

C455A -Quantum Chemistry and Spectroscopy

Exam 2

May 24, 2004

Exams will be collected at 9:25:00 am SHARP

1 ONE SIDED 8.5x11" page of notes is allowed

-ALL ANSWERS MUST BE IN THE ANSWER BOX WHEN PROVIDED

-CROSSED OUT/PARTIALLY ERASED WORK WILL BE IGNORED

-NO PARTIAL CREDIT ON NUMERICAL PROBLEMS WITHOUT A FORMULA

-NO PARTIAL CREDIT ON "PHYSICALLY IMPLAUSIBLE" ANSWERS UNLESS THE ERROR IS RECOGNIZED

*Key*

Your name: \_\_\_\_\_ *Key*

Student ID#: \_\_\_\_\_

I have neither received nor provided assistance of any kind on this exam.

Signature: \_\_\_\_\_

*I attend lecture/discussion on average: <1, 1-2, 2-3, 3-4 times per week*  
(your answer to this question will not affect your grade)

I want this exam to be left in the hallway for collection: YES / NO \_\_\_\_\_

In the following,  $u$  and  $v$  are functions of  $x$ , and  $a$  and  $n$  and  $m$  are real numbers

$$\int u \, dv = uv - \int v \, du$$

$$\frac{d}{dx}(uv) = u \frac{dv}{dx} + v \frac{du}{dx}$$

$$\int x^n \, dx = \frac{x^{n+1}}{n+1} \text{ except } n = -1$$

$$\frac{d}{dx} \left( \frac{1}{v} \right) = \frac{1}{v^2} \frac{dv}{dx}$$

$$\int \frac{dx}{x} = \ln x$$

$$\frac{d}{dx}(u^n) = nu^{n-1} \frac{du}{dx}$$

$$\int e^u \, dx = \frac{1}{a} e^{ax}$$

$$\frac{d}{dx} \left( \frac{1}{u^n} \right) = -\frac{n}{u^{n+1}} \frac{du}{dx}$$

$$\int (\sin ax) \, dx = -\frac{1}{a} \cos ax$$

$$\frac{d}{dx}[f(u)] = \frac{d}{du}[f(u)] \cdot \frac{du}{dx}$$

$$\int (\cos ax) \, dx = \frac{1}{a} \sin ax$$

$$\frac{d}{dx}(u^m v^n) = u^{m-1} v^{n-1} \left( nv \frac{du}{dx} + mu \frac{dv}{dx} \right)$$

$$\int (\sin^2 ax) \, dx = \frac{1}{2} x - \frac{1}{4a} \sin 2ax$$

$$\frac{d}{dx}(e^u) = e^u \frac{du}{dx}$$

$$\int (x \sin^2 ax) \, dx = \frac{x^2}{4} - \frac{\cos 2ax}{8a^2} - \frac{x \sin 2ax}{4a}$$

$$\frac{d \sin x}{dx} = \cos x$$

$$\int (\cos^2 ax) \, dx = \frac{1}{2} x + \frac{1}{4a} \sin 2ax$$

$$\frac{d \cos x}{dx} = -\sin x$$

$$\int (x^2 \sin^2 ax) \, dx = \frac{1}{6} x^3 - \left( \frac{1}{4a} x^2 - \frac{1}{8a^3} \right) \sin 2ax - \frac{1}{4a^2} x \cos 2ax$$

$$\frac{d \sin u}{dx} = \frac{du}{dx} \cos u$$

$$\int (x^2 \cos^2 ax) \, dx = \frac{1}{6} x^3 + \left( \frac{1}{4a} x^2 - \frac{1}{8a^3} \right) \sin 2ax + \frac{1}{4a^2} x \cos 2ax$$

$$\frac{d \cos u}{dx} = -\frac{du}{dx} \sin u$$

$$\int x^n e^u \, dx = \frac{x^{n+1}}{a} \int x^{n-1} e^u \, dx$$

$$\int \frac{dx}{x^{n+1}} = \frac{1}{n+1} x^{-n} + \frac{a}{n+1} \int \frac{dx}{x^{n+1}}$$

$$\int \sin \left( \frac{mx}{a} \right) \sin \left( \frac{nx}{a} \right) \, dx = \frac{1}{2} \cos \left( \frac{mx}{a} \right) \cos \left( \frac{nx}{a} \right) - \frac{a}{2} \sin \left( \frac{mx}{a} \right) \left[ \cos \left( \frac{nx}{a} \right) \right]_0^a$$

$$\int \sin^2 mx \, dx = \frac{1}{2} \cos^2 mx - \frac{a}{2}$$

$$\int \cos \left( \frac{mx}{a} \right) \cos \left( \frac{nx}{a} \right) \, dx = \frac{1}{2} \cos \left( \frac{(m+n)x}{a} \right) + \frac{a}{2} \sin \left( \frac{mx}{a} \right) \left[ \cos \left( \frac{nx}{a} \right) \right]_0^a$$

$$\int \frac{dx}{\sqrt{x}} = \int \frac{dx}{\sqrt{a^2+x^2}} = \frac{1}{\sqrt{a^2}} \int \frac{dx}{\sqrt{1+(x/a)^2}}$$

$$\int x^n e^{-ax^2} \, dx = \frac{n!}{a^{n+1}} (a > 0, n \text{ positive integer})$$

$$\int x^{2n} e^{-ax^2} \, dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}} (a > 0, n \text{ positive integer})$$

$$\int x^{2n+1} e^{-ax^2} \, dx = \frac{n!}{2 a^{n+1}} (a > 0, n \text{ positive integer})$$

$$\int e^{-ax^2} \, dx = \left( \frac{\pi}{4a} \right)^{1/2}$$

The First Few Spherical Harmonics

Total Points: 100

Question 1: \_\_\_\_\_ /10

Question 2: \_\_\_\_\_ /20

Question 3: \_\_\_\_\_ /30

Question 4: \_\_\_\_\_ /10

Question 5: \_\_\_\_\_ /30

Total: \_\_\_\_\_ /

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi}$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$

$$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi}$$

$$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi}$$

$$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{2i\phi}$$

$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi}$$

Potentially Useful Information:

Workfunctions of Metals:

Li	2.3 eV
Ca	2.87 eV
Al	4.28 eV
Au	5.1 eV

Values of Some Physical Constants

Constant	Symbol	Value
Atomic mass constant	$amu$	$1.660\ 5402 \times 10^{-23} \text{ kg}$
Avogadro constant	$N_A$	$6.022\ 1367 \times 10^{23} \text{ mol}^{-1}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\ 0154 \times 10^{-24} \text{ J} \cdot \text{T}^{-1}$
Bohr radius	$a_0 = 4\pi\epsilon_0^2/r_e e^2$	$5.291\ 772\ 49 \times 10^{-11} \text{ m}$
Boltzmann constant	$k_B$	$1.380\ 658 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
Electron rest mass	$m_e$	$0.959\ 468 \text{ cm}^{-1}$
Gravitational constant	$G$	$6.672\ 59 \times 10^{-11} \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-2}$
Molar gas constant	$R$	$8.3145101 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
		$0.083\ 1451 \text{ dm}^3 \cdot \text{bar K}^{-1} \cdot \text{mol}^{-1}$
		$0.082\ 0578 \text{ dm}^3 \cdot \text{atm K}^{-1} \cdot \text{mol}^{-1}$
Molar volume, ideal gas (one bar, 0°C)		$22.711\ 08 \text{ L} \cdot \text{mol}^{-1}$
(one atm, 0°C)		$22.414\ 09 \text{ L} \cdot \text{mol}^{-1}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\ 7866 \times 10^{-37} \text{ J} \cdot \text{T}^{-1}$
Permittivity of vacuum	$\epsilon_0$	$8.854\ 187\ 816 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$
Planck constant	$4\pi\epsilon_0 c$	$1.112\ 650\ 056 \times 10^{-10} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$
	$\hbar$	$6.626\ 0755 \times 10^{-34} \text{ J} \cdot \text{s}$
Proton charge	$e$	$1.054\ 572\ 66 \times 10^{-19} \text{ C}$
Proton magnetogyric ratio	$\gamma_p$	$2.675\ 221\ 28 \times 10^4 \text{ s}^{-1} \cdot \text{T}^{-1}$
Proton rest mass	$m_p$	$1.672\ 6231 \times 10^{-27} \text{ kg}$
Rydberg constant (Bohr)	$R_\infty = m_e e^4 / 8\epsilon_0^2 \hbar^2$	$2.179\ 8736 \times 10^{-23} \text{ J}$
Rydberg constant for H	$R_H$	$109\ 737.31534 \text{ cm}^{-1}$
Speed of light in vacuum	$c$	$109677.581 \text{ cm}^{-1}$
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4 / 15\hbar^3 c^2$	$299\ 792\ 458 \text{ m} \cdot \text{s}^{-4} (\text{defined})$
		$5.670\ 51 \times 10^{-8} \text{ J} \cdot \text{m}^{-2} \cdot \text{K}^{-4} \cdot \text{s}^{-1}$

### 1). Rigid rotor and spherical harmonics (10 points)

We can visualize the shape of the spherical harmonics by plotting them in 3D using the format:  $r = Y_l^m(\theta, \phi)$ .

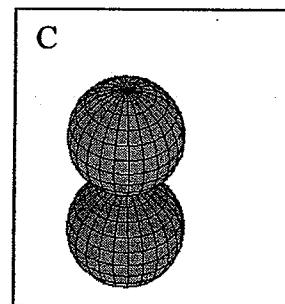
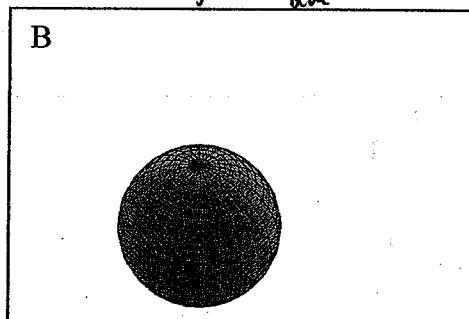
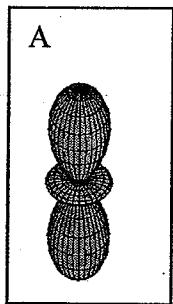
1a) We know that the spherical harmonics are the solutions to the Schrödinger equation for the diatomic rigid rotor. Order the rigid rotor wave functions shown below from lowest to highest energy. (eg A, B, C) (3 points)

$$B < C < A$$

(right or wrong order  
+3 or 0)

1b) Explain your choice of ordering based on the shapes in the figures below, in particular what tells you about the kinetic energy. (7 points)

The functions are ordered from fewest  $\rightarrow$  most # of nodes in the wave function, more nodes  $\Rightarrow$  more KE  
(sharper curvature  $\Rightarrow$  higher  $\frac{d^2}{dr^2} + l(l+1)$  term)



(most nodes + KE)  
+ 7  
(1 point for each)  
(+2 for harmonic  $l$ )  
value written

### 2) Hydrogen atom wave functions and their interpretation in 3-dimensions (20 points)

The wavefunction for the ground state of the H atom is:  $\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-r/a_0}$

2a) Sketch the radial probability distribution (probability of finding the electron at some distance between  $r$  and  $r+dr$  from the nucleus) for an electron in the  $\psi_{100}$  state. Be sure to **CALCULATE** (and label your sketch with) the **most probable value of  $r$  for this state**. (15 points)

$$+4 \quad P(r) dr / 4\pi r^2 dr = \frac{4r^2}{a_0^3} e^{-2r/a_0}$$

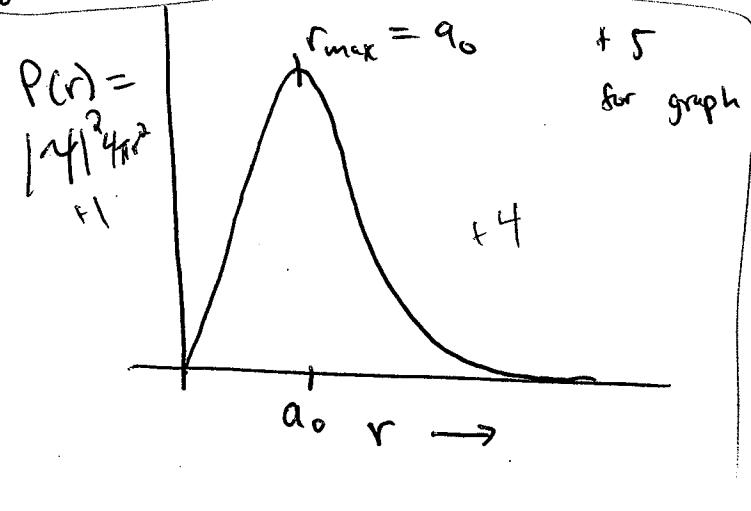
$$\text{max when } \frac{dP}{dr} = 0 = \frac{8r}{a_0^3} e^{-2r/a_0} - \frac{8r^2 e^{-2r/a_0}}{a_0^4}$$

$$+4 \quad 0 = \frac{8r e^{-2r/a_0}}{a_0^3} \left( 1 - \frac{r}{a_0} \right)$$

$$1 - \frac{r}{a_0} = 0$$

$$\boxed{r = a_0} \quad +2$$

+10 for  $a_0$  value



2b) For the H-atom, the electron energy depends ONLY on the principle quantum number n (i.e. the energy of the 2s state is the same as the 2p state). For heavier atoms, this is not the case. Explain why the energy of an electron depends on angular momentum (why the energies are ordered s < p < d < f) for atoms heavier than H but not for H. (5 points)

The effect is due to interelectron repulsion and screening concept

ie) high  $\ell$  orbitals distribute e<sup>-</sup> probability farther from nucleus where they penetrate the inner orbitals less + experience a reduced nuclear charge  $\Rightarrow$  lower energy

### 3) Multi-electron Atoms (30 points)

3a) Work out (simply listing is unacceptable) the possible term symbols for the  $1s^2 2s^2 2p^4$  configuration of O (including the possible J values). (13 points)

$M_L$	$m_S$	$M_2$	$M_{2s}$	$M_{\text{total}}$	$M_{S\text{ total}}$
0	+1/2	+	-1/2	0	0
+	+1/2	0	-1/2	1	0
-	-1/2	0	+1/2	1	0
+	+1/2	-1	-1/2	0	0
+	-1/2	-1	+1/2	0	0
+	+1/2	0	+1/2	1	0
+	-1/2	0	-1/2	1	-1
+	+1/2	-1	+1/2	0	1
+	-1/2	-1	-1/2	0	-1
0	+1/2	0	-1/2	0	0
0	+1/2	-1	+1/2	-1	1
0	+1/2	-1	-1/2	-1	0
0	-1/2	-1	-1/2	-1	-1
0	-1/2	-1	+1/2	-1	0

$$2p^4 = 2p^2 \text{ (holes same as } e^-)$$

$$\frac{6!}{2!4!} = 15 \text{ states}$$

$L=2 S=0 \Rightarrow ^1D$  term  $J=2, 0$

$L=1 S=1 \Rightarrow ^3P$  term  $J=2, 1, 0$

$L=0 S=0 \Rightarrow ^1S$  term  $S=0$

Terms: 5 points for term 3 for levels

$^1D_2, ^3P_2, ^3P_1, ^3P_0, ^1S_0$

5 points only if no work

3b) Rank the terms and levels from left to right in order from LOWEST to HIGHEST energy (level is the term symbol with total J included). EXPLAIN (briefly). (5 points) largest 5 lowest in energy,

$\cancel{^1P_1}$  filled orbital  $\Rightarrow$  largest  $J$  most stable (within a term), after that largest  $L$

$^3P_2 < ^3P_1 < ^3P_0 < ^1D_2 < ^1S_0$

3c) Passing through a rift in the fabric of space time (yet again), the crew of the Enterprise find themselves in a universe where + and - charge attract according to Coulomb's law, but - charges no longer repel one another. The electrons in this universe possess spin angular momentum (and obey the Pauli principle), but possess no magnetic moment. In this strange universe, re-rank the relative energy differences between the terms and levels you've written above (use = to indicate any that are equal). (Data remarks: "Captain, it's as if the interelectron repulsion and spin-orbit coupling terms in the atomic Hamiltonian have been made zero!") (6 points)

$^3P_2 = ^3P_1 = ^3P_0 = ^1D_2 = ^1S_0$

$\hat{H}_{\text{ee}}$  splits e<sup>-</sup> config into terms - w/o all terms have same energy,  $\hat{H}_{\text{so}}$  splits levels, w/o  $\hat{H}_{\text{so}}$  all levels are same energy

d) What are the possible terms and levels for the  $1s^2 2s^2 2p^6 4s^2 3d^{10} 4p^4$  configuration of Se? (you may simply state the answer if you know them based on your work above) (3 points)

$^1D_2, ^3P_2, ^3P_1, ^3P_0, ^1S_0$  (same as O)

e) Considering the magnitude of the spin-orbit coupling term, would the energy difference between the lowest two levels be larger or smaller for Se than for O? Why (very short answer)? (3 points)

$\hat{H}_{SO} \propto Z^4 \Rightarrow$  level splitting is larger for Se

4) In 1971 a paper was published that applied the variational function  $N e^{-(br^2/a_0^2 - cr/a_0)}$  to the hydrogen atom (where N is a normalization constant, b and c are variational parameters). The paper claimed that minimization of the variational energy with respect to the parameters b and c yielded an energy 0.7% above the true ground state energy of H). Why must the paper be incorrect? (10 points)

$N e^{-cr/a_0}$  is the form of the H-atom (true). Since the  $\phi_{trial}$  contains this term a variational approach should return  $E_{true}$ ! -ie 0% error

#### 5) Rotational/Vibrational Spectra (30 points)

5a) What is/are the selection rule(s) for the transitions between rotational states of a linear diatomic molecule? (2 points)

$$\Delta l = \pm 1$$

5b) Give one physical motivation/interpretation to the selection rule in (a) (2 points)

Conservation of angular momentum of the photon with  $l=1$

An experimental high-resolution IR spectrum for HCl is included on the last page of the exam. The units are displayed in wavenumbers. (you may tear it off for study if you wish).

5c) In two-three sentences, explain why we see a series of lines rather than a single vibrational peak in the high-resolution spectrum? (5 points)

Rotational transitions accompany vibrational transitions, the  $\Delta l = \pm 1$  selection rule leads to a series of evenly spaced rotational transitions superimposed on the vibrational spectrum ( $\Delta n = 1$ ) because (and the absence of the  $\Delta n = 2$   $\Delta l = 0$  peak) many  $l_1$  states are populated at room T

5d) Calculate the bond length of an HCl molecule using the data in the graph. (10 points)

reading  
from graph, Spacing =  $2B \approx 19.66 \text{ cm}^{-1}$  for  ${}^1\text{H} {}^{35}\text{Cl}$  peaks  
 $(= 3.899 \times 10^{-22} \text{ J})$

$$\text{in } \text{cm}^{-1} \quad B = \frac{h}{8\pi c M_0 r} =$$

$$r = \sqrt{\frac{h}{8\pi^2 c M_0 B}} = \sqrt{\frac{6.626 \times 10^{-34} \text{ Js}}{8\pi^2 (3 \times 10^8 \text{ m/s})(1.61 \times 10^{-27} \text{ kg})(9.83 \text{ cm}^{-1})}}$$

$$M = \frac{1 \times 35}{36} \times 1.66 \times 10^{-27} \text{ kg} \\ = 1.61 \times 10^{-27} \text{ kg}$$

Length:

$$1.32 \times 10^{-10} \text{ m} = 1.32 \text{ \AA}$$

e) How would the spectrum of pure  ${}^1\text{H} {}^{80}\text{Br}$  gas be different from the spectrum shown for HCl? (consider specifically i) the position/energy of the central peak (higher, lower, why?), ii) the spacing between the peaks, iii) the number of peaks, and if transitions from states with the same initial and final  $l$  values will be split and if so, by how much). (11 points)

4 i)  $\text{Br}$  is heavier/larger and HBr has a weaker bond/lower k

both Fx shift ~~an~~ peak to lower energy  $\Delta E = \hbar \sqrt{\frac{k}{m}}$

4 ii) Spacing due to ~~rotational~~ transitions goes down  
(bond length increases  $\oplus$  m goes up  $\Rightarrow$  larger I)

$$\Delta E_{\text{rot}} = \frac{\hbar^2}{2I} l(l+1)$$

4 iii) the splitting "within" the rotational peaks is due to the shift in vibrational energy due to the presence of 2 isotopes of Cl - pure  ${}^1\text{H} {}^{80}\text{Br}$  will have no isotope splitting

Note: all underlined effects must be mentioned to receive full credit