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Name \_\_\_\_\_ Student # \_\_\_\_\_

## FINAL EXAMINATION CHEMISTRY 3PA3

Fall 2009

### Part 1; Short Answer

There are 112 points possible but the exam is scored out of 100. After you have completed the “short answer” portion of the exam, turn it in and get the “long answer” portion. I will grade the exam “on the fly” so you should have some idea what your final mark is by the end of the day on Saturday.

Key integrals and identities:

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi x}{a}\right) dx$$

$$0 = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\frac{a^2}{4} = \int_0^a \left( \sin\left(\frac{n\pi x}{a}\right) \right)^2 x dx$$

$$\left(\frac{a}{2\pi n}\right)^3 \left(\frac{4\pi^3 n^3}{3} - 2\pi n\right) = \int_0^a \left( \sin\left(\frac{n\pi x}{a}\right) \right)^2 x^2 dx$$

$$\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \int_0^\infty e^{-\alpha x^2} dx$$

$$\left(\frac{1}{2} \sqrt{\frac{\pi}{\alpha}}\right) \left( \frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n} \right) = \int_0^\infty x^{2n} e^{-\alpha x^2} dx \quad n = 1, 2, 3, \dots$$

$$\left(\frac{1}{2}\right) \left(\frac{n!}{\alpha^{n+1}}\right) = \int_0^\infty x^{2n+1} e^{-\alpha x^2} dx \quad n = 0, 1, 2, \dots$$

$$2\sin(x)\sin(y) = \cos(x-y) - \cos(x+y) \rightarrow 2\sin^2 x = 1 - \cos(2x)$$

$$2\cos(x)\cos(y) = \cos(x-y) + \cos(x+y) \rightarrow 2\cos^2 x = 1 + \cos(2x)$$

$$2\sin(x)\cos(y) = \sin(\alpha+\beta) + \sin(\alpha-\beta) \rightarrow 2\sin x \cos x = \sin(2x)$$

$$\sin(x+y) = \sin x \cos y + \cos x \sin y \rightarrow \sin(2x) = 2\sin x \cos x$$

$$\cos(x+y) = \cos x \cos y - \sin x \sin y \rightarrow \cos(2x) = \cos^2 x - \sin^2 x$$

## 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	$k_B$	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
	$k_B$	$0.69509 \text{ cm}^{-1}$
Molar gas constant	$R$	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	$\epsilon_0$	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
	$\epsilon_0$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
Rydberg constant (infinite nuclear mass)	$R_\infty$	$2.179914 \times 10^{-23} \text{ J}$
	$R_\infty$	$1.097373 \text{ cm}^{-1}$
First Bohr radius	$a_0$	$5.29177 \times 10^{-11} \text{ m}$
Bohr magneton	$\mu_B$	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
Stefan-Boltzmann constant	$\sigma$	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

### CONVERSION FACTORS FOR ENERGY UNITS

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

**Short Answer Questions: (31 questions @ 2 points each = 62 points total).**

1. The *units* of the ground-state wavefunction for the Hydrogen atom,  $\psi_{1s}(\mathbf{r})$ , are

- |                                     |                                      |                                     |
|-------------------------------------|--------------------------------------|-------------------------------------|
| (a) $(\text{length})^3$             | (f) $(\text{length})^{\frac{1}{2}}$  | (k) $(\text{length})^{-1}$          |
| (b) $(\text{length})^{\frac{5}{2}}$ | (g) $(\text{length})^{-3}$           | (l) $(\text{length})^{\frac{1}{2}}$ |
| (c) $(\text{length})^2$             | (h) $(\text{length})^{-\frac{5}{2}}$ | (m) the wavefunction is unitless.   |
| (d) $(\text{length})^{\frac{3}{2}}$ | (i) $(\text{length})^{-2}$           | (n) none of the above.              |
| (e) $(\text{length})^1$             | (j) $(\text{length})^{-\frac{3}{2}}$ |                                     |

2,3. The Davisson-Germer experiment measured the electron diffraction pattern when a beam of electrons (a so-called “cathode ray,” like in the old CRT monitors) impinged on a Nickel surface at a  $90^\circ$  angle. The spacing between planes of Nickel atoms is  $d = .91 \cdot 10^{-10}$  m. In order to see a diffraction pattern, what is the (approximate) velocity of the electrons in the beam? Write your answer in meters/second.

4,5. An experimental study of the photoelectric effect is performed on a sample of Cesium, which has the work function  $\Phi = 2.14$  eV and electrons with a kinetic energy of 1.00 eV are emitted. What is the wavelength of the light that is shining on the Cesium surface? Write your answer in nanometers.

6. Write the Hamiltonian for a Harmonic Oscillator with force constant  $k$ , reduced mass  $\mu$ , and equilibrium bond length  $r_e$ .
7. Because the chemical bond in CO is so strong, the rigid rotor is an excellent approximation to the rotation of CO. It is sometimes interesting to measure rotational spectra for several different isotopes. For example, we could measure the rotational spectrum for  $^{12}_6\text{C}-^{16}_8\text{O}$  and  $^{14}_6\text{C}-^{18}_8\text{O}$ . **The spacing between the rotational energy levels is**
- |  |   |
|--|---|
| (a) greater in $^{12}_6\text{C}-^{16}_8\text{O}$ than in $^{14}_6\text{C}-^{18}_8\text{O}$ .<br>(b) greater in $^{14}_6\text{C}-^{18}_8\text{O}$ than in $^{12}_6\text{C}-^{16}_8\text{O}$ . | (c) the same in $^{14}_6\text{C}-^{18}_8\text{O}$ and $^{12}_6\text{C}-^{16}_8\text{O}$ . |
|--|---|
8. Because the chemical bond in CO (carbon monoxide) is so strong, the harmonic oscillator is an excellent approximation to the vibrations in CO. **The lowest-energy electric-dipole-allowed vibrational excitation of the CO (carbon monoxide) molecule is associated with absorbing photons with frequency  $6.42 \cdot 10^{13}$  Hz. The equilibrium bond length of CO is  $1.128 \cdot 10^{-10}$  m.**

A student forgot the exact ground state wavefunction and energy for the harmonic oscillator, so he decided to try to obtain an approximate ground state energy with the variational principle. As his trial wavefunction, he chose:

$$\psi(r) = Ae^{-\alpha(r-1.128 \cdot 10^{-10} \text{ m})^2},$$

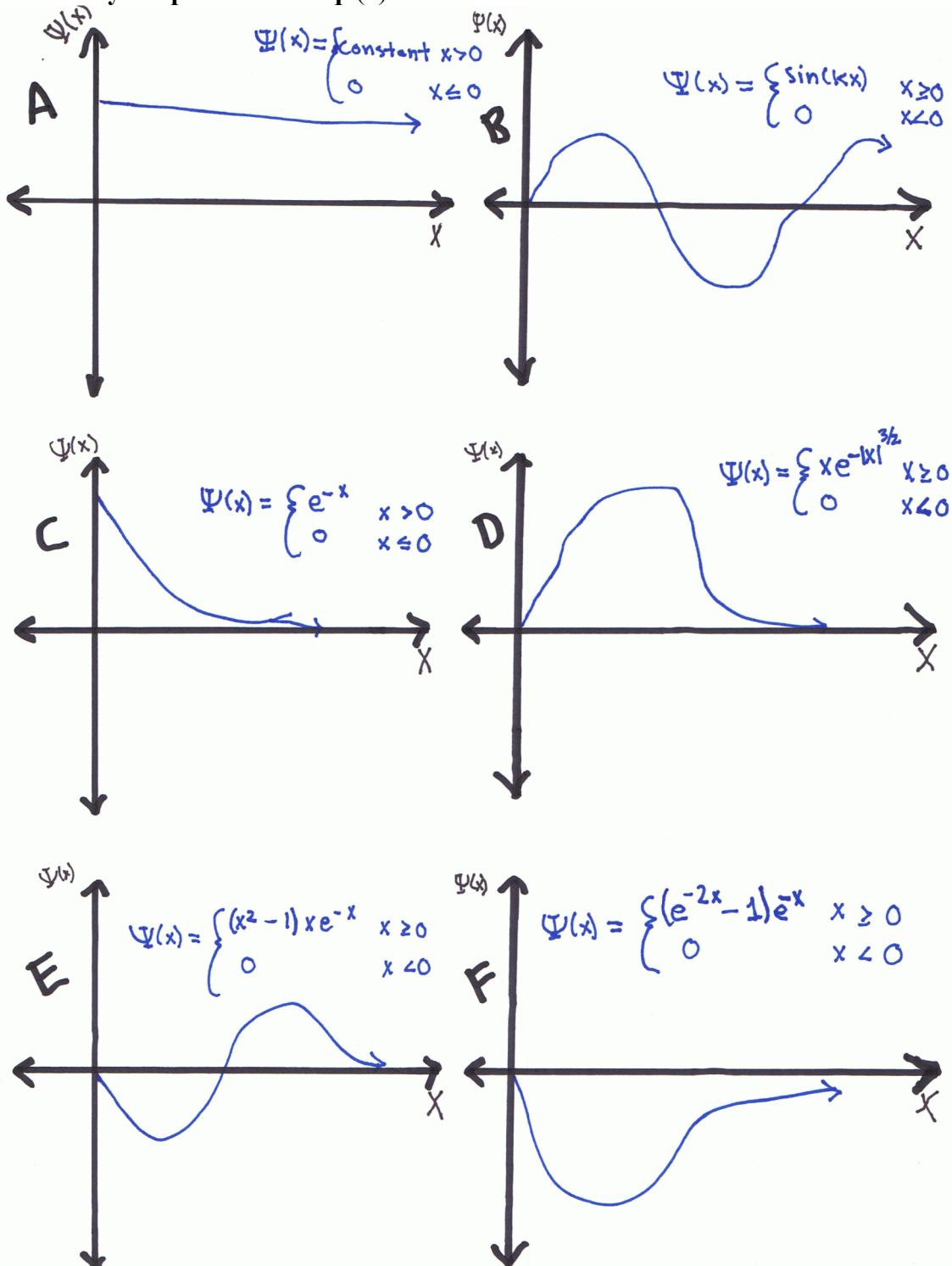
mainly because it gave easy integrals.  $A$  is the normalization constant. He then evaluated the energy of the Harmonic-Oscillator Hamiltonian and minimized the result with respect to  $\alpha$ . **The answer he obtains will be (to the given number of significant figures):**

- |  |  |
|--|--|
| (a) greater than $8.51 \cdot 10^{-20}$ J.<br>(b) equal to $8.51 \cdot 10^{-20}$ J.<br>(c) greater than $4.25 \cdot 10^{-20}$ J but less than $8.51 \cdot 10^{-20}$ J.<br>(d) equal to $4.25 \cdot 10^{-20}$ J. | (e) greater than $2.13 \cdot 10^{-20}$ J but less than $4.25 \cdot 10^{-20}$ J.<br>(f) equal to $2.13 \cdot 10^{-20}$ J.<br>(g) less than $2.13 \cdot 10^{-20}$ J but greater than zero.<br>(h) zero |
|--|--|

9. Consider the following potential,

$$V(x) = \begin{cases} +\infty & x < 0 \\ x & x \geq 0 \end{cases} \quad (1)$$

Which of the following sketches is a possible ground-state wavefunction for a particle bound by the potential in Eq. (1).



**10-11.** 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
	<b>Carbon tetrachloride</b>	
	<b>Coronene</b>	
	<b>1-butyne</b>	
	<b>propyne</b>	

**12-14.** 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**       $\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array}$  (7)  
                (14)  
                (14)  
                (14)

$\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array}$  (5)  
                (10)  
                (10)

$\begin{array}{c} \text{---} \\ \text{---} \end{array}$  (3)  
                (6)

— (1)

**B**      — (1)  
                — (1)

— (1)

— (1)

— (1)

— (1)

— (1)

— (1)

— (1)

— (1)

**C**       $\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array}$  (14)  
                (14)  
                (14)  
                (7)

$\begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array}$  (10)  
                (10)  
                (5)

$\begin{array}{c} \text{---} \\ \text{---} \end{array}$  (6)  
                (3)

— (1)

**D**      — (1)

— (1)

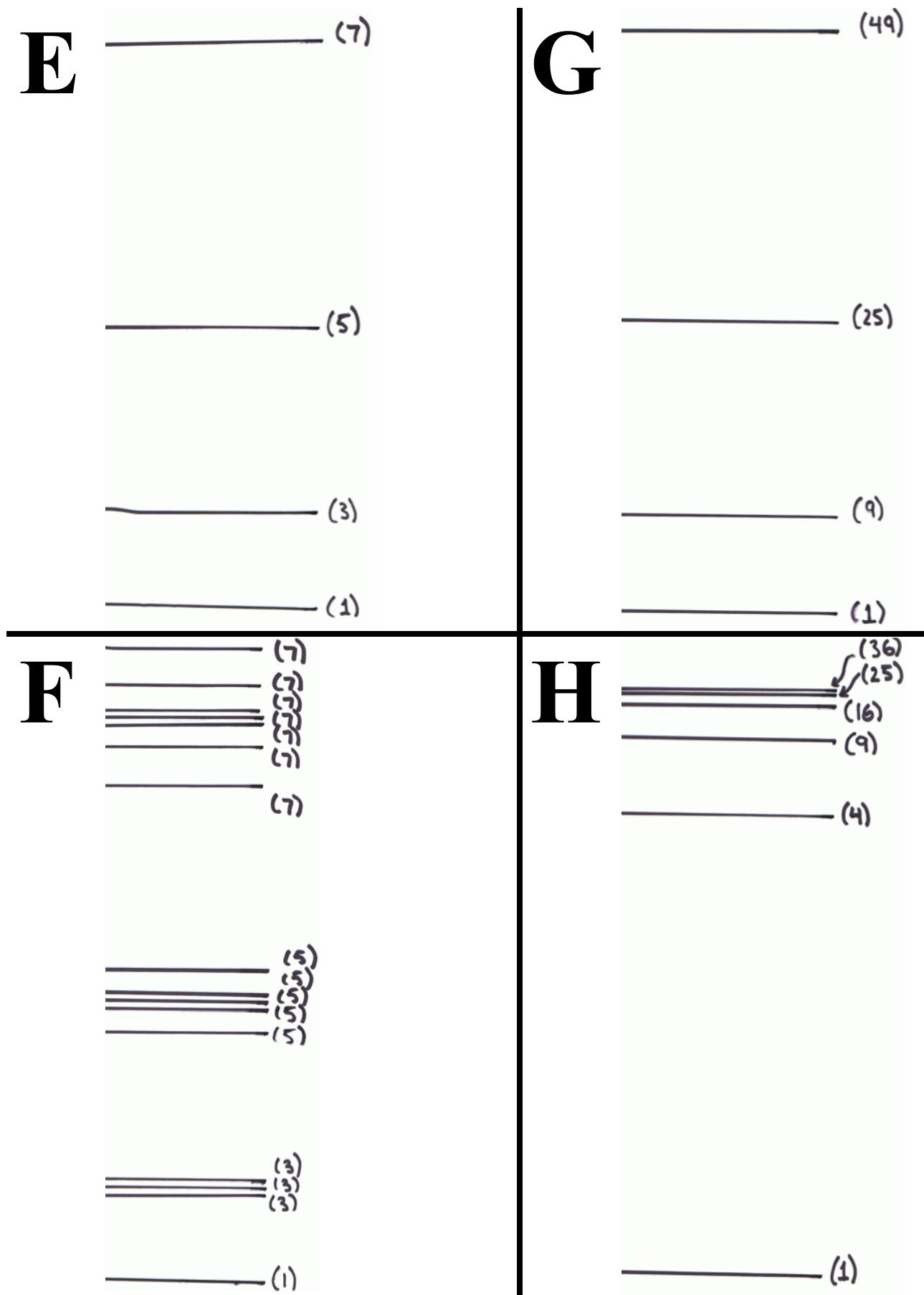
— (1)

— (1)

— (1)

— (1)

— (1)



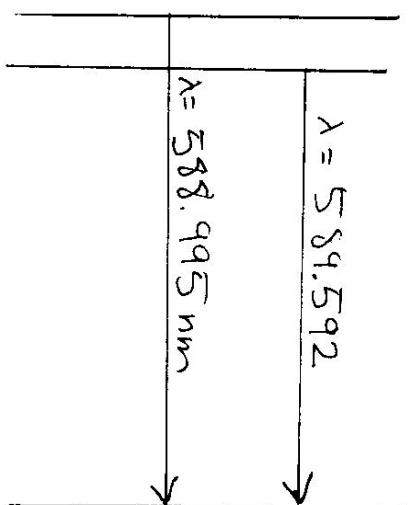
**15,16. What are the term symbols associated with the  $[\text{Ne}]3s^13p^13d^1$  excited state of the Aluminum atom?** You do not need to include the "J" levels.

**17. Assume that Hund's rules apply in #15,16. Which term symbol is associated with the lowest energy? You do not need to consider the "J" levels.**

**18. What is the degeneracy of an atomic state described by the  ${}^7G$  term symbol?**

**19. In Europe, streetlights often give off yellow light, instead of the blueish-white light that is typical in North America. This is because European streetlamps are Sodium lamps, instead of Mercury lamps. (This is a bit more efficient: Mercury emits a lot of light in the UV, while the strongest emission from a Sodium lamp is the yellow light from the "sodium D line," (where "D" stands for "doublet", not  $L = 2$ ). The sodium "D" line corresponds to the  $1s^22s^22p^63p^1 \rightarrow 1s^22s^22p^63s^1$  transition. Use term symbols to label the each state on the energy level diagram. Assume Hund's rules can be used to order the excited states.**

Term Symbol



20. In bra-ket notation, the Hermitian property of the “momentum in the  $x$  direction” operator,  $\hat{p}_x$ , can be written as

$$\langle \Phi(x) | \hat{p}_x \Psi(x) \rangle = \langle \hat{p}_x \Phi(x) | \Psi(x) \rangle$$

Write the corresponding equation as an integral, taking care to substitute in the appropriate explicit formula for  $\hat{p}_x$ .

21. Write a simple approximation for the binding molecular orbital in the Fluorine dimer;  $F_2$ . (The electron configuration of F is  $1s^2 2s^2 2p^5$ .)

22. Write a Slater determinant of molecular orbitals that is appropriate for the *ground state* of the hydrogen molecule anion,  $H_2^-$ . 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.

**23,24.** 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, $\hat{V}_{ee}$	

**25,26.** Using the notation in the first column of the table in #25-#26, write the electronic and nuclear time-independent Schrödinger equations for a molecule.

**Electronic:**

**Nuclear:**

**The following text is used in problems 27-31.**

You are given a Helium cation ( $\text{He}^+$ ) that has been prepared in a state described by the following wavefunction,

$$\Psi_{\text{He}^+}(\mathbf{r}, t) = .5774\psi_{3s}(\mathbf{r}, t) - .7071\psi_{3p_1}(\mathbf{r}, t) + .4082\psi_{3d_2}(\mathbf{r}, t)$$

Here  $\psi_{\text{label}}(\mathbf{r}, t)$  are the normalized eigenfunctions of the  $\text{He}^+$  Hamiltonian and the subscripts indicate the  $n$ ,  $l$ , and (for the double-subscript)  $m_l$  quantum number.

**27. What is the expectation value for the energy in this system?** Give your answer in atomic units.

**28. What is the expectation value of the square magnitude of the total orbital angular momentum,  $\langle \hat{L}^2 \rangle$ ?** Show the dependence of your answer on  $\hbar$ .

**29. What is the expectation value for the amount of orbital angular momentum about the  $z$  axis,  $\langle \hat{L}_z \rangle$ ?** Show the dependence of your answer on  $\hbar$ .

**30. If you measure the total orbital angular momentum of this system, what is the probability that you will obtain “zero” for the answer?**

**31. Does  $\Psi(\mathbf{r}, t)$  describe a stationary state of  $\text{He}^+$ ?**

Name \_\_\_\_\_ Student # \_\_\_\_\_

## Part 2. Problems

Pick THREE of the following SIX problems. Each problem is worth 15 points. There is a 5-point bonus after problem #6

Clearly indicate which problems you wish for me to mark by marking an “X” in the following “score sheet” for the problems that you do not want me to mark.

Problem	#1	#2	#3	#4	#5	#6	BONUS	TOTAL
Score								

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

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

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Paul

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1 cm $^{-1}$	$= 1.986 \times 10^{-23}$	$1.196 \times 10^{-4}$	$1.240 \times 10^{-4}$	$4.556 \times 10^{-6}$	$1$
1 Hz	$= 6.626 \times 10^{-44}$	$3.990 \times 10^{-13}$	$4.136 \times 10^{-15}$	$1.520 \times 10^{-16}$	$3.336 \times 10^{-11}$
					$1$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**1. The spread of bond lengths in the Harmonic Oscillator.**

The eigenvalues of the simple oscillator are given by

$$E(v) = \hbar \left( \sqrt{\frac{k_e}{\mu}} \right) \left( v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots \quad (2)$$

where the reduced mass of the oscillator is simply related to the atomic masses by  $\mu = (m_A m_B / (m_A + m_B))$ . Here,  $k_e$  is the force constant of the oscillator and  $r_e$  denotes the equilibrium bond distance. The eigenfunctions of the two lowest energy states of the harmonic oscillator are given below

$$\psi_0(r) = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}(r-r_e)^2} \quad \psi_1(r) = \left( \frac{\alpha}{\pi} \right)^{1/4} \left( \sqrt{2\alpha} \right) (r - r_e) e^{-\frac{\alpha}{2}(r-r_e)^2} \quad (3)$$

where

$$\alpha = \sqrt{\frac{k_e \mu}{\hbar^2}} \quad (4)$$

- (a) Write down the Harmonic-Oscillator Hamiltonian and show that  $\psi_0(r)$  is an eigenfunction of it. (4 points)

**(b) The lowest-energy vibrational excitation of the  $^{12}\text{C}^{16}\text{O}$  (carbon monoxide) molecule is associated with absorbing photons with frequency  $6.42 \cdot 10^{13}$  Hz. The equilibrium bond length of CO is  $1.128 \cdot 10^{-10}$  m. Use the harmonic oscillator model to estimate the spread in bond lengths,  $\sigma_r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$ , for the ground state of CO. (8 points)**

- (c) Using your result in part 1b, obtain a lower bound for the kinetic energy for the ground vibrational state of the  $^{12}\text{C}^{16}\text{O}$  molecule. (3 points)

2. Derive the “equation of motion” for the change in the expectation value of a time-dependent Hermitian operator:

$$i\hbar \frac{d\langle C(t) \rangle}{dt} = \int \Psi^*(\tau, t) [\hat{C}(\tau, t), \hat{H}(\tau, t)] \Psi(\tau, t) d\tau + i\hbar \int \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) d\tau$$

(15 points)

**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”. (10 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. (3 points)**

- 4. Energy of 2-electron atoms.** For the 2-electron atom, we considered a wave function with the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \left( \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

where

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}$$

We found that the energy of this wave function was given by the form,

$$\begin{aligned} E(\zeta) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - Z) \end{aligned}$$

where the Hamiltonian of the 2-electron atom has the form

$$\hat{H} \equiv \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- (a) Suppose we approximate the energy of the Lithium cation ( $\text{Li}^+$ ) by using first-order perturbation theory, where the electron-electron repulsion term in the Hamiltonian is treated as a perturbation. What is the approximate energy? (8 points)

- (b) Suppose we approximate the energy of the Helium atom using the variational principle, using trial wave functions with the form given by in the problem statement. What is the approximate energy? (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:

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

- (a) 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. (5 points)**

- (b) 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? (5 pts.)
- (c) Suppose that you want to design a quantum dot that absorbs red light, with wavelength  $\lambda = 680 \cdot 10^{-9} \text{ m}$ , 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  $\lambda = 680 \text{ nm}$ ?** You will probably find it helpful to work this problem in atomic units. The atomic unit of length is the Bohr, and 1 Bohr =  $.52917725 \cdot 10^{-10} \text{ m}$ . (5 points)

**6. 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  $\Psi_0(\tau)$ .

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

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

(5 pts.)

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

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

(10 points)

**BONUS:** The results in problem #6 are key results associated with the theory of infinitesimal unitary transformations. The theory of infinitesimal unitary transformations describes, among other things, how wavefunctions change in time, and was the key mathematical concept behind Julian Schwinger's development of quantum field theory, for which he shared the 1965 Nobel Prize and became justly famous. The key idea here is that the following operator,

$$\hat{U}_\epsilon = \hat{I} + i\epsilon \hat{C}$$

is an infinitesimal unitary transformation, where  $\hat{I}$  is the identity operator (i.e., “multiply by one”). Here  $\epsilon$  is a very small (“infinitesimal”) real number.

**Using equations, explain why  $\hat{U}_\epsilon$  can be interpreted as an “infinitesimal unitary transformation” if  $\hat{C}$  is a Hermitian operator, but cannot be interpreted as an “infinitesimal unitary transformation” if  $\hat{C}$  is not Hermitian. (5 points)** (This requires you to remember that a unitary transformation/matrix/operator is defined by the fact that its Hermitian conjugate is equal to its inverse.)

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Name

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Student #**FINAL EXAMINATION CHEMISTRY 3PA3****Fall 2009****Part 1; Short Answer**

**There are 112 points possible but the exam is scored out of 100. After you have completed the “short answer” portion of the exam, turn it in and get the “long answer” portion. I will grade the exam “on the fly” so you should have some idea what your final mark is by the end of the day on Saturday.**

**Key integrals and identities:**

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi x}{a}\right) dx$$

$$0 = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\frac{a^2}{4} = \int_0^a \left( \sin\left(\frac{n\pi x}{a}\right) \right)^2 x dx$$

$$\left(\frac{a}{2\pi n}\right)^3 \left(\frac{4\pi^3 n^3}{3} - 2\pi n\right) = \int_0^a \left( \sin\left(\frac{n\pi x}{a}\right) \right)^2 x^2 dx$$

$$\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \int_0^\infty e^{-\alpha x^2} dx$$

$$\left(\frac{1}{2} \sqrt{\frac{\pi}{\alpha}}\right) \left( \frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n} \right) = \int_0^\infty x^{2n} e^{-\alpha x^2} dx \quad n = 1, 2, 3, \dots$$

$$\left(\frac{1}{2}\right) \left(\frac{n!}{\alpha^{n+1}}\right) = \int_0^\infty x^{2n+1} e^{-\alpha x^2} dx \quad n = 0, 1, 2, \dots$$

$$2\sin(x)\sin(y) = \cos(x-y) - \cos(x+y) \rightarrow 2\sin^2 x = 1 - \cos(2x)$$

$$2\cos(x)\cos(y) = \cos(x-y) + \cos(x+y) \rightarrow 2\cos^2 x = 1 + \cos(2x)$$

$$2\sin(x)\cos(y) = \sin(\alpha+\beta) + \sin(\alpha-\beta) \rightarrow 2\sin x \cos x = \sin(2x)$$

$$\sin(x+y) = \sin x \cos y + \cos x \sin y \rightarrow \sin(2x) = 2\sin x \cos x$$

$$\cos(x+y) = \cos x \cos y - \sin x \sin y \rightarrow \cos(2x) = \cos^2 x - \sin^2 x$$

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	$k_B$	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
	$k_B$	$0.69509 \text{ cm}^{-1}$
Molar gas constant	$R$	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	$\epsilon_0$	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
Rydberg constant (infinite nuclear mass)	$R_\infty$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
First Bohr radius	$a_0$	$2.179914 \times 10^{-15} \text{ J}$
Bohr magneton	$\mu_B$	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
Stefan-Boltzmann constant	$\sigma$	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

**CONVERSION FACTORS FOR ENERGY UNITS**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**Short Answer Questions: (31 questions @ 2 points each = 62 points total).**

1. The *units* of the ground-state wavefunction for the Hydrogen atom,  $\psi_{1s}(r)$ , are

- |                             |                              |                                   |
|-----------------------------|------------------------------|-----------------------------------|
| (a) $(\text{length})^3$     | (f) $(\text{length})^{1/2}$  | (k) $(\text{length})^{-1}$        |
| (b) $(\text{length})^{5/2}$ | (g) $(\text{length})^{-3}$   | (l) $(\text{length})^{1/2}$       |
| (c) $(\text{length})^2$     | (h) $(\text{length})^{-5/2}$ | (m) the wavefunction is unitless. |
| (d) $(\text{length})^{3/2}$ | (i) $(\text{length})^{-2}$   | (n) none of the above.            |
| (e) $(\text{length})^1$     | (j) $(\text{length})^{-3/2}$ |                                   |

2,3. The Davisson-Germer experiment measured the electron diffraction pattern when a beam of electrons (a so-called “cathode ray,” like in the old CRT monitors) impinged on a Nickel surface at a  $90^\circ$  angle. The spacing between planes of Nickel atoms is  $d = .91 \cdot 10^{-10} \text{ m}$ . In order to see a diffraction pattern, what is the (approximate) velocity of the electrons in the beam? Write your answer in meters/second.

The wavelength of the light needs to be about twice the lattice spacing. Then, using the De Broglie relation,

$$\begin{aligned}\lambda &= 2(.91 \cdot 10^{-10} \text{ m}) = \frac{h}{p} \\ p &= \frac{h}{2(.91 \cdot 10^{-10} \text{ m})} = 3.64 \cdot 10^{-24} \frac{\text{m}}{\text{s}} \\ v &= \frac{p}{m} = \frac{3.64 \cdot 10^{-24} \frac{\text{kg} \cdot \text{m}}{\text{s}}}{9.1095 \cdot 10^{-31} \text{ kg}} \\ &= 4.00 \cdot 10^6 \frac{\text{m}}{\text{s}}\end{aligned}$$

4,5. An experimental study of the photoelectric effect is performed on a sample of Cesium, which has the work function  $\Phi = 2.14 \text{ eV}$  and electrons with a kinetic energy of  $1.00 \text{ eV}$  are emitted. What is the wavelength of the light that is shining on the Cesium surface? Write your answer in nanometers.

The total energy of the light that is impinging on the surface must be  $2.14 \text{ eV} + 1.00 \text{ eV} = 3.14 \text{ eV}$ . Then, using Planck's law,

$$\begin{aligned}h\nu &= 3.14 \text{ eV} \\ \nu &= \frac{3.14 \text{ eV}}{h} = \frac{(3.14 \text{ eV}) \cdot 1.602 \cdot 10^{-19} \frac{\text{J}}{\text{eV}}}{6.6262 \cdot 10^{-34} \text{ J} \cdot \text{s}} = 7.592 \cdot 10^{14} \frac{1}{\text{s}} \\ \lambda &= \frac{c}{\nu} = \frac{2.998 \cdot 10^8 \frac{\text{m}}{\text{s}}}{7.592 \cdot 10^{14} \frac{1}{\text{s}}} = 3.949 \cdot 10^{-7} \text{ m} \\ &= 394.9 \text{ nm}\end{aligned}$$

6. Write the Hamiltonian for a Harmonic Oscillator with force constant  $k$ , reduced mass  $\mu$ , and equilibrium bond length  $r_e$ .

$$\hat{H}_{HO} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{1}{2}k(r - r_e)^2$$

7. Because the chemical bond in CO is so strong, the rigid rotor is an excellent approximation to the rotation of CO. It is sometimes interesting to measure rotational spectra for several different isotopes. For example, we could measure the rotational spectrum for  $^{12}_6C-^{16}_8O$  and  $^{14}_6C-^{18}_8O$ . The spacing between the rotational energy levels is

(a) greater in  $^{12}_6C-^{16}_8O$  than in  $^{14}_6C-^{18}_8O$ .

(c) the same in  $^{14}_6C-^{18}_8O$  and  $^{12}_6C-^{16}_8O$ .

(b) greater in  $^{14}_6C-^{18}_8O$  than in  $^{12}_6C-^{16}_8O$ .

Method A: The more massive the molecule, the closer it is to classical and the narrower the spacing of energy levels.

Method B: The rotational energy levels of a rigid diatomic molecule are

$E_J = \frac{\hbar^2 J(J+1)}{2\mu r_e^2}$ . The larger the mass of the isotopes is, the larger  $\mu$  is, and the smaller the spacing between energy levels.

8. Because the chemical bond in CO (carbon monoxide) is so strong, the harmonic oscillator is an excellent approximation to the vibrations in CO. The lowest-energy electric-dipole-allowed vibrational excitation of the CO (carbon monoxide) molecule is associated with absorbing photons with frequency  $6.42 \cdot 10^{13}$  Hz. The equilibrium bond length of CO is  $1.128 \cdot 10^{-10}$  m.

A student forgot the exact ground state wavefunction and energy for the harmonic oscillator, so he decided to try to obtain an approximate ground state energy with the variational principle. As his trial wavefunction, he chose:

$$\psi(r) = Ae^{-\alpha(r - 1.128 \cdot 10^{-10} \text{ m})^2},$$

mainly because it gave easy integrals.  $A$  is the normalization constant. He then evaluated the energy of the Harmonic-Oscillator Hamiltonian and minimized the result with respect to  $\alpha$ . The answer he obtains will be (to the given number of significant figures):

- (a) greater than  $8.51 \cdot 10^{-20}$  J.  
 (b) equal to  $8.51 \cdot 10^{-20}$  J.  
 (c) greater than  $4.25 \cdot 10^{-20}$  J but less than  $8.51 \cdot 10^{-20}$  J.  
 (d) equal to  $4.25 \cdot 10^{-20}$  J.

- (e) greater than  $2.13 \cdot 10^{-20}$  J but less than  $4.25 \cdot 10^{-20}$  J.  
 (f) equal to  $2.13 \cdot 10^{-20}$  J.  
 (g) less than  $2.13 \cdot 10^{-20}$  J but greater than zero.  
 (h) zero

This wavefunction has the exact right form for the harmonic oscillator, so it will give the exact ground-state energy, which is  $\frac{1}{2}\hbar\nu_0$ . So the ground-state (or "zero point" energy is):  $E_0 = \frac{1}{2}\hbar\nu_0 = \frac{1}{2}(6.6262 \cdot 10^{-34} \text{ J} \cdot \text{s})(6.42 \cdot 10^{13} \frac{1}{\text{s}}) = 2.127 \cdot 10^{-20} \text{ J}$ .

9. Consider the following potential,

$$V(x) = \begin{cases} +\infty & x < 0 \\ x & x \geq 0 \end{cases} \quad (1)$$

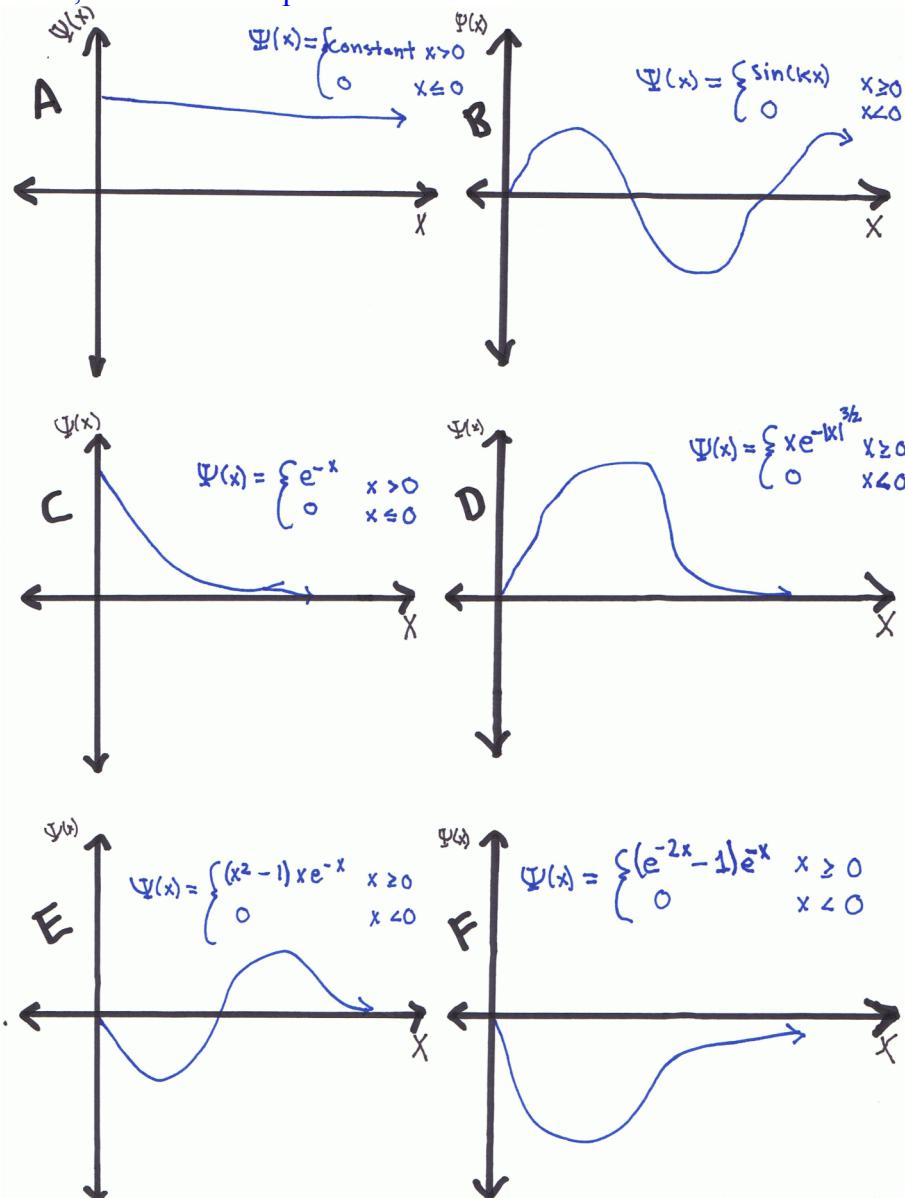
Which of the following sketches is a possible ground-state wavefunction for a particle bound by the potential in Eq. (1).

D and F are the answers.

A and B are not normalizable.

C is not zero where the potential diverges.

E has a node, and thus corresponds to an excited state.



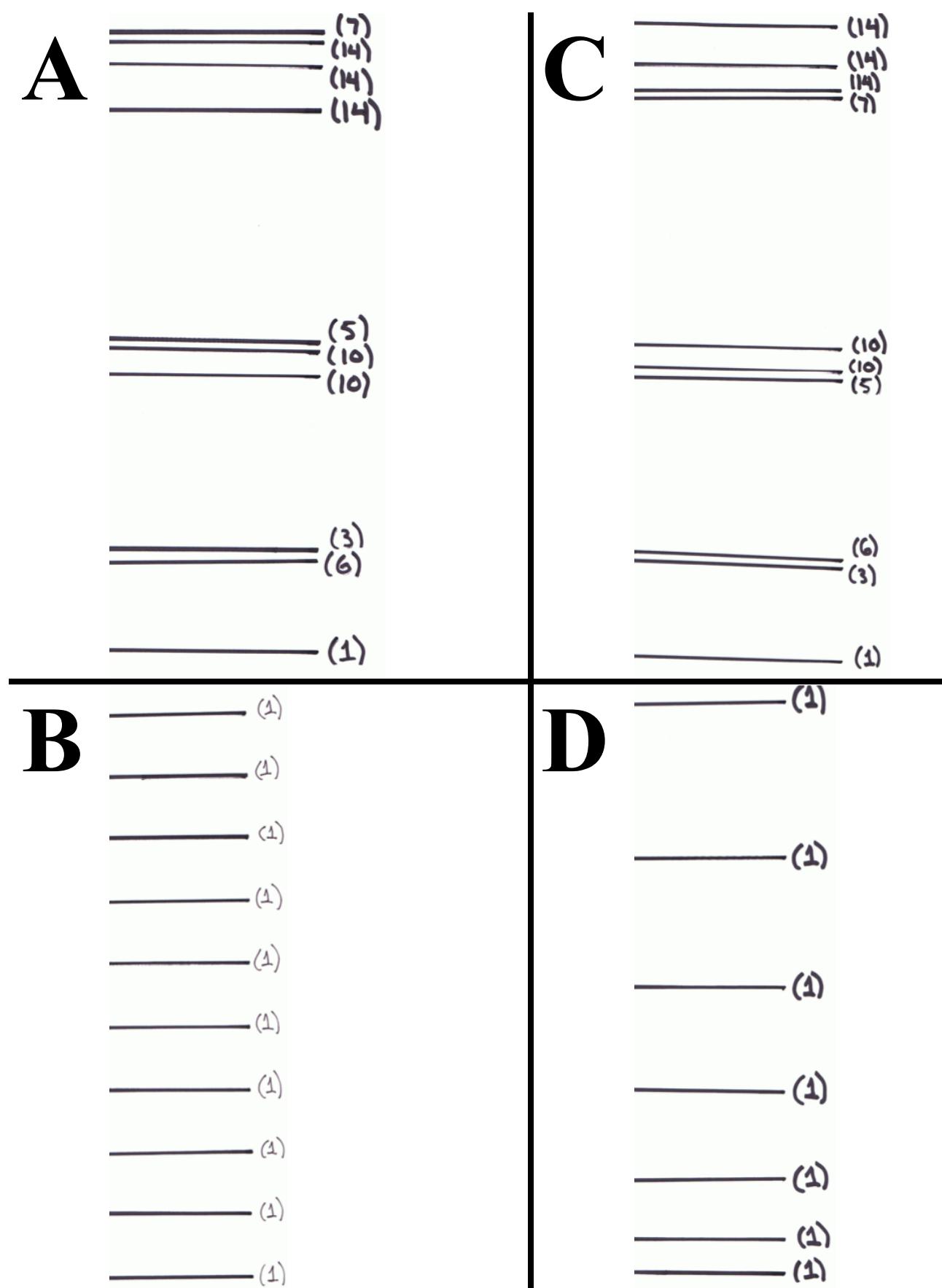
**10-11.** Fill in the first column of the following table, labelling the following molecules as:

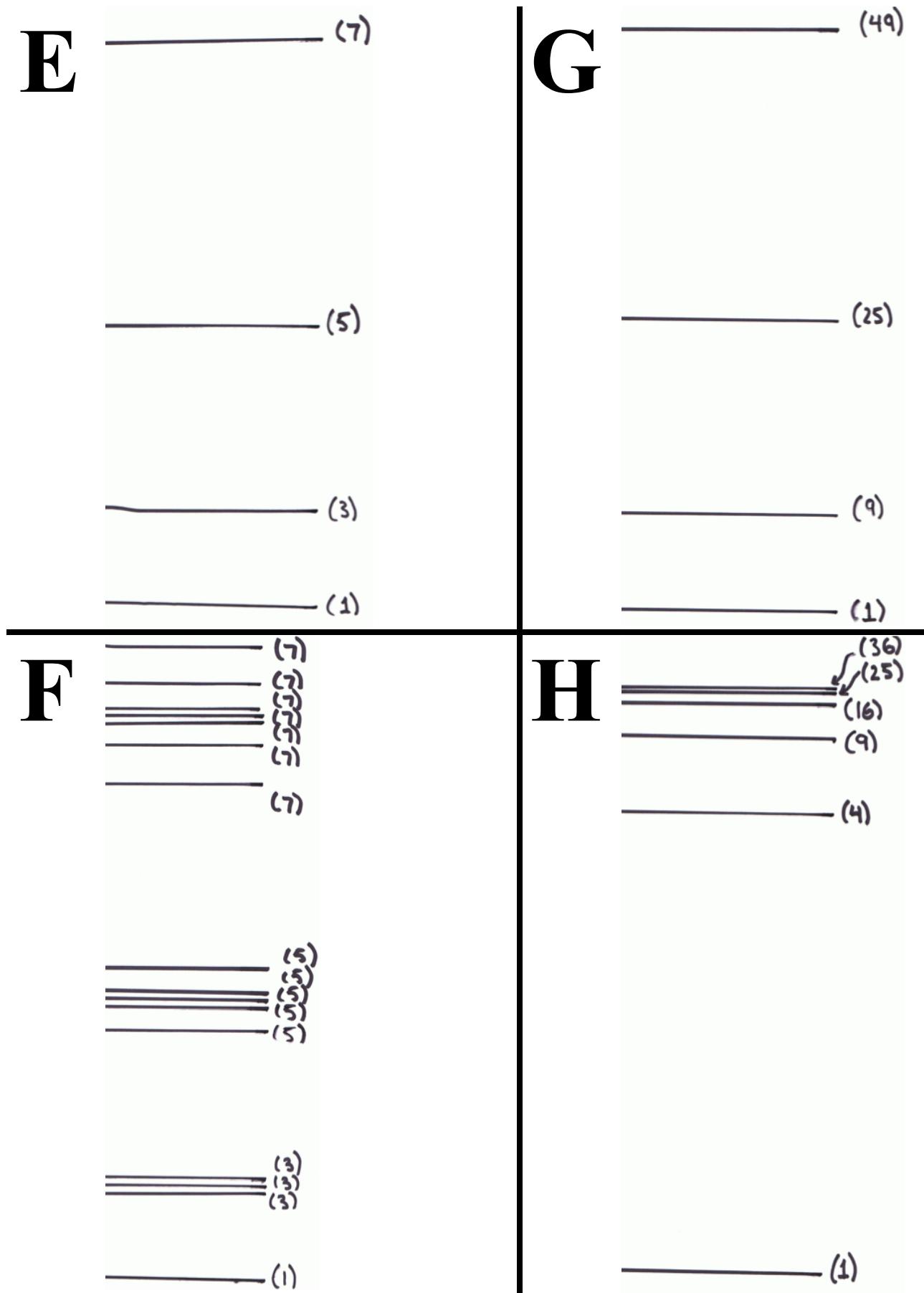
- O oblate symmetric top
- P prolate symmetric top
- S spherical top
- A asymmetric top

Type of “top”	Name of Molecule	Structure of Molecule
S (spherical)	Carbon tetrachloride	
O (oblate)	Coronene	
A (asymmetric)	1-butyne	
P (prolate)	propyne	

**12-14.** Match the following systems to the energy level diagrams on the next page. 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.

- H One-Electron Atom
- B One-Dimensional Harmonic Oscillator
- D One-Dimensional Particle in a Box with Infinite Sides
- G Rigid Rotation of a Spherical Top Molecule
- A Rigid Rotation of a Oblate Symmetric Top Molecule
- C Rigid Rotation of a Prolate Symmetric Top Molecule





**15,16. What are the term symbols associated with the  $[\text{Ne}]3s^13p^13d^1$  excited state of the Aluminum atom?** You do not need to include the “J” levels.

Always start with the “hardest” part, which in this case is the highest angular momentum case. Starting with the  $p^1d^1$  part, the possible values of  $L$  and  $S$  are given by:

$$\begin{aligned} |S_1 - S_2| &\leq S \leq S_1 + S_2 \\ \left|\frac{1}{2} - \frac{1}{2}\right| &= 0 \leq S \leq \frac{1}{2} + \frac{1}{2} = 1 \\ S &= 0, 1 \\ |L_1 - L_2| &\leq L \leq L_1 + L_2 \\ |2 - 1| &= 1 \leq L \leq 2 + 1 = 3 \\ L &= 1, 2, 3 \end{aligned}$$

So the term symbols for  $p^1d^1$  are  ${}^1\text{P}, {}^1\text{D}, {}^1\text{F}; {}^3\text{P}, {}^3\text{D}, {}^3\text{F}$

Now we couple each of these states to the  $s^1$  part. The angular momentum does not change because the  $s$  orbital has no orbital angular momentum,

$$|L_{s^1} - L_{p^1d^1}| = L_{p^1d^1} \leq L \leq L_{p^1d^1} = L_{s^1} + L_{p^1d^1}$$

By the same argument, the spin does the following

When the  $p^1d^1$  term is a singlet:

$$\begin{aligned} |S_1 - 0| &= \frac{1}{2} \leq S_{\text{total}} \leq \frac{1}{2} = S_1 + 0 \\ S_{\text{total}} &= \frac{1}{2} \end{aligned}$$

and so one has the term symbols:  ${}^2\text{P}, {}^2\text{D}, {}^2\text{F}$ .

When the  $p^1d^1$  term is a triplet:

$$\begin{aligned} \left|\frac{1}{2} - 1\right| &= \frac{1}{2} \leq S_{\text{total}} \leq \frac{3}{2} = \frac{1}{2} + 1 \\ S_{\text{total}} &= \frac{1}{2}, \frac{3}{2} \end{aligned}$$

and so one has the term symbols:  ${}^2\text{P}, {}^2\text{D}, {}^2\text{F}; {}^4\text{P}, {}^4\text{D}, {}^4\text{F}$ .

Combining the two cases, the full set of term symbols is:

$$2({}^2\text{P}), 2({}^2\text{D}), 2({}^2\text{F}); {}^4\text{P}, {}^4\text{D}, {}^4\text{F}.$$

Notice that there are *two* different states corresponding to the same term symbol in some cases.

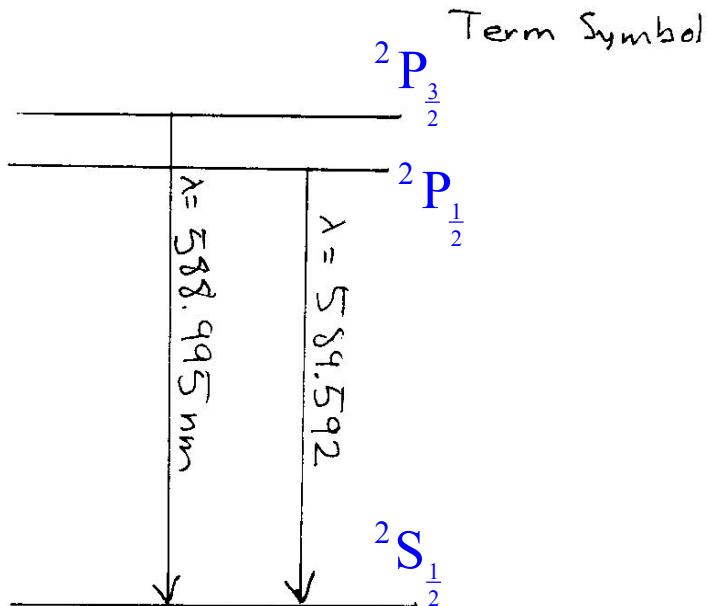
**17. Assume that Hund’s rules apply in #15,16. Which term symbol is associated with the lowest energy?** You do not need to consider the “J” levels.

${}^4\text{F}$

- 18. What is the degeneracy of an atomic state described by the  $^7G$  term symbol?  
63 (SIXTY-THREE)**

For this state,  $L=4$  and  $2S+1=7 \rightarrow S=3$ . So there are *nine*  $M_L$  states ( $M_L = -4, -3, \dots, 2, 3, 4$ ) and *seven*  $M_S$  states ( $M_S = -3, -2, \dots, 1, 2, 3$ ). So there are  $63 = 9 \cdot 7$  total states.

- 19.** In Europe, streetlights often give off yellow light, instead of the blueish-white light that is typical in North America. This is because European streetlamps are Sodium lamps, instead of Mercury lamps. (This is a bit more efficient: Mercury emits a lot of light in the UV, while the strongest emission from a Sodium lamp is the yellow light from the “sodium D line,” (where “D” stands for “doublet”, not  $L=2$ ). The sodium “D” line corresponds to the  $1s^2 2s^2 2p^6 3p^1 \rightarrow 1s^2 2s^2 2p^6 3s^1$  transition. **Use term symbols to label the each state on the energy level diagram. Assume Hund's rules can be used to order the excited states.**



The splitting here is due to the  $J$  quantum number. That gives rise to the above labels.

20. In bra-ket notation, the Hermitian property of the “momentum in the  $x$  direction” operator,  $\hat{p}_x$ , can be written as

$$\langle \Phi(x) | \hat{p}_x \Psi(x) \rangle = \langle \hat{p}_x \Phi(x) | \Psi(x) \rangle$$

**Write the corresponding equation as an integral, taking care to substitute in the appropriate explicit formula for  $\hat{p}_x$ .**

$$\int \Phi^*(x) \left( -i\hbar \frac{d}{dx} \right) \Psi(x) dx = \int \left( i\hbar \frac{d}{dx} \right) \Phi^*(x) \Psi(x) dx$$

21. Write a simple approximation for the binding molecular orbital in the Fluorine dimer;  $F_2$ . (The electron configuration of F is  $1s^2 2s^2 2p^5$ .)

If the bond is directed along the  $z$  axis, then,

$$\psi_{\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}} (\phi_{2p_z}(\mathbf{r}) - \phi_{2p_z}(\mathbf{r}))$$

22. Write a Slater determinant of molecular orbitals that is appropriate for the *ground state* of the hydrogen molecule anion,  $H_2^-$ . Label the molecular orbitals with symmetry labels, i.e.  $\sigma_u, \sigma_g, \pi_u^+, \pi_u^-, \pi_g^+, \pi_g^-$ , ... **Write out the long form of the Slater determinant, including all the rows and columns.**

$$\frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{\sigma_g}(\mathbf{r}_1)\alpha(1) & \psi_{\sigma_g}(\mathbf{r}_1)\beta(1) & \psi_{\sigma_u}(\mathbf{r}_1)\alpha(1) \\ \psi_{\sigma_g}(\mathbf{r}_2)\alpha(2) & \psi_{\sigma_g}(\mathbf{r}_2)\beta(2) & \psi_{\sigma_u}(\mathbf{r}_2)\alpha(2) \\ \psi_{\sigma_g}(\mathbf{r}_3)\alpha(3) & \psi_{\sigma_g}(\mathbf{r}_3)\beta(3) & \psi_{\sigma_u}(\mathbf{r}_3)\alpha(3) \end{vmatrix}$$

**23,24.** 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, $\hat{T}_n$	$\sum_{\alpha=1}^P -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2$
electronic kinetic energy, $\hat{T}_e$	$\sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_i^2$
nuclear-electron attraction energy, $\hat{V}_{ne}$	$\sum_{\alpha=1}^P \sum_{i=1}^N \frac{-Z_\alpha e^2}{4\pi\varepsilon_0  \mathbf{r}_i - \mathbf{R}_\alpha }$
nuclear-nuclear repulsion energy, $\hat{V}_{nn}$	$\sum_{\alpha=1}^{P-1} \sum_{\beta=\alpha+1}^P \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0  \mathbf{R}_\alpha - \mathbf{R}_\beta }$
electron-electron repulsion energy, $\hat{V}_{ee}$	$\sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\varepsilon_0  \mathbf{r}_i - \mathbf{r}_j }$

**25,26.** Using the notation in the first column of the table in #25-#26, write the electronic and nuclear time-independent Schrödinger equations for a molecule.

**Electronic:** 
$$(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn})\psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = U_{BO}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P)\psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

**Nuclear:** 
$$(\hat{T}_n + U_{BO}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P))\chi_n(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) = E_{BO}\chi_n(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P)$$

**The following text is used in problems 27-31.**

You are given a Helium cation ( $\text{He}^+$ ) that has been prepared in a state described by the following wavefunction,

$$\Psi_{\text{He}^+}(\mathbf{r}, t) = .5774\psi_{3s}(\mathbf{r}, t) - .7071\psi_{3p_1}(\mathbf{r}, t) + .4082\psi_{3d_2}(\mathbf{r}, t)$$

Here  $\psi_{\text{label}}(\mathbf{r}, t)$  are the normalized eigenfunctions of the  $\text{He}^+$  Hamiltonian and the subscripts indicate the  $n$ ,  $l$ , and (for the double-subscript)  $m_l$  quantum number.

- 27. What is the expectation value for the energy in this system?** Give your answer in atomic units.

The wavefunction is normalized, so the energy is simply

$$\begin{aligned}\langle E \rangle &= \langle \Psi | \hat{H} | \Psi \rangle = |c_{3s}|^2 \left( \frac{-\langle 2 \rangle^2}{2\langle 3 \rangle^2} \right) + |c_{3p_1}|^2 \left( \frac{-\langle 2 \rangle^2}{2\langle 3 \rangle^2} \right) + |c_{3d_2}|^2 \left( \frac{-\langle 2 \rangle^2}{2\langle 3 \rangle^2} \right) \\ &= \left( |c_{3s}|^2 + |c_{3p_1}|^2 + |c_{3d_2}|^2 \right) \left( \frac{-\langle 2 \rangle^2}{2\langle 3 \rangle^2} \right) \\ &= 1 \left( \frac{-4}{2 \cdot 9} \right) \\ &= -\frac{2}{9} \text{ Hartree} = -.2222 \text{ Hartree}\end{aligned}$$

- 28. What is the expectation value of the square magnitude of the total orbital angular momentum,  $\langle \hat{L}^2 \rangle$ ?** Show the dependence of your answer on  $\hbar$ .

$$\begin{aligned}\langle \hat{L}^2 \rangle &= \langle \Psi | \hat{L}^2 | \Psi \rangle = |c_{3s}|^2 (\hbar^2 (0)(0+1)) + |c_{3p_1}|^2 (\hbar^2 (1)(1+1)) + |c_{3d_2}|^2 (\hbar^2 (2)(2+1)) \\ &= (-.7071)^2 (2\hbar^2) + (.4082)^2 (6\hbar^2) \\ &= 2.000\hbar^2\end{aligned}$$

- 29. What is the expectation value for the amount of orbital angular momentum about the  $z$  axis,  $\langle \hat{L}_z \rangle$ ?** Show the dependence of your answer on  $\hbar$ .

$$\begin{aligned}\langle \hat{L}_z \rangle &= \langle \Psi | \hat{L}_z | \Psi \rangle = |c_{3s}|^2 (0\hbar) + |c_{3p_1}|^2 (1\hbar) + |c_{3d_2}|^2 (2\hbar) \\ &= (-.7071)^2 (\hbar) + (.4082)^2 (2\hbar) \\ &= .8332\hbar\end{aligned}$$

- 30. If you measure the total orbital angular momentum of this system, what is the probability that you will obtain “zero” for the answer?**

The probability of zero total orbital angular momentum is the same as the probability of observing the 3s state, which is

$$P_{3s} = |.5774|^2 = .3334$$

- 31. Does  $\Psi(\mathbf{r}, t)$  describe a stationary state of  $\text{He}^+$ ?**

Yes, because all of the eigenstates that contribute to the wavefunction have the same energy.

Name \_\_\_\_\_ Student # \_\_\_\_\_

## Part 2. Problems

Pick THREE of the following SIX problems. Each problem is worth 15 points. There is a 5-point bonus after problem #6

Clearly indicate which problems you wish for me to mark by marking an “X” in the following “score sheet” for the problems that you do not want me to mark.

Problem	#1	#2	#3	#4	#5	#6	BONUS	TOTAL
Score								

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

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

Paul

### SOME MATHEMATICAL FORMULAS

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	$\hbar$	$6.62618 \times 10^{-34} \text{ J}\cdot\text{s}$
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	$k_B$	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
Rydberg constant (infinite nuclear mass)	$R_\infty$	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Molar gas constant	$R$	$8.834188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
Permittivity of a vacuum	$\epsilon_0$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
$4\pi\epsilon_0$		
$a_0$		$2.179914 \times 10^{-23} \text{ J}$
First Bohr radius		$1.097373 \text{ cm}^{-1}$
Bohr magneton	$\mu_B$	$5.29177 \times 10^{-11} \text{ m}$
Stefan-Boltzmann constant	$\sigma$	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
		$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

### CONVERSION FACTORS FOR ENERGY UNITS

joule	$\text{kJ}\cdot\text{mol}^{-1}$	$eV$	$au$	$\text{cm}^{-1}$	Hz
1 joule	$6.022 \times 10^{20}$	$6.242 \times 10^{18}$	$2.2939 \times 10^{17}$	$5.035 \times 10^{22}$	$1.509 \times 10^{33}$
$1 \text{ kJ mol}^{-1}$	$= 1.661 \times 10^{-21}$	1	$1.036 \times 10^{-2}$	$3.089 \times 10^{-4}$	$83.60$
$1 \text{ eV}$	$= 1.602 \times 10^{-19}$	96.48	1	$3.675 \times 10^{-2}$	$8065$
1 au	$= 3.359 \times 10^{-8}$	2625	27.21	1	$2.195 \times 10^5$
1 cm $^{-1}$	$= 1.986 \times 10^{-23}$	1.196 $\times 10^{-4}$	$1.240 \times 10^{-4}$	$4.556 \times 10^{-6}$	1
1 Hz	$= 6.626 \times 10^{-44}$	$3.990 \times 10^{-13}$	$4.136 \times 10^{-15}$	$1.520 \times 10^{-16}$	$3.336 \times 10^{-11}$
					1

$$\begin{aligned} \sin \alpha \sin \beta &= \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta) \\ \cos \alpha \cos \beta &= \frac{1}{2} \cos(\alpha - \beta) + \frac{1}{2} \cos(\alpha + \beta) \\ \sin \alpha \cos \beta &= \frac{1}{2} \sin(\alpha + \beta) + \frac{1}{2} \sin(\alpha - \beta) \\ \cos(\alpha \pm \beta) &= \cos \alpha \cos \beta \mp \sin \alpha \sin \beta \\ \cos(\alpha \pm \beta) &= \cos \theta \pm i \sin \theta \\ e^{\pm i\theta} &= \cos \theta \pm i \sin \theta \\ \cos \theta &= \frac{e^{i\theta} + e^{-i\theta}}{2} \\ \sin \theta &= \frac{e^{i\theta} - e^{-i\theta}}{2i} \end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

### 1. The spread of bond lengths in the Harmonic Oscillator.

The eigenvalues of the simple oscillator are given by

$$E(v) = \hbar \left( \sqrt{\frac{k_e}{\mu}} \right) \left( v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots \quad (2)$$

where the reduced mass of the oscillator is simply related to the atomic masses by  $\mu = (m_A m_B / (m_A + m_B))$ . Here,  $k_e$  is the force constant of the oscillator and  $r_e$  denotes the equilibrium bond distance. The eigenfunctions of the two lowest energy states of the harmonic oscillator are given below

$$\psi_0(r) = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}(r-r_e)^2} \quad \psi_1(r) = \left( \frac{\alpha}{\pi} \right)^{1/4} \left( \sqrt{2\alpha} \right) (r - r_e) e^{-\frac{\alpha}{2}(r-r_e)^2} \quad (3)$$

where

$$\alpha = \sqrt{\frac{k_e \mu}{\hbar^2}} \quad (4)$$

- (a) Write down the Harmonic-Oscillator Hamiltonian and show that  $\psi_0(r)$  is an eigenfunction of it. (4 points)

This problem is straight off the first mid-term.

1. The Harmonic Oscillator Hamiltonian is

$$\hat{H}_{\text{HO}} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{1}{2} k_e (r - r_e)^2$$

2.  $\psi_0(r)$  is an eigenfunction of this Hamiltonian because:

$$\begin{aligned} \hat{H}_{\text{HO}} \psi_0(r) &= \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{1}{2} k_e (r - r_e)^2 \right) \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}(r-r_e)^2} \\ &= \left( \frac{\alpha}{\pi} \right)^{1/4} \left( -\frac{\hbar^2}{2\mu} \left[ \frac{d^2}{dr^2} \left( e^{-\frac{\alpha}{2}(r-r_e)^2} \right) \right] + \frac{1}{2} k_e (r - r_e)^2 \left( e^{-\frac{\alpha}{2}(r-r_e)^2} \right) \right) \\ &= \left( \frac{\alpha}{\pi} \right)^{1/4} \left( -\frac{\hbar^2}{2\mu} \left[ \frac{d}{dr} \left( \frac{d \left( e^{-\frac{\alpha}{2}(r-r_e)^2} \right)}{dr} \right) \right] + \frac{1}{2} k_e (r - r_e)^2 \left( e^{-\frac{\alpha}{2}(r-r_e)^2} \right) \right) \\ &= \left( \frac{\alpha}{\pi} \right)^{1/4} \left( -\frac{\hbar^2}{2\mu} \left[ \frac{d \left( -\alpha(r - r_e) e^{-\frac{\alpha}{2}(r-r_e)^2} \right)}{dr} \right] + \frac{1}{2} k_e (r - r_e)^2 \left( e^{-\frac{\alpha}{2}(r-r_e)^2} \right) \right) \\ &= \left( \frac{\alpha}{\pi} \right)^{1/4} \left( -\frac{\hbar^2}{2\mu} \left[ \left( -\alpha e^{-\frac{\alpha}{2}(r-r_e)^2} \right) + \left( -\alpha(r - r_e) \right)^2 e^{-\frac{\alpha}{2}(r-r_e)^2} \right] + \frac{1}{2} k_e (r - r_e)^2 \left( e^{-\frac{\alpha}{2}(r-r_e)^2} \right) \right) \\ &= \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}(r-r_e)^2} \left( \left[ -\frac{\hbar^2}{2\mu}(-\alpha) - \frac{\hbar^2}{2\mu}(\alpha^2)(r - r_e)^2 \right] + \frac{1}{2} k_e (r - r_e)^2 \right) \\ &= \psi_0(r) \left( -\frac{\hbar^2}{2\mu} \left( \sqrt{\frac{k_e \mu}{\hbar^2}} \right) + \left\{ -\frac{\hbar^2}{2\mu} \left( \sqrt{\frac{k_e \mu}{\hbar^2}} \right)^2 + \frac{1}{2} k_e \right\} (r - r_e)^2 \right) \\ &= \psi_0(r) \left( \frac{\hbar}{2} \sqrt{\frac{k_e}{\mu}} + \left( -\frac{k_e}{2} + \frac{k_e}{2} \right) (r - r_e)^2 \right) \\ &= \left( \frac{\hbar}{2} \sqrt{\frac{k_e}{\mu}} \right) \psi_0(r) = E_0 \psi_0(r) \end{aligned}$$

**(b) The lowest-energy vibrational excitation of the  $^{12}\text{C}^{16}\text{O}$  (carbon monoxide) molecule is associated with absorbing photons with frequency  $6.42 \cdot 10^{13}$  Hz. The equilibrium bond length of CO is  $1.128 \cdot 10^{-10}$  m. Use the harmonic oscillator model to estimate the spread in bond lengths,  $\sigma_r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$ , for the ground state of CO. (8 points)**

Remember that the variance can also be written as

$$\sigma_r^2 = \left\langle \psi_0 \left| (r - \langle r \rangle)^2 \right| \psi_0 \right\rangle = \left\langle \psi_0 \left| r^2 \right| \psi_0 \right\rangle - \left\langle \psi_0 \left| r \right| \psi_0 \right\rangle^2$$

It is obvious from the form of the ground-state wavefunction that the expectation value for the bond length is just  $r_e$ . (If this is not clear, you could confirm it by explicit integration.) So we need to evaluate

$$\sigma_r^2 = \left\langle \psi_0 \left| (r - r_e)^2 \right| \psi_0 \right\rangle = \left\langle \psi_0 \left| r^2 \right| \psi_0 \right\rangle - r_e^2$$

You were given the integrals that you need to evaluate this, but there is an easier way. Using the Hellmann-Feynman theorem,

$$\frac{\partial E_0}{\partial k_e} = \left\langle \psi_0 \left| \frac{\partial \hat{H}}{\partial k_e} \right| \psi_0 \right\rangle = \left\langle \psi_0 \left| \frac{1}{2} (r - r_e)^2 \right| \psi_0 \right\rangle$$

and so

$$\sigma_r^2 = 2 \frac{\partial E_0}{\partial k_e} = 2 \left( \frac{\partial \left( \hbar \left( \sqrt{\frac{k_e}{\mu}} \right) \left( \frac{1}{2} \right) \right)}{\partial k_e} \right) = \frac{\hbar}{\sqrt{\mu}} \left( \frac{1}{2} k_e^{-\frac{1}{2}} \right) = \frac{\hbar}{2\sqrt{\mu k_e}}$$

Now we need to figure out the force constant, which was not given. We know that the fundamental absorption frequency for the harmonic oscillator is twice the zero-point energy. So:

$$h\nu = \hbar \left( \sqrt{\frac{k_e}{\mu}} \right)$$

$$k_e = \left( 2\pi\nu \right)^2 \mu$$

Using the information we were given, and the definition of the reduced mass, we have:

$$k_e = \left( 2\pi \left( 6.42 \cdot 10^{13} \frac{1}{\text{s}} \right) \right)^2 \left( \frac{12 \cdot 16}{12 + 16} \right) \left( 1.661 \cdot 10^{-27} \frac{\text{kg}}{\text{u}} \right)$$

$$= \left( 1.627 \cdot 10^{29} \frac{1}{\text{s}^2} \right) \left( 1.139 \cdot 10^{-26} \text{ kg} \right)$$

$$= 1853 \frac{\text{kg}}{\text{s}^2}$$

Then

$$\begin{aligned}\sigma_r^2 &= \frac{\hbar}{2\sqrt{\mu k_e}} = \frac{1.0546 \cdot 10^{-34} \text{ J} \cdot \text{s}}{2\sqrt{(1.139 \cdot 10^{-26} \text{ kg}) \cdot (1853 \frac{\text{kg}}{\text{s}^2})}} = \frac{1.0546 \cdot 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{2\sqrt{(1.139 \cdot 10^{-26} \text{ kg}) \cdot (1853 \frac{\text{kg}}{\text{s}^2})}} \\ &= \frac{1.0546 \cdot 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{2(4.4594 \cdot 10^{-12} \frac{\text{kg}}{\text{s}})} = 1.148 \cdot 10^{-23} \text{ m}^2 \\ \sigma_r &= \sqrt{\sigma_r^2} = 3.39 \cdot 10^{-12} \text{ m}\end{aligned}$$

Notice that this is only a 3% change in the bond length...the bond length is nearly constant, which is why the rigid rotor model of molecular vibrations works so well.

- (c) Using your result in part (b), obtain a lower bound for the kinetic energy for the ground vibrational state of the  $^{12}\text{C}^{16}\text{O}$  molecule. (3 points)**

The Heisenberg uncertainty relation tells us that

$$\sigma_r \sigma_p \geq \frac{1}{2} \hbar$$

$$\sigma_p \geq \frac{\frac{1}{2} \hbar}{\sigma_r}$$

$$\sigma_p^2 \geq \frac{\hbar^2}{4\sigma_r^2}$$

However, we know that the momentum uncertainty is:

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$$

and that the expected value of the momentum is zero in any stationary state. So we have:

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 = \langle p^2 \rangle \geq \frac{\hbar^2}{4\sigma_r^2}$$

$$T = \left\langle \frac{p^2}{2\mu} \right\rangle \geq \frac{\hbar^2}{8\mu\sigma_r^2}$$

Evaluating this last expression gives us a lower bound on the kinetic energy,

$$T \geq \frac{\hbar^2}{8\mu\sigma_r^2} = \frac{(1.0546 \cdot 10^{-34} \text{ J} \cdot \text{s})^2}{8 \cdot (1.139 \cdot 10^{-26} \text{ kg}) \cdot (1.148 \cdot 10^{-23} \text{ m}^2)}$$

$$T \geq 1.06 \cdot 10^{-20} \left( \frac{\left( \frac{\text{kg} \cdot \text{m}^2}{\text{s}} \right)^2}{\text{kg} \cdot \text{m}^2} \right) = 1.06 \cdot 10^{-20} \left( \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \right)$$

$$T \geq 1.06 \cdot 10^{-20} \text{ J}$$

**2. Derive the “equation of motion” for the change in the expectation value of a time-dependent Hermitian operator:**

$$i\hbar \frac{d\langle C(t) \rangle}{dt} = \int \Psi^*(\tau, t) [\hat{C}(\tau, t), \hat{H}(\tau, t)] \Psi(\tau, t) d\tau + i\hbar \int \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) d\tau$$

**(15 points)**

This problem is straight from the notes. Starting with the definition of the expectation value

$$\frac{d\langle C(t) \rangle}{dt} = \frac{d \int \Psi^*(\tau, t) \hat{C}(\tau, t) \Psi(\tau, t) d\tau}{dt}$$

We can pull the derivative inside the integral, and then we get:

$$\frac{d\langle C(t) \rangle}{dt} = \int \left( \frac{\partial \Psi^*(\tau, t)}{\partial t} \hat{C}(\tau, t) \Psi(\tau, t) + \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) + \Psi^*(\tau, t) \hat{C}(\tau, t) \frac{\partial \Psi(\tau, t)}{\partial t} \right) d\tau$$

Substitute in the time-dependent Schrödinger equations:

$$\begin{aligned} \frac{\partial \Psi(\tau, t)}{\partial t} &= \frac{-i}{\hbar} (\hat{H}(\tau, t) \Psi(\tau, t)) \\ \frac{\partial \Psi^*(\tau, t)}{\partial t} &= \frac{i}{\hbar} (\hat{H}^*(\tau, t) \Psi^*(\tau, t)) \end{aligned}$$

to obtain

$$\begin{aligned} \frac{d\langle C(t) \rangle}{dt} &= \frac{1}{i\hbar} \int \left( -(\hat{H}^*(\tau, t) \Psi^*(\tau, t)) (\hat{C}(\tau, t) \Psi(\tau, t)) + \Psi^*(\tau, t) \hat{C}(\tau, t) H(\tau, t) \Psi(\tau, t) \right) d\tau + \int \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) d\tau \\ &= \frac{1}{i\hbar} \int \left( -(\Psi^*(\tau, t)) (\hat{H}(\tau, t) \hat{C}(\tau, t) \Psi(\tau, t)) + \Psi^*(\tau, t) \hat{C}(\tau, t) H(\tau, t) \Psi(\tau, t) \right) d\tau + \int \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) d\tau \end{aligned}$$

$$\begin{aligned} i\hbar \frac{d\langle C(t) \rangle}{dt} &= \int \Psi^*(\tau, t) (\hat{C}(\tau, t) \hat{H}(\tau, t) - \hat{H}(\tau, t) \hat{C}(\tau, t)) \Psi(\tau, t) d\tau \\ &\quad + i\hbar \int \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) d\tau \end{aligned}$$

$$i\hbar \frac{d\langle C(t) \rangle}{dt} = \int \Psi^*(\tau, t) [\hat{C}(\tau, t), \hat{H}(\tau, t)] \Psi(\tau, t) d\tau + i\hbar \int \Psi^*(\tau, t) \frac{\partial \hat{C}(\tau, t)}{\partial t} \Psi(\tau, t) d\tau$$

We used the Hermitian property of the operator to obtain the next-to-last line,

$$\int \Psi_1^*(\tau, t) \hat{C}(\tau, t) \Psi_2(\tau, t) d\tau = \int (\hat{C}^*(\tau, t) \Psi_1^*(\tau, t)) \Psi_2(\tau, t) d\tau.$$

**3a. What are the term symbols associated with the ground state electron configuration of the Vanadium atom,  $[\text{Ar}]4s^2 3d^3$ ? You do not need to show the “J labels”. (10 points)**

$M_L \setminus M_S$	$M_S = \frac{1}{2}$	$M_S = \frac{3}{2}$
$M_L = 5$ 2+2+1	$  3d_2\alpha \quad 3d_2\beta \quad 3d_1\alpha  $	
$M_L = 4$ 2+2+0 2+1+1	$  3d_2\alpha \quad 3d_2\beta \quad 3d_0\alpha  $ $  3d_2\alpha \quad 3d_1\alpha \quad 3d_1\beta  $	
$M_L = 3$ 2+1+0 2+2+-1	$  3d_2\alpha \quad 3d_1\alpha \quad 3d_0\beta  $ $  3d_2\alpha \quad 3d_1\beta \quad 3d_0\alpha  $ $  3d_2\beta \quad 3d_1\alpha \quad 3d_0\alpha  $ $  3d_2\alpha \quad 3d_2\beta \quad 3d_{-1}\alpha  $	$  3d_2\alpha \quad 3d_1\alpha \quad 3d_0\alpha  $
$M_L = 2$ 2+0+0 1+1+0 2+1+-1 2+2+-2	$  3d_2\alpha \quad 3d_0\alpha \quad 3d_0\beta  $ $  3d_1\alpha \quad 3d_1\beta \quad 3d_0\alpha  $ $  3d_2\alpha \quad 3d_1\alpha \quad 3d_{-1}\beta  $ $  3d_2\alpha \quad 3d_1\beta \quad 3d_{-1}\alpha  $ $  3d_2\beta \quad 3d_1\alpha \quad 3d_{-1}\alpha  $ $  3d_2\alpha \quad 3d_2\beta \quad 3d_{-2}\alpha  $	$  3d_2\alpha \quad 3d_1\alpha \quad 3d_{-1}\alpha  $
$M_L = 1$ 1+0+0 2+0+-1 1+1+-1 2+1+-2	$  3d_1\alpha \quad 3d_0\alpha \quad 3d_0\beta  $ $  3d_2\alpha \quad 3d_0\alpha \quad 3d_{-1}\beta  $ $  3d_2\alpha \quad 3d_0\beta \quad 3d_{-1}\alpha  $ $  3d_2\beta \quad 3d_0\alpha \quad 3d_{-1}\alpha  $ $  3d_1\alpha \quad 3d_1\beta \quad 3d_{-1}\alpha  $ $  3d_2\alpha \quad 3d_1\alpha \quad 3d_{-2}\beta  $ $  3d_2\alpha \quad 3d_1\beta \quad 3d_{-2}\alpha  $ $  3d_2\beta \quad 3d_1\alpha \quad 3d_{-2}\alpha  $	$  3d_2\alpha \quad 3d_0\alpha \quad 3d_{-1}\alpha  $ $  3d_2\alpha \quad 3d_1\alpha \quad 3d_{-2}\alpha  $
$M_L = 0$ 2+-1+-1 1+0+-1 1+1+-2 2+0+-2	$  3d_2\alpha \quad 3d_{-1}\alpha \quad 3d_{-1}\beta  $ $  3d_1\alpha \quad 3d_0\alpha \quad 3d_{-1}\beta  $ $  3d_1\alpha \quad 3d_0\beta \quad 3d_{-1}\alpha  $ $  3d_1\beta \quad 3d_0\alpha \quad 3d_{-1}\alpha  $ $  3d_1\alpha \quad 3d_1\beta \quad 3d_{-2}\alpha  $ $  3d_2\alpha \quad 3d_0\alpha \quad 3d_{-2}\beta  $ $  3d_2\alpha \quad 3d_0\beta \quad 3d_{-2}\alpha  $ $  3d_2\beta \quad 3d_0\alpha \quad 3d_{-2}\alpha  $	$  3d_1\alpha \quad 3d_0\alpha \quad 3d_{-1}\alpha  $ $  3d_2\alpha \quad 3d_0\alpha \quad 3d_{-2}\alpha  $

${}^2\text{H}$ ,  ${}^2\text{G}$ ,  ${}^4\text{F}$ ,  ${}^2\text{F}$ ,  ${}^2\text{D}$ ,  ${}^2\text{D}$ ,  ${}^4\text{P}$ ,  ${}^2\text{P}$

So, the term symbols are:  ${}^4\text{F}$ ,  ${}^4\text{P}$ ,  ${}^2\text{H}$ ,  ${}^2\text{G}$ ,  ${}^2\text{F}$ ,  $2({}^2\text{D})$ ,  ${}^2\text{P}$ .

**3b. According to Hund’s Rules, what is the ground-state term symbol for Vanadium? (2pts.)**

${}^4\text{F}$

**3c. For the ground state term symbol from #3b, what are the possible values of J? List these in order of increasing energy. (3 points)**

$|L - S| = |3 - \frac{3}{2}| = \frac{3}{2} \leq J \leq \frac{9}{2} = 3 + \frac{3}{2}$ ;  $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ . Since the shell is less than half filled:

$$E({}^4\text{F}_{\frac{3}{2}}) < E({}^4\text{F}_{\frac{5}{2}}) < E({}^4\text{F}_{\frac{7}{2}}) < E({}^4\text{F}_{\frac{9}{2}})$$

**4. Energy of 2-electron atoms.** For the 2-electron atom, we considered a wave function with the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \left( \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

where

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}$$

We found that the energy of this wave function was given by the form,

$$\begin{aligned} E(\zeta) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - Z) \end{aligned}$$

where the Hamiltonian of the 2-electron atom has the form

$$\hat{H} \equiv \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- (a) Suppose we approximate the energy of the Lithium cation ( $\text{Li}^+$ ) by using first-order perturbation theory, where the electron-electron repulsion term in the Hamiltonian is treated as a perturbation. What is the approximate energy? (8 points)

This problem is very close to one off an old exam. The perturbation theory result consists of using the wavefunction for the "hydrogenic" system (with no electron-electron repulsion) as a starting point and then evaluating the energy for that "zeroth order" wavefunction. So we want to have the energy,  $\langle \Psi | \hat{H}_{\text{Li}^+} | \Psi \rangle$ , corresponding to

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left( \sqrt{\frac{(3)^2}{\pi}} \right) e^{-3r_1} \left( \sqrt{\frac{(3)^2}{\pi}} \right) e^{-3r_2} \left( \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

This energy can be evaluated using the energy expression you are given, with  $\zeta=Z=3$ . So the energy is:

$$\begin{aligned} E(3) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H}_{Z=3} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -(3)^2 + \frac{5}{8}(3) + 2(3)(3-3) \\ &= -9 + \frac{15}{8} \\ &= -7.125 \text{ Hartree} = -7\frac{1}{8} \text{ Hartree} \end{aligned}$$

- (b) Suppose we approximate the energy of the Helium atom using the variational principle, using trial wave functions with the form given by in the problem statement. What is the approximate energy? (7 points)

To use the variational principle, we minimize the energy with respect to the effective nuclear charge,  $\zeta$ . So we solve for the optimal effective nuclear charge:

$$\begin{aligned} 0 &= \frac{\partial E(\zeta)}{\partial \zeta} = \frac{\partial \left( -\zeta^2 + \frac{5}{8}\zeta + 2\zeta^2 - 2\zeta Z \right)}{\partial \zeta} \\ &= -2\zeta + \frac{5}{8} + 4\zeta - 2Z \\ 2Z - \frac{5}{8} &= 2\zeta \\ \zeta &= Z - \frac{5}{16} \end{aligned}$$

and then substitute back into the energy expression,

$$\begin{aligned} E(Z) &= -\left(Z - \frac{5}{16}\right)^2 + \frac{5}{8}\left(Z - \frac{5}{16}\right) + 2\left(Z - \frac{5}{16}\right)\left(Z - \frac{5}{16} - Z\right) \\ E(3) &= -\left(3 - \frac{5}{16}\right)^2 + \frac{5}{8}\left(3 - \frac{5}{16}\right) - \frac{5}{8}\left(3 - \frac{5}{16}\right) \\ &= -\left(3 - \frac{5}{16}\right)^2 \\ &= -7.223 \text{ Hartree} \end{aligned}$$

### 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:

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

- (a) 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. (5 points)**

This is a spherical problem. In atomic units, the Hamiltonian for such a problem has the form,

$$\hat{H}_{\text{spherically symmetric}} \equiv -\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2}{r^2} \right) + V(r),$$

where  $V(r)$  is any radial potential (with no dependence on the angular coordinates) and  $\hat{L}^2$  is the square of the total orbital angular momentum operator. For our specific, very simple, potential, we have:

$$\begin{aligned} \hat{H}_{\text{spherical box}} &\equiv -\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2}{r^2} \right) \\ &= \left( \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{L}^2}{2r^2} \right) \quad 0 \leq r \leq a \end{aligned}$$

and the Hamiltonian is infinite (ergo “mathematically undefined”) outside this region. Substituting the wavefunction into this equation, and using the known result for the operation of  $\hat{L}^2$  on a spherical harmonic,  $\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1) Y_l^m(\theta, \phi)$ , we have

$$\begin{aligned}
& \left( \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{L}^2(\theta, \phi)}{2r^2} \right) \left( j_l(kr) Y_l^m(\theta, \phi) \right) \\
&= \left( \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) j_l(kr) Y_l^m(\theta, \phi) + \left( \frac{\hat{L}^2(\theta, \phi)}{2r^2} \right) j_l(kr) Y_l^m(\theta, \phi) \\
&= Y_l^m(\theta, \phi) \left( \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) j_l(kr) + j_l(kr) \left( \frac{\hat{L}^2(\theta, \phi) Y_l^m(\theta, \phi)}{2r^2} \right) \\
&= Y_l^m(\theta, \phi) \left( \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) j_l(kr) + j_l(kr) \left( \frac{l(l+1) Y_l^m(\theta, \phi)}{2r^2} \right) \\
&= \left( Y_l^m(\theta, \phi) \right) \left( \frac{-1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} \right) j_l(kr) \\
&= \frac{k^2}{2} Y_l^m(\theta, \phi) j_l(kr)
\end{aligned}$$

This also establishes that the energies have the form  $E_{k,l} = \frac{k^2}{2}$ .

**(b) 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? (5 pts.)**

Recall that in the particle in a box, there were many eigenfunctions that we had to discard because they did not satisfy the boundary conditions; in particular, we had to reject all the eigenfunctions of the Hamiltonian that were not zero at the edges of the box. The same thing is true here. We need to reject all the solutions that are not zero at  $r=a$ . This means that

$$j_l(ka) = 0$$

For the case  $l=0$ , the location of the zeros was simple, so we know that

$$j_0(ka) = 0 \quad \Rightarrow \quad ka = n\pi \quad n = 1, 2, 3, \dots$$

and thus

$$k = \frac{n\pi}{a}$$

Substituting this back into the equation for the energy, the energies are:

$$E_{n,l=0} = \frac{1}{2} \left( \frac{n\pi}{a} \right)^2 = \frac{n^2 \pi^2}{2a^2}$$

Notice how similar this result is to the result for the one-dimensional particle in a box.

- (c) Suppose that you want to design a quantum dot that absorbs red light, with wavelength  $\lambda = 680 \cdot 10^{-9} \text{ m}$ , 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  $\lambda = 680 \text{ nm}$ ?** You will probably find it helpful to work this problem in atomic units. The atomic unit of length is the Bohr, and  $1 \text{ Bohr} = .52917725 \cdot 10^{-10} \text{ m}$ . **(5 points)**

Just as they always are, the dipole-allowed transitions from the ground state are  $s$  to  $p$  transitions. So we need to find the lowest energy “ $p$ ” orbital, with  $l = 1$ . So:

$$j_1(ka) = 0 \quad \Rightarrow \quad ka = 4.493409$$

$$k = \frac{4.493409}{a}$$

and the energy of this state is

$$E_{k,l=1} = \frac{k^2}{2} = \frac{(4.493409)^2}{2a^2} = \frac{20.19072}{2a^2}$$

The first excitation energy is the difference between this state’s energy and that of the lowest-energy  $l=0$  state,

$$\Delta E_{1s \rightarrow 2p} = \frac{20.19072}{2a^2} - \frac{\pi^2}{2a^2} = \frac{10.32112}{2a^2} \text{ Hartree}$$

The energy we want is:

$$\begin{aligned} E = h\nu &= \frac{hc}{\lambda} = \frac{(6.6262 \cdot 10^{-34} \text{ J} \cdot \text{s}) \cdot (2.998 \cdot 10^8 \frac{\text{m}}{\text{s}})}{680 \cdot 10^{-9} \text{ m}} = 2.921 \cdot 10^{-19} \text{ J} \\ &= 2.921 \cdot 10^{-19} \text{ J} \left( 2.2939 \cdot 10^{17} \frac{\text{Hartree}}{\text{J}} \right) = .06700 \text{ Hartree} \end{aligned}$$

and so the size of the quantum dot will be:

$$\begin{aligned} \frac{10.32112}{2a^2} \text{ Hartree} &= .06700 \text{ Hartree} \\ a &= 8.776 \text{ Bohr} = 8.776 \text{ Bohr} \cdot (.52917725 \cdot 10^{-10} \frac{\text{m}}{\text{Bohr}}) \\ &= 4.64 \cdot 10^{-10} \text{ m} \end{aligned}$$

**6. 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  $\Psi_0(\tau)$ .

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

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

(5 pts.)

First expand out the commutator. Then use the eigenvalue condition,  $\hat{H}\Psi_k = E_k \Psi_k$  and the Hermitian property to simplify the expression.

$$\begin{aligned} \langle \Psi_k | [\hat{H}, \hat{C}] | \Psi_k \rangle &= \langle \Psi_k | \hat{H}\hat{C} - \hat{C}\hat{H} | \Psi_k \rangle \\ &= \langle \Psi_k | \hat{H}\hat{C}\Psi_k \rangle - \langle \Psi_k | \hat{C}\hat{H}\Psi_k \rangle \\ &= \langle \hat{H}\Psi_k | \hat{C}\Psi_k \rangle - \langle \Psi_k | \hat{C}E_k\Psi_k \rangle \quad \left. \begin{array}{l} \text{use Hermitian property in the} \\ \text{first term; use eigenvalue cond.} \\ \text{in the second term} \end{array} \right\} \\ &= \langle E_k\Psi_k | \hat{C}\Psi_k \rangle - E_k \langle \Psi_k | \hat{C}\Psi_k \rangle \\ &= E_k \langle \Psi_k | \hat{C}\Psi_k \rangle - E_k \langle \Psi_k | \hat{C}\Psi_k \rangle \\ &= 0 \end{aligned}$$

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

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

(10 points)

First expand out the double commutator,

$$\begin{aligned} \langle \Psi_0 | [\hat{C}^\dagger, [\hat{H}, \hat{C}]] | \Psi_0 \rangle &= \langle \Psi_0 | \hat{C}^\dagger [\hat{H}, \hat{C}] - [\hat{H}, \hat{C}] \hat{C}^\dagger | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{C}^\dagger (\hat{H}\hat{C} - \hat{C}\hat{H}) - (\hat{H}\hat{C} - \hat{C}\hat{H}) \hat{C}^\dagger | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{C}^\dagger \hat{H}\hat{C} - \hat{C}^\dagger \hat{C}\hat{H} - \hat{H}\hat{C}\hat{C}^\dagger + \hat{C}\hat{H}\hat{C}^\dagger | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{C}^\dagger \hat{H}\hat{C} - \hat{C}^\dagger \hat{C}\hat{H} + \hat{C}\hat{H}\hat{C}^\dagger - \hat{H}\hat{C}\hat{C}^\dagger | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{C}^\dagger \hat{H}\hat{C} | \Psi_0 \rangle - \langle \Psi_0 | \hat{C}^\dagger \hat{C}\hat{H}^\dagger | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | \hat{C}\hat{H}\hat{C}^\dagger | \Psi_0 \rangle - \langle \Psi_0 | \hat{H}\hat{C}\hat{C}^\dagger | \Psi_0 \rangle \end{aligned}$$

Use the Hermitian property,  $\langle \Psi_0 | \hat{C}^\dagger \hat{C} \Psi_0 \rangle = \langle \hat{C} \Psi_0 | \hat{C} \Psi_0 \rangle$ , and the eigenvalue property,  $\hat{H} \Psi_0 = E_0 \Psi_0$ , to simplify these terms, obtaining

$$\begin{aligned}
\langle \Psi_0 | [\hat{C}^\dagger, [\hat{H}, \hat{C}]] | \Psi_0 \rangle &= \langle \Psi_0 | \hat{C}^\dagger \hat{H} \hat{C} | \Psi_0 \rangle - \langle \Psi_0 | \hat{C}^\dagger \hat{C} \hat{H} | \Psi_0 \rangle \\
&\quad + \langle \Psi_0 | \hat{C} \hat{H} \hat{C}^\dagger | \Psi_0 \rangle - \langle \Psi_0 | \hat{H} \hat{C} \hat{C}^\dagger | \Psi_0 \rangle \\
&= \langle \hat{C} \Psi_0 | \hat{H} | \hat{C} \Psi_0 \rangle - \langle \Psi_0 | \hat{C}^\dagger \hat{C} E_0 | \Psi_0 \rangle \\
&\quad + \langle \hat{C}^\dagger \Psi_0 | \hat{H} | \hat{C}^\dagger \Psi_0 \rangle - \langle \hat{H} \Psi_0 | \hat{C} \hat{C}^\dagger | \Psi_0 \rangle \\
&= \langle \hat{C} \Psi_0 | \hat{H} | \hat{C} \Psi_0 \rangle - E_0 \langle \hat{C} \Psi_0 | \hat{C} \Psi_0 \rangle \\
&\quad + \langle \hat{C}^\dagger \Psi_0 | \hat{H} | \hat{C}^\dagger \Psi_0 \rangle - \langle E_0 \Psi_0 | \hat{C} \hat{C}^\dagger | \Psi_0 \rangle \\
&= \langle \hat{C} \Psi_0 | \hat{H} | \hat{C} \Psi_0 \rangle - E_0 \langle \hat{C} \Psi_0 | \hat{C} \Psi_0 \rangle \\
&\quad + \langle \hat{C}^\dagger \Psi_0 | \hat{H} | \hat{C}^\dagger \Psi_0 \rangle - E_0 \langle \hat{C}^\dagger \Psi_0 | \hat{C}^\dagger \Psi_0 \rangle
\end{aligned}$$

Because  $\hat{C} \Psi_0$  is itself a wavefunction, we can expand it in terms of the full set of eigenfunctions of the Hamiltonian. So

$$\begin{aligned}
\hat{C} \Psi_0 &= \sum_{k=0}^{\infty} c_k \Psi_k & \hat{H} \Psi_k &= E_k \Psi_k \\
\hat{C}^\dagger \Psi_0 &= \sum_{k=0}^{\infty} d_k \Psi_k & \hat{H} \Psi_k &= E_k \Psi_k
\end{aligned}$$

Substituting in these expressions, and using the fact that the eigenfunctions are orthogonal, we have:

$$\begin{aligned}
\langle \Psi_0 | [\hat{C}^\dagger, [\hat{H}, \hat{C}]] | \Psi_0 \rangle &= \langle \hat{C} \Psi_0 | \hat{H} | \hat{C} \Psi_0 \rangle - E_0 \langle \hat{C} \Psi_0 | \hat{C} \Psi_0 \rangle \\
&\quad + \langle \hat{C}^\dagger \Psi_0 | \hat{H} | \hat{C}^\dagger \Psi_0 \rangle - E_0 \langle \hat{C}^\dagger \Psi_0 | \hat{C}^\dagger \Psi_0 \rangle \\
&= \left\langle \sum_{l=0}^{\infty} c_l \Psi_l \middle| \hat{H} \left| \sum_{k=0}^{\infty} c_k \Psi_k \right. \right\rangle - E_0 \left\langle \sum_{l=0}^{\infty} c_l \Psi_l \middle| \sum_{k=0}^{\infty} c_k \Psi_k \right\rangle \\
&\quad + \left\langle \sum_{l=0}^{\infty} d_l \Psi_l \middle| \hat{H} \left| \sum_{k=0}^{\infty} d_k \Psi_k \right. \right\rangle - E_0 \left\langle \sum_{l=0}^{\infty} d_l \Psi_l \middle| \sum_{k=0}^{\infty} d_k \Psi_k \right\rangle \\
&= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k \langle \Psi_l | \hat{H} | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k \langle \Psi_l | \Psi_k \rangle \\
&\quad + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k \langle \Psi_l | \hat{H} | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k \langle \Psi_l | \Psi_k \rangle \\
&= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k E_k \langle \Psi_l | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k \delta_{kl} \\
&\quad + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k E_k \langle \Psi_l | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k \delta_{kl}
\end{aligned}$$

$$\begin{aligned}
\left\langle \Psi_0 \left[ \hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \Psi_0 \right\rangle &= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k E_k \delta_{kl} - \sum_{k=0}^{\infty} |c_k|^2 E_0 \\
&\quad + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k E_k \delta_{kl} - \sum_{k=0}^{\infty} |d_k|^2 E_0 \\
&= \sum_{k=0}^{\infty} |c_k|^2 (E_k - E_0) + \sum_{k=0}^{\infty} |d_k|^2 (E_k - E_0)
\end{aligned}$$

However, because we are considering the ground state wavefunction,  $E_0 \leq E_1 \leq E_2 \leq \dots$  and  $E_k - E_0 \geq 0$  for all  $k$ . Since all of the terms in the sum are positive, the sum is also positive. So,

$$\begin{aligned}
\left\langle \Psi_0 \left[ \hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \Psi_0 \right\rangle &= \sum_{k=0}^{\infty} |c_k|^2 (E_k - E_0) + \sum_{k=0}^{\infty} |d_k|^2 (E_k - E_0) \\
&\geq 0
\end{aligned}$$

**BONUS:** The results in problem #6 are key results associated with the theory of infinitesimal unitary transformations. The theory of infinitesimal unitary transformations describes, among other things, how wavefunctions change in time, and was the key mathematical concept behind Julian Schwinger's development of quantum field theory, for which he shared the 1965 Nobel Prize and became justly famous. The key idea here is that the following operator,

$$\hat{U}_\varepsilon = \hat{I} + i\varepsilon \hat{C}$$

is an infinitesimal unitary transformation, where  $\hat{I}$  is the identity operator (i.e., “multiply by one”). Here  $\varepsilon$  is a very small (“infinitesimal”) real number.

Using equations, explain why  $\hat{U}_\varepsilon$  can be interpreted as an “infinitesimal unitary transformation” if  $\hat{C}$  is a Hermitian operator, but cannot be interpreted as an “infinitesimal unitary transformation” if  $\hat{C}$  is not Hermitian. (5 points)

A unitary transformation/matrix/operator has the property that its conjugate transpose (it’s “Hermitian conjugate”) is equal to its inverse. So we need to show that

$$\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon = \hat{I}$$

Substituting in the form for the operator, we have that:

$$\begin{aligned}
\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon &= (\hat{I} + i\varepsilon \hat{C})^\dagger (\hat{I} + i\varepsilon \hat{C}) \\
&= (\hat{I}^\dagger - i\varepsilon \hat{C}^\dagger)(\hat{I} + i\varepsilon \hat{C})
\end{aligned}$$

The identity matrix is equal to its Hermitian conjugate,  $\hat{I}^\dagger = \hat{I}$  and obviously  $\hat{I} \cdot \hat{I} = \hat{I}$  for the identity. So

$$\begin{aligned}
\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon &= (\hat{I}^\dagger - i\varepsilon \hat{C}^\dagger)(\hat{I} + i\varepsilon \hat{C}) \\
&= (\hat{I} - i\varepsilon \hat{C}^\dagger)(\hat{I} + i\varepsilon \hat{C}) \\
&= \hat{I} + i\varepsilon(\hat{C} - \hat{C}^\dagger) + \varepsilon^2 \hat{C}^\dagger \hat{C}
\end{aligned}$$

Now, for very, very, very tiny (“infinitesimal”)  $\varepsilon$ , the last term is entirely negligible. So we can omit it. So

$$\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon = \hat{I} + i\varepsilon(\hat{C} - \hat{C}^\dagger).$$

If  $\hat{C}^\dagger = \hat{C}$  (i.e., the operator is Hermitian) then this is an infinitesimal unitary transformation because  $\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon = \hat{I}$ . If  $\hat{C}^\dagger \neq \hat{C}$ , then this is not true because the error term is of the same order as the change in the operator.

Speaking technically, the important point was that for unitary infinitesimal transformations, the normalization of the wavefunctions does not change to first order. The important property is related to the fact that  $[\partial \hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon / \partial \varepsilon]_{\varepsilon=0} = 0$  for an infinitesimal unitary transformation.