

Screening Constants for Gaussian-lobe Orbital Expansions of Hydrogenic Atomic Orbitals for Molecular SCF Calculations

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Abstract

Along with determination of Gaussian-lobe orbital expansions that accurately approximate hydrogen atom energies and 1s, 2s, 2p and 3d atomic orbitals, Jerry Whitten hypothesized [J. Chem. Phys., 39,349(1963)] that his hydrogen atom Gaussian-lobe orbital expansions could provide useful basis sets for all electron self-consistent field Hartree-Fock molecular orbital studies of molecules. So after fifty years have elapsed, this paper presents the first confirmation of Whitten's hypothesis by using his hydrogen atom Gaussian-lobe orbital expansions as basis sets, modified only by inclusion of screening constants, in molecular orbital calculations for ground state electronic energies and electrical charge distributions for several small inorganic and organic molecules.

Keywords: Screening constants, hydrogen atom Gaussian lobe orbital expansions, molecular orbitals calculations

1. Introduction

Whitten demonstrated the utility of using Gaussian lobe expansions as approximations for 1s, 2s, 2p and 3d hydrogen atom wave functions, Jerry L. Whitten (1963), and suggested that “*the approximations are sufficiently accurate to find use in molecular energy calculations* “. However, Whitten never actually tested his HAGLOs Hypothesis for molecular calculations, Grimmelmann and Chesick(1971). Instead, completely new groups of Gaussian lobe expansion functions were developed for 1st row atoms Li-Ne and ethylene, Whitten(1966), and for 2nd row atoms Na-Ar, Petke, Whitten and Douglas(1970) and were used in molecular calculations. Accurate approximations to hydrogen atom wave functions 1s, 2s, 2p, 3s, 3p, 3d_z and 3d_{xy} were also determined as Gaussian lobe orbital expansions and used to calculate energies for the H₂⁺ ion by Hideo Sambe(1965). This paper investigates Whitten's original Hypothesis concerning usefulness of HAGLOs modified only by introduction of appropriate screening constants to describe the first row atoms and molecules containing hydrogen and first row atoms. Screening constants for HAGLOs minimal basis sets were determined by minimizing ground state molecular electronic energies. Ab-initio energies and electrical

properties obtained with the modified HAGLOs functions are presented for several molecules and compared to values calculated using closed shell Hartree-Fock SCF-MO computer programs available in commercial quantum chemistry G98W program suite marketed by Gaussian, Inc., Frisch et. al.(2001). The G98W program suite had several Gaussian orbital basis sets already installed, including STO-3G, Hehre, Stewart and Pople(1969), 3-21G, Binkley, Pople and Hehre(1980)and 4-31Gand 6-31G, Ditchfield, Hehre and Pople(1971).

2. Basis sets for molecular calculations

Whitten's HAGLOs expansions provided useful minimal basis set for calculating properties of many-electron atoms and molecules after being modified by introduction of screening constants. In addition, multi zeta and floating orbital centers provided useful extensions to minimal basis sets.

2.1 Screening constants and Gaussian lobe functions

For this study electronic basis sets were built from Whitten's original Gaussian lobe orbital expansion functions for hydrogen atom orbitals 1s, 2s, 2p_x, 2p_y, 2p_z, 3d_{xy}, 3d_{xz}, 3d_{yz} and 3d_{x²-y²} which were referred to as HAGLOs. Whitten postulated that these HAGLOs expansions could be used in molecular SCF-MO calculations but did not indicate how to go about doing this. One way to modify HAGLOs expansions for use in many-electron atoms and molecules is by including screening constants in the HAGLOs. These modifications of Whitten's original HAGLOs are referred to as SCM-HAGLOs. Appropriate values for screening constants were determined by SCF energy optimizations for the electronic environment of the many-electron atom or molecule being studied. Primitive normalized Gaussian lobe functions with exponent **a**, center **R_i**, and electron position vector **r** as used by Whitten to define HAGLOs were written as

$G(\mathbf{r}, \mathbf{a}, \mathbf{R}_i) = (2a/\pi)^{3/4} \exp(-a|\mathbf{r} - \mathbf{R}_i|^2)$. Screening constant **S** for an atom of atomic number **Z** is introduced into a primitive Gaussian lobe function by multiplying each exponent used in Whitten's HAGLOs by $(Z - S)^2$. $G[\mathbf{r}, \mathbf{a}(Z - S)^2, \mathbf{R}_i] = [2\mathbf{a}(Z - S)^2/\pi]^{3/4} \exp[-\mathbf{a}(Z - S)^2|\mathbf{r} - \mathbf{R}_i|^2]$.

By means of an energy variational principle Whitten defined accurate approximations to hydrogen atom wave functions(**AO_k**), 1s, 2s, 2p_x, 2p_y, 2p_z, 3d_{xy}, 3d_{xz}, 3d_{yz} and 3d_{x²-y²} as sums of the primitive Gaussian-lobe orbitals. Exponents **a** and expansion coefficients **g_{n,k}** were optimized to give normalized orthogonal hydrogen atom orbitals **AO_k**: $\text{AO}(\mathbf{r})_k = \sum g_{n,k} G(\mathbf{r})_n$. Slater proposed rules for estimating screening constants **S** in atomic SCF energy calculations, Slater (1929). Only his first rule, use 0.30 for the screening constant of a core 1s atomic orbital when the core orbital configuration is 1s² was helpful because this study required SCM-HAGLOs basis sets for molecules. For example, Slater's value **S** = 0.3 for the 1s orbital in H⁻¹ agreed with the screening constant values obtained for H⁻¹ and He atoms using energy versus screening constant optimization, but differed from values, -0.1 and -0.4, obtained respectively for the 1s orbitals in H₂ and H₃⁺¹, as illustrated in Table 1. So for many-electron atoms and molecules screening constants optimization in SCM-HAGLOs basis sets lowered SCF energy and provided a pathway to obtain better minimum basis sets. Energies calculated for 1s, 2p and 3d atomic energy levels using Whitten's HAGLOs for a hydrogen atom (**Z** = 1) with **S** = 0 were identical to the energies already reported by Whitten. And when energy of the hydrogen atom was calculated for a 1s atomic orbital over range of screening constant values in Whitten's HAGLO expansion the energy was not improved. Varying screening constants here failed to improve the energy because these HAGLOs were already optimized by Whitten with respect to orbital exponents. From a variational quality viewpoint, the energy -0.4990 au obtained for hydrogen atom by Whitten was superior to the -0.4982 au calculated using a split-valence double zeta 6-31G basis set but not to the -0.4998 au calculated using a split-valence triple-zeta 6-311G basis set. Therefore, an objectives of this study was to benchmark molecular energies calculated using SCM-HAGLOs basis sets against energies obtained using STO-3G,

3-21G, 4-31G, 6-31G and 6-311G basis sets. Notation for SCM-HAGLOs used in this paper consists of orbital type with screening constant enclosed within parenthesis. For example, the notation H[1s(0.30)] indicates SCM-HAGLO for a hydrogen atom 1s orbital with screening constant 0.30.

Table 1. HAGLOs screening constant optimization for two-electron systems using one 1s atomic orbital on each nuclear center

SH(atom)H ¹ He	H ₂ (R=1.4 au)	H ₃ ⁺ (R=1.65 au)			
-0.6					-1.2209
-0.5					-1.2563
-0.4					-1.2692
-0.3			1.0813	-1.2605	
-0.2	-0.4790		-2.5763	-1.1135	-1.2300
-0.1	-0.4940	-0.3001	-2.6688	-1.1259	-1.1771
0.0	-0.4990	-0.3726	-2.7413	-1.1181	-1.1005
0.1-0.4940	-0.4251	-2.7938	1.0893		
0.2	-0.4790	-0.4578	-2.8264		
0.3		-0.4704	-2.8391		
0.4		-0.4630	-2.8318		
0.5		-0.4358	-2.8045		

Benchmark comparison G98W results, M. J. Frisch et. al.(2001).

STO-3G	-0.1586	-0.1586	-2.8078	-1.1167-1.2375	
3-21G	-0.4962	-0.4044	-2.8357	-1.1229	-1.2694
4-31G	-0.4982	-0.4224	-2.8552	-1.1267	-1.2735
6-311G	-0.4998	-0.4667	-2.8599	-1.1280	-1.2765

2.2 Multiple zeta basis sets

Minimal basis sets can be improved by using multiple values of screening constants in each orbital type at a given nuclear center. Use of two screening constant values, say 0.1 and 0.3, in 1s orbitals produces two 1s orbitals, 1s(0.1) and 1s(0.3). Such a basis set is known as a double zeta basis set. A triple zeta 1s basis set is one in which three different values, say 0.1, 0.3 and 0.5 are used as screening constants to obtain 1s(0.1), 1s(0.3) and 1s(0.5) SCM-HAGLOs. Pople's basis sets STO-3G are single zeta basis sets, 3-21G, 4-31G and 14

6-31G are split-valence double zeta basis sets, and 6-311G is a split-valence triple zeta basis set. We discuss use of single, double and triple zeta SCM-HAGLOs basis sets in energy calculations for hydrogen and other molecules. Minimal basis sets can also be improved by displacing some or all of the atomic orbitals off nuclear center.

2.3 Floating atomic orbitals

These displaced atomic orbitals are called floating atomic orbitals. Previous efforts to float atomic orbitals have been reported for Gaussian lobe orbitals rather than hydrogenic atomic orbitals, Arthur Frost(1977), Hyatt, Careless and Stanton(1977) and Schwartz and Schaad(1967). These Gaussian lobe orbitals were displaced along directions toward bond midpoints. Our program package allowed floating HAGLOs atomic orbitals in order to improve basis sets; these floating AOs were positioned at selected centers having nuclear charge $Z = 0$. Notation for floating 1s orbital with screening constant $S = 0.25$ is Float[1s(0.25, at center x,y,z)]. We can add orbitals changing a minimal basis set into a double or triple zeta basis set and at the same time use floating atomic orbitals. These basis set extensions were tested upon H_2 and other molecules.

3. Partial atomic charges using electronegativity

Oxidation numbers are atomic charges calculated assuming ionic bonding; formal charges are atomic charges calculated assuming covalent bonding. Partial atomic charges are the actual atomic charges present in polarized chemical bonds. Bond polarization arises when bonded atoms have different electronegativity; this bond polarization results in partial atomic charges for terminally bonded atoms intermediate to oxidation number and formal charge values and also specific partial atomic charges for interior bonded atoms. Starting from the Lewis electron-dot picture for the molecule, partial atomic charge δ_A for atom A was estimated using equation, $\delta_A = V_A - L_A - \chi_A \sum N_{AB} / (\chi_A + \chi_B)$ from Meek and Garner(2005). The χ_A and χ_B are electronegativity values, Pauling (1960), for atoms in the covalent bond A-B. This bond links atom B to atom A and contains N_{AB} electrons. V_A and L_A are numbers of valence electrons and lone pair electrons, respectively on atom A. The sum is over all B-A covalent bonds that connect surrounding atoms B to central atom A. Carbon dioxide molecule ::O=C=O:: provides an example. Pauling scale electronegativity values for oxygen and carbon are $\chi_O = 3.5$ and $\chi_C = 2.5$. From the Lewis picture, $N_{CO} = 4$ for each C=O bond, $V_C = 4$ for C atom, and $L_C = 0$ for C atom. There are two C=O bonds. Carbon atom C has partial atomic charge $\delta_C = 4 - 0 - 4 \times 2.5 / (2.5 + 3.5) - 4 \times 2.5 / (2.5 + 3.5) = 0.666$ au. Similarly, each oxygen atom has $V_O = 6$, $L_O = 4$ and partial atomic charge $\delta_O = 6 - 4 - 4 \times 3.5 / (3.5 + 2.5) = -0.333$. For hydrogen atoms in formaldehyde H_2CO :: the electronegativity $\chi_H = 2.1$, $V_H = 1$, $L_H = 0$, $N_{HC} = 2$, and partial atomic charge $\delta_H = 1 - 0 - 2 \times 2.1 / (2.1 + 2.5) = 0.087$ au. Again the oxygen partial atomic charge $\delta_O = -0.333$ au. There are three bonds connecting H and O atoms to carbon, two C-H and one C=O. Partial atomic charge $\delta_C = 4 - 0 - 4 \times 2.5 / (2.5 + 3.5) - 2 \times 2.5 / (2.1 + 2.5) - 2 \times 2.5 / (2.1 + 2.5) = 0.159$ au. When these electronegativity determined partial atomic charges were compared to ab-initio partial atomic charges calculated using SCM-HAGLOs basis sets and Mulliken's population charge analysis, Szabo and Ostlund (1996), similar values were often observed. For CO_2 molecule, $\delta_O = -0.333$ au versus ab-initio -0.289 au, and $\delta_C = 0.666$ au versus ab-initio 0.578 au. For formaldehyde, $\delta_H = 0.087$ au versus ab-initio 0.102 au, $\delta_O = -0.333$ au versus ab-initio -0.430 au, and $\delta_C = 0.226$ au versus ab-initio 0.159 au. For hydrogen fluoride HF, $\delta_H = 0.311$ au versus ab-initio 0.254 au.

4. Self-consistent field molecular orbital method

Molecular orbitals MOs were defined as linear combinations of atomic orbitals using AOs which were determined using SCM-HAGLOs basis sets: $MO_k = \sum C_{i,k} AO_i$. For each MO_k there was a corresponding molecular orbital energy e_k .

4.1 SCF molecular orbitals and energies

Molecular orbitals row matrix \mathbf{MO} has elements MO_k ; $\mathbf{MO} = [MO_1, MO_2, \dots, MO_N]$. Atomic orbitals row matrix \mathbf{AO} has elements AO_i ; $\mathbf{AO} = [AO_1, AO_2, \dots, AO_N]$. Expansion coefficient matrix \mathbf{C} is $N \times N$ matrix with elements $C_{i,k}$ (i refers to atomic orbital and k to molecular orbital). Matrix \mathbf{MO} is the product of matrix \mathbf{AO} and matrix \mathbf{C} , namely $\mathbf{MO} = \mathbf{AO} \times \mathbf{C}$. Molecular orbital energies matrix \mathbf{E} is $N \times N$ diagonal matrix with elements e_k . Matrices \mathbf{C} and energy \mathbf{E} were calculated as solutions to Self-Consistent Field Hartree-Fock (SCF/HF) matrix secular equation, $\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \mathbf{E}$. Symmetric and real-valued matrix \mathbf{S} consists of atomic orbitals overlap integrals $S_{i,j} = \langle AO_i | AO_j \rangle$. Fock matrix \mathbf{F} is also real-valued and symmetric; its elements consist of the sum of single-electron Hamiltonian matrix \mathbf{h} and electron-electron interactions matrix \mathbf{G} , namely $F_{i,j} = h_{i,j} + G_{i,j}$. So matrices \mathbf{h} and \mathbf{G} were needed to calculate the Fock matrix \mathbf{F} . The Born-Oppenheimer single-electron molecular Hamiltonian operator \hat{h}_i defined using atomic units is $\hat{h}_i = -1/2 \nabla_i^2 - \sum \alpha / r_{\alpha,i}$. First term $-1/2 \nabla_i^2$ is kinetic energy operator for i^{th} electron; 2nd term is potential energy operator for i^{th} electron interacting with α^{th} nucleus; α sum is over all nuclei. Single-electron Hamiltonian matrix \mathbf{h} has elements $h_{k,l} = \langle AO_k | \hat{h}_i | AO_l \rangle$. The full N_{elec} electron molecular Hamiltonian operator \hat{H} is defined as $\sum \hat{h}_i$ (sum over all electrons) + $\sum \sum 1/r_{i,j}$ (sum over all j and $i < j$). Electron-electron potential energy operator term $1/r_{i,j}$ is used to define electron-electron potential energy matrix \mathbf{Y} which has elements $Y_{i,j;k,l} = \langle AO(1)_i AO(2)_j | r_{1,2}^{-1} | AO(1)_k AO(2)_l \rangle$. Matrix \mathbf{Y} and density matrix \mathbf{P} with elements $P_{i,j} = 2 \sum C_{i,s} C_{j,s}$ (s sum is over occupied MOs only) were used to calculate Coulomb energy matrix \mathbf{J} which has elements $J_{k,l} = \sum P_{r,s} Y_{k,r;l,s}$ (sum over AOs indices r and s) and exchange energy matrix \mathbf{K} which has elements $K_{k,l} = \sum P_{r,s} Y_{k,r;l,s}$ (again, sum over AOs indices r and s). Finally, \mathbf{G} matrix has elements $G_{k,l} = J_{k,l} - 1/2 K_{k,l}$. All of these matrices $\mathbf{F}, \mathbf{G}, \mathbf{h}, \mathbf{P}, \mathbf{J}, \mathbf{K}$ and \mathbf{S} were defined using SCM-HAGLOs atomic orbitals and depended upon choices made for screening constants that converted HAGLOs into CM-HAGLOs. Coefficients matrix \mathbf{C} and molecular orbital energies matrix \mathbf{E} were calculated using numerical matrix diagonalization methods which solved matrix eigenvalue equation $\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \mathbf{E}$. The solution was iterative because part \mathbf{G} of matrix \mathbf{F} depended upon the density matrix \mathbf{P} which depended upon coefficients matrix \mathbf{C} . The iterative process was cycled sufficient times to give converged SCF ground-state energy (Takao Tsuneda, 2104) which was calculated using $E_{\text{SCF}} = 1/2 \sum P_{r,s} (h_{r,s} + F_{r,s}) = \sum P_{r,s} (h_{r,s} + 1/2 G_{r,s})$.

4.2 Molecular electric dipole moment

Also of interest were electrical properties of the molecules. Electric dipole moment vector \mathbf{M} of the molecule is the difference of nuclear and electronic dipole moment vectors: $\mathbf{M} = \mathbf{M}_{\text{nuc}} - \mathbf{M}_{\text{elec}}$. Nuclear dipole moment vector \mathbf{M}_{nuc} is $[\sum c_n X_n \mathbf{i} + \sum c_n Y_n \mathbf{j} + \sum c_n Z_n \mathbf{k}]$. Here the sum is over nuclear indices n , and c_n is nuclear charge (atomic number). The X_n, Y_n and Z_n are nuclear Cartesian position coordinates and the \mathbf{i}, \mathbf{j} and \mathbf{k} are Cartesian unit vectors. The electronic dipole moment vector \mathbf{M}_{elec} is $[\sum P_{r,s} X_{r,s} \mathbf{i} + \sum P_{r,s} Y_{r,s} \mathbf{j} + \sum P_{r,s} Z_{r,s} \mathbf{k}]$. Here the sum is over atomic orbital indices r and s ; $P_{r,s}$ are elements of density matrix \mathbf{P} . The $X_{r,s}, Y_{r,s}$ and $Z_{r,s}$ are matrix elements of the electron Cartesian position coordinates. Matrix elements $X_{r,s} = \langle AO_r | x | AO_s \rangle$, $Y_{r,s} = \langle AO_r | y | AO_s \rangle$ and $Z_{r,s} = \langle AO_r | z | AO_s \rangle$ were calculated using SCM-HAGLOs atomic orbitals. Also of interest were partial atomic charges in the molecules; these were calculated using the SCF/HF wavefunctions and Mulliken's population analysis method, Szabo and Ostlund (1996).

4.3 Mulliken partial atomic charges

Mulliken partial atomic charges were calculated as follows. Let \mathbf{n} index atom centers and \mathbf{m} index atomic orbitals on atom center \mathbf{n} . For molecule with N_{atoms} values of \mathbf{n} satisfy, $1 \leq \mathbf{n} \leq N_{\text{atoms}}$. Let the number of atomic orbitals on center \mathbf{n} be N_n . Values of atomic orbital index \mathbf{m} satisfy, $1 \leq \mathbf{m} \leq N_n$. The total number of orbitals in the molecule is $N_{\text{orb}} = \sum N_n$. For convenience the molecular orbital expansion $MO_k = \sum C_{i,k} AO_i$ was rewritten

as $MO_k = \sum C_{n,m,k} AO_{n,m}$ using atom center n and atomic orbital indices m notation. Atomic orbitals overlap matrix S has elements $S_{n,m;n',m'} = \langle AO_{n,m} | AO_{n',m'} \rangle$. For closed shell systems discussed here the number of electron pairs equals N_{pair} and the number of electrons in the system $N_{\text{elec}} = 2 N_{\text{pair}}$. These N_{elec} electrons are distributed in pairs in the occupied molecular orbitals so $N_{\text{elec}} = 2 \sum \langle MO_k | MO_k \rangle = \sum [\sum 2 \sum C_{n,m,k} C_{n',m',k} S_{n,m;n',m'}]$, where the inner k sum is over occupied molecular orbitals. In the new indices notation, density matrix P has elements $P_{n,m;n',m'} = 2 \sum C_{n,m,k} C_{n',m',k}$. The electron population is divided into amounts placed on atom centers n and amounts distributed between atom centers n and n' . The electron population on atom center n is $Q_{n,n} = \sum P_{n,m;n,m} S_{n,m;n,m}$ and the electron population shared by centers n and n' is $Q_{n,n'} = \sum [P_{n,m;n',m'} S_{n,m;n',m'} + P_{n',m';n,m} S_{n',m';n,m}]$. In this expression for shared electron population restrictions on the sum are $1 \leq n \leq N_{\text{atom}}$ and $n' < n$. Mulliken divided $Q_{n,n'}$ into two equal parts giving half to atom center n and the other half to atom center n' . The electron population on center n is $Q_n = Q_{n,n} + \frac{1}{2} \sum Q_{n,n'}$ and on center n' is $Q_{n'} = Q_{n',n'} + \frac{1}{2} \sum Q_{n,n'}$. The partial atomic charge δ_n for atom center n is the difference of its nuclear charge number Z_n and its electron population: $\delta_n = Z_n - Q_n$.

5. Discussion

All electron self-consistent-field Hartree-Fock(SCF/HF)energies and electrical properties were calculated for atoms, inorganic and organic molecules.

5.1 Atoms

Minimal basis sets and basis sets extended to multi-zeta levels were used to calculate SCF/HF wave functions and energies for helium, beryllium and neon.

5.1.1 Helium: Without screening constants the He[1s(0.0)] minimal basis set gave energy $E = -2.7413$ au. Optimization of screening constants gave minimal basis set He[1s(0.3)] and improved $E = -2.8391$ au. Penta-zeta basis set, He[1s(-0.5, -0.25, 0.0, 0.25, 0.5)] gave $E = -2.8603$ au. For bench marking purposes, commercial G98W program suite with basis set STO-3G gave $E = -2.8078$ au, with basis set 3-21G gave $E = -2.8357$ au, with basis set 4-31G gave $E = -2.8552$ au, with basis set 6-31G gave $E = -2.8552$ au and with basis set 6-311G gave $E = -2.8599$ au.

5.1.2 Beryllium: Without screening constants in HAGLOs minimal basis set the energy was $E = -13.6973$ au. Minimal basis set Be [1s(0.3)2s(1.83)] gave $E = -14.3719$ au, and double zeta basis set Be[1s(0.29, 0.31)2s(1.80, 1.85)] gave $E = -14.5035$ au. Triple zeta basis set Be[1s(0.1, 0.3, 0.5)2s(1.63, 1.83, 2.03)] gave $E = -14.5618$ au, and penta zeta basis set Be[1s(-0.1, 0.1, 0.3, 0.5, 0.7)2s(1.5, 1.75, 2.0, 2.25, 2.5)] gave $E = -14.5651$ au. Grimmelmann and Chesick(1971) obtained $E = -14.4567$ au with a small Gaussian lobe 1s, 2s, 2p basis set. G98W program suite with basis set STO-3G gave $E = -14.3519$ au, with basis set 3-21G gave $E = -14.4868$ au, with basis set 4-31G gave $E = -14.5569$ au, with basis set 6-31G gave $E = -14.5668$ au and with basis set 6-311G gave $E = -14.5719$ au.

5.1.3 Neon: Without screening constants the energy was $E = -111.8306$ au. Minimal basis Ne[1s(0.45)2s(3.8)2p(3.6)] gave $E = -126.2482$ au, and triple-zeta basis set Ne[1s(0.1, 0.3, 0.5) 2s(3.5, 4.0, 4.5)2p(3.5, 4.0, 4.5)] gave $E = -128.1544$ au. G98W program suite with basis set STO-3G gave $E = -126.6045$ au, with basis set 3-21G gave $E = -127.8038$ au, and with basis set 4-31G gave $E = -128.3562$ au.

5.2 Inorganic molecules

Optimized SCM-HAGLO basis sets for diatomic molecules of hydrogen, lithium, nitrogen, fluorine, and

molecules of lithium hydride, boron monohydride, hydrogen fluoride, lithium oxide, berylliumdihydride, boron tri-hydride, ammonia and water were used to calculate ground-state electronic energies, dipole moments and partial atomic charges. Some of these basis sets were extended to include multi-zeta and floating atomic orbitals.

5.2.1 Diatomic hydrogen: The bond length in H_2 is $R_{HH} = 1.4$ au, Huber and Herzberg(1979). HAGLOs basis set $H[1s(0.0)]$ gave $E = -1.1181$ au while optimized SCM-HAGLOs basis set $H[1s(-0.1)]$ gave $E = -1.1259$ au. Double zeta basis set $H[1s(-0.10,-0.30)]$ gave $E = -1.1264$ au, and triple zeta basis set $H[1s(0.0,-0.1562,-0.3125)]$ gave $E = -1.1275$ au. Atomic coordinates(x, y, z) for the two hydrogen atoms were (0, 0 0.7) and (0, 0 -0.7). Adding floating $1s(0.9)$ orbitals positioned at centers (0,0, 0.35) and (0,0, -0.35) to the minimal basis set $H[1s(-0.1)]$ gave $E = -1.1284$ au which was better than energies obtained with triplezeta basis sets. For H_2 bench marking purposes use of G98W program suite with basis set STO-3G gave $E = -1.1167$ au; basis set 3-21G gave $E = -1.1229$ au; basis set 6-31G gave $E = -1.1267$ au; and basis set 6-311G gave $E = -1.1280$ au.

5.2.2 Diatomic Lithium: The molecule has bond length $R_{LiLi} = 5.049$ au, Huber and Herzberg(1979). Minimal basis $Li[1s(0.28)2s(1.08)]$ gave $E = -14.7755$ au. Addition of $2p_z$ gave basis set $Li[1s(0.28)2s(1.08)2p_z(1.29)]$ and $E = -14.7845$ au. However, deleting the $2p_z$ orbital on each Li atom and placing one floating $1s(0.343)$ orbital at the mid-point of the Li-Li bond gave an $E = -14.8095$ au. Program suite G98W with STO-3G basis set gave $E = -14.6387$ au, with basis set 3-21G gave -14.7686 au, and with basis set 4-31G gave $E = -14.8601$ au.

5.2.3 Boron monohydride

BH has bond length $R_{BH} = 2.347$ au, Huber and Herzberg(1979). With H at the origin of the Cartesian coordinate system and B positioned 2.347 au along the positive z axis, minimal basis set $H[1s(-0.1)]B[1s(0.3)2s(1.1)2p_z(2.0)]$ gave $E = -24.9071$ au, partial atomic charge $\delta_H = -0.298$ au and dipole moment $M = -0.113$ au. Double zeta basis set $H[1s(-0.1, -0.2)]B[1s(0.2, 0.4)2s(1.8, 2.4)2p_z(1.7, 2.3)]$ gave $E = -25.0269$ au, $\delta_H = -0.238$ au and dipole moment $M = -0.439$ au. Using G98W program package and basis set STO-3G gave $E = -24.7525$ au, $\delta_H = -0.135$ and dipole moment $M = -0.369$ au. Basis set 3-21G gave $E = -24.9767$ au, $\delta_H = -0.127$ and $M = -0.613$ au. Basis set 4-31G gave $E = -25.0769$ au, $\delta_H = -0.153$ au and $M = -0.538$ au. Calculations with electronegativity gave $\delta_H = -0.024$ au.

5.2.4 Diatomic Nitrogen: The bond length $R_{NN} = 2.0675$ au, Huber and Herzberg (1979). Minimum basis set $N[1s(0.286)2s(1.533)2p_x(3.336)2p_y(3.336)2p_z(2.546)]$ gave energy $E = -108.0886$ au. Addition of one floating $1s(0.286)$ orbital at bond mid-point improved the energy to -108.1879 au. Program suite G98W with STO-3G basis set gave $E = -107.1645$ au, with 3-21G basis set gave -107.9828 au and with 4-31G basis set gave -108.4194 au.

5.2.5 Diatomic Fluorine: The bond length $R_{FF} = 2.711$ au, Huber and Herzberg (1979). Minimal basis set $F[1s(0.286)2s(1.533)2p_x(3.95)2p_y(3.95)2p_z(3.95)]$ gave energy $E = -196.6047$ au. Addition of Float $[1s(1.230)$, bond mid-point(0.0, 0.0, 0.0)] gave $E = -196.9294$ au. Addition of two more floating orbitals, one $1s(1.23)$ at center 0.0,0.0,1.0) and the other $1s(1.23)$ at center 0.0,0.0,-1.0) improved the energy to -196.9426 au. Program suite G98W with basis set STO-3G gave $E = -195.9609$ au, with basis set 3-21G gave $E = -197.6432$ au and with basis set 4-31G gave $E = -198.4580$ au.

5.2.6 Hydrogen fluoride: The bond length $R_{\text{HF}} = 1.733$ au, Huber and Herzberg (1979). Hydrogen was positioned at the origin of the Cartesian coordinate system and fluorine positioned at 1.733 Bohr away on positive Z axis; this allowed the sign of the dipole moment to be the same as the sign of partial atomic charge on the F atom. Minimal basis set F[1s(0.4)2s(1.95)2px(4.05)2py(4.05)2pz(4.05)]H[1s(-0.3)] gave energy $E = -99.0046$ au, dipole moment $M = -0.5462$ au and partial atomic charge $\delta_{\text{H}} = 0.1409$ au. Addition of one floating 1s orbital at the bond mid-point and extending the basis to multi-zeta level gave improved basis set F[1s(0.4, 1.0)2s(2.0, 3.0, 4.0)2px(4.05)2py(4.05)2pz(2.0, 3.0, 4.0)]H[1s(-0.3, -0.6)]Float[1s(1.03, bond midpoint)] and $E = -99.4155$ au, dipole moment $M = -0.3706$ au, and partial atomic charge $\delta_{\text{H}} = 0.2544$ au. Benchmarking with program suite G98W and basis set STO-3G gave $E = -98.5708$ au, $\delta_{\text{H}} = 0.2110$ au and dipole moment $M = -0.507$ au. Basis set 3-21G gave $E = -99.4598$ au, $\delta_{\text{H}} = 0.4533$ au and $M = -0.848$ au. Basis set 4-31G gave $E = -99.8873$ au, $\delta_{\text{H}} = 0.4785$ au and $M = 0.898$ au. Calculations with electronegativity gave partial atomic charge $\delta_{\text{H}} = 0.3115$ au.

5.2.7 Lithium hydride: The bond distance $R_{\text{LiH}} = 3.015$ au, Huber and Herzberg (1979). Minimal basis set Li [1s(0.28)2s(0.74)] H[1s(0.18)] gave $E = -7.9412$ au, dipole moment $M = 2.577$ au and atomic charge $\delta_{\text{H}} = -0.707$ au. Addition of $2p_z$ with further optimization gave basis set Li [1s(0.28)2s(0.62)2pz(0.62)]H [1s(0.16)] with $E = -7.9528$ au, dipole moment $M = 2.540$ au and partial atomic charge, $\delta_{\text{H}} = -0.707$ au. Extending the basis set to multi-zeta level gave Li[1s(-2,-1,0,1,2)2s(-2,-1,0,1,2)2pz(-2,-1,0,1,2)]H[1s(0.0,-0.1562,-0.3125)], $E = -7.9825$ au, dipole moment $M = 2.330$ au and $\delta_{\text{H}} = -0.354$ au. This partial atomic charge is consistent with partial charge $\delta_{\text{H}} = -0.355$ au calculated using Li and H electronegativity. G98W program package with basis set STO-3G gave $E = -7.8620$ au, $\delta_{\text{H}} = +0.016$ au and dipole moment $M = 1.911$ au. Basis set 3-21G gave $E = -7.9296$ au, $\delta_{\text{H}} = -0.219$ au and $M = 2.319$ au. Basis set 4-31G gave $E = -7.9771$ au, $\delta_{\text{H}} = -0.263$ au and $M = 2.315$ au. Basis set 6-31G gave $E = -7.9793$ au and $\delta_{\text{H}} = -0.263$ au. Basis set 6-311G gave $E = -7.9846$ au and $\delta_{\text{H}} = -0.398$ au.

5.2.8 Lithium oxide:

Li_2O is linear symmetric with two Li-O bonds and $R_{\text{LiO}} = 3.07265$ au, Koput and Peterson (2002). Multi-zeta basis set Li[1s(0.3094,2.0)2s(1.7208)2pz(1.2)] O[1s(0.3421,1.0,3.0)2s(1.5)2px(4.0)2py(4.0)2pz(4.0)] gave $E = -88.8835$ au with $\delta_{\text{Li}} = 0.3789$ au. Electronegativity considerations gave $\delta_{\text{Li}} = 0.5556$ au. G98W program suite with basis set STO-3G gave $E = -88.5705$ au and $\delta_{\text{Li}} = 0.111$ au, and with basis set 3-21G gave $E = -89.2857$ au and $\delta_{\text{Li}} = 0.400$ au.

5.2.9 Beryllium hydride:

The molecule is linear symmetric with two Be-H bonds and $R_{\text{HBe}} = 1.7165$ au, Koput and Peterson (2006). Minimal basis set Be [1s(0.3)2s(1.3)]H[1s(-0.05)] gave $E = -15.3933$ au and $\delta_{\text{H}} = -0.7673$ au. Including $2p_z$ in the basis set Be [1s(0.3)2s(0.9)2pz(0.9)]H[1s(-0.05)] gave $E = -15.5151$ au and $\delta_{\text{H}} = -0.4612$ au. Using triple zeta basis set Be[1s(0.0, 0.286, 0.572)2s(0.0,0.767,1.533)2pz(0.0,1.273,2.546)]H[1s(0.0,-0.1562,-0.3125)] gave $E = -15.5579$ au and $\delta_{\text{H}} = -0.2371$ au. Electronegativity calculations gave $\delta_{\text{H}} = -0.167$ au. Benchmarking with G98W program suite and STO-3G basis set gave $E = -15.3507$ au and $\delta_{\text{H}} = -0.1005$ au; with 3-21G basis set gave $E = -15.4638$ au and $\delta_{\text{H}} = -0.0258$ au; and with 4-31G basis set gave $E = -15.5477$ au and $\delta_{\text{H}} = -0.0341$ au.

5.2.10 Boron trihydride: BH_3 is a trigonal planar molecule with $R_{\text{BH}} = 2.31$ au, M. E. Schwartz and L. C. Allen (1970). Minimal basis set Be[1s(0.3)2s(1.1)2px(2.0)2py(2.0)]H[1s(-0.1)] gave $E = -26.3151$ au with $\delta_{\text{H}} = -0.1902$ au, and double zeta basis B[1s(0.2,3.0)2s(0.0,1.0)2px(0.0,1.0)2py(0.0,1.0)]H[1s(0.0,-0.3)] gave $E =$

-26.3207 au and $\delta_{\text{H}} = -0.3254$ au. Schwartz and Allen (1970) studied BH_3 using basis sets determined by Whitten (1966) for first row atoms and obtained $E = -26.3546$ au. Using G98W program suite and basis set STO-3G gave $E = -26.0636$ au and $\delta_{\text{H}} = -0.0652$ au; basis set 3-21G gave $E = -26.2356$ au and $\delta_{\text{H}} = -0.0403$ au; and basis set 4-31G gave $E = -26.3472$ au and $\delta_{\text{H}} = -0.0759$ au. Electronegativity determined partial atomic charge was $\delta_{\text{H}} = -0.0244$ au.

5.2.11 Ammonia: Ammonia molecule has trigonal pyramidal geometry, Herzberg (1966). Calculations were done for angle $\angle\text{HNH} = 106.7^\circ$ and bond length $R_{\text{NH}} = 1.9120$ Bohr. Minimal basis set $\text{N}[1\text{s}(0.25)2\text{s}(2.5)2\text{p}_x(2.5)2\text{p}_y(2.5)2\text{p}_z(2.5)]\text{H}[1\text{s}(-0.03)]$ gave energy $E = -55.5681$ au. Further screening constants optimization gave basis set $\text{N}[1\text{s}(0.25)2\text{s}(1.4)2\text{p}_x(3.2)2\text{p}_y(3.2)2\text{p}_z(3.2)]\text{H}[1\text{s}(-0.2)]$, $E = -55.8454$ au, dipole moment $M = -0.5685$ au and partial atomic charge $\delta_{\text{H}} = 0.0477$ au. G98W program suite with basis STO-3G gave $E = -55.45402$ au, $\delta_{\text{H}} = 0.1568$ au and dipole moment $M = -0.7029$ au; with basis set 3-21G gave $E = -55.87048$ au, $\delta_{\text{H}} = 0.2793$ au and dipole moment $M = -0.8552$ au; and with basis set 4-31G gave $E = -56.10248$ au, $\delta_{\text{H}} = 0.2982$ au and dipole moment $M = -0.9043$ au. Calculations using electronegativity gave $\delta_{\text{H}} = 0.176$ au.

5.2.12 Water: H_2O is a bent symmetric molecule, Herzberg (1966). Calculations were made for valence angle $\angle\text{HOH} = 105.2^\circ$ and bond length $R_{\text{OH}} = 1.8066$ Bohr. Minimal basis set $\text{O}[1\text{s}(0.3)2\text{s}(2.1)2\text{p}_x(2.9)2\text{p}_y(3.75)2\text{p}_z(3.75)]\text{H}[1\text{s}(-0.4)]$ gave $E = -75.2716$ au, dipole moment $M = -0.7212$ au and $\delta_{\text{H}} = 0.1237$ au, and multi-zeta basis set $\text{O}[1\text{s}(0.1710,0.3421,0.6842)2\text{s}(0.70168,3.5084,1.7542)2\text{p}_x(3.5468)2\text{p}_y(3.5468)2\text{p}_z(3.5468)]\text{H}[1\text{s}(0.3125,0.1562,0.0,-0.1562)]$ gave $E = -75.6295$ au, dipole moment -0.7211 au and $\delta_{\text{H}} = 0.1521$ au. G98W program suite with STO-3G basis set gave -74.9625 au, $\delta_{\text{H}} = 0.1843$ au and dipole moment $M = -0.6778$ au; basis set 3-21G gave $E = -75.5855$ au, $\delta_{\text{H}} = 0.3649$ au and dipole moment $M = -0.9538$ au; and basis set 4-31G gave $E = -75.9076$ au, $\delta_{\text{H}} = 0.3933$ au and dipole moment $M = -1.0214$ au. Calculations with electronegativity gave $\delta_{\text{H}} = 0.250$ au.

5.3 Organic molecules

Energy and electrical charge parameters were calculated for methane, ethane, ethene, ethyne, formaldehyde and carbon dioxide.

5.3.1 Methane: CH_4 has tetrahedral geometry, Herzberg (1966). With bond length $R_{\text{CH}} = 2.05$ au and multi-zeta basis set $\text{C}[1\text{s}(0.25)2\text{s}(1.3,1.7)2\text{p}_x(2.8,3.2)2\text{p}_y(2.8,3.2)2\text{p}_z(3.0)]\text{H}[1\text{s}(-0.15)]$ the energy $E = -40.0190$ au and $\delta_{\text{H}} = 0.0953$ au. Grimmelmann and Chesick (1971) obtained $E = -39.7956$ au with a small Gaussian lobe 1s, 2s, 2p optimized minimal basis set. This energy compared well with $E = -39.7269$ au from G98W program suite and basis set STO-3G, $E = -39.9769$ au from basis set 3-21G and $E = -40.1397$ au from basis set 4-31G. Partial atomic charge $\delta_{\text{H}} = 0.087$ au was calculated using Pauling's electronegativity values. G98W program suite calculations gave $\delta_{\text{H}} = 0.065$ au from STO-3G basis set, $\delta_{\text{H}} = 0.198$ au from 3-21G basis set and $\delta_{\text{H}} = 0.153$ au from 4-31G basis set.

5.3.2 Ethane: C_2H_6 has staggered and eclipsed conformations with near tetrahedral geometry at each carbon center, Herzberg (1966). Minimal basis set $\text{C}[1\text{s}(0.25)2\text{s}(1.3)2\text{p}_x(3.0)2\text{p}_y(3.0)2\text{p}_z(3.0)]\text{H}[1\text{s}(-0.15)]$ was used with both conformations and $R_{\text{CH}} = 2.052$ Bohr, $R_{\text{CC}} = 2.9059$ Bohr, methyl group valence angle $\angle\text{HCH} = 108.18^\circ$, $\angle\text{HCC} = 110.73^\circ$, and dihedral $\angle\text{HCC,H}' = 120.0^\circ$. For staggered ethane $E = -78.8816$ au and for eclipsed ethane $E = -78.8772$ au. This gave a rotation energy barrier of 2.75 kcal/mole. G98W program suite calculations gave for staggered ethane $E = -78.3062$ au from STO-3G basis set, $E = -78.7939$ au from 3-21G

basis set and $E = -79.1158$ au from 4-31G basis set. For eclipsed ethane the energies were $E = -78.3014$ au from basis set STO-3G, $E = -78.7892$ au from basis set 3-21G and $E = -79.1112$ au from basis set 4-31G. Rotation barriers were 3.00 kcal(STO-3G), 2.95 kcal(3-21G), 2.90 kcal(4-31G) and 2.93 kcal(6-31G). Using the best SCM-HAGLOs basis set gave for staggered ethane partial atomic charge $\delta_H = 0.086$ au and for eclipsed ethane $\delta_H = 0.087$ au. Both are in good agreement with the $\delta_H = 0.087$ au derived from electronegativity values. Using G98W program suite for staggered ethane the partial atomic charges δ_H were 0.058 au for STO-3G basis set, 0.200 au for 3-21G basis set, 0.150 au for 4-31G basis set and in eclipsed ethane the atomic charges were $\delta_H = 0.059$ au for STO-3G basis set, $\delta_H = 0.203$ au for 3-21G basis set and $\delta_H = 0.154$ au for 4-31G basis set.

5.3.3 Ethene: $H_2C=CH_2$ is a planar symmetric molecule, Herzberg(1966). Bond lengths $R_{CC} = 2.55102$ Bohr, $R_{CH} = 2.2236$ Bohr and valence angle $\angle HCH = 117^\circ$ were used with basis set $C[1s(0.25)2s(1.3)2px(3.0)2py(3.0)2pz(3.0)]H[1s(-0.15)]$. Calculation gave energy $E = -77.6607$ au and partial atomic charge $\delta_H = 0.0804$ au. Using G98W programs and basis set STO-3G gave $E = -77.0706$ au and $\delta_H = 0.064$ au; basis set 3-21G gave $E = -77.5995$ au and $\delta_H = 0.2142$ au; and basis set 4-31G gave $E = -77.9207$ au and $\delta_H = 0.1641$ au.

5.3.4 Ethyne: C_2H_2 is a linear symmetric molecule, HCCH, Herzberg(1966). Using $R_{CC} = 2.2828$ Bohr, $R_{CH} = 1.9994$ Bohr, and basis set $C[1s(0.25)2s(1.3)2px(3.0)2py(3.0)2pz(3.0)]H[1s(-0.15)]$ gave energy $E = -76.4420$ au and partial atomic charge $\delta_H = 0.110$ au. Using G98W program suite with basis set STO-3G gave $E = -75.8562$ au and $\delta_H = 0.109$ au; with basis set 3-21G gave $E = -76.3947$ au and $\delta_H = 0.333$ au; and with basis set 4-31G gave $E = -76.7100$ au and $\delta_H = 0.299$ au.

5.3.5 Formaldehyde: H_2CO is a planar symmetric molecule, Herzberg(1966). Using $R_{OC} = 2.28266$ Bohr, $R_{CH} = 2.0825$ Bohr, valence angle $\angle OCH = 121.1^\circ$ and minimal basis set $C[1s(0.25)2s(1.3)2px(3.0)2py(3.0)2pz(3.0)]O[1s(0.3)2s(3.0)2px(4.0)2py(4.0)2pz(4.0)]H[1s(-0.15)]$ gave energy $E = -112.5435$ au, Mulliken partial atomic charges $\delta_H = 0.088$ au, $\delta_C = 0.145$ au and $\delta_O = -0.320$ au and dipole moment $M = -1.272$ au. Using G98W procedures with basis set STO-3G gave $E = -112.3525$ au, $\delta_H = 0.060$ au, $\delta_C = 0.072$ au, $\delta_O = -0.192$ au and dipole moment $M = -0.597$ au. With basis set 3-21G the $E = -113.2200$ au, $\delta_H = 0.179$ au, $\delta_C = 0.124$ au, $\delta_O = -0.482$ au and dipole moment $M = -1.041$ au. Partial atomic charges from electronegativity were $\delta_H = 0.087$ au, $\delta_C = 0.159$ au and $\delta_O = -0.333$ au.

5.3.6 Carbon dioxide:

CO_2 is a linear non-polar symmetric, Herzberg(1966). Using $R_{OC} = 2.1961$ au and minimal SCM-HAGLOs basis set $C[1s(0.25)2s(1.3)2px(3.0)2py(3.0)2pz(3.0)]O[1s(0.3)2s(2.0)2px(4.0)2py(4.0)2pz(4.0)]$ gave $E = -185.1422$ au, Mulliken partial atomic $\delta_C = 0.578$ au and $\delta_O = -0.289$ au. G98W programs and STO-3G basis set gave $E = -185.0653$ au, $\delta_C = 0.464$ au and $\delta_O = -0.232$ au. With basis set 3-21G the $E = -186.5611$ au, $\delta_C = 1.083$ au and $\delta_O = -0.541$ au. Electronegativity based partial atomic charges were $\delta_C = 0.666$ au and $\delta_O = -0.333$ au.

6. Conclusion

This study confirmed Whitten's hypothesis that Hydrogen Atom Gaussian Lobe Orbital Expansions (HAGLOs) can provide useful basis functions for Self-Consistent-Field Hartree-Fock molecular orbital energies and property calculations.

Accuracy obtained for electronic energy for many-electron atoms and molecules in many cases—He, Be, Ne, H₂, Li₂, BH, N₂, F₂, LiH, HF, BeH₂, BH₃, Li₂O, H₂O, NH₃, CH₄, C₂H₆, C₂H₄, C₂H₂, H₂CO and CO₂ exceeded that obtained using basis sets STO-3G and often 3-21G but not 4-31G. Small but significant energy improvements were obtained using multi-zeta and floating 1s atomic orbitals at bond mid-points.

Calculated dipole moments and Mulliken partial atomic charges were consistent with values determined using G98W program suite and STO-3G, 3-21G and 4-31G basis sets as well as obtained using simple electronegativity, ionic character and bond polarization concepts, but for diatomic BH molecule the direction of the dipole moment was determined by the lone pair of electrons on B rather than by the small polarity of the H-B bond.

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