Symmetry and Molecular Orbital Theory

Some Considerations for Building Molecular Orbitals

- Molecular orbitals (MOs) are approximated as combinations of atomic orbitals (AOs)
- AOs have intrinsic energies reflected by their ease of ionization
- Lower energy orbitals are said to be more electronegative
- Valence Orbital Ionization Energy (VOIE) values a good place to start

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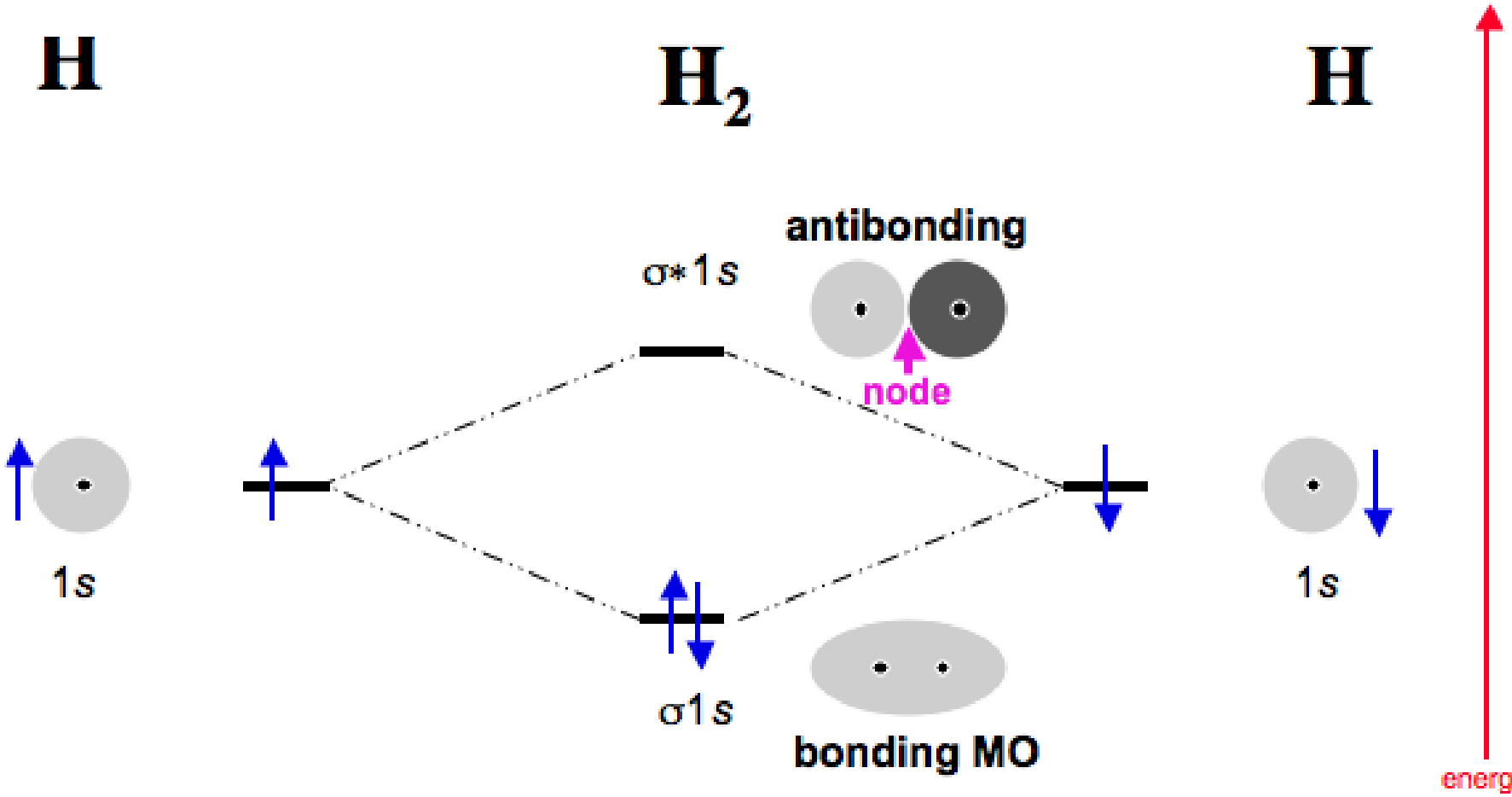
Valence Orbital Ionization Energies, eV

Atom	1*s*	2*s*	2*p*
H	13.6		
He	24.6		
Li		5.4	
Be		9.3	
B		14.0	8.3
C		19.4	10.6
N		25.6	13.2
O		32.3	15.8
F		40.2	18.6
Ne		48.5	21.6

Molecular Orbitals of the H_2 Molecule



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- For H_2 we have two AOs, χ_1 and χ_2
- Each MO, ϕ, will be approximated: $\phi = c_1\chi_1 + c_2\chi_2$
- By symmetry, the electrons have equal probability of being near either H
- $c_1^2 = c_2^2$
- $\therefore c_1 = \pm c_2$

LCAO MO Theory

MOs are approximated as linear combinations of atomic orbitals

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General Features of MO Diagrams

- Bonding MOs are found at low energy
- Non-bonding or lone-pair MOs are at higher energy
- Antibonding MOs are usually vacant and at high energy
- Highest occupied MO (HOMO) is nucleophilic/Lewis basic
- Lowest unoccupied MO (LUMO) is electrophilic/Lewis acidic

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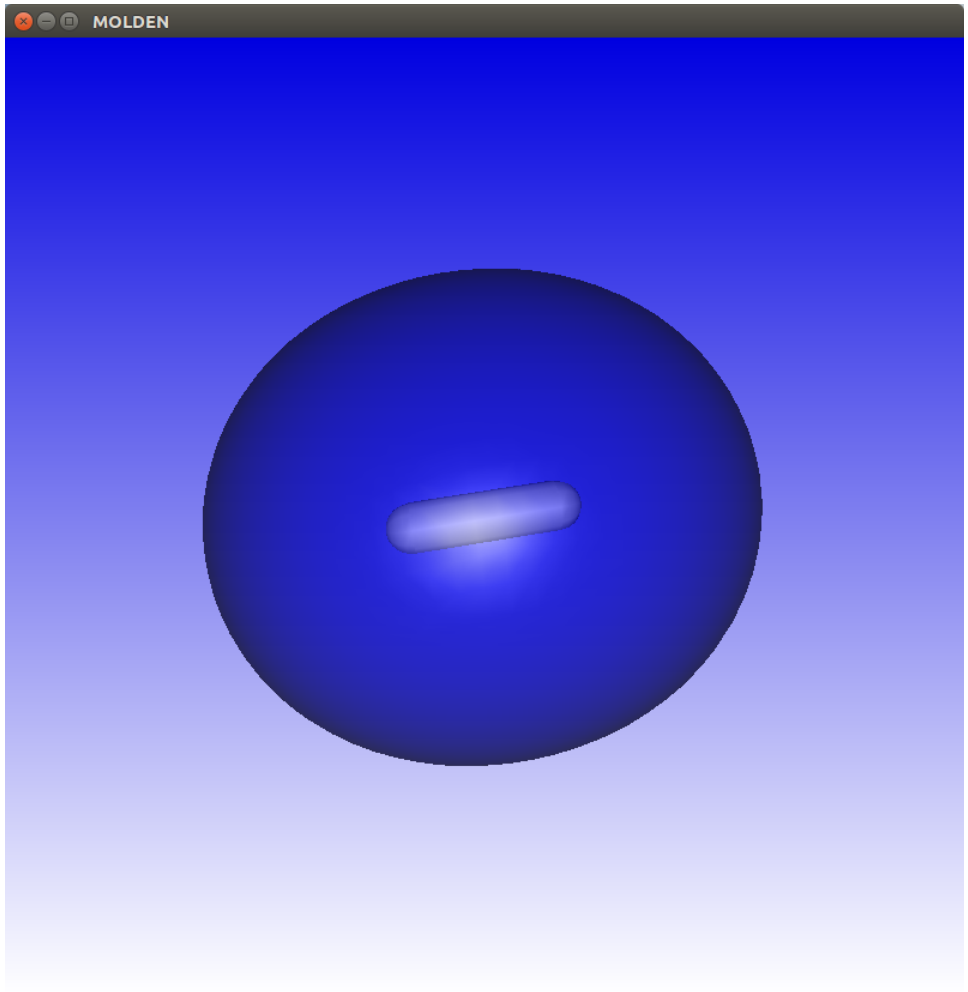

The bonding MO (HOMO): $\phi = c_1\chi_1 + c_2\chi_2$

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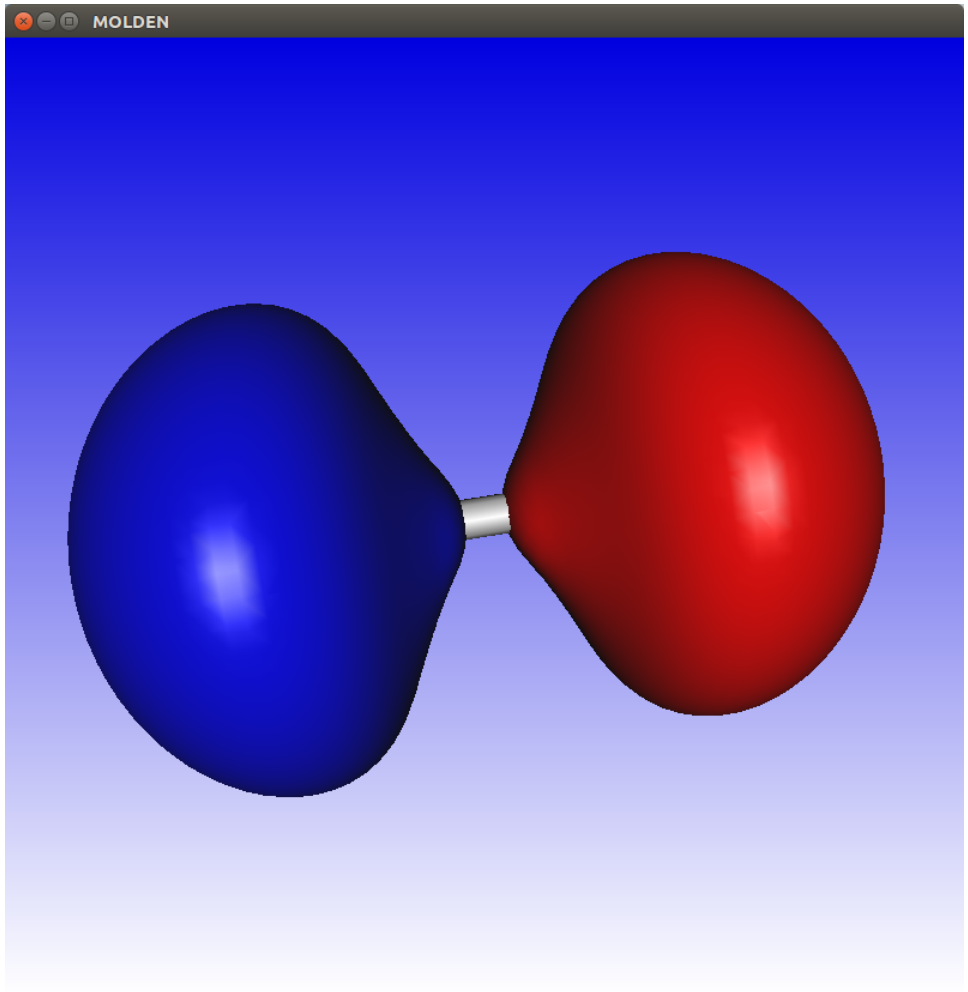

The antibonding MO (LUMO): $\phi = c_1\chi_1 - c_2\chi_2$

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Bonding in the Water Molecule

- Just as in H_2, the two H atoms in C_{2v} H_2O are equivalent by symmetry
- The two H atoms in H_2O are like a "stretched H_2" interacting with an O atom
- We will classify the oxygen atomic orbitals according to their symmetry
- We will also find the symmetry types of the stretched H_2 molecule in the C_{2v} point group
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Bonding in the Water Molecule

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

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- The oxygen $2p_x$ orbital has B_1 symmetry
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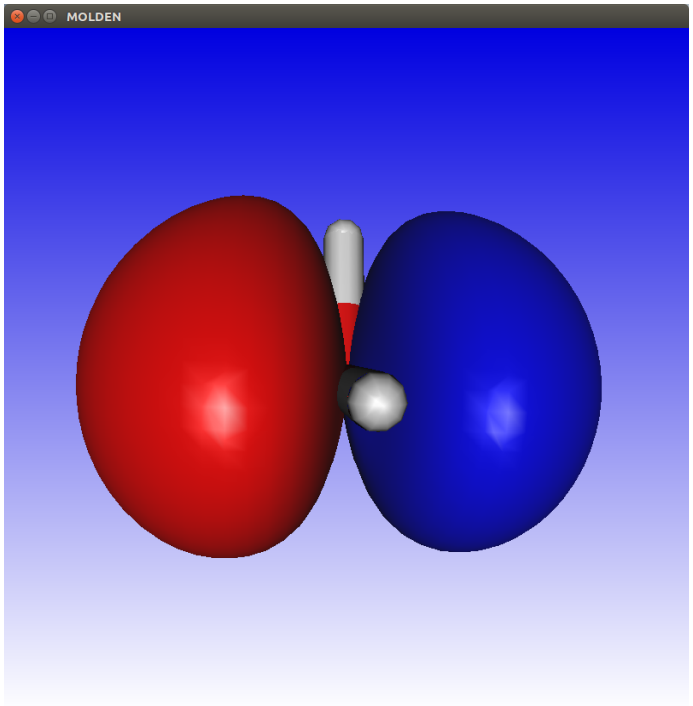
HOMO of the Water Molecule



- The water HOMO has B_1 symmetry
- The water HOMO is a pure oxygen $2p_x$ orbital and does not have any contribution from H
- This lone-pair orbital is orthogonal to the molecular plane and is responsible for the basic/nucleophilic character of the water molecule

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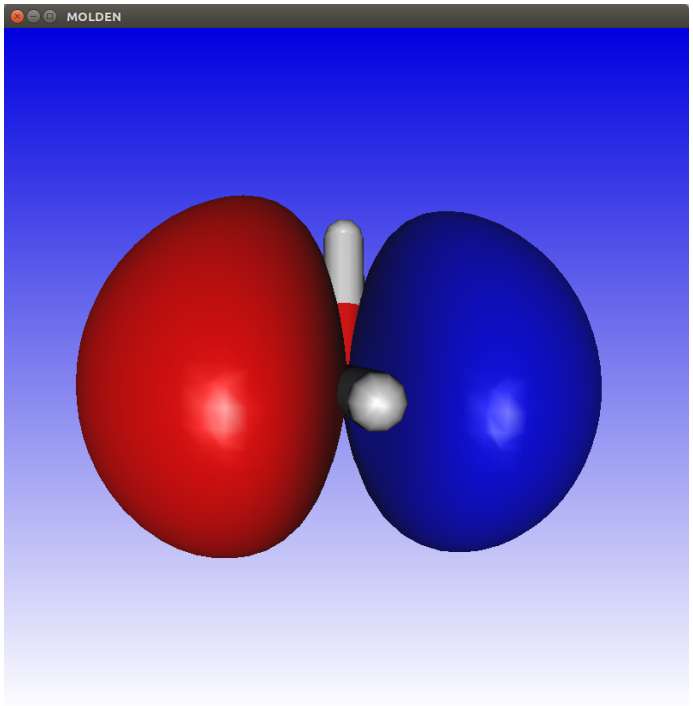
HOMO of the Water Molecule



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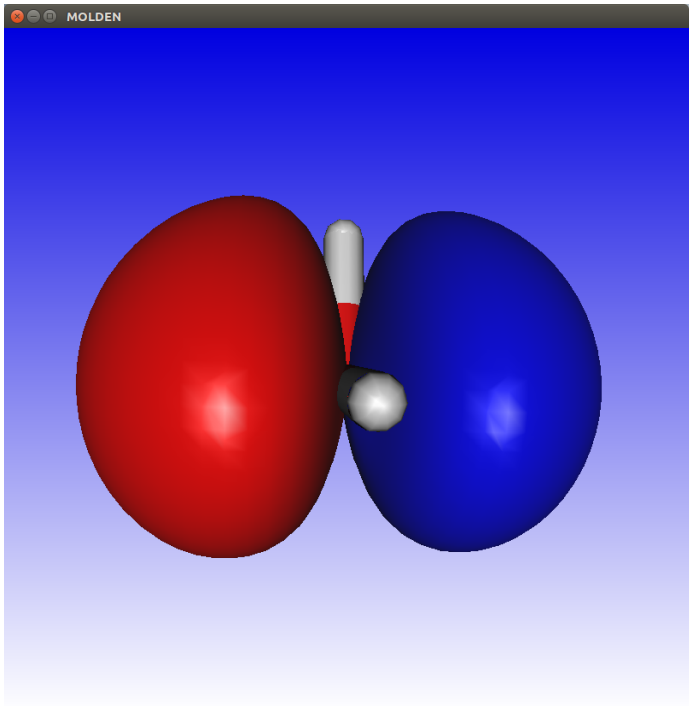

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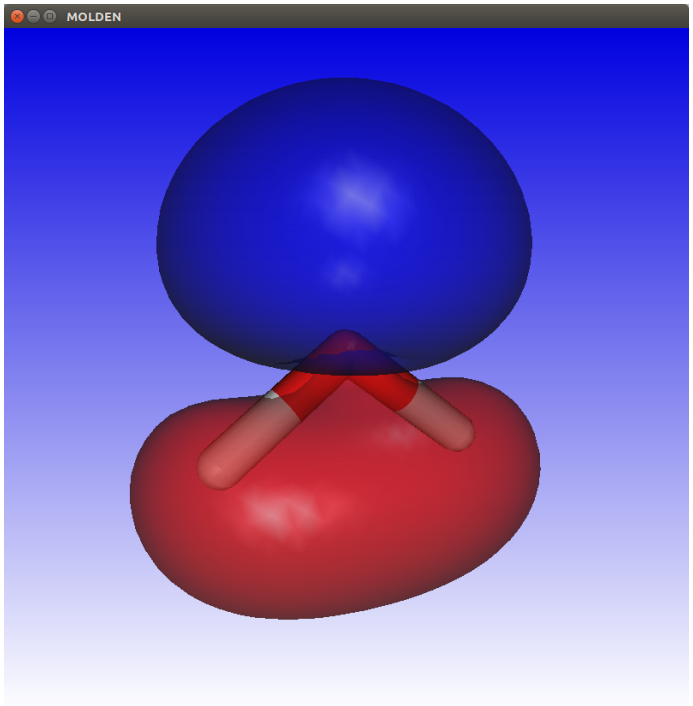

- The water HOMO-1 has A_1 symmetry
- This is a bonding MO with the O $2p_z$ orbital mixing with the bonding MO of H_2

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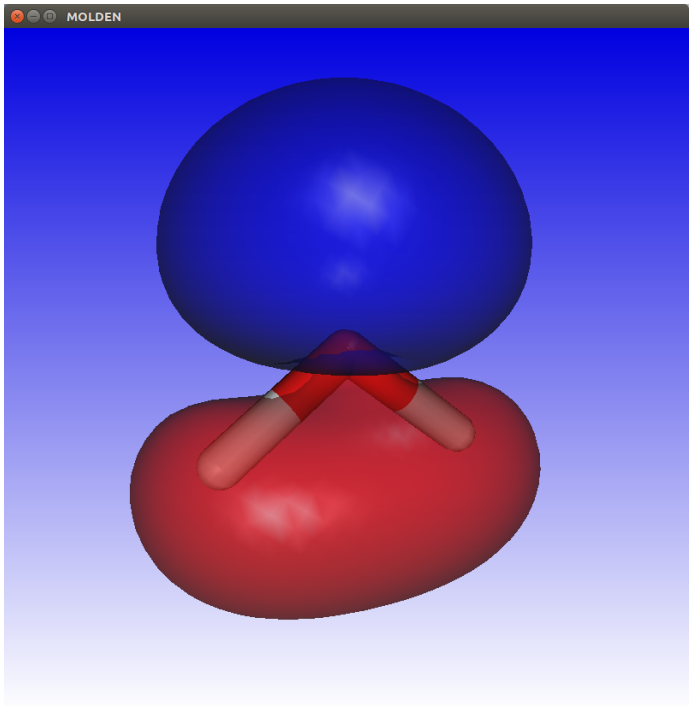
HOMO-1 of the Water Molecule



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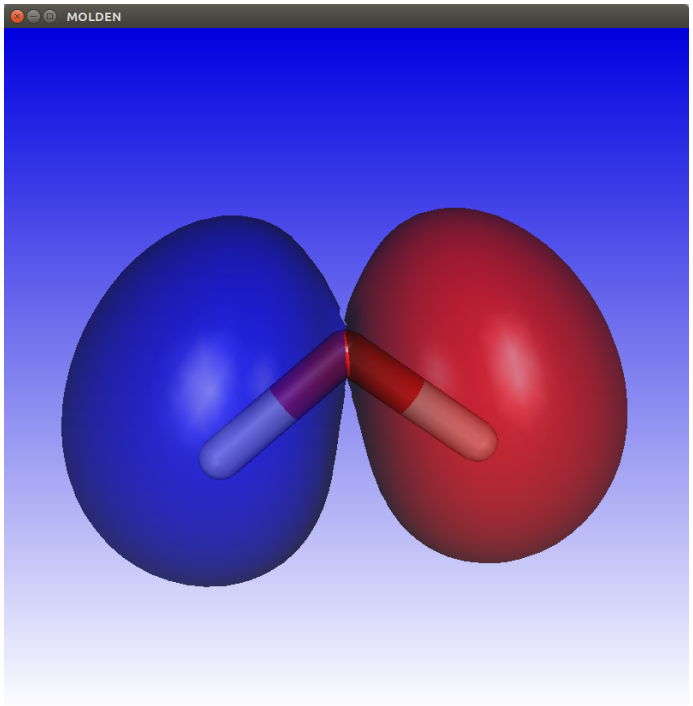
HOMO-2 of the Water Molecule



- The water HOMO-2 has B_2 symmetry
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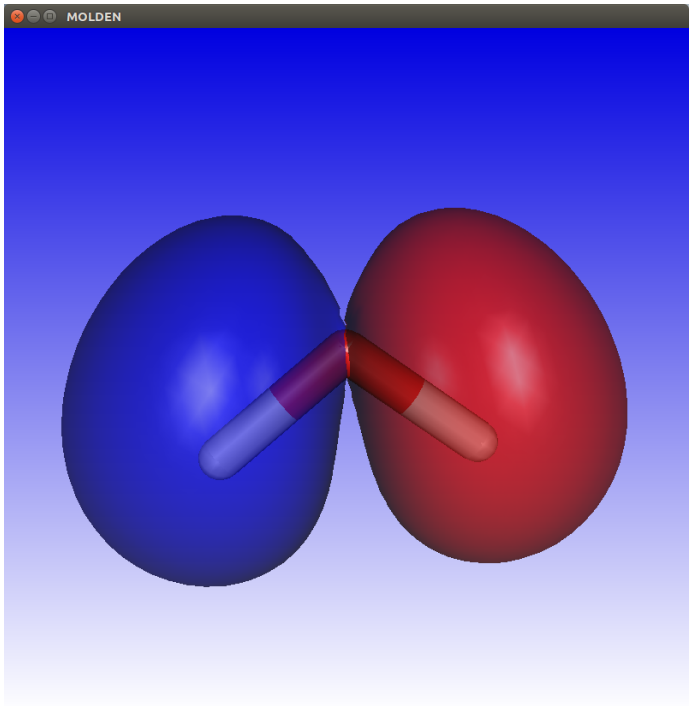
HOMO-2 of the Water Molecule



- The water HOMO-2 has B_2 symmetry
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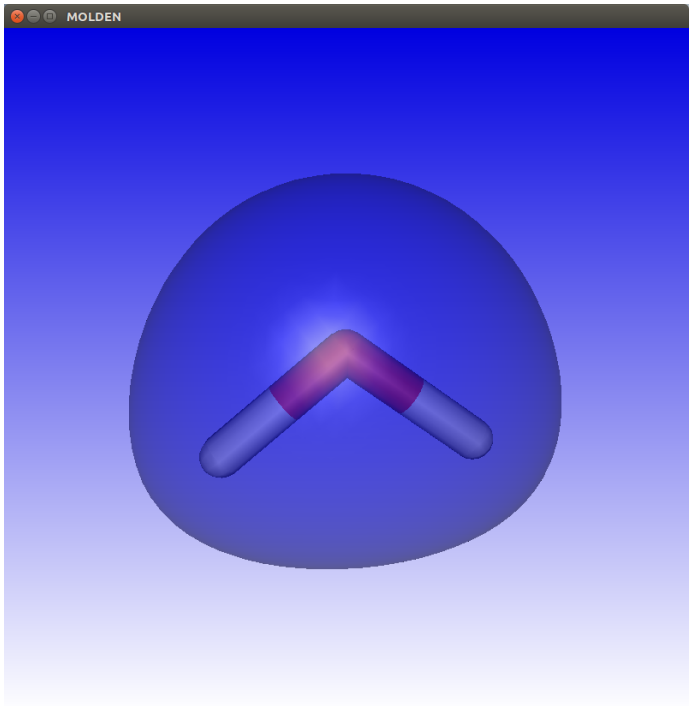
HOMO-3 of the Water Molecule



- The water HOMO-3 has A_1 symmetry
- This is a bonding MO with mostly O $2s$ AO character mixing a little with the bonding MO of H_2

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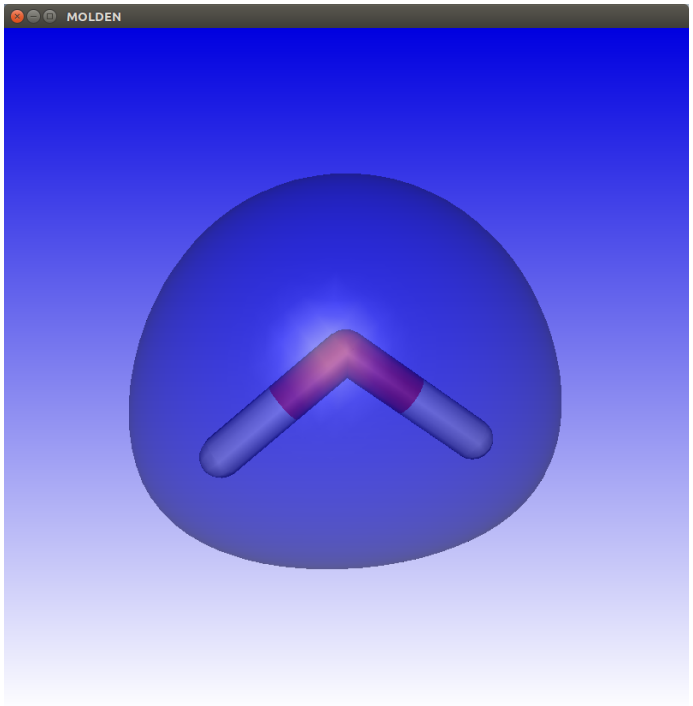

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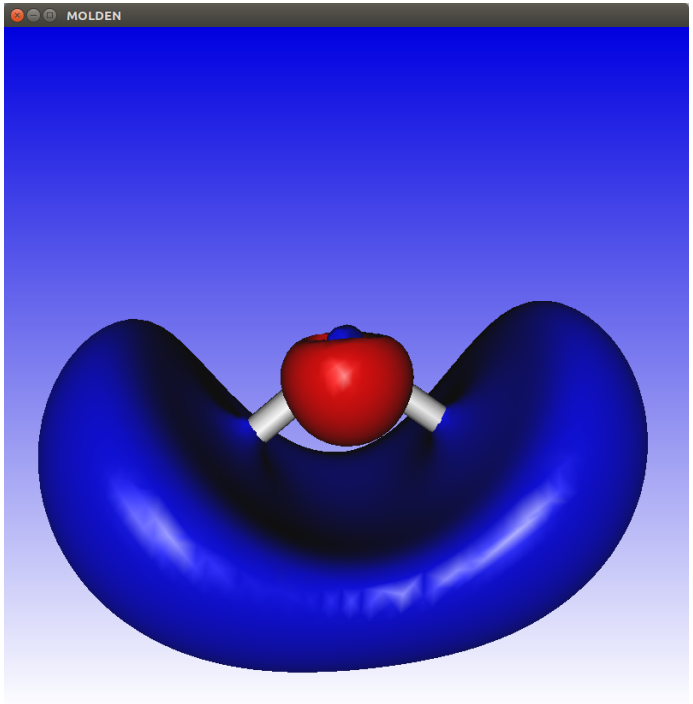
LUMO of the Water Molecule

LUMO: Lowest unnocupied molecular orbital



- The water LUMO has A_1 symmetry
- This is an antibonding MO involving the bonding MO of H_2
- This MO is responsible for the Lewis acid character of the water molecule

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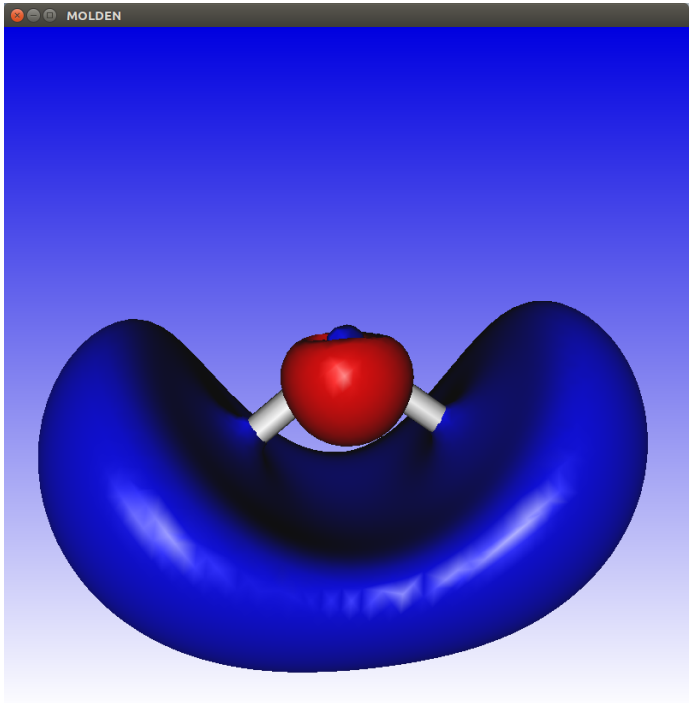

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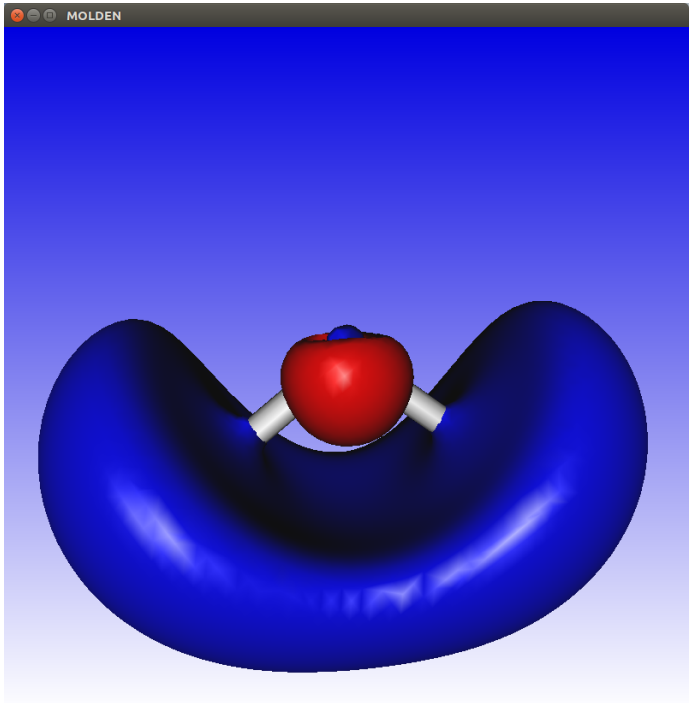

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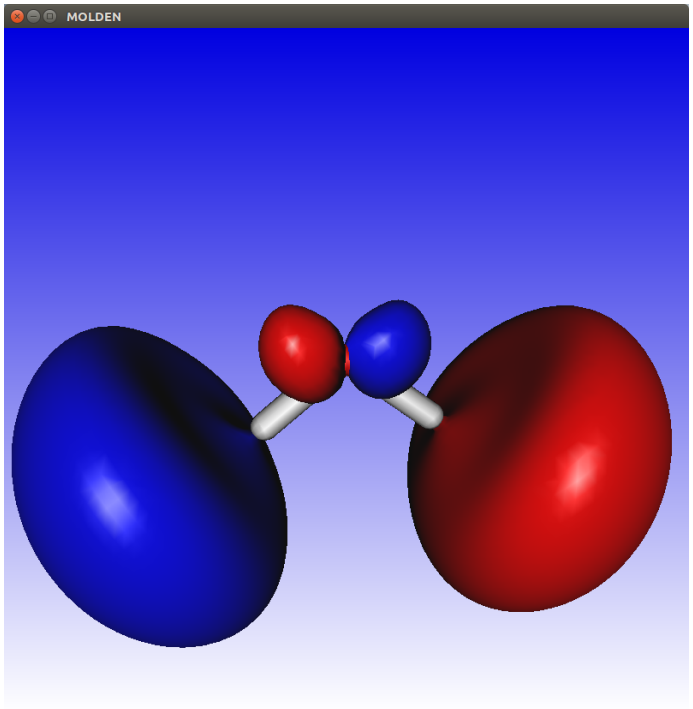
LUMO+1 of the Water Molecule



- The water LUMO+1 has B_2 symmetry
- This is an antibonding MO involving the antibonding MO of H_2 and the oxygen $2p_y$ AO
- It illustrates the idea that when the electronegativity difference between bonded atoms is large, the more electronegative partner will have bigger coefficients in the bonding MO, while the less electronegative partner contributes more to the antibonding MO

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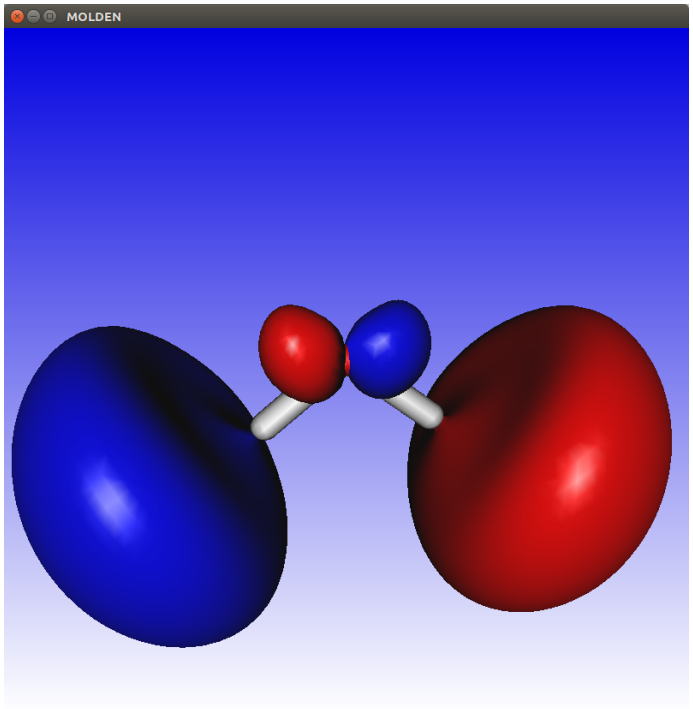
LUMO+1 of the Water Molecule



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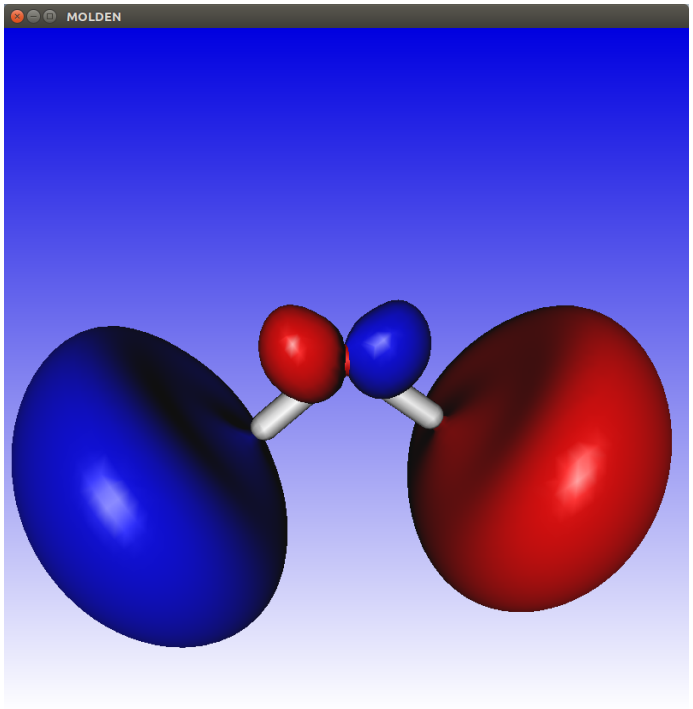

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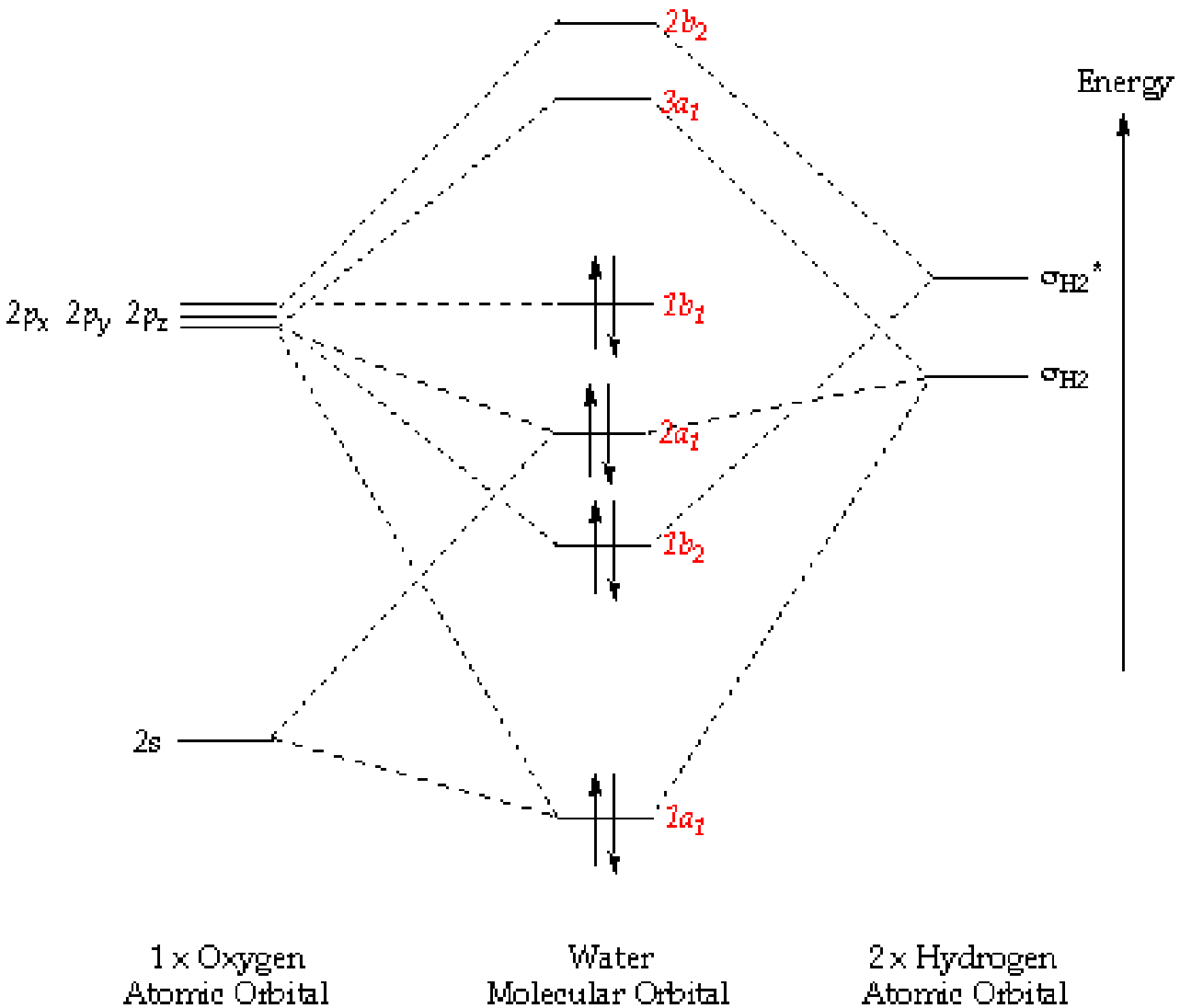
MO Diagram for the Water Molecule



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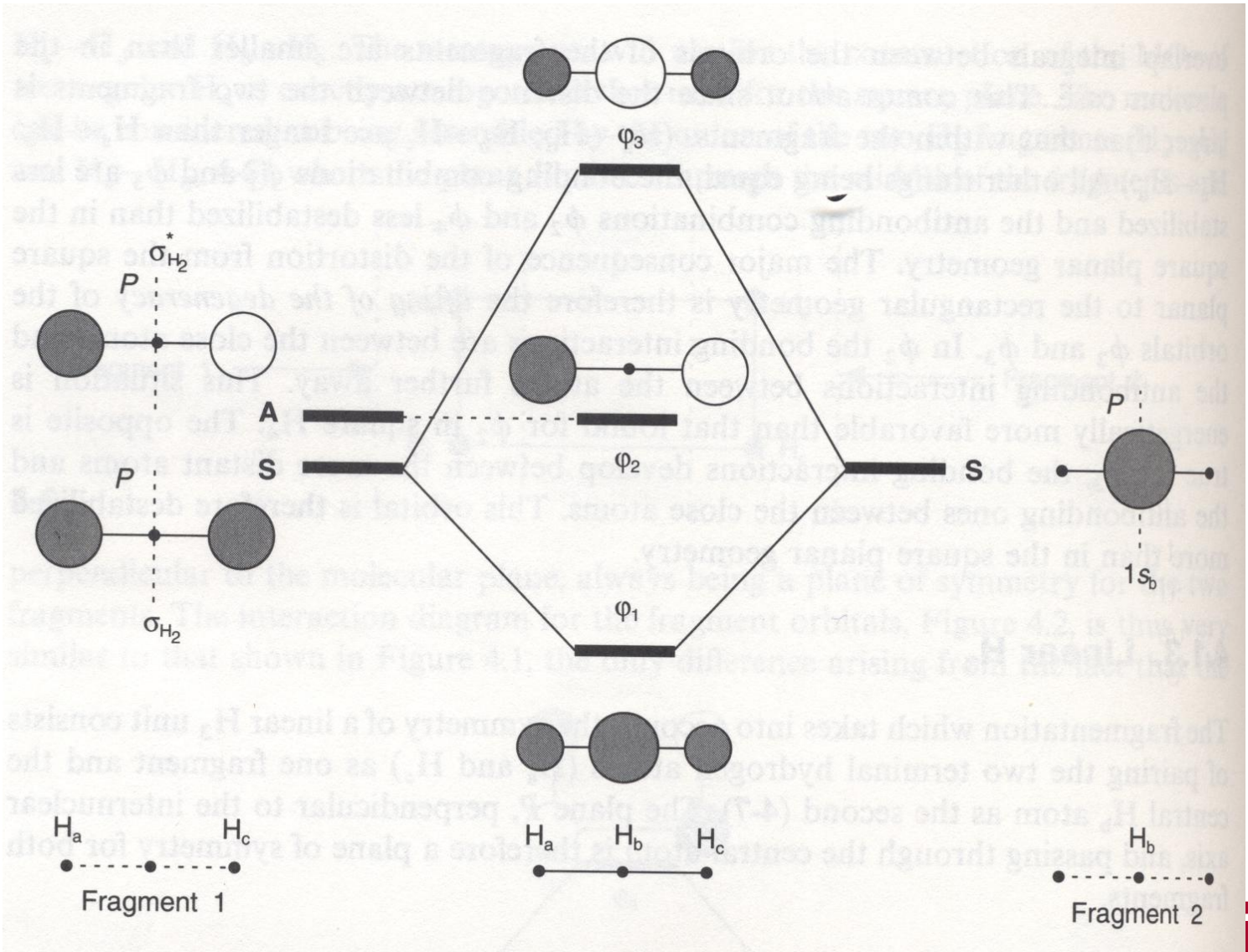
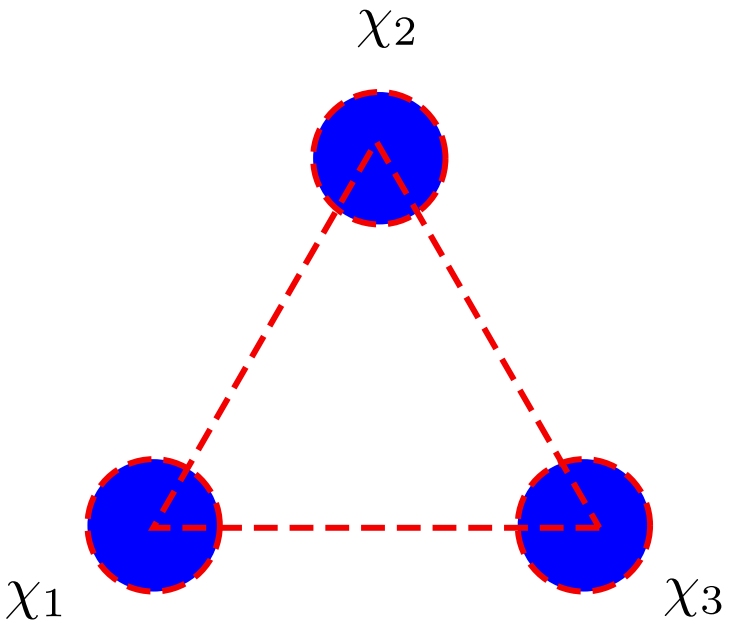
MO Diagram for Linear H_3

A fragment approach to deriving molecular orbitals





1. Carry out group operations in D_{3h}
2. Note how many atoms are unshifted
3. Reduce the reducible representation

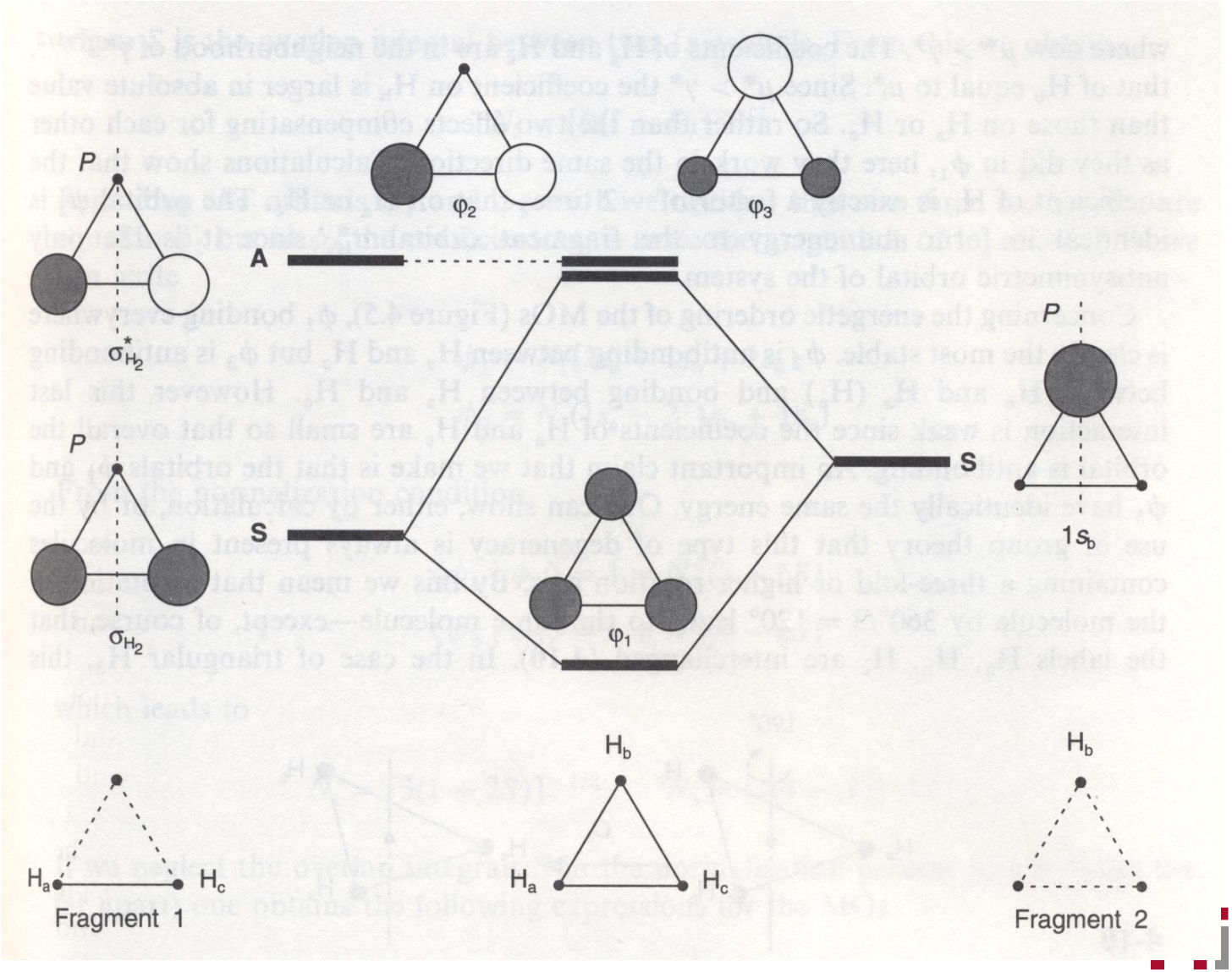
E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$
Γ 3 0 1 3 0 1
reduces to $A_1 + E'$

Symmetry Adapted Linear Combinations (SALCs) will be of the general form:

$\phi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3$

MO Diagram for Triangular H_3

A fragment approach to deriving molecular orbitals



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Triangular H_3^+ in the Universe

- H_3^+ disovered by J. J. Thomson in 1911, an abundant ion by mass spectrometry
- 1961: Martin et al. suggested that H_3^+ may be present in interstellar space
- Tasheki Oka observed (1980) the ν_2 fundamental for H_3^+; this is the E' vibration in D_{3h} symmetry
- 1996: H_3^+ first detected in the interstellar medium (ISM)
- The Central Molecular Zone (CMZ) contains H_3^+ at concentrations a million times higher than the ISM

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Massachusetts Institute of Technology

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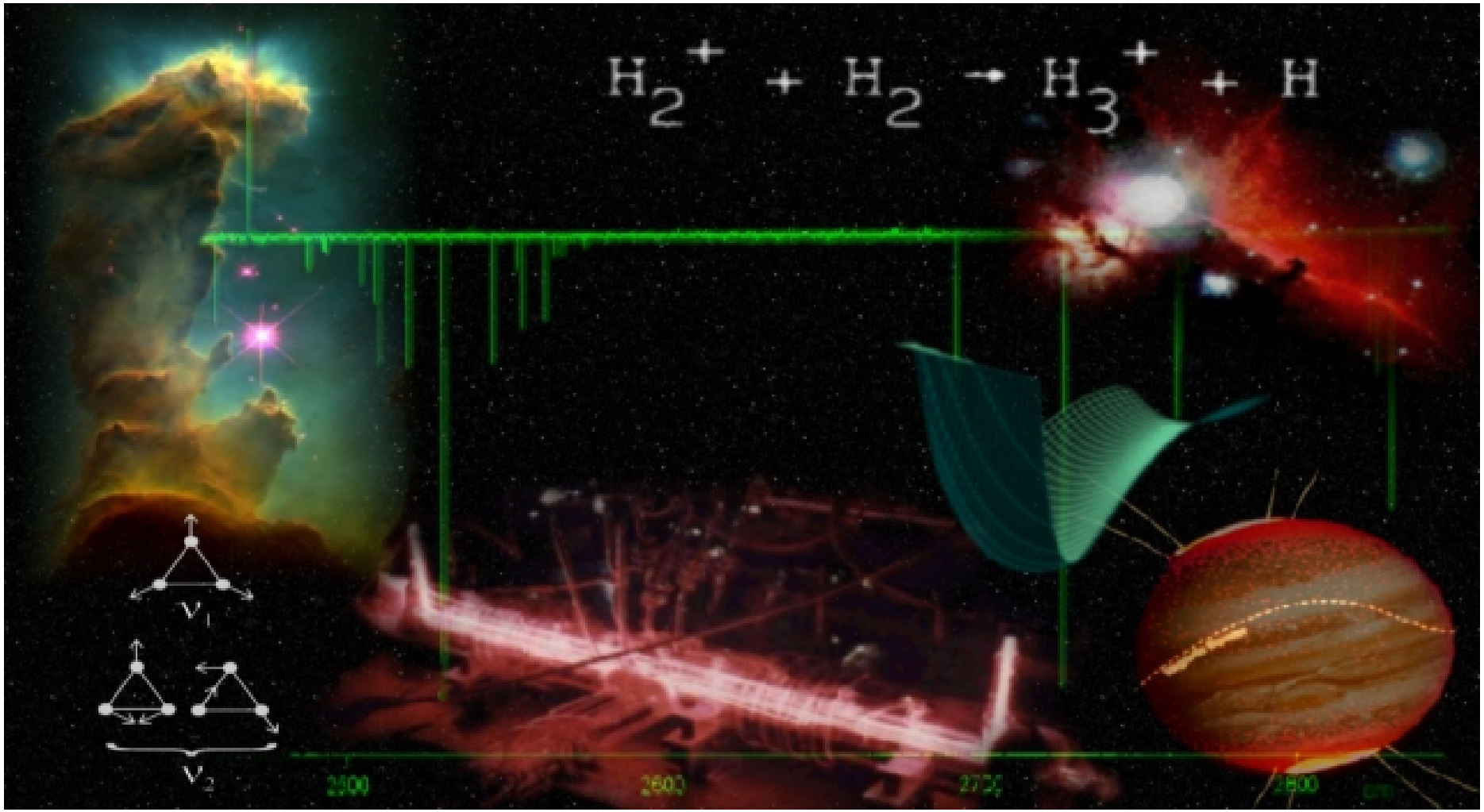
Image from the H_3^+ resource center http://h3plus.uiuc.edu/



PHYS.ORG

H3+: The molecule that made the Universe

12 April 2012

"There wouldn't be any star formation if there weren't molecules that slowly cool down the forming star by emitting light," said Michele Pavanello, who was a University of Arizona graduate student when he worked on the project. "Astronomers think that the only molecule that could cool down a forming star in that particular time is H_3^+."