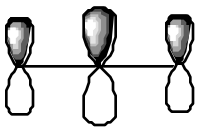
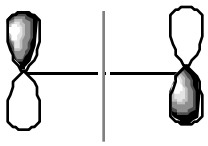
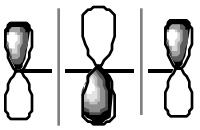
Chemistry 412, Winter Semester 1999, Dr. Glaser
Quiz 2: "HMO and EHMO", Monday, November 8, 1999, 25 minutes

Your Name:

Question 1. Allyl Radical, Cation, and Anion. (25 points)

(a) On p. 3-5, HMO outputs are given of allyl radical, cation, and anion. Sketch MOs #1, #2 and MO #3 (side views). Your drawings should reflect AO contributions. Indicate sign by shading and clearly indicate where the nodes are. (9 points)

MO #1	MO #2	MO #3
		

(b) Consider the π-densities of the three species. Which atoms carry the highest charges in the cation and the anion. Is this consistent with the use of the usual resonance forms? (8 points)

Cation: +0.5 on each terminal C-atom Anion: -0.5 on each terminal C-atom

Yes, this matches the Lewis pi-resonance forms.

(c) Show how the **C1-C2 Bond Order** is computed for the anion. Show every term, even if the term will be zero. Show how the **C1 π-density** is computed for the anion. (8 points)

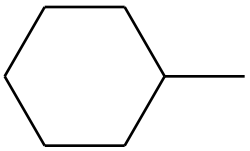
C1-C2 bond order: 2 • (0.5 • 0.707) + 2 • (0.5 • 0)

C1 pi-density: 2 • 0.5**2 + 2 • (-0.707)**2

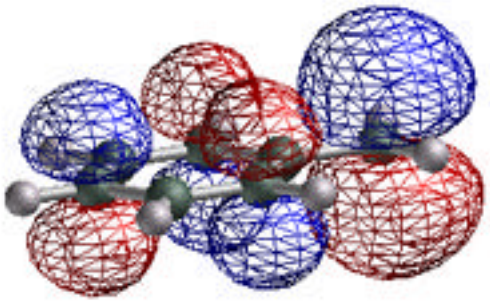
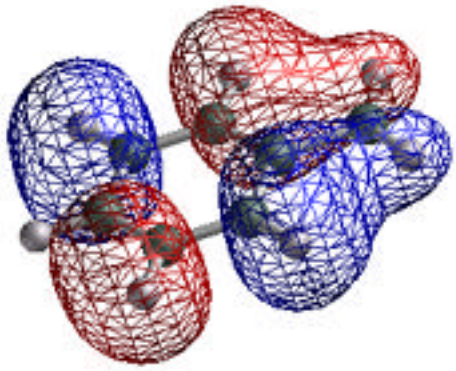
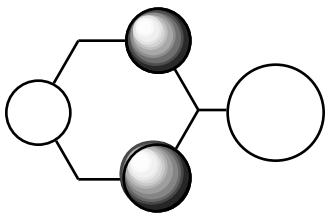
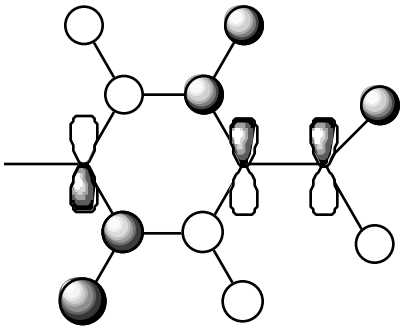
Points for Question 1:	/25		
Points for Question 2:	/25	Total Points:	/50

Question 2. HMO and EHMO of an Alternating Hydrocarbon. (25 p.)

(a) The skeleton of an alternant, benzyl radical is shown. Mark the carbons of the "stared" and "circled" sets, state whether the system is odd or even, whether its MOs are symmetric about the α-level, and give the number of non-bonding MOs. Determine the HOMO for the alternant hydrocarbon. Show work. (No need to evaluate the square root.) (12 p.)

<table>
<tr><td>  </td><td rowspan="4">See lecture notes</td></tr>
<tr><td>odd/even? odd</td></tr>
<tr><td>sym. about α? no</td></tr>
<tr><td># of non-bd. MOs? 1</td></tr>
</table>

(b) Two EHMOs are shown for benzyl radical. For each, state whether it is a pi- or a sigma-MO. State the number of nodes and, if any, indicate in the drawing where these nodes are. In the space in the bottom row, indicate schematically the LCAO that forms the MOs. (13 points)

<table>
<tr><td>  </td><td>  </td></tr>
<tr><td>A pi-MO with 3 nodes: Molecular plane and two perpendicular parallel planes
  </td><td>A sigma-MO with 2 nodes: Node planes mutually perp. and with regard to mol. plane.
  </td></tr>
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*********************************************************
*             Hueckel Molecular Orbital Program         *
*           Rainer Glaser, UMC, January 21, 1991        *
*       Written for but not limited to 30 carbon atoms  *
*********************************************************

Title: allyl_cation

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

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3
  1.414  0.000 -1.414

  0.500 -0.707  0.500
  0.707  0.000 -0.707
  0.500  0.707  0.500

The squared MO coefficient vectors are
    1      2      3
  0.250  0.500  0.250
  0.500  0.000  0.500
  0.250  0.500  0.250

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

Ground State Energy:   2 alpha + 2.828 Beta
The ground state electron configuration is:
 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:   0.707
Bond  2- 3 has pi-bond order:   0.707

Atom  1 has pi-density:   0.500
Atom  2 has pi-density:   1.000
Atom  3 has pi-density:   0.500
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*********************************************************
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*********************************************************

Title: allyl_radical

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

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3
  1.414  0.000 -1.414

  0.500 -0.707  0.500
  0.707  0.000 -0.707
  0.500  0.707  0.500

The squared MO coefficient vectors are
    1      2      3
  0.250  0.500  0.250
  0.500  0.000  0.500
  0.250  0.500  0.250

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

Ground State Energy:   3 alpha + 2.828 Beta
The ground state electron configuration is:
 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

Bond  1- 2 has pi-bond order:   0.707
Bond  2- 3 has pi-bond order:   0.707

Atom  1 has pi-density:   1.000
Atom  2 has pi-density:   1.000
Atom  3 has pi-density:   1.000
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*********************************************************
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*       Written for but not limited to 30 carbon atoms  *
*********************************************************

Title: allyl_anion

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

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3
  1.414  0.000 -1.414

  0.500 -0.707  0.500
  0.707  0.000 -0.707
  0.500  0.707  0.500

The squared MO coefficient vectors are
    1      2      3
  0.250  0.500  0.250
  0.500  0.000  0.500
  0.250  0.500  0.250

Charge:  -1    Number of Electrons:  4
Doubly occ. MOs:   2   Singly occ. MOs:   0

Ground State Energy:   4 alpha + 2.828 Beta
The ground state electron configuration is:
 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

Bond  1- 2 has pi-bond order:   0.707
Bond  2- 3 has pi-bond order:   0.707

Atom  1 has pi-density:   1.500
Atom  2 has pi-density:   1.000
Atom  3 has pi-density:   1.500
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