Exe 4: Excercises for (Physical and) Theoretical Chemistry
WS 2002/03 1^{st} IGS semester Excercises No. 4
hand out: Fr., 8.11.02, return: Wed., Nov. 13, mail-box, AR-K6 left side wall.

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13) A model based on quantum mechanics: The simple box model yields for the longest wave length absorption line of conjugated carbon chains with m double bonds and $2m$ chain atoms and a total length of $L \approx (2m+1)D$ for the wave length λ: in case of equal C-C bond length (e.g. in cyanine dyes) $\lambda \approx c_0 \cdot L \approx c_1 \cdot (2m+1)$. In the case of alternating bond lengths (e.g. merocyanines or polyenes) $\lambda \approx c_1 \cdot (2m+1)/(1+c_2 \cdot m)$. Show that $y = 1/\lambda$ versus $x = 1/(2m+1)$ yields a straight line. What is the meaning of y for $x = 0$?

14) The semiempirical approach: The first polyenes are colorless. Their UV-absorption wave lengths have been measured as: Ethene - 162 nm, Butadiene - 217 nm, Hexatriene - 257 nm, Ocatatraene - 290 nm, Decapentaene - 317 nm. Make a diagram of $1/\lambda$ versus $1/L$. (For Din A4 paper, the following cm-scales are appropriate: $3000\,\mathrm{nm}/\lambda$, and $60/(2m+1)$.) Which ployenes may have a visible color? Which color do you expect for very long chains?

15) Are closed shells stable? The Hückel rule: The ring model for a circular chain of N atoms with circumference $N \cdot D$ yields for the orbital energy levels $E_m = m^2/2\mu R^2$, where $m = 0, +1, -1, +2, -2$ etc. Assume that every atom supplies one valence electron. Occupy the energy levels with electrons according to Pauli's principle. Make a table with 3 columns: $N = 2$ (Ethene), 3, 4 (Butadiene), 5, 6 (Benzene), 7, 8, 9, 10, 11 – $|m|$ for the HOMO – E_m in units of $[2\pi^2/\mu D^2]$.

16) The hen and the egg. Make a plot: E_m versus N. a) For given quantum shell number $|m|$: how does the energy vary with the size of the system? b) Why is an energy level particularly stable? c) When is a valence electron particularly loosely bound? d) Comment on the rule: Closed shells are stable. e) The Hückel rule states: rings with $(4n+2)\pi$ electrons are particularly stable for integer $n = 0, 1, 2$ etc. Which is the "best" n according to the plot? f) An atomic s^2p^6 shell is said to be particularly stable. Comment on the stabilities of Mg^{2+}, Na^+, Ne, F^-, O^{2-}, N^{3-}.