Problem Set PS07

Issued: 10/10/01 **Due: 10/24/01**

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. What is the probability of drawing a jack from a regular deck of cards? How about drawing four jacks?

2. Plot the probabilities for each outcome for rolling one fair six-sided die. Plot the probability for each outcome for rolling two fair six-sided die. Plot the probability for each outcome for rolling three six-sided die. Based on these three distributions of outcomes, what do you think the distribution of outcomes would look like if 1000000 fair die were rolled?

3. First make a guess at the probability of getting 50 heads when flipping 100 coins. Now use Eq. (4.5) to calculate that probability. How much greater is the probability of getting 50 heads than getting 60 heads. If one were to flip 10000 coins, how much greater would the probability of getting 5000 heads than 6000 heads.

4. We can also consider a "loaded" die. This means that there is now not an equal likelihood for each of the six outcomes. To characterize the "loadedness" of the die we need a weight function which mathematically describes how each outcome is favored or disfavored. For example consider the weight function, $w(n) = \frac{1}{n}$. Now the probability of rolling a six with the loaded die is

$$P = \frac{\frac{1}{6}}{\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5} + \frac{1}{6}} = \frac{10}{147} \simeq 0.068. \tag{1}$$

The probability of rolling a one on the other hand is

$$P = \frac{\frac{1}{1}}{\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5} + \frac{1}{6}} = \frac{20}{49} \simeq 0.408. \tag{2}$$

That is, the probability of rolling a one is

$$\frac{0.408}{0.068} = 6 \tag{3}$$

times greater then rolling a six. Notice that this value is also the ratio of the weight functions

$$\frac{w(1)}{w(6)} = \frac{1/1}{1/6} = 6. \tag{4}$$

Calculate the probability of rolling a six and also compare this probability to that of rolling a one for the loaded die have the weight functions listed below. Verify that your answer is the ratio of the weight functions.

(a) $w(n) = 2 + (-1)^n$

(b) $w(n) = e^{-\frac{n}{5}}$

(c) $w(n) = e^{-n}$

5. How many ways can you permute the letters of your first name? Count only distinct permutations. What would have to be true of your first name in order for two or more permutations to be identical?

Exercises

6. When we talk about a chemical bond we say that in order for a bond to form there must be electron density found between the positively charged nuclei. Furthermore we build-up the electronic structure of a molecule by overlapping atomic orbitals. An important quantity that describes the overlap of the atomic orbitals is the overlap integral, S. These integrals are hard to evaluate (mainly because one must transform the wavefunctions to parabolic coordinates which are unfamiliar to us). Nonetheless we can use an approximate expression for the overlap integral

$$S = e^{-R}\left(1 + R + \frac{R^2}{3}\right) \tag{5}$$

where R is the internuclear separation in units of Bohr radii. Plot S as a function of R. What does this plot say physically? Let's see if we can put our general notions regarding the chemical bond in more mathematical form (n.b., we are not doing any rigorous derivation here). Let us try to estimate the bond length of H_2^+ simply by thinking about the contributions to the energy of this molecular ion. We have an energy increasing electrostatic repulsion as we decrease the internuclear separation (R). This is of the form $1/R$. We also have the energy lowering overlap integral contribution. So very roughly we might expect the total energy of H_2^+ to be of the form

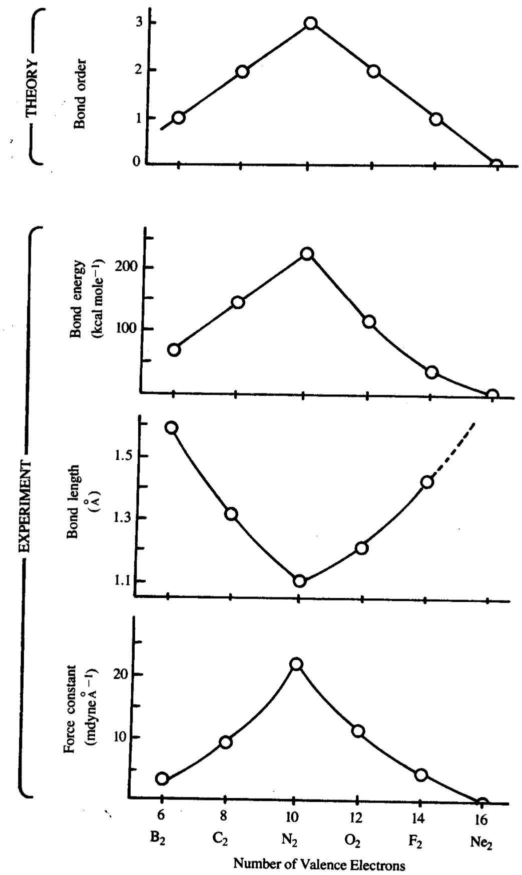
$$E(R) = 1/R - S. \tag{6}$$

Plot this function out to 5 or so Bohr radii. Use what you know from calculus to determine the value of R where $E(R)$ is a minimum (this is the equilibrium bond length). You probably will want to use MATHEMATICA to do this. Also you will need to use the `FindRoot` command rather than the `Solve` command. What is the relative error in the bond length compared with the experimental value of 1.06Å (remember you are working in units of Bohr radii so you will need to convert to angstroms; $a_0 = 0.529$Å).

Conceptual Problems

7. Can you draw the Lewis structure for OF? Construct the MO diagram for OF (Scheme II). Does this help explain your answer to the first part of this question?

8. Use the concepts of MO theory to explain the following figure from R.L. DeKock and H.B. Gray *Chemical Structure and Bonding.*



9. In organic you learned of the reaction

$$Cl_2 \stackrel{h\nu}{\rightarrow} 2Cl.$$

This process is called *photo-dissociation.* Sketch the potential energy curves for the electronic states involved in this photo-dissociation reaction.

10. Superimpose the potential energy curves for the ground state of He_2 and the first excited state of He_2 on a single graph. He_2 is not stable in the ground as we expect since Helium is a noble gas. He_2 is metastable in its first excited state. Properties of this molecule have been measured. How in the world you one make this excited helium molecule? Hint: The process is called *photo-association* in contrast to *photo-dissociation.* Draw the MO diagrams for the ground and excited states.

11. How many distinguishable 5 amino acid linear chain oligomers can one make out of the 20 "normal" amino acids?

12. A very common model to describe collective systems is a lattice model where the vertices of the lattice represent molecules which can be in one of a number of states. The 2D square lattice looks like standard graph paper. Lets say a 2D lattice models the collective spin of the system so that at each vertex the molecule is either spin up or spin down. How many distinguishable configurations of the unit cell are there assuming only nearest neighbor interaction? Hint draw a tick-tac-toe board and consider the four vertices.

Computer Problems

13. Use HYPERCHEM LITE to calculate and plot the molecular orbitals for F_2. Print these orbitals and identify the nodes and describe why the orbital is bonding or antibonding. Does the number of nodes increase with increasing energy? HYPERCHEM LITE is available one the computers in the analytical chemistry lab, but you need to have one of the CD ROMs in order to run the program (get these from me).

Reflective Exercises

14. Please read the attached paper by M. Schermer. Do you agree with nothing he says, some of what he says, or all of what he says? Has your learning about quantum mechanics changed what you had once believed to be the truth? Are the "weird things" in quantum mechanics different from the "weird things" Schermer discusses? Feel free to add any other comments you would like.

15. Please read the following excerpt from an essay entitled "The limitless power of science" by P.W. Atkins which is similar in spirit to the article by Schermer. Atkins is a distinguished professor of physical chemistry at Oxford University and a prolific textbook author. He is the author of the most widely used physical chemistry textbook in the US. He also has written an inorganic text, a general text and several other books. Do you think Atkin's statement "Someone with a fresh mind, one not conditioned by upbringing and environment, would doubtless look at science and the powerful reductionism that inspires it as overwhelmingly the better mode of understanding the world, and would doubtless scorn religion as wishful thinking." is a correct hypothesis. Why or why not?

THE STIFLING GRIP OF RELIGION

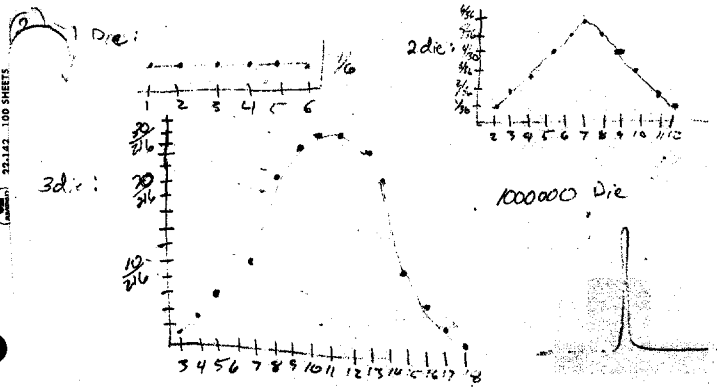
I consider that the survival of religion and the antireductionism that it represents survives merely because it is so deeply ingrained in our cultural attitudes, and its survival is independent of its intrinsic truth. The stifling grip of religion on Man's mind stems partly from its early start, when, as our ancestors dropped from the trees they first sought explanations and solace; it also stems partly from religion's control (for both benevolent and malevolent purposes) of the behaviour of individuals and societies, and it stems partly from its capture of the literature and the arts, which has given it a powerful imagery. Someone with a fresh mind, one not conditioned by upbringing and environment, would doubtless look at science and the powerful reductionism that it inspires as overwhelmingly the better mode of understanding the world, and would doubtless scorn religion as sentimental wishful thinking. Would not that same uncluttered mind also see the attempts to reconcile science and religion by disparaging the reduction of the complex to the simple as attempts guided by muddle-headed sentiment and intellectually dishonest emotion?

P. W. Atkins, "The Limitless Power of Science," in *Nature's Imagination—The Frontiers of Scientific Vision*, edited by John Cornwell (Oxford University Press, New York, 1995).

① $P(\text{Jack}) = \frac{4}{52} = \frac{1}{13}$

$P(4\text{Jacks}) = \frac{4}{52}\left(\frac{3}{51}\right)\left(\frac{2}{50}\right)\left(\frac{1}{49}\right) = 4.9\times10^{-6}$

② 1 Die: 2 die: 3 die: 1000000 Die



③ $P(p=50) = \frac{100!}{50!50!}\frac{1}{2^{100}} = 7.96\%$ $P(p=5000) = \frac{10000!}{5000!5000!}\frac{1}{2^{10000}} = 0.8\%$

$P(p=60) = \frac{100!}{60!40!}\frac{1}{2^{100}} = 1.01\%$ $P(p=6000) = \frac{10000!}{4000!6000!}\frac{1}{2^{10000}} = 2.9\times10^{-88}\%$

$\frac{P(50)}{P(60)} = 7.88$ $\frac{P(5000)}{P(6000)} = 2.74\times10^{87}$

④ ⓐ $P(1) = \frac{2-1}{(2-1)+(2+1)+(2-1)+(2+1)+(2-1)+(2+1)} = \frac{1}{12}$

$1+3+1+3+1+3$

$P(6) = \frac{2+1}{12} = \frac{3}{12} = \frac{1}{4}$

$\frac{P(1)}{P(6)} = \frac{1/12}{1/4} = \frac{1}{3}$ $\frac{\omega(1)}{\omega(6)} = \frac{2-1}{2+1} = \frac{1}{3}$ ✓

④ ⓑ $P(1) = \frac{e^{-\frac{1}{5}}}{e^{-\frac{1}{5}}+e^{-\frac{2}{5}}+e^{-\frac{3}{5}}+e^{-\frac{4}{5}}+e^{-\frac{5}{5}}+e^{-\frac{6}{5}}} = 0.260$

$P(6) = \frac{e^{-\frac{6}{5}}}{\ldots} = 0.095$

$\frac{P(1)}{P(6)} = 2.718$ $\frac{\omega(1)}{\omega(6)} = \frac{e^{-\frac{1}{5}}}{e^{-\frac{6}{5}}} = e = 2.718$

ⓒ $P(1) = \frac{e^1}{e^1+e^2+e^3+e^4+e^5+e^6} = 0.0043$

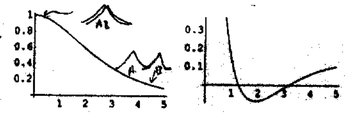
$P(6) = \frac{e^6}{e^1+e^2+e^3+e^4+e^5+e^6} = 0.63$

$\frac{P(1)}{P(6)} = 0.0067$ $\frac{\omega(1)}{\omega(6)} = 0.0067$

⑤ DARIN $\frac{5!}{1!1!1!1!1!} = 120$ If 2 or more letters were the same the some permutations would be identical

⑥

```
In[2]:= S = Exp[-R] (1 + R + (R^2) / 3);
In[11]:= ps = Plot[S, {R, 0, 5}, DisplayFunction -> Identity];
In[14]:= p = Plot[1/R - S, {R, .5, 5}, DisplayFunction -> Identity];
In[15]:= Show[GraphicsArray[{ps, p}]]
```



```
Out[15]= -GraphicsArray-
In[16]:= d = D[1/R - S, R];
In[18]:= FindRoot[d = 0, {R, 1}]
Out[18]= {R -> 1.90907}
```

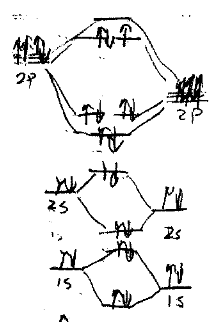
⇒ in angstroms $1.909\times0.529 = 1.01\,Å$

rel error $\frac{1.01-1.06}{1.06} = -4.7\%$

⑦ :Ö:F: you can not draw the lewis structure

$B.O. = \frac{3}{2}$

Lewis structure rules don't handle fractional bond order



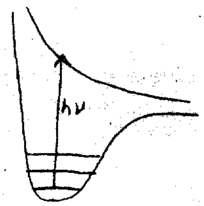
⑧ Bond order: the Bond order follows from the MO Diagrams in the notes

Bond energy: Since N_2 has the largest B.O. we expect the bond to be the most energetic

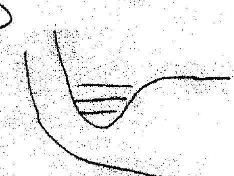
Bond length: Since N_2 has the largest B.O. we expect the nuclei to be closest together

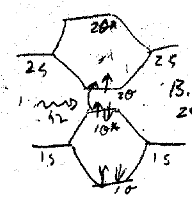
Force Constant: Since N_2 has the largest B.O. we expect the N≡N bond to be the stiffest

⑨

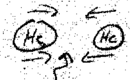


⑩





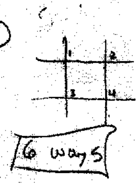
B.O. goes from zero to 1



to create the metastable excited state one must strike two colliding He atoms with light.

⑪ Straight chain: $20^5 = 3.2\times10^6$

⑫



6 ways

Vertex	1	2	3	4	
	u	u	u	u	
	u	u	u	d	= u u d u etc
	u	u	d	d	= d d u u etc
	u	d	u	d	= d u d u
	u	d	d	d	= d u d d etc
	d	d	d	d	