Chemistry 120A
Spring 2004

Name: KEY

Final Exam
May 14, 2004 - 8:00 am - 11:00 am
Lewis 100

Show all your work to get partial credit

1. (15 points) The chemical iodine atom laser is produced by photodissociating a molecule like CH_3I. The ground state is a $^2P_{3/2}$ and the excited state is $^2P_{1/2}$. Calculate the degeneracies of these two laser states and fill in the blanks.

$\uparrow E$

$^2P_{1/2}$ ______ $g =$ 2

$^2P_{3/2}$ ______ $g =$ 4

$g = 2J+1$

$J = 1/2$ and $3/2$

What is minimum ratio of $^2P_{1/2}/^2P_{3/2}$ to achieve a population inversion — fill in the blank.

$$\frac{I(^2P_{1/2})}{I(^2P_{3/2})} > \frac{0.333}{0.666} = \frac{1}{2} = \frac{2}{4}$$

(recall the term symbol is: $^{2s+1}L_J$)

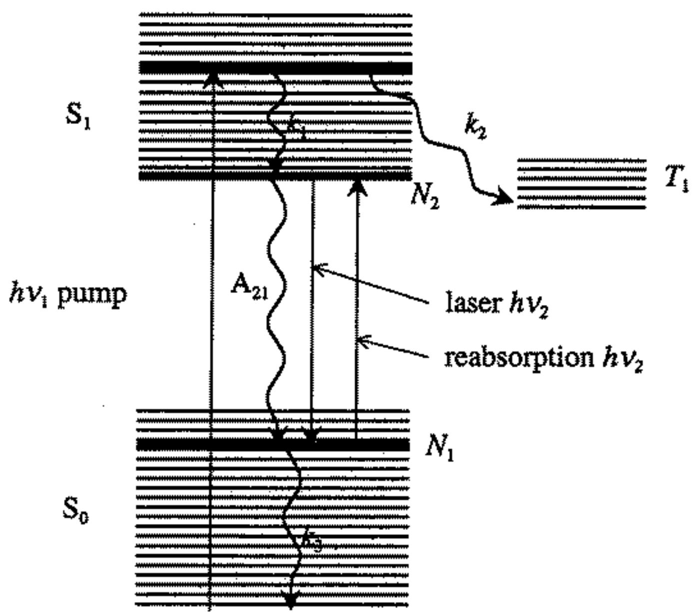
Now suppose the photolysis produces 80% $^2P_{1/2}$ and 20% $^2P_{3/2}$. If the total number of molecules dissociated is 10^{16}, how many photons of laser light could be extracted in the maximum case? Assume the ground state cannot be removed during the timescale of lasing. A picture might be helpful.

$0.80 \rightarrow 0.333$, $0.20 \rightarrow 0.666$

$(0.8 - 0.333) \times 10^{16} = 4.67 \times 10^{15}$ photons

Once 0.333 is reached, the lasing stops

2. (15 points) Consider the laser system shown below which is like a dye molecule. The banded levels are like closely spaced vibrational states. Only the processes shown can occur. Assume the laser states have the same degeneracy.



k_1, k_2, and k_3 are all first order relaxation processes that occur without any photons. Molecules that make the transition to T_1 (excited triplet), never return to S_0 or S_1 (the singlets). What is the criterion for an inversion to occur on the laser transition ($N_2 \rightarrow N_1$), before the stimulated emission starts. ($\rho_{12} = 0$)? A mathematical equation expressing N_2/N_1 in terms of A_{21} and k_3 is expected.

Ignore lasing initially, assume steady state

$$\frac{dN_1}{dt} = 0 = A_{21}N_2 - k_3 N_1$$

$$\frac{N_2}{N_1} = \frac{k_3}{A_{21}} \text{ in steady state}$$

$$\frac{N_2}{N_1} > 1 \text{ for lasing inversion}$$

$$\text{so } \frac{k_3}{A_{21}} > 1 \text{ for population inversion}$$

relaxation out of N_1 faster than population into N_1 for inversion

[redacted]

What is the maximum efficiency of the laser above when the k_2 process is taken into account? Assume $k_3 >> k_1$ and $k_3 >> k_2$, and assume A_{21} can be small compared to the laser output. Give your answer in terms of the rate processes on the figure.

If A_{21} is small, we need to look at the processes k_1, k_2, k_3. k_3 is always really large, so the efficiency depends only on k_1 and k_2. k_1 helps feed the level for lasing; k_2 permanently removes population from the laser. The percent or efficiency that goes through k_1 is

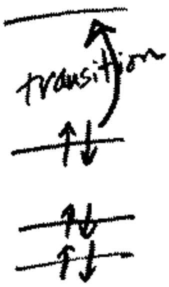
$$\text{efficiency} = \frac{k_1}{k_1 + k_2} \quad \text{or} \quad \frac{k_1}{k_1+k_2} \times 100\%$$

3. (10 points) Describe briefly in words how the transition probability for the absorption of a photon is obtained in quantum chemistry. What theory is used, what Hamiltonian is used, etc.

Time dependant perturbation theory is used, together with a Hamiltonian that includes the oscillating electric field of the light. An approximation is made to retain only the electric dipole term. The result is a matrix element like $\langle \psi_2 | \vec{\mu} | \psi_1 \rangle$ that connects ψ_1 to ψ_2 through the dipole operator.

[redacted]

4. (15 points) Hückel molecular orbital theory has a useful analogy to the particle-in-a-box energy levels. What is that analogy? Discuss several aspects of how these are similar and different: The length of the box, the filling of two electrons with opposite spins in each energy level, and the transition energy from the highest filled energy level to the lowest unfilled level. Pictures will be helpful.



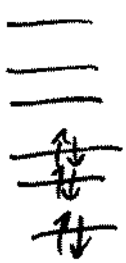
An important analogy is that the energy levels in an extended π electron system are like a particle in a box. As the box gets longer, or the extended conjugation greater, the energy levels get closer together. In the usual particle in a box, we think of one particle and it can occupy several states. In the conjugated π system, we fill orbitals with two electrons at a time until they are all filled up. The transition energy would be from the highest filled level to the lowest unoccupied level.

The Hückel theory energy levels do not exactly follow the same spacings as a particle-in-a-box. What is this difference? Comment on this point.

In Hückel theory the energy levels are more equally spaced above and below a zero level. In the particle-in-a-box the levels are increasing as n^2. But both sets of levels get closer together as the box gets longer.

The particle in a box model is not a perfect match to the Hückel result.

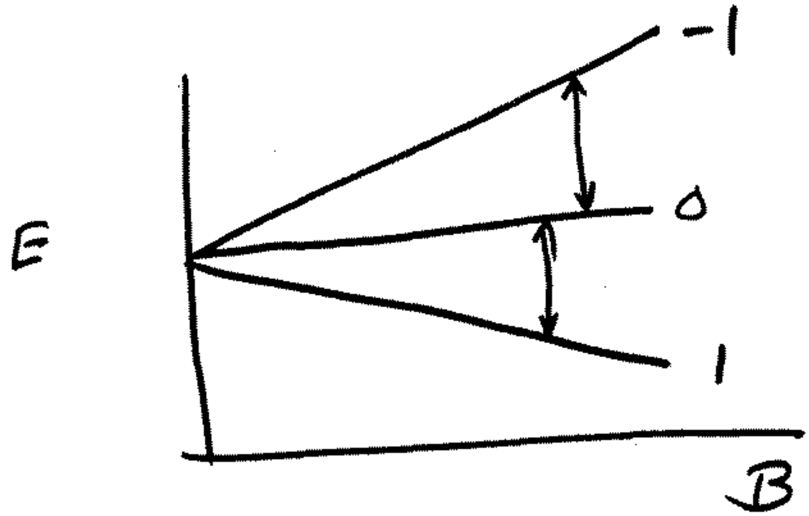
Hückel



Box

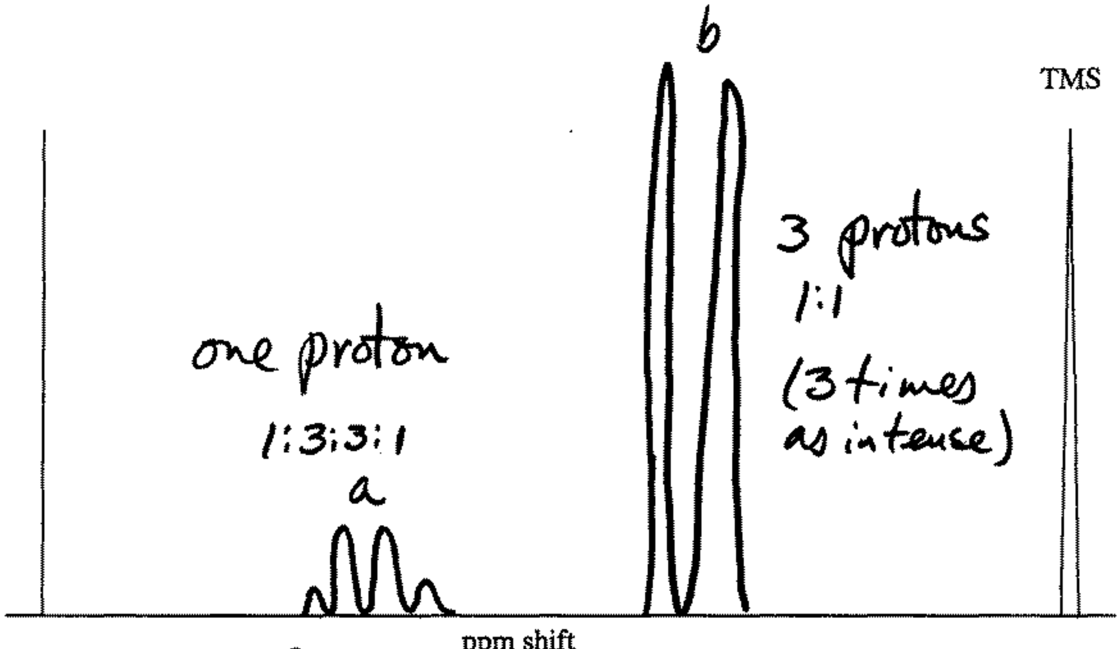
[redacted]

5. (10 points) A deuterium atom nucleus has a spin of 1. $s = 1$. Draw the splitting of the energy levels in a magnetic field, and label the states, such as would be found in nuclear magnetic resonance. Plot E vs. B_z. Show the possible transitions with radio frequency light.



6. (10 points) Consider the molecule $CF_2\overset{a}{H}\overset{b}{CH_3}$.

Take the F to be a strong electron withdrawing group, but assume no nuclear spin for F, but do include the spin-spin interaction of the H atoms, and draw an approximate nmr spectrum on the axes below. Show realistic intensities also. Label your peaks.



F atoms with draw electrons - less shielded

[redacted]

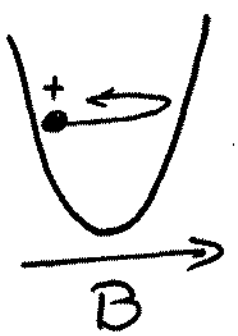
7. (10 points) Pulsed nmr was developed to overcome an important limitation in the nmr signals. What is that limitation?

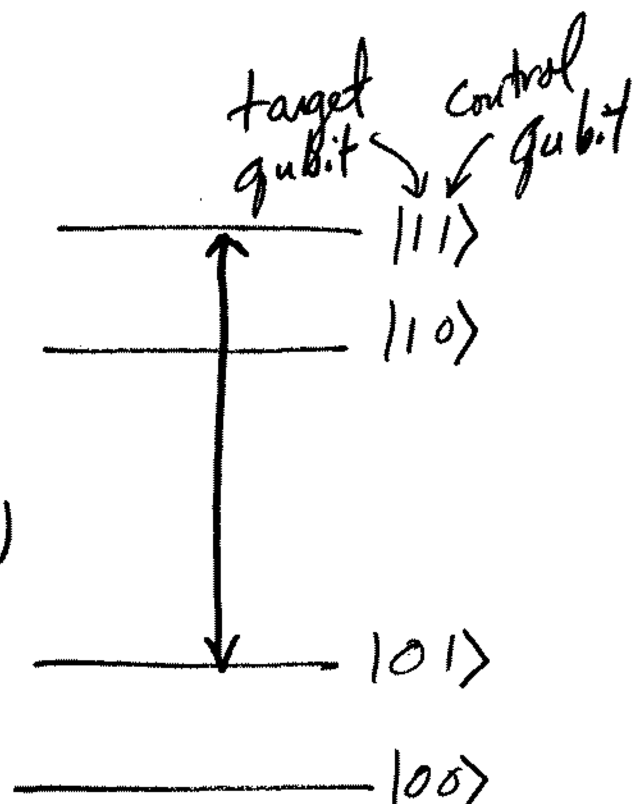
The small population difference between $+\frac{1}{2}$ and $-\frac{1}{2}$ states in a magnetic field at room temperature, by transiently flipping lots of spins all at once with coherent radio frequency pulses.

8. (10 points) A controlled NOT gate operates on two qubits, where the value of the first qubit affects the operation that is applied to the second qubit. Give any example of how this can be accomplished.

An ion in a trap with a B field

nmr example also ok.





When the ion moves to one side of the trap (motional qubit) the frequency of the light needed to make the transition changes. When control qubit is 1, flip the target qubit from $0 \rightarrow 1$

[redacted]

9. (15 points) The unnormalized wave function for finding an electron over the interval $x = 0 \rightarrow 1$ is:

$$\psi(x) = ie^{-x}$$

What is the probability of finding the electron between $x = 0 \rightarrow 0.5$? Work out all the math.

$$\text{probability} = \frac{\int_0^{0.5} (-ie^{-x})(ie^{-x})\,dx}{\int_0^{1} (-ie^{-x})(ie^{-x})\,dx} = \frac{\int_0^{0.5} \psi^* \psi\,dx}{\int_0^{1} \psi^* \psi\,dx}$$

$$= \frac{\int_0^{0.5} e^{-2x}\,dx}{\int_0^{1} e^{-2x}\,dx} = \frac{\cancel{-\tfrac{1}{2}} e^{-2x} \Big|_0^{0.5}}{\cancel{-\tfrac{1}{2}} e^{-2x} \Big|_0^{1}}$$

$$= \frac{e^{-1} - e^{-2\cdot 0}}{e^{-2} - e^{-2\cdot 0}}$$

$$= \frac{e^{-1} - e^{0}}{e^{-2} - e^{0}} = \frac{0.36788 - 1}{0.13534 - 1}$$

$$\text{probability} = 0.73$$

[redacted]

10. (10 points) Evaluate the commutator: $\left[i\hbar\frac{d}{dx}, x^2\right]$

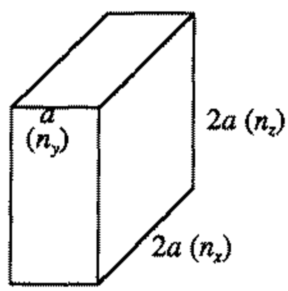
$$i\hbar\frac{d}{dx}(x^2)f(x) - x^2 \cdot i\hbar\frac{d}{dx}f(x) =$$

$$i\hbar\, 2x\, f(x) + \cancel{i\hbar x^2 \frac{d}{dx} f(x)} - \cancel{i\hbar x^2 \frac{d}{dx} f(x)}$$

$$= i\hbar\, 2x$$

$$\left[i\hbar\frac{d}{dx}, x^2\right] = i\hbar\, 2x$$

11. (15 points) Consider a 3-D particle in a box of lengths $2a$, $2a$, and a.



Write down the wave full function for a single particle (see the equations on the 1st page of the equations handout).

$$\psi_{Total} = \left[\left(\frac{2}{2a}\right)^{1/2} \sin\frac{n\pi x}{2a}\right]\left[\left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi y}{a}\right]\left[\left(\frac{2}{2a}\right)^{1/2} \sin\frac{n\pi z}{2a}\right]$$

[redacted]

Write down the total energy for the box above:

$$E_{Total} = \frac{n_x^2 h^2}{8m \cdot 4a^2} + \frac{n_y^2 h^2}{8ma^2} + \frac{n_z^2 h^2}{8m \cdot 4a^2}$$

What are the quantum numbers of the first degenerate energy levels in the box above (the lowest levels that are degenerate)? (Use labels (n_x, n_y, n_z).)

when n_x or $n_z = 2$ and all the rest are 1

(2,1,1)

(1,1,2)

12. (10 points) A wave packet is composed of a normalized superposition of three states:

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3$$

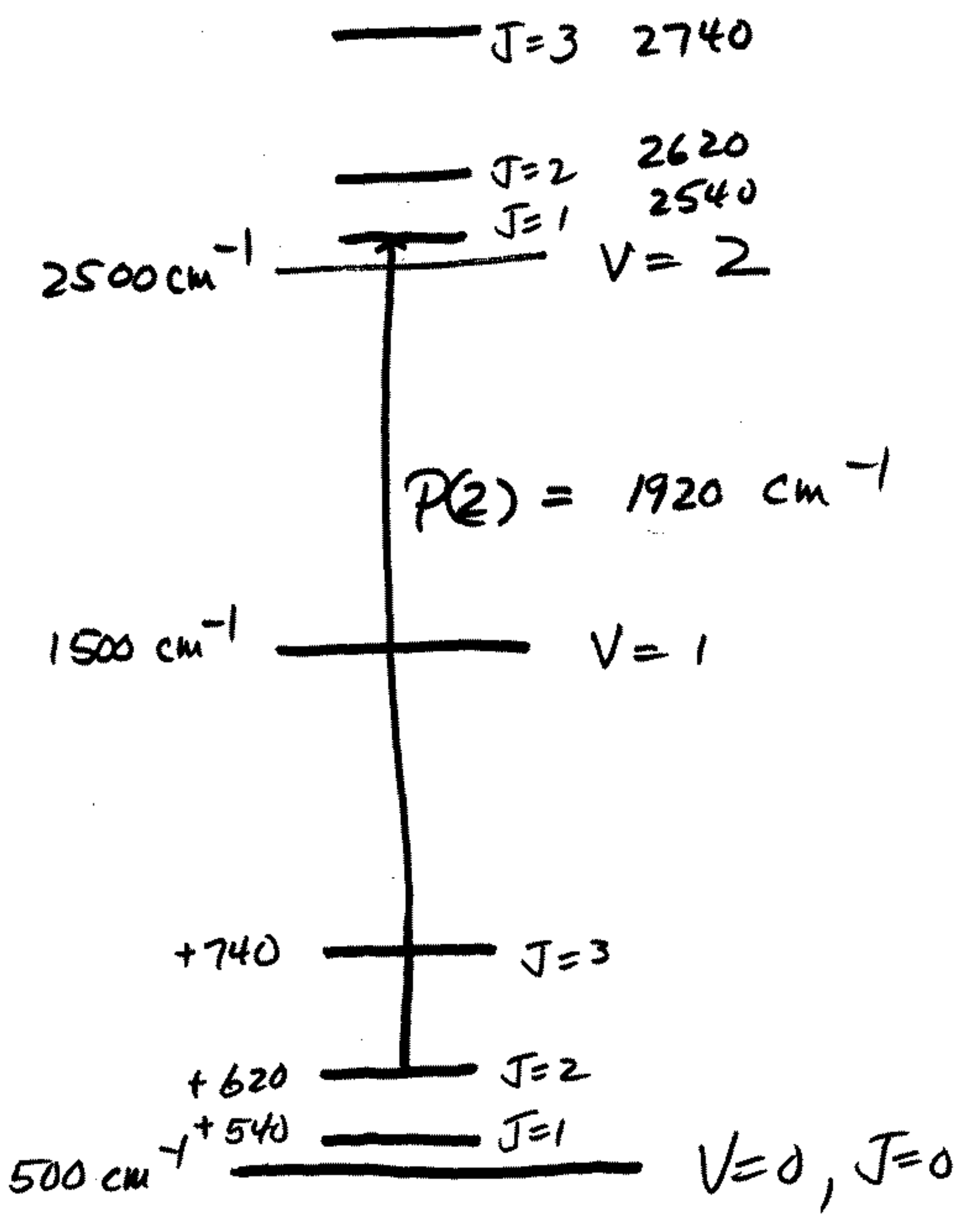
We make one measurement of the energy of the system. What is the probability that the value E_1, corresponding to $\hat{H}\psi_1 = E_1\psi_1$ is observed?

Probability $= c_1^2$

[redacted]

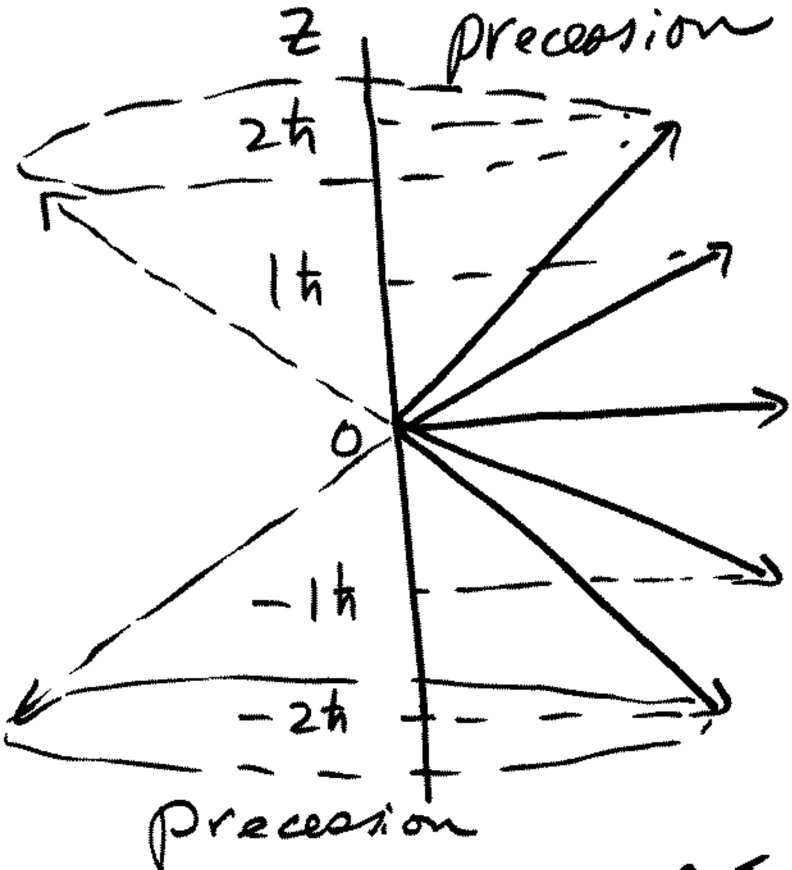
13. (10 points) A real molecule AB has a vibrational frequency $\nu_{osc} = 1000\,\text{cm}^{-1}$ and a rotational constant $\bar{B} = 20\ \text{cm}^{-1}$. Draw the first few energy levels for v = 0 and v = 2 and various J states within these two vibrational levels. Indicate the P(2) transition for the weak v = 0 → 2 absorption and calculate the energy of the P(2) transition.

$E_J = BJ(J+1)$

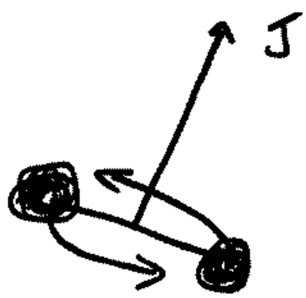


[redacted]

14. (10 points) A rotational state of a diatomic molecule has a degeneracy of 5. Draw a $\vec{J}$ vector diagram showing all 5 of these possible angular momentum states, show also their precession, and give the length of the vectors in units of $\hbar$. Draw also a diatomic molecule on one of the vectors to show how the molecule is oriented with respect to the $\vec{J}$ vector, and show the direction of its rotation to match that vector. A separate picture is ok.

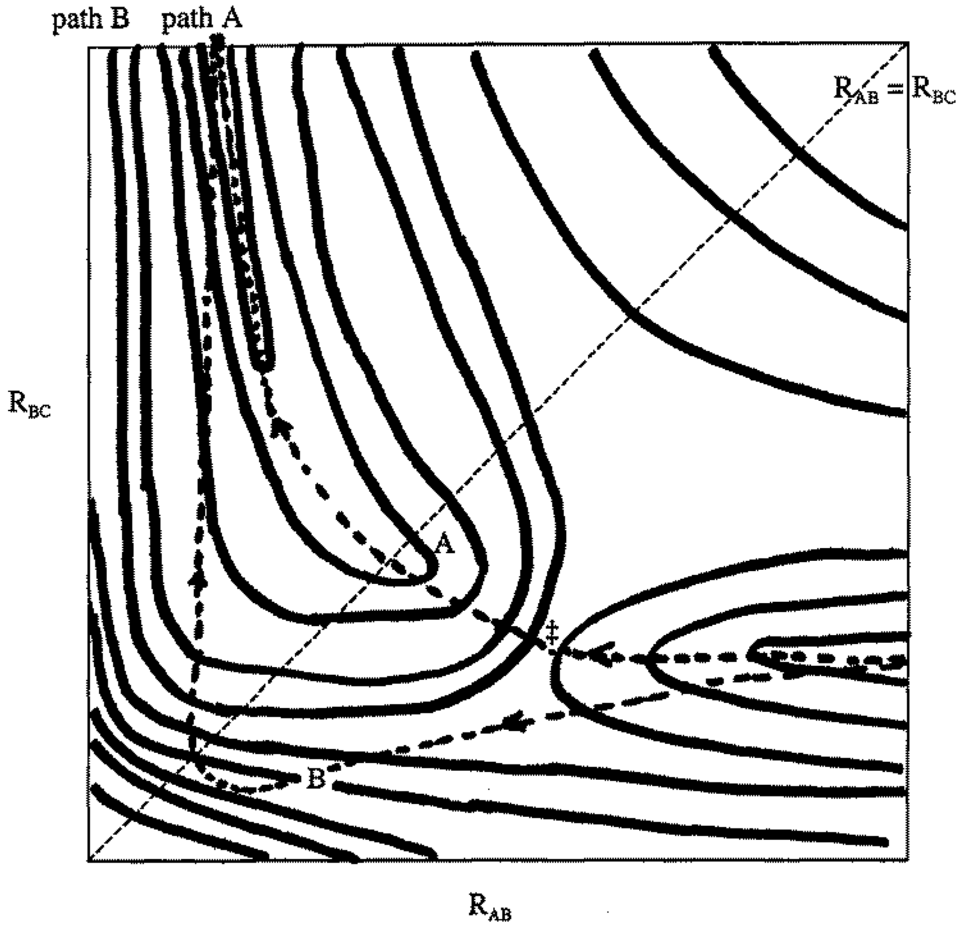


length of vector is $2.45\,\hbar$

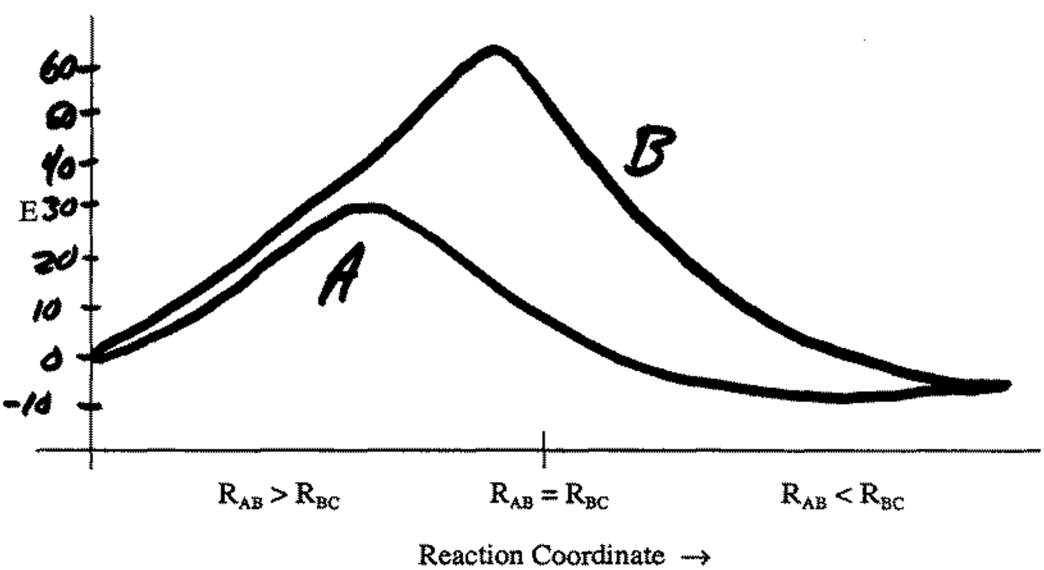


[redacted]

15. (15 points) The contour map of a 3D potential surface is shown below for the reaction $A + BC \rightarrow AB + C$. Each contour is 10 kJ/mole. ‡ is the transition state barrier.

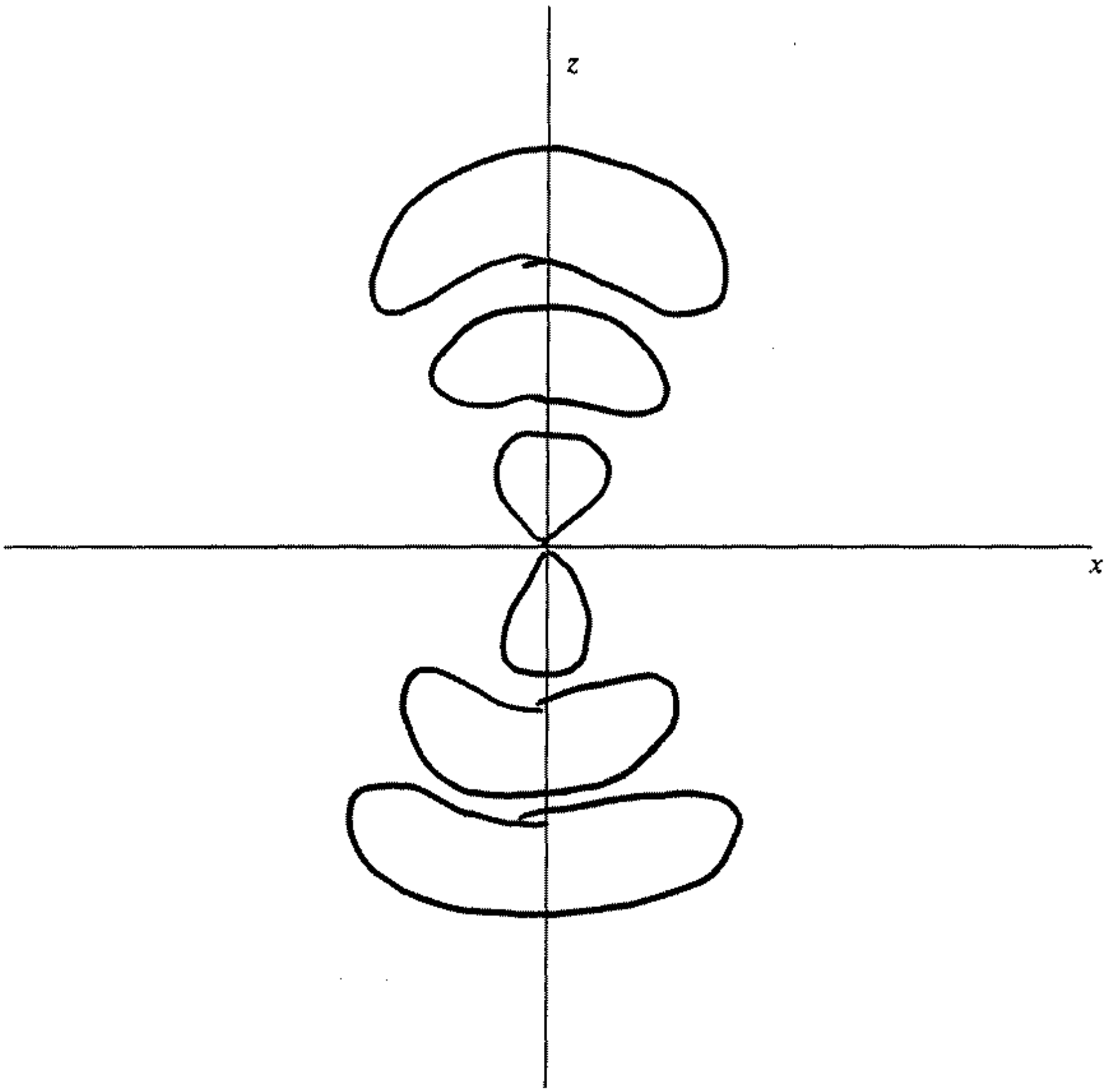


On the axis below, draw the reaction coordinate energy for the two paths A and B shown above.



[redacted]

16. (10 points) Sketch a cross section of the probability density for an electron in a $4p_z$ orbital of an H atom:



Specify the number of angular and radial nodes.

number of angular nodes = 1

number of radial nodes = 2

[redacted]

17. (10 points) A wave packet is composed of 4 states, with frequencies 3000 cm^{-1}, 3100 cm^{-1}, 3200 cm^{-1} and 3300 cm^{-1}. What are the possible different beat frequencies that will be observed?

3300 - 3200 = 100
3200 - 3100 = 100
3300 - 3100 = 200
3300 - 3000 = 300
3100 - 3000 = 100
3200 - 3000 = 200

6 possible beats

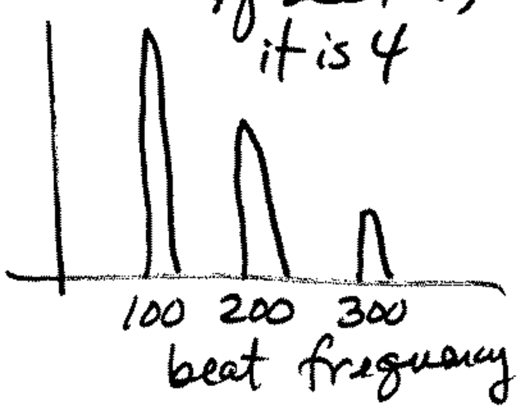
3 - 100
2 - 200
1 - 300

intensity ratio would be 3:2:1
we would only see 3 beat frequencies

If we know there are 3 or 4 states in the above superposition and we obtain the total quantum beat data, we now want to figure out whether 3 or 4 states are in the superposition. If the matrix elements for excitation and detection are all approximately equal, is it possible to detect how many states are participating in the superposition by observing the frequencies and amplitudes of the quantum beat signals? Why or why not?

Yes, If there are only 3 states, they could be 3000, 3100, and 3300. This would also give 100, 200, and 300. But the intensity ratio would be 1:1:1 - only 3 possible beats

If see this, it is 4



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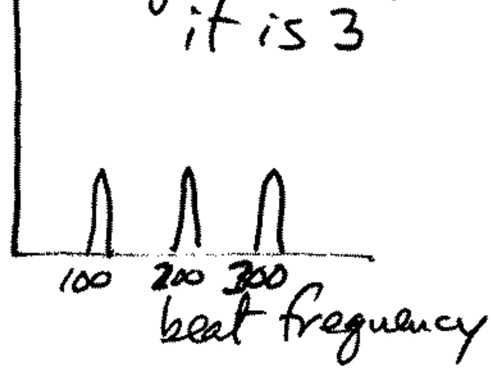

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