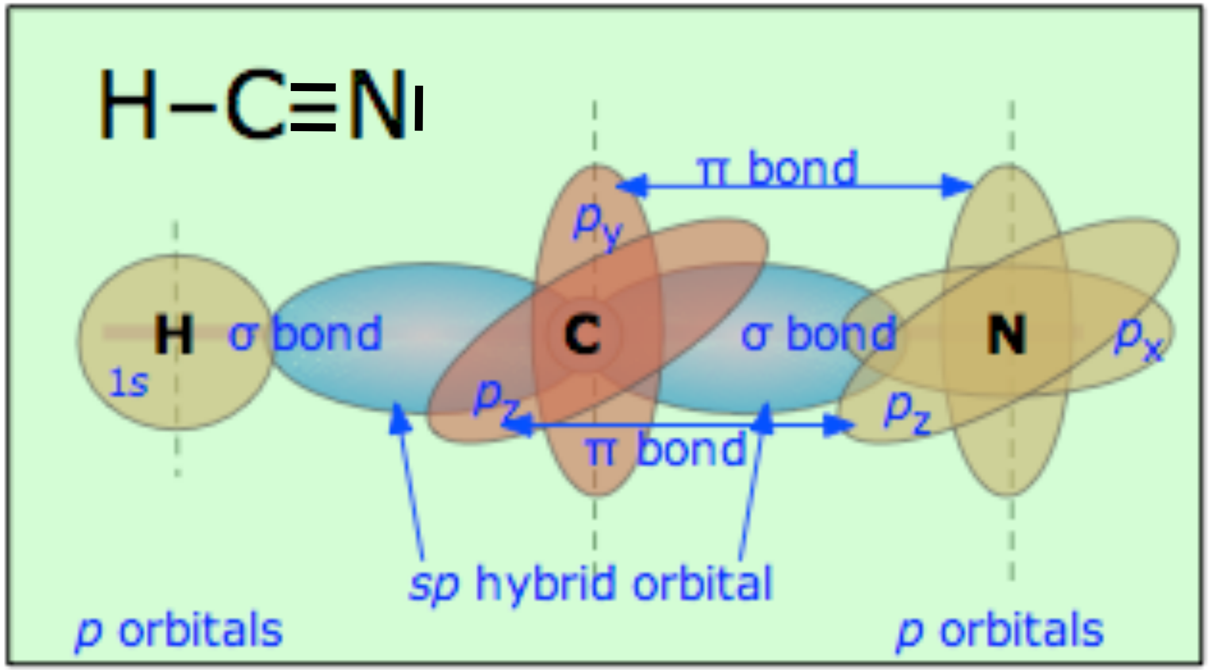


A B

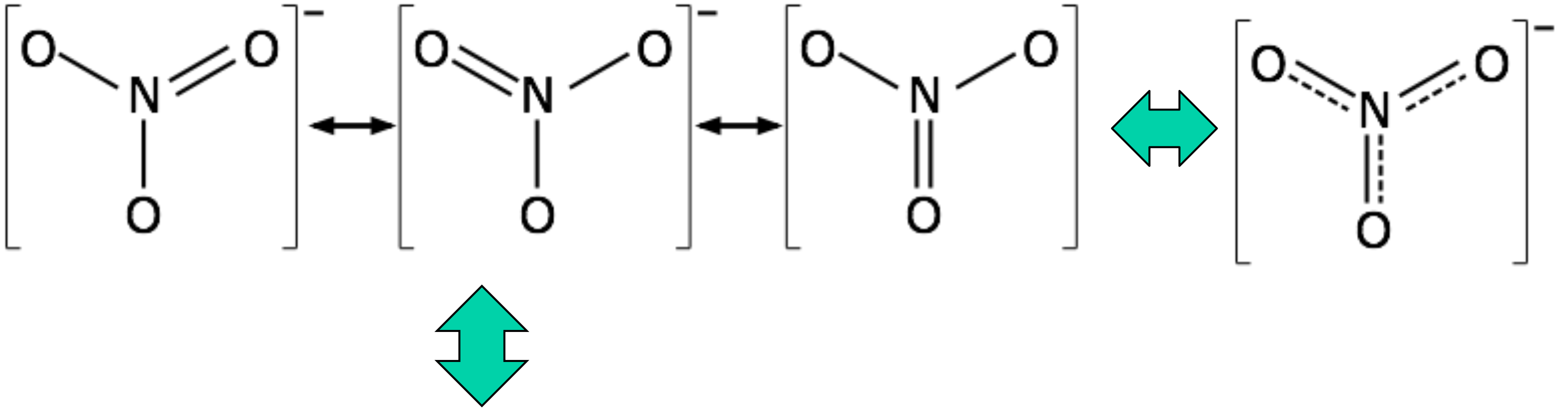
Multiple bonds between different atoms

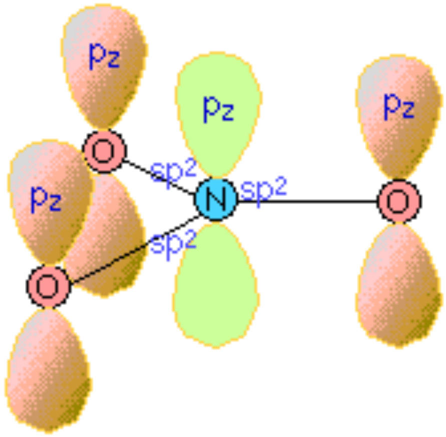


$\overline{\underline{O}}=C=\overline{\underline{O}}$

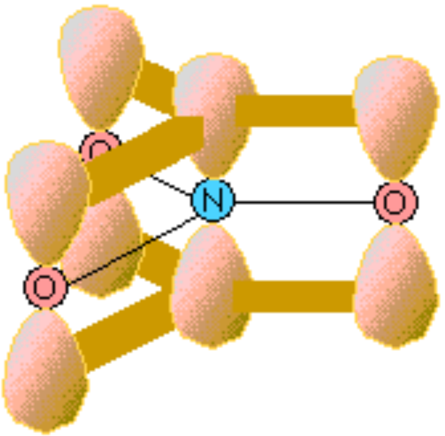


delocalized π-bonds

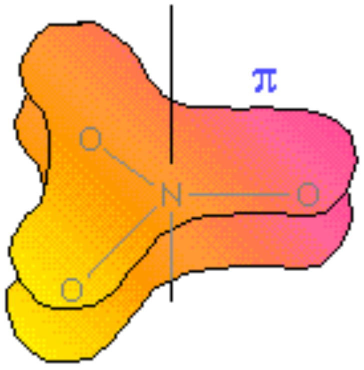




Unhybridized atomic p orbitals and σ-bonding backbone



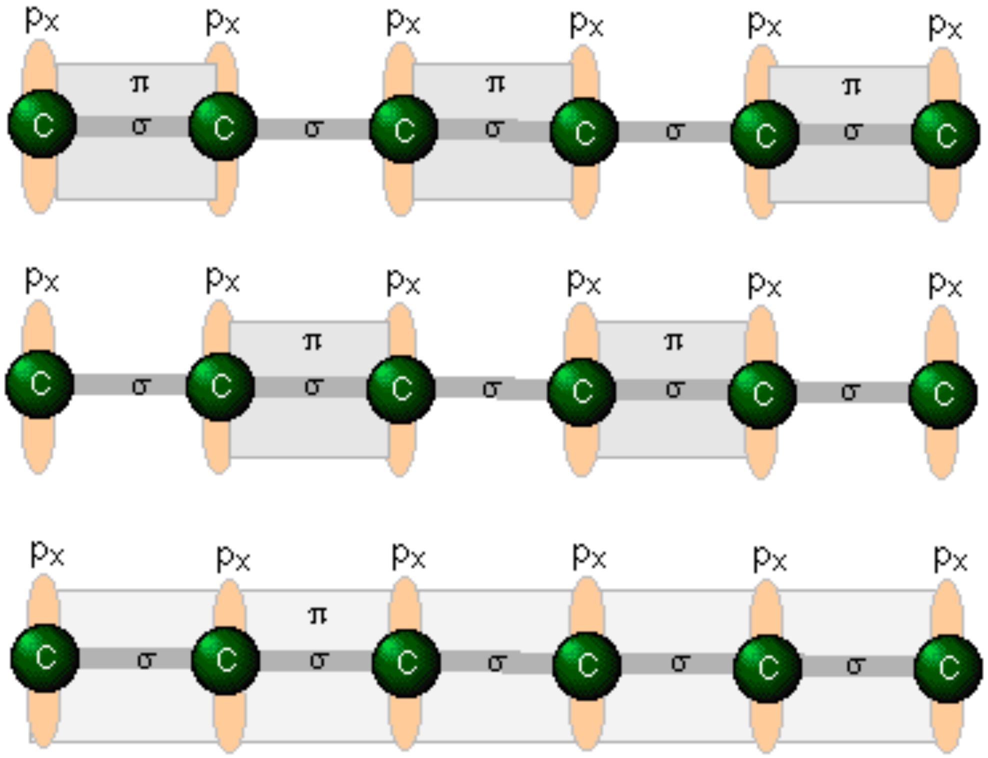
The π bonds are formed by overlap of the p_z orbitals



A representation of the entire NO_3^- molecule

4 different π-MO

delocalized π-bonds



... C = C – C = C – C ...

equivalent structures

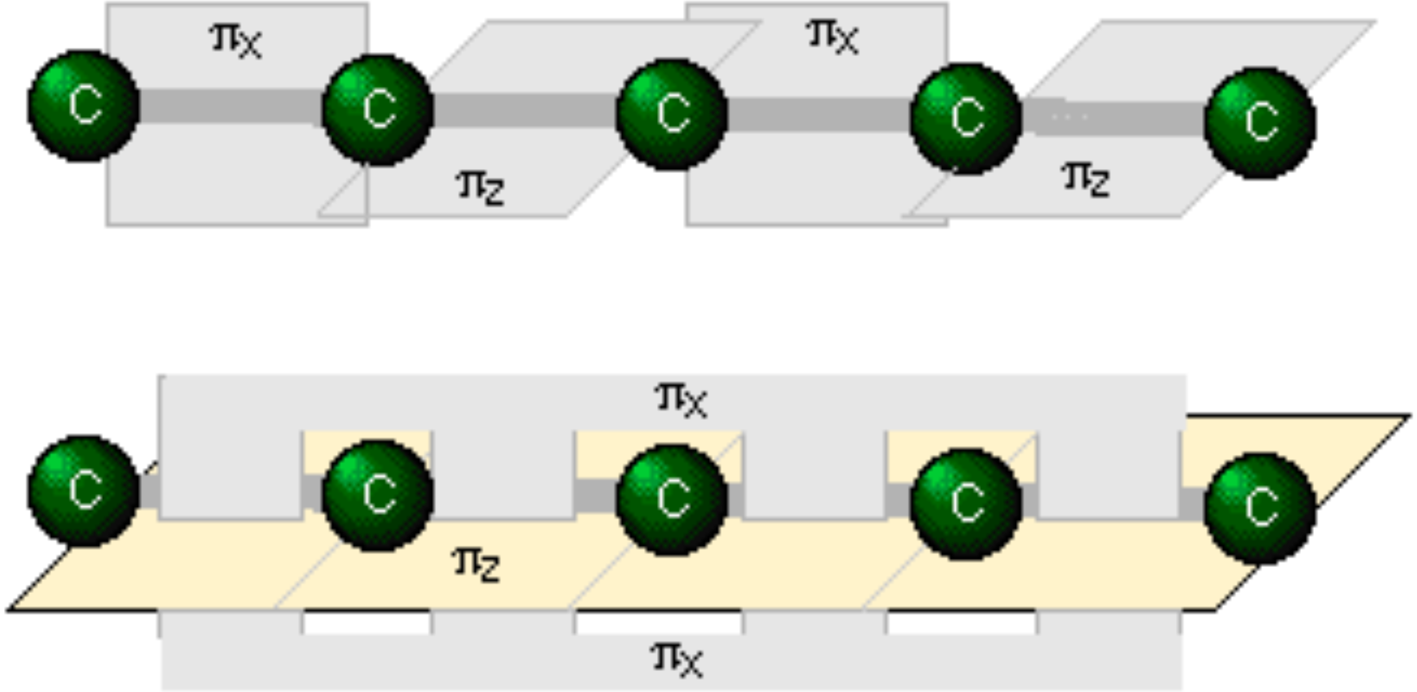
... C – C = C – C = C ...

bond order 1.5

C=C=C=C=C=

conjugated π-system

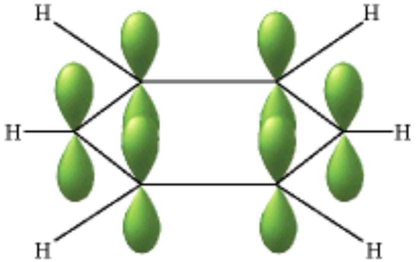
delocalized π-bonds



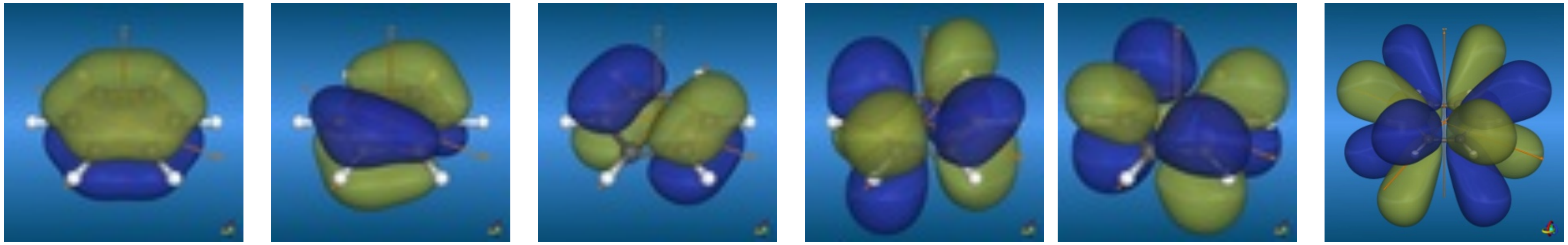
$$\ldots C = C = C = C \ldots$$

conjugated π-system - cummulens

delocalized π-bonds

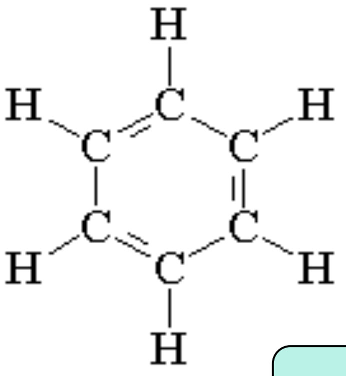


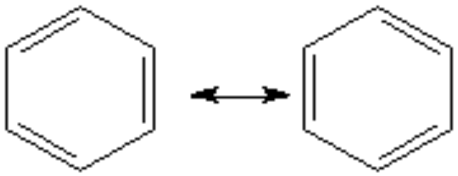
6 different π-MOs

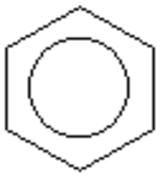


bonding

antibonding







benzene - aromatic ring