Homework # 8

Exercise 1 – Butadiene

The butadiene molecule (C_4H_6 or CH_2=CH-CH=CH_2, see Fig. 1) is a planar molecule. It is important for the chemical industry, for instance it is used as a monomer in the production of synthetic rubber.
Historical note Most rubber products are vulcanized as this massively improves their lifespan, function, and strength. Vulcanization is a range of processes for hardening rubbers, typically based on the treatment of natural rubber with sulfur. Charles Goodyear invented the process of rubber vulcanization in the 1830s, while was working to improve tube tires. By 1844 was producing it on an industrial scale.

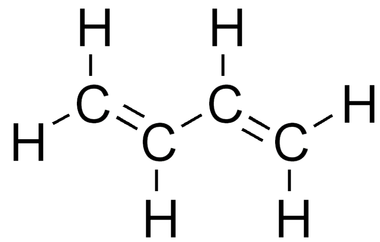

Figure 1: Structural formula of the butadiene molecule.

In the following, we will consider only the π orbitals of the molecule, having a nodal plane for $z = 0$ (the nuclei lie in the xy plane). In the simplest minimal-basis LCAO approximation these π orbitals can be written as a linear combination of p_z orbitals of carbon atoms $|\chi_j\rangle$, while hydrogen atoms do not contribute.

Recall that for variational priciple the solution of the LCAO method can be found diagonalizing the $\hat{H}$ matrix in an orthogonal basis.

We will assume $\langle\chi_i|\chi_j\rangle = \delta_{ij}$ (orthonormality) and matrix elements of the form:

$$H_{ij} = \langle\chi_i|H|\chi_j\rangle = \begin{cases} \alpha & \text{if } i = j, \\ \beta & \text{if } i, j \text{ are nearest neighbours,} \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

In the following, assume $\beta < 0$.

1. Find the energy eigenvalues ε_i. The secular problem could be solved using the change of variable $x = \frac{\alpha-\varepsilon}{\beta}$, with ε eigenvalues of the matrix, and lead to the 4-th order equation:

$$x^2(x^2 - 2) - (x^2 - 1) = 0, \tag{2}$$

2. Knowing that the molecule has 4 π-electrons, what is the energy of the highest occupied molecular orbital (HOMO)?

3. What is the total degeneracy (orbital and spin degeneracy) for the ground state of the neutral butadiene molecule? What is the total degeneracy for the molecular ions (CH_2 =CH-CH=$CH_2)^+$ and (CH_2 =CH-CH=$CH_2)^-$?
Hint: count how many equivalent ground state wavefunction you can write (orbital and spin).

Exercise 2 – CH_3Cl

In class you have discussed the symmetry operations of the water molecule. Let us consider the CH_3Cl molecule (see Fig. 2).

1. Determine all the symmetry operations of CH_3Cl.

2. Verify that the group formed by the symmetry operations is closed with respect to multiplication.

   Hint: make the table of symmetry combinations. Do all combinations belong to the group?

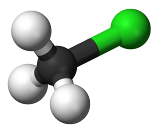

Figure 2: The CH_3Cl molecule

Exercise 3 – C_2H_4

Let us consider now ethylene: C_2H_4 (see Fig. 3). Assume that the plane of the molecule is the xy plane and that the x axis is along the direction of the C-C bond.

1. You have learned how to present symmetry operations geometrically. Another way to study symmetry is using matrix representation. For example, an arbitrary counter-clockwise rotation around x, y or z axis by $2\pi/n$ can be expressed as

$$\mathcal{C}_n(x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & cos(2\pi/n) & -sin(2\pi/n) \\ 0 & sin(2\pi/n) & cos(2\pi/n) \end{pmatrix} \quad \mathcal{C}_n(y) = \begin{pmatrix} cos(2\pi/n) & 0 & sin(2\pi/n) \\ 0 & 1 & 0 \\ -sin(2\pi/n) & 0 & cos(2\pi/n) \end{pmatrix}$$

$$\mathcal{C}_n(z) = \begin{pmatrix} cos(2\pi/n) & -sin(2\pi/n) & 0 \\ sin(2\pi/n) & cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

respectively. Write down the matrix representation for the following symmetry operations. Which ones represent C_2H_4 molecule?

   - Identity, E;
   - Inversion, i;
   - Rotation by π degree around the x axis, $\mathcal{C}_2(x)$;
   - Rotation by π degree around the y axis, $\mathcal{C}_2(y)$;
   - Rotation by π degree around the z axis, $\mathcal{C}_2(z)$;
   - Rotation by $\pi/2$ degree around the x axis, $\mathcal{C}_4(x)$;
   - Rotation by $\pi/2$ degree around the y axis, $\mathcal{C}_4(y)$;

- Rotation by $\pi/2$ degree around the z axis, $\mathcal{C}_4(z)$;
- Reflection through xy plane, $\sigma(xy)$;
- Reflection through yz plane, $\sigma(yz)$;
- Reflection through xz plane, $\sigma(xz)$.

2. Verify that the symmetries of C_2H_4 form a group.

3. Suppose now to substitute one of the H atom with a Cl atom (vinyl chloride or chloroethene). Consider again the 11 symmetry operations above, which are the ones of this new molecule?

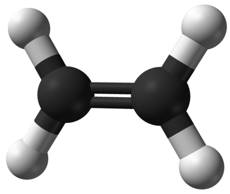

Figure 3: Ethylene molecule.