C475A – Honors Quantum Chemistry and Spectroscopy
Exam 2

Due Nov. 24 2003 at 9:30am
Open Book and Open Notes, Maple solutions are permitted

SOLUTIONS SHOULD BE WORKED ON SEPARATE SHEETS (OR PRINTOUTS) AND MUST BE SUBMITTED **IN NUMERICAL ORDER,** WITH THIS EXAM SHEET STAPLED TO THE TOP. ALL ANSWERS MUST BE CIRCLED. ALL COMPUTER WORK SHOULD BE SUFFICIENTLY ANNOTATED AS TO BE READILY UNDERSTOOD.

ALL PROBLEMS MUST HAVE SERIOUS ATTEMPTED SOLUTIONS IN ORDER TO BE GRADED ON A CURVE.

This exam, the questions within and the material pertaining to those questions, must not be discussed in any form in any manner with *anyone* inside or outside of this class (except the instructor) until *AFTER* the exams have been turned in.

By signing below I certify that I have neither given nor received assistance from *anyone* on this exam and I agree to retain the original computer files to my work and to provide them upon request.

Your name:_____

Student ID#:_____

Signature:_____

IF YOU WANT YOUR GRADED EXAM LEFT IN THE HALLWAY SIGN BELOW:

Signature:_____

Total Points: 125


Question 1:_____/20

Question 2:_____/20

Question 3:_____/25

Question 4:_____/25

Question 5:_____/10

Question 6:_____/15

Question 7: _____/20


Total: _____/135

1) a) *Work out* the possible term symbols for the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ configuration of Titanium (Ti).

b) Which term and level (level is the term symbol with total J included) is the ground state for Ti?
i) Explain why. (Be sure to mention which component in the Hamiltonian for the Hf atom is responsible for making this the lowest energy term and level).
ii) Is this state degenerate or not?
iii) If this state is not degenerate, explain why not. If it is, explain how many states make up the lowest energy level and how you could you lift this degeneracy?

c) In the **absence** of spin-orbit coupling and interelectron repulsion terms in the atomic Hamiltonian, which term(s) would be lowest in energy?

d)
i)What would the ground state terms (and levels including J) for Zr and Ti be? (short)

ii) Order the elements Ti, Zr, and Hf according to the magnitude of the difference between the lowest and next lowest terms/levels. Briefly explain the choice of ordering.

e) Repeat part (a) for the $3d^1 4p^1$ *excited* state of Ti.

**2) Quark Screening? (Perturbation Theory)**

So far we have assumed that the proton is an infinitesimal point. However, in the Standard Model the proton itself is actually just the lowest energy (ground state) of two up quarks (charge +2/3), and one down quark (charge -1/3). However, such a calculation is "beyond the scope of this course" as they say, so for our purposes why don't you approximate the proton as a uniformly charged sphere of radius $10^{-13}$ cm and *use perturbation theory to calculate a first order correction in the ground state energy of hydrogen due to the finite size of the proton.* The potential energy of an electron that has penetrated the nucleus and is at a distance $r$ from the center is $-eQ/(4\pi\varepsilon_o r)$ where Q is the amount of charge contained in a sphere of radius $r$. Hint: you may approximate the exp(-r) term in the H atom wave function

5a) What are $H^0$ and $H^1$ for this problem?

5b) What is the first order correction to the energy? What percent difference is this?

5c) Do you expect the $E^1$ correction to the energy to be bigger for the ground state or the first excited state (1s vs. 2s). *Explain why* without resorting to a calculation.

Harmonic Oscillator and Selection Rules
3) a) What is the selection rule for the transitions between the vibrational levels of the **Harmonic oscillator**?

b) To calculate the transition dipole moment you need to know the dipole moment operator for that system. If $x$ represents the internuclear coordinate for the H.O., the appropriate dipole moment operator to use is given by: $\mu = \mu_0 + \dfrac{d\mu}{dx}x + h.o.t.$. Here $\mu_0$ is the permanent dipole moment of the molecule, and $d\mu/dx$ is the change in dipole moment of the bond with internuclear separation. We can ignore the higher order terms in the Taylor expansion. ***Explicitly*** *evaluate the* ***value*** *of the transition dipole moment for a transition between the n=0 and n=1, and the n=0 and n=2 vibrational states of a harmonic oscillator* (*make sure you use properly normalized wave-functions*) (express your answer in units of the reduced mass, $\mu_m$, the force constant, $k$, the molecule dependent value $d\mu/dx$, and Planck's constant). Are your results consistent with the selection rules for the Harmonic oscillator? Explain (briefly).

c) Make an animation of the time evolution of a linear superposition of the n=0 and n=1 states for the Harmonic oscillator. *Interpret the resulting motion.* (remember, for the H.O. you are plotting the difference from the equilibrium bond length as a function of time).

d) From your calculation in "b" your animation in "c", and your qualitative understanding of how the electromagnetic field of a light wave could excite a vibration, argue why the $N_2$ and $O_2$ in the atmosphere don't absorb infrared radiation, but $CO_2$ does.

e) Consider the generic superposition of two energy eigenstates for an unspecified potential at time t=0 given by $\psi_1(x,0) + \psi_2(x,0)$. Write out the wavefunction at arbitrary time $t$. If the energies corresponding to $\psi_1$ and $\psi_2$ are energies $E_1$ and $E_2$ show that this superposition will always correspond to a physical state containing a "beat term" oscillating a frequency related to the difference in energy $E_2-E_1$ and Planck's constant (you should only need paper, pencil, and Euler, for this one).

**4) IR Spectroscopy**
An experimental high-resolution IR spectrum for HCl is included on the last page of the exam.

a) Why do we see a series of lines rather than a single vibrational peak in the high-resolution spectrum?

b) Calculate the bond length of the HCl molecule from the data in the graph.

c) Calculate the force constant of the bond from the data in the graph.

d) Why do you think each of the peaks is split into a doublet? Calculate the splitting you would expect from your answer and compare it with the data.

e) Could you use this data to estimate the temperature of the sample? If so, make a guess at the temperature and justify it. If not, explain why not.

**Hydrogen and more**
**5)** In lecture and reading you learned that the energy of an electron in a hydrogen-like atom depended *only* on the principal quantum, n.

a) Explain *in a brief paragraph* why the energy of an electron depends on orbital angular momentum, $l$, in a mulitelectron atom.

b) Now let's compare your analysis in part "a" with a calculation. First, calculate both the *most likely* **and** the *average* distance from the nucleus that you would find an electron in a 2s and a 2p orbital in doubly ionized Li. Is this what you expected? *Explain.*

**6) Stern-Gerlach and Spin**

A series of hydrogen atoms is prepared in the state:
$(3 \, \alpha(1) + i \, \beta(1))$

a) Determine if this spin function is normalized. If not, normalize it.

b) Determine if this spin function is an eigenfunction of the spin operators $S_{z\text{-tot}}$ and $S^2_{tot}$, and, if possible, determine the eigenvalues.

c) If a beam of atoms in this state were passed through an inhomogeneous magnetic field oriented along the **z**-axis (as in the Stern-Gerlach experiment), what would the idealized experimental result look like? (be as quantitative as possible).

d) What are the spin functions for each of the beams emerging from the magnet in 6c)? If these beams were each individually subjected to another pass through a magnet with a magnetic field identical to that they were subjected to in 6c) (mag field along **z**-axis) what would the experimental result look like?

6e) What do we know about the value of the projection of **S** along the **x**-axis for the the beams emerging from the magnets in 6d)? (i.e. pass the beam emerging from 6d through another experimental Stern-Gerlach setup, this time with the field at a right angle to the first field (the electrons are moving in the y direction).

**7) The Morse Potential for HCl.**
The Morse potential for the bond in $H^{35}Cl$ can be given by:

$$V(x)=D_e(1-e^{-\beta x})^2$$

With $D_e=7.31\times10^{-19}$ J/molecule, and $\beta=1.82\times10^{10}\,m^{-1}$

**Use the variational method to find the energies of the ground state, the first excited state, and the second excited state for the Morse Potential system.** Hint #1: make a wise choice of trial functions (do you know any that should be pretty close?). (Hint #2 If you want to check your values, is it possible (maybe even easier?) to solve this problem use perturbation theory).

Compare these values with the results you got by taking a Taylor expansion of this potential (remember problem 5-8) and treating it like a S.H.O. Are your variational values more or less accurate? *Compare the energy level spacing in your calculation to that expected from the S.H.O.*
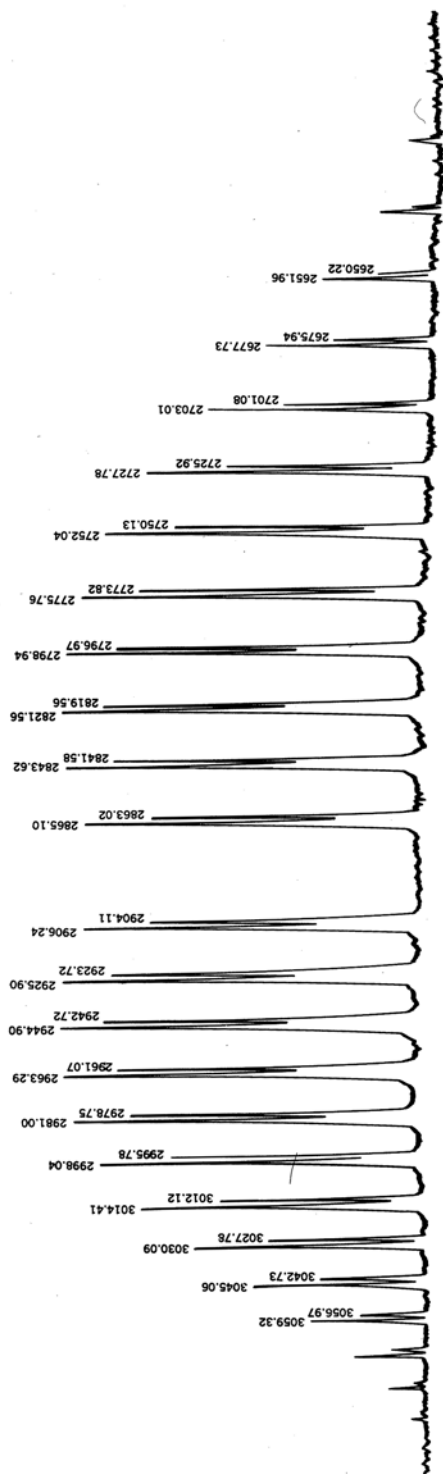
The problem will be graded by choosing the *lowest* possible score from this table:
Ground state is:

| % Above my energy | % Total Points |
|---|---|
| 1-2% | 50 |
| .001-1% | 75 |
| <.0015% | 95 |
| <.001% | 100 |

Any excited state is:

| % Above my energy | % Total Points |
|---|---|
| 5 or more % | 50 |
| 2-5% | 75 |
| 1-2% | 95 |
| <1% | 100 |

IR Spectrum of HCl, (peak positions are in cm$^{-1}$)

2650.22
2651.96
2675.94
2677.73
2701.08
2703.01
2725.92
2727.78
2750.13
2752.04
2773.82
2775.76
2796.97
2798.94
2819.56
2821.56
2841.58
2843.62
2863.02
2865.10
2904.11
2906.24
2923.72
2925.90
2942.72
2944.90
2961.07
2963.29
2978.75
2981.00
2995.78
2998.04
3012.12
3014.41
3027.78
3030.09
3042.73
3045.06
3056.97
3059.32