*Name*__________________________________

Chemistry 344

Final Exam
Tuesday December 4, 2001
3:30 -5:30 PM

NO CALCULATORS PERMITTED. Additional information, integrals, etc. are given on separate pages. Where a calculator is required, you do not need to provide a final numerical answer. Just carry through all the way up to the complete numerical expression, ready for punching numbers into the calculator.

Be sure to use the constants, variables and functions of <u>the given problem</u>, not those of some other remembered problem in answering the questions.

1. A particle of mass M is constrained to be on a line along the z axis perpendicular to the earth's surface in a gravitational field where *g* is the acceleration of gravity.

(a) *Write down the Schrödinger equation for this system.*

(b) *Determine the boundary conditions that must be satisfied by the wavefunction for this system.*

2. Consider a particle of mass M constrained to move on a circle of radius R where its potential energy is zero. $\Psi_k(\phi) = (1/\sqrt{2\pi})\exp[ik\phi]$ are the eigenfunctions of $\mathcal{H} = -(\hbar^2/2MR^2)\, d^2/d\phi^2$ and $E = k^2(\hbar^2/2MR^2)$ are the eigenvalues.

(a) *Derive the values of* k *that are allowed. Show proof!*

(b) The z component of the angular momentum of the particle is represented by the operator $L_z = (\hbar/i)\, d/d\phi$. When the angular momentum of the system is measured ***derive (show proof) the possible outcomes of the measurements.***

3. A particle of Problem 2 is in a physical state that is described by $F(\phi) = A\{\cos 2\phi + 2\cos 3\phi\}$. *Determine the results of the following sets of experiments on this system, that is, determine the typical outcomes of the experiments, the average values of the results:*

(a) The z component of the angular momentum of the system is measured

Derivation of predictions here:	Observed values here:
	Average=

(b) The energy of the system is measured

Derivation of predictions here:	Observed values here:
	Average=

4. The eigenvalues of a linear (one-dimensional) harmonic oscillator are known:

$\mathcal{H}(x)\, \varphi(x) = E\, \varphi(x)$

where $\mathcal{H}(x) = -(\hbar^2/2M)\, d^2/dx^2 + ½\, \kappa x^2$

where M is the mass of the oscillator, and κ is the Hooke's law force constant.

That is, $\{-(\hbar^2/2M)\, d^2/dx^2 + ½\, \kappa x^2\}\, \varphi(x) = (n + ½)\hbar\omega\, \varphi(x)$ where $n = 0, 1, 2, 3, \ldots$

A linear harmonic oscillator in its ground state is described by the normalized function

$\varphi(x) = [2\, \omega M/h]^{¼} \exp[-\omega M x^2/2\hbar]$

Now consider a three-dimensional anisotropic harmonic oscillator that has three different force constants for motion in the direction of each of the Cartesian coordinates, i.e., $V = ½\, [\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]$

[This is akin to the vibrations of a polyatomic molecule, in which there are several vibrational coordinates, one normal mode coordinate for each normal mode of vibration.]

Write the Schrödinger equation for this system (the three-dimensional anisotropic oscillator).

Show how you would find the eigenfunctions and eigenvalues of the three-dimensional anisotropic oscillator. [The harmonic vibrations of a polyatomic molecule are found in this way.]

Write down the eigenvalues of the ground state of the three-dimensional anisotropic harmonic oscillator.

Write down the eigenfunction of the ground state of the three-dimensional anisotropic harmonic oscillator.

Using this three-dimensional oscillator <u>as a model for the vibrations of a polyatomic molecule</u>, *derive the number of distinct frequencies that could be observed as infrared transitions of such an oscillator, specifying the attributes that are required for such observations.*

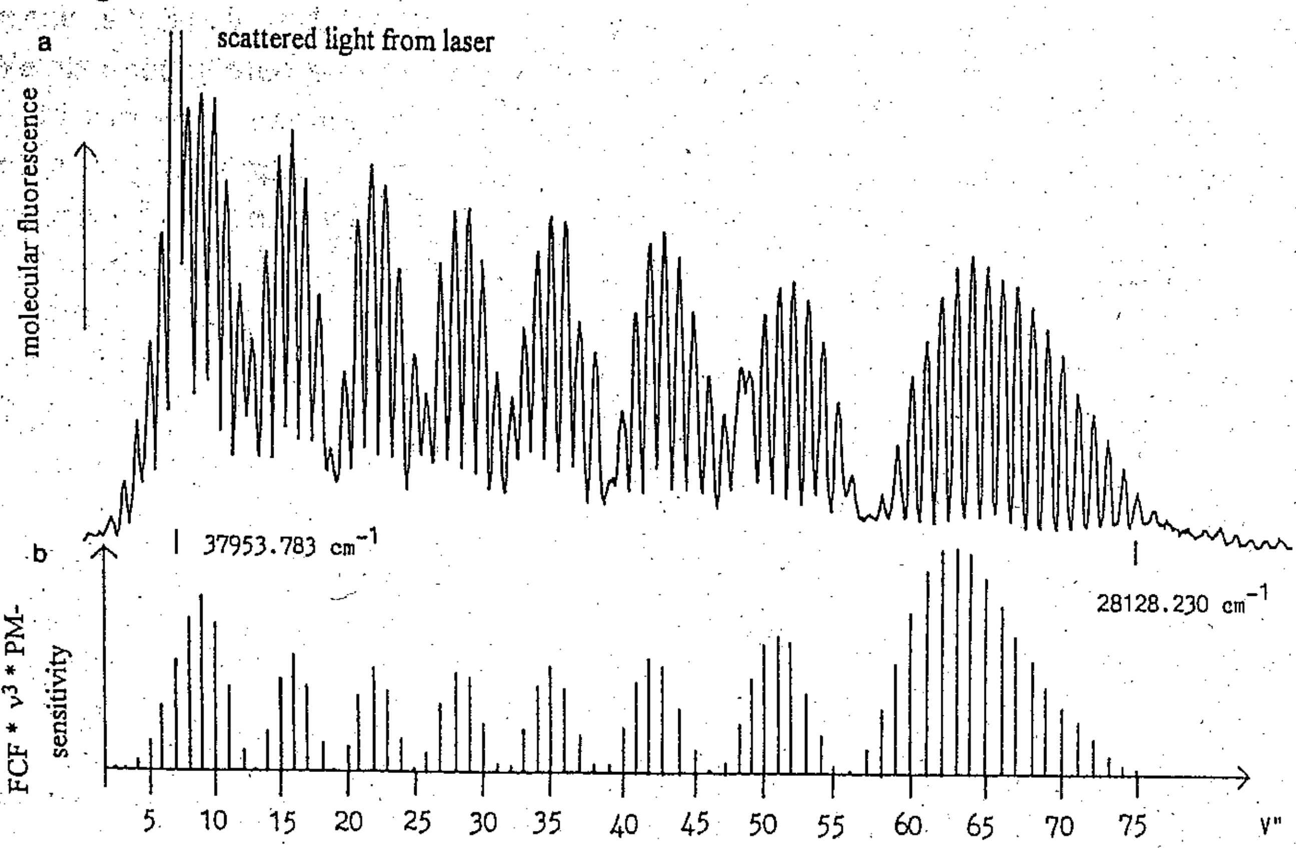
5. Interstellar molecules that have been detected by their radiofrequency or millimeter wave spectra are given below:

Diatomics	OH, CO, CN, CS, SiO, SO, SiS, NO, NS, CH, CH^-
Triatomics	H_2O, HCN, HNC, OCS, H_2S, N_2H^+, SO_2, HNO, C_2H, HCO, HCO^+, HCS^+
Tetratomics	NH_3, H_2CO, HNCO, H_2CS, HNCS, N≡C-C≡C, H_3O^+
5-atomics	HCOOH, CH_2=NH, NH_2CN,N≡C-C≡CH
6-atomics	CH_3OH, CH_3CN, etc.
9-atomics	CH_3OCH_3, CH_3CH_2OH, N≡C-C≡C-C≡C-C≡CH

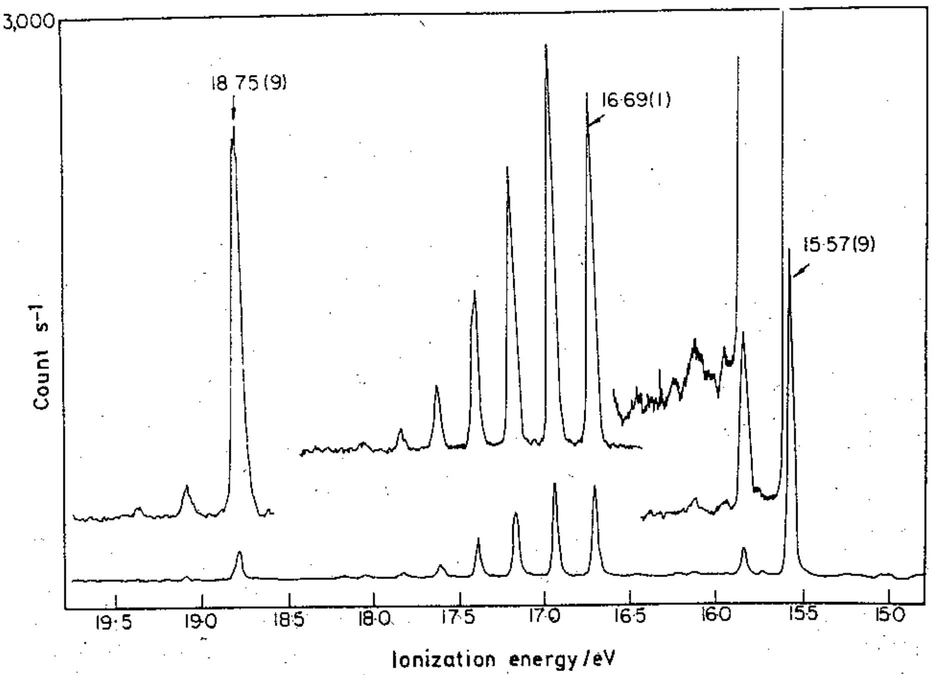
Some of them were actually found in the interstellar medium before they were searched for and found in the laboratory. In all molecules, except OH and NH_3, the transitions observed are rotational in nature.

There is known to be large quantities of H_2 and no doubt there are such molecules as C_2, N_2, O_2, HC≡CH and polyacetylenes to be found in the interstellar clouds, yet they are not listed in this table. *Explain why, from first principles.*

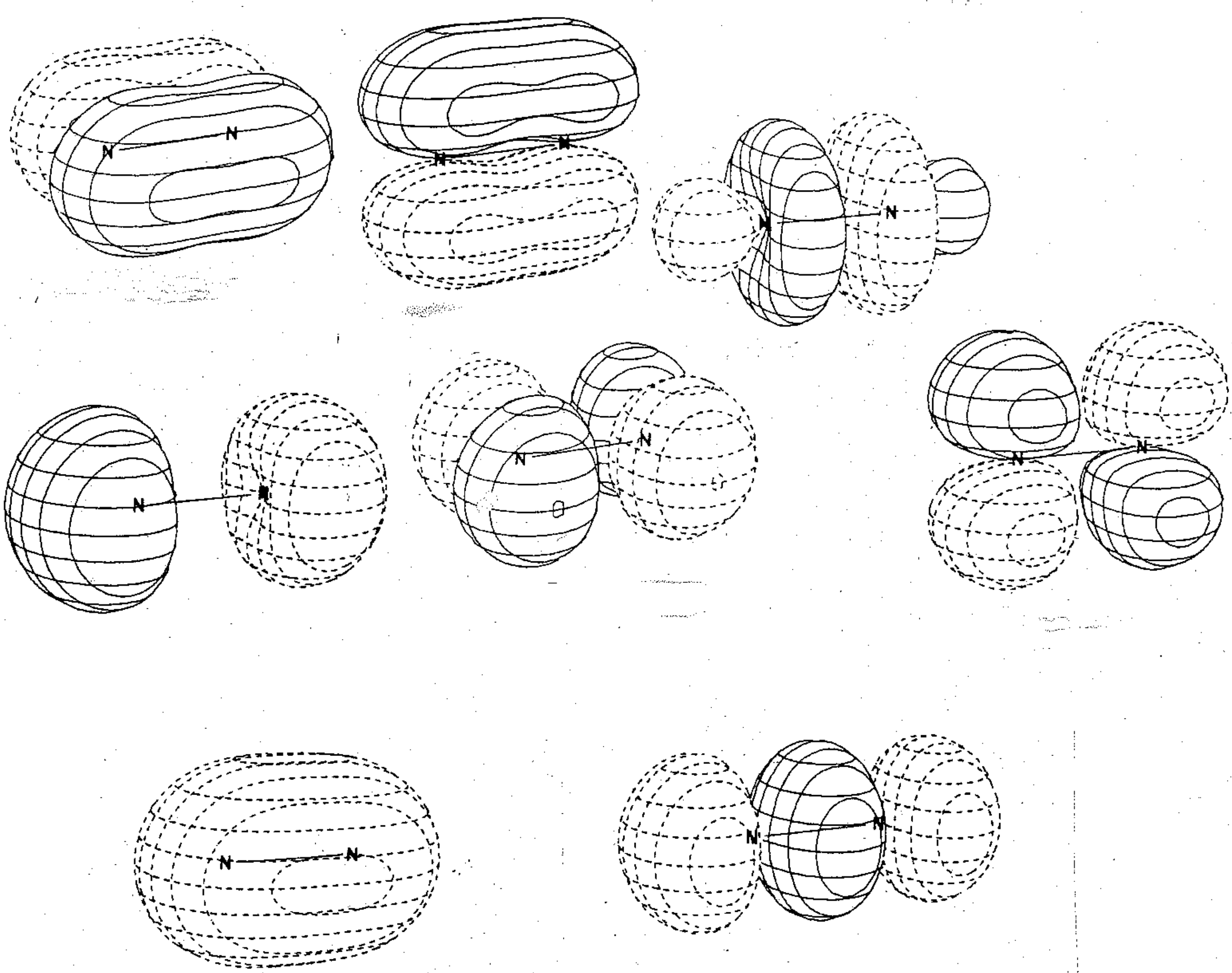
6. Alkali halides are highly ionic diatomic molecules. Very little was known about the covalent states of the alkali halides until laser spectroscopy gave some detailed information about the crossing of the ionic potential M^+X^- with some of the covalent states that asymptotically lead to neutral M and X atoms. A newly discovered excited covalent state is found to be consistent with dissociation into an excited K(...4p) and ground I(...5p5) neutral atoms. The <u>emission spectrum</u> from a specific v' level of this excited state of KI, that was reached by a 37953.783 cm^{-1} laser line in this experiment, is shown in the figure below, together with the simulation. For the ground state and the new excited covalent state, a complete analysis of the spectra (including J-resolved lines not shown here) leads to a set of spectroscopic constants that could be deduced by fitting energy differences between the states to the observed line frequencies. [e.g., The ground state of KI has a harmonic frequency that is 186.294 cm^{-1}.] For such an analysis, a provisional assignment in v′ was required. The authors had no difficulties in making this provisional assignment from the figure below. *From the observed spectrum, deduce the specific v′ level of this excited state of KI from which the emission in the figure was observed.* It is worth remembering that the intensities in emission have a cubic dependence on frequency. *Explain* your answer with the help of sketches of energy level diagrams.



7. The <u>lowest</u> ionization energy of N_2 molecule (15.58 eV) corresponds to removal of an electron from the outermost $\sigma_g 2p$ molecular orbital. The <u>second</u> (16.69 eV) and <u>third</u> (18.76 eV) lowest correspond to removal from $\pi_u 2p$ and $\sigma_u{}^*2s$ respectively. The ultraviolet photoelectron spectrum and the molecular orbitals of N_2 are shown below: ***By drawing connecting lines, associate each of the three sets of bands in the photoelectron spectrum with the molecular orbital from which the electron has been removed.***



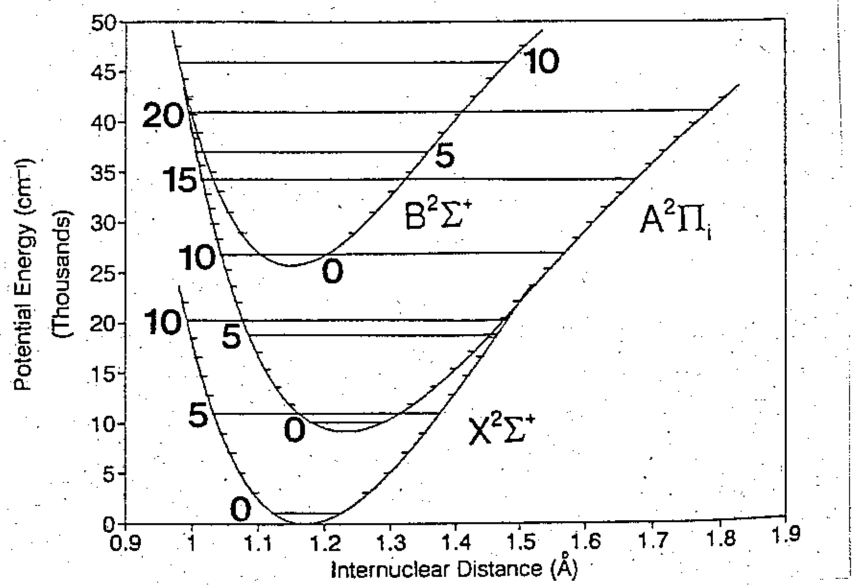
3,000
18.75(9)
16.69(1)
15.57(9)
Count s⁻¹
19.5
19.0
18.5
18.0
17.5
17.0
16.5
16.0
15.5
15.0
Ionization energy /eV



N

8. CN molecules are found in many extraterrestrial sources such as the Sun, stellar atmospheres, comets, and interstellar clouds by the techniques of microwave, infrared and ultraviolet spectroscopy.

The red system of CN ($A^2\Pi \leftrightarrow$ ground $X^2\Sigma^+$) is observed in emission from comets and in absorption in carbon stars and the Sun. The violet system ($B^2\Sigma^+ \leftrightarrow$ ground $X^2\Sigma^+$) has also been observed in the laboratory by Bernath in the University of Waterloo. The potential energy functions for these mentioned states are shown below from their paper in J. Mol. Spectroscopy, 156, 327 (1992):



From these potentials, *predict the band structure (approximate frequencies and intensities) of the red system and of the violet system of CN.*

red system bands	violet system bands

red system bands explanation	violet system bands explanation

In doing the complete analysis of excited electronic state properties, it is usually necessary to use other parts of the electromagnetic spectrum to help provide spectroscopic constants for the ground state. Can this be done for CN molecule? *Which spectroscopic constants describing the ground electronic state of CN can be obtained from which region of the electromagnetic spectrum and how? To answer, in each case, sketch a spectrum and indicate which constants correspond to which spacings.*

(1) region of electromagnetic spectrum:	(2) region of electromagnetic spectrum:

9. *Show* whether it is theoretically possible to simultaneously know the following quantities:

(a) The position and the linear momentum of a particle along the same direction in any physical system.

(b) The energy and the z component of the angular momentum of the particle in the system of Problem 2.

(c) The x position and the linear momentum along the y direction of the physical system in Problem 4.

10. Most empirical trends predicted from the Periodic Table can be predicted or explained by using the central field approximation for many-electron atoms. From a Chemistry 112 Final exam comes the following set of questions:

Problem:

(a) For each of the following properties that can be predicted from the Periodic Table, identify the trend (choose: increases, decreases, or is not systematic) and choose the most appropriate explanation(s) based on electronic configurations of the atoms (choose as many as appropriate from A,B,C,D, E):

Properties	Trend	Expln	Possible explanations
1. The first ionization energy of the atom _____ with increasing atomic number within each row (period)			A. The principal quantum number of the outermost electrons are increasing, with a corresponding increase in average distance from the nucleus
2. The first ionization energy of the atom _______ with increasing atomic number within each column (group)			B. The inner core electrons largely shield the outermost electrons from the nucleus so the effective nuclear charge seen by the outermost electrons is not varying greatly.
3. The atomic radius _______ with increasing atomic number within each row			C. As each additional electron is added to the electron configuration, the charge on the nucleus increases by one also. Because of the imperfect shielding by other electrons within the same shell, each addition leads to a net increase in the effective nuclear charge seen by the electrons within that shell.
4. The atomic and ionic radius ________with increasing atomic number within each group, but the rate of change is less after the third row.			D. Filling of the d subshells
5. The electron affinity _____ with increasing atomic number within each period with the major exception being the noble gas atoms			E. Electrons in inner shells are closer to the nucleus, on the average and more strongly bound than valence electrons.

(b) The following properties change in a way that can be predicted from the positions of the atoms in the Periodic Table. Identify the change (choose increases, decreases, or is not systematic) and choose which of the trends 1,2,3,4,5 (more than one may apply) from part (a) above are most closely associated with or responsible for the change.

Properties	Change (increases, decreases, is not systematic)	which of 1,2,3,4,5?
1. The metallic character of the elements of group 2A _______ with increasing atomic number.		
2. The shortest cation-anion distances in LiF, NaF, KF, RbF, CsF ______ with increasing atomic number.		
3. The lattice energy of the chlorides of the alkaline earths ______ with increasing atomic number.		
4. The polarity of the bond to hydrogen _______ in going from Be-H, to B-H, to C-H, to N-H, to O-H, to F-H		
5. The melting point of the solid elements of group 6A ______ with increasing atomic number.		
6. The density of the solid elements of the halogen group ______ with increasing atomic number.		

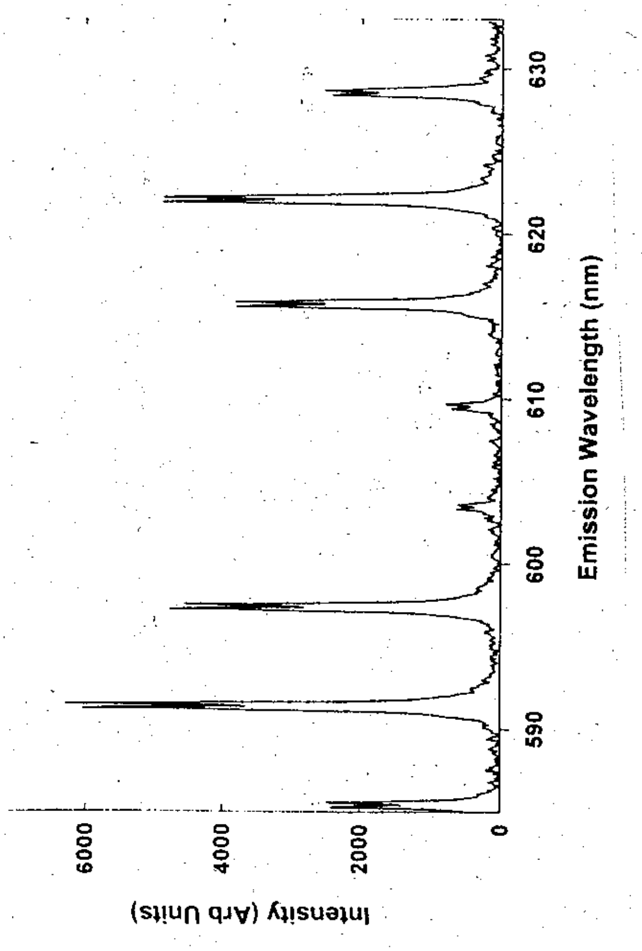
Answer the above questions, in the spaces provided, just as the Chemistry 112 student is instructed. Now, as a **Chemistry 344** student, *derive the very first trend [from part (a)] for the second row, using as examples the B and C atoms*. You may use *Slater's rules* given at the end of this exam.

The quantum numbers n, l, m_l, m_s that are strictly valid for the hydrogen atom only from solving the Schrödinger equation exactly, have been used by many a Chemistry 112 student to write electronic configurations for the ground states of the atoms. ***Demonstrate the nature of the approximation that could permit the quantum numbers l and m_l to arise for a many-electron atom*** despite the electron-electron repulsion terms in the energy.

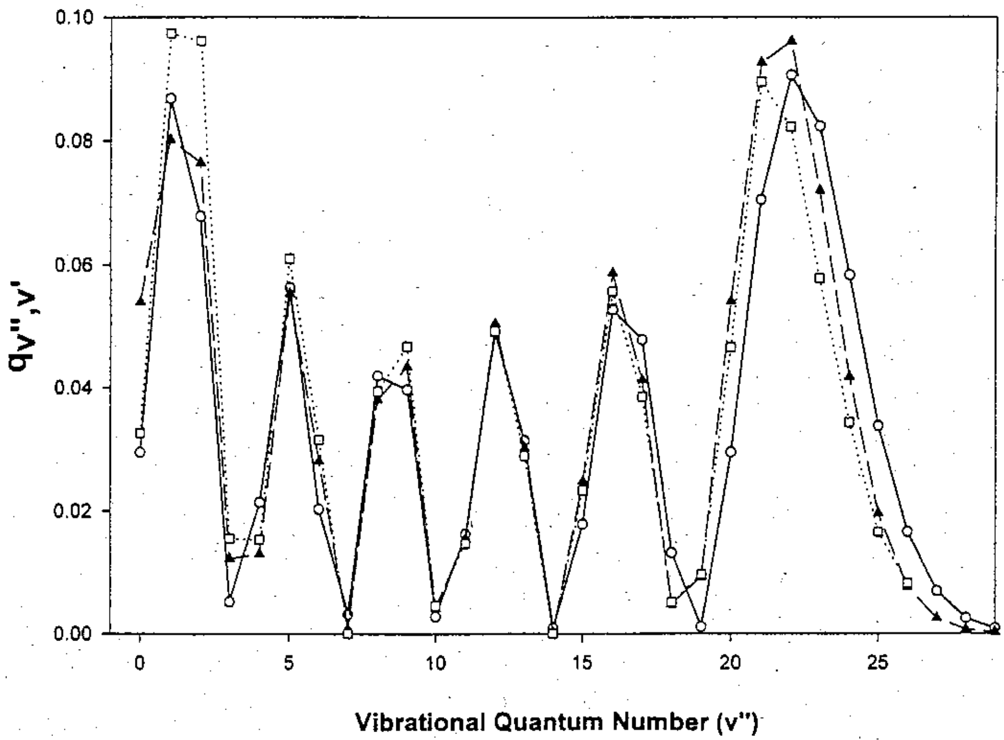
The electronic configuration learned in Chemistry 112 is an oversimplification. *Describe the ways in which the $1s^2 2s^2 2p^4$ description of the electronic ground state of the oxygen atom is incorrect or incomplete.*

The atomic radius (and the ionic radius) is an empirical quantity obtained from lattice parameters of the solid element or its compounds. *Provide a quantum-mechanical description that relates to the empirical concept of atomic radius.* For simplicity, consider the atomic radii of the rare gas elements as your example.

11. The Bi_2 spectrum obtained from the paper in Journal of Molecular Spectroscopy vol. 194, 1-7 (1999). is the subject of this problem:
The emission (fluorescence) spectrum of the Bi_2 molecule that has been prepared in the v' = 3 vibrational level of the excited state studied in this paper, is shown below. In order to show all the observed bands in the range 5800 to 6300 Å in this figure, the spectrum is displayed such that the P and R branches do not appear individually resolved, although the spectra were actually recorded for a wide range ($0 < J < 211$) of rotational levels. *Draw a set of ground and excited state potential surfaces that are consistent with the intensities of the v' = 3 → v" = 6 to 13 transitions displayed here.* Hint: The ground state is a stable diatomic molecule with a harmonic frequency of about 170 cm^{-1} and the excited state has a harmonic frequency of 132.38 cm^{-1}. *Assign* the peaks shown.



The paper also provides in the figure below the values of $|\int \Psi_{v'}(x)^{*}\Psi_{v''}(x)dx|^2$ from v' = 5 as experimentally observed (·····), compared with various calculated values (□○▲) also shown in the figure below:



Explain this figure, with the help of sketches of vibrational wavefunctions for v' and v". In other words, predict a figure that looks just like this, that would be the outcome starting from some reasonable description of the upper and ground electronic states.

List of possibly useful integrals that will be provided with each exam

$\int \sin(ax)dx = -(1/a)\cos(ax)$

$\int \cos(ax)dx = (1/a)\sin(ax)$

$\int \sin^2(ax)dx = ½\, x -(1/4a)\sin(2ax)$

$\int \cos^2(ax)dx = ½\, x +(1/4a)\sin(2ax)$

$\int \sin(ax)\sin(bx)dx = [1/2(a-b)]\sin[(a-b)x)] - [1/2(a+b)]\sin[(a+b)x)],\quad a^2 \neq b^2$

$\int \cos(ax)\cos(bx)dx = [1/2(a-b)]\sin[(a-b)x)] + [1/2(a+b)]\sin[(a+b)x)],\quad a^2 \neq b^2$

$\int x \sin(ax)dx = (1/a^2)\sin(ax) - (x/a)\cos(ax)$

$\int x \cos(ax)dx = (1/a^2)\cos(ax) + (x/a)\sin(ax)$

$\int x^2 \cos(ax)dx = [(a^2x^2 - 2)/a^3]\sin(ax) + 2x\cos(ax)/a^2$

$\int x^2 \sin(ax)dx = -[(a^2x^2 - 2)/a^3]\cos(ax) + 2x\sin(ax)/a^2$

$\int x \sin^2(ax)dx = x^2/4 - x\sin(2ax)/4a - \cos(2ax)/8a^2$

$\int x^2 \sin^2(ax)dx = x^3/6 -[x^2/4a - 1/8a^3]\sin(2ax) - x\cos(2ax)/4a^2$

$\int x \cos^2(ax)dx = x^2/4 + x\sin(2ax)/4a + \cos(2ax)/8a^2$

$\int x^2 \cos^2(ax)dx = x^3/6 +[x^2/4a - 1/8a^3]\sin(2ax) + x\cos(2ax)/4a^2$

$\int x \exp(ax)dx = \exp(ax)\,(ax-1)/a^2$

$\int x \exp(-ax)dx = \exp(-ax)\,(-ax-1)/a^2$

$\int x^2 \exp(ax)dx = \exp(ax)\,[x^2/a - 2x/a^2 + 2/a^3]$

$\int x^m \exp(ax)dx = \exp(ax) \sum_{r=0 \text{ to } m} (-1)^r\, m!x^{m-r}/(m-r)!a^{r+1}$

$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1}$ $\quad a > 0$, n positive integer

$\int_0^\infty x^2 \exp(-ax^2)dx = (1/4a)(\pi/a)^{½}$ $\quad a > 0$

$\int_0^\infty x^{2n} \exp(-ax^2)dx = (1\cdot3\cdot5\cdot\ldots\cdot(2n-1)/(2^{n+1}a^n)(\pi/a)^{½}$ $\quad a > 0$

$\int_0^\infty x^{2n+1} \exp(-ax^2)dx = n!/2a^{n+1}$ $\quad a > 0$, n positive integer

$\int_0^\infty \exp(-a^2x^2)dx = (1/2a)\,(\pi)^{½}$ $\quad a > 0$

$\int_0^\infty \exp(-ax)\cos(bx)dx = a/(a^2+b^2)$ $\quad a > 0$

$\int_0^\infty \exp(-ax)\sin(bx)dx = b/(a^2+b^2)$ $\quad a > 0$

$\int_0^\infty x\exp(-ax)\sin(bx)dx = 2ab/(a^2+b^2)^2$ $\quad a > 0$

$\int_0^\infty x\exp(-ax)\cos(bx)dx = (a^2-b^2)/(a^2+b^2)^2$ $\quad a > 0$

$\int_0^\infty \exp(-a^2x^2)\cos(bx)dx = [(\pi)^{½}/2a]\cdot\exp[-b^2/4a^2]$ $\quad ab \neq 0$

PERIODIC TABLE OF THE ELEMENTS

- Metals
- Semimetals
- Nonmetals

Transition elements: groups between II and III

I	II											III	IV	V	VI	VII	VIII
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (268)	110 Uun (269)	111 Uuu (272)	112 Uub (277)						

Lanthanide series

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04

Actinide series

89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (241)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)

ADDITIONAL INFORMATION

$a_0 = (\hbar^2/m_e e^2)$ the "Bohr radius", 0.529177×10^{-10} m
$(e^2/2a_0) = 13.6057$ eV one rydberg, a unit of energy = (1/2) hartree
c = frequency•wavelength = 2.997924×10^{10} cm sec^{-1} the speed of light
1 eV = 8065.6 cm^{-1}

Slater's rules for finding the screening :

1. For an electron in the same 1s orbital as the electron of interest $s_{1s} = 0.30$
2. For electrons with $n > 1$ and $\ell = 0, 1$

$$s_{n\ell} = 0.35k_{same} + 0.85k_{in} + 1.00k_{inner}$$

where

k_{same} = number of other electrons in the same shell as the screened electron of interest

k_{in} = number of electrons in the shell with principal quantum number n-1

k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For 3d electrons

$$s_{3d} = 0.35k_{3d} + 1.00k_{in}$$

where

k_{3d} = number of 3d electrons

k_{in} = number of electrons with $n \leq 3$ and $\ell < 2$

$$E = U_\alpha(R_e) + (v+\tfrac{1}{2})\nu_e - x_e\nu_e\,(v+\tfrac{1}{2})^2 + y_e\nu_e\,(v+\tfrac{1}{2})^3 + B_eJ(J+1) - D_e[J(J+1)]^2 - \alpha_e(v+\tfrac{1}{2})J(J+1) + Y_{00}$$

where all spectroscopic quantities are expressed in energy units (or the corresponding frequency or wavenumbers). In energy units, the following are positive quantities:

$B_e \equiv \hbar^2 / 2\mu\, R_e^2$ — B_e rotational constant

$$h x_e\nu_e \equiv \tfrac{1}{4}\, B_e^2/(h\nu_e)^2 \cdot \{\, (^{10}/_3)B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 - U^{iv}(R_e)R_e^4 \,\}$$

$x_e\nu_e$ anharmonicity constant

$D_e \equiv 4\, B_e^3/(h\nu_e)^2$

D_e centrifugal distortion constant

$$\alpha_e \equiv -\,2\, B_e^2/h\nu_e \cdot \{3 + 2\, B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2\,\}$$

α_e vibrational rotational coupling constant

$$Y_{00} \equiv B_e^2/16(h\nu_e)^2 \cdot \{\, U^{iv}(R_e)R_e^4 - (^{14}/_9)B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 \,\}$$

$h\nu_e \equiv (h/2\pi)[\, U''(R_e)/\mu\,]^{1/2}$ — ν_e harmonic frequency

μ reduced mass $1/\mu = 1/m_A + 1/m_B$

R_e equilibrium bond length

Rotational constant for the v<u>th</u> vibrational state is B_v

$$B_v = B_e - \alpha_e\,(v+\tfrac{1}{2})$$

Y_{00} same anharmonic correction to <u>every</u> vibrational level

Since Y_{00} is a constant for the electronic state, it is usually put together with $U(R_e)$.