

Name: _____
Student Number: _____
Tutorial: _____

PHYSICS 294 – QUANTUM AND THERMAL PHYSICS

TEST 1

February 7th, 2023

Duration: 90 min

No.	Maximum	Marks
1.	25	
2.	30	
3.	25	
4.	20	
5.	Bonus: 10	
Total:		/100

Answer all questions on the question paper using a pen in the space provided. Write legibly.

Use the back of a page if more space is required and indicate clearly when you have done so.

No aids allowed except for a non-programmable, non-communicating calculator

1. (25 pts) For the hydrogen atom ($E_n = -\frac{m_e Z^2 e^4}{8h^2 \epsilon_0^2} \frac{1}{n^2} = -Z^2 E_R / n^2$; $E_R = 13.6 \text{ eV}$)

a) (5pts) What is the energy of the first excited state of H? $-E_R/4$

full marks for right answer. Partial marks if the expression is written out (3) but wrong n

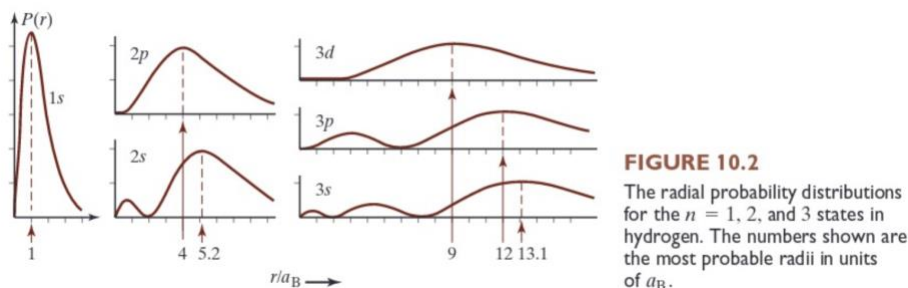
b) (5pts) What is the energy required to ionize He^+ (hydrogen like ion) to He^{2+} .

Need photon with energy at least equal to binding energy of He^+ in the $n=1$ level or $E = 4E_R$

As above.

c) (5pts) Draw the radial distribution for $n = 2, l = 0$ orbitals in comparison to the $n = 3, l = 0$ orbitals.

See Fig. 8.23 of text. $n=2, l=0$ is the 2s orbital; $n=3, l=0$ is the 3s. The radial distribution for the 2s should have a smaller maxima close to the nucleus (near a followed by a larger maxima further out. The 3s radial distribution should have 2 nodes with successively larger amplitude maxima and clearly greater area or density away from the nucleus than 2s.



The plots should show correct number of nodes (2pts)

The plots should clearly show that the average $\langle r \rangle$ in the radial probability distributions to show that it is understood the most probable positions at higher n (energies are further from the nucleus) (3pts)

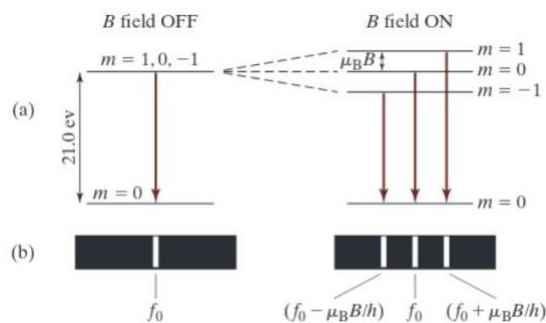
If radial function rather than radial probability distribution were drawn...but correct...3 pts

d) (5pts) Write the relation that gives the photon energy for a transition and emission of light from the $n = 5$ to the $n = 3$ in hydrogen. You don't need to evaluate it.

$$E_{\text{photon}} = h\nu = -E_R/n_i^2 - E_R/n_f^2 = -E_R/5^2 - (-E_R/3^2)$$

3 pts for writing down correct relation for photon energy of transition, 2pts for correct response.

e) (5pts) Draw the effect of a 2 T magnetic field on the $n = 2, l = 1$ levels of hydrogen in the presence of a 2 T magnetic field. Show the energy splitting explicitly in the diagram including spin (a population of excited H atoms will have equal populations of electrons with spin up and spin down). It is helpful to draw the effect on l states first then include spin. You don't need to find the specific energy splitting but show relation on how to calculate it.



Split each of the angular momentum lines to the left by the Zeeman effect due to spin by $\pm u_B B$ to give 5 lines separated by $u_B B$

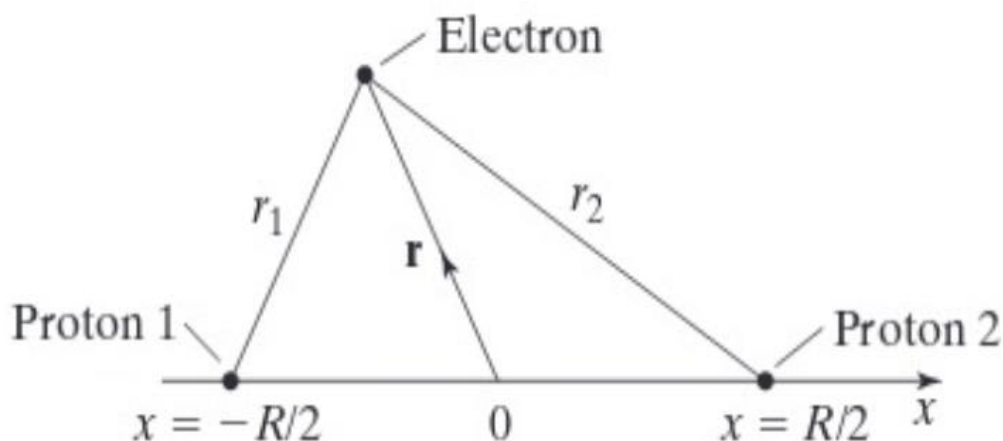
Drawing Zeeman splitting for l (L) angular momentum components – 2pts

Drawing Zeeman splitting for S (m) spin components – 2pts

Showing relation for energy splitting ΔE (as given above) – 1 pt

2. (30 pts total) This problem concerns understanding the formation of molecules with H_2 as the simplest case for the forces involved.

a) (5 pts) First consider H_2^+ . Draw a diagram showing the separation between two nuclei (labelled proton 1 and proton 2) at a distance R . Show explicitly all the coulombic interactions between the 2 protons and the one electron.



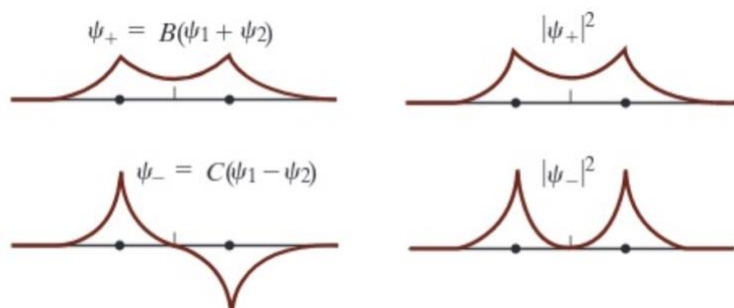
2 pts for drawing R between proton 1 and proton 2, 1 pt r1 (distance from proton to one labelled e), 1pt r2, 1pt for r showing single value distance dependence to make problem tractable.

b) (5pts) Write down possible wavefunctions to H_2^+ (consider linear combinations of H atom ψ_{1s} solutions for proton 1 and 2, showing constructive and destructive interference re: Linear Combination of Atomic Orbitals – Molecular Orbital (LCAO-MO) approach.) Draw the resulting molecular wavefunctions probability densities specifically showing the relative electron distribution giving rise to bonding and antibonding molecular orbitals. (Show where there is a buildup of electron density, or bonding, and where there is depletion or antibonding forces.)

constructive $\Psi = A(\psi_{1s1} + \psi_{1s2})$ bonding; destructive interference $\Psi = B(\psi_{1s1} - \psi_{1s2})$
antibonding -> 2pts

where ψ_1 and ψ_2 are 1s radial function solutions to the H atom corresponding to protons 1 and 2. One takes a superposition that is constructive (+) which leads to an increase in electron distribution/density between nuclei.

The other suitable function involves destructive interference leading to higher electron density away from the proton positions. Plots should resemble the two plots on the right, below – 3pts



c) (5pts) The Schroedinger equation has the following general form:

$$\mathbf{H}\Psi(r_1, r_2 \dots r_i) = [-(\hbar^2/8\pi^2m^2) \sum_i \nabla_i^2 + \sum_i U_i] \Psi(r_1, r_2 \dots r_i) = E\Psi(r_1, r_2 \dots r_i)$$

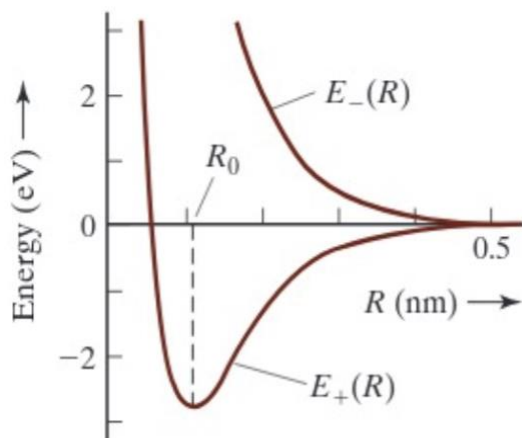
where i refers to electron labels or other particles. The solution to the Schroedinger equation always reduces to properly identifying the potential U for a given problem. For H_2^+ , write down the potential U defining the formation of a molecular bond. (Identify all the Coulombic terms involved and refer to your diagram in a) to be sure you have them all.).

$U = -e^2/4\pi\epsilon_0\mathbf{r} + e^2/4\pi\epsilon_0\mathbf{R}\mathbf{R}$ where \mathbf{r} is defined from the centre of mass and R is the repulsion between protons, note +ve sign to indicate repulsive force.

Acceptable answers would include $U = -e^2/4\pi\epsilon_0\mathbf{r1} + -e^2/4\pi\epsilon_0\mathbf{r2} + e^2/4\pi\epsilon_0\mathbf{R}\mathbf{R}$ with some comment about relation between r1 and r2. No deduction if it is clear the Coulombic attraction of both protons is involved and the repulsive Coulombic force between protons.

1pt for identifying each Coulombic term (3pts), 2 pts for correct signs,

d) (10 pts) Draw the Energy diagram for the formation of H_2^+ (E solutions to the wave equation as a function of R, the separation between nuclei) and indicate the position defining the bond length. Briefly discuss the driving forces for forming a bond as a well-defined minimum in this curve. This diagram should include the antibonding energy dependence on R as well (destructive interference between electronic wavefunctions - as both occur).



The minimum denoted as R_0 is the bond length, which defines the position at which the interproton repulsive force equals the electron-proton attractive force of both protons. The driving force for bond formation is the build up of electron density leading to a larger net attractive force or Z_{eff} as for multielectron atoms. At the point of zero force the proton-proton repulsion force equals the attractive Coulombic potential. This point defines the bond length. This interaction leads to a stable minimum in proton

separation or the formation of molecular bond (**2pts** – coulombic attractive force and build up of electron density between nuclei AND proton-proton repulsion is counter force, **1pt**. For defining potential minimum, cancellation of attractive and repulsive terms (zero force) at defines bond length **2pts** (balance of attractive and repulsive terms).

Antibonding. The opposing trend is for the electron motions to lead to increased repulsive force between nuclei or destructive interference (**2pt**). This e-e repulsion effect leads to depletion of electron density between the protons as well as away from centre of mass of each proton (**1pt**). The e-e repulsion would take work to create the same e distribution around the individual protons and as such represents a higher energy (**2pts**), repulsive state or antibonding molecular orbitals.

e) (5pts) Now consider H_2 (add one more electron to the interactions). What is the additional term needed in the potential U_i ? Briefly explain why this problem is not solvable. Discuss either the Independent Particle Approximation or Variational Method as possible means to approximate the solution to the Schrodinger equation for H_2 .

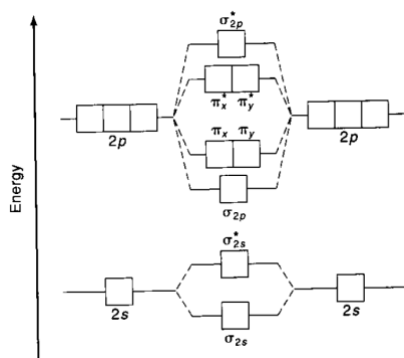
The additional term for H_2 is the $+ e^2/4\pi\epsilon_0 r_{12}$ term. **2pts** (Just need to state make this point.) You do not need to include in diagram. The problem is no longer exactly solvable as there is no way to separate orthogonal coordinates or use separation of variable methods. Approximate methods are used instead to get around this problem.

The molecular orbital case is similar to multielectron atoms for the Independent Particle Approximation. One would take an assumed solution to the wavefunctions using what would be expected to be the dominant term such as the H_2^+ molecular orbitals, use the electron distribution to create a spatially varying potential given by the electron distribution of the initial

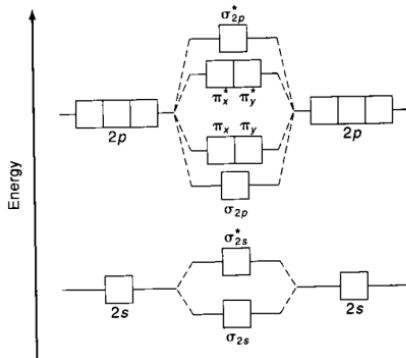
trial function. This potential U' will lead to a modified wavefunction ψ'' that would then be used to redefine U' to U'' and repeat the process calculating the E for each trial function (that satisfies Pauli Exclusion Principle, indistinguishability of electrons, and antisymmetric to exchange). With each loop in what is referred to as self consistent field method (or mean field) approach the energy will be lower than the previous as the function converges. At some acceptable level of accuracy the calculation is considered converged to the degree of accuracy and available computer power available. (3pts if IPA discussed – needs to include approximate function to determine U' , find new wavefunction, repeat to convergence)

Variation method uses trial functions in which a key parameter is used as a variable parameter. For the He case, the effective nuclear charge felt by the electrons due to electron correlation effects is used as a variable parameter. Using a trial function with the parameter used to tune the wavefunction accuracy, the operation of the Schroedinger equation yields an equation in a functional form of the variable. The minimum energy $dE/d\alpha$ (α the variational variable) is used to find the best solution within this approximation yielding corrections to energies, Z_{eff} and radial distributions. (3pts if Variational Method discussed, as above save find minimum energy by taking first derivative of E as function of variational parameter, 1pt trial function, 1 pt variational variable, 1 pt find min.)

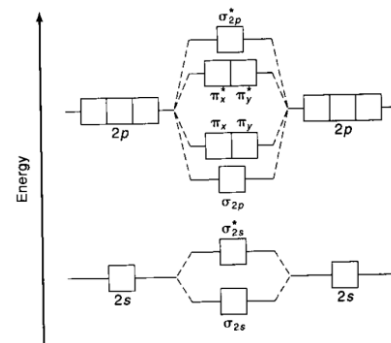
3. (25pts) For the series of Homonuclear Diatomic Molecules, Li_2 , Be_2 , O_2 , use the Molecular Orbital Energy Diagrams below.



Li Li



Be Be



O O

- a) (15 pts) Assign electron configurations to each participating atom in the above diagrams for molecular orbitals formed by linear combinations of valence orbitals (Periodic Table provided re: electron configurations). Predict the bond order for Li_2 , Be_2 and O_2 using the above diagrams to show electron configurations for molecular orbitals.

As above... $\text{Li} - 2s^1$ for each atom, bond order = 1. $\text{Be} 2s^2$, bond order = 0, $\text{O} 2s^2 2p^4$, bond order 2, paramagnetic or 2 unpaired electrons in π_x^* and π_y^* orbitals

Correct electron configurations for elements AND for molecular orbitals, as indicated by filling in boxes **10 pts**, 4 points for correct bond order, **1pt** for spins parallel for oxygen

- b) (10 pts) explain the difference in bond energy and bond length between Li_2 and O_2 in terms of Z_{eff} and electron correlation effects in multielectron atoms.

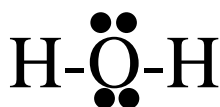
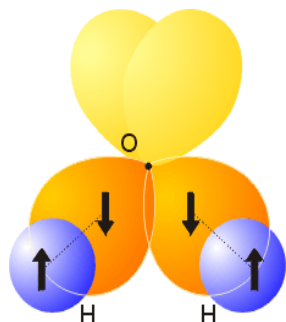
The bond order for O_2 is predicted to be a double bond so within the same row of the periodic table this bond will be shorter and more than 2x stronger than the Li_2 bond order (so much for dilithium for space travel re: Star Trek). As one goes across the periodic table each additional proton/electron to form the next element in the series experience a larger Z_{eff} as each added electron does not completely screen its complementary proton. The net effect is continuous increase in Z_{eff} , tighter binding of electrons, reduced radii of individual atoms/elements and in general shorter bonds.

<Looking primarily for a discussion of Z_{eff} across the Periodic Table (**5pts**) and difference in bond orders in terms of effect on bond lengths and bond strengths. Need to include some discussion of e-e correlation **3pts**, reduced radii with larger Z_{eff} and related increase in bond strengths (**2pts**). This question is looking for a basic understanding of e-e correlation to minimize e-e repulsion leading to increased Z_{eff} .

4. (20pts) Consider the molecular structure of water.

- a) (10pts) Draw the Lewis Dot Structure for H_2O and the corresponding hybridization of orbitals.

The hybridization is sp^3 (**5pts**). The yellow lobes hold 2 electrons each that with bonded electrons shared with H atoms gives 8 electrons around the central O atom (Lewis dot structure or indication of stable octet about central O (**5pts**)).

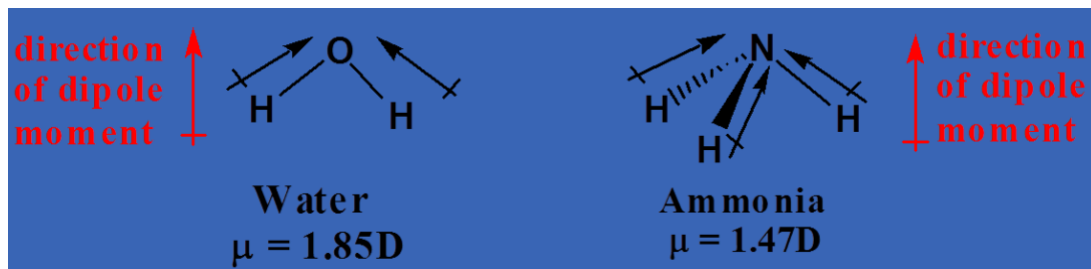


b) (5 pts) The bond angle for H-O-H is 104.7° . Explain using Valence Electron Shell Pair Repulsion concepts why this angle is not 109.5° as would be expected for a tetrahedron arrangement of electron pairs.

The bond is compressed by the more diffuse electron distributions associated with electron lone pairs creating a larger effective repulsive volume (**3pts**) for electrons in these nonbonding orbitals. The electron density is not “focused” towards another nuclei as it would be in forming a molecular bond. This larger effective repulsive volume forces the O-H bonds to a smaller angle than completely uniform forces involved in sp^3 hybridization or minimal energy distribution for 4 ligands (**2pts**).

c) (5 pts) Does water have a dipole moment? Explain briefly (see periodic table with electronegativities).

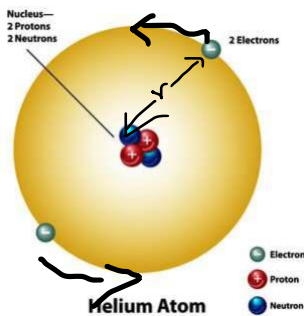
Yes. Given that O is more electronegative than H there is a net -ve charge buildup on the O site, or higher probability of finding valence electron density on the oxygen atom, leaving partially positive character to the H atoms for charge neutrality (**3pts**). Given the geometry of H_2O the vector sum of bond dipoles along each OH leads to a net observable dipole moment for H_2O (**2pts**). For example from notes. If drawn correctly, as below, full pts.



5. Bonus question (10 pts)

Let's examine electron correlation energies and the physics leading to spatial-temporal correlation in electron motion. Instead of 3D, consider a 2D world.

- a) (3pts) Draw a picture of a 2D He atom with 2 electrons showing the relative electron positions about the nucleus that would give minimum electron repulsion for motion within a stable orbit re: perfect electron correlation effects.



The electrons would be 180° apart and moving in perfect correlation to give the minimum repulsion in a stable Bohr like orbit. This configuration keeps them as far apart as possible in this mythical 2D world. Need to show spatial relation of 2 electrons and indicate the relation that would give min. e-e repulsion.

indicate the relation that would give min. e-e repulsion (180° degrees apart) – 1.5 pts.

show correlated motion of the 2 electrons - either clockwise or anticlockwise in 2D to stay 180° – 1.5 pts.

- b) (3pts) Assuming the electrons are in stable orbits about the nucleus what would Z_{eff} be? From Gauss' Law the way presented in the text Z_{eff} would be 2 as both electrons would have not intervening electrons. Full points for this solution.

More detailed. Including the $1/r^2$ dependence for Coulombic interaction. The attractive force of the nucleus to each electron would be $-Zke^2/r^2$ reduced by the $+ke^2/(2r)^2$ e-e repulsion. $Z > 1$. If you compare net Coulombic force $F = -Zke^2/r^2 - ke^2/4r^2$ gives $(-ke^2/r^2)(Z-1/4)$ where Z_{eff} could be taken to be 1.75, very close to the variational method for helium (root reason Z is so close to 2 ...very strong correlation of e motions).

1pt for identifying forces, 1pt for getting Z_{eff} correct, 1pt for some discussion on how to find Z_{eff} .

- c) (2pts) This problem is now identical to the Bohr model for the H atom but considers 2 electrons per orbit (neglecting Pauli Exclusion Principle for this 2D problem by assuming perfect correlation of electron motions). What then is the expression for the allowed energies levels, of stationary or stable, orbits about the nucleus (see table of equations)? Calculate the electron binding energy of 2D He assuming the 2D He^+ is stable long enough to measure.

Depending on answer above, this problem could be reduced to an H-like system with Z_{eff} . $E_n = -Z_{\text{eff}}^2 E_R / n^2$. So for first ionization energy of 2D-He to 2D-He⁺ one needs a photon of energy $Z_{\text{eff}}^2 E_R$ to ionize (1 pt). The resulting ion is 2D-He⁺ has a binding energy of $E_n = 4E_R / n^2$ or ionization energy requirement of $4E_R$. The total binding energy of 2D-He would be $(Z_{\text{eff}}^2 + 4)E_R$ (1 pt). Need to show you understand that the binding energy refers to removal of all electrons...both e.

- d) (2pts) Would 2D He be stable? Recall Bohr's dilemma. Would one have the same problem with 2 electrons perfectly avoiding one another in 2D in stable orbits about the nucleus?

The problem is that for one electron there would be an oscillating electric field that would act like an antennae to emit light...coupling to EM field. With 2 electrons in perfect synchronization, there would be no net field so it could be argued to be stable (+1 pt). Any discussion indicating you realize that the oscillating charge could lead to loss of energy through emission of light will be given credit (+1 pt).