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 $\sigma < \pi <$ lone pairs $< \pi^* < \sigma^*$. More nodes equals higher in energy.
  7. Label MOs.
     - σ implies a SALC with infinite-fold rotational symmetry about the bond axis; π 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: CO_2.

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

$\mathbf{D_{2h}}$	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (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.

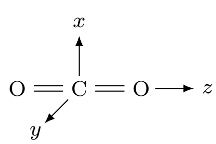


Figure 6.1: CO_2 xyz coordinates.

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 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,

$$C(2s) = a_g \qquad C(2p_z) = b_{1u} \qquad C(2p_x) = b_{3u} \qquad C(2p_y) = b_{2u}$$

6. We can now construct the following MO diagram.

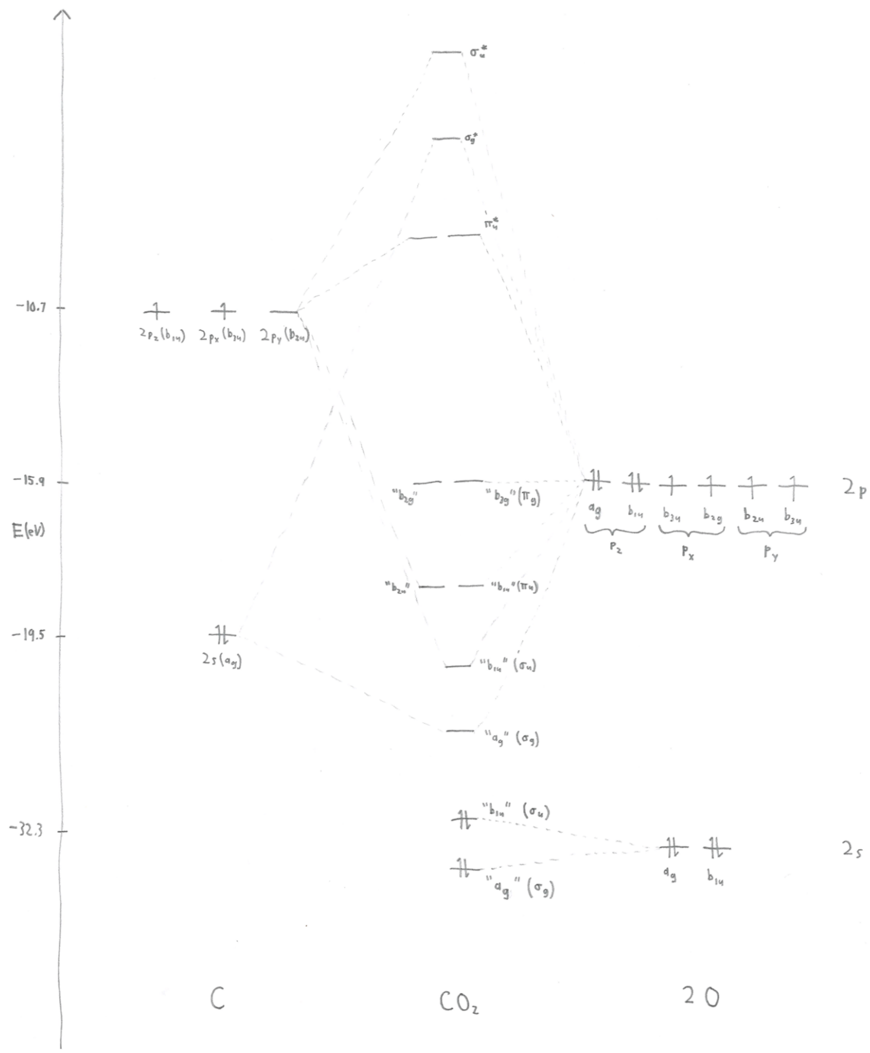
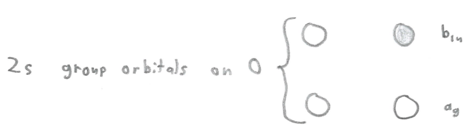
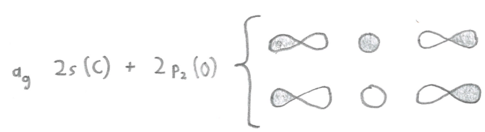


Figure 6.2: CO_2 MO diagram.

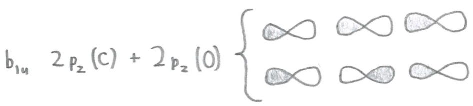
Moreover, a selection of key SALCs may be visualized as follows.



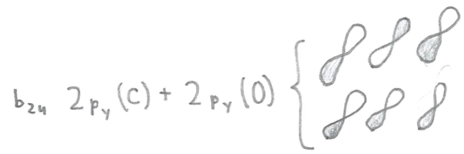
(a) O(2s).



(b) a_g.



(c) b_{1u}.



(d) b_{2u}.

Figure 6.3: Selected CO_2 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_2 MOs derived from first principles (Figure 6.2) and the MOs calculated by a computer's quantum mechanics program (Figure 6.4).

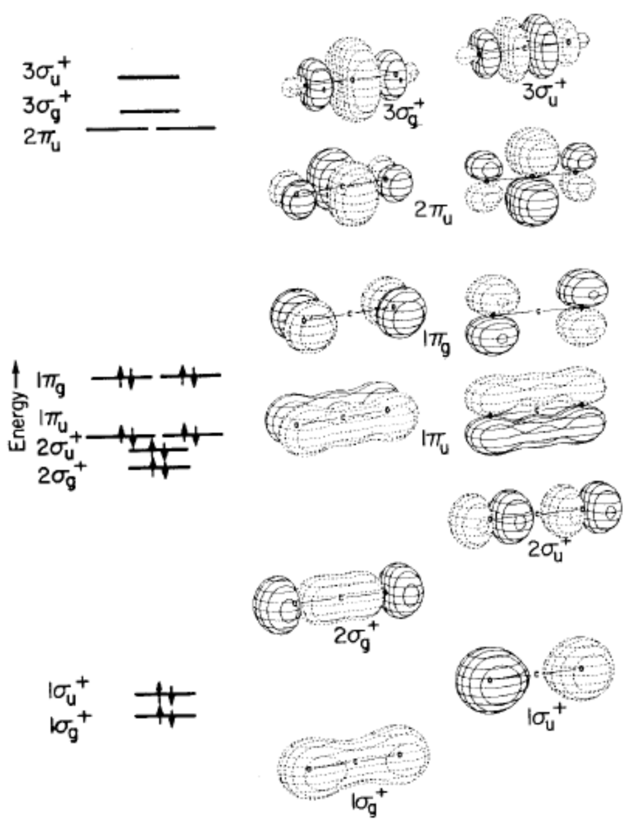


Figure 6.4: Quantum-mechanically calculated MOs for CO_2.

– 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 σ 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 $0.0675\,\text{electrons}/\text{Å}^3$ 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 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).

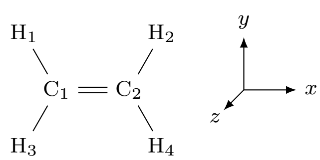


Figure 6.5: C_2H_4 xyz coordinates.

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 C_2H_4.

4. Reductions.

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

• 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.

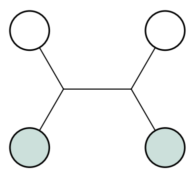
- We will visualize how these transform under b_{2u}. For H_1, we get

$$\begin{aligned}\hat{P}(\mathrm{H}_{1s})_{b_{2u}} &= \mathrm{H}_1 - \mathrm{H}_4 + \mathrm{H}_2 - \mathrm{H}_3 - \mathrm{H}_4 + \mathrm{H}_1 - \mathrm{H}_3 + \mathrm{H}_2 \\ &= 2\mathrm{H}_1 - 2\mathrm{H}_4 + 2\mathrm{H}_2 - 2\mathrm{H}_3 \\ &\approx \mathrm{H}_1 - \mathrm{H}_4 + \mathrm{H}_2 - \mathrm{H}_3\end{aligned}$$

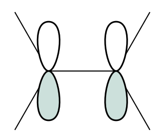
and for $C_{2p_y(1)}$, we get

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

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



(a) Peripheral atoms.



(b) Central atoms.

Figure 6.6: C_2H_4 b_{2u} SALCs.

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

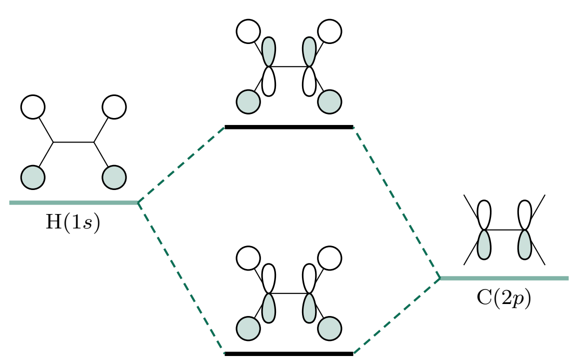


Figure 6.7: C_2H_4 b_{2u} MOs.

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

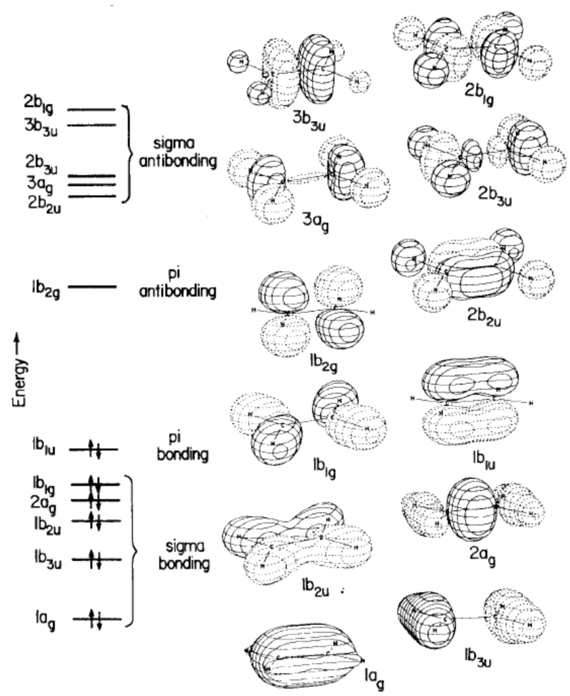


Figure 6.8: Quantum-mechanically calculated MOs for C_2H_4.

- 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)	$3C'_2$	σ_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.

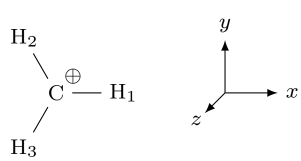


Figure 6.9: CH_3^+ xyz coordinates.

3. Representations.

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

Table 6.6: Representations for the valence orbitals of $CH_3{}^+$.

4. Reductions.

$$\begin{aligned}\Gamma_{\text{H}(1s)} &= a_1' + e' \\ \Gamma_{\text{C}(2s)} &= a_1' \\ \Gamma_{\text{C}(2p_x,2p_y)} &= e' \\ \Gamma_{\text{C}(2p_z)} &= a_2''\end{aligned}$$

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

D_{3h}	E	C_3	C_3^2	C_2	C_2'	C_2''	σ_h	S_3	S_3^{-1}	σ_v	σ_v'	σ_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 $CH_3{}^+$ orbitals transform under the D_{3h} symmetry operations operators.

  - Transformations under e'.

$$\begin{aligned}\hat{P}(\text{H}_1)_{e'} &\approx 2\text{H}_1 - \text{H}_2 - \text{H}_3 \\ \hat{P}(\text{H}_2)_{e'} &\approx 2\text{H}_2 - \text{H}_3 - \text{H}_1 \\ \hat{P}(\text{H}_3)_{e'} &\approx 2\text{H}_3 - \text{H}_1 - \text{H}_2\end{aligned}$$

  - 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.

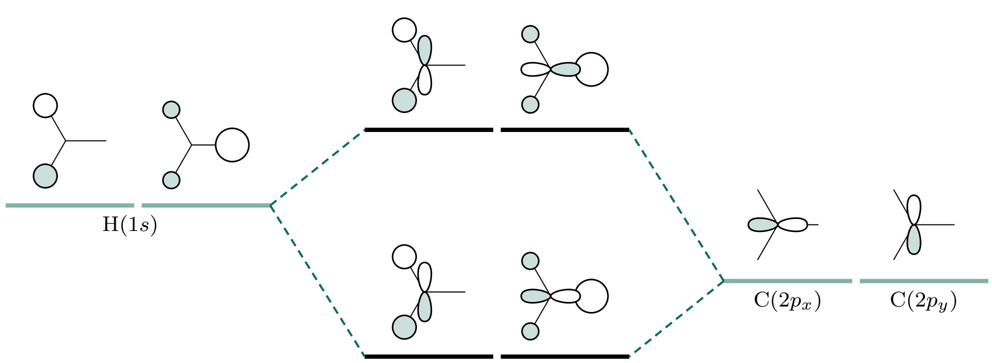


Figure 6.10: $CH_3{}^+$ e' MOs.

    - 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?