Chemistry 433, Winter Semester 1998, Dr. Glaser

Quiz II: "Basis Sets", Monday, April 20, 1998, 25 minutes.

Your Name:

Question 1. Split-Valence Basis Sets and Basis Set Augmentation. (24 points)

(a) Explain what a **split-valence basis set** is by comparison of the STO-3G and 3-21G basis sets of oxygen. (8 points)

In STO-3G there is one basis function for each atomic orbital and each of the basis functions is an expansion of three Gaussian primitives. In 3-21G, the same holds true for all core atomic orbitals. However, for every valence orbital we now use two basis functions. The inner basis function is an expansion of 2 primitives and the outer basis function is a flat Gaussian.

(b) Using an illustration, explain what **polarization functions** are. Give an example of an oxygen-containing molecule that would require polarization functions in the basis set. (8 points)

add a little p-function to a lot of s-function ===> polarized s-function (2nd * in G**)

this is automatically taken care of for the non-H atoms (since there alsways are p-BFs).

add a little d-function to a lot of p-function ===> polarized p-function (* in G*)

Polarization functions are needed whenever there are polar bonds and they also are necessary for lone pairs. So, pretty much any O-containing molecule needs them!

(c) Using an illustration, explain what **diffuse functions** are. Give an example of an oxygen-containing molecule that would require diffuse functions in the basis set. (8 points)

Augmentation by diffuse functions meas adding an extra set of valence BFs. These BF are single flat functions with small exponents. Needed mostly for anions. Example: hydroxide.

Points for Question 1:	/24		
Points for Question 2:	/14		
Points for Question 3:	/12	Total Points:	/50

Question 2. Calibrated Pople Basis Sets. (14 points)

Consider formaldehyde, $H_2C=O$, and its sulfur analog, $H_2C=S$.	$H_2C=O$	$H_2C=S$
Number of valence AOs on the heteroatom?	4	4
Number of BFs to describe the heteroatom at STO-3G?	5	9
Number of BFs to describe the heteroatom at 3-21G?	1 core + 8 valence = 9	5 core + 8 valence = 13
Number of BFs to describe the heteroatom at 6-31G*?	9+5=14 (9+6=15 OK)	13+5=18 (13+6=19 OK)
Total number of BFs at 6-31G* (1.5 p.)	14(C)+14(O)+4(H)=32	14(C)+18(S)+4(H)=36
Total number of BFs at 6-311G** (1.5 p.)	18(C)+18(O)+12(H)=48	18(C)+22(S)+12(H)=52

Question 3. Numerical Example. (12 points)

Attached is the basis set section of an output of an ab initio calculation of water.

(a) Describe the basis set shown in the attachement in the "() & []" nomenclature. (4 points)

(9s5p,4s) and [4s2p,2s]

(b) Write down the H-1s inner basis function as an expansion of the primitives. No need for normalization. Just write down the expansion using the numbers you find in the attachement. (4)

(H-1s)inner = N *(0.032*exp(-19.2r^2) + 0.231*exp(-2.89r^2) + 0.817*exp(-0.653r^2))

(c) For the calculation of the electrical dipole moment of water, would you rather use this basis set or the basis set 6-31G**? Explain in a few words. (4 points)

6-31G** - polarization is more important than more BFs for the sp AOs.