

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

Second Examination
“Hartree-Fock Theory & Approximate Methods”

Wednesday, November 17, 1999, Take-Home

Name:	
	Rainer AK

Question 1. Benzene MOs	25	
Question 2. C ₃ H ₆ MOs	15	
Question 3. CH ₂ Dimerization	20	
Question 4. HMO & EHMO	20	
Question 5. CNDO	20	
Total	100	

Question 1. Molecular Orbitals of Benzene. (25 points)

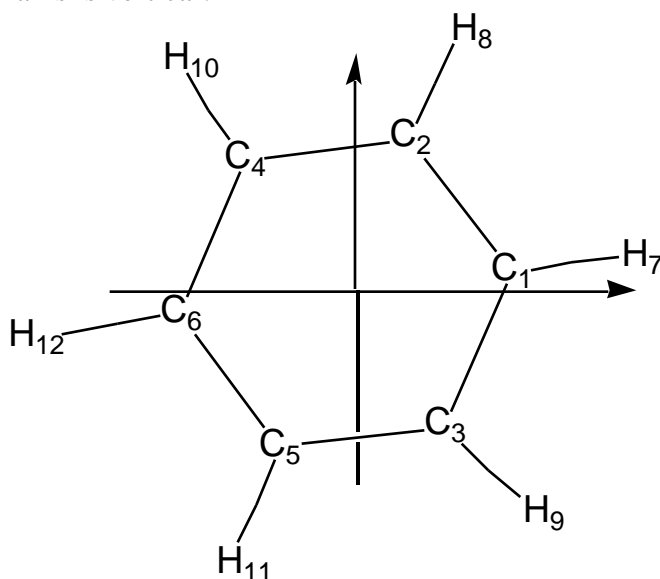
Benzene was optimized at the RHF/STO-3G level without any symmetry constraints imposed. The molecule optimized to the *de facto* D_{6h} symmetric structure. Since the optimized structure is very, very close to planar but remains not perfectly planar, the σ / π -separation in the MOs is not perfect. Ignore this imperfection and recognize what matters.

(a) Cartesian coordinates of the optimized structure are given for the molecule in its **standard orientation**. Draw the molecule in the XY-plane in the space below and label each center. (3 pts.)

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	1.379187	0.145609	-0.000034
2	6	0.563478	1.267214	0.000040
3	6	0.815702	-1.121594	-0.000003
4	6	-0.815693	1.121603	-0.000006
5	6	-0.563491	-1.267211	0.000005
6	6	-1.379182	-0.145621	-0.000008
7	1	2.455774	0.259282	-0.000086
8	1	1.003343	2.256396	0.000101
9	1	1.452430	-1.997119	0.000060
10	1	-1.452432	1.997118	-0.000082
11	1	-1.003346	-2.256399	0.000068
12	1	-2.455774	-0.259276	-0.000021

X-axis in horizontal and Y-axis is vertical!



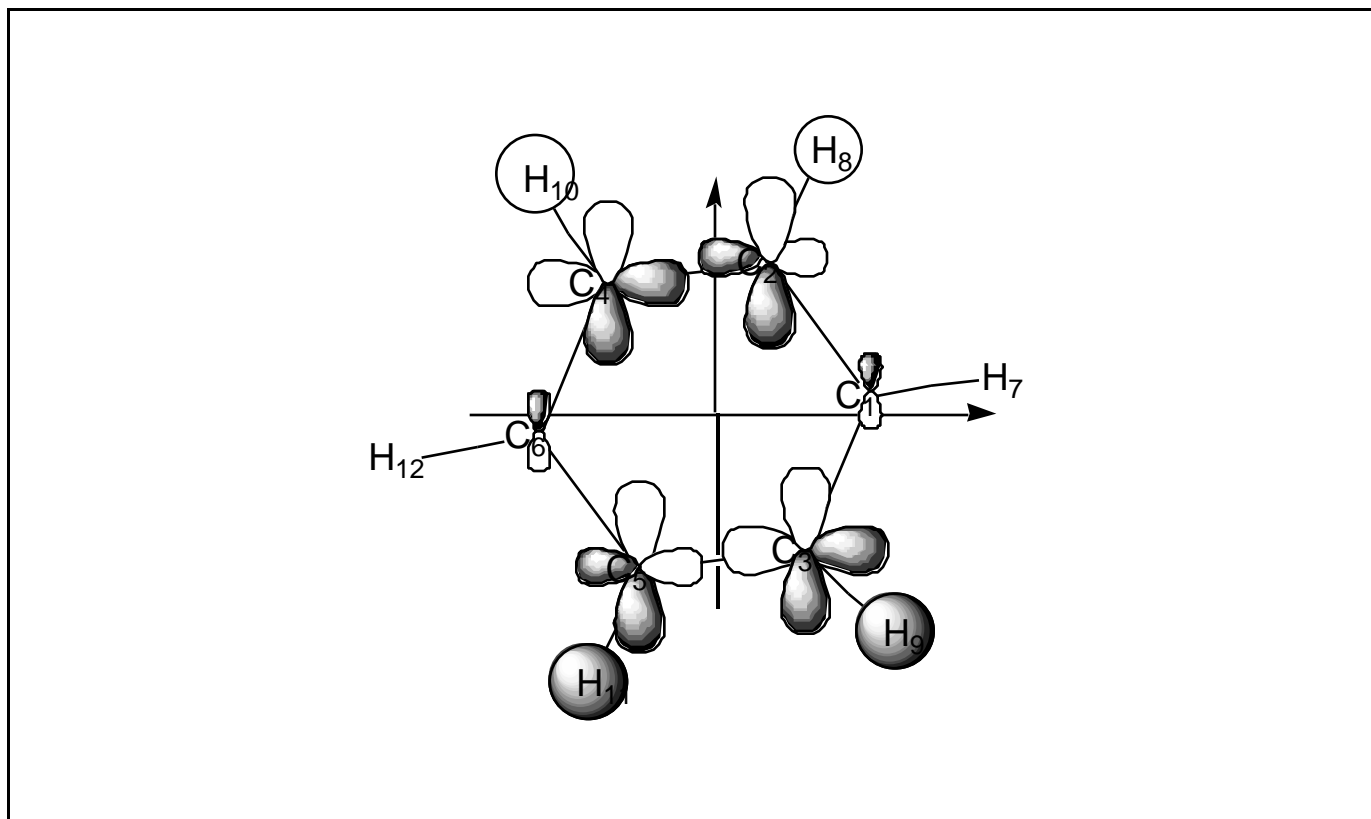
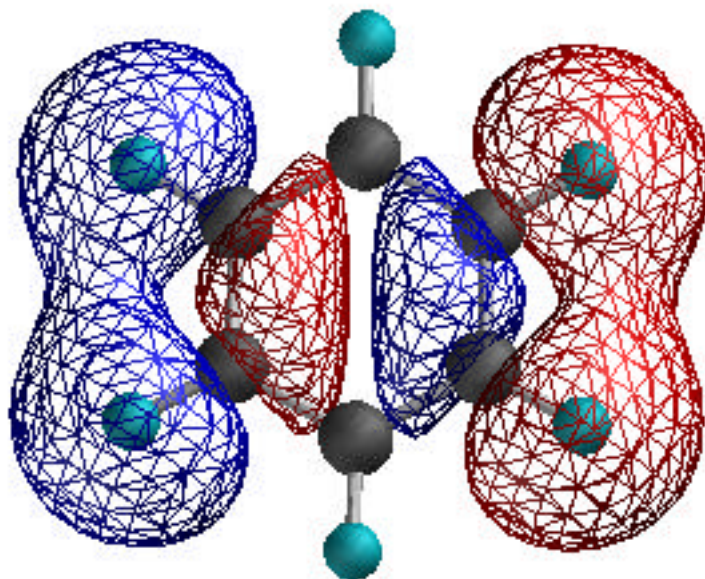
(b) The coefficients of MOs 16 – 21 are shown. Benzene contains **42** electrons and **12** of these are in core orbitals. Hence, the “space” of the valence MOs extends from MO **7** to MO **21**. Benzene contains **3** π -MOs and **2** (2, 3 or none) of these are degenerate. Indicate for each MO whether it is a π -MO or a σ -MO. For each of the π -MOs, write down how many nodes planes it contains. (12 points)

	16 (2)	17 (1)	18 (3)	19 (4)	20 (4)	21 (2)
EIGENVALUES	-0.53608	-0.46087	-0.43378	-0.43378	-0.28263	-0.28263
1 1 C 1S	-0.00010	0.00000	0.00752	-0.00089	0.00000	0.00000
2 2S	0.00030	0.00001	-0.01525	0.00180	0.00001	0.00001
3 2PX	0.00931	-0.00002	0.28354	0.00163	-0.00004	-0.00003
4 2PY	-0.10110	-0.00006	-0.00954	-0.33266	0.00001	0.00003
5 2PZ	-0.00001	0.33333	0.00001	-0.00007	-0.48565	-0.21538
6 2 C 1S	0.02304	0.00000	-0.00299	0.00696	0.00000	0.00000
7 2S	-0.07201	-0.00001	0.00605	-0.01411	-0.00001	0.00001
8 2PX	0.17652	0.00004	-0.32521	-0.01452	0.00002	0.00001
9 2PY	0.27127	0.00003	0.02245	0.29100	0.00003	-0.00004
10 2PZ	0.00001	0.33333	0.00004	-0.00002	-0.42933	0.31292
11 3 C 1S	-0.02314	0.00000	-0.00453	-0.00607	0.00000	0.00000
12 2S	0.07232	-0.00001	0.00920	0.01230	0.00001	0.00000
13 2PX	-0.22953	0.00003	-0.31556	0.02802	0.00001	0.00001
14 2PY	0.22989	0.00008	-0.02008	0.30065	0.00000	-0.00004
15 2PZ	-0.00003	0.33333	0.00003	-0.00009	-0.05633	-0.52827
16 4 C 1S	0.02314	0.00000	-0.00453	-0.00607	0.00000	0.00000
17 2S	-0.07231	0.00001	0.00918	0.01230	-0.00001	0.00001
18 2PX	-0.22955	-0.00008	0.31555	-0.02802	-0.00001	-0.00004
19 2PY	0.22990	-0.00003	0.02010	-0.30066	0.00000	0.00002
20 2PZ	-0.00003	0.33333	0.00008	-0.00003	0.05631	0.52828
21 5 C 1S	-0.02304	0.00000	-0.00299	0.00696	0.00000	0.00000
22 2S	0.07201	0.00000	0.00606	-0.01410	-0.00001	0.00001
23 2PX	0.17650	-0.00003	0.32522	0.01452	0.00000	-0.00002
24 2PY	0.27127	-0.00003	-0.02243	-0.29099	0.00002	0.00000
25 2PZ	-0.00003	0.33333	0.00004	-0.00006	0.42935	-0.31290
26 6 C 1S	0.00010	0.00000	0.00752	-0.00089	0.00000	0.00000
27 2S	-0.00030	-0.00001	-0.01525	0.00181	0.00001	0.00000
28 2PX	0.00933	0.00004	-0.28355	-0.00160	0.00000	0.00000
29 2PY	-0.10110	0.00005	0.00953	0.33267	0.00000	-0.00001
30 2PZ	-0.00002	0.33333	0.00006	-0.00006	0.48566	0.21535
31 7 H 1S	-0.00104	-0.00004	0.29706	-0.03522	-0.00002	-0.00001
32 8 H 1S	0.24420	0.00006	-0.11801	0.27489	0.00001	-0.00002
33 9 H 1S	-0.24522	-0.00004	-0.17905	-0.23964	0.00001	0.00002
34 10 H 1S	0.24523	0.00001	-0.17903	-0.23965	0.00000	0.00002
35 11 H 1S	-0.24419	0.00006	-0.11803	0.27487	0.00000	-0.00001
36 12 H 1S	0.00102	-0.00005	0.29706	-0.03524	0.00000	-0.00001

(c) Which lines in the table would be missing if these were EHMO molecular orbitals? (4 points)

EHMO uses a valence minimal basis. The **red lines** would not be there.

(d) The picture shows the isocontour depiction of one MO of MOs 16 - 21. Identify that MO. Then draw the benzene molecule in the standard orientation in the empty space below and indicate the AO contributions to this MO. As much as possible, draw the AOs in a size that reflects the AO coefficient of that MO. Finally, indicate the types and numbers of node surfaces that characterize this MO. (6 pts.)

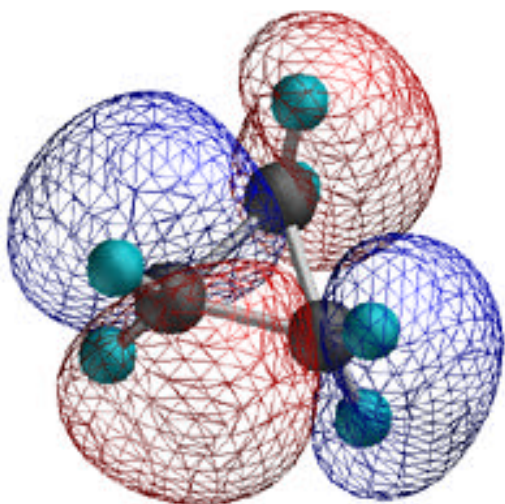


Question 2. Cyclopropane Molecular Orbitals. (15 points)

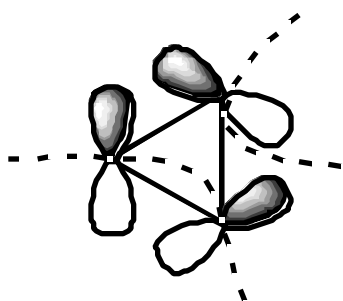
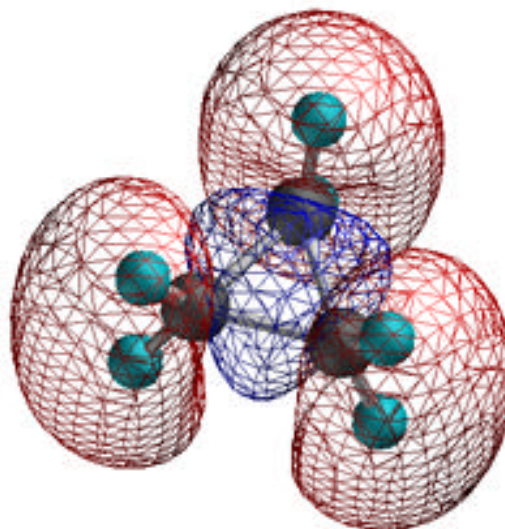
Cyclopropane is a rather strained molecule with remarkable properties. Alkanes and less strained cycloalkanes react with Br_2 by way of substitution. Yet, cyclopropane reacts with Br_2 by way of C-C bond cleavage and addition. It is for this reason that the σ -bonds in cyclopropane are said to have “ π -character.” The bonding in cyclopropane is hard to explain based on hybrid atomic orbitals. The (C-C-C) angles are 60° while a standard sp^3 hybridization is best for bonding angles of about 109° . In the context of valence bond theory, one needs to invoke the concept of “banana bonds” to describe the bonding in cyclopropane. In LCAO theory, everything is straightforward: Some of the σ -MOs are constructed mainly from carbon p-AOs. Let’s look at two of these orbitals.

For each of the MOs shown, state how many nodes it contains and what kind(s) of node(s) there is (are). Indicate the nodes in the MO depictions. The triangles symbolize the C-frame of cyclopropane. Indicate schematically the AOs at each C-atom that linearly combine to form the MO shown on top.

HOMO-1

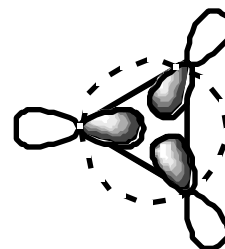


HOMO-4



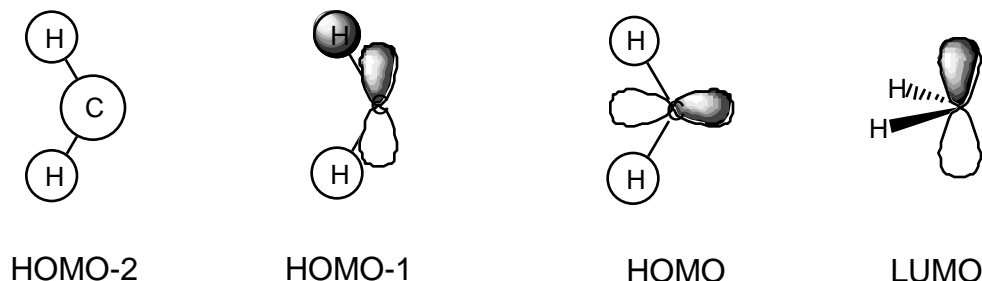
2 nodes

1 node sphere



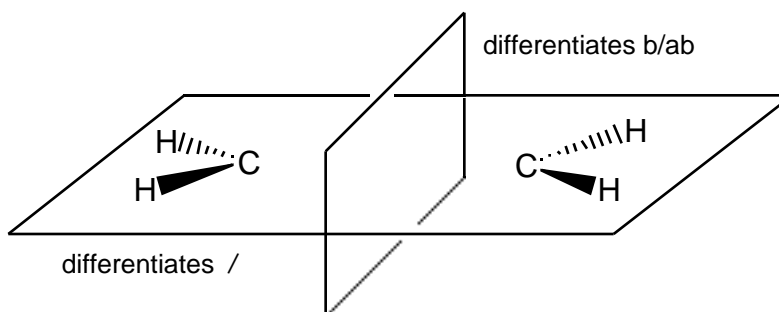
Question 3. Carbene Dimerization. (20 points)

We discussed the least motion dimerization of carbene in the lecture using a molecular orbital diagram. In the lecture, the diagram shown was qualitative. We now want to revisit the issue using some quantitative data derived from EHMO calculations. The MOs of carbene are depicted schematically and their energies are listed in the left column of the table. The right column contains the MO eigenvalues of the ethene MOs.

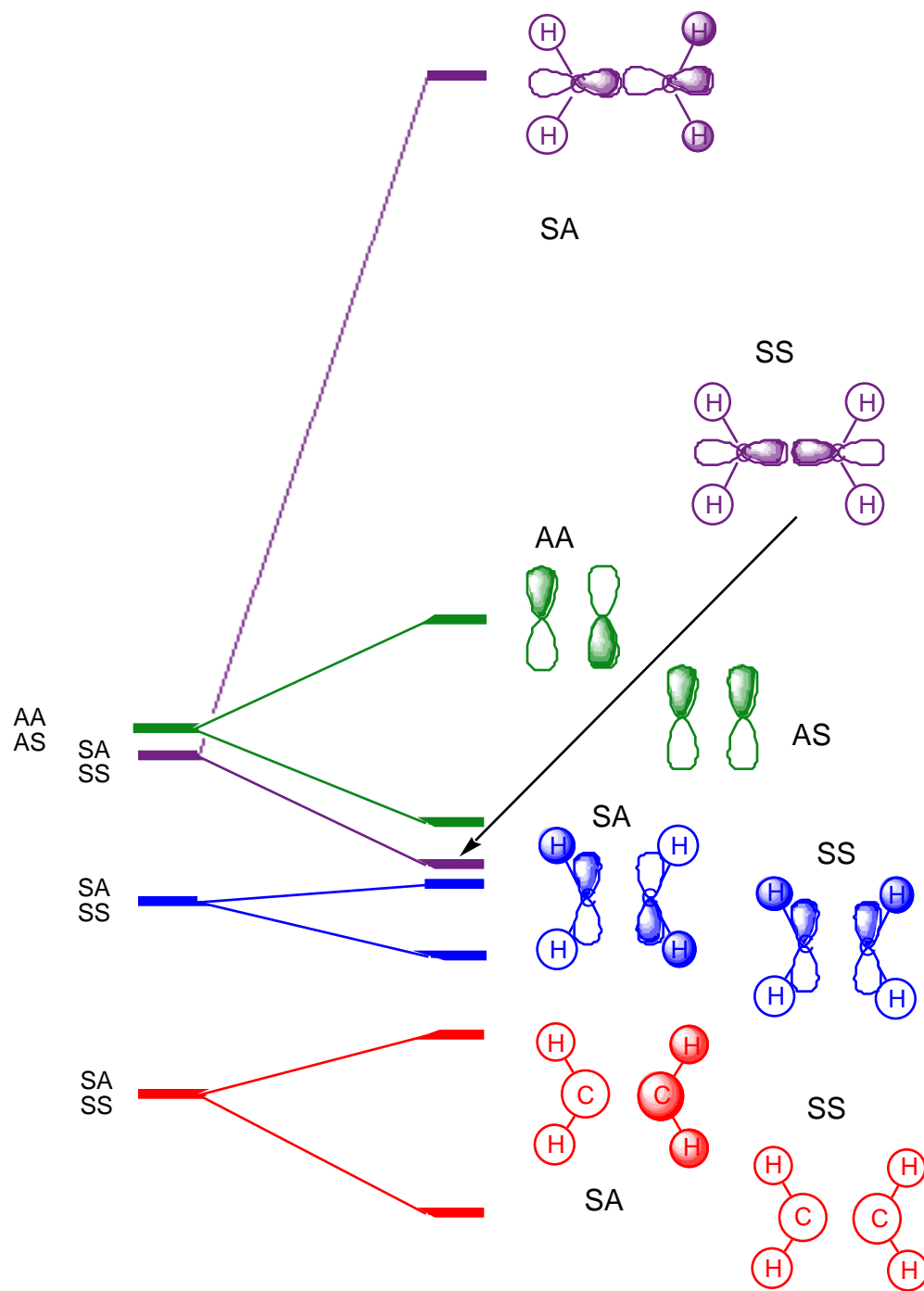


CARBENE		ETHENE	
LUMO	-11.4000 eV (pi)	LUMO+5	208.3343 eV (sigma)
HOMO	-12.6702 eV (sigma)	LUMO	-0.8435 eV (pi)
HOMO-1	-22.5927 eV (sigma)	HOMO	-17.4641 eV (pi)
HOMO-2	-35.9302 eV (sigma)	HOMO-1	-19.8112 eV (sigma)
		HOMO-2	-20.9889 eV (sigma)
		HOMO-3	-25.7388 eV (sigma)
		HOMO-4	-31.6299 eV (sigma)
		HOMO-5	-43.6332 eV (sigma)
NOTE: LUMO+1 through LUMO+4 Are C-H antibonding MOs.			

(a) The scheme shows two carbene as they approach each other along the least motion path. Indicate the symmetry elements that matter for this reaction.



(b) The MO energies range from -45 to 40 eV. Draw the molecular orbital diagram to scale (as much as possible). For each ethene MO, sketch the MO indicating clearly the types and phases of the AOs involved. For all MOs, indicate the symmetry with regard to each of the symmetry elements that matter for the reaction. Connect the appropriate molecular orbitals of the starting materials and of the product.



Question 4. Hückel Theory and Extended Hückel Theory. (20 points)

Hueckel Theory and Extended Hueckel Theory are approximations to Hartree-Fock theory. The left column lists a number of key terms of Hartree-Fock theory. In the columns to the right, indicate the approximations made in dealing with these terms in the HMO and EHMO theories.

	HMO	EHMO
H_{ii}	Alpha	One H_{ii} for each valence AO of each atom
H_{ij}	Beta	$K \cdot 1.5 \cdot (H_{ii} + H_{jj}) \cdot S_{ij}$
S_{ij}	ij	Compute all
J_{ij}	No explicit e-e repulsion!	No explicit e-e repulsion!
K_{ij}	No explicit e-e exchange!	No explicit e-e exchange!

Question 5. CNDO Theory and Parameterizations. (20 points)

(a) CNDO stands for “Complete Neglect of Differential Overlap.” Explain what this means. Make a clear distinction between “overlap” and “differential overlap.” Your explanation should state which types of repulsion integrals are affected by this approximation. Writing down the appropriate equation is desirable but not sufficient. There has to be a written statement as to the meaning of the equation.

(b) One of the essential parameters in any approximative theory is the bonding parameter β . In HMO theory, this parameter is just one number because there are only CC bonds. In EHMO and CNDO theory, this parameter is handled in a comparable manner in that β_{AB} is treated as the average between properties of atoms A and B. Below, the EHMO and CNDO equations are written in a way that demonstrates this similarity. Note that there is only one β_A° per atom A while there is two $\beta_{\mu\mu}$ per atom A. EHMO makes a difference between the s- and p-AOs when it comes to bonding, while CNDO/1 does not. (10 points)

EHMO: $H_{\mu} = 0.5 \cdot (1.75 \cdot \beta_{\mu\mu} + 1.75 \cdot \beta_A^\circ) \cdot S_{\mu}$	CNDO: $H_{\mu} = 0.5 \cdot (\beta_A^\circ + \beta_B^\circ) \cdot S_{\mu}$
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The equation for EHMO suggest how one might come up with a good guess for the β_A° . One needs to know the ionization energies from 2s and 2p and multiply their average by 1.75. The EHMO $\beta_{\mu\mu}$ are provided. Find the average ionization potentials (AIP) used to fix the $U_{\mu\mu}$ data in CNDO/1. Compute the averages and compare them to the β_A° data.

	β_A°	$-\beta_{\mu\mu}(2s)$ [eV]	$-\beta_{\mu\mu}(2p)$ [eV]	-1.75• EHMO Average	CNDO/1 -AIP(2s) [eV]	CNDO/1 -AIP(2p) [eV]	-1.75• AIP Average
Li	9	5.392	3.600	7.868	5.39	3.54	7.814
Be	13	9.322	6.000	13.407	9.32	5.96	13.370
B	17	12.930	8.298	18.574	14.05	8.30	19.556
C	21	16.590	11.260	24.369	19.44	10.67	26.346
N	25	20.330	11.260	27.641	25.58	13.19	33.924
O	31	28.480	13.620	36.838	32.38	15.85	42.201
F	39	37.850	17.420	48.361	40.20	18.66	51.003

How do the data compare?

Note the signs of all the numbers in the above table!

The betas used in CNDO are a lot smaller in magnitude than the estimates based on the ionization energies. Why might this be good? If you neglect a lot of ee-repulsion, well then you better make sure that the “bonding” also comes out a bit smaller. It is a matter of cancellation of two errors. Get it?