

LCAO-MO Theory

- ✿ In molecular orbital theory the MOs, $\{\psi_\mu\}$, are usually expanded as combinations of atomic orbitals, $\{\phi_i\}$.

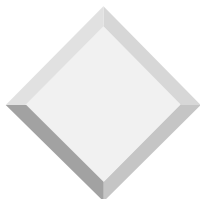
For the μ^{th} MO, we write this expansion as

$$\psi_\mu = \sum_i c_{i\mu} \phi_i = c_{1\mu} \phi_1 + c_{2\mu} \phi_2 + c_{3\mu} \phi_3 + \dots$$

- ✿ The MOs are solutions to an effective Schrödinger equation:

$$\mathcal{H}\psi_\mu = E_\mu \psi_\mu$$

Read: Harris & Bertolucci, *Symmetry and Spectroscopy...*, Chapter 4, pp. 245-99.



SALCs as basis functions

- ✿ Instead of AO basis functions, we can use “pre-combined” SALCs as basis functions. So, when we write the expansion

$$\psi_\mu = \sum_i c_{i\mu} \phi_i = c_{1\mu} \phi_1 + c_{2\mu} \phi_2 + c_{3\mu} \phi_3 + \dots$$

the basis, $\{\phi_1, \phi_2, \dots\}$, may be AOs or they may be SALCs. The ultimate form of the MOs won't change, but the coefficients in this expansion will depend on the basis.

Example: Express π MOs for allyl in AO and SALC bases.

Rewriting the Schrödinger Eqn.

$$\mathcal{H}\psi_\mu = E_\mu\psi_\mu$$

$$\mathcal{H}\psi_\mu - E_\mu\psi_\mu = (\mathcal{H} - E_\mu)\psi_\mu = 0$$

Now, we introduce the LCAO expansion,

$$\psi_\mu = \sum_j c_{j\mu}\phi_j = c_{1\mu}\phi_1 + c_{2\mu}\phi_2 + c_{3\mu}\phi_3 + \dots$$

So we obtain a different form of the eqn.:

$$(\mathcal{H} - E_\mu)\sum_j c_{j\mu}\phi_j = \sum_j c_{j\mu}(\mathcal{H} - E_\mu)\phi_j = 0$$

Matrix form of Schrödinger Eqn.

$$\sum_j c_{j\mu}(\mathcal{H} - E_\mu)\phi_j = 0$$

Mult. on the left by ϕ_i and integrate:

$$\sum_j c_{j\mu} \left(\int \phi_i \mathcal{H} \phi_j d\tau - E_\mu \int \phi_i \phi_j d\tau \right) = 0$$

$$H_{ij} \equiv \int \phi_i \mathcal{H} \phi_j d\tau \quad S_{ij} \equiv \int \phi_i \phi_j d\tau$$

$$\sum_j c_{j\mu} (H_{ij} - E_\mu S_{ij}) = 0$$

For a proper treatment using variational method, see for example Levine's *Quantum Chemistry* text.



Matrix Schrödinger Eqn., cont.

$$\sum_j (H_{ij} - E_\mu S_{ij}) c_{j\mu} = 0$$

in matrix form, this can be written as

$$[\mathbf{H} - E_\mu \mathbf{S}] \mathbf{c}_\mu = 0 \quad \text{or} \quad \mathbf{H} \mathbf{c}_\mu = E_\mu \mathbf{S} \mathbf{c}_\mu$$

where the matrix elements are

$$(\mathbf{H})_{ij} = H_{ij} \equiv \int \phi_i \mathcal{H} \phi_j d\tau \quad (\mathbf{S})_{ij} = S_{ij} \equiv \int \phi_i \phi_j d\tau$$



A 3 basis function example

$$(H_{11} - E_\mu) c_{1\mu} + (H_{12} - E_\mu S_{12}) c_{2\mu} + (H_{13} - E_\mu S_{13}) c_{3\mu} = 0$$

$$(H_{21} - E_\mu S_{21}) c_{1\mu} + (H_{22} - E_\mu) c_{2\mu} + (H_{23} - E_\mu S_{23}) c_{3\mu} = 0$$

$$(H_{31} - E_\mu S_{31}) c_{1\mu} + (H_{32} - E_\mu S_{32}) c_{2\mu} + (H_{33} - E_\mu) c_{3\mu} = 0$$

$$\begin{bmatrix} H_{11} - E_\mu & H_{12} - E_\mu S_{12} & H_{13} - E_\mu S_{13} \\ H_{21} - E_\mu S_{21} & H_{22} - E_\mu & H_{23} - E_\mu S_{23} \\ H_{31} - E_\mu S_{31} & H_{32} - E_\mu S_{32} & H_{33} - E_\mu \end{bmatrix} \begin{bmatrix} c_{1\mu} \\ c_{2\mu} \\ c_{3\mu} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

❖ This is called the *Secular Equation*.

SALCs as the Expansion Basis

Previously, we introduced the LCAO expansion,

$$\psi_\mu = \sum_j c_{j\mu} \phi_j = c_{1\mu} \phi_1 + c_{2\mu} \phi_2 + c_{3\mu} \phi_3 + \dots$$

If the functions $\{\phi_j\}$ are "precombined" SALCs, then the basis functions belong to irred. reps. We can use what we know about zero - value integrals

$$H_{ij} \equiv \int \phi_i \mathcal{H} \phi_j d\tau \neq 0 \text{ and } S_{ij} \equiv \int \phi_i \phi_j d\tau \neq 0$$

if $\Gamma_i \otimes \Gamma_j$ contains the totally symmetric representation.

$\therefore \phi_i$ and ϕ_j must belong to the same IR.

The Matrix Equation when the "basis" is the set of MOs

If we choose the MOs as basis functions to begin with, the equation simplifies drastically:

$$H_{ij} = E_i \delta_{ij} \text{ for all } i \text{ and } S_{ij} = \delta_{ij}$$

$$\begin{bmatrix} E_1 - E_\mu & 0 & \dots & 0 \\ 0 & E_2 - E_\mu & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & E_m - E_\mu \end{bmatrix} \begin{bmatrix} c_{1\mu} \\ c_{2\mu} \\ \vdots \\ c_{m\mu} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

When $E_\mu =$ one of the E_i , the matrix is singular

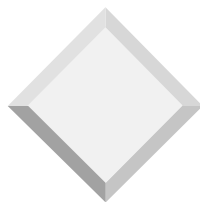
What's the use of Group Theory?

- Using SALCs as a basis simplifies the Secular Eqn. For example, when SALCs are used as the basis functions, the secular equation for H₂O becomes:

$$\begin{bmatrix}
 H_{11} - E_{\mu} & H_{12} - E_{\mu}S_{12} & H_{13} - E_{\mu}S_{13} & 0 & 0 & 0 \\
 H_{21} - E_{\mu}S_{21} & H_{22} - E_{\mu} & H_{23} - E_{\mu}S_{23} & 0 & 0 & 0 \\
 H_{31} - E_{\mu}S_{31} & H_{65} - E_{\mu}S_{65} & H_{33} - E_{\mu} & 0 & 0 & 0 \\
 0 & 0 & 0 & H_{44} - E_{\mu} & 0 & 0 \\
 0 & 0 & 0 & 0 & H_{55} - E_{\mu} & H_{56} - E_{\mu}S_{56} \\
 0 & 0 & 0 & 0 & H_{65} - E_{\mu}S_{65} & H_{66} - E_{\mu}
 \end{bmatrix}
 \begin{bmatrix}
 c_{1\mu} \\
 c_{2\mu} \\
 c_{3\mu} \\
 c_{4\mu} \\
 c_{5\mu} \\
 c_{6\mu}
 \end{bmatrix}
 =
 \begin{bmatrix}
 0 \\
 0 \\
 0 \\
 0 \\
 0 \\
 0
 \end{bmatrix}$$

Example, Usefulness of SALCs

- In the pictorial construction of the MOs of water given earlier, how many H_{ij} 's would have been zero if we had used AOs (on the O atom and both H atoms) for the basis functions?
 - How many are nonzero with the SALCs that were used?
- (Note: H_{ij} 's involving two AOs centered on the same atom are automatically zero)

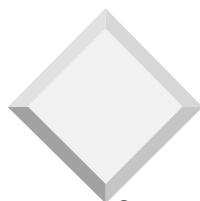


Another Example

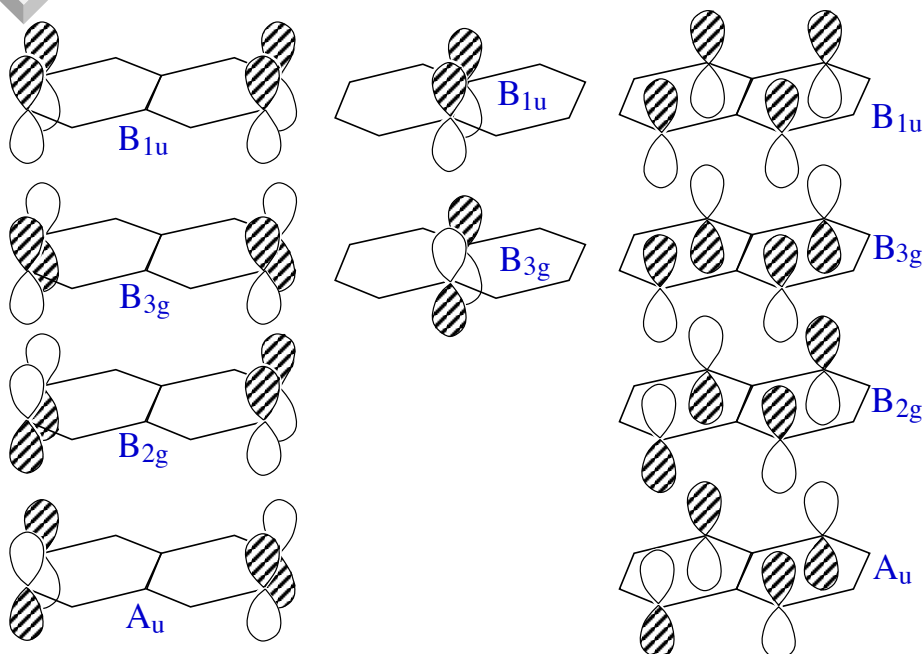
- ✿ In problem 6.1, we constructed SALCs for the π orbitals of naphthalene. The IRs spanned by the $p\pi$ orbitals were

$$B_{1u} (\times 3), B_{3g} (\times 3), B_{2g} (\times 2), A_u (\times 2)$$

- ✿ If we used the $p\pi$ orbitals as our AO basis in the secular eqn., we would have had one 10×10 matrix eqn. Using SALCs, we have two 3×3 's (for B_{1u} and B_{3g}) and two 2×2 's (for B_{2g} and A_u).



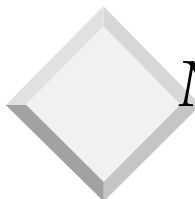
Naphthalene π -Orbital SALCs



The Crudest Approximation:

❖ In the *Hückel approximation* (applied to π systems where all the atoms are of the same type) the following substitutions are made (in this case the basis functions are understood to be AOs, not SALCs):

- $H_{ii} = \alpha$ (can choose = 0, if all atoms carbon)
- $H_{ij} = \beta$ if i and j are neighbors
- $H_{ij} = 0$ otherwise
- $S_{ii} = 1$ (normalization) and $S_{ij} = 0$



Neglect of Overlap: Consequences

A general 2×2 secular determinant is

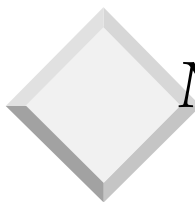
$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{vmatrix} = 0$$

expanding the determinant gives

$$E^2 - \left[\frac{H_{11} + H_{22} - 2H_{12}S_{12}}{1 - S_{12}^2} \right] E + \left[\frac{H_{11}H_{22} - H_{12}^2}{1 - S_{12}^2} \right] = 0$$

solutions are of the form: $E_{\pm} = \frac{b \pm \sqrt{D}}{2(1 - S_{12}^2)}$;

$$b = H_{11} + H_{22} - 2H_{12}S_{12}; \quad D = b^2 - 4(1 - S_{12}^2)(H_{11}H_{22} - H_{12}^2)$$



Neglect of Overlap: Consequences

A 2×2 secular determinant w/o overlap is

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

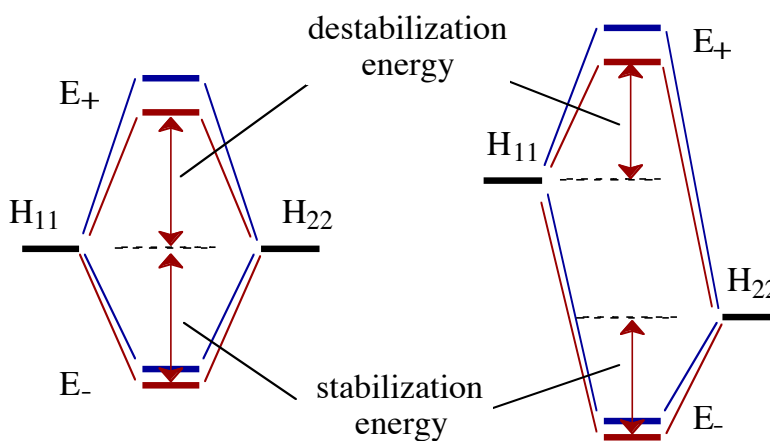
expanding the determinant gives

$$E^2 - [H_{11} + H_{22}]E + [H_{11}H_{22} - H_{12}^2] = 0$$

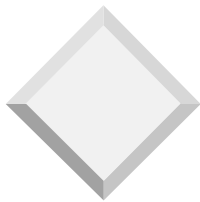
solutions are of the form: $E_{\pm} = \frac{b \pm \sqrt{D}}{2}$;

$$b = H_{11} + H_{22}; \quad D = (H_{11} - H_{22})^2 + 4H_{12}^2$$

Neglect of Overlap: Consequences

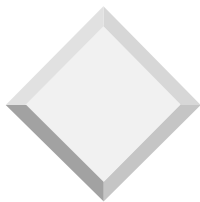


Neglect of Overlap	destabilization energy	=	stabilization energy
Overlap Included	destabilization energy	>	stabilization energy

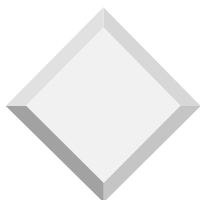


Examples

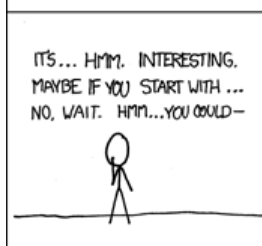
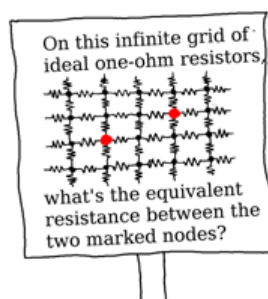
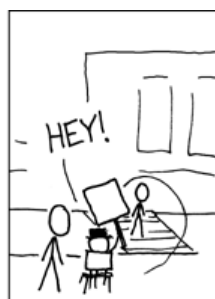
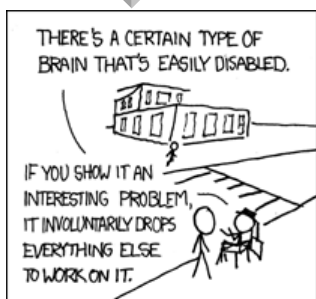
- ✿ Trivial example: ethylene π orbitals
- ✿ Cyclopropenium ion
- ✿ benzene
 - Hückel π bond-order
 - resonance energy
- ✿ other C_N symmetry systems
- ✿ ~~T_N -symmetry systems~~



D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1		
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	(R_x, R_y)	(xz, yz)
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0		
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	z	
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1		
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1	(x, y)	
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0		
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		



Nerd Sniping



“Fixing” Accidental Degeneracies

Editing tools: Show Data Table Verbose On-the-fly

Buttons: Add, Change, Erase, Clear, Minimize, Move, Rotate

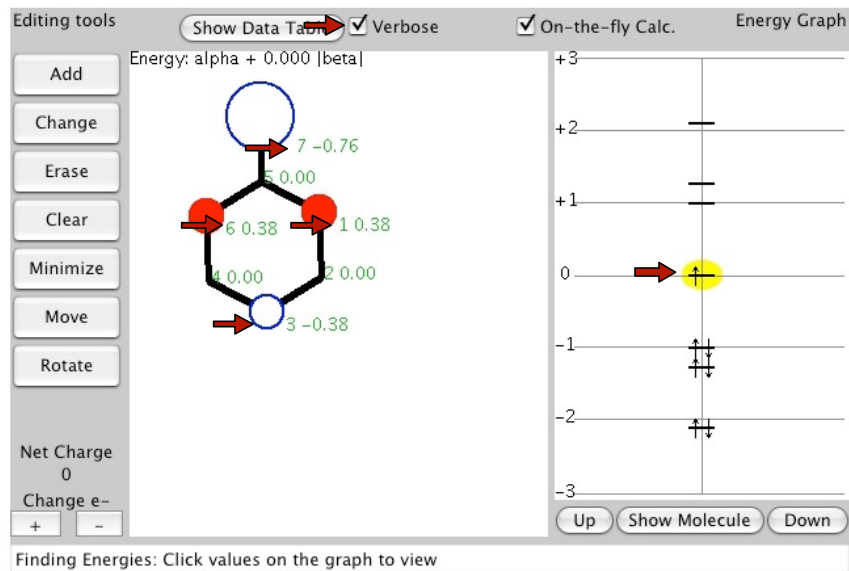
Net Charge: 0

Dialog 1: B, C, N2, N3, O1, O2, F, X, Si, P2, P3, S1, S2, Cl. hx val: 1.0E-4. Changing from C

Dialog 2: B, C, N2, N3, O1, O2, F, X, Si, P2, P3, S1, S2, Cl. hx val: 1.0E-4. Changing from C

Use “Change” button, then click the atoms shown, then type in 0.0001 for the “alpha” value, then click Ok!

Spin Density for Benzyl Radical



Turn on “Verbose” option, then read coefficients!