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Citation: *The Journal of Chemical Physics* **87**, 6562 (1987); doi: 10.1063/1.453441

View online: <http://dx.doi.org/10.1063/1.453441>

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# Ground and excited states of group IVA diatomics from local-spin-density calculations: Model potentials for Si, Ge, and Sn

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(Received 16 March 1987; accepted 17 August 1987)

LCGTO-MP-LSD results are reported for the spectroscopic constants and electronic structure of the diatomic molecules Si<sub>2</sub>, Ge<sub>2</sub>, Sn<sub>2</sub>, SiGe, SiSn, and GeSn in their low-lying electronic states. For the homonuclear molecules we found that the ground state is  $^3\Sigma_g^-$  with the most important lower-lying excited states being  $^3\Pi_u$ ,  $^1\Pi_u$ , and  $^1\Sigma_g^+$ , respectively. Our results are in good agreement with the available experimental data and also in qualitative agreement with other theoretical studies. We present here the first theoretical study on the heteronuclear molecules, for which experimental data are not available. We found the  $^3\Sigma^-$  state to be the lowest, followed by  $^3\Pi$  and  $^1\Sigma^+$  states. Model potentials (MP) are reported for the Si, Ge, and Sn atoms. The reliable results for molecules complement those for the atoms and show that the LSD model potentials presented here allow for an accurate description of chemical bonding and spectroscopic properties in the title molecules.

## I. INTRODUCTION

Most of the elements of group IVA in the Periodic Table have interesting electronic properties and important practical applications. The possibility of simulating and predicting surface, bulk and chemisorption properties of semiconductor crystals with quantum-mechanical methods is an important area of modern surface science.<sup>1,2</sup> In the framework of the cluster approach a large number of atoms are necessary to describe the crystal well and to reduce the unwanted boundary effects. But the use of clusters with a large number of atoms considerably increases the computational effort. One way to circumvent this problem is to use pseudopotentials or model potentials (MP) which allow one to treat explicitly only valence electrons. These methods, originally developed in solid-state physics<sup>3</sup> are now commonly used in molecular physics and quantum chemistry.<sup>4</sup> In a continuation of our interest in the development of model potentials<sup>5</sup> we present here the model potentials for silicon, germanium, and tin and, in order to demonstrate their accuracy, an LCGTO-MP-LSD study of homo- and heteronuclear diatomics of these elements.

The group IVA diatomics are also interesting per se and a number of studies of their electronic structure has been performed.<sup>6-25</sup> Contrary to the C<sub>2</sub> molecule which has a  $^1\Sigma_g^+$  ground state, the ground state of Si<sub>2</sub> has been found as  $^3\Sigma_g^-$ . Additionally, for both molecules many other low-lying excited states have been found experimentally,<sup>21</sup> or predicted by theoretical investigations.<sup>6-12</sup> Due to their complicated electronic structure these diatomic systems are severe tests for theoretical methods.

For the Si<sub>2</sub> molecule experimental data are available for two spectroscopic states<sup>21</sup> and a series of theoretical studies has been performed.<sup>6-12,19</sup> Experimental information on Sn<sub>2</sub>

is more scarce<sup>22,23</sup> and few quantum-mechanical investigations exist in the literature.<sup>17,18</sup> Finally, to our knowledge, the experimental work concerning Ge<sub>2</sub> is limited to a measurement of the dissociation energy from mass spectrometry data.<sup>13</sup> Several theoretical studies have been reported on Ge<sub>2</sub>.<sup>10,12-16,19,24,25</sup>

For the heterodiatomics SiGe, SiSn, and GeSn no experimental or theoretical study has been performed until now, so our results represent predictions for these diatomics and also provide ingredients for future cluster studies of the corresponding alloys.

The mixed first- and second-row system SiC has been observed in interstellar space and theoretical *ab initio* CI studies<sup>6,20</sup> have found a  $^3\Pi$  ground state. It is of interest to study mixed second, third, and fourth row systems and establish general trends in spectroscopic and electronic properties of the heteronuclear diatomics of group IVA. Before studying the unknown SiGe, SiSn, and GeSn molecules we have performed calculations for SiC. Calculated spectroscopic constants for SiC compare very well with the most recent theoretical CI study<sup>6,20</sup> so we feel confident that our new results for the other heteronuclear dimers are well founded and can be used as guidance for experimental investigations.

In Sec. II we report the computational methods and model potentials (MP) for Si, Ge, and Sn. Section III is devoted to the presentation of the results and their discussion both for homo- and heteronuclear dimers. Finally in Sec. IV we summarize some conclusions of this work and, in the Appendix, basis set and model potential details are given.

## II. METHOD

All calculations have been performed with the LCGTO-LSD method originally implemented by Sambe and Felton<sup>26</sup> and considerably developed and extended, as described elsewhere.<sup>27-31</sup> The "best" (VWN<sup>32</sup>) local spin-density potential has been used. Auxiliary basis sets, necessary to fit den-

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sity and exchange-correlation potentials, have been obtained using our fitting procedure.<sup>33</sup> For the carbon atom an all-electron basis set with (521/41/1\*) contraction pattern has been employed (for the notation see Ref. 33). The corresponding auxiliary basis set has the form (834/734). For silicon, germanium, and tin, model potentials have been developed with only the *ns* and *np* valence-shell electrons treated explicitly, as discussed further below. The short notation of the contraction pattern for the basis sets used for Si, Ge, and Sn are (311/211/1\*), (311/211/1\*), and (2211/2111/1\*), respectively. The auxiliary basis sets are of the form (634/634), (634/633), and (734/733) for Si, Ge, and Sn, respectively. Basis sets and model potential parameters are given in the Appendix.

We turn now to a discussion of the model potentials. Although the basic assumption of core–valence separability is now quite well established<sup>34</sup> the construction of both accurate and efficient pseudopotentials still represents a challenge for many elements of the Periodic Table. The first choice to be made concerns the number of electrons to be included in the valence space. This choice may be delicate if the outermost core orbitals overlap significantly with the valence orbitals and cases have been reported<sup>28,34–36</sup> where an expanded valence shell appears to be necessary for high accuracy. However, a recent Hartree–Fock MP study on As<sub>2</sub> and Sb<sub>2</sub> suggests that treating only the valence *s* and *p* orbitals explicitly should lead to rather small errors for our title molecules which involve atoms from a nearby region of the Periodic Table (0.01–0.03 Å in bond distances, 20 cm<sup>−1</sup> in vibrational frequencies, and 0.2–0.5 eV in binding energies) in comparison with all-electron calculations. Since these errors are acceptable to us we have performed calculations including only *s* and *p* orbitals in the valence shell, augmented with *d* polarization functions. Additionally we expect that the relative energies of molecular states found in this paper were obtained with higher accuracy than the individual binding energies. As will be seen, our results bear out this expectation. Our next goal will be to investigate large semiconductor clusters and it is therefore gratifying that the small, economical, MPs coupled with the LSD formalism provide reasonable accuracy.

Since our method for optimizing the model potentials has been described fully in Ref. 28, here we will discuss only the accuracy for the atoms treated here. For all atoms the radial parts of the MP valence orbitals outside the last node are nearly identical to those of the reference valence orbitals (numerical VWN solution for the atom). The MP atomic orbital energies compare very well (within 0.2 eV) with the corresponding reference values. Atomic test calculations for several excited and ionized configurations of the atoms are presented in Table I. Comparison with all electron, numerical calculations shows excellent agreement, (within 0.2 eV) for all considered states except the *stp*<sup>3</sup>(<sup>5</sup>S) state. The quality of the molecular results (see below) indicates that a more accurate description of these high spin *sp*<sup>3</sup> states is not crucial for the atoms in the molecules. In any case, for completeness and to elucidate the reason for this discrepancy, which for tin is as large as 0.8 eV, we present in Table II the splitting (Δ) between the outer core spin-polarized orbitals of tin. It

TABLE I. Atom excitation energies (in eV). Model potential (MP) and numerical (*N*) (in parentheses) results.

Configuration	Si	Ge	Sn
<i>stslp</i> <sup>2</sup>	0	0	0
<i>stslp</i> <sup>1</sup>	0.72 (0.67)	0.70 (0.61)	0.62 (0.52)
<i>stp</i> <sup>3</sup>	3.98 (4.30)	4.98 (5.56)	4.56 (5.35)
<i>stp</i> <sup>2</sup> <i>p</i> <sup>1</sup>	6.50 (6.57)	7.44 (7.54)	6.70 (6.95)
<i>stp</i> <sup>1</sup> <i>p</i> <sup>2</sup>	7.43 (7.38)	8.35 (8.23)	7.48 (7.49)
<i>stslp</i> <sup>1</sup> <sup>a</sup>	8.34 <sup>c</sup> (8.28)	8.09 <sup>d</sup> (8.07)	7.58 (7.45)
<i>stp</i> <sup>1</sup> <i>p</i> <sup>1</sup>	15.58 (15.55)	16.39 (16.38)	15.04 (15.11)
<i>stp</i> <sup>1</sup> <i>p</i> <sup>1</sup> <sup>3b</sup>	−1.30	−1.22 <sup>d</sup>	−1.38

<sup>a</sup> Ionization potential (IP).

<sup>b</sup> Electron affinity (EA).

<sup>c</sup> All electron CI result for IP is 8.06 eV (from Ref. 16).

<sup>d</sup> The corresponding all electron CI results for IP, EA are 7.68 and 1.12 eV, respectively (from Ref. 19).

can be seen that the errors in the description of the excited states (Table I) correlate with changes in the spin polarization of the outer core orbitals, particularly the 4*d* orbitals. Clearly, if one wants to reproduce exactly excited states of the atom which differ very much from the ground state for which the model potential was optimized, then at least the 4*d* orbital should not be treated as a frozen core orbital. If one wished to consider states involving high spin atomic states then it would be easy in our MP scheme to include the 4*d* level in the valence space for the diatomic molecules considered here.

Basis set superposition error (BSSE) has been calculated in the usual way.<sup>40</sup> The high quality of our basis sets results in only a small influence of BSSE on molecular properties as is shown in the next section.

The spectroscopic constants were calculated by fitting the potential curve with third-degree polynomials and the binding energies are calculated using the interpolated total energies.

### III. RESULTS AND DISCUSSION

The interaction of two atoms of group IVA in their atomic ground state gives rise to several molecular states with singlet, triplet, and quintuplet multiplicity. In the present paper we are mainly interested in the investigation of the

TABLE II. Spin splitting (eV) of the valence and outer core orbitals of Sn for several atomic configurations from numerical relativistic calculations.

		4 <i>s</i>	4 <i>p</i>	4 <i>d</i>	5 <i>s</i>	5 <i>p</i>
Sn:	<i>stslp</i> <sup>2</sup>	0.14	0.13	0.36	2.03	2.10
	<i>stp</i> <sup>3</sup>	0.36	0.44	1.04	4.76	4.46
	<i>stp</i> <sup>2</sup>	0.22	0.27	0.64	2.48	2.13
Sn <sup>+</sup> :	<i>stslp</i> <sup>1</sup>	0.08	0.10	0.23	1.25	1.36
	<i>stp</i> <sup>1</sup> <i>p</i> <sup>1</sup>	0.16	0.20	0.45	1.50	1.29

ground states and the lowest-lying excited states of the title molecules, those derived from the configurations  $\pi^2\sigma^2$ ,  $\pi^3\sigma^1$ , and  $\pi^4$ . The first two of these configurations have open shells and therefore some difficulty and ambiguity arise when treating them within the framework of local density functional theory.<sup>8,9,38-41</sup> A single determinant built from the orbitals of a given configuration would not, in general, correspond to a spin and angular momentum eigenfunction. The "state" labels used below are therefore approximate and due caution should be exercised when comparing with experiment or with results from CI calculations. The "states" we have investigated are  $^3\Sigma_g^-$  ( $\pi^2\sigma^2$ ),  $^3\Pi_u$  ( $\pi^3\sigma^1$ ),  $^1\Pi_u$  ( $\pi^3\sigma^1$ ) and two further singlet states labeled  $^1\Sigma_g^-$  ( $\pi^4$ ) and  $^1\Sigma_g^+$ ,  $^1\Delta_g$  ( $\pi^2\sigma^2$ ). The same states, minus the *g* and *u* labels, were studied for the heteronuclear molecules. For the triplet states, spin-polarized ( $\uparrow\uparrow$ ) calculations were performed, so these states should only show the usual (slight) spin contamination associated with unrestricted calculations for triplets. The singlets were treated within the spin-unpolarized approximation, which is entirely appropriate only for the closed-shell,  $\pi^4$ , configuration. For the open-shell singlet ( $\pi^2\sigma^2$ ) we have followed Dunlap<sup>8,9</sup> in assuming that the unpolarized approach is appropriate to singlet states, although this is based rather loosely on a consideration of  $S_z$  values only. Within this approximation, the  $\pi^2\sigma^2$  configuration has unresolved components of both sigma and delta symmetry, hence the notation  $^1\Sigma^+$ ,  $^1\Delta$ . The state labeled  $^1\Pi_u$  corresponds to the spin-polarized configuration  $\cdots(\pi_u\uparrow)^2(\pi_u\downarrow)^1(2\sigma_g\uparrow)^1(2\sigma_g\downarrow)^0$ . This is not a pure state but has some contamination from other multiplicities and also other states of angular momentum. Despite such ambiguities we will show below that the present calculations, interpreted with appropriate caution, are sufficiently accurate to yield useful predictions of the spectroscopic constants where they are unknown, to furnish valid information on the nature of the bonding and to provide support for the use of these techniques for larger systems. The calculated potential energy curves are reported in Figs. 1 and 2. Orbital energy diagrams for the ground state configurations are shown on Fig. 3.

As pointed out previously,<sup>8,9</sup> the degeneracy between two states in symmetry-restricted LSD theory can be removed by using fractional occupation numbers, in a spin-unpolarized calculation or by removing all symmetry constraints on the one-electron orbitals (broken-symmetry) and performing spin-polarized calculations. We have used the former technique, minimizing the LSD energy functional with respect to fractional orbital occupation numbers. Performing this calculation at every point of the potential energy curve of  $^1\Sigma_g^+$ ,  $^1\Delta_g$  ( $^1\Sigma^+$ ,  $^1\Delta$  for heteronuclear diatomics) we have obtained the lower dotted curves in Figs. 1 and 2. As in the work of Dunlap,<sup>13,14</sup> for  $C_2$  and  $Si_2$  we have denoted these states as  $^1\Sigma_g^{+*}$  and  $^1\Sigma^{+*}$  for homo- and heteronuclear molecules, respectively. The two dotted curves are equidistant from the average of the respective solid curves. In this way we have obtained potential energy curves for the  $^1\Sigma^+$ -type states that imitate the avoided crossing of the two-electron configurations. Now they are more comparable with CI results (Ref. 6 for  $Si_2$  and Ref. 14 for  $Ge_2$ ),

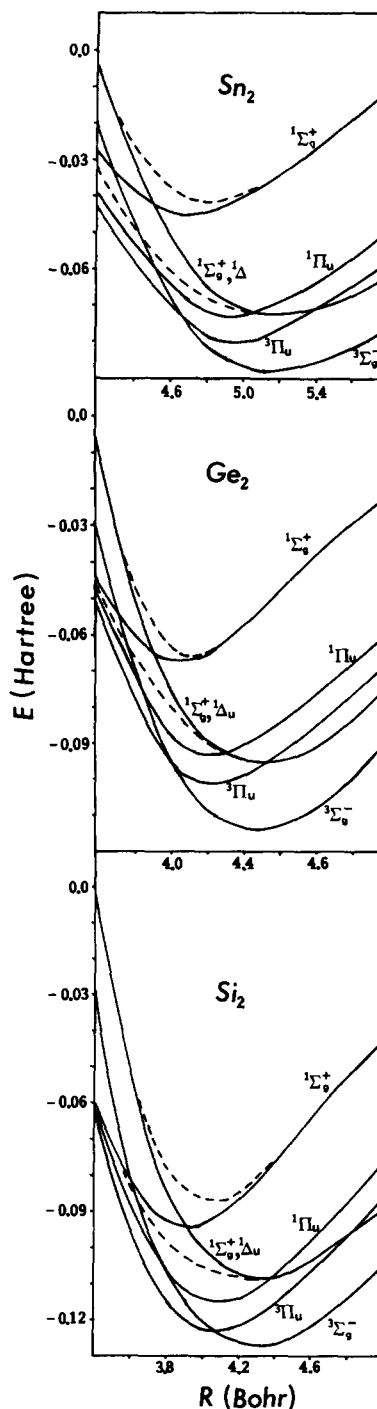


FIG. 1. Potential energy curves for ground and low-lying excited states of  $Si_2$ ,  $Ge_2$ , and  $Sn_2$ . The  $^1\Sigma_g^{+*}$  state results from a calculation with fractional occupation numbers (see the text).

and for  $Si_2$  are the same as those obtained for the all-electron LCAO- $X\alpha$  calculations.<sup>8,9</sup> Contrary to the case of the  $C_2$  molecule for which  $^1\Sigma_g^+$  is the ground state and  $^3\Pi_u$ ,  $^3\Sigma_g^-$ , and  $^1\Pi_u$  are the lowest-lying excited states, for  $Si_2$ ,  $Ge_2$ , and  $Sn_2$  (see Fig. 1)  $^3\Sigma_g^-$  appears to be the ground state. The first low-lying excited state is  $^3\Pi_u$  followed by  $^1\Pi_u$  and  $^1\Sigma_g^+$  states, respectively.

Inspection of Fig. 1 reveals that at both short and long

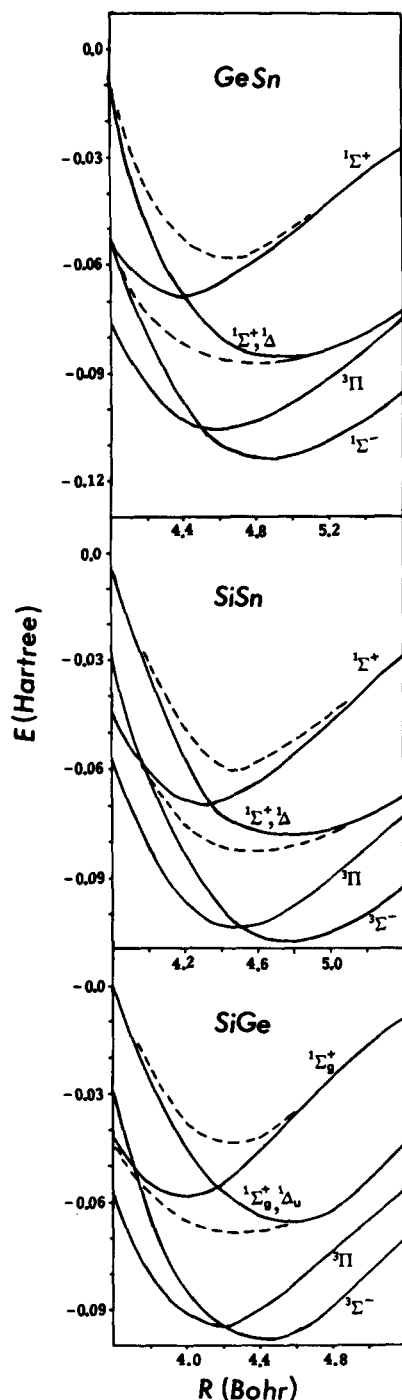


FIG. 2. Potential energy curves for ground and low-lying excited states of SiGe, SiSn, and GeSn. The  $1\Sigma_g^+$  state results from a calculation with fractional occupation numbers (see the text).

distances the relative position of the electronic states is different from that at the equilibrium distances. In particular, at short distances the  $3\Pi_u$  state is much lower than  $3\Sigma_g^-$ . Our potential energy curves are in qualitatively good agreement with those reported for  $\text{Si}_2$  both with all-electron LCAO-LSD results<sup>8,9</sup> and with *ab initio* CI studies.<sup>6</sup> The same agreement is found for  $\text{Ge}_2$  and  $\text{Sn}_2$  with the available CI studies.<sup>12-18</sup> In Tables III-V we have collected the computed spectroscopic constants of  $\text{Si}_2$ ,  $\text{Ge}_2$ , and  $\text{Sn}_2$ , respectively,

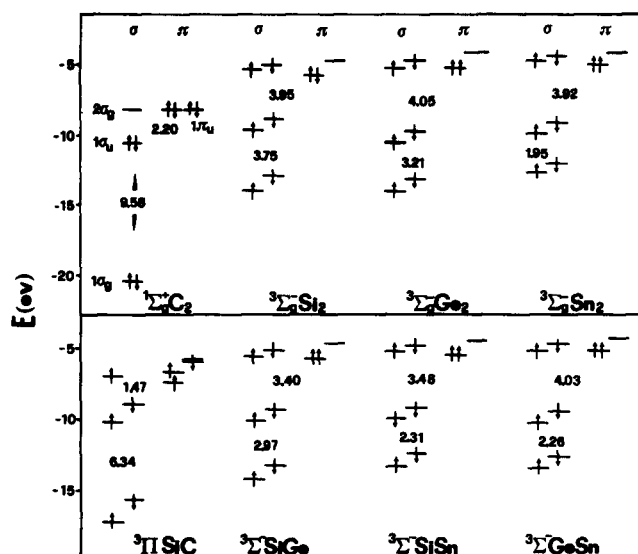


FIG. 3. Valence orbital energy levels for  $XY$  ( $X, Y = \text{C, Si, Ge, Sn}$ ) in their ground states, computed at the equilibrium distances (see the text).

together with the most recent theoretical results<sup>6-18</sup> and available experimental measurements.<sup>21</sup>

#### A. $\text{Si}_2$

Analysis of Table III shows that our results for  $\text{Si}_2$  are in very good agreement with both the experimental equilibrium distances and vibrational frequencies both for the ground state  $3\Sigma_g^-$  and for the first low-lying excited  $3\Pi_u$  state. A general good agreement is also found with most of the other theoretical studies.<sup>6-11</sup> Detailed comparison with the most recent  $X\alpha$  calculation,<sup>8,9</sup> reveals that our (VWN)  $R_e$  and  $\omega_e$  and the relative stabilities ( $T_e$ ) of different states are close to those found in Refs. 8 and 9. Differences exist, however, for the dissociation energies ( $D_e$ ) and the magnitude of  $T_e$ .

A comparison with the different *ab initio* CI studies<sup>6,11,12</sup> on  $\text{Si}_2$  shows general good agreement with our results. The best agreement is found for the most extensive CI expansions.<sup>6,11</sup> Analyzing the values of  $T_e$  we note that the relative orders of the states are correctly reproduced by LCGTO-MP-LSD calculations for all electronic states considered. The difference between the ground  $3\Sigma_g^-$  state and the first low-lying  $3\Pi_u$  state (0.11 eV) is of the same order of magnitude as the difference found in the CI calculations. Considering the limits of accuracy of our method and the very low value found for the  $3\Sigma_g^- - 3\Pi_u$  separation we can conclude that the agreement is consistent and that the two states are practically degenerate. Agreement between the  $1\Sigma_g^+$  states and the CI results is also satisfactory.

#### B. $\text{Ge}_2$

The molecular results for  $\text{Ge}_2$  are reported in Table IV. Unfortunately except for an estimate of the dissociation energy<sup>13</sup> no other experimental information is available for this

TABLE III. Spectroscopic constants for  $\text{Si}_2$  from different levels of theory and from experiment. The  $^1\Sigma_g^+ *$  state results from a calculation with fractional occupation numbers (see the text).

State	Method	$R_e$ (bohr)	$\omega_e$ ( $\text{cm}^{-1}$ )	$T_e$ (eV)	$D_e$ (eV)
$^3\Sigma_g^-$	LCGTO-MP-LSD	4.29	485	0.0	3.92
	LCGTO- $X\alpha^a$	4.31	470	0.0	5.35
	HF/SDQ <sup>b</sup>	4.26	514	0.0	2.90
	MRD/CI <sup>c</sup>	4.33	494	0.0	3.02
	HF/CI <sup>d</sup> ( $^3\Sigma_g^-$ )	4.42	469	0.0	2.89
	HF/CI <sup>d</sup> ( $^3\Pi_u$ )	4.44	473	0.0	0
$^3\Pi_u$	Expt <sup>e</sup>	4.25	511	...	3.21
	LCGTO-MP-LSD	4.07	551	0.11	3.81
	LCGTO- $X\alpha^a$	4.10	528	0.02	5.33
	HF/SDQ <sup>b</sup>	4.09	547	0.13	2.78
	MRD/CI <sup>c</sup>	4.16	517	0.02	...
	HF/CI <sup>d</sup> ( $^3\Sigma_g^-$ )	4.29	484	0.22	...
$^1\Sigma_g^+ *$	HF/CI <sup>d</sup> ( $^3\Pi_u$ )	4.26	503	0.03	...
	Expt <sup>e</sup>	4.07	548	...	...
	LCGTO-MP-LSD	4.23	387	0.51	3.40
	LCGTO- $X\alpha^a$	4.16	399	0.67	4.68
	HF/SDQ <sup>b</sup>	4.25	453	0.85	...
	MRD/CI <sup>c</sup>	4.37	370	0.70	...
$^1\Pi_u$	HF/CI <sup>d</sup> ( $^3\Sigma_g^-$ )	4.55	359	0.86	...
	HF/CI <sup>d</sup> ( $^3\Pi_u$ )	4.40	270	0.77	...
	LCGTO-MP-LSD	4.08	540	0.33	3.59
	HF/SDQ <sup>b</sup>	4.09	...	0.66	...
	MRD/CI <sup>c</sup>	4.16	580	0.55	...

<sup>a</sup> From Refs. 8 and 9.<sup>b</sup> From Ref. 11.<sup>c</sup> From Ref. 6.<sup>d</sup> From Ref. 12.<sup>e</sup> From Ref. 21.

molecule, so that the comparison can be made mainly with other theoretical studies. The calculated ground state is  $^3\Sigma_g^-$  followed by  $^3\Pi_u$ ,  $^1\Sigma_g^+ *$ , and  $^1\Pi_u$  states as was found in all other theoretical calculations.<sup>10,11-16</sup> The main differences

with respect to  $\text{Si}_2$  occur in the relative order of the two low-lying excited states  $^1\Sigma_g^+ *$  and  $^1\Pi_u$ . In fact, in the case of  $\text{Ge}_2$  the  $^1\Sigma_g^+ *$  state is more stable than  $^1\Pi_u$ . In any case we note that the energy splitting between these two states is very

TABLE IV. Structural and spectroscopic constants for  $\text{Ge}_2$  from different levels of theory.

State	Method	$R_e$ (bohr)	$\omega_e$ ( $\text{cm}^{-1}$ )	$T_e$ (eV)	$D_e$ (eV)
$^3\Sigma_g^-$	LCGTO-MP-LSD	4.50	292	0.0	3.76
	LMTO-LSD <sup>a</sup>	4.75	240	0.0	1.97
	PP-MRD-CI <sup>b</sup>	4.63	228	0.0	2.32
	PP-MRD-CI <sup>c</sup>	4.60	217	...	2.54
	LSD <sup>d</sup>	4.43	286	...	4.14
	HF/CI <sup>e,f</sup>	4.57	283	0.0	3.14
	Expt <sup>f</sup>	...	...	...	2.70
$^3\Pi_u$	LCGTO-MP-LSD	4.26	356	0.35	3.39
	LMTO-LSD <sup>a</sup>	4.49	250	0.43	1.53
	PP-MRD-CI <sup>b</sup>	4.50	195	0.06	1.81
	HF/CI <sup>e,f</sup>	4.41	306	0.01	...
	LCGTO-MP-LSD	4.53	287	0.50	3.28
$^1\Sigma_g^+ *$	LMTO-LSD <sup>a</sup>	4.76	240	...	1.55
	PP-MRD-CI <sup>b</sup>	4.77	166	0.57	...
	HF/CI <sup>e,f</sup>	4.63	196	0.76	...
	LCGTO-MP-LSD	4.26	362	0.57	3.21
$^1\Pi_u$	LMTO-LSD <sup>a</sup>	4.48	250	...	1.32
	PP-MRD-CI <sup>b</sup>	4.51	199	...	...
	HF/CI <sup>e,f</sup>	4.42	298	0.69	...
	LCGTO-MP-LSD	4.26	362	0.57	3.21

<sup>a</sup> From Ref. 10.<sup>b</sup> From Ref. 14.<sup>c</sup> From Ref. 15.<sup>d</sup> From Ref. 16.<sup>e</sup> From Ref. 12.<sup>f</sup> See Ref. 13.

TABLE V. Structural and spectroscopic constants of  $\text{Sn}_2$  from different levels of theory.

State	Method	$R_e$ (bohr)	$\omega_e$ ( $\text{cm}^{-1}$ )	$T_e$ (eV)	$D_e$ (eV)
$^3\Sigma_g^-$	LCGTO-MP-LSD	5.16	190	0.0	3.09
	HF/CI <sup>a</sup>	5.20	104	0.0	1.86
	Expt	...	188 <sup>b</sup>	...	2.04 <sup>a</sup>
					2.05 <sup>c</sup>
$^3\Pi_u$	LCGTO-MP-LSD	4.93	213	0.22	2.87
	HF/CI <sup>a</sup>	4.95	219	0.19	...
$^1\Sigma_g^+ *$	LCGTO-MP-LSD	5.18	168	0.42	2.64
	HF/CI <sup>a</sup>	5.31	140	0.77	...
$^1\Pi_u$	LCGTO-MP-LSD	4.92	230	0.42	2.64

<sup>a</sup>From Ref. 18.<sup>b</sup>From Ref. 23.<sup>c</sup>From Ref. 22.

small and we can consider that they are practically degenerate. The energy difference between the ground state and the first low-lying excited state ( $^3\Pi_u$ ) is found to be 0.35 eV, in agreement with a previous LMTO-LSD study<sup>10</sup> but much larger than the values found in CI investigations.<sup>12-15</sup>

Also in this case our computed  $D_e$  are overestimated in comparison with the experimental values but the relative trends are correctly reproduced. In fact going from  $\text{Si}_2$  to  $\text{Ge}_2$  the experimental  $D_e$  decreases by about 0.5 eV whereas our computed  $D_e$  decreases by about 0.2 eV. A similar comparison study of  $D_e$  in  $\text{Si}_2$  and  $\text{Ge}_2$  computed at the CI level<sup>12</sup> gives the reverse trend. In that work<sup>12</sup> it is pointed out that this incorrect trend in computed  $D_e$  is probably due to the different role of BSSE for both molecules. Our data are corrected for BSSE and we note that this error in our calculations is very small and has the same magnitude for both molecules (0.01 and 0.02 eV for the case of the ground state,  $^3\Sigma_g^-$ , for  $\text{Si}_2$  and  $\text{Ge}_2$ , respectively). BSSE barely influences  $D_e$  and has a negligible influence on  $R_e$  and  $\omega_e$ , in all cases studied here.

The comparison of our calculated  $R_e$  with the CI studies reveals that in general these distances are longer, by about

0.2 a.u. with respect to our results. In particular, we note that the difference is small in the case of the ground state and more pronounced in all the excited electronic states considered. This fact is not surprising if we considered that also in the case of  $\text{Si}_2$  the CI results at the same level<sup>6,12</sup> of theory give distances longer than ours. Since an "experimental estimate" of the bond length of 2.44 Å (4.61 bohr) was quoted in Ref. 15 we decided to examine this point further. We performed a calculation with our Ge MP on the GeH molecule for which the experimental  $R_e$  and  $\omega_e$  are known<sup>21</sup> in order to have another point of comparison. Our computed  $R_e$  for the  $^2\Pi$  ground state of this molecule is 3.051 bohr whereas the experimental value is 3.001 bohr. The experimental  $\omega_e$  is found to be 1834  $\text{cm}^{-1}$  and our value is 1752  $\text{cm}^{-1}$ . This means that our MP for Ge is able to reproduce reasonably both  $R_e$  and  $\omega_e$  values. The difference in  $R_e$  is about 0.05 a.u. and we think that this small contraction is partly due to the lack of relativistic corrections in our model potential. Additionally including the  $d$  orbitals in the core likely will cause an elongation of the bond.<sup>36</sup> All of this is inconsistent with the experimental estimate of  $R_e$ . Indeed examining Ref. 24 reveals that the quoted value is for the solid state.

TABLE VI. Mulliken population analysis of the valence orbitals for group IVA homonuclear dimers computed at the equilibrium distances of the ground states.

Molecule	State	Orbital	Overlap	Orbital analysis			Occup. number	
				$s$	$p$	$d$	$\downarrow$	$\uparrow$
$\text{Si}_2$	$^3\Sigma_g^-$	$1\sigma_g$	0.61	0.87	0.13	0.0	1	1
		$1\sigma_u$	-0.42	0.88	0.11	0.01	1	1
		$2\sigma_g$	0.00	0.14	0.86	0.0	1	1
		$1\pi_u$	0.49	0.0	0.97	0.03	2	0
$\text{Ge}_2$	$^3\Sigma_g^-$	$1\sigma_g$	0.54	0.89	0.11	0.0	1	1
		$1\sigma_u$	-0.44	0.94	0.05	0.01	1	1
		$2\sigma_g$	0.04	0.11	0.88	0.01	1	1
		$1\pi_u$	0.47	0.0	0.98	0.02	2	0
$\text{Sn}_2$	$^3\Sigma_g^-$	$1\sigma_g$	0.41	0.94	0.06	0.0	1	1
		$1\sigma_u$	-0.34	0.95	0.04	0.01	1	1
		$2\sigma_g$	0.10	0.08	0.91	0.01	1	1
		$1\pi_u$	0.42	0.0	0.98	0.02	2	0

### C. $\text{Sn}_2$

For the  $\text{Sn}_2$  molecule (Table V) the experimental information concerns the value of the vibrational frequency and a mass spectroscopic estimate of the dissociation energy and semiempirical<sup>19</sup> and *ab initio* CI calculations<sup>17,18</sup> have been performed. Our calculated  $R_e$  and  $\omega_e$  are in excellent agreement with experimental data and/or with the CI results. As in the other cases our  $D_e$  is overestimated but also in this case the trend of  $D_e$  with respect to  $\text{Si}_2$  and  $\text{Ge}_2$  is well reproduced. The energy difference between the  $^3\Sigma_g^-$  ground state and  $^3\Pi_u$  is found to be 0.22 eV, very close to the CI value. The relative order of the states is the same as for  $\text{Ge}_2$  with the  $^1\Pi_u$  state being slightly below  $^1\Sigma^+*$ .

In order to further characterize the electronic structure—to “understand” the bonding as far as this is possible within an orbital analysis—we report in Table VI the Mulliken population analysis for the ground state of the homonuclear diatomics, computed at the equilibrium distances. A comparative analysis for the compounds considered shows that the largest overlap populations occur for the  $1\sigma_g$  orbitals. The values of this overlap decrease on going from  $\text{Si}_2$  to  $\text{Sn}_2$  as do the values of the overlap of the antibonding  $1\sigma_u$  orbital. As judged by the Mulliken overlap populations the  $2\sigma_g$  orbitals would appear to be essentially nonbonding. However, plots of the wave functions (Fig. 4) clearly show that the orbital is bonding in the sense that the differential overlap is positive in the valence region between the atoms. The plots also show the increasing diffuseness of this wave function as the Periodic Table is descended. It may be of some interest to note that the amplitude of  $2\sigma_g$  at the bond midpoint decreases on going to heavier congeners, the same

trend as just noted for the dissociation energies. Finally the  $1\pi$  orbitals are bonding (Table VI, Fig. 5) and the overlap population is almost constant in all cases. The results of Table VI reveal the predominant *s*-type composition for  $1\sigma_g$  and  $1\sigma_u$  orbitals, whereas in the  $2\sigma_g$  and  $1\pi_u$  orbitals the *p* character dominates. The *d* participation is very small for all orbitals and in all molecules. Of course linking any or all of these orbital aspects of the electronic structure directly to a binding energy contribution remains a primary challenge for quantum chemistry. Our results provide a qualitative description of the molecule in familiar terms and we have not attempted to go beyond this stage.

### D. Heteronuclear diatomics

Turning now to the heteronuclear diatomics, we note the complete absence of experimental information and other theoretical studies on the  $\text{SiGe}$ ,  $\text{SiSn}$ , and  $\text{GeSn}$  systems. In order to touch base with experiment on a related system we have performed a preliminary study on the  $\text{SiC}$  molecule for which *ab initio* CI investigations are available.<sup>6,26</sup> In Table VII are collected all our data on the studied heteronuclear diatomics together with the CI studies for  $\text{SiC}$ .<sup>6,26</sup> We found for  $\text{SiC}$ , in agreement with both CI studies, that  $^3\Pi$  is the ground state and that the  $^3\Sigma^-$  state lies above, at 0.57 eV. The  $T_e$  values from CI are found to be 0.69 and 0.65 eV, respectively.<sup>6,26</sup> Concerning the  $R_e$  and  $\omega_e$  results we note that our results compare favorably with those of MRD-CI.<sup>11</sup> The vibrational frequencies are good to about 10%. On the basis of these encouraging results, we have performed calculations on the other heteronuclear diatomics of group IVA. Contrary to  $\text{SiC}$ , the  $\text{SiGe}$ ,  $\text{SiSn}$ , and  $\text{GeSn}$  molecules have  $^3\Sigma^-$  ground states, followed by  $^3\Pi$  and  $^1\Sigma^+$  states, respectively. The general shape of the potential curves (Fig. 2) is very similar to those for the corresponding homonuclear systems and the previous discussion remains valid. The energy differences between the ground states and the first low-lying excited states are very small as found for the homonuclear diatomics as well. In fact, as is reported in Table VII, the  $T_e$  for these two states have values of about 0.1 for  $\text{SiGe}$  and  $\text{SiSn}$  and about 0.2 for  $\text{GeSn}$ . Also for these molecules we can regard these two states as being practically degenerate. The equilibrium distances of the different states show that on going from  $^3\Sigma^-$  to  $^3\Pi$  and  $^1\Sigma^+$ , contractions occur, mainly for  $^3\Pi$  states. An inspection of the computed  $\omega_e$  shows that the trends in vibrational frequencies are the same for all the molecules and that the differences between  $\omega_e$  of the different electronic states decrease on going from  $\text{SiGe}$  to  $\text{GeSn}$ . Finally, the computed  $D_e$  decrease in the series as in the homonuclear case.

In Table VIII we report the Mulliken population analysis for the heteronuclear molecules. As in the case of homonuclear systems, the  $1\sigma$  ( $1\sigma_g$ ) orbitals are bonding and the  $2\sigma$  ( $1\sigma_u$ ) orbitals are antibonding. The  $3\sigma$  ( $2\sigma_g$ ) orbital again appears from the Mulliken analysis to be essentially nonbonding in all the molecules. However, wave function plots (Fig. 4) reveal the bonding nature of this orbital. The orbital compositions of the  $1\sigma$  and  $2\sigma$  orbitals reveal a predominant *s* character with a *p* contribution that is more significant in the case of  $\text{SiC}$ . The overlap population of these

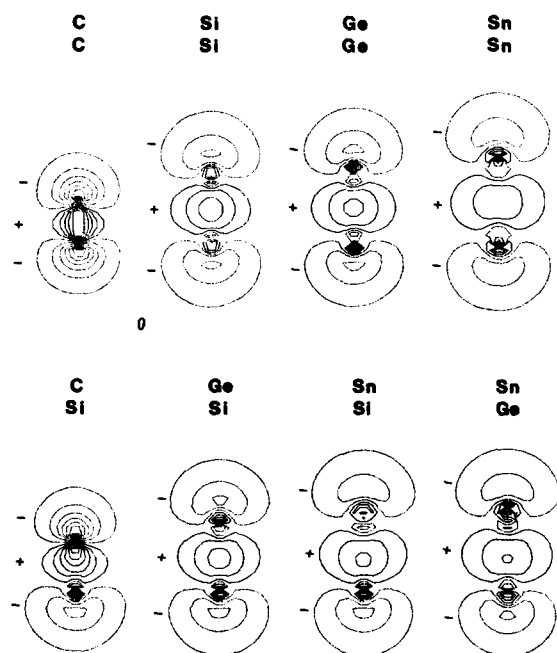


FIG. 4. Contours of the uppermost occupied  $\sigma$  valence orbitals of group IVA diatomics. The lowest contour is 0.025 a.u. and adjacent contours differ by 0.050 a.u.



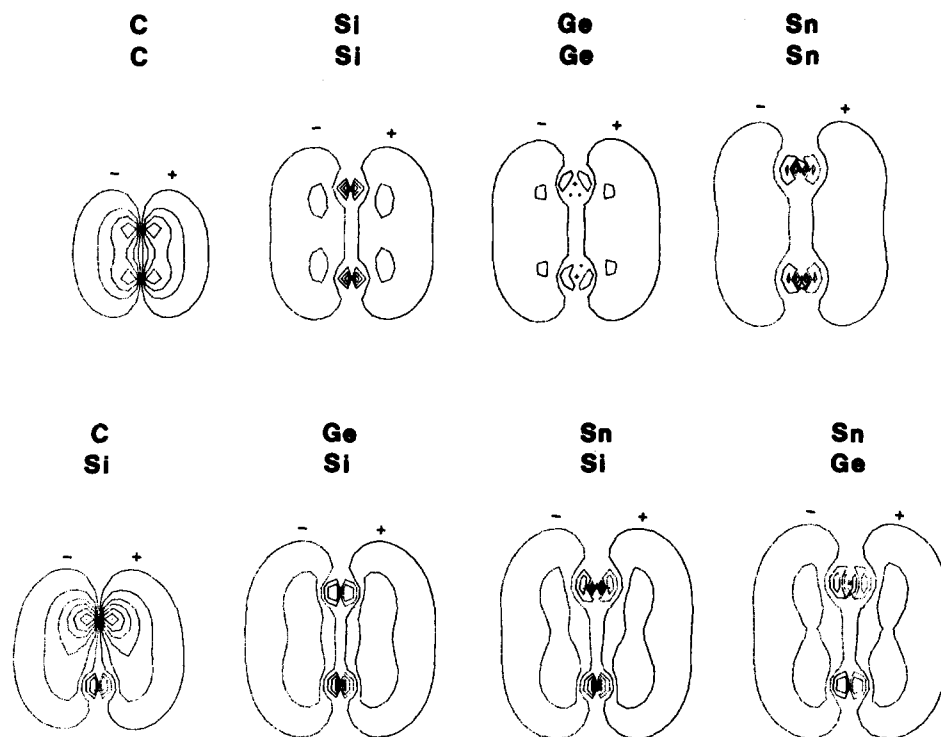


FIG. 5. Contours of the bonding  $\pi$  valence orbitals of group IVA diatomics. The lowest contour is 0.025 a.u. and adjacent contours differ by 0.050 a.u.

orbitals decreases in the series but the most appreciable variation occurs going from SiC to SiGe. The  $3\sigma_g$  orbital in the case of SiC is formed by a  $p$  orbital of C and Si with a small contribution from Si  $s$  functions. In all the other cases, the orbital compositions of  $3\sigma$  are essentially similar. Finally, the  $1\pi_u$  orbitals show a considerable overlap with a strong  $p$  participation of both partners. The only difference in the series is the higher participation of the  $p$  orbital of carbon in SiC whereas in the other cases the  $p$  values are essentially the same for the two considered atoms. For the heavier molecules, the relatively equal distribution of the valence levels between the two atoms is apparent from Figs. 4 and 5.

From our results it is clear that the molecules containing a carbon atom show a ground state that is different from the other systems. In particular,  $C_2$  and SiC have  $^1\Sigma_g^+$  and  $^3\Pi$ , respectively, as ground states whereas the ground state of all the other considered diatomics is  $^3\Sigma^-$ . We have addressed the question of why the diatomics of group IVA show these differences. Previous studies<sup>6,10,14</sup> have pointed out that this effect can be traced to the different energy gap between  $1\sigma_u$  and  $2\sigma_g$  or  $1\pi_u$  MOs. For homonuclear diatomics this gap is smaller in  $C_2$  than in other cases.<sup>10</sup> A reliable comparison of this gap has been performed so far only for  $C_2$ ,  $Si_2$ , and  $Ge_2$  at the LMTO-LSD level.<sup>18</sup> It is interesting to verify this hypothesis for all the diatomics of group IVA. In Fig. 3 we have reported the orbital energy diagrams for the ground states of the molecules studied together with the  $^1\Sigma_g^{+*}$  state of  $C_2$  computed at the equilibrium distances. As is shown in this figure the  $1\sigma_g-1\sigma_u$  splitting decreases drastically on going from  $C_2$  to  $Si_2$  and continues to decrease in the series. On the other hand, the  $1\sigma_u-2\sigma_g$ ,  $1\pi_u$  splitting shows the reverse trend. The most significant variation occurs also in this case on going from  $C_2$  to  $Si_2$  (the difference being 1.39 eV) while

the change in this splitting from  $Si_2$  to  $Ge_2$  is only 0.46 eV. The trend is slightly reversed on going from Ge to Sn, perhaps owing to the fact that the Ge model potential is nonrelativistic.

The analysis of heteronuclear diatomics shows the same trends observed previously for homonuclear ones. These trends mean that passing from  $C_2$  to  $Sn_2$  and from SiC to GeSn the possible hybridization of  $s$  and  $p$  AOs in the occupied MOs of the diatomics decreases considerably. On the other hand, this is in agreement with our population analyses (see Tables V and VII) and with the same trend found in an *ab initio* CI study for  $Ge_2$ .<sup>14</sup>

TABLE VII. Spectroscopic constants for group IVA heteronuclear dimers.

Molecule	State	$R_e$ (bohr)	$\omega_e$ ( $cm^{-1}$ )	$T_e$ (eV)	$D_e$ (eV)
SiC	$^3\Pi$	3.26	930	0.0	5.38
	$^3\Sigma^-$	3.44	826	0.57	4.81
SiC <sup>a</sup>	$^3\Pi$	3.445	983	0.0	
	$^3\Sigma^-$	3.590	606	0.69	
SiC <sup>b</sup>	$^3\Pi$	3.299	914	0.0	
	$^3\Sigma^-$	3.439	960	0.65	
SiGe	$^3\Sigma^-$	4.42	397	0.0	3.79
	$^3\Pi$	4.17	484	0.11	3.67
SiSn	$^1\Sigma^{+*}$	4.26	294	0.80	2.99
	$^3\Sigma^-$	4.76	339	0.0	3.39
	$^3\Pi$	4.48	378	0.10	3.29
	$^1\Sigma^{+*}$	4.60	308	0.66	2.70
GeSn	$^3\Sigma^-$	4.87	236	0.0	3.34
	$^3\Pi$	4.57	242	0.22	3.13
	$^1\Sigma^{+*}$	4.79	190	0.70	2.63

<sup>a</sup>From Ref. 20.

<sup>b</sup>From Ref. 16.

TABLE VIII. Mulliken population analysis of the valence orbitals for group IVA heteronuclear dimers computed at their equilibrium distances (see Table VII) of the ground states.

Molecule	State	Orbital	Orbital analysis										Occ. No.	
			Atomic population			X			Y					
			X	Y	Overlap	s	p	d	s	p	d	↑	↓	
SiC	$^3\Pi$		Si	C			Si		C					
		1s	0.0	2.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	1	1	
		1σ	0.43	0.86	0.71	0.58	0.16	0.05	1.08	0.13	0.0	1	1	
		2σ	1.39	0.83	−0.22	1.01	0.24	0.03	0.50	0.22	0.0	1	1	
		3σ	0.50	0.55	−0.05	0.18	0.29	0.0	0.05	0.48	0.0	1	0	
		1π	0.88	1.35	0.77	0.0	1.19	0.07	0.0	1.74	0.0	2	1	
		Net charge	0.203	−0.203										
SiGe	$^3\Sigma$		Si	Ge			Si		Ge					
		1σ	0.53	0.92	0.55	0.68	0.11	0.02	1.09	0.08	0.02	1	1	
		2σ	1.37	1.03	−0.40	1.10	0.05	0.02	0.71	0.11	0.01	1	1	
		3σ	1.02	0.96	0.02	0.13	0.89	0.01	0.12	0.84	0.01	1	1	
		1π	0.78	0.74	0.48	0.0	1.00	0.02	0.0	0.96	0.02	2	0	
		Net charge	−0.024	0.024										
			Si	Sn			Si		Sn					
SiSn	$^3\Sigma$	1σ	0.75	0.76	0.49	0.88	0.10	0.01	0.95	0.06	0.0	1	1	
		2σ	1.21	1.15	−0.36	0.96	0.05	0.02	0.90	0.07	0.0	1	1	
		3σ	1.03	0.91	0.06	0.10	0.95	0.01	0.11	0.83	0.0	1	1	
		1π	0.82	0.74	0.44	0.0	1.02	0.04	0.0	0.94	0.0	2	0	
		Net charge	−0.122	0.122										
			Ge	Sn			Ge		Sn					
		1σ	1.05	0.52	0.43	1.18	0.07	0.01	0.68	0.06	0.0	1	1	
GeSn	$^3\Sigma$	2σ	0.97	1.37	−0.34	0.72	0.06	0.01	1.18	0.03	0.0	1	1	
		3σ	0.99	0.94	0.05	0.08	0.95	0.01	0.10	0.86	0.0	1	1	
		1π	0.80	0.78	0.42	0.0	1.00	0.02	0.0	0.98	0.0	2	0	
		Net charge	−0.102	0.102										

## IV. CONCLUSION

In the present work we have presented the model potential for the Si, Ge, and Sn atoms and the LCGTO-MP-LSD study of homo- and heteronuclear diatomics of group IVA elements. On the basis of our results we can conclude that our model potential for these atoms at the LCGTO-MP-LSD level of theory is able to correctly reproduce the relative order of the different electronic states. The computed spectroscopic constants are in excellent agreement with the experimental data where available and in general good agreement with previous *ab initio* CI studies. In particular, the agreement is better with the most extensive CI calculations.

For the heteronuclear diatomics we confirm that for SiC the ground state is  $^3\Pi$  followed by  $^3\Sigma^-$ . For the unknown SiGe, SiSn, and GeSn molecules our theoretical study predicts the ground state as  $^3\Sigma^-$  with  $^3\Pi$  and  $^1\Sigma^+$  low-lying excited states. Additionally, we predict spectroscopic and

structural properties for these molecules which we hope will stimulate experimental studies.

For the first time the main features of the electronic structure have been ascertained and described using the same level of theory for all the molecules. We are confident that our LSD model potential technique is accurate and economical enough to allow the extension of the present method to study surface phenomena and chemisorption processes on clusters of semiconductors.

## ACKNOWLEDGMENTS

This work was carried out with financial assistance from the Natural Sciences and Engineering Research Council of Canada, the Fonds FCAR of the Government of Québec and the Institut Français du Pétrole. One of the authors (N. R.) is indebted to NSERC of Canada for a fellowship. We thank Dr. Amine Selmani for his contribution to development of the model potentials. We are grateful to the Centre de Calcul de l'Université de Montréal for providing computer services.

## APPENDIX

TABLE IX. Valence orbitals for  $\text{Si}^{4+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$  MP.

	Si		Ge		Sn	
	$\alpha$	C	$\alpha$	C	$\alpha$	C
ns	62.50	-0.0728	329.1	0.0412	981.1	-0.0169
	2.344	0.3410	17.55	-0.1982	48.58	0.1229
	0.8241	0.1818	2.080	0.5573	8.685	-0.3656
	0.2379	1	0.2100	1	1.410	0.7393
	0.0841	1	0.0770	1	0.1856	1
np					0.0709	1
	21.30	0.0338	57.49	-0.0595	160.5	-0.0260
	4.169	0.1619	3.208	0.2268	12.34	0.1092
	0.2690	1	0.2500	1	1.859	1
	0.0760	1	0.0717	1	0.1835	1
nd <sup>a</sup>					0.0574	1
	0.26	1	0.20	1	0.18	1

<sup>a</sup> d-type polarization function used in molecular calculations.

TABLE X. The MP parameters for  $\text{Si}^{4+}$ ,  $\text{Ge}^{4+}$ , and  $\text{Sn}^{4+}$ .

$\text{Si}^{4+}$		$\text{Ge}^{4+}$		$\text{Sn}^{4+}$	
$\alpha$	C	$\alpha$	C	$\alpha$	C
88.56	-3.218	807.9	-3.070	2075	-2.895
66.08	-3.289	109.3	-7.370	834.2	-7.532
1.468	-3.295	10.53	-10.33	42.18	-13.94
1.112	-0.1983	1.754	-6.878	7.485	-10.34
		0.5020	-0.3559	1.882	-6.608
				0.8820	-4.249
				0.3423	-0.4309

TABLE XI. Atomic core orbitals and values of  $2\epsilon_c$ .

$\text{Si}^{4+}$				
$\alpha$	1s	2s	$\alpha$	2p
1.342	0.0055	-0.6743	1.136	0.3334
4.896	0.0008	-0.5168	4.145	0.5834
17.86	0.4052	0.2494	15.13	0.2527
65.18	0.5235	0.1812	55.25	0.0570
237.8	0.1601	0.0475		
867.8	0.0559	0.0148		
$-2\epsilon_c$ :	130.3	10.13	$-2\epsilon_c$ :	7.012
$\text{Ge}^{4+}$				
$\alpha$	1s	2s	3s	
1.588	-0.0056	0.0301	0.9688	
5.563	0.0104	-0.2398	0.2120	
19.49	-0.0197	-0.9215	-0.7266	
68.26	0.2431	0.0942	0.0668	
239.1	0.5815	0.3009	0.1130	
837.8	0.2396	0.0783	0.0347	
2935	0.0913	0.0310	0.0112	
$-2\epsilon_c$ :	792.6	98.10	11.91	
$\alpha$	2p	3p	$\alpha$	3d
1.188	0.0062	-0.3928	0.7276	0.2883
3.729	-0.0033	-0.6917	2.598	0.5492
11.70	0.3500	-0.0032	9.276	0.3866
36.73	0.5725	0.2714	33.12	0.1010
115.3	0.2079	0.0827		
361.7	0.0548	0.0228		
$-2\epsilon_c$ :	87.42	8.376	$-2\epsilon_c$ :	2.221
$\text{Sn}^{4+}$				
$\alpha$	1s	2s	3s	4s
1.191	-0.0098	0.0053	-0.0553	-1.180
3.652	-0.0127	-0.0374	0.4460	0.0673
11.19	0.0392	0.0414	1.043	1.0176
34.33	-0.0355	-0.7991	-0.7945	-0.4881
105.2	0.0668	-0.4162	-0.2977	-0.1212
322.7	0.4123	0.3045	0.1585	0.0604
989.4	0.4535	0.1909	0.0865	0.0433
3033	0.1419	0.0598	0.0275	0.0108
9300	0.0908	0.0311	0.0139	0.0065
$-2\epsilon_c$ :	2120	320.4	61.79	9.769
$\alpha$	2p	3p	$\alpha$	4p
0.8807	-0.0039	-0.0095	0.5108	
2.519	0.0111	-0.0198	0.7223	
7.209	-0.0150	-0.6807	-0.3860	
20.62	0.1232	-0.4634	-0.3094	
59.01	0.5211	0.2783	0.1296	
168.8	0.4028	0.2039	0.0860	
483.0	0.1092	0.0556	0.0256	
1382	0.0375	0.0169	0.0069	
$-2\epsilon_c$ :	288.9	51.34	6.577	
$\alpha$	3d	4d		
0.5205	0.0068	-0.3596		
1.596	-0.0088	-0.6313		
4.893	0.2638	-0.2025		
15.00	0.6058	-0.2316		
45.99	0.3021	0.1171		
141.0	0.0697	0.0277		
$-2\epsilon_c$ :	34.82	1.897		

TABLE XII. Auxiliary set for the Coulomb fit.

$\text{Si}^{4+}$		
s	221.5, 41.9, 7.9, 1.50, 0.28, 0.05	
p	4.0, 1.3, 0.3	
d	30.0, 8.0, 1.0, 0.1	
$\text{Ge}^{4+}$		
s	660.0, 34.1, 10.2, 4.4, 0.45, 0.10	
p	6.0, 0.5, 0.14	
d	35.0, 6.0, 0.5, 0.1	
$\text{Sn}^{4+}$		
s	100.0, 30.0, 9.0, 3.0, 1.0, 0.38, 0.14	
p	3.2, 0.37, 0.12	
d	40.0, 3.7, 0.36, 0.1	
	Auxiliary set for the exchange-correlation fit	
$\text{Si}^{4+}$		
s	15.5, 4.5, 1.3, 0.4, 0.1, 0.03	
p	2.0, 0.6, 0.1	
d	10.0, 3.0, 0.3, 0.04	
$\text{Ge}^{4+}$		
s	30.5, 7.2, 2.4, 0.85, 0.22, 0.05	
p	1.5, 0.3, 0.08	
d	11.0, 0.80, 0.06	
$\text{Sn}^{4+}$		
s	50.0, 10.0, 3.0, 1.0, 0.33, 0.13, 0.05	
p	1.1, 0.12, 0.04	
d	12.0, 0.12, 0.03	

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