Final Exam

Chemistry 539
Wednesday, December 9, 2011

Your Name:

This is the final exam. You can use your notes or a textbook but cannot discuss anything with other students. You have 2 hours to complete the exam. Write ALL your derivations , especially if you wish to get partial credit.

Question 1 (5 points)

a) (3points) Arrange in order of increasing energy the terms that may arise from the $3d^2$ electron configuration.

b) (2 points) Identify the lowest energy state in that configuration.

Question 2 (28 points)

The ammonia molecule is pyramidal with nitrogen atom being 0.38Å above the plane.

a) (10 points) Identify molecular symmerty and explain using Walsh correlation diagram why the molecule is not planar. Provide the electron configuration and the total molecular symmetry in the ground state. **Hint**: consider the MO for planar and pyramidal shapes and evalute their relative energies as weel as the total energy of all electrons.

b) (2 points) Based on your diagram, will NH_3^+ more or less close to planar geometry?

c) (10 points) Identify (label and draw) vibrational modes for NH_3. How many IR-active and Raman-active fundamental frequencies are there?

d) (6 points) Sketch a microwave spectrum of NH_3.

Question 3 (49 points)

Molecule of XeF_4 is planar. How can we confirm that it is not tetrahedral? First we will use spectroscopic tools to prove it and then use MO theory to corroborate the conclusion.

a) (**2 point**) Will microwave spectroscopy be useful in answering this questions? Why?

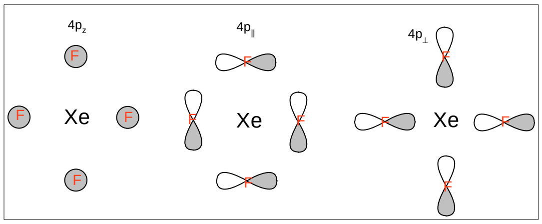
b) (**22 points**) Let us analyze vibrational frequencies using IR and Raman and see if that helps. Perform vibrational analysis for the planar, XeF_4. Show by arrows (or write in a form of displacement vectors) and classify by symmetry the normal modes, label them and identify their IR and Raman activities. **Hint:** treat stretching, bending in plane and bending out of plane modes separately.

Perform the same analysis for anticipaed tetrahedral XeF_4.

Does the information about the number of IR and Raman allowed transitions help in distinguishing between the two molecular shapes?

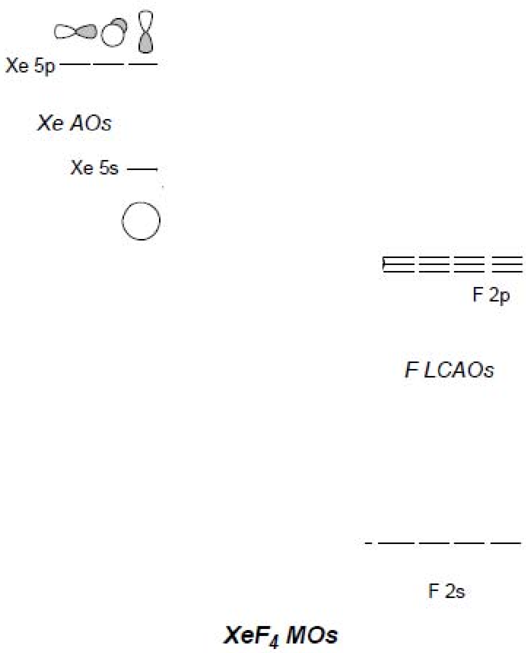
Next we will try to rationalize this structure using MO theory.

c) (15 points) Construct a molecular orbital diagram for XeF_4 that includes four valence atomic orbitals (AOs) for all five atoms, assuming that the 2s orbitals of F do not effectively take part in bonding. Do it by assigning the symmetry species of D_{4h} group to 5s and 5p AOs of Xe, the construct symmetry adapted linear combinations (SALC) of 2p AOs of F. **Hint**: reduce separately the representations of four p_z orbitals, four $p_{\parallel}$, and four $p_{\perp}$, with the reference to **II** and $\perp$ as sketched below.



Identify the symmetry species from Xe AOs and 4F p AOs that participate in bonding and sketch the result on the graph below.

NB. Don't forget that the resonance integrals for π-bonding is less than that for σ-bonding.



d) (4 points) Place the valence electrons onto MOs and identify the HOMO and LUMO. What is the bonding nature and character for each? (e.g. σ-bonding, π- antibonding, non-bonding)?

e) (2 points) What is the total bond order? Is it greater than 0?

f) (4 points) Is the transition arising from promoting HOMO electron to LUMO allowed?

Question 4 (6 points)

Calculate $\langle L^2 \rangle$, $\langle L_z \rangle$, and the probability to measure $L_z = +1$ for d_{xy} orbital. **Hint:** Represent d_{xy} via linear combination of spherical functions, Y_l^m, and use their properties to calculate the desired expectation values.

Question 5 (4 points)

Molecule	Symmetric top? What kind?	Point symmetry group
a) $H_2C{=}C{=}CH_2$		
b) CH_3Cl		
c) CO_2		
d) CF_4		

Question 6 (8 points)

Skecth the rotational Raman spectra (only Stokes part) at room temperature for $^{15}N_2$, $^{18}OC^{16}O$, SiH_4, SF_6. Take the reasonable bond lengths.

'Cheating' Sheet

Postulates:

1) $\int \Psi^*(\vec{r},t)\Psi(\vec{r},t)d\tau = 1$

2) For every **observable** → **Hermitian operator** in QM. $x \to \hat{x}$; $p_x \to \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$.

3) For any observable A: $\hat{A}\psi_k = \lambda_k\psi_k$ and any $\Psi = \sum_k c_k\psi_k \Leftrightarrow |\Psi> = \left(\sum_k\right)|k><k|\Psi>$.

4) $\langle A\rangle \equiv \frac{<\Psi|\hat{A}|\Psi>}{<\Psi|\Psi>} = \frac{\int\Psi^*\hat{A}\Psi d\tau}{\int\Psi^*\Psi d\tau} = \int\Psi^*\hat{A}\Psi d\tau$ (if $<\Psi|\Psi>=1$); $\langle A\rangle = \sum_k \lambda_k|c_k|^2 = \left(\sum_k\right)\lambda_k|<k|\Psi>|^2$

5) Time dependent Schrödinger equation: $i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}\Psi(\vec{r},t)$,

where nonrelativistic **Hamiltonian**: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

For time independent $V(x)$: $\hat{H}\psi_n(x) = E_n\psi_n(x)$

$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$

1D systems:

PIB: $|n> = \psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$ $\quad E_n = \frac{n^2h^2}{8mL^2}$

HO:

$|n> = \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{n!2^n}}H_n(\xi)e^{-\xi^2/2}$ $\quad \omega = \sqrt{\frac{k}{m}};\ \xi = \sqrt{\frac{m\omega}{\hbar}}x$

$E_n = (n+\frac{1}{2})\hbar\omega = (n+\frac{1}{2})h\nu$ $\quad \nu = \frac{\omega}{2\pi}$

$\hat{a} = \sqrt{\frac{m\omega\hbar}{2}}x + i\sqrt{\frac{1}{2\hbar m\omega}}\hat{p}$; $\quad \hat{a}^+ = \sqrt{\frac{m\omega\hbar}{2}}x - i\sqrt{\frac{1}{2\hbar m\omega}}\hat{p}$

$\hat{a}|n> = \sqrt{n}|n>$; $\quad \hat{a}^+|n> = \sqrt{n+}|n+1>$

ψ_0	$\left(\frac{1}{\pi}\right)^{1/4}e^{-\xi^2/2}$
ψ_1	$\left(\frac{4}{\pi}\right)^{1/4}\xi e^{-\xi^2/2}$
ψ_2	$\frac{2\xi^2-1}{\sqrt[4]{4\pi}}e^{-\frac{1}{2}\xi^2}$
ψ_3	$\frac{2\xi^3-3\xi}{\sqrt{3}\sqrt[4]{\pi}}e^{-\frac{1}{2}\xi^2}$

POR: $\psi_n(\varphi) = \sqrt{\frac{1}{2\pi}}e^{in\varphi}$ $\quad E_n = \frac{n^2\hbar^2}{2I}$ $\quad I = \sum m_i r_i^2\left(\frac{m_1m_2}{m_1+m_2}R_e^2 \text{ for diatomic}\right)$

3D systems:

Hamiltonian in spherical coordinates:

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] + V(r)$$

Angular momentum (and spin):

$\vec{L} = -i\hbar[\mathbf{r}\times\vec{\nabla}]$

$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \frac{-\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$

$\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\varphi}$

$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cos\varphi\cot\theta\frac{\partial}{\partial\varphi}\right)$

$\hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = i\hbar\left(\sin\varphi\cot\theta\frac{\partial}{\partial\varphi} - \cos\varphi\frac{\partial}{\partial\theta}\right)$

$\hat{L}_\pm = L_x \pm iL_y = \pm\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right)$

$\hat{L}^2 = (L_+L_- + L_z^2 - \hbar L_z)$

$\hat{L}^2|l,m> = \hbar^2 l(l+1)|l,m>$

$\hat{L}_z|l,m> = \hbar m|l,m>$

$\hat{L}_\pm|l,m> = \hbar\sqrt{l(l+1)-m(m\pm1)}\,|l,m\pm1>$

Y_0^0	$\sqrt{1/4\pi}$
Y_1^0	$\sqrt{\frac{3}{4\pi}}\cos\theta$
$Y_1^{\pm1}$	$\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\theta$
Y_2^0	$\sqrt{\frac{5}{\pi}}\frac{3\cos^2\theta-1}{4}$
$Y_2^{\pm1}$	$\sqrt{\frac{15}{2\pi}}e^{\pm i\varphi}\sin 2\theta$
$Y_2^{\pm2}$	$\sqrt{\frac{15}{32\pi}}e^{\pm 2i\varphi}\sin^2\theta$

Linear Combinations:	Names
Y_0^0	s
Y_1^0	p_z
$\frac{1}{\sqrt{2}}(Y_1^1+Y_1^{-1})$	p_x
$\frac{1}{i\sqrt{2}}(Y_1^1-Y_1^{-1})$	p_y

Linear Combinations:	Names
Y_2^0	d_{z^2}
$\frac{1}{\sqrt{2}}(Y_2^1+Y_2^{-1})$	d_{xz}
$\frac{1}{i\sqrt{2}}(Y_2^1-Y_2^{-1})$	d_{yz}
$\frac{1}{\sqrt{2}}(Y_2^2+Y_2^{-2})$	$d_{x^2-y^2}$
$\frac{1}{i\sqrt{2}}(Y_2^2-Y_2^{-2})$	d_{xy}

Hydrogen-like atom: $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}Y_l^m(\theta,\varphi) = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+1)!]^3}}\,e^{-Zr/na}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na}\right)Y_l^m(\theta,\varphi) \quad E_n = -\frac{1}{2n^2}\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}$$

R_{10}	$2\left(\frac{Z}{a}\right)^{3/2}e^{-Zr/a}$
R_{20}	$\left(\frac{Z}{2a}\right)^{3/2}\left(2-\frac{Zr}{a}\right)e^{-Zr/2a}$
R_{21}	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}$
R_{30}	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(27\text{-}18\frac{Zr}{a}+2\frac{Z^2r^2}{a^2}\right)e^{-\frac{Zr}{3a}}$
R_{31}	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)\left(6-\frac{Zr}{a}\right)e^{-Zr/3a}$
R_{32}	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2e^{-Zr/3a}$

$$\frac{s+1}{n^2}<r^s>-(2s+1)a<r^{s-1}>+\frac{s}{4}\left((2l+1)^2-s^2\right)a^2<r^{s-2}>=0$$

Constants :

Electron charge	e	$1.602177\times10^{-19}\,\mathrm{C}$
Planck's constant	h	$6.6260755\times10^{-34}\,\mathrm{J{\cdot}s}$
Electron mass	m_e	$9.1093897\times10^{-31}\,\mathrm{kg}$ or $0.511\,\mathrm{MeV}$
Proton mass	m_p	$1.672623\times10^{-27}\,\mathrm{kg}$ or $938.27\,\mathrm{MeV}$
Speed of light	c	$2.997924\times10^8 m/\mathrm{s}$
Bohr radius	$a_0 = \hbar^2\frac{4\pi\varepsilon_0}{me^2}$	$0.52918\times10^{-10}\,\mathrm{m}$
Rydberg constant	$R_\infty = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$	$2.17987\times10^{-18}\,\mathrm{J}$ or $3.28984\times10^{15}\,\mathrm{Hz}$
Hartree energy	$E_h = 2R_\infty$	$4.35975\times10^{-18}\,\mathrm{J}$ or $27.2114\,\mathrm{eV}$
Fine-structure constant	$\alpha = \frac{e^2}{2\varepsilon_0 hc}$	$7.29735\times10^{-3} = 1/137.04$
Boltzmann constant	k	$1.380658\times10^{-23}\,\mathrm{J{\cdot}K^{-1}}$
Bohr magneton	μ_B	$9.274\times10^{-24}\,\mathrm{J/T}$
Nuclear magneton	μ_N	$5.051\times10^{-27}\,\mathrm{J/T}$
Mag. permeability of free space	μ_o	$1.25664\times10^{-6}N\bullet A^{-2}$
Permeability of free space	$\varepsilon_o = 1/c^2\mu_o$	$8.854187817\times10^{-12}F/m$
Avogadro's number	N_A	$6.0221367\times10^{23}\,\mathrm{mol^{-1}}$

Virial theorem: for $V(x) = ax^s, < K >= \frac{s}{2} < V >$