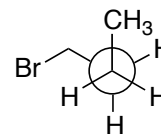
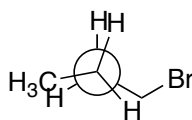
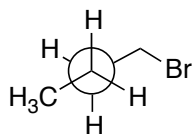


<b>Score (4 pts)</b>		<b>Lectures</b>	5, 6, 7	<b>Name</b>	
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1. Draw the sawhorse and bond-line notation (with dashes and wedges) for the Newman projections below. Sawhorse projections should site down the C2-C3 bond. Bond-line drawings should place the C2-C3 bond in the place of the paper horizontally.



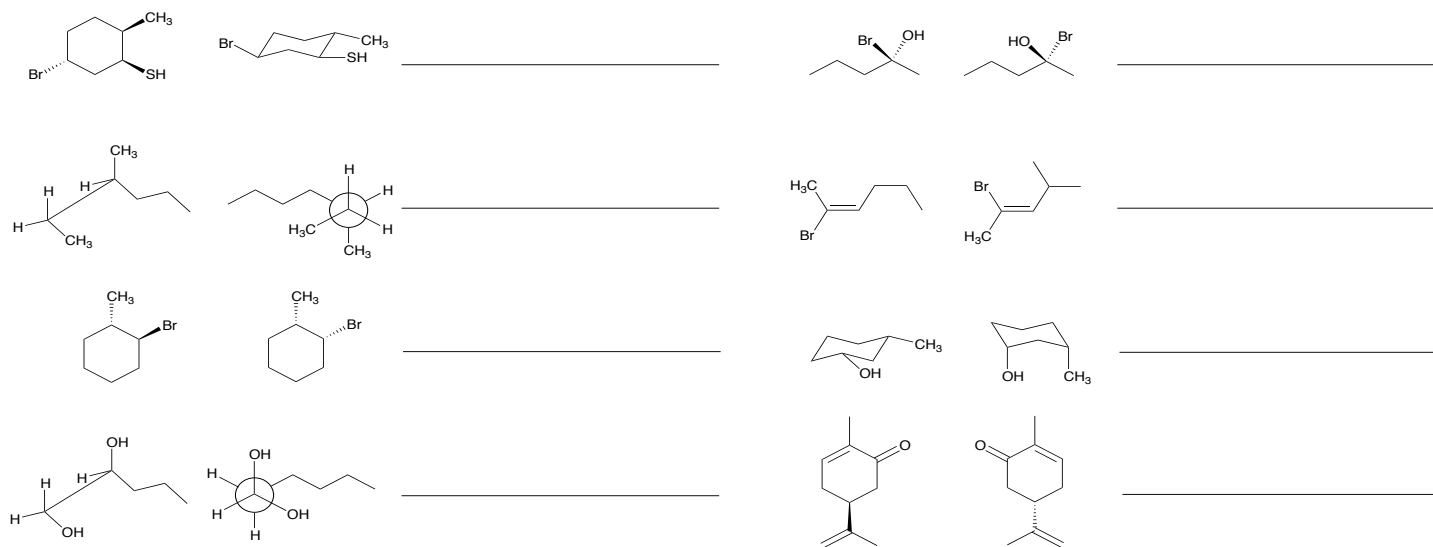
<b>Sawhorse</b>			
<b>Bond-line (Dash-Wedge)</b>			

2. **First**, using Newman projections, draw three conformations of 1,2-dibromoethane—two staggered and one eclipsed. **Second**, circle the conformation you'd expect to have the largest dipole moment. **Third**, explain your choice.

3. Draw the most stable conformation for each of following molecules using both Newman projections and dash-wedge notation.

	2,3-dimethylbutane (sight down C2-C3 bond)	4-isopropylheptane (sight down C3-C4 bond)	2-fluorobutane (sight down C2-C3 bond)
Newman			
Dash-Wedge			

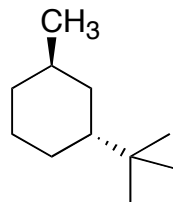
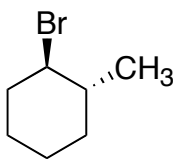
4. For each pair of molecules write whether they are constitutional isomers, conformational isomers, configurational isomers or not isomers.



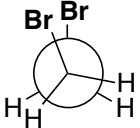
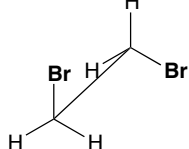
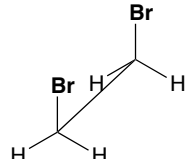
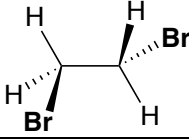
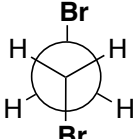
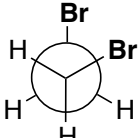
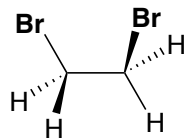
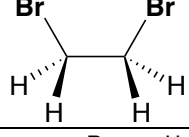
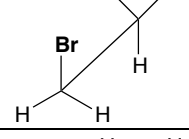
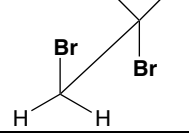
5. Draw the most stable conformation for each of following molecules using both Newman projections and dash-wedge notation.

	2,3-dimethylbutane (sight down C2-C3 bond)	4-isopropylheptane (sight down C3-C4 bond)	2-fluorobutane (sight down C2-C3 bond)
Newman			
Dash-Wedge			

6. First, draw a chair conformation for each molecule below. Second, draw the new chair conformation after ring inversion. Third, place a check mark in the box representing the most stable conformation. You *may* need to consult the tables of strain energies at the end of the exam.

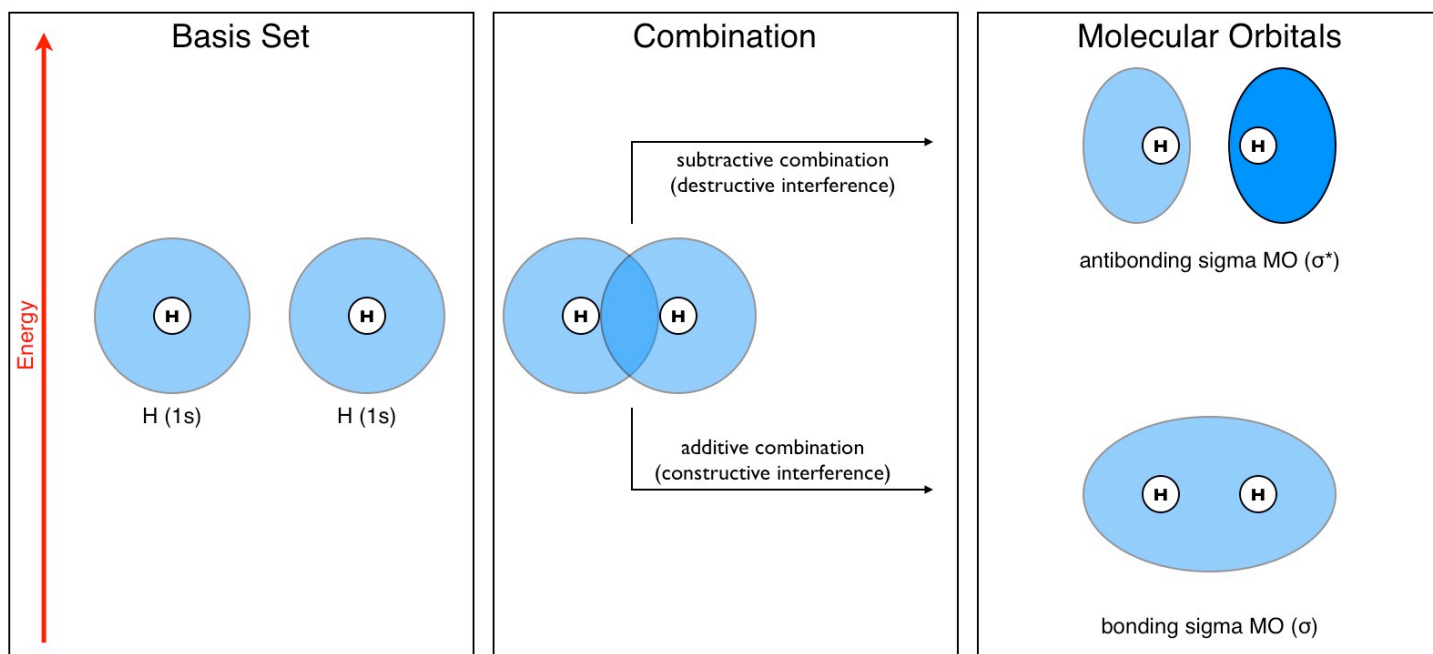
	<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;"> <input style="width: 20px; height: 20px; margin: 0 auto 20px auto;" type="checkbox"/> </div>	ring inversion $\rightleftharpoons$	<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;"> <input style="width: 20px; height: 20px; margin: 0 auto 20px auto;" type="checkbox"/> </div>
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7. Consider the conformations of 1,2-dibromoethane. **First**, determine the dihedral angle formed by each of the C-Br bonds. **Second**, write the relationship between the two bromine atoms in the conformation. **Third**, write the name of the conformation.

Compound	Dihedral Angle	Relationship	Conformation Name
	0°	Eclipsed	Eclipsed
		NA for us	
			
			
			
			
			
			
			
			

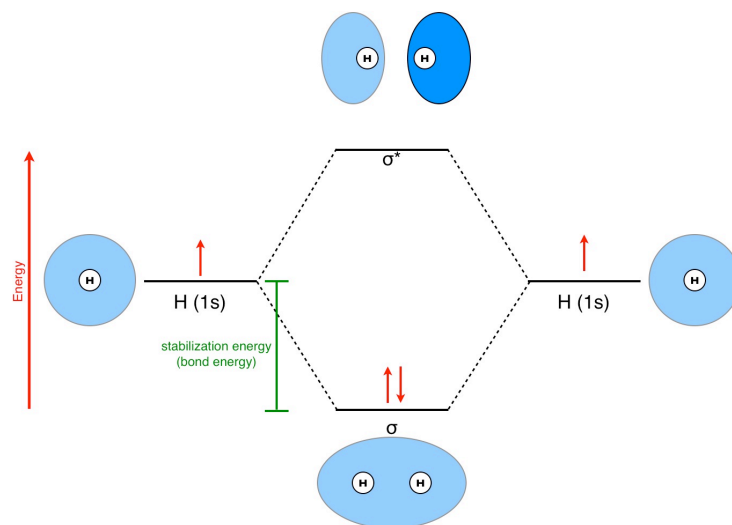
**Quick Review on Molecular Orbital Theory (Homework questions follow.)**

The molecular orbitals for a  $H_2$  molecule can be thought of as arising from the combination of the valence atomic orbitals on two individual hydrogen atoms (Figure 1). These atomic orbitals (AOs) are referred to as the *basis set*. In valence bond theory, we envision the basis set of orbitals overlapping with each other, much like a Venn diagram. The area of overlap represents increased electron density and thus increased shielding between the two nuclei (a covalent bond!). Molecular orbital (MO) theory takes one more step. Rather than stopping at overlap, MO theory states that all the atomic orbitals are combined to produce an equal number of brand new orbitals encompassing the entire molecule. This combination can be additive, leading to a lower energy bonding MO, or it can be subtractive, leading to a higher energy antibonding ( $\sigma^*$ ) MO. Since both MOs involve head-to-head combinations in this case, they are examples of sigma bonds ( $\sigma$ ). Notice that the antibonding MO ( $\sigma^*$ ) contains a node between the two H nuclei as indicated by the change in shading between the two lobes of the orbital. (A change in shading is just another way of indicating different signs of the wavefunction.) This node represents a point where no electron density is found. Since it is between the two H nuclei, there will be zero electron shielding between those same nuclei (an antibond!).



**Figure 1: Molecular orbitals of  $H_2$  derived from combination of basis set.**

While both MOs of  $H_2$  always exist, they may not necessarily both contain electrons. It may seem odd, but orbitals can and do exist even when they are empty. In order to determine which MOs are occupied, a MO orbital diagram like the one shown in Figure 2 can be helpful. Here, each atomic orbital involved in the molecular bond are placed to the right and left of the newly produced molecular orbitals. Horizontal lines are drawn to represent the AOs and the MOs just like in electron configuration diagrams. Each hydrogen atom contributes one valence electron. This is represented with one red arrow occupying each 1s AO. Those electrons are then placed into the MOs following the Aufbau's rule (fill lowest orbitals first), Hund's rule (fill degenerate orbitals half way first) and the Pauli principle (electrons have opposite spins when in the same orbital). Two total electrons originated from the basis set of AOs, which means two electrons go into the MOs. The MO diagram, then, shows that only the bonding MO is filled. The antibonding orbital, although it still exists, does not contribute to the overall bonding picture since it is empty. This is the most abstract part of MO theory, but probably the most important in terms of describing physical phenomena (e.g., conformational analysis) and chemical reactivity. One more time, then: Even though the antibonding orbital in  $H_2$  is empty and doesn't contribute to the bonding picture, it is still present and can still interact with the physical world around it.

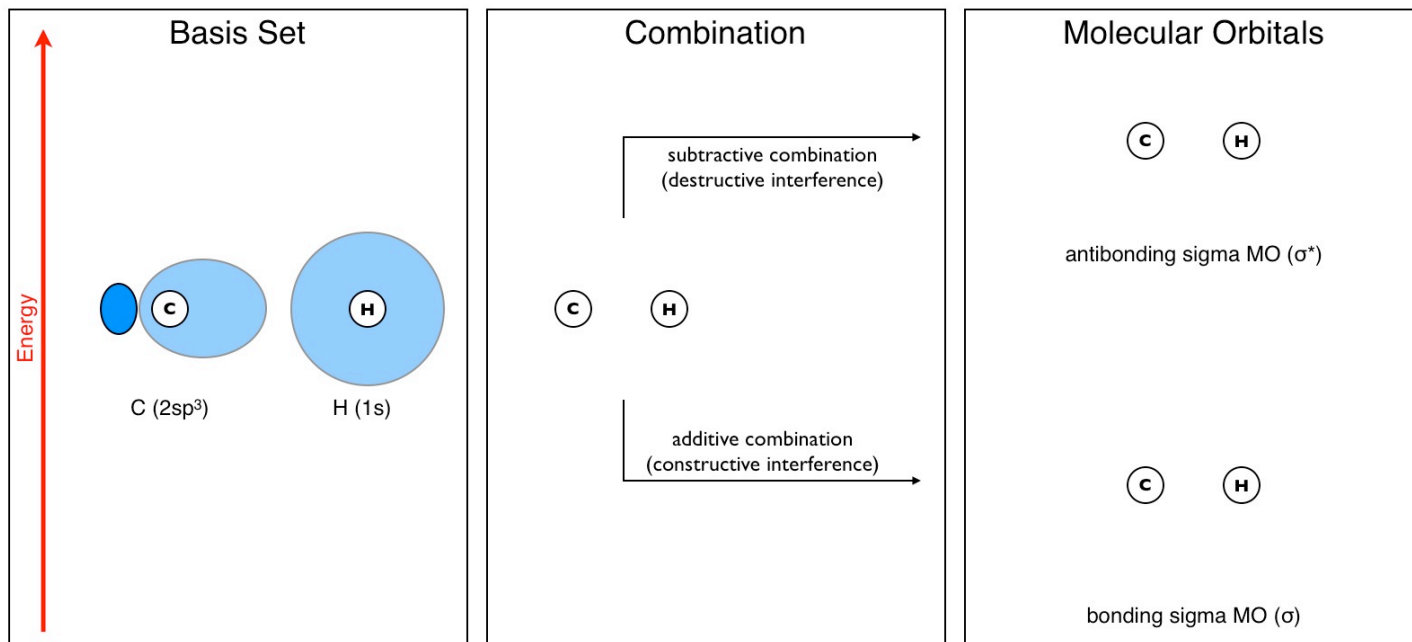


**Figure 2: Molecular orbital diagram for H<sub>2</sub>.**

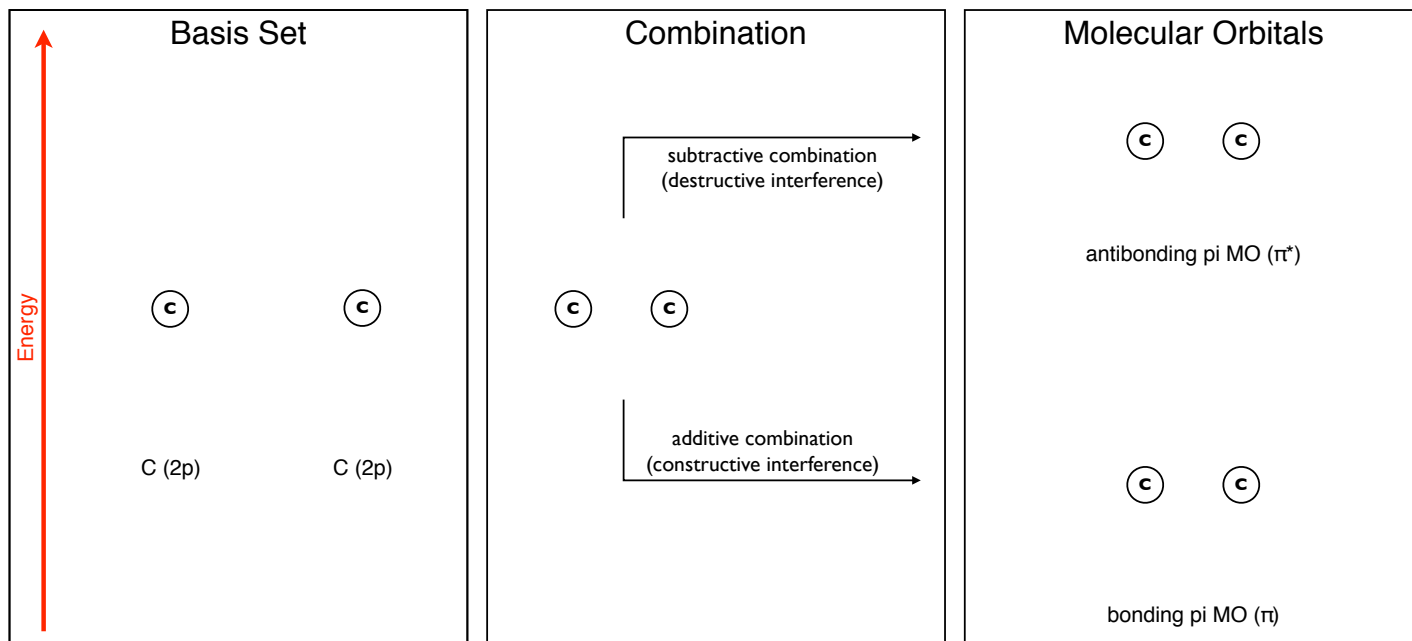
*Note: It is not always necessary to include the graphical pictures of the basis set atomic orbitals or of the molecular orbitals. In most cases the graphical representations are not included in MO diagrams.*

8. What would you predict would happen to H<sub>2</sub> if an external Lewis base was able to donate an electron pair to the antibonding orbital of H<sub>2</sub>?
9. Draw a molecular orbital diagram for He<sub>2</sub>. Based on the MO diagram you drew what conclusions could you draw about He<sub>2</sub>? Explain. (You do not have to draw the orbitals themselves, but be sure to label all atomic and molecular orbitals appropriately.)

10. Draw the MOs that result from the combination of a carbon  $sp^3$ -orbital with a hydrogen  $1s$ -orbital. The basis set has been drawn for you. Start by drawing the overlap expected in the *Combination* box. Be sure to use shading to indicate where the wavefunction changes sign (nodes!).

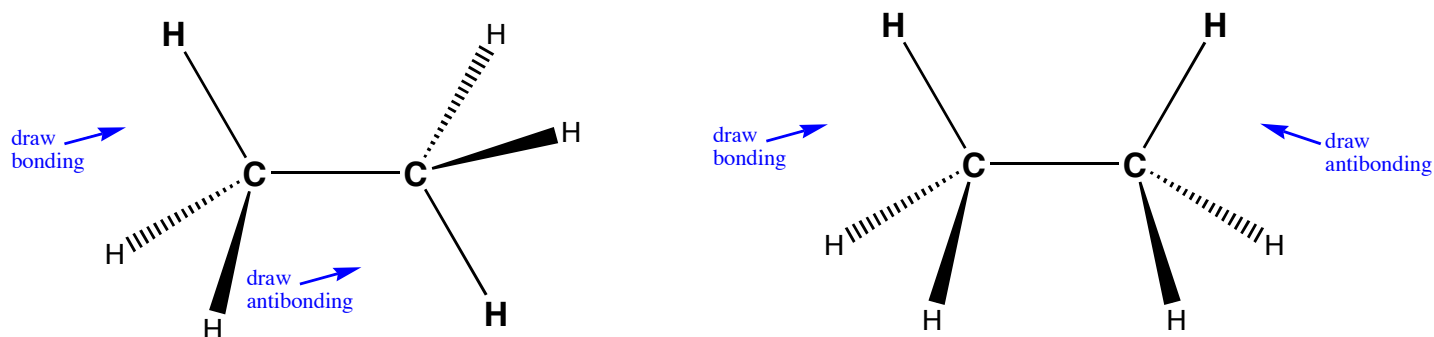


11. Repeat this process for the  $\pi$ -bond formed by the combination of two carbon  $2p$ -orbitals. This time begin by drawing the basis set first.



**Hyperconjugation in Conformational Analysis (Homework questions follow.)**

Now that you can draw both the bonding and antibonding MOs for a C-H bond, let's consider the molecule of ethane below. In class we said that when two adjacent C-H bonds are planar (the solid lines in Figure 3), the bonding MO of one C-H bond was able to donate some of its electron density to the antibonding MO of the other and vice versa. This electron density donation from a filled orbital to an adjacent empty orbital is called hyperconjugation. This effect can be stabilizing since it delocalizes (spreads out) the electron density over more atoms. Importantly, in order for hyperconjugation to occur, the filled MO and adjacent empty MO must be able to overlap. Remember that as you consider the questions below.



**Figure 3: Staggered and eclipsed conformations of ethane.**

- Draw the bonding and antibonding MO orbital for the pair of adjacent C-H bonds indicated in Figure 3. Draw them directly on top of the Lewis structures in Figure 3. Let the letter represent the nucleus of each atom. Use your answer to question 7 for guidance.
- Using the MOs you've superimposed on the Lewis structures in Figure 3, explain why the staggered conformation is more stable than the eclipsed conformation. (Do not use the steric argument.)