

Applications of Group Theory

PD Dr. Andrea Donarini

Lectures

Exercises

9.2.01, Mondays, 14:15

H34, Wednesdays, 14:00

Sheet 9

1. Molecular stability

Why would the octahedral configuration of Fig. 1b be more stable for a hypothetical SH_6 than the planar configuration in Fig. 1a? Consider the angular momentum states required for the S atom to make the appropriated equivalent valence bonds to the six hydrogens in the planar SH_6 hypothetical molecule.

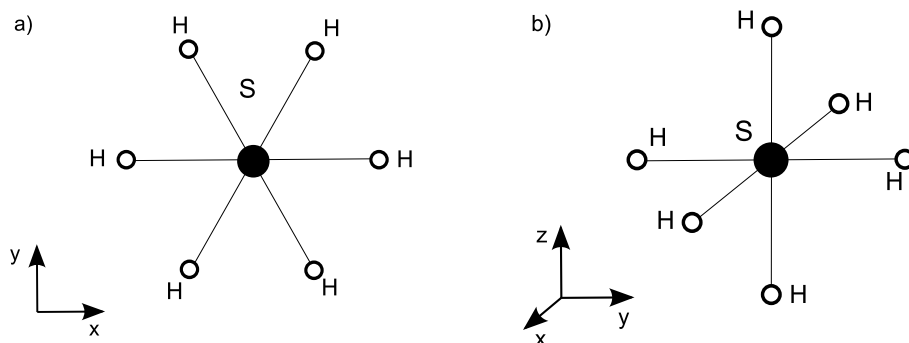


Figure 1: Two possible configurations of the hypothetical molecule SH_6 .

2. Ethylene

Ethylene (C_2H_4) is a planar molecule which has the configuration shown in Fig. 2.

1. Identify the appropriate point group for C_2H_4 .
2. Construct the character system for the representations of the point symmetry group of ethylene associated to a) the valence orbitals of the 2 carbon atoms; b) the valence orbitals of the 4 hydrogen atoms.
3. By reducing the representation obtained at the previous point, prove that there are molecular orbitals on ethylene which do not involve the hydrogens. Construct explicitly the basis function associated to the irreducible representations. Predict the degeneracies of the spectrum of ethylene.
4. Prove that, by restricting to the nearest neighbours tight binding, ethylene can be described by the following 12×12 Hamiltonian, written in the basis $|C_1, 2s\rangle$, $|C_1, 2p_x\rangle$, $|C_1, 2p_y\rangle$, $|C_1, 2p_z\rangle$,

$|C_2, 2s\rangle, |C_2, 2p_x\rangle, |C_2, 2p_y\rangle, |C_2, 2p_z\rangle, |H_1, 1s\rangle, |H_2, 1s\rangle, |H_3, 1s\rangle, |H_4, 1s\rangle$, (for the labelling of the atoms and the directions of the associated p orbitals see Fig. 2):

$$H = \begin{pmatrix} H_{CC} & H_{CH} \\ H_{CH}^\dagger & H_{HH} \end{pmatrix}$$

where

$$H_{HH} = \epsilon_{Hs} \mathbf{1}_4, \quad H_{CC} = \begin{pmatrix} H_{C_1C_1} & H_{C_1C_2} \\ H_{C_1C_2}^\dagger & H_{C_1C_1} \end{pmatrix}$$

with

$$H_{C_1C_1} = \begin{pmatrix} \epsilon_{Cs} & 0 & 0 & 0 \\ 0 & \epsilon_{Cp} & 0 & 0 \\ 0 & 0 & \epsilon_{Cp} & 0 \\ 0 & 0 & 0 & \epsilon_{Cp} \end{pmatrix} \quad \text{and} \quad H_{C_1C_2} = \begin{pmatrix} V_{ss\sigma}^{CC} & 0 & 0 & V_{sp\sigma}^{CC} \\ 0 & -V_{pp\pi}^{CC} & 0 & 0 \\ 0 & 0 & -V_{pp\pi}^{CC} & 0 \\ V_{sp\sigma}^{CC} & 0 & 0 & V_{pp\sigma}^{CC} \end{pmatrix}.$$

Finally, the coupling between the carbon and hydrogen atoms is given by

$$H_{CH} = \begin{pmatrix} H_{C_1H_{12}} & 0 \\ 0 & H_{C_1H_{12}} \end{pmatrix} \quad \text{with} \quad H_{C_1H_{12}} = \begin{pmatrix} V_{ss\sigma}^{CH} & V_{ss\sigma}^{CH} \\ 0 & 0 \\ V_{sp\sigma}^{CH} \sin(\alpha/2) & -V_{sp\sigma}^{CH} \sin(\alpha/2) \\ -V_{sp\sigma}^{CH} \cos(\alpha/2) & -V_{sp\sigma}^{CH} \cos(\alpha/2) \end{pmatrix}$$

Take the following parameters (in eV):

ϵ_{Hs}	ϵ_{Cs}	ϵ_{Cp}	$V_{ss\sigma}^{CC}$	$V_{sp\sigma}^{CC}$	$V_{pp\pi}^{CC}$	$V_{pp\sigma}^{CC}$	$V_{ss\sigma}^{CH}$	$V_{sp\sigma}^{CH}$
-13.6	-19.37	-11.07	-6.03	-7.93	-3.49	-13.96	-8.98	-11.8

For the \widehat{HCH} angle (see Fig. 2) assume $\alpha = 118^\circ$. Diagonalize numerically the Hamiltonian. Verify the predicted degeneracy of the spectrum and assign each eigenvector to the corresponding irreducible representation.

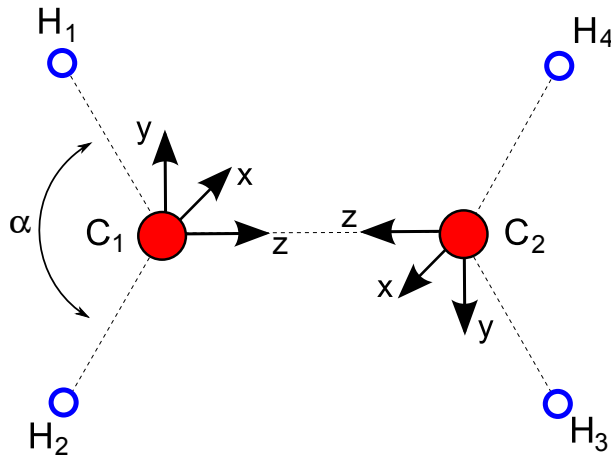


Figure 2: Geometrical configuration of ethylene (C_2H_4).

Frohes Schaffen!