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

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) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- **The first page portion 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. **40 points.**

(a) What are the values of L and S for the ground electron configurations of any of the noble gases?

(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.

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2m_e}\left[\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_4^2 + \nabla_{\mathrm{He}}^2 + \nabla_{\mathrm{A}}^2 + \nabla_{\mathrm{B}}^2\right] \\ &+ \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}}\right] \\ &- \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{\mathrm{A1}}} + \frac{1}{r_{\mathrm{A2}}} + \frac{1}{r_{\mathrm{A3}}} + \frac{1}{r_{\mathrm{A4}}} + \frac{1}{r_{\mathrm{B1}}} + \frac{1}{r_{\mathrm{B2}}} + \frac{1}{r_{\mathrm{B3}}} + \frac{1}{r_{\mathrm{B4}}}\right) \\ &+ \frac{e^2}{4\pi\epsilon_0 R_{\mathrm{AB}}}\end{aligned}$$

(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:

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

(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.

2. Find the term states, including J values, of neutral platinum atom in its ground electron configuration, $[\mathrm{Xe}]6s^1 4f^{14} 5d^9$. Rank these **from left to right** in order of increasing energy.

lowest energy **highest energy**

3. A table is started below for data from nitrogen NMR spectra of the atoms at each end of the linear azide anion, NNN^-. Separate entries are given for two common reference substances, NH_3 ($\sigma_0 = 269\,\mathrm{ppm}$) and CH_3NO_2 ($\sigma_0 = -112\,\mathrm{ppm}$)

   (a) Fill out the remaining entries in the table.

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

   (b) Which of the following describes the δ value of nitrogen atom N_a in neutral hydrozoic acid, $HNN^{15}N_a$, at $B_0 = 9.4\,\mathrm{T}$ using NH_3 as a reference (circle one):

   $< 99\,\mathrm{ppm}$ $99\,\mathrm{ppm}$ $> 99\,\mathrm{ppm}$