

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

Name:
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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 methyldiazonium ion (my favorite ion, no doubt about it!) in a highly exothermic  $S_N2$  reaction to form methylchloride 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, 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.

(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.)

**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 \_\_\_\_\_ coordinates  $r$ , \_\_\_\_\_, and \_\_\_\_\_. The angular part depends on the quantum number(s) \_\_\_\_\_ but not on the quantum number(s) \_\_\_\_\_. 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.

Give the correct functional form of the **2s** AO.

Give the correct functional form of the **2p** AO.

Give the functional form of the Slater-type orbital of the **2s** AO.

Give the functional form of the Slater-type orbital of the **2p** AO.

Give the functional form of the Gaussian-type orbital of the **2s** AO.

Give the functional form of the Gaussian-type orbital of the **2p** AO.

Give the functional form of the Gaussian-type orbital of the **4s** AO.

How many spherical nodes are there in the **4s** AO?

Give the functional form of the Slater-type orbital of the **4s** AO.

**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  $M_{\text{Li}}$  and  $M_{\text{H}}$  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.

nucl. kin. energy		Enters $H_{\text{el}}$ ? Enters $H_{\text{core}}$ ? Enters “Total Energy”? Leads to 1-e-integrals? Leads to 2-e-integrals?
elect. kin. energy		Enters $H_{\text{el}}$ ? Enters $H_{\text{core}}$ ? Enters “Total Energy”? Leads to 1-e-integrals? Leads to 2-e-integrals?
nucl.-nucl. rep.		Enters $H_{\text{el}}$ ? Enters $H_{\text{core}}$ ? Enters “Total Energy”? Leads to 1-e-integrals? Leads to 2-e-integrals?
elect.-elect. rep.		Enters $H_{\text{el}}$ ? Enters $H_{\text{core}}$ ? Enters “Total Energy”? Leads to 1-e-integrals? Leads to 2-e-integrals?
elect.-nucl. attraction		Enters $H_{\text{el}}$ ? Enters $H_{\text{core}}$ ? Enters “Total Energy”? Leads to 1-e-integrals? Leads to 2-e-integrals?

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

The Li—H molecule contains two occupied MOs and both of these are  $\sigma$ -MOs. Let us denote the lower lying MO as  $\psi_1$  and the higher-lying one as  $\psi_2$ .

(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).

$\psi_1$ MO is LCAO of	$\psi_2$ MO is LCAO of
MO Energy Level Diagram	Hartree Product of Li—H

(b) The Hartree Product is not a correct solution of the Schrodinger equation since it does not satisfy the \_\_\_\_\_ 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.)

