

The use of parameter ratios to characterize the formal order of chemical bonds

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Abstract

While bonding parameters such as electron localization function (ELF) bond basin populations and atoms-in-molecules (AIM) delocalization indices may not in an absolute sense reflect our simple ideas of bond orders, ratios of these parameters referenced to a suitable standard may be a more viable measure of the bonding situation. In the present paper we have calculated both these quantities for the bonds between heavy atoms for all the simple two-heavy-atom hydrides and diatomics capable of multiple bond formation for elements in the first two long rows of the periodic table and have compared the ratios of these parameters relative to the arbitrarily chosen double bond case. We find that a division into clearly defined formal bond-order classes occurs for the AIM delocalization index and is apparent though less clear for ELF bond basin populations. The division agrees with our intuitive chemical ideas regarding formal bond order and should be a useful tool in characterizing general bonding situations. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The chemical bond is one of the most important ideas in science although attempts to associate it with a single quantitative label continue to be elusive. The accompanying idea of “bond order” is pervasive throughout chemistry and qualitatively important and useful. We tend to think of the isoelectronic H_2CCH_2 , H_2CNH , and H_2CO molecules as all containing heavy atom bonds of order two, yet clearly these bonds must all differ because of the asymmetry and accompanying polarization in the latter two cases. Attempts to obtain a robust quantitative definition have not been par-

ticularly successful since most are based on orbital concepts and are often basis set and method dependent. Except for one-electron systems, orbitals are generally a mathematical construct (although most necessary and useful) and not observables, and we understand that a quantitative measure of bond order must be relatively insensitive to method or basis set.

Two approaches have emerged in recent years that show great promise of fulfilling our desire to better pin down the nature of chemical bonding. These are the delocalization index of Fradera et al. [1] based on the electron pair density in the atoms-in-molecules (AIM) approach [2], and bond basin populations from the electron localization function (ELF) approach of Becke and Edgecombe [3] as extensively developed by Savin and coworkers [4–10].

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Both the AIM and ELF approaches are topological and divide a system's space into basins and basin attractors based on the gradients of particular scalar fields. Any such topological division will be sensitive to the approach used to define the scalar field. The AIM approach in which atomic basins are derived from the scalar field of the electron density is a very natural one, but, while atomic basin properties seem natural in this regard, the electron pair density divided up into inter-basin contributions is not as transparent. ELF basins are defined quantities although based on strong physical arguments regarding the Fermi hole [11,12] and the corresponding tendency of electron pairs to occupy different regions of space. It is, indeed, striking that ELF basin populations correspond as closely as they do to our chemical expectations of electron pairs. Complications to our simplistic expectations do arise in both approaches, however, when lone pairs are nearby or when bonds are polarized [13–15].

We note that Bader's delocalization index is equivalent to the covalent bond order defined by Ángyán et al. [16] at the Hartree–Fock or density functional theory levels; the Ángyán et al. expression is an invariant form of a similar bond index based on population-localized orbitals proposed by Cioslowski and Mixon [17]. These latter two measures of covalent bond order are quite useful, although Frederica et al. [1] state that their expression (the delocalization index) is non-arbitrary, being determined by the second-order density matrix at all levels of theory. However, the fact that the delocalization index at some levels is taken as a measure of covalent bond order is worth noting and is appropriate here because the examples we treat are done so in the single determinant density functional approach.

We have indicated before [18] that, while the bonding parameters (both ELF bond basin populations and AIM delocalization indices) may not in an absolute sense reflect our simple ideas of bond orders, ratios of these parameters referenced to a suitable standard may be a more viable measure of the bonding situation. In the present paper we have calculated both delocalization indices and bond basin populations for the bonds between heavy atom for all the simple two-heavy-

atom hydrides and diatomics capable of multiple bond formation for elements in the first two long rows of the periodic table and have compared the ratios of these parameters relative to the arbitrarily chosen double bond case. We find that a division into clearly defined formal bond-order classes occurs for the AIM delocalization index and is apparent though less clear for ELF bond basin populations. The division agrees with our intuitive chemical ideas regarding formal bond order and should be a useful tool in characterizing general bonding situations.

2. Theoretical background

2.1. The electron localization function

ELF is a robust descriptor of chemical bonding based on topological analyses of local quantum mechanical functions related to the Pauli exclusion principle. The local maxima of the function define localization attractors corresponding to core, bonding (located between the core attractors of different atoms) and non-bonding electron pairs and their spatial arrangement. It is of special interest to chemists in that the resulting isosurfaces of ELF density tend to conform to the classical Lewis picture of bonding.

Becke and Edgecombe [3] pointed out that the conditional pair probability for same spin electrons has the form

$$P_{\text{cond}}^{\sigma\sigma}(\vec{r}, s) = \frac{1}{3} \left[\sum_j^\sigma |\nabla \varphi_j|^2 - \frac{1}{4} \frac{|\nabla \rho_\sigma|^2}{\rho_\sigma} \right] s^2 + \dots \quad (1)$$

for an electron at point \vec{r} and another a distance s away (averaged over a spherical shell of radius s). When the coefficient of the quadratic term is small the Fermi hole at \vec{r} is large and one would expect to find pairs of electrons of opposite spin in the region; when it is large, the converse is true.

For a closed shell single determinantal wave function built from Hartree–Fock or Kohn–Sham orbitals, φ_j , the ELF of position \vec{r} is defined as

$$\eta = \frac{1}{1 + (D/D_h)^2}, \quad (2)$$

where

$$D = \frac{1}{2} \sum_{j=1}^N |\nabla \varphi_j|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho},$$

$$D_h = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}, \quad (3)$$

$$\rho = \sum_{j=1}^N |\varphi_j|^2$$

and where the scaling factor is chosen to be the homogeneous electron gas kinetic energy density of a system of the same electron density. The term D is the local Pauli kinetic energy density, the excess kinetic energy electrons have (due to the Pauli exclusion principle) compared to a bosonic system of the same density [6]. The ELF can be viewed as a local measure of the Pauli repulsion between electrons due to the exclusion principle and allows one to define regions of space that are associated with different electron pairs in a molecule or solid. The position where ELF attains a maximum value (the attractor) can be used as an electron pair's signature [9].

Using the vector field of the gradient of the ELF, the topology of the ELF can be used to define basins within which one or more electron pairs are to be found [5–7,10]. These subsystems are defined in terms of zero flux surfaces; the gradient paths end at what are called attractors within each subsystem. The region of three-dimensional space traversed by all gradient paths that terminate at a given attractor defines the basin of the attractor. ELF basins are labeled as either core or valence basins. Core basins contain a nucleus while valence basins do not; hydrogen basins are taken as exceptions since, although they contain a proton, they represent a shared pair interaction. A valence basin is characterized by its number of connections to core basins, referred to as its synaptic order. Basins are connected if they are bounded by part of a common surface. A simple covalent bond basin would be connected to two core basins and be of synaptic order two; a lone pair basin would

be monosynaptic. More complex bonding basins can be polysynaptic.

The population of a basin Ω_i , N_i , is given by integrating the total electron density, $\rho(\vec{r})$, over the basin volume. These populations are particularly important in

$$N_i = \int_{\Omega_i} \rho(\vec{r}) d\vec{r} \quad (4)$$

that they tend to reflect delocalization effects and, in the case of bond basins, the bond order.

2.2. The delocalization index

Bader's AIM approach [2] is based on the electron density, $\rho(\vec{r})$, a key observable in a molecule's description. The gradient field of the electron density is used to define atomic basins which can be integrated over to obtain AIM atomic basin electron populations. The delocalization index is defined in terms of the electron pair density as it relates to the AIM atomic basins.

The electron pair density [11,12], $P_2(\vec{r}_1, \vec{r}_2)$, is the diagonal part of the reduced second-order density matrix and is normalized as

$$\int d\vec{r}_1 \int d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) = \int d\vec{r}_1 (N-1) \rho(\vec{r}_1) = N(N-1), \quad (5)$$

where $\rho(\vec{r}_1)$ is the electron number density and N the total number of electrons. It proves convenient to define the pair density in terms of a quantity explicitly referencing the antisymmetric character of electron wave functions,

$$P_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1) \rho(\vec{r}_2) [1 + f(\vec{r}_1, \vec{r}_2)], \quad (6)$$

so that

$$\frac{P_2(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_2)} - \rho(\vec{r}_1) = \rho(\vec{r}_1) f(\vec{r}_1, \vec{r}_2). \quad (7)$$

The quantity on the left is the conditional probability of finding an electron at \vec{r}_1 given that there is one at \vec{r}_2 , minus the number density at \vec{r}_1 , $\rho(\vec{r}_1)$, where integration over the coordinates of all other electrons has taken place. This quantity (either

side of Eq. (7)) is the Fermi hole [11,12] associated with the reference electron at \vec{r}_2 .

If we integrate the pair density over two AIM basins, Ω_i and Ω_j , we obtain by definition the quantity N_{ij} , the inter-basin pair number, and, using Eq. (6) we can write [2,19,20]

$$\begin{aligned} N_{ij} &= \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) \\ &= \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 \rho(\vec{r}_1) \rho(\vec{r}_2) [1 + f(\vec{r}_1, \vec{r}_2)] \\ &= N_i N_j + \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 \rho(\vec{r}_1) \rho(\vec{r}_2) f(\vec{r}_1, \vec{r}_2) \\ &= N_i N_j - F_{ij}, \end{aligned} \quad (8)$$

where N_i and N_j are the basin electron numbers and where here, in contrast to Frederica et al. [1], we have explicitly introduced the negative sign in the definition of F_{ij} because it is generally positive. Because of the relations in Eqs. (5) and (6) the following sum rule for F_{ij} obtains:

$$\begin{aligned} \sum_j N_{ij} &= N_i(N - 1) = N_i N - \sum_j F_{ij}, \\ \sum_j F_{ij} &= N_i. \end{aligned} \quad (9)$$

The diagonal elements of F_{ii} are also important since it can be shown that they are intimately related to the variance, s_i^2 , of the electron number in a basin [19,20] by

$$s_i^2 = N_{ii} - N_i(N_i - 1) = N_i - F_{ii}. \quad (10)$$

These relations have also been clearly presented by Savin and coworkers [6,10].

It is the sum of the off-diagonal terms $F_{ij} + F_{ji} = 2F_{ij} \equiv \delta_{ij}$ in the AIM approach that Frederica et al. [1] refer to as the delocalization index and use as a quantitative measure of the sharing of electrons between basins Ω_i and Ω_j ; they also denote F_{ii} as the atomic localization index.

3. Theoretical details

The AIM and ELF calculations were carried out employing the TopMod Package of Noury and

coworkers [21] in the B3LYP approach [22,23]. Step sizes of 0.1 a.u. and box sizes that extended 5.0 a.u. from the outermost atomic coordinates in each direction were typically used. The TopMod package sacrifices some accuracy for efficiency and, according to the authors [21], is thought to be accurate to a few percent, sufficient for comparative studies. Optimizations and minimum-confirming frequency calculations were carried out at the MP2(FC)/6-31+G(d,p) level with GAUSSIAN98 [24].

The ground triplet states of O₂, S₂, and SO were employed as representing double bonds for these molecules. The *trans*-bent structures for H₂SiSiH₂ [25,26] and HSiSiH [27,28] were employed although this form for HSiSiH is not the global minimum. Likewise, the *trans*-bent form of HSiCH was employed although the silavinylidene form is the global minimum [29].

4. Results and discussion

4.1. The general case

Frederica et al. [1] point out that molecular formation reduces the number of pairs between two atoms (N_{ij} is reduced as F_{ij} increases, Eq. (8)) while increasing the pair formation within each (AIM) atomic basin. They take the reduction in N_{ij} to be the result of the formation of shared pairs between atoms and is the basis for their contention that $F_{ij} + F_{ji} = 2F_{ij} \equiv \delta_{ij}$, the delocalization index, provides a quantitative measure of the sharing of electrons between atoms. They do not, however, identify the delocalization index with a bond order because, with the exception of equally shared pairs (no bond polarization), it does not in their view determine the number of contributing Lewis electron pairs. They illustrate this with the delocalization indices from Hartree–Fock calculations on N₂, NO⁺, CN[−], and CO of 3.04, 2.40, 2.21, and 1.57, respectively, for this isoelectronic sequence with increasing bond polarization. On the other hand, as we noted earlier, the delocalization index is equivalent to the covalent bond order defined by Ángyán et al. [16] at the Hartree–Fock or density

functional theory levels and is, for these cases, a valid definition of covalent bond order.

In a like manner, while the ELF bond basins population, N_i , can be taken as a measure of a topological bond order [6] (more properly $0.5N_i$), when atoms of differing electronegativity are involved or lone pairs are nearby this simple picture becomes more complex [13–15].

Our working premise here is that, if polarization effects are kept relatively constant, the ratios of delocalization indices and bond populations appropriately referenced should provide insight into the nature of the formal bond order involved. We are proposing a principle of local electronic similarity whereby the formal bond order is derived from a comparison of the same two (heavy) atoms in differing states of bond multiplicity.

The delocalization indices (δ_{ij}) and heavy atom bond basin populations (N_i) for first and second long row hydrides and diatomics are contained in Table 1. The data are divided into intra- and inter-row compounds and are arranged for easy comparison between first and second row analogues. We note that the range of the delocalization index is from 0.48 in H_3SiOH to 3.04 in P_2 , and for the bond basin populations from 0.50 in HOOH to 5.83 in HSiSiH . We have arbitrarily chosen the double bond as the reference bond and have determined ratios of the two parameters relative to it for each molecular species.

For purposes of clarity of presentation and interpretation we have then multiplied each ratio by two so that in the “ideal” case a formally single bond will have a scaled ratio of 1.0 and a triple bond 3.0. These scaled data are shown in Figs. 1 (for the delocalization index) and 2 (for bond basin populations); the abscissa in Fig. 1 is δ_{ij} while in Fig. 2 it is the so-called topological bond order, $0.5N_i$. A division into three classes is quite clear in Fig. 1 for the delocalization index and evident but with more scatter in Fig. 2 for the bond basin populations. The third class in each case corresponds to the CO, CS, SiO, and SiS diatomics which we discuss below. Table 2 gives the means and standard deviations for the two types of bond-order-measuring parameters; a quantitative argument can be made for three separate classes for the delocalization index, but for the bond basin popu-

Table 1

Delocalization indices (δ_{ij}) and heavy atom bond basin populations (N_i) for first and second long row hydrides and diatomics^a

	δ_{ij}	N_i		δ_{ij}	N_i
<i>(a) Intra-row compounds</i>					
H_3CCH_3	0.95	1.78	H_3SiSiH_3	0.72	1.95
H_2CCH_2	1.89	3.44	H_2SiSiH_2	1.33	3.77
HCCH	2.85	5.20	HSiSiH	2.05	5.83
H_3CNH_2	0.99	1.63	H_3SiPH_2	0.64	1.88
H_2CNH	1.77	2.91	H_2SiPH	1.41	2.81
HCN	2.57	4.37	HSiP	2.53	4.05
H_3COH	0.90	1.26	H_3SiSH	0.60	1.76
H_2CO	1.58	2.41	H_2SiS	1.27	2.71
CO	1.70	3.11	SiS	1.49	2.74
H_2NNH_2	1.24	1.29	H_2PPH_2	0.99	1.75
HNNH	2.03	2.26	HPPH	1.93	2.36
NN	3.03	3.47	PP	3.04	3.04
H_2NOH	1.22	0.89	H_2PSH	1.05	1.51
HNO	2.14	1.83	HPS	1.86	2.20
HOOH	1.27	0.51	HSSH	1.29	1.28
OO	2.23	0.99	SS	2.29	1.89
<i>(b) Inter-row compounds</i>					
H_3SiCH_3	0.55	1.94			
H_2SiCH_2	1.17	3.64			
HSiCH	2.02	4.09			
H_3SiNH_2	0.52	2.36	H_3CPH_2	0.86	1.76
H_2SiNH	1.12	3.14	H_2CPH	1.65	2.96
HSiN	2.22	(0.0) ^b	HCP	2.53	4.16
H_3SiOH	0.48	1.49	H_3CSH	1.13	1.55
H_2SiO	0.98	(0.0) ^b	H_2CS	2.06	2.62
SiO	1.16	3.50	CS	2.64	2.62
H_2PNH_2	0.85	2.03			
HPNH	1.64	2.50			
PN	2.52	3.09			
H_2POH	0.81	1.23	H_2NSH	1.21	1.36
HPO	1.50	1.75	HNS	2.08	2.11
HSOH	1.15	0.86			
SO	1.99	1.32			

^a The data are divided into intra- and inter-row compounds and are arranged for easy comparison between first and second row analogues.

^b There is no heavy atom bond basin for this molecule; see text.

lations one cannot distinguish the triple bond and CO-type cases.

We believe the case is made, then, that if one uses ratios of either parameter relative to the double bond case, formal bond orders of essentially one or three arise. The division into classes is more important than the absolute values of the ratios although it is satisfying that the numbers confirm

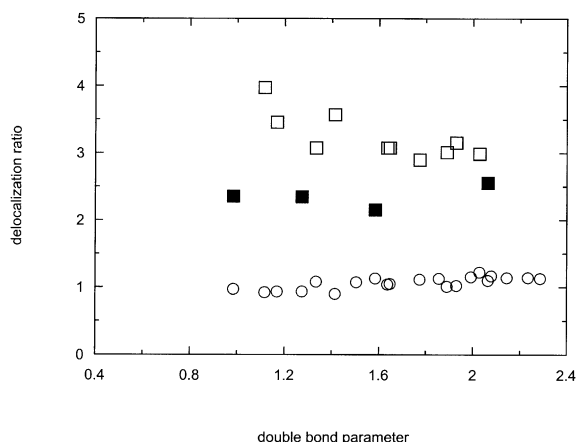


Fig. 1. Ratios of delocalization indices as a function of the delocalization index (δ_{ij}).

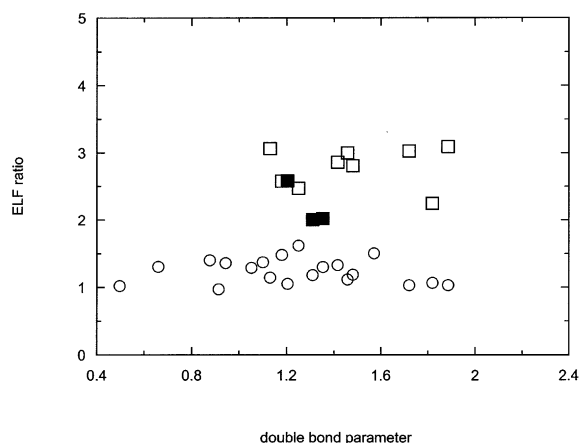


Fig. 2. Ratios of bond basin populations as a function of the ELF topological bond order ($0.5N_i$).

Table 2

Means (\bar{x}) and standard deviations (σ) for the scaled delocalization index (δ_{ij}) and bond basin population (N_i) ratios^a

	Comparative single order	Comparative triple order	CO-type
δ	1.06 ± 0.09	3.23 ± 0.32	2.35 ± 0.14
N	1.24 ± 0.18	2.79 ± 0.28	2.22 ± 0.29

^a The “CO”-type species are treated as a separate category.

our intuitive impressions regarding these types of multiple bonds.

Table 3

ELF populations (number of electrons) for core (C), lone pair (LP) and bond basins (BB) for the CO-type species made up of atoms A and B and their H_2AB counterparts^a

A ... B	LP/H(A)	C(A)	BB(AB)	C(B)	LP(B)
CO	2.56	2.07	3.11	2.12	4.14
H ₂ CO	2.13	2.09	2.41	2.11	5.13
CS	2.46	2.06	2.63	10.06	4.79
H ₂ CS	2.13	2.08	2.62	10.06	4.98
SiS	2.26	10.06	2.74	10.08	4.86
H ₂ SiS	2.04	10.07	2.71	10.07	5.08
SiO	2.14	10.06	3.50	2.10	4.20
H ₂ SiO	2.04	10.06	(0.0) ^b	2.12	7.74

^a The entry under LP/H(A) represents the population of each proton basin in the diprotonic molecule. The molecules are arranged in order of calculated increasing absolute dipole moment of the diatomics.

^b There is no heavy atom bond basin in this molecule.

4.2. The CO-type species

The CO-type species consisting of CO, CS, SiO, and SiS are usually thought of as triply bonded, yet the delocalization indices (Fig. 1, Table 2) suggests that the scaled parameter ratio is closer to 2 than 3, classifying them in our approach as formally double bonds. We cannot separate the CO-type species and the formally triply bound species in the bond basin approach (Fig. 2, Table 2) unless the value for CO itself is considered an outlier and omitted, which we have no justification in doing. In Table 3 we compare all the basin populations for these species next to their diprotonated counterparts. Comparing SiO to H₂SiO is made complicated because the latter has no SiO bond basin. The molecule in the ELF picture is basically ionic with charge being transferred from the SiO bonding region to the oxygen lone pairs. We do note from Table 1 and from Fig. 1 that the delocalization index ratio classifies the bond in SiO as a formally double. The CS and SiS molecules differ very little from the (assumed) doubly bonded H₂CS and H₂SiS molecules; we must conclude that in the ratio of parameters case they should be considered as formally doubly bonded. CO is strange in that the ELF picture likely classifies it as triple while the delocalization picture would call it double. This discrepancy probably points out a problem in the current approach; obviously one

would like the two methods of describing bonding to yield equivalent results.

4.3. Some special cases

The HSiN and H₂SiO molecules are unusual compared to the others studied here.

H₂SiO does not exhibit a bond basin, revealing only core and valence basins as shown in Fig. 3 for an η -value of 0.81. In that figure one is looking down on the planar molecule; the various basin populations (in electrons) are 2.04 (each hydrogen), 10.06 (silicon core), 2.12 (oxygen core), and 7.74 (oxygen valence). Although the oxygen valence basin does ultimately move to two attractors, what one is seeing here is essentially ionic oxygen of approximate charge -2 ; likewise, taking into account the hydrogen basin populations the silicon–hydrogen fragment is basically of charge $+2$. This case illustrates the fact that one cannot discuss covalent character of a bond in terms of bond

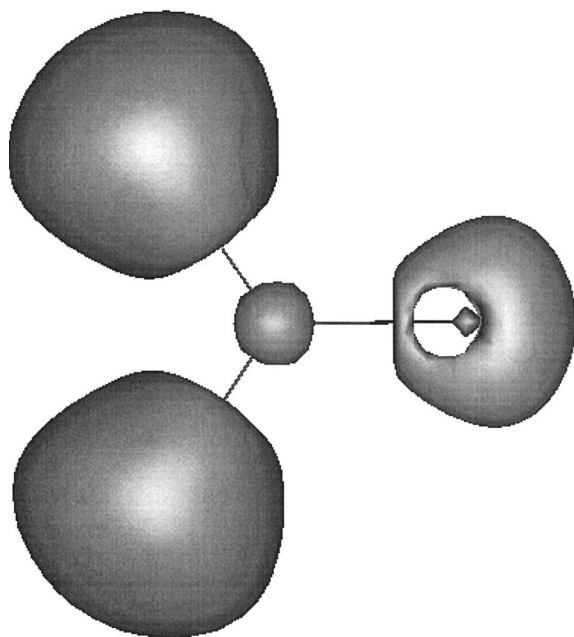


Fig. 3. ELF basins for H₂SiO (left to right) for $\eta = 0.81$. The view is looking down on the planar molecule and reveals the hydrogen, silicon and oxygen core basins along with the oxygen valence shell.

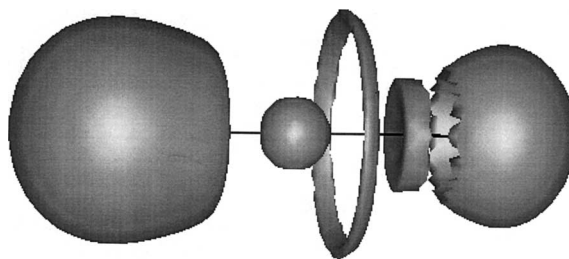


Fig. 4. ELF basins for HSiN (left to right) for $\eta = 0.80$. Note the unusual valence rings for silicon and oxygen.

basin populations if there are no clear bond basins! The SiO bond here is characterized by ELF as essentially ionic.

HSiN is a more difficult case, as is seen in Fig. 4 for an η -value of 0.80. Here the molecule is shown with hydrogen on the left ($N_i = 2.06$), the silicon core ($N_i = 10.06$), what we shall term the silicon valence ($N_i = 2.73$), an oxygen valence “neck” ($N_i = 0.55$) (vide infra), and the oxygen core ($N_i = 4.49$). The linear symmetry of the molecule requires that the various basins have cylindrical symmetry. The usual basin structure of this molecule is due, we believe, to the usual mixture of ionic and covalent bonding as illustrated by the silicon valence basin somewhat to the right of the silicon core and the oxygen “neck” just to the left of the oxygen core and valence (lone pair) basins. As η is increased higher than the value shown in Fig. 4 the oxygen “neck” quickly merges with the oxygen valence (lone pair) basin and the ionic nature of the bond is more apparent. This example shows that basin structures are not always straightforward; that is, one cannot always describe an interaction as either simple covalent or ionic.

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