Exam II – 4/5/06

You are to answer a total of 10 questions on this exam for a total of 100 points. (Some choice of questions is provided at the end.) Answer all questions in the blue examination book provided. No written materials or notes in other forms are to be used for this exam.

1. (8 points) Is \( \exp(-ax^2) \) an eigenfunction of the operators \( \hat{O} \) listed below? If not explain why not; if so, what is its eigenvalue?
   
   (a) \( \hat{O} = x \)  
   (b) \( \hat{O} = \frac{d}{dx} \)  
   (c) \( \hat{O} = x^{-1} \frac{d}{dx} \)

2. (10 points) The normalized wavefunction of the 1s state of H is given by:
   
   \[
   \psi_{1s} = N_{1s} \exp(-r/a_0)
   \]
   
   where
   
   \[
   N_{1s} = (\pi a_0^3)^{-1/2}
   \]
   
   Write the complete expression required to evaluate the average distance of an electron from the nucleus in this state. Be as explicit as possible but don’t bother to actually evaluate the integral over \( r \) involved.

3. (8 points) The sketch at the right is qualitatively incorrect as a representation of the radial distribution function of the 2s orbital of H.
   
   (a) What is wrong with this sketch?
   (b) Provide a corrected version of this sketch.

4. (10 points) Estimate ionization energies of electrons in the orbitals listed below. State your energy units. (If you don’t know how to estimate energies, at least rank them.)
   
   (a) 1s in H  
   (b) 1s in Li\(^{2+} \)  
   (c) 1s in Li\(^+ \)  
   (d) 1s in Li  
   (e) 2s in Li

5. (12 points) The variational principle is of central importance in electronic structure theory.
   
   (a) State the variational principle in an equation, and describe its meaning.
   (b) Explain how the variational principle is used in electronic structure calculations.

6. (12 points) Using the variables defined at the right, express the electronic Hamiltonian of the diatomic ion LiH\(^{2+} \) in atomic units and define the meanings of the various terms involved.

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7. (10 points) According to the Hückel molecular orbital (HMO) theory, the energies of the \( \pi \)-type molecular orbitals of ethylene are \( \alpha \pm \beta \). As we saw in Assignment 8 these \( \pi \) MOs are the HOMO and LUMOs in ethylene.

(a) According to the HMO theory, what is the 1st ionization potential of ethylene?

(b) According to the HMO theory, how much energy do \( \pi \) electrons contribute to the C-C bond in ethylene?

8. (8 points) Give the secular determinant (in terms of \( \alpha \) and \( \beta \)) that would appear in a Hückel molecular orbital description of the molecule cyclobutadiene shown at the right. (You need not solvent the determinant.)

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Chose any two of the questions below. Your answer will be judged both on its correctness and completeness. (If you work on more than two of these questions, be sure to indicate which two you want to be graded.)

9. (10 points) Discuss what is meant by electron correlation and why it is important in chemical problems.

10. (10 points) Discuss the basis functions used in \textit{ab initio} electronic structure calculations.

11. (10 points) Describe some of the similarities and differences between \textit{ab initio} and semi-empirical electronic structure methods. Consider both the nature of the calculations involved as well as the types of systems for which they are best suited.

12. (10 points) Discuss the meaning and aptness of Michael Dewar’s analogy between calculating chemical energies using \textit{ab initio} methods and “weighing the captain of a ship by first weighing the ship with the captain on board, then weighing the ship without her, and then taking the difference.”