CHEM356: Physical Chemistry II
Homework Set V - due 21^{th} of May, 5.00 pm
Each problem is worth 5 points, 25 pts in total.

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Problem I

Show that sp^2 hybrid orbitals are orthogonal.

Problem II

Using Hückel model, derive the molecular orbital energies for the cyclobutadiene molecule. Compare the stability of the cyclobutadiene with two isolated ethene molecules.

Problem III

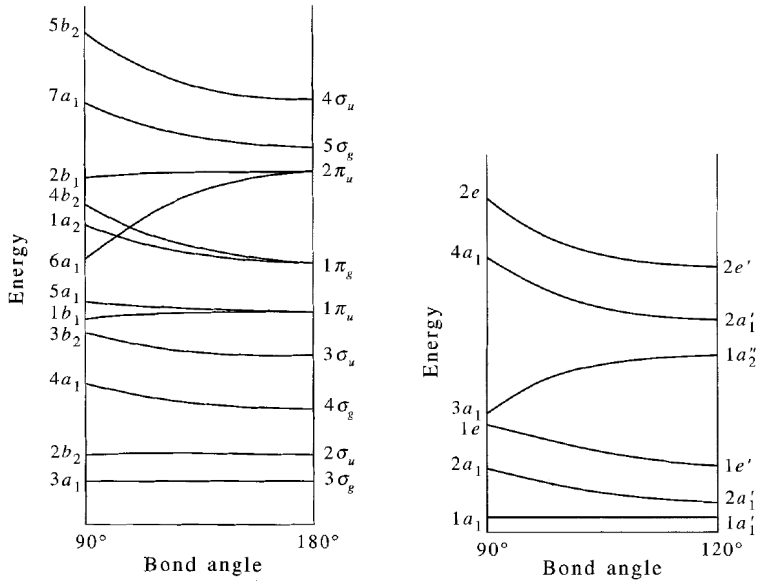
The energies E_j of the j-th molecular orbitals in a linear conjugated polyene composed of N carbon atoms is given by:

$$R_j = \alpha + 2\beta \cos \frac{j\pi}{N_1}$$

Validate the formula for butadiene and hexatriene. Next, show that extrapolation of the model to hypothetical 1-dimensional solid leads to formation of essentially a continuous band of the width of 4β.

Problem IV

Use the Walsh correlation diagram for the valence electrons of XY_2 (left) and XH_3 (right) molecules to predict whether following molecules are linear or bent: CO_2, CO_2^-, CO_2^+, CF_2, CN_2, NO_2^+, NO_2; and planar or pyramidal: BH_3, CH_3, CH_3^+, CH_3^-, NH_3. 'e' means that the state is double-degenerate.



Problem V

Consider allyl cation, $CH_2 = CH - CH_2^+$ which features delocalized π-network. From Hückel model, derive the molecular orbital energies. Next, derive the energies for cyclopropene cation and compare energetics of these two molecules. Does the relative stability changes if we consider anions instead of catiosn?