Homework #3

Assigned: 11.11.2021 **Due: 24.11.2021**

Hückel approximation for the benzene molecule

Hückel appoximation is a simple model for estimation of the energies of binding molecular orbitals (MO) in some organic molecules, which can be used to assess the stability of those molecules. It is based on the MO-LCAO method (molecular orbitals as linear combinations of atomic orbitals) with additional restrictions on the matrix elements of the Hamiltonian in the basis of atomic orbitals (AO) as well as on the overlap integrals of the AOs.

In the case of the benzene molecule (point group D_{6h}), the stability can be understood considering only the p_z orbitals on individual carbon atoms ($\langle z \rangle$ axis is identified with the principal C_6 rotational axis). Thus, we have a basis consisting of six orbitals ϕ_i, and we assume that the Hamiltonian matrix elements can be expressed as follows:

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = \begin{cases} \alpha & (i = j) \\ \beta & (|i - j| = 1) \\ 0 & (|i - j| > 1) \end{cases}$$

The basis is assumed to be orthonormal, i.e., the overlap matrix S is diagonal:

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j). \end{cases}$$

Tasks:

1. *(4 points)* Reduce the 6-dimensional representation in the basis of the p_z orbitals to the irreducible representations of D_{6h}.

2. *(6 points)* Find the corresponding invariant subspaces (symmetrize the basis).

3. *(6 points)* Determine the eigenenergies and eigenstates of the above Hamiltonian and classify them according to the irreducible representations of D_{6h}.

4. *(4 points)* Based on the results of the previous task, try to ascertain whether the benzene molecule is stable, i.e., whether the total energy of the six electrons occupying the obtained MOs is lower compared to the electrons occupying the atomic p_z orbitals.