CHEM 455A –Quantum Chemistry and Spectroscopy
Exam 2 Friday May 19, 2006
Exams will be collected at 9:20:00 am SHARP
1 ONE SIDED 8.5x11" page of notes is allowed

2006

-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

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

$$\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$$
$$\frac{d}{dx}\frac{u}{v} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx}$$
$$\frac{d}{dx}(u^n) = nu^{n-1}\frac{du}{dx}$$
$$\frac{d}{dx}\left(\frac{1}{u^n}\right) = -\frac{n}{u^{n+1}}\frac{du}{dx}$$
$$\frac{d}{dx}[f(u)] = \frac{d}{du}[f(u)]\cdot\frac{du}{dx}$$
$$\frac{d}{dx}(u^n v^m) = u^{n-1}v^{m-1}\left(nv\frac{du}{dx} + mu\frac{dv}{dx}\right)$$
$$\frac{d}{dx}(e^u) = e^u\frac{du}{dx}$$
$$\frac{d\sin x}{dx} = \cos x$$
$$\frac{d\cos x}{dx} = -\sin x$$
$$\frac{d\sin u}{dx} = \frac{du}{dx}\cos u$$
$$\frac{d\cos u}{dx} = -\frac{du}{dx}\sin u$$
$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha\cos\beta = \frac{1}{2}\cos(\alpha-\beta) + \frac{1}{2}\cos(\alpha+\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

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:

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

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

Total Points: 100

Question 1:_________/25

Question 2:_________/20

Question 3:_________/19

Question 4:_________/21

Question 5:_________/15

Total: ____________/

Potentially Useful Information:

Workfunctions of Metals:

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

The First Few Spherical Harmonics

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

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

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

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

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

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

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

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

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

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	$\mu B = e\hbar/2m_e$	$9.274\,0154 \times 10^{-24}$ 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, 0^0C)		22.711 08L · mol^{-1}
(one atm, 0^0C)		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) Hydrogen Atom (25 points) ***(Note: some H-atom wave functions are included on the front cover)***

1A) Draw an energy level diagram for the first 6 energy levels of the hydrogen atom. Label the energy levels both by principal quantum number and energy. (Hint: you may want to calculate the energies before sketching so you get the spacings about right).

E (in eV)

-0.377 ——— n=6 n=∞

-0.544 ——— n=5

-0.85 ——— n=4

-1.5 ——— n=3

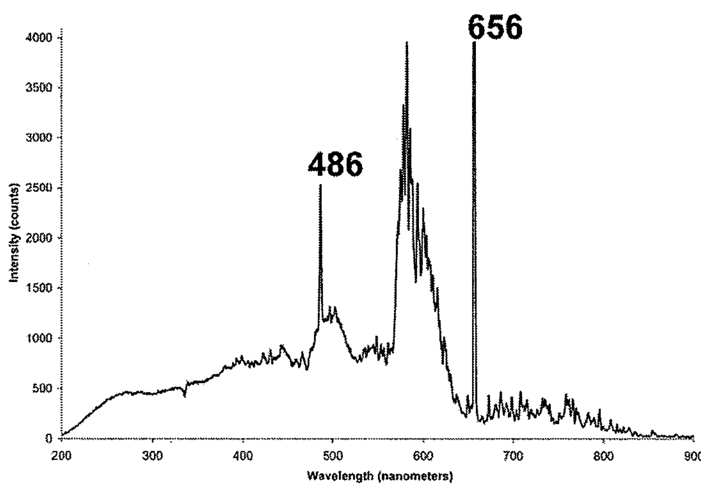
E ↑ -3.4 ——— n=2

-13.6 ——— n=1

$$E_n = \frac{-13.6\ eV}{n^2}$$

+5/5

1B) Below is an emission spectrum from a hot gas. Discuss the evidence for or against the presence of H in this spectrum (refer to any spectral lines seen by the principal quantum numbers of the levels involved in the transition).



$$\frac{1240\ eV\text{-}nm}{486\ nm} = 2.55\ eV$$ +5/5

$$\frac{1240\ eV\text{-}nm}{655\ nm} = 1.89\ eV$$

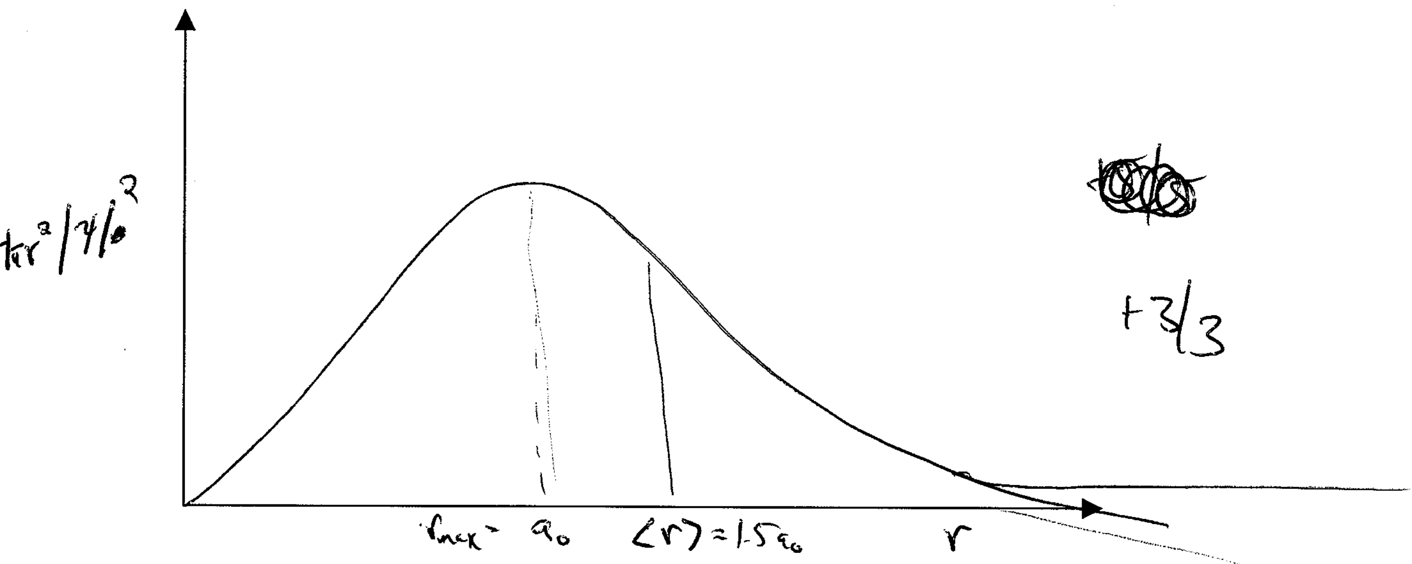
These are H-atom transitions

From graph above for H atom

$E_2 - E_4 = 3.4 - 0.85 = 2.55\ eV$ ✓

$E_2 - E_3 \quad 3.4 - 1.51 = 1.89\ eV$ ✓

1C) Use the space below to sketch the radial distribution function for the electron P(r) as a function of r for a ground state electron in the Hydrogen atom



+3/3

1D) What is the most likely distance (r) at which you will find the electron from the proton in the Hydrogen atom? Give your answer in units of a_0 (You must explicitly calculate this here for credit).

$$P(r) = 4\pi r^2|\psi|^2 dr = 4\pi r^2 \frac{1}{\pi}\frac{1}{a_0^3} e^{-2r/a_0}$$

$$\frac{dP(r)}{dr} = \frac{8r}{a_0^3} e^{-2r/a_0} - \frac{8r^2}{a_0^4} e^{-2r/a_0} = 0$$

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

+7/7

$$\therefore \quad r - \left(\frac{r^2}{a_0}\right) = 0 \qquad \boxed{r = a_0} \checkmark$$

1E) If you were to calculate <r> how would you do so? (You should set up, but need not evaluate this integral). *Label your graph in 1C with where you expect to find <r> that you would expect.* Will <r> be different than your answer in **1D**).

$$\boxed{\langle r\rangle = \int_{r=0}^{\infty} 4\pi r^2 \psi^* r \psi \, dr}$$

or

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

$\langle r\rangle$ will be ~~larger~~ larger than r_{max} b/c of exponential tail in e^{-r/a_0} function ✓

+5/5

1/5 for $\langle r\rangle$ label

2) Operators and Observables (20 points)

A) Write down the Hamiltonian for the *He* atom (you don't need to expand the ∇^2 operator into specific coordinates), and explain the origin/meaning of each term. Which term(s) preclude(s) an analytical solution of the Schrödinger equation with this Hamiltonian?

$$\underbrace{\frac{-\hbar^2}{2m_e}\nabla_1^2}_{\text{KE of } e^- \#1} + \underbrace{\frac{-\hbar^2}{2m_e}\nabla_2^2}_{\text{KE of } e^- \#2} + \underbrace{\frac{-2e^2}{4\pi\epsilon_0 r_1}}_{\text{Coulombic PE betw } e_1^- + \text{nucleus}} + \underbrace{\frac{-2e^2}{4\pi\epsilon_0 r_2}}_{\text{coulombic PE betw } e_2^- + \text{nucleus}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\text{Coulombic PE due to } e^- - e^- \text{ repulsion}}$$

This term is not separable! ⇑

+8/8

B) Is the total energy eigenfunction of the H atom $\psi(r,\theta,\phi) = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0} - \frac{r^2}{a_0^{\,2}}\right)^{3/2} e^{-r/3a_0}\cos(\theta)$ an eigenfunction of any operators other than the Hamiltonian? *If so which ones? What are their eigenvalues?*

Yes/No:

+1/12

Fill out table with all operators for which the above psi is an eigenvalue (points will be *subtracted* for incorrect guesses):

Operator:	Eigenvalue:	Physical Observable:
$\hat{H}$	$\frac{-13.6\text{ eV}}{9} = -1.51\text{ eV}$ +1.5	Total Energy +1.5
? L_z +1	$m_\ell = 0 \Rightarrow 0\hbar$ +1.5	z-component of angular momentum +1.5
? L^2 +1	$\ell = 1 \Rightarrow \hbar^2 1(1+1)$ $2\hbar^2$ +1.5	total square of angular momentum +1.5
?		

+12/12

11/12 for table

3) Electron Spin (19 points)

3A) State the CHEM 455 version of the Pauli exclusion principle in 2-3 sentences

All fermionic wave functions must be antisymmetric upon exchange of any two fermions. All bosonic wave functions must be symmetric upon exchange of any 2 bosons.

+6/6

3B) Write down the acceptable wave functions for the 1s2s excited state configuration of He as products of spatial and spin functions. Identify the triplet and singlet wave functions as such.

singlet $\frac{1}{\sqrt{2}}[1s(1)2s(2) + 1s(2)2s(1)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

triplets $\frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)]$ $\alpha(1)\alpha(2)$

+6/6

" $\times$ $\beta(1)\beta(2)$

1.5 pts ea.

" $\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1))$

3C) Check, by explicit application of the $S_{z\text{-tot}} = s_{z1}+s_{z2}$ operator, if the singlet wave function for the excited 1s2s state of He above is an eigenfunction of $S_{z\text{-tot}}$ or not. If so, what is the eigenvalue?

$S_{ztot}(S_{z_1} + S_{z_2})\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

$= \frac{1}{\sqrt{2}}\left(\cancel{\frac{\hbar}{2}\alpha(1)\beta(2)} + \cancel{\frac{\hbar}{2}\alpha(2)\beta(1)}\right) + \frac{1}{\sqrt{2}}\left(-\cancel{\frac{\hbar}{2}\alpha(1)\beta(2)} - \cancel{\frac{\hbar}{2}\alpha(2)\beta(1)}\right)$

+7/7

$= 0\,\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

$\boxed{\text{Yes}}$ it is an eigenfunction w/ eigenvalue $\boxed{S_z = 0}$

4) Spectroscopy (21 points)
An IR spectrum of HF gas is given **on the last page of the exam**.
4A) Use the data in that spectrum to find the force constant for HF

$\Delta E = \hbar\omega = \hbar\sqrt{\frac{K}{\mu}}$ = center of vib./rot spectrum = $3975\,cm^{-1}$

$3975\,cm^{-1} \Rightarrow \dfrac{6.626\times10^{-34}\,Js \cdot 3\times10^{10}\,m/s}{\frac{1}{3975\,cm^{-1}}} = 7.903\times10^{-20}\,J$

$\mu = \dfrac{m_H m_F}{m_H + m_F} = \dfrac{19}{20}\,1.67\times10^{-27} = 1.587\times10^{-27}\,kg$

Force constant:
890 N/m

7/7

$\Delta E = \hbar\sqrt{\frac{K}{\mu}} \therefore K = \dfrac{E^2\mu}{\hbar^2}$

$= \dfrac{(7.9\times10^{-20}\,J)^2}{(1.054\times10^{-34}\,J\cdot s)^2}\,1.58\times10^{-27}\,kg = 888\,N/m$

4B) Use the information in the graph(s) to calculate the length of the HF bond.

Spacing between two peaks on graph = $40\,cm^{-1} = 2B$

$40\,cm^{-1} \Rightarrow \Delta E = \dfrac{6.626\times10^{-34}\,Js\;3\times10^{10}\,m/s}{.02\,cm} = 9.939\times10^{-22}\,J$

$\Delta E = 2B = \dfrac{2\hbar^2}{2I} = \dfrac{\cancel{2}\hbar^2}{\cancel{2}\mu r^2}$ $\quad r = \sqrt{\dfrac{\hbar^2}{E\mu}}$

$= \sqrt{\dfrac{1.054\times10^{-34}\,J\text{-}s}{(1.587\times10^{-27}\,kg)(9.39\times10^{-22}\,J)}}$

-or-

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

$B = 20\,cm^{-1}$

$c = 3\times10^{10}\,m/s$

$\mu = 1.587\times10^{-27}$

Bond Length:
0.84 Å

7/7

~ good to ~1 sig fig

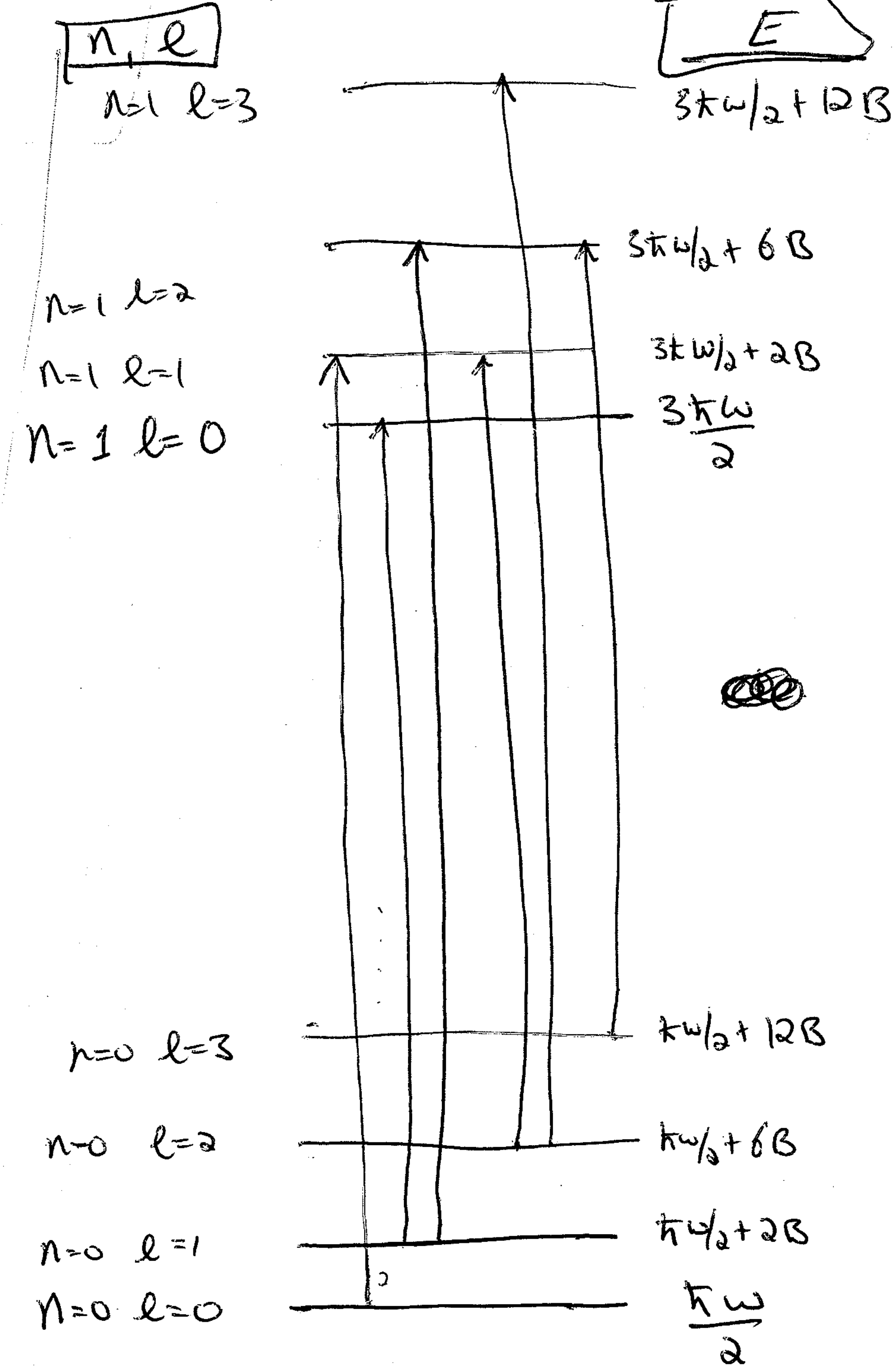
4C) Draw an ENERGY LEVEL diagram for the energy levels of the HF molecule that are being probed in the absorption spectrum. Label i) the energies of each level, ii) the quantum numbers of each level, iii) the ALLOWED transitions between different levels.

Allowed transitions $\Delta l = \pm 1$ $\Delta n = +1$ for absorption

Level

Energy

for first 4 rot levels & first 2 vib levels



E ↑

7/7

5) (15 pts) Variational Theorem

5a) Since the eigenfunctions of a quantum mechanical operator form a complete orthogonal set, you can rewrite any trial function as a linear combination of the true energy eigenfunctions ψ_i, i.e., $\phi_{trial} = \sum_i^{\infty} c_i \psi_i$ Explain in your own words why then carrying out the integral in 5a) for any trial function must give an $\langle E_\phi \rangle$ that is larger than the energy of the true ground state ψ_0?

$$\langle E_\phi \rangle = \frac{\int \phi^* H \phi}{\int \phi^* \phi}$$ (+3)

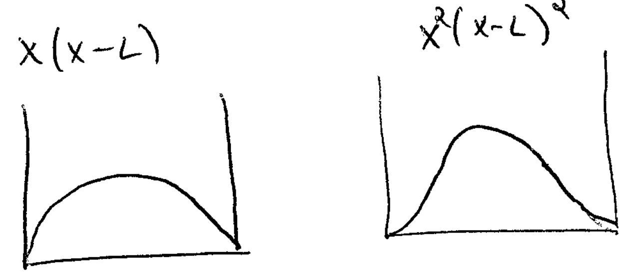
10/10

if you expand ϕ in terms of the ψ_i then

$\langle E_\phi \rangle = \sum |c_i|^2 E_i$ since each of the E_i are greater than the ground state any ϕ_{trial} that is not the ground state will have a large $\langle E \rangle$

5b) If you were to use $\phi_{trial} = c_1 x(x-L) + c_2 x^2 (x-L)^2$ as a trial function to estimate the particle in a box energies using the variational theorem, would you expect c_1 or c_2 to be larger for the best possible trial function? Why? Be concise.

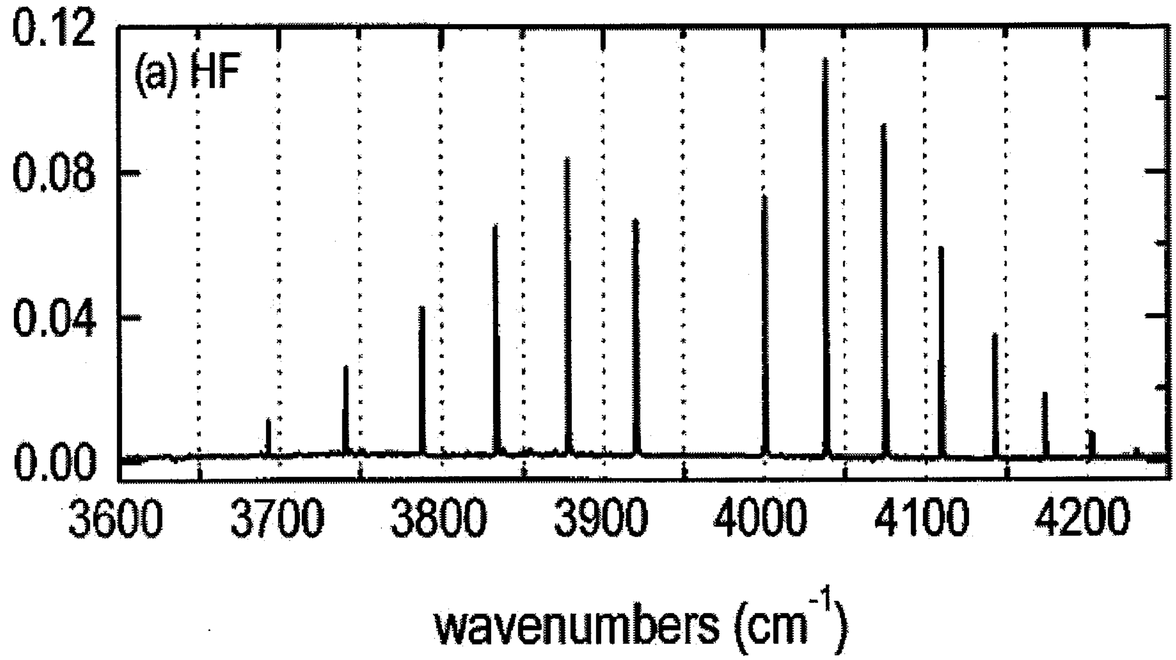
5/5



By itself $x(x-L)$ gives a slightly better E_{trial} than $x^2(x-L)^2$. So one might guess $x(x-L)$ since it looks slightly closer to true ψ_i but we know that optimum E_{trial} came w/ c_2 just larger than c_1 so c_2 is correct answer.

Both look similar to ψ

Note: Points are for discussion of similarity of shapes, not for one answer or the other.



0.12
0.08
0.04
0.00
(a) HF
3600
3700
3800
3900
4000
4100
4200
wavenumbers (cm^{-1})