

1.6: LCAO and Hückel Theory 1 (Eigenfunctions)

A common approximation employed in the construction of molecular orbitals (MOs) is the **linear combination of atomic orbitals (LCAOs)**. In the LCAO method, the k^{th} molecular orbital, ψ_k , is expanded in an atomic orbital basis,

$$|\psi_k\rangle = c_a\phi_a + c_b\phi_b + \dots + c_i\phi_i \quad (1.6.1)$$

where the ϕ_i s are normalized atomic wavefunctions and . Solving Schrödinger's equation and substituting for ψ_k yields,

$$\begin{aligned} H\psi_k &= E\psi_k \\ |H - E|\psi_k\rangle &= 0 \end{aligned}$$

Substitute Equation 1.6.1

$$|H - E|c_a\phi_a + c_b\phi_b + \dots + c_i\phi\rangle = 0 \quad (1.6.2)$$

Left-multiplying by each ϕ_i yields a set of i linear homogeneous equations,

$$\begin{aligned} c_a \langle \phi_a | H - E | \phi_a \rangle + c_b \langle \phi_a | H - E | \phi_b \rangle + \dots + c_i \langle \phi_a | H - E | \phi_i \rangle &= 0 \\ c_a \langle \phi_b | H - E | \phi_a \rangle + c_b \langle \phi_b | H - E | \phi_b \rangle + \dots + c_i \langle \phi_b | H - E | \phi_i \rangle &= 0 \\ &\vdots \\ c_a \langle \phi_i | H - E | \phi_a \rangle + c_b \langle \phi_i | H - E | \phi_b \rangle + \dots + c_i \langle \phi_i | H - E | \phi_i \rangle &= 0 \end{aligned}$$

Solving the secular determinant,

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} & \dots & \dots & H_{ai} - ES_{ai} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} & \dots & \dots & H_{bi} - ES_{bi} \\ \vdots & & \ddots & & \vdots \\ \vdots & & & \ddots & \vdots \\ H_{ia} - ES_{ia} & H_{ib} - ES_{ib} & \dots & \dots & H_{ii} - ES_{ii} \end{vmatrix} = 0$$

where $H_{ij} = \int \phi_i H \phi_j d\tau$; $S_{ii} = \int \phi_i \phi_i d\tau = 1$; $H_{ij} = \int \phi_i H \phi_j d\tau$; $S_{ij} = \int \phi_i \phi_j d\tau$

In the Hückel approximation,

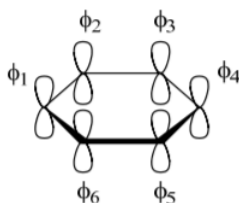
- $H_{ii} = \alpha$
- $H_{ij} = 0$ for ϕ_i not adjacent to ϕ_j
- $H_{ij} = \beta$ for ϕ_i not adjacent to ϕ_j
- $S_{ij} = 1$
- $S_{ij} = 0$

The foregoing approximation is the simplest. Different computational methods treat these integrals differently. Extended Hückel Theory (EHT) includes all valence orbitals in the basis (as opposed to the highest energy atomic orbitals), all S_{ij} s are calculated, the H_{ii} s are estimated from spectroscopic data (as opposed to a constant, α) and H_{ij} s are estimated from a simple function of S_{ij} , H_{ii} and H_{ij} (zero differential overlap approximation).

The EHT (and other Hückel methods) are termed **semi-empirical** because they rely on experimental data for quantification of parameters. Other semi-empirical methods include CNDO, MINDO, INDO, etc. in which more care is taken in evaluating H_{ij} (these methods are based on self-consistent field procedures). Still higher level computational methods calculate the pertinent energies from first principles – *ab initio* and DFT. Here core potentials must be included and high order basis sets are used for the valence orbitals.

Benzene

As an example of the Hückel method, we will examine the frontier orbitals (i.e. determine eigenfunctions) and their associated orbital energies (i.e. eigenvalues) of benzene. The highest energy atomic orbitals of benzene are the C $p\pi$ orbitals. Hence, it is reasonable to begin the analysis by assuming that the frontier MO's will be composed of LCAO of the C $2p\pi$ orbitals:



The matrix representations for this orbital basis in D_{6h} is,

$$\begin{aligned}
 E \cdot \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} &= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} = \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} & x_{\text{trace}} = 6 \\
 C_6 \cdot \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} &= \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} = \begin{bmatrix} \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \\ \phi_1 \end{bmatrix} & x_{\text{trace}} = 0 \\
 C_2' \cdot \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} &= \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{bmatrix} = \begin{bmatrix} \bar{\phi}_1 \\ \bar{\phi}_6 \\ \bar{\phi}_5 \\ \bar{\phi}_4 \\ \bar{\phi}_3 \\ \bar{\phi}_2 \end{bmatrix} & x_{\text{trace}} = -2
 \end{aligned}$$

The only orbitals that contribute to the trace are those that transform into +1 or -1 themselves (i.e. in phase or with opposite phase, respectively). Thus the trace of the remaining characters of the $p\pi$ basis may be determined by inspection:

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_v$	$3\sigma_d$
$\Gamma_{p\pi}$	6	0	0	0	-2	0	0	0	0	-6	2	0

(1.6.3)

The $\Gamma_{p\pi}$ representation is a reducible basis that must be decomposed into irreducible representations.

Decomposition of reducible representations may be accomplished with the following relation:

$$a_i = \frac{1}{h} \sum_R \left(\text{character of } \Gamma_{\text{red}} \text{ under operation } R \cdot \text{character of } \Gamma_{\text{irr}} \text{ under operation } R \cdot \text{no. of members in the class} \right)$$

the number of times Γ_{irr} contributes to Γ_{red} \rightarrow a_i \leftarrow order

Returning to the above example,

$$a_{A_{1g}} = \frac{1}{24} [6 \cdot 1 \cdot 1 + 0 \cdot 0 \cdot 0 + (-2)(1)(3) + 0 + 0 + 0 + 0 + (-6)(1)(1) + 2 \cdot 1 \cdot 3 + 0] = 0$$

thus A_{1g} does not contribute to $\Gamma_{p\pi}$

How about $a_{A_{2u}}$?

$$a_{A_{2u}} = \frac{1}{24} [6 \cdot 1 \cdot 1 + 0 \cdot 0 \cdot 0 + (-2)(-1)(3) + 0 + 0 + 0 + 0 + (-6)(1)(-1) + 2 \cdot 1 \cdot 3 + 0] = 1$$

Continuing the procedure, one finds,

$$\Gamma_{p\pi} = A_{2u} + B_{2g} + E_{1g} + E_{2u} \quad (1.6.4)$$

these are the symmetries of the MO's formed by the LCAO of $p\pi$ orbitals in benzene.

With symmetries established, LCAOs may be constructed by "projecting out" the appropriate linear combination. A projection operator, $P^{(i)}$, allows the linear combination of the i^{th} irreducible representation to be determined,

$$P^{(i)} = \frac{\text{dimension of } \Gamma_i}{h} \sum_R \left[\chi^{(i)}(R) \right] \bullet R$$

dimension of Γ_i
operator
order
character of Γ_i under operator R

A drawback of projecting out of the D_{6h} point group is the large number of operators. The problem can be simplified by dropping to the pure rotational subgroup, C_6 . In this point group, the full extent of mixing among ϕ_1 through ϕ_6 is maintained; however the inversion center, and hence u and g symmetry labels are lost. Thus in the final analysis, the Γ_i s in C_6 will have to be correlated to those in D_{6h} . Reformulating in C_6 ,

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5
$\Gamma_{p\pi}$	6	0	0	0	0	0

$$\Gamma_{p\pi} = A + B + E_1 + E_2$$

\downarrow
 A_{2u}

\downarrow
 B_{2g}

\downarrow
 E_{1g}

\downarrow
 E_{2u}

in D_{6h}

The projection of the SALC that from ϕ_1 transforms as A is,

$$P^{(A)}\phi_1 = \frac{1}{6} \left[1 \cdot E \cdot \phi_1 + 1 \cdot C_6 \cdot \phi_1 + 1 \cdot C_6^2 \cdot \phi_1 + 1 \cdot C_6^3 \cdot \phi_1 + 1 \cdot C_6^4 \cdot \phi_1 + 1 \cdot C_6^5 \cdot \phi_1 \right]$$

$$\equiv \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$$

drop constant since LCAO will be normalized

Continuing,

- $P^{(B)}\phi_1 = \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6$
- $P^{(E_{1a})}\phi_1 = \phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6$
- $P^{(E_{1b})}\phi_1 = \phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6$
- $P^{(E_{2a})}\phi_1 = \phi_1 - \varepsilon^*\phi_2 - \varepsilon\phi_3 + \phi_4 - \varepsilon^*\phi_5 - \varepsilon\phi_6$
- $P^{(E_{2b})}\phi_1 = \phi_1 - \varepsilon\phi_2 - \varepsilon^*\phi_3 + \phi_4 - \varepsilon\phi_5 - \varepsilon^*\phi_6$

The projections contain imaginary components; the real component of the linear combination may be realized by taking \pm linear combinations:

For $\psi(E_{1a})$ SALC's:

$$\psi'_3(E_{1a}) + \psi'_4(E_{1b}) = 2\phi_1 + (\varepsilon + \varepsilon^*)\phi_2 - (\varepsilon + \varepsilon^*)\phi_3 - 2\phi_4 - (\varepsilon + \varepsilon^*)\phi_5 + (\varepsilon + \varepsilon^*)\phi_6$$

$$\psi'_3(E_{1a}) - \psi'_4(E_{1b}) = (\varepsilon - \varepsilon^*)\phi_2 + (\varepsilon - \varepsilon^*)\phi_3 + (\varepsilon^* - \varepsilon)\phi_5 + (\varepsilon^* - \varepsilon)\phi_6$$

where in the C_6 point group,

$$\varepsilon = \exp\left(\frac{2\pi}{6}\right)i = \cos \frac{2\pi}{6} - i \sin \frac{2\pi}{6}$$

$$\therefore \varepsilon + \varepsilon^* = \cos \frac{2\pi}{6} - i \sin \frac{2\pi}{6} + \cos \frac{2\pi}{6} + i \sin \frac{2\pi}{6} = 2 \cos \frac{2\pi}{6} = 1$$

$$\varepsilon^* - \varepsilon = -\cos \frac{2\pi}{6} + i \sin \frac{2\pi}{6} - \cos \frac{2\pi}{6} + i \sin \frac{2\pi}{6} = 2i \sin \frac{2\pi}{6} = i\sqrt{3}$$

$$\varepsilon - \varepsilon^* = \cos \frac{2\pi}{6} - i \sin \frac{2\pi}{6} - \left(\cos \frac{2\pi}{6} + i \sin \frac{2\pi}{6}\right) = -2i \sin \frac{2\pi}{6} = -i\sqrt{3}$$

\therefore the E_{1a} LCAO's reduce to (again ignoring the constant prefactor),

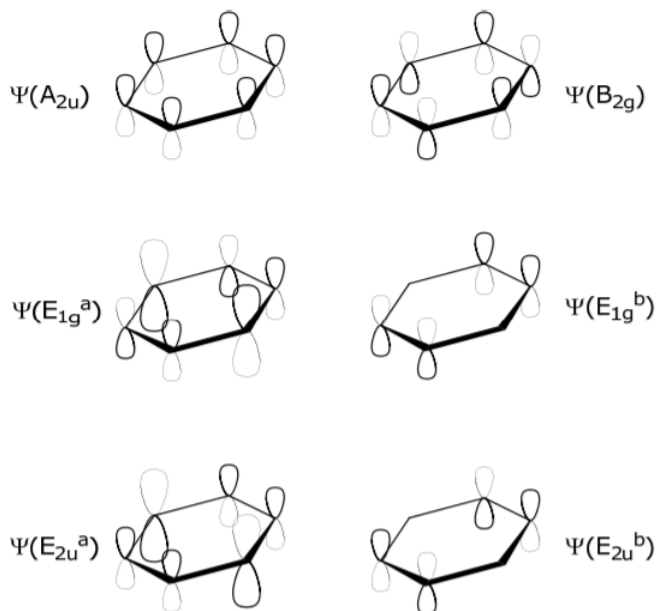
$$\psi_3(E_1) = \psi'_3(E_{1a}) + \psi'_4(E_{1b}) = 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6$$

$$\psi_4(E_1) = \psi'_3(E_{1a}) - \psi'_4(E_{1b}) = \phi_2 + \phi_3 - \phi_5 - \phi_6$$

Similarly for the $\psi_5(E_2)$ and $\psi_6(E_2)$ LCAO's... normalizing the SALC's

$$\begin{aligned}\psi_1(A) &= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) & \psi_2(B) &= \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 + \phi_6) \\ \psi_3(E_1) &= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) & \psi_4(E_1) &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6) \\ \psi_5(E_2) &= \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) & \psi_6(E_2) &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)\end{aligned}$$

The pictorial representation of the SALC's are,



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