Visualization is important. In group theory this can be done using projection operators.

Definition of a projection operator: \( \hat{P}^j \) (no proof)

\[
\hat{P}^j = \left( \frac{\ell}{\hbar} \right) \sum_{T} \chi_j(T) \hat{T}
\]

A projection operator projects out from a function (of your choice), \( \phi \), the sum of all basis functions that transform according to the IR \( \Gamma_j \).

If \( \Gamma_j \) is 1D, \( \phi \) is a starting basis function for \( \Gamma_j \).

If \( \Gamma_j \) is > 1D, repeat the procedure \( l_j \) times, each time with a new \( \phi \), to obtain \( l_j \) linearly independent functions.

Best understood by doing an example:
**π-electron systems**

Electronic charge density in a MO extends over the whole molecule, and therefore, MO must form bases for the symmetry point group of the molecule.

Symmetry-adapted MOs will be expressed as linear combinations of atomic orbitals (LCAO)

\[ \psi^j = \sum_r c_{jr} \phi_r \quad \text{or} \quad |\psi^j\rangle = \sum_r c_{jr} |\phi_r\rangle \]

\( \{\phi_r\} \) = orthonormal basis set of atomic orbitals

**Example:** MOs of benzene using as basis 6 2p\(_x\) orbitals, one on each C

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![Benzene molecular diagram](image)
Recall, a 2p orbital looks like:

Therefore, use contour of \( \varphi = 2p_z \) on carbon \( r \) to determine \( \varphi' \) under each operation in the point group of the molecule = \( D_{6h} \), and recognize that \( \varphi' \) contributes to the trace, \( \chi \), of the matrix representation under an operation T only when it transforms into \( \pm \varphi \),

\[
\begin{array}{ccccc}
D_{6h} & E & 2C_6 & C_2 & 2C'_2 & 3C'_2 & i & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v
\end{array}
\]

\[
\chi(\Gamma_v) \begin{pmatrix} 6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}
\]

Using \( a_j = h^{-1} \sum_k c_k \chi_j(T_k) \chi(T_k) \)

can show \( \Gamma_v = A_{2u} \oplus B_{2g} \oplus E_{1u} \oplus E_{2u} \)

**Example:** \( a(A_{2u}) = \frac{1}{24} \left[ (1)(1)(6) + (3)(-1)(-2) + (1)(1)(-6) + (3)(1)(2) \right] = 1 \)

**Note:** for \( \Gamma_v \), 6 AOs yield 6 MOs: one with \( A_{2u} \) symmetry, one with \( B_{2g} \) symmetry, two degenerate orbitals with \( E_{1u} \) symmetry and 2 degenerate orbitals with \( E_{2u} \) symmetry.

In a cyclic (CH)\(_n\) molecule with rotational \( C_n \) symmetry, one will form \( n \pi \) MOs, one belonging to each IR of the point group \( C_n \). The IRs for \( C_6 \) are \( A, B, E_1, E_2 \). However for benzene need to use \( D_{6h} \) because there are other symmetries at play.

Basis functions for the IRs of benzene can be obtained using projection operators:

\[
\psi' = N_j \sum_T \chi_j(T) \tilde{T} \phi
\]

\( N_j \) is a normalization constant and \( \phi \) is an arbitrary function defined in the subspace of the functions for which in this example are the 6 \( 2p_z \) orbitals.
For simplicity use $\phi_1 = 2p_z$ orbital on carbon 1.

\[
\psi(A_{2u}) = N(A_{2u})[1\phi_1 + 1(\phi_2 + \phi_6) + 1(\phi_3 + \phi_5) + 1\phi_4 - E]
\]

\[
-1(-\phi_1 - \phi_2 - \phi_5) - 1(-\phi_2 - \phi_4 - \phi_6) - 1(-\phi_4) - 1(-\phi_3 - \phi_5)
\]

\[
3C_2^r \quad 3C_2^r \quad i \quad 2S_3
\]

\[
-1(-\phi_2 - \phi_6) - 1(-\phi_1) + 1(\phi_2 + \phi_3 + \phi_6) + 1(\phi_1 + \phi_3 + \phi_5)
\]

\[
2S_6 \quad \sigma_h \quad 3\sigma_d \quad 3\sigma_v
\]

\[
\therefore \psi(A_{2u}) = 4N(A_{2u})[\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6]
\]

\[
= N(A_{2u})[\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6]
\]

**Normalization**

\[
\therefore \psi^j = N_j \sum_r c_{jr} \phi_r
\]

\[
\Rightarrow \langle \psi^j | \psi^j \rangle = |N_j|^2 \left( \sum_r c_{jr} \phi_r \right) \left( \sum_s c_{sj} \phi_s \right)
\]

\[
= |N_j|^2 \left[ \sum_r |c_{jr}|^2 + \sum_{rs} \sum_s c_{jr}^* c_{sj} S_{rs} \right] = 1
\]

$S_{rs}$ = overlap integral

Useful approximation = zero overlap approximation (ZOA): $S_{rs} = 0$ for $r \neq s$

Typically, $S_{ss} \sim 0.2 - 0.3$ for C(2p_z), but ZOA yields $N_j$ easily, and the ratio of the coefficients still exact.
\[ a_{2u} = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \]

Label for MO of A\textsubscript{2u} symmetry

Pictorially, indicate the relative magnitude of the coefficients on the structure of benzene:

No nodal plane

Can show using projection operators:

- **e\textsubscript{1g}(1):**
  - 1 nodal plane

- **e\textsubscript{1g}(2):**
  - 1 nodal plane

- **e\textsubscript{2u}(1):**
  - 2 nodal planes

- **e\textsubscript{2u}(2):**
  - 2 nodal planes

- **b\textsubscript{2g}:**
  - 3 nodal planes

> Energy of an orbital, > # nodes
Therefore expect \( E(a_{2u}) < E(e\textsubscript{1g}) < E(e\textsubscript{2u}) < E(b\textsubscript{2g}) \)
Note:
For a 2-fold degeneracy use $P_j$ first for $\varphi_1$ and then again for $\varphi_2$. Then find linear combinations of the two wave functions which are orthogonal and normalized. In the case of benzene, do this for $E_{1g}$ set, and then again for the $E_{2u}$ set.

Note:
Since wave functions $\psi$ can be multiplied by an arbitrary phase factor without changing the charge density it is common practice if need be to multiply $\psi$ by -1 so that the LCAO does not start with a negative sign.

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**Energy of MOs**

\[
E^{' \prime} = \langle \psi^{' \prime} | \hat{H} | \psi^{' \prime} \rangle = \left| N_j \right|^2 \left\{ \sum_{r} c_{rj} \varphi_r | \hat{H} | \sum_{s} c_{sj} \varphi_s \right\} \\
= \left| N_j \right|^2 \left[ \sum_{r} |c_{rj}|^2 H_{rr} + \sum_{r \neq s} \sum_{s} c_{rj}^* c_{sj} H_{rs} \right]
\]

where \( H_{rg} = H_{gr}^* = \langle \phi_r | \hat{H} | \phi_g \rangle \)

Hermitian
**Hückel Approximation**

If $s = r$  
$H_{ss} = \alpha$ “very” negative

If $s$ is joined to $r$: $s \leftrightarrow r$  
$H_{sr} = \beta$ negative

If $s$ is not joined to $r$  
$H_{ss} = 0$

\[ \therefore E' = \left| N_j \right|^2 \sum_r |c_{rf}|^2 + \sum_{r \neq s} \sum_s c_{rf}^* c_{sf} \beta \]

There is double counting here

**Example:**  
\[ a_{2_u} = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \]

\[ \therefore E(a_{2_u}) = \frac{1}{6} [6\alpha + 2(c_1c_2 + c_2c_3 + c_3c_4 + c_4c_5 + c_5c_6 + c_6c_1)\beta] \]

Find for benzene:

\[ = \frac{1}{6} [6\alpha + 12\beta] = \alpha + 2\beta \]

Agrees with “nodal prediction”.

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