CHEM 555-75 **WORKSHEET 10** **Fall 2021**

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1. From the TZ, 6-311G, 6-31+G and 4-31G* Gaussian basis sets, explain which you would expect to produce the most accurate results in Hartree-Fock calculations of:

   a) Deprotonation energies of sulphuric acid.

   b) Structure of chloroethane.

   c) Nuclear magnetic resonance (NMR) chemical shifts of molecules.

   a) 6-31+G – diffuse functions allow for calculation of electrons far from the center of electron density, such as in anionic molecules.

   b) 4-31G* – Molecular orbitals constructed from just split valence basis sets are not sufficiently flexible to accurately calculate geometries. Addition of CGs with higher angular momenta provides this flexibility.

   c) TZ – NMR requires description of both core and valence electrons as both affect chemical shifts so need a basis set that treats both sets of electrons equally.

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2. For the basis sets STO-2G, 3-21G, DZP and 4-31+G, determine:

   a) How many contracted Gaussians they contain for each core and valence atomic orbital.

   b) How many primitive Gaussians are contained in each contracted Gaussian.

   c) How many and what type (e.g. s, p or d) of contracted Gaussians they involve for the H and C atoms.

   a) STO-2G – 1 valence CG and 1 core CG; 3-21G – 2 valence CG and 1 core CG; DZP – 2 valence CG and 2 core CG; 4-31+G – 2 valence CG and 1 core CG.

   b) STO-2G – 2 pG in valence CG and 2 pG in core CG; 3-21G – 2 pG in first valence CG, 1 pG in second valence CG and 3 pG in core CG; DZP – not specified; 4-31+G – 3 pG in first valence CG, 1 pG in second CG and 4 pG in core CG.

   c) STO-2G – 1×1s in H, 1×1s + 1×2s + 3×1×2p in C; 3-21G – 2×1s in H, 1×1s + 2×2s + 3×2×2p in C; DZP – 2×1s in H; 2×1s + 2×2s + 3×2×2p in C; 4-31+G – 2×1s in H; 1×1s + 2×2s + 3×2×2p + 1×3s + 3×1×3p.

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3. For a H atom whose nucleus is centered at point **R**, described by the STO-2G basis set with exponents 1.31 and 0.23 and with corresponding contraction coefficients 0.43 and 0.67 respectively, write down the form of the contracted Gaussian function.

$G(\mathbf{r}) = 0.43e^{-1.31(\mathbf{r}-\mathbf{R})^2} + 0.67e^{-0.23(\mathbf{r}-\mathbf{R})^2}$

4. A Hartree-Fock calculation on a nitrogen molecule gives energies of -108.7 Hartree and -107.4 Hartree when run with two different basis sets. The two basis sets are STO-3G and 4-31G. Which basis set leads to which energy and why?

N_2 contains 10 CGs in STO-3G and 18 CGs in 4-31G so there is more variational flexibility in 4-31G than STO-3G. As Hartree-Fock is a variational method, greater variational flexibility leads to a lower energy that better approximates the exact solution. Therefore 4-31G gives -108.7 Hartree and STO-3G gives -107.4 Hartree.