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FSGO Calculations of Geometries and Electronic Structures of "Argon-Core" Third-Row Hydrides

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A series of *ab initio* calculations using the FSGO method and including geometry optimizations are reported for the lowest singlet states of KH, CaH_2, ScH, ScH_3, TiH_4, VH_3, CrH_2, and MnH. Both core and valence orbital exponents are shown to vary systematically. The description of the M-shell electrons is uneven, in that p orbitals are more accurately described than the $3s$ orbital. The bond angles of VH_3 and CrH_2 are predicted to be unexpectedly large (94.1° and 103.1°, respectively). Orbital energies, bond lengths and angles, dipole moments, and electron populations are reported for all systems.

Key words: FSGO Calculations – Third-row hydrides

1. Introduction

Numerous theoretical calculations of the properties of first- and second-row hydrides in the gaseous state have been performed [1]. In conjunction with the extensive spectral studies reported in recent years, the lowest singlet states of these systems are, for the most part, well-characterized. The same cannot be said for the third-row hydrides, particularly those which contain a transition metal atom. These molecules have low volatilities and stabilities, and are therefore not amenable to standard spectral analyses. At the same time, the number of electrons and the necessity of including d orbitals in the LCAO basis set makes conventional *ab initio* calculations – especially those which optimize geometries – rather expensive. Consequently, few such computations have been reported [2–8], and many species have not been studied either experimentally or theoretically.

We now report the results of a series of geometry-optimized calculations using the FSGO method on the lowest singlet state of some third-row hydrides. The molecules studied, which possess $1s^2 2s^2 2p^6 3s^2 3p^6$ core electron systems, are KH, CaH_2, ScH, ScH_3, TiH_4, VH_3, CrH_2, and MnH. The FSGO method is a particularly attractive computational tool in this instance, since 1) the method lends itself to rapid geometry optimizations [9, 10], and 2) the method does not require any special treatment for "d-orbital" valence electrons. The FSGO procedure represents each pair of electrons in a closed-shell atom or molecule by a floating spherical Gaussian orbital, with no direct reference to atomic s, p, or d functions. In addition, Frost and coworkers and others have shown that the FSGO method predicts with reasonable accuracy the nuclear and electronic

Table 1. Orbital Exponents

	Ar	KH	CaH_2	ScH	ScH_3	TiH_4	VH_3	CrH_2	MnH
K shell	97.672	109.487	121.765	134.927	134.966	148.791	163.355	178.507	194.398
L shell	6.603	7.646	8.767	9.962	9.960	11.260	12.627	14.067	15.617
M shell	0.430	0.549	0.686	0.824	0.834	0.997	1.169	1.361	1.568
Bonding		0.144	0.160	0.176	0.187	0.217	0.228	0.234	0.269
Lone pair				0.075			0.131	0.146	0.179

structures of many molecules [11, 12] including the first- and second-row hydrides [13, 14].

Previous FSGO calculations appear to have been restricted to molecules containing first- or second-row atoms (and hydrogen and helium); thus, the computations reported here are the first to extend the method to third-row species. Consequently, the computations are interesting for what they reveal about FSGO wavefunctions as well as for specific information about individual molecules. We have, therefore, analyzed our results in terms of the quality of the FSGO representation of the core electron systems and the size, location, and energy of valence orbitals, in addition to the nature of the optimized molecular structures.

Information concerning computational techniques and our computer program has been given elsewhere [12].

2. Core Systems

The argon-like core systems were approximated by a single (1*s*) Gaussian centered at the metal nucleus, four *L*-shell Gaussians located at the vertices of an inner tetrahedron, and four *M*-shell Gaussians at the vertices of an outer tetrahedron inverted with respect to the first. The core orbital exponents were optimized in each of the molecular calculations, and results are shown in Table 1. As expected, the exponents vary systematically, and given a few members of the sequence it is relatively easy to estimate core exponents for the others. Furthermore, the core exponents are hardly affected by molecular environment. The *K* and *L* shell exponents of ScH and ScH_3, for example, are virtually identical and the *M* shell exponents differ by less than two per cent. Thus, core exponents could be frozen at these values in future calculations on systems containing these metals with little loss of accuracy and a considerable reduction in computer time.

If the sizes of the *L* or *M* shell tetrahedra are allowed to vary, they tend to coalesce on the nucleus. To avoid this problem, we have frozen the inner tetrahedron at a distance of 0.01732 bohr from the metal nucleus, as suggested by Frost [14], and located the outer tetrahedron at a distance of 0.0300 bohr. Test calculations on the argon atom revealed that a collapsing of the outer tetrahedron would decrease the energy by only ~ 0.02 hartree (out of a total of 456.0601 hartree). In light of earlier work [11], it seems very unlikely that a variation in the *M*-shell distance would significantly affect molecular properties.

The FSGO's of the various molecules were transformed to molecular orbitals

Table 2. Orbital Energies[a]

Ar[b]	KH	CaH_2	ScH_3[c]
$1s$ −101.409 (−118.610)	1σ −114.420	1σ −128.252	$1a_1$ −142.891 (−166.102)
$2s$ − 9.240 (− 12.322)	2σ − 10.929	2σ − 12.786	$2a_1$ − 14.783 (− 19.058)
$2p$ − 6.930 (− 9.571)	1π − 8.572	1π − 10.372	$3a_1$ − 12.309 (− 15.761)
$3s$ − 0.589 (− 1.277)	3σ − 8.571	3σ − 10.371	$1e$ − 12.309 (− 15.760)
$3p$ − 0.289 (− 0.591)	4σ − 0.833	4σ − 1.079	$4a_1$ − 1.352 (− 2.672)
	5σ − 0.595	2π − 0.932	$2e$ − 1.285 (− 1.713)
	2π − 0.591	5σ − 0.931	$5a_1$ − 1.285 (− 1.719)
	6σ − 0.135	6σ − 0.243	$3e$ − 0.307 (− 0.379)
		7σ − 0.236	$6a_1$ − 0.269 (− 0.431)

ScH	TiH_4	VH_3	CrH_2	MnH
$1\sigma_1$ −142.880	$1a_1$ −158.331	$1a_1$ −174.650	$1a_1$ −191.794	1σ −209.729
2σ − 14.795	$2a_1$ − 16.892	$2a_1$ − 19.247	$2a_1$ − 21.759	2σ − 24.367
1π − 12.291	$1t_2$ − 14.396	$3a_1$ − 16.683	$1b_1$ − 19.136	1π − 21.726
3σ − 12.291	$2t_2$ − 1.669	$1e$ − 16.683	$3a_1$ − 19.134	3σ − 21.724
4σ − 1.474	$3a_1$ − 1.627	$4a_1$ − 2.135	$1b_2$ − 19.134	4σ − 3.143
2π − 1.261	$3t_2$ − 0.361	$2e$ − 2.119	$4a_1$ − 2.622	2π − 3.142
5σ − 1.261	$4a_1$ − 0.269	$5a_1$ − 2.075	$2b_2$ − 2.619	5σ − 2.898
6σ − 0.270		$6a_1$ − 0.395	$2b_1$ − 2.619	6σ − 0.493
7σ + 0.026		$3e$ − 0.380	$5a_1$ − 2.502	3π − 0.242
		$7a_1$ + 0.086	$6a_1$ − 0.447	7σ + 0.260
			$3b_2$ − 0.442	
			$3b_1$ − 0.198	
			$7a_1$ + 0.175	

[a] Energies are in hartrees.

[b] Values in parentheses are Hartree-Fock values from Ref. [15].

[c] Values in parentheses are LCAO-SCF values from Ref. [2].

so that orbital energies could be obtained and used to further assess the quality of the wavefunctions. FSGO orbital energies are reported in Table 2. Comparable results from larger basis set *ab initio* calculations are available for Ar and ScH_3 [2, 15]. In these cases the ordering of "core" molecular orbitals is correct (the $2e$ and $5a_1$ orbitals of ScH_3 are nearly degenerate), but the quality of the description is uneven. The $3s$ orbital ($4a_1$ in ScH_3) is relatively poorly described as compared to the $3p$ ($2e$ or $5a_1$ in ScH_3). The relative inaccuracy of the $3s$ orbital increases throughout the sequence; in TiH_4 and subsequent molecules the orbital which is primarily $3s$ in character ($3a_1$ for TiH_4) is higher in energy than the $3p$-like ($2t_2$) orbitals. This weakness of the FSGO description might have structural ramifications if it also affects the admixture of $4s$ and $4p$ orbitals in bonding situations.

3. Valence Orbitals

Optimized values for bonding and lone pair orbital exponents are included in Table 1. They show the expected systematic variation with respect to nuclear charge and bond length, and we anticipate that one could now readily estimate near-optimal exponents for species such as CaH^-, TiH_2, or VH. Molecular properties and electronic structures are sensibly insensitive to the orientation of valence orbitals with respect to core tetrahedra. The results cited here were obtained using the following orientations: KH, bond orbital located on a radial extension through an *L* shell vertex; CaH_2, bond orbitals arranged symmetrically on opposite sides of Ca nucleus in a plane defined by the nucleus and two *L* shell vertices; ScH, bonding orbital as in KH and lone pair orbital on opposite side of Sc; ScH_3, bonding orbitals at 120° intervals in plane defined by Sc nucleus and two *L* shell vertices, with one bonding orbital on the bisector of an *L* shell "orbital angle"; TiH_4, bond orbitals on radial extensions of the inner tetrahedron; VH_3, bonding orbitals in a plane as in ScH_3, which has been displaced perpendicularly, lone pair orbital below the vanadium nucleus; CrH_2, bonding orbitals symmetrically arranged in a plane defined by two inner vertices and nucleus, and lone pair orbitals similarly located in plane of nucleus and other two inner vertices; MnH, bond orbital along a bisector of an *L* shell "orbital angle", lone pair orbitals in a plane on opposite side of the Mn nucleus. In CrH_2 and MnH, the locations of the lone pair orbitals were suitably restricted to prevent coalescense.

The valence orbital energies of KH, CaH_2, ScH_3, and TiH_4, as presented in Table 2, are not surprising and are presumably of acceptable accuracy. The $3e$ and $6a_1$ orbitals of ScH_3 are inverted as compared to the minimum basis set LCAO-MO-SCF result of Stevenson and Lipscomb [2], but the differences between the orbital energies are small in both calculations. What is rather striking, however, is that in all the systems which contain lone-pair electrons there is one molecular orbital with a positive orbital energy. The 7σ orbital of ScH is only marginally positive, $\varepsilon_{7\sigma}=0.026$ h, but this value increases through the sequence and for MnH we find $\varepsilon_{7\sigma}=0.260$ h. Positive orbital energies obtained in this manner suggest that either (a) these systems, in the closed shell singlet states, are indeed marginally stable or even unstable with respect to their positive ions, or (b) FSGO valence orbitals of these systems are not sufficiently accurate to yield orbital energies. There is a precedent for (b), in that a previous FSGO calculation [12] on Li_2O yielded positive orbital energies [although the geometry was accurately predicted]. Further calculations employing more accurate wavefunctions would thus be desirable.

The species examined here are usually regarded as being primarily ionic, and our results support that interpretation. Bond orbitals were found to be located near the protons, on the bond axes. Following Blustin and Linnett [16], the bond orbital locations can thus be specified by orbital multiplers, where orbital multiplier = distance from heavy atom to bond orbital/bond length. As shown in Table 3, these multipliers decrease regularly throughout the sequence, and thus lend themselves to analyses concerning electron distributions or the ionic characters of their respective bonds. The simplest procedure of this type would be to apportion each pair of bonding electrons between the metal and hydrogen according to its multiplier, and thereby define electron population of atoms in molecules. Populations generated in this manner for first- and second-row diatomics [17], including hydrides, agree well with populations determined by Bader and co-

Table 3. Charge Distributions[a]

XH_n	Multiplier[b]	$N(X)$[c]	$N(H)$[c]
KH	0.951	18.098	1.902
CaH_2	0.902	18.392	1.804
ScH	0.884	20.232	1.768
ScH_3	0.864	18.816	1.728
TiH_4	0.830	19.360	1.660
VH_3	0.800	21.200	1.600
CrH_2	0.735	23.060	1.470
MnH	0.700	24.600	1.400

[a] Bonding electrons are divided according to orbital multipliers.
[b] Multiplier = Distance from metal to bond orbital/bond length.
[c] Number of electrons associated with an atom.

workers [18–20] using zero flux surfaces. Electron populations for third-row hydrides are included in Table 3.

4. Molecular Structures

Total energies for the molecules in our study are presented in Table 4. As in previous computations [11], FSGO energies appear to be ~85% of Hartree-Fock values. Using FSGO energies for ScH, ScH_3, and H_2 ($E = -0.9559$ h), one predicts that ScH_3 will be unstable with respect to decomposition to ScH and H_2 by 25 kcal. (The singlet state is apparently the ground state of ScH [6]). Although comparable quantitative data is unavailable, the qualitative stability prediction is reasonable since vapor phase ScH has been detected [21] but ScH_3 has not, and attempts to prepare solid ScH_3 have not been successful [22].

Bond lengths, bond angles, and dipole moments are reported in Table 5. In the case of KH, theoretical and experimental bond lengths agree to within 1.5%. In accord with FSGO calculations on first- and second-row hydrides with electropositive atoms [13, 14], the predicted KH bond is slightly overlong. This should also be true for the other hydrides. In the sequence BH, AlH, and ScH, for example, we find that BH and AlH are predicted to be 0.16 and 0.12 bohr longer than their respective Hartree-Fock bond lengths. This suggests that the actual singlet ScH bond length should be ~3.9 bohr; surprisingly, this is considerably larger than the value of 3.34 bohr calculated by Scott and Richards [6].

Computed bond angles confirm the expected linearity of CaH_2, planarity of ScH_3, and tetrahedral nature of TiH_4. The results for VH_3 and CrH_2 were unanticipated, however, in that bond angles were respectively larger than the FSGO values for second-row hydrides. The VH_3 angle was 94.1° as compared to 90.9° for PH_3, and the CrH_2 angle was computed to be 103.1° compared to 87.7° for H_2S. In a series such as H_2O, H_2S, H_2Se, H_2Te, bond angles monotonically decrease; our calculations suggest that the same trend may not hold for H_2O, H_2S, H_2Cr, H_2Mo. Further, the particularly large angle for H_2Cr is not consistent with the analysis of FSGO bond angles developed by Blustin and Linnett [23], in that they suggest a bias towards "natural" bond angles of 90°. Perhaps the

Table 4. Total Energies[a]

System	Energy
Ar	-456.0601 $(-526.8171)^{b}$
KH	-520.0352
CaH_2	-588.7854
ScH	-661.4219
ScH_3	-662.3381 $(-779.7923)^{c}$
TiH_4	-740.7798
VH_3	-823.0654
CrH_2	-910.3020
MnH	-1002.6453

[a] Energies are in hartree, 1 h $=4.398\times10^{-18}$ J.
[b] Hartree-Fock energy from Ref. [15].
[c] LCAO-SCF energy from Ref. [2].

Table 5. Optimized Molecular Structures[a]

Molecule	Bond Length	Bond Angle	Dipole Moment[b]
KH	4.303(4.241)[c]	–	-10.20
CaH_2	4.193	180.0	0.00
ScH	4.001	–	-2.40
ScH_3	3.783	120.0	0.00
TiH_4	3.503	109.5	0.00
VH_3	3.421	94.1	-0.98
CrH_2	3.257	103.1	0.18
MnH	3.028	–	0.10

[a] Bond lengths are in bohr, angles are in degrees, dipole moments are in Debye.
[b] $\mu<0$ implies a positive metal atom.
[c] Experimental value from: Herzberg,G.: Spectra of diatomic molecules. Princeton, New Jersey: Van Nostrand 1950.

polarized V–H and Cr–H bonds should be interpreted in terms of negatively charged hydrogens (Table 3) which repel each other and open up the bond angle.

It is difficult to evaluate quantitatively the predicted dipole moments, particularly since they are sensitive to geometries. The predicted moment for KH is presumably fairly accurate (as in the case of LiH [24]), but the FSGO description of lone-pair electrons in ScH, VH_3, CrH_2, and MnH may introduce larger errors. Again considering the BH, AlH, ScH sequence, for example, we note [17] that for BH $\mu_{\mathrm{FSGO}}-\mu_{\mathrm{Hartree\text{-}Fock}}=1.049$ debye and that for AlH the deviation is 1.024 debye. If an extrapolation is valid, the FSGO dipole moment for ScH should be in error by ~ 1.0 debye, and an estimated Hartree-Fock dipole moment would be 1.4 debye.

5. Concluding Remarks

The singlet states of some third-row hydrides have been examined with regard to orbital energies, population distributions, and nuclear geometries. Although

FSGO wavefunctions are not highly accurate, the results presented here are, in most cases, the first ones available for these species and should prove to be of at least semi-quantitative value.

In addition, the strengths and weaknesses of the FSGO method as applied to "argon-core" systems have been demonstrated. We suggest that for the most part the results are satisfactory, and that one could now perform economical calculations of certain properties of bioinorganic species which contain the metals K – Mn. Key elements of such future studies will include the use of standard metal core exponents which need not be reoptimized for each molecule, and the estimation of near-optimal exponents and multipliers for valence orbitals.

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