Applications: π-electron systems

C734b

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

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

$$\hat{P}^j = \left(\frac{\ell_j}{h}\right)\sum_T \chi_j(T)^*\hat{T}$$

A projection operator projects out from a function (of your choice), φ, the sum of all basis functions that transform according to the IR Γ^j

If Γ^j is 1D, φ is a starting basis function for Γ^j

If Γ^j is > 1D, repeat the procedure l_j times, each time with a new φ, to obtain l_j linearly independent functions

Best understood by doing an example:

π-electron systems

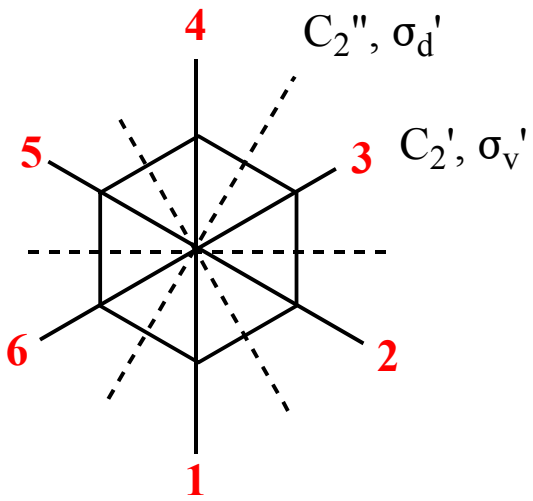
Electronic charge density in a MO extends over the whole molecule, and therefore, MO must form bases for the symmetry point group of the molecule

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

$$\psi^j = \sum_r c_{rj}\phi_r \quad \text{or} \quad \left|\psi^j\right\rangle = \sum_r c_{rj}\left|\phi_r\right\rangle$$

$\{\varphi_r\} \equiv$ orthonormal basis set of atomic orbitals

Example: MOs of benzene using as basis 6 $2p_z$ orbitals, one on each C



Recall, a 2p orbital looks like: 

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

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
$\chi(\Gamma_\phi)$	6	0	0	0	-2	0	0	0	0	-6	0	2

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

can show $$\Gamma_\phi = A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$$

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

Note: for Γ_φ 6 AOs yield 6 MOs: on 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 nπ 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:

$$\psi^j = N_j \sum_T \chi_j(T)^* \hat{T}\phi$$

N_j is a normalization constant and φ 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 $\varphi_1 \equiv 2p_z$ orbital on carbon 1.

$$\psi(A_{2u}) = N(A_{2u})[1\phi_1 + 1(\phi_2 + \phi_6) + 1(\phi_3 + \phi_5) + 1\phi_4$$
$$E \qquad 2C_6 \qquad 2C_3 \qquad C_2$$
$$-1(-\phi_1 - \phi_3 - \phi_5) - 1(-\phi_2 - \phi_4 - \phi_6) - 1(-\phi_4) - 1(-\phi_3 - \phi_5)$$
$$3C_2' \qquad 3C_2'' \qquad i \qquad 2S_3$$
$$-1(-\phi_2 - \phi_6) - 1(-\phi_1) + 1(\phi_2 + \phi_4 + \phi_6) + 1(\phi_1 + \phi_3 + \phi_5)]$$
$$2S_6 \qquad \sigma_h \qquad 3\sigma_d \qquad 3\sigma_v$$

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

Normalization

$$\because \psi^j = N_j \sum_r c_{jr}\phi_r$$
$$\Rightarrow \langle \psi^j | \psi^j \rangle = |N_j|^2 \left\langle \sum_r c_{rj}\phi_r \middle| \sum_s c_{sj}\phi_s \right\rangle$$
$$= |N_j|^2 \left[\sum_r |c_{rj}|^2 + \sum_{r \neq s} \sum_s c_{rj}^* c_{sj} S_{rs} \right] = 1$$

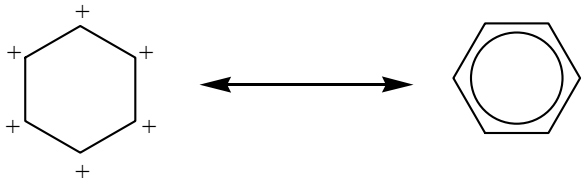
$S_{rs} \equiv$ overlap integral

Useful approximation = **zero overlap approximation** (ZOA): $S_{rs} = 0$ for $r \neq s$
Typically, $S_{rs} \sim 0.2$ - 0.3 for $C(2p_z)$, but ZOA yields N_j easily, and the ratio of the coefficients still exact.

$$\Rightarrow a_{2u} = \frac{1}{\sqrt{6}}\left(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\right)$$

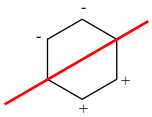
Label for MO of A_{2u} symmetry

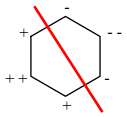
Pictorially, indicate the relative magnitude of the coefficients on the structure of benzene



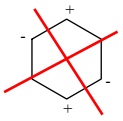
No nodal plane

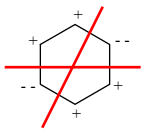
Can show using projection operators:

$e_{1g}(1)$: 

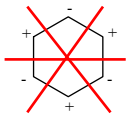
$e_{1g}(2)$: 

1 nodal plane

$e_{2u}(1)$: 

$e_{2u}(2)$: 

2 nodal planes

b_{2g}: 

3 nodal planes

> Energy of an orbital, > # nodes
Therefore expect $E(a_{2u}) < E(e_{1g}) < E(e_{2u}) < E(b_{2g})$

Note:
For a 2-fold degeneracy use P^j first for φ_1 and then again for φ_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 ψ can be multiplied by an arbitrary phase factor without changing the charge density it is common practice if need be to multiply ψ by -1 so that the LCAO does not start with a negative sign.

Energy of MOs

$$E^j = \left\langle \psi^j \middle| \hat{H} \middle| \psi^j \right\rangle = \left| N_j \right|^2 \left\langle \sum_r c_{rj}\phi_r \middle| \hat{H} \middle| \sum_s c_{sj}\phi_s \right\rangle$$

$$= \left| N_j \right|^2 \left[\sum_r \left| c_{rj} \right|^2 H_{rr} + \sum_{r \neq s} \sum_s c_{rj}^* c_{sj} H_{rs} \right]$$

where $H_{rs} = H_{sr}^* = \left\langle \phi_r \middle| \hat{H} \middle| \phi_s \right\rangle$

Hermitian

Hückel Approximation

If s = r	$H_{rr} = \alpha$	"very" negative
If s is joined to r: s ↔ r	$H_{rs} = \beta$	negative
If s is not joined to r	$H_{rs} = 0$	

$$\therefore E^j = |N_j|^2 \left[\sum_r |c_{rj}|^2 + \sum_{r \neq s} \sum_s c_{rj}^* c_{sj} \beta \right]$$

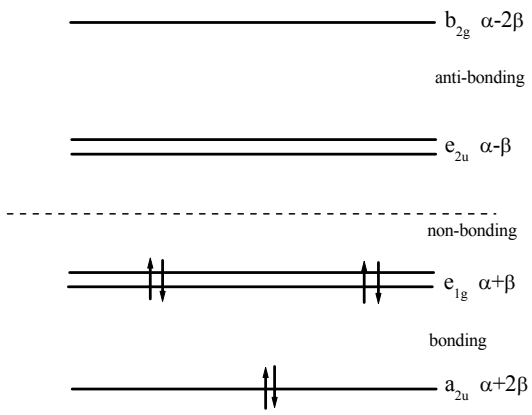
There is double counting here

Example: $a_{2u} = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$

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

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

Find for benzene:



Agrees with "nodal prediction".