Exam 2 Retest Solutions

1. Consider this excited electron configuration of ~~phosphorus~~ aluminum: Al [Ne]$2s^1 2p^1 3p^1$

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

$S_1 = \frac{1}{2}$ $S_2 = \frac{1}{2}$ $S_3 = \frac{1}{2}$

$\hat{S} = \frac{1}{2} + \frac{1}{2}, \ldots |\frac{1}{2} - \frac{1}{2}| = 1, 0$

$\frac{\hat{S}}{1} \quad \frac{S_3}{\frac{1}{2}} \quad S = 1 + \frac{1}{2}, \ldots, |1 - \frac{1}{2}| = \frac{3}{2}, \frac{1}{2}$

$\ell_1 = 0 \quad \ell_2 = 1 \quad \ell_3 = 1$

$\hat{L} = 0 + 1, \ldots, |0 - 1| = 1$

$\hat{L} = 1 + 1, \ldots, |1 - 1| = 2, 1, 0$

L	S	J				
2	$\frac{3}{2}$	$2 + \frac{3}{2}, \ldots, |2 - \frac{3}{2}| = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$	$^4D_{7/2}$	$^4D_{5/2}$	$^4D_{3/2}$	$^4D_{1/2}$
2	$\frac{1}{2}$	$2 + \frac{1}{2}, \ldots, |2 - \frac{1}{2}| = \frac{5}{2}, \frac{3}{2}$	$^2D_{5/2}$	$^2D_{3/2}$		
1	$\frac{3}{2}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}$	$^4P_{5/2}$	$^4P_{3/2}$	$^4P_{1/2}$	
1	$\frac{1}{2}$	$\frac{3}{2}, \frac{1}{2}$	$^2P_{3/2}$	$^2P_{1/2}$		
0	$\frac{3}{2}$	$\frac{3}{2}$	$^4S_{3/2}$			
0	$\frac{1}{2}$	$\frac{1}{2}$	$^2S_{1/2}$			

(b) There are many allowed spectroscopic transitions between these terms. Give at least 5 allowed transitions. Explain the basis of your reasoning.

$\Delta S = 0 \quad \Delta L = 0, \pm 1 \quad \Delta J = 0, \pm 1$

$^4D_{7/2} \longleftrightarrow {}^4D_{5/2}$ $^4D_{5/2} \longleftrightarrow {}^4D_{3/2}$ $^4D_{3/2} \longleftrightarrow {}^4D_{1/2}$

$^4D_{7/2} \longleftrightarrow {}^4P_{5/2}$ $^4D_{5/2} \longleftrightarrow {}^4P_{5/2}$ $^4D_{5/2} \longleftrightarrow {}^4P_{3/2}$

$^4D_{3/2} \longleftrightarrow {}^4P_{5/2}$ $^4D_{3/2} \longleftrightarrow {}^4P_{5/2}$ $^4D_{3/2} \longleftrightarrow {}^4P_{3/2}$ $^4P_{3/2} \longleftrightarrow {}^4P_{1/2}$

$^4D_{1/2} \longleftrightarrow {}^4P_{3/2}$ $^4D_{1/2} \longrightarrow {}^4P_{1/2}$

$^4P_{5/2} \longleftrightarrow {}^4S_{3/2}$ $^4P_{5/2} \longleftrightarrow {}^4P_{3/2}$ $^4P_{3/2} \longleftrightarrow {}^4P_{1/2}$

$^2D_{5/2} \longleftrightarrow {}^2D_{3/2}$ $^2P_{3/2} \longleftrightarrow {}^2P_{1/2}$ $^2D_{5/2} \longleftrightarrow {}^2P_{3/2}$ $^2D_{3/2} \longleftrightarrow {}^2P_{3/2}$

$^2D_{3/2} \longleftrightarrow {}^2P_{1/2}$ $^2P_{3/2} \longleftrightarrow {}^2S_{1/2}$ $^2P_{1/2} \longleftrightarrow {}^2S_{1/2}$
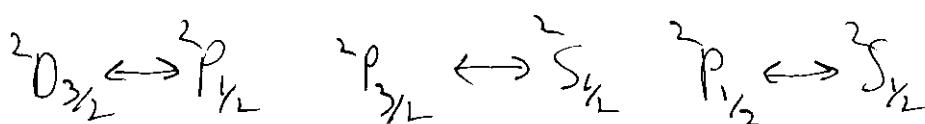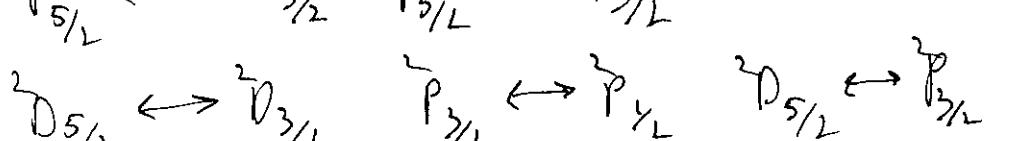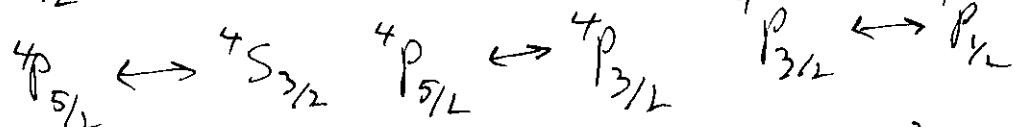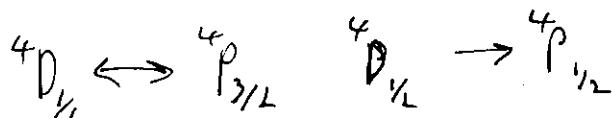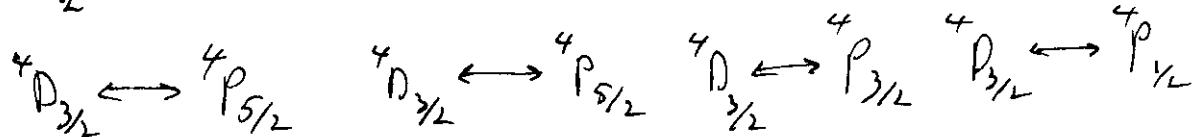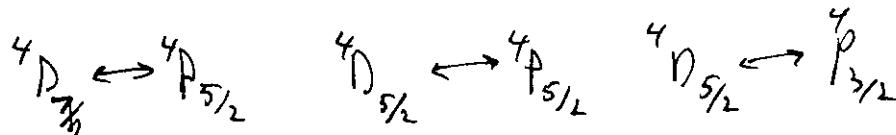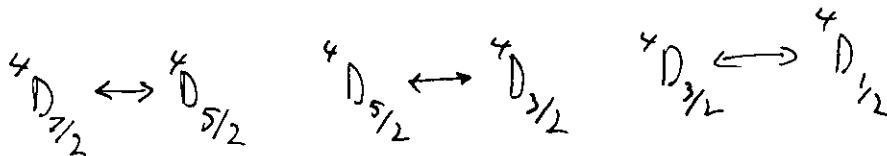
2. Consider the F_2 (F has atomic number 9).

(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.


F   7 valence e's

F_2 14   "   "
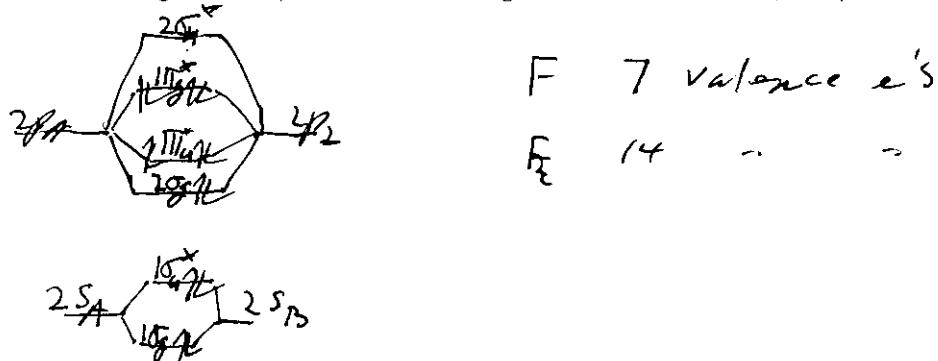
(b) Determine the electron configuration.

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

(c) (i) Determine whether adding an electron to form the F_2^- anion will increase or decrease the bond length (you must state why). (ii) Determine whether removing an electron to form the F_2^+ cation will increase or decrease the bond length (you must state why).

F_2 $b = \frac{1}{2}(n - n^{\perp}) = \frac{1}{2}(8-6) = 1$

F_2^- $b = \frac{1}{2}(8-7) = \frac{1}{2}$ increase bond length

F_2^+ $b = \frac{1}{2}(8-5) = \frac{3}{2}$ decrease "   "

(d) In the molecular orbital energy level diagram, state all AOs (atomic orbitals) that can contribute to the $2\sigma_g$ and $1\pi_u$ orbitals, and why.

$2\sigma_g$: $2s_A, 2s_B, 2p_{zA}, 2p_{zB}$

$1\pi_u$: $2p_{xA}, 2p_{xB}$ (or for other degenerate $1\pi_u$, $2p_{yA}, 2p_{yB}$)

AOs from $\ell = 3$ & higher will also contribute, but these are enough

4. Consider the molecule HCN.

(a) Draw a Lewis structure, including any lone pairs.

$$H-C\equiv N:$$
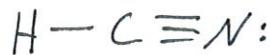
(b) Identify all σ and π bonds, determine any hybridization of the atoms, and make a sketch of the molecule using Valence Bond concepts, i.e., showing the σ and π bonds and giving the right geometry (correct bond angle).

2σ bonds ($C-H$, $C-N$)

$$H-C\equiv N$$

$180°$

2π .. ($C-N$, $C-N$)

$C: Sp$ (2 sp orb + 2 p orbs)

$N: Sp$ (-.   -.
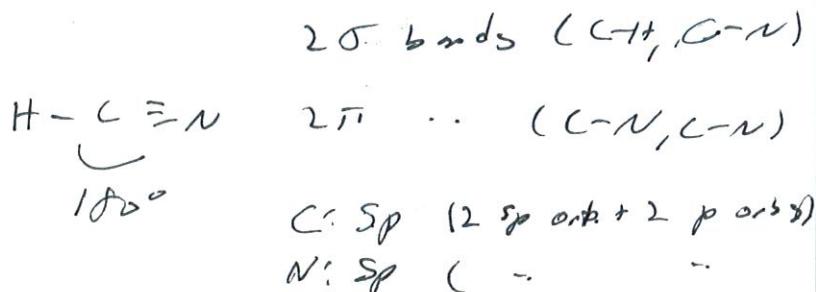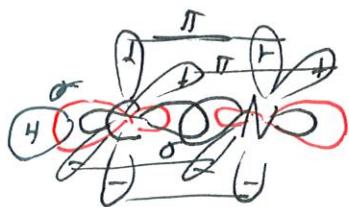
(c) Write wavefunctions for the σ and π bonds using AOs or hybrid orbitals as appropriate. If there are any lone pairs, describe what orbital(s) they occupy.

$\sigma_{CH}:$ $\psi = \psi_{H1s}^{(1)} \psi_{Ch_1}^{(2)} + \psi_{H1s}^{(2)} \psi_{Ch_1}^{(1)}$

$\pi_y:$ $\psi = \psi_{CP_y}^{(1)} \psi_{NP_y}^{(2)} + \psi_{CP_y}^{(2)} \psi_{NP_y}^{(1)}$

$\sigma_{CN}:$ $\psi = \psi_{Ch_2}^{(1)} \psi_{Nh_1}^{(2)} + \psi_{Ch_2}^{(2)} \psi_{Nh_1}^{(1)}$

$h_1 = $ hybrid sp orbital #1

$h_2 = $ . .   . .

$\pi_x:$ $\psi = \psi_{CP_x}^{(1)} \psi_{NP_x}^{(2)} + \psi_{CP_x}^{(2)} \psi_{NP_x}^{(1)}$

(d) Write an improved wavefunction for the σ bond that takes into account the difference in negativity between C and N.

$$\psi_\sigma = \psi_{cov} + \lambda \psi_{ion}$$

$$\text{where } \psi_{cov} = \psi_{\sigma_{CN}} \text{ above}$$

$$\psi_{ion} = \psi_{NP_x}^{(1)} \psi_{NP_x}^{(2)}$$

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.")

$$\psi = Nr^2 e^{-\frac{r}{3}}(3\cos^2\theta - 1)$$

(a) Identify any radial nodes or ~~nodal planes~~ *angular nodes*.

2 angular nodes: $\cos\theta = \pm\sqrt{3}$

0 radial nodes

(b) Identify the orbital (1s, 2s, 2p$_x$ etc)?

$n = \#\text{ nodes} + 1 = 3$ 2 angular nodes/nodal planes $\Rightarrow \ell = 2$

no ϕ-dependence $\Rightarrow m_\ell = 0$

$3d_{z^2}$

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

$P_{(r)} = r^2 R^2$ $R = M r^2 e^{-r/3}$ (r-part of ψ; M is some norm. const.)

$P_{(r)} = M^2 r^6 e^{-2r/3}$

Max @ $\frac{dP}{dr} = 0 = M^2 \left(6r^3 - \frac{2}{3}r^4\right) e^{-2r/3}$

We can anticipate single max from form of P

$6r^3 - \frac{2}{3}r^4 = 0$ $r^3\left(6 - \frac{2}{3}r\right) = 0$ $\frac{2}{3}r = 6$ $\underline{r_{mp} = 9}a_0$

(d) Write an equation for calculating the average distance of the electron from the nucleus. Do not evaluate it. Tell whether you expect the average distance to be the same as the most probable distance, and why.

$\langle r \rangle = \int \psi^* r \psi \, d\tau = N^2 \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^5 e^{-2r/3}(3\cos^2\theta - 1)^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi$

$= N^2 \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^5 e^{-2r/3}(3\cos^2\theta - 1) \sin\theta \, dr \, d\theta \, d\phi$

There is no reason to expect $\langle r \rangle$ to be equal to r_{mp}. Most likely $r_{mp} < \langle r \rangle$ because of the shape of P.