A

# Chemistry 3502/4502

# Exam IV

## April 19, 2006

**1) Fill in the blank on each question with the correct answer, by letter, from the list provided on the last page of the exam (you may tear the list off if you like).**

**2) There is *one* correct answer to every fill-in-the-blank problem. There is no partial credit. No answer will be used more than once. There *are* answers that are *not* used, however.**

**3) On the short-answer problem, show your work in full.**

**4) You should try to go through all the problems once quickly, saving harder ones for later.**

**5) There are 25 fill-in-the-blank problems. Each is worth 3 points. The short-answer problem is worth 25 points.**

**6) There is no penalty for guessing.**

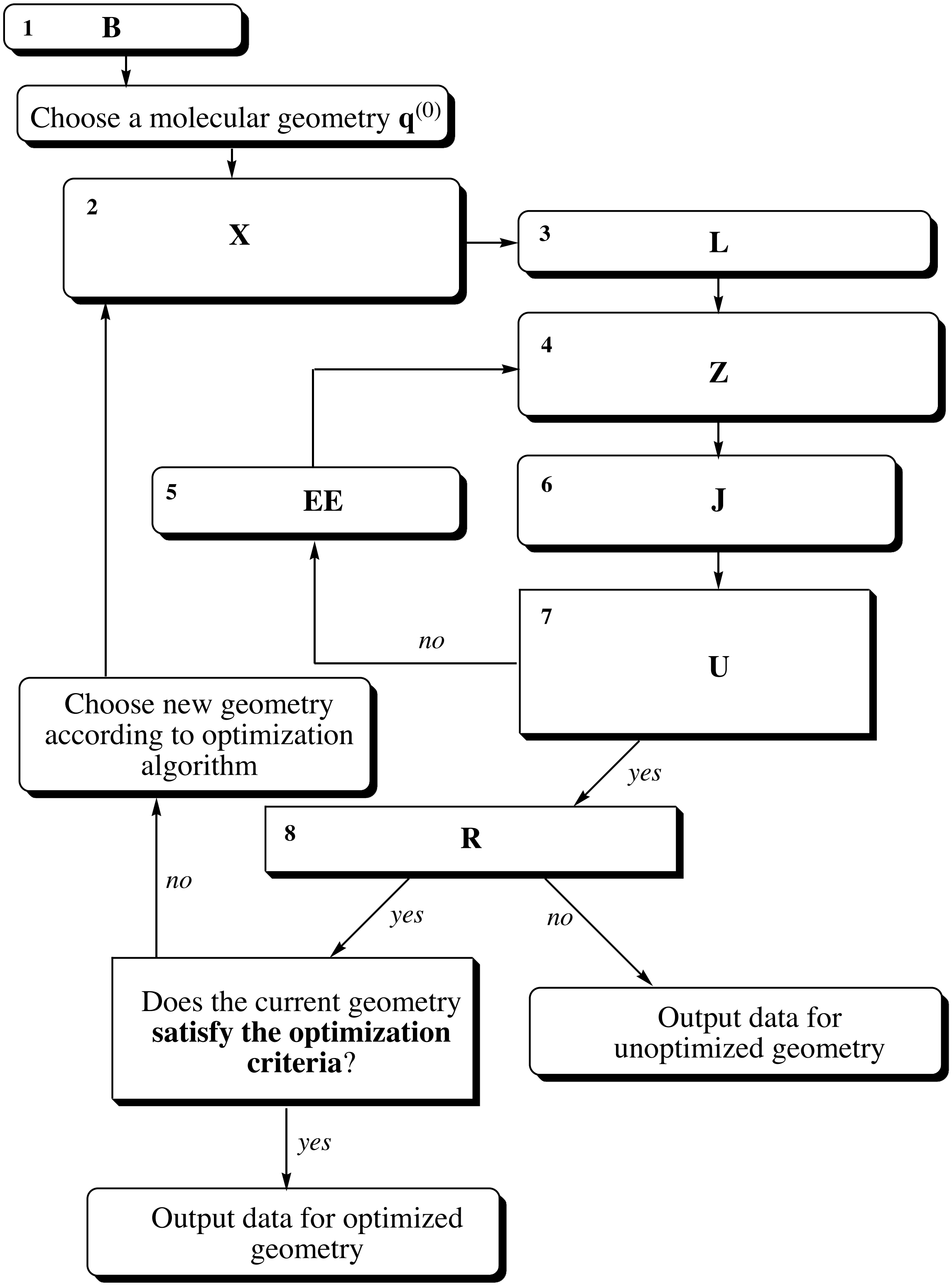
**7) Please write your name at the bottom of each page.**

**8) Please mark your exam with a pen, not a pencil. If you want to change an answer, cross your old answer out and circle the correct answer. Exams marked with pencil or correction fluid will not be eligible for regrade under any circumstances.**

**Score on Next Page after Grading**

NAME: ______________________________________________

Fill in the numbered boxes on the HF calculation flowchart (from lecture 28) with the appropriate steps from the answer list (use the letters—don't write the phrases).



NAME: ______________________________________________

9. An integral equal to –1: ___**N**___

10. An operator $H = h_1 + h_2 + h_3$ where $h_1\psi_1 = 4\psi_1$, $h_2\psi_2 = 2\psi_2$, and $h_3\psi_3 = 1\psi_3$.
    If $\psi_1$, $\psi_2$, and $\psi_3$ are normalized,
    what is $< \psi_1\psi_2\psi_3 \mid H \mid \psi_1\psi_2\psi_3 >$? ___**W**___

11. A generic density matrix element $P_{\mu\nu}$: ___**H**___

12. The exchange integral $K_{ab}$ involving orbitals $a$ and $b$: ___**Y**___

13. A Hartree-product many-electron wave function: ___**DD**___

14. A generic Fock matrix element $F_{\mu\nu}$ (atomic units): ___**A**___

15. The Coulomb integral $J_{ab}$ between an electron in
    orbital $a$ and another electron in orbital $b$: ___**T**___

16. A generic overlap matrix element $S_{\mu\nu}$: ___**HH**___

17. An integral equal to zero: ___**O**___

18. A generic 4-index integral $( \mu\nu \mid \lambda\sigma )$: ___**K**___

19. An antisymmetric, many-electron wave function
    with normalization implicit: ___**BB**___

20. Equating the ionization potential of a molecule with the negative of the
    energy of the highest occupied molecular orbital (HOMO) is known as: ___**E**___

NAME: ______________________________________________

The following 5 questions refer to a HF/STO-6G calculation on neutral hydroxylamine, $H_2NOH$. The atomic numbers of H, N, and O are 1, 7, and 8 respectively.

21. By what factor will the number of one-electron integrals over primitive basis functions exceed the number of one-electron integrals over contracted functions? ___**S**____

22. As a linear combination of how many contracted basis functions will each molecular orbital be expressed? ___**AA**____

23. What is a reasonable value for the final HF energy in a.u.? ___**V**____

24. Ignoring symmetry and the turnover rule, how many two-electron integrals over contracted basis functions would need to be evaluated in the calculation? ___**I**____

25. How many occupied orbitals will be used to construct the Slater determinantal many-electron wave function that would result from a restricted Hartree-Fock calculation? ___**GG**____

NAME: ______________________________________________________

## Hückel Theory

Consider the simplest possible Hückel system, ethylene, $H_2C{=}CH_2$, which has 2 $\pi$ electrons.

How many basis functions are needed to carry out a Hückel theory calculation of the molecular orbitals of ethylene? What are the basis functions, specifically?

***There are 2 basis functions. They are $2p_z$ orbitals, one on each carbon, where the z axis is the axis orthogonal to the plane of the atoms (i.e., the p orbitals forming the $\pi$ system).***

In terms of 0, 1, $\alpha$, and $\beta$, what are the specific values of all matrix elements that will appear in the secular determinant for ethylene? To what experimental quantities do $\alpha$ and $\beta$ refer, specifically?

$S_{11} = S_{22} = 1, S_{12} = 0, H_{11} = H_{22} = \alpha, H_{12} = \beta$

***$\alpha$ is the negative of the ionization potential of the methyl radical (the energy of an electron in a free $2p_z$ orbital) and $\beta$ is one half the rotational barrier in ethylene.***

Write the Hückel theory secular equation for ethylene. What values of $E$ permit solution of the secular equation? You may find the equation $a^2 - b^2 = (a + b)(a - b)$ to be helpful.

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

***The solution to this secular equation is***

$$\begin{aligned} 0 &= (\alpha - E)^2 - \beta^2 \\ &= (\alpha - E + \beta)(\alpha - E - \beta) \end{aligned}$$

***which is satisfied by $E = \alpha + \beta$ and $E = \alpha - \beta$. The first root is lower in energy since $\alpha$ and $\beta$ are negative quantities.***

NAME: ____________________________________________

What does Hückel theory predict for the singlet-triplet splitting in ethylene? Explain your answer.

***The energy of the singlet is computed from placing the two ethylene $\pi$ electrons in the lowest energy orbital. Given the energy determined above, that makes the total energy $2\alpha + 2\beta$. Making the triplet will require removing one electron from the lowest energy orbital and moving it to the higher energy orbital (since we can't have two electrons of the same spin in the same orbital). So, now we have the energy of each orbital taken once and added together, which gives $\alpha + \beta + \alpha - \beta = 2\alpha$. The difference is $2\beta$ and that is the singlet-triplet splitting.***

***For those interested in the chemistry, notice that this is, by definition of $2\beta$, equal to the rotational barrier in ethylene. This is exactly what one expects, since the triplet has one electron in the bonding orbital and one in the antibonding, there is no net $\pi$ bond, which is the same thing that happens at the rotational transition state: the $\pi$ bond is destroyed.***

**A:** $\left\langle \mu \left| -\frac{1}{2}\nabla^2 \right| \nu \right\rangle - \sum_{k}^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma}\left[ (\mu\nu \mid \lambda\sigma) - \frac{1}{2}(\mu\lambda \mid \nu\sigma) \right]$

**B:** Choose a basis set

**C:** 21

**D:** $\left\langle 1s_{H_a} \middle| 1s_{H_b} \right\rangle$ where $H_a$ and $H_b$ are the two H atoms in water

**E:** Koopmans' theorem

**F:** 16

**G:** $-\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}}$

**H:** $2 \sum_{i}^{\text{occupied MOs}} a_{\mu i} a_{\nu i}$

**I:** $13^4$

**J:** Construct density matrix from occupied MOs

**K:** $\iint \phi_\mu(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2)d\mathbf{r}(1)d\mathbf{r}(2)$

**L:** Guess initial density matrix $\mathbf{P}^{(0)}$

**M:** 41.818 911 429

**N:** $\left\langle -2p_{x,\mathrm{N}} \middle| 2p_{x,\mathrm{N}} \right\rangle$

**O:** $\left\langle 2p_{x,\mathrm{N}} \middle| 2p_{z,\mathrm{O}} \right\rangle$ where N and O are both on the $x$ axis

**P:** The Born-Oppenheimer approximation

**Q:** $16^4$

**R:** Optimize molecular geometry?

**S:** 36

**T:** $\iint a(1)b(2)\frac{1}{r_{12}}a(1)b(2)d\mathbf{r}(1)d\mathbf{r}(2)$

**U:** Is new density matrix $\mathbf{P}^{(n)}$ sufficiently similar to old density matrix $\mathbf{P}^{(n-1)}$ ?

**V:** –130.505 204 660

**W:** 7

**X:** Compute and store all overlap, one-electron, and two-electron integrals

**Y:** $\iint a(1)b(1)\frac{1}{r_{12}}a(2)b(2)d\mathbf{r}(1)d\mathbf{r}(2)$

**Z:** Construct and solve Hartree-Fock secular equation

**AA:** 13

**BB:** $\Psi = \left|\chi_1\chi_2\chi_3\cdots\chi_N\right\rangle$ where the various $\chi_i$ are one-electron spin orbitals

**CC:** $\pi$

**DD:** $\Psi = \psi_1\psi_2\cdots\psi_N$ where the various $\psi_i$ are one-electron orbitals

**EE:** Replace $\mathbf{P}^{(n-1)}$ with $\mathbf{P}^{(n)}$

**FF:** $21^4$

**GG:** 8

**HH:** $\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})d\mathbf{r}$

NAME: ____________________________________________________________