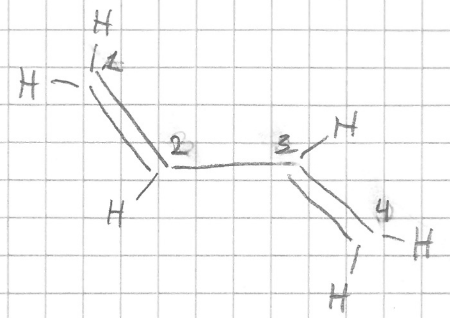
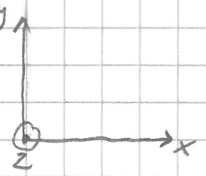
CB2070 Ex. session 9

① Trans-butadiene





a) $\hat{C}_2$ rotation around z-axis

$\hat{\sigma}$ in xy plane, horizontal to $\hat{C}_2^z$ $\Rightarrow \hat{\sigma}_h$

$\hat{i}$ through center C–C bond

$\Rightarrow$ C_{2h}

b) Introduce basis $\{p_z^\alpha\}_{\alpha=1}^{4}$

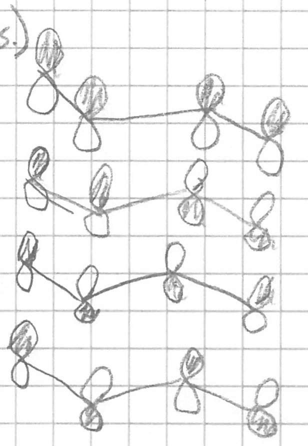
The SAOs are (ener. decreas.)

χ_1^{SAO} $p_z^1 + p_z^2 + p_z^3 + p_z^4$

χ_2^{SAO} $p_z^1 + p_z^2 - p_z^3 - p_z^4$

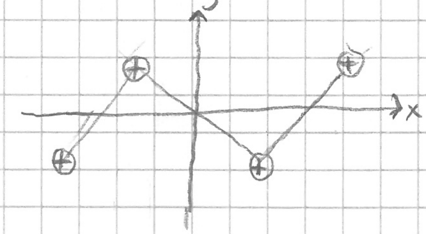
χ_3^{SAO} $p_z^1 - p_z^2 - p_z^3 + p_z^4$

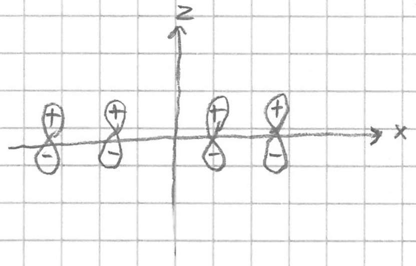
χ_4^{SAO} $p_z^1 - p_z^2 + p_z^3 - p_z^4$



c) We investigate the effect of the symmetry operations on our basis

χ_1^{SAO}

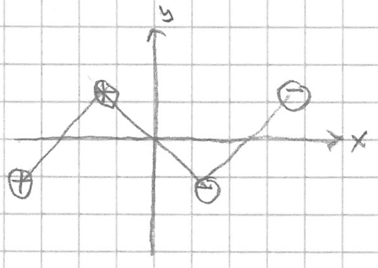


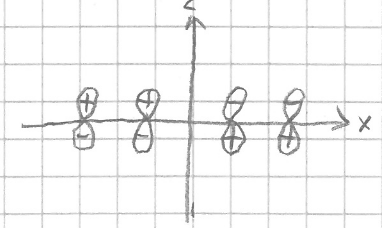


$\hat{C}_2^z$	$\hat{i}$	$\hat{\sigma}_h$
+1	−1	−1

$\underline{\underline{A_u}}$

χ_2^{SAO}



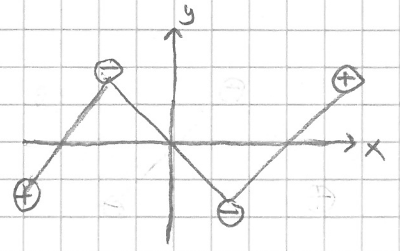


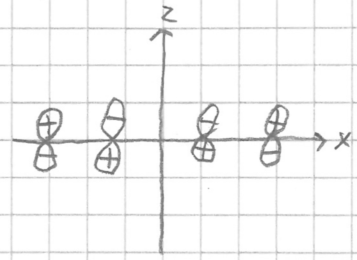
$\hat{C}_2^z$	$\hat{i}$	$\hat{\sigma}_h$
−1	+1	−1

$\underline{\underline{B_g}}$

c) cont'd

χ_3^{SAO}:

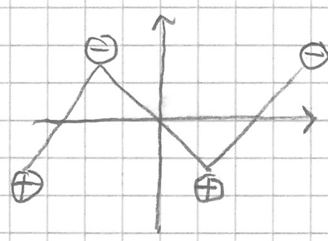


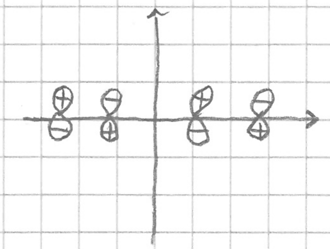


$\hat{C}_2^z$	$\hat{i}$	$\hat{\sigma}_h$
+1	−1	−1

$\underline{\underline{A_u}}$

χ_4^{SAO}:





$\hat{C}_2^z$	$\hat{i}$	$\hat{\sigma}_h$
−1	+1	−1

$\underline{\underline{B_g}}$

d) In the SCF output from veloxchem, we look at the printed tables for the MOs.
Basis set: STO-3G

MOs # 14 and 15 are HOMO-1 and HOMO

MOs # 16 and 17 are LUMO and LUMO+1

The energy ordering is

HOMO-1:	χ_1^{SAO}	$p_z^1 + p_z^2 + p_z^3 + p_z^4$	A_u
HOMO:	χ_2^{SAO}	$p_z^1 + p_z^2 - p_z^3 - p_z^4$	B_g
LUMO:	χ_3^{SAO}	$p_z^1 - p_z^2 - p_z^3 + p_z^4$	A_u
LUMO-1:	χ_4^{SAO}	$p_z^1 - p_z^2 + p_z^3 + p_z^4$	B_g

e) The symmetry of the HF ground state is the same as the HOMO

$\Rightarrow B_g$

The symmetry of the lowest $\pi\pi^*$ excited state is the same as the LUMO

$\Rightarrow A_u$

f) The matrix element $\langle \Psi_\pi^{\pi^*} | \hat{\mu}_\alpha | \Psi_{HF} \rangle \neq 0$

only if $\Gamma(\Psi_\pi^{\pi^*}) \otimes \Gamma(\hat{\mu}_\alpha) \otimes \Gamma(\Psi_{HF}) = A_g$

We have – closed-shell wave functions span the $\Gamma(\hat{I})$ irrep

– the symmetry of the S_1 state is $\Gamma(S_1) = \Gamma(\phi_{HOMO}) \otimes \Gamma(\phi_{LUMO})$

f) cont'd

$$\Gamma(\Psi_{\pi}^{\pi^*}) = B_g \otimes A_u = B_u$$

$$\Gamma(\Psi_{HF}) = A_g$$

From character table we have

$$\Gamma(\hat{x}) = \Gamma(\hat{y}) = B_u \quad , \quad \Gamma(\hat{z}) = A_u$$

The symmetries of the matrix elements then become

$$\Gamma(\langle \Psi_{\pi}^{\pi^*} | \hat{\mu}_x | \Psi_{HF} \rangle) = B_u \otimes B_u \otimes A_g = A_g \Rightarrow$$ x, y components couple the states

$$\Gamma(\langle \Psi_{\pi}^{\pi^*} | \hat{\mu}_z | \Psi_{HF} \rangle) = B_u \otimes A_u \otimes A_g = B_g \Rightarrow$$ z gives <u>zero</u>