PHYSICS 294 – QUANTUM AND THERMAL PHYSICS
TEST 1

February 17th, 2022
Duration: 120 min

No.	Maximum	Marks
1.	5	
2.	20	
3.	15	
4.	25	
5.	5	
6.	20	
7.	10	
8. 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 <u>except </u>for a non-programmed calculator**

1. (5 pts) For the hydrogen atom, state <u>whether the following statements are true or false</u>.

a) The state defined by $n = 2$ is the first excited state. <u>T</u>

b) It takes more energy to ionize (remove) the electron from the $n = 2$ state than from the ground state. <u>F</u>

c) The electron is farther from the nucleus (on average) in the $n = 4$ state than in the n =2 state. <u>T</u>

d) The wavelength of light emitted when the electron drops from n=5 to the n = 3 in hydrogen is longer than from n= 4 to n= 2 (See equation for energies of the hydrogen atom; $E \propto n^2$). <u>T</u>

e) The energy required to ionize an H atom is higher for the n= 2, l = 0, m = 0 state than the n = 2, l=1 m = 1 state in the presence of a 2 T magnetic field. <u>F</u>

2. (20 pts total) Consider the radial functions for the hydrogen wavefunction solutions.

a) (10 pts) The relative radial probability distributions (i.e. $4\pi r^2 [R(r)]^2$) for the 1s, 2s and 2p orbitals are shown below.   On the figure showing the 1s probability distribution, sketch the corresponding orbital for 3s. On the figure for 2s, sketch the 3p orbital probability distribution. On the 2p plot, sketch the corresponding radial probability distribution for 3d orbitals – as indicated. Show the nodes and trend for the maxima in probability distribution as a function of r as n and l increases.

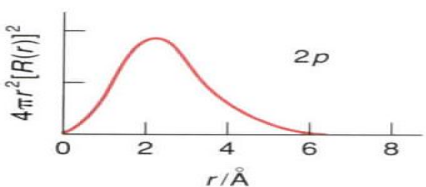Plot radial prob. for **3s overlayed on 1s** in this figure.
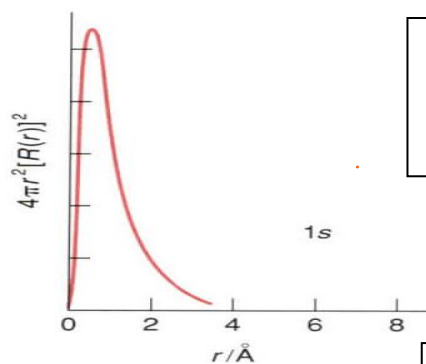
Drawing should show 2 nodes with increasing maxima and obvious <r> further from nucleus.

Plot radial prob. for **3p overlayed on 2s** in this figure.
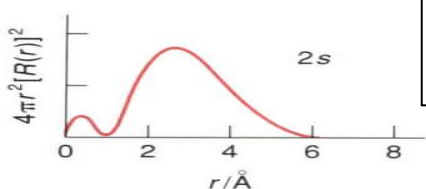
Drawing should show 1 node with second maxima further than the 2s..obvious increase in <r>.

Plot radial prob. for **3d overlayed on 2p** in this figure.

Drawing should show 0 nodes with increasing maxima and obvious <r> further from nucleus for 3d relative to 2p

2

See text, p. 279, Figure 8.23 for specific details. Only qualitative features were required.
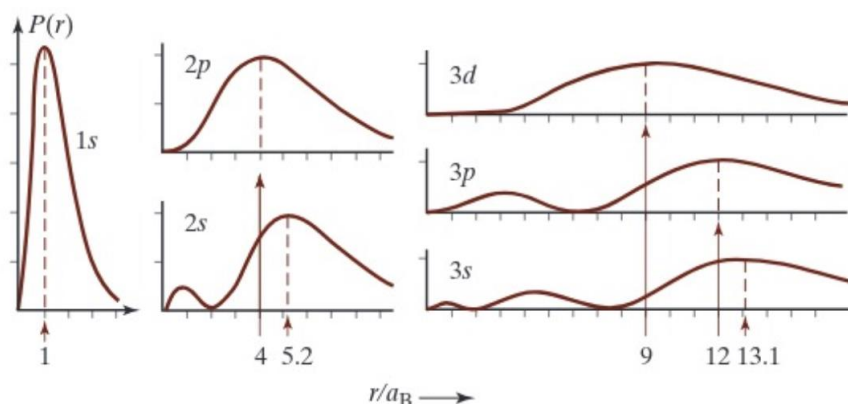
b) (10 pts) For the hydrogen atom, the energy of the different states depends only on the principal quantum number n, e.g. the binding energy of 2s and 2p electrons is the same in hydrogen. Is the energy of the 2s and 2p orbitals the same for multielectron atoms? Explain how this difference in electron distribution with angular momentum quantum number, l, gives rise to differences in Z_{eff} and to decreasing atomic radii across a row of the periodic table and increased ionization energies.

The energy of the valence orbitals described by hydrogenic wavefunctions 2s and 2p are no longer degenerate. The differences is the details of the radial distribution account for the different. As shown in comparing the radial distributions for 2s and 2p, the 2s orbital has a maximum in the electron probability distribution that is closer to the nucleus than that for 2p. The electrons in 2s orbitals will experience less screening and a larger Zeff than electrons in 2p orbitals. This difference in screening can be rationalized by extrapolation of Gauss's law for which U(r) approximates $-Zke^2/r$ as r $\rightarrow$ 0 (closer to the nucleus) and U(r) goes to -ke2/r (Z=1) as r$\rightarrow\infty$ (further from the nucleus). The larger Zeff experienced by electrons in 2s orbitals will feel a larger Zeff than for 2p and will therefore be lower in energy or more tightly bound. (Coulomb force goes as $1/r^2$ is another way of stating this..held more tightly.)

The difference in Zeff also means that the electrons will be held more tightly and will be closer on average to the nucleus. The 2s radial distribution will condense more closely to the nucleus than the 2p as one goes across the periodic table and will cause a decrease in the radii of the elements of higher Z as one goes across a given row or shell in the periodic table. The increase in number of protons in the nucleus, or increase in Z, is not offset by the complementary electron due to the spatial distributions and incomplete screening of the charge (Z) of the nucleus. This leads to an increase in the relative binding energy for each addition electron for each incremental

increase in Z. The effect is smaller radii and higher ionization energies across a row with increasing Z.

Main points, effects of radial distribution on the screening of the nucleus. The electron distributions do not completely screen their complementary proton at the nucleus as Z increases across a row. The l dependence on the radial distribution for which there are larger probabilities for being closer to the nucleus will be lower in energy and higher IE. The corresponding increase on Coulomb force (higher Zeff) gives rise to correspondingly smaller atomic radii.

3. (15pts) Consider the He atom.

a) (5pts) Write down the Schroedinger equation (Hamiltonian) for the Helium atom. Be sure to include a drawing and explicitly show the spatial variables you used to define the relevant Schroedinger equation. Be sure to identify and include all terms relating to the potential energy, U.
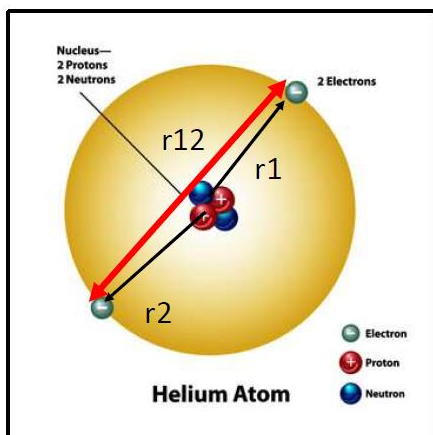
$$\mathbf{H}\Psi(r_1, r_2) = [-(h^2/8\pi^2 m^2)(\nabla_1^2 + \nabla_2^2) - Ze^2/4\pi\varepsilon_0 r_1 - Ze^2/4\pi\varepsilon_0 r_2 + \boxed{e^2/4\pi\varepsilon_0 r_{12}}]\,\Psi(r_1, r_2) = E\Psi(r_1, r_2)$$

$\boxed{e^2/4\pi\varepsilon_0 r_{12}}$ $\Rightarrow$ No Longer Mathematically Separable/Solvable ....classic intractable problem

Need to show 2 electrons and 2 protons, with the nucleus representing a larger mass and/or central force (figure as above) For Schroedinger equation, any suitable form in which the spatial dependence for 2 electrons is included would be accepted. The key is the potential. It should include the attractive Coulombic attraction of the Z nuclear charge for both electrons and the all important e-e repulsion term.

b) (5pts) This classic 2-body problem is not exactly solvable. Identify the term in the above expression that makes the problem intractable - with a brief explanation.

Red box above. The spatial relationship between the 2 electrons can not be written in terms of independent variables. This term is intrinsically inseparable. Mathematically, the method of separation of variables can no longer be used. Main points are that the electron-electron repulsion terms in intrinsically coupled and can not be separated. The electron motion and forces affecting their spatial relationship in space and time is strongly correlated through this e-e repulsion term.

c) (5pts) What approximate methods are used to treat multielectron atoms such He. Explain the Independent Particle Approximation (IPA) in your response.

See section 10.2 of text. The discussion should include that each electron is assumed to be independent of the other as evident in the name of this approximation. Each electron moves within the effective potential created by the electron distribution of the other electron(s), which partially screens the nucleus. Approximate wavefunction solutions are used to define an effective potential (Ueff or IPA potential) that is then used to solve for improved electron wavefunctions that are then used again to determine a refined or more accurate Ueff. This approach leads to calculated energies and wavefunctions that become closer to the exact solution with each iteration. The whole process is repeated until the basis used converges to a predicted energy that does not change within some threshold to state the calculation has converged. The use of the electron wavefunctions to defined an effective potential is a mean field approach that improves each successive calculation in what is referred to as a self-consistent manner or Hartree-Fock method who introduced this methodology. Any method is which a proper trial function is used to calculate the atomic or molecular energy and some means of refining the guess would be acceptable.

The other approach discussed on class is the Variational Method discussed below.

4. (25 pts) The Variational Theorem is important in providing reasonable approximations to the operating physics in multi-electron atoms. The exact solution is always lower in energy than any approximate solution.

A particular trial function for He, using H 1s wavefunctions, we can be written as:

$$\psi(\mathbf{r_1}, \mathbf{r_2}) = \psi_{1s}(r_1)\psi_{1s}(r_2) = e^{-Z(r_1+r_2)}$$

Using the nuclear charge Z as a Variational Variable (replacing Z in the exponent with α) we can find the lowest energy, and effective nuclear charge (Z_{eff}), assuming 1s electron distributions. Using the above trial function with the Schroedinger equation to calculate the energy (E), after a bit of math, one arrives at the relation for energy for the He atom in terms of the variation variable as:

$E(\alpha) = \alpha^2 - (27/8)\alpha$

Note this expression is in atomic units or Hartrees to keep simple (1 Hartree = 27.211 eV or $2E_R$)

a) (5 pts) Using the above expression for $E(\alpha)$, what is the effective nuclear charge (Z_{eff} or α) felt by the electrons in this approximation? (Find the minimum energy with respect to the variational variable, α.) Offer an explanation why Z > 1, i.e. that each electron does not screen its full complement of a proton charge in the nucleus.

Find $dE/d\alpha$ and set to 0, gives $\alpha = 27/16$ or **1.688 for Zeff**. The fact that Z>1 is due to the incomplete screening of the nucleus by the electrons. This variational calculation is using the static distribution of 1s orbitals in which electrons in similar distributions will feel a larger Z due to the spatial relationship leaving unscreened fields per r dependence on degree of screening. See equation sheet for IPA potential.

b) (5pts) With your estimated Z_{eff} (or α value giving the lowest E) calculate the energy of the He atom within this approximation (you need to convert Hartrees to eV).

With $\alpha=27/16$, the relation for $E(\alpha)$ gives $(1.688)^2 - (27/8)(1.688) = -2.85$ Ha

Converting to eV gives 2.85 Ha x 27.211eV/Ha = - 77.49 eV as the binding energy for He.

c) (10 pts) We would like to compare this approximation using the Variational Method to the exact energy. Since this problem can not be solved exactly, we need to experimentally measure it. The first ionization energy ($He + h\nu \rightarrow He^+ + e$) is found to be 24.6 eV. With this information, what is the exact energy of the He atom. (Hint: you need to calculate the second ionization energy for He^+ to He^{2+}.)

The energy of the He atom is defined to be the energy to break it up, completely separate electrons and nucleus with 2 protons, which is defined to be E=0. *This problem is direct from the problem sets.* You are given the energy to remove 1 electron. The remaining electron ionization energy can now be exactly calculated as it corresponds to an H-like atom with only 1 electron (separable central force problem). In this case, from the equation sheet:

$E_n = -\frac{m_e Z^2 e^4}{8h^2\varepsilon_0^2}\frac{1}{n^2} = -Z^2 E_R/n^2$; E_R= 13.6 eV …Z = 2 so $He^+ \rightarrow He^{2+}$ is $-Z^2 E_R$(n=1 for lowest energy state or intrinsic binding energy) or $-4E_R = -4(13.6)eV = -54.4$ eV. One would need a photon of this energy to ionize He^+ to He^{2+}.

The exact He total binding energy (from 1 experimental measurement) is the sum of these two ionization processes or $E_{exact} = -IE1 - IE2 = -24.6 + (-54.4) = -79.0$ eV

d) (5pts) The error in this simple calculation is quite small (2-3%). Please describe physically what the difference in the approximate energy and exact solution is due to. The interesting point is that this energy is comparable to chemical bonds and it is for this reason accurate calculations

with higher levels of approximation are used in quantum calculations of atomic/molecular properties.

The use of the trial function in the Variational Method assumes a static charge distribution, or mean field the electrons experience. As discussed in class (and demo), the e-e repulsion will strongly correlate their motion to be as far apart as possible for a given energy about the nucleus. The missing physics is the correlation of the electron motion in time, which is referred to as electron correlation energies..

5. (5pts total) Which molecule would have the <u>longer bond length</u>: F_2 or F_2^+? Explain in terms of molecular-orbital theory using the MO energy level diagram for homonuclear atoms below to assign the electron configuration for F_2^+ and compare to F_2. <u>Assign electrons into the boxes provided for either F_2 or F_2^+ and state bond order.</u>
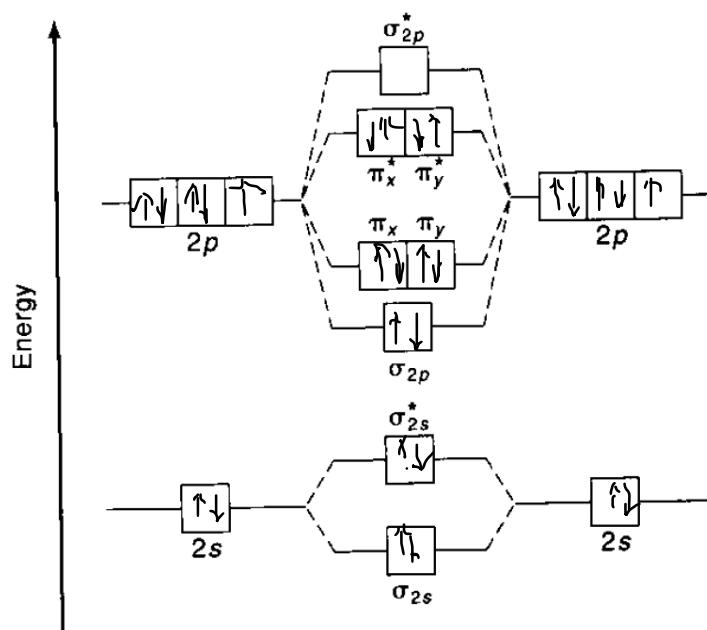
The above is for F_2, total of 7 valence electrons. The 4 electrons in antibonding π^* MO's constitute cancelling the effect of 4 electrons in bonding π MO's, to give a bond order of 1, as can be seen in the above MO diagram for electron configurations.

For F_2^+, there is one less electron in antibonding π^* MO's so the bond order is 1.5. F_2^+ has the stronger bond relative to F2, even though one less electron, and is shorter.

This problem was directly from the assigned problems.

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6. (20 pts total) Consider the hydroxyl radical (OH•). This species plays an important role in atmospheric chemistry because it is a strong oxidant. Assume the molecular orbitals result from the overlap of an oxygen $2p_x$ orbital and a hydrogen 1_s orbital.

a) (3pts) Draw pictures of the σ and σ* molecular orbitals for OH•.

b) (2 pts) Which of the two molecular orbitals has more hydrogen 1_s character? Brief explanation.

c) (5 pts) Use the molecular-orbital energy-level diagram below. Give the electron configuration for the OH• radical by assigning valence electrons from O and H into the molecular orbitals (boxes) in the figure. Label which side is for H and which for O valence electron contributions to the MO's. Note that the electrons in the nonbonding orbitals on oxygen have π character and should be assigned as such.

 d) (5 pts) Estimate the bond order of OH•. Compare this value with that for OH⁻.

This part of the problem is directly from the assigned problems. Solution as posted:

(a)
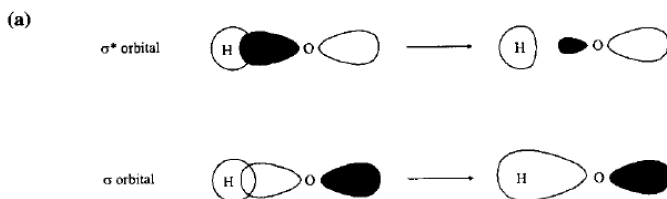
(b) Since the H 1s atomic orbital is higher in energy, the antibonding σ* will have the greater hydrogen 1s character.

(c)
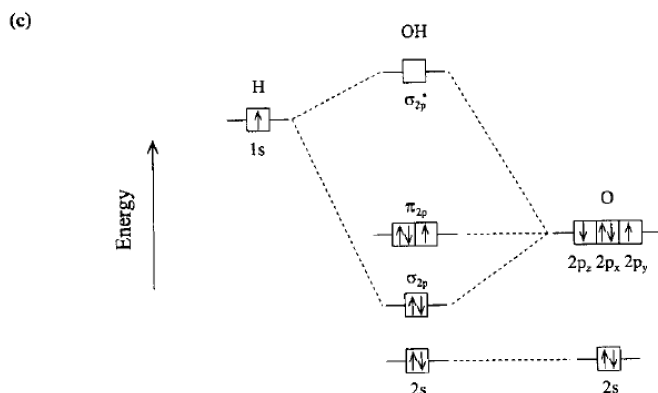
(d) There are two bonding electrons in OH and 5 nonbonding electrons. The bond order is 1. In forming OH⁺, an electron is removed from a nonbonding orbital, and the bond order of OH⁺ is also 1.

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Inspection of this figure shows that the addition of 1 electron to generate OH⁻ will also have a bond order of 1.

e) (5 pts) Comment on the position of the H 1s orbital with respect to binding energy relative to the 2p and 2s orbitals of O and their relative contributions to molecular orbitals. In this context, explain electronegativity and difference in electron withdrawing power of different atoms.

The binding energy of O for its valence electrons is larger than H. The Zeff is >1 whereas H has only 1 proton and 1 electron so Z = 1. The larger unscreened effective charge of the nucleus leads to an increase of electron density around the O atom. Is this difference in unscreened nuclear charge, and e-e correlations that further increasing the reduced screening of each additional electron's complementary proton, that leads to higher IE across the periodic table and increase in electronegativities or drawing powers across the periodic table.

7. (10 pts total) DNA encodes the genetic sequence for the key condition of self replication for living systems. The specific structure and how the molecules fit together to form a double helix secures the code. There are 4 nucleobases for the genetic code. The structure of the Adenine-Thymine interaction is shown below.


Adenine   Thymine
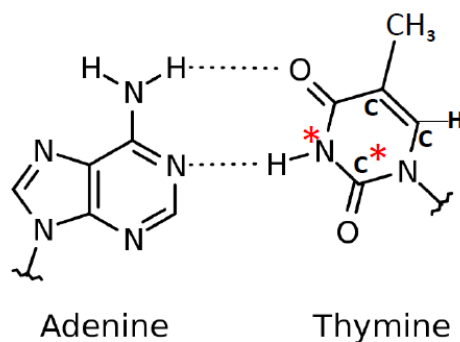
a) (4 pts) <u>For the starred carbon atom</u> (C*) for Thymine give the valence orbital *hybridization* <u>and</u> the *expected bond angles* between all 3 ligands. (Is the carbon s, p, sp, sp², sp³..?). <u>Draw or state</u> the specific overlap of orbitals on the carbon and oxygen that <u>lead to the double bond</u> as drawn for C=O in the figure.

The C* is sp² hybridized with 120^0 bond angles between ligands. The unhybridized p orbital is then available for sidewise overlap to create a double, π, bond with a p orbital of the O. (The O atom has 2 lone pairs to complete an octet or filled valence shell, so it will also be sp² hybridized with the lone pairs in sp² orbitals and remaining p orbital forming this double bond.)

b) (3 pts) <u>What is the valence orbital hybridization for the starred **N*** atom</u> in the above figure? The bond angles are 120^0 and all atoms line in the same plane as C*. Please note, N has a filled shell or satisfies the octet rule. There is a lone pair not shown in the figure<u>. In which hybridization orbital would the lone pair be formally assigned?</u> <u>Draw at least one resonance structure</u>, rearranging the electrons in this orbital to form double bonds to adjacent atoms or rearrange the double bonds in the provided Lewis structure to show the resonance or electron delocalization. <u>What is the approximate bond order in the ring structure</u>?

The N atom must be sp^2 hybridized based on the given bond angles and planar nature. The 3 bonds to N that form a plane must all be $\sigma(sp^2)$ bonds. This leaves the remaining lone pair to complete N's octet in the unhybridized p orbital.

Resonance structures are easily created by simply interchanging double bonds in Lewis structures. The electrons are mobile and don't know what atom they atom to which they are assigned to create a filled shell and maximum over Zeff, by being spatially delocalized to experience the net Coulombic binding force of multiple nucleii. If there is a way to rearrange electrons in Lewis diagrams, the electrons of course will find these structures, which will be intermediate between localized end points for the electron distribution. Resonant structures = spatial delocalization of electrons = attractive force of more nucleii or increase on Zeff = lower energy.

Thymine   Thymine
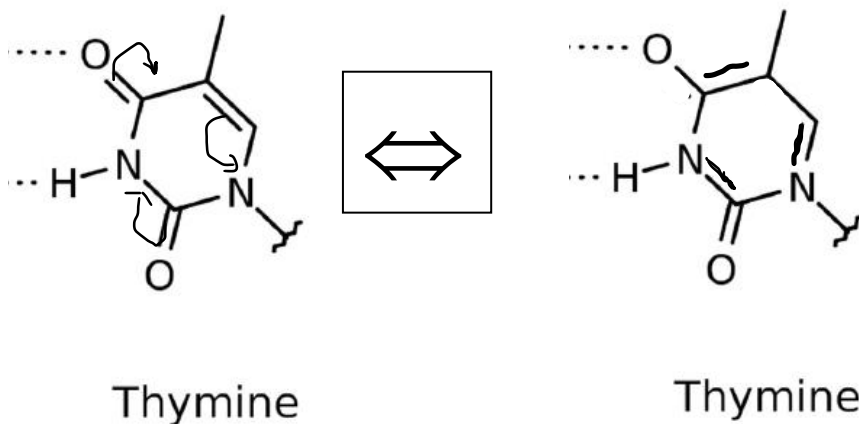
From the above bond order for atoms in the ring is approximately <u>1.5</u> for all atoms not alternating between single and double bonds.

The above are only a few resonance structures. The electrons for DNA nucleobases are extensively delocalized, with additional resonance stabilization, lower energy, due to the increase in collective Zeff with electrons within the p orbitals, for all the ring atoms in sp2, to experience the full unscreened nuclear charge, of the entire ring. It was thought that this extra stabilization is why DNA is intrinsically stable to UV radiation so that mutation rates are not much higher than observed, based on UV photodegradation of similar biomolecules.

c) (3 pt) In the figure below, circle any <u>polar bonds</u> (i.e. bond dipoles) in the Thymine molecule. This partially polar character directs molecular recognition and conservation of the DNA sequence. The electronegativities of the different elements, if needed, are attached back of the exam.
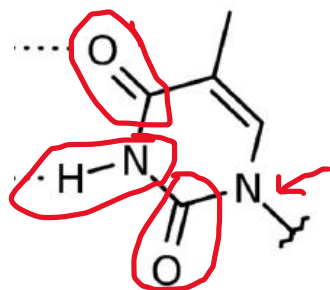
If circled <u>also accepted</u>. However no atom was indicated here to allow you to decide based on electronegativities if this bond would be polar.

Thymine

8. (**bonus question - 10 pts total**) The Stern-Gerlach Experiment shown schematically below illustrated that electrons have spin with quantized spin states corresponding to spin magnetic moments with projections $S_z = \pm \frac{1}{2}\hbar$ along an applied field. This work was based on the Ag atom.
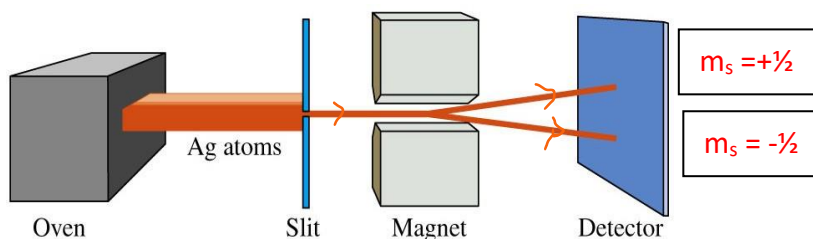
a) (4 pts) Calculate the transverse velocity of the Ag atoms (vertical direction shown in the figure), assuming a <u>net change in the</u> <u>B field in traversing the magnetic field gradient of 1T</u>, (atomic mass of Ag is 1.79 x 10^{-25} kg, 1 eV = 1.6x10^{-19} J, μ_B = 5.79 x 10^{-5} eV/T). The two emerging beams have the same kinetic energy but displaced in opposite directions. (Hint: consider the energy splitting for spin ½ and spin -½ electrons. Draw the splitting in energy for electron spin states in an applied field showing the energy difference. This potential energy is converted to kinetic energy in a magnetic field gradient.)

a) cont.

The energy imparted to the Ag atom is just the force generated on the magnetic moment of an unpaired electron. The beam is shown to split into 2 with the measured component corresponding to spin.

The magnetic field gradient was given to you and stated to lead to a net change in energy corresponding to 1T.

$$\Delta E = \pm \frac{e\hbar}{2m_e} B = \pm \mu_B B$$

For electron spin the Zeeman effect leads to a change in energy of:

for electron spin with a total separation of $2\mu_B B$ for $\pm 1/2$ spin states. From the center of the beam (0 transverse velocity reference), the spin $+\frac{1}{2}$ will be increased in energy by $\mu_B B$ and $-1/2$ by the same but in the opposite direction, as shown in the figure. The increase in energy being converted to KE is $\mu_B B$ or KE(vertical direction) = 5.79 x 10^{-5} eV/Tx1T = 5.79 x 10^{-5} eV or 9.26 x 10^{-24} J.

This gives for the Ag atom transverse velocity (one beam up, other down) of:

v_{Ag} = [2KE/m_{Ag}]$^{\frac{1}{2}}$ = [2x9.26x10^{-24} (kgm^{2}s^{-2})/1.79x10^{-25}kg]$^{\frac{1}{2}}$ = 10.2 m/s.

b) (3 pts) It turns out there was something very unusual in this experiment in that the classical energy ordering of valence orbitals to define the electron configuration of Ag would give [Kr]$5s^2 4d^9$ (see attached periodic table, [Kr] configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$). If this was the case, the orbital angular momentum for the electron distribution would be defined by the quantum number l and the total magnetic moment would be the sum of orbital and spin moments. <u>How many spots should Stern and Gerlach have observed if [Kr]$5s^2 4d^9$ was the actual electron configuration?</u> <u>Draw the splitting of energy levels</u> due to the interaction of resulting magnetic moments along the field direction (taken as z component) for both orbital angular momentum and spin.

In this problem it is important to realize that it is the total L and S magnetic moments that count. The electrons that are in levels with spin paired electrons have 0 net magnetic moment as the two spin moments cancel. Similarly for orbital angular magnetic moments from angular motions. However for the [Kr]5s24d9 configuration, all the levels in the 5s are filled and m=0 in any case, so no splitting from these electron contributions. The $4d^9$ orbital arrangement however has 1 unpaired electron, so there will be at least 1 spin magnetic moment and within an ensemble measurement, there will be $\pm \frac{1}{2}$ spin moments possible. The 4d electrons are in l=2 levels. Here it is important to realize that all the l=2 levels are 5 fold degenerate. The sole unpaired d electron can be in any of the 5 possible d orbitals with corresponding orbital angular magnetic moments, i.e.:

B field OFF   B field ON
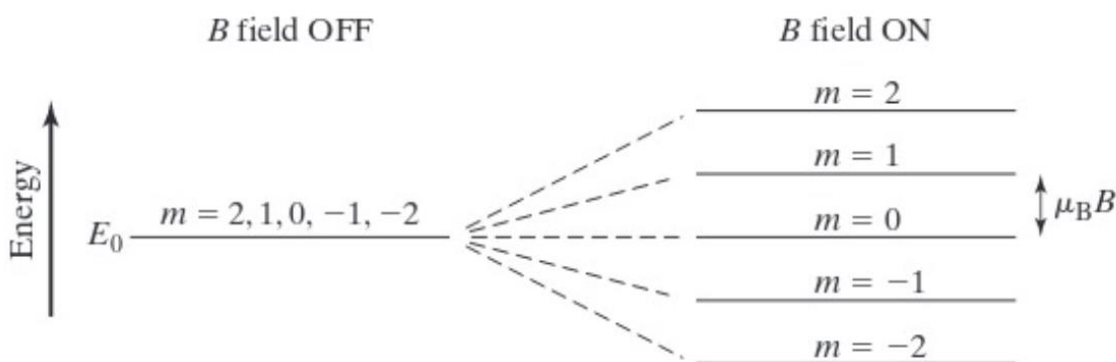
Each of the above will be split into the 2 possible spin states with splitting $2\mu B$. If you plot the splitting of each of the above levels by $\pm\mu_B B$ corresponding to the spin splittings, you will see 7 lines or spots (of maximum amplitude at the centre). Partial credit for recognizing l

c) (3 pts) Given the experimental observation (only 2 spots corresponding to electron spin magnetic moments), it was determined that the energy electron configuration for Ag is $[Kr]4d^{10}5s^1$. Offer an explanation.

This difference reflects the convergence of change in energy for electron binding in going to higher valence shells or principle quantum number for central force driven electron distributions and the effect of screening that has a angular dependence on the radial distribution of electrons. The cost of pairing an electron in the same spatial distributions is offset by the opposing magnetic dipole moments. This is the heart of the Pauli Exclusion principle the additional magnetic field interaction ensures the electrons do not occupy the same space at the same time – self avoidance. The cost of pairing the electrons is offset by this effect such that it costs less to pair two electrons, and leave the unpaired electron in the 5s orbital, which has a large <r>. This point was discussed in class, there is additional stabilization energy for ½ filled valence (l) shells due to Hunds rule, and filled shells due to the competition between cost for pairing electrons vs promoting to a higher valence level. This effect could not have been predicted and we only understand this after developing very accurate methods, albeit not exact, for calculating wavefunctions and energies for multielectron atoms (Ag is nontrivial). Note, here that the closed shell with the smaller <r> leads to contraction of the distribution, which then exposes the 5s shell as being higher in energy.

The main point is to discuss the cost of pairing electrons to create a filled shell is less than the cost to promote to a higher valence shell.