Chem 452 – Exam III
April 8, 2009

Cover Sheet
Closed Book, Closed Notes

There are 6 problems. The point value of each part of each problem is indicated.

Useful Equations:

\[ \hat{T} = -\frac{\hbar^2}{2m} \nabla^2 \]

\[ V(r_{ab}) = \frac{Z_a Z_b e^2}{4\pi \varepsilon_o r_{ab}} \]

\[ (\alpha_A - E)c_A + (\beta - ES)c_B = 0 \]

\[ (\beta - ES)c_A + (\alpha_B - E)c_B = 0 \]

\[ A_{1\rightarrow 0} = \left( \frac{8\pi \hbar^3}{e^4} \right) B_{1\rightarrow 0} \]

\[ B_{1\rightarrow 0} = \frac{\mu_{00}^2}{6\varepsilon_o \hbar^2} \]

\[ A = \varepsilon(v) Cl \]

\[ E_J = \hbar c F(J) \]

\[ F(J) = BJ(J + 1) \]

\[ B = \frac{\hbar}{4\pi cl} \]

\[ E_v = \hbar c G(v) \]

\[ G(v) = \left( v + \frac{1}{2} \right) \tilde{v} - \left( v + \frac{1}{2} \right)^2 \chi_e \tilde{v} \]

\[ \tilde{v} = \frac{1}{2\pi e} \sqrt{\frac{k}{\mu}} \]

\[ x_e = \frac{\tilde{v}}{4D_e} \]

Useful Constants

\[ e = 1.6022 \times 10^{-19} \text{ C} \]

\[ \varepsilon_o = 8.8542 \times 10^{-12} \text{ C}^2/\text{Jm} \]

\[ eV/J = 6.2414 \times 10^{18} \]

\[ \text{amu} = 1.6605 \times 10^{-27} \text{ kg} \]

\[ c = 2.9979 \times 10^8 \text{ m/s} \]

\[ h = 6.6261 \times 10^{-34} \text{ Js} \]
Name: 

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<thead>
<tr>
<th>Problem</th>
<th>Possible Score</th>
<th>Your Score</th>
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1. (12 points) The following questions regard the Born-Oppenheimer approximation.
   
a. (6 points) Write the electron and the nuclear Hamiltonians for $H_2$ making the *orbital approximation* and the *Born Oppenheimer approximation*. Clearly indicate the physical meaning of each term in the operators. Write the Laplacian for each electron or nucleus $i$ as $\nabla_i^2$. Label electrons with numbers and nuclei with letters. Hint: you should draw and label all electrons and nuclei for clarity.

b. (6 points) The potential energy function in the nuclear Hamiltonian, $V(a,b)$, contains two terms one of which is the internuclear repulsion. *What* is the second term, and from *where* is the second term obtained?
a. The ground state electronic configuration of $O_2$ is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^2 1\pi_g^4 1\pi_g^2$.

i. (8 points) Match the bond lengths to the following molecules or ions. Justify your answers. You may find it helpful to review the molecular orbital energy level diagrams at the end of the exam.

<table>
<thead>
<tr>
<th>Molecule/ion</th>
<th>Bond length</th>
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<tr>
<td>$O_2$</td>
<td>132 pm</td>
</tr>
<tr>
<td>$O_2^+$</td>
<td>112 pm</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>110 pm</td>
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</table>
ii.  (5 points) Explain why ground state O₂ molecule has a triplet spin state but the N₂ molecule with electronic configuration $1\sigma_g^21\sigma_u^22\sigma_g^22\sigma_u^21\pi_u^43\sigma_g^2$ is a singlet.

b.  (5 points) Sketch the shape(s) of the highest occupied molecular orbital(s) of ground state O₂. If there is more than one orbital, clearly indicate their relative orientations with a drawing or with a short description.
3. (17 points) The following questions regard the Variation Method.

a. (5 points) Set-up and evaluate the secular determinant for H$_2$ in the minimal basis set where the Coulomb integral is $\alpha$ and the resonance integral is $\beta$. You do not need to solve for the energies. Do not make the Hückel approximations.

b. (5 points) The solutions of the secular determinant you wrote in part a) are

$$E_s = \frac{\alpha \pm \beta}{1 \pm S}$$

where the + subscript designates the energy of the bonding molecular orbital.

Write the expression for the total energy (electronic + nuclear) for the ground state of the H$_2$ molecule. Use $r_{ab}$ for the internuclear separation.

c. (7 points) Using the information below, calculate the total energy of the H$_2$ molecule in electron-volts for an internuclear separation, $r_{ab} = 100$ pm. Show your work.

| $\alpha = -26.4$ eV | $\beta = -19.0$ eV | $E_{1s} = -13.6$ eV | $S = 0.586$ |
4. (13 points) The following questions regard the Huckel method.

a. Huckel molecular orbital calculations are used to obtain $\pi$ electron energies for the molecules shown below.

\[
\begin{align*}
E_6 &= \alpha - 1.80\beta \\
E_5 &= \alpha - 1.25\beta \\
E_4 &= \alpha - 0.445\beta \\
E_3 &= \alpha + 0.445\beta \\
E_2 &= \alpha + 1.25\beta \\
E_1 &= \alpha + 1.80\beta
\end{align*}
\]

(7 points) **Calculate** the $\pi$ electron stabilization energy, $E_{\text{stab}}$, for hexatriene and benzene, $E_{\text{stab}} = \frac{E_\pi}{\#e^{-}}$. **Use** your results to explain the relative stability of benzene.
b. (6 points) Add electrons to the appropriate molecular orbitals in the Huckel molecular orbital energy level diagrams below. Use these diagrams to explain why benzene is more stable than cyclo-octatetraene.

**Benzene: 6 π electrons**

**Cyclo-octatetraene: 8 π electrons**
5. (15 points) The following questions regard transition probabilities in spectroscopy
   a. (6 points) Calculate the ratio of the Einstein coefficients for spontaneous and stimulated emission for transitions with the following characteristics:
      i. 2.5 GHz microwave radiation
      ii. 589 nm visible radiation
   b. (5 points) Do you expect spontaneous emission to occur more readily in comparison to stimulated emission for a rotational transition at 2.5 GHz or for an electronic transition at 589 nm? Justify your answer.
c. (4 points) Calculate the optical density of a $1.00 \times 10^{-3}$ molar ethanolic solution of coumarin 343 at the peak of the visible absorption spectrum at 445 nm for a path length of 150 μm. The peak molar absorption coefficient of coumarin 343 at 445 nm is 45,000 M$^{-1}$cm$^{-1}$.
6. (25 points) The following questions regard specific applications of rotational and vibrational spectroscopy.

a. (5 points) Sketch the normal vibrational modes of CS$_2$ and determine which modes will be IR active. Justify your answers.

b. Below is a rotational spectrum of carbon monoxide, $^{12}$C$^{16}$O.

   i. (5 points) The transition marked (c) corresponds to a transition with $J_{\text{initial}} = 7$. The value of $J_{\text{final}}$ is smaller than $J_{\text{initial}}$. Determine the value of $J_{\text{final}}$. 


ii. (10 points) Line (a) is at 23.058 cm\(^{-1}\) and line (b) is at 26.920 cm\(^{-1}\). Calculate the molecular bond length from the information in this spectrum. Table 13.1 at the end of the exam may be helpful for this. Ignore the centrifugal distortion.
c. (5 points) Draw the relevant transitions for Stokes, Rayleigh, and Anti-Stokes Raman scattering on the diagram below.
Figure 8. MO energy level schemes appropriate for
a) O₂, F₂, Ne₂, and for
b) Li₂, Be₂, B₂, C₂, N₂.
Table 13.1  Moments of inertia*

1. Diatomic molecules

\[ I = \mu R^2 \quad \mu = \frac{m_A m_B}{m} \]

2. Triatomic linear rotors

\[ I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_c R')^2}{m} \]

\[ I = 2m_A R^2 \]

* In each case, \( m \) is the total mass of the molecule.