

Name: _____
Student Number: _____
Tutorial: _____

PHYSICS 294 – QUANTUM AND THERMAL PHYSICS

TEST 1

February 6th, 2024
Duration: 90 min

No.	Maximum	Marks
1.	30	
2.	30	
3.	20	
4.	20	
5.	Bonus Question: 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. (30 pts). Lessons from the Exact Solution of Hydrogen

a) (5pts) What is the binding energy of H? (See equation sheet.)

$$E_n = -\frac{m_e Z^2 e^4}{8h^2 \epsilon_0^2} \frac{1}{n^2} = -Z^2 E_R / n^2; E_R = 13.6 \text{ eV for } n=1 \text{ lowest energy state}$$

2pts for right equ, 2 pts for $n=1$ and maximum energy to remove electron (intrinsic binding energy of H atoms) and 1 pt for correct answer. Answer can be left in eV.

b) (5pts) Calculate the binding energy of He assuming that each electron completely screens its complement of proton charge, i.e. assume $Z=1$ for first ionization step. (You need to calculate the energy for $\text{He} + E_1 \rightarrow \text{He}^+$ and $\text{He}^+ + E_2 \rightarrow \text{He}^{2+}$).

1st ionization step $Z=1$, $n=1$ as 2 electrons per orbital $E_1 = 13.6 \text{ eV}$ (required to remove electron)

2nd ionization step now $Z=2$, $n=1$ and $E_2 = (2)^2 13.6 \text{ eV}$ or 54.4 eV

Total energy required = 68 eV

2 pts for recognizing the right equation and $n=1$ is lowest energy

2pts for use of $Z=2$ in second ionization step (removal of other electron screening nucleus)

1 pt for correct over all answer.

c) (5pts) The ionization energy of $(\text{He} + h\nu \rightarrow \text{He}^{+1})$ is experimentally determined to be 24.6 eV . What is the exact binding energy of He? Why is this value different than that calculated in b)?

1st ionization step (experimental) = 24.6 eV

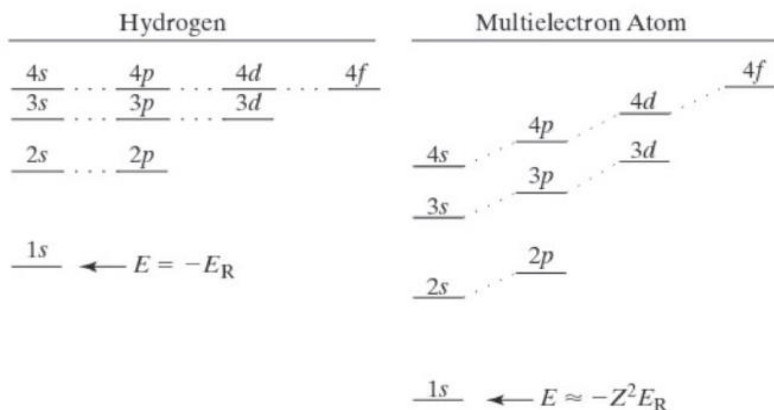
2nd ionization step (He^+ , hydrogen like with $Z=2$) = 54.4 eV

Total binding energy is 79 eV

The difference is in the first ionization step. The 2 electrons, as part of the He structure, spatially correlate their motion so there is incomplete screening of the nucleus. The e-e coulombic repulsion between electrons keeps them as far apart as possible while still interacting with the +ve charge of the nucleus. This spatial correlation or e-e correlation of motion leads to a larger Z_{eff} felt by both electrons such that the first ionization is found to be larger than if each electron completely screened its proton complement. The variation method shows that to within 2% accuracy, the Z_{eff} is close to 1.7 rather than 1 (or 2).

Grades as above. 1 pt for identifying correction experimental ionization for E_1 and 1pt for identifying He^+ as a hydrogen like ion with $Z=2$ and exact solution and 3pts for explaining e-e correlation energy and incomplete screening of nucleus for first ionization step.

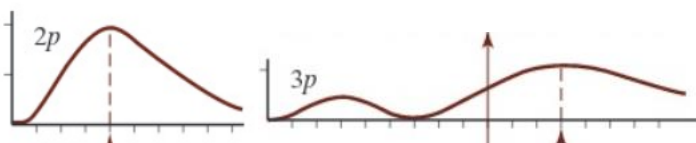
d) (5 pts) Draw the relative energy position of the different levels of H relative to He energy levels from $n=1$ up to $n=3$ (all n, l, m levels) using the above energy for the $n=1$ levels for H and He (exact ground state energy). Be sure to show which element has the highest binding energy and relative energy positions for the different levels. Briefly explain the difference between H and He, especially the difference in degeneracy for different quantum numbers.



As above, but only up to $n = 3$ is sufficient. **1 pt** for showing that H has degeneracy n^2 (including m states) whereas for multielectron atoms $E_{2s} < E_{2p}$, and $E_{3s} < E_{3p} < E_{3d}$ as above. An additional **1 pt** for showing the $1s$ energy level of He is lower than H.

Brief explanation – 3pts. The binding energy of He (more negative energy position of $1s$ core electrons) is larger than H due to the additional proton at the nucleus (increased positive charge) and incomplete screening of each electron of its proton complement. This effect is referred to as the electron-electron correlation energy – **1pt**. The breaking of degeneracy in the degeneracy for $n > 1$ is due to the difference in radial distribution for different values of l , in which the lower l value has a maxima in the electron density (probability distribution) closer to the nucleus than higher l value quantum states – **1pt**. This effect leads to higher Z_{eff} for lower l values and lower energy than the otherwise degenerate l states for the hydrogen atom – **1pt**. This latter point is distinct from the binding energy as it is necessary to explain difference in binding energies for different l quantum states.

e) (5pts) Based on the solution to the hydrogen atom, we know the electron is farther from the nucleus (on average) in the $n = 3$ state than in the $n = 2$ state. Draw the radial distribution for $n = 2, l = 1$ orbitals in comparison to the $n = 3, l = 1$ orbitals.



As above, main point is to identify $n=2, l=1$ is the $2p$ orbital, $n=3, l=1$ is the $3p$ – 2pts

Radial distributions showing no nodes for $2p$ and 1 node for $3p$ – 2pts

Showing schematically or stating the average r in the radial distribution is larger for $3p$ than $2p$, electron is further from the nucleus on average for $3p$ rather than $2p$ – 1pt (stated in the problem just have to show it schematically)

f) (5pts) Write the relation that gives the photon energy for a transition involving the emission of light from the $n = 3, l=1$ to the $n = 2, l=0$ level in hydrogen. Calculate the wavelength of the light emitted.

Emission = initial state is the higher energy state ($n=3$) – 2pts

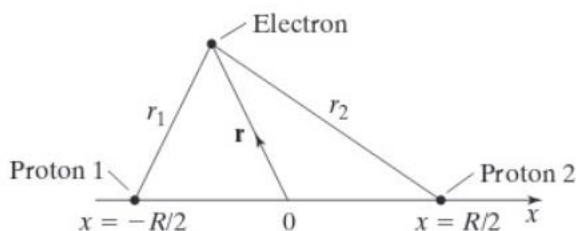
$$\Delta E = [-E_R/3^2 - (-E_R/2^2)]E_R = .139 (13.6 \text{ eV}) = 1.89 \text{ eV or } 1.89 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV} = 3.02 \times 10^{-19} \text{ J}$$

$$\Delta E = h\nu \text{ or } \nu = \Delta E/h = 3.02 \times 10^{-19} \text{ J} / 6.63 \times 10^{-34} \text{ J.s} = 4.56 \times 10^{14} \text{ s}^{-1} - 2\text{pts}$$

$$\lambda = c/\nu = 6.57 \times 10^{-7} \text{ m or } 650 \text{ nm.} - 1\text{pt}$$

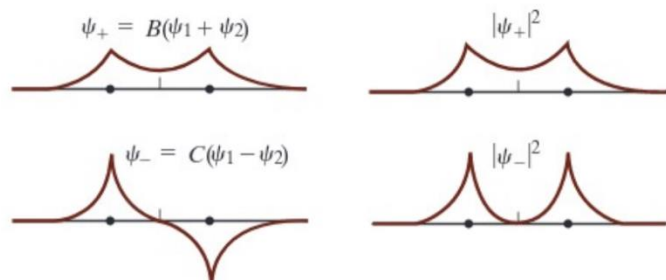
2. (30pts) This problem concerns understanding the formation of molecules with H_2 as the simplest case for the forces involved.

a) (5pts) 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 and write down the corresponding potential needed for setting up the Schrodinger equation.



1pt for R , 1pt for r_1 , 1pt for r_2 and 2 pts for $U(r_1, r_2, R) = -e^2/4\pi\epsilon_0 r_1 - e^2/4\pi\epsilon_0 r_2 + e^2/4\pi\epsilon_0 R$

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. (Clearly show where there is a buildup of electron density and where there is depletion of electron density.)

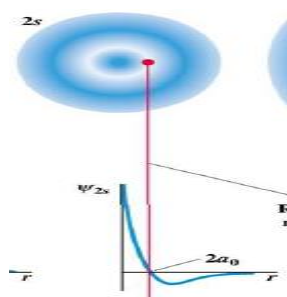


1 pt each for each AO superposition (eq with linear combinations of $1s$ orbitals) – 2pts (constructive/destructive)

Plots showing mod squared with build up e density between nuclei for bonding and depletion of e density from nuclei for antibonding– 3pts

c) (10 pts) Repeat the above for Li_2^+ . To simplify the problem, you can treat the 1s electrons as core electrons that do not mix to form molecular orbitals and completely screen their complement of protons in the nucleus to give a net +1 charge at each Li centre. Write down the electron configuration and trial wavefunction for Li_2^+ using the appropriate valence orbitals, for constructive (bonding) and destructive (antibonding) interference. Draw the corresponding orbital picture, explicitly showing the 1s core shell of electron probability density screening the nucleus. Qualitative descriptions of the molecular orbitals may help convey your response.

As above except now ψ_{2s} orbitals must be used, which have a node in the radial distribution.

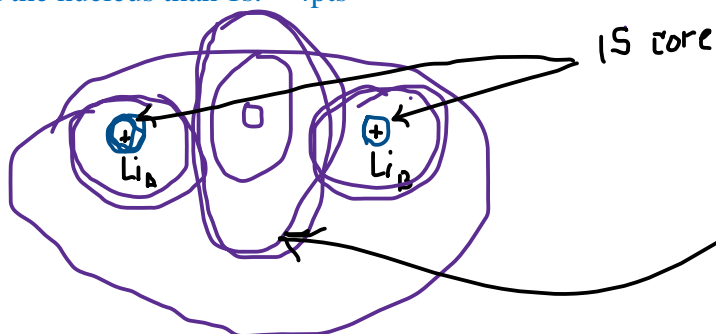


There should be superposition of two 2s hydrogenic orbitals with a node, as shown in the left.

$\psi_+ = \psi_{A2s} + \psi_{B2s}$ – re: constructive interference/bonding – 3pts

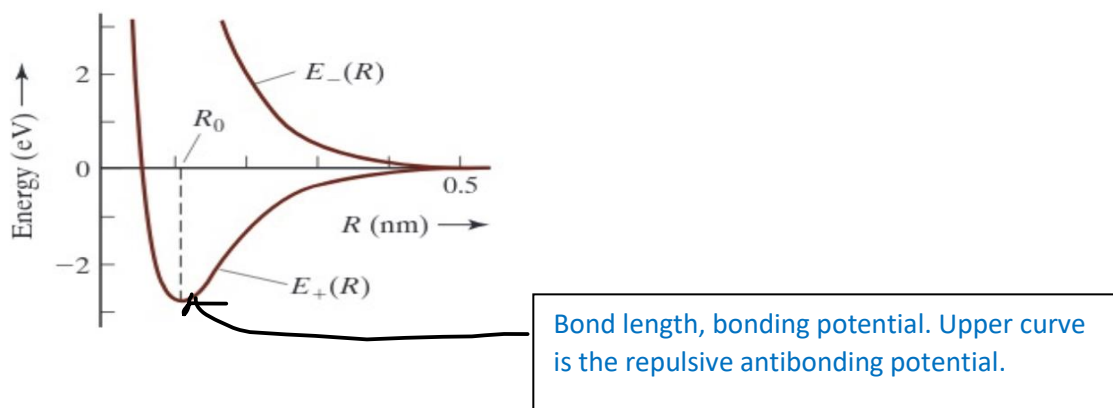
$\psi_- = \psi_{A2s} - \psi_{B2s}$ – to represent antibonding orbital – 3pts

The figure should show build up of electron density for bonding with a node...no penalty if not. Main point is to recognize you need to use 2s orbitals that are further from the nucleus than 1s. – 4pts

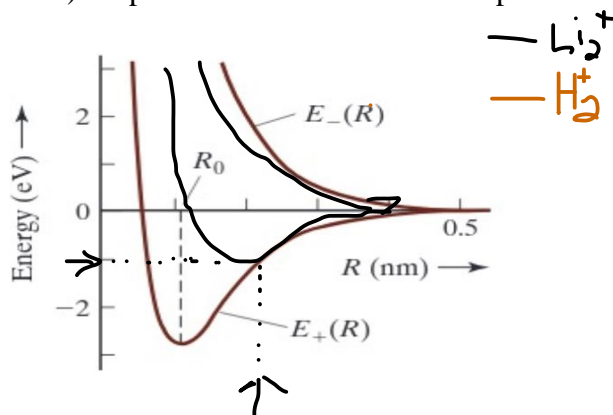


Constructive interferences post node in 2s radial function

d) (5 pts) Draw the Energy diagrams for the formation of H_2^+ (E 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).



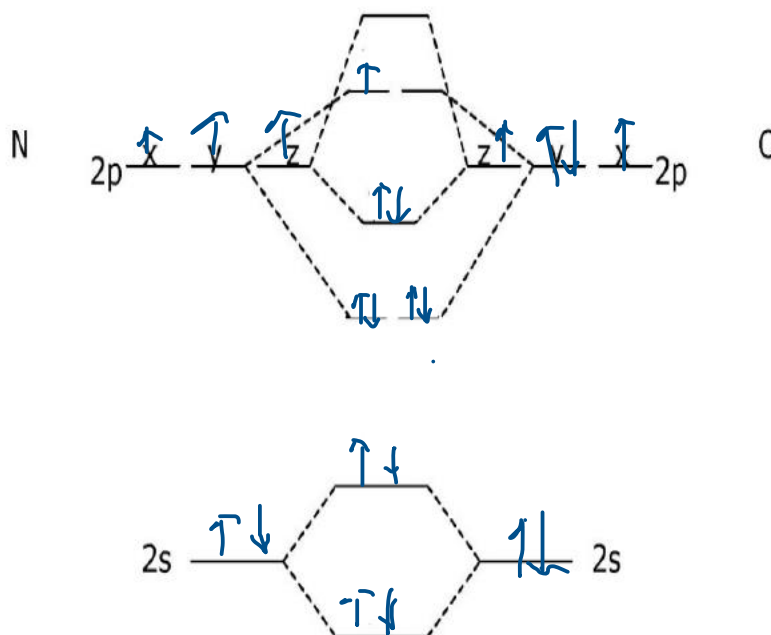
e) (5pts) Repeat the above (E vs. R plot) for Li_2^+ and compare directly to H_2^+ showing the expected difference in bond length and bond strength between Li_2^+ and H_2^+ , i.e., show clearly which molecule has the shortest bond length and largest bond enthalpy (energy needed to break the bond). Explain the difference in the expected bond energy and bond length.



The above curves should show a minimum at a larger distance than H_2^+ . The net Z_{eff} is 1 for both and the valence electron in Li_2^+ is in $n=2$ not $n=1$. The bond length will be longer and the bonding energy less than H_2^+ . Showing longer bond length for Li_2^+ - 2pts. Showing weaker bond for Li_2^+ - pts, Showing bonding and antibonding equal stabilizing and destabilizing relative to bonding and anti bonding of Li_2^+ - 1pt.

3. (20pts) The molecule nitric oxide, NO, was only discovered to have important biological properties in 1988 as an important cardiovascular regulating molecule which was awarded the Nobel Prize in Medicine in 1998. Its properties are determined by the charge separation between N and O atoms.

a) (5pts) Assign the electronic configurations to N and O using the energy level diagram below and the Pauli Exclusion Principle. Show how the electrons in the different valence orbitals would mix to form molecular bonds, i.e., assign valence electrons to the mixed electronic levels schematically shown by dashed lines.



1pt for correct e config for O, 1pts e config for N, 3pts for correct MO electron config,

b) (5pts) What is the bond order in NO? 2.5

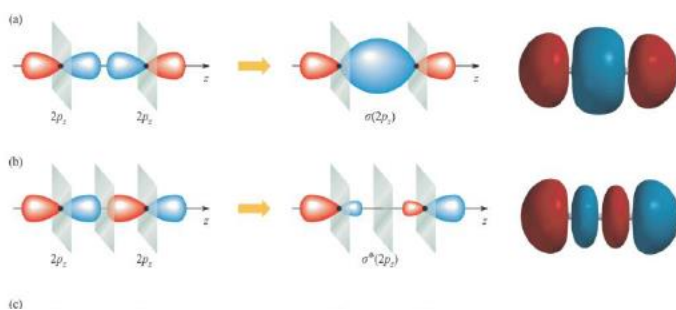
c) (5pts) Which element is lowest in energy (highest binding energy for electrons) and would have the highest electron density. Briefly explain using trends in the periodic table and concept of electronegativity.

From the table on electronegativity O would have the highest Z_{eff} and would be lower in energy wrt to binding electrons – 1pt. The higher electronegativity scale indicates the electron density will be greatest on the O atom in the NO molecule – 1pt. The effect of electron correlation, to minimize e-e repulsion leads to decreased screening of the electron of its complementary proton for each element across a row in the periodic table – 1pt. The ionization energy increases and radii decrease. Both factors lead to increase electron density on the atom that is more

electronegative across a row in the periodic table – 2pts. It is not until one goes up one row, corresponding to a higher level, n quantum shell, that the electrons are on average further away from the nucleus and less tightly bound. The trends down a row are increasing atomic radii and decreased electron ionization (less energy needed to remove an electron) and lower electronegativity.

For N there is a higher ionization energy relative to O due to the extra stability of a half filled shell re: Hund's rule. If N was discussed on the basis to have the higher electron density rather than O and made this point clear...full points.

- d) (5pts) The overlap of the highest bonding MO is p_z in character. Draw the overlap of the p_z orbitals to form a bonding MO showing (or stating) specifically which atom will have the higher electron density on either the N or O atom. Show the corresponding antibonding orbitals.



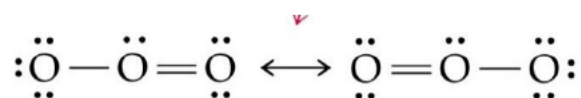
Upper is bonding orbital for σ_{pz} showing the build up radially symmetrically along the bond axis for a sigma covalent bond with most electron density near the O atoms due to the larger electronegativity – 3pts

Bottom is overlap leading to a node intersecting the bond axis and depletion of electron density. N is the less electronegative element so the electron density in the antibonding orbital will be larger near N – 2pts

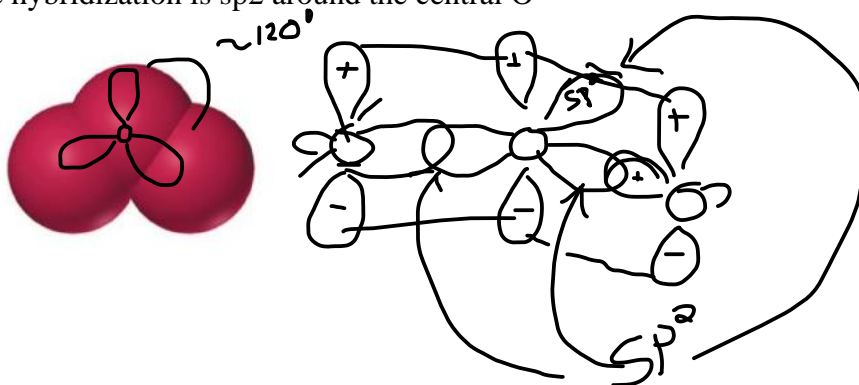
Note, if N was stated due to Hund's rule and same logic – full pts

4. (20pts) Ozone (O_3) strongly absorbs UV in the stratosphere to protect living systems from mutagenic UV photochemistry. We came dangerously close to depleting this layer through the UV induced creation of ChloroFluorocarbon (CFC) radicals. CFC were used as refrigerants in air conditioning and propellants for household goods that were thought to be inert but form radicals from UV absorption and catalytically degrade O_3 . Understanding the structure and bonding of O_3 was essential to figuring out the photochemistry in the stratosphere – and save the planet from an ecological disaster.

a) (5pts) Draw the Lewis Dot Structure for ozone, O_3 and the corresponding hybridization of orbitals of the central O atom (skeletal structure: O-O-O).



The hybridization is sp^2 around the central O



b) (10 pts) Is Ozone linear or bent? If bent, what do you expect the bond angles to be? Explain in terms of valence electron shell pair repulsion concepts.

There are formally 8 electrons around the central O atom to fill its $n=2$ shell. There are 2 possible resonances or spatial distributions of electrons with respect to the other two O. Each of these 2 O atoms, with lone pairs also has a full complement of shared electrons to fill the $n=2$ valence shell about each O. The net effect is that there is a redistribution of electron density between the 3 O atoms by which the central O has 3 different arrangements of molecular orbitals with the full complement of electrons in single and formally double bonds. These electron distributions are not fixed in space but are free to rearrange in space about the central O to minimize e-e repulsion between the corresponding electron densities for each MO. This effect is referred to as valence hybridization that leads to a minimum energy arrangement in space by which 3 spatially polarized electron distributions by the nuclei and lone pairs can arrange to give the lowest possible e-e repulsion ...at 120° apart. The angle will be slightly smaller than 120° between Os as the lone pair does not have another nucleus or positive charge to more direct the density along a bond axis. The net effect is that lone pairs occupy more volume with respect to electron-electron repulsion and will decrease this angle. The measured angle turns out to be 117° .

3pts – for some mention of Lewis Octet Rule or ability for each O to accommodate 8 electrons to maximize Z_{eff} felt by all electrons

3pts – for discussion of e-e repulsion between the polarized electron density between the other 2 O surrounding the central O

3pts – for discussion the maximum distance apart, min. e-e repulsion, lowest energy is 120° .

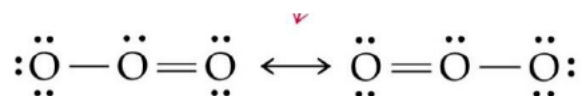
1pt – for realizing the bond angle will be less than 120° due to the increased e-e repulsion volume of lone pairs. The bond angle is close to 120° , slightly less (117°) due to the larger volume of the lone pair.

c) (5 pts) What is the bond order of O₃?

Based on the above resonant structures the bond order is 1.5. This bond order could also be deduced from the sp² hybridization and overlap with p orbitals on neighbouring O atoms

2 pts for resonant structures in arranging electrons...spatially delocalized means electrons feel the net attraction of more nuclei = large Z_{eff} for molecular structure.

3 points – 1.5 bond order. Equal mixture of double bond and single bond.



5. Bonus question (10 pts)

a) (5pts) Given the wavefunctions below, write down the expression for the expectation value $\langle r \rangle$ for 2s and 2p wavefunctions for the H atom. Recall the expectation value or average value is found by multiplying r by the probability of finding r in the interval $r+dr$ and integrating over all r (0 to ∞), i.e., $\langle r \rangle = \int rP(r)dr$. Given the time limits, you do not have to evaluate the integrals.

The first few radial functions $R_{nl}(r)$ for the hydrogen atom. The variable ρ is an abbreviation for $\rho = r/a_B$ and a stands for a_B .

	$n = 1$	$n = 2$	$n = 3$
$l = 0$	$\frac{2}{\sqrt{a^3}}e^{-\rho}$	$\frac{1}{\sqrt{2a^3}}\left(1 - \frac{1}{2}\rho\right)e^{-\rho/2}$	$\frac{2}{\sqrt{27a^3}}\left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right)e^{-\rho/3}$
$l = 1$		$\frac{1}{\sqrt{24a^3}}\rho e^{-\rho/2}$	$\frac{8}{27\sqrt{6a^3}}\left(1 - \frac{1}{6}\rho\right)\rho e^{-\rho/3}$
$l = 2$			$\frac{4}{81\sqrt{30a^3}}\rho^2 e^{-\rho/3}$

You need to recognize that 2s is the function listed in the above table, first row, second column, $n=2, l=0$, i.e., $R_{2,0}$ AND to use $r^2 |R_{nl}|^2$ for the integration, i.e.,

$$\begin{aligned}
\langle r \rangle_{20} &= \frac{4\pi}{32\pi a_0^3} \int_0^\infty dr r^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \\
&= \frac{a_0}{8} \int_0^\infty dx x^3 (2-x)^2 e^{-x} = \frac{a_0}{8} (4 \cdot 3! - 4 \cdot 4! + 5!) \\
&= 6a_0
\end{aligned}$$

$$\begin{aligned}
\langle r \rangle_{21} &= \frac{2\pi}{32\pi a_0^3} \int_0^\infty d\theta \sin \theta \cos^2 \theta \int_0^\infty dr r^3 \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} \\
&= \frac{a_0}{16} \left(\frac{2}{3}\right) \int_0^\infty dx x^5 e^{-x} \\
&= \frac{a_0}{16} \left(\frac{2}{3}\right) (5!) = 5a_0
\end{aligned}$$

The above integrals would be needed for full credit with proper limits. The integral does not have to be evaluated.

The problem is 2pts for writing correctly the radial distribution function for R2,0 and R2,1. For correctly setting up the integral to find $\langle r \rangle$ - 3pts

b) (5pts) Without evaluating the integrals, you should see that the $\langle r \rangle$ will be different for 2s and 2p orbitals. The expectation value for r can be shown to have the general form:

$$\langle r_{n,l} \rangle = a_B [3n^2 - l(l+1)].$$

The average $\langle r_{2,1} \rangle$ for the 2p orbital is $5a_B$ and is actually smaller than the average distance $\langle r_{2,0} \rangle$ of $6a_B$ for the 2s orbital.

How is it possible for the 2s and 2p to have the same energy then, depend only on n, the principle quantum number related to the r dependence?

This problem is interesting as if you go through to look at $\langle U \rangle$, which has a $1/r$ functional form will also not give the same value for 2s and 2p orbitals even though the same n and E only depends on n. The energy is both in the form of kinetic energy (KE) and potential energy for the electron (U), i.e., $E = \langle KE \rangle + \langle U \rangle$. The difference in radial distribution for the 2s and 2p leads to offsetting differences in KE to lead to the same energy.

Realizing the $E = \langle KE \rangle + \langle U \rangle$ - 3pts

Difference must be attributable to specific details of r dependence in $\langle KE \rangle$ to explain degeneracy – 2pts.