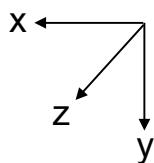
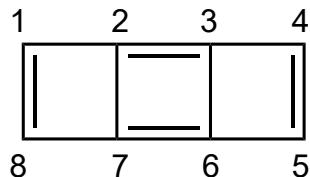


*Chemistry 6330*  
*Problem Set 4 Answers*

(1)



There are 2 sets of p- $\pi$  orbitals in this molecule that are exchanged by operations of the D<sub>2h</sub> point group (1, 4, 5, 8) and (2, 3, 6, 7).

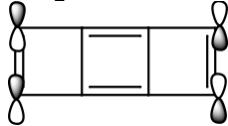
D <sub>2h</sub>	E	C <sub>2</sub> (z)	C <sub>2</sub> (y)	C <sub>2</sub> (x)	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma_{(1,4,5,8)}$	4	0	0	0	0	-4	0	0	$\Rightarrow B_{2g} + B_{3g} + A_u + B_{1u}$
$\Gamma_{(2,3,6,7)}$	4	0	0	0	0	-4	0	0	$\Rightarrow B_{2g} + B_{3g} + A_u + B_{1u}$
$\Gamma\phi_1$	$\phi_1$	$\phi_5$	$-\phi_4$	$-\phi_8$	$-\phi_5$	$-\phi_1$	$\phi_8$	$\phi_4$	
$\Gamma\phi_2$	$\phi_2$	$\phi_6$	$-\phi_3$	$-\phi_7$	$-\phi_6$	$-\phi_2$	$\phi_7$	$\phi_3$	

The first thing we need to do is use the projection operators on  $\phi_1$  and  $\phi_2$  to find the wavefunctions.

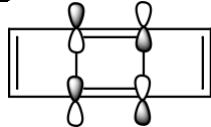
**B<sub>2g</sub>:**

$$\Psi_1 = N(\phi_1 - \phi_5 - \phi_4 + \phi_8 - \phi_5 + \phi_1 + \phi_8 - \phi_4)$$

$$\Psi_1 = \frac{1}{2}(\phi_1 - \phi_4 - \phi_5 + \phi_8)$$

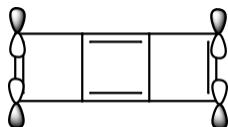


$$\Psi_2 = \frac{1}{2}(\phi_2 - \phi_3 - \phi_6 + \phi_7)$$

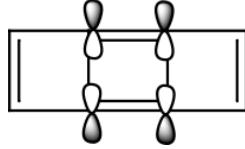


**B<sub>3g</sub>:**

$$\Psi_3 = \frac{1}{2}(\phi_1 + \phi_4 - \phi_5 - \phi_8)$$

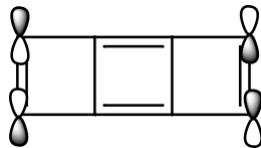


$$\Psi_4 = \frac{1}{2}(\phi_2 + \phi_3 - \phi_6 - \phi_7)$$

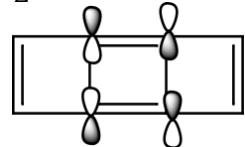


**A<sub>u</sub>:**

$$\Psi_5 = \frac{1}{2}(\phi_1 - \phi_4 + \phi_5 - \phi_8)$$

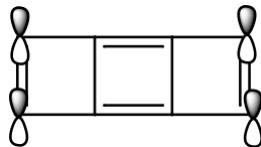


$$\Psi_6 = \frac{1}{2}(\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

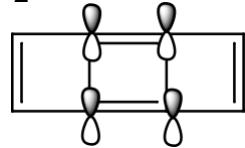


**B<sub>1u</sub>:**

$$\Psi_7 = \frac{1}{2}(\phi_1 + \phi_4 + \phi_5 + \phi_8)$$



$$\Psi_8 = \frac{1}{2}(\phi_2 + \phi_3 + \phi_6 + \phi_7)$$



Next, we need to use these wavefunctions to find the secular determinants, which will give us the energies.

**B<sub>2g</sub>:**

$$\begin{aligned}\Psi(B_{2g}) &= c_1\Psi_1 + c_2\Psi_2 \\ \widehat{H}\Psi &= E\Psi \\ (\widehat{H} - E)[c_1\Psi_1 + c_2\Psi_2] &= 0\end{aligned}$$

This can be separated into:

$$[c_1(\widehat{H})\Psi_1 + c_1(E)\Psi_1] - [c_2(\widehat{H})\Psi_2 + c_2(E)\Psi_2] = 0$$

If we left multiply by  $\Psi_1$  and integrate, this gives:

$$\begin{aligned}c_1\langle\Psi_1|\widehat{H}|\Psi_1\rangle + c_1(E)\langle\Psi_1|\Psi_1\rangle - c_2\langle\Psi_1|\widehat{H}|\Psi_2\rangle + c_2(E)\langle\Psi_1|\Psi_2\rangle &= 0 \\ = c_1(H_{11} - E) + c_2H_{12} &= 0\end{aligned}$$

Then we need to left multiply by  $\Psi_2$  and integrate, which leads to:

$$\begin{aligned}c_1\langle\Psi_2|\widehat{H}|\Psi_1\rangle + c_1(E)\langle\Psi_2|\Psi_1\rangle - c_2\langle\Psi_2|\widehat{H}|\Psi_2\rangle + c_2(E)\langle\Psi_2|\Psi_2\rangle &= 0 \\ = c_1H_{21} + c_2(H_{22} - E) &= 0\end{aligned}$$

This gives us the matrix:

$$\begin{bmatrix} (H_{11} - E) & H_{12} \\ H_{12} & (H_{22} - E) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

Now we must solve for  $H_{11}$ ,  $H_{12}$  and  $H_{22}$ :

$$\begin{aligned}H_{11} &= \frac{1}{4}\langle\phi_1 - \phi_4 - \phi_5 + \phi_8|\widehat{H}|\phi_1 - \phi_4 - \phi_5 + \phi_8\rangle \\ &= \frac{1}{4}[h_{11} - h_{14} - h_{15} + h_{18} - h_{41} + h_{44} + h_{45} - h_{48} - h_{51} + h_{54} + h_{55} - h_{58} + h_{81} - h_{84} - h_{85} + h_{88}] \\ &= \frac{1}{4}[\alpha - 0 - 0 + \beta - 0 + \alpha + \beta - 0 - 0 + \beta + \alpha - 0 + \beta - 0 - 0 + \alpha] \\ &= \alpha + \beta \approx \beta = 1\end{aligned}$$

$$H_{12} = \beta = 1$$

$$H_{22} = \alpha \approx 0$$

Substituting this into the matrix:

$$\begin{bmatrix} (1 - E) & 1 \\ 1 & (-E) \end{bmatrix} = 0$$

Therefore, the determinant is:

$$E^2 - E - 1 = 0$$

and:

$$E = +1.618\beta, -0.618\beta$$

**B<sub>3g</sub>:**

If we do the same for the b<sub>3g</sub> orbitals, we get:

$$\Psi(B_{3g}) = c_3\Psi_3 + c_4\Psi_4$$

$$\begin{aligned}c_3\langle\Psi_3|\hat{H}|\Psi_3\rangle + c_3(E)\langle\Psi_3|\Psi_3\rangle - c_4\langle\Psi_3|\hat{H}|\Psi_4\rangle + c_4(E)\langle\Psi_3|\Psi_4\rangle &= 0 \\&= c_3(H_{33} - E) + c_4H_{34} = 0\end{aligned}$$

and:

$$\begin{aligned}c_3\langle\Psi_4|\hat{H}|\Psi_3\rangle + c_3(E)\langle\Psi_4|\Psi_3\rangle - c_4\langle\Psi_4|\hat{H}|\Psi_4\rangle + c_4(E)\langle\Psi_4|\Psi_4\rangle &= 0 \\&= c_3H_{43} + c_4(H_{44} - E) = 0\end{aligned}$$

This gives us the matrix:

$$\begin{bmatrix}(H_{33} - E) & H_{34} \\ H_{34} & (H_{44} - E)\end{bmatrix} \begin{bmatrix}c_3 \\ c_4\end{bmatrix} = 0$$

Solving for H<sub>33</sub>, H<sub>34</sub> and H<sub>44</sub> gives us:

$$\begin{aligned}H_{33} &= \alpha - \beta = -\beta = -1 \\H_{34} &= \beta = 1 \\H_{44} &= \alpha = 0\end{aligned}$$

And our matrix becomes:

$$\begin{bmatrix}(-1 - E) & 1 \\ 1 & (-E)\end{bmatrix} = 0$$

Solving for E gives:

$$E^2 + E - 1 = 0$$

and:

$$E = +0.618\beta, -1.618\beta$$

**A<sub>u</sub>:**

$$\Psi(A_u) = c_5 \Psi_5 + c_6 \Psi_6$$

This leads to the matrix:

$$\begin{bmatrix} (H_{55} - E) & H_{56} \\ H_{56} & (H_{66} - E) \end{bmatrix} \begin{bmatrix} c_5 \\ c_6 \end{bmatrix} = 0$$

$$\begin{aligned} H_{55} &= \alpha - \beta = -\beta = -1 \\ H_{56} &= \beta = \beta = 1 \\ H_{66} &= \alpha - 2\beta = -2\beta = -2 \end{aligned}$$

$$\begin{bmatrix} (-1 - E) & 1 \\ 1 & (-2 - E) \end{bmatrix} = 0$$

Solving for E leads to:

$$\begin{aligned} E^2 + 3E + 1 &= 0 \\ E &= -0.382\beta, -2.618\beta \end{aligned}$$

**B<sub>1u</sub>:**

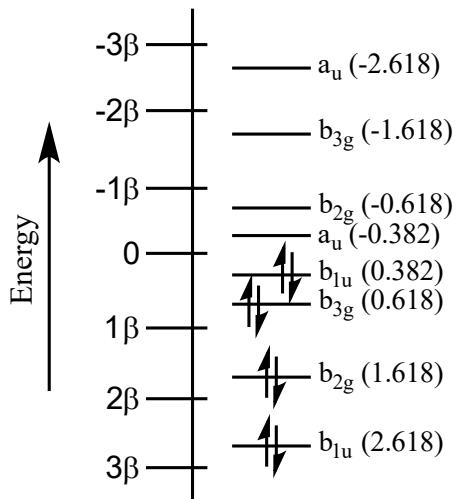
$$\Psi(B_{1u}) = c_7 \Psi_7 + c_8 \Psi_8$$

$$\begin{bmatrix} (H_{77} - E) & H_{78} \\ H_{78} & (H_{88} - E) \end{bmatrix} \begin{bmatrix} c_7 \\ c_8 \end{bmatrix} = 0$$

$$\begin{aligned} H_{77} &= \alpha + \beta = \beta = 1 \\ H_{78} &= \beta = 1 \\ H_{88} &= \alpha + 2\beta = 2\beta = 2 \end{aligned}$$

$$\begin{bmatrix} (1 - E) & 1 \\ 1 & (2 - E) \end{bmatrix} = 0$$

$$\begin{aligned} E^2 - 3E + 1 &= 0 \\ E &= +2.618\beta, +0.382\beta \end{aligned}$$



$\pi$ -stabilization energy:

$$= 2(2.618) + 2(1.618) + 2(0.618) + 2(0.382)$$

$$= 10.472\beta$$

delocalization energy:

$$= 10.472\beta - 4(2\beta)$$

$$= 2.472\beta$$

$\pi$ -bond order:

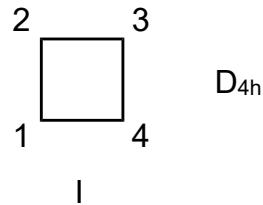
$$= \frac{8 - 0}{2}$$

$$= 4$$

(2) For this question, we will consider each of the structures separately.

First, Structure I:

(a)



D <sub>4h</sub>	E	2C <sub>4</sub>	2C <sub>2</sub>	2C <sub>2'</sub>	2C <sub>2''</sub>	i	2S <sub>4</sub>	σ <sub>h</sub>	2σ <sub>v</sub>	2σ <sub>d</sub>	
Γ <sub>ϕ1-ϕ4</sub>	4	0	0	-2	0	0	0	-4	2	0	⇒ E <sub>g</sub> + A <sub>2u</sub> + B <sub>2u</sub>

To simplify things, we can apply the projection using the C<sub>4</sub> pure rotational subgroup.

D <sub>4h</sub>	→	C <sub>4</sub>
A <sub>2u</sub>	→	A
B <sub>2u</sub>	→	B
E <sub>g</sub>	→	E

C <sub>4</sub>	E	C <sub>4</sub>	C <sub>2</sub>	C <sub>4</sub> <sup>3</sup>
ϕ <sub>1</sub>	ϕ <sub>1</sub>	ϕ <sub>4</sub>	ϕ <sub>3</sub>	ϕ <sub>2</sub>

$$P^A(\phi_1) = N[\phi_1 + \phi_4 + \phi_3 + \phi_2]$$

$$\Psi_1 = \frac{1}{2}[\phi_1 + \phi_2 + \phi_3 + \phi_4]$$

$$P^B(\phi_1) = N[\phi_1 - \phi_4 + \phi_3 - \phi_2]$$

$$\Psi_2 = \frac{1}{2}[\phi_1 - \phi_2 + \phi_3 - \phi_4]$$

$$\begin{aligned} P^{E(1)}(\phi_1) &= N[\phi_1 + i\phi_4 - \phi_3 - i\phi_2] \\ P^{E(2)}(\phi_1) &= N[\phi_1 - i\phi_4 - \phi_3 + i\phi_2] \end{aligned}$$

$$\Psi_3 = P^{E(1)}(\phi_1) + P^{E(2)}(\phi_1) = \frac{\sqrt{2}}{2}[\phi_1 - \phi_3]$$

$$\Psi_4 = \frac{P^{E(1)}(\phi_1) + P^{E(2)}(\phi_1)}{i} = \frac{\sqrt{2}}{2}[\phi_4 - \phi_2]$$

(b) In this case, all of the secular determinants are going to be 1x1 matrices.

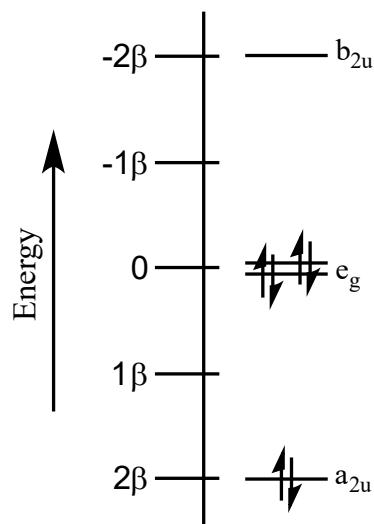
$$\begin{aligned} E(\Psi_1) &= \langle \Psi_1 | \hat{H} | \Psi_1 \rangle \\ &= \alpha + 2\beta = 2\beta \end{aligned}$$

$$\begin{aligned} E(\Psi_2) &= \langle \Psi_2 | \hat{H} | \Psi_2 \rangle \\ &= \alpha - 2\beta = -2\beta \end{aligned}$$

$$\begin{aligned} E(\Psi_3) &= \langle \Psi_3 | \hat{H} | \Psi_3 \rangle \\ &= \alpha = 0 \end{aligned}$$

$$\begin{aligned} E(\Psi_4) &= \langle \Psi_4 | \hat{H} | \Psi_4 \rangle \\ &= \alpha = 0 \end{aligned}$$

(c, d)



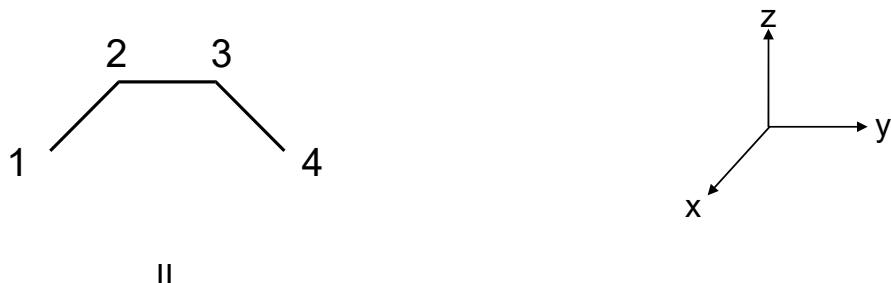
$$\begin{aligned}\pi\text{-stabilization energy:} \\ = 2(2\beta) = 4\beta\end{aligned}$$

$$\begin{aligned}\text{delocalization energy:} \\ = 4\beta - 2(2\beta) = 0\end{aligned}$$

$$\begin{aligned}\pi\text{-bond order:} \\ = \frac{4-0}{2} \\ = 2\end{aligned}$$

Now for Structure II:

(a)



$C_{2v}$	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$		
$\Gamma_{\phi 1, \phi 4}$	2	0	0	-2	$\Rightarrow$	$A_2 + B_1$
$\Gamma_{\phi 2, \phi 3}$	2	0	0	-2	$\Rightarrow$	$A_2 + B_1$

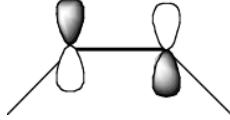
This is not a carbocyclic molecule, so we cannot use the pure rotational group for the projections.

**A<sub>2</sub>:**

$$\Psi_1 = \frac{\sqrt{2}}{2} [\phi_1 - \phi_4]$$



$$\Psi_2 = \frac{\sqrt{2}}{2} [\phi_2 - \phi_3]$$

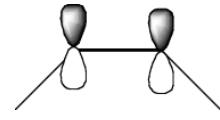


**B<sub>1</sub>:**

$$\Psi_1 = \frac{\sqrt{2}}{2} [\phi_1 + \phi_4]$$



$$\Psi_2 = \frac{\sqrt{2}}{2} [\phi_2 + \phi_3]$$



(b)

$$\Psi(A_2) = c_1 \Psi_1 + c_2 \Psi_2$$

$$\begin{bmatrix} (H_{11} - E) & H_{12} \\ H_{12} & (H_{22} - E) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$$\begin{aligned} H_{11} &= \alpha = 0 \\ H_{12} &= \beta = 1 \\ H_{22} &= \alpha - \beta = -1 \end{aligned}$$

$$\begin{bmatrix} (-E) & 1 \\ 1 & (-1 - E) \end{bmatrix} = 0$$

$$\begin{aligned} E^2 + E - 1 &= 0 \\ E &= -1.618\beta, +0.618\beta \end{aligned}$$

$$\Psi(B_1) = c_3 \Psi_3 + c_4 \Psi_4$$

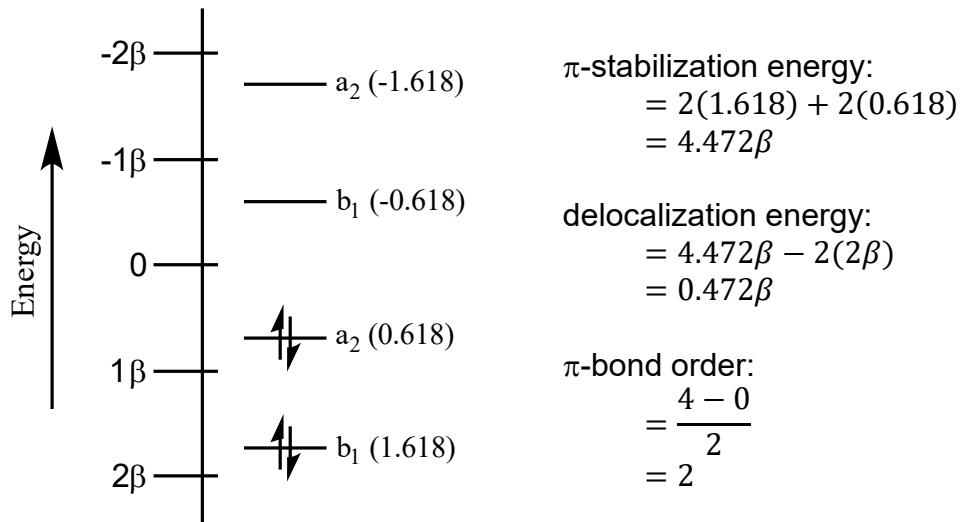
$$\begin{bmatrix} (H_{33} - E) & H_{34} \\ H_{34} & (H_{22} - E) \end{bmatrix} \begin{bmatrix} c_3 \\ c_4 \end{bmatrix} = 0$$

$$\begin{aligned} H_{33} &= \alpha = 0 \\ H_{34} &= \beta = 1 \\ H_{44} &= \alpha + \beta = 1 \end{aligned}$$

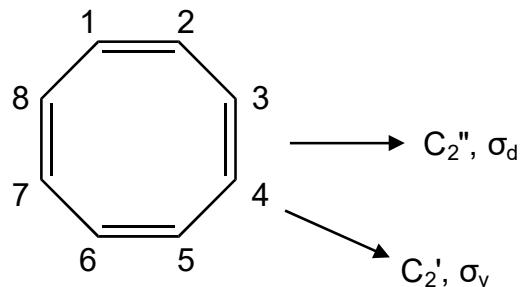
$$\begin{bmatrix} (-E) & 1 \\ 1 & (1 - E) \end{bmatrix} = 0$$

$$\begin{aligned} E^2 - E - 1 &= 0 \\ E &= +1.618\beta, +0.618\beta \end{aligned}$$

(c, d)

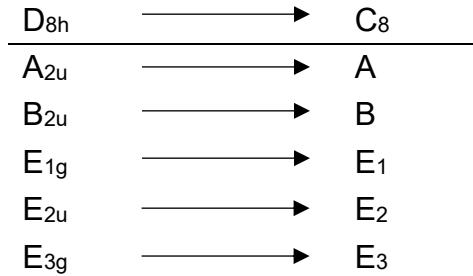


(3)



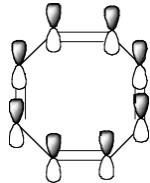
$D_{8h}$	E	$2C_8$	$2C_8^3$	$2C_4$	$C_2$	$4C_2'$	$4C_2''$	i	$2S_8^3$	$2S_8$	$2S_4$	$\sigma_h$	$4\sigma_v$	$4\sigma_d$
$\Gamma_{\phi 1-\phi 8}$	8	0	0	0	0	-2	0	0	0	0	0	-8	2	0

$$\Gamma_{\phi 1-\phi 8} = E_{1g} + E_{3g} + A_{2u} + B_{2u} + E_{2u}$$

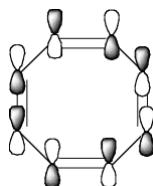


$C_8$	$E$	$C_8$	$C_4$	$C_8^3$	$C_2$	$C_8^5$	$C_4^3$	$C_8^7$
$\Gamma_{\phi_1}$	$\phi_1$	$\phi_8$	$\phi_7$	$\phi_6$	$\phi_5$	$\phi_4$	$\phi_3$	$\phi_2$

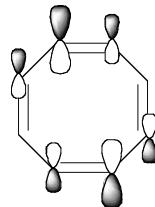
$$P^A(\phi_1) = \Psi_1 = \frac{\sqrt{2}}{4} [\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 + \phi_7 + \phi_8]$$



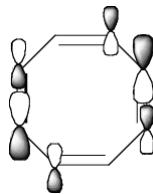
$$P^B(\phi_1) = \Psi_2 = \frac{\sqrt{2}}{4} [\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 + \phi_7 - \phi_8]$$



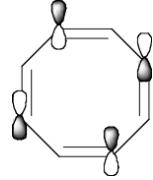
$$\Psi_3 = P_1^{E_1}(\phi_1) + P_2^{E_1}(\phi_1) = \frac{\sqrt{2}}{4} [\sqrt{2}\phi_1 + \phi_2 - \phi_4 - \sqrt{2}\phi_5 - \phi_6 + \phi_8]$$



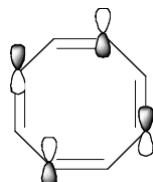
$$\Psi_4 = \frac{P_1^{E_1}(\phi_1) - P_2^{E_1}(\phi_1)}{i} = \frac{\sqrt{2}}{4} [\phi_2 + \sqrt{2}\phi_3 + \phi_4 - \phi_6 - \sqrt{2}\phi_7 - \phi_8]$$



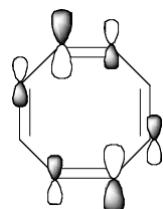
$$\Psi_5 = P_1^{E_2}(\phi_1) + P_2^{E_2}(\phi_1) = \frac{1}{2} [\phi_1 - \phi_3 + \phi_5 - \phi_7]$$



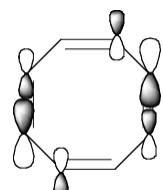
$$\Psi_6 = \frac{P_1^{E_2}(\phi_1) - P_2^{E_2}(\phi_1)}{i} = \frac{1}{2} [\phi_2 - \phi_4 + \phi_6 - \phi_8]$$



$$\Psi_7 = P_1^{E_3}(\phi_1) + P_2^{E_3}(\phi_1) = \frac{\sqrt{2}}{4} [\sqrt{2}\phi_1 - \phi_2 + \phi_4 - \sqrt{2}\phi_5 + \phi_6 - \phi_8]$$



$$\Psi_8 = \frac{P_1^{E_3}(\phi_1) - P_2^{E_3}(\phi_1)}{i} = \frac{\sqrt{2}}{4} [\phi_2 - \sqrt{2}\phi_3 + \phi_4 - \phi_6 + \sqrt{2}\phi_7 - \phi_8]$$



$$E(\Psi_1) = \alpha + 2\beta \quad E(\Psi_2) = \alpha - 2\beta \quad E(\Psi_3) = \alpha + \sqrt{2}\beta \quad E(\Psi_4) = \alpha + \sqrt{2}\beta$$

$$E(\Psi_5) = \alpha \quad E(\Psi_6) = \alpha \quad E(\Psi_7) = \alpha - \sqrt{2}\beta \quad E(\Psi_8) = \alpha - \sqrt{2}\beta$$