Molecular Physics (Prof. Käs) **WS 2007/08**
Universität Leipzig
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Problem Set 12a
Due date: January 21, 2008

Problem 45)
The four p_z orbitals of the three O atoms and of the N atom of the NO_3^- ion are oriented perpendicular to the plane of the molecule and give rise to a π system, which is occupied by two delocalized electrons. Apply the Hückel approximation for molecular orbitals and express the energies in terms of the Coulomb integrals α_O and α_N and the resonance integral β. Solve the relevant secular equations by usage of a determinant and calculate the delocalization energy of the ion. Hint: use energies which you would obtain for one hypothetic electron pair localized between N and O.
(5 points)

Problem 46)
Calculate the ratio of the Einstein coefficients of spontaneous and stimulated emission, A and B, for transitions with the following characteristics: a) 1.542 Å (x-ray), b) 470 nm (visible) c) 2900 cm^{-1} (mid-infrared) d) 98.3 MHz (radio). Show graphically how A/B behaves as a function of frequency.
(5 points)

Problem 47)
A rotation absorption spectrum for $^1H^{35}Cl$ gas was experimentally recorded and the observed lines had the following wavenumbers: 83,32; 104,13; 124,73; 145,37; 165,89; 186,23; 206,60; 226,86 cm^{-1}. From the latter results, calculate the moment of inertia I of the $^1H^{35}Cl$ molecule and its bond length R. Calculate the wavenumbers of the analogous lines for $^2H^{35}Cl$.
Given: reduced masses $\mu(^1H^{35}Cl) = 1{,}6266 \cdot 10^{-27}$ kg and $\mu(^2H^{35}Cl) = 3{,}1624 \cdot 10^{-27}$ kg
(4 points)