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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.

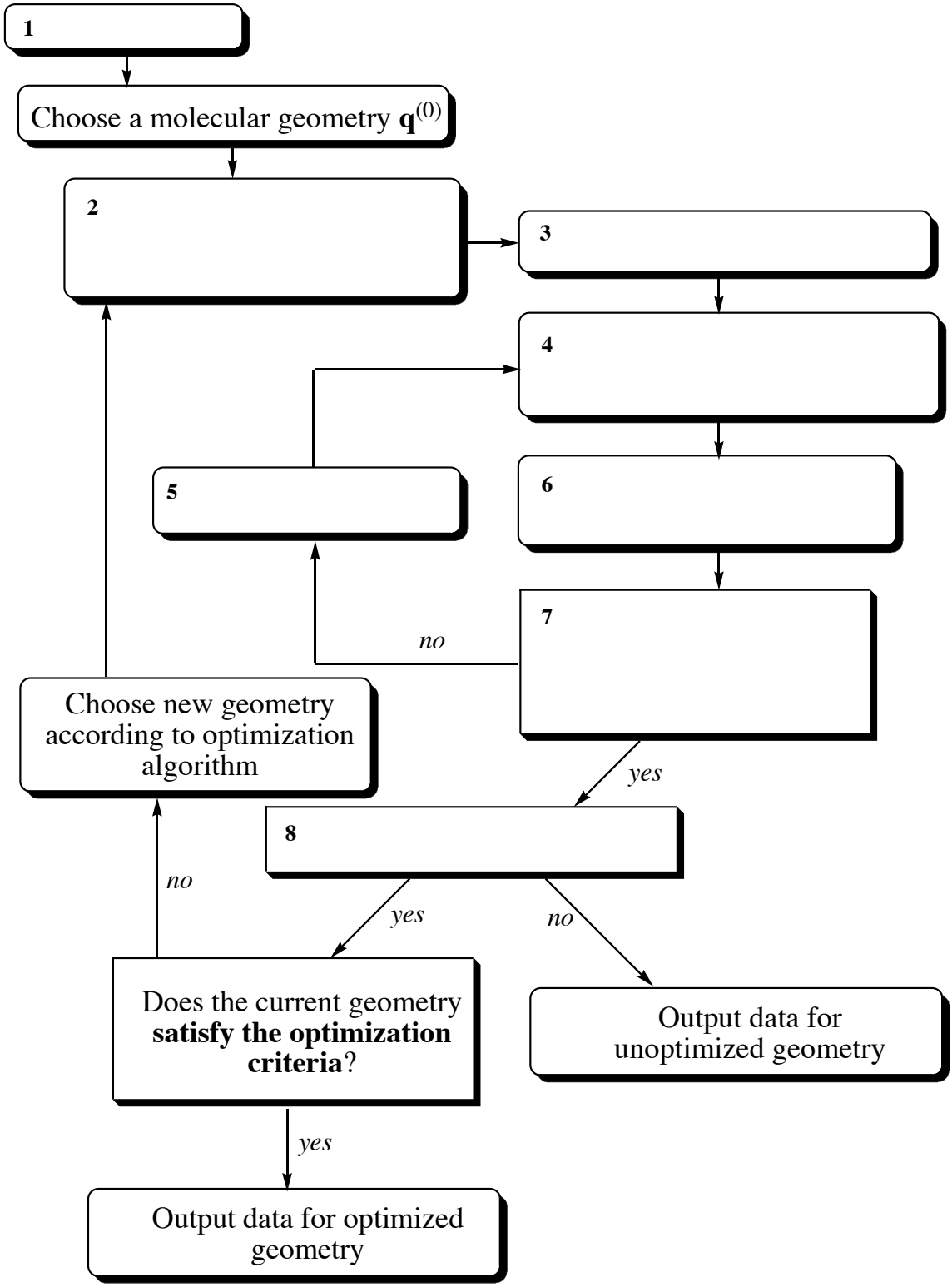
7) Please write your name at the bottom of each page.

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: _____

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 ψ_1, ψ_2, and ψ_3 are normalized,
what is $< \psi_1\psi_2\psi_3 \mid H \mid \psi_1\psi_2\psi_3 >$? _____

11. A generic density matrix element $P_{\mu\nu}$: _____

12. The exchange integral K_{ab} involving orbitals a and b: _____

13. A Hartree-product many-electron wave function: _____

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

15. The Coulomb integral J_{ab} between an electron in
orbital a and another electron in orbital b: _____

16. A generic overlap matrix element $S_{\mu\nu}$: _____

17. An integral equal to zero: _____

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

19. An antisymmetric, many-electron wave function
with normalization implicit: _____

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

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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? _____

22. As a linear combination of how many contracted basis functions will each molecular orbital be expressed? _____

23. What is a reasonable value for the final HF energy in a.u.? _____

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

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? _____

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Hückel Theory

Consider the simplest possible Hückel system, ethylene, $H_2C{=}CH_2$, which has 2 π 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?

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

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.

NAME: _____

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

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

O: $\left\langle 2p_{x,N} \middle| 2p_{z,O} \right\rangle$ 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 χ_i are one-electron spin orbitals

CC: π

DD: $\Psi = \psi_1\psi_2\cdots\psi_N$ where the various ψ_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: _____