CHM 673
Lecture 9: Molecular symmetry

Suggested reading:

https://en.wikipedia.org/wiki/Molecular_symmetry

http://www.huntresearchgroup.org.uk/teaching/year2_mos.html

Group theory in chemistry

Application of group theory in chemistry:
- predicting molecular properties (dipole moment, polarity, chirality)
- predicting allowed/forbidden electronic transitions
- predicting active modes in IR and Raman spectra
- construction and labelling of molecular orbitals
- ligand-field theory
- crystal symmetry of solids

Group theory in computations:
- as molecular Hamiltonian commutes with symmetry operators, eigenstates of the Hamiltonian will preserve symmetry of the molecule
- only symmetry-unique information (integrals etc) need to be computed --> calculations for symmetric molecules can be times faster
- symmetry can be used in performing geometry optimizations --> only symmetry-allowed steps will be performed (effectively decreasing number of degrees of freedom)

Symmetry analysis

Symmetry operation: an action that leaves the molecule in a state indistinguishable from the starting state

Symmetry element: location of a symmetry operation (point, line, plane)
        Operation leaves at least one point in the molecule unchanged

Symmetry operations of an object form a symmetry group.

The successive application of one or more symmetry operations of a molecule has an effect equivalent to that of some single symmetry operation of the molecule. Such groups are called point groups. They leave at least one point of a molecule unchanged.

Differently, symmetry of a crystal is described by space groups because symmetry operations include transitions in space.
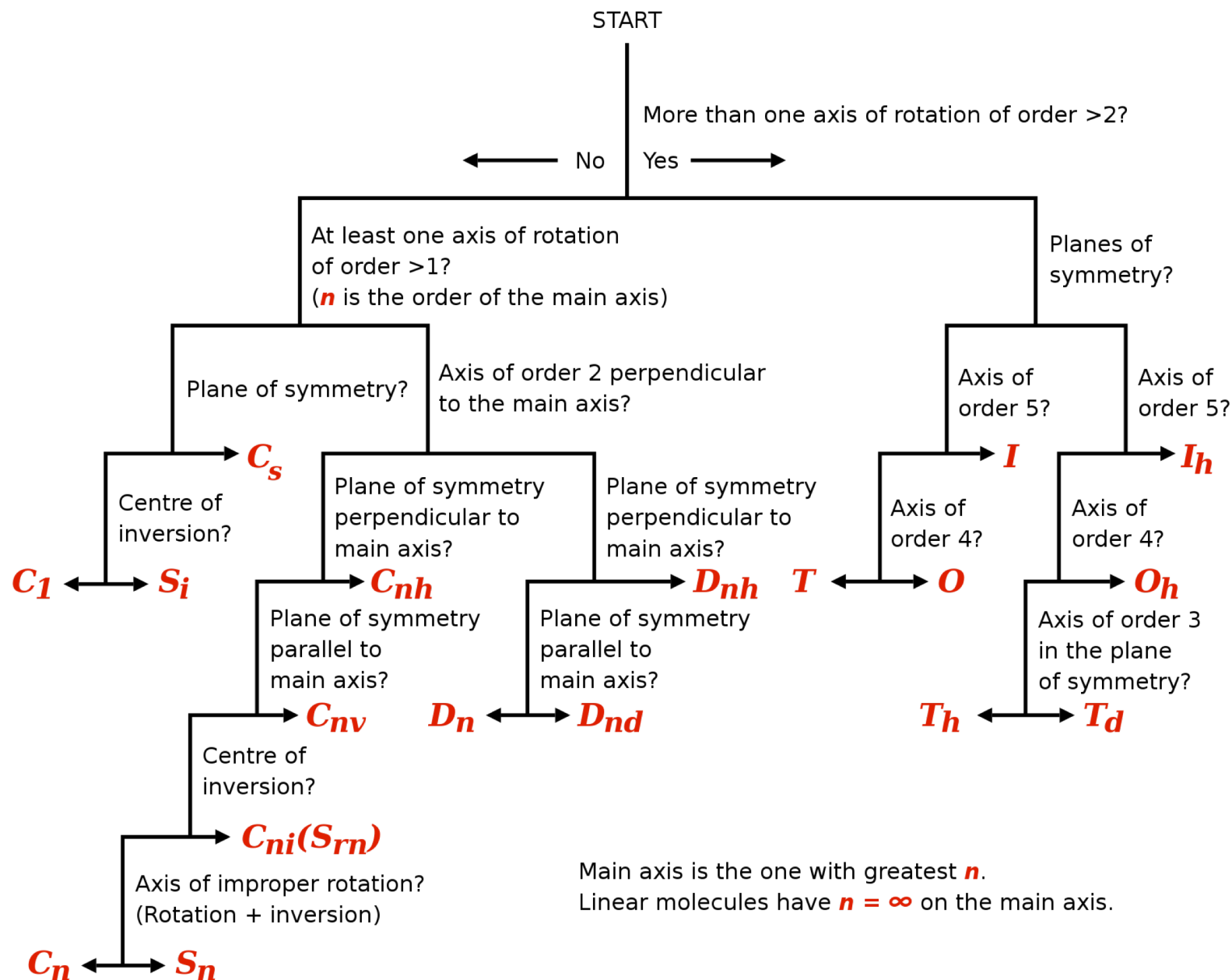
Symmetry operations

Symmetry element	Symmetry operation	Symbol
	Identity	E
n-fold symmetry axis	Rotation by $2\pi/n$	C_n
Mirror plane	Reflection	σ
Center of inversion	Inversion	i
n-fold axis of improper rotation	Rotation by $2\pi/n$ followed by reflection perpendicular to rotation axis	S_n

Common symmetry groups

Point group	Symmetry operations	Typical geometry	examples
C_1	E	No symmetry, chiral	
C_s	E, σ	mirror plane	ClOH, CH_2BrCl
C_i	E, i	Inversion center	*meso*-tartaric acid
$C_{\infty v}$	E, $2C_\infty$, $\infty\sigma_v$	linear	HCl, N_2O
$D_{\infty h}$	E, $2C_\infty$, $\infty\sigma_i$, i, $2S_\infty$, $2C_i$	Linear with inversion center	CO_2, O_2, C_2H_2
C_{2h}	E, C_2, i, σ_h	Planar with inversion center, no vertical plane	Trans-1,2-dichloroethylene
C_{2v}	E, C_2, σ_v, σ_v'	Angular, or see-saw, or T-shape	Water, ClF_3
D_{3h}	E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$	trigonal planar or trigonal bipyramidal	BF_3, cyclopropane
D_{2d}	E, $2S_4$, C_2, $2C_2'$, $2\sigma_d$	90% twist	allene
T_d		tetrahedral	methane
O_h		Octahedral or cubic	SF_6

Determining point group of a molecule

START

More than one axis of rotation of order >2?

No ← | Yes →

At least one axis of rotation
of order >1?
(n is the order of the main axis)

Planes of
symmetry?

Plane of symmetry? | Axis of order 2 perpendicular
to the main axis?

Axis of
order 5?

Axis of
order 5?

C_s

I

I_h

Centre of
inversion?

Plane of symmetry
perpendicular to
main axis?

Plane of symmetry
perpendicular to
main axis?

Axis of
order 4?

Axis of
order 4?

C_1 ← → S_i

C_{nh}

D_{nh}

T ← → O

O_h

Plane of symmetry
parallel to
main axis?

Plane of symmetry
parallel to
main axis?

Axis of order 3
in the plane
of symmetry?

C_{nv}

D_n ← → D_{nd}

T_h ← → T_d

Centre of
inversion?

$C_{ni}(S_{rn})$

Axis of improper rotation?
(Rotation + inversion)

Main axis is the one with greatest n.
Linear molecules have $n = \infty$ on the main axis.

C_n ← → S_n

Irreducible representations (irrep)

Symmetry operations can be represented by matrices
Left-multiplying any vector (representing a point in Cartesian space) by the matrix of a symmetry operation results in a new vector (i.e. a new location of the point)

Composition of symmetry operations = matrix multiplication
Within a symmetry group, composition of two symmetry operations (a multiplication of two matrices) leads to another symmetry operation in the same group

$$\underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{C_2} \times \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma_v} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma_v'}$$

Example for C_{2v} group

Typically, irreducible representations (or irreps) of the group are used.
Other representations can be obtained as linear combinations of irreps.

Character tables

Character table summarizes information on symmetry operations of the group and on its irreducible representations

Character tables are square, as the numbers of irreducible representations is equal to the number of classes of symmetry operations

Conventions for irreducible representation labels:

A: rotation around the principal axis is symmetrical

B: rotation around the principal axis is asymmetrical

E: doubly degenerate representation

T: triply degenerate representation

Subscripts g (gerade) and u (ungerade): designate no change in sign (g) and a change in sign (u) for the groups with inversion center

Σ, Π, Δ (aka notations of the angular momentum) for point groups $C_{\infty v}$ and $D_{\infty h}$

Character tables

symmetry operations

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

symmetry labels

Characters show how irrep transforms when a symmetry operation is applied
-1 (antisymmetric): vector changes sign (direction), orbital changes phase
1 (symmetric): no change in vector or orbital

Character tables

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

irreducible representation

show how Cartesian vectors (x,y,z), rotations (Rx, Ry, Rz) and quadratic functions (components of the second-order tensors, xy, xz, yz, x2, y2, z2) transform

applicable for p and d orbitals, and IR and Raman intensities

Molecular orbitals: definitions

σ orbitals: no node along the bond → no sign change with rotation around the bond
π orbitals: one node along the bond → sign change with C_2 rotation around the bond
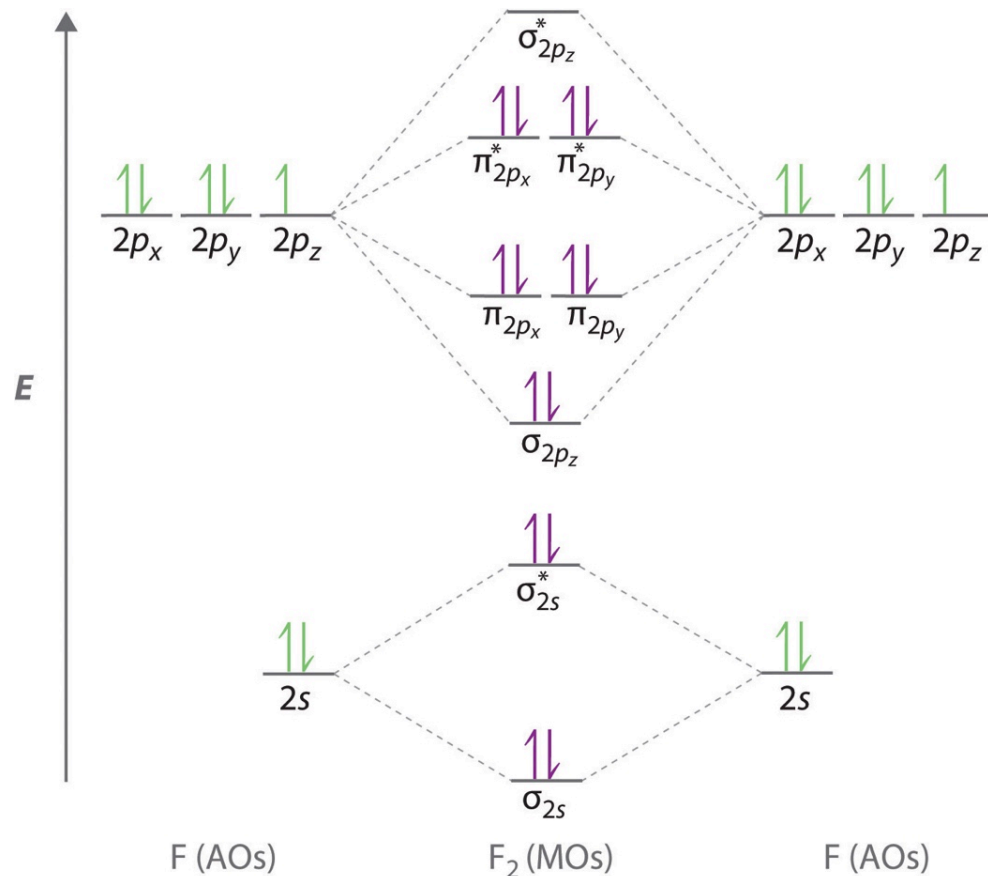δ orbitals: two nodes along the bond → sign change with C_4 rotation around the bond

Orbitals with a node perpendicular to the bond are antibonding
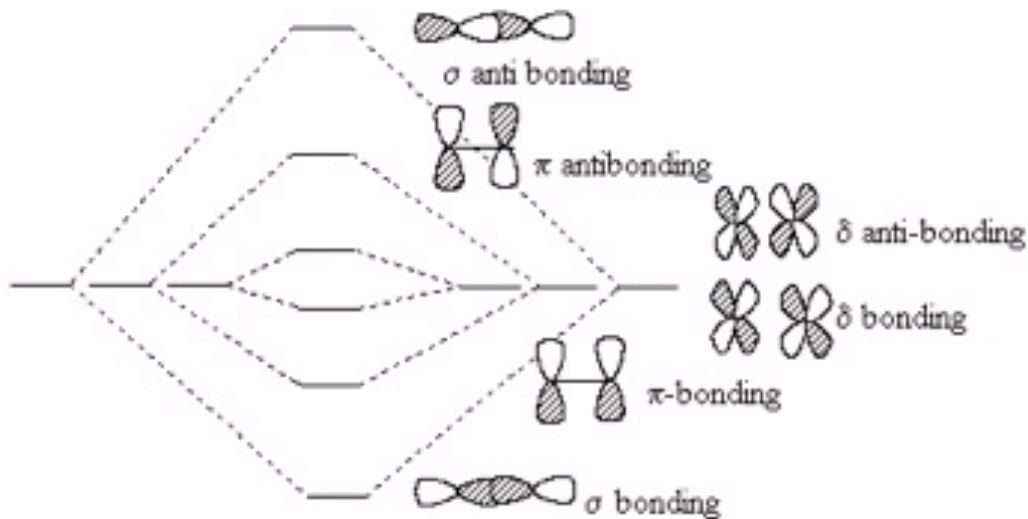
Molecular orbitals and symmetry

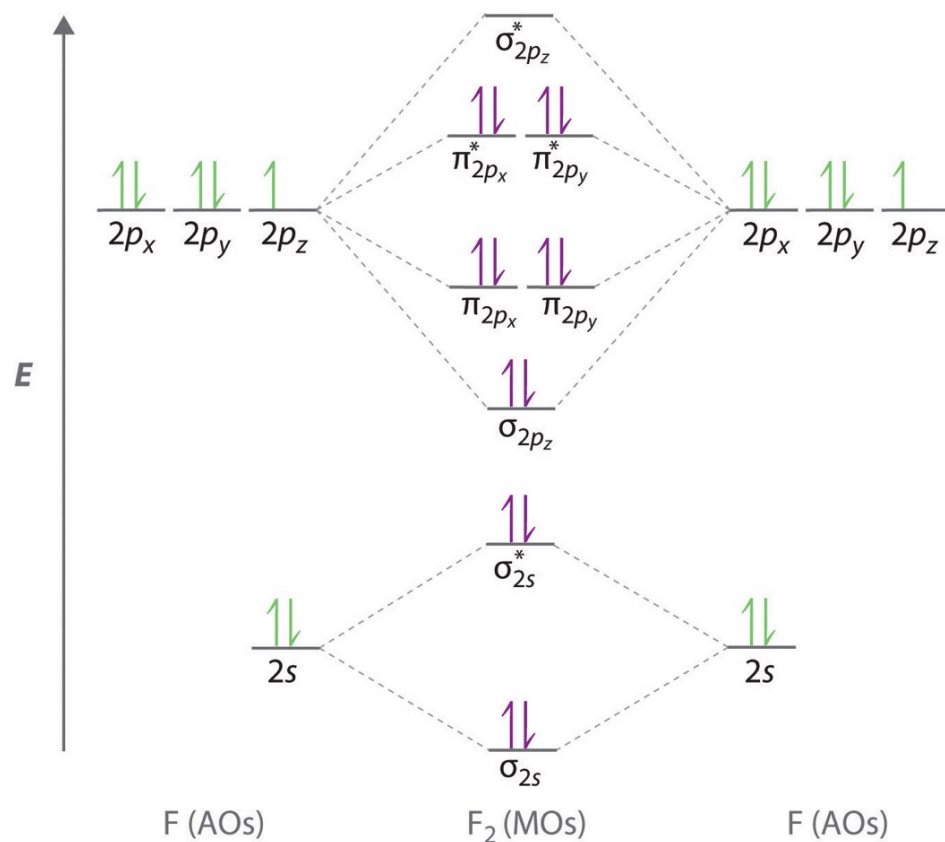Molecular (or canonical) orbitals are combinations of atomic orbitals with imposed symmetry constraints
Only orbitals of the same irreps can interact (mix)
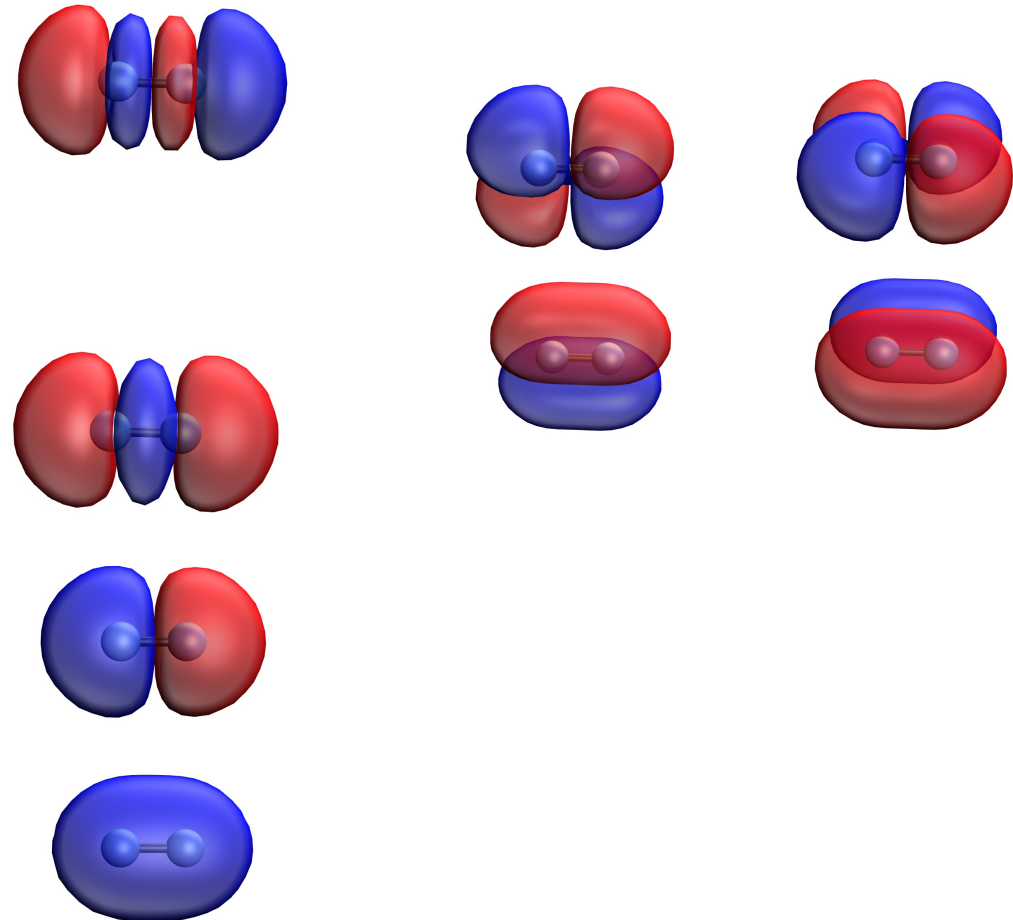
Molecular orbitals: diatomic molecules

Molecular (or canonical) orbitals are combinations of atomic orbitals with imposed symmetry constraints

Only orbitals of the same irreps can interact (mix)

- Orbitals with larger number of nodes are higher in energy
- Sigma orbitals typically have higher overlap and split more than pi orbitals, resulting in:
  - bonding sigma orbitals are more bonding (lower in energy) than corresponding pi orbitals
  - antibonding sigma orbitals are typically more antibonding than antibonding pi orbitals
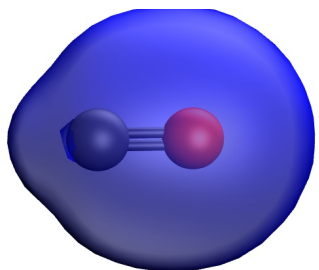
Molecular orbitals: diatomic molecules

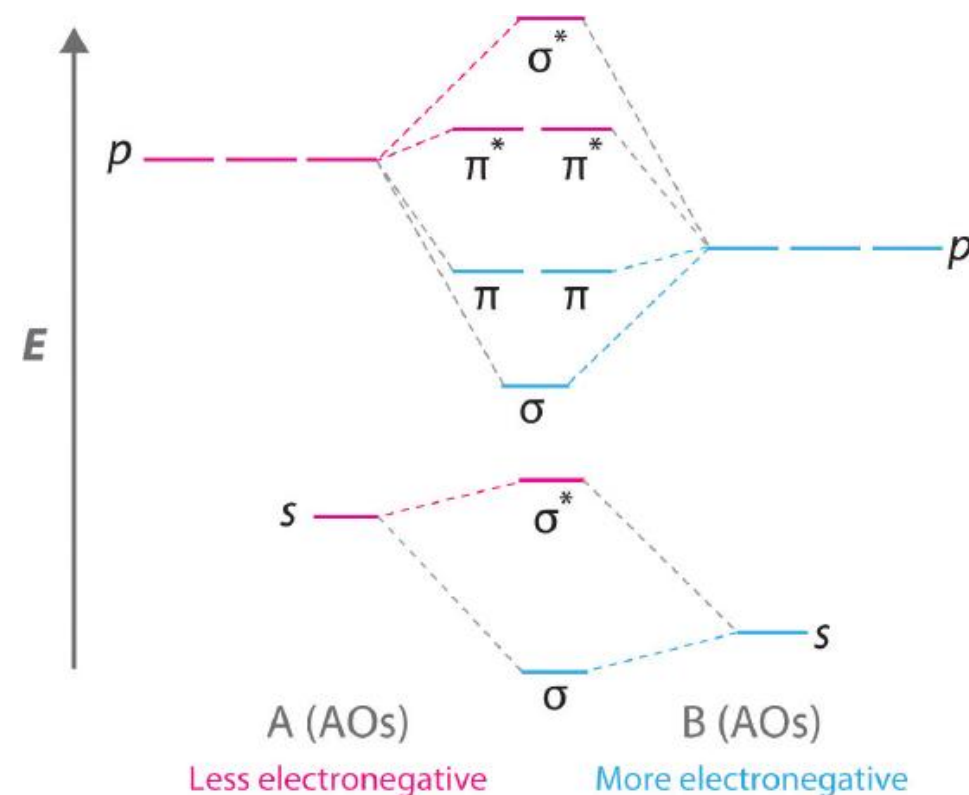Atomic orbitals of more electronegative atom are lower in energy

Molecular orbital that are energetically closer to a corresponding atomic orbital inherits more of its shape and properties, e.g., in CO molecule:
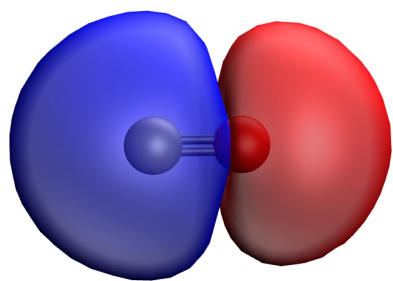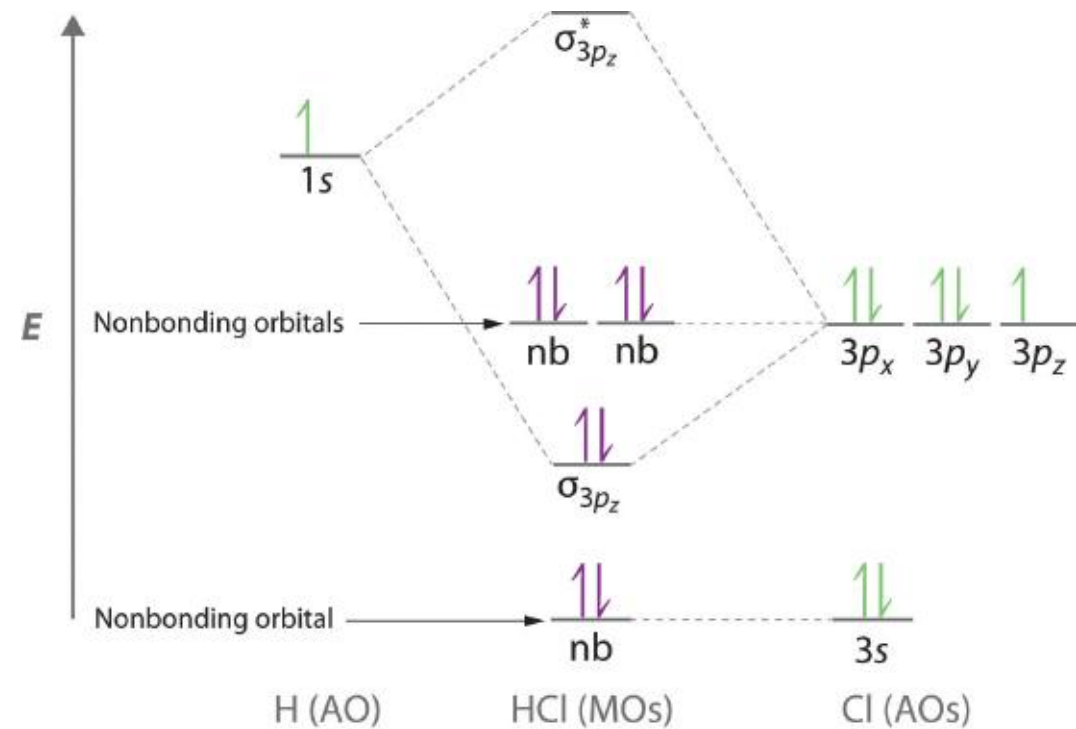
σ* antibonding:
located mainly on C

σ bonding:
located mainly on O

Molecular orbitals in a heterogeneous diatomic molecule

Molecular orbitals: diatomic molecules

Non-bonding orbitals do not delocalize between two centers, do not change energy (compared to corresponding orbitals) and do not contribute to bonding.
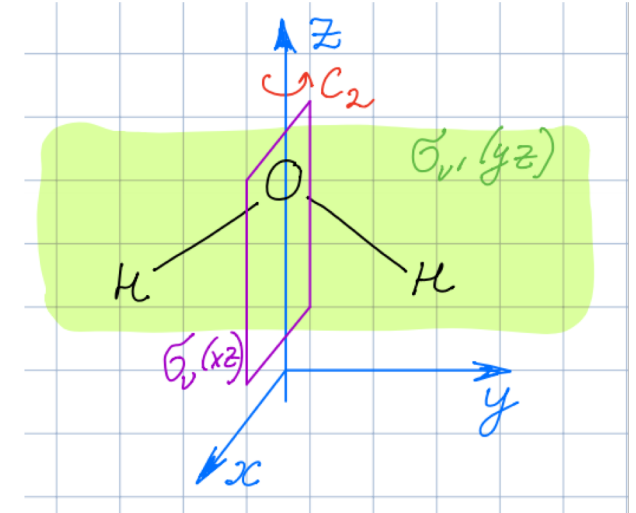

Molecular orbitals in a heterogeneous diatomic molecule

Molecular orbitals: polyatomic molecules

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	R_z
B_1	1	−1	1	−1	x, R_y
B_2	1	−1	−1	1	y, R_x

O					
1s					
2s					
$2p_x$					
$2p_y$					
$2p_z$					
2H					
$1s_A + 1s_B$					
$1s_A - 1s_B$					

Water H_2O
C_{2v} symmetry

Molecular orbitals. Example: C_2H_4

D_{2h}	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear functions, rotations	quadratic functions
A_g	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2, y^2, z^2
B_{1g}	+1	+1	-1	-1	+1	+1	-1	-1	R_z	xy
B_{2g}	+1	-1	+1	-1	+1	-1	+1	-1	R_y	xz
B_{3g}	+1	-1	-1	+1	+1	-1	-1	+1	R_x	yz
A_u	+1	+1	+1	+1	-1	-1	-1	-1	-	-
B_{1u}	+1	+1	-1	-1	-1	-1	+1	+1	z	-
B_{2u}	+1	-1	+1	-1	-1	+1	-1	+1	y	-
B_{3u}	+1	-1	-1	+1	-1	+1	+1	-1	x	-

4S (H)	4	0	0	0	0	4	0	0	
2S (C)									
2pz (C)									
2px (C)									
2py (C)									
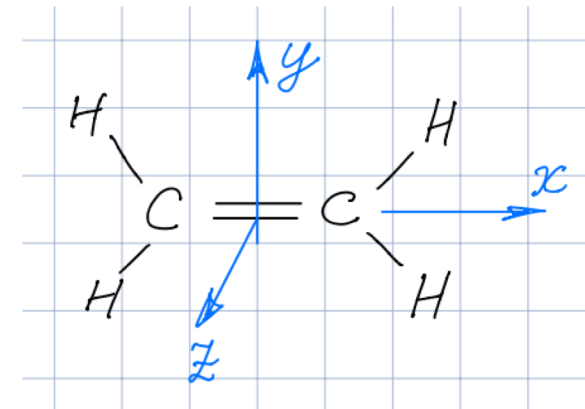
1. determine "stationary" atoms (or rather stationary orbitals) – atoms/orbitals not moved by the symmetry operation

2. Decompose stationary orbitals into unique linear combinations of irreps, e.g. (4S(H) x A_g)/# oper = (4+4)/8 = 1