MO Diagrams for Linear and Bent Molecules

Chapter 5

Monday, October 12, 2015

Molecular Orbitals for Larger Molecules

1. Determine point group of molecule (if linear, use D_{2h} and C_{2v} instead of $D_{\infty h}$ or $C_{\infty v}$)

2. Assign *x*, *y*, *z* coordinates
   (*z* axis is principal axis; if non-linear, *y* axes of outer atoms point to central atom)

3. Find the characters of the **reducible representation** for the combination of valence orbitals on the outer atoms. Treat *s*, p_x, p_y, p_z, etc. separately (as for vibrations, orbitals that change position = 0, orbitals that do not change = 1; and orbitals that remain in the same position but change sign = -1)

4. Find the irreducible representations (they correspond to the symmetry of *group orbitals*, also called **S**ymmetry **A**dapted **L**inear **C**ombinations, **SALC**s of the orbitals)

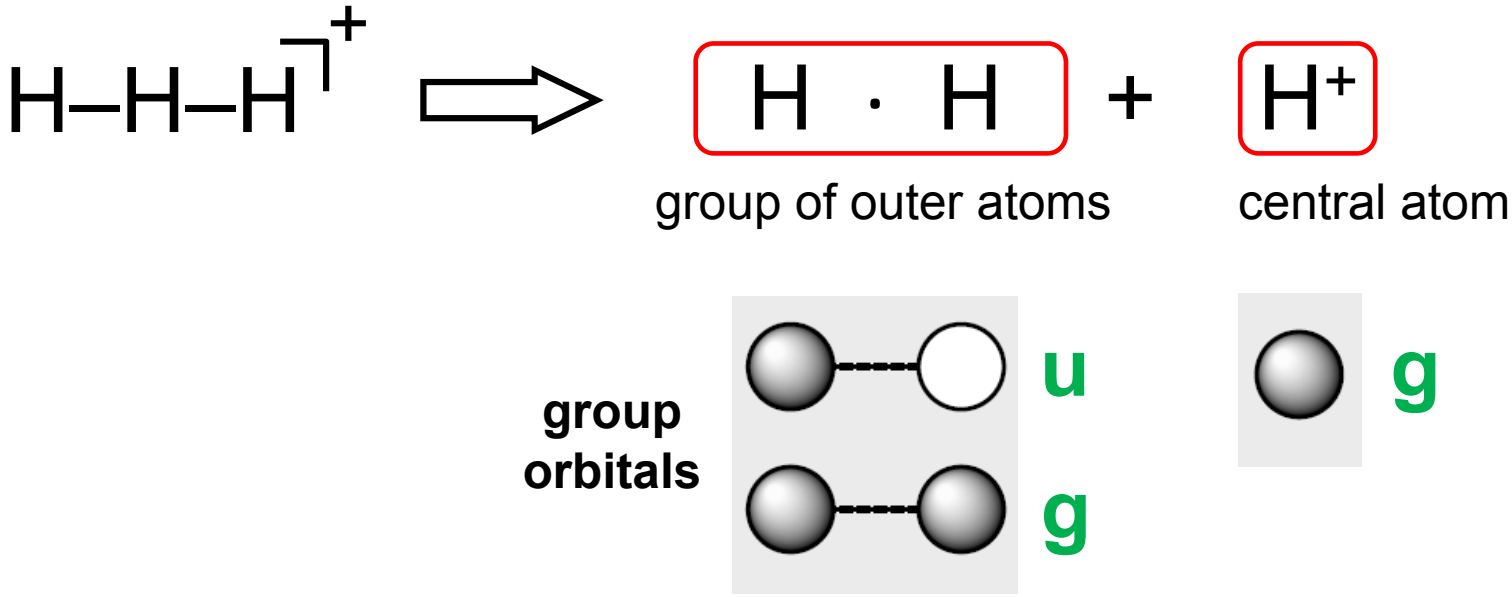
5. Find AOs on central atom with the same symmetry

6. Combine AOs from central atom with those group orbitals of same symmetry and similar energy to make the MO diagram

Linear H_3^+ by Inspection

Among the easiest multi-atom molecules to build is linear H_3^+.

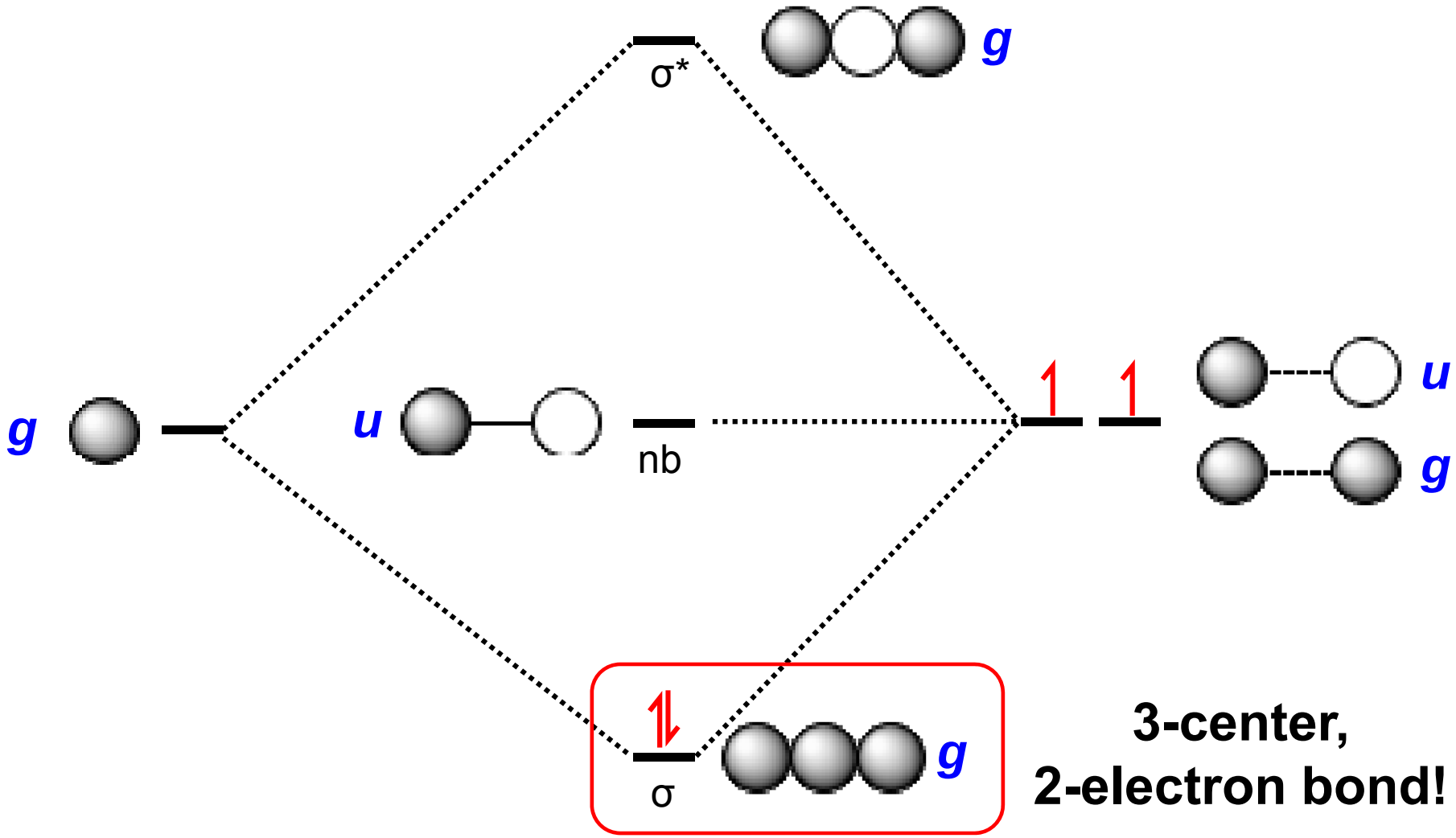
General procedure for simple molecules that contain a central atom: build *group orbitals* using the outer atoms, then interact the group orbitals with the central atom orbitals to make the MOs.



Only group orbitals and central atom orbitals with the same symmetry and similar energy will interact.

Linear H_3^+

***g* orbitals interact, while *u* orbital is nonbonding.**

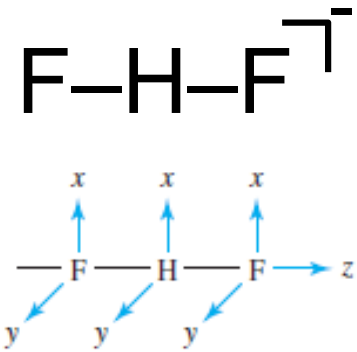


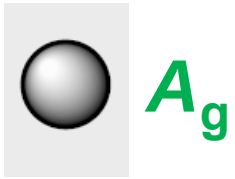
3-center,
2-electron bond!

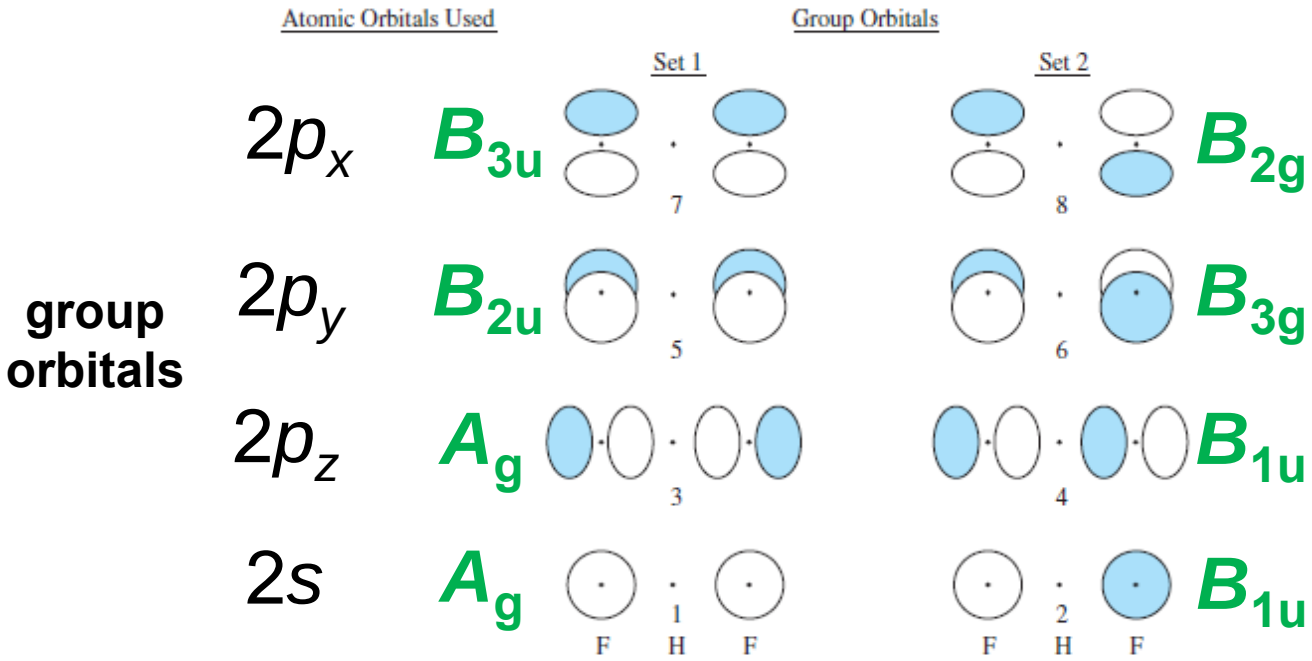
H^+ $\quad$ $H{-}H{-}H^{+}$ $\quad$ $H \cdot H$

Linear FHF^- by Inspection

In building the group orbitals for FHF^-, we must consider the 2*s* and 2*p* orbitals of the two fluorines (8 AOs in total). Use point group D_{2h}.







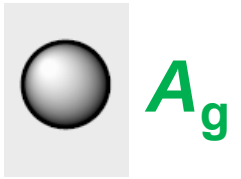
Linear FHF^-

In building the group orbitals for FHF^-, we must consider the 2*s* and 2*p* orbitals of the two fluorines (8 AOs in total). Use point group D_{2h}.

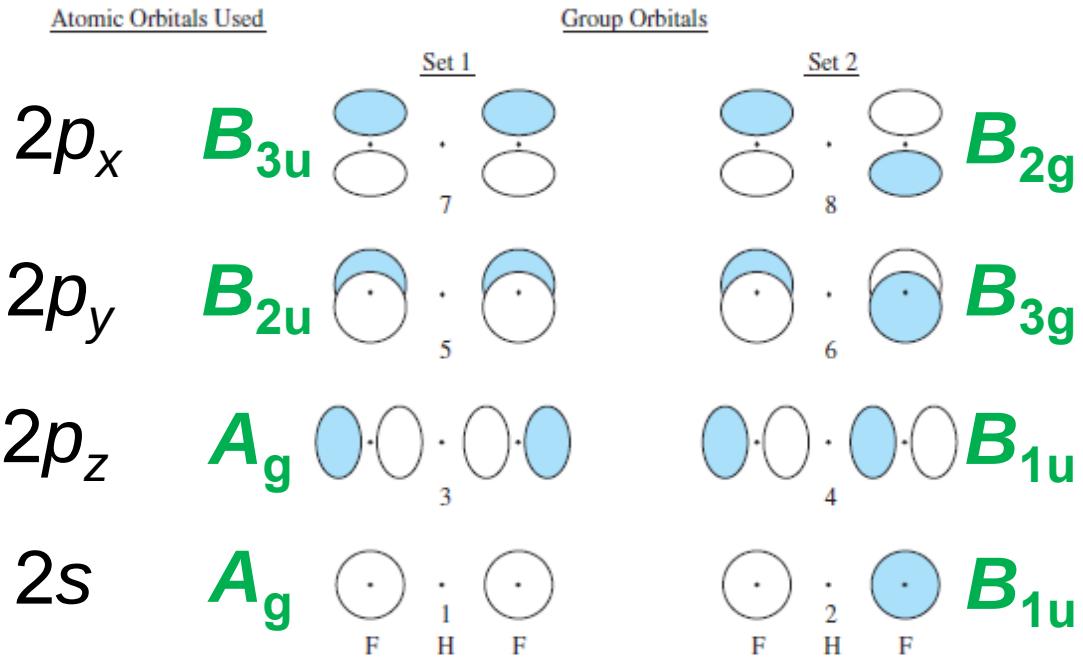
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

H^-

central atom

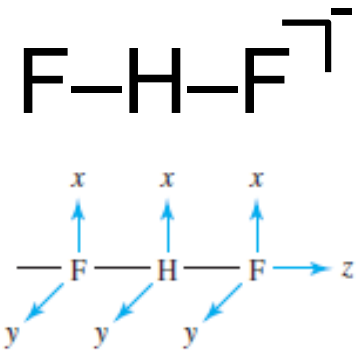


A_g



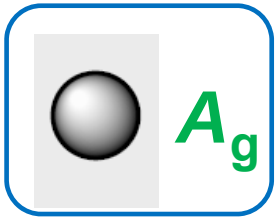
Linear FHF^-

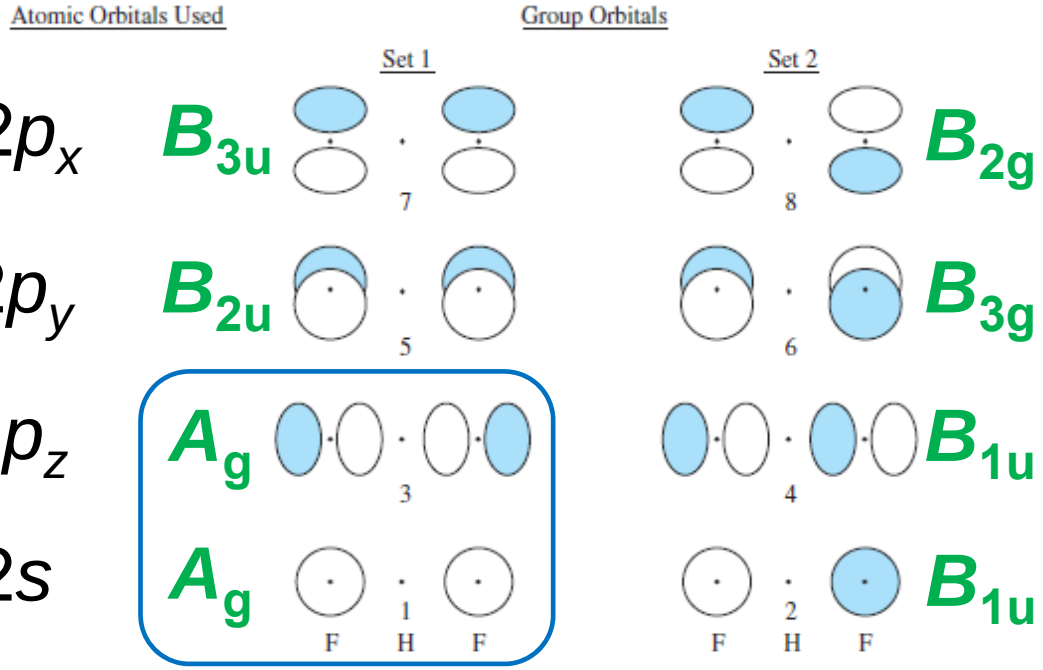
In building the group orbitals for FHF^-, we must consider the 2*s* and 2*p* orbitals of the two fluorines (8 AOs in total). Use point group D_{2h}.



$F–H–F^-$ ⟹ $F \cdot F$ + H^-

group of outer atoms — central atom

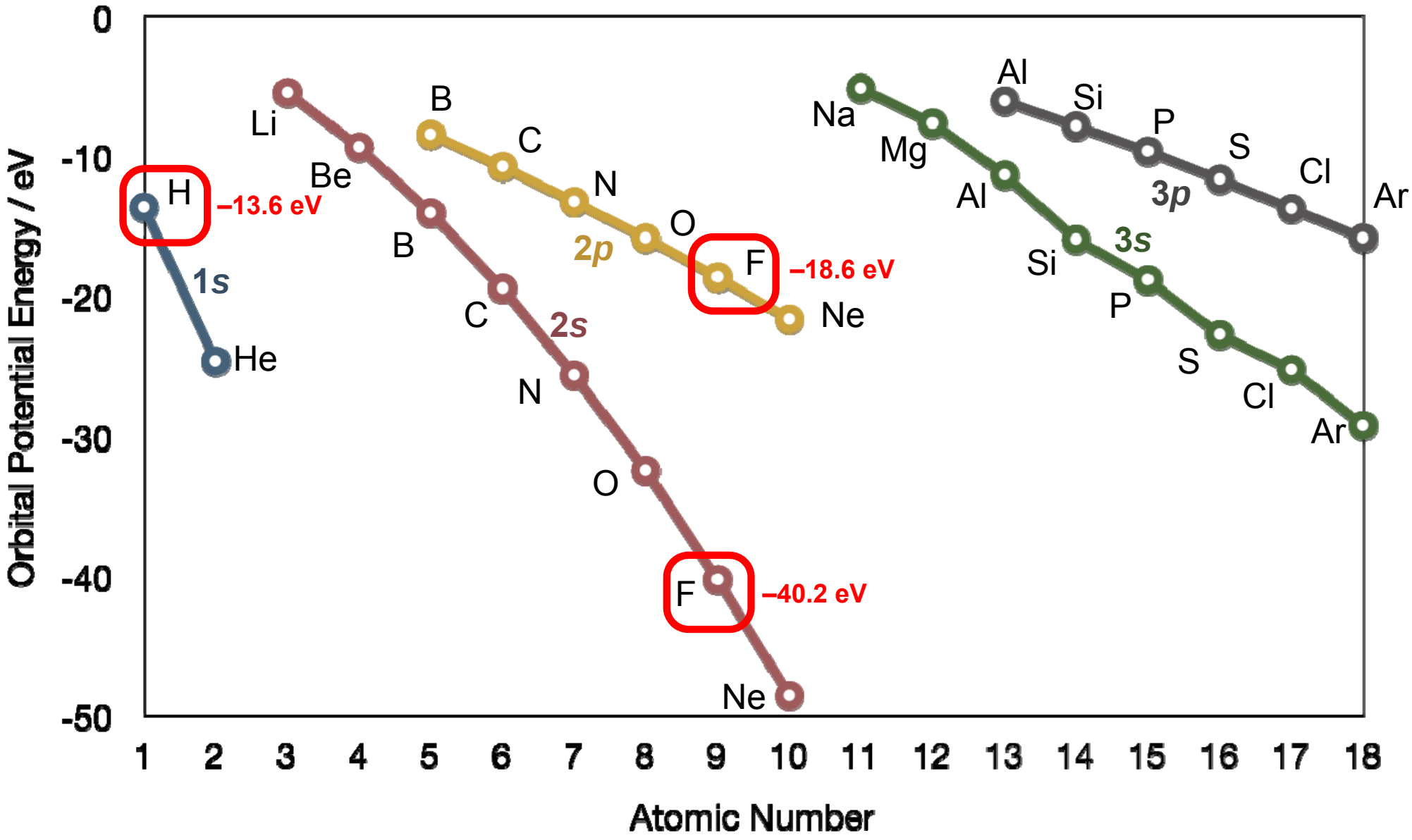




The central atom has proper symmetry to interact only with group orbitals 1 and 3.

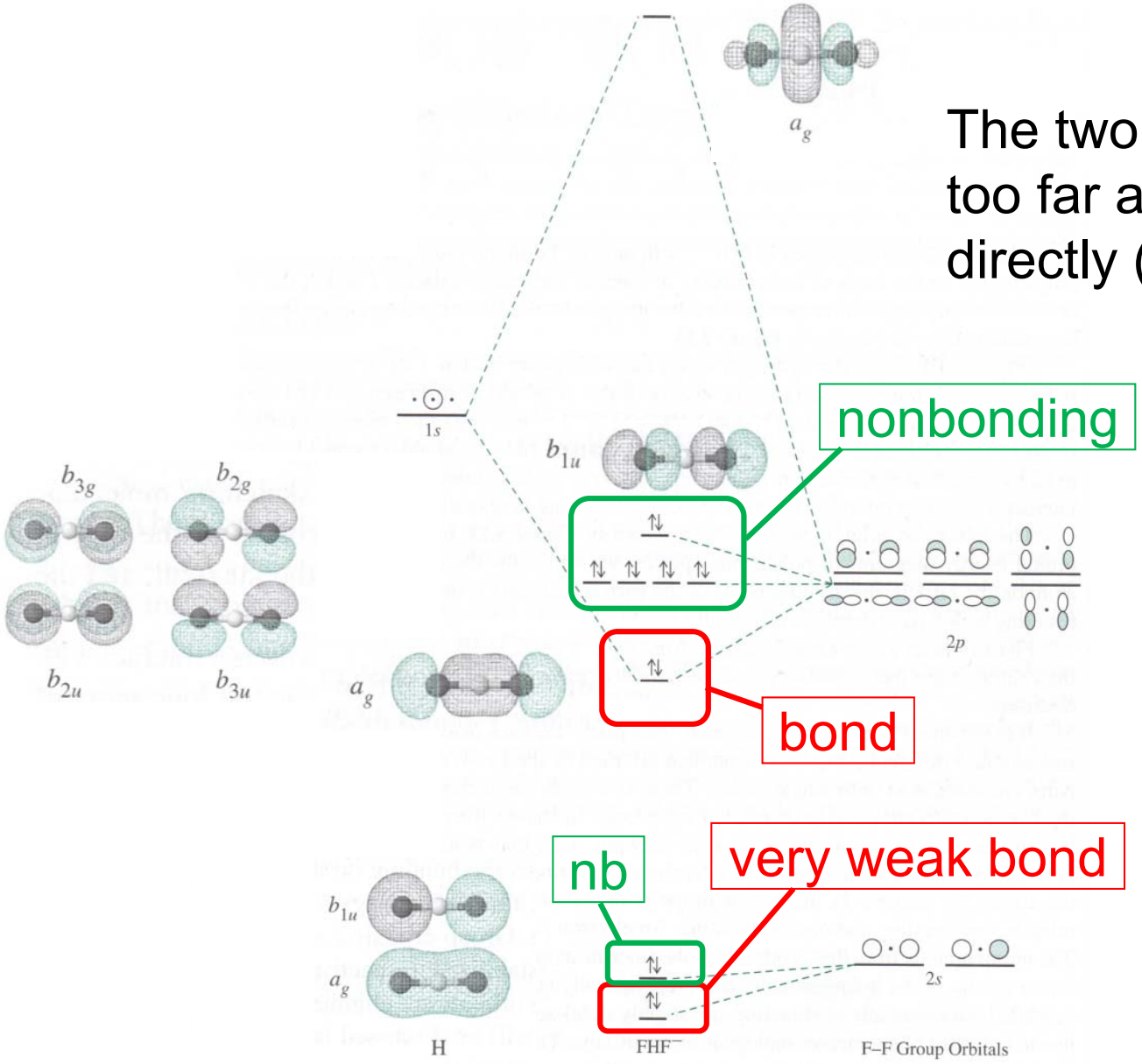
Relative AO Energies for MO Diagrams

F 2s orbital is very deep in energy and will be essentially nonbonding.



Linear FHF^-

F 2*s* orbitals are too deep in energy to interact, leaving an interaction (σ) only with group orbital 3. Some *sp* mixing occurs between a_g and b_{1u} MOs.



The two fluorines are too far apart to interact directly (*S* very small).

Lewis:

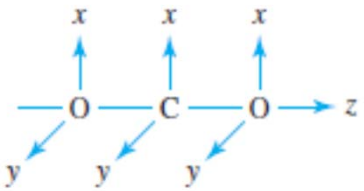
MO:
<2 bonds,
>6 lone pairs

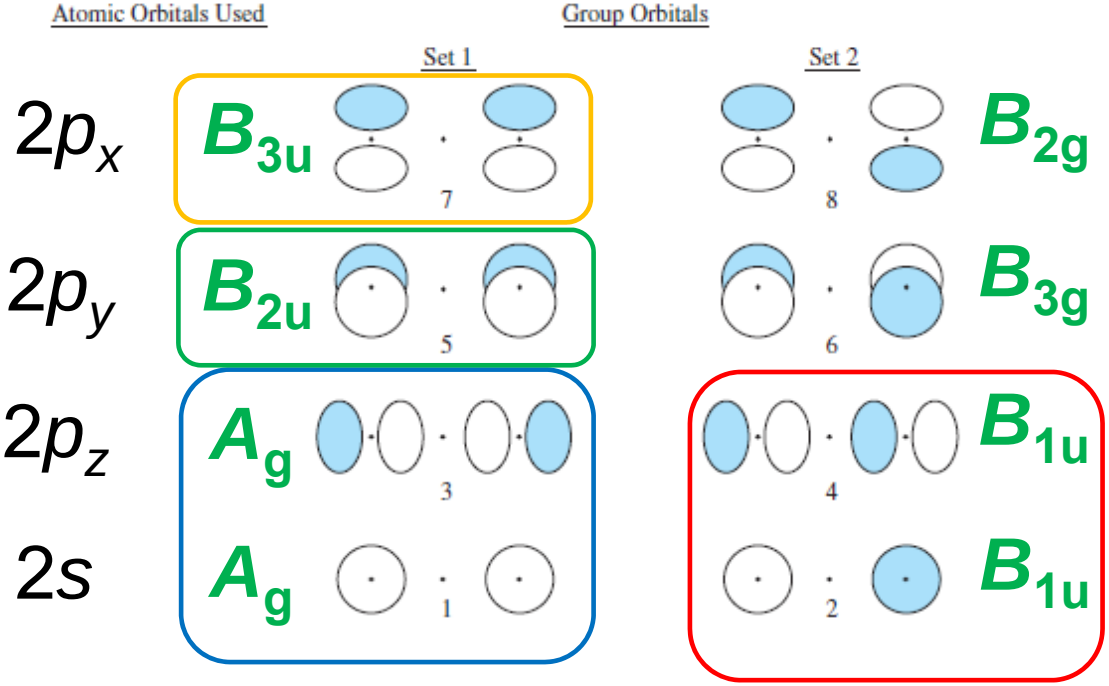
Carbon Dioxide by Inspection

CO_2 is also linear. Here all three atoms have 2*s* and 2*p* orbitals to consider. Again, use point group D_{2h} instead of $D_{\infty h}$.

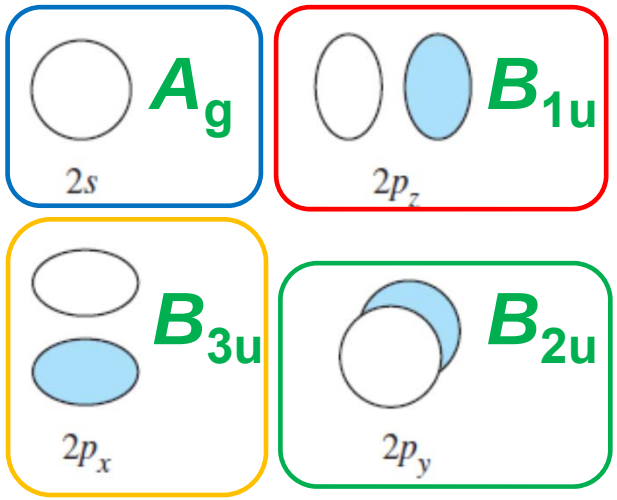
O=C=O ⟹ [O · O] + [C]

group of outer atoms central atom





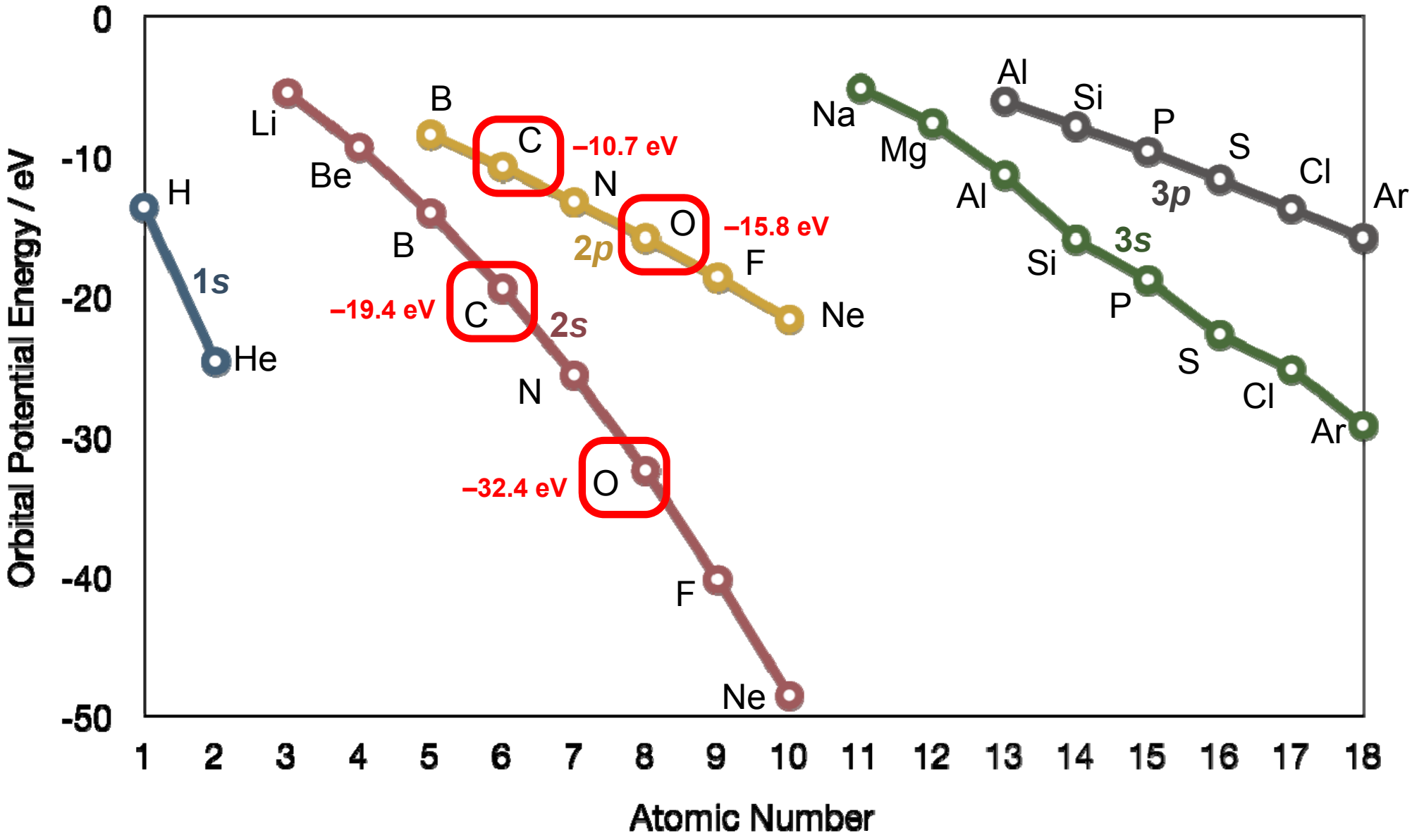
group orbitals same as F- -F



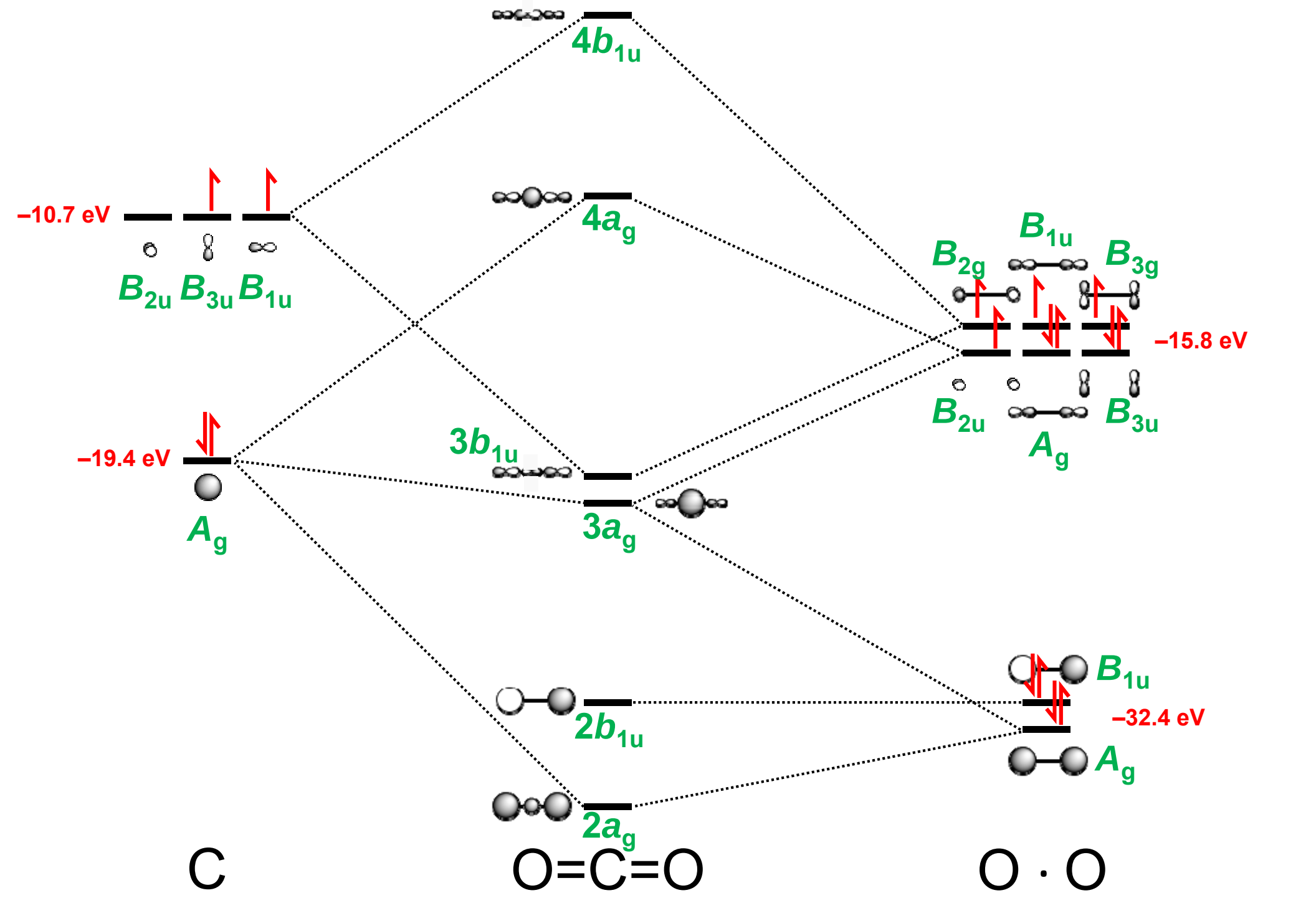
carbon has four AOs to consider!

Relative AO Energies in MO Diagrams

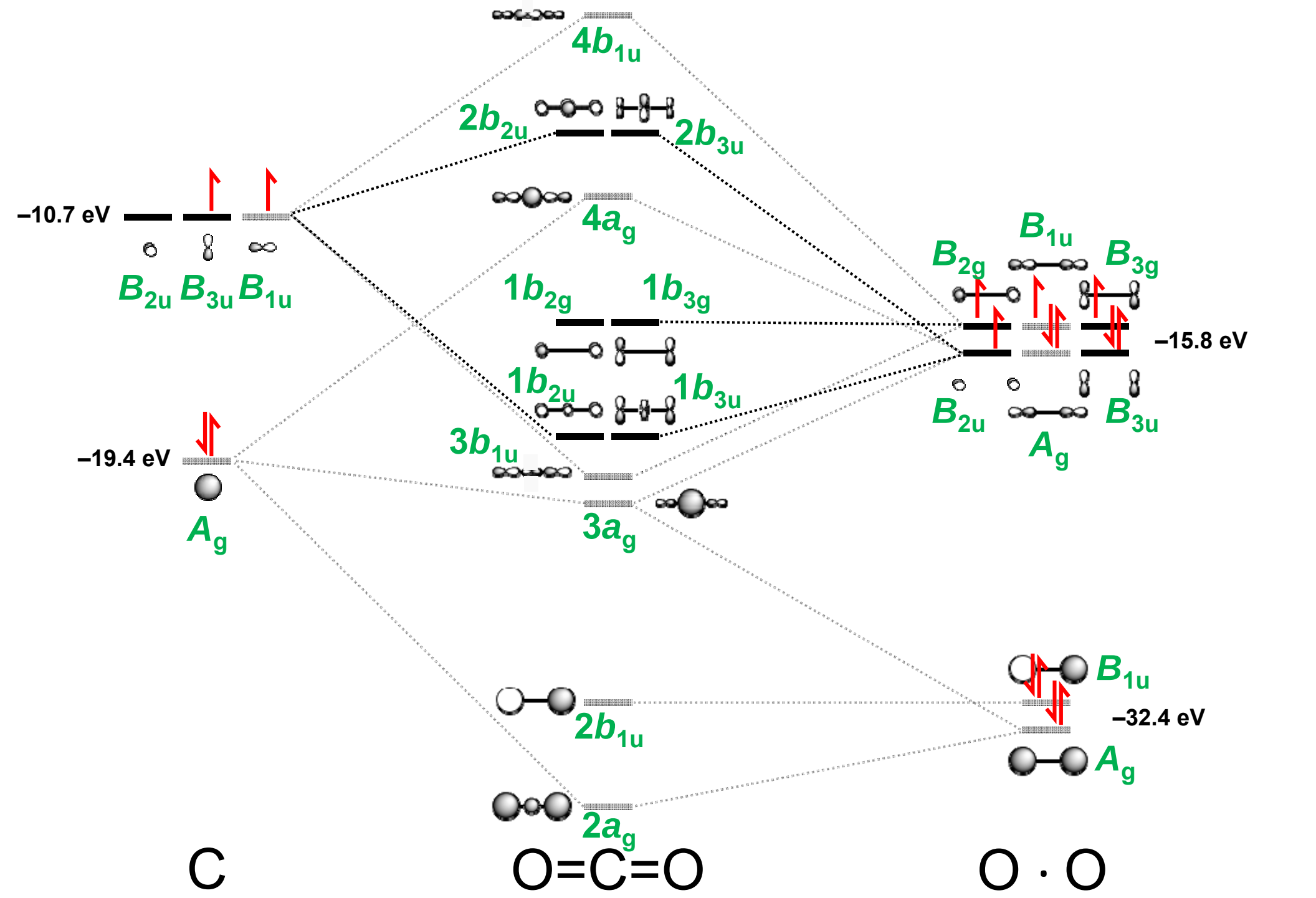
Use AO energies to draw MO diagram to scale (more or less).



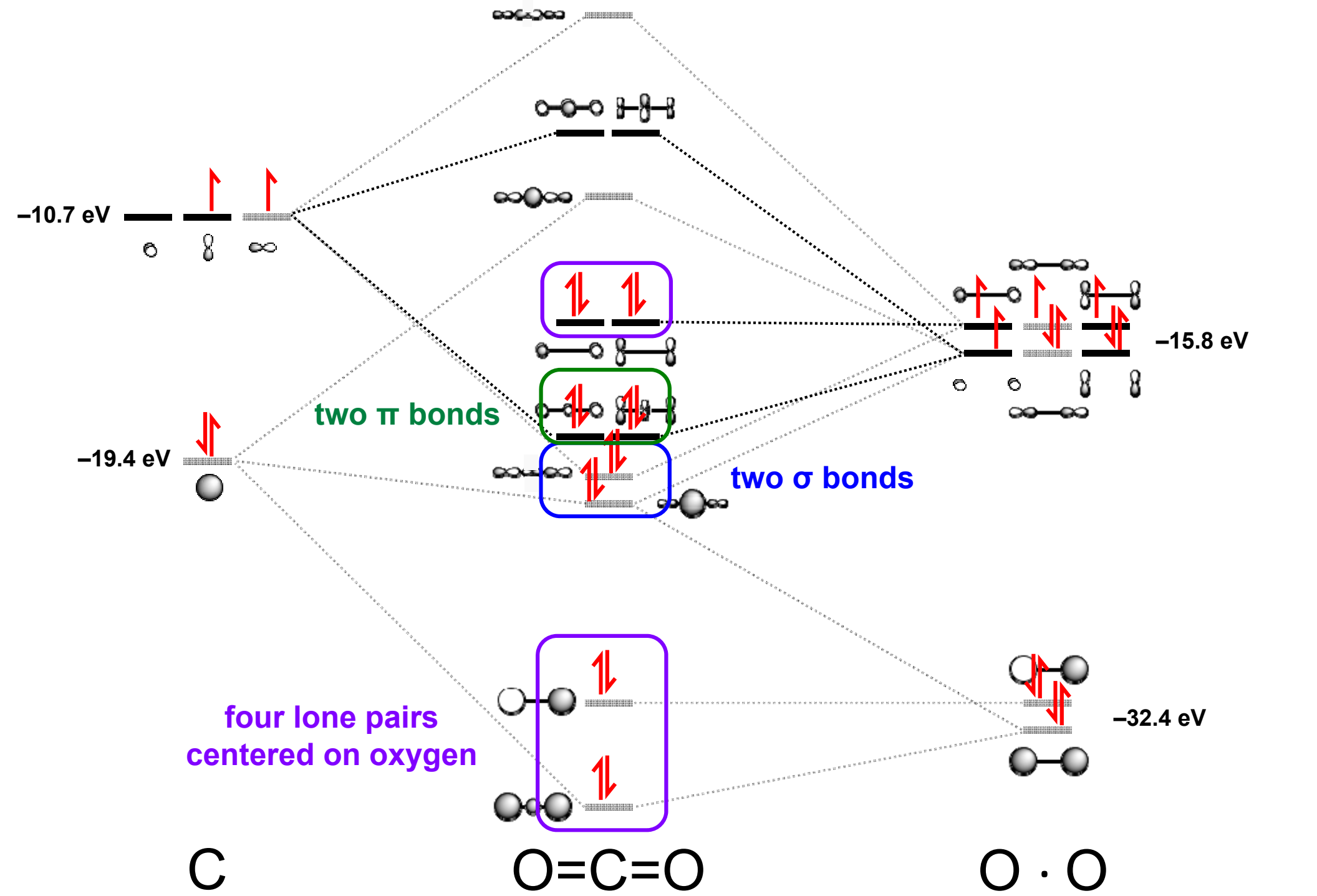
Carbon Dioxide



Carbon Dioxide



Carbon Dioxide



Molecular Orbitals for Larger Molecules

To this point we've built the group orbitals by inspection. For more complicated molecules, it is better to use the procedure given earlier:

1. Determine point group of molecule (if linear, use D_{2h} and C_{2v} instead of $D_{\infty h}$ or $C_{\infty v}$)

2. Assign *x*, *y*, *z* coordinates
   (*z* axis is principal axis; if non-linear, *y* axes of outer atoms point to central atom)

3. Find the characters of the **reducible representation** for the combination of valence orbitals on the outer atoms. Treat *s*, p_x, p_y, p_z, etc. separately (as for vibrations, orbitals that change position = 0, orbitals that do not change = 1; and orbitals that remain in the same position but change sign = -1)

4. Find the irreducible representations (they correspond to the symmetry of *group orbitals*, also called **S**ymmetry **A**dapted **L**inear **C**ombinations, **SALC**s of the orbitals)

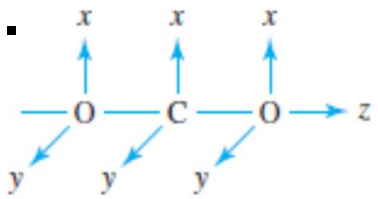
5. Find AOs on central atom with the same symmetry

6. Combine AOs from central atom with those group orbitals of same symmetry and similar energy

Carbon Dioxide by Reducible Representations

1. Use point group D_{2h} instead of $D_{\infty h}$ (this is called *descending in symmetry*).

2.



D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
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	

3. Make reducible reps for outer atoms

Γ_{2s}	2	2	0	0	0	0	2	2
Γ_{2pz}	2	2	0	0	0	0	2	2
Γ_{2px}	2	-2	0	0	0	0	2	-2
Γ_{2py}	2	-2	0	0	0	0	-2	2

4. Get group orbital symmetries by reducing each Γ

$$\text{\# of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_R \left(\text{\# of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

$\Gamma_{2s} = A_g + B_{1u}$ $\quad$ $\Gamma_{2px} = B_{2g} + B_{3u}$

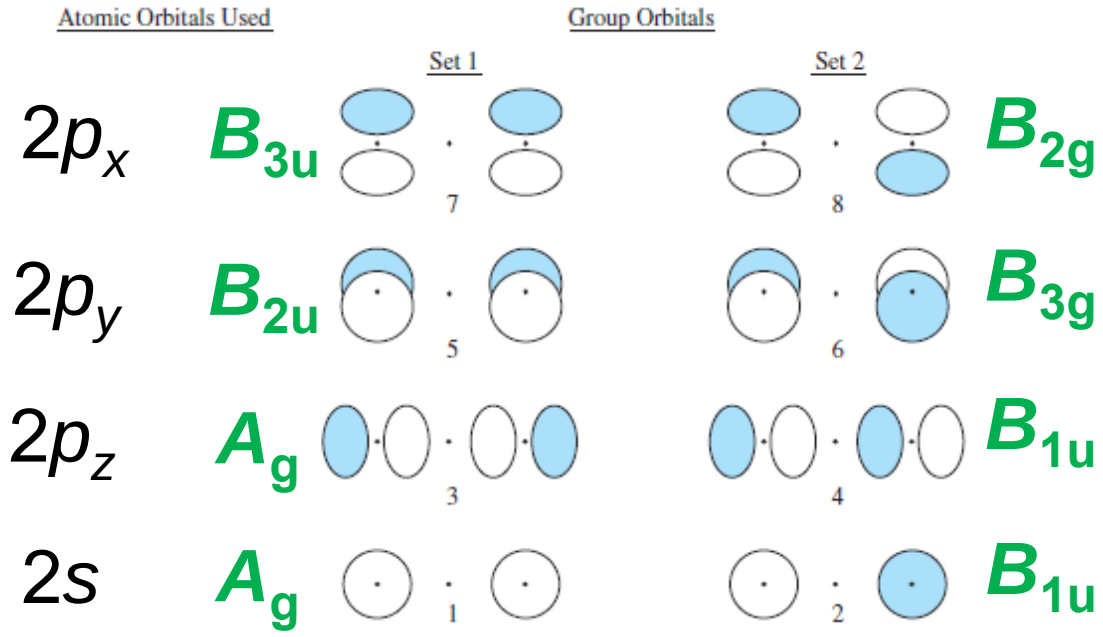
$\Gamma_{2pz} = A_g + B_{1u}$ $\quad$ $\Gamma_{2py} = B_{3g} + B_{2u}$

Carbon Dioxide by Reducible Representations

$\Gamma_{2s} = A_g + B_{1u}$ $\Gamma_{2px} = B_{2g} + B_{3u}$

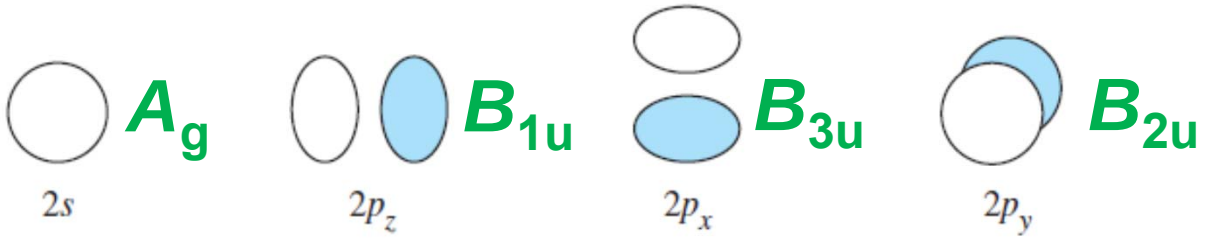
$\Gamma_{2pz} = A_g + B_{1u}$ $\Gamma_{2py} = B_{3g} + B_{2u}$

These are the same group orbital symmetries that we got using inspection. We can (re)draw them.

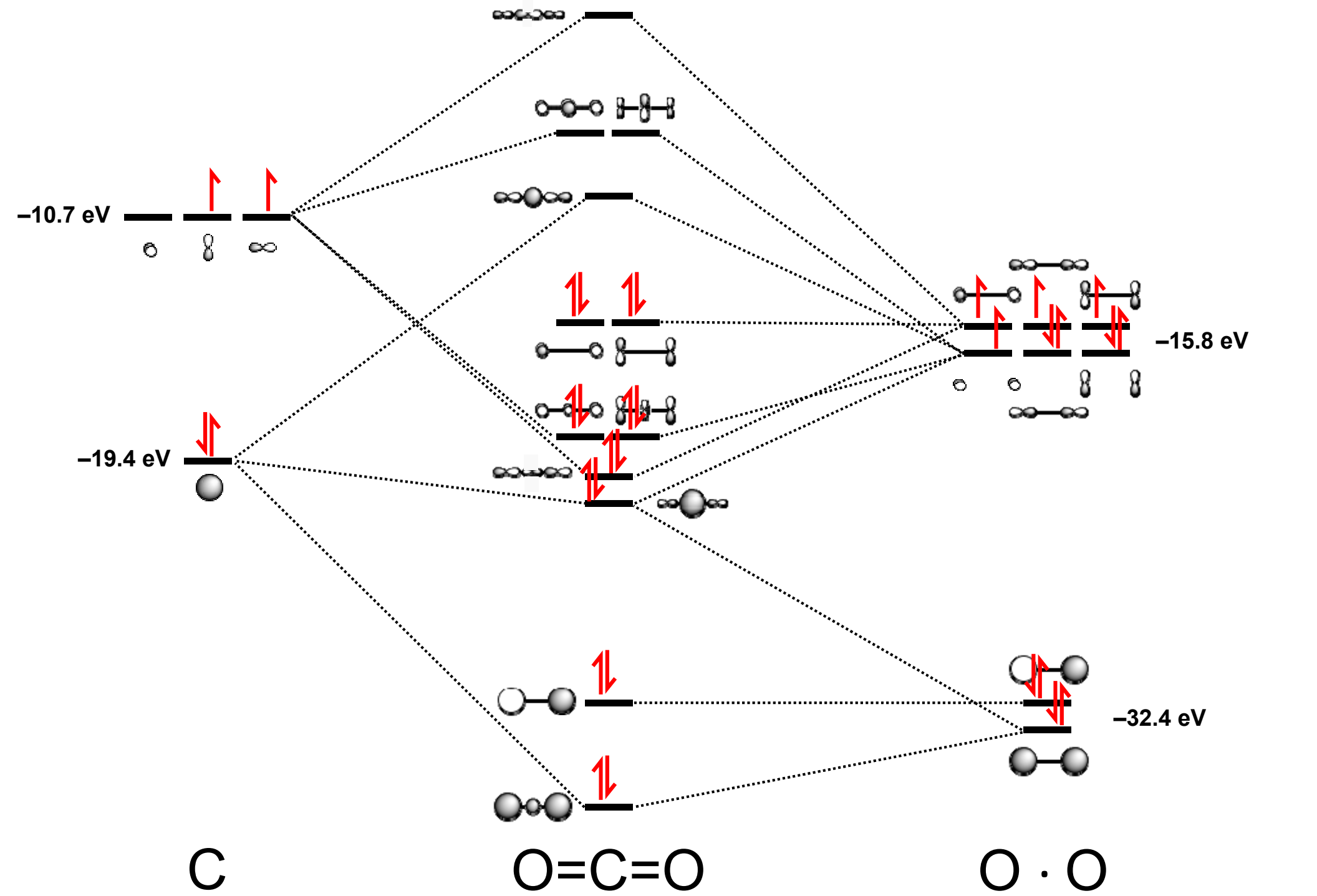


6. Build MO diagram…

5. Find matching orbitals on central atom



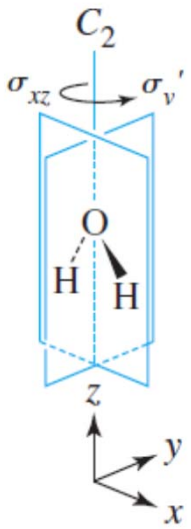
Carbon Dioxide



Water

1. Point group C_{2v}

2.



3. Make reducible reps for outer atoms

C_{2v} Character Table

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
Γ_{1s}	2	0	2	0		

4. Get group orbital symmetries by reducing Γ

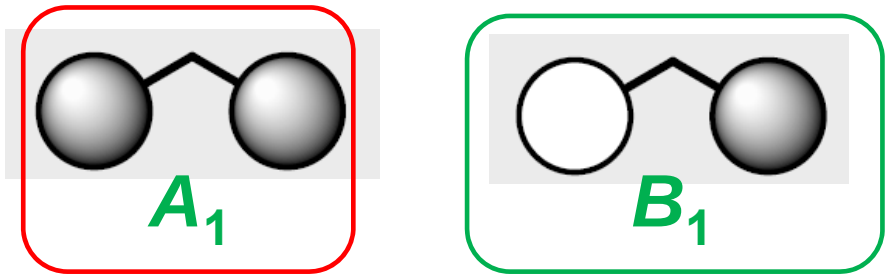
$$\text{\# of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_R \left(\text{\# of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

$$\Gamma_{1s} = A_1 + B_1$$

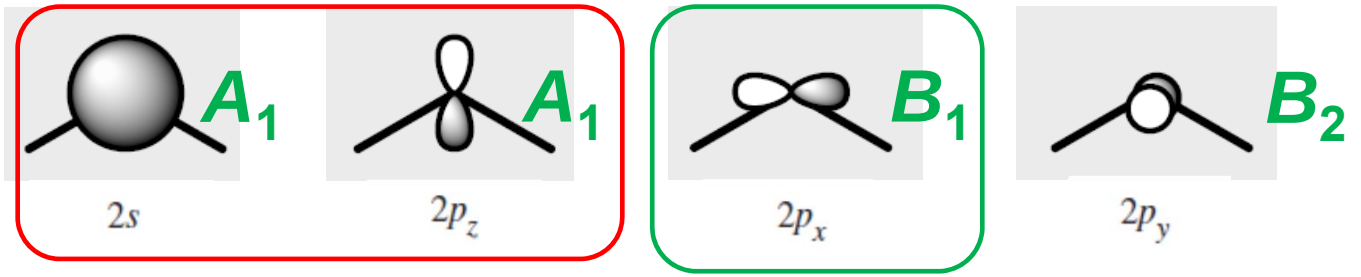
Water

$\Gamma_{1s} = A_1 + B_1$

The hydrogen group orbitals look like:



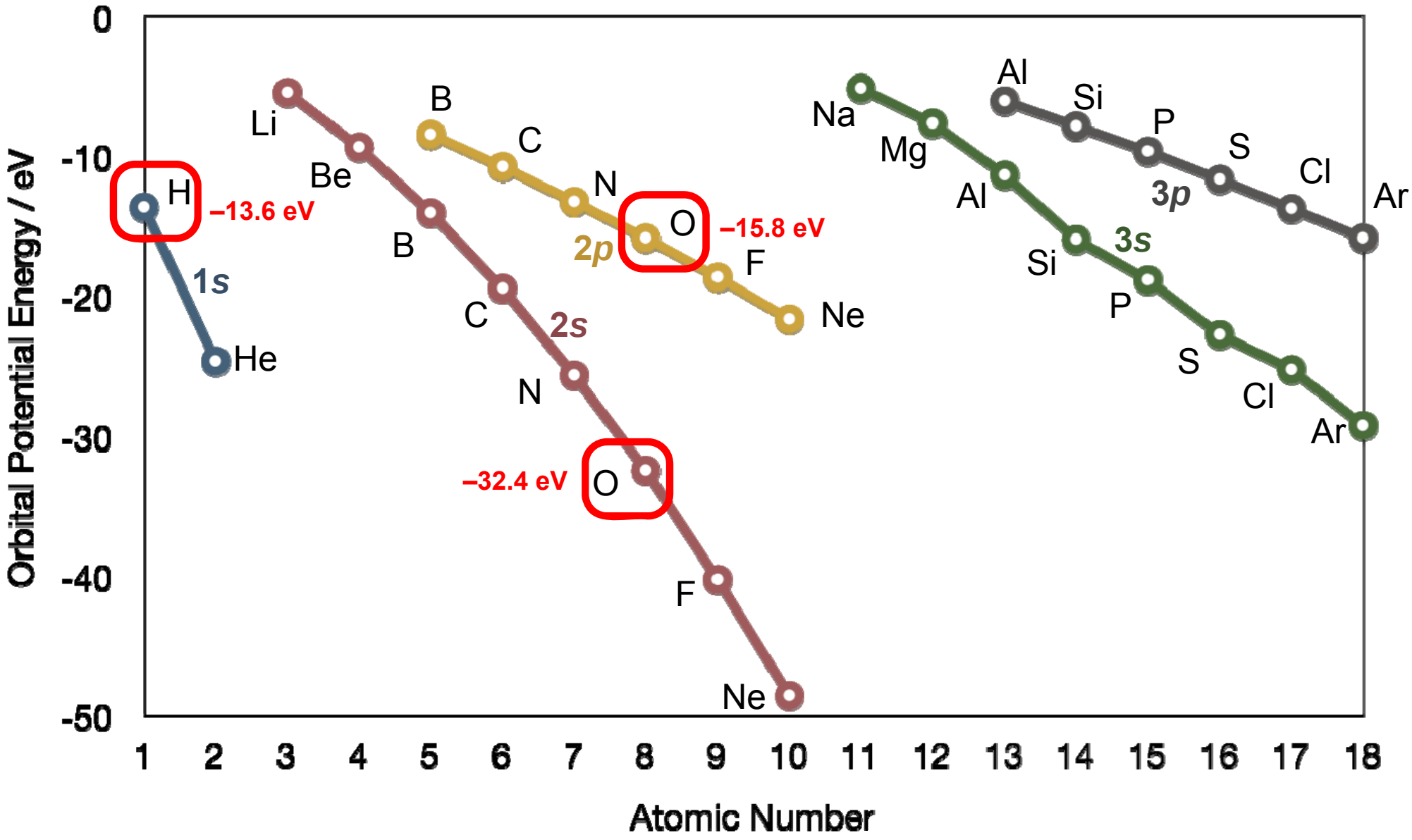
5. Find matching orbitals on central O atom



6. Build MO diagram. We expect six MOs, with the O $2p_y$ totally nonbonding.

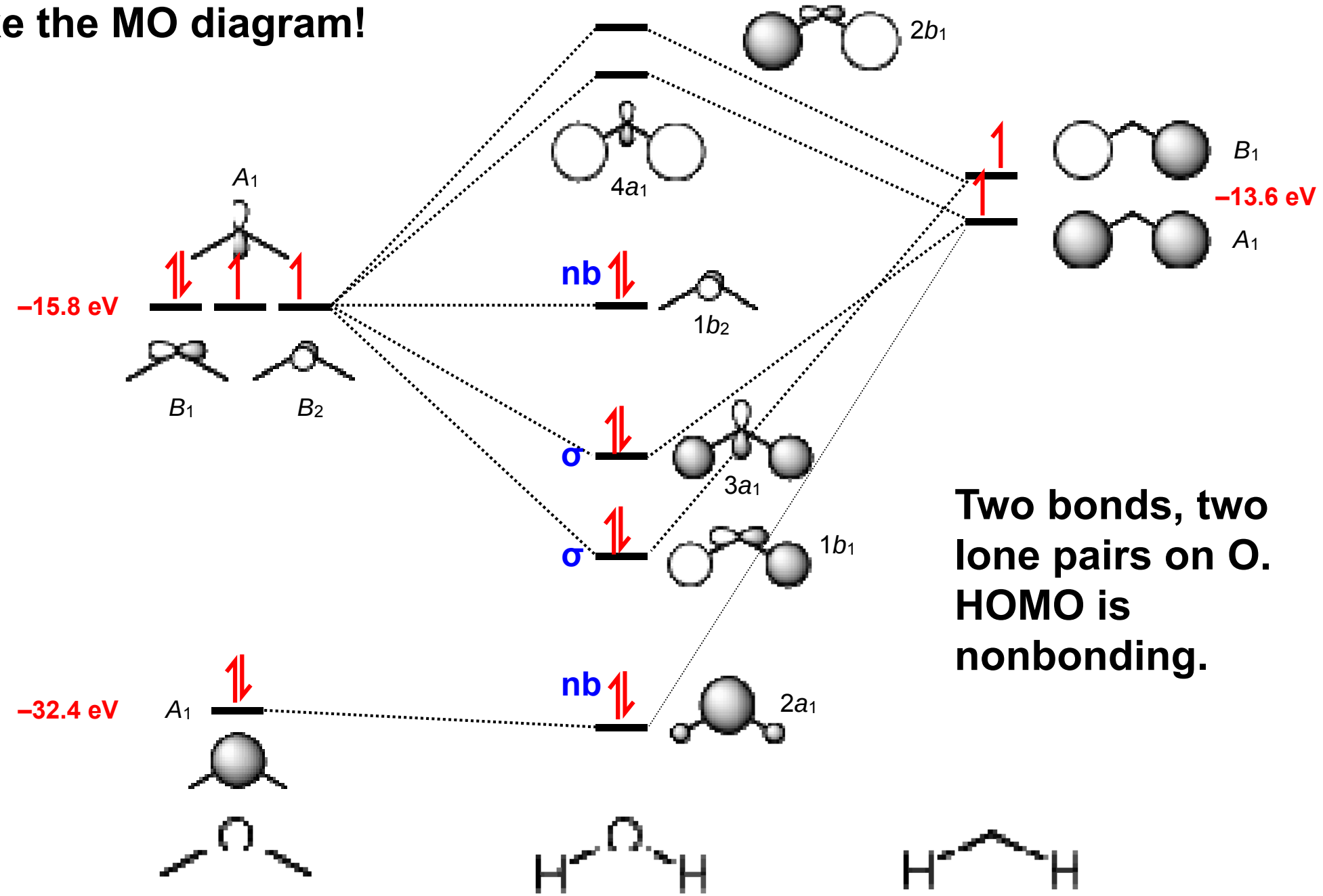
Water

Based on the large ΔE, we expect O 2*s* to be almost nonbonding.



Water

With the orbital shapes, symmetries, and energies in hand we can make the MO diagram!



Two bonds, two lone pairs on O. HOMO is nonbonding.