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)

United-atom allows us to take the methyl groups as single units, which I'll call "Me". The simplest force field would be a harmonic one, and we'll need force constants for Me-C and C=O bond stretches, Me-C-Me and Me-C=O angle bending, and we'll need some term associated with non-planarity of the four sites (two Me sites, C, and O). One approach would be a harmonic expression involving the out-of-plane (oop) angle of the O from the plane defined by the two Me sites and the C (another possibility would be an improper torsion term using the dihedral angle Me-C=O-Me, but I like the oop angle better). As it's an isolated molecule, we don't need to worry about non-bonded terms (e.g., Lennard-Jones terms or partial atomic charges). The total energy expression is thus:

$$E = \sum_{i}^{\text{Me-C,C=O}} \frac{1}{2} k_i \left(r_i - r_{i,\text{eq}} \right)^2 + \sum_{j}^{\text{Me-C-Me,Me-C=O,oop}} \frac{1}{2} k_j \left(\theta_j - \theta_{j,\text{eq}} \right)^2$$

where the force constants have already been named above and the associated equilibrium values are parameters that would also need to be selected.

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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)

1) Choose an argon atom at random
2) Move that atom a random distance in some randomly chosen direction
3) Compute the energy of the new configuration (to save computer time, you can compute the new energy as the old energy plus the *difference* in all interactions involving the moved atom, which will require computing only a very small *subset* of *all* interatomic interactions)
4) If the new energy is *below* the last energy, "accept" the move and go to step 9 below
5) Else, choose a random number p on the interval [0,1]
6) Compute $z = \exp[-(E_{new} - E_{old})/k_B T\,]$
7) If $z > p$, accept the move and go to step 9 below
8) Else, record the *last* set of atomic positions (i.e., that from before the random move) *again*, as well as any other properties that are being accumulated, and return to step 1
9) Record the *current* set of atomic positions, as well as any other properties that are being accumulated, and return to step 1

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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

The U parameters are approximate ionization potentials for valence s and p electrons, which would be expected to be *larger* in magnitude for oxygen than sulfur, since the orbitals are 2s and 2p vs. 3s and 3p. The ζ parameters dictate how quickly the s and p atomic orbitals decay radially, and since 2s and 2p orbitals decay more quickly than 3s and 3p orbitals, we would again expect oxygen parameters to be *larger* than sulfur. The β parameters are one electron "resonance" terms associated with integrals involving basis functions on two different atoms, but since total energies are determined by multiplying these terms by overlap integrals, which will be different for S vs. O, their variation is not simple to predict. The G and H terms are electron-electron repulsion integrals for the various valence atomic orbitals. As the 2s and 2p valence orbitals of oxygen are smaller in spatial extent than the 3s and 3p valence orbitals of sulfur, one would expect *larger* magnitudes for oxygen.

G_{pp} refers to the repulsion between 2 electrons in the *same* valence p orbital while G_{p2} refers to the repulsion between 2 electrons in 2 *different* p orbitals. The spatial separation between the electrons will be greater on average for the latter case and hence it has a smaller positive value.

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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)

The minimal basis will comprise a single 1s, 2s, and three 2p functions (x, y, and z) on each oxygen. That's five basis functions total, times three oxygen atoms, is fifteen basis functions. The split valence basis set will add an extra 2s and three extra 2p functions, and one set of five 3d functions. That's a total of fourteen basis functions per oxygen atom, so forty-two basis functions in total.

As MP2 theory scales as the 5th power of the number of basis functions, the time for the second calculation compared to the first will be formally $(42/15)^5$.

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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)

> Overestimated. As the basis set lacks diffuse functions, the energy of the phenolate anion will be computed to be too high, thus making it "want" its proton back more than would be the case with a more complete basis set. The chosen level of theory, CCSD(T), is quite good, so we would expect the error to come almost entirely from choice of basis set.

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)

> Symmetry considerations may render the overlap integral zero. Thus, for instance, in carbon monoxide, if the z axis is taken to be the axis of the molecule, the overlap integral of a 2s function on carbon with a $2p_x$ function on oxygen would be expected to be zero because the positive and negative regions of overlap will exactly cancel one another.

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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.

G

(2) The single-reference post-HF "gold standard" that scales as N^7, where N is the number of basis functions.

O

(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.

M

(4) To compute the statistical mechanical partition function, these are required.

E

(5) Something to which correlated methods are more sensitive than the HF model.

J

(6) Computation of the mixed second derivative of the energy with respect to an external magnetic field **B** and a nuclear spin **I** predicts this.

H

(7) A useful chemical idea that does *not* have a uniquely defined quantum mechanical operator, so that many different models exist for its prediction.

D

(8) A model that permits no spin polarization of doubly-occupied orbitals but guarantees wave functions that are eigenfunctions of S^2.

C

(9) The proper value of S^2 for a singlet state.

F

(10) The number of imaginary frequencies associated with a transition-state structure.

A

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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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