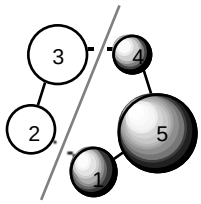
Chemistry 433, Winter Semester 1998, Dr. Glaser
Quiz I: "HMO", Wednesday, March 11, 1998, 20 minutes, not announced

Your Name:

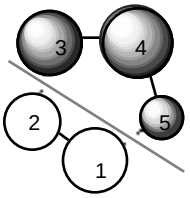
Question 1. Cyclopentadienyl Radical, Cation, and Anion. (18 points)

(a) On p. 3-5, HMO outputs are given of cyclopentadienyl radical, cation, and anion. Sketch MO #2 and MO #3 drawing circles whose radii reflect the AO contribution and use black and white circles to indicate sign. Clearly indicate where the nodes are. (6 points)

MO #2



MO #3



(b) Consider the π-densities of the three species. For the cation and the anion, all C-atoms have the same π-density. Yet, for the neutral, the present calculation would indicate different π-densities for each C-atom? Does that make sense? Why or why not? (6 points)

No, not really. You can draw five resonance forms that all are degenerate.
That would imply that there is 0.2 unpaired electron on each C.
The configuration is: Norm [pi(2)pi'(1) + pi(1)pi'(2)]

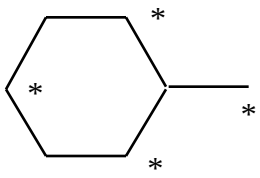
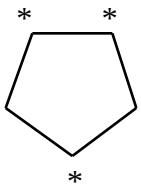
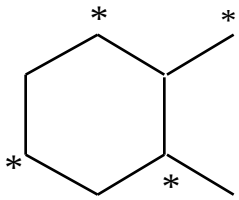
(c) Show how the **C1-C2 Bond Order** is computed for the cation. Show how the **C1 π-density** is computed for the anion. (6 points)

bond order C1-C2 in cation: 2*(0.447*0.447)-(0.497*0.219)+(0.593*0.392)=0.524
C1 pi-density: 2*(0.200)+2*(0.048)+2*(0.352)=1.2

Points for Question 1:	/18		
Points for Question 2:	/15		
Points for Question 3:	/7		
Points for Question 4:	/10	Total Points:	/50

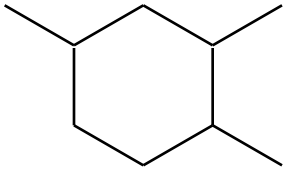
Question 2. Alternating and Non-Alternating Hydrocarbons.

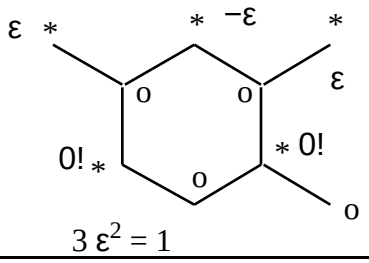
For each of the unsaturated hydrocarbon, mark the carbons of the "stared" and "circled" sets, state whether it is alternant or non-alternant, whether it is odd or even, whether its MOs are symmetric about the α-level, and, finally, give the number of non-bonding MOs. (15 points)

		
alt./non-alt.? alternant	alt./non-alt.? non-alternant	alt./non-alt.? alternant
odd/even? odd	odd/even? odd	odd/even? even
sym. about α? Yes	sym. about α? No	sym. about α? Yes
# of non-bd. Mos? 1	# of non-bd. MOs? 0	# of non-bd. MOs? 0

Question 3. (7 points)

Determine the HOMO for the alternant hydrocarbon shown. Show work. No need to evaluate the square root that will show up.





Question 4. Heteroatoms. (10 points)

Write down the secular determinant for **pyrrole** in two ways: First consider only how H_{ii}(N) is accounted for. In the second approximation also consider polarization effects on the C-atom(s) to which N is attached. For the N-atom in pyrrole, the δ-value is 0.5 and the ρ-value is 0.8.

1. Approx. (assume N is atom 3)	2. Approx. (assume N is atom 3)
aC bC 0 0 bC bC aC 0.8bC 0 0 0 0.8bC aC+0.5bC 0.8bC 0 0 0 0.8bC aC bC bC 0 0 bC aC	aC bC 0 0 bC bC 1.05aC 0.8bC 0 0 0 0.8bC aC+0.5bC 0.8bC 0 0 0 0.8bC 1.05aC bC bC 0 0 bC aC

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**********************************************************
*             Hueckel Molecular Orbital Program          *
*           Rainer Glaser, UMC, January 21, 1991         *
*       Written for but not limited to 30 carbon atoms   *
**********************************************************

Title: neutral

HMO Connectivity Matrix:
  0.  1.  0.  0.  1.
  1.  0.  1.  0.  0.
  0.  1.  0.  1.  0.
  0.  0.  1.  0.  1.
  1.  0.  0.  1.  0.

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3      4      5
  2.000  0.618  0.618 -1.618 -1.618

  0.447  0.219 -0.593  0.580  0.253
  0.447 -0.497 -0.392 -0.618  0.136
  0.447 -0.526  0.351  0.419 -0.473
  0.447  0.172  0.609 -0.061  0.630
  0.447  0.632  0.025 -0.321 -0.545

The squared MO coefficient vectors are
    1      2      3      4      5
  0.200  0.048  0.352  0.336  0.064
  0.200  0.247  0.153  0.381  0.019
  0.200  0.277  0.123  0.176  0.224
  0.200  0.029  0.371  0.004  0.396
  0.200  0.399  0.001  0.103  0.297

Charge:   0    Number of Electrons:  5
Doubly occ. MOs:   2   Singly occ. MOs:   1

Ground State Energy:   5 alpha + 5.854 Beta
The ground state electron configuration is:
 2 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

Bond  1- 2 has pi-bond order:   0.415
Bond  1- 5 has pi-bond order:   0.662
Bond  2- 3 has pi-bond order:   0.785
Bond  3- 4 has pi-bond order:   0.433
Bond  4- 5 has pi-bond order:   0.632

Atom  1 has pi-density:   0.848
Atom  2 has pi-density:   1.047
Atom  3 has pi-density:   1.077
Atom  4 has pi-density:   0.829
Atom  5 has pi-density:   1.199
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*********************************************************
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*       Written for but not limited to 30 carbon atoms  *
*********************************************************

Title: cation

HMO Connectivity Matrix:
  0.  1.  0.  0.  1.
  1.  0.  1.  0.  0.
  0.  1.  0.  1.  0.
  0.  0.  1.  0.  1.
  1.  0.  0.  1.  0.

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3      4      5
  2.000  0.618  0.618 -1.618 -1.618

  0.447  0.219 -0.593  0.580  0.253
  0.447 -0.497 -0.392 -0.618  0.136
  0.447 -0.526  0.351  0.419 -0.473
  0.447  0.172  0.609 -0.061  0.630
  0.447  0.632  0.025 -0.321 -0.545

The squared MO coefficient vectors are
    1      2      3      4      5
  0.200  0.048  0.352  0.336  0.064
  0.200  0.247  0.153  0.381  0.019
  0.200  0.277  0.123  0.176  0.224
  0.200  0.029  0.371  0.004  0.396
  0.200  0.399  0.001  0.103  0.297

Charge:   1    Number of Electrons:  4
The HOMO is degenerate, DIRADICAL
Doubly occ. MOs:   1   Singly occ. deg. MOs:   2

Ground State Energy:   4 alpha + 5.236 Beta
The ground state electron configuration is:
 2 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

Bond  1- 2 has pi-bond order:   0.524
Bond  1- 5 has pi-bond order:   0.524
Bond  2- 3 has pi-bond order:   0.524
Bond  3- 4 has pi-bond order:   0.524
Bond  4- 5 has pi-bond order:   0.524

Atom  1 has pi-density:   0.800
Atom  2 has pi-density:   0.800
Atom  3 has pi-density:   0.800
Atom  4 has pi-density:   0.800
Atom  5 has pi-density:   0.800
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*********************************************************
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*       Written for but not limited to 30 carbon atoms  *
*********************************************************

Title: anion

HMO Connectivity Matrix:
  0.  1.  0.  0.  1.
  1.  0.  1.  0.  0.
  0.  1.  0.  1.  0.
  0.  0.  1.  0.  1.
  1.  0.  0.  1.  0.

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3      4      5
  2.000  0.618  0.618 -1.618 -1.618

  0.447  0.219 -0.593  0.580  0.253
  0.447 -0.497 -0.392 -0.618  0.136
  0.447 -0.526  0.351  0.419 -0.473
  0.447  0.172  0.609 -0.061  0.630
  0.447  0.632  0.025 -0.321 -0.545

The squared MO coefficient vectors are
    1      2      3      4      5
  0.200  0.048  0.352  0.336  0.064
  0.200  0.247  0.153  0.381  0.019
  0.200  0.277  0.123  0.176  0.224
  0.200  0.029  0.371  0.004  0.396
  0.200  0.399  0.001  0.103  0.297

Charge:  -1    Number of Electrons:  6
Doubly occ. MOs:   3   Singly occ. MOs:   0

Ground State Energy:   6 alpha + 6.472 Beta
The ground state electron configuration is:
 2 2 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

Bond  1- 2 has pi-bond order:   0.647
Bond  1- 5 has pi-bond order:   0.647
Bond  2- 3 has pi-bond order:   0.647
Bond  3- 4 has pi-bond order:   0.647
Bond  4- 5 has pi-bond order:   0.647

Atom  1 has pi-density:   1.200
Atom  2 has pi-density:   1.200
Atom  3 has pi-density:   1.200
Atom  4 has pi-density:   1.200
Atom  5 has pi-density:   1.200
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