Virtual previous exam questions in chemical physics

(Incompletely formulated, but should still be of some help.)
(The exam on May 26 2006 will be available in Norwegian and English, of course.)

Exercise 1
Carbon dioxide, CO_2, is a linear molecule with double bonds between C and both O-atoms. Due to its high symmetry, the geometry of the molecule is determined by a single bond length (C-O). In the basis set 3-21G(*), one includes three s- and six p-orbitals on both C and O. The three atoms lie along the z-axis, with C at the origin.

Determine the total number of electrons in a carbon dioxide molecule. How many basis functions are included in the construction of molecular orbitals (MOs) for CO_2, within the LCAO approximation and with the 3-21G(*) basis set? How many of these MOs are occupied by electrons (in the ground state)?
The figure below illustrates some of the MOs that are occupied by electrons in CO_2. Discuss the parity of these MOs. What kind of atomic orbitals (basis functions) contribute to the various MOs in the figure?

…figure with several MOs...Do a Hartree-Fock calculation yourself
and play around with some of the MOs in CO_2….!

Carbon dioxide has four vibrational modes. These are illustrated in the figure below. The arrows illustrate the vibrational motion in each of the modes. Which modes are IR-active and which are IR-inactive? (A mode is IR-active if it represents an oscillating dipole.)

…figure which illustrates the vibrational modes in CO_2… Do a Hartree-Fock calculation yourself
and inspect the vibrational modes in CO_2….!

Exercise 2
The reaction A + B = C proceeds from a complex "A+B" via a transition state to a more stable product C. We may model this reaction with en empirical energy function

E(x,y) = ……(see for example exercise 2, however, in that example, E(x,y) has two energy minima that are equally stable)…..

where x and y are two (dimensionless) coordinates. Show that (x,y) = (..,..) represents a local energy minimum. From this position, the reaction proceeds along (increasing values of) x. Find the position of the transition state, x(TS), and the position of the final energy minimum, x(C). Determine the activation energy of this reaction, as well as the total reaction energy E(C) – E(A+B). Verify that the three stationary points are two minima and one saddle point, by evaluating the matrix of 2. derivatives of E. (see exercise 2)

Exercise 3
a) What is meant by the Born-Oppenheimer approximation? (see lecture notes)
b) Describe the iterative process of a geometry optimization. Use a two-atomic molecule as example, where the energy E(R) depends on the interatomic distance R as shown in the figure

below (see page 6 in lecture notes). Assume that dE/dR and also the second derivative can be calculated for a “guessed” value of R. (Hint: Taylor expansion to 2. order of E(R), Newton’s method.)

c) Show that the vibrational frequency of a one-dimensional harmonic oscillator is proportional to the square root of the second derivative of V(x). How is this generalized to a multi-dimensional harmonic oscillator potential, e.g., a molecule with N atoms moving in an approximately harmonic potential E(x1, y1, z1, …, xN, yN, zN)?

d) In the figure below (see figure on page 10 in lecture notes), discuss the relation between the energies E_a and Delta E on one hand, and the kinetics and thermodynamics of the reaction A + B = C on the other hand. How will the speed of this reaction depend upon the temperature? How will the relative concentrations of A+B and C depend upon the temperature?

Exercise 4

What kind of bonds is responsible for stabilizing the double helical structure of DNA? Roughly, what is the bond strength (“binding energy”) of one such bond, say, in comparison to a covalent bond between two H-atoms in the H_2 molecule?