

Problem Set PS07

ISSUED: 10/12/00 Due: 10/26/00

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

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

The probability of rolling a one on the other hand is

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

That is, the probability of rolling a one is

$$\frac{0.408}{0.068} = 6 \quad (3)$$

times greater than rolling a six. 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.

(a) $w(n) = 1/n^2$

- (b) $w(n) = e^{-\frac{n}{6}}$
- (c) $w(n) = e^{-\frac{n}{3}}$
- (d) $w(n) = e^{-\frac{n}{2}}$

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 coordinate which is unfamiliar to us). Nonetheless we can use an approximate expression for the overlap integral

$$S = e^{-R} \left(1 + R + \frac{R^2}{3} \right) \quad (4)$$

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

$$E(R) = 1/R - S. \quad (5)$$

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 1.06\AA (remember you are working in units of Bohr radii so you will need to convert to angstroms; $a_0 = 0.529\text{\AA}$).

7. The energies of the molecular orbitals are obtained from the Schrödinger equation $\hat{H}\Psi = E\Psi$. Alternatively we may use the expression for average value $E = \langle \hat{H} \rangle = \int \Psi^* \hat{H} \Psi$. The wavefunctions are linear combinations of atomic orbitals so for diatomics $\Psi = \frac{1}{\sqrt{2}}(c_A\psi_A + c_B\psi_B)$ where the c 's are constants. Substituting these linear combinations into the expression for energy we find

$$E = \frac{1}{2} \int (c_A\psi_A + c_B\psi_B)^* \hat{H} (c_A\psi_A + c_B\psi_B) \quad (6)$$

$$= \frac{1}{2} \underbrace{\int c_A^2 \psi_A^* \hat{H} \psi_A}_{J_A} + \underbrace{\int c_B^2 \psi_B^* \hat{H} \psi_A}_{K_{BA}} + \underbrace{\int c_A c_B \psi_A^* \hat{H} \psi_B}_{K_{AB}} + \underbrace{\int c_A c_B \psi_B^* \hat{H} \psi_B}_{J_B}.$$

The integrals J_A and J_B are called the coulomb integrals and the integrals K_{AB} and K_{BA} are called the exchange integrals.

- (a) Show that the energy corresponding to Φ_+ of the notes (Eq. (3.23)) is equal to $J+K$ and for Φ_- (Eq.(3.24)) it is $J-K$, where $J = J_A = J_B$ and $K = K_{AB}+K_{BA}$. (Note C_+ and C_- are $1/\sqrt{2}$)
 - (b) Explicitly calculate J , K , E_{Φ_+} and E_{Φ_-} for H_2^+ . Is $E_{\Phi_+} < E_{\Phi_-}$ as we expect?
8. Use MO theory to order the following set according to stretching frequency (lowest to highest)
 - (a) CO, CO^{2+} , CO^- (Scheme II)
 - (b) SiS, SiS^{2+} , SiS^- (Scheme II).
 9. Use MO theory to determine which is most stable: N_2^+ , O_2^- , Li_2^+ .
 10. A mixture of the amino acids leucine, isoleucine, asparagine and aspartate is placed under conditions in which they link to form small oligomers. All the oligomers containing four monomer units were isolated. What is the entropy of an ensemble of four unit oligomers solutions? (It is not the case that all amino acid units must appear in the oligomer. Also remember that one end of the oligomer is called the N terminal and the other the C terminal—these are different.)

Conceptual Problems

11. Can you draw the Lewis structure for NO? Construct the MO diagram for NO (Scheme II). Does this help explain your answer to the first part of this question?
12. In organic you learned of the reaction



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

13. 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?
14. Superimpose the potential energy curves for the ground state of O_2 and the first excited state of O_2 on a single graph.

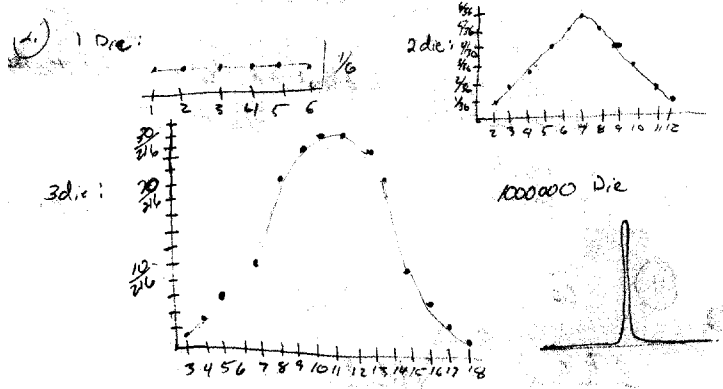
Computer Problems

15. 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 on 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

16. 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.

① $P(1 \text{ Jack}) = \frac{4}{52}$
 $P(4 \text{ Jacks}) = (\frac{4}{52})(\frac{3}{51})(\frac{2}{50})(\frac{1}{49})$



③ your guess

⑤ DARIN $W = \frac{5!}{1!1!1!1!1!} = 120$ 3 of 7
 Two permutations will be the same if two letters are identical.

⑥

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In[1]: B = Exp[-R] (1 + R + (R^2) / 3)
Out[1]: e^{-R} (1 + R + \frac{R^2}{3})
In[2]: Plot[B, {R, 0, 5}]
Out[2]: Graphics-
In[5]: Plot[1/R - B, {R, .5, 5}]
Out[5]: Graphics-
In[12]: d = D[1/R - B, R]
In[13]: FindRoot[d = 0, {R, 2}]
Out[13]: {R -> 1.90907} => in angulus 1.909 * 0.5298 = 1.010 A
    
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rel error = $\frac{1.010 - 1.06}{1.06} = -4.7\%$

④ $P_w(6) = \frac{w(6) P_{w,r}(6)}{\sum w(n) P_{w,r}(n)}$ $P_w(1) = \frac{w(1) P_{w,r}(1)}{\sum w(n) P_{w,r}(n)}$

① $P_w(6) = \frac{1/6^2}{\frac{1}{1} + \frac{1}{4} + \frac{1}{9} + \frac{1}{16} + \frac{1}{25} + \frac{1}{36}} = 0.019$
 $P_w(1) = \frac{1}{1 + \frac{1}{4} + \frac{1}{9} + \frac{1}{16} + \frac{1}{25} + \frac{1}{36}} = 0.67$

② similarly
 $P_w(6) = 0.106$
 $P_w(1) = 0.242$

③ $P_w(6) = 0.062$
 $P_w(1) = 0.328$

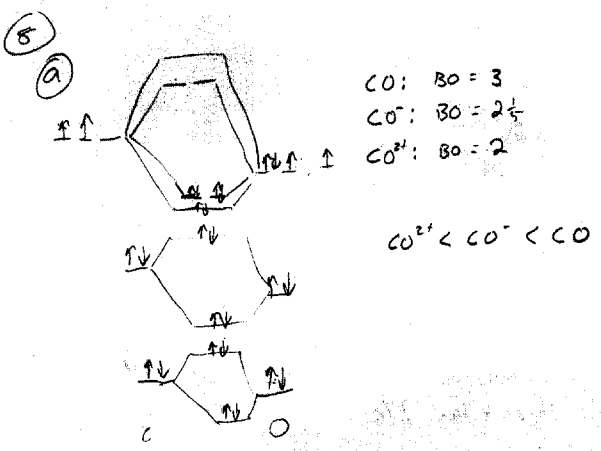
④ $P_w(6) = 0.034$
 $P_w(1) = 0.414$

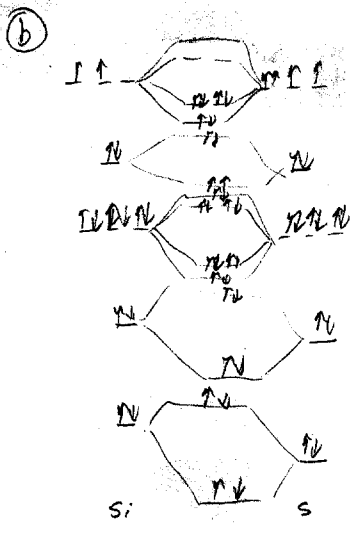
⑦ $\Phi_i = (1s_A + 1s_B)$ $\bar{E}_i = (1s_A - 1s_B)$ 4 of 7

$E_{\Phi_i} = \frac{1}{2} (\int (1s_A \pm 1s_B) H (1s_A \pm 1s_B))$
 $= \frac{1}{2} (\int 1s_A H 1s_A + \int 1s_A H 1s_B + \int 1s_B H 1s_A + \int 1s_B H 1s_B)$
 $E = J \pm K$

⑧

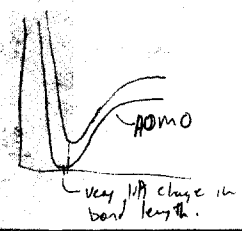
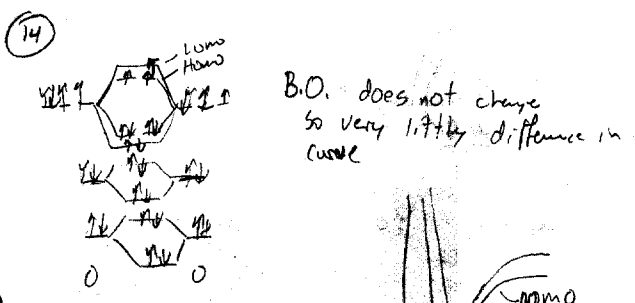
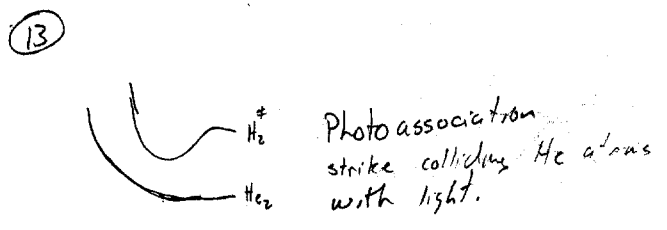
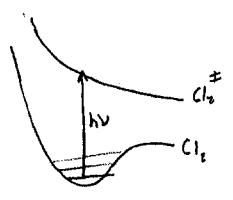
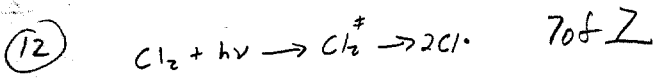
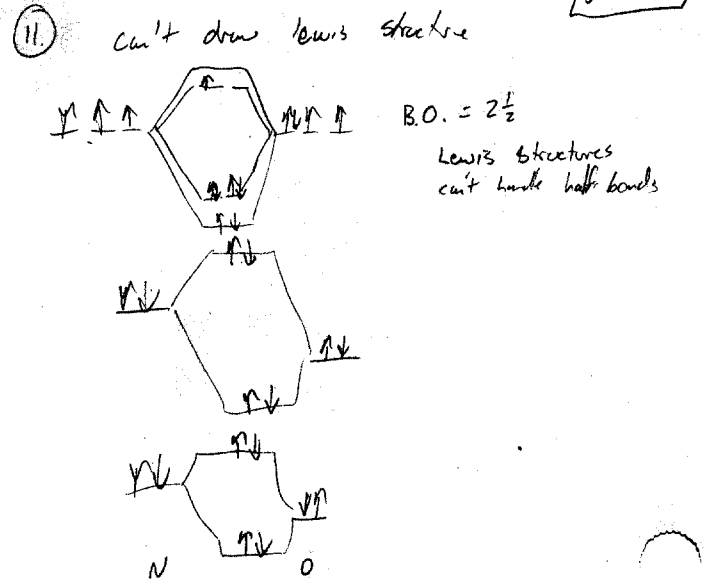
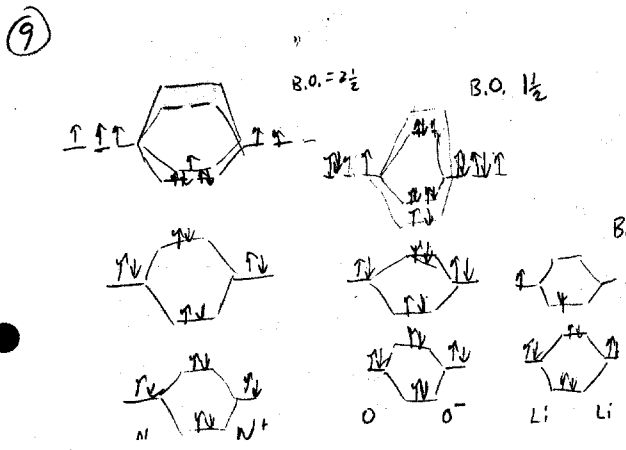
$J = \int 1s_H 1s = \int 1s E_{1s} 1s = E_{1s} \int 1s 1s = -\frac{me a_0}{2a_1^2}$
 $K = \int 1s H k = \dots$
 $E = 0$
 $E = -\frac{me a_0}{2a_1^2}$
 $E = -\frac{me a_0}{n^2 a_1^2}$





$SiSi: B.O. = 3$
 $SiSi^{\ddagger}: B.O. = 2$
 $SiSi^{\ominus}: B.O. = 2\frac{1}{2}$
 $SiSi^{\oplus} < SiSi^{\ominus} < SiSi$

(10) There is 1 way to use four different A.A.
 There are 24 permutations $\Rightarrow 24$
 12 ways to use 3 different A.A.
 12 permutations $\Rightarrow 144$
 6 ways to use 2 different A.A. each twice
 6 permutations $\Rightarrow 36$
 12 ways to use 2 different A.A. 3 of 1 and 1 of the other
 4 permutations $\Rightarrow 48$
 4 way to use 1 type of AA
 1 permutation $\Rightarrow 4$
 $\frac{256}{256} = 1$ $S = 1.25 \times 10^6$
 $S = 5.55 \times 10^6$



(15) Hyperchan etc.