Chemistry 410A                           Exam 5                          Spring 2016

# NAME:

**Instructions:**

1. Keep this exam closed until instructed to begin.

2. **Please write your name on this page but not on any other page.**

3. Please silence any noisy electronic devices you have.

4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.

5. To receive full credit for your work, please

   (a) put your name on your exam;

   (b) show all your work, using only the exam papers, including the back of this sheet if necessary;

   (c) specify the correct units, if any, for your final answers;

   (d) use an appropriate number of significant digits for final numerical answers;

   (e) **stop writing and close your exam immediately when time is called.**

**Other notes:**

- **Problem 1 (covering all of page 3) of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.

- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. (a) What is the order $Q$ of the point group $O_h$. The character table is given in Problem 2 of this exam.

(b) Give the bond order for the $Al_2$ molecule, which has MO configuration (including core electrons)

$$1\sigma_g^2\,1\sigma_u^2\,2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,3\sigma_u^2\,1\pi_u^4\,1\pi_g^4\,4\sigma_g^2\,4\sigma_u^2\,2\pi_u^2.$$

(c) The Cartesian $d$ orbitals are labeled $d_{z^2}$ (lies along $z$ axis), $d_{xz}$ (lies in $xz$ plane), $d_{yz}$ (lies in $yz$ plane), $d_{xy}$, and $d_{x^2-y^2}$ (which both lie in $xy$ plane). When we combine these five $d$ orbitals centered on different atoms to form MOs, what is the symmetry of each MO that is formed? The same question is solved for the $p$ orbitals as an example.

- $p_z \quad \to \sigma_g, \sigma_u$
- $p_x, p_y \to \pi_g, \pi_u$

(d) The $C_2$ molecule has a $X^1\Sigma_g^+$ ground state. The lowest energy bound excited electronic states are listed below. Write **F** next to any of these states that will fluoresce to return to the ground state and **P** for any that will phosphoresce.

   i. $a^3\Pi_u$

   ii. $b^3\Sigma_g^-$

   iii. $A^1\Pi_u$

| $D_{\infty h}$ | $\hat{E}$ | $\hat{C}_\infty$ | $\infty\hat{\sigma}_v$ | $\hat{I}$ | $\infty\hat{C}_2$ | Functions |
|---|---|---|---|---|---|---|
| $\Sigma_g^+(\sigma_g)$ | 1 | 1 | 1 | 1 | 1 | $x^2+y^2, z^2$ |
| $\Sigma_g^-$ | 1 | 1 | $-1$ | 1 | $-1$ | $R_z$ |
| $\Sigma_u^+(\sigma_u)$ | 1 | 1 | 1 | $-1$ | $-1$ | $z$ |
| $\Sigma_u^-$ | 1 | 1 | $-1$ | $-1$ | 1 | |
| $\Pi_g(\pi_g)$ | 2 | $2\cos\phi$ | 0 | 2 | 0 | $xz, yz; R_x, R_y$ |
| $\Pi_u(\pi_u)$ | 2 | $2\cos\phi$ | 0 | $-2$ | 0 | $x, y$ |
| $\Delta_g(\delta_g)$ | 2 | $2\cos 2\phi$ | 0 | 2 | 0 | $xy$ |
| $\Delta_u(\delta_u)$ | 2 | $2\cos 2\phi$ | 0 | $-2$ | 0 | |

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2. There is an allowed transition from the $^3T_{1u}$ state to an upper state $Y$ for a molecule in the point group $O_h$. If the representation for $Y$ is $\Gamma_Y$, we find

$$T_{1u} \otimes \Gamma_Y = A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}.$$

(a) Find the term symbol for state $Y$.

(b) Is the transition allowed by electric dipole selection rules, Raman, or both?

(c) The $^3T_{1u}$ state has a molecular orbital configuration in which all the orbitals are filled except two, which have one electron each. One of those is an $a_{2u}$ MO, Fill in the missing symmetry representation:

$$[\text{filled MOs}]\, a_{2u}^1 \underline{\qquad}^1.$$

| $O_h$ | $\hat{E}$ | $8\hat{C}_3$ | $6\hat{C}_2$ | $6\hat{C}_4$ | $3\hat{C}_2(=\hat{C}_4^2)$ | $\hat{I}$ | $6\hat{S}_4$ | $8\hat{S}_6$ | $3\hat{\sigma}_h$ | $6\hat{\sigma}_d$ | Functions |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_{1g}\ (a_{1g})$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $x^2+y^2+z^2$ |
| $A_{2g}\ (a_{2g})$ | 1 | 1 | $-1$ | $-1$ | 1 | 1 | $-1$ | 1 | 1 | $-1$ | |
| $E_g\ (e_g)$ | 2 | $-1$ | 0 | 0 | 2 | 2 | 0 | $-1$ | 2 | 0 | $2z^2-x^2-y^2, x^2-y^2$ |
| $T_{1g}\ (t_{1g})$ | 3 | 0 | $-1$ | 1 | $-1$ | 3 | 1 | 0 | $-1$ | $-1$ | $R_x, R_y, R_z$ |
| $T_{2g}\ (t_{2g})$ | 3 | 0 | 1 | $-1$ | $-1$ | 3 | $-1$ | 0 | $-1$ | 1 | $xz, yz, xy$ |
| $A_{1u}\ (a_{1u})$ | 1 | 1 | 1 | 1 | 1 | $-1$ | $-1$ | $-1$ | $-1$ | $-1$ | |
| $A_{2u}\ (a_{2u})$ | 1 | 1 | $-1$ | $-1$ | 1 | $-1$ | 1 | $-1$ | $-1$ | 1 | |
| $E_u\ (e_u)$ | 2 | $-1$ | 0 | 0 | 2 | $-2$ | 0 | 1 | $-2$ | 0 | |
| $T_{1u}\ (t_{1u})$ | 3 | 0 | $-1$ | 1 | $-1$ | $-3$ | $-1$ | 0 | 1 | 1 | $x, y, z$ |
| $T_{2u}\ (t_{2u})$ | 3 | 0 | 1 | $-1$ | $-1$ | $-3$ | 1 | 0 | 1 | $-1$ | |

3. (a) Draw the best Lewis structure you can for the diatomic molecule BO. Boron does
   not normally take an octet in Lewis structures.

   (b) From this Lewis structure, write an MO configuration for the valence electrons (skip
   the core electrons). Don't worry about the energy ordering of the orbitals, except
   for the highest energy MO which you should put last.

   (c) Complete the MO diagram started below for the $2p$ orbitals of the B and O atoms.

   B $\uparrow$ _____

                        $\uparrow$ $\uparrow$ $\uparrow\downarrow$ O
                        _____

4. We start with 1,3,5-trichlorobenzene, which has $D_{3h}$ symmetry, and use a laser to break one of the C—Cl bonds, to form 1,3-dichlorobenzene, which has $C_{2v}$ symmetry. We could draw a correlation diagram connecting the MOs in each case. In the space below:

(a) Label the coordinate axes for both molecules (more than one correct answer).

(b) Write the symmetry elements that are preserved from one side to the other of this correlation diagram. (If the label changes from one side to the other, give both labels with the $D_{3h}$ label on the left and the $C_{2v}$ label on the right.)

(c) For each of the MOs listed on one side, write the representation(s) that it correlates to on the other side.

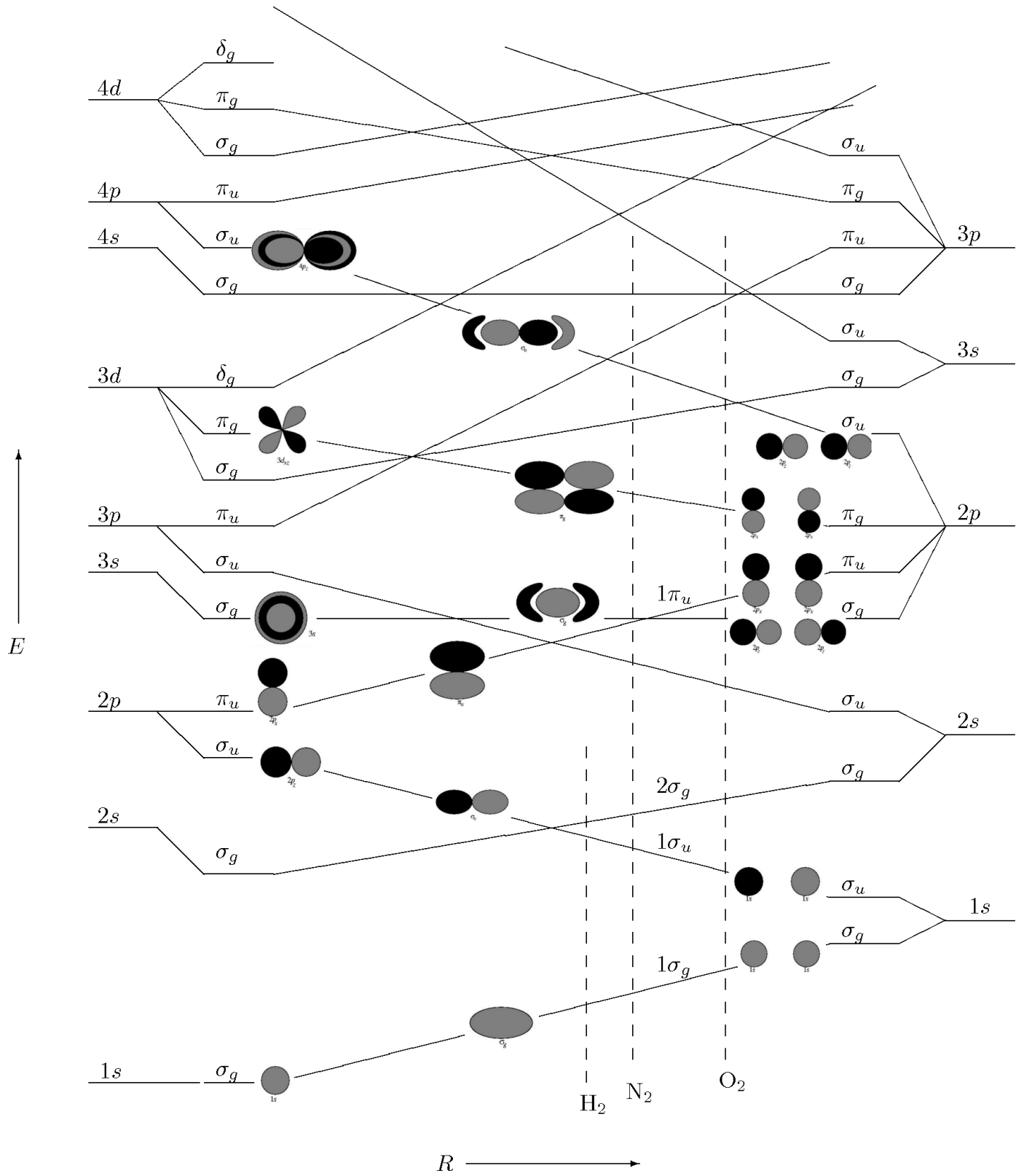(a)
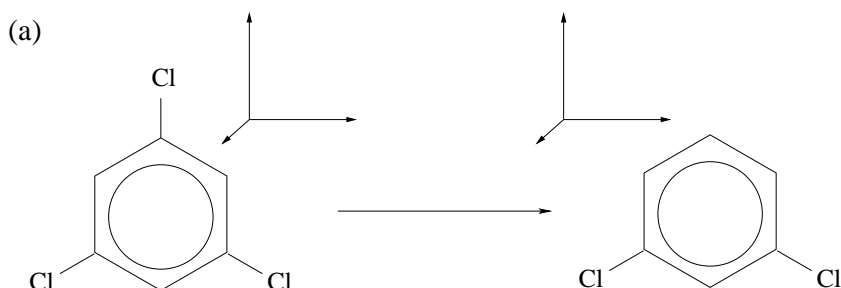


(b)　　　　　　preserved symmetry elements

(c)

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - $a_1$

- - - - - - - - - - - - - - - - - - - - - - - - - - - - $b_2$

$a_2$'' - - - - - - - - - - - - - - - - - - - - - - - - - - - -

| $D_{3h}$ | $\hat{E}$ | $2\hat{C}_3$ | $3\hat{C}_2$ | $\hat{\sigma}_h$ | $2\hat{S}_3$ | $3\hat{\sigma}_v$ | Functions |
|---|---|---|---|---|---|---|---|
| $A_1'(a_1')$ | 1 | 1 | 1 | 1 | 1 | 1 | $z^2, x^2+y^2$ |
| $A_2'(a_2')$ | 1 | 1 | −1 | 1 | 1 | −1 | $R_z$ |
| $E'(e')$ | 2 | −1 | 0 | 2 | −1 | 0 | $(x,y); (x^2-y^2, xy)$ |
| $A_1''(a_1'')$ | 1 | 1 | 1 | −1 | −1 | −1 | |
| $A_2''(a_2'')$ | 1 | 1 | −1 | −1 | −1 | 1 | $z$ |
| $E''(e'')$ | 2 | −1 | 0 | −2 | 1 | 0 | $(xz, yz); (R_x, R_y)$ |

| $C_{2v}$ | $\hat{E}$ | $\hat{C}_2(z)$ | $\hat{\sigma}_v(xz)$ | $\hat{\sigma}_v'(yz)$ | Functions |
|---|---|---|---|---|---|
| $A_1(a_1)$ | 1 | 1 | 1 | 1 | $z; x^2, y^2, z^2$ |
| $A_2(a_2)$ | 1 | 1 | −1 | −1 | $xy; R_z$ |
| $B_1(b_1)$ | 1 | −1 | 1 | −1 | $x; xz; R_y$ |
| $B_2(b_2)$ | 1 | −1 | −1 | 1 | $y; yz; R_x$ |

## Fundamental Constants

| | | | |
|---|---|---|---|
| Avogadro's number | $\mathcal{N}_A$ | | $6.0221367 \cdot 10^{23}$ mol$^{-1}$ |
| Bohr radius | $a_0$ | $= \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ | $5.29177249 \cdot 10^{-11}$ m |
| Boltzmann constant | $k_{\mathrm{B}}$ | | $1.380658 \cdot 10^{-23}$ J K$^{-1}$ |
| electron rest mass | $m_e$ | | $9.1093897 \cdot 10^{-31}$ kg |
| fundamental charge | $e$ | | $1.6021773 \cdot 10^{-19}$ C |
| permittivity factor | $4\pi\epsilon_0$ | | $1.113 \cdot 10^{-10}$ C$^2$ J$^{-1}$ m$^{-1}$ |
| gas constant | $R$ | | $8.314510$ J K$^{-1}$ mol$^{-1}$ |
| | $R$ | | $0.08314510$ L bar K$^{-1}$ mol$^{-1}$ |
| | $R$ | | $0.08206$ L atm K$^{-1}$ mol$^{-1}$ |
| hartree | $E_{\mathrm{h}}$ | $= \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$ | $4.35980 \cdot 10^{-18}$ J |
| Planck's constant | $h$ | | $6.6260755 \cdot 10^{-34}$ J s |
| | $\hbar$ | | $1.05457266 \cdot 10^{-34}$ J s |
| proton rest mass | $m_p$ | | $1.6726231 \cdot 10^{-27}$ kg |
| neutron rest mass | $m_n$ | | $1.6749286 \cdot 10^{-27}$ kg |
| speed of light | $c$ | | $2.99792458 \cdot 10^8$ m s$^{-1}$ |

## Unit Conversions

| | K | cm$^{-1}$ | kJ mol$^{-1}$ | kcal mol$^{-1}$ | erg | kJ |
|---|---|---|---|---|---|---|
| kHz $=$ | $4.799 \cdot 10^{-8}$ | $3.336 \cdot 10^{-8}$ | $3.990 \cdot 10^{-10}$ | $9.537 \cdot 10^{-11}$ | $6.626 \cdot 10^{-24}$ | $6.626 \cdot 10^{-34}$ |
| MHz $=$ | $4.799 \cdot 10^{-5}$ | $3.336 \cdot 10^{-5}$ | $3.990 \cdot 10^{-7}$ | $9.537 \cdot 10^{-8}$ | $6.626 \cdot 10^{-21}$ | $6.626 \cdot 10^{-31}$ |
| GHz $=$ | $4.799 \cdot 10^{-2}$ | $3.336 \cdot 10^{-2}$ | $3.990 \cdot 10^{-4}$ | $9.537 \cdot 10^{-5}$ | $6.626 \cdot 10^{-18}$ | $6.626 \cdot 10^{-28}$ |
| K $=$ | 1 | 0.6950 | $8.314 \cdot 10^{-3}$ | $1.987 \cdot 10^{-3}$ | $1.381 \cdot 10^{-16}$ | $1.381 \cdot 10^{-26}$ |
| cm$^{-1}$ $=$ | 1.4388 | 1 | $1.196 \cdot 10^{-2}$ | $2.859 \cdot 10^{-3}$ | $1.986 \cdot 10^{-16}$ | $1.986 \cdot 10^{-26}$ |
| kJ mol$^{-1}$ $=$ | $1.203 \cdot 10^2$ | 83.59 | 1 | 0.2390 | $1.661 \cdot 10^{-14}$ | $1.661 \cdot 10^{-24}$ |
| kcal mol$^{-1}$ $=$ | $5.032 \cdot 10^2$ | $3.498 \cdot 10^2$ | 4.184 | 1 | $6.948 \cdot 10^{-14}$ | $6.948 \cdot 10^{-24}$ |
| eV $=$ | $1.160 \cdot 10^4$ | $8.066 \cdot 10^3$ | 96.49 | 23.06 | $1.602 \cdot 10^{-12}$ | $1.602 \cdot 10^{-22}$ |
| hartree $=$ | $3.158 \cdot 10^5$ | $2.195 \cdot 10^5$ | $2.625 \cdot 10^3$ | $6.275 \cdot 10^2$ | $4.360 \cdot 10^{-11}$ | $4.360 \cdot 10^{-21}$ |
| erg $=$ | $7.243 \cdot 10^{15}$ | $5.034 \cdot 10^{15}$ | $6.022 \cdot 10^{13}$ | $1.439 \cdot 10^{13}$ | 1 | $10^{-10}$ |
| J $=$ | $7.243 \cdot 10^{22}$ | $5.034 \cdot 10^{22}$ | $6.022 \cdot 10^{20}$ | $1.439 \cdot 10^{20}$ | $10^7$ | $10^{-3}$ |
| dm$^3$ bar $=$ | $7.243 \cdot 10^{24}$ | $5.034 \cdot 10^{24}$ | $6.022 \cdot 10^{22}$ | $1.439 \cdot 10^{22}$ | $1.000 \cdot 10^9$ | 0.1000 |
| kJ $=$ | $7.243 \cdot 10^{25}$ | $5.034 \cdot 10^{25}$ | $6.022 \cdot 10^{23}$ | $1.439 \cdot 10^{23}$ | $10^{10}$ | 1 |

| | | | |
|---|---|---|---|
| **distance** | 1 Å $=$ | $10^{-10}$ m | |
| **mass** | 1 amu $=$ | $1.66054 \cdot 10^{-27}$ kg | |
| **energy** | 1 J $=$ | 1 kg m$^2$ s$^{-2}$ | $= 10^7$ erg |
| **force** | 1 N $=$ | 1 kg m s$^{-2}$ | $= 10^5$ dyn |
| **electrostatic charge** | 1 C $=$ | 1 A s | $= 2.9979 \cdot 10^9$ esu |
| | 1 D $=$ | $3.3357 \cdot 10^{-30}$ C m | $= 1 \cdot 10^{-18}$ esu cm |
| **magnetic field strength** | 1 T $=$ | 1 kg s$^{-2}$ A$^{-1}$ | $= 10^4$ gauss |
| **pressure** | 1 Pa $=$ | 1 N m$^{-2}$ | $= 1$ kg m$^{-1}$ s$^{-2}$ |
| | 1 bar $=$ | $10^5$ Pa | $= 0.98692$ atm |