Exe 5: Excercises for (Physical and) Theoretical Chemistry

WS 2002/03 1^{st} Master semester Excercises No. 5

hand out: Fr., 15.11.02, return: Wed., Nov. 20, mail-box, AR-K6 left side wall.

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17) First order perturbation theory. There are two dye molecules, (I) $[R_2N \cdot \Phi \cdot CH \cdot \Phi \cdot NR_2]^+$ and (II) $[R_2N \cdot \Phi \cdot N \cdot \Phi \cdot NR_2]^+$ (Φ is a benzene ring). Their names are (II) Bindschedler's B, (I) Michler's Hydrol-M, where M and B are names of colors, such as red, green, etc. One of the dyes absorbs at 600 nm, the other one at 725 nm. a) How many π-pairs do (I) and (II) have? b) Which one of the two, (I) and (II), has shorter wave length absorption? c) Which are the colors of these two dyes? d) What are the names (such as Bindschedler's Black)?

18) The harmonic vibrator. The UV-spectrum of H_2 exhibits a vibrational structure corresponding to quantum level differences of wave length $\lambda = \text{mm}/440$. What is the vibrational wave number $\tilde{\nu}$, the vibrational energy quantum in eV, in atomic units? Give the reduced mass in AMU and in a.u.. Give the force constant in a.u. and in N/cm.

19) Quantum smearing of atoms. The vibrational ground state function ist $\psi(r) = \exp(-R^2\sqrt{k\mu}/2)$ Determine $\pm R_{sm}$ where the probablity of the nuclei has decreased from its maximum value at the equilibrium ($R = 0$) to $1/e$. Compare the zero point positional smearing $2R_{sm}$ with the bond length of 74.17 pm (give the %-age).

20) Two "parallel" spins. An angular momentum vector of quantum numbers $l = \frac{1}{2}, m = \frac{1}{2}$ is given by $\vec{l}_i^+ = (\cos\phi_i/\sqrt{2}, \sin\phi_i/\sqrt{2}, 1/2)$ with undefined angle ϕ_i. Couple two such vectors $\vec{l}_1(\phi_1)$ and $\vec{l}_2(\phi_2)$ to a sum vector $\vec{l}$ with quantum numbers $l = 1, m = 1, \vec{l}^+ = (\cos\phi, \sin\phi, 1)$. Determine the angle γ between $\vec{l}_1$ and $\vec{l}_2$.
Hint: $\cos\phi = (\cos\phi_1 + \cos\phi_2)/\sqrt{2}$ etc. ; $\cos^2\phi + \sin^2\phi = 1$. $\cos|\phi_1 - \phi_2| = \cos\phi_1\cos\phi_2 + \sin\phi_1\sin\phi_2$ What is $|\phi_1 - \phi_2|$? While ϕ_1 and ϕ_2 are arbitrary, their difference is fixed! Choose, for instance, $\phi_1 = 0$. Then you have one possible pair $\vec{l}_1$ and $\vec{l}_2$. The calculate γ.

21) $\pi-$electron density in benzene. Choose the 3 real canonical orbitals $\phi(\alpha) = \cos(0\alpha)/\sqrt{2\pi}$, $\cos(1\alpha)/\sqrt{\pi}$, $\sin(1\alpha)/\sqrt{\pi}$. What is $\rho(\alpha) = 2\cdot\Sigma|\phi|^2$? Now choose the 3 complex canonical orbitals $\phi(\alpha) = e^0/\sqrt{2\pi}$, $e^{+i\alpha}/\sqrt{2\pi}$, $e^{-i\alpha}/\sqrt{2\pi}$.