Chemistry 433
“Computational Chemistry”
Winter Semester 1998
Dr. Rainer Glaser

Final Examination
“Mostly ab Initio Molecular Orbital Theory”

Tuesday, May 5, 1998, 3:30 - 5:30

Name:

Question 1 (MOs)	26	
Question 2 (Basis Sets)	30	
Question 3 (Homolysis)	20	
Question 4 (Scenarios)	24	
Total	100	

Question 1. Extended Hückel Theory, Molecular Orbitals and Walsh Diagrams. (26 points)

Inspired by the article “Theoretical Aspects of A Novel Mode of Hydrogen-Hydrogen Bonding.” by Qiang Liu and Roald Hoffmann, *J. Am. Chem. Soc.* **1995**, *117*, 10108-10112. We discussed this article on the ch433w98-l discussion list. You might remember the discussion was quite shall we say “lively”.

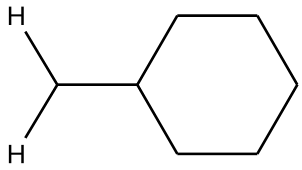
(a) Using structural fomulas, write down the structure of the compound synthesized by the Morris group and the structure of the c_{2v}-symmetrical model compound used in the computational study. (4 points)

Actual structure:	Model used in computational study:

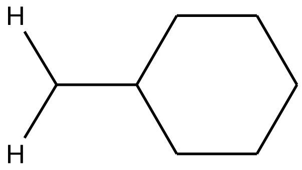
(b) In Table 1, the authors present the EHMO parameters they used. Consider the data given for Ir, briefly explain the meaning of each of the terms and where the values come from (measured, fitted to ..., guessed). Keep in mind that 1 eV equals ______ kcal/mol. (1.5+6x1.5=10.5 points)

H_{ii}(6s) = -11.36 eV	
ζ_{i1} = 2.50	
H_{ii}(6p) = -4.50 eV	
ζ_{i1} = 2.20	
H_{ii}(5d) = -12.17 eV	
ζ_{i1} = 2.80 and ζ_{i2} = 2.56	

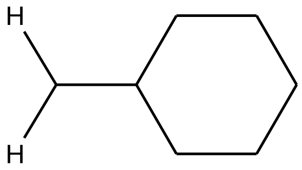
(c) In appendix 2, the authors point out that the ligand $[HSC_5H_4NH]^+$ is isoelectronic with benzyl anion. Let's take a look at **benzyl anion**. Schematically draw the four occupied MOs and the LUMO (MO#1 is most bonding ...) and clearly indicate the node planes as dashed lines. (7.5 points)



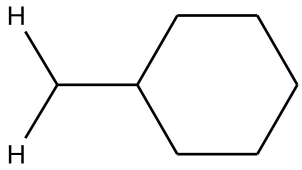
MO2



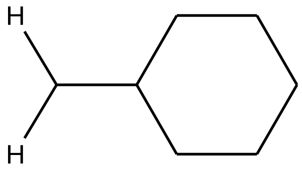
MO4



LUMO



MO1



MO3

(d) Look at Figure 4, the **Walsh diagram** for the HOMO and LUMO of the $[HSC_5H_4NH]^+$ ion. Briefly explain why the HOMO energy goes up while the LUMO energy comes down with rotation about the C-S bond. (4 points)

Question 2. Hartree-Fock and Perturbation Theory, Basis Sets and Reaction Mechanisms. (30 points)

Inspired by the article "Theoretical Studies of Eliminations. 5. Intermolecular vs Intramolecular Eliminations: An ab Initio Study of the Gas-Phase Reaction of NH_2^- with $CH_3CH_2SCH_3$." by Scott Gronert and Peter Freed, *J. Am. Chem. Soc.* **1996**, *61*, 9430-9433. The authors studied the amide anion promoted methanethiolate elimination from $CH_3CH_2SCH_3$ at the MP2/6-31+G**//MP2/6-31+G* level.

(a) What does "MP2/6-31+G**//MP2/6-31+G* level" mean? (3 points)

(b) What is the meaning of "+" in the basis set descriptor? (3 points)

(c) What is the difference between 6-31+G* and 6-31+G**? (3 points)

(d) Why have the zero-point energies been scaled by a factor of 0.9135? (3 points)

(e) Orbitals, basis functions, primitives! (15 points, -0.5 for every wrong or missing)

	NH_2^- Anion	**H_3CS^- Anion**	**$CH_3CH_2SCH_3$**
Number of **valence electrons**:			
Number of **valence atomic orbitals** on all atoms combined:			
Number of all **basis functions** on all non-H atoms combined at 6-31+G*:			
Number of all **basis functions** on all H-atoms combined at 6-31+G*:			
Number of all **basis functions** combined for all atoms at 6-31+G**:			
Number of all **basis functions** combined for all atoms at 6-311+G**:			
Number of all **primitive functions** combined for all atoms at 6-31G*:			
Number of all **primitive functions** combined for all atoms at 6-311+G**:			

(f) All of the basis sets used contain **"d-functions"** for the description of the heavy atoms. What is the purpose of these "d-functions"? Could we do without them? What is the numerical value of a typical d-orbital exponent for a C-atoms? Would the d-orbital coefficient for an S-atom be smaller or larger than the d-exponent for the C-atom? (3 points)

Question 3. Correlation Effects on Homolytic Bond Cleavage Reactions. (20 points)

Inspired by the article “Investigation of Cyclopropane Stereomutation by Quasiclassical Trajectories on the an Analytical Potential Energy Surface.” by David A. Horvat, Shu Fang, and Thatcher Borden, *J. Am. Chem. Soc.* **1997**, *119*, 5253-5254.

(a) Using structural formulas, write down the mechanism for cyclopropane stereomutation predicted by transition state theory (TST) which involves disrotatory opening and conrotatory closure. Use cyclopropane-1,2-d_2 in your discussion. (4 points)

(b) Using structural formulas, write down the mechanism for cyclopropane stereomutation predicted by the dynamic model. Use cyclopropane-1,2-d_2 in your discussion. (4 points)

(c) The authors use a rather high level of electron correlation for the potential energy surface, CASPT2N. This method combines complete active space computations (CAS) with second-order perturbation theory (PT2). The CAS method involves a CI for a limited number of occupied and unoccupied orbitals, the “active space”. In the present case only one pair of electrons is included in the active space. State why it is essential to use such a highly correlated level for this problem. Use the terms “static” and “dynamic” electron correlation. Explain how these correlations are taken into account by the “CASPT2N” method. (8 points)

(d) Can this problem be approximated using RHF or UHF theory. Briefly, explain why or why not. (4)

Question 4. Scenarios. (4 points each, total 24 points)

For each of the problems, briefly state what method would be most appropriate. Chose among the semi-empirical (HMO, EHMO, CNDO, MNDO varieties), Hartree-Fock (RHF, UHF, ROHF), post-Hartree Fock (MPx, (Q)CI, MCSCF, G%, CBS) and density functional methods (X-Corr). Also specify a basis set if your method of choice demands the selection of a basis set. [It is understood that several answers are possible. Try to give "the best" answer given the computing environment you are enjoying.]

Problem	**Suggested Theoretical Treatment**
The binding energy of the van-der-Waals complex between He and Ar.	
The structure of vitamin C, L-ascorbic acid. Vitamin C has the formula $C_6H_8O_6$ and contains two intramolecular H-bonds.	
Intercalation of anthracene into a DNA piece consisting of two strands with two nucleotides each.	
The energy of the acid dissociation reaction of hydrogen peroxide.	
The homolytic dissociation energy of hydrogenperoxide.	
A study of the facial selectivity of the Diels-Alder reaction. (Do you think that the levels used in *JOC* **1998**, *63*, 105-112 are appropriate? Can you do better?)	

Na endlich ist das lamge Final zu Ende!!