

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

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.

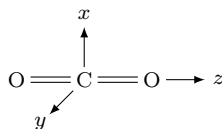


Figure 6.1: CO_2 xyz coordinates.

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.

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

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

Hand-drawn molecular orbital diagram for CO_2 . The diagram shows the energy levels of the atomic orbitals (AOs) of Carbon (C), Carbon Dioxide (CO_2), and Oxygen (O) and how they combine to form the molecular orbitals (MOs) of CO_2 .

Energy Axis (eV):

- 10.7
- 15.9
- 19.5
- 32.3

Carbon (C) Orbitals (Left):

- $2p_x (b_{1u})$
- $2p_y (b_{1u})$
- $2p_z (b_{2u})$

Carbon Dioxide (CO_2) Orbitals (Middle):

- σ_u^{**}
- σ_g^*
- π_u^*
- π_g (labeled as π_g in the diagram)
- σ_g (labeled as σ_g in the diagram)

Oxygen (O) Orbitals (Right):

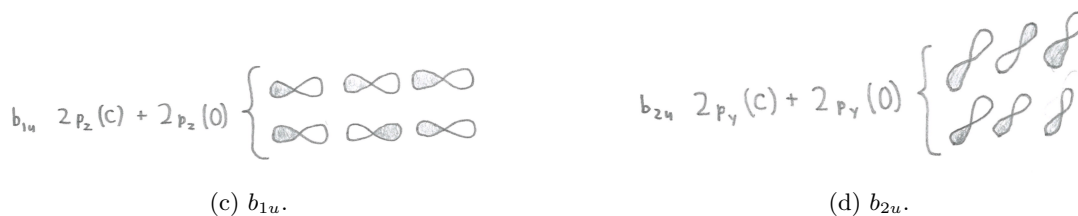
- $2p_x$ (labeled as $2p_x$ in the diagram)
- $2p_y$ (labeled as $2p_y$ in the diagram)
- $2p_z$ (labeled as $2p_z$ in the diagram)
- a_g
- b_{1u}
- b_{2u}
- b_{3u}
- b_{1g}
- b_{2g}
- b_{3g}

Connections (Dashed Lines):

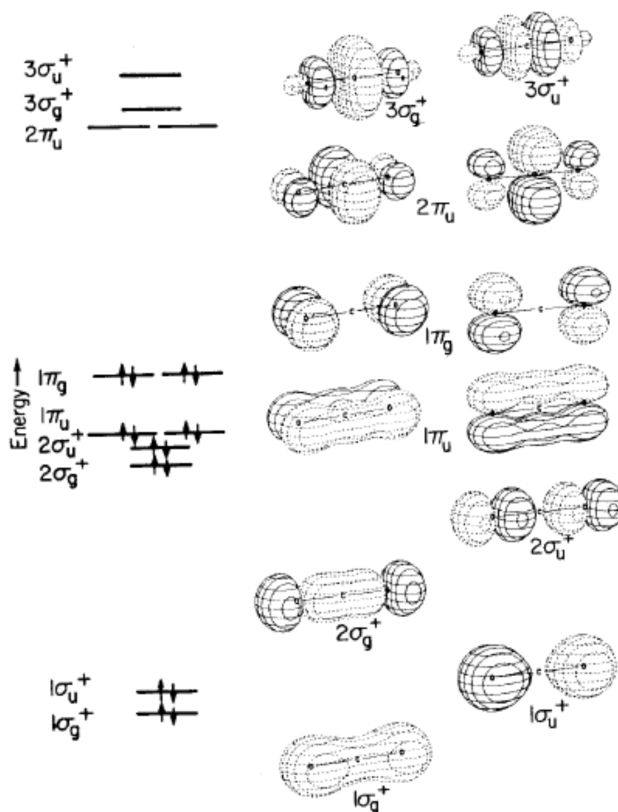
- $2p_x (b_{1u})$ and $2p_y (b_{1u})$ of C connect to π_u^* of CO_2 .
- $2p_z (b_{2u})$ of C connects to σ_u^{**} of CO_2 .
- $2p_x$ and $2p_y$ of O connect to π_u^* of CO_2 .
- $2p_z$ of O connects to σ_u^{**} of CO_2 .
- a_g of O connects to σ_g of CO_2 .
- b_{1u} of O connects to π_u^* of CO_2 .
- b_{2u} and b_{3u} of O connect to π_u^* of CO_2 .
- b_{1g} and b_{2g} of O connect to π_g of CO_2 .
- b_{3g} of O connects to σ_g of CO_2 .

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



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 $0.0675 \text{ electrons}/\text{\AA}^3$ for one-electron wave functions. This value was chosen merely for satisfactory visual display of the orbitals.