Hückel approximation for the benzene molecule

Deadline for submission: ideally by Friday **20.12.2024**

The Hückel approximation is a simple model for determining the energies of molecular orbitals (so-called π-orbitals) of some organic molecules (in which double and single bonds alternate, as in benzene). This approximation can be used to estimate the stability of these molecules. It is based on the LCAO-MO method (i.e., on the construction of molecular orbitals using a linear combination of atomic orbitals), but with additional conditions on the matrix elements of the Hamiltonian in the basis of atomic orbitals and on the overlap integrals of these orbitals.

In the case of the benzene molecule (point group of symmetry D_{6h}), to explain the bond according to this approximation, it is sufficient to consider only the p_z orbitals on the carbon atoms (it is assumed that the other orbitals are not important for the bond; we will identify the z axis with the C_6 rotational axis of the benzene molecule, which is a planar molecule in the ground state and carbon atoms form a regular hexagon). We therefore have a basis of six orbitals and we assume that the following matrix elements for the Hamiltonian

$$H_{ij} = \int \phi_i^* H \phi_j d^3x = \begin{cases} \alpha & \text{for } i = j, \\ \beta & \text{for } i \text{ adjacent to } j, \\ 0 & \text{in other cases (the Hückel approximation)} \end{cases} \tag{1}$$

and for overlap integrals

$$S_{ij} = \int \phi_i^* \phi_j d^3x = \begin{cases} 1 & \text{for } i = j, \\ 0 & \text{for } i \neq j, \quad \text{(again Hückel approximation).} \end{cases} \tag{2}$$

1. (4 points) Determine the decomposition of the reducible representation, the basis of which consists of 6 p_z orbitals of carbon atoms, into irreducible representations.

2. (6 points) Using the symmetrization (projection) operators corresponding to these irreducible representations, determine a symmetrically adapted basis from these p_z orbitals.

3. (4 points) Using this basis, determine the eigenstates and energies of the Hamiltonian (1) and classify them according to the irreducible representations of the group D_{6h}.

4. (2 points) Based on the results obtained, estimate whether the benzene molecule will be stable, i.e. whether the resulting energy of 6 electrons placed in the specified molecular orbitals according to the Pauli exclusion principle is lower than in the situation when the electrons would be directly in the atomic orbitals and not interacting, i.e. if each had the corresponding energy α).

5. (4 points) If we replace two opposite hydrogen atoms in the benzene molecule with deuterium atoms, we will break its symmetry. Determine the symmetry group of this deuterated molecule and determine to which irreducible representations of this group (this is a subgroup of the group D_{6h}) the eigenstates of the Hamiltonian (1) will now belong, i.e. determine the decomposition of the corresponding irreducible representations of the group D_{6h} when subducted to the symmetry group of this deuterated molecule.

6. (bonus 10 points) What does the Hückel approximation predict about the stability of cyclobutadiene, which would have 4 carbon atoms located at the vertices of a square, compared to benzene? Will the binding energy of cyclobutadiene be higher or lower? Again, consider only the p_z orbitals on the carbon atoms.