

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	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
	ϵ_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_∞	$2.179914 \times 10^{-23} \text{ J}$
	R_∞	1.097373 cm^{-1}
First Bohr radius	a_0	$5.29177 \times 10^{-11} \text{ m}$
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

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)

C

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

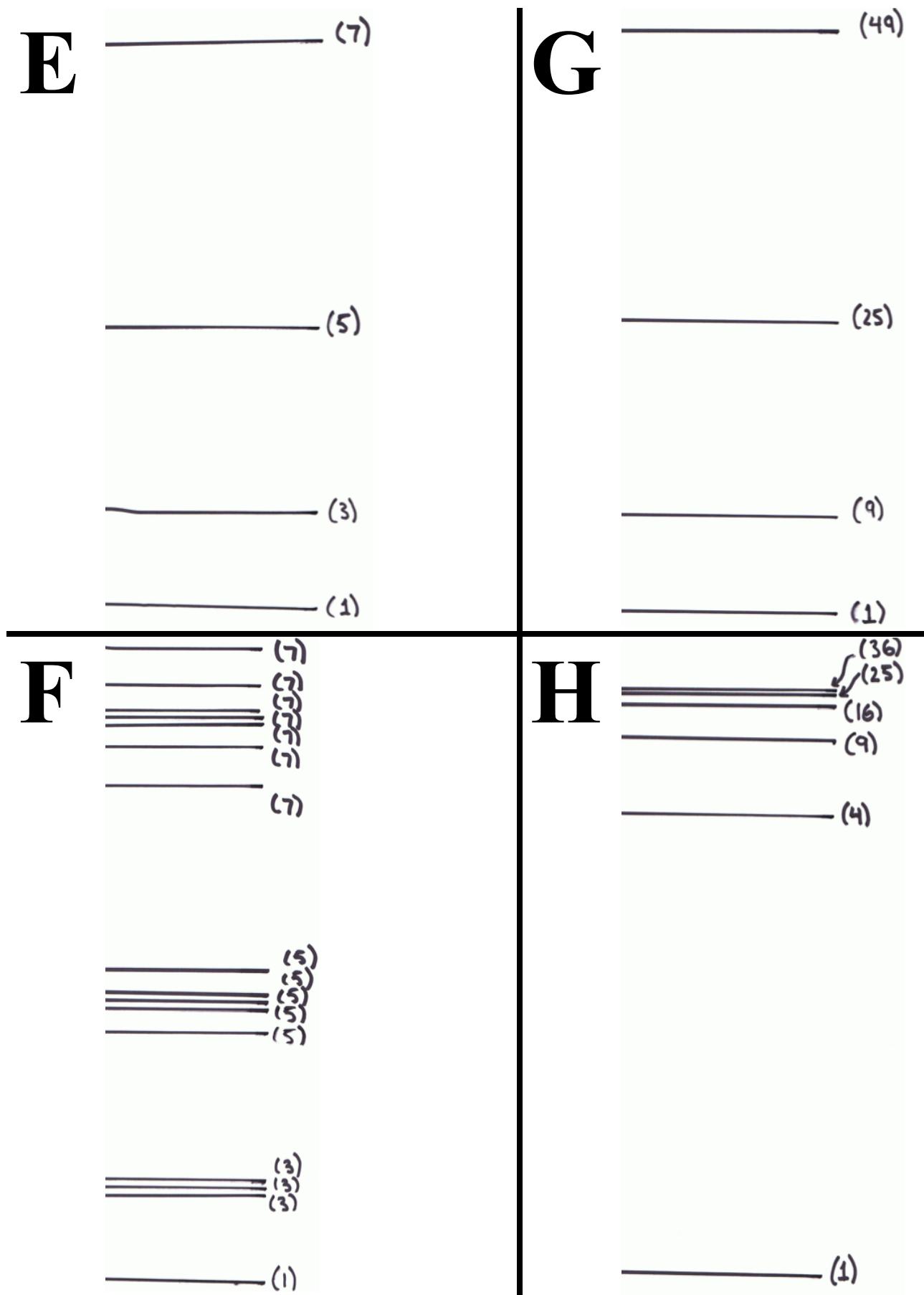
(10)
(10)
(5)

(6)
(3)

(1)

D

(1)
(1)
(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,

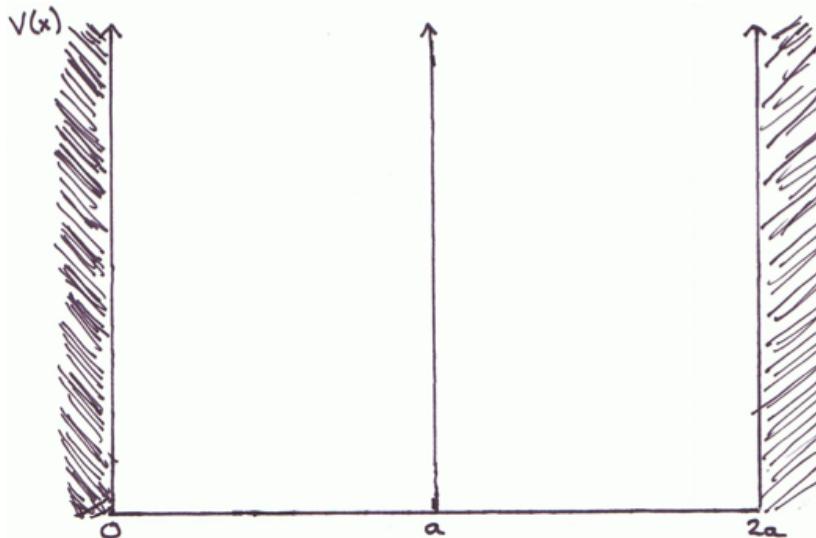
$$V_Y(r) = \frac{q_1 q_2 e^{-\lambda r}}{4\pi\epsilon_0 r}$$

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)**