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Journal of Molecular Structure 450 (1998) 59–68

Journal of
MOLECULAR
STRUCTURE

Analysis of the delocalization in the topological theory of chemical bond

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Received 29 September 1997; accepted 7 November 1997

Abstract

The topological analysis of the gradient field of the electron localization function provides a convenient theoretical framework for the partition of the molecular space into basins of attractors having a clear chemical meaning. The basin populations are evaluated by integrating the one-electron density over the basins. The variance of the basin population provides a measure of the delocalization. The behavior of the core C(X) and protonated valence basins V(X, H) populations have been investigated. The analysis of the population variance in terms of cross-contributions is presented for aromatic and antiaromatic systems, hypervalent molecules and hydrogen-bonded complexes. For hypervalent molecules this analysis emphasizes the importance of the ionic resonance structures. © 1998 Elsevier Science B.V.

Keywords: Delocalization; Chemical bond; Topological theory

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1. Introduction

The bonding in many molecular systems is not fully explained by considering a single Lewis structure. As a classical example we can mention the conjugated hydrocarbons for which a straightforward application of the valence concepts led Huggins to propose chimerical structures [1]. Within the standard quantum chemical approaches such systems are understood either as the superposition of resonant valence-bond structure [2] or in terms of occupied molecular orbital delocalized over the whole carbon skeleton [3]. Both approaches rely upon the calculational procedure and as mentioned by Coulson: ‘‘There is an interesting contrast between the VB and MO descriptions of benzene. Both require complete delocalization, but whereas the VB method introduces it by superposition of Kekulé (and other) structures, in the MO method there is nothing that even remotely resembles a structure. This situation warns us once more against any too literal belief in the reality of our structures.’’ [4].

An alternative point of view, which does not give sense to intermediates in the calculation, is provided by partitioning techniques of the molecular space pioneered by Daudel in the framework of the loge theory [5] in order to reconcile the global picture provided by quantum mechanics with the localized description of the bonding taught by the chemical experience. Within this framework, delocalization dialectically arises as consequence of the contradiction between these two latter pictures. The loge theory realizes a partition of the molecular space into spatial domains, the loges, which maximizes the probability of finding a given number of electrons within each of them. The determination of the loge boundary is hardly feasible because it requires to work with the *N*-particle density

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PII S0022-2860(98)00413-X

matrix. Two alternative partition schemes, mainly based on topological methods, have been proposed so far. On the one hand is the theory of atoms in molecules of Richard Bader which analyzes the gradient field of the one-electron density [6] and on the other hand is the analysis of Silvi and Savin [7] which works with the Becke and Edgecombe's electron localization function ELF [8] as potential function. This latter method allows a partition of the molecular space into basins of attractor having a clear chemical meaning. Within these two methods, the basin population $\bar{N}_i$ are evaluated by integration the one-electron density over the volume of the basin Ω_i. Moreover, a measure of the delocalization is provided by considering the fluctuations of the basin populations $\sigma^2(\bar{N}_i)$ [9,10]. The importance of the fluctuation of the number of particles contained in a limited region of space has been addressed at a rather high epistemological level by Diner and Claverie [11]

In this paper we investigate the properties of the variance of the basin populations in order to build up a method of analysis of the delocalization in terms of basin contributions. The applicability of the method is exemplified by results on typical molecular system such as the water molecule, aromatic and anti-aromatic compounds, substituted benzenes, hypervalent molecules ionic systems and hydrogen-bonded complexes.

2. Theory

Consider a partition of the molecular space into n adjacent non-overlapping basins. The average basin population, $\bar{N}_i$, can be defined as the expectation value

$$\bar{N}_i = \langle \psi | \hat{N}_{\Omega_i} | \psi \rangle \tag{1}$$

of the operator $\hat{N}_{\Omega_i}$:

$$\hat{N}_{\Omega_i} = \sum_i^N \hat{Y}_{\Omega_i}(\mathbf{r}_i) \tag{2}$$

where N is the number of particles and

$$\hat{Y}_{\Omega_i}(\mathbf{r}_i) = \begin{cases} 1 & \text{if } \mathbf{r}_i \in \Omega_i \\ 0 & \text{otherwise} \end{cases} \tag{3}$$

and thus in terms of the one-electron density $\rho(\mathbf{r})$

$$\bar{N}_i = \int_{\Omega_i} \rho(\mathbf{r})\, d\mathbf{r} \tag{4}$$

Its variance, i.e. the square of the standard deviation, is given by [9]:

$$\sigma^2(\bar{N}_i) = \langle (\hat{N}_{\Omega_i} - \bar{N}_i)^2 \rangle = \int_{\Omega_i} d\mathbf{r}_1 \int_{\Omega_i} P_2(\mathbf{r}_1,\ \mathbf{r}_2)\, d\mathbf{r}_2 + \bar{N}_i - \bar{N}_i^2 = \bar{N}_{ii} - \bar{N}_i(\bar{N}_i - 1) \tag{5}$$

in which $P_2(\mathbf{r}_1,\ \mathbf{r}_2)$ is the spinless pair function, i.e. the probability of finding one electron at position $\mathbf{r}_1$ and another at $\mathbf{r}_2$, $\bar{N}_{ii}$ is the actual number of electron pairs within Ω_i whereas $\bar{N}_i(\bar{N}_i - 1)$ is the number of pairs in an isolated system containing $\bar{N}_i$ particles. Therefore, $\sigma^2(\bar{N}_i)$ has the meaning of an excess in the number of pairs due to the interaction of Ω_i with the other basins. It is worth noting that $\bar{N}_i(\bar{N}_i - 1)$ is the lower bound of the actual number of pairs $\bar{N}_{ii}$ since $\sigma^2(\bar{N}_i) \geq 0$. It is possible to rewrite $\sigma^2(\bar{N}_i)$ in order to make the dependence clearer. The properties of $P_2(\mathbf{r}_1, \mathbf{r}_2)$ [12] imply that:

$$\int_{\Omega_i} d\mathbf{r}_1 \sum_{j=1}^{n} \int_{\Omega_j} [\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - P_2(\mathbf{r}_1, \mathbf{r}_2)]\, d\mathbf{r}_2 = \sum_{j=1}^{n} \bar{N}_i\bar{N}_j - \bar{N}_{ij} = \bar{N}_i \tag{6}$$

Substituting Eq. (6) into Eq. (5) yields:

$$\sigma^2(\bar{N}_i) = \sum_{j \neq i} \left(\bar{N}_i\bar{N}_j - \bar{N}_{ij} \right) \tag{7}$$

Therefore, the variance of the population of a given basin can be written as the sum of the contributions of all the other basins. These contributions

$$B_{ij} = \bar{N}_i\bar{N}_j - \bar{N}_{ij} \tag{8}$$

are just the difference in the number of pairs between Ω_i and Ω_j expected in the limit of non-interacting basins (the product of their populations) and the actual number of pairs. An alternative expression of the B_{ij}

$$B_{ij} = -\int_{\Omega_i} d\mathbf{r}_1 \int_{\Omega_j} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \tag{9}$$

can be derived by rewriting $P_2(\mathbf{r}_1, \mathbf{r}_2)$ as:

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)[1 + h(\mathbf{r}_1, \mathbf{r}_2)] \tag{10}$$

in which $h(\mathbf{r}_1, \mathbf{r}_2)$ stands for the exchange correlation hole.

Though any partition of the variance of the basin population is somewhat arbitrary, it is rather disconcerting to find an expression in terms of additive contributions having a clear physical meaning. Moreover, Eq. (9) is closely related to Mayer's definition of bond orders [13,14] and happens to be one half of the topological bond orders derived by Ángyán et al. in the framework of Bader's theory of atoms in molecules [15]. For a practical analysis of the delocalization, the B_{ij} functions can be either used as they stand or divided by $\sigma^2(\Omega_i, \Omega_j)$ in order to obtain these contributions in percentages.

In actual calculations performed with single determinantal wave functions, the B_{ij} functions are evaluated from molecular or natural orbitals $\phi_\mu(\mathbf{r})$ and from the occupation numbers n_μ^α, n_μ^β:

$$B_{ij} = \sum_\mu \sum_\nu (n_\mu^\alpha n_\nu^\alpha + n_\mu^\beta n_\nu^\beta)\langle\phi_\mu|\phi_\nu\rangle_{\Omega_i}\langle\phi_\nu|\phi_\mu\rangle_{\Omega_j} \tag{11}$$

Following Bader [9] it is useful to introduce the relative fluctuation

$$\lambda(N_i) = \frac{\sigma^2(\bar{N}_i)}{\bar{N}_i} \tag{12}$$

which is positive and expected to be less than one in most cases.

3. The topological analysis of ELF

The electron localization function of Becke and Edgecombe [8] is defined as:

$$\eta(\mathbf{r}) = \frac{1}{1 + [D(\mathbf{r})/D_h(\mathbf{r})]^2} \tag{13}$$

For a single determinantal wave function built from Hartree–Fock or Kohn–Sham orbitals ϕ_i

$$D(\mathbf{r}) = \frac{1}{2}\sum_i |\nabla\phi_i(\mathbf{r})|^2 - \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \tag{14}$$

and

$$D_h(\mathbf{r}) = C_F \rho(\mathbf{r})^{5/3} \tag{15}$$

$D(\mathbf{r})$ has the physical meaning of the excess local kinetic energy density due to Pauli repulsion [16] and $D_h(\mathbf{r})$ is the Thomas–Fermi kinetic energy density $D_h(\mathbf{r})$, which can be regarded as a ''renormalization'' factor. In Eq. (9), C_F is the Fermi constant with value $C_F = 2.871$ a.u. The range of values of η is: $0 \le \eta \le 1$.

Where electrons are alone, or form pairs of antiparallel spins, the Pauli principle has little influence on their behavior and the excess local kinetic energy has a low value, whereas at the boundaries between such regions the probability of finding parallel spin electrons close together is rather high and the excess local kinetic energy has a high value. The gradient field analysis of ELF allows one to locate attractors and basins with a clear chemical meaning [7]. Usually, the attractors of a gradient field are single points as it is the case for the gradient field of the density. However, for the ELF function, they can also be circles and spheres if the system belongs to a continuous symmetry group (here, cylindrical and spherical symmetry respectively).

3.1. Classification of basins

There are basically two types of basins. On the one hand are core basins organized around nuclei (with $Z > 2$) and on the other are valence basins in the remaining space. The structure provided by the core basins closely matches the inner atomic shell structure. A valence basin is characterized by its synaptic order which is the number of cores to which it is connected [10]. To be connected to a core a valence basin must fulfil the three following conditions:

1. It is bounded to the core basin by a part of a common separatrix.
2. The valence attractor lies within the smallest (reducible or irreducible) valence f-localization domain[1] which totally surrounds another f-localization domain which contains one or more core attractors.
3. The proton is counted as a formal core.In principle, a core is always totally encapsulated by at least one valence basin and therefore propositions 1 and 2 are redundant when f tends to zero unless the valence localization domains and a core domain have already merged into a single domain. In our description of the chemical bond a basin which

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[1] An f-localization domain localization domain is a volume bounded by at least one isosurface $\eta(\mathbf{r}) = f$. It is said to be irreducible when it contains only one attractor, and to be reducible otherwise.

Table 1
Nomenclature of attractors and basins

Synaptic order	Nomenclature	Symbol
0	core	$C(X_i)$
1	monosynaptic	$V(X_i)$
2	disynaptic	$V(X_i, Y_j)$
≥ 3	polysynaptic	$V(X_i, Y_j, \ldots)$

contains a proton is considered as a valence basin except for the peculiar case of the very strong hydrogen bond for which a pseudo-core shell is found around the bridging proton. The valence basins are therefore divided into mono-, di- and polysynaptic ones. As an example, a C–H bond is characterized by a disynaptic basin which encompasses the proton and shares a common separatrix with the carbon core basin. The nomenclature adopted to label core and valence attractors and basins is given in Table 1. The attractors and basins are labeled as $T_{[i]}$(atom labels). T denotes the type of attractor, V for valence, C for core; *i* is an optional running number in the case of multiple attractors related to the same atom(s). For example, in the water molecule there is one core attractor for the oxygen K-shell labeled C(O), two protonated disynaptic attractors $V(H_1, O)$ and $V(H_2, O)$, and two monosynaptic attractors corresponding to the lone pairs $V_1(O)$ and $V_2(O)$. In ethane, the disynaptic attractor of the C–C bond will be named $V(C_1, C_2)$ accordingly.

The classification of bonds proposed previously [7] remains valid with this new nomenclature. The shared

Table 2
Molecular and atomic systems studied

System	Basis set	Method	►Geometry
LiH	6-311 + G(3df,2p)	B3LYP	r(LiH) = 1.5905 Å
LiF	6-311 + G(3df,2p)	B3LYP	r(LiF) = 1.5718 Å
BeH_2	6-311 + G(3df,2p)	B3LYP	r(BeH) = 1.3251 Å
B	6-311 + G(3df,2p)	B3LYP	
B^+	6-311 + G(3df,2p)	B3LYP	
B^{2+}	6-311 + G(3df,2p)	B3LYP	
B_4H_4	6-31G**	B3LYP	T_d, r(BB) = 1.6785 Å, r(BH) = 1.187 Å
$B_6H_6^{2-}$	6-31G**	B3LYP	O_h, r(BB) = 1.729 Å, r(BH) = 1.225 Å
C_2H_4	6-31G**	B3LYP	D_{2h}, r(C=C) = 1.3405 Å, r(CH) = 1.0935 Å, ∠CCH = 121.8°
C_4H_4	6-31G**	B3LYP	D_{2h}, r(C=C) = 1.1.3347 Å, r(C–C) = 1.5785 Å, r(CH) = 1.0833 Å
C_6H_6	6-31G**	B3LYP	D_{6h}, r(CC) = 1.386 Å, r(CH) = 1.0935 Å
C_6H_5F	6-31G**	HF	C_{2v}, r(CC) = 1.3831 Å, r(CH) = 1.1.0752 Å, r(CF) = 1.3262 Å
$C_6H_5NO_2$	6-31G**	HF	C_{2v}, r(CC) = 1.3855 Å, r(CN) = 1.4533 Å, r(CNO) = 1.1937 Å
NH_3	6-311 + G(3df,2p)	B3LYP	r(NH) = 1.313 Å, ∠HNH = 107.3°
H_2O	6-311 + G(3df,2p)	B3LYP	r(OH) = 0.927 Å, ∠HOH = 105.2°
$(HF)_2$	6-31G**	B3LYP	r(FH) = 0.9259 Å, r(FF) = 2.7256 Å
FHNH3	6-311 + G(3df,2p)	B3LYP	r(FH) = 0.9425 Å, r(FN) = 2.72 Å
Ne	6-311 + G	B3LYP	
NaH	6-311 + G	B3LYP	r(NaH) = 1.8818 Å
$MgAlF_5$	6-311 + G(3df,2p)	B3LYP	C_{3v}, $r(AlF_{eq})$ = 1.7375 Å, r(AlF_{ap}) = 1.6343 Å, $r(MgF_{eq})$ = 2.0709 Å, $r(MgF_{ap})$ = 1.7501 Å
F_2SiO	6-311 + G(3df,2p)	B3LYP	r(SiO) = 1.5059 Å, r(SiF) = 1.5747 Å, ∠FSiO = 127.7°
Cl_2SiO	6-311 + G(3df,2p)	B3LYP	r(SiO) = 1.5112 Å, r(SiCl) = 2.0278 Å, ∠ClSiO = 125.8°
PF_5	6-311 + + G**	HF	D_{3h}, $r(PF_{ap})$ = 1.596 Å, $r(PF_{eq})$ = 1.561 Å
SF_6	6-311 + + G**	HF	O_h, r(SF) = 1.538 Å
SF_3N	6-311 + + G**	HF	C_{3v}, r(SF) = 1.544 Å, r(SN) = 1.388 Å, ∠NSF = 122.9°
SF_4O	6-311 + + G**	HF	C_{2v}, $r(SF_{ap})$ = 1.562 Å, $r(SF_{eq})$ = 1.522 Å, r(SO) = 1.41 Å, $\angle OSF_{eq}$ = 123.38°
ClO	6-311 + G(3df,2p)	B3LYP	r(ClO) = 1.5761 Å
ClO_2	6-311 + G(3df,2p)	B3LYP	r(ClO) = 1.4791 Å, ∠OClO = 117.3°
Ar	6-311 + G(3df,2p)	B3LYP	

Table 3
Basis set dependence of basin populations $\bar{N}$ and standard deviations σ of water All calculations have been performed at the B3LYP level

Basis set	C(O)		V(O, H)		V(O)	
	$\bar{N}$	σ	$\bar{N}$	σ	$\bar{N}$	σ
STO-3G	2.06	0.52	1.38	0.81	2.59	1.03
3-21G	2.15	0.59	1.43	0.84	2.50	1.05
6-31G	2.15	0.59	1.43	0.84	2.50	1.05
6-31G**	2.14	0.59	1.60	0.87	2.33	1.03
6-311 + G(3df,2p)	2.14	0.59	1.60	0.88	2.33	1.04

electron interaction (a more consistent name is shared valence basin interaction) is characterized by a di- or polysynaptic basin. The lone pairs give rise to monosynaptic basins. It is important to note that this picture of the chemical bond implies a somewhat different point of view than that currently adopted in chemistry. In the standard pictures a bond is considered as a link joining an atom to another one. Here, what is important is the number of cores a given piece of glue (the valence basin) is stuck on.

4. Examples of application

The method of analysis outlined above has been applied to a selection of chemical systems (see Table 2) in order to investigate how the basin populations and their variances (or standard deviations which represent the quantum mechanical uncertainties on the populations) can help to understand the bonding. The calculations of the wave functions have been performed either at the Hartree–Fock or at the hybrid functional B3LYP [17,18] levels with the Gaussian94 software [19]. The calculations on large and small systems have been carried out with the 6-31G** and 6-311 + G(3df,2p) basis sets respectively. The ELF function analysis and the integration of the density matrices over the basins have been done with the TopMoD package [20] developed in our laboratory.

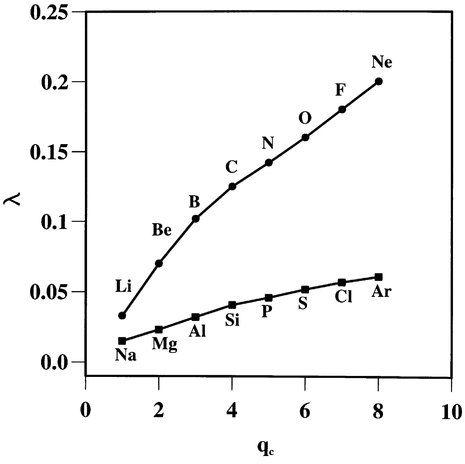


Fig. 1. Relative fluctuation of the core basin population vs. core formal charges for first row ($Z-2$) and second row ($Z-8$) elements.

In contrast with other population analysis, the topological partition provides populations which are not so much basis set dependent as illustrated by the values listed in Table 3. The only noticeable effect is due to polarization functions for which a difference of the order of 0.2 e^- with respect to unpolarized sets is found for valence basins. In the discussion we will first present some general trends concerning given types of basins and after more particular examples exhibiting a specific chemical behavior.

4.1. Fluctuation of the core basin atomic density

In molecules the core basin population of a given element is almost independent of the nature of the molecule in which the atom is involved. Representative values of core populations, standard deviations and relative fluctuations have been selected in results on molecules listed in Table 2. The core basin population of the first row atoms is calculated to lie between 2.01 for Li and 2.26 for Ne whereas the corresponding variances range from 0.07 to 0.46. For the second row atoms, it is convenient to gather the two core shells into a single superbasin the population of which is close to 10.05 throughout the series whereas the variance is comprised between 0.16 and 0.61. Fig. 1 displays the evolution of the relative fluctuation λ of

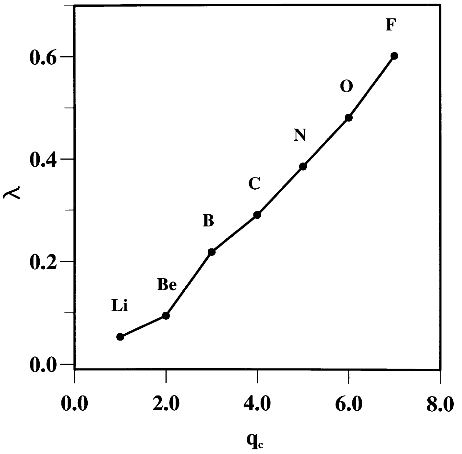


Fig. 2. Relative fluctuation of the V(H) and V(X, H) populations vs. X core formal charge. X = Li, …, F.

the core basins of the first and second rows atoms as a function of core formal charge. For the whole periodic classification, the relative fluctuation of the core basin populations is bounded by 0.2 the neon value. For both rows λ increases almost linearly with *Z*. For molecules, this can be interpreted according to the following picture: in lithium the core radius is large and the effective potential felt by the valence electron is not strong enough to allow it to enter the core zone easily, whereas in neon the core radius is small and the core net charge large, which favors the visit to the core region by the valence electrons. It is worth noting that for a given atom the variance decreases upon ionization, for B, B^+ and B^{2+} $\lambda = 0.4$, 0.35 and 0.32 respectively, therefore the number of electrons in the valence shell plays a similar role as the core net charge.

In an ionic bond the cation is often a bare core and therefore $\lambda = 0.2$ appears to be an upper bound for the variance of the cation population.

Table 4
Cross contribution to the population variance of water. Note that $\sum_j B_{ij} = \bar{N}_i$, $\sum_{j \neq i} B_{ij} = \sigma^2(\bar{N}_i)$

	$V(O, H_2)$	$V_1(O)$	$V(O, H_1)$	C(O)	$V_2(O)$
$V(O, H_2)$	0.826	0.291	0.128	0.061	0.291
$V_1(O)$	0.291	1.238	0.291	0.113	0.393
$V(O, H_1)$	0.128	0.291	0.826	0.061	0.291
C(O)	0.061	0.113	0.061	1.793	0.113
$V_2(O)$	0.291	0.393	0.291	0.113	1.238

Table 5
C_2H_4 molecule. Basin populations $\bar{N}_i$, standard deviation $\sigma(\bar{N}_i)$, relative fluctuation $\lambda(\bar{N}_i)$ and contributions of the other basins (%) to $\sigma^2(\bar{N}_i)$

Basin	$\bar{N}_i$	$\sigma(\bar{N}_i)$	$\lambda(\bar{N}_i)$	Contribution analysis
$C(C_1)$	2.10	0.51	0.12	$V(C_1, H_1)$ 27%, $V(C_1$, H2) 27%, $V_1(C_1, C_2)$ 20%, $V_2(C_1, C_2)$ 20%
$V_1(C_1, C_2)$	1.80	1.0	0.55	$V(C_1,H_1)$ 16%, $V(C_2$, H3) 16%, $V(C_2$, H4 16%, $V_2(C_1, C_2)$ 27%
$V(C_1, H_1)$	2.05	0.79	0.30	$V(C_1$, H2) 29%, $V_1(C_1, C_2)$ 25%, $V_2(C_1, C_2)$ 25%

4.2. Fluctuation of the V(H) and V(X, H) basin population

The populations and population variances of the V(H) and V(X, H) basins also follow a regular variation with respect to the core formal charge within the first row as shown by Fig. 2. For LiH and BeH_2, the relative fluctuations of V(H) are both lower than 0.2 indicating the ionic character of the bond. Table 4 shows the cross-contributions to the population variance of H_2O. On the other end of the plot, the large values of the relative fluctuations of H_2O and HF are explained by populations less than 2: 1.6 and 1.2 respectively. For the water molecule V(O, H) basin, the delocalization mainly involves the two monosynaptic basins of the lone pairs which contribute to 76% of the variance whereas the other V(O, H) basin only accounts to 17%. In FH, 88% of the variance is due to the fluorine lone pairs.

4.3. Two cases of high delocalization

High values of the standard deviation σ occur for the disynaptic basins of double bonds [10] and for the monosynaptic basins of lone pairs. Table 5 reports the basin populations and their standard deviations of ethylene together with the variance contribution analysis. The rather large standard deviations of the $C_1(C_1, C_2)$ and $C_2(C_1, C_2)$ disynaptic basins which forms the double bond is explained by the rather large mutual contribution. In the case of H_2O and H_2S lone pairs, Table 6 shows that the mutual

Table 6
H_2O and H_2S molecules. Basin populations $\bar{N}_i$, standard deviation $\sigma(\bar{N}_i)$, relative fluctuation $\lambda(\bar{N}_i)$ and contributions of the other basins (%) to $\sigma^2(\bar{N}_i)$

Basin	$\bar{N}_i$	$\sigma(\bar{N}_i)$	$\lambda(\bar{N}_i)$	Contribution analysis
H_2O				
C(O)	2.14	0.59	0.16	V(O, H_1) 17.5%, V(O, H_2) 17.5%, V_1(O) 32.5%, V_2(O) 32.5%
V_1(O)	2.33	1.04	0.47	V(O, H_1) 26%, V(O, H_2) 26%, V_2(O) 36%
V(O, H_1)	1.60	0.88	0.48	V(O, H_2) 17%, V_1(O) 38%, V_2(O) 38%
H_2S				
C(S)	10.06	0.72	0.05	V(S, H_1) 18%, V(S, H_2) 18%, V_1(S) 32%, V_2(S) 32%
V_1(S)	2.17	1.0	0.46	V(S, H_1) 25%, V(S, H_2) 25%, V_2(S) 34%
V(S, H_1)	1.79	0.84	0.39	V(S, H2) 17%, V_1(S)

contribution to the variance of the monosynaptic basins accounts for 36% and 34% respectively of the total population variance of these basins.

4.4. Aromatic and antiaromatic systems

Monocyclic conjugated hydrocarbons which follow the $4n+2$ Hückel rule are aromatic whereas those having $4n$ electrons in their π systems are antiaromatic. Benzene and cyclobutadiene are academical examples of aromatic and antiaromatic hydrocarbons. The basin populations, their standard deviations and the contribution analysis of the population variance are presented in Table 7.

In benzene there is only one disynaptic basin between two successive carbons with a population intermediate between a single and a double bond (i.e. 2.8 e^-) and a rather large standard deviation ($\sigma = 1.14$). The largest contributions to the population variance come from the adjacent V(C, C) basins (22%) and to a lesser extent from the V(C, H) basins involving the two carbons of the bond (17%). In C_4H_4, there are two single bonds and two double bonds in the conventional representation, the molecule has the D_{2h} symmetry. A disynaptic basin with a population of 1.91 e^- corresponds to each single bond. The standard deviation of these basins is 0.99 and the analysis of the variance shows a noticeable contribution of the hydrogens. The double bonds give rise to a pair of disynaptic basins symmetrically located on each side of the molecular plane. Their population is 1.83 e^- with a standard deviation of 1. The leading term of the variance decomposition is the mutual contribution which accounts for 26%.

4.5. Hypervalent systems

The SF_6, SF_3N and SF_4O molecules have been chosen as examples of hypervalent systems. Table 8 presents the basin populations, the standard deviation, relative fluctuations and variance contribution leading

Table 7
C_6H_6 and C_4H_4 molecules. Basin populations $\bar{N}_i$, standard deviation $\sigma(\bar{N}_i)$, relative fluctuation $\lambda(\bar{N}_i)$ and contributions of the other basins (%) to $\sigma^2(\bar{N}_i)$

Basin	$\bar{N}_i$	$\sigma(\bar{N}_i)$	$\lambda(\bar{N}_i)$	Contribution analysis
C_6H_6				
C(C_1)	2.10	0.50	0.12	V(C_1, C_2) 31%, V(C_1, C_6) 31%, V(C_1, H_1) 27%
V(C_1, H_1)	2.08	0.78	0.29	V(C_1, C_2) 35%, V(C_1, C_6) 35%
V(C_1, C_2)	2.80	1.14	0.46	V(C_1, H_1) 17%, V(C_2, H_2) 17%, V(C_1, C_6) 22%, V(C_2, C_3) 22%
C_4H_4				
C(C_1)	2.10	0.51	0.12	V(C_1, C_2) 19%, V_1(C_1, C_3) 21%, V_2(C_1, C_3) 21%, V(C_1, H_1) 29%
V(C_1, H_1)	2.10	0.80	0.31	V(C_1, C_2) 24%, V_1(C_1, C_3) 25%, V_2(C_1, C_3) 25%, C(C_1) 12%
V(C_1, C_2)	1.91	0.99	0.51	V_1(C_2, C_4) 12%, V_2(C_2, C_4) 12%, V_1(C_1, C_3) 12%, V_2(C_1, C_3) 12%, V(C_1, H_1) 16%, V(C_2, H_2 16%
V_1(C_1, C_3)	1.83	1.0	0.54	V(C_1, C_2) 12%, V(C_3, C_4) 12%, V(C_1, H_1) 16%, V(C_3, H_3) 16%, V_2(C_1, C_3) 26%

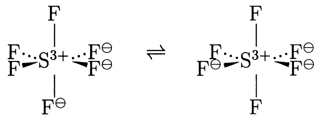
Table 8
SF_6, SF_3N and SF_4O. Basin populations $\bar{N}_i$, standard deviation $\sigma(\bar{N}_i)$, relative fluctuation $\lambda(\bar{N}_i)$ and contributions of the other basins (%) to $\sigma^2(\bar{N}_i)$

Basin	$\bar{N}_i$	$\sigma(\bar{N}_i)$	$\lambda(\bar{N}_i)$	Contribution analysis
SF_6				
C(S)	10.04	0.69	0.05	6 × V(S, F) 10%
C(F)	2.13	0.62	0.18	V(F) 90%
V(S, F)	0.97	0.90	0.86	V(F) 57%
V(F)	6.88	1.06	0.16	V(S, F) 38%
SF_3N				
C(S)	10.04	0.71	0.05	3 × V_1(S, N) 15%, 3 × V(S, F) 8%
C(N)	2.07	0.54	0.14	V(N) 60%
C(F)	2.11	0.63	0.18	V_1(F) 36%, V_2(F) 56%
V_1(S, N)	1.35	0.95	0.66	2V_2(S, N) 15%, V(N) 35%
V(S, F)	0.73	0.77	0.81	V_1(F) 25%, V_2(F) 35%
V(N)	4.01	1.19	0.35	3 × V_1(S, N) 24%
V_1(F)	2.50	1.10	0.48	V_2(F) 69%
V_2(F)	4.54	1.23	0.33	V_1(F) 56%
SF_4O				
C(S)	10.06	0.70	0.05	V(S, O) 27%
C(O)	2.11	0.58	0.16	V(O) 80%
C(F)	2.13	0.62	0.18	V(F) 90%
V_1(S, O)	1.15	0.91	0.74	V(O) 47%
V_2(S, O)	1.15	0.91	0.74	V(O) 47% V_1(S, O) 15%
V(S, F_{ap})	0.90	0.84	0.77	V(F) 56%
V(S, F_{eq})	0.94	0.85	0.76	V(F) 56%
V(O)	5.79	1.19	0.24	V(S, O) 56%
V(F)	6.90	1.05	0.16	V(S, F) 38%

terms of these compounds. In both systems the S–F bond is rather depleted since its population is always less than 1 e^-, moreover the standard deviation of the V(S, F) basin population is of the order of $\bar{N}$ indicating a strong delocalization with the fluorine lone pairs. In fact the around the fluorine core the different basins tend to merge in a valence shell with a total population close to 8 e^-, therefore the S–F bond is mostly ionic. The octet rule is also verified around the nitrogen and oxygen centers whereas there is only about 6 electrons around the sulfur core. In SF_3N, the S–N bond gives rise to three disynaptic basins though the total population, 4.05 e^-, is rather what one could expect for a double bond. Each V(S, N) disynaptic basin interacts with the two others and with the single V(N) basin of the two lone pairs. This shows that the number of basins of a given type is ruled more by symmetry than by perfect pair formation. Finally, the S–O bond in SF_4O appears to be delocalized with the oxygen lone pairs which form a single basin.

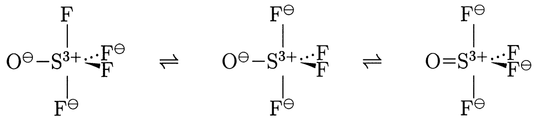
Table 9
C_6H_5F and $C_6H_5NO_2$ molecules. Basin populations $\bar{N}_i$, standard deviation $\sigma(\bar{N}_i)$, relative fluctuation $\lambda(\bar{N}_i)$

Basin	C_6H_5F			$C_6H_5NO_2$		
	$\bar{N}_i$	$\sigma(\bar{N}_i)$	$\lambda(\bar{N}_i)$	$\bar{N}_i$	$\sigma(\bar{N}_i)$	$\lambda(\bar{N}_i)$
V(C_1, C_2)	2.85	1.13	0.45	2.86	1.14	0.45
V(C_2, C_3)	2.87	1.15	0.46	2.80	1.14	0.46
V(C_3, C_4)	2.81	1.14	0.46	2.77	1.13	0.46

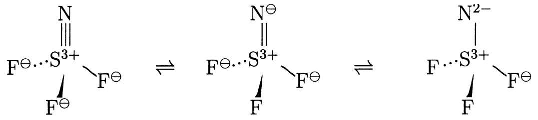


For SF_6, the basin populations suggest a model of superposition of resonance Lewis structures such as those involving SF_3^{3+} which correctly account for the calculated basin populations.

In this model there is no need for a promotion of electrons into the vacant d orbitals of the sulfur atom [2] as this has been established by Magnusson [21] and by Reed [22]. The same kind of resonance explains the bonding in SF_4O where the dominant participating Lewis structures are



whereas in SF_3N three resonance structure are involved



with approximate respective weights of 0.25, 0.25 and 0.5.

4.6. Substituted benzene

The substitution of the hydrogen located on the carbon labeled by C_1 by an electron donor substituent, such as F, or by an electron acceptor such as NO_2 modify the delocalization in benzene in two different ways. As shown in Table 9 in both cases the disynaptic basin $V(C_1, C_2)$ population is slightly increased with respect to benzene (Table 7) by an amount of about 0.05 e^-. In the electron donor case population of the basin between the carbons in position *ortho* and *meta* with respect to the substituted one increase whereas for the electron acceptor it keeps its benzene value. Finally, between the *meta* and *para* position the population decreases for the electron acceptor and is not altered for the electron donor. The same trends are observed for the cross-contributions to the population variance. This is consistent with the enhancement of the electrophilic substitution reactivity of the *ortho* site in C_6H_5F and of the *meta* one in $C_6H_5NO_2$.

4.7. Ionic and hydrogen-bonded systems

For ionic systems it is convenient to gather the cation basins into a single domain. This is generally already done in the case of monatomic cations such as alkali and alkaline earth positive ions. The relative fluctuation of the cation population is always very low. For example, in LiF, it is 0.042 for C(Li) to be compared with the C(F) value 0.18. Therefore, the delocalization between the valence and core basins of the anion is much more larger than between the cation and the anion.

The same trend is magnified in hydrogen-bonded complexes. The relative fluctuation of the proton donor population is generally calculated to be one order of magnitude smaller than that of the cation in ionic bonds. For $(FH)_2$ and $FHNH_3$, in which the proton donnor is one FH molecule, it is found to be 0.006 and 0.010 respectively. The respective magnitudes of these two values follows the order of the observed hydrogen bond strengths.

5. Conclusion

For the electron density produced by a given potential of the nuclei, ELF provides a structuring of the molecular space into basins that may be associated with the electronic regions and have therefore a chemical meaning. The population analysis presented here allows one to calculate the basin populations, their variance and also to analyze the variance in term of cross-contributions arising from the interactions with the other basins. It is worth noting that such an analysis allows the bonding to be successfully modeled into traditional resonance structures. The examples presented in this paper illustrate the applicability of the method.

Acknowledgements

The authors gratefully acknowledge Frank Fuster for providing the wave functions of C_6H_5F, $C_6H_5NO_2$, $(FH)_2$ and $FHNH_3$.

References

[1] M.L. Huggins, Science 55 (1922) 679.

[2] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, NY, 1948.
[3] L. Salem, The Molecular Orbital Theory of Conjugated Systems, W.A. Benjamin, Reading, MA, 1966.
[4] C.A. Coulson, Valence, Clarendon Press, Oxford, 1952.
[5] R. Daudel, Quantum Theory of The Chemical Bond, Reidel, Dordrecht, 1974.
[6] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1990.
[7] B. Silvi, A. Savin, Nature 371 (1994) 683.
[8] A.D. Becke, K.E. Edgecombe, J. Chem. Phys. 92 (1990) 5397.
[9] R.F.W. Bader, in: O. Chalvet, R. Daudel, S. Diner, J.P. Malrieu (Eds.), Localization and Delocalization in Quantum Chemistry, vol. I, Reidel, Dordrecht, 1975, pp. 15–38.
[10] A. Savin, B. Silvi, F. Colonna, Can. J. Chem. 74 (1996) 1088.
[11] S. Diner and P. Claverie, in: O. Chalvet, R. Daudel, S. Diner, J.P. Malrieu (Eds.), Localization and Delocalization in Quantum Chemistry, vol. II, Reidel, Dordrecht, 1976, pp. 395–448.
[12] R. McWeeny, Methods of Molecular Quantum Mechanics, 2nd ed., Academic Press, London, 1989.
[13] I. Mayer, Theor. Chim. Acta 67 (1985) 315.
[14] I. Mayer, Int. J. Quantum Chem. 29 (1986) 73.
[15] J.G. Ángyán, M. Loos, I. Mayer, J. Phys. Chem. 98 (1994) 5244.
[16] A. Savin, A.D. Becke, J. Flad, R. Nesper, H. Preuss, H.G. von Schnering, Angew. Chem. Int. Ed. Engl. 30 (1991) 409.
[17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[18] C. Lee, Y. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, Revision D.4, Gaussian, Pittsburgh, PA, 1995.
[20] S. Noury, X. Krokidis, F. Fuster, B. Silvi, TopMod package, 1997.
[21] E. Magnusson, J. Am. Chem. Soc. 112 (1990) 7940.
[22] A.E. Reed, P. von Ragué Schleyer, J. Am. Chem. Soc. 112 (1990) 1434.