Theor Chim Acta (1996) 93: 165–176

Theoretica Chimica Acta

On the definition of valence of functional groups in molecules

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Received December 27, 1994/Final revision received July 3, 1995/Accepted August 11, 1995

Abstract. The quantum chemical definition of valence as a property of an atom in a molecule was generalized to functional groups in molecules. The new definition was applied to a series of functional groups in simple organic molecules. The results were found to be in agreement with expectation on the basis of classical valence rules. CH_2, N_2 and CO group valences in selected organic molecules are compared. Group valences for systems violating the classical valence rules are also briefly discussed with an emphasis on the role of multicenter bonding in the phenomenon of hyper- and subvalence. Finally, Si_2 groups serve to probe the bulk character of small and medium silicon clusters.

Key words: Group valence – Functional groups – Multicenter bonding

1 Introduction

Quantum chemical calculations have become the routine tool for the elucidation of the molecular electronic structure. Yet the interpretation and understanding of wave functions still rely on the use of simple qualitative concepts. One of the most useful of such concepts is the concept of valence.

Although the first intuitive ideas related to the concept of valence date back to the time of Kekulé [1], the modern theory of valence is based on the Lewis electron pair model of the chemical bond [2]. In terms of this model the valence of an atom is a measure of its ability to share its valence electrons and to enter thus into covalent bonding with its neighbours. Because of its enormous impact to chemistry, the concept of valence has become the subject of numerous theoretical analyses aiming at putting this concept into the conceptual framework of modern

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quantum chemical models of chemical structure [3–11]. Among the numerous studies which contributed to putting the concept of valence on safer theoretical footing those by Gopinathan and Jug [3–5] have found wide acceptance [7, 8, 10, 12, 13] and have become the basis of a majority of more recent extensions. Mayer [6, 7] generalized the original approach beyond the scope of semiempirical methods with orthogonal or orthogonalized basis sets to the level of *ab initio* methods with generally nonorthogonal bases. Another important recent extension is due to Angyan et al. [14], who found it possible to incorporate the valence concept into the framework of Bader's theory of atoms in molecule [15].

In all these cases valence has been regarded as the property of an atom in a molecule. One could, however, also ask whether it would not be possible to attribute the valence also to some functional group in a molecule. An example could be, e.g., the valence of a methyl group in ethane or of an acetyl group in acetaldehyde. This problem was recently addressed by Giambiagi et al. [16], who proposed a definition of group valence in terms of the so-called bond indices. In this study, we report an alternative way of obtaining group valences and apply the resulting formalism to the visualization of bonding in several simple molecules. First of all we demonstrate this for *normal* molecules with well localized 2c–2e bonds. The resulting group valences fit well into the intuitive expectations based on classical structural formulas. Then functional groups in organic systems with localized and partially delocalized bonds are treated. In addition to these simple cases, some examples of unusual systems violating the standard valence rules are also discussed especially in connection with the concept of the so-called sub- and/or hypervalence [17]. Among these we show how Si_2 units can serve to determine the bulk character in silicon clusters.

2 Group valence

According to Gopinathan and Jug [3–5], the valence of the atom A in a molecule is defined as

$$V_A = \sum_{B \neq A} V_{AB} = \sum_{B \neq A} \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu}^2, \tag{1}$$

where $P_{\mu\nu}$ is a matrix element of the usual density matrix over symmetrically orthogonalized atomic orbitals λ in a closed-shell case on the SCF level

$$P_{\mu\nu} = 2 \sum_{i}^{\text{occ}} c_{\mu i} c_{\nu i} \tag{2}$$

for molecular orbitals ψ

$$\psi_i = \sum_{\mu} c_{\mu i} \lambda_{\mu}. \tag{3}$$

Starting from the idempotency of the matrix $\frac{1}{2}\mathbf{P}$

$$\mathbf{P}^2 = 2\mathbf{P}, \tag{4}$$

we sum over the diagonal elements and obtain

$$\sum_{\mu}^{A} \sum_{B} \sum_{\nu}^{B} P_{\mu\nu}^2 = 2 \sum_{\mu}^{A} P_{\mu\mu}. \tag{5}$$

Rearrangement of the left-hand side of Eq. (5) yields

$$\sum_B V_{AB} = 2N_A. \tag{6}$$

Here V_{AB} is the valence between atoms A and B and N_A is the number of electrons on atom A. We now partition the molecular system in two exclusive groups G_1 and G_2 and rewrite the sum over B accordingly. Equation (6) takes the form

$$\sum_{B \in G_2} V_{AB} = 2N_A - \sum_{B \in G_1} V_{AB}. \tag{7}$$

The group valence of group G_1 is now defined as the sum of bond valences V_{AB} of the atoms A of group G_1 with the atoms B of group G_2

$$\begin{aligned} V_{G_1} &= \sum_{A \in G_1} \sum_{B \in G_2} V_{AB} \\ &= 2 \sum_{A \in G_1} N_A - \sum_{A \in G_1} \sum_{B \in G_1} V_{AB}. \end{aligned} \tag{8}$$

It is apparent from Eq. (8) that the group valences are related by the equation

$$V_{G_1} = V_{G_2}, \tag{9}$$

which says that the valence of group G_1 and of its complementary group G_2 are always the same. An example of such a partitioning can be, e.g., the dissection of CH_4 into CH_3 and H, and Eq. (9) then says that $V_{CH_3} = V_H$.

Insertion of the density matrix elements $P_{\mu\nu}$ into Eq. (8) yields the explicit form

$$V_G = 2 \sum_{A \in G} \sum_{\mu}^{A} P_{\mu\mu} - \sum_{A \in G} \sum_{B \in G} \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu}^2. \tag{10}$$

The most significant observation of this relation is that the group valence of a group, which is defined via the bond valence of the atoms of group G and the remainder of the system, can be calculated from the density matrix elements *within* group G only. If the group involves the whole molecule, the group valence V_G is zero, because there is no possible interaction with another group left. If G consists of a single atom, V_G reduces to V_A.

Other derivations of V_G via effective pair populations [18] are also possible and heuristic arguments can be given to introduce the valence idea [14] into the framework of Bader's theory of atoms in a molecule [15]. We shall not elaborate on these directions here.

3 Results and discussion

3.1 Molecules with localized and partially delocalized bonds

The simplest situation is for molecules with well-localized 2c–2e bonds where the group valences usually closely agree with what could be expected on the basis of classical structural formula. In order to demonstrate this simple behaviour of these systems we calculated the atomic and group valences for a series of simple molecules, both saturated and unsaturated. For a uniform comparison all calculations were performed by the semiempirical SINDO1 method [19]. The resulting values V_G for optimized molecular geometries are summarized in Table 1. As can be seen, the calculated valences do not display any unexpected behaviour and the

Table 1. Group valences V_G for several simple molecules with well localized 2c–2e bonds

Molecule	Group	V_G
C_2H_6	C_2H_5, H	1.000
	CH_3	1.044
CH_3NH_2	CH_3, NH_2	1.079
CH_3OH	CH_3, OH	1.076
CH_3Cl	CH_3, Cl	0.975
CH_4	CH_3, H	1.000
	CH_2	2.000
	CH	3.000
C_2H_4	$CH{=}CH_2$	1.000
	CH=CH	1.988
	CH_2	2.079
C_2H_2	C≡CH	0.989
	CH	3.008
NH_3	NH_2, H	0.994
	NH	1.983
H_2O	OH, H	0.973

values are in all cases close to classical expectations. The key to the understanding of this simple behaviour lies in the reported results of pair population analysis [18]. The pair populations Π^{eff} relate to the valences V in the following way [18]:

$$\Pi^{\text{eff}}_{AA} = \tfrac{1}{4} V_{AA}, \qquad \Pi^{\text{eff}}_{AB} = \tfrac{1}{2} V_{AB}. \tag{11}$$

Substituting Eq. (11) into Eq. (6) and summing up over all atoms A we obtain

$$\sum_A \Pi^{\text{eff}}_{AA} + \sum_{A<B} \Pi^{\text{eff}}_{AB} = N/2. \tag{12}$$

This means that the sum of electron pairs Π^{eff}_{AA} on all atoms A and the sum of electron pairs Π^{eff}_{AB} in all bonds AB equals the total number of electron pairs $N/2$. Systems which are well characterized by a classical structural formula display negligible pair populations between classically nonbonded atoms. As a consequence, the normalization, Eq. (12) can be replaced by the approximate equation

$$\sum_A \Pi^{\text{eff}}_{AA} + \sum_{A<B}^{\text{bonded}} \Pi^{\text{eff}}_{AB} \approx N/2, \tag{13}$$

so that atomic valences generally defined by Eq. (1) can also be written as a sum over contributions from bonded pairs only

$$V_A \approx 2 \sum_{B \neq A}^{\text{bonded}} \Pi^{\text{eff}}_{AB}. \tag{14}$$

It was demonstrated that these contributions were practically insensitive to the nature of bonding atoms and their values are nearly proportional to classical bond multiplicities with the proportionality factor 2 [15]. As a consequence of this, the contributions to valence are practically identical with the expectations of the classical structural theory.

After these test calculations it seems suggestive to see trends in a series of organic molecules with both localized and partially delocalized bonds. We have

Table 2. Trends for external valences V_G and internal group valences V'_G in groups for organic molecules

Molecule	Group	V_G	V'_G
CH_2N_2	CH_2	1.514	1.93
CH_2CO	CH_2	1.880	1.91
$C_2H_4O^a$	CH_2	2.027	1.94
$C_5H_4CH_2^b$	CH_2	2.078	1.94
CH_2O	CH_2	2.134	1.86
HN_3	NN^c	1.216	2.68
N_2O	NN	1.363	2.63
CH_2N_2	NN	1.514	2.47
N_2H_2	NN	1.714	2.39
N_2H_4	NN	3.616	1.50
HN_3	NN^d	3.860	0.95
CH_2CO	CO	1.880	2.07
CH_2O	CO	1.939	2.05
CF_2O	CO	1.947	1.93
HCOOH	CO^c	2.082	1.92
CO_2	CO	2.127	1.87
HCOOH	CO^d	3.91	1.02

[a] oxirane; [b] fulvene; [c] outer; [d] inner

therefore collected group valences V_G for a few molecules with CH_2, N_2 and CO groups in Table 2. We notice that the spread of values in N_2 and CO is high. It is complementary to the valence V'_G within the group. Here V'_G is defined as

$$V'_G = \sum_{A<B\in G} V_{AB}. \tag{15}$$

On the whole, the following trend can be observed: The higher the valence V'_G is within the group, the lower is the group valence V_G. Even for CH_2 the situation is not uniform with V_G values ranging from 1.514 to 2.134. Somewhat closer are the values for the carbonyl groups ranging from 1.880 to 2.127.

3.2 Hypervalent and subvalent systems

3.2.1 Molecules

Although certainly interesting from a theoretical point of view, the group valences of the previous simple systems bring practically no completely new information. Therefore, much more interesting would be to apply the above formalism to systems with more complex bonding patterns. As the representatives of such systems we have chosen the sulphurhexafluoride SF_6 and ammoniaoxide H_3NO. In our calculations we used again the semiempirical SINDO1 method and the calculated values of atomic and group valences are summarized in Table 3.

As can be seen, the valence of sulphur in SF_6 is slightly lower than one would normally expect from the presence of six F ligands. On the other hand, the valence of F and consequently also of SF_5 is close to a normal value of unity. Similarly the values for SF_4 and SF_3 groups are also rather close to classical expectations while

Table 3. Atomic and group valences for SF_6 and H_3NO

Molecule	Group	V_G
SF_6	SF_5, F	1.011
	SF_4	2.006
	SF_3	2.857
	SF_2	3.628
	SF	4.382
	S	5.052
H_3NO	Group	V_G
	H_3N, O	0.878
	H_2NO	0.991
	HNO	1.979
	NO	2.965
	N	3.671

greater deviations are observed for SF_2 and SF groups. Since all SF bonds are equivalent and no long-range interactions exist, there is no valence difference between, e.g., SF_4 groups of C_{2v} or D_{4h} symmetry. In order to get more insight it is useful to look at the values of effective pair populations which are summarized in Table 4. We see that the effective pair population for the S–F bond is slightly lower than for a normal single bond (0.42 vs. 0.50). As a consequence, the valence of sulphur which is twice the sum of S–F pair populations over six S–F bonds, is slightly reduced compared to the value of 6. The reduced pair contribution from the S–F bonds has to be compensated by the increase of other pair populations. The only possibility for such an increase are the interactions between formally nonbonded F atoms. As can be seen from Table 4 small contributions of these F ... F formally nonbonded pair populations do indeed appear. Let us now look from this point of view at the valence of F (and SF_5). The main contribution to fluorine atomic valence comes from the S–F pair population. However, without the F ... F interactions the valence of F would be 0.842 and it is just the presence of these interactions which increases the valence to the final value 1.01. Similar F ... F interactions then operate also in the case of the remaining SF_n groups and their effect is again the appropriate correction to the dominant contributions from S–F pair populations.

Another example of a system with a slightly unusual bonding pattern is ammoniaoxide H_3NO in which the oxygen atom is subvalent and the nitrogen is hypervalent. As can be seen from Table 3, the actual valences for O and N are indeed consistent with these expectations. The explanation for the observed subvalence of oxygen can again be found in the values of effective pair populations which are summarized in Table 5. As can be seen, the N–O bond population is much less than would correspond to an N=O double bond and in fact is even slightly lower than the value for the normal single bond. In this case the lack of electron pairs in the N–O bond is not compensated by pair populations between nonbonded atoms, because the O ... H pair populations are weaker and less numerous than the F ... F interactions in the previous case. The main compensation comes from the relatively high atomic pair population on oxygen, which is rather consistent with the *zwitterionic nature* of the N–O bond. Consequently, the

Table 4. Effective pair populations for SF_6

Term	Effective pair population
Monoatomic	Π_{AA}^{eff}
S	0.865
F	3.392
Diatomic	Π_{AB}^{eff}
SF	0.421
$F \ldots F_{\mathrm{adjacent}}$	0.020
$F \ldots F_{\mathrm{trans}}$	0.004

Table 5. Effective pair populations for H_3NO

Terms	Effective pair population
Monoatomic	Π_{AA}^{eff}
O	2.988
N	1.519
H	0.204
Diatomic	Π_{AB}^{eff}
NO	0.396
HN	0.480
O ... H	0.014

valence of oxygen is strongly reduced below the standard value of 2 observed in other oxygen compounds. On the other hand, even the single bond character of N–O is sufficient to increase the valence of N over the standard value of 3 so that the nitrogen atom is effectively hypervalent in this case. This combination of subvalence and hypervalence was previously proposed as a criterion for a zwitterion [17, 18]. As a consequence the group valence of the H_3N group is not negligible.

3.2.2 Clusters

As a last example for a small system we have chosen the rhombic Li_4 cluster with D_{2h} symmetry whose structure was investigated by various authors [22, 23]. In our calculations we used again the semiempirical SINDO1 method and calculated values of atomic and group valences are summarized in Table 6. Atoms *a* and *c* refer to the long diagonal, *b* and *d* to the short diagonal. The brief inspection of this table suggests that the valences of both different types of lithium atoms differ considerably and while the valence of lithium atoms Li_a and Li_c is very close to the *normal* value of 1, the valence of the remaining two atoms is much higher. It is possible to say that Li_b and Li_d are hypervalent. The same hypervalence can then also be detected for the groups $Li_aLi_bLi_c$ and $Li_aLi_cLi_d$.

Table 6. Atomic and group valences for rhombic Li_4 cluster with D_{2h} symmetry

Group	V_G
Li_a, Li_c	1.054
Li_b, Li_d	1.441
Li_aLi_b	1.543
Li_aLi_c	1.901
$Li_aLi_bLi_d$	1.054
$Li_aLi_bLi_c$	1.441

Table 7. Effective pair populations Π^{eff} from linear population analysis for rhombic Li_4 cluster

Terms	Effective pair population
Monoatomic	Π^{eff}_{AA}
Li_a	0.254
Li_b	0.123
Diatomic	Π^{eff}_{AB}
Li_aLi_b	0.238
Li_aLi_c	0.052
Li_bLi_d	0.245

In order to get insight into these calculated results it is useful to look at the values of effective pair populations which are summarized in Table 7. Let us discuss now the conclusions suggested by these values. The approximate normalization (13) which was of crucial importance for *normal* behaviour of valences is not satisfied with satisfactory precision since instead of the required value of approximately 2, the normalization sum amounts to 1.706 only.

$$\sum_j \Pi^{\text{eff}}_{\text{Li}_j} + \Pi^{\text{eff}}_{\text{Li}_a\text{Li}_b} + \Pi^{\text{eff}}_{\text{Li}_b\text{Li}_c} + \Pi^{\text{eff}}_{\text{Li}_c\text{Li}_d} + \Pi^{\text{eff}}_{\text{Li}_d\text{Li}_a} = 1.706 . \tag{16}$$

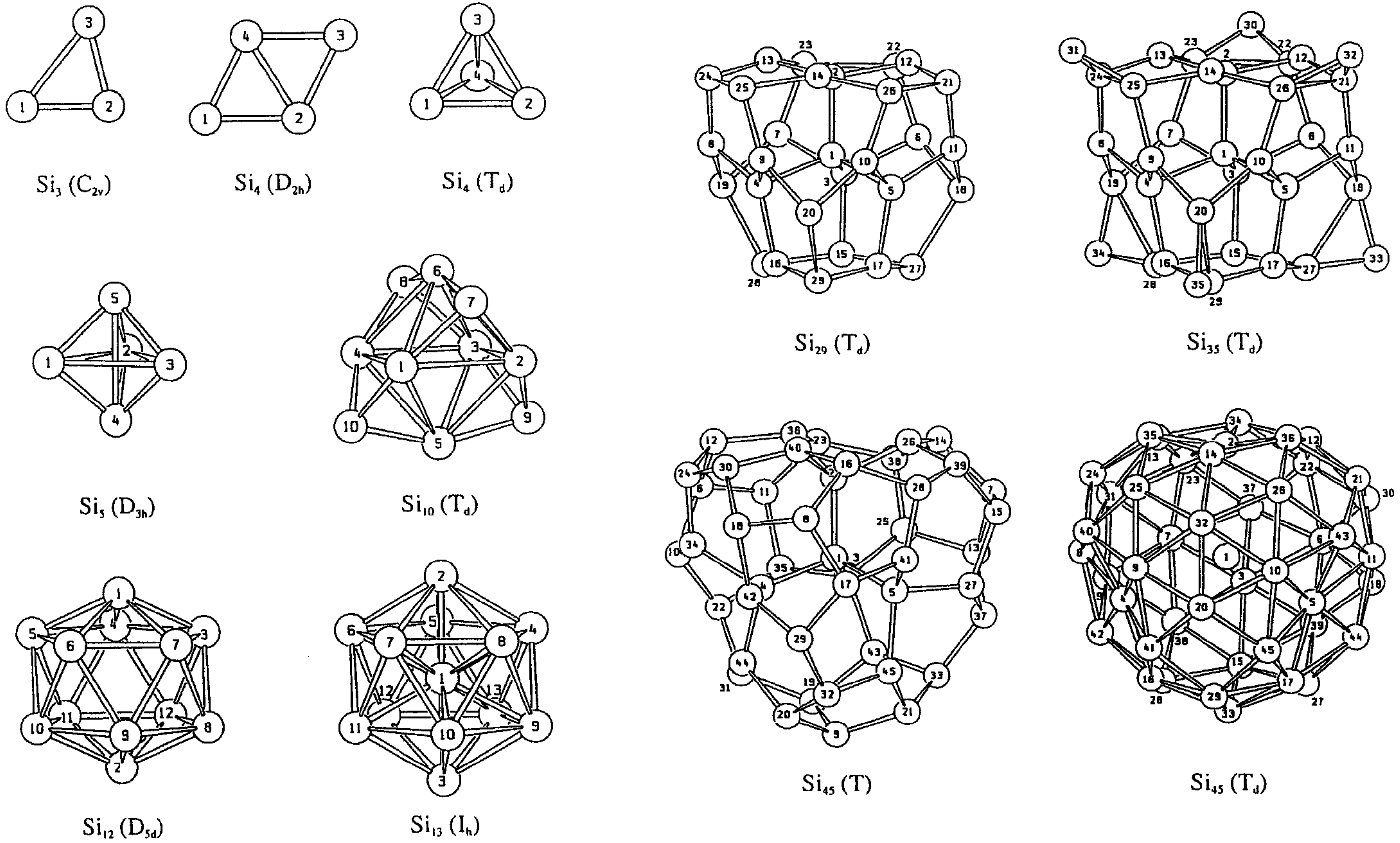
This indicates that the interactions between nonadjacent atoms are here more important than in the case of SF_6. As can be seen in Table 6, such interactions do indeed exist and can mainly be attributed to the Li_bLi_d pair of atoms. A detailed breakdown reveals that the Li_bLi_d valence is due to π bonding, whereas the Li_aLi_b valence is due to σ bonding. The existence of such nonadjacent pair interactions then determines to a considerable extent the valence of the Li_b and Li_d atoms, as well as of $Li_aLi_cLi_d$ and $Li_aLi_bLi_c$ groups (Table 6). In the case of an ideally localized bonding model described by (13), the valence of all Li atoms could be expected to be close to 1. As can be seen, the valences of Li_a and Li_c satisfy this expectation quite well. On the other hand, the contributions of nonadjacent interactions dominated by $Li_b \ldots Li_d$, increase the valence of Li_b and Li_d to the observed value 1.441 and thus cause these lithium atoms to be hypervalent. Similarly, the relatively lower values of contributions of $Li_a \ldots Li_c$ interactions are the primary cause of normal values of valences of Li_a and Li_c atoms.

Table 8. Effective pair populations Δ^{eff} from nonlinear population analysis for rhombic Li_4 cluster

Terms	Effective pair populations
Monoatomic	$\Delta^{\mathrm{eff}}_{AA}$
Li_a	0.064
Li_b	0.009
Diatomic	$\Delta^{\mathrm{eff}}_{AB}$
Li_aLi_b	0.230
Li_aLi_c	0.054
Li_bLi_d	0.125
Triatomic	$\Delta^{\mathrm{eff}}_{ABC}$
$Li_aLi_bLi_d$	0.342
$Li_aLi_bLi_c$	0.034
Tetraatomic	$\Delta^{\mathrm{eff}}_{ABCD}$
LiLiLiLi	0.007

In connection with the observed hypervalence of Li, it is possible to mention yet another interesting consequence of the existence of nonbonded pair interactions. According to our experience such contributions are frequently the indicator of multicenter bonding and the existence of such three-center LiLiLi bonds was suggested in the rhombic Li_4 cluster by Cooper et al. [23]. Here it is interesting to remark that in pursuing the development of the general methodology of pair population analysis we recently proposed the so-called nonlinear pair population analysis [24] in which the existence of three- and four-center bonds can be directly detected. The derivation of Δ^{eff} is analogous to the derivation of Π^{eff}, but based on $\mathbf{P}^2$ instead of $\mathbf{P}$. The sum of one-center, two-center, three-center and four-center contributions is equal to the number of electron pairs. The results of such an analysis are summarized in Table 8. As can be seen, the values of individual pair populations do indeed confirm the considerable importance of the three-center $Li_aLi_bLi_d$ bond expected by Cooper while the other possible three-center interaction $Li_aLi_bLi_c$ is considerably weaker. In view of this result it is possible to say that they are apparently just these nonclassical bonding interactions which cause the deviations of atomic and group valences from the values expected on the basis of classical valence rules.

Finally, we want to demonstrate that the group valence concept can be relevant in areas of present day research. Such an area is the field of cluster studies. We have selected silicon clusters to study the growth of clusters in the context of solid state properties. For this purpose Si_2 units were chosen to probe the bulk character of silicon clusters up to 45 atoms (Fig. 1). We now denote the external group valence V_G of an Si_2 group as V_{SiSi} and the internal group valence V'_G of such a group by V'_{SiSi}. If we tentatively assume that the bonding of silicon atoms in a diamond lattice is such that each atom is tetracoordinated with single bonds to each neighbour atom, then the external group valence V_{SiSi} of an Si_2 unit is 6 and the bond valence V'_{SiSi} between the two Si atoms in the unit is 1. A region in a cluster would be the more bulk-like, the closer its Si_2 units approach these values. The



Si_3 (C_{2v}) Si_4 (D_{2h}) Si_4 (T_d) Si_{29} (T_d) Si_{35} (T_d)

Si_5 (D_{3h}) Si_{10} (T_d)

Si_{12} (D_{5d}) Si_{13} (I_h) Si_{45} (T) Si_{45} (T_d)

Fig. 1. Structures for Si_n clusters with $n = 3, 4, 5, 10, 12, 13, 29, 35, 45$

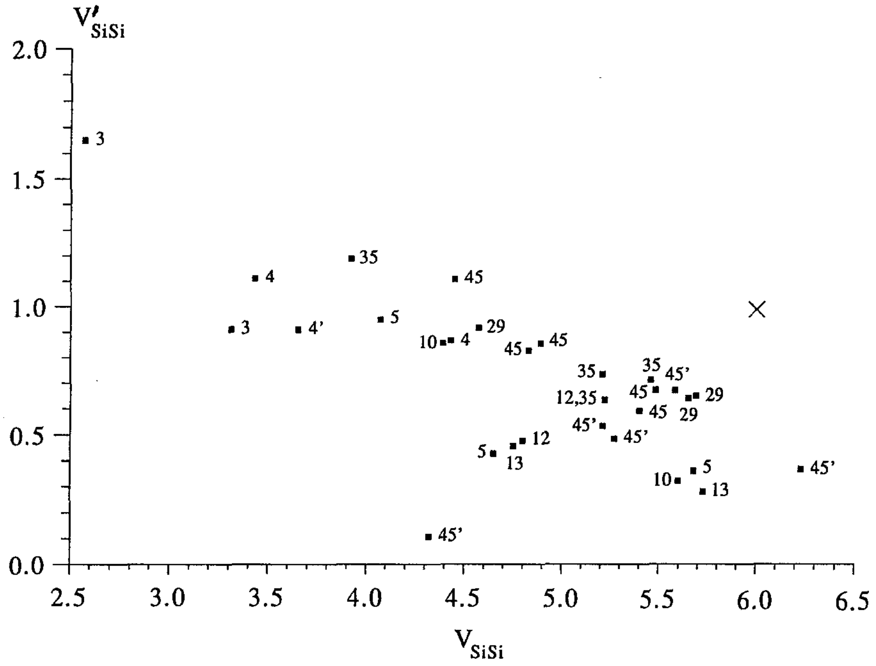


Fig. 2. Distribution of external group valences V_{SiSi} and internal group valences V'_{SiSi} of Si_2 units in Si_n clusters with $n = 3$ (C_{2v}), 4 (D_{2h}), 4′ (T_d), 5 (D_{3h}), 10 (T_d), 12 (D_{5d}), 13 (I_h), 29 (T_d), 35 (T_d), 45 (T), 45′ (T_d); hypothetical bulk value ×

results for SINDO1 calculations are in Fig. 2. The structures (Fig. 1) were taken either from previous work [25, 26] or were optimized with the new parametrization for silicon [27]. The figure shows that the smaller clusters are not bulk-like at all and even medium size clusters with 29, 35 or 45 atoms are quite different from the bulk. The points for Si_2 units on the surfaces are usually quite distant from the bulk point in the (V_{SiSi}, V'_{SiSi}) plane. Only points for Si_2 units with tetracoordinated inner cluster atoms are found in the vicinity of the hypothetical bulk point. This is particularly important since the Si_{45} cluster was the subject of extensive discussion in recent years [28–30, 25]. We observe that Si_2 units of the Si_{29}, Si_{35} and Si_{45} structures [25] have the closest values to the hypothetical bulk values $V_G = 6$ and $V'_G = 1$. This conclusion would hold, even if the hybridization in the diamond-structure of bulk silicon would not be exactly sp^3, but would have a somewhat lesser hybridization, because in that case both V_{SiSi} and V'_{SiSi} would be linearly reduced. For Si_{29} these values are related to the 1–2 and 2–12 bonds, for Si_{35} to the 1–2 bond and for Si_{45} (T) to the 1–2 bond. But for Si_{45} (T_d) the surface bond 2–36 is more bulk-like than the 1–2 bond, because the inner atom 1 is not strongly bonded to the surface atoms.

Acknowledgements. R.P. thanks Deutscher Akademischer Austauschdienst for the support of his stay at Universität Hannover. The cluster calculations were performed on the Siemens S400/40 at Universität Hannover.

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