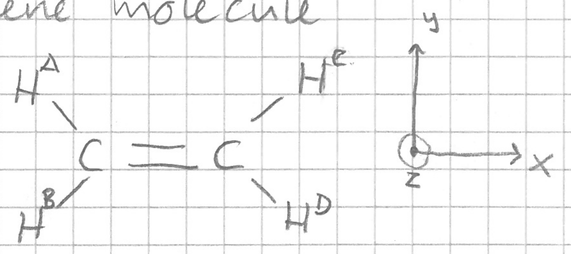
CB2070 Ex. session 8

① The ethylene molecule



a) C_2 axis on all cartesian axes

2 C_2 axes perpendicular to each axis

σ_h mirror plane on all C_2 axes

$\Rightarrow \boxed{D_{2h}}$

b) $\hat{I}$, $\hat{C}_2^x$, $\hat{C}_2^y$, $\hat{C}_2^z$, $\hat{\sigma}_{xy}$, $\hat{\sigma}_{xz}$, $\hat{\sigma}_{yz}$, $\hat{i}$

↑all symmetry operations of the group

c) Group table

	$\hat{I}$	$\hat{C}_2^x$	$\hat{C}_2^y$	$\hat{C}_2^z$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	$\hat{i}$
$\hat{I}$	$\hat{I}$	$\hat{C}_2^x$	$\hat{C}_2^y$	$\hat{C}_2^z$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	$\hat{i}$
$\hat{C}_2^x$	$\hat{C}_2^x$	$\hat{I}$	$\hat{C}_2^z$	$\hat{C}_2^y$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{xy}$	$\hat{i}$	$\hat{\sigma}_{yz}$
$\hat{C}_2^y$	$\hat{C}_2^y$	$\hat{C}_2^z$	$\hat{I}$	$\hat{C}_2^x$	$\hat{\sigma}_{yz}$	$\hat{i}$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$
$\hat{C}_2^z$	$\hat{C}_2^z$	$\hat{C}_2^y$	$\hat{C}_2^x$	$\hat{I}$	$\hat{i}$	$\hat{\sigma}_{yz}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{xy}$
$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	$\hat{i}$	$\hat{I}$	$\hat{C}_2^x$	$\hat{C}_2^y$	$\hat{C}_2^z$
$\hat{\sigma}_{xz}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{xy}$	$\hat{i}$	$\hat{\sigma}_{yz}$	$\hat{C}_2^x$	$\hat{I}$	$\hat{C}_2^z$	$\hat{C}_2^y$
$\hat{\sigma}_{yz}$	$\hat{\sigma}_{yz}$	$\hat{i}$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	$\hat{C}_2^y$	$\hat{C}_2^z$	$\hat{I}$	C_2^x
$\hat{i}$	$\hat{i}$	$\hat{\sigma}_{yz}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{xy}$	$\hat{C}_2^z$	$\hat{C}_2^y$	$\hat{C}_2^x$	$\hat{I}$

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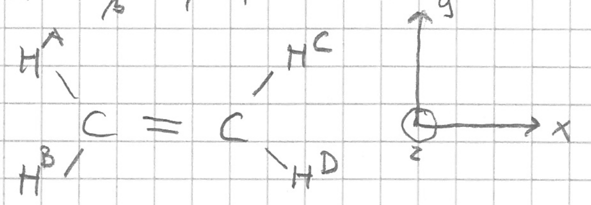
d) Introducing an AO basis for H 1s-AOs:

$$\{\chi_\alpha\}_{\alpha=1}^{4} \rightarrow (H_{1s}^{A}, H_{1s}^{B}, H_{1s}^{C}, H_{1s}^{D})$$

Determine the action of the symmetry operations that is, the matrix representations $\Gamma(\hat{G})$ from $\hat{G}\chi_\alpha = \sum_\beta \chi_\beta \Gamma_{\beta\alpha}(\hat{G})$



$$\Gamma(\hat{I}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(\hat{C}_2^x) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad \Gamma(\hat{C}_2^y) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix}, \quad \Gamma(\hat{C}_2^z) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

$$\Gamma(\hat{\sigma}_{xy}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad \Gamma(\hat{\sigma}_{xz}) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad \Gamma(\hat{\sigma}_{yz}) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

$$\Gamma(\hat{i}) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

renaming for simplicity

We see that: $\Gamma(\hat{I}) = \Gamma(\hat{\sigma}_{xy}) = \mathbb{I} \rightarrow C$

$\Gamma(\hat{C}_2^x) = \Gamma(\hat{\sigma}_{xz}) \rightarrow D$

$\Gamma(\hat{C}_2^y) = \Gamma(\hat{\sigma}_{yz}) \rightarrow E$

$\Gamma(\hat{C}_2^z) = \Gamma(\hat{i}) \rightarrow F$

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e) Find a unitary matrix that transforms all $\Gamma(\hat{G})$ into block-diagonal matrices determined by

$$\Gamma'(\hat{G}) = U^{\dagger}\Gamma(\hat{G})U$$

We have the four matrices

$$C = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \qquad D = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$E = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \qquad F = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

They can be further reduced to 2x2 matrices

$$C' = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad D' = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

The following is an attempt at formalizing the process of finding a unitary matrix:

By diagonalizing D' (with Python) I get the eigenvectors

$$\bar{v}_1 = \frac{1}{\sqrt{2}}(1 \quad 1), \quad \bar{v}_2 = \frac{1}{\sqrt{2}}(-1 \quad 1)$$

Because of reasons I want first row and first column to all have positive values, so I scale $\bar{v}_2$ by -1 and create my 2×2 unitary matrix

$$U_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

which diagonalizes both C' and D'

$$U_2^{\dagger} C' U_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad U_2^{\dagger} D' U_2 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

I decide to build my 4x4 unitary matrix with the 2x2 one, keeping in mind that all columns (and rows) must be orthogonal (and unique).

I can get this far without getting in trouble:

$$X_4 = \begin{pmatrix} U_2 & U_2 \\ U_2 & ? \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & a & b \\ 1 & -1 & c & d \end{pmatrix}$$

(calling it X until it is actually unitary)

e) cont'd

From that point we can either "just look at it" and see that the columns will be orthogonal if the lower right block is equal to $-U_2$

One can also carry out the $U_4^+ U_4$ multiplication and determine a, b, c, d from the condition of unitary matrix ☆

In either case, we get

$$U_4 = \frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}$$

where the normalization factor is now $\frac{1}{2}$.

We now get

$$\Gamma^{'} = U_4^+ \mathbb{C} U_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad \Gamma^{''} = U_4^+ \mathbb{D} U_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\Gamma^{'''} = U_4^+ \mathbb{E} U_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad \Gamma^{IV} = U_4^+ \mathbb{F} U_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Each matrix contains 4 irreps of one dimension

f)

$\Gamma^{'}$: $\hat{I}$, $\hat{\sigma}_{xy}$ $\rightarrow$ 1

$\Gamma^{''}$: $\hat{C}_2^x$, $\hat{\sigma}_{xz}$ $\rightarrow$ 1, −1

$\Gamma^{'''}$: $\hat{C}_2^y$, $\hat{\sigma}_{yz}$ $\rightarrow$ 1, −1

Γ^{IV}: $\hat{C}_2^z$, $\hat{i}$ $\rightarrow$ 1, −1

f cont'd p. 5 →

☆ determine a, b, c, d. We require that $X_4^+ X_4$ is diagonal

$$X_4^+ X_4 = \frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & a & c \\ 1 & -1 & b & d \end{pmatrix}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & a & b \\ 1 & -1 & c & d \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 4 & 0 & 2+a+c & b+d \\ 0 & 4 & a-c & 2+b-d \\ 2+a+c & a-c & 2+a^2+c^2 & ab+cd \\ b+d & 2+b-d & ab+cd & 2+b^2+d^2 \end{pmatrix}$$

we see that the first two diags = 4. I want to be one normalization factor away from the identity, so I require all other diagonal elements to be 4

$2+a^2+c^2 = 4$

$2+b^2+d^2 = 4$

All other elements must be zero

$2+a+c = 0$

$b+d = 0$

$a-c = 0$

$2+b-d = 0$

cont'd page 4.b →

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e) cont'd: determination of $\mathcal{U}$.

We can determine a and c straightforwardly

$$\begin{aligned} a+c &= -2 \\ a &= c \end{aligned} \quad \Rightarrow a = c = -1$$

For b and d, we have

$$\begin{aligned} b-d &= -2 \\ b &= -d \end{aligned} \quad \Rightarrow \begin{aligned} b &= -1 \\ d &= 1 \end{aligned}$$

Thus, we get

$$\mathcal{U}_4 = \frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}$$

where the factor $\frac{1}{2}$ normalizes such that $\mathcal{U}_4^{+} \mathcal{U}_4 = \mathbb{I}$

f) ~~Here,~~ I write the characters in the order they appear in the transformed matrix representations.
We only get 4 irreps from our procedure, but a group has as many irreps as it has symmetry operations (hence, 8)

	$\hat{I}$	$\hat{C}_2^x$	$\hat{C}_2^y$	$\hat{C}_2^z$	$\hat{\sigma}_{xy}$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	$\hat{i}$
A_g	1	1	1	1	1	1	1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1
B_{3u}	1	1	-1	-1	1	1	-1	-1
B_{1g}	1	-1	-1	1	1	-1	-1	1

This is because our basis is insufficient

The irreps have been identified by comparing to the character table in Appendix.

cont'd →

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g) Construct the symmetry-adapted basis functions

$$\{\chi_\alpha^{SAO}\}_\alpha^4 = \frac{1}{2}\begin{pmatrix} H_{1s}^A & H_{1s}^B & H_{1s}^C & H_{1s}^D \end{pmatrix}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}$$

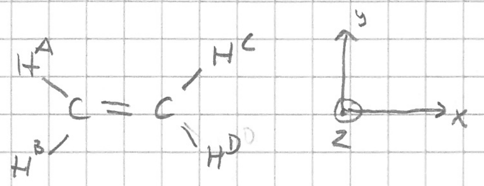
$$= \frac{1}{2}\big(H_{1s}^A + H_{1s}^B + H_{1s}^C + H_{1s}^D, \quad \leftarrow \chi_1^{SAO}$$

$$H_{1s}^A - H_{1s}^B + H_{1s}^C - H_{1s}^D, \quad \leftarrow \chi_2^{SAO}$$

$$H_{1s}^A + H_{1s}^B - H_{1s}^C - H_{1s}^D, \quad \leftarrow \chi_3^{SAO}$$

$$H_{1s}^A - H_{1s}^B - H_{1s}^C + H_{1s}^D\big) \quad \leftarrow \chi_4^{SAO}$$

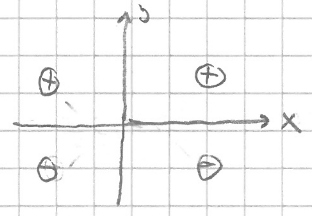
h)



I write the operations in same order as character table in appendix

χ_1^{SAO}: all H_{1s} have the same sign $\Rightarrow A_g$

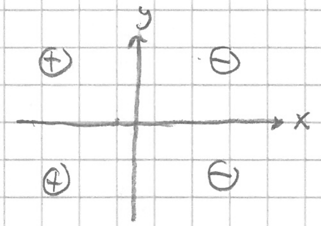
χ_2^{SAO}:



$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	$\hat{i}$	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$
1	−1	1	−1	−1	1	−1	1

$\Rightarrow B_{2u}$

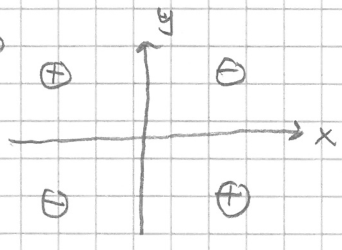
χ_3^{SAO}



$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	$\hat{i}$	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$
1	−1	−1	1	−1	1	1	−1

$\Rightarrow B_{3u}$

χ_4^{SAO}



$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	$\hat{i}$	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$
1	1	−1	−1	1	1	−1	−1

$\Rightarrow B_{1g}$

i) We need AOs that are out of the xy plane $\Rightarrow 2p_z$