CHEM 5210 – Final Exam
May 11, 2015

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Four (4) digit number for posting.

(05) 1. The calculated Hartree-Fock (HF) value of the ionization energy of a nitrogen atom is 1452 kJ/mol. **EXPLAIN** why you would expect the exact experimental value of the ionization energy to be *higher* or *lower* than the Hartree-Fock value?

The answer is *higher* because it accounts for the Forces that the core energy in the N⁺ ion is *less than* that in N.

(06) 2. Calculate the value of the commutator, \[ \left[ \frac{d}{dx}, \frac{d}{dx} + x^2 \right] q \]

\[ \left( \frac{d}{dx} \right) \left( \frac{d}{dx} + x^2 \right) q = \frac{d^2 q}{dx^2} + 2x \frac{dq}{dx} + 2xq \]

\[ \left( \frac{d}{dx} \right) \frac{d}{dx} q = \frac{dq}{dx} + x \frac{dq}{dx} \]

\[ \left[ \frac{d}{dx}, \frac{d}{dx} + x^2 \right] q = \left[ \frac{d}{dx} + x^2 \right] q - \left[ \frac{d}{dx} \right] q = 2xq + 2xq - 2xq = 2xq \]

\[ \left\{ \frac{d}{dx}, \frac{d}{dx} + x^2 \right\} q = 2xq \]
3. Consider a particle in a one-dimensional box with the approximate ground state wavefunction:

\[ \psi = Ax^2(a-x) \quad 0 \leq x \leq a \]
\[ \psi = 0 \quad x < 0, \quad x > a \]

Determine the normalization constant, \( A \), and the probability that the particle's position will be between 0 and \( a/2 \).

**Note:** You should end up with a numerical answer for the probability.

\[
1 = \int_{0}^{a} 4x^2 \, dx = A \int_{0}^{a} x^2 (a-x)^2 \, dx = A^2 \int_{0}^{a} a^2 x^4 - 2ax^5 + x^6 \, dx
\]
\[
= A^2 \int \left[ \frac{a^2 x^5}{5} - \frac{2ax^6}{6} + \frac{x^7}{7} \right]_0^a = A^2 \left[ \frac{a^7}{5} - \frac{a^7}{3} + \frac{a^7}{7} \right]_{[0]}
\]
\[
1 = A^2 \left( \frac{21a^7 - 35a^7 + 15a^7}{60} \right) \Rightarrow A^2 a^7 = 1
\]
\[
A = \sqrt{\frac{105}{a^7}}
\]

\[
P(0 \leq x \leq \frac{a}{2}) = \int_{0}^{\frac{a}{2}} 4x^2 \, dx = A^2 \int \left[ \frac{a^2 x^5}{5} - \frac{ax^6}{3} + \frac{x^7}{7} \right]_0^{\frac{a}{2}}
\]
\[
= A^2 \left[ \frac{a^2 (0.5a)^5}{5} - \frac{a (0.5a)^6}{3} + (0.5a)^7 \right] - [0]
\]
\[
= A^2 a^7 \left( 0.25 \times 10^{-3} - 5.208 \times 10^{-3} + 1.116 \times 10^{-3} \right)
\]
\[
= A^2 a^7 (2.158 \times 10^{-3})
\]
\[
P = \frac{105}{a^7} a^7 \left( 2.158 \times 10^{-3} \right) = 0.227 \approx 0.23
\]
(15) 4. The C≡C and C-H bond lengths in the linear molecule, acetylene \([ H-^{12}\text{C}≡^{12}\text{C}-\text{H}]\), are 1.20 Å and 1.06 Å, respectively. Assume that the masses of the H and \(^{12}\text{C}\) atoms are 1.00 and 12.00.

The selection rule for rotational Spookman spectra is \(\Delta J = \pm 4\)

Calculate the frequencies (in cm\(^{-1}\)) of the first two lines in the rotational Spookman spectrum of acetylene.

\[ \text{H} - \text{C} ≡ \text{C} - \text{H} \]

\[ J = 2 \text{amu} \cdot \text{C} \cdot 2 \text{amu} \cdot \text{H} \]

\[ \nu = \frac{2}{2} (12.00 \text{amu}) (0.06 \text{Å})^2 \]

\[ = 14.75 / \text{amu} \text{Å}^2 \times 1.66 \times 10^{-24} \text{ kg m}^2 / \text{amu} \]

\[ = 2.349 \times 10^{-46} \text{ s}^{-1} \]

\[ \beta = \frac{k}{2 \pi^2 \beta} = \frac{6.63 \times 10^{-34} \text{ s m}^2 / \text{kg}}{8 \pi^2 (2.349 \times 10^{-46} \text{ s}^{-1}) (3.00 \times 10^8 \text{ m/s})} = 1.19 \text{ cm}^{-1} \]

\[ \Delta = 6 \text{ cm}^{-1} \]

Line 1: \(J = 2 \rightarrow J = 4\)

\[ \tilde{v} = 4(\Delta) \beta = 0(1) \beta \]

\[ = 20 \beta = 20 (1.19 \text{ cm}^{-1}) \]

\[ = 23.8 \text{ cm}^{-1} \]

Line 2: \(J = 1 \rightarrow J = 3\)

\[ \tilde{v} = 5/6) \beta - 1(2) \beta = 288 \]

\[ = 288 / (1.19 \text{ cm}^{-1}) = 243.3 \text{ cm}^{-1} \]
5. The Radial part of a hypothetical hydrogen atom wavefunction is:

\[ R(r) = r^2 e^{-r/a_0} \]

\[ P(r) = R^2 \Phi(r) = Br^2 \Phi^2 = Br^2 \left( r^2 e^{-r/a_0} \right)^2 \]

\[ = Br^6 e^{-2r/a_0} = Br^6 e^{-ar} \text{ where } a = \frac{3}{a_0} \]

\[ \int_0^\infty P(r)dr = 1 = B \int_0^\infty r^6 e^{-ar}dr = \frac{6!}{a^7} = \frac{720}{(2/3a_0)^7} \]

\[ 1 = B \left( 5.625a_0^7 \right) \]

\[ B = \frac{1}{5.625a_0^7} \]
5. (Cont'd).

(10) (b) The average Potential Energy \( \langle V \rangle \) of attraction between an electron and proton in a hydrogen atom is given by:

\[
\langle V \rangle = \left\langle \frac{-e^2}{4\pi\varepsilon_0 r} \right\rangle = -\frac{e^2}{4\pi\varepsilon_0} \langle \frac{1}{r} \rangle
\]

Use your normalized Radial Distribution Function to determine \( \langle V \rangle \)

You should simplify your answer as much as possible, but can leave it in terms of \( e, \varepsilon_0, \pi \) and \( a_0 \)

\[
\langle \frac{1}{r} \rangle = \int_0^\infty \frac{1}{r} P(r) dr = \int_0^\infty \frac{1}{r} B r e^{-ar} dr \quad [a = \frac{2}{a_0}]
\]

\[
= B \int_0^\infty r e^{-ar} dr = B \frac{5}{a^6} = B \frac{120}{(2a_0)^6}
\]

\[
= B \left( \frac{1}{1875 a_0} \right)^6
\]

\[
= \frac{1}{5.625 a_0} \left( 1.875 a_0^6 \right) = \frac{0.333}{a_0} = \frac{1}{3a_0}
\]

\[
\langle V \rangle = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{3a_0} = -\frac{e^2}{12\pi\varepsilon_0 a_0}
\]
(20) 6. The bonding in Hydrogen Iodide (HI) can be described by a two orbital interaction between the 1s orbital on Hydrogen and the 5p orbital on Iodine. The Hamiltonian matrix elements (and overlap) are:

\[ H_{HH} = -14. \text{eV} \quad H_{II} = -10. \text{eV} \quad H_{HI} = -3. \text{eV} \quad S_{HH} = 0 \]

Assume that the molecular wavefunction is: \( \psi = c_H 1s_H + c_I 5p_I \)

(8) a) Set up the Secular Determinant and solve for the energy of the **Anti-Bonding** Orbital.

**Note:** In case you need a reminder, the quadratic equation and its solutions is given on the information sheet.

\[
\begin{vmatrix}
H_{HH} - \langle E \rangle & H_{HI} \\
H_{HI} & H_{II} - \langle E \rangle
\end{vmatrix} = 0 = 
\begin{vmatrix}
-14 - \langle E \rangle & -3.0 \\
-3.0 & -10 - \langle E \rangle
\end{vmatrix}
\]

\[
(-14 - \langle E \rangle)(-10 - \langle E \rangle) - (-3)^2 = 0
\]

\[
\langle E \rangle^2 + 24 \langle E \rangle + 140 - 9 = 0 = \langle E \rangle^2 + 24 \langle E \rangle + 131 = 0
\]

\[
\langle E \rangle_{AB} = -\frac{24 + \sqrt{576 - 4(1)(131)}}{2} = -8.39 \text{ eV} - 8.40 \text{ eV}
\]

Use \( \psi \) of ground state to find the energy of the **Anti-Bonding** orbital.
6. (Cont'd)

(8) b) Use your answer in part (a) to calculate the coefficients, \( c_H \) and \( c_I \), in the normalized anti-bonding orbital.

**Note:** If you don't like your answer for part (a), assume that \( E_{\text{antibond}} = -8.0 \text{ eV} \) (not the right answer) to work this part.

\[
\left( -\psi_{5s} \right) \psi_{11s} - 3\psi_{2s} = 0 = -5.6\psi_H - 3\psi_I
\]

\[
\psi_I = \frac{-5.6\psi_4}{3} = -1.87\psi_4
\]

\[
\psi_4 = \psi_{\text{H}(1s)} + 1.87\psi_{\text{I}(5p_z)}
\]

\[
\text{Normaliz. } c_H^2 + (-1.87c_I)^2 = 1 \rightarrow 4.497c_H^2 = 1
\]

\[
\psi = 0.47\psi_{\text{H}(1s)} - 0.88\psi_{\text{I}(5p_z)}
\]

\[
4.497c_H^2 = 1 \rightarrow c_H = 0.472 \approx 0.47
\]

\[
\psi_4 = -1.87 \psi_4
\]

(4) c) Assume for this part that the bonding orbital is: \( \psi = N\left[ (0.5) \cdot 1s_H + (0.9) \cdot 5p_I \right] \)

What fraction of the charge of an electron in the bonding orbital is on the iodine atom?

\[
\frac{c_H^2}{c_H^2 + c_I^2} = \frac{(0.9)^2}{(0.5)^2 + (0.9)^2} = 0.76
\]
7. Consider the chloroethene molecule (on right). The Secular Determinant is:
\[
\begin{vmatrix}
 x & 1 & 0 \\
 1 & x & 0.4 \\
 0 & 0.4 & x + 2.0 \\
\end{vmatrix} = 0 
\]
where \( x = \frac{\alpha - E}{\beta} \)

The two lowest energy solutions to the Secular Determinant are \( x_1 = -2.10 \) and \( x_2 = -0.93 \). Note: The Cl atom contributes two (2) electrons to the \( \pi \) system.

(10) a) The normalized wavefunction corresponding to \( x_1 \) is:
\[
\phi_1 = 0.115 \chi_1 + 0.241 \chi_2 + 0.964 \chi_3. \]
[I'm giving this for use in parts (b) and (c)]

Determine the normalized molecular orbital, \( \phi_2 \), corresponding to \( x_2 \), as a linear combination of the basis functions, \( \chi_1, \chi_2 \) and \( \chi_3 (\chi_3 \text{ is on Cl}) \).

\[
\begin{align*}
19x_1 + 60x_2 &= 0 \\
\chi_2 &= -x_1 + 60 \text{ or } 0.93 \chi_1 \\
0.4x_2 + 0.4 \chi_3 &= 0 \\
0.4 \chi_3 &= -x_2 - 0.4 \chi_1 = -c_1 \left( -0.93 \right) \left( 0.93 \chi_1 \right) \\
&= 0.13c_1 \chi_1 \\
\chi_3 &= -0.34 c_1 \\
\end{align*}
\]

\[
\phi_2 = 0.71 \chi_1 + 0.93 \chi_1 \chi_2 - 0.34c_1 \chi_3
\]

\[
\text{Normaliz.} \quad c_1 \left( \frac{1}{2} \right) ^{0.93^2 + (-0.34)^2} = 1 = c_1 \left( 1.98 \right)
\]

\[
\begin{align*}
\chi_2 &= 0.71 \chi_1 + 0.66 \chi_2 - 0.24 \chi_3
\end{align*}
\]
7. (Cont'd)

(3) b) Determine the $\pi$ electron charge on C$_2$.

$\rho = 2(0.241)^2 + 2(0.66)^2 = 0.89$

(3) c) Determine the $\pi$ bond order, between C$_2$ and Cl$_3$ [P$_{23}$].

$P_{12} = 2(0.155)(0.241) + 2(0.71)(0.66) = 0.71$

(08) 8. Consider the molecule, ethanedial (right)

\[ \text{O}_1 \equiv \text{C}_2 \equiv \text{C}_3 \equiv \text{O}_4 \]

The oxygen Hückel parameters are: $\alpha_o = \alpha + \beta$

$\beta_o = 0.8\beta$

Write the Secular Determinant in terms of (i) $\alpha$, $\beta$ and E, (ii) $\times [=(\alpha-E)/\beta]$

\[
\begin{vmatrix}
\alpha - E & B_0 & 0 & 0 \\ B_0 & \alpha - E & B_0 & 0 \\ 0 & B_0 & \alpha - E & B_0 \\ 0 & 0 & B_0 & \alpha - E \\
\end{vmatrix} = 0 =
\]

\[
\begin{vmatrix}
\alpha + \beta - E & 0.8\beta & 0 & 0 \\ 0.8\beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & 0.8\beta \\ 0 & 0 & 0.8\beta & \alpha + \beta - E \\
\end{vmatrix} = 0
\]
Consider a particle in a two dimensional box of length \( a \times b \), where \( b = \sqrt{2} a \).

Draw a diagram containing the lowest 6 energy levels of a particle in this two dimensional box. Put your answer in units of \( \frac{\hbar^2}{ma^2} \).

**Note:** Give the set(s) of quantum numbers corresponding to each level.

\[
\Sigma = \frac{n_x^2 \hbar^2}{8ma^2} + \frac{n_y^2 \hbar^2}{8m(\sqrt{2}a)^2} = \frac{n_x^2 \hbar^2}{8ma^2} + \frac{n_y^2 \hbar^2}{16ma^2}
\]

\[
= \frac{\hbar^2}{ma^2} \left[ \frac{2n_x^2 + n_y^2}{16} \right]
\]

\[
\begin{array}{l}
\frac{2^2}{16} = 0.25 \\
\frac{2^2}{16} = 0.25 \\
\frac{3}{16} = 0.188 \\
\frac{1}{16} = 0.063 \\
\frac{2}{16} = 0.125 \\
\frac{3}{16} = 0.188 \\
\end{array}
\]
10. The data in the table to the right was obtained from QM studies at 100\(^\circ\)C.

<table>
<thead>
<tr>
<th>Molec.</th>
<th>E(el) (au)</th>
<th>H(^0) (au)</th>
<th>S(^0) (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)O(_4)</td>
<td>-409.331</td>
<td>-409.298</td>
<td>325.5</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>-204.652</td>
<td>-204.638</td>
<td>253.3</td>
</tr>
</tbody>
</table>

(6) a) What 3 "corrections" are made to the QM electronic energy to determine the enthalpy in the table?

1) ZPC, PC, VE (ZPE)

2) Thermal correction to ZPE, PC

3) PV = RT

(9) b) Calculate the equilibrium constant for the reaction, N\(_2\)O\(_4\)(g) \(\leftrightarrow\) 2 NO\(_2\)(g) at 100 \(^\circ\)C.

\[
N\(_2\)O\(_4\) \rightleftharpoons 2 \text{NO}_2
\]

\[
\Delta H^\circ = 2 \Delta H(\text{NO}_2) - \Delta H(N\(_2\)O\(_4\)) = 2(-204.688) - (-409.298)
\]

\[
= 1072.92 \frac{\text{au}}{\text{mol-K}} \times \frac{1 \text{au}}{1 \text{eV}} = 657,780 \text{ eV}
\]

\[
\Delta S^\circ = 2 \Delta S(\text{NO}_2) - \Delta S(N\(_2\)O\(_4\)) = 2(253.3) - 1(353.5) = 618.1 \text{ eV-K}
\]

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 657,780 - 373(181.1) = -98,000 \text{ J}
\]

\[
\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-98,000}{8.314(353)} = 3.16
\]

\[
K = e^{3.16} = 23.6
\]
11. Consider a hypothetical \( \text{AH}_2 \) molecule with \( C_{2v} \) symmetry and a triplet ground state electronic configuration: \((a_1)^2(a_1^2)(b_2)^1\)

For the electronic transition below, show whether or not the transition is allowed, and if it is allowed, is it polarized parallel or perpendicular to the principal axis. You MUST show your work to receive credit!!

\[
\begin{align*}
\tau(\nu_0) &= a_1 \times b_2 = B_2^1 \\
\tau(\nu_1) &= b_2 \times b_2 = a_2^1
\end{align*}
\]

**IR Active**

12. Quantum Mechanics Basis Sets and Methods

3. (a) In the basis set, 4-21G (aka STO-4-21G), what does each number stand for?

- Core STO's and of 4-21G

3. (b) In the CCSD(T) method, what does each letter stand for?
(3) (c) Describe what it means to perform a Quantum Mechanical Calculation at the CISD/6-311+G(d,p)//HF/6-31G(d) level. Why is this an acceptable approach?

Some by optimized by HF/6-31G(d) level.
Some by Dunning basis set (at fixed geometry).
Some by CI5D/6-31+G(d,p) level.

(9) (d) Consider using a 6-31++G(2df,p) basis for a Quantum Mechanical calculation on HCP. Describe the types and numbers of STOs that are used on each of the three atoms (H, C, and P).

\[ \begin{align*}
\text{H:} & \quad 2 \times 1s \quad 1 \times 1s \quad 1 \times 1s \quad 1 \times 3-2p' \quad \text{Polyatomic} \\
\text{C:} & \quad 1 \times 1s \quad 2 \times 2s \quad 2 \times 3s \quad 1 \times 3p' \quad 1 \times 3p' \quad \text{Polyatomic} \\
\text{P:} & \quad 1 \times 1s \quad 1 \times 1s \quad 2 \times 3s \quad 2 \times 3p' \quad 1 \times 3p' \quad \text{Polyatomic} \\
\end{align*} \]