

CHEMISTRY 4021/8021
MIDTERM EXAM 1 – SPRING 2014

Q1) Propose a simple, *united-atom* molecular mechanics force-field needed to generate a potential energy surface for an *isolated* molecule of acetone (Me_2CO). I.e., provide an energy expression clearly explaining the nature of all constants that may appear. (15 points)

use the backs of pages as needed

CHEMISTRY 4021/8021
MIDTERM EXAM 1 — SPRING 2014

2

Q2) Explain all of the computations and actions that are associated with taking a “step” in a Monte Carlo simulation of a box of Ar atoms in the NVT ensemble. (15 points)

use the backs of pages as needed

Q3) Some AM1 parameters are listed below for sulfur. For each parameter, decide whether the equivalent parameter for oxygen would be expected to be larger or smaller in magnitude (or perhaps difficult to say) and briefly explain your reasoning. All units are eV except for ζ , which has units of bohr⁻¹. Finally, why is G_{pp} larger than G_{p2} ? (15 points)

U_s , -56.7

U_p , -48.7

ζ_s , 2.36

ζ_p , 1.67

β_s , -3.92

β_p , -7.91

G_{ss} , 11.8

G_{pp} , 10.0

G_{p2} , 7.8

G_{sp} , 8.7

H_{sp} , 2.5

Q4) Doing a calculation on ozone (O_3), you switch from a minimal basis set (e.g., STO-3G) to a split-valence, polarized basis set (e.g., cc-pVDZ). How many contracted basis functions are involved in total for each level of theory? Formally, how much longer will the second calculation take than the first at the MP2 level of theory (you can provide a mathematical expression that is not reduced to a final integer)? (15 points)

Q5) Would you expect the gas-phase proton affinity (which is the opposite of acidity) of phenol to be overestimated, or underestimated, at the CCSD(T)/6-311G(d) level of theory? Explain your answer. (10 points)

Q6) Under what circumstances might the overlap integral between two gaussian basis functions, one on atom 1 and one on atom 2, be equal to zero when the two atoms are *not* separated by a large distance (a picture as part of your explanation will likely be helpful)? (10 points)

Select by letter from the list on the next page the proper answer to the following questions (you may tear the list from the exam for convenience). There is only one best answer to each question. (2 points each)

- (1) The post-HF model with the most favorable scaling, namely, N^5 , where N is the number of basis functions.
- (2) The single-reference post-HF “gold standard” that scales as N^7 , where N is the number of basis functions.
- (3) A model is said to have this property if the energy computed for five infinitely separated molecules is equal to five times the energy computed for a single molecule.
- (4) To compute the statistical mechanical partition function, these are required.
- (5) Something to which correlated methods are more sensitive than the HF model.
- (6) Computation of the mixed second derivative of the energy with respect to an external magnetic field \mathbf{B} and a nuclear spin \mathbf{I} predicts this.
- (7) A useful chemical idea that does *not* have a uniquely defined quantum mechanical operator, so that many different models exist for its prediction.
- (8) A model that permits no spin polarization of doubly-occupied orbitals but guarantees wave functions that are eigenfunctions of S^2 .
- (9) The proper value of S^2 for a singlet state.
- (10) The number of imaginary frequencies associated with a transition-state structure.

CHEMISTRY 4021/8021
MIDTERM EXAM 1 — SPRING 2014

7

A: 1	B: UHF	C: ROHF
D: Partial atomic charge	E: An optimized geometry with associated vibrational frequencies	F: 0
G: MP2	H: Nuclear chemical shift	I: Hyperfine coupling constant
J: Basis-set incompleteness	K: 2	L: CISD
M: Size extensivity	N: MNDO	O: CCSD(T)
P: $\pi/2$	Q: Electric dipole moment	R: Spin contamination
S: Acid reflux	T: Slater-type orbitals	U: MP4SDQ

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