
Name

Student #**CHEMISTRY 3PA3 Section #1
VERSION # 1****DAY CLASS****DURATION OF EXAM: 3 Hours.****INSTRUCTOR: Paul W. Ayers (x24505; ayers@mcmaster.ca)****McMASTER UNIVERSITY DEFERRED FINAL EXAMINATION****February, 2010**

THIS EXAMINATION PAPER CONTAINS 13 PAGES AND 25 QUESTIONS. YOU ARE RESPONSIBLE FOR ENSURING THAT YOUR COPY OF THE PAPER IS COMPLETE. BRING ANY DISCREPANCY TO THE ATTENTION OF THE INVIGILATOR.

SPECIAL AIDS:

Any calculator can be used.

Immediately following this page is a list of formulas and experimental data that you may find helpful.

In all portions of this exam, be very careful to record the units in which you are giving your answer.

Instructions:

The exam is scored out of 100 points.

There are TWENTY short-answer questions in this exam. Answer all of them. Use the exam booklet when there is not room to write your answer on the exam paper. When you use the exam booklet, write on the exam "in booklet" so that I know to look there. Each short-answer question is worth 3 points.

There are FIVE long-form problems in this exam. Pick FOUR of the problems and answer them in the exam booklet. Each problem is worth 10 points.

Write your work clearly and neatly. Clearly label the problems you work in the exam booklet. Be careful with your units. Partial credit is available, but only if your work is clear, neat, and easy to follow.

Page 2: Periodic Table

Pages 3 & 4: formula sheet & conversion factors.

Pages 5-10: 20 short-answer questions.

Pages 11-13: 5 long-form problems. (Pick 4 of 5).

hydrogen 1 H 1.0079														helium 2 He 4.0026			
lithium 3 Li 6.941	beryllium 4 Be 9.0122																
sodium 11 Na 22.990	magnesium 12 Mg 24.305																
potassium 19 K 39.098	calcium 20 Ca 40.078																
rubidium 37 Rb 85.468	strontium 38 Sr 87.62																
caesium 55 Cs 132.91	barium 56 Ba 137.33	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	aluminium 10.811 Al 26.982	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
francium 87 Fr [223]	radium 88 Ra [226]	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
		lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
		lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]	ununquadium 114 Uuq [289]					

* Lanthanide series

** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europtium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Key integrals and identities:

$$\begin{aligned}
 \left(\frac{a}{2}\right)\delta_{mn} &= \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx \\
 \left(\frac{a}{2}\right)\delta_{mn} &= \int_0^a \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi x}{a}\right) dx \\
 0 &= \int_0^a \cos\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx \\
 \frac{a^2}{4} &= \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right) \right)^2 x dx \\
 \left(\frac{a}{2\pi n}\right)^3 \left(\frac{4\pi^3 n^3}{3} - 2\pi n \right) &= \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right) \right)^2 x^2 dx \\
 \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} &= \int_0^\infty e^{-\alpha x^2} dx \\
 \left(\frac{1}{2} \sqrt{\frac{\pi}{\alpha}}\right) \left(\frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n} \right) &= \int_0^\infty x^{2n} e^{-\alpha x^2} dx \quad n = 1, 2, 3, \dots \\
 \left(\frac{1}{2}\right) \left(\frac{n!}{\alpha^{n+1}} \right) &= \int_0^\infty x^{2n+1} e^{-\alpha x^2} dx \quad n = 0, 1, 2, \dots
 \end{aligned}$$

$$\begin{aligned}
 2 \sin(x) \sin(y) &= \cos(x-y) - \cos(x+y) &\rightarrow 2 \sin^2 x &= 1 - \cos(2x) \\
 2 \cos(x) \cos(y) &= \cos(x-y) + \cos(x+y) &\rightarrow 2 \cos^2 x &= 1 + \cos(2x) \\
 2 \sin(x) \cos(y) &= \sin(\alpha+\beta) + \sin(\alpha-\beta) &\rightarrow 2 \sin x \cos x &= \sin(2x) \\
 \sin(x+y) &= \sin x \cos y + \cos x \sin y &\rightarrow \sin(2x) &= 2 \sin x \cos x \\
 \cos(x+y) &= \cos x \cos y - \sin x \sin y &\rightarrow \cos(2x) &= \cos^2 x - \sin^2 x
 \end{aligned}$$

SOME MATHEMATICAL FORMULAS

Paul

VALUES OF SOME PHYSICAL CONSTANTS

Constant	Symbol	Value
Avgadro's number	N_0	$6.02205 \times 10^{23} \text{ mol}^{-1}$
Proton charge	e	$1.60219 \times 10^{-19} \text{ C}$
Planck's constant	\hbar	$6.62618 \times 10^{-34} \text{ J}\cdot\text{s}$
	\hbar	$105459 \times 10^{-34} \text{ J}\cdot\text{s}$
Speed of light in vacuum	c	$2.997925 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Atomic mass unit	amu	$1.66056 \times 10^{-27} \text{ kg}$
Electron rest mass	m_e	$9.10953 \times 10^{-31} \text{ kg}$
Proton rest mass	m_p	$1.67265 \times 10^{-27} \text{ kg}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
	k_B	0.69509 cm^{-1}
Molar gas constant	R	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	ϵ_0	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
Rydberg constant (infinite nuclear mass)	R_∞	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
First Bohr radius	a_0	$2.179914 \times 10^{-15} \text{ J}$
Bohr magneton	μ_B	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
Stefan-Boltzmann constant	σ	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

CONVERSION FACTORS FOR ENERGY UNITS

joule	$\text{kJ}\cdot\text{mol}^{-1}$	eV	au	cm^{-1}	Hz
1 joule	6.022×10^{20}	6.242×10^{18}	2.2939×10^{17}	5.035×10^{22}	1.509×10^{33}
1 kJ mol $^{-1}$	$= 1$	1	1.036×10^{-2}	3.089×10^{-4}	83.60
1 eV	$= 1.602 \times 10^{-19}$	96.48	1	3.675×10^{-2}	8065
1 au	$= 3.359 \times 10^{-8}$	2625	27.21	1	2.195×10^5
1 cm $^{-1}$	$= 1.986 \times 10^{-23}$	1.196×10^{-4}	1.240×10^{-4}	4.556×10^{-6}	1
1 Hz	$= 6.626 \times 10^{-44}$	3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}
					1

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

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

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

$$\cos(\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

$$\cos(\alpha \pm \beta) = \cos \alpha \cos \beta \pm \sin \alpha \sin \beta$$

$$e^{\pm i\theta} = \cos \theta \pm i \sin \theta$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

$$f(x) = f(a) + f'(a)(x - a) + \frac{1}{2!} f''(a)(x - a)^2 + \frac{1}{3!} f'''(a)(x - a)^3 + \dots$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \dots$$

$$(1 \pm xy)^n = 1 \pm nx \pm \frac{n(n-1)}{2!} x^2 \pm \frac{n(n-1)(n-2)}{3!} x^3 \pm \dots$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2} \quad (n \text{ positive integer})$$

$$\int_0^a \sin \frac{m\pi x}{a} \sin \frac{m\pi x}{a} dx = \int_0^a \cos \frac{m\pi x}{a} \cos \frac{m\pi x}{a} dx = \frac{a}{2} \delta_{mn}$$

$$\int_0^a \cos \frac{m\pi x}{a} \sin \frac{m\pi x}{a} dx = 0 \quad (m \text{ and } n \text{ integers})$$

Short Answer Questions: (20 questions @ 3 points each = 60 points total).

1.2. Fill in the first column of the following table, labelling the following molecules as:

- O** oblate symmetric top
- P** prolate symmetric top
- S** spherical top
- A** asymmetric top

Type of “top”	Name of Molecule	Structure of Molecule
	Carbon tetrachloride	
	Coronene	
	1-butyne	
	propyne	

3-5. Match the following systems to the energy level diagrams on the next two pages. Each line indicates an energy level, and the number in parenthesis next to the line indicates the degeneracy of that level. That is, the positions of the lines give the relative energies of the ground state (the first line) and a few excited states, and the number in parenthesis indicates the number of states with that energy.

 One-Electron Atom

 One-Dimensional Harmonic Oscillator

 One-Dimensional Particle in a Box with Infinite Sides

 Rigid Rotation of a Spherical Top Molecule

 Rigid Rotation of a Oblate Symmetric Top Molecule

 Rigid Rotation of a Prolate Symmetric Top Molecule

A

(7)
(14)
(14)
(14)

(5)
(10)
(10)

(3)
(6)



(1)

B

(1)
(1)
(1)
(1)
(1)
(1)



(1)



(1)



(1)



(1)



(1)



(1)



(1)



(1)

C

(14)
(14)
(14)
(7)

(10)
(10)
(5)

(6)
(3)



(1)

D

(1)
(1)



(1)



(1)



(1)



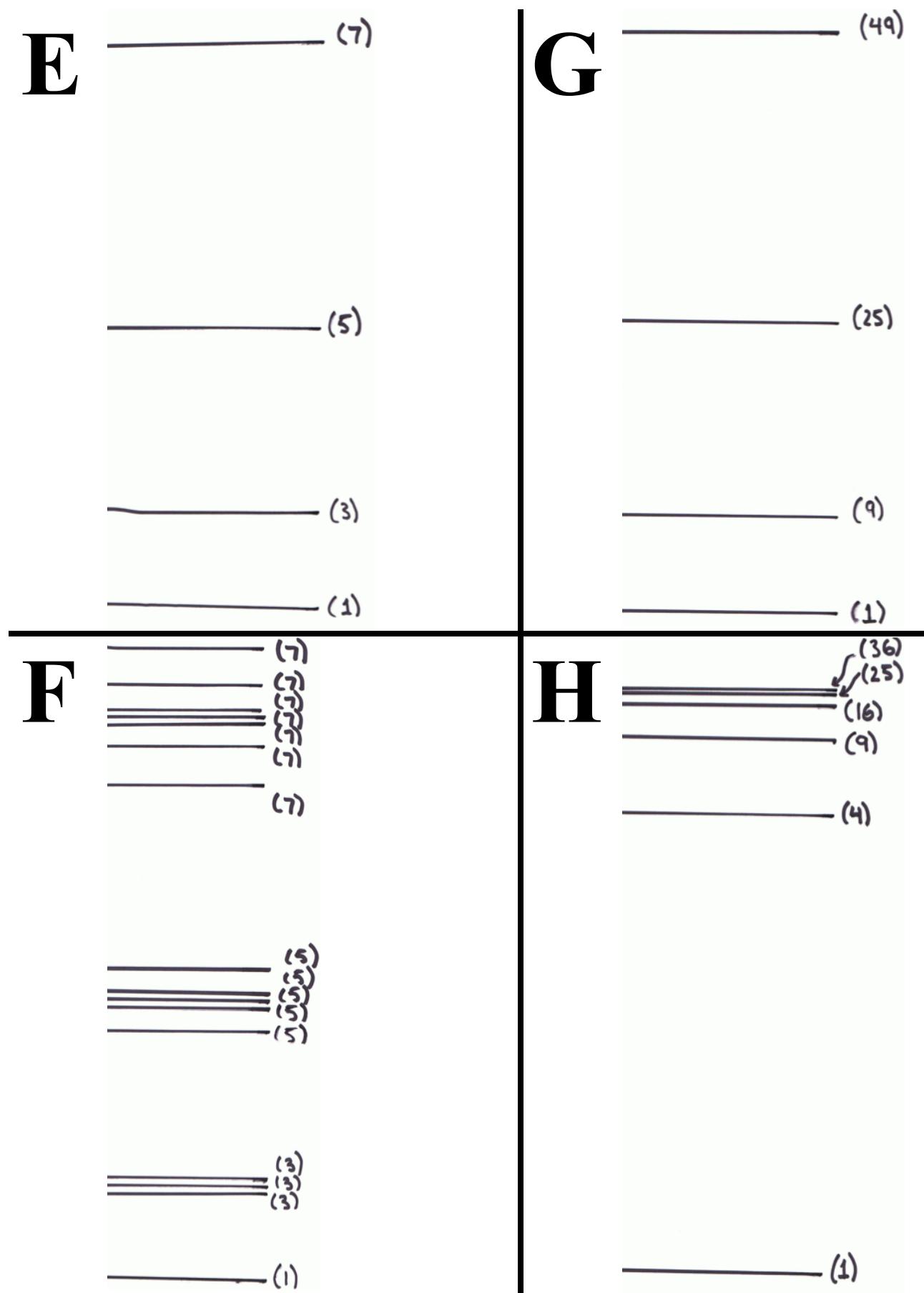
(1)



(1)



(1)



The following text refers to problems 6-8.

Among the many possible wavefunctions associated with the 7G term symbol, suppose you are given the one with the largest possible values for the J quantum number (total angular momentum) and the M_J quantum number (total angular momentum about the z -axis). This wavefunction is denoted $\Psi_{J^{(\max)} M_J^{(\max)}}^{^7G}$.

- 6. What is the degeneracy of an atomic state described by the 7G term symbol?**

- 7. What are the maximum values for the total angular momentum and the total angular momentum around the z -axis.**

_____ $J^{(\max)}$

_____ $M_J^{(\max)}$

- 8. What are the eigenvalues of the following operators. Be sure to show the dependence on \hbar .**

-
- 9. Write the key equation known as “Fermi’s Golden Rule.”**

- 10. Write a Slater determinant of molecular orbitals that is appropriate for the *ground state of the Lithium Hydride cation*, LiH^+ . Label the molecular orbitals with symmetry labels, i.e. $\sigma_u, \sigma_g, \pi_u^+, \pi_u^-, \pi_g^+, \pi_g^-$,.... Use the long form of the Slater determinant, writing out all the rows and columns.**

11. Because of the presence of other electrons and the positive nuclei, electrons in large molecules and solids do not experience the full Coulomb potential. Instead, they experience a screened Coulomb potential. (You learned about this in thermodynamics, as it is a key component of the Debye-Hückel theory of electrolyte solutions.) A common model for the screened Coulomb potential is the Yukawa potential,

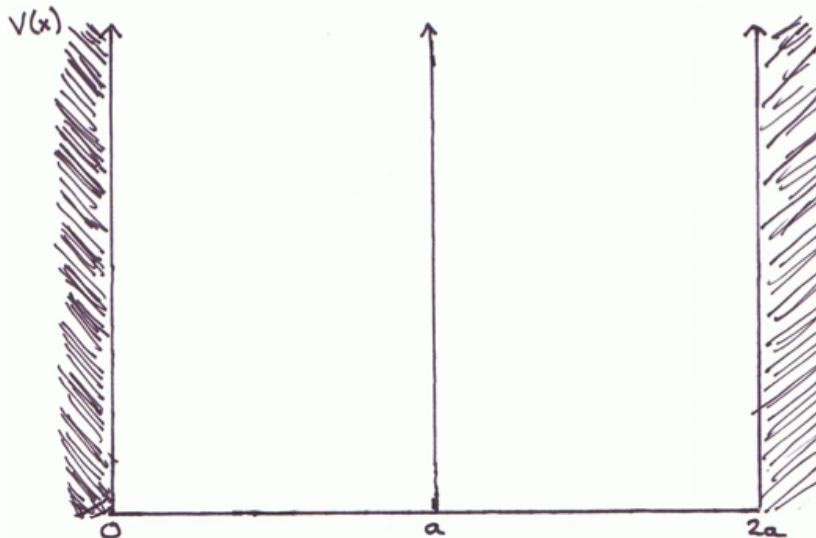
$$V_Y(r) = \frac{q_1 q_2 e^{-\lambda r}}{4\pi\epsilon_0 r}$$

where r is the separation between the particles. **Write the Hamiltonian for two particles, with charges q_1 and q_2 and masses m_1 and m_2 whose interaction is described by the Yukawa potential.**

The following text refers to problems 12-15.

Consider an electron confined to two one-dimensional boxes with infinitely repulsive sides. The two boxes are adjacent to each other but separated by an infinite barrier, as shown in the following figure and encapsulated by the following equation:

$$V(x) = \begin{cases} +\infty & x \leq 0 \\ 0 & 0 < x < a \\ +\infty & x = a \\ 0 & a < x < 2a \\ +\infty & x \geq 2a \end{cases}$$



12. The system is prepared in its ground state and then its absorption spectrum is taken. The largest-wavelength absorption that is observed has wavelength 1000 nm. **How wide are the boxes? (I.e., what is the value of a ?)**
13. **What is the ground state energy of this system?**
- 14,15. An experiment reveals that the system has a 90% chance of being observed in the first box and a 10% chance of being observed in the second box. **Write TWO wavefunctions, which differ from each other by more than a constant factor, that are consistent with this observation.**

16-18. Write expressions for each of the following operators in a general N -electron, P -nucleus molecule. *Show the dependence on the fundamental physical constants, $\hbar, m_e, e, \varepsilon_0$, etc..*

Quantity	Quantum-Mechanical Operator in <u>SI units</u>
nuclear kinetic energy, \hat{T}_n	
electronic kinetic energy, \hat{T}_e	
nuclear-electron attraction energy, \hat{V}_{ne}	
nuclear-nuclear repulsion energy, \hat{V}_{nn}	
electron-electron repulsion energy, \hat{V}_{ee}	

19,20. Using the notation in the first column of the table in #18,19, write the electronic and nuclear time-independent Schrödinger equations for a molecule.

Electronic:

Nuclear:

Part 2. Problems

There are **FIVE** problems, each worth **10** points. Pick **FOUR** of the five problems and clearly indicate which problem you do not wish for me to grade.

1. Properties of the Second Derivative Operator.

In this problem, you will derive some properties of the second derivative operator,

$$\left\langle \Psi(x) \left| \frac{d^2}{dx^2} \right| \Psi(x) \right\rangle$$

1a. Explicitly show that the second derivative operator is Hermitian. [6 points]

1b. Explicitly show that the second derivative operator is negative semidefinite.

That is, show that for any wavefunction, $\Psi(x)$,

$$\left\langle \Psi(x) \left| \frac{d^2}{dx^2} \right| \Psi(x) \right\rangle \leq 0.$$

[4 points]

2. Atomic Diffraction and Neutron Diffraction.

Suppose we use a beam of Helium-4 atoms to image a crystal, in a manner similar to *X-ray* crystallography. Assume that the ${}^4_2\text{He}$ atoms are in thermal equilibrium at temperature T . From fundamental thermodynamics, we know that the kinetic energy of the Helium atoms is

$$\text{kinetic energy} = \frac{3}{2} k_B T \quad (1)$$

where k_B is Boltzmann's constant. Suppose that the substance we want to diffract the Helium atoms from crystallizes in a simple cubic lattice with lattice constant (i.e., nearest-neighbor distance) $a = 3.0 \cdot 10^{-10}$ m.

2a. At what temperature would diffraction of the ${}^4_2\text{He}$ atoms become appreciable? (6 points)

2b. Suppose we use thermal neutrons, instead of ${}^4_2\text{He}$ to diffract off the crystal. Would the optimal temperature of the neutrons be smaller or larger than that of the Helium atoms in part (a)? (2 points)

(i) $T_{\text{neutrons}} > T_{\text{Helium}}$

(ii) $T_{\text{neutrons}} < T_{\text{Helium}}$

2c. Suppose we now decide to diffract ${}^4_2\text{He}$ from a cubic lattice with a slightly smaller lattice constant, $a = 2.8 \cdot 10^{-10}$ m. Should the temperature of the Helium atom beam be increased or decreased in order to optimize diffraction. (2 points)

(i) $T_{\text{He for .28 nm}} > T_{\text{He for .20 nm}}$ (increase T) (ii) $T_{\text{He for .28 nm}} < T_{\text{He for .20 nm}}$ (decrease T)

3. Term symbols for the Vanadium Atom.

- 3a. What are the term symbols associated with the ground state electron configuration of the Vanadium atom, $[\text{Ar}]4s^23d^3$? You do not need to show the “J labels”. (6 points)
- 3b. According to Hund’s Rules, what is the ground-state term symbol for Vanadium? (2 points)
- 3c. For the ground state term symbol from #3b, what are the possible values of J? List these in order of increasing energy. (2 points)

4. Mathematical results related to infinitesimal unitary transformations.

Let $\hat{C}(\tau)$ be a time-independent Hermitian operator. Let $\Psi_k(\tau)$ denote the eigenfunctions of the Hamiltonian, $\hat{H}(\tau)$. Denote the ground-state wavefunction as $\Psi_0(\tau)$.

- 4a. Show that for any eigenfunction of the Hamiltonian, the following expectation value is zero:

$$\langle \Psi_k | [\hat{H}, \hat{C}] | \Psi_k \rangle = 0$$

(3 points)

- 4b. Show that the expectation value of the following double-commutator is always greater than or equal to zero for the ground-state wavefunction,

$$\langle \Psi_0 | [\hat{C}, [\hat{H}, \hat{C}]] | \Psi_0 \rangle \geq 0$$

(7 points)

5. The electron in a spherical well.

In the third-year chemistry laboratory, you made “quantum dots.” An electron in a quantum dot can be approximated as a particle in a spherical well,

$$V(r) = \begin{cases} 0 & r \leq a \\ +\infty & r > a \end{cases}$$

The eigenfunctions of this system are products of spherical Bessel functions and spherical Harmonics,

$$\Psi_{klm}(r, \theta, \phi) \propto j_l(kr) Y_l^m(\theta, \phi)$$

The two lowest-order spherical Bessel functions are:

$$j_0(x) = \frac{\sin(x)}{x} \quad j_1(x) = \frac{\sin(x)}{x^2} - \frac{\cos(x)}{x}$$

These functions have the property that they are zero at the following values:

$$\begin{array}{ll} 0 = j_0(x_i) & x_0 = \pi; x_1 = 2\pi; x_3 = 3\pi; \dots \\ 0 = j_1(x_i) & x_0 = 4.493409; x_1 = 7.725252; x_3 = 10.904122; \dots \end{array}$$

The spherical Bessel functions are eigenfunctions of the following differential equation:

$$\left(\frac{-1}{2} \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right) + \frac{l(l+1)}{2r^2} \right) j_l(kr) = \frac{k^2}{2} j_l(kr)$$

- 5a. Confirm, by explicit substitution, that the proposed wavefunction, $\Psi_{klm}(r, \theta, \phi) \propto j_l(kr) Y_l^m(\theta, \phi)$ is an eigenfunction for the “electron in a spherical well” Hamiltonian. (4 points)**
- 5b. What are the energy levels for the s-type “electron in a spherical well” states? What is the ground-state energy for the electron in a spherical well? (3 points)**
- 5c. Suppose that you want to design a quantum dot that absorbs red light, with wavelength $\lambda = 680 \cdot 10^{-9}$ m, and assume that the “electron in a spherical well” is an adequate model for the quantum dot. What radius for the quantum dot will cause the lowest-energy electric-dipole-allowed absorption from the ground state to have wavelength $\lambda = 680$ nm? You will probably find it helpful to work this problem in atomic units. The atomic unit of length is the Bohr, and 1 Bohr = $.52917725 \cdot 10^{-10}$ m. (3 points)**