

## Week 6

# Complex MO Diagrams

### 6.1 MO Theory: LCAOs and Group Orbitals

10/31:

- Last time: Building MO diagrams by qualitatively identifying a basis of atomic orbitals (e.g., 1s for H, 2s and 2p for F) and intuitively determining an axis to about which they transform within the linear point group  $C_{\infty v}$ .
- Today: Making this process more formal, as is necessary for more complex, polyatomic molecules.
- For polyatomic molecules, we need to determine how the basis atomic orbitals transform. This will allow us to approximate molecular orbitals with linear combinations of them (the AOs) that transform with the same symmetry.
  - To do this, we need to understand how to group together valence atomic orbitals, i.e., how to construct **group orbitals**.
- **Group orbital**: An MO of a complex molecule.
- Strategy for building group orbitals and creating the relevant MO diagram.
  1. Determine the point group of the molecule. If it is a linear molecule, substituting a simpler point group that still retains the symmetry of the orbitals (ignoring the signs) makes the process easier by eliminating infinite-fold rotation axes.
    - We will substitute the 2-fold **subgroup** of the relevant point group in these cases.
    - In particular, substitute  $D_{2h}$  for  $D_{\infty h}$  and  $C_{2v}$  for  $C_{\infty v}$ .
  2. Assign  $xyz$  coordinates.
  3. Construct reducible representations for the valence orbitals on the peripheral atoms.
  4. Reduce each representation to its IRRs (i.e., find the symmetry of the group orbitals). Group orbitals are the combinations of atomic orbitals that match the symmetry of the IRRs.
  5. Identify the atomic orbitals on the central atom with the same symmetries (IRRs) as those found in step 4.
  6. Combine the atomic orbitals with matching symmetry and similar energy. The total number of MOs must be equal to the number of atomic orbitals used from all the atoms.
    - Energy scaling of MOs  $\sigma < \pi < \text{lone pairs} < \pi^* < \sigma^*$ . More nodes equals higher in energy.
  7. Label MOs.
    - $\sigma$  implies a SALC with infinite-fold rotational symmetry about the bond axis;  $\pi$  implies a SALC with 2-fold rotational symmetry about the bond axis.
    - No superscript implies a bonding interaction; superscript  $*$  implies an antibonding interaction.

- Subscript  $g$  implies symmetrical with respect to inversion; subscript  $u$  implies asymmetrical with respect to inversion.

8. Fill in the electrons.

- Example:  $\text{CO}_2$ .

1.  $D_{\infty h} \rightarrow D_{2h}$ .

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	linear functions, rotations	quadratic functions	cubic 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	-	-	xyz
$B_{1u}$	+1	+1	-1	-1	-1	-1	+1	+1	z	-	$z^3, y^2z, x^2z$
$B_{2u}$	+1	-1	+1	-1	-1	+1	-1	+1	y	-	$yz^2, y^3, x^2y$
$B_{3u}$	+1	-1	-1	+1	-1	+1	+1	-1	x	-	$xz^2, xy^2, x^3$

Table 6.1:  $D_{2h}$  character table.

2.  $xyz$  coordinates are chosen as per Figure 6.1.

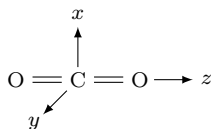


Figure 6.1:  $\text{CO}_2$   $xyz$  coordinates.

3. The two oxygen atoms are peripheral; their valence orbitals are  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$ . Thus, we have from the  $D_{2h}$  character table and Figure 6.1 that

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\text{O}(2s)}$	2	2	0	0	0	0	2	2
$\Gamma_{\text{O}(2p_z)}$	2	2	0	0	0	0	2	2
$\Gamma_{\text{O}(2p_x)}$	2	-2	0	0	0	0	2	-2
$\Gamma_{\text{O}(2p_y)}$	2	-2	0	0	0	0	-2	2

Table 6.2: Representations for the valence orbitals of  $\text{CO}_2$ .

- We get 0 characters for  $\Gamma_{\text{O}(2p_z)}$  because the individual orbitals move, even though the “overall basis” inverts.

4. As follows.

$$\begin{aligned}
 \Gamma_{\text{O}(2s)} &= \Gamma_{\text{O}(2p_z)} = a_g + b_{1u} \\
 \Gamma_{\text{O}(2p_x)} &= b_{3u} + b_{2g} \\
 \Gamma_{\text{O}(2p_y)} &= b_{2u} + b_{3g}
 \end{aligned}$$

5. Carbon AOs: From the  $D_{2h}$  character table,

$$C(2s) = a_g$$

$$C(2p_z) = b_{1u}$$

$$C(2p_x) = b_{3u}$$

$$C(2p_y) = b_{2u}$$

6. We can now construct the following MO diagram.

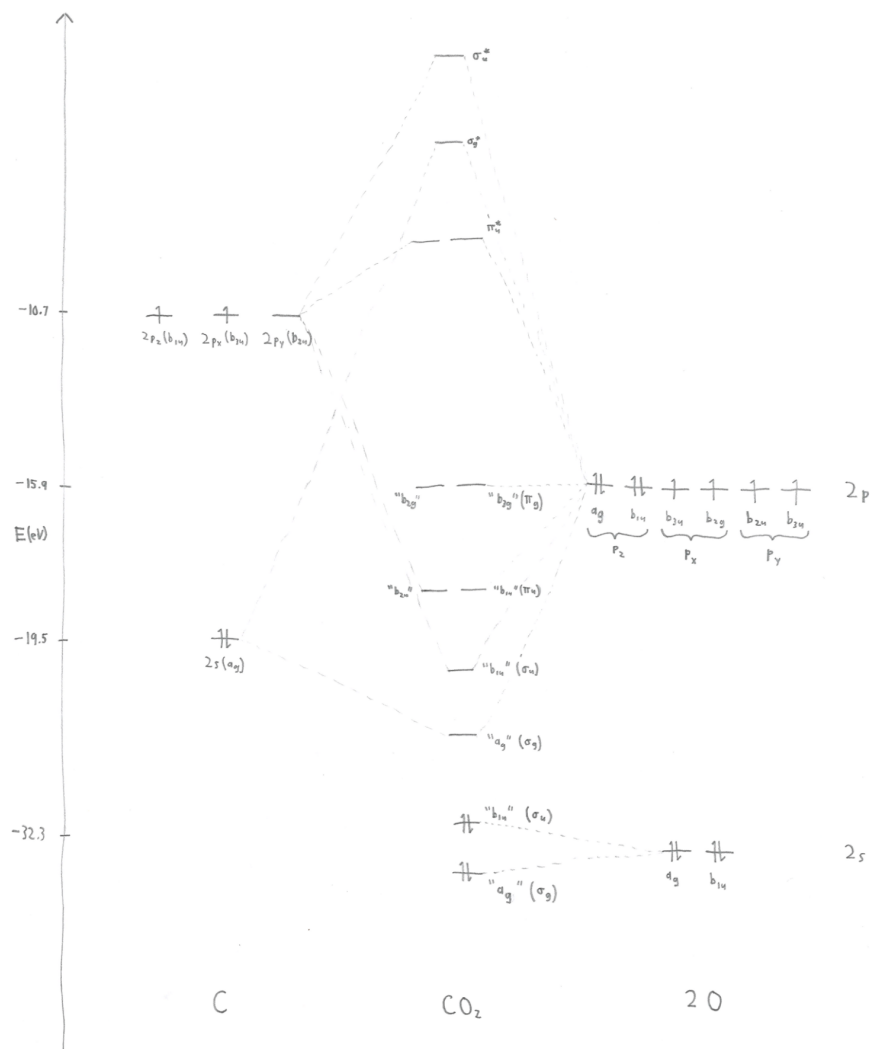
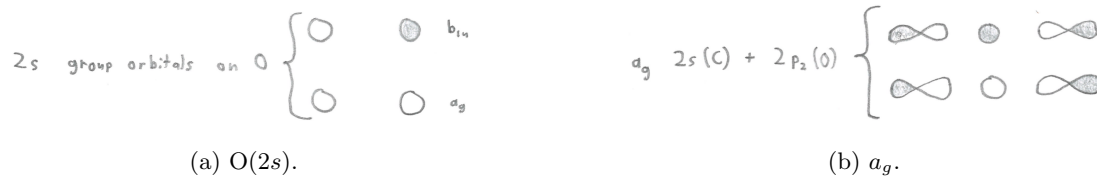
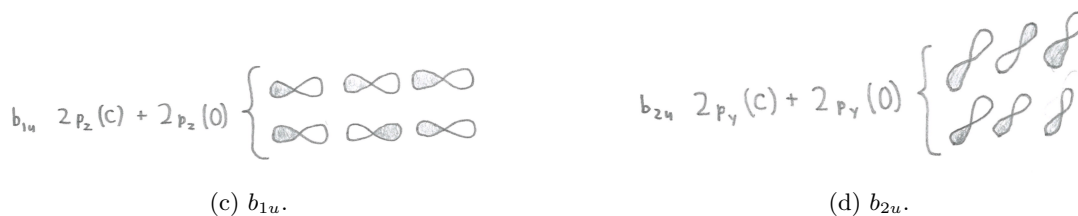


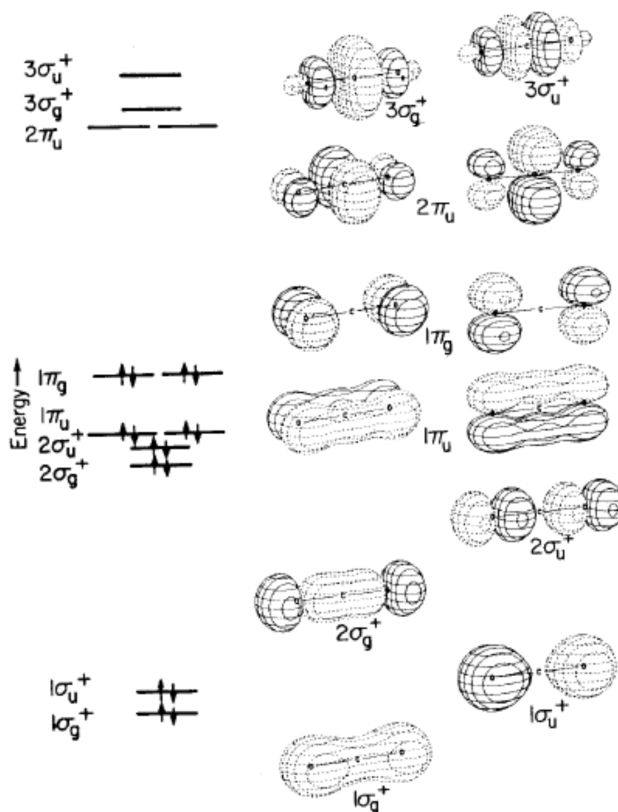
Figure 6.2: CO<sub>2</sub> MO diagram.

Moreover, a selection of key SALCs may be visualized as follows.



Figure 6.3: Selected CO<sub>2</sub> SALCs.

- From the 1 Rydberg rule, oxygen 2s orbitals will not significantly overlap with carbon 2s or 2p orbitals.
    - However, we still know that the bonding orbital is slightly lower in energy than the antibonding orbital by counting nodes
    - A bit of mixing also occurs, though (see the discussion surrounding Figure 6.4).
  - We have so many oxygen electrons since we have *two* oxygens and we are considering their *group* orbitals.
  - We can draw SALCs intuitively by combining orbitals in a bonding or antibonding fashion, or rigorously using the projection operator.
  - *Redraw & add electrons later!*
7. Done (see Figure 6.2).
8. Done (see Figure 6.2).
- Differences between the CO<sub>2</sub> MOs derived from first principles (Figure 6.2) and the MOs calculated by a computer's quantum mechanics program (Figure 6.4).

Figure 6.4: Quantum-mechanically calculated MOs for CO<sub>2</sub>.

- In the calculated version,  $1\sigma_g$  does not have a node at the carbon atom. This differs from the corresponding SALC we derived from first principles. Thus, in reality, we have some mixing between  $1\sigma_g$  and  $2\sigma_g$ . It follows that we can describe the orbital a bit better as O(2s) lone pairs plus CO  $\sigma$  bonds.
- Takeaway: The MOs we get from first principles do not take into account all of the interactions that the computer can.
- Note that in Figure 6.4, the electron density at each contour surface is  $0.0675 \text{ electrons}/\text{\AA}^3$  for one-electron wave functions. This value was chosen merely for satisfactory visual display of the orbitals.

## 6.2 Group Orbitals for Nonlinear Molecules

- 11/2:
- Last time: Making MOs for combinations that have two linear “outer atoms” like  $\text{CO}_2$ .
  - Today: Making MOs for cases in which we can’t just add and subtract two valence orbitals to visualize the group orbitals.
  - Strategy: Make group orbitals for “central atoms” and “peripheral atoms” and combine.
  - Example: MO diagram for ethylene.
    1. Point group:  $D_{2h}$ .
    2.  $xyz$  coordinates (and numbering for the projection operator).

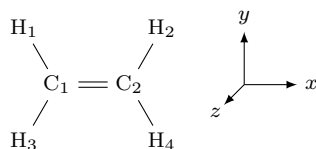


Figure 6.5:  $\text{C}_2\text{H}_4$   $xyz$  coordinates.

### 3. Representations.

$D_{2h}$	$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\text{H}(1s)}$	4	0	0	0	0	4	0	0
$\Gamma_{\text{C}(2s)}$	2	0	0	2	0	2	2	0
$\Gamma_{\text{C}(2p_x)}$	2	0	0	2	0	2	2	0
$\Gamma_{\text{C}(2p_y)}$	2	0	0	-2	0	2	-2	0
$\Gamma_{\text{C}(2p_z)}$	2	0	0	-2	0	-2	2	0

Table 6.3: Representations for the valence orbitals of  $\text{C}_2\text{H}_4$ .

### 4. Reductions.

$$\Gamma_{\text{H}(1s)} = a_g + b_{1g} + b_{2u} + b_{3u}$$

$$\Gamma_{\text{C}(2s)} = a_g + b_{3u}$$

$$\Gamma_{\text{C}(2p_x)} = a_g + b_{3u}$$

$$\Gamma_{\text{C}(2p_y)} = b_{1g} + b_{2u}$$

$$\Gamma_{\text{C}(2p_z)} = b_{2g} + b_{1u}$$

- Let’s get a handle on what some of these orbitals look like using the projection operator.

- Let's see how  $H_1$  and  $C_{2p_y(1)}$  transform.

$D_{2h}$	$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$H_1$	$H_1$	$H_4$	$H_2$	$H_3$	$H_4$	$H_1$	$H_3$	$H_2$
$C_{2p_y(1)}$	$C_{2p_y(1)}$	$-C_{2p_y(2)}$	$C_{2p_y(2)}$	$-C_{2p_y(1)}$	$-C_{2p_y(2)}$	$C_{2p_y(1)}$	$-C_{2p_y(1)}$	$C_{2p_y(2)}$

Table 6.4: How selected  $C_2H_4$  orbitals transform under the  $D_{2h}$  symmetry operations operators.

- We will visualize how these transform under  $b_{2u}$ . For  $H_1$ , we get

$$\begin{aligned}
 \hat{P}(H_{1s})_{b_{2u}} &= H_1 - H_4 + H_2 - H_3 - H_4 + H_1 - H_3 + H_2 \\
 &= 2H_1 - 2H_4 + 2H_2 - 2H_3 \\
 &\approx H_1 - H_4 + H_2 - H_3
 \end{aligned}$$

and for  $C_{2p_y(1)}$ , we get

$$\begin{aligned}
 \hat{P}(C_{2p_y(1)})_{b_{2u}} &= C_{2p_y(1)} + C_{2p_y(2)} + C_{2p_y(2)} + C_{2p_y(1)} + C_{2p_y(2)} + C_{2p_y(1)} + C_{2p_y(1)} + C_{2p_y(2)} \\
 &= 4(C_{2p_y(1)} + C_{2p_y(2)}) \\
 &\approx C_{2p_y(1)} + C_{2p_y(2)}
 \end{aligned}$$

- Thus, individually, these group orbitals may be visualized as follows.

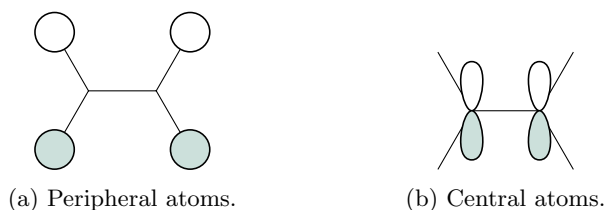


Figure 6.6:  $C_2H_4$   $b_{2u}$  SALCs.

- Now we take two orthogonal linear combinations of the two to get our MOs.

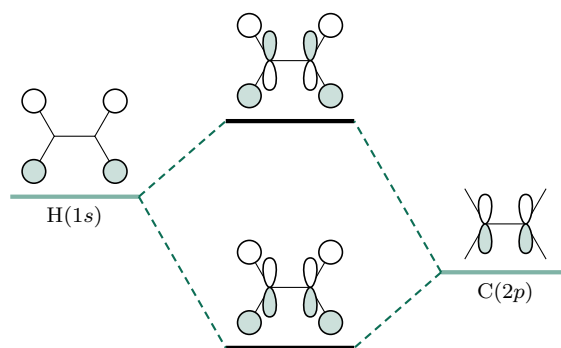
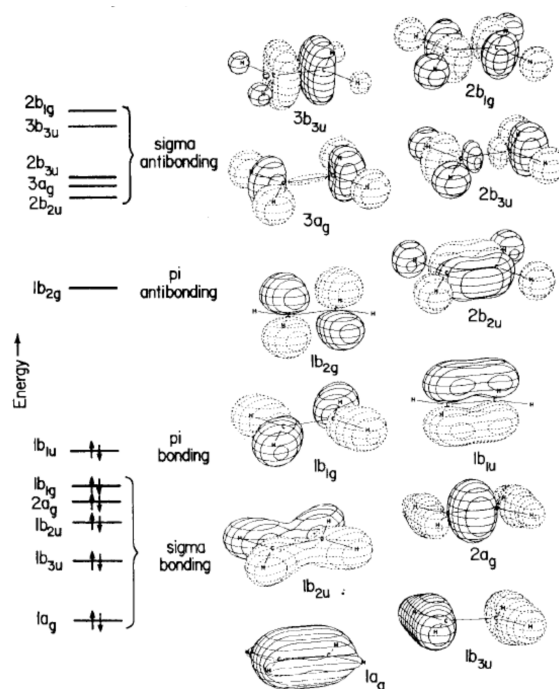


Figure 6.7:  $C_2H_4$   $b_{2u}$  MOs.

- Note that we label the MOs by comparing to the computed orbitals in Figure 6.8.

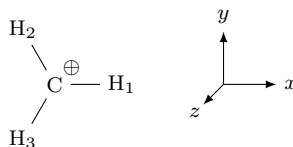
Figure 6.8: Quantum-mechanically calculated MOs for  $\text{C}_2\text{H}_4$ .

- What about how we make MOs for group orbitals that transform with  $e$  symmetry?
- Example: Methyl cation.
  1. Point group:  $D_{3h}$ .

$D_{3h}$	E	$2C_3$ (z)	$3C'_2$	$\sigma_h$ (xy)	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
$A'_1$	+1	+1	+1	+1	+1	+1	-	$x^2+y^2, z^2$	$x(x^2-3y^2)$
$A'_2$	+1	+1	-1	+1	+1	-1	$R_z$	-	$y(3x^2-y^2)$
$E'$	+2	-1	0	+2	-1	0	(x, y)	$(x^2-y^2, xy)$	$(xz^2, yz^2) [x(x^2+y^2), y(x^2+y^2)]$
$A''_1$	+1	+1	+1	-1	-1	-1	-	-	-
$A''_2$	+1	+1	-1	-1	-1	+1	z	-	$z^3, z(x^2+y^2)$
$E''$	+2	-1	0	-2	+1	0	$(R_x, R_y)$	$(xz, yz)$	$[xyz, z(x^2-y^2)]$

Table 6.5:  $D_{3h}$  character table.

2.  $xyz$  coordinates.

Figure 6.9:  $\text{CH}_3^+$   $xyz$  coordinates.

## 3. Representations.

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$\Gamma_{H(1s)}$	3	0	1	3	0	1
$\Gamma_{C(2s)}$	1	1	1	1	1	1
$\Gamma_{C(2p_x, 2p_y)}$	2	-1	0	2	-1	0
$\Gamma_{C(2p_z)}$	1	1	-1	-1	-1	1

Table 6.6: Representations for the valence orbitals of  $\text{CH}_3^+$ .

## 4. Reductions.

$$\begin{aligned}\Gamma_{H(1s)} &= a'_1 + e' \\ \Gamma_{C(2s)} &= a'_1 \\ \Gamma_{C(2p_x, 2p_y)} &= e' \\ \Gamma_{C(2p_z)} &= a''_2\end{aligned}$$

- The projection operator is only necessary for what group orbitals look like.

– How hydrogen orbitals transform.

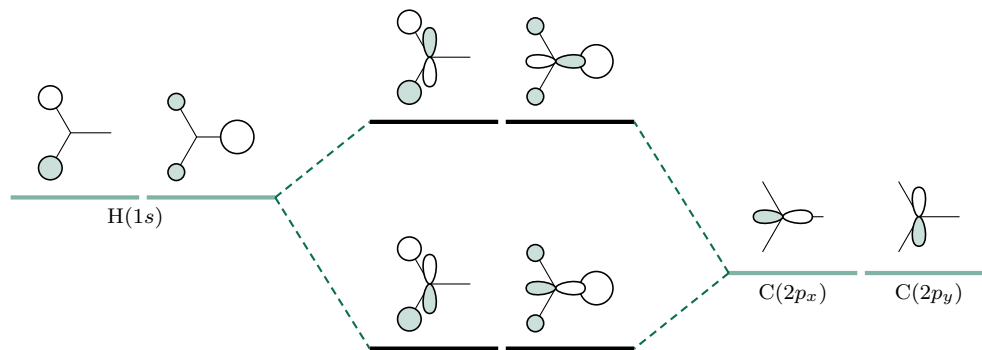
$D_{3h}$	$E$	$C_3$	$C_3^2$	$C_2$	$C_2'$	$C_2''$	$\sigma_h$	$S_3$	$S_3^{-1}$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$H_1$	$H_1$	$H_2$	$H_3$	$H_1$	$H_3$	$H_2$	$H_1$	$H_2$	$H_3$	$H_1$	$H_2$	$H_3$
$H_2$	$H_2$	$H_3$	$H_1$	$H_2$	$H_1$	$H_3$	$H_2$	$H_3$	$H_1$	$H_2$	$H_3$	$H_1$
$H_3$	$H_3$	$H_1$	$H_2$	$H_3$	$H_2$	$H_1$	$H_3$	$H_1$	$H_2$	$H_3$	$H_1$	$H_2$

Table 6.7: How selected  $\text{CH}_3^+$  orbitals transform under the  $D_{3h}$  symmetry operations operators.

– Transformations under  $e'$ .

$$\begin{aligned}\hat{P}(H_1)_{e'} &\approx 2H_1 - H_2 - H_3 \\ \hat{P}(H_2)_{e'} &\approx 2H_2 - H_3 - H_1 \\ \hat{P}(H_3)_{e'} &\approx 2H_3 - H_1 - H_2\end{aligned}$$

- We take the first and subtract the second two to get  $H_2 - H_3$  as our second orthogonal orbital.
- To draw MOs, we either pair  $C_{2p_x}$  with  $2H_1 - H_2 - H_3$  and  $C_{2p_y}$  with  $H_2 - H_3$  or vice versa.

Figure 6.10:  $\text{CH}_3^+$   $e'$  MOs.

- Note that the two bonding and the two antibonding MOs here are pairwise degenerate.



- Should we label the MOs via PES as in CHEM 201?
  - Yes.
- Finding energies from SALCs?

## 6.3 Photoelectron Spectroscopy and MO Diagrams of Coordination Complexes

11/4:

- The problem set is deceptively hard; get started early!
- Today: Experimental verification of molecular orbitals.
- **Photoelectron spectroscopy:** A widely used technique that allows us to obtain information about the energies of the electrons in orbitals.
- Key equation.

$$BE = h\nu - KE$$

- BE is the binding energy of the expelled electron.
- $h\nu$  is the incident photon energy.
- KE is the kinetic energy of the expelled electron.
- Fine structure in PES comes from the interaction of the electronic levels with the vibrational levels. This yields multiple peaks for a single given electronic transition.
- Example: How many peaks in the PES should we expect for each occupied MO of ethylene? Label each peak with the relevant valence molecular orbitals for ethylene.

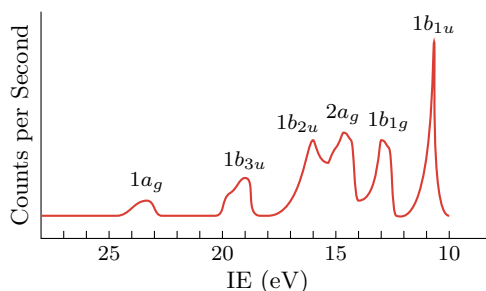


Figure 6.11: Photoelectron spectrum of C<sub>2</sub>H<sub>4</sub>.

- 1 peak for each occupied MO.
- Highest IE corresponds to the most core orbital. Decreases in energy as we get to higher energy orbitals.
- When Wuttig says in the homework that she wants us to draw a qualitative photoelectron spectrum, this is what she means.
- We now translate the principals of MO diagrams we've developed to understand bonding and structure in coordination complexes. We abbreviate the metal as M and the ligand as L.
- Basis sets are denoted by  $\phi$ .
- Basis sets.
  - M:  $(n+1)p$ ,  $(n+1)s$ , and  $nd$ .

- L:  $\sigma \rightarrow \sigma$  interactions,  $\pi \rightarrow \pi$  interactions, and  $\pi^* \rightarrow \pi^*$  interactions.
- Today: The  $\sigma \rightarrow \sigma$  case only.
- A few general rules for M-L bonding (these are essentially a rephrasing of those we have developed for the MOs of the organic species we have discussed this far).
  1. M-L atomic orbital mixing is proportional to the overlap of the M and L orbitals.
    - (a) But only orbitals of correct symmetry can mix.
    - (b)  $\sigma$  interactions typically give rise to larger interaction energies than  $\pi$  interactions which, in turn, typically give rise to larger interaction energies than  $\delta$  interactions. This is because we have more directional bonding as we move from  $\sigma \rightarrow \pi \rightarrow \delta$ .
  2. M-L atomic orbital mixing is inversely proportional to energy difference of mixing orbitals.
  3. The order of the  $E_L$  and  $E_M$  energy levels almost always is the following.

$$\sigma(L) < \pi(L) < nd < (n+1)s < (n+1)p$$

- (a) Energy ordering origin: Metal/main group VOIEs and ligand electronic spectra.
- Impact of VOIE as you move later in the periodic table.
  - Metals.
    - More covalency with L.
    - Less d-s-p mixing.
  - Common ligands.
    - More mixing with lone pairs compared to bonding orbitals.
- Conclusions from examining VOIEs.
  1. The  $s$  orbitals are generally too low in energy to participate in bonding.
  2. The filled  $p$  orbitals are the frontier orbitals, and they have VOIEs that place them below metal orbitals.
  3. For ligands, since the frontier orbitals comprise  $s$  and  $p$  orbitals, filled ligand orbitals have energies  $E$  that are stabilized relative to metal orbitals.
- Symmetry.
- We will now build the  $\sigma$ -only MO diagram for the important  $ML_6$  octahedral case.

1. Point group:  $O_h$ .

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear	quadratic
$A_{1g}$	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
$A_{2g}$	1	1	-1	-1	1	1	-1	1	1	-1		
$E_g$	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
$T_{1g}$	3	0	-1	1	-1	3	1	0	-1	-1	$(R_x, R_y, R_z)$	
$T_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1		$(xy, xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	-1	-1	1	-1	1	-1	-1	1		
$E_u$	2	-1	0	0	2	-2	0	1	-2	0		
$T_{1u}$	3	0	-1	1	-1	-3	-1	0	1	1	$(x, y, z)$	
$T_{2u}$	3	0	1	-1	-1	-3	1	0	1	-1		

Table 6.8: Character table for the  $O_h$  point group.

2. A coordinate system is not particularly necessary here since the molecule is symmetric along every Cartesian axis.
3. Reducible representation for the  $\sigma$  orbitals.

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_\sigma$	6	0	0	2	2	0	0	0	4	2

Table 6.9: Representation for the  $\sigma$  orbitals of  $ML_6$ .

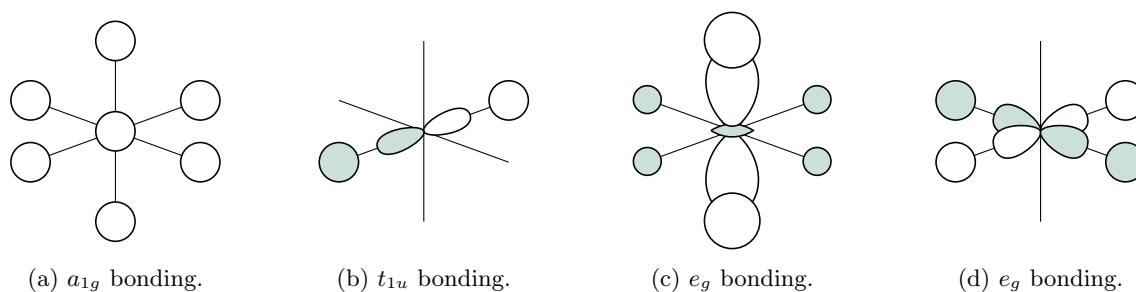
4. Reduction.

$$\Gamma_\sigma = a_{1g} + e_g + t_{1u}$$

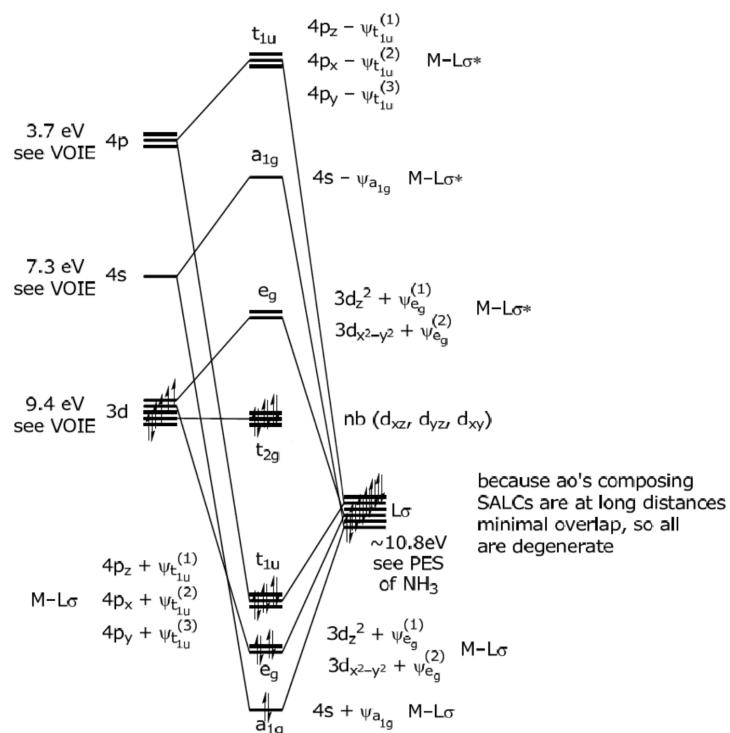
5. Symmetries of the metal atomic orbitals (from Table 6.8).

$$s \sim a_{1g} \quad p_x, p_y, p_z \sim t_{1u} \quad d_{z^2}, d_{x^2-y^2} \sim e_g \quad d_{xz}, d_{yz}, d_{xy} \sim t_{2g}$$

6. What the SALCs end up looking like.

Figure 6.12:  $ML_6$  SALCs.

- Note that the  $t_{2g}$  set will end up being nonbonding.
  - Wuttig did not explicitly compute these; she took a shortcut of guessing their shape inspired by the symmetry of the central orbital and assured us that the guess is what you get from the projection operator.
  - Doing the SALC for the  $d_{z^2}$   $e_g$  set gives you twice the electron density for the  $z$ -axis regions as for the  $xy$ -plane regions.
7. Now we can make sense of the full  $\sigma$ -only MO diagram (see Figure 6.13).
    - In particular, we want to be able to determine what all of the MOs on the diagram look like.
- $\pi$ -donating ligands.
    - Typical  $\pi$ -donating ligands include halides (X), amides ( $\text{CONH}_2$ ), sulfides ( $\text{S}^{2-}$ ), and oxides ( $\text{O}^{2-}$ ).
    - Pictures of  $\sigma$ - and  $\pi$ -donation (see Figure VI.4 of Labalme (2022)).
  - $\pi$ -accepting ligands.
    - Typical  $\pi$ -accepting ligands include CO,  $\text{NO}^+$ ,  $\text{CN}^-$ , CNR, and  $\text{PPh}_3$ .
    - Pictures of  $\sigma$ -donation and  $\pi$  acceptance (see Figure VI.4 of Labalme (2022)).

Figure 6.13:  $ML_6$  MO diagram.