

CHEMISTRY 4021/8021
MIDTERM EXAM 1 – SPRING 2013 – KEY

Q1) In molecular mechanics, what are the advantages and disadvantages of having multiple atom types for a single element? Use at least one example in the context of your answer. (15 points)

The clear advantage is being able to use simple (e.g., harmonic) potentials for bond stretches having different minima rather than having to develop possibly very complex potentials that would place multiple minima along a given stretching coordinate based on other factors (e.g., coordination number). Thus, for example, the 1.54 Å equilibrium distance for two sp³ bonded C atoms is different than the 1.34 Å equilibrium distance for two sp² bonded C atoms. Using different atom types permits much greater accuracy in the force field by permitting separate parameters to be optimized to different bonding situations.

That is also to some extent the chief disadvantage: with each new atom type a rather large number of new parameters (for bonds, angles, torsions, and non-bonded interactions) involving that atom type need to be optimized, and that requires an ever larger body of validation data.

Q2) What is a "polarizable" force field? What are the advantages and disadvantages of using a polarizable force field. (15 points)

A polarizable force field includes dipole polarizabilities on atoms or groups. The fixed charges of the atoms induce dipoles on polarizable sites, and those induced dipoles interact with the charges, one another, and the polarizabilities, to give a net electrostatic interaction. Iteration is required to converge the induced dipoles to final values.

The advantage of a polarizable force field is that it is more physical in nature (atoms and groups are indeed polarizable). The disadvantage is the significant increase in computational cost associated with the self-consistent solution of the electrostatic polarization.

Q3) You have an output file containing one million snapshots from a 298 K Monte Carlo simulation of a box of liquid water containing 512 flexible molecules under periodic boundary conditions and constant pressure. Explain how you would compute the expectation value of the H–O–H bond angle (you may use words or equations). If the bending potential is harmonic, what shape would you expect for the continuous angle distribution function? (10 points)

The expectation value is simply the average of the values for all 512,000,000 water molecules (512 per snapshot, 1,000,000 snapshots).

Since Monte Carlo sampling accepts structures with probability proportional to $\exp(-\Delta E)$, and since ΔE varies with the square of the displacement for a harmonic potential, we'd expect the shape $\exp[-(\theta-\theta_{eq})^2]$ which is a gaussian function.

Q4) What is a four-index integral, often abbreviated $(\mu\nu | \lambda\sigma)$? Why do semiempirical theories approximate these integrals, and what approximations do they employ? (15 points)

The shorthand implies $\iint \varphi_{\mu}(1)\varphi_{\nu}(1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\varphi_{\lambda}(2)\varphi_{\sigma}(2)d\mathbf{r}_1d\mathbf{r}_2$

where the lower case Greek letters index atomic-orbital basis functions, and the double integral ranges over the volume coordinates \mathbf{r} of electrons 1 and 2 (so this can also be called a 2-electron integral). As each index can be any of the N basis functions in a given basis set, the number of 4-index integrals scales as N^4 , making their computation the bottleneck in Hartree-Fock calculations.

Semiempirical theories set many to zero to avoid the cost of computing them, and simplifies the computation of those that remain. In particular, CNDO eliminates all integrals other than $(\mu\mu | \lambda\lambda)$, evaluating these remaining integrals from atomic parameters (γ) and interatomic distances. INDO relaxes this simplification somewhat by using separate parameters for *one*-center integrals ($ss | ss$), ($ss | pp$), ($pp | pp$), ($pp | p'p'$), and ($sp | sp$). NDDO further relaxes from this point by considering all *diatomic* integrals $(\mu\nu | \lambda\sigma)$ where $\mu\nu$ and $\lambda\sigma$ are replaced by point charges, dipoles, or quadrupoles depending on whether they are ss , sp , or pp/pp' , and the interaction energy is then computed from classical electrostatics.

Q5) How many contracted basis functions are required for a calculation on H₂O with the 6-311G(d) basis set (which by default uses a set of 6 cartesian d functions)? (5 points)

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Q6) If instead of 6-311G(d) we were to use 6-311+G(2df,2pd), which energy would you expect to go down by more, the HF energy, or the CCSD(T) energy? Why? (5 points)

CCSD(T), because correlated methods are more sensitive to basis-set incompleteness than the HF method.

Q7) An atomic orbital basis function is to a molecular orbital as a Slater determinant is to a configuration interaction wave function. (5 points)

Q8) What does a hyperfine coupling constant indicate and what kind of spectroscopy is involved in its measurement? (10 points)

In electron spin (or paramagnetic) resonance (ESR (or EPR)) spectroscopy, the hyperfine coupling constant measures the magnitude of unpaired spin density at a magnetically active nuclear position.

Q9) What is the ideal gas molecular partition function and what approximations are involved in computing it for a given molecule? For what is the partition function useful? (20 points)

A general partition function is
$$\sum_i^{\text{levels}} g_i e^{-E_i/k_B T}$$

where the sum runs over energy levels, g is the degeneracy of the level having energy E , k_B is Boltzmann's constant, and T is temperature. For a molecule, the general partition function can be expressed as a product of electronic, translational, rotational, and vibrational partition functions. Each of these can be solved fairly easily, if one assumes classical behavior for the translation, rigid rotation, and harmonic oscillator vibrational frequencies. Thus, one needs an optimized structure and a frequency calculation to compute the partition function. Once in hand, all thermodynamic state functions can be computed from it, making it particularly useful for computing enthalpy, entropy, and free energy, for example.