1) Draw a Lewis structure for a chemical species whose bonding is not accurately described by a Lewis Structure, and draw a more realistic delocalized / hybrid representation of that species. (3pts)

2) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (15pts)

3) Draw (Z)-1,3-hexadiene in its s-trans conformation. (4pts)
4) By applying the polygon rule to the below cyclic hydrocarbon:

[Diagram]

a) draw out the MO energy level diagram
b) label the MO’s using $\pi_1$...$\pi_4^*$
c) circle one pair of degenerate orbitals
d) draw in the electrons and explain whether this compound is predicted to be aromatic or antiaromatic. (8pts)
5) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (21pts)

\[
\begin{align*}
&\text{Br} \quad \text{Br} \\
&\text{NC} \equiv \text{CN} \quad \text{heat} \\
&\text{H} \quad \text{CH}_2\text{CH}_3 \\
&\text{Br}_2 \\
&\text{Br}_2 \\
&\text{O} \\
&\text{1) NaOH} \\
&\text{2) CH}_3\text{CH}_2\text{Br} \\
&\text{NO}_2 \\
&\text{CH}_3\text{Cl}, \text{AlCl}_3 \\
&\text{UV Light}
\end{align*}
\]
6) The nitronium ion NO$_2^+$ is the active electrophile in nitration EAS reactions. It is formed when nitric and sulphuric acid react via an acid promoted dehydration.

\[
\begin{array}{c}
\text{H}_2\text{SO}_4^-
\end{array} \xrightarrow{\text{H}^+} \begin{array}{c}
\text{H}_2\text{O} + \text{HSO}_4^-
\end{array}
\]

Draw a correct Lewis structure for the nitronium cation, and mechanistically show how it is formed.

(10pts)
7) Please fill in the blanks. (18pts)

- NO₂
- Cl
- NO₂
- PhO
- O
- CH₂CF₂H
- excess HBr
- heat
- PhCH₂C₆H₄CH₃
8) When the below allylic alcohol is treated with H-Br, two isomeric allylic bromides are formed.

\[
\text{OH} \quad \xrightarrow{\text{H-Br}} \quad \text{two isomeric allylic bromides}
\]

Draw the two products and provide a step-by-step mechanism which explains the generation of both products. (9pts)
9) For both below substitution reactions (i) draw the expected product, and (ii) explain why the bromine substitutes at that specific site for each reaction. (10pts)

\[
\begin{align*}
\text{Br}_2, \text{uv light} & \quad \text{CH}_2\text{CH}_3 \quad \text{Br}_2, \text{FeBr}_3 \\
\text{CO}_2\text{H} & \\
\text{Br}_2, \text{FeBr}_3 &
\end{align*}
\]
10) What is the definition of a *Pericyclic reaction*? (2pts)

*Bonus question* (up to 2pts)
Show how the carbon p orbitals overlap to form the LUMO of the allyl anion.
1) Draw a Lewis structure for a chemical species whose bonding is not accurately described by a Lewis Structure, and draw a more realistic delocalized / hybrid representation of that species. (3pts)

\[
\begin{align*}
R-\overset{\circ}{\cdot}\cdot\cdot-O^\ominus & \quad \text{and} \quad R-\overset{\circ}{\cdot}\cdot\cdot\overset{\circ}{\cdot}\cdot\cdot\overset{\circ}{\cdot}\cdot\cdot\overset{\circ}{\cdot}\cdot\cdot-\overset{\circ}{\cdot}\cdot\cdot-\text{ch} \\
\end{align*}
\]

2) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (15pts)

\[
\begin{array}{ccc}
\text{NON} & \text{NON} & \text{ANTI} \\
\text{Cyclpentadiene} & \text{Cyclhexadiene} & \text{Cyclpentadiene} \\
\text{Cyclpentadiene} & \text{Cyclhexadiene} & \text{Cyclpentadiene} \\
\text{Cyclpentadiene} & \text{Cyclhexadiene} & \text{Cyclpentadiene} \\
\end{array}
\]

3) Draw (Z)-1,3-hexadiene in its s-trans conformation. (4pts)

\[
\begin{align*}
\text{(Z)-1,3-hexadiene in s-trans conformation}
\end{align*}
\]
4) By applying the polygon rule to the below cyclic hydrocarbon:

a) draw out the MO energy level diagram
b) label the MO's using $\pi_1 \ldots \pi_4^*$
c) circle one pair of degenerate orbitals
d) draw in the electrons and explain whether this compound is predicted to be aromatic or antiaromatic. (8pts)

\[ \text{Unpaired Electrons } = \text{ Anti-Aromatic} \]
5) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (21 pts)

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} & \quad \text{NC} = \text{C} = \text{CN} \\
\text{Heat} & \quad \rightarrow \\
\text{Benzyne} & \quad \text{HNO}_3, \text{H}_2\text{SO}_4 \\
\text{benzene} & \quad \text{NaOCH}_3, \text{CH}_3\text{OH} \\
\text{Br}_2 & \quad \rightarrow \\
\text{Br}_2 & \quad \rightarrow \\
\text{phenol} & \quad 1) \text{NaOH} \\
& \quad 2) \text{CH}_3\text{CH}_2\text{Br} \\
\text{nitrobenzene} & \quad \text{CH}_3\text{Cl}, \text{AlCl}_3 \\
\text{UV Light} & \quad \rightarrow
\end{align*}
\]
6) The nitronium ion NO$_2^+$ is the active electrophile in nitration EAS reactions. It is formed when nitric and sulphuric acid react via an acid promoted dehydration.

\[
\begin{align*}
\text{H}_2\text{SO}_4 \quad \text{H}_2\text{NO}_2^- & \rightarrow \quad \text{NO}_2^+ \quad \text{H}_2\text{O} \quad \text{HSO}_4^- \\
\end{align*}
\]

Draw a correct Lewis structure for the nitronium cation, and mechanistically show how it is formed.

(10pts)
7) Please fill in the blanks. (18pts)

\[
\begin{align*}
\text{PhO-} & \quad \text{O-CH}_2\text{CF}_2\text{H} \quad \text{excess HBr} \quad \text{PhOH} \quad \text{Br}-\text{[ ]-Br} \quad \text{Br-CH}_2\text{CH}_3
\end{align*}
\]
8) When the below allylic alcohol is treated with H-Br, two isomeric allylic bromides are formed.

\[
\text{two isomeric allylic bromides}
\]

Draw the two products and provide a step-by-step mechanism which explains the generation of both products. (9pts)
9) For both below substitution reactions (i) draw the expected product, and (ii) explain why the bromine substitutes at that specific site for each reaction. (10pts)

This is free radical substitution
Br-Br → 2Br•
This Br• selectively abstracts the β-hydrogen to give a resonance stabilized radical

This radical reacts with Br• to give the product once a Br• to carry on the chain

Ethyl is ortho directing and -CO2H is meta directing.
There is double reinforcement para for the to the ethyl.
Sterics favor the para attack
10) What is the definition of a *Pericyclic reaction*? (2pts)

A reaction that involves a closed loop of interacting orbitals

*Bonus question* (up to 2pts)
Show how the carbon p orbitals overlap to form the LUMO of the allyl anion.

Allyl Anion: \[ \bigvee \theta = 4 \pi e^{-5} \]

Allyl Mo's:
- \[ \pi_3^* \]
- \[ \pi_2 \]
- \[ \pi_1 \]

LUMO = Lowest Unoccupied MO = \[ \pi_3^* \]