

Theoretical study of the adsorption of H on Si n clusters, ($n = 3 - 10$)

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Theoretical study of the adsorption of H on Si_n clusters, (n=3–10)William Tiznado^{a)}*Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile*

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A recently proposed local Fukui function is used to predict the binding site of atomic hydrogen on silicon clusters. To validate the predictions, an extensive search for the more stable Si_nH ($n=3-10$) clusters has been done using a modified genetic algorithm. In all cases, the isomer predicted by the Fukui function is found by the search, but it is not always the most stable one. It is discussed that in the cases where the geometrical structure of the bare silicon cluster suffers a considerable change due to the addition of one hydrogen atom, the situation is more complicated and the relaxation effects should be considered. © 2005 American Institute of Physics.

[DOI: [10.1063/1.2128675](https://doi.org/10.1063/1.2128675)]**INTRODUCTION**

The study and understanding of binary hydrogen silicon clusters has become an active subject of research in the last years. This is in part because silicon hydrides, neutral, and ions participate in important chemical reactions such as the formation of silicon thin films by chemical-vapor deposition,¹⁻³ hydrogenated amorphous silicon film growth,^{4,5} and silicon nanoparticle production.⁶ In addition, the nature of silicon-hydrogen bond in silicon hydrides containing more than one silicon atom is of significant interest. Computationally, it is very difficult to handle large systems to understand how the addition of hydrogen alters the electronic structure of bare silicon systems. For this reason, theoretical studies of small systems such as disilyne (Si₂H₂) (Refs. 7 and 8) and small monohydrides silicon clusters (Si_nH) (Refs. 9–13) are important. In the study of the Si_nH clusters one important issue is to know how the hydrogen atom is bonded to the silicon cluster and at which position. As the cluster grows the possible binding sites augment considerably and it is desirable to have a methodology to predict them.

In this paper, in an attempt to understand the reactivity

of silicon clusters, a recently proposed local Fukui function¹⁴ will be used to predict the most probable site where a hydrogen atom would bind to the silicon clusters. Since the hydrogen atom is more electronegative than the silicon clusters, it acts as an acceptor of charge. Therefore, it is expected that the reactivity will be driven by the highest occupied molecular orbital (HOMO) of the bare silicon cluster. In order to check the reliability of the predictions a detailed search for the more stable isomers of each Si_nH ($n=3-10$) has been done using a modified genetic algorithm.¹⁵ This methodology has already been used to search for the more stable isomers of the bare silicon¹⁶ and small Si_nCu¹⁷ clusters.

In the past there have been various studies of the reactivity of clusters. Fuentealba and Savin¹⁸ have analyzed the bonding of hydrogen to lithium clusters using the electron localization function (ELF).¹⁹ Galvan *et al.* have studied the reactivity of Si₄ with a single atom (Si or Ga)²⁰ using the reactivity indices defined in the density-functional theory (DFT). The topology of the frontier orbitals were used by Chrétien *et al.*^{21,22} to propose simple rules which can be used to predict the binding site of propene to Au and Ag clusters. Mañanes *et al.*²³ have used the topology of the Fukui function and the atomic condensed Fukui function analysis to study the bonding and reactivity of H and Al₁₃ clusters. In a

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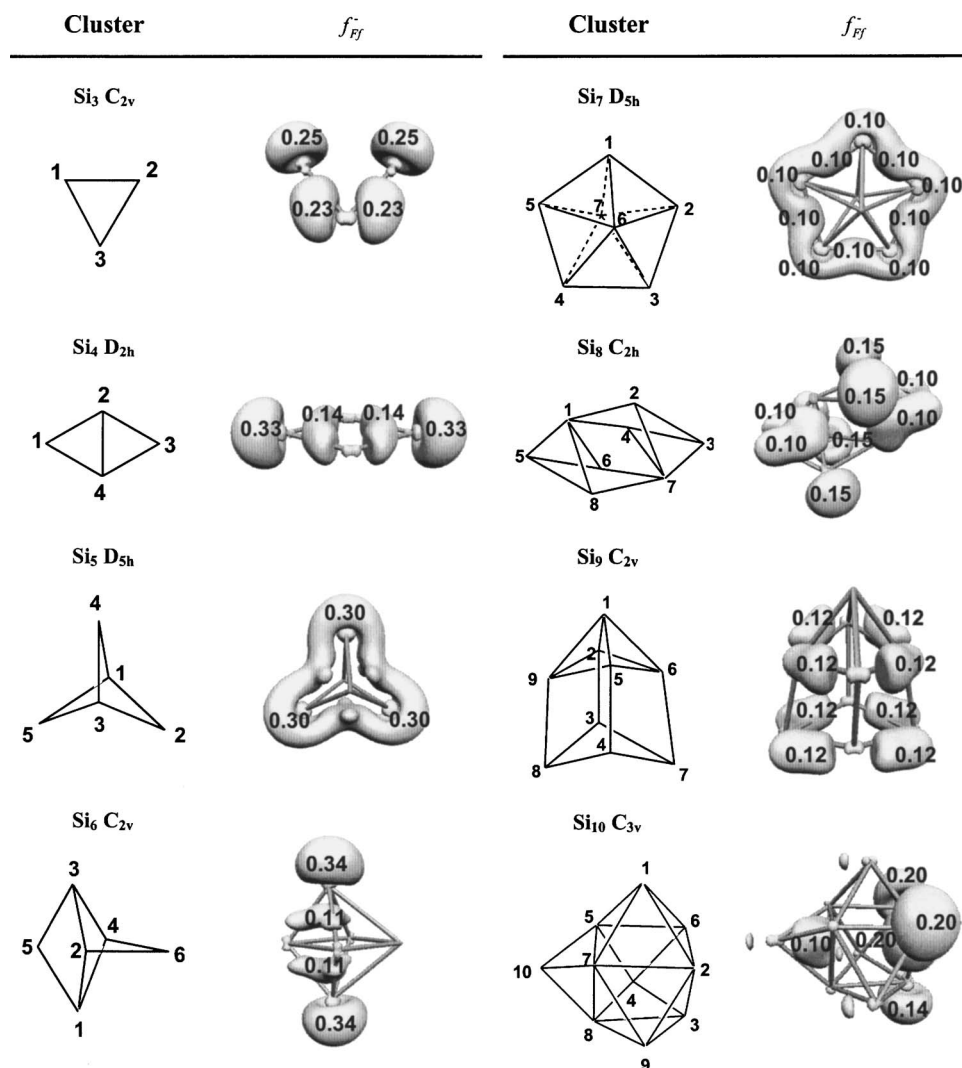


FIG. 1. Condensed donor Fukui functions f_{FF}^- for more stable Si_n ($n=3-10$) clusters, at the B3LYP/6-311+G* level of theory.

previous paper,¹⁴ some of us have shown condensed Fukui functions for Li₄ and Si₄ clusters which are not related with atomic centers but with bonding regions, and the predictions are in good agreement with the results of Fuentealba *et al.*¹⁸ and Galvan *et al.*²⁰ related to the reactivity of these clusters.

METHODOLOGY

Parr and Yang²⁴ defined the Fukui function as

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta\nu(\mathbf{r})} \right]_N, \quad (1)$$

which gives a measurement of the change of the chemical potential μ when a local change is induced in the external potential $\nu(\mathbf{r})$. N is the number of electrons in the system. It has been shown²⁵ that, in a first approximation, the Fukui function is equal to the square of the respective frontier orbital, the HOMO when the derivative is taken from the left, f^- , and the lowest unoccupied molecular orbital (LUMO) when the derivative is taken from the right, f^+ . In the Kohn-Sham scheme the Fukui function can be defined as²⁵

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta\nu_{KS}(\mathbf{r})} \right]_N, \quad (2)$$

where $\nu_{KS}(\mathbf{r})$ is the effective Kohn-Sham potential. Now, this derivative is exactly equal to the square of the respective frontier orbital,

$$f(\mathbf{r}) = |\phi^\alpha(\mathbf{r})|^2, \quad (3)$$

where ϕ^α is the frontier orbital (α =HOMO or LUMO). This is an exact equation, and the so-implemented Fukui function is a positive definite function which normalizes to unity.²⁶⁻²⁸ In a previous work¹⁴ the condensation of this function using a numerical integration of the Fukui function over the basins of the Fukui function itself has been proposed and named f_{FF}^\pm for an acceptor or donor system. In this work, this function has been used to analyze the reactivity of the silicon clusters against a hydrogen atom.

In addition to this, for the search of the more stable isomers, a stochastic method which uses a parallel genetic algorithm (PGA) has been used. Bazterra *et al.* have implemented the MGAC package using parallel techniques²⁹ mak-

ing it very portable as well as easy to maintain and upgrade. The coding method used here allows the treatment of the cluster represented by a genome of dimension $3N$, where N is the number of atoms in the cluster. Moreover, any genetic operator, mating, crossover, mutation, etc., applied to this genome produces a valid individual, i.e., a possible structure for the desired cluster size. The GA operations of mating, mutations, and also the “cut and splice” operator introduced by Johnston and Roberts³⁰ are used to evolve one generation into the next one. All the energy calculations for the GA optimization were done with the MSINDO (Refs. 31–33) code. More details of the algorithm used here can be found in Refs. 15 and 16. The isomers selected by the MGAC/MSINDO calculations were fully optimized using the DFT method with the local spin-density approximation (LSDA),³⁴ B3LYP exchange correlation functionals,³⁵ and the MP2 method employing the 6-311++G** basis sets.³⁶ Vibrational frequencies were calculated for the optimized structures to check that no imaginary frequencies are present. All these calculations were done using the package of programs GAUSSIAN 98.³⁷ The calculations of the condensed Fukui function were done over the more stable Si_n ($n=3-10$) clusters^{16,38–40} with a modified version of the TOP_MOD set of programs.⁴¹

RESULTS AND DISCUSSION

The chemical potential, the negative of the absolute electronegativity, of the hydrogen atom is of -7.25 eV and the chemical potential of the silicon clusters ranges between -5.1 and -4.5 eV. Therefore it can be expected that silicon clusters act as a donor system and the donor Fukui function f_{Fr}^- should indicate the reactivity of the different regions of the clusters. In Fig. 1, the basins associated to this function for the different clusters are depicted. The numerical value inside each volume represents the condensed Fukui function and it is calculated as the integration of the Fukui function over the respective volumes. The bigger is the number the more reactive is this region. Hence, the hydrogen atom should bind the cluster at the position where the condensed Fukui function presents the biggest value. In all cases the addition of a hydrogen atom at this position, after a complete optimization, produces a stable Si_nH cluster without imaginary frequencies. The resulting structures are depicted in Fig. 2.

To find the most stable hydrogenated silicon cluster for each value of n , the MGAC method has been applied to search for other isomers. All the obtained structures have been further optimized using the B3LYP/6-311++G** level of theory. They are shown in Fig. 3. It is important to note that all isomers predicted by the Fukui function have also been founded by the MGAC/MSINDO method. The isomers are ordered according to their relative energies with respect to the most stable isomer, and the ordering includes the clusters presented in Fig. 2. It can be observed that f_{Fr}^- always predicts one of the stable isomers. In the cases of Si_5H , Si_6H , Si_7H , and Si_8H clusters the function does not predict which

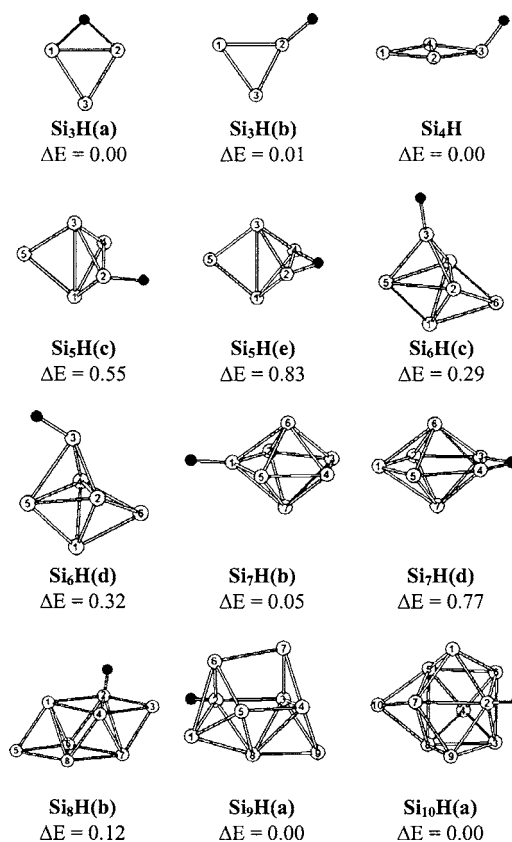


FIG. 2. Relaxed geometries of Si_nH at B3LYP/6-311++G** level of theory obtained by f_{Fr}^- predictions. ΔE is the excess energy of an isomer as compared to the energy of the most stable one (including the isomers of Fig. 3). Silicon atoms are numbered and the hydrogen atom is shown by a small dark circle.

the most stable one is. For Si_7H the one predicted by f_{Fr}^- is only 0.05 eV less stable than the isomer labeled (a). The possibility that the Si_nH isomer does not come from the most stable Si_n cluster has also been investigated.

The Fukui function of Si_5 in a triplet state and of Si_8 with a C_s symmetry has been studied, and the results are presented in Fig. 4. It is observed that the predictions yield the isomers $\text{Si}_5\text{H}(\text{b})$ and $\text{Si}_8\text{H}(\text{a})$ of Fig. 3. It has also been observed that in the cases where the Si_n skeleton of the Si_nH cluster differs markedly from the structure of the parent Si_n cluster, the Fukui function is not able to indicate the most stable isomer. To validate this point, for some clusters, the Fukui function of the Si_n skeleton has been calculated. The results are presented in Fig. 5 where it can be observed that the maximum of the Fukui function is always in the positions where the hydrogen atom binds. It seems that the f_{Fr}^\pm is, in part, a quantitative application of the rules proposed by Chrétien *et al.*^{21,22}

Next, it is important to assess the quality of the obtained results. Therefore, the total energy and the binding energy per atom, $\text{BE} = [E(\text{Si}_n\text{H}) - nE(\text{Si}) - E(\text{H})]/n$, of all the clusters have been calculated using the already presented B3LYP/6-311++G**, the LSDA/6-311++G**, and the MP2/6-311++G** methodologies. The results are presented in Table I. In a few cases, the self-consistent-field (SCF)

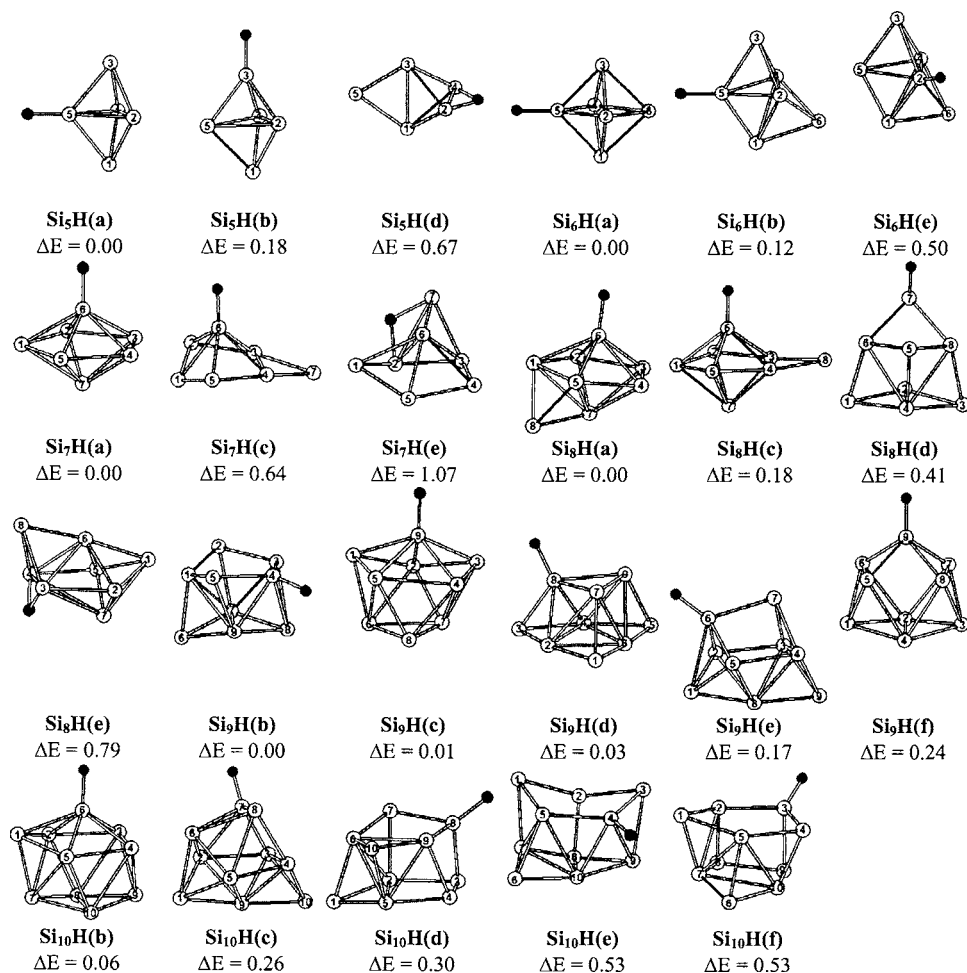


FIG. 3. Lowest-energy isomers of Si_nH clusters ($n=3-10$) calculated by the MGAC method in combination with B3LYP/6-311++G** calculations. ΔE is the excess energy of an isomer as compared to the energy of the most stable isomer (including the isomers of Fig. 2). Silicon atoms are numbered and the hydrogen atom is shown by a small dark circle.

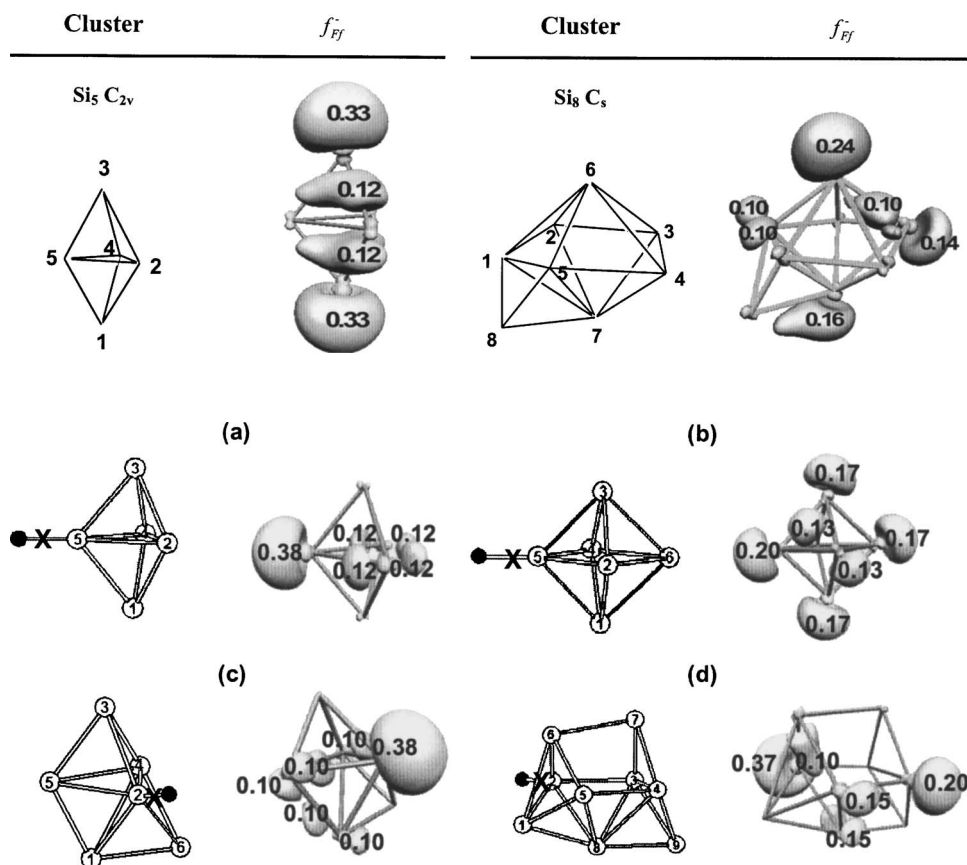


FIG. 4. Condensed donor Fukui functions f_{FR}^- for Si_5 $^3C_{2v}$ and Si_8 C_s clusters, at the B3LYP/6-311+G* level of theory.

FIG. 5. Condensed donor Fukui functions f_{FR}^- for Si_n in geometry of Si_nH clusters, at the B3LYP/6-311+G* level of theory. (a) Si_5H , (b) Si_6H , (c) Si_9H , and (d) Si_9H .

TABLE I. Binding energy per atom (BE/atom), calculated with B3LYP, LSDA, and MP2 methods and 6-311++G** basis set, for Si_nH ($n=3-10$) († indicates nonconverged results).

Cluster	Isomer	B3LYP/6-311++G**		LSDA/6-311++G**		MP2/6-311++G**	
		Energy (a.u.)	BE (eV/n)	Energy (a.u.)	BE (eV/n)	Energy (a.u.)	BE (eV/n)
Si ₃ H	a	-869.0390	-3.202	-866.4176	-4.082	-867.2563	-4.053
	b	-869.0389	-3.201	-866.4147	-4.057	-867.2639	-4.121
Si ₄ H		-1158.5684	-3.320	-1155.0826	-4.250	-1156.1988	-4.210
Si ₅ H	a	-1448.0959	-3.380	-1443.7076	-4.132	-1445.0314	-3.700
	b	-1448.0890	-3.340	-1443.7520	-4.370	-1445.1274	-4.228
	c	-1448.0755	-3.267	-1443.7364	-4.288	†	
	d	-1448.0712	-3.243	-1443.7329	-4.269	†	
	e	-1448.0654	-3.212	-1443.7327	-4.268	†	
Si ₆ H	a	-1737.6202	-3.403	-1732.4279	-4.480	-1734.0679	-4.290
	b	-1737.6158	-3.383	-1732.4267	-4.480	-1734.0547	-4.230
	c	-1737.6091	-3.353	-1732.4197	-4.450	-1733.9310	-3.680
	d	-1737.6082	-3.349	-1732.4195	-4.446	-1734.0472	-4.200
	e	-1737.6017	-3.319	-1732.4102	-4.400	-1733.9266	-3.660
Si ₇ H	a	-2027.1326	-3.370	-2021.0887	-4.510	-2022.8486	-3.720
	b	-2027.1308	-3.370	-2021.0837	-4.490	-2022.8417	-3.700
	c	-2027.1089	-3.280	-2021.0530	-4.410	-2022.8221	-3.620
	d	-2027.1041	-3.264	-2021.0691	-4.430	-2022.9267	-4.030
	e	-2027.0934	-3.220	-2021.0650	-4.370	-2022.8016	-3.540
Si ₈ H	a	-2316.6378	-3.330	-2309.7415	-4.500	-2311.7294	-3.630
	b	-2316.6333	-3.310	-2309.7336	-4.470	-2311.7242	-3.620
	c	-2316.6309	-3.310	-2309.7217	-4.430	-2311.7360	-3.660
	d	-2316.6227	-3.280	-2309.7242	-4.440	-2311.7230	-3.610
	e	-2316.6086	-3.230	-2309.7158	-4.410	-2311.6746	-3.450
Si ₉ H	a	-2606.1567	-3.340	-2598.4009	-4.510	-2600.6323	-3.630
	b	-2606.1566	-3.330	-2598.4002	-4.500	†	
	c	-2606.1563	-3.330	-2598.4074	-4.530	-2600.8108	-4.168
	d	-2606.1557	-3.330	-2598.3981	-4.500	-2600.6367	-3.644
	e	-2606.1503	-3.320	-2598.3980	-4.500	-2600.6243	-3.606
	f	-2605.9573	-2.730	-2598.3969	-4.490	-2600.6166	-3.583
Si ₁₀ H	a	-2895.6936	-3.880
	b	-2895.6915	-3.380	-2887.0922	-4.600
	c	-2895.6841	-3.360	-2887.0830	-4.580
	d	-2895.6826	-3.360	-2887.0661	-4.530
	e	-2895.6743	-3.340	-2887.0899	-4.600
	f	-2895.6741	-3.340	-2887.0628	-4.520

procedure could not converge, and the results are marked with a † in the table. The MP2/6-311++G** results for Si₁₀H are not presented because the computational cost becomes prohibitive.

It can be seen that in many cases the energy differences among different isomers are very small and outside the range of accuracy of the calculations. Hence, it is not possible to decide which one is the most stable isomer. In general, the MP2 results seem to separate better the energy of the various isomers but in many cases the energy ordering of the isomers differs with respect to the B3LYP results. It is clear that more elaborated calculations, which are not feasible at the present time, should be employed in order to elucidate the point. In Table II, the average Si–Si bond lengths with the respective standard deviations and the Si–H bond lengths are presented.

There is a good concordance among the three used theoretical methods. The LSDA bond lengths tend to be a little too short. Si–H distances for all the studied clusters are near to 1.5 Å when H atom binds only to one silicon atom and near to 1.7 Å when the H atom is in a bridge position reflecting the different type of bond. These results are in good agreement with the values reported by Prasad and co-workers^{12,13} and Yang *et al.*⁴²

Other properties are presented in Figs. 6 and 7. Figure 6(a) displays the vertical ionization potentials of the most stable silicon clusters. They have been calculated through an energy difference between the neutral and the cation at the equilibrium geometry of the neutral one and they are compared to the energy of the HOMO which after Koopmans' approximation or Janak's theorem⁴³ can be considered as an

TABLE II. The average Si–Si distances ($d_{\text{Si-Si}}$), standard deviation of Si–Si distances (σ), and Si–H distances ($d_{\text{Si-H}}$) calculated with B3LYP, LSDA, and MP2 methods and 6-311++G** basis set for Si_nH ($n=3-10$) (\dagger indicates nonconverged results).

Cluster	Isomer	B3LYP/6-311++G**			LSDA/6-311++G**			MP2/6-311++G**		
		$d_{\text{Si-Si}}$	σ	$d_{\text{Si-H}}$	$d_{\text{Si-Si}}$	σ	$d_{\text{Si-H}}$	$d_{\text{Si-Si}}$	σ	$d_{\text{Si-H}}$
Si ₃ H	a	2.286	0.009	1.488	2.264	0.007	1.501	2.259	0.006	1.478
	b	2.351	0.002	1.660	2.321	0.002	1.671	2.331	0.002	1.644
Si ₄ H		2.598	0.325	1.500	2.568	0.323	1.513	2.581	0.318	1.492
Si ₅ H	a	2.568	0.143	1.479	2.581	0.171	1.473	2.540	0.147	1.469
	b	2.587	0.136	1.488	2.542	0.136	1.502	2.549	0.142	1.478
	c	2.643	0.154	1.497	2.598	0.145	1.511	†		
	d	2.728	0.296	1.694	2.683	0.288	1.698	†		
	e	2.659	0.160	1.747	2.616	0.152	1.748	†		
Si ₆ H	a	2.685	0.182	1.490	2.644	0.176	1.506	2.659	0.179	1.481
	b	2.965	0.680	1.490	2.930	0.383	1.504	2.720	0.317	1.490
	c	2.751	0.315	1.486	2.706	0.312	1.498	2.723	0.309	1.477
	d	2.744	0.295	1.499	2.697	0.292	1.510	2.712	0.289	1.490
	e	2.814	0.435	1.480	2.767	0.426	1.491	2.772	0.429	1.472
Si ₇ H	a	2.883	0.429	1.494	2.839	0.426	1.508	2.859	0.431	1.487
	b	2.880	0.366	1.483	2.833	0.364	1.495	2.846	0.362	1.475
	c	3.144	0.830	1.481	3.077	0.784	1.496	3.061	0.758	1.477
	d	2.897	0.381	1.706	2.846	0.378	1.710	2.860	0.377	1.712
	e	3.043	0.588	1.662	2.902	0.489	1.633	3.000	0.569	1.653
Si ₈ H	a	3.052	0.581	1.487	2.999	0.573	1.501	3.051	0.581	1.487
	b	3.097	0.721	1.496	3.047	0.729	1.507	3.064	0.758	1.482
	c	3.165	0.846	1.495	3.116	0.824	1.506	3.139	0.833	1.480
	d	3.133	0.584	1.503	3.000	0.514	1.497	3.063	0.543	1.491
	e	3.120	0.636	1.708	3.037	0.602	1.712	3.053	0.603	1.698
Si ₉ H	a	3.198	0.656	1.484	3.135	0.638	1.493	3.148	0.643	1.481
	b	3.203	0.608	1.493	3.141	0.596	1.508	†		
	c	3.143	0.558	1.483	3.083	0.538	1.491	3.146	0.560	1.481
	d	3.206	0.631	1.481	3.145	0.644	1.499	3.162	0.658	1.487
	e	3.249	0.729	1.478	3.175	0.745	1.492	3.213	0.749	1.465
	f	3.160	0.550	1.479	3.096	0.553	1.489	3.109	0.522	1.465
Si ₁₀ H	a	3.213	0.632	1.490
	b	3.239	0.589	1.484	3.173	0.567	1.493
	c	3.283	0.704	1.484	3.215	0.689	1.495
	d	3.339	0.738	1.491	3.275	0.718	1.504
	e	3.343	0.812	1.495	3.193	0.641	1.486
	f	3.341	0.812	1.495	3.277	0.803	1.508

approximation to the ionization potential. Both curves show the same trends. However, the energy of the HOMO underestimates the ionization potential by 2.0 eV, approximately. These calculated values are in good agreement with those reported in the literature.^{44,45} The hardness of the more stable Si_n and Si_nH clusters is depicted in Figs. 6(b) and 6(c), respectively. They were calculated in two different ways. First, as the difference between the vertical ionization potential and the electron affinity and second, as the difference between the energy of the LUMO and the energy of the HOMO. Both values follow the same trend. In comparing the hardness for the two families of clusters, Si_n and Si_nH , it is observed that there is no correlation between them which can be attributed to the changes in the geometrical structure when a hydrogen atom is added. These have been also observed by Li and

Gong between neutral and charged silicon clusters.⁴⁵ A comparison between the mean polarizability calculated from the polarizability tensors as $\langle\alpha\rangle=1/3(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$ for the most stable Si_n and Si_nH isomers is presented in Fig. 6(d). In both families of clusters the dipole polarizability increases almost linearly with the number of atoms, and the effect of adding a hydrogen atom is almost negligible. The reason for this behavior should lie on the small value of the dipole polarizability of a hydrogen atom in comparison to the value in the silicon cluster. In Fig. 7(a) the adsorption energy of H atom to the Si_n cluster, $D_c=E[\text{Si}_n]+E[\text{H}]-E[\text{Si}_n\text{H}]$, are displayed and compared with the inverse of the binding energy per atom of the corresponding silicon cluster. Both quantities present a good correlation after considering the fact that for

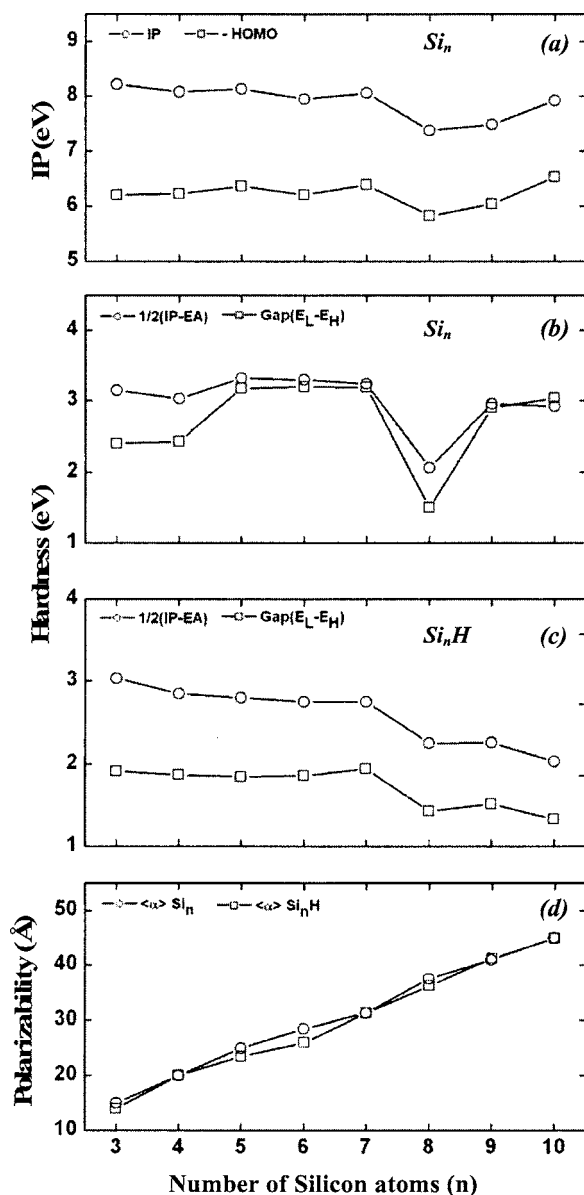


FIG. 6. Calculated properties for Si_n and Si_nH clusters. (a) Ionization potentials (IPs) of Si_n clusters, (b) chemical hardness and HOMO-LUMO gap of Si_n clusters, (c) chemical hardness and HOMO-LUMO gap of Si_nH clusters, and (d) comparison between calculated average polarizabilities (in $\text{Å}^3/\text{cluster}$) of Si_n and Si_nH clusters.

$n=5$ and 8 the more stable hydrogenated clusters do not come from the most stable silicon clusters but from the ones depicted in Fig. 4. It can be observed that those values for those clusters improve considerably the correlation. This good correlation implies that the more stable the cluster is, the less reactive it is.

To study the geometrical relaxation of a silicon cluster when a hydrogen atom is added to it, the energy difference between the silicon skeleton of the hydrogenated cluster and the equilibrium geometry of the corresponding silicon cluster has been calculated. The results are presented in Fig. 7(b). It can be seen that Si_4 , Si_5 , Si_7 , and Si_{10} clusters are geometrically more stable. The results are in good agreement with those presented by Balamuragan and Prasad¹³ with the exception of Si_5 . This difference can be explained because they compared the geometrical sta-

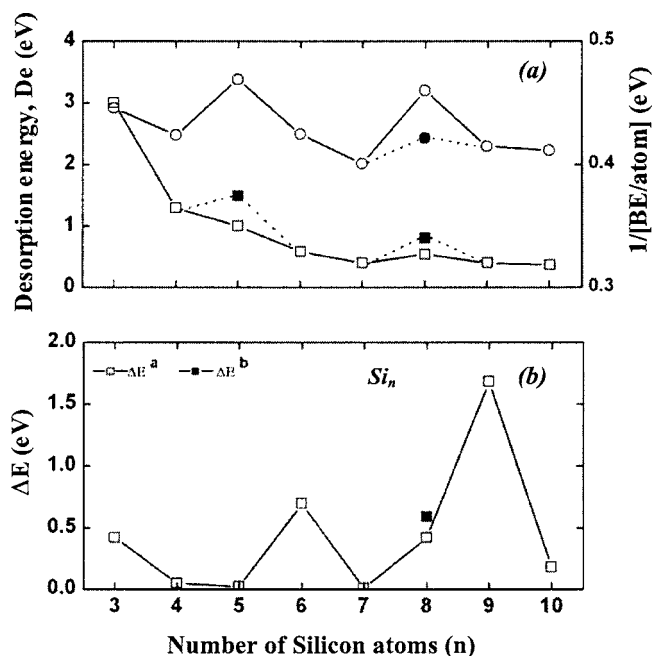


FIG. 7. (a) Comparison between desorption energy De (eV) for H atom from Si_n clusters and the inverse of the binding energy per atom of Si_n clusters. The dark symbols correspond to the less stable isomers, (b) difference ΔE , between the total energy of Si_n in the Si_nH geometry and the ground-state energy of Si_n cluster.

bility of Si_5 with respect to the D_{3h} singlet structure and here it is compared with respect to the Si_5C_{2v} triplet structure.

CONCLUDING REMARKS

The bonding of a hydrogen atom on small silicon clusters, Si_n ($n=3-10$), has been studied. In particular, it has been shown that the recently introduced condensed Fukui function is able to predict the most favorable bonding site in all the cases where the skeleton of the silicon cluster does not change significantly. The results corroborate that the use of the Fukui function is only valid when the adsorption process does not induce strong deformations in the cluster. In those cases, it is necessary to consider the possibility that the most stable hydrogenated cluster does not come from the most stable parent silicon cluster. To validate this conclusion, a stochastic genetic algorithm has been used to explore the complete configurational space available for each Si_nH . The so-constructed clusters have been further optimized by three different all-electron methods, and various properties have been studied. In particular, it has been found that the average dipole polarizability for both series of clusters, Si_n and Si_nH , increases linearly with the number of atoms, and the effect of adding a hydrogen atom is almost negligible.

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