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Chemistry 218
Final Exam
February 3, 1999

Time: 120 minutes

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Useful information

Planck's constant	$h = 6.6260755 \times 10^{-34}$ J s
	$\hbar = 1.05457266 \times 10^{-34}$ J s
Boltzmann constant	$k_B = 1.3806568 \times 10^{-23}$ J K^{-1}
Mass of electron	$m_e = 9.1093897 \times 10^{-31}$ kg
Speed of light	$c = 2.99792458 \times 10^{8}$ m s^{-1}
Charge of electron	$e = 1.60217733 \times 10^{-19}$ C
Bohr's Magneton	$\mu_B = 9.2740154 \times 10^{-24}$ J T^{-1}
Bohr's radius	$a_0 = 0.529177249 \times 10^{-10}$ m

$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$; $\left[\hat{L}_x, \hat{L}_z\right] = -i\hbar\hat{L}_y$; $\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$

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GRADE:

1. (5%) One of the most powerful modern techniques for studying structure is neutron diffraction. This technique involves generating a collimated beam of neutrons at a particular temperature from high-energy neutron source and is accomplished at several accelerator facilities around the world. If the speed of a neutron is given by

$$v_n = \sqrt{\frac{3k_BT}{m}},$$

where m is the mass of a neutron, then what temperature is needed so that the neutrons have a de Broglie wavelength of 50 pm? Take the mass of a neutron to be $1.67 \times 10^{-27} Kg$.

2. (10%)The Shrödinger equation for a particle of mass m constrained to move on circle of radius a is

$$-\frac{\hbar^2}{2I}\frac{d^2\psi(\theta)}{d\theta^2} = E\psi(\theta) \qquad 0 \le \theta \le 2\pi,$$

where $I = ma^2$ is the moment of inertia and θ is the angle that describes the position of the particle around ring.

   a. Find the appropriate physical boundary condition for $\psi(\theta)$ and fully determine the eigenfunctions and the energy eigenvalues.
   b. Discuss how you might use these results for a free-electron model for benzene.

3. (10%) Define the two operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \qquad and \qquad \hat{L}_- = \hat{L}_x - i\hat{L}_y.$$

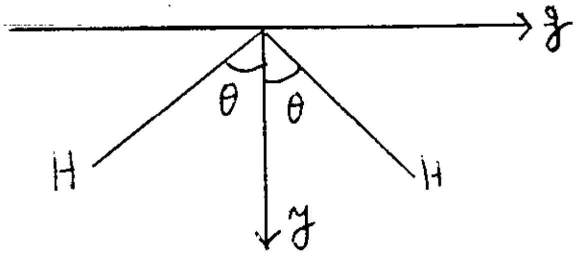
   a. Show that $[\hat{L}_z, \hat{L}_+] = \hbar\hat{L}_+$ and $[\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-$.
   b. Show that $[\hat{L}_+, \hat{L}^2] = [\hat{L}_-, \hat{L}^2] = 0$.

4. (5%)Find all term symbols for the excited state of zirconium with the following configuration

$$KLM4s^2 4p^6 4d^1 5s^2 5f^1.$$

What is the ground-state term?

5. (15%)Use the following coordinate system for the water molecule



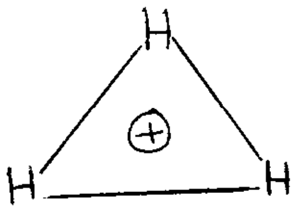
   a. What is the second bonding hybrid molecular orbital on the oxygen atom, ξ_2, if the first one, ξ_1, is given by

$$\xi_1 = N[\gamma(\theta)2s + (\sin\theta)2p_y + (\cos\theta)2p_z],$$

   where $\gamma(\theta)$ is function of θ and N is a normalization constant. At this stage write it in terms of $\gamma(\theta)$ and N.
   b. Find $\gamma(\theta)$ and N if the angle θ for water is 104.5°.
   c. Determine the third hybrid, ξ_3, if it is along the z-axis.
   d. For the lone pairs of electrons, write down two equivalent, normalized, fully determined,

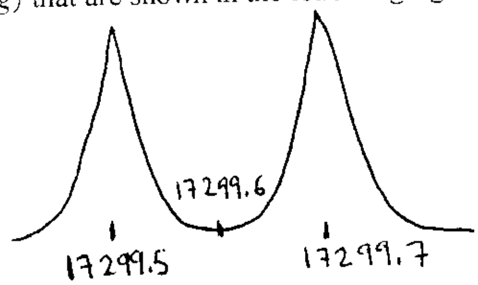
nonbonding molecular orbitals.

6. (15%)Using Hückel molecular-orbital theory, determine whether the linear state ($H-H-H^+$) or the triangular state



of H_3^+ is the more stable state. Repeat the calculation for H_3 and H_3^- to determine which geometry is the most stable. [Hint: $x^3-3x+2=(x+2)(x-1)^2$].

7. (15%)In this problem, we will determine the excited-state rotational quantum number for the $X \to A$ absorption bands of $ICl(g)$ that are shown in the following figure:



The transition is from the $v''=0$ state of the X state to highly excited vibrational level of the A state ($v'=32$). To accurately calculate the vibrational term $G(v)'$ for the excited state for the excited state A, we will need to include a second order a harmonic correction to take into account the shape of the potential curve. First order corrections will be sufficient for the ground electronic state. We would write

$$G(v)' = G(v) + \tilde{v}_e\tilde{y}_e\left(v+\frac{1}{2}\right)^3,$$

where $G(v)$ is the usual vibrational term with first order correction. Some of the spectroscopic constants for the X ground state and the excited state A of ICl are given by

State	$\tilde{T}_e/cm^{-1}$	v_e/cm^{-1}	$\tilde{v}_e\tilde{x}_e/cm^{-1}$	$\tilde{v}_e\tilde{y}_e/cm^{-1}$	$\tilde{B}_e/cm^{-1}$	$\tilde{\alpha}_e/cm^{-1}$
A	13745.6	212.39	1.927	−0.03257	0.08389	0.00038
X	0	384.18	1.46			

a. Write down explicitly $G(v)'$ and determine the value of $\tilde{v}$ corresponding to the transition $X(v''=0,\ J''=0) \to A(v'=32,\ J'=0)$.

b. Given that the ground state of the lines shown in the above figure is the $v''=0,\ J''=2$ level of the X state and the rotational term for this level is $F(2)=0.65\ cm^{-1}$, determine the closest value of J', the rotational level of the $v'=32$ level of the excited A state that gives the two observed spectral lines.

8. (25%)In the photolysis of $ICN(g)$, the $CN(g)$ fragment can be generated in several different vibrational and rotational states.

a. Discuss the IR spectrum of the ICN molecule: Draw all the vibrational modes of the molecule, indicate the active and inactive ones, write down the selection rule and sketch the expected spectrum.

Consider the following spectroscopic information:

State	$\tilde{T}_e/cm^{-1}$	ν_e/cm^{-1}	$\tilde{\nu}_e\tilde{x}_e/cm^{-1}$	$\tilde{B}_e/cm^{-1}$	$\tilde{\alpha}_e/cm^{-1}$
$B^2\Sigma^+$	25751.8	2164.13	20.25	1.970	0.0222
$X^2\Sigma^+$	0	2068.71	13.14	1.899	0.0174

Use this table to answer the following:

b. At what wavelength would you set your probe laser to excite the $v'' = 0, J'' = 3$ of the $X^2\Sigma^+$ ground state to the $v' = 0$, $J' = 3$ level of the $B^2\Sigma^+$ excited state.

c. Calculate the energy-level spacing between the $v'' = 0, J'' = 3$ level and the $v'' = 0, J'' = 4$ level.

d. If the width of the duration of an electromagnetic pulse, Δt, and the width of the frequency distribution of the pulse, $\Delta\nu$, are related by $\Delta t\Delta\nu = 1/2\pi$, can the formation dynamics of a single vibrational state of $CN(g)$ can be monitored by a femtosecond laser experiment?

Good Luck!