Chemistry 483 Examination 4
December 4, 2009

Student Name Key

1. (40 points) Define and/or characterize

a. Normal coordinate

one which permits the vibrational potential energy to be written as $\frac{1}{2}\sum_j F_j Q_j^2$

b. Trace of a matrix

sum of diagonal elements

c. A (mathematical) group

a group is a set of entities that satisfy certain requirements:

1. multiplication rule
2. associative
3. identity
4. inverse

d. sp^2 hybrid orbital

ψ_i = atomic orbital consisting of p & s character.

there are 3 possible sp^2 hybrid orbitals & they are separated by 120°.

$$\psi = \frac{p_R + \lambda s}{\sqrt{1+\lambda^2}} \; ; \; \lambda = \sqrt{\frac{-1}{\cos\theta}} \; : \theta = 120$$

e. The five symmetry elements

E identity

C_N ~~rotation by~~ axis of rotation

σ plane of symmetry

i center of symmetry

S_n N fold rotation - reflection.

f. Order of a group

The number of operators in group

g. Huckel approximation

$H_{ii} = \alpha$; $H_{ij} = \beta$ if $i \neq j$ correspond to adjacent (bonded) atoms

$H_{ij} = 0$ otherwise

$S_{ij} = 0$ if $i \neq j$

$S_{ij} = \delta_{ij}$

h. Matrix representation of a group.

a set of matrices that multiply together in the same manner as a group multiplication table.

Key

2.(15 points)

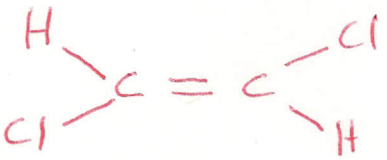
a. How many normal modes of vibration does *trans*-dichloroethene have?

b. Determine their symmetries.

a) For a non-linear molecule with 6 atoms,

$3N-6 = 3(6)-6 = 12$ vibrational modes

b)



C_{2h}	$\hat{E}$	$\hat{C}_2$	$\hat{i}$	$\hat{\sigma}_h$
Γ	18	0	0	6

$$a_{A_g} = \frac{1}{4}\left[(1)(18)(1) + (1)(6)(1)\right] = 6$$

$$a_{B_g} = \frac{1}{4}\left[(1)(18)(1) + (1)(6)(-1)\right] = 3$$

$$a_{A_u} = \frac{1}{4}\left[(1)(18)(1) + (1)(6)(-1)\right] = 3$$

$$a_{B_u} = \frac{1}{4}\left[(1)(18)(1) + (1)(6)(1)\right] = 6$$

$$\Gamma_{3N} = 6A_g + 3B_g + 3A_u + 6B_u$$

$$\Gamma_{trans} = 1A_u + 2B_u$$

$$\Gamma_{rot} = 1A_g + 2B_g$$

$$\Gamma_{3N} - \Gamma_{trans} - \Gamma_{rot} = \boxed{5A_g + 1B_g + 2A_u + 4B_u = \Gamma_{vib}}$$

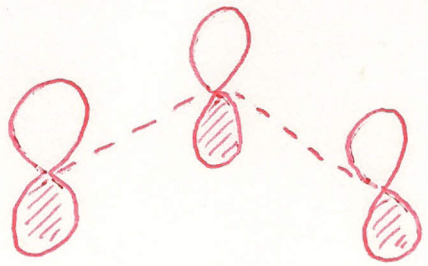
Key

3. (15 points) The allyl radical, C_3H_5 has C_{2v} symmetry and three pi electrons in three atomic pi orbitals.

a. Determine the characters of the reducible representation generated by these orbitals.

b. Decompose this reducible representation into its irreducible components.

c. Using the generating (projection) operator method determine the linear combination of these atomic orbitals that belong to these irreducible representations.



a)

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
Γ	3	-1	1	-3

b) $a_{A_1} = \frac{1}{4}[(1)(3)(1) + (1)(-1)(1) + (1)(1)(1) + (1)(-3)(1)] = 0$

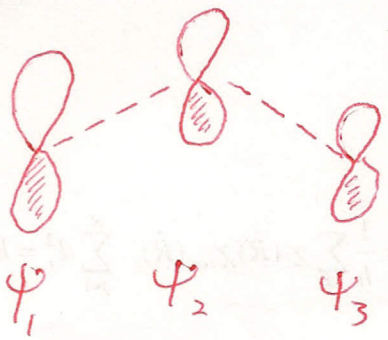
$a_{A_2} = \frac{1}{4}[(1)(3)(1) + (1)(-1)(1) + (1)(1)(-1) + (1)(-3)(-1)] = 1$

$a_{B_1} = \frac{1}{4}[(1)(3)(1) + (1)(-1)(-1) + (1)(1)(1) + (1)(-3)(-1)] = 2$

$a_{B_2} = \frac{1}{4}[(1)(3)(1) + (1)(-1)(-1) + (1)(1)(-1) + (1)(-3)(1)] = 0$

$\Gamma = A_2 + 2B_1$

Key



$$\hat{P}_{A_1}\psi_1 \propto (1)\hat{E}\psi_1 + (1)\hat{C}_2\psi_1 + (1)\hat{\sigma}_v\psi_1 + (1)\hat{\sigma}_v'\psi_1$$

$$\psi_1 \quad -\psi_3 \quad +\psi_3 \quad -\psi_1 = 0$$

↳ No A_1 in Γ. (Should only project on A_2 & B_1)

$$P_{A_2}\psi_1 \propto (1)\hat{E}\psi_1 + (1)\hat{C}_2\psi_1 + (-1)\hat{\sigma}_v\psi_1 + (-1)\hat{\sigma}_v'\psi_1$$

$$\psi_1 \quad -\psi_3 \quad -\psi_3 \quad +\psi_1$$

$\phi_1 = N(\psi_1 - \psi_3)$ → LCAO belonging to A_2 (only B_1's left)

$$P_{B_1}\psi_1 \propto (1)\hat{E}\psi_1 + (-1)\hat{C}_2\psi_1 + (1)\hat{\sigma}_v\psi_1 + (-1)\hat{\sigma}_v'\psi_1$$

$$\psi_1 \quad +\psi_3 \quad +\psi_3 \quad +\psi_1$$

$\phi_2 = N(\psi_1 + \psi_3)$ → LCAO belonging to B_1

$$P_{B_1}\psi_2 \propto (1)\hat{E}\psi_2 + (-1)\hat{C}_2\psi_3 + (1)\hat{\sigma}_v\psi_2 + (-1)\hat{\sigma}_v'\psi_2$$

$$\psi_2 \quad +\psi_2 \quad +\psi_2 \quad +\psi_2$$

$\phi_3 = N(\psi_2)$ → LCAO belonging to B_1

Key

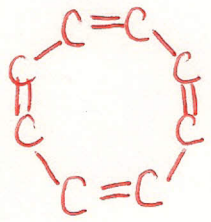
4. (15 points)

a. Calculate the Huckel energy levels for the *cyclo*-octatetraene molecule, C_8H_8.

b. What is the pi electron energy of *cyclo*-octatetraene?

c. Calculate the delocalization energy of *cyclo*-octatetraene

Keep in mind the formula : $E_n = \alpha + 2\beta\cos\left(\frac{2\pi n}{N}\right)$; $N = 0, \pm1, \pm2, \cdots, N/2$

(a.) 

8 π electrons

$N = 8$ (# carbon atoms)

$E_0 = \alpha + 2\beta$

$E_{1,} = E_{-1} = \alpha + 1.414\beta = \alpha + \sqrt{2}\beta$

$E_2 = E_{-2} = \alpha$

$E_3 = E_{-3} = \alpha - 1.414\beta = \alpha - \sqrt{2}\beta$

$E_4 = \alpha - 2\beta$

8 values for 8 E_n's

— $E_4 = \alpha - \beta$

— — $E_3 = E_{-3} = \alpha - 1.414\beta = \alpha - \sqrt{2}\beta$

↑ ↑ $E_2 = E_{-2} = \alpha$

↑↓ ↑↓ $E_1 = E_{-1} = \alpha + 1.414\beta = \alpha + \sqrt{2}\beta$

↑↓ $E_0 = \alpha + 2\beta$

(b.) $E_\pi = 2(\alpha + 2\beta) + 4(\alpha + 1.414\beta) + 2\alpha$

$= 2\alpha + 4\beta + 4\alpha + 5.656\beta + 2\alpha$

$\boxed{E_\pi = 8\alpha + 9.656\beta}$

(c.) $E_{deloc} = E_\pi(\text{cyclo-octatetraene}) - 4E_\pi(\text{ethene})$

$= 8\alpha + 9.656\beta - 4(2\alpha + 2\beta)$

$= \boxed{1.656\beta} < 0$

key

5. (15 points) Given the two orbitals $\varphi_1 = p_x \cos\phi + p_y \sin\phi$ and $\varphi_2 = -p_x \cos\phi + p_y \sin\phi$
Express the overlap integral as a function of ϕ

$$\phi_1 = \frac{1}{\sqrt{2}}(2s - 2p_x)$$

Overlap integral, $S_{ij} = \int \phi_i^* \phi_j \, d\tau$

$$S_{12} = \int (p_x \cos\phi + p_y \sin\phi)^* (-p_x \cos\phi + p_y \sin\phi) \, d\tau$$

$$= -\int p_x^* p_x \cos^2\phi \, d\tau + \int p_x^* \cos\phi \, p_y \sin\phi \, d\tau - \int p_y^* \sin\phi \, p_x \cos\phi \, d\tau + \int p_y^* p_y \sin^2\phi$$

$$= -\int p_x^* p_x \cos^2\phi \, d\tau + \int p_y^* p_y \sin^2\phi \, d\tau$$

$$= -\cos^2\phi \int p_x^* p_x \, d\tau + \sin^2\phi \int p_y^* p_y \, d\tau$$

$$= -\cos^2\phi + \sin^2\phi$$