Assembling Small Silicon Clusters Using Criteria of Maximum Matching of the Fukui Functions

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ABSTRACT: In this work, we present a methodology inspired by criteria of "maximum matching" between the Fukui functions to predict the best interaction between small silicon clusters to form larger ones. The model is based on the topological analysis of the Fukui functions. We tested the methodology in the formation of Si_4-Si_8 using a set of small Si_2-Si_6 clusters as building blocks in ground state structures in singlet and triplet multiplicities. In all of the cases, the Fukui function predicts the formation of the large cluster in its ground state structure, but the number of reaction channels increases with the cluster size.

INTRODUCTION

Since the advent of advanced laser vaporization techniques,[1-5] atomic and nanocluster semiconductors have become an active subject of research, both experimentally and theoretically.[6-10] Spectroscopic experiments have been utilized to infer the most stable structures of small atomic clusters, but measurements provide only indirect information about the geometries. Moreover, there is not conclusive experimental evidence on what is the mechanism of formation of the more stable structures in atomic clusters. Silicon nanoclusters have been extensively studied because of their intrinsic interest from the point of view of chemical structure and bonding as well as their importance in the microelectronics industry.[11,12] Motivated by the fundamental importance of understanding properties of silicon-based materials with increasing size, especially the transition, atom → cluster → bulk, considerable experimental and theoretical efforts have been devoted to determine geometric structures of small and midsized silicon clusters.[8,13-15]

In the past three decades the development of chemical-reactivity density functional theory[16-20] has provided a formal framework for many empirical chemical concepts like electronegativity,[21] hardness,[22-26] Fukui function,[27-32] electrophilicity,[33-35] et cetera. These descriptors have been widely applied to study chemical reactivity in organic chemistry, less in inorganic chemistry, and little in solid state surfaces[36,37] and clusters.[38-40]

The aim of this paper is to use a criterion of "maximum matching" between the Fukui functions of small clusters to predict how large clusters can be formed from the small ones. This criterion indicates that where electrostatic effects are not decisive, at the offset of the cluster formation, the clusters prefer to orient such that their Fukui functions maximize their overlap. To check this criterion, we assemble pairs of small silicon clusters in a "maximum matching" orientation and then relax the structure and check whether the final geometry corresponds to a known stable structure of the resulting cluster. The organization of the present paper is as follows. In the next section, we will

address some formal issues like the approximation used to calculate the Fukui function and the information obtained from their topological analysis and how the attractors of the Fukui functions are used to predict the most efficient interaction between two small clusters to produce a larger one, the "maximum matching" criteria. The Fukui function information is used to predict the most favorable interaction of the small clusters in each considered reaction; the efficiency of the Fukui function in predicting the most stable isomers is discussed.

THEORETICAL MODEL

In the density-functional theory approach to phenomenological chemical reactivity theory (chemical DFT),[16,20,41,42] the reactive site of an acceptor of electrons is associated with a large positive value of the Fukui function:[29,30]

$$f^+(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^+_{\nu(\mathbf{r})} = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \qquad (1)$$

The superscript "+" on the derivative indicates that the derivative is taken from above; this is essential because the derivative from above and the derivative from below

$$f^-(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^-_{\nu(\mathbf{r})} = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \qquad (2)$$

are not equal when the number of electrons is an integer, owing to the derivative discontinuity of the energy,[43,44] density, and other molecular properties.[31,45] Similarly, the Fukui function from below is the key regioselectivity indicator for the donor of electrons.

The link between the chemical DFT description and the frontier MO theory description is clear when one approximates

the Fukui functions using the frontier molecular orbitals:[28,46]

$$f^-(\mathbf{r}) = |\varphi_{\text{HOMO}}(\mathbf{r})|^2$$
$$f^+(\mathbf{r}) = |\varphi_{\text{LUMO}}(\mathbf{r})|^2 \tag{3}$$

These approximations are sufficient except for the seemingly rare cases where orbital relaxation effects are important.[47−49] When the HOMO or LUMO belongs to a degenerate irreducible representation of the cluster's point goup, an average over the set of degenerated orbitals is used.[50−52]

The following approximation for the total interaction energy of a donor and acceptor has been deduced elsewhere:[25,53]

$$\Delta W_{\text{int}} = (\mu_{\text{acceptor}} - \mu_{\text{donor}})\Delta N$$
$$+ \int \left(\sum_{\alpha \,\in\, \text{donor}} Z_\alpha \delta(\mathbf{r} - \mathbf{R}_\alpha) - \rho_{\text{donor}}(\mathbf{r}) \right) \Phi_{\text{acceptor}}(\mathbf{r})\, d\mathbf{r}$$
$$+ \Delta N \int \left(f_{\text{acceptor}}^+(\mathbf{r}')\, \Phi_{\text{donor}}(\mathbf{r}) - f_{\text{donor}}^-(\mathbf{r})\, \Phi_{\text{acceptor}}(\mathbf{r}) \right) d\mathbf{r}$$
$$- (\Delta N)^2 \iint \frac{f_{\text{donor}}^-(\mathbf{r})\, f_{\text{acceptor}}^+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \tag{4}$$

where donor and acceptor stand for properties of the donor and acceptor, and the charge and position of the nuclei are indexed by α. The chemical potential, μ, determines who is the acceptor (the one with the most negative μ) and who is the donor (the one with less negative μ). ΔN is the number of electrons transferred from the donor to the acceptor. $\delta v_{\text{donor}}(\mathbf{r})$ is the change in the external potential of the acceptor due to the presence of the donor. $\delta(\mathbf{r} - \mathbf{R}_\alpha)$ is the Dirac δ function centered at the position of the nucleus α, which accounts for the electrostatic interaction between the nuclei of both species, which are considered point charges. $\Phi(\mathbf{r})$ is the molecular electrostatic potential. The first term in eq 4 is independent of the orientation of the molecule and does not play a role in regioselectivity. The second term is a pure electrostatic interaction, and it is generally either small for reagents with noncharged sites (atoms) or negative for reagents with charged sites (atoms). In our case of neutral homonuclear silicon clusters, this term must be very small because the charge on Si atoms is negligible. The third term is the correction to the electrostatic interaction because of the electron transfer between both molecules. This term is usually positive: electron transfer weakens the strength of the electrostatic interaction because electron flow from the donor to the acceptor tends to equalize the charges of the reactive sites. This term, again, should be small in our case, as there is not significant charge to equalize. Finally, the integrand in the last term is usually positive because the Fukui function is positive, with some exceptions only in small regions around the nuclei of molecules with nodes of the frontier orbitals in the nuclear positions.[49,54] This term, then, is stabilizing and depends entirely on the relative orientation between the "frontier" densities of the molecules;[55] this term is decisive for explaining the regioselectivity of systems like homonuclear clusters, where electrostatic interactions are expected to be negligible. Therefore, information on the optimal orientation between two small clusters to form a large one is enclosed in this term: the orientation should be such that the integrand is a maximum. This is what we called the *maximum matching* criterion. Summarizing, the relative
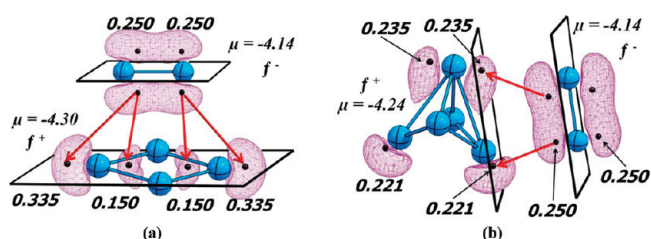
Figure 1. Interaction of $Si_2^t + Si_m^t$ ($m = 4, 5$) guided by the respective Fukui functions. Black spheres correspond to attractors, and numbers correspond to the value of the Fukui function integrated in each basin.

orientation between reactants is optimal when

$$\iint \frac{f_{\text{donor}}^-(\mathbf{r})\, f_{\text{acceptor}}^+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \tag{5}$$

is maximum.

Optimizing eq 5 is not an easy task, as it not only depends on the orientation between the reactants but also on the distance between them. A systematic approach to this problem would be to fix a distance between the center of mass of both clusters and optimize the orientation between the molecules and then repeat for different distances until it is certain that the maximum had been achieved. However, for small clusters, one can approach the problem in an empirical way that uses information of the topology of the Fukui function gradient field.[56] Associated with the Fukui function, there is a gradient vector field, $\nabla f(\mathbf{r})$. This field is characterized by so-called critical points, where $\nabla f(\mathbf{r}) = (0, 0, 0)$. They represent local maxima, minima, and saddle points of $f(\mathbf{r})$. From a Hessian matrix, $\underline{H}(f(\mathbf{r}_c))$, analysis associated with each critical point defines four different types of nondegenerate critical points: attractor $(3, -3)$, repellor $(3, 3)$, and saddle points $(3, 1)$ and $(3, -1)$. A basin, roughly speaking, is a region of the space, Ω, given by all points whose gradient paths end at the same attractor. The integral of the Fukui function in each basin, f_k, is a measure of the "abundance (population)" of the Fukui function around the attractor k. It is, then, reasonable to assume that at a given distance between the reactants (fragments), an assembling of the fragments that makes small the total distance between the attractors corresponding to the more populated basins (f_k large) translates into a large overlap of the Fukui functions.

The details and steps of the method proposed above are as follows:

(i) The first step is to determine which cluster is expect to be the donor and which the acceptor. The acceptor between two clusters is the one with the smallest chemical potential (more negative).

(ii) From a topological analysis of $\nabla f(\mathbf{r})$, all basins should be identified. Then, proceed with the integration of the Fukui function to obtain the set of $f_k^\pm$.

(iii) In each cluster should be plotted planes which include as many attractors as possible with large $f_k^\pm$.

(iv) The plane of the acceptor should be placed parallel to the plane of the donor "minimizing" the distance between attractors. In a symmetric cluster where the plane is the same as the molecular plane or a face in 3D clusters, the distance between planes is set to 1.0 Å; otherwise, it is set to 0.5 Å. Figure 1 shows how this procedure is done for the formation of Si_6^s from the pairs $\{Si_2^t + Si_5^t\}$.

Structure	μ	f^{+}	f^{-}
Si_2^s C_∞ 2.063	-4.98	0.366 0.244 0.366	0.500 0.500
Si_2^t C_∞ 2.167	-4.14	0.363 0.245 0.363	0.250 0.250 / 0.250 0.250
Si_3^s C_{2V} 2.185	-4.52	0.257 / 0.166 0.166 / 0.200 0.200	0.237 0.237 / 0.249 0.249
Si_3^t D_{3h} 2.295	-4.25	0.256 / 0.071	0.253 0.253 / 0.214 / 0.253
Si_4^s D_{2h} 2.185	-4.64	0.245 0.245 / 0.245 0.245	0.327 0.327 / 0.158 0.158
Si_4^t D_{2h} 2.293	-4.31	0.335 0.335 / 0.150 0.150	0.245 0.245 / 0.245 0.245
Si_5^s D_{3h} 2.330	-4.35	0.332 / 0.054 / 0.054 / 0.332	0.270 0.270 / 0.270
Si_5^t C_{2V} 2.463 2.751 2.328	-4.24	0.235 0.235 / 0.221 / 0.221	0.332 0.332 / 0.152 0.152
Si_6^s C_{2V} 3.080 2.342 2.496 2.419	-4.27	0.070 0.070 / 0.297 0.297 / 0.070 0.070	0.341 0.341 / 0.235 0.235
Si_6^t D_{4h} 5.534 2.374	-4.11	0.181 0.181 / 0.062 / 0.181 0.181	0.067 / 0.176 0.176

Figure 2. Structures, chemical potential μ (eV), and donor and acceptor Fukui functions with their corresponding condensed values for Si_n ($n = 2-8$) global minimum structures of singlet and triplet configurations.

(v) Finally, from this starting point, the structures should be relaxed using an *ab initio* calculation.

In the present work, we study the formation of closed shell clusters. We have used the Fukui function information to predict the best interaction between fragments, and then we relaxed the systems fixing the multiplicity. Obeying the principle of spin conservation, we have combined the following: singlet + singlet → singlet and triplet + triplet → singlet. If we would like to explore higher spin states, we can fix the multiplicity before relaxing the formed cluster, for example: singlet + triplet → triplet, triplet + triplet → quintuplet, and/or exciting the clusters before relaxing.

This methodology is in total agreement with the working equations applied to use the local hard and soft acids and bases principle, which relies on matching of the local softness of the atoms in the fragments. These working equations use the local softness which corresponds to the softness of an atom in a molecule to estimate the maximum matching between both fragments; if we consider the local softness as obtained by the Sf_k expression, where S is the global softness and f_k is the condensed Fukui function on atom k, then, it is the f_k value which determines the local reactivity of the system.[41] In the present methodology, we used a different strategy to locally condense the Fukui function using a topological analysis to localize regions where this function is maximum (attractors), obtaining local reactive regions around these maximum values (basins), which are not necessarily atomic regions.

■ COMPUTATIONAL DETAILS

The most stable structures for Si_n ($n = 2-8$) were taken from the literature[8,13,14] and reoptimized at the B3LYP[57,58]/6-311 +G(d,p)[59] level. Total energies were recalculated using CCSD-(T). All of these calculations were done using the Gaussian 03 program.[60] For the calculation of Fukui functions, we used the HF wave function of the CCSD(T)[61] calculation. The

Table 1. Reaction Energies Associated with the Formation of Si$_n$ (n = 4−8) Clusters^a

cluster	entry	reaction	reaction energy	ΔE_{rx}
Si$_4^s$	1	Si$_2^s$ + Si$_2^s$ → Si$_4^s$	−146.1	25.1
	2	Si$_2^t$ + Si$_2^t$ → Si$_4^s$	−121.0	0.0
Si$_5^s$	1	Si$_3^s$ + Si$_2^s$ → Si$_5^s$	−124.2	11.9
	2	Si$_3^t$ + Si$_2^t$ → Si$_5^s$	−112.3	0.0
Si$_6^s$	1	Si$_4^t$ + Si$_2^t$ → Si$_6^s$	−127.3	11.6
	2	Si$_4^s$ + Si$_2^s$ → Si$_6^s$	−121.0	10.4
	3	Si$_3^t$ + Si$_3^t$ → Si$_6^s$	−116.9	6.3
	4	Si$_3^s$ + Si$_3^s$ → Si$_6^s$	−106.2	0.0
Si$_7^s$	1	Si$_5^t$ + Si$_2^t$ → Si$_7^s$	−133.7	28.0
	2	Si$_5^s$ + Si$_2^s$ → Si$_7^s$	−130.7	5.4
	3	Si$_4^t$ + Si$_3^t$ → Si$_7^s$	−128.3	3.0
	4	Si$_4^s$ + Si$_3^s$ → Si$_7^s$	−105.7	0.0
Si$_8^s$	1	Si$_4^t$ + Si$_4^t$ → Si$_8^s$	−108.4	37.6
	2	Si$_5^t$ + Si$_3^t$ → Si$_8^s$	−103.5	21.1
	3	Si$_6^t$ + Si$_2^t$ → Si$_8^s$	−102.0	12.6
	4	Si$_6^s$ + Si$_2^s$ → Si$_8^s$	−95.8	6.4
	5	Si$_5^s$ + Si$_3^s$ → Si$_8^s$	−87.3	4.9
	6	Si$_4^s$ + Si$_4^s$ → Si$_8^s$	−70.8	0.0

^{a} Values of energy are in kcal mol^{-1}. In all cases, the reactants and products are the global minimum structures at the corresponding multiplicity.

topological analysis of the Fukui function was done with the DGrid 4.4 set of programs.[62]

■ RESULTS AND DISCUSSION

Figure 2 shows the geometry, chemical potential μ (eV), Fukui functions isosurfaces at 0.003 au, and the $f_k^{\pm}$ for each one of the small clusters Si$_n$ (n = 2−6) used in the formation reactions in their two lowest spin multiplicities (singlet and triplet). All structures in singlet configuration are more stable than those in triplet configuration, except for the case of Si$_2$, whose global minimum configuration is triplet.[8,13,14] The chemical potential of the closed shell configurations is more negative than its open shell counterpart in all cases.

Table 1 presents the proposed reaction channels of the type $si_x^{\alpha} + si_y^{\alpha} \rightarrow si_n$ where α denotes singlet or triplet configurations and $x + y = n$. As it is known that for $n = 4-8$, a Si$_n$ cluster in singlet configuration is the most stable; only this product channel has been studied. The number of reactive channels increases with the size of the cluster. The most probable reaction channel will be the one with the most stable reactants because all of the reactions are exothermic, and the probability to populate the isomers higher in energy is low. Therefore, in Table 1, the relative energies ΔE_{rx} are taken with respect to the most probable reaction channels. Hence, Si$_6$ will be most probably formed by the combination of two Si$_3$'s in their singlet state. In the second column of Table 1, each combination to obtain the large cluster is numbered
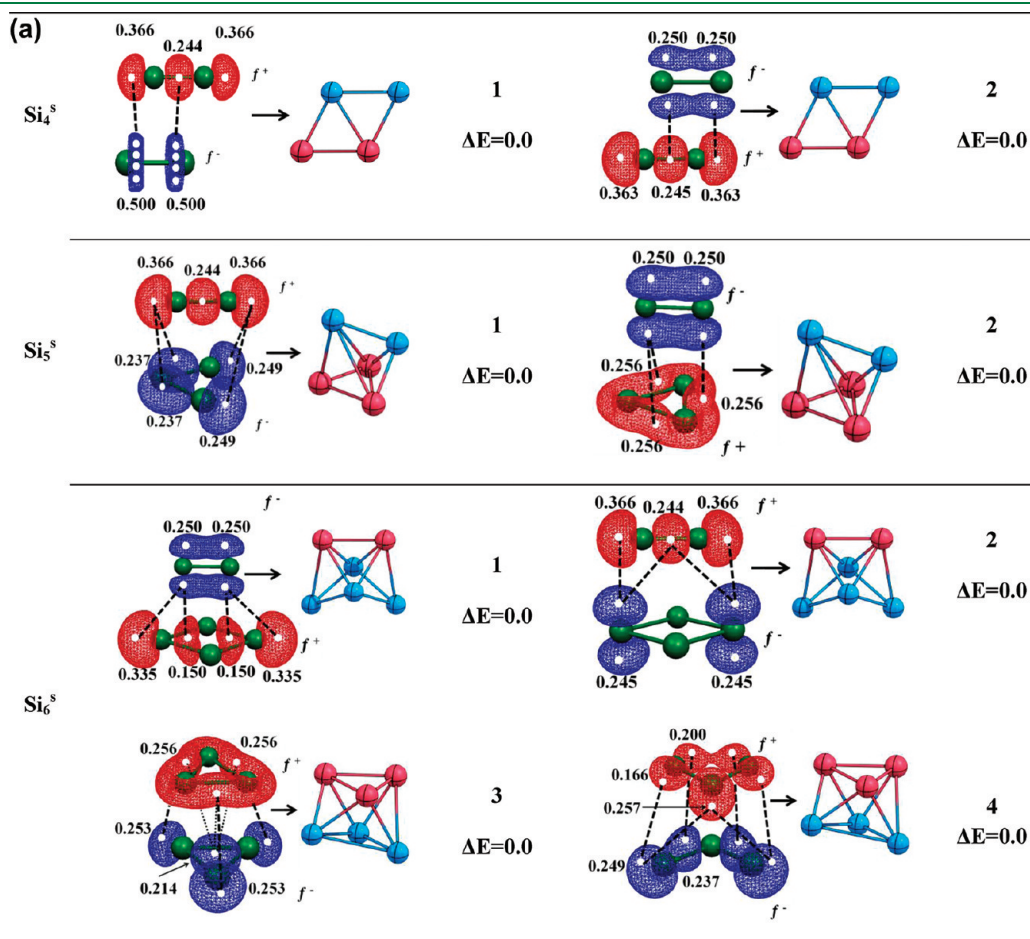
Figure 3. Continued
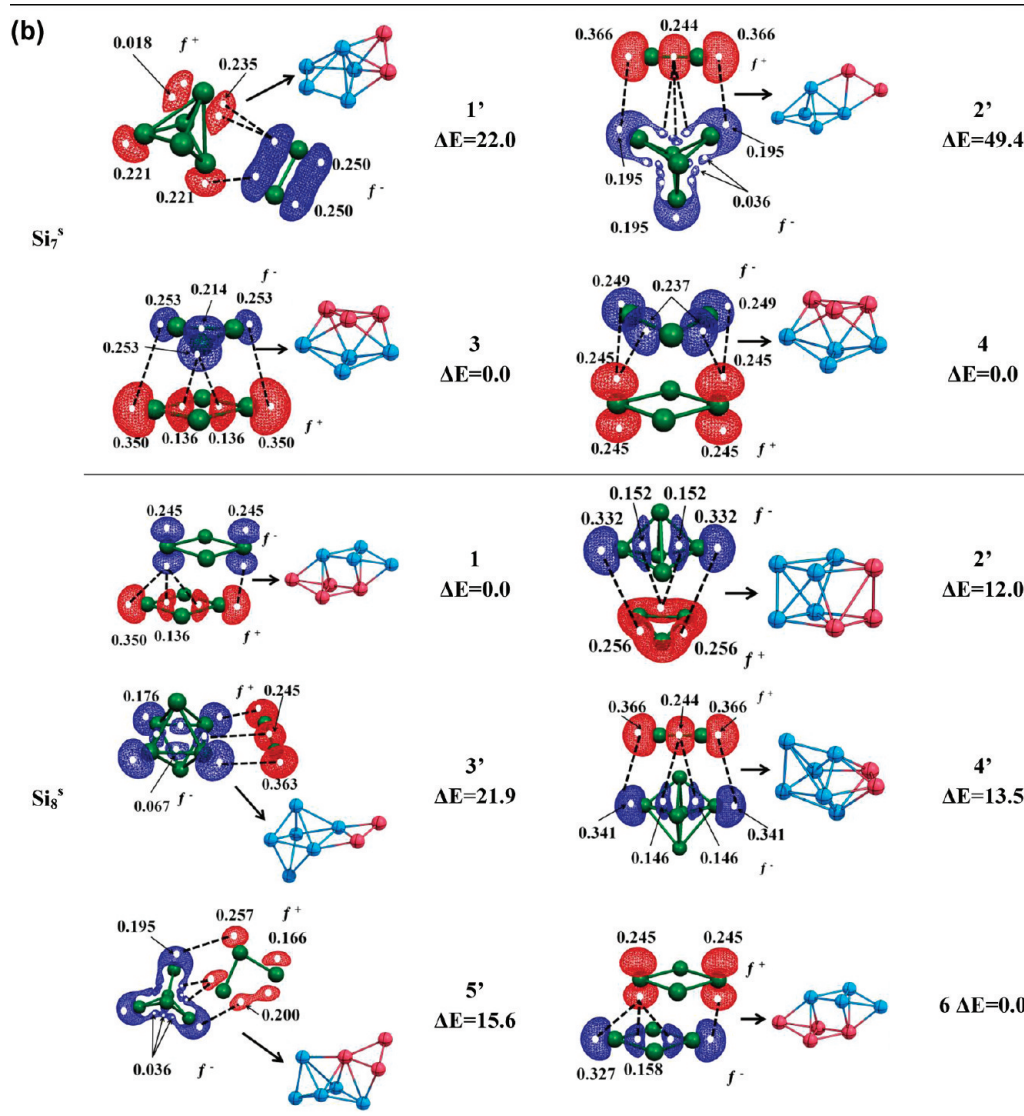
Figure 3. (a) Orientation that produces the maximum matching of the Fukui functions of two small clusters to form a large cluster (Si_4-Si_6). f^+ (in red) is used for the clusters that accept electrons and f^- (in blue) for the donors. White dots represent the attractors' position of each Fukui function. The numbers represent the reaction channel according to Table 1, and ΔE is the isomer relative energy compared to the global minimun structure. (b) Orientation that produces the maximum matching of the Fukui functions of two small clusters to form a large cluster (Si_7-Si_8). f^+ (in red) is used for the clusters that accept electrons and f^- (in blue) for the donors. White dots represent the attractors' position of each Fukui function. The numbers represent the reactions channel according to Table 1, and ΔE is the isomer relative energy compared to the global minimun structure. The prime identifies the cases where the global minimum structures are not obtained by the Fukui predictions.

(1, 2, ...) in a decreasing order of probability of the reaction to happen. It is important to remark that in Table 1, the reactions are proposed to produce the global minimum isomer.

Figure 3a and b show the position of the reactant clusters according to the maximum matching of the Fukui function. All of the predicted interactions lead to the formation of a stable cluster. The relative energies of the formation of clusters are also reported in Figure 3. All of the zero values correspond to cases where the most stable isomer was formed. In all of the cases the most stable reactants form the most stable product following the matching of the Fukui function criteria. There are cases where a cluster higher in energy is formed. For example, the Si_7 singlet formed following channels 1 and 2 of Table 1. It is also found that as the number of atoms in the cluster increases, a greater number

of low-lying energy isomers appear. This explains the variety of structures found in Si_8. It is, therefore, gratifying to see that the criterion of maximum matching of the Fukui function is able to predict the most stable structure of Si_8, which is the most challenging one among the studied cases.

■ CONCLUSIONS

The information obtained from topological analysis of the Fukui function, basins, attractors, and condensed values has been used to propose an empirical model to predict the best interaction between small silicon clusters to form larger clusters using a criterion of "maximum matching" between the Fukui functions. This criterion says that in reactions where electrostatic interactions are

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negligible, two clusters prefer to orient such that the overlap, in the sense of eq 5, between their Fukui functions maximizes. Here, we show that in a significant number of examples of formation of small silicon clusters, this criterion successfully predicts the structure of the most stable isomers. In this study, we have not optimized the matching of the Fukui function in a rigorous way, but we have used information already contained in the gradient field of the Fukui functions. It is clear that in more complicated cases, as could be in systems with low symmetry or that are too big, an adequate maximization or eq 5 must be done. We have also devised how this can be done in a general way.

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Notes
The authors declare no competing financial interest.

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