CHEMISTRY 8003
MIDTERM EXAM

1. FORCE FIELDS

The force field of Cornell et al. has the following published form:

$$E_{\text{total}} = \sum_{\text{bonds}} K_r \left(r - r_{\text{eq}} \right)^2 + \sum_{\text{angles}} K_\theta \left(\theta - \theta_{\text{eq}} \right)^2 + \sum_{\text{dihedrals}} \sum_{n=1}^{3} \frac{V_n}{2} \left[1 + \cos(n\phi) \right]$$

$$+ \sum_{\substack{\text{atoms} \\ i<j}} \left[\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^{6}} \right] + \sum_{\substack{\text{atoms} \\ i<j}} \frac{q_i q_j}{r_{ij}}$$

It is designed for equilibrium structures. Let us imagine that you wanted to modify this force field so that bonds could be made or broken. Describe as completely as possible what changes you would make to the above functional form to allow for bond making/breaking. (**40 points**)

Most critically, the bond stretching term would have to be modified from a harmonic potential to something like a Morse potential. Moreover, some choice would need to be made about what constitutes "connected" atoms, so that a broken bond would not be used in, say, an angle term (for instance, the angle and torsion terms could each be cross-coupled with some switching function going to zero with increasing bond length while the non-bonded terms would go to zero with decreasing bond length). Ideally partial atomic charges would be updated during optimization so that the charge on an atom could reflect its changing chemical environment. The nature of atom "types" would also need some attention. Either smooth switching functions would need to be developed carrying one type to another, or, more simply, atom types would reduce simply to atomic number.

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2. Basis Sets

Remember our old friend the allyl cation? List the total number of basis functions, *and the kind of functions involved*, that would be employed at the following levels of theory: Huckel MO theory, AM1, HF/6-31G*, MP2/6-31+G**. **(30 points)**
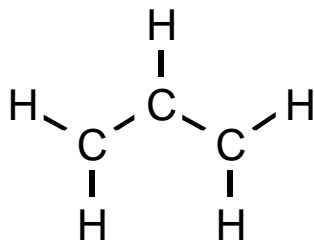
   Huckel theory uses simply one (conjugated) p orbital on each heavy atom—the total number of functions is 3 since there are 3 carbon atoms.
   AM1 uses Slater functions for valence atomic orbitals; 6-31G* and 6-31+G** use gaussian functions for core and valence atomic orbitals. AM1 is a minimal basis (1 basis function (bf) per orbital); 6-31G* is minimal in the core, double- in the valence region, and includes 6 cartesian d functions on heavy atoms; 6-31+G** adds p functions on hydrogen atoms and a diffuse sp set on heavy atoms to 6-31G*. The tables below provide totals.

AM1:

Atom	(a) \# of atoms	orbital	(b) degeneracy	(c) bfs per orbital	(a) x (b) x (c) subtotal
H	5	1s	1	1	5
C	3	2s	1	1	3
C	3	2p	3	1	9
				Total:	**17**

6-31G*:

Atom	(a) \# of atoms	orbital	(b) degeneracy	(c) bfs per orbital	(a) x (b) x (c) subtotal
H	5	1s	1	2	10
C	3	1s	1	1	3
C	3	2s	1	2	6
C	3	2p	3	2	18
C	3	3d	6	1	18
				Total:	**55**

6-31+G**:

Atom	(a) \# of atoms	orbital	(b) degeneracy	(c) bfs per orbital	(a) x (b) x (c) subtotal
H	5	1s	1	2	10
H	5	2p	3	1	15
C	3	1s	1	1	3
C	3	2s	1	2	6
C	3	2p	3	2	18
C	3	diffuse s	1	1	3
C	3	diffuse p	3	1	9
C	3	3d	6	1	18
				Total:	**82**

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3. Electron Repulsion Integrals

Explain what is meant by the shorthand notation $< \mu \quad | \quad >$. How are the relevant integrals evaluated at different levels of molecular orbital theory? Exact mathematical formulae are not required for full credit—you can express any key approximations/issues in words, if you prefer. **(40 points)**

In cartesian coordinates:

$$< \mu \quad | \quad > = \quad \frac{\mu(1) \quad (1) \quad (2) \quad (2)}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}} \, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

where the indices 1 and 2 refer to two different electrons and the numerator in the integral is the product of the four basis functions with indices μ, , , and .

At the CNDO level, these integrals are zero unless $\mu =$ and $=$, in which case they are replaced by a single parameter if all on the same atom, and by evaluation of a simple function depending on interatomic distance and atomic number if on different atoms.

At the INDO level, the CNDO approximation is relaxed slightly by including different parameters for the monatomic integrals. In particular, there are separate parameters for the one-center integrals $< ss \mid ss >$, $< ss \mid pp >$, $< sp \mid sp >$, $< pp \mid pp >$, and $< pp \mid p'p' >$.

At the NDDO level, the ERIs are evaluated if μ and are on the same atom (but not necessarily the same function) and and are on the same atom (which may be a different atom from the one on which μ and reside). The integral is evaluated by approximating the charge clouds as multipole distributions and assuming a 1/r-like dependence.

At the ab initio level, every ERI is evaluated. Using gaussian functions as basis functions facilitates this process by rendering solution of the integrals analytic.

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4. Molecular Properties

Detail all the purposes for which second derivatives of the energy with respect to atomic motion can be used. **(40 points)**

1) **Accurate second derivatives speed geometry optimization.**

2) **The signs of the second derivatives determine the nature of a stationary point (minimum, transition state, etc.)**

3) **Vibrational (infrared) frequencies are determined from second derivatives.**

4) **Knowledge of vibrational frequencies permits computation of zero-point vibrational energy and equilibrium and kinetic isotope effects.**

5) **Together with molecular formula, geometry, and spin multiplicity, vibrational frequencies permit computation of entropy and of thermal contributions to enthalpy and free energy.**

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