CHEM 455A –Quantum Chemistry and Spectroscopy
Exam 2 May 20, 2004
Exams will be collected at 9:20:00 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

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 (circle ONE)
(your answer to this questions will not affect your grade)

I want this exam to be left in the hallway for collection: YES / NO _____(Initial here)

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

$$\int u\,dv = uv - \int v\,du$$
$$\int x^n dx = \frac{x^{n+1}}{n+1} \text{ except } n=-1$$
$$\int \frac{dx}{x} = \ln x$$
$$\int e^{ax} dx = \frac{1}{a} e^{ax}$$
$$\int (\sin ax)\,dx = -\frac{1}{a}\cos ax$$
$$\int (\cos ax)\,dx = \frac{1}{a}\sin ax$$
$$\int (\sin^2 ax)\,dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax$$
$$\int (x\sin^2 ax)\,dx = \frac{x^2}{4} - \frac{\cos 2ax}{8a^2} - \frac{x\sin 2ax}{4a}$$
$$\int (\cos^2 ax)\,dx = \frac{1}{2}x + \frac{1}{4a}\sin 2ax$$
$$\int (x^2\sin^2 ax)\,dx = \frac{1}{6}x^3 - \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax - \frac{1}{4a^2}x\cos 2ax$$
$$\int (x^2\cos^2 ax)\,dx = \frac{1}{6}x^3 + \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax + \frac{1}{4a^2}x\cos 2ax$$
$$\int x^m e^{ax} dx = \frac{x^m e^{ax}}{a} - \frac{m}{a}\int x^{m-1} e^{ax} dx$$
$$\int \frac{e^{ax}}{x^m} dx = -\frac{1}{m-1}\frac{e^{ax}}{x^{m-1}} + \frac{a}{m-1}\int \frac{e^{ax}}{x^{m-1}} dx$$
$$\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cdot\sin\left(\frac{m\pi x}{a}\right)dx = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cdot\cos\left(\frac{m\pi x}{a}\right)dx = \frac{a}{2}\delta_{nm}$$
$$\int_0^a \left[\sin\left(\frac{n\pi x}{a}\right)\right]\cdot\left[\cos\left(\frac{n\pi x}{a}\right)\right]dx = 0$$
$$\int_0^a \sin^2 mx\,dx = \int_0^a \cos^2 mx\,dx = \frac{\pi}{2}$$
$$\int_0^\infty \frac{\sin x}{\sqrt{x}}dx = \int_0^\infty \frac{\cos x}{\sqrt{x}}dx = \sqrt{\frac{\pi}{2}}$$
$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (a>0,\ n \text{ positive integer})$$
$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}} \quad (a>0,\ n \text{ positive integer})$$
$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2\,a^{n+1}} \quad (a>0,\ n \text{ positive integer})$$
$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$$
$$\frac{d}{dx}\frac{u}{v} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx}$$
$$\frac{d}{dx}(u^n) = nu^{n-1}\frac{du}{dx}$$
$$\frac{d}{dx}\left(\frac{1}{u^n}\right) = -\frac{n}{u^{n+1}}\frac{du}{dx}$$
$$\frac{d}{dx}[f(u)] = \frac{d}{du}[f(u)]\cdot\frac{du}{dx}$$

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

$$\frac{d}{dx}(e^u) = e^u\frac{du}{dx}$$
$$\frac{d\sin x}{dx} = \cos x$$
$$\frac{d\cos x}{dx} = -\sin x$$
$$\frac{d\sin u}{dx} = \frac{du}{dx}\cos u$$
$$\frac{d\cos u}{dx} = -\frac{du}{dx}\sin u$$

$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha\cos\beta = \frac{1}{2}\cos(\alpha-\beta) + \frac{1}{2}\cos(\alpha+\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

Some H-Atom wave functions:

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\psi_{200}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)^{3/2} e^{-r/2a_0}$$

$$\psi_{310}(r,\theta,\phi) = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right)^{3/2} e^{-r/3a_0}\cos(\theta)$$

Some H-Atom radial wave functions:

$$R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$R_{20}(r) = \frac{1}{\sqrt{8}}\left(2-\frac{r}{a_0}\right)^{3/2} e^{-r/2a_0}$$

46 present counted 2x

46 scores recorded

[redacted]

Total Points: 100

Question 1:_____/20

Question 2:_____/25

Question 3:_____/15

Question 4:_____/30

Question 5:_____/10

Total: _____/

The First Few Spherical Harmonics

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

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

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

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

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

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

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

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

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

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*	$1.660\,5402 \times 10^{-27}$ kg
Avogadro constant	N_A	$6.022\,1367 \times 10^{23}$ mol^{-1}
Bohr magneton	$\mu B = eh/2m_e$	$9.274\,0154 \times 10^{-24}$ J · T^{-1}
Bohr radius	a_0	$5.291\,772\,49 \times 10^{-11}$ m
Boltzmann constant	k_B	$1.380\,658 \times 10^{-23}$ J · K^{-1}
		0.695 038 cm^{-1}
Electron rest mass	m_e	$9.109\,3897 \times 10^{-31}$ kg
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ · m^3 · kg^{-1} · s^{-2}
Molar gas constant	R	8.3145101 J · K^{-1} · mol^{-1}
		0.083 1451 dm^3 · bar K^{-1} · mol^{-1}
		0.082 0578 dm^3 · atm K^{-1} · mol^{-1}
Molar volume, ideal gas		
(one bar, 0°C)		22.711 08L · mol^{-1}
(one atm, 0°C)		22.414 09 L · mol^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,7866 \times 10^{-27}$ J · T^{-1}
Permittivity of vacuum	ε_0	$8.854\,187\,816 \times 10^{-12}$ C^2 · J^{-1} · m^{-1}
	$4\pi\varepsilon_0$	$1.112\,650\,056 \times 10^{-10}$ C^2 · J^{-1} · m^{-1}
Planck constant	h	$6.626\,0755 \times 10^{-34}$ J · s
	$\hbar$	$1.054\,572\,66 \times 10^{-34}$ J · s
Proton charge	e	$1.602\,177\,33 \times 10^{-19}$ C
Proton magnetogyric ratio	γ_p	$2.675\,221\,28 \times 10^8$ s^{-1} · T^{-1}
Proton rest mass	m_p	$1.672\,6231 \times 10^{-27}$kg
Rydberg constant (Bohr)	$R_\infty = m_e e^4 / 8\varepsilon_0^2 h^2$	$2.179\,8736 \times 10^{-23}$ J
		109 737.31534 cm^{-1}
Rydberg constant for H	R_H	109677.581 cm^{-1}
Speed of light in vacuum	c	299 792 458 m · s^{-1} (defined)
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4 / 15h^3c^2$	$5.670\,51 \times 10^{-8}$ J · m^{-2} · K^{-4} · s^{-1}

1) Spherical Harmonics and the Rigid Rotor. (20 points)

1A) What is the average (expectation) value for the energy (<E>) for a series of rigid rotors with moment of inertia I and (non-normalized) rotational wave function: $\psi(\theta,\phi) = 3Y_0^0(\theta,\phi) + Y_1^0(\theta,\phi) + iY_1^1(\theta,\phi)$ (where Y_l^m denotes the corresponding spherical harmonic function) (10 points)

probability $\propto$ |coefficient|^2

1) normalization $|3|^2 + |1|^2 + |i|^2 = 9 + 1 + 1 = 11 = \frac{1}{N^2}$

$$\psi = \frac{3}{\sqrt{11}} Y_0^0 + \frac{1}{\sqrt{11}} Y_1^0 + \frac{i}{\sqrt{11}} Y_1^1 + 2PC$$

we know $\boxed{\hat{H} Y_\ell^m = \frac{\hbar^2}{2I} \ell(\ell+1)}$ $+ 4PC$ so

$$\langle E \rangle = \frac{9}{11}(0) + \frac{2}{11} \hbar^2 1(1+1) = \frac{4}{11} \frac{\hbar^2}{2I}$$

1B) What is the probability that the square of the total angular momentum (eigenvalue of the L^2 operator) for the rigid rotor described by the wave function in part 1A will be measured as $2\hbar^2$? (10 points)

$$\boxed{\hat{L}^2 Y_\ell^m = \hbar^2 \ell(\ell+1)} + 4PC$$

prob $\propto$ |coefficient|^2

$$2\hbar^2 = \hbar^2 \ell(\ell+1)$$

$$\Rightarrow \ell = 1$$

from 1A $\frac{2}{11}$

2) Hydrogen Atom (25 points) ***(Note: some H-atom wave functions are included on the front cover)***

2A) What *wavelength photon* is needed to excite an electron from the ψ_{100} to the ψ_{310} (using the ψ_{nlm} notation) energy eigenstate of the hydrogen atom. (10 points)

PC: $\Delta E = \frac{hc}{\lambda}$ +2

$n = 1 \rightarrow n = 3$

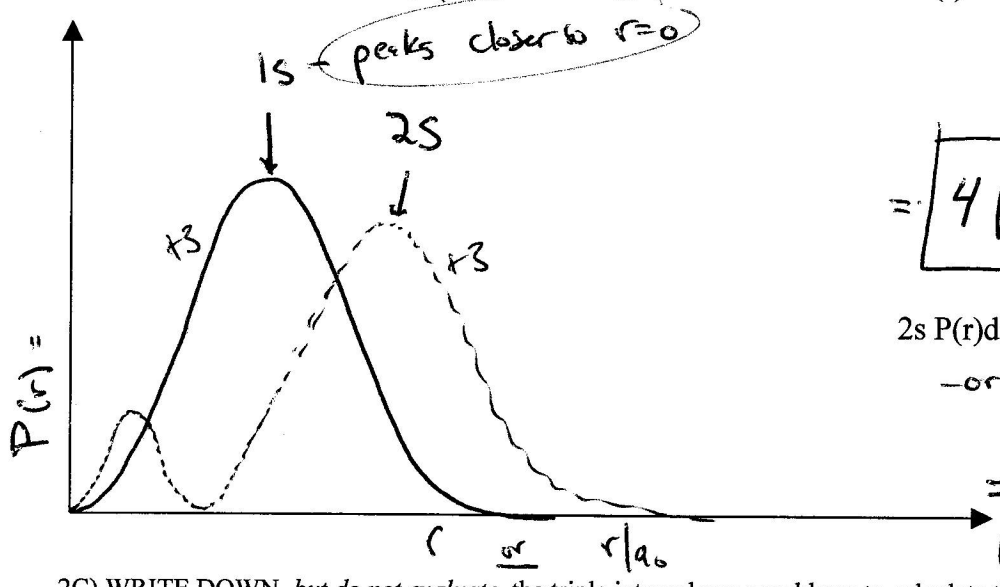
$$\Delta E = |E_1 - E_3| = \left| \frac{-13.6}{1^2} - \frac{-13.6}{3^2} \right| = 12.1 \text{ eV} = \frac{hc}{\lambda} \quad +2$$

$$\lambda = \frac{hc}{E} = \frac{1240 \text{ nm/eV}}{12.1 \text{ eV}} = 103 \text{ nm}$$

−2 for not in nanometers

2B) In the space below, *WRITE DOWN* the functions (using the ψ_{nlm} shorthand where possible) that give the probability of finding the electron at some distance r from the proton for both the 1s and 2s states of the H-atom. *SKETCH* the probability of finding the electron at a distance r from the proton (radial probability distribution) for the 1s (ψ_{100}) and the 2s (ψ_{200}) states. Make sure your graph axes are labeled. *INDICATE* for which curve the most likely position of finding the electron is closer to the proton. (12 points)

−1 if not indicated



1s $P(r)dr = |\psi_{1s}|^2 4\pi r^2 dr$ +2 PC

or

$|R_{1s}(r)|^2 r^2 dr$

$$= \boxed{4\left(\frac{1}{a_0}\right)^3 e^{-2r/a_0} r^2 dr}$$ +3 fnl cnd

2s $P(r)dr = |\psi_{2s}|^2 4\pi r^2 dr$ +2 PC

−or− $|R_{2s}(r)|^2 r^2 dr$

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

2C) WRITE DOWN, *but do not evaluate,* the triple integral you would use to calculate the average (expectation) value *of the angle that the electron makes with the z-axis* when the H atom is in the ψ_{210} state. (USE the ψ_{nlm} shorthand for the wave-function). (8 points)

up to $\frac{4}{8}$ for correct form of $\langle\theta\rangle$ w/ math errors (ie. missing r^2 or $\sin\theta$ in dV)

$$\langle\theta\rangle = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} \psi_{210}^* \, \theta \, \psi_{210} \, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

3) (15 Points) Acceptable wave functions. **CIRCLE** Acceptable or Unacceptable to indicate if each of these functions is an acceptable wave function for a He atom. Then ***briefly explain*** why or why not. (5 points each no credit w/o explanations)

a) $(1/2)^{1/2}\ 1s(1)2s(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ Acceptable / Unacceptable

e^- are distinguishable (not antisymmetric)

b) $(1/2)\ [1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ Acceptable / Unacceptable

$\hat{P}_{12}\psi = +1\psi \Rightarrow$ Symmetric

$= [1s(2)2s(1) - 1s(1)2s(2)][\alpha(2)\beta(1) - \alpha(1)\beta(2)]$

c) $(1/2)^{1/2}[1s(1)2s(2)\alpha(2)\beta(1) - 2s(1)1s(2)\alpha(1)\beta(2)]$ Acceptable / Unacceptable

1.) e^- indistinguishable

2.) $P_{12}\psi = -1\psi \Rightarrow$ antisymmetric

$= \frac{1}{\sqrt{2}}\left(1s(2)2s(1)\alpha(1)\beta(2) - 2s(2)1s(1)\alpha(2)\beta(1)\right) = -1\psi$ ✓

4) Spectroscopy (30 points)
FTIR monitoring is one method that can be used to identify gaseous pollutants emitted from refineries, chemical plants, and power stations. An experimental high-resolution FTIR spectrum for CO gas is included on the last page of the exam. (you may tear it off for study if you wish). ***Note that the x-axis units are displayed as wavelengths in units of MICROMETERS (so you will need to convert to E or cm^{-1} depending on your preference).***

4A) 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—right or wrong, so be concise). must mention rotational & Δl selection rule

Rotational transitions accompany vibrational transitions in diatomic molecules because

+5

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 many rotational states are populated @ room T

4B) Calculate ***the force constant*** of a CO bond using the data in the graph. (10 points)

$$\Delta E = h\nu = \frac{hc}{\lambda} = \hbar\sqrt{\frac{K}{\mu}}$$ ← for the S.H.O (+3 pc)

for C=O (+1 pc)

$$\mu = \frac{(16)(12)}{16+12} 1.66\times10^{-27}\,kg = 1.14\times10^{-26}\,kg$$

10

from graph: peak center → $\lambda = \frac{4.6573 + 4.6743}{2} \times10^{-6}\,m = 4.6658\times10^{-6}\,m$ (+2 pc)

$$\Delta E = \frac{6.626\times10^{-34}\,J\text{-}s \times 3\times10^{8}\,m/s}{4.6658\times10^{-6}\,m} = 4.26\times10^{-20}\,J = \frac{6.626\times10^{-34}}{2\pi}\sqrt{\frac{K}{1.14\times10^{-26}\,kg}}$$

solving for

$K = 1860\ N/m$

Force constant:
1860 N/m

4C) Calculate the ***length*** of a CO bond using the data in the graph. (10 points)

Spacing between rotational peaks gives 2B convert to cm^{-1}

to use our favorite B formula (could also convert "B" to cm^{-1}

or J or eV)

$\lambda = 4.6573 \times 10^{-6}\ m = 4.6573 \times 10^{-4}\ cm \Rightarrow \bar{\nu} = \frac{1}{4.6573 \times 10^{-4}\ cm} = 2,147\ cm^{-1}$

$\lambda = 4.6496 \times 10^{-6}\ m = 4.6496 \times 10^{-4}\ cm \Rightarrow \bar{\nu} = \frac{1}{4.6496 \times 10^{-4}\ cm} = 2150.7\ cm^{-1}$

note taking average of 2B spacings would be more accurate but full credit for "short" approach spacing betw lines

$2B \approx 3.55\ cm^{-1}$ $B \approx 1.78\ cm^{-1}$

+10

$B = \frac{h}{8\pi^2 \mu c r_0^2}$

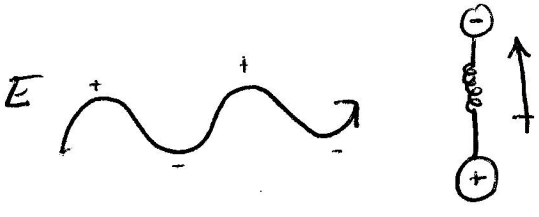
$r = \sqrt{\frac{h}{8\pi^2 \mu c B}} = \sqrt{\frac{6.626 \times 10^{-34}\ J\,s^2 \cdot m^2}{8\pi^2\ 1.14 \times 10^{-26}\ kg\ 3 \times 10^{10}\ \frac{cm}{s} \times 1.78\ cm^{-1}}} = 1.17 \times 10^{-10}\ m$

Bond Length:
1.17 Å

4D) Burning fossil fuel leads to an increased CO_2 level in the atmosphere. From your knowledge of how electromagnetic radiation excites vibrations in molecules, explain (qualitatively in a FEW CONCISE SENTENCES) why gases like CO and CO_2 in the atmosphere will absorb infrared radiation (preventing the escape of heat to space and contributing to the greenhouse effect) while most of atmosphere (the N_2 and O_2) is transparent to IR light. (5 points)

+5

For a bond to absorb IR radiation it must undergo a change in dipole moment upon stretching (the molecule absorbs light because the oscillating E-field excites the bond vibration) Homonuclear diatomic molecules like O_2 + N_2 are non-polar & don't change dipole moments upon stretching.



5) Variational Theorem (10 Points)

On a homework assignment, a student guesses a trial function for the quantum harmonic oscillator, and, with this trial function optimized, calculates a ground state energy of $.493\hbar\sqrt{\frac{k}{\mu}}$ (where k is the spring constant of the bond, and μ is the reduced mass of the oscillator). The student is excited because his trial function gave the lowest energy of any functions that the members of his study group could come up with. Has he done the best possible job? Should he search for a better trial function? Has something gone horribly wrong (not with your memory, with the student's calculation). **Explain.**

+10

Something gone wrong! Variational theorem tells us the lowest trial energy must be greater than or equal to the true energy

$(E_{trial} \geq E_{true})$ we <u>know</u> E_0 for HO is

$$\frac{\hbar\omega}{2} = \frac{\hbar}{2}\sqrt{\frac{k}{\mu}}$$

FTIR spectrum of absorbance versus wavelength (in microns) for a sample of carbon monoxide