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Discussion Section #/TA_____
Midterm #2 (100 pts total)   Wednesday 5AM.   **Chem 20A, Winter 2016**
March 4th, 2016 (11:00 - 11:50 a.m.)

This exam is closed book but you are allowed one 8.5" x 11" sheet of notes. Non-programmable calculators are allowed. Please read the questions carefully and make sure you answer all (and only!) the questions that are asked and be sure that your answers in the appropriate units with a reasonable number of significant figures. Be sure to show all your work as explicitly as possible if you want to receive partial credit, and circle or box your final answer(s); significant figures an units are an important part of each answer. Remember, a correct sentence or two explaining your reasoning and choice of equations will earn most of the points for a problem even if there is a numerical error. (Conversely, incorrect reasoning with a correct answer will result in points being deducted.) If you need additional space, use the back of the page and indicate on the front of the page that your work is continued on the back.

CONSTANTS:

N_{Av} = 6.0223 x 10^{23} atoms/mole c = 2.9979 x 10^8 m/s
e = 1.6022 x 10^{-19} C m_e = 9.1094 x 10^{-31} kg
ε_0 = 8.8542 x 10^{-12} C^2/(J m) m_p = 1.6726 x 10^{-27} kg
h = 6.6261 x 10^{-34} J s g = 9.8067 m/s^2
π = 3.14159 $1/(4\pi\varepsilon_0)$ = 8.9875 x 10^9 (J m)/C^2
C atom: Z = 6; atomic weight = 12.011 g/mole; $[He](2s)^2(2p)^2$
N atom: Z = 7; atomic weight = 14.0067 g/mole; $[He](2s)^2(2p)^3$
O atom: Z = 8; atomic weight = 15.9994 g/mole; $[He](2s)^2(2p)^4$
S atom: Z = 16; atomic weight = 32.06 g/mole; $[Ne](3s)^2(3p)^4$
Ba atom: Z = 56; atomic weight = 137.327 g/mole; $[Kr](2s)^2$

#1	12
#2	30
#3	50
Total	92

CONVERSION FACTORS:

1 atomic mass unit = 1.6605 x 10^{-27} kg; 1 Å = 1 x 10^{-10} m = 0.1 nm ; 1 nm = 1 x 10 m
1 eV = 1.6022 x 10^{-19} J = 96.485 kJ/mole "=" 8065.5 cm^{-1}; 1 kJ = 1000 J

FORMULAS:

K.E. = $1/2\, m v^2$; $F = -\Delta U/\Delta x$

E_{ph} = $h\nu$ = hc/λ; deBroglie Wavelength: $\lambda = h/p$; $\hbar = h/2\pi$

Coulomb Potential: $U(r) = q_1 q_2/(4\pi\varepsilon_0 r)$; Coulomb Force: $F_C = q_1 q_2/(4\pi\varepsilon_0 r^2)$

Moment of Inertia for a Diatomic Molecule: $I = \dfrac{m_1 m_2}{m_1 + m_2} R^2$

Reduced mass for a Diatomic Molecule: $\mu_{red} = m_1 m_2/(m_1 + m_2)$

Frequency for a vibrating diatomic molecule: $\omega_{osc} = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu_{red}}}$

Bragg Formula for maxima: $n\lambda = d \sin\theta$; n = 1, 2, 3, ...

One-e^- Atom Electronic Energy Levels: $E = -\dfrac{m(2\pi)^2 e^4 Z^2}{2h^2(4\pi\varepsilon_0)^2 n^2} = -\dfrac{Z^2}{n^2}E_0$; n = 1, 2, 3, ...

Energy Levels for a Rotating Diatomic: $E = \dfrac{\hbar^2}{2I}J(J+1)$; J = 0, 1, 2, 3, ...

Energy Levels for a Vibrating Diatomic: $E = h\omega_{osc}(v + 1/2)$; v = 0, 1, 2, 3, ...

Dipole Moment (for μ in Debye; R in Å; δ in e^- units): $\mu = R\delta/0.2082$

This v. 1 exam has 5 total pages, including this cover page

Midterm (Continued)

1. (20 pts total) The Lewis structure (but not necessarily the chemical structure!) for the hydrocarbon molecule propene (C_3H_6) is shown at right. Keep in mind that although the structure is drawn co-planar with bonds at right angles, the actual chemical structure and bond angles are likely to be different. Note: No MO diagram is needed for this problem!

$$\begin{array}{ccc} H & & H \\ | & b & | \\ {}^{a}\,C = C - C - H \\ | & |\,c & |\,d \\ H & H & H \end{array}$$
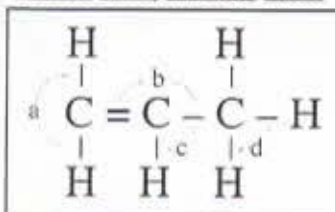
(a) (16 points) Use the ideas of the VSEPR theory to estimate the four bond angles (a, b, c and d) shown in the picture. For each of the 4 bond angles, do you expect the actual bond angle to be slightly larger, slightly smaller, or equal to your estimate? Briefly explain why for each angle.

< smaller
> greater.

a — $\sim < 120°$ — dbe on opposite site of large charge density (double bond).

b — $\sim > 120°$ — adjacent to a double bond, when charge density will be higher.

c — $\sim < 120°$ — on opposite side of large charge density (double bond).

d — exactly $109.5°$ — no lone pairs / double bonds / 0

(b) (4 points) List the hybridization of each of the three C atoms (left, center, and right) in the molecule; no justification is needed.
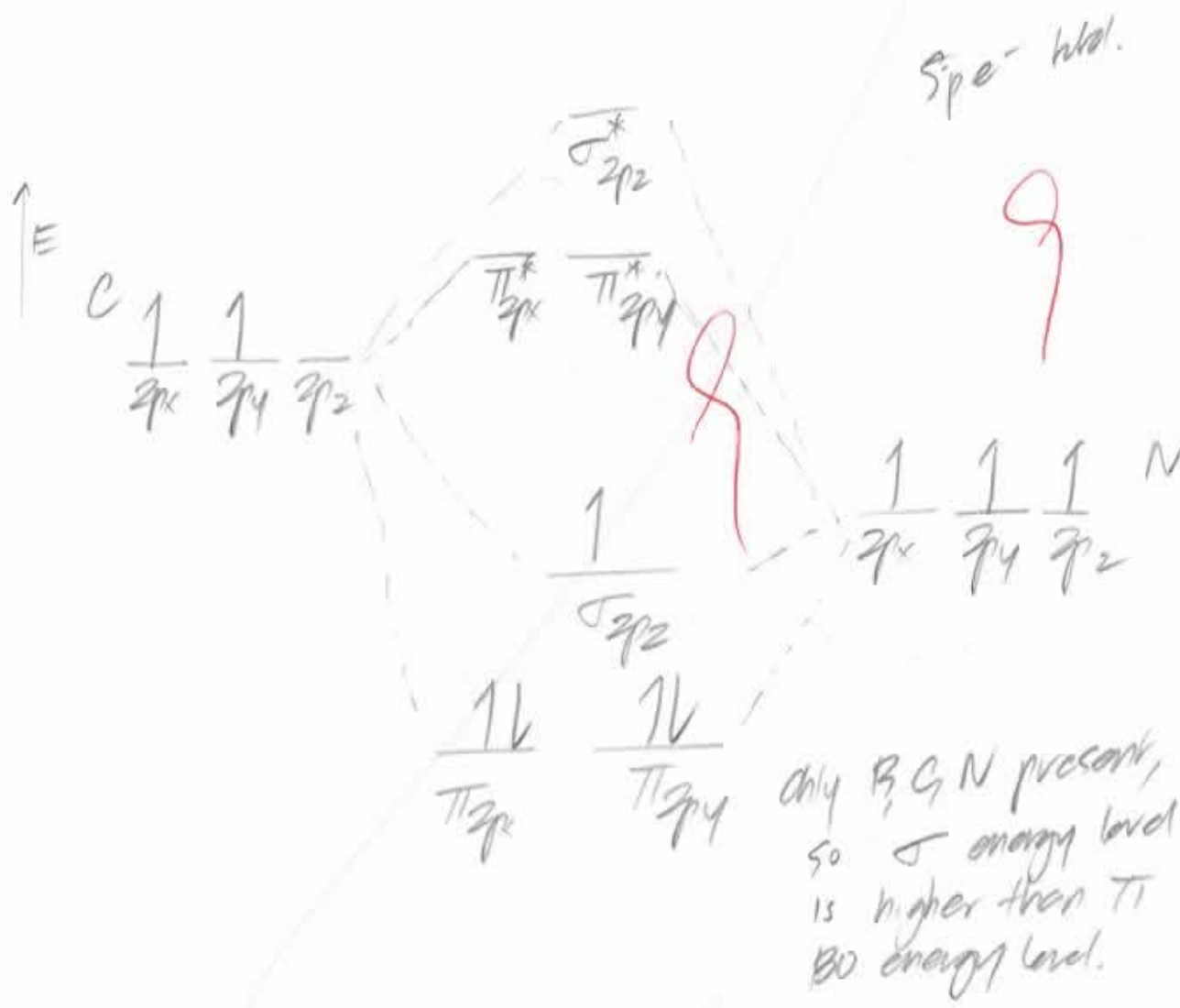
$sp^2 \, s$ $\quad sp^2, \; sp^2, \; sp^3$

2. (30 points total) The cyanogen molecule (CN) is known to be a stable although highly reactive diatomic, and its structure has been deduced in various spectroscopy experiments.

(a) (20 points) Write down a molecular orbital energy (correlation) diagram for the CN molecule; you do *not* need to include the filled MO's formed by LCAOs of the 1s or 2s orbitals, only those formed from the LCAO's of the 2p valence electrons. Be sure to fill the molecular energy levels with the appropriate number of electrons for CN. Label each of the AO's and MO's in your diagram, and be sure to *briefly* justify how you picked the ordering of the MO energy levels.

$5p e^-$ htd.

E

C $\uparrow$ $\uparrow$ $\overline{}$
      $2p_x$ $2p_y$ $2p_z$

$\sigma^*_{2p_z}$

$\pi^*_{2p_x}$ $\pi^*_{2p_y}$

$\uparrow$
σ_{2p_z}

$\uparrow\downarrow$ $\uparrow\downarrow$
π_{2p_x} π_{2p_y}

$\uparrow$ $\uparrow$ $\uparrow$ N
$2p_x$ $2p_y$ $2p_z$

only B, C, N present, so σ energy level is higher than π BO energy level.

3

(20)

2. (Continued)

(b) (10 points) Write down a Lewis structure for CN, and make sure to indicate formal charges on each atom. Based on your MO diagram in part (a), what is the bond order of CN? Does this agree with the Lewis structure (yes or no)? Would you expect CN to be paramagnetic or diamagnetic?

C: 4 valence e's
N: 5 valence e's

$4 + 5 = 9$

$$?\ \ :C \!\!\equiv\!\! N: \ \ ?$$

Since N is more electronegative, assume N has the lone pair + C has single e⁻.

:C⋮⋮N:
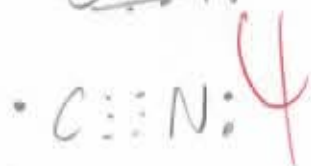
C formal charge: $4 - (1_p + 3_b) = 0$
N formal charge: $5 - (2_p + 3_b) = 0$

bond order of CN according to MO diagram: $\frac{5}{2} = 2.5$

No, LS shows BO of 3, so they disagree.

paramagnetic.

3. (50 points) A microwave spectroscopy experiment on the $^{137}Ba-^{16}O$ molecule shows a series of evenly spaced absorption lines, with the lowest frequency line having a wavelength of 16.0 mm (= 0.016 m). An infrared absorption experiment on this same molecule shows a single line at 127 cm^{-1}. The bond dissociation energy of BaO is 561 kJ/mole. The dipole moment of BaO is 7.05 D units. Calculate the fraction ionicity (that is, the degree of charge separation) of the Ba–O bond.

vibrational

rotational

$$\mu = \frac{m_{Ba} \, m_O}{m_{Ba} + m_O} = 14.33 \ g/md \Rightarrow 2.3788 \times 10^{-26} \ kg/atom.$$

$5

Rotational

$$hf = \frac{h^2}{8\pi^2 (\mu R^2)} J(J+1) \Rightarrow \left(\frac{c}{h\lambda}\right)(h) \cdot \left(\frac{\mu \cdot 8\pi^2}{8\pi^2}\right) \cdot \frac{1}{2} = \frac{1}{R^2}$$

$$8\pi^2 \mu \cdot 0.016 = \frac{h^2}{R^2} (h)(2 = (0))$$

$$R = 1.9405 \times 10^{-10} \ m$$

$$= 1.94 \ A°$$

less

$$\mu = R\delta/.2082.$$

$$7.05 = R\delta/.2082.$$

$$\delta = .7564 e^-   +50$$

charge separation: $\dfrac{\delta}{r}$ (?)

$$= .7564e \cdot 1.6022 \times 10^{-19} \frac{C}{e^-}$$

$$1.94 \times 10^{-10} \ m \ =$$

$$6.2469 \times 10^{-10} \ C/m$$