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Advance P. Chem. Problems (I) Populations, Partition Functions, Particle in Box, Harmonic Oscillators, Angular Momentum and Rigid Rotor

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Problems for the Advanced Physical Chemistry Student
Part 1, Populations, Partition Functions, Particle in a Box, Harmonic Oscillators, Angular Momentum and the Rigid Rotor

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I. SYNOPSIS

This is a set of problems that were used near the turn of the century and which will be lost when the web site they were on disappears with my demise. Because these problems are being taken from the web and are being edited, their statements and the hints/answers offered are subject to the typical editorial errors that ensue when such work is undertaken in the vacuum of a non-teaching situation. Therefore, I claim any errors for myself, and hate to note that there most likely is no point in contacting me about them for obvious reasons.

II. POPULATIONS

1. Obtain a formula for the ratio of the number of harmonic oscillators expected to populate the n=1,J=2 state relative to the n=0,J=3 state.

Answer and/or Hint

We know that

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

for vibration, and

$$E_J = B * J * (J + 1)$$

so the number of oscillators in the higher energy state, (n=1,J=2) will be proportional to

$$\#_{n=1;J=2} \propto (2*2+1)e^{-\beta\left(\left(1+\frac{1}{2}\right)\hbar\omega + B*2*(2+1)\right)}$$

while the number of oscillators in the lower energy state, (n=0,J=3) will be proportional to

$$\#_{n=0;J=3} \propto (2*3+1)e^{-\beta\left(\left(0+\frac{1}{2}\right)\hbar\omega + B*3*(3+1)\right)}$$

(where $\beta = \frac{1}{kT}$, and remember the degeneracy, $2 * J + 1$) from which the answer follows.

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2. The rotational constant (B) for a certain molecule is 10.4 reciprocal centimeter (cm^{-1}). In a high resolution infra red absorption experiment, the intensity of the {n=0,J=1} to {n=1,J=2} transition had an intensity ratio of 0.7174 relative to that of the {n=0,J=2} to {n=1,J=3} transition. What was the temperature of the sample (in K)?

Answer and/or Hint

From the above problem, we have:

$$\frac{(1*2+1)e^{-\beta\left(\left(0+\frac{1}{2}\right)\hbar\omega + B*1*(1+1)\right)}}{(2*2+1)e^{-\beta\left(\left(0+\frac{1}{2}\right)\hbar\omega + B*2*(2+1)\right)}} = 0.7174$$

where $k = 1.38 \times 10^{-16} \frac{ergs}{K}$, and the conversion factor from cm^{-1} to $ergs$ is $1.986 \times 10^{-16} \frac{ergs}{cm^{-1}}$

Notice that ω is not given for this molecule [1] since it cancels (top and bottom). Solving for T is left as an exercise, but here is some Maple code which might help:

```
>   #temp
>   restart;
>   eqn1 := 3*exp(-10.4*1.986e(-16)*2
>   /(1.38e(-16)*T));
>   eqn2 := 5*exp(-10.4*1.986e(-16)*6
>   /(1.38e(-16)*T));
>   ratio := eqn1/eqn2;
>   solve(ratio=0.7174,T);
```

$$eqn1 := 3\,e^{\left(-\frac{29.93391305}{T}\right)}$$

$$eqn2 := 5\,e^{\left(-\frac{89.80173914}{T}\right)}$$

$$ratio := \frac{3\,e^{\left(-\frac{29.93391305}{T}\right)}}{5\,e^{\left(-\frac{89.80173914}{T}\right)}}$$

$$3xy.z$$

Smile; surely you didn't expect me to do all the work!

3. Obtain a formula for the ratio of the number of H atoms (free radicals) expected to populate the $n=2$

electronic state relative to the $n=1$ electronic state.

$$E_n = -\frac{Ry}{n^2}$$

Answer and/or Hint

We know that the population of a state will be proportional to a degeneracy times an exponential (of the energy/kT), i.e.,

$$\#_n \propto g_n e^{-\frac{E_n}{kT}}$$

and we have to figure out the degeneracy of the states we are dealing with.

For the $n = 1$ state, $g_1 = 2$, while for the $n = 2$ state, $g_2 = 8$. Thus, we have for the desired ratio:

$$\frac{8e^{-\frac{Ry}{2^2 kT}}}{2e^{-\frac{Ry}{1^2 kT}}}$$

4. Consider a system which has several energy levels as shown (see Figure 1). Use a unit system

$$k = 1.38 \times 10^{-16}\frac{ergs}{K} \times 5.04 \times 10^{15}\frac{cm^{-1}}{ergs}$$

and express energies in cm^{-1}. The diagram shows a doubly degenerate ground state, and 4 excited states. What is the numerical value of the partition function at the temperature corresponding to $kT = 10cm^{-1}$?

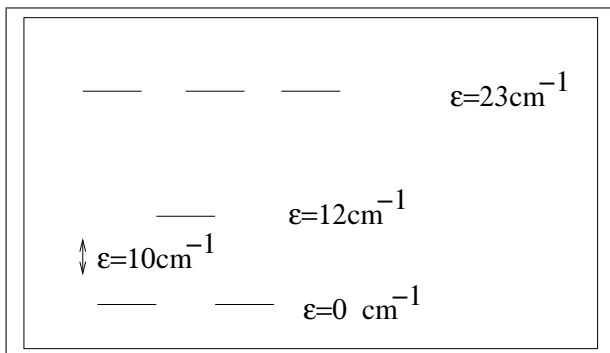FIG. 1: A make believe energy level scheme

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Answer and/or Hint

$$Z = 2*e^0 + e^{-\frac{12}{10}} + 3e^{-\frac{23}{10}}$$

which has to be numerically evaluated.

5. Considering the same energy level structure as in the above problem, Compute the thermodynamics (average) energy of the system at 350K. Report your answer in cm^{-1}.

Answer and/or Hint

We know that

$$k = 1.38 \times 10^{-16}\frac{ergs}{K} \times 5.04 \times 10^{15}\frac{cm^{-1}}{ergs} = 0.695\frac{cm^{-1}}{K}$$

so $350K$ is $0.695*350cm^{-1}$ which is $243.4cm^{-1}$. Then

$$E = \frac{12*e^{\frac{-12}{243.4}} + 3*23*e^{\frac{-23}{243.4}}}{2 + e^{\frac{-12}{243.4}} + 3*e^{\frac{-23}{243.4}}}$$

It is interesting, in this case, to plot the average energy as a function of temperature, to see that it rises from zero to a saturated, in a sense, value: It
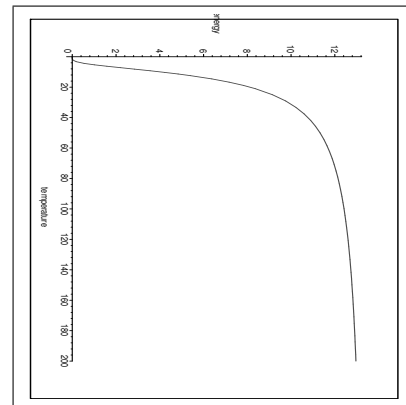
FIG. 2: The Thermodynamic Energy as a function of temperature for an artificial energy level scheme.

is also interesting to plot the heat capacity $\left(\frac{\partial E}{\partial T}\right)$ as a function of temperature, but this is left as an exercise for the "interested student".

One should verify that the Energy asymptotically approaches a fixed (and obtainable) value,

$$\lim_{T \to \infty} E =?$$

6. In the accompanying diagram, two electronic energy levels of a diatomic molecule are shown, and in balloons at the side, the appropriate vibrational

and rotational energy levels. If the rotational constant (B) is 6 cm^{-1}, calculate the ratio of the number of molecules expected in the $J = 2, n = 1$ state of the excited electronic state relative to the number of molecules expected in the $J = 1, n = 0$ state of the ground electronic state assuming a temperature of 1200K .
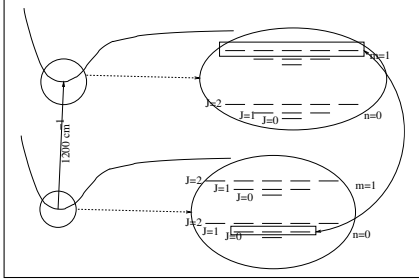

FIG. 3: Two electronic energy levels for a diatomic molecule undergoing vibration and rotation

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Answer and/or Hint

The upper state's population is proportional to

$$5e^{-\frac{1200+360*\left(1+\frac{1}{2}\right)+6*2*3}{kT}}$$

while the lower state's population is proportional to

$$3e^{-\frac{0+360*\left(0+\frac{1}{2}\right)+6*1*2}{kT}}$$

so the ratio will be

$$\frac{5e^{-\frac{1200+360*\left(1+\frac{1}{2}\right)+6*2*3}{kT}}}{3e^{-\frac{0+360*\left(0+\frac{1}{2}\right)+6*1*2}{kT}}}$$

III. SPECTROSCOPY

1. The spacing between adjacent microwave absorptions for the AlH molecule is 12.604 cm^{-1}. Calculate the internuclear distance in AlH. Assume the 27-isotope of Aluminum ($^{27}_{13}$Al) has mass 26.98 grams/mole, and the 1-isotope of H($^{1}_{1}$H) has mass 1.009 grams/mole. Give your answer in Angstrom (Å).

Answer and/or Hint

The rotational energy levels for a diatomic molecule whose internuclear distance is fixed is given by

$$E_J = \frac{\hbar^2}{2I}J(J+1)$$

and the selection rules say that $\Delta J = \pm 1$. For the $0 \rightarrow 1$ transition, for instance, the change in energy is

$$E_1 - E_0 = \frac{\hbar^2}{2I}1*2 - \frac{\hbar^2}{2I}0*1$$

while for the $1 \rightarrow 2$ transition, we would have

$$E_2 - E_1 = \frac{\hbar^2}{2I}2*3 - \frac{\hbar^2}{2I}1*2 = \frac{\hbar^2}{2I}(6-2) = 4\frac{\hbar^2}{2I}$$

The frequency of the first "line" cited above would be

$$\nu_{0\rightarrow 1} = \frac{2\frac{\hbar^2}{2I}}{h}$$

while that of the second "line" cited above would be

$$\nu_{1\rightarrow 2} = \frac{4\frac{\hbar^2}{2I}}{h}$$

so the difference in frequencies (the spacing between adjacent lines) of the two lines, which is given as 12.604 cm^{-1} in the statement of the problem, would be

$$\Delta\nu = \nu_{1\rightarrow 2} - \nu_{0\rightarrow 1} = \frac{2\frac{\hbar^2}{2I}}{h} = 12.604 cm^{-1}$$

Since the moment of inertia I is μr_{eq}^2 where μ is the reduced mass of the AlH molecule, we can, once all the units have been worked out, compute r_{eq}.

We would have

$$12.604 cm^{-1} = \frac{\hbar}{2\pi\mu r_{eq}^2}$$

which would be

$$12.604 cm^{-1} = \frac{\frac{6.62\times10^{-27} erg\ sec}{2\pi}}{2\pi\mu r_{eq}^2}$$

$$12.604 cm^{-1} \times c\frac{cm}{sec} = \frac{6.62 \times 10^{-27} dyne\ cm\ sec}{(2\pi)^2 \mu r_{eq}^2}$$

$$12.604 \cancel{cm^{-1}} \times 3 \times 10^{10} \frac{cm}{sec} = \frac{6.62 \times 10^{-27} \left(gram\ \frac{cm}{sec^2}\right) cm\ sec}{(2\pi)^2 \mu r_{eq}^2}$$

$$12.604 \times 3 \times 10^{10} \frac{1}{\cancel{sec}} = \frac{6.62 \times 10^{-27} gram\ \frac{cm^2}{\cancel{sec}}}{(2\pi)^2 \mu r_{eq}^2}$$

We now have

$$\mu r_{eq}^2 = \frac{12.604 \times 3 \times 10^{10} \times \pi^2}{6.627 \times 10^{-27}} gram\ cm^2$$

where

$$\frac{1}{\mu} = \left(\frac{1}{\frac{1.009}{6.023 \times 10^{23}}} + \frac{1}{\frac{26.98}{6.023 \times 10^{23}}}\right) \frac{1}{grams}$$

Note that this value is per molecule! The rest is arithmetic. But don't forget to convert your answer to Angstrom (Å).

2. If the internuclear distance in AlH is 1.66 Å, calculate the rate of rotation (in radians per second) of an AlH molecule when it is in the J=17 state, B = 6.302 cm^{-1}, which is 1.252×10^{-15} (in ergs). The moment of inertia for this molecule is $\sim 4.439 \times 10^{-40}$ (in $gram * cm^2$). Assume the 27-isotope of Aluminum, with mass 26.98 grams/mole, and the 1-isotope of H, mass 1.009 grams/mole (as above).

Answer and/or Hint

Here we need to first compute the energy (rotational) of this molecule, and then we need to remember that

$$E = \frac{1}{2} I \left(gram\ cm^2\right) \omega^2 \left(\frac{rad}{sec}\right)^2$$

from elementary physics. The units are

$$gram\ cm^2 \left(\frac{rad}{sec}\right)^2 = gram\ \frac{cm^2}{sec^2} = dyne\ cm = erg$$

But the energy, quantum mechanically, is

$$E = B(J)(J+1) = 6.302(17)(18)cm^{-1}$$

which needs to be converted to ergs. The conversion factor is $1.986 \times 10^{-16}(hc)$. We have

$$E = 6.302(17)(18)cm^{-1} \times 1.986 \times 10^{-16} \frac{ergs}{cm^{-1}}$$

This energy is $\frac{1}{2}I\omega^2$, and we can solve for ω.

3. In the far infrared, HCl absorbs at 83 cm^{-1}. It is known that the B_e value for this particular isotopic form of the molecule is about 10 cm^{-1}. What J value increased by one to give this transition?

Answer and/or Hint

We will have

$$10(J)(J+1) \rightarrow 10(J+1)(J+2) \rightarrow 83 cm^{-1}$$

i.e.,

$$83 = 10(J+1)(J+2) - 10(J)(J+1)$$

which is an equation solvable for J, i.e.,

$$\cancel{10J^2} + 3(J)(10) + 20 - \cancel{10J^2} - 10J = 83$$

i.e.,

$$20J + 20 = 83$$

Notice that the equation will give a fractional value for J, which means that we are going to have to figure out where the "error" is.

4. The force constant for $_1^1H_{17}^{35}Cl$ is 4.903×10^5 dynes/cm. How many vibrations per second does $_1^2D_{17}^{35}Cl$ make? Check that your answer is not in radians/sec.
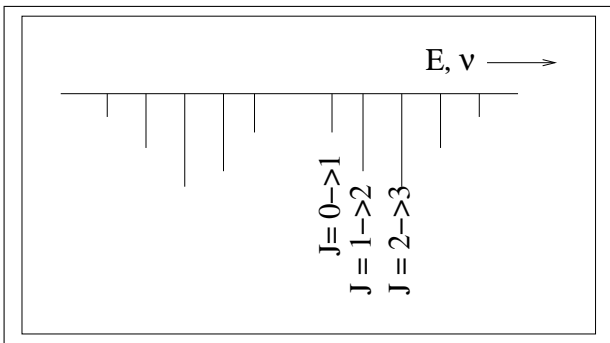
FIG. 4: The high resolution infra-red spectrum of a diatomic molecule. The hypothetical $J = 0 \rightarrow J = 0$ transition is the one used for the force constant computation.

FIG. 5: The Birge Sponer extrapolation.

Answer and/or Hint

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\left(\sqrt{\frac{\frac{dyne}{cm}}{gram}}\right)$$

where the units work out to be

$$\sqrt{\frac{gram\,\frac{\not{cm}}{sec^2}}{\frac{\not{cm}}{gram}}}$$

so

$$\sqrt{\frac{\not{gram}\,\frac{1}{sec^2}}{\not{gram}}}$$

i.e., sec^{-1} and

$$\frac{1}{\mu} \sim \frac{1}{\frac{2}{6.023\times10^{23}}} + \frac{1}{\frac{35}{6.023\times10^{23}}}$$

We know the force constant k, we know the reduced mass, μ, and we can therefore obtain the frequency of vibration ν.

n''	$\nu(cm^{-1})$	$\Delta\nu(cm^{-1})$
22	25419	
		90
23	25509	
		85
24	25694	
		80
25	25774	
		75
26	25849	
		70
27	25919	

5. The Birge Sponer extrapolation procedure is employed in the P. Chem. Lab, traditionally, for analyzing the visual spectrum of iodine, which is usually obtained at high resolution in absorption. Since this is the only example of this procedure one is likely to see, it has remained mysterious to generations of students. This made up example should clear up the situation. For a certain molecule, the following electronic transitions have been observed:
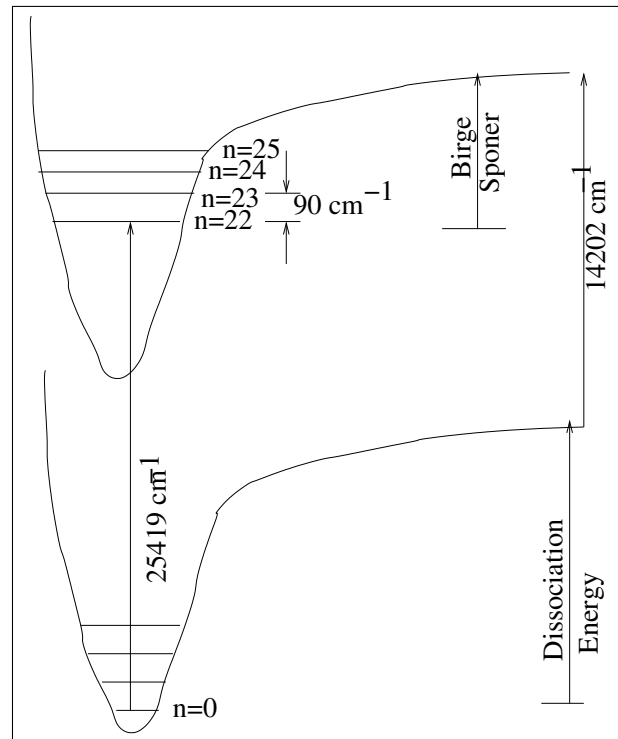
Answer and/or Hint

The Birge Sponer extrapolation is a specialized computation for diatomic molecule energy levels which, given all the information shown in Figure 5, allows one to compute the Dissociation Energy approximately.

From Figure 6 we can, assuming the trend continues, determine the equation of the line
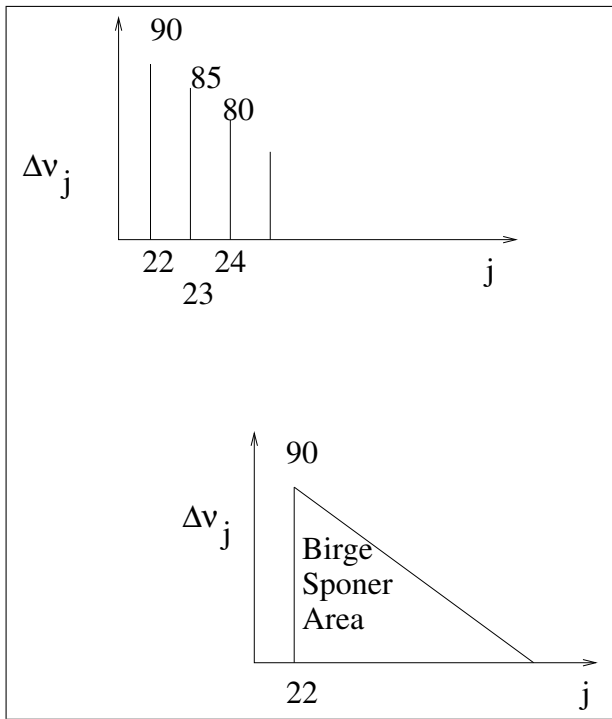
$$\Delta\nu = mj + b$$

FIG. 6: The Birge Sponer extrapolation.

i.e.,

$$\Delta\nu = -5j + 200 \sim \sum \Delta\nu_j \Delta j \overset{1}{\sim} area$$

This means that the area denoted as the "Birge Sponer Area" is

$$\frac{1}{2}(90)(j^* - 22)$$

where j^* is the extrapolated value when $\Delta\nu \to 0$. Obviously, $j^* = 40$. From Figure 5 we have

$$25419 + \frac{(40-22)(90)}{2} = 14202 + E_{dissoc}$$

which gives us the value of the dissociation energy directly.

6. In the photo dissociation of a homo-nuclear diatomic molecule, the exciting photon's energy is 28,000 cm^{-1}, and the dissociation energy of the molecule is 25,413 cm^{-1}. If the atomic mass of the nuclei is 16 grams/mole (i.e. oxygen), and if the velocity of each of the oxygen atoms are equal in magnitude, compute the value of the velocity of the resultant oxygen atoms when the internuclear distance in infinite. Assume that the molecule was initially at rest (we actually compute the velocity relative to the center of mass). Report your answer in cm/sec.
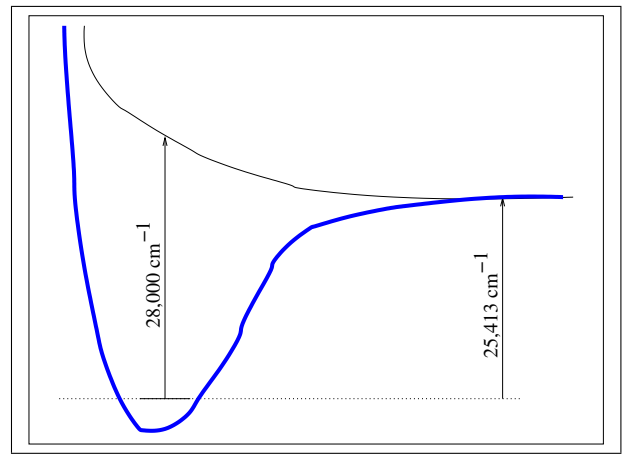

FIG. 7: Potential Energy Curves for Diatomic Molecule Undergoing Photo Dissociation

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Answer and/or Hint

The excess energy, above that required for dissociation, is

$$E_{excess} = 28000 - 25413 \ cm^{-1}$$

which needs to be converted into ergs, divided by 2 (partitioning between the two (now) independent separating nuclei), and, knowing the mass of these nuclei, used to obtain the velocity.

7. The dipole moment of an arbitrary molecule is

$$\vec{\mu} = \mu_x\hat{i} + \mu_y\hat{j} + \mu_z\hat{k}$$

which, in spherical polar coördinates is

$$\vec{\mu} = \mu_0 sin\vartheta \cos\varphi\hat{i} + \mu_0 sin\vartheta sin\varphi\hat{j} + \mu_0 cos\vartheta\hat{k}$$

What is the value of the integral

$$\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} d\varphi \psi_{p_z}\mu_x\psi_{p_y} =$$

$$\int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \cos\vartheta\mu_x \sin\vartheta \sin\varphi \sin\vartheta$$

(which is related to the x-dipole selection rule for a transition from ψ_{p_z} to ψ_{p_y})? Notice that the radial part of the wave functions has been suppressed.

Answer and/or Hint

$$\int_0^\pi \sin\vartheta\, d\vartheta \int_0^{2\pi} d\varphi \cos\vartheta \left\{ |\vec{\mu}| \sin\varphi \cos\varphi \right\} \sin\vartheta \sin\varphi$$

$$|\vec{\mu}| \int_0^\pi d\vartheta \sin^2\vartheta \cos\vartheta \int_0^{2\pi} d\varphi \sin^2\varphi \cos\varphi$$

which is

$$|\vec{\mu}| \left.\frac{\sin^3\vartheta}{3}\right|_0^\pi \left.\frac{\sin^3\varphi}{3}\right|_0^{2\pi}$$

What does this result mean?

8. Matsushima, Oka, and Takagi (Phys. Rev. Letters, 78,1664(1997)) reported the observation of spectral transitions of $_2^4\text{He}\,\text{H}^+$ in the THz region. One such line occurs at 2010.18392 GHz (Giga = 10^9). It corresponds to a J=0 to 1 transition. What is the bond length of the molecule (in Angstrom)?

IV. PARTICLES IN BOXES

1. For a one dimensional "particle in a box (of length L)" (variable = x), obtain a formula for the probability density ($P(x)$) of the described particle if the total range (domain) of x is $a \le x \le b$ where $a < b$ (a and $b > 0$), assuming the wave function over this domain is

$$\psi(x) = \frac{A}{x^{1/2}} = \frac{A}{\sqrt{x}}$$

We know that we need to integrate $\psi^*\psi$ which is the probability density, over the domain of interest, and divide it by the integral of the probability density over the entire domain of the variable x. We have

$$P(a,b) \sim \frac{\int_a^b \frac{\cancel{A^2}}{x} dx}{\int_0^L \frac{\cancel{A^2}}{x} dx}$$

which leads to logarithm integrals which are straightforward.

2. For a one dimensional particle in a box of length L, compute the probability of finding the particle in the center third of the box when the particle is in the first excited state.

Here, we have a more traditional problem

$$\frac{\int_{L/3}^{2L/3} \sin^2\left(\frac{2\pi x}{L}\right) dx}{\int_0^L \int_0^L \sin^2\left(\frac{2\pi x}{L}\right) dx}$$

Why have we dropped the normalization constants? Again, the integrals are straightforward, and are left to the interested and/or motivated student.

3. For a two dimensional "particle in a box", calculate the number of states which lie between (in energy) (but not including) the states from {3,5} to {6,6}, when the box is square. The notation is as follows, $\{n_x, n_y\}$ labels each state, where n_x is the quantum number associated with the x-direction, and n_y is the quantum number associated with the y-direction. The wave function is a product of sines, one for the x-direction and one for the y-direction. Further, the energy is equal to

$$E_{n_x,n_y} = a\ constant\ times(n_x^2 + n_y^2)$$

This question is addressing the question of degeneracy, and asking you to count the number of states by, in essence, explicitly listing them in ascending (usually) order of energy, according to their $\{n_x, n_y\}$ values. We start, but do not finish the job. The lower bound is $\{3,5\} \to 34a$ while the upper bound is $\{6,6\} \to 72a$ Thus

{3,6}	$(9+36)a = 45a$
{3,7}	$(9+49)a = 58a$
⋮	⋮
{1,8}	$(1+84)a = 65a$
⋮	⋮
{2,8}	$(4+84)a = 68a$
⋮	⋮
{7,1}	$(49+1)a = 50a$

So there are lots (and lots) of states, and a full list would take too much space here.

4. For butadiene, assuming that it is 'straight' and made up of 3 C-C bonds of length 1.5 Å, calculate the expected absorption wavelength assuming that the electrons are Fermi filled into the molecular orbitals generated using the particle in a box model, i.e., that the electrons are 1) independent of each other, and 2) ignore the presence of nuclei, and just notice the ends of the molecule.

Answer and/or Hint

We are asked to think of this molecule as a particle in a box problem, where the box is the total length of the molecule, i.e., 4.5 Å. With 4 electrons, we know that the ground ($n = 1$) and the first state ($n = 2$) will be occupied in the ground electronic state of the molecule, and that one of the $n = 2$ electrons will transit to $n = 3$ in absorbing a photon, so we need to compute the change in energy in going from the $n = 2 \rightarrow n = 3$ states. We have

$$\Delta E_{n=2 \rightarrow 3} = \frac{\hbar^2}{2m_e L^2} \left(3^2 - 2^2\right)$$

where $L = 4.5 \times 10^{-8} cm$.

Knowing ΔE allows us to compute the energy of the photon which "did the work", i.e.,

$$\Delta E_{n=2 \rightarrow 3} = h\nu_{photon}$$

and

$$\lambda_{photon}\nu_{photon} = c(velocity\ of\ light)$$

allows us ultimately to compute λ_{photon}.

5. The Schrödinger Equation for the particle in a box (stretching from $x = 0$ to $x = L$) is:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = \epsilon\psi$$

and, given two eigenfunctions:

$$\psi_1 = \sqrt{\frac{2}{L}}\sin\left(\frac{1\pi x}{L}\right)$$

and

$$\psi_2 = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$$

a state is prepared which is one half ψ_1 and one half ψ_2, i.e., a linear combination with equal coëfficients

$$\psi_{combination} = c_1\psi_1 + c_2\psi_2$$

with $c_1 = c_2$, what is the expected energy (ϵ) of the resultant state?

Answer and/or Hint

Notice, this "LCAO" is midway between the $n = 1$ state and the $n = 2$ state so we expect the energy to be likewise positioned. We can get the explicit value in several ways, but the best from a pedagogical point of view is to evaluate

$$H_{op}\left(\psi_1 + \psi_2\right)$$

and see if we can obtain

$$\epsilon\left(\psi_1 + \psi_2\right)$$

This means we apply the Hamiltonian operator,

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

in the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2\left(\psi_1 + \psi_2\right)}{\partial x^2}$$

and see what we recover when we factor out the term $(\psi_1 + \psi_2)$ from the resultant.

6. For an electron in a 3-dimensional box, compute the wavelength (in Å) assuming that the box has dimension $(a, a/2, 2a)$ where a is 1.5Å, for a transition from the 4'th excited state to the 2'nd excited state.

Answer and/or Hint

The energy levels are given by the expression:

$$E_{n_x,n_y,n_z} = -\frac{\hbar^2}{2m_e}\left\{\left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{a/2}\right)^2 + \left(\frac{n_z}{2a}\right)^2\right\}$$

and we need to evaluate this expression for the choice of quantum numbers which "create" the two different states (there's no particular algorithm for searching for these two sets of quantum numbers that I know of). The ground state would be

$$E = -\frac{\hbar^2}{2m_e a^2}\left\{\left(\frac{1}{1}\right)^2 + \left(\frac{1}{1/2}\right)^2 + \left(\frac{1}{2}\right)^2\right\}$$

Therefore, making a list of candidate states, sorting them in ascending order, and picking out the appropriately required ones is left as an exercise.
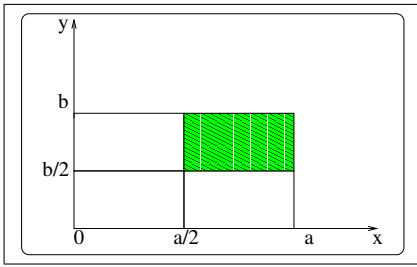
FIG. 8: A particle in a 2D box.

7. For a particle in a two dimensional box (area $= ab$, perimeter $= 2(a+b)$), find the probability of finding it in the area bounded by $a/2 < x < a$ and $b/2 < y < b$. Assume the particle is in the ground state.

Answer and/or Hint

Your answer better be $\frac{1}{4}$! You can obtain this by inspection, introspection, or direct integration (which is the preferred method). You would be evaluating two integrals as a fraction, the numerator of which would be

$$\int_{a/2}^{a} dx \int_{b/2}^{b} dy \psi^2$$

and the denominator would be

$$\int_{0}^{a} dx \int_{0}^{b} dy \psi^2$$

where

$$\psi = \sqrt{\frac{2}{a}} \sqrt{\frac{2}{b}} \sin \frac{1\pi x}{a} \sin \frac{1\pi y}{b}$$

Parenthetically, notice that there are no degeneracy problems here until $b \to a$, whereupon the situation becomes a little muddled.

$$\int_{a/2}^{a} dx \int_{b/2}^{b} dy \left(\sqrt{\frac{2}{a}} \sqrt{\frac{2}{b}} \sin \frac{1\pi x}{a} \sin \frac{1\pi y}{b} \right)^2$$

which is separable into the product of two integrals which can be done independent of each other.

What happens if we are in an excited state?

8. A particle is trapped in a two-dimensional rectangular box of sides A and $2A$. How many states exist whose energy (E) obeys the relation

$$E \leq \frac{2\hbar^2 \pi^2}{2m_{particle} A^2}$$

Answer and/or Hint

Since the energy expression is

$$E_{n_x, n_y} = \frac{n_x^2 \hbar^2 \pi^2}{2m_{particle} A^2} + \frac{n_y^2 \hbar^2 \pi^2}{2m_{particle} (2A)^2}$$

or

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2m_{particle} A^2} \left(\frac{n_x^2}{1^2} + \frac{n_y^2}{2^2} \right)$$

with $n_x = 1, 2, 3, \cdots$ and $n_y = 1, 2, 3, \cdots$ etc., we can evaluate a sequence of increasing values of the energy as the two quantum numbers increase until we've crossed the threshold of the desired maximum.

9. For a particle in a 3-dimensional (x, y, z) box of lengths $(a, 2a, 3a)$: $0 \leq x \leq a$, $0 \leq y \leq 2a$, $0 \leq z \leq 3a$ calculate the probability of finding the particle in the range: $0 < x < a/2$, $0 < y < a$, $0 < z < 3a/2$

Answer and/or Hint

---

2 dimensions, 3 dimensions, what's the big deal? See above!!!!

10. Assume that a particular argon atom is constrained to exist in a two-dimensional square box of length L on each side. A particular state of this system is a combination of the ground state (in one coördinate) and the first excited state (in the other coördinate): i.e.,

$$\psi_{1,2} = \frac{2}{L} \sin\left(\frac{1\pi x}{L} \right) \sin\left(\frac{2\pi y}{L} \right)$$

and the alternative form

$$\psi_{2,1} = \frac{2}{L} \sin\left(\frac{2\pi x}{L} \right) \sin\left(\frac{1\pi y}{L} \right)$$

There are two possibilities for the $\{n_x, n_y\}$ shown, and therefore a proper state of the particle is a linear combination of the two possibilities, i.e.,

$$\psi_{question} = a\psi_{1,2} + b\psi_{2,1}$$

(here, we take $a = b$ for our "LCAO") i.e.,

$$\psi_{question} = K_{normalization} \left[\sin\left(\frac{1\pi x}{L} \right) \sin\left(\frac{2\pi y}{L} \right) \right.$$
$$\left. + \sin\left(\frac{2\pi x}{L} \right) \sin\left(\frac{1\pi y}{L} \right) \right)$$

where L is 10Å. Obtain the energy of the argon atom (in ergs).

Answer and/or Hint

Remember that the Hamiltonian is

$$-\frac{\hbar^2}{2m_{Argon}}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)$$

which can be applied to the wave function shown.

11. Assuming that benzene's electrons can be approximated as being in a two dimensional square box which completely encloses the molecule, and assuming that the C-C distance in benzene is 1.3 , calculate the expected HOMO-LUMO energy gap (in ergs/molecule) for benzene.

Answer and/or Hint

The actual benzene molecule fits into a rectangle of length 1.502 by 2.6 Angstrom, so let's assume the square has the same area, i.e., 1.5*2.6 Å^2. Thus, let's take the square's edge length at 1.98 Å for this problem. Then, we need to find the energy
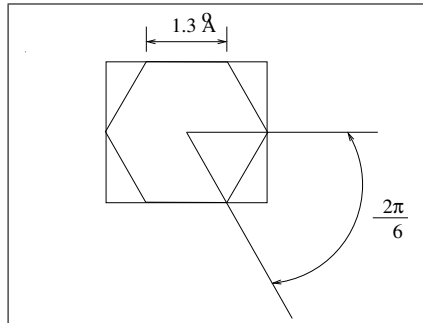

FIG. 9: A particle in a benzene like 2D box.

levels in terms of the $\{n_x, n_y\}$ sets, determine where the 6 electrons go, so that the highest filled orbital becomes the HOMO, and the next in sequence of energy becomes the LUMO. The energy difference between these two needs to be computed, and the rest, as they say, is trivial.

V.   HARMONIC OSCILLATORS

1. For the Semi-Harmonic Oscillator (SHO) shown in Figure 11 (where $V(x)$ is the potential energy), what is the energy of the second excited state.
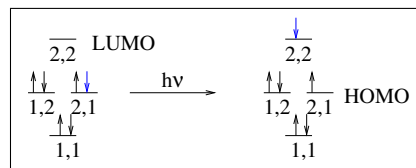

FIG. 10: Energy level scheme for this particle in a box model, showing the HOMO → LUMO transition.
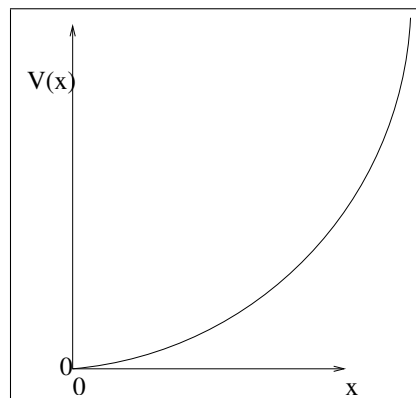

FIG. 11: A particle in a semi-harmonic oscillator potential.

Answer and/or Hint

The ground state of the SHO is the same as the n=1 state of the HO, while the first excited state of the SHO is the same as the 3rd state of the HO.
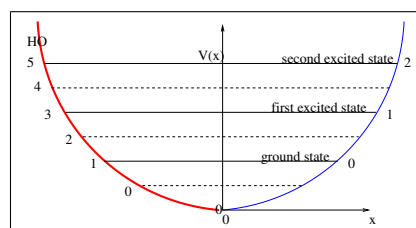

FIG. 12: The energy levels of a harmonic oscillator with the semi-harmonic oscillator energy levels selected out and displayed.

For the state of the SHO in question

$$E_{2^{nd}\ excited\ state}=\left(5+\frac{1}{2}\right)\hbar\omega$$

(see Figure 12). This is because half of the HO eigenfunctions are finite at $x = 0$ which violates the boundary conditions of the SHO, so they have to be eliminated. Only the "odd" states survive

the winnowing process. The state in question, the second excited state of the SHO corresponds to the $n = 5$ state of the HO.

2. The Schrödinger Equation (in dimensionless form, so called atomic units) for the Harmonic Oscillator is:

$$-\frac{\partial^2 \psi}{\partial y^2} + y^2 \psi = \epsilon \psi$$

and the eigenfunctions are:

$$\psi_n = (Hermite\ polynomial\ in\ y) \times e^{-\frac{y^2}{2}}$$

For n=2, the Hermite Polynomial is $4y^2 - 2$. Obtain the value of ϵ for the $n = 2$ state.

Answer and/or Hint

The first partial of the trial wave function is

$$\frac{\partial \psi}{\partial y} = 8ye^{-\frac{y^2}{2}} - y(4y^2 - 2)e^{-\frac{y^2}{2}}$$

The second partial

$$\frac{\partial \left(8ye^{-\frac{y^2}{2}} - y(4y^2 - 2)e^{-\frac{y^2}{2}}\right)}{\partial y}$$

is also obtained in elementary fashion, allowing substitution into the appropriate equation (indicated above), leading to the resultant energy through simple cancellations.

3. Assuming the $Na^{35}C\ell$ molecule, with k = 1.086 × 10^5 erg/cm and $\mu = 2.30314 \times 10^{-24}$ grams, obtain the value of the distance from the r_e (in Å) so that the probability of finding the oscillator is 0.5.

Answer and/or Hint

The Schrödinger Equation for the isotropic 1-dimensional Harmonic Oscillator is

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2 \psi}{\partial x^2}\right) + k\frac{x^2}{2}\psi = E\psi$$

which has as ground state solution ($\psi_0(x)$),

$$\psi_0(x) = N \times e^{\frac{-\sqrt{k\mu}}{2\hbar}x^2}$$

where k is $\frac{dynes}{cm}$, μ is $\frac{grams}{molecule}$, and x is in centimeters.

It is inconvenient to work in units like this *vide infra*, so we wish to convert to a dimensionless distance, say ρ. Let

$$\rho = \alpha x$$

where α is to be determined by some (future) measure of convenience. Then, from the chain rule we have

$$\frac{\partial}{\partial x} = \frac{\partial \rho}{\partial x}\frac{\partial}{\partial \rho} = \alpha \frac{\partial}{\partial \rho}$$

so we have, for the transformed equation is

$$-\frac{\hbar^2}{2\mu}\left(\alpha^2\frac{\partial^2\psi}{\partial\rho^2}\right) + k\frac{\left(\frac{\rho}{\alpha}\right)^2}{2}\psi = E\psi$$

so, cross-multiplying, we have

$$\left(\frac{\partial^2\psi}{\partial\rho^2}\right) - \frac{2k\mu}{\alpha^4\hbar^2}\frac{\rho^2}{2}\psi = -E\frac{2\mu}{\alpha^2\hbar^2}\psi$$

The <u>choice</u> that makes most sense is

$$\frac{k\mu}{\alpha^4\hbar^2} \to 1$$

so

$$\left(\frac{\partial^2\psi}{\partial\rho^2}\right) - \rho^2\psi = -\epsilon\psi$$

where ϵ's definition in terms of E and α is obvious. We have achieved a more "textbook" appearance of our differential equation.

Let's check the units:

$$\alpha^4 = \frac{k\mu}{\hbar^2} \mapsto \frac{gram\frac{dyne}{cm}}{erg^2 sec^2}$$

$$= \frac{gram\frac{dyne\ cm}{cm^2}}{erg^2 sec^2} = \frac{gram\frac{1}{cm^2}}{erg\ sec^2} = \frac{gram\frac{1}{cm^2}}{dyne\ cm\ sec^2}$$

$$= \frac{gram\frac{1}{cm^2}}{\frac{gram\ cm}{sec^2}cm\ sec^2} = \frac{1}{cm^4}$$

In the new units, the ground state solution is

$$Ne^{-\rho^2/2}$$

so

$$\left(\frac{\partial\psi}{\partial\rho}\right) = -\rho\psi$$

and

$$\left(\frac{\partial^2 \psi}{\partial \rho^2}\right) = -\psi + \rho^2 \psi$$

so, in this unit system $\epsilon = 1$.

The question asks, what is x_{answer} for the following integral:

$$P(\rho_{answer}) = \frac{1}{2} = \frac{2\int_0^{x_{answer}} N e^{-2\alpha^2 x^2/2} dx}{2\int_0^{\infty} N e^{-2\alpha^2 x^2/2} dx}$$

(why the factor of 2 in front?)

The denominator is a standard Gaussian integral, but the numerator is related to the error function.

$$P(\rho_{answer}) = \frac{1}{2} = \frac{\int_0^{\rho_{answer}} N e^{-\rho^2} d\rho}{\int_0^{\infty} N e^{-\rho^2} d\rho}$$

The Error function, defined as

$$Erf(t) \equiv \frac{2}{\sqrt{\pi}} \int_0^t e^{-u^2} du$$

so we have:

$$P(\rho_{answer}) = \frac{1}{2} = \frac{Erf(x_{answer})}{Erf(\infty)}$$

t	Erf(t)
0.00	0.000
0.1	0.112
0.2	0.223
0.3	0.329
0.4	0.428
0.47	0.4937450509
0.4769	0.5
0.48	0.5027496707
0.5	0.521

Since

$$P(x) \propto \psi^2 dx$$

The question requires that we define

$$\frac{1}{2} = \int_0^{x_{answer}} e^{-\alpha x^2} dx$$

where $\alpha^4 = \frac{k\mu}{\hbar^2}$

4. The Schrödinger Equation for the 1-dimensional Harmonic Oscillator is

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 \psi}{\partial x^2} + \frac{kx^2}{2}\psi = E\psi$$

which has a proposed solution:

$$\psi_{problem} = (x^4 - \beta x^2)e^{-\alpha x^4}$$

What follows is some Maple code to carry out the mechanics of this problem.

```
psi := (x^4- beta*x^2)*exp(-alpha*x^2);
ham := expand(-(hbar^2/(2*m))*
diff(psi,x$2) + (k/2)*(x^2)*psi-E*psi);
ham_1 := subs(exp(alpha*x^2)=1,ham);
ham_1 := collect(ham_1,x);
```

$$\psi := \left(x^4 - \beta x^2\right) e^{(-\alpha x^2)}$$

$$ham := -6\frac{hbar^2 x^2}{m e^{(\alpha x^2)}} + \frac{hbar^2 \beta}{m e^{(\alpha x^2)}} + 9\frac{hbar^2 \alpha x^4}{m e^{(\alpha x^2)}} - 5\frac{hbar^2 \alpha x^2 \beta}{m e^{(\alpha x^2)}} - 2\frac{hbar^2 \alpha^2 x^6}{m e^{(\alpha x^2)}}$$
$$+ 2\frac{hbar^2 \alpha^2 x^4 \beta}{m e^{(\alpha x^2)}} + \frac{1}{2}\frac{k x^6}{e^{(\alpha x^2)}} - \frac{1}{2}\frac{k x^4 \beta}{e^{(\alpha x^2)}} - \frac{E x^4}{e^{(\alpha x^2)}} + \frac{E \beta x^2}{e^{(\alpha x^2)}}$$

$$ham\_1 := -6\frac{hbar^2 x^2}{m} + \frac{hbar^2 \beta}{m} + 9\frac{hbar^2 \alpha x^4}{m} - 5\frac{hbar^2 \alpha x^2 \beta}{m} - 2\frac{hbar^2 \alpha^2 x^6}{m}$$
$$+ 2\frac{hbar^2 \alpha^2 x^4 \beta}{m} + \frac{1}{2}k x^6 - \frac{1}{2}k x^4 \beta - E x^4 + E \beta x^2$$

$$ham\_1 := (\frac{1}{2}\,k - 2\,\frac{hbar^2\,\alpha^2}{m})\,x^6 + (9\,\frac{hbar^2\,\alpha}{m} - E - \frac{1}{2}\,k\,\beta + 2\,\frac{hbar^2\,\alpha^2\,\beta}{m})\,x^4$$
$$+ (-6\,\frac{hbar^2}{m} - 5\,\frac{hbar^2\,\alpha\,\beta}{m} + E\,\beta)\,x^2 + \frac{hbar^2\,\beta}{m}$$

We conclude, from the absence of cancellations, that the trial wave function is NO GOOD!

VI.   ANGULAR MOMENTUM

1. The operator for angular momentum (squared) (L_{op}^2) in spherical polar coördinates is

$$L_{op}^2 = -\hbar^2 \left\{ \frac{1}{\sin\vartheta}\frac{\partial \sin\vartheta \frac{\partial}{\partial\vartheta}}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \right\}$$

so, for an eigenfunction of this operator one would have

$$L_{op}^2\psi(\vartheta,\varphi) = \ell(\ell+1)\hbar^2\psi(\vartheta,\varphi)$$

$$L_{op}^2 = -\hbar^2 \left\{ \frac{\cos 2\varphi}{\sin\vartheta}\frac{\partial \sin\vartheta \frac{\partial(\sin^2\vartheta)}{\partial\vartheta}}{\partial\vartheta} + \frac{\sin^2\vartheta}{\sin^2\vartheta}\frac{\partial^2(\cos 2\varphi)}{\partial\varphi^2} \right\}$$

is a straightforward exercise in partial differentiation.

2. The operator for angular momentum (squared) (L_{op}^2) in spherical polar coördinates is

$$L_{op}^2 = -\hbar^2 \left\{ \frac{1}{\sin\vartheta}\frac{\partial \sin\vartheta \frac{\partial}{\partial\vartheta}}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \right\}$$

and the operator for L_{op}^z is

$$L_{op}^z = -\hbar\frac{\partial}{\partial\varphi}$$

so, for an eigenfunction of this operator one would have

$$L_{op}^2\psi(\vartheta,\varphi) = \ell(\ell+1)\hbar^2\psi(\vartheta,\varphi)$$

and

$$L_{op}^z\psi(\vartheta,\varphi) = m_\ell\hbar\psi(\vartheta,\varphi)$$

Is the function

$$\sin^2\vartheta\cos 2\varphi$$

What is the ℓ value associated with the function

$$\sin^2\vartheta\cos 2\varphi$$

Answer and/or Hint

an eigenfunction of L_{op}^z?

Answer and/or Hint

We need to form

$$L_{op}^z\psi(\vartheta,\varphi) = L_{op}^z\left(\sin^2\vartheta\cos 2\varphi\right) \overset{?}{=} m_\ell\hbar\psi(\vartheta,\varphi)$$

and ask if m_ℓ is an integer?

$$L_{op}^z\left(\sin^2\vartheta\cos 2\varphi\right) = -\hbar\frac{\partial\left(\sin^2\vartheta\cos 2\varphi\right)}{\partial\varphi}$$

which equals

$$-2\hbar\left(\sin^2\vartheta\sin\varphi\right)$$

so the answer is NO!

3. If two eigenfunctions of angular momentum are orthogonal to each other then the integral

$$\int_a^b \sin\vartheta d\vartheta \int_c^d d\varphi \left\{ \psi_1^* \psi_2 \right\}$$

must have a certain value. What are a, b, c, and d and what is the value of the integral assuming the functions are

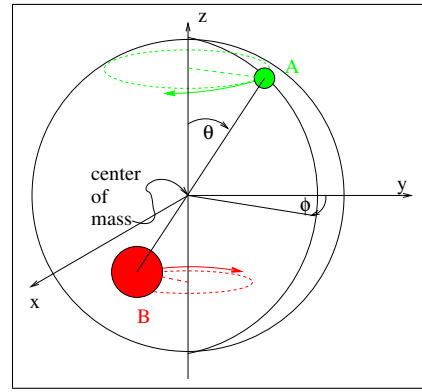$$\psi_1 = \cos\vartheta$$

and

$$\psi_2 = \sin\vartheta \cos\varphi$$

FIG. 13: A diatomic molecule, in the center of mass coördinate system, undergoing rotation as a rigid rotor.

$$\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} d\varphi \left\{ \cos\vartheta \sin\vartheta \cos\varphi \right\}$$

which can be written

$$\int_0^\pi \sin^2\vartheta \cos\vartheta d\vartheta \int_0^{2\pi} \cos\varphi d\varphi$$

which is trivially integrable.

4. The proposed function

$$\sin^2\vartheta \cos\vartheta \cos\varphi \sin\varphi$$

is an eigenfunction of angular moment (L_{op}^2). What is the quantum number (ℓ) associated with this function?

Again, all we need do is operate on the function with the appropriate operator (see above) and look for regeneration in the eigenfunction sense.

VII. RIGID ROTORS

1. The Schrödinger Equation (in dimensionless form) for the Rigid Rotor is:

$$-\left\{ \frac{1}{\sin\vartheta} \frac{\partial \sin\vartheta \frac{\partial\psi}{\partial\vartheta}}{\partial\vartheta} + \frac{1}{\sin^2\vartheta} \frac{\partial^2\psi}{\partial\varphi^2} \right\} = \epsilon\psi$$

and a purported eigenfunction is $\sin^3\vartheta \cos(3\varphi)$. Obtain the value of ϵ for this function, verifying at the same time that it is truly an eigenfunction.

$$-\left\{ \frac{1}{\sin\vartheta} \frac{\partial \sin\vartheta \frac{\partial \sin^3\vartheta \cos(3\varphi)}{\partial\vartheta}}{\partial\vartheta} + \frac{1}{\sin^2\vartheta} \frac{\partial^2 \sin^3\vartheta \cos(3\varphi)}{\partial\varphi^2} \right\} = \epsilon\psi$$

After appropriate partial differentiation one need only collect terms.

2. The energy operator in spherical polar coördinates when r is not a variable ($r = R$, a constant) is

$$-\frac{\hbar^2}{2\mu R^2} \left\{ \frac{1}{\sin\vartheta} \frac{\partial \sin\vartheta \frac{\partial\psi}{\partial\vartheta}}{\partial\vartheta} + \frac{1}{\sin^2\vartheta} \frac{\partial^2\psi}{\partial\varphi^2} \right\}$$

which, for planar rotation, with $\varphi = \frac{\pi}{2}$, would be

$$-\frac{\hbar^2}{2\mu R^2} \left\{ \frac{1}{\sin^2\vartheta} \frac{\partial^2\psi}{\partial\varphi^2} \right\}$$

Obtain an expression for the eigenvalues associated with this operator.

$$-\frac{\hbar^2}{2\mu R^2} \left\{ \frac{1}{\sin^2\frac{\pi}{2}} \frac{\partial^2\psi}{\partial\varphi^2} \right\}$$

is the Hamiltonian for this problem, which becomes

$$-\frac{\hbar^2}{2I} \left\{ \frac{\partial^2\psi}{\partial\varphi^2} \right\}$$

which is a "particle in a box" Hamiltonian, i.e., is one whose eigenfunctions and eigenvalues are already known. Notice how the moment of inertia evolves naturally.

3. Consider a molecule of $^1\text{H}^{35}\text{Cl}$ in the n'th vibrational state and the J'th rotational state. Calculate the value of J such that

$$E_{n,J} > E_{n+1,0}$$

i.e., a highly rotating molecule's energy is greater than the next highest vibrational energy level of the "non-rotating" molecule. The vibrational force constant for this molecule is 4.9×10^{-5} dynes/cm (said another way, the energy difference between the $n = 0, J = 0$ and the $n = 1, J = 0$ state is about 2886 cm^{-1}). The rotational constant, B, is about $10 cm^{-1}$. Remember, J is an integer!

Answer and/or Hint

$$E_{n,J} = \left(n + \frac{1}{2}\right)\hbar\omega + J(J+1)B$$

---

where B is the rotational constant. We are asked to solve the "equation"

$$\left(n + \frac{1}{2}\right)\hbar\omega + J(J+1)B \geq \left(n + 1 + \frac{1}{2}\right)\hbar\omega + 0(0+1)B$$

which is a straightforward task.

VIII. EPILOGUE

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it up and send this off. If, in the years 2008-2010 or so, you come across an error, and you e-mail me, I will try to have it corrected.

But since this material is written in there is some doubt whether or not I'll have access to a Linux machine, and access to the digitialcommons site. You can try; we'll see what happens, if anything. Thanks to all the students over the last 45 years who've taught me Physical Chemistry.

[1] OK, it's HCℓ and ω is 2886 cm^{-1}