Ab initio cluster-model study of the on-top chemisorption of F and Cl on Si(111) and Ge(111) surfaces

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The interaction of atomic F and Cl with Si_4H_9 and Ge_4H_9 cluster models has been studied by using *ab initio* pseudopotentials and basis sets of increasing complexity. The results show that the effect of d orbitals is important in order to reproduce the experimental findings. However, the use of polarization functions in the atoms which are directly involved in the chemisorption bond leads to results which are very close to those obtained using extended basis sets. The local nature of the chemisorption bond is also interpreted by means of a Mulliken population analysis. For F-Si_4H_9 and Cl-Si_4H_9 the present results are in good agreement with previous *ab initio* all-electron calculations, and for the chemisorption of Cl on Si(111) and Ge(111) surfaces, good agreement is found with respect to the available experimental results as well as with previous slab calculations based on the local-density-functional formalism.

INTRODUCTION

Recent investigations of the chemisorption of Cl on Si(111) and Ge(111) surfaces have finally concluded that, among the several high-symmetry sites usually assumed for the interpretation of bonding at those surfaces, the on-top site is, without doubt, the preferred one. In fact, surface-extended x-ray-absorption fine-structure (SEXAFS) measurements[1] show that the adsorption of Cl on annealed Si(111)-(7×7), annealed Ge(111)-(2×8), and quenched Si(111)-($\sqrt{19}\times\sqrt{19}$) occurs at the onefold on-top site, and also permits the structural determination of the bond distance between the adsorbate and the substrate. Thus, from the experimental viewpoint it is clear that bonding between Cl and the Si(111) surface is of a covalent nature, while chemisorption on the threefold site, which implies an ionic bond, is unfavored.

On the other hand, the theoretically determined geometries[2] based on the local-density-functional formalism (LDF) and on the use of atomic pseudopotentials, for a six-layer slab of substrate and two overlayers of adsorbate, agree quantitatively with the SEXAFS measurements and also suggest that the bridging sites are not minima, but are saddle points. These authors also find that the inclusion of d orbitals in the atomic basis set is important.

The evidence for on-top chemisorption of Cl on Si(111) has been also found by Seel and Bagus[3] through *ab initio* all-electron cluster-model calculations at the double-ζ level, and they report similar results for F on Si(111). However, the bondlengths reported by Seel and Bagus are larger than both the experimental ones and those calculated using LDF slab calculations. At this point it is difficult to assess whether the effect on the distance comes from the inclusion of the d orbitals on the atomic basis set,

from the effect of correlation energy, which is partly taken into account in LDF theory, but not at all in the *ab initio* self-consistent-field (SCF) calculations, or even from both effects.

It should be noted that the use of an extended basis set in cluster-model calculations is very expensive due to the size of the cluster model. Even with the use of a relatively small model for the Si(111) surface the computational effort is enormous, and for the Ge(111) cluster model, extended-basis all-electron *ab initio* calculations are out of the question.

In order to solve such a dilemma the use of *ab initio* atomic pseudopotentials is very valuable and, as only valence electrons are treated explicitly, the computation of cluster models for Si(111) and Ge(111) surfaces using an extended basis is possible at an identical level of accuracy and with the same computational effort.

In this paper the chemisorption of F and Cl on cluster models simulating the Si(111) and Ge(111) surfaces is studied at the SCF *ab initio* level and by using the *ab initio* pseudopotentials of Durand and Barthelat.[4] As the inclusion of d orbitals seems necessary, several basis sets of different complexities are used, and mixed basis sets are also proposed. Such a choice will permit a direct comparison between the present calculations and available SCF all-electron *ab initio* calculations, LDF slab calculations, and experimental results.

METHOD OF CALCULATION

All of the present calculations were carried out by using an UNIVAC 1100/80 version of PSHONDO program, a version of the HONDO package[5] including the *ab initio* pseudopotentials of Durand and Barthelat,[4] and the effective recombination of $6d$ to $5d$ atomic orbitals.[6]

The pseudopotentials are derived from the double-ζ atomic Hartree-Fock calculations of Clementi and Roetti.[7] From an all-electron calculation, a pseudo-orbital is obtained; this pseudo-orbital reproduces the SCF valence atomic orbital in the valence region, but cancels the orthogonality tails in the core region. Once this pseudo-orbital is obtained, a radial potential is determined for each l symmetry, leading to an effective Fock operator, the solution of which is the pseudo-orbital, but with the energy of the all-electron valence orbital. Such a procedure effectively reproduces results of double-ζ quality in the inner shells and permits the use of an extended basis set in the valence ones. Thus, the pseudopotential results are at least of double-ζ quality.

In this work, we use pseudopotentials on Si, Ge, Cl, and F atoms, which have already used in molecular calculations.[8−11]

The determination of wave functions for the cluster with and without the corresponding adatom is carried out by using the SCF Hartree-Fock linear combination of atomic orbitals (HF LCAO) method for closed shells. The open shells are treated by the approximate method described by Nesbet,[12] and in the present work this method is only used to determine the wave functions and total energy of isolated clusters.

The atomic orbitals are described by means of contracted Gaussian orbitals (CGO's) which constitute the atomic basis set. In this work several basis sets have been used, including mixed basis sets of the same kind as previously used in dealing with atomic hydrogen chemisorption on Be(0001).[13]

The basis sets used here can be summarized as follows:

Basis 1. This basis set is of double-ζ quality in Si, Ge, F, and Cl atoms. The ns orbitals are described by four primitive basis functions which are contracted by means of a $3+1$ procedure. For the np orbitals a similar approach is used, except for Si and Ge, where a $2+2$ procedure is used. Thus, we can designate this basis as (44/22). The hydrogen basis set, at this level, consists of four primitive functions and is contracted to the minimum basis quality; this is designated as (4/1).

Basis 2. This basis set uses the previous basis set for Si, Ge, Cl, and F, but is also of double-ζ quality for the hydrogen atoms, the four initial primitive functions now being contracted through a $3+1$ procedure. This can be written in the form (4/2) for the atomic hydrogen basis set and (44/22) for the corresponding Si, Ge, F, and Cl ones.

Basis 3. This basis set the effect of polarization on the adatom. Thus, a single d function was added to the previous F and Cl basis sets. The exponents were taken from Sieghban and Ross[14] and were 1.62 and 0.56, respectively. Basis 2 is used for the remaining atoms. The basis sets are then (441/221) for Cl and F, (44/22) for Si and Ge, and (4/2) for hydrogen.

Basis 4. This basis set accounts for the polarization on the first-layer Si and Ge atoms (see next section for a description of the cluster models), and, as in basis 3, a single d function was added to the first-layer Si and Ge atoms; the d exponents were taken from Ref. 9. For the remaining atoms, basis 3 is used. Consequently, this can

be summarized as (441/221) for F, Cl, and first-layer Si and Ge atoms, (44/22) for the second-layer Si and Ge atoms, and (4/2) for the hydrogen-embedding atoms.

Basis 5. Use of this basis set is an attempt to obtain basis-set-limiting results. It is of double-ζ—plus—polarization quality on all atoms, except for hydrogen, where a double-ζ—quality basis set is used. This leads to a (441/221) basis set for F, Cl, Si, and Ge, and (4/2) for H, the exponents being those described above.

By using the basis sets described above, SCF calculations were carried out for the isolated cluster models as well as the adatom-substrate systems. In the latter case, the energy was computed versus the vertical distance to the cluster model, and the equilibrium positions were determined. Binding energies particular to the isolated systems were also calculated.

The vibrational frequencies for the perpendicular vibration to the surface were calculated from the binding-energy curves in the harmonic approximation and by assuming the mass of the substrate to be infinite. Thus, the vibrational energy can be expressed as

$$\hbar\omega_e = \hbar(k/m_x)^{1/2} , \tag{1}$$

m_x being the halogen mass. The use of such an approximation has been widespread in dealing with atomic chemisorption on cluster-model surfaces, and the computed force constants are in error by about 15%.[15,16] Finally, the results obtained are interpreted in terms of a Mulliken population analysis.

All of the present calculations have been carried out in the C_{3v} symmetry group and, consequently, the computation of integrals is greatly reduced, and final eigenvectors belong to the irreducible representations of the C_{3v} punctual group.

CLUSTER MODELS

When using a cluster model to represent the surface, a choice has to be made about the cluster size, that is, the number of atoms which are treated explicitly in the calculation, and the level of precision of the required computation. Fortunately, the chemisorption of atoms on surfaces seems to be of local character. This fact is strongly supported by earlier *ab initio* cluster-model calculations[3,15,16] and particularly by the calculations reported by Seel and Bagus for the on-top chemisorption of F and Cl on Si(111) surface.[3] These authors showed that the binding-energy curves for X-Si$_4$H$_9$ (X = F,Cl) and X-Si$_{10}$H$_{15}$ were substantially the same. This makes possible the use of the Si$_4$H$_9$ cluster model for the simulation of the Si(111) surface. As has been argued in several papers,[3,17−19] the use of embedded hydrogen atoms provides an adequate environment for the second-layer atoms and forces them to have the bulk sp^3 hybridization. In this way, use of embedded hydrogen atoms is also expected to minimize edge effects.

For Si$_4$H$_9$ we used the geometric parameters previously used by Seel and Bagus.[3] Thus, values of $d_{\text{Si-Si}} = 4.44$ bohrs and $d_{\text{Si-H}} = 2.80$ bohrs have been used. In the case of Ge$_4$H$_9$ the values were taken from Wyckoff[20] and Pietro *et al.*,[21] the values then being $d_{\text{Ge-Ge}} = 4.63$ bohrs and $d_{\text{Ge-H}} = 2.912$ bohrs, the latter being the experimental

TABLE I. Binding energy for isolated Si_4H_9 and Ge_4H_9 clusters according to the definition in Eq. (2). (Note that basis set 3 includes only polarization in the adatom and hence does not affect result of basis set 2 in the calculation for the isolated cluster.)

Basis set	E_B (hartrees)	
	Si_4H_9	Ge_4H_9
1	0.86	0.79
2	0.89	0.80
4	0.92	0.82
5	1.04	0.88
All electron, DZ[a]	0.91	
All electron, DZ + P[b]	1.05	

[a]DZ denotes double-ζ, Ref. 3.
[b]DZ + P denotes double-ζ plus polarization, Ref. 18.

Ge-H distance in Ge_2H_6.

In the present calculation no relaxation or reconstruction effects were considered and, consequently, the cluster geometry was preserved during the computation of the halogen-substrate potential-energy curves. For the Si(111) surface, there is evidence that the displacements of the surface Si atoms are small,[22,23] and similar trends are expected for the Ge(111) surface. In any case, the effect of relaxation will produce only a slight decrease in the binding-energy curves for the halogen-substrate systems. This is also supported by the ab initio LDF slab calculations on Cl-Si(111) and Cl-Ge(111) systems which use an ideal unreconstructed unrelaxed surface.[2]

The cluster binding energies are defined in the usual way[3] as

$$D = -[E_{tot}(X_4H_9) - 4E_{tot}(X) - 9E_{tot}(H)] , \qquad (2)$$

with $X = $Si,Ge. The energy of the isolated atoms are calculated at the SCF restricted-Hartree-Fock (RHF) open-shell level using the basis sets previously described. Atomic calculations were carried out by using the

PSATOM program, a modification of the ATOM-SCF program,[24] which also permits the use of pseudopotentials at the atomic level.

For the two clusters used here, the values obtained for the cluster binding energies are reported in Table I. From these results it can be seen that the agreement between the pseudopotential and all-electron calculations is excellent, as expected. The adequacy of the pseudopotential approach can further be illustrated by comparing the orbital-energy values of the lowest and highest closed-shell molecular orbitals (ε_l and ε_h) with those obtained by all-electron ab initio calculations on Si_4H_9 with the double-ζ (Ref. 3) and double-ζ—plus—polarization (Ref. 18) basis sets (Table II). The difference between these orbital energies can be compared with the experimental[25] and calculated[26] bandwidths of silicon, which are 12.4 (Ref. 25) and 12.20 eV (Ref. 26), respectively, higher than a value which ranges from 11.28 to 10.75 eV, depending on the basis set employed. For the Ge_4H_9 cluster the range of the bulk valence-band width obtained here is 13.39—11.10 eV, which is also comparable with the experimental and LDF-calculation values, which are 12.6 (Ref. 27) and 12.46 eV (Ref. 26), respectively. However, the information coming from orbital energies must be handled cautiously since the energies can be arbitrarily shifted by different SCF procedures, which use the level-shift[28,29] technique to improve convergence.

The population analysis for both cluster models are reported in Table III. Of particular interest is the agreement found for Si_4H_9 with respect to previous all-electron ab initio calculations.[3,18] The difference at the double-ζ—plus—polarization level in the d population with respect to the value reported in Ref. 18 is due to the s contribution, which is partially taken into account when $6d$ functions are used to represent the d orbitals. This is not the present case since the effective recombination $6d \rightarrow 5d$ is carried out in our computational framework.

The differences between the values obtained using different basis sets are small and illustrate the usefulness of mixed basis sets. However, in the latter case the information must be treated in a qualitative way since small dis-

TABLE II. Oribtal-energy range for the valence levels in Si_4H_9 and Ge_4H_9 isolated clusters. The energy of the lowest (highest) doubly occupied valence molecular orbital is denoted ε_l (ε_h); the range is denoted $\Delta\varepsilon$. All energies are in hartrees. DZ and DZ + P as in Table I.

	Basis set	ε_l	ε_h	$\Delta\varepsilon$
Si_4H_9	1	−0.810	−0.396	0.413
	2	−0.801	−0.384	0.417
	4	−0.795	−0.387	0.408
	5	−0.782	−0.387	0.395
	All electron DZ[a]	−0.801	−0.383	0.418
	All electron DZ + P[b]	−0.776	−0.332	0.440
Ge_4H_9	1	−0.797	−0.378	0.418
	2	−0.791	−0.370	0.421
	4	−0.785	−0.371	0.414
	5	−0.777	−0.368	0.408

[a]Reference 3.
[b]Reference 18.

TABLE III. Electronic population according to the Mulliken analysis. The s, p, and d contributions are explicitly given for the atoms on each substrate layer. The layer is denoted by a superscript.

		Si4H9				Ge4H9			
		$N(Si^1)$	$N(Si^2)$	$N(H^1)$	$N(H^3)$	$N(Ge^1)$	$N(Ge^2)$	$N(H^1)$	$N(H^3)$
Basis set 1	s	1.58	1.00	1.30	1.30	1.58	1.07	1.28	1.28
	p	2.77	1.99			2.68	2.00		
	Total	4.35	2.99	1.30	1.30	4.26	3.07	1.28	1.28
Basis set 2	s	1.56	1.30	1.13	1.13	1.57	1.29	1.16	1.16
	p	2.69	2.22			2.65	2.15		
	Total	4.25	3.52	1.13	1.13	4.21	3.44	1.16	1.16
Basis set 4	s	1.56	1.28	1.14	1.14	1.57	1.29	1.17	1.17
	p	2.69	2.19			2.65	2.07		
	d	0.08				0.12			
	Total	4.33	3.47	1.14	1.14	4.48	3.22	1.17	1.17
Basis set 5	s	1.49	1.25	1.10	1.10	1.44	1.23	1.05	1.05
	p	2.66	2.20			2.64	2.36		
	d	0.07	0.16			0.10	0.19		
	Total	4.22	3.61	1.10	1.10	4.18	3.79	1.05	1.05

tortions are introduced through the basis set, i.e., when a d orbital is used in the first-layer Si or Ge atoms, leaving the basis set in the remaining atoms at the double-ζ level, the electronic population of first-layer atoms can be polarized, leading to a slightly different value with respect to either double-ζ or double-ζ—plus—polarization basis-set values, where all atoms are treated at the same level.

The use of minimal basis sets on the hydrogen-embedding atoms, although it does not introduce quantitative changes in the population analysis, leads to a slight exaggeration between the polarities of the atoms of the two layers. It should be noted that, even in this case, the population analysis for the first-layer atom is almost the same as that obtained using more extended basis sets. As will be shown in the next section, the charge transfer between the adsorbate and the cluster model is mainly due to the first-layer atoms and, consequently, small changes in the electronic distribution induced by the use of a different basis does not lead to important changes in the results for the adsorbate-substrate systems.

From the results in Table III it is also seen that, in both cases, and regardless of which basis set is used, a charge difference between the atoms of the first and second layers does appear. This fact has been interpreted as the tendency to pull the first-layer atoms toward the second layer,[3] which would produce surface-relaxation effects. However, as pointed out by Seel and Bagus,[3] the cluster models used here are too small to reproduce the variation of the electron density between the different layers. In the cluster models used here the atoms of the two substrate layers have different environments due to the embedding hydrogen atoms, which are also responsible for the different populations.

Finally, the ns and np contributions on both clusters clearly indicate the tendency to adopt a sp^3 hybridization, and the absence of strong redistribution charges on the edge atoms on both Si4H9 and Ge4H9 cluster models is an indication of the effective use of H atoms in order to avoid edge effects. identical results were found by *ab initio* all-electron calculations in Si4H9.[3,18]

RESULTS FOR THE ADSORBATE-CLUSTER SYSTEMS

The binding energy for the interaction of F and Cl with the Si4H9 and Ge4H9 clusters was calculated, using the five basis sets previously described, as a function of the perpendicular distance to the surface atom. The binding energy is defined, as usual, as the difference between the total energy of the adsorbate-cluster system and the total energies of the isolated fragments, using the same basis set in both cases. This can be expressed as

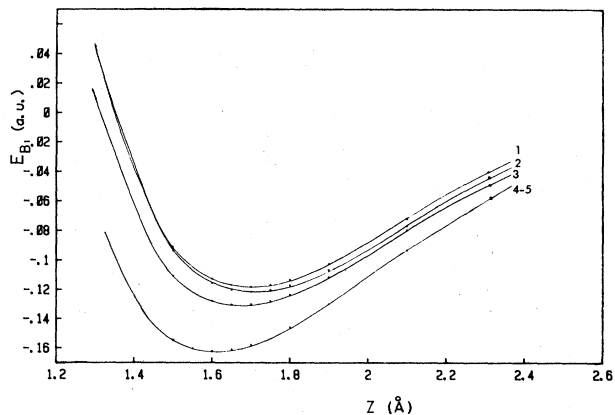$$E_B = E_{tot}(X_4H_9 - Y) - [E_{tot}(X_4H_9) + E_{tot}(Y)] , \qquad (3)$$

FIG. 1. Binding-energy curves for the on-top interaction of atomic F with a Si4H9 cluster model simulating the Si(111) surface. The different curves (1—5) correspond to the results using different basis sets (see text).

where $X = Si, Ge$ and $Y = F, Cl$.

In Fig. 1 the binding-energy curves for the F-Si$_4$H$_9$ system have been reproduced for the different basis sets used here. Note the closeness between results obtained using basis sets 1 and 2, as well as between results obtained using basis sets 4 and 5. These results illustrate the usefulness of mixed basis sets in such calculations, particularly the fact that a good description is obtained by using double-ζ basis set for all the atoms except the embedding hydrogen atoms. By using a minimal basis set for the embedding hydrogen atoms, leaving the remaining atoms at the double-ζ level would permit one to go beyond the Hartree-Fock approximation at a lower cost. Similar arguments are also applicable to the results using basis sets 4 and 5. In this case it can be seen that the effect of including polarization functions in the atoms directly involved in the interaction is sufficient to obtain results which are effectively of extended-basis quality.

It is also interesting to note that the use of *ab initio* pseudopotentials permits the use of more extended basis sets without introducing a minimal basis set in the inner shells. This fact is confirmed by the numerical results summarized in Table IV. From these results it is seen that, by the use of pseudopotentials, confined to the use of basis 2, one is able to reproduce results which have been obtained by all-electron *ab initio* calculations at the double-ζ level, with the slight differences resulting from the use of a nonsegmented basis set in Ref. 3.

Of particular interest is the influence of d orbitals in the bonding between F and the Si$_4$H$_9$ cluster model, which, apart from leading to an increase in the binding energy, as could be expected, also produces a relative increase in the vibrational frequencies perpendicular to the surface and a considerable decrease in the equilibrium position of the adsorbate above the surface.

At this point, it should be noted that the binding energies corresponding to basis set 5 are slightly smaller than those corresponding to basis set 4, a difference that can be attributed to the nonvariational calculation of the open-shell Si$_4$H$_9$ and Ge$_4$H$_9$ systems.

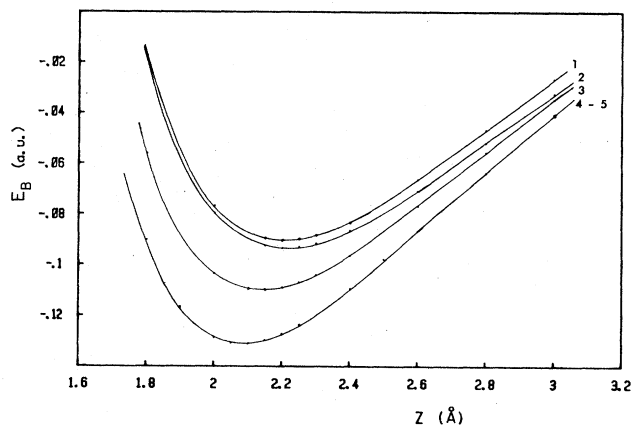Results for the Cl-Si$_4$H$_9$ system follow similar trends.

FIG. 2. Same as Fig. 1 for the on-top chemisorption of atomic Cl over a Si(111) model surface.

However, in this case it becomes clear that the effect of d orbitals is important (Fig. 2). In fact, results obtained by using basis sets 1, 2, or 3 lead to a bond distance which is larger than both the experimental value[1] and that coming from LDF calculations.[2] The results for the bond distance obtained by Bagus *et al.*[3] using double-ζ basis set in the valence and minimal basis sets in the core electrons are even larger, and the binding energy for the Cl-Si$_4$H$_9$ system obtained by these authors is considerably smaller than the present values. As the pseudopotential calculations effectively reproduce results of double-ζ quality in the cores, the difference between the present results and those reported in Ref. 3 should be attributed to the use of a minimal basis set for the Cl core electrons.

With respect to the experimental value for the bond distance, it is seen that, although the present results are in good agreement with experiment, the SCF procedure leads to values for the equilibrium distance that are still slightly larger than the experimental findings, and the difference could be attributed to the correlation effects. Such a con-

TABLE IV. Summary of results for the interaction of fluorine and chlorine with the Si$_4$H$_9$ cluster model. The calculated values for the equilibrium bond distance (r_e), vibrational energy perpendicular to the surface (ω_e), and binding energies (E_B) are given for the five basis sets used here and are compared with available experimental and calculated data.

	Si$_4$H$_9$-F			Si$_4$H$_9$-Cl		
	r_e (Å)	ω_e (cm^{-1})	E_B (eV)	r_e (Å)	ω_e (cm^{-1})	E_B (eV)
Basis set 1	1.69	623.0	3.21	2.20	320.0	2.45
Basis set 2	1.70	623.0	3.30	2.21	320.0	2.55
Basis set 3	1.67	668.0	3.69	2.14	336.0	3.00
Basis set 4	1.61	705.0	4.41	2.08	359.0	3.57
Basis set 5	1.61	708.0	4.40	2.09	362.0	3.63
All electron[a]	1.68		3.25	2.24	326.0	1.66
Experimental[b]				2.03 ($\pm$0.03)		
LDF[c]				2.02	338.0	

[a]Reference 3.
[b]Reference 1.
[c]Reference 2.

TABLE V. Summary of results for the interaction of fluorine and chlorine with the Ge_4H_9 model.

| | Ge₄H₉-F | | | Ge₄H₉-Cl | | |
	r_e (Å)	ω_e (cm⁻¹)	E_B (eV)	r_e (Å)	ω_e (cm⁻¹)	E_B (eV)
Basis set 1	1.79	595	2.94	2.27	328.609	2.45
Basis set 2	1.80	595	2.99	2.27	328.228	2.49
Basis set 3	1.77	647	3.18	2.22	346.278	2.88
Basis set 4	1.77	646	3.55	2.20	345.795	3.23
Basis set 5	1.77	649	3.56	2.21	346.157	3.21
Experimentalᵃ				2.07 (±0.03)		
LDFᵇ				2.09	322.620	

ᵃReference 1.
ᵇReference 2.

clusion is also supported by the LDF calculations of Bachelet and Schlüter.[2]

As is well known, the chemical properties of Si and Ge are very similar; this is also related to the behavior of the Si and Ge surfaces upon F and Cl chemisorption. In Table V a summary of results for F and Cl on Ge(111) is presented. With respect to the F-Ge₄H₉ system, no experimental or calculated data are available for comparison. However, it can be seen that the bond distances, vibrational frequencies, and binding energies are quite similar to the Si₄H₉-F results reported in Table IV. The general trends previously described are also preserved. Binding-energy curves for F-Ge₄H₉ and Cl-Ge₄H₉ are plotted in Figs. 3 and 4, respectively.

In the case of F-Ge₄H₉, the effect of d orbitals on the bond distance is small, although the other properties are greatly affected. For the Cl-Ge₄H₉, the situation is similar to that of the Cl-Si₄H₉ system, but the present calculated bond distance, even using the more extended basis set, 5, still differs by 6% with respect to the experimental value. Thus, to obtain more precise results with the atomic orbitals as the basis set, the effect of electron correlation should be included. However, in view that such computations are very expensive, a rather good description can be obtained at the SCF level.

From a Mulliken population analysis it is seen that the net charge on the adsorbate is quite independent of the basis set used. Particularly, results obtained using basis sets 1 and 2 and basis sets 4 and 5 are very similar. It is also interesting to note that the net charge on the adatom comes mainly from the first-layer atoms in all cases, although the inclusion of d orbitals leads to qualitative changes. In fact, for the F-Si₄H₉ and F-Ge₄H₉ systems, the inclusion of polarization leads to a partial charge transfer from the second-layer atoms, while for the Cl-Si₄H₉ and Cl-Ge₄H₉ supermolecules the effect of the second-layer atoms appears even at the double-ζ level (basis sets 1 and 2). The total net charges on the adsorbate are summarized in Table VI.

The population on the embedding hydrogen atoms is almost constant in all cases and is coincident with the values obtained for the isolated cluster. This is an indication of the role played by such saturators as has been previously described.[3,17,18]

With respect to the population analysis for the remaining atoms in the cluster model, it must be pointed out that, although it leads to an electronic population which is near the corresponding one in the isolated cluster model for the second-layer atoms the population analysis is very different from that of the first-layer atoms, and it changes depending on the basis set. These effects are particularly important when using mixed basis sets, such as basis sets 3 or 4, and they can produce some anomalies with respect to the results obtained by using other basis sets, such as basis sets 1, 2, or 5. This is due to the different treatment of identical atoms, and this information must be handled
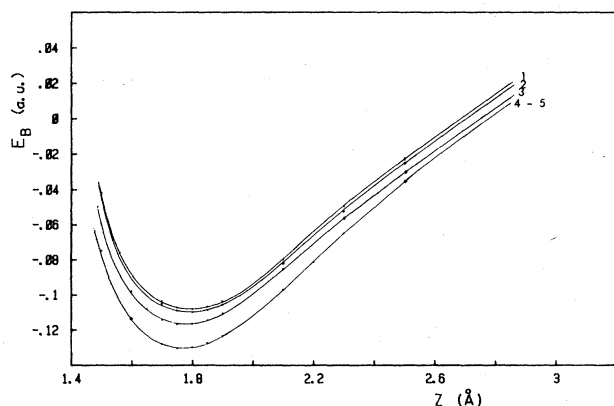

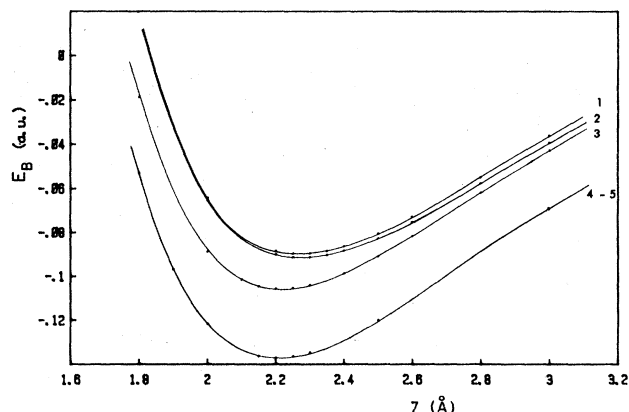FIG. 3. Same as Fig. 1 for the on-top chemisorption of atomic F over a Ge(111) model surface.

FIG. 4. Same as Fig. 1 for the on-top chemisorption of atomic Cl over a Ge(111) model surface.

TABLE VI. Net charges on the adatom (F,Cl) at the equilibrium position on the Si(111) and Ge(111) model surfaces as a function of the different basis sets.

	Basis set 1	Basis set 2	Basis set 3	Basis set 4	Basis set 5
F (on Si)	−0.64	−0.65	−0.66	−0.50	−0.51
F (on Ge)	−0.64	−0.64	−0.65	−0.58	−0.58
Cl (on Si)	−0.36	−0.37	−0.41	−0.35	−0.36
Cl (on Ge)	−0.40	−0.41	−0.43	−0.35	−0.35

cautiously.

Finally, in Table VII we report the relations for the binding energies E_B(F-X)$/E_B$(Cl-X) (X =Si,Ge) and vibrational frequencies ω_e^2(F-X)$/\omega_e^2$(Cl-X), and compare them with the recently proposed empirical relations for chemisorption on surfaces.[30] Although these relations have been mainly proposed for chemisorption on metals, we find rather good agreement between our *ab initio* calculated data and the corresponding empirical relations. This fact is particularly important since, in such relations, F and Cl are treated as exceptions to the empirical rules, which are, consequently, modified.

CONCLUSIONS

From the present calculations it can be concluded that the effect of d orbitals is important in order to reproduce experimental values. However, the use of mixed basis sets suggests that the inclusion of d orbitals in the atoms that are directly involved in the interaction with the adsorbate will be sufficient to obtain results of extended-basis-set quality. The effect of d orbitals appears decisive in the calculation of bond distances, in the view that even by using these limiting basis sets results for the equilibrium distances are still within 3–7 % of error with respect to the experimental value. This fact is attributed to the approximate character of the SCF wave function, which does not include the electronic correlation. The use of mixed basis sets also leads to the possibility of including such electronic correlation effects at a reasonable cost.

On the other hand, the use of atomic *ab initio* pseudopotentials permits the treatment of the valence shell at a high level of accuracy without the necessity of introducing minimal basis sets in the inner shells. Thus, it is ex-

pected that the combined use of atomic pseudopotentials and mixed basis sets will permit the inclusion of the electron correlation effects in the near future. For instance, the use of a basis set like basis set 1 will surely permit one to obtain the effect of electron correlation, at least at the double-ζ level.

For the F-Si$_4$H$_9$ and Cl-Si$_4$H$_9$ clusters, the present results are in good agreement with the previous all-electron *ab initio* calculations reported in Ref. 3, except for the binding energy of Cl on Si$_4$H$_9$, which was found to be too small via use of all-electron calculations. For the chemisorption of Cl on Si(111) and Ge(111) surfaces, quite good agreement with the available experimental data,[1] as well as with previous LDF calculations,[2] is found. These results also illustrate the local character of chemisorption and add further information for use in subsequent studies. The local nature of the chemisorption of F and Cl on Si(111) and Ge(111) can also be found through the electronic populations derived from Mulliken analysis which reflect that the main interaction occurs between the adatom and the first-layer atom of the cluster model.

ACKNOWLEDGMENTS

TABLE VII. Comparison between the present values for the relations E_B(F-X)$/E_B$(Cl-X) (X =Si,Ge), ω_e^2(F-X)$/\omega_e^2$(Cl-X), and those calculated using the empirical equations of Ref. 30.

X	Basis set 1	Basis set 2	Basis set 3	Basis set 4	Basis set 5	All electron[a]	Empirical relations[b]
			E_B(F-X)$/E_B$(Cl-X)				
Si	1.31	1.29	1.23	1.23	1.24	1.97	1.17
Ge	1.20	1.20	1.10	1.10	1.11		1.17
			ω_e^2(F-X)$/\omega_e^2$(Cl-X)				
Si	3.80	3.80	3.96	3.85	3.82		3.12
Ge	3.27	3.29	3.49	3.47	3.50		3.12

[a]Reference 3.
[b]Reference 30.

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