CHEMISTRY 8003
MIDTERM EXAM

1. FORCE FIELDS

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

$$E_{\text{total}} = \sum_{\text{bonds}} K_r\left(r - r_{\text{eq}}\right)^2 + \sum_{\text{angles}} K_\theta\left(\theta - \theta_{\text{eq}}\right)^2 + \sum_{\text{dihedrals}} \sum_{n=1}^{3} \frac{V_n}{2}\left[1 + \cos(n\omega)\right]$$
$$+ \sum_{i<j}^{\text{atoms}} \left(\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^{6}}\right) + \sum_{i<j}^{\text{atoms}} \frac{q_i q_j}{\varepsilon r_{ij}}$$

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)**

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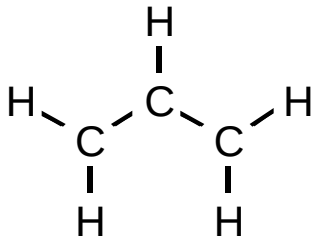
2. Basis Sets

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)**



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3. Electron Repulsion Integrals

Explain what is meant by the shorthand notation $< \mu\nu \mid \lambda\sigma >$. 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)**

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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)**

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