

Chem 344 Final Exam

Tuesday, Dec. 11, 2007, 3-?? PM

Closed book exam, only pencils and calculators permitted. You may bring and use one 8 1/2 x 11" paper with anything on it. No Computers. Put all of your work in the answer book. If you need graph paper there are sheets available. If you work out graphical values like slope and intercept on your calculator, you should fully explain your method, put in intermediate values and describe the result. "Floating" answers without substantiation receive little credit. Possibly useful information is at the end of the exam.

Good Luck!!

1. (19) Consider the cyclopropane molecule, C_3H_6 . Quantum mechanically, this presents a complex multi-variable problem due to its 9 nuclei and 24 electrons. Separation of variables for cyclopropane is a major problem, but it can be accomplished with a series of approximations.

- Give an expression for the complete molecular Hamiltonian (energy operator)
- Indicate the physical meaning of each term

Answer only 3 of the following

- Describe the approximation used to separate the nuclear motion from the electron motion.
- How are internal nuclear motions separated from the translation and rotational motion?
- What terms make the vibrational coordinates (internal motions of the nuclei) not separable?
- What approximation can be used to separate the vibrations into one-dimensional harmonic oscillator problems. Include a brief statement of what is lost.
- What term in the Hamiltonian prevents separation of the electron wavefunction into one-electron equations? What approximation is used to overcome this?

2. (4) Give the lowest energy electron configuration for **only one of the following pairs**:

- Os^{+4} , and Mo
- Li_2 and F_2

3. (12) The H-atom solution is the basis for all of our understanding of the electronic structure of atoms and functionally of molecules, so it is important to know the shapes and forms of these solutions. **Sketch only 3 of the following** pairs of H-atom-related wavefunctions/orbitals:

- $Y_{lm}(\theta, \phi)$ for $l = 2, m = 1$ and $l = 3, m = 0$
- $R_{nl}(r)$ for $n = 4, l = 3$, and $n = 3, l = 0$
- $4\pi r^2 R_{nl}^2(r)$ for the same values of n, l as in *part b*
- π -bonding orbital on N_2 composed of $2p_x$ and $2p_y$ orbitals on N
- σ -anti-bonding orbital on N_2 composed of $2p_z$ orbitals on N

4. (5) In class we discussed two separate methods of using spectroscopy to determine secondary structure in proteins and peptides, using IR or CD spectra. Briefly describe **one of these**.

5. (12) We used a postulate approach to learning quantum mechanics in the Schrodinger picture:

Answer only 4 of the following:

- Briefly explain the physical interpretation of the wavefunction (this relates to Postulate 1).
- Briefly discuss the physical meaning of the eigenvalue if the state is an eigenfunction of an operator that corresponds to some observable (this would relate to Postulate 3).
- What is the angular momentum projected on the z-axis for an electron in the H-atom $3d_{-2}$ ($m_l = -2$) orbital? Explain your answer (*one line answer*).
- Briefly discuss how to evaluate some observable when the state of the system (atom or molecule) does not correspond to an eigenvalue of the operator for that observable (this would relate to Postulate 4).
- ~~What is the angular momentum projected on the z-axis for an electron in the H-atom $3d_{xz}$ orbital? Explain your answer (*set up, do not solve—but answer is simple if you recognize it*)~~
- Explain how to determine the probability of finding an electron within Bohr's radius of the nucleus.
- Briefly explain why s-orbitals have a non-zero value for R_{nl} at the nucleus, but the $l \neq 0$ solutions (p,d,f etc.) do not. Hint: think about the function.

6. ~~By use of a molecular orbital diagram, describe the bonding and anti-bonding orbitals in BH_3 , which has a trigonal geometry and is planar.~~

- ~~Sketch out the diagram for the valence orbitals (you may ignore the B(1s), but do not miscount the electrons). Label the orbitals in a consistent manner. Hint: it is NOT linear.~~
- ~~Fill in the occupied orbitals, and determine the lowest energy configuration.~~

Answer only 2 of the following:

- ~~Is this a paramagnetic or diamagnetic configuration? Why?~~
- ~~Describe the bond order for EACH bond.~~
- ~~Describe the filling arrangement (configuration) for the first excited electronic state.~~
- ~~Under what conditions for this excited configuration above (give some specific properties of the state?) will the transition from the ground state be allowed?~~

7. (8) Electronic spectra of atoms are very sharp (line spectra) and those of molecules are normally broad (band spectra).

Answer only 2 of the following:

- Please give a brief explanation of the source of this difference between atomic and molecular electronic spectra.
- Briefly explain why fluorescence spectra have vibrational characteristics of the ground state and absorption those of the excited state.
- Briefly explain why the lowest energy absorption transitions (the low frequency part of the band) will tend to be at a lower frequency as temperature increases for large molecule.
- Describe the expected absorbance and fluorescence band profiles if the potential surfaces of ground and excited states are identical in shape and displacement

8. Energy levels for the particle in a box problem diverge (get further apart) as n increases and those for a harmonic oscillator have a constant separation, however for a truncated (finite potential) box, for the anharmonic oscillator and for the H-atom problem, the separation between energy levels collapses as the quantum numbers increase.

Answer only 2 of the following:

- Briefly give a physical explanation for this behavior.
- The particle in a box wave functions terminate ($\psi=0$) at the walls, but the shortened box wave functions do not. Briefly explain this OR describe a consequence of this behavior if you had two boxes with a barrier between them.
- The anharmonic wave functions shift with regard to the harmonic ones. Briefly explain.

9. (12) We used the Jablonski diagram to trace the flow of energy in an excited molecule:
- Sketch a Jablonski diagram and label the states and possible energy conversion pathways

Answer only 1 (one) of the following:

- use it to explain why the lifetime of fluorescence can be made shorter by addition of heavy atom containing solvent, such as Iodoform, CHI_3 .
- Differentiate between internal conversion and vibrational relaxation.
- Non-radiative decay rates normally increase with increase in temperature. Use this to determine the effect of temperature on fluorescence quantum yield and lifetime.

10. (10) Consider the vibrational spectra of the CO diatomic molecule in its ground electronic state.

Answer either a or b of the following

- If the fundamental frequency of CO is 2170 cm^{-1} , what is k ? (watch your units!, MW: C = 12, O = 16)
- How much would the vibrational frequency shift (and to where) for $^{13}\text{C}^{18}\text{O}$?

Answer either c or d of the following

- In the gas phase, the CO IR spectrum has rotational structure. Describe which bands are observed and to what transitions they correspond and what the observed spacings are.
- How will the Raman spectra differ? (Bands, spacings, selection rules?)

11. (9) Consider Methane, CH_4 , vibrational spectra:

Answer only 3 of the following

- Explain why if all 4 C-H bonds stretch in phase for methane, the corresponding normal mode is not observed in the IR spectrum but it is in the Raman.
- Propose a different mixture of C-H stretching motions that is observed in the IR, and explain why.
- For the methane spectrum there are two dominant IR transitions at $\sim 2850 \text{ cm}^{-1}$ and at $\sim 1450 \text{ cm}^{-1}$. Explain how they differ in terms of local vibrational motion.
- The transition in part c are $v=0 \rightarrow v=1$, briefly explain what you would predict for the $v=0 \rightarrow v=2$ vibrational spectrum if the potential were more realistic, i.e. anharmonic.
- Determine the total number of fundamental vibrational modes for methane and fluoromethane, CFH_3 . How would you expect their IR spectra to differ?.

12. (15) Glycogen synthase kinase 3 β (GSK-3 β) phosphorylates the protein τ , and this process accompanies the onset of Alzheimer's disease. A compound Ro31-8220 seems to inhibit the process. From the following Rate ($10^{-8} \mu\text{M s}^{-1}$) data:

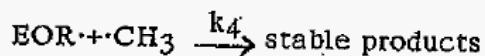
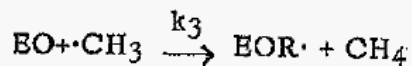
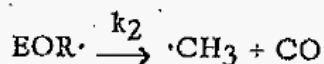
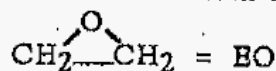
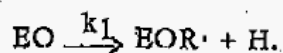
[S] (μM)	Rate ($10^{-8} \mu\text{M s}^{-1}$) Data	
	[I] = 0	[I] = 200 μM
66.7	4.17	3.33
40.0	3.97	2.98
20.0	3.62	2.38
13.3	3.27	1.81
10.0	2.98	1.39
6.67	2.31	1.04

Determine K_m and V_{max} for GSK-3 β , and for the inhibitor determine K_m^* and K_i

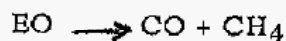
13. (15) Answer the following mechanism question:

The following mechanism has been proposed for the thermal decomposition of ethylene oxide.

- a. Derive a rate law for this decomposition consistent with this mechanism



- b. Which steps propagate a chain?
- c. What approximations are necessary to make the rate law agree with the observed first order dependence on EO?
- d. Since the reaction is first order, you might have proposed a one-step mechanism, eg.



How could you determine which was correct?

