

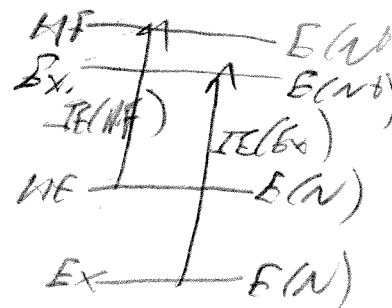
Name Solomon

If you wish to have your final exam and course grade posted on the Web site, please provide me with a four (4) digit number which will be the ID number for your grade.

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 ~~approx~~ is higher because it accounts for the fact that the correlation in the N^+ ion is less than in N .



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

$$\frac{d}{dx} \left(\frac{d\psi}{dx} + x^2 \psi \right) = \frac{d^2\psi}{dx^2} + x^2 \frac{d\psi}{dx} + 2x\psi$$

$$\left(\frac{d}{dx} + x^2 \right) \frac{d\psi}{dx} = \frac{d^2\psi}{dx^2} + x^2 \frac{d\psi}{dx} + 2x\psi$$

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

$$= \boxed{2x\psi} \quad \text{OK, To}$$

$$\left[\frac{d}{dx}, \frac{d}{dx} + x^2 \right] = \boxed{2x}$$

- (15) 3. Consider a particle in a one dimensional box with the approximate ground state wavefunction:

$$\psi = Ax^2(a-x) \quad 0 \leq x \leq a$$

$$\psi = 0 \quad x < 0, x > a$$

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.

Normal

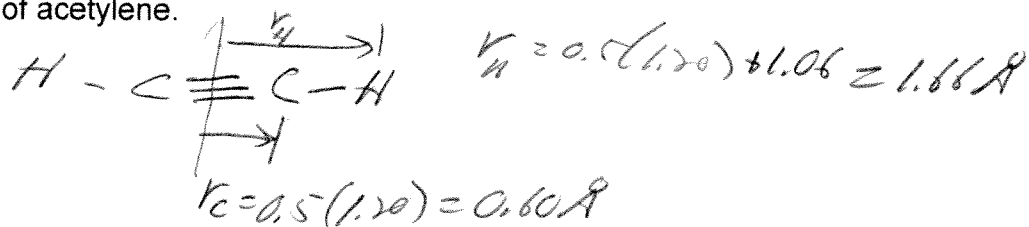
$$\begin{aligned} 1 &= \int_0^a \psi^2 dx = A^2 \int_0^a x^4 (a-x)^2 dx = A^2 \int_0^a [a^2 x^4 - 2ax^5 + x^6] dx \\ &= A^2 \left[\frac{a^2 x^5}{5} - \frac{2ax^6}{6} + \frac{x^7}{7} \right]_0^a = A^2 \left[\frac{a^7}{5} - \frac{a^7}{3} + \frac{a^7}{7} \right] - [0] \\ 1 &= A^2 \left(\frac{21a^7 - 35a^7 + 15a^7}{105} \right) = A^2 \frac{a^7}{105} \\ A^2 &= \frac{105}{a^7} \quad A = \sqrt{\frac{105}{a^7}} \end{aligned}$$

$$\begin{aligned} P(0 \leq x \leq a/2) &= \int_0^{a/2} \psi^2 dx = A^2 \left[\frac{a^2 x^5}{5} - \frac{ax^6}{3} + \frac{x^7}{7} \right]_0^{a/2} \\ &= A^2 \left[\frac{a^2 (0.5a)^5}{5} - \frac{a(0.5a)^6}{3} + \frac{(0.5a)^7}{7} \right] - [0] \\ &= A^2 a^7 \left[0.25 \times 10^{-3} - 5.208 \times 10^{-3} + 1.116 \times 10^{-3} \right] \\ &= A^2 a^7 (2.158 \times 10^{-3}) \\ &= \frac{105}{a^7} a^7 (2.158 \times 10^{-3}) = 0.227 \approx \boxed{0.23} \end{aligned}$$

- (15) 4. The $\text{C}\equiv\text{C}$ and $\text{C}-\text{H}$ bond lengths in the linear molecule, acetylene [$\text{H}-^{12}\text{C}\equiv^{12}\text{C}-\text{H}$], are $1.20 \text{ \AA}$ and $1.06 \text{ \AA}$, respectively. Assume that the masses of the H and ^{12}C atoms are 1.00 and 12.00 .

The selection rule for rotational Spookman spectra is $\Delta J = +4$

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



$$\begin{aligned}
 I &= 2m_{\text{C}}r_{\text{C}}^2 + 2m_{\text{H}}r_{\text{H}}^2 = 2(12.00 \text{ amu})(0.60 \text{ \AA})^2 + 2(1.00 \text{ amu})(1.66 \text{ \AA})^2 \\
 &= 14.754 \text{ amu \AA}^2 \times \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \times \left(\frac{10^{-10} \text{ m}}{1 \text{ \AA}}\right)^2 \\
 &= 2.349 \times 10^{-46} \text{ kg m}^2
 \end{aligned}$$

$$\begin{aligned}
 \bar{B} &= \frac{h}{8\pi^2 I c} = \frac{6.63 \times 10^{-34} \text{ J s}}{8\pi^2 (2.349 \times 10^{-46} \text{ kg m}^2) (3.00 \times 10^{10} \text{ cm/s})} = 1.192 \\
 &= \boxed{1.19 \text{ cm}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \Delta J = +4 \quad \text{Line 1: } J=0 \rightarrow J=4 \quad \bar{\nu} &= 4(5)\bar{B} - 0(1)\bar{B} \\
 &= 20\bar{B} = 20(1.19 \text{ cm}^{-1}) \\
 &= \boxed{23.8 \text{ cm}^{-1}}
 \end{aligned}$$

Line 2: $J=1 \rightarrow J=5$

$$\begin{aligned}
 \bar{\nu} &= 5(6)\bar{B} - 1(2)\bar{B} = 28\bar{B} \\
 &= 28(1.19 \text{ cm}^{-1}) = \boxed{33.3 \text{ cm}^{-1}}
 \end{aligned}$$

(20) 5. The Radial part of a hypothetical hydrogen atom wavefunction is::

$$R(r) = r^2 e^{-r/a_0}$$

(10) (a) Calculate the normalization constant, B, of the Radial Distribution Function.
Your answer should be in terms of a_0 .

$$\begin{aligned} P(r) &= R^2(r) = B^2 r^4 / R^2 = B^2 r^4 (r^2 e^{-r/a_0})^2 \\ &= B^2 r^6 e^{-2r/a_0} = B^2 r^6 e^{-ar} \text{ where } a = 2/a_0 \end{aligned}$$

$$\begin{aligned} \int_0^\infty P(r) dr &= 1 = B^2 \int_0^\infty r^6 e^{-ar} dr = \frac{6!}{a^7} = \frac{720}{(2/a_0)^7} \\ 1 &= B^2 (5.625 a_0^7) \end{aligned}$$

$$\therefore B = \frac{1}{\sqrt{5.625 a_0^7}}$$

5. (Cont'd).

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

$$\langle V \rangle = \left\langle -\frac{e^2}{4\pi\epsilon_0 r} \right\rangle = -\frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle$$

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 , ϵ_0 , π and a_0

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \frac{1}{r} P(r) dr = \int_0^\infty \frac{1}{r} B r^6 e^{-ar} dr \quad \left[a = \frac{2}{a_0} \right]$$

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

$$= B (1.875 a_0)^6$$

$$= \frac{1}{5.625 a_0^7} (1.875 a_0)^6 = \boxed{\frac{0.333}{a_0} = \frac{1}{3a_0}}$$

$$\langle V \rangle = \boxed{-\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{3a_0} = -\frac{e^2}{12\pi\epsilon_0 a_0}}$$

- (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.

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

$$(-14 - \langle E \rangle)(-10 - \langle E \rangle) - (-3)(-3) = 0$$

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

$$\langle E \rangle_{AB} = \frac{-24 + \sqrt{24^2 - 4(1)(131)}}{2} = \boxed{-8.39 \approx -8.40 \text{ eV}}$$

Use (+) sign to get higher Energy AB orb

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.

$$(-14.55)c_H - 3c_I = 0 = -5.6c_H - 3c_I$$

$$\therefore c_I = \frac{-5.6c_H}{3} = -1.87c_H$$

$$\psi = c_H(1s_H) - 1.87c_H(5p_I)$$

$$\text{normalize } c_H^2 + (-1.87c_H)^2 = 1 \rightarrow 4.497c_H^2 = 1$$

$$\psi = 0.47(1s_H) - 0.88(5p_I)$$

$$c_H = 0.472 \approx 0.47$$

$$c_I = -1.87c_H = -0.88$$

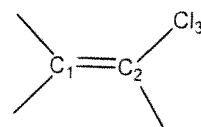
- (4) c) Assume for this part that the bonding orbital is: $\psi = N[(0.5) \cdot 1s_H + (0.9) \cdot 5p_I]$

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

$$f_I = \frac{c_I^2}{c_H^2 + c_I^2} = \frac{(0.9)^2}{(0.5)^2 + (0.9)^2} = \boxed{0.76}$$

- (16) 7. Consider the chloroethene molecule (on right).
The Secular Determinant is:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 0.4 \\ 0 & 0.4 & x+2.0 \end{vmatrix} = 0 \quad \text{where } x = \frac{\alpha - E}{\beta}$$



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 π system.

- (10) a) The normalized wavefunction corresponding to x_1 is:

$$\phi_1 = 0.115\chi_1 + 0.241\chi_2 + 0.964\chi_3. \text{ [I'm giving this for use in parts (b) and (c)]}$$

Determine the **normalized** molecular orbital, ϕ_2 , corresponding to x_2 , as a linear combination of the basis functions, χ_1 , χ_2 and χ_3 (χ_3 is on Cl).

$$x_1 \chi_1 + \chi_2 = 0 \rightarrow \chi_2 = -x_1 \chi_1 = +0.93 \chi_1$$

$$1 \chi_1 + x_2 \chi_2 + 0.4 \chi_3 = 0 \rightarrow 0.4 \chi_3 = -\chi_1 - x_2 \chi_2 = -\chi_1 - (-0.93)(0.93 \chi_1) = -0.1351 \chi_1$$

$$\chi_3 = -0.34 \chi_1$$

$$\therefore \phi_2 = \chi_1 + 0.93 \chi_2 - 0.34 \chi_3$$

Normalize $C_1^2 [1^2 + 0.93^2 + (-0.34)^2] = 1 = C_1^2 (1.98)$

$$C_1 = 0.71$$

$$\phi_2 = 0.71 \chi_1 + 0.66 \chi_2 - 0.24 \chi_3$$

$$q_1 = 0.115\chi_1 + 0.241\chi_2 + 0.984\chi_3 \quad 1V$$

$$q_2 = 0.71\chi_1 + 0.66\chi_2 - 0.24\chi_3 \quad 1V$$

7. (Cont'd)

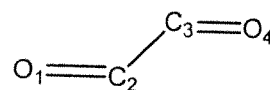
(3) b) Determine the π electron charge on C_2 .

$$q_2 = 2(0.241)^2 + 2(0.66)^2 = \boxed{0.99}$$

(3) c) Determine the π bond order, between C_2 and C_3 [P_{23}].

$$P_{12} = 2(0.115)(0.241) + 2(0.71)(0.66) = \boxed{0.71}$$

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



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

$$\beta_o = 0.8\beta$$

Write the Secular Determinant in terms of (i) α , β and E , (ii) $x = (\alpha - E)/\beta$

$$\begin{vmatrix} \alpha - E & \beta_o & 0 & 0 \\ \beta_o & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta_o \\ 0 & 0 & \beta_o & \alpha - E \end{vmatrix} = 0 = \begin{vmatrix} \alpha + \beta - E & 0.8\beta & 0 & 0 \\ 0.8\beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & 0.8\beta \\ 0 & 0 & 0.8\beta & \alpha + \beta - E \end{vmatrix}$$

$$\begin{vmatrix} x+1 & 0.8 & 0 & 0 \\ 0.8 & x & 1 & 0 \\ 0 & 1 & x & 0.8 \\ 0 & 0 & 0.8 & x+1 \end{vmatrix} = 0$$

- (8) 9. 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 h^2/ma^2 .

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

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8m(\sqrt{2}a)^2} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{16ma^2}$$

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

$$\frac{h^2}{8ma^2}$$

$\frac{23}{16} = 1.06$
$\frac{22}{16} = 0.75$
$\frac{13}{16} = 0.688$
$\frac{21}{16} = 0.563$
$\frac{12}{16} = 0.375$
$\frac{11}{16} = 0.188$

- (15) 10. The data in the table to the right was obtained from QM studies at 100°C.

Molec.	E(el) au (hart)	H° au (hart)	S° J/mol-K
N ₂ O ₄	-409.331	-409.298	325.5
NO ₂	-204.652	-204.638	253.3

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

- 1) zero p⁰ vib. E (ZPE)
- 2) thermal contrib to E, rot, vib, etc
- 3) PV = RT

- (9) b) Calculate the equilibrium constant for the reaction, N₂O₄(g) ↔ 2 NO₂(g) at 100 °C.



$$\Delta H^\circ = 2H^\circ(\text{NO}_2) - H^\circ(\text{N}_2\text{O}_4) = 2(-204.638) - (-409.298)$$

$$= +0.022 \text{ au} \times \frac{2625 \text{ KJ/mol}}{1 \text{ au}} \times \frac{10^3 \text{ J}}{1 \text{ KJ}}$$

$$= +57,750 \text{ J}$$

$$\Delta S^\circ = 2S^\circ(\text{NO}_2) - S^\circ(\text{N}_2\text{O}_4) = 2(253.3) - 1(325.5) = +181.1 \text{ JK}$$

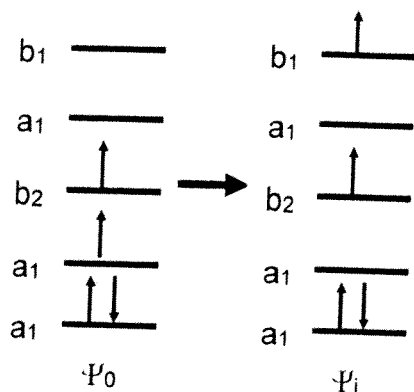
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 57750 - 373(181.1) = -9800 \text{ J}$$

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{(-9800)}{8.31(373)} = +3.16$$

$$K = e^{3.16} = 23.6$$

- (8) 11. Consider a hypothetical AH_2 molecule with C_{2v} symmetry and a triplet ground state electronic configuration: $(a_1)^2(a_1)^1(b_2)^1$

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!!



$$M_{ox} = A_2 \times B_1 \times B_2 = A_1 \checkmark$$

$$M_{oy} = A_2 \times B_2 \times B_2 = A_2 \times$$

$$M_{oz} = A_2 \times A_1 \times B_2 = B_1 \times$$

$$\Gamma(\Psi_0) = a_1 \times b_2 = B_2$$

$$\Gamma(\Psi_1) = b_2 \times b_1 = A_2$$

IR Active

Perpendicular

(18) 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?

4 - core STO's, contrs of 4 GTO's

Only split valence - Valence contrs - Inner STO = contrs of 2 GTO's
Outer STO = 1 GTO

- (3) (b) In the CCSD(T) method, what does each letter stand for?

Coupled Cluster with Single & Double Excitations
plus Approx Extrapol for Triple Excitations

12. (Cont'd)

- (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?

Geometry optimised at HF/6-31G(d) level.
Single Point Energy Calc. (at fixed geom.)
at CISD/6-311+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).

H: 2x1s DSU (only split value.)
1x4s Diffuse
1x3-2p's Polarized

C: 1x1s Core.
2x2s DSU
2x3 2p's "
1-4s Diffuse
1-3p's Diffuse
2x5d's Polarized
1x7f's Polarized

P
1x1s Core.
1x2s Core.
1x3-2p's Core.
2x3s DSU
2x3-3p's "
1-4s Diffuse
1-3p's Diffuse
1x3-2p's Polarized
2x5d's Polarized
1x7d's Polarized