

## ***Ab initio* Studies, Using the FSGO-pseudopotential Method, of the Electronic Structure in Group IV Cluster Molecules $M(LH_3)_4$ ; M, L = C, Si, Ge**

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*Ab initio* FSGO-pseudopotential studies are reported for the nine molecules  $M(LH_3)_4$ ; M, L = C, Si, Ge. We report orbital energies, calculated geometries, bonding parameters, and predicted energies of reaction. Comparison with experimental data shows the results to be quite satisfactory. Comparison with the tetrahedral group IV solids affords some clues to the nature of the doped materials. The outstanding observation, from all parameters calculated, is the similarity of (Si, Ge) and their difference from carbon. Comments on possible stability of the compounds are ventured.

**Key words:** FSGO – Semiconductor cluster – Silicon cluster – Germanium cluster.

### **1. Introduction**

The chemistry of group IV is marked by particularly large changes on progressing from the lightest member (carbon, a predominantly tetravalent nonmetal) to the heaviest (lead, a predominantly divalent metal). Much of this change is already accomplished by the time Ge is reached. Perhaps the most significant difference between carbon and its heavier congeners lies in the much reduced tendency

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toward catenation, and the relative inability to form multiple bonds, exhibited by the four heavier elements. This manifests itself even in the element: graphite contains trigonal carbon, but no stable trigonal allotropes of the heavier elements are known. The simplest bonding description would impute these differences largely to the exceptional ability of carbon (and other first-row atoms) to form  $p\pi$  bonds. In silicon, the usual discussions of  $\pi$  bonding are given in terms of the participation of  $d$ -orbitals, and this explanation is commonly used [1, 2] to explain a wealth of experimental data, including acid strengths of silanols, planarity of trisilylamine, bond angles of near  $150^\circ$  in siloxanes, etc. The participation of Si  $d$ -functions has indeed tended to dominate the discussion of bonding differences between Si and C. This discussion tends to be somewhat ill-focused [3], since atomic orbitals are simply convenient in an LCAO description; they really have no physical significance per se in a molecular situation in which spherical symmetry is lost.

In this paper we present *ab initio* calculations, of FSGO-pseudopotential type, on the species  $M(LH_3)_4$ , where  $M, L = C, Si, Ge$ . These are studied both because of their intrinsic molecular interest and because they form a model for local sites in tetrahedral group IV semiconductors. The FSGO procedure is a quantum-mechanical version of Lewis' electron pair concept, and permits the electron pair, represented in a spherical Gaussian orbital to migrate freely about the nuclear framework until it finds the energetically most favorable geometry [4]. No atom-centered basis function of  $l > 0$  are ever employed, so that the question of  $d$ -orbital participation is never encountered. Thus the FSGO description does not contain any pi bonding, and, indeed, corresponds to an absolute minimum sigma basis. Since the basis functions are not atom-centered, the ( $sp$ ) versus ( $d$ ) question does not arise, although in principle the FSGO's could be expanded in an atom-centered set to estimate the  $d$  contribution. The bonding description is entirely local, within the bonding pairs. The present study was undertaken partly to see how well the FSGO procedure can describe these covalent-cluster species. We find, in accordance with our expectations, that the geometric results are quite good indeed, and that the orbital character can be subsumed in a very simple, purely covalent bonding description, in which the concept of  $d\pi$  bonding need never be considered. In addition, the nature of the bonding orbitals provides some insight into the electronic structure in mixed group IV tetrahedral semiconductor solids. In section 2, we outline the FSGO-pseudopotential procedure. Section 3 presents the results for geometries, orbital energies and electron distributions in  $M(LH_3)_4$ , and some remarks on the relevance of our studies for solid-state behavior.

## 2. The FSGO-pseudopotential Method

The FSGO (floating spherical Gaussian orbital) method was developed as a quantum-mechanical version of Lewis' bonding theory [4]. It is the simplest *ab initio* molecular electronic structure technique. It has been quite successful at calculation of geometries for a large number of covalent molecules, and has also

been applied to solids, to open-shell systems [5] to molecular fragment calculations [6], to predicted structures for unstable species [7], and even to large biomolecules [8]. For  $2N$ -electron closed-shell species of the type considered here, the FSGO wavefunction is simply a Slater determinant of doubly-occupied spherical Gaussian functions  $\phi_i$  of the form

$$\Psi = \left\| \begin{array}{c} \phi_{1\alpha}(1)\phi_{1\beta}(1)\phi_{2\alpha}(2) \cdots \cdots \phi_{N\beta}(2) \\ \vdots \cdots \cdots \cdots \phi_{N\beta}(2N) \end{array} \right\| \quad (1)$$

$$\phi_i(\mathbf{r}) = \left( \frac{2}{\pi\rho_i^2} \right)^{3/4} \exp \{ -(r-r_i)^2/\rho_i^2 \} \quad (2)$$

Here the orbital is centered at the point  $r_i$  with the orbital radius  $\rho_i$ . The  $r_i$  and  $\rho_i$  for the  $N$  differing  $\phi_i$ , as well as the nuclear geometry of the molecule, are treated as variational parameters. These values are optimized by a direct minimization of the energy

$$\delta \left\{ \frac{\langle \Psi | \mathbf{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right\} = 0 \quad (3)$$

as a function of all the parameters. Physically, the  $\phi_i$  simply represent electron pair bonds, lone pairs and the other constructs of Lewis theory [9]. Since the interpretation of FSGO results is always given in terms of valence behavior, and since the FSGO core representation does not ever enter directly into the valence description, we have recently developed a pseudopotential procedure for use in FSGO calculations [10]. This pseudopotential replaces the entire effect of the core on the valence by a one-body effective potential, of the type

$$V^{pp} = \sum_{\alpha} \sum_{L=0}^{L_{\max}} \sum_{M=-L}^{L_{\max}} \left| LM\alpha \right\rangle \langle LM\alpha | [V_L(r_{\alpha}) - V_{L_{\max}+1}(r_{\alpha})] + V_{L_{\max}+1}(r_{\alpha}) \quad (4)$$

Here  $\alpha$  labels the various nuclei, the projectors are onto the angular momentum states on each nucleus, and  $V_L(r_{\alpha})$  is a smooth function, conveniently given as a Gaussian over a power of  $r_{\alpha}$ . The cutoff at  $L_{\max}+1$  is made for reasons of computational convenience; we have found  $L_{\max}+1$  = the highest occupied angular momentum in the neutral atom to yield highly satisfactory results for small species [10, 11]; the form of Eq. (4) was suggested by the work of Melius, Kahn, and Goddard [12]. Values for  $V_L(r_{\alpha})$  are given in Table 1 of Ref. [11].

Local tetrahedral symmetry is assumed and bonding pairs are assumed centered on intermolecular lines, the  $M(\text{LH}_3)_4$  species contain six parameters to be variationally optimized in the valence-only FSGO calculation; these are the M—L and L—H bondlengths, and the  $\rho_i$  and  $r_i$  for the M—L and the L—H bonds. Our computations consist simply of minimizing the energy (3) with respect to these parameters. Full tetrahedral point-group symmetry holds for the calculated geometry.

### 3. Results

The computed geometries for the nine species  $M(LH_3)_4$  are presented in Table 1, along with experimental bondlength data. We also give the computed orbital radii  $\rho_i$  as well as the fractional position of the orbital centers along the M—L bonds. Table 2 presents calculated total energies (valence only) and orbital energies for the nine species.

The first observation to be made is that, as expected, the geometric parameters are quite good. Direct comparison with experiment is possible only for neopentane ( $C_5H_{12}$ ) tetramethylsilane and older data for tetramethylgermane. The bondlength deviation for the first two is less than two per cent; that for the germane is larger, but the error may lie in the experimental data (note the 0.055 Å disparity between the recent tetramethylsilane data of Beagley et al. and the electron diffraction results of Brockway (Table 1)). This gives us some confidence in the remaining geometric parameters.

The calculated geometries show some obvious trends. The clearest is the similarity between Ge and Si, and their large difference from C. For instance, our calculated atomic radii are 1.19, 1.13, and 0.76 Å for Ge, Si, and C, respectively; the difference between C and Si is six times that between Ge and Si. In the carbon-containing systems, the heteronuclear bondlengths are less than the sum of radii, but in the Ge—Si compounds they are greater. (It is tempting to attribute this to carbon's higher electronegativity.) In all cases, the L—M distance is greater for heavier L and lighter M than vice versa. This may simply be due to steric effects (crowding) about the smaller central atom. For Ge—Si, however, this difference is only 0.003 Å, while for C—Si and C—Ge it is 0.030 Å and 0.035 Å, respectively.

**Table 1.** Experimental and Calculated Geometric Data

Compound	$r_i^{[a]}$	Orbital radius (Å)	L—H Bond Length (Å)	M—L Bond Calc.	Length (Å) Expt.
$C(CH_3)_4$	0.527	0.886	1.119	1.519	1.539 <sup>d</sup>
$Si(CH_3)_4$	0.716	0.995	1.129	1.848	1.875 <sup>e</sup>
$Ge(CH_3)_4$	0.734	1.01	1.126	1.903	1.98 ± 0.03 <sup>c</sup>
$C(SiH_3)_4$	0.248	1.06	1.478	1.878	—
$Si(SiH_3)_4$	0.486	1.24	1.487	2.263	2.35 <sup>b</sup>
$Ge(SiH_3)_4$	0.504	1.27	1.487	2.328	—
$C(GeH_3)_4$	0.219	1.08	1.534	1.938	—
$Si(GeH_3)_4$	0.452	1.14	1.542	2.324	—
$Ge(GeH_3)_4$	0.488	1.29	1.543	2.367	2.45 <sup>b</sup>

<sup>a</sup> This is the fractional position along the bond; it is 0. at M, 1. at L.

<sup>b</sup> These are distances for the crystalline element, not the compound.

<sup>c</sup> Electron diffraction data: L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.* **58**, 2036 (1936).

<sup>d</sup> B. Beagley, et al., *J. Mol. Struct.* **4**, 233 (1969).

<sup>e</sup> B. Beagley, et al., *J. Mol. Struct.* **8**, 401 (1971).

Table 2. Calculated Total and Valence Energies

Molecule	Total energies (neg. hartrees)	$3t_2$	$1t_1$	$e$	$2t_2$	$2a_1$	$1t_2$	$1a_1$
$C(CH_3)_4$	30.4251	0.299(0.415) <sup>a</sup>	0.373(0.463)	0.406(0.518)	0.471(0.562)	0.684(0.654)	0.915	1.113
$Si(CH_3)_4$	29.1290	0.278(0.382) <sup>b</sup>	0.402(0.423)	0.413(0.485)	0.431(0.518)	0.547(0.570)	0.915(0.798)	0.965(0.882)
$Ge(CH_3)_4$	28.9631	0.275(0.376) <sup>c</sup>	0.407(0.478)	0.416(0.509)	0.430(0.509)	0.527(0.584)	0.917	0.957
$C(SiH_3)_4$	25.4933	0.287	0.379	0.388	0.426	0.627	0.694	0.944
$Si(SiH_3)_4$	24.3585	0.287	0.394	0.397	0.408	0.571	0.706	0.785
$Ge(SiH_3)_4$	24.2260	0.278	0.394	0.396	0.404	0.558	0.704	0.767
$C(GeH_3)_4$	24.9082	0.281	0.377	0.385	0.419	0.616	0.671	0.927
$Si(GeH_3)_4$	23.8005	0.281	0.389	0.391	0.402	0.567	0.682	0.765
$Ge(GeH_3)_4$	23.6714	0.289	0.392	0.394	0.402	0.559	0.686	0.762

<sup>a</sup> Experimental data: W. Schmidt and B. J. Wilkins, *Ang. Chem. Int. Ed.* **11**, 222 (1972).

<sup>b</sup> Experimental data: W. B. Perry and W. L. Jolly, *J. El. Spectros.* **4**, 219 (1974).

<sup>c</sup> Experimental data: S. Evans et al., *J. Chem. Soc. Far. II* **68**, 905 (1972).

These bond distances thus mirror the general conclusion, from a host of other properties, that carbon differs strongly from its congeners.

The same trends occur in the calculated bonding energies. In all cases, we find that the bond to carbon is stronger than that to silicon, which is stronger than that to germanium. Indeed, reactions of the type  $(\text{LH}_3)_4\text{M} + (\text{L}'\text{H}_3)_4\text{M}' \rightarrow (\text{LH}_3)_4\text{M}' + (\text{L}'\text{H}_3)_4\text{M}$ , are calculated to favor always that side which has carbon bonded to carbon if possible, or next best, carbon bonded to Si. There is a weak preference for Si—Si bonds over Si—Ge. This tendency toward disproportionation has been noted previously for the carbon case [13]. The tabulated bond energies (from Huheey [1]: C—C, C—Si, C—Ge, Si—Si, Ge—Ge are 83, 76, 51, 53, and 45 kcal/mol, respectively) agree exactly with this prediction, despite maximum overlap arguments which might predict the homopolar bond to be the strongest.

Experimental thermochemical data do not exist for all of these molecules (indeed, one suspects that  $\text{C}(\text{SiH}_3)_4$  and  $\text{C}(\text{GeH}_3)_4$  might not be stable for simple steric reasons). From studies on the tetramethyl compounds and on  $\text{ML}(\text{CH}_3)_6$  species, however, Lappert and co-workers have calculated rough bond energies<sup>13</sup> for the bonds, giving 82.1, 68.5, 59.9, 68.0, 63.3, and 59.3 kcal/mol for the C—C, C—Si, C—Ge, Si—Si, Si—Ge, and Ge—Ge bonds, respectively. Although these numbers are not strictly comparable to our calculated values, we compare, in Table 3, the predicted thermochemical differences for various scrambling reactions as calculated directly from the FSGO method and as computed from Lappert's approximate bond energies. The qualitative agreement is perfect, and the quantitative agreement is quite good. The only really substantial disagreements occur for the reactions (1, 2, 5, 8) involving neopentane.

The photoemission spectral data for these molecules is very sparse. In Table 2 we present the orbital energies obtained from our calculations, and comparison with the experimental data where available. Note that the comparison (assuming the validity of Koopmans' theorem) yields the correct ordering, and that the error, which is large for the highest-energy orbitals, decreases as the orbitals become

**Table 3.** Calculated Reaction Energies

Number	Reaction	$\Delta E_{\text{Thermochem}}^a$	$\Delta E_{\text{calc}}(\text{Kcal/mol})$
(1)	$\text{C}_5\text{H}_{12} + \text{Si}_5\text{H}_{12} \rightarrow \text{CSi}_4\text{H}_{12} + \text{SiC}_4\text{H}_{12}$	52	101
(2)	$\text{C}_5\text{H}_{12} + \text{Ge}_5\text{H}_{12} \rightarrow \text{CGe}_4\text{H}_{12} + \text{GeC}_4\text{H}_{12}$	86	141
(3)	$\text{Si}_5\text{H}_{12} + \text{Ge}_5\text{H}_{12} \rightarrow \text{SiGe}_4\text{H}_{12} + \text{GeSi}_4\text{H}_{12}$	2.8	2.0
(4)	$\text{SiC}_4\text{H}_{12} + \text{Ge}_5\text{H}_{12} \rightarrow \text{SiGe}_4\text{H}_{12} + \text{GeC}_4\text{H}_{12}$	18	23
(5)	$\text{SiGe}_4\text{H}_{12} + \text{C}_5\text{H}_{12} \rightarrow \text{SiC}_4\text{H}_{12} + \text{CGe}_4\text{H}_{12}$	68	118
(6)	$\text{CGe}_4\text{H}_{12} + \text{Si}_5\text{H}_{12} \rightarrow \text{SiGe}_4\text{H}_{12} + \text{CSi}_4\text{H}_{12}$	-16	-17
(7)	$\text{CSi}_4\text{H}_{12} + \text{Ge}_5\text{H}_{12} \rightarrow \text{CGe}_4\text{H}_{12} + \text{GeSi}_4\text{H}_{12}$	18	19
(8)	$\text{GeSi}_4\text{H}_{12} + \text{C}_5\text{H}_{12} \rightarrow \text{GeC}_4\text{H}_{12} + \text{CSi}_4\text{H}_{12}$	68	122
(9)	$\text{GeC}_4\text{H}_{12} + \text{Si}_5\text{H}_{12} \rightarrow \text{GeSi}_4\text{H}_{12} + \text{SiC}_4\text{H}_{12}$	-16	-21

<sup>a</sup> Based on bond energies estimated by M. F. Lappert et al., *J. Organomet. Chem.* **29**, 1951 (1971).

more strongly bound; this is typical of FSGO pseudopotential calculations, and arises from the fitting procedure employed to generate the pseudopotentials [10]. Within the tetramethyls, the differences in ionization potentials for the HOMO level  $3t_2$  on going from  $M = C$  to  $Si$  to  $Ge$  are calculated as 0.58 and 0.08 eV; experimentally these data are [14] 0.50 and 0.06 eV. The actual values demonstrate yet again the  $Ge-Si$  difference and the  $C$  similarity. The deepest levels ( $1a_1$ ,  $1t_2$ ,  $2a_1$ ) are most strongly bound by the most electronegative species, carbon.

There is really not a very significant variation in our calculated valence ionization potentials. It does seem noteworthy that, on comparison of species for fixed  $L$  and varying  $M$  or for fixed  $M$  and varying  $L$ , the most strongly bound HOMO occurs for  $M = L$ ; this is in keeping with the maximum overlap criterion for the strengths of chemical bonds [14, 15]. The order of the MO's is as expected from earlier empirical studies of the bonding [15]. The HOMO ( $3t_2$ ) is very largely  $ML$  bonding, and the next three levels ( $1t_1$ ,  $e$ ,  $2t_2$ ) are principally localized in the  $L-H$  bond. The deeply bound valence levels do show more substantial differences with varying  $M$ ,  $L$ , and all five of them ( $2a_1$ ,  $1t_2$ ,  $1a_1$ ) are strongly mixed with substantial contributions from all sixteen FSGO's. Since bonding in the  $ML_4$  skeleton is mostly due to ( $3t_2$ ,  $1t_2$ ,  $2a_1$ ,  $1a_1$ ), we expect these orbital energies to be lowest in the most stable molecules. Comparison of data from Table 2 shows that this is indeed so\*<sup>1</sup>

In the calculated orbital energies, the similarity of  $Si$  and  $Ge$ , and the uniqueness of  $C$ , are again clear. For the  $M-L_4$  bonding orbitals  $2a_1$  and  $1a_1$ , the  $M = C$  orbital energies lie considerably below the  $M = (Si, Ge)$ , but the latter two are close for all  $L$ . This holds also for the bonding orbital  $1t_2$ , and just the opposite is true for the largely  $L-H$  orbitals  $1t_1$ ,  $e$ . The delocalized bonding set  $1t_2$  is roughly independent of the identity of  $M$ , but is more deeply bound for  $L = C$  than for  $L = (Si, Ge)$ .

Turning now from experimental comparison to analysis of the valence interactions, we present in Table 1 the orbital radii and positions along the  $L-M$  bonds. In earlier work [11], we have attempted to correlate these parameters with electronegativities, but such comparisons were made difficult by complications due to atomic size—comparing  $HF$  and  $HCl$ , for instance, FSGO would put the bonding pair relatively closer to  $H$  in  $HCl$ , due to the larger ionic radius of  $Cl$  [17]. While this is in agreement with the relative electronegativities here [18], it shows that FSGO location is not terribly sensitive to electronegativity; ionic or covalent radius is at least as important in determining positions, and, indeed, we suspect that this criterion with a given group of the periodic table will always indicate decreasing electronegativity with increasing charge. The orbital radius parameter indicates how diffuse the bonding is. In the present series, we again note that

\*<sup>1</sup> The FSGO absolute minimum basis defines a Slater determinant [4] and is a solution to the molecular SCF equations. Thus Koopmans' theorem holds, and the ionization potentials may properly be compared with FSGO orbital energies. Of course, the basis is small and inflexible, and therefore considerable inaccuracy in predicted IP's is expected. For tight covalent Lewis-like bonds, the FSGO IP should be at their best, and the molecules studied here are just such cases.

Tables 1, 2 show large similarities between Ge and Si, both of which differ greatly from carbon. For instance, in the tetramethyl compounds the FSGO results show an FSGO M—L bonding orbital radius change of 0.11 Å from C to Si, but only 0.016 from Si to Ge; likewise, in the tetrasilyl compounds, the center of the bonding orbital moves out 24% of the way on changing from C to Si, but only another 2% on going to Ge. The valence forces in the compounds reflect these changes, of course—perhaps the most obvious examples are the great hardness of diamond as compared to Si or Ge, and the large extent of delocalization of electronic effects in silane, as opposed to alkane, chains [19]. The very tightly held electrons in the C—C bond would be expected to confer greater rigidity than the more diffuse orbitals in the Ge—Ge or Si—Si bonds, but that very diffuseness should mean greater overlap from bond to bond, hence greater tendency toward delocalization.

The frequencies of the totally symmetric M—L stretch mode in the tetramethyl compounds is given as 731, 592, and 560  $\text{cm}^{-1}$  for L = C, Si, and Ge, respectively [20]. The ratios  $\nu_{\text{Si-C}}/\nu_{\text{C-C}}$  and  $\nu_{\text{Ge-C}}/\nu_{\text{C-C}}$  are then 0.81 and 0.77, respectively. The analogous ratios for our calculated bond lengths are 0.82 and 0.80 and for the square of the M—L orbital radii 0.79 and 0.77. Thus the FSGO size is related both to bond length (as has been pointed out previously) [21] and to bond stiffness: the tighter the FSGO, the stiffer the bond.

Our results are relevant to group IV solids such as pure Si and doped Ge. For instance, experimental data show quite clearly that the standard molar enthalpy of vaporization of diamond, Ge, and Si is very close to the expected value of twice the bond enthalpy. Thus the enthalpies of the individual bonds are reasonably close to additive, and we can use the calculated data of table 2 for drawing some conclusions. The most obvious is, once more, the far greater lattice energy of diamond. Second is the far greater thermodynamic ease of doping Si or Ge: note that to change the central atom in the  $\text{C}_5$  cluster always requires  $\sim 0.2$  hartree = 120 kcal/mol, roughly ten times the energy required in the  $\text{Ge}_5$  or  $\text{Si}_5$  clusters. As might be expected by ionic size considerations, it is even harder to form  $\text{Ge}_4\text{C}$  than  $\text{Si}_4\text{C}$ . The very small energy difference in reaction (3) suggested (as is found) that Si/Ge mixed crystals should be very easily prepared. The orbital compositions of the highest occupied orbitals (corresponding to the band states closest to the Fermi level, for the infinite solid) are roughly constant in the series of nine molecules: the highest occupied orbital is a  $t_2$  state which is largely M—L bonding ( $\sim 80\%$ ). The orbital parameters suggest that a carbon impurity in Si or Ge will act as an electron trap in a tighter local orbital, while a Si or Ge impurity in diamond would be hard to form, and, if made, would act as a hole center in a more diffuse orbital. The  $1t_2$  energies would, indeed, support the relative electronegativity  $\text{C} \gg \text{Ge} > \text{Si}$ , in agreement with standard assignments [18]. The significant differences between the bond lengths calculated for some of these molecules and those observed in the tetrahedral solids (1.52, 1.86, 2.26, 2.37 Å calculated for C—C, C—Si, Si—Si, Ge—Ge in molecules; 1.54, 1.94, 2.35, 2.45 observed in crystals) [22] probably reflect the altered environment of the L atom in the periodic crystal as compared with its (M;H<sub>3</sub>) coordination in the molecules. These



differences are larger for Ge and Si than for C, in agreement with the trends observed for  $XYH_6$  (X,Y = C, Si, Ge) in Ref. [11].

Finally, the calculated total energies of Tables 2, 3 permit suggestions to be ventured about as yet unreported molecules. The large endoergicity of reaction (1) suggests that  $C(SiH_3)_4$  will be difficult to prepare (this might be suspected on simple steric grounds). Likewise, reactions (2) and (5) would seem to militate against any stability for  $C(GeH_3)_4$ . On the other hand, the predicted exoergicity of reaction (9), coupled with the known stability of  $Si_5H_{12}$  and  $Ge(CH_3)_4$  suggest that  $Ge(SiH_3)_4$  might well be stable [23].

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