Chemistry 410A | **Exam 4** | **Fall 2011**

Solutions

1. **40 points.**

   (a) What are the values of L and S for the ground electron configurations of any of the noble gases? **Solution:** The electrons fill every occupied subshell in the noble gases, so all the m_l and m_s values cancel: $\boxed{L = 0 \text{ and } S = 0.}$

   (b) A partial Hamiltonian for the HeH_2^+ molecule is given below, with the hydrogens labelled A and B. Cross out or replace any *incorrect* terms, and then add any missing *correct* terms.

   $$\hat{H} = -\frac{\hbar^2}{2m_e}\left[\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_{He}^2 + \nabla_A^2 + \nabla_B^2\right]$$

   $$+ \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right] + \frac{e^2}{4\pi\epsilon_0 R_{AB}} + \frac{2e^2}{4\pi\epsilon_0 R_{HeA}} + \frac{2e^2}{4\pi\epsilon_0 R_{HeB}}$$

   $$- \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{A2}} + \frac{1}{r_{A3}} + \frac{1}{r_{B1}} + \frac{1}{r_{B2}} + \frac{1}{r_{B3}} + \frac{2}{r_{He1}} + \frac{2}{r_{He2}} + \frac{2}{r_{He3}}\right)$$

   Solution: There are 3 electrons (so all the electron 4 terms should be crossed off) and all the potential energy terms (attraction by electrons and repulsion by H nuclei) involving the He atom were missing.

   (c) A $2s$ orbital and a $2p_z$ orbital are combined to make a pair of non-equivalent sp hybrids, sp_a and sp_b. If the sp_a hybrid has the formula below, give the formula for the normalized function sp_b:

   $$(sp_a) = \sqrt{\frac{3}{5}}(2s) - \sqrt{\frac{2}{5}}(2p_z).$$

   Solution: If we start from

   $$(sp_b) = c_1(2s) + c_2(2p_z).$$

   The squares of the coefficients need to equal 1 (for it to be normalized, so $c_1^2 + c_2^2 = 1$) and the products of the sp_a and sp_a coefficients need to cancel (for the two hybrids to be orthogonal, so $\sqrt{2/5}c_1 - \sqrt{3/5}c_2 = 0$). That gives:

   $$(sp_b) = \sqrt{\frac{2}{5}}(2s) + \sqrt{\frac{3}{5}}(2p_z).$$

   (d) Find the chemical shift of the carbon atoms in the ^{13}C NMR spectrum of benzene if the shielding constant is 65.2 ppm, while the shielding constant for the carbons in TMS is 192.3 ppm. **Solution:** The chemical shift is inversely proportional to the shielding constant:

   $$\delta \approx \sigma_0 - \sigma = 192.3 - 65.2 = \boxed{127.1\,\text{ppm.}}$$

2. Find the term states, including J values, of neutral platinum atom in its ground electron configuration, $[Xe]6s^1 4f^{14} 5d^9$. Rank these **from left to right** in order of increasing energy. **Solution:** This is tractable using the vector model (20 microstates), but can also be managed by seeing that we have one s electron with $s = 1/2$ and $l = 0$, and 9 d electrons, for which all the angular momenta must cancel except for the s and l of one electron (or more accurately, one electron "hole"). The one uncancelled electron has $s = 1/2$ and $l = 2$, so we are coupling two spins of $1/2$ (which give 0 and 1 as possible results) and have only the net $l = 2$ of the uncancelled d electron. Therefore the terms are ^1D and ^3D, and applying Hund's rules we get the ranking $\boxed{^3D_3 <\, ^3D_2 <\, ^3D_1 <\, ^1D_2.}$

3. The data below are from nitrogen NMR spectra of the atoms at each end of NNN^-. Two common reference substances are NH_3 ($\sigma_0 = 269\,\text{ppm}$) and CH_3NO_2 ($\sigma_0 = -112\,\text{ppm}$).

(a) Fill out the remaining entries in the table. **Solution:** The shielding constant $\sigma = \sigma_0 - \delta = 170\,\text{ppm}$ is unchanged when we change the reference, so we can calculate the new chemical shift as $\delta' \approx \sigma_0' - \sigma$. The local magnetic field is given by $B_{\text{local}} = B_0(1-\sigma)$, so $B_0 - B_{\text{local}} = \sigma B_0$. Keep in mind that the σ's and δ's are in ppm, so need to be multiplied by 10^{-6} when comparing to other numbers. The chemical shift is not affected by change in magnetic field.

nucleus	^{15}N	^{15}N	^{15}N
field (T)	9.4	9.4	14.1
reference	NH_3	CH_3NO_2	NH_3
δ (ppm)	99	-282	99
$B_0 - B_{\text{local}}$ (T)	0.0016	0.0016	0.0024

(b) Which of the following describes the δ value of nitrogen atom N_a in neutral hydrozoic acid, $HNN^{15}N_a$, at $9.4\,\text{T}$ using NH_3 as a reference (circle one):

$< 99\,\text{ppm}$ $\qquad\qquad\qquad$ $99\,\text{ppm}$ $\qquad\qquad\qquad$ $\boxed{> 99\,\text{ppm}}$

Solution: Adding a proton to N^{3-} will take electron density away from the atoms in the anion, which reduces the shielding and *increases* the chemical shift.

4. The bonds along the molecular axis of carbon dioxide can be thought of as forming from combinations of hybrid orbitals on each of the three atoms. Assume the molecule lies on the z axis.

(a) What is the hybridization at each oxygen atom? **Solution:** Each oxygen has one double bond and two lone pairs, which is three groups, so the hybridization is $\boxed{sp^2.}$

(b) What is the hybridization at the carbon atom? **Solution:** The carbon has two double bonds and no lone pairs, so two groups and the hybridization is $\boxed{sp.}$

(c) Write a formula in terms of the *atomic orbitals* of these atoms for the wavefunction that forms the $C{-}O_B$ bonding orbital. Assume the hybrid orbitals at each atom are all equivalent. **Solution:** The equivalent sp and sp^2 hybrids that lie on the z axis must be

$$(sp_\pm)_C = \sqrt{\frac{1}{2}}(2s)_C \pm \sqrt{\frac{1}{2}}(2p_z)_C$$

$$(sp_\pm^2)_O = \sqrt{\frac{1}{3}}(2s)_O \pm \sqrt{\frac{2}{3}}(2p_z)_O.$$

To point the $(sp_\pm)_C$ orbital towards O_B, we want $(sp_+)_C$, and to point $(sp_\pm^2)_O$ towards the C atom we want $(sp_-^2)_O$. To increase bonding density between the C and the O atom, we now add these two together. The phase of each hybrid is positive in the bonding region, between the two atoms, so they constructively interfere and increase the density of the electron:

$$\sqrt{\frac{1}{2}}(2s)_C + \sqrt{\frac{1}{2}}(2p_z)_C + \sqrt{\frac{1}{3}}(2s)_O - \sqrt{\frac{2}{3}}(2p_z)_O.$$

(d) Sketch the amplitude of that wavefunction along z below.