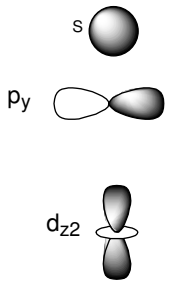
Polyatomic Molecular Orbital Theory

Transformational properties of atomic orbitals

- When bonds are formed, atomic orbitals combine according to their symmetry.
- Symmetry properties and degeneracy of orbitals and bonds can be learned from corresponding character tables by their inspection holding in mind the following transformational properties:

Atomic orbital	Transforms as
s	$x^2+y^2+z^2$
p_x	x
p_y	y
p_z	z
d_{z2}	z^2, $2z^2-x^2-y^2$
d_{x2-y2}	x^2-y^2
d_{xy}	xy
d_{xz}	xz
d_{yz}	yz



Examples of atomic orbitals symmetry analysis

Atomic orbital	Mulliken labels				
	C_{2v}	D_{3h}	D_{4h}	T_d	O_h
s	a_1	a_1'	a_{1g}	a_1	a_{1g}
p_x	b_1	e'	e_u	t_2	t_{1u}
p_y	b_2	e'	e_u	t_2	t_{1u}
p_z	a_1	a_2''	a_{2u}	t_2	t_{1u}
d_{z2}	a_1	a_1'	a_{1g}	e	e_g
d_{x2-y2}	a_1	e'	b_{1g}	e	e_g
d_{xy}	a_2	e'	b_{2g}	t_2	t_{2g}
d_{xz}	b_1	e''	e_g	t_2	t_{2g}
d_{yz}	b_2	e''	e_g	t_2	t_{2g}

C_{2v}		
A_1	z	x^2, y^2, z^2
A_2	R_z	xy
B_1	x, R_y	xz
B_2	y, R_x	yz

D_{3h}		
A_1'		x^2+y^2, z^2
A_2'	R_z	
E'	(x,y)	(x^2-y^2, xy)
A_1''		
A_2''	z	
E''	(R_x,R_y)	(xz, yz)

D_{4h}		
A_{1g}		x^2+y^2, z^2
B_{1g}		x^2-y^2
B_{2g}		xy
E_g	(R_x,R_y)	(xz, yz)
A_{2u}	z	
E_u	(x, y)	

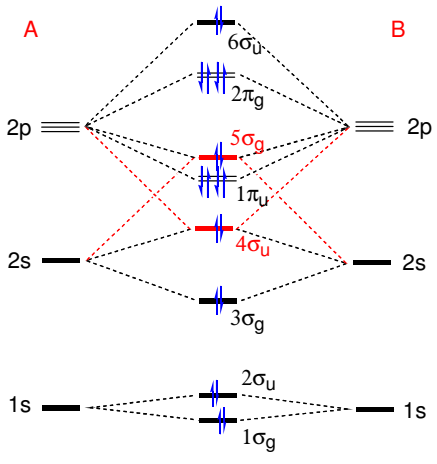
T_d		
A_1		$x^2+y^2+z^2$
A_2		
E		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	(R_x,R_y,R_z)	
T_2	(x,y,z)	(xz, yz, xy)

O_h		
A_{1g}		$x^2+y^2+z^2$
E_g		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	(R_x,R_y,R_z)	
T_{2g}		(xz, yz, xy)
T_{1u}	(x,y,z)	
…		

MO diagram of homonuclear diatomic molecules

- Filling the resulting MO's of homonuclear diatomic molecules with electrons leads to the following results:

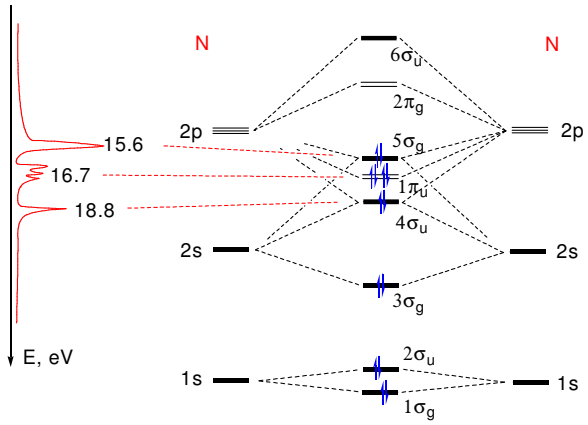
AB	# of e's	Bond order	# unpair. e's	Bond energy, eV
Li_2	6	1	0	1.1
Be_2	8	0	0	-
B_2	10	1	2	3.0
C_2	12	2	0	6.4
N_2	14	3	0	9.9
O_2	16	2	2	5.2
F_2	18	1	0	1.4
Ne_2	20	0	0	-



Bond order = ½ (#Bonding e's - #Antibonding e's)

MO-energy levels in N_2 molecule

- Photoelectron spectroscopy of simple molecules is an invaluable source of the information about their electronic structure.
- The He-I photoelectron spectrum of gaseous N_2 below proves that there is the σ-π level inversion in this molecule. It also allows identify bonding (peaks with fine vibronic structure) and non-bonding MO (simple peaks) in it.



Let's Play with some MO's

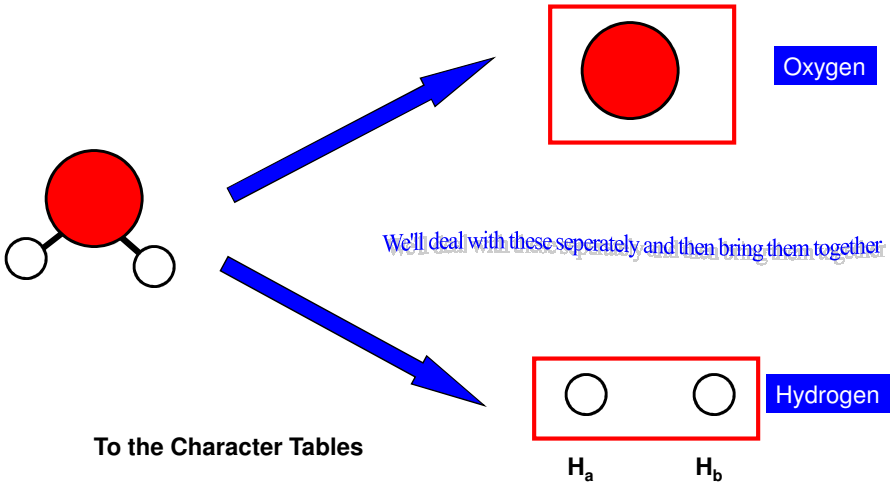
water…water…water….

To begin….How to Deal with more than two atoms?

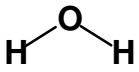
You use some Acronyms! Sounds Good!

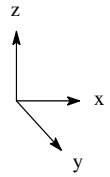
- SALCs – **S**ymmetry **A**dapted **L**inear **C**ombinations
- LGOs – **L**igand **G**roup **O**rbitals

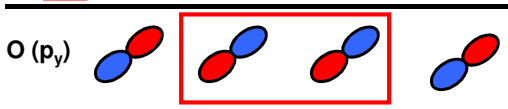
Lets Separate the O for the H H



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

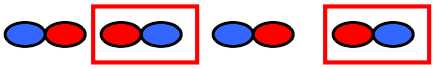




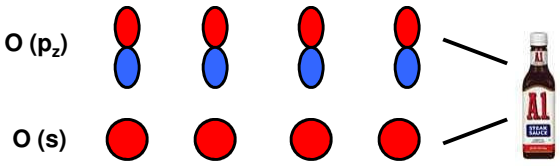


B_2

Oxygen

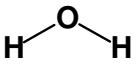


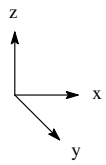
B_1

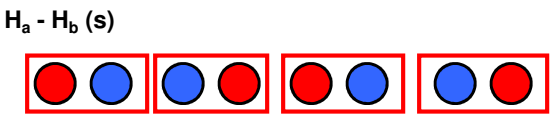


A_1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

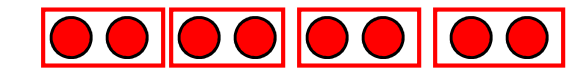




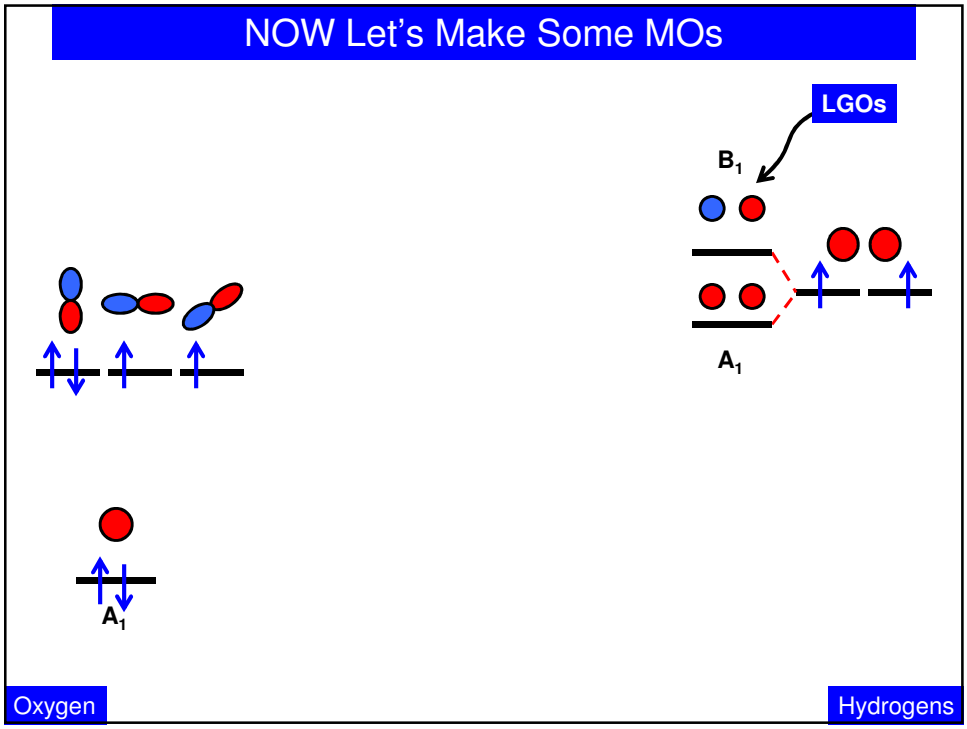


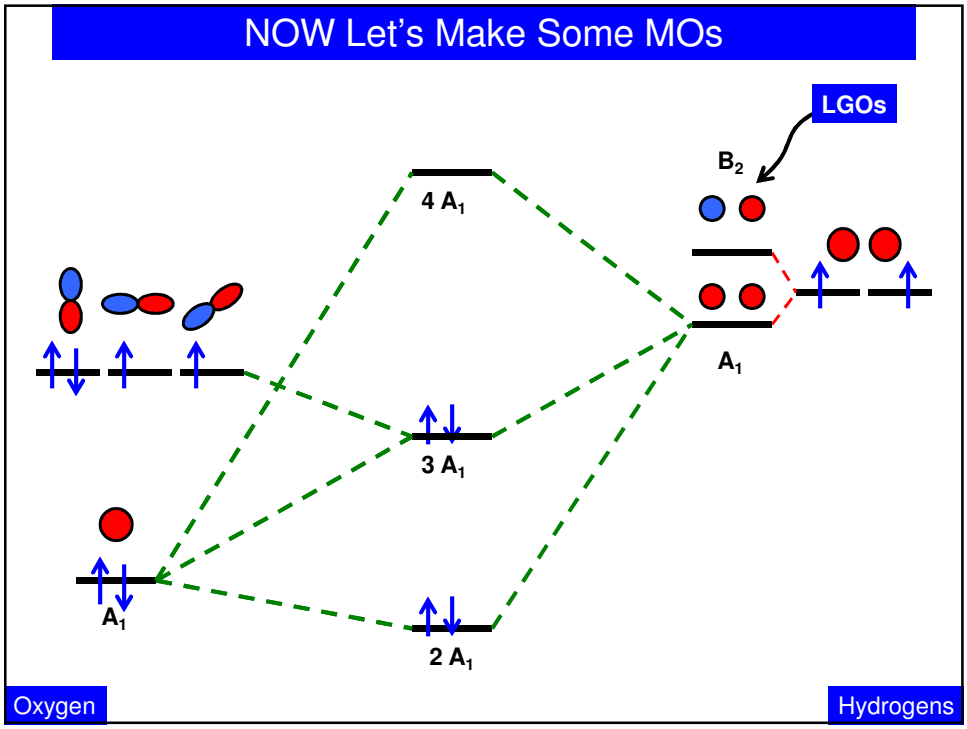
Hydrogen

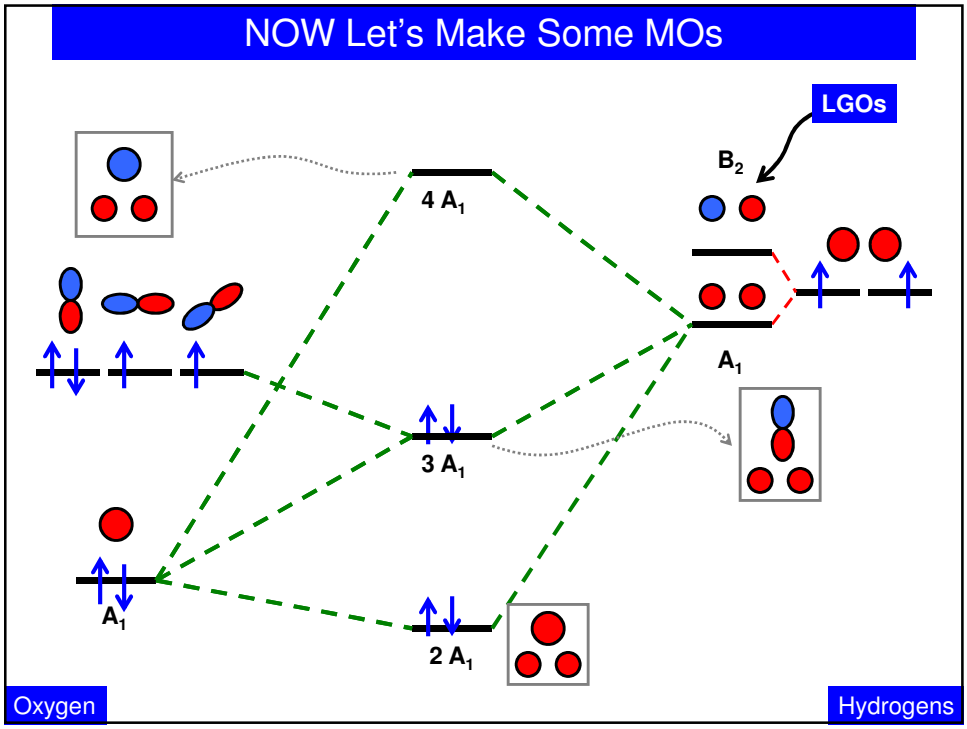
B_1

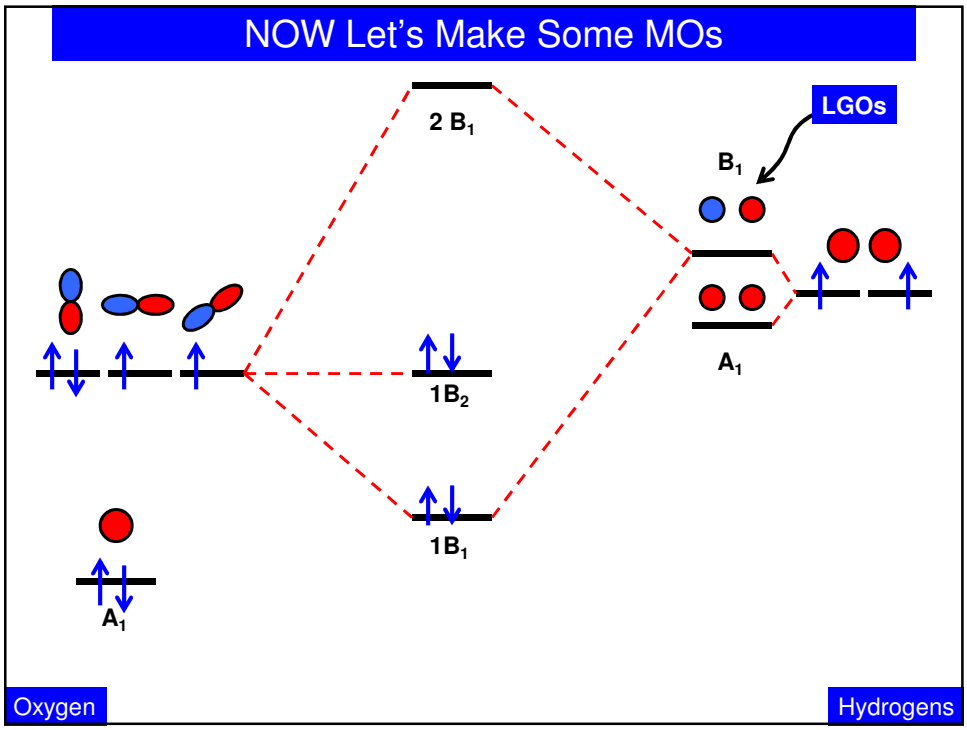


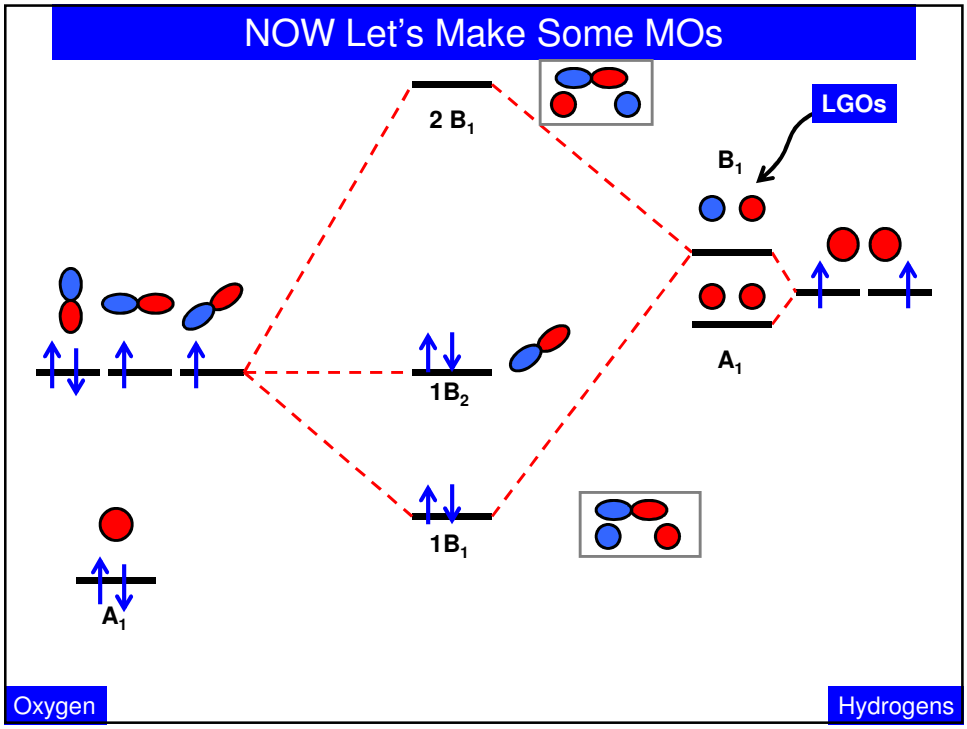
A_1


NOW Let's Make Some MOs
LGOs
B1
A1
A1
Oxygen
Hydrogens


NOW Let's Make Some MOs
LGOs
B2
4 A1
A1
3 A1
A1
2 A1
Oxygen
Hydrogens


NOW Let's Make Some MOs
LGOs
B2
4 A1
A1
3 A1
A1
2 A1
Oxygen
Hydrogens


NOW Let's Make Some MOs
2 B1
LGOs
B1
A1
1B2
1B1
A1
Oxygen
Hydrogens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2 B1
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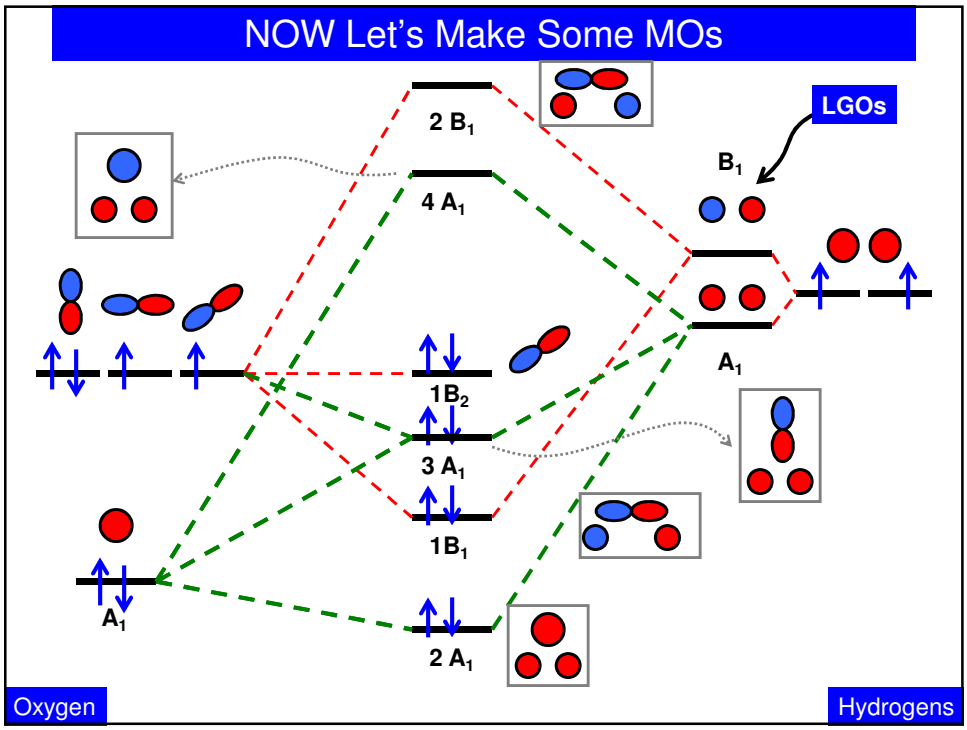
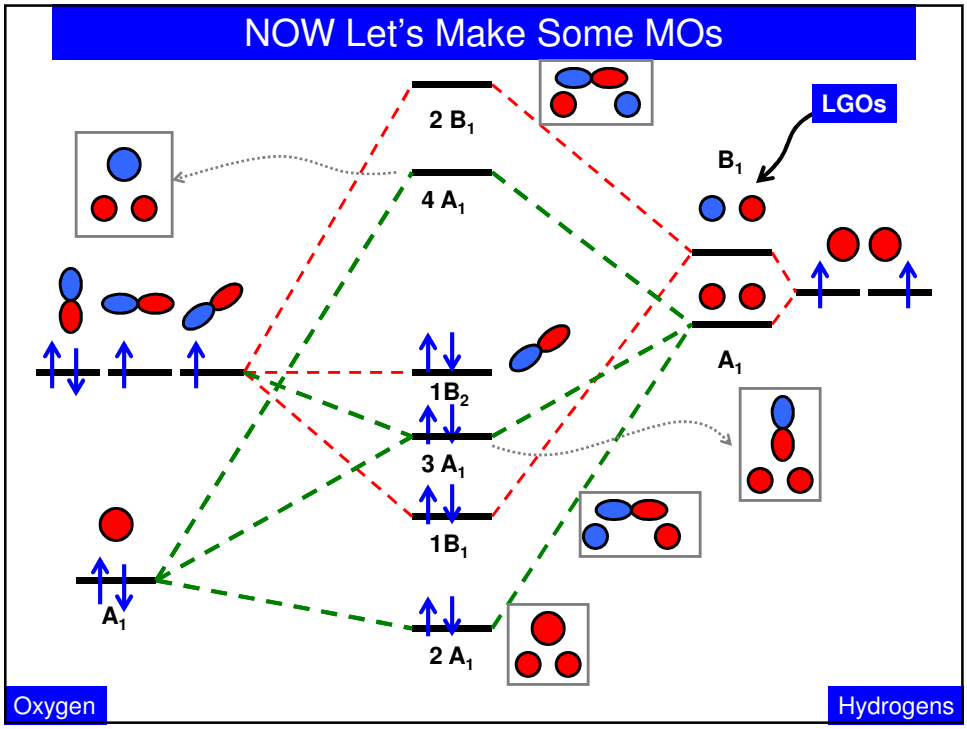
Oxygen
Hydrogens

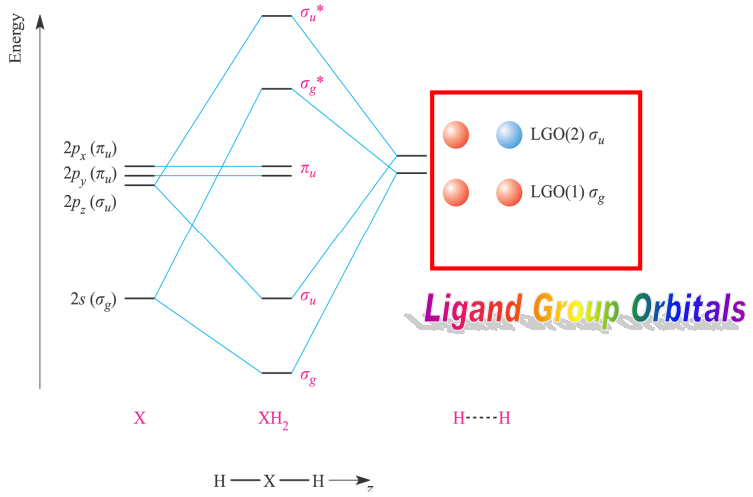

NOW Let's Make Some MOs
2 B1
LGOs
B1
4 A1
A1
1B2
3 A1
1B1
A1
2 A1
Oxygen
Hydrogens



Now for the Million Dollar Question

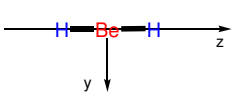
Why is Water Bent???

Molecular Orbital Theory – linear XH_2 molecules

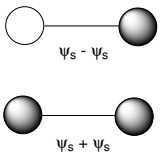


Molecular Orbitals of BeH_2

- BeH_2 ($D_{\infty h}$)

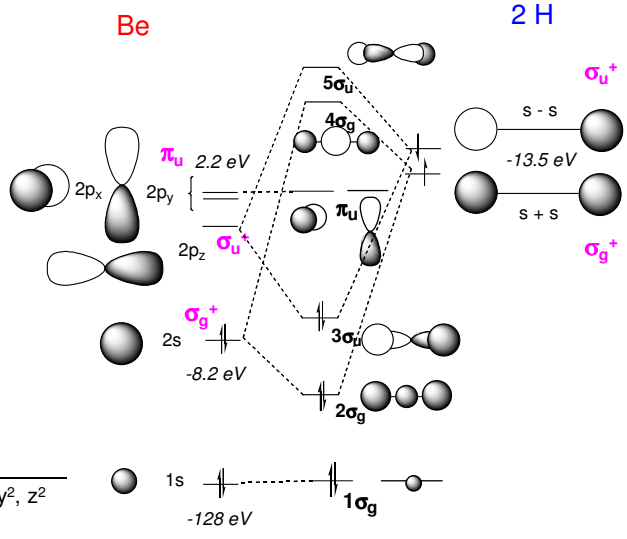


Group orbitals of 2H's:

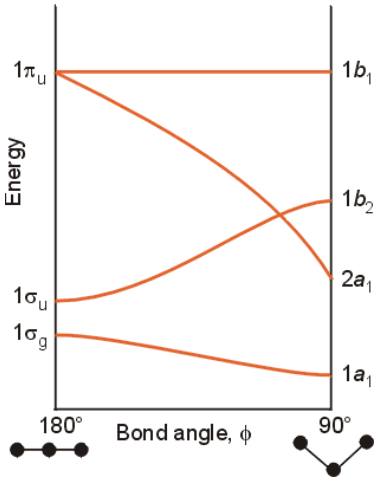


$1\sigma_g^2 2\sigma_g^2 3\sigma_u^2$

$D_{\infty h}$	$\infty\sigma_v$	i		
Σ_g^+	1	1		$x^2+y^2,\ z^2$
Σ_u^+	1	-1	z	
Π_u	0	-2	(x,y)	



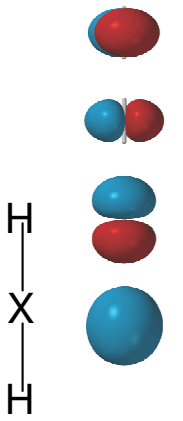
Molecular Orbital Theory – Walsh diagram

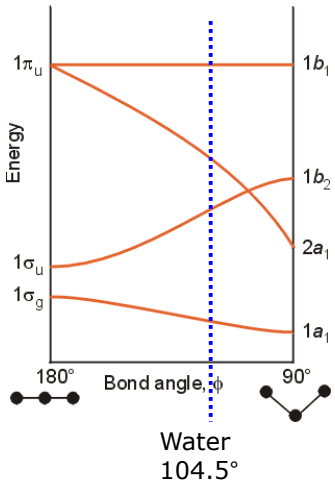


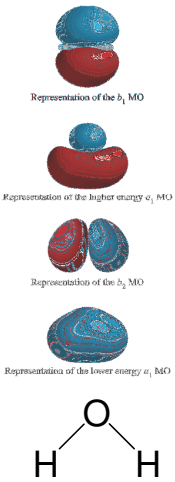
The Walsh diagram shows what happens to the molecular orbitals for a set of molecules which are related in structure.

In this case, the difference is the H-X-H bond angle which decreases from 180° to 90°

Molecular Orbital Theory – Walsh diagram

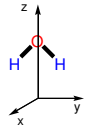


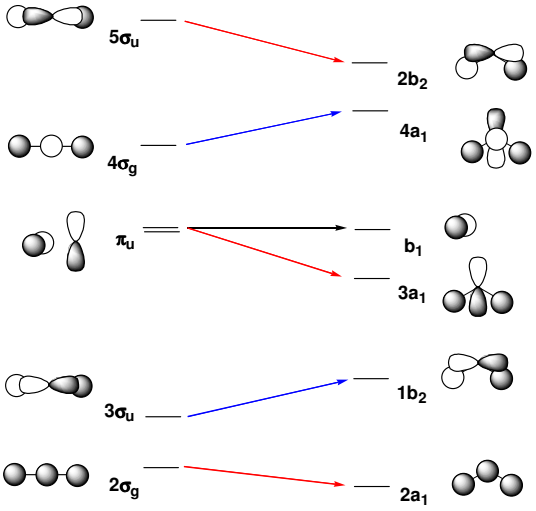




4) MO theory and molecular geometry (Walsh diagrams)

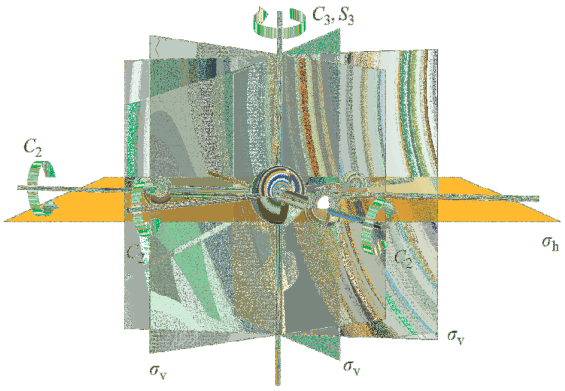
- Correlate changes in energy of MO's between species AB_x of high and lower symmetry, such as BeH_2 and H_2O.





BeH_2 $2\sigma_g^2 3\sigma_u^2$ linear
BH_2 $2a_1^2 1b_2^2 3a_1^1$, 131°
CH_2 $2a_1^2 1b_2^2 3a_1^2$, 102°
NH_2 $2a_1^2 1b_2^2 3a_1^2 1b_1^1$, 103°
OH_2 $2a_1^2 1b_2^2 3a_1^2 1b_1^2$, 105°
FH_2^+ $2a_1^2 1b_2^2 3a_1^2 1b_1^2$, 113°

Molecular Orbital Theory – BH_3



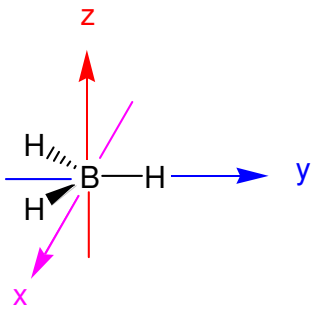
BH_3 has a C_3 principal axis of symmetry, 3 C_2 axes ($\perp C_3$), 3 σ_v, and σ_h – it is in a D_{3h} point group

Molecular Orbital Theory – BH_3

The BH_3 molecule exists in the gas phase, but dimerizes to B_2H_6 (which we will look at a bit later)

$2\ BH_3 \rightleftharpoons B_2H_6$

The BH_3 molecule is trigonal planar and we will make the C_3 principal axis of symmetry the z axis, with the x and y axes in the plane of the molecule. The y axis (arbitrary) will be along one of the B-H bonds.

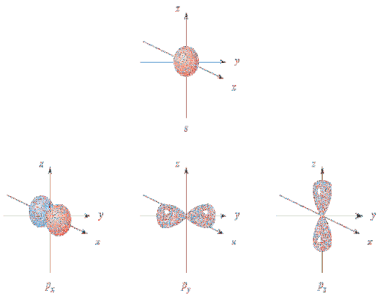


Molecular Orbital Theory – D_{3h} Character Table

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

Molecular Orbital Theory – D_{3h} Character Table

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0



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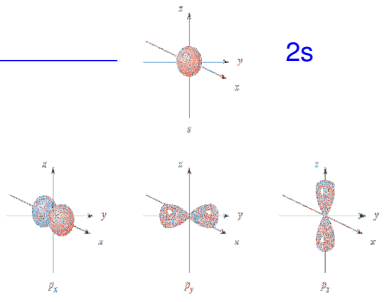
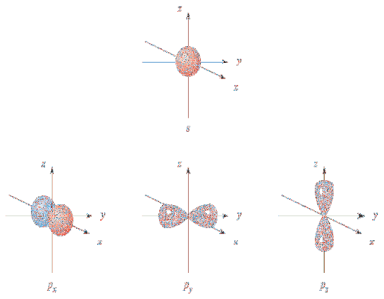
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0



Molecular Orbital Theory – D_{3h} Character Table

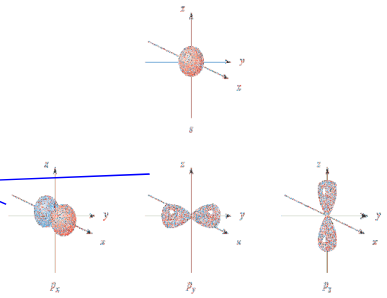
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0



$2p_z$

Molecular Orbital Theory – D_{3h} Character Table

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

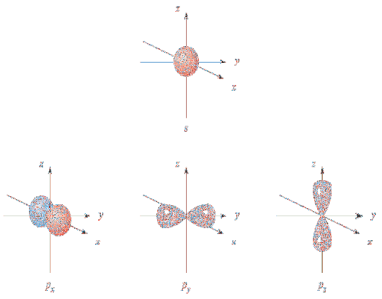


$2p_x$ $2p_y$

doubly degenerate

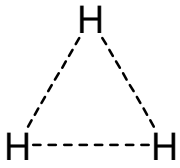
Molecular Orbital Theory – D_{3h} Character Table

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0



Molecular Orbital Theory – LGOs on H atoms

In BH_3 we need three LGOs, formed from linear combinations of the H 1s orbitals



What happens if we carry out the D_{3h} symmetry operations on this group of H 1s orbitals? How many remain unchanged?

E	C_3	C_2	σ_h	S_3	σ_v
3	0	1	3	0	1

Molecular Orbital Theory – LGOs on H atoms

E	C_3	C_2	σ_h	S_3	σ_v
3	0	1	3	0	1

The resulting row of characters is also obtained by adding the characters of the A_1' and E' representations

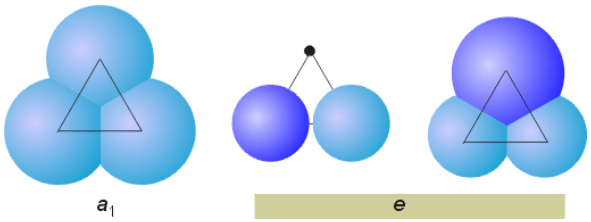
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
E'	2	-1	0	2	-1	0
LGOs	3	0	1	3	0	1

Molecular Orbital Theory – LGOs for BH_3

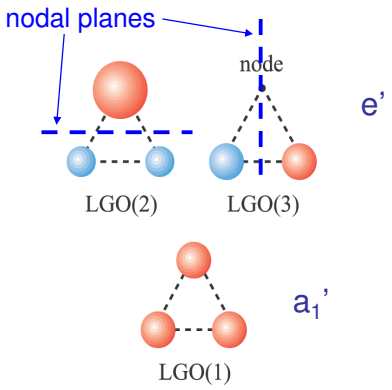
$$\Psi(a_1') = (1/\sqrt{3})(\Psi_1 + \Psi_2 + \Psi_3)$$

$$\Psi(e')_1 = (1/\sqrt{6})(2\Psi_1 - \Psi_2 - \Psi_3)$$

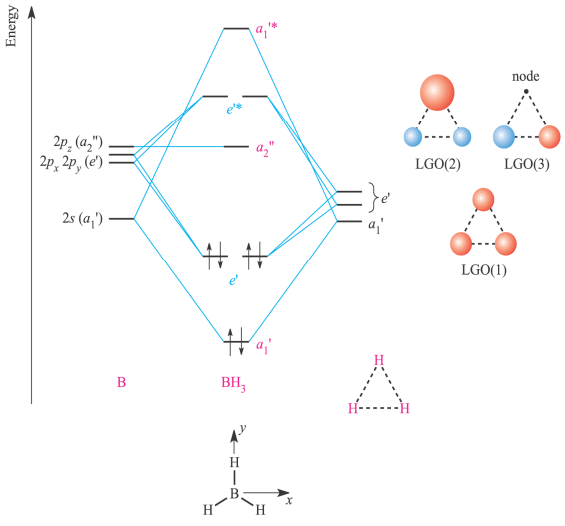
$$\Psi(e')_2 = (1/\sqrt{2})(\Psi_2 - \Psi_3)$$



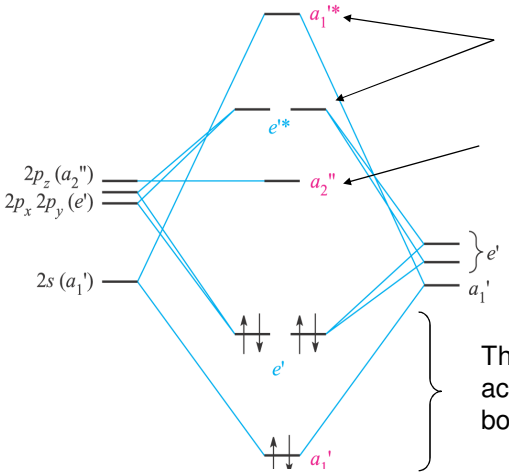
Molecular Orbital Theory – LGOs for BH_3



Molecular Orbital Theory



Molecular Orbital Theory – BH_3

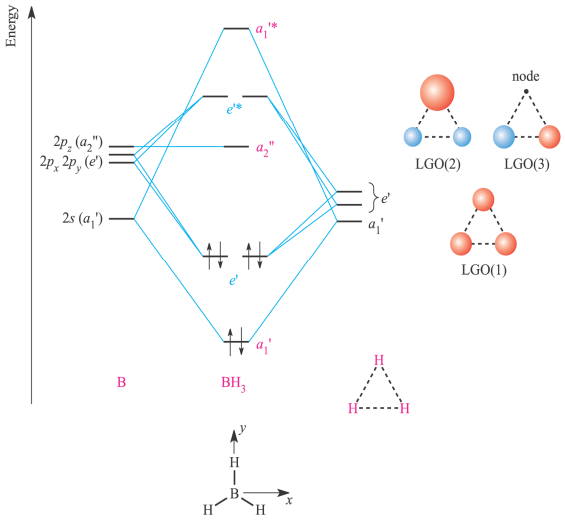


Empty anti-bonding MOs

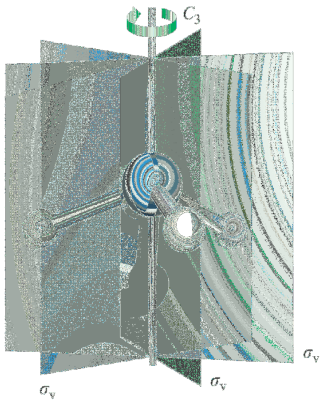
Empty non-bonding MO

Three bonding MOs are filled, accounting for the three B-H σ bonds

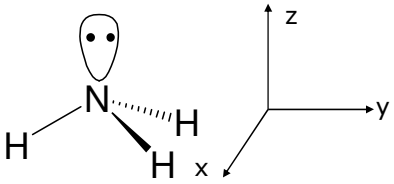
Molecular Orbital Theory



Molecular Orbital Theory – NH_3



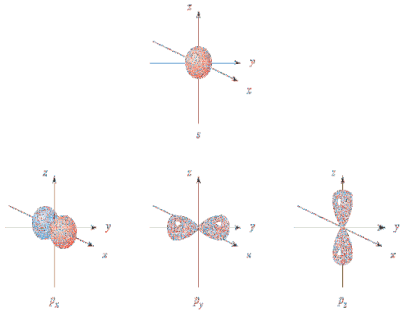
The ammonia molecule, NH_3, has C_{3v} symmetry, with a C_3 principal axis of symmetry and 3 vertical planes of symmetry



Molecular Orbital Theory – NH_3

Part of the character table of C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0



Molecular Orbital Theory – NH_3

Part of the character table of C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

2s and $2p_z$ orbitals on N

Molecular Orbital Theory – NH_3

Part of the character table of C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$2p_x$ and $2p_y$ orbitals on N

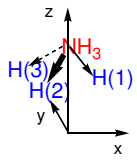
Molecular Orbital Theory – NH_3

Part of the character table of C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
LGOs	3	0	1	← $a_1 + e$

2) Molecular Orbitals of NH_3 (C_{3v})

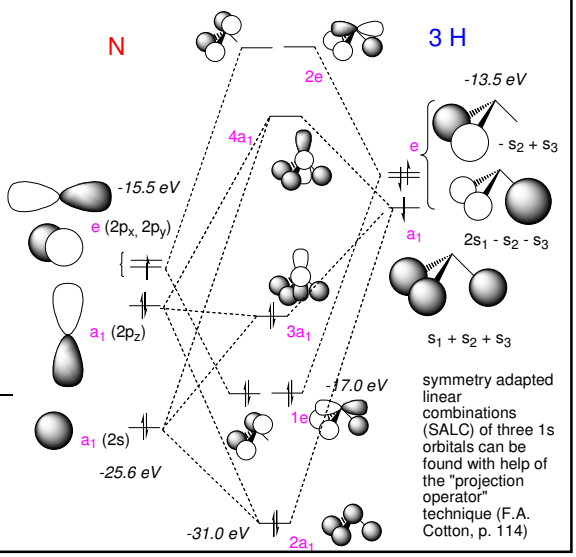
- NH_3 (C_{3v}: E, $2C_3$, $3\sigma_v$)



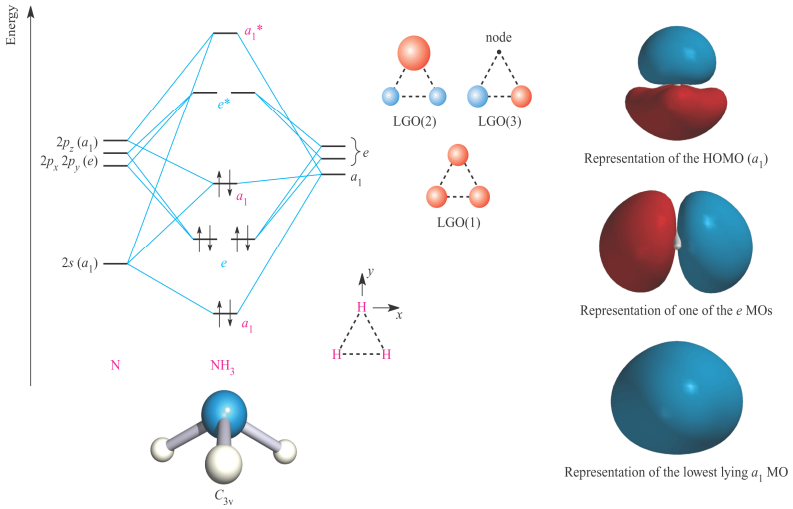
The symmetry of 3H's group orbitals:

$\Gamma_r = 3E+0C_3+\sigma_v = A_1 + E$

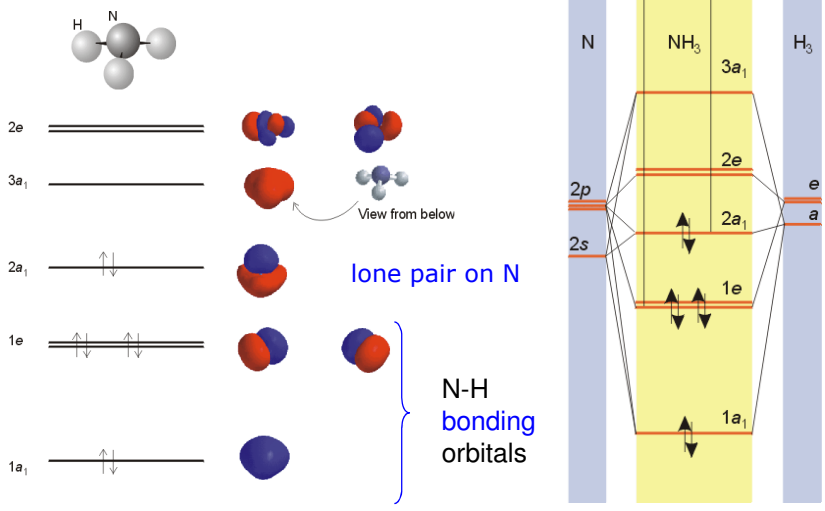
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	



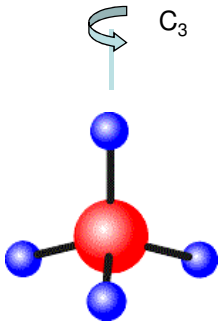
Molecular Orbital Theory



Molecular Orbital Theory –



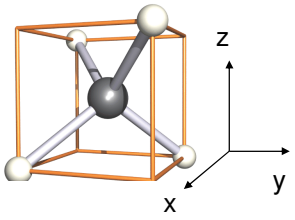
Molecular Orbital Theory – Methane T_d



Methane has T_d symmetry, a cubic point group

The C_3 axes in CH_4 coincide with the C-bonds

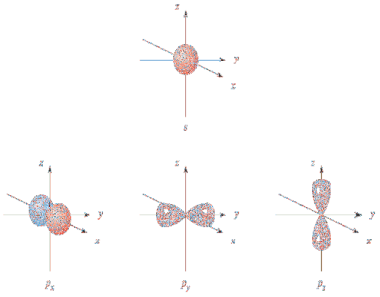
The C_2 and S_4 axes coincide with the x, and z axes



Molecular Orbital Theory – T_d character table

Part of the T_d Character Table

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6s_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1



Molecular Orbital Theory – T_d character table

Part of the T_d Character Table

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6s_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

2s of C

Molecular Orbital Theory – T_d character table

Part of the T_d Character Table

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6s_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$2p_x$, $2p_y$, and $2p_z$ are triply degenerate

Molecular Orbital Theory – T_d character table

Part of the T_d Character Table

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6s_d$	
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	
T_1	3	0	-1	1	-1	
T_2	3	0	-1	-1	1	
LGOs	4	1	0	0	2	$= a_1 + t_2$

Molecular Orbital Theory – T_d character table

Wavefunctions for the LGOs for methane hydrogens

$$\psi(a_1) = \tfrac{1}{2} (\psi_1 + \psi_2 + \psi_3 + \psi_4)$$

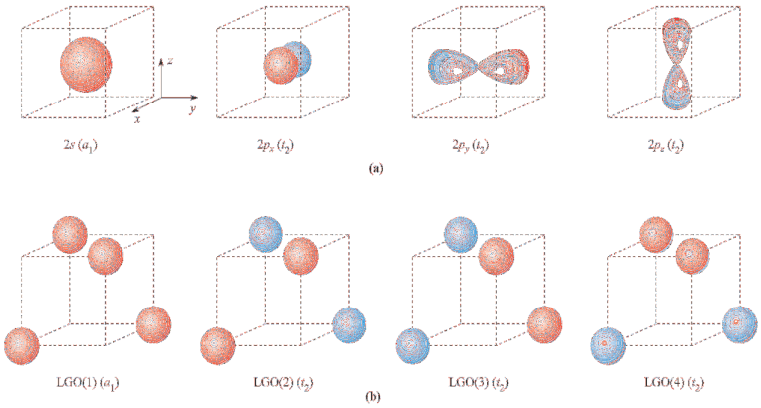
$$\psi(t_2)_1 = \tfrac{1}{2} (\psi_1 - \psi_2 + \psi_3 - \psi_4)$$

$$\psi(t_2)_2 = \tfrac{1}{2} (\psi_1 + \psi_2 - \psi_3 - \psi_4)$$

$$\psi(t_2)_3 = \tfrac{1}{2} (\psi_1 - \psi_2 - \psi_3 + \psi_4)$$

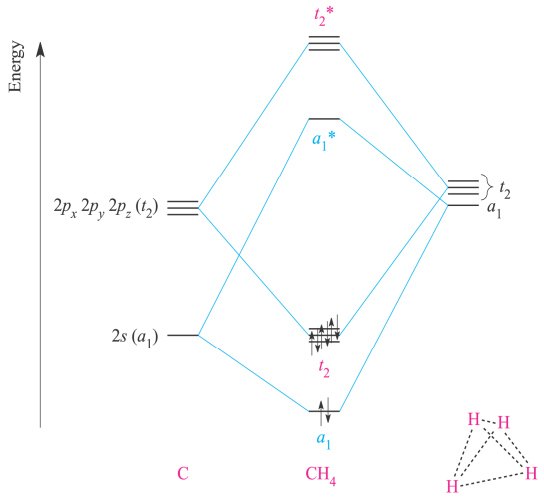
Molecular Orbital Theory – LGOs for methane

C atomic orbitals



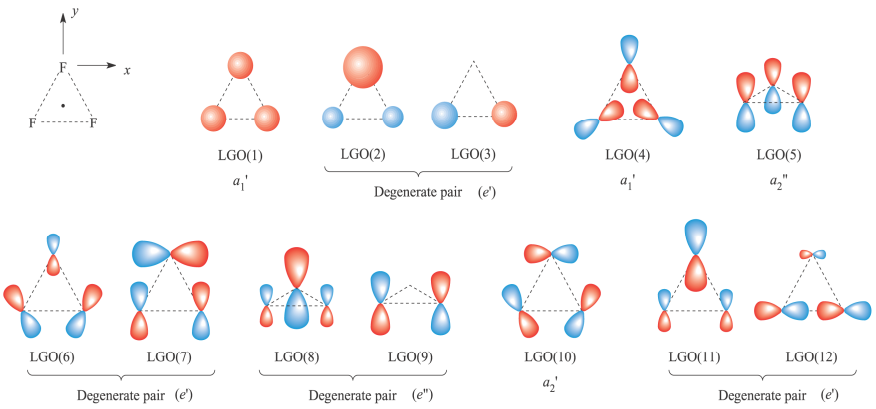
H ligand group orbitals

Molecular Orbital Theory - methane



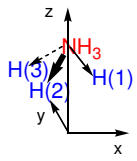
Molecular Orbital Theory – LGOs for F atoms

What if the atoms attached to the central atom are not H, and have valence p orbitals, such as fluorines?



2) Molecular Orbitals of NH_3 (C_{3v})

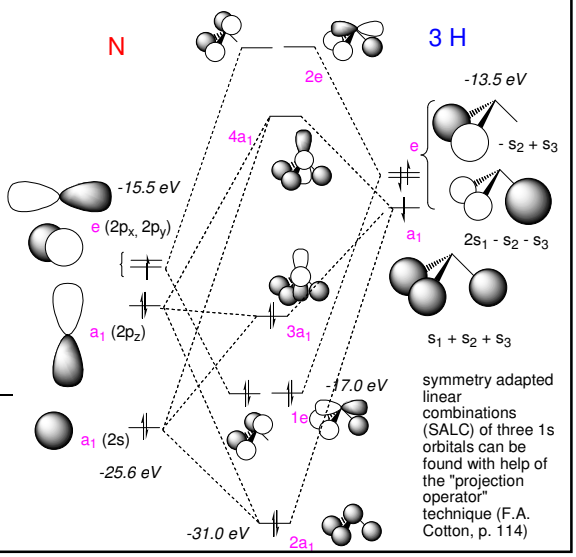
- NH_3 (C_{3v}: E, $2C_3$, $3\sigma_v$)



The symmetry of 3H's group orbitals:

$\Gamma_r = 3E+0C_3+\sigma_v = A_1 + E$

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	

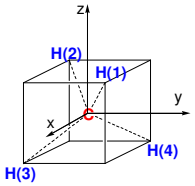


symmetry adapted linear combinations (SALC) of three 1s orbitals can be found with help of the "projection operator" technique (F.A. Cotton, p. 114)

3) Molecular Orbitals of CH_4 (T_d)

The symmetry of 4H's group orbitals:

$\Gamma_r = 4E+1C_3+0C_2+0S_4+2\sigma_d = A_1 + T_2$



T_d		
A_1		$x^2+y^2+z^2$
A_2		
E		
T_1		
T_2	(x,y,z)