

Chemistry 412  
“Computational Organic Chemistry”  
Fall Semester 1999  
Dr. Rainer Glaser

Third and Final Examination  
“Electronic Structure Theory”

Friday, December 10, 1999, Take-Home over Weekend

Name:
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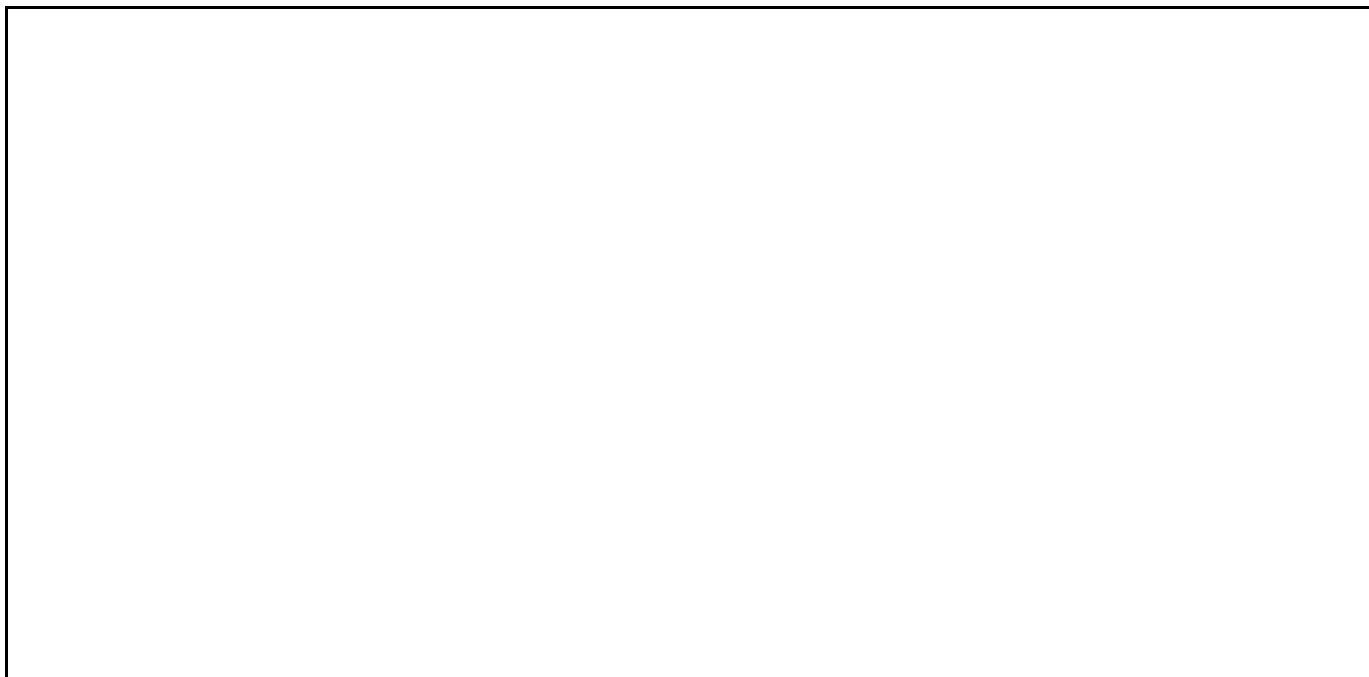
Question 1. Virtual Spaces	20	
Question 2. OCNCO <sup>+</sup>	20	
Question 3. H-Transfer	20	
Question 4. Disulfanes	20	
Question 5. Spin density	20	
Total	100	
Total of final counts <b>twice</b>	• 2	

**Question 1.** Occupied and Virtual Spaces. (20 points)

Electron correlation treatments seek to reduce electron-electron repulsion. This is accomplished by adding correction terms to the Hartree-Fock wavefunction and these corrections terms most conveniently are expressed in terms of small contributions of excited states. These excited states are generated by the excitation of one, two, three, four or more electrons from occupied molecular orbitals into unoccupied molecular orbitals. The ensemble of all the unoccupied MOs is called the “virtual space.” Let’s take a look as to how this virtual space changes with the choice of basis set.

Consider dinitrogen at its experimental bond distance of  $d(\text{N}-\text{N}) = 1.097685 \text{ \AA}$ . Carry out single-point RHF calculations of  $\text{N}_2$  at its experimental geometry using the following basis sets: STO-3G, 3-21G, 6-311G\*, and 6-311+G\*. Furthermore, carry out CISD(full) calculations of  $\text{N}_2$  at its experimental geometry and again using the following basis sets: STO-3G, 3-21G, 6-311G\*, and 6-311+G\*. In the outputs of the RHF calculations, you can find the eigenvalues of all of the occupied and of all of the unoccupied molecular orbitals. In the table provided on the following page, indicate as horizontal lines each of these MO eigenvalues at each of the theoretical levels. Make sure that your drawings are (roughly) to scale.

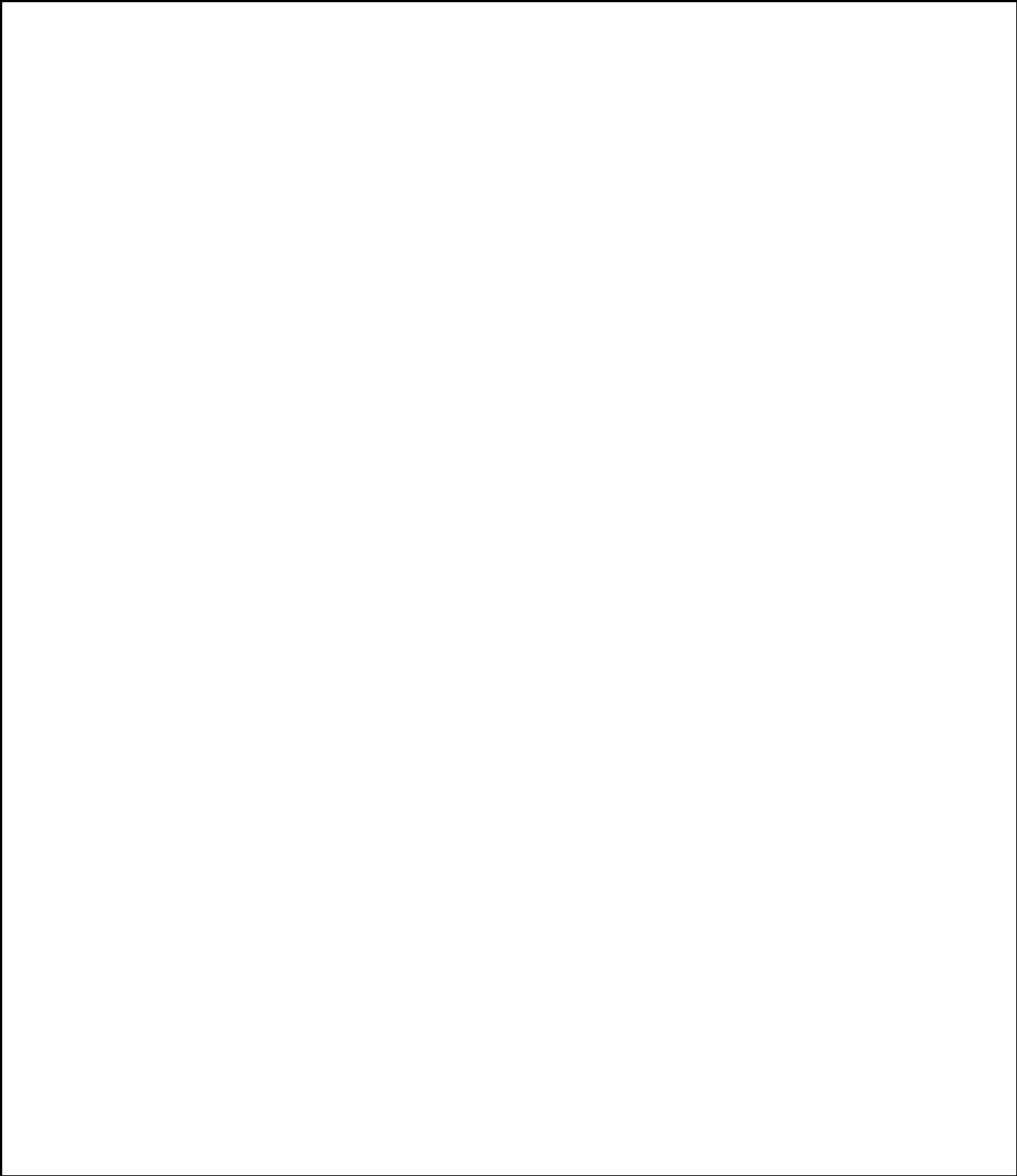
(a) When you have drawn these MO-level diagrams on the following page, return to this page and report the electron correlation energies computed using the different basis sets, e.g.  $E(\text{CISD})-E(\text{RHF})$ . Report these energy differences in *atomic units* and also in the units of *kcal/mol*.



(b) Draw the molecular orbital level diagrams. Indicate which MOs are occupied and which ones are empty in the RHF wavefunction.

Indicate Energy Scale	MO-Levels Using STO-3G	MO-Levels Using 3-21G	MO-Levels Using 6-311G*	MO-Levels Using 6-311+G*

(c) Discuss how the virtual spaces differ, what they have in common, and what the consequences are of these similarities and differences in the correlation treatments.



**Question 2.** Isolation and Structure of OCNCO<sup>+</sup> ion. (20 points)

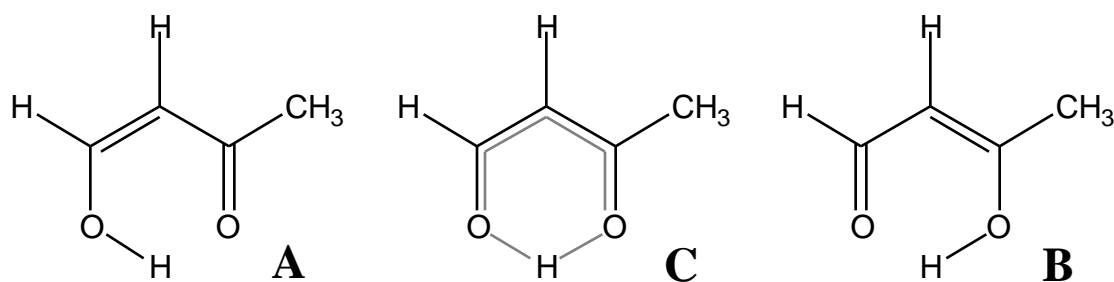
Inspired by the article “Isolation and Structure of OCNCO<sup>+</sup> Ion” by Seppelt *et al.* (*ACIE* **1999**, *15*, 2232.)

(a) The authors have computed the structure of the OCNCO<sup>+</sup> ion at the MP2/6-31G\*\* level of theory. Both the linear and the bent structures were considered and the bent structure was found to be preferred. Using the MP2/6-31G\*\* structure of the bent OCNCO<sup>+</sup> ion reported by these authors, compute the natural populations for the atoms in this ion using the keywords POP=NPA and density=current. The keyword density=current will provide the charge distribution of the correlated wave function. From the log file of this calculation, provide the following items: The MP2 energy, the dipole moment, the NPA charges on N, C, and O. On the basis of the **structural parameters** and the **computed atom charges**, discuss which Lewis structure(s) is (are) best to describe this ion.

**Question 3.** Hydrogen Transfer Reaction. (20 points)

Inspired by the article “Competition Between Wolff Rearrangement and 1,2-Hydrogen Shift in  $\alpha$ -Oxyketocarbenes.” By Quirante *et al.* (*JPC B* **1999**, *103*, 7145.)

The product of 1,2-H- shift in  $\alpha$ -oxyketocarbene **1** is a vinyl ketone **3** (numbers refer to the paper). Let's take a look at a small vinyl ketone in which the RO-group is an HO-group. This system comes in two structure isomers **A** and **B**. The structure isomers **A** and **B** can be interconverted into each other *via* a transition state structure **C** in which a H-atom is shifted between the O-atoms. At the *ab initio* level RHF/6-31G\*, optimize the minima **A** and **B** (make sure you consider the correct methyl conformation) and locate the transition state structure **C**. Compute vibrational frequencies for **A** - **C**. Provide the data requested in the table.



Parameter	<b>A</b>	<b>B</b>	<b>C</b>
RHF/6-31G* total energy in a.u.			
Total <u>unscaled</u> vibrational zero-point vibrational energy computed at RHF/6-31G* in kcal/mol.			
Total <u>scaled</u> vibrational zero-point energies (RHF/6-31G*, kcal/mol). Use scale factor of _____.			
Relative energy (relative to the most stable structure) in kcal/mol <u>without</u> consideration of vibrational zero-point energies.			
Relative energy (relative to the most stable structure) in kcal/mol <u>with</u> consideration of scaled vibrational zero-point energies.			

**Question 4.** Rotational Barrier in Peroxides HO-OH. (20 points)

Inspired by the article “How Unstable are Thiosulfoxides? An *ab Initio* MO Study of Various Disulfanes RSSR (R=H, Me, Pr, All), Their Branched Isomers R<sub>2</sub>SS and the Related Transition States.” By R. Steudel, *et al.* *J. Am. Chem. Soc.* **1997**, *119*, 1990-1996.

Using **Gaussian** and z-matrix inputs optimize three structures of HO-OH – *trans*, *cis*, and *gauche* – at three semi-empirical levels – MNDO, AM1 and PM3 – and at RHF/6-31G\*. Discuss the theoretical model dependency of the relative energies. Which levels are best, worst and why?

<b>Parameter</b>	<i>trans</i>	<i>cis</i>	<i>gauche</i>
Heat of formation MNDO AM1 PM3 RHF/6-31G*			
Relative energy (relative to the most stable structure) MNDO AM1 PM3 RHF/6-31G*			

Discussion:

**Question 5.** Molecular Orbitals and Spin Densities. (20 points)

Sort of inspired by “Direct observation of d-orbital holes and Cu-Cu bonding in Cu<sub>2</sub>O.” J. M. Zuo, *et al.* *Nature* **1999**, 401, 49-52.

Using **Chem3D ULTRA** on the PCs in the computer laboratories, compute allyl radical using PM3 semi-empirical theory. Optimize allyl radical at the PM3 level as an open-shell system and compute properties (again at PM3 and selecting open-shell system). Compute and plot the following items: (1): Isocontour plot of the HOMO and provide the energy of this MO on the plot. (2) and (3): An isocontour plot of the spin density with a *positive* isocontour level setting and an isocontour plot of the spin density with a *negative* isocontour level setting. Select the magnitudes as you see fit. Submit plots of these items. The HOMO describes the MO of the unpaired electron. What does it mean that spin density occurs also at other places and that there is spin density of both kinds (*alpha* and *beta*)?

Discussion: