

Time: 2½ hours

Chemistry 218
Molecular Structure
Final Exam

January 30, 1996
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NAME: _____

1. (15 pts)

The one-dimensional harmonic oscillator Hamiltonian is:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + 2\pi^2\nu^2 m \hat{x}^2$$

The raising and lowering operators for this problem are defined as:

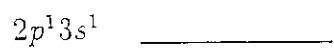
$$\hat{A}_+ = \frac{1}{(2m)^{1/2}} [\hat{p}_x + 2\pi i\nu m \hat{x}], \quad \hat{A}_- = \frac{1}{(2m)^{1/2}} [\hat{p}_x - 2\pi i\nu m \hat{x}]$$

where $i = \sqrt{-1}$.

Evaluate the operators $\hat{A}_+ \hat{A}_-$ and $\hat{A}_- \hat{A}_+$;

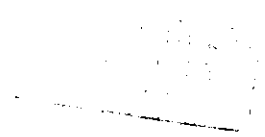
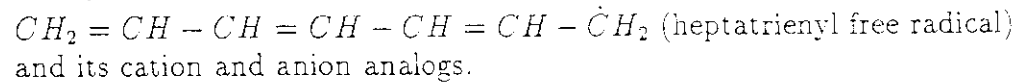
then show that $[\hat{A}_+, \hat{A}_-] = -\hbar\nu$.

2. (10 pts) Consider the following diagram showing two electronic configurations:



Draw an energy diagram showing all the terms and the levels arising from these two configurations (No magnetic field).

3. (52 pts) Consider from the viewpoint of Hückel molecular orbital π -electron theory, the heptatrienyl molecular systems:



- a. Write the secular determinant for these seven-carbon systems in terms of $x = \alpha - E/\beta$. (4 pts)
- b. Now draw structures for the cycloheptatrienyl carbonium ion, free radical and carbanion; then write the secular determinant for these *cyclic* seven-carbon systems. (7 pts)
- c. The solutions for the two problems (acyclic and cyclic π -electron systems) are as follows:

ACYCLIC: $x = 0, \pm 0.765, \pm 1.414, \pm 1.848$

CYCLIC:

$$x_1 = -2, \quad x_2 = x_3 = -1.247, \quad x_4 = x_5 = 0.445, \quad x_6 = x_7 = 1.802$$

Construct the MOED for each of the acyclic and cyclic seven-carbon systems showing the energies of the various molecular orbitals (draw two separate diagrams). (14 pts)

- d. Calculate the delocalization energy (D.E) for each of the three acyclic and the three cyclic molecules. Organize your results in a table as follows:

Table 1: DELOCALIZATION ENERGIES

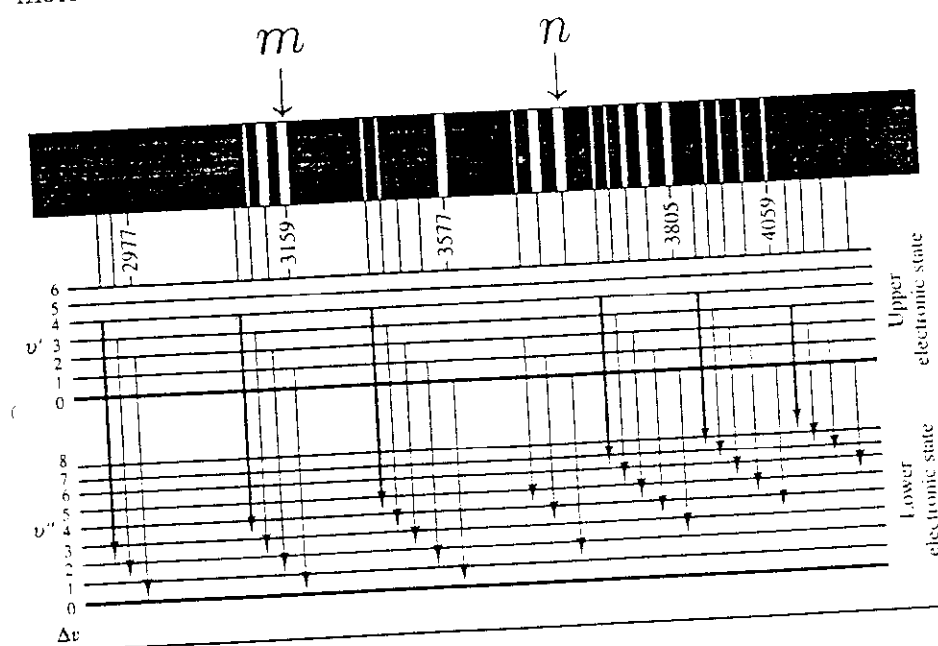
	cation	radical	anion
acyclic			
cyclic			

GIVEN: Energy of lowest MO in ethylene: $\alpha + \beta$ (20 pts)

- e. Compare the different extents of delocalization of the considered molecules. Which system is the most delocalized and what property does it illustrate? Explain. (7 pts)
4. (45 pts) 4 *independent* parts

- a. What molecular terms would result if two atoms, each in a 3P term, combined to form a homonuclear diatomic molecule? (Ignore the parity and $+/-$ symbols) (10 pts)

- b. Arrange the following molecules in order of decreasing bond length: N_2^- , F_2 , N_2 , O_2 , O_2^+ , O_2^- . (10 pts)
- c. The lower energy states of the oxygen (O_2) molecule are $^3\Sigma$, $^1\Sigma$ and $^1\Delta$. Give the electronic configurations corresponding to each of these states then write the corresponding *complete* term. What term is the ground state? (10 pts)
- d. The following diagram illustrates the high resolution structure of a broad band in the emission electronic spectrum of the nitrogen molecule.



1. Label the various groups (called sequences) of vibrational bands with the corresponding value of Δv . What restriction exists on the value of Δv for the transition to be allowed? (5 pts)
2. The most intense vibrational bands are the ones labeled m and n . Sketch the potential energy curves of the lower and the upper electronic states, in a manner which clearly illustrates these observed intensities. Explain your reasoning. (10 pts)

5. (38 pts)

- a. Write the Hamiltonian operator \hat{H} (in atomic units) for the HeH^+ molecule (a drawing labeled with the distances used is helpful). (8 pts)
- b. Write out the secular determinant for this molecule in terms of

$$\langle 1s_H | \hat{H} | 1s_H \rangle \equiv \alpha, \quad \langle 1s_{He} | \hat{H} | 1s_{He} \rangle = 4\alpha.$$

$$\text{and } \langle 1s_H | \hat{H} | 1s_{He} \rangle = 2.5 \alpha.$$

Then solve the determinantal equation in terms of α . (15 pts)

- c. Now let $\alpha = -1.0 \text{ eV}$. Calculate the energies of the obtained molecular orbitals, then give clear numerical expressions for the molecular wavefunctions. (15 pts)
6. (40 pts) The infrared spectrum of gaseous hydrogen bromide includes an intense band centered at a wave number of 2559 cm^{-1} whose successive lines are 16.94 cm^{-1} apart. If the anharmonicity constant is 0.01706 ,
- a. calculate:
 - * the harmonic wave number,
 - * the wave number at which the first overtone is observed.
 - * the force constant of the HBr bond.
 - * the rotational constant and hence the internuclear distance in the molecule (in \AA).
$$M_H = 1.008 \text{ g/mol}, M_{Br} = 79.904 \text{ g/mol} \quad (25 \text{ pts})$$
 - b. Given that at the dissociation limit, the spacing between the vibrational energy levels becomes practically zero, determine the maximum vibrational quantum number. (5 pts)
 - c. From your calculation in c), estimate a value of the bond dissociation energy (in eV). (10 pts)

NOTE: The grade totals up to 200 points.

Good Luck

APPENDIX

PHYSICAL CONSTANTS:

Planck's constant $h = 6.626 \times 10^{-34}$ Js

Speed of light $c = 2.998 \times 10^8$ m s⁻¹ = 2.998×10^{10} cm s⁻¹

Avogadro's number $N_A = 6.023 \times 10^{23}$ molec/mol

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J