University of Regensburg Summer Term 19

Applications of Group Theory

Lectures	Tue	10:00 - 11:30	PHY 9.1.09
	Thu	10:00 - 11:30	PHY 9.1.09
Exercises	Fri	10:00 - 11:30	PHY 5.0.21

Sheet 7

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1. Ethylene

Ethylene (C_2H_4) is a planar molecule which has the configuration shown in Fig. 1.

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 functions associated to the different irreducible representations. Predict the degeneracies of the spectrum of ethylene.
4. Construct the nearest neighbours tight binding Hamiltonian of ethylene. Prove that it can be cast into the form of 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. 1):

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

where

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

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 $\alpha = 118°$. Diagonalize numerically the Hamiltonian. Verify the predicted degeneracy of the spectrum and assign each eigenvector to the corresponding irreducible representation.

5. On the basis of the analysis performed in the previous points, discuss the stability of non-planar ethylene. In particular, consider the case in which the two pairs of hydrogens are orthogonal to each other.

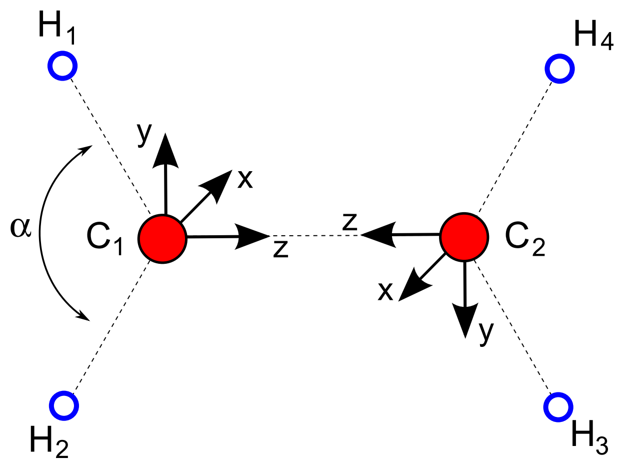

Figure 1: Geometrical configuration of ethylene (C_2H_4).

Frohes Schaffen!