MO diagrams of small molecules:

- \( \text{N}_2 \): HOMO is \( 3\sigma_g \) \( \Rightarrow \) end-on coordination (linear \( \text{MoN}_2 \)); reduction weakens the \( \pi \)-bonds (lone pair formation, which are protonated to form N-H bonds - orbital picture of proton coupled electron transfer)
- \( \text{O}_2 \): HOMO \( 1\pi^*_g \) \( 1\pi_g^* \) \( \Rightarrow \) side on coordination (\( \text{Cu}_2\text{O}_2 \), \( \text{Fe}_2\text{O}_2 \) rhombs) with instantaneous 2 e\(^-\) transfer \( \Rightarrow \) peroxide formation; end-on coordination (bent \( \text{FeO}_2 \)) with 1e\(^-\) transfer \( \Rightarrow \) superoxide formation
- \( \text{CO} \): HOMO \( \sigma_{\text{nb},\text{C}} \) \( \Rightarrow \) end-on coordination at the C side

MO diagrams for bonding with many atoms/ligands (Group Theoretical Treatment)

General guidelines:

1. need to know the point group and be able to identify all symmetry elements (\( \text{PF}_5 \) is \( D_{3h} \), \( \text{SF}_6 \) is \( O_h \))
2. separate \( \sigma \) (no angular momentum) and \( \pi \) (non-zero angular momentum) bonding (\( \text{PF}_5 \) has \( \sigma_{\text{ax}}, \sigma_{\text{eq}} \))
3. generate reducible representations and find their irreducible representations
4. obtain SALC using the projection operator method
5. combine SALC with central atom's orbitals to obtain the MO (non-bonding orbitals: lack of matching irreps between the central and pendant atom)
6. sketch MO diagram (better overlap gives larger splitting/lower energy + take into account double (E), triple (T)-degeneracy

Example: Problem set 4.19 - \( \text{PF}_5 \) – point group \( D_{3h} \)

A. \( \sigma \) orbitals (hybrid orbitals from VB theory):

- can be separated, since axial does not transfer to equatorial
- count the operations, which do not change the position of the bonds

<table>
<thead>
<tr>
<th>( D_{3h} )</th>
<th>E</th>
<th>2C(_3)</th>
<th>3C(_2)</th>
<th>( \sigma_h )</th>
<th>2S(_3)</th>
<th>3( \sigma_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{\text{eq}} )</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( \Gamma_{\text{ax}} )</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

- reduce \( \Gamma_{\text{eq}} \) and \( \Gamma_{\text{ax}} \): can be guessed by using the characters of irreps. \( \Rightarrow \) \( \Gamma_{\text{eq}} = A_{1}' + E' \) and \( \Gamma_{\text{ax}} = A_{1}' + A_{2}'' \)
- orbitals on P need to be hybridized: s, \( d_{z^2} \) from \( A_{1}' \), \( p_z \) from \( A_{2}'' \), and \( p_x,p_y \) from \( E' \), thus axial \( \sigma \)-bonds are based on \( p_z, d_{z^2} \); for equatorial \( \sigma \)-bonds are based on s, \( p_x, p_y \) orbitals

I. Equatorial \( \sigma \) orbitals

- for the hybrid orbitals need to apply the projection operator – take a bond and apply all symmetry operation (everything within all classes - must know every single symm.ops.). First for \( A_{1}' \)

<table>
<thead>
<tr>
<th>( \sigma_1 )</th>
<th>( \sigma_3 )</th>
<th>( \sigma_2 )</th>
<th>( \sigma_1 )</th>
<th>( \sigma_2 )</th>
<th>( \sigma_3 )</th>
<th>( \sigma_1 )</th>
<th>( \sigma_2 )</th>
<th>( \sigma_3 )</th>
<th>( \sigma_1 )</th>
<th>( \sigma_2 )</th>
<th>( \sigma_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi(A_{1}) )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

- multiply the results of each operation with the character of the irreps.

\[
\phi(a_1') = \frac{1}{\sqrt{4^2 + 4^2 + 4^2}} ( 4\sigma_1 + 4\sigma_2 + 4\sigma_3 ) = \frac{1}{\sqrt{3}} ( \sigma_1 + \sigma_2 + \sigma_3 )
\]
For \( E' \), use the above projection and multiply with the characters of \( E' \)

\[
\begin{array}{cccccccccc}
E & C_3 & C_3^2 & C_2 & C_2' & C_2'' & \sigma_h & S_3 & S_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\
\sigma_1 & \sigma_1 & \sigma_3 & \sigma_2 & \sigma_1 & \sigma_2 & \sigma_3 & \sigma_1 & \sigma_1 & \sigma_3 & \sigma_2 & \sigma_1 \\
E' & 2 & -1 & -1 & 0 & 0 & 2 & -1 & -1 & 0 & 0 & 0 & 0 \\
\end{array}
\]

\[
\phi(e') = \frac{1}{\sqrt{4^2 + 2^2 + 2^2}} (4\sigma_1 - 2\sigma_2 - 2\sigma_3) = \frac{1}{\sqrt{6}} (2\sigma_1 - \sigma_2 - \sigma_3)
\]

- need to find the second set for \( E' \) (which is orthogonal) ⇒ use a symmetry operation and the results should be either ±1 itself, the second set, or linear combination of both

\[
(2\sigma_1 - \sigma_2 - \sigma_3) \text{ applying } C_3 \text{ gives } (2\sigma_3 - \sigma_1 - \sigma_2) \text{ not ±1, not orthogonal, therefore}
\]

a linear combination of the two sets ⇒ (2\(\sigma_3 - \sigma_1 - \sigma_2\)) = 1/2 \(\chi(C_3)\) (1st set) + 1/2 \(\chi(C_3)\) (2nd set)

- the combination of the two results give (3\(\sigma_3 - 3\sigma_2\)), therefore

\[
\phi(e') = \frac{1}{\sqrt{3^2 + 3^2}} (3\sigma_3 - 3\sigma_2) = \frac{1}{\sqrt{2}} (\sigma_3 - \sigma_2)
\]

- use the three \(\phi\)'s for defining the hybrid orbitals from SALC:

\[
\begin{bmatrix}
\phi(a_1') \\
\phi(e') \\
\phi(e')
\end{bmatrix} = \begin{bmatrix}
1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\
2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\
0 & 1/\sqrt{2} & -1/\sqrt{2}
\end{bmatrix} \begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3
\end{bmatrix}
\]

since orthogonal ⇒ SALC\(^{-1}\):

\[
\begin{bmatrix}
1/\sqrt{3} & 2/\sqrt{6} & 0 \\
1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\
1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2}
\end{bmatrix}
\]

hybrid orbitals in VB theory

\[
h_1 = \frac{1}{\sqrt{3}} [s + \frac{\sqrt{2}}{2} p_x] \quad h_2 = \frac{1}{\sqrt{3}} [s - \frac{\sqrt{2}}{2} p_x + \sqrt{\frac{3}{2}} p_y] \quad h_3 = \frac{1}{\sqrt{3}} [s - \frac{\sqrt{2}}{2} p_x - \sqrt{\frac{3}{2}} p_y]
\]

II. Axial \(\sigma\) orbitals:

- apply the projection operator and multiply with the characters of \(A_1'\) and \(A_2''\) irred.reps.

\[
\begin{array}{cccccccccc}
E & C_3 & C_3^2 & C_2 & C_2' & C_2'' & \sigma_h & S_3 & S_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\
\sigma_4 & \sigma_4 & \sigma_4 & \sigma_5 & \sigma_5 & \sigma_5 & \sigma_4 & \sigma_4 & \sigma_4 & \sigma_4 & \sigma_4 \\
\end{array}
\]

\[
\phi(a_1') = \frac{1}{\sqrt{6^2 + 6^2}} (6\sigma_4 + 6\sigma_5) = \frac{1}{\sqrt{2}} (\sigma_4 + \sigma_5)
\]

\[
\phi(a_2'') = \frac{1}{\sqrt{6^2 + 6^2}} (6\sigma_4 - 6\sigma_5) = \frac{1}{\sqrt{2}} (\sigma_4 - \sigma_5)
\]
• use the two $\phi$'s for defining the hybrid orbitals using SALC:

$$
\begin{bmatrix}
\phi(a_1') \\
\phi(a_2'')
\end{bmatrix}
= \begin{bmatrix}
1/\sqrt{2} & 1/\sqrt{2} \\
1/\sqrt{2} & -1/\sqrt{2}
\end{bmatrix}
\begin{bmatrix}
\sigma_1 \\
\sigma_2
\end{bmatrix}
$$

since orthogonal, the transpose = $\text{SALC}^{-1}$

$$
\begin{bmatrix}
1/\sqrt{2} & 1/\sqrt{2} \\
1/\sqrt{2} & -1/\sqrt{2}
\end{bmatrix}
\begin{bmatrix}
d_{z^2} \\
p_z
\end{bmatrix}
$$

hybrid orbitals in VB theory

$$
h_4 = \frac{1}{\sqrt{2}}[d_{z^2} + p_z] \quad h_5 = \frac{1}{\sqrt{2}}[d_{z^2} - p_z]
$$

B. $\pi$ orbitals:

• in-plane and out-of-plane can be separated in addition to axial and equatorial components since there is no symmetry operation to transform in between these
• this example is worked out for the equatorial, out-of-plane $\pi$-orbitals
• obtain the reducible representation for the three $\pi$-bonds in $D_{3h}$

$$
\begin{array}{cccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2\sigma_v & 3\sigma_v \\
\Gamma & 3 & 0 & -1 & -3 & 0 & 1
\end{array}
$$

note the negative sign for $C_2$ and $\sigma_h$, which means leaves the $\pi$ orbital on the atom, however changes its sign

• $\Gamma$ can be reduced to $A_2''$ and $E''$, i.e. orbitals need to be combined on P are $p_z$ and (xz, yz).
• For $A_2''$, use the projection operator and multiply with the characters of $A_2''$

$$
\begin{array}{cccccccccc}
E & C_3 & C_3^2 & C_2 & C_2' & C_2'' & \sigma_h & S_3 & S_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\
\pi_1 & \pi_1 & \pi_3 & \pi_2 & -\pi_1 & -\pi_3 & \pi_1 & -\pi_3 & -\pi_1 & -\pi_3 & \pi_1 & \pi_3 & \pi_2 \\
\chi & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1
\end{array}
$$

$$
\phi(a_2'') = \frac{1}{\sqrt{3^2 + 3^2 + 3^2}} (3\pi_1 + 3\pi_2 + 3\pi_3) = \frac{1}{\sqrt{3}} (\pi_1 + \pi_2 + \pi_3)
$$

• For $E''$, use the projection operator and multiply with the characters of $E''$

$$
\begin{array}{cccccccccc}
E & C_3 & C_3^2 & C_2 & C_2' & C_2'' & \sigma_h & S_3 & S_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\
\chi & 2 & -1 & -1 & 0 & 0 & -2 & 1 & 1 & 0 & 0 & 0 & 0
\end{array}
$$

$$
\phi(e'') = \frac{1}{\sqrt{4^2 + 2^2 + 2^2}} (4\pi_1 - 2\pi_2 + 4\pi_3) = \frac{1}{\sqrt{6}} (2\pi_1 - \pi_2 - \pi_3)
$$

$$
\phi(e'') = \frac{1}{\sqrt{3^2 + 3^2}} (3\pi_3 - 3\pi_2) = \frac{1}{\sqrt{2}} (\pi_3 - \pi_2)
$$