*Name*____________________________________

Chemistry 344

Final Exam *ANSWERS*
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 the given problem, 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 in a 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.*

$\{ - (\hbar^2/2M)\, d^2/dz^2 + Mgz\}\Psi(z) = E\, \Psi(z)$

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

$\Psi(z)$ must be single-valued, continuous and finite, and its first derivatives also continutous and finite. Since $V(z) = \infty$ for $z < 0$, then $\Psi(z < 0) = 0$. This means that one boundary condition is that $\Psi(z = 0) = 0$ in order for the wavefunction to be single-valued and continuous. A second boundary condition is that $\Psi(z\rightarrow\infty) = 0$, that is, we must have a finite wavefunction.

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!*

The wavefunction that describes the state of a system must be single valued. Since the position on the circle corresponding to a value of ϕ is the same point that corresponds to $\phi + 2\pi$, and $\phi + 4\pi$, etc. then

$\Psi_k(\phi) = (1/\sqrt{2\pi})\exp[-ik\phi]$ must equal $(1/\sqrt{2\pi})\exp[-ik(\phi+ 2\pi)]$

or $\exp[-ik\phi] = \exp[-ik(\phi+ 2\pi)] = \exp[-ik\phi]\bullet\exp[-ik2\pi)]$

Thus, the condition that has to be satisfied is that $\exp[-ik2\pi)] = 1$

Since $\exp[-ix] \equiv \cos x - i\sin x$

$\exp[-ik2\pi)] = \cos k2\pi - i\sin k2\pi$ must equal 1

This can only be satisfied if $\cos k2\pi = 1$ and also $\sin k2\pi = 0$, conditions that are satisfied by $k = 0$ or $k =$ any integer, positive or negative. Thus, we find that the single-valued condition for the wavefunction can be satisfied only by

$k = 0, \pm 1, \pm 2, \pm 3, \ldots$

(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.*

The possible outcomes of measurements of the z component of the angular momentum are the eigenvalues of L_z .

Since $L_z = (\hbar/i)(d/d\phi)$ commutes with $\mathcal{H} = -(\hbar^2/2MR^2)\, d^2/d\phi^2$, then the eigenfunctions of $\mathcal{H}$ are also the set of eigenfunctions for L_z.

So let us use those functions to find the eigenvalues of L_z.:

$L_z \Psi_k(\phi) = (1/\sqrt{2\pi})\exp[-ik\phi] = (\hbar/i)\, d/d\phi\, (1/\sqrt{2\pi})\exp[-ik\phi]$

$= (\hbar/i)\,(1/\sqrt{2\pi})\,(d/d\phi)\exp[-ik\phi] = (\hbar/i)\,(1/\sqrt{2\pi})\,(-ik)\exp[-ik\phi]$

$= (-\hbar k)\,(1/\sqrt{2\pi})\exp[-ik\phi] = (-\hbar k)\,\Psi_k(\phi)$

Thus, the possible outcomes of measurements of the z component of the angular momentum, the eigenvalues of L_z, are $-\hbar k$, that is, the possible outcomes are

$0\hbar, \mp 1\hbar, \mp 2\hbar, \mp 3\hbar, \ldots$

Aside: Note that the results of having the wavefunction be either $(1/\sqrt{2\pi})\exp[ik\phi]$ or $(1/\sqrt{2\pi})\exp[-ik\phi]$ are the same! When calculating any average values with these wavefunctions, we use $\Psi_k^*(\phi)$ and $\Psi_k(\phi)$ together. Thus, for average values, the results are not changed at all whether we choose to have the wavefunctions be the set of functions $\{ (1/\sqrt{2\pi})\exp[ik\phi] \}$ or the set $\{ (1/\sqrt{2\pi})\exp[-ik\phi] \}$.

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:
$F(\phi)$ is not one of the eigenfunctions given in Prob. 2 Expand $F(\phi)$ in terms of the complete orthonormal set of functions $(1/\sqrt{2\pi})\exp[ik\phi]$. $F(\phi) = \sum_k c_k \Psi_k(\phi)$ and find the coefficients: $c_k = \int_0^{2\pi} \Psi_k^*(\phi)\, F(\phi)\, d\phi = \int_0^{2\pi} \Psi_k^*(\phi) A\{\cos 2\phi + 2\cos 3\phi\}\, d\phi$ Since we can write $\cos 2\phi = \frac{1}{2}[\exp(i2\phi) + \exp(-i2\phi)]$ and $\cos 3\phi = \frac{1}{2}[\exp(i3\phi) + \exp(-i3\phi)]$, then $c_k = \int_0^{2\pi} \Psi_k^*(\phi)\frac{1}{2}A\{\exp(i2\phi)+\exp(-i2\phi)+2\exp(i3\phi)+2\exp(-i3\phi)\}\, d\phi$ $c_k = (1/\sqrt{2\pi})^{-1}\frac{1}{2}A \int_0^{2\pi} \Psi_k^*(\phi)\{\Psi_2(\phi) + \Psi_{-2}(\phi) + 2\Psi_3(\phi) + 2\Psi_{-3}(\phi)\}\, d\phi$ $c_k = (1/\sqrt{2\pi})^{-1}\frac{1}{2}A\, \{\delta_{k,2} + \delta_{k,-2} + 2\delta_{k,3} + 2\delta_{k,-3}\}$ in shorthand where $\delta_{k,2} = 1$ if k=2 or else it is zero, since it was an orthonormal set A can be obtained by integration $\int_0^{2\pi} F^*(\phi)F(\phi)\, d\phi$: $A = [5\pi]^{-\frac{1}{2}}$ $c_k = (10)^{-\frac{1}{2}}\{\delta_{k,2} + \delta_{k,-2} + 2\delta_{k,3} + 2\delta_{k,-3}\}$ $c_2^2 = c_{-2}^2 = (1/10)$ $c_3^2 = c_{-3}^2 = (4/10)$	$2\hbar$ $-2\hbar$ $3\hbar$ $3\hbar$ $3\hbar$ $3\hbar$ $-3\hbar$ $-3\hbar$ $-3\hbar$ $-3\hbar$ Average = $0\hbar$

(b) The energy of the system is measured

Derivation of predictions here:	Observed values here:
The average value is obtained by $\int_0^{2\pi} F^*(\phi)\, (L_z \text{ or } \mathcal{H})\, F(\phi)\, d\phi$: which by above algebra leads to $\sum_k c_k^2 \bullet k\hbar$ or $\sum_k c_k^2 \bullet k^2(\hbar^2/2MR^2)$ The observed values should be 10% of the time the eigenvalue for k=2, 10% of the time the eigenvalue for k=-2, 40% of the time the eigenvalue for k=3, 40% of the time the eigenvalue for k=-3, according to the probabilities given by the corresponding c_k^2	$2^2\,(\hbar^2/2MR^2)$ $(-2)^2(\hbar^2/2MR^2)$ $3^2\,(\hbar^2/2MR^2)$ $3^2\,(\hbar^2/2MR^2)$ $3^2\,(\hbar^2/2MR^2)$ $3^2\,(\hbar^2/2MR^2)$ $(-3)^2(\hbar^2/2MR^2)$ $(-3)^2(\hbar^2/2MR^2)$ $(-3)^2(\hbar^2/2MR^2)$ $(-3)^2(\hbar^2/2MR^2)$ Average = $8\,(\hbar^2/2MR^2)$

4., The eigenvalues of a linear (one-dimensional) harmonic oscillator are known:
$\mathcal{H}(x)\,\varphi(x) = E\,\varphi(x)$
where $\mathcal{H}(x) = -(\hbar^2/2M)\, d^2/dx^2 + \tfrac{1}{2}\kappa x^2$
where M is the mass of the oscillator, and κ is the Hooke's law force constant.
That is, $\{-(\hbar^2/2M)\, d^2/dx^2 + \tfrac{1}{2}\kappa x^2\}\,\varphi(x) = (n+\tfrac{1}{2})\hbar\omega\,\varphi(x)$ where $n = 0, 1, 2, 3, \ldots$
A linear harmonic oscillator in its ground state is described by the normalized function
$\varphi(x) = [2\,\omega M/h]^{1/4} \exp[-\omega M x^2/2\hbar]$
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., $V = \tfrac{1}{2}[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]$
[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).

$$\{-(\hbar^2/2M)[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2] + \tfrac{1}{2}[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]\}\Psi(x,y,z) = E\,\Psi(x,y,z)$$

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.]

Use separation of variables:
Let $\Psi(x,y,z) = P(x)\bullet Q(y)\bullet R(z)$, substitute it into the Schr. equation:

$$\{-(\hbar^2/2M)[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2] + \tfrac{1}{2}[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2]\}\, P(x)\bullet Q(y)\bullet R(z) = E\, P(x)\bullet Q(y)\bullet R(z)$$

Then divide both sides of the equation by $P(x)\bullet Q(y)\bullet R(z)$ to get

$$\frac{[-(\hbar^2/2M)\partial^2/\partial x^2 + \tfrac{1}{2}\kappa_x x^2]\,P(x)}{P(x)} + \frac{[-(\hbar^2/2M)\partial^2/\partial y^2 + \tfrac{1}{2}\kappa_y y^2]\,Q(y)}{Q(y)} + \frac{[-(\hbar^2/2M)\partial^2/\partial z^2 + \tfrac{1}{2}\kappa_z z^2]\,R(z)}{R(z)} = E$$

Since each term involves only x or only y or only z, then each must be equal to a constant and the sum of the constants must equl the eigenvalue E
Therefore we find that we have to solve 3 equations, one in x, one in y, one in z.

$$[-(\hbar^2/2M)\partial^2/\partial x^2 + \tfrac{1}{2}\,\kappa_x\, x^2]\, P(x) = e\, P(x)$$

and the others look just like this except in the variables y and z.
We already have the eigenfunctions and eigenvalues of the x equation:

$\varphi(x)$ and energies are $(n + \tfrac{1}{2})\hbar\omega$

Since the y and z equations are analogous then we know those eigenfuncitons and energies as well. We need the x, y, z subscripts to identify the various quantum numbers and harmonic frequencies which are different from each other (since $\kappa_x \neq \kappa_y \neq \kappa_z$) :

$E = (n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z$

$\Psi(x,y,z) = \varphi(x)\bullet \varphi(y)\bullet \varphi(z)$

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

$E = (n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z$ are the general eigenvalues of this system where $n_x = 0,1,2,3,4 \ldots$ $n_y = 0,1,2,3,4 \ldots$ $n_z = 0,1,2,3,4 \ldots$

Ground state $E = (0 + \tfrac{1}{2})\hbar\omega_x + (0 + \tfrac{1}{2})\hbar\omega_y + (0 + \tfrac{1}{2})\hbar\omega_z$

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

$$\Psi(x,y,z) = \varphi(x)\bullet \varphi(y) \bullet\varphi(z)$$
$$= [2\omega_x M/h]^{1/4}\exp[-\omega_x M x^2/2\hbar]\bullet[2\omega_y M/h]^{1/4}\exp[-\omega_y M y^2/2\hbar]$$
$$\bullet\ [2\omega_z M/h]^{1/4}\exp[-\omega_z M z^2/2\hbar]$$

Using this three-dimensional oscillator as a model for the vibrations of a polyatomic molecule, *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.*

Three fundamental frequencies ω_x ω_y ω_z will be observed in the infrared, provided that $(\partial\mu/\partial x)_{x=0}$ and $(\partial\mu/\partial y)_{y=0}$ and $(\partial\mu/\partial z)_{z=0}$ are non-zero .

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

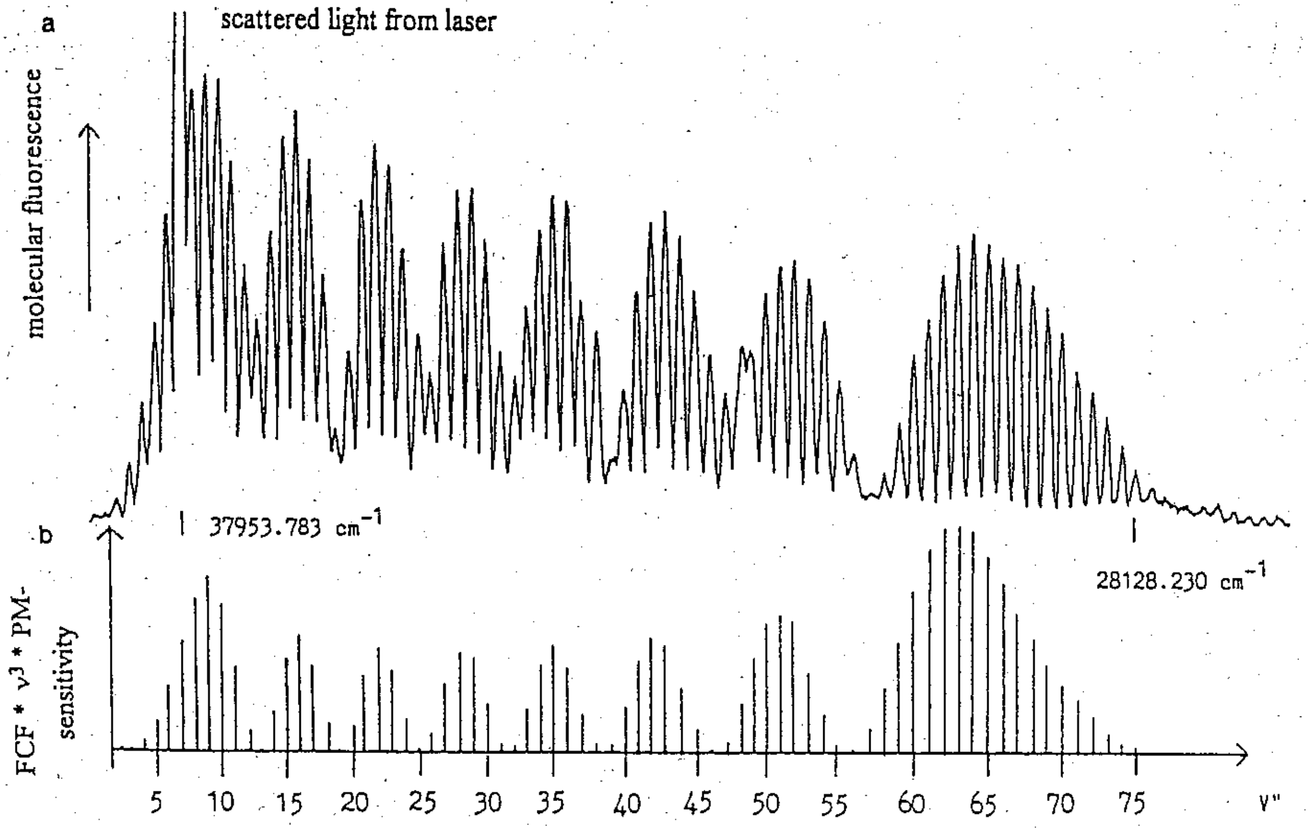
Some of them were actually found in the interstellar medium before they were searched for and found in the laboratory. In all molecules, except OH and NH_3, the transitions observed are rotational in nature.

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.*

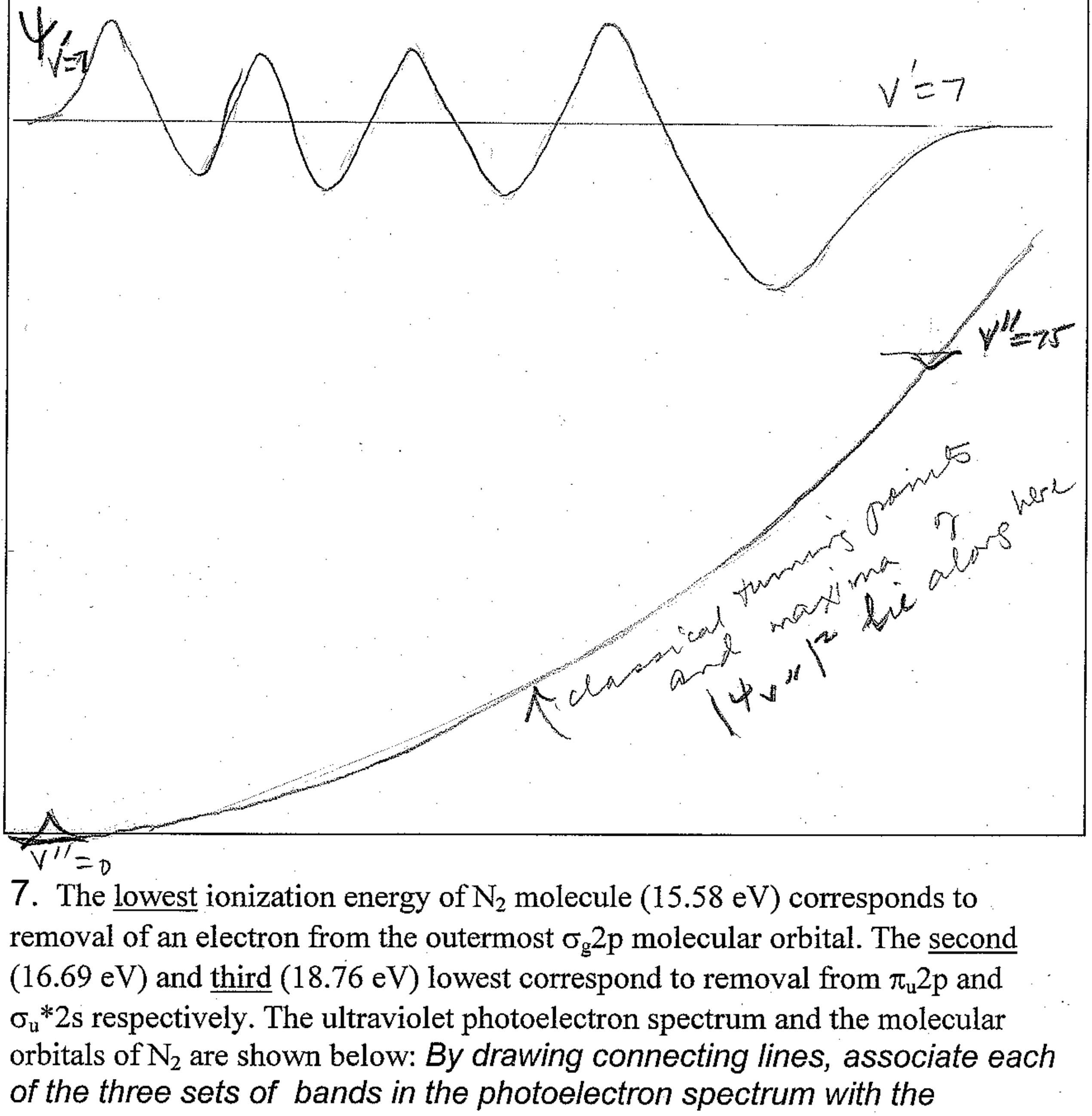
The probability that a transition will be observed within the <u>same</u> electronic state and the <u>same</u> vibrational state, changing only rotational states is given by $\iint \psi^*_{elec}\psi^*_{v}\left[\mu(R_e)+\left(\frac{d\mu}{dR}\right)_{R_e}(R-R_e)+\frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{R_e}(R-R_e)^2\right]\psi_{elec}\psi_{vib}$.

$\cdot \int Y^*_{J'M'}(\theta,\phi)\begin{pmatrix}\sin\theta\cos\phi\\ \text{or}\\ \sin\theta\sin\phi\\ \text{or}\\ \cos\theta\end{pmatrix}Y_{J''M'}(\theta,\phi)\sin\theta\, d\theta\, d\phi$. <u>Pure</u> rotational transitions, only the first term $\mu(R_e)$ survives. So if $\mu(R_e)$ is zero no pure rotational spectra can be observed. H_2 C_2 N_2 O_2 HCCH all have zero dipolemoment therefore can not be observed in pure rotation.

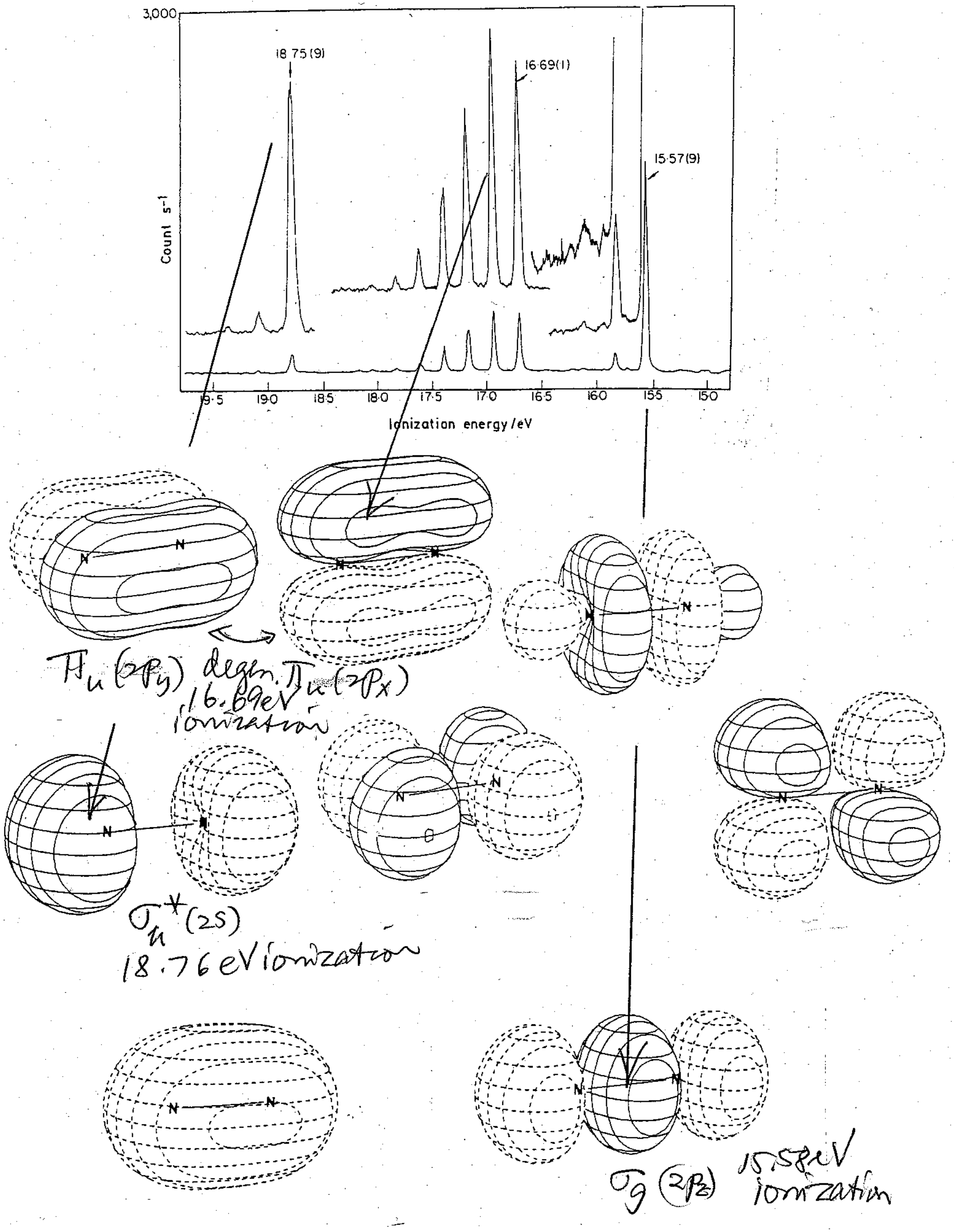
6. Alkali halides are highly ionic diatomic molecules. Very little was known about the covalent states of the alkali halides until laser spectroscopy gave some detailed information about the crossing of the ionic potential M^+X^- with some of the covalent states that asymptotically lead to neutral M 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.



The spectrum shows that from $v''=4$ to $v''=75$, electronic transitions occurred between the unknown v' state of the upper electronic state to these various v'' levels of the ground electronic state. The shape of the envelope is an image of the $\psi_{v'}^{*}\psi_{v'}$ of the unknown state simply because such a large number of v'' levels were favorable in overlapping with it. Thus v' must have 7 nodes, that is, $v'=7$.



7. The lowest ionization energy of N_2 molecule (15.58 eV) corresponds to removal of an electron from the outermost $\sigma_g 2p$ molecular orbital. The second (16.69 eV) and third (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.*



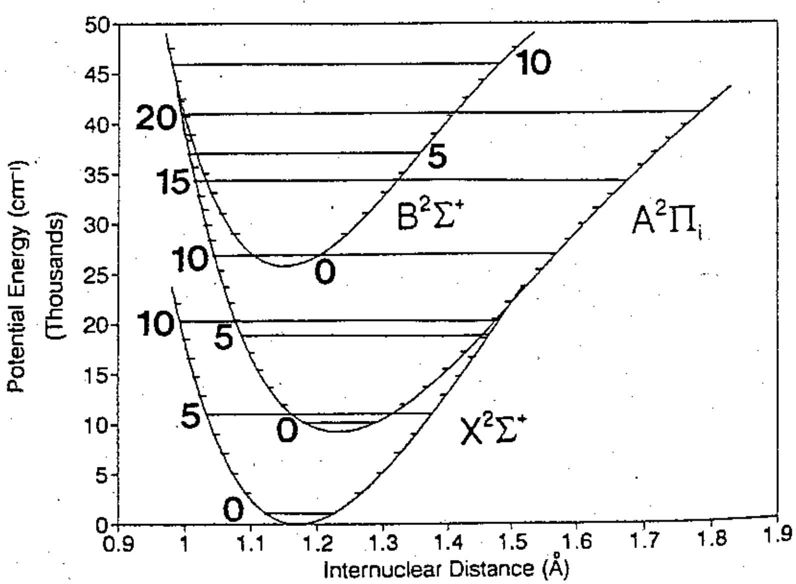
$\Pi_u(2p_y)$ degen. $\Pi_u(2p_x)$
16.69eV
ionization

$\sigma_u^*(2s)$
18.76 eV ionization

$\sigma_g(2p_z)$ 15.58eV
ionization

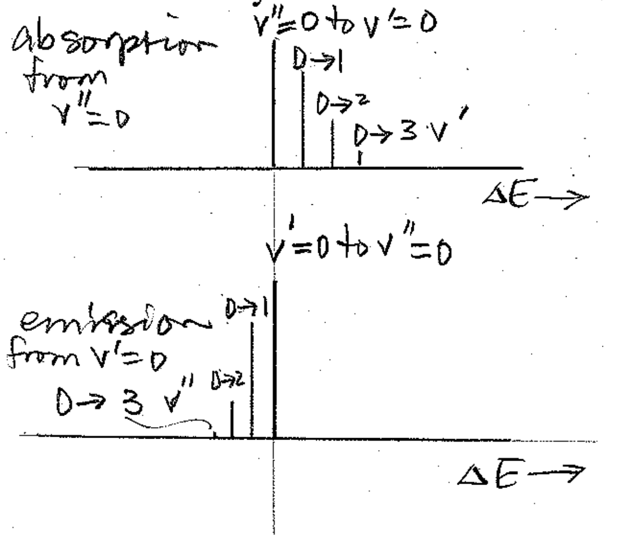
8. CN molecules are found in many extraterrestrial sources such as the Sun, stellar atmospheres, comets, and interstellar clouds by the techniques of microwave, infrared and ultraviolet spectroscopy.

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):

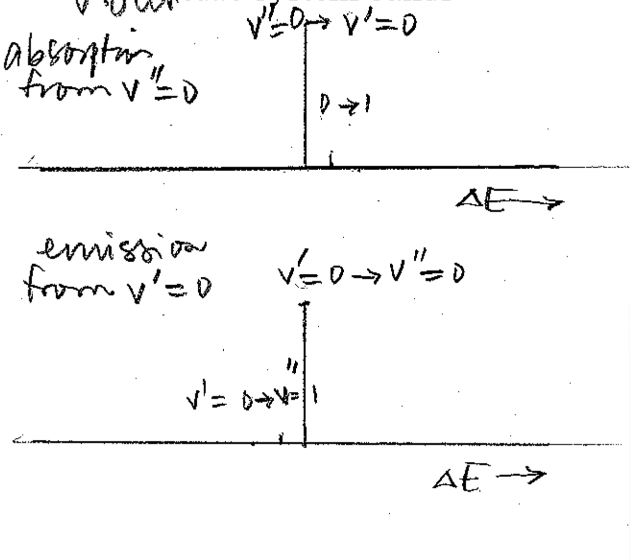


From these potentials, *predict the band structure (approximate frequencies and intensities) of the red system and of the ~~blue~~ violet system of CN.*

red system bands



violet ~~blue~~ system bands



Transitions have to be vertical (no change in R of nuclei)

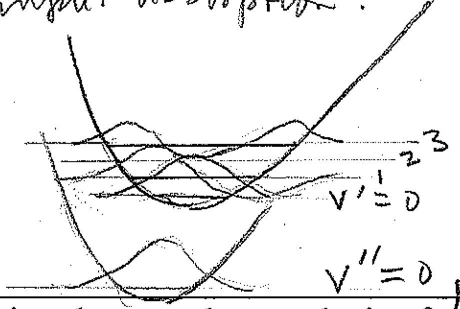
red system bands explanation

overlap $\int_{-\infty}^{+\infty}\psi_{v'}^{*}\psi_{v''}\,dx$ is maximum for 0-0

only a bit less for 0-1

less again for 0-2

Example: absorption:



only v'' = 0 is populated

violet system bands explanation

superior overlap for 0-0

much smaller for 0-1, 0-2 etc

Example: absorption

$\int_{-\infty}^{+\infty}\psi_{v'}^{*}\psi_{v''}\,dx$

Re nearly identical

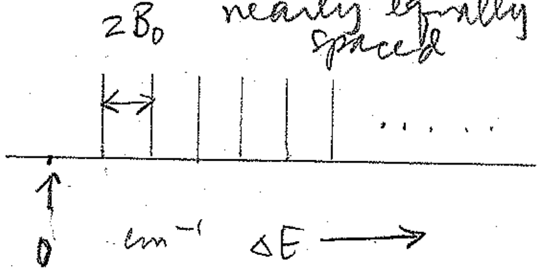
In doing the complete analysis of excited electronic state properties, it is usually necessary to use other parts of the electromagnetic spectrum to help provide spectroscopic constants for the ground state. Can this be done for CN molecule? *Which spectroscopic constants describing the ground electronic 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:

microwave

pure rotational transitions

provides $B_0 = B_e - \frac{1}{2}\alpha_e$



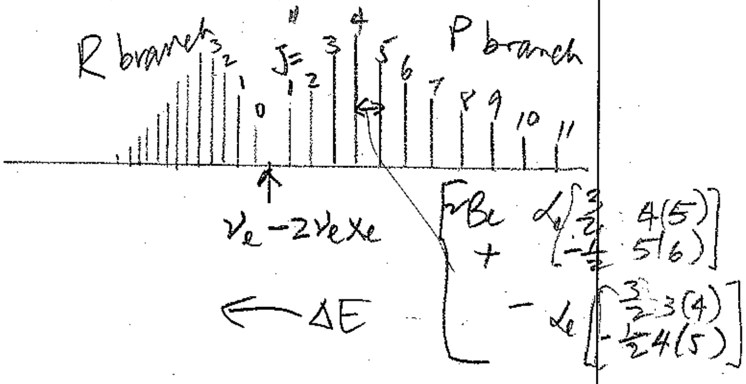
(2) region of electromagnetic spectrum:

infrared

vibrational transition

accompanied by

rotational transitions



Provides α_e, B_e and

$(\nu_e - 2\nu_e x_e)$

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.

The product of the standard deviations is ≥ 0 if the two operators commute. If that is the case then, $\sigma_A \cdot \sigma_B \geq 0$, =zero is a possibility and it is theoretically possible to simultaneously know the two quantities. Therefore we just need to evaluate the commutator $[A, B]$ in each case:

$$\left[\frac{\hbar}{i}\frac{\partial}{\partial x}, x\right]\psi = \frac{\hbar}{i}\frac{\partial}{\partial x}(x\psi) - x\frac{\hbar}{i}\frac{\partial \psi}{\partial x} = \frac{\hbar}{i}\frac{\partial \psi}{\partial x}\cdot x + \frac{\hbar}{i}\psi\overset{1}{\overset{\parallel}{\frac{\partial x}{\partial x}}} - x\frac{\hbar}{i}\frac{\partial \psi}{\partial x}$$

$$\left[\frac{\hbar}{i}\frac{\partial}{\partial x}, x\right] = \frac{\hbar}{i}$$ do not commute

NOT possible to know both p_x and x

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

$$\left[\frac{\hbar}{i}\frac{\partial}{\partial \phi}, \frac{-\hbar^2}{2MR^2}\frac{\partial^2}{\partial \phi^2}\right] = 0$$ since both $L_z\mathcal{H}$ and $\mathcal{H}L_z$ give $\frac{\partial^3}{\partial \phi^3}$

They commute

YES it is possible to know both at the same time.

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

$$\left[x, \frac{\hbar}{i}\frac{\partial}{\partial y}\right]\psi = x\frac{\hbar}{i}\frac{\partial \psi}{\partial y} - \frac{\hbar}{i}\frac{\partial (x\psi)}{\partial y} = x\frac{\hbar}{i}\frac{\partial \psi}{\partial y} - \frac{\hbar}{i}\frac{\partial \psi}{\partial y} + 0$$

$$= 0$$

They commute

YES it is possible to know both at the same time.

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
1. The first ionization energy of the atom _____ with increasing atomic number within each row (period)	increases	B,C
2. The first ionization energy of the atom _______ with increasing atomic number within each column (group)	decreases	A
3. The atomic radius _______ with increasing atomic number within each row	decreases	C
4. The atomic and ionic radius ________with increasing atomic number within each group, but the rate of change is less after the third row.	increases	A,D
5. The electron affinity _____ with increasing atomic number within each period with the major exception being the noble gas atoms	increases	C

Possible explanations

A. The principal quantum number of the outermost electrons are increasing, with a corresponding increase in average distance from the nucleus

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.

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.

D. Filling of the d subshells

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.	increases	2
2. The shortest cation-anion distances in LiF, NaF, KF, RbF, CsF ______ with increasing atomic number.	increases	4
3. The lattice energy of the chlorides of the alkaline earths ______ with increasing atomic number.	decreases	4
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	increases	5
5. The melting point of the solid elements of group 6A ______ with increasing atomic number.	increases	4
6. The density of the solid elements of the halogen group ______ with increasing atomic number.	increases	4

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.

$Z=5 \quad 1s^2 2s^2 2p^1 \quad E_{atom} = -\left[\frac{(5-0.3)^2}{1^2}\cdot 2 + \frac{(5-2\times0.35-2\times0.85)^2}{2^2}\cdot 3\right]\frac{e^2}{2a_0}$

$1s^2 2s^2 \quad E_{+ion} = -\left[\frac{(5-0.3)^2}{1^2}\cdot 2 + \frac{(5-0.35-2\times0.85)^2}{2^2}\cdot 2\right]\frac{e^2}{2a_0}$

$I.E. = E_{+ion} - E_{atom} = -\left[\frac{3(5-2\times0.35-2\times0.85)^2 - 2(5-0.35-2\times0.85)^2}{2^2}\right]\frac{e^2}{2a_0}$

$= +\frac{2.875}{4}(13.6\ eV) = 9.775\ eV$

$$C: \; Z=6 \quad 1s^2 2s^2 2p^2 \quad E_{atom} = -\left[\frac{(6-0.3)^2}{1^2}\cdot 2 + 4\cdot\frac{(6-\overset{-2\times .85}{3\times .35})^2}{2^2}\right]\frac{e^2}{2a_0}$$

$$1s^2 2s^2 2p^1 \quad E_{+ion} = -\left[\frac{(6-0.3)^2}{1^2}\cdot 2 + 3\cdot\frac{(6-\overset{-2\times .85}{2\times .35})^2}{2^2}\right]\frac{e^2}{2a_0}$$

$$I.E. = E_{+ion} - E_{atom} = -\left[\frac{4\,(6-2.75)^2 - 3\,(6-2.4)^2}{2^2}\right]\frac{e^2}{2a_0}$$

$$= +\frac{3.37}{4}\,(13.6\,eV) = 11.458\,eV$$

First I.E. of C is greater than that of B

And if we were to do the entire row, the trend of increasing ionization energy with increasing atomic number within a row of the Periodic Table would be found.

The quantum numbers *n, l, m*

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.

When a central field approximation is used, the $\left[\frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \dots + \frac{e^2}{r_{23}} + \frac{e^2}{r_{24}} + \dots\right]$ repulsive terms are replaced by an average function $V_{rep}(r_1) + V_{rep}(r_2) + V_{rep}(r_3) + V_{rep}(r_4) + \dots$ each one of which depends on the wavefunction (orbital) used to describe each of the other $N-1$ electrons. When this is done the hamiltonian becomes separable into N one-electron hamiltonians and each one becomes solvable in the exact same way as the H atom problem, except for the last step, that is, the solution of the r-dependence. Thus, the θ and ϕ parts separate out in exactly the same way as in the H atom leading to $Y_{lm}(\theta,\phi)$ the same eigenfunctions of the angular part, with the quantum numbers l and m_l.

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.*

A central field approximation has been used so as to lead to <u>orbitals</u>, that is, one-electron wavefunctions. By eliminating the position-explicit dependence of the Coulomb repulsion terms and replacing them with a central field term, the separation into individual one-electron problems become possible. Also the electronic config. as such does not include the antisymmetric nature of the total wavefunction with respect to interchange of any two electrons (fermions). Another approximation is the neglect of spin angular momentum coupling with orbital angular momentum.

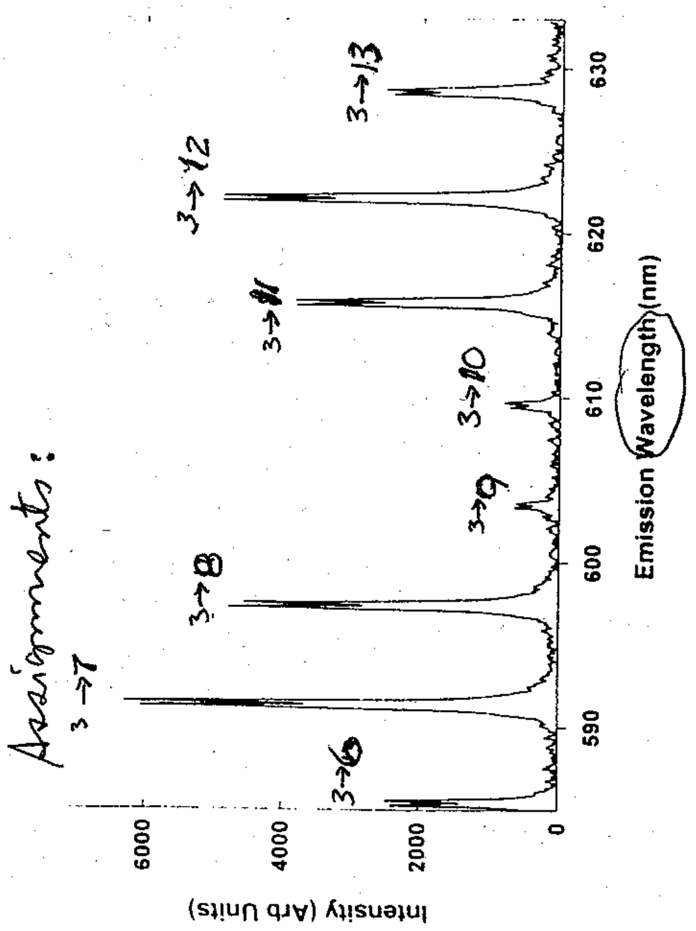
The atomic radius (and the ionic radius) is an empirical quantity obtained from lattice parameters of the solid element or its compounds. *Provide a quantum-mechanical description that relates to the empirical concept of atomic radius.* For simplicity, consider the atomic radii of the rare gas elements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

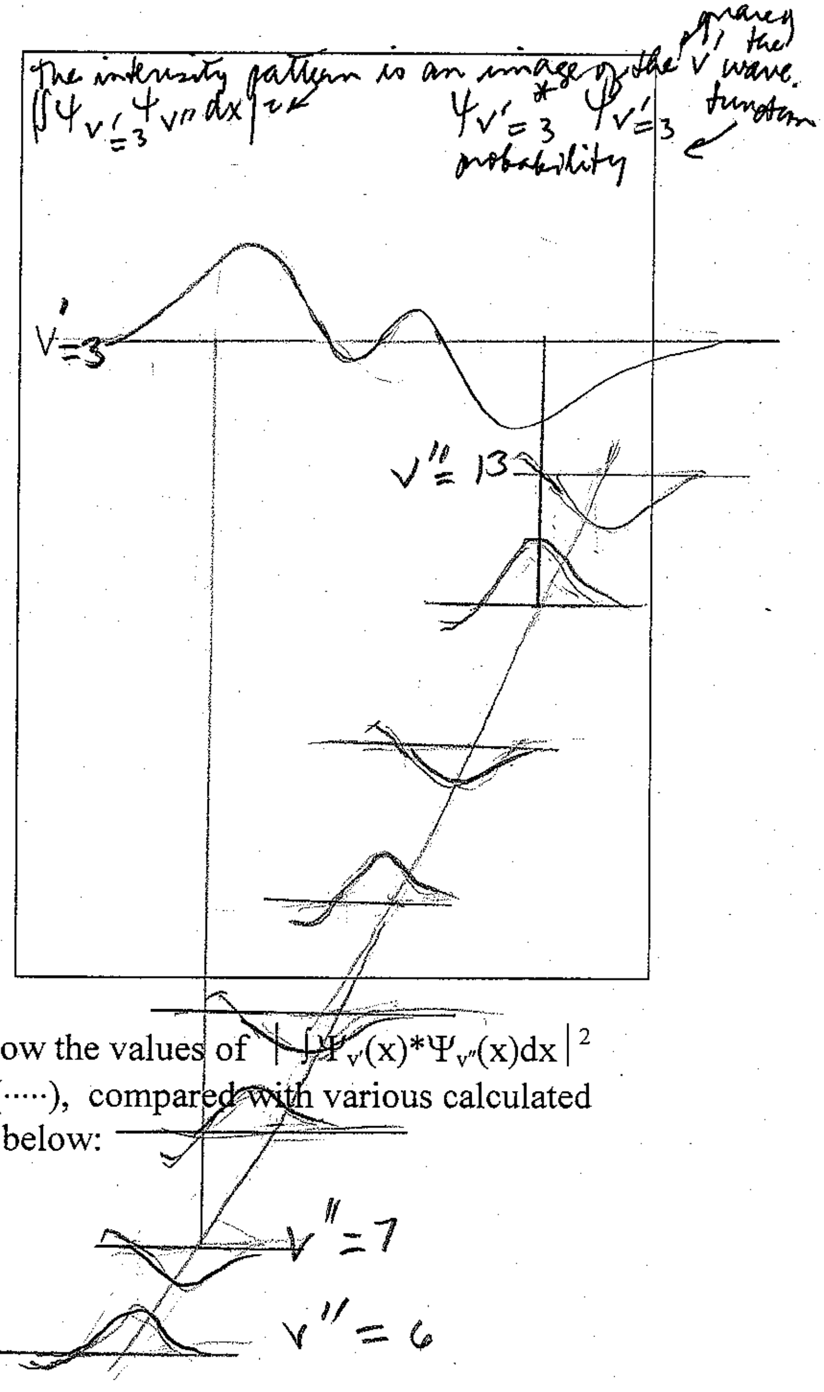
The probability of finding an electron within a distance r_a of the nucleus in a one-electron atom is given by the integral

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{0}^{r_a} \psi^*_{(r,\theta,\phi)}\psi(r,\theta,\phi)\, r^2 dr \sin\theta\, d\theta\, d\phi \qquad (1)$$

In terms of a central field approximation, for a many-electron atom, the core orbitals have much smaller values of $\langle r\rangle = \int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} \psi^* r \psi\, r^2 dr \sin\theta\, d\theta\, d\phi$. Thus, we should be looking at the valence orbitals. One possible definition of an atomic radius is to find the r_a value such that integral (1) for the core orbitals $= 0.95$, for 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}.



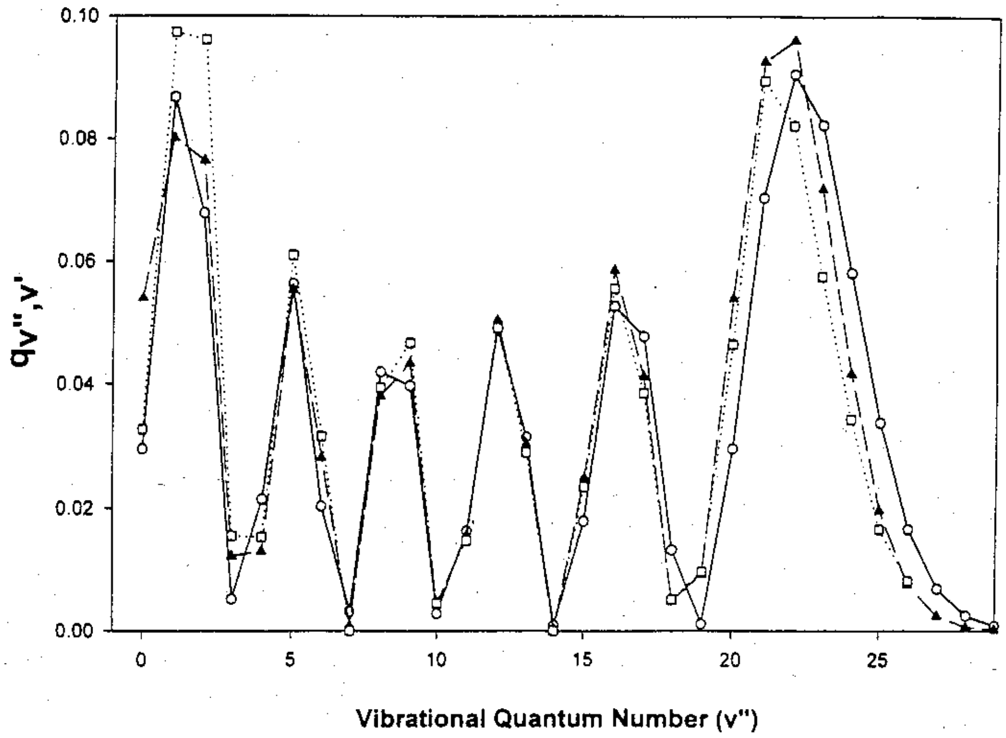


The intensity pattern is an image of the squares the v' wave. function

$|\int \psi_{v'=3}\psi_{v''}dx|^2$

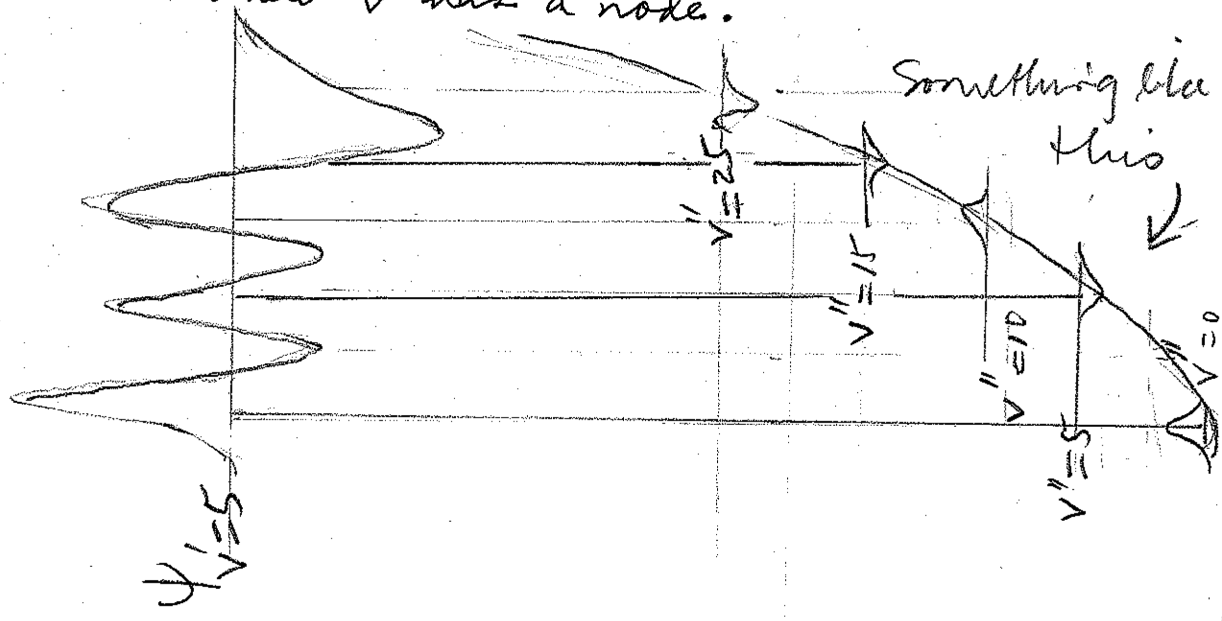
$\psi_{v'=3}^{*}\psi_{v'=3}$ probability

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.

v' = 5 has 5 nodes and it is quite clear from the above figure that the intensity given by $\left|\int \psi_{v'}(x)^* \psi_{v''}(x)dx\right|^2$ has very small (nearly zero) intensities at 5 frequencies which correspond roughly to v" = 4, 7, 10, 14, 19. These lower vibrational states have maxima in their wavefunctions where v' has a node.



Something like this