

Name: \_\_\_\_\_

**CHEMISTRY 8003  
MIDTERM EXAM**

**1. FORCE FIELDS**

a) In a general sense, describe the various terms that contribute to a generic molecular mechanics force field. For at least one term, discuss two or more different functional forms that might reasonably be adopted for that term. **(40 points)**

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b) Given some chemical question that can be studied using molecular mechanics, how should one go about choosing a force field? You are welcome to use hypothetical situations in your answer. **(20 points)**

c) Why are metals typically harder to handle in force fields than, say, second-row atoms? **(20 points)**

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## 2. COMPARISONS AND CONTRASTS

Provide a *specific, practical* example of a chemical question for which computational study using semimpirical molecular orbital theory would be a better choice than molecular mechanics. Provide a different example where the converse would be true. Describe, briefly, why you chose your examples. **(40 points)**

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### 3. HUCKEL THEORY

You are transported to an unusual universe, where carbon p orbitals can interact with each other only in a “skip-bonding” fashion. That is, interactions between them do *not* occur when they are adjacent, but only if another atom is inserted between them. Except for this difference, all other fundamental chemical phenomena in the two universes are the same. To impress the local natives, you decide to explain the allyl system to them using Huckel MO theory.

a) What modification(s) will you need to make to the Huckel theory we discussed in class in order for it to be valid in *their* universe? **(15 points)** *Our* universe’s theory is recapitulated here:

1. Basis functions are one p orbital per carbon atom, i.e.,

$$\psi_k = \sum_{i=1}^N a_{ki} p_i^C$$

where  $\psi_k$  is a molecular orbital wavefunction having energy  $E_k$  and  $N$  is the number of carbon atoms.

2. The overlap integral for any two basis functions,  $S_{ij}$  is defined as

$$S_{ij} = \int \psi_i \psi_j$$

3. The resonance integral for any two basis functions,  $H_{ij}$ , is defined as

$$H_{ij} = \begin{cases} H_{ii}, & i = j \\ H_{ij}, & i, j \text{ are neighbors} \\ 0, & \text{otherwise} \end{cases}$$

where  $H_{ii}$  is the ionization potential of the methyl radical and  $2H_{ij}$  is the rotational barrier in ethylene.

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b) Recall orbital energies  $E_k$  are found by solving the secular equation

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

Based on your answer above, what is the secular determinant for the allyl system in this new universe? **(15 points)**

c) What three values for  $E$  make your above secular equation true? **(15 points)**

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d) Sketch the MO's corresponding to each energy for skip-allyl. I'll remind you that orbital coefficients for MO having energy  $E$  are found from solving the linear equations

$$\sum_{i=1}^N a_i (H_{ji} - ES_{ji}) = 0 \text{ for all } j = 1, N$$

but if you think about it, you might be able to avoid the math. Explain your reasoning, if you don't work through the equations. If you *do* go through the equations, explain why the natives in your new universe were quite unimpressed with your results. **(35 points)**

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7

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