Solutions

Name _____

CHM 3411, Dr. Chatfield, March 26, 2018

Exam 2

You may use a calculator (non-graphing), but nothing else. If you need extra room, use the back of exam pages and direct the grader where to look. You may also use scratch paper, but **put all final answers on the exam itself and attach any scratch paper with work the grader should read. Read all problems carefully**. Set up problems methodically, show your work, and be neat. Partial credit will be given when it is possible for me to follow your work. If you are having trouble with a problem, go on to the next and come back.

GOOD LUCK!

Constants:

$h = 6.626 \times 10^{-34}\, Js$ $\hbar = \frac{h}{2\pi}$ $m_e = 9.11 \times 10^{-31}\, kg$ $c = 3.00 \times 10^8\, m\, s^{-1}$

$k = 1.38 \times 10^{-23}\, J\, K^{-1}$ $N_A = 6.022 \times 10^{23}\, mol^{-1}$ $amu = 1.66 \times 10^{-27}\, kg$ $a_o = 52.9\, pm$

$\tilde{R}_\infty = 1.097 \times 10^5\, cm^{-1}$ $e = 1.602 \times 10^{-19}\, C$ $\epsilon_0 = 8.854 \times 10^{-12}\, J^{-1}C^2 m^{-1}$

Equations (others are given directly in exam questions):

$\lambda = \frac{h}{p}$ $\Delta x \Delta p \geq \frac{\hbar}{2\pi}$ $\lambda v = c$ $\tilde{v} = \frac{1}{\lambda}$ $\Delta E = hv = \hbar \omega$ $d\tau = r^2 \sin\theta\, dr\, d\theta\, d\phi$

$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$ $\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + \hat{V}(x)$ $E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \frac{Z^2}{n^2} = -hc\tilde{R}_\infty \cdot \frac{Z^2}{n^2}$ $E = \frac{l(l+1)\hbar^2}{2I}$

$P(r) = 4\pi r^2 \psi^2$ $P(r) = r^2 \mathcal{R}^2(r)$ $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

1. Consider this excited electron configuration of silicon: Si $[Ne]3s^23p^13d^1$

(a) Determine all possible term symbols, using Russell-Saunders coupling.

We only need to consider partially filled subshells

$\Rightarrow 3p^13d^1$

$\ell_1 = 1 \quad \ell_2 = 2 \quad L = 2+1, \ldots, |2-1| = 3, 2, 1$

$S_1 = \frac{1}{2} \quad S_2 = \frac{1}{2} \quad S = \frac{1}{2} + \frac{1}{2}, \ldots, |\frac{1}{2} - \frac{1}{2}| = 1, 0$

L	S	J			
3	1	$J = 3+1, \ldots, |3-1| = 4, 3, 2$	$^3F_4$	$^3F_3$	$^3F_2$
3	0	3	$^1F_3$		
2	1	3, 2, 1	$^3D_3$	$^3D_2$	$^3D_1$
2	0	2	$^1D_2$		
1	1	2, 1, 0	$^3P_2$	$^3P_1$	$^3P_0$
1	0	1	$^1P_1$		

Term symbol $= {}^M\!\boxed{L}_J$

$M = 2S+1$ multiplicity

$\boxed{L} = S(L=0), P(L=1), D(L=2), F(L=3)\ldots$

(b) There are many allowed spectroscopic transitions between these terms. To keep it simple, list just the pairs that include at least one P term. Explain the basis of your reasoning.

Selection rules: $\Delta S = 0 \qquad \Delta L = 0, \pm 1 \qquad \Delta J = 0, \pm 1$
but $J=0 \xleftarrow{1} \rightarrow J=0$

Transitions involving at least one P term
_____

represents
both absorp.
+emission

$^3P_2 \leftrightarrow {}^3D_3 \qquad {}^3P_2 \leftrightarrow {}^3D_2 \qquad {}^3P_2 \leftrightarrow {}^3D_1$

$^3P_1 \leftrightarrow {}^3D_2 \qquad {}^3P_1 \leftrightarrow {}^3D_1$

$^3P_0 \leftrightarrow {}^3D_1$

$^3P_2 \leftrightarrow {}^3P_1 \qquad {}^3P_1 \leftrightarrow {}^3P_0$

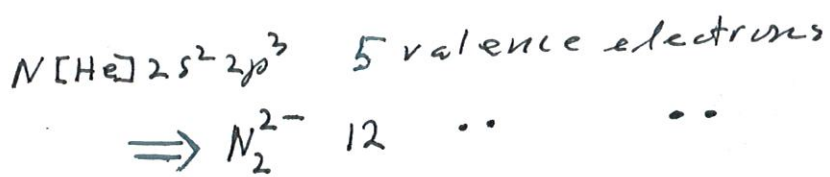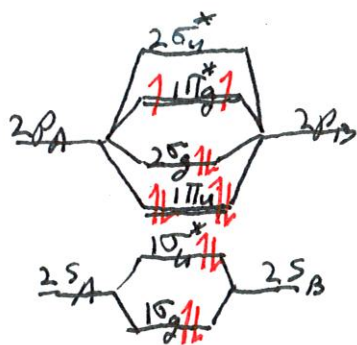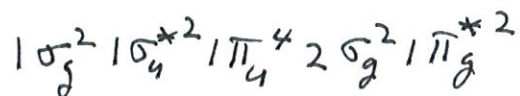$^1P_1 \leftrightarrow {}^1D_2$

2. Consider the N_2^{2-} di-anion *and fill it with electrons*

(a) Construct an MO energy level diagram for the ground state. Label the MOs and indicate which are antibonding. You may use either labeling scheme we discussed, but you must be consistent. Assume the ordering of MOs is the same as for neutral N_2 neutral.

$N [He] 2s^2 2p^3$ 5 valence electrons

$\Rightarrow N_2^{2-}$ 12

(b) Determine the electron configuration.

$$1\sigma_g^2 \, 1\sigma_u^{*2} \, 1\pi_u^4 \, 2\sigma_g^2 \, 1\pi_g^{*2}$$

(c) Suppose one electron is removed to form the N_2^- mono-anion. Determine whether removing the electron will increase or decrease the bond dissociation energy. You must provide your reasoning for credit.

N_2^{2-} $b = \frac{1}{2}(N - N^*) = \frac{1}{2}(8 - 4) = 2$

N_2^- $1\sigma_g^2 \, 1\sigma_u^{*2} \, 1\pi_u^4 \, 2\sigma_g^2 \, 1\pi_g^{*1}$ $b = \frac{1}{2}(8 - 3) = \frac{5}{2}$

N_2^- has the larger bond order

Therefore removing the electron $\boxed{increases}$ the bond dissociation energy.

3. Answer the following multiple choice or short answer questions by circling the correct answer(s) or giving information as indicated.

a. Which of the following AOs contribute to a σ bond in a diatomic molecule (circle all that apply):
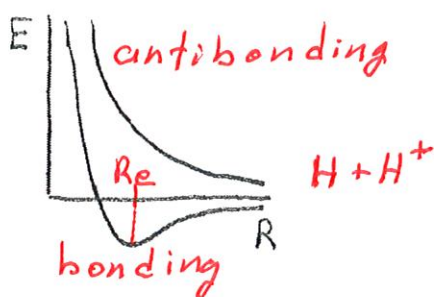
(A) 2s

(B) $2p_x$
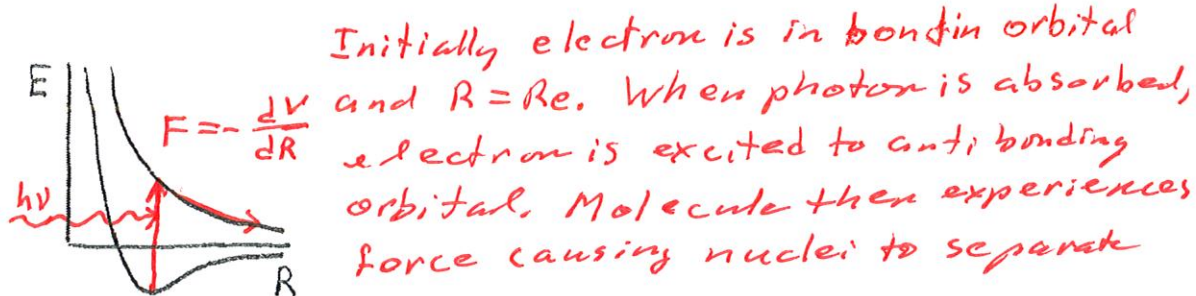
(C) $2p_y$

(D) $2p_z$

b. Below is a sketch of a pair of potential energy surfaces (PES's) for H_2^+. One PES is for a bonding orbital and one PES is for an antibonding orbital. (i) Label the PES's as bonding or antibonding, (ii) identify the equilibrium bond distance, and (iii) label the species present as R gets very large.

E

antibonding

R_e

$H + H^+$

R

bonding

c. Below is same the sketch of PES's for H_2^+ as in (c). Add markings to demonstrate the process of photodissociation.

E

$F = -\dfrac{dV}{dR}$

$h\nu$

R

Initially electron is in bondin orbital and R = Re. When photon is absorbed, electron is excited to anti bonding orbital. Molecule then experiences force causing nuclei to separate

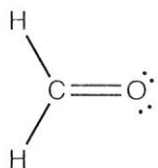d. Which of the following spatial functions belongs to a triplet state?

(A) $\psi_{1s}(1)\,\psi_{2s}(2)$

(B) $\psi_{1s}(1)\,\psi_{1s}(2)$

(C) $\psi_{1s}(1)\,\psi_{2s}(2) - \psi_{1s}(2)\,\psi_{2s}(1)$

(D) $\psi_{1s}(1)\,\psi_{2s}(2) + v\,\psi_{1s}(2)\,\psi_{2s}(1)$

4. The Lewis structure for formaldehyde is shown below.

a) Give a complete Valence Bond (VB) description of the bonds. Include any hybridization and give the atomic orbitals (regular or hybrid) that contribute to each bond.

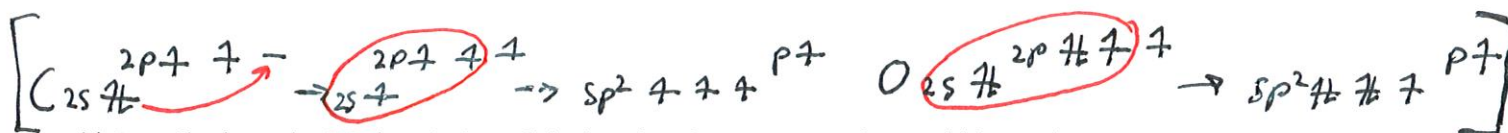C and O are both sp^2 hybridized, so each has 3 sp^2 hybrid orbitals (h_1, h_2, h_3) and 1 p orbital

Bonds

2 C–H σ bonds, each formed from a C sp^2 hybrid and an H 1s orbital

1 C–O σ bond, formed from a C sp^2 hybrid and an O sp^2 hybrid orbital

1 C–O π bond, formed from a C p and an O p orbital

[The two lone pairs on O fill the remaining O sp^2 hybrids]

$$\left[C\; 2s\uparrow\downarrow\; 2p\uparrow\uparrow\uparrow\_ \to 2s\uparrow\; 2p\uparrow\uparrow\uparrow \to sp^2\uparrow\uparrow\uparrow\uparrow\; p\uparrow \qquad O\; 2s\uparrow\downarrow\; 2p\uparrow\downarrow\uparrow\uparrow \to sp^2\uparrow\downarrow\uparrow\downarrow\uparrow\; p\uparrow \right]$$

b) Describe how the VB description of the bonding between C and O could be made more accurate.

The description above implicitly describes both the C–O σ and the C–O π bond as covalent. Since the bonds are really polar, including an ionic component to create an ionic–covalent resonance hybrid will improve the VB representation.

$$\Psi = \Psi_{cov} + \lambda \Psi_{ion}$$

adjustable parameter

ignoring spin

$$\Psi_{cov} = \Psi_{Ch_1}(1)\Psi_{Oh_1}(2) + \Psi_{Ch_1}(2)\Psi_{Oh_1}(1) \qquad \Psi_{ion} = \Psi_{Oh_1}(1)\Psi_{Oh_1}(2)$$

and analogous expressions for the π bond.

5. A wave function for the hydrogen atom is given below. (To keep things simple, r is in terms of the a_o, the Bohr radius. This is called an "atomic unit of distance" or just an "atomic unit.")

$$\psi = N(2-r)e^{-r/2}$$

(a) Identify any radial nodes or nodal planes.

1 radial node @ $r = 2a_o$

(b) Identify the orbital (1s, 2s, 2p_x etc)?

1 node $\Rightarrow$ n = 2

No θ dependence $\Rightarrow$ $l = 0$ $\Rightarrow$ S

$\boxed{2S}$

(c) Determine the most probable distance of the electron from the nucleus.

$P(r) = r^2 R^2$ and because there is no θ or ϕ dependence, $Y(\theta, \phi)$ is a constant $\Rightarrow$ $\psi \propto R$

includes constant of proportionality $\downarrow$

$P(r) = M^2 r^2 (2-r)^2 e^{-r}$

P_{max} obtained by setting $\frac{dP}{dr} = 0$

$0 = M^2 [2r(2-r)^2 - 2r^2(2-r) - r^2(2-r)^2] e^{-r}$

$= 0$ divide by $r(2-r)$

$0 = 2(2-r) - 2r - r(2-r) = r^2 - 6r + 4$

$r = \frac{6 \pm \sqrt{36-16}}{2} = 3 \pm \sqrt{5} = 5.24, 0.76$

Plug each value into expression for P to see which is larger

$P(5.24) = 1.71 M^2$

$P(0.76) = 0.42 M^2$

$\boxed{5.24 a_o \text{ is most probable distance}}$

6. Give brief explanations for **2 of the following 3** concepts, using examples where possible. *If you give more than 2 answers, only the first 2 will be graded.*

(a) Spin-correlation

The Pauli principle causes electrons to be correlated by their spins. As a result, electrons with like spin have a smaller probability of being close to each other than electrons with opposite spin.

⟹ Electrons with like spin experience less el.-el. repulsion

⟹ Basis for Hund's maximum multiplicity rule

(b) Orbital approximation

The approximation that the total wavefunction can be expressed as a product of one-electron wavefunctions (properly antisymmetrized via a Slater determinant).

⟹ Justified by neglecting el.-el. repulsion terms to create separable Hamiltonian.

(c) Born-Oppenheimer approximation

The assumption that electrons adjust instantaneously to any change in the nuclear coordinates, because the nuclei are much more massive.

⟹ The adjustment is actually very fast but no instantaneous. Hence this is an approx.