EXAM II

Name: _____________________________________________________________

Student ID No.: ____________________________________________________

Note: The exam time is 1 hr 15 min; the total number of points is 100. In the case of multiple choice questions, there is only one correct answer. You must show your work or reasoning for partial credit. A periodic table of the elements is in the back of the exam. A $D_{2h}$ character table and point group flow chart are also provided.

1) ____________  (20 pts)

2) ____________  (6 pts)

3) ____________  (4 pts)

4) ____________  (20 pts)

5) ____________  (10 pts)

6) ____________  (20 pts)

7) ____________  (10 pts)

8) ____________  (10 pts)

TOTAL ____________  (100 pts)
Symmetry and Group Theory

(1) Determine the point groups for the following molecules:

(a) 1,1'-Dichloroferrocene

(b) Dibenzenechromium (eclipsed conformation)

(c)  

Cs
(d) $\text{H}_3\text{O}^+$

\[ C_{3v} \]

(e) $\text{O}_2\text{F}_2$

\[ C_2 \]

(f) Formaldehyde, $\text{H}_2\text{CO}$

\[ C_{2v} \]

(g) $\text{S}_8$ (puckered ring)

\[ D_{4d} \]

(h) Borazine (planar)

\[ D_{3h} \]
(i) \([\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}\)

(j) A tennis ball (ignoring the label, but including the surface pattern)

\(D_{2d}\)
(2) Sketch the following atomic orbitals and determine the point group of each. Be sure to include the signs on the orbital lobes:

(a) \( p_x \)

(b) \( d_{xy} \)

(c) \( d_{z^2} \)
(3) Which molecules from problem #1 are chiral? List three items that are chiral.

$O_2F_2$ and [tris(oxalato)chromate(III)] are chiral from problem #1

Other items from everyday life include a human foot ($C_1$), a piece of paper with two identical spiral designs printed on one side ($C_2$), and many organisms when small asymmetric details are considered.
(4) For trans-1,2-dichloroethylene, of $C_{2h}$ symmetry,

(a) List all the symmetry operations for this molecule

$C_{2h}$ molecules have $E$, $C_2$, $i$, and $\sigma_h$ operations.

(b) Write a set of transformation matrices that describe the effect of each symmetry operation in the $C_{2h}$ group on a set of coordinates $x$, $y$, $z$ for a point.

$$
\begin{align*}
E: & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
C_2: & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
i: & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
\sigma_h: & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\end{align*}
$$
(2) (cont)

(c) Obtain as many irreducible representations as possible from the transformation matrices in (b).

These matrices can be block diagonalized into three $1 \times 1$ matrices, with the representations shown in the table.

<table>
<thead>
<tr>
<th>$\chi(E)$</th>
<th>$\chi(C_2)$</th>
<th>$\chi(i)$</th>
<th>$\chi(\sigma_h)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The total is $\Gamma = 2B_u + A_u$.

(d) Using the $C_{2h}$ character table, verify that the irreducible representations are mutually orthogonal.

Multiplying $B_u$ and $A_u$:

$1 \times 1 + (-1) \times 1 + (-1) \times (-1) + 1 \times (-1) = 0$, proving they are orthogonal.
Molecular Orbitals

(5) Using all three $p$ orbitals of atom A and all five $d$ orbitals of atom B, indicate which atomic orbitals have the necessary symmetry to interact as bonding and antibonding orbitals.

There are three possible bonding interactions:

\[ p_z \quad d_{z^2} \quad p_y \quad d_{yz} \quad p_x \quad d_{xz} \]

All other combinations have both positive and negative overlaps, resulting in no bonding.
(6) Consider the molecules NO, NO\(^+\), and NO\(^-\)

(a) Prepare a molecular orbital energy level diagram for NO, showing clearly how the atomic orbitals interact to form MOs.
(6) (cont.)

(b) How does your diagram illustrate the difference in electronegativity between N and O?

O is more electronegative than N, so its orbitals are slightly lower in energy. The bonding orbitals are slightly more concentrated on O.

(c) Predict the bond order and number of unpaired electrons.

The bond order is 2.5, with one unpaired electron.

(d) NO⁺ and NO⁻ are also known. Compare the bond orders of these ions with the bond order of NO. Which of the three would you predict to have the shortest bond? Why?

NO⁺ Bond Order = 3
NO Bond Order = 2.5
NO⁻ Bond Order = 2

NO⁺ will have the shortest bond because it has the highest bond order.
(7) Methylene, CH₂, plays an important role in many reactions. One possible structure of methylene is linear.

(a) Construct a molecular orbital energy level diagram for this species. Include sketches of the group orbitals, and indicate how they interact with the appropriate orbitals of carbon.
(7) (cont.)

(b) Would you expect linear methylene to be diamagnetic or paramagnetic?

CH₂ is a paramagnetic diradical, with one electron in each of the pₓ and pᵧ orbitals of the C. The singlet state, with these electrons paired in one of these nonbonding orbitals, has a significantly higher energy. Bonding orbitals are derived from the 2s of the C atom and the two 1s orbitals of the hydrogen atoms and from the 2p of the C atom and the two 1s orbitals from the hydrogen atoms. All these orbitals are close enough in energy (-10 to – 19 eV) to interact easily. More careful calculations show that the H-C-H angle is about 130°.
(8) In addition to the doping described in this chapter, n-type semiconductors can be formed by increasing the amount of metal in ZnO or TiO₂; whereas p-type semiconductors can be formed by increasing the amount of nonmetal in Cu₂S, CuI, or ZnO. Explain how this is possible. BE CONCISE!

In ZnO or TiO, additional Zn or Ti would have two more electrons than the metallic ions. As a result, any nonstoichiometry in the direction of excess Zn or Ti would supply extra electrons, making an n-type semiconductor.

In Cu₂S, CuI, or ZnO, excess S, I, or O would have fewer electrons than the corresponding ions. Therefore, the result of excess nonmetals in the lattice would be a p-type semiconductor.