Chemistry 433
"Computational Chemistry"
Winter Semester 1998
Dr. Rainer Glaser

Second 1-Hour Examination
"Extended Hückel Theory & Semi-Empirical MO Theory"

Wednesday, April 8, 1998, 8:00 - 8:50

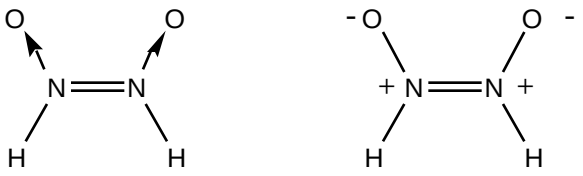
Name:

Question 1 (LCDs)	30	
Question 2 (CNDO *vs* NDDO)	20	
Question 3 (SE Parameters)	20	
Question 4 (HNO dimer)	30	
Total	100	

Question 1. Level Correlation Diagram and Extended Hückel Theory. (30 points)

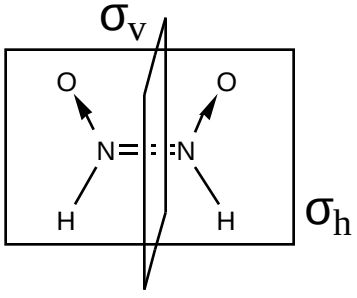
In lecture, we discussed the paper "Non-Least-Motion Potential Surfaces. The Dimerization of Methylenes and Nitroso Compounds" by Roald Hoffmann et al., *J. Am. Chem. Soc.* **1970**, *92*, 1460, in some detail. For the nitroso compound, the dimerization can proceed in two ways in that the *cis* or the *trans* isomer can be formed (compounds **5** and **6** in the paper). The formation of **5** was discussed in the paper and a **level correlation diagram** was presented for this reaction in Figure 2 of that article. Here, we will be concerned with the level correlation diagram for the formation of the *trans* isomer via the least motion path.

(a) Draw Lewis structures of the *cis* HNO dimer. Make sure that you write down formal charges as appropriate. (Hoffmann *et al.* write the NO bonds as dative bonds. Give that Lewis structure. Then also give the Lewis structures in which the NO bonds are covalent.) (2 points)

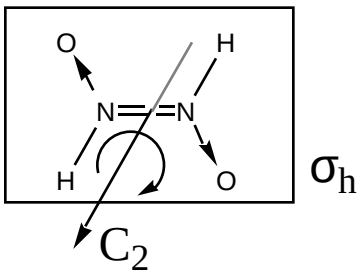


(b) Symmetry Elements. Draw the *cis* and *trans* isomers of the dimer of HNO. For each isomer, indicate the **two** symmetry elements (mirror plane, rotational axis, inversion center) that are necessary to describe the **least motion paths** for the two dimerizations. (2 points)

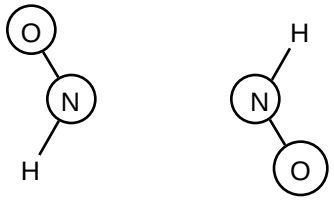
Cis Isomer

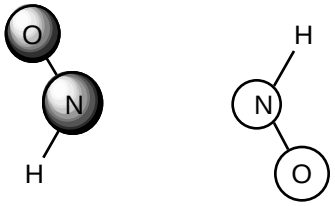


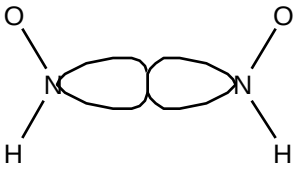
Trans Isomer

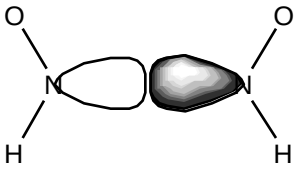


(c) For the construction of the level correlation diagram of the ***trans* isomer**, the six relevant orbitals are, on the **monomer** side, the two *N* lone pairs, and the π and π* levels of the two HNO groups. Sketch each of the associated orbitals (use p-AO and sp^2 lobes, indicate phase information) and specify the symmetry of each orbital with regard to the two symmetry elements you chose in section (b). (9 points)

<table>
<tr>
<td>π-MO #1
 

σ_h: A C_2: S</td>
<td>π-MO #2
 

σ_h: A C_2: A</td>
</tr>
<tr>
<td>n-MO #1
 

σ_h: S C_2: S</td>
<td>n-MO #2
 

σ_h: S C_2: A</td>
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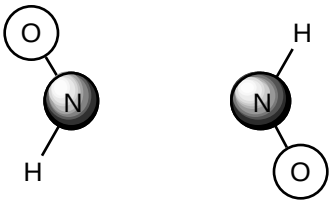
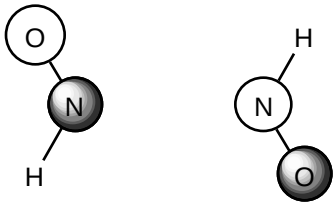
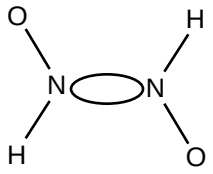
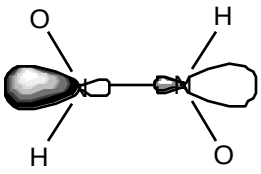
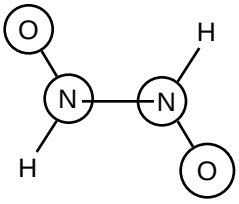
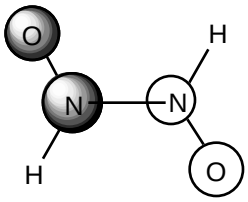
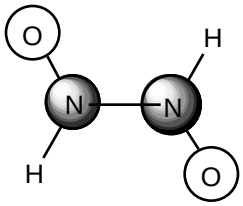
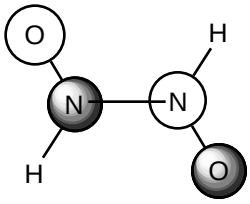
<tr>
<td>π -MO #1
 

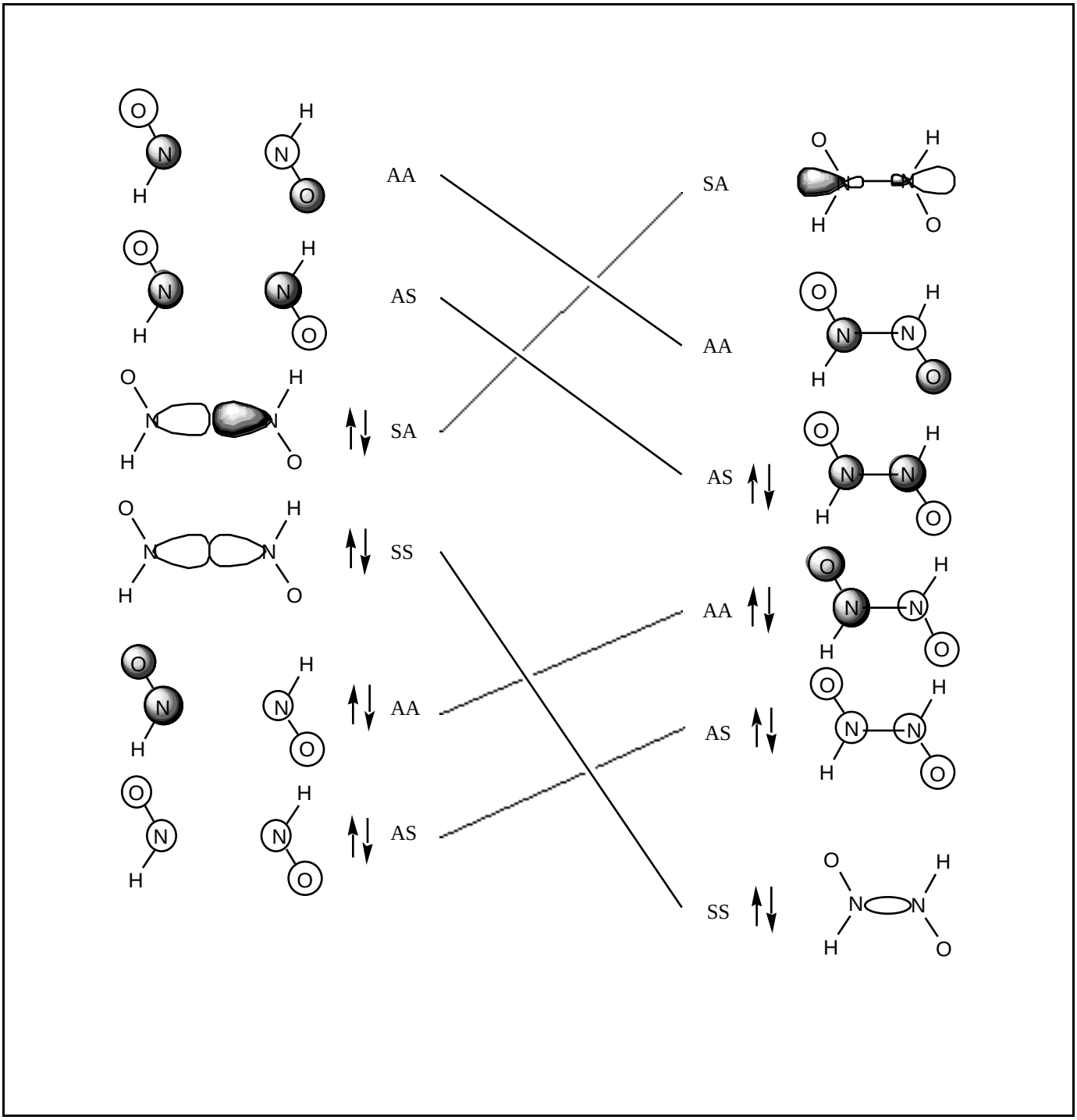
σ_h: A C_2: S</td>
<td>π -MO #2
 

σ_h: A C_2: A</td>
</tr>
</table>

(d) For the construction of the level correlation diagram of the ***trans* isomer**, the six relevant orbitals are, on the **product** side, the σ and σ* MOs and the four π and π levels. Sketch each of these orbitals (use p-AO and sp^2 lobes, indicate phase information) and specify the symmetry of each orbital with regard to the two symmetry elements you chose for the trans isomer in section (b). (9 points)

σ-MO #1  σ_h: S C_2: S	σ -MO #2  σ_h: S C_2: A
π-MO #1  σ_h: A C_2: S	π-MO #2  σ_h: A C_2: A
π-MO #3  σ_h: A C_2: S	π-MO #4  σ_h: A C_2: A

(e) Construct of the **level correlation diagram** for the ***trans* isomer**. Give the HNO monomer levels on the left, give the HNO dimer levels on the right. Give the symmetry symbols for each level. Make sure that the ordering of the MOs is correct (high energy on top of page). Indicate occupancies of the orbitals with up & down arrows as usual. Connect the appropriate MO levels on the monomer and dimer sides. (8 points)



Question 2. CNDO *versus* NDDO. (20 points)

(2 points) CNDO stands for: COMPLETE NEGLECT OF DIFFERENTIAL OVERPAP
(2 points) NDDO stands for: NEGLECT OF DIATOMIC DIFFERENTIAL OVERLAP

(a) Briefly explain what "differential overlap" means. Your written explanation should be accompanied by an illustration. Pick a simple molecule, such as CO for example, for your illustration. (8 points)

Simply the overlap between different Aos.
In the zero differential overlap methods (ZDO), this overlap is assumed to be zero! Bold.
Draw CO, for example, and show the overlap between one AO on C and one AO on O.
In the ZDO approximation, that overlap is assumed to be zero.

(b) Briefly explain what part of "the hamiltonian" is most affected by approximate methods that neglect "differential overlap". (8 points)

The Js and the Ks. Expand a bit.
The electron-electron repulsion is affected most.

Question 3. Semi-Empirical Parameters. (20 points)

List five parameters which enter any of the semi-empirical theories you encountered in Chemistry 433 (EHMO, CNDO, CNDO/2, INDO, MNDO, AM1, PM3). Specify (1) the symbol and (2) the name of the parameter, (3) state how the parameter is determined (fitted to ..., derived from ...), and (4) state which part of the hamiltonian is determined by this parameter. (1 p. each part for each parameter)

Question 4. Computed Semi-Empirical Results on the HNO Dimerization. (30 points)

(a) The (rather long despite editing) supplementary material to this questions contains the output files of MNDO, AM1, PM3, and CNDO calculations of HNO monomer and of the *trans*-dimer. Go through these outputs and collect the data needed to complete the table. Then spend a some five minutes to compute the ***trans* preference energy** (state by how many kcal/mol the *trans* isomer is preferred; negative number if *cis* is more stable) and the **dimerization energy** (always compute for the *trans* isomer). (10 points for getting the table completed)

Method	E(HNO)	E(*Cis*-Dimer)	E(*Trans*-Dimer)	*Trans*-Preference Energy	Energy of Dimerization (for *trans*)
	in a.u.	in a.u.	in a.u.	in kcal/mol	in kcal/mol
MNDO	0.006011	0.100707	0.088688	7.54	48.11
AM1	0.003426	0.084729	0.066833	11.23	37.64
PM3	0.021961	0.088719	0.067787	13.68	14.98
CNDO	-30.741898	-61.655293	-61.662744	4.68	-112.29

(b) Discuss the data compiled in the table. State what you think are the best and the worst numbers and say why you think so. Be brief and concise and precise. (10 points)

The best data suggest a *trans*-preference energy of 4.4 kcal/mol
The best data suggest the dimerization to be slightly exothermic, -15.8 kcal/mol.
The best data can be found in *J. Org. Chem.* **1996**, *61*, 1047-1058.

Thus: CNDO matches the TPE best and it is the only method to get the sign of the DE while the number for the DE is obviouslt nonsense (of by over 100 kcal/mol).

Among the NDDO methods, the sign of the TPE is always right and that for the DE is always wrong. Not too encouraging!
MNDO happens to give the better TPE, PM3 happens to give the closer (but still very wrong) DE value.

Most people would expect PM3 to do best because of its parameterization. Yet, for molecules that are polar and not in the test set, anything can happen and that is the lesson to learn here!

(c) Now consider only the level you think is the best level among the four levels for this specific problem. Find the Mulliken populations of HNO and of the *trans* dimer. Comment on the electron density shifts that are associated with the formation of the dimer. (10 points)

This part of the question was graded irrespctove of your choice of method in the previous part. All I wanted to see is that you can find the correct numbers in the given outputs (5 p).
In addition that had to be some statement as to the relaxation. (3 p)
Finally, there were 2 points in it for saying something as to what might cause the relaxation.

For the PM3 data, you would find Atom (monomer, *trans* dimer)
H(0.027, 0.129)
N(0.246,0.501)
O(-0.273,-0.630)

Dimerization shifts electron density from N to O.

Maximize electron density on most electronegative atom.
Generate large quadrupole moment.

For a recent discussion of the HNO dimerization, see: "Why Do Nitroso Compounds Dimerize While Their Oxime Tautomers Do Not? A Structural Study of the *trans*-Dimer of 2-Chloro-2-methyl-3-nitrosobutane and Higher Level ab Initio Study of Thermodynamic Stabilities and Electronic Structures of Configurational Isomers of Diazene Dioxides." R. Glaser, R. K. Murmann, and C. L. Barnes *J. Org. Chem.* **1996**, *61*, 1047-1058.

Na endlich ist der Test zu Ende!!