# Problem Set PS04

ISSUED: 9/20/01 **Due: 9/27/01**

Prof. Darin J. Ulness Name _____

**Instructions.** Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

### Mathematical Exercises

1. Plot $f = \sin^2 x$, $f = \cos^2 x$, and $f = \sin x \cos x$.

2. How does the decay of the function $f = e^{-\frac{x}{n}}$ behave as $n$ is increased?

### Exercises

3. Using your handout on hydrogenic wavefunctions and average values, plot $\left\langle \frac{1}{r} \right\rangle$ for each value of $n$ and $l$ up through $n = 7$ (work in units of Bohr radius, i.e., set $a_0 = 1$). $\frac{1}{r}$ is the functional form of the potential felt by the electron in the hydrogen system. What does this say about the behavior of average potential felt by the electron in a hydrogen atom as the principle quantum number increases? How about as the angular momentum quantum number increases? Does this make sense?

4. Using your handout on hydrogenic wavefunctions and average values, plot $\left\langle \frac{1}{r^2} \right\rangle$ for each value of $n$ and $l$ up through $n = 7$ (work in units of Bohr radius, i.e., set $a_0 = 1$). When you learned Newton's laws in physics the primary property determining the dynamics of the system was force. As you are learning, in quantum mechanics the concept of force is not as useful as energy for determining dynamics. Nonetheless $\left\langle \frac{1}{r^2} \right\rangle$ can be considered as a kind of "force." What does this say about the "force" on the electron for the hydrogen atom as the principle quantum number increases? How about as the angular momentum quantum number increases? Does this make sense?

5. Derive the $3d_{xy}$ and $3d_{x^2+y^2}$ wavefunctions from the $3d_2$ and $3d_{-2}$ wavefunctions.

### Conceptual Problems

6. Much of general chemistry and particularly inorganic chemistry can be explain using two simple ideas: i) penetration and ii) shielding. Penetration deals with the fact that outer shell electrons which are normally found far from the nucleus have a non-zero probability of being found near the nucleus and, in fact, inside inner shell electrons. Shielding arrises in atoms that have more than one electron and is a result of the interaction between the electrons. Each electron "shields" each of the other electrons from feeling the full nuclear charge. Electrons that are closer to the nucleus shield electrons that are farther from the nucleus. The figures below shows the so-called radial probability distribution functions for various numbers. This represents the probability of finding an electron at a given distance $r$ from the nucleus irrespective of angle.

(a) Considering the s electrons and their radial distribution functions given below, can the 3s electrons penetrate inside the average radius of the 2s electrons? How about inside the 1s electron radius.

(b) Considering the figure showing the $n = 3$ electrons, which type of electrons do you think are more effective penetrators s, p or d?. Which are more effective shielders?

**Computer Problems**

7. Use MATHEMATICA to make a density plot of the $|\psi_{1s}|^2$ and $|\psi_{2s}|^2$. What do these plots tell us? (Hint: Define $\sigma = \sqrt{x^2 + y^2}$ and plot versus $x$ and $y$. Turn the `Mesh` to false and use a sufficient number for `PlotPoints` and appropriate ranges to make the plots look like the ones you've seen in freshman chemistry.)

8. Use MATHEMATICA to make a density plot of the $\left|\psi_{2p_x}\right|^2$ and $\left|\psi_{2p_y}\right|^2$. What do these plots tell us? (Hint: Define $\sigma = \sqrt{x^2 + y^2}$, $\phi = \arctan \frac{y}{x}$, $\theta = \pi$ (this puts us on the $x$-$y$ plane) and plot versus $x$ and $y$. Turn the `Mesh` to false and use a sufficient number for `PlotPoints` and appropriate ranges to make the plots look like the ones you've seen in freshman chemistry.)

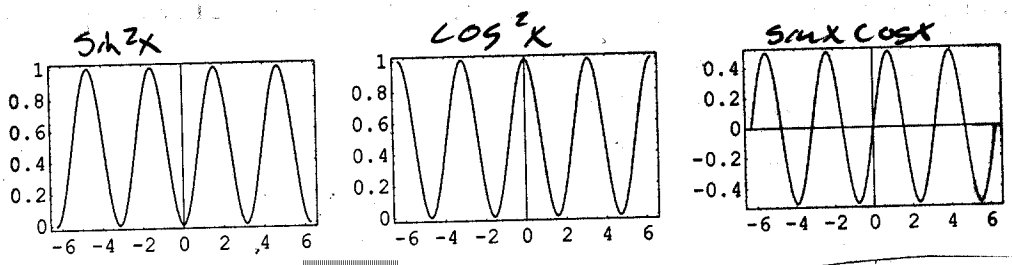
9. Use MATHEMATICA to make a density plot of the $\left|\psi_{2d_{xy}}\right|^2$ and $\left|\psi_{2d_{x^2+y^2}}\right|^2$. What do these plots tell us? (Hint: Define $\sigma = \sqrt{x^2 + y^2}$, $\phi = \arctan \frac{y}{x}$, $\theta = \pi$ (this puts us on the $x$-$y$ plane) and plot versus $x$ and $y$. Turn the `Mesh` to false and use a sufficient number for `PlotPoints` and appropriate ranges to make the plots look like the ones you've seen in freshman chemistry.)

**Reflective Exercises**

10. A popular play called *Copenhagen* deals with a mysterious visit of Heisenberg to his mentor Bohr that occurred during World War II. At the time, Heisenberg was head of the German nuclear project and Bohr was in German occupied Denmark. Heisenberg claimed that the German nuclear project was focussed on creating nuclear power for use by Germany rather then focussed on the atomic bomb. Anyway, the question is raised as to whether or not it is ethical to work on nuclear power of any reason. Suppose that at some point in the future, your job required you to use your training to work on something that may be of tremendous benefit to society (such as nuclear power) but could potentially be very destructive (such as the atomic bomb). Also suppose that it was out of your control as to how your results would be used. How would you react to this situation?

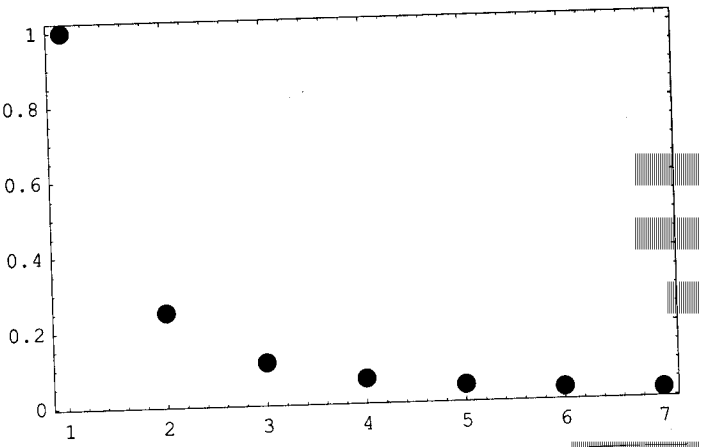
11. What are the five traditional areas of chemistry? What do these areas deal with? Make all possible pairs of areas (e.g., biochemistry + inorganic chemistry = bioinorganic chemistry) and think of one modern problem that each of the 10 hybrid fields might tackle.

(1)



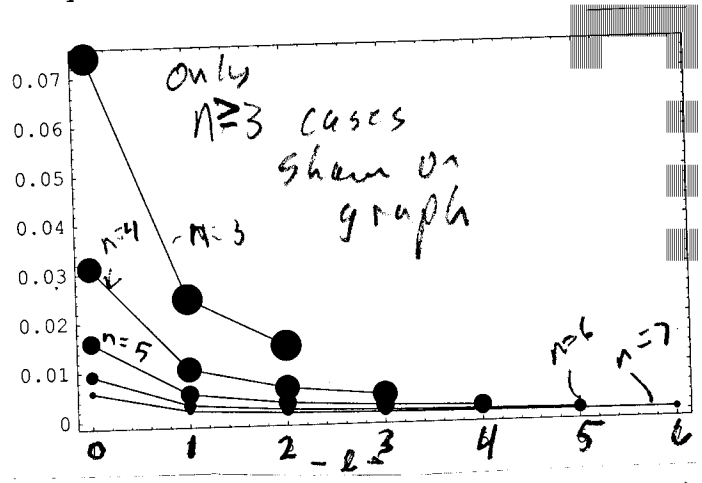

(2) f decays at a slower rate as n increases

(3)



The potential felt by the electron decreases with n as expected since on average it is further away from the nucleus at higher n. This is independent of angular momentum (l)

(4)




Generally the "force" decreases with n as expected since the electron is further from the nucleus. Also the "force" decreases with l. As l increases there is greater "centrifugal force" which counters the columbic force

(5)

$$3d_{xy} = \frac{1}{\sqrt{2}}\left[3d_2 + 3d_{-2}\right] = \frac{1}{\sqrt{2}}R_{32}(\sigma)\sin^2\theta e^{2i\phi} + \frac{1}{\sqrt{2}}R_{32}(\sigma)\sin^2\theta e^{-2i\phi}$$

$$= \frac{2}{\sqrt{2}}R_{32}(\sigma)\sin^2\theta\cos 2\phi \quad \checkmark$$

$$3d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left[3d_2 - 3d_{-2}\right] = \frac{1}{\sqrt{2}}R_{32}(\sigma)\sin^2\theta e^{2i\phi} + \frac{1}{\sqrt{2}}R_{32}(\sigma)\sin^2\theta e^{-2i\phi}$$

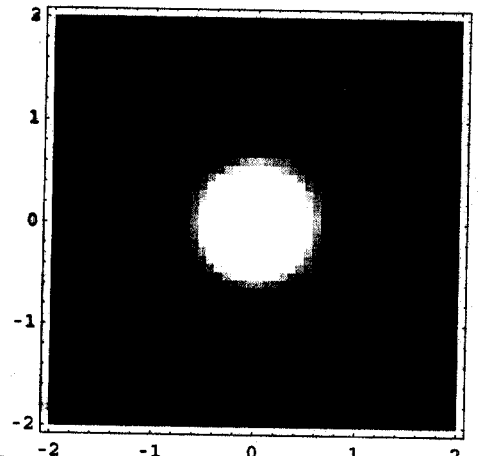
$$= \frac{2}{\sqrt{2}}R_{32}(\sigma)\sin^2\theta\sin 2\phi$$

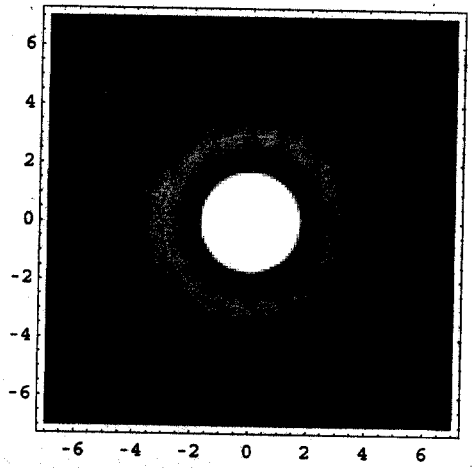
where $R_{32} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\frac{\sigma}{3}}$ and $\sigma = \frac{Z}{a_0}r$

(6) (a) We see that the 3s electron can penetrate inside the average radius for the 2s electron. It can penetrate to about the ave radius of the 1S electron but not significantly inside OR that.

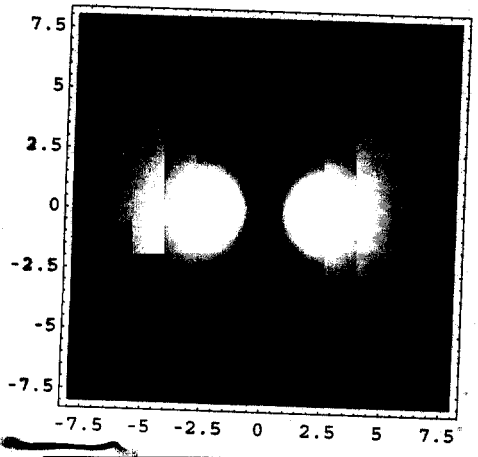
(b) The s is the best penetrater, then the p, the 3d essentially doesn't penetrate much. The penetration of the of the s and p electrons make them also more effective shielders. The 3d electrons will shield 3rd level electrons to some degree.

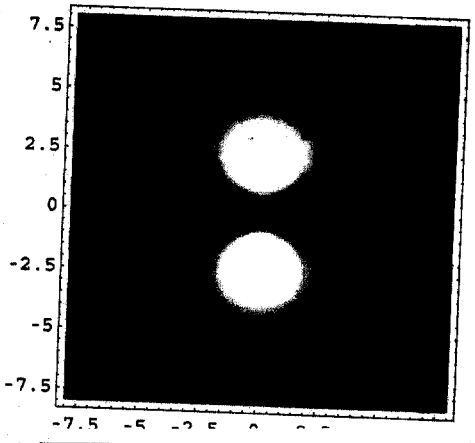
(7)



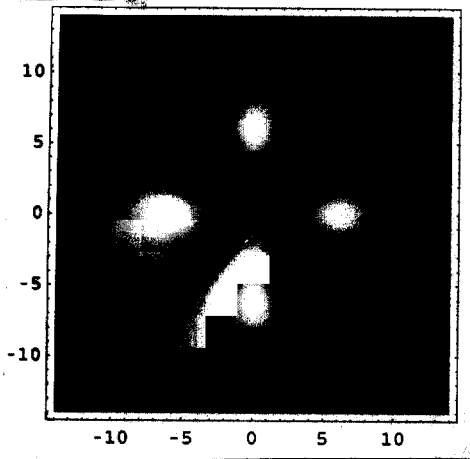



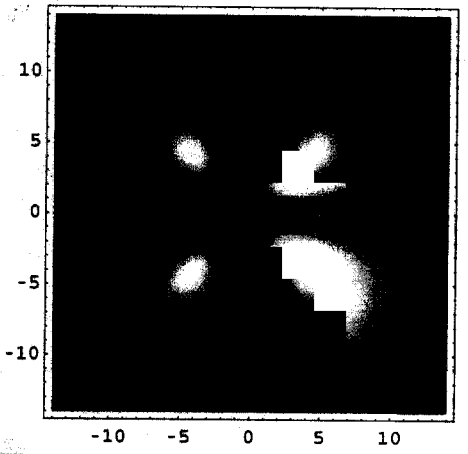

(8)




(9)




(10) + (11) your words