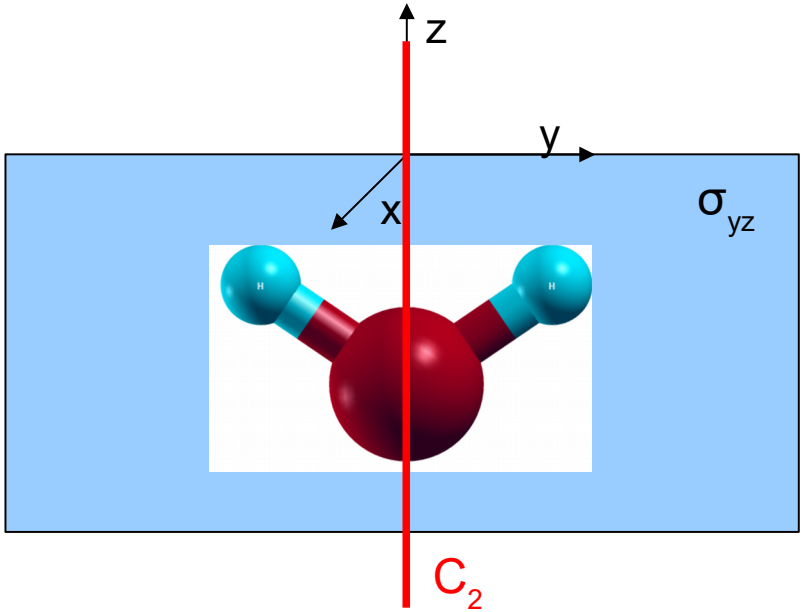
Group Theory applied to Molecules



Jens Kortus

Jens.Kortus@physik.tu-freiberg.de

Topics you hopefully already know

- Matrix properties and operations
- Formal aspects of group theory:
  - → groups, order of groups,
  - → characters,
  - → reducible and irreducible representations,
  - → orthogonality theorem
- Basic quantum mechanics (H-atom, s-, p-, d-orbitals)
- Vibrations (normal modes)
- Whatever else I forgot to mention
- …

If you have any questions please ask!

Wherrett, Brian S.: “Group theory for atoms, molecules and solids” Englewood Cliffs NJ : Prentice-Hall Internat., 1986

Yu, P.Y., Cardona, M. “Fundamentals of Semiconductors” Springer: Chapter “A Pedestrian’s Guide to Group Theory”

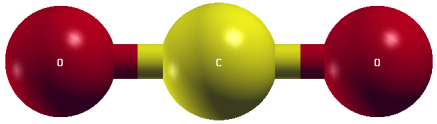
Character tables: http://symmetry.jacobs-university.de/

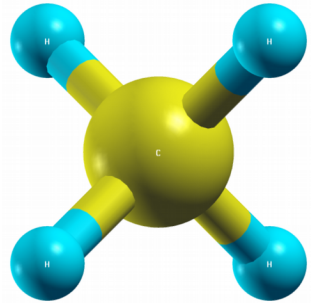
Jens.Kortus@physik.tu-freiberg.de

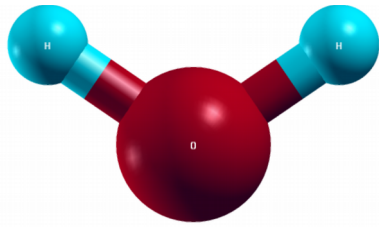
Motivation

• Molecules may have symmetries described by point groups, which leave the molecule invariant under these operations.
• The symmetries can be represented by matrices.
→ representation theory

• The functions describing the physical properties must show corresponding behavior under the symmetry operation of the molecule.
→ electronic wavefunctions
→ normal vibrational modes
→ dipole moments
→ whatever ...



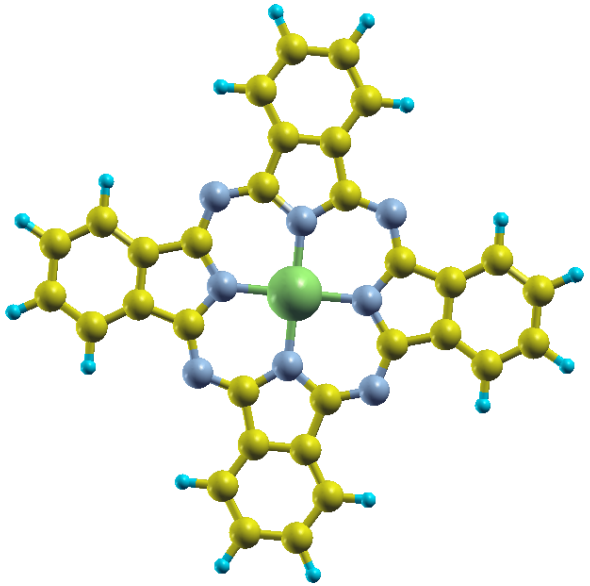


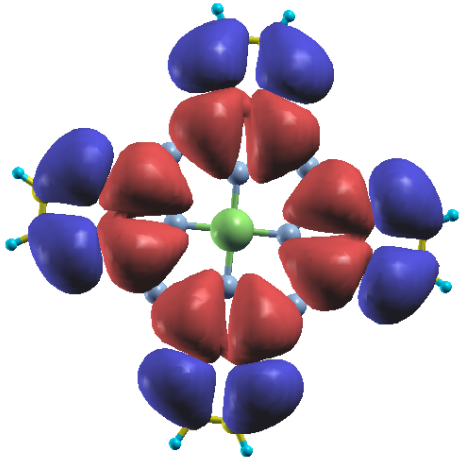


No dipole moment for molecules with inversion.

Jens.Kortus@physik.tu-freiberg.de

Symmetry of molecule determines symmetry of electronic wavefunctions





There exist a whole family of phtalocyanine with different metal atoms (Cu, Co, Ni, Fe, Zn ...).

The HOMO for CoPc involves ligand states. The molecule has spin ½.

Jens.Kortus@physik.tu-freiberg.de

Schönflies notation

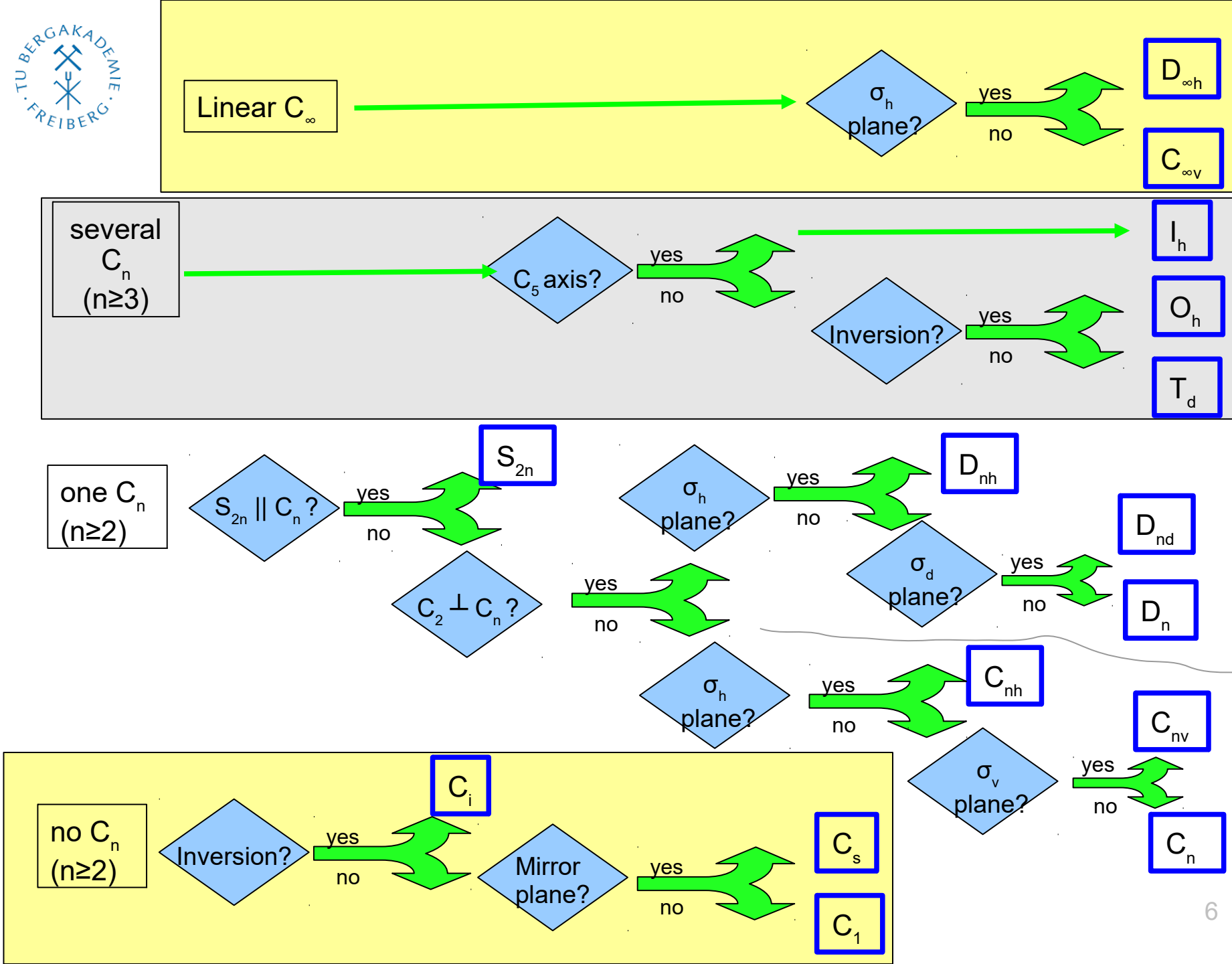
E: identity
I: inversion
σ: reflection
σ_v plane is parallel to principal axis
σ_h plane is perpendicular to principal axis

C_n: clockwise rotation around an axis by 2π/n (n-fold axis)
For molecules with more than one symmetry axis, the axis with the largest n is called the principal axis.

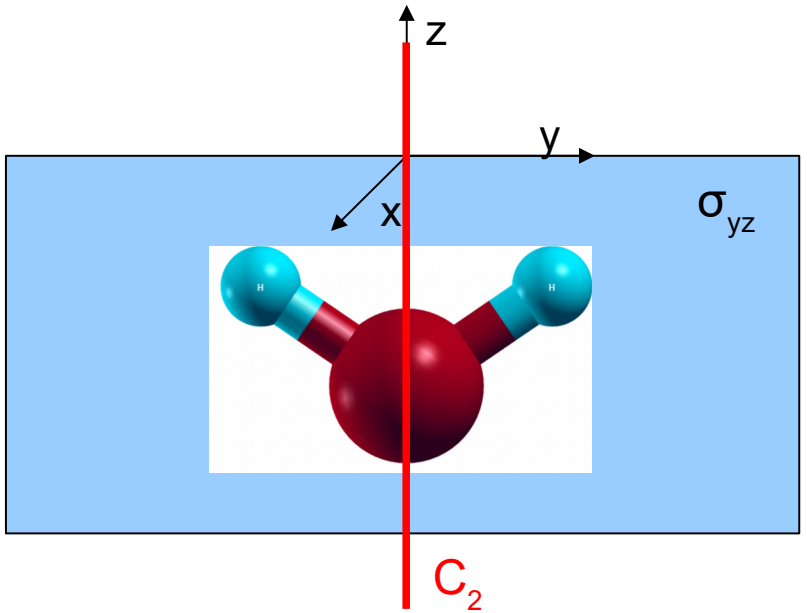
S_n: rotation C_n followed by a reflection through a plane perpendicular to the rotation axis (improper rotation)

Definitions:
Order: total number of symmetry operations in a group
Class: subset of symmetry operations that transform into each other
e.g. any C_n axis will have a subgroup of order n
Character: trace = sum of diagonal elements in a matrix

Jens.Kortus@physik.tu-freiberg.de


Linear C_∞
σ_h plane?
yes
no
$D_{\infty h}$
$C_{\infty v}$
several C_n ($n \geq 3$)
C_5 axis?
yes
no
I_h
Inversion?
yes
no
O_h
T_d
one C_n ($n \geq 2$)
$S_{2n} \parallel C_n$?
yes
no
S_{2n}
$C_2 \perp C_n$?
yes
no
σ_h plane?
yes
no
D_{nh}
σ_d plane?
yes
no
D_{nd}
D_n
σ_h plane?
yes
no
C_{nh}
σ_v plane?
yes
no
C_{nv}
C_n
no C_n ($n \geq 2$)
Inversion?
yes
no
C_i
Mirror plane?
yes
no
C_s
C_1

Symmetry group: C_{2v} (water)



Symmetry elements:

E: identity
C_2: rotation by π
σ_{yz} : mirror plane (yz)
σ_{xz} : mirror plane (xz)

Multiplication table C_{2v}:

C_{2v}	E	C_2	σ_{yz}	σ_{xz}
E	E	C_2	σ_{yz}	σ_{xz}
C_2	C_2	E	σ_{xz}	σ_{yz}
σ_{yz}	σ_{yz}	σ_{xz}	E	C_2
σ_{xz}	σ_{xz}	σ_{yz}	C_2	E

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): Identity E as 9x9 matrix

$$E \circ H_2O = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x(\mathrm{H1}) \\ y(\mathrm{H1}) \\ z(\mathrm{H1}) \\ x(O) \\ y(O) \\ z(O) \\ x(\mathrm{H2}) \\ y(\mathrm{H2}) \\ z(\mathrm{H2}) \end{pmatrix} = \begin{pmatrix} x(\mathrm{H1}) \\ y(\mathrm{H1}) \\ z(\mathrm{H1}) \\ x(O) \\ y(O) \\ z(O) \\ x(\mathrm{H2}) \\ y(\mathrm{H2}) \\ z(\mathrm{H2}) \end{pmatrix}$$

$$\chi(E) = 9$$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): Rotation C2 as 9x9 matrix

$$C_2 \circ H_2O = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x(\mathrm{H1}) \\ y(\mathrm{H1}) \\ z(\mathrm{H1}) \\ x(O) \\ y(O) \\ z(O) \\ x(\mathrm{H2}) \\ y(\mathrm{H2}) \\ z(\mathrm{H2}) \end{pmatrix} = \begin{pmatrix} -x(\mathrm{H2}) \\ -y(\mathrm{H2}) \\ z(\mathrm{H2}) \\ -x(O) \\ -y(O) \\ z(O) \\ -x(\mathrm{H1}) \\ -y(\mathrm{H1}) \\ z(\mathrm{H1}) \end{pmatrix}$$

$$\chi(C_2) = -1$$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): mirror plane xz as 9x9 matrix

$$\sigma_{xz} \circ H_2O = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x(\mathrm{H1}) \\ y(\mathrm{H1}) \\ z(\mathrm{H1}) \\ x(O) \\ y(O) \\ z(O) \\ x(\mathrm{H2}) \\ y(\mathrm{H2}) \\ z(\mathrm{H2}) \end{pmatrix} = \begin{pmatrix} x(\mathrm{H2}) \\ -y(\mathrm{H2}) \\ z(\mathrm{H1}) \\ x(O) \\ -y(O) \\ z(O) \\ x(\mathrm{H1}) \\ -y(\mathrm{H1}) \\ z(\mathrm{H2}) \end{pmatrix}$$

$$\chi(\sigma_{xz}) = 1$$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): mirror plane yz as 9x9 matrix

$$\sigma_{yz} \circ H_2O = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x(\mathrm{H1}) \\ y(\mathrm{H1}) \\ z(\mathrm{H1}) \\ x(O) \\ y(O) \\ z(O) \\ x(\mathrm{H2}) \\ y(\mathrm{H2}) \\ z(\mathrm{H2}) \end{pmatrix} = \begin{pmatrix} -x(\mathrm{H2}) \\ y(\mathrm{H2}) \\ z(\mathrm{H1}) \\ -x(O) \\ y(O) \\ z(O) \\ -x(\mathrm{H1}) \\ y(\mathrm{H1}) \\ z(\mathrm{H2}) \end{pmatrix}$$

$$\chi(\sigma_{yz}) = 1$$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): reducible representation as 9x9 matrix

These four 9 × 9 matrices reproduce our multiplication table (check as homework). They form a reducible representation of the group C_{2v}.

Is this representation unique? No!

The following set of four 3x3 matrices will also reproduce our multiplication table (check as homework):

$$E=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \quad C_2=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix} \quad \sigma_{xz}=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix} \quad \sigma_{yz}=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

They are also a representation of point group C_{2v}.

$$\Gamma\left(C_{2\mathrm{v}}\right)=\left\{E,C_{2,}\sigma_{xz},\sigma_{yz}\right\}$$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): irreducible representations

Can we even find simpler representations? Note that z is not changing, therefore we can break the 3x3 matrices in 2x2 and 1x1 blocks further. We get two representations (Γ_z and Γ_A) both reproducing our multiplication table:

$$\Gamma_z(C_{2v}) = \{(1),(1),(1),(1)\}$$

$$\Gamma_A(C_{2v}) = \left\{\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix},\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix},\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}\right\}$$

Γ_z can not be reduced any further, it is an irreducible representation of C_{2v}. However Γ_A can be reduced into two 1x1 representations according to x and y.

$$\Gamma_x(C_{2v}) = \{(1),(-1),(1),(-1)\}$$

$$\Gamma_y(C_{2v}) = \{(1),(-1),(-1),(1)\}$$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} : character table

There is still one irreducible representation missing.

$$\Gamma_{A2}(C_{2v}) = \{(1),(1),(-1),(-1)\}$$

The point group C_{2v} has four irreducible representations resulting in the following **character table**

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

Mulliken symbols = symmetry labels: A, B: 1D e: 2D t: 3D

A: 1D symmetric with respect to principal axis (C_2)

B: 1D anti-symmetric with respect to principal axis (C_2)

Jens.Kortus@physik.tu-freiberg.de

Reducing a reducible representation

$$a_i = \frac{1}{h} \sum_R \chi_\Gamma(R) * \chi_{\Gamma_i}(R) N_R$$

a_i = the number of times the irreducible representation is in the reducible representation
h = order of group, NR= number of elements in class
R = symmetry operation (sum of all symmetry operations)
χ_Γ = character of reducible representation
$\chi_{\Gamma i}$ = character of irreducible representation (from character table)

For example our 3x3 matrices can be reduced:

$$\Gamma\left(C_{2v}\right) = \left\{E, C_2, \sigma_{xz}, \sigma_{yz}\right\} \qquad \chi_\Gamma = \{3, -1, 1, 1\}$$

A1: $\frac{1}{4}\left(3\cdot 1 + (-1)\cdot 1 + 1\cdot 1 + 1\cdot 1\right) = 1$

A2: $\frac{1}{4}\left(3\cdot 1 + (-1)\cdot 1 + 1\cdot(-1) + 1\cdot(-1)\right) = 0$

B1: $\frac{1}{4}\left(3\cdot 1 + (-1)\cdot(-1) + 1\cdot 1 + 1\cdot(-1)\right) = 1$

B2: $\frac{1}{4}\left(3\cdot 1 + (-1)\cdot(-1) + 1\cdot(-1) + 1\cdot 1\right) = 1$

$$\Rightarrow \Gamma = A1 + B1 + B2$$

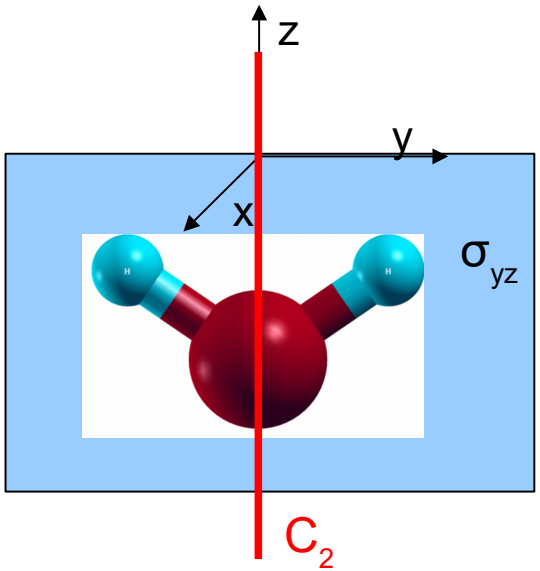
Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): oxygen orbitals

The relevant oxygen orbitals are 2s, $2p_x$, $2p_y$ and $2p_z$.

2s is spherically symmetric and does not change under any of the symmetry operations (A1). Note, that the 2p-orbitals have a phase.

	E	C2	σ_{xz}	σ_{yz}	
$2p_y$	1	-1	-1	1	= B2
$2p_x$	1	-1	1	-1	= B1
$2p_z$	1	1	1	1	= A1



Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): overlap integrals

Overlap integral: $\langle \phi | \psi \rangle = \int d V \, \phi * \psi$

Any nonzero integral must contain the totally symmetric representation A.

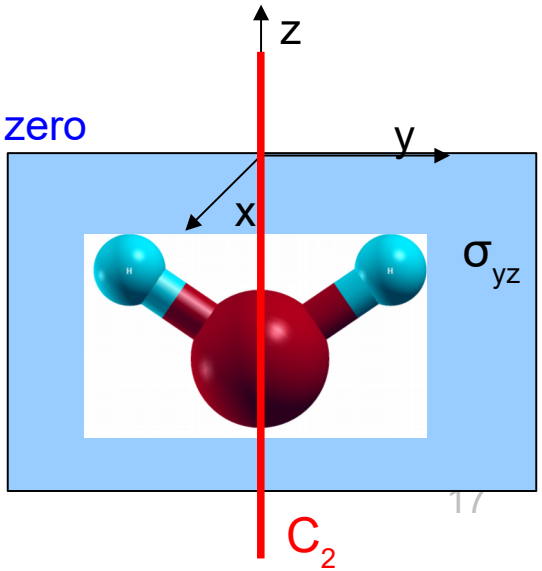
1) apply symmetry operations to each orbital, φ , ψ
2) multiply characters of the orbitals
3) find irreducible representation
4) if the irreducible representation does not contain a totally symmetric representation, then the integral will be zero otherwise we have to calculate the integral.

Overlap integral of |1s> and $|2p_z>$orbital in a C_{2v} molecule: possibly nonzero

Γ(1s) = 1 1 1 1 = A1
$\Gamma(2p_z)$ = 1 1 1 1 = A1
$\Gamma(1s)*\Gamma(2p_z)$ = 1 1 1 1 = A1

Overlap integral of |1s> and $|2p_x>$ orbital in a C_{2v} molecule: definitely zero

Γ(1s) = 1 1 1 1 = A1
$\Gamma(2p_x)$ = 1 −1 1 −1 = B1
$\Gamma(1s)*\Gamma(2p_x)$ = 1 −1 1 −1 = B1



Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): dipole matrix elements

Dipole matrix element: $\vec{p} = \langle \phi | e\vec{r} | \psi \rangle = e \int$

1) find symmetry of each orbital, φ , ψ
2) character of the components of the dipole operator (character of x, y, z),
3) multiply characters of the orbitals and character of component of dipole operator
4) find irreducible representation
5) if the irreducible representation does contain the totally symmetric representation (A1), then the dipole transition will be allowed between these states

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

<A1| x | A1> = 0 forbidden
<A1| z | A1> ≠ 0 allowed
<A1| y | B2> ≠ 0 allowed
<A2| x | B2> ≠ 0 allowed

This can be generalized to any operator C, where one can ask for which symmetry of the operator a transition will be allowed.

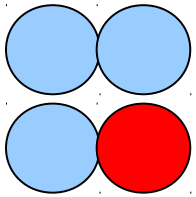
Jens.Kortus@physik.tu-freiberg.de

Molecular orbitals: LCAO

Molecular orbitals can be formed from linear combinations of atomic orbitals (LCAO).
For example the two H-atoms in H_2O provide each a 1s-orbital giving two possible LCAO.

$$\Phi_+ = c_1 \psi_{1s}^{H1} + c_2 \psi_{1s}^{H2}$$

$$\Phi_- = c_1 \psi_{1s}^{H1} - c_2 \psi_{1s}^{H2}$$



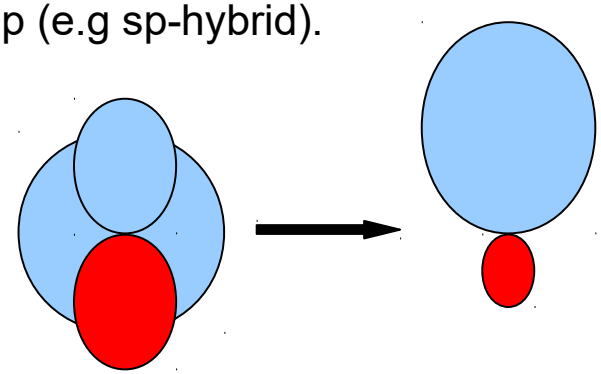
A1

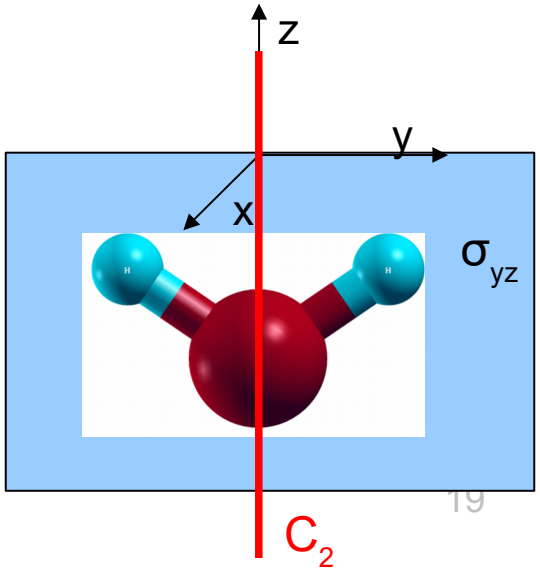
B2

Together with the oxygen orbitals H_2O has 3 A_1(2s, $2p_z$, Φ_+), 2 B_2 ($2p_y$, Φ_+) and 1 B_1 ($2p_x$) molecular orbitals, which can be filled with 2 electrons (Pauli principle) starting from lowest one. Using only symmetry adapted linear combinations (SALC) the lowest bonding MO would be:

$$MO = c_1 \psi_{2s}^{O} + c_2 \psi_{2p_z}^{O} + c_3 \Phi_+$$

The MO correspond to a delocalized view of the orbitals and are used to construct hybrid orbitals due to constructive/destructive overlap (e.g sp-hybrid).



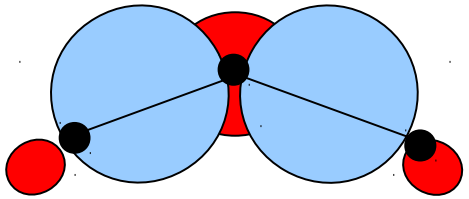


Jens.Kortus@physik.tu-freiberg.de

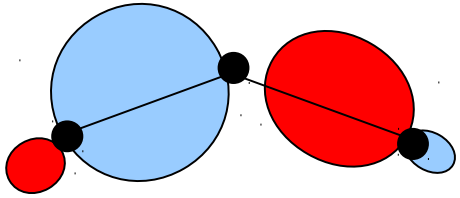
MO for systems with central atom (AB_n)

- start from symmetry of molecule AB_n
- find symmetry of relevant orbitals of central atom (A) and the SALC for B_n
- Molecular orbitals are constructed from orbitals of same symmetry
- depending on overlap of the orbitals and energies the resulting MO can be classified as bonding, nonbonding, or antibonding orbitals

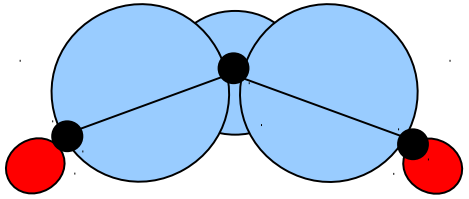
Antibonding



Non-bonding

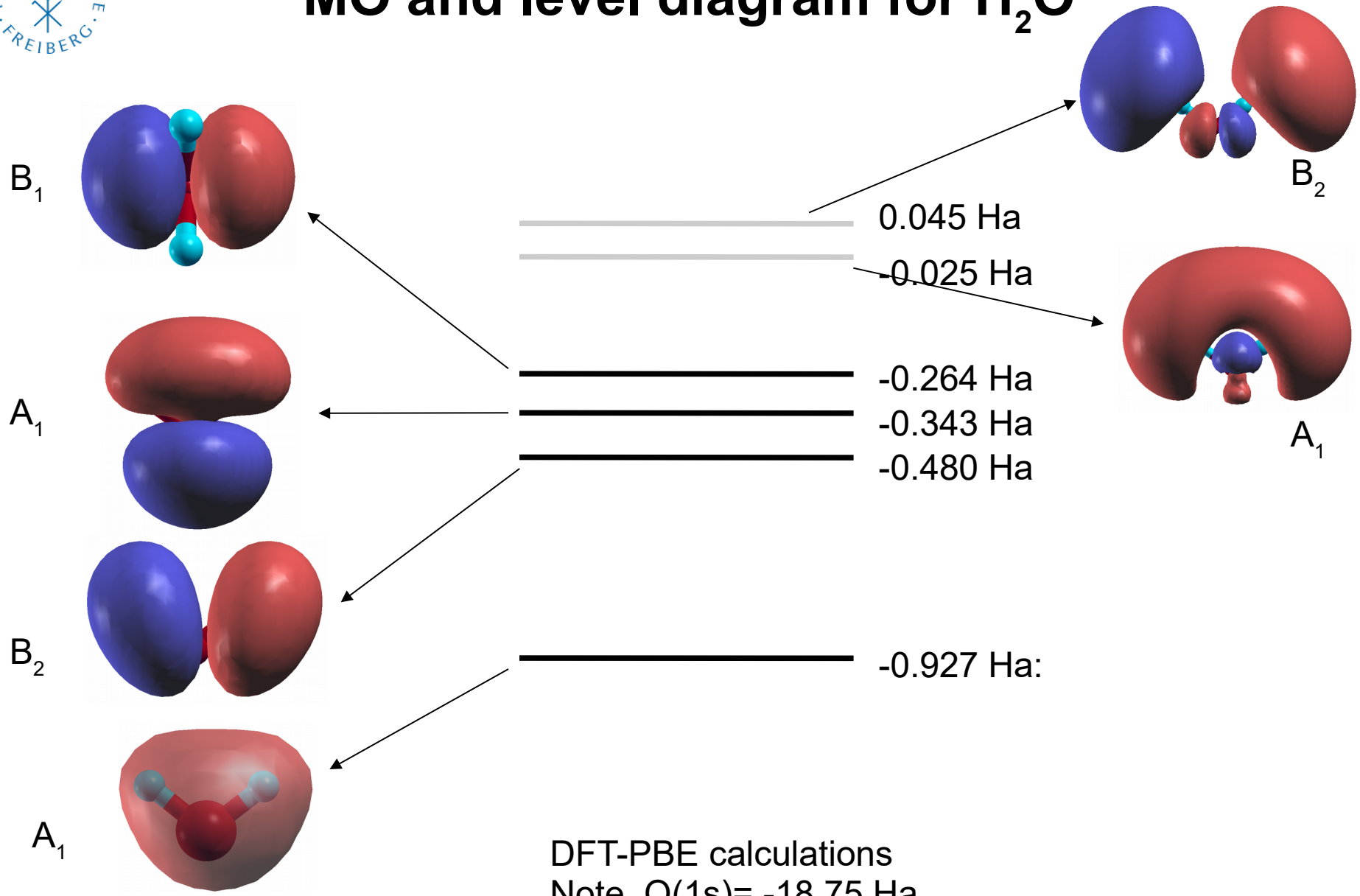


Bonding



Jens.Kortus@physik.tu-freiberg.de

MO and level diagram for H_2O

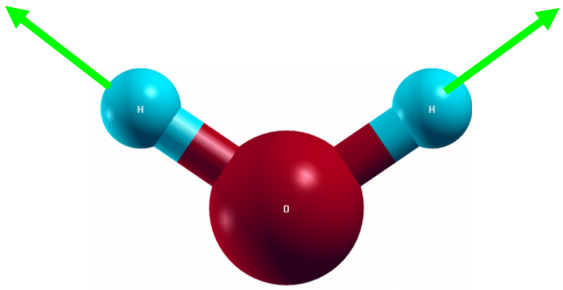


DFT-PBE calculations
Note, O(1s)= -18.75 Ha

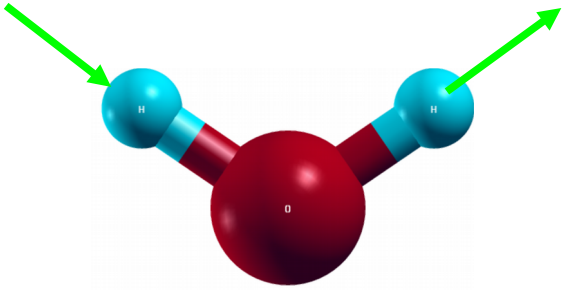
Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): vibrational modes

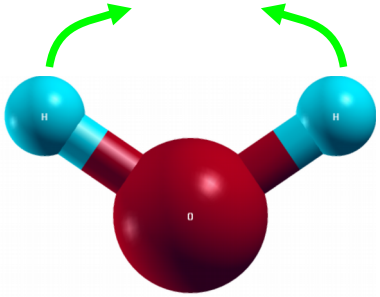
Any non-linear molecule has 3N-6 vibrational modes. In case of H_2O we expect therefore only 3 vibrational modes.
The displacement vectors of the normal modes will transform according to the irreducible representations.



Symmetric stretch (v1)



anti-symmetric stretch (v2)



bending (v3)

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

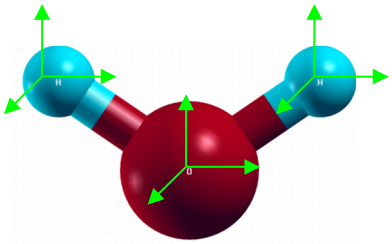
C_{2v}	E	C_2	σ_{xz}	σ_{yz}
v_1	1	1	1	1
v_2	1	-1	-1	1
v_3	1	1	1	1

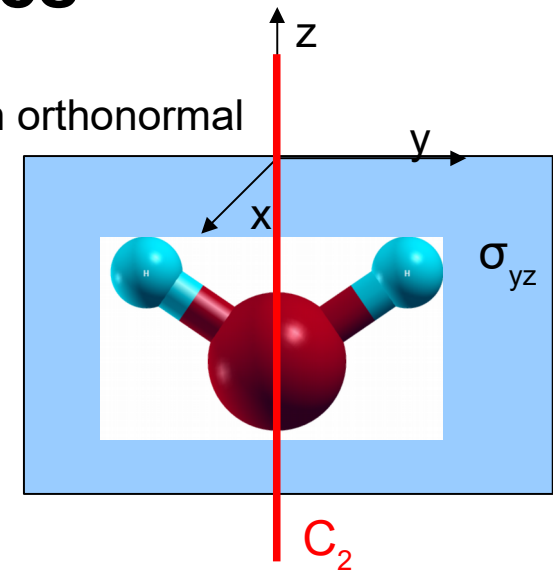
$\Gamma_{vib} = 2\,A_1 + B_2$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): normal modes

The displacement of the atoms can be described by vectors in an orthonormal coordinate system attached to each atom of the molecule.





We need the transformation behavior under the symmetry operations of the molecule.

E:	$(x_1,y_1,z_1,x_2,y_2,z_2,x_3,y_3,z_3) \rightarrow (x_1,y_1,z_1,x_2,y_2,z_2,x_3,y_3,z_3)$	$\chi(E) = 9$
C_2:	$(x_1,y_1,z_1,x_2,y_2,z_2,x_3,y_3,z_3) \rightarrow (x_3,y_3,z_3,-x_2,-y_2,z_2,x_1,y_1,z_1)$	$\chi(C_2)= -1$
σ_{xz}:	$(x_1,y_1,z_1,x_2,y_2,z_2,x_3,y_3,z_3) \rightarrow (x_3,-y_3,z_3,x_2,-y_2,z_2,x_1,-y_1,z_1)$	$\chi(\sigma_{xz})= 1$
σ_{yz}:	$(x_1,y_1,z_1,x_2,y_2,z_2,x_3,y_3,z_3) \rightarrow (-x_1,y_1,z_1,-x_2,y_2,z_2,-x_3,y_3,z_3)$	$\chi(\sigma_{yz})= 3$

The reducible representation for vibrations is then $\Gamma_{3N}= \{9,-1,1,3\}$.

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): normal modes

With help of the reduction formula we find the irreducible representation in Γ_{3N} = {9,-1,1,3}.

$$a_i = \frac{1}{h}\sum_R \chi_\Gamma(R) * \chi_{\Gamma_i}(R) N_R$$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy, Rz
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

$$\text{A1:}\quad \frac{1}{4}\left(9\cdot 1+(-1)\cdot 1+1\cdot 1+3\cdot 1\right)=3$$

$$\text{A2:}\quad \frac{1}{4}\left(9\cdot 1+(-1)\cdot 1+1\cdot(-1)+3\cdot(-1)\right)=1$$

$$\text{B1:}\quad \frac{1}{4}\left(9\cdot 1+(-1)\cdot(-1)+1\cdot 1+3\cdot(-1)\right)=2$$

$$\text{B2:}\quad \frac{1}{4}\left(9\cdot 1+(-1)\cdot(-1)+1\cdot(-1)+3\cdot 1\right)=3$$

$$\Rightarrow \Gamma = 3A_1 + A_2 + 2B_1 + 3B_2$$

Γ_{3N} contains translational, rotational and vibrational degrees of freedom.
The translations correspond to irreducible representations x, y and z (A_1,B_1,B_2)
The rotatations are given by rotation around the axes R_x, R_y and R_z.

Γ_{vib} (H_2O) = ($3A_1 + A_2 + 2B_1 + 3B_2$) - ($A_1 + B_1 + B_2$) - ($A_2 + B_1 + B_2$) = $2A_1 + B_2$

Jens.Kortus@physik.tu-freiberg.de

C_{2v} (water): IR and Raman activity

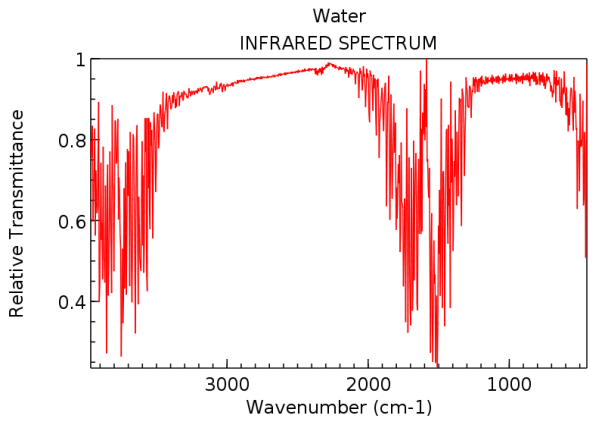
If Γ_{vib} contains irreducible representations corresponding to x, y, and z (dipole matrix element) then the mode will be IR active.

For H_2O the modes A_1 and B_2 are IR active since Γ_{vib} contains $2A_1 + B_2$.

Raman activity is proportional to a change of the polarizability. Raman active modes must contain irreducible representations corresponding to z^2, x^2-y^2, xy, xz or yz in Γ_{vib}.

For H_2O, z^2 and x^2-y^2 transform as A_1, xy as A_2, xz as B_1 and yz as B_2, therefor the modes A_1 and B_2 maybe also Raman active.

The IR spectrum of H_2O shows three bands. The two stretch modes v1 and v2 occur at 3756 and 3657 cm^{-1} whereas the bending v3 mode occurs at 1595 cm^{-1}. (NIST reference gas phase data)



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Jens.Kortus@physik.tu-freiberg.de

Summary

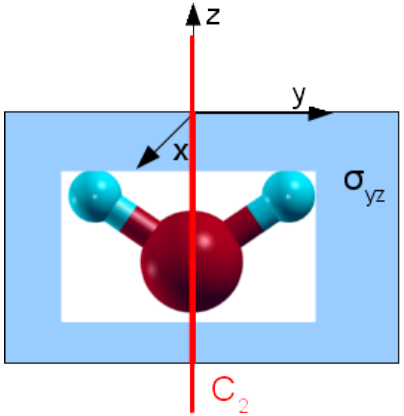
Group theory is a very powerful tool to investigate vibrational or electronic properties of molecular systems!

Electronic or vibronic wavefunctions can be classified using irreducible representations. The symmetry then decides on possible interactions which will result in splittings of levels or transition matrix elements.

Group theory is therefore often used to understand:

- vibrational IR and Raman spectra (normal modes, selection rules)

- electronic wavefunctions (MO levels, LCAO method, Hückel-theory, π-electron approximation, Valence Shell Electron Pair Repulsion Theory = VSPER, ...)



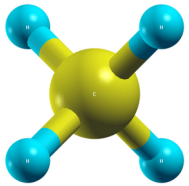
Jens.Kortus@physik.tu-freiberg.de

Jens.Kortus@physik.tu-freiberg.de

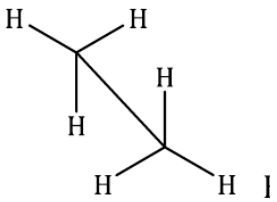
Character tables:
http://symmetry.jacobs-university.de/

1) Find the point group of the following molecules and list the symmetry elements of the group.

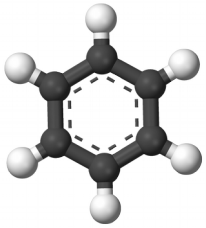
Methene

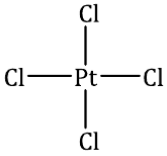


Ethane (staggered)

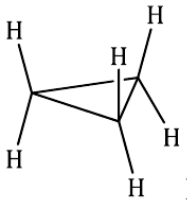


Benzene





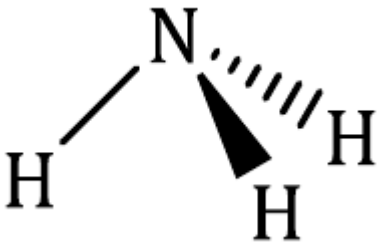
Cyclopropane



2) If a molecule has an improper rotation (S_n), then it is optically inactive.

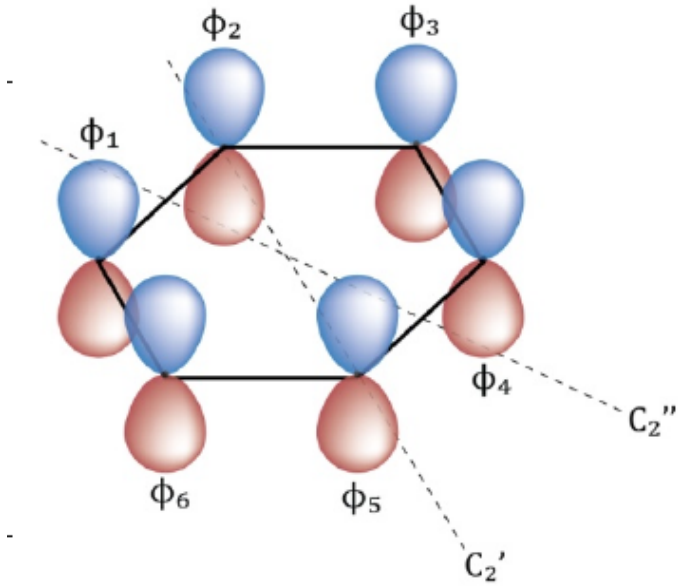
Which of the following molecules may have a dipole moment or is optically inactive?
Methene, benzene, ethane, CO_2, H_2O, NH_3, $PtCl_4$

3) Find the normal modes of ammonia NH_3 and discuss IR/Raman activity of the modes!



Jens.Kortus@physik.tu-freiberg.de

4) Use the subgroup D_6 and sketch possible molecular orbitals for benzene considering only p_z-orbitals! (Construction of benzene π-states)



Jens.Kortus@physik.tu-freiberg.de

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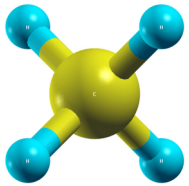
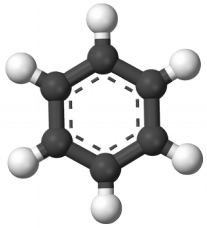
Methene

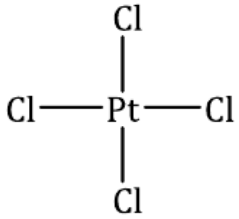


T_d

Benzene

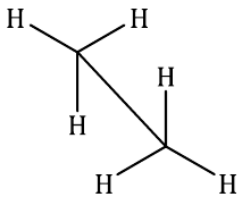


D_{6h}



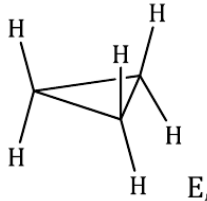
D_{4h}

Ethane (staggered) – D_{3d}



E, $2C_3$, $3C_2$, i, $2S_6$, $3\sigma_d$

Cyclopropane – D_{3h}



E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$

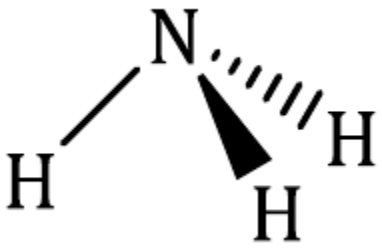
2) If a molecule has an improper rotation (S_n), then it is optically inactive.

Which of the following molecules may have a dipole moment or is optically active?
Methene, benzene, ethane, CO_2, H_2O, NH_3, $PtCl_4$

Dipole: H_2O, NH_3

Jens.Kortus@physik.tu-freiberg.de

3) Find the normal modes of ammonia NH_3 and discuss IR/Raman activity of the modes!



C_{3v}	E	2 C_3	3σ_v
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ^{3N}	12	0	2

$\Gamma_{vib}(H_2O) = (3A_1 + A_2 + 4E) - (A_1 + E) - (A_2 + E) = 2A_1 + 2E$

Modes are IR and Raman active.

i) Add 1 to the character if the basis function is unchanged by the symmetry operation
ii) Add –1 to the character if the basis function changes sign under the symmetry operation;
iii) Add 0 to the character if the basis function moves when the symmetry operation is applied.

Jens.Kortus@physik.tu-freiberg.de

Using a character table:

The character for the 3N Cartesian basis is simply the sum of the characters for the x, y and z functions listed in the character table.

Just multiply this by the number of atoms in the molecule that are not changed by the symmetry operation.

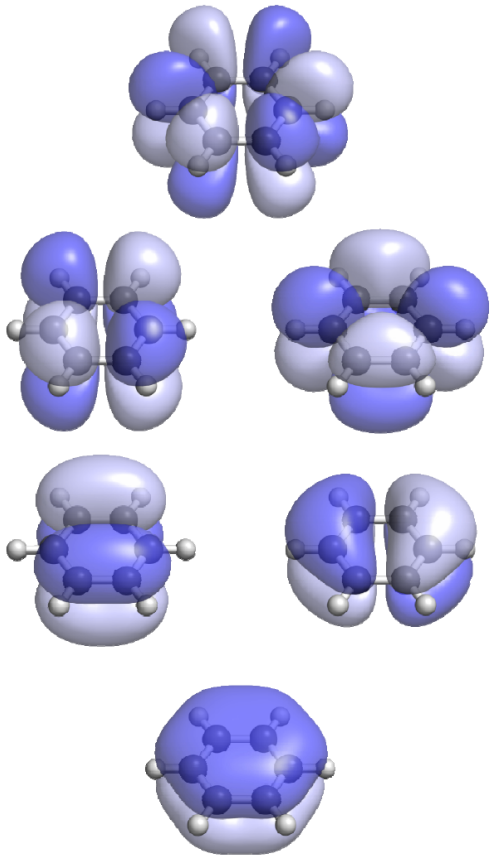
(x,y) transforms like E and z transforms like A1:

E	C3	σ	
3	0	1	sum of characters x,y,z
4	1	2	atoms unchanged by symmetry operation
12	0	2	product of above lines

Jens.Kortus@physik.tu-freiberg.de

4) Use the subgroup D_6 and sketch the possible molecular orbitals for benzene considering only p_z-orbitals! (Construction of benzene π-states)

D_6	E	2 C_6	2 C_3	C_2	3 C_2'	3 C_2''
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0



Jens.Kortus@physik.tu-freiberg.de

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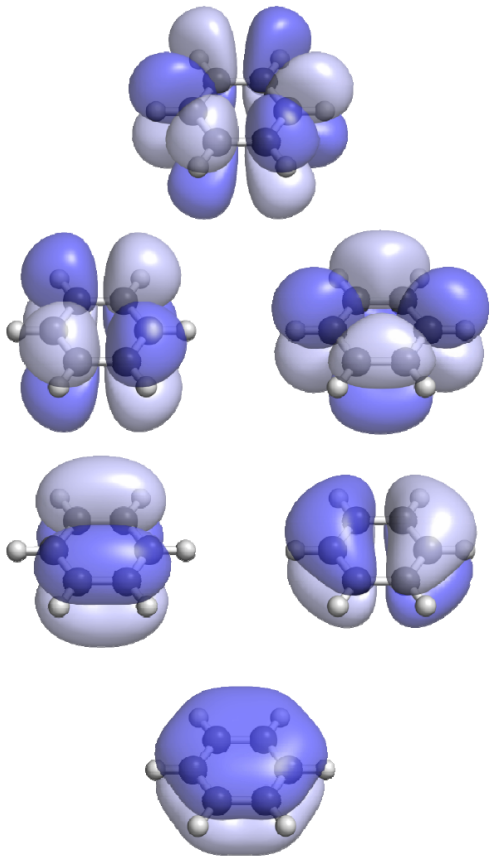
D_6	E	2 C_6	2 C_3	C_2	3 C_2'	3 C_2''
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0



Jens.Kortus@physik.tu-freiberg.de