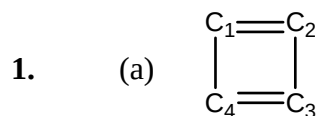
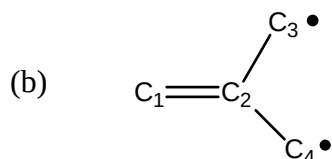


Chapter 10
Semiempirical Methods and Applications of Symmetry
Homework Solutions

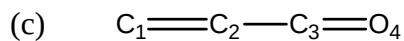
PART A: The Hückel Model and other Semiempirical Methods



$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0 \rightarrow \begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$



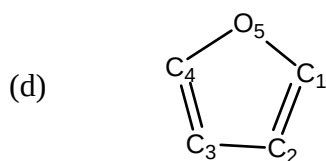
$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & \beta \\ 0 & \beta & \alpha - E & 0 \\ 0 & \beta & 0 & \alpha - E \end{vmatrix} = 0 \rightarrow \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 1 \\ 0 & 1 & x & 0 \\ 0 & 1 & 0 & x \end{vmatrix} = 0$$



$$\alpha_{=O} = \alpha + 1.0\beta = \alpha + \beta \quad \beta_{C=O} = 1.0\beta = \beta$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta_{C=O} \\ 0 & 0 & \beta_{C=O} & \alpha_{=O} - E \end{vmatrix} = 0 \rightarrow \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha + \beta - E \end{vmatrix} = 0$$

$$\rightarrow \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x+1 \end{vmatrix} = 0$$



$$\alpha_{-O-} = \alpha + 2.0\beta = \alpha + 2\beta \quad \beta_{C-O} = 0.8\beta$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & \beta_{C-O} \\ \beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & \beta_{C-O} \\ \beta_{C-O} & 0 & 0 & \beta_{C-O} & \alpha_{-O-} - E \end{vmatrix} = 0 \rightarrow$$

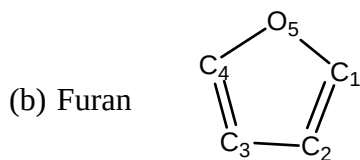
$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0.8\beta \\ \beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & 0.8\beta \\ 0.8\beta & 0 & 0 & 0.8\beta & \alpha + 2\beta - E \end{vmatrix} = 0 \rightarrow$$

$$\begin{vmatrix} x & 1 & 0 & 0 & 0.8 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 0.8 \\ 0.8 & 0 & 0 & 0.8 & x + 2 \end{vmatrix} = 0$$

2. (a) Acrolein: $C_1 = C_2 - C_3 = O_4$

Contributes 1 electron

Oxygen has 6 valence electrons. 1 electron is involved in the σ bond to carbon, 4 more electrons are used in 2 oxygen lone-pairs, leaving 1 electron which contributes to the π system.

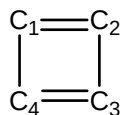


Contributes 2 electrons

Oxygen has 6 valence electrons. 2 electrons are involved in σ bonds to carbon, 2 more electrons are used in an oxygen lone-pair, leaving 2 electrons which contribute to the π system.

3.

Cyclobutadiene:



(a) Energies

$x^4 - 4x^2 = 0$ factors into: $x \cdot x \cdot (x^2 - 4) = 0$, with solutions: $x = +2, 0, 0, -2$

Below, I number the values in order of increasing energy (remembering that $\beta < 0$)

$$x_1 = -2 = \frac{\alpha - E_1}{\beta} \rightarrow E_1 = \alpha + 2\beta$$

$$x_2 = 0 = \frac{\alpha - E_2}{\beta} \rightarrow E_2 = \alpha$$

$$x_3 = 0 = \frac{\alpha - E_3}{\beta} \rightarrow E_3 = \alpha$$

$$x_4 = +2 = \frac{\alpha - E_4}{\beta} \rightarrow E_4 = \alpha - 2\beta$$

(b) Normalized Molecular Orbitals

$$(1) \phi_1 = c_1(\chi_1 + \chi_2 + \chi_3 + \chi_4)$$

$$\begin{aligned} \langle \phi_1 | \phi_1 \rangle &= 1 = \langle c_1(\chi_1 + \chi_2 + \chi_3 + \chi_4) | c_1(\chi_1 + \chi_2 + \chi_3 + \chi_4) \rangle \\ &= c_1^2 \left[(1)^2 + (1)^2 + (1)^2 + (1)^2 \right] = 4c_1^2 \end{aligned}$$

$$\text{Therefore: } c_1 = \frac{1}{\sqrt{4}} = \frac{1}{2} \text{ and } \phi_1 = \frac{1}{2}(\chi_1 + \chi_2 + \chi_3 + \chi_4)$$

In the above calculation, we have assumed that the atomic orbitals are orthonormal.

$$\text{i.e. } \langle \chi_i | \chi_j \rangle = \delta_{ij}$$

$$(2) \phi_2 = c_1(\chi_1 - \chi_3)$$

$$\begin{aligned} \langle \phi_2 | \phi_2 \rangle &= 1 = \langle c_1(\chi_1 - \chi_3) | c_1(\chi_1 - \chi_3) \rangle \\ &= c_1^2 \left[(1)^2 + (-1)^2 \right] = 2c_1^2 \end{aligned}$$

$$\text{Therefore: } c_1 = \frac{1}{\sqrt{2}} \text{ and } \phi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3)$$

$$(3) \phi_2 = c_2(\chi_2 - \chi_4)$$

$$\begin{aligned}\langle \phi_3 | \phi_3 \rangle &= 1 = \langle c_2(\chi_2 - \chi_4) | c_2(\chi_2 - \chi_4) \rangle \\ &= c_2^2 [(1)^2 + (-1)^2] = 2c_2^2\end{aligned}$$

$$\text{Therefore: } c_2 = \frac{1}{\sqrt{2}} \text{ and } \phi_3 = \frac{1}{\sqrt{2}}(\chi_2 - \chi_4)$$

$$(4) \phi_4 = c_1(\chi_1 - \chi_2 + \chi_3 - \chi_4)$$

$$\begin{aligned}\langle \phi_4 | \phi_4 \rangle &= 1 = \langle c_1(\chi_1 - \chi_2 + \chi_3 - \chi_4) | c_1(\chi_1 - \chi_2 + \chi_3 - \chi_4) \rangle \\ &= c_1^2 [(1)^2 + (-1)^2 + (1)^2 + (-1)^2] = 4c_1^2\end{aligned}$$

$$\text{Therefore: } c_1 = \frac{1}{\sqrt{4}} = \frac{1}{2} \text{ and } \phi_4 = \frac{1}{2}(\chi_1 - \chi_2 + \chi_3 - \chi_4)$$

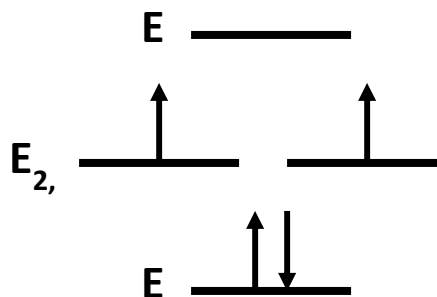
Summary:

$$\phi_1 = \frac{1}{2}(\chi_1 + \chi_2 + \chi_3 + \chi_4) \quad E_1 = \alpha + 2\beta$$

$$\phi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad E_2 = \alpha$$

$$\phi_3 = \frac{1}{\sqrt{2}}(\chi_2 - \chi_4) \quad E_3 = \alpha$$

$$\phi_4 = \frac{1}{2}(\chi_1 - \chi_2 + \chi_3 - \chi_4) \quad E_4 = \alpha - 2\beta$$



(c) π Energy and Delocalization Energy

$$E_\pi = 2E_1 + 2E_{2,3} = 2(\alpha + 2\beta) + 2\alpha = 4\alpha + 4\beta$$

The localized energy is simply twice the energy of a C_2H_4 molecule: $E_{C_2H_4} = 2(\alpha + \beta)$

$$E_{Loc} = 2[2(\alpha + \beta)] = 4\alpha + 4\beta$$

$$E_{Deloc} = E_\pi - E_{Loc} = 0$$

(d) π Electron Charge

$$q_1 = \sum_i^{Occ\ Orbs} n_i c_{i1}^2 = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{\sqrt{2}}\right)^2 + 1(0)^2 = 1.0$$

$$q_2 = \sum_i^{Occ\ Orbs} n_i c_{i2}^2 = 2\left(\frac{1}{2}\right)^2 + 1(0)^2 + 1\left(\frac{1}{\sqrt{2}}\right)^2 = 1.0$$

$$q_3 = \sum_i^{Occ\ Orbs} n_i c_{i3}^2 = 2\left(\frac{1}{2}\right)^2 + 1\left(-\frac{1}{\sqrt{2}}\right)^2 + 1(0)^2 = 1.0$$

$$q_4 = \sum_i^{Occ\ Orbs} n_i c_{i4}^2 = 2\left(\frac{1}{2}\right)^2 + 1(0)^2 + \left(-\frac{1}{\sqrt{2}}\right)^2 = 1.0$$

(e) π Bond Order

$$p_{12} = \sum_i^{Occ\ Orbs} n_i c_{i1} c_{i2} = 2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) + 1\left(\frac{1}{\sqrt{2}}\right)(0) + 1(0)\left(\frac{1}{\sqrt{2}}\right) = \frac{1}{2}$$

$$p_{23} = \sum_i^{Occ\ Orbs} n_i c_{i2} c_{i3} = 2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) + 1(0)\left(-\frac{1}{\sqrt{2}}\right) + 1\left(\frac{1}{\sqrt{2}}\right)(0) = \frac{1}{2}$$

$$p_{34} = \sum_i^{Occ\ Orbs} n_i c_{i3} c_{i4} = 2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) + 1\left(-\frac{1}{\sqrt{2}}\right)(0) + 1(0)\left(-\frac{1}{\sqrt{2}}\right) = \frac{1}{2}$$

$$p_{41} = \sum_i^{Occ\ Orbs} n_i c_{i3} c_{i4} = 2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) + 1(0)\left(\frac{1}{\sqrt{2}}\right) + 1\left(-\frac{1}{\sqrt{2}}\right)(0) = \frac{1}{2}$$

4. Solutions to all parts are given in the PowerPoint Presentation

(a) Secular Determinant: Slide 27

(b) Energy Levels: Slide 29

(c) MO Normalized Coefficients: ϕ_1 on Slides 31-32

The other 3 MO's are obtained by the identical procedure, and are tabulated on Slide 33

(d) π Energy and Delocalization Energy: Slide 30

(e) π Electron Charge: Slide 34

(f) π Bond Order: Slide 35

5. See MO coefficients (from Slide 33)

$$\phi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$

$$\phi_2 = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4$$

$$\phi_3 = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4$$

$$\phi_4 = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4$$

(a) π Electron Charge

$$q_1 = \sum_i^{Occ\ Orbs} n_i c_{i1}^2 = 2(0.372)^2 + 1(0.602)^2 + 1(0.602)^2 = 1.0$$

$$q_2 = \sum_i^{Occ\ Orbs} n_i c_{i2}^2 = 2(0.602)^2 + 1(0.372)^2 + 1(-0.372)^2 = 1.0$$

$$q_3 = \sum_i^{Occ\ Orbs} n_i c_{i3}^2 = 2(0.602)^2 + 1(-0.372)^2 + 1(-0.372)^2 = 1.0$$

$$q_4 = \sum_i^{Occ\ Orbs} n_i c_{i4}^2 = 2(.372)^2 + 1(-0.602)^2 + 1(-0.602)^2 = 1.0$$

(b) π Bond Order

$$p_{12} = \sum_i^{Occ\ Orbs} n_i c_{i1} c_{i2} = 2(0.372)(0.602) + 1(0.602)(0.372) + 1(0.602)(-0.372) = 0.45$$

versus $p_{12} = 0.90$ for the ground state

$$p_{23} = \sum_i^{Occ\ Orbs} n_i c_{i2} c_{i3} = 2(0.602)(0.602) + 1(0.372)(-0.372) + 1(-0.372)(-0.372) = 0.72$$

versus $p_{23} = 0.45$ for the ground state

$$p_{34} = \sum_i^{Occ\ Orbs} n_i c_{i3} c_{i4} = 2(0.602)(0.372) + 1(-0.372)(-0.602) + 1(-0.372)(0.602) = 0.45$$

versus $p_{34} = 0.90$ for the ground state

Notes: The 1-2 and 3-4 bonds are weakened in the excited state.

This is because the positive overlap between these atoms in ϕ_2 is replaced by negative overlap in ϕ_3 .

The 3-4 bond is strengthened in the excited state.

This is because the negative overlap between these atoms in ϕ_2 is replaced by positive overlap in ϕ_3 .

6. Methylenecyclopropene

(a) $\Gamma(\Psi_0) = A_1$ (all spins paired) $\Gamma(\Psi_i) = b_2 \times b_2 = A_1$

$$\Gamma(M_{oi}^x) = A_1 \times B_1 \times A_1 = B_1 \neq A_1$$

$$\Gamma(M_{oi}^y) = A_1 \times B_2 \times A_1 = B_2 \neq A_1$$

$$\Gamma(M_{oi}^z) = A_1 \times A_1 \times A_1 = A_1$$

Therefore, this **IS** an allowed transition and polarized **parallel** to the principal axis.

(b) $\Gamma(\Psi_0) = A_1$ (all spins paired) $\Gamma(\Psi_i) = b_2 \times a_2 = B_1$

$$\Gamma(M_{oi}^x) = A_1 \times B_1 \times B_1 = A_1$$

$$\Gamma(M_{oi}^y) = A_1 \times B_2 \times B_1 = A_2 \neq A_1$$

$$\Gamma(M_{oi}^z) = A_1 \times A_1 \times B_1 = B_1 \neq A_1$$

Therefore, this **IS** an allowed transition and polarized **perpendicular** to the principal axis (along y axis).

7. Methylenecyclopropene Cation

(a) $\Gamma(\Psi_0) = B_2$ (ignore paired spins) $\Gamma(\Psi_i) = A_2$ (ignore paired spins)

$$\Gamma(M_{oi}^x) = B_2 \times B_1 \times A_2 = A_1$$

$$\Gamma(M_{oi}^y) = B_2 \times B_2 \times A_2 = A_2 \neq A_1$$

$$\Gamma(M_{oi}^z) = B_2 \times A_1 \times A_2 = B_1 \neq A_1$$

Therefore, this **IS** an allowed transition and polarized **perpendicular** to the principal axis (along x axis).

(b) $\Gamma(\Psi_0) = B_2$ (ignore paired spins) $\Gamma(\Psi_i) = B_2$ (ignore paired spins)

$$\Gamma(M_{oi}^x) = B_2 \times B_1 \times B_2 = B_1 \neq A_1$$

$$\Gamma(M_{oi}^y) = B_2 \times B_2 \times B_2 = B_2 \neq A_1$$

$$\Gamma(M_{oi}^z) = B_2 \times A_1 \times B_2 = A_1$$

Therefore, this **IS** an allowed transition and polarized **parallel** to the principal axis.

8. Trans Butadiene treated with Symmetry Adapted MO's.

(a) Determination of the SALCs.

$$S_j = N_j \sum_R Tr_j(R) \cdot R(\chi_i). \quad N_j \text{ is the normalization constant.}$$

B_g SALCs

$$\begin{aligned} S_1(B_g) &= N_1 [1 \cdot E(\chi_1) + (-1) \cdot C_2(\chi_1) + (1) \cdot i(\chi_1) + (-1) \cdot \sigma_h(\chi_1)] \\ &= N_1 [\chi_1 + (-1) \cdot \chi_4 + (1) \cdot (-\chi_4) + (-1) \cdot (-\chi_1)] = N_1' (\chi_1 - \chi_4) \\ &= \frac{1}{\sqrt{2}} (\chi_1 - \chi_4) \end{aligned}$$

$$\begin{aligned} S_2(B_g) &= N_2 [1 \cdot E(\chi_2) + (-1) \cdot C_2(\chi_2) + (1) \cdot i(\chi_2) + (-1) \cdot \sigma_h(\chi_2)] \\ &= N_1 [\chi_2 + (-1) \cdot \chi_3 + (1) \cdot (-\chi_3) + (-1) \cdot (-\chi_2)] = N_1' (\chi_2 - \chi_3) \\ &= \frac{1}{\sqrt{2}} (\chi_2 - \chi_3) \end{aligned}$$

A_u SALCs

$$\begin{aligned} S_3(A_u) &= N_1 [1 \cdot E(\chi_1) + (+1) \cdot C_2(\chi_1) + (-1) \cdot i(\chi_1) + (-1) \cdot \sigma_h(\chi_1)] \\ &= N_1 [\chi_1 + (+1) \cdot \chi_4 + (-1) \cdot (-\chi_4) + (-1) \cdot (-\chi_1)] = N_1' (\chi_1 + \chi_4) \\ &= \frac{1}{\sqrt{2}} (\chi_1 + \chi_4) \end{aligned}$$

$$\begin{aligned} S_4(A_u) &= N_2 [1 \cdot E(\chi_2) + (+1) \cdot C_2(\chi_2) + (-1) \cdot i(\chi_2) + (-1) \cdot \sigma_h(\chi_2)] \\ &= N_1 [\chi_2 + (1) \cdot \chi_3 + (-1) \cdot (-\chi_3) + (-1) \cdot (-\chi_2)] = N_1' (\chi_2 + \chi_3) \\ &= \frac{1}{\sqrt{2}} (\chi_2 + \chi_3) \end{aligned}$$

(b) Secular Determinants.

B_g Secular Determinant

$$\begin{aligned} H_{11} &= \langle S_1 | H | S_1 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 - \chi_4) \left| H \right| \frac{1}{\sqrt{2}}(\chi_1 - \chi_4) \right\rangle \\ &= \frac{1}{2} (\langle \chi_1 | H | \chi_1 \rangle - \langle \chi_1 | H | \chi_4 \rangle - \langle \chi_4 | H | \chi_1 \rangle + \langle \chi_4 | H | \chi_4 \rangle) \\ &= \frac{1}{2} (\alpha - 0 - 0 + \alpha) = \alpha \end{aligned}$$

$$\begin{aligned} H_{22} &= \langle S_2 | H | S_2 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 - \chi_3) \left| H \right| \frac{1}{\sqrt{2}}(\chi_2 - \chi_3) \right\rangle \\ &= \frac{1}{2} (\langle \chi_2 | H | \chi_2 \rangle - \langle \chi_2 | H | \chi_3 \rangle - \langle \chi_3 | H | \chi_2 \rangle + \langle \chi_3 | H | \chi_3 \rangle) \\ &= \frac{1}{2} (\alpha - \beta - \beta + \alpha) = \alpha - \beta \end{aligned}$$

$$\begin{aligned} H_{12} &= \langle S_1 | H | S_2 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 - \chi_4) \left| H \right| \frac{1}{\sqrt{2}}(\chi_2 - \chi_3) \right\rangle \\ &= \frac{1}{2} (\langle \chi_1 | H | \chi_2 \rangle - \langle \chi_1 | H | \chi_3 \rangle - \langle \chi_4 | H | \chi_2 \rangle + \langle \chi_4 | H | \chi_3 \rangle) \\ &= \frac{1}{2} (\beta - 0 - 0 + \beta) = \beta \end{aligned}$$

$$\text{B}_g \text{ Secular Determinant: } \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = \begin{vmatrix} x & 1 \\ 1 & x - 1 \end{vmatrix} = 0$$

A_u Secular Determinant

$$\begin{aligned} H_{33} &= \langle S_3 | H | S_3 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 + \chi_4) \left| H \right| \frac{1}{\sqrt{2}}(\chi_1 + \chi_4) \right\rangle \\ &= \frac{1}{2} (\langle \chi_1 | H | \chi_1 \rangle + \langle \chi_1 | H | \chi_4 \rangle + \langle \chi_4 | H | \chi_1 \rangle + \langle \chi_4 | H | \chi_4 \rangle) \\ &= \frac{1}{2} (\alpha + 0 + 0 + \alpha) = \alpha \end{aligned}$$

$$\begin{aligned} H_{44} &= \langle S_4 | H | S_4 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 + \chi_3) \left| H \right| \frac{1}{\sqrt{2}}(\chi_2 + \chi_3) \right\rangle \\ &= \frac{1}{2} (\langle \chi_2 | H | \chi_2 \rangle + \langle \chi_2 | H | \chi_3 \rangle + \langle \chi_3 | H | \chi_2 \rangle + \langle \chi_3 | H | \chi_3 \rangle) \\ &= \frac{1}{2} (\alpha + \beta + \beta + \alpha) = \alpha + \beta \end{aligned}$$

$$\begin{aligned}
 H_{34} &= \langle S_3 | H | S_4 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 + \chi_4) \left| H \right| \frac{1}{\sqrt{2}}(\chi_2 + \chi_3) \right\rangle \\
 &= \frac{1}{2} (\langle \chi_1 | H | \chi_2 \rangle + \langle \chi_1 | H | \chi_3 \rangle + \langle \chi_4 | H | \chi_2 \rangle + \langle \chi_4 | H | \chi_3 \rangle) \\
 &= \frac{1}{2} (\beta + 0 + 0 + \beta) = \beta
 \end{aligned}$$

$$\text{A}_u \text{ Secular Determinant: } \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = \begin{vmatrix} x & 1 \\ 1 & x + 1 \end{vmatrix} = 0$$

(c) Energies and Wavefunctions.

Note: I'll be relabeling the energies and wavefunctions as a,b,c,d, corresponding to relative energies (from lowest to highest)

B_g Energies

$$\begin{vmatrix} x & 1 \\ 1 & x + 1 \end{vmatrix} = 0 \rightarrow x^2 - x - 1 = ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{1 \pm \sqrt{5}}{2}$$

$$x_b = -0.618 = \frac{\alpha - E_b}{\beta} \rightarrow E_b = \alpha + 0.618\beta$$

$$x_d = +1.618 = \frac{\alpha - E_d}{\beta} \rightarrow E_d = \alpha - 1.618\beta$$

B_g Wavefunctions

Note: I'm going to drop the coefficients on the SALCs because we'll have to renormalize them at the end, anyway.

$$S_1 = \chi_1 - \chi_4$$

$$S_2 = \chi_2 - \chi_3$$

$$\begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0 \rightarrow \begin{aligned} xc_1 + c_2 &= 0 \\ c_1 + (x-1)c_2 &= 0 \end{aligned} \quad \text{We only need to use one of these (will use first one)}$$

$$x_b = -0.618 \rightarrow -0.618c_1 + c_2 = 0 \rightarrow c_2 = +0.618c_1$$

$$\phi_b = c_1[S_1 + 0.618S_2] = c_1[(\chi_1 - \chi_4) + (0.618)(\chi_2 - \chi_3)] = c_1[\chi_1 + 0.618\chi_2 - 0.618\chi_3 - \chi_4]$$

$$c_1 = \frac{1}{\sqrt{1^2 + (0.618)^2 + (-0.618)^2 + (-1)^2}} = 0.602$$

$$\boxed{\phi_b = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4}$$

$$x_d = +1.618 \rightarrow +1.618c_1 + c_2 = 0 \rightarrow c_2 = -1.618c_1$$

$$\phi_d = c_1[S_1 - 1.618S_2] = c_1[(\chi_1 - \chi_4) + (-1.618)(\chi_2 - \chi_3)] = c_1[\chi_1 - 1.618\chi_2 + 1.618\chi_3 - \chi_4]$$

$$c_1 = \frac{1}{\sqrt{1^2 + (-1.618)^2 + (+1.618)^2 + (-1)^2}} = 0.372$$

$$\boxed{\phi_d = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4}$$

A_u Energies

$$\begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0 \rightarrow x^2 + x - 1 = ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1 \pm \sqrt{5}}{2}$$

$$x_c = +0.618 = \frac{\alpha - E_c}{\beta} \rightarrow E_c = \alpha - 0.618\beta$$

$$x_a = -1.618 = \frac{\alpha - E_d}{\beta} \rightarrow E_d = \alpha + 1.618\beta$$

A_u Wavefunctions

Note: I'm going to drop the coefficients on the SALCs because we'll have to renormalize them at the end, anyway.

$$S_3 = \chi_1 + \chi_4$$

$$S_4 = \chi_2 + \chi_3$$

$$\begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0 \rightarrow \begin{matrix} xc_1 + c_2 = 0 \\ c_1 + (x+1)c_2 = 0 \end{matrix} \quad \text{We only need to use one of the equations.}$$

$$x_c = +0.618 \rightarrow +0.618c_1 + c_2 = 0 \rightarrow c_2 = -0.618c_1$$

$$\phi_c = c_1[S_3 - 0.618S_2] = c_1[(\chi_1 + \chi_4) - (0.618)(\chi_2 + \chi_3)] = c_1[\chi_1 - 0.618\chi_2 - 0.618\chi_3 + \chi_4]$$

$$c_1 = \frac{1}{\sqrt{1^2 + (-0.618)^2 + (-0.618)^2 + (-1)^2}} = 0.602$$

$$\boxed{\phi_c = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4}$$

$$x_a = -1.618 \rightarrow -1.618c_1 + c_2 = 0 \rightarrow c_2 = +1.618c_1$$

$$\phi_a = c_1[S_1 + 1.618S_2] = c_1[(\chi_1 - \chi_4) + (+1.618)(\chi_2 - \chi_3)] = c_1[\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4]$$

$$c_1 = \frac{1}{\sqrt{1^2 + (+1.618)^2 + (+1.618)^2 + 1^2}} = 0.372$$

$$\boxed{\phi_a = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4}$$

Energy/Wavefunction Summary

$$\phi_a = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4 \quad E_a = \alpha + 1.618\beta$$

$$\phi_b = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4 \quad E_b = \alpha + 0.618\beta$$

$$\phi_c = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4 \quad E_c = \alpha - 0.618\beta$$

$$\phi_d = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4 \quad E_d = \alpha - 1.618\beta$$