

Chemistry 433
“Computational Chemistry”
Winter Semester 1998
Dr. Rainer Glaser

First 1-Hour Examination
“Potential Energy Surfaces & Quantum-Mechanical Background”

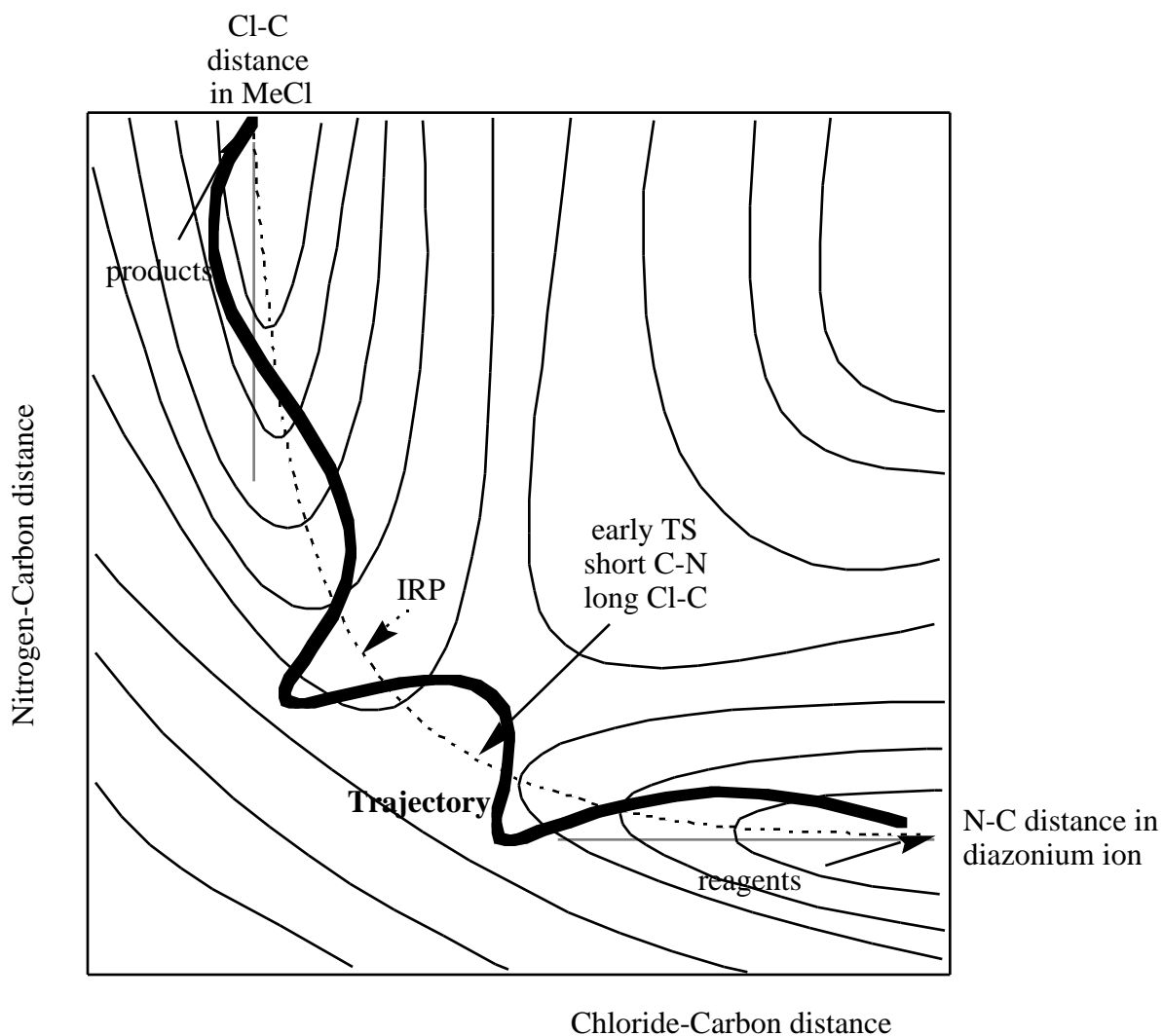
Wednesday, February 11, 1998, 8:00 - 8:50 am

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| Name: |
| Answer Key |

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|------------------------------|-----|--|
| Question 1 (PES Features) | 20 | |
| Question 2 (PES Searching) | 20 | |
| Question 3 (Atomic Orbitals) | 20 | |
| Question 4 (Hamiltonians) | 20 | |
| Question 5 (Wave Functions) | 20 | |
| Total | 100 | |

Question 1. Potential Energy Surfaces. (20 points)

Chloride reacts with methyl diazonium ion (my favorite ion, no doubt about it!) in a highly exothermic S_N2 reaction to form methyl chloride and dinitrogen. The potential energy surface of this reaction can be described, to a first approximation, as a function of the two distances $a = d(\text{Cl-C})$ and $b = d(\text{C-N})$. Draw a **schematic contour map** of the potential energy surface. The x-axis should correspond to the internal coordinate “a” and the y-axis should correspond to the internal coordinate “b”. Your scheme should indicate the minima corresponding to starting materials and products. Your scheme should reflect that the reaction is exothermic and that the transition state therefore is early (early, late). When done with the contour plot, draw a dashed line that indicates the intrinsic reaction path. Then draw as solid lines two possible trajectories (which ever you like) that lead from starting materials to products.



Question 2. PES Searching for Minima and Transition State Structures. (20 points)

(a) Suppose you want to locate the transition state structure for the S_N2 reaction between chloride and methyldiazonium ion using the “**coordinate driving**” method. How would you proceed? What computations would have to be carried out? Briefly describe.

Drive coordinate “a”

Find the optimized structure with a fixed Cl-C distance of 4 Angstrom.

Reduce the Cl-C distance. e.g. use stepsize of 0.2 Angstrom.

Find the optimized structure with a fixed Cl-C distance of 3.8 Angstrom.

and so on ... This will produce structures on the IRC between TS and products.

Drive coordinate “b”

Find the optimized structure with a fixed C-N distance of 4 Angstrom.

Reduce the C-N distance. e.g. use stepsize of 0.2 Angstrom.

Find the optimized structure with a fixed C-N distance of 3.8 Angstrom.

and so on ... This will produce structures on the IRC between TS and reagents.

(b) Suppose you carried out a “**gradient norm minimization**” search on the potential energy surface and you located a structure that looks like the transition state structure for the S_N2 reaction between chloride and methyldiazonium ion. Now you want to make sure that you do in fact have located the correct transition state structure. How would you proceed? What computations would have to be carried out? Briefly describe. (Your answer should contain such words as Hessian, eigenvalues, symmetry of transition vector.)

Gradient norm minimizations find minima, shoulders or saddle points.

In simple cases (such as the present one), it is easy to tell (using chemical sense) what type of stationary structure one is looking at.

The computation of the second derivative matrix of the energy with respect to the internal coordinates, the Hessian matrix, will tell. A saddle point of the first order (a TS) will have one and only one negative eigenvalue. The imaginary mode should be asymmetric with regard to a displacement that transforms reagents to products.

Question 3. Atomic Orbitals. (20 points)

The solutions to the Schroedinger equation for 1-nucleus 1-electron systems are “atomic orbitals” and the simplest ones are the AOs of hydrogen. The AOs are best expressed in polar coordinates r , θ , and ϕ . The angular part depends on the quantum number(s) l and m but not on the quantum number(s) n . Chemists are quite familiar with the shape of s, p, d ... AOs and the location of the node planes. So, here, let's be concerned with the radial functions and the number of spherical nodes.

| | |
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| Give the correct functional form of the 2s AO. | $A (B - r) \exp(-\zeta r)$ |
| Give the correct functional form of the 2p AO. | $A r \exp(-\zeta r)$ |
| Give the functional form of the Slater-type orbital of the 2s AO. | $A r \exp(-\zeta r)$ |
| Give the functional form of the Slater-type orbital of the 2p AO. | $A r \exp(-\zeta r)$ |
| Give the functional form of the Gaussian-type orbital of the 2s AO. | $A r \exp(-\zeta r^2)$ |
| Give the functional form of the Gaussian-type orbital of the 2p AO. | $A r \exp(-\zeta r^2)$ |
| Give the functional form of the Gaussian-type orbital of the 4s AO. | $A r^3 \exp(-\zeta r^2)$ |
| How many spherical nodes are there in the 4s AO? | there are 3 |
| Give the functional form of the Slater-type orbital of the 4s AO. | $A r^3 \exp(-\zeta r)$ |

Question 4. Hamiltonians. (20 points)

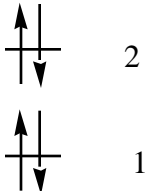
In the first column, write down the general expression for the Hamiltonian describing the indicated interaction. In the second column, write down the specific expression for that Hamiltonian for the molecule Li-H in columns 1 - 3 (give all terms that show up in the sums in the general expression and use M_{Li} and M_{H} as appropriate). For rows 4 and 5, it is sufficient to state how many terms will have to be considered for LiH. In column 3, indicate for each term (YES or NO) whether this term shows up in the “electronic Hamiltonian”, whether it shows up in the “core-Hamiltonian”, whether it is considered in the computation of the “total energy”. Finally, for each term indicate whether this term will lead to one-electron integrals or two-electron integrals.

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| nucl. kin. energy sum over all nuclei of terms $-(\hbar^2/8 M_A)^{-2}$ | 2 terms, one for each atom $-(\hbar^2/8 M_{\text{Li}})^{-2}$ $-(\hbar^2/8 M_{\text{H}})^{-2}$ | Enters H_{el} ? NO Enters H_{core} ? NO Enters “Total Energy”? NO Leads to 1-e-integrals? NO Leads to 2-e-integrals? NO |
| elect. kin. energy sum over all electrons of terms $-(\hbar^2/8 M_e)^{-2}$ | one term per electron there are four electrons 4 times $-(\hbar^2/8 M_e)^{-2}$ | Enters H_{el} ? YES Enters H_{core} ? YES Enters “Total Energy”? YES Leads to 1-e-integrals? YES Leads to 2-e-integrals? NO |
| nucl.-nucl. rep. sum over all unique pairs of atoms A and B terms $+e^2 Z_A Z_B / r_{AB}$ | one term $+3e^2 / r_{\text{LiH}}$ | Enters H_{el} ? NO Enters H_{core} ? NO Enters “Total Energy”? YES Leads to 1-e-integrals? NO Leads to 2-e-integrals? NO |
| elect.-elect. rep. sum over all unique electron pairs of terms $+e^2 / r_{pq}$ | there are four electrons pairs 12, 13, 14, 23, 24, and 34 thus, six terms of this sort | Enters H_{el} ? YES Enters H_{core} ? NO Enters “Total Energy”? YES Leads to 1-e-integrals? NO Leads to 2-e-integrals? YES |
| elect.-nucl. attraction sum over all atoms sum over all electrons of terms $-e^2 Z_A / r_{Ap}$ | one term for each electron per atom there will be eight such terms | Enters H_{el} ? YES Enters H_{core} ? YES Enters “Total Energy”? YES Leads to 1-e-integrals? YES Leads to 2-e-integrals? NO |

Question 5. Many-Electron Wave Functions. (20 points)

The Li—H molecule contains two occupied MOs and both of these are σ -MOs. Let us denote the lower lying MO as σ_1 and the higher-lying one as σ_2 .

(a) Describe the two occupied orbitals of Li—H in terms of the AOs of Li and H. Provide a molecular orbital energy level diagram for Li—H (indicate electron spin using up and down arrows). Write down Hartree Product for Li—H (give spatial and spin part).

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| σ_1 MO is LCAO of basically 1s(Li) | σ_2 MO is LCAO of 2s(Li) and 1s(H) |
| MO Energy Level Diagram <div style="text-align: center;">  </div> | Hartree Product of Li—H $\sigma_1(1) \sigma_1(2) \sigma_2(3) \sigma_2(4)$ |

(b) The Hartree Product is not a correct solution of the Schrodinger equation since it does not satisfy the antisymmetry principle. To overcome this problem, we use a linear combination of Hartree Products as described by Slater. Write down the Slater Determinant for **the valence electrons only** Li—H, $\Psi_{\text{LiH}}(3,4)$, and expand the determinant. (Use “N” as the normation constant.)

$$\Psi_{\text{LiH}}(3,4) = N \begin{vmatrix} \sigma_2(3) & \sigma_2(3) \\ \sigma_4(4) & \sigma_4(4) \end{vmatrix} \quad (\text{Imagine the vertical bars})$$

$$\Psi_{\text{LiH}}(3,4) = N \{ \sigma_2(3) \sigma_4(4) - \sigma_2(3) \sigma_4(4) \}$$

