Chem 452 – Exam III
Nov. 10, 2010

Cover Sheet
Closed Book, Closed Notes

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

Useful Equations:

\[
\hat{T} = -\frac{\hbar^2}{2m} \nabla^2 \\
V(r_{ob}) = \frac{Z_a Z_b e^2}{4\pi \epsilon_0 r_{ob}}
\]

\[(\alpha_a - E)c_x + (\beta - ES)c_z = 0\]

\[(\beta - ES)c_y + (\alpha_b - E)c_t = 0\]

\[
N_\pm = 1/(2 \pm 2S)^{1/2} \\
E_{n \sigma} = E_{n \pi} + \sum_{n \sigma}
\]

\[
A = \varepsilon(\nu) Cl \\
\varepsilon(\nu) = N_a \sigma(\nu) \\
\sigma(\nu) = \frac{A_{1\rightarrow 0} \nu c^2}{8\pi \nu^2} \left(1 - e^{-\nu \tau_0}\right) \\
A_{1\rightarrow 0} = \frac{8\pi \hbar^3}{c^3} B_{1\rightarrow 0} \\
B_{1\rightarrow 0} = \frac{\mu_{10}^2}{6\varepsilon_0 \hbar^2}
\]

\[
E_J = \hbar f(J) \\
F(J) = BJ(J + 1) \\
B = \frac{\hbar}{4\pi cI}
\]

\[
E_\nu = \hbar c G(\nu) \\
G(\nu) = \left(\nu + \frac{1}{2}\right)\nu - \left(\nu + \frac{1}{2}\right)^2 \frac{\nu^2}{2} \\
V_{Morse} = \hbar c D_e \left\{1 - \exp\left(-a(R - R_e)\right)\right\}^2 \\
a = \left(\frac{\mu a_0^2}{2\hbar c D_e}\right)^{1/2}
\]

Useful Constants

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

\[
\varepsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2/\text{Jm}
\]

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

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

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

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

\[
N_A = 6.022 \times 10^{23} \text{ mol}^{-1}
\]
## Point Total

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1. (18 points) Answer 3 of the 4 questions. Clearly mark which question you do not want graded.

   a. Identify the diatomic molecule or ion to which the following Hamiltonian corresponds. Be sure to indicate the charge on the molecule/ion. Refer to the periodic table at the end as needed.

   \[
   \hat{H} = -\hbar^2 \left( \frac{\nabla_a^2}{2m_a} + \frac{\nabla_b^2}{2m_b} \right) - \frac{\hbar^2}{2m_e} \sum_{i=1}^{14} \nabla_i^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_{i=1}^{14} \left( \frac{7}{r_{ia}^3} + \frac{8}{r_{ib}^3} \right) + \frac{e^2}{4\pi\varepsilon_0} \left( \frac{56}{r_{ab}} + \sum_{j=1}^{14} \frac{1}{r_{ij}} \right) + \frac{14}{m_a} e^- \quad \text{(only 14 e}^-\text{on molecule)}
   \]

   \[m_a = 14\text{amu} \quad m_b = 16\text{amu}\]

   

   neutral would be \(15e^-\)

   \[\text{N}_2^+\]

   b. Is the above Hamiltonian exact? If not, what approximations have been made? Justify your answer.

   Yes, includes K.E. of nuclei and e
   P.E. of e− attraction to nuclei
   e−−e− repulsion
   nuclear repulsion

   c. Describe the Bom Oppenheimer approximation and explain why the approximation is justified for most molecules.

   The B.O. approx. assumes that nuclei move much more slowly than e− so that the nuclear K.E. term can be removed from the Hamiltonian for e−. This is justified because nuclei weigh >1000 times as much as e−.

   (+2 bonus points)

   d. Argue from the wave-nature of matter why molecular orbital theory provides a better (lower energy) description of benzene (and other conjugated molecules) than does valence bond theory.

   Valence bond theory describes conjugated \(\pi\)-bonds as existing only between pairs of atoms, \(\square\), and thus predicts short deBroglie wavelengths. For e−'s in the \(\pi\)-bond "boxes" which have higher energy. MO theory properly molec. orbitals that extend over the entire molecule, \(\bigcirc\), thus permitting longer \(3\) deBroglie wavelengths (lower energy).
2. (18 points) The following questions regard molecular orbital theory.

a. (8 points) Use the MO energy level diagrams at the end of the exam to determine how many of the following neutral diatomic molecules have triplet spin states (two unpaired electrons) in their ground state electronic configurations. Identify the molecules. Justify your answers.

B₂ and O₂ have unpaired e⁻ in their 1π_u and 1π_g MO's, respectively.
b. (4 points) Sketch the shape of a \( \pi_u \) molecular orbital and determine whether it is a bonding or an antibonding orbital. Justify your answer.

\[ \pi_u \]

bonding because \( e^- \) density concentrated between nuclei

c. (6 points) The antibonding molecular orbital of \( \text{H}_2 \), \( \psi_- = N_- (1s_a - 1s_b) \), has a normalization constant, \( N_- = 1.103 \). From this information, calculate the value of the integral, \( \int 1s_a \cdot 1s_b \, d\tau \). Assume the individual atomic orbitals are normalized. Show your work and define all symbols.

\[
\text{Normalization integral:}
\int_{-\infty}^{\infty} |\psi_-|^2 \, d\tau = 1 = N_-^2 \int_{-\infty}^{\infty} \left| 1s_a - 1s_b \right|^2 \, d\tau
\]

\[
= N_-^2 \left[ \int_{-\infty}^{\infty} |1s_a|^2 \, d\tau + \int_{-\infty}^{\infty} |1s_b|^2 \, d\tau - 2 \int_{-\infty}^{\infty} |1s_a| |1s_b| \, d\tau \right]
\]

\[
= 1 = \frac{1}{2} \left( 1.103^2 \right)
\]

\[
1 - \int |1s_a| |1s_b| \, d\tau = \frac{1}{2} \left( \frac{1}{1.103^2} \right)
\]

\[
\int |1s_a| |1s_b| \, d\tau = 1 - \frac{1}{2} \left( \frac{1}{1.103^2} \right) = 0.589
\]
3. (18 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.

$$\text{Sec. Det.} \begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES' & \alpha - E \end{vmatrix} = 0 = (\alpha - E)^2 - (\beta - ES')^2$$

b. (5 points) The solutions of the secular determinant you wrote in part a) are $E_\pm = \frac{\alpha \pm \beta}{1 \pm S}$ 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.

$$H_2, \quad \sigma_u, \quad E_- = \frac{\alpha - \beta}{1 - S}$$

$$\sigma_g, \quad E_+ = \frac{\alpha + \beta}{1 + S}$$

$$E_{\text{tot}} = 2E_+ + \frac{\epsilon^2}{4\pi\epsilon_0 r_{ab}} = 2\frac{\alpha + \beta}{1 + S} + \frac{\epsilon^2}{4\pi\epsilon_0 r_{ab}}$$
c. (8 points) Using the information below, calculate the bond dissociation energy of the $\text{H}_2$ molecule in electron-volts for an internuclear separation, $r_{ab} = 100 \text{ pm}$. Show your work.

\[
\begin{array}{c|c|c|c|c}
\alpha & \beta & E_{ls} & S \\
-26.4 \text{ eV} & -19.0 \text{ eV} & -13.6 \text{ eV} & 0.586 \\
\end{array}
\]

\[\text{Bond diss. energy} = E_{\text{dissociated}} - E_{\text{molecule}}\]

\[E_{\text{dissociated}} = 2E_{ls} = -27.2 \text{ eV}\]

\[E_{\text{molecule}} = 2 \frac{\alpha + \beta}{1 + S} + \frac{e^2}{4\pi\varepsilon_0 r_{ab}}\]

\[= 2 \left(\frac{-26.4 - 19.0}{1 + 0.586}\right) \text{ (eV)} + \frac{(1.60 \cdot 10^{-19} \text{ C})^2/(1.60 \cdot 10^{-19} \text{ J/eV})}{4\pi(8.85 \cdot 10^{-12} \text{ C}^2/\text{J/m})(1.00 \cdot 10^{-10} \text{ m})}\]

\[E_{\text{molecule}} = -57.3 \text{ eV} + 14.4 \text{ eV} = -42.9 \text{ eV}\]

\[\text{B. D. E.} = -27.2 + 42.9 = 15.7 \text{ eV}\]
4. (12 points) The following questions regard the Hückel method.

a. (6 points) Hückel molecular orbital calculations are used to obtain π electron energies for the molecules shown below.

\[
\begin{align*}
E_6 &= \alpha - 1.80\beta & E_6 &= \alpha - 2\beta \\
E_5 &= \alpha - 1.25\beta & E_4 &= E_5 = \alpha - \beta \\
E_4 &= \alpha - 0.445\beta & E_2 &= E_3 = \alpha + \beta \\
E_3 &= \alpha + 0.445\beta & E_1 &= \alpha + 2\beta \\
E_2 &= \alpha + 1.25\beta & \quad & E_1 &= \alpha + 1.80\beta
\end{align*}
\]

Calculate the total energy of the π electrons for each molecule. Which molecule is predicted to have lower energy?

\[
\text{hexatriene}
\]

\[
E_{\pi} = 2E_1 + 2E_2 + 2E_3 = 2(\alpha + 1.8\beta) + 2(\alpha + 1.25\beta) + 2(\alpha + 0.445\beta)
\]

\[
E_{\pi} = 6\alpha + 6.99\beta
\]

\[
\text{benzene}
\]

\[
E_{\pi} = 2E_1 + 4E_2 = 2(\alpha + 2\beta) + 4(\alpha + \beta)
\]

\[
E_{\pi} = 6\alpha + 8\beta
\]
b. (6 points) Add electrons to the appropriate molecular orbitals in the Hückel molecular orbital energy level diagrams below. Use these diagrams to explain why cyclo-octatetraene is more easily oxidized (electrons more easily removed) in comparison to benzene.

Cyclo-octatetraene is more easily oxidized because two electrons reside in MOs with non-bonding character (high energy). All electrons in benzene reside in bonding MOs.

Benzene: 6 $\pi$ electrons

Cyclo-octatetraene: 8 $\pi$ electrons
5. (30 points) Below is a pure rotational absorption spectrum of carbon monoxide, $^{12}$C$^{16}$O.

![Graph showing absorption spectrum]

a. (10 points) The transition marked (a) occurs at 23.058 cm$^{-1}$, and the spacing between transitions (a) and (b) is 3.862 cm$^{-1}$. Calculate what would be the corresponding frequency of transition (a) for isotopically substituted carbon monoxide, $^{14}$C$^{18}$O. Assume the same bond lengths both molecules.

\[
\text{wavenumber of (a)}
\]

\[
\omega = 23.058 \text{ cm}^{-1} = 2BJ
\]

\[B \text{ is different for } ^{14}\text{C}^{18}\text{O due to different reduced mass.}\]

\[
B = \frac{\hbar}{4\pi c I}, \quad I = MR^2, \quad M = \frac{m_c m_o}{m_c + m_o}
\]

\[
B = \frac{\hbar}{4\pi c M R^2}
\]

\[
\frac{\omega_{^{14}\text{C}^{18}\text{O}}}{\omega_{^{12}\text{C}^{16}\text{O}}} = \frac{2B_{^{14}\text{C}^{18}\text{O}} J}{2B_{^{12}\text{C}^{16}\text{O}} J} = \frac{1}{\omega_{^{14}\text{C}^{16}\text{O}}} = \frac{1}{M_{^{14}\text{C}^{18}\text{O}}} = \frac{1}{7.875 \text{ amu}} = 0.871
\]

\[
\omega_{^{14}\text{C}^{18}\text{O}} = (0.871) \omega_{^{12}\text{C}^{16}\text{O}} = 20.08 \text{ cm}^{-1}
\]
b. (4 points) The transition marked (c) corresponds to a transition with $J_{\text{initial}} = 7$. What is the value of $J_{\text{final}}$ for the transition?

$$\text{selection rule: } \Delta J = \pm 1$$

spectrum is an absorption spectrum $J_{\text{final}} > J_{\text{initial}}$

$$J_{\text{final}} = 8$$

c. (8 points) Regarding Einstein coefficients, if two transitions have the same values of their transition dipole moments, which transition do you expect to have a larger molar absorption coefficient, $\varepsilon(v)$: a transition at 100 MHz or one at 100 GHz? You must justify your answer with appropriate formulae to receive full credit.

same trans. dipole moment means same $B_{1\rightarrow 0}$

$$B_{1\rightarrow 0} = \frac{M_i^2}{6 \mu \alpha}$$

$$\varepsilon(v) = N_A \sigma(v) = N_A \left( \frac{8\pi \hbar v^3}{C^3} B_{1\rightarrow 0} \frac{C^2}{8\pi v^2} \right) g(v-v_0)$$

$$\varepsilon(v) = N_A \left( \frac{\hbar v}{C} B_{1\rightarrow 0} \right) g(v-v_0)$$

$$\frac{\hbar v}{C} \text{ is larger for } v = 100 \text{ GHz than for } v' = 100 \text{ MHz}$$

so $\varepsilon(v)$ is larger for 100 GHz transition.
d. (8 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 $45,000 \text{ M}^{-1}\text{cm}^{-1}$.

Use Beer's law:

$$A = E \cdot c \cdot l$$

$$E = 45,000 \text{ M}^{-1}\text{cm}^{-1} \text{ at } 445 \text{ nm}$$

$$C = 1.00 \cdot 10^{-3} \text{ M}$$

$$l = 150 \mu \text{m} = 0.0150 \text{ cm}$$

$$A = (45,000 \text{ M}^{-1}\text{cm}^{-1}) (1.00 \cdot 10^{-3} \text{ M}) (0.0150 \text{ cm})$$

$$A = 0.675$$
6. (4 points)

Thanksgiving is coming!
Figure 8. NO energy level schemes appropriate for
a) O₂, F₂, Ne₂, and for
b) Li₂, Be₂, B₂, C₂, N₂.
**Table 13.1 Moments of inertia**

1. **Diatonic molecules**
   
   \[ I = \mu R^2 \quad \mu = \frac{m_A m_B}{m} \]

2. **Triatomic linear rotors**
   
   \[ I = m_A R^2 + m_C R^2 \quad I = 2m_A R^2 \]

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

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

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*Table 13-1 part 1*
Atkins Physical Chemistry, Eighth Edition
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